Surfactant action in heteroepitaxy: Growth of Co on (4×4)Pb/Cu(111) studied by LEED and STM

J. E. Prieto,[1,*] Ch. Rath,[2] S.Müller,[2] L. Hammer,[2] K. Heinz,[2] and R. Miranda[1]

[1]*Departamento de Física de la Materia Condensada and Instituto Universitario de Ciencia de Materiales ''Nicolás Cabrera,''
Universidad Autónoma de Madrid, Cantoblanco, E-28049 Madrid, Spain*

[2]*Lehrstuhl für Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstrasse 7, D-91058 Erlangen, Germany*

(Received 29 November 1999)

The magnetic properties of ultrathin Co films and Co/Cu heterostructures grown on Cu(111) have been shown to improve when Pb is used as a surfactant: the thickness range of Co films displaying perpendicular magnetic anisotropy is extended and a complete antiferromagnetic coupling between them is made possible. In this paper, we aim to understand the origin of these magnetic properties by illuminating the crystallographic structure and morphology of the films. We apply low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) to ultrathin epitaxial Co films grown on the Cu(111) surface precovered by 1 monolayer (ML) of Pb in the (4×4) superstructure. The Pb layer is found to segregate to the surface of the growing films and STM images show that the growth of Co proceeds in the layer-by-layer mode for coverages higher than 2 ML. For lower coverages, a coexistence of 1 ML and 2 ML high islands is observed on the terraces. A quantitative comparison of experimental LEED spectra shows that the structural transition from fcc to hcp stacking with increasing thickness of the Co films deposited on the Cu(111) substrate is not significantly affected by the surfactant. Instead, the latter induces the formation of sharp interfaces that favor the interface contribution to the magnetic anisotropy and allow the growth of rather smooth films with well-defined thicknesses.

I. INTRODUCTION

Thin metallic films and superlattices containing magnetic materials show phenomena like the oscillatory magnetic coupling (OMC) across nonmagnetic layers; the associated giant magnetoresistance effect allows interesting applications in magnetic reading devices such as spin valves.[1] The Co/Cu system is one of the most extensively studied due to the similarity of the lattice parameters (mismatch is only 1.9%) and the possibility of growing highly perfect fcc Co films by epitaxy, as demonstrated earlier for the Cu(100) substrate,[2] where the OMC has been unambiguously shown.[3,4] The growth of Co on Cu(111) has also been studied, because of the presence of (111) oriented domains in heterostructures grown by sputtering[5] or molecular-beam epitaxy (MBE).[6] However, the latter show poor magnetic properties: for example, antiferromagnetic (AF) coupling of Co layers is absent[7] or incomplete[8,9] because large regions of the samples remain ferromagnetically (FM) coupled.

Recent work has shown that the magnetic properties of Co/Cu heterostructures grown on Cu(111) improve significantly when the substrate is precovered by 1 monolayer (ML) of Pb, which acts as a surfactant for the subsequent growth of Co[10] and Cu layers:[11,12] first, the thickness of the Co films displaying perpendicular magnetic anisotropy (PMA) is extended;[10] second, the residual FM coupling between Co layers is reduced by a factor of 10 in sputtered films[1] and even a complete AF coupling between them is made possible for the appropriate thickness of the Cu spacer layers in structures grown by MBE.[10,13]

It is well known that, in systems of reduced dimensionality, the structure and morphology drastically affect the magnetic properties like the saturation magnetization or the Curie temperature.[14] Therefore, a detailed characterization of the films grown with the aid of the surfactant is essential in order to understand the origin of the reported improvements in their magnetic properties. Pb induces the growth of Co[10] and Cu[11] on Cu(111) in the layer-by-layer (lbl) mode and suppresses the twinning in the capping Cu layers,[15] but a systematic characterization of surfactant-grown Co films is still lacking. The aim of the present paper is to provide a structural and morphological study of Co epitaxial layers grown in the presence of Pb on Cu(111). To this end, scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) are applied. The combination of these two surface-sensitive techniques, complementary in several aspects, has been shown to provide a very complete characterization of epitaxial films.[16,17]

II. EXPERIMENT

Experiments were carried out in an ultrahigh vacuum chamber equipped with a homemade STM unit of the inertial approach type and a rear-view four-grid LEED optics also suitable for performing auger electron spectroscopy (AES). The Cu(111) substrate was electrochemically polished and afterwards cleaned by cycles of ion sputtering and annealing inside the vacuum chamber until no contaminants were present in AES spectra and a sharp (1×1) LEED pattern with low background was observed. Under these conditions, STM images show clean Cu(111) terraces several tens of nanometers wide and separated by monoatomic steps.

