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Critical island size for Ag thin film growth on ZnO $(000\bar{1})$

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ABSTRACT

Island growth of Ag on ZnO is investigated with the development of a new technique to approximate critical island sizes. Ag is shown to attach in one of three highly symmetric sites on the ZnO surface or initial monolayers of grown Ag. Due to this, a lattice based adaptive kinetic Monte Carlo (LatAKMC) method is used to investigate initial growth phases. As island formation is commonly reported in the literature, the critical island sizes of Ag islands on a perfect polar ZnO surface and a first monolayer of grown Ag on the ZnO surface are considered. A mean rate approach is used to calculate the average time for an Ag ad-atom to drop off an island and this is then compared to deposition rates on the same island. Results suggest that Ag on ZnO $(000\bar{1})$ will exhibit Stranski–Krastanov (layer plus island) growth.

1. Introduction

Silver thin films make common appearances in low-emissivity (low-e) window production due to their reflective properties of certain wavelengths in the electromagnetic spectrum [1]. A thin film of Ag, when accompanied by the rest of a low-e coating, has the ability to reflect infra red radiation whilst allowing visible light to pass through. Ag is typically grown on a seed layer via a magnetron sputtering device [2,3]. These devices are run just above room temperature (300 K) and typically deposit single Ag atoms on a substrate at low energies (≈ 3 eV) at near normal incidences. The seed layer considered in this work is zinc oxide.

The formation of islands during Ag thin film growth on ZnO has been witnessed experimentally [4] and investigated via *ab initio* methods [5]. Further investigation is conducted by using a lattice based adaptive kinetic Monte Carlo (LatAKMC) model to simulate initial growth phases of Ag on a perfect O-terminated ZnO $(000\bar{1})$ surface. A mean rate method approach is used for predicting island size on a perfect ZnO surface and a single Ag layer applied to a perfect ZnO surface.

2. Lattice AKMC

During single point deposition simulations [6] and off-lattice AKMC, it is seen that Ag ad-atoms most commonly sit in highly symmetric sites on the perfect polar ZnO $(000\bar{1})$ surface (Fig. 1). This is also the case when Ag diffuses on an existing first layer of Ag on the ZnO surface. Due to this behaviour of deposited Ag atoms, a lattice based system can be assumed and used with KMC simulation to increase the efficiency of reusing previously found transitions and eliminate the need to use single ended search methods to find final transition positions.

For LatAKMC, all possible initial and final positions are assumed to be on a lattice. For the ZnO $(000\bar{1})$ surface, a hexagonal lattice is considered. The first layer ad-atom can move in three different directions in the surface plane and possibly also jump up to the second layer. A second layer ad-atom can move in 3 directions on the Ag plane with the possibility to jump down or up a layer if appropriately sited. To calculate barriers between states, the initial and final states are first minimised using a conjugate gradient minimiser [7] then the nudged elastic band (NEB) [8] method is used. To calculate the rate of transition, the Arrhenius equation is used:

$$\text{Escape Frequency} = \alpha \cdot e^{-E_B/k_B T}. \quad (1)$$

In Eq. (1), E_B, k_B and T represent the barrier height, the Boltzmann constant and system temperature respectively. The prefactor, α, can be calculated via the Vineyard method [9] but has been shown that taking it as a constant (10^{13}) is a reasonable assumption [10]. All energy and force calculations performed are done using the ReaxFF potential developed for Ag on ZnO surfaces [6]. Transitions are stored on objects that identify local initial and final states such that the atoms outside of a certain local radius

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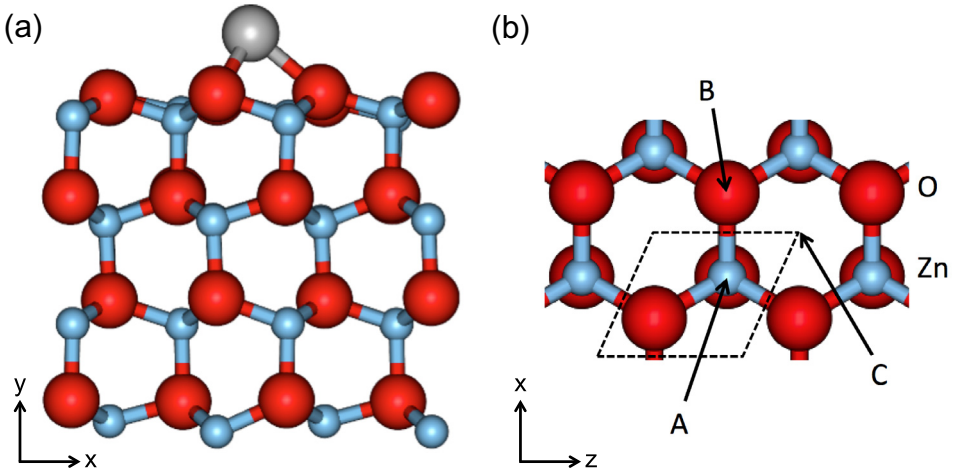

