Novel Microscopic Mechanism of Intermixing during Growth on Soft Metallic Substrates

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Generic computer simulations using empiric interatomic potentials suggest a new, collective mechanism that could be responsible for mixing at heteroepitaxial interfaces. Even if single adsorbate atoms diffuse by hopping on the substrate surface and do not mix at the terraces, two-dimensional islands formed by nucleation may become unstable above a certain critical size and explode upwards forming clusters of several atomic layers. This process is accompanied by strong distortions of the underlying atomic layers, and on soft materials it can result in surface etching and incorporation of substrate atoms into the islands.

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Obtaining atomically sharp and morphologically flat interfaces between the different layers is one of the main difficulties for the preparation of thin films and super-lattices. Intermixing is common even between two materials immiscible in volume [1]. Roughness develops frequently right from the beginning of deposition. A typical example is furnished by the STM image in Fig. 1a. It shows a Cu(111) surface after growing 0.3 monolayer of Co at room temperature. Several remarkable features can be seen: atomic steps are decorated with clusters of irregular shape, all of the islands (both on the terraces and at the steps) have two or more atomic layers, and also some "pools" or clusters of single-atomic-depth vacancies can be seen interspersed among the islands. These observations reveal the importance of interfacial etching reactions. The total volume of islands and clusters present on the surface and measured in many of these images exceeds the amount of Co deposited. The vacancy clusters are never observed on the Cu surface in absence of Co. The appearance of multiple-atomic-height islands is confined to the interface region; beyond that, Co grows in single layers. Finally, the segregation of Cu atoms to the surface of the growing Co film has been confirmed by ion scattering spectroscopy [2] and chemical titration [3] experiments. The existence of another Co layer buried below the islands has also been detected [4]. On the other hand, these undesirable effects can be reduced or even suppressed by depositing Co at low temperature [5] or by using a surfactant [6].

Atomic place exchange during growth of metal films on single-crystal metallic substrates is now accepted as common on fcc(100) and (110) surfaces, and results in either surface alloying [7] or in the formation of patches within the surface layer, often encapsulated by a layer of substrate atoms [8]. These site exchanges take place between *single* atoms, both during diffusion [9] and after adsorption at certain sites [10,11]. Theoretically, they have been predicted both from computer simulations [12] and first-principle calculations [13] for many different combinations of adsorbate/substrate metals. Different explanations have been provided, such as stress relief [14], surface energy [15], or even magnetic effects [16]. However, collective phenomena involving groups of atoms have only rarely been considered [17].

In this paper we describe a new intermixing path not related to single-atom behavior but rather to the instability of *islands* larger than a certain critical size. This
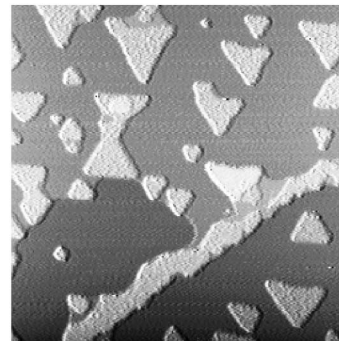

FIG. 1. Typical STM image of a submonolayer Co film grown on Cu(111) at 300 K, showing bilayer islands, decorated substrate steps, and clusters of monatomic-depth vacancies. The image size is 1000×1000 Å^2.

novel mechanism seems common on mechanically soft substrates. We have studied through Monte Carlo (MC) simulations and static relaxation (SR) the effects that appear at the interfaces during metal heteroepitaxy. Both methods employ the same empirical atomic potentials adjusted to reproduce the bulk properties of each material [18]; they have been obtained using the second-moment approximation of the tight-binding scheme and include many-body effects. Further information can be found elsewhere [19]. We have successfully used this procedure to study the homoepitaxial growth of Cu on Cu(111) and its modification by a surfactant Pb layer [20]. Here we have resorted to the same procedure to explore different mechanisms that can produce interfacial alloying.

Our most relevant finding is the observation that, while single Co atoms diffuse freely by hopping over the Cu(111) surface and do not get incorporated into the terraces, Co islands of single atomic height become unstable after reaching a certain size and break up forming clusters of several atomic layers. This phenomenon is frequently accompanied by the etching of some Cu atoms from the crystal surface. As a result, the clusters finally contain a mixture of Co and Cu atoms, while some vacancies are left behind on the surface.

The process is graphically demonstrated by the simulation depicted in Fig. 2. We have studied the behavior of Co islands as a function of their size, by generating flat Cu samples with single-layer Co islands of different sizes on it, and running the simulations to follow the system's

evolution. Our islands are in general triangular, with compact edges of either [111] or [100] orientation, and fcc stacking; some test runs have shown no appreciable difference in island behavior associated with these parameters. Above a certain size (that we can tentatively fix around 25 atoms, although this number should be taken as a rough estimate) the Co islands become unstable and explode upwards, dragging also some Cu atoms from the surface layer. The Co island shown in Fig. 2 contains 28 atoms. The two upper panels in this figure show side and top views of the surface configuration shortly after starting the simulation. The island center starts to swell and drags the Cu atoms directly underneath (middle panels). Finally, an island of mixed Co and Cu atoms with two or more layers is formed, leaving a cluster of vacancies on the surface (lower panels).

