Surfactant effect of Pb in the growth of Fe on Cu(111): A kinetic effect

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The effect of predepositing 1 ML of lead on the substrate surface in the growth of Fe on Cu(111) is studied both at room and high temperature (400 K). The results show that, even though the Pb monolayer floats efficiently over the Fe film, the thermodynamic equilibrium state of the film consists of three-dimensional iron clusters over the copper surface, and consequently, that the room-temperature surfactant action of the Pb monolayer results merely from its effect on the kinetics of the growth, in particular decreasing the mobility of the Fe atoms.

I. INTRODUCTION

In the continuous search for the capability to control the structure and morphology of newly developed nanostructures, small amounts of adsorbed gases or metals, usually known as surfactants, are currently being used in molecular-beam epitaxy to promote a two-dimensional (2D) layer-by-layer growth in systems that naturally grow in a three-dimensional (3D), island mode and where an increase of the deposition temperature would lead to a dissolution of the deposited material into the substrate rather than to an enhancement of surface diffusion. Known for a long time in the field of crystal growth from solutions,[1] the use of surfactants was recently extended to epitaxial growth both in metal[2] and semiconductor systems.[3] Usually, in molecular-beam epitaxy a layer of the surfactant material is deposited on the substrate surface before the actual deposition of the film. With a low surface free energy and a lack of chemical affinity toward the growing materials, the surfactant tends to float during growth; thus it is not incorporated into the growing film and somehow changes the growth mechanism, leading to smoother films.

Despite all the work devoted to understanding surfactant action, at the present time there is no consensus about the fundamental mechanisms involved, or if these are valid for every system. It has not even been clarified whether the contaminant affects mainly the energetics via the surface energy or the kinetics of growth, and many different models have been proposed.[4] Most of these models can be classified into one of the following categories: (a) The surfactant modifies the thermodynamic balance of the surface and interface free energies, in such a way that the equilibrium state in the presence of the surfactant layer is a smooth flat film;[3] within this model the adatoms exchange place locally with the surfactant atoms, with minimum surface diffusion, thus preventing nucleation and growth of 3D islands.[5–7] (b) The surfactant favors interlayer diffusion, either by directly lowering the barrier at the step edges (the Schwoebel barrier)[8–11] or by increasing the terrace barrier, thus reducing the additional edge barrier.[12–19] (c) The surfactant passivates the island edges, thus leading to a high density of islands and preventing 3D islanding.[20] (d) The surfactant effect results as a combination of a small diffusion barrier on top of the surfactant layer, a rate-limiting exchange barrier for nucleation, and a second highest barrier for the aided exchange of adatoms to get incorporated into islands.[21,22]

Although the very first models focused on the thermodynamic approach, it is hard to justify the surfactant action solely for thermodynamic reasons. A higher island density was experimentally observed in many systems when a surfactant is used,[14,15,23] and this was considered by many authors to be the main effect of the surfactant (although different atomic mechanisms were proposed to explain this increase in the island density[13,16,19,20,24]). However, to our knowledge, no direct proof has been reported showing that, in fact, the thermodynamic equilibrium state of the system, even in the presence of the surfactant, is that of a 3D island film. In this paper we show that, for the growth of Fe on Cu(111), where Pb has been proven to be an efficient surfactant for the early stages of growth at room temperature,[25] this is indeed the case, i.e., although thermodynamic reasons (a very low surface energy) make the surfactant float on top of the Fe film, the equilibrium configuration consists of 3D iron islands on top of the copper surface. Consequently, the main role of the surfactant layer can unambiguously be ascribed to kinetic reasons: the reduction of the surface mobility of the Fe adatoms over the Cu surface when Pb is present.

