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Atomistic Modelling of Titania Grown using PVD Methods

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Abstract—Results are presented for the atomistic modelling of titania growth, specifically the rutile {110} surface. Long time scale dynamics techniques are used to model the growth of thin films at realistic growth rates. Between deposition events, the system is evolved through an on-the-fly Kinetic Monte Carlo (off-KMC) method, finding diffusion pathways and barrier heights without any prior knowledge of transitions. Off-KMC allows thorough investigation of transitions and barriers observed during the film growth, giving a deeper understanding of growth mechanisms. An important rutile growth mechanism observed during all simulations, involves the upward diffusion of Ti interstitials below an O rich surface, with a barrier of 0.61 eV. The energy required for a single O ad-atom to diffuse on the surface is higher (between 0.65 eV - 0.85 eV). Methods used also allow examination of the effects of varying the experimental parameters, such as substrate bias, plasma density and stoichiometry of the deposited material. Conclusions drawn from the film growth suggest that the evaporation process produces an incomplete structure with voids, which is interesting for dye cell use. The inclusion of a low energy ion-beam assist does however add enough kinetic energy to the substrate to enable the completion and densification of layers, producing a film with greater crystallinity. The sputtering process produces highly crystalline growth, which is useful for anti-reflection coatings.

Index Terms—Titanium dioxide, thin film, evaporation, sputtering, ion assist, modelling, dye sensitized solar cells.

I. INTRODUCTION

Titania in its rutile form is an important material with industrial scale applications. Uses range from pigment to sunscreen to photovoltaic devices, and it is the latter which is the focus of this work. The high refractive index and UV radiation absorption abilities of dense, crystalline TiO₂ films lends to multilayer optical coating uses [1]. TiO₂ in its porous form is required for dye sensitized solar cells [2].

Thin films, specifically metal-oxide films in this case, can be deposited using numerous industrial-scale processes [3]. Evaporation, ion-beam assisted evaporation [4], [5], [6] and reactive magnetron sputtering [7], [8], [9] are typical processes used. The deposition rate of TiO₂ in industry is typically anywhere between 1/2 - 2 monolayers per second; here we use 1/2 monolayer per second. Evaporation deposition is simulated by deposition of TiO_x ad-clusters onto the rutile {110} surface, arriving with typical kinetic energy of <1 eV. An ion source, in this case Ar, is used to aid the densification of the film and to introduce extra energy into the substrate in order to increase atomic mixing and surface diffusion. The use of both low and medium energy ion sources was simulated, where Ar arrived at the surface with either 40 eV or 100 eV kinetic energy respectively. The

arrival rate of Ar was matched to that of the TiO_x ad-clusters, equivalent to 1.6×10^{15} atoms/cm²/s, it is expected that most of the Ar will leave the surface during the simulation. Sputter deposition deposits TiO₂ thin films using either RF, DC or pulsed DC power. Targets in the magnetron can be TiO₂ (RF), Ti (DC), or TiO_x (pulsed DC). As with evaporation, TiO_x ad-clusters arrive at the surface. The ad-units are sputtered from the target and arrive at the substrate with increased kinetic energy, typically 40 eV. Ar present within the magnetron is used as the working gas in order to sputter the material from the target, thus it is known that Ar will also bombard the substrate with a similar kinetic energy (40 eV). This Ar bombardment during deposition is known to affect the density and stoichiometry of the resulting oxide film [10]. Ar impacts on the substrate can also transfer momentum thus enhance surface mobility and diffusion, increasing film quality, leading to a higher refractive index [11].

Atomistic simulation has been used to complement experiment to understand the mechanisms involved. However, despite advances in computational power, using traditional Molecular Dynamics (MD) alone to model systems over long time scales is computationally infeasible. Traditional MD allows simulation for a few milliseconds, whereas the time required to grow one monolayer of TiO₂ is ~ 2 seconds. This is because a typical time step in the numerical integration scheme is around 1×10^{-15} s. Thus to simulate the deposition of one monolayer would require 10^{16} integration time steps. Each step requires the evaluation of the forces on all the atoms and is computationally expensive, especially for the variable charge model used here. Thus it is not possible to simulate thin film growth over realistic time scales using MD alone. If the deposition rate is artificially enhanced to allow the MD simulations to be carried out, then the system dynamics is biased. Long time scale dynamics combines MD with new techniques, allowing simulation over experimental time scales without biasing the system dynamics. On-the-fly Kinetic Monte Carlo (off-KMC) [12] is combined with MD allowing simulation of systems over several seconds of real time. Off-KMC methods also allow detailed investigation of individual transitions, enabling a deeper understanding of the growth mechanisms involved.

