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Ion bombardment induced alloying as layer by layer promoter in heteroepitaxial growth

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Abstract

By means of numerical simulations (Monte Carlo and Molecular Dynamics), we have studied the atomistic mechanisms involved in the growth of Co over Cu(1 1 1). We determined the role of the interface alloying as layer by layer growth promoter, and explored the capability of using direct ion beam deposition to tailoring this alloying. We found that tuning the bombarding kinetic energy we are able of achieving a large grade of interface alloying limiting it, at the same time, to the first couple of layers.

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1. Introduction

From tailoring electrical properties, through doping of semiconductors, to synthesizing surface compounds, ion beam deposition has suffered a large evolution along the past decade [1]. From the widely known methods like sputter deposition and ion plating, to the more recently developed ones, like direct ion beam deposition [2], energetic beams are widely used in thin film growth. The energetic bombardment during film growth necessarily involves surface modifications [3,4], which depend on several factors, including mass and kinetic energy of the bombarding particle, substrate temperature, and so on. While these surface modifications are sometimes looked for, the improvement of film adhesion in ion plating for instance, in other cases they introduce some restrictions to the use of ion bombardment. The restriction of keeping bombarding induced defects limited to the very surface in the manufacture of nanoscale devices is a good example of the last group. In this work we study the effect of ion induced mixing, produced during direct ion beam deposition, on the stability of the Co/Cu(1 1 1) interface. This interface is known to develop large instabilities due to the surface stress [5], and only through the use of surfactants it is possible to achieve device quality superstructures [6].

2. Numerical details

The interaction potentials employed in our simulations have been obtained using the

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second-moment approximation of the tight-binding scheme [7] (TB-SMA), including a short-range, repulsive pair potential plus a long-range, many-body contribution based on a tight-binding description of the electronic structure [8]. These potentials are used for all the involved interactions, i.e. Co–Co, Co–Cu, Co–Pb, Cu–Pb, Pb–Pb and Cu–Cu, with their corresponding physical parameters [9]. In each step of our MC simulation, every atom in the sample is randomly displaced a fraction of a lattice constant; the energy of the resulting configuration is then calculated, based on a set of interatomic potentials. Configurations are then accepted or rejected in the usual way: those with an energy lower than the former one are automatically adopted; if the final energy is higher, the decision is taken after comparing the Boltzmann factor of the energy increment with a random number.

The Cu(1 1 1) sample used in our calculations consists of six layers with 128 Cu atoms in each. The two lowest Cu layers were frozen to simulate the bulk, while all the remaining atoms in the sample were allowed to move. Most of the MC calculations have been performed at a sample temperature of 540 K in order to speed up the diffusion processes and improve the statistics, but the same qualitative results were obtained for simulation performed at 270 K. The initially mixed CoCu islands are randomly formed. The Molecular Dynamics simulations were performed for an initial distribution of energetic atoms near the surface. The reported energies correspond to the initial ones, and only normal incidence was considered.

3. Results and discussion

There are at least two mechanisms through which mild ion bombardment induces layer by layer growth (LbL): the generation of surface vacancies lowering the adatom mobility and increasing the island density [10,11], and the ballistic destruction of small islands due to the hyperthermal energy of the impinging atoms. Both these effects favour the interlayer mass transport, promoting LbL growth [12]. On the other hand, we have already shown that the enhancement of interlayer mass transport may be not enough to ensure LbL growth. In fact, surface stress can

