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.

Keywords: Silver, Zinc Oxide, Critical Island Size, Kinetic Monte Carlo, Thin Film Growth

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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.

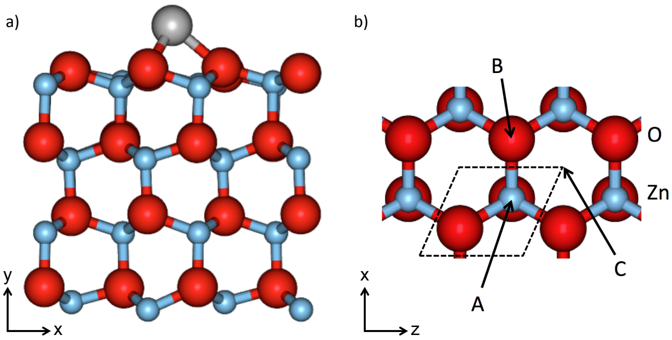

Figure 1 – Schematic structures of the O-terminated polar ZnO (000$\bar{1}$) surface with (a) an Ag ad-atom and (b) potential adsorption sites for deposited Ag atoms labelled A, B and C. Red, blue and grey spheres represent O, Zn and Ag atoms respectively. When the first layer of Ag forms, only sites 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.)

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

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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 300K.

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

Table 2 – Two possible transitions within the basin and the two escaping transitions with corresponding barrier heights and calculated rates above a first layer, 'C' stacked, island. E_B denotes barrier height and corresponding rates are calculated at 300K.

Initial	Final	E_B (eV)	Rate (s^{-1})
AboveZn	Above O	0.17	1.56×10^{10}
Above O	Above Zn	0.30	8.77×10^{7}
Above Zn	Escape	0.35	1.32×10^{7}
Above O	Escape	0.72	8.02

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:

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

In equation (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 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 0.4-0.6 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).

Table 3 – Two possible transitions within the basin and two escaping transitions with corresponding barrier heights and calculated rates on a second layer 'B' stacked island (above an existing 'C' stacked Ag monolayer). E_B denotes barrier height and corresponding rates are calculated at 300K.

Initial	Final	E_B (eV)	Rate (s^{-1})
Above Ag	Above Zn	0.01	6.79×10^{12}
Above Zn	Above Ag	0.06	9.82×10^{11}
Above Ag	Escape	0.75	2.51
Above Zn	Escape	0.89	1.12×10^{-2}

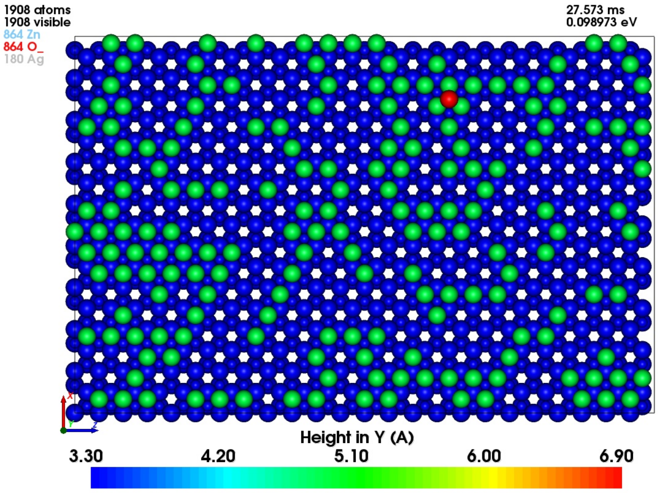

Figure 2 – Example growth structure after 27.6ms of simulation. The ZnO surface consists of 864 Zn and O atoms and 180 additional Ag ad-atoms are deposited at an average rate of 12 monolayers per second. Atoms are coloured by height in the y direction (Å). Large blue represent O and small blue Zn surface atoms whereas green and red denote first and second layer Ag atoms respectively.