II. METHODOLOGY

Simulations were carried out using a modified variable charge TiO₂ interatomic potential [13], [14]. The original

potential, by Hallil et al. [15] was modified on the basis of ab-initio calculations [13] that were carried out to determine energy migration barriers. It was found that the original potential gave a much higher barrier for subsurface Ti interstitials to migrate to the surface and this migration mechanism was found to be one that was crucial to the way in which growth could take place. Periodic boundary conditions were employed for the substrate, mimicking the bulk in the lateral direction. The bottom layer of atoms was held fixed and the two layers above connected to a heat bath, maintained at a temperature of 350 K. Typical system sizes were 5 monolayers deep with ~ 200 atoms in each layer, simulations beginning with a perfect $\{110\}$ rutile surface. An ad-unit was deposited onto the surface with a prescribed energy by running MD for up to 10 ps, allowing the lattice return to 350 K and defects to stabilize. The system was then relaxed and diffusion between deposition events was simulated using otf-KMC. At each step either a deposition event or a diffusion event is chosen, according to their relative probabilities. Growth continues in this way until we have grown the number of layers we wish. The key point here is that the growth technique involves MD and otf-KMC working together.

During deposition, a variety of small molecular species arrive at the surface. We assume that these consist of a mixture of O and Ti atoms, O_2 molecules, TiO and TiO_2 units, resulting in the stoichiometric deposition of TiO_2 . These are assumed to impact normally on the surface with an energy of 1 eV for the model of e-beam deposition and with energies that vary up to 40 eV for modelling magnetron sputtering. A very useful part of the simulation is that the species mix and energy can be varied in the simulation to determine the most appropriate stoichiometry and energy for crystalline growth. In addition to the deposition species Ar atoms can also be introduced into the model. In magnetron sputtering these will have a similar energy to the deposition species but in ion beam assist the energy can be much higher. In our model we investigate simultaneous Ar bombardment also at normal incidence up to energies of 100 eV.

Otf-KMC specifically calculates all available transitions on-the-fly, enabling us to simulate much more defective and complicated systems. First, defects are identified along with all neighbouring atoms. This defines a defect region in which transitions from one local minimum to another are sought. Next, transition (saddle) points surrounding a metastable state (local minimum) are approximately located using a saddle point searching method [14]. Finally the climbing image Nudged Elastic Band method (NEB) [16] determines the barrier heights, more exactly. Typically > 200 searches are carried out per step. The transition frequency ν , of every unique transition is determined using the Arrhenius equation

$$\nu = \nu_0 \exp(-E/kT) \quad (1)$$

with an assumed constant prefactor ν_0 , usually taken as 10^{12} ,

where E is the barrier height, k is Boltzmanns constant and T is temperature. Transition searches together with a deposition event are carried out in parallel, on typically between 24-48 cpu cores, where the deposition event runs MD on a single core and searches are employed on multiple cores. Either a transition or deposition event is chosen from a roulette algorithm, which is used to evolve the system in time. Further details of the algorithm can be found elsewhere [12].

III. RESULTS

A. Typical Growth Mechanisms

Titania growth quality is dependant on the deposition process used, however, there are growth mechanisms observed during all processes that allow surface diffusion and more complete structures to form. A key feature of the deposition process is that O atoms and O_2 molecules nearly always attach to the surface whereas isolated Ti atoms almost invariably implant below the surface. Figure 1 illustrates a simple example of the rutile growth mechanism, a mechanism aiding the growth of titania via the migration of Ti interstitials up to the surface when surface is O rich [17], [18]. This is a key mechanism in enabling completion of layers and the annealing of Ti interstitials [13].

Fig. 1. Example of a rutile growth mechanism. Only the Ti atoms are shown; a Ti in an interstitial site diffuses upwards to fill a Ti vacancy in the surface with an energy barrier of 0.61 eV. There is O present on the surface above the Ti vacancy, this reduces the transition barrier and helps the Ti to diffuse upwards. Atoms are coloured by height using the key.