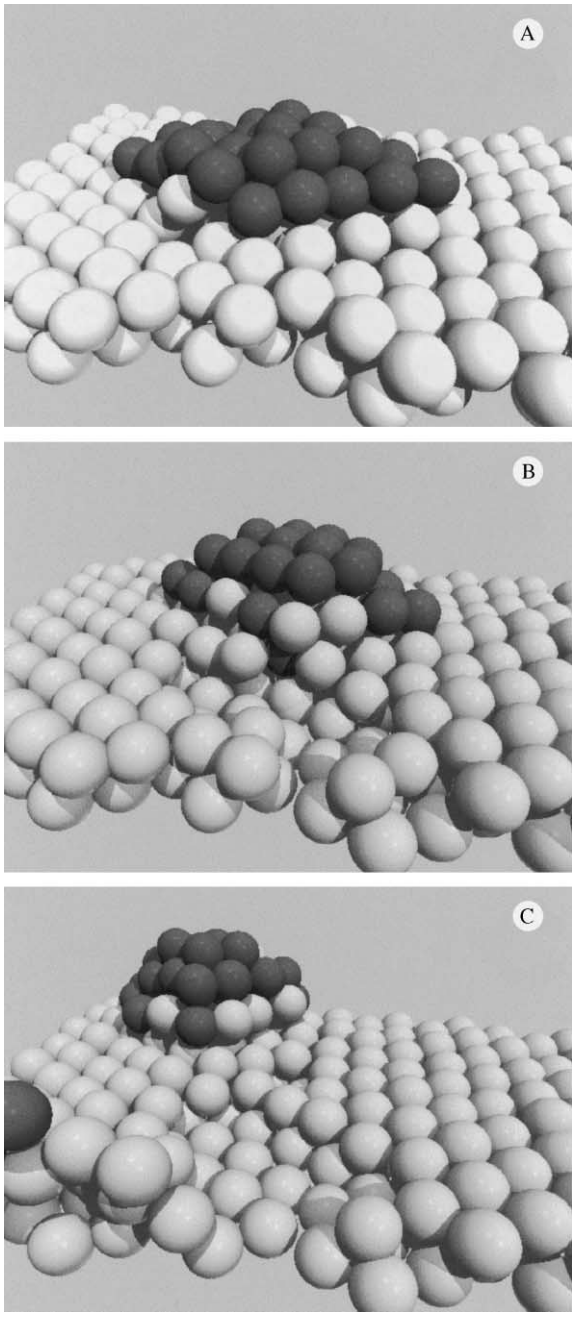

Fig. 1. MC evolution of a Co island (dark spheres) over a pure Cu(1 1 1) terrace (light spheres).

produce the collapse of an initially flat and sharp interface [6].

Let us analyze in details the case of Co growing over Cu(1 1 1). This system is characterized by the appearance of two or more atomic height alloyed islands, pools of single atomic vacancies, and the decoration of atomic steps [13]. In Fig. 1 we show the evolution of a Co island over a Cu(1 1 1) surface obtained by means of a Monte Carlo simulation. The surface stress of the initially flat Co island increases with size up to a critical value. Beyond this size, the interface collapses producing the etching of the copper surface, generating mixed CuCo islands of several atomic heights and pools of vacancies like the experimentally observed [13].

Pre-covering the Cu(1 1 1) surface with a ML of Pb promotes the LbL growth, suppressing most of these unwanted features [5,14]. In Fig. 2, we show the changes produced on the surface diffusion mechanisms by the presence of the surfactant, obtained by means of MC simulations. In Fig. 2(A), the evolution of the z-coordinate of the absorbed Co atom, for several MC simulations, is depicted. The first drop of the z-coordinate,

