Effect of CoO/Ni orthogonal exchange coupling on perpendicular anisotropy of Ni films on Pd(001)

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The effect of orthogonal exchange coupling between antiferromagnetic CoO and ferromagnetic Ni/Pd(001) on the perpendicular anisotropy of Ni films is studied. The thickness range in which Ni films show a perpendicular easy magnetization axis is extended by growing CoO on top of them, however, only at temperatures below $T_K$ of CoO. The perpendicular orientation of Ni spins and the in-plane orientation of CoO spins are confirmed by the magneto-optic Kerr effect/x-ray magnetic circular dichroism and x-ray magnetic linear dichroism, respectively. Additionally, a perpendicular exchange bias shows up at low temperature.

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I. INTRODUCTION

The interface exchange coupling mechanism in the antiferromagnet (AFM)/ferromagnet (FM) system has been widely investigated in the last few decades. A lot of attention has been given to distinguish the coupling direction between the FM and AFM spins in such systems [1–3]. It is of particular interest to exploit the FM/AFM coupling which modifies magnetic anisotropy and switches the easy magnetization axis from in plane to out of plane. This is very important for many novel applications where perpendicular magnetization is strongly required, in particular, for tunneling magnetoresistance (TMR) based reading heads and for magnetic random access memory (MRAM) [4,5]. Very recently, it was shown that the magnetic easy axis of FM layers can be changed from in plane to out of plane due to the collinear coupling between the perpendicularly oriented unpinned magnetic moments of the Mn AFM layer in the Mn/Fe system [6].

Existing models explain the exchange bias effect for systems with an uncompensated AFM surface (i.e., all spins are oriented in the same direction) and with collinear (i.e., parallel or antiparallel) FM/AFM exchange coupling at the interface [7]. However, theoretical calculations for compensated interfaces (i.e., neighboring spins of the interfacial AFM plane are oriented antiparallel) show that the AFM and FM spins may be coupled orthogonally due to the “spin-flop” mechanism [8].

In the last decade, the compensated antiferromagnet (AFM) surface, e.g., CoO(001) in contact with a ferromagnetic layer, has been deeply investigated [9–11]. A lot of attention has been paid to the system with a CoO layer, because as an AFM layer, it has strong magnetic anisotropy [12,13] and an ordering temperature close to room temperature (RT) [13,14]. Moreover, recently, it was experimentally and theoretically shown that the orientation of the magnetic moments of CoO can be controlled via the strain applied to that layer [15,16], which can open new opportunities to investigate the coupling direction in CoO/FeM systems. Up to now, one of the main interests was focused on the CoO/Fe system to distinguish the direction of the coupling between CoO and Fe spins [14,17,18]. It was found that this interfacial coupling favors perpendicular alignment [17], however, due to the substrate influence, collinear coupling was also observed [18]. It should be noted that the quality of the CoO/Fe interface plays an important role because the large number of uncompensated spins in the nominally compensated surface of CoO can change the coupling direction from orthogonal to collinear [14].

Theoretically, it is well known that such an orthogonal coupling can generate an effective uniaxial anisotropy [19]. This has been observed experimentally for many FM systems with in-plane anisotropy, for instance, NiO/Fe or CoO/Fe bilayers grown on a Ag(001)-stepped surface [18,20,21]. However, there are only a few reports regarding orthogonal coupling in the layered system with perpendicular magnetic anisotropy (PMA) [22–24]. In magnetron sputtered CoO/[Co/Pt] multilayers, it was observed that the in-plane spin orientation of the CoO layer supplies the additional in-plane contribution to the anisotropy of the Co/Pt, thereby reducing the PMA of the Co/Pt multilayer [22]. On the other hand, in a well-crystallized CoO/Fe/Pt(L10) bilayer, where the FM layer shows perpendicular anisotropy, it was reported that the Co spins were aligned in the sample plane [23,24]. However, such a robust orthogonal coupling has never been shown as a source of additional uniaxial anisotropy favoring perpendicular magnetization.

