Biasing Plasmonic Nanocavities



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Declaration

I hereby declare that except where specific reference is made to the work of others, the contents of this dissertation are original and have not been submitted in whole or in part for consideration for any other degree or qualification in this, or any other university. This dissertation is my own work and contains nothing which is the outcome of work done in collaboration with others, except as specified in the text and Acknowledgements. This dissertation contains fewer than 65,000 words including appendices, bibliography, footnotes, tables and equations and has fewer than 150 figures.

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Abstract

Molecular electronics promises a new generation of ultralow-energy information technologies, based around functional molecular junctions where two electrodes are bridged by just a few molecules. How molecules exactly behave in a real junction however is still not well understood, since interactions with the electrode materials and neighbouring molecules at the nanoscale is difficult to model and probe experimentally. Many studies so far have characterised in detail the electrical response of molecular junctions by statistical analysis of many repeated measurements, but without monitoring in real time the behaviour of individual devices. The main difficulty of in situ measurements is the absence of characterisation tools that can provide direct access to the dynamics of nm-sized junctions during device operation.

This thesis explores two novel approaches used to create optically accessible nanoscale junctions. One method is based on graphene electrodes, used to fabricate extended junctions with a metal oxide spacer. These graphene junctions are found to behave as memristive devices, where a solid state redox reaction releases gas from the oxide spacer that remains trapped under the graphene, resulting in an actuating mechanism. Displacement of the surface layers can be optically tracked in real time using metallic nanoparticles deposited on the sample, whose plasmonic coupling with the bottom electrode is modulated by the actuation mechanism.

The second method used to construct nanoscale junctions is more appropriate for molecular junctions, and is based on electrical contacting of individual metallic nanoparticles with a conductive transparent cantilever. Nanoparticles are deposited on a molecular monolayer and represent one electrode of a molecular junction, and at the same time allow to optically probe the junction itself by enabling plasmonic confinement of light to volumes <100nm³. Darkfield and Raman spectroscopy are performed on single nanoparticle junctions in real time while voltage is applied, and a modulation of the optical response with voltage is observed, revealing that molecules undergo conformational changes during device operation.

List of publications

- <u>Dean Kos</u>, Giuliana Di Martino, Alexandra Boehmke, Bart de Nijs, Dénes Berta, Tamás Földes, Edina Rosta, Jeremy J. Baumberg. "Optical Probes of Molecules as Nano-Mechanical Switches", *in review*, 2019.
- H. Hou, Y. Kozuka, Jun-Wei Liao, L. W. Smith, <u>Dean Kos</u>, J. P. Griffiths, J. Falson, A. Tsukazaki, M. Kawasaki, and C. J. B. Ford. "Quantized conductance of onedimensional strongly correlated electrons in an oxide heterostructure". *Physical Review B*, 99(12):121302, March 2019.
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Chapter 1

Introduction

A couple of decades ago, nanotechnology was seen as one of the most promising frontiers of scientific research, predicted to bring about a technological revolution across many fields in a short period of time [1]. The ideal concept was to construct materials and systems from basic nm-sized building blocks, that would assemble themselves into specific structures tailored for each application [2]. Fast forward to today, major technological disruptions driven by nanotechnology are still relatively sparse, with most practical applications relating to adoption of "passive" nanomaterials to improve existing technologies, although in a vast range of sectors including flexible and transparent electronics [3], batteries [4], disease detection [5], construction [6] and the food industry [7]. The reason behind the limited number and sophistication of applications lies in the intrinsic complexity of matter at the nanoscale. Simply isolating a nanostructure to expose its fundamental properties is often already a challenge, and any interaction with other objects immediately adds multiple layers of complexity. The vast amount of research conducted in nanoscience over the last couple of decades has unveiled many properties of nanomaterials, and these now need to be exploited to produce more "active" nanostructures.

Electronics was among the sectors on which nanotechnology was expected to have the highest impact. Although the scaling of commercial integrated circuits to component sizes as small as ~10nm is one of the great successes of the modern semiconductor industry, this level of miniaturisation has been achieved by pushing the boundaries of traditional lithography, rather than by introducing a radically different approach in the fabrication of electronics. As further reduction in size becomes increasingly difficult, alternative designs in electronics are being proposed to break the fabrication barrier of lithography, and reduce the energy required for computation.

One example of an alternative electronic device is the *memristor*, a component that can change its resistance state when a voltage is applied. The change in resistance is non-volatile, and thus the device can be used as both a switch and a memory unit in one. Memristors potentially represent a new practical paradigm for neural computing [8], where computation is performed concurrently with memory operations, rather than by a central processing unit exchanging information with a separate memory module. Memristive circuits could perform some operations faster than a normal CPU-memory architecture and with higher energy efficiency.

Another promising frontier for computing is *molecular electronics*, whose aim is to use an individual molecule or set of molecules as a fundamental electronic component. Single molecule functionality possibly represents the ultimate scaling limit of electronics, that could enable devices with even higher density and lower power requirements. Molecular structures tailored to particular applications could provide a specific electronic response in a junction with sub-nm dimensions, that would otherwise require multiple semiconductor devices.

Before device concepts such as memristors or molecular junctions can be rationally designed and integrated into practical circuits, their behaviour in realistic device geometries needs to be fully understood. A basic nanoscale electronic junction is made of a dielectric layer (molecules or an inorganic material) positioned between two electrodes, and an important challenge is to characterise junction functionality in real time during device operation. While the electrical response is measured by applying a voltage, identifying the fundamental mechanism responsible for such response is not straightforward. Common characterisation tools used in nanoscience, such and scanning or transmission electron microscopy, atomic force microscopy, or X-ray spectroscopy, are often difficult to integrate with real time junction measurements, and can alter the electronic functionality of devices. There is a strong need for non-invasive in situ characterisation methods, and the work presented in this thesis explores the use of optical spectroscopy for this application.

Visible light is generally not a useful tool for direct inspection of objects in the sub-100nm scale, because resolution is limited by diffraction to a few hundred nm. However, metallic nanostructures such as nanoparticles can interact with light and amplify the electromagnetic field near their surface, effectively concentrating light to much smaller volumes ~100nm³. This effect is due to the strong interaction of free electrons with light, also called *localised surface plasmon*, observed when the size of metallic objects is scaled down to ≤ 200 nm. The peculiar optical response of nanoparticles makes them very useful as optical probes to directly investigate nm-sized surface layers with spectroscopy.

The main objective of this thesis is to optically access the functional layer of memristors and molecular junctions in real time. This is achieved by integrating metallic nanoparticles into working devices, and tracking the evolution of the functional layer during device operation with optical spectroscopy.

Chapter 2 provides an overview of plasmonics, and shows the origin and implications of the optical response of nanoparticles. Particular attention is dedicated to coupled plasmonic systems, specifically the nanoparticle on mirror geometry, which is adopted in all fabricated devices described in later chapters.

Chapter 3 is an overview of nanoscale electronics. Transport properties of materials radically change when the size of electronic junctions is pushed to the nanoscale, with the onset of nonlinear quantum effects. This is evident in memristors, but even more dramatically in molecular junctions, where electrical currents are driven through single molecules or sets of molecules.

Chapter 4 presents the experimental methods used in this thesis for imaging and spectroscopy of electronic devices. An optical microscope in darkfield configuration is the main tool used to observe nanoparticles. Raman spectroscopy is extensively used to characterise molecules in molecular junctions, so the method is presented with a brief theoretical introduction followed by the practical implementation used in experiments.

Chapter 5 reports the results of electrical and optical measurements on memristors fabricated with a graphene top electrode and an inorganic oxide spacer. While the memristive devices discussed in this Chapter were initially only designed as test samples for the subsequent development of molecular junctions, they exhibit a peculiar actuating response driven by solid state redox reactions, that has potential applications for nanoactuation. The device geometry presented in this Chapter was then abandoned as a scheme for molecular junctions due to difficulties in fabrication.

Chapter 6 describes the experimental setup developed to create optically accessible molecular junctions. A conductive but transparent cantilever is used to electrically contact

a single metallic nanoparticle, that represents the electrode of a molecular junction. Plasmonic localisation of the optical response allows to directly investigate in situ the molecules responsible for conduction. The various stages of setup development are described, together with testing of the electrical and optical performance.

Chapter 7 finally reports the experimental data obtained from simultaneous electric and spectroscopic measurements on single nanoparticle molecular junctions. A modulation of the Raman scattering intensity with applied voltage is observed for biphenyl molecular layers, originating from a conformational change in the molecules, where phenyl rings twist with respect to their equilibrium position with no bias. A simple circuit model based on junction capacitances supports the observations, indicating that the twisted configuration is energetically favoured.

Chapter 2

Plasmonics of nanostructures

In the experimental work presented in this thesis, nanoparticles are used as optical probes to detect changes in nanoscale electrical junctions during operation of a device. An understanding of their optical properties is thus essential to interpret the spectroscopic data obtained from measurements and correctly infer what mechanisms are responsible for a given response. This Chapter reviews the origin, characteristics, and applications of nanoparticles as optical probes.

Plasmons are collective oscillations of free electrons in a metal. While they exist in the bulk and are responsible for the external appearance of metallic materials, as discussed in Sections 2.1 and 2.2, these oscillations become particularly interesting when the size of a metallic object is scaled down below the wavelength of visible light, where they give rise to localised plasmons. As electrons can rapidly move across the entire metallic nanostructure within a single oscillation of the electromagnetic field, they can resonantly interact with light, and this results in amplified fields around the nanostructure itself, described in Section 2.3. The resonant behaviour of metallic nanostructures with respect to light leads to enhanced light-matter interaction and widespread applications in sensing that are crucial for the work presented in this thesis.

One of the simplest and most reproducible structures that support localised plasmons are metallic nanoparticles. They represent a convenient system to exploit plasmonics at the nanoscale because of their availability, tunable size, versatility and ease of detection. Metallic nanoparticles easily bind to a number of different substrates and molecules, and compound structures such as nanoparticle dimers or aggregates can also be fabricated, further modifying their optical response (Section 2.4). Nanoparticles deposited on a flat substrate can be imaged with an optical microscope, and their scattered light collected to perform spectroscopy. In Section 2.5, it is shown how they can represent invaluable tools to optically access the behaviour of complex systems at the nanoscale.

2.1 Electron oscillations in metals

Electrons in the valence band of a metal are bound to the atomic lattice, whereas electrons of the conduction band are relatively free to move. These free electrons are responsible for interaction of the metal with electromagnetic fields, and the interaction is best described with the dielectric function $\varepsilon(\omega)$ of the metal, that depends on the field frequency ω .

An external electric field **E** induces a polarisation **P** in a material as a consequence of the alignment of its microscopic dipoles, and the dielectric function $\varepsilon(\omega)$ is related to these quantities by [9]:

$$\mathbf{P} = \varepsilon_0 \left(\varepsilon(\omega) - 1 \right) \mathbf{E} , \qquad (2.1)$$

where ε_0 is the vacuum permettivity. In general $\varepsilon(\omega)$ also depends on position and time, causing nonlocal effects, but these are not considered here.

A simple expression for the dielectric function of metals can be calculated starting from the Drude model [9]. In this classical model, the metal is assumed to be composed of a gas of free electrons that move against a background of fixed positive ion cores, and electron-electron interactions are neglected. The application of an external electric field accelerates the electrons, which move in a straight line and collide against the ions with a frequency $\gamma = 1/\tau$, where τ is the mean free time between collisions (typically $\tau \sim 10^{-14}$ s at room temperature, corresponding to $\gamma = 100$ THz). The effect of the atomic lattice potential can be partially accounted for by defining an effective electron mass obtained from the band structure of the material [9]. Following this model, the equation of motion for an electron with effective mass *m* and charge -e can be written as:

$$m\ddot{\mathbf{x}} + m\gamma\dot{\mathbf{x}} = -e\mathbf{E}$$
.

Assuming harmonic time dependence for the electric field, $\mathbf{E}(t) = \mathbf{E}_0 e^{-i\omega t}$, a solution of this equation is:

$$\mathbf{x}(t) = \frac{e}{m(\omega^2 + i\gamma\omega)} \mathbf{E}(t) \,.$$

This is the expression of the displacement of a single electron, which can be used to calculate the macroscopic polarisation \mathbf{P} of a gas with number density *n*:

$$\mathbf{P} = -\frac{ne^2}{m(\omega^2 + i\gamma\omega)}\mathbf{E}$$

and thus, using equation (2.1),

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} , \qquad (2.2)$$

where ω_p is the plasma frequency defined by $\omega_p^2 = ne^2/\varepsilon_0 m$. The plasma frequency depends on the material and usually corresponds to energies between 5 and 15 eV, typical of UV radiation. It is useful to decompose the expression for $\varepsilon(\omega)$ into its real and imaginary parts, called respectively $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$:

$$\varepsilon_1(\omega) = 1 - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2}$$
(2.3)

$$\varepsilon_2(\omega) = \frac{\omega_p^2 \tau}{\omega(1 + \omega^2 \tau^2)} , \qquad (2.4)$$

where $\gamma = 1/\tau$. Analysing equations (2.3) and (2.4), different frequency regimes can be identified. At very high frequency, when $\omega \gg \omega_p$, $\omega \tau \gg 1$ so there is negligible damping, and $\varepsilon(\omega)$ is mainly real:

$$\varepsilon(\omega) \approx 1 - \frac{\omega_p^2}{\omega^2}$$
 (2.5)

In this regime the metal is therefore predicted to be transparent, which is an important limitation of the Drude model, because it neglects electrons of the valence band that can be excited by interband transitions in this frequency range. On the contrary, when $\omega \tau \ll 1$, $\varepsilon_1(\omega)$ is large and negative, while $\varepsilon_2(\omega)$ is large and positive. This leads to high absorption, and radiation in this frequency range can penetrate into the metal only for very short distances.

For $1 < \omega \tau < \omega_p \tau$, which corresponds to energies approximately between 1 and 10 eV, there is a less clear boundary between free and bound charges, and there is no dominant behaviour. In this regime the energy required to trigger interband transitions is particularly important, and depends on the material. An example of values of $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ is shown in Figure 2.1 for the case of gold. The graphs show the behaviour predicted by



Fig. 2.1 Au dielectric function. Real and imaginary parts of the dielectric function $\varepsilon(\omega)$ of gold. The solid line shows the prediction of the Drude model, the dotted line the experimentally measured values. The deviation from the model due to interband transitions is evident above 2 eV. Data from [10].

the Drude model compared to the real material. The model agrees with the experimental data up to approximately 2 eV, a value that marks the onset of interband transitions. It is possible to go beyond the Drude approximation, with more accurate classical models that consider also the bound electrons (for example the Drude-Lorentz model), or with quantum treatments that take into account the electron-electron interactions (Drude-Sommerfeld model). These more sophisticated models are not discussed here, since the Drude theory applies well to metals such as Ag or Au below the interband transition frequencies, which is sufficient to provide a fundamental description of plasmonics.

2.2 Surface plasmon polaritons

The Drude model of the dielectric function applies to all harmonic charge oscillations in a metal. This includes longitudinal oscillations called *volume plasmons* that occur in the bulk of a metal, but these do not couple to light, that has a transverse nature. Instead, light can interact with a different type of excitation, that happens near the metal surface. Under certain conditions, an electromagnetic wave can induce a charge oscillation at the surface, that remains bound to and propagates along the metal-dielectric interface. These propagating oscillations are hybrid states formed by the interaction of the electromagnetic wave and the plasmon, called *surface plasmon polaritons* (SPP).

To see how the interface between a metal and a dielectric can sustain a surface plasmon polariton, the system can be reduced to one dimension (Figure 2.2a), with the propagation happening along the *x* axis and no spatial variation along the *y* axis, so $\varepsilon = \varepsilon(z)$.



Fig. 2.2 Propagation of surface plasmon polaritons. **a**, Illustration of a propagating SPP, with the coupling between light and charge oscillations in the metal. **b**, Profile along z of the electric field at the interface between metal and dielectric. Figure adapted from [12].

The starting point of the analysis is the Helmholtz equation for the electric field \mathbf{E} , which is the equation for a propagating wave with harmonic time dependence [11]:

$$\nabla^2 \mathbf{E} + k_0^2 \varepsilon \mathbf{E} = 0 , \qquad (2.6)$$

where $k_0^2 = \omega/c$ is the wave vector, with *c* speed of light in vacuum. An analogous equation holds for the magnetic field. Including the harmonic time dependence, the electric field in the considered geometry can be expressed as:

$$\mathbf{E}(x, y, z) = \mathbf{E}(z)e^{i(k_x x - \omega t)}$$

where k_x is the *x* component of the wave vector. Substituting into (2.6) gives the wave equation:

$$\frac{\partial^2 \mathbf{E}(z)}{\partial z^2} + \left(k^2 \varepsilon - k_x^2\right) \mathbf{E} = 0 , \qquad (2.7)$$

and a similar equation can be obtained for the magnetic field **H**. It can be shown that the solutions to this equation can be separated into two sets, depending on the polarisation of the electromagnetic wave. One set is represented by the *transverse electric* (TE) modes, or *s* modes, for which only the components H_x , H_z and E_y are nonzero; the other set is represented by the *transverse magnetic* (TM) modes, or *p* modes, for which only the components E_x , E_z and H_y are nonzero. TE-polarised modes cannot be sustained by a metal-air interface, so only TM modes are acceptable solutions for modes bound to the surface.

For TM modes the solutions of equation (2.7) are:

$$H_{y}(z) = A_{m} e^{ik_{x}x} e^{k_{m,z}z}$$

$$E_{x}(z) = -i A_{m} \frac{k_{m}}{\omega \varepsilon_{0} \varepsilon_{m}} e^{ik_{x}x} e^{k_{m,z}z} \qquad (z < 0) ,$$

$$E_{z}(z) = -A_{m} \frac{k_{x}}{\omega \varepsilon_{0} \varepsilon_{m}} e^{ik_{x}x} e^{k_{m,z}z}$$

and

$$H_{y}(z) = A_{d} e^{ik_{x}x} e^{-k_{d,z}z}$$

$$E_{x}(z) = i A_{d} \frac{k_{d}}{\omega \varepsilon_{0} \varepsilon_{d}} e^{ik_{x}x} e^{-k_{d,z}z} \qquad (z > 0)$$

$$E_{z}(z) = -A_{d} \frac{k_{x}}{\omega \varepsilon_{0} \varepsilon_{d}} e^{ik_{x}x} e^{-k_{d,z}z}$$

where ε_d and ε_m are the dielectric functions of the insulator and metal, respectively. Continuity of H_y and εE_z along *z* requires that $A_m = A_d$ and also

$$\frac{k_d}{k_m} = -\frac{\varepsilon_d}{\varepsilon_m} \ . \tag{2.8}$$

Combining this with the condition of confinement to the surface $\operatorname{Re}(k_m)$, $\operatorname{Re}(k_d) > 0$, and assuming that for the dielectric medium $\varepsilon_d > 0$, equation (2.8) can only be valid if $\operatorname{Re}(\varepsilon_m) < 0$. This is exactly what happens in metals, as described in section 2.1. Figure 2.2a schematically shows an intuitive picture of SPP propagation, as a combination of moving charges in the metal and electromagnetic waves in the dielectric. The electric field $E_z \propto e^{\pm k_z z}$ decays rapidly away from the surface (Figure 2.2b), with the field decreasing to 1/e of its initial amplitude within a distance δ_d in the dielectric and δ_m in the metal according to [13]:

$$\delta_d = \frac{1}{k_0} \left| \frac{\mathsf{Re}(\varepsilon_m) + \varepsilon_d}{\varepsilon_d^2} \right|^{1/2} \quad , \quad \delta_m = \frac{1}{k_0} \left| \frac{\mathsf{Re}(\varepsilon_m) + \varepsilon_d}{\mathsf{Re}(\varepsilon_m)^2} \right|^{1/2} \; .$$

In the visible range δ_d is of the order of a few hundred nm, while δ_m is up to a few tens of nm in noble metals such as Ag or Au.



Fig. 2.3 Dispersion diagram of SPPs for air-metal and silica-metal interfaces. The dispersion curves do not cross the respective light lines ($\omega = k_0 c/n$), and thus SPPs do not couple directly to light on the surface of a metal. The lines above ω_p represent the volume plasmons. Figure adapted from [11].

By inserting the expression for H_y into the analogous of equation (2.7) for the magnetic field the following expression is obtained:

$$k_m^2 = k_x^2 - k_0^2 \varepsilon_m$$
$$k_d^2 = k_x^2 - k_0^2 \varepsilon_d$$

which, combined with (2.8), gives:

$$k_{\rm SPP} = k_0 \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} , \qquad (2.9)$$

where k_x is relabelled as k_{SPP} . Equation (2.9) is the dispersion relation of surface plasmon polaritons propagating at the interface between a metal and a dielectric. Figure 2.3 shows the dispersion diagram of SPPs for a Drude metal and two dielectrics, air ($\varepsilon_d = 1$) and fused silica ($\varepsilon_d = 2.25$). The dispersion of SPPs corresponds to the curves on the right of the respective light lines of air and silica, meaning that they have a higher wavevector than light. Because these curves do not cross, SPPs cannot be excited with light directly incident on the surface of the metal. The typical propagation length for a SPP is of the order of a few tens of μ m for excitation in the visible, and up to a few hundred μ m in the near IR, and depends on the type of metal, dielectric, and on the quality of the film [11].

To excite SPPs on a metal, the wave vector of light near the surface has to be increased. Several techniques can be used to achieve this, the simplest being prism



Fig. 2.4 Excitation of SPPs. Prism (**a**) and grating (**b**) coupling of light to SPPs. Figure adapted from [11].

coupling and grating coupling [11]. In the first, a metal film is positioned on one side of a prism, with air on the opposite side (Figure 2.4a). A beam reflected at the interface between the prism and the metal excites an oscillation with wave vector $k_x = k_0 \sqrt{\varepsilon} \sin \theta$, where ε is the dielectric function of the prism. While this wave vector cannot excite a SPP at that same interface, it can excite a SPP at the metal-air interface whenever $k_x = k_{SPP}$. This corresponds to the intersection of the light line of the prism material (silica in Figure 2.3) with the dispersion of the metal-air SPP.

The increase in wave vector can also be obtained by patterning the metal surface with a grating of grooves or holes with a lattice constant *a* (Figure 2.4b). In this case, coupling is achieved whenever $k_{\text{SPP}} = k_0 \sin \theta \pm mg$, where $g = 2\pi/a$ and *m* is a positive integer number. With this technique, the reverse process is also possible: SPPs propagating along a surface modulated by a grating can couple to light and thus emit radiation.

2.3 Localised surface plasmons

The previous section discussed plasmons that propagate along a surface and can couple to light only under particular conditions. A direct coupling between a photon and a plasmon can however be obtained in metallic nanostructures with a size much smaller than the wavelength of light. In such nanostructures, the plasmon does not propagate and is confined to a limited volume inside a metal, and is thus called *localised surface plasmon*. The simplest structure that supports localised plasmons is a spherical metallic nanoparticle (NP), which is of particular importance for the work presented in this thesis.

