ISLAND NUCLEATION IN METAL THIN-FILM GROWTH

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Abstract. Island nucleation and growth during thin-film epitaxy is typically described using mean-field rate equations. Assuming that interactions between adatoms do not extend beyond the short range and that deposited atoms remain on top of the substrate, among other things, these equations can be solved to yield a scaling relationship that predicts the density of stable islands as a function of the deposition rate and the diffusivity of an isolated adatom Recent theoretical and experimental studies indicate that the assumptions behind this "standard" nucleation theory are not always upheld. Medium- and long-range interactions between adatoms may change the picture that nucleation theory provides. Also, intermixing of deposited atoms into the substrate can occur in heteroepitaxy. We review our recent theoretical studies, in which we have used density-functional theory calculations and kinetic Monte Carlo simulations to probe the initial stages of thin-film epitaxy for: (i) the growth of Ag on a strained Ag(111) surface and (ii) the growth of Co on Cu(001). We discuss the "novel" growth modes in these systems and related experimental work.

1. Introduction

Achieving a quantitative understanding of the morphology that evolves when atoms are deposited onto a solid substrate is important for both fundamental and practical reasons. In the initial stages of thin-film epitaxy, before a complete layer has been deposited, atoms typically diffuse on the

M. Kotrla et al. (eds.), Atomistic Aspects of Epitaxial Growth, 87–97.

solid surface and aggregate to form islands. Certain aspects of island nucleation and growth appear to be common to many different systems and this has motivated the development of a theory [1–4] to describe the general process. In this description, gas-phase species are deposited onto an initially bare, solid substrate with a rate F. These species diffuse on the surface with a rate $D = \nu_0 e^{-E_b^0/k_B T}$, where ν_0 is the pre-exponential factor, E_b^0 is the diffusion-energy barrier for an isolated species, k_B is Boltzmann's constant, and T is temperature. Diffusion mediates the aggregation of ad-species into nuclei, which either dissociate if they are below a critical size, or grow subsequently to become stable islands. Initially, the formation of island nuclei is the main process taking place. As the surface coverage increases, it becomes increasingly likely that deposited species will add to stable islands and promote their growth instead of forming new nuclei. These features can be captured in a mean-field theory for the stable island density in the island-growth regime N_x [1–4]. In the limit of low temperatures, where all deposited atoms stick to the surface and aggregate irreversibly to form islands, this expression has the form

$$N_x \sim (F/D)^{1/3}. \tag{1}$$

The validity of Eq. (1) has been investigated experimentally in several studies of homo- and heteroepitaxial growth [4–14]. Perhaps the best documented success of Eq. (1) is for the growth of Ag on Pt(111), which has been probed experimentally with low-temperature scanning-tunneling microscopy (STM) by Brune and co-workers [7], as well as theoretically by Brune *et al.* [6], who used kinetic Monte Carlo (KMC) simulations to model the growth, and by Ratsch and Scheffler [15, 16], who used first-principles calculations to quantify the diffusion barriers and pre-exponential factors. All of these studies confirm that the assumptions of Eq. (1) are upheld for the growth of Ag on Pt(111).

The success of Eq. (1) for Ag/Pt(111) heteroepitaxy is not universally achieved and, here, we review two examples of classes of systems for which Eq. (1) fails. Our first example is the growth of Ag on a strained Ag(111) surface. This example typifies growth on substrates for which the adatom diffusion barrier is small and comparable to the magnitude of adatom-adatom interactions. Here, we discuss our studies with density-functional theory (DFT) and KMC simulations [17–19], which show that, when this is the case, the island density may differ markedly from that predicted by Eq. (1). Our second example is the growth of Co on Cu(001) – a prototype for understanding heteroepitaxial growth involving intermixing. In this system, Co adatoms incorporate into the Cu(001) substrate and eject Cu atoms into the growing layer. Using DFT, we obtain energy barriers characterizing the hopping, exchange, and break-away from substitutional

Co of Cu and Co adatoms on the Cu(001) surface. With KMC simulations, we demonstrate a pronounced deviation from Arrhenius behavior in the island density, which is contrary to that predicted by Eq. (1) [20]. We discuss related experimental work.