Pb was evaporated at a rate of 1 ML per several minutes by resistively heating a Ta basket containing the material. The coverage was calculated from the measured intensities

of the low-energy AES signals Pb$_{94}$ and Cu$_{61}$; the Stranski-Krastanov mode of growth of Pb on Cu(111) (see below) allows a precise detection of the completion of the first Pb monolayer. Deposition of Co was made from a high-purity rod heated by electron bombardment, at a rate of about 1 ML min^{-1}, on the Pb-precovered surface at RT. The Co coverage was calculated from the ratio of the high energy AES peaks Cu$_{920}$ and Co$_{716}$ following the procedure described in detail in Ref. 18. It was cross checked with similar relations for the low-energy AES transitions and measurements of covered areas in STM images, whenever possible. We define 1-ML Co as the atomic density in the Cu(111) surface, 1.8×10^{15} cm^{-2}, while for 1-ML Pb, we take the atom density in the close-packed (4×4)Pb/Cu(111) surface layer, i.e., $(\frac{3}{4})^2 \approx 0.56$ times the former figure.

The STM and LEED measurements were applied to the same film surfaces. STM images were recorded in the constant current mode with bias voltages of up to 2 V and typical currents of 1 nA. LEED intensity vs energy spectra (*I-V* curves) for various diffraction spots were taken at normal incidence of the primary beam using an automated, computer-controlled video technique.[19] The Pendry *R* factor[20] R_P was used for quantitative comparison of experimental spectra for different film thicknesses.

III. RESULTS

After an initial lattice-gas phase at very small coverages,[21] Pb grows in the Stranski-Krastanov mode on Cu(111) at room temperature (RT),[22] as shown by unambiguous breaks in the uptake curves of the Pb$_{94}$ and Cu$_{61}$ AES signals as a function of deposition time:[22,23] the first ML of Pb covers the Cu(111) surface homogeneously, while further deposition results in the formation of three-dimensional (3D) Pb crystallites well separated from each other. In order to obtain a surface completely covered by a Pb layer, a coverage slightly larger than 1 ML was deposited. The excess material concentrates in the 3D clusters, which occupy a very small fraction of the surface, as verified by STM images (not shown). At this coverage, a sharp (4×4) LEED pattern is observed, due to the formation of an hexagonal close-packed Pb layer with a lateral lattice parameter close to $\frac{4}{3}$ of that of Cu(111).[23,24] On this (4×4)Pb/Cu(111) surface, Co films of different thicknesses were deposited and analyzed by STM and LEED.

An efficient segregation of the surfactant to the surface of the growing films is necessary for a good surfactant action: first, to maintain continuously a high concentration on the surface; second, to avoid incorporation into the growing film, so causing structural defects. Our results confirm[1,10] the practically complete segregation of the Pb layer for Co depositions at RT and rates within a factor of 10 with respect to the typical rate of 1 ML min^{-1}. Figure 1(a) shows how the Cu$_{61}$ AES signal of the (4×4)Pb/Cu(111) surface is completely attenuated by the deposition of 7-ML Co, while the Pb$_{94}$ signal remains almost unchanged. The LEED patterns of the (4×4)Pb/Cu(111) surface and the 7-ML Co film grown on it are shown in Figs. 1(b) and 1(c), respectively. Preliminary intensity evaluations show that both phases have an hexagonally close-packed lead adlayer in common. The broader spots in the case of the Co film can be adscribed to smaller
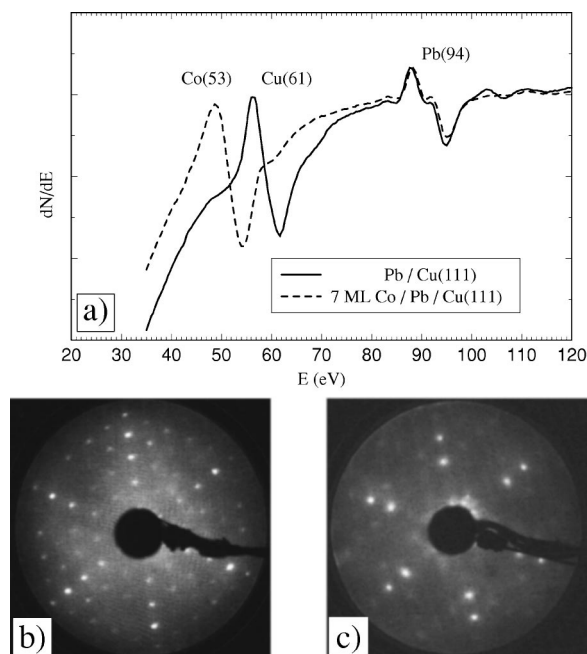