The dielectric response of a metallic NP can be studied in a quasi-static approximation, which holds for particles with size ≤ 100 nm and assumes that all the electrons of the particle respond simultaneously to an external electric field [11]. Indicating the dielectric functions of the metallic NP and of the surrounding medium respectively with $\varepsilon_m(\omega)$ and

 ε_d (assumed to be independent of ω), the dipole moment of the NP can be written as:

$$\mathbf{p} = \varepsilon_0 \varepsilon_d \alpha \mathbf{E}_0 ,$$

where E_0 is the applied electric field and α the complex polarisability of the nanoparticle. The polarisability can be obtained by solving the Laplace equation $\nabla^2 \phi = 0$ for the electric potential ϕ ; by assuming that the dielectric medium is isotropic and non-absorbing, the polarisability of the NP is found to be [11]:

$$\alpha = 4\pi a^3 \frac{\varepsilon_m(\omega) - \varepsilon_d}{\varepsilon_m(\omega) + 2\varepsilon_d}$$

where *a* is the radius of the particle. From this expression it is evident that the polarisability undergoes a resonant enhancement when $|\varepsilon_m(\omega) + 2\varepsilon_d|$ is a minimum. In the case of a slowly-varying Im ($\varepsilon_m(\omega)$) this condition translates into the so called *Fröhlich condition*:

$$\operatorname{Re}\left(\varepsilon_m(\omega)\right) = -2\varepsilon_d ,$$

and the oscillatory mode corresponding to this resonance is called *dipole surface plasmon*. The frequency dependence of the dielectric function of the metal in the Fröhlich condition makes the plasmon resonance wavelength very sensitive to the refractive index of the surrounding medium.

From the solution of the Laplace equation for the NP, the expression of the electric field inside and on the surface of the particle can also be extracted [11]:

$$\mathbf{E} = \frac{3\varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \mathbf{E}_0 \; .$$

This equation shows that the electric field is strongly enhanced in the neighbourhood of the NP when the resonance condition is fulfilled, with enhancement factors as high as 200 [14]. The enhancement is concentrated at opposite sides of the particle along the polarisation axis of incident radiation (Figure 2.5a,c). Away from the surface the NP behaves as an electric dipole, and the magnitude of the electric field decays as $1/r^3$, while in the far field the NP is seen as a point dipole that resonantly absorbs and scatters light.

Beyond the dipole approximation, higher order modes appear with more complex charge distributions, for example the quadrupole mode (Figure 2.5b,d). Even though



Fig. 2.5 Calculated plasmonic modes of a single metallic nanoparticle. Electric field for 30nm diameter AgNP at dipole resonance wavelength with (**a**) first order dipole mode in the plane defined by propagation and polarisation axes of incident radiation and (**c**), in a plane perpendicular to propagation axis. **b**,**d**, Analogous plots for quadrupole mode in a 60nm AgNP at the quadrupole resonance wavelength. Asymmetries are due to mixing of the modes. **e**, Scattering cross section of single AuNPs with different diameters, measured in solutions with identical Au mass concentrations. **a**-d adapted from [15], e from [16].

higher order modes show a progressively smaller field enhancement, they also couple to light and combine with the dipole mode to give the final field profile around the nanoparticle.

Near the plasmon resonance the NP strongly scatters light, since the incident field excites electron oscillations that then re-emit light as an antenna at optical frequencies. The scattered wavelength is tied to the plasmon resonance, and depends on the NP size (Figure 2.5e) and surrounding dielectric medium. Smaller particles tend to primarily absorb light, whereas bigger ones have a larger scattering cross section and higher ratio of scattering to overall extinction [16].

2.4 Coupled plasmonic systems

Since the field enhancement rapidly decays away from a NP, multiple NPs in free space do not interact when the inter-particle distance is greater than 2-3 times the particle radius. However, when the spacing between two particles is reduced, charge oscillations start to couple, giving rise to effects that cannot be observed for an isolated nanoparticle.



Fig. 2.6 Coupled plasmonic modes of a metallic nanoparticle dimer. **a**, Modes parallel to the dimer axis. **b**, Modes perpendicular to the dimer axis. Figure adapted from [19].

Coupled plasmonic modes have been extensively studied for the nanoparticle dimer system [17, 18], and are of great importance for the work presented in this thesis.

A NP dimer geometry is obtained when two NPs are brought close to each other at a distance smaller than their radius [14], and the result is a coupling of their plasmonic modes that gives rise to a new set of *hybridised* modes [18]. The situation is analogous to the case of two atoms that bind together to form a molecule: the states of the individual atoms combine to form hybridised modes, which characterise the behaviour of the molecule as a whole.

The set of hybridised modes arising in a NP dimer system to the lowest order is shown in Figure 2.6 [18]. This picture considers only the dipole mode of each individual particle, and thus neglects any other higher order hybridisation. For dipole modes parallel to the dimer axis (Figure 2.6a), the hybridised mode with aligned dipoles has the lowest energy, whereas in the higher energy mode the dipoles are anti-parallel. The first of the two modes mode is called "bright", because it has a non-vanishing dipole moment and can thus couple to light. This is not true for the second mode, which is therefore termed "dark". A similar picture holds for dipole modes perpendicular to the dimer axis (Figure 2.6b). In this case the energies are swapped between the parallel and anti-parallel hybridised modes, but they can still be classified as "bright" or "dark" according to the net dipole moment.

Excitation of the hybridised modes in the NP dimer geometry is very sensitive to the polarisation of incident light. If the incident electromagnetic field is polarised parallel to



Fig. 2.7 Field enhancement in coupled plasmonic systems. **a**-**d**: Electric field enhancement in a AgNP (radius 60nm) dimer as gap size is increased from 1nm to 30nm (colours in logarithmic scale of ratio $|E/E_0|$). Field enhancement increases for smaller gaps, while hotspot volume drops. Figure adapted from [20].

the dimer axis it mainly excites the bright mode of Figure 2.6a, while if it is polarised perpendicular to the dimer axis it excites the bright mode of Figure 2.6b.

An important property of NP dimers that is particularly relevant for applications is the additional field enhancement produced in the dimer gap compared to single NPs. The field enhancement factor $|E/E_0|$, where E is the field of the dimer and E_0 the maximum field of a single NP, can reach values as high as 10^2 - 10^3 (Figure 2.7a-d) at the point of maximum field intensity in the middle of the dimer gap [21, 20]. The region of high field intensity between NPs is therefore called plasmonic hotspot. Plasmonic hotspots in NP aggregates, where high field intensities greatly increase light-matter interactions, have enabled for the first time the optical detection of single molecules at room temperature [22, 23] (see also Raman spectroscopy, Section 4.2). The volume of the hotspot, as well as the field enhancement, depend on the NP size, shape and material, and on the dielectric properties of the surrounding medium. Stronger fields are obtained when the gap size is reduced, particularly in the range of a few nm and below (Figure 2.7a), and when particles have sharp corners [21]. The field enhancement starts to drop off when inter-particle separation is pushed below ≈ 0.5 nm, with the onset of nonlocal effects in the dielectric response [24] and nonlinear tunnelling currents between the NPs of the dimer [25]. The hotspot volume scales with dimer separation distance and NP size, which allows to concentrate intense electric fields into volumes <100nm³.

The hybridised modes of a NP dimer can be observed in its scattering or extinction spectrum (Figure 2.8). For incident light polarised along the dimer axis, the prevalent feature is the broad resonance peak corresponding to aligned dipoles in the individual



Fig. 2.8 Extinction spectrum of NP dimers. Calculated extinction cross section for 60nm radius AgNP dimers, with electric field polarised parallel to dimer axis. Wavelength of parallel dipole mode is tuned by size of dimer gap. Figure adapted from [20].

NPs. The peak position is highly sensitive to the dimer gap size, spanning \approx 200nm as the separation is increased from 1nm to 30nm. Additional peaks are visible around the 400-500nm region, corresponding to quadrupolar and other higher order modes, with less pronounced dependence on dimer gap. As the inter-particle distance is further increased, the coupling gets progressively weaker and the spectrum resembles that of individual NPs (Figure 2.5e).

2.5 Nanoparticle on mirror geometry

In this section I discuss the nanoparticle on mirror geometry (NPoM), which consists of a metallic NP positioned near a flat metallic substrate. Any displacement of charges in the NP induces a movement of charges on the metallic surface, and from the method of image charges [26], the system behaves as if the entire surface was replaced by an image particle on the side of the substrate (Figure 2.9). The NPoM geometry has a central role in most of the experimental results presented in later chapters, where it is used to probe structures and molecules at the nanoscale.

The NPoM geometry behaves similarly to the NP dimer system, with the difference that any charge in the image particle is of the opposite sign with respect to the real NP (Figure 2.9), and these charges cannot move independently. Of the hybridised plasmonic modes of a NP dimer, those supported by the NPoM system are the bright



Fig. 2.9 Nanoparticle on mirror geometry. Electric charges in the real AuNP are mirrored by charges of the opposite sign in the image nanoparticle.

mode of Figure 2.6a and the dark mode of Figure 2.6b. The first can be excited with light polarised perpendicular to the metallic surface, whereas the latter interacts weakly with light and only when the polarisation is parallel to the surface. Higher order modes are also supported and couple to light according to their net dipole moment.

The crucial advantage of the NPoM structure compared to a dimer is the reproducibility and simplicity of fabrication. Conventional dimers are normally fabricated chemically by assembly in solution, starting from a stabilised colloidal suspension of single NPs, and driving assembly with the controlled addition of an electrolyte [27]. These methods however tend to have low yield, since they are accompanied by production of trimers and larger aggregates, while some particles do not assemble at all [28], and in the dimers that are created the facet size of individual NPs is different. An alternative approach is to define dimer arrays with e-beam lithography on a metallic film [29], but this method is fabrication intensive and particle separation is difficult to control below 10nm.

Instead, the NPoM geometry is created by simply casting a droplet of colloidal NP solution onto a sample with a flat metallic surface, and waiting for NPs to deposit before rinsing away the excess. NP deposition rate can be increased or decreased by adding an electrolyte or functionalising the target surface. The result is a sample with thousands of NPoM structures/mm² assembled across the surface, uniformly distributed, that differ from each other only for the polydispersity of the starting colloidal solution and because of local variations in surface roughness.

The critical element in the NPoM fabrication process is the spacer that separates the NP from the mirror. Together with NP size, shape and material, it determines the optical response of the NPoM structure. The spacer can range from thin inorganic films [30], to layered polyelectrolytes [31], 2D materials [32] and organic molecules [33]. The high



Fig. 2.10 Gap size dependence of an Au NPoM system. Scattering spectrum of a 60nm diameter AuNP for various distances from an Au mirror, and corresponding darkfield images. Figure adapted from [31].

sensitivity of the plasmonic coupling between NP and mirror, combined with the large scale reproducibility of the structure, makes the NPoM construct an extremely versatile platform to optically investigate materials in the sub-10nm scale. The NPoM structure has been applied for this purpose to a vast number of different systems [34], and in the rest of this section I focus on a few applications that are particularly relevant for the work presented in this thesis.

The NPoM gap size dependence is studied in [31] for the case of an AuNP on an Au surface. In [31] the spacer is fabricated with multiple layers of polyelectrolyte, and scattering spectra of individual NPoMs are collected using white light illumination (Figure 2.10). When the particle is in contact with the surface the coupled mode scatters around 660nm, and as the spacer thickness is increased, the resonance peak gradually blueshifts until reaching \approx 540nm for a gap size of 22nm. This occurs because the increasing distance from the surface weakens the screening effect that image charges have on the charge oscillations in the real NP, leading to stronger restoring forces on the electrons in the NP, and thus a higher energy is required to sustain the oscillation [35]. The appearance of each NPoM in darkfield microscopy (Figure 2.10, see also Section 4.1) also changes as the NP is lifted away from the surface, from a red ring to a green spot. The red ring is generated by the NPoM coupled mode radiating at high angles, with preferential polarisation perpendicular to the surface. As the NP moves away from the



Fig. 2.11 Refractive index dependence of an Au NPoM system. Scattering intensity of NPoM coupled mode plotted against resonance wavelength for a range of refractive index values (blue vertical lines) shows redshift with increasing refractive index. Figure from [36].

mirror, it tends to behave as a single NP, whose dipole can be oriented in any direction thus producing a symmetric spot.

The refractive index of NPoM spacer layers also affects the plasmonic coupling. This is demonstrated in [36], where a barrel-shaped molecule (CB, cucurbit[7]uril) is used as the spacer, that can be loaded with methyl viologen to increase the refractive index. The NPoM coupled mode redshifts with increasing refractive index, because of decreased effective electric fields in the gap due to the dielectric. The refractive index *n* of the spacer, together with the NP facet radius *R* and gap size *d* also sets the spatial FWHM Δx of the electric field hotspot in the gap through the expression [34]:

$$\Delta x = \frac{\sqrt{2Rd}}{n}$$

Finally, the electric conductivity of the spacer can play an important role in determining the plasmonic resonances of an NPoM system. In [33], NPoM structures are fabricated



Fig. 2.12 Conductance dependence of an Au NPoM system. **a**, NPoM structure is fabricated with 60nm diameter AuNP on a self assembled monolayer. **b**, A blueshift of 50nm in the NPoM coupled mode resonance is observed when insulating BPT is completely replaced by more conductive BPDT. **c**, Blueshift and conductance values for mixed BPT/BPDT SAMs. Figure adapted from [33].

with AuNPs on an Au mirror, and the spacer is a molecular self assembled monolayer (SAM). SAMs are single uniform layers of individual molecules, that spontaneously adsorb on a solid surface from solution, and arrange themselves in a closely packed film [37] (Figure 2.12a). They are often used to assemble NPoM geometries, given the reproducible \leq 1nm spacing they can provide, and in [33] they are formed with two organic molecules with the same structure but functional groups of different conductivity, BPT (biphenyl-4-thiol, insulating) and BPDT (biphenyl-4,4'-dithiol, conductive). NPoM structures are made with pure and mixed SAMs of BPT and BPDT, and the corresponding scattering spectra are measured. An increasing blueshift in the NPoM coupled mode resonance is observed as insulating BPT is replaced by more conductive BPDT (Figure 2.12b,c), due to the screening effect of the charge transfer between real and image NP, made possible by the formation of an increasingly conductive link [38]. A molecular conductance of 1.3×10^{-5} S/molecule is inferred for BPDT (Figure 2.12c).

2.6 Conclusions

From the review of coupled plasmonic systems presented in this Chapter it is clear that the "nanoparticle on mirror" geometry is a powerful tool that can be used to probe thin dielectric and molecular layers. There are two crucial elements that make this structure eminently suited for this application:

- the coupled NPoM plasmonic oscillations strongly enhance the electric field of incident optical radiation in the gap, and thus both *amplify* and *concentrate* lightmatter interaction to a hotspot volume ≤100nm³;
- the properties of matter in the hotspot can be *optically tracked* with spectroscopy in real time.

The focus of the work presented in this thesis is the optical investigation of nm-sized electrical junctions, and these two points are the rationale behind the use of metallic nanoparticles in the fabrication of electronic devices described in later experimental chapters. Before presenting the methods used to approach the problem and the experimental results, in the next Chapter the second essential ingredient of this work is introduced: nanoscale electrical junctions.

Chapter 3

Nanoelectronics

This Chapter provides an overview of nanoscale electronics. The discussion starts in Section 3.1 from aspects that make nanoscale electronics different from macroscopic transport, with particular attention to the nanostructure of junctions and contacts and their behaviour with respect to electrical currents. These concepts are then used in Section 3.2 to address resistive switches, or memristors, a class of resistive memory devices based on the formation and dissolution of a nm-scale conductive filament within a dielectric. The properties of memristors are linked to the results presented in Chapter 5, where the measured electronic devices share the structure and functionality of resistive switches. The effect of pushing electronics to the scaling limit of molecular junctions is described in Section 3.3. Measuring transport across molecules involves challenges in junction design, control of geometry, and interpretation of electrical data, and different approaches to the problem are presented in Section 3.4, with particular focus on outstanding research questions that could be addressed with the experimental approach described in Chapters 6 and 7.

3.1 Transport at the nanoscale

The electrical response of macroscopic conductors at temperatures above \approx 100K is well described by Ohm's law, which states that the potential *V*, electric current *I* and resistance *R* of a conductor are related by the simple linear expression

V = RI.

The resistance in this equation is usually calculated using the expression:

$$R = \rho \frac{l}{A} ,$$

where *l* and *A* are the length and cross-sectional area of the conductor and ρ the resistivity of the material. Although these two expressions describe very well the behaviour of macroscopic conductors, they start to fail when one of the conductor dimensions approaches the nanoscale. To form an intuitive picture of the difference between macro and nanoscale, consider a simple "particle in a box" quantum description of an electron in a cubic conductor of side *L*. The time-independent Schrödinger equation for such a system is:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi_k(x, y, z) = E_k\psi_k(x, y, z) \ .$$

By imposing the boundary condition $\psi_k(0, y, z) = \psi_k(L, y, z) = 0$, and the same for *y* and *z*, the eigenvalues of the equation above can be shown to be [39]:

$$E_k = \frac{\pi^2 \hbar^2}{2m_e L^2} (l^2 + m^2 + n^2) ,$$

where *l*, *m* and *n* are integer numbers and m_e is the mass of the electron. The spacing in energy between the first and the second level is then:

$$\Delta E_k = \frac{3\pi^2\hbar^2}{2mL^2} \; .$$

Considering two cubic pieces of conductor, one with side of 1 mm and one 10 nm, ΔE_k in the first case has a value of 1.5×10^{-12} eV, whereas in the second case it is 11 meV. Macroscopic conductors thus behave as if their electrons were distributed in a continuum of states, whereas at the nanoscale the energies between their discrete states is comparable to the thermal energy of electrons even at room temperature (\approx 25meV). The scale directly affects the eigenmodes, which in the case of conductors are called *transport channels* [40]. In a macroscopic conductor the electric signal is transported by a continuum of modes, but at the nanoscale only a limited and discrete number of channels is available for the electronic transport, leading to the so called *quantisation of conductance*.

The current flow in nano-sized conductors is governed by Landauer's formula, which determines the conductance G as a sum of the transmission coefficients T_n of the



Fig. 3.1 Conductance quantisation in a constriction. **a**, Design of the constriction, with a gate (black) inducing a depleted region (grey) in a two-dimensional electron gas to tune the channel width with voltage. **b**, Conductance quantisation with varying constriction width determined by the gate voltage. Figure adapted from [40].

transport channels [39]:

$$G = \frac{2e^2}{h} \sum_n T_n(E) \; .$$

The factor $2e^2/h$ is called *conductance quantum*; it has a numerical value of 77.5 µS and is labelled G_0 . Landauer's formula does not imply that the conductance is always a multiple of G_0 , because the value of the transmission coefficient can in principle be anywhere between 0 and 1, which depends on the potential profile within the conductor. The case of T = 1 is however of particular interest, because it corresponds to the so called *ballistic conduction*. In this regime the conductor is small enough so an electron travelling along its length does not undergo any scattering with phonons.

Conductance quantisation in the ballistic conduction regime has been experimentally demonstrated in [41]. In [41], the conductor is represented by a GaAlAs-GaAs heterostructure, which confines electrons into a thin layer by creating a two-dimensional electron gas with high mobility. Two metal gates on the top of the heterostructure modulate the depletion region in the electron gas underneath, changing the width of the conduction channel (Figure 3.1a). As the depleted area becomes larger, current is constricted to a narrower channel, until conductance quantisation becomes evident in the stepwise dependence on the gate voltage, with step height G_0 (Figure 3.1b).

The number of transport channels (transport eigenmodes) is determined by the minimum width of the constriction, and can be approximately estimated with a simple one dimensional model that disregards the potential inside the electron gas and assumes an

infinite potential barrier outside the conductive neck. The energy of the *n*-th level is:

$$E_n = \frac{\pi^2 \hbar^2}{2m_e a^2} n^2 ,$$

where a is the width of the constriction. The energy of the level increases with the index n, while it decreases with the width of the constriction. With increasing a, a new transport channel with index n opens each time the energy of the level goes above the Fermi energy:

$$E_n \ge E_F = \frac{\hbar^2 k_F^2}{2m_e} \; .$$

By solving for the level index, the number of open transport channels can be estimated as:

$$N = \left\lfloor \frac{k_F^2 a^2}{\pi} \right\rfloor \,, \tag{3.1}$$

where brackets denote the floor function. This equation explains quantitatively why the conductance is expected to change in discrete steps when the gate voltage is varied.

3.1.1 Atomic-sized contacts

Contacts between metals with an atomic-sized diameter are discussed in this section. The Fermi wavelength in metals is of the order of the atomic diameter, $\lambda_F \sim 0.5$ nm, which means that the mode splitting for a conductive channel of this size is of the order of $\pi^2 \hbar^2 / 2m\lambda_F \sim 1$ eV, sufficient to observe quantum effects at room temperature. The number of transport channels in a single-atom contact can be estimated with equation (3.1), and is between 1 and 3 for most metals. Quantisation of conductance is therefore expected to be evident in atomic sized contacts, and each atom is predicted to contribute $\sim 1G_0$ to the total conductance.

In [42], a gold tip is brought into contact with a thin gold sample attached to a cantilever (inset Figure 3.2a). The tip is pressed against the gold sample to create a small dent, and is then gradually retracted while applying a voltage between tip and sample to measure conductance. On the other side of the cantilever, a separate AFM system is used to detect displacement and determine the force exerted on the sample by the gold tip.

When the gold tip is retracted after indentation, an atomic sized neck is formed, which undergoes a number of atomic rearrangements and eventually breaks. Electrical


Fig. 3.2 Contact formation and breaking with an Au tip on a cantilever. **a**, A cantilever is approached with an Au tip, and the tip is retraced during conductance measurements (decreasing tip diplacement corresponds to increasing retraction from the cantilever). **b**, Force on the cantilever as a function of tip displacement. Figure adapted from [42].

measurements show that conductance decreases in discrete steps, which reflect the discrete size and shape changes of the conductive neck (Figure 3.2a). The last two steps have a height of $\approx 1G_0$, which indicates a single-atom contact before the constriction is broken. Within the displacement corresponding to a single conductance plateau, the force applied to the cantilever grows approximately linearly, but an abrupt relaxation is observed when the value of conductance changes (Figure 3.2b). This relaxation is due to rearrangement of atoms in the contact, and the force required to break the conductive neck at its thinnest state is around 1.5 nN.

Although one is tempted to associate the height of the conductance plateaus in Figure 3.2a with multiples of G_0 , this is in general not the case. The only highly reproducible jump in conductance is usually the last one before the contact is broken. The height of this plateau has been consistently found to be near $1G_0$ for Au and other monovalent metals. For sp and sd-metals, such as Al or Pt, plateaus are generally less regularly spaced, and the last plateau before contact is broken can be a factor two away from G_0 [43].

