Reentrant Surface Anisotropy in the Antiferromagnetic/Ferromagnetic Bilayer Mn/Co/Cu(001)

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We investigated the magnetic anisotropy energy of monatomic surface-step atoms in antiferromagnetic/ferromagnetic (AF/FM) epitaxial Mn/Co bilayers grown on vicinal Cu(001) surfaces. The step-induced anisotropy of the Co/Cu(001) films was quenched upon submonolayer Mn deposition, but a reentrant uniaxial surface anisotropy was observed for Mn thickness (t_{Mn}) between 1 and 2 monolayers, which disappears for Mn thickness above 2 monolayers. In the Mn/Co/Cu(001) system, Mn films undergo a t_{Mn}-dependent transition from FM to AF in the 1–2 Mn monolayer thickness range, which entails the coexistence of FM and AF Mn phases in the film. The observation of a sizeable uniaxial anisotropy exclusively in the Mn-thickness range of coexistence of the FM and AF phases points out the crucial role of the boundaries between FM and AF regions within the Mn film. A symmetry-breaking mechanism of a magnetic type, rather than a purely geometric one, is therefore proposed as the origin of the reentrant anisotropy.

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The magnetic anisotropy energy (MAE) plays a key role in defining many fundamental properties of magnetically ordered materials [1–3]. The magnitude and functional form of the MAE define the so-called easy and hard magnetization axes, determine the stability of the magnetization, and influence the magnetization reversal behavior and the domain wall (DW) width. MAE has been the subject of great attention, experimental and theoretical, in ferromagnets (FM), either in bulk or nanostructure form, where it is controlled by low-coordinated atoms [4–7]. MAE is also a defining property of antiferromagnets (AF), yet in this class of materials it is much less investigated, especially in nanostructures [8,9]. This is mainly because accessing the MAE in AF surfaces, ultrathin films, or nanoparticles is experimentally challenging, both by direct [9,10] or by indirect methods [11–14]. Thus, the possibly crucial influence of low-coordinated atoms in these systems is so far largely unexplored.

In this Letter, we report an investigation of the MAE of low-coordinated atoms at the surface of a Mn film in Mn/Co bilayers grown on a slightly miscut Cu(001) surface. In the early stages of growth on Co/Cu(001), Mn undergoes a thickness-dependent transition from FM to AF ordering in the 1–2 monolayer (ML) thickness range, which entails the coexistence of FM and AF Mn phases in the film [15]. We exploited such phase coexistence to investigate the influence of the local magnetic structure on the MAE of Mn atoms at low-coordinated surface-step sites. Such a MAE was made detectable by the substrate miscut, chosen to be sufficiently low to affect neither the Mn film structure nor its almost perfect layer-by-layer growth mode [4,5]. We observed that the pristine step-induced uniaxial magnetic anisotropy in the Co/Cu(001) film, quickly quenched upon submonolayer Mn deposition, exhibits a reentrant behavior for Mn thickness (t_{Mn}) in the range between 1 and 2 ML, and finally disappears for $t_{Mn} > 2$ ML. We ascribed the reentrant magnetic anisotropy to the contribution of Mn atoms located at the boundary between FM and AF phases within the Mn film. In particular, we propose that in this system the boundaries between FM and AF Mn phases act as symmetry-breaking elements which can induce a modification of the MAE of the atoms located in their proximity, in analogy with the geometrical symmetry-breaking mechanism responsible for the onset of the peculiar magnetic anisotropy experienced by atoms at low-coordinated surface sites [16].

The experiments were performed in an ultrahigh vacuum chamber with a base pressure of 1×10^{-10} mbar, described in previous publications [17]. The chamber is equipped with Co and Mn molecular beam epitaxy evaporators, medium-energy electron diffraction (MEED), an ion-sputter gun, and a combined low-energy electron diffraction (LEED) and Auger electron spectroscopy instrument (Omicron SPECTALEED) for assessing the sample structure and chemical composition. The experimental setup allows performing *in situ* variable temperature magneto-optical Kerr effect (MOKE) ($130\ \mathrm{K} < T < 800\ \mathrm{K}$) in the longitudinal configuration, with a maximum applied field H_{max} of about 600 Oe.

