Magnetic and Electronic Properties of Reduced Rutile $Ti_{1-x}Mn_xO_{2-\delta}$ Thin Films

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Magnetic and electronic properties of reduced rutile titanium dioxide ($TiO_{2-\delta}$) thin films doped by Mn have been investigated. The present sol-gel-grown semiconducting $TiO_{2-\delta}$:Mn films exhibit a ferromagnetic behavior at room temperature for a limited range of Mn content. The Mn-doped films have p-type electrical conductivity with the carrier concentration near 10^{19} cm^{-3}. The observed room-temperature ferromagnetism is believed to be intrinsic but not related to free carriers such as holes. Oxygen vacancies are likely to contribute to the room-temperature ferromagnetism—trapped carriers in oxygen vacancies can mediate a ferromagnetic coupling between neighboring Mn^{3+} ions. The energy band-gap change due to the Mn doping measured by spectroscopic ellipsometry exhibits a red-shift compared to that of the undoped sample at low Mn content. It is explainable in terms of strong spin-exchange interactions between Mn ion and the carrier.

Key words : ferromagnetism, titanium dioxide, oxygen vacancy, Mn-doping

1. Introduction

Oxide semiconductors have been paid a great deal of attention since the discovery of room-temperature ferromagnetism in Co-doped TiO_2 thin films with anatase structure [1]. Such ferromagnetic semiconductors with Curie temperature higher than room temperature are desirable for realizing spintronics. It is necessary to have materials that show both ferromagnetism and semiconducting properties for exploiting spins as information carriers. So far, numerous experimental and theoretical investigations have been performed on magnetic properties and the related structural and electronic properties of transition-metal-doped TiO_2 and the films doped by V, Cr, Fe, and Ni have also been found to exhibit room-temperature ferromagnetism [2-5].

However, despite the intensive research on such 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, several 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 oxide semiconductors has yet been reached.

In this work, rutile $TiO_{2-\delta}$ thin films (of oxygen deficiency δ) doped by Mn have been grown by a sol-gel method and their physical properties investigated by X-ray diffraction (XRD), vibrating sample magnetometry (VSM), Hall effect, and spectroscopic ellipsometry (SE) measurements. The present reduced rutile $TiO_{2-\delta}$ films exhibit ferromagnetism at room temperature for some range of Mn doping. Change of the magnetic properties of the oxides related to their electronic properties is examined. Possible physical mechanism for the observed ferromagnetic properties of the $TiO_{2-\delta}$:Mn films is discussed.

2. Experimental

Rutile TiO_2 thin films were deposited on $Al_2O_3(0001)$ 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

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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 hr to increase its homogeneity. The substrates were spin-coated by the precursor solution with 3000 rpm for 20 sec 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. Prior to the film deposition the substrates were cleaned by acetone followed by methanol in ultrasonic bath. After the spin-coating process, the precursor films were annealed at 600°C for 4 hr 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 XRD in θ-2θ geometry using Cu $K\alpha$ radiation. The transport properties were investigated by Hall effect measurements, performed in the van der Pauw configuration under a magnetic field of 0.5 T. Magnetization measurements on the films were made with Lake-Shore 7300 vibrating sample magnetometer at room temperature.

3. Results and Discussion

Figure 1 exhibits the evolution of the XRD pattern for the present rutile $TiO_{2-\delta}$:Mn films. The thickness of the films was around 1 μm, estimated by scanning electron microscopy. These films are transparent in the visible-ultraviolet range due to their large band-gap energy of ~3.2 eV [9]. It is seen that the XRD peak positions of the
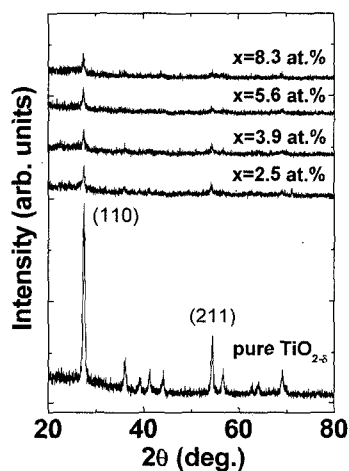
Mn-doped samples hardly shift from those of the pure $TiO_{2-\delta}$. The ionic radii of octahedral Mn^{2+}, Mn^{3+}, and Mn^{4+} ions are known to be 0.970, 0.785, and 0.670 Å, respectively, while that of octahedral Ti^{4+} ion 0.745 Å [10]. The comparison of the ionic radius between Mn and Ti ions suggests that Mn^{3+} with ionic radius close to that of Ti^{4+} is a dominant impurity ionic state in the Mn-doped films. $MnTiO_3$ phase was detected in the Mn-doped films for x > 0.1.

Hall measurements revealed that the samples have p-type conductivity 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. It is seen that the change of the hole concentration is not consistent with that of the Mn content. The undoped rutile $TiO_{2-\delta}$ samples have n-type conductivity with the carrier concentration of 3×10^{18} cm^{-3}. The oxygen vacancies contribute to the electrical conductivity as n-type carriers. The p-type character is mainly attributable to the substitution of the octahedral Ti^{4+} sites by Mn^{3+} ions.

