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Research articles

Exchange bias and major coercivity enhancement in strongly-coupled CuO/Co films

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ABSTRACT

The exchange-bias properties of ferromagnetic, either Co or Ni, thin films deposited onto polycrystalline multiferroic CuO are investigated. After field cooling, the CuO/Co magnetization hysteresis loops show exchange bias at temperatures lower than 200 K, while the CuO/Ni system exhibits bias below about 5 K only. It is suggested that the exchange bias of CuO/Co is determined mainly by the magnetization reversal that takes place on the descending branch of the loop. Rather high values of both the interface coupling energy, 0.89 erg/cm^2, and coercivity, 2.44 kOe, of the CuO/Co film are obtained at 5 K.

1. Introduction

Multiferroicity [1], electromagnons [2] and a toroidal moment [3] related to orbital currents have recently triggered an additional interest to cupric oxide (CuO) which, unlike other 3*d* metal monoxides, has a monoclinic crystal structure (centrosymmetric space group $C2/c$). Antiferromagnetic (AF) order sets in at the Néel temperature $T_{N2} \simeq 230$ K and the magnetic moments order [4–6], in the so-called AF2 phase in an incommensurate helix with an envelope oblique to the propagation vector. This AF2 magnetic structure supports polar order, i.e. multiferroicity. Another transition to a collinear commensurate AF structure, AF1, with moments aligned with the monoclinic *b* axis, occurs at $T_{N1} \simeq 213$ K. The later is not polar.

Apart from being the only known binary multiferroic (MF) compound, CuO has a much higher transition temperature into the MF state (i.e., T_{N2}) than any other known material in which the electric polarization is induced by spontaneous magnetic order at temperatures typically lower than 100 K. Recently, intriguing magnetoelectric phase diagrams of CuO have been revealed and strong magnetoelectric effect has been demonstrated [7]. It has also been suggested [8] that CuO should be MF at elevate temperatures under pressure. This opens the possibility for strain-engineered thin films and eventually room temperature multiferroicity.

It is tempting to use AF multiferroic materials with coupled magnetic and polar order parameters in heterostructures to pin the orientation of the spins in adjusted ferromagnetic (FM) layer, which should allow manipulating of the ferromagnetism through the application of an electric field to the MF counterpart. The first observation of the electric-field-controlled exchange bias (EB) has been reported [9] in a Py/$YMnO_3$ at 2 K and later in several other systems containing MFs, see, e.g., Refs. [10,11] and the references therein, including the prominent $BiFeO_3$ [12,13]. Although the knowledge of the EB mechanism in such MF/FM heterostructures is still not settled, the effect could be of interest in new device technologies, particularly in the dissipationless spintronic applications.

The EB [14] has been widely-studied through the last decades and is already employed in magnetic sensing and storage applications. Its best-known manifestation, i.e., the hysteresis loop shift along the axis of the magnetic field (H) referred to as EB-field (H_{EB}), results from exchange coupling between FM and uncompensated spins (UCSs) at its interface with an AF. The EB could be set by applying magnetic field during either the sample's production or by cooling down the sample through T_N or by post-deposition ion irradiation [15–17], or even by applying sufficiently large magnetic fields at a fixed temperature [18]. In the literature, one can find more detailed information on the origin [19,20] and the classification [21–27] of the UCSs as unstable (i.e., superparamagnetic

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and rotatable [28–31]) and stable [set (responsible for the bias) and unset].

CuO nanoparticles where reported to present uncompensated surface Cu^{2+} spins resulting in a weak FM component, enhanced coercivity, H_C, remanence and EB below 40 K [32]; ball-milled CuO nanoparticles also showed an EB-like effect [33,34]. CuO nanowires exhibited EB below a blocking temperature (T_B) of about 19 K [35], and FM-like behavior and long-range AF ordering [36]. $BiFeO_3$ nanocrystals dispersed into CuO matrix revealed EB below 170 K [37]. In our opinion, some of the EB results claimed in the above studies of CuO nanoparticles should be taken with precaution since they are based on unsaturated hysteresis loops. To the best of our knowledge, there are no reports on EB in CuO-based thin films.

In this study we report the observation of EB and significant H_C enhancement in polycrystalline CuO/Co and CuO/Ni films. The former system exhibits EB at temperatures lower than 200 K, while the latter shows bias at 5 K only. We estimated that the EB of CuO/Co is determined mainly by the magnetization reversal that takes place on the descending branch of the hysteresis loops. It is worthwhile to emphasize the rather high values of both interface coupling energy and coercivity presented by the CuO/Co film at 5 K.

2. Experimental

Thin films, each of them containing an FM (either Co or Ni) layer, were deposited from targets of nominally identical compositions onto CuO layers. Ru buffer layers were grown before the CuO ones onto naturally oxidized Si(100) substrates in order to set the CuO preferential (1 1 1) orientation growth; aiming to avoid oxidation, Ru cap layers were finally grown onto the FM ones. The films with nominal compositions Si(1 0 0)/Ru(5 nm)/CuO(220 nm)/Co (7 nm)/Ru(5 nm) and Si(1 0 0)/Ru(5 nm)/CuO(220 nm)/Ni(7 nm)/ Ru(5 nm), (henceforth CuO/Co and CuO/Ni), together with a film which does not contain an FM layer referred to as CuO, i.e., Si (1 0 0)/Ru(5 nm)/CuO(220 nm), were produced at room temperature by dc magnetron sputtering under base pressure of 2.0×10^{-8} Torr from Ru, Co and Ni targets with a 99.99% pure Ar at 20 sccm constant flow and power of 100 W for Ru and 300 W for Co and Ni. The CuO layers were produced by RF magnetron sputtering under a total pressure of 5×10^{-3} Torr kept constant in a Ar + O_2 reactive atmosphere, and under 45% O_2 partial pressure using 250 W power.

