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# Ferromagnetism and transport properties of Fe-doped reduced-rutile $\text{TiO}_{2-\delta}$ thin films

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We have investigated  $\text{Fe}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$  ( $x=0.02, 0.06, \text{ and } 0.08$ ) thin films grown on  $\alpha\text{-Al}_2\text{O}_3$  substrates by pulsed-laser deposition. X-ray diffraction results indicate that the films are single phase and of reduced-rutile type. Detailed microstructural observations reveal no measurable magnetic impurities in the films. Vibrating sample magnetometer measurements show the films are ferromagnetic at room temperature with coercivity ranging from 340 to 770 Oe. The temperature dependence of the resistivity shows nearly metallic behavior at room temperature but semiconducting behavior at lower temperatures. The extraordinary Hall effect with coercivities similar to those in magnetic hysteresis curves was observed at room temperature. The carriers are  $p$  type with a carrier density of about  $10^{22}/\text{cm}^3$ . © 2003 American Institute of Physics.

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## I. INTRODUCTION

It has been reported that the ferromagnetic state exists in Co-doped anatase  $\text{TiO}_2$  semiconductors at room temperature.<sup>1-3</sup> X-ray absorption spectroscopy study of Co-doped anatase films suggests that Co is in the 2+ oxidation state rather than forms metal clusters.<sup>2</sup> Room temperature ferromagnetism has also been indicated when rutile, another common structure of  $\text{TiO}_2$ , is doped with Co.<sup>4,5</sup>  $\text{TiO}_2$  has three common forms: anatase, rutile, and brookite. Stoichiometric rutile has a band gap of 3.05 eV. It crystallizes in a tetragonal lattice and is easily reduced by forming oxygen vacancies or titanium interstitials. Large concentrations of vacancies or interstitials condense into platelets that are removed from the structure by forming Magnéli shear planes.<sup>6</sup> The shear planes are (101) planes when referring to the stoichiometric rutile tetragonal lattice, and the reduced rutile forms a homologous series of compounds  $\text{Ti}_n\text{O}_{2n-1}$  ( $n=4, \dots, 10$ ) with a triclinic structure. Electrical properties of Fe-doped  $\text{TiO}_2$  have been studied before,<sup>7,8</sup> and no ferromagnetism was reported. In this study, we report ferromagnetism and associated transport properties of  $\text{Fe}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$  ( $x=0.02, 0.06, \text{ and } 0.08$ ) thin films of substantially reduced-rutile structures.

## II. EXPERIMENT

$\text{Fe}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$  ( $x=0.02, 0.06, \text{ and } 0.08$ ) thin films were grown on  $\alpha\text{-Al}_2\text{O}_3(012)$  substrates by pulsed-laser deposition.  $\text{Fe}_x\text{Ti}_{1-x}\text{O}_2$  targets were prepared using standard ceramic synthesis techniques. The films were prepared in vacuum at a substrate temperature of 980 K. The pressure during deposition was  $2 \times 10^{-6}$  Torr. The pulsed excimer la-

ser uses KrF ( $\lambda=248$  nm) and produces a laser beam intensity of  $1\text{--}2$  J/cm<sup>2</sup> and repetition rate of 4–20 Hz. The deposition rate is between 0.3 and 0.6 Å/s, and the film thickness varies from 120 to 300 nm. The crystalline structure was investigated by x-ray diffraction (XRD) with Cu  $K\alpha$  radiation and by transmission electron microscopy. The transport properties were measured with a physical property measurement system (PPMS) from Quantum Design. The Hall effect of the films was measured with a four-probe method at room temperature.

