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Adsorption site, growth, and structure of Co on Cu(111) determined by multiple-scattering analysis of x-ray-absorption spectra

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The growth of cobalt on a Cu(111) single crystal is studied using x-ray-absorption spectroscopy. A polarization-dependent multiple-scattering analysis up to the fourth shell of neighbors using the FEFF code clearly shows that the thick films have a local hcp stacking (*ABAB* planes) and not the fcc stacking (*ABCABC*) of the substrate. Moreover, we determine that on a *C* surface type of the *ABC* Cu substrate, the Co atoms are first adsorbed on *A* sites, the second layer on *B* sites continues the Cu lattice, but the third Co layer already starts a hcp stacking, by mainly choosing *A* sites again.

Magnetic thin films and multilayers have received considerable attention, since it was discovered that these systems have original properties: enhanced magnetic moments, surface magnetic anisotropy, and giant magnetoresistance. Epitaxial growth of magnetic metal films with metastable crystal structures provides important extensions of the family of simple elemental magnetic crystals and gives different elements for the comparison with the predictions of electronic structure calculations. Then, a precise knowledge of the crystallography of these metastable magnetic films is the key for the understanding of their unusual magnetic properties. We show here that multiple-scattering (MS) analysis of x-ray-absorption spectra is a unique tool for a precise structural characterization of these systems. In addition to the well known strengths of surface extended x-ray-absorption fine structure (EXAFS) (like selectivity, polarization dependence, high sensitivity, and high precision in the measure of the first-shell radial distribution function), a quantitative simulation of the x-ray-absorption spectra including higher shell contributions allows us to identify unambiguously the stacking sequence and the local symmetry of the adsorption site. This is now possible within the MS formalism. We have used here the FEFF6 code developed by Rehr, Zabinsky, and Albers,[1] which takes the polarization of the light into account in a curved wave formalism.

Co-Cu systems have been widely studied: while Co-Cu multilayers grown with a (100) orientation have giant magnetoresistance and oscillations in the magnetic coupling with a thickness of Cu,[2] the results for (111)-oriented multilayers are not clear:[3] the presence of antiferromagnetic coupling seems to depend on growth conditions.[4] Is that related to differences in the structure of the films? On Cu(100), we have shown[5] that cobalt is in perfect epitaxy on copper in a tetragonal face-centered structure. On Cu(111), the problem is different since the symmetry of the fcc Cu(111) surface is that of the hcp Co(0001) surface. Then the structure of cobalt can be fcc or hcp, the difference between the two structures lying in the stacking sequence of the hexagonal planes: *ABCABC* for fcc and *ABAB* for hcp. Many papers were already devoted to the study of the structure and growth mode of these films.[6–9] Concerning the stacking sequence, from x-ray photoelectron diffraction (XPD) studies, Scheuch *et al.*[8] think that the Co atoms start to grow in a fcc stacking untwinned with the substrate (*ABCabc*, where the upper case letters denote the Cu substrate, and the lowercase ones the Co layers), while Figuera *et al.*[7] interpret their scanning tunneling microscopy (STM) data as evidence for the existence of twinned fcc crystallites (*ABCabc* and *ABCbac*). But up to now, the adsorption site of the first layer remains unknown. All the diffraction studies show a sixfold symmetry[8–10] for films thicker than 3 or 4 ML. This can be interpreted as two twinned fcc structures or as an hcp structure. EXAFS, which is sensitive only to the local order, can solve this controversy. In an fcc local environment, the first and the fourth neighbors are aligned and give the well-known focusing effect,[11] while in an hcp environment, this focusing effect exists only in the hexagonal planes. Thus, at the EXAFS scale, twinned fcc crystallites will look like bulk fcc, while hcp crystallites will look like bulk hcp. Moreover, an original result of this surface EXAFS study will be to use the power of multishell analysis to unambigously establish that at the very early stages of growth, the cobalt atoms are mainly adsorbed on fcc continuation sites (*ABCa*).

