Laterally confined THz Sources and Graphene based THz Optics

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To the hands who nourished the seed,
To the winds that made it stronger,
To the sun that gave it warmth,
To the earth which held it on.
Declaration

This dissertation is the result of work carried out in the Semiconductor Physics group at the Cavendish Laboratory from October 2009 to May 2014. This dissertation is the result of my own work and includes nothing which is the outcome of work done in collaboration except where specifically stated in the text. This work is not the same as any I have already submitted, or I am in the process of submitting, for any degree at this, or any other university. This dissertation contains 95215 words including appendices, bibliography, tables and equations and has 200 figures.

Shruti Badhwar,

Cambridge, May 2014
"Behind the wall of objective science, a thousand emotions collide"

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Abstract

The region between the infrared and microwave region in the electromagnetic spectrum, the Terahertz (THz) gap, provides an exciting opportunity for future wireless communications as this band has been underutilized. This doctoral work takes a two-pronged approach into closing the THz gap with low-dimensional materials. The first attempt addresses the need for a compact THz source that can operate at room temperature. The second approach addresses the need to build optical elements such as filters and modulators in the THz spectrum.

Terahertz quantum cascade lasers (THz QCLs) are one of the most compact, powerful sources of coherent radiation that bridge the terahertz gap. However, their cryogenic requirements for operation limit the scope of the applications. This is because of the electron-electron scattering and heating of the 2-dimensional free electron gas which leads to significant optical phonon scattering of the hot electrons. Theoretical studies in laterally confined QCL structures have predicted enhanced lifetime of the upper state through suppression of the non-radiative intersubband relaxation, which leads to lower threshold, and higher temperature performance. Lithographically defined vertical nanopillar arrays with electrostatic radius less than tens of nm offer a possible route to achieve lateral confinement, which can be integrated into QCL structures. A typical gain medium in a QCL consists of at least 100 repeat periods, with a thickness of 6-14 µm. For practical implementation of the top-down approach, restrictions are imposed by aspect ratios that can be achieved in present dry-etching systems. Typically, for sub-200 nm radius pillars, the thickness ranges from 1-3.5 µm. It is therefore necessary to work with THz QCLs based on 3-4 quantum well active regions, so as to maximize the number of repeat periods (hence gain) within a ≤ 3.5 µm thin active region.

After an introductory chapter, Chapter 2 presents a theoretical treatise on the realistic electrostatic potential in a lithographically defined nanopillar by scaling from a single quantum well (resonant tunneling diode) to a THz QCL.
Chapter 2 also discusses, the effect of lateral confinement on the intersubband states and the plasmonic mode in a THz QCL. One of the key experimental challenges in scaling down from QCLs to quantum-dot cascade lasers is the electrical injection into the nanopillars. This involves insulation and planarization of the high aspect-ratio nanopillar arrays. Furthermore, the choice of the planarizing layer is critical since it determines the loss of any optical mode. This experimental challenge is solved in Chapter 3. Chapter 4 presents the electro-optic performance of low-repeat period QCLs with an active region thickness $\leq 3.5 \, \mu m$.

Another topic of recent interest in the THz optics community is plasmonics in graphene. This is because the bound electromagnetic modes (plasmons) are tightly confined to the surface and can also be tuned with carrier concentration. Plasmonic resonance at terahertz (THz) frequencies can be achieved by gating graphene grown via chemical vapor deposition (CVD) to a high carrier concentration. THz time domain spectroscopy of such gated monolayer graphene shows resonance features around 1.6 THz superimposed on the Drude-like frequency response of graphene which may be related to the inherent polycrystallinity of CVD graphene. Chapter 5 discusses these results, as an understanding of these features is necessary for the development of future THz optical elements based on CVD graphene. Chapter 5 finally describes how the gate tunability of THz transmission through graphene can be exploited to indirectly modulate a THz QCL.

Chapter 6 presents ideas from this doctoral work, which can be developed in future to address the issues of enhanced temperature performance of Thz QCLs and to realize realistic THz devices based on graphene.
Publications

Some ideas and concepts have appeared or will appear in the following publications and conferences.

PUBLISHED JOURNAL ARTICLES


TO BE SUBMITTED


2. *Fabrication of suspended contact to high aspect ratio nanopillars*, Shruti Badhwar, Harvey E. Beere, Jon Griffiths, Geb Jones, David A. Ritchie

3. *Parallel conduction through 500 x 500 laterally confined RTDs*, Shruti Badhwar, Joshua R. Freeman, Anthony Brewer, Harvey E. Beere, Jon Griffiths, Geb Jones, David A. Ritchie

CONFERENCES

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1. *THz optics - the route to faster wireless communications*, Shruti Badhwar, Indian Institute of Technology, Gandhinagar, India (December 2013)

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Abbreviation

THz.............. Terahertz
Mid IR............. Mid infrared
RTD................. Resonant tunneling diode
QCL................. Quantum cascade laser
BtC................. Bound to continuum
LO phonon.......... Longitudinal optical phonon
TDS................. Time domain spectroscopy
RIE................. Reactive ion etching
ICP RIE............. Inductively coupled plasma reactive ion etching
SOG................. Spin on glass
BHF................. Buffered hydrofluoric acid
CVD................. Chemical vapour deposition
PECVD.............. Plasma enhanced chemical vapour deposition
NDR............... Negative differential resistance
LIV................. Light current voltage
QW................. Quantum well
AR............... Active region
FOM............... Figure of merit
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Chapter 1

Introduction

1.1 Terahertz (THz) gap

The Terahertz (THz) gap lies in a very unique position in the electromagnetic spectrum. On the lower end of the gap are the radio and microwave frequencies, commonly associated with communications owing to the distance these long wavelengths can propagate. On the higher end lie the infrared frequencies (shorter wavelengths), which are exploited by the optical fiber communication techniques owing to higher bandwidth and data rates.

Applications of the THz band are not limited to communication. The THz gap is so called as it is sandwiched between the realms of electronics and photonics. The gap exists as there is no easy solution to generating and detecting such low energies (1-10 THz, 4-40 meV). Historically, much of the interest in developing optical elements in this region...
1. INTRODUCTION

- sources and detectors - came from the fields of astrophysics and atmospheric sciences, where the small energy associated with THz frequencies corresponds to strong rotational and vibration modes of molecules [8, 9]. Development in the field of THz sources over the past few years have expanded the potential to biomedical imaging, ultrafast spectroscopy, security screening, and non-destructive evaluation [8, 9, 10].

1.2 THz sources

THz sources in the literature can be classified as (i) broadband sources (ii) narrow band sources.

1.2.1 Broadband sources

Broadband sources use a variety of mechanisms to generate THz radiation. These include (i) photocarrier acceleration in photoconducting antennas [11], (ii) second-order non-linear effects in electro-optic crystals such as ZnTe, ionic salts [12, 13], (iii) non-linear generation by optical parametric conversion in materials such as LiNbO$_2$ [14] and (iv) plasma oscillations [15]. However, these sources are indirect in nature and the conversion efficiencies in all of these sources are very low. Consequently, average THz beam powers tend to be in the nW to µW range, whereas the average power of the femtosecond optical source is in the region of 1 W. A comprehensive review of broadband THz sources is provided elsewhere [9, 16, 17].

1.2.2 Narrowband sources

Narrowband sources are relevant for high-resolution spectroscopy applications. In the past, the only fundamental terahertz oscillators available were optically pumped molecular gas lasers using continuous wave CO$_2$ lasers. However, not only were these lasers bulky, the type of gas (for example, methanol, chloroform and ethanol) determined the operating frequency, denying tunability of operation [18]. Tunable emission from semiconductor lasers was obtained from exotic gain mechanisms such as the p-Ge hot-hole lasers. These lasers achieved population inversion between the heavy-hole and the light-hole valence band in crossed electric and magnetic fields [19]. High power THz radiation (1W-10$^3$W range) can be obtained from electron beams, such as free electron lasers [20], relativistic accelerators [21] and synchrotrons [22]. More recently there have been claims on achieving peak powers from laser-driven particle accelerators, which are greater than synchrotrons [23]. These high power sources require dedicated facilities and involve prohibitive costs.
THz sources motivated from oscillators in electronics are limited by transit time and resistance-capacitance effects at high frequencies, operating slightly above 1 THz ($\lambda \approx 300 \ \mu m$) at below mW level at best [24]. These approaches include the Gunn diode, IMPact ionization Avalanche Transit Time (IMPATT) diode and resonant tunneling diodes (RTD) all of which employ negative differential resistance [9]. Some of the electronic approaches to generate THz radiation employ frequency up conversion using nonlinear reactive multiplication of lower-frequency microwave oscillators.

The photonic approaches on the other hand, are restricted by the lack of appropriate materials with sufficiently small band gaps to allow optical transitions below 15 THz. A few semiconductor lasers, operating at $\approx 6.5$ THz based on narrow gap lead-salt materials were demonstrated in the 1980s [25]. However, these devices once fabricated suffer from rapid aging and are particularly sensitive to Auger processes in which the energy and momentum of the recombining electron-hole pair are transferred to a third carrier, rather than to a photon. Semiconductor lasers based on intersubband transitions in quantum wells dramatically altered the focus from finding a material with a band gap in the THz range to engineering band gaps with THz frequencies. These semiconductor lasers were given the name THz quantum cascade laser, and are described below.

### 1.3 THz quantum cascade lasers (THz QCLs)

Among the THz sources discussed above, THz quantum cascade lasers (THz QCLs) are unrivalled in performance in terms of their size and power. Here, we review the principles behind THz QCLs and how they evolved from their mid IR counterparts. Note that this review here is by no means complete and the interested reader is directed to comprehensive books written on QCLs [10, 26].

#### 1.3.1 The paradigm change: intersubband transitions

Conventional semiconductor lasers, including quantum well lasers are bipolar in the sense that they rely on transitions between conduction and valence bands in a forward-biased p-n junction device where the electrons and holes radiatively recombine across the material bandgap. It is this band gap, which determines the emission wavelength. Furthermore, the gain spectrum is broad and reflects the distribution of charge carriers in the conduction and valence bands (having opposite curvature) according to the Fermi’s statistics, see figure 1.2(a).

In the early 1970s, Kazarinov and Suris proposed a paradigm shift from interband
transitions to intersubband transitions in quantum wells to achieve generation and light amplification by electrical pumping [27], [28]. This proposal followed on the seminal work by Esaki and Tsu [29] who introduced the concept of negative differential resistance (NDR) in a superlattice. The proposal by Kazarinov and Suris was based on unipolar photon assisted tunneling. Intersubband transitions unlike interband transitions, are unipolar in nature, which rely on optical transitions within the quasi-two-dimensional electronic states in semiconductors (called subbands) formed due to confinement of the electron wavefunction in the growth dimension. In these unipolar devices, the radiative frequency can be engineered by changing the well width. Also, the emission frequency is limited only by the heterostructure offset, $\Delta E_c$ ($\Delta E_v$) for conduction (valence) band. Since the initial and final states have the same curvature if non-parabolicity is ignored, the joint density of states is very sharp which gives rise to a narrow gain linewidth, see figure 1.2(b).

Figure 1.2: (a) Interband laser transition (b) Intersubband laser transition. Here, $\rho(E)$ and $g(E)$ refer to the joint density of states and gain as a function of optical transition [10].

1.3.2 The journey from mid-infrared QCLs to THz QCLs

Since the energy separation between subbands is independent of the fundamental band gaps of the material system, the bands can be engineered such that operation at any long
wavelength is possible. However, the biggest stumbling block in designing any arbitrary frequency is the reststrahlen band, or the longitudinal phonon energy of the constituent material. The initial attempts at achieving emission from intersubband transitions focussed on energies below the reststrahlen band so as to avoid the extremely fast non-radiative intersubband relaxation of electrons via the emission of optical phonons\[30, 31\]. The major breakthrough came in 1994 when Faist et al. \[32\] demonstrated the first intersubband laser in the mid infrared region. This laser operated at energy $E_{32} \gg E_{LO}$ ($\lambda \approx 4.6 \mu m, f = 70 \text{THz}, E = 290 \text{meV}$), see figure 1.3. Here, $E_{32}$ is the energy difference between the diagonal levels 3 and 2. Aided by LO phonon scattering, the electrons in the lower lasing level 2 are depopulated to level 1. In addition to the three quantum wells, a digitally graded alloy is implemented within the superlattice period. This region forms a miniband of levels that helps in the extraction of electrons from the lower lasing levels 2 and 1, to the upper lasing level 3 of the next period. This doped region termed as the injector serves as a Bragg reflector for hot electrons in the upper lasing level 3, preventing them from escaping into the continuum over the barriers.

Figure 1.3: Schematic conduction band diagram of the first quantum cascade laser showing the radiative levels 3 and 2. Reproduced from [32].

Note that the electron phonon scattering element is proportional to $1/\Delta k$, where $\Delta k$ is the momentum exchanged in the scattering process. In order to achieve $E_{32} \gg E_{LO}$, the momentum exchange involved for LO phonon scattering from level 3 to level 2 is an order of magnitude higher than the momentum exchange involved for LO phonon scattering from level 2 to level 1 \[32, 33\]. This is illustrated in figure 1.4.

Since the inception of the first mid infrared quantum cascade laser, the field developed rapidly. Within a span of two years, the mid infrared quantum cascade laser started to
1. INTRODUCTION

Figure 1.4: Schematic representation of the dispersion relationship $E(k_{//})$, where $E_{32} \gg E_{LO}$, and $k_{//}$ is the corresponding wavevector parallel to the layers. Adapted from [33].

operate at room temperature [34]. A comprehensive review on mid infrared quantum cascade laser is provided by Gmachl et al. [35].

Inspite of the developments in the mid infrared QCLs, the move to THz QCLs ($E = 4$ to 20 meV) was met with several roadblocks. The first promising example of THz electroluminescence was reported in 1998, at a frequency of 8 THz ($\lambda = 37.4 \ \mu m$, $E = 33$ meV) [36]. Figure 1.5 shows the dispersion relation for a three level quantum cascade laser where $E_{32} < E_{LO}$. In GaAs, $E_{LO} = 36$ meV. Due to the small energy spacing between the upper lasing level 3 and lower lasing level 2, various intersubband mechanisms such as electron-electron, electron-impurity and interface roughness come into play, which reduces the amount of population inversion [33]. A small transition energy $E_{32}$ makes it difficult to selectively inject into the upper lasing level. At the same time, it becomes difficult to selectively extract from the lower lasing level. Note that the momentum exchange involved for electron LO phonon scattering from level 3 to level 1 ($\Delta k_{31}$) is very close to the momentum exchange involved for electron LO phonon scattering from level 2 to level 1 ($\Delta k_{21}$).

Besides these challenges, one of the major hurdles in development of the first THz QCL was the waveguiding of the THz radiation. Conventional dielectric based waveguides used in the mid IR could not be used without hitting against practical limitations of growing waveguides to support long wavelengths. Owing to these difficulties, it took eight years to go from mid IR QCL to a THz QCL, with the breakthrough coming in the year 2002, when Koehler et al. demonstrated a THz laser operating at 4.4 THz ($\lambda = 67 \mu m$, $E = 18$ meV) [37]. This laser required a waveguiding approach that was radically different to it’s mid infrared counterpart. Making use of surface plasmons that exist at the interface of two
1.3 THz quantum cascade lasers (THz QCLs)

Figure 1.5: Schematic representation of the dispersion relationship $E(k_{//})$, where $E_{32} < E_{LO}$, and $k_{//}$ is the corresponding wavevector parallel to the layers. Adapted from [33].

Since 2002, a lot of progress has been made in achieving better lasing performance
1. INTRODUCTION

through active region design [39]. In the next section, we describe some of the most common active regions used for THz QCLs.

1.3.3 THz QCL active regions

The merit of different active regions is evaluated in terms of material gain $G_P$ and the normalized oscillator strength $f_{ul}$. Here, $f_{ul}$ is the ratio of the quantum optical strength of the optical transition between upper (u) and lower (l) lasing levels to that of a classical electron oscillator. The oscillator strength characterizes the overlap and symmetry of the initial and final wavefunctions. The material gain $G_P$, discussed in section 4.1.1, is proportional to the product of oscillator strength and population inversion. $G_P$ is also inversely proportional to linewidth of the optical transition.

Figure 1.7(a-d) shows the schematic conduction band diagram of common THz QCL active regions. Apart from the chirped superlattice (CSL) active region, QCL designs come in two main variants - the bound to continuum (BtC) design and resonant phonon (LO phonon) design. More recently, the scattering assisted (SA) design has gained prominence in the THz community.

The BtC design employs the same miniband based extraction scheme as the CSL design, see figure 1.7(b). The difference in the two designs comes in the upper lasing level, which is made to be a bound 'defect' state in the minigap. Designed to be more diagonal in real space, the upper state lifetime increases as the non-radiative scattering reduces. However, the diagonality of the transition also impairs the oscillator strength of the radiative transition. Compared to the CSL design, the oscillator strength reduces from $f_{21} = 2.5 - 3$ to $f_{21} = 1.5 - 2$.

The LO phonon design deviates from BtC and CSL design in that it uses resonant tunneling to inject into the upper state, but employs the LO phonon scattering to depopulate the lower lasing level, see figure 1.7(c). In section 1.3.2, we brought out the difficulty of achieving population inversion posed by LO phonon scattering when the energy of radiative transition is lower than the phonon energy. This challenge was addressed by Williams et al. [41] where the authors identified that the lower lasing state must be brought into a broad tunneling with the adjacent quantum wells so that it’s wavefunction is spread over several quantum wells. The lack of a miniband state implies that the LO phonon designs have a smaller oscillator strength when compared to BtC and CSL designs, $f_{21}$ is approximately $0.5 - 1$. However, one of the biggest advantages of LO phonon design lies in the reduction of the period length from 105-110 nm to nearly half.

Like the LO phonon design, the scattering assisted (SA) design, also has a small period
1.3 THz quantum cascade lasers (THz QCLs)

Figure 1.7: Schematic conduction band diagram of common THz QCL active regions: (a) chirped superlattice (CSL) (b) bound to continuum (BtC) (c) resonant phonon (LO phonon / RP) (d) scattering assisted (SA). Adapted from [39, 40]
1. INTRODUCTION

length. However, the SA design does not employ resonant tunneling to inject electrons into the upper lasing level, instead it uses resonant phonon relaxation to selectively inject into the upper lasing level as well as extract the electrons out from the lower lasing level [40]. The oscillator strength \( f_{ul} \approx 0.6 \) is similar to that of the LO phonon. Note that currently, the SA design holds the record for the highest operating temperature within the literature. This is important since the operating temperature holds the key to commercialization of THz QCLs for various applications.

1.3.4 THz QCLs: quest for room temperature operation

Over the last decade, rapid advancements in the design of gain medium as well as improvement in the fabrication and wave guiding techniques have led to significant improvements in the operating performance of the THz QCLs. THz QCLs now cover a wide spectral range \((0.45 - 5.0 \text{ THz})\) [39]. They also exhibit high bandwidth (up to 1 THz) [42] and operate at a power exceeding 1 W [43]. However, room temperature operation still continues to elude THz QCLs, making this subject a holy grail in this field. What is encouraging is that THz QCLs have come a long way in terms of their operating temperature since their first demonstration in 2002 at a maximum operating temperature of 50 K. Figure 1.8 shows the maximum operating temperatures achieved with improvements made in active region design, heat sinking and confinement of optical mode. As one can see, the relationship between the operating temperature \( T \) and the operating frequency \( \omega \) is linear. This is because at low frequencies, the energy carried by the photon \( (E_{ul} \sim 8 \text{ meV at 2 THz}) \) is similar to the typical energy broadening of the subbands (a few meV). Hence, it becomes difficult to selectively inject from the injector into the upper lasing level.

There are however three design principles that deviate from this trend. The first approach makes use of a unique scattering assisted injection scheme, first shown to work at 1.8 THz by Kumar et al. Based on this work, the SA design was made more diagonal to achieve a record operating temperature of 200 K at a frequency of 3.6 THz [44]. The second approach is more recent and employs intracavity difference frequency generation from mid IR QCLs, to achieve room temperature emission between 3.3 to 4.6 THz [45]. The third approach makes use of very high magnetic field to suppress the non-radiative scattering by LO phonon emission. By imposing zero-dimensional confinement on the carriers, this technique has shown to improve the operating temperature of a standard resonant phonon design from \( \approx 178 \text{ K} \) to 225 K [46]. Below, we focus our attention to zero-dimensional confinement as a route to higher temperature performance.
1.4 Zero-dimensional confinement in QCLs

Figure 1.8 shows the schematic dispersion relationship for a laterally confined three-level THz QCL. Note that the non-radiative LO phonon scattering from the upper lasing level 3 to the lower level 1, which is particularly dominant at high electron density in the upper subband [47, 48], is suppressed due to quantization of the in-plane momentum. The in-plane quantization of the momentum wavevector can be imposed in several ways. First, we survey the different approaches explored in the literature to attain zero-dimensional confinement, aside from a very high magnetic field. The term bottom-up refers broadly to quantum-dots, quantum-dashes or nanowire structures grown by epitaxial methods.

1.4.1 Bottom up approach

Theoretical proposals for quantum dot cascade structures

The first proposal by Wingreen et. al (figure 1.10(a)) in visioning a quantum-dot cascade structure [49], predates the demonstration of THz electroluminescence from quantum-well cascade structures [37, 51]. Suggested for operation at mid-infrared frequencies, this proposal made use of a vertical cascade of a pair of quantum dots to achieve radiative transition between energy levels with an energy difference $E \geq h\omega_{LO}$. Following this proposal,
1. INTRODUCTION

Figure 1.9: Schematic representation of the dispersion relationship $E(k_{||})$, where $E_{32} < E_{LO}$. The wavevector parallel to the layers $k_{||}$ is discretized due to zero-dimensional confinement.

another design which made use of radiative transition in a single quantum-dot with energy splitting $E \geq 2\hbar \omega_{LO}$ was suggested by Chia-Fu et. al (figure 1.10(b)). Infact, Chia-Fu was one of the very few authors who actually proposed a lasing architecture for a quantum-dot cascade structure, with a dielectric cladding surrounding the quantum-dot gain medium to act as a waveguide. Both, Wingreen et. al and Chia-Fu et. al estimated the lateral dimension of the quantum dot to be $\sim 20$ nm. With increasing electron-population, the Coulomb interaction between electrons may start to effect radiative transitions described in figure 1.10. Compared to a noninteracting system, this interaction may result in a blueshift of the luminescence spectra [52, 53].

Mid infrared emission from quantum dot cascade structures

The first experimental observation of electroluminescence from a quantum-dot cascade structure, at mid-infrared frequencies came a few years after the theoretical proposals were made. Instead of replacing the quantum wells with quantum dots, as suggested by Wingreen et. al, this design employed a cascade with each period consisting of self assembled InAs dots grown on top of GaAs wells, see figure 1.11. While pure quantum-well systems (without dots) showed emission that was transverse-magnetic (TM) polarized, the radiation emitted from these 'quantum-dot in quantum-well' system was observed to be only slightly polarized. The lack of polarization was attributed to an elliptical cross section of the quantum-dots [54]. Similar cascade structures, with InAs dots grown on top of AllnGaAs wells were shown to emit p-polarized electroluminescence due to hybrid radiative transitions. These transitions occurred from the excited and ground state of the quantum-
1.4 Zero-dimensional confinement in QCLs

Figure 1.10: (a) Schematic energy band diagram showing diagonal radiative transition in a pair of coupled dots, i.e. between the first-excited state of one dot and the ground state of a second dot. The density of the coupled dots in an array determines the gain. To achieve lasing, these coupled dots are stacked vertically as well as repeated in a planar array [49]. (b) Schematic energy band diagram, showing radiative transition in a single quantum dot. The Bragg mirror in the direction of growth achieves the same purpose as the coupled dots in figure (a) i.e it reduces the leakage of electrons in the upper lasing level. The dots are arranged in a planar array to achieve the required gain, and make use of only one repeat period in the vertical direction [50].

dot to the ground state of the following quantum well, at mid-infrared frequencies [55] and did not depend upon the size of the quantum-dot.

Anisotropically polarized mid-infrared emission from quantum-dot cascade structures that relied on transitions within the InAs quantum dot was observed in an active region very similar to the vertical transition design proposed by Chia-Fu [56]. The schematic band diagram showing vertical transition from the excited to the ground state of the quantum dot is shown in figure 1.12. Transitions within a single InAs quantum dot on AlInAs, supported with superlattices on either side for efficient injection and extraction were exploited recently, to achieve room temperature anisotropic, transverse-electric (TE) polarized emission at mid-infrared frequencies, which depended on the amount of lateral confinement [57]. A quantum dot in InAs modeled as a semi-cylinder with width = 15 nm, length = 65 nm and height = 2.5 nm, corresponds to an energy difference of $|2, 1, 1\rangle - |1, 1, 1\rangle = 120 \text{ meV}$, which agrees with an electroluminescence peak at 110 meV [57] when the minibands are aligned to the dot energy states.

**THz absorption from quantum dot cascade structures**

The transition energies in a vertical design, quantum-dot cascade structure depend upon the quantum dot dimensions and the growth material. Absorption at THz frequen-
Figure 1.11: Energy band diagram indicating the radiative transition levels in the quantum-dot cascade structure (3 and 2) used in [54]. The excited energy levels of the quantum dot (3 and 2) are coupled to the quantum-well states. The schematic shows the energy levels of the 'quantum-dot embedded in quantum-well' structure for a single period, under the conditions of (a) no electrical bias and (b) with electrical bias [54].

Species was reported in 2009 from THz pump-probe experiments on quantum-dot cascade structures based on self-assembled InGaAs quantum dots [58]. Transition energy between the first excited state and the ground state, in these InGaAs dots lie in the range of 40-60 meV \((f = 9.6 - 14.5\text{THz})\). By annealing the quantum-dots post-growth, the transition energy can be brought down below the longitudinal phonon energy, \(\hbar \omega_{LO}\). The InGaAs quantum-dots modeled as truncated cones of base (top) radius 12 nm (6 nm) and height 4.9 nm, correspond to a transition energy of 48 meV \((f = 12 \text{THz})\), which reduces to 10 meV \((f = 2.4 \text{THz})\) when the radius of the dot is increased to 25 nm by post-growth annealing. Unlike previous designs in the mid-infrared, this quantum-dot cascade structure did not employ any Bragg mirror to improve electron injection and extraction. However, each dot layer was separated from the other by a thick GaAs barrier to prevent structural and electronic coupling between the layers. Figure 1.13 shows the absorption spectra below Reststrahlen band due to intersublevel transitions between the excited p-state and the s-like ground state in a stack of self-assembled InGaAs quantum dots. While the quantum-dot structure holds promise at higher energies, the spectra around 10 meV \((f = 2.4 \text{THz})\) is quite weak and broad possibly due to intermixing, suggesting the need for better dot size.
1.4 Zero-dimensional confinement in QCLs

Figure 1.12: Energy band diagram, under an electrical bias, showing the radiative transition levels in the quantum-dot cascade structure used in [56]. The superlattice minibands, grown on top of the quantum-dot, are tailored to block leakage of electrons from the upper lasing levels (excited states of the dot) at the injector energy. Furthermore, these minibands (shaded in blue) promote extraction of electrons from the ground state of the quantum dot. This superlattice structure is similar to the Bragg mirror shown in figure 1.10(b). However, unlike [50], in spite of the vertical transition in a single quantum dot, this structure makes use of stacking of the active periods in the growth direction to improve gain [56].

Growth of nanowires

In the year 2010, Williams et. al, proposed that intersubband transitions within semiconductor nanowires with axial and core-shell geometries might have potential for THz lasers operating at high temperature $^1$. However, while such nanowire geometries have shown promise as photodetectors through intersubband absorption [59, 60], their applicability to THz emitters still remains as an area of active research.

1.4.2 Top down Cavendish approach

We can now introduce the subject of this thesis - zero dimensional confinement in THz QCLs through a top down nanofabrication approach. So far, the most optimistic result of zero-dimensional confinement leading to intersubband transitions at THz frequencies comes from Zibik et. al [58]. However, the need to realize a 25 nm wide quantum dot or wider through epitaxial growth, for emission at $\leq 2.4$ THz has been inhibiting the development of THz quantum dot cascade lasers through a bottom up approach. The challenge of the top down approach to realize such structures is exactly the opposite. While it is relatively straightforward to fabricate structures that are a few $\mu$m wide over

$^1$Url: https://www.collectiveip.com/grants/NSF:1002387
1. INTRODUCTION

Figure 1.13: (a) Calculated wavefunction of the s and p states in the quantum dot (b) Schematic energy diagram showing vertical transitions between s and p states. The two transitions, $p_x$-s and $p_y$-s are separated by an energy difference equal to $\Delta_{pp}$. (c) Absorption spectra of quantum dots as a function of annealing temperature [58].

In section 1.3.2, we mentioned that the development of THz QCLs struggled initially because of the absence of a low loss THz waveguide. Dielectric waveguides cannot be used at THz frequencies, as the thickness of the cladding layer scales linearly with the free space wavelength, which makes it prohibitive to implement. On the other hand, the very high free-carrier absorption at THz frequencies prevents the use of doped layers. The optimal solution for THz frequencies uses an alternate approach to waveguiding as opposed to techniques borrowed from the microwave and the optical frequencies [62, 63, 64, 65, 66]. This solution relies on using surface plasmon waves at the interface of two materials with dielectric constants of opposite signs, typically a metal and a semiconductor. Below, we
describe the theory behind surface plasmons.

### 1.5.1 Surface plasmons

Surface plasmons are charge density oscillations that exist at the interface of a dielectric and a conductor, and propagate along the surface of the conductor, see figure 1.14. Technically, surface plasmons should be addressed as surface plasmon polaritons owing to the hybrid nature of the interaction between a photon (of electromagnetic radiation) and free electrons (on the surface of the conductor) which respond collectively by oscillating with the light wave. The normal component of the electric field decays exponentially with distance from the surface. The decay length in the metal $\delta_m$ depends upon the skin depth of the conductor and the decay length $\delta_d$ in the dielectric is approximately of half of the incident wavelength.

![Figure 1.14: Surface plasmons at the interface between a metal and a dielectric](image)

If the surface plasmon propagates in the x-direction, the electric and magnetic fields in the dielectric ($E_d$ and $H_d$, $z > 0$) and in the metal ($E_m$ and $H_m$, $z < 0$) can be expressed as:

\[
E_d(r, t) = (e_x E_{d,x} + e_z E_{d,z})e^{-k_d z}e^{i(k_x x - \omega t)} \quad (1.1)
\]
\[
H_d(r, t) = (e_y H_d) e^{-k_d z}e^{i(k_x x - \omega t)} \quad (1.2)
\]
\[
E_m(r, t) = (e_x E_{m,x} + e_z E_{d,z})e^{k_m z}e^{i(k_x x - \omega t)} \quad (1.3)
\]
\[
H_m(r, t) = (e_y H_m) e^{-k_m z}e^{i(k_x x - \omega t)} \quad (1.4)
\]
1. INTRODUCTION

The surface wave corresponding to a frequency of \( \omega \) is characterized by the wavenumbers \( k_x \), \( k_y \) and \( k_z \). Solving the generic wave equation

\[
\nabla^2 E = \varepsilon \mu \frac{\partial^2 E}{\partial t^2}
\]

(1.5)

using for electric and magnetic fields given by eqns. 1.2 - 1.4 yields the dispersion relations:

\[
k_x^2 - k_d^2 = \varepsilon_d \frac{\omega^2}{c^2}
\]

(1.6)

\[
k_x^2 - k_m^2 = \varepsilon_m \frac{\omega^2}{c^2}
\]

(1.7)

Here, \( \varepsilon_d \) and \( \varepsilon_m \) are the relative permittivity values of the dielectric and the metal. The permeability values for both the dielectric and the metal are assumed to be equal to 1, for non-magnetic materials. The ratio of \( \kappa_d \) to \( \kappa_m \) can be expressed in terms of the propagation wavevector \( k_x \) and frequency \( \omega \) as:

\[
\frac{\kappa_d^2}{\kappa_m^2} = \frac{k_x^2 - \varepsilon_d \omega^2 / c^2}{k_x^2 - \varepsilon_m \omega^2 / c^2}
\]

(1.8)

Applying the Maxwell equation, \( \text{curl}(E) = -\mu \frac{\partial H}{\partial t} \), the respective magnetic fields can be written in terms of the electric field as:

\[
H_{d,y} = -i \varepsilon_o \frac{\varepsilon_d \omega}{\kappa_d} E_{d,x}
\]

(1.9)

\[
H_{m,y} = i \varepsilon_o \frac{\varepsilon_m \omega}{\kappa_m} E_{m,x}
\]

(1.10)

Since, \( H_{d,y} = H_{m,y} \) and \( E_{d,x} = E_{m,x} \) at the surface, the boundary conditions reduce eqn. 1.9 and eqn. 1.10 to

\[
\frac{\varepsilon_d}{\varepsilon_m} = -\frac{\kappa_d}{\kappa_m}
\]

(1.11)

On substituting eqn. 1.11 into eqn. 1.8 one obtains the dispersion relation of surface plasmons, which can be written as:

\[
k_x = \frac{\omega}{c} \left( \frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m} \right)^{1/2}
\]

(1.12)

Thus, the wavevector \( k_x \) of the surface plasmon wave is larger than the wavevector
1.5 THz waveguides

of the incident electromagnetic radiation, given as \( k_0 = \omega/c \). This dispersion relationship is plotted in figure 1.14(c). This implies that the electromagnetic energy is confined within a dimension that is much smaller than the wavelength of light. This is the reason why an incident THz wave, which has a long wavelength, can be supported by a surface plasmon which can propagate in subwavelength dimensions. Below, we describe the two main categories of waveguide configurations based on surface plasmons, which enable the functioning of THz QCLs.

1.5.2 Plasmonic waveguides in THz QCL

The waveguide developed for the first THz QCL relied on semi-insulating GaAs substrates, which were relatively free from absorption related losses. This approach also made use of the highly doped bottom contact layer, grown directly beneath the active region \[37\]. A surface plasmon mode then exists between the top metal contact and the bottom doped \( n^+ \) GaAs layer, with a substantial extension into the GaAs substrate, see figure 1.15(a). This kind of a waveguide is commonly known as a single plasmon waveguide. Although the mode extends into the substrate, the overlap with the doped semiconductor layer is small, so the free carrier absorption loss is curtailed. In the single-plasmon design, the overlap factor, \( \Gamma \) typically ranges from 0.1 to 0.5. Here, the overlap factor is defined as the percentage of the optical mode interacting with the active region. The exact formalism is discussed in section 2.11.1.

Figure 1.15: THz QCL waveguides: schematic diagram and 2-dimensional mode profile (a) single-plasmon (b) double-metal \[39\]
Recent developments have seen the emergence of the double metal waveguides, which provide an overlap factor $\Gamma \approx 1$ \[67\]. Double metal waveguides have metal layers on the top and bottom of the active region, causing two surface plasmon modes to be formed, see figure 1.15(b). As compared to single plasmon waveguides, the double-metal waveguides supports smaller ridge widths and have better heat sinking properties, which allows for a greater temperature performance. Furthermore, as the mode is confined between the two metal surfaces, the ridge width can be considerably shrunk, leading to smaller devices with lower drive currents. However, because of the strong confinement, there exists no cutoff frequency for the TM mode in this waveguide structure. This implies greater impedance mismatch with vacuum at the ridge facets, which considerably increases the reflectance at the facet. Although, the increased reflectance minimizes the mirror loses, it also acts detrimental to the beam profile and the output powers extracted from the device.

1.5.3 Graphene: a material for THz plasmonics

In a THz QCL, the gain medium and the waveguide are two disparate entities. The optical gain arises from intersubband transitions in GaAs/AlGaAs materials, and the optical wave is supported by the plasmonic mode at the metal/active region interface. In the year 2008, another material came to the attention of the THz community. This exotic material was called graphene, a two dimensional monolayer of carbon atoms arranged in a hexagonal lattice, with zero bandgap. Pitched as a conducting material that could support THz plasmons as well as provide plasmon gain, monolayer graphene quickly gained wide interest from the optical community \[68\].

Compared to traditional metals, graphene is only one atom thin. Therefore, the bound electromagnetic modes (plasmons) are tightly confined to the surface. Furthermore, the conductivity of graphene can be tuned externally with bias by changing the carrier concentration. This implies that the plasmon frequency $\omega_p$, which is function of carrier concentration $n$, can be controlled externally. The plasmon frequency $\omega_p$ of a conventional two dimensional electron gas (2DEG) can also be varied externally with carrier concentration. However, to obtain plasmon frequencies in the THz range, one generally requires low temperatures (4.2 K) \[69, 70\]. In contrast, the plasmon frequencies in graphene can approach THz frequencies at room temperature by external gating \[71\]. The differences between graphene and a 2DEG are summarized in table 1.1.

Figure 1.16(a) illustrates the typical absorption spectrum from graphene. Note that the
### 1.5 THz waveguides

<table>
<thead>
<tr>
<th>Property</th>
<th>Monolayer graphene</th>
<th>2DEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy dispersion</td>
<td>Linear, no gap</td>
<td>Quadratic, energy gap &gt; 1 eV</td>
</tr>
<tr>
<td>Mass of electron</td>
<td>Massless</td>
<td>0.067 m&lt;sub&gt;e&lt;/sub&gt;</td>
</tr>
<tr>
<td>Carrier concentration</td>
<td>10&lt;sup&gt;9&lt;/sup&gt; to 10&lt;sup&gt;13&lt;/sup&gt; cm&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>10&lt;sup&gt;9&lt;/sup&gt; to 10&lt;sup&gt;12&lt;/sup&gt; cm&lt;sup&gt;-2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Gating efficiency</td>
<td>Dielectric/Chemical</td>
<td>Dielectric</td>
</tr>
<tr>
<td>Plasmon frequency ω&lt;sub&gt;p&lt;/sub&gt; dependence on carrier concentration n</td>
<td>Varies as n&lt;sup&gt;1/4&lt;/sup&gt;</td>
<td>Varies as n&lt;sup&gt;1/2&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Table 1.1: Difference between monolayer graphene and 2DEG. Data sourced from [71, 72].

Figure 1.16: (a) Schematic diagram showing typical absorption spectrum of graphene, with Drude peak at THz frequencies, minimal absorption at mid-infrared frequencies due to Pauli blocking and transition to universal 2.3 % absorption in near infrared to visible frequencies. (b) Illustration of the various optical processes corresponding to THz, mid-infrared and visible regions in the absorption spectrum. Reproduced from [73]
Drude peak lies in the THz spectrum, indicated by 1. This is followed by minimal absorption at mid-infrared frequencies due to Pauli blocking, indicated by 2 and finally, a transition to universal 2.3 % absorption in the near infrared to visible frequencies, indicated by 3 [73]. The optical processes corresponding to absorption in the THz, mid-infrared and near-infrared to visible regions is shown in figure 1.16(b). At low energies, where $\hbar \omega$ is less than the thermal energy, transitions occurs via the intraband processes, indicated by 1. At a finite $\hbar \omega < 2 E_F$, where $E_F$ marks the position of the fermi level, disorder can play a role in imparting the momentum for the optical transition, indicated by 2. A transition occurs around $\hbar \omega = 2 E_F$, where direct interband processes lead to a universal 2.3 % absorption, indicated by 3 [73].

The potential for graphene based THz optics ranging from modulators, filters, polarizers and photodetectors is a rapidly evolving field and is discussed in references [73, 74]. Room temperature optical elements that can be a part of an optical system involving compact THz sources such as THz QCLs, would bring the THz technology one step closer to applications in the real world. In this thesis, we explore whether graphene can fulfill some of these needs at the THz frequency.

So far, our definition of a THz gap was restricted to THz sources and waveguides. At times, this absence of a fast, reliable THz detector cripples the development of other THz optical elements. In the next section, we discuss some common detectors that are used in the measurement of a THz response.

### 1.6 THz detectors

Most detectors at THz frequencies (4-40 meV, 1-10 THz) face a problem from high thermal background noise ($k_B T$ at 300 K $\sim$ 25.8 meV). In general all THz detection schemes can be classified as (i) incoherent detection systems, which involve direct detection of signal amplitude and (ii) coherent detection system, which involve detection of phase and amplitude of the THz signal. For an excellent review of current THz detection techniques, the reader is directed to reference [75, 76].

**Direct detection scheme**

Under the direct detection scheme, there are several techniques that can be used to measure the signal amplitude. Some of these schemes are summarized in table 1.2 and are primarily based upon thermal absorption. These detection schemes include thermopiles, golay cells, pyroelectrics and bolometers. Thermopiles are essentially arrays of thermocou-
1.6 THz detectors

Thermopiles, which convert temperature to an electrical output. Golay cells rely upon changes in gas pressure with heat absorption, to detect the THz signal amplitude. Pyroelectrics detectors are based on crystals such as Lithium Niobate and Lithium Tantalate, which measure change in polarization as a function of temperature. Bolometers typically operate at cryogenic temperatures and are based upon the temperature dependent electrical resistance of semiconducting materials such as Si, Ge or InSb. They can also be based upon superconducting materials such as Niobium, where the change in resistance with temperature measures the amplitude of the THz signal. The merit of a detector is assessed in terms of noise equivalent power (NEP), optical responsitivity and rise time, see table 1.2.

<table>
<thead>
<tr>
<th>Detector</th>
<th>Operating temperature</th>
<th>Noise equivalent power $W/\sqrt{Hz}$</th>
<th>Optical responsitivity $V/W$</th>
<th>Rise time $ms$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermopile</td>
<td>300</td>
<td>4.8</td>
<td>$10^4$</td>
<td>16</td>
<td>Roithner-laser¹</td>
</tr>
<tr>
<td>Golay Cells</td>
<td>300</td>
<td>100</td>
<td>$4.8 \times 10^3$</td>
<td>25</td>
<td>Microtech Instruments²</td>
</tr>
<tr>
<td>Pyroelectric detector</td>
<td>300</td>
<td>2</td>
<td>$4.2 \times 10^{-3}$</td>
<td>10-100</td>
<td>Gentec-EO³</td>
</tr>
<tr>
<td>Composite Bolometer</td>
<td>4.2</td>
<td>0.02</td>
<td>$10^4$</td>
<td>0.4</td>
<td>QMC Instruments⁴</td>
</tr>
</tbody>
</table>

Table 1.2: Comparision between different commercially available THz detectors. Data was sourced from manufacturer specifications and reference[76].

Although, the specifications listed in table 1.2 reflect only a small subset of detectors, in general, the uncooled bolometers display the highest sensitivity (low noise equivalent power) among the commercially available detection schemes. At liquid He temperatures, the bolometers display a noise equivalent power approaching $pW/\sqrt{Hz}$. Cryogenic bolometers also measure the THz signal with the lowest response times (< 1 ms). More recently, the field of THz detection has caught renewed interest with development of plasma wave detection in field effect transistors based on low-dimensional materials such as graphene and semiconducting nanowires [77]. Some THz detectors based on graphene use Landau level quantization to detect energies of 10 meV, at a very small magnetic field (0.5 T) [78]. Reports on the bolometric response of graphene and carbon nanotube con-

¹http://www.roithner-laser.com
²http://www.mtinstruments.com
³https://www.gentec-eo.com/
⁴http://www.terahertz.co.uk/

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tinues to gain traction \[79, 80, 81\], but so far these techniques are still in their infancy.

**Coherent detection scheme**

The methods discussed above only measure the intensity of THz radiation and not the temporal profile of the radiation. Electro-optic sampling and photoconductive antennas enable the measurement of the THz waveform over time. Both these methods work in the same manner as their emitter counterparts, except in reverse. In the first case, an optical beam enters along with the THz pulse into an electro-optic crystal. The THz field modulates the polarization ellipticity of the optical probe passing through the crystal. The \(x\) and \(y\) components of the polarization give information about the amplitude and phase of the THz pulse. The photoconductive antenna measures an induced current across the antenna as a result of the incident THz radiation, which is probed by the femtosecond pulse. Other methods of detection THz radiation include heterodyne techniques, which requires a local oscillator emitting at the THz frequency of interest. The THz signal is mixed with local oscillator, for example a Schottky diode and is down converted signal. This technique offers a high spectral resolution and a high sensitivity.

1.7 Thesis outlook

This thesis is organized as follows. Chapters 2 to Chapter 4 are driven by the motivation to achieve higher operating temperature in THz QCLs through lateral confinement. In **Chapter 2**, we develop our understanding of lateral confinement from a simple system - a resonant tunneling diode to a more complicated structure - a THz quantum cascade laser. Building on from theoretical predictions, in **Chapter 3** we discuss the various processing routes explored to meet the requirements of lateral confinement in THz QCLs. **Chapter 4** discusses THz quantum cascade lasers with an active region of thickness \(\leq 3.5 \, \mu\text{m}\). Termed as ultrathin THz QCLs, these lasers form the foundations of a gain medium that is suitable for studying effects of lateral confinement. In **Chapter 5**, we move away from THz QCLs and investigate plasmonic properties of a two-dimensional material - monolayer graphene, which promises interesting applications at THz frequencies owing to voltage tunability of carrier concentration. Finally, conclusions and future work discussed in **Chapter 6** reflect on some of ideas built upon in this doctoral work.
Chapter 2

Nanopillars in RTDs and QCLs: Theory

2.1 Introduction

Considering the compact and powerful nature of QCLs as a source bridging the THz gap, achieving room temperature operation would open up doors to a plethora of opportunities in both academic and commercial areas of sensing, spectroscopy and imaging.

In Chapter 1, we discussed that the maximum operating temperature of THz QCLs is limited by optical phonon scattering of hot electrons in the upper lasing level. These electrons gain sufficient in-plane kinetic energy to relax non-radiatively into the lower lasing level. This decay which occurs at a very fast time scale (2-3 ps), lowers the population inversion (and hence gain), in THz QCLs. Discretization of in-plane momentum may suppress this non-radiative inter-sub-band relaxation mechanism, and enhance the upper state lifetime \[61\]. By imposing a lateral potential, i.e. confining the electrons in-plane, the momentum can be discretized. These predictions have been verified by application of high magnetic fields to THz QCLs \[82\], where electrons are confined by the cyclotron radius, and also in a cascade of self-assembled quantum dots \[58\], where electrons are confined spatially by the dot radius.

In this chapter, we explore a top down approach to obtain lateral confinement in THz QCLs. This lateral confinement is imposed in the radial direction by nanofabrication methods. This radial potential is superimposed on top of the epitaxially imposed confinement in the longitudinal growth direction, which gives rise to 3-D confinement in these nanopillar arrays.

Before we delve into the energy spectrum and optical properties of a laterally confined
THz QCL, it is useful to study the effect of lateral confinement in a simpler III-V heterostructure - a resonant tunneling diode. Consisting of a single well, sandwiched between two barriers, a resonant tunneling diode (RTD) exhibits negative differential resistance (NDR) as the applied voltage aligns with energy states associated with the longitudinal confinement of the two-dimensional electron gas \([83]\). Unlike a THz QCL, which is a cascade of several repeat periods, an RTD is a single stage oscillator. RTDs by themselves have been proven to oscillate at frequencies approaching 1 THz, at room temperature \([84]\). However, their gain is derived from the negative differential resistance, unlike QCLs which rely on intersubband transitions. Here, we do not use the RTD as a THz oscillator, but exploit its simplicity to understand the effects of lateral confinement on intersubband transitions in THz QCLs.

The enormous advantage of RTDs is that they exhibit a very clear NDR peak upon alignment in their transport characteristics. This transport behavior will be influenced by discretization of energy states due to an additional potential - imposed by nanopillars. Therefore, RTDs act as a very useful testbed to probe effects of a top-down approach on vertical transport of electrons. We use the RTDs to answer the following questions. The first question, is whether enough optical gain can be achieved by the array of nanopillars. In the first approximation, this translates to whether the nanopillar array can carry a current density that approaches the threshold current densities of THz QCLs, which is typically in the order of hundreds of \(A/cm^2\). The second question relates to the cascade nature of the QCL. Given a fixed nanopillar radius, what is the true lateral potential across the height of the nanopillar, as this may depend upon the surface states and doping of each layer? The third question relates to electron transport through more than a thousand nanopillars, connected in parallel to achieve sufficient gain required for lasing. The question therefore is how statistical deviations arising from fabrication, influences the vertical transport in an ensemble of quantum dots?

In this chapter, we seek to learn from existing models of lateral confinement in an RTD, and translate the ideas to the more complicated QCL structure. We also probe the effect of such lateral confinement on the band structure of the THz QCLs used in this work. Vertical transport through a nanopillar array necessitates the use of a planarizing material and formation of a top electrical contact. This process can influence the optical mode inside a nanopillar array. Therefore, in the final section, we discuss the effect of lateral confinement on the plasmonic mode in a THz QCL nanopillar array and identify optimum geometries.
2.2 General description of RTDs

In this section we provide a general discussion on the band diagram and electrical characteristics of large-area RTDs. The electrons in these large-area RTDs have in-plane momentum, and are confined only in the longitudinal growth direction.

First, let us look at the material composition of an RTD. Figure 2.1(a) shows the band gaps and conduction (valence) band $\Delta E_c (\Delta E_v)$ discontinuities for GaAs, Al$_{0.33}$Ga$_{0.67}$As and AlAs. As is seen from the figure, Al$_{0.33}$Ga$_{0.67}$As and AlAs are higher band gap materials as compared to GaAs. Electrons in GaAs surrounded by either Al$_{0.33}$Ga$_{0.67}$As layers on both sides, or AlAs layers on both sides, will be confined in a potential well, leading to quantization of energy states in the growth direction. It is this quantization, which leads to negative differential resistance (NDR) in RTDs.

Figure 2.1(b) shows the schematic diagram of an epitaxially grown double barrier RTD. This system is described by the time independent Schrödinger equation in the growth ($z$) direction, given as:

$$-rac{\hbar^2}{2m^*} \frac{\partial^2}{\partial z^2} \psi(z) + V(z) \psi(z) = E \psi(z) \quad (2.1)$$

Here, $m^*$ is the effective mass of electrons inside the quantum well and $V(z)$ is the potential in the growth direction. At the well boundaries, $V(z) = V_o = \Delta E_c$, which is typically 0.26 eV in Al$_{0.33}$Ga$_{0.77}$As/GaAs/Al$_{0.33}$Ga$_{0.67}$As structures and 1.1 eV in AlAs/GaAs/AlAs structures. The wavefunction of the electron is described by the eigen function $\psi(z)$.

By solving eqn. 2.1 under appropriate boundary conditions, the energy states in the quantum well of finite height $V_o$, can be calculated by solving the transcendental equation:

$$E_n = -\frac{\hbar^2}{2m^* L_w} \left( \frac{\pi(n + 1)}{\sqrt{E_n/V_o}} \right)^2, \quad n = 0, 1, 2, ... \quad (2.2)$$

It is easy to see from eqn. 2.2, that the energy levels can be engineered by changing the width, $L_w$, of the quantum well [87]. The tunneling rate depends upon the width of the barrier $L_b$. Figure 2.1(c) shows the ground and excited energy states in an Al$_{0.33}$Ga$_{0.67}$As / GaAs / Al$_{0.33}$Ga$_{0.67}$As double barrier RTD, with $L_w = 10$ nm and $L_b = 5$ nm. The transmission probabilities of electrons tunneling through the Al$_{0.33}$Ga$_{0.67}$As / GaAs / Al$_{0.33}$Ga$_{0.67}$As double barrier RTD is described by the following equation, and plotted in figure 2.1(d).

$$T(E) = T_n \frac{(1/2\Gamma)^2}{(1/2\Gamma)^2 + (E - E_n)^2}. \quad (2.3)$$
2. NANOPILLARS IN RTDS AND QCLS: THEORY

Figure 2.1: (a) Band gaps, conduction (valence) band $\Delta_c$ ($\Delta_v$) discontinuities for GaAs, Al$_{0.33}$Ga$_{0.67}$As and AlAs. (b) Schematic of the epitaxially grown barrier/well/barrier structure. (c) Conduction band diagram of unbiased double barrier resonant tunneling diode showing the energy levels in the well. (d) Transmission function as a function of energy. The bound states and the transmission coefficients have been calculated for an Al$_{0.33}$Ga$_{0.67}$As/GaAs/Al$_{0.33}$Ga$_{0.67}$As double barrier structure using RTD NEGF tool [85, 86]. The thickness of the GaAs well is 10 nm, and the thickness of the Al$_{0.33}$Ga$_{0.67}$As barrier is 5 nm.

Here, $\Gamma$ is the full width half maximum (FWHM) of the resonance peak and $T_n$ is the transmission when energy $E = E_n$.

The tunneling current density $J$, for each contact, can be evaluated by integrating the density of states $g(E)$, with the Fermi function $f(E)$, the electron charge $e$, the electron velocity $v$ and the transmission coefficient $T(E)$. This is given as

$$J = \int_{0}^{\infty} g(E)f(E)evT(E)dE \quad (2.4)$$

In the case of a large area RTD, the contacts can be treated as bulk and the electrons confined in the well can be treated as a two-dimensional electron gas.

Figure 2.2 plots the theoretical current density of an Al$_{0.33}$Ga$_{0.67}$As / GaAs / Al$_{0.33}$Ga$_{0.67}$As
2.2 General description of RTDs

Figure 2.2: Theoretically evaluated current-voltage characteristics of an RTD, showing (i) current before alignment due to non-resonant processes (ii) current at alignment of the Fermi level with the ground state (iii) maximum current at alignment of the conduction band with the ground state followed by negative differential resistance due to misalignment (iv) increase in current through barriers due to thermionic emission and scattering assisted tunneling. The current was calculated for a double barrier RTD with 5 nm thick Al$_{0.33}$Ga$_{0.67}$As barriers and a 10 nm GaAs well, using RTD NEGF tool [85, 86].
double barrier RTD, with the energy states indicated in figure 2.1. Also shown in figure 2.2 is the band structure of the RTD under different bias conditions. At a low bias, case (i), a small current flows due to non-resonant processes such as thermionic emission over barriers and scattering assisted tunneling. As the bias is increased to a point (ii) on figure 2.2, the Fermi level of the left contact \(E_{LF}\) aligns with the ground state of the well \(E_o\). Here, the current starts to flow due to resonant tunneling of electrons. This point is indicated by a threshold bias \(V_{th}\). On further increase in bias, the conduction band of the left contact \(E_c\) aligns with the ground state of the well \(E_o\). When this occurs, maximum current tunnels into the resonant level. This is the bias at which peak current is measured, and is indicated by (iii) in figure 2.2. The voltage and current density at the point of resonance is indicated by \(V_p\) and \(J_p\), respectively. Since \(V_p\) is the voltage dropped across the two contacts, the resonance condition for the ground state is met when \(E_o = V_p/2\). In an RTD, a clear NDR signature is obtained when the conduction band aligns with the ground state, and the current reduces as the bias is increased, creating a so called valley. The voltage and current density at the valley is indicated by \(V_v\) and \(J_v\), respectively. The difference between the peak voltage \(V_p\) and the voltage \(V_v\) at the valley is called \(\Delta V_{NDC}\), and the ratio between the peak to valley currents \((J_p/J_v)\) is called PVCR. The current rises again due to non-resonant processes, case (iv) in figure 2.2, until the Fermi level meets the next energy state given by eqn. 2.2.

The exact mechanism of resonant tunneling depends upon the width of the barrier \(L_b\). For example, resonant tunneling may occur by coherent (Fabry-Perot) mechanism, which preserves the phase of the electron wavefunction or by incoherent (sequential) mechanism, which destroys the phase coherence of electrons [88]. The latter mechanism dominates RTD transport in the case where \(L_b\) is greater than 7 nm. Since the barrier width for RTDs used in this work is \(L_b \leq 7\) nm, we will assume coherent tunneling of electrons. Theoretical description of RTD transport is detailed in [83] and the interested reader is directed towards the references listed within [83].

### 2.3 Confinement in a single nanopillar RTD

In the previous section, we discussed quantization of energy states in a double barrier RTD due to confinement of electrons in the longitudinal (growth) direction. When a lateral potential is imposed upon the two-dimensional electrons, the energy levels in the well split into multiple energy levels. This is shown in figure 2.3(a), in a schematic diagram, where the energy states denoted as \(E_0, E_0, E_1\) in figure 2.1 split into multiple energy states, with a difference \(\Delta E\). The splitting of the energy levels, \(\Delta E\) depends upon the radial potential
V(r) that is imposed upon the electrons.

Figure 2.3: (a) Schematic diagram, showing splitting of energy levels due to lateral confinement (b) Current voltage characteristics of the first zero-dimensional RTD, as a function of temperature. The arrows indicate the voltage positions corresponding to lateral quantization. Reproduced from [89].

In the year 1988, Reed et. al were the first to demonstrate lateral confinement in RTDs [90]. Using a top-down nanofabrication approach to impose a lithographically imposed potential, Reed et. al showed that discretization of energy states in laterally confined RTD can be observed by measuring the transport characteristics of such structures, see figure 2.3. They were the first to correlate lateral quantization with the fine structure observed at low temperatures, appearing as multiple NDR peaks in the current-voltage spectrum.

We will now discuss the simplistic model that Reed et. al employed to compute the energy splitting $\Delta E$, in laterally confined RTDs.

### 2.4 Reed’s simplistic model for a zero-dimensional RTD

Figure 2.4 shows the schematic diagram of the longitudinal and lateral potential in a zero-dimensional RTD. Lateral confinement is imposed by etching a nanopillar of physical radius $R_p$. The epitaxial composition of the double barrier RTD is given in figure 2.4(a).
2. NANOPILLARS IN RTDS AND QCLS: THEORY

Figure 2.4: (a) Epitaxial structure of the double barrier RTD used by Reed et. al (b) Schematic description of the conduction band diagram plotted in the longitudinal direction. The schematic shows energy splitting of energy states due to lateral confinement. (c) Schematic description of the parabolic potential, in the radial direction, which arises due to surface depletion. Adapted from [90].
The density of interface states at the exposed surface of the nanopillar causes the conduction band to bend upwards with respect to the Fermi level, causing a depletion of carriers over a length $R_d$, in order to maintain charge neutrality in the complete structure. The electrostatic radius is then described as $R_e = R_p - R_d$. The bending of conduction band leads to the formation of a parabolic potential in the radial direction.

Reed et al. [89] described this parabolic potential as:

$$\Phi(r) = \Phi_T (1 - (R_p - r)/R_d)^2$$ \hspace{0.5cm} (2.5)$$

where $\Phi_T$ is the height of the potential determined by Fermi pinning, at $r = R_p$. The above model is equivalent to a harmonic potential of the form $V(r) = m_e^* \omega^2 r^2 / 2$, with the boundary condition that $V(R_p) = m_e^* \omega^2 R_p^2 / 2 = \Phi_T$. Solving the Schrödinger equation in the radial direction, the energy level splitting is evaluated as

$$\Delta E = \hbar \omega = \frac{\hbar}{R_p} \sqrt{\frac{2\Phi_T}{m_e^*}}$$ \hspace{0.5cm} (2.6)$$

where $m_e^*$ is the effective mass of electron and $\Phi_T$ is assumed to be 0.7 eV for GaAs.

The model proposed by Reed et al. [89] suffers from significant simplifications. Firstly, Reed et. al’s model does not include intersubband mixing effects, that occurs if the lateral potential is not harmonic. Therefore, any slight deviation from cylindrical geometry is likely to have an influence on the energy splitting $\Delta E$. Secondly, Reed et. al did not calculate the three-dimensional potential across the RTD, which arises due to differences in the doping densities within each epitaxial layer. This problem has been addressed in later work, for example see [83, 91, 92]. Differences in doping densities can also lead to mode mixing. For a bulk material, the depletion width $R_d$ is inversely proportional to $\sqrt{N_d}$ [93]. This implies that the undoped well will have a greater $R_d$, as compared to the doped contact [94]. In three-dimensions, this leads to the formation of an hour-glass potential with a neck in the undoped well. Calculation of energy states for this potential requires a scattering matrix approach, shown by Mizuta et. al in [83]. The third simplification lies in the estimation of the potential $\Phi_T$ at $r = R_p$. The potential $\Phi_T$ depends upon the doping of the material and the density of interface states, which exist at the sidewalls of the nanopillar. However, this has been kept constant at 0.7 eV in the above calculation.

In 2012, Chia et. al calculated the lateral potential for a homogeneous GaAs nanopillar, taking this dependence into account [95]. However, so far, these calculations have not been extended to understand electron transport in laterally confined RTDs. Therefore, in the next subsection, using Chia et. al’s model for homogeneous GaAs nanopillars, we
attempt to estimate the lateral potential $\phi(r)$ taking into account (i) the doping of each layer, and (ii) the density of interface states, in a nanopillar RTD.

