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Crystallography of epitaxial face centered tetragonal Co/Cu(100) by low energy electron diffraction

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A crystallographic LEED I/V characterization of thin Co/Cu(100) films is presented. Results from dynamical LEED calculations are compared with experiments via Pendry's reliability factor. The first Co layer grows with a small, but noticeable, amount of Co atoms in the second layer. For thicker films up to at least 10 ML, Co is found to grow on Cu layer by layer in a tetragonally distorted structure. The film adopts the lateral Cu spacing with an in-plane lattice expansion and a contraction of the vertical interplanar distances. By subsequent Cu on Co deposition, lateral and vertical Cu spacings are kept, reproducing the initial substrate structure.

The growth of epitaxial thin films of ferromagnetic materials on non-magnetic substrates under ultrahigh vacuum conditions has long been of interest. It offers the possibility of producing materials that are not present in nature, and that may exhibit new properties of a high technological interest [1–3]. In particular, the magnetic properties of ultrathin fcc-Co films [4,5] and Co/Cu superlattices [6] grown on Cu(001) have been studied in detail. A strong dependence of the magnetic properties on the structure and growth conditions has been found.

Several structural techniques such as TEAS [6], LEED [7], X-ray diffraction [8], XPD [9], STM [10] and SEXAFS [11], have been applied to study Co films grown on Cu(100). In spite of the effort, a quantitative description of the crystallography of the overlayer film has not yet been achieved. We report here on a LEED study of this system carried out for 5 different Co coverages, from 1 to 10 ML. Connecting with the first stages of growth of a Co/Cu superlattice, the structure of a 5 ML Cu film grown on a 5 ML Co/Cu(100) surface is also studied and compared with a clean Cu(100) surface.

The lattice parameter of fcc Co at room temperature is 3.548 Å, while the one of Cu is 3.615 Å. During growth on Cu(100), the symmetry of the LEED, MEED and RHEED patterns is 1×1 indicating that the lateral lattice parameter of Cu is adopted by the growing Co film. Now, in order to be strictly fcc, the Co film would have a perpendicular interplanar distance of 1.80 Å. This represents a uniform 2% expansion with a calculated energy cost of 68 meV/atom [12]. This large value of strain energy can be minimized by compressing the vertical distances in the Co film (i.e. introducing a tetragonal distortion) or by developing a lattice of misfit dislocations and changing the film to unstrained fcc Co with a vertical distance of 1.77 Å. We demonstrate here

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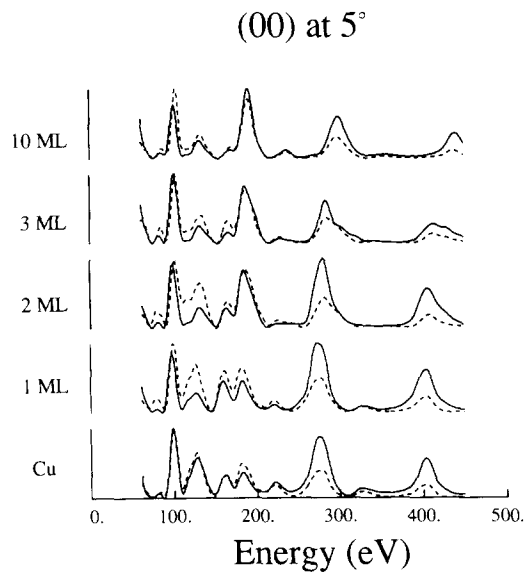

Fig. 1. Evolution with Co coverage of experimental (continuous lines) and theoretical (dashed lines) I/V curves for (00) beams at 5° incidence.

that nature has chosen the tetragonal distortion for thickness up to 10 ML.

