Crystallography and morphology of the early stages of the growth of Co/Cu(111) by LEED and STM

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Abstract

We report on a quantitative investigation of the structure and morphology of ultrathin films of Co deposited on Cu(111) by an in situ combination of real space (STM) and diffraction (LEED) techniques. The film grows initially as bilayer islands with strict fcc stacking. Part of them are covered by Cu. The lateral distribution of Co- and Cu-terminated domains as well as of uncovered patches is both quantitatively determined by intensity analysis and visualized by STM images. Their simultaneous presence correlates nicely to known magnetic properties of ultrathin films, in particular with the observed magnetic anisotropy.

Keywords: Cobalt; Copper; Growth; Low energy electron diffraction (LEED); Magnetic films; Metallic films; Scanning tunneling microscopy (STM); Single crystal epitaxy

1. Introduction

Because of their technical potential, thin magnetic films and superlattices have long been of interest. Their attraction recently has increased because today techniques are at hand to characterize these films both magnetically and structurally with high precision - a prerequisite of the quantitative understanding of their properties and growth. In this light we concentrate in the present paper on the quantitative and detailed investigation of the structure and morphology of ultrathin Co films epitaxially grown on Cu(111) at room temperature (RT). Emphasis is on the very low coverage regime at 1.5 monolayers (ML) average coverage. For such films, regions with magnetization parallel to the surface and regions with spontaneous perpendicular magnetization have been observed as revealed by the surface magneto-optical Kerr effect (SMOKE) signal in longitudinal and polar geometries, respectively (Ref. [1]). Furthermore, it has been reported that upon deposition of 2 ML Cu on top of 1.5 ML Co only perpendicular magnetization is observed (Ref. [1]). Thus, capping with Cu obviously enhances the perpendicular anisotropy. The Cu covered Co films exhibit a magnetization temperature dependence described by the 2D Ising model and a critical temperature of \(T_c = 434 \text{ K} \) (Ref. [2]). It will turn out that our structural results nicely correlate with these magnetic properties of the films.

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We also set out to demonstrate that a particularly useful strategy for the structural characterization of the films is an in situ combination of Low Energy Electron Diffraction (LEED) and Scanning Tunneling Microscopy (STM). While STM is invaluable to visualize the morphology and electronic structure in real space, LEED is able to provide quantitative and high precision structural information both in the surface and extending to deeper layers. In particular, the dominant perpendicular momentum transfer makes LEED very sensitive to vertical interlayer distances and stacking sequences in the first few layers, parameters to which the STM is essentially blind.

In spite of a number of structural investigations of Co/Cu(111) films (Refs. [3–10]) their structural characterization is still incomplete. Contradictions abound with respect to the mode of growth at RT, which has been reported to be layer-by-layer (Refs. [3,5]) or 3D islands (Refs. [4,7]) with the initial stage being a flat monolayer (Ref. [5]) or bilayer islands (Ref. [6]). The film has been described initially as fcc turning to hcp at Co coverages ranging from 4 (Ref. [7]) to 8 (Ref. [3]) ML as deduced from the six-fold symmetry of the diffraction patterns. Alternatively, this change from threefold to six-fold symmetry has been ascribed recently to the growth of twinned fcc crystallites (Ref. [6]). To further complicate things, Cu has been detected at the external surface for Co films thinner than 3 ML (Refs. [4,8]) which was suggested to result by a spontaneous etching process induced by Co deposition at RT or above (Ref. [11]).

### 2. Experimental and data evaluation procedure

The experiments were performed at room temperature in a UHV chamber equipped with a home made STM unit and a rear-view four-grids LEED optics, which was also used to record Auger spectra. The sample holder allowed in situ transfer from the LEED optics to the STM head. The Cu(111) substrate was cleaned by cycles of argon ion sputtering and annealing. Evaporation of Co was carried out by electron bombardment of a Co reservoir. The LEED pattern of the Co films was always 1 × 1 with low background. The coverage was deduced from the evaporation time and cross-checked by the ratio of low energy Auger peaks of Co and Cu. Calibration was made by measuring the fraction of covered surface in the STM images at low coverages. Considering the uncertainties involved, the error in the coverage is estimated to be 20%. The STM tip was a polycrystalline W wire. The piezodrives were calibrated laterally by images at atomic resolution and vertically by the step height of clean Cu(111).