In this paper, we show both that orthogonal FM/AFM coupling may occur in a plane perpendicular to the sample surface and that the easy magnetization axis of the FM layer can be reoriented perpendicular to the sample plane due to this coupling. We have previously demonstrated that

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epitaxial Ni layers on Pd(001) show a perpendicular easy axis up to a thickness of about 17 monolayers (ML), above which a spin reorientation transition (SRT) occurs [25]. In this paper, we describe how the deposition of CoO on top of the Ni/Pd(001) layer extends the thickness range of the perpendicular easy magnetization axis up to a thickness of at least 25 ML of Ni. Remarkably, the persistence of the perpendicular anisotropy caused by the coupling, together with the emergence of a perpendicular exchange bias effect, are observed. By combining grazing incidence x-ray diffraction (GIXRD), temperature-dependent magneto-optic Kerr effect (MOKE), and x-ray absorption spectroscopy (XAS) measurements, we demonstrate unambiguously that the spin axis of CoO lies in the sample plane (while the Ni layer presents an easy axis perpendicular to the sample plane). These results reveal an orthogonal coupling between Co and Ni spins. Hence, we demonstrate that the orthogonal exchange coupling between CoO and Ni spins introduces another contribution term to perpendicular anisotropy, which is responsible for the persistence of the perpendicular easy magnetization axis in the CoO-coated Ni films at much higher thicknesses than the ones which occur in the uncovered Ni/Pd(001) films.

II. EXPERIMENT

The experiments were performed in multichamber ultrahigh vacuum systems with pressure below \(2 \times 10^{-10}\) mbar during deposition. Pd(001) substrates were prepared with cycles of 0.8 keV Ar ion sputtering and subsequent annealing at \(\sim 900\) K. The Ni and CoO films were grown by molecular beam epitaxy at RT and at \(\sim 380\) K, respectively. After the growth of the Ni underlayer, one single layer of Co was grown in order to avoid Ni oxidation. This first layer was then exposed to oxygen for 200 s at a pressure of \(7.7 \times 10^{-7}\) mbar. Keeping the substrate temperature at \(380\) K, and the same oxygen pressure and Co deposition rate, the oxidized first Co layer was covered with 2 CoO monolayers (ML), resulting in a total of 3 ML of CoO. Exactly the same growth conditions were applied to CoO grown directly on Pd(001) and then covered with Ni. Except for the GIXRD experiment, the samples were grown in the shape of a wedge. The wedge samples guarantee the same conditions for substrate preparation and for layer deposition, thus reducing the source of uncontrollable variables.

For structural analysis we used \textit{in situ} GIXRD done at the BM32 beamline at the European Synchrotron Radiation Facility (ESRF, France). We performed a detailed analysis of Ni films in the thickness range between 0 and 25 ML grown on clean Pd(001).

The magnetic properties were probed by \textit{in situ} polar and longitudinal MOKE. MOKE measurements were performed with a laser diode (wavelength 670 nm, incidence angle 69° and 30°, respectively, and a beam diameter <0.2 mm), in the external magnetic field up to 6 kOe, in a wide range of temperatures (from RT down to \(T = 5\) K) and Ni thicknesses (from 10 to 25 ML). Note that MOKE is sensitive only to the FM Ni film, however, it is affected by the AFM CoO(001)/FM Ni interface interaction.

Additionally for coupling direction analysis, soft x-ray absorption spectroscopy (XAS) was performed at the ID08 beamline of the ESRF, France, on the CoO(001)/Ni(001)/Pd(001) sample at both the Ni and Co \(L_{2,3}\) edges. In this spectral range (760–890 eV), the energy resolution is \(E/\Delta E = 6000\) and the degrees of linear and circular polarizations are close to 100%. The sample was allowed to rotate about a vertical axis, with the polar angle \(\theta\) defined as the angle between the surface normal and the x-ray propagation. XAS measurements were performed after magnetic field cooling from 350 K down to 10 K under an applied field of +5 kOe along the normal to the sample surface.