These results offer a consistent explanation for the experimentally observed formation of multiple-atomic-height islands accompanied by the appearance of the pools of vacancies. Our simulations imply that this is a *collective phenomenon,* requiring a certain number of Co atoms acting together and involving also large displacements of the substrate atoms situated below the Co island. Additional simulations have been performed in order to cross-check these assertions. Figure 3 shows one moment in the evolution of a Co island of only 21 atoms. In panel (a), all Co and Cu atoms have been allowed to move freely except for the two deepest Cu layers, which are frozen in order to simulate the crystal volume. The Co island also swells upwards inducing a strong buckling of several Cu layers below it. However, the amount of energy stored in this smaller island seems to not be enough to etch surface Cu atoms. Finally, a double-layer Co cluster appears, without any Cu atoms incorporated to it nor vacancies on the surface. Nevertheless, the displacements of the substrate atoms are an essential ingredient in the
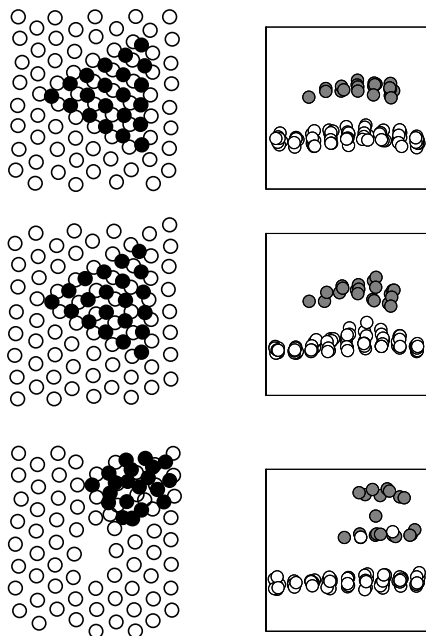
FIG. 2. Monte Carlo snapshots showing the breakup of a Co island (left: top view; right: side view). The instability starts developing at the island center that rises up pulling the underlying Cu atoms. Finally, an island with a mixture of Co and Cu and several atomic layers is formed, leaving some Cu vacancies on the surface.
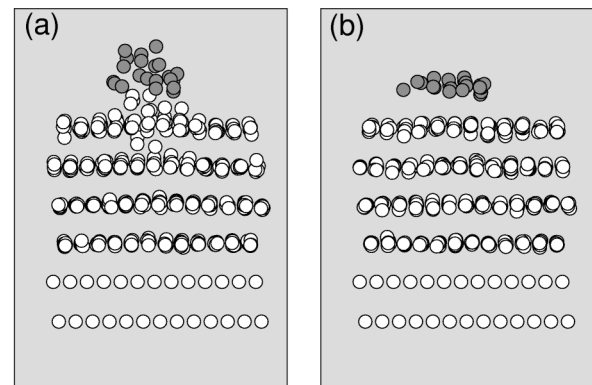
FIG. 3. Evolution of a Co island of subcritical size: (a) the strong substrate distortion facilitates the formation of a double-layer cluster; however, no Cu atoms are etched from the substrate. (b) When the same simulation is repeated but the uppermost Cu atoms are not allowed to move upwards, the breakup of the single-layer Co island is suppressed.

process of island distortion. The simulation of Fig. 3b is identical to the previous one except that the Cu atoms in the uppermost layer are not allowed to rise above their initial average height. The Co island shows the same tendency to inflate upwards, but now the Cu atoms cannot assist this movement and, as a result, the formation of the double-layer cluster is inhibited.

The tendency to form clusters of multiple atomic height must be driven by the need of the heteroepitaxial islands to relieve their excess energy. The balance of surface free energies for the growth of flat Co islands on Cu(111) is $\Delta E = \gamma_{Cu} - (\gamma_{Co} + \gamma_{CuCo} + \gamma_{st})$, with γ_{CuCo} and γ_{st} being the energies associated to the Co-Cu interface and to the strain in the pseudomorphic film, respectively. Taking $\gamma_{Cu} = 1.9$ J/m^2, $\gamma_{Co} = 2.7$ J/m^2 [21], and $\gamma_{CuCo} = 0.2$ J/m^2 [22], we see that this energy increment is relatively large and negative, indicating that 2D growth will not be thermodynamically favored. Although the applicability of a macroscopic criterion such as this to small islands is doubtful, it still provides a hint about the possible instability of the Co islands that we observe. It does not explain, however, the distortions provoked in the Cu substrate and the formation of vacancies. We think that this effect might be of elastic nature, since the islands of pure Co are under tensile strain. Elastic properties are accurately described by our empirical potentials, because they have been fitted to the materials' bulk properties [18,19]. The substrate hardness, understood as the difficulty to extract atoms from its surface, plays a crucial role. In other simulations for Fe/Cu(111) we have found that these effects (multiple-layer island formation, step decoration, and terrace etching) are even stronger than for Co on Cu(111), in agreement with experimental observations [23]. Double-layer islands have also been found for growth on other soft substrates, such as Co/Au(111) [11] or Ni/Au(110) [17]. On the other hand, on hard substrates such as W(110) [24] or Ru(0001) [25] single-layer islands are found in all cases, in spite of the large values of lattice mismatch (~10%).

