Non-Arrhenius Behavior of the Island Density in Metal Heteroepitaxy: Co on Cu(001)

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We present a combined theoretical and experimental study of island nucleation and growth in the deposition of Co on Cu(001)—a prototype for understanding heteroepitaxial growth involving intermixing. Experimentally, ion scattering is employed. Using density-functional theory, we obtain energy barriers for the various elementary processes and incorporate these into a kinetic Monte Carlo program to simulate the heteroepitaxial growth. Both the simulations and the experiments show a unique $N$-shape dependence of the island density on temperature that stems from the interplay and competition of the different processes involved.

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Heteroepitaxial metallic structures, such as Co/Cu multilayers represent a new material that has high potential for the development of magnetoelectronic devices. In order to control the interfacial properties it is important to achieve a quantitative understanding of the morphology that develops during growth and its dependence on the growth conditions. A standard model for the initial stages of growth is given by nucleation theory [1], on the growth conditions. A standard model for the initial order to control the interfacial properties it is important to achieve a quantitative understanding of the morphol-

order for the development of magnetoelectronic devices. In multilayers represent a new material that has high potential for the development of magnetoelectronic devices. In order to control the interfacial properties it is important to achieve a quantitative understanding of the morphology that develops during growth and its dependence on the growth conditions. A standard model for the initial stages of growth is given by nucleation theory [1], where the island density $n_s$ is expressed in terms of the deposition rate $F$, the adatom hopping rate $D = D_0 \exp(-E_d/k_B T)$, and the binding energy $E_b$ of the critical nucleus of size $i$.

$$n_s \propto (F/D)^{i/(i+2)} \exp[-E_b/(i + 2)k_B T]. \quad (1)$$

The linear dependence of $\ln n_s$ on $1/T$ is widely used to deduce quantities such as activation barriers from island-density measurements, when adatoms form islands on top of the substrate [2]. However, in heteroepitaxial systems, deposited atoms may incorporate into the substrate displacing substrate atoms into the growing layer [3–9]. The effect of site exchange is not considered in Eq. (1).

A prototypical system where intermixing takes place is Co on Cu(001). A broad [5,6] and bimodal [6] island-size distribution was observed in submonolayer growth studies using scanning-tunnelling microscopy (STM)—in contrast to a Poisson-like distribution anticipated in standard nucleation theory [1]. In addition Nouvertne et al. reported that the island density at 415 K is slightly higher than at 295 K [6], which is at variance with the predictions of Eq. (1). The island composition was found to depend on the growth conditions and to vary from mostly Co to mostly Cu. Moreover, a correlation has been observed between island composition and island size [5,6].

From a fundamental standpoint, it is important to extend nucleation theories to account for intermixing. However, to date, only a few studies have attempted this [4,10–13]. Chambliss and Johnson proposed that substitutional Fe atoms constitute stable nuclei for the growth of Fe on Cu(001) [4]. By accounting for monomer stability [$i = 0$ in Eq. (1)] at substitutional Fe pinning sites, they found that the island density is independent of $F/D$. Meyer and Behm assumed irreversible pinning of adatoms at substitutional nucleation centers and found that the island density goes through a minimum with increasing temperature—consistent with that seen in Ni/Ag(111) heteroepitaxy [10]. By choosing two different surface mobilities for deposited and displaced substrate atoms and assuming a critical coverage to limit adatom exchange, Miranda and Gallego obtained a monotonic decrease in the island density with increasing temperature [13]. In contrast to Eq. (1), this temperature dependence reflects the mobilities of both the deposited and the displaced substrate atoms. Although these studies capture different aspects of heteroepitaxial growth with intermixing, none provides a comprehensive picture integrating all aspects of this complex process over a wide range of growth conditions, e.g., Miranda and Gallego neglect adatom pinning at substitutional sites [13], while other groups do not consider the effect of substrate adatoms ejected onto the surface [4,10]. Further, because diffusion barriers of two-component systems are difficult to obtain in experiments, these approaches rely on rather rough estimates of the diffusion parameters.