2. Growth of Ag on Strained Ag(111)

One indication that Eq. (1) may not be appropriate for describing growth is when the parameters that must be employed to fit experimental island-density data do not seem physically reasonable. Barth and colleagues have described efforts to obtain the activation energy and pre-exponential factor for diffusion using Eq. (1) to analyze low-temperature STM data [14]. The parameters obtained in three of these studies are shown in Table 1. A striking feature of the experimental results is that the pre-exponential factors are significantly smaller than would be anticipated for systems such as these. For example, from *ab initio* calculations, Ratsch and Scheffler [16] find a pre-exponential factor of $\nu_0 = 1.3 \times 10^{12}$ s^{-1} for a Ag adatom on 1-ML-Ag/Pt(111), with a diffusion barrier of $E_b^0 = 63$ meV. Inserting the experimental and theoretical values for the diffusion parameters into Eq. (1), we see that the experimental island densities are about an order of magnitude higher than predictions based on the theoretical diffusion parameters. While it has been suggested that such low pre-exponential factors are, indeed, possible [14], we concluded [17] that these discrepancies indicate that the assumptions on which Eq. (1) is based are not upheld for all epitaxial growth systems – even for those that are seemingly related.

TABLE 1. Experimentally determined diffusion-energy barriers and pre-exponential factors using Eq. (1).

System	E_b^0 (meV)	ν_0 (s^{-1})	Reference
Al on Au(111)	30	7×10^3	[13]
Al on Al(111)	42	8×10^6	[14]
Ag on 1-ML-Ag/Pt(111)	60	10^9	[7]

In our work, we probed the influence of substrate-mediated interactions on island nucleation and growth [17–19], in an attempt to understand the anomalies in Table 1. The electronic, substrate-mediated interaction between two adsorbates is understood to arise from the electron-density perturbation that occurs when an atom binds to a surface and modifies the charge density nearby [21–24]. Oscillatory, ring-like, charge-density waves

associated with the electronic interaction have been imaged around adatoms and defects in STM studies of the (111) surfaces of Ag, Au, and Cu [25–31]. These interactions have been observed to extend to as far as 70 Å from the adatom or defect of their origin. Recently, Repp and co-workers [27] confirmed the interactions predicted [21–24] to stem from charge-density waves. The first (and deepest) minimum in the interaction-energy profile observed by Repp *et al.* [27] lies at $d = 12.5$ Å, with a depth of -0.4 meV. Beyond this distance, the interactions are weaker. For the Ag(111) surface, the first minimum of the long-range interaction occurs at ~ 30 Å and the interactions between Co adatoms on Ag(111), probed in low-temperature STM studies by Knorr *et al.*, are weaker than those seen for the Cu(111) surface [31].

There is evidence that substrate-mediated interactions can also occur at "intermediate" distances, greater that the distances over which direct chemical bonds form and less than the Fermi wavelength. For example, Einstein and Schrieffer showed in tight-binding calculations that the intermediate-range interaction is present and is more significant than the long-range interaction [22]. The STM studies of Repp also indicate this is the case for Cu adatoms on Cu(111) [27]. Thus, while the long-range interactions are well understood and are weak compared to k_BT in typical growth experiments, there is evidence that the "medium-range" interactions, which are poorly understood by comparison, can be strong enough to influence growth under experimental conditions. Additionally, these "medium-range" interactions can be accessed in modern, electronic-structure calculations.

We used DFT, within the plane-wave pseudopotential method [32], to quantify these "medium-range" interactions on a strained Ag(111) surface, which we use as a model of Ag on 1-ML-Ag/Pt(111) [17, 18]. The electronic, pair interaction that we find is shown in Fig. 1 for various, ranked distances of an adatom from a central adatom. In Fig. 1, we see that the magnitude of the repulsive interaction at distances 11, 12, and 13 is significant compared to the diffusion-energy barrier, which has a value of $E_b^0 = 52$ meV [17]. We found that these "medium-range" interactions are primarily pairwise and electronic in origin [17, 18]. Similar results are found in electronic-structure calculations by Bogicevic and co-workers [33] for Cu adatoms on Cu(111) and for Al on Al(111).

We incorporated the interactions shown in Fig. 1 into a KMC model to simulate thin-film epitaxy [17, 19] over temperatures ranging between 40-70 K and we determined island densities in the island growth regime. These low temperatures are in the range of the experimental studies (cf. Table 1). Figure 2 shows an Arrhenius plot of the island density from our DFT-KMC model as a function of temperature. Also shown in Fig. 2 is the island density predicted by Eq. (1) for $F = 0.1$ ML/s, $\nu_0 = 10^{12}$ s^{-1} , and $E_b^0 =$