FIG. 1. (a) Low-energy Auger spectra in the derivative mode corresponding to the (4×4)Pb/Cu(111) surface (solid line) and to a 7 ML thick Co film deposited on it (dashed line). Both spectra were recorded in the same experimental conditions. (b) and (c) LEED patterns, at an electron energy of 135 eV, of the mentioned surfaces: Pb/Cu(111) and Pb/7 ML Co/Cu(111), respectively.

domains due to the formation of islands (see below).

A. Morphology of Co deposited on (4×4)Pb/Cu(111)

Figure 2 shows a representative STM image of 0.3 ML Co deposited on (4×4)Pb/Cu(111). The following features are evident:

there is no apparent preferential decoration of the substrate steps;

there is no apparent etching of the substrate: no formation of vacancy islands;

islands nucleated on terraces are 1 and 2 atomic layers high, as shown by the profile at the right of the image; at RT, there is about the same amount of islands of either type for the deposition rate used.

These observations are in clear contrast to the Co deposition on the *clean* Cu(111) surface. In that case, a practically continuous step decoration is observed even for coverages
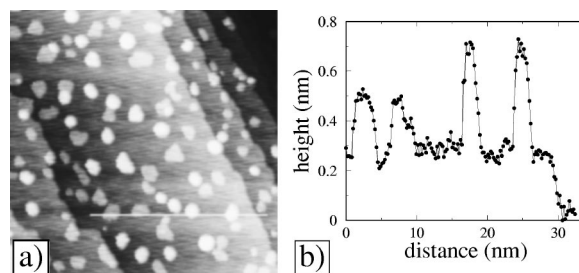

FIG. 2. (a) STM image of the (4×4)Pb/Cu(111) surface after deposition of 0.3 ML Co. Image size is 50 nm $\times$ 50 nm. (b) Profile along the line drawn in (a).
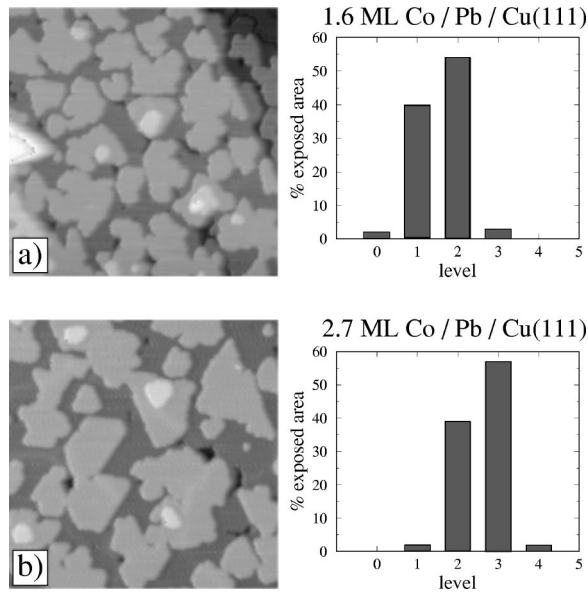
FIG. 3. STM images (40 nm×40 nm) of the surfaces of Co films of (a) 1.6 ML and (b) 2.7 ML deposited on (4×4)Pb/Cu(111). At the right of the images, the fraction of exposed area of each atomic level is plotted.

well below 1 ML;[25-27] islands attach to both sides, because a bilayer island nucleated at the lower side of a monoatomic step represents an ascending step for adatoms in the upper terrace. Furthermore, islands nucleated on the terraces are 2 atomic layers high at RT and display highly regular triangular shapes. On the contrary, in the presence of Pb, a coexistence of 1 and 2 layers-high islands is found. Although the shapes of the islands are now not so clearly defined, a tendency towards straight edges can be seen. Edge diffusion in the presence of Pb has to be efficient enough to produce compact instead of dendritic shapes, in contrast, e.g., with the surfactant action of Sb in the homoepitaxial growth on Ag(111).[28] The island density measured in Fig. 2 amounts to 4×10^{12} (islands) cm^{-2}. This is an order of magnitude larger than the typical values without surfactant for similar deposition rates at RT.[25,26]