III. RESULTS AND DISCUSSION

A. GIXRD structural analysis of CoO/Ni bilayer

It was shown that the Ni layer grows epitaxially on Pd(001) and displays a large tetragonal distortion of \(c/a = 0.81(1)\) up to about 6 ML. After that, it starts to relax in the in-plane strain. Above 15 ML, it is almost completely relaxed, keeping the epitaxial relation Ni(100)/Pd(100). At a thickness of 23 ML, the lattice constants parallel \((a)\) and perpendicular \((c)\) to the surface are 3.59(2) and 3.47(2) Å, respectively, giving \(c/a = 0.97(1)\) [25]. The deposition of 1 ML of Co leads the Ni diffraction rods to increase intensity and to decrease the peak width, indicating that the Co layer grows pseudomorphically on the Ni(001) surface. Exposure to oxygen results in the formation of an epitaxially (001) oriented rocksaltlike oxide film with an in-plane lattice constant of 4.15(2) Å. Both a decrease of intensity and a widening of the peaks were observed from the metallic (Ni+Co) rods. This widening corresponds to a thickness reduction of 2 ML (1 ML Co and 1 ML Ni). Further deposition of 2 ML Co under partial oxygen pressure results in an increase of the oxide layer thickness. The lattice constants parallel and perpendicular to the surface are 4.18(2) and 4.31(1) Å, respectively, indicating a slightly in-plane compressed oxide layer with a \(c/a\) of 1.03(1). The average Co(Ni)O oxide layer thickness has been estimated to be around 1.3 nm, i.e., about three CoO lattice parameters. Despite the oxidation of about 1 ML of Ni, the reactive thermal deposition of CoO on pure Ni(001) does not induce other structural changes. In particular, no additional strain is induced in the Ni layer since its lattice parameters remain unchanged after CoO deposition. As seen in the following, these structural properties have a strong impact on the magnetic anisotropy of both the Ni and CoO layers.

B. MOKE evidence of spin reorientation

in Ni films by covering with CoO

Ni films epitaxially grown on Pd(001) exhibit a perpendicular easy magnetization axis from the thickness of 2 ML up to 17 ML, where it undergoes an SRT [25]. For both 5 K and RT, it exhibits in-plane magnetization for thicker films [as shown for a 23 ML thick Ni film in Fig. 1(a)]. The perpendicular anisotropy of the Ni film is attributed to the strong tetragonal distortion (measured by GIXRD) and corresponding modification of the electronic structure at the Fermi level [26]. Accordingly, the observed structural relaxation for thicker Ni layers causes the in-plane SRT. At RT the polar MOKE signal is detectable only after a sufficiently thick Ni film is grown, i.e., when the Curie temperature...
The coercivity and an exchange bias effect at low temperatures. A strong perpendicular exchange coupling, which causes large perpendicular magnetic anisotropy, CoO/Ni/Pd(001) shows a perpendicular easy magnetization axis, i.e., below TN of CoO(001). The rectangular loop and increased Kerr ellipticity in remanence correspond to the perpendicular anisotropy of Ni at 5 K after covering with CoO, whereas the large Hc and the measurable HEB refer to the exchange coupling between AFM CoO and FM Ni.

FIG. 1. (Color online) Polar hysteresis loops at 5 K and at RT for 23 ML of Ni on Pd(001): (a) before and (b) after covering with 3 ML of CoO(001). The rectangular loop and increased Kerr ellipticity in remanence correspond to the perpendicular anisotropy of Ni at 5 K after covering with CoO, whereas the large Hc and the measurable HEB refer to the exchange coupling between AFM CoO and FM Ni.

After covering the Ni films with 1.3 nm of uniform CoO, polar Kerr loops at RT were collected along the wedge, i.e., for different Ni thicknesses, showing the same anisotropy of the films as before covering with CoO. Then, the samples were heated up to 450 K and cooled down to 5 K with or without a magnetic field applied perpendicular to the sample plane. After such a procedure, the CoO/Ni/Pd(001) system presented a perpendicular easy magnetization axis in the Ni thickness range 17–25 ML at temperatures below 250 K. This thickness range the magnetization of Ni films reorients towards the film plane at temperatures above 250 K. The corresponding hysteresis loops for a 23 ML thick Ni film covered with 3 ML of CoO are shown in Fig. 1(b). Besides perpendicular magnetic anisotropy, CoO/Ni/Pd(001) shows a strong perpendicular exchange coupling, which causes large coercivity and an exchange bias effect at low temperatures. The HEB value is of the order of 100 Oe at 5 K. The Kerr signal in remanence versus the Ni film thickness at different temperatures is plotted in Fig. 2, which is equivalent to the temperature dependence of the squareness of the loops since the saturation magnetization is constant for all thicknesses of Ni. At RT the magnetization tends to be oriented in the film plane. After such a procedure, the CoO/Ni/Pd(001) system presented a perpendicular easy magnetization axis in the Ni thickness range of 17–25 ML, i.e., for Ni/CoO(3 ML)/Pd(001). Note that in the Ni thickness range 17–25 ML, there is a contribution to the Kerr signal from spin-polarized Pd [27]. This contribution is strong only at low temperature, when the Ni films in this thickness range show a perpendicular easy magnetization axis, i.e., below Tc of CoO, and polarize Pd perpendicularly. After growing the CoO on top of the Ni films, the RT polar Kerr signal in remanence decreases slightly. This indicates that the effective Ni thickness is reduced, which may imply a formation of an antiferromagnetic Ni-O layer (no more than 1 ML thick), as already observed from GIXRD experiments. Ni oxidation causes the SRT to occur at a slightly increased nominal thickness of Ni, however, it cannot explain a perpendicular magnetization of a 23 ML thick Ni film covered with CoO. Moreover, the orientation of the NiO spins is found to follow the CoO spin orientation due to a strong exchange interaction at the interface and a stronger anisotropy of CoO [28]. Such a Ni oxide component leads to an increase of the Néel temperature of the NiO layer observed both by MOKE and x-ray magnetic linear dichroism (XMLD) studies.

