Journal of Magnetism and Magnetic Materials 321 (2009) 1955–1958

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Exchange bias in thin-film $(Co/Pt)_3/Cr_2O_3$ multilayers

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ARTICLE INFO

Article history:
Received 26 April 2008
Received in revised form
30 November 2008
Available online 24 December 2008

Keywords:
Exchange bias
Cr_2O_3
Magnetoelectric
Thin film
Multilayer

ABSTRACT

We have fabricated exchange-biased Co/Pt layers ((0.3 nm/1.5 nm) × 3) on (0 0 1)-oriented Cr_2O_3 thin films. The multilayered films showed extremely smooth surfaces and interfaces with root mean square roughness of ≈0.3 nm for 10 μm × 10 μm area. The Cr_2O_3 films display sufficient insulation with a relative low leakage current (1.17×10^{-2} A/cm^2 at 380 MV/m) at room temperature which allowed us to apply electric field as high as 77 MV/m. We find that the sign of the exchange bias and the shape of the hysteresis loops of the out-of-plane magnetized Co/Pt layers can be delicately controlled by adjusting the magnetic field cooling process through the Néel temperature of Cr_2O_3. No clear evidence of the effect of electric field and the electric field cooling was detected on the exchange bias for fields as high as 77 MV/m. We place the upper bound of the shift in exchange bias field due to electric field cooling to be 5 Oe at 250 K.

Cr_2O_3 is an antiferromagnet (AFM) showing antiferromagnetic ordering of Cr^{3+} spins aligned along the *c*-axis of its rhombohedral unit cell below the Néel temperature ($T_N = 307$ K) [1]. Cr_2O_3 was the first compound in which the magnetoelectric (ME) effect was theoretically predicted and experimentally observed [2–5]. Recently, the ME effect on exchange bias was observed on a Co/Pt multilayer on a *c*-axis oriented Cr_2O_3 single crystal [6,7]. Such an effect can be the basis for a new type of memory and/or logic devices where both electric and magnetic fields serve as external control parameters.

Thin-film multilayer devices are desirable since rather large electric fields can be applied to the Cr_2O_3 layer, and thus the ME effect on exchange bias is expected to be larger. To this end, in our present study, we have fabricated Co/Pt multilayers on Cr_2O_3 thin films with extremely smooth interfaces. Out-of-plane magnetized exchange-biased dual hysteresis loops were clearly observed whose detailed features were found to be delicately controlled by demagnetizing ac magnetic field with different amplitude offset during magnetic field cooling (MFC). The effect of high electric field (~77 MV/m) cooling (EFC) as well as direct electric field *E* at a fixed temperature after magnetic field cooling were investigated.

The 130 nm-thick Cr_2O_3 thin films were grown on Al-doped ZnO (Al-ZnO) buffered *c*-axis-oriented sapphire (Al_2O_3) substrates by pulsed laser deposition. Cr_2O_3 and Al-ZnO targets were ablated using a KrF excimer laser ($\lambda = 248$ nm) with a typical fluence of 2 J/cm^2. The epitaxial Al-ZnO (170 nm) layer was used for the bottom electrode to apply an electric field on the Cr_2O_3 thin film. Subsequently, the sample was taken out of the pulsed laser deposition chamber and transferred to an electron beam deposition chamber. $[Co(\sim0.3\,nm)/Pt(\sim1.5\,nm)]_3$ layers were deposited alternately on Cr_2O_3 at 500 K. Pt (~0.5 nm) was the first layer deposited to prevent oxygen diffusion from Cr_2O_3 and subsequent potential formation of antiferromagnetic CoO [8]. It was then capped with another ~2 nm of Pt. Previously, exchange bias of out-of-plane magnetized Co/Pt layers has been reported by a number of groups [9–11].