The magnetization vs. applied field curves obtained by VSM measurements on the rutile $TiO_{2-\delta}$:Mn films at room temperature are exhibited in Fig. 2. It is seen that the x = 3.9 and 5.6 at.% films exhibit hysteresis loop with non-zero cbercivity, indicating that these samples are ferromagnetic at room temperature. On the other hand, the x = 2.5 and 8.3 at.% samples exhibit paramagnetic behavior. The observed ferromagnetism is mainly attributable to high-spin Mn^{3+} ions substituting the Ti^{4+} sites. The saturation magnetic moment (M_S) of the x = 3.9 at.% sample reaches to 0.7 μ_B/Mn.

It is seen that the magnetic properties of the $TiO_{2-\delta}$:Mn samples change significantly with Mn content while the hole concentration does not. According to Dietl et al., holes are essential for stabilizing the RKKY-induced ferromagnetic state at room temperature [11]. However,
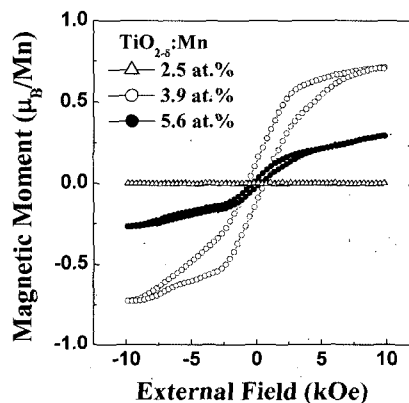

Fig. 1. XRD patterns of rutile $TiO_{2-\delta}$:Mn films.

Fig. 2. Results of magnetic hysteresis measurements on rutile $TiO_{2-\delta}$:Mn films at room temperature.

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 ferromagnetism at room temperature. ⸱

Thus, the room-temperature ferromagnetism observed from the $TiO_{2-\delta}$:Mn films is not likely to be related to free carriers but related to some other interactions among the impurity spins and the carriers. One possible interaction mechanism is F-center-mediated exchange, as recently proposed by Coey et al. [12]. It is a direct ferromagnetic coupling between two neighboring Mn^{3+} ions via an electron trapped in oxygen vacancy nearby. The present sol-gel-grown films annealed in the air, thus containing little oxygen vacancies compared to the vacuum-annealed samples and electrically insulating, exhibited no ferromagnetic behavior. 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 decrease of the net magnetization with the increase of the Mn content is attributable to an increase of antiferromagnetic superexchange interaction between two neighboring Mn^{3+} ions via a nearby O^{2-} ion [13].

In order to investigate the electronic structure of rutile $TiO_{2-\delta}$:Mn SE measurements were performed on the samples at room temperature. Figure 3 exhibits the absorption coefficient α ($=4\pi k/\lambda$) of the $TiO_{2-\delta}$:Mn films obtained from the SE data, where k represents the imaginary part of complex refractive index and λ the wavelength of light. The band-gap energies of the films were determined to be 3.25, 3.10, 3.20, and 3.25 eV for the $x = 0$, 3.9, 5.6, and 8.3 at.% samples, respectively, at which α becomes 1.0×10^6 m^{-1}. Such band-gap variation indicates that the Mn ions substitute the Ti sites randomly to construct
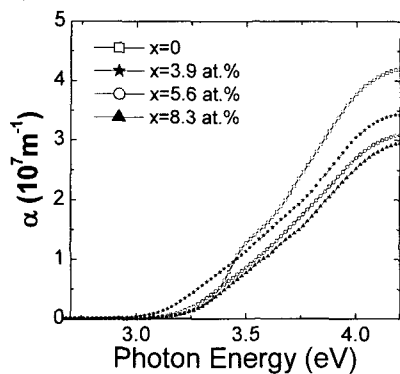
disordered alloy with a different band structure rather than forming clusters. Also, an initial decrease of the band-gap energy is observed at low Mn content. Such red-shift of the band-gap energy has been attributed to spin-exchange interactions between the sp electrons near the Fermi level and the localized spins from the impurity ions [14]. The s-d and p-d exchange interactions tend to give rise to a downward and upward correction to the conduction- and the valence-band edges, respectively. The red-shift was also observed for Mn-doped ZnO, a wide band-gap semiconductor (E_g = 3.25 eV) [15]. The strong spin-exchange interactions between the Mn ions and the carriers are likely to induce strong coupling between neighboring Mn^{3+} ions, possibly leading to room-temperature ferromagnetism.

4. Conclusions

Ferromagnetic behavior was observed from semiconducting rutile $TiO_{2-\delta}$:Mn thin films at room temperature for a limited range of Mn doping. The observed net magnetic moment is mainly attributable to Mn^{3+} ions substituting the octahedral Ti^{4+} sites. The rutile films exhibited p-type semiconducting properties but the observed ferromagnetism is not likely to directly involve the free holes. Oxygen vacancies are believed to be crucial for achieving the room-temperature ferromagnetism. Red-shift of the band-gap energy was observed at low Mn doping, explainable in terms of spin-exchange interactions between Mn ions and the carriers.

Acknowledgments

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