Curie Temperature of Ultrathin Films of fcc Cobalt Epitaxially Grown on Atomically Flat Cu(100) Surfaces

C. M. Schneider, P. Bressler, P. Schuster, and J. Kirschner

Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-1000 Berlin 33, West Germany

J. J. de Miguel and R. Miranda

Departamento de Fisica de la Materia Condensada, Universidad Autonoma de Madrid, Cantoblanco, 28049, Madrid, Spain

(Received 24 July 1989; revised manuscript received 15 January 1990)

We have explored the relationship between epitaxial growth and magnetism in the case of ultrathin fcc-Co films by means of a multitechnique approach. For high-quality fcc-Co films less than 3 monolayers thick the Curie temperatures T_C are dramatically lower than T_C^B of bulk fcc-Co and decrease distinctly with film thickness. In contrast to previous claims, T_C of a single monolayer appears to be far below 300 K. Substrate topology is found to strongly influence the structural perfection of the films which in turn determines their magnetic properties (Curie temperature, coercive field, and anisotropies).

PACS numbers: 75.70.Ak

In recent years the influence of dimensionality on magnetism has become a matter of considerable interest in both experiment and theory. In particular, the transition from 3D to 2D and the resulting changes in the magnetic properties of a system are discussed controversially. Experimentally, a quasi-2D magnetic system may be realized by growing a few atomic layers of a ferromagnet on top of a nonmagnetic substrate. This task requires the solution of some major problems: (i) the determination of the growth mode and growth conditions; (ii) the precise calibration of the coverage, i.e., the meaning of the quantity "monolayer" for the investigated system; and (iii) the characterization of the structural perfection of the grown film. Further complications may arise by interdiffusion processes between overlayer and substrate. A careful evaluation of these parameters seems to be mandatory considering the contradictory findings on magnetic behavior of thin films. For example, in the case of iron films on silver, both an in-plane magnetization as well as an orientation of the magnetic moments perpendicular to the film plane have been reported for the same range of coverages.[1-5] There seems to be a growing consensus now that such strong discrepancies are most likely due to differing preparation procedures. This elucidates once more the demand to comprehensively examine the growth conditions.

An important but often neglected parameter in epitaxial growth is the topology of the substrate surface. In particular, to interpret results on magnetism in the monolayer range, one should take into account the microscopic structure of a *real* surface, e.g., its roughness (step height and step density). In this Letter we report on the first use of scanning tunneling microscopy (STM) to characterize the topology of various substrate surfaces. Epitaxial growth on top of these substrates is investigated by applying *simultaneously* medium-energy electron diffraction (MEED) and Auger-electron spectroscopy (AES). This yields for the first time a direct correlation between MEED and AES data obtained from the same film *during* the growth process.

Our approach to characterize the magnetic behavior of these Co films is twofold. On the one hand, we perform spin- and angle-resolved photoemission experiments using synchrotron radiation. By this method we obtain information on both the electronic structure and the magnetic properties, in particular, the orientation of the magnetization vector. For the investigated range of coverages and temperatures (see below) the analysis of the spin-polarization vector proves the remanent magnetization to lie within this film plane. Further results from these experiments are the subject of a forthcoming publication.[6] On the other hand, we use the surface magneto-optical Kerr effect (SMOKE) to determine the macroscopic magnetic properties of the system. The value of this method for the magnetic characterization of thin films has already been demonstrated.[7,8] Our experimental Kerr setup allows us to determine the magnetization of a sample both parallel and normal to the film plane. A good signal-to-noise ratio, being the basic requirement for monolayer sensitivity, is achieved by a lock-in technique. The main results from these experiments are as follows.

(a) The Curie temperature T_C of ultrathin fcc-cobalt films is drastically lower than T_C of bulk fcc-cobalt.

(b) T_C depends strongly on the film thickness.

(c) In the temperature range from 150 to 500 K the remanent magnetization is found to be in plane for the investigated cobalt coverages between 1.5 and 20 ML (ML denotes monolayer).

