Thickness Dependence of Magnetic and Transport Properties of Chromium Dioxide (CrO_2) Strained Epitaxial Thin Films

A. Anguelouch, A. Gupta, and Gang Xiao

***Abstract*—Chromium dioxide (CrO_2) thin films of different thicknesses (120–2600 Å) have been grown epitaxially on (100)-oriented TiO_2 substrates by the chemical vapor deposition technique. The thicker films, with a Curie temperature of 395 K, exhibit in-plane magnetocrystalline anisotropy with the magnetic easy axis along the c-axis direction. At low temperatures, the easy axis is deflected from the c- toward the b-axis in the thickness range 1500–600 Å. For even smaller thicknesses, the c-axis and the magnetic easy axis coincide again. However, at 300 K, the c-axis is always the magnetic easy axis in every film studied. Resistivity measurement in the temperature range of 4.2 to 420 K has also been performed. Temperature dependence of the resistivity is highly anisotropic between the b- and the c-axis, due to thickness induced anisotropic strain in the CrO_2 films.**

I. Introduction

CHROMIUM dioxide (CrO_2) is a ferromagnetic oxide that has been widely used as a particulate magnetic recording medium [1]. Theoretical [2] and experimental [3], [9] studies have confirmed that CrO_2 is a half-metallic solid with a nearly 100% spin polarization in the conduction band. This half-metallicity property makes CrO_2 a good material candidate for magnetic tunnel junctions and other magnetoelectronic devices that require a large spin polarization. Fabrication and characterization of epitaxial CrO_2 films are essential for basic studies and potential applications. It remains a challenging task to synthesize CrO_2 films, as this particular phase is a metastable oxide. So far, high-quality single-crystal CrO_2 films have been prepared using the technique of chemical vapor deposition (CVD) on the single crystal substrate of TiO_2. The close lattice matching between CrO_2 and the substrate is necessary to stabilize the growth of the CrO_2 phase. The lattice constant difference between CrO_2 and TiO_2 is -3.79% along $\langle 100\rangle$ and $\langle 010\rangle$ crystalline axes, and -1.48% along the $\langle 001\rangle$ axis. Therefore the induced strain in the CrO_2 film is expected to be anisotropic for films with in plane b- and c-axis. Earlier, our group [4] has shown that the strain in CrO_2 films affects the magnetic anisotropy significantly in the thickness range of 800 Å–1.2 μm. The present work extends our research of magnetic properties of strained CrO_2 films to thinner films. Furthermore, we have measured the temperature and thickness dependence of resistivity of these films. We will show that the induced strain also plays an important role on the electron transport.

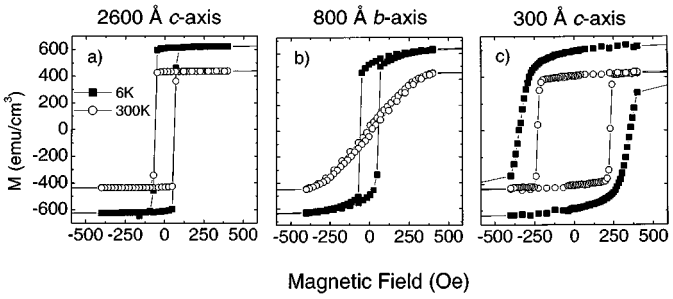

Fig. 1. Magnetization hysteresis loops obtained at 6 K and 300 K for film thickness: (a) 2600 Å and field along c-axis, (b) 750 Å and field along b-axis (c) 300 Å and field along c-axis.

We have grown CrO_2 films with varying thicknesses (120–2600 Å) on single crystal TiO_2 substrates using the CVD technique. The details of the synthesis have been published elsewhere. [5] The b- and c-axis of the films are in-plane and the a-axis is along the growth direction. Thickness profilometry and Rutherford backscattering analysis have been used for thickness determination. Magnetic hysteresis loops have been measured in the Quantum Design SQUID magnetometer at temperatures of 6, 150, and 300 K. The magnetic field was along both the b- and c-axis directions for the characterization of magnetic anisotropy. We have used the standard four-probe technique to measure resistivity on photo-lithographically patterned samples.

We have measured the magnetic properties of eight films in the thickness range of 300–2600 Å. No significant influence of the film thickness on the Curie temperature has been observed. However, marked changes in the hysteresis loops have been seen as the films become thinner. As shown in Fig. 1(a) for a 2600 Å thick film, the hysteresis loops are square with the field along the c-axis both at 6 K and 300 K, indicating that the c-axis is the magnetic easy axis in thick films. As the film thickness is reduced to below 1500 Å, the c-axis loops become gradually more rounded. The coercivity in the b-axis loops starts to appear and increase. This is an indication of a gradual reorientation of the magnetic easy axis from c- to the b-axis. A similar behavior has also been observed recently in magnetic susceptibility measurements [6]. An example of the easy axis reorientation is shown

Manuscript received October 16, 2000.

The work was supported by NSF Grant Nos. DMR-0080031 and DMR-0071770.