Figure 3 shows two STM images of 1.6 and 2.7-ML Co films deposited on (4×4)Pb/Cu(111). In both cases, monoatomic-high islands above the lower level can be seen, resulting in a strong similarity. The histograms at the right-hand side of the images confirm that two atomic levels dominate in the distribution of exposed areas of both films. Since their thicknesses differ by 1 ML, we conclude that the mode of growth of Co on (4×4)Pb/Cu(111) is lbl by means of two-dimensional (2D) nucleation for coverages above 1.5 ML. This mode of growth is very different from that of Co on clean Cu(111) at RT, where initially only bilayer-high islands are formed. This is related to the presence of copper at the outer surface of the films.[16,18,29,30] Further growth on top of the bilayer islands proceeds in a 3D mode as a consequence of limited interlayer mass transport.[25,26]

B. Structure of Co deposited on (4×4)Pb/Cu(111), compared to Co/Cu(111)

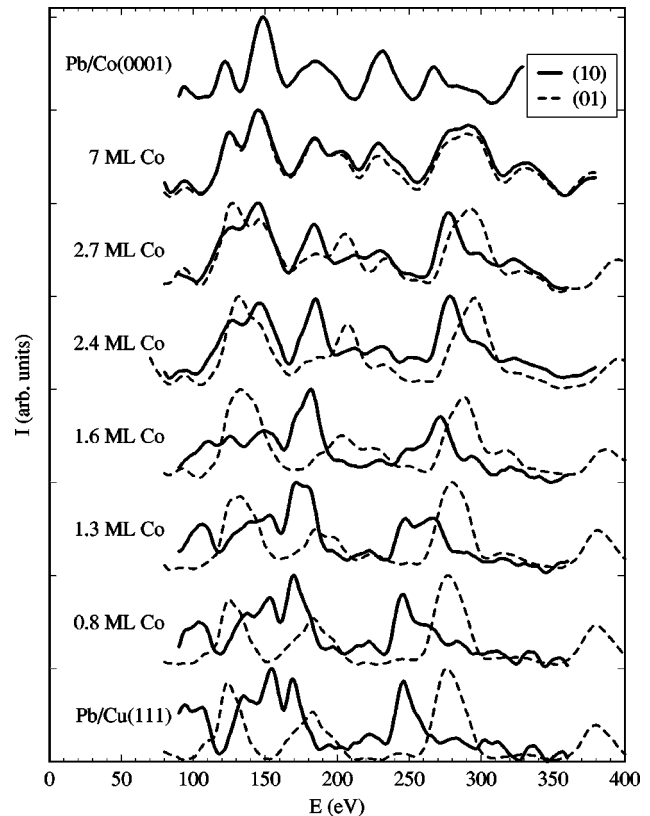Figure 4 shows the evolution of the LEED *I-V* curves of the (10) and (01) beams of Co films of increasing thick-

FIG. 4. LEED *I-V* curves of the (10) and (01) beams of Co films of the indicated thicknesses deposited on the (4×4)Pb/Cu(111) surface. For comparison, the curves of the (4×4) structures formed by 1-ML Pb on the Cu(111) and Co(0001) substrates are included at the bottom and top, respectively.

nesses deposited on (4×4)Pb/Cu(111). For comparison, the curves corresponding to the (4×4)Pb/Cu(111) and (4×4)Pb/Co(0001) surfaces are included, at the bottom and the top of the figure, respectively. The latter were obtained by deposition of 1-ML Pb on an hcp-Co single crystal. While the corresponding (10) and (01) beams are very different from each other at low Co coverages, they become almost identical for thicker films. This reflects the gradual evolution from threefold towards sixfold symmetry as the Co thickness increases. In addition, the similarity between the low-coverage curves and those of the substrate, as quantified by $R_P=0.19$ for 0.8 ML, points to an fcc stacking sequence in the early stages of growth. The also favorable comparison of the 7-ML curves with those of the Pb-covered Co(0001) surface ($R_P=0.27$) indicates dominant hcp stacking in thick Co films.

