Dynamic evolution of the magnetic anisotropy of ultrathin Co/Cu(110) films

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We have studied the magnetic properties of the Co/Cu(110) system ($5\ \mathrm{ML} < d_{\mathrm{Co}} < 40\ \mathrm{ML}$) at 300 K, using the magneto-optic Kerr effect. The magnetic easy axis is found to switch through 90° for a constant Co thickness, typically over a period of one hour. We attribute this behavior to the reversal in sign of the effective in-plane uniaxial anisotropy constant, due to the adsorption of submonolayer quantities of residual CO gas in the UHV chamber. Scanning tunnel microscope images reveal the growth of elongated island structures preferentially oriented along the [001] direction providing edges for gas adsorption. [S0163-1829(98)01214-4]

It has become clear in recent years that the morphology, growth mode, and crystalline structure of ultrathin magnetic films can strongly affect the magnetic behavior. For example, it has been shown that variations of the film roughness when going from a filled to an incompletely filled layer can cause oscillations in the uniaxial anisotropy in Co/Cu(001).[1,2] The reduced symmetry at surface steps in the same system, which result in an additional twofold contribution to the surface anisotropy has also received a great deal of attention. Weber *et al.* have observed that submonolayer coverages of Cu, Fe, Ag, or O on the deliberately miscut Co/Cu(001) stepped surface can cause the magnetic easy axis to switch 90°, from a direction parallel to the step edges to one perpendicular to the step edges.[3,4] Similarly, Buckley *et al.*[5] have observed easy axis direction changes, when submonolayer coverages of Cu are grown on Co/Cu(001) for crystal miscuts of only 0.5° (three times smaller than the miscuts on the substrates used by Weber). The question arises as to whether or not in-plane easy axis switching can occur in structures that have not been miscut.

The Co/Cu(110) system has received relatively little attention. However, with the combination of a three-dimensional (3D) growth mode[6] and a lower order twofold symmetric surface, one might expect the Co/Cu(110) system to display very different magnetic properties to the Co/Cu(001) system. The (110) orientation contains the ⟨111⟩ directions (the bulk easy axis of fcc Co) as well as the ⟨001⟩ and ⟨110⟩ directions, which are the symmetry axes for uniaxial anisotropies. The (110) surface therefore allows us to differentiate between the cubic and uniaxial anisotropy contributions due to different symmetry axes.

In this paper, we present the results of a study of the magnetic properties of the Co/Cu(110) system at 300 K in the thickness range $5\ \mathrm{ML}(6.15\ \text{Å}) < d_{\mathrm{Co}} < 40\ \mathrm{ML}(49.2\ \text{Å})$ using the magneto-optic Kerr effect (MOKE) in the transverse geometry. For a given thickness of Co in the range mentioned above, the system exhibits a uniaxial anisotropy favoring an in-plane easy magnetization direction along [001]. With no further Co deposition, the uniaxial anisotropy switches 90° to favor the [1-10] direction over a repeatable duration dependent on the thickness of the Co film and the time elapsed since chamber bakeout. To our knowledge no such temporal evolution of the magnetic properties of ultrathin films has been seen before. We discuss these results in terms of the effect of residual gas adsorption at sites revealed by scanning tunnel microscope (STM) images.

The magnetic measurements were carried out under UHV conditions with a base pressure of 1.0×10^{-10} mbar. The single-crystal Cu(110) substrate was prepared via cycles of 1 kV Ar^+ sputtering and annealing to 700 K, until Auger electron spectroscopy (AES) and low-energy electron-diffraction measurements indicated a clean, well-ordered surface. Co was evaporated from a commercial electron-beam evaporator with an integral flux monitor, at a constant rate of around $0.4\ \mathrm{ML\ min^{-1}}$. The pressure remained below 3.0×10^{-10} mbar during Co deposition and the thickness of the films was evaluated from the relative heights of the Co and Cu Auger peaks recorded at the end of the experiment. This procedure gives an error in the absolute thickness of ≈25%. However, by keeping the evaporation rate constant, the relative thicknesses are known much more accurately. The STM measurements were performed at Liverpool IRC using the same crystal under the same pressure conditions, and using the same model of Omicron evaporator.