Intensity versus energy spectra, $I(E)$, for the different diffraction spots were recorded by an automated video method (Ref. [12]). The primary beam incidence was adjusted within 0.5° to the surface normal by comparison of symmetrically equivalent beams, whose intensities eventually were averaged in order to improve the data quality. Full dynamical calculations were applied for their structural analysis, whereby standard codes (Refs. [13,14]) with matrix inversion for the layer diffraction and layer doubling for the stacking of layers were used. Calculated spectra were quantitatively compared to the experimental data by means of the Pendry R-factor (Ref. [15]). The best fit structure was retrieved by a grid search whereby error limits were determined by the variance of the Pendry R-factor.

### 3. Results

Fig. 1 displays experimental $I(E)$ spectra for the (10) and (01) diffracted beams recorded for increasing coverages. The STM images displayed in parallel correspond to the very same film in each case and are of the same magnification.

As is obvious from the diffraction spectra, there is a clear evolution from three- to six-fold symmetry. In fact, as described in more detail in a separate paper (Ref. [16]) stacking faults are gradually introduced with increasing film thickness. So, there is a transition from pure fcc stacking in the low coverage regime with both Co/Co and Cu/Co bilayers (see below) to pure hcp stacking of Co layers for thicker films (Ref. [16]).

For 1.5 ML coverage, on which we concentrate in the following, 75% of the surface is covered by
islands of triangular-like shape with a density of $1.2 \times 10^{12}$ islands/cm$^2$. A relative area of 25% of the substrate is uncovered. The islands have an apparent height of $3.8 \pm 0.1$ Å, i.e. they correspond to double-layer patches (Ref. [6]). They are mostly interconnected suggesting that they all have the same stacking sequence with respect to the substrate. There is only a small (5%) population of the third layer, 1.9 Å above the bilayer.

In order to determine the structure of the initial bilayer, the four possible stacking combinations (ABCab, ABCac, ABCbc and ABCba) were tried as a first step of the LEED analysis assuming a homogeneous film. For this idealized morphology only the fcc stacking (ABCab) gave a reasonably good fit ($R_p=0.25$) as a start for further structural refinement. All other stacking sequences could be unambiguously discarded ($R_p>0.6$).

The STM pictures (revealing a morphology characterized by uncovered surface patches and only a negligible population of the third layer level) guided the following structural refinement. It was realized by a weighted addition of the intensities calculated for the various domains as allowed by the absence of positional correlations between them.

Fig. 2 compares experimental and calculated best fit $I(E)$ spectra for the (10) and (01) beams of the 1.5 ML film whose morphology is illustrated by the corresponding STM images in Fig. 3. The resulting best fit model with a convincingly low Pendry $R$-factor, $R_p=0.17$, as averaged over all beams, consists of three types of domains: one of them is due to 2 ML of fcc Co occupying 45% of the surface. The second is formed by 2 ML of fcc CuCo islands, i.e. islands terminated by Cu, with a relative area of 30%. The rest of the surface (25%) is clean Cu(111). The amount of uncovered area resulting from the LEED analysis is in excellent agreement with the corresponding area seen in the STM images. The two kinds of film domains are pseudomorphic with Cu(111) having the same lateral lattice constant. The vertical interlayer distances in the CoCo domain are $d_{12}=2.08 \pm 0.04$ Å and $d_{23}=2.07 \pm 0.05$ Å, i.e. they practically coincide with the spacing of bulk Cu. The interlayer dis-
Fig. 4. Schematic model of the crystallographic arrangement of CoCo and CuCo bilayers on Cu(111). The filled circles represent Co atoms.

tances in the CuCo domain are $d_{12} = 2.00 \pm 0.04$ Å and $d_{23} = 2.07 \pm 0.05$ Å, respectively. For the clean Cu(111) patches, $d_{12} = 2.07 \pm 0.04$ Å results, in agreement with the value of the bulk layer distance of the Cu(111) surface. The Debye temperature of the Co top layer was determined to be 380 K. In all cases the error limits result by the variance of the $R$-factor, $\text{var}(R_p) = 0.032$ as resulting from the energy width of the experimental data base, 1120 eV.