To characterize the microstructure of the multilayer, phi (φ) scans and theta (θ) scans were performed with a 4-circle X-ray diffractometer (Bruker D8 Discover). Transmission electron microscopy (TEM) images and selected area diffraction (SAD) patterns of the films were obtained at an accelerating voltage of 200 keV with a JEOL 2010F field emission TEM. The Co/Pt multilayer atop the Cr_2O_3 layer was patterned into 200 μm × 200 μm square dots by ion milling to make capacitor devices. A magneto-optical Kerr effect (MOKE) system was used to detect the Kerr rotation of Co spins in the Co/Pt multilayer and measure the hysteresis loops directly on individual capacitor devices.

The θ–2θ X-ray diffraction (XRD) spectrum in Fig. 1(a) shows that the Al-ZnO and Cr_2O_3 layers, which have the hexagonal and rhombohedral crystal structures, respectively, grew *c*-axis oriented on the (0 0 1) oriented Al_2O_3 substrate, which has a rhombohedral crystal structure. The sheet resistance of the Al-ZnO bottom electrode layer was less than 10 kΩ. The Cr_2O_3 film showed sufficient insulation for applying a high electric field. As

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doi:10.1016/j.jmmm.2008.12.022

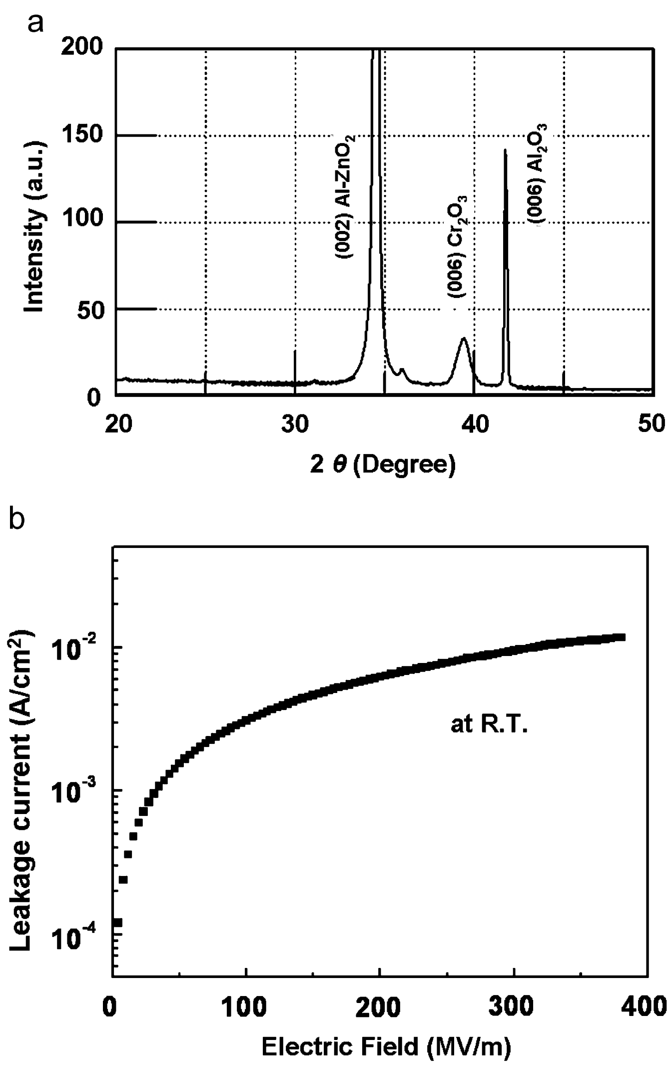

Fig. 1. (a) XRD 2-θ scan of a Co/Pt/Al-ZnO/Cr_2O_3 film. (b) The leakage current density of Cr_2O_3 film was measured using Pt (top) and Al-ZnO (bottom) electrodes at room temperature. The observed highly insulating properties of Cr_2O_3 film were suitable for applying high electric field.

shown in Fig. 1(b), the leakage current density of the Cr_2O_3 film measured at room temperature was $\sim 10^{-2}$ A/cm^2 even for electric fields as high as 380 MV/m at room temperature. This allowed us to apply up to ± 100 MV/m continuously without breakdown.