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

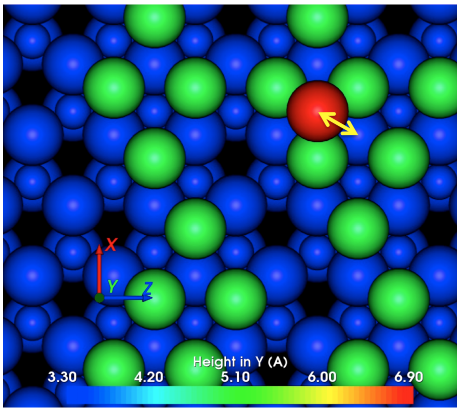

Figure 3 – Example configuration of a second layer Ag atom that will flip between adsorption sites above first layer Ag atoms with the relative transition rates shown in Table 2. Atoms are coloured by height in the y direction (Å). Large blue represent O and small blue Zn surface atoms whereas green and red denote first and second layer Ag atoms respectively.

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.

3. Critical Island Size

The question of finding the critical size of islands in growth simulations has been asked for many systems [12, 13, 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 island than an existing atom is to drop off and thus more likely to continue island growth.

3.1. Methodology

The mean rate method (MRM) [15] is used to calculate the mean residence time in basin states before leaving the basin. Here it is used to estimate the time to escape an island. To calculate the probability that an atom will exit the basin (or island), we first calculate the probability matrix $\underline{\mathbf{T}}$ (only including states within the basin), with elements

$$\begin{aligned} T_{j,i} &= \frac{R_{i\to j}}{\sum_k R_{i\to k}} = \tau_i^1 R_{i\to j} \\ \tau_i^1 &= \frac{1}{\sum_k R_{i\to k}} \end{aligned} \tag{2}$$

where $R_{i\to j}$ is the rate to go from state i to state j within the basin. The summation $\sum_k$ is over all states within and out of the basin. The reciprocal of the sum τ_i^1 is the mean residence time in state i each time that state is visited. To find the probability that a state is occupied after in-basin move m, an occupation probability vector of all basin states is given by repeat application of $\underline{\mathbf{T}}$ to the initial occupation probability:

$$\begin{aligned} \mathbf{\Theta}(m) &= \underline{\mathbf{T}}^m \mathbf{\Theta}(0) \\ \mathbf{\Theta}_i(0) &= \begin{cases} 1 & \text{if state } i \text{ is the initial state} \\ 0 & \text{otherwise.} \end{cases} \end{aligned} \tag{3}$$

The mean residence time in basin state i before leaving the basin is then given by:

$$\tau_i = \tau_i^1 \mathbf{\Theta}_i^{sum} \tag{4}$$

where,

$$\mathbf{\Theta}_i^{sum} = \sum_{m=0}^{\infty} \underline{\mathbf{T}}\mathbf{\Theta}(0) = (\mathbf{I} - \underline{\mathbf{T}})^{-1}\mathbf{\Theta}(0). \tag{5}$$

Thus, the mean time to escape the basin (or island) is then given as the sum of mean residence times within the basin.

3.2. Results

For the case of a single layer Ag island - in the energetically preferable ABC (FCC) stacking - on the ZnO surface, we assume that there are 2 different types of basin states (directly above an O atom or Zn atom) and that a basin state of one type can only move to a basin state of the other type or escape the basin. The rates to move between states are calculated by using NEB to find the barrier height and the Arrhenius equation (Eq. 1) to convert the barrier height to a rate depending on system temperature (Table 2). Islands are assumed to be in regular hexagonal shapes on the surface for simplicity.

The mean time to escape a first layer Ag island on the perfect ZnO surface is compared against the average time between subsequent depositions (see Fig. 4). The results indicate that small changes in system temperature can largely affect the critical island size. For a deposition rate of 12 monolayers per second (ml/s), at temperatures below room temperature (293 K), the critical island size is less than 350 Ag atoms. Whereas for higher temperatures, critical island sizes can be in excess of 500 atoms. As well as temperature, deposition rate also has a significant effect on critical island sizes.

