

Plasma Enhanced Chemical Vapor Deposition of P-type Cu₂O from Metal Organic Precursors

D. E. Gomersall^{1, a)} and A. J. Flewitt¹

*Department of Engineering, University of Cambridge,
JJ Thompson Avenue, Cambridge, CB3 0FA*

(Dated: 10 May 2022)

The scope of this work was to optimise the reactant delivery parameters for the PECVD of p-type Cu₂O films from Cu(hfac)(tmvs), with the aim to explore an alternative to other large area deposition techniques such as sputtering. Whilst n-type metal oxide semiconductors such as amorphous indium gallium zinc oxide have now been developed and offer significantly improved device performance over hydrogenated amorphous silicon, with devices achieving mobilities $>10\text{ cm}^2(\text{Vs})^{-1}$, there is still an absence of good p-type inorganic semiconductors that provide similar performance. Cu₂O is a promising p-type metal oxide, but there remain limitations on the industrial scalability of some of the deposition processes demonstrated so far. Plasma enhanced chemical vapor deposition (PECVD) has been scaled for uniform deposition on Generation 10 display glass (2.88 m × 3.13 m) and so provides a viable alternative. The Cu₂O films deposited in this work achieved a Hall mobility of $\sim 1\text{ cm}^2(\text{Vs})^{-1}$ and were stable over a period of months. Contrary to previous reports of an 'incubation' period, the initial growth rate during and immediately following nucleation was ($\sim 40\text{ nm/pulse}$) 10 times greater than the steady state growth ($\sim 4\text{ nm/pulse}$) achieved later in the deposition. Topographical scaling methods and fractal analysis of the film surface morphology using atomic force microscopy, at different stages during growth development, link this shift to a regime transition from growth dominated by surface diffusion to volume diffusion.

^{a)} Author to whom correspondence should be addressed: deg28@cam.ac.uk

I. INTRODUCTION

Thin film silicon based technologies remain of importance in large-area electronics and the advance and development of both display and solar cell technology is limited by the low carrier mobilities ($\sim 0.5\text{--}1.0\text{ cm}^2 (\text{Vs})^{-1}$), high optical opacity, poor current-carrying capacity and modest mechanical flexibility of hydrogenated amorphous silicon (a-Si:H) devices or the high processing temperature and/or high cost of polycrystalline silicon (poly-Si) devices.¹ This has led to the development of metal oxide semiconductors such as amorphous indium gallium zinc oxide (a-IGZO),² which has emerged as an alternative to thin film silicon and offers significantly improved device performance or lower cost. However, whilst these n-type metal oxide semiconductors allow the fabrication of high performing TFT devices (high carrier mobilities of $>10\text{ cm}^2 (\text{Vs})^{-1}$, switching ratios exceeding 10^7 and subthreshold swing of 0.2 V dec^{-1}),³ there is still an absence of p-type inorganic thin-film semiconductors that can achieve equivalent device performance, which would be required by both the solar cell industry whose devices are based on a p-n junction, and the display industry who are looking to utilise CMOS logic to reduce their device power consumption. Therefore, the development of a p-type semiconductor that can achieve similar electrical performance is crucial for the further integration of metal oxide thin film semiconductors into the large-area electronic display and solar cell industries.

The inherent material properties of metal oxides have traditionally made this difficult, with most exhibiting poor p-type behaviour due to a valence band maximum (VBM) dominated by anisotropic oxygen 2p orbitals, leading to low hole mobilities and high carrier localisation.^{4,5} However, cuprous oxide (Cu_2O), with a direct band gap of $2.1\text{--}2.6\text{ eV}$,³ has emerged as a promising p-type metal oxide, with p-type behaviour provided by the presence of negatively ionised copper vacancies³. It exhibits less localisation and higher hole mobilities due to a valence band formed of fully occupied and hybridised Cu 3d¹⁰ and O 2p orbitals and a VBM dominated by the Cu 3d antibonding states.⁶ Although Hall mobilities have been reported in the range $10^{-1}\text{--}10^2\text{ cm}^2 (\text{Vs})^{-1}$,^{7–13} it remains a challenge to realise high performing TFT devices, with reported Cu_2O devices exhibiting field effect mobilities of $10^{-4}\text{--}10^1\text{ cm}^2 (\text{Vs})^{-1}$ and on/off current ratios $<10^7$.^{10,12–19} The origin of the low field effect mobilities and high off-state currents for thin film devices has been linked to two mechanisms: the presence of CuO in the grain boundaries of Cu_2O films providing a highly conductive shunting path for the off-state current^{20,21}; and to the ionisation of intrinsic donors, either oxygen vacancies²² or copper interstitials²³ in the grain

boundaries. These grain boundary effects highlight the fundamental difficulties in depositing a material that is metastable at room temperature and readily precipitates into secondary phases, demonstrating that control over the grain boundaries will be fundamental to improving Cu₂O device performance.²¹ Perhaps the Cu₂O TFT devices with one of the highest on/off ratio reported to date, were deposited using pulsed laser deposition (PLD) and achieved a field effect mobility of $4.3 \text{ cm}^2(\text{Vs})^{-1}$ and on/off current ratio of 10^6 .¹⁸ However, current technology leaves PLD unsuitable for large-area applications, whereas plasma enhanced chemical vapor deposition (PECVD), which like PLD provides a high level of stoichiometric control, gives the potential for significantly higher growth rates and high uniformity over very large deposition areas, with Generation 10 display glass ($2.88 \text{ m} \times 3.13 \text{ m}$) being routinely coated by this technique.

This work demonstrates the deposition of Cu₂O from copper(I) hexafluoroacetylacetonate trimethylvinylsilane (Cu(hfac)(tmvs), trade name CupraSelect) using PECVD, with the precursor delivered using pulsed liquid injection. Cu(hfac)(tmvs) is a liquid at room temperature, making it ideal for this type of delivery, as it is not necessary to dissolve it in a carrier solvent, thereby diluting the precursor and introducing additional species into the reaction chamber. There have been previous reports of successful deposition using Cu(hfac)(tmvs), of both phase pure Cu₂O using an atmospheric atomic layer deposition (AALD) system⁹ and copper (rather than copper oxide) films using CVD^{24–29} with a liquid precursor delivery system similar to the system used in this work. However, whilst Cu₂O films and TFT devices have been reported using CVD,⁷ sputtering,^{12–14} ALD^{10,15} (all of which are also suitable for large area deposition), PLD,^{18,19} thermal oxidation¹⁶ and solution-processing,¹⁷ no previous reports of PECVD Cu₂O using Cu(hfac)(tmvs) have been identified. Therefore, the scope of this work is to identify a suitable deposition process to achieve the successful growth of p-type Cu₂O, whilst avoiding the often lengthy ‘incubation’ period reported elsewhere for this particular precursor.^{24–28} To do this, *in-situ* plasma treatment of the substrate surface was employed, immediately prior to deposition and the effect of independently varying the oxygen flow and both the precursor injection pulse width and frequency, which together define the liquid precursor injection pattern, has been explored. In addition, with a focus on producing device quality thin films, this work employs scaling analysis based on surface topographies determined by atomic force microscopy (AFM) to analyse the dominant surface smoothing mechanism and identifies a shift from surface diffusion to volume diffusion as the deposition progresses. This understanding of the varying growth mechanism will allow for further process optimisation, thereby providing precise control over the film morphology and ensuring good

homogeneity throughout the device thickness, something which is essential for thin film devices where the device cannot rely on ‘bulk’ properties to compensate for poor interface properties.

II. EXPERIMENTAL METHOD

The films were deposited using a capacitively coupled PECVD system with separate reaction and load-lock chambers and pulse liquid injection precursor delivery. The precursor is delivered to the process chamber through a showerhead, which acts as the top capacitor plate, with the oxygen delivered separately through a ring source between the substrates and the showerhead. This is shown in Figure 1a.

The precursor is vaporized using a Kemstream Vapbox 300 precursor delivery system, which is designed to vaporize and inject liquid precursors. The Vapbox system consists of a mixing chamber, which mixes the liquid precursor and carrier gas, and a second, separate vaporisation chamber. The liquid precursor is pulse injected into the mixing chamber, where it is mixed with the Ar carrier gas. There is then a second injector which injects this precursor/carrier gas mixture into the heated vaporisation chamber, where the mixture undergoes flash vaporisation, and with both carrier gas and liquid lines held at high pressure (3.5 bar and 4.5 bar respectively) the vaporised mixture is drawn down rapidly into the high vacuum process chamber. The two separate injectors provide precise, independent control of the precursor flow and carrier gas flow, with the injection pattern defined by the pulse width and frequency, and where necessary, the system can be operated in closed loop mode with the flow controlled by mass flow controllers fitted to the precursor and carrier gas lines.