The experiments are performed at the Laboratoire pour l'Utilisation du Rayonnement Electromagnetique, on the surface EXAFS setup installed on the wiggler beam line of DCI storage ring, using a Si(311) double-crystal monochromator. The Co is deposited at room temperature on a clean Cu(111) single crystal in ultrahigh vacuum. Preparation and control of the substrate, and determination of film thickness have been detailed elsewhere.[5] The EXAFS spectra ($\chi(k)$) are recorded *in situ* at the Co *K* edge (7710 eV) in the fluorescence yield mode. During the measurements, the sample is maintained at 77 K in order to reduce the thermal disorder. We have studied films from 0.5 to 8 ML. The linear polarization of the x rays renders the technique sensitive to the crystallographic anisotropy. For each sample, two spectra are recorded: one in the normal incidence (NI), with the polarization of the x rays parallel to the surface, and one in the grazing incidence (GI), where the polarization of the x-rays is about 20° from the surface normal. The angular dependence of the single-scattering (SS) part of the EXAFS signal is $\cos^2\alpha$, where α is the angle between the bond and the polarization direction of the x rays. Whatever the stacking is on the (111) surface (hcp or fcc), each Co atom has six nearest neighbors (nn) in its plane, three above (missing for the top layer), and three below. Then, concerning the first shell of neighbors, in GI, only the bonds out of the (111) planes (interlayer bonds) are contributing to the EXAFS signal, while the NI, the bonds parallel to the (111) planes (intralayer bonds) have a weight three times larger than the out of planes ones.

The frequency of the main EXAFS oscillation is the nn distance. From the raw data presented on Fig. 1, it is clear that the NI spectrum is oscillating faster than the GI one, denoting an intralayer bond longer than the interlayer one. By back transforming in *k* space the first peak of the Fourier transform (FT) of an EXAFS spectrum, one can extract the contribution to the signal of the nn shell. This contribution is then fitted in the SS approximation, using the classical EXAFS formula and experimental Co backscattering amplitude and phase shift. For each sample, we begin by a fit of the GI spectrum, to obtain the interlayer bond length; then we can extract the intralayer bond length from the NI spectra. For all the fits, a good simulation of the experimental spectra is obtained assuming a number of *nn* calculated for a flat film. The presence of large flat clusters[7] (lateral size larger than 100 Å) would not modify significantly these numbers. The free parameters for the fit of the GI (NI) spectrum are, therefore, only the interlayer (intralayer) bond length and associated Debye-Waller factor. For all the Co thicknesses, the in-plane nn distance is 2.54±0.01 Å, the out-of-plane nn distance is 2.50±0.01 Å, and the static disorder at 77 K is very similar to its value in bulk cobalt. The Cu substrate, which has a nn distance of 2.55 Å, forces the Co atoms to adopt parallel to the interface a larger in-plane parameter than in bulk Co. This distortion does not vary when the film thickness increases up to 8 ML.

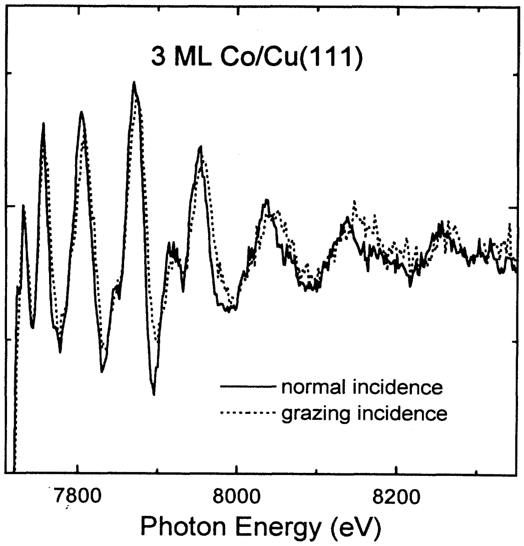

FIG. 1. EXAFS raw spectra recorded at 77 K at the Co *K* edge on a 3-ML Co/Cu(111) film in the NI (solid line) and the GI (dotted line).

As noted before, it is impossible to determine the stacking of the Co films from the analysis of the first shell. In the FT of the EXAFS spectra (see Fig. 2, for example) we can see well-defined peaks up to a distance of 6 Å. They are due to SS involving neighbors located at higher distances, but also to MS phenomena. Between these MS contributions, the most important ones are those concerning three aligned atoms. In particular, in an fcc structure, each first neighbor at a distance *R* of the

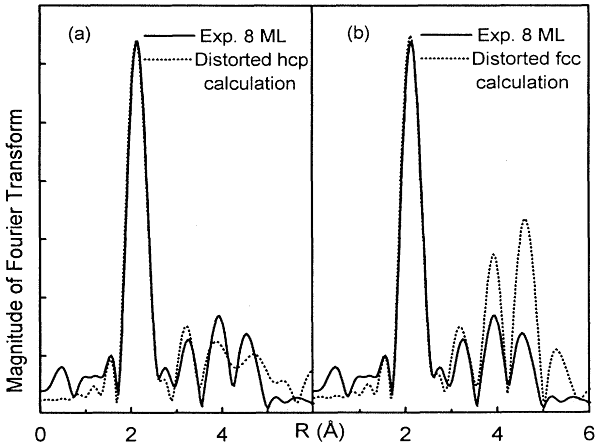

FIG. 2. FT (from $k = 3.14$ to 12.66 $Å^{-1}$) of $k^3\chi(k)$ in the GI for a 8-ML Co/Cu(111) film (solid line) and FEFF6 simulations (dotted line) for (a) a distorted hcp Co(0001) crystal and (b) a distorted fcc Co(111) crystal.