Our model can also explain the decoration of Cu steps by intermixed islands, as a result of preferential nucleation of Co islands near a descending Cu step. Isolated Co atoms diffuse on Cu(111) by hopping; in no case have we detected any site exchanges with Cu atoms on the terraces. When they reach an ascending step, they stick to it and remain mostly immobile. On the other hand, Co atoms arriving to the edge of a descending step push a Cu one out of it and roll over to occupy its position. These two processes are visualized in Fig. 4a, which shows the outcome of our MC simulations for both cases. These results are in complete agreement with previous findings on the system Ni/Cu(111) [12], and recent experimental data on Co/Pt(111) [26].

During the early stages of deposition many Co atoms are able to reach the surface steps from both sides, form-
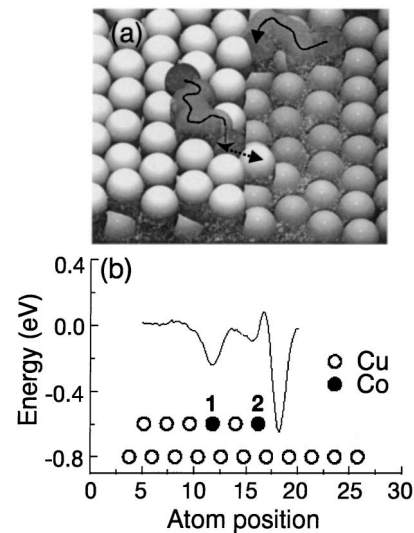

FIG. 4. (a) Monte Carlo simulation showing how a Co atom arriving to a descending step expels a Cu one and takes its place; at an ascending step, Co atoms stick to the edge and do not mix. (b) Energy profile, obtained by static relaxation, for a Co atom moving perpendicularly to a Cu step after the incorporation of two Co atoms as described above.

ing two nearly straight rows parallel to the edge. The inset in Fig. 4b shows schematically a transverse cut across such an atomic step. Co atoms are represented by the filled circles. The one labeled "1" has arrived to the step from the upper terrace, displacing the edge Cu atom to the right; atom "2" comes from the lower terrace. From SR calculations we find that the adsorption sites above these Co atoms are energetically preferred. The curve in Fig. 4b shows the energy felt by another Co atom moving perpendicularly to the step. A rather deep binding well (0.24 eV) is found above atom 1, and a shallower one (0.10 eV) above atom 2. These positions can trap other diffusing Co atoms and thus constitute preferential nucleation sites. Islands formed at them, or on the lower terrace by the step, could also break up upon reaching the critical size and provoke the experimentally observed step decoration. Of course, we cannot rule out other possible mechanisms, such as enhanced interdiffusion at the step. However, it is tempting to explain nearly all morphological features observed in the STM images by a single mechanism.

The effects of temperature or surfactant agents can also be easily understood. In the first case, lowering the growth temperature results in the formation of smaller islands, many of which may not reach the critical size and compact shape needed to etch Cu atoms from the surface; after coalescence, the overall reduction in the growth kinetics also helps preserve the metastable morphology. For the same reason, ultrafast deposition rates such as those achieved by pulsed laser deposition [27] also result in strongly reduced interfacial intermixing. On the other hand, with the same energetic argument given above, the balance of energies in the presence of a monolayer of Pb acting as a surfactant

reads $\Delta E = (\gamma_{Pb} + \gamma_{PbCu}) - (\gamma_{Pb} + \gamma_{PbCo} + \gamma_{CoCu})$, which is only very slightly negative, since $\gamma_{PbCu} \simeq \gamma_{PbCo}$, and γ_{CoCu} is rather small. Accordingly the quasiequilibrium mode of growth is 2D. In this case we do not need to consider the elastic strain term because, in the presence of the surfactant, islands of pure Co are never formed at the interface. We have shown in a previous work that in the presence of a compact surfactant layer, deposited Cu atoms diffuse below it by exchange [20]. Co atoms behave in an identical way. The deposited Co atoms diffuse under the Pb overlayer by exchanging places with the Cu atoms from the substrate. Thus, most of the islands formed in this case contain a mixture of Co and Cu atoms. As a result the elastic strain is reduced with respect to clean deposition of Co on Cu(111).

In summary, from generic computer simulations with empiric interatomic potentials we propose the existence of a novel, collective mechanism responsible for interfacial mixing. We find that two-dimensional Co islands become unstable above a certain critical size, and eventually break up forming clusters several layers high. This phenomenon should be especially relevant for soft metallic substrates, where it could be accompanied by etching of surface atoms and creation of vacancies. Step decoration could also result from the same phenomenon, combined with preferential island nucleation above individual Co atoms inserted at the upper step edge. These findings have an obvious importance for the growth of metallic superlattices, because the processes described determine the interface quality. An accurate understanding of these phenomena at the atomic scale will allow us to devise strategies to control them and suppress undesirable effects.

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