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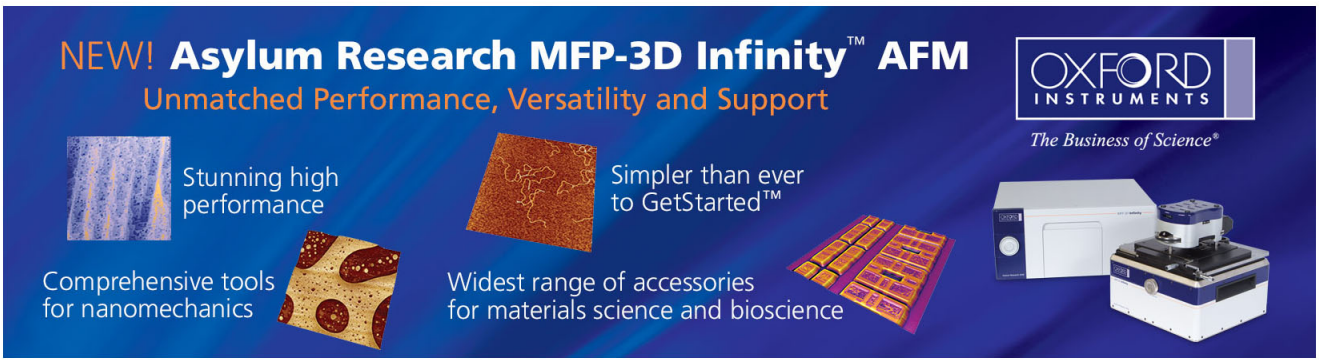

Transport properties of CrO_2 (110) films grown on TiO_2 buffered Si substrates by chemical vapor deposition

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Epitaxial CrO_2 (110)-oriented films were fabricated on Si (100) substrates buffered by rutile TiO_2 derived from oxidation of a pulsed-laser-deposited TiN layer. The epitaxial films of CrO_2 were prepared by chemical vapor deposition in a two-zone furnace with oxygen flow from a CrO_3 precursor. The transport measurements show that the CrO_2 films are metallic with a Curie temperature of about 380 K. The temperature dependence of resistivity was best described by a phenomenological expression $\rho(T)=\rho_0+AT^2e^{(-\Delta/T)}$ over the range of 5–350 K with $\Delta=94$ K. The magnetic measurements show the in-plane coercive fields are about 30 and 60 Oe at 300 and 5 K, respectively. The temperature dependent spontaneous magnetization follows Bloch's $T^{3/2}$ law and the slope suggests a critical wavelength of $\lambda_\Delta \sim 30.6$ Å beyond which spin-flip scattering becomes important. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1481534]

The metallic ferromagnet CrO_2 has received much attention due to its interesting physical properties and great application potential. Band structure calculations have predicted that CrO_2 is a half-metallic ferromagnet with 100% spin polarization of conduction electrons since the minority spin band structure has a gap at the Fermi energy.[1] Recently, a number of experiments including photoemission experiments,[2] superconducting point-contact experiments,[3,4] and vacuum tunneling measurements[5] have unambiguously demonstrated the half-metallicity of this material. The highly spin polarization of CrO_2 makes it a promising candidate for spin-dependent devices.[6] However, the nature of CrO_2 is still, in some cases, not yet in consensus. Thus, a viable method of producing this material in a controlling manner is needed to further delineate some of the issues. Due to the same crystal structure, the rutile TiO_2 should serve as a favorable substrate for growing CrO_2 films. However, rutile TiO_2 substrates are quite expensive. Other crystalline substrates have been used to prepare CrO_2 films including sapphire[7] and RuO_2.[2] Buffer layers on fused quartz and glass have also been used.[8,9] In this letter, we report the growth and magnetotransport properties of epitaxial CrO_2 (110)-oriented film on Si (100) substrate with TiO_2 buffer layer.

It is difficult to directly grow epitaxial TiO_2 layer on Si from TiO_2 targets.[10] However, our recent studies have indicated that, by oxidation, TiN can be converted into rutile TiO_2 while keeping the original epitaxy of TiN with substrate.[11] To obtain the epitaxial TiO_2 buffer layer on Si, a similar concept was adopted. Briefly, prior to the deposition, the Si substrate was cleaned ultrasonically in acetone, followed by oxide removal in 20% HF solution. The substrates were then loaded into the deposition chamber and evacuated immediately to prevent from the native oxidation. TiN layers were deposited by pulsed laser deposition on Si (100) substrates at 650 °C with a laser energy density of 4 J/cm^2. The chamber was maintained under a pressure of 4×10^{-5} Torr during the deposition. After the deposition, the substrates with TiN layer were annealed at 750 °C in 0.3 Torr O_2 for 10 mins to oxidize TiN to rutile TiN_2 (110). The as-deposited TiN is golden yellow in color and becomes transparent after being oxidized. The epitaxial CrO_2 films were grown by chemical vapor deposition using a two-zone tube furnace based on the process reported by Ishibashi.[12] CrO_3 was used as precursor and placed in the first zone at a temperature of 260 °C. CrO_3 sublimes at 260 °C. Oxygen was used as the carrier gas to transfer the vapor from the first zone to the second zone. The substrates were placed in the second zone at 400 °C, onto which the CrO_3 vapor completely decomposes into CrO_2. It took 3 h to obtain 550-nm-thick CrO_2 films.