The Cu(001) crystal was cleaned by repeated cycles of 1 keV-Ar^+ sputtering and annealing at 830 K. Co (Mn) films were deposited at a pressure lower than 3×10^{-10} mbar, with a deposition rate of 1.3 (0.6) ML/ min. Co films (8 ± 0.1 ML thick) were grown on Cu(001) with the substrate held at room temperature, while Mn was deposited onto the 8 ML-thick Co/Cu(001) films at $T = 250$ K, in order to limit interdiffusion and alloying [18]. Mn was deposited in the form of a thickness wedge, making use of a movable shutter placed in front of the sample. The Co and Mn thickness were calibrated monitoring the MEED (00) spot intensity during growth. Typical MEED curves for Co/Cu(001) and Mn/Co/Cu(001) deposition are reported in Fig. 1. The Co/Cu(001) case shows the well-defined MEED oscillations characteristic of its layer-by-layer (LBL) growth. If grown on Co/Cu(001), Mn is stabilized in an expanded-fct γ-phase structure and grows dislocation-free up to 40 ML [19–22]. During Mn deposition, though previous STM studies have proven that the growth occurs in the LBL mode [23], the MEED oscillations become evenly spaced only from the third oscillation onwards. Thus, the periodicity of the MEED oscillations from the third oscillation on, which scales back to the deposition start, has been used to define the Mn deposition rate and coverage. This initial lack of regularity may stem from the evolution of the film structure in the early stages of the growth of Mn on Co/Cu(001). In particular, LEED analysis shows the onset of a $c(12 \times 8)$ superstructure that sets in at about 1.5 and persists above 5 ML Mn thickness in agreement with Refs. [22] and [24]. Thus, the periodicity of the MEED oscillations from the third oscillation on, which scales back to the deposition start, has been used to define the Mn deposition rate and coverage. All measurements have been performed at $T = 250$ K.

The Cu(001) substrate was miscut by 0.3° along the $[1\bar{1}0]$ direction. The imbalance in the density of monatomic steps aligned perpendicular or parallel to the miscut direction endows the system with an in-plane step-induced uniaxial magnetic anisotropy which adds to the pristine in-plane biaxial anisotropy of the Co/Cu(001) film [25,26]. The interplay between the uniaxial and biaxial anisotropies influences the magnetization reversal mechanism and, consequently, the shape of the hysteresis loops. In particular, the hysteresis loops of the stepped Co/Cu(001) films measured with external field $\mathbf{H}\perp[1\bar{1}0]$, i.e., along the step-induced anisotropy hard axis [Fig. 2(a)], exhibited a characteristic split shape, due to the Co magnetization reversal occurring in two distinct 90°-rotation jumps.

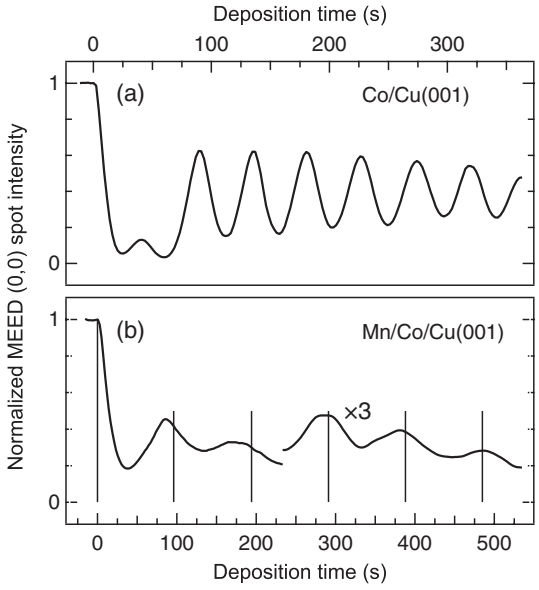

FIG. 1. Intensity of the (00) MEED spot during the deposition of Co on Cu(001) (a) and Mn on Co/Cu(001) (b). The evenly spaced vertical lines in panel (b) correspond to the full Mn ML.