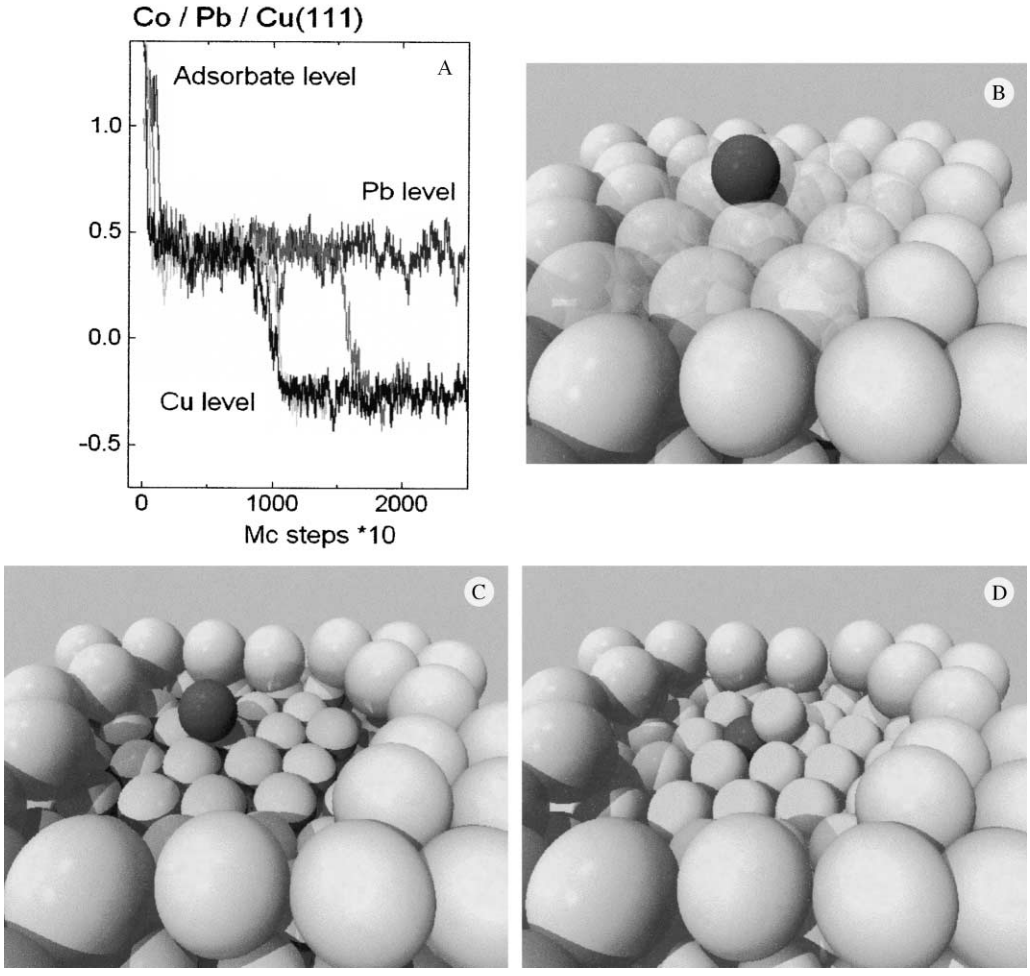

Fig. 2. MC evolution of a Co atom (dark sphere) over a Cu surface (lighter spheres) pre-covered with a monolayer of Pb (larger white spheres). (A) Evolution of the Z coordinate (z units are $R_0 = 2.56$ Å). (B)–(D) Snapshots of the same evolution. In (C) and (D), Pb atoms were partially erased to facilitate the observation.