Fig. 2(a) shows the high-resolution cross-sectional TEM image of the (Co/Pt)/Cr_2O_3 interface region. As shown in an electron diffraction pattern in Fig. 2(b) and (c), the Cr_2O_3 and Al-ZnO layers grew epitaxially on the (0 0 1)-oriented Al_2O_3 substrate. The growth orientation relationship between different layers indexed from the diffraction pattern were $[0\,0\,1]_{Al_2O_3} \| [0\,0\,1]_{Al\text{-}ZnO} \| [0\,0\,1]_{Cr_2O_3}$ along the out-of-plane direction and $(1\,0\,0)_{Al_2O_3} \| [1\,1\,0]_{Al\text{-}ZnO} \| [1\,0\,0]_{Cr_2O_3}$ along the in-plane direction (Fig. 2(c)).

The interface roughness between ferromagnetic (FM) and AFM layers is known to influence the AFM spin configuration and cause complex exchange bias behavior affecting the exchange bias field (H_E) and coercive field (H_C) [12]. In our sample, the Co/Pt layer on the Cr_2O_3 layer showed a continuous structure with a sharp interface in the observed wide lateral range (several hundred microns) of the film which we attribute to the extremely smooth surface of the Cr_2O_3 layer. The surface roughness (root mean square) of a Cr_2O_3 layer deposited on an Al-ZnO film (170 nm) measured by atomic force microscopy was $\sim$0.3 nm over a $10\,\mu m \times 10\,\mu m$ area. The selected area diffraction pattern (not shown here) obtained from this region (Fig. 2(a)) indicated that the Co/Pt multilayer was polycrystalline. The bright band seen in Fig. 2(a) at the interface between Cr_2O_3 and Co/Pt layers is attributed to a defocusing effect in TEM or due to slight tilting from the zone axis.

Fig. 3(a) shows the out-of-plane hysteresis loops of our (Co/Pt)/Cr_2O_3 structure at room temperature after magnetic field cooling through the Néel temperature following heating the sample to 325 K, where H_C of the Co/Pt multilayer was 15 Oe. We found clear exchange bias with cooling in a field of only 20 Oe. As the temperature decreased from 325 to 299 K, H_E was seen to gradually increase to $\sim$170 Oe, and the sign of H_E was consistent with the direction of the applied field. Even at 299 K, with the exchange bias present, H_C of Co/Pt remained narrow at 15 Oe. At this temperature, we estimate the exchange bias energy to be approximately 1.7×10^{-5} J/m^2. Upon raising the temperature slightly, the exchange bias disappears at 305 K, 2 K below T_N of Cr_2O_3. Thus, we rule out the possibility that there is an antiferromagnetic CoO layer ($T_N = 291$ K) giving rise to the observed exchange bias.

We have found that a tunable dual hysteresis loop can be obtained by varying the magnetic field during the MFC process. Dual hysteresis loops are a result of an uneven up/down spin fraction set up in the AFM layer at the interface [13]. To achieve this, we have superposed a slow (0.02 Hz) ac field with constant amplitude of 0.7 kOe with dc offsets of either 0, $\pm$0.02, or $\pm$0.2 kOe. The ac field during the cooling process ($\sim$30 min) provided a demagnetizing effect on the Co/Pt layer, and the dc offset created the uneven up/down spin fraction depending on its sign and the amplitude.

For the +0.2 kOe offset case, the ac magnetic field oscillates between +0.9 and −0.5 kOe. The net positive magnetic field swing (+0.4 kOe) in this case is sufficient to saturate and align all magnetic spins of the Co along the positive field direction. This leads to the Co magnetic moments imprinting their homogenous magnetic spin orientation into the very top layer spins of AFM Cr_2O_3 during the cool and resulted in a fully uncompensated interface and negative H_E. Similarly, in the −0.2 kOe offset case, the magnetic field is swept between +0.5 and −0.9 kOe with the net negative magnetic field (−0.4 kOe) which aligned all magnetic spins along the negative field direction and resulted in the positive value of H_E.

