

# EFFECTS OF Co-DOPING LEVEL ON THE MICROSTRUCTURAL AND FERROMAGNETIC PROPERTIES OF LIQUID-DELIVERY METALORGANIC-CHEMICAL-VAPOR-DEPOSITED $Ti_{1-x}Co_xO_2$ THIN FILMS

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## 1. Introduction

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.<sup>[1]</sup> 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.<sup>[5]</sup> Titanium dioxide is wide gap oxide semiconductor and in addition, anatase has high mobility of n-type charge carrier and large thermopower of  $-200 \mu V/K$  at 300 K<sup>[6]</sup>. Co-doped anatase thin films as DMS materials were prepared by pulsed laser ablation<sup>5</sup>, oxygen-plasma-assisted molecularbeam epitaxy (OPA-MBE)<sup>[7]</sup>, and sol-gel process<sup>[8]</sup> for epitaxial or polycrystalline growth.

In this work, polycrystalline  $Ti_{1-x}Co_xO_2$  thin films on  $SiO_2$  (200 nm)/Si (100) substrates were prepared using liquid-delivery metalorganic chemical vapor deposition, and the microstructure and ferromagnetic properties were investigated as a function of doped Co concentration. Ferromagnetic behaviors of polycrystalline films were observed at room temperature, and the magnetic and structural properties strongly depended on the Co distribution, which varied widely with doped Co concentration.

## 2. Experimental

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  $700^\circ C$  for 1 h in the vacuum chamber which was evacuated to  $1.0 \times 10^{-6}$  Torr.

## 3. Results and discussion

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.<sup>[5]</sup> 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.<sup>[9]</sup> 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

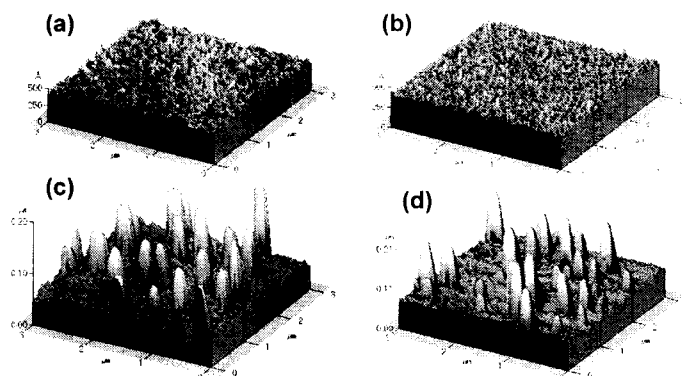


Figure 1. AFM images of  $Ti_{1-x}Co_xO_2(x=0)$  thin films annealed at  $700^\circ C$  for 60 min in  $\sim 10^{-6}$  torr with Co contents of (a)  $x=0.03$ , (b)  $x=0.05$ , (c)  $x=0.07$ , (d)  $x=0.12$

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.<sup>[5]</sup>

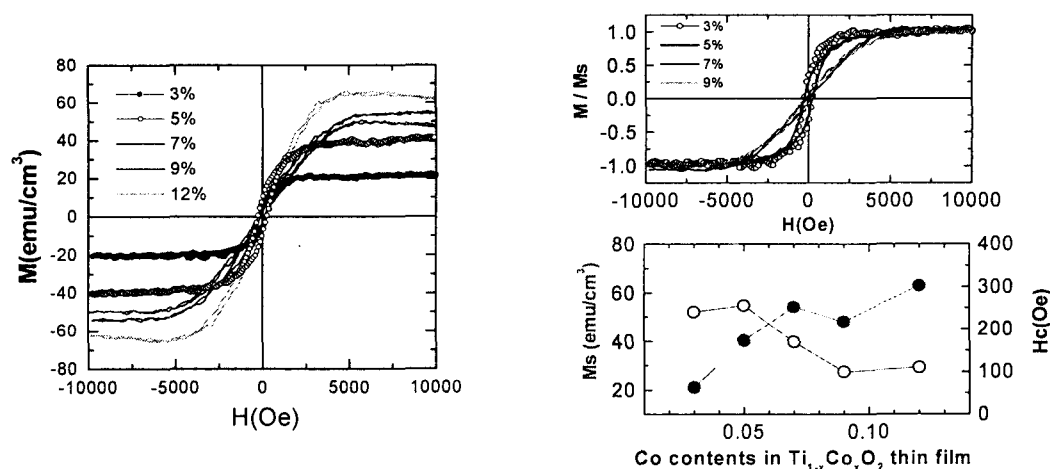


Figure 2. Magnetization hysteresis loops of  $Ti_{1-x}Co_xO_2$  thin films with various Co contents (at Room temperature.)

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  $M_s$  abruptly increases and the coercive field  $H_c$  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  $H_c$  (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  $T_c$  higher than room temperature.

#### 4. Conclusions

the polycrystalline  $Ti_{1-x}Co_xO_2$  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. 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  $FM_{TCO}$  and  $SM_{Co-Ti}$ .  $Co_{1-x}Ti_x$  clusters with about 150 nm size decreases the value of  $H_c$  (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

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