Growth of Co nanostructures on Cu(110): Atomic-scale simulations

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Performing atomic-scale simulations we study the growth of Co on Cu(110) in the early stages of heteroepitaxy. The energetics of various diffusion processes relevant for this system is investigated. We reveal that the interface intermixing occurs at room temperature. Our results lead to the conclusion that Cu nanoislands grow on top of embedded Co adatoms in the submonolayer regime.

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Precise control over matter at the atomic scale is one of the most challenging tasks in modern nanoscience and is central to the engineering of nanostructures. Magnetic nanostructures on surfaces are considered to be one of the candidates for the development of high-density magnetic storage data. A detailed understanding of a growth process of nanostructures is essential for future progress of nanotechnology. Exploiting atomistic processes on surfaces allows one to create a wide range of nanostructures using different techniques.[1]

During the last decade many experimental and theoretical studies have been performed on Co/Cu heterostructures, which are of great interest for spintronic applications.[2] Growth processes of Co on Cu(100) and Cu(111) have been investigated and understood at the atomic scale. For example, in the case of a Cu(100) surface, both experiments and calculations have revealed that at low coverage Co adatoms occupy substitutional sites in the Cu substrate acting as pinning centers for subsequent island nucleation.[3–5] As the result of such process, small Co clusters are distributed on a surface with a high density and large Co-decorated Cu islands are formed. The onset of Co/Cu exchange has been shown to significantly change island morphologies.[3–5] On the Cu(111) the intermixing of Co and Cu is usually associated with the formation of vacancy islands in the Cu substrate.[6,7] Experiments have shown that at temperatures below 300 K, no vacancies are observed.[7] Both experiments and calculations have revealed formation of triangular bilayer Co islands on Cu(111) at room temperature.[7] In contrast, a detailed understanding of the growth process of Co on Cu(110) at the atomic scale is still missing.

During the last few years several experimental studies have been performed on Co nanostructures on Cu(110). For example, structural studies have indicated that growth of Co on Cu(110) does not exhibit the near ideal layer-by-layer growth mode seen for a Cu(100) substrate.[8] The Co initially grows via formation of elongated three-dimensional (3D) islands with the long edges preferentially aligned parallel to the [1–10] direction.[9,10] Fassbender *et al.*[11] reported that low-energy electron diffraction patterns of Co/Cu(110) can be explained in terms of an anisotropic surface diffusion of the deposited atoms resulting in anisotropic island shapes. Scanning tunneling microscope studies of Co film grown on clean Cu(110) at room temperature have been reported in the literature and anisotropic 3D islands have been found.[9,10] Results of Kief and Egelhof[8] on growth of Co on Cu(110) have suggested the existence of Co-Cu agglomerates. York and Leibsle[10] have concluded that Co islands on Cu(110) contain significant fraction of Cu atoms, while Hope *et al.*[9] reported on pure 3D Co islands on Cu(110). The later authors have assumed a small Co-Cu intermixing during percolation to explain their magnetic measurements. Tölkes *et al.*[12] concluded that pure and flat Co(110) films cannot be obtained by depositing Co on the bare Cu(110). The above-mentioned works have provided important insights into the structure of Co nanoislands and layers on Cu(110). However, a deeper understanding of the growth process requires knowledge of atomistic processes occurring at the Co/Cu(110) interface.

In this Brief Report we present the results of the molecular static (MS) calculations of energy barriers for different atomic events determining the growth of Co on Cu(110) in submonolayer regime. The kinetic Monte Carlo (kMC) simulations are performed to reveal the growth at the atomic scale. Our results indicate that the atomic exchange between Co and Cu atoms at the interface and surface diffusion of expelled Cu adatoms are the driving forces of growth mode in the early stages of heteroepitaxy.

To perform large-scale atomic simulations, we combine MS and kMC methods. In order to get an atomic-scale insight into the self-organization of Co nanostructures on a Cu(110) surface, first we consider dominant atomic events driving the growth process. Calculations of diffusion barriers are carried out by means of MS simulations. They are performed with a finite slab of ten layers, where each layer contains 1260 atoms. Four bottom layers are kept fixed and periodic boundary conditions are applied in the surface plane. *Ab-initio*-based many-body interatomic potentials formulated in the second moment of tight-binding approximation[13] are used for the system of Cu and Co atoms. These potentials are adopted to reproduce bulk properties of Cu and Co crystals and to describe binding energies of small embedded and supported Co clusters on different types of Cu surfaces [100 (Ref. 14) and 111 (Ref. 7)]. Previous studies have demonstrated that the combination of *ab initio* and tight-binding methods allows one to construct many-body potentials for low-dimensional structures and to investigate large systems in fully relaxed geometries.[15] The parameters of our potentials are given in Ref. 16.