In tip "pull-off" experiments the conductance steps are so steep that the slopes cannot be resolved in the time scale of measurements, which is ~1ms. Conductance traces are also different for each measurement, as can be expected considering that each time the shape of the contact evolves through a different sequence of structures that cannot be controlled [43]. To extract more information from these experiments, it is common



Fig. 3.3 Conductance histogram. Tip pull-off experiments are performed multiple times to account for variability in contact behaviour, and conductance values are collected into histograms with peaks at preferred configurations. Figure from [44].

to represent the measurement data in conductance histograms [43]. These diagrams are constructed using large sets of individual conductance-displacement curves, usually obtained from thousands of measurements. The total range of conductance values is divided into a finite number of bins and one count is added to the bin for each value of conductance that falls within the bin range. Under the assumption that all possible configurations of the atomic-sized conductive neck are equally likely, it is expected that any peaks in the histogram correspond to conductance values that are preferred by the electronic system (Figure 3.3).

The evidence collected in tip pull-off experiments is not consistent with a smoothly varying contact radius and steps resulting directly from quantization of conductance. Instead, it strongly supports the idea that the contact has a stable atomic geometry over the length of a conductance plateau, where the total energy is in a local minimum. At the jumps in conductance, the local energy minimum for a new geometry drops below that of the present state as a result of stress in the contact, and the contact shape abruptly changes.

Interesting phenomena also occur while the tip is still approaching a conductive surface. At sufficiently large distances, up to a few nm, a current due to tunnelling is observed, which decreases exponentially with the distance between the metals (see also Section 3.3). At small distances, simulations [45] and experimental studies [46] show the *jump to contact* phenomenon: when the distance between two metals is reduced to a critical value (fraction of a nm), a conductive bridge is formed through the rearrangement

of the atoms in the approaching metal. The process is very fast, believed to occur in a time of a few ps. When distance is further reduced, the same rearrangement processes discussed for tip pull-off experiments are observed, with similar stepwise conductance changes.

The forces between metals in this regime originate from two contributions [43]. The first is the image potential that a tunnelling electron experiences from the metallic surfaces, which modifies the potential barrier. The second is due to electronic wave functions of the two metals extending in the space between them, which causes a certain degree of overlap and results in a bonding force characteristic of metallic adhesion. The overall force has been experimentally measured using an STM tip with a sample mounted on a cantilever beam [47]. The tunnelling regime is evident as the resistance changes linearly on a log scale upon approach (Figure 3.4a), and the transition to the contact regime is denoted by an approximately constant resistance in the remaining displacement range. A negative interaction force gradient (Figure 3.4b) signals an attractive force during approach, with a peak force of 2.5nN at 0.25nm.

Simulations predict that the attractive force between two metal surfaces leads to an intrinsic instability at a distance of 0.1-0.3 nm [48]. The adhesion process causes surfaces to snap together on a time scale of the order of the time it takes a sound wave to travel the inter-planar spacing, ~ 100 fs. It is therefore impossible in general to bring two metal surfaces together in a continuous way, even though the atoms are strongly bound to their nearest neighbours. The elastic response of many atomic layers produces an effective spring constant which holds the surface atoms, but when the gradient of the force pulling the surface atoms across the gap becomes greater than this spring constant, the surfaces snap together. To fabricate electrical junctions in this size range without shorting, electrodes need to be separated by a thin spacer, for example a molecular layer as discussed in Section 3.3.

3.1.2 Electromigration

Electromigration is the process by which material is transported by the flow of electric current, and is known to be a common cause of failure of conventional current carrying wires and connections, especially in integrated circuits [39]. When a wire supports a current, it heats up due to the electron-phonon interaction, and metal atoms become more mobile. The atoms move against the direction of current flow, propelled by the



Fig. 3.4 Jump to contact. **a**, Resistance drops exponentially with decreasing tip-sample distance, with jump to contact position marked with an arrow. Inset highlights the region of transition from tunnelling to contact. **b**, Negative interaction force gradient indicates an attractive force during approach. From [47].

momentum transfer provided by the "electron wind", and the rate of movement increases with temperature. Generally the devices to which wires are connected carry lower current densities than the wires themselves, giving rise to smaller Joule heating in that region; as a consequence, material flowing along the wire is not replaced at the ends at the same rate as it leaves, and voids form at one of the electrodes. These voids eventually merge, leading to failure [39] (Figure 3.5). The process is influenced by the material of the contact or wire, its geometry, microstructure, temperature, and the value of the current density.

The force exerted by the electron wind on the contact atoms is [50]:

$$F_w = 2 \frac{Ja^2}{e} m_e v_F \eta \; ,$$



Fig. 3.5 Electromigration. Migration of metal atoms in a 60nm wide constriction creates a gap as a high current is maintained from \mathbf{a} to \mathbf{c} . Figure adapted from [49].

where *J* is the current density, *a* the size of the contact, m_e the electron mass, v_F the Fermi velocity and η a constant that depends on the scattering geometry and takes values between 0 (forward scattering) and 1 (backscattering). Assuming a single-atom contact and substituting for Ja^2 a current of $\approx 1\mu$ A, the electron wind force reaches a few nN, which can be well above the force of ≈ 1.5 nN required to break a single-atom contact. However, the force value depends on the contact geometry and the coefficient η . If the conductance is perfectly quantised, the wind force is expected to vanish since $\eta = 0$, which allows conductance plateaus at multiples of G_0 to exist for extended periods of time.

3.2 Resistive switching

Following the background discussion in the previous section, dealing mostly with nanoscale contacts between two metals separated by vacuum or air, attention is now directed to resistive switches. In this section, a brief overview is provided of what happens when a solid state medium is placed between two metals. In particular, discussion is focussed on devices called *ReRAMs*, short for *redox-based resistive switching random access memory*, which can be thought of as small capacitors with an insulating layer just a few nm thick. Another common name for these devices is *memristors*, since they can act as non-volatile memories, and the state of the memory is changed through resistive switching. Following [51], the term ReRAM is used when referring to devices and processes with a two-level binary state, and the term memristive when referring to the general characteristics of devices and the presence of multilevel states. The field of



Fig. 3.6 Structure of a memristor. A dielectric layer (here SiO₂) is sandwiched between two metallic electrodes to make a memristor, and a conductive filament (here Ag) grows or retracts with applied voltage to produce a switching response. Figure adapted from [52].

memristive switches is very broad, as memristive switching can be achieved with a number of different mechanisms, materials and geometries.

In a typical ReRAM cell, two electrodes are separated by a thin insulating layer, usually made of a metal or semiconductor oxide [51] (Figure 3.6). When a sufficiently high voltage is applied, a conductive filament forms between the electrodes, causing the resistance of the device to drop significantly. This first step is called electroforming, or shortly forming; after forming, the device is in a low-resistance state. In a ReRAM cell this process is reversible: when a voltage of the opposite sign is applied, the filament retracts, breaking the conductive bridge and creating a high-resistance state. The lowand high-resistance conditions represent the two states of the resistive memory. The state of the memory can be determined by applying a small voltage, sufficient to measure the resistance but much lower than the one required to modify the system. More precisely, the forming process should be distinguished from actual switching. Forming is the first phase of device operation, during which switching behaviour is enabled. It normally requires higher voltages than switching itself, but only happens once in the initial stage. The process is very similar to the breakdown of a dielectric, and for this reason it is often important to limit current through the device to prevent permanent damage. After forming, the two processes of switching from high- to low-resistance state (set) and from low- to high-resistance state (reset) require lower voltages.

A representative *I*-*V* curve of a ReRAM cell is shown in Figure 3.7. The set transition occurs at positive voltage, while the reset transition is operated at negative voltage. To avoid damaging the device during operation, the current is limited to a compliance current



Fig. 3.7 Typical *I-V* curve of a ReRAM cell. Current increases/drops sharply at the set/reset transitions used for state switching, but is linear at small voltages for readout. Figure adapted from [51].

 I_C . In the set phase, the current increases sharply when the filament forms, as the resistance is strongly reduced, until the compliance current is reached. When the bias voltage is reversed, the response is approximately linear in a certain range, until the reverse current is high enough to trigger the reset process. This usually happens with a current that is close to I_C , and causes the resistance to sharply increase.

A more detailed discussion of ReRAM cells requires to classify them according to the switching mechanism. There are three types of ReRAM cells: *valence change mechanism* (VCM) cells, *electrochemical metallisation mechanism* (ECM) cells and *thermochemical mechanism* (TCM) cells. The following sections provide an overview of each type. In all cells the switching is due to the reversible formation and dissolution of a conductive filament, but the specific mechanism that leads to the process is different.

3.2.1 Valence change mechanism cells

In VCM cells the resistive switching mechanism relies on the movement of oxygen vacancies within the insulating layer, followed by a redox reaction [51] (Figure 3.8). When a positive voltage is applied to the cell (forming and set operations), oxygen is extracted from the insulating layer near the anode, leaving oxygen vacancies behind. These vacancies migrate through the insulating layer towards the cathode interface, following the direction of the applied electric field, and gradually accumulate at the cathode. The resulting oxygen-deficient region is well-conducting and keeps growing towards the anode, representing a virtual cathode. Depending on the material of the insulating layer,



Fig. 3.8 VCM cell. The conductive filament grows from the cathode (right) towards the anode (left), usually made of a high work function metal, due to migration of oxygen vacancies. Figure adapted from [51].

this migration of oxygen vacancies can be associated with a reduction of the metal in the oxide, that leads to a phase transition in which the metal atoms convert into their metallic form. For the reset operation, the voltage polarity is inverted and the opposite process occurs, with a reduction reaction happening at the cathode and the oxidation occurring on the filament. The electrical response is of the type described in Figure 3.7.

3.2.2 Electrochemical metallisation mechanism cells

ECM cells are based on redox reactions and on the migration of ions through the insulating layer [53]. For this reason, they are fabricated using an oxidisable active electrode, usually made of Ag or Cu, an inert counter electrode, commonly made of Pt or W, and an oxide or chalcogenide as insulating layer (Figure 3.9a, with Cu active electrode and Pt counter electrode). The electrical response of these cells is analogous to the one reported in Figure 3.7.

The operation of ECM cells is an electrochemical process. A basic requirement for ECM cells is that the oxidation potential of the metal is greater than that of the electrolyte. When a metal atom becomes oxidised at a certain location, it acquires a charge and migrates through the solid electrolyte (insulating layer) as a cation (Figure 3.9b). When this ion receives an electron at a different location, it is reduced and turns back into a neutral metal atom. This electrochemical process allows the transfer of metal across different regions of the device and the formation of a filament (Figure 3.9c). A continuous flow of material requires a source of ions at one location and a sink at another, which in an ECM cell are represented by the active and counter electrodes, respectively.

3.2 Resistive switching



Fig. 3.9 ECM cell operation. **a**, Structure of a typical ECM cell with a Cu active electrode and Pt counter electrode. **b**, metal atoms oxidise and migrate through the solid electrolyte in the set phase, reducing and depositing on the opposite electrode until a conductive filamente is formed (**c**). **d**, Opposite voltage stimulates migration in the inverse direction for the reset process. Figure adapted from [51].

In real ECM cells, the roughness of the electrode material and nonuniformities in the ion concentration tend to promote localised nucleation and deposition. The ions closer to the electon-supplying cathode are more likely to be reduced first, and even though multiple nuclei may initially form, the one with the highest field and best ion supply is favoured for additional growth. The result of this process is that a filament starts to grow from the cathode towards the anode. As long as the potential drop between the top of the filament and the cathode is above the reduction potential, the filament grows in length and diameter. Growth normally stops when current compliance is reached, which happens when the residual resistance of the system drops below a certain threshold.

As opposed to the growth process, the reset mechanism (Figure 3.9d) is much less understood. It is generally accepted that the filament retracts because of the oxidation reaction triggered by the application of a reverse bias. For this process to start, however, any conductive links physically connecting the filament to the counter electrode must be broken. This most likely happens at the narrowest part of the filament, which has the highest resistance, and the process can be thermally activated.

3.2.3 Thermochemical mechanism cells

The growth and dissolution of the conductive filament in TCM cells is caused by thermally assisted diffusion of oxygen or metal ions [51]. This requires oxides whose conductivity is thermally activated, such as NiO, Al_2O_3 , TiO₂ or HfO₂. The switching mechanism is due to a conductive filament because the behaviour of a cell does not depend on the contact



Fig. 3.10 TCM cell electrical response. Forming (black), set (blue) and reset (red) are all induced by the same voltage polarity, by changing the voltage operation range and current compliance. Figure from [51].

area. As other types of cells, TCM cells require a forming phase to start operating in the low-voltage reversible regime.

When a voltage is applied for the first time, a small current starts flowing through the device, due to the residual conduction of the oxide. This initial current leads to Joule heating, and as the oxide conductivity is thermally activated, the current further increases. Beyond a certain point, a thermal runaway occurs which causes the thermally induced dielectric breakdown. The conductive filament can be formed by oxygen vacancies or metal atoms of the lattice, which convert into their metallic form. As a consequence of the strong temperature gradient that occurs during breakdown between the hot conduction channel and the surrounding material, oxygen starts to diffuse out of the hot region and metal atoms towards it. The hot filament region thus gets partially reduced to a metallic phase, while the surrounding oxide gets further oxidized to higher valence numbers. The compliance current controls the conductive filament diameter.

As opposed to VCM and ECM cells, TCM cells are are *unipolar*, in that the set and reset processes both happen with the same bias polarity (Figure 3.10). The system is reset (red line in Figure 3.10) by releasing the current compliance and increasing the voltage until the cell abruptly turns into the off state at the reset voltage. Thereafter, the entire cycle can be repeated, with the difference that the set process (blue line) is performed at a voltage lower than the forming voltage.

The reset process in TCM cells is not very well understood. The increased current compliance in the reset process causes the current to rise significantly, leading to an intense heating in the region of the conductive filament. The higher temperature activates the migration of oxygen from O-rich regions outside the conductive filament to O-deficient regions inside it, with the opposite migration direction occurring for metal atoms. As the switching is unipolar in nature, this process is expected to happen in the lateral direction by diffusion mechanisms.

3.3 Molecular transport

In the context of nanoscale electronics, the idea of shrinking electronic components down to single molecules by fabricating *molecular junctions* possibly represents the ultimate frontier for miniaturisation, that could lead to lower energy devices, higher component density, and new functionalities. Molecular electronics has been an active field of research for at least a couple of decades, gaining momentum when fundamental transport mechanisms at the nanoscale were unveiled as described in Section 3.1, but practical applications are currently still beyond reach [54]. A number of outstanding challenges need to be addressed before molecular junctions can be turned into useful devices, as discussed in this Section.

A molecular junction is an electronic component where two electrodes are bridged by a single molecule or a nanoscale collection of molecules [55]. The first element to consider in such a system is the junction structure, which is determined by the type of molecule and the shape of the electrodes.

Linear alkane or phenyl chains (Figure 3.11a) are common choices for the bridging molecules, as their linear size can be tuned by changing the length of the chain from a fraction of a nm to several nm [56]. At least one end of the chain is usually functionalised with a group that chemically binds to the electrode material (for example, thiol groups for Au [57]), but other functional groups can be added to ensure binding to both electrodes, affect the steric configuration of molecules [58], or change their conductance [59]. An additional reason for using molecules with the structure in Figure 3.11a with a binding group is that they form uniform self assembled monolayers (SAMs) [37], which is essential for a more defined junction geometry. While generic molecules can be deposited on surfaces by non-specific adsorption from liquid or gas phases (Figure 3.11b), they form



Fig. 3.11 Molecules used in molecular junctions. **a**, Alkane and phenyl chains are common in molecular electronics because their length is tunable and they can be functionalised with different terminal or side groups. **b**, Self assembled monolayers are preferred to non-specific adsorption in molecular junctions for more defined molecular orientation and junction geometry. Figure adapted from [54].

films with uneven thickness, pinholes, and undefined molecular orientation. On the other hand, SAM formation by functionalised alkane and phenyl molecules is self-limiting and results in closely packed films that are one molecule thick [37]. The key elements of molecules that form SAMs are a head, or binding group, and a tail, also called backbone. The binding group must have a much higher affinity to the substrate than the rest of the molecule, to ensure that bonding with the surface occurs in the same position for all molecules. The tail dictates the interactions of a molecule with its neighbours, and thus determines the orientation and packing order of the layer. Interactions occur through van der Waals forces, π stacking for aromatics, and also H bonding or Coulombic repulsion if specific chemical groups are present [60]. The final positioning of molecules in a SAM is given by the tendency to minimise the overall configuration energy of the layer, and in well defined SAMs this implies that all binding groups are bound to the surface, while tails are vertically aligned (often at an angle). In molecular electronics applications, often a second binding group is added to the other end of the tail, to enable binding of a second electrode. Many SAMs define surface domains with areas ranging from a few tens of nm^2 to a few μm^2 , where the exact orientation of individual molecules is different from the neighbouring domains. Domain boundaries, combined with surface roughness and metal atom mobility, contribute to the formation of local defects in the SAM that can lead to pinholes.

Consistently defining the precise geometry of the electrodes in a molecular junction is one of the biggest challenges of molecular electronics. The size of molecules determines the separation between electrodes, and thus sets some constraints on the size of the electrodes themselves or their roughness. Electrodes are prevalently made of a noble metal to prevent oxidation, with Au being the most common choice, for its high conductivity and convenience in shaping sharp tips either electrochemically, by lithography, or with electromigration. More recently, electrodes based on other materials such as semiconductors [61] or carbon [62] have also been demonstrated. All types of electrodes for molecular electronics can be broadly divided into two categories: those used to make single molecule junctions, and those bridging ensembles of molecules [55]. The first are generally based on trapping a molecule at the end of a sharp tip used to approach either another tip, or a flat surface coated with a SAM. Molecular ensembles instead are contacted with extended electrodes whose typical area is >100nm², defined with a surface patterning technique. Experimental examples of both types of junctions are described in Section 3.4, while the rest of this section deals with transport models in molecular junctions.

It is widely accepted that transport through molecular junctions is driven by electron tunnelling [63–65]. The molecule in the junction gap represents a tunnelling barrier, and conduction is a quantum effect due to the nonzero probability of an electron crossing the barrier when a voltage is applied. A number of transport models can be applied to electron tunnelling, including the Wentzel–Kramers–Brillouin (WKB) approximation for rectangular barriers, the Simmons model for trapezoidal barriers, the Fowler–Nordheim (F-N) equation for triangular barriers, and the Landauer formalism mentioned in Section 3.1 based on conduction channels with a finite transmission probability [55, 66]. The Simmons model is often used, because it applies to the general case of a trapezoidal barrier, and gives the expression of the tunnelling current density *J* as [65]:

$$J = \frac{e}{4\pi^2 \hbar d^2} \times \left[\left(\Phi - \frac{eV}{2} \right) \exp\left(-\frac{2(2m)^{1/2}}{\hbar} \alpha \left(\Phi - \frac{eV}{2} \right)^{1/2} d \right) , \qquad (3.2)$$
$$- \left(\Phi + \frac{eV}{2} \right) \exp\left(-\frac{2(2m)^{1/2}}{\hbar} \alpha \left(\Phi + \frac{eV}{2} \right)^{1/2} d \right) \right]$$

with Φ and *d* the barrier height and thickness, *m* the electron mass, α an effective mass term that controls the barrier shape ($\alpha = 1$ for a rectangular barrier), and *V* the voltage applied across the junction. The potential barrier height is normally approximated with the energy gap between the Fermi energy of the metallic electrode and the HOMO (Highest Occupied Molecular Orbital) or LUMO (Lowest Unoccupied Molecular Orbital) energies when these are close to the Fermi energy [55]. Different regimes can be identified as V is increased (Figure 3.12a,b), which can be visualised by plotting the current-voltage response in Fowler–Nordheim coordinates as $\ln I/V^2$ against 1/V (Figure 3.12c). In the limit of $V \rightarrow 0$ the barrier has a rectangular shape, and [67]:

$$I \propto V \exp\left(-\frac{2d\sqrt{2m\Phi}}{\hbar}\right),$$

so $\ln I/V^2 \propto \ln 1/V$ (Figure 3.12c), and this regime is called *direct tunnelling*. On the other hand, for $V > \Phi$, the barrier becomes triangular, and the current [67]:

$$I \propto V^2 \exp\left(-\frac{4d\sqrt{2m\Phi^3}}{3\hbar eV}\right)$$

so the response is linear in F-N coordinates (Figure 3.12c), and the regime is called Fowler–Nordheim tunnelling or *field emission*. In the transition region between these two regimes, a transition voltage V_{trans} can be extracted from the F-N plot (Figure 3.12c), which represents the effective barrier height for electron transport and corresponds to the energy offset between the electrode Fermi level and the closest molecular energy level.

From equation (3.2) it is evident that the tunnelling current decays exponentially with the thickness *d* of the barrier. This behaviour can be probed experimentally [65], which is another reason why alkane-thiol and phenyl-thiol chains are particularly convenient for demonstrating molecular electronic devices, since molecules with various lengths are readily available. An additional parameter that can be used to identify tunnelling, and distinguish it from hopping, is the temperature dependence of the current [65, 54]. Hopping probability scales as $\exp(-E_a/k_BT)$, where E_a is the activation energy of the hopping mechanism. Pure tunnelling instead is independent of temperature, except for the broadening of the Fermi-Dirac distribution of carriers in the electrodes with increasing temperature.

Alkane and phenyl chains are convenient barrier molecules that are widely used for their availability and modularity, but they can be replaced with more sophisticated molecules to access new electronic functionalities, that also complicate the electric response and modelling of the junctions. An interesting example is that of negative differential resistance (NDR) [69], that employs a molecule with a redox centre that can host additional electrons (Figure 3.13a). A junction containing this molecule works as



Fig. 3.12 Tunnelling regimes in molecular junctions. **a**,**b**, As voltage is increased from 0V, the tunnelling barrier of a molecular junction goes from purely rectangular (a, direct tunnelling), to trapezoidal, and finally to purely triangular (b, F-N tunnelling or field emission). **c**, Direct tunnelling and field emission can be identified when plotting *I* and *V* in F-N coordinates. Figure adapted from [68].

a normal tunnelling molecular junction for low voltages, but as the voltage is increased above the reduction potential of the molecule, negative charge is stored in the molecule that stops electron transport and drops the conductance, giving NDR. A different example is related to quantum interference, which can be observed when electrons can tunnel through a molecule along separate converging paths [70]. If the phase difference is such that the electron wave functions interfere destructively, conductance through the molecule is strongly reduced (Figure 3.13b).

3.4 Types of molecular junctions

This section describes some common types of molecular junction geometries and fabrication techniques. As mentioned at the beginning of Section 3.3, these can be broadly divided into two categories: single molecule and ensemble junctions. While single molecule systems enable to investigate transport at a fundamental level, they typically show strong variability in their geometry and electrical properties from one junction to another, and are not suitable for device applications. On the other hand, ensemble



Fig. 3.13 Nonlinear effects in molecular junctions. **a**, Redox molecules in a junction can undergo reduction and produce negative differential resistance; adapted from [69]. **b**, Molecules with multiple conduction pathways can lead to destructive quantum interference and reduce conductance even though in the tunnelling regime; adapted from [71].

molecular junctions tend to have more realistic device geometries, but their response originates from a large number $(10^2 \text{ to } 10^7)$ of molecules, although they can retain some nonlinear properties. Some examples are given for both types, that can be compared to the junction geometry described in this thesis (Chapter 6), which belongs to the category of ensemble junctions.

