Surfactant effect in heteroepitaxial growth. The Pb - Co/Cu(111) case

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A MonteCarlo simulations study has been performed in order to study the effect of Pb as surfactant on the initial growth stage of Co/Cu(111). The main characteristics of Co growing over Cu(111) face, i.e. the decorated double layer steps, the multiple layer islands and the pools of vacancies, disappear with the pre-evaporation of a Pb monolayer. Through MC simulations, a full picture of these complex processes is obtained. Co quickly diffuses through the Pb monolayer exchanging place with Cu atoms at the substrate. The exchange process diffusion inhibits the formation of pure Co islands, reducing the surface stress and then the formation of multilayer islands and the pools of vacancies. On the other hand, the random exchange also suppress the nucleation preferential sites generated by Co atoms at Cu steps, responsible of the step decoration.

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I. INTRODUCTION

The startling, and sometimes surprising physical properties observed in the new series of artificial materials, has catapulted an intensive work around the world. The experimental conditions needed to obtain atomically clean and nearly perfect flat substrates are achieved in most surface labs. Currently, almost any atom can be deposited over almost any surface, allowing the creation of phases that are not found in nature. But, the way the atoms diffuse over the terrace (intra layer diffusion) and the ability to overcome terrace steps (inter layer transport) before binding other walking atoms, will determine the morphology of the growing film. Being intermixing and surface roughness development the most common artifacts in the preparation of these materials, the obtainting of flat films through layer by layer growth (LbL) is mostly the exception than the rule. External parameters, like substrate temperature and evaporation rate among the most usual, and internal ones, like interaction potentials, Ehrlich-Schwoebel barrier, diffusion type, surface orientation and so on, are crucial in determining the type of film growth [1-4]. On the other hand, the evaporation or adsorption of some materials, known as surfactants, previous to the metal deposition has proved to promote LbL growth [6]. A perfect example of this behavior is the growth of Cu over Cu(111). In fact, while in absence of surfactant Cu grows in a 3D fashion over Cu(111), after the pre evaporation of a monolayer of Pb, LbL growth in a wide range of temperatures and evaporation rates can be obtained. [8] In a recent work, we showed that the monolayer of Pb changes the diffusion mechanism of Cu over the surface from hopping to atomic concerted exchange, turning the diffusion over Cu(111) surface like over the Cu(100) one, where LbL growth is usually obtained [8].

The growth of Co over Cu(111), on the other hand, is a good example of hetero-epitaxial non LbL growth. Multiple height island formation, step decoration, vacancy (pools) islands and Cu-Co intermixing are common features in this system [9]. In a recent work, we showed that this behavior depends on the adsorbate - substrate interaction, and it should be awaited any time materials of these types are put into contact [11]. As in the case of Cu/Cu(111), the pre-evaporation of a monolayer of Pb acts as a surfactant promoting 2D growth, and allowing the fabrication of good quality magnetic multilayer. In this work we present results, based on MonteCarlo simulation about the effect of Pb as surfactant for heteroepitaxial growth, in particular we analyze the case Co/Cu(111)

II. COMPUTATIONAL DETAILS

The interaction potentials employed in our MC simulations have been obtained using the second-moment approximation of the tight-binding scheme (TB-SMA) [12]. They include a short-range, repulsive pair potential plus a long-range, many-body contribution based on a tight-binding description of the electronic structure [13]. They have been successfully used previously to study the properties of transition metal surfaces [14], noble metals [15] and microclusters [16]. This potential will be used for the six involved interactions, i.e. Co-Co, Pb-Pb, Cu-Cu, Co-Cu, Co-Pb and Cu-Pb with their correspond-
ing physical parameters. The potential at the $i-th$ atom is given by

$$V_i(r_{ij}) = U \{ A \sum_j \exp[-p(r_{ij} - r_0)]$$

$$- \{ \sum_j \exp[-2q(r_{ij} - r_0)] \}^{1/2} \}$$

(1)