For the zero offset case, the magnetic field oscillates between +0.7 and −0.7 kOe. After cooling, a dual hysteresis loop is observed. This is marked as "zero offset" in Fig. 3(b). In this case, the demagnetizing process led to up and down domains in the Co/Pt multilayers such that there were equal numbers of up and down spins. Upon cooling, these domains were imprinted onto the very top layer of Cr_2O_3. They in turn resulted in exchange biasing "half" of the Co spins in one direction while the other half was biased in the opposite direction [13], giving rise to the double loop. For the intermediate offset values (Fig. 3(b)), uneven distributions of up and down magnetic domains were imprinted on the top layer of Cr_2O_3 resulting in vertically asymmetric dual hysteresis loops reflecting the distributions (curves marked $\pm$0.02 kOe offsets). Thus, by adjusting the dc field offset, we can tune the shape of the dual hysteresis loop.

To investigate the ME effect on exchange bias in the thin-film devices, the hysteresis loops were compared after different (simultaneous) magnetic and electric field cooling (MEFC) conditions (magnetic field = 0.7 kOe and $E = \pm 77$ MV/m). Based on previous measurements of the ME susceptibility (tensor) in Cr_2O_3, we have performed the MEFC down to 250 K in order to maximize the ME effect in Cr_2O_3 [14]. Typical H_E was 550 Oe in the Co/Pt multilayer at this temperature. No difference in the shape of the

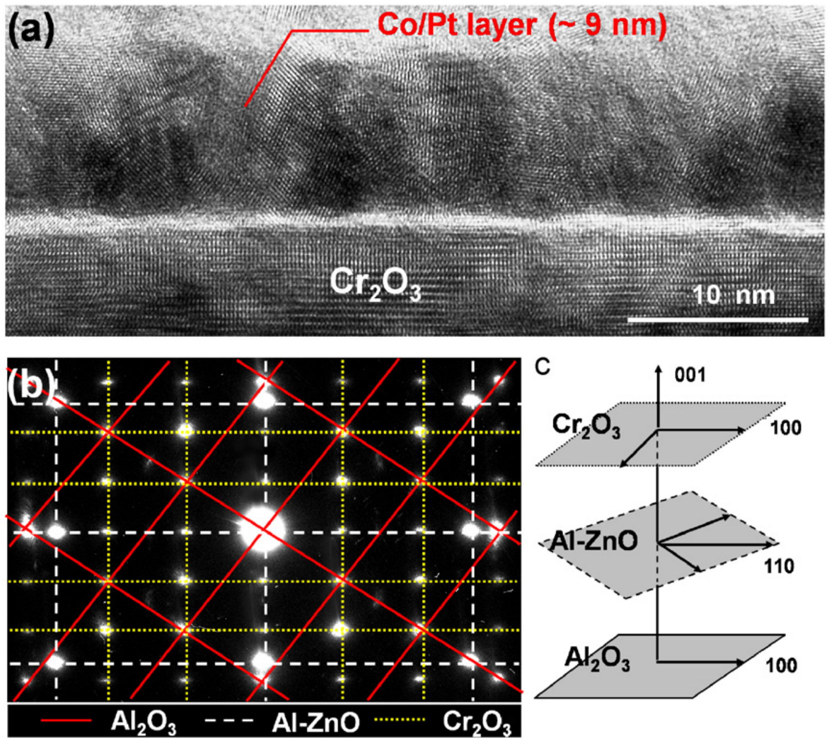

Fig. 2. (a) High-resolution TEM image of Co/Pt layer. Co particles were embedded in Pt matrix. The thickness of Co/Pt layer was ~9 nm (including the top Pt capping layer of ~2 nm). (b) The electron diffraction patterns and (c) schematics of crystal orientation relation. The film showed epitaxial growth of Al-ZnO, Cr_2O_3 layer on *c*-axis sapphire substrate.

