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Electronic and Magnetic Properties of $Ti_{1-x}M_xO_{2-\delta}$ (M=Co and Fe) Thin Films Grown by Sol-gel Method

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Electronic and magnetic properties of $Ti_{1-x}M_xO_{2-\delta}$ (M=Co and Fe) thin films grown by sol-gel method have been investigated. Anatase and rutile $Ti_{1-x}Co_xO_{2-\delta}$ films were successfully grown on Al_2O_3 (0001) substrates and exhibited p-type electrical conductivity while the undoped films n-type conductivity. Room temperature vibrating sample magnetometry measurements on the anatase and rutile $Ti_{1-x}Co_xO_{2-\delta}$ films with same x (=4.8 at.%) showed quite similar magnetic hysteresis curves with the saturation magnetic moment of ~4 μ_B per Co ion despite their differences in structural and electronic properties. Such giant magnetic moment is attributable to the unquenched orbital moment of the Co^{2+} ions substituting the octahedral Ti^{4+} sites. Similar ferromagnetic behavior was observed for $Ti_{1-x}Fe_xO_{2-\delta}$ films that are highly resistive compared to the Co doped samples. Saturation magnetic moment was found to decrease for higher x, i.e., ~2 and ~1.5 μ_B per Fe ion for x=2.4 and 5.8 at.%, respectively. Conversion electron Mössbauer spectroscopy measurements predicted the coexistence of Fe^{2+} and Fe^{3+} ions at the octahedral sites of $Ti_{1-x}Fe_xO_{2-\delta}$.

Key words : ferromagnetism, TiO_2, magnetic moment, orbital moment quenching

1. Introduction

Semiconducting oxides have been under considerable attention recently due to room temperature ferromagnetic properties achieved by doping 3d transition metal elements. These ferromagnetic oxides have been found to exhibit higher Curie temperatures (T_C) compared to those obtained from existing non-oxide semiconductors such as GaAs.

Since the first discovery of ferromagnetism at room temperature in Co doped anatase TiO_2 [1], numerous experimental and theoretical investigations have been performed on structural, electronic, and magnetic properties of it along with other transition metal doped TiO_2. Recently, Fe and V doped TiO_2 has also been found to exhibit similar magnetic properties as in Co doped TiO_2 [2, 3].

Despite the remarkable attention on such magnetic oxides, the results reported by different research groups have frequently been controversial on the origin of the exhibited ferromagnetic properties. Such transition metal doped semiconductors become true diluted magnetic semiconductor (DMS) if the observed magnetization is induced from the interaction of the magnetic dopant with itinerant carriers.

In the present work, structural, electronic, and magnetic properties of $TiO_{2-\delta}$ thin films doped by Co and Fe have been investigated by X-ray diffraction (XRD), vibrating sample magnetometry (VSM), conversion electron Mössbauer spectroscopy (CEMS), and Hall effect measurements. Large magnetic moments were observed from the present Co and Fe doped rutile and anatase $TiO_{2-\delta}$ films. The origin of their ferromagnetic properties is discussed.

2. Experimental

Anatase and 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

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by dissolving titanium butoxide, $Ti[O(CH_2)_3CH_3]_4$, into the solvent at 70 °C. When 2-methoxyethanol was used as the solvent, the resultant TiO_2 films exhibited anatase structure. On the other hand, when the solvent consists of a mixture of 2-methoxyethanol and monoethanolamine, rutile films were produced. Fe or Co doping was achieved by dissolving $Fe(NO_3)_3 \cdot 9H_2O$ or $Co(C_2H_3O_2)_2 \cdot 4H_2O$ together with titanium butoxide in the solvent. The amount of Fe or Co doping is denoted as the fraction (at.%) of number of impurity atoms to the sum of those of Ti and impurity atoms in the prepared precursor solution.

The concentration of titanium butoxide in the precursor solution was about 0.375 mol/l. The precursor solution was stirred at 70 °C for 2 hr to increase its homogeneity. The substrates were then spin-coated by the precursor solution with 3,000 rpm for 20 sec to make precursor films which were then pre-heated in the air at 300 °C for 5 min. This process was repeated for increasing the film thickness. Before film deposition the substrates were cleaned by acetone followed by methanol in ultrasonic bath. After the spin-coating, the precursor films were annealed at 600 °C for 4 hr in an evacuated chamber with the pressure of about 10^{-3} Torr. Such vacuum annealing has been known as being effective for creating oxygen vacancies for some oxide materials.

The crystalline quality of the deposited films was investigated by XRD in θ-2θ geometry using Cu K_α radiation. The transport properties were investigated by Hall effect measurements, performed in the van der Pauw configuration under a magnetic field of 0.51 T. Magnetic property measurements on the films were performed by VSM and CEMS with a ^{57}Co source in a rhodium matrix at room temperature.

