Rutile $Ti_{1-x}Co_xO_{2-\delta}$-based p-type Diluted Magnetic Semiconductor Thin Films

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An attempting to produce a p-type diluted magnetic semiconductor (DMS) using $Ti_{1-x}Co_xO_{2-\delta}$ thin films was made by suitable control of the deposition parameters including deposition temperature, deposition pressure, and doping level using a pulsed laser deposition method. The $Ti_{0.97}Co_{0.03}O_{2-\delta}$ (TCO) films deposited at 500 °C at a pressure of 5 x 10^{-6} Torr showed an anomalous Hall effect with p-type characteristics. On the other hand, films deposited at 700 °C at 5 x 10^{-6} Torr showed n-type behaviors by a decreased solubility of cobalt. The charge carrier concentration in the p-type TCO films was approximately 7.9 x 10^{22}/cm^3 at 300 K and the anomalous Hall effect in the p-type TCO films was controlled by a side-jump scattering mechanism. The magnetoresistance (MR), measured at 5 K in p-type TCO films showed a positive behavior in an applied magnetic field and the MR ratio was approximately 3.5 %. The successful preparation of p-type DMS using the TCO films has the potential for use in magnetic tunneling junction devices.

Keywords : Rutile $Ti_{1-x}Co_xO_{2-\delta}$, p-type DMS, Anomalous hall effect, Magnetoresistance

1. INTRODUCTION

Because of recent developments in the physics of spin-dependent phenomena, spintronics has become a subject of considerable interest. For use in spintronic materials, dilute magnetic semiconductors (DMS) are under consideration as spin injectors for spintronic devices[1]. Numerous investigators have studied DMS, in which transition metal atoms are introduced into a lattice, thus inserting local magnetic moments into the lattice.

Co-doped anatase TiO_2 thin films were recently reported to show ferromagnetic properties, even at temperatures above 400 K[2-5] and the magnetic ordering was explained in terms of carrier-induced ferromagnetism, as observed for a III-V based DMS. An anomalous Hall effect (AHE) in reduced Co-doped rutile $TiO_{2-\delta}$ films[6,7], and the co-occurrence of superparamagnetism in highly reduced Co-doped rutile $TiO_{2-\delta}$ films[7] have also been reported. These ferromagnetic properties and Hall effects are only observed at n-type Co-doped TiO_2 films. The efficiency of spin-injection is higher in the p-type rather than the n-type DMS because exchange coupling between ferromagnetic ions and holes is more effective than coupling with electrons. The p- or n-type semiconducting characteristics in TiO_2 ceramic materials could be controlled by deposition temperature, oxygen partial pressure, and the doping level[8]. The solubility limit of Co in rutile TiO_2 is approximately 5 mol % and saturation magnetization (M_S) in 5 mol % Co-doped TiO_2 films is approximately 1.0 μ_B/Co at room temperature[5]. In this study, M_S in 3 mol % Co-doped TiO_2 films shows 1.0 μ_B/Co atom and M_S in films doped above 3 mol % Co increases above 1.0 μ_B/Co atom. Therefore, Co-doping concentration in rutile TiO_2 films was fixed as 3 mol %.

In this letter, an attempt to produce a p-type DMS using $Ti_{1-x}Co_xO_{2-\delta}$ thin films was made by suitable control of the deposition parameters including deposition temperature, deposition pressure, and doping level using a pulsed laser deposition method. We have studied the magnetic and electrical properties and have observed the p-type ferromagnetic characteristics in the $Ti_{0.97}Co_{0.03}O_{2-\delta}$ (TCO) films.

2. EXPERIMENTAL

The rutile TCO thin films were deposited on R-Al_2O_3 (1102) substrates by pulsed laser deposition (PLD) using a KrF excimer laser (λ = 248 nm) at various temperatures in an operating pressure of 5 x 10^{-6} Torr. The laser repetition rate was 2 Hz and the pulse energy density was 1.5 J/cm^2. The deposition rate was 0.2 Å/shot and the film thickness was approximately 200 nm. X-ray diffraction (XRD, Rigaku D/MAX-RC) experiments using Cu K_α radiation and a Ni filter were carried out to determine the crystal structure and preferred orientation of the films. The surface morphologies were examined by atomic force microscopy (AFM, AUTOPROBE CP). The detailed composition of the film surface was analyzed by scanning Auger microscopy (SAM, VG scientific Microlab 350) using a mapping technique and the depth profiles of the films were measured by secondary ion mass spectroscopy (SIMS, Cameca ims-4f). The resistivity of thin films was measured with an electrometer (CMT-SR 1000) using a four-point probe method, and the Hall effect of the films was measured in a van der pauw configuration with physical property measurement system (PPMS, Quantum design). Magnetic measurements were performed in a dc superconducting quantum interference device (SQUID) magnetometer and a vibrating sample magnetometer (VSM). Spin transport properties in DMS can be identified through magnetoresistance (MR) characteristics. Using a physical property measurement system (PPMS), an external magnetic field was applied to the perpendicular to the film surface in the range between −9 T and 9 T.