central atom is aligned with a fourth neighbor at a distance $2R$ of this central atom. These alignments enhance the intensity of the fourth peak in the FT,[11] both in NI and GI. In an hcp structure, these alignments still exist in the (0001) planes, but are lost out of these planes. It causes an absence of focusing in the GI, and gives the strong polarization dependence of the fourth peak in the FT of bulk hcp cobalt.[5] So, it will be possible to conclude on the structure of the cobalt films, fcc or hcp, by measuring the polarization dependence of the EXAFS spectra and comparing it to simulations involving MS phenomena. We have done the calculations with an FEFF 6.0, considering the single-, double-, and triple-scattering processes; the accuracy of this code for simulating polarization-dependent experimental data of bulk hcp cobalt has been demonstrated previously.[5] The only free parameter is the amplitude reduction factor S_0^2 (it is between 0.65 and 0.80), the Debye temperature being fixed to its bulk value (445 K for Co and 343 K for Cu).

We first consider the 8-ML-thick film. The first-shell analysis has determined that the Co in-plane nn distance is 2.54 ± 0.01 Å and the out-of-plane one is 2.50 ± 0.01 Å. The Co crystals constructed for the FEFF calculation with the two stacking sequences (distorted hcp and distorted fcc) are supposed in perfect epitaxy on Cu(111) with an in-plane nn distance of 2.55 Å and an out-of-plane nn distance of 2.50 Å. As expected, the NI calculations are very similar for the two simulations and well reproduce the NI experimental data (they are all very similar to the NI spectra presented further for the 3-ML-thick film). On the other hand, in the GI, there is a dramatic decrease of the high distant peaks of the FT for the hcp distorted simulation as compared to the fcc distorted one. These results are presented in Fig. 2 and compared to the experiment. Unambiguously, the distorted hcp simulation is much better fitting the experiment. Nevertheless, we cannot exclude the presence of some "defects" with local fcc stacking, but we can say that they represent less than 20% of the total signal. We have done also calculations on a nondistorted hcp Co: the FT is in disagreement with the experiment. This multishell analysis, therefore, confirms the first-shell analysis, i.e., the nonisotropic shape of the nn shell. Furthermore, it demonstrates clearly that an 8-ML film has already a mainly hcp structure, a result in agreement with a recent XPD study.[8]

The x-ray-absorption near-edge structures (XANES) are also very sensitive to the local structure and to the polarization effects. The XANES spectra of fcc Cu are isotropic and present two bumps in the region from 10 to 20 eV above the edge, while for an hcp cobalt single crystal with a (0001) free surface, there are two bumps in the NI, but only one bump in the GI [Fig. 3(a)]. These results are totally expected since in the hcp structure, the full point group (D_{6h}) confers to the electric dipole K edge absorption cross section a dichroic dependence, whereas in the fcc structure, i.e., in a cubic symmetry (O_h), the electric dipole absorption cross section is isotropic.[12] Convergence of the cluster size (about 200 atoms) has been thoroughly checked for both structures. The accuracy of the FEFF6 code in the XANES region for such edges is demonstrated in Fig. 3(b): the XANES spectra anisotropy measured on a bulk hcp Co(0001) is very well reproduced by the calculation, with the two bumps in the NI, and only one in the GI. The experimental spectra on the 8-ML-thick film present the same anisotropy, confirming the hcp stacking in this film.

What happens now at the very beginning of the Co growth? Cu is fcc, and has a $ABCABC$ stacking sequence of the (111) planes. If we assume that the surface