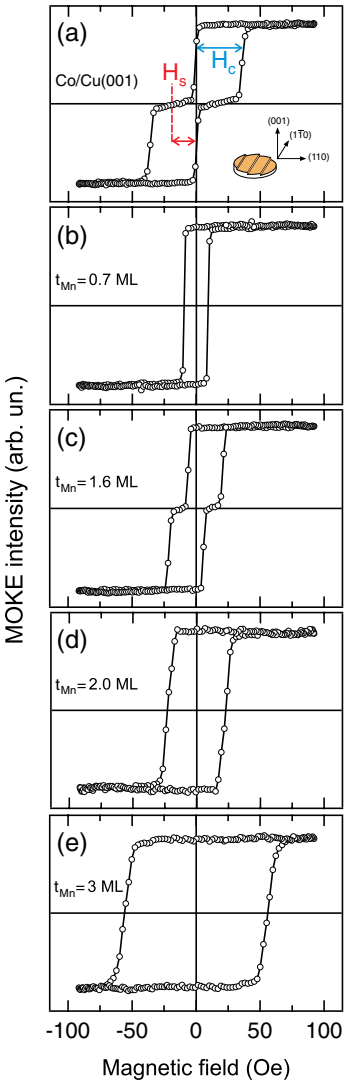

FIG. 2 (color online). Hysteresis loops measured with external field $\mathbf{H}\perp[1\bar{1}0]$ for Co/Cu(001) (a) and for increasing Mn coverage: 0.7 (b), 1.6 (c), 2 (d), and 3 ML (e).

The so-called shift field H_s, i.e., the separation between the subloops and the zero-field axis, is proportional, in first approximation, to the uniaxial MAE [25,26]. For the clean 8 ML Co/Cu(001) films [Fig. 2(a)], we find $H_s \approx 17$ Oe [26].

In Figs. 2(b)–(e), a set of hysteresis loops for the Mn/Co/Cu(001) system in correspondence of selected values of t_{Mn} are reported. The full t_{Mn} dependence of H_s and of the coercive field H_c is summarized in Fig. 3(a). For increasing Mn coverage, the coercive field stays roughly constant below 20 Oe until the 2 ML mark, thereafter it quickly and monotonically increases, reaching 500 Oe at $t_{Mn} \approx 8$ ML. The shift field has instead a more complex t_{Mn} dependence. In the very early stages of Mn growth, H_s monotonically drops, reaching zero at $t_{Mn} \approx 0.4$ ML. H_s stays zero until about 1 ML, then reappears, and reaches a local maximum of $H_s \approx 10$ Oe at $t_{Mn} \approx 1.5$ ML before decreasing again, becoming null at $t_{Mn} \approx 2$ ML. For further increasing t_{Mn}, H_s remains zero. No sign of loop splitting was observed for hysteresis loops measured with **H** aligned along the step-anisotropy easy axis.

In Fig. 3(b) we report the x-ray magnetic circular dichroism (XMCD) asymmetry at the Mn-L_3 edge as a function of t_{Mn}, defined as $I^+ - I^-/I^+ + I^-$, where $I^{+(-)}$ represents the absorption spectra measured for right (left) circularly polarized x rays. XMCD measurements have been performed at the high-energy branch of the Advanced Photoemission Experiment (APE) beamline at the Elettra synchrotron light source [27], on a wedged Mn/Co/Cu(001) sample analogous to the one measured by MOKE. In agreement with Ref. [15], the Mn XMCD signal decreases for $1 < t_{Mn} < 2$ ML, reaching zero at $t_{Mn} \approx 2$ ML, and thereafter remaining zero for increasing t_{Mn}. The decrease of the Mn XMCD signal is compatible with a linear trend which, according to O'Brien and Tonner [15], stems from the peculiar evolution of the Mn magnetic structure: Mn is fully FM up to 1 ML thickness. As soon as the second Mn ML nucleates, 2 ML-thick islands become AF, while 1 ML-thick regions remain FM, thus implying a FM-AF phase coexistence in the $1 < t_{Mn} < 2$ ML thickness range. At the completion of the second Mn ML, the film finally becomes fully AF.

