RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 52, NUMBER 20 15 NOVEMBER 1995-II

Submonolayers of adsorbates on stepped Co/Cu(100): Switching of the easy axis

W. Weber
IBM Research Division, Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

C. H. Back, U. Ramsperger, and A. Vaterlaus
Laboratorium für Festkörperphysik, ETH Hönggerberg, CH-8093 Zürich, Switzerland

R. Allenspach
IBM Research Division, Zurich Research Laboratory CH-8803 Rüschlikon, Switzerland

(Received 16 June 1995; revised manuscript received 2 August 1995)

We report a striking sensitivity of the easy magnetization axis in epitaxial Co films upon adsorption of submonolayers of Cu, Ag, Fe, and O if the Cu substrate is a stepped surface slightly miscut from the (100) orientation. All adsorbates cause a switch of the easy axis by 90° within the plane. The key role of this switching phenomenon is played by the atoms at the step sites and their influence on the magnetic surface anisotropy.

The concept of magnetic anisotropy is fundamental for predicting the magnetization direction in ferromagnets without an external field applied. Néel[1] pointed out that symmetry breaking at a surface can create an additional anisotropy term compatible with the changed symmetry, even for perfectly flat surfaces. The microscopic origin, however, is not yet understood very well, particularly because the *ab initio* calculation of anisotropies is a formidable task.[2] Imperfect surfaces pose an even greater challenge. Epitaxial films with defects or steps have locally changed symmetry, which must necessarily influence magnetic anisotropies. Investigations of the energetics at steps or defect sites are rare.[3] For an understanding of real systems, however, they will become essential. We have performed experiments to probe magnetic anisotropies at stepped surfaces by covering magnetic films with adsorbates.

Nonmagnetic adsorbates are known to affect the magnetic anisotropies on flat surfaces. Upon coverage with Cu, Ag, Au, or Pd, the perpendicular anisotropy showed a nonmonotonic dependence on the overlayer thickness in Co/Pd(111) (Ref. 4) and Co/Au(111).[5] Interestingly, in-plane magnetized systems also exhibit such behavior. Fe/W(110) changes its easy magnetization axis upon coverage with Au,[6] which is connected to a surface reconstruction. Coverages of the order of a complete layer are needed to obtain these changes. Only a few experiments have addressed the influence of very small coverages. The perpendicular surface anisotropy was found to change strongly in Ni/Re(0001) (Ref. 7) and Fe/Ag(100) films[8] upon coverage with a small amount of oxygen. The influence of minute amounts of Cu on the magnetism of thin Co(100) films was investigated by Schumann *et al.*[9] A distinct drop of the coercive field H_c occurs. Unfortunately, this H_c dependence does not provide definite information about the anisotropy changes because the connection between coercivity and anisotropy is complicated by various physical processes such as domain-wall nucleation and motion. All these experiments concentrated on surfaces that are as flat and perfect as possible.

In this paper we investigate changes of the magnetic anisotropy on well-defined stepped surfaces. We present data on Cu, Ag, Fe, and O-covered Co films, which show drastic changes of the magnetic anisotropy for submonolayer coverages, provoking a switching of the easy axis within the plane. We performed a systematic study of the magnetic behavior as a function of the adsorbate coverage and species, and relate our observations to the preferential step structure of the films.