In this Letter we describe metal heteroepitaxy by employing density-functional theory (DFT) to characterize the major rate processes. We incorporate these processes into a kinetic Monte Carlo (kMC) simulation to model growth on time and length scales relevant for experiments. The target of our efforts is to achieve microscopic understanding of the island densities developing in the initial growth of Co on Cu(001), as well as their scaling behavior. We demonstrate that the interplay between deposition, adsorbate diffusion, and intermixing gives rise to the experimentally observed features [6]. By simulating growth over a wide temperature range, we predict that the island density has an $N$-shape with a minimum
and a maximum as a function of temperature. The $N$ shape is evidenced in our experimental studies and represents a significantly different scaling behavior than anticipated by standard nucleation theory.

The experimental technique used is grazing scattering of fast atoms. A Cu(001) single crystal surface is prepared in situ by cycles of Ar$^+$ sputtering and annealing. Co is deposited from a high-purity wire by electron beam heating. A well-collimated beam of 25 keV He atoms is directed upon the Cu(001) surface at a grazing angle of 1.75$^\circ$ ± 0.1$^\circ$ and an azimuthal angle of a few degrees to the [110] surface lattice direction. specularly reflected atoms are recorded as a function of deposition time for constant growth temperature and deposition rate. Growth-induced irregularities such as nucleated islands affect the correlated scattering process and the specular-beam intensity. Thus island densities are deduced from best fits of the measured intensities to computer simulations using classical trajectories [14,15]. We find that the density is saturated and nearly constant in a wide range of coverages between about 0.2 and 0.6 monolayers (ML). Grazing scattering of He atoms from Cu surfaces is affected by inelastic processes and the macroscopic surface topography [16]. Considering these effects in the experimental analysis gives rise to a simple displacement of $n(T)$ towards higher densities. Because this additive constant is rather empirical, we tied the ion scattering data to STM results [6].

The energy barriers characterizing rate processes of Co and Cu adatoms on Cu(001) are obtained using DFT with the full-potential linearized augmented plane wave method in the WIEN97 [17] implementation. For the exchange-correlation functional, we use the generalized gradient approximation (GGA) [18]. Results are obtained in a $p(3 \times 3)$ unit cell with 16 $k_{\parallel}$ points in the Brillouin zone. The energy cutoff of the basis set is 13.8 Ry, which provides a numerical accuracy of 0.02 eV in the surface energy of a 5 ML-thick Co(001) slab [19]. The structural optimization along the diffusion path is performed with damped Newton dynamics [20].

Using DFT-GGA, we quantify the major processes in the initial growth of Co on Cu(001), namely, hopping of a Cu and Co adatom between adjacent fourfold hollow sites over a bridge site and exchange of an adatom with a substrate atom that is ejected onto the surface. The values for the diffusion barriers are summarized in Table I. For Cu, the barrier for diffusion via hopping is 0.49 eV, in good agreement with previous DFT [21] and experimental values [22], while the exchange process has a much higher barrier. Because of a substantial gain in magnetic energy at the twofold coordinated transition state compared to the fourfold initial state, the barrier for Co hopping is lowered from 0.92 eV (nonmagnetic case) to 0.61 eV (spin-polarized case). Interestingly, the energy barriers for exchange are similar for Co (1.00 eV) and Cu (1.02 eV). A detailed analysis of the energetic, structural, and magnetic properties during the diffusion process will be presented elsewhere [23]. We are aware of only one previous study, based on the second-moment, tight-binding approximation, which reports diffusion barriers for Co on Cu(001) [24]. The value for Co hopping (0.66 eV) is in good agreement with our result, while the one for exchange (0.86 eV) is somewhat lower.

The pinning of adatoms at substitutional Co is an important feature in this system. In previous work [6,25,26] we calculated the binding energies of Co and Cu adatoms at substitutional Co sites and proposed that these sites act as nucleation centers for on-surface adatoms. Here, we present the barriers for Co and Cu adatoms to detach from a substitutional Co atom. We find (cf. Table I) that substitutional Co atoms hinder Cu hopping by increasing the barrier 0.15 eV beyond the bare-surface value, while Co adatoms need an additional 0.48 eV to overcome the attractive potential of substitutional Co. The attraction of the substitutional site is short ranged and the barriers for both species to hop toward this site are essentially equal to the bare-surface values. Our DFT results also show that pinned Co atoms can exchange into the surface with a barrier comparable to the one on clean Cu(001) [25]. This provides a mechanism for forming compact Co inclusions in the surface.