We find that a Co adatom on Cu(110) [Fig. 1(a)] diffuses along the [1–10] direction with a barrier E_1 of 0.29 eV. At room temperature a Co adatom easily overcomes this barrier. The activation energy for diffusion along the perpendicular

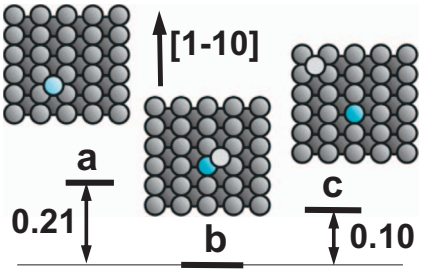

FIG. 1. (Color) Top view of a Cu(110) surface with a Co adatom. The gray circles represent Cu atoms, while the blue circles correspond to Co. (a) Initial configuration: a Co atom is on the surface. (b) Configuration with an embedded Co atom and a substituted Cu atom nearby. (c) Expelled Cu atom is located far from the buried Co atom. The relative energies between the configurations (in eV) are presented. The activation barriers are given in the text.

direction is found to exceed 1.0 eV; therefore, such motion is suppressed. Incorporation of a Co adatom into the topmost substrate layer [Fig. 1(b)] decreases the total energy of the system by $\Delta E=0.21$ eV and takes place with a barrier E_2 of 0.30 eV. Due to the fact that barriers E_1 and E_2 are close, deposited Co atoms embed into the substrate shortly after landing.

To demonstrate that the activation barriers computed by means of many-body potentials[16] correctly describe basic details of atomic motion on a Cu(110) surface, we have performed additional *ab initio* density-functional theory calculations. We have used VASP code[17] in Perdew-Wang 1991 version of generalized gradient approximation.[18] Ultrasoft pseudopotentials have been exploited within our calculations.[19] Our VASP calculations indicate that the diffusion barrier E_1 of a Co adatom along the [1–10] direction on Cu(110) is 0.35 eV. Incorporation of a Co adatom into the substrate leads to the energy gain ΔE of 0.22 eV and takes place with a barrier E_2 of 0.32 eV. The values computed by means of VASP code are close to those obtained using potentials.[16] Therefore, we are convinced that our potentials are well suited for the large-scale atomic simulations.

Now we turn back to the results of MS calculations and concentrate on the behavior of substituted Cu atoms. The diffusion barrier of a Cu adatom on Cu(110) along the [1–10] direction is found to be 0.26 eV. In contrast to Co atoms, Cu atoms may migrate along the [001] direction via exchange with one of the Cu atoms at the topmost layer. The barrier for this transition is only 0.30 eV. As a result, a substituted Cu atom follows a two-dimensional (2D) random motion on the Cu(110) surface. It is worthy to note that not all hollow sites are energetically equal for the diffusing Cu and there are preferable positions: hollow sites in a vicinity of embedded Co atoms [Fig. 1(b)]. When the Cu adatom is located near an embedded Co, the energy gain is 0.10 eV [Fig. 1(c)]. Migrating Cu atoms tend to coalescence into small clusters (dimers and trimers), and nucleation is energetically favorable in a vicinity of embedded Co atoms.

Figure 2 depicts the evolution of a small Cu cluster. The most stable configuration of two Cu atoms is dimer, which is oriented along the [1–10] direction near an embedded Co atom [Fig. 2(a)]. If the third Cu atom approaches the dimer,

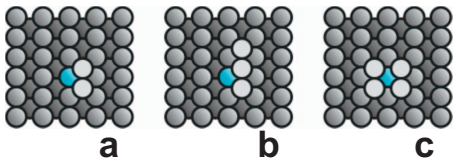

FIG. 2. (Color) Initial stages of growth of small Cu clusters on Cu(110) during epitaxy of Co. The most stable configurations of (a) two, (b) three, and (c) four expelled Cu atoms are demonstrated. The colors are the same as in Fig. 1.