3. Results and Discussion

The thickness of the prepared oxygen deficient $TiO_{2-\delta}$ films was estimated to be in the 600~700 nm range by scanning electron microscopy. In Fig. 1, the XRD patterns of Co doped $TiO_{2-\delta}$ ($Ti_{1-x}Co_xO_{2-\delta}$) films with anatase (a) and rutile (b) structures are compared to that of undoped film prepared under the present deposition conditions. The doped films show reduced crystalline quality but negligible XRD peak shift compared to the undoped films. Also, the doped anatase and rutile films are seen to be single phase without any Co related crystallites due to segregations. Hall measurements indicated that the undoped films exhibit n-type electrical conductivity with carrier concentration (resistivity) of 1.3×10^{19} cm^{-3} (0.44 Ω·cm) and 3.4×10^{18} cm^{-3} (1.6 Ω·cm) for anatase and rutile films, respectively. On the other hand, the air-annealed films

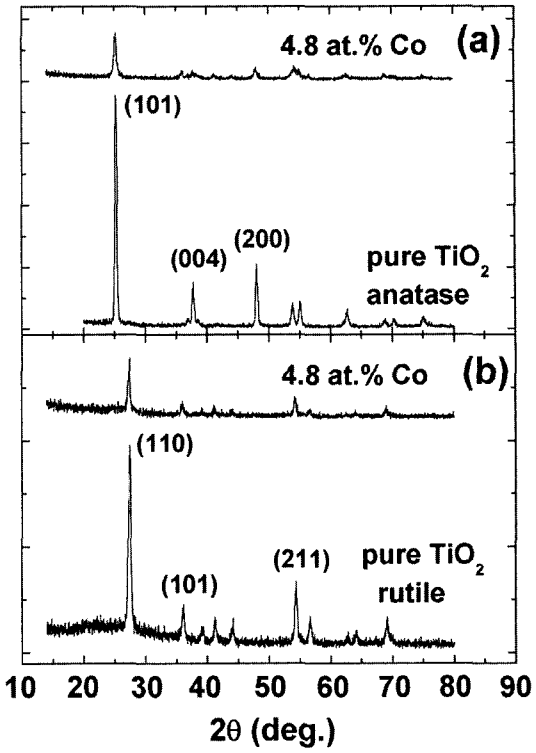

Fig. 1. XRD patterns of anatase (a) and rutile (b) $Ti_{1-x}Co_xO_{2-\delta}$ (x=4.8 at.%) films compared to undoped samples.

were found to be insulating. The vacuum-annealing on the TiO_2 samples is likely to generate intrinsic oxygen vacancies. Such off-stoichiometry is known to form shallow donor levels that are expected to contribute n-type carriers [4]. Thus, the decrease of resistivity by vacuum annealing is attributed to the increase of oxygen vacancies in the sample.

By Co doping of 4.8 at.% both the anatase and rutile films exhibited the change of conductivity to p-type. The Co doped anatase and rutile films exhibited the p-type carrier concentration (resistivity) of 4.4×10^{19} cm^{-3} (0.44 Ω·cm) and 1.6×10^{18} cm^{-3} (1.7 Ω·cm), respectively. That is, both anatase and rutile films are semiconducting as well as optically transparent. The doped Co ions substituting octahedral Ti^{4+} sites are known to have the ionic valence of +2 mostly [5]. Thus, the substituting Co ions are expected to create holes, inducing the n-p conductivity transition.

Figure 2 exhibits the result of the VSM measurements on the anatase and rutile $Ti_{1-x}Co_xO_{2-\delta}$ films at room temperature. Despite the differences in structural and electronic properties, both films show quite similar magnetic hysteresis behavior with the saturation magnetic moment per Co ion (~4 μ_B) being larger than any other values so far reported for Co doped TiO_2 samples. It is even larger than the value

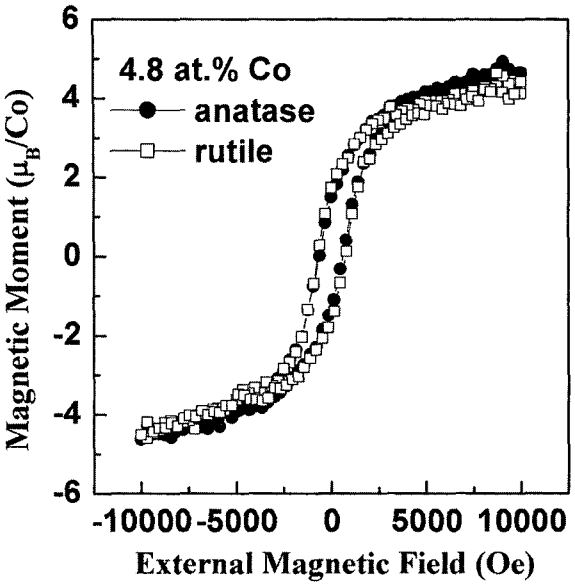

Fig. 2. VSM measurement result of anatase and rutile $Ti_{1-x}Co_xO_{2-\delta}$ (x=15 at.%) films.

of ~1.67 μ_B/Co reported for metallic cobalt or ~2.1 μ_B/Co for nano-sized Co clusters. Thus, the present $Ti_{1-x}Co_xO_{2-\delta}$ films with such giant magnetic moment are not expected to contain Co clusters. Such large magnetic moment is probably due to unquenched orbital moment of Co ion, possible when the surrounding ions have gained a moment via electronic effects [6].