To describe island nucleation, growth, and restructuring, we need to take many more adatom-adatom interactions into account. We do this using a bond-cutting model, where the activation energy for hopping or exchange depends linearly on the number and type of nearest neighbors in the initial state. It is known that long-range electronic interactions can influence growth for Cu(111) and Ag(111) [27,28], where their strength is comparable to the energetics of diffusion on the bare surface. However, this is not the case for the (001) surfaces. The diffusion barrier for species $i$ ($i = \text{Co}, \text{Cu}$) is given by $E_d^i = E_d^{i/1} + N_{\text{Cu}}E_{i-\text{Cu}} + N_{\text{Co}}E_{i-\text{Co}} + N_{\text{Co,sub}}E_{i-\text{Co,sub}}$, where $N_{\text{Cu(Co)}}$ is the number of Cu (Co) on-surface neighbors. The barrier for an isolated species to hop or exchange, $E_d^{i/1}$ (cf. Table I), is enhanced by $E_{\text{Cu-Co}} = 0.1$ eV, $E_{\text{Cu-Co}} = 0.15$ eV, and $E_{\text{Co-Co}} = 0.2$ eV per Cu-Cu, Cu-Co, and Co-Co bond, respectively. These energies correlate

<table>
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<tr>
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<th>$E_d^\text{Co}$ (eV)</th>
<th>$E_d^\text{Cu}$ (eV)</th>
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<tbody>
<tr>
<td>On the clean Cu(001) surface</td>
<td>0.49</td>
<td>0.61 (0.92)</td>
</tr>
<tr>
<td>Exchange</td>
<td>1.02</td>
<td>1.00</td>
</tr>
<tr>
<td>On Cu(001)-p(3 × 3)-Co sub</td>
<td>0.64</td>
<td>1.09</td>
</tr>
<tr>
<td>Break away from Co sub</td>
<td>0.55</td>
<td>0.60</td>
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with the DFT dimer binding energies on Cu(001): 0.16, 0.23, and 0.37 eV/atom for Cu-Cu, Cu-Co, and Co-Co dimers, respectively, calculated in a (4 \times 2)-unit cell with \( E_{\text{Cu}} = 13.8 \text{Ry} \). The interaction parameters are chosen to be lower than the dimer binding energies to account for the influence of adsorbate interactions on the transition-state energies and they represent the barriers for a wide spectrum of surface processes. In the presence of Co in the substrate layer the hopping barrier is enhanced by \( N_{\text{Co,sub}}E_{\text{r,Co,sub}} \), where \( N_{\text{Co,sub}} \) is the number of substitutional neighbors and \( E_{\text{r,Co,sub}} = 0.15 (0.48) \text{ eV} \) for Cu(Co). These values reproduce the DFT detachment barriers given in Table I.

Recently Stepanyuk et al. [24] showed that surface strain can change hopping barriers especially in the close vicinity of Co islands by approximately 0.1 eV (the relative height of the energy barriers of different processes remains essentially unchanged). We note that a change of the diffusion rate at edges would affect primarily the shape of the islands, but would play only a minor role for island nucleation and densities discussed in this paper.

We incorporated these rate processes into a kMC simulation, following the general method of Fichthorn and Weinberg [29]. The surface is represented by a fcc lattice and the simulated region contains \( 256 \times 256 \) surface unit cells. The prefactors for hopping and exchange are set to values obtained from a molecular-dynamics study using an embedded-atom-method (MD-EAM) potential for Cu on Cu(001) [21], \( D_h^n = 2 \times 10^{13} \text{s}^{-1} \) and \( D_h^\text{ex} = 4.37 \times 10^{14} \text{s}^{-1} \). Recent calculations with \( N \)-body potentials fitted to first-principles values find the same prefactor for hopping of Co on a Co island on Cu(001) \( (2 \times 10^{13} \text{s}^{-1}) \) [30]. The MD-EAM values reflect the trend that prefactors for concerted processes such as exchange are higher due to the difference of the vibrational spectrum at the transition state.

Co was deposited randomly onto an initially bare Cu(001) surface at two different rates of 0.0045 and 0.1 ML/s. We simulated growth in the temperature range between 240–460 K and determined the island density \( n_s(T) \) at a coverage of 0.2 ML [31]. Figure 1 shows Arrhenius plots of the island density obtained from kMC simulations as well as from our ion scattering experiments.

A monotonic decrease of the island density with increasing temperature is anticipated in standard nucleation theory [cf. Eq. (1)]. In clear contrast to this, the island density here exhibits a complex \( N \) shape.