Structural studies indicate that that growth of Co on Cu(110) does not exhibit the near ideal layer-by-layer growth mode seen for Cu(001) substrates.[6,7] Studies at 300 K indicate that the growth is far from layer-by-layer below 5 ML. Even after 5 ML of deposited Co, 20% of uncovered Cu still remains.[6] To our knowledge no *in situ* magnetic measurements have been performed on the Co/Cu(110) system in the ultrathin regime. Brillouin light scattering (BLS) measurements of fcc Au/Cu/Co/Cu(110) *ex situ*, between 8 and 110 Å Co thickness, show an unexpected suppression of the magnetocrystalline anisotropy contribution below 50 ± 10 Å Co.[8–10] The magnetocrystalline anisotropy contribution K_1 becomes vanishingly small at Co thicknesses below ≈15 ML. They find a strong in-plane uniaxial anisotropy that they attribute to magnetoelastic effects at the Co/Cu substrate interface.[8]

Measurements of a 6 ML Co film grown on Cu(110) are shown in Fig. 1. The top and bottom panels show M-H loops obtained with the field applied parallel to the [001] and [1-10] directions, respectively. The time elapsed after the end of the Co deposition is given in minutes underneath each loop. A square loop with unity remanence is observed along the [001] direction five minutes after the end of the Co deposition, indicating that this is a magnetic easy axis. Angle-dependent studies show that the [1-10] direction is a mag-

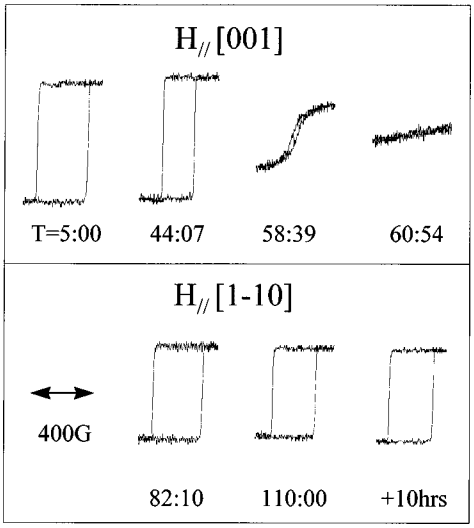

FIG. 1. The time evolution of the M-H loops for a 6 ML Co/Cu(110) film. The magnetic easy axis is observed to switch by 90° from the [001] to [1-10] direction in a duration of the order of 1 h. The time in minutes after the end of the Co deposition is given in minutes underneath each M-H loop.

netic hard axis at this time. With no further Co deposition, the M-H loops are observed to evolve continuously in time until the [001] direction has become a magnetically hard axis after 60 min. Rotating the sample so that the field is now applied along the [1-10] direction we observe an easy axis square loop with unity remanence along this direction. Therefore, the magnetic easy axis has switched 90° to favor the [1-10] direction over a period of approximately 1 h. The bottom panel shows that once the easy axis has switched, there is only a very small reduction in coercive field up to 110:00 min, after which the loops stop evolving and we find no further changes in the easy axis direction. We observe qualitatively equivalent behavior for all Co thicknesses studied in the range 5 ML$<d_{\mathrm{Co}}<$40 ML.

To investigate the M-H loop evolution in greater detail, we have plotted the loop squareness S and coercive field H_c as a function of time for the same sample as in Fig. 1. We have defined the loop squareness as the ratio of the remanent to saturation magnetization $S=M_{\mathrm{rem}}/M_{\mathrm{max}}$, and M_{max} is the loop amplitude measured from the maximum Kerr intensity. The top and bottom panels of Fig. 2 are each split in two by a dotted line that separates data taken when the field is applied parallel to the [001] and [1-10] directions, respectively. The top panel shows that S remains constant along [001] at $S=1$ over $\approx$60 min, before dropping sharply to zero, then rising sharply to $S=1$ along [1-10] where there are no further changes. The behavior of the coercive field H_c (bottom panel) in contrast, displays an almost linear decrease with the field applied parallel to the [001] axis over $\approx$60 min at which time it drops sharply to zero. This sharp drop is accompanied by an initial sharp rise of H_c as observed with the field applied along [1-10]. From 60 to 85 min H_c increases almost linearly for fields applied parallel to [1-10] in a mirror image behavior to that observed along [001] during the first 60 min. This initial [1-10] behavior is not shown in Fig. 2 due to the practical difficulties in performing an angle-dependent MOKE study during a time-dependent

