

Atomistic Mechanism of Surfactant-Assisted Epitaxial Growth

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Experiments and simulations on the effect of a surfactant on atomic diffusion are presented. Cu adatoms deposited on a Cu(111) surface covered with a monolayer of Pb quickly get buried and diffuse under the Pb layer by exchanging sites with other Cu atoms from the substrate. The surfactant induces layer-by-layer growth by suppressing the hopping mechanism of diffusion over the terraces and promoting atomic exchange, both at the terraces and across the steps. This mechanism may be rather general and has profound implications for the synthesis of artificial materials. [S0031-9007(98)06721-0]

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Our comprehension of the atomistic mechanisms of epitaxial growth has increased significantly in the past few years [1]. This improved understanding had led to the fabrication of elaborated artificial structures, such as magnetic superlattices, which involve the growth of flat and structurally perfect layers [2]. At high enough temperature, step flow growth always takes place, at least for homoepitaxial growth. In heteroepitaxy, however, elevated temperatures must usually be avoided due to the risk of massive interdiffusion that would destroy these structures. On the other hand, lowering the growth temperature leads to the periodic nucleation of islands on the terraces, which grow laterally until coalescence occurs. Ideally, it would be desirable that no level starts to grow before the preceding one is completely filled. This "layer-by-layer" (LbL) mode of growth, unfortunately, is the exception rather than the rule, and films frequently grow in a multilayer fashion.

Let us focus on the homoepitaxial growth of a fcc metal such as Cu. On Cu(100) one can always find conditions for growth to take place in a LbL fashion [3]. In that case many surface properties (work function, step density, etc.) oscillate with monolayer (ML) periodicity, thus allowing us to monitor growth with atomic precision. As an illustration of LbL growth, Fig. 1a shows that during the evaporation of Cu on Cu(100) at 300 K, the specularly reflected intensity of a beam of He atoms of thermal energy (TEAS) oscillates with a period of precisely 1 ML [3]. On the contrary, when Cu is deposited at 300 K on Cu(111), surface roughness increases continuously, the film morphology is 3D, and the specular intensity (Fig. 1b) decreases smoothly. In fact, in the temperature range from 125 to 500 K LbL growth is not observed in agreement with previous reports [4,5]. These findings are quite general: while for homoepitaxial growth on fcc (100) substrates oscillations are common [6], on (111)-oriented substrates they have only rarely been observed [7].

Recently it was found that covering fcc (111) faces with a compact layer of some additives, termed surfactants [8–10], prior to the deposition of the corresponding metal promotes LbL growth. Figure 1c shows oscillations of the reflected He intensity recorded during the evaporation of Cu on a Cu(111) crystal previously covered by a monolayer of Pb. These oscillations, detected in a wide range of temperatures and evaporation rates [11], are very

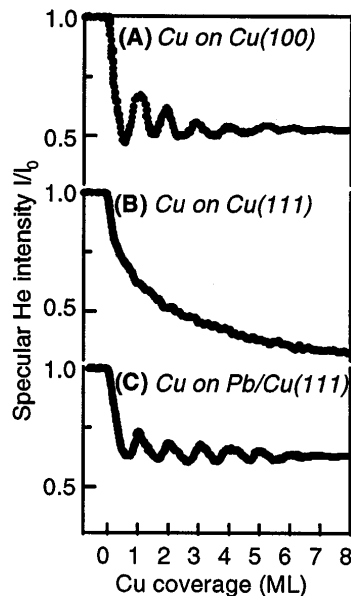


FIG. 1. Normalized specular intensity of a beam of 67 meV He atoms reflected from the sample under antiphase conditions during homoepitaxial growth of Cu at 300 K: (a) On Cu(100), layer-by-layer (LbL) growth is revealed by the periodical oscillations of the specular intensity; (b) on clean Cu(111), the monotonic decrease of the intensity signals 3D growth; (c) using Pb as surfactant, LbL growth is induced on Cu(111). The deposition rate was 0.02 ML/s in all cases.

similar to the ones shown in Fig. 1 for Cu(100) and indicate that the growth mode has changed to LbL. Suitable surfactants have also been shown to facilitate LbL growth of heteroepitaxial films, e.g., Co/Cu(111) [12,13], Cu/Ru(0001) [14], and Cu/Co superlattices [15] at reduced temperatures. In particular, the use of Pb as a surfactant allows a precise control and a substantial improvement of the resulting magnetic properties [2,12]. However, the atomistic mechanism of its surfactant action remains unknown.