More intuitive transitions also take place to enable growth to occur; single O ad-atoms, for example, diffuse on the surface with energy barriers of 0.65 eV - 0.85 eV. The lower range of these barriers result in the diffusion of O ad-atoms along the trenches, above the 5-fold co-ordinate Ti row, as illustrated in figure 2. If the O ad-atoms adhere above a Ti interstitial this lowers the energy barrier for the Ti interstitial to diffuse to the surface, this enables the formation of TiO_2 units on the surface. With slightly higher energy barriers, the O ad-atom can fill any vacancies in the O ad-rows, aiding the completion of layers as shown in figure 3.

Fig. 2. An O ad-atom sitting above 5-fold Ti in the trench diffuses up and down the trench with energy barriers ranging typically between 0.65 eV and 0.75 eV. Ad-atoms may diffuse towards a Ti interstitial, thus lowering the energy required for the interstitial to diffuse upwards and join the O ad-atom as a ad-cluster on the surface. Larger, red spheres represent O and the smaller, grey spheres represent Ti.

Fig. 3. An O ad-atom sitting above 5-fold co-ordinate Ti in the trench moves across to fill a vacancy in the O ad-row. This takes place with an energy barrier of 0.81 eV. Transitions similar to this enable layers to become complete.

The mechanisms shown in figures 1-3 are the most important in terms of producing good crystalline growth but there are also many other concerted mechanisms that take place. Figure 4 illustrates the concerted movement of an ad-unit on the surface. The O ad-row has a TiO_2 ad-cluster joined to it, with a O ad-atom on top. The off-KMC methods allow investigation of these concerted, multi atom transitions. The O atoms rotate around a point to effectively slide the unit down the trench. Transitions such as this allow layer by layer growth to occur as this unit would perhaps enable the drawing out of the Ti interstitials below.

Fig. 4. A TiO_2 unit with a O sitting on top diffuses down the trench above the 5-fold coordinated Ti row with a barrier of 0.83 eV. This image shows only the involved atoms, along with the neighbouring O ad-row, to avoid confusion.

However, the barriers for these mechanisms are relatively high compared to the growth of metal films [19]. This implies that they require some added energy into the system to activate. This is discussed in the subsequent sections of the

paper where we consider first evaporation growth without any added energy and then two experimental deposition methods that do add energy to the system. The various resulting growth structures are compared.

B. Evaporation Deposition and Ion-Beam Assist

Four monolayers of atoms have been deposited onto the substrate via the evaporation process, simulating up to 6 seconds of experimental time. Ad-units arrive at the substrate with kinetic energy of <1 eV. During ion-beam assist, Ar arrives at the same rate and at either low or high energy (40 eV or 100 eV). Growth from evaporation deposition alone, without ion-beam assist, produces highly incomplete layers, with both oxygen and titanium atoms missing. Low kinetic energy of the arriving ad-clusters does not transfer sufficient energy to the substrate for much surface diffusion to occur, thus leaving the layers incomplete and void filled.

Both low and high energy ion-beam assist on the evaporation growth have been simulated. It is clear that the addition of low energy ion-beam assist (Ar arriving with 40 eV kinetic energy) produces layers which are more crystalline, as illustrated in figure 5. The Ar depositions introduce more energy into the system thus allowing more mixing, diffusion and growth mechanisms to take place, producing a more crystalline structure to form over time. The higher energy ion-beam assist (Ar arriving with 100 eV kinetic energy), however, introduces too much energy to the system, causing damage to the surface and producing voids, thus disrupting the crystallinity whilst appearing to densify the film. Implantation of Ar into the substrate is observed during the ion-beam assist, with deep implantation from the higher energy Ar bombardments, up to 4 layers deep into the substrate. From the experimental results it was expected that the ion-beam assist would improve film density [8], however, from our calculations an increased density effect cannot be definitely concluded, as growth has not yet reached a steady state.

Ar within the lattice preferentially sits in one of two locations; in an interstitial location between layers or as a substitutional atom in a Ti site after knocking the Ti into a deeper interstitial site within the lattice. The higher energy Ar assist creates increased Ti interstitials deeper within the lattice than the less disruptive 40 eV ion assist. The rutile growth mechanism allows some Ti interstitials to anneal, however, Ti interstitials very deep within the lattice require more time to diffuse upwards and thus often remain stuck in the lattice over the time to grow one or two monolayers.