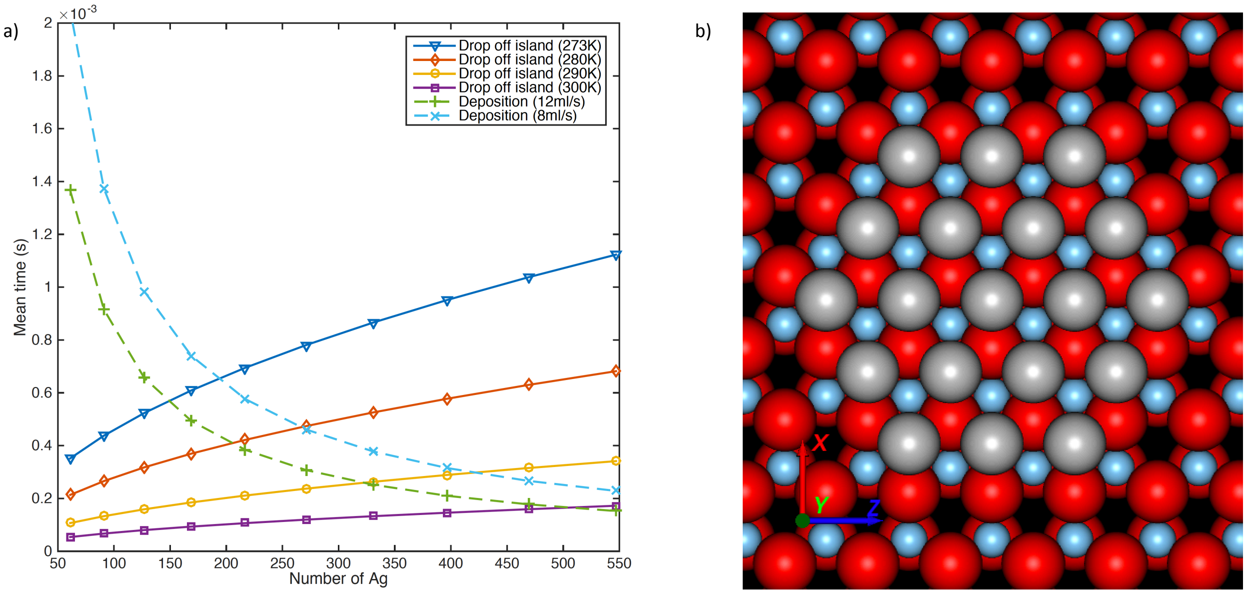

Figure 4 – A graph (a) comparing the mean time for ad-atoms to drop off a first layer Ag island at various temperatures and the time of new atoms being deposited on the island and (b) an example (19 atom) hexagonal first layer island of Ag on the ZnO surface.

For second layer islands (Table 3) in a favourable ABCB (first layer FCC and second layer HCP) stacking configuration, transition rates between states within the island are 2-3 orders of magnitude larger than in first layer islands. In addition, transition rates to escape the island are smaller and thus result in critical islands sizes of less than 7 atoms when considering a deposition rate of 12 ml/s. For our system setup (temperature at 300 K and a deposition rate around 12 ml/s), we would expect large or no islands forming on the first layer of growth but many small islands forming on subsequent layers of Ag growth.

4. Summary

Critical island analysis on perfect ZnO surfaces predicts a layer plus island growth model at initial growth phases (less than 2 layers high). However, island sizes may differ on defective ZnO surfaces. For our model, in order to simulate a system that may include multiple initial islands, we would have to either consider a system with a surface of at least a few thousand atoms, decrease our deposition rate or increase our system temperature. Despite this, an investigation of further island formation on subsequent layers of grown Ag could be conducted on a much smaller surface with typical system temperatures and deposition rates.

Experimental results show a large quantity of small islands forming after 8 monolayers of Ag growth [4] but island formation on the first layer is unclear. Our critical island analysis agrees that small islands are likely to form after an initial layer of Ag growth.

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