### 2.5 Effect of surface states

Figure 2.5 shows the schematic band diagram of an n-doped homogeneous GaAs nanopillar in the radial direction proposed by Chia et. al, which suggests that parabolic potential $\phi_T = 0.7$ eV, is not a constant but dependent upon many interdependent parameters.

#### 2.5.1 Interface charge density

From figure 2.5, we note that the bands bend upwards to maintain charge neutrality, as an opposite and an equal space charge $Q_{sc}$ builds up to compensate for the interface states $Q_{it}$ (per unit area), which exists at the surface. It is this space charge $Q_{sc}$ that gives rise to depletion of carriers inside the nanopillar. The interface charge $Q_{it}$ can be written in terms of the charge neutrality level $E_{CNL}$, the Fermi energy $E_F$ and the density of interface states (traps per unit area per eV), $D_{it}$ as:

$$Q_{it} = -e \int_{E_{CNL}}^{E_F} D_{it} \, dE \quad (2.7)$$

Before we delve into the origin of the surface states, let us examine eqn. 2.7 qualitatively. $Q_{it}$ depends upon charge neutrality level $E_{CNL}$ which depends upon the doping of the material and the processing conditions of the nanopillar. The Fermi level $E_F$ remains constant as a function of nanopillar radius and depends only on the doping of the material. The density of interface states $D_{it}$ may depend upon the doping. Out of these three parameters, only $E_F$ can be estimated accurately.

#### 2.5.2 Charge neutrality level

Although Chia et. al evaluate the parabolic potential in terms of $E_{CNL}$ and $D_{it}$, they assume $E_{CNL}$ to be 0.53 eV, referred from the top of the valence band [95]. From our survey of literature, we feel that this common assumption may not be accurate. We find that $E_{CNL}$ depends upon material doping, processing conditions and measurement method. In some cases, the error associated with the measurement of $E_{CNL}$ is nearly 60%.

The origin of the interface states can be traced to the Ga-type or As-type dangling bonds in a UHV cleaved GaAs (110) surface. These dangling bonds have energies lying in
2.5 Effect of surface states

Figure 2.5: Schematic diagram of conduction and valence band of an n-doped GaAs nanopillar, in the radial direction. The diagram shows band bending due to interface states. Adapted from [95].

between the band gap of the material [96]. The charge neutrality level $E_{CNL}$ separates the donor As states from the acceptor Ga states. In an n-doped GaAs, the Fermi level $E_F$ is pinned close to $E_{CNL}$ such that the bands bend upwards to compensate for the negatively charged occupied acceptor states with $E_{CNL}$ close to midgap. In p-doped GaAs the bands bend downwards to compensate for the positively charged empty donor states with $E_{CNL}$ in the lower half of the band gap. The position of the charge neutrality level, $E_{CNL}$ (and consequently $Q_{it}$) is also affected by surface processing such as etching, ion-bombardment and exposure to gases like oxygen and atomic hydrogen, varying from 0.65 to 0.8 eV for n-doped GaAs and 0.45 to 0.55 eV for p-doped GaAs [96].

Reported values of $E_{CNL}$ also vary depending upon the measurement method. For example, measurements based on metal-GaAs studies report $E_{CNL}$ to be equal to 0.53 eV, with an error of ±0.33 eV [93, 97]. However, measurements based on photoelectric
studies suggest an $E_{CNL}$ of 0.76 eV for n-doped GaAs. According to the authors, this value may further depend upon the crystallographic plane [97].

Since we are interested in the depletion width of the undoped GaAs well to understand lateral confinement in nanopillar RTDs, we would like to point out that it is difficult to rely completely on $E_{CNL}$ evaluated from studies on n-doped or p-doped GaAs. However, independent of this assumption, Chia’s model provides an analytical understanding of surface depletion in nanopillars as a function of $E_{CNL}$ and $D_{it}$. Therefore, in the following discussion, we use the same value of $E_{CNL}$ as the authors, i.e. $E_{CNL} = 0.53$ eV, referred from the top of the valence band.

### 2.5.3 Chia et. al’s model for homogeneous GaAs nanopillar

The potential distribution in a GaAs nanopillar can be described by writing Poisson’s equation in cylindrical coordinates. For a long homogeneous nanopillar, i.e. neglecting any confinement in the growth direction, Poisson’s equation can be simplified to an ordinary differential equation in $r$, as follows:

\[
\frac{\partial^2 \phi}{\partial r^2} + \frac{1}{r} \frac{\partial \phi}{\partial r} = -\frac{\rho}{\epsilon} \tag{2.8}
\]

Here $r$ is the radial distance, $\rho$ is the density of charge carriers in bulk GaAs and $\epsilon$ is the permittivity of GaAs. The solution to the differential eqn. 2.8 is given by

\[
\Phi(r) = -\frac{\rho}{4\epsilon} r^2 + C_1 \ln(r) + C_2 \tag{2.9}
\]

where $C_1$ and $C_2$ are constants. The constants can be determined by imposing appropriate Neumann and Dirichlet boundary conditions. From figure 2.5, we see that in the case of a partially depleted nanopillar, $R_d < R_p$, the following boundary conditions hold.

\[
\Phi(R_e) = \Phi_o \quad (R_d < R_p) \tag{2.10}
\]

\[
\frac{d\Phi(r)}{dr} \bigg|_{r=R_d} = 0 \tag{2.11}
\]

where eqn. 2.11 merely states that the radial component of the electric field is zero in the steady state. We note that the above boundary conditions are also applicable to the case of undoped GaAs, where $E_F$ approaches midgap. In the case of undoped GaAs, $\phi_o$ in eqn. 2.10 approaches 0.

On substituting the boundary conditions (eqns. 2.10-2.11) in to eqn. 2.9, the following
solution is obtained for the radial potential:

\[ \Phi(r) = \frac{\rho R_e^2}{2e} \left( -\frac{r^2}{2R_e^2} + \ln \left( \frac{r}{R_e} \right) + \frac{1}{2} \right) + \Phi_o \] (2.12)

Eqn. 2.12 dictates that \( \Phi(r) \big|_{r=R_p} = \Phi_s \), where \( \Phi_s \) is the surface potential and is equal to

\[ \frac{\rho R_e^2}{2e} \left( -\frac{R_p^2}{2R_e^2} + \ln \left( \frac{R_p}{R_e} \right) + \frac{1}{2} \right) + \Phi_o. \]

Under the assumption of complete ionization in the space charge region, the charge density \( \rho = eN_d \) where, \( N_d \) is the number of dopants per unit volume. Therefore, the radial potential given by eqn. 2.12 can be rewritten in terms of doping density as:

\[ \Phi(r) = \Phi_o, \quad 0 < r < R_e \] (2.13)

\[ \Phi(r) = \frac{eN_d R_e^2}{2e} \left( -\frac{r^2}{2R_e^2} + \ln \left( \frac{r}{R_e} \right) + \frac{1}{2} \right) + \Phi_o, \quad R_e < r < R_p \] (2.14)

The position of the Fermi level \( E_F \) referred to the intrinsic level \( E_i \) at the center of the nanopillar is determined from the Boltzmann approximation as

\[ N_e \exp \left( \frac{-(E_c - E_F)}{kT} \right) = N_e \exp \left( \frac{-(E_g / 2 - \Phi_o)}{kT} \right) = N_d \] (2.15)

Here, \( E_c \) is the conduction band and \( N_e = 2 \left( m^* kT / 2\pi\hbar^2 \right)^{3/2} \) is the effective density of states in the conduction band. \( N_e = 4.7 \times 10^{17} \text{ cm}^{-3} \) in GaAs. Given the doping density \( N_d \), we can estimate the potential \( \Phi_o \) at the center of the nanopillar.

Finally, the depletion width \( R_d \) and hence, the electrostatic radius \( R_e \) are determined by invoking the charge neutrality condition given below, where the sum of all bulk and surface charges is zero.

\[ \pi(R_p^2 - R_e^2) eN_d + 2\pi R_p Q_{it} = 0 \] (2.16)

where \( Q_{it} \) is determined by eqn. 2.7. From figure 2.5, we note that \( Q_{it} \) can be expressed in terms of the surface potential \( \Phi_s \) and \( \Delta \), which is the difference between \( E_i \) and \( E_{CNL} \) at the surface of the nanopillar. Therefore \( Q_{it} \) can be written as:

\[ Q_{it} = -e \int_{E_{CNL}}^{E_F} D_{it} \, dE = -e \int_{E_i - \Delta}^{E_i + \Phi_s} D_{it} \, dE = -e D_{it} (\Delta + \Phi_s) \] (2.17)

The surface potential \( \Phi_s \) can be determined by substituting eqn. 2.17 into eqn. 2.16.

\[ ^{1}\text{From the online semiconductor database, url: http://www.ioffe.ru/SVA/NSM/Semicond/GaAs/bandstr.html} \]
This is given below.

\[ \phi_s = \frac{(R_p^2 - R_e^2) e N_d}{2 R_p e D_{it}} - \Delta \]  

(2.18)

The surface potential \( \phi_s \) can be equated to eqn 2.12 at \( r = R_p \). Therefore, the eqns. 2.15, 2.14 and 2.16 can be written as:

\[ \frac{(R_p^2 - R_e^2)e N_d}{2 R_p e D_{it}} - \Delta = \frac{e N_d R_p^2}{2 e} \left( - \frac{R_p^2}{2R_e^2} + \ln \left( \frac{R_p}{R_e} \right) + \frac{1}{2} \right) + \Phi_o \]  

(2.19)

Eqn. 2.19 is a transcendental equation. Given \( N_d, D_{it} \) and \( E_{CNL} \), eqn. 2.19 can be solved to estimate \( R_e \). Before proceeding on to the results, let us reiterate the key features of Chia et. al’s model.

The first point of significance is that the electrostatic radius \( R_e \) and the surface potential \( \phi_s \) are dependent upon each other. Knowledge of \( \phi_s \) determines \( R_e \) according to eqn. 2.17. However, \( \phi_s \) depends upon \( R_e \) as \( \rho \frac{R_e^2}{2e} \left( - \frac{R_p^2}{2R_e^2} + \ln \left( \frac{R_p}{R_e} \right) + \frac{1}{2} \right) + \Phi_o \). Solution of eqn. 2.12, and therefore \( \phi_s \) and \( R_e \) requires us to invoke the charge neutrality condition (eqn. 2.16).

Note, that the charge neutrality condition in bulk is different from charge neutrality condition in the nanopillar. Text book calculations of depletion width are typically based on p-n junction models. In the case of a one-sided abrupt semiconductor junction (i.e \( p^+n \) or \( n^+p \)), the depletion width is equal to \( \sqrt{\frac{2e \phi_r}{\epsilon N_d}} \), where \( \phi_r \) is the amount of band bending at the surface of the junction [93]. Previous studies on lateral confinement in RTDs inaccurately translate this depletion width, derived for bulk Schottky junctions, to surface depletion in nanopillars, with \( R_d = R_p - R_e = \sqrt{\frac{2e (\phi_o - \phi_s)}{\epsilon N_d}} \), where \( \phi_o - \phi_s = 0.7 \text{ eV} \) [91, 94]. In a finite sized homogeneous nanopillar, the correct charge neutrality condition is calculated by balancing the interface charge around the curved surface of the nanopillar, with the space charge inside the volume of the nanopillar. This is the second point of importance, and is described by eqn. 2.16.

The third salient feature of Chia et. al’s model is that the electrostatic radius \( R_e \) depends upon the doping density \( N_d \), the density of interface states \( D_{it} \) and \( E_{CNL} \). We know from section 2.5.2 that \( E_{CNL} \) may depend upon \( N_d \) as well as other material and measurement parameters. Furthermore, \( D_{it} \), which is typically quoted as \( 1.25 \pm 1 \times 10^{14} \text{ cm}^{-2} \text{eV}^{-1} \) in GaAs may not be a constant or uniformly distributed in the forbidden gap [93, 97, 98]. In the calculations below, we neglect any functional or phenomenological dependence of \( E_{CNL} \) and \( D_{it} \) on other parameters.
2.6 Results: extension of Chia’s model to double barrier RTD

Figure 2.6(a) shows the schematic diagram of a double barrier RTD. The $n^+$ doped GaAs contact, GaAs spacer, AlAs (or, Al$_x$Ga$_{1-x}$As) barrier and undoped GaAs well are indicated in the diagram. For surface depletion calculations, we ignore the thin barrier layers, typically $\leq 7$ nm. The structure and doping concentrations listed in figure 2.6(a) are representative of real RTD structures used in this thesis, see Chapter 3. In the results discussed below, we neglect the depletion of carriers at the interface of each epitaxial layer, i.e. $n^+$ doped GaAs contact, GaAs spacer and undoped GaAs well are assumed to be non-interacting.

In figure 2.6(b-e), we plot the electrostatic radius $R_e$, estimated from eqn. 2.19, as a function of density of interface states $D_{it}$ for a homogeneous GaAs nanopillar of a constant $R_p$. The doping $N_d$ is varied according to the epitaxial layer considered in the calculation. For example, the doping $N_d$ of the homogeneous nanopillar in figure 2.6(b), is equal to the intrinsic carrier concentration in an undoped quantum well. Therefore, we use $N_d = N_i = 2 \times 10^6$ cm$^{-2}$, which is the intrinsic carrier concentration in GaAs. Figure 2.6(c) shows the variation of $R_e$ as a function of $D_{it}$, in a homogeneous GaAs nanopillar with a doping concentration $N_d$ equal to $1 \times 10^{16}$ cm$^{-2}$, which is the typical doping concentration of a GaAs spacer. Figure 2.6(d-e) shows the electrostatic radius $R_e$ as a function of $D_{it}$, in a homogeneous GaAs nanopillar, with doping concentration $N_d$ equal to $5 \times 10^{16}$ cm$^{-2}$ and $8 \times 10^{16}$ cm$^{-2}$, respectively, which is an order of magnitude less than the heavily $n^+$ doped GaAs contact. The reason for these values of $N_d$ is explained in section 2.6.3.

2.6.1 Undoped GaAs Well

Let us first consider the behavior of $R_e$ vs $D_{it}$, in the undoped well. We note from figure 2.6(a) that there exists a critical density of states $D_{it}^c$, for each pillar size, beyond which the nanopillar is fully depleted, or pinched off. This density depends upon the physical radius of the nanopillar, i.e. $D_{it}^{200}$ for a 200 nm radius nanopillar is higher than the $D_{it}^{50}$ for a 50 nm nanopillar. This is a consequence of the charge neutrality condition. Therefore, while a high $Q_{it}$ may cause complete depletion of charge carriers in a 50 nm pillar, it will only cause partial depletion in a 200 nm pillar. From the calculations at $N_d = N_i$, we infer that the electrostatic radius $R_e$ falls rapidly with $D_{it}$ for all sizes of nanopillars, i.e. $R_p = 50$ nm to $R_p = 200$ nm as a function of $D_{it}$, as it approaches the critical density, which separates the partially depleted regime from the fully depleted regime.

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$^1$From the online semiconductor database, url: http://www.ioffe.ru/SVA/NSM/Semicond/GaAs/bandstr.html
2. NANOPILLARS IN RTDS AND QCLS: THEORY

Figure 2.6: (a) Schematic diagram of a double barrier RTD, showing the n+ doped GaAs contacts, GaAs spacer, AlAs (or AlxGa1−xAs) barrier and undoped GaAs well. (b) Electrostatic radius $R_e$ as a function of interface states $D_{it}$, in the undoped GaAs well. The doping density is assumed to be equal to intrinsic carrier concentration, which is $N_d = 2 \times 10^6$ cm$^{-2}$. (c) Electrostatic radius $R_e$ as a function of interface states $D_{it}$, in the GaAs spacer doped with a carrier concentration $N_d = 1 \times 10^{16}$ cm$^{-2}$. (d) Electrostatic radius $R_e$ as a function of interface states $D_{it}$, in n+ GaAs doped with a carrier concentration $N_d = 5 \times 10^{16}$ cm$^{-2}$. (e) Electrostatic radius $R_e$ as a function of interface states $D_{it}$, in n+ GaAs doped with a carrier concentration $N_d = 8 \times 10^{16}$ cm$^{-2}$. 
2.6 Results: extension of Chia’s model to double barrier RTD

Figure 2.7: Schematic diagram of surface depletion in undoped GaAs nanopillars. Four different cases of $R_p$ are discussed, i.e. $R_p$ ≤ 100 nm, 100 nm, 150 nm and 200 nm. **Top panel** shows partial depletion in undoped GaAs nanopillars, in all four cases of $R_p$. The density of interface states is constant ($2 \times 10^{13}$ cm$^{-2}$eV$^{-1}$) and less than the critical density of states for all the nanopillars. **Bottom panel** shows partial depletion in undoped GaAs nanopillars with $R_p \leq 100$ nm, and complete depletion in the smallest nanopillar with $R_p = 50$ nm. The density of interface states is constant in all four cases and is equal to $1 \times 10^{14}$ cm$^{-2}$eV$^{-1}$. This density is greater than $D_{it}^{50}$ but less than $D_{it}^{100}$, $D_{it}^{150}$ and $D_{it}^{200}$.
Figure 2.7 illustrates this idea in a schematic diagram. The top panel in figure 2.7 shows partial depletion in undoped GaAs nanopillars with size $R_p$ varying from 50 nm to 200 nm. Note, that the density of interface states is constant ($2 \times 10^{13} \text{ cm}^{-2} \text{eV}^{-1}$) for all four nanopillars. Theoretically, $Q_{it}$ depends upon $D_{it}$ and the surface potential $\phi_s$, which is $\propto R_e^2$, see eqn. 2.17. For simplicity in understanding the result, we have used $Q_{it} \propto D_{it}$ and $R_e^2$ in figure 2.7. At low doping densities, dopants within the nanopillar volume, ionize to balance the interface charge. At a density of states equal to $2 \times 10^{13} \text{ cm}^{-2} \text{eV}^{-1}$, the 200 nm pillar has an electrostatic radius $R_e = 192$ nm, the 150 nm pillar has an electrostatic radius $R_e = 141$ nm, the 100 nm pillar has an electrostatic radius $R_e = 91$ nm and the 50 nm pillar has an electrostatic radius $R_e = 42$ nm.

The bottom panel in figure 2.7 shows the smallest nanopillar with $R_p = 50$ nm pinching off when $D_{it}$ is increased to $1 \times 10^{14} \text{ cm}^{-2} \text{eV}^{-1}$, which is greater than $D_{it}^{50}$. At this density of states, the larger nanopillars are still partially depleted, but their depletion width increases to accommodate the higher amount of interface charge. The 200 nm pillar has an electrostatic radius $R_e = 159$ nm, the 150 nm pillar has an electrostatic radius $R_e = 109$ nm, the 100 nm pillar has an electrostatic radius $R_e = 54$ nm and the 50 nm pillar is fully depleted ($R_e = 0$).

### 2.6.2 Doped GaAs Spacer

Compared to the undoped GaAs well, the doping density in a GaAs spacer is much higher, typically $N_d = 1 \times 10^{16} \text{ cm}^{-2}$. At this density, the results plotted in figure 2.6(c) show counter-intuitive behavior. Similar to the results evaluated for the undoped well, the electrostatic radius $R_p$ in a GaAs spacer falls rapidly with $D_{it}$, as it approaches the critical density. However, at this doping density, the critical density $D_{it}^{50}$ for a doped 50 nm pillar is lower than the $D_{it}^{50}$ for an undoped 50 nm pillar, see figure 2.6(b). This is true for all sizes of nanopillars, between $R_p = 50$ nm to $R_p = 200$ nm. We believe that this behavior occurs because $R_e$ does not depend upon $N_d$ in a straightforward way for a finite-sized, cylinder. This is unlike the case of a planar slab (bulk surface) where the depletion width is $\propto 1/\sqrt{N_d}$. The dependence of $R_e$ on $N_d$, at different values of $D_{it}$ is shown in figure 2.9 and will be discussed in section 2.6.4.

### 2.6.3 Doped GaAs contact

At $N_d = 5 \times 10^{16} \text{ cm}^{-2}$ and $8 \times 10^{16} \text{ cm}^{-2}$, see figure 2.6(d-e), the behavior of $R_e$ as a function of $D_{it}$ is different from what we observe in figure 2.6(b-c). At $N_d = 5 \times 10^{16} \text{ cm}^{-2}$, see figure 2.6(d), $R_e$ is nearly equal to $R_p$, for a 200 nm pillar, decreasing to $\approx$
180 nm as $D_{it}$ approaches $1 \times 10^{15}$ cm$^{-2}$eV$^{-1}$. As $N_d$ is increased further, up to $8 \times 10^{16}$ cm$^{-2}$, see figure 2.6(e), the depletion width for a 200 nm pillar is negligible. The interface charge $Q_{it}$ due to dangling bonds outside the nanopillar sidewall is balanced by an equal and opposite space charge $Q_{sc}$ due to a high density of ionized donors inside the sidewall. Therefore, at these high doping densities, the 200 nm pillar never pinches off for the entire range of $D_{it}$ plotted in figure 2.6. In the case of a 50 nm and a 100 nm pillar, the surface area is small when compared to the 200 nm nanopillar. Hence, to maintain the charge neutrality condition, carriers from inside the nanopillar volume provide the charge needed to compensate the $Q_{it}$. This can cause a 50 nm (100 nm) pillar to deplete completely at the critical density of interface states given by $D_{it}^{50}$ ($D_{it}^{100}$). Note, the critical density of states $D_{it}^{c}$ required to pinch off a 50 nm or a 100 nm pillar is higher when the doping density $N_d$ is $8 \times 10^{16}$ cm$^{-2}$, as compared to $5 \times 10^{16}$ cm$^{-2}$. This agrees with our intuitive understanding of depletion, i.e. it requires a higher amount of interface charge $Q_{it}$ at the surface to completely deplete a volume that contains a higher density of ionized donors forming the total space charge. $Q_{sc}$. The electrostatic distribution of space charge as a function of $D_{it}$ in a 150 nm pillar, lies in between the two responses, i.e. (i) flat $R_e$ in a 200 nm pillar, and (ii) rapidly varying $R_e$ in a 50 nm (100) nm pillar. Even though the electrostatic radius $R_e$ decreases with increase in $D_{it}$, the roll-off does not cause the 150 nm pillar to pinch off completely.

Figure 2.8 shows the schematic diagram illustrating surface depletion in GaAs nanopillars, doped at $N_d = 5 \times 10^{16}$ cm$^{-2}$ at a $D_{it}$ equal to $2 \times 10^{13}$ cm$^{-2}$eV$^{-1}$ (greater than $D_{it}^{50}$). At this density of states, the 200 nm pillar shows negligible depletion ($R_e = 198$ nm), the 150 nm and 100 nm pillars show partial depletion ($R_e = 137$ nm and 77 nm, respectively) and the 50 nm pillar is depleted completely ($R_e = 0$).

At $N_d = 2 \times 10^{18}$ cm$^{-2}$, we find that the doping density at the surface of the nanopillar, in all four cases, $R_p = 50$ nm, 100 nm, 150 nm and 200 nm, is sufficient to balance the interface charge. Therefore, GaAs contacts doped to a density of $N_d = 2 \times 10^{18}$ cm$^{-2}$ have $R_e = R_p$, independent of the density of interface states. In the next section, we summarize the dependence of $R_e$ on the doping density $N_d$. 

2.6 Results: extension of Chia’s model to double barrier RTD
DOPED GaAs CONTACT, $N_d = 5 \times 10^{16} \text{ cm}^{-2}$

At constant $D_{it} = 2 \times 10^{13} \text{ cm}^{-2}\text{eV}^{-1}$

$egin{align*}
R_p &= 200 \text{ nm} \\
R_p &= 150 \text{ nm} \\
R_p &= 100 \text{ nm} \\
R_p &= 50 \text{ nm}
\end{align*}$

Figure 2.8: Schematic diagram of surface depletion in doped GaAs nanopillar at a constant density of interface states, labeled as $D_{it}$, showing negligible depletion in pillars with $R_p = 200 \text{ nm}$, partial depletion in 150 nm and 100 nm pillars and pinch off in 50 nm pillar. The schematic is shown for the case where $N_d = 5 \times 10^{16} \text{ cm}^{-2}$ and $D_{it} = 2 \times 10^{13} \text{ cm}^{-2}\text{eV}^{-1}$, which is greater than $D_{it}^{50}$.
2.6 Results: extension of Chia's model to double barrier RTD

2.6.4 Depletion as a function of doping density

In figure 2.9, we plot the electrostatic radius $R_e$ as a function of doping density $N_d$ for all four cases of $R_p$ discussed in the previous section. In GaAs $D_{it}$ is typically quoted as $1.25 \pm 1 \times 10^{14} \text{ cm}^{-2}\text{eV}^{-1}$ [93, 97, 98]. To remain consistent with realistic estimates of $D_{it}$, we discuss the behavior of $R_e$ vs. $N_d$ as it varies from $1 \times 10^{12} \text{ cm}^{-2}\text{eV}^{-1}$ to $1 \times 10^{14} \text{ cm}^{-2}\text{eV}^{-1}$ on a log scale.

We note three distinctive regimes in all four sets of calculations. The first regime, occurs at low doping densities $N_d$, where for certain values of $D_{it}$, the extent of depletion increases with the number of ionized donors available in the volume. This occurs for all $N_d$ to the left of the dashed red line in figures 2.9(a-d). Decrease in $R_e$ with increase in $N_d$ is counter intuitive to the textbook understanding of surface depletion due to interface states. As discussed previously, this is because the finite size of the nanopillar and the density of interface states was not accounted in the textbook explanation surface depletion[93]. The solution to $R_e$ as a function of $N_d$ is determined by the transcendental equation, given by eqn. 2.19. The second regime, occurs at values of $N_d$ in between the dashed red line and the continuous red line in figure 2.9. In this regime, the electrostatic radius $R_e$ increases with increase in $N_d$. In the third regime, indicated by the right side of the continuous red line, no surface depletion occurs. In this regime, the dopant density is sufficiently high at the surface to balance any interface charge on the sidewall.

The transition between the first regime and the second regime occurs at a point determined by the physical radius $R_p$ and the density of interface states $D_{it}$. Similarly, the transition between the second regime and the third regime depends upon $R_p$ and $D_{it}$. For certain values of $D_{it}$ and $N_d$, the solution to $R_e$ approaches zero, i.e. the nanopillar is completely pinched off. For example, in the case of a 200 nm nanopillar, no solutions exist for $13.3 \text{ cm}^{-3} \leq \log_{10}(N_d) \leq 15.5 \text{ cm}^{-3}$ at $D_{it} = 1 \times 10^{14} \text{ cm}^{-2}\text{eV}$, see figure 2.9(d). We know from eqn. 2.12 that in the limit of $R_e \to 0$, the surface potential $\phi(r)$ reaches a singularity. Therefore, it is difficult to identify a clear transition between the three regimes discussed above at these values of $D_{it}$ and $N_d$.

In the next section, we discuss the implication of these results on the observation of fine NDR features in a laterally confined RTD.

2.6.5 Implication of surface states on NDR peaks

In 1988, the same year as Reed et. al’s experimental observation of NDR peaks in laterally confined RTDs (see section 2.3), Chou et. al argued that if the lateral confinement ($R_e$) is the same throughout the structure (i.e. contacts, barriers, spacers and well), then one
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Figure 2.9: Electrostatic radius $R_e$ as a function of doping density, $N_d$, plotted for four different values of physical radius $R_p$ (a) 50 nm (b) 100 nm (c) 150 nm (d) 200 nm. The density of interface states varies from $1 \times 10^{12}$ cm$^{-2}$eV to $1 \times 10^{14}$ cm$^{-2}$eV on a logarithmic scale.
2.6 Results: extension of Chia’s model to double barrier RTD

applied bias will align all of the subband states in the well with the corresponding subbands in the contact [99]. This would then destroy any fine structure (NDR peaks) associated with the splitting of energy levels in the current-voltage spectra. Following this work, Bryant et. al suggested that fine structure may be observed if the lateral confinement is different in each region of the RTD [91].

Extending this analysis to include the effect of surface states, we find that depending upon the physical radius of the pillar $R_p$, the density of interface states in each region of the nanopillar $D_{it}$ and the doping density $N_d$, the lateral confinement ($R_e$) may be same for the undoped well and the doped GaAs contact. For example, in a 50 nm nanopillar RTD, if the density of interface states $= 6 \times 10^{13} \text{ cm}^{-2} \text{eV}$ on the sidewalls of an undoped well, then the electrostatic radius $R_e = 23 \text{ nm}$. See point A in figure 2.10. This undoped well may be contacted in the growth direction with a doped GaAs layer, which has a density of interface states $= 2 \times 10^{13} \text{ cm}^{-2} \text{eV}$ on the sidewalls. Under this scenario, the lateral confinement in the contact equals 23 nm, which is the same as the undoped well, see point B in figure 2.10. If these conditions were to exist, no fine feature will be observed even when quantization due lateral confinement occurs [91, 99].

![Figure 2.10: Electrostatic radius $R_e$ as a function of doping density, $N_d$, plotted for $R_p = 50 \text{ nm}$. The density of interface states varies from $1 \times 10^{12} \text{ cm}^{-2} \text{eV}$ to $1 \times 10^{14} \text{ cm}^{-2} \text{eV}$ on a logarithmic scale. For certain values of $D_{it}$, the electrostatic radius may be same for undoped GaAs well, and doped GaAs contacts. The points of intersection A and B highlight these combinations.](image)

In the next section we discuss the potential along the growth direction in laterally confined RTD.
2.7 Three dimensional potential in laterally confined RTDs

Figure 2.11 shows the schematic diagram of the longitudinal potential in a nanopillar RTD [100]. Numerical calculations of the longitudinal potential in a laterally confined RTD, predict a non-uniform hour-glass potential along the growth direction. The neck of this hour-glass shaped potential exists in the undoped well, where depletion is maximum.

![Schematic diagram showing hour-glass potential in a nanopillar RTD](image)

We now extend our understanding of surface depletion in homogeneous nanopillars to heterogeneous nanopillars, where all regions i.e. doped GaAs contacts, doped spacer and undoped GaAs well are integrated into a single structure. Using the modified expression for lateral confinement estimated from eqn. 2.19, we calculate the longitudinal potential of the lithographically defined nanopillar RTD.

Given a constant \( D_{it} \) and \( N_d \), the surface potential \( \phi(r = R_p) \) can be calculated for each epitaxial layer using eqns. 2.19 and 2.18. We assume azimuthal symmetry of the potential, which agrees with realistic devices.

Neglecting surface depletion at the interface of the epitaxial layers, the complete Poisson equation, given below:

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \zeta(r, z)}{\partial r} \right) + \frac{\partial^2 \zeta(r, z)}{\partial r^2} + \frac{\partial^2 \zeta(r, z)}{\partial z^2} = \frac{eN_d^i}{\epsilon} \quad (2.20)
\]

can be solved numerically by applying the Dirichlet condition \( \zeta(r, z)_{r=R_p} \) for all \( z \in [L_{i-1}, L_i] = \phi_o \cdot \phi_i(r=r_{R_p}) \), where \( L_i \cdot L_{i-1} \) is the thickness of \( i \)-th layer and \( \phi_i(r=r_{R_p}) \) is the surface potential calculated using eqn. 2.19 at that layer. At the interface between two
layers, the tangential component of the electric field is zero and the normal component of the displacement field can be written as:

\[
\varepsilon_i \frac{\partial \zeta(r,z)}{\partial z} |_{z \to L^-_i} = \varepsilon_{i+1} \frac{\partial \zeta(r,z)}{\partial z} |_{z \to L^+_i}
\]  

(2.21)

We use COMSOL 4.3 to numerically solve eqn. 2.20 for the RTD structure shown in figure 2.12. We ignore the barrier layers in the simulation, and only consider the GaAs layers. The three dimensional potential calculated using eqn. 2.20, agrees with the hour-glass potential shown in figure 2.11 under certain conditions. These conditions exist when the density of interface states \(D_{it}\) is different for each epitaxial layer, and are such that \(R_e\) in the undoped well is less than the \(R_e\) in the injector. Therefore, if for example, \(D_{it}\) in the injector is equal to \(1 \times 10^{13}\) cm\(^{-2}\)eV and \(D_{it}\) in the undoped well is equal to \(5 \times 10^{13}\) cm\(^{-2}\)eV, then the three-dimensional potential \(\zeta(r,z)\) shown in figure 2.12 is shaped as an hour-glass. Under this scenario \(R_e = 27\) nm in the undoped well, and is equal to 35 nm in the GaAs spacer \((N_d = 1 \times 10^{16}\) cm\(^{-3}\)). Note that the depletion width of each epitaxial layer evaluated by solving the complete three-dimensional potential in an RTD (see figure 2.12) is slightly different from the width evaluated by solving eqn. 2.19. This is because eqn. 2.19 assumes homogeneity throughout the nanopillar and does not account for boundary conditions at the interface of each epitaxial layer.

There are other combinations of \(D_{it}\) and \(N_d\), which satisfy the above mentioned condition for an hour-glass potential. These values can be evaluated from figure 2.9(a). The solution to energy states \(E_n\), in a laterally confined RTD, may then determined by three-dimensional scattering matrix theory that takes the non-uniform potential into account. This approach is beyond the scope of this work, and has been discussed in detail by Mizuta et. al [83].

While the first device structure to obtain laterally confined RTDs involved lithographic definition of nanopillars [89, 101], most of the latter techniques used an external gate bias to control the depletion of charge carriers [102, 103]. This allowed an external control over the electrostatic radius such that the lateral potential imposed on the quantum well remained uniform along the z-direction. Figure 2.13 shows the schematic diagram of an RTD with external gates that control the lateral potential in the quantum dot, with it’s associated electrical characteristics.

This approach can not be scaled to achieve lateral confinement in QCLs, which requires an array of hundred thousand laterally confined pillars connected in parallel to achieve the gain required for lasing. An immediate consequence of restricting to the top-down nanopillar approach implies an hour-glass (non-uniform) potential \(\zeta(r,z)\) because
Figure 2.12: Three-dimensional potential $\zeta(r, z)$ in a nanopillar RTD, with $R_p = 50$ nm.

of surface depletion repeating with each period along the $z$-direction.

In the next section, we discuss lateral confinement in QCLs and calculate the three-dimensional potential $\zeta(r, z)$ for a laterally confined QCL structure.

### 2.8 Three dimensional potential in laterally confined QCLs

As discussed above, although, the use of an external gate bias to control the lateral confinement is an appealing concept, it is difficult to scale this approach from a single dot in an RTD to an array of dots in QCLs.

Figure 2.14 shows the epitaxial structure of a typical QCL used in this thesis. Each period in the quantum cascade comprises of (i) a doped GaAs injector and, (ii) undoped quantum GaAs wells that form the upper and lower lasing levels. If we assume, $D_{it}$ in the injector is equal to $1 \times 10^{13}$ cm$^{-2}$eV and $D_{it}$ in the undoped well is equal to $5 \times 10^{13}$ cm$^{-2}$eV, then from figure 2.9(a) we obtain an $R_e = 27$ nm in the undoped well and $R_e = 35$ nm in the doped GaAs injector ($N_d = 2 \times 10^{16}$cm$^{-3}$).

As before, we use COMSOL 4.3 to numerically solve eqn. 2.20 for the three dimensional
potential $\zeta(r,z)$ in a laterally confined QCL. We ignore the barrier layers in the simulation, and only consider the GaAs layers. The three-dimensional potential $\zeta(r,z)$ is shown in figure 2.14.

We observe that the curvature of the parabolic potential in the undoped active region in a laterally confined QCL is weaker than the laterally confined RTD. This is because the thickness per period of the undoped GaAs is 31.9 nm, which is more than the thickness of the undoped GaAs well in an RTD (9 nm). As opposed to a single undoped quantum well RTD, there are multiple undoped quantum wells in a QCL, which form part of a period. These periods repeat in the growth direction. Therefore, the parabolic potential also repeats each time with the period.

The complete three dimensional potential $\zeta(r,z)$ can now be introduced into the three dimensional time-independent Schrödinger equation, given below:

$$\left( -\frac{\hbar^2}{2m^*} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial z^2} \right) + \zeta(r,z) \right) \Psi(r,\theta,z) = E \Psi(r,\theta,z) \quad (2.22)$$

The solution to eqn. 2.22 yields the spectrum of energy states $E_n$ in a laterally confined QCL. Electron transport through such zero-dimensional cascade structure can be calculated using a three dimensional multi-mode scattering matrix theory [104]. This is beyond the scope of this work.

For simplicity in calculations, we use Reed’s simplistic model for harmonic potential in
nanopillars and use it to study the effect of lateral confinement on the bandstructure of a THz QCL. This is discussed below.

2.9 Effect of lateral confinement on THz QCL bandstructure

In this section, we extend Reed's simplistic model for lateral confinement in RTDs to understand splitting of energy levels in a THz QCL. We then compare the quantized energy states of carriers that are lithographically constricted in a THz QCL to a scenario where they are confined by the application of an external magnetic field. Before we discuss the effect of lateral confinement on THz QCLs, it is useful to understand the difference between the bandstructure of a typical THz QCL with a single quantum well RTD.
2.9 Effect of lateral confinement on THz QCL bandstructure

2.9.1 Comparison between RTD and THz QCL bandstructure

We know from our understanding of an RTD that the thickness of the wells determine the energy states in a simple double barrier structure. A THz QCL is far more complex than an RTD - it comprises of multiple wells within each period. This period is repeated in the growth direction to obtain gain. The thickness of the wells governs the energy states (or subbands) within each period of a THz QCL. The energy states involved in radiation, i.e. the injector, upper lasing level, lower lasing level and extractor are determined by optimizing various design parameters to achieve maximum population inversion.

Figure 2.15: Schematic bandstructure diagram of (a) RTD and (b) THz QCL.

Figure 2.15 shows the schematic bandstructure diagram of an RTD and a THz QCL. The ground state \( E_0 \) and the first excited state \( E_1 \) in a single quantum well RTD structure is highlighted in red, see figure 2.15(a). On the right, we show only those energy states that take part in four-stage lasing mechanism in a typical THz QCL, see figure 2.15(b). These states are labeled from the bottom of the conduction band, in the order of energy. We call these states as \( E_1, E_2, E_3, E_4 \) and \( E_5 \). In this particular design of THz QCL, the extraction of the electrons from the lower lasing level occurs through resonant LO phonon scattering. The radiative transition occurs between the upper lasing \( E_5 \) and the lower lasing level \( E_4 \).

We next discuss splitting of energy states in RTDs and THz QCLs due to lateral confinement.

2.9.2 Magnetic field vs. lithographic confinement of carriers

On application of an external magnetic field in the growth direction, the two-dimensional electron gas gets constricted in the ‘xy’ plane to a cyclotron radius. This cyclotron radius is given by \( \frac{\sqrt{\hbar e B}}{c} \). Here, \( c \) is the speed of light and \( e \) is the charge of the electron. Figure 2.16(a) shows the schematic diagram of an RTD under the influence of an external...
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magnetic field, $B$. Each subband $|i\rangle$, in the quantum well, splits into a ladder of Landau states $|i,m\rangle$ with energies given by:

$$E_{i,m} = E_i + (m + 1/2)\hbar\omega_c, m = 1, 2, 3...$$  \hspace{1cm} (2.23)

where $\omega_c = eB/cm^*_e$ is the cyclotron frequency, and $m^*_e$ is the effective mass of electron.

![Figure 2.16: Schematic diagram of RTD bandstructure under the influence of (a) an external magnetic field, B (b) lithographic confinement of carriers to a physical radius $R_p$.](image)

Application of a magnetic field is analogous to creating an artificial quantum dot. A real quantum dot is created upon lithographic confinement of electrons in the 'xy' plane, which also quantizes the energy states. Figure 2.16(b) shows the schematic diagram of an RTD when it is laterally constricted to a nanopillar of physical radius $R_p$. In this case, each subband $|i\rangle$, in the quantum well, splits into a ladder of states $|i,m\rangle$ with energies given by

$$E_{i,m} = E_i + (m + 1/2)\hbar\omega, m = 1, 2, 3...$$  \hspace{1cm} (2.24)

where $\hbar\omega = \hbar / R_p \sqrt{2\Phi / m_i^*}$ is the in-plane quantization energy obtained using Reed’s simplistic harmonic potential discussed in section 2.3.

An important difference in the energy states $E_{i,m}$ of artificial quantum-dots (assisted
by magnetic field) and lithographically defined quantum-dots comes from the in-plane quantization energy $\delta E = \hbar \omega$ which varies proportionally with $B$ and inversely with $R_p$. Note that as $R_p \to 0$, $E_{i,m} \to \infty$.

In the case of a simple structure such as an RTD, the number of energy states $E_i$ are limited. Therefore, the energy spectrum of laterally confined RTDs $E_{i,m}$, is relatively easier to interpret from transport or optical measurements. In the case of a THz QCL, there are multiple energy states $E_i$ which split upon lateral confinement, see figure 2.17. This lateral quantization creates additional subbands that influences electron scattering and transport in a THz QCL. While magnetotransport behavior of THz QCLs is generally understood [82], it offers us useful insights into transport and spectroscopic behavior of lithographically confined THz QCLs.

We extend Reed’s harmonic potential to evaluate ladder states in a THz QCL using eqn. 2.17. Note that this is a very simple picture of the confining potential. In reality, $\hbar \omega$ would be dictated by the true depletion width in each quantum well described by figure 2.14.

The same resonance conditions that determine optical selection rules of THz QCLs under a magnetic field, apply to lithographically confined THz QCLs (nanopillars). As is the case with the application of a B field, we propose that the physical radius $R_p$ would modulate the lifetime of the laser transition states. Similar to the magneto-photon resonance conditions, the resonance condition in the case of zero-dimensionality can be written as:

$$E_{i,m} - E_{j,m'} - p\hbar \omega_{LO} = 0, \quad (2.25)$$

Here, $i$ is the upper or lower lasing level, $j$ is the lower subband. In the above equation, $p = 0, m = 0, m' = 0, 1, 2$ etc for elastic scattering and $p = 1, m' = 0, m = 0, 1, 2$ etc for inelastic scattering. The term $\hbar \omega_{LO} = 36$ meV in eqn. 2.25 is the energy associated with resonant LO phonon scattering. When the upper lasing level is at resonance, the elastic and inelastic scattering will cause quenching of any radiation. However, when the lower lasing level is at resonance, the enhanced relaxation of charge carriers will lead to higher power and operating temperature.

For the design shown in figure 2.17, the upper lasing level is labeled as $E_5$, and the lower lasing level is labeled as $E_4$. Therefore, upon lateral confinement, for those radial dimensions $R_p$ that cause the upper lasing level $E_5$ to be at resonance, no emission will be observed. This happens when the following condition is met.
2. NANOPILLARS IN RTDS AND QCLS: THEORY

Figure 2.17: Schematic diagram of THz QCL bandstructure under the influence of (a) an external magnetic field (b) lithographic confinement of carriers.

\[ E_{5,0} = E_{4,m} \quad \text{Elastic scattering} \quad (2.26) \]
\[ E_{5,m} - E_{4,0} = \hbar \omega_{LO} \quad \text{LO phonon scattering} \quad (2.27) \]

Here, \( m = 0, 1, 2 \) and so on. On the other hand, for those radial dimensions \( R_p \) that cause the lower lasing level to be resonance, emission will be observed. In this particular example there are two lower lasing levels \( E_4 \) and \( E_3 \) that are close to each other in energy (coupled to each other) and the condition for enhanced relaxation is applied to the lower most level \( E_3 \).

\[ E_{3,0} = E_{2,m} \quad \text{Elastic scattering} \quad (2.28) \]
\[ E_{3,m} - E_{2,0} = \hbar \omega_{LO} \quad \text{LO phonon scattering} \quad (2.29) \]
Here, \( m = 0, 1, 2 \) and so on. Therefore, in a laterally confined THz QCL, the resonance conditions determine which radial dimensions would lead to enhanced emission. At these radial dimensions, the radiative states that take part in the energy transition are determined by the optical selection rules which follow from conservation of energy and momentum. For simplicity, we do not assume any broadening of states.

\section*{2.10 Results: radiative states in laterally confined THz QCLs}

Here, we look at two important THz QCLs designs that are used in this thesis, with the intention of improved temperature performance due to quantization of energy states in the in-plane direction. The two designs (i) 3 THz 3 QW Paris design, and (ii) 3 THz 4 QW ETH design have been discussed in detail in Chapter 4. In this section, we are only concerned with the position of the injector, upper lasing level, lower lasing level and the extractor with respect to each other at the alignment field.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{3_THz_3_QW_Paris_design.png}
\caption{Band diagram of 3 THz 3 QW Paris design showing energy states at alignment field \( E = 12.1 \) kV/cm. For epitaxial structure and simulation details, see section 4.7.}
\end{figure}

Figure 2.18 shows the band diagram of the 3 THz 3 QW Paris design at the alignment field. Also shown are the energy levels \( E_4, E_3, E_2 \) and \( E_1 \), labeled as quantum well (QW) states because they arise due to confinement in the growth direction. \( E_4 \) and \( E_3 \) form the upper and lower lasing level, respectively. The lower lasing level \( E_3 \) is coupled to \( E_2 \). The electrons resonantly relax from \( E_2 \) to the extractor through LO phonon scattering.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{3_THz_4_QW_ETH_design.png}
\caption{Band diagram of 3 THz 4 QW ETH design, at the alignment field. In this design, the QW states \( E_5 \) and \( E_4 \) form the upper and lower lasing levels, respectively. Compared to the 3 THz 3 QW Paris design, there are more number of states}
\end{figure}

Figure 2.19 shows the band diagram of the 3 THz 4 QW ETH design at the alignment field. In this design, the QW states \( E_5 \) and \( E_4 \) form the upper and lower lasing levels, respectively. Compared to the 3 THz 3 QW Paris design, there are more number of states.
2. NANOPILLARS IN RTDS AND QCLS: THEORY

Figure 2.19: Band diagram of 3 THz 4 QW ETH design showing energy states at alignment field $E = 7.6 \text{ kV/cm}$. For epitaxial structure and simulation details, see section 4.9.

that take part in the extraction of carriers from the lower lasing level. This is because this designs employs a miniband of states $E_4$, $E_3$ and $E_2$, that are resonantly coupled to the extractor $E_1$ through LO phonon scattering.

2.10.1 Radiative states in laterally confined 3 THz 3 QW Paris design

Figure 2.20 shows ladder states as a function of nanopillar radius $R_p$ for the 3 THz 3 QW Paris design. The QW states are calculated by solving Poisson-Schrödinger equation self-consistently in the growth direction, as shown above. For clarity, we separate the ladder states into four groups, i.e. those involved in (a) elastic scattering of electrons in the lower lasing level $E_2$ with the extractor $E_1$ (b) inelastic scattering of electrons in the lower lasing level $E_2$ with the extractor $E_1$ (c) elastic scattering of electrons in the upper lasing level $E_4$ with the lower lasing level $E_3$, and finally (d) inelastic scattering of electrons in the upper lasing level $E_4$ with the lower lasing level $E_3$.

Scattering of electrons in the lower lasing level $E_2$ leads to enhanced relaxation of carriers in $E_3$, leading to enhanced population inversion. This happens when the resonance condition for scattering are met, see figure 2.20 (a-b). At these resonance positions, the two states $E_2$ and $E_1$ cross each other. The dashed arrows coloured in orange, indicate the resonance positions that maximise carrier relaxation from $E_2$ to the extractor state $E_1$. Scattering of electrons can also quench radiation of photons. This occurs when carriers in the upper lasing level $E_4$ scatter non-radiatively into the lower lasing level $E_3$. These resonance positions are highlighted with dashed black arrows in figure 2.20 (c-d). Table 2.1
summarizes the resonance positions in the order of increasing $R_p$.

<table>
<thead>
<tr>
<th>Scattering process</th>
<th>Energy levels</th>
<th>Physical radius, $R_p$ (nm)</th>
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</thead>
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<tr>
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<td></td>
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<td>$E_{2,1} = E_{1,0} + 2\hbar\omega_{LO}$</td>
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<td>$E_{2,2} = E_{1,0} + 3\hbar\omega_{LO}$</td>
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<td></td>
<td>$E_{2,4} = E_{1,0} + 2\hbar\omega_{LO}$</td>
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<td>$E_{4,4} = E_{3,0} + 2\hbar\omega_{LO}$</td>
<td>85.05</td>
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<tr>
<td></td>
<td>$E_{4,2} = E_{3,0} + \hbar\omega_{LO}$</td>
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<tr>
<td></td>
<td>$E_{4,3} = E_{3,0} + \hbar\omega_{LO}$</td>
<td>165.5</td>
</tr>
</tbody>
</table>

Table 2.1: Summary of resonance positions in laterally confined 3 THz 3 QW Paris design at a constant electric field $E = 12.1$ kV/cm. The resonance positions are listed in the order of increasing nanopillar radius.

Looking at figure 2.20, we propose that only those nanopillars whose radial dimensions meet the criterion of enhanced relaxation of carriers in the lower lasing level will show improved temperature performance. For radial dimensions that encourage scattering of carriers in the upper lasing level, lateral confinement would be detrimental. Therefore, we identify three windows of $R_p$, labeled as $P$, $Q$ and $R$ for nanopillars that meet the requirements of emission discussed above. The position of the windows in figure 2.20 is determined by the resonance positions shown in figure 2.20(a) and figure 2.20(b). The width of the windows is governed by the resonance positions shown in figure 2.20(c) and figure 2.20(d) that should be avoided as they quench emission.

The first window $P$ is identified by including the resonances $E_{2,0} = E_{1,1}$ at $R_p = 33.71$ nm, $E_{2,2} = E_{1,0} + 3\hbar\omega_{LO}$ at 35.5 nm and $E_{2,1} = E_{1,0} + 2\hbar\omega_{LO}$ at 36.29 nm. The range of the first window is limited by the resonance $E_{4,2} = E_{3,0} + 2\hbar\omega_{LO}$ at 43.03 nm. The resonance $E_{2,3} = E_{1,0} + 3\hbar\omega_{LO}$ at 53.33 nm, which enhances relaxation lies very close to the resonance $E_{4,1} = E_{3,0} + \hbar\omega_{LO}$ at 54.72 nm that quenches emission. Therefore, the
Figure 2.20: Ladder states as a function of \( R_p \) in 3 THz 3 QW Paris design at an electric field, \( E = 12.1 \text{ kV/cm} \), showing (a) elastic scattering of the lower lasing level (b) inelastic scattering of the lower lasing level (c) elastic scattering of the upper lasing level (d) inelastic scattering of the upper lasing level.
second window Q is identified in between the resonances $E_{4,3} = E_{3,0} + 2\hbar\omega_{LO}$ at 64.04 nm and $E_{4,4} = E_{3,0} + 2\hbar\omega_{LO}$ at 85.05 nm. This window includes the resonance $E_{2,2} = E_{1,0} + 2\hbar\omega_{LO}$ at 74.14 nm that enhances relaxation of carriers. At higher radial dimensions, the resonance $E_{2,3} = E_{1,0} + 2\hbar\omega_{LO}$ at 110.8 nm that enhances relaxation lies very close to the resonance $E_{4,2} = E_{3,0} + \hbar\omega_{LO}$, which quences radiation. Hence, the third window R is identified such that it lies between the resonance $E_{4,2} = E_{3,0} + \hbar\omega_{LO}$ at 108.2 nm and the resonance $E_{4,3} = E_{3,0} + \hbar\omega_{LO}$ at 165.5 nm. This window includes the resonance $E_{2,4} = E_{1,0} + 2\hbar\omega_{LO}$ that enhances electron relaxation from the lower lasing level.

Now that we know which radial dimensions permit THz emission, it is useful to estimate the energy states that are involved in THz emission. These radiative states are determined by the optical selection rule that dictates conservation of energy and momentum during an intersubband transition. We therefore propose that in the case of nanopillars fabricated from 3 THz 3 QW Paris design, only those transitions will radiate, that meet the optical selection rule given below, i.e.

$$E_{4,m} = E_{3,m'} \text{ for all } m = m'$$

where, m and $m'$ = 0, 1, 2, 3 and so on.

For radial dimensions in the window $P \leq 42$ nm, the transitions $E_{4,0} \rightarrow E_{3,0}$ at 3.16 THz and $E_{4,1} \rightarrow E_{3,1}$ at 3.15 THz are likely to be radiative levels. In the second window Q, $65 \leq R_p \leq 84$ nm, electron transition between the states $E_{4,2} \rightarrow E_{3,2}$ is likely to yield a photon of energy at 3.14 THz. For larger pillars $110 \leq R_p \leq 164$ nm, transition between $E_{4,0} \rightarrow E_{3,0}$ and $E_{4,4} \rightarrow E_{3,4}$ are likely to form part of the radiative routes with an energy difference of 3.52 THz and 3.13 THz, respectively.

2.10.2 Radiative states in laterally confined 3 THz 4 QW ETH design

Let us now look at the ladder states in a second design, that uses a miniband of energy states as well as a resonant LO phonon stage for extraction of carriers from the lower lasing level. Figure 2.22 shows a plot of the ladder states in nanopillars etched in 3 THz 4 QW ETH design as a function of $R_p$. As before, the ladder states are separated into four panels, i.e. those involved in (a) elastic scattering of electrons in the lower miniband state $E_2$ with the extractor $E_1$ (b) inelastic scattering of electrons in the lower miniband state $E_2$ with the extractor $E_1$ (c) elastic scattering of electrons in the upper lasing level $E_5$ with the lower lasing level $E_4$, and finally (d) inelastic scattering of electrons in the upper lasing level $E_5$ with the lower lasing level $E_4$. Table 2.2 summarises the energy states with the corresponding radial dimensions that are involved in scattering processes that lead
2. NANOPILLARS IN RTDS AND QCLS: THEORY

Figure 2.21: Ladder states as a function of nanopillar radius $R_p$ in 3 THz 3 QW ETH design at an electric field, $E = 12.1 \text{ kV/cm}$, showing optically permitted radiative transitions within the windows P, Q and R.

enhanced relaxation or suppressed emission.

From figure 2.22, we identify four windows, labeled as P, Q, R and S that meet the requirements of emission in laterally confined 3 THz 4 QW ETH design. The first window P is identified by excluding the resonance $E_{2,0} = E_{1,1}$ at $R_p = 40.65 \text{ nm}$ that leads to suppressed emission. Therefore, the first window P lies in the range of $R_p \leq 39 \text{ nm}$. The second window Q is identified by avoiding the resonances at $E_{5,3} = E_{4,0} + 2\hbar \omega_{LO}$ at 64.04 nm and $E_{5,4} = E_{4,0} + 2\hbar \omega_{LO}$ at 85.44 nm, that quenches emission. The third window R, includes the resonance at $E_{2,3} = E_{1,0} + 2\hbar \omega_{LO}$ at 92.58 nm that enhances relaxation of carriers from the lower miniband states. This window avoids the resonance at $E_{5,4} = E_{4,0} + 2\hbar \omega_{LO}$ at 85.44 nm and at $E_{5,2} = E_{4,0} + \hbar \omega_{LO}$ at 107 nm, which leads to suppressed emission. The fourth window S includes the resonances $E_{2,0} = E_{1,3}$ at 122.3 nm and $E_{2,4} = E_{1,0} + 2\hbar \omega_{LO}$ at 123 nm. The width of this window is determined by the position of the resonances $E_{5,2} = E_{4,0} + \hbar \omega_{LO}$ at 107 nm and $E_{5,3} = E_{4,0} + \hbar \omega_{LO}$ at 162.1 nm which quenches emission.

In the case of nanopillars fabricated from 3 THz 4 QW ETH design, only those transitions will radiate, that meet the optical selection rule given below, i.e.

$$E_{5,m} = E_{4,m'} \text{ for all } m = m'$$  \hspace{1cm} (2.31)
Figure 2.22: Ladder states as a function of $R_p$ in 3 THz 4 QW ETH design at an electric field, $E = 7.6$ kV/cm, showing (a) elastic scattering of the lowest miniband state (b) inelastic scattering of the lowest miniband state (c) elastic scattering of the upper lasing level (d) inelastic scattering of the upper lasing level.
Nanopillars in 3 THz 4 QW ETH design

<table>
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<th>Scattering process</th>
<th>Energy levels</th>
<th>Physical radius, $R_p$ (nm)</th>
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<td>$E_{2,0} = E_{1,3}$</td>
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<td></td>
<td>$E_{2,0} = E_{1,4}$</td>
<td>163.3</td>
</tr>
<tr>
<td>Inelastic scattering $E_2$</td>
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<td>$E_{3,2} = E_{4,0} + 2\hbar\omega_{1,0}$</td>
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<td>$E_{3,3} = E_{4,0} + 2\hbar\omega_{1,0}$</td>
<td>162.1</td>
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</table>

Table 2.2: Summary of resonance positions in laterally confined 3 THz 4 QW ETH design at a constant electric field $E = 7.5$ kV/cm. The resonance positions are listed in the order of increasing nanopillar radius.

where, $m$ and $m' = 0, 1, 2, 3$ and so on. Figure 2.23 plots ladder states as a function of nanopillar radius $R_p$ in 3 THz 4 QW ETH design at an electric field, $E = 7.6$ kV/cm, showing optically permitted radiative transitions. In the first window $P$, the intersubband transition, $E_{5,1} \rightarrow E_{4,1}$ will dominate emission at 2.9 THz. In the second window, $66 \leq R_p \leq 84$ nm, the transition would occur between the ground states $E_{5,0} \rightarrow E_{4,0}$, with an energy difference equal to 3.07 THz. The transitions $E_{5,3} \rightarrow E_{4,3}$ at $R_p = 92.58$ nm and at $R_p = 123.7$ nm would form part of the radiative routes in windows $R$ and $S$, with an energy difference equal to 3.82 THz and 3.00 THz respectively.

### 2.10.3 Accurate estimation of radiative states

In the calculations above, we have not evaluated the dipole moment $\langle z_{ul} \rangle$ and oscillator strength $f$ between the two radiative states. In a QD cascade structure, these design parameters need to be determined from the complete wavefunction $\Psi(\theta, r, z) = \Theta(\theta)\psi(r, z)$. Here, $\Theta(\theta)$ is the azimuthal part of the solution to the 3D Schrödinger equation (eqn. 2.22). The potential $\zeta(r, z)$ is determined from eqn. 2.20. Assuming azimuthal symmetry $\Theta(\theta) = \ldots$
2.10 Results: radiative states in laterally confined THz QCLs

Figure 2.23: Ladder states as a function of nanopillar radius $R_p$ in 3 THz 4 QW ETH design at an electric field, $E = 7.6$ kV/cm, showing optically permitted radiative transitions within the windows P, Q, R and S.

$$e^{im\theta}/\sqrt{2\pi},$$ which implies that $\Psi(\theta,r,z) = e^{im\theta}/\sqrt{2\pi}\psi(r,z)$.

Furthermore, the intersubband transitions (QD states) identified as the radiative paths in laterally confined 3 THz 4 QW ETH design and laterally confined 3 THz 3 QW Paris design have only been calculated at the alignment field of the QW states. For a more accurate estimate of the radiative states in laterally confined THz QCLs, the simulation has to be swept over a range of applied bias values, taking into account alignment between the extraction stage of one period with the injector stage of the neighbouring period.

What is important to note is that this model predicts the tolerance in $R_p$ that allows THz emission in laterally confined THz QCLs. This tolerance depends upon the QCL design and width of the window. The minimum tolerance is for pillars with radial dimensions in the window R, fabricated in 3 THz 4 QW ETH design, where $\pm 3.5$ nm accuracy in fabrication is required for observation of THz emission, see figure 2.21. For pillars fabricated from 3 THz 3 QW Paris design, the minimum tolerance is $\pm 10$ nm, which is slightly higher. This tolerance is estimated for pillars with radial dimensions in the window Q shown in figure 2.23.

Inspite of the simplifications, the model provides a theoretical framework to predict radiative states in laterally confined THz QCLs. This theoretical framework is necessary to
2. NANOPILLARS IN RTDS AND QCLS: THEORY

understand the THz energy spectra of laterally confined QCLs. So far, we have discussed the effect of lateral confinement on the QCL bandstructure. We now focus on the plasmonic mode of laterally confined THz QCLs.

2.11 Effect of lateral confinement on plasmonic mode in THz QCLs

In the previous section, we focussed on the effect of nanopillar radius on intersubband transitions in laterally confined THz QCLs. While it is essential to be within the range of radial dimensions that permit emission of photons, it is also equally crucial to (i) achieve enough gain to overcome losses, and (ii) support a plasmon with freespace wavelength equal to the emitted photon (100 µm = 3 THz). The free space wavelength is $10^2$-$10^3$ times larger than the nanopillar radius (50-200 nm). The two constrains necessitate the fabrication of a nanopillar array that is packed into an area equal to the area of a THz QCL. Typically, a standard THz QCL processed in a double metal waveguide geometry comprises of a 2 mm long Fabry Pérot ridge, that is 100 µm wide, see figure 2.24. Therefore, the surface area of the ridge translates to $\approx 10^7$ nanopillars of radius $R_p = 50$ nm, connected in parallel.