II. EXPERIMENT

The experiments were performed in an ion-pumped ultrahigh-vacuum chamber equipped with a homemade scanning tunneling microscopy (STM) unit and a rear-view four-grid low-energy electron-diffraction (LEED) optics, which was also used to acquire Auger electron spectroscopy (AES) spectra. The substrate was a Cu(111) single crystal mechanically polished and cleaned by cycles of Ar$^+$ sputtering (500 eV) and annealing at 850 K, until no contamination was present in the AES spectrum. The LEED pattern of this surface presented the expected 1×1 threefold symmetry char-

acteristic of the (111) face of the fcc substrate. Deposition of Pb and Fe was carried out by evaporation from Pb and Fe dispensers heated by electron bombardment. Although this procedure was reported to produce metal ions that can modify the growth behavior,[26] no noticeable differences were found when comparing with results obtained with a Knudsen-type effusion cell.[27] For low coverages, the deposition rate was calibrated by measuring the fraction of covered surface in the STM images. Larger coverages were deduced from the evaporation time, and cross-checked by the ratios of the low- and high-energy Auger peaks of Fe and Pb with respect to that of Cu. The error in the coverage was estimated to be around 20%. The STM tip was a chemically etched, polycrystalline tungsten wire. The piezodrives were calibrated vertically by measuring the step height in the clean Cu(111) surface, and laterally by measuring the nearest-neighbor distance in images with atomic resolution. Two sets of experiments were made. In the first, the substrate was kept at room temperature during the Fe deposition, while in the second it was kept at 400 K. The substrate was always at room temperature during the Pb deposition. STM images were recorded at 300 K in the constant current mode.

III. RESULTS

The Pb-aided growth of Fe on Cu(111) was recently the subject of a detailed STM study,[25] whose main results are summarized in Fig. 1: The left panel shows typical STM images taken after depositing, at room temperature, increasing amounts of Fe on the bare Cu(111) surface, while the images in the right panel have been taken when similar amounts of Fe have been deposited on the Cu(111) surface precovered with one monolayer of Pb.

As previously reported,[27] during the early stages of growth on the clean surface the deposited Fe forms three-dimensional islands whose height increases quickly with the Fe coverage Θ. For $\Theta \sim 1.3$ ML [Fig. 1(a)] approximately 50% of the Cu surface is covered by islands of a quasihexagonal (or triangular) shape and mostly two layers high. The island density (for a deposition rate of ~ 1 ML/min) is $(7.3 \pm 0.2) \times 10^{11}$ cm^{-2}, and remains constant between 0.5 and 2.5 ML. When the coverage increases to ~ 2.0 ML [Fig. 1(b)] the shape of the islands becomes more irregular and their height increases, most of the islands now being four layers high. Further Fe deposition [see Fig. 1(c), $\Theta \sim 3.0$ ML] makes the islands grow laterally until they cover completely the Cu surface. The uncomplete coalescence of the islands leaves voids between them, giving rise to a granular, discontinuous film where the individual grains will eventually transform to a bcc structure upon further deposition.

The most evident effect of the Pb overlayer during the beginning of growth [see Fig. 1(d), $\Theta \approx 0.8$ ML] is to increase the island density [which now becomes $(30 \pm 2) \times 10^{11}$ cm^{-2}, almost four times larger than in the absence of Pb], and consequently to decrease the lateral size of the islands, which are still mostly bilayer high. Increasing the Fe coverage [see Fig. 1(e), $\Theta \approx 1.6$ ML] makes the islands grow laterally until they completely cover the Cu surface. Now the
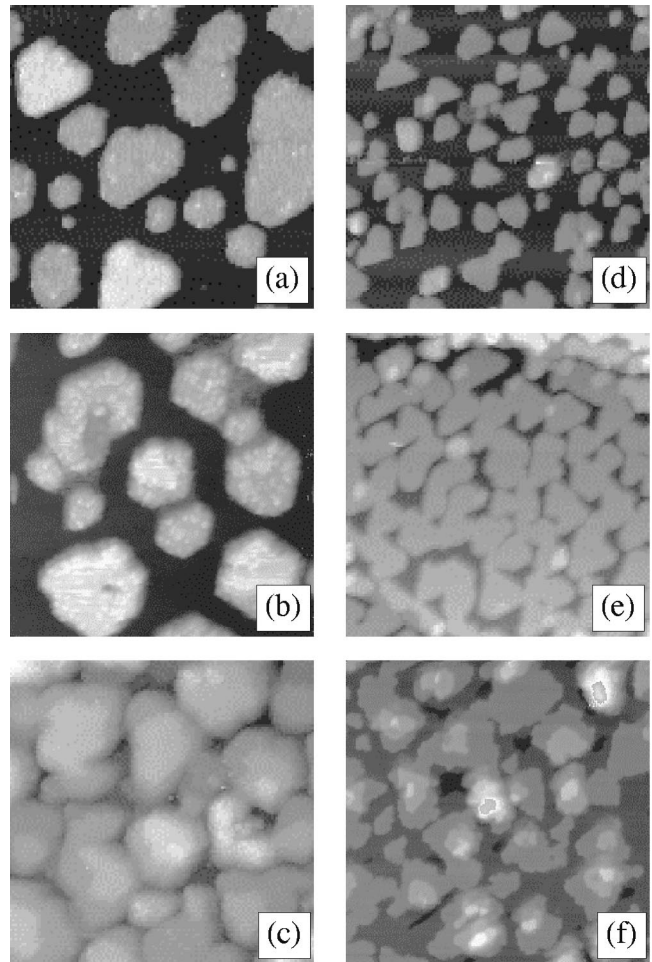