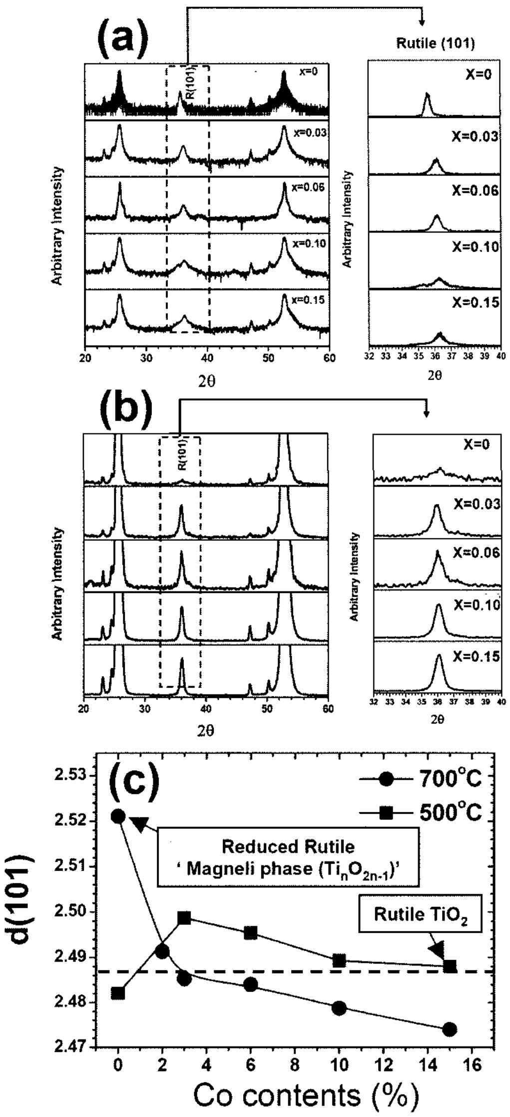

Fig. 1. XRD patterns of $Ti_{1-x}Co_xO_{2-\delta}$ thin films deposited at (a) 700 °C and (b) 500 °C with various cobalt concentrations and (c) the variation of d(101) in thin films with various cobalt concentrations.

3. RESULTS AND DISCUSSION

The TCO films were grown with an epitaxial relationship with a sapphire (1102) single crystal at various deposition temperatures. The films with a growth direction of (101) and (202) have a rutile structure and the patterns do not show a second phase such as Co metal. The variation of crystal structure as a function of Co concentration in $Ti_{1-x}Co_xO_{2-\delta}$ thin films grown at 700 and 500 °C was shown in Fig. 1(a) and (b), respectively. As shown in Fig. 1(a), (101) peak shape in the films deposited at 700 °C was broaden with increasing Co concentration and (101) peak in non-doped $TiO_{2-\delta}$ films shifts remarkably toward a low angle from a peak position of an normal rutile structure. This was due to the formation of Magneli phase (Ti_nO_{2n-1}, n<10)[9,10] deviated from the stoichiometric composition in case of films deposited in an ultra-high vacuum atmosphere. When the lattice was substituted by atoms larger than those of the matrix, the main peaks shift toward a low angle by a volume expansion of the lattice. However, the substitution of Co atoms (ionic radius : 0.72 Å) larger than Ti atoms (ionic radius : 0.68 Å) in Co-doped $TiO_{2-\delta}$ films shifts toward a high angle the (101) peak with increasing Co concentration. This result suggests that the substitution of Co in Ti site is not efficient in the films deposited at 700 °C.

On the other hand, as shown in Fig. 1(b), non-doped films deposited at 500 °C exhibit a broad shape of (101) peak indicating an unstable phase formation and the rutile peak intensity increases with increasing Co concentration followed by a shift toward a low angle of