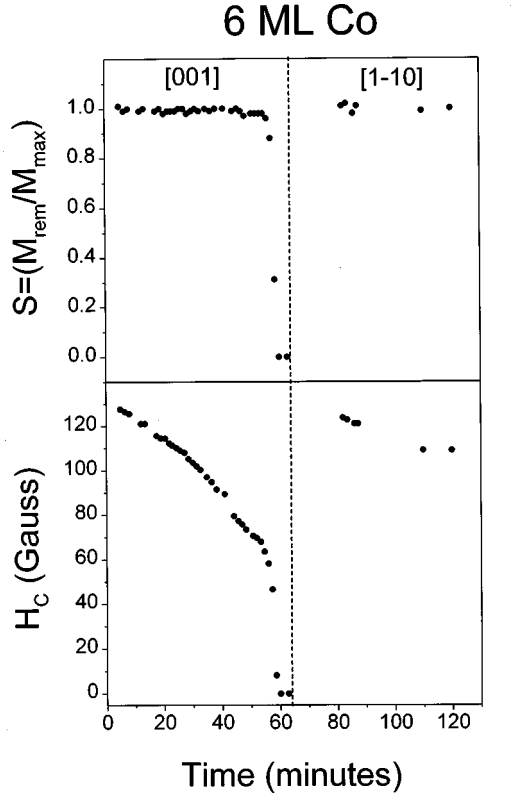

FIG. 2. The evolution of the loop squareness S and coercive field H_c for the sample discussed in Fig. 1, as a function of time during the period of magnetic easy axis switching. The dashed line separates data collected when the magnetic easy axis is found along [001] and [1-10], respectively.

process on the same sample. However, we have observed this behavior with experiments performed with the field applied exclusively along the [1-10] direction during the easy axis switch. After reaching a maximum along [1-10] at 85 min, H_c then reduces slightly before reaching a constant level. The loop evolution is in qualitative agreement with the results shown in Fig. 2 for all Co thicknesses studied.

Although it is found initially that the time taken to switch easy axes remains constant at a given Co thickness, the same experiments are observed to slow down by more than an order of magnitude as a function of the time the system has remained under UHV conditions after bakeout. We emphasize that this slowing down occurs even though there is no measurable change in the base pressure of the system (1×10^{-10} mbar). This finding immediately rules out the processes of surface reconstructions, thermally driven Co adatom diffusion or room temperature substrate Cu segregation as the driving mechanisms responsible. Although AES detected no contamination within its resolution limit ($\approx$0.5 ML) we conclude that the adsorption of minute quantities of a residual gas from the UHV chamber is responsible for the magnetic switching. Residual gas analyzer readings indicate that hydrogen, oxygen, or carbon monoxide may be responsible. Dosing experiments on a 15 ML Co film show that only a 0.08 ML of CO gas is required in order to cause the easy axis to switch. Dosing O only serves to destroy the sample magnetism (a 1 Langmuir dose is found to destroy the magnetism in a 8 ML Co film). Ar dosing is also found to be unable to switch the easy axis. Although we have not