The essential physical processes determining the growth mode are diffusion and nucleation, and, in particular, the relative efficiency of intra- and interlayer mass transport. If interlayer diffusion is only slightly less efficient than intralayer diffusion, a reasonably perfect LbL growth results, whereas if step crossing is much slower than surface diffusion, 3D growth sets in. Interlayer mass transport is usually controlled by an additional energy barrier to descend the steps, known as the Ehrlich-Schwoebel (ES) barrier [16]. On Cu(100) the ES barrier is relatively small and the activation energy for diffusion rather large (0.4 eV) [3], which results in the desired LbL growth. On clean Cu(111), on the other hand, the energy barrier for hopping over the surface is extraordinarily small, e.g., ~ 0.03 eV [4]. Intralayer diffusion is, thus, very efficient while interlayer mass transport is strongly hindered by a significant ES barrier (e.g., 0.12 eV at 100 steps [17]). Thus, nucleation on top of the islands occurs well before coalescence takes place, resulting in 3D, pyramidal growth.

In the following we concentrate on the influence of Pb as a surfactant in changing the diffusion mechanism and accordingly the growth of Cu on Cu(111). Deposition

of 1 ML of Pb on clean Cu(111) produces a (4×4) superstructure detected by low energy electron diffraction (LEED) [15] and scanning tunneling microscopy (STM). The (4×4) superstructure is due to a compact, quasi-hexagonal layer of Pb atoms residing on top of the Cu(111) surface [18]. The left panel in Fig. 2 reproduces TEAS oscillations measured during deposition of Cu on Pb/Cu(111) at 280 K under antiphase conditions. The intensity at each layer's completion ($\sim 60\%$ of the initial value) indicates that a reasonably perfect LbL growth (e.g., $\sim 95\%$ of the first layer population for 1 deposited ML) is taking place. After deposition, the increased width of the specular peak (not shown) signals the existence of smaller (80 \AA) ordered domains due to the Cu islands formed below the Pb layer. Indeed, the STM images of the central panel in Fig. 2, recorded after deposition on the surfactant-covered surface, show that the LbL growth is associated with a large ($1.4 \times 10^{12} \text{ cm}^{-2}$) density of islands nucleated at the terraces with only two levels exposed, in agreement with previous results for other systems [10]. The atomically resolved image of the inset proves that the (4×4) superstructure of Pb still exists on top of every terrace and island. Thus, the surfactant efficiently floats at the external surface, and LbL growth occurs.

Since the island density is more than 2 orders of magnitude larger than for growth on clean Cu(111), the effective adatom diffusion in the presence of the surfactant must be smaller. How does the diffusion process take place? There are two possibilities: either the Cu atoms diffuse on top of the surfactant layer first and get buried then or they exchange positions with a surfactant atom near the point of impact and diffuse later under the Pb overlayer. The left

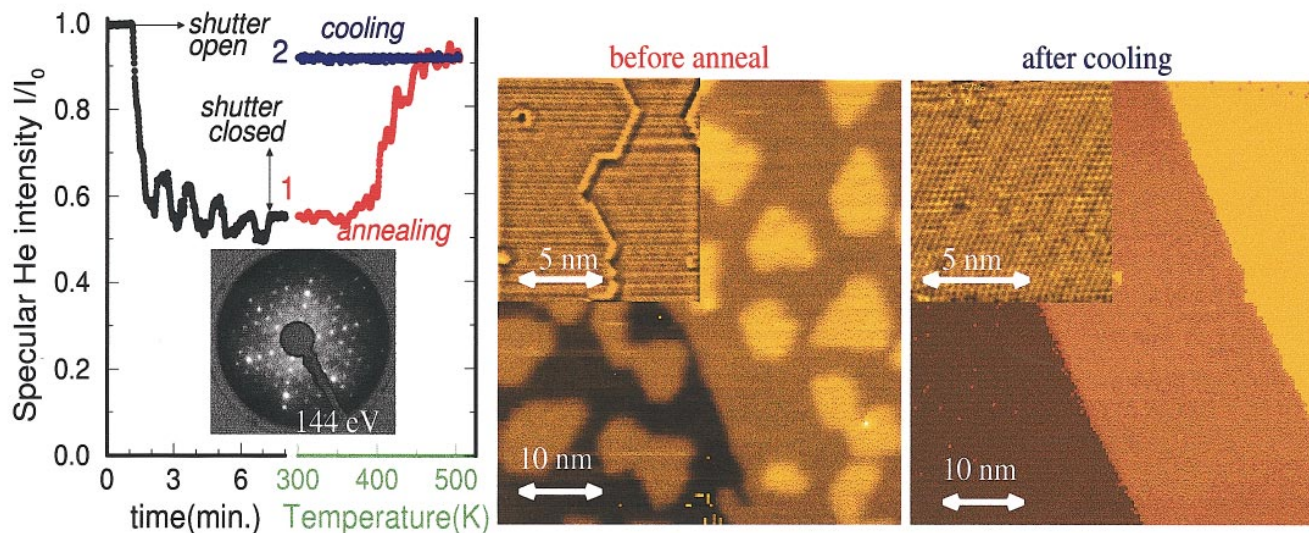


FIG. 2(color). Left: Normalized specular intensity of He (under antiphase conditions) during Cu deposition at 280 K on Pb/Cu(111), annealing to 500 K and cooling to 300 K. The intensity increase indicates a recovery of the original surface morphology. Inset: LEED pattern observed continuously during the process. Center: STM image of the surface at stage 1 showing Cu islands covered by Pb (4×4) . Right: STM image at stage 2. The islands formed during LbL growth have dissolved upon annealing.