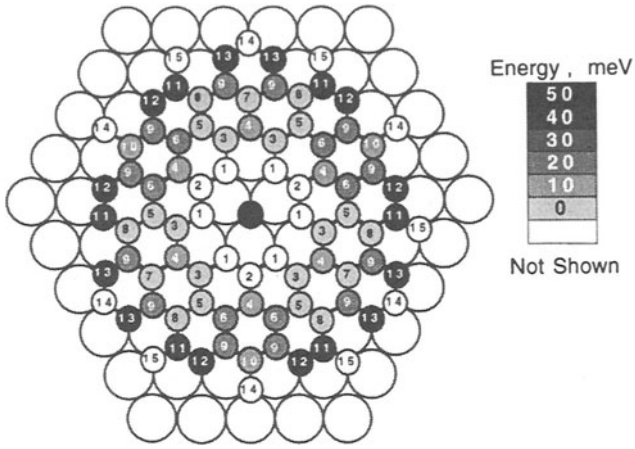

Figure 1. Pair interaction for Ag atoms on strained Ag(111) as a function of ranked distance from a central Ag adatom, shown in black.

52 meV – the values used in the KMC simulations. A proportionality coefficient η is needed to quantitatively compare nucleation theory with the simulations [i.e., $N_x = \eta \times (F/D)^{1/3}$]. We use the theoretical estimate by Bales and Chrzan [34] of $\eta = 0.25$. In Fig. 2, we see that the DFT-KMC island densities are an order of magnitude (or more) above the values predicted by Eq. (1). Returning to our discussion of the experimental results shown in Table 1, we point out that the order-of-magnitude difference between the island densities predicted from *ab initio* calculations [16] and those found experimentally for Ag on 1-ML-Ag/Pt(111) [7] is also seen in our study, comparing the island densities predicted by nucleation theory to those found in our DFT-KMC "computer experiments" (cf. Fig. 2). Thus, substrate-mediated interactions can play a significant role in determining island densities during thin-film epitaxy. This is especially so when the diffusion barrier of the deposited species is comparable to the magnitude of the interactions.

3. Growth of Co on Cu(001)

It is currently a significant challenge to predict with theory and to characterize with experiment the formation of intermixed structures during heteroepitaxy. A prototypical example is the non-equilibrium heteroepitaxial growth of Co on Cu(001). Studies of submonolayer growth with STM reveal that Co atoms can incorporate into the Cu(001) substrate and displace Cu atoms into the growing layer [35, 36]. Although submonolayer growth in the

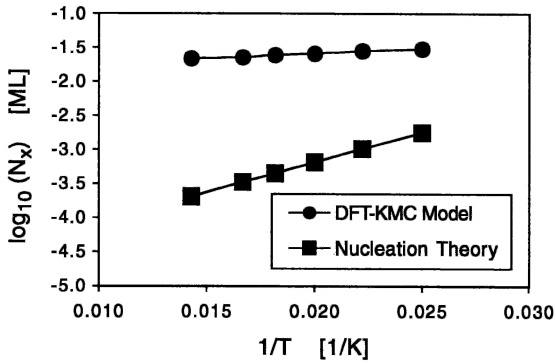

Figure 2. Arrhenius plot of the island density obtained from the DFT-KMC simulations (circles) and the island density predicted by nucleation theory (squares).

presence of intermixing has been treated theoretically with rate equations and KMC simulations [37-40], an assumption in these studies is that the impact of the ejected substrate atoms is negligible. An interesting observation in the STM studies is that ejected Cu atoms can break away from substitutional Co atoms to diffuse and aggregate with other Cu and Co adatoms [35, 36]. The interplay between deposition and the temperature-dependent rates of Co and Cu hopping, exchange, and break-away can lead to an interesting variety of heteroepitaxial structures and growth modes. Evidence for these phenomena is seen in recent STM studies, which indicate that the island-size distribution is broad [35, 36] and bimodal [36] – in distinct contrast to the Poisson-like distribution predicted in standard nucleation theory [2, 3]. The composition of the islands ranges from mostly Co to mostly Cu, and appears to correlate with island size [35, 36]. Nouvertné *et al.* found that the island density at 415 K is higher than that at 295 K [36]. Again, this phenomenon is not anticipated in standard nucleation theory. In this work, we characterize the temperature dependence of the island density using DFT calculations and KMC simulations.