The substrates we chose were Cu single crystal oriented 1.6° and 3.4° off the (100) surface, their step direction running along the $[1\bar{1}0]$ direction. After sputtering and annealing cycles up to 800 K, scanning tunneling microscopy (STM) revealed atomically flat terraces having an average width of 6 nm and 3.5 nm, respectively, and an average length of $\approx$300 nm. All metal films were grown by molecular-beam epitaxy at room temperature with deposition rates of 0.5–1 ML/min for Co and 0.02–0.05 ML/min for the other metals (1 ML=0.18 nm for Cu, Co, and Fe, and 0.20 nm for Ag, respectively). The evaporation rates were determined by Auger spectroscopy. In addition, the Cu evaporation rate was calibrated with a stylus profilometer on thicker films. We conclude that the absolute thickness calibration is accurate to within 20% for Cu, and to 50% for the other metals. For the experiments with oxygen, the clean Co film was exposed to a O dose of 0–50 L ($1\ \mathrm{L}\equiv 10^{-6}$ Torr sec) at room temperature. Spot analysis of digitized low-energy electron diffraction (LEED) images reveals a maximum intensity of the $c(2\times 2)$ pattern characteristic for ordered O adsorption between 12 and 20 L. Auger-electron spectroscopy clearly distinguishes between two different stages of adsorption, a pure chemisorption stage between 0 and 20 L and an oxidation stage for larger exposures. As the complete formation of the $c(2\times 2)$ reconstruction corresponds to an O coverage of 0.5 ML, and by taking the LEED analysis as a calibration point for the Auger measurements, we are able roughly to determine the O coverage for all exposures. The magnetic measurements have been performed using the magneto-optical Kerr effect[10] in both the longitudinal and the transverse ge-

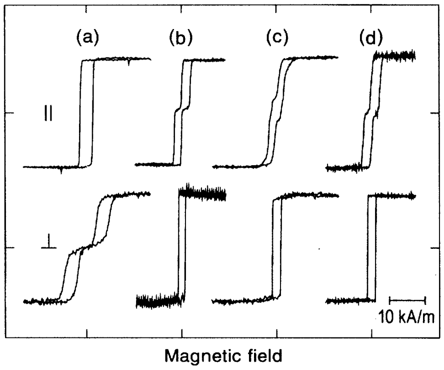

FIG. 1. Hysteresis loops $M(H)$ obtained using the magneto-optical Kerr effect on a 7-ML Co film. Top row, H parallel to the steps; bottom row, H perpendicular to the steps within the plane. (a) Uncovered, (b) covered with 0.08 ML of Cu, (c) covered with 0.27 ML of Ag, and (d) exposed to 20 L of oxygen.

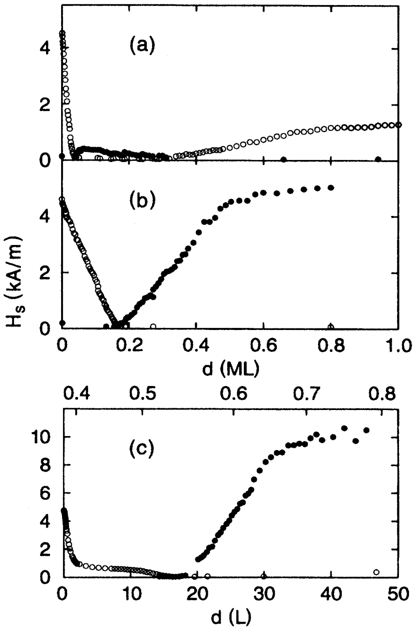

FIG. 2. The shift field H_s of a 7-ML Co film vs coverage for the three adsorbates (a) Cu, (b) Ag, and (c) O, derived from the $M(H)$ loops. Solid circles: H parallel to the steps; open circles: H perpendicular to the steps.

ometry in order to determine the magnetic hysteresis loops $M(H)$ parallel and perpendicular to the preferential Cu substrate step direction without changing the sample orientation.

The drastic changes of the $M(H)$ loops of a 7-ML Co film upon small coverage with various elements are shown in Fig. 1. The loops for the uncovered Co film differ markedly for the magnetic field parallel to the step direction (along $[1\bar{1}0]$) and perpendicular to it (along $[110]$), see Fig. 1(a). For H along $[1\bar{1}0]$ a rectangular loop is found, the typical signature of an easy magnetization axis. In contrast, the loop along the $[110]$ direction is composed of two single shifted loops. This difference must be attributed to the preferential step direction of the substrate. On a perfectly oriented (100) surface, the hysteresis loops along the $[110]$ and the $[1\bar{1}0]$ directions have to be identical, owing to crystal symmetry. The slight miscut of 1.6° reduces the symmetry from fourfold to twofold and changes the $M(H)$ loops. Such a symmetry breaking has previously been observed on Co films grown on Cu(1 1 13) (Ref. 11) and Cu(1 1 17).[12] As a result, the $[110]$ direction, being magnetically equivalent to the $[1\bar{1}0]$ direction in Co on Cu(100), is no longer an easy axis. Actually, the $[110]$ direction is an intermediate rather than a hard axis, because it combines the easy character of the fourfold anisotropy term $(K_1/4)\sin^2(2\phi)$ with the hard character of the uniaxial term $K_u\sin^2(\phi)$, where ϕ denotes the angle between the magnetization vector and the $[1\bar{1}0]$ axis. For positive values of both K_u and K_1, the existence of an intermediate loop requires that the ratio K_u/K_1 be smaller than 1.

