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# Ferromagnetism in chromium-doped reduced-rutile titanium dioxide thin films

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Cr-doped reduced-rutile TiO<sub>2</sub> thin films were grown on *R*-plane sapphire substrates by pulsed-laser deposition. X-ray diffraction and transmission electron microscopy results indicate that the films are single phase and reduced-rutile type. Superconducting quantum interference device magnetometer measurements show the films are ferromagnetic up to 400 K. A large magnetic moment of 2.9 μ<sub>B</sub> per Cr atom is found for 6% Cr-doped reduced films at room temperature, and the saturation magnetization of the films decreases with increasing Cr doping. The temperature dependence of the resistivity shows semiconducting behavior. © 2004 American Institute of Physics.

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## I. INTRODUCTION

Because of the combined magnetic and transport properties in dilute magnetic semiconductors and the potential technological applications, a growing effort is directed toward studies of magnetic semiconductors with practical ordering temperature.<sup>1,2</sup> Recently, above room temperature, ferromagnetism has been reported<sup>3,4</sup> in Fe-doped reduced-rutile TiO<sub>2</sub> and in Co-doped SnO<sub>2</sub> of rutile structure.<sup>5</sup> Rutile TiO<sub>2</sub> crystallizes in a tetragonal lattice and is easily reduced by forming oxygen vacancies or titanium interstitials, and the reduced rutile forms a homologous series of compounds Ti<sub>n</sub>O<sub>2n-1</sub> with triclinic structure. Although the earlier investigations of the phase relations within the composition range MO<sub>1.75-2.0</sub> (M=Ti,Cr,...) of the titanium-chromium-oxygen system revealed the existence of analogous series of oxides Ti<sub>n-2</sub>Cr<sub>2</sub>O<sub>2n-1</sub> (6 ≤ n ≤ 9) with triclinic structure,<sup>6-9</sup> ferromagnetic properties at RT have not been reported in titanium-chromium-oxygen system.

In this work, following the study of Fe-doped reduced-rutile TiO<sub>2</sub> films,<sup>3,4</sup> we have investigated the magnetic and transport properties of Cr-doped reduced-rutile TiO<sub>2</sub> thin films.

## II. EXPERIMENT

Cr<sub>x</sub>Ti<sub>1-x</sub>O<sub>2-δ</sub> (x=0.06, 0.08, 0.12, 0.14) thin films were grown on α-Al<sub>2</sub>O<sub>3</sub>(012) substrates by pulsed-laser deposition (PLD). Cr<sub>x</sub>Ti<sub>1-x</sub>O<sub>2-δ</sub> targets were prepared using standard ceramic techniques. The films were prepared in vacuum at a substrate temperature of 800–1000 K. The pressure during deposition was 2 × 10<sup>-6</sup> Torr. The pulsed excimer laser uses KrF (λ = 248 nm) and produces a laser beam of intensity of 1–2 J/cm<sup>2</sup> and repetition rate of 4 Hz. The

deposition rate is between 0.2 and 0.4 Å/s, and the film thickness varies from 50 to 100 nm. The Cr concentrations of the films were measured with energy dispersive x-ray analysis in TE mode, and they were consistent with those of the targets. The crystalline structure was investigated by x-ray diffraction (XRD) with Cu K<sub>α</sub> radiation and transmission electron microscopy (TEM). The magnetic properties were studied with a superconducting quantum interference device (SQUID) magnetometer. The transport properties were measured with a physical property measurement system from Quantum Design.

## III. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern for a Cr<sub>0.06</sub>Ti<sub>0.94</sub>O<sub>2-δ</sub> film grown on *R*-plane α-Al<sub>2</sub>O<sub>3</sub> (012). The film is single phase and of reduced-rutile type with (202) plane, referred to the stoichiometric rutile tetragonal cell, parallel to the film

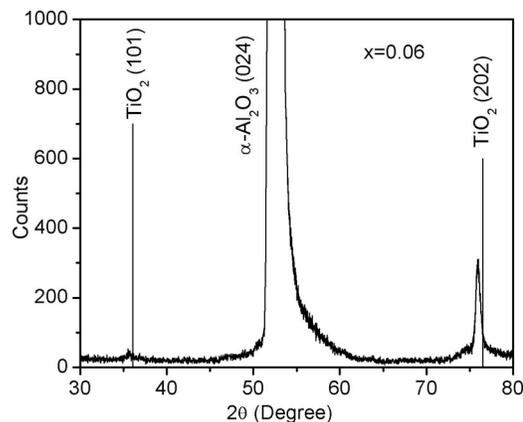


FIG. 1. XRD pattern of a Cr<sub>0.06</sub>Ti<sub>0.94</sub>O<sub>2-δ</sub> film grown on α-Al<sub>2</sub>O<sub>3</sub> (012) substrate showing reduced-rutile structure.

