PHYSICAL REVIEW B, VOLUME 64, 180408(R)

Near-complete spin polarization in atomically-smooth chromium-dioxide epitaxial films prepared using a CVD liquid precursor

A. Anguelouch,[1] A. Gupta,[2] Gang Xiao,[1] D. W. Abraham,[2] Y. Ji,[3] S. Ingvarsson,[2] and C. L. Chien[3]

[1]*Department of Physics, Brown University, Providence, Rhode Island 02912*

[2]*IBM T.J. Watson Research Center, Yorktown Heights, New York 10598*

[3]*Department of Physics and Astronomy, The Johns Hopkins University, Baltimore, Maryland 21218*

(Received 27 June 2001; published 23 October 2001)

We have fabricated single crystal chromium dioxide (CrO_2) films using chemical vapor deposition with chromyl chloride (CrO_2Cl_2) as a liquid precursor. Their electrical and magnetic properties have been investigated. These films are atomically smooth with a rms roughness of less than 5 Å for 1000 Å thick films. We have obtained a spin polarization of $P=98.4\%$, as determined by the technique of point-contact Andreev reflection. Magnetization and resistivity measurements on these films are in good agreement with those measured on films made with the CrO_3 solid precursor. The process using the liquid precursor is superior to other existing techniques for the preparation of single crystal single- and multilayers containing CrO_2, especially the structure of magnetic tunnel junctions.

DOI: 10.1103/PhysRevB.64.180408 PACS number(s): 75.70.Ak, 75.50.Cc

Chromium dioxide (CrO_2) is a ferromagnetic oxide that has been widely used as a particulate magnetic recording medium.[1] Another unique property of CrO_2 has received increased attention in recent years. Theoretical studies[2] have predicted it to be half-metallic, i.e., having a full spin polarization of 100%. The half-metallicity makes CrO_2 a good magnetic component in magnetoelectronic devices that require a large spin polarization. These devices include magnetic tunnel junctions (MTJ) and spin valves. In addition to this property, a number of other factors, such as film smoothness, small coercivity, and a single-domain-like hysteresis loop, are also crucial for potential applications. We have fabricated CrO_2 epitaxial films that exhibit all of these desirable characteristics. We used a chemical vapor deposition (CVD) process with a liquid precursor that is more advantageous than the solid precursor used in earlier CVD processes. We have experimentally verified, using the point-contact Andreev reflection (PCAR) technique, that our CrO_2 film has an actual spin polarization of 98.4%.

The synthesis of CrO_2 films has been a difficult task due to the metastable nature of this oxide. It has not been possible to obtain CrO_2 films using standard high-vacuum deposition methods (e.g., molecular beam epitaxy or sputtering). The CVD technique seems to be the most effective method to fabricate epitaxial CrO_2 films on single-crystal TiO_2 substrates.[3] DeSisto *et al.* have recently used CVD with a CrO_2Cl_2 liquid precursor to produce CrO_2 films.[4] While these films are epitaxial, they are not of very high quality, have a relatively large roughness (30–60 Å), a smaller than expected spin polarization (81%) and a considerable hard axis saturation field (4 kOe). Our group has previously used CrO_3 powder as a solid precursor to produce high-quality films.[5] The use of a solid precursor is cumbersome in preparing CrO_2-based multilayers, such as MTJ's. In this paper, we describe a CVD process with a CrO_2Cl_2 liquid precursor which yields films whose properties compare favorably with those grown using CrO_3 as a precursor. For these reasons, we believe this method is preferable to other fabrication techniques.

Our CVD deposition reactor consists of a quartz tube placed inside a furnace and kept at 400 °C. After being cleaned with organic solvents and dilute hydrofluoric acid, single-crystal (100) TiO_2 substrates are placed on a tilted glass susceptor. The quality of substrates and substrate cleaning is critical for obtaining high quality films. The liquid precursor CrO_2Cl_2 is placed in a bubbler and kept at 0 °C. The flow rate of the oxygen carrier gas is 40 cc^3/min, yielding a deposition rate of about 72 Å/min. The results of x-ray diffraction are in good agreement with those obtained on single crystal epitaxial samples grown using CrO_3. The full width at half maximum (FWHM) of the rocking curve for the (200) CrO_2 peak is on the order of 0.1 degrees.