Similar ferromagnetic behavior was also observed for Fe doped anatase $Ti_{1-x}Fe_xO_{2-\delta}$ films as shown in Fig. 3. Two samples, containing 2.4 and 5.8 at.% Fe, were

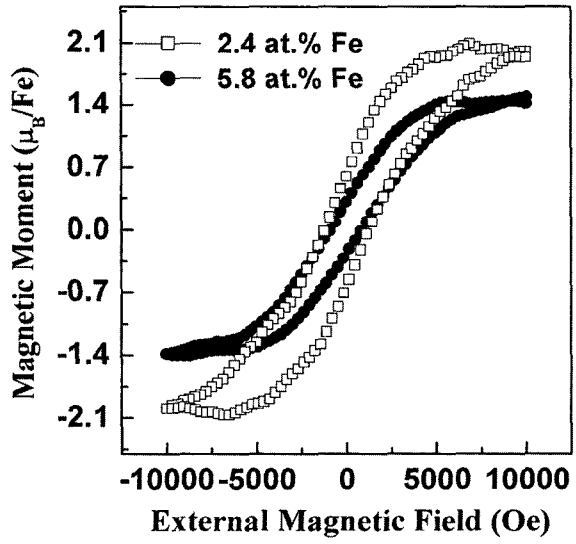

Fig. 3. VSM measurement result of anatase $Ti_{1-x}Fe_xO_{2-\delta}$ (x= 2.4 and 5.8 at.%) films.

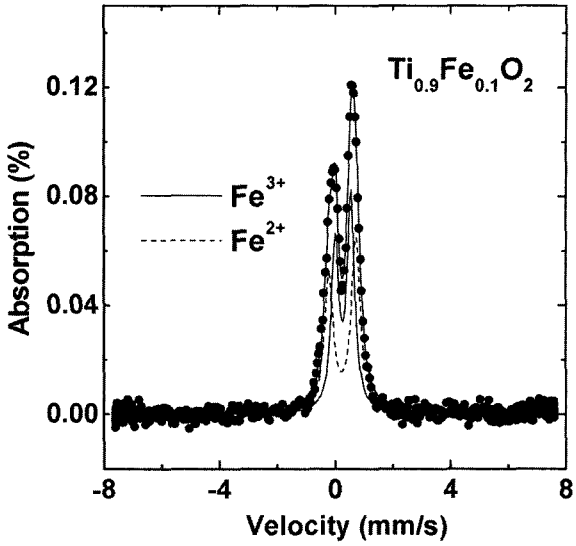

Fig. 4. CEMS spectra of rutile $Ti_{1-x}Fe_xO_{2-\delta}$ (x=10 at.%) films at room temperature.

examined by VSM at room temperature. As in the Co doped samples, the XRD peak shift of the Fe doped samples is found to be negligible. Hall measurements revealed that both samples are more resistive than the Co doped samples (the 2.4 at.% Fe sample is p-type with 8.3×10^{16} cm^{-3} and 21 Ω·cm and the 5.8 at.% Fe sample is insulating). It is seen that the saturation magnetic moment is ~2 μ_B/Fe and ~1.5 μ_B/Fe for 2.4 and 5.8 at.% Fe, respectively. Both samples exhibit large magnetic moments despite their high electrical resistivity. A magnetic moment of ~1.5 μ_B/Fe was reported for an 8 at.% Fe doped TiO_2 film recently [7]. The decrease of the magnetic moment for increasing Fe concentration in the present Fe doped $TiO_{2-\delta}$ samples can also be explained by the unquenched orbital contribution. That is, the decrease of the magnetic moment is attributable to the enhancement of the orbital quenching due to the increase of the dopant-dopant interactions [3]. The large magnetic moment in the Fe doped oxides also indicates the dominance of the Fe^{3+} ions in the samples [8]. As shown in Fig. 4, the CEMS spectrum of a $Ti_{1-x}Fe_xO_{2-\delta}$ film consists of two components, due to Fe^{3+} with high-spin state, with isomer shifts of 0.28 and 0.27 mm/s relative to iron metal. Two paramagnetic doublets have quadrupole splitting of 0.57 and 0.99 mm/s. The smearing-out of the CEMS spectrum due to small amount of ^{57}Fe in the film may prevent the detection of ferromagnetic phase.

4. Conclusion

Co and Fe doped anatase and rutile $TiO_{2-\delta}$ samples

prepared by the present sol-gel method exhibit p-type semiconducting or insulating properties. Anatase and rutile films with the same Co content but different electrical resistivity exhibit ferromagnetic hysteresis behavior close to each other. The saturation magnetization obtained from the samples is ~4 μ_B/Co, largest value reported so far. Large magnetic moment was also observed for Fe doped anatase $TiO_{2-\delta}$ samples with ~2 μ_B/Fe and ~1.5 μ_B/Fe for 2.4 and 5.8 at.% Fe, respectively. Such large magnetic moments can be explained in terms of the unquenched orbital moment of Fe and Co ions in TiO_2.

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