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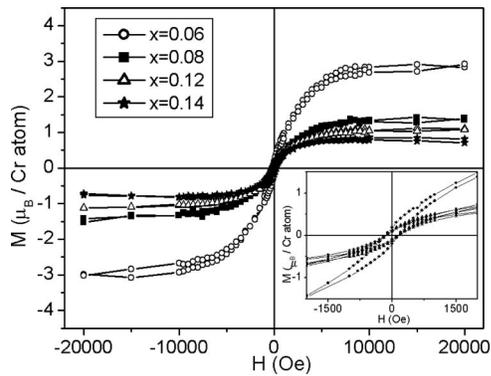


FIG. 2. Magnetic hysteresis loops  $\text{Cr}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$  ( $x=0.06, 0.08, 0.12, 0.14$ ) films measured with a SQUID at RT. The inset shows the low-field region of the hysteresis loop for the four films.

plane. The two vertical lines show (101) and (202) reflections of the stoichiometric rutile. The peak at the center of the scans is that of the substrate  $\alpha\text{-Al}_2\text{O}_3$  (024). The (202) peaks are shifted toward lower  $2\theta$  angles. The (101) peak is absent due to substantial reduction that forms the Magnéli shear plane. Similar XRD patterns were obtained for all films with different Cr content. The XRD results are similar to that of the Fe-doped reduced-rutile  $\text{TiO}_2$ .<sup>3,4</sup> XRD and TEM observation indicate no sign of the existence of any impurity phase up to  $x=0.14$  in this study. In fact, much higher Cr content can be sustained in the analogous series of oxides  $\text{Ti}_{n-2}\text{Cr}_2\text{O}_{2n-1}$  ( $6 \leq n \leq 9$ ) with triclinic structure.<sup>8,9</sup> The TEM observation showed the films are epitaxially grown.

In Fig. 2, we show magnetic hysteresis loops at RT for  $\text{Cr}_{0.06}\text{Ti}_{0.94}\text{O}_{2-\delta}$ ,  $\text{Cr}_{0.08}\text{Ti}_{0.92}\text{O}_{2-\delta}$ ,  $\text{Cr}_{0.12}\text{Ti}_{0.88}\text{O}_{2-\delta}$  and  $\text{Cr}_{0.14}\text{Ti}_{0.86}\text{O}_{2-\delta}$ . The hysteresis loops show that all the films are ferromagnetic at RT. The coercivity of the films at RT is 149, 134, 140, and 148 Oe for  $x=0.06, 0.08, 0.12,$  and  $0.14$ , respectively. The inset shows the low-field region of the hysteresis loops for the four films. The magnetic moment for the  $\text{Cr}_{0.06}\text{Ti}_{0.94}\text{O}_{2-\delta}$  film is about  $2.9 \mu_B/\text{Cr}$ , and the magnetic moment decreases with increasing  $x$ , as shown in Fig. 2. This result indicates that, as the Cr concentration in the material increases, a decreasing fraction of their spins participate in the ferromagnetism.

Figure 3 shows the temperature dependence of the magnetization  $M$  for  $\text{Cr}_{0.06}\text{Ti}_{0.94}\text{O}_{2-\delta}$  film measured from 2 to 400 K using SQUID with a magnetic field of 300 Oe applied in film plane.  $M$  is constant up to 400 K except at very low temperature. The temperature dependence of the magnetization near 400 K suggests that there is no  $\text{CrO}_2$  impurity phase ( $T_C \sim 398$  K) in the films and confirms the XRD and TEM results.

In earlier investigations, the analogous series of oxides  $\text{Ti}_{n-2}\text{Cr}_2\text{O}_{2n-1}$  ( $6 \leq n \leq 9$ ) with triclinic structure<sup>6-9</sup> were synthesized at high temperature. The corresponding Cr/Ti ratio of the oxides is in the range of  $2/7 \leq \text{Cr}/\text{Ti} \leq 1/2$ . They are not ferromagnetic at RT. According to our results,  $M$  decreases with increasing Cr content in the low Cr concentration region. This is consistent with earlier results on oxides with higher Cr content. It should be mentioned that, in the earlier investigations, the crystal structure of the high-

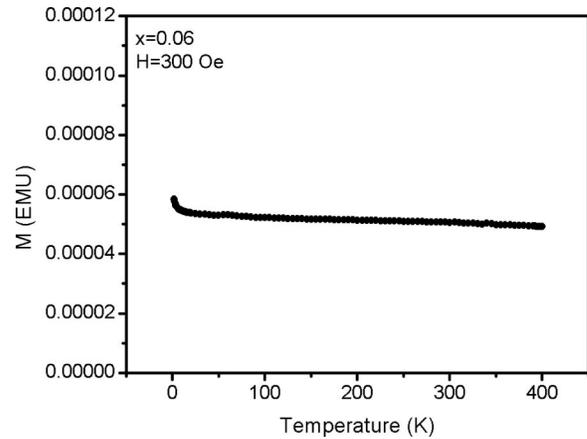


FIG. 3. Magnetization as a function of temperature for the  $\text{Cr}_{0.06}\text{Ti}_{0.94}\text{O}_{2-\delta}$  film measured from 2 to 400 K in a field of 300 Oe. The Curie temperature is above 400 K.

temperature-synthesized oxides was not triclinic for  $n < 6$  or  $n > 9$  ( $\text{Cr}/\text{Ti} < 2/7$  or  $\text{Cr}/\text{Ti} > 1/2$ ).<sup>6-9</sup> On the other hand, the structure is triclinic for our films prepared by PLD even though  $\text{Cr}/\text{Ti} < 2/7$ .