FIG. 1. STM images (500×500 Å^2) taken after depositing increasing amounts of Fe at room temperature on clean Cu(111) (left panel) and on Cu(111) precovered with 1 ML of Pb (right panel). (a) 1.3 ML of Fe. (b) 2.0 ML of Fe. (c) 3.0 ML of Fe. (d) 0.8 ML of Fe. (e) 1.6 ML of Fe. (f) 2.9 ML of Fe.

coalescence of the islands proceeds in a smooth way, which makes this Fe bilayer continuous and epitaxial rather than granular. However, once the first bilayer is completed the growth proceeds in a Poisson-like mode,[25] i.e., there is no interlayer mass transport [see Fig. 1(f), $\Theta \approx 2.9$ ML], which gives rise to a multilevel, although still continuous, Fe film. During all these processes the Pb overlayer is floating on top of the surface, forming a 4×4 superstructure, just as on the clean Cu surface.

Thus the Pb overlayer seems to be an efficient surfactant during the early stages of the growth of Fe on Cu(111) although, contrary to the case of Co on Cu(111),[23,28] its effects are not enough to promote layer-by-layer growth for large Fe coverages. Nevertheless, the role of the Pb layer during the early stages is able to transform a granular, polycrystalline iron film, into a continuous and epitaxial one (although with many different levels) even for high Fe coverages (up to $\sim 6-7$ ML). As mentioned above, the most visible mechanism through which this surfactant action proceeds is an increase in the island density, which admits, in principle, a
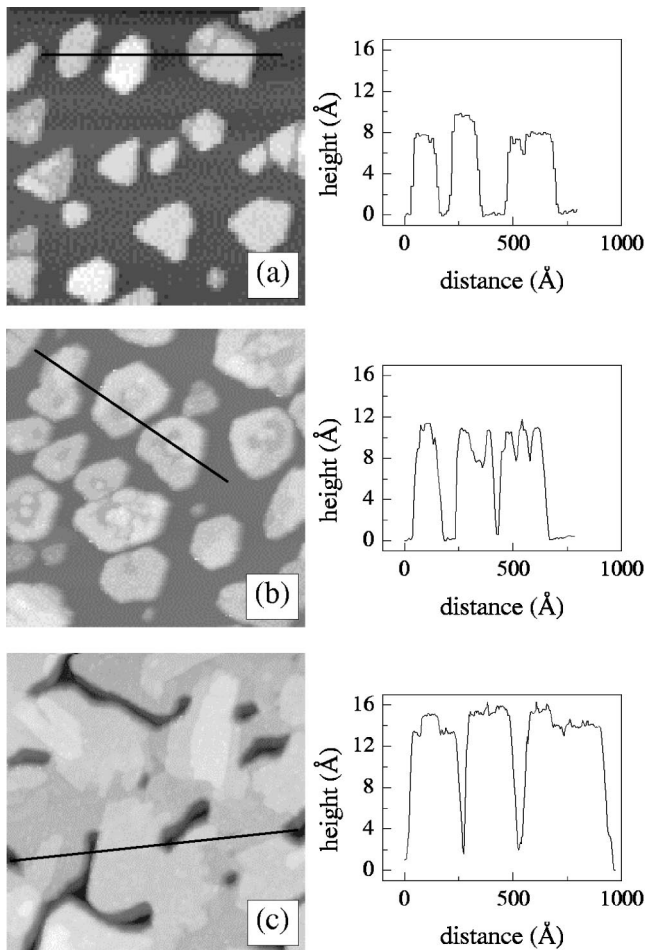
FIG. 2. STM images (1000×1000 Å^2) taken after depositing increasing amounts of Fe at 400 K on clean Cu(111). (a) 0.8 ML of Fe. (b) 2.4 ML of Fe. (c) 6.0 ML of Fe. The right panel shows representative line scans along the lines drawn in the images.