3.4.1 Single molecule break junctions

A widely adopted type of single molecule junction is the scanning tunneling microscope (STM) break junction, obtained by approaching a molecular SAM on a flat metallic surface with a sharp STM tip, and then retracting it until a molecular junction is formed [72]. Control of the vertical position of the tip with respect to the surface is critical for this method, and this is normally achieved by applying a small voltage and maintaining a desired current by controlling the tip position with piezoelectric scanners in a closed loop feedback system [55]. A single junction is formed in several steps. First, the tip is brought into full contact with the sample, creating an ohmic conductive metallic bridge. The tip is then gradually retracted, and the conductive link gets progressively narrower, showing stepwise changes in conductance of height G_0 (Figure 3.14a and conductance histogram in Figure 3.14b) typical of local rearrangements in atomic sized constrictions described in Section 3.1. As the last atom is pulled off the surface, in most cases the tip is completely



Fig. 3.14 STM break junctions. Molecular junctions are created by contacting a SAM on a metallic surface with a tip. Conduction is initially dominated by residual metal atoms (\mathbf{a} , \mathbf{b}), but then shows characteristic conductance values when only one or more molecules bridge the gap (\mathbf{c} , \mathbf{d}). These small conductance values are not observed without SAMs (\mathbf{e} , \mathbf{f}). Figure from [72].

detached from the surface, interrupting any conduction. In some cases however, one or more molecules remain attached to the tip, and bridge the tip-surface gap creating a molecular junction (Figure 3.14c) before the tip is completely retracted. Conductance in this regime is much smaller that G_0 , typically 10^{-6} - $10^{-2} G_0$, because conduction occurs via tunnelling through the molecule (as described in Section 3.3) rather than through an atomic-sized metallic filament. Conductance histograms in the molecular regime (Figure 3.14d) show peaks evenly spaced by multiples of a fundamental conductance value, which are attributed to a discrete number of molecules contributing to the total conductance. This is confirmed by the same experiment performed on a sample with no molecular SAM, which does not show any peaks in this conductance range (Figure 3.14e,f).

STM break junctions have the important advantage of enabling the acquisition of thousands of independent conductance traces by repeatedly approaching and retracting the tip on the same sample. Once a molecular junction is formed, the tip can be kept fixed and the molecule conductance characterised thoroughly [73]. This has allowed to



Fig. 3.15 Mechanically controllable break junctions. **a**, Suspended metallic membranes with narrow channels are fabricated on a flat substrate, and then (**b**) mechanically pulled apart by bending the sample against a pushing screw. Figure from [74].

accurately measure the conductance of a range of molecules, and observe nonlinear effects such as NDR, redox switching and spin-split molecular orbitals [55].

A different type of single molecule junction can be obtained with mechanically controllable break junctions [75, 76]. In these systems, a suspended metallic membrane with a narrow channel is lithographically defined on the surface of a sample (Figure 3.15a). The sample is then held in position at two anchor points, and elastically deformed with a pushing screw (Figure 3.15b). The narrow channel is thus pulled apart by the deforming sample, until snapping to produce a narrow gap. This part of the sample can be immersed in a solution containing a molecule of interest (or can be previously coated with a SAM), to fill the gap with a molecular bridge and form a molecular junction, where the two ends of the broken channel become the electrodes. Since the overall sample deformation is elastic, the gap size can be mechanically controlled with the pushing screw. This junction geometry is similar to STM break junctions, with the important advantage that it provides purely mechanical, reproducible control with <0.1nm precision over the junction spacing. Measurements are typically performed similarly to STM junctions, by repeatedly forming and breaking molecular junctions, and identifying statistically relevant features in the conductance histograms.

A third type of break junction, less widespread than STM and mechanical ones, can be formed by electromigration [55]. As described in Section 3.1.2, high currents passed through a thin wire can create small gaps, that can be filled with molecules by previous deposition of a SAM or by immersion in a solution. Although electromigrated junctions are simple to fabricate, gap size is difficult to control and repeatable measurements with the same junction cannot be made.

In some configurations, break junctions allow optical access to the molecules for spectroscopy [77]. In STM break junctions this can be achieved with optical components positioned on the side of the probe [78], or by in- and out-coupling of light through the STM probe itself [79]. Modulation of molecular fluorescence [78], luminescence [80, 81] and Raman response [79] due to conformational and transport changes induced by the applied voltage have been demonstrated with these techniques.

For mechanical and electromigrated break junctions, imaging and spectroscopy can be simply performed from the top. Several studies employing these systems and Raman spectroscopy in combination with electrical measurements [82–84] have confirmed that Raman scattering is strongly enhanced in the molecular junction gap as a result of amplified local optical fields (see Section 4.2). In particular, it is possible to detect an optical signal from the same molecules involved in the electrical transport, and even use this signal to monitor heating of the junction [85]. However, a consistent optical response is difficult to observe for the same junction, and the modulation has not been linked to specific conformational or transport changes in the molecules.

3.4.2 Ensemble junctions

Ensemble molecular junctions fundamentally differ from break junctions because they are fabricated with static electrodes and defined geometries [54]. A typical ensemble junction is obtained by sandwiching a molecular SAM between two metallic electrodes patterned with lithography (Figure 3.16a), although a number of other approaches have been proposed, including vertical bridging of a gap, buffer layers, and assembly on existing nanostructures (3.16b-d).

The main challenges in the fabrication of these devices are the preservation of SAM and electrode integrity during processing, the uniformity of films and the chemical interactions between SAM and metal. A molecular functional group that binds strongly to the substrate is preferred to produce dense SAMs, but if the molecule-metal bond strength is comparable to metal-metal bonds (as is the case for Au-S and Au-Au bonds [86]), the bound species can diffuse across the surface. Molecules then migrate until they find the most thermodynamically favourable position, and form highly ordered domains with grain boundaries [86], which represent defects in the SAM that can short the junction



Fig. 3.16 Ensemble junction geometries. Molecular devices with many molecules can be fabricated with a vertical sandwich structure (**a**), but also in a trench geometry using the edges of a metallic film (**b**), by indirect contacting through a conductive buffer layer (**c**), or by bridging electrodes with a SAM coated nanostructure (**d**). Figure adapted from [54].

over large areas. Migration of metal atoms from the electrodes into the junction gap can also occur during device operation, altering the transport properties in ways that may resemble molecular conduction [87].

In a sandwich configuration, which is the most widely adopted, the fabrication of the top electrode is still challenging. Most organic molecules are sensitive to heat and high energies, which limits the applicability of direct physical vapor deposition methods common in standard microelectronics fabrication. Similarly, standard lithography protocols employ photoresists and solvents that can damage or alter organic films. A universally accepted method to fabricate top electrodes, and verify the integrity of the underlying SAM after processing, is still not available [54]. The most common strategy to address this issue is to reduce the junction area by fabricating sandwich structures in nanopores [69] or cross-bar geometries, cooling of the sample during metal evaporation, and lowering of material deposition rate. After fabrication, ensemble molecular junctions must be tested individually to identify those that successfully represent the desired structure, which can exhibit the same properties of single molecule junctions but at a device level [88] (Figure 3.17).



Fig. 3.17 Electrical properties of ensemble junctions. When correctly fabricated, ensemble sandwich junctions (**a**) made with alkanethiols (**b**) show exponential dependence of conductance on gap size (**c**) and transport properties typical of tunnelling junctions (**d**). Figure adapted from [88].

3.5 Conclusions

Electrical transport in nm-sized conductors is characterised by a range of unexpected nonlinear effects, ranging from quantum tunnelling to quantisation of conductance and redox reactions. Turning these properties into practical applications however is a huge challenge, mostly because the exact junction geometry is very difficult to define for a particular system and to reproduce across multiple devices. An additional complication is that the small gap between two electrodes at the nanoscale is hard to access with external characterisation methods, and the electrical response of the device itself is often the only tool available to infer the underlying transport mechanism.

There is a strong need to develop reproducible molecular junctions that can be probed in real time during operation. The work presented in this thesis tries to address this need by exploring nanoscale junction geometries and contact materials that allow to optically access the junction gap, and track its evolution in situ as voltage in applied.

Chapter 4

Methods for imaging and spectroscopy

Optical spectroscopy is an essential analytical tool used throughout the work presented in this thesis. Plasmonic nanostructures such as the NPoM geometry strongly interact with light, and their optical response is tightly bound to light-matter interactions that occur in the small volume where electrical fields are strongly enhanced. Darkfield imaging and spectroscopy, described in Section 4.1, are used to image nanoparticles and identify the morphology of the NPoM gap. Raman spectroscopy, introduced in Section 4.2, allows to observe molecular vibrations and thus characterise molecular layers.

4.1 Brightfield and darkfield spectroscopy

A modified Olympus BX51 optical microscope (Figure 4.1), is the main tool used in this work to observe nanostructures. Since samples are fabricated on opaque silicon substrates, the microscope is used in reflection configuration with Köhler illumination [89]. All microscope objectives are infinity corrected, allowing simple in- and out-coupling of light along the optical path [90].

Conventional white light spectroscopy is performed by out-coupling the light collected by the microscope objective with a beam splitter, and focussing it at the end of a multimode optical fibre with core diameter $50\mu m$. The other end of the fibre is directed into an OceanOptics QE65000 spectrometer for spectral acquisition. The fibre core size and objective magnification set the physical size of the collection spot, which has a



Fig. 4.1 Microscopy setup. Olympus BX51 microscope used for imaging and spectroscopy. The microscope tube is extended with beam splitter slots for in- and out-coupling of light for darkfield and Raman spectroscopy. Sample position is controlled with a motorised stage.

diameter of $1-2\mu m$ for a $100 \times$ (Olympus LMPLFLN100xBD) objective. Spectral acquisition is therefore restricted to a localised region of the sample containing the nanostructure of interest, for example a single nanoparticle. A halogen bulb is used as the white light source, which combined with the transmission characteristics of the microscope objectives allows spectroscopy in the 400-900nm wavelength range. Since light from the source follows a black-body radiation profile, a diffuse reflectance standard is used at the start of each experiment to record the source white light spectrum then used for referencing of acquired spectra.

The magnification of an optical microscope at the diffraction limit is sufficient to observe metallic nanoparticles with a size of a few tens of nm and larger deposited on a



Fig. 4.2 Darkfield microscopy. A darkfield stop (spatial filter) and elliptical mirror shape light into a ring, and direct it at high angles on the sample surface through a darkfield objective. Only scattered light enters the collection path.

flat substrate, where they appear as small spots with a diffraction-limited size. However, in a conventional brightfield reflection configuration, in which the eyepiece or imaging camera collect all the light that is reflected and scattered by the sample, the reflected light from the flat specimen surface overwhelms the signal coming from scattering by the particle. Due to all the reflected light, in such a configuration the particles are hardly visible, and it is impossible to measure their characteristic scattering spectrum.

For nanoparticles to be clearly visible under a microscope, the light coming into the eyepiece due to specular reflection must be separated from that scattered by the sample surface. This can be achieved using the microscope in darkfield configuration (Figure 4.2). Light from the lamp source is sent towards the sample in the shape of a ring by blocking the central part of the beam with a *darkfield stop*, and directing the remaining light with an elliptical mirror. A specially designed darkfield objective deflects light towards the sample at high angles with an annular reflector located in the objective collar, and only the scattered signal is collected by the central part of the objective. Any light undergoing specular reflection off the sample surface is not collected.



Fig. 4.3 Scattering angles of a NPoM system. The horizontal dipole mode scatters at low angles, the coupled mode scatters at high angles. Adapted from [19].

As with conventional brightfield objectives, numerical aperture must be considered when observing a sample. The numerical aperture is defined as:

$$N.A. = n \sin \theta ,$$

where *n* is the refractive index of the medium between the sample and the objective lens and θ is the half angle of collection or illumination. As darkfield objectives include an external collar for annular illumination, the angle used for illumination has to be greater than the one used for collection, and the two angular ranges have to be separate. When the scattering of a sample is observed with a darkfield configuration, the only collected light is that scattered within the angles corresponding to the N.A. of the central part of the objective.

In the scattering profile of an Au NPoM system (Figure 4.3, also see Section 2.5), the single-particle (green) mode produces light scattering at low angles, and is therefore easily collected by any darkfield objective. The coupled mode, however, scatters most strongly around 60° from the normal [91]. This means that to effectively collect light scattered by this mode an objective with an N.A. ~ 0.85 is needed, and illumination has to be performed at N.A. > 0.85.

4.2 Raman spectroscopy

4.2.1 Theoretical introduction

In a classical approach [92], an external electric field ${\bf E}$ induces a dipole moment ${\bf p}$ in a molecule that can be expressed as:

$$\mathbf{p} = \alpha \mathbf{E} \ . \tag{4.1}$$

where α is the polarisability tensor, that depends on the shape and dimensions of the chemical bonds inside the molecule. Since bonds change due to molecular vibrations, α can be expanded as:

$$\alpha = \alpha_0 + \sum_k \left(\frac{\partial \alpha}{\partial Q_k}\right) Q_k + \frac{1}{2} \sum_{k,l} \left(\frac{\partial^2 \alpha}{\partial Q_k \partial Q_l}\right) Q_k Q_l + \dots , \qquad (4.2)$$

where Q_i is the normal coordinate of the molecule corresponding to the *i*th normal vibration. In a first order approximation all normal vibrations are assumed to be independent, and no cross-terms are included in the expansion of α . Considering a particular *v*th normal vibration, equation (4.2) is then reduced to:

$$\alpha_v = \alpha_0 + \alpha'_v Q_v \tag{4.3}$$

where $\alpha'_v = (\partial \alpha / \partial Q_v)_{Q_v=0}$ is the derivative of the polarisability tensor to the normal coordinate Q_v in equilibrium conditions.

In a first order approximation, the normal coordinate Q_v is assumed to behave as a harmonic oscillator, oscillating in time as:

$$Q_v = Q_{v0} \cos\left(2\pi v_v t + \varphi_v\right)$$

where Q_{v0} is the amplitude of the normal vibration, v_v its characteristic frequency, and φ_v a phase term. Substituting this expression into (4.3) gives:

$$\alpha_v = \alpha_0 + \alpha'_v Q_{v0} \cos\left(2\pi\nu_v t + \varphi_v\right) \quad . \tag{4.4}$$

In the context of Raman spectroscopy, the external electric field in equation (4.1) is due to incident electromagnetic radiation, represented by an oscillating electric field vector \mathbf{E} expressed at time instant *t* as:

$$\mathbf{E} = \mathbf{E}_0 \cos\left(2\pi\nu_0 t\right),\tag{4.5}$$

where v_0 is the frequency of the incident radiation. Plugging (4.4) and (4.5) into (4.1), the induced dipole moment **p** becomes:

$$\mathbf{p} = \alpha_0 \mathbf{E}_0 \cos\left(2\pi\nu_0 t\right) + \alpha'_v \mathbf{E}_0 Q_{v0} \cos\left(2\pi\nu_0 t\right) \cos\left(2\pi\nu_v t + \varphi_v\right) \,,$$

which can be rewritten as:

$$\mathbf{p} = \alpha_0 \mathbf{E}_0 \cos (2\pi v_0 t) + \frac{1}{2} \alpha'_v \mathbf{E}_0 Q_{v0} \cos [2\pi (v_0 + v_v) t + \varphi_v] + \frac{1}{2} \alpha'_v \mathbf{E}_0 Q_{v0} \cos [2\pi (v_0 - v_v) t - \varphi_v] .$$

The total induced dipole moment can thus be split into three components as a function of the vibrational frequencies of the molecule (v_v) and of the incident radiation (v_0):

$$\mathbf{p} = \mathbf{p}(\nu_0) + \mathbf{p}(\nu_0 + \nu_v) + \mathbf{p}(\nu_0 - \nu_v) .$$
(4.6)

The first term in equation 4.6 has the same frequency (and thus energy) of the incident radiation, and represents the elastic scattering contribution of the induced dipole, also called *Rayleigh scattering*. The other two terms correspond to inelastic scattering, also termed *Raman scattering*. In one case the dipole frequency is higher than that of the incident radiation ($v_0 + v_v$, anti-Stokes scattering), while in the second case the frequency is lower than that of the incident radiation ($v_0 - v_v$, Stokes scattering).

In Raman spectroscopy, a monochromatic laser beam is focussed onto the sample, and the intensity of the scattered radiation is measured as a function of wavelength. Each molecular vibration from each molecule in the illuminated area contributes with its own Raman scattering signal, and the collection of these signals represents the detected Raman spectrum (Figure 4.4). Since generally $\alpha_0 \gg \alpha'_v$ elastic Rayleigh scattering is much more intense than Raman signals, with simple specular laser reflection dominating



Fig. 4.4 Example of Raman Spectrum. Stokes Raman spectrum of biphenyl-4,4'-dithiol (BPDT), with Rayleigh scattering region filtered out by a notch filter below $\approx 200 \text{ cm}^{-1}$, and labelled peaks for some characteristic Raman bands of the molecule (see also Table 4.1).

both scattering contributions. This strong signal concentrated near v_0 easily saturates most detectors, compromising the detection of the weaker Raman scattering, so light collected from the sample is spectrally filtered around v_0 with edge filters (long- or shortpass, for either Stokes or anti-Stokes) or notch filters (for simultaneous Stokes and anti-Stokes).

The spectral position of a Raman band, or peak, is determined by the energy difference between the ground state and the first excited vibrational state of the bond, which in turn depends on the atomic species involved, the bond position in the molecule, the strength of the bond, and the size and density of the electron cloud around the atoms. It is customary to define the Raman peak positions in terms of shift from the excitation wavelength, and to express the values in wavenumbers \tilde{v}_v with units of cm⁻¹:

$$ilde{v}_v = ilde{v}_m - ilde{v}_0 = rac{1}{\lambda_m} - rac{1}{\lambda_0} \; ,$$

where λ_m is the measured wavelength of the Raman peak, λ_0 the wavelength of the excitation source, and $\tilde{\nu}_m$ and $\tilde{\nu}_0$ the corresponding wavenumbers. When plotting Raman data the absolute value of $\tilde{\nu}_v$ is taken, with the anti-Stokes and Stokes regions respectively placed at the left and right of the laser line.

Characteristic Raman lines can be attributed to many functional groups in organic chemistry, with some of the relevant ones to this work listed in Table 4.1. The exact

Functional group/vibration	wavenumber [cm ⁻¹]
CC aromatic ring chain vibrations	1000, 1580 – 1600
inter-ring (aromatic) C-C stretching	1280
C≡N stretching	2200 – 2250
C _{ring} -S stretching (aromatic)	1080 – 1150
C-H in plane bending (aromatic)	1180 – 1200
Au-S stretching	270 - 300

Table 4.1 Raman lines in aromatics. Raman bands of selected groups typical of aromatic molecules on metallic surfaces [92–94].

position, intensity, and width of these lines depend on the overall structure of the molecule, its local environment in the sample, and its orientation with respect to the excitation and collection directions, as well as the efficiency and spectral response of the measuring instrument. In particular, the molecular neighbourhood can lead to line broadening, as different molecules within the excitation region experience different local environments, leading to slightly different vibrational frequencies for the same type of functional group. Rotational degrees of freedom within the functional group introduce an additional source of broadening, since they couple to vibrational modes producing roto-vibrational states that are closely spaced in energy and strongly dependent on the local steric conditions. Nevertheless, each molecule has its own Raman fingerprint, which is the collection of its Raman bands. Identifying a molecule solely from its Raman spectrum however is challenging as the same functional group in different molecules generates similar Raman lines, so the measurement is very sensitive to contamination, and Raman bands often overlap in complex molecules.

Equation 4.4 implies that the Raman scattering effect only occurs if $\alpha'_v = (\partial \alpha / \partial Q_k)_{Q_k=0} \neq 0$, which requires a change in polarisability as a result of the corresponding molecular vibration. For complex molecules this is evaluated from symmetry considerations with group theory, and quantum mechanics is used to determine the allowed transitions and their energy requirements. In quantum mechanical terms, molecular vibrations are described with electron wave functions that at a given point in time are either in their ground state or in one of the higher energy excited states, separated by discrete energy steps. In the quantum harmonic potential approximation, it can be shown that the dipole moment selection rules are only satisfied if the vibrational state quantum



Fig. 4.5 Energy levels of Raman transitions. Electrons in the ground state are excited by incoming photons with energy hv_0 to a virtual excited state, from which they decay elastically back to the ground state (Rayleigh scattering, emitted photon energy hv_0) or inelastically to a molecular vibrational state (Stokes scattering, energy $hv_s = h(v_0 - v_v)$). If they decay to the ground state following excitation from a vibrational state (anti-Stokes scattering) they emit a photon with energy $hv_{as} = h(v_0 + v_v)$.

number changes by either 0 or ± 1 , which corresponds to Rayleigh or Stokes/anti-Stokes scattering, Figure 4.5. For the Rayleigh case, the incoming photon from the laser is re-emitted with the same energy. In Stokes transitions, the electron is first excited to a high-energy state, that generally does not correspond to a real electronic state and is thus called *virtual* excited state. This state is very short-lived, and the electron quickly relaxes into an allowed vibrational state above the ground level, emitting a photon with energy $hv_S = h(v_0 - v_v) < hv_0$. If the electron is already in an excited vibrational level, it can relax from the virtual state directly into the vibrational ground state, emitting a photon of higher energy $hv_{aS} = h(v_0 + v_v) > hv_0$.

The population $N_{v,j}$ in the *j*-th energy level of the *v*-th vibrational mode follows a Boltzmann distribution:

$$N_{v,j} = N rac{e^{-E_{v,j}/k_BT}}{\sum\limits_{i} e^{-E_{v,i}/k_BT}} \; ,$$

which implies that at finite temperatures the ground energy level is always more populated than the first excited vibrational state. For this reason the anti-Stokes transition always has a lower probability than a Stokes scattering event, translating into less intense anti-Stokes Raman peaks compared to the Stokes bands.

4.2.2 Surface Enhanced Raman Scattering

It is found experimentally that Raman scattering is strongly enhanced when molecules are positioned on a nanostructured metallic surface, through a process called *surface*

enhanced Raman scattering (SERS). The nanostructured material can range from simple disordered roughness on a planar surface, to specifically nanofabricated structures in a metallic film, all the way to colloidal suspensions of metallic nanoparticles in a liquid. Enhancement factors of 10³ to 10⁶ are easily achieved, and higher factors of 10¹⁰ and above can be obtained with structures optimised to maximise the SERS [95]. The exact origin of the SERS effect is still an active field of research, mainly because of our limited understanding of how molecules bind and adsorb on a surface, how neighbouring molecules interact with each other and spatially arrange themselves, how the metallic surface itself is modified by molecular binding, and how surface oxide layers, residual ligands, contaminants, and surface functionalisation affect the local environment.