For comparison, the intensity spectra of the (10) and (01) beams of Co films deposited on *clean* Cu(111) are displayed in Fig. 5. With increasing film thickness, a similar evolution from threefold to sixfold symmetry can be observed as above, with the largest change occurring at Co coverages between 1.5 and 2 ML. The first two Co monolayers are known to be predominantly fcc stacked,[16,18] although a small fraction of faulted domains can be detected;[18] this is the origin of the minority orientation of the triangular Co islands observed by STM,[25,26] as supported by a recent analysis by tunneling spectroscopy.[31] Structural models retrieved by full-dynamical calculations confirm that the symmetry change is due to a stacking transformation from fcc to hcp.[18,32]
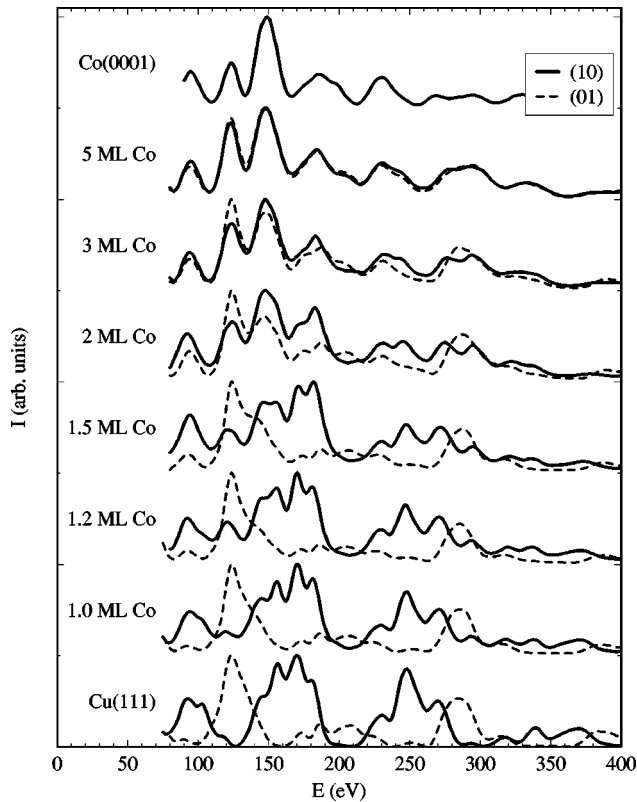
FIG. 5. LEED *I-V* curves of the (10) and (01) beams of Co films of the indicated thicknesses deposited on the clean Cu(111) surface. For comparison, the curves of the Cu(111) and Co(0001) substrates are included at the bottom and top, respectively.

FIG. 6. Values of the Pendry *R* factor, R_P, between the LEED intensity curves of Co films deposited on clean Cu(111) and on (4×4)Pb/Cu(111), and these respective starting surfaces, as a function of the Co-film thickness. Displayed values are the average between the (10) and (01) beams.

A complete structural characterization of the epitaxial (4×4)Pb/Co/Cu(111) films by full dynamical analyses of the LEED intensities presently seems to be out of range due to the complexity of the system. For each coverage, in addition to the difficulties inherent to the large (4×4) unit cells, different domains, whose presence is evident through the STM images, need to be considered. They might exhibit different stacking sequences and surface terminations, causing the total parameter space to grow beyond any practical limits even when the powerful perturbation method TensorLEED (Ref. 33) is applied. With only a single domain present, the latter method can resolve the structure, as shown for the (4×4)Pb/Cu(111) surface.[23] The quantitative structural analysis of the single domain system (4×4)Pb/7 ML Co/Cu(111) is in progress.