The spin-polarization experiments were performed using PCAR, as described previously.[6] The PCAR data are shown in Fig. 1. Representative measurements (shown as open circles) of normalized conductance $G(V)/G_n$ vs bias voltage V for Pb/CrO_2 films at ~1.6 K are shown in Figs. 1(a)–1(c).

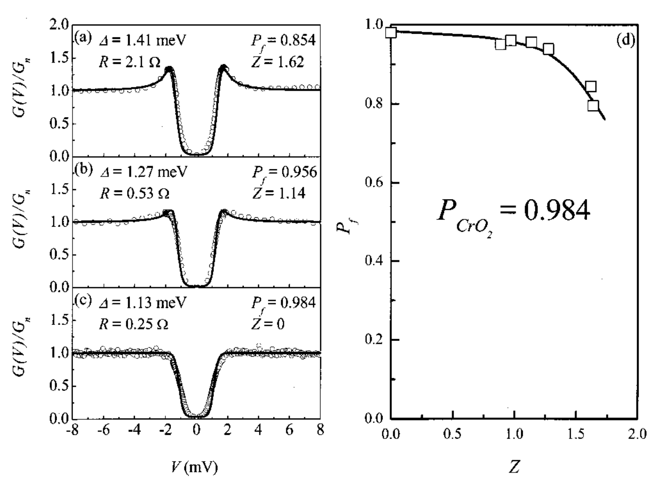

FIG. 1. (a)–(c) Measured $G(V)/G_n$ vs V of Pb/CrO_2 point contacts at $T=1.6$ K (open circles). The solid lines are best fits to the data using the modified BTK model. (d) Fitted polarization P_f as a function of Z.

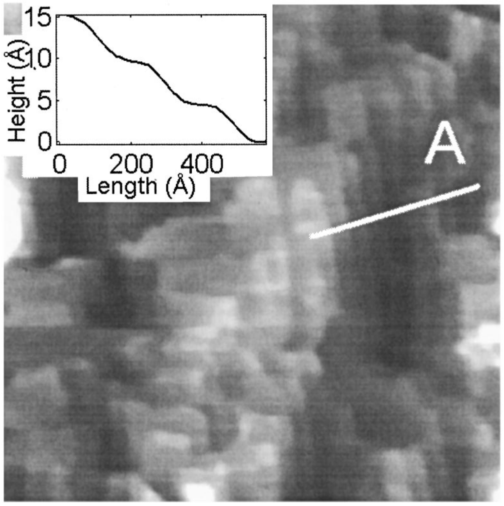

FIG. 2. AFM image of a 1050 Å thick CrO_2 film. The distinguishable lines correspond to atomic planes of CrO_2. Inset shows a sample cross section of region marked A with 4.4 Å steps.

A modified version[7] of Blonder-Tinkham-Klapwijk (BTK) theory[8] has been used to analyze the experimental data in order to obtain the value of spin polarization. The conductance curves can be reasonably well described by this model. The solid lines in Figs. 1(a)–1(c) represent best-fit lines to this model using the spin polarization P_f, the interfacial scattering barrier strength Z, and the superconductor energy gap Δ as fitting parameters. The fitted values of these parameters are given in the figures. Figure 1(d) shows the Z dependence of the value of P_f, which is consistent with previous PCAR measurements.[6,7] In the limit of transparent interface $Z=0$, the value of polarization is 98.4%.

Figure 1(c) shows the experimental results obtained with such an interface. The conductance curve is completely flat outside of the energy gap, indicating clean metallic contact between the Pb and CrO_2 layers. Assuming a clean interface, the formula for spin polarization reduces[6,7] to $G(0)/G_n=2(1-P)$. Since $G(0)/G_n=0.032$ in this case, P is determined to be 98.4%, which agrees with the fitting result. This is the largest spin polarization ever determined in any ferromagnetic metal, affirming convincingly the half-metallic nature of CrO_2. As a comparison, conventional ferromagnetic metals, Fe, Co, Ni, etc., have much lower polarization, in the range of 25 to 45%.