The currently accepted model for SERS includes two contributions, one called electromagnetic enhancement, and one termed charge transfer or chemical enhancement. Electromagnetic enhancement is the result of the large increase in the local electromagnetic field induced by the incident excitation source due to surface plasmons, discussed in Section 2.3. Since the local field is amplified, all molecules within the nanostructure hotspots experience a boost in polarisation. A simple surface with random roughness features of typical size ≤ 200 nm is sufficient to produce this effect, and the field is mostly enhanced near the tip of individual protrusions. Given the random nature of these features, in- and out-coupling of light is rarely optimal, limiting the effective enhancement and overall experimental reproducibility. Well-defined geometries, such as the NPOM structure (see Section 2.5), offer a repeatable system that provides consistent amplification of the local field and can be modelled in simulation and theory. An alternative approach is to use aggregates of colloidal suspensions, for example metallic nanoparticles such as spheres or rods. As particles aggregate in solution or are dried onto a substrate, molecules are trapped in the inter-particle gaps, that are plasmonic hotspots of the aggregated system.

Plasmonically active metallic nanostructures generally have a resonant behaviour, showing maximum coupling with incident light around a specific wavelength set by the size, shape and material of the system. For spherical metallic nanoparticles, for example, this occurs near the Frölich condition discussed in Section 2.5. While SERS can be observed above the interband transition of the metal throughout the visible and near IR ranges, additional enhancement is obtained by operating near the plasmon resonance of the nanostructure, Figure 4.6. The electromagnetic Raman enhancement factor G_{em} can



Fig. 4.6 Optimal SERS conditions | Maximum SERS signal is generated when both the excitation wavelength λ_0 and the Raman wavelengths λ_s and λ_{as} are within the resonance peak of the plasmonic nanostructure. The optimal excitation wavelength is shifted left/right of the resonance peak if only Stokes/anti-Stokes scattering is collected.

be written as [96]:

$$G_{em} = \left(\frac{E_{loc}(\nu_0)}{E_0}\right)^2 \left(\frac{E_{loc}(\nu_m)}{E_0}\right)^2 ,$$

where E_0 is the electric field of incident light, v_0 its frequency, $v_m = v_0 \pm v_v$ the frequency of the Raman emission, and E_{loc} the local electric field in the plasmonic hotspot at the respective frequencies. The metallic structure then has a double effect: it enhances the light intensity at the surface by boosting the incoming field (v_0), and amplifies the Raman scattering itself (v_m) by increasing the molecular emission rate. Ideally, to maximise the SERS enhancement, the position of the plasmon resonance and the wavelength of the excitation laser should be tuned so v_0 and v_m are both within the plasmon resonance peak width.

The contribution to SERS of chemical enhancement is believed to arise from the creation of a surface species, where a bond forms between the molecule and a few atoms of the metal surface [97, 98]. This bond allows charge transfer of electrons or holes from the metal into the molecule, increasing the molecular polarisability by creating new electronic states that act as resonant intermediates in Raman scattering. In this model a charge carrier is transferred into the molecule-metal surface species, the Raman process occurs, the excitation is transferred back into the metal and the emission process happens from the metal surface. This chemical enhancement is known to be a smaller contribution to the overall SERS than electromagnetic enhancement.



Fig. 4.7 Diagram of spectroscopy setup. Excitation and collection paths of the Raman spectroscopy setup based on the modified Olympus BX51 microscope.

4.2.3 Experimental setup

The experimental setup for Raman spectroscopy employs the same Olympus BX51 microscope used for darkfield spectroscopy shown in Figure 4.1, with the additional components illustrated in Figure 4.7. The setup is built by Dr Bart de Nijs from the Department of Physics, University of Cambridge, and aligned by myself before each experiment.

A 633nm CW diode laser (MatchBox series, Integrated Optics) is used as the excitation source. Power is adjusted using an acousto-optic modulator (AOM), which splits the input beam into 0th and 1st order diffraction beams in a ratio that can be changed electronically, with only the 1st order directed towards the rest of the setup. The AOM can be used to perform fast and programmable modulation of the laser power, and when the diffraction ratio is maximised, it operates as an optical switch up to frequencies of ~Mhz.

The input beam is sent through a 3nm bandpass cleanup filter centred on 633nm to eliminate spurious spectral lines, and directed towards the microscope with a 90:10

(R:T) beam splitter. This significantly drops the input excitation power, but ensures higher collection efficiency for the signal in the return path. The beam is coupled into the microscope tube with a dichroic mirror, it reaches the back aperture of the objective, and is focussed into a diffraction-limited spot on the sample surface. The reflected and scattered signals are collected by the objective and propagate back to the 90:10 beam splitter to enter the collection path. The Rayleigh scattering signal and residual laser light are removed with a 25nm notch filter centred on 633nm, before the beam is directed into the spectrometer (Horiba Triax 320 with liquid cooled Andor Newton 970 CCD) for analysis.

A power of up to a few mW can be delivered onto the sample, but this is normally limited to $200 \,\mu$ m when observing organic molecules to prevent damage. The laser input and white light illumination from the microscope can be switched with shutters, to avoid cross-talk during spectroscopy and imaging.
Chapter 5

Contacting nanoparticles with graphene layers

The initial approach adopted to electrically contact metallic nanoparticles is based on a top graphene layer electrode. Graphene is a good conductor and is optically transparent, so it allows access to the contacted particles for spectroscopy. On the other hand, reproducible fabrication of junctions with a defined geometry requires transfer of graphene membranes grown by chemical vapour deposition, and a number of lithography steps. Graphene-based junctions with a thin inorganic oxide spacer are presented in this chapter, characterised both electrically and optically, and the advantages and drawbacks of this contacting approach are discussed. While initially designed as test devices for subsequent replacement of the inorganic oxide with molecular layers, the oxide material combined with the strength of the graphene sheet lead to interesting electrochemical reactions, producing an actuating effect that could be exploited for nano and micro actuation.

Following a brief overview of other nanoactuation schemes, Section 5.1 presents the design and fabrication of graphene devices. Their electrical and optical properties are described in Section 5.2, showing that the response resembles resistive switching. Interesting actuation properties due to the oxide layer are first introduced in Section 5.3, and the actuation mechanism is explained in Section 5.4. Finally, actuation is characterised in more detail in Section 5.5. A significant portion of this chapter is contained in [99].

5.1 Device design and fabrication

Advances in nanotechnology rely on miniaturising functional components, which is a particular problem for nanoactuators required to control nanostructures and manipulate matter at the nanoscale [100]. Several microactuators have been demonstrated based on electrostatic, electro-thermal, magnetic and piezoelectric forces [101] as well as bimorphs [102]. However, the transition to the nanoscale raises a number of fabrication and cost/complexity challenges. Small-scale bimorphs, such as carbon-nanotube/aluminium nanoactuators [103], are hard to fabricate and position. Polymer films have been used for large scale devices, but they lack local control, and are complex to switch electrically [104]. Organic molecules such as DNA can be folded into structures with chemically triggered actuating capabilities in liquid environments [105], but these are inherently slow (typically seconds). All these systems face challenges in fabrication and operation when device size is pushed towards the sub-100 nm scale [106], where high actuation stresses (>1MPa) are particularly important since van der Waals interactions, capillary forces, and electrostatic forces become dominant.

Here an electrically driven nanoactuator based on memristive switches is demonstrated, that is compatible with large scale fabrication and incorporates optical readout capabilities. Memristive devices (see Section 3.2) have been proposed in [107] and demonstrated in [108], and can be obtained with thin layers of oxide material by electrically inducing a reversible local change in conductivity via ion migration at the nanoscale. This ion migration triggers a redox reaction that is often accompanied by gas release from the oxide, which is usually fatal for the memristive switch [? 109, 110]. In the present work, gas is instead trapped in micrometre-sized tanks to create an electrically-driven reversible actuator based on memristive switching.

The functional component of the actuator is a thin AI_2O_3 film, sandwiched between a graphene electrode and a flat gold substrate. Device fabrication starts with 20 nm of Ti for adhesion followed by 100 nm of Au deposited by evaporation onto a 285 nm thick SiO₂ on Si substrate in a pattern defined using optical lithography. The AI_2O_3 layer is deposited by ALD, without any prior adhesion layer, and using 60 and 90 layer deposition cycles to provide different thickness *t* for comparison, $t \sim 8$ nm and $t \sim 12$ nm respectively. The ALD is performed at a temperature of 180 °C in a vacuum chamber, which ensures a water-free Au-AI₂O₃ interface. The AI₂O₃ layer is subsequently patterned via optical



Fig. 5.1 Device design. **a**, The Al₂O₃ layer (thickness $t \sim 8$ or 12 nm) is sandwiched between separately contacted top graphene and bottom Au substrate to which a potential *V* is applied relative to the graphene. Low density 80 nm Au NPs under the graphene allow optical tracking. **b**,**c**, SEM images of device with Au fingers (false colour yellow) contacting graphene pads (blue) sitting on Al₂O₃ (green). Scale bar in b is 200µm.

lithography and chemically etched using Microposit MF-319. Gold nanoparticles (AuNPs, 80 nm diameter) from BBI Solutions are drop-cast on the substrate to obtain a number density of ~ $0.1 \,\mu m^{-2}$ on the Al₂O₃ surface. Single layer graphene grown by chemical vapour deposition (CVD) [111] is then deposited onto the chip via wet transfer and subsequently patterned with lithography and reactive ion etching. The schematic design of a junction is represented in Figure 5.1a, with the real overall junction array structure in Figure 5.1b,c. Design and patterning of the devices is done by Dr Hippolyte Astier from the Department of Physics, University of Cambridge, and devices are characterised by myself.

By incorporating AuNPs under the graphene layer in a nanoparticle-on-mirror (NPoM) geometry [36, 112] (see Section 2.5), the state of the thin Al₂O₃ film under bias can be optically tracked. Incident light is trapped in the plasmonic hotspot tightly localised within the nanoscale gap between AuNP and Au substrate, providing optical access to changes

in the thin film morphology and its dielectric properties [113]. Because AuNPs can be easily deposited over wide areas and their optical response is highly reproducible, large regions of the thin film are probed in real time. The NPs are drop-cast over the surface with a number density controlled by the deposition time, and optimised to ensure light collection for spectroscopy from individual NPs within the collection spot.

The graphene and gold contacts are arranged as independent junctions (Figure 5.1b,c) electrically isolated from each other so that a voltage V can be applied across independent graphene-Al₂O₃-Au structures. Graphene is used as the top electrode for its conductivity, transparency (making the encapsulated NPs optically accessible), flexibility (conforming to mechanical deformations in the underlying structure), and impermeability to gases [114, 115]. Using large CVD graphene sheets and optical lithography allows parallel fabrication of an arbitrary number of junctions.

Single layer graphene (SLG) is prepared via chemical vapour deposition (CVD) on 35µm thick Cu, following the recipe in [111]. Initially, Cu is annealed in H₂ atmosphere (\approx 200mTorr), by raising the temperature up to 100°C and keeping it constant for 30 minutes. Then, 5 sccm of CH₄ are added to the 20 sccm flow to initiate the growth, which lasts 30 minutes. The sample is then cooled in vacuum (\approx 1 mTorr) to room temperature and unloaded from the chamber. Single layer graphene is then transferred by wet transfer on top of the Al₂O₃/Au/SiO₂/Si substrate as follows: a PMMA layer is spin-coated on the surface of SLG/Cu and then placed in a solution of ammonium persulfate (APS) and DI water for Cu etching [116]. The PMMA membrane with attached single layer graphene is then transferred to a beaker filled with DI water for cleaning APS residuals and is finally lifted with the target substrate. Graphene growth, transfer, and characterisation, as well as ALD of Al₂O₃, are done by the group of Prof Andrea Ferrari from the Department of Engineering, University of Cambridge.

5.2 Device operation

Electrical measurements are used to characterise the junctions at room temperature. The initial state of the junctions is insulating with conductance in the 0.1 to 10 pS range for junctions of area $\sim 500 \,\mu\text{m}^2$ and Al₂O₃ thickness of \sim 8nm, corresponding to conductance per unit area ranging from 0.1 to 10 nS/mm². Each junction can be made conductive (switched on) by applying a critical voltage across it. In the case of devices with 8nm Al₂O₃



Fig. 5.2 Device dynamics under applied potential. **a**, *I*-*V* plot of transitions between on and off states driven by changing junction voltage to positive or negative polarities. Magnitude of current |I| shown on logarithmic scale, legend colour indicates order in which measurements are taken, while a current compliance limits the maximum current. **b**, Junction conductance in on and off states for cycles shown in a. **c**, Single device finger with graphene (blue) on 8nm Al₂O₃ (green) thin film on Au back contact. Low density 80nm Au NPs (red) are sandwiched between graphene and Al₂O₃. **d**-f, Darkfield images for (d) 0V, (e) 5V, and (f) 6V applied. Strong light scattering is observed for increasing voltages. Scale bar is 5 µm.

layers, this voltage is around 5V (for 12.5nm thick layers devices switch on around 7V). The turn-on transition appears as a sudden jump in current, in which the conductance rises to values in the 1nS to $100 \,\mu$ S range, i.e. 1μ S/mm² to 0.1mS/mm². In a given cycle, on-off resistance ratios as high as 10^8 are observed (Figure 5.2a,b), which compares favourably to some of the highest ratios observed in memristors [117–119]. Reversing the voltage polarity across the junction drives the opposite reaction and decreases the conductance back towards the initial state, seen either in a sudden drop in current or a more gradual transition (Figure 5.2a). Approximately 5 cycles can be switched in this way (Figure 5.2b), before the memristive behaviour is compromised. In either state, the junction remains stable when varying the voltage within a small range, between -1V and 1V. The junctions at 0V for times in the range of tens of hours are stable (Figure



Fig. 5.3 Stability of switching cycles. Conductance as a function of time over 48h. On (red) and off (blue) states retain their conductance values, and the device state can be read using voltage pulses with amplitude ≤ 0.1 V. Switching is performed by applying a voltage of ± 5 V until current compliance is reached.

5.3), however a slight decrease in conductivity in the conductive state can sometimes be observed.

Further electrical measurements are performed while optically imaging the graphene pad from the top (Figure 5.2c). When a field exceeding 5×10^8 Vm⁻¹ is applied ($V \approx 5$ V for $t \sim 8$ nm, $V \approx 7$ V for $t \sim 12$ nm), strong scattering is observed arising from different regions of the graphene pad (Figure 5.2d-f). These bright regions (which as shown below are caused by micro-bubbles) expand faster as V is further increased, and merge into fewer larger regions as they expand more. The AuNPs within the bright regions change colour from red to yellow (Figure 5.4a,b), signalling a modification of the NPoM gap. Such behaviour is consistently observed for all NPs in the device. The NPoM geometry is thus a helpful tool to investigate the real time dynamics of such thin films or bubbles.

The formation of each bubble results in a prompt blueshift of the NP coupled mode seen in dark-field scattering spectroscopy (Figure 5.4c,d) together with a simultaneous increase in current (Figure 5.4e). Reversing the voltage causes the bubbles to gradually shrink, enabling voltage-driven height manipulation. Complete bubble deflation can be achieved, fully recovering the initial NP spectrum (Figure 5.4f,g). The switching process in the devices can typically be repeated approximately 5 times (Figure 5.4f,g). In a given junction, the location and relative size of the bubbles when a device is first turned *on* is random. However, the location, size, and height of the bubbles are maintained in successive switching cycles when using the same electrical parameters, enabling the NPs on bubbles to undergo repeatable transitions (Figure 5.4g). Once the voltage is turned off, the position and size of the bubbles remain stable for months.



Fig. 5.4 Optical evolution with applied potential. **a**,**b**, NP colour switching in dark field imaging, with **c**, corresponding scattering spectra from this NP. **d**, NP scattering spectrum for increasing voltages with **e**, corresponding measured current (line is guide to the eye). **f**, Scattering spectra when plasmon resonance switches under voltage cycling $-V \leftrightarrow +V$ over time sequence shown in **g**. Positive voltages trigger blueshifts while negative *V* promptly recovers the initial condition.

5.3 Formation of O₂ gas reservoirs

The NP blueshifts can arise from three different scenarios: refractive index changes in the medium surrounding the NP (scenario S1), alterations in spacer conductivity (S2), or variations in distance from the mirror, where it is sensitive to nanometre displacements (S3). Scenario S1 requires an unfeasibly high refractive index variation (in excess of $\Delta n = 0.4$) to account for a 50 nm shift [13]. Variations in conductivity (S2) can induce a shift due to shorting of the optical charge oscillations between the NP and the substrate [27], but require a much larger increase in Al₂O₃ conductivity than measured and should be localised under the NPs. Similarly a vertical displacement of the NP (S3) could cause a shift of the coupled mode resonance [28] needing the NP to be moved away from the mirror to induce the observed blueshift. Proving this latter scenario thus requires morphological analysis of the surface.

Angled scanning electron microscopy (SEM) images of the bubbles reveal an inflation of the device surface with the AuNPs sitting on top (Figure 5.5a), confirming scenario S3. Atomic force microscopy (AFM) topography measurements are used to quantify the size of the larger bubble reservoirs (visible in darkfield microscopy), which can reach up to



Fig. 5.5 Imaging of bubble reservoir. **a**, SEM image of inflated reservoir, with NPs sitting on top. Scale bar is $1\mu m$. **b**, AFM topography image with **c**, cross section showing reservoir height along line.

tens of μ m in diameter and up to 1 μ m in height (Figure 5.5b,c). The bubbles observed in darkfield microscopy thus correspond to vertical displacements of the device surface, which match the blueshift in the NPoM scattering spectra [31]. In the early stage of inflation when the bubble diameter is <2 μ m, bubble actuation can only be detected in real time through the NP scattering spectra, sensitive to sub-nm displacements. The height of such bubbles is 10-20nm, and the AuNP plasmonic coupling with the gold electrode thus provides a unique tool to detect their formation and growth in real time.

Figure 5.4f,g shows the spectrum of a AuNP sitting on top of a bubble displaying multiple switching cycles. Positive voltages inflate the bubble, lifting the NP and causing a 10nm blueshift in the coupled mode peak from 645 to 635nm, whereas negative voltages fully deflate the bubble, inducing a redshift and restoring the initial NP spectrum. Applying the switching voltage for a longer time or increasing its magnitude inflates larger bubbles and causes greater NP spectrum shifts (50 nm shift in Figure 5.4d). This demonstrates the use of a plasmonic ruler to measure the actuation, the repeatability of subsequent cycles, and the ability to control height of actuation through the voltage applied. The additional rise in scattering intensity of the NPoMs (Figure 5.4c) is caused by interference effects when the distance exceeds 100 nm [120], which agrees with the height range measured using AFM.

The reservoir inflation could arise from several types of deformation. Bulging of the Au bottom contact due to electrostatic forces between the electrodes is ruled out since bubble formation is not observed for negative applied voltages, and electrostatic forces should be independent of voltage polarity. Corrugations of the graphene layer alone would not cause the bright scattering regions observed in dark-field, because the graphene monolayer itself is barely visible in microscopy. The AuNPs play no active role, since the initial position of the bubbles is unrelated to the NP positions. It is therefore concluded that changes in the Al_2O_3 layer are responsible for reservoir inflation.

Thin Al₂O₃ films are known to allow migration of oxygen ions [121], and have widely been used in resistive switching devices [? 122, 123]. In such devices, a voltage applied across an oxide layer such as TiO₂ or AI_2O_3 drives O^{2-} ions towards one of the electrodes. This leaves oxygen vacancies in the material, effectively doping the oxide and changing the resistivity of the layer, thus making it suitable for resistive switching applications. In the case of TiO₂, such O²⁻ ion migration and vacancy formation mechanisms have been confirmed by spatially resolved X-ray spectromicroscopy [124]. When using inert Pt electrodes, the ions can then oxidise upon reaching the positive electrode via the reaction $2 O^{2-} \rightarrow 4 e^- + O_2^{(g)}$, forming bubbles of oxygen gas [110]. Bubbles however only persist while the voltage is applied, rapidly disappearing once the bias is removed. Modifications in the density of oxygen vacancies under applied voltage have also been studied in NiO films, where growth of a metallic Ni phase has been proposed as the switching mechanism [109], although with no direct evidence in working devices [125, 126]. The exact oxide reduction mechanisms are therefore still unclear. Studying this mechanism in typical resistive switching devices based on planar metal/oxide/metal junctions is problematic as they prevent in situ access for optical or electron microscopy.

5.4 Reservoir inflation mechanism

The devices presented in this work share the same structure of valence change mechanism resistive switches. It can thus be concluded that reservoir inflation is similarly caused by drift of O^{2-} ions which move towards the positive electrode, there converting into oxygen gas. The data confirm the observation of oxygen bubbles reported so far only for TiO₂ [110]. The dynamics of the reservoirs and the increased expansion speed with higher voltage also agrees with previous reports [110]. The currently accepted view of the resistive switching mechanism in valence-change cells is that the high-conductivity state is due to a localised conductive filament [127], but its composition and structure have not yet been directly observed in situ. Formation of these filaments has often been associated with local deformation of the device in the form of crater-like structures [128], and this seems consistent with the formation of a gas reservoir bursting due to



Fig. 5.6 Al₂O₃ redox into Al and O₂. **a**, Thin Al₂O₃ film (V = 0) separates into metallic Al and O₂ gas (V > 5V) with a growing bubble reservoir. **b**, Ratio of measured reflectivity after (R_f) and before (R_i) reservoir inflation (solid line), compared to the thin film model (dashed) with increasing Al thickness d_{Al} , identifying $d_{Al} \sim 10$ nm, and predicting the same inflation height as that found from AFM.

excessive pressure. In the devices described in this work, conduction through the Al_2O_3 film likely starts at a site where O^{2^-} ion conductivity is locally higher than the surroundings. Rapidly this local migration of O^{2^-} ions forms O_2 gas at the Au electrode which lifts the graphene/Al₂O₃ film away from the Au, interrupting the conductive path. Conduction can then only occur through the migration of O^{2^-} at the boundaries of the reservoir via new migration paths formed in the Al₂O₃, thereby continually producing more O_2 gas and enlarging the reservoir laterally (Figure 5.6a). A corresponding solid-state electrochemical reaction is then driven at the graphene electrode, $Al^{3^+} + 3e^- \rightarrow Al^0$ producing a thin metallic Al film. Rather than localised conductive filaments found in most other memristors, which would be unable to grow the bubble, this scenario suggests a uniform Al film forms near the surface of the reservoir.

To confirm this picture, reflectivity measurements on a bubble region are compared before and after reservoir inflation. The transparent graphene electrode in the devices is crucial for enabling this real time optical tracking of the redox underlayer. Initial brightfield reflectivity spectra R_i are collected before any voltage is applied on the top of each bubble with a 50× objective, to focus broadband white light which is confocally collected at a detection fibre. After forming the reservoir the modified reflectivity R_f is measured, and the ratio R_f/R_i is plotted to highlight spectral changes. This experimental ratio is compared with transfer matrix calculations using a multilayer model of the inflated reservoir structure [129] (Figure 5.6b). The transfer matrix method represents each individual layer with a propagation matrix, and the interfaces between layers with a matrix defined by Fresnel coefficients of reflection and transmission. The spectrum of reflected



Fig. 5.7 Bubble multilayer model. Vertical layer profile used in bubble reflectivity calculations.

light is then calculated by propagating incident plane waves through the multilayer, as a product of consecutive propagation and interface matrices.

