Surfactant-Mediated Modification of the Magnetic Properties of Co/Cu(111) Thin Films and Superlattices

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Deposition of Pb on Cu(111) prior to the growth of Co/Cu superlattices changes the magnetic properties of the latter. The use of a surfactant induces layer-by-layer growth of Co and delays the fcc to hcp structural transition. As a consequence, the easy axis of magnetization remains perpendicular to the plane for Co/Cu films grown with Pb. On the other hand, the elimination of twinning in the Cu spacers grown with surfactants allows the observation of complete antiferromagnetic coupling in Co/Cu superlattices for both in-plane and out-of-plane magnetization. [S0031-9007(96)00377-8]

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In thin films and in short-period superlattices, many magnetic properties such as the saturation magnetization or the Curie temperature, T_C, become extremely sensitive to the crystal structure [1]. Furthermore, magnetic and nonmagnetic multilayers show new phenomena such as antiferromagnetic (AF) coupling [2], oscillatory magnetic coupling [3], and oscillatory giant magnetoresistance (GMR) [4]. Some characteristic properties of these phenomena, such as the switching fields, the magnitude of GMR, or the lack of complete AF coupling [5–10] are believed to be strongly influenced by structural defects. In these artificial systems it is, thus, very important to control the microstructure at the atomic level in order to manipulate the magnetic properties. This can be achieved in various cases by employing suitable surfactants [11] during the growth of the films [12]. In particular, it has been reported that the deposition of a monolayer of Pb prior to the growth of Co/Cu superlattices on Cu(111) suppresses the twinning of the Cu spacer layers [12]. It was further suggested [12] that the twinned Cu spacers, which are commonly obtained when growing without surfactants, are not continuous. They yield magnetic bridges responsible for the observed [5,6,8] partial ferromagnetic (FM) coupling of adjacent Co layers separated by Cu spacers of thickness appropriate to show AF coupling. It has yet to be demonstrated, however, that the use of surfactants results in actual changes of the magnetic behavior of the material grown by this method.

In this Letter we describe experimental evidence for such changes: We show first that the predeposition of Pb extends the thickness range of perpendicular magnetization for a single Co film grown on Cu(111), and second that it produces perfect Cu spacers through which *complete* AF coupling for *both* perpendicular and parallel magnetization of adjacent Co layers can be detected. The surfactant influences the magnetic properties via a modification of the crystal structure of the deposited films. It eliminates defects in the stacking sequence of the Co layers, removes the twinning of the Cu spacers, and reduces the interface roughness [13,14]. The results presented here provide a clear-cut example of the close relation that exists between microstructure and magnetic properties in thin films and superlattices.

The experiments were performed in two ultrahigh vacuum (UHV) chambers. The substrates were Cu(111) crystals with a maximum miscut of 1°. They were cleaned by repeated cycles of Ar+ sputtering and annealing until no signal of contamination was detected by Auger electron spectroscopy (AES). Co, Cu, and Pb overlayers were deposited from *e*-gun evaporators with the substrate held at room temperature (RT) except during Pb deposition (at 490 K). The quality of the growth was continuously monitored by thermal-energy atom scattering (TEAS) in one UHV chamber, and by medium-energy electron diffraction (MEED) in the other. The deposited coverage was calibrated by AES spectra measured with a cylindrical mirror analyzer (CMA). With predeposition of Pb the MEED intensity displays oscillations with monolayer periodicity which were consistent with the AES calibration. The deposition rate of Co was ~ 0.5 ML/min. Under these conditions the density of islands is 3×10^{11} cm^{-2} as detected by scanning tunneling microscopy (STM) [15]. The coverage is given in monolayers (ML), with 1 ML = 1.77×10^{15} atoms cm^{-2}, i.e., the surface density of Cu(111). The magnetic characterization at RT was carried out *in situ* by means of surface magneto-optical Kerr effect (SMOKE) performed in both polar and longitudinal geometries, which are sensitive, respectively, to the magnetization perpendicular and parallel to the film plane. Hysteresis loops of the Kerr intensity were used to determine the Kerr saturation, remanence, and coercivity. The maximum applied magnetic field was 560 Oe. The

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easy axis of magnetization was ascertained by comparing Kerr loops for perpendicular (polar) and in-plane (longitudinal) applied fields.