Co films were deposited on a Cu(100) substrate prepared by several sequences of 3 kV Ne bombardment and 1000 K heating in a chamber with a 5×10^{-10} Torr base pressure. Co was evaporated from a pure rod and Cu from a tantalum oven via 1.2 kV, 10 mA electron bombardment. Both evaporators featured manual shutters and water cooling. The pressure during the evaporation was in the range of 10^{-10} Torr. Deposition was performed at 325 K with rates of 1–2 ML per minute. Thicknesses of the different films were controlled by MEED oscillations cross checked with a previous Auger calibration [4]. The LEED optics was a retractile OMICRON with a computer controlled Autoleed system, which records the evolution of the intensity–voltage (I/V) curves for several diffracted beams at RT with a CCD camera. Fig. 1 shows the evolution with Co coverage of both theoretical (broken lines) and experimental (continuous lines) I–V curves for the (00) beam at 5° incidence.

It is known that identical crystalline structures of different chemical elements which are close in the periodic table give LEED I–V spectra difficult to distinguish. The spectra in fig. 1 differ in energy position of the Bragg peaks and lineshape, excluding inmediately the possible growth of thick fcc strained films of Co(100). In order to be more specific we have performed a theoretical calculation of the I–V curves for different structures.

The I–V curves were calculated using the fast renormalized forward scattering method [13], known to converge within a wide range of parameters yielding accurate results for the clean Cu(001) surface [14].

As will be seen below, the Co adlayers can also be treated by RFS with very good agreement. At the highest energy a total of 101 beams were involved in the interlayer multiple scattering. We used 8 phase shifts, which were calculated according to the prescription of Matheiss [15], starting from the atomic wavefunctions [16]. The exchange contribution was taken proportional to $\alpha\rho(r)^{1/3}$, where α is an optimized parameter taken from ref. [17]. Actual computations were done using the code provided by Van Hove and Tong [18]. Finally, we have considered thermal effects as isotropic for all systems via the use of a surface Debye temperature for the first Co adlayer which was given a value of $\Theta_D^S(\mathrm{Co}) = \Theta_D^{\mathrm{bulk}}(\mathrm{Co})/\sqrt{1.4} = 330$ K (for clean Cu we chose $\Theta_D^S(\mathrm{Cu}) = 280$ K). On the other hand, the structural determination is based on the use of Pendry's correlation R-factor [19]. All R-factor calculations included minimization with respect to the different interlayer spacings (to be specified in each section), as well as the inner potential V_0.

The accuracy of the calculations has been tested with the data from clean Cu(100). The known oscillatory relaxation of the perpendicular distances [14], $d_{12} = (1.78 \pm 0.02)$ Å, $d_{23} = (1.82 \pm 0.02)$ Å and $d_{\mathrm{bulk}} = 1.805$ Å has been reproduced with an excellent value of the R-factor (0.21). For Co-covered samples, the Cu–Cu distances were set to the bulk lattice spacing of 1.805 Å.

For 1 ML Co/Cu(100), seven beams were available. Only adsorption at the hollow site was considered, since Clarke et al. [7] gave a strong evidence for this position. It has been suggested by ARXPS [9], X-ray diffraction [8] and STM [10]

that below 2 Co ML average coverage, the growth mode deviates slightly from an ideal layer-by-layer model with the adsorbed metal forming a small, but detectable ($\approx 20\%$) percentage of 2 ML-thick islands. Following this approach, we have simulated these islands by averaging (with equal weights) the calculated clean Cu surface beams with those corresponding to 2 full Co ML p (1×1). The averaged beams were mixed with beams calculated for 1 ML of Co with weights chosen in such a way that the sum of both sets always yields an average coverage of 1 ML. From the calculations, the most probable island percentage is found in the 20–40% range. The important point to notice here, is that the R-factor variance excludes a layer by layer perfect growth for this coverage, as was assumed by Clarke et al. [7]. The optimum Co perpendicular distances obtained are: $d_{12} = (1.77 \pm 0.02)$ Å for the 1 ML platform and $d_{12} = (1.76 \pm 0.02)$ Å and $d_{23} = (1.78 \pm 0.02)$ Å for the 2 ML islands, with an R-factor $R = 0.22$. The structural values obtained suggest that these islands essentially keep both the lateral and vertical distances of the clean substrate. We shall shortly see that this apparent tendency to grow in a pseudomorphic (strained fcc) form is finally abandoned by the Co films.