We have probed the surface quality of our CrO_2 films using atomic force microscopy (AFM) and have verified that these films grow as a single crystal. Figure 2 shows one AFM image of a 1050 Å thick film. The clearly distinguishable lines on the scan correspond to atomic planes of CrO_2. The rms roughness over an area of 1 μm^2 is 4.6 Å, while the height of each individual step is 4.4 Å or 8.8 Å. Since the out-of-plane lattice constant of CrO_2 is 4.4 Å, these steps correspond to single or double atomic planes, indicating that the films are atomically smooth. A scan over a region with atomic steps is shown as an inset in the figure. The roughness at the interfaces greatly affects the magnetic and resistive properties of MTJ. It has been shown that magnetic properties are strongly affected by Néel "orange-peel" coupling.[9]

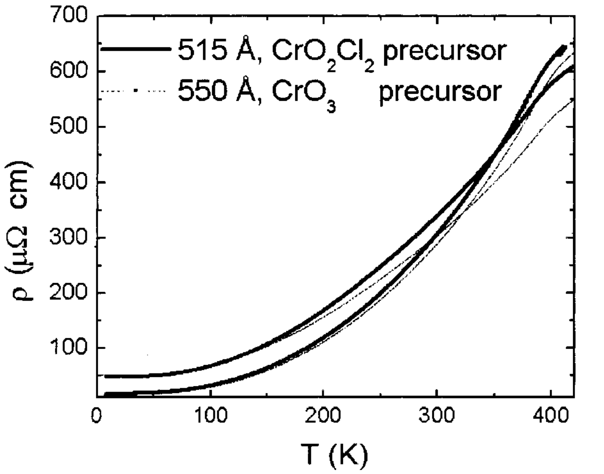

FIG. 3. Resistivity vs temperature curves for the c axis (low residual resistivity) and the b axis (high residual resistivity). The films with comparable thickness are made with solid CrO_2 (thin lines) and liquid CrO_2Cl_2 (thick lines) precursors.

Large roughness can also lead to imperfections in the tunnel barrier, causing highly nonuniform current distributions. When we compare the roughness values obtained for our CrO_2 films with those determined in state-of-the-art MTJ devices,[10] we find that the surface quality of the CrO_2 films makes it ideal for MTJ devices.

We have measured the temperature dependence of resistivity using the standard four-probe technique. The results of the CrO_2 films made using CrO_3 and CrO_2Cl_2 as precursors are compared in Fig. 3. It is evident that the resistive properties of these films are similar in comparable thickness range. Both types of films have the same Curie temperature $T_c \sim 390$ K, indicative in the slope change of the resistivity vs T curve.

Magnetic measurements were performed using a superconducting quantum interference device (SQUID) magnetometer and a vibrating sample magnetometer (VSM). Figure 4 shows two typical magnetic hysteresis loops taken at different temperatures for a 1375 Å thick film. It can be seen that the easy-axis (in-plane c axis) hysteresis loops are square-like, especially at room temperature. The in-plane b axis is the hard axis.

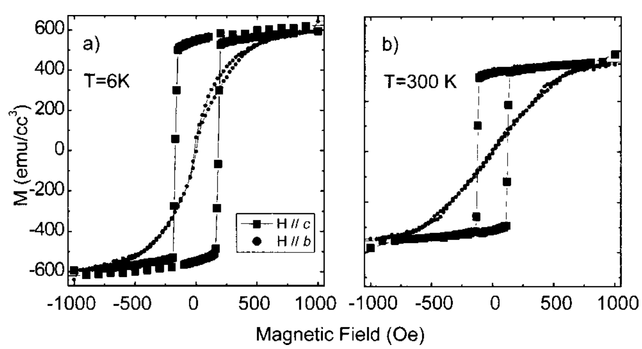

FIG. 4. Magnetic hysteresis loops taken at (a) 6 K($M_s=650$ emu/cc^3) and (b) 300 K($M_s=465$ emu/cc^3) for a 1375 Å thick film.

