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Room-temperature ferromagnetic properties in Mn-doped rutile $TiO_{2-\delta}$ thin films

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Abstract

Room-temperature ferromagnetic properties of Mn-doped reduced titanium dioxide ($Ti_{1-x}Mn_xO_{2-\delta}$) thin films with rutile structure synthesized by a sol–gel method have been detected for a limited range of Mn composition (x). The $Ti_{1-x}Mn_xO_{2-\delta}$ films were found to be p-type semiconducting with hole concentration near 10^{19} cm^{-3}. The observed ferromagnetism in the $Ti_{1-x}Mn_xO_{2-\delta}$ films is not related to the hole concentration but related to x. The room-temperature ferromagnetism is attributable to magnetic polaron formed by trapped electron in oxygen vacancy and magnetic ions around it. Thus, the existence of oxygen vacancies is necessary for the room-temperature ferromagnetism.

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Keywords: Ferromagnetism; Titanium dioxide; Oxygen vacancy; Doping

1. Introduction

Ferromagnetic semiconductors have been under considerable attention recently for realizing spintronics by manipulating charge and spin degrees of freedom in single material. Numerous experimental and theoretical investigations have been performed on magnetic properties and the related structural and electronic properties of semiconducting metal oxides such as ZnO, TiO_2, and SnO_2 that have been reported to exhibit room-temperature ferromagnetism.

As one of those metal oxides, transition-metal-doped (V, Cr, Fe, Ni, etc.) TiO_2 alloys have been under numerous experimental and theoretical investigations [1–4] on their magnetic properties and the related structural and electronic properties since the discovery of room-temperature ferromagnetism in Co-doped anatase TiO_2 thin films [5]. Despite the intensive research on TiO_2-based magnetic oxides, the interpretations for the observed ferromagnetic properties have often been controversial, e.g., on whether the exhibited ferromagnetism is intrinsic or not [6,7]. The spintronic applications require that ferromagnetism in semiconductors needs to be intrinsic, that is, not from magnetic clusters of the doped transition-metal impurities. Also, a number of recent studies showed that the observed ferromagnetism tends to depend on methods and conditions used in the sample preparation. Thus, no consensus on the proper origin for the room-temperature ferromagnetism in such metal-oxide semiconductors has been reached yet.

In the present work, rutile $TiO_{2-\delta}$ thin films (of oxygen deficiency δ) doped by Mn have been synthesized by a sol–gel method and their physical properties investigated by X-ray diffraction (XRD), Hall effect, vibrating sample magnetometry (VSM), X-ray photoelectron spectroscopy (XPS), and superconducting quantum interference device (SQUID) measurements. The present reduced rutile

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$Ti_{1-x}Mn_xO_{2-\delta}$ films exhibit ferromagnetism at room temperature for a limited range of Mn doping. Effects of the structural and electronic properties on the magnetic properties of the $Ti_{1-x}Mn_xO_{2-\delta}$ films are discussed and possible physical origin for the observed room-temperature ferromagnetism is proposed.

2. Experimental

The present $Ti_{1-x}Mn_xO_{2-\delta}$ thin films were deposited on $Al_2O_3(0\,0\,0\,1)$ substrates by a sol–gel method employing spin-coating process. The precursor solution was prepared by dissolving titanium butoxide, $Ti[O(CH_2)_3CH_3]_4$, into solvent at 70 °C. The solvent consists of a mixture of 2-methoxyethanol and monoethanolamine. Mn doping was achieved by dissolving $(C_2H_3O_2)_2Mn \cdot 4H_2O$ together with titanium butoxide in the solvent. The amount of doping (x), measured by energy-dispersive X-ray spectroscopy, is denoted as the fraction (at%) of number of impurity atoms to the sum of those of Ti and impurity atoms in the film.

The precursor solution was stirred at 70 °C for 2 h to increase its homogeneity. The substrates were spin-coated by the precursor solution with 3000 rpm for 20 s to make precursor films that were then pre-heated in the air at 300 °C for 5 min after each deposition in order to remove the organic substance. This process was repeated until desired film thickness was attained. After the spin-coating process, the precursor films were annealed at 600 °C for 4 h in an evacuated chamber with a pressure of about 10^{-3} Torr. Such oxygen-deficient annealing has been proven to be efficient for creating oxygen vacancies [8], resulting in an increase of the electrical conductivity.

The crystalline quality of the deposited films was investigated by using XRD in $\theta-2\theta$ geometry with Cu Kα radiation. The transport properties were investigated by using Hall effect measurements performed in the van der Pauw configuration under a magnetic field of 0.5 T. Magnetization measurements on the films were done with VSM and SQUID.