Figure 4 compares the transport properties of the undoped reduced-rutile  $\text{TiO}_2$  and  $\text{Cr}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$  ( $x=0.06, 0.08, 0.12, 0.14$ ) films. The films show increasing resistivity with decreasing temperature. All films exhibit nearly metallic conductance at RT and semiconducting behavior at lower temperatures. The resistivity at 300 K for  $x=0.06$  is  $0.0025 \Omega \text{cm}$ , which is lower than that of the undoped film ( $0.004 \Omega \text{cm}$ ). The resistivity increases with increasing Cr concentration. In addition, Cr doping also changes the shape of  $R-T$  curves.

The mechanism of the RT ferromagnetism in our films is not understood. Park *et al.*, who have investigated the electronic structure of Co/Mn/Fe/Ni-doped anatase  $\text{TiO}_2$  with the local-spin-density approximation, suggest the ferromagnetism in the metallic phase is accounted for by the double-exchange-like mechanism.<sup>10</sup> The carriers are expected to be  $n$ -type. Such a mechanism cannot explain the experimental results presented here because the carriers of our films are

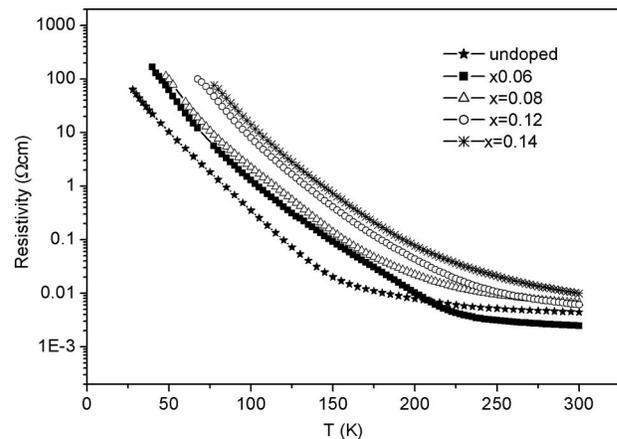


FIG. 4. Temperature dependence of the resistivity for the  $\text{Cr}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$  ( $x=0.06, 0.08, 0.12, 0.14$ ) films.

*p*-type. The origin of the magnetism should be related to the Zener-type, hole-mediated Ruderman–Kittel–Kasuya–Yosida interaction, which is responsible for the known magnetic semiconductor such as (Ga,Mn)As.<sup>11</sup> It turns out that, according to Dietl's model, holes are favored over electrons in order to achieve a ferromagnetic state at RT. The holes in our samples may play an important role in the coupling between the magnetic moments.

The highest magnetic moment of  $2.9 \mu_B$  per Cr atom found in our samples is larger than expected. Although it is possible that the entire contribution to the moment is from the Cr ions, it does not exclude the possibility that Ti moments are involved. When one pays attention to the unique structure of the reduced rutile, which produces  $Ti^{3+}$  ions with a *3d* moment, both Cr and Ti may contribute to the magnetization. This may lead to exchange couplings other than, or in addition to, the hole-mediated, Zener-type mechanism. The possible involvement of Ti *3d* electrons makes this system even more interesting and its understanding, possibly, more challenging.

So far, we have observed RT ferromagnetism in Fe-, Mn-, and Cr-doped reduced-rutile films. *P*-type carriers have been found in all films suggesting the importance of the holes in the observed ferromagnetism. When grown under similar conditions, Co-doped  $TiO_2$  films contain nanoparticles of Co metal, and the films themselves are not ferromagnetic. The large magnetic moments for the Cr-doped films provide an opportunity for further exploring this interesting material.

#### IV. CONCLUSIONS

The Cr-doped reduced-rutile  $TiO_2$  films are magnetic semiconductors up to 400 K. The saturation magnetization of  $Cr_xTi_{1-x}O_{2-\delta}$  films decreases with increasing Cr doping and the saturation magnetic moment of the 6% Cr-doped reduced films is  $2.9 \mu_B$  per Cr atom at RT. The large magnetic moments may originate from a number of sources. One such possibility is the involvement of the *3d* electrons of the  $Ti^{3+}$  ions. Another possibility is the formation of acceptor bound magnetic polarons, in which the spins of the holes and chromium are aligned via exchange interaction. The resistivity of the  $Cr_xTi_{1-x}O_{2-\delta}$  films increases with increasing Cr concentration and with decreasing temperature.

#### ACKNOWLEDGMENTS

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