where $r_{ij}$ is the distance between the two atoms at $r_i$ and $r_j$, respectively, $r_0$ is the nn distance of the bulk crystal, $U$, $A$, $p$ and $q$ are parameters. In this paper, the sums are performed over all atoms within a sphere of radius equal to 3.2 times the Cu nn distance. We have checked that including interaction between further atoms does not alter the conclusion of this paper. The many-body interactions are included in the potential through the square root of the second sum. This term takes into account the essential band character of the metallic bonds. The value of $A$ is determined minimizing the cohesive energy of the bulk crystal with nn distance $r_0$, while the values of $U$, $p$ and $q$ are determined in such a way that the bulk cohesive energy and the bulk modulus calculated using (1) and the experimental value of $r_0$ are in good agreement with the experimental bulk cohesive energy and bulk modulus. The values $p = 9/r_0$ and $q = 3/r_0$ are found to be appropriate for the surface. The interactions between the different types of atoms are determined by sets of six parameters $\{ U_i, p_i, q_i \}$: $i = 1$ stands for Cu-Pb pairs, $i = 2$ for Pb-Pb, and so on. $r_0$ are the bulk nearest-neighbor (nn) distances. The validity of this approximation has been tested in previous studies with this combination of elements. The ordered structures and melting behav-

III. RESULTS AND DISCUSSION

As different as the growth processes of Cu and Co over Cu(111) is, the effect of Pb as surfactant recognizes the same root. Cu grows over Cu(111) in 3D from the beginning. This is so due to the low intralayer diffusion barrier compared to the interlayer one (Ehrlich-Schwoebel barrier). The presence of a monolayer of Pb changes the diffusion mechanism from hopping to exchange, making both barriers of the same order. In absence of any other effect, this is enough to promote 2D growth. The heteroepitaxial growth of Co over Cu(111) is by far more complex. The growth of Co over nude Cu presents the formation of double atomic height decorated steps, multilayer islands and pools of vacancies. Through ion scattering spectroscopy and chemical titration it has been shown that these islands are actually formed by a mixture of Co and Cu atoms. In a recent paper we showed that the diffusion mechanisms, the larger surface energy of Co as compared to Cu, and the Co-Co and Co-Cu interaction potentials are the responsible of these features. Over the Cu terrace Co diffuses through hopping. In this way, the adatom nucleation gives place to the formation of pure Co island. Once the Co islands reach a critical size, they explode forming multilayer alloyed islands, and leaving pools of vacancies. On the other hand, the interlayer mass transport is produced, as in the case of Cu-Cu, through the exchange mechanism. But, in this case the process gives place to alloyed steps that act as nucleation sites for the diffusing Co adatoms, forming the double atomic height decorated steps.

The question to answer is then if the effect of Pb on Co/Cu(111) growth is similar to the homoepitaxial case. And if the change in the diffusion mechanism is enough to suppress all the different features appearing in Co/Cu(111), promoting 2D growth. This is just the case; in Fig.1 we show the evolution of a Cu (left panel) and a Co adatom (right one) over a Cu(111) surface pre-covered with a Pb monolayer, obtained through MC simulations. In the upper panel the evolution of the z coordinate (normal to the surface) is depicted vs. MC steps. As we know, a drop in the Z coordinate is a fingerprint of a concerted exchange process. Thus, the first drop observed in both cases represents the exchange of Cu (Co) atom with the surfactant. This exchange is very fast and it is the responsible of the floating of the Pb monolayer. The second drop in z coordinate (not always occurring within the elapsed time analyzed) corresponds to the CoCu (CuCu) exchange. As we showed for Cu, the Co diffusion over Pb/Cu(111) system occurs below the Pb layer and through the exchange mechanism. We should note that although Co and Cu adatom diffusion below Pb are quite similar, they are not identical as well. In the lower panel of Fig.1 we show a couple of snapshots of the MC diffusion simulations. We can see that substrate atoms involved in the concerted exchange mechanism are no the same in both cases. While CuCu exchange involves next nearest neighbors, the process in the CoCu case is between nearest neighbors. This difference is maintained for the following steps, always in the vicinity of the implanted Co atoms. Thus, although the adatom diffusion below the surfactant layer is still through concerted exchange, the presence of Co as impurity modifies the nature of the exchanging mecha-
anism. This difference with Cu/Cu exchange may have important physical consequences. In fact, we have already shown [1] that the interaction CoCu produces a dip binding well, locating the evolving atom in the near defect zone. Thus, the hopping mechanism will be more restricted than in the case of Cu/Cu. In fact, we are resembling the situation responsible of the step decoration [11], but in the middle of the terrace. Additionally, the probability of a Cu Co reverse exchange, i.e. extracting the Co atom again, will be larger than in a "long jump exchange "like in CuCu case, increasing in this way the probability of reacher Co island formation.