(d) Films with $d_{Co} \geq 2$ ML exhibit a distinct in-plane magnetocrystalline anisotropy with the easy axes of magnetization along the $\langle 110 \rangle$ directions.

(e) For nonperfect films a number of anomalous effects have been found: an apparent decrease in T_C, an increase in the coercive field, and modifications of the in-plane anisotropy.

All experiments were carried out *in situ* at UHV conditions (base pressure $< 2\times10^{-10}$ Torr). To avoid any possible contamination from crucible materials, the films were sublimated by electron-beam evaporation from a cobalt tip. During growth the substrate was held at a temperature of $T_S = 450$ K, the growth rate being 1–2 ML/min. This value of T_S was chosen to obtain optimum growth conditions without the presence of interdiffusion. Cobalt films prepared under these conditions showed essentially the same LEED patterns as the clean copper substrate.

For various Co coverages the hysteresis loops $I_K(H)$ have been taken as a function of the sample temperature (inset, Fig. 1). Thus, for a given film thickness one may determine a critical temperature marked by the disappearance of the hysteresis. The Curie temperature T_C has been obtained by extrapolating $I_K(T)$ to $I_K = 0$ at zero field.[9] The results of these SMOKE experiments are summarized in Fig. 1, showing the dependence of T_C on the Co film thickness. The dramatic decrease from

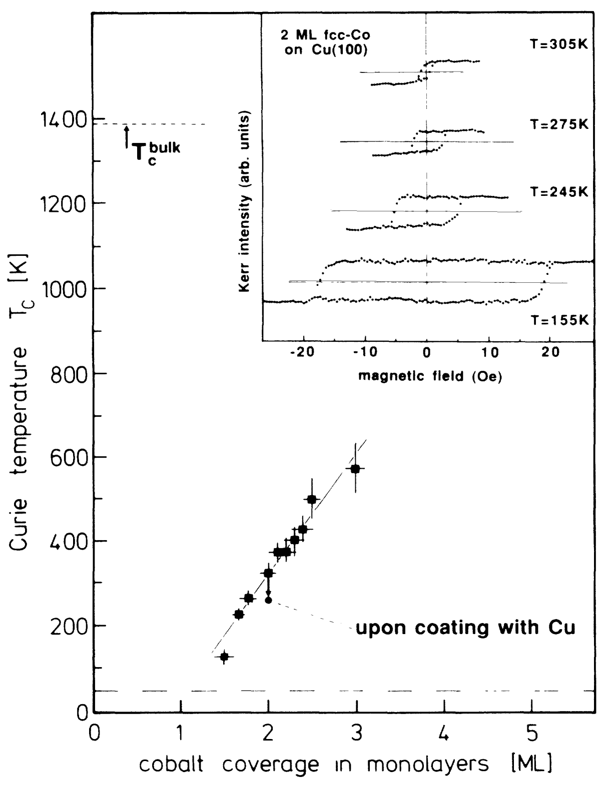


FIG. 1. Coverage dependence of the Curie temperature of fcc-Co films as determined from the SMOKE experiments (the thin line serves to guide the eye). The film thickness in monolayers (ML) has been determined as described in the text. Inset: Variation of the hysteresis loop of a 2-ML film with sample temperature. This temperature dependence has been used to determine $T_C(d_{ML})$ (see also Ref. 10).

$T_C \approx 500$ K (2.5 ML) to $T_C \approx 130$ K (1.5 ML) is clearly visible. Furthermore, these critical temperatures are strongly reduced compared to the value of fcc-bulk cobalt [$T_C^{bulk} = 1388$ K (Ref. 10)]. In particular, a single Co monolayer did not exhibit a ferromagnetic signal above $T = 50$ K which is the lowest temperature we can achieve currently.