FIG. 3. STM images (1000×1000 Å^2) taken after depositing increasing amounts of Fe at 400 K on the Cu(111) surface precovered with one monolayer of Pb. (a) 0.8 ML of Fe. (b) 2.4 ML of Fe. (c) 6.0 ML of Fe. The right panel shows representative line scans along the lines drawn in the images.

simple explanation: the presence of the Pb layer decreases the effective mobility of the Fe atoms by, probably, increasing the energy barrier for terrace diffusion. Actually, it has been shown that in the homoepitaxial growth of Cu on Cu(111) the Pb overlayer not only modifies the energy barrier for terrace diffusion, but also changes the diffusion mechanism of the Cu atoms, which instead of moving by hopping now diffuse by exchange under the Pb layer.[19] Although there are no results for the Fe/Pb/Cu(111) system, it is reasonable to assume that the Pb overlayer will at least modify the diffusion parameters (energy barrier and/or diffusion coefficient). In this case, the surfactant action could be explained entirely as a kinetic effect. However, an alternative explanation is also possible. The low surface free energy of lead makes the Pb overlayer float during growth, and modifies the state of thermodynamic equilibrium of the system, which now consists of an iron film (not 3D islands) covered by the Pb monolayer, the increase in the island density just being the way to reach this new state. Although at room temperature the net effect could be the same, the difference between these two explanations is not insubstantial, because what is at stake is the real equilibrium configuration of the
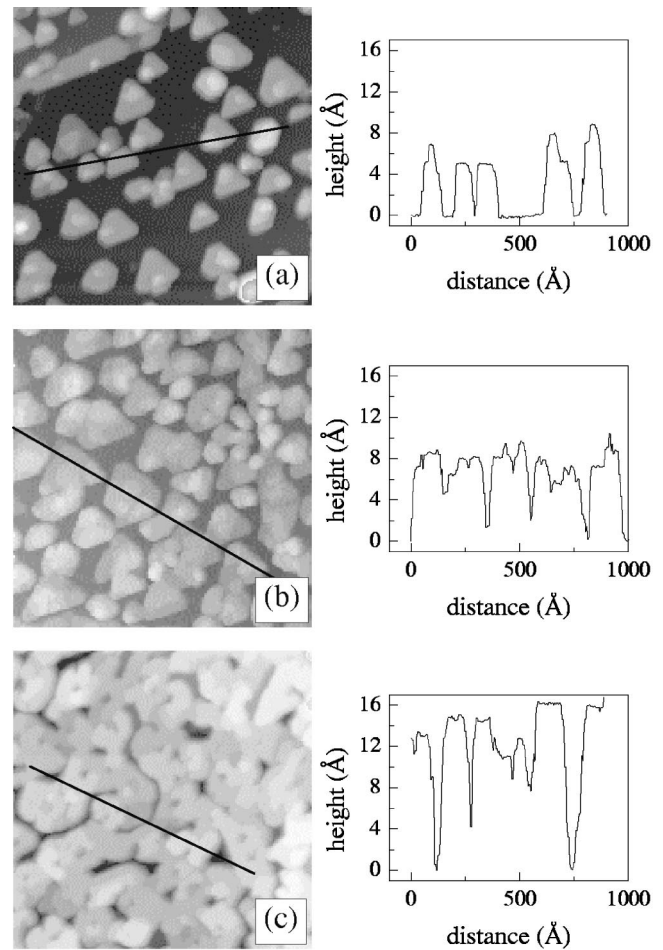
system: if this is a 2D iron film, an increase in the deposition temperature will produce a smoother Fe film; on the other hand, if the energy balance favors the growth of 3D clusters, a higher temperature will remove the kinetic limitations imposed by the presence of the Pb layer, leading again to a Volmer-Weber mode of growth.