Surprisingly, the adsorption of small amounts of Cu, Ag, or O causes a complete change of the loop shapes, see Figs. 1(b)–(d). For Cu coverages exceeding 0.03 ML the roles of the easy and the intermediate axes are interchanged. The rectangular loop occurs now with magnetic field perpendicular to the steps: The easy axis has switched 90° from the $[1\bar{1}0]$ to the $[110]$ direction. Exactly the same behavior is found for slightly larger coverages of Ag, 0.27 ML, see Fig. 1(c), and for an O dosage of 20 L, see Fig. 1(d). This abrupt switching of the easy axis must be ascribed to a sign reversal of the uniaxial anisotropy term.

A more quantitative evaluation can be deduced from the analysis of the hysteresis loops taken parallel and perpendicular to the steps with increasing adsorbate coverage d. More specifically, we analyzed the intermediate axis loops with respect to the shift field H_s. We define H_s as the magnetic-field difference between zero field and the center of the single loops. It is a direct measure of the anisotropy and, in the limiting case $K_u \ll K_1$, $H_s = K_u/M_s$, with M_s the saturation magnetization. We find that the uniaxial anisotropy field of our Co films is of the order of several kA/m, whereas the cubic anisotropy field determined earlier is of the order of 100 kA/m.[13]

Figure 2 shows $H_s(d)$ both perpendicular and parallel to the steps for Cu, Ag, and O. We start with an uncovered Co film of 7 ML thickness and $H_s \approx 5$ kA/m. For minute Cu coverages, H_s perpendicular to the steps is strongly reduced and vanishes for $d \approx 0.03$ ML, see Fig. 2(a). The corresponding H_s parallel to the steps is still zero. Consequently, for Cu coverages around 0.03 ML, the Co film has fourfold symmetry. For $d > 0.03$ ML a nonvanishing H_s appears parallel to the steps, i.e., the anisotropy has changed its sign. After reaching a maximum at $d = 0.06$ ML, H_s decreases again until $d = 0.3$ ML. Then, surprisingly, the magnetization flips again from perpendicular to the steps to parallel. Subsequent Cu coverage leads to an increase of H_s and finally to saturation at $d \approx 1$ ML. Even so, however, the observed switching of the magnetization is a change of the easy axis rather than a metastable magnetization reorientation, because $H_s > H_c$.[14]

The Ag/Co system behaves differently, see Fig. 2(b). After the switching of the easy axis from parallel to perpendicular to the steps at $d = 0.16$ ML, the shift of the single loops reaches essentially the original value of the uncovered film