## III. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of  $\text{Fe}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$  with  $x=0.02$  and 0.06. The films are single phase and of reduced-rutile type with a (202) plane, referred to as a stoichiometric rutile tetragonal cell, parallel to the plane of the film. The

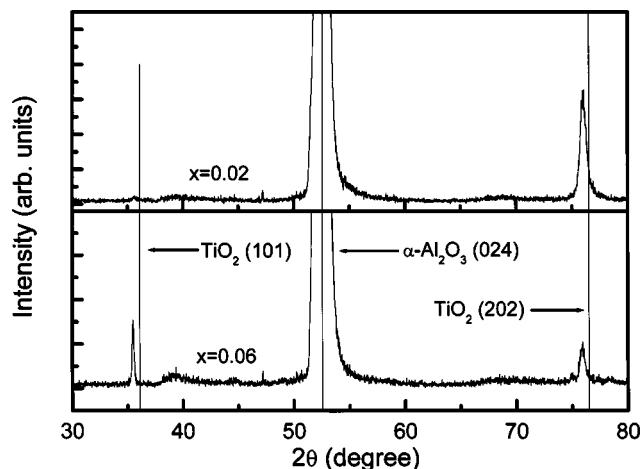


FIG. 1. XRD patterns of  $\text{Fe}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$  with  $x=0.02$  and 0.06, showing reduced-rutile phase and no impurity peaks.

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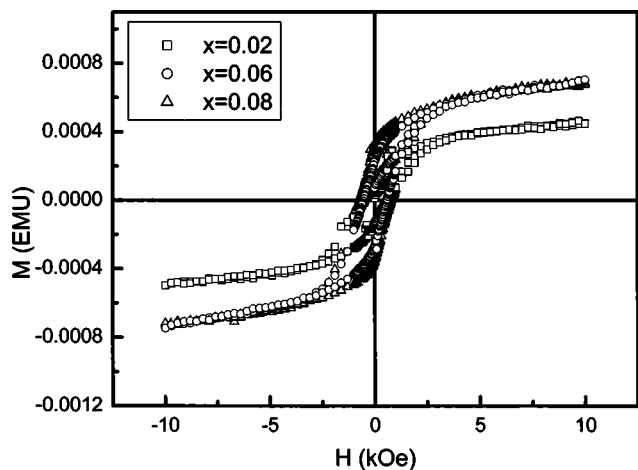


FIG. 2.  $M-H$  curves of films with  $x=0.02$ ,  $0.06$ , and  $0.08$  on  $\text{Al}_2\text{O}_3(012)$  substrates measured with a vibrating sample magnetometer at room temperature. The magnetic field was applied parallel to the film surface.

two vertical lines show (101) and (202) reflections of 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 relative to stoichiometric rutile. The (101) peak is absent in sample  $x=0.02$  (and  $x=0.08$ , not shown) due to the substantial reduction that forms the Magnéli shear plane. The degree to which sample  $x=0.06$  is reduced is different from that with  $x=0.02$  and  $0.08$ . However both (101) and (202) peaks are shifted toward lower angles, which is consistent with the formation of Magnéli reduced rutile<sup>9</sup> and may also be influenced by the Fe doping. Transmission electron microscopy (TEM) observation indicates no sign of segregation of impurity phase up to  $x=0.08$ .

The magnetization versus field ( $M-H$ ) curves measured at 300 K exhibit hysteresis with coercivity ranging from 340 to 770 Oe as shown in Fig. 2. The saturation magnetization of the films is estimated to be  $2.3-2.4 \mu_B$  per Fe atom. The  $M-H$  curves indicate that these films are ferromagnetic at 300 K. The remaining internal magnetization at zero external magnetic field, remanence, varies from 26% to 52%.

All films exhibit nearly metallic conductance at room temperature and semiconducting behavior at lower temperatures. Positive magnetoresistance (MR) is observed at low temperatures in high fields. Figure 3 shows the temperature dependence of the resistivity for  $\text{Fe}_{0.06}\text{Ti}_{0.94}\text{O}_{2-\delta}$  film, and the inset of Fig. 3 shows the MR for the same sample, which is about 5% at 2 K in a field of 5 T applied normal to the plane. The MR of the sample is negative and less than 0.1% at room temperature.