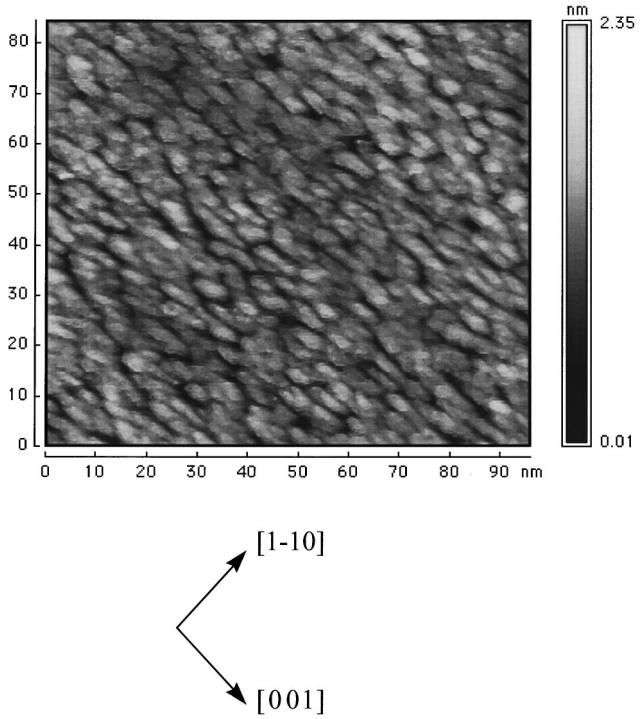

FIG. 3. STM image of 6 ML Co/Cu(110). The image shows that the Co grows via the formation of three-dimensional elongated island clusters preferentially oriented along the [001] direction. The island lengths vary between 9 and 15 nm and the widths vary between 1 and 5 nm.

directly dosed hydrogen into the chamber, we can study the effect of increasing the amount of hydrogen indirectly by allowing the cold trap to warm up to room temperature thereby significantly worsening the base pressure of the system. This was found to have no effect on the time taken for the easy axis to switch and therefore we believe that the system is not sensitive to hydrogen adsorption.

Figure 3 shows an STM image of a 6 ML Co/Cu(110) film. It is clear from Fig. 3 that the growth proceeds via the formation of three dimensional elongated island clusters preferentially oriented along the [001] axis, parallel to the initial easy axis direction of the system. The island lengths vary between 9 and 15 nm and the widths vary between 1 and 5 nm. Although our crystal is not stepped (miscut less than 0.25°), Fig. 3 does indicate that the elongated Co structures do provide ''step like'' edge sites for the gas adsorption in analogy to the vicinal surfaces studied by Weber.

Noting that the shape anisotropy keeps the magnetization in the plane of the film[8] we can model the magnetic anisotropy of the system as follows:

$$E_{\mathrm{tot}}=\frac{K_1}{4}\,(\sin^4\varphi+\sin^2 2\varphi)+K_u^{\mathrm{eff}}\cos^2\varphi,$$

where K_1 is the cubic anisotropy constant and the angle φ is measured from the [001] axis. The second term is the effective in-plane uniaxial anisotropy term. Since both K_1 and K_u^{eff} are known to be negative,[8] then the cubic term favors the $\langle 111\rangle$ axes, and the uniaxial term favors the $\langle 001\rangle$ axes as easy magnetization directions. To explain our results we modify the above equation by replacing K_u^{eff} with a time-dependent term $K_u^{\mathrm{eff}}(t)$, which changes sign as the residual CO gas/Co interface grows, thereby switching the easy axis to the [1-10] direction. At $t=0$ min after Co deposition, K_u^{eff} is negative, hence the easy axis initially lies along [001]. From Fig. 2, H_c reduces initially almost linearly over the first 60 min as is consistent with a reducing in-plane anisotropy strength along [001]. Near the transition S and H_c drop sharply to zero (corresponding to $K_u^{\mathrm{eff}}=0$) and then rise sharply as a function of time, implying that once a very small positive K_u^{eff} exists, the easy axis behavior is re-established, but this time along [1-10]. If K_1 was nonzero for this Co thickness (6 ML), then as K_u^{eff} tends to zero, the easy axis would tend to shift towards the $\langle 111\rangle$ direction and S would not be expected to remain at unity during this time. The fact that S remains at unity at all times except briefly at the easy axis cross over region implies that the cubic anisotropy K_1 is negligible at this thickness. Therefore our results are in agreement with the (BLS) measurements of Hillebrands *et al.* that show that the cubic anisotropy component of the total anisotropy is vanishingly small for Co thicknesses below 15 ML.[8]