Due to the difficulties described, we have resorted to an approximate method to gain some insight into the structural evolution of the (4×4)Pb/Co/Cu(111) films. The idea is to compare, by means of the Pendry *R* factor R_P, the *I-V* curves of the Co films of different thicknesses with those of the starting structure, i.e., the (4×4)Pb/Cu(111) and Cu(111) surfaces, for the cases of growth with and without surfactant, respectively. The (10) and (01) beams were used for the comparison. The resulting *R* factors, plotted as a function of the Co coverage, are shown in Fig. 6. The very similar behaviors of the two curves towards the respective end structures, which possess the same stacking sequence, as shown by $R_P = 0.11$ between the Co(0001) and the (4×4)Pb/Co(0001) surfaces, point to comparable evolu-
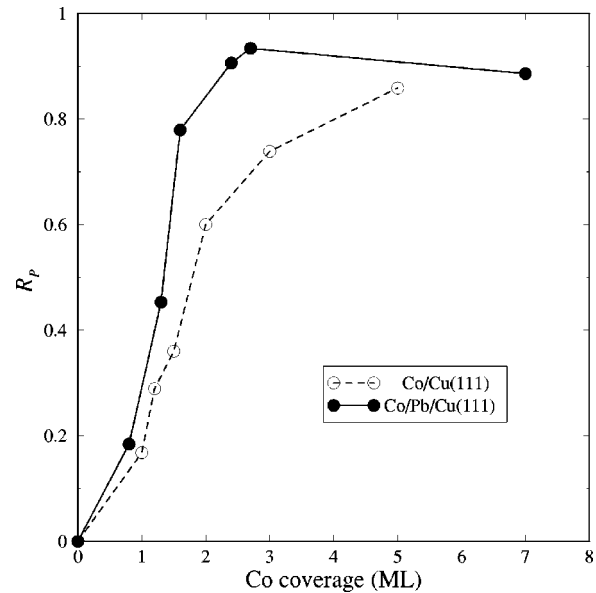
tions with Co-film thickness towards the hcp structure in both cases. Thus, our analysis finds no evidence of a significant effect of the surfactant on the stacking sequence of the Co layers grown at RT.

IV. DISCUSSION

The STM results show that the growth of Co on (4×4)Pb/Cu(111) proceeds in the lbl mode by 2D nucleation *from the second monolayer on*. Earlier, a coexistence of islands of one and two atomic layers is found on the surface. This explains the reported absence of the first maximum in the intensity of diffracted electrons, which would correspond to the completion of the first ML.[10] The low surface energy of Pb, $\gamma_{Pb(111)} = 0.5$ Jm^{-2} (Ref. 34), explains its segregation to the surface and thus the weakening of the driving force for Co to cluster on Cu(111) and to get capped by Cu [$\gamma_{Co(0001)} = 2.74$ Jm^{-2}, $\gamma_{Cu(111)} = 1.96$ Jm^{-2} (Ref. 35)]. As a consequence, the etching of the substrate is reduced, as shown by the absence of the conspicuous monolayer-deep holes that develop in the substrate upon submonolayer Co depositions on clean Cu(111)[26,36] and of the almost continuous mixture of Co and Cu decorating the steps.[27]

There are, however, two reasons to consider kinetics, in addition to thermodynamics, in order to understand the surfactant action of the Pb layer. First, the effect of Pb on the growth of Co is very similar to that on the *homoepitaxy* of Cu on Cu(111), where differences in surface energies between substrate and film are obviously absent. In the latter case, Pb also segregates to the surface maintaining the (4×4) superstructure and changing the growth mode of Cu from 3D to 2D[11] in much the same way as reported here for Co. The only difference is that, since all the islands are monoatomic high in homoepitaxy, the surfactant-induced lbl growth takes place already for the first ML. Second, the increase of the Co island density by an order of magnitude

caused by the Pb layer, also found in homoepitaxy,[11] suggests an effect of the surfactant on the surface diffusivity.

An atomistic mechanism for the surfactant action of the (4×4)Pb/Cu(111) surface in homoepitaxy has been recently proposed.[11] According to it, the change in the diffusion mechanism of Cu adatoms from hopping to atomic exchange with the substrate atoms underneath the Pb layer is the cause of a reduced diffusivity on the terraces, leading to a higher island density and to the decrease of the efficiency of the Ehrlich-Schwoebel (ES) barrier hindering interlayer mass transport. The ES barrier is defined as the activation energy that adatoms have to surmount to descend a step *in addition* to the barrier for surface diffusion. This reduction allows lbl growth to take place, since the holes remaining in a given atomic level can be filled up before nucleation in the next layer starts. The proposed mechanism might be favored by the noticeable distortion of the topmost Cu layers induced by the presence of the (4×4)Pb/Cu(111) structure,[23] since exchange seems to dominate as the degree of coordination in the surface diminishes.[37] The similarity between the homo- and the heteroepitaxy of Co, as discussed above, suggests a similar origin of the surfactant action of Pb in both systems.