During the deposition optimisation, where the frequency and pulse width of the precursor injection pattern were varied, the Ar flow was set to 150 sccm at an injection frequency of 1 Hz. The Vapbox vaporisation chamber was held at 40°C, with the delivery pipework held at 43°C, and the substrates were heated to 200°C and chamber pressure held at 1.0 mbar, which were both chosen based on work in the literature looking at the effect of substrate temperature and chamber pressure on the ‘incubation time’²⁴ and carbon contamination.^{30,31} During deposition, the plasma was set to 10 W (83 mW/cm²), but during the 5 minute pre-deposition *in-situ* plasma surface treatment, the power was 100 W with an O₂ flow (Ar where relevant) of 100 sccm and pressure of 1.0 mbar. The as-deposited Cu₂O was annealed in vacuum in an Aixtron Cambridge Nanoinstruments Black Magic 2 system under a base pressure of 9.5x10⁻⁴ mbar at 700°C for 10 min, based on work by

PECVD of P-type Cu_2O from Metal Organic Precursors

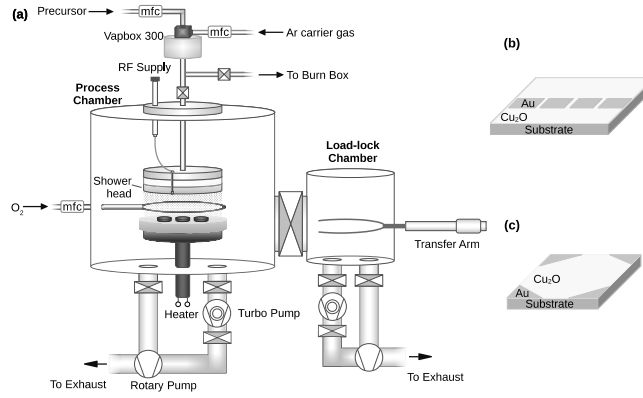


FIG. 1. (a) Schematic showing the PECVD and Vapbox 300 precursor delivery system, and (b) the gap cell and (c) square Au contact configurations used for the electrical characterisation.

Han et al.¹³ The work here presents the material properties and electrical performance for a single deposition (with a range of substrates) at each set of deposition conditions (19 in total), and as such is based on the assumption that the process is highly controllable and reproducible. This assumption is based on consistency across additional depositions that haven't been considered here, for example all the films that delaminated during the annealing process were repeated and behaved in exactly the same way, the 3 s deposition consisting of a single pulse of precursor was completed on six different occasions and produced the same film, and the variation in the growth shown in the SEM analysis was consistent across all the longer depositions.

The XRD data was taken on a Bruker D8 Davinci XRD system in the Bragg Brentano geometry and the AFM images on a 5420 Agilent Technologies AFM in non-contact mode and tip radius of 8 nm; for both, the samples were deposited on glass substrates (Corning 7059). The AFM images were processed (levelled and denoised) using Gwyddion, but the scaling analysis completed using python. The absorption coefficient has been calculated from transmission and reflection data measured using an ATI Unicam UV/Vis spectrometer over a wavelength range of 200–1100 nm, with the films deposited on quartz substrates (Spectrosil B polished windows). For the electrical measurements, Au contacts were evaporated on the Cu_2O films deposited on glass substrates, in either a gap cell configuration (contact width of 4 mm and gap of 0.13 mm) or a square configuration (for the Hall measurement), shown in Figure 1b and 1c respectively. The resistivity was measured over a range of 10 V to –10 V and the magnetic field applied for the Hall measurement was 2000 Gauss. To measure the thermally activated current, a voltage of –1 V was applied and the current measured whilst the substrates were heated on a hot plate from room temperature

up to 100°C. Therefore, assuming an Arrhenius relationship, the activation energy (E_a) and the thermally activated conductivity prefactor (σ_0) could be calculated using:

$$\sigma_D = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad (1)$$

All measurements were taken at ambient temperature and pressure, with all the electrical characterisation completed in the dark to remove photoconductivity and illumination effects. The samples were kept in a dessicator between measurements, where they remained stable over a period of months, which would be satisfactory for the purposes of microfabrication and encapsulation, where the major concern for degradation would be oxidation to CuO.

III. RESULTS AND DISCUSSION

A. Substrate Pretreatment

Several papers depositing Cu from Cu(hfac)(tmvs), have reported the presence of an ‘incubation’ period during thermal CVD processes, whereby the initial growth is inhibited and there is a delay before the film fully nucleates on the substrate surface and blanket growth is achieved.^{24–28} This was clearly demonstrated by Kim et al.,²⁴ (fig. 2) where the length of this incubation period and the dependence on substrate material, substrate temperature, chamber pressure and carrier gas was explored. They reported that the apparent incubation period decreased as the conductivity of the substrate was increased and when the carrier gas was switched from Ar to H₂. This meant that for their SiO₂ (insulating) substrate and argon as the carrier gas, the measured incubation time could be as high as ~40 minutes, which is significant for this work given the aim to develop a process suitable for TFT fabrication, necessitating deposition on insulating substrates. Work looking into the mechanism behind this inhibited growth period, has linked higher initial growth rates (a shorter incubation period) to the density of silanol (O-H) groups on the substrate surface for both Cu(hfac)(tmvs)^{24,32,33} and similar precursors.³⁴ Plasma treatment is regularly used to clean substrates and remove organic contaminants and thereby expose silanol groups on the substrate surface.³⁵

Figure 2 compares the effect of *in-situ* O₂ and Ar plasma pretreatment of the substrate, immediately prior to deposition, in terms of the growth rate and film properties. Firstly, looking at Figure 2a, it can be seen that the growth per pulse, which is calculated by taking the film thickness and dividing by the total number of precursor injections to give an average growth rate per

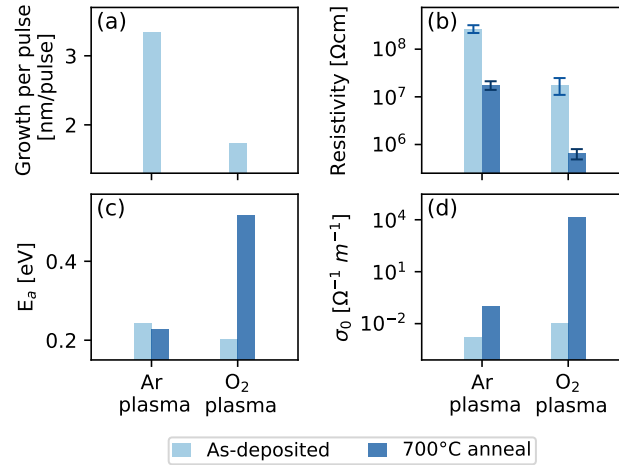


FIG. 2. Comparison of plasma pretreatment both before and after high temperature vacuum annealing, looking at (a) the growth per pulse of precursor, (b) the resistivity, (c) the activation energy (E_a) and (d) the thermally activated conductivity prefactor (σ_0)

pulse, for the substrates pretreated with Ar plasma, is double the rate for the O_2 plasma. This difference in growth rate could be due to a shorter incubation period or to a variation in the growth process, as work elsewhere has shown that when the growth of copper films from $\text{Cu}(\text{hfac})(\text{tmvs})$ is too high, the films grow with a porous microstructure, as vertical growth dominates over lateral growth,^{28,36} leading to overall thicker but less dense films. Secondly looking at Figure 2b, c and d which compare the resistivity, E_a and σ_0 respectively, it can be seen that O_2 plasma improves the conductivity of the film, relative to the Ar plasma, by a factor of 10 and this improvement is extended further after high temperature vacuum annealing at 700°C (a factor of $\sim 10^2$), with the corresponding increase in σ_0 (5 orders of magnitude after annealing) suggesting conduction deeper into the extended states.³⁷ The positive values of E_a , representing an increase in conductivity with increasing temperature, demonstrates clear semiconductor behaviour.

These factors combine to determine that the O_2 plasma provides improved electrical performance and despite a lower growth rate for O_2 than Ar plasma, the average growth of ~ 1.75 nm per 1 ms injection of precursor, still represents rapid film growth compared with other techniques such as ALD. Therefore the use of *in-situ* O_2 plasma immediately prior to deposition has been used throughout the rest of this work. However, it is important to recognise that the role of the plasma density has not been explored here, but is likely to impact the film growth, given the halving in the growth rate, which is a growth parameter reported to effect both the film density and incorporation

of contaminants,^{28,30,31,36} and the factor of 100 increase seen for the films conductivity. Therefore, there is substantial opportunity for this process to be further explored and optimised.