Co grows on Cu(111) at RT by first forming bilayer islands, followed at higher coverage by simultaneous multilayer growth, i.e., forming terraced pyramids [15]. The corresponding monotonic increase in the step density produces no oscillations in TEAS [12], nor in MEED as shown in Fig. 1(a). Co films thicker than 2 ML start to develop stacking faults and contain regions of hcp stacking [13,16]. As a result, these Co films are rough, with many layers simultaneously exposed, characterized by a Gaussian growth front of FWHM of $\sim$ 4–5 ML [17]. Deposition of $\sim$ 1.5 ML of Pb on Cu(111) prior to the evaporation of Co results in the layer-by-layer growth of a highly perfect, strictly fcc Co film [14]. The periodic variation of the surface step density characteristic of layer-by-layer growth gives rise to oscillations in the MEED intensity as displayed in Fig. 1(b). The period of the oscillations corresponds to 1 ML of Co coating. The Pb overlayer floats on top of the growing Co film as verified by AES, low-energy electron diffraction (LEED) [12], and surface-sensitive x-ray diffraction [14], the latter two detecting the 4×4 surface reconstruction associated with the Pb overlayer.

At RT spontaneous magnetization is detected for Co/Cu(111) at a coverage of about 2 ML [10], with the magnetization vector perpendicular to the film plane [10]. Increasing the Co coverage above 2 ML immediatly leads to regions of the sample being magnetized *in* the plane and with smaller coercivities [18]. At even larger coverages the easy axis of magnetization lies in the plane of the film [19]. The top panels of Fig. 2 show that 3 ML Co/Cu(111) exhibits a hysteresis loop only for in-plane magnetization in agreement with previous data [19]. At this thickness the volume (shape) anisotropy ($K_V = -1.2 \times 10^6$ J/m^3) overcomes the (weak) Co/Cu interface anisotropy which has been estimated to be 0.18 mJ/m^2 [19]. Covering the 3 ML Co film with 4 ML of Cu produces a second Co/Cu interface. However, the existence of many atomic levels (up to 6 for 3 ML coverage [15]) in Co films grown without Pb results in a high degree of interfacial roughness between the Co and the capping layer. This reduces the influence of the interface anisotropy which is not large enough to overcome the volume anisotropy, and the magnetization remains in the plane, as demonstrated in the second panel of Fig. 2. It has to be kept in mind that the 3 ML Co film already contains regions of hcp stacking [14] which may contribute additionally to the observed difficulty to rotate the easy axis out of the plane.

On the contrary, the easy axis of magnetization of Co films grown on Cu(111) with a Pb surfactant layer can be rotated from in plane to perpendicular to the plane by adding a Cu capping layer. The third panel of Fig. 2 shows that 3 ML Co/Pb/Cu(111) displays similar hysteresis loops as 3 ML Co/Cu(111). Notice that in spite of the large spin-orbit coupling of Pb, the Pb–Co interface

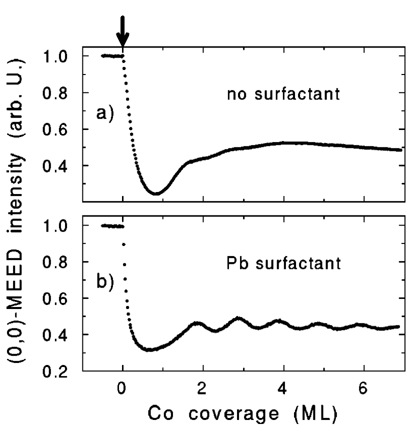

FIG. 1. MEED specular beam intensity for Co films grown at room temperature on Cu(111) (a) without Pb and (b) with 1.5 ML of Pb deposited on the substrate prior to the growth. The arrow indicates the opening of the shutter. The electron beam energy was 2.4 keV. The deposition rate of Co was 0.5 ML/min.