FIG. 2. (Color online) Polar Kerr ellipticity in remanence vs thickness of the Ni film after covering with 3 ML of CoO at RT before field cooling and from 5 to 311 K after field cooling (at 3.8 kOe). The arrow indicates how the Kerr signal in remanence decreases with increasing temperature. Inset: Polar Kerr ellipticity in remanence vs temperature for a 23 ML thick Ni film covered with 3 ML of CoO. The signal decreases rapidly above 270 K due to the rotation of the easy magnetization axis towards the sample plane.

There is a simple method to prove whether the temperature at which the perpendicular anisotropy starts to decrease is related to the antiferromagnetism of CoO. In order to change the Néel temperature of the coupled AFM layer, we oxidized the existing Ni film (in reality, only the topmost two to three atomic layers became oxidized) and then covered it with another 3 ML of CoO. This procedure results in the increased Néel temperature of NiO up to the value dependent on x and approaching 525 K for x = 1, i.e., for bulk NiO [28]. In other words, the Néel temperature of the Co1−xNi,O layer can be tuned by a proper choice of x. The procedure causes perpendicular magnetization to be restored in the Ni thickness range 17–25 ML, even above RT. Since the same effect is observed for the Ni/O/Ni/Pd(001) system (i.e., with no CoO), it confirms that metallic, i.e., not fully oxidized Co eventually existing, does not play any decisive role in the recovery of perpendicular anisotropy of the Ni film.
The perpendicular exchange bias must be related to a unidirectional anisotropy perpendicular to the sample plane. In the CoO/FePt/Pt(001) system, a very small amount of Co uncompensated spins (responsible for the exchange bias) has been detected [23]. Such a unidirectional source of anisotropy, which probably comes from a slight canting, has not been detected in this case and should be within the noise. It should be emphasized that, also for Mn/Fe bilayers, a perpendicular arrangement of unpinned moments in antiferromagnetic Mn at the Mn/Fe interface forces the Fe layer to be magnetized perpendicular to the sample plane [6].

The interface spins of AFM CoO couple to the interface spins of the FM Ni film. Since the exchange coupling is much stronger than the effective in-plane anisotropy of the Ni film underneath (of a thickness just above SRT), the coupling can affect the orientation of the magnetization of the Ni film, making it perpendicular to the sample plane. The only question is about the coupling mechanism: Is it orthogonal or collinear, i.e., are the CoO spins oriented parallel or perpendicular to the sample plane?

C. XMLD and XMCD evidence of spin orientation in CoO and Ni layers

In order to answer this question, the orientation-dependent Co L$_3$-edge XAS spectra was measured at 10 K with $\Theta$ varying from 0° (normal incidence) to 70° (grazing incidence), with horizontal light polarization (Fig. 3). In this experimental geometry, the variation of the escape length of the electrons with the angle should be corrected in order to recover the real XAS signal. This has been systematically done using the standard procedure for electron yield saturation effects [29].