Figure 2.24: Schematic diagram showing the three-dimensional view of a THz QCL in a double metal waveguide.
2.11 Effect of lateral confinement on plasmonic mode in THz QCLs

2.11.1 Plasmon mode simulations in THz QCLs

Before we discuss the effect of various device parameters on the plasmonic mode of a laterally confined THz QCL, it is useful to revisit the plasmonic mode in a double metal THz QCL (discussed in section 1.5.2). Figure 2.25 shows the cross-sectional view of the THz QCL ridge illustrating the different material layers.

The problem of evaluating the eigen mode solution to plasmons propagating inside a THz QCL is analogous to the multilayer slab waveguide problem. The complex propagation constant, \( \tilde{n} \) determined by solving the multilayer problem comprises of a real component \( n \) that characterizes the effective refractive index of the medium and an imaginary component \( \kappa \), also known as the extinction coefficient that characterizes the losses in the medium. This is given below:

\[
\tilde{n} = n + i\kappa
\]  

(2.32)

The extinction coefficient \( \kappa \) characterizes the absorption losses in the waveguide. For a freespace wavelength \( \lambda \), the absorption losses are written as \( \alpha_w = \frac{4\pi\kappa}{\lambda} \).

The overlap \( \Gamma \), is another parameter that is crucial to the waveguide and is defined as the percentage of the optical mode interacting with the active region. This is written as:

\[
\Gamma = \frac{\int_{AR} |E(z)|^2 dz}{\int_{-\infty}^{+\infty} |E(z)|^2 dz}
\]

(2.33)

Here \( E(z) \) is the z-component of the electric field and AR is the QCL active region excluding the top and bottom \( n^+ \) GaAs doped contacts.

The figure of merit (FOM) defines the quality of a waveguide in terms of both the absorption losses \( \alpha_w \) and the overlap factor \( \Gamma \), and has units of length. Defined as the ratio
between $\Gamma$ and $\alpha_w$, FOM can be written as:

$$FOM = \frac{\Gamma}{\alpha_w} \quad (2.34)$$

These parameters, i.e. $\text{Re}(\bar{n})$, $\alpha_w$, $\Gamma$ and FOM depend upon (a) the geometry of each layer, and (b) the complex dielectric constant of each layer. In the case of the GaAs active region, the $n^+$ doped GaAs contacts and the gold layers, the complex dielectric constants can be estimated from the Drude model. The accuracy of this model to estimate the optical behavior of semiconductors and metals at THz frequencies has been described in great detail before [5, 41]. Here we only present the key formulae that we use to estimate the complex dielectric constant, that is dependent on frequency ($\omega$), effective mass $m^*_e$ and doping $N_d$.

The complex dielectric constant can be written as:

$$\epsilon(\omega) = \epsilon' + i\epsilon'' = \left(1 - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2} + i \frac{\tau \omega_p^2}{\omega(1 + \omega^2 \tau^2)}\right). \quad (2.35)$$

Here, $\omega_p = \sqrt{\frac{N_d e^2}{m^*_e \epsilon_o}}$ is the volume plasma frequency and $\epsilon_o$ is the permittivity of vacuum. The carrier lifetime $\tau$ is equal to 0.1 ps for undoped GaAs and 1 ps for $n^+$ doped GaAs.

We use COMSOL v4.3 to evaluate the mode profile supported by the waveguide. In the COMSOL environment, for every material layer included in the COMSOL simulation, i.e. the active region, doped contacts and metal contacts, we input the real part of the dielectric constant $\epsilon'$ and the dc conductivity $\sigma_{dc}$. The dc conductivity $\sigma_{dc} = \frac{N_d e^2 \tau}{m^*_e}$ is related to the imaginary part of the dielectric constant as:

$$\epsilon'' = \frac{\sigma_{dc}}{1 + \omega^2 \tau^2} \quad (2.36)$$

We notate $\epsilon'$ as $\epsilon_r$ for every material. For simplicity we also drop the subscript in dc conductivity and notate it as $\sigma$.

Figure 2.26(a) shows the optical constants associated with each material layer in a double metal THz QCL. The active region is characterized by optical constants $\epsilon_{GaAs}^r$ and $\sigma_{GaAs}$. The top (bottom) doped $n^+$ GaAs contact layers are characterized by the optical constants $\epsilon_{r}^{top\,GaAs}$ ($\epsilon_{r}^{bot\,GaAs}$) and $\sigma_{top\,GaAs}$ ($\sigma_{bot\,GaAs}$). The $n^+$ GaAs substrate is characterized by optical constants $\epsilon_{r}^{substrate}$ and $\sigma^{substrate}$, and finally, the metal contacts are characterized by optical constants $\epsilon_{r}^{Au}$ and $\sigma^{Au}$. Figure 2.26(b-c) show that in a double metal THz QCL, the THz wave is confined as a surface plasmon between the top and bottom metal layers. The surface plasmon propagates perpendicular to the plane and the mode profile varies in the
2.11 Effect of lateral confinement on plasmonic mode in THz QCLs

growth direction. The dipole selection rule in intersubband lasers only permit radiation that has it’s electric field polarized perpendicular to the growth direction, and hence only transverse magnetic (TM) modes are considered in plasmon simulations [5].

![Diagram](image)

Figure 2.26: (a) Schematic diagram showing the optical constants corresponding to the material layers in a THz QCL in double metal waveguide (b) Plasmon mode calculated for a full-stack THz QCL in a double metal waveguide, where the optical constants of the different material layers correspond to the 3 THz 4 QW ETH design (c) Cross-sectional view of the mode confinement in the QCL active region.

2.11.2 Effective medium approximation in laterally confined QCLs

As discussed before, the freespace wavelength of intersubband transitions in a THz QCL (100 µm = 3 THz) is much larger than the radial dimensions (R_p ≤ 200 nm) of the nanopillars. Therefore, an array of nanopillars is required to support the plasmonic mode in a laterally confined THz QCL. The nanopillars, fabricated from a THz QCL active region are planarized with an insulator and contacted on the top and bottom with metal layers. Figure 2.27 shows the schematic diagram of a laterally confined THz QCL, detailing the cross-sectional and top view of the nanopillars. The packing density of the nanopillar array is determined by the pitch p, defined as the distance between the center of two closest nanopillars. Here we use a square lattice to pack the nanopillars. In theory a different lattice arrangement can also be used to pack the nanopillars. For the same p, a hexagonal lattice allows for a higher packing density than a square lattice.
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Figure 2.27: Schematic diagram showing (a) the cross-sectional view of laterally confined THz QCL (nanopillars) in a double metal waveguide and (b) the top-view of nanopillars fabricated in THz QCL and planarized with an insulator.

Assuming that the radiation emitted from a laterally confined THz QCLs is TM polarized and is perpendicular to the plane, we suggest that the losses due to free carrier absorption in laterally confined THz QCLs can be calculated in the same way as standard double metal ridges in THz QCLs. From figure 2.27, we note that the optical constants $\varepsilon_{Au}$ and $\sigma_{Au}$ of the two top and bottom metal layers which electrically connect the nanopillars remain unaffected by lateral confinement. However, the optical constants of the laterally confined active region layer as well as the top and bottom $n^+$ doped GaAs layers must now include the surrounding medium, be it air or a planarizing dielectric medium. The planarizing material will have its own optical constant at THz frequencies. In this work, we label the electrical permittivity as $\varepsilon_{r}^{ins}$ and conductivity as $\sigma_{r}^{ins}$. In the case of air, $\varepsilon_{r}^{ins} = \varepsilon_{r}^{air} = 1$ and $\sigma_{r}^{ins} = \sigma_{r}^{air} = 0$ S/m. For most planarizing materials $\varepsilon_{r}^{ins}$ ranges from 2.5 to 4 and $\sigma_{r}^{ins}$ ranges from $10^{-10}$ - $10^{-15}$ S/m.

Figure 2.28 shows the schematic diagram of the laterally confined THz QCL illustrating the effective medium approximation approach to evaluate the optical constants of the active region (2) and the top and bottom $n^+$ doped layers (1 and 3). Note that the optical constant of each epitaxial layer is governed by the surrounding medium, the radius $R_p$ of

---

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Figure 2.28: Schematic diagram showing (a) the cross-section view of laterally confined THz QCL (nanopillars) in double metal waveguide and, (b) the top-view of nanopillars fabricated in THz QCL and planarized with an insulator of permittivity $\varepsilon_{\text{ins}}^r$ and conductivity $\sigma_{\text{ins}}$.

the nanopillar array and, the pitch $p$ of the nanopillar array. The optical constants of the laterally confined active region $\varepsilon_{r}^{NP}$ and $\sigma_{NP}$ can be calculated as:

$$
\varepsilon_{r}^{NP} = \varepsilon_{r}^{GaAs} \pi R_p^2 + \varepsilon_{r}^{\text{ins}} (p^2 - \pi R_p^2)
$$

(2.37)

$$
\sigma_{NP} = \sigma_{r}^{GaAs} \pi R_p^2 + \sigma_{\text{ins}} (p^2 - \pi R_p^2)
$$

(2.38)

Here, $\varepsilon_{r}^{GaAs}$ is the real part of the complex dielectric constant of the QCL active region and $\sigma_{r}^{GaAs}$ is the conductivity of the QCL active region. The optical constants of the laterally confined doped layers can be evaluated using eqns. 2.37 and 2.38, by substituting the permittivity ($\varepsilon_{r}^{\text{topGaAs}}, \varepsilon_{r}^{\text{botGaAs}}$) and conductivity ($\sigma_{\text{topGaAs}}, \sigma_{\text{botGaAs}}$) of the top and bottom doped layers.

We find that the effective medium approximation is a very useful tool to analyse the losses in a laterally confined THz QCL and optimize for the best device geometry. In the next sub-sections, we discuss the effect of active region height, packing density of the nanopillar array and planarizing material on the optical properties of laterally confined THz QCLs. The active region of choice in all the calculations discussed below is the 3 THz
2. NANOPILLARS IN RTDS AND QCLS: THEORY

4 QW ETH design. This design has an average doping per period equal to $5.609 \times 10^{15}$ cm$^{-2}$. In the simulations, the thickness of the top and bottom $n^+$ GaAs contact layer is 100 nm, which is doped with a carrier concentration $N_d$ equal to $5 \times 10^{18}$ cm$^{-2}$.

2.11.3 Simulation results: effect of active region thickness

In general the thickness of a full-stack THz QCL ranges from 6 - 14 µm depending upon the design. In the case of the 3 THz 4 QW ETH design, a full-stack THz QCL with 150 repeats has a thickness of 10 µm. Ideally, to achieve the same gain as a standard THz QCL, one should implement the top-down approach on full-stack structures. Experimental considerations, however, limit the thickness of the active region to approximately 3 to 3.5 µm (ultrathin THz QCLs). This is discussed in detail in section 3.5. An important concern while implementing the top-down approach would be whether a plasmonic mode can be supported in a THz QCL with active region thickness less than 3 µm in a standard double metal geometry. Extending the argument to laterally confined THz QCLs, it would be important to know whether a common plasmonic mode can exist within the effective medium comprising of nanopillars and insulation between the top and bottom metal contacts.

Figure 2.29: Plasmonic mode calculated for (a) a THz QCL in a double metal waveguide, with active region thickness equal to 3 µm (b) a suspended nanopillar array ($\varepsilon^{\text{ins}} = \varepsilon^{\text{air}}$, $\sigma^{\text{ins}} = \sigma^{\text{air}}$), with active region thickness equal to 3 µm and pitch/diameter ($p/2R_p$) ratio = 4. Also shown is the cross-sectional view of the mode profile confined between the top and bottom metal contacts.

Figure 2.29(a) shows the plasmonic mode calculated for a 3 µm thick, Fabry-Pèrot ridge, with optical constants corresponding to a 3 THz 4 QW ETH design, in a double metal waveguide configuration. The mode is confined within the top and bottom metal
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contacts, similar to a standard full-stack laser. A comparison between the mode properties of ultrathin active regions with full stacks is discussed in section 4.10. Here, we limit the discussion to low-repeat period THz QCLs and their comparison with laterally confined THz QCLs. Figure 2.29(b) shows the plasmonic mode calculated for the same design, with optical constants corresponding to a nanopillar array of radius 50 nm, p/2R_p equal to 4 and active region height of 3 µm. For simplicity, we use air as the surrounding medium around the nanopillars. The use of the effective medium approach eliminates the need to define the number of nanopillars considered in the simulation and the same mesh can be used for standard THz QCLs and the laterally confined THz QCLs. It is interesting to note that a plasmonic mode exists in this effective medium. Furthermore, the plasmonic mode shown in figure 2.29 is confined within the top and bottom metal contacts, similar to THz QCLs with a double metal waveguide. This allows us to compare the waveguiding properties of THz QCLs with laterally confined THz QCLs.

Figure 2.30 compares the THz QCL with laterally confined THz QCL as a function of active region thickness. In a double metal ridge, the waveguide loss $\alpha_w$ increases from 9.6 cm$^{-1}$ to 10.5 cm$^{-1}$ as the thickness of the active region is reduced from 5 µm to 2 µm. This increase is explained in terms of greater field intensity at the metal/semiconductor interface as the active region thickness is reduced [3]. The overlap factor $\Gamma \sim 0.97$ increases very slightly with increase in thickness. The figure of merit (FOM) also varies slightly (0.09 cm to 0.1 cm), when the thickness is increased from 2 µm to 5 µm. Finally, we note that the effective refractive index or the propagation constant decreases with increase in active region thickness. Between a thickness of 2-5 µm the effective refractive index of a THz QCL in a double metal waveguide is estimated to be $\approx 3.65$. Similar to the 100 µm wide double metal ridge, the optical losses in a laterally confined THz QCL increases with decrease in thickness. This is shown in figure 2.30 for nanopillars surrounded by air as an insulating medium (also called suspended nanopillars). What is striking is the reduction in waveguide losses upon introducing lateral confinement. Let us compare a 3 µm thin THz QCL, with a 3 µm thin laterally confined THz QCL. As opposed to an optical loss of 9.45 cm$^{-1}$ in a 3 µm thin double metal ridge, the optical loss in 3 µm tall nanopillar array yields a significantly lower value (2.47 cm$^{-1}$). The low loss is attributed to the low conductivity of the surrounding medium ($\sigma_{ins}$), which is equal to 0 S/m in the case of air. The disadvantage of suspended nanopillars is that the optical mode leaks into the surrounding air. Hence, the overlap factor reduces from 0.97 in a 3 µm thin QCL to 0.70 in a 3 µm tall suspended nanopillar structure. The figure of merit of suspended nanopillars, still remains higher than the Fabry-Perot ridge. For example the figure of merit of a 3 µm tall suspended nanopillar array is three times more than the double metal ridge of the same
2.11.4 Simulation results: effect of pitch/diameter ratio

Here, we discuss the effect of pitch/diameter \((p/2R_p)\) ratio on the waveguide properties of the suspended nanopillar arrays. The \(p/2R_p\) characterises the packing density of the nanopillar array. As \(p/2R_p \to 0\), the optical properties of laterally confined THz QCLs \((\varepsilon_{NP}, \sigma_{NP})\) approaches the optical properties of a standard THz QCL \((\varepsilon_{GaAs}, \sigma_{GaAs})\), see eqns. 2.37-2.38. In reality, experimental considerations constrain the packing density that can be achieved. For the smallest pillars, a \(p/2R_p < 2\) suffers from two challenges.
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The first challenge arises from the proximity effect while directly writing a pattern using e-beam. The second issue pertains to incomplete etching of trench passage between the nanopillars, also called as reactive ion etching (RIE) lag. These problems are discussed in detail in Chapter 3. For these reasons we restrict our discussion to cases where the \( p/2R_p \) ratio \( \geq 2 \).

While it might seem that a small \( p/2R_p \) is ideal as it maximizes the number of pillars in an area, figure 2.31(a) shows that the optical losses of a suspended nanopillar array are highest when \( p/2R_p = 2 \). This loss is due to absorption by free carriers in the active region and the doped layers. As the \( p/2R_p \) ratio is increased, the losses decrease from \( 4 \) cm\(^{-1} \) to a lowest of \( 2.5 \) cm\(^{-1} \) at \( p/2R_p = 4 \). This decreases is due to the zero conductivity of air which forms part of the effective medium that supports the optical mode. As the \( p/2R_p \) is increased further, the optical mode weakens as it leaks out of the cavity. The overlap factor shown in figure 2.31(b) decreases with the \( p/2R_p \) ratio. From figure 2.31, we note that the highest figure of merit that is experimentally possible for laterally confined THz QCLs is achieved when the top contact is suspended and the pillars are packed with a \( p/2R_p = 4 \).

Let us now discuss what these results mean for nanopillar dimensions highlighted in figure 2.23. The gain of a nanopillar array is decided by the strength of the optical transition. The losses are dictated by the \( p/2R_p \) ratio. Therefore, if we were to pattern a nanopillar array, with \( R_p = 35 \) nm that permits intersubband transition (window P in figure 2.23), at a pitch equal to \( 4 \) times \( 2R_p \) (280 nm), the figure of merit would be maximum. To achieve the same figure of merit in a nanopillar array with \( R_p = 120 \) nm (window S in figure 2.23), the pillars have to be separated by a larger distance. The pitch equals \( 4 \) times \( 2R_p = 960 \) nm. Figure 2.32 shows the schematic diagram illustrating the optimum spacing for \( R_p = 35 \) nm and \( R_p = 120 \) nm nanopillars when the array is insulated by air, i.e. the nanopillars have a suspended top contact.
Figure 2.31: Effect of $p/2R_p$ on the optical properties of suspended nanopillar array fabricated from 3 THz 4 QW ETH design. Shown in the figure is a comparison of (a) waveguide losses (b) overlap (c) figure of merit and, (d) propagation constant $\text{Re} (\tilde{n}) = n$. Simulations have been performed using COMSOL v4.3, with active region thickness kept constant at 3 $\mu$m.
2.11 Effect of lateral confinement on plasmonic mode in THz QCLs

![Schematic diagram illustrating the optimum spacing of nanopillars when the array is insulated by air (\(\varepsilon_{\text{ins}} = \varepsilon_{\text{air}}, \sigma_{\text{ins}} = \sigma_{\text{air}}\)).](image)

**Figure 2.32:** Schematic diagram illustrating the optimum spacing of nanopillars when the array is insulated by air (\(\varepsilon_{\text{ins}} = \varepsilon_{\text{air}}, \sigma_{\text{ins}} = \sigma_{\text{air}}\)).

**2.11.5 Simulation results: effect of planarising material**

The planarizing material plays a critical role in the fabrication of potential quantum dot cascade lasers based on a top-down approach. Commonly used planarizing materials such as spin-on-glass, polyimide and cyclotene have a finite electrical conductivity, which can range from \(10^{-10} - 10^{-15}\) S/m \([105, 106, 107]\). Considering the variability in \(\varepsilon_{\text{ins}}\) and \(\sigma_{\text{ins}}\) arising out of differences in curing temperature, humidity and other processing parameters, we do not differentiate between available planarizing materials. Instead, we compare the optical mode parameters of a nanopillar array planarized with an insulator characterized with an \(\varepsilon_{\text{ins}} = 3.9\) and \(\sigma_{\text{ins}} = 10^{-10}\) S/m, with a nanopillar array that has a suspended top contact and is surrounded by air, which is characterized with an \(\varepsilon_{\text{air}} = 1\) and \(\sigma_{\text{air}} = 0\) S/m.

Figure 2.33(a) shows the waveguide losses of a planarized array as a function of \(p/2R_p\) ratio. Compared to a suspended array, the waveguide losses in an insulated array increase nearly exponentially as \(p/2R_p\) increases from 2 to 6. The minimum loss in an insulated array of pillars is achieved when \(p/2R_p\) ratio = 2, which is commensurate with the suspended array. To achieve the minimum loss, nanopillars with radial dimensions in the range of 35 nm to 150 nm (figure 2.23) must be separated by a pitch \(p\) equal to \(2(2R_p)\). Figure 2.34 shows the schematic diagram of the pillar arrangement, illustrating the optimum spacing for \(R_p = 35\) nm and \(R_p = 120\) nm nanopillars when the array is insulated by a dielectric medium.

In general, the minimum distance that an insulator can fill is determined by the fill
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Figure 2.33: Comparison of (a) waveguide losses (b) overlap (c) figure of merit, FOM (d) propagation constant, $\text{Re}(\tilde{n}) = n$ as a function of $p/2R_p$ ratio of the nanopillar array with a suspended top contact (red) and an unsuspended/insulated top contact (black), calculated using COMSOL v4.3. The nanopillar thickness is constant at 3 $\mu$m.

Figure 2.34: Schematic diagram illustrating the optimum spacing of nanopillars when the array is insulated by a dielectric ($\varepsilon_r^{\text{ins}} = 3.9$, $\sigma^{\text{ins}} = 10^{-10}$ S/m).
properties of the planarizing materials. Typically, this minimum distance is equal to 300 nm. For a pitch density $p/2R_p = 2$ that yields the lowest optical loss, the fill distance $p - 2R_p$ equals $2R_p$. In the case of pillars with radial dimensions in the range with $R_p = 35$ (to 150 nm), the optimum spacing that ensures the lowest optical loss is equal to 70 nm (to 300 nm). This distance is less than the fill length of typical planarizing materials (> 300 nm). For these range of pillar dimensions, it is not experimentally viable to achieve the lowest optical loss ($5 \text{ cm}^{-1}$) in insulated nanopillars. If we increase the $p/2R_p$ ratio to 4, the waveguide loss in an insulated array is $\approx 10 \text{ cm}^{-1}$. At the same $p/2R_p$ ratio, the waveguide loss of a suspended array is $2.5 \text{ cm}^{-1}$, which is four times lower than the insulated array. An advantage of retaining insulation is that the optical mode is confined more strongly in an insulated array as compared to a suspended array and decreases only slightly with increasing $p/2R_p$. In fact, the overlap factor in an insulated array approaches 0.9, which is close to what is observed in standard double metal THz QCLs. However, the suspended nanopillar array shows a higher figure of merit compared to the insulated array.

These simulations provide useful design considerations for optimizing the performance of a laterally confined THz QCL. Finally, we summarize the key results of this chapter below.

2.12 Summary and conclusions

In the first part of the chapter, we explored the effect of lateral confinement on the energy states of a simple structure, the resonant tunneling diode (RTD). Using Chia’s model for homogeneous nanopillars, we calculated the effect of surface states on the electrostatic potential of a laterally confined RTD. We found that the estimation of electrostatic radius is non-trivial as it depends upon many factors, such as density of interface states, doping of the epitaxial layer and the physical radius of the nanopillar. Using these results, we simulated the three-dimensional potential of an RTD nanopillar. We also extended the model to simulate the three-dimensional potential of a laterally confined THz QCL.

In the second part of the chapter, we used resonance conditions and optical selection rules to identify intersubband states that would permit radiation in laterally confined THz QCLs. We also identified windows of radial dimensions that permit emission between those that suppress emission.

Finally, we developed an effective medium approach to simulate plasmonic modes in laterally confined THz QCLs. From our simulations, we found that nanopillar arrays with a suspended top contact and a pitch/diameter ratio = 4, yielded a 2 to 4 times higher figure of merit compared to a double metal Fabry–Pérot ridge from the same active region.
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Chapter 3

Nanopillar arrays in RTDs and QCLs: Experimental realization

3.1 Introduction

In Chapter 2, we identified geometrical constraints under which the top-down nanofabrication approach would possibly yield improved temperature performance of THz QCLs. These constraints require the development of new processing routes that can achieve a suspended electrical contact simultaneously to \( \sim 10^7 \) nanopillars (section 2.11). Additionally, the constraints on the nanopillars only allow for a vertical sidewall profile with a tolerance such that the radius lies within the dimension windows, which permit radiative intersubband transitions.

Fabrication of such electrically connected nanopillar arrays is non-trivial as it can directly influence the electro-optic performance of laterally confined THz QCLs. It requires optimization of several experimental processes and their parameters, some of which are unique to THz QCLs. Furthermore, one processing stage can impact subsequent processing stages, which necessitates identification of processing steps that do not conflict with each other. In this chapter, we discuss the experimental challenges that were encountered during the fabrication of electrically connected nanopillar arrays in THz QCLs.

In chapter 2, we discussed that RTDs serve as a useful test bed to examine the electrical robustness of this top-down fabrication approach as the effect of device geometry can be clearly seen in the electrical behavior. However, fabrication of nanopillars in RTDs requires either the addition or omission of certain processing stages, which pertain only to the RTDs. In this chapter we demonstrate fabrication routes that are compatible with both RTDs and QCLs. Therefore, we first test the validity of our nanofabrication approach on RTDs. We
also present electrical characteristics of laterally-confined RTDs that allow us to comment on the electrical stability of these nanopillar arrays. In addition to electrical contact, we show evidence that suggests quantization effects in these nanopillar arrays, which is in agreement with quantization effects observed in a single nanopillar [89, 94, 102, 108].

In the next section, we discuss the RTD active regions that are compatible with the THz QCLs in terms of similar current density and material system. These RTD active regions are used to demonstrate the validity of our fabrication process.

### 3.2 RTD active region used: relevance to QCLs

The most pertinent material system to the growth of high-quality THz QCLs is the GaAs / Al\(_x\)Ga\(_{1-x}\)As system. What is in favour of this particular system is that both GaAs and AlAs have almost identical lattice constants [109]. Therefore, independent of the Aluminium concentration \(x\), the entire layered structure, that is typical of a QCL, is lattice matched. Furthermore, this system allows flexibility in engineering the barrier height for the electrons, based upon the concentration of Aluminium. Owing to these reasons, THz QCLs discussed in this thesis, were grown in the GaAs / Al\(_x\)Ga\(_{1-x}\)As system, exclusively.

Naturally, the simple single quantum well structures, i.e. the RTDs, were also grown in the same material system. The RTD active regions that we chose as test structures had to meet the following two criteria. The first and foremost requirement is that of peak current density \(J_p\), which is defined as the maximum current density due to resonant tunneling of electrons from the contacts into the quantum well (see section 2.2). In order to test electrical robustness of nanopillar arrays, this peak current density must be comparable to the threshold current density \(J_{th}\) of THz QCLs, which is defined as the current density at which the QCL overcomes losses and starts to exhibit lasing (see section 4.2). The second condition demanded that the RTD of choice must exhibit a negative differential peak at room temperature, i.e. the tunneling current must be larger than the background current due to crystal defects. This condition allowed us to test the electrical contacts of laterally-confined RTDs at 4 K as well as at room temperature.

Within the existing repository of wafers grown at Cavendish, we found that two RTD structures met with our requirements. These two wafers were labelled W0021 and A1700. While W0021 used AlAs barriers, A1700 used Al\(_x\)Ga\(_{1-x}\)As barrier where \(x = 0.33\). The barrier height of both these RTDs is higher than the barrier height of THz QCLs discussed in Chapter 3 which use \(x= 0.15\). However, this slight difference is not important to demonstrate the proof of principle. The epitaxial structure of W0021 is given as \(2/9/2\) where the thickness is expressed in nm and the AlAs barriers are highlighted in bold. The epitaxial
structure of A1700 is given as $5/10/5$ where the thickness is expressed in nm and the Al$_{0.33}$Ga$_{0.67}$As barriers are highlighted in bold. The complete layer structure that includes the thickness of spacers and contacts is detailed in appendix A. The electrical characteristics of these RTDs are discussed in sections 3.8 and 3.9.

Before proceeding to discuss the fabrication of nanopillar arrays, it is imperative to describe the growth of high-quality GaAs / Al$_x$Ga$_{1-x}$As layered structures, fashioned with atomic level precision. This precise control is enabled by molecular beam epitaxy, which is described below.

### 3.3 Molecular beam epitaxy

Molecular beam epitaxy (MBE) relies on deposition of atoms or cluster of atoms, with monolayer control, under an ultra high vacuum (typically $10^{-10}$ mTorr base pressure). These atoms are produced by heating high-purity solid elemental sources to their sublimation temperatures. Figure 3.1 shows the schematic diagram of a typical molecular beam epitaxy system. After loading the sample, a few preparatory steps are taken. Moisture is removed and a standard thermal degas is performed to remove the native oxides, following which the layer-by-layer growth of the III-V structure is performed. This occurs under the ultra high vacuum, where the vapourized elemental flux impinges upon a rotating, heated substrate.

Growth rate is determined by the group III flux rate under standard growth conditions, which includes optimal substrate temperature and group V excess. Individual layer composition and thickness are governed by a combination of deposited materials by use of shutters. Since the operation of the shutters is faster than typical growth rates, abrupt 'monolayer' interface can be achieved.

Growth rates can be determined by several techniques, such as reflection high-energy electron diffraction (RHEED), ex-situ X-Ray measurements, flux gauge and optical band pass pyrometer [110, 111]. Wafers discussed in this thesis were monitored prior to growth using an optical band pass pyrometer [110]. This technique detects oscillations in the surface temperature occuring during the growth of heteroepitaxial structures due to Fabry-Pérot cavity interference. The oscillation period can be related to the growth rate of the material that is being deposited [111]. Accurate growth rate are a key parameter in the QCL performance [112].
3.4 General methods: fabrication of nanopillar arrays

In the previous section, we described monolayer level control over the growth of the epitaxial layers to obtain confinement in the growth direction. In this section, we describe the techniques that are employed to achieve the designed lateral potential in nanopillars that are processed from layered structures grown using MBE.

Our philosophy behind fabrication of nanopillar arrays is given below.

The geometrical constraints described in Chapter 2 require precise control over the processing of nanopillars. It is therefore, essential that the final device geometry after multiple processing stages is as close as possible to the designed geometry, within the tolerance limits described in section 2.9. For control over the energy states due to lateral quantization, any deviation between the final geometry and the expected geometry must be accounted for at each processing stage. This is of use to subsequent iterations, where the disparity between the final and expected geometry is incorporated at the design stage itself.

The device geometry, i.e. the radial dimensions of the nanopillar and the pitch of the nanopillar array is defined using electron beam lithography. This lithography helps in defining the etch mask for the nanopillars. Although, there are other routes such as deposition of a colloidal solution of nanoparticles, which can act as an etch mask [113], such lithographic techniques do not allow control over the device geometry in terms of size and pattern.
3.4 General methods: fabrication of nanopillar arrays

Following the definition of an etch mask, the nanopillars are etched using plasma processing. Plasma processing (or dry etching) is far superior to wet chemical etching techniques in terms of obtaining a vertical sidewall profile \[114\]. Moreover, for radial dimensions in the range of sub-200 nm, dry etching is the only way to achieve pillars with a high-aspect ratio (diameter/height ratio). Unlike wet chemical etching, which is isotropic in nature and causes a rounded profile due to underetching of the mask, dry etching can be used to obtain any desired profile. This can be achieved by adding reactive species in the plasma. Therefore, the etch profile is controlled by a balance of physical sputtering, which is anisotropic in nature, and chemical etching, which reacts with the sample to be etched.

Following etching, the nanopillar arrays are planarized with an insulator. This insulation is etched back to expose the top n$^+$ doped GaAs contact, without compromising on the electrical integrity of the planarizing material. Finally, the nanopillars are connected in parallel by lithography and deposition of a top metal contact. Figure 3.2 shows the general process flowchart to fabricate electrically connected nanopillar arrays. These processing stages are common to both RTDs and QCLs.

![General process flowchart to fabricate electrically connected nanopillar arrays. These processing stages are common to both RTDs and THz QCLs.](image)

Below, we describe the general experimental techniques that we used to fabricate electrically connected nanopillar arrays.
3.3.1 Electron beam lithography

Electron beam lithography (or e-beam lithography) uses a focused beam of electrons to write patterns directly on to a resist, which is spin-coated on the sample [114]. The e-beam pattern is generated in a computer aided design software (AutoCAD), and transferred directly to a computer system which controls the exposure of the e-beam as it scans the sample.

E-beam lithography has the benefit of ultra high resolution (1-5 nm), that is not limited by the diffraction of light. Instead, the minimum pattern dimensions are determined by the beam spot size that is achievable with the electron optics and the interactions of electrons with the resist and substrate during the writing process.

In this work, e-beam patterns were written using Vistec VB6, ultra high resolution (UHR), extra wide field (EWF) deflection system. This system employs a Gaussian beam step and exposure strategy, with the thermal field emission gun operating at a maximum accelerating voltage of 100 KV. The maximum writing speed of the system is 50 MHz. The deflection coils allow the electron beam to be steered electromagnetically, around a fixed region, allowing selective exposure within that area without any movement of the sample relative to the column. Under the technical specifications listed for the above-mentioned system, the maximum possible deflection is 1.3 mm at 100 KV.

The e-beam pattern is written on a Poly (methyl) methacrylate (PMMA), a positive tone resist that has the advantage of long film life. PMMA also offers extremely high-resolution, has excellent surface adhesion characteristics and is not sensitive to white light. We use an undiluted solution of PMMA (A5) with a molecular weight of 950,000, which is spun at 5000 rpm for 1 minute. After coating the sample, we follow 10 min post-bake at 150°C to achieve a final resist thickness of ∼160-180 nm. The thickness of the e-beam resist is chosen keeping further processing stages in mind. If the thickness of the PMMA film is higher than 180 nm, then the dosage requirement would constrain the resolution of the e-beam pattern. On the other hand, if the PMMA film is lower than 160 nm, it would limit the thickness of the evaporated metal that serves as an etch mask (see section 3.5.2).

At this film thickness, the minimum radius (of a circular pattern) that can be written on a ∼500 µm GaAs substrate under optimized dosage conditions is restricted to 50 nm. This feature size is larger than the minimum resolution than can be theoretically achieved by the Vistec e-beam tool. This is because any pattern that is written by the e-beam system is broken down to smaller shapes, which are realizable by the pattern generator. The fracture process splits larger shapes into trapezoidal sub-shapes. In the case of writing an array of

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1Microchem PMMA data sheet, URL: http://microchem.com
3.4 General methods: fabrication of nanopillar arrays

circles, each circle is broken into trapezoidal sub-shapes. Therefore, the e-beam tool only writes a feature that best approximates the circle, with a grid size of 5 nm. Together with these approximations, and the interaction of electrons with the PMMA and the substrate, the minimum radius that can be conveniently achieved by the Vistec tool, is restricted to 50 nm. Therefore, the e-beam lithography step imposes a minimum radius of the nanopillar, which can be written on the sample.

3.4.2 Optical lithography

For patterns larger than 1 \( \mu \text{m} \), e-beam lithography can be prohibitively expensive and time consuming. For such feature sizes, optical photolithography is a convenient alternative. Photoresists are patterned by selective exposure to a UV light source, when the resist-coated sample is brought in contact with the optical mask. The selective exposure is performed using this mask, which has pre-defined regions that are either transparent or opaque to UV light. Patterns related to different processing stages can be included on a single optical mask. Using carefully designed alignment marks, the sample can be brought into alignment and subsequently exposed to the desired pattern. For all lithographic stages, apart from the definition of nanopillars, we use UV light to expose the desired feature. Depending upon the processing stage, these features may either be used to form metal contacts or to etch material.

After a standard clean with acetone and IPA, followed by a prebake step, we spin-coat the sample with a positive photoresist. In this work, we use Shipley series: 1805 and 1813, where the last two digits in the product number indicate the thickness of the photoresist film after spin coating at 5000 rpm for 1 min. Therefore, a sample coated with Shipley 1805 (1813) yields a film thickness of 500 nm (1800 nm). The minimum resolution that can be obtained by optical lithography often depends upon the thickness of the resist, the exposure time and the development time.

A sample coated with Shipley 1805, exposed between 3 to 3.5 secs and developed in a KOH based solution (MF319) for 15 to 30 secs, yields a minimum feature size of 1-2 \( \mu \text{m} \). This occurs when the optical mask is in complete contact with the resist. Shipley 1805 is used while performing lithography for metal contacts, where high alignment or high resolution is critical. In the case where the photoresist serves to protect the underlying features during a wet chemical etch, it is important to use a thicker photoresist to avoid underetching of the mask. Under this scenario, we use Shipley 1813 exposed between 6.5 to 7 secs and developed for 1 min.

There is a slight difference in the photoresist profile when it is used as a mask for wet
chemical etching versus when the resist is used for metal evaporation. In the former case, the resist is heated at 115 °C post exposure to hardbake it for chemical etching. Whereas, in the latter case, the resist is softbaked at 90 °C post exposure and dipped in chlorobenzene before development to obtain a sloping undercut resist profile. This is necessary to produce a shadow profile to facilitate a discontinuity in the metal film deposition. Figure 3.3 summarizes the process flow for optical photolithography.

Figure 3.3: Schematic diagram describing the photolithographic process flow. The process flow shows (a) photoresist spin-coated over the sample (b) exposure of the photoresist under UV light (c) photoresist after UV exposure (d) photoresist after development. Also shown in (d) is the resist profile when it is used as a mask during wet chemical etching and when it is used for metal evaporation.

3.4.3 Dry etching

In this section we discuss the principle behind etching highly vertical nanopillars using plasma processing (dry etching). Plasma processing involves a mechanism to generate ions, and impart these ions with the momentum that is directed towards the sample. This plasma consists of (i) neutral and ionized ions that etches material by physical sputtering, and (ii) electrons and free radicals that etches material by reacting with it chemically. In order to obtain highly vertical sidewall profile using plasma etching, it is necessary to obtain the right balance between these two processes. Unlike sputtering which removes material by physical bombardment of ions, chemical etching depends upon the formation of volatile products with the exposed surface and offers etch selectivity over the mask.
3.4 General methods: fabrication of nanopillar arrays

Generation of this plasma requires a chamber that is maintained at a low pressure (typically 0.01 to 1 Torr). When a high frequency voltage is applied between the electrodes, current flows forming a plasma which emits a characteristic glow. Figure 3.4 shows the schematic diagram of the etching chamber after the plasma is struck upon introduction of the feed gas. This plasma is an ionized gas with equal number of positive and negative charges. In etching systems, the extent of ionization is quite small, typically only one charged particle per $10^6 - 10^7$ neutral atoms or molecules. The difference in the mobility of the positive and negative charges causes the formation of a plasma sheath at the boundaries of the discharge.

![Schematic diagram showing plasma chamber. The particle motion is shown for the positive half cycle of the RF bias. Adapted from [2].](image)

Figure 3.4: Schematic diagram showing plasma chamber. The particle motion is shown for the positive half cycle of the RF bias. Adapted from [2].

Figure 3.5 shows the multiple processes that are involved in etching. Under the influence of the electric field, the ions are directed perpendicular to the sample causing anisotropic etching (figure 3.5(a)). If the pressure is high, these ions may cause (i) mask erosion and (ii) mechanical damage of the sample. Therefore, one of the necessary conditions to control when sputtering is dominant is to maintain a chamber pressure that is less than 60 mT. In the case where chemical etching is dominant, the etch is selective but isotropic (figure 3.5(b)). Since chemical etching requires a suitable density of reactive species to etch the surface, it is dependent upon the RF power that is applied to generate the plasma. Reliable chemical etching also depends upon the volatility of the reaction products. Higher volatility of the reaction products would ensure a uniform etch rate of the
3. NANOPILLAR ARRAYS IN RTDS AND QCLS: EXPERIMENTAL REALIZATION

Figure 3.5: Schematic diagrams showing four basic methods of plasma etching: (a) Sputtering of ions physically removes substrate material, causing directional etching. (b) Thermalized neutral radicals chemically react with the substrate material to form volatile products, causing isotropic etching. (c) In the case where neutral radicals cannot form a volatile product, the impinging ion flux can modify substrate reactivity, leading to energetic ion-enhanced anisotropic etching. (d) There may be a case where the substrate and the etchant would react spontaneously and etch isotropically, if it were not for the inhibitor species - leading to inhibitor ion-enhanced etching. The inhibitors form a thin film on vertical surfaces, which acts as a barrier to the etchant and prevents attack of sidewalls, leading to anisotropic etching. Adapted from [115].
3.4 General methods: fabrication of nanopillar arrays

sample. Depending upon the sample and the reactant species in the plasma, there may be other mechanisms that dominate etching. For example, neutral radicals alone may not be able to react with the substrate. However, if the surface is modified by an impinging flux of ions, either by formation of dangling bonds, or by introduction of defects/dislocations in the lattice, the neutral radicals may chemically react with the substrate (figure 3.5(c)). This ion-enhanced chemical etching occurs in a direction that is perpendicular to the growth, and is therefore anisotropic. The etch rate is dependent upon many empirical parameters such as ion-density, chamber pressure, RF power and substrate to reactant chemistry. In the fourth case, neutral radicals may spontaneously react with the surface, causing rapid isotropic etching. In the presence of an inhibitor species, a passivating layer protects the sidewalls of the feature. Since the direction of the ion flux is perpendicular to the surface, the ions remove the protective layer on the surface, thereby allowing the neutral radicals to chemically react with the surface. This mechanism of etching falls under the category of inhibitor ion-enhanced etching and leads to vertical sidewalls (figure 3.5(d)).

There is a wide choice of dry etching systems and gases that can etch III-V materials [116, 117, 118]. However, not all chemistries and etch systems, can achieve high-aspect ratio nanopillars with vertical sidewalls. These reasons may vary from corrosiveness of gas, control over ion energies, control over ion trajectories, selectivity over the etch mask and so on. Below, we discuss the systems and gas chemistries that we used to achieve nanopillars in GaAs / Al\textsubscript{x}Ga\textsubscript{1-x}As materials.

### 3.4.3.1 Reaction ion etching system (RIE)

The schematic diagram of a typical reactive ion etching (RIE) system is shown in figure 3.4. This system uses a single RF coil operating at 13.56 MHz, and an anode that is larger than the cathode. Often, the entire chamber is used as an anode. Increasing the anode size with respect to the cathode raises the voltage drop across the plasma sheath, increasing the ion energy and therefore etch anisotropy [2, 115]. In this work, an RIE system is employed under two scenarios. In the first scenario, an RIE system is used to etch SiO\textsubscript{2} (see section 3.5.2.2 and section 3.5.4.3). In the second scenario, an RIE system is used directly to etch nanopillars, see section 3.5.3.5.

**I. OXIDE ETCH**

Figure 3.6 shows the schematic diagram of the RIE system, a JLS designs Ltd bench-top plasma pod, that is used to etch SiO\textsubscript{2}. The SiO\textsubscript{2} layer is etched in a CHF\textsubscript{3} and O\textsubscript{2}
plasma. The plasma etching system has an aluminium chamber (280 mm diameter, 150 mm high) with a substrate electrode (125 mm diameter) that is water-cooled. The top electrode is grounded and is accompanied with an internal gas distribution head. The plasma chemistry of CHF$_3$ etching of SiO$_2$ is quite complex and is mediated by several gas phase reactions \cite{119}. However, the overall reaction can be summarized as $2\text{CHF}_3 + \text{O}_2 \rightarrow 2\text{CO} + \text{H}_2 + \text{SiF}_4$ \cite{120}.

Figure 3.6: Schematic diagram of the reactive ion etching system, used for etching silicon oxide

**II. GaAs / Al$_x$Ga$_{1-x}$As ETCH**

Figure 3.7 shows the schematic diagram of a Plasmatherm load-locked RIE system (SLR 720), that is used to etch GaAs / Al$_x$Ga$_{1-x}$As. The samples are mounted onto a Si wafer which rests on an alumina platen in a manually operated load-locked chamber. Prior to etching, this alumina platen is transferred to the plasma chamber using a mechanical arm. A load-lock system minimizes exposure of the plasma chamber to ambient moisture and oxygen which can cause the aluminium in Al$_x$Ga$_{1-x}$As to oxidize, reducing it’s reactivity to chemical etching.

The plasma etching system is equipped with a 500 W RF generator and has a substrate
3.4 General methods: fabrication of nanopillar arrays

electrode that is 280 mm in diameter. The feed gas that forms the reactive plasma uses SiCl₄ and Ar. Under ideal conditions, this chemistry, selective over a wide range of dielectric, photoresist and metal mask, etches GaAs and AlₓGa₁₋ₓAs at an equal rate. In the first step SiCl₄ dissociates into Si and 2Cl₂. These chlorine molecules collide with electrons to form atomic chlorine, which gets adsorbed on the surface as GaAs-Cl. This leads to the following reaction GaAs-Cl → GaClₓ + AsClᵧ, where x and y may range from 1 to 3. In the case of Al, atomic chlorine reacts with the surface to form AlCl₃. Other reactive species in the plasma such as energetic ions (Cl₂⁺, Cl⁺) and electrons may assist the reaction on the surface [121]. The benefit of introducing Si in the feed gas is that it acts as the inhibitor species in the plasma, reacting with the oxygen present in the chamber to form SiOₓ protective layer over the sidewalls (see Figure 3.5(d)).

![Figure 3.7: Schematic diagram of the reactive ion etching system, used for etching GaAs / AlₓGa₁₋ₓAs](image)

### 3.4.3.2 Inductively coupled plasma (ICP) RIE system

As described in figure 3.5(a), one of the important criteria to maintain directionality of the etch is low chamber pressure. Reducing the pressure increases the mean free path of the ions which limits scattering within the reactive plasma and ensures a trajectory per-
3. NANOPILLAR ARRAYS IN RTDS AND QCLS: EXPERIMENTAL REALIZATION

perpendicular to the sample. While this ensures vertical sidewalls of the feature (nanopillars), reduction in pressure limits the etch rate and hence the etch depth of the feature. Furthermore, reduction in pressure adversely influences the convective cooling of the substrate, which raises the temperature of the sample for plasma reactions. To compensate for the reduced etch rate, one can increase the RF power in an RIE, which increases the density of the reactive species. However, this may influence several other reaction parameters at the same time.

To circumvent this problem, high aspect ratio structures are generally etched in inductively coupled (ICP) RIE systems [122]. In an ICP RIE, two independent RF sources operating at 13.56 MHz are used, where one RF coil (chamber) is used to create a high-density plasma and the other RF coil (table) is used to direct and accelerate the reactive species from the plasma to the sample. The two RF generators allow independent control of ion density and the kinetic energy of the reactive species [116, 117, 118].

Figure 3.8: Schematic diagram of the in-house ICP RIE

Figure 3.8 shows the schematic diagram of the in-house inductively coupled reactive ion etcher (ICP RIE). By adding an additional 300 W RF coil to an existing RIE80 system (JLS Instruments Ltd), this system was modified to generate the ion density using this
3.5 Fabrication of electrically connected nanopillar arrays

In this section, we present the sequential progress of fabricating electrically connected nanopillar arrays, starting from definition of etch-mask to removal of insulation post top-contact deposition. For each sequence, we specify the parameters that we use to gauge the quality of processing and then discuss the experimental results.

3.5.1 Processing guidelines

Before listing our processing guidelines, it is useful to collate the ideal characteristics of a top-down laterally confined THz QCL derived from our theoretical analysis in Chapter 2.

(a) The device should comprise of nanopillars with sub-200 nm radius. Pillars of only those radial dimensions will lead to emission, which are allowed by the optical selection rules. The sidewall profile should be vertical, with a tolerance that is dictated by the resonance conditions.

(b) The height of the nanopillar must approach the height of a standard THz QCL. This is
required to achieve sufficient gain to overcome optical losses.

(c) The device architecture should comprise an array of nanopillars, electrically connected in parallel. This is required to ensure that the material gain of a top-down laterally confined THz QCL is comparable to the gain of a standard Fabry-Perot ridge. Under first approximation, this condition requires that the array must be electrically and structurally robust to carry a current density that is comparable to the threshold current density of a THz QCL (100-900 A/cm² [6, 37, 123]). As discussed in section 2.11, a Fabry-Perot ridge of dimensions that is 2 mm long and 100 μm wide is equivalent to $10^7$ nanopillars $\times (\pi R_p^2)$, where $R_p = 50$ nm.

(d) To minimize optical losses in the device architecture the nanopillar array must have the flexibility of removal of planarization at a later stage to obtain a suspended contact if so required.

(e) Finally, the nanopillar array should be packed such that the pitch/diameter ratio $= 4$. For a square lattice, this ratio ensures maximum figure of merit of the device architecture.

Based on the simulation results described in section 2.11, table 3.1 summarizes the ideal device parameters of a sub-200 nm pillar array in a QCL that is optimized for THz emission.

<table>
<thead>
<tr>
<th>Example radius, $R_p$ in nm</th>
<th>Ideal pitch, $p$ in nm</th>
<th>Ideal Pitch/diameter ($p/2R_p$) Ratio</th>
<th>Ideal number of pillars in an array</th>
<th>Ideal equivalent physical area in $\mu m^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>280</td>
<td>4</td>
<td>$5.1 \times 10^7$</td>
<td>200000</td>
</tr>
<tr>
<td>50</td>
<td>400</td>
<td>4</td>
<td>$2.5 \times 10^7$</td>
<td>200000</td>
</tr>
<tr>
<td>120</td>
<td>960</td>
<td>4</td>
<td>$4.4 \times 10^6$</td>
<td>200000</td>
</tr>
<tr>
<td>150</td>
<td>1200</td>
<td>4</td>
<td>$2.8 \times 10^6$</td>
<td>200000</td>
</tr>
<tr>
<td>200</td>
<td>1600</td>
<td>4</td>
<td>$1.6 \times 10^6$</td>
<td>200000</td>
</tr>
</tbody>
</table>

Table 3.1: Ideal device parameters of a sub-200 nm pillar array optimized for emission in a THz QCL.

A direct implementation of this ideal device architecture on THz QCLs would be arduous. Furthermore, it would impede troubleshooting of processing-related problems, as well as hinder the understanding of electro-optic characteristics which are correlated with geometry. Therefore, in this work, we have attempted to adhere to some of these ideal characteristics, which at the same time allow us to demonstrate the proof of principle.
These processing guidelines have been designed such that when the nanopillar array is fabricated in THz QCLs, it meets the stringent structural requirements of THz QCLs and when fabricated in test RTDs, it meets the electrical requirements imposed by the test RTD. These processing guidelines are given below.

(a) Multiple arrays of nanopillars are defined using e-beam lithography, where nanopillars in each array have a constant radius. This radius varies between arrays and ranges from $R_p = 50 \text{ nm}$ to $200 \text{ nm}$. While the minimum radius is limited by e-beam lithography (section 3.4.1), we have not attempted to define the radius such that it necessarily permits intersubband emission.

(b) The etching is optimized to achieve the maximum height that is possible for 50 - 200 nm radius pillars using available dry etching capabilities. This is to experimentally identify the optimum device dimensions that are structurally stable in top-down laterally confined THz QCLs.

(c) The device architecture is designed to electrically connect an array of nanopillars in parallel. The optical mask is flexible to simultaneously connect to any number of pillars defined by e-beam within a footprint of 500 $\mu\text{m} \times 500 \mu\text{m}$. However, to be consistent in our measurements, we keep the number of nanopillars in an array as constant and equal to 500 $\times$ 500. The electrical stability of the array is tested on those RTD active regions, which can support current densities that are comparable to the threshold current densities of THz QCLs.

(e) The processing route is designed for flexibility in removal of insulation post top-contact metallization. Therefore, the designed fabrication process allows for both suspended and unsuspended top-contact.

(f) Independent of the diameter, the pitch of the nanopillar array is kept constant at 1 $\mu\text{m}$. Therefore, the pitch/diameter ratio varies for each array. This distance was chosen to meet gap-fill specifications of conventional planarizing materials in the first instance.

Table 3.2 summarizes the key parameters that were used in the definition of nanopillar arrays while processing. Note that the parameters of the array shown below do not follow the optimum array pattern predicted for optimizing the emission from a THz QCL, see table 3.1. However, they bridge the gap in our understanding of lateral confinement in a single nanopillar to an array of nanopillars. The physical transport area of the nanopillars...
3. NANOPILLAR ARRAYS IN RTDS AND QCLS: EXPERIMENTAL REALIZATION

is equivalent to the physical transport area of typical large-area RTDs (100 to 40000 \( \mu \text{m}^2 \)).

<table>
<thead>
<tr>
<th>Radius, ( R_p ) in nm</th>
<th>Pitch, ( p ) in ( \mu \text{m} )</th>
<th>Pitch/diameter ((p/2R_p)) Ratio</th>
<th>Number of pillars in an array</th>
<th>Equivalent physical area in ( \mu \text{m}^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1</td>
<td>10</td>
<td>500 x 500</td>
<td>490</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>5</td>
<td>500 x 500</td>
<td>1963</td>
</tr>
<tr>
<td>150</td>
<td>1</td>
<td>3.3</td>
<td>500 x 500</td>
<td>4417</td>
</tr>
<tr>
<td>200</td>
<td>1</td>
<td>2.5</td>
<td>500 x 500</td>
<td>7854</td>
</tr>
</tbody>
</table>

Table 3.2: Device parameters that define the nanopillar pattern while processing.

Figure 3.9 shows the schematic diagram of the nanopillar pattern written using e-beam lithography, keeping the above-mentioned processing guidelines in mind. Note that the footprint of the array on the chip is constant. Also shown in figure 3.9 is the position of the top and bottom-contact pads relative to the nanopillar pattern.

![Figure 3.9: Schematic diagram showing (a) the nanopillar pattern written using e-beam lithography (b) the top and bottom-contact pads relative to the the nanopillar pattern.](image)

3.5.2 Etch mask definition

Upon e-beam lithography of the array pattern, the first stage of processing is to transfer the pattern written on the resist to an etch mask. This etch mask may be a dielectric or a metal. The choice of etch mask material determines the etch quality and the type of top-contact to the nanopillar array. Below we discuss the parameters used to assess the merit of an etch mask.
3.5 Fabrication of electrically connected nanopillar arrays

3.5.2.1 Etch-mask assessment parameters

So far we have used \( R_p \) to indicate the radius of the nanopillar that is written on the resist. After transferring the pattern from the e-beam resist to the etch mask, the radial dimensions may vary depending upon material and process conditions. We call the radius of the etch mask as \( R_{\text{mask}} \). The difference between \( R_{\text{mask}} \) and \( R_p \), quantifies the consistency of transfer, which is our first assessment parameter. The second parameter that we use to assess the integrity of an etch mask is its durability, i.e. the resistance to withstand physical erosion and chemical reaction during plasma processing of nanopillars. The endurance of the etch mask may depend upon the thickness, shape and material of the etch mask, but can affect the aspect ratio and the sidewall profile of the etched nanopillar. While these conditions may be relaxed for nanopillars in RTDs, they are of significant importance to nanopillars in THz QCLs where etch depth and sidewall uniformity is a big concern (see section 2.8).

3.5.2.2 Dielectric mask: results

Here, we describe the process of transferring the e-beam pattern on to a dielectric mask which is generally used in inductively coupled plasma RIE systems to etch high aspect ratio features. We review the experimental results for nanopillars in light of the above-mentioned assessment parameters. The process of transferring the pattern from an e-beam resist to a dielectric mask is a two stage process. In the first stage, the pattern on the resist is transferred on to a sacrificial mask. In the second stage, the pattern from the sacrificial mask is transferred on to the dielectric layer. This process is summarized in Figure 3.10.

As described in section 3.4.1, the array pattern is written on an e-beam resist (160-180 nm thick PMMA). This resist is spin-coated over a 100 nm thick dielectric that is deposited using plasma enhanced chemical vapour deposition (PECVD) on a pre-cleaned chip cleaved from the wafer of choice. This dielectric layer is essentially SiO\(_2\) deposited at a temperature of 300 °C at a rate of 7 nm/sec. The dielectric thickness was chosen to be equal to the minimum nanopillar diameter defined using e-beam (2 x 50 nm), to maintain a mechanically stable mask profile, i.e. an aspect ratio of 1:1. Following e-beam exposure the resist is developed for 3-4 sec in a solution of MIBK:MEK:IPA (5:1:15) followed by a rinse in IPA for 30 sec. A thin layer of Ti/Al (5/50 nm) is evaporated, which acts as a sacrificial mask for the underlying SiO\(_2\). Figure 3.11 shows the scanning electron microscope (SEM) images of Ti/Al disks with a radius \( R_p = 50 \text{ nm}, 100 \text{ nm and 150 nm} \) after metal liftoff. Note that the pattern defined by e-beam is transferred from the resist to the sacrificial mask Ti/Al with a high degree of consistency, i.e. \( R_p = R_{\text{Ti/Al}} \).
3. NANOPILLAR ARRAYS IN RTDS AND QCLS: EXPERIMENTAL REALIZATION

Figure 3.10: Process Schematic (a) 100 nm SiO$_2$ deposited on a clean 6 mm x 7 mm chip (b) e-beam lithography and development of resist (c) evaporation of Ti/Al and lift-off (d) dry etch of SiO$_2$

Figure 3.11: Scanning electron micrograph of Ti/Al disks after e-beam lithography and lift-off, shown for three different arrays (a) $R_p = 50$ nm (b) $R_p = 100$ nm (c) $R_p = 150$ nm.
3.5 Fabrication of electrically connected nanopillar arrays

In the second stage of pattern transfer, the Ti/Al serves as an etch mask for the underlying SiO$_2$ layer. The SiO$_2$ layer is etched in the plasma-pod in a CHF$_3$ and O$_2$ plasma, see figure 3.6. At an RF power of 75 W, CHF$_3$ (O$_2$) flowrate at 30 (4) sccm and base pressure of 60 mTorr, the plasma etches 100 nm of SiO$_2$ in 6 mins. The sacrificial Ti/Al mask is removed by rinsing in Microposit developer - MF319 (a N(CH$_3$)$_4$OH$^-$ based alkaline solution) for 3 mins, followed by a rinse in DI water.

![Figure 3.12: Scanning electron micrograph of SiO$_2$ disks etched in CHF$_3$ and O$_2$ plasma using Ti/Al mask with (a) R$_{Ti/Al}$ = R$_p$ = 50 nm (b) R$_{Ti/Al}$ = R$_p$ = 100 nm (c) R$_{Ti/Al}$ = R$_p$ = 150 nm.](image)

Figure 3.12: Scanning electron micrograph of SiO$_2$ disks etched in CHF$_3$ and O$_2$ plasma using Ti/Al mask with (a) R$_{Ti/Al}$ = R$_p$ = 50 nm (b) R$_{Ti/Al}$ = R$_p$ = 100 nm (c) R$_{Ti/Al}$ = R$_p$ = 150 nm.

![Figure 3.13: (a) Schematic diagram of SiO$_2$ disks after etching (b) schematic diagram of SiO$_2$ disks after removal of Ti/Al layer (c) Scanning electron micrograph of SiO$_2$ disks after etching, isometric view.](image)

Figure 3.13: (a) Schematic diagram of SiO$_2$ disks after etching (b) schematic diagram of SiO$_2$ disks after removal of Ti/Al layer (c) Scanning electron micrograph of SiO$_2$ disks after etching, isometric view.

Figure 3.12 shows the scanning electron microscope (SEM) images of SiO$_2$ disks after etching, using the Ti/Al pattern shown in figure 3.11. We note that the etched SiO$_2$ disks...
are larger than the Ti/Al masks, i.e. $R_{SiO_2} \cdot R_{Ti/Al} = R_{SiO_2} \cdot R_p \approx 50$ nm. Figure 3.13(a-b) shows the schematic diagram of the SiO$_2$ disks immediately after etching, and after removal of the Ti/Al sacrificial mask. This schematic is corroborated with the isometric view of the SiO$_2$ disks recorded immediately after etching, using scanning electron microscopy, see figure 3.13(c). The increase in the difference between $R_{SiO_2}$ and $R_{Ti/Al} \approx 140$ nm instead of 50 nm, is due to reduced CHF$_3$ content in the plasma. In the case of figure 3.13(c), we used 30:10 sccm, instead of the optimized process involving CHF$_3$ to O$_2$ ratio of 30:4 sccm.

The positive slope associated with the sidewall profile of the etch mask indicates insufficient ion energy and density during reaction ion etching, leading to reduced sputtering and chemical removal. Increasing the RF power and pressure of the reactive species can correct the sidewall profile, reducing the difference between $R_{SiO_2}$ and $R_p$. However, attempts in the direction of high pressure prompted plasma instabilities within the chamber. Improvements in power from 75 W to 100 W, and changes in the ratio of CHF$_3$ to O$_2$ from 30:4 to 30:3, 50:2 returned similar enlargement of feature sizes. Under these constraints, we found that a dielectric etch mask compromised on the consistency of pattern transfer, even before etching the nanopillars. To correct this inconsistency, we removed the second stage of pattern transfer and instead focused on using a metal mask directly. Below, we discuss the fabrication procedure and reproducibility of pattern transfer from e-beam resist to a metal mask.