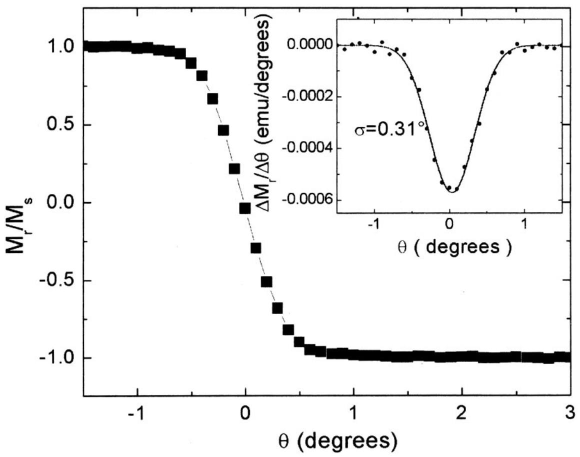

FIG. 5. Remanence M_r/M_s parallel to the sample's easy axis, as a function of saturation angle θ. The inset shows a Gaussian fit to the derivative $\Delta M_r/\Delta\theta$ vs θ.

To estimate the in-plane dispersion of the magnetization, we have measured their magnetic remanence M_r/M_s as a function of saturation angle θ. The sample relaxes to its easy axis in one of the two energetically favorable directions. As the saturation field direction approaches the sample's hard axis there is a narrow transition region where the sample changes from relaxing along the easy axis in one direction to relaxing along an antiparallel direction. Figure 5 shows the remanent magnetization parallel to the sample's easy axis. The derivative of this transition gives a peak, whose width characterizes the dispersion of the in-plane angular distribution of the magnetization. A Gaussian fit to this peak, which is shown in the inset, gives a small standard deviation of only 0.31 deg. In similar measurements, the narrowest transition we have seen in permalloy ($Ni_{80}Fe_{20}$) films has a standard deviation of 0.57 deg.

In summary, we have fabricated atomically-smooth single-crystal half-metallic CrO_2 films using CrO_2Cl_2 as a liquid CVD precursor. The films exhibit a large spin polarization of 98.4%, larger than that of any other ferromagnet. The electrical and magnetic properties of these films compare favorably with single-crystal CrO_2 samples prepared by other methods.

We wish to thank B.D. Schrag for help and useful discussions. This work was supported by NSF Grant Nos. DMR-0080031 and DMR-0071770.

[1] B. L. Chamberland, CRC Crit. Rev. Solid State Mater. Sci. **7**, 1 (1977).

[2] K. Schwarz, J. Phys. F: Met. Phys. **16**, L211 (1986); M. A. Korotin, V. I. Anisimov, D. I. Khomskii, and G. A. Sawatzky, Phys. Rev. Lett. **80**, 4305 (1998).

[3] X. W. Li, A. Gupta, T. R. McGuire, P. R. Duncombe, and Gang Xiao, J. Appl. Phys. **85**, 5585 (1999).

[4] W. J. DeSisto, P. R. Broussard, T. F. Ambrose, B. E. Nadgorny, and M. S. Osofsky, Appl. Phys. Lett. **76**, 3789 (2000).

[5] A. Anguelouch, A. Gupta, and Gang Xiao, IEEE Trans. Magn. **37**, 2135 (2001).

[6] Y. Ji, G. J. Strijkers, F. Y. Yang, C. L. Chien, J. M. Byers, A. Anguelouch, Gang Xiao, and A. Gupta, Phys. Rev. Lett. **86**, 5585 (2001).

[7] G. J. Strijkers, Y. Ji, F. Y. Yang, C. L. Chien, and J. M. Byers, Phys. Rev. B **63**, 104510 (2001).

[8] G. E. Blonder, M. Tinkham, and T. M. Klapwijk, Phys. Rev. B **25**, 4515 (1982).

[9] L. Néel, Acad. Sci., Paris, C. R. **255**, 1676 (1962).

[10] B. D. Schrag, A. Anguelouch, S. Ingvarsson, Gang Xiao, Yu Lu, P. L. Trouilloud, A. Gupta, R. A. Wanner, W. J. Gallagher, P. M. Rice, and S. S. P. Parkin, Appl. Phys. Lett. **77**, 2373 (2000).