B. Deposition Optimisation

Figure 3 provides a comparison of the growth rate and film properties as the reactant delivery parameters (the oxygen flow, the precursor injection frequency and the precursor injection pulse width) are varied. The films have all undergone post deposition annealing at 700°C to improve the film conductivity. Considering first the oxygen flow, Figure 3a shows there is no significant variation in the growth per pulse as the O₂ flow is increased, with the average growth of 2.25 nm/pulse corresponding to an apparent growth rate of 34 nm/min. This is perhaps to be expected given that the precursor flow rate hasn't changed. However, increasing the O₂ flow rate whilst keeping the chamber pressure constant, simultaneously changes the O₂ partial pressure and precursor partial pressure during deposition, and as both the Ar and precursor flows remain constant, it will also change the residency time of the gases in the deposition chamber (higher inflow at constant pressure, means higher outflow). Given that there is no change, perhaps indicates, as expected for low pressure CVD, that the deposition is surface reaction limited³⁸ and that within this range, the partial pressure of the precursor remains high enough for the surface to be saturated³⁹. Looking at Figure 3b shows that the growth per pulse actually decreases linearly as the frequency increases, representing a decrease in the efficiency of the deposition, which is in contrast to the apparent growth rate, measured in nm/min, which increases linearly with frequency (not shown here). This is consistent with the reports that increasing the pulse frequency led to higher apparent growth rates of Cu from Cu(acac)₂, but a lower growth rate per cycle, and that for higher apparent growth rates there is a greater incorporation of impurities and less control of the film morphology.³⁸ By comparison, Figure 3c shows a very clear linear increase in the thickness and growth per pulse as the pulse width increases. This is to be expected as increasing the pulse width increases the amount of precursor introduced to the deposition chamber each pulse and therefore greater surface coverage of adsorbed precursor molecules, with the linear fit highlighting the precise control of the precursor delivery. However at a pulse width of 2 ms, the film delaminated during annealing, likely due to higher stress incorporated during deposition due to the high deposition rate, which could be further exacerbated by the fact that the annealing temperature is above the annealing temperature of the Corning glass substrates. This damage to the film is the reason for the higher value

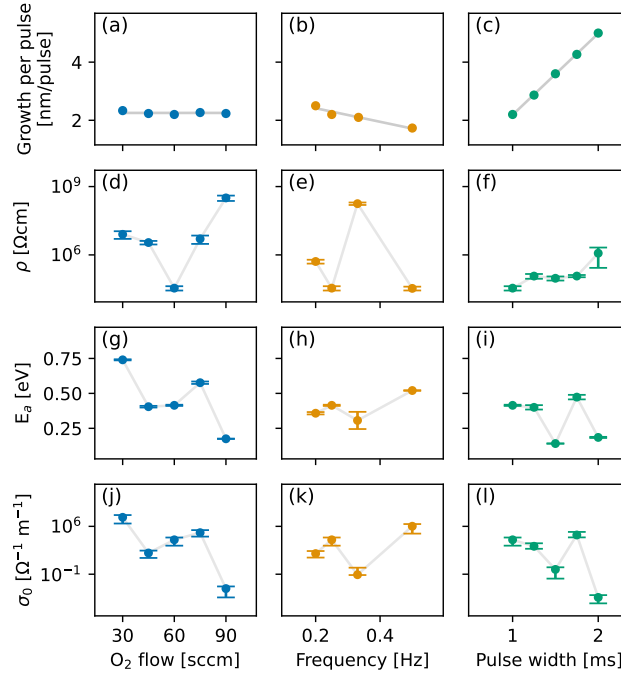


FIG. 3. Comparison of growth and film properties: (a-c) the growth per pulse, (d-f) the resistivity (ρ), (g-i) the activation energy (E_a) and (j-l) the thermally activated conductivity prefactor σ_0 ; for varying oxygen flow (with precursor injection pulse width of 1 ms at 0.25 Hz), injection frequency (with oxygen flow of 60 sccm and 1 ms precursor pulse width) and precursor pulse width (with oxygen flow of 60 sccm and 0.25 Hz injection frequency).

and greater uncertainty seen for the resistivity in Figure 3f.

Now turning to the electrical properties and starting with the variation of the oxygen flow, it can be seen that the resistivity (Figure 3d) drops as the flow is increased from 30 to 60 sccm, where it then increases again as the oxygen flow is increased further to 90 sccm. This suggests that there is some transition in the film composition or morphology. This is supported by the trend seen in Figure 3g and 3j, where there is a step down from 30 to 45 sccm, then both E_a and σ_0 increase with increasing oxygen flow, before stepping down again at 90 sccm, suggesting two transitions, between 30 and 45 sccm and between 75 and 90 sccm. These step changes are reminiscent of the large step changes in resistivity and carrier concentration seen by Meyer et al.,⁴⁰ (fig. 19-20) where sputter deposited films transitioned from Cu_2O , to Cu_4O_3 and finally to CuO as the oxygen flow was varied. Therefore, this could suggest that within the range of oxygen flows here, the film is transitioning from a Cu-rich state to an O-rich state. Keeping an oxygen flow of 60 sccm (due to

the lower resistivity) and looking now at the variation of precursor injection frequency, there again appears to be some transition between 0.25 Hz and 0.333 Hz, seen by the large step up in resistance seen in Figure 3e at 0.333 Hz and corresponding step down in E_a and σ_0 . When looking at the variation of resistivity with pulse width and ignoring the point at a pulse width of 2 ms, Figure 3f, the resistivity is fairly constant at $\sim 10^5 \Omega\text{cm}$. However, when looking at the variation in E_a and σ_0 (Figure 3i and 3l) there is a significant drop in both E_a and σ_0 at a pulse width of 1.5 ms. It is important to note here that the activation energy represents the energy required to excite a carrier to a higher state and σ_0 represents the inherent conductivity of the state it is excited into.³⁷ Therefore, an increase in σ_0 indicates that activated carriers are being excited further into the extended states where conduction is less localised, and the linear relationship between E_a and σ_0 , shown by the similar trend for values of E_a in Figure 3g-i and for values of σ_0 in Figure 3j-l, indicates that higher activation energies consistently result in more extended type conduction, across the variation in all three reactant delivery parameters. Finally, due to the high growth rates and therefore film thickness for the film deposited with a pulse width of 1.75 ms (O_2 flow of 60 sccm and injection frequency of 0.25 Hz), a valid Hall measurement was achieved, giving p-type behaviour with a Hall mobility of $1.48 \text{ cm}^2(\text{Vs})^{-1}$, resistivity of $1.92 \times 10^5 \Omega\text{cm}$ and carrier density of $3.09 \times 10^{13} \text{ cm}^{-3}$. Although, the measured resistivity is still quite high to be suitable for TFT fabrication and the carrier concentration at the lower end of reported values (see Table I for a comparison), a Hall mobility of $1.48 \text{ cm}^2(\text{Vs})^{-1}$ with p-type conduction, although also quite low, is very promising and suggests that with further process optimisation, it will be possible to deposit optimised films more suited to TFT devices.

Figure 4 shows XRD patterns for a selection of the deposited films, comparing a) annealed films deposited with varying reactant delivery parameters and b) the as-deposited and annealed film deposited at 60 sccm of O_2 , and precursor delivery at 0.25 Hz and 1.75 ms pulse width. Starting with Figure 4a it can be seen that the pattern for the film deposited with 30 sccm of O_2 shows a strong peak matching Cu(111) and a smaller peak at Cu(200), suggesting that the O_2 flow is too low. This is supported by the absence of these two peaks as the O_2 flow is increased to 60 sccm and 90 sccm, where instead there are possibly very small broad peaks at the Cu₂O (111) and (200) orientations, which fits with the transition in electrical properties seen in Figure 3. These broad peaks become clearer as both the pulse width is increased to 1.75 ms and the frequency is increased to 0.5 Hz (shown in the bottom two patterns of 4a), for which a higher delivery rate of the precursor resulted in thicker films for the same deposition length of 600 s. Using Scherrer's

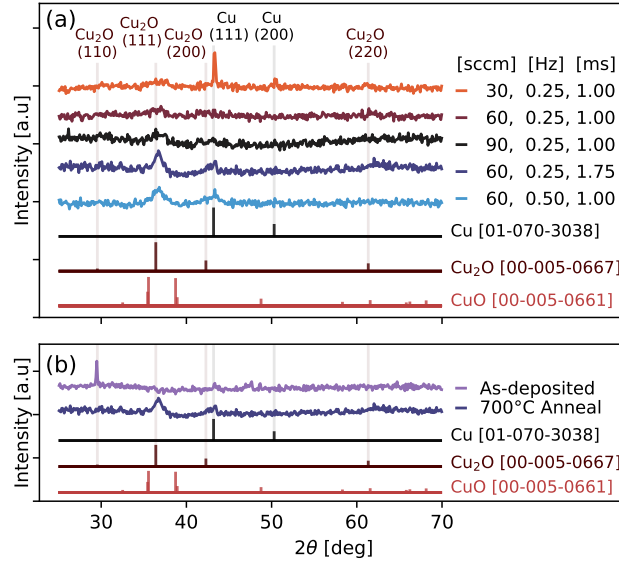


FIG. 4. XRD pattern comparison: (a) annealed films at varying oxygen flow [sccm], precursor delivery frequency [Hz] and pulse width [ms]; and (b) film deposited at 60 sccm of Oxygen, and precursor delivery of 0.25 Hz and 1.75 ms, both before and after annealing. Reference peaks: Cu_2O [JCPDS 00-005-0667]; Cu [JCPDS 01-070-3038]; CuO [JCPDS 00-005-0661].

formula⁴¹ to calculate the crystallite size for the bottom two patterns of Figure 4a, where the peaks are clearest, gave values of 8.1 nm and 4.3 nm for the film deposited at 1.75 ms and 0.5 Hz respectively, showing a nanocrystalline film. The pattern for the film deposited with a pulse width of 1.75 ms is repeated in Figure 4b and compared to the as-deposited film. Interestingly, it can be seen that the peaks shift from a sharp peak at Cu_2O (110) to the two broader peaks seen at the Cu_2O (111) and (200) orientations after high temperature vacuum annealing. This suggests that some further optimisation of the annealing process should be explored, to see if it is possible to improve the electrical performance, whilst still retaining the original crystal orientation.