Fig. 4 illustrates schematically the best fit model structure of the 1.5 ML Co film. Neglect of the CuCo domains worsens the quality of the fit ($R_p = 0.20$) and additionally produces a structure with unusual properties: the percentage of uncovered Cu would rise to 45%, in clear disagreement with the STM images. Also, its first interlayer distance would be expanded by 5% in contradiction to the clean surface result. We also tried to mix Co and Cu in the various layers according to the formation of a random surface alloy, but this model can be discarded as well. Consequently, the presence of Cu capped cobalt layers is a safe result.

Another important conclusion from the quantitative structure determination is that no hcp fraction can be detected. There is no stacking fault at the Co/Cu interface, nor between the layers of the bilayer islands. The 1.5 ML film contains only fcc-stacked double-height islands, at least within the detection limit of LEED I–V measurements. This is a conclusive answer to the long-standing question of the initial stacking of the film with respect to the Cu substrate. The existence of faulted island,
inferred from previous STM studies at lower coverages (Refs. [6,11]), may play a role in the very first stages of nucleation, but the present work shows that their presence at a coverage of 1.5 ML is not relevant for the LEED I–V analysis. Furthermore, Cu found to be present at 30% of the external surface in addition to the uncovered surface, is also fcc stacked with respect to the layer underneath.

The existence of Cu at the surface of Co films deposited on Cu(111) has also been recently concluded from X-Ray Photoelectron Diffraction (Ref. [4]) and time-dependent Ion Scattering (Ref. [8]) data. The present LEED analysis fixes the weight and structure of these domains quantitatively. An additional confirmation is possible by STM. Chemically selective imaging on metal surfaces has been achieved in STM by tunneling into image (Ref. [17]) or surface (Ref. [18]) states. The necessary contrast between Co and Cu terminated areas can also be produced by chemical titration of the film components if they have a different reactivity. It is known that at RT CO adsorbs on Co but not on Cu (Ref. [19]). So, we expect that exposing the film to CO decorates the Co terminated islands enhancing the contrast in the STM images. Fig. 5 shows the result of such an approach. The exposure to 50 L of CO produces STM images with enhanced contrast between different parts of the CO-covered surfaces. Fig. 5a shows an image 300 Å wide of a submonolayer Co film including several bilayer islands plus a nearby stepped zone. Every island shows brighter and darker regions imaged with an apparent height difference that can be larger than 1 Å (Fig. 5b) depending on the tunneling conditions. The existence of both types of domains along the step edge is also evident. The brighter regions display the same height before and after CO titration and are, therefore, ascribed to the Cu-terminated domains revealed by the LEED analysis. The darker regions within the islands correspond to the Co-terminated domains. Another image of a bilayer island (Fig. 5c) allows us to quantify the fraction of its surface that corresponds to the brighter (Cu-terminated) domains. In this particular case (for a lower coverage) a value of about 20% is found, in reasonable agreement with the result of the LEED analysis.

Thus, this real-space chemical titration visualizes the spatial distribution of Co and Cu revealing that the Cu-coated regions on the bilayer islands are 20 × 10 Å² wide on average and randomly distributed, being much larger close to the steps.

This is a confirmation of the conclusions of the LEED analysis. Some Co bilayer islands are embedded by a monolayer of Cu “shores” (Fig. 5c). Both CoCo and CoCu domains are fcc stacked with respect to the surface and constitute the building blocks of the “fcc” film of Co that initially grows on Cu(111) (Refs. [3–10]). The presence of Cu seems to be essential for the stabilization of fcc Co in this orientation. In effect, as soon as the segregation of Cu stops, the Co film starts to develop stacking faults that change the local structure from fcc to hcp. This is indicated by the detailed analysis of the incipient six-fold symmetry.
of the \( I(E) \) spectra for 5 ML to be reported elsewhere (Ref. [20]).