3. Results and discussion

The XRD data for the present rutile $Ti_{1-x}Mn_xO_{2-\delta}$ films are shown in Fig. 1. The thicknesses of the films were around 1 μm, as estimated by using scanning electron microscopy. For $x > 0.1$ $MnTiO_3$ phase was detected in the film. The Mn-doped samples show poor crystalline quality compared to that of pure $TiO_{2-\delta}$. It is also seen that the XRD peak positions of the Mn-doped samples hardly shift from those of the pure $TiO_{2-\delta}$. The ionic radii of octahedral Mn^{2+}, Mn^{3+}, and Mn^{4+} ions are known to be 0.970, 0.785, and 0.670 Å, respectively, while that of octahedral Ti^{4+} ion is 0.745 Å [9]. By comparing the ionic radii of these Mn and Ti ions, Mn^{3+} and Mn^{4+} are likely to be main impurity ions in the films.

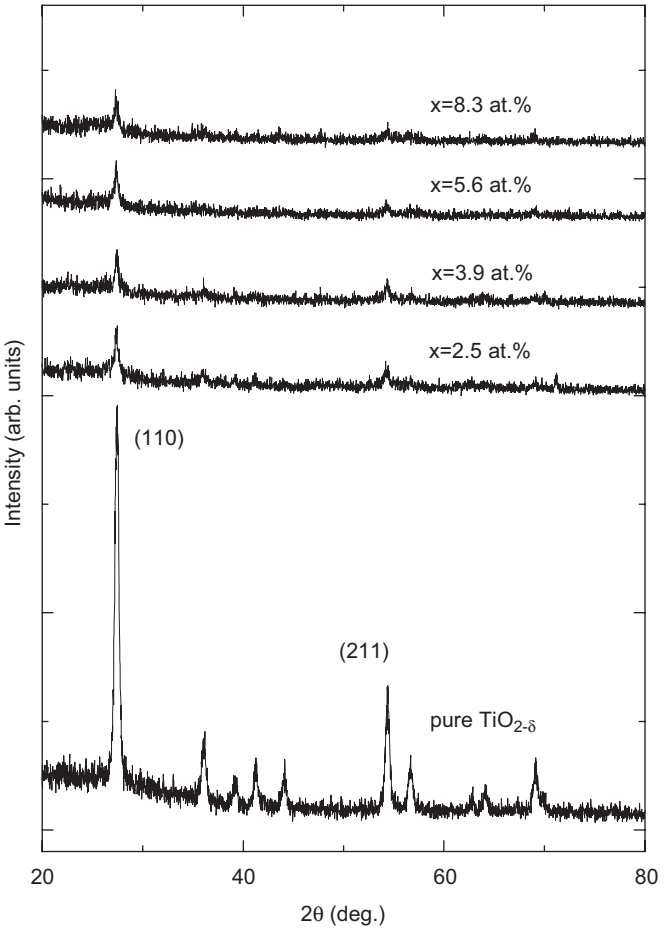

Fig. 1. XRD data for rutile $Ti_{1-x}Mn_xO_{2-\delta}$ films.

The present $Ti_{1-x}Mn_xO_{2-\delta}$ samples were found to have p-type electrical conductivity by Hall effect measurements with the carrier concentration of 7×10^{18}, 1×10^{19}, 9×10^{18}, and 7×10^{18} cm^{-3}, respectively, for the $x = 2.5$, 3.9, 5.6, and 8.3 at% samples. The change of the hole concentration is not proportional to that of the Mn content, indicative of increasing defects with increasing Mn doping. The p-type character for the $Ti_{1-x}Mn_xO_{2-\delta}$ samples is mainly attributable to the substitution of the octahedral Ti^{4+} sites by Mn^{3+} ions. The undoped rutile $TiO_{2-\delta}$ samples were found to have n-type conductivity with the carrier concentration of 3×10^{18} cm^{-3}, attributable to oxygen vacancies [8].

Fig. 2 exhibits the magnetization vs. applied field curves of the films obtained by VSM measurements at room temperature. It is seen that the $x = 3.9$ at% sample exhibits hysteresis loop with nonzero coercivity (H_C) and saturation magnetic moment (M_S), indicative of a ferromagnetism. The values of M_S and H_C of the $x = 3.9$ at% sample reach to 0.7 μ_B/Mn ion and 0.75 kOe, respectively. For the $x = 5.6$ at% sample, H_C and M_S are significantly reduced compared to those of the $x = 3.9$ at% sample.