Figure 5 shows the extraction of the direct optical bandgap (E_g) from a Tauc plot of $(\alpha h\nu)^2$ against $h\nu$, for the annealed films deposited with varying (a) oxygen flow, (b) precursor injection frequency and (c) precursor injection pulse width. The extracted values of E_g are all in the range 2.53 – 2.59 eV, which is consistent with reported values for thin Cu_2O films^{9,42–44} and thus lending validity to the interpretation of the broad peaks seen in the XRD patterns of Figure 4.

Given the promising electrical characterisation and Hall measurements for the film deposited with an O_2 flow of 60 sccm and injector pulse width and frequency of 1.75 ms and 0.25 Hz, these

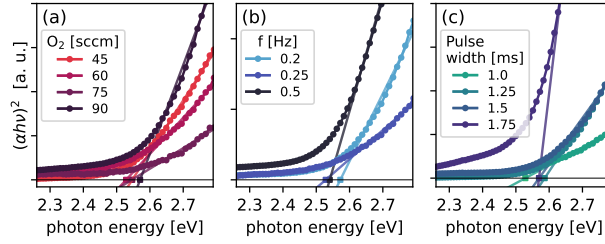


FIG. 5. Tauc plots showing the extraction of the direct optical band gap for films deposited on quartz substrates and vacuum annealed at 700°C , for varying a) oxygen flow rate, b) precursor injection frequency and c) precursor injection pulse width.

deposition parameters were taken forward for the growth analysis discussed in the next section.

C. Growth Analysis

In order to aid material characterisation, the deposition time to this point was kept at 600 s, resulting in a minimum film thickness of ~ 300 nm. However, this is far greater than the < 50 nm required for thin film devices and therefore this section looks at the effect of reducing the deposition length from 600 s down to a single injection of precursor.

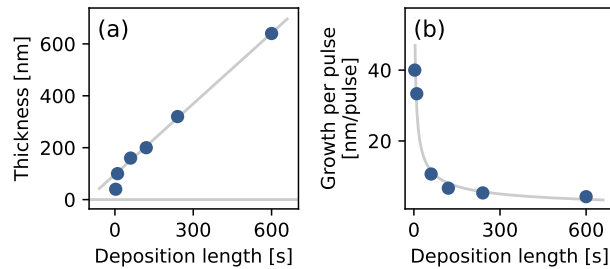


FIG. 6. Evolution of (a) the film thickness and (b) the growth per pulse with time.

Figure 6 shows a) the evolution of film thickness with time and b) the variation of the growth per pulse as the deposition length increases. Figure 6a shows that for the longer depositions, steady state growth is reached, with the thickness showing a linear trend (grey line). However, this trend would give zero thickness at negative time and therefore, the initial growth is significantly higher. This is shown more clearly in Figure 6b, which shows that the growth per pulse for the 3 s deposition, which consisted of a single pulse, is 10 times higher than for the 600 s deposition.

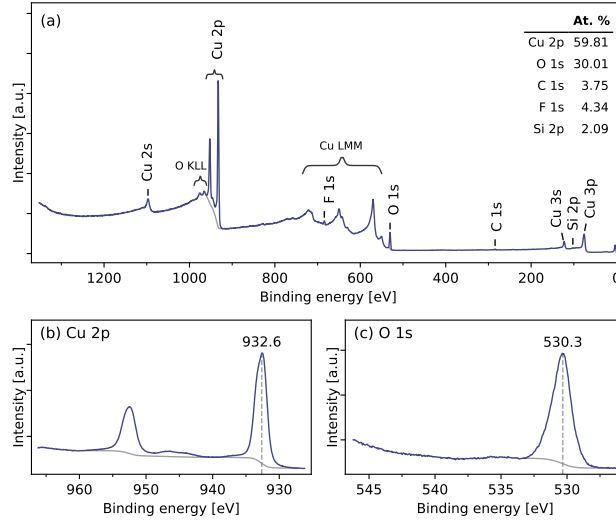


FIG. 7. XPS of 3 s deposition after vacuum annealing: (a) wide scan; (b) Cu 2p scan showing the Cu $2p_{3/2}$ peak at 932.6 eV and the smaller Cu $2p_{1/2}$ peak; and (c) O 1s peak at 530.3 eV.

After the initial high growth of 40 nm/pulse, the growth drops off and settles to a steady growth rate; as the growth per pulse is calculated by dividing the thickness at the end of each deposition by the total number of pulses, it provides an average over the deposition and will therefore be distorted by the initially high growth. This means that in reality the growth per pulse must drop off even faster than Figure 6b shows. Section III A discusses the sensitivity of the growth reaction to the state of the substrate surface. However, as the film grows and the substrate is covered, it would follow that the growth reaction would be equally sensitive to the state of the film surface. The exceptionally high growth rate for the very first injection of precursor shows that the efforts to remove the incubation period reported elsewhere in the literature have been successful. However, given TFTs will normally have a thickness of 5-30 nm, meaning the initial growth will set the performance of the device, it also demonstrates how important the substrate surface state is for the fabrication of working devices.

With that in mind, Figure 7 shows XPS of the film deposited for 3 s, to explore the film stoichiometry and contamination. The measurement has been taken for the annealed film after a 30 s etch to remove surface contamination. It can be seen that C, F and Si have been incorporated into the film from the $\text{Cu}(\text{hfac})(\text{TMVS})$ precursor, but all at < 5 At. %. The Cu 2p scan, in Figure 7b, shows the Cu $2p_{3/2}$ at 932.6 eV and the O 1s scan in Figure 7c, shows a peak at 530.3 eV. This is consistent with the deposition of Cu_2O with peaks at 932.4 eV and 520.2 eV observed by

Ghijsen et al.⁴⁵ and 932.5 eV and 530.3 eV observed by Sung et al.⁴⁶, for the Cu 2p_{3/2} and O 1s respectively.

D. AFM and Scaling Analysis

AFM provides a method to analyse the surface of the growing film and Figure 8 shows AFM images for the films deposited for varying lengths of time. The color scale shows the variation in surface height relative to the mean height averaged over the whole surface. Figure 8a shows a clear difference in appearance, with much less variation in height than the longer depositions, with Figure 8b and 8c looking fairly similar and then by visual inspection, there is a step change in the appearance of the film surface on the second row of images (deposition length ≥ 120 s). Given the crystallite size of 8.1 nm calculated for the film shown in figure 8f, after annealing, and the fact that the AFM tip radius was 8 nm, it is important to note that the ‘particles’ seen in the AFM image are unlikely to be individual crystallites, but larger surface morphology features determined by the growth and smoothing mechanisms present.

To quantify the differences seen in Figure 8, the RMS roughness (δ), which defines the vertical variation across the surface, and the lateral correlation length (σ), which provides a measure of the length of in-plane features, were estimated from the autocovariance function of each AFM image, averaged and binned radially, over the radius (r), to give a 1-dimensional profile. Although both δ and σ provide a quantitative comparison of the film surface, they provide only a snapshot of the surface state at a specific time and do not, by themselves, provide any insight to differences in the growth mechanism. However, it turns out that these quantities scale with time, allowing the use of topographical scaling methods and fractal geometry to explore the film development and growth mechanism.⁴⁷

Fractal geometry provides a way of describing the scaling as either self-similar or self-affine. An object can be described as self-similar if $H(r)$ scales as $kH(kr)$, where k is a constant. The scaled object can then be considered either a deterministic fractal, for which the scaled object overlaps the original exactly, or a statistical fractal (also called random fractal), where inherent randomness makes the objects self-similar in a purely statistical sense.⁴⁸ Similarly, self-affine fractals allow for anisotropic scaling such that $H(r)$ scales as $k^\alpha H(kr)$. Of course for the special case where $\alpha = 1$, the system becomes self-similar, meaning self-affinity is just a more general case of self-similarity. Assuming the surface of growing films to be statistically self-affine, Family and Viscek, showed