Figure 1 shows the typical θ–2θ x-ray diffraction (XRD) pattern of the $CrO_2/TiO_2/Si$ multilayer structure. Except for

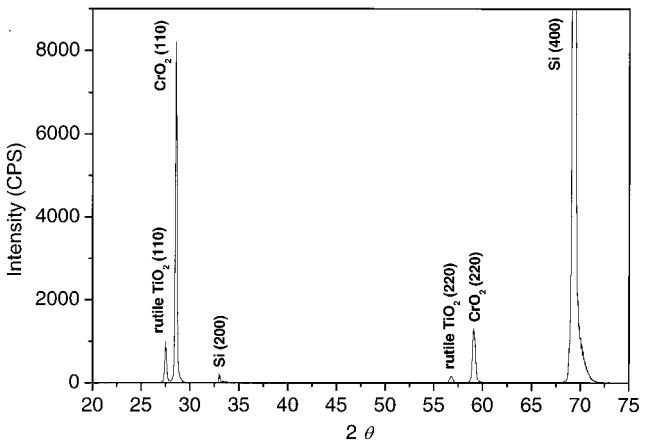

FIG. 1. XRD pattern of the CrO_2 film grown on the TiO_2 buffered Si substrate. Both CrO_2 and TiO_2 are completely (110) oriented.

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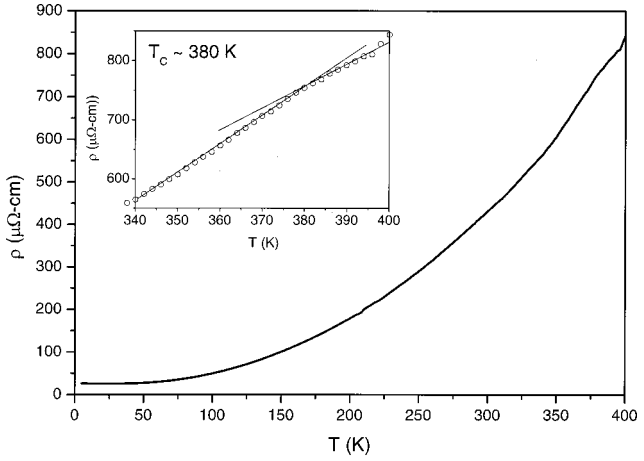

FIG. 2. Resistivity plotted as a function of temperature. The CrO_2 film grown on TiO_2 buffer layer is metallic. T_C is 380 K as indicated in the slope change of the $R-T$ curve shown in the inset.

the peaks of the TiO_2 buffer layer and Si substrate, only the (110) and (220) peaks of CrO_2 are observed. The XRD scans indicate that the TiO_2 buffer layer and the CrO_2 film are both epitaxial and completely (110) oriented.

It is evident from Fig. 2 that the CrO_2 films grown on TiO_2-buffered silicon substrates are metallic. The inset of Fig. 2 shows that the Curie temperature (T_C) of the CrO_2 films obtained here is about 380 K, as depicted by the slope change in the $R-T$ curve. This is slightly lower than the bulk value of 390 K for CrO_2. However, the resistivities at 300 K (~430 $\mu\Omega$ cm) and 5 K (~26 $\mu\Omega$ cm) are much higher than the respective bulk value of 250 and 5 $\mu\Omega$ cm. The smaller residual resistivity ratio (RRR) suggests that the grain boundaries may have played a prominent role in the earlier mentioned results. To further elucidate this speculation, the magnetoresistance (MR) of the as-grown films was measured. A negative MR at room temperature was observed, which is consistent with that observed in CrO_2 films grown on single crystalline and polycrystalline TiO_2 substrates.[6] The result has been attributed to the effect of magnetic field suppression of spin disorder scattering. However, unlike a positive MR observed at low temperatures in the epitaxial films grown on single crystalline TiO_2, which has been attributed to the Lorentz force effect, the MR of CrO_2 films obtained by the present method exhibits a negative change at 5 K in a field up to 5 T (~−3%). In the works of Hwang and Cheong[13] and Gupta *et al.*,[6] the negative MR at low temperatures has been interpreted as a manifestation of spin-polarized transport across grain boundary. We believe that similar arguments may also account for the smaller RRR value obtained in the present films.