The change in the diffusion mechanism, from hopping to exchange is, as in the case of Cu over Cu(111), enough to explain all the features of the surfactant effect over the heteroepitaxial growth. In fact, through the exchange mechanism, very quickly the diffusing atoms turn to be Cu ones, and no pure Co island could be formed. The alloyed islands lowers the surface energy affecting the critical size instabilities we found for Co over nude Cu [10]. The non-adiabatic production of these alloyed islands, coming from the unstable pure Co islands, was the responsible of the appearance of the pools of vacancies and the multiple height island, which are hardly formed in the new scenario. The suppression of the decorated steps is based on the same mechanism. Since the diffusing atoms are mostly Cu ones, the CoCu alloyed steps, and thus the preferential nucleation sites located there, are not formed. The interlayer diffusion is still through concerted exchange, but the morphology of the steps does not change, since the exchanging process is mostly CuCu.

We have established that the 1 surface energy is the reason for the explosion of the Co islands., i.e. pure Co islands over Cu(111) surface are naturally unstable. The exchange diffusion mechanism will tend, as we discussed in the previous paragraph, to the formation of mixed Co-Cu islands, lowering the surface energy. But, we have not shown still to what extent this effect is sufficient to suppress the double height island formation. In fact, it could occur that the double height islands are still formed under different experimental conditions. For instance they may form with larger critical size, or they could depend on either coverage or evaporation rate. Actually, we have found that the CoCu islands are stable below the surface energy of Co over Cu(111) (middle). The complete process of multilayer mixed island and the appearance of vacancy pools is apparent. In the lateral sight (the right one) the mixed composition of the island is evident. In the upper vision (left one), the mobility of the island is also apparent. In the third lower panel, the surfactant assisted case, the Pb stabilized island is shown. Thus, the Pb modification of the diffusion mechanism not only prevent the formation of pure Co islands, promoting 2D growth, but also, in the remote, but statistically possible case that either Co pure or Co rich island are formed, the Pb layer acts stabilizing them.

IV. CONCLUSIONS

Through MC simulation, we have studied the growth of Co over Cu(111) in the presence of a surfactant (Pb) layer. We found that the surfactant changes the diffusion mechanism of Co over the surface from hopping to concerted exchange. An important difference with the previously reported surfactant effect on Cu/Cu growth, is that the exchange process involves nearest neighbor atoms. This effect reduces even more the hopping mechanism, and increase the probability of reverse exchange, only important in hetero epitaxy. The surface diffusion through exchange diminishes the probability of pure Co islands formation, which are the responsible of the multiple height and vacancy island formation. In the same way, the exchange mechanism suppresses the formation of the binding alloyed steps, responsible of the step decoration. Additionally, the coverage of the Co by Pb atoms diminishes the effect of the different surface energy between Cu and Co stabilizing even the pure Co island. This effect turns irrelevant the non zero probability of the formation of pure Co island.

[1] See F.Besembacher e.al in Growth and properties of ultrathin epitaxial layers, edited by D.A.King and D.P.Woodruff, The Chemical Physics of Solid Surfaces Vol. 8 (Elsevier, Amsterdam, 1997), Chap. 6, and references therein.
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FIG. 1. Surface diffusion of Cu and Co over Cu(111) pre-covered with a monolayer of Pb obtained by means of MC. First column, x, y and z evolution of Cu over Pb/Cu(111). The first drop corresponds to the initial Cu/Pb exchange; Second column: as in a, for Co adatom diffusion. Lower panel: top views showing the exchange between the Cu substrate atoms (gray clear - gray obscuro circle) and the subsurface evolving adatom, i.e. Cu or Co (black circle). Note that while the exchange Cu/Cu is with the next-nearest neighbor, in the Co case is with the nearest one. The Pb atoms are not shown in the last frames for clarity.

FIG. 2. Co comparative island stability over Cu(111) with and without a surfactant layer. Upper (first column) and lateral (second column) view. Upper panel: Original situation for a Co island over the critical size. Middle panel: snapshot of the Co island over nude Cu, the multilayer island formation, together with the pools of vacancies can be observed. Lower panel: the evolution of the same Co island, under the surfactant layers is shown. The island, as well as the substrate, shows some kind of corrugation, but for comparative times, the island stability is proved.
Co / Pb / Cu(111)

adatom level

Pb level

Cu level

Height (z)

Mc steps *10
Initial pure Co island

without surfactant

with surfactant