These results are also consistent with a recent publication on surfactant-assisted growth of 3 ML Cu/3 ML Co/Cu(111) sandwiches (Ref. [21]). The interpretation given there for the 6-fold symmetric LEED pattern of this structure (grown without surfactant) in terms of fcc Cu twins remains valid in the light of the present work: after the first two layers, fcc-stacked, the third Co layer may already begin the transition to the hcp structure (Refs. [9,10]). Cu grown on top of an at least partial hcp Co film will unavoidably present the two fcc-twin-related domains, because of the local unequivalence of a- and b-terminated regions of the hcp (ababab...) structure, thus leading to a 6-fold symmetry in the diffraction pattern.

4. Discussion and conclusion

As evident from the above results, the initial stage of epitaxial growth of Co on Cu(111) is pseudomorphic, i.e., the films exhibit the lateral lattice parameter of Cu, \( a_p = 2.556 \) Å. The interlayer distances of the cobalt bilayers are practically identical to the bulk copper value. This means that these cobalt regions exhibit a uniformly expanded unit cell. Total energy calculations (Ref. [22]) indicate a minimum in the energy of fcc Co at a lattice parameter of \( a = 3.54 \) Å which is close to the experimentally determined value. The calculations further predict that fcc Co with a uniformly expanded lattice parameter of 3.61 Å, i.e., such as of Cu in the present case, costs an extra amount of energy of 65 meV/atom. This energy is much larger than the energy difference between fcc and hcp Co (27 meV/atom). Thus, at first glance it seems difficult to imagine that fcc Co exists at the lattice parameter of Cu. However, it has been known for more than 30 years that fine grain precipitates of fcc Co do exist with the Cu lattice parameter within a Cu matrix (Ref. [23]). They are stable up to a size of 500 Å. We interpret the Co/Cu regions that exist in the 1.5 ML film as the analog of these fcc Co precipitates. They are surrounded by Cu capped regions and in many cases laterally decorated by additional Cu removed from the substrate.

Besides the Co bilayers, the existence of Cu capped domains and their precise structural characterization is the second important result of the present paper. They correlate to the magnetic anisotropy of Cu-coated Co films grown on Cu(111) which was analyzed earlier (Ref. [24]). In these investigations a volume anisotropy constant of \( K_{\text{vol}} = -1.2 \times 10^6 \) J/m\(^3\) and a surface anisotropy of \( K_s = 0.18 \) mJ/m\(^2\) was obtained. The negative bulk anisotropy causes films thicker than 2 ML to be magnetized in-plane while the positive surface anisotropy provokes a perpendicular magnetization for films thinner than 2 ML. The crystallographic result described in the present paper suggests an explanation of these magnetic properties: since the Co/Cu regions have an expanded volume, the volume anisotropy term can be due to a strain induced magneto-elastic energy which can be estimated (Ref. [25]) from the bulk magneto-elastic constant \( K_{\text{me}} \). If we use the values for hcp Co, assuming that there is not much difference to fcc Co, and use the experimentally observed strain \( \epsilon = (3.61 - 3.54) / 3.54 = 1.97\% \) we obtain \( K_{\text{vol}} \approx K_{\text{me}} \approx -6.48 \times 10^7 \times \epsilon = -1.28 \times 10^6 \) J/m\(^3\). This is in surprisingly good agreement with the experimental value (Ref. [24]).

On the other hand, the positive surface anisotropy observed experimentally is probably related to the presence of a Cu capping layer since Linear Muffin-Tin Orbital (LMTO) first principles calculations predict a negative magnetic anisotropy \((-1.20 \) meV/atom\) for a free-standing Co(111) layer and only a positive value \((0.20 \) meV/atom\) for a Co layer sandwiched in between Cu layers (Ref. [26]).

In conclusion, our results describe in quantitative detail the structure of the early stages of the epitaxial growth of Co on Cu(111). In addition, our observations of Cu covered and Co terminated domains on the 1.5 ML film nicely explain the existence of perpendicular and parallel magnetized regions in RT-deposited films. Cu-capped and Co-terminated zones correspond to perpendicular and surface parallel magnetization, respectively. This demonstrates impressively the correlation.
between structure and chemistry on the one hand and magnetism on the other.

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