the formation of a linear chain is found to be energetically favorable [Fig. 2(b)]. When the fourth substituted Cu atom nucleates, the most stable structure is the cluster "two-by-two" [Fig. 2(c)]. To explain the driving force for this phenomenon, we note that the interaction between Cu and Co atoms is stronger than that between two Cu atoms.[4] As a result, an embedded Co atom acts as a pinning center for expelled Cu atoms. This result is very similar to the findings of Pentcheva *et al.*[3,4] for Co on a Cu(100) surface. Configuration shown in Fig. 2(c) is the nucleation center for a growing island, which increases its size due to the approaching of next expelled Cu atoms.

A shape of a nanoisland is determined by a delicate balance between the activation barriers of atomic events involved in the growth process. Previous studies have revealed that the main factor affecting the morphology of a Cu(110) surface is the interplay between the barriers for attachment and detachment.[20–22] When increasing temperature T at a fixed flux F, one can reveal the following growth regimes: (i) small atomic clusters at low T; (ii) one-dimensional-like strips along the in-channel direction at intermediate T (when T is not enough to break in-channel Cu-Cu bonds); and (iii) 2D anisotropic islands at high T (when T is high enough to break in-channel Cu-Cu bonds). Figure 3 presents basic diffusion events on a Cu(110) surface in the vicinity of a Cu nanoisland. The barrier for the step edge diffusion of Cu along the [1–10] direction is 0.29 eV, while along the perpendicular island edge is 0.52 eV. A Cu adatom diffusing along the [1–10] direction detaches the island with a barrier of 0.34 eV (0.29 eV, when it is at the corner of the island). The barrier required for the breaking of in-channel Cu-Cu bond is 0.46 eV. All these events are operative at room temperature.[21] Thus according to Ref. 20, we expect the for-

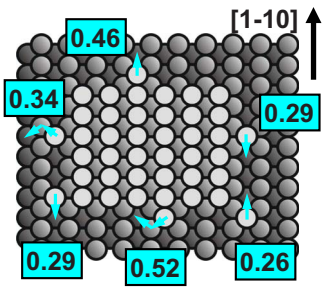

FIG. 3. (Color online) Basic atomic events responsible for the growth of Cu nanoislands elongated along the [1–10] direction. The colors are the same as in Fig. 1. The activation barriers are given in eV.

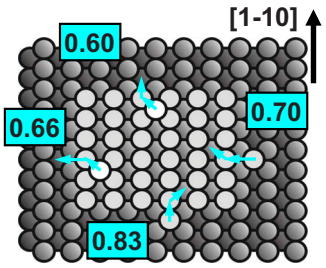

FIG. 4. (Color online) Atomic events responsible for the formation of the second overlayer of nanoislands: interlayer mass transport at the step edges. The gray (light gray, white) circles represent Cu atoms of the surface (the first and second) overlayers. The activation barriers are given in eV.

mation of Cu islands elongated along the [1–10] direction.

When the size of a Cu nanoisland is large enough, there is a certain probability that a deposited Co atom settles on top of it. The landed Co adatom exhibits the atomic site exchange with Cu atoms of the island, similar to the flat Cu(110) surface. To understand the behavior of an expelled Cu atom, we now consider atomic events of the interlayer mass transport between the first overlayer and the top of the island (Fig. 4). The Cu adatom, which is located on top of the island in a vicinity of the step edge parallel to the [1–10] direction, induces downward diffusion via exchange with a barrier of 0.66 eV. The backward transition takes place with a barrier of 0.70 eV. The Cu adatom, which is located on top of the island in a vicinity of the edge parallel to the [001] direction, exhibits downward mass transport with a barrier of 0.60 eV (Fig. 4). The opposite transition takes place with a barrier of 0.83 eV. Barriers for all interlayer diffusion events are quite high. Therefore, the probability that the Cu atom, being on top of the island, would reach its edge and would diffuse downward strongly depends on the value of flux F. When F is large enough, the migrating Cu atoms do not have enough time to induce downward mass transport to the first overlayer and the 3D growth regime takes place.