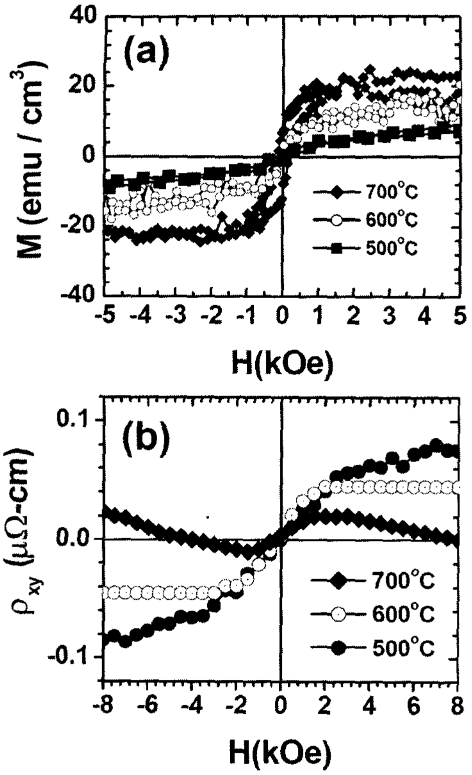

Fig. 2. The variation in (a) Magnetization and (b) Hall resistance (ρ_{xy}) as a function of an applied magnetic field in $Ti_{0.97}Co_{0.03}O_{2-\delta}$ thin films deposited at various temperatures.

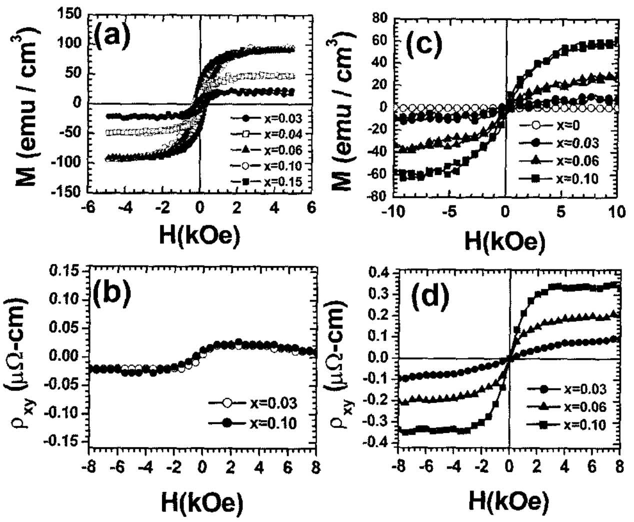

Fig. 3. The variation in (a,c) Magnetization and (b,d) Hall resistance (ρ_{xy}) as a function of an applied magnetic field in $Ti_{1-x}Co_xO_{2-\delta}$ thin films deposited with various Co concentrations at (a, b) 700 °C and (c, d) 500 °C.

(101) peak. The shift toward a low angle is the largest in the films doped with a cobalt of 3 %, resulting in the largest substitution of Co and the order of shift decreases with increasing Co concentration. The result for the variation of d (101), lattice constant, in Co-doped $TiO_{2-\delta}$ films deposited at 700 and 500 °C as a function of Co concentration was summarized in Fig. 1(c). The ferromagnetic and electrical properties of Co-doped $TiO_{2-\delta}$ films were characterized in the films with a cobalt concentration of 3 %.

Magnetization and Hall resistivity of $Ti_{0.97}Co_{0.03}O_{2-\delta}$ films grown at various deposition temperatures under a operating pressure of 5 x 10^{-6} Torr are shown in Fig. 2(a) and (b), respectively. As the deposition temperature increases, M_S (saturation magnetization) increases and ρ_{xy} (Hall resistivity) decreases. As shown in Fig. 2(b), films deposited at 700 °C exhibit a negative slope for ρ_{xy} in a high magnetic field, resulting in n-type behavior.

On the other hand, films deposited at 500 °C exhibit p-type behavior, indicating the highest Hall resistivity. The dependence of n- or p-type of a TiO_2-based DMS on deposition temperature at 5 x 10^{-6} Torr can be explained as follows. Non-doped TiO_2 films deposited at 500 °C and 5 x 10^{-6} torr exist at the boundary state of p- or n-type semiconducting characteristics through a Hall measurement, and the films exhibit n-type semiconducting properties with increasing deposition temperature above 500 °C. The valence of Co in the ferromagnetic $Ti_{0.97}Co_{0.03}O_{2-\delta}$ films was the +2 formal oxidation state, corresponding to the CoO phase[11]. When cobalt substitutes for Ti site in TiO_2, cobalt plays a role of an acceptor. A high deposition temperature such as 700 °C induces the precipitation of Co in the films and decreases the role of Co as an acceptor, resulting in the n-type behavior. On the other hand, a low deposition temperature of 500 °C increases the solubility of Co in the films followed by an increase of the role of Co as an acceptor in a Ti site, resulting in the p-type.