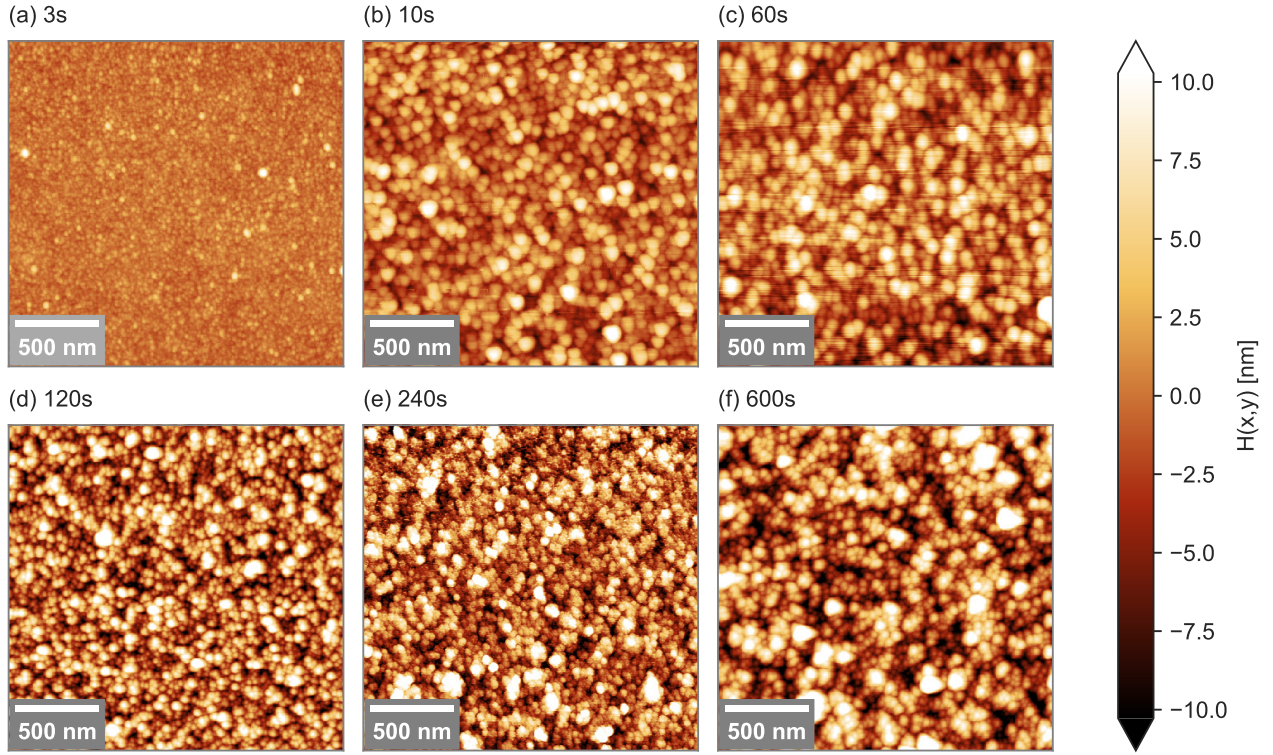


FIG. 8. AFM images of the as-deposited film surface (a-f) as the deposition length is increased from 3 s to 600 s.

that the surface roughness scales as:

$$\delta(L, t) \approx L^\alpha f\left(\frac{t}{L^\beta}\right) \quad (2)$$

where t is time, L is the length-scale of the measurement, α and β are the spatial and temporal scaling exponents and the function f is given by:^{47,49,50}

$$f(x) \sim \begin{cases} t^\beta & \text{for } x \ll 1 \\ \text{constant} & \text{for } x \gg 1 \end{cases} \quad (3)$$

Typically the variation of δ with time consists of two regimes.^{48,50} Initially, at small t , the roughness will increase with time as t^β . At some characteristic time (t_c), δ saturates and becomes time invariant, at which point the length over which fluctuations are correlated (σ) becomes comparable to L (i.e. $\sigma = L$ for $t \gg t_c$).⁵⁰ However if L is increased, the saturated value of δ is expected to

scale as $\delta(L, t \rightarrow \infty) \approx L^\alpha$.⁵⁰ Therefore, δ scales as:

$$\delta(L, t) \sim \begin{cases} t^\beta & \text{for } t \ll t_c \\ L^\alpha & \text{for } t \gg t_c \end{cases} \quad (4)$$

Suggesting that from Equation 2, t_c scales with L as:⁵⁰

$$t_c \sim L^{\frac{\alpha}{\beta}} \quad (5)$$

At the characteristic time (t_c), $\sigma = L$, hence substituting for L in Equation 5 gives $\sigma = t_c^{\frac{1}{z}}$ where $z = \frac{\alpha}{\beta}$ and it can be shown that this relationship also holds for $t < t_c$.⁴⁸ Therefore:

$$\sigma(L, t) \sim \begin{cases} t^{\frac{1}{z}} & \text{for } t \ll t_c \\ L & \text{for } t \gg t_c \end{cases} \quad (6)$$

Finally, combining Equation 4 and 6 gives the following relationship for σ and δ :

$$\sigma \sim t^{\frac{1}{z}} = t^{\frac{\beta}{\alpha}} = \delta^{\frac{1}{\alpha}} \quad \text{for } t \ll t_c \quad (7)$$

The variation of δ and σ with deposition length is plotted in Figure 9 allowing the extraction of a) the temporal scaling exponent, β , b) the dynamic scaling exponent, z , and c) the spatial scaling exponent, α . It should be noted that β is often extracted from the gradient of δ against film thickness. However, as the film thickness does not scale linearly with time at short deposition lengths, it was important in this case to plot δ against time instead.

At first glance, Figure 9a showing the evolution of δ with time, looks as expected with an initial increase with time until a deposition time of about 120 s, before the curve flattens off and appears to saturate. However, Figure 9b showing the evolution of σ , clearly demonstrates two separate regimes, with the transition occurring between a deposition time of 60 and 120 s and has not yet reached the saturation regime. Therefore, rather than δ saturating, it has also entered a new scaling regime. The existence of these two regimes of growth is consistent with the order of magnitude change in growth rate measured as the deposition progresses. Therefore two distinct values of β and z have been extracted for these two regimes by fitting a straight line, the values of which are shown in the legend. The presence of these two regimes is perhaps more clearly shown in Figure 9c. It can be seen that initially during the deposition (<120 s), $\alpha = 1$, which means the crystals on the film surface are growing vertically at the same rate as laterally along the surface. However, as

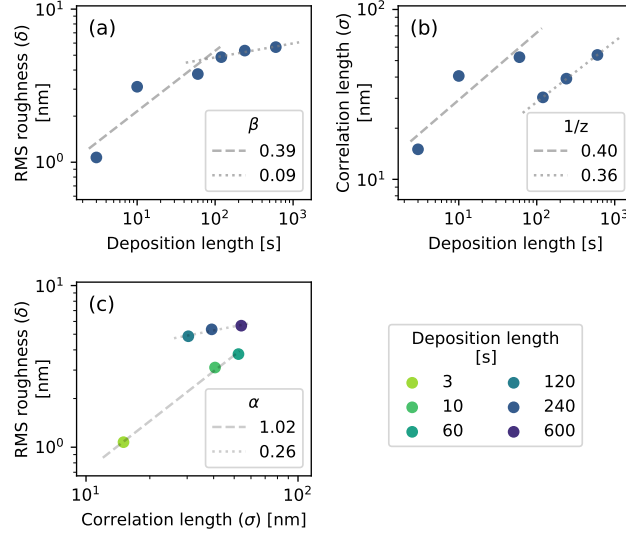


FIG. 9. Evolution of (a) the RMS roughness, δ , and (b) the lateral correlation length, σ with time, and (c) the scaling relationship between σ and δ . The dashed and dotted lines show linear fits for two distinct scaling regimes, allowing the extraction of the temporal scaling exponent (β), the dynamic scaling exponent (z) and the spatial scaling exponent (α).

the deposition progresses, α reduces to 0.26, meaning that later during the deposition, the crystals are scaling laterally along the film surface at a greater rate than the vertical growth.

This scaling nature of growing self-affine films is determined by the balance between competing roughening and smoothing mechanisms.⁴⁷ Deposition of thin films has an inherent randomness associated with the stochastic nature of the deposition flux on the surface; if there were no additional smoothing or roughening mechanisms, the surface will grow under the mechanism of stochastic roughening and will have a β value of $1/2$ and α of 0, as growth is completely random and therefore there is no correlation along the surface.⁴⁸ If additional smoothing mechanisms are introduced, the values of α and β will change, therefore α and β provide a fingerprint of the dominant smoothing mechanisms that control the surface state. Four of these smoothing mechanisms that oppose stochastic roughening were considered in 1950 by Herring,⁵¹ who analysed the scaling processes of sintering. By considering the size of two “clusters” of particles given by radii R_1 and R_2 respectively, where $R_1 = \lambda R_2$, the analysis described, for each mechanism, the relationship between the time Δt_1 , required to produce a change in R_1 and the time Δt_2 required to produce the same change in R_2 as:

$$\Delta t_2 = \lambda^i \Delta t_1 \quad (8)$$

where i takes an integer value depending on the dominant smoothing mechanism.⁵¹

The four smoothing mechanisms considered were: **Viscous flow** ($i=1$) or creep of an amorphous material which is driven by higher surface tension under a convex surface than under a concave surface, thus driving material from convex to concave regions; **Evaporation and condensation** ($i=2$) driven by the higher vapour pressure over a convex surface than a concave surface; **Volume diffusion** ($i=3$) or bulk diffusion of material driven by a local gradient in the chemical potential; **Surface diffusion** ($i=4$) or surface migration of material driven by a gradient in the chemical potential within the surface plane.^{51,52} For the case where stochastic roughening dominates the surface morphology, $i = 0$.

In 1959, the relationship in Equation 8 was shown by Mullins⁵³ to be most easily analysed in Fourier space, using:

$$\frac{\partial h(|\mathbf{q}|, t)}{\partial t} \propto -|\mathbf{q}|^i h(|\mathbf{q}|, t) \quad (9)$$

where

$$h(|\mathbf{q}|) = \mathcal{F}\{H(\mathbf{r})\} \quad (10)$$

and i is the same exponent given by Herring in Equation 8.