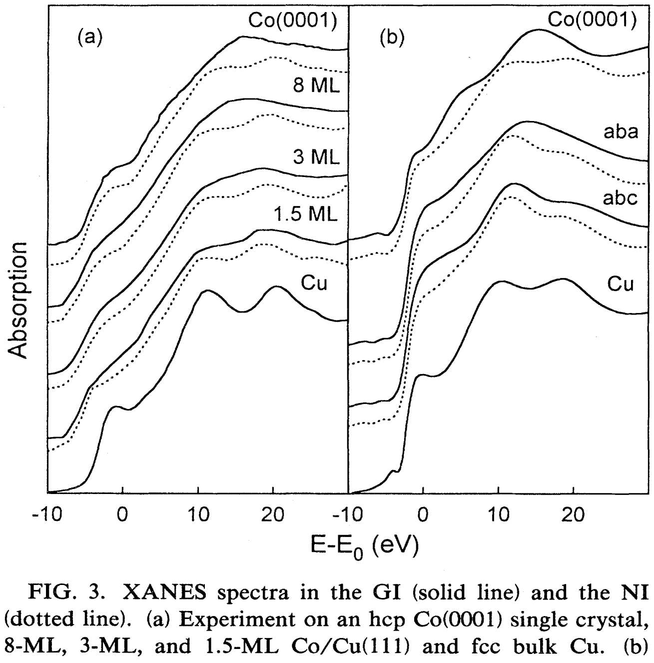

FIG. 3. XANES spectra in the GI (solid line) and the NI (dotted line). (a) Experiment on an hcp Co(0001) single crystal, 8-ML, 3-ML, and 1.5-ML Co/Cu(111) and fcc bulk Cu. (b) FEFF6 simulations for hcp Co(0001), 3-ML Co/Cu(111) (*ABCaba* and *ABCaba* stackings) and fcc Cu. The abscissa is the energy relative to the threshold (7710 eV for Co and 8980 eV for Cu). The instrument broadening is 2 eV.

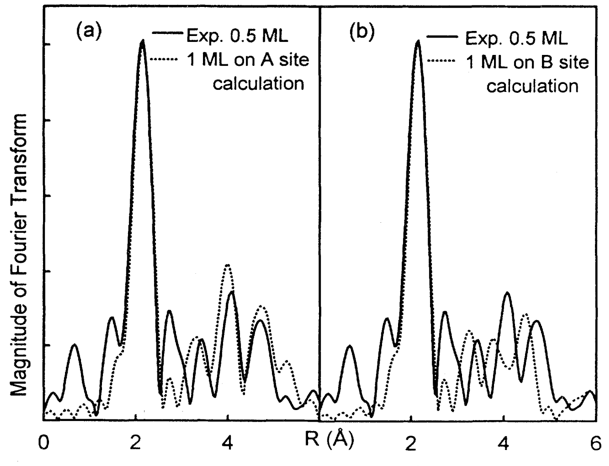

FIG. 4. FT (from $k = 3.14$ to 12.66 Å^{-1}) of $k\chi(k)$ in the GI of a 0.5-ML Co/Cu(111) film (solid line) and FEFF6 simulations (dotted line) for 1 ML of Co on an ABC terminated Cu(111) on A sites (a) or on B sites (b).

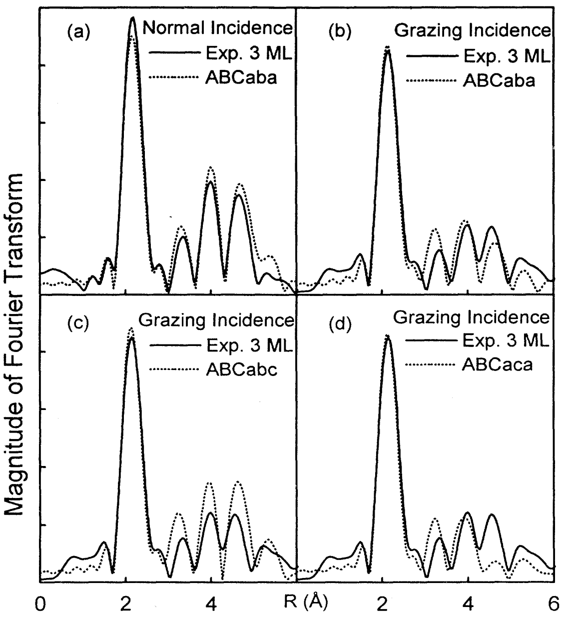

FIG. 5. FT (from $k = 3.14$ to 12.66 Å^{-1}) of $k^3\chi(k)$ of 3-ML Co/Cu(111): experiment (solid line) and FEFF6 simulations (dotted line).