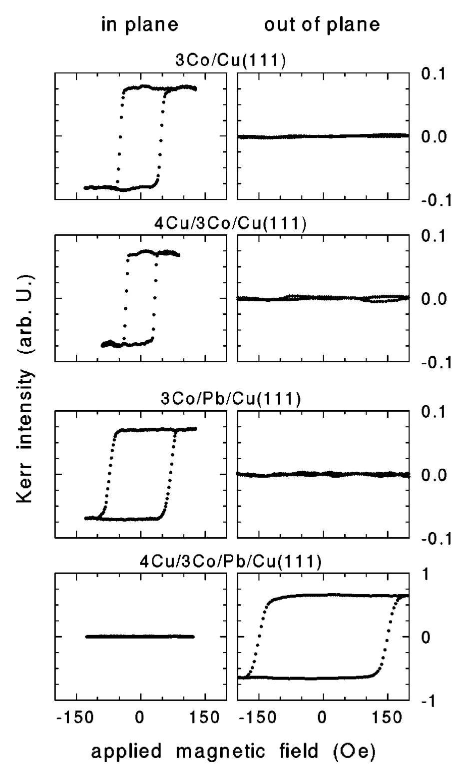

FIG. 2. Kerr hysteresis loops measured at room temperature in longitudinal (left panels) and polar (right panels) geometries. They correspond from top to bottom to films of 3 ML Co, (4 ML Cu)/(3 ML Co), (3 ML Co)/(1.5 ML Pb), and (4 ML Cu)/(3 ML Co)/(1.5 ML Pb), respectively. The polar Kerr signal is larger than the longitudinal signal, accounting for the different y-axis of the bottom panels. A sloping background has been subtracted from the loops.

anisotropy is not large enough to rotate the easy axis of magnetization out of the plane. However, when covering the Co film with 4 ML of Cu, i.e., producing a 4 ML Cu/3 ML Co/Pb/Cu(111) structure, the magnetization rotates to perpendicular to the plane, as illustrated in the bottom panel of Fig. 2. This rotation has its origin in the use of the Pb surfactant which yields a flat fcc Co film with only two atomic levels simultaneously exposed and with smooth Co/Cu interfaces. As a consequence, the interface anisotropy can overcome the shape anisotropy. The fact that the Cu capping does rotate the easy axis of magnetization, while the Pb capping does not, highlights the importance of hybridization in establishing the interface anisotropy.

The Pb surfactant technique affects yet another magnetic property, namely coupling between adjacent Co layers across Cu spacers. It has been established that Co/Cu (111)-oriented multilayers, both polycrystalline and grown by molecular beam epitaxy (MBE), display AF coupling of maximum intensity for Cu spacers of ~ 8 Å (4 ML) thickness. The AF coupling can be obtained for Co thicknesses corresponding to both perpendicular [10] and parallel [4] magnetization. In all cases, however, the coupling has been found to be incomplete, with large fractions (up to 80%) of the sample showing FM coupling [5,8], as indicated by large remanent magnetization in zero field. The reason for this (extrinsic) FM coupling is not yet known, although magnetic bridges [10,15], magnetostatic "orange peel" [20] coupling due to conformal roughness [21] and pinholes [8] in the Cu spacer have been invoked.

Figure 3 compares polar SMOKE loops recorded for single and doubly repeated 4 ML Cu/(2–3 ML Co)/ superstructures grown with and without Pb on Cu(111). At these Co coverages the magnetization is perpendicular to the plane [22]. The thickness of the Cu spacer (4 ML) has been chosen to maximize the AF coupling between the Co layers. In spite of this, the multilayer grown without Pb displays hysteresis loops for single and double periodicity, indicating that large parts of the 4 ML Cu/2 ML Co/4 ML Cu/2 ML Co/Cu(111) film remain FM-coupled (although some regions of the sample might be AF-coupled). This is in agreement with observations by other groups [10]. The use of the Pb surfactant produces a *complete* cancellation of the signal indicative of perfect perpendicular AF coupling, i.e., the two Co layers of identical thickness have their magnetization vector antiparallel aligned (bottom right panel of Fig. 3). Co/Cu superlattices grown by MBE tend to show conformal roughness. The pyramidal growth commonly observed on (111) fcc substrates induces bumps. They are reproduced in the following layers in a correlated way. The resulting (conformal) waviness of the magnetic layers yields magnetic dipole fields which lead to FM interlayer coupling. This magnetostatic coupling can be as large as the RKKY exchange coupling [21] and competes with the antiferromagnetism of the latter. We have shown [12] that the predeposition of Pb, apart from maintaining the fcc stacking sequence of the Co layers, removes the twinning of the Cu spacers. In addition, the use of the surfactant produces smoother and flatter films, eliminating the conformal roughness. These structural effects are essential for the observation of perfect AF coupling through thin Cu spacers.