For coverages $d_{Co} > 2.5$ ML the procedure used to determine T_C no longer yields reliable results. This is due to interdiffusion between Cu and Co, becoming a significant effect above 500 K. Since cobalt atoms within a copper matrix no longer contribute to the magnetism,[11] this interdiffusion process reduces the magnetically active layer thickness, which explains the already reported changes of T_C upon annealing.[9] For comparison, films have been grown also at RT onto annealed flat surfaces. Whereas the Curie temperature of these samples agreed with the above values, much higher coercive fields could be observed. This illustrates the sensitivity of thin-film magnetism on the preparation conditions.

A similar coverage dependence of T_C as shown above has been found for iron[2] and nickel films.[12] Therefore this behavior appears to be a phenomenon of general nature, correlated to the reduced dimensionality in magnetic thin-film systems.

In order to assure a correct calibration of the deposited coverage, we employ a variety of experimental techniques,[5,9] namely MEED and TEAS (thermal-energy atom scattering) in addition to AES. In both techniques one may observe intensity oscillations in the diffracted beams during the deposition procedure. This behavior is well known as being due to a layer-by-layer growth and may be explained by a periodically varying density of steps at the surface induced by condensing adatoms.[13] For that reason the intensity variations should have monolayer periodicity. We have been able to confirm this point by simultaneously recording the MEED specular intensity I_M and the Auger signals of Co(I_{54}) and Cu(I_{62}) during growth (Fig. 2). The direct comparison reveals the particular correlation between a relative maximum in $I_M(t)$ and a break in the $I_A(t)$ curves. Within the experimental uncertainty, both events coincide marking the completion of a monatomic layer. Since the underlying physical mechanisms of MEED intensity oscillations and Auger breaks are different, each method confirms the layer-by-layer growth independently. Consequently, the Co coverage in monolayers may be determined very precisely by the number of periods in $I_M(t)$. The finding of layer-by-layer growth for fcc-Co on Cu(100) agrees with the results of Gonzalez *et al.*[14] based on an AES analysis.

Finally, to define the expression "monolayer," it is necessary to know whether the first layer really forms a 2D coverage. This may be checked by titration experiments,[14,15] which proved the copper surface to be covered completely at the equivalent of a monatomic lay-