### 3.5.2.3 Metal mask: results

In the case of a metal mask, the pattern is transferred from the e-beam resist to 100-140 nm, thick gold. The schematic diagram of the process is shown in figure 3.14.

![Figure 3.14: Process Schematic (a) E-beam lithography and development of resist (c) evaporation of NiCr/Au](image)

The thickness of the gold mask is limited by the thickness of the e-beam resist. Evaporation of gold over GaAs requires the use of a wetting layer, which promotes the adhesion
3.5 Fabrication of electrically connected nanopillar arrays

of gold to the surface. This wetting layer may be 5-10 nm of Ti or Nichrome (NiCr), which is a non-magnetic alloy of Ni and Cr. While NiCr/Au forms a permanent self-aligned Schottky contact with the top n+ doped GaAs layer, Ti/Au etch-mask can be easily removed in buffered hydrofluoric (BHF) acid if an additional non-aligned ohmic contact is desired. However, the merits of NiCr/Au contact supersede that of Ti/Au. Unlike NiCr/Au, Ti/Au is unsuitable for processes such as etch-residue and insulation removal (section 3.5.6). These processes involve buffered hydrofluoric acid, which rapidly reacts with Ti with an etch rate of 1000 nm/min [124]. Figure 3.23 shows the Ti/Au mask partially removed after cleaning the samples in BHF. On these grounds, we prefer to use a NiCr/Au etch mask over a Ti/Au etch mask.

Figure 3.15 shows the scanning electron micrograph of the NiCr/Au etch mask after lift off. Note that the pattern is transferred from the e-beam resist to gold, with high degree of fidelity, i.e. \( R_{\text{NiCr/Au}} \approx R_p \).

![Figure 3.15: Scanning electron micrograph of NiCr/Au etch mask after lift off, shown for three different arrays (a) \( R_p = 50 \) nm (b) \( R_p = 100 \) nm (c) \( R_p = 200 \) nm.](image)

3.5.2.4 Etch mask summary

In terms of pattern transfer, we note that a metal mask offers a higher degree of fidelity, as compared to a dielectric mask. This metal mask may either comprise of NiCr/Au deposition or a Ti/Au deposition. While NiCr/Au forms a permanent self-aligned Schottky contact to the nanopillars, both Ti/Au and SiO\(_2\) can be removed in BHF to deposit a non-aligned, shallow ohmic contact. This contact may be formed from (a) an AuGeNi slug annealed at 400°C for 40 secs or (b) the evaporation of Pd/Ge (25/75 nm) subsequently scintered at 350°C for 300 secs. However, a secondary contact that involves rapid thermal annealing jeopardises the integrity of the planarising material [125].

A self-aligned ohmic contact can be formed using a two-stage metal etch mask. This involves a primary evaporation step of AuGeNi or Pd/Ge, followed by a secondary evap-
oration step involving NiCr/Au. However, the combined thickness of the mask increases with two-stage evaporations, which poses a structural problem for masks with \( R_p \approx 50 \text{ nm} \) [94].

Table 3.3 compares the different masks, in terms of consistency of pattern transfer, type of contact and suitability for further processing. So far, we have not commented on the endurance of the etch mask to plasma processing. In the following section, we describe the etch of high aspect ratio pillars in GaAs / Al\(_x\)Ga\(_{1-x}\)As materials using both SiO\(_2\) and NiCr/Au etch masks.

<table>
<thead>
<tr>
<th>Etch mask assessment parameters</th>
<th>Dielectric</th>
<th>Metal</th>
<th>Metal (reports)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO(_2)</td>
<td>NiCr/Au</td>
<td>Two stage evaporation: AuGeNi (PdGe) + Ti/Au [94]</td>
</tr>
<tr>
<td>Fidelity of transfer</td>
<td>( R_{SiO_2} - R_p \geq 50 \text{ nm} ) ( R_p = 50 - 200 \text{ nm} )</td>
<td>( R_{NiCr/Au} \approx R_p, R_p = 50 - 200 \text{ nm} )</td>
<td>Combined metal thickness ( \geq 200 \text{ nm} ), not suitable for ( R_p = 50 \text{ nm} )</td>
</tr>
<tr>
<td>Type of contact</td>
<td>Not aligned: Schottky or ohmic</td>
<td>Aligned: Schottky</td>
<td>Aligned: ohmic</td>
</tr>
<tr>
<td>Suitability for planarization and insulation removal</td>
<td>Yes, with Schottky contact</td>
<td>Yes, with Schottky contact</td>
<td>Untested in this work</td>
</tr>
</tbody>
</table>

Table 3.3: Comparison of etch masks in terms of fidelity of pattern transfer, type of contact and suitability for further processing.

3.5.3 Etch of high aspect ratio pillars

The central step in realizing top-down laterally confined THz QCLs is the high quality etching of high aspect ratio nanopillars. In this work, we have attempted to identify experimental processes and systems that maximize the aspect ratio and maintain a vertical sidewall profile for pillars with sub-200 nm radial dimensions. Below, we describe the factors that limit the aspect ratio of nanopillars in GaAs / Al\(_x\)Ga\(_{1-x}\)As materials.

3.5.3.1 Factors affecting the aspect ratio

There are two factors that limit the aspect ratio of the nanopillar during plasma processing. The first factor that comes into play is the mask erosion. Ideally, the resistance of an etch mask to plasma processing should be infinite. In reality, the energy of ions erodes
the material of the mask, albeit at a much lower rate as compared to GaAs (Al\textsubscript{x}Ga\textsubscript{1-x}As). Therefore, the height of the nanopillar that can be successfully etched is equal to the thickness of the etch mask times the ratio of the etch rates between the mask and the GaAs (Al\textsubscript{x}Ga\textsubscript{1-x}As). The second factor that influences the etch depth is the aspect ratio dependent etching (ARDE) \cite{126}. This second parameter encompasses multiple processes that cause the etch rate to reduce with time. These processes include aspect ratio dependent transport of neutrals, and shadowing of ions and neutrals \cite{126}. In the first case, transport of neutrals is attenuated due to reflections from the sidewalls as they travel to the surface. This occurs when the neutrals have mean free path length larger than the channel length, which in the case of an array is p - 2R\textsubscript{p}. In the second case, as the etch depth increases, the angular spread function of the ions and neutrals decreases. This reduces the number of ions and neutrals reaching the etch surface. Under this scenario, the radicals dominate the etching and attack the sidewalls of the etched feature, which leads to undercutting and structural instability of the nanopillar array. This effect worsens if the channel length, or the p - 2R\textsubscript{p}, reduces, and is commonly described as RIE lag \cite{116, 126}.

### 3.5.3.2 Etch assessment parameters

In this section we define the parameters employed to assess the quality of the etch. In an ideal scenario, the radial dimensions of the nanopillar should be transferred with high degree of fidelity, from the e-beam stage to the etch-mask stage and finally to the etched pillar stage. This implies that R\textsubscript{p} = R\textsubscript{mask} = R\textsubscript{etch}, where R\textsubscript{etch} is the radial dimension of the pillar after etching. Furthermore, the nanopillar of height H and aspect ratio R\textsubscript{etch} \mid z=0 : H should have a vertical profile, i.e. R\textsubscript{etch} \mid z=H = R\textsubscript{etch} \mid z=0, see figure 3.16(a). However, the dimensions and the sidewall profile may alter significantly from the ideal geometry after processing the nanopillars in a reactive ion etching system. In order to quantify this deviation, we characterize the quality of plasma processing with the following parameters.

The first parameter quantifies the consistency of pattern transfer from the e-beam stage to the etch stage. Accounting for dimension variations along the growth direction (z), we define the average radius of the nanopillar as R\textsubscript{etch} \mid z=H/2 = \frac{R\textsubscript{etch} \mid z=H + R\textsubscript{etch} \mid z=0}{2}. The difference between this average radius and the radius defined on the e-beam resist R\textsubscript{p}, is defined as \Delta R\textsubscript{etch} and it quantifies the consistency or fidelity of pattern transfer. The second parameter quantifies the profile of the sidewall. The inclination of the sloping sidewall with the vertical axis, defined as \theta = \tan^{-1} \frac{R\textsubscript{mask} \mid z=H - R\textsubscript{mask} \mid z=0}{H} characterizes the closeness of the sidewall profile to the ideal geometry. While a positive \theta indicates insufficient etching, see figure 3.16(b), a negative \theta implies an undercut of the nanostructure due to enhanced...
chemical reactivity, figure 3.16(c).

![Figure 3.16: Sidewall profile of nanopillars after reactive ion etching, shown in the case of (a) ideal conditions (b) insufficient physical and chemical etching, and (c) undercutting due to greater chemical reactivity.](image)

3.5.3.3 Etch in ICP using a dielectric mask: results

In this section we discuss the results obtained from etching nanopillars in the in-house ICP RIE, see section 3.4.3.2, using a dielectric etch mask. Before etching, the chamber is pre-cleaned in CHF$_3$/O$_2$ plasma at low and high pressures for 30 min each. This pre-treatment cleans the ICP tube of any depositions, identified as containing Si-O-F-Cl [127] that can start to detach from the tube walls after multiple etches. The chamber is cleaned further in an O$_2$ plasma to remove any hydrocarbon residue on the chamber walls. To ensure reproducibility of the etch, the chamber is preconditioned with the SiCl$_4$/Ar etch process without loading the samples. This involves tuning a network of reactive elements to match the impedance of the RF coil with the reactive load (the plasma). The temperature of the substrate electrode is maintained at 18°C.

**I. ETCHING UNDER STANDARD RECIPE**

The samples were post-baked at 80°C for 10 min to expel all solvents. Following the bake, the samples were mounted on the substrate using fomblin oil onto a 6" Si wafer clamped to the substrate electrode. After pumping the plasma chamber for 12 hours, post
mounting, the GaAs/AlxGa1-xAs nanopillars were etched in a SiCl₄/Ar chemistry with a flow of 5/2 sccm and a pressure of 4 mTorr.

Figure 3.17 shows the scanning electron microscope images of nanopillars etched at a table power of 55 W and a chamber power of 100 W. It is encouraging to note that pillars of $R_p \geq 200$ nm show a high degree of fidelity ($\Delta R_{etch} \approx -10$ nm) and maintain a vertical profile, with $\theta = -1.14^\circ$. However, pillars with $R_p \leq 100$ nm do not survive the plasma processing and collapse due to undercutting.

Below, we discuss the effect of chamber power on the fidelity and sidewall profile of the nanopillars.

**II. EFFECT OF CHAMBER POWER**

Upon reducing the chamber power from 100 W to 70 W, the density of ions is reduced, which improves the etch profile of nanopillars with $R_p = 100$ nm, see figure 3.18. We measure an undercut angle $\theta = -1.96^\circ$ and the fidelity of pattern transfer to be $\Delta R_{etch} \approx -20.5$ nm. The undercut angle of pillars with $R_p = 200$ nm improves from $\theta = -1.14^\circ$, figure 3.17(c) to $\theta = -0.16^\circ$, figure 3.18(c). However, the improvement in the sidewall profile of pillars with $R_p = 200$ nm comes at the cost of a lower fidelity of pattern transfer, with $\Delta R_{etch} \approx 16$ nm. In both the scenarios, figures 3.17 and 3.18, $R_{etch}$ is less than $R_{mask}$. This indicates mask erosion in the initial stages of the etch, followed by anisotropic etching.
of nanopillars resulting in an undercut. The schematic diagram of the process is shown in figure 3.19.

Figure 3.18: Scanning electron micrograph of nanopillars after being etched at 55 W table power and 75 W chamber power, in ICP-RIE, using 100 nm thick SiO$_2$ etch mask. The profile is shown for radial dimensions (a) $R_p = 50$ nm, $p/2R_p = 10$ (b) $R_p = 100$ nm, $p/2R_p = 5$ (c) $R_p = 200$ nm, $p/2R_p = 2.5$.

Figure 3.19: Schematic diagram, showing etching of nanopillars in ICP-RIE using a dielectric etch mask.

III. EFFECT OF MOUNTING

We also note that the mounting procedure can often introduce variability in the etch profile as the temperature influences the plasma reactions at the etch surface. If the sam-
3.5 Fabrication of electrically connected nanopillar arrays

Samples are glued to a 2" Si wafer with a silver epoxy compound for enhanced thermal dissipation instead of mounting them using the procedure followed in figure 3.17, the results can vary. We note that if the epoxy is applied uniformly over the backside of the chip, the undercutting of the nanopillars is reduced, see figure 3.20. At the same process conditions as figure 3.17, we observe a positive inclination of the sidewall profile instead of undercutting. We further note that although pillars of $R_p = 50$ nm survive the plasma processing, the fidelity of the pattern transfer is severely compromised. For instance, pillars with $R_p = 100$ nm (200 nm) in figure 3.20, show $\Delta R_{etch} = 52$ nm (75 nm). This is nearly 2 (3) times higher than $\Delta R_{etch} = 20.5$ nm (16 nm), in figure 3.18.

Figure 3.20: Scanning electron micrograph of nanopillars after being etched at 55 W table power and 100 W chamber power, in ICP-RIE, using 100 nm thick SiO$_2$ etch mask. The samples are mounted to enhance thermal dissipation. The profile is shown for radial dimensions (a) $R_p = 50$ nm, $p/2R_p = 10$ (b) $R_p = 100$ nm, $p/2R_p = 5$ (c) $R_p = 200$ nm, $p/2R_p = 2.5$.

IV. EFFECT OF INCLUDING PUMPING STAGE DURING ETCH

From figure 3.17 and figure 3.18, we infer that two processes limit the aspect ratio of the nanopillars. In the initial stages of the etch, the sputtering of ions modifies the shape of the etch mask. In the later stages of the etch, plasma reactions cause anisotropic etching of the nanopillar. A common strategy to inhibit lateral etching and improve the aspect ratio, is to employ alternate cycles of etching and passivation achieved by introducing appropriate feed gas at each cycle [128]. This strategy was difficult to implement on the in-house ICP
RIE, with dedicated gas lines. We therefore replaced the cycle of passivation with pumping to minimize the amount of non-volatile reactive species present on the surface. Therefore, between etch cycle, we introduced a pumping cycle to bring the chamber back to the base pressure.

Figure 3.21: Scanning electron micrograph of nanopillars after being etched in three stages, interspersed with two pump cycles at 55 W table power and 100 W chamber power, in ICP-RIE, using 100 nm thick SiO$_2$ etch mask. The profile is shown for radial dimensions (a) $R_p = 50$ nm (b) $R_p = 100$ nm (c) $R_p = 200$ nm.

Figure 3.21 shows the scanning electron micrograph of nanopillars etched in three steps, interspersed with two pump cycles. The effective etch rate is 306 nm/min. The aspect ratio of pillars with alternate etch-pump cycles (figure 3.21) is far superior to the aspect ratio shown in figure 3.17. Compared to the collapse of $R_p = 100$ nm nanopillars in figure 3.17(b), we observe pillars of the same dimension demonstrating an aspect ratio of 1:12. It is interesting to note that the stability of the $R_p = 100$ nm pillars is not affected by the undercut at the base of the etched surface as shown in figure 3.17(b). The attenuated transport of the reactant species in the vertical direction, and scattering with the sidewalls of the nanopillars leads to lateral etching of the nanopillars at various places, figure 3.21(b). From figure 3.21, we further note that even though all the nanopillar arrays are etched at the same time, the etch depth of $R_p = 200$ nm pillars is less than the etch depth of the $R_p = 100$ nm pillars. This is a consequence of the RIE lag that arises due to the packing density of the array which contains nanopillars of $R_p = 200$ nm. The distance between the nanopillars of radial dimensions $R_p = 200$ nm ($p = 2R_p = 1000 - 400 = 600$
3.5 Fabrication of electrically connected nanopillar arrays

nm), is less than the distance between the nanopillars of radial dimensions $R_p = 100$ nm ($p - 2R_p = 1000 - 200 = 800$ nm).

3.5.3.4 Etch in ICP using a metal mask: results

In the previous section, we discussed that high fidelity of pattern transfer from the e-beam resist to the mask can be obtained using a dielectric mask. This requires etch conditions that promote mask erosion and anisotropic etching. High consistency of pattern transfer through the dielectric route comes at the cost of destroying nanopillars with radial dimensions that are defined to be close to 50 nm. Etch conditions can be engineered to obtain structurally stable nanopillars of $R_p = 50$ nm. However, such conditions are non-ideal and lead to enlargement of nanopillar dimensions after the etch. In this section we assess the consistency of pattern transfer from the e-beam resist to the nanopillars using a metal mask.

I. ETCHING UNDER OPTIMIZED RECIPE

Figure 3.22 shows the scanning electron micrograph of nanopillars etched at 55 W table power and 100 W chamber power in the in-house ICP RIE using a 100 nm thick Ti/Au etch mask. The samples are mounted on a 2" Si wafer with a silver epoxy compound for enhanced thermal dissipation and etched in a SiCl$_4$/Ar chemistry with a flow 5/2 sccm and a pressure of 4 mTorr. Compared to figure 3.20, we observe an improvement in the sidewall profile and consistency of pattern transfer for nanopillars with all radial dimensions, i.e. between 50 nm and 200 nm, see figure 3.22. For example, nanopillars defined with an $R_p = 200$ nm, but etched with a dielectric mask in the in-house ICP RIE show a fidelity $\Delta R_{etch} = 75$ nm and a sidewall inclination $\theta = 2.64^\circ$. On the other hand, nanopillars of the same dimensions, but etched with a metal mask in the in-house ICP RIE show a fidelity $\Delta R_{etch} = 9$ nm and a sidewall inclination $\theta = 2.45^\circ$.

The scanning electron micrograph shown in figure 3.22 has been recorded after rinsing the nanopillars in buffered hydrofluoric acid to remove the polymer residue deposited on the surface during the etch. However, the etchant reacts with Ti, removing the self-aligned contact from the pillars. To correct this, we use NiCr/Au as the etch mask instead of Ti/Au, which yields similar etch profile as the latter.

II. EFFECT OF INCLUDING PUMPING STAGE DURING ETCH
3. NANOPILLAR ARRAYS IN RTDS AND QCLS: EXPERIMENTAL REALIZATION

Figure 3.22: Scanning electron micrograph of nanopillars after being etched at 55 W table power and 100 W chamber power, in ICP RIE, using 100 nm thick Ti/Au etch mask. The samples are mounted to enhance thermal dissipation. The profile is shown for radial dimensions (a) $R_p = 50$ nm, $p/2R_p = 10$ (b) $R_p = 100$ nm, $p/2R_p = 5$ (c) $R_p = 200$ nm, $p/2R_p = 2.5$.

Figure 3.23 shows the scanning electron micrograph of nanopillars, with a Ti/Au mask etched in three steps, interspersed with two pump cycles. The effective etch rate is 293 nm/min. The pillars were etched in the same active region, and at the same time as the pillars shown in figure 3.21. The results indicate one of the best aspect ratios that have been demonstrated at Cavendish Labs. Although, nanopillars with $R_p = 50$ nm are destroyed completely, nanopillars with $R_p = 100$ nm remain structurally stable with an aspect ratio of $\approx 1:15$. The maximum height of the nanopillars shown in figure 3.23(b) is limited by underetching at the base of the nanopillar, unlike lateral etching near the mask and sidewalls as shown in figure 3.21(b). This implies that perhaps the endurance of the metal mask is better than the endurance of the dielectric mask. We also note once again, that when the pillars are etched with a metal mask, the fidelity of pattern transfer ($\Delta R_{etch} = 9$ nm, $R_p = 200$ nm) is superior to the fidelity of pattern transfer, when the pillars are etched under the same conditions with a dielectric mask ($\Delta R_{etch} = 40$ nm, $R_{etch} = 200$ nm).

Although, a metal etch mask yields better sidewall profile and consistency of pattern transfer, it’s use as an etch material is limited in most ICP RIE systems due to possibilities of micromasking. Micromasking is a phenomenon that occurs under high powers and feed gas flow rates, which promotes sputtering of the gold mask on to the GaAs surface [129].
It is for this reason, we abstained from processing the nanopillars in the in-house ICP RIE and shifted the process to a Plasmatherm load-locked RIE system, which permits metal-based processing. The results obtained from etching nanopillars in an RIE system, with a metal mask are discussed below.

Figure 3.23: Scanning electron micrograph of nanopillars after being etched in three stages, interspersed with two pump cycles at 55 W table power and 100 W chamber power, in ICP-RIE, using 100 nm thick Ti/Au etch mask. The profile is shown for radial dimensions (a) \( R_p = 50 \text{ nm}, \frac{p}{2R_p} = 10 \) (b) \( R_p = 100 \text{ nm}, \frac{p}{2R_p} = 5 \) (c) \( R_p = 200 \text{ nm}, \frac{p}{2R_p} = 2.5 \).

3.5.3.5 Etch in RIE using a metal mask: results

A major convenience of the Plasmatherm (SLR 720) RIE system is that it offers a load-lock system. This reduces the pumping time from 12 hours to 0.5 hours, allowing multiple etches in a 24 hour period and faster optimization of the etch conditions. Before mounting the samples, the chamber is cleaned with SF\(_6\)/O\(_2\) and O\(_2\) plasma, which is followed by conditioning with the desired SiCl\(_4\)/Ar etch recipe. The samples were mounted onto a 6" Si wafer with a drop of fomblin oil which rests on an alumina platen. The temperature of the substrate electrode was maintained at 20°C.

The effect of etch parameters on the rate and quality of etching nanopillars in the load-locked RIE system is shown in figure 3.24. As the pressure is increased from 10 mTorr to 25 mTorr, the etch rate increases. This is a result of increased ion energy causing enhanced physical sputtering of the etched species. Therefore, as the pressure is increased, nanopillars start to collapse. At a pressure of 25 mTorr, all nanopillars with radial dimensions \( R_p \leq 200 \text{ nm} \) collapse after 10 min of etching. Only those nanopillars survive reaction ion
etching whose radial dimensions are larger than $R_p = 250$ nm. It is only at a pressure of 10 mTorr, where nanopillars of $R_p = 50$ nm survive plasma etching.

Figure 3.24: Etch rate vs. process parameters to etch nanopillars in an RIE, with a NiCr/Au etch mask (a) at constant power of 100 W and SiCl$_4$/Ar flow rate of 4/10 sccm (b) at constant pressure of 10 mTorr and SiCl$_4$/Ar flow rate as 4/10 sccm (c) at constant pressure of 25 mTorr and constant power of 100 W (d) scanning electron micrograph of nanopillars etched at a pressure of 10 mTorr and an RF power of 150 W in SiCl$_4$/Ar (4/8 sccm) chemistry.

At this pressure, the etch rate is only 85 nm/min. Etch rate can be increased by increasing the RF power, which leads to enhancement in the density of ions. We find that the etch rate increases from 85 nm/min to 100 nm/min by increasing the RF power from 100 W to 150 W, beyond which the rate saturates, see figure 3.24(b). The etch rate can also be enhanced by increasing the ratio of the SiCl$_4$ to Ar flow rate, figure 3.24(c). However, this increase must be made with care as a higher SiCl$_4$ content in the gas mixture promotes anisotropic chemical etching, leading to undercutting of the pillars.

Figure 3.24(d) shows the scanning electron micrograph of GaAs / Al$_x$Ga$_{1-x}$As nanopillars etched with a NiCr/Au mask, in the Plasmatherm RIE system at a pressure of 10 mTorr,
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RF power of 150 W and SiCl₄/Ar gas flowrate of 4/8 sscm. While the fidelity of pattern transfer (ΔR_{etch} = -32 nm, R_p = 150 nm) is not among the best that has been reported in this work, the sidewall profile and the aspect ratio are satisfactory (θ = -0.38 °, aspect ratio = 1:7). The etch depth is limited by mask erosion which starts to play a role beyond 2.3 μm. For the pillars shown in figure 3.24(d), except towards the end where the dimensions of the pillar are 2R_{etch} | z=0 = 214 nm, the variation in the sidewall profile falls within the acceptable tolerance in radial dimensions calculated for the larger pillars (R_p = 108.2 to 165.5 nm, window R in figure 2.21 and R_p = 107 nm to 162.1 nm, window S in figure 2.23).

3.5.3.6 Nanopillar etching summary

According to the processing guidelines discussed in section 3.5.1, the etch processes were developed in view of maximizing the aspect ratio of GaAs / Al_xGa_{1-x}As nanopillars. In table 3.4, we compare the etch quality of nanopillars that demonstrated the highest aspect ratio under three different types of processes: (i) nanopillars etched with a dielectric etch mask in an ICP RIE (ii) nanopillars etched with a metal etch mask in an ICP RIE, and (iii) nanopillars etched with a metal etch mask in an RIE.

<table>
<thead>
<tr>
<th>Etch assessment parameters</th>
<th>ICP RIE</th>
<th>RIE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest aspect ratio achieved</td>
<td>1:12</td>
<td>1:15</td>
</tr>
<tr>
<td>Etch depth</td>
<td>3.56 μm</td>
<td>3.4 μm</td>
</tr>
<tr>
<td>Fidelity of transfer, R _mask \cdot R_p</td>
<td>≈ 50 nm</td>
<td>≈ 2 nm</td>
</tr>
<tr>
<td>Fidelity of transfer, R _etch \cdot R_p</td>
<td>ΔR_{etch} = +35 nm (R_p = 100 nm)</td>
<td>ΔR_{etch} = -15 nm (R_p = 100 nm)</td>
</tr>
<tr>
<td>Sidewall inclination</td>
<td>+0.53°</td>
<td>-1.1°</td>
</tr>
<tr>
<td>Endurance of etch mask</td>
<td>Mask erosion occurs as etch depth approaches 3 μm</td>
<td>No mask erosion occurs as etch depth approaches 3 μm</td>
</tr>
<tr>
<td>Suitability for THz QCL</td>
<td>High aspect ratio, but sputtering may occur upon reaching end point.</td>
<td>High aspect ratio and fidelity, but sputtering may occur upon reaching end point.</td>
</tr>
</tbody>
</table>

Table 3.4: Comparison of systems and processes in terms of etch assessment parameters and suitability for processing laterally confined THz QCLs.

Nanopillars etched with a metal mask in an ICP RIE show the highest aspect ratio among the three processes. Furthermore, this process demonstrates the highest fidelity of pattern transfer and resistance to plasma processing. In spite of superior credentials,
nanopillars etched in an ICP RIE with a metal mask may not be appropriate for processing laterally confined THz QCLs. This is because of micromasking from metal erosion, which is a risk while etching GaAs/Al$_x$Ga$_{1-x}$As deep features in an ICP RIE. Etching nanopillars with an improved dielectric mask in an ICP RIE may also not be suitable for processing laterally confined THz QCLs. From table 3.4, we infer that the highest etch depth, for GaAs/Al$_x$Ga$_{1-x}$As nanopillars is limited to 2.3 to 3.56 $\mu$m. Such low etch depths impose an additional constraint on the processing of laterally confined THz QCLs. The laterally confined THz QCL must use metal-metal waveguide configuration. Therefore, unlike nanopillars in described in this section, which have a GaAs end point, the nanopillars etched in a lasing ultrathin THz QCL would have a metal contact as the end point. This increases the risk of metal exposure to the plasma chamber in an ICP RIE system. Exposure of the plasma chamber to the metal can be minimized in an ICP RIE by using a hybrid mask and by stopping the etch a few nanometers before the metal contact by using in-situ monitoring. However, the feasibility of these processes was beyond the timescale of this work.

Instead of using the ICP RIE for etching THz QCLs, we have attempted to optimize etching of sub-200 nm pillars on an RIE system. Although, the quality of etch in terms of the aspect ratio is not the best (1:7) and the etch depth is limited to 2.3 $\mu$m, the result holds promise to investigate lateral confinement.

### 3.5.4 Insulation

One of the most crucial steps in the fabrication of electrically connected nanopillar arrays is the insulation of the nanopillars. This involves sidewall insulation and planarization of the underlying topography to enable top-contact fabrication. The processing guidelines, discussed in section 3.5.1, require a planarizing material which offers the flexibility of removal post top-contact fabrication. The foremost rationale behind this requirement is that the insulation adds significant absorption losses, which are detrimental to the observation of any weak electroluminescence from laterally confined THz QCLs, see section 2.11.5. Besides the optical properties of the active region, the electrical permittivity and conductivity of the insulation plays a big role in determining the figure of merit of the waveguide. The second argument behind ensuring flexibility of removal is that the insulating layer may passivate the charge on the sidewall of the nanopillars defined in RTDs and QCLs [97]. While this is difficult to quantify, the choice of insulation may influence the density of surface states $D_{it}$, which in turn affects the Fermi level pinning at the nanopillar surface and hence the depletion width, see sections 2.5.2 and 2.6. In the next section, we discuss the qualities of an ideal planarizing material and assess the merits of some of the commercially
3.5 Fabrication of electrically connected nanopillar arrays

available insulators.

3.5.4.1 Insulation assessment parameters

From the perspective of device processing it is essential to choose an insulator that shows planarising properties, i.e. it can non-conformally coat the underlying topography. Furthermore, the insulator must have good gap fill properties, i.e. a small L, see figure 3.25. Here, \( L = p - 2R_p \), where \( p \) is the pitch and \( R_p \) is the radial dimension of the nanopillar. Finally, the thickness of the insulator must be sufficient to planarize nanopillars of etch depth \( H \), which is typical of ultrathin THz QCLs. The thickness of the insulator after planarization generally depends on its viscosity. While certain materials may planarize a feature of height \( H \) upon a single coat, others may need to be coated multiple times to reach the desired height.

In general, the percent planarization is evaluated empirically in terms of the equation:

\[
\%P = \left( 1 - \frac{Z}{H} \cdot \frac{\text{abs}(\gamma)}{90} \right) \cdot 100
\]  \hspace{1cm} (3.1)

where \( Z \) is the height of the insulator over the nanopillars and \( \gamma \) is the angle that measures the smoothness of the insulator after planarising, see figure 3.25. For uniform planarization and insulation it is necessary to reduce \( Z \), the buildup of the insulator above the nanopillar. At the same time, it is also necessary to reduce \( \gamma \), the angle subtended by the insulation with the horizontal surface, to ensure a robust insulation.

![Figure 3.25: Planarization schematic](image)

Apart from these processing parameters, the criteria used while evaluating the merit of each insulator is the ability to form suspended top-contact to the nanopillars. Table 3.5 compares a selection of standard insulators against parameters such as single coat thickness and ease of removal. Table 3.5 also lists the reported refractive index of the insulators at THz frequencies.
3. NANOPILLAR ARRAYS IN RTDS AND QCLS: EXPERIMENTAL REALIZATION

Table 3.5: A comparison of planarizing materials against single coat thickness on a bare substrate, ease of removal and refractive index at THz frequencies. Thickness has been compared against the following product suppliers - SU8 from MicroChem (SU-8 2), Polyimide from Dupont (HD4104), Benzocyclobutene (BCB) from Dow Chemicals (Cyclotene 4022-35), Resist from Shipley (1828), Hydrogen siloxane (HSQ) from Dow Corning (XR 1541-E), Spin-on-glass (SOG) from Filmtronix (Methylsiloxane 500 F).

<table>
<thead>
<tr>
<th>Material</th>
<th>Processing parameter</th>
<th>Optical parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thickness</td>
<td>Ease of Removal</td>
</tr>
<tr>
<td>SU8 (SU-8 2)</td>
<td>2.0 µm at 2000 rpm</td>
<td>Dry etch, difficult to</td>
</tr>
<tr>
<td></td>
<td></td>
<td>remove after cure</td>
</tr>
<tr>
<td>Polyimide (HD4104)</td>
<td>3 µm at 5000 rpm</td>
<td>Removed in oxygen plasma</td>
</tr>
<tr>
<td></td>
<td></td>
<td>and HF after cure</td>
</tr>
<tr>
<td>BCB (Cyclotene 4022-35)</td>
<td>2.6µm at 5000 rpm</td>
<td>Dry etch, difficult to</td>
</tr>
<tr>
<td></td>
<td></td>
<td>remove after cure</td>
</tr>
<tr>
<td>Resist (1828)</td>
<td>2.8µm at 5000 rpm</td>
<td>Removed in Acetone</td>
</tr>
<tr>
<td>HSQ (XR 1541-E)</td>
<td>200 nm at 1000 rpm</td>
<td>Can be removed in HF</td>
</tr>
<tr>
<td></td>
<td></td>
<td>after cure</td>
</tr>
<tr>
<td>SOG (Methylsiloxane 500 F)</td>
<td>640 nm at 2000 rpm</td>
<td>Can be removed in HF</td>
</tr>
<tr>
<td></td>
<td></td>
<td>after cure</td>
</tr>
</tbody>
</table>

Although the single coat thickness of the three planarizing materials SU8, polyimide and BCB is in the range of typical ultrathin THz QCLs, they are difficult to remove post top-contact fabrication. On the other hand, while the single coat thickness of the photoresist is suitable for ultrathin THz QCLs, it can be easily removed in a common cleanroom solvent (acetone). Ideally, the planarization layer must be removable by chemistries that do not interfere with lithographic stages. HSQ and SOG, are planarizing materials that can be left as is or be removed in acid, if required. However, use of HSQ to planarize features is experimentally tasking. With a single coat thickness of 200 nm, it requires 10 to 18 spin-coating stages to planarize features of etch depth in the range of 2 to 3.5 µm. On the contrary, with SOG, it requires 3 to 5 coats to planarize features of the same etch depth. For these reasons, we have chosen the SOG process to planarise the nanopillars.

3.5.4.2 Trilayer spin-on-glass process

The SOG process necessitates two conformal depositions CVD1 and CVD2, before and after spin coating, hence the name trilayer process, see figure 3.26(a)-(d). In an SOG trilayer process, the first conformal layer improves the adhesion of the spin on glass on metallized contacts [134]. Following the deposition of CVD1, the chip is planarized with SOG. Multiple spin coating stages may be required to planarize features if the etch depth is larger than the single coat thickness. Because the planarised SOG is quite smooth, a second thin
3.5 Fabrication of electrically connected nanopillar arrays

A thin layer of SiO$_2$ (CVD2) is deposited by PECVD to improve ball bonding of gold contacts on top of the insulator. Following the trilayer insulation process, the n$^+$ GaAs layer (or self aligned mask) on top of the nanopillars is exposed by etching the insulator back in a plasma chamber. This process is called etch back of the planarizing material, see figure 3.26.

Figure 3.26: Trilayer planarisation process schematic showing (a) nanopillars processed by reactive ion etching (b) conformal coating of first PECVD layer, CVD1 (c) planarisation by SOG, spin coated in multiple stages (d) conformal coating of second PECVD layer, CVD2 (e) etch back of planarized nanopillars, with exposed top-contact. The arrows show the cross-section of the planarised and etched back nanopillars.

Figure 3.26(a) illustrates the deposition of a thin layer of SiO$_2$ (CVD1) by plasma enhanced chemical vapour deposition (PECVD) at a rate of 7 nm/min. Following a pre-bake at 125°C, SOG is spin coated under nitrogen atmosphere, humidity ≤ 30 %, at a speed determined by the height, H. This is shown in figure 3.26(b). For a longer shelf life, it is important to store SOG at a temperature of 4°C. However, the solution must be allowed
to warm up to the ambient temperature before spin coating to prevent condensation of water vapour. Another essential requirement while spin coating is to use a plastic syringe, as spin-on-glass tends to coagulate in a glass syringe or pipette. Following the spin-coating process, the sample is post baked at 65°C, 115°C, 125°C and 200°C for a minute each, after which it is cooled to 125°C and 115°C for a minute, bringing it to bake at 65°C for 10 minutes, see figure 3.27(a). The above process is repeated when applying a second coat. It is important to post bake and cool slowly as SOG can tend to crack. The resist is then cured under nitrogen gas at a ramp rate of 2.0 °C per min from ambient temperature to 400°C and dwelled for an hour at 400 °C. Figure 3.26(c) illustrates the deposition of the second layer of SiO₂ (CVD2) by plasma enhanced chemical vapour deposition (PECVD) at a rate of 7 nm/min. It is important to note that to obtain a lower leakage current density, the insulation has to be free of voids typically associated with a poor or a rough etch back. After curing the spin-on-glass at 400 ° C, and depositing the second PECVD layer, windows are selectively opened by optical lithography in the photoresist so as to protect the majority of the insulation, and expose only those regions on the chip that define the nanopillar array, see figure 3.26(e). The exposed insulation is etched in a CHF₃/O₂ (30/2 sccm) plasma, at a pressure of 60 mTorr and RF power of 75 W in the plasma pod described in section 3.4.3.1.

The three parameters that need to be engineered to ensure smooth planarisation and etch back are: (i) thickness \( t_1 \), of the first conformal layer CVD1 (ii) SOG spin speed and number of coats, which determines thickness \( t_{SOG} \), of the spin on glass, and (iii) thickness \( t_2 \), of the second conformal layer CVD2. A high \( t_1 \), has the benefit of reducing the thickness of SOG required to planarise the nanopillars, thereby reducing the number of coats required to fill a certain etch depth. On the other hand, a low \( t_1 \) improves the gap filling length, which is given as \( L = p - 2R_p - 2t_1 \). The minimum gap filling length that can be achieved using SOG 500F is limited by the manufacturer's specifications to \( \sim 200 \) nm [125]. As discussed in Chapter 3, pitch \( p \) determines the effective refractive index of the nanopillar array, see eqns. 2.37 and 2.38. Therefore, given \( L \) and \( t_1 \), we can estimate the lower limit to the value of \( p \) that is feasible using the SOG process. This lower limit is given by \( L + 2t_1 + 2R_p \). Therefore, the minimum \( p/2R_p \) ratio that can be experimentally achieved by the SOG process is given by \( p/2R_p = t_1/R_p + 200/2R_p + 1 \), where \( t_1 \) and \( R_p \) is in nm. Table 3.6, shows the minimum \( p/2R_p \) ratio that is constrained by planarization, for each radial dimension in the case when the thickness of the CVD1 layer \( t_1 \) is 25 nm and when it is 130 nm.
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Figure 3.27: Schematic diagram, showing (a) the optimized post baking procedure after spin coating SOG and, (b) optimized curing procedure of SOG in nitrogen.
3. NANOPILLAR ARRAYS IN RTDS AND QCLS: EXPERIMENTAL REALIZATION

<table>
<thead>
<tr>
<th>Minimum Pitch/diameter (p/2R_p) ratio constrained by planarization</th>
<th>CVD1 thickness, t_1 in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius, R_p in nm</td>
<td>25 nm</td>
</tr>
<tr>
<td>50</td>
<td>p/2R_p = 3.5</td>
</tr>
<tr>
<td>100</td>
<td>p/2R_p = 2.25</td>
</tr>
<tr>
<td>150</td>
<td>p/2R_p = 1.83</td>
</tr>
<tr>
<td>200</td>
<td>p/2R_p = 1.63</td>
</tr>
</tbody>
</table>

Table 3.6: Pitch/diameter (p/2R_p) ratio constrained by planarization for each radial dimension, when t_1 = 25 nm and when t_1 = 130 nm.

Figure 3.28 shows the leakage characteristics of the etched back insulation at room temperature. The trilayer comprises of 130 nm thick CVD1, approximately 500 nm thick spin on glass and 30 nm thick CVD2 layer. The footprint of the top-contact is the same as the footprint of a standard 500 x 500 nanopillar array, which is equal to 250000 µm², see inset in figure 3.28(a). Sample 1 and 2 represent two reference devices for leakage test on the same chip. The measured current through the test device is 500 nA, which is flat in the voltage range 0 to 3 V. This current corresponds to a current density of 0.1 mA/cm², which is four-five orders lower than the current density through the nanopillars in RTDs (hundred to thousand A/cm²). For comparison, the leakage current of the two samples is plotted together with the room-temperature current through three 500 x 500 nanopillar arrays, that were contacted in the same manner as the test devices, figure 3.28(b). The nanopillar characteristics, which show increasing current with applied bias and a distinct NDR peak, correspond to nanopillars processed from W0021, with radial dimensions R_p = 50 nm, 100 nm and 150 nm. Further details about the experimental set-up are discussed in section 3.7.

3.5.4.3 Results from trilayer spin-on-glass process

In this section, we discuss the optimization of planarization and etch back process. Figure 3.29(a) shows the cross-sectional view of nanopillars imaged after deposition of the first conformal layer (100 nm of SiO₂) and planarisation by SOG, spin coated once at 2000 rpm. Since the deposition of the third layer (CVD2) is conformal, the SEM after spin coating and cure of SOG is representative of the insulation topography. From figure 3.29(a), we note that the nanopillars have been planarized well (γ ≈ 0). In spite of good planarization, the etch back of the complete insulation (CVD1 (t_1 = 100 nm)/SOG (2000 rpm, once)/CVD2 (t_2 = 100 nm)) leaves it rough, and open to current leakage, see
3.5 Fabrication of electrically connected nanopillar arrays

Figure 3.28: (a) Leakage current and current density through the trilayer insulation at room temperature. The size of the devices is 500 µm by 500 µm. The inset shows the schematic diagram of the device. (b) Leakage current through the insulation in comparison to an array of nanopillars with a footprint of 500 µm by 500 µm, measured at 300 K. The array of nanopillars, with radial dimensions R_p = 50 nm, 100 nm and 150 nm were processed from wafer W0021.

Two mechanisms play a role in producing this microstructure after etch back. In the first scenario, the etch rate of SOG is faster than the etch rate of PECVD deposited SiO_2 layer, see figure 3.30(a). Therefore, the insulation between the pillars is removed faster than the insulation over the nanopillar. The roughening of the insulator is a result of physical sputtering during reactive ion etching. The roughening is exacerbated if the thickness of the insulator above the nanopillars after removal of CVD2 layer (t_1 + Z) is high, see figure 3.30(b). It is possible to reduce the etch rate of SOG with respect to PECVD SiO_2 by decreasing the percentage of O_2 in the plasma. However, we find that the etch rate of SOG remains unaffected by decreasing the O_2 percentage from 11.4 % to 6.2 %.

A smooth etch back is achieved by reducing both Z and t_1. At the same time, t_1 and t_2 are chosen to maintain a t_1+t_2 ≥ 100 nm for a good insulation. We achieve this by reducing t_1 from 100 nm to 25 nm, and by spin coating SOG to a thickness t_{SOG}, which is less than H+t_1, see figure 3.31(b). This is obtained by increasing the spin speed from 2000 rpm to 4000 rpm. Although the thickness of the spin glass decreases with increase in speed of spin coating [125], in practice it may also vary depending upon the height H and the pitch p of the nanopillar array. This implies that the trilayer planarization process has to be optimized separately for each active region.

Note that reducing Z and t_1 also reduces γ. For example, in the current example γ re-
3. NANOPILLAR ARRAYS IN RTDS AND QCLS: EXPERIMENTAL REALIZATION

Figure 3.29: Scanning electron micrograph showing cross-sectional view of (a) nanopillars imaged after deposition of CVD1 (100 nm of SiO$_2$) and planarisation by SOG (spin coated once at 2000 rpm) (b) nanopillars insulated by CVD1/SOG/CVD2 (100 nm/2000 rpm/100 nm) and etched back in CHF$_3$/O$_2$ plasma for 6 min. The cross-sectional view of pillars is obtained by cleaving the pillars through the insulation.

Figure 3.30: Schematic diagram showing a poor etch back (a) when the etch rate of SOG is higher than the etch rate of SiO$_2$ (b) when the thickness of insulation above the nanopillars after removal of CVD2 layer ($t_1 + Z$) is high.
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duces from $0^\circ$ to $-35^\circ$, see figure 3.31(b), which shows the scanning electron micrograph of nanopillar arrays after conformal coating by CVD1 ($t_1 = 25$ nm) and planarization by SOG (spin coated once at 4000 rpm). Since the deposition of the third layer (CVD2) is conformal, the SEM after spin coating and cure of SOG is representative of the insulation topography. Following the conformal deposition of CVD2 ($t_2 = 75$ nm) layer, the nanopillars are etched in CHF$_3$/O$_2$ plasma for 2.5 mins, see figure 3.31(c). Note, that the top-contact of the nanopillars is only partly exposed after 2.5 mins. For complete etch-back, the nanopillars are etched for a minute more. Figure 3.31(d) shows the scanning electron micrograph of nanopillars after 3.5 min of etching. The increase in the apparent dimensions of the nanopillars measured by the SEM after etch back (diameter = 222 nm in figure 3.31(d)), as compared to the original dimensions (diameter = 174 nm in figure 3.31(a)), is most likely due to charging at the insulator surface, which is aggravated by roughness - a consequence of etch back. However, the roughness of the insulator is not as severe as compared to figure 3.29, which opens up voids in the insulation.

Figure 3.31: Scanning electron micrograph of nanopillars (a) imaged after reactive ion etching (b) imaged after deposition of CVD1 (25 nm of SiO$_2$) and planarisation by SOG (spin coated once at 4000 rpm) (c) etched back in CHF$_3$/O$_2$ plasma for 2.5 min (d) etched back in CHF$_3$/O$_2$ plasma for 3.5 mins. The cross-sectional view of pillars shown in (b), (c) and (d) is obtained by cleaving the pillars vertically.
The height of the nanopillars will vary depending upon the active region of choice. For example, in the case of a double barrier RTD, the height $H$ of the nanopillar would range from 600 nm - 900 nm. On the other hand, in the case of THz QCLs, the height $H$ of the nanopillar would range from 2 - 3.5 $\mu$m. Therefore, the thickness of the conformal layer, the spin speed of the spin on glass and the number of coats required, must be engineered for each active region. However, optimization of the planarization parameters requires detailed calibration.

The flexibility of the insulation removal provides another huge benefit. It allows device recovery after an etch back. Both spin on glass and $\text{SiO}_2$ can be removed in buffered hydroflouric acid. However, buffered hydroflouric acid also etches aluminium, aggressively. Therefore, this method of device recovery is not suitable for active regions with AlAs barriers. Active regions that contain $\text{Al}_x\text{Ga}_{1-x}\text{As}$ barriers with low aluminium content ($x \leq 0.7$), may be suitable for device recovery as they are resistant to buffered hydroflouric acid. While complete device recovery may be possible in theory, certain challenges may need to be overcome.

Figure 3.32(a) shows the scanning electron micrograph of nanopillars fabricated using a double barrier RTD structure - test wafer A1700. As mentioned in section 3.2, A1700 comprises of a 10 nm well, sandwiched between two 5 nm thick $\text{Al}_{0.33}\text{Ga}_{0.67}\text{As}$ barriers. The first barrier is at a distance of 438 nm from the top GaAs surface, and the second barrier is at a distance of 453 nm from the top GaAs surface. The average position of the barriers is indicated in figure 3.32(a). The height of the nanopillar is $\approx 629$ nm. When planarized by the trilayer process, the combined height of the insulation reaches $\approx 884$ nm. The height of the insulation is inferred from figure 3.32(b), showing the unexposed area of the planarized chip on the right. The scenario shown in figure 3.32(b) is very similar to the one discussed in figure 3.30(b). When the planarized nanopillar array is etched back in the $\text{CHF}_3/\text{O}_2$ plasma for 6 mins, the insulation is left rough and open to voids, see the exposed area of the chip in figure 3.32(b). To test the removal of insulation, a nominally similar sample to the one shown in figure 3.32(a-b) is etched in stagnated buffered hydroflouric acid for 12 hours. What is promising to note, is that the barrier remains unaffected by the etch. However, in spite of the long etch, we find remnants of SOG and $\text{SiO}_2$ between the nanopillars and on the GaAs surface. This is a consequence of etching a very large-area of the insulation (standard chip size : 6 x 7 mm) under stagnated buffered hydroflouric acid. In order to overcome this problem, we etched the planarized nanopillars in magneti-

\footnote{http://terpconnect.umd.edu/browns/wetetch.html}
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cally stirred buffered hydrofluoric acid. While the insulation was completely removed, we observed narrowing of the pillars around the Al$_{0.33}$Ga$_{0.67}$As barriers. This narrowing also caused a few nanopillars to collapse at the neck. This observation leads us to speculate that agitated buffered hydrofluoric acid reacts with the Al$_{0.33}$Ga$_{0.67}$As barrier, while the static acid does not.

![Figure 3.32: Scanning electron micrograph of nanopillars (a) imaged after reactive ion etching (b) imaged after trilayer insulation (CVD1 (50 nm)/SOG (2500 rpm, once)/CVD2 (50 nm)) and plasma etch back for 6 mins (c) imaged after chemical etching in still buffered hydrofluoric acid for 12 hours (d) imaged after chemical etching in buffered hydrofluoric acid, magnetically stirred for 1 hour. The cross-sectional view of pillars shown in (b) is obtained by cleaving the pillars through the insulation.](image)

Although the device cannot be recovered completely, we can still contact the remaining nanopillars. This is important to keep in mind while optimizing the etch back process for a laterally confined THz QCLs based on GaAs / Al$_x$Ga$_{1-x}$As material system. Perhaps, a suitable device recovery process should comprise of two stages, with the first stage involving a long etch in stagnated buffered hydrofluoric acid and the second stage involving a fast removal of the etch residue in magnetically stirred buffered hydrofluoric acid. Optimization of the device recovery process was beyond the scope of the present work. In the following section, we summarize the key points necessary for a structurally and an electrically robust
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insulation.

3.5.4.5 Nanopillar insulation summary

We have demonstrated a planarization technique that can be designed to insulate nanopillars in a range of GaAs/AlxGa1−xAs active regions. While meeting the height requirements imposed by laterally confined THz QCLs (H = 2 - 3.5 µm), this planarization technique is compatible with the processing of laterally confined RTDs (H = 600 - 900 nm). This insulation technique involves a trilayer process where the thickness of each layer is engineered to ensure smooth planarization and etch back, which is a requirement for structural and electrical stability of the device. Among most insulation techniques, this trilayer spin on glass process has the advantage of removal by wet chemical etching. While this quality can be exploited to achieve a suspended top-contact if required, it also allows for partial device recovery after a poor etch back. In the next section we describe the fabrication of top-contact after the trilayer insulation process.

3.5.5 Fabrication of top-contact and bond pads

Figure 3.33(a) shows the schematic diagram of the nanopillar array after etch back in a plasma chamber. Windows patterned by optical lithography, allow only the nanopillar array to be exposed to reactive ion etching, leaving the rest of the insulation unexposed. Following the etch back, the optical photoresist, which is baked during the plasma processing is removed in acetone. The next step involves deposition of the top-contact, a rotatilt evaporation of NiCr/Au, figure 3.33(b). Following the deposition of the top-contact, bond pads are evaporated over the insulator which electrically connect to the top of the nanopillar array, figure 3.33(c). The bond pads over the top-contact give the flexibility to produce both insulated and suspended contact. Since the top-contact bond pads do not come in contact with the hydrofluoric acid at any stage of processing, we choose to use Ti as a wetting layer for gold. Finally, the bottom-contact pads are exposed by chemically etching the trilayer insulation through an optically defined window, figure 3.33(d). In the next section, we discuss the fabrication of suspended top-contact to the array of nanopillars.

3.5.6 Suspended top-contact

From table 3.5, we recognized that most insulating materials require plasma processing for removal. However, plasma processing, being anisotropic in nature does not allow the formation of a suspended top-contact after metal evaporation, see general process flowchart
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Figure 3.33: Schematic diagram showing nanopillars after (a) etch back in a plasma chamber (b) deposition of top-contact (c) deposition of top-contact bond pad, and (d) removal of insulation over the bottom-contact pads.
3. Nanopillar Arrays in RTDS and QCLS: Experimental Realization

for fabricating electrically connected nanopillar arrays (figure 3.2). From table 3.5, we also noted the possibility of using two insulating materials that fulfill the height requirements of laterally confined THz QCLs, which can be removed by wet chemical processing. These two materials were (i) spin on glass, and (ii) standard optical photoresist. Below we discuss the processing routes of the two insulating materials, and evaluate their feasibility for forming suspended top-contacts to laterally confined THz QCLs (and the test RTDs).

3.5.6.1 Possible routes to suspended contact

Spin on Glass Route

As discussed previously, spin on glass and SiO$_2$ can be chemically etched using buffered hydrofluoric acid. Since the nature of wet etch is isotropic, the etchant removes the insulation in the lateral direction as well as the vertical direction, which can be exploited to remove the trilayer insulation between the nanopillars. Note that the top of the insulation over the nanopillars is protected by the metal and is inaccessible for etching in the vertical direction, see figure 3.34(a). To overcome this problem, a window defined using optical lithography is opened in the insulation layer, 20-30 microns away from the nanopillar array, see 3.34(b). On a chip with multiple array patterns, this window is approximately 360 µm away from the opposite array.

We note that until the insulation below the window is removed, the etch through the airgap window is isotropic, i.e. the etch rate in the vertical direction is equal to the etch rate in the lateral direction. Once the insulation below the window is removed, the etch progresses at a much faster rate owing to increased surface area available to the etchant. For a 1.25 µm thick insulation, buffered hydrofluoric acid etches at a rate of $\approx 6.5\,\mu\text{m/min}$ through a 10 µm wide x 250 µm long window as opposed to 80 nm/min in the vertical direction. Figure 3.34(c) shows the trilayer insulation first etched in the vertical direction, followed by etching in the lateral direction, see figure 3.34(d).

Note that the length of the airgap window (250 µm) for a 500 x 500 array is intentionally designed to be less than 500 µm inorder to protect the lateral etch from extending to the bottom-contact and the other arrays on the chip. Furthermore, depending upon the height of the insulation, the etch has to be calibrated in time to ensure that the etchant does not attack the insulation near the edge 3, to protect the mechanical stability of the suspended top-contact. Figure 3.35 shows a rough schematic diagram illustrating the extent of the lateral etch for each nanopillar array on the chip. This extent (radius = 320 to 360 µm) is limited by the shape of the window, the placement of the arrays and the
3.5 Fabrication of electrically connected nanopillar arrays

Figure 3.34: Suspended top-contact process schematic (not to scale), showing (a) Ti/Au bond pads evaporated on planarized (and etched back) nanopillars (b) Optical lithography to define a window at a distance from the array (c) Trilayer insulation vertically etched at a rate of $\approx 80$ nm/min (d) Trilayer insulation laterally etched at a rate of $\approx 6.5$ $\mu$m/min to form air gaps between the nanopillars.

Figure 3.35: Schematic diagram showing the lateral etch of insulation through the airgap window in relation to all nanopillar arrays on the chip.
placement of the bottom-contact. Improvements in the optical mask will help optimize the extent of the lateral etch and at the same time maintain the mechanical stability of the top-contact. However, these improvements were beyond the timescale of the current work.

The advantage of this method is that the removal of insulation is the last step in the process flow. Therefore, this processing route offers the flexibility to obtain electrical measurements with a robust insulation and optical measurements with the insulation removed.

**PHOTORESIST ROUTE**

In 2010, Offermans et. al demonstrated suspended contacts to individual InAs nanowires, obtained by using an optical photoresist as a planarizing material [135]. In Offermans work, a vertical InAs nanowire was grown using a bottom-up technique on an InP substrate. The bottom-contact and the top-contact were electrically isolated from each other by selective patterning of an insulator after the growth of InAs nanowires.

Here, we evaluate the feasibility of Offermans approach to top-down nanopillar arrays in THz QCLs and the test RTDs. Akin to Offermans work on InAs wires where the bottom layer is conducting, the end point of a laterally confined THz QCL and the test RTD structure is also conducting. In the case of metal-metal THz QCLs (section 4.2), this layer is a gold contact, whereas in the case of RTDs (section 3.6) this layer is an $n^+$ GaAs contact, see figure 3.36(a). Therefore, the first step after reactive ion etching of nanopillars, would involve deposition and selective patterning of an insulator on the conducting layer, figure 3.36(b). Following planarization by an optical photoresist, see figure 3.36(c), windows would be patterned by optical lithography that selectively expose the bottom-contact, the nanopillar array and the oxide, see figure 3.36(d). Finally, a rotatilt evaporation would allow the formation of top and bottom-contact to the nanopillar arrays, figure 3.36(d).

Note that Offerman’s approach combines top-contact and bond pad fabrication in the same step. Furthermore, this approach only allows for the formation of suspended contacts, i.e. this process does not have the flexibility to achieve an unsuspended top-contact. Offermans approach can be extended to THz QCLs using the process flow described in figure 3.36. Extending the process to RTDs requires a few intermediate steps, which are briefly discussed in section 3.6.2. While the photoresist route is an appealing alternative, it requires a redesign of the existing processing flow, which was not within the timescale of the current work.
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Figure 3.36: Schematic diagram showing fabrication of suspended top-contact using Of-fermans approach. The process flow involves (a) reactive ion etching of nanopillars in THz QCLs or RTDs (b) deposition and patterning of oxide (c) spin coating of photoresist (d) selective exposure with windows for bottom-contact, nanopillar array and oxide (e) evaporation of metal contact.
3.5.6.2 Spin on glass route to suspended contact: results

Figures 3.37 and 3.38 show the scanning electron micrograph of nanopillars imaged after the formation of suspended contact. The cross-section of the nanopillars is imaged by cleaving the array in the centre, in a direction perpendicular to the length of the window.

Figures 3.37(a-b) show the scanning electron micrograph of a 500 x 500 array of \( R_p = 200 \) nm nanopillars processed from an RTD active region (\( H = 850 \) nm). The lateral etch rate of the trilayer insulation is equal to \( 3.15 \mu\text{m/} \text{min} \). For clarity, the 270 nm airgap is shown at a higher magnification in figure 3.37(b). In section 3.5.4.3, we discussed that the insulator etched back in the plasma and the underlying topography may not be planar, see figure 3.31. The shape of the underlying insulator, when etched back gets mapped onto the top-contact. Therefore, the apparent buckling of the top-contact, shown in figure 3.38(a-b), is not a consequence of the weight of the top-contact, but a consequence of the insulator shape derived after plasma etching.

![Direction of view](image)

![Figure 3.37](image)

Figure 3.37: Scanning electron micrograph (a-b) imaged after the formation of suspended top-contact in nanopillar arrays that are planarized and etched back in a reactive ion plasma. Figure 3.38(b), shows the 270 nm airgap, formed in RTD active region, at higher magnification for clarity.

Figure 3.37(a) shows the formation of a 1.25 \( \mu\text{m} \) high airgap in an array of \( R_p = 150 \) nm, \( H = 1.75 \mu\text{m} \) pillars. The insulation etches at a rate of 6.5 \( \mu\text{m/} \text{min} \) in the
3.5 Fabrication of electrically connected nanopillar arrays

lateral direction. This was the very first demonstration of a suspended top-contact using a trilayer process at the Cavendish labs. The 500 x 500 nanopillar array was processed from a THz QCL active region, with $n^+$ GaAs as the end point during reactive ion etching. Figure 3.37(a) shows the airgap stretching over 36 µm. The magnified image of the airgap is shown in figure 3.37(b). The collapse of a few pillars occurred partly during the stage of reactive ion etching (section 3.5.3) and partly during cleaving. Note that in the case of figure 3.37(a-b), the nanopillars were planarized but not etched back. Therefore, the top-contact, which follows the topography of the underlying insulator is also planar. Note that this process is equally compatible with nanopillars etched in both GaAs / Al$_x$Ga$_{1-x}$As based RTD and THz QCL active regions, where the end point is an $n^+$ doped GaAs contact. Therefore, figure 3.38(a-b) is a good representative of a suspended top-contact in a THz QCL active region using the trilayer process.

![Figure 3.38: Scanning electron micrograph (a-b) imaged after the formation of a suspended top-contact in planarized nanopillars. Figure 3.37(b), shows the 1.25 µm airgap formed in THz QCL active region, at higher magnification for clarity.](image-url)
3.6 Fabrication of RTDs

In section 3.5, we discussed processing techniques that are common to nanopillars in GaAs / AlₙGa₁₋ₙAs based RTD and THz QCL active regions. In this section, we elaborate on additional processing stages that are unique to the test structures, i.e. the RTDs. Before we delve on the additional complexities of fabricating nanopillar arrays in RTDs, it is useful to discuss the fabrication of large-area RTDs. The fabrication process described below was used to process large-area RTDs with a Schottky top-contact to ensure consistency with the non-aligned metal-based NiCr/Au process described in section 3.5.2. Although the same fabrication process can be used for large-area RTDs with an ohmic top-contact, these devices already existed in the lab and hence we did not attempt to reprocess them.

3.6.1 Large-area RTDs

The term large-area refers to an area where the effects of surface depletion and hence quantum confinement in the lateral direction are negligible, i.e. the area of the device is $\gg R_d^2$. Instead of circular pillars, large-area RTDs were defined as square mesas. The size of these mesas ranged from 10 µm x 10 µm to 50 µm x 50 µm. Figure 3.39 shows the various processing steps used to fabricate the large-area RTDs.