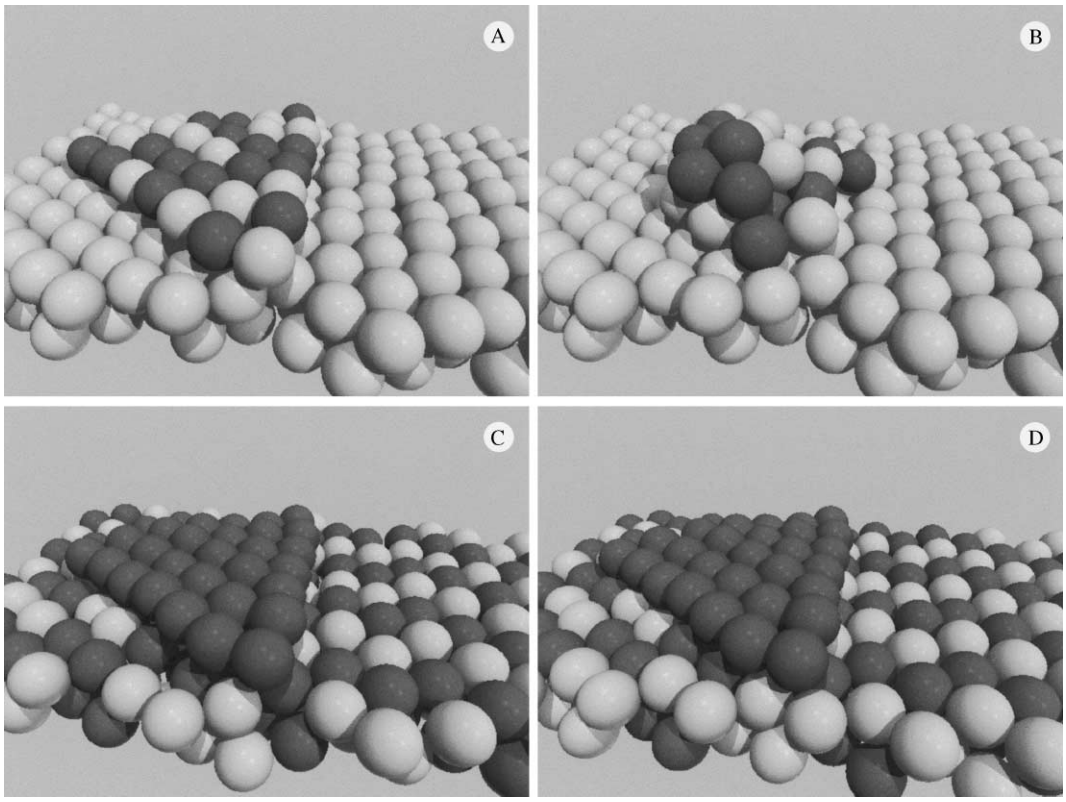

Fig. 3. MC evolution of a mixed CuCo island over a pure Cu(1 1 1) substrate ((A)–(B)), and of a pure Co island over an alloyed interface ((C)–(D)). Light spheres correspond to Cu, and dark ones to Co.

changing from the absorbate to the Pb level, represents the exchange with the surfactant layer (evolution from Fig. 2(B) to (C)). This exchange is fast, and occurs always at the landing site, i.e. no surface diffusion over the surfactant layer is ever observed. The second drop represents the atomic exchange with the sub-surface Cu atoms (evolution from Fig. 2(C) to (D)), meaning a change in the nature of the surface diffusion, from hopping to atomic exchange over the compact (1 1 1) Cu face [5,9,14]. We have already shown that the change from hopping to concerted atomic exchange, over the compact faces, is enough to ensure LbL growth in homoepitaxy [14]. However, although the large surface mobility of adsorbates over compact faces would prevent also in this case LbL growth, it is not responsible for the Co/Cu instability. In fact, the explosive situation resembled in the set of Fig. 1 has its origin on the surface stress, and it would occur even if we are able of ensuring a large atomic interlayer transport. On the other hand, the atomic exchange provides itself a stabilizing mechanism. The atomic exchange ensures both, a LbL growth through changing the intra- versus interlayer diffusion ratio, and the surface stability by lowering the surface stress through the induced interface mixing. In Fig. 3 we present MC results that support this affirmation. Fig. 3(A) shows a mixed CuCo (3/7Cu-4/7Co) island as initial stage. This is the kind of island we would obtain with a large atomic exchange probability. After several MC steps the island has evolved to form a double atomic height one, but no atomic etching is observed (Fig. 3(B)). This result is in quite well agreement with experimental results, that show LbL growth after double height