A. Anguelouch and G. Xiao are with the Department of Physics, Brown University, Providence, RI 02912 (e-mail: anguelou@barus.physics.brown.edu; xiao@physics.brown.edu).

A. Gupta is with IBM T.J. Watson Research Center, Yorktown Heights, NY 10598 (e-mail: agupta1@us.ibm.com).

Publisher Item Identifier S 0018-9464(01)06167-2.

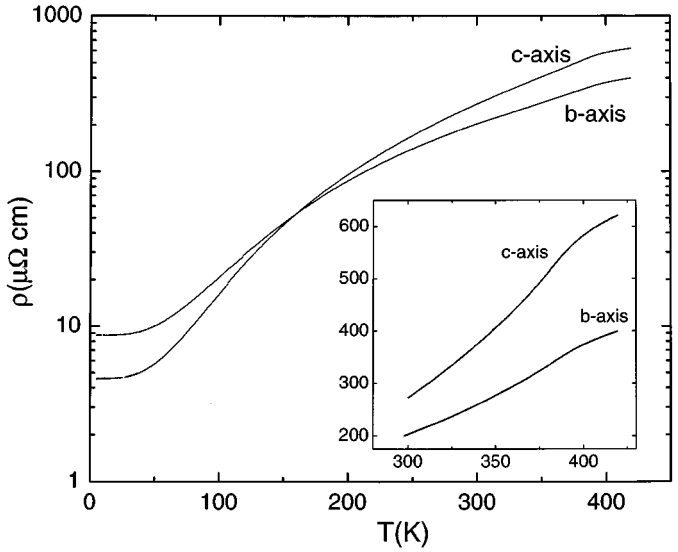

Fig. 2. Resistivity vs. temperature along b- and c-axis for a 2600 Å film (Note the log resistivity scale). The inset shows the resistivity near the Curie temperature (395 K).

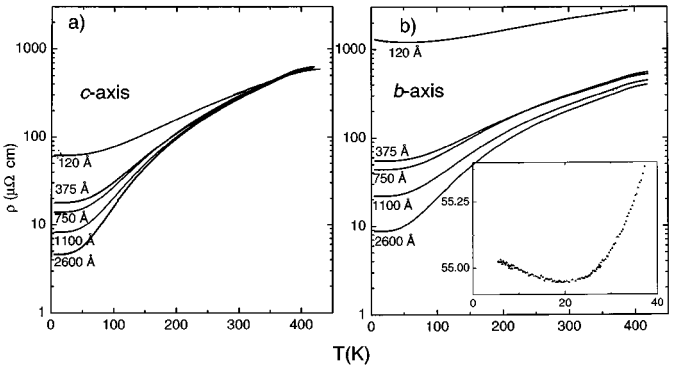

Fig. 3. Temperature dependence of the resistivity for: (a) c-axis and (b) b-axis for various thicknesses. Inset shows the low-temperature region for the b-axis measurement of the 375 Å film (note the resistivity upturn).

in Fig. 1(b) for an 800 Å film. In this hysteresis loop, the field is along the b-axis. The fact that the loop at 6 K is close to be square-like indicates that the easy axis is nearly aligned with the b-axis. As we increase the temperature to 300 K, the easy axis switches back to the c-axis as in the thicker films.

Interestingly, when we reduce the thickness further to, e.g., 300 Å, the easy axis becomes the c-axis again at both 6 and 300 K. This can be seen in Fig. 1(c), where the magnetic hysteresis loops at 6 and 300 K are square-like with the field along the c-axis. These results show that the magnetic anisotropy in strained CrO_2 films can be easily affected by the thickness as well as temperature. Furthermore, the evolution of the anisotropy is not monotonic against a varying thickness. Another interesting observation from Fig. 1 is that the coercivity of the CrO_2 film is strongly thickness dependent, ranging from tens of Oe in the thicker films to hundreds of Oe in the thinner films. One should be particularly aware of this fact if CrO_2 is intended to be a magnetic component in any magnetoelectronic devices.

We have measured the resistivity, $\rho(T)$, of the films as a function of thickness (120–2600 Å) in the temperature range of 4.2–420 K. The temperature dependence of resistivity is shown in Fig. 2 for a bulk 2600 Å film. The resistivity was measured along both the b- and the c-axis, with results similar to those obtained in earlier studies on thicker films [7]. The resistivity curves for the b- and the c-axis intercept at about 160 K. The resistivity changes nearly two orders of magnitude between 4.2 and 420 K, with the film being highly metallic at low temperatures. The magnetic phase transition temperature ($T_c \sim 395$ K for the bulk film) can be obtained from the resistivity versus temperature curve (see inset of Fig. 2). Due to magnetic disorder scattering, there appears to be a slope change in the curve as temperature moves across T_c. Using this signature, we were able to determine T_c for films of different thicknesses.