![Figure 3.39: Process schematic (a) mesa etch (b) lithography and deposition of bottom-contact (c) deposition of SiO₂ (d) opening of windows, deposition of top Schottky contact and bottom bond pad.](image)

The square mesa was wet etched in a solution of H₂SO₄ : H₂O₂ : H₂O mixed in a ratio of 1:8:80 which results in sloping sidewalls caused by lateral chemical etching, see fig-
3.6 Fabrication of RTDs

To avoid isotropic etching, the mesa can be dry etched in a reactive ion etcher, which results in more vertical sidewalls. This is described in section 3.4.3.1. Following the mesa definition, AuGeNi contacts were evaporated and annealed at 430°C for 80 s in forming gas atmosphere to form ohmic bottom-contacts, figure 3.39(b). Windows for top and bottom-contact were opened in an insulating layer of 100 nm thick SiO$_2$ deposited by plasma-enhanced chemical vapor deposition (PECVD), figure 3.39(c). The evaporation of the top-contact and the bottom-contact pad were combined in a single evaporation step, figure 3.39(d). The bond pads to the top-contact were evaporated over the SiO$_2$ insulation (see section 3.5.5). Before characterization, the device was wire bonded to the top and bottom bond pads.

3.6.2 Nanopillar arrays in RTDs: bottom-contact dilemma

In a GaAs / Al$_x$Ga$_{1-x}$As based active region, where the end point after etching nanopillars is an n$^+$ doped GaAs contact, bottom-contact fabrication poses a big challenge. This is specially true for our test double well RTD structures which terminate in an n$^+$ doped GaAs contact. As described in section 3.6.1, the bottom n$^+$ doped GaAs layer is contacted by AuGeNi contacts which are evaporated and annealed at 430°C for 80 s. This annealing step has two ramifications. First, the metal etch mask, which is in contact with the top of the nanopillars diffuses down to the GaAs / Al$_x$Ga$_{1-x}$As layers during the annealing stage of the bottom-contact, resulting in a short circuit. Second, if the bottom-contacts are evaporated after planarization, the spin on glass layer cracks upon rapid thermal annealing.

Figures 3.40(a-b) show the flowchart for the fabrication of electrically connected nanopillar arrays in RTDs. Similar to large-area RTD processing, the bottom-contacts for nanopillar RTDs, were fabricated before etching the nanopillars, in the case where the etch mask was a metal, figure 3.40(a). However, inclusion of bottom-contacts before etching exposes the reactive ion chamber to a high metallic content on the chip for the entire duration of the etch, restricting this process to RIE systems alone. While the metallic content on the chip as a result of using a metal etch mask is around 0.02 %, the metallic content on the chip due to bottom-contacts is around 3.3 %. Consequently, even using an RIE process, we protect the bottom-contacts and bond pads by SiO$_2$ before e-beam lithography, to avoid a potential risk of micromasking as a result of etch related debris. However, this process increases the number of lithographic stages. In the case of a dielectric etch mask, electrical shorting is not an issue. Therefore, we prefer to deposit the bottom-contact and bond pads after the etching stage but before the planarization stage, figure 3.40(b).
3. NANOPILLAR ARRAYS IN RTDS AND QCLS: EXPERIMENTAL REALIZATION

Figure 3.40: Process flowchart to fabricate electrically connected nanopillar arrays in RTDs (a) in the case of a metal etch mask, and (b) in the case of a dielectric etch mask.

3.7 Experimental set-up for characterizing RTDs

Four terminal (4T) measurements as opposed to two terminal (2T) measurements allow the true device electrical characteristics of the device to be measured as it eliminates lead resistance, see figure 3.41. In the 4T measurement, the voltmeter indirectly measures the voltage drop across the device ($r_{RTD}$), and the top and bottom doped contacts ($r_{tc}$, $r_{bc}$) that form part of the device, see figure 3.41(a). In the 2T measurement, the voltmeter measures the voltage drop across the lead resistances $r_{lead}$, resistance across the device $RTD$, and the top and bottom doped contacts ($r_{tc}$, $r_{bc}$) that form part of the device, see figure 3.41(b). Unlike 2T measurements which require only two contacts, 4T measurements require four contacts to allow for the elimination of the lead resistance. While this is straightforward to implement on a large-area device, these measurements are not trivial to carry out on electrically connected nanopillar arrays as this necessitates two top-contacts and two bottom-contacts. To allow for a useful comparison between large-area devices and the nanopillar arrays, all the Schottky RTD devices discussed in this work were characterized by 2T measurements.
3.8 Results from RTDs: A1700

Figure 3.41: Experimental set up for characterizing RTDs using (a) four terminal measurements, and (b) two terminal measurements.

These measurements were made using an HP 4155 A semiconductor parameter analyzer at room temperature (300 K) and at liquid helium temperature (4K). To avoid Joule heating, the voltage was pulsed at a period of 10 ms with a duty cycle of 10%.

3.8 Results from RTDs: A1700

A1700 was used as the main test structure for the nanopillars as it is based upon Al$_x$Ga$_{1-x}$As barriers, which closely resembles the epitaxial structure of the THz QCLs used in this work. Results from large-area RTDs processed from ohmic contacts are presented first, as a reference. This is the ideal configuration of RTDs under the absence of any constraints and involves using a shallow ohmic top-contact such as Pd/Ge and a deep ohmic bottom-contact such as AuGeNi. Next, we present the electrical characteristics of large-area RTDs fabricated with a Schottky top-contact and an ohmic bottom-contact. This contact geometry is representative of the contact geometry used for an array of nanopillars. Finally, we discuss the results from nanopillar arrays processed from A1700.

3.8.1 Large-area RTDs: ohmic contact

Figure 3.42 shows the 4T measurements of a large-area RTD processed from A1700, with an ohmic top and bottom-contact at 77 K. The large-area device, which has a mesa size of approximately 70 $\mu$m x 70 $\mu$m, shows a distinct NDR under positive and negative polarities. From theoretical calculations, we should expect three NDR peaks under both positive...
and negative polarities, which correspond to three resonance states in A1700, see section 2.2. These NDR peaks should occur at \( \text{abs}(V_p) = 2E_i \), where \( i = 0, 1 \) and 2 [136]. Here, \( V_p \) is the voltage associated with each resonant state at which the current is maximum. The three NDR peaks should occur at a bias \( \text{abs}(V_p) \) equal to 0.064 V, 0.254 V and 0.514 V, corresponding to energy levels \( E_0 \sim 32 \text{ meV} \), \( E_1 \sim 127 \text{ meV} \) and \( E_2 \sim 257 \text{ meV} \). In reality, there is a slight discrepancy between the experimentally measured NDR peak and the NDR peak predicted from simplistic theoretical calculations based on the epitaxial structure. In a 4T measurement, this deviation occurs primarily because of the depletion region formed in the GaAs layers between the contact and the barriers [102, 137]. Therefore, while the theoretical calculations predict the first NDR peak to be at \( \text{abs}(V_p) = 0.064 \) V, this peak is observed at -0.31 V under negative bias upon alignment with the ground state, see figure 3.42. The peak current density associated with resonant tunneling of electrons is \( J_p = -85 \text{ A/cm}^2 \). Under positive bias, the first NDR appears at +0.36 V upon alignment with the ground state and the peak current density associated with the NDR is \( J_p = +92 \text{ A/cm}^2 \). A record of device behavior at 4K is absent, however this should not influence the discussion of results in section 3.8.2 by a great extent.

Figure 3.42: Electrical characterization of large-area RTD, with mesa size 70 \( \mu \text{m} \times 70 \mu \text{m} \) processed from A1700, with an ohmic top-contact. The measurement was carried out at 77K, in a 4T configuration and the voltage was swept from -1 V to +1 V in steps of 5 mV. The data was provided by Dr. Patrick Sze.

Figure 3.43 shows the 4T electrical characteristics for a range of mesa areas varying from 70 \( \mu \text{m} \times 70 \mu \text{m} \) to 200 \( \mu \text{m} \times 200 \mu \text{m} \). All the devices exhibit an NDR peak in the

\[ ^1 \text{An approximate numerical solution to 2.2} \]
3.8 Results from RTDs: A1700

Figure 3.43: Electrical characterization of large-area RTDs with mesa sizes varying from 70 µm x 70 µm to 200 µm x 200 µm. The devices were processed from A1700, with an ohmic top-contact. The measurement was carried out at 77K in a 4T configuration and the voltage was swept from -1 V to +1 V in steps of 5 mV. The data was provided by Dr. Patrick Sze.

As the mesa area increases from 70 µm by 70 µm to 200 µm by 200 µm, the peak voltage associated with the ground state NDR increases from $V_p = -0.31$ V to $V_p = -0.46$ V under negative bias and from $V_p = +0.36$ V to $V_p = +0.81$ V under positive bias. This voltage drop is associated with the additional series resistance of the doped contacts, which scales with device area and is independent of whether the measurement is 4T or 2T [138, 139]. The other parameters which are influenced by an increase in mesa area include the peak current density and the peak to valley current ratio. The peak current density associated with the NDR peak decreases from $J_p = -85$ A/cm$^2$ to $J_p = -33$ A/cm$^2$ under negative bias and from $J_p = +92$ A/cm$^2$ to $J_p = +66$ A/cm$^2$ under positive bias. The peak to valley current ratio ($J_p/J_v$) falls from 11.6 to 1.78 under negative bias (and from 10.8 to 1.66 under positive bias) for the same increase in mesa dimensions. Even though there exists a slight variability among large-area RTD devices, the threshold voltage remains nominally identical for all the different mesa sizes, i.e. $V_{th} = -0.065$ V in the case of negative polarity and $V_{th} = +0.05$ V in the case of positive polarity.

3.8.2 Large-area RTDs: Schottky contact

Figure 3.44(a) shows a comparison between a large-area RTD device processed from A1700 with a Schottky contact and a large-area RTD device processed from A1700 with an
ohmic contact. The dimensions of the large-area RTDs with a Schottky contact are equal to 10 µm by 10 µm and the dimensions of the large-area RTDs with an ohmic contact are equal to 70 µm by 70 µm. At these dimensions, the quantum confinement effects due to surface depletion are negligible [139].

Figure 3.44: (a) 2T measurements of large-area RTDs (processed from A1700 with a Schottky top-contact) at 4K in comparison with 4T measurements of large-area RTDs (processed from A1700 with an ohmic top-contact) at 77 K. The dimensions of the large-area RTDs with a Schottky contact are equal to 10 µm by 10 µm and the dimensions of the large-area RTDs with an ohmic contact are equal to 70 µm by 70 µm (b) Forward and backward voltage sweep during the 2T measurements of the 10 µm by 10 µm RTD at 4K. The applied voltage was swept in steps of 10 mV.

We note a very clear shift in bias between the first NDR peaks of the two devices. Considering that the peak current density associated with the NDR peak is similar, $J_p = -85$ A/cm$^2$ (-126 A/cm$^2$) for the RTD with the ohmic (Schottky) contact, it is highly probable that the NDR peak seen at $V_{p,\text{abs}} = -1.04$ V from the Schottky device corresponds to alignment with the ground state. The shift in bias between the two peaks may be attributed to the following causes. First, this shift may just perhaps occur because of a difference in the resistance of the doped contacts arising from a difference in the mesa size of the two devices that are being compared. Second, this shift may occur due to the additional lead resistance picked up in a 2T measurement as opposed to a 4T measurement. Finally, this shift may occur due to a voltage drop of 0.7 V on the collector end due to the Schottky barrier. The first reason can be eliminated on the basis that the difference in mesa size would have resulted in a larger $V_p$ as opposed to a smaller $V_p$ for the 70 µm by 70 µm device, when compared to the 10 µm by 10 µm device. Furthermore, even if the shift in the NDR peak was due to a difference in mesa size, the threshold voltage of the two...
3.8 Results from RTDs: A1700

devices would have been similar (see figure 3.43). While the second reason is a possibility that can not be discounted, the difference in the two peak voltages (0.74 V) between the devices suggests that this additional voltage is dropped across the Schottky barrier at the top-contact. The ground state resonance under negative bias for the large-area RTD device with a Schottky top-contact is shown in greater detail in figure 3.44(b). Note, that the two separate curves indicate forward and reverse voltage sweep. The hysteresis observed in figure 3.44(b) is characteristic of RTD behavior, and can be attributed to a combination of intrinsic charge bistability \[140\] and extrinsic biasing effects \[141\].

Figure 3.45: 2T measurements of large-area RTDs processed from A1700 with a Schottky top-contact. The device has a mesa size of 10 µm by 10 µm. The voltage was swept in steps from -5 V to +5 V of 10 mV and the measurement was carried out at 4K and 300 K.

Figure 3.45 shows the 2T measurements of a large-area RTD, with a Schottky top-contact and an ohmic bottom-contact, under an extended voltage range (-5 to +5 V). Unlike the 4T measurements of large-area RTDs processed with an ohmic top and bottom contact (figure 3.43), these measurements show an asymmetry under positive and negative bias. This asymmetry may arise out of a difference in lead resistance that is not excluded in a 2T measurement or it may also arise out of a difference in the contact resistance at the emitter and the collector end. We note that the first NDR peak under the positive polarity appears at a very high voltage (\(V_p = +4.29\) V) as compared to the negative polarity (\(V_p = -1.04\) V). The peak current \(J_p = 109\) A/cm² is approximately equal to the peak current observed in the negative bias when the device is in resonant alignment with the
ground state. Therefore, it is probable that the NDR peak at \( V_p = +4.29 \) V corresponds to alignment with the ground state. The shift in bias from the expected \( V_p \) at approximately +1.04 V to +4.29 V may then perhaps occur primarily due to an additional voltage drop across the lead resistance, which may be eliminated with a 4T measurement.

Going back to the device characteristics under negative polarity between 0 to -5 V, we observe three distinct NDR peaks at 4 K (\( V_p = -1.04 \) V, -1.8 V and -3.75 V). Although weak, these peaks are also observed when the device is at room temperature. The observation of three NDR peaks suggest that they correspond to alignment with the ground state (\( E_0 \)) and the two excited states (\( E_1 \) and \( E_2 \)), which is in agreement with the theoretical calculations discussed in section 3.8.1. We also note an increase in peak current and the peak current density associated with resonant alignment with the subsequent higher energy states. For example, the peak current density \( J_p \) associated with the third NDR peak is approximately -5018 A/cm\(^2\), which is much larger than the peak current density \( J_p \) associated with the first and second NDR peaks (\( J_p = -126 \) A/cm\(^2\) and -532 A/cm\(^2\), respectively). This behavior is expected from large-area RTDs with multiple energy states [142].

We also tested multiple devices processed from A1700 with a Schottky top-contact and an ohmic bottom-contact. The mesa dimensions of these devices ranged from 10 \( \mu \)m by 10 \( \mu \)m to 50 \( \mu \)m by 50 \( \mu \)m, see figure 3.46. All the devices exhibit an NDR peak in the positive and negative polarity. As the mesa area increases from 10 \( \mu \)m by 10 \( \mu \)m to 50 \( \mu \)m by 50 \( \mu \)m, the peak voltage associated with the ground state NDR increases from \( V_p = -1.04 \) V to \( V_p = -2.37 \) V under negative bias and from \( V_p = +4.28 \) V to \( V_p = +4.54 \) V under positive bias. This increase is associated with the additional series resistance of the doped contacts, which scales with device area and is independent of whether the measurement is 4T or 2T [138, 139]. All the devices exhibit similar peak current density upon alignment with the ground state, i.e. \( \text{abs}(J_p) = 134 \pm 27 \) A/cm\(^2\). We further note that even though the threshold voltage is different under opposite polarities due to asymmetry in lead resistance, i.e. \( V_{th} = -0.77 \) V under negative bias and \( V_{th} = +1.9 \) V under positive bias, it is nominally identical for all the large-area devices that were measured. Similar to large-area RTD devices processed with an ohmic top-contact, section 3.8.1, we note that the device with the largest mesa size, i.e. mesa length equal to 50 \( \mu \)m, exhibits the smallest peak to valley current ratio (\( J_p/J_v = 1.82 \) under negative bias and \( J_p/J_v = 1.61 \) under positive bias). The device with the smallest mesa dimensions, i.e. mesa length equal to 10 \( \mu \)m, exhibits a peak to valley current ratio (\( J_p/J_v \)) that is equal to 23.3 under negative polarity and 2.54 under positive polarity.

It is encouraging to note that the Schottky barrier on the top-contact of a large-area RTD does not impede the observation of a resonance. This allows us to test the electrical
3.8 Results from RTDs: A1700

Figure 3.46: 2T measurements of large-area RTDs processed from A1700 with a Schottky top-contact. The mesa dimensions vary from 10 μm by 10 μm to 50 μm by 50 μm. The voltage was swept from -5 V to +5 V in steps of 10 mV and the measurement was carried out at 4K.

robustness of an array of insulated (unsuspended) nanopillars, processed from A1700 with a Schottky top-contact, see below.

3.8.3 Nanopillar arrays

3.8.3.1 Results from 500 x 500 array, \( R_p = 100 \text{ nm} \)

Figure 3.47 shows the first result of a successful top-contact to an array of insulated nanopillars. Processed from A1700, this chip consisted of three 500 x 500 array of nanopillars, with pillar sizes defined as \( R_p = 50 \text{ nm} \), \( R_p = 100 \text{ nm} \) and \( R_p = 150 \text{ nm} \). Out of these three arrays, pillars with \( R_p = 100 \text{ nm} \) and \( R_p = 150 \text{ nm} \) survived the etch and processing. Here, we discuss the results from pillars with \( R_p = 100 \text{ nm} \), see figure 3.47 inset. The necking around the quantum well is a result of agitated stirring in buffered hydrofluoric acid during the planarization recovery process. We note distinct NDR peaks at 4 K and at 300 K. These peaks appear at \( V_p = -2.6 \text{ V} \) in the negative bias, and at \( V_p = +5.52 \text{ V} \), \( V_p = +6.66 \text{ V} \) in the positive bias.

Figure 3.48 shows the peak at \( V_p = -2.6 \text{ V} \), in more detail. The appearance of NDR during forward and the reverse voltage sweeps confirms transport through the nanopillars. Unlike pA to nA current flowing through single nanopillars processed from RTDs, we observe a current in the range of \( \mu \text{A} \) flowing through nanopillars connected in parallel. This is at least three orders of magnitude improvement over the previously reported values of...
Figure 3.47: 2T measurements of 500 x 500 nanopillar array processed from A1700, with radial dimension $R_p = 100$ nm measured at 4K and 300 K. The voltage was swept in steps of 10 mV. The inset shows the scanning electron micrograph of the nanopillar array, before final insulation and top-contact processing.

Figure 3.48: Negative differential peak corresponding to the ground state of 500 x 500 array of nanopillars processed from A1700, at negative bias, and at a temperature of 4K. The radial dimensions of the pillars was defined as $R_p = 100$ nm. The voltage was swept in steps of 10 mV and the measurement was carried out in 2T configuration.
nanopillar RTDs [89, 94, 102, 108].

### 3.8.3.2 Challenges associated with NDR mapping

While it is relatively straightforward to attribute NDR peaks to energy states \( E_i \) for large-area RTDs, it is not trivial to map NDR peaks to energy states in the case of an array of nanopillars. This complexity arises due to discretization of energy states from lateral quantization in a nanopillar. We can however safely assume, that the strongest NDR peak in an array of nanopillars occurs due to strong confinement in the longitudinal direction, and hence can be attributed to alignment with any of the longitudinal states \( E_i \).

Besides the mapping of NDR peaks in an array of nanopillars, it may also be non-trivial to estimate the number of pillars \( N_t \) taking part in transport and the electrostatic radius \( R_e \) simultaneously. This ambiguity arises from the problem of mapping NDR peaks to the energy states. The position of the fine feature superimposed upon the NDR peak can be related to the electrostatic radius \( R_e \). In the absence of fine features, we can estimate \( R_e \) and \( N_t \) from the peak current \( I_p \) that is experimentally observed during a measurement. This current is a product of the current density \( J_p \) associated with the resonance, the electrostatic area of a single nanopillar \( \pi R_e^2 \) and the number of pillars taking part in transport \( N_t \), see eqn. below.

\[
I_p = J_p \pi R_e^2 N_t \quad (3.2)
\]

To estimate \( R_e \), we assume that all the nanopillars in the 500 x 500 array are in contact and take part in transport. This assumption is true when the processing preserves the number of pillars defined at the e-beam stage. Eqn. 3.2 then gets modified to:

\[
I_p = 250000 J_p \pi R_e^2 \quad (3.3)
\]

Since previous attempts only focused on single nanopillars [89, 94, 102, 108], it is useful to gain an insight into how many nanopillars in a 500 x 500 array take part in the transport. This estimate requires the knowledge of \( R_e \). In order to estimate the minimum number of pillars that are in contact \( N_t \), we ignore sidewall depletion and assume that \( R_e = R_p \). Therefore, eqn. 3.2 gets modified to:

\[
I_p = J_p \pi R_p^2 N_t \quad (3.4)
\]

In reality, as \( R_e \) is less than \( R_p \), the number of pillars taking part in the transport will be higher than the \( N_t \) estimated using eqn. 3.4. We can now discuss the results shown in
3. NANOPILLAR ARRAYS IN RTDS AND QCLS: EXPERIMENTAL REALIZATION

figures 3.47 and 3.48 in view of the analysis presented above.

3.8.3.3 Discussion

Mapping of NDR peaks

It is highly probable that the first NDR peak seen under negative bias at $V_p = -2.6$ V in figure 3.47, actually corresponds to the ground state $E_0$. However, since the position of the ground state and the position of the first excited state are quite close (figure 3.45), this peak can also correspond to the first excited state. Since we observe two peaks that are close to each other under positive bias, it is probable that the first NDR peak at $V_p = +5.53$ V in figure 3.47 corresponds to the ground state $E_0$ and the second NDR peak at $V_p = +6.66$ V in figure 3.47 corresponds to the first excited state $E_1$. However, multiple peaks may also imply multiple devices coming into alignment.

Estimation of number of pillars

Let us assume that the peak at $V_p = -2.6$ V corresponds to the ground state. From figure 3.47, we note that the peak current at $V_p = -2.6$ V is equal to $-72 \mu$A. The density of current flowing through the device upon alignment must be equal to the density of current flowing through a large-area RTD, i.e. $J_p = -126$ A/cm$^2$ (figure 3.46). Assuming that only one nanopillar with $R_p = 100$ nm was contacted successfully, the peak current flowing through the device, in the best-case scenario, i.e. ignoring depletion, would be 39 nA. Clearly, our result implies that multiple nanopillars are conducting in parallel. If there was no depletion and all the nanopillars were contacted successfully, the current flowing through the device would be 9.9 mA. Since the current flowing through the array of nanopillars shown in figure 3.47 is less than 9.9 mA but greater than 39 nA, this implies that either only a few nanopillars are contacted or the current path is constrained due to surface depletion. It is likely, that in this particular device both the scenarios hold true. Using eqn. 3.4 we can estimate the minimum number of pillars that are in contact and take part in the transport (i.e. $N_t$). For an array of nanopillars with physical radius $R_p = 100$ nm to pass a peak current of 72 $\mu$A, at least 1820 nanopillars must be in contact. From the inset in figure 3.47, which shows the SEM image of the pillars after etching, we note that the radial dimensions of the nanopillar is less than 100 nm around the quantum well (for details see section 3.5.4.4). Substituting the radius as 57 nm in eqn. 3.4, we note that the minimum number of pillars in contact increases to 7730. The number of pillars
calculated using this approach is an under estimate and would increase if we account for surface depletion in the nanopillars.

**Estimation of electrostatic radius**

Reversing the argument, assuming that all the 500 x 500 nanopillars are connected, the empirical electrostatic radius \( R_e \) can be calculated using eqn. 3.3 by equating \( 250000 \pi R_e^2 J_p \) to the absolute value of the peak current observed at \( V_p = -2.6 \) V, which is -72 \( \mu \)A. From here, we derive \( R_e = 8.3 \) nm.

**Absence of fine features**

According to Reed et. al, for a 100 nm nanopillar, we expect fine features superimposed upon the NDR peak due to lateral quantization which should be equally spaced at \( 2\Delta E = 25.2 \) meV [89]. However, in spite of a very clear NDR peak and an SEM image indicating reduced dimensionality, we do not observe fine features in the current-voltage characteristics. The absence of fine features can be attributed to several causes. Perhaps, the fine features were washed out due to large statistical variations in the radial dimensions of the pillars within the array in this particular batch of processing. It may also be that the fine features were averaged during the measurement. For nanopillars processed from A1700 (figures 3.47 and 3.48), the voltage was swept in steps of 10 mV. If the lateral quantization was weak, i.e. the splitting of energy levels (\( \Delta E \)) was less than 10 meV, these features were not picked up during the measurement. Finally, if the electrostatic radius of the doped contact was equal to electrostatic radius of the undoped well, the fine feature might have been destroyed due to alignment of the subbands in the doped contact with the subbands in the undoped well, see section 2.6.5.

### 3.9 Results from RTDs: W0021

Although, A1700 was the main test structure for the nanopillars, a second wafer W0021 was also investigated. The rationale behind this study can be attributed to the peak current density which is higher in W0021 as compared to A1700 and commensurate with the operation of the THz QCLs. Unfortunately, a higher current density requires the use of thin barriers, which is why W0021 is based on AlAs barriers. The transport behavior of electrons tunneling through an AlAs/GaAs system is significantly different from that of \( \text{Al}_{0.33}\text{Ga}_{0.67}\text{As}/\text{GaAs} \) system. This difference originates from a difference in the potential
profile of the double barrier structure. In the case of Al$_{0.33}$Ga$_{0.67}$As, the potential profile is derived from Γ-point energies such that Al$_{0.33}$Ga$_{0.67}$As barriers acts as a tunnel barrier and GaAs acts as a well. In the case of AlAs, the potential profile can also be derived from the X-point energy states which causes AlAs to serve as a well for the electrons tunneling through GaAs barrier. It is also possible that the real potential profile is not based purely on Γ and X-point energies, but exists as a mixture of the two profiles [143]. Since this adds additional complexity to the analysis, we do not discuss these states in detail. The purpose of this section is to introduce the electrical measurements of large-area RTDs, followed by a discussion of results from the nanopillar arrays. In comparing the empirically observed NDR peaks, we assume that the longitudinal states that take part in the electron transport through large-area RTDs are the same states that are also involved in the nanopillar arrays.

### 3.9.1 Large-area RTDs: ohmic contact

Figure 3.49 shows the 2T measurements of large-area RTDs processed from W0021, with an ohmic top and bottom-contact at 4 K. The large-area device, with a mesa size of approximately 20 µm x 20 µm, shows distinct NDR peaks under positive and negative polarities. Assuming a Γ profile of the AlAs/GaAs structure, the first NDR peak should occur at a bias $|V_p| = 2E_i = 0.1 \text{ V}$ corresponding to alignment with the energy states $E_0 \approx 51.7 \text{ meV}$.

Experimentally however, the position of the measured NDR peaks deviates slightly from the theoretically predicted NDR peaks. In a 4T measurement, this deviation occurs primarily because of the depletion region formed in the low-doped GaAs layers between the contact and the barriers [102, 137]. In a 2T measurement, an additional contribution comes from the voltage that is dropped across the leads. Therefore, while the theoretical calculations predict the ground state NDR peak at $|V_p| = 0.10 \text{ V}$ the first peak is observed at $V_p = +1.08 \text{ V}$ under positive polarity and at $V_p = -0.56 \text{ V}$ under negative polarity, when the voltage is swept from negative to positive. What is interesting to note is that the peak current density associated with these two peaks is quite different. The peak current density associated with the NDR at $V_p = +1.08 \text{ V}$ is $J_p = 690 \text{ A/cm}^2$ as compared to $J_p = -245 \text{ A/cm}^2$, which is associated with the peak at $V_p = -0.56 \text{ V}$. This suggests that the two peaks correspond to different bound states. The behavior is reversed when the direction at which the voltage is swept is reversed. In the reverse voltage sweep, the first peak is observed at $V_p = +0.60 \text{ V}$ with $J_p = 266 \text{ A/cm}^2$ under positive polarity, and at $V_p = -1.03 \text{ V}$ with $J_p = 675 \text{ A/cm}^2$ under negative polarity. The similarity in the peak current density between the peak at $V_p = -0.56 \text{ V}$ (forward bias) and the peak at $V_p = +0.60 \text{ V}$ (reverse bias) suggests

\[^1\text{An approximate numerical solution to 2.2}\]
3.9 Results from RTDs: W0021

that the two peaks occur due to alignment with the same state, let’s call it \( E_0 \). In the same way, the similarity in peak current densities between the peak at \( V_p = +1.08 \) V (forward bias) and the peak at \( V_p = -1.03 \) V (reverse bias) suggests that the two peaks occur due to alignment with the same state, let’s call it \( E_1 \). Here, we refrain from specifying the origin of \( E_0 \) and \( E_1 \) states, which may belong to \( \Gamma \)-point energy, \( X \)-point energy, a mixture of the \( \Gamma \) and \( X \)-point energies, or arise due to accumulation of electrons in the GaAs layer adjacent to the barrier [137, 143]. We also note the appearance of a small peak at \( V_p = -0.81 \) V (\( J_p = -124 \) A/cm\(^2\)) and at \( V_p = +0.86 \) V (\( J_p = +127 \) A/cm\(^2\)), which is observed in conjunction with the peak attributed to state \( E_0 \), i.e. at \( V_p = -0.56 \) V and at \( V_p = +0.60 \) V. We call this peak as \( E_0' \), since it always appears with \( E_0 \).

![Figure 3.49: Electrical characterization of large-area RTD, with mesa size 20 \( \mu \)m x 20 \( \mu \)m processed from W0021, with an ohmic top-contact. The measurement was carried out at 4K in a 2T configuration and the voltage was swept in steps of 5 mV. The device was fabricated by Ken Cooper and Melanie Tribble.](image)

Figure 3.50 shows the 2T measurements of the 20 \( \mu \)m x 20 \( \mu \)m RTD under an extended voltage range. At higher voltages, we note the appearance of an NDR peak at \( V_p = +4.06 \) V (\( J_p = +2488 \) A/cm\(^2\)) and at \( V_p = -3.76 \) V (\( J_p = -2321 \) A/cm\(^2\)). Since the peak current density associated with the two peaks is similar, it implies that both the peaks correspond to the same state, which we label as \( E_2 \).

Figure 3.51 shows the electrical characteristics for a range of mesa areas varying from 20 \( \mu \)m x 20 \( \mu \)m to 50 \( \mu \)m x 50 \( \mu \)m, as the voltage is swept from negative bias to positive bias. All the devices exhibit NDRs corresponding to state \( E_0 \) (negative polarity), \( E_0' \) (negative polarity) and \( E_1 \) (positive polarity). Although the peak voltage \( V_p \) corresponding to state \( E_0 \) increases with mesa area due to an increase in the contact resistance (\( V_p = -0.56 \) V...
3. NANOPILLAR ARRAYS IN RTDS AND QCLS: EXPERIMENTAL REALIZATION

Figure 3.50: Electrical characterization of large-area RTD, with mesa size 20 μm x 20 μm processed from W0021, with an ohmic top-contact. The measurement was carried out at 4K in a 2T configuration and the voltage was swept from -5 V to +5 V in steps of 10 mV. The device was fabricated by Ken Cooper and Melanie Tribble.

Figure 3.51: Electrical characterization of large-area RTD, with mesa size varying from 20 μm x 20 μm to 50 μm x 50 μm. The devices were processed from W0021, with an ohmic top-contact. The measurement was carried out at 4K in a 2T configuration and the voltage swept in steps of 10 mV. The inset shows the NDR peaks under negative bias in more detail. The device was fabricated by Ken Cooper and Melanie Tribble.
3.9 Results from RTDs: W0021

V to -0.81 V), the threshold voltage remains nominally identical ($V_{th} = -0.23$ V). We also note a decrease in the peak current density from $J_p = -245$ A/cm$^2$ to -84 A/cm$^2$, as well as a decrease in the peak to valley current ratio, which falls from $J_p/J_v = 5.83$ to $J_p/J_v = 1.86$, as the mesa size is increased from 20 $\mu$m x 20 $\mu$m to 50 $\mu$m x 50 $\mu$m. This behavior also holds true for the first NDR peak observed under positive polarity (state E$_1$), where the peak voltage increases from $V_p = +1.08$ V to $+4.18$ V as the area is increased. The threshold voltage for all the devices remains nominally identical ($V_{th} = +0.26$ V). The peak to valley current ratio tends to decrease with mesa area ($J_p/J_v = 7.26$ to $J_p/J_v = 1.37$), and the devices exhibit a peak current density of 654 ± 36 A/cm$^2$.

3.9.2 Nanopillar arrays

Although we only compared the electrical behavior of A1700 with ohmic and Schottky contacts (section 3.8.2), it is reasonable to assume that the Schottky barrier on the top-contact would introduce similar changes to W0021. We can now discuss the results obtained from nanopillar arrays processed from W0021.

3.9.2.1 500 x 500 array, $R_p = 150$ nm

Results

Figure 3.52 shows the electrical characteristics of a 500 x 500 nanopillar array with pillar size defined as $R_p = 150$ nm. We note distinct NDR peaks at 4 K and at 300 K, indicating successful top-contact to the nanopillar array. Under negative bias, we observe NDR peaks at $V_p = -0.52$ V, -0.92 V, -1.36 V, -2.2 V, -2.38 V, -2.69 V. Under positive bias, the NDR peaks are observed at $V_p = +0.48$ V, +0.80 V, +1.77 V, +3.68 V. The peaks observed under negative polarity are shown in detail in figure 3.53. The appearance of NDR peaks under forward as well as reverse voltage sweeps confirms transport through the nanopillars, see figure 3.53. What makes the analysis challenging is the appearance of multiple NDR peaks, which do not necessarily correspond to the states observed in the large-area RTDs (figure 3.49).

Mapping of NDR peaks

In large-area RTDs processed with an ohmic contact, the first NDR peak was observed at $V_p = -0.56$ V (figure 3.49). This state was labelled as E$_0$. Assuming a 0.7 V drop due to the Schottky top-contact, the first NDR peak due to alignment should occur at an absolute bias of 1.24 V. However, from figure 3.52, we note two peaks ($V_p = -0.52$ V and $V_p = -0.94$
Figure 3.52: (a) 2T measurements of 500 x 500 nanopillar array processed from W0021, with radial dimension $R_p = 150$ nm measured at 4K and 300 K. The inset, on the top left shows the scanning electron micrograph of the nanopillar array, before final insulation and top-contact processing. (b) 2T measurements of the 500 x 500 nanopillar array at 4K, shown separately at low-voltage. The voltage was swept from -5 to +5 V in steps of 10 mV.

Figure 3.53: 2T measurements of 500 x 500 nanopillar array processed from W0021 at 4K, during forward and reverse voltage sweeps. The pillar size was defined as $R_p = 150$ nm. The voltage was swept in steps of 10 mV.
V) that appear before reaching this bias. These peaks are also symmetric with polarity, i.e. we note two similar peaks in the positive polarity ($V_p = +0.48$ V and at $V_p = +0.80$ V) which appear at approximately the same position and exhibit the same peak current. Perhaps, these peaks appear due to subband states in the contact and do not necessarily reflect bound states in the well. It is probable that the peak observed at $V_p = -1.36$ V corresponds to alignment with the state $E_0$. Similarly, it is probable that the peak at $V_p = +1.77$ V corresponds to alignment with the state $E_1$ and the next highest peak at $V_p = +3.68$ V corresponds to $E_2$. However, it is difficult to identify the origin of the three peaks at $V_p = -2.2$ V, -2.38 V or -2.69 V and attribute a suitable cause to the multiplicity of the peaks.

**Estimation of number of pillars**

When the device is in resonance with the state $E_0$ at $V_p = -1.34$ V, the nanopillar array supports a peak current of $-154$ $\mu$A. The density of current flowing through the device upon alignment must be equal to the density of current flowing through a large-area RTD, i.e. $J_p = -245$ A/cm$^2$. Assuming that only one nanopillar with $R_p = 150$ nm was contacted successfully, the peak current flowing through the device, ignoring depletion would be $-173$ nA. This current is much less than the peak current that we observe, i.e. $I_p = -154$ $\mu$A. This implies that multiple nanopillars are indeed in contact and take part in the current transport. The ratio of the two currents ($154/0.173$), see eqn. 3.4, leads us to believe that at least 890 nanopillars are in contact. Note that the number of pillars calculated using this approach is an under estimate and would increase if we account for surface depletion in the nanopillars.

**Estimation of electrostatic radius**

If we reverse the argument and assume that all 500 x 500 nanopillars are in contact, the electrostatic radius $R_e$ can be calculated by equating $250000\pi R_e^2 J_p$ to the peak current at $V_p = -1.34$ V. Substituting $-154$ $\mu$A as the peak current and $J_p = -245$ A/cm$^2$ in eqn. 3.3, we estimate the electrostatic radius to be 8.9 nm.

**Probing for fine features**

In section 2.3, we discussed that the splitting between the energy levels due to quantization should lead to fine features superimposed upon the NDR peak. According to Reed
et. al, these features should be equally separated by $2\Delta E = 16.8 \text{ meV}$ for a 150 nm pillar. It is likely that these features were not picked up in figure 3.53, where the voltage was incremented in steps of 10 mV. To probe this further we remeasured the electrical characteristics at a higher resolution, i.e. in steps of 5 mV and 2 mV.

Figure 3.54: (a) Electrical characteristics of 500 × 500 nanopillar array, processed from W0021 with $R_p$ defined as 150 nm. The electrical characteristics were measured at a voltage step of 5mV and 2mV in a 2T configuration at a temperature of 4K. For clarity, the current voltage characteristics at 2 mV voltage step have been displaced vertically by 100 $\mu$A. The NDR peaks corresponding to $E_0$ and $E_1$ have been shown separately in (b) and (c), respectively.

The 2T measurements at a voltage step of 5 mV and 2 mV (figure 3.54) are consistent with the measurements carried out earlier (figure 3.53), in that the same NDR peaks are observed under nominally identical positions. The position of these NDR peaks only shifts slightly because of the inherent hysteresis in RTD devices [140, 141]. In addition to these peaks (highlighted through red arrows), we observe four peaks (highlighted through green arrows) that are weak.

Let us look closely at the peaks at $V_p = -1.36 \text{ V}$ and $V_p = -1.38 \text{ V}$. The difference between the two peaks is 20 meV. Perhaps, this additional shoulder peak is a consequence of resonant alignment with $E_0 + (m+1/2)\Delta E$ state, where $m=1$ is an integer and $\Delta E$ is the energy splitting due to lateral quantization, see eqn. 2.24. The peaks corresponding to $E_0$ and $E_0 + (3/2)\Delta E$ are shown separately in figure 3.54(b) for greater clarity. The additional
peaks at $V_p = -1.71$ V, $V_p = -2.24$ V and at $V_p = -2.61$ V, shown clearly in figure 3.54(b-c), can not be easily mapped onto the corresponding energy states. Perhaps, these peaks occur as a consequence of different pillars coming into alignment. It may also be that these peaks appear as a result of lateral mode mixing, which is not accounted by Reed's simplistic model [144]. While it is challenging to map all the NDR peaks to the corresponding states, due to the complexity introduced by multiple transport pathways it is certain that a 500 x 500 nanopillar array processed from W0021 with $R_p = 150$ nm can support parallel conduction. Our results clearly indicate an electrically robust contact to multiple nanopillars, with a peak current of -154 $\mu$A flowing through the device upon alignment with the $E_0$ state. As the bias is increased, the array can support a maximum peak current of -1565 $\mu$A flowing through the nanopillars. To verify the electrical robustness of smaller pillars, we reduced the dimensionality of the pillar from 150 nm to 100 nm. We describe these results below.

3.9.2.2 500 x 500 array, $R_p = 100$ nm

Results

Figure 3.55 shows the electrical characteristics of a 500 x 500 nanopillar array with pillar size defined as $R_p = 100$ nm, measured at 4K and 300 K. While the NDR peak at 300 K is relatively weak, we observe a distinct NDR peak at 4K under negative bias ($V_p = -2.72$ V). This NDR peak is observable in both forward and reverse voltage sweeps, confirming resonant tunneling as the dominant transport mechanism through the nanopillar array, figure 3.56. However, the main NDR peak in this device appeared to shift with voltage with each measurement. This may be a consequence of a large hysteresis due to intrinsic charge instability [140, 141].

Mapping of NDR peaks and estimation of number of pillars

Even though the peak at $V_p = -2.72$ V is the first distinct NDR peak that we observe, the high peak current associated with the NDR implies that this peak corresponds to an excited state and not the ground state. A similar peak is also observed when measuring the nanopillar arrays processed with $R_p = 150$ nm. For a comparison, see figure 3.57. Since the position of the peak is lower than -3.76 V it is unlikely that the peak at $V_p = -2.72$ V corresponds to alignment with $E_2$ (figure 3.49), seen in the large-area RTDs. The absence of a clear ground state in this device, as well as ambiguity in assignment of the observed peak makes it difficult to directly estimate the minimum number of pillars in contact.
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Figure 3.55: 2T measurements of 500 x 500 nanopillar array processed from W0021, with radial dimension $R_p = 100$ nm measured at 4K and 300 K. The voltage was swept from -5 V to 0 V in steps of 5 mV. The inset shows the scanning electron micrograph of the nanopillar array, before final insulation and top-contact processing.

Figure 3.56: 2T measurements of 500 x 500 nanopillar array processed from W0021 at 4K, during forward and reverse voltage sweeps. The pillar size was defined as $R_p = 100$ nm. The voltage was swept in steps of 5 mV.
However, we can put a lower limit to the number of pillars in contact by correlating the peak current tunneling through the 100 nm array at $V_p = -2.72$ V to the peak current tunneling through the 150 nm array at $V_p = -2.38$ V.

![Figure 3.57: A comparison of electrical characteristics between a 500 x 500 array ($R_p = 100$nm) and a 500 x 500 array ($R_p = 100$nm), measured in a 2T configuration at 4K. The voltage was swept from -5 V to 0 V in steps of 5 mV. For clarity, the main NDR peak shown by the 100 nm array is indicated with a red arrow and some of the peaks corresponding to the 100 nm array are highlighted with a green arrow.](image)

We know from our analysis of the 150 nm array, that at least 890 nanopillars take part in the transport (see section 3.9.2.1). This array supports a peak current that is equal to -1562 µA at $V_p = -2.38$ V. Substituting these values of $N_t$ and $I_p$ in eqn. 3.4, we obtain a peak current density that is equal to -241 A/cm$^2$. Since this peak current density can be equated to the peak current density associated with the NDR at $V_p = -2.72$ V, we can estimate the number of 100 nm pillars that take part in transport. Substituting $J_p = -241$ A/cm$^2$ and $I_p = -2720$ µA in eqn. 3.4, we obtain $N_t = 2388$.

**Analysis of fine features**

According to Reed’s simplistic model, we should observe equally separated fine features superimposed upon each NDR peak corresponding to the bulk RTD states. For a 100 nm pillar, the features would be separated by $2\Delta E = 25.2$ meV. From figure 3.57, we do observe a fine structure in the electrical characteristics. One might dismiss the few peaks
shown in green occurring as a consequence of parasitic pathways through the insulation, which can open upon application of a very high bias. However, since we reproducibly observe the main NDR peak (shown in red) upon multiple measurements, there is merit in studying the energy distribution of these additional peaks. Since every NDR peak is accompanied by an increase in the conductance, it is easier to identify the peaks by plotting the derivative of current with respect to voltage. Figure 3.58 shows the differential conductance of the 100 nm and 150 nm arrays, plotted as a function of bias. The position of the suspected NDR peaks corresponding to the 100 nm array, is highlighted in blue.

![Figure 3.58: A comparison of differential conductance at 4K, between a 100 nm pillar size 500 x 500 array, with a 150 nm pillar size 500 x 500 array processed from W0021. The voltage was swept in steps of 5 mV. For clarity, the main NDR peak shown by the 100 nm array is indicated with an red arrow and the other peaks corresponding to the 100 nm array are highlighted with a green arrow.](image)

If the peaks were distributed randomly, i.e. if the energy separation between consecutive peaks was not a constant, then these peaks would occur as a result of unwanted parasitic effects. However, if Reed’s model was to hold true, the energy distribution of the peaks would be biased around $2\Delta E$. If we denote the difference between two consecutive peaks shown in figure 3.58 as $\Delta E'$, we can plot a histogram that counts the number of peaks with respect to $\Delta E'$. The bin size is limited by the voltage step of the measurement, which is 5 meV in this case. In an ideal scenario, we should have observed multiple instances (counts $> 1$) where the peaks are separated by $\Delta E' = 2\Delta E = 25.2$ meV and one instance (count $= 1$) where the peaks are separated by $\Delta E' = 2E_1 - 2(E_0 + (m+1/2)\Delta E)$. Here $E_0$...
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Figure 3.59: Histogram showing the energy distribution of peaks at 4K corresponding to a 500 x 500, 100 nm nanopillar array processed from W0021. The inset shows the ideal energy distribution of peaks at 4K, evaluated from Reed’s simplistic model.

+ (m+1/2)\Delta E is the highest energy level that is a result of splitting E0. This distribution holds true if all the nanopillars in the array have the same dimensions. The ideal distribution according to Reed’s model is shown as an inset to figure 3.59. Our observations agree partially with Reed’s model, i.e. we do observe that some of the peaks are equally separated, see figure 3.59. In the histogram shown, we note that there are four instances where the peaks are separated by \( \Delta E' = 40-45 \) meV. We also note that there are three instances where the peaks are separated by \( \Delta E' = 30-35 \) meV. Perhaps, the bias around two energy splittings (\( \Delta E' = 30-35 \) meV and \( \Delta E' = 40-45 \) meV) indicates bimodal distribution of nanopillar sizes within the array. We do note that the experimentally observed energy separation (\( \Delta E' \)) is slightly higher than the energy splitting estimated from Reed’s model (\( 2\Delta E \)). The single instance at \( \Delta E' = 200-205 \) meV may correspond to the difference between \( E_i \) and \( E_{i-1} + (m+1/2)\Delta E. \) The other peaks, which show a count of 1 or 2, suggest that the energy distribution is not entirely governed by the Reed’s simplistic model. For an accurate explanation of energy distribution of peaks other effects such as estimation of depletion, lateral mode mixing due to non-uniform potential, mixed valley through AlAs barriers and multimodal distribution of dimensions should be taken into account.

Below, we describe the electrical characteristics of another array of nanopillars, where the radial dimension of the pillar is reduced from 100 nm to 50 nm.
3.9.2.3 500 x 500 array, $R_p = 50$ nm

Results

Figure 3.60 shows the electrical characteristics of a 500 x 500 nanopillar array with pillar size defined as $R_p = 50$ nm. In agreement with earlier samples, we note distinct NDR peaks at 4 K and at 300 K, indicating successful top-contact to the nanopillar array. We observe several NDR peaks at 4K. Under negative bias, these peaks are observed at $V_p = -1.23 \, \text{V}, -1.57 \, \text{V}, -1.83 \, \text{V}, -2.85 \, \text{V}, -3.02 \, \text{V}, -5.91 \, \text{V}, -6.32 \, \text{V}$ and $-7.1 \, \text{V}$. Under positive bias, these peaks are observed at $V_p = 0.71 \, \text{V}, 1.17 \, \text{V}, 5.52 \, \text{V}$ and $7.59 \, \text{V}$. We also observe that the negative differential resistance peaks appear during both forward and reverse voltage sweeps, which confirms transport through the nanopillars, see figure 3.61. The appearance of multiple peaks makes it extremely challenging to map the NDR peaks to the bound states.

![Figure 3.60: 2T measurements of 500 x 500 nanopillar array processed from W0021, with radial dimension $R_p = 50$ nm measured at 4K and 300 K. The inset shows the scanning electron micrograph of the nanopillar array, before final insulation and top-contact processing. (b) 2T measurements of the 500 x 500 nanopillar array at 4K shown separately at 4K. The voltage was swept from -8 V to +8 V in steps of 10 mV.](image)

Mapping of NDR peaks
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Figure 3.61: 2T measurements of 500 x 500 nanopillar array, pillar size 50 nm processed from W0021 at 4K, during forward and reverse voltage sweeps. The voltage was swept in steps of 10 mV.

Under negative bias, the first peak is observed at $V_p = -1.23 \text{ V}$. After accounting for the voltage drop across the Schottky contact, this peak corresponds to the $E_0$ state observed in the large-area device. Similar to the large-area device, an additional peak is observed at $V_p = -1.57 \text{ V}$, which perhaps corresponds to the $E_0'$ state. It is difficult to identify the origin of the peak at $V_p = -1.83 \text{ V}$. The 2T measurements of the 50 nm array also indicate a peak at around $V_p = -2.85 \text{ V}$ and at $V_p = -3.02 \text{ V}$. Perhaps these peaks corresponding to the 50 nm array occur due to the same bound state responsible for the NDR peak at $V_p = -2.72 \text{ V}$ in 100 nm arrays and the NDR peaks around $V_p = -2.38 \text{ V}$ in 150 nm arrays. It is encouraging to note fine features superimposed upon main NDR peaks. However, this feature appears at a very high voltage. Perhaps, these NDR peaks at $V_p = -5.91 \text{ V}$, $V_p = -6.32 \text{ V}$, and $V_p = -7.1 \text{ V}$ corresponds to the $E_2$ state seen in large-area devices. Similar NDR peaks at higher voltages under positive bias at $V_p = +5.52 \text{ V}$ and $V_p = +7.59 \text{ V}$ suggest that these peaks can also be associated with the $E_2$ state seen in large-area devices. The low-voltage peaks at $V_p = +0.71 \text{ V}$ and at $V_p = +1.17 \text{ V}$ may not correspond to a bound state within the quantum well, but occur as a result of quantization within the contacts.

**Estimation of number of pillars**

When the device is in resonance with the state $E_0$ at $V_p = -1.24 \text{ V}$, the nanopillar array
supports a peak current of \(-13 \mu A\). The density of current flowing through the device upon alignment must be equal to the density of current flowing through a large-area RTD, i.e. \(J_p = -245 \text{ A/cm}^2\). Assuming that only one nanopillar with \(R_p = 50 \text{ nm}\) was contacted successfully, the peak current flowing through the device, ignoring depletion would be \(-19 \text{ nA}\). This current is much less than the peak current that we observe, i.e. \(I_p = -13 \mu A\). Clearly, multiple nanopillars are in contact and participate in resonant tunneling of electrons in parallel. The ratio of the two currents, i.e. the experimentally observed \(I_p\) and the expected current through a single nanopillar \((13/0.019)\), provides an estimate of the minimum number of pillars in contact, see eqn. 3.4. Here, we believe that at least 623 nanopillars are in contact and take part in transport. Note that the number of pillars calculated using this approach is an under estimate and would increase if we account for surface depletion in the nanopillars.

**Analysis of fine features**

Figure 3.62 shows the differential conductance of the 50 nm array plotted as a function of applied bias. The position of the main NDR peaks is highlighted with red arrows and the fine features are highlighted with green arrows. Assuming that Reed’s model is applicable, the energy distribution of the peaks shown in figure 3.62 would be biased around \(2\Delta E = 50.2 \text{ meV}\) for \(R_p = 50 \text{ nm}\). This distribution can be obtained from a histogram, which counts the number of peaks with respect to \(\Delta E’\), where \(\Delta E’\) is the difference between two consecutive peaks. The bin size is limited by the voltage step, which was equal to 10 mV in this case. In an ideal scenario, we should have observed multiple instances (counts \(> 1\)), where the peaks are separated by \(\Delta E’ = 2\Delta E = 50.2 \text{ eV}\). Also, we should have observed one instance (count = 1), where the peaks are separated by \(\Delta E’ = 2E_1 - 2(E_0 + (m+1/2)\Delta E)\). Here \(E_0 + (m+1/2)\Delta E\) is the highest energy level that is a result of splitting \(E_0\). The ideal distribution for an array of pillar size 50 nm is shown as an inset to figure 3.63(a), assuming that all the nanopillars in the array have the same radial dimensions.

The energy distribution of peaks shown in figure 3.63 agrees in part with the Reed’s model. While we do observe that some of the peaks are equally separated and the energy distribution is biased, it is spread across \(\Delta E’\). We see that there are four instances where the peaks are separated by \(\Delta E’ = 45-55 \text{ meV}\). We also note that there are four instances where the peaks are separated by \(\Delta E’ = 25-35 \text{ meV}\) and three instances where the peaks are separated by \(\Delta E’ = 15-25 \text{ meV}\). The single instance at \(\Delta E’ = 1.25 \text{ V}\) corresponds to the difference between the bulk states \(2E_1\) and \(2E_0\), figure 3.63(b). Perhaps a bias around multiple energy bands implies a multimodal distribution of nanopillar sizes within the
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Figure 3.62: Differential conductance of a 50 nm pillar size 500 x 500 array processed from W0021, and measured at 4K. The voltage was swept in steps of 10 mV.

Array. Appearance of peak’s in the histogram which show a count of unity or 2 suggest that factors such as mixed valley transport in AlAs barriers and lateral mode mixing due to non-uniform potential need to be taken account while calculating the estimated energy distribution.

To conclude, we have demonstrated successful electrical contact to a 500 x 500 array of nanopillars processed from double barrier RTDs. Clear NDR signatures for a range of radial dimensions (50 nm - 150 nm) and wafer structures (A1700/W0021) implies that the process is robust. From our measurements, it is apparent that multiple nanopillars take part in electron transport allowing us to reach currents that are at least four orders of magnitude higher than what has been achieved so far in laterally confined RTDs [89, 94, 102, 108]. For example, when the applied bias is in resonance with the ground state, the nanopillar array processed from W0021 can carry a current of 13 µA (R_p = 50 nm) to 154 µA (R_p = 150 nm). At higher bias, i.e. when the device is in resonance with the excited states, the array can support a current of up to 2000-4000 µA. We acknowledge that not all NDR peaks can be easily mapped onto corresponding energy states, owing to the inherent complexity introduced by factors such as multiple transport pathways within a single nanopillar, non-uniform lateral potential and parallel conduction of pillars. However, for a test structure, appearance of NDR peaks is sufficient proof to scale the process to nanopillar arrays in THz QCLs.
Figure 3.63: (a) Histogram showing the energy distribution of peaks at 4K corresponding to a 500 x 500, 50 nm nanopillar array processed from W0021. For clarity, the energy scale is limited to 0-250 meV. The inset shows the ideal energy distribution of peaks at 4K, evaluated from Reed’s simplistic model (b) Complete histogram showing the energy distribution of peaks at 4K corresponding to a 500 x 500, 50 nm nanopillar array processed from W0021.
3.10 Fabrication of nanopillar arrays in metal-metal THz QCLs

In section 3.5 we discussed processing techniques that were common to nanopillars in GaAs/Al$_x$Ga$_{1-x}$As active regions. We then validated the processes on test RTD structures. The next step - i.e. scaling the process to nanopillar arrays in THz QCLs, requires us to address some additional challenges that are unique to QCL active regions. In section 3.5, we noted that the highest etch depth for GaAs/Al$_x$Ga$_{1-x}$As structures was limited to 2.3 to 3.56 $\mu$m. At this height, the gain is low and the only waveguide configuration that allows an ultrathin THz QCL to lase is the metal-metal waveguide configuration, 4.2. This implies that nanopillars etched in an ultrathin THz QCL have a metal contact at the bottom.

Typically, in a THz QCL, a metal contact at the bottom comprises of a titanium wetting layer and a thermocompressed gold layer 4.3. Note that post etching, the nanopillars adhere to the gold contact and the host substrate through the titanium layer. This effects any subsequent stage of processing, which involves buffered hydrofluoric acid. As mentioned in section 3.5, buffered hydrofluoric acid is necessary to remove etch residue as well as the insulation for a suspended contact. However, buffered hydrofluoric acid etches titanium at a rate faster than the etch residue or the insulation. This problem was identified at a much later stage of this doctoral work, and could not be rectified within the time limit. Therefore, for successful scaling of our process to metal-metal THz QCLs, it is essential to investigate the possibility of using NiCr as the wetting layer for gold, while evaporating the bottom-contact. In the next section we summarize the key points discussed in this chapter.

3.11 Summary and conclusions

In this chapter, we first discussed techniques that allow a top-down fabrication of nanopillar arrays. We then demonstrated fabrication of pillars in GaAs/Al$_x$Ga$_{1-x}$As systems with sub-200 nm radius and a high aspect ratio (1:15) nanopillars. This involved a careful optimization of etch mask, etching system and choice of insulation. Each processing stage was designed in view of structural and electrical stability of the array, with due consideration to compatibility with the final laterally confined THz QCL device for improved temperature performance. Using test RTD structures, which show similar current densities as THz QCLs, we then validated the electrical robustness of the nanopillar arrays. Finally, using test RTDs, we demonstrated parallel conduction through an array of 500 x 500 sub-200 nm nanopillars.
3. NANOPILLAR ARRAYS IN RTDS AND QCLS: EXPERIMENTAL REALIZATION
Chapter 4

Ultrathin QCLs

4.1 Introduction

In the previous chapter we noted that in order to implement the top-down nanofabrication approach to THz QCLs, the thickness of the active region needs to be scaled down to 3.5 \( \mu m \) or less. We refer this scaled down THz QCL, as an ‘ultrathin’ THz QCL. A THz QCL typically contains a cascade of more than 100 repeat periods. Each period consists of an injection stage, upper lasing level, lower lasing level and an extraction stage. Depending upon the design, the thickness of a THz QCL can range from 6 - 14 \( \mu m \). This implies that in general, ultrathin QCLs are low-gain active regions. This is because the peak modal gain, \( G_M \) is proportional to the number of periods, \( N_p \) and inversely proportional to length of the period, \( L_p \).

Detailed derivation of the gain can be found in [10, 38]. A simplistic description is provided below.

4.1.1 Effect of active region thickness on gain

In a single period of the active region, the intersubband radiative transition between the upper lasing level ‘u’ and the lower lasing level ‘l’ can be quantified in terms of a parameter called the material gain, \( G_p \). This material gain, \( G_p \) is calculated by solving the rate-equations describing the radiative transition in terms of (a) the injection efficiency, \( \eta_i \), of the charge carriers into the upper lasing level (b) the charge carrier lifetime in the lower lasing level, \( \tau_l \), and, (c) the charge carrier lifetime in the upper lasing level, \( \tau_u \). The charge carrier lifetime in the upper lasing level can be expressed as \( \tau_u^{-1} = \tau_{ul}^{-1} + \tau_{ug}^{-1} + \tau_{esc}^{-1} \). Here, scattering of charge carriers from \( u \) to \( l \) is defined by a time constant of \( \tau_{ul} \). This is the direct path to non-radiative relaxation of electrons in the upper lasing level. The electrons...
4. ULTRATHIN QCLS

in the upper lasing level can also parasitically scatter into the ground state with a time constant indicated by $\tau_{ug}$. Another contributor to the parasitic leakage is the tunneling of electrons through the barriers from the upper lasing level into the extractor state. This process is associated with a time constant defined by $\tau_{escp}$. All of these processes are illustrated in figure 4.1.

Figure 4.1: Schematic diagram showing radiative (curly arrow) and non-radiative (straight arrows) processes across the lasing levels in a THz QCL.

The material gain, $G_p$, is a function of the dipole matrix element $\langle z_{ul} \rangle$ which describes the probability of the electron extending in the growth direction. The material gain, $G_p$, is adversely affected by the length of the period, $L_p$ and the broadness of the energy transition, $2\gamma$, which can lead to electron scattering when large.

Mathematically, the material gain is expressed as:

$$G_p = \frac{4\pi Je^2 \langle z_{ul} \rangle^2}{\varepsilon_0 \varepsilon_r 2\gamma \lambda L_p} \eta_g \tau_u \left(1 - \frac{\tau_l}{\tau_{ul}}\right). \quad (4.1)$$

where, $J$ is the current density describing the number of electrons injected into the upper lasing level and $\lambda$ is the wavelength associated with the energy transition. Dividing the material gain $G_p$ with the current density $J$, one obtains the so-called gain-coefficient $g = G_p/J$ associated with the intersubband transition.

The peak modal gain, $G_M$ is proportional to the material gain $G_p$, which measures the strength of the intersubband transition, and the spatial overlap of the optical mode with the gain medium. Therefore, the peak modal gain $G_M$ can be written in terms of the
waveguide confinement factor $\Gamma$ as:

$$G_M = \Gamma G_p = \Gamma_p N_p G_p = \Gamma_p N_p g J \quad (4.2)$$

Here, $\Gamma = \Gamma_p N_p$ where $\Gamma_p$ is the overlap factor per period.

As is seen from eqn. 4.2, there is no threshold to achieve population inversion. The gain is present from the first electron injected into the device as long as the condition $\tau_u \geq \tau_l$ is satisfied and population inversion is achieved.