plane is of *C* type, the first deposited Co atoms can be located on *A* sites ("fcc sites") or on *B* sites ("hcp sites"). If the Co atom chooses a fcc site, it will have its fourth Cu neighbor aligned with its first Cu neighbor. This alignment will not exist if the Co atom is located on a hcp site. We have calculated the EXAFS spectra of 1 ML of Co adsorbed on *A* or *B* sites on a Cu(111) surface, with Co-Co nn distance of 2.55 Å, Co-Cu nn distance of 2.50 Å, and Cu-Cu nn distance of 2.55 Å. The FT of the GI spectra are represented on Fig. 4 together with an experimental GI spectrum recorded on a 0.5-ML-thick film. Both the positions and the intensities of the peaks of the experiment are better reproduced by the simulation of 1-ML Co adsorbed on *A* sites. The STM study quoted above reported that, at this coverage, there were already 2-ML high Co islands. These islands are flat and wide triangles, with edges of around 150 Å. EXAFS being a very local probe, such islands can be considered as a flat homogeneous 2-ML film. We have compared the experimental data of the 0.5-ML film with simulations done on 2 ML of Co on a Cu substrate for all the possible configurations (*ABCab*, *ABCac*, *ABCbc*, and *ABCba*). The *ABCab* calculation is nearly identical to the *ABCa* one, and the other possibilities are clearly to be excluded. We conclude that, at the early stages of growth, the Co atoms continue the fcc Cu lattice, with an adsorption site of *A* type on a *C* surface type of the *ABC* Cu substrate.

Finally, the study of a 3-ML-thick film is of great interest, since we have established that the first Co layer was adsorbed on fcc sites, but, at high coverage the structure is mainly hcp. What is the stacking at this intermediate thickness? Starting on a *C* surface and the first layer on the *A* site, the stacking can be *ABCabc* (fcc stacking type) or *ABCaba* or *ABCaca* (hcp stacking types). We have proceeded the same way as for the study of the adsorption site by comparing FEFF6 simulations on 3 ML of Co/Cu(111) with experiment. The crystals are constructed again with an in-plane nn distance of 2.55 Å (for Co-Co and Cu-Cu) and out-of-plane nn distances of 2.50 Å (for Co-Co and Co-Cu) and 2.55 Å (for Cu-Cu). For each configuration, a total absorption spectrum is the average of three calculations with the absorbing atom on each different Co layer. The FT of the results for both the NI and the GI are presented in Fig. 5, together with the FT of the spectra recorded on a 3-ML-thick film. In the NI, the agreement between calculation and experiment is very good and quite independent of the stacking sequence. In the GI, the positions of the peaks are well reproduced by the three simulations, but the respective intensities are better reproduced by the *ABCaba* simulation. Other stacking sequences like *ABCbcb* and *ABCbab* give simulations with very small high distant peak clearly different form the experiment.

To confirm the *aba* stacking, we have compared the XANES spectra of the different simulations. As can be seen in Fig. 3, the experimental spectra recorded on the 3-ML film present a clear anisotropy, with two bumps in the NI and mainly one in the GI, while the XANES of a 1.5-ML film is isotropic. The 3-ML anisotropy is only described by the *ABCaba* simulation, whereas the XANES of the *ABCabc* simulation is nearly isotropic with two bumps in the two incidences, and look more alike the fcc Cu ones. Calculations of XANES spectra have also been performed, using the full MS code developed by Natoli and co-workers.[13] They give the same results with the same minor discrepancy in the relative amplitudes of the two bumps, which is probably due to the muffin-tin approximation. Here also, the XANES spectra confirm the result of the EXAFS multishell analysis. Both the 0.5 ML and the 1.5-ML-thick films have two bumps in the XANES region in the NI and in the GI: this is the signature of fcc continuation sites for the two first layers. The 3-ML film has anisotropic XANES spectra well reproduced, assuming a third layer in hcp sites.

As a conclusion, we found that thin Co films are in epitaxy on Cu(111) and that, for all the thicknesses, they have a distorted structure with in-plane nn distances of 2.54 Å very close to the Cu one, and out-of-plane nn distances of 2.50 Å. A polarization-dependent MS analysis of both EXAFS and XANES data allows us to determine the Co first location on the Cu surface and the structure of the films. This result shows that while cobalt adopts the fcc stacking of copper on a (100) surface[5] (which has a square two-dimensional symmetry not existing in hcp structures), cobalt grows on a (111) surface of copper with its own hcp structure, the sixfold symmetry of the (111) fcc surface becoming the (0001) basal plane of the cobalt film. The hcp stacking starts at the third deposited layer, as soon as the Co has to choose between the fcc and the hcp structure.

This study which uses the power of the multiple-scattering calculations opens very wide prospects in the thin-film research field. X-ray-absorption spectroscopy sensitivity to local environment removes the ambiguities, due to the possible existence of domains with different orientations on different parts of the sample, and it is the only selective technique where the signal recorded on a submonolayer film gives access to the location of the adatoms with respect to the substrate.

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