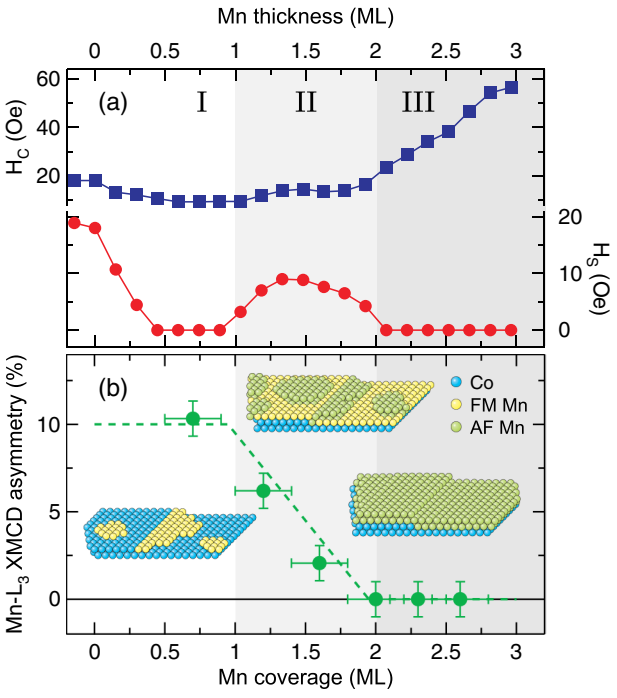

FIG. 3 (color online). Panel (a): Coercive (squares) and shift (circles) fields as a function of t_{Mn} in Mn/Co/Cu(001). Panel (b): XMCD asymmetry at the Mn-L_3 edge as a function of t_{Mn}. Error bars account for the uncertainty of the x-ray absorption measurement (about 0.5% of the total electron yield signal) and the thickness estimation performed by XPS (±0.2 ML). The dashed line is drawn according to the model of Ref. [15]. The insets schematically show the growth model (see text).

Based on the thickness dependence of the Mn magnetic phase, we can readily understand the Mn-thickness dependence of H_c. In the bare Co/Cu(001) film the magnetization reversal is expected to proceed mostly by DW propagation, as testified by the sharp transitions observed in the hysteresis loops, where the main factor that determines the coercive field is the DW depinning field. Since the DW depinning field is not directly influenced by magnetic anisotropy and the uniaxial MAE and its changes as a function of Mn coverage are much smaller than the pristine cubic MAE of the Co film [25], the evolution of H_c doesn't trace the evolution of H_s. However, in agreement with what is generally observed in AF/FM systems below the critical AF thickness for the onset of the exchange bias [28], H_c increases for increasing thickness of the AF overlayer [21].

The t_{Mn} dependence of H_s is definitely more intriguing and reflects the influence of the magnetic phase evolution of the film on its surface MAE. We propose here an interpretation to account for it, based on few simple assumptions. First, concerning the system morphology, we recall that the terrace width is large enough not to strongly modify the film growth mode (cf. the well-defined MEED oscillations observed during the Co growth). The substrate-induced step imbalance is preserved almost unaltered during film growth [25].

Second, we assume that we can detect a contribution of Mn atoms to the uniaxial anisotropy, hence to H_s, only by those spins that are exchange coupled to the underlying Co magnetization, and whose configuration in the cases of Co magnetization parallel (perpendicular) to the miscut direction is macroscopically anisotropic. This automatically includes the Mn FM fraction, which is FM exchange coupled to Co, and may possibly include AF Mn spins, provided their collective spin orientation changes between $[1\bar{1}0]$ and [110] as a consequence of a 90° rotation of the Co magnetization.

We can thus model the H_s thickness dependence as follows, making explicit reference to the schemes I–III reported in Fig. 3. In the early growth stages ($t_{\mathrm{Mn}} < 0.5$ ML), Mn will eventually decorate the Co steps and quench their uniaxial anisotropy. This leads to a gradual drop and eventual disappearance of H_s (I). Upon approaching the 1 ML mark, we expect that, due to its LBL growth, the Mn film is conformal to the underlying Co film, thus replicating its step imbalance. This implies that, not only does Mn quench the Co step anisotropy, but Mn atoms at the monatomic steps bounding Mn islands also yield no measurable uniaxial MAE of their own.