The threshold current density, $J_{th}$, is related only to the optical cavity losses, which occurs due to waveguide losses ($\alpha_w$) and mirror losses ($\alpha_m$). While the waveguide loss $\alpha_w$ depends upon the scattering and absorption inside the resonator, the mirror loss $\alpha_m = -\ln(R_1 R_2)/2L$ depends upon the reflectivity of the facet ($R_1, R_2$) and the cavity length $L$. The threshold condition can be obtained by balancing the gain $G_M$ with the total losses ($\alpha_w + \alpha_m$). Therefore, we obtain the condition for threshold current density, $J_{th}$, as:

$$J_{th} = \frac{\alpha_w + \alpha_m}{g \Gamma_p N_p} \quad (4.3)$$

It is easily seen that as $N_p$ reduces, $J_{th}$ increases.

### 4.1.2 Ultrathin QCLs: finding the right active region

Practical implementation of top-down nanopillars in QCLs necessitates the use of very thin active regions to ensure a pillar thickness of less than 3.5 $\mu$m, which can be etched in a reactive ion etching system (see Chapter 3 for processing details). The key to achieving lasing in a thin QCL is to maximize the total gain, $G_M$ in the active region and minimise the total waveguide loss ($\alpha_w + \alpha_m$). Let us first focus on the gain medium. To maximize $G_M$, it is necessary to choose an active region with a higher number of repeat periods per unit height, i.e. a small $L_p$. As described in the introductory chapter, active regions based on resonant LO phonon designs typically require 3-4 quantum wells per period as opposed to bound-to-continuum (BtC) designs, which require 9-10 quantum wells for efficient injection and extraction within each period. Therefore, resonant LO phonon active regions do appear likely candidates for implementing the top-down approach to lateral confinement.

Another point to note is that BtC designs are not ideal to observe lateral confinement effects. This is because we expect the radial potential to split the energy levels by $\sim 5$-$10$ meV. In absorption or an electroluminescence spectra, energy states associated with the lateral potential would be superimposed upon the energy states associated with the longitudinal confinement. These small differences may not be easy to recognize particularly
4. ULTRATHIN QCLS

in a superlattice structure that relies on minibands where the energy levels are separated by \( \leq 5 \text{ meV} \).

Interestingly, there exists a third alternative that lies in between the two mechanisms that we have discussed (LO phonon and BtC) - a hybrid that uses both resonant LO phonon and a miniband of energy states for electron extraction. This 4 quantum well design, is robust in terms of growth fluctuations, and relies on a BtC transition in which a miniband is coupled to the extraction stage by resonant LO mechanism [6]. We refer this design as 3 THz 4 QW ETH design throughout this work.

4.2 Ultrathin QCLs in literature

Prior work on achieving THz lasing from ultra-thin (\( \leq 3.5 \mu\text{m} \)) active regions has been primarily based on resonant LO phonon designs, processed in a metal-metal waveguide configuration. The two reports that demonstrate lasing from ultrathin THz QCLs use (i) a 3 quantum-well (QW) design [3], and (ii) a 4 quantum-well (QW) design [4].

Figure 4.2 shows the IV and spectral characteristics of the 3 QW design, as a function of active region thickness. Note that the laser shows observable emission between 3 to 3.5 THz as the active region thickness is reduced from 10 \( \mu\text{m} \) to 1.75 \( \mu\text{m} \). It is important to point out that three of the five lasers compared in figure 4.2 were processed from three distinct wafers with active region thickness 10 \( \mu\text{m} \), 5 \( \mu\text{m} \) and 2.5 \( \mu\text{m} \). All these lasers retained the top n\(^+\) doped layer. Lasers with active region thickness 2 \( \mu\text{m} \) and 1.75 \( \mu\text{m} \) were derived from the 2.5 \( \mu\text{m} \) active region, by chemically thinning the wafer.

![Figure 4.2](image-url)

Figure 4.2: (a) IV characteristics of 3 quantum-well LO phonon design at 10 K, as a function of active region thickness. The inset plots the electric field as a function of current density. (b) Spectral characteristics of the 3 quantum-well LO phonon design showing blue shift with decreasing active region thickness. Adapted from [3].

The effect of reducing the active region thickness is seen noticeably in the threshold
current density, which reduces from 925 A/cm² to 680 A/cm² at 10K, as the active region thickness is reduced from 10 µm to 1.75 µm, see figure 4.3. This behavior follows from eqn. 4.3, which predicts that the threshold current density is inversely proportional to the number of periods. Another important change brought about by reduction in the active region thickness is on the maximum operating temperature of the laser. The maximum operating temperature reduces from 146 K in the case of 10 µm thick laser to 79 K in the case of 1.75 µm laser.

Figure 4.3: Threshold current density as a function of temperature for 3 quantum-well LO phonon design, reported for active region thickness varying from 10 µm to 1.75 µm. The table on the right shows threshold current density for lasers with different active region, at a temperature of 10 K. Adapted from [3].

Figure 4.4 shows the LIV characteristics of the 4 QW design at 10 K for three different active regions. Also shown in the inset is the spectral behavior of the 4 QW design and the threshold current density as a function of operating temperature. All three lasers were derived from the same wafer, i.e. lasers with thickness 5.1 µm and 2.8 µm were obtained by chemically thinning the 10 µm wafer. Therefore, while the 10 µm thick laser retained the top n⁺ doped layer, the other two lasers were processed without it. Similar to the behavior of the 3 QW design discussed earlier, the threshold current density of the 4 QW lasers increases with decrease in active region thickness. The threshold current density increases from 440 A/cm² to 575 A/cm², as the thickness of the active region is reduced from 10 µm to 2.8 µm. The maximum operating temperature of the lasers decreases from 166 K in the case of 10 µm active region to 117 K in the case of 2.8 µm active region.

From the epitaxial structure detailed in references [3, 4, 33, 145] we note that the 2.8 µm-thin 4 QW design shown in figure 4.4 has lower repeat periods, $N_p = 50$, as compared to $N_p = 56$ in the 2.5 µm-thin 3 QW design shown in figures 4.2 and figure 4.3. Despite the lower number of repeat periods, the maximum operating temperature of the former
4. ULTRATHIN QCLS

Figure 4.4: LIV characteristics as a function of temperature shown for 4 quantum-well LO phonon design with an active region thickness of (a) 2.8 µm (b) 5.1 µm (c) 10.0 µm. Inset in (a) shows spectral characteristics of the ultrathin device, with emission at 2.9 THz. Inset in (c) shows the threshold current density $J_{th}$ varying as a function of temperature. The table on the right shows threshold current density for lasers with different active region, at a temperature of 10 K. Adapted from [4].

(166 K) is nearly two times higher than the latter (95 K). One of the reasons for superior performance is perhaps due to the improved heat sinking of the 2.8 µm thin 4 QW device, implemented by employing a Cu-Cu waveguide [4, 33]. Therefore, both the gain medium and the choice of the waveguide play a crucial role in the operating performance of an ultrathin THz QCL.

4.3 Fabrication of ultrathin QCLs

THz QCLs can be fabricated in single plasmon (SP) waveguide configuration or in double metal (DM) waveguide configuration. As discussed in the introduction, a single plasmon waveguide requires a thick (700 nm) n+ doped GaAs layer, which when suitably processed acts as an ohmic bottom contact, and confines the plasmon mode to the active region. In a double metal waveguide, this layer is not necessary as the plasmon mode is predominantly confined between the top and bottom metal contacts. Therefore, to maximize the number of repeat periods per unit height, the double metal (DM) waveguide configuration
4.3 Fabrication of ultrathin QCLs

is preferable for ultrathin THz QCLs. Further more, a major motivation behind this work is higher temperature performance, and since DM waveguide devices have superior heat-sinking properties as compared to SP waveguides, we focus on the former in this chapter. The latter is discussed separately in [5].

4.3.1 Wafer bonding and host-substrate removal

The fabrication of double metal QCLs involves thermocompression bonding of active region grown via molecular beam epitaxy (MBE) onto a host n+ GaAs substrate. Prior to bonding, both the MBE wafer and the host wafer are evaporated with a ~ 500 nm thick layer of Ti/Au (figure 4.5(a-b)). Ti acts as a wetting layer which improves the adhesion of Au to the GaAs surface. The thickness of the Au layer, as well as the surface quality before and after evaporation determines the quality of the wafer bond. To achieve a good surface quality before evaporation, it is common to clean the wafers in deionized water, acetone and IPA before evaporation. A 30 sec dip in 1:10 solution of HCl:H2O removes the oxide layer on the GaAs surface. We find that removal of the oxide layer in HCl introduces stains on the wafer surface, detrimental to the surface quality. These arise due to drying of water droplets on the hydrophilic GaAs surface. It is therefore essential to rinse in DI water for 2-3 minutes until the resistance of the water reads ≥ 10 Ohm. Care must also be taken to blow dry water droplets from the tweezers, which are used to handle the MBE and host substrate. Any residues that remain may be cleaned gently with a lens wipe. During the evaporation, it is important to melt the Au before evaporation to avoid spitting of Au. The best surface finish is obtained at an evaporation rate of ≤ 0.3 nm/sec, and when the wafer is placed away from the normal axis of the Au boat. It is also possible to evaporate Pd/Ge (25/75 nm) before the Ti/Au evaporation which forms a shallow ohmic contact to the bottom n+ GaAs. However, Pd/Ge metallizations are susceptible to degradation owing to oxidation of Ge and decomposition of PdGe, which is why this step is avoided in our processing.

The thermocompression bonding (figure 4.5(c)) is performed at Applied Microengineering Limited (AML) where the bonding is carried out under a uniform pressure of 2 MPa across the wafer at a temperature ~ 300°C [146]. The MBE substrate is thinned to 200µm by mechanical polishing (figure 4.5(d)). Further substrate thinning is achieved chemically by using a 5:1 solution of anhydrous citric acid (1g:1ml of H2O) and H2O2 [147]. This solution etches GaAs at a rate of 0.33 µm/min until it reaches the Al0.5Ga0.5As etch stop layer.

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4. ULTRATHIN QCLS

4.3.2 Mesa etch and metallization

Further processing of laser ridges can be performed either using dry etching, which is anisotropic and enables smooth vertical walls or using wet etching, which is isotropic and leads to sloping sidewall etch profiles.

4.3.2.1 Dry etching

When the ridges are processed using reactive ion etching, the etch stop layer is removed with hydrofluoric acid to ensure a smooth surface (figure 4.6(b)). Following the etch stop removal, the etch mask is lithographically defined which also forms the self-aligned top contact (figure 4.6(c)). In the case of dry etching laser ridges, it is important to deposit a thick layer of Ti/Au, preferably 300-400 nm to account for mask erosion during plasma etching. It is good to note that because the thickness of ultra-thin QCLs is small, it is relatively easy to obtain vertical sidewalls with minimum mask erosion in a reactive ion chamber. Powerful BtC designs that employ active regions of thickness $\geq 10 \mu m$ might require a dielectric mask for vertical etching, in which case the etch mask does not form a self-aligned top contact. See section 3.5.3 for details about reactive ion etching.

Figure 4.5: Process steps in the wafer-bonding of a double metal QCL (a-c) Au-Au thermo-compression bonding of MBE grown active region onto $n^+$ GaAs substrate (d) Mechanical thinning and polishing of MBE substrate (e) Removal of substrate in a selective etchant.
4.3 Fabrication of ultrathin QCLs

4.3.2.2 Wet etching

An alternative approach would be to process laser ridges with widths $\sim 100\mu$m using chemical etching (see, figure 4.7). A primer (hexamethyldisilazane) is utilized to increase the adhesion of the photoresist etch mask to the active region. Retaining the etch stop layer during wet chemical etching prevents the etchant from opening up growth defects in the active region. Following the mesa etch in a 1:8:80 solution of $\text{H}_2\text{SO}_4$:$\text{H}_2\text{O}_2$:H$_2$O, the photoresist and etch stop layers are removed in acetone and hydrofluoric acid, respectively (figure 4.7(d)). A Ti/Au layer (20/100 nm) forms a Schottky contact to the mesa and facilitates wire bonding to the top of the laser ridge (figure 4.7(e)).

The host substrate may be mechanically thinned down from 500 $\mu$m to 200 $\mu$m to allow better optical confinement and improved heat sinking. In the single plasmon waveguide geometry, the optical mode is confined within a top metal contact and a doped n$^+$ GaAs layer and hence thinning of the host substrate reduces optical losses. Another layer of Ti/Au is deposited on the backside of the substrate, which acts as a diffusion barrier for
indium that is used while mounting the chips. The laser ridges are formed into Fabry-Pèrot cavities of length \( \sim 1-2 \text{ mm} \) by cleaving along a crystal axis to produce parallel laser facets. The cavity length determines the mirror losses as well as the current required to achieve lasing. Since our measurement set-up has a maximum current range of 4 A, this allows for a maximum current density of 2000 A/cm\(^2\) to flow through a 2 mm long, 100 \( \mu \text{m} \) wide cavity, which is sufficient for the typical threshold current density observed for ultrathin THz QCLs. Following indium soldering to copper blocks which ensures good thermal contact, the devices are bonded with gold wires to gold contact pads evaporated on the Cu blocks. The devices are then mounted on Cu blocks for electrical characterization in the cryostat.
4.4 Characterization of ultrathin QCLs: methods

4.4.1 Mounting

THz QCL devices are mounted onto the cold finger of a continuous flow liquid helium cryostat (Janis Research Company, model ST-300). Brass contacts attached to the cryostat’s cold finger with nylon screws, clamp the copper block to the cold finger and electrically connect the device. The contacts are electrically connected to a series of BNC connectors on the outside of the cryostat via micro-coaxial cables. Optical access to the sample space is achieved using a polyethylene window, which is transparent to THz radiation.

4.4.2 Electro-optic measurements

The QCL can be operated in either pulsed mode or in continuous wave (cw) mode. To avoid Joule heating in the ultra-thin QCLs (as well as nanopillars), the QCLs reported in this work were operated in the pulsed mode. CW measurements may be carried out with an HP 1200 DC power supply.

Figure 4.8 shows the experimental set-up employed to measure the electro-optic char-
4. ULTRATHIN QCLS

acteristics of THz QCLs. The QCL is powered with 10 kHz pulses at 5-10 % duty cycle, supplied by an Agilent 8114A pulse generator. The 10 kHz pulses are gated externally by a low frequency 5V square pulse that is supplied by a separate pulse generator. The same low frequency pulse is used as an external trigger on the Tektronics TCS 2014 digital oscilloscope to measure the voltage and current across the device. The frequency of this external gate or trigger is determined by the response time of the photodetector. If a golay is used as a THz detector, then the reference frequency is 15 Hz. For spectral and low power measurements a bolometer is used to measure the THz output, and the reference frequency is 300 Hz \(^1\). The output of the detector is sent as input to EG&G 5210 lock-in amplifier, which measures the THz signal at the reference frequency. The instruments are interfaced to the computer through labview.

4.4.3 Spectral measurements

4.4.3.1 Above lasing threshold

![Experimental set-up](image)

Figure 4.9: Experimental set-up used to collect spectra above lasing threshold. Diagram from [5].

For results presented in this chapter, we measured the emission spectra above lasing threshold at Manchester using a Bruker VERTEX 80 Fourier Transform Infra-Red (FTIR) Spectrometer set up in the rapid scan mode. A liquid-He cooled Si-bolometer was used as

\(^1\)Optimum operating frequency may vary from 80 Hz - 333 Hz between bolometers.
the THz detector. This is shown in figure 4.9. The maximum spectral resolution attainable using this FTIR Spectrometer is 2.1 GHz (0.07 cm\(^{-1}\)). The FTIR is essentially a Michelson Interferometer, where the radiation from the source (THz QCL) is directed to a beam splitter. Half of the radiation is reflected from a fixed mirror while the other half is reflected from a mirror moving continuously over a specific distance. When the two beams are recombined at the detector (Si-bolometer), an interferogram is produced. The beam path between cryostat and detector is purged with N\(_2\) gas in an attempt to minimize losses due to water vapor absorption. In the rapid scan mode mode, the mirror moves continuously over a fixed distance. One complete movement comprises a single scan. While the mirrors are moving, the output detected from the bolometer is sent to the input of the FTIR, which performs the Fourier transform of the signal. This signal is fed into the computer. To avoid beating, the QCL is operated without the slow modulation and is pulsed with fast modulation alone (10 kHz, continuously triggered, duty cycle of 1-2 %).

4.4.3.2 Below lasing threshold

Figure 4.10: Experimental set-up used to collect spectra below lasing threshold. Diagram from [5].

In the case of below threshold operation, we operated the Bruker VERTEX 80 FTIR at Manchester in the step-scan mode to allow collection of the weak signal. In the step-scan mode, the QCL is pulsed with both fast and slow modulation on. The mirror moves in steps. The signal collected from the bolometer at each step of the mirror is fed into the
lock-in. The reference signal provided is the same as the slow modulation (300 Hz). The
DC signal from the lock-in is fed into the FTIR, which is collected and processed by the
computer. The experimental set-up is shown in figure 4.10.

4.5 Ultrathin active regions used

The various active regions investigated for suitability as ultrathin THz QCLs during this
doctoral work are summarized in table 4.1. Corresponding to each design (highlighted
in green) and wafer number grown at Cavendish (highlighted in magenta), we list the
reference design published in literature (highlighted in blue). Among all the reference
designs listed in table 4.1, L422 (full-stack reference L421, L420) is the only ultrathin
wafer which emits at lower repeat periods. While all other wafers, i.e. L207, FL178C-M7
and EV1116, are likely candidates for ultrathin devices, a direct comparison between the
performance of these reference designs and the in-house grown QCLs can only be made
for full-stack wafers. While the first three active regions, i.e. 2.7 THz 3 QW Paris, 3 THz
3 QW Paris and 3 THz 4 QW MIT are resonant phonon designs, the final active region
listed in table 4.1 as 3 THz 4 QW ETH design can be categorized as a BtC design. The 3
QW Paris designs emitting at 2.7 THz and 3 THz are similar as they both exploit a vertical
lasing transition and have nominally same anticrossing energies with injection/extraction
levels. With the exception of W0798 (2.7 THz 3 QW Paris design), which was grown in the
W chamber, all wafers in the V series were grown in the Veeco chamber at the Cavendish
Labs. All QCLs labelled in the table as ‘ultrathin’ were grown thin epitaxially. V674-[T],
which is mentioned later in this chapter is also an ultrathin QCL. However, unlike its other
counterparts, V674-[T] was chemically etched down to a thickness of 3 µm.

<table>
<thead>
<tr>
<th>Design</th>
<th>Wafer number</th>
<th>Reference in literature</th>
<th>Previous growths</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7 THz 3 QW Paris</td>
<td>V671 Ultrathin</td>
<td>L207 in [148]</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>W0798 Ultrathin</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>V692 Ultrathin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 THz 3 QW Paris</td>
<td>V702 Ultrathin</td>
<td>L421 L420, L422 in [3], Also in [145, 149]</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>V703 Full-stack</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 THz 4 QW MIT</td>
<td>V704 Ultrathin</td>
<td>FL178C-M7 in [150]</td>
<td>V569 Full-stack</td>
</tr>
<tr>
<td></td>
<td>V705 Full-stack</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 THz 4 QW ETH</td>
<td>V674 Full-stack</td>
<td>EV1116 in [6]</td>
<td>V696 Full-stack</td>
</tr>
</tbody>
</table>

Table 4.1: Summary of active regions and wafers used in this work, with the corresponding
references to the literature.
Figure 4.11: Energy band diagram of 2.7 THz 3 QW Paris design evaluated using in-house code at an electric field, $E = 11.2 \text{kV/cm}$. The modulii-squared wavefunctions are shown in blue for the upper (4) lasing level and in red for the lower (3) lasing level. Starting from the injection barrier, the growth sequence in nanometers is given as $4.8/9.4/2.4/7.2/4.2/15.7$ where Al$_{0.15}$Ga$_{0.85}$As barrier layers are in bold. The center 5.5 of the 15.7 nm injection well is doped with Si to $N_d = 5 \times 10^{16} \text{cm}^{-2}$. The dashed lines enclose one period of the active region.

### 4.6 2.7 THz 3 QW Paris design

Figure 4.11 shows the energy band structure of the 2.7 THz 3 QW Paris design computed using the in-house solver [5]. Based upon one of the first 3 QW designs [145], this design employs two tunnel-coupled wells for lasing and one well for both resonant-phonon depopulation and carrier injection. A single well for injection also implies lower intersubband absorption loss, a parameter crucial to the observation of emission in ultrathin QCLs. Shown in table 4.2, is a comparison of the lasing parameters reported in [148] with those calculated using the in-house Poission-Schrodinger solver.

<table>
<thead>
<tr>
<th>2.7 THz 3 QW Paris design</th>
<th>Literature [148]</th>
<th>In-house</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{ul}$ (meV)</td>
<td>11.15</td>
<td>11.2</td>
</tr>
<tr>
<td>Field (kV/cm)</td>
<td>12.5</td>
<td>12.0</td>
</tr>
<tr>
<td>$(z_{ul})$ (nm)</td>
<td>5.1</td>
<td>6.25</td>
</tr>
<tr>
<td>$f_{ul}$</td>
<td>0.52</td>
<td>0.77</td>
</tr>
</tbody>
</table>

Table 4.2: Summary of the design parameters calculated for 2.7 THz 3 QW Paris design
4. ULTRATHIN QCLS

The calculated energy difference between upper and lower lasing levels $E_{ul}$ and the alignment field agree with the corresponding values reported in literature [148]. However, we overestimate the dipole matrix element $\langle z_{ul} \rangle$ and the normalized oscillator strength $f_{ul}$. This difference may be explained if we look at $\langle z_{ul} \rangle$ and $f_{ul}$, closely.

The dipole matrix element $\langle z_{ul} \rangle$ for an optical transition can be expressed in terms of the envelope wavefunction as:

$$\langle z_{ul} \rangle = \int_{-\infty}^{+\infty} dz \psi_f^*(z) z \psi_i(z)$$  \hspace{1cm} (4.4)

The oscillator strength is proportional to the square of the dipole matrix element and is given as:

$$f_{ul} = \frac{2m \ast (E_f - E_i) \langle z_{ul} \rangle^2}{\hbar^2}$$  \hspace{1cm} (4.5)

Therefore, both $\langle z_{ul} \rangle$ and $f_{ul}$ depend upon the integral of the envelope wavefunction in the direction of growth, i.e. z-axis. Typically, this relies upon (i) the summation method used for numerical integration, and (ii) the distance $z$, to which the wavefunction is truncated. In our solver, the wavefunctions are truncated up to 3 periods. It is probable that slight differences in the integral method and the domain of integral between solvers, influences the calculation of dipole matrix element and oscillator strengths.

We next describe the electro-optic characteristics of ultrathin 2.7 THz 3 QW Paris design grown thrice at the Cavendish labs.

4.6.1 Ultrathin QCL (V671)

V671 was the first ultrathin QCL grown for this work towards the end of a growth campaign in November 2010. However, none of the devices processed from V671 appeared to lase. XRD data from this wafer (reproduced in appendix B) showed that this wafer was thinner than the target thickness by 0.56%. Table 4.3 lists the target specifications of V671 in terms of active region thickness, period length $L_p$, number of periods $N_p$ and waveguide structure, i.e. thickness and doping of the top and bottom n+ doped GaAs. Perhaps, V671’s failure to lase is a consequence of insufficient gain due to reduced active region thickness, see section 4.1.1. Apart from the active region and number of periods, the waveguide structure plays an equally important role in determining some of operating characteristics. The influence of n+ GaAs layers on the waveguide losses in an ultrathin THz QCL is discussed in detail in section 4.10.
4.6 2.7 THz 3 QW Paris design

Table 4.3: Wafer structure of the ultrathin 2.7 THz 3 QW Paris design.

<table>
<thead>
<tr>
<th>Wafer</th>
<th>Length per period, $L_p$ (nm)</th>
<th>Number of repeats, $N_p$</th>
<th>Waveguide</th>
<th>Thickness without etch stop ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V671, W0798, V692</td>
<td>43.7</td>
<td>45</td>
<td>Top 75 nm (2e18), Bottom 75 nm (2e18)</td>
<td>2.121</td>
</tr>
</tbody>
</table>

Figure 4.12: (a) LIV characteristics of ultrathin 2.7 THz 3 QW Paris design (V671) double-metal ridge, measured at 4K using golay for THz detection (b) Optical image of 2.7 THz 3 QW Paris design (V671) showing appearance of growth defects, at 5x magnification (c) Optical image of a growth defect at 50x magnification.

Another possible explanation to device failure may rest in the examination of the electrical characteristics. Figure 4.12 shows that the devices processed from V671 appeared to short-circuit. As this wafer was processed multiple times into 80-150 $\mu$m wide ridges, by chemical and dry etching, it may have been short circuiting due to growth defects that resulted in the top Ti/Au contact spiking down to the bottom contact during evaporation, see figure 4.12(b-c). Since spiking occurs over a length of 1-2 $\mu$m, it is not a problem that influences full-stack THz QCLs, which are 6-14 $\mu$m in height. In an ultrathin THz QCL, the spiking depth approaches the thickness of the active region, which adversely affects their performance.
4. ULTRATHIN QCLS

The existence of interface homogeneities and alloy disorders manifests as increase in the full width half maximum (FWHM) of the satellite peak recorded by XRD measurements. Therefore, the poor performance of V671 can be attributed to interface inhomogeneities and alloy disorders through the FWHM of the satellite peaks (appendix B). Unfortunately, the FWHM of all the peaks, the substrate peak (43 arc.sec) and the satellite peak (40 to 43 arc.sec), is limited by the resolution of the XRD system, which makes it harder to ascertain the cause of failure for V671.

4.6.2 Ultrathin QCL (W0798)

During the MBE downtime on the V chamber, V671 was repeated in the W chamber as W0798. XRD data from this wafer showed a deviation of +0.96 % from the target thickness. The FWHM derived from the substrate peak (43 arc.sec) and the satellite peak (40 to 43 arc.sec) suffered from the same resolution issues as V671, making it difficult to assess the epitaxial growth of W0798.

Figure 4.13 shows the LIV characteristics of a double metal ridge processed from this wafer. From the LIV characteristics, it appears that the device short-circuits and fails to lase. After multiple attempts at characterization, this wafer was discarded from analysis as this was the first THz QCL attempted in the W chamber, which gave rise to many floating experimental parameters related to growth in a different system. Issues with thermo-compression bonding may have also affected the performance of the laser. Furthermore, W0798 suffered from the same issues as V671 with regards to reduced gain due to active region design, number of repeat periods and waveguide structure (table 4.3).

4.6.3 Ultrathin QCL (V692)

Grown in December 2012, at the beginning of a new growth cycle, devices processed from wafer V692 did not lase, see figure 4.14. However, unlike V671 and W0798 these devices did not short. XRD data (reproduced in appendix B) showed that V692 was grown thinner than the target thickness by approximately 1.99 %. Broadening of the FWHM derived from the substrate peak (50 arc.sec) and the satellite peak (50-70 arc.sec) suggested inhomogeneity in the growth, possibly due to an arsenic drift. Subsequent to the failure of the previous two attempts, we found that all three wafers V671, W0798 and V692 were grown in the reverse order as reported by Chassagneux et al. [148], i.e. the injection barrier was closer to the bottom contact as opposed to the top. This motivated us to test the V692 in both forward and reverse bias.

We use results previously reported in [148] to understand the electrical characteristics
of V692, shown in figure 4.14. THz QCLs processed from the full-stack wafer (L207) in [148] show a $J_{th} \sim 900$ A/cm$^2$. At this current density, the authors in [148] report an alignment bias of $\sim 12.5$ V, which corresponds to an alignment electric field of 12.5 kV/cm. At the same current density, i.e. at $J = 900$ A/cm$^2$, the voltage dropped across V692 is $\approx 3.1$ V in the reverse bias and $\approx 2.7$ V in the forward bias, see figure 4.14. Accounting for the voltage dropped across the top and bottom Schottky contacts (0.7 V+0.7 V), the measured bias (1.7 V and 1.4 V, respectively) corresponds to an electric field of 8.1 kV/cm in the reverse sense and 6.2 kV/cm in the forward sense.

In the above analysis, we ignored the increase in threshold current density introduced by reducing the number of periods (eqn. 4.3). In reality, the $J_{th}$ expected for the ultrathin V692 is higher than the threshold current density reported for L207 (900 A/cm$^2$). This implies that the measured electric field corresponding to alignment is actually higher than the value calculated from figure 4.14, i.e. greater than 8.1 (6.2) kV/cm in reverse (forward) bias. The results from V692 show that the measured electric field associated with alignment ($\geq 8.1$ kV/cm) agrees with the 12.5 kV/cm expected from the 2.7 THz 3 QW Paris design. This result is encouraging in spite of the absence of observable emission or a clear NDR signature in the LIV.

In short, while we did not observe emission from all three attempts of the ultrathin 2.7 THz 3 QW Paris design, we found that the electro-optic characteristics of V692 were in closest agreement with the reported electro-optic characteristics [148]. This then leads us to examine the points of failure of emission from V692. In addition to XRD data, problems
4. ULTRATHIN QCLS

with growth (more specifically, higher III-V composition, due to Arsenic drift) were further investigated by comparing the electro-optic characteristics of another design (3 THz 4 QW ETH design, wafer V696) grown under nominally identical conditions as V692. Any differences between the LIV characteristics of double metal ridges processed from V696 and V674 (both grown with 3 THz 4 QW ETH design but at different times) may provide insights to any growth anomaly in V692. This is discussed in detail in section 4.9.3. The more likely cause behind the device failure appeared to be the choice of active region, the number of repeat periods and the choice of waveguide geometry, which plagued the performance of all three attempts of the 2.7 THz 3 QW Paris design. In the next section, results from double metal ridges processed from 3 THz 3 QW Paris design are discussed. Very similar in design in terms of anticrossing energies with injection and extractor states, the only difference between 2.7 THz 3 QW Paris design and 3 THz 3 QW Paris design, is in the emission frequency.

Figure 4.14: LIV characteristics of ultrathin 2.7 THz 3 QW Paris design (V692) double-metal ridge, measured on golay.
4.7 3 THz 3 QW Paris design

Figure 4.15 shows the energy band structure of the 3 THz 3 QW Paris design computed using the in-house solver. Reported in 2007, this design was the first THz QCL structure which employed only three quantum wells per period [145]. This design was later used by Belkin et al. to break the record in 2008 of the highest operating temperature in THz QCLs (178 K) by using copper-copper waveguides [149]. In 2011, Strupiechonski et al. from Université Paris-Sud 11 first published lasing from ultrathin THz QCL using the same design as [3]. Since the present work relates to ultrathin QCLs, the nomenclature of this design rests with Paris, although its origins can be traced to Luo et al. from National Research Council, Canada.

Table 4.4 lists the transition energy, alignment bias, dipole matrix element and the normalized oscillator strength for the 3 THz 3 QW Paris design. Also shown is a comparison between the design parameters computed in-house and those reported in the literature by Luo et al. and Belkin et al. For the same epitaxial structure, Luo et al. and Belkin et al. report slightly different $E_{ul}$ and $\langle z_{ul} \rangle$ values. The normalized oscillator strength $f_{ul}$,
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reported as 0.51 by Luo et al. is not explicitly reported by Belkin et al. in [149]. For comparison here, we estimate \( f_{ul} \) in [149] from eqn. 4.4 using the reported values of \( E_{ul} \) and \( \langle z_{ul} \rangle \). We find that \( f_{ul} = 0.67 \) in [149]. For the same epitaxial structure, our calculations of the transition energy between the upper and lower lasing level, \( E_{ul} = 12.8 \) meV are closer to Luo et al. (\( E_{ul} = 12.9 \) meV) as opposed to Belkin et al. (\( E_{ul} = 14 \) meV). Compared to Luo et al.’s calculations, our solver slightly overestimates both \( \langle z_{ul} \rangle \) and \( f_{ul} \).

<table>
<thead>
<tr>
<th>3 THz 3 QW Paris design</th>
<th>Literature [145], [149]</th>
<th>In-house</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{ul} ) (meV)</td>
<td>12.9(^a)</td>
<td>12.8</td>
</tr>
<tr>
<td>Field (kV/cm)</td>
<td>12.5</td>
<td>12.1</td>
</tr>
<tr>
<td>( \langle z_{ul} \rangle ) (nm)</td>
<td>4.7(^b)</td>
<td>5.74</td>
</tr>
<tr>
<td>( f_{ul} )</td>
<td>0.51(^c)</td>
<td>0.74</td>
</tr>
</tbody>
</table>

\(^a\) 12.9 meV in Ref [145], 14 meV in Ref [149]
\(^b\) 4.7 nm in Ref [145], 6.1 nm in Ref [149]
\(^c\) 0.51 in Ref [145], 0.67 in Ref [149].

Table 4.4: Summary of the design parameters calculated for 3 THz 3 QW Paris design

Note that in section 4.6, all the attempts at ultrathin QCLs grown using the 2.7 THz, 3 QW Paris design failed to lase, with reasons attributed to number of repeat periods, choice of active region, anomalous growth, and poor waveguide geometry. For a systematic analysis, the ultrathin QCLs are compared with their corresponding full-stack version, grown under nominally identical conditions. Below, we discuss experimental results obtained from double metal ridges processed from full-stack and ultrathin THz QCLs, grown at Cavendish with the 3 THz 3 QW Paris design.

4.7.1 Full-stack (V703)

XRD data from the full-stack 3 THz 3 QW Paris design (reproduced in appendix B) showed that the layer thickness deviated from the target thickness by +1.86 %. The FWHM of the substrate peak (47 arc.sec) and the satellite peak (47-54 arc.sec) of V703 was found to have reduced when compared to V692, suggesting a stabilization of the drift observed in the earlier samples. Grown in-house for the first time, devices processed from V703 demonstrated lasing with a threshold current density \( J_{th} \) of \( \approx 910 \) A/cm\(^2\) and a peak current density \( J_{peak} \) of \( \approx 1250 \) A/cm\(^2\), see figure 4.16. \( J_{peak} \) is defined as the current density at which maximum lasing output is obtained. From figure 4.16(a), we note that at \( J_{th} = 910 \) A/cm\(^2\) the voltage dropped across the double metal ridge is \( \approx 14.5 \) V. Once again, accounting for the top and bottom Schottky contacts, the actual alignment voltage dropped...
across a 10.8 µm active region \( (N_p = 226) \) is 14.5 \(-\) 2(0.7) = 13.1 V, which corresponds to an alignment electric field of 12.1 kV/cm. This is in agreement with the theoretically estimated alignment field calculated for the 3 THz 3 QW Paris design using the in-house solver listed in table 4.4. From figure 4.16(a), we note that \( J_{th} \) increases exponentially with temperature, and the full-stack operates up to a maximum temperature of 70 K.

**Figure 4.16:** (a) LIV characteristics of double-metal ridges processed from full-stack 3 THz 3 QW Paris design (V703) at 10 K (b) Threshold current density \( J_{th} \) as a function of temperature

Figure 4.17 shows the differential resistance of V703 plotted along with the IV characteristics, measured at 10 K in the pulsed mode (figure 4.16(a)). We note from figure 4.17 that the dynamic range, defined as \( \frac{J_{th} - J_{ph}}{J_{th}} \) can be estimated to be \( \frac{1420 - 910}{1420} \) which is \( \approx \) 36% of the entire current range.

For lasers with electro-optic characteristics shown in figure 4.16 and figure 4.17, the frequency spectrum measured using FTIR spectroscopy is shown in figure 4.18. The spectral characteristics are measured as a function of current, which is increased in steps of 100 mA starting from 1500 mA, i.e. \( J = 862 \text{ A/cm}^2 < J_{th} \) to a current of 2300 mA, i.e. \( J = 1320 \text{ A/cm}^2 \). We observe that the experimental results deviate slightly from the theoretical calculations of the design frequency, \( E_{ul} = 12.8 \text{ meV} = 3.1 \text{ THz} \), listed in table 4.4. Just above threshold (\( J = 920 \text{ A/cm}^2 \), current = 1600 mA), we note that the first lasing mode appears at a frequency of 3.22 THz. We also note the appearance of a second lasing mode at 3.32 THz as the current is increased to 1800 mA (\( J = 1034 \text{ A/cm}^2 \)). As the current is raised further to about 2100 mA, corresponding to \( J = 1206 \text{ A/cm}^2 \), which in fact approaches the \( J_{peak} \) shown in figure 4.16, we observe the appearance of a very strong lasing...
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Figure 4.17: Differential resistance of double metal ridges processed from 3 THz 3 QW Paris design (V703) at 10 K

![Differential resistance graph](image)

Figure 4.18: Spectral characteristics of double metal ridges processed from full-stack 3 THz 3 QW Paris design (V703) shown as a function of current, increasing from 1500 mA to 2300 mA, in steps of 100 mA.

![Spectral characteristics graph](image)
We next discuss the performance of the full-stack 3 THz 3 QW Paris design (V703) in comparison to the performance of L421 reported in literature [3, 145, 149].

4.7.2 Comparison of V703 with Literature

In section 4.2, we discussed results from Strupiechonski et al.’s work on 3 THz 3 QW Paris design, which demonstrated lasing emission from ultrathin active region (L422) and the corresponding 10 µm thick full-stack wafer (L421), see figure 4.2. From figure 4.2, we note that the 10 µm thick active region (L421) exhibits a \( J_{th} \approx 910 \) A/cm\(^2\). This is lower than \( J_{th} \approx 700 \) A/cm\(^2\), which we measure from double-metal ridges processed from V703, see figure 4.16(b). Another point of comparison is the maximum operating temperature, which varies from 70 K in our measurements to 146 K reported by Strupiechonski et al. In spite of these shortcomings, we find that the dynamic range of L421, calculated as \( \frac{J_{NDR} - J_{th}}{J_{NDR}} \times 100 \% \), is 37.5 % is only slightly better than the dynamic range exhibited by V703 (36 %). While our results from the full-stack 3 THz 3 QW Paris design show suboptimal performance, it still holds promise for ultrathin THz QCLs based on the same design, and grown under nominally identical conditions. Below we discuss results from double metal ridges processed from V702, which is an ultrathin 3 THz 3 QW Paris design, grown just before V703.

4.7.3 Ultrathin QCL (V702)

XRD data suggests that the layer thickness of V702 deviated from the target thickness by +1.46 %, see appendix B. Table 4.5 summarizes the target structure of the ultrathin 3 THz 3 QW Paris design (V702) in terms of period length, number of periods and waveguide geometry. Compared to the symmetric top and bottom n\(^+\)GaAs contact used in ultrathin 2.7 THz 3 QW Paris design (V692), see table 4.3, we use asymmetric top and bottom n\(^+\)GaAs contacts in V702.

<table>
<thead>
<tr>
<th>Wafer</th>
<th>Length per period, ( L_p ) (nm)</th>
<th>Number of repeats, ( N_p )</th>
<th>Waveguide</th>
<th>Thickness without etch stop (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V702</td>
<td>44.1</td>
<td>57</td>
<td>Top 75 nm (2e18), Bottom 50 nm (2e18)</td>
<td>2.668</td>
</tr>
</tbody>
</table>

Table 4.5: Wafer structure of the ultrathin 3 THz 3 QW Paris design.

Figure 4.19 shows the LIV characteristics of double metal ridges processed from V702. Devices processed from V702 were characterized with a very unusual LIV, and an absence of any simultaneous emission. Given that the alignment electric field is 12.1 kV/cm for the
3 THz 3 QW Paris design, the alignment bias for a 2.66 µm thick active region works out to be 4.5 V. At this voltage, the current density $J \approx 50 \text{ A/cm}^2$. This is nearly twenty times less than $J_{th} = 910 \text{ A/cm}^2$ observed for the full-stack THz QCL. This may be indicative of a high resistive layer within the active region, perhaps a problem that may be attributed to doping within the first few periods, which severely impediments the electrical performance in a reduced active region device.

![Figure 4.19: (a) LIV characteristics of V702 double-metal ridge, measured on golay at 4K (b) Differential resistance at 4K](image)

FWHM derived from the substrate peak (32 arc.sec) and the satellite peak (36-43 arc.sec) suggest that these values are limited by the resolution of the system, which hints at absence of inhomogeneity during the epitaxial growth of V702. While doubts over the choice of waveguide remain, the main question that arises is whether under-doping and not inhomogeniety plagued the performance of the full-stack V703 wafer, and these issues also played a role in degrading the performance of the ultrathin V702 wafer. This is harder to analyze in an active region grown for the first time at Cavendish, with no previous in-house data to compare. In order to answer this question, we probed the electro-optic performance of the 3 THz 4 QW MIT design grown at the same time as the 3 THz 3 QW Paris design. The full-stack 3 THz 4 QW MIT design is a regrowth of V569, a wafer previously grown and characterized at the Cavendish Labs. The next section discusses results from double metal ridges processed from full-stack and ultrathin 3 THz 4 QW MIT design.
4.8 3 THz 4 QW MIT design

Figure 4.20 shows the energy band structure of the 3 THz 4 QW MIT design. The 3 THz 4 QW MIT design has lower number of repeat periods per unit length as opposed to its successor - the (2.7/3) THz 3 QW Paris design. However, compared to its 3 QW counterpart, the performance of the 3 THz 4 QW MIT design, which consists of an additional well, is much more robust in terms of growth variations. This is because THz QCLs based on resonant phonon designs, rely crucially on the alignment of energy states between periods. Therefore, a change of a few monolayers can dramatically influence the performance of a THz QCL.

![Energy band diagram of 3 THz 4 QW MIT design evaluated using in-house code at an electric field, E = 13.0 kV/cm.](image)

Figure 4.20: Energy band diagram of 3 THz 4 QW MIT design evaluated using in-house code at an electric field, $E = 13.0$ kV/cm. The modulii-squared wavefunctions are shown in blue for the upper (5) lasing level and in red for the lower (4) lasing level. Starting from the injection barrier, the growth sequence in nanometers is given as $4.1/6.6/2.5/7.9/4.9/9.0/3.3/15.6$ where $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$ barrier layers are in bold. The thickest well is doped with Si to $N_d = 1.9 \times 10^{16}$ cm$^{-2}$. The dashed lines enclose one period of the active region.

Shown in comparison to lasing parameters reported in [150], is a summary of the transition energy, alignment field, dipole matrix and oscillator strength calculated for the 3 THz 4 QW MIT design, using the in-house solver, see, table 4.6. Our estimates of the transition energy and alignment bias agree with that of [150]. However, unlike the (2.7/3) THz 3 QW Paris design, where we overestimated $\langle \varepsilon_{ul} \rangle$, $f_{ul}$, in the case of 3 THz 4 QW MIT design, our estimates of $\langle \varepsilon_{ul} \rangle$, $f_{ul}$ are less than those reported by [150].

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<table>
<thead>
<tr>
<th>3 THz 4 QW MIT design</th>
<th>Literature [150]</th>
<th>In-house</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{ul}$ (meV)</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>Field (kV/cm)</td>
<td>10.2</td>
<td>10.2</td>
</tr>
<tr>
<td>$z_{ul}$ (nm)</td>
<td>6.1</td>
<td>4.39</td>
</tr>
<tr>
<td>$f_{ul}$</td>
<td>0.86</td>
<td>0.61</td>
</tr>
</tbody>
</table>

Table 4.6: Summary of the design parameters calculated for 3 THz 4 QW MIT design

In the next sub-section, we discuss results from double metal ridges processed from the full-stack 3 THz 4 QW MIT design.

### 4.8.1 Full-stack V705 and comparison to V569

Figure 4.21 shows the LIV characteristics of the 3 THz 4 QW MIT design (V705), in comparison to a 3 THz 4 QW MIT design (V569), grown previously at the Cavendish Labs under optimal conditions. We note that double metal ridges processed from V569 exhibit a $J_{th} \approx 720 \text{ A/cm}^2$. However, similar ridges processed from V705 exhibit a $J_{th} \approx 755 \text{ A/cm}^2$. We also note the difference in alignment bias between V705 and V569. While V569 shows an alignment bias $\approx 9.2 \text{ V}$, V705 shows a much higher alignment bias even after accounting for the top and bottom Schottky contact, i.e. $13.4 - 2(0.7) = 12 \text{ V}$. Another point of comparison is the $J_{peak}$, which departs from $\approx 1000 \text{ A/cm}^2$ in V569 to $860 \text{ A/cm}^2$ in V705. As can be seen from figure 4.21(b), the maximum operating temperature falls from 125 K in THz QCLs processed from V569 to 70 K in the THz QCLs processed from V705. Although the devices processed from V705 have been wet-etched and not dry-etched unlike V569, we do not expect the performance to shift this significantly.

Figure 4.21 shows the differential resistance for both V569 and V705, measured at 10 K in pulsed mode. Shown in figure 4.21 is the dynamic range which is seen to reduce from $\frac{J_{th,N69}}{J_{th,N68}} = \frac{1170 - 720}{1170} = 38 \%$ in V569 to $\frac{960 - 755}{960} = 21 \%$ in V705. Even though the III-V composition that affected V692 and V696 was corrected in the growth run of wafers V702 to V705, a comparison between V569 and V705 appears to reconfirm that the wafers with 2.7/3 THz, 3 QW Paris design were grown under suboptimal growth conditions, possibly due to variations in higher background impurity levels due to start of growth campaign. The high background impurity levels may have compensated the intentional doping causing an under-doped structure, thereby adversely affecting the laser performance. From XRD data shown in appendix B, we observe that the layer thickness of V705 deviated by $+2.91 \%$ from the target structure. The rocking curves of V705 indicate a FWHM of approximately 50 arc.sec and 60-61 arc.sec measured from the substrate peak and satellite
4.8 3 THz 4 QW MIT design

Figure 4.21: Comparison of (a) LIV characteristics of 3 THz 4 QW MIT design (V705) double-metal ridge at 10 K with 3 THz 4 QW MIT design (V569) (b) Threshold current density ($J_{th}$) as a function of operating temperature of 3 THz 4 QW MIT design (V705) with respect to 3 THz 4 QW MIT design (V569). The data on 3 THz 4 QW MIT design (V569) was taken by Anthony Brewer.

peak, respectively.

4.8.2 Ultrathin QCL (V704)

Here, we present results from double metal ridges processed from ultrathin 3 THz 4 QW MIT design (V704). XRD data suggests that the layer thickness of V704 deviated by $\pm 2.84\%$ from the target structure, see appendix B. It is however promising to note an absence of broadening in the FWHM derived from the substrate peak (32 arc.sec) and the FWHM derived from the satellite peak (36-43 arc.sec).

Table 4.7 summarizes the target wafer structure of the ultrathin 3 THz 4 QW MIT (V704) design in terms of period length, number of periods and waveguide geometry. Note that the thickness and doping of the top and bottom $n^+$ GaAs contacts is consistent with the ultrathin 3 THz, 3 QW, MIT (V702) design (see, table 4.5), i.e. asymmetric waveguide geometry is employed.

<table>
<thead>
<tr>
<th>Wafer</th>
<th>Length per period, $L_p$ (nm)</th>
<th>Number of repeats, $N_p$</th>
<th>Waveguide</th>
<th>Thickness without etch stop ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V704</td>
<td>53.9</td>
<td>47</td>
<td>Top 75 nm ($2e18$), Bottom 50 nm ($2e18$)</td>
<td>2.712</td>
</tr>
</tbody>
</table>

Table 4.7: Wafer structure of the ultrathin 3 THz 4 QW MIT design.

The electro-optic characteristics of 3 THz 4 QW MIT design (V704) are very similar
Figure 4.22: Comparison of differential resistance characteristics between 3 THz 4 QW MIT design (V705) and 3 THz 4 QW MIT design (V569), measured at 10 K in pulsed mode. The data on V569 was taken by Anthony Brewer.

to that of 3 THz 3 QW Paris design (V702). As in the case of V702, double metal ridges processed from V704 show a very unusual IV, see figure 4.23. We note from table 4.6, that the alignment field for the 3 THz 4 QW MIT design is 10.2 kV/cm. For a 2.66 µm thick active region, alignment is expected at a bias of 2.7 V. At this voltage, the current density $J \approx 10$ A/cm$^2$. This is nearly two orders less than $J_{th} = 755$ A/cm$^2$ observed for the full-stack THz QCL. Similar to 3 THz 3 QW Paris design (V702), this may be indicative of a high resistive layer within the active region, perhaps a problem that may be attributed to doping within the first few periods, which severely impediments the electrical performance in a reduced active region device.

The possibility of an open circuit is excluded as multiple devices processed from 3 THz 4 QW MIT design (V704) show a room temperature resistance between 15-20 kilohm, which is similar to the 7-10 kilohm resistance obtained from THz QCLs proceesed out of full-stack 3 THz 4 QW MIT design (V705) wafer. Note that we do not measure any light emission using both golay and the more sensitive Si-Ge bolometer as a detector from these devices.

The poor performance of a full-stack 3 THz 4 QW MIT design (V705) which is a regrowth of previously characterized 3 THz 4 QW MIT design (V569), in addition to the failure of ultrathin 3 THz 4 QW MIT design (V704) necessitated a reassessment of our options. It compelled us to review in-house grown full-stack designs, which were known
4.9 3 THz 4 QW ETH design

This section presents results from double metal ridges processed from full-stack 3 THz 4 QW ETH design and also an ultrathin 3 THz 4 QW ETH design, which is derived by chemical etching the full-stack wafer post growth. These results are the first demonstration of emission from ultrathin active regions at the Cavendish, and to our knowledge the first demonstration of emission in a BtC design.

Figure 4.24 shows the energy band diagram of 3 THz 4 QW ETH design. Although we have discussed this hybrid design in the introductory chapter, we present the salient features once again. Compared to the 3 THz 4 QW MIT design, where lasing transition occurs across energy states in the same well (4 → 3 in figure 4.20), the 3 THz 4 QW MIT design employs a lasing transition (5 → 4 in figure 4.24) between energy states in adjacent wells, which makes it much more diagonal in the real space. As we can see from figure 4.24, states 3 and 2 form a miniband which is coupled to a resonant phonon extraction stage, i.e. state 1.

Table 4.8 lists the lasing parameters of the 3 THz 4 QW ETH design computed with the
Figure 4.24: Energy band diagram of 3 THz 4 QW ETH design evaluated using in-house code at an electric field, $E = 7.5$ kV/cm. The modulii-squared wavefunctions are shown in blue for the upper (5) lasing level and in red for the lower (4) lasing level. Starting from the injection barrier, the growth sequence in nanometers is given as $5.5/11.0/1.8/11.5/3.8/9.4/4.2/18.4$ where $\text{Al}_{0.15}\text{Ga}_{0.85}\text{As}$ barrier layers are in bold. The thickest well is doped with Si to $N_d = 2 \times 10^{16}$ cm$^{-2}$. The dashed lines enclose one period of the active region.

in-house solver, in comparison to the values reported by Amanti et al. \cite{6}. We note that the transition energies and alignment fields agree with each other. Also, the calculated dipole matrix element $\langle z_{ul} \rangle$, is consistent with Amanti et al. to within an accuracy of 6\%. We find that unlike the resonant phonon designs (sections 4.6 - 4.8), our solver is more robust for BtC designs in calculating $\langle z_{ul} \rangle$ and $f_{ul}$. Note that $\langle z_{ul} \rangle$ and $f_{ul}$ depend upon the length over which the envelope wavefunctions extend in the growth direction ($3L_p$, where 3 is the number of periods over which the wavefunction is truncated). Besides the actual number of periods included in the simulation (section 4.6), it is probable that the in-house solver is more accurate for the BtC design as opposed to the resonant phonon design as this length is higher in the former as compared to the latter.
4.9 3 THz 4 QW ETH design

<table>
<thead>
<tr>
<th>3 THz 4 QW ETH design</th>
<th>Literature [6]</th>
<th>In-house</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{ul} ) (meV)</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Field (kV/cm)</td>
<td>7.6</td>
<td>7.6</td>
</tr>
<tr>
<td>( \langle x_{ul} \rangle ) (nm)</td>
<td>4.4</td>
<td>4.19</td>
</tr>
<tr>
<td>( f_{ul} )</td>
<td>0.36</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Table 4.8: Summary of the design parameters calculated for 3 THz 4 QW ETH design

Below, we discuss results obtained from full-stack 3 THz 4 QW ETH design (V674), which was grown in the 2010 growth cycle, without under-doping and III-V composition issues. We also compare the performance of full-stack 3 THz 4 QW ETH design (V674) with devices processed from 3 THz 4 QW ETH design (V696). V696 is a regrowth of V674 grown in V chamber under nominally similar conditions as V692, V702-V705 (wafers discussed in sections 4.6 - 4.8). Therefore, a comparison between full-stack 3 THz 4 QW ETH design (V674) and full-stack 3 THz 4 QW ETH design (V696) should give us the confidence that the performance of an ultrathin QCL derived from the former wafer would not be plagued with growth-related problems. Finally, we present results from V674\(^T\), with the superscript \( T \), indicating that it has been obtained by thinning the full-stack 3 THz 4 QW ETH design (V674) post growth, unlike the other ultrathin wafers mentioned in this thesis which were epitaxially grown with reduced repeat periods.

4.9.1 Full-stack (V674)

XRD data suggests that V674 was grown thinner than the target structure by 0.33 %. The rocking curves of V674 indicate a FWHM of approximately 47 arc.sec and 47-50 arc.sec measured from the substrate peak and satellite peak, respectively (see appendix B). Figure 4.25 shows the LIV characteristics of double metal ridges processed from full-stack 3 THz 4 QW ETH design (V674). From figure 4.25, we note that the device exhibits a \( J_{th} \) of 155 A/cm\(^2\). At 4 K, we obtain an average power of 3.2 \( \mu \)W at the peak current density. We also note from figure 4.25, that the full-stack 3 THz 4 QW ETH design (V674) operates up to a maximum temperature of 134 K. In accordance with general THz QCL behavior, the threshold current density, \( J_{th} \), increases exponentially with temperature as the gain reduces with temperature due to thermally assisted scattering.

Figure 4.26 plots the differential resistance along with the IV characteristics. From the figure 4.26, we estimate the alignment bias at \( J_{th} = 155 \) A/cm\(^2\) to be 10.8 V. Taking into account the 2 x 0.7 V voltage drop due to top and bottom Schottky contacts, for a 11.8 \( \mu \)m thick active region, this implies an electric field \( \approx 7.9 \) kV/cm. This agrees very well with
4. ULTRATHIN QCLS

Figure 4.25: (a) LIV characteristics of 3 THz 4 QW ETH design (V674) measured on golay, in pulsed mode at different operating temperatures (b) Threshold current density $J_{th}$ as a function of temperature.

The theoretical alignment field of 7.6 kV/cm predicted for the 3 THz 4 QW ETH design, see table 4.8. From figure 4.26 we note that the NDR occurs at a $J_{NDR} \approx 280 \text{ A/cm}^2$. Therefore, the dynamic range for the full-stack 3 THz 4 QW ETH design (V674) can be estimated as $\frac{J_{NDR} - J_{th}}{J_{NDR}} = \frac{280 - 155}{280} = 44\%$ of the entire current range.

Note that among all the full-stack lasers of different designs presented in this chapter, the 3 THz 4 QW ETH design (V674) shows the maximum operating temperature, and also the maximum dynamic range.

4.9.2 Comparison of full-stack V674 with literature

To confirm that results from full-stack 3 THz 4 QW ETH design (V674) are indeed representative of a good device, we compare our results to those reported by Amanti et al. from the same design (see figure 4.27). The dynamic range in Amanti et al. can be estimated as $\frac{J_{NDR} - J_{th}}{J_{NDR}} = \frac{410 - 180}{410} = 56\%$ from figure 4.27. This is more than what we measure, however we feel that a lower $J_{th}$ in our devices may be to our advantage when we subsequently reduce the number of repeat periods. We also note that the maximum operating temperature reported by Amanti et al. is 150 K (figure 4.27), as opposed to a slightly lower temperature (134 K) observed in our devices, see figure 4.25. However, we expect a 10-20 K improvement in performance of the full-stack 3 THz 4 QW ETH design (V674) by thinning the host-substrate.
4.9.3 Comparison of full-stack V674 and full-stack V696

We now compare the electro-optic performance of two wafers, V674 and V696, both of which are full-stack 3 THz 4 QW ETH designs, and grown in-house at the Cavendish Labs. We expect V674 to have a superior performance over V696, as the latter was grown under sub-optimal growth conditions. XRD data suggests that the layer structure of V696 deviated from the target structure by +0.44%.

We note from figure 4.28, that while double metal ridges processed from full-stack 3 THz 4 QW ETH design (V674) shows a $J_{th} \approx 155$ A/cm$^2$, similarly processed ridges from full-stack 3 THz 4 QW ETH design (V696) show a $J_{th} \approx 187$ A/cm$^2$. Compared to V674, devices from V696 show an alignment bias of 7.2 V. Accounting for the 2 x 0.7 V drop due to Schottky contacts, for a 10 $\mu$m active region, this corresponds to an electric field of 5.8 kV/cm. This field deviates from 7.6 kV/cm, which is the theoretically predicted alignment field for this design. The dynamic range of V696, estimated as $\frac{J_{NDR} - J_{th}}{J_{NDR}} = \frac{212 - 187}{212} = 12\%$ is nearly one third of the dynamic range exhibited by V674. From figure 4.28(b), we also observe that the maximum operating temperature reduces from 134 K to 85 K, in moving from V674 to V696.

A minor point to keep in mind is that, while the full-stack 3 THz 4 QW ETH design

![Graph showing alignment bias and dynamic range](image)
4. ULTRATHIN QCLS

Figure 4.27: LIV characteristics of 3 THz 4 QW ETH design as reported in the literature [6]. The inset shows the laser spectra. Adapted from [6] to indicate $J_{th}$, $J_{NDR}$, alignment bias and dynamic range.

(V674) incorporates 180 repeat periods, the full-stack 3 THz 4 QW ETH design (V696) is grown with 160 repeat periods. This difference in $N_p$ also contributes to higher $J_{th}$ and a lower maximum operating temperature. It is useful at this point to remind ourselves of eqn. 4.3, which states that $J_{th}$ varies inversely with $N_p$. For an active region thickness greater than 5 µm, a difference of 20 repeat periods should not introduce a difference of more than 10% in $J_{th}$ and the maximum operating temperature for QCLs processed and grown under nominally identical conditions [3]. Therefore, if 3 THz 4 QW ETH design (V696) was grown under the exact same conditions as 3 THz 4 QW ETH design (V674), we should have observed a $J_{th} = 165$ A/cm$^2$ and a maximum operating temperature of 120 K. The discrepancy in observed characteristics of wafer V696 can therefore be attributed to problems with III-V composition. In particular, V696 is rich in Gallium making it more conductive than V674.

We next discuss our process of obtaining ultrathin QCLs from full-stack 3 THz 4 QW ETH design (V674), and subsequently present electro-optic results obtained from this chemically thinned wafer (V674$^T$).
4.9 3 THz 4 QW ETH design

Figure 4.28: Comparison of (a) LIV characteristics of 3 THz 4 QW ETH design (V674) double-metal ridge at 4 K with 3 THz 4 QW ETH design (V696) (b) Threshold current density ($J_{th}$) as a function of operating temperature of 3 THz 4 QW ETH design (V674) with respect to 3 THz 4 QW ETH design (V696). The data on 3 THz 4 QW ETH design (V696) was taken by Yash D. Shah.

4.9.4 Chemical etching of ultrathin QCLs

While an ultrathin THz QCL can be grown epitaxially, the conventional route reported in the literature employs chemically thinning of a full-stack THz QCL (see section 4.2). In figure 4.29(a), we show the optical image of 3 THz 4 QW ETH design (V674) after thinning in a solution of $\text{H}_2\text{SO}_4$:$\text{H}_2\text{O}_2$:$\text{H}_2\text{O}$, diluted to a ratio of 1:8:80. The solution etches GaAs/Al$_{0.15}$Ga$_{0.75}$As at a rate of 500 nm/min. A consequence of chemical thinning is the roughening of the GaAs surface, which poses a problem for further processing of dry-etched photonic devices from a thinned THz QCL. Also seen in figure 4.29(b) are defect etch pits which open up due to isotropic nature of the chemical etch. Careful selection of defect free areas enable mesa processing via wet chemical routes, as shown in figure 4.29(b).

While previous reports on ultrathin QCLs do not comment on the surface roughness of the processed THz QCLs, it may be possible to optimize the etch rate to improve the surface quality of the thinned wafer. However, substrate quality after chemical thinning is unlikely to compete with the surface quality of as grown THz QCLs.