Finally, we present the results of kMC simulations based on the activation barriers for different atomic events. The kMC model applied within our study describes epitaxial growth in terms of rates of elementary stochastic processes (deposition, atomic diffusion, and interlayer mass transport) in order to avoid explicit calculations of unsuccessful attempts.[23] This model has been recently used in a certain number of investigations.[20–22,24] The rate of an atomic process is calculated using the Arrhenius expression $\nu = \nu_0 \times \exp[-E_D/(k_B T)]$, where $\nu_0 = 10^{12}$ Hz is the prefactor, T is the temperature, and E_D is the activation barrier. The kMC simulations are carried out on a close-packed (110) lattice consisting of 166×234 atoms (50×50 nm^2) and periodic boundary conditions are applied in a surface plane. We set $F = 0.01$ ML/s and $T = 290$ K, i.e., close to the experimental setup of Hope *et al.*[9] The results of the kMC simulations are presented in Figs. 5 and 6. Figure 5 demonstrates the morphology of a Cu(110) surface exposed by 0.07 ML of Co atoms. Formation of 1 ML high randomly distributed nanoislands elongated along [1–10] direction is observed. In Fig. 5(b) we present the atomic-scale resolution of the area

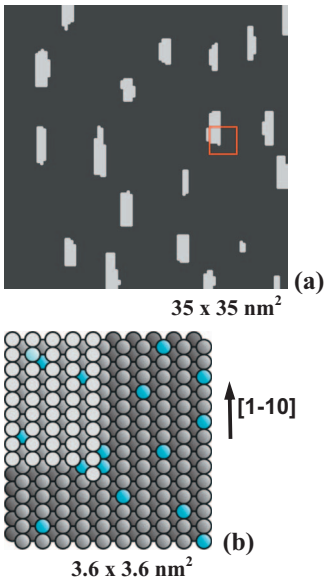

FIG. 5. (Color) (a) The morphology of a Cu(110) surface exposed by 0.07 ML of Co atoms at 290 K: the kMC simulation. (b) An atomic-scale view of the area marked in (a) with the red rectangle. The gray (light gray, white) circles represent Cu atoms of the surface (the first and second overlayers). The blue (pale blue) circles correspond to Co atoms embedded into the surface layer (in the first overlayer).

marked with the red rectangle in Fig. 5(a). A strong intermixing between deposited and substrate atoms is seen and growing nanoislands consist of Cu atoms. Figure 6(a) shows the morphology of Cu(110) at higher level of coverage: 0.45 ML of Co. Cu nanoislands increase their sizes and even become 2 ML high. The atomic-scale resolution [Fig. 6(b)] indicates

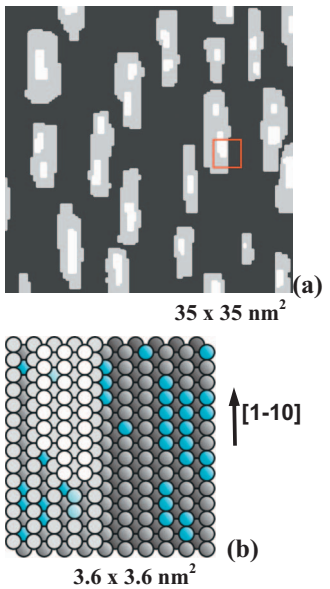

FIG. 6. (Color) (a) The morphology of Cu(110) exposed by 0.45 ML of Co atoms at 290 K: the kMC simulation. (b) An atomic-scale view of the area marked in (a) with the red rectangle. The colors are the same as in Fig. 5.

that the second overlayer consists of Cu atoms, and a small fraction of Co atoms appears in the first overlayer.

Our results shed light on the paramagnetic behavior of thin films, surprisingly observed during early stages of heteroepitaxy of Co on Cu(110).[9] Two factors could quench the magnetic signal of Co deposited on Cu(110): (i) Co atoms are buried in the nonmagnetic substrate and part of them are covered by expelled Cu and (ii) buried Co atoms form Co clusters of few atoms, which could exhibit paramagnetic behavior due to their small sizes.

In summary, we have demonstrated the scenario of Co growth on the Cu(110) at the atomic scale. We have found that the interface intermixing occurs in the early stages of heteroepitaxy. Our results reveal that embedded Co atoms serve as nucleation centers for substituted Cu atoms. Surface diffusion of expelled Cu adatoms is shown to lead to an elongated form of nanoislands consisting mainly of Cu atoms.

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