By combining Equation 9 with a noise term to represent the stochastic roughening mechanism and solving analytically gives:⁴⁷

$$g(|\mathbf{q}|, t) = \Omega \frac{1 - \exp(-2c_n |\mathbf{q}|^i t)}{c_n |\mathbf{q}|^i} \quad (11)$$

where $g(|\mathbf{q}|, t)$ is the radially averaged power spectrum density (PSD), calculated from the Fourier transform of the AFM images.

Therefore for large q , it can be seen that the PSD approaches

$$g(|\mathbf{q}|, t) \propto \frac{1}{|\mathbf{q}|^i} \quad (12)$$

and that by plotting $\log\{g(|\mathbf{q}|)\}$ against $\log\{|\mathbf{q}|\}$ will produce a straight line for large q , of gradient $-i$, where i is the Herring exponent identifying the dominant smoothing mechanism.⁵²

From this and using an approximation for $g(|\mathbf{q}|)$ in terms of α , Tong and Williams⁴⁷ showed that i could be related to α with the following:

$$i = 2(\alpha + 1) \quad (13)$$

Figure 10 shows the PSD, averaged and binned radially, as the deposition length increases, which provides information about the dominant smoothing mechanism during the film growth. The size

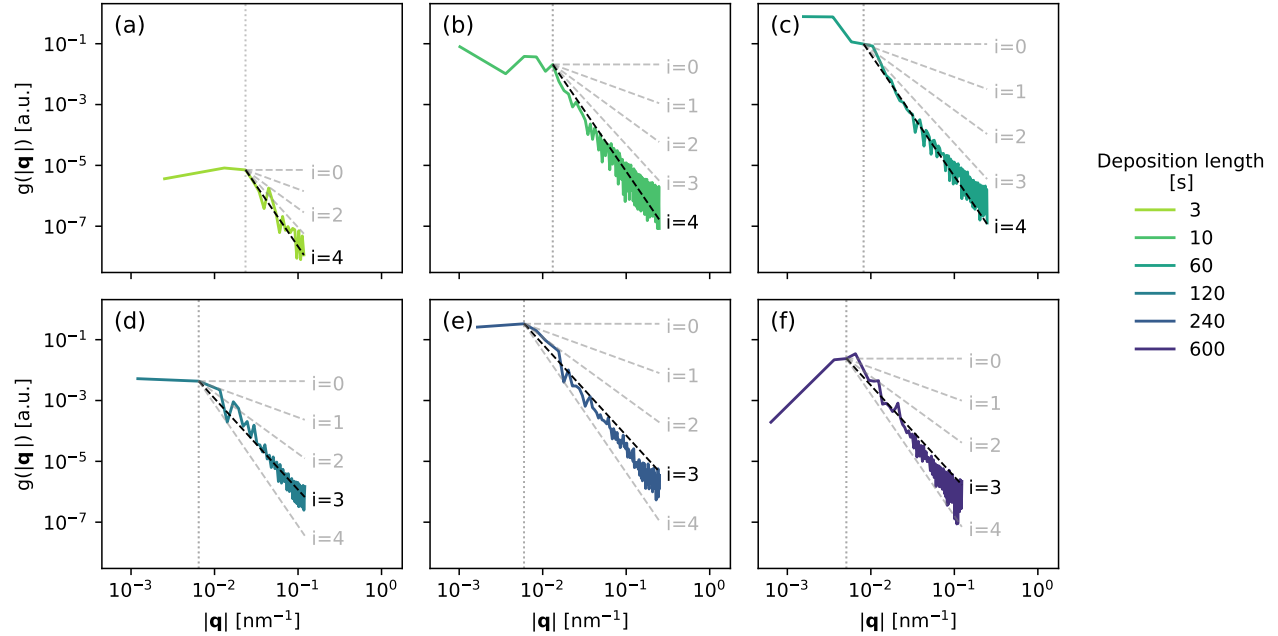


FIG. 10. Radially averaged power spectrum density of the AFM images (a-f) as the deposition length is increased from 3 s to 600 s. Straight line fits for the 4 theoretical smoothing mechanism are provided as a guide (dashed grey lines), with the best fit highlighted in black.

of the image used has been chosen to ensure that the x- and y- dimensions are larger than the lateral correlation length calculated from each corresponding AFM image, but that the majority of the data is at a large enough q to approach the straight line fit given in Equation 12. Rather than fit a straight line using a linear regression, lines representing each of the different smoothing mechanisms ($i = 0, 1, 2, 3, 4$) have been plotted in as a guide (dashed lines), with the best fit highlighted in black. As with Figure 9c, there appear to be two regimes, with the dominant smoothing mechanism transitioning from surface diffusion ($i = 4$) to volume diffusion ($i = 3$). Using Equation 13 ($i = 2(\alpha + 1)$), gives α equals 1 for surface diffusion and 0.5 for volume diffusion. The value of $\alpha = 1$ exactly matches the value of α extracted from Figure 9c for deposition length less than 2 minutes. The fact that both methods agree so closely provides confidence that the analysis is valid. Whereas, for deposition times of 120 s and greater, $\alpha = 0.5$ is different to the value of α extracted from Figure 9. However, i has been confined to an integer value, only identifying a single, dominant smoothing mechanism. Given that $\alpha = 0.26$ does not give an integer value of i , it is likely that the surface morphology is, in fact, caused by a combination of different smoothing mechanisms and possibly even roughening mechanisms.⁴⁷ In addition, the value of α from Figure

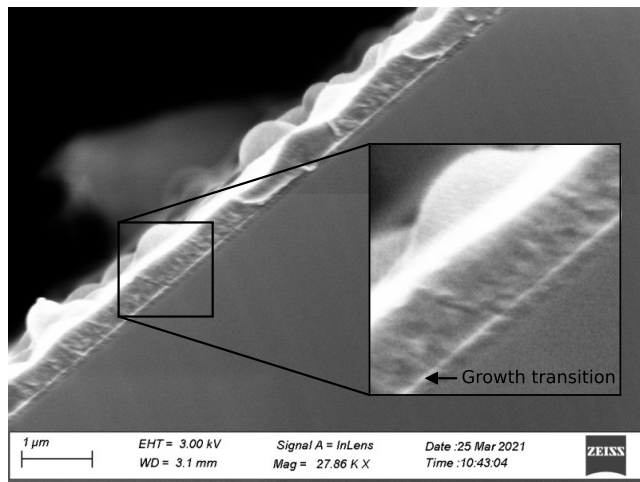


FIG. 11. Cross-sectional SEM image showing a clear boundary at the transition in growth regime.

9 is only for 3 data points, one of which could be very close to the transition, therefore to gain more insight into the growth mechanisms would perhaps require further depositions and analysis to provide more data.

Having identified these two separate regimes, cross-sectional scanning electron microscopy (SEM) used to determine whether these two separate growth regimes could be distinguished. Figure 11 shows a clear boundary in the Cu_2O layer showing that as indicated by the scaling analysis, there is a significant and rapid change in the growth mechanism.

Overall, the topographical scaling analysis shows that there are two distinct regimes of growth, which when considered in combination with the growth rate analysis, suggests that the initial regime, which is of most significance when depositing thin films, is determined by the state of the substrate surface. Further to this, initial attempts to fabricate devices identified issues etching this initial growth (the film nucleation stage) and measured higher resistivities, suggesting that the favourable electrical performance seen when optimising the reactant delivery parameters, should be attributed to the bulk film achieved in the longer depositions. Therefore with further optimisation of the initial growth mechanism and the use of fractal analysis to identify a deposition dominated by volume diffusion, rather than surface diffusion, it is believed that TFT device quality films can be achieved.

IV. CONCLUSION

This work has demonstrated the successful deposition of p-type Cu₂O thin films using PECVD from Cu(hfac)(tmvs), which remained stable over a period of months stored in a desiccator, achieving a Hall mobility of $\sim 1 \text{ cm}^2(\text{Vs})^{-1}$ and a high apparent deposition rate of 64 nm/min (relative to reported values of 1 nm/min using AALD,⁹ and 6 nm/min using PLD¹⁹) or 4.27 nm/pulse. Table I provides a comparison of how the electrical parameters compare to those reported elsewhere in the literature. The resistivity reported here is 2 orders of magnitude larger and the Hall mobility and carrier concentration are at the lower extreme of reported values. The Hall mobility of $\sim 1 \text{ cm}^2(\text{Vs})^{-1}$ in particular, is significantly smaller than the $256 \text{ cm}^2(\text{Vs})^{-1}$ reported by Li et al.¹¹, where the films were deposited using RF magnetron sputtering, a deposition method that is equally suited to large area deposition, indicating that further optimisation of the PECVD process is required. Previous studies have highlighted the significance of the substrate surface condition by identifying the presence of an ‘incubation period’, where there is a delay before the film fully nucleates on the substrate surface and blanket growth is achieved. In contrast to these reports, using a plasma enhanced deposition process and incorporating *in-situ* oxygen plasma pretreatment, led to very rapid initial growth, achieving $\sim 40 \text{ nm}$ from a single 1.75ms injection of precursor. Using fractal geometry and topographical scaling methods, two distinct growth regimes have been identified, with the transition caused by a shift in the dominant smoothing mechanism from surface diffusion to volume diffusion. Of the two regimes, the bulk growth where volume diffusion dominates, leads to more favourable electrical characteristics. The deposition optimisation in this work focused on the reactant delivery parameters, but there is scope for further optimisation of the deposition process to allow for better performance in the thinner films, especially in terms of the role of the plasma during the pretreatment process and the deposition itself. It has been assumed that the role of the plasma has been to provide gas-phase activation of the reactants, providing ionisation of the oxygen and possibly of the organic precursor. However, it is clear that the plasma power and by extension ion energies will impact the activation of the organic precursor and therefore the growth mechanism and potential incorporation of contaminants.^{28,30,31,36} The relatively low plasma power of 10 W has been chosen here to try to limit the chance of the precursor breaking into its constituent parts, but this should be explored in further work. Therefore, with careful optimisation of the substrate pretreatment process and precise control over the surface nucleation this work provides the potential for a highly industry compatible PECVD process for high growth

rate deposition of p-type Cu₂O devices.