4.9.5 Ultrathin QCL (V674$^T$)

Table 4.9 summarizes the wafer structure of the ultrathin 3 THz 4 QW ETH design (V674$^T$). There are two main differences between epitaxially grown ultrathin THz QCLs and chem-
4. ULTRATHIN QCLS

Figure 4.29: (a) Optical image of 3 THz 4 QW ETH design (V674) after chemical etching, showing growth defects opening as a result of etch (b) optical image of processed ridges showing ridge with top and bottom Ti/Au contacts.

ically etched ultrathin THz QCL. The first difference relates to the definite absence of the top n⁺ doped GaAs contact layer. The second difference relates to number of periods $N_p$ estimated to be contained within the active region. While this is straightforward to know in an epitaxially grown ultrathin THz QCLs, for a chemically etched ultrathin THz QCL this number is determined by the target etch thickness and the roughness of the wafer post etching. We measure a variation of about ±0.5 µm across the wafer, due to surface roughness introduced after thinning the 3 THz 4 QW ETH design (V674) to a thickness of ≈3 µm. Therefore, we can only estimate a range for the number of periods $N_p$. As shown in table 4.9, we estimate the ultrathin 3 THz 4 QW ETH design (V674T) to contain $N_p$ between 38-53.

<table>
<thead>
<tr>
<th>Wafer</th>
<th>Length per period, $L_p$ (nm)</th>
<th>Number of repeats, $N_p$</th>
<th>Waveguide</th>
<th>Thickness without etch stop ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V674T</td>
<td>65.6</td>
<td>38-53</td>
<td>Top (None), Bottom 100 nm (Se18)</td>
<td>3.0 ± 0.5</td>
</tr>
</tbody>
</table>

Table 4.9: Summary of the chemically etched ultra-thin QCLs

Figure 4.30(a) shows the LIV characteristics of the double-metal ridges processed from ultrathin 3 THz 4 QW ETH design (V674T), as a function of operating temperature. Compared to a threshold current density of $J_{th} \sim 155$ A/cm² in full-stack 3 THz 4 QW ETH design (V674), the threshold current density $J_{th}$ in ultrathin 3 THz 4 QW ETH design (V674T) increases to 188 A/cm² as $N_p$ reduces from 180 to 45 ± 7. It is encouraging to see clear alignment at $J_{th}$ and breaking in the IV characteristics of the ultrathin device. The threshold current density $J_{th}$ follows an exponential increase with operating temperature as shown in figure 4.30(b). From figure 4.30(a), we note that the device shows an alignment bias of 3.8 V. Accounting for the 2 x 0.7 V voltage drop across the top and
4.9 3 THz 4 QW ETH design

bottom Schottky contacts, this corresponds to an electric field of $8 \pm 1.6$ kV/cm, for an active region of height $3 \mu m \pm 0.5 \mu m$. The alignment field of the thinned wafer $V674^T$ is consistent with the alignment field observed in the full-stack 3 THz 4 QW ETH design ($V674$).

Compared to the full-stack power of $3.2 \mu W$, the power emitted from this device is quite small $\sim 64$ nW. What is promising is that the ultrathin 3 THz 4 QW ETH design ($V674^T$) operates up to a maximum temperature of 86K.

Figure 4.31 shows the differential resistance of ultrathin 3 THz 4 QW ETH design ($V674^T$), measured in pulsed mode at 10 K. If we compare this to figure 4.26, we note that the ultrathin device breaks earlier than the full-stack, i.e. $J_{NDR} = 244$ A/cm$^2$ of ultrathin 3 THz 4 QW ETH design ($V674^T$) is less than $J_{NDR} = 280$ A/cm$^2$ of full-stack 3 THz 4 QW ETH design ($V674$). A lower value of $J_{NDR}$ implies reduction in population inversion between the upper and lower lasing levels. This may perhaps occur as a consequence of surface roughness over the top of the ridge where different regions are biased differently, causing instability and forcing the device into NDR. Increase in $J_{th}$ and reduction in $J_{NDR}$, adversely impacts the dynamic range of the ultrathin 3 THz 4 QW ETH design ($V674^T$), lowering it from 44% in full-stack to 23%. The dynamic range of ultrathin 3 THz 4 QW ETH design ($V674^T$) is calculated from figure 4.31 as $J_{NDR} - J_{th} = J_{NDR} - 244 - 188 = \frac{244 - 188}{244}$.

Figure 4.32 shows the spectral characteristics of 3 THz 4 QW ETH design ($V674^T$), measured on Bruker VERTEX 80/80v in the rapid-scan mode. In agreement with the designed frequency of the 3 THz 4 QW ETH design, the first lasing mode appears at 3.15
THz, as the current density approaches $J_{th}$ which continues to be the most prominent lasing mode as the current density approaches $J_{peak} = 235 \text{ A/cm}^2$.

In both the reports of emission from ultra-thin QCLs [3, 4], the authors’ chemically etched a full-stack active region down to $\sim 1.75 - 2.8 \text{ µm}$. At the Cavendish Labs, we observed lasing from V674$^T$, obtained by chemically etching 3 THz 4 QW ETH design (V674), grown with $N_p = 180$ down to $\sim 3.0 \text{ µm}$. Note that the previous reports on ultrathin QCLs came from LO phonon designs, whereas in this work we show emission from a 4 QW BtC design, with a resonant phonon extraction stage [6].

These results are the first demonstration of a working ultrathin QCL at the Cavendish Labs, which is very promising for studying the effects of lateral confinement in nanopillars fabricated using this material. However, as is seen from the figure 4.29, wet chemical etching of the full-stack QCL leaves the final surface of the ultra-thin QCL quite rough and unsuitable for further fabrication detailed in Chapter 3. For use as a material to process nanopillars, it is important to obtain simultaneous emission from epitaxially grown ultrathin THz QCLs. It is also possible that in the early stages of growth, outgassing from the substrate, cells and manipulator results in dopant migration in the active region, which

Figure 4.31: Differential resistance of double metal ridges processed from 3 THz 4 QW ETH design (V674$^T$).
comes into play while growing the ultra-thin QCL. In an etched 'full-stack' structure, this region is removed from the active region, resulting in better performance. Perhaps, this explains the difficulty in the growth of ultra-thin THz QCLs.

The next section investigates the effect of waveguide losses on the performance of epitaxially grown ultrathin THz QCLs. For a low gain medium to overcome losses and achieve simultaneous emission, it is necessary to identify a waveguide designed for reduced repeat period QCLs.

4.10 Waveguide losses in ultrathin THz QCLs

4.10.1 Effect of contact thickness and doping on waveguide losses

In chapter 2, we discussed how active region thickness influences the waveguide losses $\alpha_w$ in a Fabry Pérot ridge. As discussed before, $\alpha_w$ depends upon the extinction coefficient, $\kappa$ and wavelength of emission, $\lambda$, as $4\pi\kappa/\lambda$. In chapter 2, we showed that the waveguide losses $\alpha_w$ increase with active region thickness. These results, calculated using the Eigen mode analysis in COMSOL v4.3, hold true for an active region with average doping $5.609 \times 10^{15} \text{ cm}^{-2}$ per period, and a 100 nm thick top and bottom $n^+$ doped GaAs contact with a doping of $5 \times 10^{18} \text{ cm}^{-2}$.
The extinction coefficient $\kappa$ and hence the waveguide losses $\alpha_w$, depend upon the thickness and average doping of the active region. Consistent with section 2.11, and unless explicitly stated, our plasmon mode calculations assume an average doping of $5.609 \times 10^{15}$ cm$^{-2}$ per period, which is the average doping of the 3 THz 4 QW ETH design.

Equally important, is the thickness and average doping of the top and bottom $n^+$ doped GaAs contacts. The role of top and bottom contacts is tabulated in 4.10. The losses, overlap and figure of merit is calculated for a Fabry Pérot waveguide in an ultrathin THz QCL of active region thickness equal to 3 $\mu$m.

<table>
<thead>
<tr>
<th>Wafer</th>
<th>Bottom Contact</th>
<th>Top Contact</th>
<th>Doping</th>
<th>Loss</th>
<th>Overlap</th>
<th>FOM</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 100</td>
<td></td>
<td></td>
<td>5 x 10^{18}</td>
<td>9.4384</td>
<td>0.9636</td>
<td>0.1021</td>
</tr>
<tr>
<td>75 75</td>
<td></td>
<td></td>
<td>5 x 10^{18}</td>
<td>8.6745</td>
<td>0.9632</td>
<td>0.1110</td>
</tr>
<tr>
<td>50 75</td>
<td></td>
<td></td>
<td>5 x 10^{18}</td>
<td>8.3675</td>
<td>0.9629</td>
<td>0.1151</td>
</tr>
<tr>
<td>3 THz 4 QW ETH (V674)</td>
<td>100 100</td>
<td></td>
<td>5 x 10^{18}</td>
<td>8.2749</td>
<td>0.9640</td>
<td>0.1164</td>
</tr>
<tr>
<td>75 0</td>
<td></td>
<td></td>
<td>5 x 10^{18}</td>
<td>7.8950</td>
<td>0.9627</td>
<td>0.1219</td>
</tr>
<tr>
<td>50 0</td>
<td></td>
<td></td>
<td>5 x 10^{18}</td>
<td>7.5897</td>
<td>0.9624</td>
<td>0.1268</td>
</tr>
<tr>
<td>2.7 THz 3 QW Paris (V671, W0798, V692)</td>
<td>75 75</td>
<td></td>
<td>2 x 10^{18}</td>
<td>10.5091</td>
<td>0.9618</td>
<td>0.0915</td>
</tr>
<tr>
<td>3 THz 3 QW Paris (V702), 3 THz 4 QW MIT (V704)</td>
<td>50 75</td>
<td></td>
<td>2 x 10^{18}</td>
<td>9.9126</td>
<td>0.9617</td>
<td>0.0970</td>
</tr>
<tr>
<td>75 0</td>
<td></td>
<td></td>
<td>2 x 10^{18}</td>
<td>8.7998</td>
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<td>0.1093</td>
</tr>
<tr>
<td>50 0</td>
<td></td>
<td></td>
<td>2 x 10^{18}</td>
<td>8.2127</td>
<td>0.9619</td>
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</tr>
<tr>
<td>Ideal</td>
<td>0</td>
<td>0</td>
<td>None</td>
<td>7.1166</td>
<td>0.9617</td>
<td>0.1351</td>
</tr>
</tbody>
</table>

Table 4.10: Summary of waveguide losses at 3 THz of a 100 $\mu$m wide metal-metal waveguide ridge in a 3 $\mu$m active region, with an average doping of $5.609 \times 10^{15}$ cm$^{-2}$, per period calculated using COMSOL v4.3. See text for explanation of colors.

Table 4.10 reveals interesting trends in the waveguide losses $\alpha_w$ and mode overlap $\Gamma$. Among the tabulated waveguide configurations, a top and bottom contact of 75 nm thickness, doped to a carrier concentration of $2 \times 10^{18}$ cm$^{-2}$ shows the highest waveguide losses at 10.5091 cm$^{-1}$ and the lowest figure of merit (FOM) at 0.0921 cm. On closer inspection, a top and bottom contact of any thickness, doped at $2 \times 10^{18}$ cm$^{-2}$ introduces higher losses, when compared to contacts of same thickness but a higher doping of $5 \times 10^{18}$ cm$^{-2}$.

Note that the waveguide configuration highlighted in blue was actually employed in double metal ridges processed from 2.7 THz 3 QW Paris designs (V671, W0798, V692), see table 4.3. It is therefore very likely that the higher optical losses influenced the emission from these wafers. While the exact values indicated in table 4.10 would vary from design to design, i.e. it would depend upon the average doping per period, the general trend
4.10 Waveguide losses in ultrathin THz QCLs

would remain the same. Correcting the results shown in blue for the 2.7 THz 3 QW Paris designs (V671, W0798, V692), with each period doped at $6.264 \times 10^{15}$ cm$^{-2}$, we obtain a waveguide loss of $11.358 \text{ cm}^{-1}$ and a figure of merit (FOM) of $0.0847$ for a 3 µm thick active region.

While the waveguide configuration highlighted in green, employed in double metal ridges processed from 3 THz 3 QW Paris design (V702) and the 3 THz 4 QW MIT design (V704) performs better than the one used in 2.7 THz 3 QW Paris designs (V671, W0798, V692), it is still extremely lossy. As before, correcting the results for 3 THz 3 QW Paris design (V702) and 3 THz 4 QW MIT design (V704), we obtain waveguide losses $\alpha_w = 10.1359 \text{ cm}^{-1}$ and $9.7694 \text{ cm}^{-1}$, given an average doping of $5.782 \times 10^{15}$ cm$^{-2}$ and $5.499 \times 10^{15}$ cm$^{-2}$, respectively.

These losses are higher than the losses incurred in the waveguide configuration used in 3 THz 4 QW ETH design (V674$^T$), shown in red in table 4.10. These results indicate that perhaps, apart from growth problems, the n$^+$ doped GaAs contact geometry and doping influenced the observation of emission from ultrathin THz QCLs discussed in this chapter.

The Eigen mode analysis of plasmon mode solutions listed in table 4.10 further implies that the best waveguide configuration exists when there are no n$^+$ doped GaAs contacts. This is highlighted in pink in table 4.10. Compared to the poorest waveguide (75 nm/75 nm, $2 \times 10^{15}$), the FOM of ultrathin THz QCLs without the top and bottom contacts, improves by $\sim 40 \%$. Note, that the doped contacts only play a role in the laser performance by improving the current injection if they are ohmic. For a Schottky-contact on either sides of the active region, these layers only add to additional losses within the gain medium.

We next discuss the effect of top contact removal on plasmonic mode, in full-stack and ultrathin THz QCLs.

### 4.10.2 Effect of removal of top contact on waveguide losses

In table 4.10, we showed that a double metal waveguide in an ultrathin THz QCL, which consists of a bottom n$^+$ GaAs contact of 100 nm thickness, doped with a carrier concentration of $5 \times 10^{15}$ cm$^{-2}$ and top contact removed, performs better than a waveguide which consists of a top and bottom n$^+$ GaAs contact of 100 nm thickness, doped with a carrier concentration of $5 \times 10^{15}$ cm$^{-2}$. Here, we probe how the performance varies over the thickness of the active region, assuming the average doping of the 3 THz 4QW ETH design.

Figure 4.33 plots the key defining features of the plasmon mode i.e. waveguide losses, overlap, figure of merit and effective refractive index, varying as a function of active region thickness. The plasmon modes have been calculated for the case of double-metal ridges,
which are 100 µm and 150 µm wide, with and without an $n^+$ doped GaAs layer. In the case of 100 µm (150 µm) wide ridge, with a top $n^+$ contact, the waveguide losses increases from 8 cm$^{-1}$ to 10.5 cm$^{-1}$ as the active region thickness is reduced from 11.8 µm to 2 µm.

![Figure 4.33](image)

Figure 4.33: (a) Waveguide losses (b) Optical overlap (c) Figure of merit (FOM) (d) Real part of the refractive index, Re($n$), as a function of active region thickness with an average doping of $5.609 \times 10^{15}$ cm$^{-2}$ per period, calculated using COMSOL v4.3.

An interesting point to note from figure 4.33 is the nonlinear reduction in waveguide losses by removing the top $n^+$ doped GaAs contact, as a function of active region thickness. This decrease in waveguide losses is particularly significant in thin active regions, with $\alpha_w$ reducing by about 22.7 % by etching the top contact in an active region of thickness 2 µm. In the case of full-stack active region, this decrease in loss is only about 6.2 %. By removing the top contact, we also increase the overlap of the plasmon mode with the gain-medium, thus improving the figure of merit (FOM) defined as $FOM = \Gamma/\alpha_w$. Note that in a low gain medium such as the ultra-thin QCL, it is crucial to reduce the waveguide loss $\alpha_w$ and increase the FOM for improved laser performance.

From figure 4.33(a), we can calculate the ratio $\alpha_w(V674^T)/\alpha_w(V674)$ to be 1.128,
where $\alpha_w(V674^T)$ is the waveguide losses associated with a 100 $\mu$m wide double-metal ridge \textit{without} the top n$^+$ doped contact layer processed from 3 THz 4 QW ETH design and $\alpha_w(V674)$ is the waveguide losses associated \textit{with} a 150 $\mu$m wide double-metal ridge with the top n$^+$ doped contact layer processed from 3 THz 4 QW ETH design. This ratio matches closely with the ratio of the respective threshold current density, defined as $J_{th}(V674^T)/J_{th}(V674)$. From figures 4.26 and 4.31, we estimate the ratio of the threshold current density to be 1.2, which agrees with eqn. 4.3 assuming that the mirror losses $\alpha_m$ are constant.

The same analysis can easily extend to a different active region design. While the general trend remains as shown in figure 4.33, an active region with average doping higher than the 3 THz 4 QW ETH design, such as the 2.7/3 THz 3 QW Paris design leads to higher waveguide losses. On the other hand, an active region with average doping less than the 3 THz 4 QW ETH design, such as the 3 THz 4 QW MIT design leads to lower waveguide losses.

We now move on to discuss the problem of spontaneous emission measurement from double metal ridges.

\section*{4.11 Measurement of spontaneous emission}

In this chapter, we discussed various active region designs in an attempt to identify a suitable THz QCL structure to study lateral confinement effects. Without an optical cavity to amplify the emission, any observable electroluminescence from nanopillars in ultrathin QCLs is expected to be incoherent or spontaneous. To gain an understanding of the energy spectra of laterally confined THz QCL structures, it is necessary to compare the spontaneous emission from an array of nanopillars to a Fabry Pérot ridge processed from the same ultrathin THz QCL. As highlighted previously, the functional requirement of ultrathin THz QCLs is that they employ 3-4 QW structures, and are processed with a double metal waveguide. In this section we discuss some of the problems associated with measuring spontaneous emission from THz QCLs employing double metal waveguides, which are relevant for ultrathin THz QCLs.

Figure 4.34 shows the measurement of simultaneous emission from double-metal ridge processed from full-stack 3 THz 4QW MIT design (V705), taken in pulsed mode. From the LIV characteristics presented in section 4.8, we know that the full-stack 3 THz 4QW MIT design (V705) exhibits lasing at a $J_{th} = 755$ A/cm$^2$. The $J_{th}$, $J_{peak}$ and $J_{NDR}$ are highlighted in the LIV characteristics shown on the right in figure 4.34. Corresponding to each value of current, which is increased in steps of 20 mA starting from 1760 mA, i.e. $J = 782$ A/cm$^2$
(just above lasing threshold) to a current of 2080 mA, i.e. $J = 924 \text{ A/cm}^2$ (just above NDR), the spectra is recorded in an FTIR set-up using rapid-scan mode. Just above the threshold, we note the appearance of a lasing mode at 3.14 THz, at $J = 782 \text{ A/cm}^2$. At a current of 1820 mA, i.e. $J = 808 \text{ A/cm}^2$, we observe the appearance of a second mode at 3.22 THz, which is the prominent mode at the peak current density. This is in agreement with the design frequency of 3 THz 4QW MIT design (see, $E_{ul} = 13 \text{ meV} = 3.14 \text{ THz}$ in table 4.6).

Figure 4.34: Frequency spectra of full-stack 3 THz 4QW MIT design (V705), taken above lasing threshold using FTIR spectroscopy in rapid-scan mode. Shown on the right, are LIV characteristics of the same device measured in pulsed mode, at an operating temperature of 10 K.

The measurement of spontaneous emission from the same double-metal ridge processed from full-stack 3 THz 4QW MIT design (V705) can be challenging to observe as it is much weaker and broader than the simultaneous emission of a laser. Measurement of spontaneous emission makes use of a more sensitive, lock-in based technique discussed in section 4.4.3.2. In this technique, the FTIR is operated in the step-scan mode. Figure 4.35 shows the step-scan measurements of the device shown in Figure 4.34. At a current of 1675 mA, i.e. $J = 744 \text{ A/cm}^2$, the device is just at the threshold current density ($J_{th} = 755 \text{ A/cm}^2$) and exhibits a broad electroluminescence centered at 3.14 THz with a full-width-half-maxima (FWHM) of $\sim 100 \text{ GHz}$. Below the threshold, at 1663 mA ($J = 739$
4.11 Measurement of spontaneous emission

A/cm²), any spontaneous emission is hardly discernable from the noise floor. This might not be very surprising, considering the optical power due to simultaneous emission from the double metal, full-stack 3 THz 4 QW MIT design (V705) was only 2.5 µW. One of the reasons associated with reduced power output is inherent in the choice of waveguide - the double metal configuration. Owing to impedance mismatch and large beam divergence, only a fraction of the emitted radiation is collected by the detector.

Figure 4.35: Electroluminescence measurements of full-stack 3 THz 4 QW MIT design (V705), at and below threshold

Figure 4.36 shows a survey of reported peak powers (due to simultaneous emission) in THz QCLs. The first point to note from figure 4.36, is that at a constant design frequency of 3 THz, the BtC designs are more powerful than the resonant LO phonon designs. The second point to note is that at this frequency, THz QCLs processed in an SP waveguide configuration emit higher power (∼ 100 mW, pulsed, BtC) as compared to THz QCLs processed in a double metal (DM) waveguide configuration (∼ 2 mW, cw, LO phonon), indicating that QCLs processed in an SP waveguide are more powerful. The highest record of power across frequencies is shared by THz QCLs in SP waveguide configuration, i.e. 250 mW in LO phonon [151] and 100 mW in BtC design [152].

Interestingly, spontaneous emission has only been observed from THz QCLs, processed in the more powerful SP waveguide configuration [37, 41, 153]. In our survey of previous work, we have not found reports of spontaneous emission i.e. below threshold measurement of THz QCLs in a DM waveguide configuration. This may perhaps imply that below threshold emission of DM THz QCLs is weaker than the sensitivity of currently available,
commercial detectors. Measurement of spontaneous emission is an area, which we identify as one of the major experimental challenges in (i) the characterization of ultrathin THz QCLs and (ii) the study of lateral confinement in ultrathin THz QCLs.

### 4.12 Summary and Conclusions

One of the first building blocks in the study of lateral confinement effects in QCLs is the demonstration of an ultra-thin QCL, with an active region thickness that is suitable for top down processing. In chapter 3, we identified this thickness to be $\leq 3.5 \mu m$, to process nanopillars of a physical radius $\leq 200$ nm. In this chapter, we demonstrate simultaneous emission from an ultrathin THz QCL, which has an active region thickness of $\approx 3 \mu m$. We achieved this by chemically etching a full-stack, active region (3 THz 4 QW ETH design), post growth. Compared to the full-stack QCL (thickness $\sim 11.8\mu m$), the threshold current density $J_{th}$ increases by 1.22 times as the thickness is scaled down to $3 \mu m$. Also associated with the decrease in the number of repeat periods, is the proportional decrease in power. The strict requirements of nanopillar processing require the ultrathin QCL to have a smooth surface instead of being chemically thinned down. This surface is typically associated with epitaxially grown layers of III-V materials. However, in spite of lasing from full-stack 3-4 quantum well QCLs, challenges in the growth of ultra-thin QCLs have so far limited this work. We also note that the top doped n$^+$ contact plays a significant role in waveguide losses, and an optimum waveguide geometry is necessary to obtain lasing from as grown ultrathin QCLs.
Chapter 5

Graphene based THz optics

5.1 Introduction

Chapters 2 to 4 focussed on achieving a higher temperature performance of THz QCLs, through lateral confinement. In this chapter we change gears from THz QCLs to THz optics based on graphene, as an attempt towards closing the THz gap. At the same time, realizing that THz QCLs are advocated as the only powerful, compact sources of THz radiation, we position our work on graphene towards optical elements that may in future be compatible with the frequencies emitted by most common THz QCLs (2-3 THz).

In section 1.5.3, we discussed that the optical response of graphene can be tuned externally by changing the carrier concentration. By controlling the electrostatic bias on external gates, the carrier concentration $n$ in graphene can be pushed to a level of $\sim 10^{12} - 10^{13}\ \text{cm}^{-2}$. It is at this carrier concentration, the plasmon resonance in graphene appears in the infrared (IR) and terahertz (THz) range [154, 155]. While this can in principle be attained at room temperature in graphene, it requires cryogenic capabilities to achieve the same in two dimensional electron gases [69]. Plasmons in graphene were imaged recently using near-field microscopy by exciting graphene with an IR pulse [156]. The purpose of this chapter is to first spectroscopically investigate the plasmonic properties of graphene at THz frequencies. After a background discussion on the electronic structure and properties of graphene, we look at THz time domain spectroscopy of graphene under different gating configurations. The second half of the chapter focusses on two applications of graphene to THz optics. In the first instance, we attempt to engineer the plasmonic frequency by patterning graphene into a one dimensional grating. This may have potential for tunable filters operating in the THz range. In the second scenario, we tune the free-carrier THz absorption by graphene with an external bias, and exploit this to indirectly modulate the
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radiation from a THz QCL.

5.2 Electronic structure of graphene

Graphene, a 2D allotrope of carbon is $sp^2$ hybridized (with one $s$ and two $p$ orbitals) which leads to a trigonal planar structure. The carbon atoms are held together with a sigma $\sigma$ bond, at a separation of 1.42 Å. The unaffected $p$ orbital is perpendicular to the planar structure, which can bind covalently with neighbouring carbon atoms leading to the formation of a $\pi$ bond. Figure 5.1 compares the structure of graphene with graphite, which is a 3D allotrope of carbon, carbon nanotubes which can be viewed as a rolled up sheet of graphene and fullerenes where carbon atoms are arranged spherically.

Figure 5.1: Graphene (top left) is a honeycomb lattice of carbon atoms. Graphite (top right) can be viewed as a stack of graphene layers. Carbon nanotubes are rolled-up cylinders of graphene (bottom left). Fullerenes (C$_{60}$) are molecules consisting of wrapped graphene by the introduction of pentagons on the hexagonal lattice. Figure from [157]

The dispersion relation of graphene can be derived from the tight-binding approach. As shown in figure 5.2, the structure of graphene can be considered to have a triangular

Figure 5.2: Honeycomb lattice and its Brillouin zone. Figure from [157]
5.2 Electronic structure of graphene

lattice with a basis of two atoms per unit cell. The lattice vectors may then be written as

\[ a_1 = \frac{a}{2}(3, \sqrt{3}), a_2 = \frac{a}{2}(3, -\sqrt{3}) \quad (5.1) \]

where \( a = 1.42 \text{Å} \) is the carbon-carbon distance. The reciprocal-lattice vectors are given by

\[ b_1 = \frac{2\pi}{3a}(1, \sqrt{3}), b_2 = \frac{2\pi}{3a}(1, -\sqrt{3}) \quad (5.2) \]

The two points \( K \) and \( K' \) at the corners of the graphene Brillouin zone are called Dirac points. Their positions in momentum space are given by:

\[ K = \left( \frac{2\pi}{3a}, \frac{2\pi}{\sqrt{3}a} \right), \quad K' = \left( \frac{2\pi}{3a}, -\frac{2\pi}{\sqrt{3}a} \right) \quad (5.3) \]

The three nearest-neighbour vectors in real space are given by

\[ \delta_1 = \frac{a}{2}(1, \sqrt{3}), \delta_2 = \frac{a}{2}(1, -\sqrt{3}), \delta_3 = -a(1,0) \quad (5.4) \]

while the six second-nearest neighbours are located at \( \delta'_1 = \pm a_1, \delta'_2 = \pm a_2, \delta'_3 = \pm (a_2, -a_1) \).

Considering that electrons can hop to both nearest and next-nearest-neighbour atoms, the tight-binding Hamiltonian for electrons in graphene has the form given below.

\[ H = -t \sum_{<i,j>,\sigma} (a_{\sigma,i}^\dagger b_{\sigma,j} + H.c) - t' \sum_{<<i,j>>,\sigma} (a_{\sigma,i}^\dagger a_{\sigma,j} + b_{\sigma,i}^\dagger b_{\sigma,j} + H.c) \quad (5.5) \]

Here, \( a_{i,\sigma}(a_{i,\sigma}^\dagger) \) annihilates (creates) an electron with spin \( \sigma \) (\( \sigma = \uparrow, \downarrow \)) on site \( R_i \) on sublattice A. Similarly, \( b_{i,\sigma}(b_{i,\sigma}^\dagger) \) annihilates (creates) an electron with spin \( \sigma \) (\( \sigma = \uparrow, \downarrow \)) on site \( R_i \) on sublattice B. The nearest-neighbour hopping energy (between different sublattices A and B) is given as \( t = 2.8 \text{eV} \) and the next nearest-neighbour hopping energy (hopping in the same sublattice) is given as \( t' = 0.1 \text{eV} \). The energy bands derived from this Hamiltonian can be written as:

\[ E_{\pm}(k) = \pm t \sqrt{3 + f(k)} - t'f(k) \quad (5.6) \]

where \( f(k) \) is given as

\[ f(k) = 2\cos(\sqrt{3}k_y a) + 4\cos \left( \frac{\sqrt{3}}{2}k_y a \right) \cos \left( \frac{3}{2}k_y a \right) \quad (5.7) \]
In eqn. 5.6 the plus sign applies to the upper ($\pi^*$) band and the minus sign applies to the lower ($\pi$) band. Figure 5.3 shows the complete band structure of graphene. For $t' = 0$, the spectrum is symmetric around zero energy. Figure 5.3 also shows the band structure close to the Dirac points (K or K' on Brillouin zone). Close to the Dirac point, the dispersion relation can be obtained by expanding the full band structure (eqn. 5.6 and eqn. 5.7) close to K (or K') vector as $k = K + q$, where $|q| \ll |K|$. This leads to following relation for energy dispersion in graphene:

$$E_{\pm}(q) \approx \pm v_F|q| + O\left((q/K)^2\right)$$  \hspace{1cm} (5.8)

Here, $q$ is the momentum measured relatively to the Dirac points and $v_F$ is the Fermi velocity $= 3ta/2$, with a value $v_F = 1 \times 10^6$ m/s.

The dispersion relationship of graphene is remarkably different from traditional semiconductor materials, which follow a quadratic response given as $E(q) = q^2/2m_e^*$, where $m_e^*$ is the effective electron mass. Unlike graphene where the Fermi velocity is independent of energy, the velocity in conventional materials varies with energy as $v = \sqrt{2E/m_e^*}$.

The unique band structure of graphene leads to many interesting electronic and optical properties, which is beyond the scope of this work. Some of these properties are reviewed in references [72, 157]. In the next section, we discuss the Drude model of conductivity.
5.3 Optical conductivity of graphene

According to the free electron (Drude) model for a conventional system (carrier concentration $n$, mass of electron $m_e^*$, the frequency dependent conductivity can be written as

$$\sigma(\omega) = \frac{\sigma_{dc}}{1 - i\omega\tau} \quad (5.9)$$

Here $\sigma_{dc} = \frac{ne^2}{m_e^*}$ is the Drude dc conductivity and $\tau$ is the relaxation time. The above can be rearranged in terms of the Drude weight $D$ and the scattering constant $\Gamma$, where, $D = \frac{\pi n e^2}{m_e^*}$ and the scattering constant $\Gamma$ is the inverse of the relaxation time $\tau$. This leads to the following expression for ac conductivity.

$$\sigma(\omega) = \frac{iD\Gamma}{\pi(\omega + i\Gamma)} \quad (5.10)$$

The optical conductivity $\sigma(\omega)$ of graphene consists of two contributions. The first contribution, $\sigma_{\text{intra}}(\omega)$ arises from intraband transitions. The second contribution arises from the interband transitions $\sigma_{\text{inter}}(\omega)$ [158]. The Drude model can be applied to the intraband optical conductivity of graphene [159]. The difference in free electron model for a conventional two dimensional material and graphene arises in the Drude weight. In the case of graphene the Drude weight has the value $D = \frac{\nu e^2}{h}\sqrt{\pi n}$, when electron-electron interactions are neglected.

Experimental observations in graphene confirm the Drude like response of the intraband conductivity. However, the Drude weight extracted from experiments is significantly lower than theoretical predictions [159, 160]. Figure 5.4 shows the experimentally derived Drude weight for graphene from AC measurements, in comparison to the theoretical results. Note, that at high bias, i.e. high carrier concentration, the experimentally derived Drude weight deviates from the theoretical results based on Boltzmann theory. Furthermore, the experimental results show an electron-hole asymmetry that is not explained by the Boltzmann theory [159].

5.4 Plasmons in graphene

The plasmonic modes in graphene were first calculated by Hwang et. al from a detailed calculation of the dielectric function $\epsilon(q,\omega)$ at an arbitrary wave vector $q$ and frequency $\omega$
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Figure 5.4: A comparison of experimentally derived Drude weight with the Drude weight theoretically predicted from Boltzmann theory, as a function of gate bias \[159\].

The zeros to the dynamical dielectric function $\epsilon(q, \omega)$ yields the plasmonics modes $\omega_p(q)$ in graphene.

In the long wavelength limit ($q \to 0$), the plasmon resonance in monolayer graphene varies relativistically with carrier concentration, $n$ as:

$$\omega_p(q \to 0) = \left( \frac{e^2 v_F q}{\kappa \hbar} \sqrt{\frac{\pi n g_s g_v}{\kappa h^*}} \right)^{1/2}$$ \hspace{1cm} (5.11)

The spin ($g_s$) and valley degeneracies ($g_v$) are both equal to 2. The dielectric constant of the surrounding medium, $\kappa$ appears as an average of the top and bottom dielectric layers. In the case of a two dimension electron gas, the plasmon mode can be calculated as:

$$\omega_p(q \to 0) = \left( \frac{2\pi n e^2}{\kappa m_e^*} q \right)^{1/2}$$ \hspace{1cm} (5.12)

Note that the plasmonic frequency has a square root dependence in the case of a conventional two dimensional electron gas (eqn. 5.12). In the case of graphene the plasmonic frequency varies as $n^{1/4}$ (eqn. 5.11). Plasmons in graphene were imaged recently using near-field microscopy by exciting graphene with an infrared pulse \[156\]. Interestingly, in the presence of a gate potential, the plasmon waves may be modified by the electric field to have a linear dispersion relation, $\omega_p = sq$, where $s$ is the wave velocity \[161, 162\].
5.5 Growth and processing

Historically, graphene was first isolated from graphite by mechanical exfoliation \cite{163}. High-quality graphene films obtained from exfoliation can have mobilities exceeding 15,000 cm\(^2\)/Vs, however their size is limited up to 100 \(\mu\)m. Graphene flakes obtained from this method can be very difficult to identify over a large area. For many electronic and optical device applications, it is necessary to use graphene with an area greater than a few hundred microns. For use in THz optical elements, obtaining an area larger than the beam waist is a challenge. As described in previous chapters, the most common THz QCLs operate in the wavelength region of 100-150 \(\mu\)m (2-3 THz). The radiation from these sources can at best be focussed to a beam size of a few mm. This implies that graphene obtained through exfoliated means is not suitable for THz applications.

The other alternatives to obtaining graphene include epitaxial growth of graphene and chemical vapour deposition of graphene. Both these processes allow for a contiguous sheet of large area of graphene. The first process involves thermal decomposition of SiC, leaving a layer of carbon behind on the surface \cite{164}. Theoretically, the surface area of the graphene sheet processed using this annealing method is only limited by the size of the SiC wafer, which can be as large as 100 mm. The second process involves chemical vapor deposition of carbon by passing a mixture of methane and hydrogen over a Cu foil in a heated furnace \cite{165}. The size of the graphene sheet deposited over the foil is controlled by the size of the Cu foil used in the furnace. In fact, using chemical vapour deposition Bae et al demonstrated graphene sheets that were about 700 mm across \cite{166}.

In this work, we use graphene grown by chemical vapour deposition (CVD) means. This is described below.

5.5.1 Chemical vapour deposition (CVD) of graphene

Figure 5.5 illustrates the process of chemical vapour deposition over foils composed of transition metals such as Cu. A mixture of methane and hydrogen flows through a furnace that is heated to up to 1000\(^\circ\)C. The reaction causes the carbon atoms from methane to chemically adsorb on the Cu surface. Once a carbon atom occupies a position on the surface, it pushes the other carbon atoms to the side, limiting the thickness of the carbon atoms to a monolayer. As the temperature is lowered the carbon crystallizes to graphene. Crystallization of graphene can initiate in parallel at random locations on the surface before the entire sheet of graphene has formed a lattice. These random locations are referred to as nucleation sites, from which the crystal grains grow, coalesce and merge to form a complete sheet of graphene.
Naturally, this kind of growth creates boundaries between different grains that merge. After the growth, the crystalline grains are called domains and the boundaries between them are called domain boundaries. These domain boundaries represent defects in the graphene sheet. This is because, along these boundaries, the bonding of carbon atoms does not follow the simple Bravais lattice from a repetition of the unit cell. These grain boundaries are determined by the crystallinity of the Cu foil and the growth conditions. While they can adversely influence the electrical and mechanical properties of the graphene sheet, they can also effect the optical properties of the graphene sheet.

In this work, CVD graphene was obtained from Stephan Hoffman’s group, grown by Dr. Kidambi in the Centre for Advanced Photonics Engineering, Engineering Department, Cambridge [7]. Kidambi et. al report that that CVD graphene on Cu is not inherently self-limited to a single layer. Rather, this is dependent upon the CVD conditions and growth kinetics. These conditions influence the density of nucleation sites, the percentage of multilayer nuclei and the uniformity of the film. Figure 5.6 shows the scanning electron micro-
5.5 Growth and processing

graphene used in this work. The thickness of the copper foil used for growth was 25 \( \mu \text{m} \), and the purity of the Cu foil was 99.999 \%. Note the nucleation and stitching of grain boundaries in CVD graphene. From the micrograph, Kidambi et al estimated the graphene sheet to contain monolayer domains ranging from 30 to 40 \( \mu \text{m}^2 \), with a few isolated areas 2-4 \( \mu \text{m}^2 \) of multilayer graphene.

Graphene deposited over the copper foil can be transferred to any arbitrary substrate for characterization or post processing. This is discussed below.

5.5.2 Transfer of CVD graphene to arbitrary substrate

Figure 5.7 describes the process flow involved in the transfer of graphene from the Cu foil to an arbitrary substrate. After the graphene is removed from the CVD chamber, a layer of PMMA is drop casted on top of it, see figure 5.7(a-b). Following this, the Copper foil is removed in Ferric Chloride, figure 5.7(c). The film of graphene supported by PMMA floats on top of the water, which is scooped using the new substrate, see figure 5.7(d). Finally, the PMMA is removed in acetone, figure 5.7(e).

Figure 5.7: Process schematic: Transfer of as grown CVD graphene onto the substrate.

At this point, it is important to comment on the choice of substrate used for the transfer of graphene. The choice of substrate is dictated by the type of measurements to be performed. Transport measurements using the backgate require the substrate to be doped such that the carrier concentration in graphene can be altered, see section 5.6. Optical measurements on the other hand, require that the substrate be transparent to the incident signal, see section 5.7. An ideal substrate should meet both the requirements.

For this work, we were provided with graphene samples transferred on p-doped Si
wafer covered with a 300 nm thick SiO$_2$ layer. The Si wafer, with $\langle 100 \rangle$ crystal orientation, had a thickness of 525 $\mu$m $\pm$ 25 $\mu$m and a resistivity of 1 to 100 ohm-cm. This substrate can be used for both transport as well as the optical measurements.

### 5.5.3 Characterization of growth quality

The quality of graphene growth was characterized extensively by Kidambi et. al and can be referred in [7]. Here, we provide the Raman spectra and the atomic force microscope image of graphene, to illustrate that the CVD graphene used is indeed a monolayer and of good quality. Figure 5.8 shows the Raman spectra of the CVD graphene obtained from a 532 nm excitation. The spectra is characteristic of monolayer graphene, with a G peak at 1580 cm$^{-1}$ and a 2D peak at 2700 cm$^{-1}$ [168]. The absence of a D peak at 1360 cm$^{-1}$ shows that graphene is free from a large number of defects. The ratio between the 2D peak and the G peak ($I_{2D}/I_G$) is around 2.35, and the ratio between the D peak and the G peak ($I_D/I_G$) is around 0.1.

![Figure 5.8: Raman spectroscopy of monolayer graphene, with 2D peak higher than G peak. Data was provided by Piran R. Kidambi](image)

Figure 5.9 shows the atomic force microscope (AFM) image of graphene. The bright specks in the image correspond to PMMA residue after rinsing in acetone. The bright lines in the AFM are due to wrinkles in the graphene sheet which appear during the transfer of graphene from Cu foil to the substrate.
5.5 Growth and processing

We next describe the process of device fabrication after the CVD graphene is transferred from a Cu foil to the substrate of choice, in our case SiO$_2$/Si.

5.5.4 Device fabrication post transfer

Back-gated graphene

The fabrication of a back-gated graphene device is quite straightforward. First, a large area of graphene (8 mm x 8 mm) is isolated on the wafer. A lithography step, protecting the desired area followed by an etch in the oxygen plasma cleans the edges of any residual graphene or organic matter, see figure 5.10(a-b). After a gentle rinse in acteone and IPA, another lithography step is performed which allows the deposition of metal contacts (Ti/Au) on the sides. These two contacts form the source and drain electrodes, figure 5.10(c). Note, that the contacts overlap partly with graphene and partly with the underlying SiO$_2$. The gold on the SiO$_2$ surface serves as a bondpad for the wires, so as to connect the device to the packaging board. The doped Si serves as the back-gate for the final device.

Top-gated graphene

The carrier concentration in graphene can be controlled with an additional gate. This gate is implemented on top of the device, and uses chemical gating to achieve control over the carrier concentration in graphene. While this additional gate can be implemented on top of the device, it can lead to a large leakage current. To avoid this gate leakage, we employ a coplanar gate which is separated from the graphene edge by a distance, $d \sim 200$ $\mu$m, see figure 5.11. Note that in this work we still use the term top-gate to reflect the use
Figure 5.10: Schematic diagram showing graphene (a) after transfer on SiO$_2$/Si substrate (b) after isolation (c) after deposition of metal contacts.

of an ionic gate geometry. Following the metallization of source, drain and gate contacts, a solution comprising 2 mg LiClO$_4$ in 9 mg PEO dissolved in acetonitrile, is drop casted over the device. This kind of gating was first demonstrated by Das et. al in the year 2008 [169]. While drop casting, care is taken to avoid the overlap of the LiClO$_4$ ionic gel with the source and drain contacts. We find that it is helpful to drop cast the gel while the device is on a hotplate. Finally, the device is baked overnight (> 12 hours) at 90°C.

5.6 Transport measurements of CVD graphene

Kidambi et. al extracted the transport behavior of their samples from Hall bar measurements. They estimated the sheet resistance of their samples to be in the range of 400-800 ohm and mobilities to be in the range of 2000-3000 cm$^2$V$^{-1}$s$^{-1}$. They further observed that their samples were predominantly p-doped after transfer, with a doping of a few 10$^{12}$ cm$^{-2}$ [7, 170]. The origin of this hole doping was attributed to the PMMA residue left on the surface after transfer. In this section, we independently measure the transport characteristics of CVD graphene in the presence of a back-gate and a top-gate.

Before, we go into the details of the measurement, it is useful to revisit the band structure of graphene and understand how the position of the Fermi level $E_F$ in graphene relates to the transport behavior. Figure 5.12 plots the band structure of graphene under three con-
Figure 5.11: Schematic diagram showing graphene (a) after deposition of coplanar gate, source and drain contacts (b) after drop casting of the ionic gel.

5.6 Transport measurements of CVD graphene

In the first case, graphene is pristine, i.e. the Fermi level $E_F$ is at the Dirac point. Notice, that the charge neutrality point ($V_{CNP}$), defined as the point where the charge transport transitions from predominantly hole carriers to predominantly electron carriers is at 0 V, see figure 5.12(a). In the second scenario, graphene is p-doped. This implies that the Fermi level $E_F$ is below the Dirac point, i.e. it exists in the valence band. At zero gate bias the transport is mediated by predominantly hole carriers and the charge neutrality point ($V_{CNP}$) shifts to the right, see figure 5.12(b). In the third scenario, graphene is n-doped and the Fermi level $E_F$ is above the Dirac point. In this case, the predominant charge carriers at zero gate bias are electrons. The charge neutrality point ($V_{CNP}$) occurs at a negative gate bias.

5.6.1 Results from back-gated graphene

The experimental set-up for measuring the transport behavior of graphene is similar to any field effect transistor measurement, see figure 5.13 Grounding the source contact, we apply a constant bias on the drain contact. We call this voltage, the drain-source bias ($V_{ds}$). The current flowing through graphene between the two contacts is called the drain-source current ($I_{ds}$) and is proportional to the width $W$ of the graphene channel and inversely proportional to the length $L$ of the graphene channel.
Figure 5.12: Schematic diagram of the band structure, and the corresponding electrical characteristics when (a) graphene is pristine (b) graphene is p-doped (c) graphene is n-doped.

Figure 5.13: Circuit diagram, showing source, drain and gate contacts for transport measurements.
5.6 Transport measurements of CVD graphene

The expression for the drain-source current is given by the following expression:

\[ I_{ds} = e\mu W \frac{\int_{0}^{V_{ds}} n dV}{L - \mu \int_{0}^{V_{ds}} 1/v_{sat} dV} \]  \hspace{1cm} (5.13)

where, \( \mu \) is the mobility of carriers in graphene and \( v_{sat} \) is the saturation velocity [171]. The carrier concentration \( n \), is controlled by the applied bias on the back-gate \( V_{bg} \). The relationship between \( V_{bg} \) and \( n \) can be evaluated from simple electrostatics, and is given by the following expression:

\[ V_{bg} - V_{CNP} = ne/C_{bg} \]  \hspace{1cm} (5.14)

Here, \( C_{bg} \) is the geometrical capacitance and is equal to \( \frac{\epsilon_{r} \epsilon_{0} d}{d} \). In the expression for capacitance, \( d \) is the thickness of the SiO\(_2\) layer, which is equal to 300 nm in our device and \( \epsilon_{r} \) is the dielectric constant of the SiO\(_2\) layer, which is typically equal to \( \sim 4 \). Using these values, we obtain a back-gate capacitance of 12 nF cm\(^{-2}\) for our device.

Figure 5.14: Drain-source current \((I_{ds})\) as a function of back-gate bias \(V_{bg}\), at room temperature 300 K. The drain-source voltage \(V_{ds}\) was kept constant at 0.01 V.

Figure 5.14 shows the transport characteristics of graphene at a constant drain-source bias equal to 0.01 V. The drain-source current was measured at room temperature using a Keithley SMU. The back-gate leakage current was negligible in this device and was always below 1 nA. On comparing the electrical behavior of the device to the characteristics shown...
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In figure 5.12, we infer that the graphene is p-doped. Note that the charge neutrality point is not reached even at a gate bias of +60 V. We do not apply a bias greater than +60 V to avoid device failure due to Joule heating. On extrapolating the measured characteristics (blue dashed curve), we estimate that the charge neutrality point lies at around +123 V. However, this is an overestimate of $V_{CNP}$ as the drain-source current does not reach zero in practice. Since $V_{CNP}$ lies in the range of +60 V to +123 V, we can evaluate the carrier concentration $n$ at zero bias using eqn. 5.14. This value lies in the range of $4.5 \times 10^{12}$ to $9.2 \times 10^{12}$ cm$^{-2}$, and agrees with the Hall bar estimates made by Kidambi et. al [7]. The position of the Fermi level $E_F$ at a given carrier concentration can be estimated using the equation:

$$E_F = h \nu_F \sqrt{\frac{\pi n}{n}} \quad (5.15)$$

This implies that at zero gate bias the position of the Fermi level $E_F$ is approximately 0.24 to 0.35 eV below the Dirac point. The mobility can be estimated using the formula $\mu = \sigma_{\text{sheet}}/(en)$, where $\sigma_{\text{sheet}}$ is the sheet conductance of graphene. We find that at zero gate bias, the sheet conductance ($I_{ds}/V_{ds}$) is equal to $21.8 \, e^2/h$. Assuming a carrier concentration of $4.5 \times 10^{12}$ to $9.2 \times 10^{12}$ cm$^{-2}$, we estimate the mobility of charge carriers to lie somewhere in the range of 1190 to 582 cm$^2$V$^{-1}$s$^{-1}$ at zero gate bias.

One of the major disadvantages of using a back-gate on graphene is the absence of a clear $V_{CNP}$ at accessible voltages. While we can still extract the transport parameters ($n$, $E_F$ and $\mu$) from the device behavior, it gives us a broad range of values. A $V_{CNP}$ to the right of voltage axis also implies that we can not access the electron transport in graphene using a back-gate as it requires a bias $V_{bg} > V_{CNP}$. Using an ionic gate, the $V_{CNP}$ can be made to approach zero enabling access to hole and electron transport at very low voltages. This is described below.

5.6.2 Results from top-gated graphene

In the previous scenario, access to high carrier concentrations as well as access to both types of carriers, was limited by the extremely small capacitance between the back-gate and graphene. The capacitive coupling can be enhanced dramatically by using an ionic (top) gate, see figure 5.15. In our devices we an ionic (top) gate comprising of LiClO$_4$ in Polyethylene oxide matrix. When a bias is applied, free cations (Li$^+$) accumulate near the negative electrode, creating a positive charge layer and a negative charge near the interface. This layer of charge around the electrode is called the Debye layer and is characterized by a thickness $d_{tg}$, which is approximately 1-5 nm. The capacitance between the
top gate and graphene is governed by the thickness of this Debye layer and is given by \( C_{tg} = \epsilon_r \epsilon_0 / d_{tg} \). Here, \( \epsilon_r \) is the dielectric constant of the Polyethylene oxide matrix, which is equal to 5 [169]. This results in a top-gate capacitance of about 2.2 \( \mu F \) cm\(^{-2}\). It is important to emphasize that even though the thickness of the ion gel varies across the area, the capacitance remains constant as it is dominated by a monolayer of ions, which forms the Debye layer. This technique of ionic gating has also been used by other THz groups to modulate plasmonic modes inside a QCL [172].

Figure 5.15: Schematic diagram illustrating gating using an ion gel.

Figure 5.16 shows the drain-source current \( (I_{ds}) \) of the graphene device as a function of top-gate bias \( (V_{tg}) \). These measurements were carried out using HP 4155 A semiconductor parameter analyser at room temperature. The drain-source bias \( (V_{ds}) \) was constant at 0.1 V. The gate voltage was ramped at a rate of 20 mV/min.

Note that we can access both electrons and holes using the top-gate configuration. The forward and reverse voltage sweeps show hysteresis in the transconductance behavior. We note that the charge neutrality point in the forward voltage sweep \( V_{CNP}^f = 0.04 \) V is less than the charge neutrality point in the reverse voltage sweep \( V_{CNP}^r = 0.14 \) V. This hysteresis is dependent upon the ramp rate. Transfer of holes (electrons) from the ionic gel to graphene can result in the right (left) shift of conductance, which can causes negative hysteresis [173]. In our devices, we observe a positive hysteresis with gate voltage sweep. Positive hysteresis occurs when the ion changes the local electrostatic potential around the graphene, thereby pulling more charges from the contacts [173]. Figure 5.17 shows the transconductance behavior of top-gated graphene at different ramp rates. At large gate bias \( (V_{tg} \approx 0.8 \) V\), the drain-source current is nearly five times larger when the voltage is ramped at 50 mV/min as opposed to when it is ramped at 5 mV/ms. The effect of the ramp rate is also seen on the area under the hysteresis curve, which is larger when the voltage is ramped at 5 mV/ms, as compared to 50 mV/min.

From figure 5.16 and figure 5.17, we also observe that at large gate bias, the drain-
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Figure 5.16: Drain-source current ($I_{ds}$) as a function of top-gate bias $V_{tg}$, at room temperature 300 K. The drain-source voltage $V_{ds}$ was kept constant at 0.1 V. The gate voltage was ramped from -0.5 V to 0.5 V at a rate of 20 mV/min.

Figure 5.17: Drain-source current ($I_{ds}$) as a function of top-gate bias $V_{tg}$, at room temperature 300 K. The drain-source voltage $V_{ds}$ was kept constant at 0.1 V. The gate voltage was ramped from 0 to 0.8 V at a rate of 50 mV/min, 100 mV/min and 5 mV/ms. For more clarity, the fastest scan is shown separately in the inset.
source current grows slowly and at times shows a dip. Perhaps, this occurs due to the chemical doping of graphene. This phenomenon is different from inducing a surface charge at the interface as it can alter the sheet conductance of graphene.

Figure 5.18: (a) Top-gate leakage current ($I_{gs}$) as a function of top-gate bias $V_{tg}$. The drain-source voltage $V_{ds}$ was kept constant at 0.1 V. (b) Drain-source current ($I_{ds}$) as a function of drain-source bias $V_{ds}$, at different $V_{tg}$.

From figure 5.18(a), we observe that the gate leakage current $I_{gs}$ through an ionic gate is higher than the leakage through a conventional dielectric. This is because an ionic gel is not a complete insulator. We note that the leakage current increases with voltage, i.e. when the top-gate bias is increased from 0 to 0.5 V, the gate-source current increases from 0 to 0.3 μA. However, this increase is nearly two orders less than the increase in the drain-source current, which changes from approximately 15 μA to 45 μA when the top-gate bias is increased from 0 to 0.5 V, see figure 5.16. This implies that the transconductance characteristics observed in figure 5.16 is indeed indicative of ionic gating. Figure 5.18(b) shows the $I_{ds}$ as a function of $V_{ds}$. The dashed vertical line shown in figure 5.18(b) compares $I_{ds}$ at $V_{ds} = 0.1$ V, for different $V_{tg}$ and agrees with results shown in figure 5.16.

The asymmetry in the drain-source current with respect to the charge neutrality point agrees with reports of electron-hole asymmetry observed by Horng et al. [159]. However, contact effects may also introduce an asymmetry in the drain-source current. Note that in a top-gated device, the ionic gel does not overlap with the source and drain contacts. Therefore, the ionic gel does not completely cover the graphene sheet, see figure 5.11. These ungated regions near the contacts add to the resistance and hence lead to the asymmetry shown in figure 5.16 and figure 5.18(b) [174]. The transport characteristics although similar in form can vary from device to device. Therefore it is useful to quote the
gate bias in terms of $V_{tg} - V_{CNP}$. In our devices, we typically observe a charge neutrality point between 0 to $+0.5$ V, suggesting slight p-doping at zero gate bias.

![Graphene Based THz Optics](image)

Figure 5.19: Transport parameters in a top-gated graphene field effect transistor, showing (a) carrier concentration, $n$ (b) Fermi level, $E_F$ and (c) mobility, $\mu$ of charge carriers.

Below, we extract the transport parameters ($n$, $E_F$ and $\mu$) from the device behavior, shown in figure 5.19. The carrier concentration $n$ is related to top-gate bias as:

$$V_{tg} - V_{CNP} = \frac{h\nu_F \sqrt{\pi n}}{e} + ne/C_{tg}$$

(5.16)

Given the carrier concentration, the Fermi level and the mobility can be calculated using $E_F = \frac{h\nu_F \sqrt{\pi n}}{e}$ and $\mu = \sigma_{\text{sheet}}/(en)$, where $\sigma_{\text{sheet}}$ is the sheet conductance of graphene.

We note that carrier concentrations approaching $1x10^{13}$ cm$^{-2}$ can be easily achieved in both directions, on application of bias as low as 0.36 V referred to the charge neutrality point, figure 5.19(a). At this bias, the fermi level $E_F$ is 0.368 eV above or below the Dirac point, depending upon the polarity (see figure 5.19(b)). A consequence of high
carrier concentration is that the mobility of the carriers reduces. In a top-gated graphene device, the mobility may also be influenced by the disorder introduced by the ions. This is seen in the reduction of mobility from 1190 (582) cm$^2$V$^{-1}$s$^{-1}$ in the case when no top-gate is implemented (section 5.6.1), to approximately 280 cm$^2$V$^{-1}$s$^{-1}$ when a top-gate is implemented but no voltage on the top-gate is applied ($V_{tg} = 0$), figure 5.19(c).

We now move on to discuss the optical response of CVD graphene at THz frequencies. The optical response of graphene is studied using THz time domain spectroscopy (THz TDS). In the next section, we first describe the experimental set-up used for spectroscopy and then discuss the results obtained from graphene.

5.7 THz time domain spectroscopy (THz TDS) of CVD graphene

THz time domain spectroscopy (THz TDS) uses the coherent detection of broadband pulses, at room temperature to analyse the spectral response of materials [175]. The THz TDS set-ups used in this work are based in the Department of Chemical Engineering and Biotechnology, Cambridge. These set-ups are routinely used by to characterize biochemical molecules and pharmaceutical drugs which have sensitivity in the THz spectrum, and can easily be adapted to make optical measurements on thin films such as graphene as a function of bias.

THz TDS systems can be operated in the transmission mode as well as reflection mode. Below we provide description for both the set-ups.

5.7.1 Experimental set-up in transmission mode

The THz TDS system comprises of an ultrafast femtosecond (12 fs) pulse laser, with a repetition rate of 80 MHz, incident on a photoconductive antenna which is used as a broadband THz source (see figure 5.20). The ultrafast NIR source (Femtolasers, Femtosource cM1, Vienna, Austria) operates at a centre wavelength of 800 nm. Using two parabolic off-axis mirrors the terahertz pulses are focused onto the samples (graphene). The transmitted pulses are collected using an identical set of parabolic mirrors. The transmitted radiation is detected using the electro-optic sampling method, which utilizes the birefringent ZnTe crystal [176]. To increase the speed of data acquisition as well as to improve spectral resolution and signal-to-noise ratio, a 50 ps rapid optical delay is used. Between 200 and 300 scans are averaged at a scanning frequency of 0.5 Hz for each spectrum. The resulting timedomain waveform is apodized using a Hamming function. Figure 5.21(a) shows the THz waveform through dry air in the time domain. The spectrum in the frequency do-
main is obtained by taking a fast Fourier transform (FFT) of the time domain waveform, figure 5.21(b).

Theoretically, the total bandwidth of the FFT signal is determined by the resolution of the time domain signal, which is 0.03 ps in our measurements \(^{177}\). This yields a total signal bandwidth that is equal to 33 THz. In reality, the total signal bandwidth is determined by the source and detection optics of the set-up. From figure 5.21(b), we note that the signal is highest around 0.5 THz and falls down as the frequency moves away, limiting the total signal bandwidth to less than 3 THz.

The resolution of the THz spectra is inversely proportional to the acquisition length of the time domain waveform \(^{177}\). This holds true for samples investigated using THz TDS that are more than 1 mm thick. The spectral resolution of the FFT spectra derived from the time-domain signal for these thick samples can be as small as 30 GHz. In the case where the samples are thin (\(< 1 \text{ mm}\)), the detector records the reflection of the THz wave from the substrate. In these samples, the spectral resolution is determined by the thickness of the substrate.

In this work the thickness of the Si substrate is approximately 525 \(\mu\text{m}\). The reflections from the substrate restricts the acquisition length to \(\approx 12 \text{ ps}\) and the spectral resolution to
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≈70 GHz.

Figure 5.22 shows the time domain waveform transmitted through a SiO$_2$/Si substrate. The first pulse transmitted through the substrate is denoted by $E_1^T(t)$ and has the maximum amplitude. This is often called the primary pulse. The appearance of a secondary pulse is marked by $E_2^T(t)$ and is a consequence of the first reflection from the substrate. This pulse travels three times through the substrate. The magnitude of the secondary pulse is lower than the magnitude of the primary transmitted pulse owing to the losses incurred within the substrate. We also observe a tertiary pulse, called $E_3^T(t)$. This pulse travels through the substrate five times and is significantly lower in magnitude. Assuming a refractive index of 3.42 for Si, the time difference $\Delta t$ between the pulses passing through a 525\,$\mu$m thick substrate can be calculated as 11.9 ps, which agrees with the measured $\Delta t$, see figure 5.22.

From figure 5.22, we note that the magnitude of the electric field corresponding to the primary pulse $E_1^T(t)$ (1.5 a.u.) is less than the strength of the THz signal transmitted through dry air (2.5 a.u., in figure 5.21) $^1$. This reduction in the THz signal arises due to free carrier absorption by the p-doped Si substrate.

In our treatment of the THz signal transmitted through the substrate (figure 5.22), we ignored the effects of the 300 nm thin SiO$_2$ layer. In reality, the incident broadband THz signal sees three interfaces - Air/SiO$_2$, SiO$_2$/Si and Si/air. While these interfaces are not a

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$^1$THz time domain waveforms shown in figure 5.22 and figure 5.21 were measured one after the other, and so the experimental conditions are the same.
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5.7.2 Experimental set-up in reflection mode

The THz TDS setup in the reflection mode consists of a modified TPI imaga 2000 supplied by Teraview Ltd., Cambridge, UK. This set-up was used with a set of 2D linear stages, controlled at a step of 100 µm to generate a THz map of the graphene device.