Fig. 1. Schematic structures of the O-terminated polar ZnO $(000\bar{1})$ surface with (a) an Ag ad-atom and (b) potential adsorption sites for deposited Ag atoms labelled A, B and C. Red, blue and grey spheres represent O, Zn and Ag atoms respectively. When the first layer of Ag forms, only sites A and C are stable but when an Ag ad-atom is deposited in the second layer, on top of Ag, it can sit above the A, B or C sites in the ZnO layer. (For interpretation of the reference to colour in this figure legend, the reader is referred to the web version of this article.)

have a negligible effect on barrier heights. For this system, the radius is taken to be 5.9 Å. Calculated barrier heights and corresponding rates for transitions on the perfect ZnO surface are given in Table 1.

In LatAKMC either a diffusion event or a deposition event occurs as in off-lattice KMC [11]. Newly deposited atoms are randomly placed on stable lattice sites on the current exposed surface. During initial growth simulation, single ad-atoms diffuse readily across the surface. Ag dimers can form and split at similar rates (with transition barriers typically between 0.4 and 0.6 eV). Once clusters of three or more Ag ad-atoms start to form, the energy barriers to escape the cluster become much larger and so act as nucleation sites on the surface. Many small clusters form initially and can then attach via single atoms strings (Fig. 2). Once atoms begin to deposit on existing Ag clusters, small energy barrier transitions can dominate the simulation. This can result in vast amounts of computational time being used without any significant evolution within the system. Fig. 3 shows an example pair of transitions with energy barriers being 0.17 eV and 0.3 eV. These are much lower than the relative barriers to escape (drop down to the first layer) or the equivalent barrier for deposition (0.6 eV).

As islands are seen experimentally when growing Ag on ZnO, simulating island growth is of interest. To investigate island formation and interaction, we must first know how large Ag islands are expected to be on the surface and then use LatAKMC to model a system large enough to incorporate multiple islands of this size. Having determined transitions on the first (Table 1) and second layers (Table 2), third layer transitions were also investigated. The results of these are shown in Table 3. Some of the barriers for diffusion in the third layer are even lower than those barriers in the second layer whilst escape (in this case jump down to second layer) barriers are very high. Including these small barriers in a traditional KMC approach is even more expensive computationally than including the second layer events. Normally a mean rate method would be used to overcome the low energy barrier problem. This is described in the next section but has only been used in this paper in determining the critical island size rather than performing LatAKMC calculations using the methodology.

Table 1
Example transitions of first layer Ag ad-atom on the perfect ZnO surface. Adsorption site labels refer to those in Fig. 1. Note that 'B' adsorption sites are unstable. E_B denotes barrier height and corresponding rates are calculated at 300 K.

Initial	Final	E_B (eV)	Rate (s^{-1})
A	C	0.16	2.05×10^{10}
C	A	0.56	3.91×10^{3}

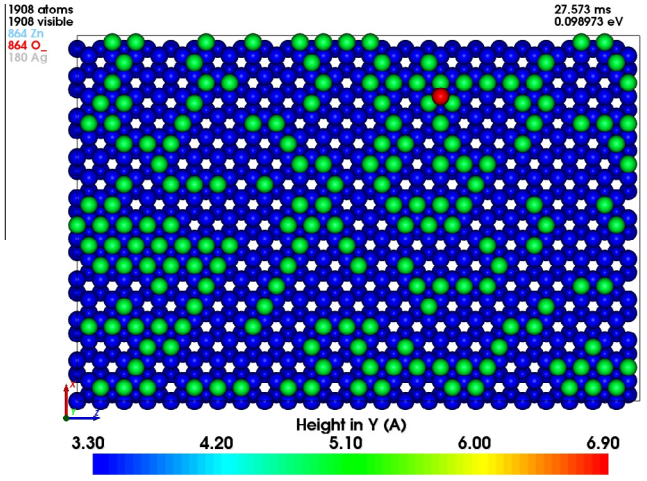

Fig. 2. Example growth structure after 27.6 ms of simulation. The ZnO surface consists of 864 Zn and O atoms and 180 additional Ag ad-atoms are deposited at an average rate of 12 monolayers per second. Atoms are coloured by height in the *y* direction (Å). Large blue represent O and small blue Zn surface atoms whereas green and red denote first and second layer Ag atoms respectively. (For interpretation of the reference to colour in this figure legend, the reader is referred to the web version of this article.)

3. Critical island size

The question of finding the critical size of islands in growth simulations has been asked for many systems [12–14]. A new approach to answering this question is presented. An atom above an island is considered in a "super-basin" as long as it stays on the island and has exited the "super-basin" once it drops off and joins the layer below. This means that a mean rate method (MRM) approach can be used to find the mean residence time of an atom on an island. This residence time can be compared to the mean time between new deposition events on the island to find a critical island size. Any island larger than the critical island size would suggest a new atom is more likely to be deposited on the

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