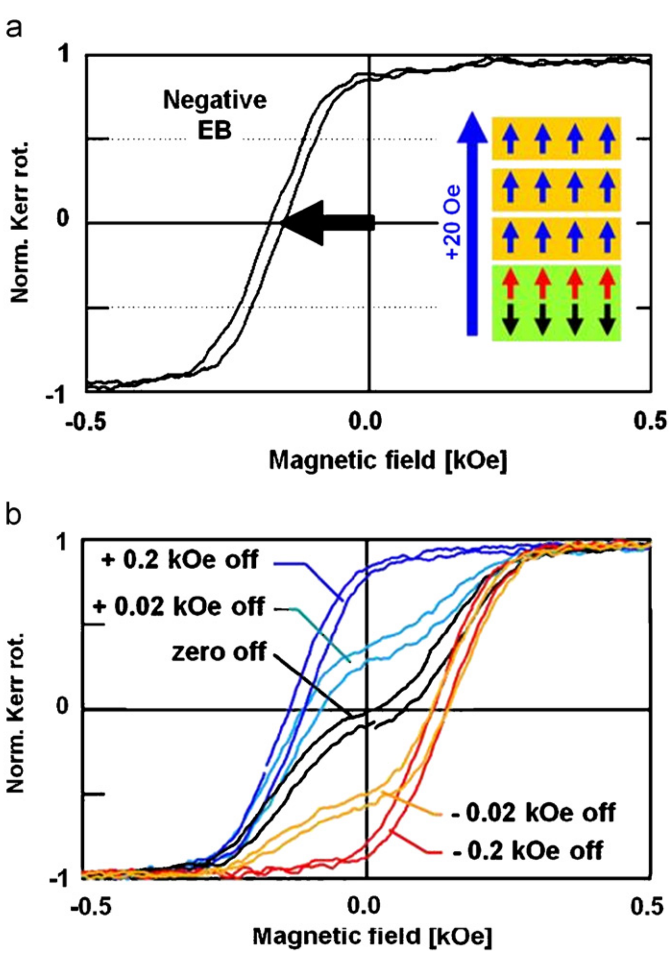

Fig. 3. Magnetic hysteresis loops measured by MOKE after field cooling at room temperature. (a) Hysteresis loop when the cooling field was +20 Oe. (b) Control of magnetic hysteresis by sweeping magnetic field with various dc offset values superposed on ac field with amplitude of 0.7 kOe during field cooling.

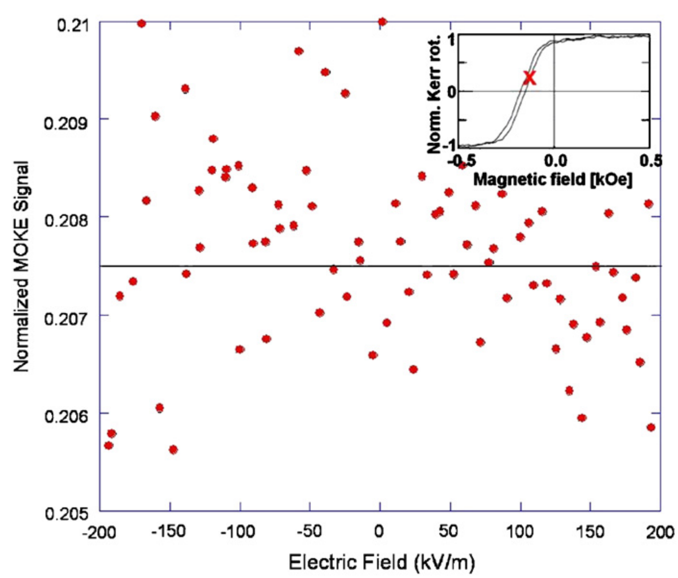

Fig. 4. Electric field versus MOKE signal measured at room temperature while the applied magnetic field is kept constant so that the system is at the "x" position in the hysteresis curve as shown in inset. The multilayer was field cooled through the Néel temperature. The vertical scale is the same as in Fig. 3(a), but magnified to display the limit of the MOKE measurement sensitivity. For this plot, the electric field was swept from 200 to −200 kV/m.

dual hysteresis was detected for the two MEFC conditions ($\pm$ electric field). Given the ability of our measurement set up to determine the magnetic field, we place the upper bound in the shift of the H_E to be 5 Oe, which is less than 1% of H_E at this temperature.