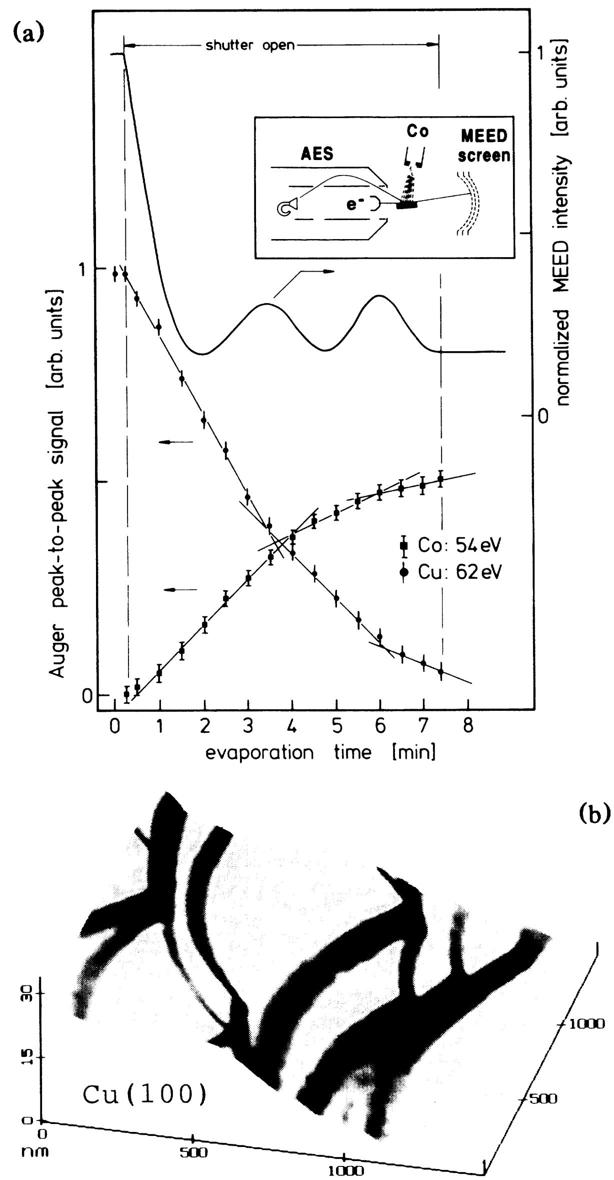


FIG. 2. (a) MEED specular intensity and peak-to-peak amplitudes of the Auger transitions Co_{54} and Cu_{62} vs deposition time. Inset: Experimental setup. The data have been obtained simultaneously. (b) The surface topology of an annealed substrate as observed with a scanning tunneling microscope (STM) showing large terraces on the scale of μm. In contrast to as-sputtered surfaces the terraces are atomically flat and separated from each other by a band of piled-up monatomic steps.

er of Co. Hence, we define a monolayer as the amount N_{Co} of Co adatoms required to form a 2D coverage in registry with the Cu(100) substrate ($N_{Co}=1.54\times10^{15}$ cm^{-2}).

However, contradictory to our results, recently for a Co monolayer a Curie temperature $T_C > 430$ K has been reported.[16] In addition, these authors did not find any variation of their magnetic signal with temperature up to 430 K. This discrepancy with our findings may be due to their incorrect thickness calibration. In the following, we will outline the reasons which make us believe that the film in Ref. 16 is actually thicker than the claimed monolayer.

First of all, from the Auger data forming the basis of their thickness calibration[17] one may determine the inelastic mean free path (IMFP) λ_{in} of the Auger electrons. Assuming that the first break in Fig. 1 of Ref. 17 corresponds to the completion of the first monolayer results in a value of $\lambda_{in} \sim 5$ Å for Auger electrons of 920-eV kinetic energy. This is surprisingly small and does neither agree with experimentally determined[5] nor calculated IMFP values[18] in that energy range. Second, no change of the hysteresis loop with temperature is reported in Ref. 16. In particular, the authors did not notice the striking sensitivity of the coercive force H_c on the temperature as clearly visible in the inset of Fig. 1. Our experiments indicate that changes of H_c with temperature—in the temperature range in question—become less pronounced at higher coverages. Third, in a very recent publication[19] referring to the same thickness calibration the author claims that his cobalt monolayer does not change magnetically, even when covering it with a copper overlayer. This is quite astonishing considering the fact that the d bands of copper and fcc-cobalt are within the same range of binding energies and one could expect a considerable hybridization between them. At least in the interface region this may give rise to a different electronic structure and it is questionable whether such changes would leave the magnetic properties unaffected. This question becomes particularly important in the case of the sandwiched monolayer which principally consists of only two barely separated Cu/Co interfaces. Indeed, if we coat the 2-ML film of fcc-cobalt (inset, Fig. 1) with several layers of copper, we find a significant reduction of the Curie temperature (as indicated by the circle in Fig. 1). It appears reasonable that this effect will become less important with increasing Co film thickness. From these arguments we conclude that only a film significantly thicker than a monolayer would exhibit the properties described in Refs. 16 and 19.

Discussing the physical properties of ultrathin films one should carefully distinguish between an idealized picture and the real surface within experimental reach. This becomes evident by looking at the surface topology on a microscopic scale. Our studies point out a strong correlation between surface topology and the occurrence of intensity oscillations in MEED or TEAS. The latter have been observed solely on clean and well-annealed surfaces like the one shown in the STM image in Fig. 2(b).[20] In the STM only this kind exhibited large, flat terraces, separated from each other by a band of piled-up monatomic steps. The lateral dimensions of the flat areas are in the range of 0.3–0.5 μm. In contrast to this, much smaller terraces (50–100 Å) have been found on the "nonoscillating" surfaces. These results suggest the following conclusion: An almost ideal layer-by-layer growth requires a surface which is atomically flat over large distances. This condition seems to be necessary to obtain reliable results on the magnetism of ultrathin films.