The temperature dependence of resistivity of CrO_2 films also represents a much discussed issue of this material. In conventional ferromagnets, such as Fe, Co, and Ni, a T^2 temperature dependence of resistivity, arising from the electron-magnon scattering, is usually observed at low temperatures. Suzuki and Tedrow[14] have observed a T^2 dependence in CrO_2 films deposited on ZrO_2 substrates between 130 and 240 K. A model of invoking the metallic majority and semiconducting minority electrons being acting in parallel and independently was proposed account for the observation. However, the electron-magnon scattering, which is a spin-flip scattering process, is theoretically forbidden in a perfect half metal due to the absence of minority spin states. On the other hand, a T^3 dependence has been observed below 40 K in (100)-oriented CrO_2 films epitaxially grown on single crystal (100) TiO_2 substrates.[6] The T^3 dependence has been considered as an unconventional electron-magnon scattering in a half metal due to spin fluctuations at finite temperature, which results in the nonrigid band behavior of the minority band. However, it is not clear why such a behavior does not sustained to higher temperatures.

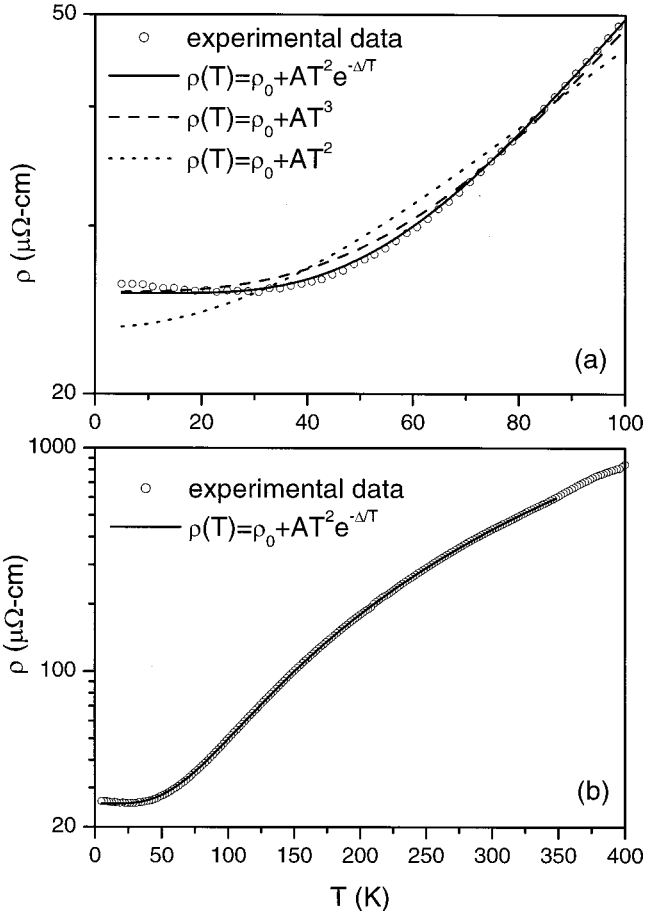

FIG. 3. A detailed comparison of fits at low temperatures is presented in (a). The resistivity data is best fitted with Eq. (1), slightly better than T^3 dependence. The $\rho(T)$ curve can well fit Eq. (1) from 5 K up to 350 K by taking $\rho_0 = 25.5\ \mu\Omega$ cm, $A = 0.00617\ \mu\Omega\ \mathrm{cm\,K^{-2}}$ and $\Delta = 94$ K, as shown in (b).

Alternatively, a phenomenological expression

$$\rho(T) = \rho_0 + AT^2 e^{(-\Delta/T)} \tag{1}$$

has been used to fit the resistivity data of epitaxial CrO_2 films grown by high pressure thermal decomposition.[15] Although our data may be reasonably fitted by T^3 dependence [dash curve in Fig. 3(a)], for $T < 100$ K, it is best described by Eq. (1) over the temperature range of 5–350 K [Fig. 3(b)] with $\rho_0 = 25.5\ \mu\Omega$ cm, $A = 0.006\,17\ \mu\Omega\ \mathrm{cm\,K^{-2}}$ and $\Delta = 94$ K, respectively. The existence of the "gap" in Eq. (1), though has found no relevant evidence from neither magnetization nor specific heat measurements as being related to magnon spectrum, has been interpreted as a means of the critical wavelength where spin-flip scattering becomes