panel of Fig. 2 shows that annealing the Pb-covered film leads to an unexpected result: the intensity of the specular beam (corrected by the experimentally determined Debye-Waller behavior of Pb) starts increasing at 400 K and at 450 K reaches $\sim 90\%$ of the value corresponding to the original surface. This intensity recovery is accompanied by the corresponding decrease in the width of the specular peak. As shown in the inset, the (4×4) LEED pattern due to the Pb superstructure is visible during the whole process. STM images recorded after annealing (Fig. 2, right panel) show the complete disappearance of the islands and the persistence of the (4×4) arrangement of Pb atoms: the morphology of the starting surface has been recovered. Since the islands were initially buried below the surfactant, we are forced to consider the possibility that their dissolution and the diffusion of Cu atoms to the steps have taken place underneath the compact Pb overlayer.

To get insight into these phenomena we have resorted to computer simulation. We use a Monte Carlo (MC) method that employs realistic potentials including a density-dependent term to account for many-body interactions [19]. The potentials have been optimized to reproduce the cohesive energy, bulk modulus, and phonon spectrum of bulk Pb and Cu, and have reproduced the ordered structure and melting behavior of Pb overlayers on Cu(100) [20]. The MC simulation considers a compact layer of 72 atoms of Pb plus 6 layers of 128 atoms of Cu each; the last 2 Cu layers were frozen, while all other atoms were allowed to move. The system correctly predicts the (4×4) superstructure of the Pb overlayer on Cu(111). The upper panel in Fig. 3 displays the evolution of the z coordinate of a Cu adatom deposited at a random position on the Pb surface for several representative MC runs at 540 K. The lower panels visualize the actual atomic configuration at four selected instants of a particular simulation run. The picture that emerges from these results is quite surprising: upon arrival (panel 1), the Cu adatom immediately displaces a Pb one and gets buried (panel 2) without any lateral displacement beyond what is necessary to reach the nearest high-symmetry adsorption site. This direct Cu-Pb exchange has been found in all simulations and even at temperatures as low as 50 K. The extreme efficiency of the lifting process justifies the floating of Pb at the external surface experimentally reported after growth of 100-Å-thick Co/Cu superlattices [2]. Once that the Cu atom is below the surfactant layer, the only diffusion process that we have observed consists in exchange with another Cu from the layer underneath the Pb. Instead of hopping, the lateral diffusion of the incoming adatom is achieved by a concerted, simultaneous displacement of another one that is pushed out from the Cu surface layer (panel 3) and replaced by the former. The displaced Cu atom is not the one closest to the incoming one but the next-nearest neighbor, as shown in the 4th panel of Fig. 3. This is in agreement with previous molecular dynamics simulations on Cu(100) [21]. Then, in turn, the displaced

