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Structure and properties of Co doped TiO_2 thin films on Si(100) by a pulsed laser deposition method

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We report on the crystal structure and magnetic properties of $Co_xTi_{1-x}O_2$ thin films ($0.03 \le x \le 0.07$), grown on Si(100) substrates by pulsed laser deposition (PLD) as a function of Co concentration, substrate temperature, oxygen flow rate and working pressure. The crystal structure exhibiting ferromagnetism at room temperature was found to originate from the anatase phase in the $Co_xTi_{1-x}O_2$ thin films, which grew well on Si substrates. The saturation magnetization (M_s) was observed to increase with increasing Co concentration in the range x = 3-7%. The $Co_xTi_{1-x}O_2$ film with x = 7% exhibits M_s = 5.31 emu/cm^3 and H_c = 92.5 Oe. The magnetic moment in the films is likely to depend upon the extent of crystallization of the anatase phase, which is related to the resistivity of the films.

Key words: $Co_xTi_{1-x}O_2$ thin film, anatase, ferromagnetism, resistivity, PLD.

Introduction

In recent years, the discovery of novel dilute magnetic semiconductors (DMS) or ferromagnetic semiconductors with Curie temperatures (T_c) exceeding room temperature has been of central importance scientifically and technologically in spintronics. The spin of charge carriers (electrons or holes) is expected to deliver prospects for fundamentally-novel functionality with respect to semiconductor device physics [1]. Comprehensive studies have focused on the (Ga,Mn)As [2], (In,Mn)As [3], and MnGe [4] systems, which exhibit very intriguing magnetic and transport properties for spintronics, but suffer from very low Curie temperatures (T_C) below 120 K for practical device applications. Wide bandgap semiconductors are of particular importance in this context, since Dietl et al. [5] predicted T_c exceeding room temperature for GaN and ZnO containing 5% of Mn and a high hole concentration (3.5×10^{20} cm^{-3}) on the basis of the mean-field Zener model of ferromagnetism. However, room temperature ferromagnetism based on GaN and ZnO still remains controversial.

One of the major methods to obtain ferromagnetic semiconductors is by doping semiconducting oxides with magnetic components. In particular, TiO_2 as an n-type semiconducting material has been widely investigated due to its high dielectric constant, excellent optical transmittance and photo-catalytic properties. Since Matsumoto et al. [6] reported room temperature ferromagnetism in anatase TiO_2:Co grown by laser molecular beam epitaxy, TiO_2-based ferromagnetic semiconductors have been of great interest. Regardless of whether epitaxial or polycrystalline, $Co_xTi_{1-x}O_2$ films grown by oxygen-plasma-assisted molecular-beam epitaxy were found to be ferromagnetic semiconductors at and above room temperature [7]. The Co-doped TiO_2 thin films grown by reactive co-sputtering were also observed to be ferromagnetic at room temperature [8]. On the other hand, a study by magnetic circular dichroism (MCD) claimed that ferromagnetism in TiO_2:Co is due to Co nano-clusters [9].

It is well known that the anatase polymorph of TiO_2 is not stable thermodynamically compared to rutile at room temperature. It is difficult to stabilize the anatase phase in the TiO_2 film without utilizing a template effect of a substrate [10], while the proper selection of a substrate material promotes anatase to grow in the film.

Epitaxial cobalt-doped anatase thin films on $LaAlO_3$ (001) and $SrTiO_3$ (001) and rutile (101)-oriented thin film on α-Al_2O_3 ($10\bar{1}2$) single crystals have been extensively investigated due to a small lattice mismatch [2-4]. However, to date, anatase deposition on a silicon substrate has not been studied, since it is complicated by a large lattice mismatch (–6.1%) between anatase and the silicon substrate. In the present study, we investigated the crystal structure and magnetic properties of $Co_xTi_{1-x}O_2$ thin films ($0.03 \le x \le 0.07$), grown on Si(100) substrates by pulsed laser deposition (PLD) as a function of Co concentration, substrate temperature, oxygen flow rate and working pressure. We will dis-

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cuss the correlation between the crystal structure and magnetic properties of $Co_xTi_{1-x}O_2$ thin films.

Experiments

$Co_xTi_{1-x}O_2$ ceramic targets (x = 0.03, 0.05, and 0.07) were prepared by a conventional solid-state reaction method. Anatase TiO_2 powders (> 99.9%) were mixed with Co (> 99.9%) and ground for 12 hour by wet ball milling using alcohol as a solvent and pressed into targets at a pressure of 98 MPa. A cold isostatic press (CIP) method was adopted to obtain very high-densified targets. The targets were made 5 mm thick and 25 mm in diameter after sintering at 1450 for 6 hr. $Co_xTi_{1-x}O_2$ films with x ($0.03 \le x \le 0.07$) have been grown on Si(100) and $LaAlO_3$(100) substrates by a pulsed laser deposition (PLD) technique. The base pressure was brought down to 0.13×10^{-9} MPa and the thin films were deposited at a working pressure of 0.13×10^{-5}~0.13×10^{-6} MPa in an ultra-high pure oxygen atmosphere. The $Co_xTi_{1-x}O_2$ targets were ablated with KrF excimer laser pulses (248 nm) that were synchronized with rotational motion. Typical laser power and repetition rate were 200 mJ and 10 Hz, respectively. The substrate temperature varied from room temperature to 700 °C and post-annealing was performed in-situ under an oxygen atmosphere at 800 °C for 30 minutes. The crystal structures of $Co_xTi_{1-x}O_2$ films were investigated by x-ray diffraction (XRD) and electron probe microanalysis (EPMA). The thickness and resistivity of the films were measured by α-step and 4-point probe methods, respectively. Hysteresis loops were measured with a high-sensitivity (10^{-7} C) alternating gradient magnetometer (AGM).