Figure 4 reproduces SMOKE loops recorded in the longitudinal geometry for Co/Cu multilayers grown with and without Pb on Cu(111). In this case the thickness (4–6 ML) of Co corresponds to in-plane magnetization while the Cu spacer (4 ML) should yield maximum AF coupling. Again there exists partial FM coupling for all coverages in the sample grown without Pb, while

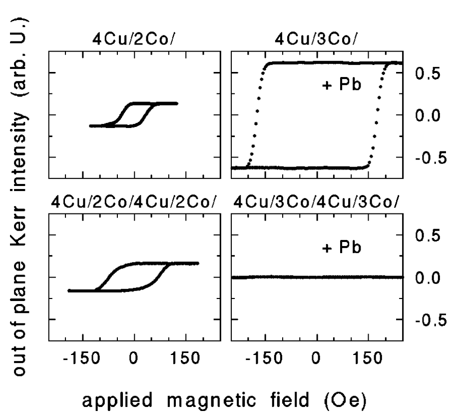

FIG. 3. Polar Kerr hysteresis loops measured on Co/Cu films grown at room temperature without (left panels) and with predeposited Pb (right panels) on Cu(111). The cancellation of signal for the bilayer grown with Pb indicates complete AF coupling between the Co layers.

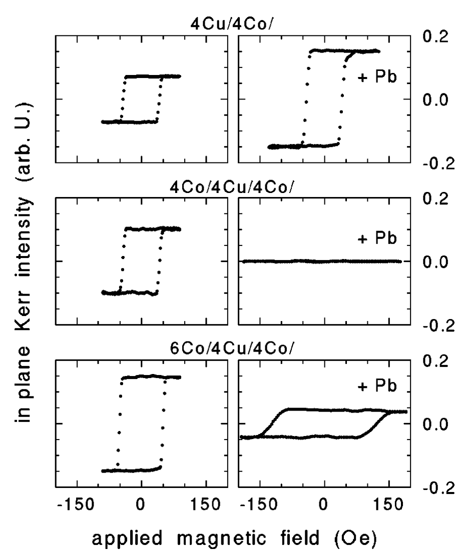

FIG. 4. Longitudinal Kerr hysteresis loops for Co/Cu films grown without (left panels) and with predeposited Pb (right panels) on Cu(111).

the (4 ML Co)/(4 ML Cu)/(4 ML Co)/trilayer fabricated with Pb displays total AF coupling. After additional Co coating the Kerr intensity recovers and shows the hysteresis loop expected for a perfectly grown, AF-coupled, asymmetric trilayer (bottom right panel). The coercivity is enhanced due to the AF exchange coupling, and the saturation magnetization is reduced by roughly a factor of 2 compared to the (4 ML Cu)/(4 ML Co)/ structure. The data clearly illustrate the dramatic effects on the magnetic coupling resulting from the use of the surfactant. The role of the surfactant is again to catalyze the growth of the films by suppressing the twinning of the Cu spacers and by eliminating other defects which may act as magnetic bridges and short out the indirect exchange coupling between the Co layers.

In summary, we have demonstrated that the use of specific surfactants, such as Pb, modifies the magnetic properties of thin Co films and Co/Cu superlattices via substantial reduction of the layer roughness and elimination of structural defects such as twins and stacking faults.

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Note added.—While writing this manuscript we have become aware of work by Egelhoff *et al.* [23] which indicates that the use of Pb as a surfactant in polycrystalline Co/Cu spin valves improves the GMR behavior of these devices, in line with the findings described here.

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