In Fig. 3, Mn 2p core-level spectra measured by XPS from the $x = 3.9$ at% sample are exhibited. It is seen that

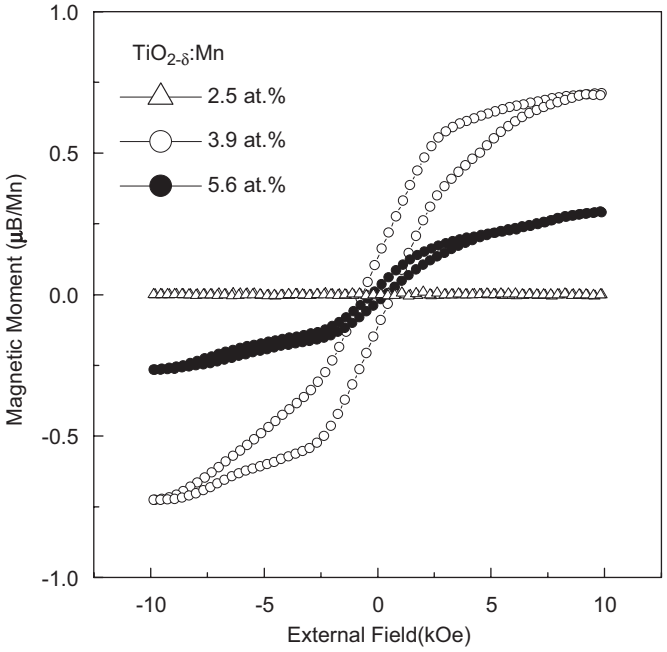

Fig. 2. Results of magnetic hysteresis measurements on rutile $Ti_{1-x}Mn_xO_{2-\delta}$ films at room temperature.

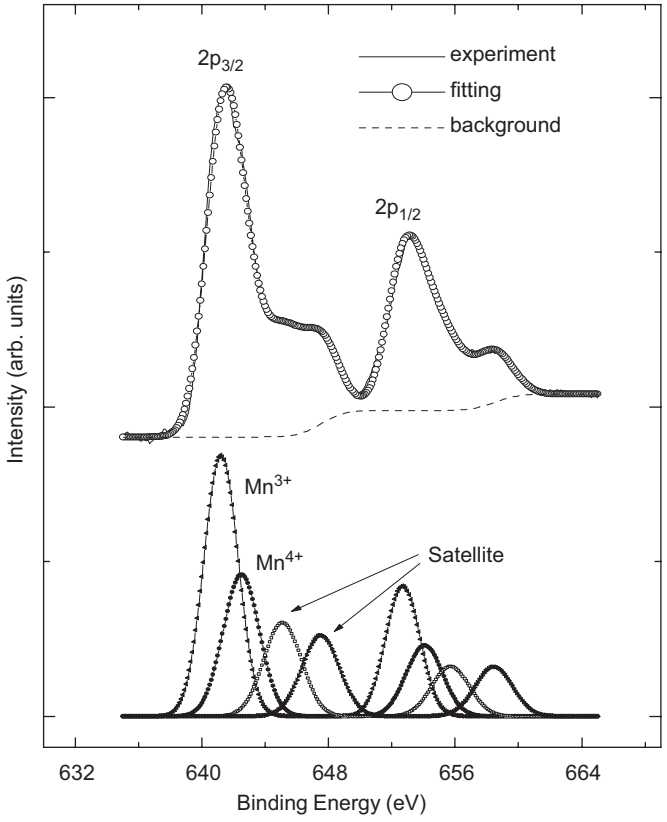

Fig. 3. XPS spectra of Mn 2p core levels of $Ti_{1-x}Mn_xO_{2-\delta}$ ($x = 3.9$ at%) film and the result of Doniach–Sunjic line-shape fitting on the spectra.

the $2p^{3/2}$ and $2p^{1/2}$ peaks are clearly resolved from their satellites at higher binding energies. Each peak could be well fitted by two lines, representing the contribution from the Mn^{3+} and Mn^{4+} ions, by the Doniach–Sunjic Lorentzian line shape convoluted with the Gaussian factor [10]. Due to a stronger Coulomb attraction, the 2p core electrons in the Mn^{4+} ion have larger binding energies than those in the Mn^{3+} ion. The present fitting result indicates that the 2p core electrons in the Mn^{4+} ion have binding energies larger by about 1.2 eV than those in the Mn^{3+} ion. Thus, the XPS investigation gives an evidence for the coexistence of Mn^{3+} and Mn^{4+} ions in the present $Ti_{1-x}Mn_xO_{2-\delta}$ films, consistent with the result of XRD analysis. Also, it is seen that the intensity of the Mn^{3+} line is stronger than that of the Mn^{4+} line by 2:1, indicating that the Mn^{3+} ions are more populated than the Mn^{4+} ions by a factor of 2.