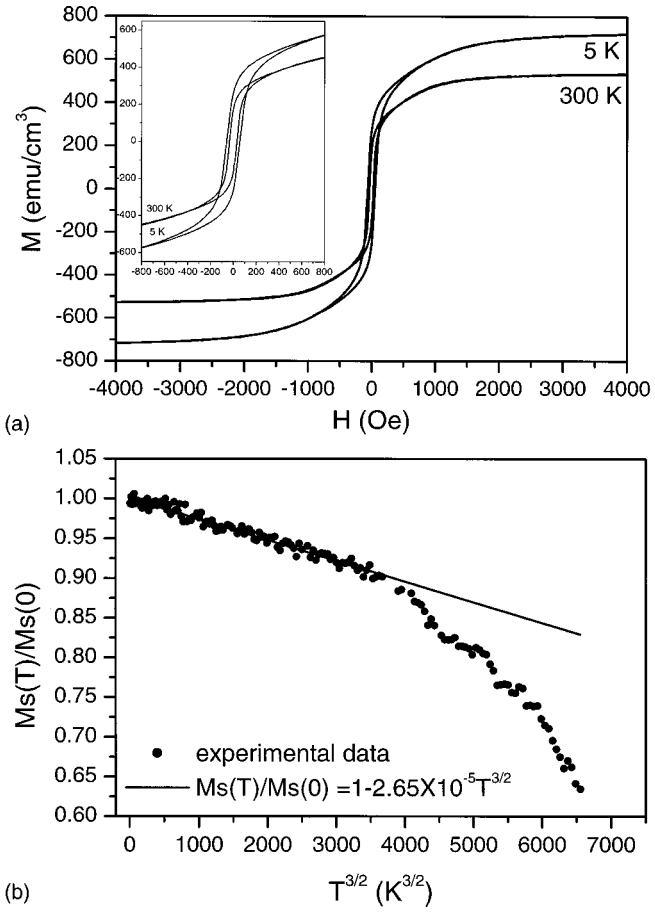

FIG. 4. Hysteresis curves measured at 5 and 300 K with the field oriented along the film. The coercive fields are 60 and 30 Oe at 5 and 300 K, respectively. A field of 2500 Oe is needed to saturate the magnetization. Inset shows a linear dependence of the spontaneous magnetization as a function of $T^{3/2}$, which is predicted by Bloch's law.

important.[15] It is, thus, interesting to see if the magnetic measurement can further lend support for applying the same argument to the present results.

The magnetic properties of the CrO_2 films are measured using a Quantum Design physical property measurement system. The hysteresis measurements were made at temperatures of 5 and 300 K with the magnetic field applied parallel to the film. As shown in Fig. 4(a), the coercive fields are 60 and 30 Oe at 5 and 300 K, respectively. The magnetic field needed to saturate the magnetization is about 2500 Oe. All the evidences indicate that the films are indeed a ferromagnet. The spontaneous magnetization measurement shows that the CrO_2 films are ferromagnetic below 350 K, consistent with the result deduced from the resistivity data. Furthermore, as shown in Fig. 4(b), the spontaneous magnetization curve $[Ms(T)]$ follows closely to the Bloch's $T^{3/2}$ law $Ms(T)=Ms(0)(1-AT^{3/2})$. From the slope "*A*," the spin-wave stiffness constant *D* was estimated to be approximately 193 meV Å^2.[15] By using $kT=Dq_T^2=4\pi^2 D/\lambda_T^2$ to define the shortest wavelength of magnons excited at a temperature *T*, the gap $\Delta=94$ K obtained previously, would imply a critical wavelength $\lambda_\Delta \sim 30.6$ Å beyond which the spin-flip scattering becomes important. This value of λ_Δ is indeed very close to that obtained by Barry *et al.*,[15] except that they had used CrO_2 powders to perform the magnetization measurements.

It is clear from the earlier analyses that the CrO_2 (110) films obtained by the present are indeed a half-metallic ferromagnet with high degree of orientation control. Since CrO_2 is difficult to be etched by any contemporary techniques, our method of using TiN as the intermediate template may offer significant advantages in realizing $CrO_2/TiO_2/Si$ spin-dependent devices based on the existing silicon technologies.

In summary, epitaxial CrO_2 (110) films have been grown on Si by using TiO_2 as buffer layers. The as grown CrO_2 film is ferromagnetic with the Curie temperature of 380 K. The temperature dependence of resistivity can be fitted with $\rho(T)=\rho_0+AT^2e^{(-\Delta/T)}$. The in-plane magnetic measurements show the coercive fields are about 30 and 60 Oe at 300 and 5 K, respectively. The temperature dependent spontaneous magnetization follows Bloch's $T^{3/2}$ law. The present process suggests a viable way of preparing patterned CrO_2 films and enhance the possibilities of fabricating spin-polarization dependent devices based on CrO_2.

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