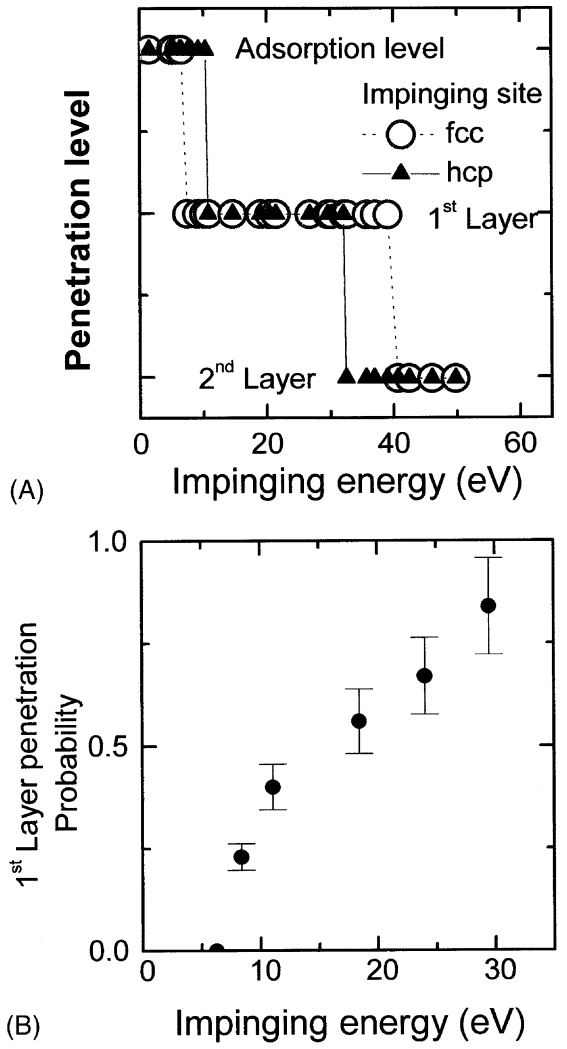

Fig. 4. Molecular Dynamics results for Co energetic atoms impinging over a Cu(111) surface. (A) Penetrating level as a function of the impinging energy, for two different impact sites. (B) First layer alloying probability as a function of the impinging energy.

island formation on Pb pre-covered Cu(1 1 1) surface [6]. In Fig. 3(C) we show the situation after a complete ML of Co has been grown. Since, we are considering a high exchange probability, two CoCu mixed layers are obtained. Over this kind of surface, even a pure Co island is stable. Fig. 3(C) and (D) shows this complete stabilization of the system, pointing out that the mixed interface lowers the surface stress enough to allow the growth of pure Co islands over it.

Once we have shown the ability of the mixing mechanism to suppress the instability of Co/Cu(1 1 1) interface, the question is our capability of obtaining this interface alloying by means of direct ion beam deposition. The ion mixing is a common experimental artifact in ion beam deposition, thus the key point here is the ability of achieving an interface alloying large enough to ensure LbL and stable growth, but low enough to preserve the quality of the interfaces. In summary, we need to obtain a large amount of ion mixing, but limited to the first couple of atomic layers. The MD results displayed in Fig. 4 show the capability of direct ion beam deposition to achieve this goal. In fact, in Fig. 4(A) we show the level of penetration of Co atoms impinging on a Cu(1 1 1) surface, as a function of its initial kinetic energy, for two different impinging sites (namely fcc and hcp hollow sites). This result shows the factibility of inducing a surface alloying, and limiting it to the first atomic layer, by tuning the impinging energy. Since we must ensure the first layer penetration, in order to alloying the interface, we need to keep the impinging energy over 10 eV. On the other hand, the energy must be kept below 30 eV, to prevent second layer penetration. Within these restrictions, it is not clear that the adequate amount of alloying can be achieved. In Fig. 4(B) we show the energy dependence of the alloying probability, calculated as the ratio among penetrating and launched ions. The results in Fig. 4(B) show our ability to tailoring the grade of interface alloying between a totally sharp, but unstable interface, up to a properly alloyed interface. Once the interface has been stabilized, either normal thermal LbL growth can be initiated, or the impinging energy lowered depending on the searched properties.

4. Conclusions

We have shown that interface mixing acts as a stabilizing factor for high cohesive elements growing over soft metals. Based on this result, we proposed the use of direct ion beam deposition to tailoring a slight alloying at the interface, by

tuning the bombardment energy. This slight alloying is similar to the surfactant induced alloying on compact (1 1 1) surfaces. After the stability of the interface is ensured by this method, ion bombardment should be used to promote layer by layer growth through the usual way, i.e. limited diffusion by vacancy generation and ballistic island destruction.

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