However, our experiments indicate that films grown on such topologically different surfaces do not exhibit the same magnetic properties. This is shown exemplarily for a 2.2-ML film grown on top of an *as-sputtered* (5 keV Ne^+, 3 μA, 15 min) surface. STM investigations revealed the microscopic roughness induced by the sputtering process. At RT the film did not show any ferromagnetic signal in the SMOKE experiment. However, after a short anneal up to $T=450$ K we observed a distinct hysteresis loop and within the experimental uncertainty the Curie temperature of this film agreed with the value of 2.2-ML films grown on a flat surface at RT and $T=450$ K. It should also be mentioned that annealing a film usually lowers its coercive field irreversibly, whereas its magnetization remains the same. This indicates a certain influence of structural defects on the movement of ferromagnetic domains during the magnetization reversal. This influence—and very likely the number of defects—is reduced by the annealing procedure. The observation itself points out that the coercive force is not a useful quantity when comparing results from films of different origin. Furthermore, the structural defects may play an important role in the discussion of magnetic anisotropies. For example, the in-plane anisotropy in fcc-Co films recently reported from the Kerr effect[19,21] and domain imaging experiments[22] seems to require an extremely flat and well-annealed surface to be observable.

In summary, in ultrathin fcc-Co films we found a pronounced thickness dependence of the Curie temperature. In particular, T_C of the single monolayer appears to be below 50 K. The key element in these experiments is a careful thickness calibration which was performed by simultaneously applying medium-energy electron diffraction and Auger-electron spectroscopy. The magnetic properties of these Co films, such as Curie temperature, coercive force, and magneto-crystalline anisotropies, are strongly influenced by the perfection of the substrate surface and structural defects in the layer.

[1]B. Heinrich, K. B. Urquhart, A. S. Arrott, J. F. Cochran, K. Myrtle, and S. T. Purcell, Phys. Rev. Lett. **59**, 1756 (1987).

[2]M. Stampanoni, A. Vaterlaus, M. Aeschlimann, and F. Meier, Phys. Rev. Lett. **59**, 2483 (1987).

[3]N. C. Koon, B. T. Jonker, F. A. Volkening, J. J. Krebs, and G. A. Prinz, Phys. Rev. Lett. **59**, 2463 (1987).

[4]B. T. Jonker, K.-H. Walker, E. Kisker, G. A. Prinz, and C. Carbone, Phys. Rev. Lett. **59**, 142 (1986).

[5]C. M. Schneider, J. J. de Miguel, P. Bressler, J. Garbe, R. Miranda, S. Ferrer, and J. Kirschner, J. Phys. (Paris), Suppl. **C8**, 1657 (1988).

[6]C. M. Schneider, J. J. de Miguel, P. Bressler, P. Schuster, R. Miranda, and J. Kirschner, J. Electron Spectrosc. Relat. Phenom. (to be published).

[7]S. D. Bader, E. R. Moog, and P. Grünberg, J. Magn. Magn. Mater. **53**, L295 (1986).

[8]C. Liu, E. R. Moog, and S. D. Bader, Phys. Rev. Lett. **60**, 2422 (1988).

[9]J. J. de Miguel, A. Cebollada, J. M. Gallego, S. Ferrer, R. Miranda, C. M. Schneider, P. Bressler, J. Garbe, K. Bethke, and J. Kirschner, Surf. Sci. **211/212**, 732 (1989).

[10]J. Crangle, Philos. Mag. **46**, 499 (1955).

[11]W. Wei and G. Bergmann, Phys. Rev. B **37**, 5990 (1988).

[12]R. Bergholz and U. Gradmann, J. Magn. Magn. Mater. **45**, 389 (1984).

[13]J. H. Neave, B. A. Joyce, P. J. Dobson, and N. Norton, Appl. Phys. A **31**, 1 (1983); L. J. Gomez, S. Bourgeal, J. Ibanez, and M. Salmeron, Phys. Rev. B **31**, 2551 (1985).