To distinguish between the two possible explanations, we have deposited different amounts of Fe, on both the clean Cu surface (Fig. 2) and the Pb-precovered Cu surface (Fig. 3) at a slightly higher temperature, which should lead the system closer to a true equilibrium state. The image in Fig. 2(a), taken after depositing $\sim$0.8 ML of Fe on clean Cu(111) at 400 K, clearly illustrates the main effects of the higher deposition temperature: first, due to a larger surface diffusion, the island density has decreased with respect to the deposition at room temperature [Fig. 1(a)] down to $(3.0 \pm 0.5) \times 10^{11}$ cm^{-2}; second, the average height of the islands, that now cover only $\sim$20% of the substrate surface, has increased to $\sim$8 Å. As demonstrated by the line profile, most of the islands are now four layers high. These results are in agreement with the predicted thermodynamic equilibrium state of
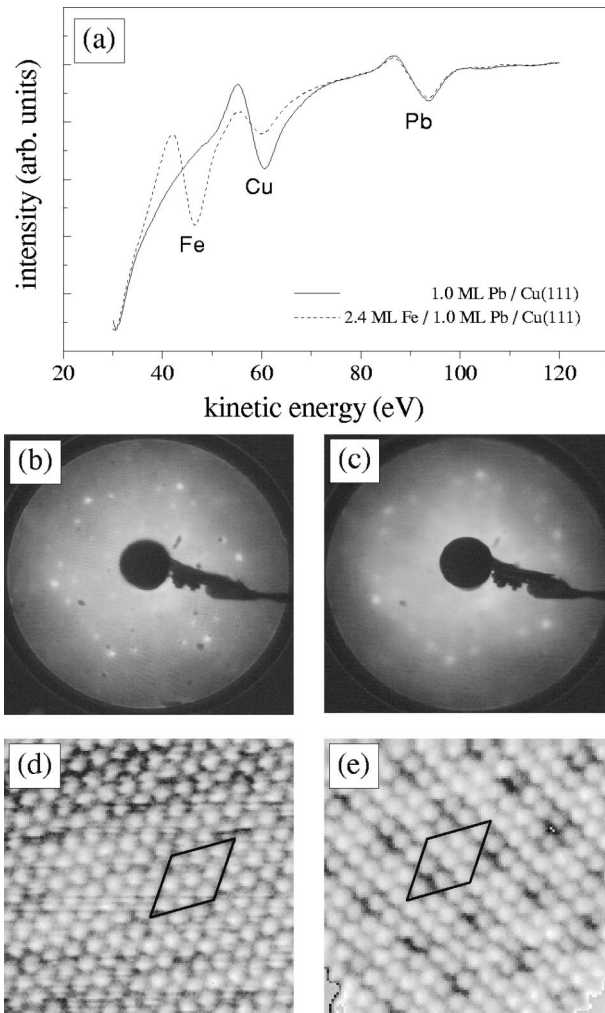
FIG. 4. (a) Auger spectra taken before (solid line) and after (dotted line) depositing 2.4 ML of Fe at 400 K on a Cu(111) surface precovered with 1 ML of Pb. (b) and (c) LEED patterns taken before and after the Fe deposition. (d) and (e) Atomic resolution STM images taken before and after the Fe deposition.

the system: since the surface free energy of iron (2.9 J/m^2) is much larger than the surface free energy of copper (1.9 J/m^2), the iron film does not wet the copper surface, but tends to agglomerate into clusters, growing in the form of 3D islands. At room temperature, kinetic considerations restrict both the terrace and the upward diffusion of the deposited atoms in such a way that, for low coverages, only bilayer islands are formed [Fig. 1(a)].