For 2 ML Co/Cu(100) eleven beams were available. For this and the rest of coverages, the in plane Co–Co distance is found to be equivalent to the Cu one, and the Cu–Cu vertical distance in the substrate was set to 1.805 Å. This time, although island formation was also studied, the best agreement was obtained by assuming no islands present. The optimized vertical distances are: $d_{12} = (1.77 \pm 0.02)$ Å and $d_{23} = (1.73 \pm 0.03)$ Å with an R-factor $R = 0.22$.

Six beams were collected for 3 ML Co/Cu(100). In the calculation we assumed that the system had already achieved a perfect layer-by-layer growth. Now the R-factor analysis included variations of the 3 Co interlayer spacings. The optimized perpendicular distances obtained were: $d_{12} = (1.76 \pm 0.02)$ Å, $d_{23} = (1.74 \pm 0.02)$ Å and $d_{34} = (1.76 \pm 0.03)$ Å; with an overall minimum of $R = 0.23$. These values indicate that the Co film is tetragonally compressed since none of these parameters match with the bulk Cu interlayer spacing of 1.805 Å. Earlier rocking curves measured with TEAS for Co films deposited at 420 K [6] indicate that the first interlayer spacing d_{12} is (1.74 ± 0.04) Å for thicknesses between 1.5 and 4.5 ML, in reasonable agreement with the values reported here.

For 5 and 10 ML Co/Cu(100), with five beams available in both cases, the limited penetration of electrons of the energy range used here makes both set of data indistinguishable and equivalent to a semi-infinite Co crystal. The interlayer spacings obtained from the analysis for both coverages are found to be: $d_{12} = (1.72 \pm 0.02)$ Å, $d_{23} = (1.74 \pm 0.03)$ Å and $d_{Co} = (1.73 \pm 0.03)$ Å for the rest of the Co layers, with an R factor of $R = 0.23$. Thus the Co film grows up to 10 ML (at least) with a tetragonally compressed structure ($a = 3.61$ Å, $c = 3.47$ Å) and a negligible contraction (if any) of the first layer spacing.

For 10 ML Co/Cu(100), the experimental I–V curves were also compared with those calculated for unstrained fcc Co (i.e. with a 2.51 Å surface unit cell and $d_z = 1.77$ Å), but the agreement was certainly poorer ($R = 0.37$) than the one obtained for the optimized fct structure.

The lateral coherent growth of the Co on Cu(100) described above can be confirmed by (and it is essential for) growing Cu on top of the Co(100) film. Only two beams were available for this sample. In order to test how perfect would Cu grow on a 5 ML thick Co film, we compared the I/V curves for these beams with those calculated for the clean surface. The result yielded an extremely good agreement ($R = 0.15$ and 0.12 for (10) and (11) beams, respectively), confirming the fact that Cu grows on Co keeping both lateral and vertical Cu(100) substrate spacings. In this way, Co/Cu superlattices will grow in a very stable way, keeping the strain accumulated in the Co film, so that on top of it, Cu grows as if the substrate were also that metal. The I/V LEED data are only sensitive to the 5 ML Cu overlayer and no information can be obtained from the sandwiched Co film. EXAFS data taken in Co/Cu superlattices, however, indicate that they maintain the structure described here for 10 ML uncovered films [20].

In summary, an important percentage of 2

ML-high islands is found for nominal Co thicknesses of 1 ML. For Co thicknesses from 2 up to 10 ML, the expansion in the in plane Co distances dictated by the Cu substrate produces a vertical contraction; the Co(100) film grows in a fct structure without misfit dislocations that could release accumulated stress. Cu deposited on this Co(100) film recovers the substrate structure (both lateral and vertically) and therefore subsequent Co depositions will be structurally equivalent to the one performed on a clean Cu(100) substrate.

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