The structural results point to a negligible influence of the surfactant on the stacking sequence of the layers; its main effect is thus the reduction in the roughness of the growing films: the interface between the Co film and Cu(111) is smoother than when grown without Pb, where large portions of the substrate remain uncovered after deposition of comparable amounts.[25,26] A small effective increase of the contribution of the fcc stacking sequence, restricted to the first 2-ML Co, might secondarily result as a consequence of the smoother morphology achieved by the surfactant and the associated favored relative occupancy of the lowest levels, predominantly fcc stacked.[16,18] The roughness reduction due to the induced lbl growth outweighs a possible intermixing caused by the proposed exchange mechanism, which would be limited to the close vicinity of the Co/Cu interface by the immiscibility of both metals in the bulk and by the lowered surface diffusivity achieved by the Pb. Since Cu has been shown also to grow smoothly on Pb-covered Co,[12] the surfactant allows the fabrication of (111) oriented Co/Cu heterostructures with a high degree of structural perfection.

A direct consequence is an increase of the contribution of the interface term to the magnetic anisotropy. This explains the extension of the range of Co thicknesses showing PMA.[10] Furthermore, the sharp interfaces achieved allow the growth of films of well-defined thicknesses. This is the origin of the observed reduction of the residual FM coupling between Co layers grown by sputtering[1] and the achievement of complete AF coupling in heterostructures grown by MBE.[10] For this effect to be observed, an homogeneity in film thickness and a structural perfection of the layers down to the atomic level is required, since the oscillation periods of OMC are of the order of a few monolayers, as determined by the Fermi surface topology of the material in the spacer layers.[38]

In conclusion, our STM analysis shows that the deposition of Co on the (4×4)Pb/Cu(111) surface leads to films growing in the lbl mode from the second ML on, while the LEED data indicate that their stacking sequence is not significantly modified by the surfactant. For small coverages, a coexistence of islands one and two atomic layers high is observed on the terraces. The island density is an order of magnitude larger than in the growth without surfactant. The reduced surface roughness accounts for the improved magnetic properties of the films grown in the presence of Pb.

*Corresponding author. Electronic address: joseemilio.prieto@uam.es, FAX: (34) 91 397 39 61.

[1] W.F. Egelhoff, Jr., P.J. Chen, C.J. Powell, M.D. Stiles, R.D. McMichael, C.-L. Lin, J.M. Sivertsen, J.H. Judy, K. Takano, and A.E. Berkowitz, J. Appl. Phys. **80**, 5183 (1996).

[2] J.R. Cerdá, P.L. de Andres, A. Cebollada, R. Miranda, E. Navas, P. Schuster, C. M. Schneider, and J. Kirschner, J. Phys.: Condens. Matter **5**, 2055 (1993).

[3] A. Cebollada, R. Miranda, C.M. Schneider, P. Schuster, and J. Kirschner, J. Magn. Magn. Mater. **102**, 25 (1991).

[4] M.T. Johnson, S.T. Purcell, N.W.E. McGee, R. Coehoorn, J. aan de Stegge, and W. Hoving, Phys. Rev. Lett. **68**, 2688 (1992).

[5] S.S.P. Parkin, R. Bhadra, and K.P. Roche, Phys. Rev. Lett. **66**, 2152 (1991).

[6] J.P. Renard, P. Beauvillain, C. Dupas, K. Le Dang, P. Veillet, E. Vélu, C. Marlière, and D. Renard, J. Magn. Magn. Mater. **115**, L147 (1992).

[7] W.F. Egelhoff, Jr. and M.T. Kief, Phys. Rev. B **45**, 7795 (1992).

[8] S.S.P. Parkin, R.F. Marks, R.F.C. Farrow, G.R. Harp, Q.H. Lams, and R.J. Savoy, Phys. Rev. B **46**, 9262 (1992).

[9] A. Schreyer, K. Bröhl, J.F. Ankner, C.F. Majkrzak, Th. Zeidler, P. Bödeker, N. Metoki, and H. Zabel, Phys. Rev. B **47**, 15 334 (1993).

[10] J. Camarero, T. Graf, J.J. de Miguel, R. Miranda, W. Kuch, M. Zharnikov, A. Dittschar, C.M. Schneider, and J. Kirschner, Phys. Rev. Lett. **76**, 4428 (1996).