The magnetic properties of the $Ti_{1-x}Mn_xO_{2-\delta}$ samples are seen to change significantly with the Mn density rather than the hole density. According to Dietl et al., mobile holes are essential for stabilizing the RKKY-induced ferromagnetic state in semiconductors at room temperature [11]. However, the observed ferromagnetism shown in Fig. 2 seems to be hardly related to the hole concentration of the samples although it is considered as being intrinsic. The hole concentrations of the $x = 2.5$, 3.9, 5.6, and 8.3 at% samples are close to each other but only the $x =$ 3.9 and 5.6 at% samples exhibit a ferromagnetic behavior at room temperature.

Thus, the room-temperature ferromagnetism observed from the $Ti_{1-x}Mn_xO_{2-\delta}$ films is not likely to involve itinerant carriers but to involve localized carriers. A possible mechanism for the ferromagnetism involving localized carriers is magnetic polaron formed by electron trapped in oxygen vacancy and surrounding magnetic impurity ions [12,13]. The $M-T$ curve shown in Fig. 4 for the $x = 3.9$ at% film measured by SQUID method exhibits

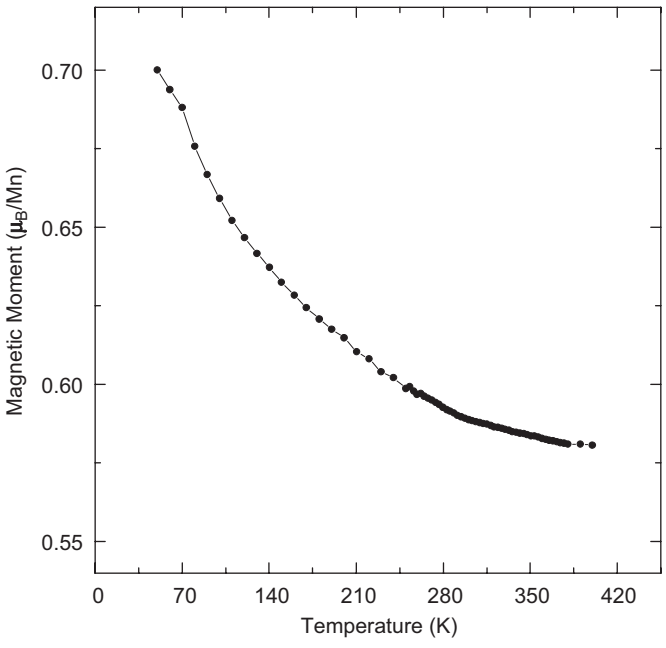

Fig. 4. Magnetization vs. temperature curve of $Ti_{1-x}Mn_xO_{2-\delta}$ ($x =$ 3.9 at%) film measured by SQUID.

the temperature variation of magnetization similar to the one obtained by a theoretical estimation based on a percolation of bound magnetic polarons [12]. Thus, the existence of oxygen vacancies is believed to be a necessary condition for the room-temperature ferromagnetism in the present Mn-doped rutile $TiO_{2-\delta}$ films. The present sol–gel-grown films annealed in the air, thus containing little oxygen vacancies compared to the vacuum-annealed samples, exhibited no ferromagnetic behavior. The decrease of the net magnetization with the increase of the Mn content is attributable to an increase of antiferromagnetic superexchange coupling strength between two neighboring Mn^{3+} ions via a nearby O^{2-} ion [14].

4. Conclusions

Room-temperature ferromagnetic behavior was observed from semiconducting rutile $Ti_{1-x}Mn_xO_{2-\delta}$ thin films for a limited range of Mn doping. The rutile films exhibited p-type semiconducting properties but the observed ferromagnetism is not likely to directly involve the mobile holes. The ferromagnetism in rutile $Ti_{1-x}Mn_xO_{2-\delta}$ is attributable to magnetic polaron formed by trapped electron in oxygen vacancy and magnetic ions around it. Existence of oxygen vacancies is believed to be crucial for achieving the room-temperature ferromagnetism in the $Ti_{1-x}Mn_xO_{2-\delta}$ films.

Acknowledgments

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