(i) Between 240 and 310 K, the island density decreases monotonically with increasing \( T \). We apply Eq. (1) assuming dimer stability \( (i = 1) \), \( n_s \propto (F/D)^{1/3} \), and find a diffusion barrier of 0.59 ± 0.02 eV from the kMC simulations. The activation energy obtained from the experimental data between 250 and 310 K is 0.54 ± 0.1 eV. These values correspond to the DFT hopping barrier for spin-polarized Co, 0.61 eV, which is the dominant diffusion mechanism in the kMC simulation in this temperature range. As a result, small, compact, on-surface Co islands evolve with preferential orientation along [110] and [110] directions.

(ii) The activation of Co exchange results in a minimum in the \( n_s(T) \) curve at ~320 K and a subsequent enhancement of the island density due to pinning of Co adatoms at substitutional Co. Cu adatoms ejected onto the surface are primarily incorporated into the Co islands.

(iii) At 370 K, the island density reaches a maximum. Here, approximately 50% of the deposited Co adatoms have exchanged into the substrate. For every Co atom that exchanges into the surface, a highly mobile Cu atom is ejected into the first layer. These Cu atoms are not as strongly pinned to substitutional Co as Co atoms and they tend to form large, on-surface islands on top of Co inclusions. On-surface Co atoms decorate the edges of Cu islands or aggregate at substitutional Co to form small islands that are mostly Cu. Thus, the effect of bimodality, i.e., the formation of two different types of islands with respect to chemical composition and size observed in STM [6], is reproduced in the kMC simulation. In the inset of Fig. 1 we resolve the density of Co and Cu islands, defining islands with more than 50% of Cu(Co) as Cu(Co) islands. While up to 350 K, islands contain predominantly Co with small amounts of Cu; at 350 K \( n_s^{\text{Cu}} \) starts to grow and a crossover of Co- and Cu-island densities takes place at approximately 380 K.

Theoretical (solid diamonds) and experimental (solid circles) island-density curves at the same deposition rate of 0.0045 ML/s are parallel with a good agreement in the positions of the minimum and the maximum. The
absolute values differ by a factor of 2 between theory and experiment. Taking into account uncertainties in the barriers and preexponential factors of some of the processes considered here, as well as experimental uncertainties, the agreement between theory and experiment is good, indicating that our kMC simulation captures the main atomistic processes that influence the scaling of \( n_x \).

We further test the influence of deposition rate on the island density by increasing the flux to \( F = 0.1 \text{ ML/s} \). Considering the low- and high-temperature regimes, the island density increases with increasing flux, as anticipated from Eq. (1). However, in the regime between minimum and maximum, the island density can actually decrease with increasing flux. Additionally, the minimum and maximum shift toward higher temperatures. At a fixed temperature, kinetic processes occur more slowly on the time scale of deposition, when the deposition rate is increased. Thus, Co exchange and the subsequent release of Cu atoms are pushed to higher temperatures.

In conclusion, we find a pronounced deviation from the typical Arrhenius behavior of island growth. A complex \( N \)-shape dependence of the island density on temperature is predicted theoretically and confirmed in an ion scattering experiment for Co on Cu(001). We identify the interplay of several microscopic mechanisms as the origin of this unusual behavior: activation of atomic exchange, pinning at substitutional Co, and aggregation of Cu adatoms, generated on the surface by exchange processes. We find that the scaling relationship from nucleation theory is only valid below the activation temperature of atomic exchange. A non-Arrhenius behavior may be present more often than anticipated so far, necessitating thus a reconsideration of some basic assumptions in the analysis of growth phenomena. Indeed, experimental results for Fe/Cu(001) [4], Fe/Au(001) [7], Ni/Cu(001) [8], and Co on Ag(001) [9] imply that the scenario described above could be relevant for a broader class of materials. A kMC approach based on reliable DFT parameters could be a useful tool to guide the fabrication of metal interfaces with controlled properties.

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[31] For the low coverages discussed in this paper the probability of island formation on top of already existing islands is negligible.
[32] Island densities at high temperatures (450 K) may be affected by finite terrace widths of the Cu substrate (some hundred Å), which favors growth from step edges not considered in the computer simulation. Low-temperature measurements (below 250 K) may suffer from small contaminations due to residual gas adsorption. Both effects tend to underestimate island densities.