The structural characterization of the films was performed via X-ray diffractometry (XRD) with Cu $K\alpha$ radiation employing a Bruker AXS D8 Advance diffractometer in a θ-2θ Bragg-Brentano geometry.

The magnetic measurements were done using a commercial SQUID magnetometer from Quantum Design. Magnetization (M) hysteresis loops were obtained for **H** applied in the plane of the films after either zero-field cooling (ZFC) or field cooling (FC) from 240 K to the measurement temperature (T) in H = 50 kOe. To avoid uncertainties related to differences between the first and the next-measured loops (the so called "training effect" [38–41]), the FC procedure was repeated prior the measurement at each temperature and all the reported loops are the first measured ones. In order to account for the contribution from the substrate, diamagnetic correction was applied on each measured curve; we also assured that the magnitude of the maximum magnetic field used was sufficiently high to avoid EB overestimation due to minor-loop effects [42,43].

Conventional four-probe measurements of resistivity (ρ) versus T were performed on the CuO film using an equipment based on signal detection by a dual-phase lock-in amplifier. The experiment was performed while cooling the film from 300 to 25 K at a rate of 1.5 K/min in zero magnetic field employing a sinusoidal 200 mV voltage at 37 Hz and a current of $\simeq$ 0.1 mA.

3. Results and discussion

Fig. 1 presents XRD patterns obtained at room temperature for the as-deposited samples. In both patterns, a narrow peak is observed at $2\theta = 35.55^\circ$ corresponding to the monoclinic CuO($\bar{1}$1 1) plane. Others, less intensive peaks, corresponding to the (2 0 0), (1 1 1) and (1 1 0) planes of CuO, are also observed. A semi-quantitative analysis was performed to evaluate the texture characteristics of our polycrystalline CuO films. It was estimated that both CuO/Co and CuO/Ni films show a preferential growth along the ($\bar{1}$1 1) direction and a slight compressive stress, ranging from 0.2% to 0.28%, for grains with ($\bar{1}$1 1) out-of-plane orientation; nevertheless, an in-plane stress cannot be discarded.

Magnetization hysteresis loops were traced at temperatures ranging from 5 to 300 K. All $M(H)$ curves have a well-defined shape typical for single-phase FM systems. The loops obtained at any measurement temperature after ZFC and those measured at $T \geqslant 200$ K after FC are symmetrical along both H and M axes. However, the loops traced at $T < 200$ K after FC for the CuO/Co film present the characteristic for exchange-coupled FM/AF systems shift along the H-axis, i.e., H_{EB}. Representative loops for the CuO/Co system, obtained after FC together with that traced after ZFC at 5 K, are shown in Fig. 2; for a better visualization, only the low-field region is presented.

The temperature dependencies of H_{EB} and H_C, measured after FC on the CuO/Co film, are plotted in the top panel of Fig. 3. The temperature of 200 K above which the EB vanishes is slightly lower than both T_{N1}($\simeq$ 213 K) and T_{N2}($\simeq$ 230 K) of bulk CuO. The temperature variations of the coercive fields H_{C1} and H_{C2}, estimated as the fields for which M = 0 at the respective descending and ascending branches of $M(H)$, are given in the inset of Fig. 3. It is seen that, from 5 to 100 K, H_{C2} decreases very weakly and both H_C and H_{EB} variations are determined mainly by that of H_{C1}. Between 100 and 200 K, H_{C2} decreases more significantly and for $T > 200$ K becomes equal to H_{C1}, thus resulting in zero bias.

The inset in the top of Fig. 3 shows that, in the range where $H_{EB} \neq 0$, the decrease of H_{C1} is well represented by a straight line which, remarkably, intersects the T-axis at $\simeq T_{N2}$. This, together with the dominant role of the variation of H_{C1} for that of H_{EB}, might indicate that, in our FM/AF system, the magnetization reversal

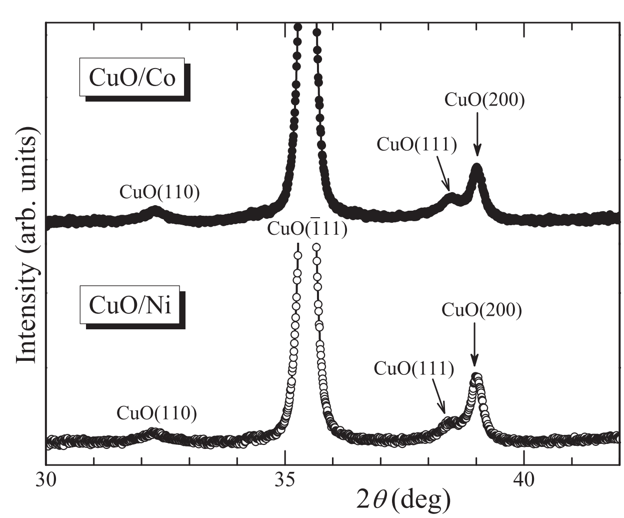

Fig. 1. Room temperature XRD patterns obtained for the CuO(220 nm)/Co(7 nm) and CuO(220 nm)/Ni(7 nm) films.