On the other hand, at 400 K, when the Fe coverage increases to ~2.4 ML [Fig. 2(b)], the density of islands increases slightly as well as the lateral size and height of the 3D islands. The shape of the island is no longer triangular, but hexagonal-like, and the top surface displays a rather peculiar morphology. As indicated by the line profile, they seem to be composed of a higher rough external shell, a lower, smoother, intermediate layer, and a higher, again rough, inner core. We think that this difference in roughness is related to a different crystalline structure: if the outer and inner layers are bcc-like, the intermediate layer is still fcc.

Further Fe deposition causes the islands to coalesce, al-

though even after depositing ~6.0 ML of Fe [Fig. 2(c)] the film does not perfectly cover the substrate surface, but deep voids have been left behind. The line profile shows that the top surface presents a very small roughness, with only 2–3 levels exposed simultaneously.

Representative results for deposition at 400 K on the Pb-precovered surface are shown in Fig. 3. As expected, after depositing ~0.8 ML of Fe [Fig. 3(a)] the island density [$(7.6 \pm 0.5) \times 10^{11}$ cm^{-2}] is larger than without Pb, confirming that the Pb overlayer decreases the surface mobility of the Fe atoms. The islands are truncated triangles, all of them with the same orientation, which indicates that we are closer to equilibrium. The islands are bilayer high, but many of them present substantial populations of third to fifth layers. When compared with the room-temperature deposition the height of the islands has increased. This trend is confirmed when the coverage increases to ~2.4 ML [Fig. 3(b)]: the islands grow both in lateral size and height, the average height now being four layers. These comprise clear evidence of a 3D growth mode, which clearly demonstrates that the thermodynamic equilibrium state of the system consists of 3D iron cluster over the Cu surface even in the presence of the Pb surfactant layer. The floating of the Pb layer is clearly shown in Fig. 4, where the Auger spectra taken before (solid line) and after (dashed line) the deposition of ~2.4 ML of Fe at 400 K on the Pb [Fig. 3(b)] reveal that the intensity of the signal coming from the Pb overlayer remains constant. It must be noted that the detected Cu signal [Fig. 4(a), dashed line] comes from the part of the original surface still visible between the Fe islands [Fig. 3(b)]. In addition, the LEED patterns and the atomic resolution STM images of the surface shown in Fig. 4 indicate that this Pb layer shows similar 4×4 superstructures both before and after Fe deposition at 400 K. Further Fe deposition on the Pb-precovered surface [see Fig. 3(c), ~6.0 ML of Fe] gives rise to a surface very similar to that in Fig. 2(c) for deposition on the clean Cu(111) surface, with only a smaller size of the characteristics features of the surface. At this point the Auger Cu signal has disappeared almost completely.

IV. CONCLUSIONS

In the preceding discussion we have not taken into account the possibility of any interdiffusion taking place between the deposited Fe and the Cu substrate. According to the bulk phase diagram,[29] the mutual solubility of Cu and Fe is negligible (<0.1 at %) below 850 K. Although surface segregation of Cu to the surface of the iron film occurs for growth at 300 K on the Cu(100) surface,[30] on the (111) surface it appears to be a minor effect below 400 K.[31] Actually, calculations using a many-body interaction potential showed that atomic exchange of Fe on Cu(111) has a barrier of over 1 eV due to the close-packed nature of the (111) surface.[32] Thus, although interdiffusion cannot be completely excluded, especially near the steps[33] or at high temperatures, it seems not to play a major role during growth. Nevertheless, since the surface free energy of Fe is higher than for Cu, it is expected that the tendency to agglomerate into clusters of any Fe-Cu mixture will be smaller than the one of pure Fe.

Since Fe clusters are formed, even with the Pb overlayer, this must be the real equilibrium state of the Fe film.

Thus we have demonstrated that the presence of a Pb overlayer in an Fe/Cu system does not modify the thermodynamic equilibrium state, but merely freezes the kinetics of the system, decreasing both the lateral and upwards diffusion of the Fe atoms. An increase in the deposition temperature overcomes these limitations, and drives the system closer to the true equilibrium state: a 3D iron film over the Cu surface, even if covered by the Pb layer.

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