Figure 3 shows M-H loops and Hall resistance (ρ_{xy}) of $Ti_{1-x}Co_xO_{2-\delta}$ thin films deposited at 700 and 500 °C as a function of Co concentration. As shown in Fig. 3(a) and 3(b), the films deposited at 700 °C showed an increase of M_s and a constant value of Hall resistance with increasing Co concentration. The films with a Co concentration of 3 % showed a M_s of 20 emu/cm^3 and ρ_{xy} of 0.02 μΩ-cm. A constant Hall resistance irrespective of an increase of Co concentration has a close relationship with a precipitation of Co metal in TCO films deposited at 700 °C.

On the other hand, as shown in Fig. 3(c) and 3(d), the films deposited at 500 °C showed an increase of M_s and Hall resistance with increasing Co concentration. The increase of an anomalous Hall effect with increasing Co concentration was attributed to the increase of Co con-

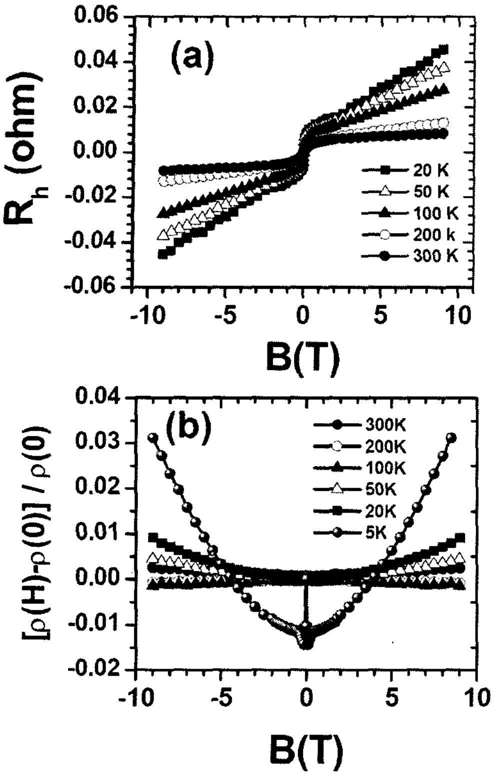

Fig. 4. (a) Temperature dependent Hall resistance as a function of magnetic field and (b) normalized magnetoresistance in $Ti_{0.97}Co_{0.03}O_{2-\delta}$ thin films measured at different temperatures.

centration substituted in $TiO_{2-\delta}$ films and an anomalous Hall effect was controlled by a side-jump scattering mechanism. These anomalous Hall effect observed with a variation of deposition temperature can also provide an evidence of an intrinsic ferromagnetism in TCO films.

Figure 4(a) shows the variation of Hall resistivity as a function of measurement temperature at a magnetic field of 9 Tesla. The slope for the variation of Hall resistance as a function of applied magnetic field at various temperatures has positive values, resulting in a p-type DMS. The carrier concentrations in TCO films measured at 300 K and 20 K are approximately 7.9 x 10^{22} and 7.4 x 10^{21} (p, /cm^3), respectively. An increase of Hall resistance with decreasing temperature suggests that an anomalous Hall effect is controlled by a side-jump scattering mechanism. Spin transport properties in DMS can be identified through magnetoresistance (MR) characteristics. Using a physical property measurement system (PPMS), an external magnetic field was applied to the perpendicular to the film surface in the range between −9 T and 9 T. The normalized magnetoresistance of the TCO films measured at various temperatures was shown in Fig. 4(b). The films show a positive magnetoresistance at 5 K and a decrease of positive values with increasing temperature. The ratio of magnetoresistance at 5 K is below 4 %. The magnetoresistance measured at the lowest temperature of 5 K is a valuable value in DMS because the lattice scattering with increasing temperature reduces the magnetoresistance of films. The positive behavior of the magnetoresistance measured at 5 K as a function of magnetic field is attributed to the s-d exchange coupling between the conduction electrons and localized Co spins.

3. CONCLUSION

An attempt to produce a p-type DMS using $Ti_{1-x}Co_xO_{2-\delta}$ thin films was made by suitable control of the deposition parameters including deposition temperature, deposition pressure, and doping level using a pulsed laser deposition method. The $Ti_{0.97}Co_{0.03}O_{2-\delta}$ films deposited at 500 °C at a pressure of 5 x 10^{-6} Torr showed an anomalous Hall effect with p-type DMS characteristics. On the other hand, films deposited at 700 °C at 5 x 10^{-6} Torr showed n-type behaviors by a decreased solubility of Co. The charge carrier concentration in the p-type TCO films was approximately 7.9 x 10^{22}/cm^3 at 300 K and the anomalous Hall effect in the p-type DMS was controlled by a side-jump scattering mechanism. The magnetoresistance (MR), measured at 5 K in p-type DMS showed a positive behavior in an applied magnetic field and the MR ratio was approximately 3.5 %.

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