TABLE I. Summary of reported resistivity (ρ), Hall mobility (μ_H) and carrier concentration (N). Abbreviations: AALD = atmospheric ALD; RF-MS = RF magnetron sputtering; Hitus = high target utilisation sputtering.

Reference	Method	ρ Ωcm	μ_H $\text{cm}^2(\text{Vs})^{-1}$	N cm^{-3}
Jeong, 2010 ⁷	Thermal CVD	190	32	10^{14}
Munoz-Rojas, 2012 ⁹	AALD	100	5	10^{16}
Napari, 2021 ¹⁰	ALD	300	0.6	10^{16}
Li, 2009 ¹¹	RF-MS	100	256	10^{14}
Fortunato, 2010 ¹²	RF-MS	10^3	0.65	10^{15}
Han, 2016 ¹³	HiTUS	10^3	28	10^{13}
Figueiredo, 2013 ¹⁶	Thermal oxidation	100	2.2	10^{16}
Matsuzaki, 2008 ¹⁹	PLD	-	70	10^{14}
Kim, 2013 ⁵⁴	Solution	-	18.9	10^{15}
Murali, 2015 ⁵⁵	Vac. annealing	149	51	10^{15}
This work	PECVD	10^5	1.48	10^{13}

ACKNOWLEDGMENTS

The authors thank Dr. Kham M. Niang for assistance with the XRD and XPS measurements and Dr. Gwen Wyatt-Moon for assistance with the SEM. This work is supported by the EPSRC through the Centre for Doctoral Training in Integrated Photonic and Electronic Systems (IPES) under Grant No. EP/L015455/1, and through project grants EP/M013650/1 and EP/P027032/1.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

- ¹X. Yu, T. J. Marks, and A. Facchetti, “Metal oxides for optoelectronic applications,” *Nat. Mater.* **15**, 383–396 (2016).
- ²K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, and H. Hosono, “Room-temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors,” *Nature* **432**, 488–492 (2004).
- ³E. Fortunato, P. Barquinha, and R. Martins, “Oxide Semiconductor Thin-Film Transistors : A Review of Recent Advances,” *Adv. Mater.* **24**, 2945–2986 (2012).
- ⁴H. Raebiger, S. Lany, and A. Zunger, “Origins of the p-type nature and cation deficiency in Cu₂O and related materials,” *Phys. Rev. B* **76**, 045209 (2007).
- ⁵Z. Wang, P. K. Nayak, J. A. Caraveo-frescas, and H. N. Alshareef, “Recent Developments in p-Type Oxide Semiconductor Materials and Devices,” *Adv. Mater.* **28**, 3831–3892 (2016).
- ⁶H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, and H. Hosono, “p-type electrical conduction in transparent thin films of CuAlO₂,” *Nature* **389**, 939–942 (1997).
- ⁷S. Jeong and E. S. Aydil, “Structural and electrical properties of Cu₂O thin films deposited on ZnO by metal organic chemical vapor deposition,” *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **28**, 1338–1343 (2010).
- ⁸J. Hsieh, P. Kuo, K. Peng, S. Liu, J. Hsueh, and S. Chang, “Opto-electronic properties of sputter-deposited Cu₂O films treated with rapid thermal annealing,” *Thin Solid Films* **516**, 5449–5453 (2008).
- ⁹D. Muñoz Rojas, M. Jordan, C. Yeoh, A. T. Marin, A. Kursumovic, L. A. Dunlop, D. C. Iza, A. Chen, H. Wang, and J. L. MacManus Driscoll, “Growth of $\sim 5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ mobility, p-type Copper(I) oxide (Cu₂O) films by fast atmospheric atomic layer deposition (AALD) at 225°C and below,” *AIP Adv.* **2**, 042179 (2012).
- ¹⁰M. Napari, T. N. Huq, D. J. Meeth, M. J. Heikkilä, K. M. Niang, H. Wang, T. Iivonen, H. Wang, M. Leskelä, M. Ritala, A. J. Flewitt, R. L. Z. Hoye, and J. L. MacManus-Driscoll, “Role of ALD Al₂O₃ Surface Passivation on the Performance of p-Type Cu₂O Thin Film Transistors,” *ACS Appl. Mater. Interfaces* **13**, 4156–4164 (2021).
- ¹¹B. S. Li, K. Akimoto, and A. Shen, “Growth of Cu₂O thin films with high hole mobility by introducing a low-temperature buffer layer,” *J. Cryst. Growth* **311**, 1102–1105 (2009).

- ¹²E. Fortunato, V. Figueiredo, P. Barquinha, E. Elamurugu, R. Barros, S.-h. K. Park, C.-s. Hwang, R. Martins, E. Fortunato, V. Figueiredo, P. Barquinha, and E. Elamurugu, “Thin-film transistors based on Cu₂O p-type thin films produced at room temperature,” *Appl. Phys. Lett.* **96**, 2102 (2010).
- ¹³S. Han, K. M. Niang, G. Rughoobur, and A. J. Flewitt, “Effects of post-deposition vacuum annealing on film characteristics of p-type Cu₂O and its impact on thin film transistor characteristics,” *Appl. Phys. Lett.* **109**, 3502 (2016).
- ¹⁴Z. Q. Yao, S. L. Liu, L. Zhang, B. He, A. Kumar, X. Jiang, W. J. Zhang, and G. Shao, “Room temperature fabrication of p-channel Cu₂O thin-film transistors on flexible polyethylene terephthalate substrates,” *Appl. Phys. Lett.* **101**, 042114 (2012).
- ¹⁵J. D. Lenef, J. Jo, O. Trejo, D. J. Mandia, R. L. Peterson, and N. P. Dasgupta, “Plasma-enhanced atomic layer deposition of p-type copper oxide semiconductors with tunable phase, oxidation state, and morphology,” *J. Phys. Chem. C* **125**, 9383–9390 (2021).
- ¹⁶V. Figueiredo, J. V. Pinto, J. Deuermeier, R. Barros, E. Alves, R. Martins, and E. Fortunato, “P-Type Cu_xO thin-film transistors produced by thermal oxidation,” *IEEE/OSA J. Disp. Technol.* **9**, 735–740 (2013).
- ¹⁷A. Liu, S. Nie, G. Liu, H. Zhu, C. Zhu, B. Shin, E. Fortunato, R. Martins, and F. Shan, “In situ one-step synthesis of p-type copper oxide for low-temperature, solution-processed thin-film transistors,” *J. Mater. Chem. C* **5**, 2524–2530 (2017).
- ¹⁸X. Zou, G. Fang, L. Yuan, M. Li, W. Guan, and X. Zhao, “Top-Gate Low-Threshold Voltage p-Cu₂O Thin-Film Transistor Grown on SiO₂/Si Substrate Using a High-k HfON Gate Dielectric,” *IEEE Electron Device Lett.* **31**, 827–829 (2010).
- ¹⁹K. Matsuzaki, K. Nomura, H. Yanagi, T. Kamiya, M. Hirano, and H. Hosono, “Epitaxial growth of high mobility Cu₂O thin films and application to p-channel thin film transistor,” *Appl. Phys. Lett.* **93**, 202107 (2008).
- ²⁰J. Deuermeier, H. F. Wardenga, J. Morasch, S. Siol, S. Nandy, T. Calmeiro, R. Martins, A. Klein, and E. Fortunato, “Highly conductive grain boundaries in copper oxide thin films,” *J. Appl. Phys.* **119** (2016), 10.1063/1.4954002.
- ²¹J. Deuermeier, H. Liu, L. Rapenne, T. Calmeiro, G. Renou, R. Martins, D. Muñoz-Rojas, and E. Fortunato, “Visualization of nanocrystalline CuO in the grain boundaries of Cu₂O thin films and effect on band bending and film resistivity,” *APL Mater.* **6** (2018), 10.1063/1.5042046.