Using DFT with the full potential-linearized augmented plane wave method [41], we characterized two types of diffusion mechanisms: hopping between adjacent four-fold hollow sites and exchange of an adatom with a substrate atom that is ejected onto the surface. The values of these diffusion barriers are summarized in Table 2. Also, an important interaction here is that of Co and Cu adatoms with substitutional Co atoms. In previous work [36, 42], we found that substitutional Co acts as a nucleation center for on-surface Co and Cu adatoms. The binding energy of a Cu adatom is enhanced by 0.25 eV when one of its neighbors in the Cu(001) surface is replaced by a Co atom. This effect is stronger for a Co adatom, which in-

creases its binding energy by 0.49 eV near substitutional Co [36, 42]. With such a substantial gain in binding energy, Co adatoms are assumed to be irreversibly pinned to substitutional Co. Pinned Co adatoms are allowed to exchange into the surface and form compact inclusions in the substrate. Preliminary DFT results show that the exchange barrier in this case is comparable to the one on the clean Cu(001) surface [42]. More weakly bound Cu adatoms are allowed to hop away from a substitutional Co atom with a barrier that is 0.15 eV higher than that for Cu hopping on Cu(001). This value accounts for the fact that both the initial and transition states are altered in the vicinity of the incorporated Co atom. The remaining interactions in this study are described in a bond-cutting model, in which the activation energy depends linearly on the number and type of neighbors in the initial state [20, 42].

TABLE 2. DFT diffusion-energy barriers for hopping, E_d^h, and exchange, E_d^{ex}, of Cu and spin-polarized Co on Cu(001).

System	E_b^h (eV)	E_b^{ex} (eV)
Cu on Cu(001)	0.49	1.02
Co on Cu(001)	0.61	1.00

Figure 3 shows a plot of the island density at 0.2 ML obtained from DFT-KMC simulations of submonolayer growth as a function of temperature for a deposition rate of $F = 0.1$ ML/s. A monotonic decrease of the island density with increasing temperature is predicted by Eq. (1). Instead, for Co on Cu(001) $N_x(T)$ exhibits complex behavior. Between 280–330 K, the island density decreases monotonically with increasing T. In this regime, hopping of Co adatoms is the dominant diffusion mechanism. Hopping of Co leads to small, compact, on-surface islands. The activation of atomic exchange results in a minimum in the $N_x(T)$-curve at approximately 350 K and a subsequent enhancement of the island density due to pinning at substitutional Co. Cu adatoms ejected onto the surface are primarily incorporated in the Co islands. The influence of exchange processes on the scaling properties of the island density have been addressed in several studies in the literature [37–40]. The fact that the island density as a function of temperature possesses a minimum was first observed by Meyer and Behm [38] for Ni/Ag(111) based on a model in which deposited atoms can either exchange into the surface or hop on top of it and nucleate islands. However, the motion of the "kicked out" substrate atoms is not considered in their

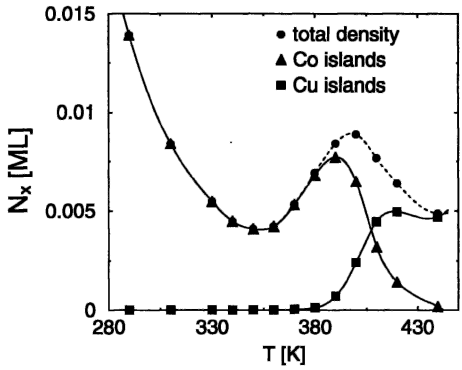

Figure 3. Island density as a function of temperature obtained from DFT-KMC simulations of the growth of Co on Cu(001) (circles). Also resolved are the densities of Co (triangles) and Cu (squares) islands.

work. This aspect turns out to have important consequences in the initial growth of Co on Cu(001).

With increasing T, both the number of on-surface Cu adatoms and their ability to overcome the attractive potential of the incorporated Co atoms increase. At 390 K, the island density reaches a maximum. Here, approximately 50% of the deposited Co adatoms have exchanged into the substrate and there is a substantial amount of substrate material in the first layer. The hopping rate of these Cu adatoms is very high and leads to large Cu islands that are decorated at the edges by Co. Coexisting with these is a number of small, predominantly Co islands. In Fig. 3, we also resolve the density of Co and Cu islands, defining islands with more than 50% of Cu(Co) as Cu(Co)-islands. While up to 380 K, islands contain predominantly Co with small amounts of Cu incorporated, at 380 K the density of Cu islands begins to grow and a crossover of the Co- and Cu-island densities takes place at approximately 400 K. Thus, the effect of *bimodality*, i.e. the formation of two different islands with respect to chemical composition and size, observed in STM [36], is reproduced in the DFT-KMC simulation. Additionally, our DFT-KMC model quantitatively reproduces the temperature-dependence of the island density observed in recent ion-scattering experiments of the growth of Co on Cu(001) [20].

4. Conclusions

Using first-principles DFT calculations and KMC simulations, we have characterized two epitaxial growth systems of current interest and quanti-

fied their deviations from "standard" nucleation theory. Such studies, with increasingly accurate atomic-scale detail, have significant potential for enhancing our understanding of thin-film growth.

Acknowledgements. This research is supported by the Alexander von Humboldt Foundation and NSF grant No. DMR-9617122.

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