To test this conclusion further we have grown another sample (~5 ML Co) and observed the easy axis switching with the external field always applied along the [1-11] direction, i.e., the easy axis favored by the cubic anisotropy term. At no time did the M-H loop display unity remanence indicating that this axis does not become an easy axis when $K_u^{\mathrm{eff}}=0$, and hence K_1 must be negligible at this thickness. An important consequence of this result is that when $K_u^{\mathrm{eff}}=0$ the sample becomes briefly magnetically isotropic for Co thicknesses below 15 ML.

Unfortunately, the extremely small quantities of CO involved were not visible with STM. However, it is possible to learn something of the preferred CO adsorption sites from annealing experiments. Before the easy axis has switched, a 6 ML Co film is found to be extremely susceptible to thermally induced Cu segregation to the surface. Auger measurements show that up to 0.5 monolayers of Cu can be segregated at temperatures as low as 325 K. We attribute this to the presence of gaps/pinholes in the trough regions between Co islands.[11] For slightly higher temperatures (380 K), a thermally induced segregation of 1 ML of Cu is found to stop the easy axis switch from occurring. This amount of Cu cannot be expected to entirely cover the surface area of the Co and therefore the Cu must occupy specific sites preferred by the CO molecules. Surprisingly, for the same Co thickness, there is no Cu segregation when the film is annealed after the easy axis has switched. This can be explained by the CO molecules ''plugging'' the pinholes along island edge sites. This is reasonable since CO would not desorb from the Co until the temperature was in the region of 400 K or more.[12] Therefore, Co island edge sites are the preferred CO adsorption sites or at least it is only at these sites that the CO can promote easy axis switching.

Annealing Co films after the easy axis has switched, reverses the switch and there are no further easy axis changes. CO desorption can be ruled out as the mechanism responsible since it would readsorb on cooling, switching the easy axis again. STM reveals that the Co surface undergoes a slight morphological rearrangement during the anneal and so

it is possible that the CO molecular bond is broken by this atomic rearrangement. Evidence to suggest the CO molecular bond is easily perturbed is given by the work of Tracy *et al.*[13] that shows that CO molecules can be dissociated (freeing the oxygen atom and leaving the carbon atom behind) simply by exposing the surface to an electron beam of energy greater than 15 eV. We have found that the easy axis switch can indeed be reversed by exposing the film to a 3 kV Auger electron beam for ~ 40 min. CO molecules tend to adsorb vertically onto Co with the carbon atom in contact with the Co atoms.[14] Therefore, our electron-beam experiment reveals the remarkably subtle nature of the CO induced electronic structure change to the Co, since both atoms of the CO molecule are needed to promote easy axis switching yet the oxygen atom is not in contact with the Co surface.

In summary, we have shown the easy axis of magnetization is observed to switch through 90° over a period of about 1 h as minute quantities of CO gas are adsorbed onto the Co surface for all Co thicknesses studied in the range $5\ \text{ML} < d_{\text{Co}} < 40\ \text{ML}$. This is a new phenomenon and is surprising because the temporal evolution in magnetic behavior occurs at a fixed Co thickness. The CO gas in the UHV chamber causes a reversal in sign of the effective uniaxial anisotropy. STM images and annealing experiments reveal that the CO molecules are adsorbed along island edge sites. The edge sites appear as a consequence of the ''natural'' nanometer scale morphology resulting from the 3D growth mode in this system. The easy axis switch can be reversed by annealing the Co film to 380 K for 40 min or by exposing the film surface to an electron beam, thereby dissociating the CO molecules. Our results highlight the extreme sensitivity of the magnetic behavior of ultrathin films to the surface morphology and to subtle electronic changes at the surface. The work also has important implications for all *in situ* magnetics research since even at the best UHV pressures obtainable, residual gas can still have a dramatic influence on the magnetic properties of thin films as highlighted here.

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