Between 1 and 2 Mn ML, we notice that the t_{Mn} dependence of H_s resembles the cyclic variation of the monatomic step density at a surface during LBL growth. In the ideal case, such a density reads zero in correspondence of full layers, and is at its maximum in correspondence of half-filled layers. We accordingly propose that there is a finite contribution to the uniaxial surface MAE from Mn atoms located in correspondence of 2 ML-island boundaries. The simplest picture is that the Mn atoms responsible for such an anisotropy are the ones belonging to the FM fraction (i.e., to the first Mn layer), yet in contact with the 2 ML-thick islands (II). Such atoms find themselves within an electronically and magnetically complex environment, since the edge of 2 ML-thick islands represents the border between AF and FM phases where complex magnetic patterns may emerge due to the minimization of the exchange energy. The corresponding symmetry breaking, of a magnetic rather than a purely geometric type, might be the factor that triggers the appearance of the aforementioned uniaxial anisotropy.

The disappearance of the uniaxial anisotropy above 2 ML is clearly correlated with the disappearance of the FM Mn fraction within the film (III). This has two implications: First, either the AF spins are decoupled from the underlying Co magnetization, or AF Mn atoms at surface steps do not sustain a uniaxial MAE. Second, there is no residual uniaxial anisotropy from the buried Co steps. This last implication points to the fact that the reentrant uniaxial MAE is most likely ascribable to the surface Mn atoms, and not to a spurious contribution from the buried Co steps. Concerning the contribution of AF Mn atoms, the increase of H_c for increasing Mn coverage above 2 ML and the absence of exchange bias in the investigated thickness range [21] undermine the complete decoupling of the Mn overlayer from the underlying Co film, rather supporting a null or vanishing small MAE of Mn step atoms in AF film portions.

Assuming, after Weber *et al.* [25], that the island aspect ratio during LBL growth is only slightly affected by the stepped Co film surface, the uniaxial MAE of Mn atoms at the 1–2 ML border can be simply estimated from the loop splitting and the step density, as

$$K_u = \frac{a^3}{4} H_s M_s \frac{t_{\mathrm{Co}}}{\tan \alpha}, \quad (1)$$

where a is the lattice parameter of Cu (neglecting here the 4% out-of-plane compression of fcc Co), H_s is the maximum reentrant loop splitting, $M_s = 1430$ emu/cm^3 is the saturation magnetization of fcc Co, t_{Co} is the Co film thickness in monolayers, and α is the vicinal angle. In Eq. (1), the contribution of the FM fraction of the Mn film, which for $t_{\mathrm{Mn}} = 1.5$ ML amounts to about 0.5 ML, and the reduction of Co magnetization upon the Mn deposition [29] have been neglected. This yields $K_u \approx 85$ μeV/atom, about half the value of the uniaxial MAE of Co atoms at step edges [6].

In conclusion, we observed an unconventional evolution of the step-induced anisotropy in exchange-coupled Mn/Co/Cu(001) bilayers. As a function of Mn thickness, the pristine Co step uniaxial anisotropy is quenched below 1 Mn layer, and then reappears in the thickness range between 1 and 2 ML, for which AF and FM phases of Mn coexist within the film. We suggest that such phase coexistence is the origin of the reentrant anisotropy, and we propose that the observed anisotropy originates from the surface Mn atoms located at the borders between the monolayer-thick FM Mn phase and the 2 ML-thick AF islands.

Our work shows that the elusive surface anisotropy of low-coordinated Mn atoms has a complex dependence from the magnetic configuration of their atomic scale environment. Furthermore, our data show that the magnetic anisotropy of low-coordinated atoms may not be the sole consequence of a geometric symmetry breaking, but rather arise at the boundary between two different magnetic phases. Analogous phenomena might indeed be a general feature of AF/FM interfaces, whose wide range of magnetic properties can be often traced to the appearance of characteristic MAE arising at the heteromagnetic contact of the two phases.

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