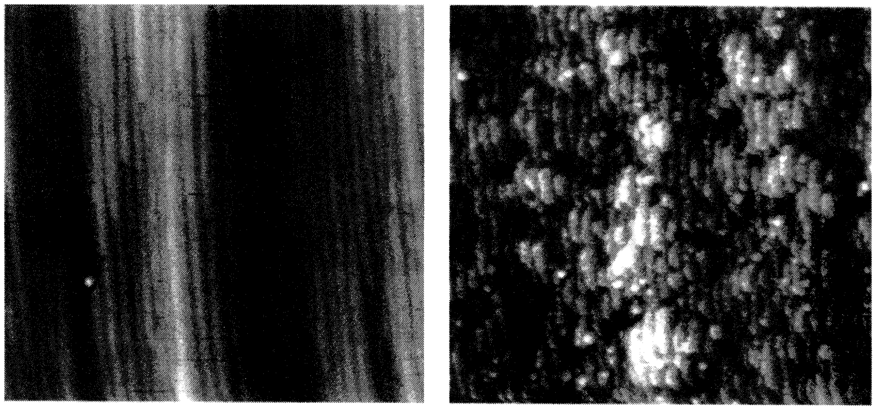

FIG. 3. 100 nm × 100 nm STM images of the clean stepped Cu surface (left) and of a 9.2-ML Co film grown on the Cu surface (right). The gray scale range is 0.56 nm and 0.68 nm, respectively. A plane was subtracted in order to compensate the 3.4° miscut of the substrate.

and saturates at $d \approx 0.7$ ML. No subsequent switching back to the original magnetization direction is observed, however, up to $d = 3$ ML, in contrast to coverage with Cu.

An entirely different adsorbate than the metals Cu and Ag is oxygen. Again, coverage of the Co film with O leads to a decrease of H_s followed by a switching of the easy magnetization axis perpendicular to the steps at a dosage of 18 L, see Fig. 2(c), which still lies in the chemisorption regime. We thus conclude that the observed switching of the easy magnetization axis is caused by adsorbed O and not by a possible Co-oxide phase having different magnetic properties. Thus Co films covered by O display qualitatively the same behavior as metallic adsorbates: The easy magnetization direction switches discontinuously from being parallel to the steps for the uncovered Co film to being perpendicular to the steps upon adsorption of small amounts of an element, be it Cu, Ag, or O.

The origin of this strikingly general observation is attributed to the steps of the Cu substrate. STM experiments on a Cu surface miscut by 4.7° show that Co films for thicknesses above 5 ML replicate the underlying step structure.[15] Our own STM images for a miscut of 3.4° confirm this behavior, see Fig. 3. The consequence is that the morphology of the Co films depends on the step structure of the substrate, and, in particular, that the fourfold symmetry is broken at the Co steps, leading to an additional surface anisotropy term.[11,12,16,17] In particular, the detailed considerations in Ref. 3 were able to explain the observed step anisotropy in Fe/W(110) within the Néel model. Thus for a step Co atom the local magnetic anisotropy is uniaxial and the twofold symmetry direction is within the plane. The symmetry around a terrace atom, on the other hand, is fourfold to the lowest order, reflecting the atomic arrangement on the (100) plane. It is likely, however, that the presence of the steps distorts the lattice on the terraces slightly, and hence also introduces uniaxial magnetic anisotropy to a terrace site. Experimentally we have set an upper limit for such a distortion: On a 7-ML Co film it is $<1\%$ deduced from LEED.

The symmetry arguments alone are not sufficient to predict the magnitude or even the sign of the anisotropy and hence the easy magnetization direction. Assumptions concerning the physical mechanism behind Néel's surface anisotropy have to be made, such as whether crystalline or magnetoelastic anisotropy is the leading energy term.[16] We shall not speculate at this point as to which contribution plays the key role, but rather comment on the consequences of the existence of Co step sites on the adsorbed atoms.

STM experiments show that the adsorbed Cu atoms attach to the Co steps.[18] The observed switching thickness is ≈ 0.03 ML for a miscut of $\alpha = 1.6°$. The ratio of step atoms to the total number of surface atoms is also 0.03 for this miscut. The exact agreement between this ratio and the switching thickness might be fortuitous: If, for instance, the step anisotropy per atom is sufficiently large, even an incomplete filling of the step sites by the Cu atoms is able to revert the sign of the anisotropy. Together with the observation that the Cu atoms decorate the steps, on the other hand, it clearly shows the relevance of the step atoms for the magnetization direction switching. Further support comes from experiments on Co films grown on a substrate having a different miscut, namely, $\alpha = 3.4°$. Again, as expected for the step anisotropy model, several hundredths of a monolayer are sufficient to rotate the magnetization. We note, however, that the simple model cannot be expected to hold for all values of α. If α is large, the magnetic behavior is not expected to be an extrapolation from small miscuts. For instance, the step-induced anisotropy observed for thin Fe films on a 4° miscut $W(100)$ crystal is not found for a 6° off crystal.[17] On the other hand, if α is too small, the average step distance is too large for the Co spins on the terrace to overcome the anisotropy energy barrier and to flip its direction as well.