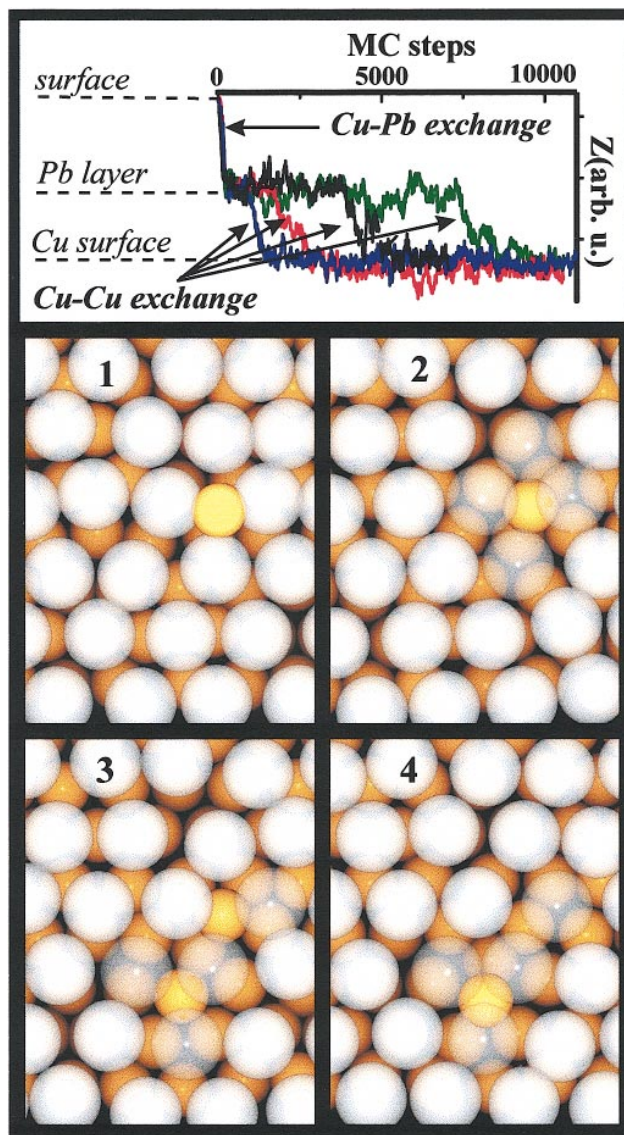


FIG. 3(color). Upper panel: Evolution of the z coordinate of a Cu adatom during several MC runs for growth on Pb-covered Cu(111). The deposited atom exchanges position with a Pb one after arrival and later diffuses below the Pb layer by successive Cu-Cu exchanges. Lower panels: Top view of the actual atomic configuration at four selected moments of the simulation. The Cu adatom (yellow) sits on top of the Pb overlayer (1), gets buried below it (2), and starts entering the Cu surface, pushing out another Cu atom (3), which eventually goes out while the original adatom occupies a site in the Cu surface (4). The color of Cu atoms is keyed to the local height. Pb atoms are white, except those just above the Cu ones involved in the exchange.

atom repeats the process (not shown). We have never observed diffusion of Cu on top of the Pb overlayer or hopping underneath it. This is completely different from the mechanism of hopping over the surface by which the simulations indicate that the diffusion of Cu on clean Cu(111) proceeds. Furthermore, exchange diffusion under the Pb surfactant is considerably slower than hopping on

clean Cu(111). This is consistent with the larger density of islands observed by STM and TEAS.

Now, in order to modify the growth mode, the presence of the surfactant should vary the relative importance on intra- and interlayer diffusion. In our simulations we have found that isolated adatoms approaching a descending step on clean Cu(111) at and above 300 K almost always are able to descend the step edge. They do it by pushing out one edge atom rather than jumping over the edge. This exchange mediated descent occurs for both types of steps, i.e., A type, 100 oriented and B type, 111 oriented. It seems to be somewhat easier to jump down B-type steps, but the difference in our simulations is not significant. Thus, the exchange-at-steps mechanism is the dominant mode of interlayer transport [22]. Since on clean Cu(111) it is always slower than the fast diffusion by hopping on terraces, interlayer mass transport is less efficient than intralayer diffusion and the adatoms nucleate islands before they fill the previous level, causing 3D growth.

Our simulations also show that on Pb-covered Cu(111) surfaces exchange is still operative at steps. In this way the push-out exchange process at island edges becomes an efficient channel for step crossing, in a way that resembles the model proposed by Zhang and Lagally [23]. From these results we conclude that the main effect of the Pb surfactant is to modify the mechanism of atomic diffusion on the terraces of Cu(111), which now takes place below the surfactant layer and by exchange. In the case that we have studied, surfactant-assisted exchange diffusion on the terraces promotes LbL growth by slowing down intralayer diffusion with respect to the clean surface, while the interlayer transport, once that Cu islands are formed under the Pb overlayer, still occurs by exchange with step atoms with only a minor increase in its efficiency. The deposited Cu adatom is incorporated so easily into the Pb layer that the hopping mechanism of diffusion, previously dominant, is suppressed. The concerted exchange process, practically impossible on clean Cu(111), is now facilitated by both the increased coordination offered by the surrounding Pb atoms and the prolonged residence time of the adatom at a given adsorption site which favor the correlated displacement required for the exchange process [24]. If this model is correct, the effect is strictly local and requires a compact layer of surfactant to act. In fact, the films with the best structural quality are obtained when the whole substrate surface is covered with a full monolayer of Pb.

The mechanism proposed here is probably also operative in explaining the reported changes to LbL growth for other cases of surfactant-assisted homoepitaxy [10] and heteroepitaxy [12–14]. If this is the case, one may predict that there will be an unavoidable, albeit limited, intermixing at the interfaces. As a result, good LbL growth can be obtained for systems that grow spontaneously with a very large roughness at the cost of a small interdiffusion.

In summary, we have presented evidence suggesting an atomistic interpretation of surfactant activity in terms of

very basic alterations of the elementary mechanisms of surface diffusion. The processes involved in this phenomenon are general enough to guarantee that many different surfactant agents will produce similar results. Besides, our increased understanding of the factors that control atomic diffusion opens up the possibility to develop novel procedures to achieve the desired degree of perfection in epitaxial heterostructures.

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