Effects of Co-doping level on the microstructures and ferromagnetic properties of $Ti_{1-x}Co_xO_2$ thin films by liquid-delivery metal-organic chemical vapor deposition

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Spintronics is a rapidly expanding research area because of recent developments in the physics of spin-dependent phenomena. For use as spintronic materials, dilute magnetic semiconductors (DMS) are of considerable interest as spin injectors for spintronic devices.[1] Many researchers have studied DMS, in which transition metal atoms are introduced into the lattice, thus inserting local magnetic moments into the lattice. Recently, Co-doped TiO_2 anatase, grown by pulsed laser ablation, has been demonstrated to be ferromagnetic and semiconducting for doping levels up to around 8 at. %, and temperatures of up to 400 K.[5] Titanium dioxide is wide gap oxide semiconductor and in addition, anatase has high mobility of n-type charge carrier and large thermopower of -200 μV/K at 300 K. [6]

In this study, the $Ti_{1-x}Co_xO_2$ thin films onto SiO_2/Si substrates using liquid-delivery MOCVD were successfully prepared and characterized for ferromagnetic properties as a function of Co-doping concentration. Ferromagnetic behaviors of polycrystalline films were observed at room temperature and the magnetic and structural properties depend critically on the Co distribution, which varies widely with Co-doping concentration. Anatase $Ti_{1-x}Co_xO_2$ thin films were prepared by liquid delivery metalorganic chemical vapor deposition using $(C_{11}H_{19}O_2)_2(C_3H_7O)_2Ti$ (Inorgtech Chemicals, Inc.) and $Co(C_{11}H_{19}O_2)_3$ (Strem Chemicals, Inc.) as the source materials for Ti and Co, respectively. The organic precursors were dissolved in a solvent (THF : tetrahydrofran, C_4H_8O, Sigma-Aldrich Chemical Co., Inc.) to form a source solution of 0.05 mol concentration of $(C_{11}H_{19}O_2)_2(C_3H_7O)_2Ti$ and $Co(C_{11}H_{19}O_2)_3$. Solutions of each precursor were mixed together and single-mixture solutions with various concentrations were used for the preparation of $Ti_{1-x}Co_xO_2$ thin films. The thickness of the grown films was approximately 70 nm. After deposition, the thermal annealing was carried out at 700°C for 1 h in the vacuum chamber which was evacuated to 1.0×10^{-6} Torr.

The annealed $Ti_{1-x}Co_xO_2$ thin films having a composition below x = 0.05 showed uniform and smooth morphologies similar to those of as-deposited films. However, samples having above x = 0.05 showed a severe precipitation on the annealed $Ti_{1-x}Co_xO_2$ thin films. Matsumoto et al.[5] reported that a sizable amount of Co, at least up to x = 0.08, is soluble, i.e., homogeneously distributed in anatase. The size of clusters was approximately 150 nm and amount of precipitates increased with increasing Co content in $Ti_{1-x}Co_xO_2$ thin films. The composition of clusters analyzed by SAM was Co-rich $Co_{1-x}Ti_x$ phase, which it has a soft magnetic property. Microstructural results suggested that the solid solubility of Co was approximately 5 at. % in MOCVD-$Ti_{1-x}Co_xO_2$ polycrystalline thin films. The resistivities of thin films varied from about 0.8 to 2 ohm-cm at room temperature, being independent on the Co doping concentration up to x = 0.12. The resistivity values obtained in polycrystalline $Ti_{1-x}Co_xO_2$ thin films are comparable to those reported in epitaxial thin films.[5]

Figure 2 shows the relationship between magnetic properties and Co-doping level in polycrystalline $Ti_{1-x}Co_xO_2$ thin films. As shown in Fig. 2, hysteresis was observed, indicating that the Co-doped anatase TiO_2 thin films are ferromagnetic even at room temperature. As the Co content increases, the saturation magnetization Ms abruptly increases and the coercive field Hc markedly decreases. Magnetic properties of $Ti_{1-x}Co_xO_2$ thin films depend on the critical Co-doping level. The annealed thin films at $x \leq 0.05$ showed a homogeneous structure without any clusters and pure ferromagnetic properties of thin films are only attributed to the $Ti_{1-x}Co_xO_2$ (TCO) phases. On the other hand, above x=0.05, Co-rich $Co_{1-x}Ti_x$ clusters having a soft magnetic (SM) properties are formed in homogeneous $Ti_{1-x}Co_xO_2$ phases and then overall ferromagnetic (FM) properties depend on both FM_{TCO} and FM_{Co-Ti}. $Co_{1-x}Ti_x$ clusters having a soft magnetic property decrease the value of Hc (coercive field) and increase the saturation magnetic field. As shown in Fig. 2, thin films above x = 0.05 showed a saturation magnetic field of about 6,000 Oe compared with 2,500 Oe of those below x = 0.05. From above results, the homogeneous $Ti_{1-x}Co_xO_2$ thin films below x = 0.05 are considered to have a Curie transition temperature Tc higher than room temperature.

In summary, the annealed $Ti_{1-x}Co_xO_2$ thin films at $x \leq 0.05$ showed a homogeneous structure without any clusters and pure ferromagnetic properties of thin films are only attributed to the $Ti_{1-x}Co_xO_2$ (TCO) phases. On the other hand, in case of thin films above x=0.05, $Co_{1-x}Ti_x$ clusters are formed in homogeneous $Ti_{1-x}Co_xO_2$ phases and overall ferromagnetic (FM) properties depend on both FMTCO and SM_{Co-Ti}. $Co_{1-x}Ti_x$ clusters with about 150 nm size decreases the value of Hc (coercive field) and increases the saturation magnetic field. The polycrystalline anatase $Ti_{1-x}Co_xO_2$ thin films prepared by liquid-delivery MOCVD are advantageous for high density device application in ferromagnetic semiconductor fields.

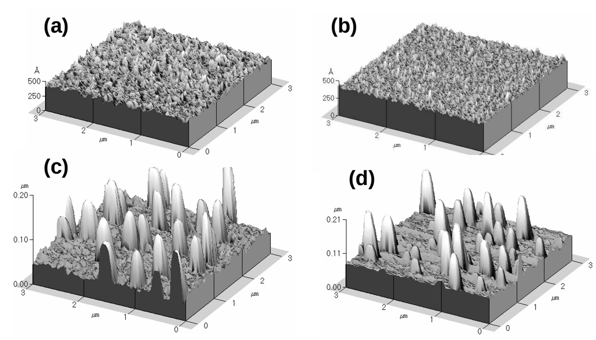

Figure 1. AFM images of $Ti_{1-x}Co_xO_2$(x=0) thin films annealed at 700°C for 60 min in $\sim 10^{-6}$ torr with Co contents of (a) x=0.03, (b) x=0.05, (c) x=0.07, (d) x=0.12

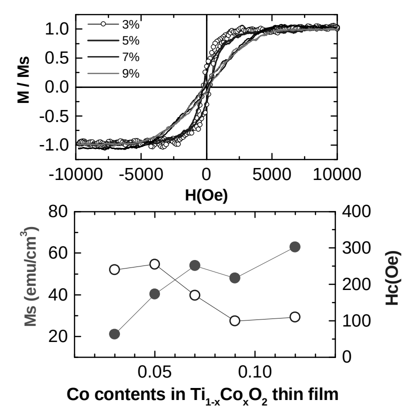

Figure 2. Magnetic properties of $Ti_{1-x}Co_xO_2$ thin films with various Co contents (at Room temperature.)

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