C. Sputter Deposition

Four monolayers of atoms have been deposited via magnetron sputtering, where ad-units arrive at the substrate with 40 eV. Biasing the substrate is possible in order to increase the

Fig. 5. Comparison of growth of TiO_2 from evaporation and low energy ion-beam assisted evaporation, where Ar arrived at the surface with equal probability as a TiO_x cluster and with 40 eV. Both surfaces are shown, with a breakdown of the newly grown layers. Evaporation produces a void filled, incomplete film whereas the ion-beam assist adds enough energy to the system for more complete layers to form thanks to increased diffusion. Atoms in the surface image are coloured by height using the key. Larger, red spheres represent O, the smaller, grey spheres represent Ti and small, green spheres represent Ar left in the film.

deposition energy as high as 100 eV. However, depositing at such high energy actually damages the substrate too much, resulting in a highly incomplete, porous structure with Ti interstitials as deep as the 4th layer, too deep for the rutile growth mechanism to be able to draw them out. Optical properties of the film would significantly alter in this case, therefore only the 40 eV sputter deposition case is discussed. Simulation of the sputtering process of TiO_2 , firstly ignoring the effect of Ar in the plasma, produces a highly crystalline and complete film, shown in figure 6. The 40 eV depositions transfer enough kinetic energy to the substrate to allow surface diffusion to occur and O atoms present on the surface enable the rutile growth mechanism to take place promoting increased crystallinity. It is clear that in the magnetron sputtering case, Ar does not cause any dramatic changes in the quality of growth produced as results are very similar, the only difference being that Ar bombardments disrupt the original substrate more thus enhancing atomic mixing. Experimental results report that Ar impacts improve film density, however, as our simulations have not reached a steady state no firm conclusions can be drawn. Ar bombardment produced a higher proportion of Ti interstitials in the substrate, which would aid the rutile growth mechanism in forming more crystalline rutile, however, a significant difference in growth quality is not evident.

IV. CONCLUSIONS

Otf-KMC partnered with traditional MD allows simulation of thin film growth over realistic, experimental time scales. In this work, simulations have modelled up to 6 seconds of film growth; using traditional MD this would require millions

Fig. 6. Growth of TiO_2 from magnetron sputtering, where atoms arrive at the substrate with 40 eV. The surface is shown with a breakdown of new layers, which are highly crystalline and complete. The higher energy depositions have enabled surface diffusion and mixing to produce this crystalline film. Atoms in the surface image are coloured by height using the key. Larger, red spheres represent O, and smaller, grey spheres represent Ti.

of computing hours.

The otf-KMC methods allow thorough investigation of transitions observed and growth mechanisms involved. The

rutile growth mechanism, shown in figure 1, is one of the most important observed; Ti interstitials below the surface are drawn upwards by the presence of an O rich surface. This key mechanism encourages the annealing of Ti interstitials and the completion of layers above. With a barrier of 0.61 eV, this mechanism is observed during all simulations; but of course the deposition processes transferring the most kinetic energy to the substrate will encourage a higher diffusion rate, however Ti interstitials must be only in the first layer for the mechanism to work. Diffusion of single O ad-atoms was also investigated and found to occur requiring slightly higher energy (0.65 eV - 0.85 eV). O ad-atoms were found to diffuse up and down the trench, above the 5-fold Ti rows, enabling units to form and hence completion of layers. Vacancies in the O ad-rows noticeably are filled in by the same O ad-atoms which may be diffusing up and down the trenches. Understanding specific mechanisms occurring during growth allows a deeper understanding of the growth itself.

Evaporation deposition was modelled by depositing ad-clusters with <1 eV kinetic energy onto the rutile {110} surface. Incomplete layers were grown with voids throughout, as illustrated in figure 5. With such low kinetic energy involved in the depositions, little surface diffusion occurs, hence leaving layers incomplete and porous. Inclusion of the low energy (40 eV) ion-beam assist transfers increased kinetic energy to the substrate, encouraging increased surface diffusion and thus a more crystalline and complete structure. Ion-beam assist, both low and high energy, produced denser films, although as the system has not reached a steady state we cannot be sure that this is a real effect. For a better insight growth would need to continue for several more layers.

Sputter deposition was modelled by depositing ad-clusters with 40 eV kinetic energy onto the surface; this was found to be the optimal deposition energy to produce dense and crystalline thin films [17], [20]. Resulting growth was crystalline and almost complete. The Ar within the working gas in the magnetron was included in simulations by bombarding with Ar at the same rate as the TiO_x and with the same deposition energy of 40 eV. Ar bombardments lead to an increase in mixing with the original substrate via damage and repair; an increase in Ti interstitials was also observed, however none of these changes improved the quality of the film significantly. From experimental reports it was thought that Ar impacts would increase film density, however the systems have not yet reached steady states so no clear conclusions can be drawn on density improvement.

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