All samples show the extraordinary Hall effect, one of the characteristics of a ferromagnetic semiconductor. Figure 4 shows the Hall voltage hysteresis loop for sample  $\text{Fe}_{0.06}\text{Ti}_{0.94}\text{O}_{2-\delta}$ . The hysteretic behavior, demonstrated by the open loop in the inset of Fig. 4, is an unambiguous signature of the interaction between itinerant carriers and localized electron spins of the Fe ions. The Hall effect data obtained in high magnetic fields (ordinary Hall effect) suggest the carriers of magnetic semiconductors are  $p$  type. The carrier density calculated from the slope in the high field region

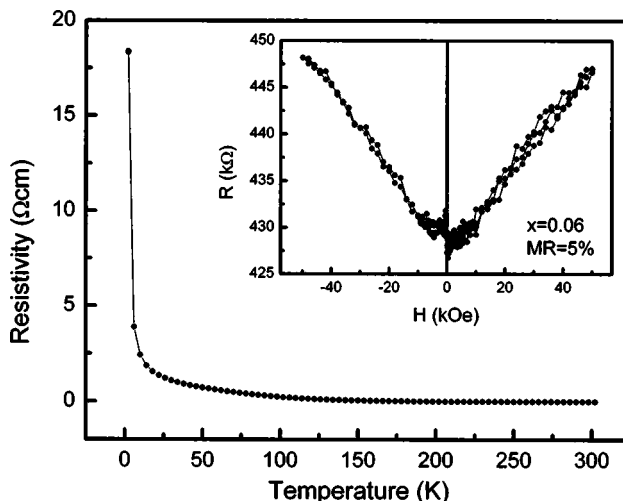


FIG. 3. Temperature dependence of the resistivity for film with  $x=0.06$ , showing semiconducting behavior. The inset shows the magnetoresistance (5%) at 2 K in a field of 5 T applied normal to the film surface.

of the Hall data is about  $10^{22}/\text{cm}^3$ . The  $p$ -type carriers found in our samples suggest that the mechanism responsible for the ferromagnetism may be related to hole-mediated Zener-type Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction.<sup>10</sup> According to such a model holes are favorable for mediating the exchange interaction between local moments and induce ferromagnetism. It should be noted here that the  $p$ -type conduction of our samples is fundamentally different from the  $n$  type observed in Co-doped anatase,<sup>1,2</sup> although more theoretical and experimental studies are needed to understand the phenomena observed.

#### IV. CONCLUSIONS

Room temperature ferromagnetic semiconductor  $\text{Fe}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$  ( $x=0.02, 0.06$ , and  $0.08$ ) thin films were successfully grown by pulsed-laser deposition. Magnetic and

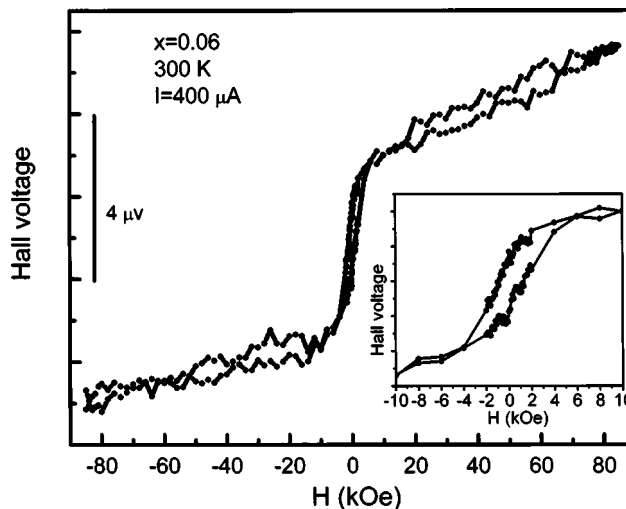


FIG. 4. Hall voltage vs applied magnetic field at 300 K for  $x=0.06$ . The extraordinary Hall effect dominates at low field and shows hysteretic behavior, as shown in the inset.

transport properties of the films were investigated. The saturation magnetization of the films was estimated to be 2.3–2.4  $\mu_B$  per Fe atom at room temperature. The resistivity shows semiconducting behavior for all of the samples at low temperature and becomes nearly metallic at room temperature. The room temperature ferromagnetic nature of the films was confirmed by the hysteretic behavior of the extraordinary Hall effect. The carriers of magnetic semiconductors are  $p$  type.

#### ACKNOWLEDGMENTS

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