[11] J. Camarero, J. Ferrón, V. Cros, L. Gómez, A.L. Vázquez de Parga, J.M. Gallego, J.E. Prieto, J.J. de Miguel, and R. Miranda, Phys. Rev. Lett. **81**, 850 (1998).

[12] J.E. Prieto, Ch. Rath, K. Heinz, and R. Miranda, Surf. Sci. **454-456**, 736 (2000).

[13] W. Kuch, A. Dittschar, M.-T. Lin, M. Salvietti, M. Zharnikov, C.M. Schneider, J. Kirschner, J. Camarero, J.J. de Miguel, and R. Miranda, J. Magn. Magn. Mater. **170**, L13 (1997).

[14] See, for instance, U. Gradmann, in *Handbook of Magnetic Materials*, edited by K.H.J. Buschow (Elsevier, Amsterdam, 1993), Vol. 7/1, pp. 1–96.

[15] J. Camarero, L. Spendeler, G. Schmidt, K. Heinz, J.J. de Miguel, and R. Miranda, Phys. Rev. Lett. **73**, 2448 (1994).

[16] J. de la Figuera, J.E. Prieto, G. Kostka, S. Müller, C. Ocal, R. Miranda, and K. Heinz, Surf. Sci. **349**, L139 (1996).

[17] J.E. Prieto, Ch. Rath, S. Müller, R. Miranda, and K. Heinz, Surf. Sci. **401**, 248 (1998).

[18] Ch. Rath, J.E. Prieto, S. Müller, R. Miranda, and K. Heinz, Phys. Rev. B **55**, 10 791 (1997).

[19] K. Heinz, Rep. Prog. Phys. **58**, 637 (1995).

[20] J.B. Pendry, J. Phys. C **13**, 937 (1980).

[21] C. Nagl, O. Haller, E. Platzgummer, M. Schmid, and P. Varga, Surf. Sci. **321**, 237 (1994).

[22] C. Ocal, E. Martínez, and S. Ferrer, Surf. Sci. **136**, 571 (1984).

[23] S. Müller, J.E. Prieto, Ch. Rath, L. Hammer, R. Miranda, and K. Heinz (unpublished).

[24] J. Henrion and G.E. Rhead, Surf. Sci. **29**, 20 (1972).

[25] J. de la Figuera, J.E. Prieto, C. Ocal, and R. Miranda, Phys. Rev. B **47**, 13 043 (1993).

[26] J. de la Figuera, J.E. Prieto, C. Ocal, and R. Miranda, Surf. Sci. **307-309**, 538 (1994).

[27] J. de la Figuera, M.A. Huerta-Garnica, J.E. Prieto, C. Ocal, and R. Miranda, Appl. Phys. Lett. **66**, 1006 (1995).

[28] J. Vrijmoeth, H.A. van der Vegt, J.A. Meyer, E. Vlieg, and R.J. Behm, Phys. Rev. Lett. **72**, 3843 (1994).

[29] A. Rabe, N. Memmel, A. Steltenpohl, and Th. Fauster, Phys. Rev. Lett. **73**, 2728 (1994).

[30] M.Ø. Pedersen, I.A. Bönicke, E. Lægsgaard, I. Stensgaard, A. Ruban, J.K. Nørskov, and F. Besenbacher, Surf. Sci. **387**, 86 (1997).

[31] A.L. Vázquez de Parga, F.J. García-Vidal, and R. Miranda (unpublished).

[32] J.E. Prieto, Ph.D. thesis, Universidad Autónoma de Madrid, 1998 (unpublished).

[33] P.J. Rous, J.B. Pendry, D.K. Saldin, K. Heinz, K. Müller, and N. Bickel, Phys. Rev. Lett. **57**, 2951 (1986).

[34] M. Mansfield and R.J. Needs, Phys. Rev. B **43**, 8829 (1991).

[35] H.L. Skriver and N.M. Rosengaard, Phys. Rev. B **46**, 7157 (1992).

[36] S. Speller, S. Degroote, J. Dekoster, G. Langouche, J.E. Ortega, and A. Närmann, Surf. Sci. **405**, L542 (1998).

[37] L. Hansen, P. Stoltze, K.W. Jacobsen, and J.K. Nørskov, Phys. Rev. B **44**, 6523 (1991).

[38] P. Bruno and C. Chappert, Phys. Rev. B **46**, 261 (1992).