The model reproduces the vertical layer structure of the bubble: the bottom semiinfinite Si substrate, a 285nm insulating SiO₂ layer, a 100 nm gold contact, layers of air, Al_2O_3 and metallic Al with thickness t_{air} , $t_{Al_2O_3}$, and t_{Al} respectively, a 0.34nm layer of graphene, and a semi-infinite air superstrate (Figure 5.7). To highlight the contribution to the reflectivity given by the bubble alone, the reflectivity R_f calculated using the structure in Figure 5.7 is normalised to the reflectivity R_i of a region without any bubble, for which $t_{air} = t_{AI} = 0$ and $t_{AI_2O_3}$ has the nominal thickness of the AI_2O_3 layer. In the calculations, the values t_{air} , $t_{Al_2O_3}$ and t_{Al} are varied in the bubble model to match the spectrum of R_f/R_i obtained from reflectivity measurements. The major contribution to the reflectivity is provided by the metallic AI layer, whereas variations in the values of t_{air} and $t_{AI_2O_3}$ have a marginal effect. By fitting the model parameters to the experimental data, complete disagreement is found unless a metallic Al film is present. Optimising the fits resolves an Al thickness of 10nm, with Al₂O₃ residual film of 4.5nm, and reservoir height of 165nm (in good agreement with the 175nm average height from AFM for bubbles of this size, Figure 5.11). Similar reflectivity changes are seen on other bubbles. This optical modelling also confirms that the AI nanolayer separates from the Au substrate, storing the oxygen gas in between.

5.5 Characterisation of bubble reservoirs

The presence of gas is further demonstrated by cooling down and optically tracking the changing size of a 1μ m high bubble from 292K to 6K in situ. Images taken at different



Fig. 5.8 Bubble reservoir cooling. **a**, Interference between light reflected from the top and bottom of the bubble reservoir. **b**, Cross-section of O_2 reservoir, with fitted shape compared to measured AFM profile at room temperature. **c**,**d**, Interference fringes of bubble reservoir inside the cryostat at 292K and 6K. Dashed lines show region used for the fit. **e**, Exemplar fit of interference pattern along the reservoir diameter at a temperature of 70K.

temperatures are used to infer the bubble height by fitting interference fringes from light reflected off the surface of the bubble and off the bottom gold substrate with a simple model.

The inflated bubble is modelled as a spherical cap with base radius *a* and height *h* (Figure 5.8a). The height and diameter measured with AFM represent the values of *a* and *h* at room temperature (Figure 5.8b). The devices are cooled from 292K to 6K in an optical cryostat (Oxford Instruments Microstat He) with the sample held on a cold finger in vacuum. The bubble evolution is observed in situ through the cryostat window with a 50× microscope objective (0.4 N.A.) using a monochromatic LED light source ($\lambda = 665$ nm). A set of images is recorded at different temperatures (Figure 5.8c,d) and the light intensity pattern along the bubble diameter is extracted. Fringes are observed

that result from the interference between the light reflected off the top surface of the bubble and off the bottom gold substrate (Figure 5.8c,d). The interference pattern is given by the phase difference between the two light paths, which is $\Delta \varphi = 2\pi n h/\lambda$, where *h* is the height of the point along the cross section, $\lambda = 665$ nm, and n = 1 is the refractive index. The geometric parameters in the model of the bubble are varied to find the height that matches the interference pattern (Figure 5.8e). This simple two-dimensional model allows the bubble height to be reliably inferred from the observed temperature-dependent interference patterns.

A stronger decrease in reservoir height is observed as the temperature is lowered below 150K (Figure 5.9), reducing finally by about a factor two. The shape and size of the reservoir are fully restored when the sample is heated back to 292K, suggesting that temperature control can also be used for nanoactuation and height fine-tuning, in addition to electrical driving. The presence of water in the devices is excluded since ALD growth occurs at 180°C epitaxially layer by layer in cycles. Each atomic layer is grown by successively flushing the deposition chamber with one of two Al₂O₃ precursors (trimethylaluminium and DI water) in gas phase, that adsorb on the sample surface and react to form a monolayer. Any excess precursor is pumped out of the chamber at each cycle, thus preventing accumulation of precursors such as water in the chamber. Traces of water can remain underneath the graphene layer during wet transfer, but water presence would also affect the electrical response of the device. Water splitting into H_2 and O_2 gas occurs at 1.2V, and this would result in an increase in current around such voltage that is not observed. Additionally, H₂ and O₂ gas would remain trapped under the graphene during this reaction, inflating bubbles and lifting the NPs on top. Instead bubbles are not observed directly, nor do NPs show spectral changes at this voltage. Therefore water residue within the device is either absent, or present in traces with negligible effect on device structure and functionality.

The internal pressure P of the O₂ bubble reservoir, which has the shape of a spherical cap, is related to its geometrical properties by [130]:

$$P = \frac{E}{1 - \nu} \frac{8th^3}{3a^4}$$
(5.1)

where *E* is the Young's modulus of the wall material, ν its Poisson's ratio, *t* the wall thickness, *h* the height of the cap and *a* the base radius. The pressure therefore scales as $P \propto h^3/a^4$, rapidly decreasing with decreasing reservoir aspect ratio. By



Fig. 5.9 Temperature dependence of bubble height. Bubble height decreases as temperature is lowered, due to decreasing volume of internal O₂. Fit (line) shows ideal gas dependence $h \propto T^{1/4}$.

considering the wall composed of both Al_2O_3 (t = 12.5 nm, E = 170 GPa, v = 0.24) [131, 132] and graphene (t = 0.34 nm, E = 2.4 TPa, v = 0.17) [133, 134], pressures in the range of 20 ± 10 atm are obtained for the majority of bubbles. Because many reservoirs start forming simultaneously across the whole area of a device when voltage is applied, equation (5.1) is found to be valid up to a reservoir diameter of approximately 5µm. Beyond this limit the boundaries of adjacent reservoirs start touching, leading to geometry rearrangements and mergers that do not preserve uniform wall thickness and increase the base areas (Figure 5.10).

Once the reservoir size and pressure are known, the number of moles n_{O_2} of O_2 inside the bubble is calculated from the ideal gas law:

$$n_{O_2} = \frac{PV}{RT} \tag{5.2}$$

where *V* is the bubble volume, *T* is the temperature and $R = 8.3 \text{ JK}^{-1}\text{mol}^{-1}$. Assuming the oxygen is extracted from the Al₂O₃ layer, using the density [135] $d = 2.8 \text{ g/cm}^3$ and molar mass $MM_{\text{Al}_2\text{O}_3} = 101.96 \text{ g/mol}$ of Al₂O₃, the fraction *f* of the layer that is converted at room temperature is derived as:

$$f = \frac{n_{O_2}}{n_{Al_2O_3}} = n_{O_2} \frac{MM_{Al_2O_3}}{\pi a^2 td}$$
(5.3)

Applying these calculations to the largest bubble shown in Figure 5.11, on which the above mentioned reflectivity measurements are performed, a conversion fraction f = 60% is obtained. Completing analogous calculations on Al (d = 2.7 g/cm³, $MM_{Al} = 26.98$ g/mol),



Fig. 5.10 Distribution of bubble height vs diameter measured with AFM. In the small bubble regime (diameter <5 μ m), where reservoirs are separated from each other, most bubbles have an internal pressure of 20 ± 10 atm. In the large bubble regime (diameter >5 μ m), the reservoirs merge and the pressure scaling breaks down.

a metallic Al layer thickness on the reservoir around 6nm is inferred, which is compatible with what is obtained experimentally considering the adopted approximations and the use of nominal parameter values in the calculation.

From the bubble pressure, the scaling of the bubble height with temperature can also be extracted. The volume *V* of a spherical cap with height *h* and base radius *a*, with $a \gg h$, is:

$$V = \frac{\pi}{6}h(3a^2 + h^2) \approx \frac{\pi}{2}ha^2$$
 (5.4)

Combining equation (5.4) with (5.1) and the ideal gas law gives:

$$T = \frac{PV}{nR} = \frac{E}{1 - \nu} \frac{4\pi t}{3nRa^2} h^4 \propto h^4$$

and thus the height of the bubble scales with temperature as $h \propto T^{1/4}$, which is observed experimentally (Figure 5.9).

The strain in the bubble surface film is found from [130] $\varepsilon = 2h^2/3a^2$, and ranges from 0.35% to 1% depending on the aspect ratio of the bubble, corresponding to a stress level well below the ultimate tensile strength of either graphene [136] or Al₂O₃ [137]. Raman spectroscopy can be used to monitor the presence of defects, doping, and strain in the graphene [138–144]. Strain in particular is determined through shifts in the G and 2D Raman peaks of graphene.



Fig. 5.11 High aspect ratio bubble AFM. Topography (**a**) and cross section (**b**) of a bubble with particularly high aspect ratio measured with AFM. With a height of 260nm and a base diameter of 4.26 μ m the calculated internal O₂ pressure is 73atm, corresponding to an O₂ conversion fraction of 60% and Al film thickness of 6nm.

The G peak is located around 1587cm⁻¹ and originates from in-plane vibrations corresponding to optical phonon modes given by the graphene lattice geometry. Its exact position is sensitive to the number of stacked graphene layers, with single layer graphene being characterised by a sharp narrow line located exactly at 1587cm⁻¹. The D band is linked to disorder in the lattice and is given by the breathing mode of sp^2 carbon rings, and the mode is only activated if the ring is adjacent to an edge or defect. A weak D band signals a good quality graphene layer with few defects. The 2D peak is the second order of the D band and results from a two phonon vibrational process that satisfies momentum conservation, and thus unlike the D band it does not require proximity to a defect to be activated and gives a strong signal in most samples. The position as well as the shape of this band are linked to the number of graphene layers, with single layer graphene showing a single band without shoulders around 2700cm⁻¹ with FWHM around 30cm⁻¹ [143]. Both the G and 2D bands have been shown to shift linearly with biaxial strain, with $\partial \tilde{v}_G / \partial \varepsilon = -57 \text{ cm}^{-1} / \%$ and $\partial \tilde{v}_{2D} / \partial \varepsilon = -160 \text{ cm}^{-1} / \%$ [145]. In the samples measured here, graphene before transfer onto the sample shows a G peak located at 1587cm⁻¹, a 2D peak without shoulders and no D band, indicating single layer graphene with negligible defects (Figure 5.12). As the graphene is transferred onto the device it acquires some strain, visible in the blueshift of the 2D line, which is typical of the wet transfer method on most substrates. Acquiring the Raman spectrum of single layer graphene on a bubble, and comparing it to the spectrum of deflated junctions, yields an observable blueshift in the G and 2D peaks by 9 and 18cm⁻¹ respectively (Figure 5.12), corresponding to a value of strain in the graphene of order 0.1%, consistent with the estimate for the full



Fig. 5.12 Raman spectroscopy of single layer graphene on different substrates. Red: on Cu substrate (before transfer onto device), blue: on junction before applying voltage bias, green: on inflated junction outside of a bubble, orange: on inflated bubble. Shifts in the graphene on bubbles are attributed to doping and strain.

SLG/Al₂O₃ film. Such strain values imply typical internal bubble pressures in the range of 20 ± 10 atm. It is found that the amount of oxygen required to give this pressure is indeed a sizeable fraction, up to 60%, of that locked up in the Al₂O₃ film.

Generally, smaller bubbles have higher internal actuation stress, thus likely requiring an overpotential to initially drive the reaction. As a simple estimate, a typical current of 1nA applied for 1 minute across junctions such as these would correspond to the migration of 10^{11} O^{2-} ions. This matches an equally simple estimate of the number of oxygen atoms trapped as O₂ in the bubbles assuming a pressure of 20 atm and typical bubble sizes after inflation. This is thus consistent with oxygen migration being a major conduction mechanism in our film.

5.6 Conclusions

This work demonstrates reversible room temperature and low voltage conversion of >60% of thin AI_2O_3 films to metallic AI and back on demand. The specific choice of electrode/electrolyte materials, forming chemically stable graphene/AI/AI₂O₃ and Au/O₂

interfaces, is what allows the reservoirs to remain stable for months when the bias is removed. A negative voltage triggers oxygen recombination with Al thus reforming the AI_2O_3 film. This is enabled by the impermeability of graphene to O_2 , while the strength of the graphene/Al/Al₂O₃ film allows O_2 gas to be locally stored at high pressures without rupturing its flexible container. The internal pressure can be tuned by choice of layer thicknesses.

The graphene/Au electrodes form a unique combination with the solid state electrolyte thin film to produce electrically controlled nano-actuators capable of high stress actuation. The applied electrical field drives O^{2-} drift, creating local chemical energy storage in the AI metal and O_2 gas which can be triggered to recombine, thereby deflating the actuator. This device geometry has much in common with memristive switches, but with an optically accessible electrode, and the flexible graphene layer improves the reliability and resilience of resistive switching. Plasmonic rulers allow the dynamics of this process to be studied in real time.

While the AuNP contacting technique described in this chapter leads to interesting actuation mechanisms, the observed effects are due to the electrochemical properties of the oxide layer, which reversibly turns into a metallic film and gas. AuNPs do not play any active role in the junction, and are only used to passively track the actuation in the oxide layer through spectroscopy. Since bubbles initially appear in random positions across each junction, there is no evidence suggesting that conduction occurs preferentially where AuNPs are located. Considering the sample design in Figure 5.1a, it is reasonable to assume that the graphene-AuNP interface represents an additional barrier to conduction due to contact resistance, and thus that current would flow directly from graphene towards the Au substrate through the oxide layer via a path of locally smaller resistance away from the AuNP. The area of a single junction is also several hundreds of μ m², orders of magnitude larger than the surface covered by AuNPs, and the contribution to conductance through AuNPs is therefore a negligible fraction of the measured value.

The issue of large junction area was particularly apparent in test devices fabricated replacing the oxide spacer with a self-assembled molecular monolayer. All junctions in such samples were shorted, through pinholes in the molecular layer or damage to the molecules during the fabrication procedure. Since conduction in these devices is distributed across a number of individual conductive paths within the whole junction area, even maintaining the integrity of the molecular layer does not guarantee that conduction

occurs through the AuNPs. To ensure this is the case, the size of the entire junction must be shrunk down to a single AuNP, that must be contacted individually while maintaining optical access for spectroscopy. In such a configuration, an NPoM structure with a molecular spacer could be used to track in real time the behaviour of all the molecules contributing to the junction conductance. This approach is discussed in the next chapter.

Chapter 6

Cantilever contacting setup

Fabrication of molecular devices with sub-100 nm junction size and a consistent number of molecules per junction is challenging, as discussed in Section 3.4. Break junction systems, whether mechanical, STM, or electromigrated, provide useful tools to access single or few molecule dynamics, but are difficult to implement at a device level. On the other hand, evaporation of metals directly onto molecular monolayers to fabricate traditional junctions can easily damage or displace the molecules, shorting the electrodes and compromising the functionality of the device. Use of "soft" electrode materials deposited in ambient conditions, like graphene, is an interesting option but also brings its own fabrication challenges, such as control of junction area, interfacing between graphene and molecules, and additional processing steps as described at the end of Chapter 5.

An alternative molecular junction geometry is presented here, where a single gold nanoparticle positioned on top of a molecular monolayer represents one of the electrodes. The nanoparticle is contacted from the top with a conductive transparent cantilever, which is key to enable real time optical access to the junction for spectroscopy. The facet size of the nanoparticle sets the number of molecules in the junction, but accurate fabrication and precise control of the cantilever are crucial to probe the junction experimentally.

The conceptual design of the cantilever contacting method and device geometry is described in section 6.1. Section 6.2 presents the challenges of cantilever control and the development of the contacting setup. Sample fabrication also requires a specific geometry, which is discussed in Section 6.3. Finally, the electrical and optical performance of the setup is tested in Section 6.4.

6.1 Experiment design

The aim of the work presented in this thesis is to optically probe molecular junctions in real time during device operation. Optical spectroscopy is a non-invasive method that can access information difficult to obtain from repeated electrical measurements or in situ electron microscopy, such as molecular vibrations that occur while a voltage is applied across the junction.

Fabricating a molecular junction in the form of a device with a small (≤ 1000) and reproducible number of molecules requires the use of self assembled monolayers (SAMs) sandwiched between electrodes, as opposed to break junctions, but more importantly it demands a shrinkage of electrode size. At the same time, in an optically accessible device light must be able to reach the functional region between the electrodes, and the optical response must be concentrated in the active part of the junction. In this context, the nanoparticle on mirror (NPoM) geometry described in Section 2.5 thus represents an ideal system, capable of consistently trapping a set number of molecules in a nm-sized gap that is also the hotspot of a plasmonic oscillation. The number of molecules in the junction is set by the size of the nanoparticle facet, which can be tuned from a few nm to tens of nm, while the coupling to the mirror enhances the electromagnetic field in the gap and creates a strong optical response that can be exploited with both darkfield spectroscopy and SERS (see Sections 4.1 and 4.2.2).

For an NPoM structure to be a molecular junction device, the AuNP needs to represent one electrode, with the mirror being the other. While the mirror can be easily contacted electrically with a probe away from the NP, contacting an individual AuNP while maintaining optical access to the junction is challenging. The concept used here to address this challenge is illustrated in Figure 6.1. The NPoM structure is contacted from the top with a conductive transparent cantilever, with a size similar to typical cantilevers used for AFM imaging applications, but without a sharp tip at the end. The cantilever (AppNano HYDRA6R-200N-TL) is made of Si_3N_4 , is 200µm long, 35µm wide and 600nm thick, and is transparent at optical frequencies.

A transparent conductive coating is required to make electrical contacts with NPs. Preliminary tests performed with indium tin oxide, a material commonly used for transparent electronics, showed that a film thickness of at least 50nm is needed to obtain good conductivity when contacting an Au surface. Strain in the indium tin oxide film however



Fig. 6.1 Cantilever contacting method. Single AuNP electrodes in NPoM geometry with a molecular spacer, embedded in a dielectric layer, are individually contacted with a transparent conductive cantilever. Elements are not to scale except for the indicated vertical sections.

caused warping, so both sides need to be coated to produce a flat, straight cantilever. Given this additional fabrication step and the inferior electrical properties of indium tin oxide, a thin metallic coating of 3nm Cr and 6nm Au (transmission \approx 25% in visible range [146]) was finally chosen for this application.

The position of the cantilever is controlled with a set of translation and rotation stages, which allow precise placement on top of the AuNP, but a number of fabrication steps are needed to ensure contacting of individual particles in NPoM geometry.

6.2 Control of cantilever position

Since imaging and spectroscopy of AuNPs are performed using an existing microscopy setup based on a modified Olympus BX51 microscope (see Sections 4.1 and 4.2.3), the main design challenge is the integration of the cantilever contacting system with the existing apparatus. The most important design constraints are compatibility with the microscope stage and optics, mechanical stability, and modularity, so the contacting setup can be quickly removed to allow access to the microscope to other users.



Fig. 6.2 AFM chip and cantilever. The transparent silicon nitride cantilever HYDRA6R-200N-TL from AppNano is fabricated on a standard AFM chip and used in all contacting experiments.

Spectroscopy of single AuNPs is performed with a $100\times$ darkfield objective (see Section 4.1), with working distance of 3.3mm. Objective working distance and vertical travel range of the microscope stage set the constraints on the overall size of the contacting setup. The transparent cantilever is located at the edge of a standard AFM chip with a rectangular size of $3 \times 1.5 \times 0.3$ mm (Figure 6.2), and must be positioned within the field of view of the objective for imaging, and on its axis for spectroscopy.

6.2.1 Initial setup design

Given the limited space available underneath the objective, the initial setup design (Figure 6.3a) was based on a horizontally mounted cantilever that could only contact the edge of a sample (Figure 6.3b).

Cantilever position was controlled using manual ball bearing translation stages with micrometre screws in *x* and *y*, a motorised actuator (resolution \approx 100nm) for the *z* direction, and a fully motorised rotation stage for axial rotation (Figure 6.3a). A travel range of 25mm in *x* and *y* allowed to navigate the entire size of a manually positioned sample. A set of custom made adapters was required to mount the cantilever sufficiently far away from the motion stages to allow rotation and swapping of the microscope objectives during a measurement. In the initial stages of setup design, samples were made using a uniform Au film on the entire surface without any patterning, so no additional control of sample alignment was required.

The AFM chip with the cantilever was mounted with a clip (not shown in Figure 6.3a) at the end of a supporting arm, and given the bulk of the setup, only the edge of a sample could be contacted while keeping access to all required microscope objectives (Figure 6.3b). While some preliminary electrical and optical testing was performed with this system, edge contacting creates a number of issues that preclude any measurements



Fig. 6.3 Initial design of contacting setup. **a**, In the initial design, the cantilever was parallel to the sample surface and could only contact the sample edge. The x and y axes were controlled manually, while z and rotation were motorised. Components highlighted in red were designed and made by myself in the student's workshop of the Department of Physics. **b**, Darkfield image of cantilever contacting the edge of a flat sample. **c**, Shorter and thinner variant of cantilever in b.

on single NPs. The edge of a sample, even though obtained from a freshly cut Si wafer, is uneven and easily damaged during sample handling, so the usable sample regions are only a fraction of the total edge length, which is itself a minimal fraction of the total entire area. Deposition of AuNPs is also difficult to control accurately near the edges due to nonuniform wetting of the sample by colloidal AuNP solutions. Finally, since the cantilever is parallel to the substrate, it tends to bend against the edge when lowered, so the contact area between the cantilever and the sample is impossible to control.

Some tests were performed with a shorter and thinner (100µm long and 200nm thick) variant of the AppNano HYDRA6R-200N-TL cantilever (Figure 6.3c). This was found to be more susceptible to bending and twisting, even only as a result of applied voltage (most likely from electrostatic forces). Additionally, the reduced distance from the AFM



Fig. 6.4 Improved contacting setup. Cantilever rotation is achieved with a compact manual stage, and longitudinal tilt is added with an angle plate. A brass holding arm is used to mount the cantilever. Electrode patterns on the sample are aligned with a dedicated manual rotation stage and contacted with probe from the side. Components highlighted in red were designed and made by myself in the student's workshop of the Department of Physics.

chip caused higher background during darkfield spectroscopy measurements, due to scattered light from the chip entering the collection path of the microscope objective. For these reasons the smaller cantilever variant was abandoned for all subsequent experiments.

6.2.2 Setup development

An improved version of the setup was developed to address the encountered issues (Figure 6.4). The motorised rotation stage was replaced with a more compact, manual stage, since rotation adjustment is only required at the beginning of each experiment to eliminate axial tilt of the cantilever with respect to the sample plane. An angled plate was added to introduce a longitudinal tilt of 5° , that enables a gradual control of the contact area with vertical displacement. Importantly, a thin brass arm was added to hold the AFM chip, and mounted with a tapered plastic (electrically insulating) adapter onto the rotation stage. The low-profile design of these components allowed to move the cantilever within the entire field of view of the microscope without colliding with the $100 \times$ objective, and thus the whole sample surface became accessible for electrical contacting and spectroscopy, while keeping objectives interchangeable. To contain the size of the brass arm, the AFM chip was fixed with conductive Ag-based glue inside a notch, whose dimensions also ensured coaxial movement with the rotation stage. The uniform Au film over the whole sample surface was replaced with a striped electrode pattern (see



Fig. 6.5 Damage to conductive coating by mechanical drift. **a**, A static NP on a surface can rip and damage the thin conductive coating of a cantilever, forming a rippled cluster and exposing the underlying material. Scale bar is 200nm. **b**, AuNPs (false colour yellow) can be displaced from the sample surface and remain attached to the cantilever. Scale bar is 100nm.