For the steps to be effectively decorated the diffusion length of the adsorbed atomic species must be larger than the mean terrace width in order to reach the step edge. Diffusion length as a thermodynamically driven quantity depends exponentially on temperature. We therefore adsorbed Cu onto a Co film kept at 150 K instead of room temperature. Again, a change of the easy magnetization direction is observed, but at a far larger Cu coverage. For the 3.4° off crystal we find a switching thickness of 0.56 ML at low temperatures compared to 0.07 ML at room temperature. Qualitatively, this result can be explained by a strong suppression of Cu diffusion to the step edges at low temperatures.

The situation is different for Ag and O adsorbed on Co. For Ag adsorption at 150 or 300 K, the switching thickness is identical. It could be that the heavy Ag atom already has a small diffusion constant at room temperature that keeps a sizable portion of Ag from reaching the step sites. More Ag atoms are then needed to sufficiently decorate the steps and to switch the magnetization direction, in agreement with observation.

From the LEED study it is clear that O takes the terrace sites leading to the $c(2\times 2)$ reconstruction. This means that the step sites are not preferentially occupied, and again a higher coverage is needed to observe a magnetization switching. Hybridization between O and Co wave functions is unlikely, owing to the negligible band overlap between them. In this context it is interesting to note that even a coverage with H at 180 K reduces the shift field H_s of a 7-ML Co film by a factor of 2. Although no easy axis switch was observed, the H_s dependence clearly shows the tendency of H coverage to weaken the magnetic anisotropy and to make the [110] direction magnetically "easier," quite analogous to the other adsorbates.

The anomalous anisotropy behavior observed by adsorbing metals onto Co/Pd(111) (Ref. 4) and Co/Au(111),[5] respectively, is interpreted to arise from the hybridization between Co and the overlayer electronic states. The maximum of the anisotropy, which is reached for adsorbate coverages of about 1 ML, seems to be related to the existence of interface states.[19] In our study the 90° switching of the easy magnetization axis occurs for much smaller coverages far below the completed monolayer of adsorbate. If step decoration occurs, hybridization could be the mechanism responsible for the switching of the easy magnetization direction, but this is more likely to occur at the step atom positions than at terrace sites. On the other hand, the increase of the shift field, and hence the uniaxial anisotropy, for larger adsorbate coverages and the subsequent saturation at about 1 ML may be due to hybridization at terrace sites. In the case of Cu, this might also cause the second magnetization switch at $\approx$0.3 ML for $\alpha=1.6°$ and 0.6 ML for $\alpha=3.4°$. Moreover, we find that submonolayers of Fe, which is known to hybridize considerably with Co, also switch the easy axis by 90° into the [110] direction (0.15 ML for $\alpha=3.4°$). For the nonmetallic coverages of O and H, on the other hand, hybridization cannot explain the observed effect because the required band overlap is small.

In conclusion, we have studied the influence of submonolayers of Cu, Ag, Fe, and O on the magnetic properties of Co films grown on stepped Cu(100) single crystals. Magnetic hysteresis loops taken by the magneto-optical Kerr effect show that all adsorbates cause a switching of the easy magnetization axis from the $[1\bar{1}0]$ to the [110] direction, caused by a strong change of the uniaxial magnetic surface anisotropy. We find that even H coverages cause a reduction of the anisotropy, albeit not sufficient to switch the magnetization direction. Thus irrespective of the adsorbate's specific electronic structure and its capability to hybridize, Co films exhibit drastic alterations of their anisotropy upon coverage with an adsorbate. Despite the similarity of the general behavior, the details are different. In particular a further easy axis switching back into its original direction is only observed in the Cu/Co system. The key role of the step atoms for the observed effect has been elucidated.

We thank A. Bischof and U. Maier for expert technical support, Ch. Würsch for help with the experiments, and E. Mächler for performing the digital LEED analysis. Financial support by the KWF and the Schweizerischer Nationalfonds is gratefully acknowledged.