[14]L. Gonzalez, R. Miranda, M. Salmeron, J. A. Verges, and F. Yndurain, Phys. Rev. B **24**, 3245 (1981).

[15]F. Falo, I. Cano, and M. Salmeron, Surf. Sci. **143**, 303 (1984).

[16]T. Beier, H. Jahrreiss, D. Pescia, T. Woike, and W. Gudat, Phys. Rev. Lett. **61**, 1875 (1988).

[17]A. Clarke, G. Jennings, R. F. Willis, P. J. Rous, and J. B. Pendry, Surf. Sci. **187**, 327 (1987).

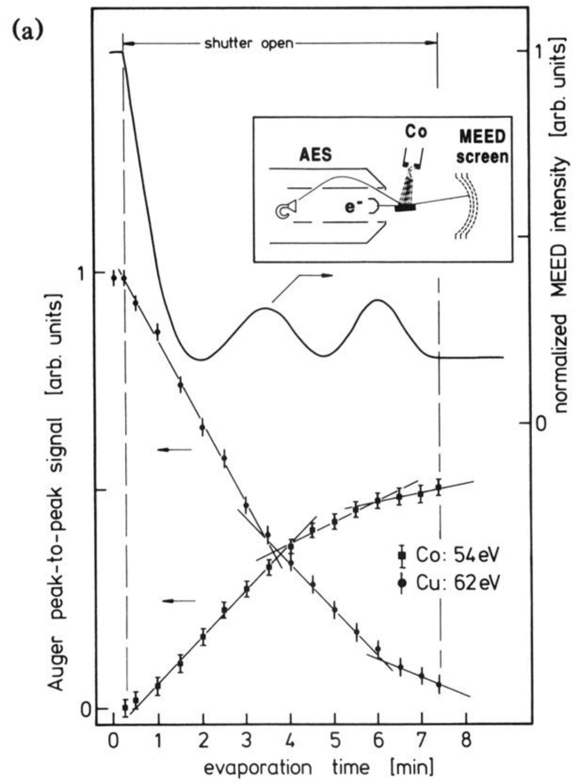
[18]M. P. Seah and W. A. Dench, Surf. Interface Anal. **1**, 2 (1979).

[19]D. Kerkmann, Appl. Phys. A **49**, 523 (1989).

[20]A. Schmid and J. Kirschner (private communication).

[21]C. M. Schneider, J. J. de Miguel, P. Bressler, S. Ferrer, P. Schuster, R. Miranda, and J. Kirschner, Vacuum (to be published).

[22]H. P. Oepen, M. Benning, C. M. Schneider, and J. Kirschner, Vacuum (to be published).



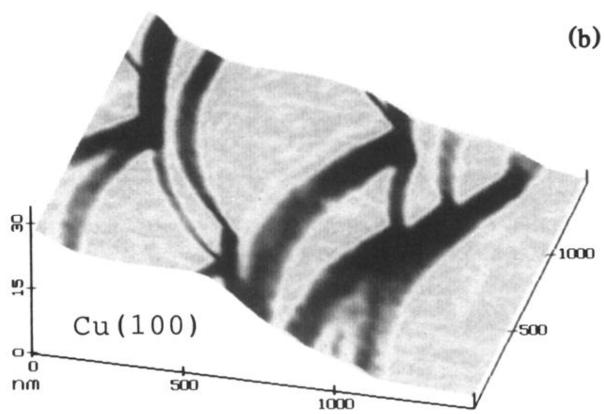


FIG. 2. (a) MEED specular intensity and peak-to-peak amplitudes of the Auger transitions Co_{54} and Cu_{62} vs deposition time. Inset: Experimental setup. The data have been obtained simultaneously. (b) The surface topology of an annealed substrate as observed with a scanning tunneling microscope (STM) showing large terraces on the scale of μm. In contrast to as-sputtered surfaces the terraces are atomically flat and separated from each other by a band of piled-up monatomic steps.