- ²²K. Matsuzaki, K. Nomura, H. Yanagi, T. Kamiya, M. Hirano, and H. Hosono, “Effects of post-annealing on (110) Cu₂O epitaxial films and origin of low mobility in Cu₂O thin-film transistor,” *Phys. Status Solidi A* **206**, 2192–2197 (2009).
- ²³S. Han and A. J. Flewitt, “The Origin of the High Off-State Current in p-Type Cu₂O Thin Film Transistors,” *IEEE Electron Device Lett.* **38**, 1394–1397 (2017).
- ²⁴S. Kim, J. M. Park, and D. J. Choi, “Carrier gas effects on the selectivity in chemical vapor deposition of copper,” *Thin Solid Films* **315**, 229–237 (1998).
- ²⁵S. Kim, J. M. Park, and D. J. Choi, “The carrier gas and surface passivation effects on selectivity in chemical vapor deposition of copper films,” *Thin Solid Films* **320**, 95–102 (1998).
- ²⁶G. A. Petersen, J. E. Parmeter, C. A. Appleby, M. F. Gonzales, P. M. Smith, T. R. Omstead, and J. A. T. Norman, “Enhanced Chemical Vapor Deposition of Copper from (hfac)Cu(TMVS) Using Liquid Coinjection of TMVS,” *J. Electrochem. Soc.* **142**, 939–943 (1995).
- ²⁷G. Braeckelmann, D. Manger, A. Burke, G. G. Peterson, A. E. Kaloyeros, C. Reidsema, T. R. Omstead, J. F. Loan, and J. J. Sullivan, “Chemical vapor deposition of copper from Cu^I hexafluoroacetylacetonate trimethylvinylsilane for ultralarge scale integration applications,” *J. Vac. Sci. Technol., B: Microelectron. Nanom. Struct.* **14**, 1828 (1996).
- ²⁸W.-J. Lee, J.-S. Min, S.-K. Rha, S.-S. Chun, C.-O. Park, and D.-W. Kim, “Copper chemical vapour deposition using copper(I) hexafluoroacetylacetonate trimethylvinylsilane,” *J. Mater. Sci.: Mater. Electron.* **7** (1996).
- ²⁹J. C. Chiou, Y. J. Chen, and M. C. Chen, “Copper chemical vapor deposition from Cu(hexafluoroacetylacetonate)trimethylvinylsilane,” *J. Electron. Mater.* **23**, 383–390 (1994).
- ³⁰G. S. Girolami, P. M. Jeffries, and L. H. Dubois, “Mechanistic studies of copper thin-film growth from CuI and CuII .beta.-diketonates,” *J. Am. Chem. Soc.* **115**, 1015–1024 (1993).
- ³¹J. A. Norman, B. A. Muratore, P. N. Dyer, D. A. Roberts, A. K. Hochberg, and L. H. Dubois, “A new metal-organic chemical vapor deposition process for selective copper metallization,” *Mater. Sci. Eng., B* **17**, 87–92 (1993).
- ³²L. H. Dubois and B. R. Zegarski, “Selectivity in copper chemical vapor deposition,” *J. Electrochem. Soc.* **139**, 3295 (1992).
- ³³A. Jain, K. M. Chi, M. J. Hampden-Smith, T. T. Kodas, J. D. Farr, and M. F. Paffett, “Chemical vapor deposition of copper via disproportionation of hexafluoroacetylacetonato(1,5-cyclooctadiene)copper(i), (hfac)Cu(1.5-COD),” *J. Mater. Res.* **7**, 261–264 (1992).

- ³⁴S. L. Cohen, M. Liehr, and S. Kasi, "Selectivity in copper chemical vapor deposition," *Appl. Phys. Lett.* **60**, 1585–1587 (1992).
- ³⁵K. Nagashio, T. Yamashita, T. Nishimura, K. Kita, and A. Toriumi, "Electrical transport properties of graphene on SiO₂ with specific surface structures," *J. Appl. Phys.* **110**, 024513 (2011).
- ³⁶P. J. Lin and M. C. Chen, "CVD growth of Cu films using H₂ as carrier gas," *J. Electron. Mater.* **28**, 567–571 (1999).
- ³⁷P. G. Le Comber, "Electrical conduction in amorphous semiconductors," *Sci. Prog., Oxf.* **66**, 105–118 (1979).
- ³⁸P. Premkumar, N. Bahlawane, and K. Kohse-Höinghaus, "CVD of Metals Using Alcohols and Metal Acetylacetonates, Part I: Optimization of Process Parameters and Electrical Characterization of Synthesized Films," *Chem. Vap. Deposition* **13**, 219–226 (2007).
- ³⁹G. G. Condorelli, G. Malandrino, and I. Fragala, "Metal-Organic Chemical Vapor Deposition of Copper and Copper(I) Oxide: Kinetics and Reaction Mechanisms in the Presence of Oxygen," *Chem. Mater.* **7**, 2096–2103 (1995).
- ⁴⁰B. K. Meyer, A. Polity, D. Reppin, M. Becker, P. Hering, P. J. Klar, T. Sander, C. Reindl, J. Benz, M. Eickhoff, C. Heiliger, M. Heinemann, J. Bläsing, A. Krost, S. Shokovets, C. Müller, and C. Ronning, "Binary copper oxide semiconductors: From materials towards devices," *Phys. status solidi* **249**, 1487–1509 (2012).
- ⁴¹L. De Los Santos Valladares, D. H. Salinas, A. B. Dominguez, D. A. Najarro, S. I. Khondaker, T. Mitrelias, C. H. Barnes, J. A. Aguiar, and Y. Majima, "Crystallization and electrical resistivity of Cu₂O and CuO obtained by thermal oxidation of Cu thin films on SiO₂/Si substrates," *Thin Solid Films* **520**, 6368–6374 (2012).
- ⁴²B. Balamurugan and B. R. Mehta, "Optical and structural properties of nanocrystalline copper oxide thin films prepared by activated reactive evaporation," *Thin Solid Films* **396**, 90–96 (2001).
- ⁴³F. M. Li, R. Waddingham, W. I. Milne, A. J. Flewitt, S. Speakman, J. Dutson, S. Wakeham, and M. Thwaites, "Low temperature (< 100 °C) deposited P-type cuprous oxide thin films: Importance of controlled oxygen and deposition energy," *Thin Solid Films* **520**, 1278–1284 (2011).
- ⁴⁴P. Pouloupoulos, S. Baskoutas, S. D. Pappas, C. S. Garoufalidis, S. A. Droulias, A. Zamani, and V. Kapaklis, "Intense quantum confinement effects in Cu₂O thin films," *J. Phys. Chem. C* **115**, 14839–14843 (2011).
- ⁴⁵J. Ghijsen, L. H. Tjeng, J. Van Elp, H. Eskes, J. Westerink, G. A. Sawatzky, and M. T. Czyzyk, "Electronic structure of Cu₂O and CuO," *Phys. Rev. B* **38** (1988), 10.1103/Phys-

RevB.38.11322.

- ⁴⁶S. Y. Sung, S. Y. Kim, K. M. Jo, J. H. Lee, J. J. Kim, S. G. Kim, K. H. Chai, S. J. Pearton, D. P. Norton, and Y. W. Heo, "Fabrication of p-channel thin-film transistors using CuO active layers deposited at low temperature," *Appl. Phys. Lett.* **97**, 222109 (2010).
- ⁴⁷W. M. Tong and S. R. Williams, "KINETICS OF SURFACE GROWTH: Phenomenology, Scaling, and Mechanisms of Smoothing and Roughening," *Annu. Rev. Phys. Chem.* **45**, 401–439 (1994).
- ⁴⁸A.-L. Barabási and H. E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge University Press, 1995).
- ⁴⁹F. Family and T. Vicsek, "Scaling of the active zone in the Eden process on percolation networks and the ballistic deposition model," *J. Phys. A: Math. Gen.* **18**, 75–81 (1985).
- ⁵⁰F. Family, "Dynamic scaling and phase transitions in interface growth," *Phys. A (Amsterdam, Neth.)* **168**, 561–580 (1990).
- ⁵¹C. Herring, "Effect of change of scale on sintering phenomena," *J. Appl. Phys.* **21**, 301–303 (1950).
- ⁵²A. J. Flewitt, J. Robertson, and W. I. Milne, "Growth mechanism of hydrogenated amorphous silicon studied by in situ scanning tunneling microscopy," *J. Appl. Phys.* **85**, 8032 (1999).
- ⁵³W. W. Mullins, "Flattening of a Nearly Plane Solid Surface due to Capillarity," *J. Appl. Phys.* **30**, 77 (1959).
- ⁵⁴S. Y. Kim, C. H. Ahn, J. H. Lee, Y. H. Kwon, S. Hwang, J. Y. Lee, and H. K. Cho, "P-channel oxide thin film transistors using solution-processed copper oxide," *ACS Appl. Mater. Interfaces* **5**, 2417–2421 (2013).
- ⁵⁵D. S. Murali, S. Kumar, R. J. Choudhary, A. D. Wadikar, M. K. Jain, and A. Subrahmanyam, "Synthesis of Cu₂O from CuO thin films: Optical and electrical properties," *AIP Adv.* **5**, 047143 (2015).