In addition, we have also looked for the direct electric field effect (Fig. 4). Following an MFC process (+20 Oe) through the Néel temperature, we have fixed the magnetic field bias at +0.13 kOe at room temperature (position "x" on the hysteresis curve shown in the inset), and swept the electric field while carefully monitoring the MOKE signal. No discernible change in the hysteresis was observed upon application of $\pm$200 kV/m. The measured signal is plotted in the figure as a function of the sweeping electric field, where the vertical scale of the normalized signal is the same as in Fig. 3(a), but the plotted range has been magnified. There is no discernible electric field effect even at this magnified range, and the scatter of the points shows that this is the sensitivity limit of the measurement. From the slope of the hysteresis loop at this magnetic field, we estimate that the magnitude of the noise signal as represented in the scatter of the points seen in the MOKE signal corresponds to the effective difference in the exchange bias field of about 0.25 Oe, which we take to be the upper bound on the direct electric field tunable shift in the exchange bias. This corresponds to about 0.2% of the overall exchange bias value here.

Thus, despite the fact we have been able to apply electric field about 150 times higher than that used in the previous experiment on a Cr_2O_3 single crystal, the apparent ME effect on the exchange bias appears to be minimal. One possible reason for the lack of electric field effect is that the magnetic spin orientations of the very top AFM layer in Cr_2O_3 are mostly affected by the magnetic spin configuration of the Co layer through exchange interaction rather than the ME effect in Cr_2O_3. Further studies are being carried out to understand the present results. Investigation of the possible ME effect on other exchange-biased multiferroic systems is also currently underway.

This work was supported by NSF-MRSEC under Grant nos. DMR 0520471, NSF DMR 0603644, and ARO W9IINF-07-1-0410. We acknowledge the Maryland NanoCenter and the use of the TEMs in the Nanoscale Imaging Spectroscopy and Properties (NISP) laboratory at the University of Maryland.

References

[1] D.N. Astrov, Sov. Phys. JETP 11 (1960) 708.
[2] I.E. Dzyaloshinskii, Sov. Phys. JEPT 10 (1960) 628.
[3] D.N. Astrov, Sov. Phys. JETP 13 (1961) 729.
[4] V.J. Folen, G.T. Rado, E.W. Stalder, Phys. Rev. Lett. 6 (1961) 607.
[5] S. Shtrikman, D. Treves, Phys. Rev. 130 (1963) 986.
[6] P. Borisov, A. Hochstrat, X. Chen, W. Kleemann, Ch. Binek, Phys. Rev. Lett. 94 (2005) 117203.
[7] X. Chen, A. Hochstrat, P. Borisov, W. Kleemann, Appl. Phys. Lett. 89 (2006) 202508.
[8] W.H. Meiklejohn, C.P. Bean, Phys. Rev. 102 (1956) 1413.
[9] M. Kiwi, J. Magn. Magn. Mater. 234 (2001) 584.
[10] J. Nogues, Ivan K. Schuller, J. Magn. Magn. Mater. 192 (1999) 203.
[11] S. Maat, K. Takano, S.S.P. Parkin, Eric E. Fullerton, Phys. Rev. Lett. 87 (2001) 087202-1.
[12] O. Hellwig, S. Maat, J.B. Kortright, Eric E. Fullerton, Phys. Rev. B 65 (2002) 144418-1.
[13] S. Brück, J. Sort, V. Baltz, S. Suriñach, J.S. Muñoz, B. Dieny, M.D. Baro, J. Nogués, Adv. Mater. 17 (2005) 2978.
[14] S. Shtrikman, D. Treves, Phys. Rev. 130 (1963) 986.