Section 6.3) to guarantee a more precise contact geometry, which required the addition of a separate x-y-z manipulator for positioning of a sharp electrical probe, and a manual rotation stage below the sample to align the electrode pattern to the cantilever.

The setup in Figure 6.4 was used to perform extensive tests (see Section 6.4), and enabled for the first time to electrically contact individual AuNPs. However, longer measurements of the order of minutes suffered from mechanical instabilities, with the cantilever drifting sideways by a few µm without any external input. This was particularly apparent in many measurements where the thin metallic coating on the cantilever was damaged by sliding over the static AuNP that was being contacted (Figure 6.5a). Inspection of the damage clearly showed a rippled film with exposed underlying SiN from the cantilever. On one hand, a locally damaged coating could induce a change in the optical response of a NP due to additional scattering, which would be difficult to distinguish from a genuine change in the NP spectrum. On the other hand, a rippled coating could pierce through the insulating layer surrounding the NP (see Section 6.3) and cause a short in the device. In some experiments, mechanical drift during the initial stage of cantilever approach resulted in NPs being knocked off their position on the sample, and in rare cases in them remaining attached to the cantilever (Figure 6.5b).

Since replacing a cantilever implies removing the setup from the microscope, disassembling the holding arm, and repositioning a new cantilever on top of the sample, damage of the coating by mechanical drift became the major bottleneck in repeating experiments with many samples. The main causes of drift were identified in the large size of the cantilever translation stages, and in the length and material of the plastic



Fig. 6.6 Side view of cantilever contacting setup. The cantilever is attached to a metallic arm, mounted through an adapter onto the x-y-z and rotation stages for positioning. The sample is placed on a separate manual rotation stage, and is imaged from the top using a microscope objective.

adapter supporting the holding arm. Additionally, using manual actuators for *x* and *y* positioning requires lifting the cantilever to a safe distance away from the surface whenever repositioning is needed, to avoid destructive vibrations when operating the actuators by hand. These problems were addressed in the final design of the setup, by replacing all ball bearing stages and their actuators with miniature piezoelectric scanners controlled electronically.

6.2.3 Final design

The final setup design (Figure 6.6) employs a set of low-profile SmarAct SLC-17 series stick-slip piezoelectric stages for *x*-*y*-*z* cantilever positioning, and a SmarAct SR-2812 stick-slip rotation stage for control of rotation around the cantilever axis. The AFM chip with the cantilever is attached with conductive silver glue to a 40mm long brass arm, in turn mounted on a brass adapter fixed onto the rotation stage, designed to ensure cantilever rotation is coaxial with the axis of the stage. An additional adapter plate is inserted between the rotation and *z* translation stages, to tilt the cantilever by 5° with respect to the sample surface and allow gradual contacting by controlling the *z* position.



Fig. 6.7 Control of cantilever position. **a**, Cantilever and electrode bias scheme, and wedge fringes upon first contact with the surface, **b**, intermediate position, and **c**, cantilever completely flat. **d**, Angled fringes for 1° cantilever tilt.

The $100 \times$ microscope objective can be used without touching the brass arm only when the cantilever is within a few hundred μ m from the sample, which can be monitored with lower magnification objectives that have longer working distances. The setup is robust to mechanical vibrations and shows no drift even in measurements lasting tens of minutes.

As the cantilever is lowered along the *z* direction onto a flat reflective sample, dense wedge interference fringes appear upon first contact with the surface, that can be used to infer the vertical distance from the sample. Fringe spacing progressively increases with further approach, until disappearing when the cantilever is flat and parallel to the surface (Figure 6.7a-c). Vertical displacement of <100nm can be monitored from the position and spacing of the fringes. Any axial tilt of the cantilever is also detected from the angle of the fringes (Figure 6.7d) and can be corrected to <0.2°. Reliable electrical measurements and spectroscopy on AuNPs are only possible when the cantilever is completely flat and parallel to the surface with no tilt. Positioning resolution of the *x*-*y*-*z* stages is a few nm, and <0.01° for the rotation stage, so instrument precision is not a limiting factor in cantilever positioning.

6.3 Fabrication of isolated NPoM junctions

Even with precise positioning, the 35μ m wide and 200μ m long cantilever is approximately 10^3 - 10^4 times larger than a single AuNP. Directly approaching an AuNP on a flat conductive surface inevitably creates areas of contact between the cantilever and the surface itself, shorting the circuit, so any applied voltage bypasses the AuNP molecular junction and current flows through the Au-Au cantilever-sample interface. The electrode





Fig. 6.8 Au pattern. **a**, Pattern of Au stripes as bottom electrodes after shadow mask evaporation through a TEM grid. Scale bar is 500μ m. b, A single Au stripe (electrode) is contacted with a probe and approached with the cantilever.

area surrounding the AuNP must therefore be protected with an insulating layer, while exposing the top of the NP for contacting with the cantilever.

The overall structure of the modified NPoM geometry used here is shown in Figure 6.1. Fabrication starts with deposition of the bottom electrode (mirror) as a pattern of 10nm-Cr/100nm-Au stripes of width 30μ m, evaporated onto a SiO₂ substrate via shadow mask evaporation (Figure 6.8) through a parallel-bar TEM grid (Agar Scientific). Using a shadow mask and avoiding lithography for this step maintains a clean surface free from photoresist or organic solvent contamination, and allows faster processing.

Next the molecular monolayer is assembled onto the patterned Au electrodes. The sample is immersed in a 1mM ethanol solution of the molecule of choice, and left to soak overnight. After SAM deposition, the sample is rinsed with ethanol and blow dried with N₂. AuNPs with 100 nm diameter (BBI Solutions) are then deposited onto the surface by simple drop casting, where a droplet of NP solution is placed onto the sample and rinsed away after a certain time. The exact position of AuNPs on the sample cannot be controlled, but the average density can be adjusted by changing the NP concentration in the cast solution and the deposition time. Correct AuNP density on the surface is critical to produce single particle junctions, while accommodating many devices on each sample. This is achieved by diluting the stock AuNP solution 1:5 by volume in DI water, and rinsing off the cast droplet immediately by dipping the sample in DI water, before finally washing with DI water and blow drying with N₂. Deposition rate of AuNPs varies for different SAM molecular species, and deposition time is adjusted accordingly. The 100 nm diameter is chosen because it still retains the plasmonic properties of smaller

particles (single NP and coupled NPoM scattering modes), while being easier to image and contact electrically. With a typical facet size of ≈ 20 nm, the NPoM gap contains a few hundred molecules, with about 100 within the 7 nm wide NPoM plasmonic hot spot (see Section 2.5). The number of contacted molecules in the junction can be scaled by changing the AuNP diameter.

Parylene-C (poly-para-xylylene) is used as an insulating barrier to prevent contact between the cantilever surface and the bottom electrode, so molecular junctions are only produced through the AuNPs. Parylene is a common polymer coating in the electronics industry [147], chosen here for the conformal coating properties and room temperature processing, preserving the SAM. The polymer is deposited from vapour phase with dedicated equipment (SCS Labcoter 2), starting from [2.2]paracyclophane dimer in granular form, that is vaporised and broken down into monomers by pyrolysis [148] in a furnace. The monomer molecules enter the deposition chamber in gas phase, and polymerise on the sample surface forming a solid, conformal, and uniform film. Raman spectroscopy is performed on the NPoM structures before and after deposition, and the signature of the molecular monolayer is preserved during the process with no evidence of parylene penetration in the NPoM gap.

To achieve the insulating layer only around, and not on top of the AuNPs, a 350nm thick parylene film is first deposited on the entire sample. Even though deposition is conformal, since the film is over three times thicker than the particle diameter this gives a near-smooth profile above the AuNPs, with a 400-500nm wide parylene dome whose height is 20-30nm (Figure 6.9a,b). The film is then isotropically dry etched in steps with O_2 plasma until the AuNP crown is exposed, leaving a 30nm thick parylene layer on the surrounding area of the electrode (Figure 6.9c,d). Each etching step is monitored with atomic force microscopy to achieve the correct device structure. Parylene has a dielectric strength between 0.2 and 0.3V/nm [149], so breakdown of the insulating layer around NPs can be expected only above 6V for a 30nm thick film. This voltage is never exceeded in any of the measurements, and molecular conduction properties are typically measured at |V| < 2V.

The stripe pattern of the bottom Au (Figure 6.8a) is used to reduce the electrode overlap area when creating a cross junction upon approach with the transparent cantilever from the perpendicular direction (Figure 6.8b). Since the cantilever is tilted with respect to the sample surface, the parylene layer can be scratched by the cantilever front edge



Fig. 6.9 Deposition and etching of parylene coating | **a**, AFM topography image of an AuNP coated with a thick parylene film with **b**, wide dome profile on top of the NP along dashed line in a. **c**, Surface topography after etching with **d**, profile showing exposed AuNP protruding outside of the residual parylene dome. a-d are taken on a test sample with ≈ 200 nm particle diameter.

during its lowering. The stripe pattern allows this to occur on the insulating SiO_2 region of the sample, thus preventing short circuits in the electrode area.

6.4 Setup testing

The cantilever contacting setup and sample design are tested to verify performance with electrical and spectroscopy measurements.

A Keithely 2635A source measure unit (SMU) in four-wire configuration [150] is used for initial testing and all subsequent electrical measurements. The cantilever is wired by attaching a shielded measurement lead to the brass mounting arm. The platform of the SR-2812 rotation stage is electrically isolated from the rest of the positioning system as part of the stage specifications, which separates these metallic components from the measurement circuit.

The ability to electrically contact nanoscale objects with the cantilever is first tested with a lithographically defined Au pattern. A set of Au lines of width ranging from $500\mu m$ to

6.4 Setup testing



Fig. 6.10 Contacting tests on lithographic pattern. **a**, Darkfield image of lithographically defined Au lines for contacting tests, in this image respectively 10, 5, 2, 1 and 0.5 μ m wide from bottom to top. Scale bar in bottom right corner is 100 μ m. **b**, Linear *I-V* response of contacting tests on 50nm and 100nm wide wires.

50nm and height 100nm is defined by e-beam lithography on an insulating SiO₂ substrate and contacted from the top with the cantilever (Figure 6.10a). E-beam lithography is performed by Dr Stefan Tappertzhofen from the Department of Engineering, University of Cambridge. A linear *I-V* response is generally observed as soon as the front edge of the cantilever is in contact with the Au pattern, down to lines of width 50nm (Figure 6.10b), for which a conductance value of $\approx 30G_0 = 2.3$ mS is obtained. This is comparable with the conductance of ≈ 2.2 mS of a rectangular Au ohmic wire that is 50nm wide, 100nm thick, and 100µm long. The calculation suggests that at this scale the 50nm wide Au line pattern is the limiting factor in the conductance. Contacting of a 100nm wide pattern however gives conductance values in the 60-80 G_0 range (Figure 6.10b), and contacting of even wider wires never gives a conductance higher than $\approx 100G_0$, suggesting that $100G_0$ is the conductance limit of the cantilever contacting technique.

In samples with AuNPs, any Au stripe from the pattern in Figure 6.8 can represent the bottom electrode, or mirror, illustrated in Figure 6.1. The chosen electrode is contacted with a sharp tungsten probe, held by a brass clamp connected to the SMU by a shielded wire, and positioned with an x-y-z dovetail manipulator, Figure 6.11. The sample can be independently rotated with respect to the cantilever using a dedicated manual rotation stage, visible in Figure 6.6. This is used for fine adjustment of the angle between cantilever and striped pattern to 90°, to minimise the cantilever-electrode overlap area



Fig. 6.11 Front view of contacted sample. Bottom Au electrodes are contacted with a sharp probe from the left side, while AuNPs are contacted with the transparent cantilever from the front. The sample is held in position with a spring clip at the back. The evaporated pattern shown in Figure 6.8 is located here within the illumination spot of the objective, with a diameter of ≈ 2 mm.

and prevent tilt originating from the edge of the Au pattern. The sample is held in place by an isolated metallic spring clip.

In a typical measurement, the striped electrode pattern is inspected to find an isolated AuNP with a strong darkfield and Raman signal, and the corresponding Au stripe to be used as bottom electrode is electrically contacted with the probe. The transparent cantilever is positioned on top of the AuNP and gradually lowered until contact is achieved, and then imaging, spectroscopy, and electrical measurements are performed. Once all measurements are completed, the cantilever is lifted and moved to another isolated AuNP junction. Several hundred single NP junctions are available to contact in a typical sample.

The electrical conductance of the NPoM structure itself when contacted with the cantilever is measured by preparing a sample with no molecular SAM in the NPoM gap. Electrical measurements of these junctions consistently show a linear ohmic response, Figure 6.12, with conductance $G_{NPoM} = 10^{-3} \text{ S} = 13 G_0$. This is significantly less than the ideal conductance $G_{wire} = 10^3 G_0$ of an Au wire with length 100nm (NP size) and diameter 20nm (NP facet width), assuming that the AuNP itself is the limiting factor in the conductance of the circuit. The reduced conductance could be due to surface roughness on the bottom Au electrode, that can decrease the effective contact region, or small cantilever-AuNP contact area. The measured conductance G_{NPoM} is still 10^5



Fig. 6.12 *I-V* curves of contacted NPoM without SAM. Linear ohmic characteristic of NPoM junctions without molecular SAM contacted with cantilever. Each curve corresponds to a different contacted AuNP, and curves are offset vertically by integer multiples of 3μ A for visibility. Current compliance is set to 9μ A.



Fig. 6.13 Electromigration in cantilever coating.

times larger than the typical conductance of single molecules [151], suggesting that the intrinsic resistance of the NPoM system and contacting method are unlikely to affect measurements of real devices made with molecular SAMs.

A current compliance is set on the Keithley SMU for all electrical measurements, which defines the maximum current allowed through the circuit at any time. If for a set voltage this value would be exceeded, the real output voltage is automatically adjusted by the instrument so the actual current is below the compliance limit. This functionality is essential to measure the electrical properties of molecular layers in the range of 1V and beyond without causing a destructive breakdown of the spacer, since heating effects and electromigration are restricted by the limit on the current.

Setting a current compliance is particularly important in measurements with the cantilever, since the thin conductive coating is very sensitive to high currents. Electromigration (see Section 3.1.2) is readily observed is contacts made with AuNPs as described above when the compliance current is set to 10µA or higher. Figure 6.13a



Fig. 6.14 Spectroscopy through cantilever. **a**, Darkfiled microscope view of an Au nanoparticle on SAM (NPoM geometry) electrically contacted by the conductive transparent cantilever, giving real-time optical access to the junction. Scale bar is 10µm. **b**, Darkfield spectroscopy through the cantilever shows a blueshift in the NPoM coupled-mode peak. **c**, Raman spectroscopy of BPDT molecular layer in NPoM through the cantilever shows molecules are unperturbed. Laser power at sample is 0.2mW, $\lambda = 633$ nm, focussed to sub-µm spot.

shows the start of a test measurement with current compliance of 100µA with multiple AuNPs within the cantilever contact area. When the voltage is increased and the current goes above \approx 10µA (Figure 6.13b), electromigration draws Au from the coating and forms a large metallic cluster in the point of maximum current flow, readily visible by its strong scattering in darkfield. Apart from being destructive for the AuNP junction and compromising spectroscopy, the process damages the conductive coating by removing Au in a circular region around the point of conduction, and leaves additional metallic clusters in the same area (Figure 6.13c). Electromigration in this system occurs in a time scale of \sim 1s, so it is difficult to manually interrupt given the typical integration time of the imaging camera in darkfield (0.2-0.4s).

Testing of darkfield and Raman spectroscopy without voltage is performed on samples with a biphenyl-4,4'-dithiol (BPDT) SAM, which provides uniform gap spacing over large areas [33] and has a strong Raman signature. AuNPs are easily imaged in darkfield through the cantilever (Figure 6.14a). The transparent cantilever does affect the darkfield spectrum of AuNPs, because of the increased refractive index this introduces on top of the NPoM structure. A ≈ 40 nm blueshift in the resonance wavelength of the NPoM coupled mode is consistently observed, together with a slight decrease in intensity of the single particle mode (Figure 6.14b). The coupled mode peak remains clearly distinguishable, but can be affected by tilt or bending of the cantilever along its edges, and this possible artefact must be taken into account during darkfield measurements.
Raman spectra, on the other hand, are largely unaffected by the cantilever, showing no detectable peak shifts and preserving peak intensity, Figure 6.14c.

Chapter 7

Cantilever contacting of molecular junctions

The contacting setup described in Chapter 6 is used to probe molecular junctions fabricated with 100 nm AuNPs in NPoM geometry with a range of different molecules in the junction gap. The sample design presented in Section 6.3 allows to selectively contact an individual AuNP, that represents the top electrode.

Compared to break junction methods discussed in Section 3.4, the AuNP junction is more representative of practical molecular electronic devices, where a molecular SAM is sandwiched between electrodes. In probe break junctions [152, 72], where a tip is used to approach a SAM on a flat surface (Figure 7.1a) and is then retracted, molecule-electrode bonds are repeatedly created and broken, and the electrical response of the junction itself is generally used as the feedback parameter to control probe position. While this allows to create single or few-molecule junctions (Figure 7.1b), it can neglect to show phenomena related to fixed electrode size or cooperative effects due to molecular packing in the SAM. An alternative probe junction structure is provided by liquid metal electrodes [153], such as EGaIn alloys (Figure 7.1c), but these involve a very large number of molecules (>10⁷). Molecular devices can also be created by indirect contacting through nanoparticles using an electrolyte in an electrochemical cell [154], Figure 7.1d, but the electrode area then spans the entire sample and the ions in solution affect the transport properties.

In this work the focus is on probing molecules in an individual sub-100nm wide junction in real time during device operation. Junction morphology and molecular behaviour are tracked in situ with darkfield and Raman spectroscopy, whose signals are enhanced



Fig. 7.1 Schemes for creating molecular junctions. \mathbf{a} , \mathbf{b} , Junctions formed by scanning tunnelling microscope (STM) tip pull-off from (a) SAMs or (b) single molecules. \mathbf{c} , Eutectic GaIn alloy contacts. \mathbf{d} , Large area electrochemical cells indirectly contact AuNPs on SAMs and \mathbf{e} , scheme described in this work using a single plasmonic nanoparticle contact.

and localised within the junction gap by the AuNP plasmon resonance. The molecules contributing to the transport properties of the NPoM device are thus located within the plasmonic hotspot. The experimental data presented here, and in particular the real time optical readout of molecular structure, reveal a nanomechanical rotational degree of freedom that is not normally observed, which could have implications on the transport properties of molecular devices. A simple circuit model is used to interpret the data, suggesting molecular rearrangement is the result of a dynamic energy balance between the steric configuration of molecules and capacitive charging across the junction.

7.1 In situ electrical and optical measurements

The fabrication of molecular junctions based on AuNPs and the technique used to electrically contact them are described in detail in Chapter 6. AuNPs with 100nm diameter are deposited on a molecular SAM on a flat Au electrode to create an NPoM geometry, and are individually contacted from the top using a transparent conductive cantilever (Figure 7.1e). The molecules used to prepare the SAMs are biphenyl-4-thiol (BPT), biphenyl-4,4'-dithiol (BPDT), 4,4'-bis(mercaptomethyl)biphenyl (BMMBP), 4'-mercaptobiphenylcarbonitrile (CN-BPT), and 2-naphthalenethiol (NPT), as discussed in the following sections. All molecules have a thiol terminal group to create a chemical bond with the Au electrodes and form a self-assembled monolayer, without producing molecular layers on the SiO₂ substrate. Biphenyl SAMs, in particular BPDT, are widespread in molecular electronics, and known to form closely-packed uniform SAMs [155]. They also



Fig. 7.2 Raman (SERS) and darkfield switching under bias in single junction with BPDT. **a**,**b**, Real-time SERS for increasingly negative bias voltage. **c**, SERS spectra decrease tenfold by -1V bias. **d**-**f**, Dark-field scattering intensity under bias, with decrease in amplitude and coupled plasmon redshift for |V| > 1 V but (f) no change for -1V bias.

provide large Raman cross-sections, giving consistent SERS, and are thus the molecules of choice for this study.

Each NPoM is optically accessed through the cantilever for imaging and spectroscopy in real time during electrical measurements. The enhanced optical field within the NPoM plasmonic gap enables strong surface enhanced Raman spectroscopy of the molecular spacer (see Section 4.2), giving >100 kcounts/mW/s and thus allowing short integration times for tracking dynamics. Changes in refractive index, thickness or conductivity of the molecular spacer can be tracked in real time through darkfield scattering spectroscopy of the electrically-contacted NPoMs.

For each measurement, the cantilever is lowered until flat and parallel to the surface to make an ohmic contact with an isolated NPoM. Elastic forces from cantilever bending are exerted at the cantilever front edge where the sample is first touched, away from the bottom electrode, thus avoiding AuNP displacement. Electrical measurements are performed simultaneously with continuous Raman or darkfield spectral acquisitions. Voltage is typically applied in a linear ramp (Figure 7.2a,d), with two spectral acquisitions



Fig. 7.3 In-situ darkfield scattering spectroscopy of BPDT junctions. **a**, AuNP is monitored with darkfield spectroscopy in real time (normalised at each time point) while **b**, electrical measurements are recorded on the AuNP molecular junction. Coupled mode amplitude and position are stable for |V| < 1.5 V. Shaded regions indicate a voltage >1V.

for each voltage step, and a 0V step after each voltage increment to highlight V_{on}/V_{off} contrast and account for spectrum variability and signal drift throughout the measurement. Voltage is kept constant during each spectral acquisition, and *I*-*V* data are continuously collected at a rate of ≈ 50 datapoint/s set by the Keithley 2635A SMU, so tens of *I*-*V* data points are collected for each spectrum acquisition.

A reduction in SERS is observed when voltage is applied (Figure 7.2b), with the effect becoming evident at $|V| \approx 0.5$ V and saturating above 1.0 V with over a ten-fold decrease (Figure 7.2c). In darkfield no changes are detected for |V| < 1 V (Figure 7.2d-f). The decrease in SERS by |V| = 0.5 V occurs before any variation in darkfield scattering spectrum (Figure 7.2e), showing cantilever artefacts cannot be responsible. The conductance is <0.1nS for |V| < 1.5 V and remains in the tunnelling regime $G < 10^{-5}G_0$ in that range, rising above the noise only for higher bias (Figure 7.2a,d) where redshifts of the NPoM coupled mode are observed (saturating at $\Delta\lambda \approx 80$ nm). Similar effects are seen with both positive and negative bias.