---

[1] L. Néel, J. Phys. Rad. **15**, 376 (1954).

[2] C. Li *et al.*, Phys. Rev. B **42**, 5433 (1990).

[3] M. Albrecht *et al.*, J. Magn. Magn. Mater. **113**, 207 (1992).

[4] B.N. Engel *et al.*, Phys. Rev. B **48**, 9894 (1993).

[5] S. Ould-Mahfoud *et al.*, in *Magnetic Ultrathin Films—Multilayers and Surfaces, Interfaces and Characterization*, edited by B.T. Jonker, S.A. Chambers, R.F.C. Farrow, C. Chappert, R. Clarke, W.J.M. de Jonge, T. Egami, P. Grünberg, K.M. Krishnan, E.E. Marinero, C. Rau, and S. Tsunashiwa, MRS Symposia Proceedings No. 313 (Materials Research Society, Pittsburgh, 1993), p. 251.

[6] H.J. Elmers and U. Gradmann, Surf. Sci. **304**, 201 (1994).

[7] H.J. Elmers and U. Gradmann, Surf. Sci. **193**, 94 (1988).

[8] J. Chen, M. Drakaki, and J.L. Erskine, Phys. Rev. B **45**, 3636 (1992).

[9] F. Schumann, O. Buckley, and J.A.C. Bland, J. Appl. Phys. **76**, 6093 (1994).

[10] S.D. Bader, J. Magn. Magn. Mater. **100**, 440 (1991).

[11] P. Krams *et al.*, Phys. Rev. B **49**, 3633 (1994).

[12] W. Wulfhekel *et al.*, Phys. Rev. B **50**, 16 074 (1994).

[13] P. Krams *et al.*, Phys. Rev. Lett. **69**, 3674 (1992).

[14] W. Weber *et al.*, Nature (London) **374**, 788 (1995).

[15] M. Giesen, F. Schmitz, and H. Ibach, Surf. Sci. **336**, 269 (1995).

[16] D.S. Chuang, C.A. Ballentine, and R.C. O'Handley, Phys. Rev. B **49**, 15 084 (1994).

[17] J. Chen and J.L. Erskine, Phys. Rev. Lett. **68**, 1212 (1992).

[18] U. Ramsperger *et al.* (unpublished).

[19] D. Hartmann *et al.*, J. Magn. Magn. Mater. **121**, 160 (1993).

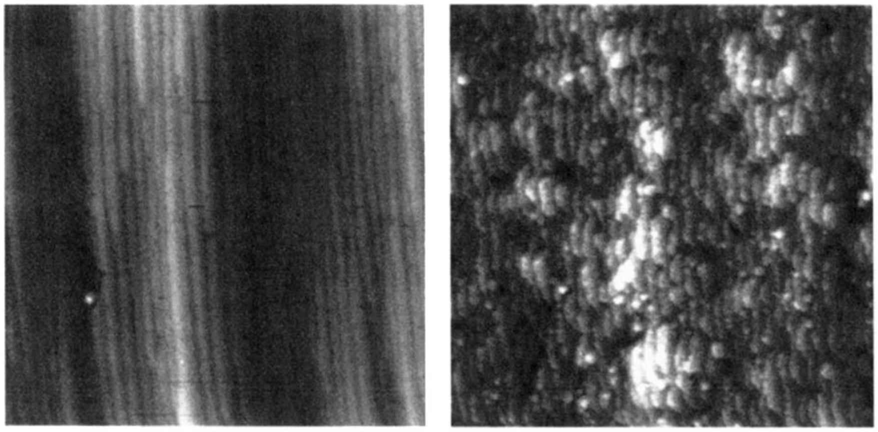

FIG. 3. 100 nm × 100 nm STM images of the clean stepped Cu surface (left) and of a 9.2-ML Co film grown on the Cu surface (right). The gray scale range is 0.56 nm and 0.68 nm, respectively. A plane was subtracted in order to compensate the 3.4° miscut of the substrate.