The spectra, normalized far from the L$_{2,3}$ edges, show a clear linear dichroism effect. Four main multiplet features are labeled (A–D) in the XAS and x-ray linear dichroism (XLD) signals. They correspond to transitions towards the orbitals of different symmetries and then show distinct variations as a function of $\Theta$. Taking the spectrum at $\Theta = 0°$ as a reference, features C and D (at energies higher than 781 eV) only slightly increase in intensity. On the other hand, features A and B decrease considerably as a function of $\Theta$. The amplitude of both features A and B fits well to the cos$^2\Theta$ function, with a minimum at $\Theta = 90°$ (as shown in the inset of Fig. 3). From XAS multiplet calculations, it has been demonstrated that the amplitude minimum corresponds to the situation when the polarization vector is perpendicular to the spin axis [30]. We can then conclude, within an accuracy of a few degrees, that the Co spins are parallel to the sample plane oriented along the main axes ([100] or [010]). This is not surprising, since for CoO on Ag(001), a compressive in-plane strain (and thus the tetragonal distortion) leads to a modified electronic structure and resulting spin axis in the sample plane [15]. One could expect the same behavior in the case of CoO on Ni/Pd(001) ($c/a = 1.03$).

The Ni L$_{2,3}$-edge XAS, measured for right and left circular polarizations at 10 K and $\Theta = 0°$, are shown in Fig. 4, along with the XMCD data, obtained as the difference between them. The XAS display a metallic fingerprint, with a small multiplet structure corresponding to the oxidation of the Ni surface. The XMCD fingerprint has a metallic character. One can observe that the XMCD amplitude at the L$_3$ edge is the same for 10 and 0.2 kOe (close to remanence) (the inset in Fig. 4). These results confirm the perpendicular magnetization of the ferromagnetic Ni layer after the deposition of the CoO oxide layer on top of it.

D. Exchange coupling energy between CoO and Ni layers

The exchange coupling energy between the Ni layer and CoO layer, $K_{sf}$, can be estimated quantitatively from our experimental results. Before CoO deposition, there are two contributions to the effective magnetic anisotropy, $K_{sf}(Ni)$, of the Ni film: (1) magnetocrystalline anisotropy ($K_{vol,perp}$) due to the tetragonal distortion of Ni grown on Pd(001), which forces the magnetization to be oriented perpendicular to the sample plane, and (2) shape anisotropy ($K_{shape}$), which forces the magnetization to be oriented in the sample plane.
From about 10 to 25 ML of Ni the tetragonal distortion is rather constant and we can assume that the volume contribution $K_{\text{vol,perp}}$ does not change throughout this thickness range. Since there is an SRT at a thickness of 17 ML, i.e., $K_{\text{eff}}(17\text{ ML}) = 0$, $K_{\text{vol,perp}}$ can be calculated as $K_{\text{vol,perp}} = -K_{\text{shape}}(17\text{ ML})$. After deposition of CoO on top of the Ni film, the total effective anisotropy writes $K_{\text{eff}}(\text{CoO}/\text{Ni}) = -K_{\text{shape}}(17\text{ ML}) + K_{\text{shape}} + K_{\text{sf}}$. For nominally 25 ML of Ni covered with CoO, and considering 1 ML of Ni oxidized, we have $K_{\text{eff}}(\text{CoO}/24\text{ ML}) = K_{\text{shape}}(7\text{ ML}) + K_{\text{sf}}$. Therefore, as the spin reorients perpendicular below the $T_N$ of CoO, the conclusion is that $K_{\text{sf}}$ is larger than $-K_{\text{shape}}(7\text{ ML})$. Quantitatively, for $M_s = 486\text{ emu/cm}^3$, we establish that $K_{\text{sf}}$ has a lower bound of 0.183 erg/cm$^2$, which is larger than, e.g., the exchange coupling energy of 0.12 erg/cm$^2$ reported for the Fe/NiO bilayers on Ag(1,1,10) [20].

In summary, we have studied the effect of the exchange coupling between AFM CoO and FM Ni on the perpendicular anisotropy and the perpendicular exchange bias of CoO/Ni and Ni/CoO bilayers on Pd(001). At temperatures below the $T_N$ of CoO, the CoO/Ni bilayers are perpendicularly magnetized in a thickness range clearly extended when compared to the thickness range of the perpendicularly magnetized uncovered Ni films grown on Pd(001). Since the AFM/FM coupling supports the perpendicular anisotropy of the Ni film (as obtained from MOKE and XMCD experiments) and the CoO spin axis of the CoO layer is settled in the sample plane (as obtained from XMLOD), the coupling between CoO and Ni spins at the interface is concluded to be orthogonal. Additionally, CoO/Ni/Pd(001) shows perpendicular exchange bias. A combination of both effects causes the phenomenon to be more interesting for applications.

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