Fig. 3(a) and (b) show that temperature dependence of resistivity for films with varying thickness from 120 to 2600 Å, along the c- and b-axis, respectively. The value of T_c, as indicated by the slope change in the $\rho(T)$ curves, remains a constant independent of thickness, which is consistent with results obtained from magnetic measurements.

Comparison between Fig. 3(a) and (b) shows that the thickness has a more dramatic effect on the b-axis resistivity than the c-axis resistivity. In the thickness range studied, the residual resistivity increases about one order of magnitude along the c-axis, whereas it increases more than two orders of magnitude along the b-axis. This is due to the fact that lattice mismatch between the TiO_2 substrate and the CrO_2 film is 3.79% along the b-axis, and 1.48% along the c-axis. Therefore, the strain in the film is highly anisotropic, stronger along b-axis than c-axis.

We have found that the functional forms of $\rho(T)$ taken along the c-axis do not change appreciably with thickness. The most important effect of the thickness variation is the change in the residual resistivity as temperature approaches zero. Our analysis has shown that the residual resistivity is inversely proportional to the thickness. This is consistent with surface induced disorder scattering, as the thickness becomes a limiting scale for the electron mean free path [8].

In the thickness range of interest, all CrO_2 films remain metallic over the temperature range measured. However, in the thin film limit and at low temperatures, there appears an upturn in resistivity along the b-axis as temperature is lowered. This behavior is best seen in the inset of Fig. 3 for the CrO_2 film with a thickness of 375 Å. We think that it is due to the large induced strain in the thin film limit. Such a strain tends to reduce the wavefunction overlap and, possibly, causes electron localization at low temperatures.

In summary, the anisotropic strain in CrO_2 films has a profound effect on both the magnetic and electron transport properties of this half-metallic solid. As the thickness of the film decreases, the magnetic easy axis reorients twice, first from c- to b-axis and then back to c-axis again at low temperatures. The magnetic coercivity also changes appreciably with thickness. The main effect of thickness on the resistivity is the surface induced disorder scattering, which increases the residual resistivity as films become thinner. There exists a large anisotropy in resistivity along the b- and the c-axis, due to the anisotropic strain in the CrO_2 films. In the thin film limit, resistivity at low temperatures exhibits nonmetallic behavior along the b-axis

which is heavily strained. The reduced wavefunction overlap is a potential cause for this behavior.

ACKNOWLEDGMENT

The authors wish to thank C. H. Shang and C. L. Chien at the Johns Hopkins University for some of the X-ray measurements and analysis and X. W. Li at Seagate Corp. for useful discussions.

REFERENCES

[1] B. L. Chamberland, "The chemical and physical properties of CrO_2 and tetravalend chromium oxide derivatives," *CRC Crit. Rev. Solid State Mat. Sci.*, vol. 7, pp. 1–31, 1977.

[2] K. Schwarz, "CrO_2 predicted as a half-metallic ferromagnet," *J. Phys. F*, vol. 16, pp. L211–L215, 1986. M. A. Korotin, V. I. Anismov, D. I. Khomskii, and G. A. Sawatzky, "CrO$_2$: A self-doped double exchange ferromagnet," *Phys. Rev. Lett.*, vol. 80, pp. 4305–4308, 1998.

[3] R. J. Soulen Jr., J. M. Byers, M. S. Osofsky, B. Nadgorny, T. Ambrose, S. F. Cheng, P. R. Broussard, C. T. Tanaka, J. Nowak, J. S. Moodera, A. Barry, and J. M. D. Coey, "Measuring the spin polarization of a metal with a superconducting point contact," *Science*, vol. 282, pp. 85–88, 1998.

[4] X. W. Li, A. Gupta, and G. Xiao, "Influence of strain on the magnetic properties of epitaxial (100) chromium dioxide (CrO_2) films," *Appl. Phys. Lett.*, vol. 75, pp. 713–715, 1999.

[5] X. W. Li, A. Gupta, T. T. McGuire, P. R. Duncombe, and G. Xiao, "Magnetoresistance and Hall effect of chromium dioxide epitaxial thin films," *J. Appl. Phys.*, vol. 85, pp. 5585–5587, 1999.

[6] L. Spinu, H. Srikanth, A. Gupta, X. W. Li, and G. Xiao, "Probing magnetic anisotropy effects in epitaxial CrO_2 thin films," *Phys. Rev. B.*, vol. 62, pp. 8931–8934, 2000.

[7] A. Gupta, X. W. Li, and G. Xiao, "Magnetic and transport properties of epitaxial and polycrystalline chromium dioxide thin films," *J. Appl. Phys.*, vol. 87, pp. 6073–6078, 2000.

[8] C. R. Tellier and A. J. Tosser, *Size Effects in Thin Films*, Amsterdam: Elsevier Scientific Publishing Company, 1982.

[9] K. P. Kamper, W. Schmitt, G. Güntherodt, R. J. Gambino, and R. Ruf, "CrO_2—A new half-metallic ferromagnet?," *Phys. Rev. Lett.*, vol. 59, pp. 2788–2091, 1987.