On an expanded time scale (Figure 7.3), the NPoM coupled mode remains clearly distinguishable throughout the in-situ measurements. No change in the amplitude or position of this peak is observed in the tunnelling regime for |V| < 1.5 V, and voltage can be cycled repeatedly in this range for tens of minutes without detectable spectral



Fig. 7.4 In-situ Raman spectroscopy of BPDT junctions. **a**,**b** In-situ Raman spectroscopy of a single AuNP junction with BPDT molecular layer. **c**, Corresponding voltage (black) and SERS intensity ratio (blue) calculated as SERS(V)/SERS(V = 0) for the 1590 cm⁻¹ ring-ring CC stretching mode. Each data point is the average of consecutive measurements taken at the same voltage. **d**, Ratio of amplitudes for peaks at 1590 cm⁻¹/1140 cm⁻¹, showing that modulation is stronger for the 1590 cm⁻¹ peak corresponding to the inter-ring CC bond.

changes. For |V| > 1.5 V rapid increase in conductance is generally observed (Figure 7.3b) accompanied by a redshift of the coupled mode (Figure 7.3a). The redshift is possibly due to a compression of the molecular layer, that decreases the vertical NPoM gap size changing the coupling between the AuNP and its mirror image (see Section 2.5). This redshift is sometimes irreversible, in which case it suggests a morphological change in the junction structure, possibly a disruption of the molecular layer and formation of metallic conductive links across the junction that increase conductance and short the coupled plasmonic mode. An integration time of 0.5-1s is typical for all darkfield spectroscopy measurements presented here.



Fig. 7.5 *I*-*V* characteristic of AuNP molecular junctions. **a**, Representative *I*-*V* characteristic of an AuNP junction for the case of a BPDT SAM. **b**, Detail of (a) in Fowler-Nordheim coordinates, showing transition from pure tunnelling to field emission around $1/V \approx 1.8 \text{ V}^{-1}$.

The plasmonic enhancement of optical field in the junction gap amplifies light-matter interactions enabling SERS with a typical signal of >10⁵ counts/mW/s for the molecular vibrational signatures, leading to real time spectroscopy with 0.5s typical integration time. Reduction in the Raman intensity for voltages above 0.5 V is consistently observed for BPDT in more than 70% of the single AuNP junctions contacted with the cantilever (Figure 7.4a,b). The remaining cases are accounted for by variations in AuNP size or local imperfections in the parylene insulating layer leading to poor contact with the AuNP crown. In-situ spectroscopic and electrical measurements on a particular junction in the |V| < 1.5 V regime can typically be cycled for tens of minutes before mechanical vibrations of the cantilever cause displacement of the AuNP, that leads to permanent modifications.

A decrease of up to 95% is observed in the SERS intensity for the Raman signal of BPDT for |V| > 1 V (Figure 7.2a,c). The effect is symmetric for positive/negative voltages in most experimental realisations (Figure 7.4a,b). The SERS peak near 1590 cm⁻¹, corresponding to the stretching of the C=C bonds in the rings, shows a stronger modulation than the other peaks in the 1100-1250 cm⁻¹ region (Figure 7.4c,d), meaning that this vibration is more affected by the applied voltage.

A representative *I*-*V* characteristic for a BPDT junction is reported in Figure 7.5a, that shows a low conductance regime for |V| < 2V. This regime is better highlighted in Figure 7.5b in Fowler-Nordheim coordinates, suggesting that the junction operates in a tunnelling regime for V < 0.5V, and transitions to field emission for V > 0.5V. In this field

emission regime the tunnelling barrier for the charge carriers is completely triangular, leading to a rapid increase in current.

For |V| > 2V a sharp jump to the compliance current in generally observed, occasionally preceded by individual spikes reaching the same set current limit. The exact voltage at which this jump is observed varies from one junction to another, being sometimes symmetric and other times asymmetric in voltage, and also depends on the molecule used in preparing the SAM. While no damage to the cantilever and its transparent conductive coating is observed if the compliance current is set to <1µA, these current jumps are often accompanied by strong and irreversible changes in the SERS and darkfield spectra, likely indicating damage in the molecular layer and formation of metallic conductive paths across the junction gap.

7.2 Molecular origin of SERS modulation

Although the light intensity in the NPoM gap does not change, as indicated by constant dark-field spectra, the 20-fold decrease in SERS shows that the molecular Raman cross-sections reduce. Biphenyl molecules have a delocalised π electron distribution [155] due to near-alignment of the π orbitals across the C atoms connecting the two rings, but misalignment of π orbitals across this CC link could disrupt the delocalisation, reducing the molecule polarizability. Modulation of SERS due to twisting between the phenyl rings is reported in [154, 79], but as opposed to the results presented here, an increase in SERS signal is observed when voltage is applied. The effect is attributed to net charging of the molecule: when the molecule is charged the stable steric configuration shifts to smaller inter-ring angles, which favours further electron delocalisation and increases the polarisability, and thus the Raman cross section.

The concept of molecular twisting is explored here through density functional theory (DFT) performed on a BPDT molecule bound to Au atoms at both thiol terminal groups (structure in Figure 7.6). DFT calculations are performed by Dénes Berta from King's College London. The molecule is progressively twisted by changing the dihedral angle θ between the two ring planes from 0° (in-plane) to 90° (rings perpendicular to each other). The energy $U_{DFT}(\theta)$ and Raman signal intensity are computed for each configuration. The calculations reveal that the energy minimum is located at $\theta \approx 35^\circ$, which is then likely the initial molecular state in the junction when no bias is applied. The simulated Raman



Fig. 7.6 DFT structures. BPDT molecule used in DFT calculations anchored at two Au atoms shown at 0° (**a**) and 65° (**b**) twist.

intensity is maximum for $\theta = 0^{\circ}$, since π orbitals are perfectly aligned across the central ring-ring bond, and decreases with increasing twist angle until reaching its minimum at $\theta = 90^{\circ}$, when electron delocalisation is disrupted resulting in low Raman cross-section, Figure 7.7a [156].

DFT calculations predict a small redshift of a few cm⁻¹ as the twist angle between the BPDT rings is increased from 0 to 90° (Figure 7.7a). This shift is not experimentally observed in our measurements nor in previous reports [79, 154], suggesting it is due to inaccuracies in the DFT model at this order. DFT calculations involve a single molecule attached to individual Au atoms, whereas a real device includes extended Au electrodes and close-packed molecules in a SAM, so calculations do not perfectly reproduce the real structure of the junction.

The experimental data reproduce the Raman suppression trend predicted for molecular twisting by DFT, but as a function of increasing voltage (Figure 7.7b) across the junction, suggesting twisting could be linked to the observed decrease in SERS signal. The ratio of calculated amplitudes for the 1590 cm^{-1} peak with respect to the 1100- 1250 cm^{-1} peaks also highlights that the C=C ring bonds are more affected by the twist between rings, and is in agreement with the same trend observed experimentally. This is supported by experiments on 2-naphthalenethiol (NPT, Figure 7.7c and 7.8), which has two rings that are locked in the same plane since they share two carbon atoms, so they are unable to twist like biphenyl molecules. NPT shows no correlation with voltage in the small fluctuations of SERS peak intensity observed for any of the molecular vibrations (Figure 7.8).



Fig. 7.7 Comparison of Raman vs twist θ in theory and experiment. **a**, DFT calculations show decrease in Raman intensity with increasing dihedral angle for BPDT. **b**, Experimental reduction in SERS intensity as voltage increases from 0V to 1V. **c**, SERS intensity reduction quantified as ratio at ± 1.5 V vs 0 V for a range of biphenyl molecules with different functional groups (using Raman peak intensity at 1590 cm⁻¹, 1070 cm⁻¹ for NPT).

Other biphenyl molecules with different functional groups still show SERS switching, but with decreased on/off SERS ratios and larger voltage thresholds when only one thiol group is present, Figure 7.7c.

Conductive AFM and STM break-junction experiments in liquid indicate that the total conductance G_t through biphenyl molecules is controlled by the twist between rings:

$$G_t = G_{CC}(1 + g\cos^2\theta), \qquad (7.1)$$

where $G_{CC} \approx 9 \,\mu\text{S}$ and $10 \leq g \leq 50$ is a scaling factor depending on the measurement method and functional groups of the molecule [151, 157, 158]. Previous models for biphenyl [154] and terphenyl systems considered charging effects [79] that modify the Raman cross-sections. In [154], NPoM structures are gated electrochemically and an increase in Raman signal is observed with increasing bias voltage, attributed to accumulation of charge from the electrolyte at the bottom Au electrode near the AuNP. This charge is claimed to reduce the equilibrium twist angle of the BPDT molecule, boosting the Raman cross section through enhanced electron delocalisation (as discussed for the DFT results above), and also increase AuNP-electrode plasmonic coupling, leading to an amplified field in the NPoM gap. Similarly, in [79] an increase in Raman is reported when voltage is applied across a methylated terphenyl molecule, whose near-90° angle



Fig. 7.8 SERS of 2-naphtalenethiol. **a**, SERS signal from an AuNP junction fabricated with 2-naphtalenethiol. **b**, Corresponding voltage applied across the junction (black) and SERS intensity of the 1070cm⁻¹ peak (blue) calculated as SERS(*V*)/SERS(*V* = 0). Each data point is the average of consecutive measurements taken at the same voltage.

between adjacent rings is sterically favoured by the presence of methyl groups. The voltage is said to cause charging of the molecule, with a net 1+ charge shifting the stable angle to $\approx 50^{\circ}$, thus increasing electron delocalisation and Raman signal. The same is not observed for the non-methylated species, where DFT predicts a negligible effect of molecular charging on molecule geometry.

Although ring twisting mechanisms are central in the reports just mentioned, that provide experimental evidence of Raman modulation by changes in molecular geometry, the molecular charging models cannot explain the results shown here. Specifically, electrical measurements on BPDT SAMs in NPoM geometry in electrochemical environment apply the potential across the gap through an additional electrolyte-NP interface. Extensive studies conducted in this field [159, 160] reported that the electrochemical current-voltage characteristic of NP terminated SAMs is very close to that of clean Au electrodes with no SAM at all, and essentially independent of molecular length, instead of showing an exponentially decreasing tunnelling current with increasing molecular size. This response is explained in terms of different charge transfer rates across the electrolyte-NP-SAM-electrode system [161]: the electron tunnelling rate across the NPoM gap is about 12 orders of magnitude higher than the charge transfer rate between the electrolyte-NP interface. Since this interface is the limiting factor in conduction, the

potential applied experimentally is concentrated near the top of the NP rather than being localised across the gap, and so electrochemical gating does not directly probe the effect of electrical bias on the SAM molecules. In the present work experiments are performed in air at ambient conditions, so no electrolyte is present, and a decrease in SERS signal is observed as opposed to an increase. To explain this observation, a simple model is introduced here based on capacitive charge stored at both ends of the molecule and across the twisting strut in the centre.

7.3 Circuit model of molecular junction

In the proposed model (Figure 7.9a), the molecular junction is divided into three sections: the top and bottom molecule-Au interfaces, characterised by a fixed conductance $G_1 = G_3$ and capacitance $C_1 = C_3$, and the central twisting strut with capacitance C_2 and variable conductance $G_2(\theta)$ according to equation (7.1). The tunnelling current through the molecule sets the total potential drop across the junction, but the voltage is distributed along the molecule according to the conductance of each section:

$$V_i = \frac{G_t}{G_i} V_t$$
 , $G_t(\theta) = \frac{1}{G_1} + \frac{1}{G_2(\theta)} + \frac{1}{G_3}$,

where $G_t(\theta)$ is the total conductance of the molecule. The capacitive energy U_c stored in the junction across the three sections then also depends on the molecular twist angle:

$$U_C(\theta) = \sum_i \frac{1}{2} C_i V_i^2(\theta) \,.$$

It is assumed that end capacitances dominate the twist capacitance, $C_2 \ll C_1 = C_3$, because the Au electrodes provide a much larger effective area for charge storage compared to the molecular backbone. With this assumption, it follows that U_C is reduced as θ is increased, since the potential drop is concentrated across the central molecular section which carries a smaller capacitance.

However since $\theta \approx 35^{\circ}$ at no bias, obtained from the DFT calculations above, energy is required to change the molecular geometry to higher twist angles. The overall energy balance is then $U_t(\theta) = U_C(\theta) + U_{DFT}(\theta)$, with a new equilibrium angle for each voltage, given by the interplay between decreasing capacitive energy and increasing molecular configuration energy with θ . Calculating the total energy U_t as a function of θ shows that



Fig. 7.9 Twist model. **a**, Circuit model for BPDT molecules in the junction gap, with each section 1-3 of the junction characterised by its conductance and capacitance; central CC bond has variable conductance. **b**, Calculated energy profile $U = U_{DFT}(\theta) + U_Q(\theta)$ as voltage is increased, shifting stable angle towards larger twists. **c**, Voltage-dependent twist angle $\theta_{eq}(V)$ from energy model (green) and resulting SERS intensity (at 1590cm⁻¹) from DFT (dashed) compared to experiment (points). **d**, Voltage-induced shift of central CC twist vibration to smaller wavenumbers (arrows). SERS normalised using a T = 320 K thermal ratio between Stokes and anti-Stokes.

the energy minimum shifts from $\theta \approx 35^{\circ}$ at 0V towards $\theta \approx 80-90^{\circ}$ at 1V, Figure 7.9b, thus indicating that rising levels of twist are more energetically favoured as the voltage bias is increased. Beyond 1V U_{DFT} cannot be further reduced, so the stable twist configuration remains at 90°, reproducing the saturation behaviour observed experimentally.

The exact numerical values of model parameters C_i , G_i and g (equation (7.1)) are extracted from previous reports [151], as well as nominal values for bond lengths [162, 163] to fit the experimental and DFT data. The voltage V applied across the junction is an experimental quantity, and the value of θ corresponding to each V can be calculated from the energy model, but also obtained by directly comparing the measured decrease in SERS with the expected decrease from DFT (Figure 7.7). Plotting the resulting curves on the same graph (Figure 7.9c), shows a good match confirming the validity of the proposed model.

To further confirm the molecular twisting, the central CC twist of BPDT is directly observed at low wavenumbers in both Stokes and anti-Stokes SERS (Figure 7.9d). Compared to other Lorentzian SERS lines (<10cm⁻¹ FWHM), the CC twist (peak at $65cm^{-1}$) is a broad Gaussian (100cm⁻¹ FWHM), suggesting each molecule is sensitive to its subtly different molecular environment within the layer. As bias is applied, a $10cm^{-1}$ shift to smaller wavenumbers of this CC twist is observed, in agreement with the 27% reduction in curvature of the full potential $U(\theta)$ at 0.5V in the energy model (Figure 7.9b) that should lead to $\sqrt{0.27} = 15\% = 10cm^{-1}$ reduction in vibrational energy. Adjacent SERS lines corresponding to the S-Au bond stretch show no detectable shift, while the Stokes:antiStokes ratio shows no change in temperature with bias.

Different functional groups at the ends of the biphenyl ring structure affect the conductance of the AuNP junction near the molecule-electrode interfaces, producing different effects in the capacitive-molecular energy balance discussed above. For BPDT the maximum level of modulation is observed, with a symmetric decrease in SERS with voltage as high as 95% (Figure 7.10a). BMMBP shows a modulation of up to 75%, but stronger for negative voltages than for positive ones (Figure 7.10b). Even though the BMMBP molecule itself is also symmetric, the additional bonds at its ends compared to BPDT could introduce variations in the SAM packing during assembly on the substrate or AuNP, causing the observed asymmetry in SERS modulation. Finally, for BPT and CN-BPT a symmetric SERS change is observed of up to 30%, with the modulation occurring only at |V| > 2 V for CN-BPT.

7.4 Single molecule switching

The ≈ 20 nm wide facets of 100nm AuNP nanogaps accommodate hundreds of molecules in a single junction. However an effect explored in the last few years [34] allows single molecule SERS to be tracked in real time in the same nanocavities. Strong enough optical fields in the NPoM gap can transiently pull out atoms from the facet surface, which further enhances light confinement and produces transient SERS lines in addition to the normal Raman signal. Individual Au atoms on Au surfaces are known to transiently



Fig. 7.10 Role of functional groups in SERS modulation. Change in SERS intensity as a function of voltage for a, BPDT, b, BMMBP, c, BPT, and d, CN-BPT.

protrude from the crystal lattice, forming so called *adatoms* [164], that normally do not directly interact with light due to their small scale. Within an NPoM gap however, Au adatoms create an additional level of local near-field enhancement by confining light in a volume <1nm³, called a *picocavity*. This tight localisation creates intense field gradients that induce scattering from Raman-inactive IR vibrational modes, that appear in addition to the SERS signal generated by the surrounding NPoM gap. Picocavities are transient events whose lifetime can be extended by operating at low temperatures and decreasing the laser power used for SERS excitation.

Picocavity events are also detected here, revealing the same SERS intensity modulation on the lines generated by molecular interactions with the Au adatom, Figure 7.11. In particular, the voltage-induced suppression of single molecule SERS matches that of the main molecular SERS peaks (dashed box). This shows that the same voltage-induced twist model applies to single molecule junctions (Figure 7.11b). The SERS signals due to these Au adatoms do not seem to be modulated by varying levels of bias, and generally all observed picocavities show the same type of switching as the main SERS peaks. The typical lifetime of picocavity events detected here is of the order of a few seconds, and their transient Raman lines fluctuate in spectral position as previously reported [**?**].



Fig. 7.11 Single molecule switching from picocavities. **a**, Single molecule switching for BPT showing transient picocavities observed in SERS spectra (dashed box). **b**, Enhanced optical field in vicinity of protruding Au adatom inside nanogap enhances SERS to single molecule level.

7.5 Time scale of molecular switching

The time scale of the molecular twisting mechanism in BPDT is investigated by applying an AC electric signal across the junction and performing fast power modulation of the excitation laser.

The measurement is executed as illustrated in Figure 7.12a. A square wave AC voltage with amplitude V_{high} is applied to the junction, and an acousto optic modulator (AOM, see Section 4.2.3) driven in phase with the AC signal is used to modulate the incident power of the laser used for Raman spectroscopy (laser power \approx 200µW when ON, <1µW when OFF). With this method an integration time of the order of seconds can be maintained for the Raman measurements, while the dynamics of molecular twisting can be investigated down to time scales limited mainly by the performance of the AOM, which can be driven at up to 1MHz.

Raman spectra are collected during a frequency ramp ranging from 1Hz to 1MHz, with an intermediate V = 0 interval between steps, (Figure 7.12b). Preliminary results show that reproducible SERS modulation similar to that recorded for DC experiments is observed up to 1-10kHz. However, for 100kHz and above, the SERS intensity is very close to that observed when V = 0, suggesting that the voltage modulation is faster than the molecular twisting motion. Starting from its equilibrium position of $\theta \approx 35^{\circ}$ at V = 0, the molecule begins to twist when the voltage jumps to $V = V_{high}$, but then the voltage drops before the motion is completed, so the average Raman cross section during this



Fig. 7.12 Modulation of SERS response with AC signal. **a**, Raman excitation is modulated in phase with the AC square wave input applied to the NPoM junction, to explore fast dynamics with long integration times. **b**, SERS modulation with voltage drops off at frequencies \geq 100kHz.

period remains high. It follows that the time scale of the twisting motion is of the order of 10-100µs.

Additional testing and development of the setup with AC signals is required to measure the AC current and exclude effects of junction heating or parasitic capacitances. The reported effect is only observed for $V_{high} > 3V$, which is normally destructive for all junctions in DC bias, but does not appear to compromise the molecular SERS signal in these measurements. Significant power reflection could occur as a result of impedance mismatch between the source and the measurement circuit, and this needs to be investigated before final conclusions can be drawn from the collected data.

7.6 Conclusions

The experimental results presented in this work indicate that molecules trapped in nmsized molecular junctions undergo conformational changes when a voltage is applied. When designing molecular devices, molecules cannot be considered as static components whose behaviour is independent from the junction structure. On the contrary, the model presented here shows that theories of molecular conductance based simply on carrier transmission probabilities are incomplete, and inclusion of junction geometry, local potentials, charges, and steric properties is needed. In the tunnelling regime of junctions presented in this work, the capacitive energy saved by dropping potential across molecular rings yields elastic potential energy to twist a molecular "torsion spring". Compared to conformational changes in molecules in break junctions or in electrochemical environments, the direct contacting of NPoM structures is performed in ambient conditions and without feedback currents passing through the molecule for tip positioning, in a geometry close to realistic device configurations.

The versatile contacting method demonstrated for NPoM could be applied to a wide variety of other nanostructures, such as plasmonic dimers or metasurfaces. Coupling molecular twisting, tunnelling electronic transport, and plasmonics with specifically engineered molecular species may lead to novel nonlinear electronic devices and new modes of light emission.

Chapter 8

Conclusions and outlook

Throughout this thesis, the challenge of creating optically accessible electrical contacts with molecular junctions has been approached from two different directions. The first strategy was to use a graphene layer as a "soft" top contact over an extended area. While this was found to be a viable approach to create junctions with inorganic oxide films, yielding memristive devices with actuating capabilities, the complicated fabrication steps would damage molecular layers when used in the same junction geometry. The second contacting method was based on a conductive transparent cantilever, used to contact single gold nanoparticle junctions, with sufficient stability to perform electrical and spectroscopy measurements, requires precise positioning of the cantilever and careful sample, that can be individually contacted by simply repositioning the cantilever.

The cantilever contacting method in its final design allows to routinely measure molecular junctions in ambient conditions, and thus represents a promising platform for studies of molecular electronics in a realistic device geometry. Real time optical spectroscopy, and in particular surface enhanced Raman spectroscopy enabled by nanoparticles, has proved crucial in revealing the hidden molecular mechanisms that occur in a junction when voltage is applied. In the case of biphenyl molecules studied here, the tendency of a molecular junction to minimise capacitive energy causes a conformational change in the molecule that is readily detected in its Raman signature.

The work of this thesis could be naturally extended in a number of directions, all relating to the measurement of single nanoparticle junctions with the cantilever contacting setup:

- a deeper electrical characterisation of the nanoparticle junction would help to better define conduction through the nanoparticle itself, the precise nature of the cantilever-nanoparticle contact, and the uniformity of the particle-molecule-surface contact. This could be achieved following common characterisation protocols used to inspect new junction geometries, namely the exponential decay of the tunnelling current with increasing molecular length, and the absence of a temperature dependence of the tunnelling regime. The first point could be tested using readily available alkanethiol molecules, while the second point would be more difficult to implement since it requires cooling of the entire contacting setup;
- dependence of junction conductance on nanoparticle size could be used to infer the effective number of molecules actually contributing to conductance. Contacting tests performed on nanoparticles without any molecular layers show that conductance is smaller than that expected for a metallic wire with the geometry of the nanoparticle, suggesting that the effective junction area is smaller, possibly because of surface roughness. If conductance was found to scale with nanoparticle size, roughness effects would be at least partially ruled out, or at least quantified;
- molecules whose optical response can be altered electrically could be placed in a nanoparticle junction to directly observe transitions in real time. Molecules that undergo redox reactions triggered by electron transfer, such as viologens and other electrochromic molecules, should display an immediate modulation of their optical response with applied voltage. The localised nature of nanoparticle on mirror gaps would enable to study fundamental electrochromic processes in situ at the single or few molecule level.

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