Figure 5.23(a) shows the THz waveform through dry air in the time domain. The spectrum in the frequency domain is obtained by taking a fast Fourier transform (FFT) of the time domain waveform, figure 5.23(b). From figure 5.23(b), we note that the signal is highest around 1.1 THz and falls down as the frequency moves away. The source and detection optics limits the total signal bandwidth to less than 3.5 THz.

Figure 5.24 shows the THz time domain waveform reflected from the SiO$_2$/Si substrate. In the reflection mode, the incident beam is focussed to a spot size of 200 µm, which is incident onto the surface at angle of 30° [178]. This allows the detector to collect the primary reflected peak $E^1_R(t)$ and the secondary reflected peak $E^2_R(t)$. Similar to the analysis of the THz time-domain waveform obtained using the transmission mode setup, the difference $\Delta t$ between the two peaks, in the reflection mode, can be estimated from the time it takes for the incident pulse to travel twice the thickness of the Si substrate.
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Figure 5.23: THz waveform through dry air in (a) time domain and (b) frequency domain, using the TDS set-up in reflection mode.

For a 525 µm thick Si substrate, Δt can be estimated as 11.9 ps, which agrees with the measured Δt shown in figure 5.24.

![THz waveform and schematic diagram](image)

Figure 5.24: THz time domain waveform reflected from the SiO$_2$/Si substrate. The schematic diagram shows the incident and the reflected peaks.

5.7.3 Transmission mode vs. reflection mode set-up

Both the THz TDS systems discussed above have their pros and cons. One of the major advantages of using the TDS in the reflection mode is for THz spectoscopy of highly absorbing...
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materials \((E_1^T \approx 0)\). This includes graphene deposited on highly doped Si substrates that would otherwise not be suitable for optical measurements.

The transmission mode set-up on the other hand is more suitable for samples (or substrates) which have a thickness less than 1 mm. This is because in the transmission mode, the beam is incident normal to the surface, figure 5.22. This implies that the primary transmitted pulse \(E_1^T(t)\) and the secondary transmitted pulse \(E_2^T(t)\) carry the spectral information of the same point in space. In the reflection mode on the other hand, the beam is incident at an angle of 30°, figure 5.24. This implies that the primary reflected pulse \(E_1^R(t)\) and the secondary reflected pulse \(E_2^R(t)\) carry the spectral information of two different points in space and can not be compared.

5.7.4 Theory behind THz transmission through graphene

We are now in the position to discuss the THz time domain spectroscopy of graphene. THz transmission through graphene is a function of its conductance, i.e. available density of states for intraband transitions \([159, 179]\). Given the frequency dependent conductivity \(\sigma(\omega)\), the THz transmission \(T(\omega)\) through graphene can be expressed as:

\[
T(\omega)/T_s(\omega) = \left| (1 + Z_o \sigma(\omega)/(n_s + 1)) \right|^{-2}
\]

Since \(T(\omega)\) also contains a component of absorption by the SiO\(_2\)/Si substrate, an estimate of transmission through graphene sheet alone is obtained by normalizing \(T(\omega)\) to \(T_s(\omega)\), which is the transmission through the SiO\(_2\)/Si substrate. In eqn. 5.17 \(n_s\) is the refractive index of the silicon substrate (\(\sim 3.42\)) and \(Z_o\) is the vacuum impedance (376.7 Ω) \([180]\). The conductivity \(\sigma(\omega)\) can be tuned by varying the position of the Fermi level. The relationship between intraband conductivity and the Fermi level \(E_F\) can be expressed as:

\[
\frac{\sigma(\omega)}{\sigma_o} = \frac{8k_BT}{\pi\hbar} \ln(e^{-E_F/2k_BT} + e^{E_F/2k_BT}) \frac{1}{1/\tau - i\omega}.
\]

Here, \(T\) is the temperature, \(k_B\) is the Boltzmann constant, \(\sigma_o = \pi e^2/2h\) is the quantum conductance and \(\tau\) is the relaxation time of carriers. The relaxation time can be estimated from the mobility of charge carriers \(\mu\) and the carrier concentration \(n\) as \(\tau = \mu\hbar/\sqrt{\pi n/eV_F}\).

Note that the expression for intraband conductivity (eqn. 5.18) is similar to the Drude like behavior discussed in section 5.3 at high carrier concentrations. At high carrier concentrations, i.e. \(E_F \gg k_BT\), eqn. 5.18 reduces to:

\[
\sigma(\omega) = \frac{4E_F}{\pi\hbar} \frac{1}{1/\tau - i\omega}
\]
5.7 THz time domain spectroscopy (THz TDS) of CVD graphene

At low carrier concentrations, $E_F \ll k_B T$, eqn. 5.18 can be written as:

$$\sigma(\omega) = \frac{8k_B T}{\pi\hbar} \frac{\ln(2)}{1/\tau - i\omega}$$  \hspace{1cm} (5.20)

Therefore, when the Fermi level is close to the Dirac point, the optical conductivity is independent of carrier concentration and only depends upon the temperature. We now discuss the results obtained from THz spectroscopy of monolayer CVD graphene under different gating conditions.

5.7.5 Results from back-gated graphene

Figure 5.25 shows the THz transmission of monolayer CVD graphene in time domain as a function of back-gate voltage, $V_{bg}$. The peaks of the primary and secondary transmission pulses have been plotted separately for clarity. Note that the transmission is highest when the back-gate voltage on graphene $V_{bg} = +50$ V. At this bias, the p-doped graphene is closest to the Dirac point. As the Fermi level is moved away from the Dirac point, towards $V_{bg} = -50$ V, the concentration of holes increases. This causes free carrier absorption within graphene, which can be observed as reduced transmission at $V_{bg} = -50$ V.

The THz spectrum is obtained by taking a fast Fourier transform of the signal shown in figure 5.25. If we take the Fourier transform of the entire waveform shown in figure 5.25(a), the spectrum suffers from spurious oscillations due to etalon effects \[181\]. While algorithms exist to deconvolve the spectrum from the oscillations, they are harder to implement in multilayered structures. The other alternative is to take the fourier transform of the primary peak and secondary peak seperately, where the length of the time domain waveform is equal to $\Delta t$. We follow the latter approach to estimate the spectrum of graphene on SiO$_2$/Si substrate.

In order to obtain the transmission (or absorption) spectrum of graphene, one of the most critical step is obtaining a reference. It is common in the literature to refer the transmission of graphene at different applied bias to the transmission of the SiO$_2$/Si substrate or the transmission of graphene at zero gate bias \[179\]. However, this is not entirely accurate. In the first case, it is difficult to decovolve the transmission through graphene from the multiple-stack graphene/SiO$_2$/Si system using this method, especially when trying to obtain weak resonance features of graphene based metamaterials. In the second case, transmission at zero-gate bias is not necessarily at maximum. Absorption referred to the charge neutrality point $V_{CNP}$ eliminates artifacts arising from laser drift, thin-film approximations and slight thickness variations across different substrates \[160\]. However, this can be prohibitive in graphene samples that require a very large back-gate bias to reach...
Figure 5.25: THz time domain waveform transmitted through monolayer graphene as a function of back-gate voltage $V_{bg}$ (a) Complete waveform (b) Primary transmitted pulse, $E_1^T(t)$ (b) Secondary transmitted pulse, $E_2^T(t)$
5.7 THz time domain spectroscopy (THz TDS) of CVD graphene

the Dirac point. For example, in the sample shown in figure 5.25, $V_{CNP}$ lies beyond our measurement range (+50 V).

Since, the THz transmission is maximum at this point, we can assume that the Fermi level is closest to the Dirac point at $V_{bg} = +50$ V. This allows us to calculate the effect of back-gate on the absorption of graphene with respect to +50 V. If the Fourier transform of the THz pulse transmitted through graphene at a bias of +50 V is given by $T_{50V}(\omega)$, the normalized absorption at each back-gate potential can be calculated as $1 - T_{bg}(\omega)/T_{50V}(\omega)$.

Figure 5.26: Normalized absorption spectra of p-doped graphene referred to $V_{bg} +50$ V, (a) derived from primary pulse (b) derived from secondary pulse.

Figure 5.26 shows the normalized absorption through monolayer CVD graphene as function of gate bias. The first spectrum, figure 5.26(a) is derived from the Fourier transform of the primary transmitted pulse $E_{1T}$ and the second spectrum figure 5.26(b) is derived from the secondary transmitted pulse $E_{2T}$. Figure 5.26(a) shows that the absorption is gate tunable and increases by 5% as graphene is gated away from the Dirac point, into the valence band. This is consistent with what has been obtained in literature [160, 179]. The absorption spectrum at $V_{bg} = +30$ V and $V_{bg} = -10$ V rolls off to negative values at frequencies higher than 1 THz. It is likely, that this feature, appearing at voltages close to +50 V, is an artifact introduced by referring the absorption to a bias that is not the charge neutrality point. The negative absorption vanishes when more signal is collected from graphene, i.e. when the absorption spectrum is derived from the secondary transmitted pulse. This pulse traverses through graphene twice. Therefore, the absorption obtained from graphene, figure 5.26(b) is more than twice the value shown in figure 5.26(a). While
interesting features are seen in the absorption spectrum of back-gated graphene at frequencies $> 1$ THz, the absence of a charge neutrality point in the sample prohibits detailed analysis.

We can still extract the optical conductivity from the THz transmission. Using eqn. 5.17, we can evaluate $\sigma(\omega)$ from the transmission $T(\omega)$, for each back-gate voltage. Note, that eqn. 5.17 only holds true when the spectrum is derived from the primary pulse [182]. Figure 5.27 plots the AC conductivity $\sigma(\omega)$ at $\omega = 1$ THz, as a function of back-gate bias. In agreement with previous reports [179], the frequency dependent conductivity shown in figure 5.27 varies non-linearly with $V_{bg}$. At voltages close to the Dirac point, the conductivity does not vary significantly with voltage. However, as the gate bias drives the Fermi level away from the Dirac point, the ac conductivity increases proportionally. This is consistent with the theoretical predictions of intraband conductivity under conditions of low and high carrier density, see eqns. 5.18 to 5.20. Note that when $V_{bg} = 0$, the frequency dependent conductivity is $\sigma(\omega)$ at 1 THz is equal to $21 \frac{e^2}{h}$. This is in agreement with the dc conductivity (sheet conductance) extracted from the transport measurements of back-gated graphene, discussed in section 5.6.1.

Figure 5.27: AC conductivity of graphene as a function of back-gate voltage, $V_{bg}$

The absence of a charge neutrality point, can be corrected by using a top ionic gate as discussed in section 5.6.2. In the next section, we review the results obtained from THz spectroscopy of top-gated, monolayer CVD graphene.
5.7.6 Results from top-gated graphene

Figure 5.28 shows the THz transmission of monolayer CVD graphene in time domain as a function of top-gate voltage $V_{tg} \leq 0.5 \text{ V}$. The primary and secondary transmission pulses have been plotted separately for clarity. Note that the transmission is highest when the top-gate bias $V_{tg} = +0.5 \text{ V}$. At voltages below $+0.5 \text{ V}$, i.e. $V_{tg} = 0.4 \text{ to } 0 \text{ V}$, the transmission drops, suggesting that the Fermi level has moved away from the Dirac point.

![Figure 5.28: THz time domain waveform transmitted through monolayer graphene as a function of top-gate voltage $V_{bg} < V_{CNP}$ (a) Complete waveform (b) Primary transmitted pulse, $E_1^T(t)$ (b) Secondary transmitted pulse, $E_2^T(t)$](image)

Decrease in transmission is also observed when the top-gate voltage is increased beyond $+0.5 \text{ V}$, i.e. $V_{tg} = 0.6 \text{ to } 1.0 \text{ V}$. Figure 5.29 shows the THz transmission of monolayer
CVD graphene in time domain as a function of top-gate voltage $V_{tg} \geq 0.5$ V. Once again, the primary and secondary transmission pulses have been plotted separately for clarity.

Figures 5.28 and 5.29 suggest that the charge neutrality point in this sample exists when $V_{tg} = +0.5$ V. Below $+0.5$ V, graphene is p-doped and the predominant charge carriers are holes. Above $+0.5$ V, graphene is n-doped and the predominant charge carriers are electrons. Note that this charge neutrality point is higher than 0.14 V observed using transport measurements for the same sample 4 weeks ago, see section 5.6.2. However, this is not very surprising as graphene is susceptible to changes in the environment, which inadvertently dopes graphene. Although the exposure is minimized by storing graphene in an environment purged with nitrogen, it is probable that it gets doped while in transit from...
cleanroom to the measurement lab. It is therefore essential that the charge neutrality point
for the graphene sample is measured each time an optical or an electrical experiment is
repeated. The device behavior is independent of where the charge neutrality point exists.
Therefore, the gate bias is best referred in terms of $V_{tg} - V_{CNP}$. In future, rebaking the
device before each experiment may yield a reproducible charge neutrality point.

Figure 5.30(a-b) shows the absorption spectrum of graphene derived from the Fourier
transform of the primary pulse $E^T_{1}$. The normalised absorption is calculated using the
expression $1 - T_{tg}(\omega)/T_{CNP}(\omega)$. Note that close to the Dirac point, at $V_{tg} - V_{CNP} = -0.1$ V, graphene is lightly p-doped ($n = 5 \times 10^{12}$ cm$^{-2}$) and the absorption increases with
frequency by up to about 10% at $\omega = 2$ THz. Similar behavior is obtained at $V_{tg} - V_{CNP} = +0.1$ V when graphene is doped with electrons. This is in agreement with a Drude like
response of the frequency dependent optical conductivity, see eqn. 5.10.

At higher voltages, the THz absorption is tunable with gate voltage. We observe that
the absorption shows flat response with frequency until $\omega = 1$ THz. However, at 1.6
THz, we observe a distinct absorption feature superimposed on the Drude like response of
graphene as the gate voltage is increased to $\pm 0.5$ V (i.e. carrier concentration $n$ is equal to
$\pm 1.2 \times 10^{13}$ cm$^{-2}$). From figure 5.30(a), we note an absorption peak at $\sim 1.6$ THz when
graphene is p-doped and $E_F$ is below the Dirac point. This feature however reverses in
figure 5.30(b) when graphene is n-doped and $E_F$ is above the Dirac point. These features
are not observed in the absorption spectrum of the ion gel, which absorbs 2-4 % incident
THz radiation when referred to the SiO$_2$/Si substrate, shown in Figure 5.31.

Figure 5.30: Normalized absorption spectra of top-gated graphene, derived from primary
transmitted pulse, referred to $V_{CNP} = +0.5$ V when graphene is (a) p-doped (b) n-doped.
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Figure 5.31: THz absorption spectra of ionic gate (LiClO$_4$), derived from the primary transmitted pulse, referred to the SiO$_2$/Si substrate.

Figure 5.32: Normalized absorption spectra of top-gated graphene, derived from secondary transmitted pulse, referred to $V_{CNP} = +0.5$ V when graphene is (a) p-doped (b) n-doped. Phase difference shows change in sign at the absorption resonance when graphene is (c) p-doped (d) n-doped. For clarity, the sign change in phase difference between 1.5 and 1.8 THz is shown in the inset.
It is likely that the absorption spectrum derived from the secondary transmitted pulse $E_T^2$ would give a stronger signal as it passes through graphene twice. This is indeed what we observe in the absorption spectrum of graphene shown in figure 5.32. Note, as the THz pulse travels twice through graphene in the case of Figure 5.32, the 10% change in absorption at highest doping is nearly twice the 5% change in absorption observed at low frequencies in figure 5.30. Superimposed upon the flat absorption spectrum we observe peaks evolving with voltage at 1.1 THz and 1.6 THz. The resonance at 1.6 THz appears to be strong in the case of p-doped graphene. At a doping of $5 \times 10^{12}$ cm$^{-2}$ ($V_{tg} - V_{CNP} = \pm 0.1$ V), the normalized absorption referred to CNP is nearly zero. As the doping increases to $1.6 \times 10^{13}$ cm$^{-2}$ ($V_{tg} - V_{CNP} = \pm 0.5$ V), the absorption increases by 10% and the peak shows 20% change in absorption at 1.6 THz. Corresponding to the absorption resonance at 1.6 THz in figure 5.32(a), we see the phase difference, $d\delta$, changing sign from positive to negative in figure 5.32(c). Interestingly, for the case of n-doped graphene, $d\delta$ undergoes a phase change from negative to positive, see figure 5.32(d).

Similar absorption features are seen in other samples. Figure 5.33 shows the absorption spectrum of another top-gated graphene device, referred to it's charge neutrality point. The absorption spectrum, shown for hole transport is derived from the secondary transmitted pulse. Similar to figure 5.32, this device also shows a similar gate tunable, absorption peak at 1.6 THz when graphene is p-doped. The peak at 1.1 THz observed in figure 5.32, reverses in this device. We do not yet understand the origin of this peak and the reason for it's reversal.

We note from our measurements of back-gated graphene (figure 5.26) and those shown in the literature that the absorption features are unique to top-gated graphene [160, 179, 183]. We note that the absorption spectrum $1 - T_{bg}(\omega)/T_{+50V}(\omega)$ is flat until 2 THz at $V_{bg} = -50$ V, with no absorption peak at 1.6 THz which we observe in top-gated, p-doped CVD graphene.

In the next section, we discuss possible causes that may explain the absorption features at 1.6 THz.

5.7.7 Role of domains in spectroscopic response

In section 5.4, we discussed that graphene can support THz plasmons. The plasmon frequency $\omega_p$ is a function of carrier concentration and varies as $n^{1/4}$. Ideally, for an un-patterned, ungated sheet of graphene, the plasmon frequency is given by eqn. 5.11. If graphene is patterned into circular disks, the patterned two dimensional free electron gas can act as two dimensional plasmonic grating [184], where the resonance frequency is
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Figure 5.33: Normalized absorption spectra of another top-gated graphene device. The absorption spectrum, shown for hole transport, is derived from secondary transmitted pulse and is referred to $V_{CNP}$

dependent upon the radius of the disk.

We note from our earlier discussion in section 5.5.1, that CVD graphene is inherently polycrystalline. We suggest that these growth domains can themselves act as a two dimensional plasmonic grating, which causes scattering of plasmons. In our samples, the domain size is observed to be of the order of 30-40 $\mu m^2$ from microscopy studies of CVD graphene, see figure 5.6. Assuming an $r = 3.4$ $\mu m$ (which corresponds to an area of 36 $\mu m^2$), the plasmon frequency $\omega_p$ can be calculated using the model for an ungated graphene disk. The plasmon frequency is then given by the following expression, where the radius of the domain $r$ is assume to be equal to the radius of the disk [184].

$$\omega_p = \sqrt{\frac{3\nu_F e^2 \sqrt{\pi \hbar}}{16r\hbar\kappa}}$$  \hspace{1cm} (5.21)

Here, $\kappa$ is the average dielectric constant of the surrounding medium (PEO and SiO$_2$), which is equal to $(5 + 3.9)/2$. For an $r = 3.4$ $\mu m$, eqn. 5.21 predicts that we should observe resonances at 2.01 THz, 2.20 THz, 2.34 THz, 2.45 THz and 2.55 THz as $V_{tg} - V_{CNP}$ is varied from 0.1 to 0.5 V in steps of 0.1 V.

While we observe gate tunability of the absorption peak, we do not measure a shift in the resonance frequency as the gate bias is swept away from the Dirac point. Note that eqn. 5.21 ignores the effect of gating on the plasmon frequency. The effect of gate on the propagation of plasmons was first calculated in conventional semiconductor field effect
transistors to predict oscillations at THz frequency under asymmetric source-drain bias due to reflection from the device boundaries [185]. This model was later extended to suggest plasma oscillations in graphene under asymmetric boundary conditions [162]. Because the instability conditions require a low drain current, asymmetric boundary conditions may also be introduced if only one of the contacts is grounded, which was the case in our experiments. The plasma wave velocity $s$, under these conditions is higher than $v_F$ and given as:

$$s = \frac{v_F}{\sqrt{1 - \left(\frac{\alpha_g}{1+\alpha_g}\right)^2}}$$

(5.22)

Here $\alpha_g$ is the gate-voltage dependent parameter given by the following equation.

$$\alpha_g = 4\sqrt{\frac{e^2 (V_{tg} - V_{CNP})}{2 C_{tg} \hbar^2 v_F}}$$

(5.23)

These plasmon waves may then reflect from the domain boundaries of monolayer graphene grown via CVD [186]. In the expression for plasma frequency $\omega_p = sq$, the wavevector $q$ can be replaced as $(2m - 1)\pi/2r$, where $r$ is the radial dimension of the crystal and $m = 1, 2, 3...$

Assuming an $r = 3.4 \mu m$ (which corresponds to an area of $36 \mu m^2$), the plasmon frequency $\omega_p$ is calculated as 1.6 THz at $V_{tg} - V_{CNP} = 0.2$ V. This agrees with the experimentally observed resonance in figure 5.32. The plasmon wave velocity $s$ at $V_{tg} = 0.2$ V is calculated as $4.3 \times 10^8$ cm/s. Ideally, the plasmon frequency should shift with electric field, which is not so in our experiments. Perhaps, at high carrier concentration the plasmon wave velocity experiences saturation with gate electric field [187].

Perhaps, the absorption and emission at different charge polarity can be explained within the framework of plasmon scattering. Over the crystalline domain boundary, we may assume short-circuit conditions at the end closer to the source and open-circuit conditions on the diametrically opposite end closer to the drain. Under these conditions, when holes are the predominant charge carriers, the current flows towards the source, i.e. towards low impedance. This may cause the plasmon wave to be reflected back with the opposite polarity thereby destructively interfering with the incident surface plasmon. In the case where electrons are the predominant charge carriers, the current flows towards the drain, i.e. towards high impedance. This may cause the plasmon wave to reflect back, but with same polarity leading to constructive interference and hence absorption.

We therefore observe that in the case where the surface current is carried by holes,
the scattering of plasmons due to domain boundaries leads to energy absorption, whereas, when the surface current in graphene is carried by electrons, the scattering of plasmons leads to emission. It is probable that the true absorption spectrum and hence the plasmon resonances, is a superposition of multiple effects, i.e. reflects the statistical distribution of domains, kinks and wrinkles in CVD graphene.

Interestingly, intrinsic plasmonic resonances have been observed in unpatterned graphene epitaxially grown on SiC [188], with a background carrier concentration, $n \sim 8 \times 10^{12}$ cm$^{-2}$ at no bias. The origin of these resonances corroborated microscopically has been attributed to uniform defects in epitaxial graphene. While it is known that the application of magnetic field splits these intrinsic plasmons into bulk and edge states, there have been no studies on the effect of charge disorder induced externally on the appearance of these plasmonic resonance modes. We observe similar plasmonic resonances in CVD grown, monolayer graphene monolayer. Near-field scanning microscopy of plasmons scattered in graphene at THz frequencies may provide additional insight to the origin of these resonances [156].

For completeness, we present the THz image of the top-gated graphene device. While this technique is not suitable for imaging plasmons, it gives us an insight into the conductivity distribution within the device.

### 5.7.8 THz imaging of top-gated graphene

Figure 5.34 shows the THz image of a top-gated graphene device measured at a spatial resolution of 100 $\mu$m. The THz image was obtained in the reflection mode by exciting graphene with a broadband THz source, incident at 30° to the surface normal. In the image shown, the source is grounded, the drain is left unbiased and the voltage on gate is equal to $V_{CNP}$. The incident THz radiation is reflected strongly from regions of highest conductivity, which in this case are the Ti/Au source, drain and gate contacts. The THz reflectance $E_R^1$ in these highly conducting regions is $\sim 0.7$ to 0.8. The dashed lines between the source and drain enclose the area covered by graphene. The position of the drop casted ionic gel can be seen in the THz image as it takes a coffee ring shape at the center [189]. The THz reflection $E_R^1$ corresponding to the ionic gel is $\sim 0.5$ to 0.6.

On careful inspection of the image, we note that the coplanar gate contact is not uniformly conducting. Perhaps, this is a ramification of the floating potential on the drain, which adds to the hypothesis that an asymmetric potential distribution across the device contributes partly to the spectroscopic signatures that we observe.
5.8 Graphene ribbons as THz filters

While unpatterned graphene exhibits a THz response that is dominated by intrinsic plasmons, it is theoretically possible to engineer the plasmonic response at THz frequencies by lithographically defining them into ribbons [71, 190]. Demonstrated first for frequencies between 3-6 THz by Ju et. al, microribbons in graphene can become particularly exciting if demonstrated below 3 THz for use as tunable filters with THz sources such as QCLs. The relationship between the plasmonic frequency and the width $w$ of the ribbon is given by the following expression.

$$\omega_p \propto n^{1/4}w^{-1/2} \quad (5.24)$$
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Our initial attempts at defining microribbons in graphene were focussed towards designing a THz filter with a plasmonic frequency of 2 THz using the scaling law mentioned in eqn. 5.24. Assuming the same carrier concentration as Ju et. al \( n = 1.5 \times 10^{13} \text{ cm}^{-2} \), ribbons with width \( w \sim 9 \mu\text{m} \) were patterned with a pitch of 1:1, using photolithographic techniques over an area equal to the THz beam spot size. However, since the design frequency approached the tail end of the detection bandwidth (see figure 5.21), we failed to observe a reasonable THz response from these ribbons. Subsequent designs were focussed at a plasmon frequency centered around \( \omega_p = 0.6 \text{ THz} \) (width \( w \sim 100 \mu\text{m}, n = 1.5 \times 10^{13} \text{ cm}^{-2} \)) where the signal to noise ratio of the THz TDS set-up is maximum.

Figure 5.35 shows the absorption spectrum of 100 \( \mu\text{m} \) wide graphene ribbons, as a function of top-gate bias, when the incident THz beam is polarized parallel and perpendicular to the length of the ribbon. The absorption spectrum is derived from the secondary transmitted pulse and is referred to the charge neutrality point of the ribbons. We observe that the absorption is tunable with gate voltage. However, the normalized absorption of the microribbons (2 to 4 %) is less than the normalized absorption of large-area graphene (10 %), see figure 5.32. This is to be expected since the effective area of graphene is reduced by nearly half after patterning into ribbons.

![Normalized absorption spectra of graphene microribbons](image)

Figure 5.35: Normalized absorption spectra of graphene microribbons when the incident THz radiation is polarized (a) parallel to the length of the ribbons (b) perpendicular to the length of the ribbons. The absorption spectrum, shown for hole transport, is derived from secondary transmitted pulse and is referred to \( V_{CNP} \)
When the THz radiation is polarized parallel to the length of the ribbons, the absorption increases with frequency, which is consistent with the Drude like response of the optical conductivity. We observe weak signatures of an absorption peak at $\sim 1.6$ THz, which suggests a contribution due to intrinsic plasmons. From the scaling law (eqn. 5.24), we expect a resonance feature at $\omega_p = 0.6$ THz when the THz radiation is polarized perpendicular to the length of the 100 $\mu$m wide ribbons. The absence of a resonance feature at the design frequency $\omega_p = 0.6$ THz inspite of reaching the required carrier concentration ($n = 1.5 \times 10^{13} \text{ cm}^{-2}$ at $V_{tg} \cdot V_{CNP} = -0.8$ V), suggests that either the resonance is destroyed by scattering due to the intrinsic polycrystallinity of graphene or the resonance suffers broadening at longer wavelengths [186, 190]. This implies that scaling the plasmon frequency of monolayer CVD graphene to longer wavelengths may not be ideal. A better understanding of the resonance features of patterned graphene ribbons can be obtained from FTIR spectroscopy which offers higher resolution and bandwidth in terms of frequency [71]. However, this was beyond the scope and time limit of this work.

### 5.9 THz modulator

In this section, we demonstrate a graphene based THz modulator operating at room temperature, which can be used to control the transmission from a QCL emitting at 2.0 THz. Here, graphene has been used in back-gated geometry. Previous means of modulating the transmission of a THz QCL relied on direct modulation of the bias voltage by application of an RF signal (up to a few GHz) together with a dc bias [191]. External THz QCL modulators based on electrically-driven active metamaterial structures fabricated on semi-insulating GaAs have been reported in the past, with modulation depth $\sim 60$ % [192]. This work builds upon the work of Rodriguez et. al, who demonstrated a large-area graphene-based modulator for carrier frequencies $\sim 570$-630 GHz [193]. Theoretical predictions suggest that it is possible to achieve a modulation depth $> 90$ % by exploiting the gate tunability of THz transmission through graphene [194].

Rodriguez’s work on broadband modulation relied on Schottky-diode detection of the amplitude modulated carrier frequency signal from ‘high’ to ‘low’ by switching the applied gate voltage on graphene over millisecond time scales [193]. However, in the frequency range of 1-5 THz, switching of amplitude-modulated THz signals is difficult to detect in time, primarily because of the slow response (4-300 Hz) of the available THz detectors. In this work we record the modulated THz transmission by sweeping the frequency of applied gate voltage ($f_{mod}$) on graphene while applying a second, slow modulation to the QCL ($f_{ref}$). The response is detected by measuring the average THz power as $P_{avg}$. The
average power can be expressed in terms of the peak power \(P_{\text{peak}}\) as follows:

\[
P_{\text{avg}} = P_{\text{peak}}(f_{\text{mod}}) \cdot \frac{f_{\text{ref}}}{f_{\text{mod}}}
\]

(5.25)

Note that the peak power measured by the detector is a function of the modulation frequency on graphene. In eqn. 5.25, this relationship is expressed as \(P_{\text{peak}}(f_{\text{mod}})\). Independent of this dependency, the modulation frequency determines the average power transmitted through graphene and measured by the detector. The choice of the modulation frequency determines the time over which the THz power is measured.

### 5.9.1 Experimental setup

The experimental setup used for indirectly modulating the THz transmission from a QCL using back-gated graphene is shown in figure 5.36. The THz QCL operating at 2.0 THz (figure 5.37) was grown epitaxially on a semi-insulating GaAs substrate in a bound to continuum design \[195\]. A 250 \(\mu\)m x 3mm single plasmon waveguide laser was mounted on to a copper block and operated at 4.2 K. In pulsed mode, the QCL operates up to a maximum temperature of 70 K (figure 5.37).

Figure 5.36: Experimental Set-Up. Pulser 1 provides continuous pulses at 60 Hz, such that the THz QCL operates at \(J_{\text{max}}\) in a quasi-cw mode. Pulser 2 provides a burst of fast modulation to the back-gate of graphene.

The QCL is biased at \(J_{\text{max}} \sim 150\) A/cm\(^2\) and is operated in a quasi-cw mode by electrically pulsing at \(f_{\text{ref}} = 60\) Hz. The duty cycle of this slow pulse is kept at 15\%. This
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Figure 5.37: (a) Spectral characteristics of THz QCL measured using Bruker IFS/66v FTIR spectrometer at $J_{\text{max}} \sim 150 \text{ A/cm}^2$ in the pulsed mode (b) Pulsed LIV of THz QCL at varying temperatures, showing a lasing threshold of 110 A/cm$^2$ at 4.2 K.

Envelope frequency ($f_{\text{ref}}$) is applied because most THz detectors have optimal sensitivity when operating at low frequencies. For completeness, we have carried out the experiments with two different THz detectors: a Golay cell and a composite Si bolometer cryogenically cooled at 4.2 K. To be consistent we choose $f_{\text{ref}} = 60 \text{ Hz}$ for both measurements. While the responsivity of a bolometer is flat for $f_{\text{ref}} < 300 \text{ Hz}$, the responsivity of a Golay cell falls by a factor of around seven as the $f_{\text{ref}}$ is increased from 15 Hz to 60 Hz. However, the amount of signal detected on the lock-in amplifier for both is significantly above the noise floor of our measurement set up ($\text{SNR}_{\text{dB}} > 25$). The radiation emitted by the QCL source is collected by a pair of F2 parabolic mirrors and is focussed on to the THz detector. The graphene based FET is placed directly in front of the THz detector at a maximum spacing of 5 mm. The source contact on graphene is grounded and the drain contact is left unbiased. The average THz power is modulated by changing the pulse frequency applied to the back-gate of graphene. The back-gate is pulsed from 0 to +50 V at a frequency which we denote as $f_{\text{mod}}$. The duty cycle of this pulse is the same as the duty cycle of the reference pulse, i.e. 15 %. The modulated signal is measured as the average THz power $P_{\text{avg}}$ carried in the 60 Hz envelope on the lock-in amplifier. For better alignment, the beam spot can be further reduced by placing an aperture in front of graphene.

5.9.2 Results from indirect modulation of a THz QCL by graphene

Figure 5.38 shows the measured THz response as a function of $f_{\text{mod}}$, detected by a Golay cell. The modulation frequency, $f_{\text{mod}}$ is swept from 200 Hz to 80 KHz. The average
detected THz power $P_{avg}$ is normalized to the average detected power at the initial modulation frequency $f_{mod} = 200$ Hz. The signal is averaged over 10 scans. We observe that the average THz power ($P_{avg}$) detected by the Golay first falls to a certain minimum at $f_{mod} = f_{cutoff}$, the cutoff frequency. This is where the drain-source current, $I_{ds}$, given by eqn. 5.13 (inset, figure 5.38) remains constant, which implies that the peak THz power $P_{peak}$ transmitted through graphene remains constant. However, the time period at which the peak power is transmitted changes due to an inverse dependence upon $f_{mod}$. The THz detector measures the average power, which is directly proportional to the $P_{peak}/f_{mod}$, see eqn. 5.25.

Figure 5.38: Average THz power measured as a function of $f_{mod}$ normalized with power at $f_{mod} = 200$ Hz using a Golay cell at room temperature. The inset shows drain-source current $I_{ds}$ measured as a function of gate modulation at $V_{ds} = 1$ mV.

The drain-source current starts to roll off at $f_{3dB} = 10$ KHz. This roll off is explained by the capacitance of the large area $SiO_2$ gate, at which point the carrier density $n$, induced by the gate falls. Therefore, at this point, the transmitted THz power through graphene, i.e. $P_{peak}$ increases. Note that eqns. 5.17 and 5.13 suggest that the transmitted power is proportional to $I_{ds}^{-2}$. The average THz power $P_{avg}$ detected by the Golay starts to increase in spite of the inverse dependence on frequency. For an $f_{mod} = 80$ KHz, the depth of modulation is observed to be $\sim 15\%$.

Figure 5.39 shows the amplitude modulated THz signal as function of time. The average THz power is switched from a ‘high’ to ‘low’ state by switching the frequency of the back-gate voltage on graphene from high ($f_{mod} > f_{cutoff}$) to low ($f_{mod} < f_{cutoff}$). The
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back-gate on graphene is switched from $V_{bg} = 0 \, V$, $f_{mod} = 0$ to a 20 sec burst of high frequency pulses ($V_{bg} = 0 \, V$ to $+50 \, V$, $f_{mod} = 20 \, \text{KHz}$). In the first 20 secs, $f_{mod} = 0$, the THz transmission through graphene corresponds to the free-carrier absorption due to holes, which we call as the 'initial' state. There is a general drift in the average power detected over a period of time, which can be attributed to the stability of the QCL source when operated in a quasi-continous mode. It is likely that over a period of time, the Joule heating of the QCL source causes a drop in the power output. This behaviour is recorded in the first 20 secs, by Golay (figure 5.39(a)) as well as the bolometer (figure 5.39(b)).

![Figure 5.39: Amplitude modulated THz signal recorded with time on (a) golay cell at room temperature (b) composite Si bolometer cryogenically cooled to 4.2 K. The last pane (c) shows the switching of $f_{mod}$ from 0 Hz to a 20 sec burst of 20 KHz pulses.](image)

In the next 20 secs $f_{mod} = 20 \, \text{KHz}$ and the transmission increases by $\sim 7\%$, corresponding to the normalized $P_{avg}(f_{mod} = 20 \, \text{KHz})$ (figure 5.38). However, we observe that
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the measured signal is limited by the response time of the Golay (figure 5.39(a)). When the same experiment is repeated using a bolometer (figure 5.39(b)), we note an overshoot which is followed by a decay of the THz signal. The difference in the transient behavior between the two detectors arises possibly because of a difference in the measurement method. In the case of the Golay, the signal is measured across a capacitor, whereas in the case of the bolometer, the signal is measured across a resistor \(^1\).

When the back-gate is switched back to \(V_{bg} = 0\), the transmission through graphene is in the ‘low’ state. Ideally, the transmission should be constant when the Fermi level is held constant. However, the Golay responds to the change in the detected signal slower than the bolometer. We note that after the Fermi level is swept to and fro, at a high frequency across the valence band, the transmission in the ‘low’ state attempts to reach the ‘initial’ state. While we do not yet understand this behavior, a possible explanation may come from the inherent hysteresis in the graphene device due to surface charge traps at the oxide/graphene interface or due to intraband carrier relaxation within graphene itself.

The cycle shown in figure 5.39 is repeated multiple times to generate an amplitude modulated THz signal from a QCL source. The measurements shown in figure 5.39 describe the results of THz modulation when the entire area of graphene is exposed to the incident beam, i.e. the fluence is maximum. The absolute change in transmission remains nominally identical as the fluence of the incident beam is decreased from 360 mW/cm\(^2\) (iris diameter = 5 mm) to 32 mW/cm\(^2\) (iris diameter = 1.5 mm). Figure 5.40 shows that at a fluence of 290 mW/cm\(^2\) (iris diameter = 4.5 mm) the difference in the transmitted power between the ‘high = 0.057’ state and the ‘low = 0.050’ state is 0.007 a.u. At a fluence of 32 mW/cm\(^2\) (iris diameter = 1.5 mm), the difference in the transmitted power between the ‘high = 0.01’ state and the ‘low = 0.006’ state is 0.004 a.u. Since the depth of modulation is expressed as the ratio of change in transmission to the original transmission, the modulation efficiency increases with decrease in fluence \(^2\).

With improvements in the modulation efficiency and the speed of modulation, graphene shows considerable promise as a THz modulator. These improvements are discussed in section 6.2.6.

\(^1\)Note that this explanation for the difference in detector response has been amended after thesis review and publication of the manuscript [183].

\(^2\)Note that this is correction to the manuscript [183], where we expressed that instead of the absolute change in transmission, the depth of modulation is independent of the fluence.
5.10 Summary and conclusions

This chapter focussed on graphene, a material that can operate at room temperature for applications in THz optics. We showed that THz transmission through wafer scale graphene grown by chemical vapour deposition (CVD) can be tuned by applying an external bias. One of the problems with CVD graphene is the inherent polycrystalline nature of the material due to random nucleation. We demonstrate that this can effect the spectroscopic response of graphene and present additional challenges in the design of THz filters. Finally, we were able to exploit the gate tunability properties of graphene to demonstrate a graphene based THz modulator for operation with THz QCLs.
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Chapter 6

Conclusions and future work

6.1 Conclusions

This thesis has taken a two pronged approach to close the THz gap. In the first approach, we looked at improving the operating temperature of THz QCLs. Towards this end, we developed the building blocks required to implement lateral confinement in THz QCLs. In the second approach, we investigated the properties of a novel two dimensional material at THz frequencies and demonstrated it’s applicability to THz optics.

Lateral confinement in THz QCLs through a top-down nanofabrication has been an elusive dream. The challenge in realizing a top-down array of nanopillars that is electrically and structurally robust is the least of the problems, as shown in this work. The bigger challenge lies in the understanding of the radiative transitions within such a structure and the measurement of THz emission from these structures.

The problem of lateral confinement in THz QCLs was broken into three parts. In the first part, that is Chapter 2, we attempted to gain an understanding of the electrostatic potential within a lithographically defined nanopillar. Using a simple quantum well structure as the basis, we found that the electrostatic potential was dependent upon many processing and growth parameters. Following the discussion on lateral potential, we realized that the task of fabricating a nanopillar structure was not restricted to obtaining sub-200 nm radial dimensions. Instead, the challenge of obtaining simultaneous emission from intersubband states rested on obtaining a few correct radial dimensions. These dimensions exist as windows where light is allowed, and depend upon the active region used. Along with these constraints, observation of simultaneous emission from such a structure depends upon the optical loss within the device. We found, almost counter-intuitively that the highest packing density is not the criteria for lowest losses within an array of nanopillars. To obtain the
The second part of the problem is demonstrating that such a nanopillar array can be fabricated. This was discussed in Chapter 3. The processing routes were validated on simple resonant tunneling diode structures (RTDs). While our intent was not to improve upon the current carrying capabilities of zero-dimensional RTDs but to test our processing, we succeeded in contacting a 500 x 500 array of nanopillars. This allowed vertical transport through thousands of nanopillars in parallel, pushing the current to four orders of magnitude higher than what has been achieved in zero-dimensional RTDs so far. At higher bias, i.e. when the device is in resonance with the excited states, the array can support a current of up to 2000-4000 $\mu$A. This result improves our confidence in nanopillars processed from THz QCLs which require high current densities for simultaneous emission.

Implementing nanopillars in THz QCLs requires active regions that are ultrathin. While this problem has been solved in the literature, it required growth and characterization of suitable active regions inhouse. Chapter 4 discusses various active region designs and wafers that were tested for emission in the hope of implementing the top-down approach for lateral confinement. While challenges in growth and choice of waveguide affected many of the results discussed in Chapter 4, we were able to demonstrate lasing in an ultrathin THz QCL, derived from a full-stack. Since this laser was derived by chemical etching, it was not found suitable for the extremely surface sensitive processing of nanopillars. However, by building upon the steps developed in this work towards lateral confinement, we hope that some of the theories and processing routes can be tested on ultrathin THz QCLs in future.

Chapter 5 of this thesis looks to graphene for tangible THz optical elements that can operate at room temperature. Graphene grown by chemical vapour deposition (CVD) techniques was studied using THz time domain spectroscopy. Our measurements of gated-graphene devices suggested that polycrystallinity in CVD graphene influences the propagation of THz plasmons. This is an important finding to realize, since many applications of graphene such as THz filters and resonators involve THz plasmons. In the final section, we exploit the gate tunable properties of graphene to modulate a THz QCL.

In the next section, we present ideas that have originated from this work, that can provide opportunities for development in future.
6.2 Opportunities for future

6.2.1 Optical spectroscopy of nanopillars processed from THz QCLs

Chapters 2-4 have been driven by the quest to achieve electroluminescence from nanopillars etched in ultrathin THz quantum cascade lasers based on 3-4 quantum well (per period) designs. In future, the design of an epitaxial structure for nanopillars in THz QCLs should be independently tailored and not be based on a working ultrathin quantum cascade laser alone. The design of this active region must include the solution to the radiative states under the influence of a lateral potential. Feedback derived from techniques such as ultrafast THz spectroscopy [196] and microphotoluminescence [197] should be given to the epitaxial growth of these designs in order to identify and understand the transition states, electron relaxation mechanisms and associated relaxation times.

6.2.2 Waveguides for quantum-dot cascade structures

In a THz QCL, a Fabry Pèrot cavity formed by parallelly cleaved laser facets supports the optical mode. In this case, laser feedback is provided by the two atomically smooth facets which act as mirrors at the end of the gain medium. The fundamental mode in the laser spectrum is then determined by the length of the cavity.

The difficulty of achieving electroluminescence in quantum-dot cascade structures has meant that there has been no research done in the area of identifying a suitable waveguide for a future quantum-dot cascade based amplifier or a laser. The lack of research in this direction extends to mid infrared frequencies as well.

This work (Chapter 4) relied on an edge emitter geometry, to observe electroluminescence. There have been suggestions on obtaining laser feedback in quantum-dot cascade structures fabricated by the top-down approach. This involves etching external mirrors at the same time as the nanopillars. However, planarization of nanopillars, which depends upon the topography of the underlying structure is likely to be a problem in this design. It may also prove to be difficult to cleave the mirrors with an accuracy of $\leq 10 \, \mu m$, which is the least count of typical scribing and cleaving equipment. Realistic estimates of mirror thickness lie in the range of 200-500 $\mu m$, depending upon experimental skill. This would add an additional; variable parameter in characterizing the power from these devices.

In the optical mask designed for edge emission in nanopillars we made a provision to add surface gratings over the top contact. Separated by a period $\lambda = \lambda_{GaAs}$, where

\(^1\)Private communication with Prof. A. Tredicucci
6. CONCLUSIONS AND FUTURE WORK

$\lambda_{GaAs} = 28 \, \mu m$ in GaAs for 3 THz free space radiation, these slits enable surface out-coupling of the radiation \[198, 199\]. As described in Chapter 3, the effective refractive index of the nanopillar array is likely to depend upon the physical radial dimension of the nanopillars, the pitch of the nanopillar array and the planarizing material. Therefore, the period $\Lambda$ would be governed by the intended quantum-dot cascade structure. The slit width (typically, 2-3 $\mu m$ in our design) should be kept larger than the pitch.

Untested on actual nanopillars in THz QCL, these surface gratings also serve as air-gap windows for lateral etch of the planarizing material which allow for suspended top contact and hence lower losses. Figure 6.1 shows the proposed schematic diagram for fabricating suspended top-contact in a surface emitting quantum-dot cascade laser. Note that the windows opened in the photoresist, subsequent to top metal evaporation are orthogonal to the emitter gratings, so as to achieve a criss-cross pattern. This minimizes the area open to the etchant during insulation removal.

Figure 6.1: Process schematic of suspended top contact in surface emitting quantum-dot cascade laser, showing (a) planarized nanopillar array after top contact evaporation, with surface gratings (b) definition of air-gap windows in the photoresist (c) equirate lateral and vertical etch of the insulation through the area shown in dashed lines (d) laterally etched insulation after removal of the photoresist in acetone. The dimensions are not to scale.

Note that these suggestions are only speculative and the waveguide design of quantum-
6.2 Opportunities for future
dot cascade lasers should take the polarization of the emitted radiation into account, which in itself is a subject of dedicated research.

6.2.3 Lateral confinement in THz QCLs - Nanofences

The current state of art THz QCLs are based on a cascade of quantum wells and barriers where electrons are confined in the growth direction but free in the other two dimensions. This means that traditionally, electrons have in-plane momentum parallel to the direction of epitaxial growth. This work explored the feasibility of achieving zero-dimensional confinement in THz QCLs. An intermediate step between the present day THz QCLs and quantum-dot THz QCLs would be the demonstration of lateral confinement in one-dimensional THz quantum cascade structures. We coin the term 'nanofences' to describe the design of these intermediary THz quantum cascade structures. Instead of etching pillars, this proposal is based on etching holes. As described later in this section, our proposal (nanofences) circumvents the problems of planarization and top-contact faced during the fabrication of nanopillars.

Just as the history of top-down zero-dimensional structures can be traced back to resonant tunneling diodes [89], the first demonstration of one-dimensional laterally confined electrons can be traced back to resonant tunneling devices [200]. Shown in figure 6.2, is the device schematic and the corresponding scanning electron microscope image of a grid gate which imposes a periodic potential that confines the electrons laterally, governed by the width of the metal lines. In figure 6.2, this width is \( t = 50 \text{ nm} \). In work done by Allee et al. [200], lateral confinement is achieved electrostatically by applying a suitable bias on the patterned top gate.

While this work has inspired the design of nanofences, it can not be adapted in a straightforward manner to the THz QCLs. In fact, lateral confinement in THz QCLs is theoretically impossible to obtain by electrostatic means. This is because the depletion of charge carriers which needs to occur throughout the height of THz QCLs (3 \( \mu \text{m} \), in ultra-thin QCLs) can not extend beyond a few nm in the growth direction, depending upon the doping of epitaxial layers. The nanofence proposal is based on using the metal grid pattern shown in figure 6.2 as a mask to etch holes in an ultra-thin THz QCL. This etch mask also forms the self-aligned top contact to the active region.

Depending upon the grid dimensions \( L_x \) and \( L_y \), the periodic lateral potential can be classified into two main categories. A pseudo-zero dimensional potential may occur for metal width \( t \leq 300 \text{ nm} \) (similar to nanopillar radius, \( R_p \leq 150 \text{ nm} \)) and \( L_x = L_y \leq 2t \). Under this condition, the in-plane moment of electrons would be constrained in both


CONCLUSIONS AND FUTURE WORK

Figure 6.2: First demonstration of resonant tunneling of one-dimensional electrons in a 3-dimensional array of confined potential. (a) Device schematic of laterally confined resonant tunneling field effect transistor (b) Scanning electron micrograph of the top gate. Adapted from [200]

If \( t \leq 300 \text{ nm} \) and \( L_x \) (and/or \( L_y \)) \( \gg 2t \), the electrons would have in-plane momentum in the \( x \) (and/or \( y \)) direction, which is akin to having an array of one-dimension electron wires. Under this condition, the electrons at the intersection of the grid would still be confined in both \( x \) and \( y \) directions.

The lower limit to \( t \) is determined by e-beam dose energy, exposure time, resist thickness and polarity which in our preliminary work at Cavendish is set at 100 nm. Furthermore, as \( t \) approaches 100 nm, a high pattern density, \( L_x(\text{or} \ L_y) - t \approx t \), is typically difficult to achieve in practice as it causes e-beam proximity effects resulting in significant pattern distortion and incomplete lift-off of metal. This is shown in figure 6.3(a), where an over exposure of the e-beam causes reduction in \( t \) from 100 nm to 43.8 nm and increase in pitch, \( L_x(\text{or} \ L_y) - t \) from 100 nm to 130 nm. Incomplete lift-off is not a problem however for larger values of \( t \) and \( L_x(\text{or} \ L_y) - t \) as shown in figure 6.3(b), where \( t \) shrinks from 300 nm to 260 nm and \( L_x(\text{or} \ L_y) - t \) increases from 900 nm to 917 nm. Depending upon whether the defined \( t \) is closer to the lower limit \( \sim 100 \text{ nm} \) or the higher limit \( \sim 300 \text{ nm} \), the periodic potential can be categorized as a weak or strong lateral potential.

It may also be possible to do away with the grid altogether and have a grating structure instead to obtain pure one-dimensional effects. However, structural stability of a grating structure for THz QCL emitter structures is likely to be a cause for concern.

Figure 6.4 shows the processing route developed for integrating nanofences with a THz QCL structure. After the thermocompression bonding and etch stop removal, the first mesa
6.2 Opportunities for future

Figure 6.3: Scanning electron micrograph of nanofences etch mask showing (a) incomplete metal lift off at a lithographically defined \( t = 100 \text{ nm} \) and \( L_x - t = 100 \text{ nm} \), for a grid simulating a strong pseudo-zero dimensional potential (b) metal mask at a lithographically defined \( t = 300 \text{ nm} \) and \( L_x - t = 900 \text{ nm} \), for a grid simulating weak one dimensional potential.

is chemically etched (figure 6.4(a)). In the second step, the \( n^+ \) GaAs layer is removed by dry etching around the second mesa. Note that it is the second mesa that forms the active region, which finally takes part in the electron transport. Once the second mesa and the first mesa are isolated, the first mesa naturally acts as the support for the top contact. This is shown in figure 6.4(c) where the conformally deposited SiO\(_2\) layer forms the insulation for the device. This layer can be thin (~100 nm). The advantage of using the first mesa for support, insulated by PECVD oxide over the planarization process discussed in Chapter 4 for nanopillars is clear. There is no necessity to spin-coat an insulator.

The next step (figure 6.4(d-e)) is the key to the observation of lateral confinement effects in nanofences. This step involves opening up of windows in the oxide layer to enable e-beam lithography of the nanofences (top contact windows) and connection to the bottom contact (bottom contact windows). The e-beam lithography defines the etch mask (figure 6.4(f-g)), which at the same time forms a self aligned top contact for the nanofences (figure 6.4(h)). The window etched into the oxide (top contact windows) must be aligned to a very high precision with the second mesa. If the window dimensions are larger than the second mesa dimensions, it is likely that e-beam lithography would result in shorting of the device. If however, the window dimensions are smaller than the mesa dimension, say for example by 5 \( \mu \text{m} \) on either sides, then these two 5 \( \mu \text{m} \) channels would dominate transport and optical profile over that of the nanofences. To observe lateral confinement effects, it is therefore necessary to reduce the overlap of the oxide with the second mesa, and at the same time maintain the electrical stability of the structure.

Theoretically, it is possible to optically align the windows in the oxide layer with the
6. CONCLUSIONS AND FUTURE WORK

Figure 6.4: Processing route for nanofences showing (a) wet etch of first mesa (b) reactive ion etch of second mesa i.e. removal of the $n^+$ GaAs layer (c) conformal deposition of SiO$_2$ via. PECVD (d) optical lithography of windows in the oxide layer (e) device schematic after removal of oxide via dry etching (f) PMMA spin-coated over device (g) e-beam lithography of nanofences etch mask and formation of self-aligned top contact (h) reactive ion etching of active region and formation of natural air gap between laterally confined regions.
second mesa, within an accuracy of 200 nm using Moire techniques [201]. Based on an observation of diffraction patterns (fringes) due to misalignment between a circular grating etched on the wafer and a grating on the mask plate, we have been able to achieve a high degree of alignment precision (figure 6.5).

Figure 6.5: Moire patterns showing (a) computer generated image of perfectly circular fringes (1 and 2) on alignment (b) optical microscope image of fringes indicating slight misalignment ($\leq 0.5 \mu m$) in the direction of the arrow (c) optical microscope image of fringes indicating misalignment by 2 $\mu m$ in the direction shown.

While the nanofences approach has its advantages over the nanopillars approach to lateral confinement, it comes at a cost of different but equally important processing issues. As mentioned before, e-beam lithography and optical alignment are likely to be bottle neck steps in development of the nanofences architecture.

6.2.4 Characterization of graphene domain boundaries by THz TDS

In Chapter 4, we suggested that the absorption features at 1.6 THz, occurred as a consequence of scattering by domain boundaries. Understanding of the exact mechanism behind the absorption features requires a systematic study of the THz absorption with dependence on the underlying microscopic structure of the grain boundaries. This can be investigated by performing THz TDS of CVD graphene grown at different growth conditions [7].

Other parameters to explore the origin of the absorption features include a systematic study of THz absorption as a function of device geometry (gate length, distance of gate from graphene, thickness and overlap of ionic gel) and device bias conditions (symmetric and asymmetric).
6. CONCLUSIONS AND FUTURE WORK

6.2.5 THz filters from graphene anti-dots

Soon after the demonstration of plasmonic resonances in graphene ribbons[71], disks[184] and rings[202], Nikitin et. al predicted another novel geometry for plasmon scattering. This geometry used antidots (or holes), in a sheet of graphene instead of isolated disks or rings [203]. The advantage of this geometry over the other two dimensional gratings is that it provides electrical continuity in addition to periodicity.

Over the course of this work, we designed an optical mask to pattern antidot arrays in graphene based on Nikitin et. al’s proposal. The plasmonic frequency corresponding to these arrays lies in the range of 0.46 to 2 THz. Although, these gratings were not implemented owing to a lack of time, they can tested in future for suitability as THz filters. This assumes that polycrystallinity is not a limitation and large area single crystal sheets of graphene can be obtained [204].

6.2.6 THz amplitude modulators

The key performance indicators of a modulator are modulation speed and modulation depth. The modulation speed can be enhanced by reducing the footprint of the graphene sheet. Modulation speeds as high as GHz can be obtained by using an array of high frequency graphene FETs. [205].

Theoretically, the modulation depth can be increased by employing multiple graphene layers stacked on top of each other but separated by an insulator [184, 193]. In this type of device architecture when one layer is biased at the Dirac point and the other layer is biased away from the Dirac point, it is possible to completely suppress THz transmission through graphene.

It is also possible to achieve a narrow band metamaterial-based modulator in graphene [71, 184]. On tuning the graphene in and out of plasmon resonance by changing the carrier concentration, the transmission can be switched from 'high ' to 'low '. All these separate approaches suggest that there still remains an opportunity to optimize and design a highly efficient, compact graphene based THz modulator.
Chapter 7

Appendix A

7.1 Epitaxial structure of RTDs

The epitaxial structure of the two test RTD structures: A1700 and W0021 is given below.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness (nm)</th>
<th>Doping (cm$^{-3}$)</th>
<th>Mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>333</td>
<td>2e18</td>
<td></td>
</tr>
<tr>
<td>GaAs</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlGaAs</td>
<td>5</td>
<td></td>
<td>0.33</td>
</tr>
<tr>
<td>GaAs</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>AlGaAs</td>
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<td></td>
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</tr>
<tr>
<td>GaAs</td>
<td>100</td>
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</tr>
<tr>
<td>GaAs</td>
<td>333</td>
<td>2e18</td>
<td></td>
</tr>
</tbody>
</table>

Table 7.1: Epitaxial structure of A1700

<table>
<thead>
<tr>
<th>Material</th>
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<th>Doping (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
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</tr>
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<td></td>
</tr>
<tr>
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</tr>
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<td>2e18</td>
</tr>
</tbody>
</table>

Table 7.2: Epitaxial structure of W0021
Chapter 8

Appendix B

Systematic changes in the global or well thickness in the QCL superlattice structure can directly influence the transport and the frequency of THz emission \([5]\). The layer thickness, length of the superlattice period and the interface quality of the designed QCL structure grown by molecular beam epitaxy can be verified using X-Ray diffraction. Below, we present a brief overview of the X-Ray diffraction (XRD) technique, followed by the rocking curves (diffraction pattern) for the THz QCLs studied in this thesis. All the rocking curves shown below were provided by Dr. Harvey E. Beere.

8.1 X-ray diffraction technique

In the X-ray diffraction pattern of a THz QCL, the strongest peak arises from the \([004]\) reflection of the bulk GaAs crystal. This pattern from the bulk GaAs crystal is modulated by the diffraction pattern obtained from the artificial supelattice structure.

The superlattice period is much larger than the unit cell spacing. Therefore, the diffraction pattern exhibits additional closely spaced satellite peaks in the reciprocal space. The spacing between the satellite peaks is inversely proportional to the length of the period \(L\). This can be described in a simple formula as:

\[
L = \frac{(N_i - N_j)\lambda}{2(sin\theta_i - sin\theta_j)},
\]

(8.1)

Here, \(\lambda\) is the X-ray wavelength and \(\theta_i, \theta_j\) are the angles of diffraction \([206]\). A comparison between the observed rocking curve (measured using the PBrucker D8 Discover...
8. APPENDIX B

High Res System) and the simulated curved (on the Philips X’pert software suite) gives an indication of the wafer quality.

8.2 Rocking curves of THz QCLs

Figures 8.1 to 8.9 show the X-ray diffraction rocking curves measured using the Bruker D8 Discover High Res System of all the THz QCLs presented in this thesis. Measurements made using the Bruker D8 Discover show a full-width-half-maxima (FWHM) of approximately 35-40 arc.sec for the GaAs substrate peak and approximately 35-50 arc.sec for the satellite peak, depending on the optics used. The full width half maximum (FWHM) of all the peaks, i.e. the substrate peak and the satellite peak is limited by the resolution of the system. Ideally, the substrate peak should show an FWHM of approximately 15-20 arc.sec and the satellite peak should show an FWHM of approximately 20-30 arc.sec. Therefore, it is difficult to discern any noticeable broadening of the satellite peaks, which would give insights on inhomogeneity such as flux drift, arising during the epitaxial growth. However, if there was a big drift, it would be observable in the XRD data measured using the Bruker system.

![Figure 8.1: X-ray diffraction rocking curve from ultrathin 2.7 THz 3 QW Paris design (V671).](image)

Figure 8.1: X-ray diffraction rocking curve from ultrathin 2.7 THz 3 QW Paris design (V671).
Figure 8.2: X-ray diffraction rocking curve from ultrathin 2.7 THz 3 QW Paris design (V692).

Figure 8.3: X-ray diffraction rocking curve from ultrathin 2.7 THz 3 QW Paris design (W0798).
Figure 8.4: X-ray diffraction rocking curve from full-stack 3 THz 3 QW Paris design (V702).

Figure 8.5: X-ray diffraction rocking curve from ultrathin 3 THz 3 QW Paris design (V703).
8.2 Rocking curves of THz QCLs

Figure 8.6: X-ray diffraction rocking curve from full-stack 3 THz 4 QW MIT design (V704).

Figure 8.7: X-ray diffraction rocking curve from ultrathin 3 THz 4 QW MIT design (V705).
Figure 8.8: X-ray diffraction rocking curve from full-stack 3 THz 4 QW ETH design (V674).

Figure 8.9: X-ray diffraction rocking curve from full-stack 3 THz 4 QW ETH design (V696).
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[147] G. C. DeSalvo, W. F. Tseng, and J. Comas. Etch rates and selectivities of Citric Acid/Hydrogen Peroxide on GaAs , Al\textsubscript{0.3}Ga\textsubscript{0.7}As , In\textsubscript{0.2}Ga\textsubscript{0.8}As , In\textsubscript{0.53}Ga\textsubscript{0.47}As , In\textsubscript{0.52}Al\textsubscript{0.48}As , and InP. *Journal of Electrochemical Society*, 139:831–833, 1992.


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