Results and Discussion

In the present study, the crystal structure and electric and magnetic properties of $CoxTi_{1-x}O_2$ films have been investigated as a function of Co content, substrate temperature, working pressure, and O_2 flowing rate. Figure 1 presents x-ray diffraction (XRD) patterns of $Co_xTi_{1-x}O_2$ films with (a) x=0.03, (b) x=0.05 and (c) x=0.07, grown on Si substrates, whose temperature was 500 °C. Single-phase anatase was observed in the $Co_xTi_{1-x}O_2$ film with x=0.07, whereas anatase phase mixed with traces of unknown and rutile phases were found to appear in the $Co_xTi_{1-x}O_2$ films with x=0.03 and x=0.05, respectively. The correlation between the crystal structure and magnetic properties in the Co-doped TiO_2 system still remain unclear. The crystal structure exhibiting ferromagnetism in the Co-doped TiO_2 has been reported to be anatase [6, 7, 9, 11] and rutile [8, 12]. The discrepancies can be attributed to different growth methods such as molecular beam epitaxy (MBE) [6, 7, 9], sputtering [8], PLD [11], solid-state reaction [12] or to different Co content in the

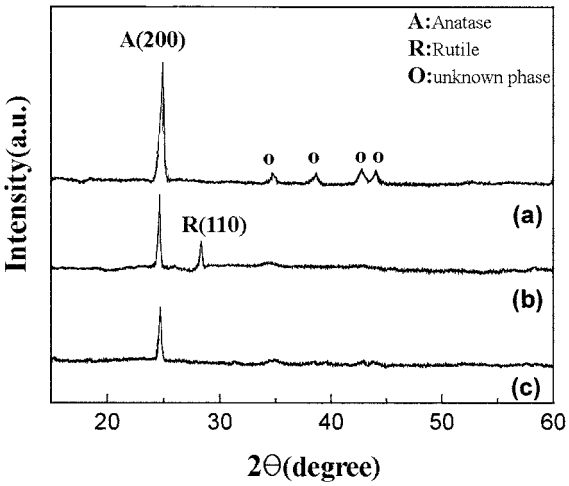

Fig. 1. X-ray diffraction patterns of $Co_xTi_{1-x}O_2$ films with (a) x=0.03, (b) x=0.05 and (c) x=0.07, grown on Si substratse, whose temperature was 500 °C.

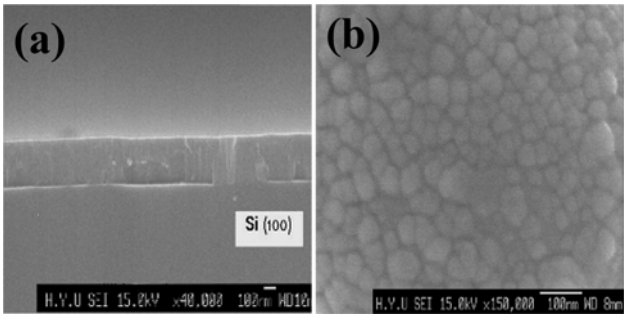

Fig. 2. SEM micrographs of (a) cross-section and (b) top view for the $Co_xTi_{1-x}O_2$ thin film with x=7 at % grown on a Si substrate at a working pressure 0.13×10^{-5} MPa using an oxygen flow rate of 50 sccm.

range 1-7% [6-9, 11, 12]. In this study, we found that the ferromagnetic behavior of Co-doped TiO_2 is due to anatase rather than rutile. We will discuss this later in detail.

We also found that the anatase phase in the films grew well when the total pressure and oxygen partial pressure was low in the deposition chamber (not shown). This is attributable to the enhanced atomic mobility and mean free path due to lower collision probability between oxygen gas and sputtered atoms from the target surface. Our XRD results, therefore, suggest that the anatase phase in the Co-doped TiO_2 thin films are grown by PLD in spite of a large lattice mismatch (–6.1%) between anatase and the silicon substrate. The $Co_{0.07}Ti_{0.93}O_2$ thin film on the Si substrate were found to be 150 nm and 300 nm thick as shown in Fig. 2(a). The grain size of the $Co_{0.07}Ti_{0.93}O_2$ thin film on the Si(100) substrate was observed to be in the range of 20-30 nm [see Fig. 2(b)]. A dense columnar microstructure was found to appear with a high oxygen content. The deposition rate was increased by lowering the operating pressure in the deposition chamber. The route mean square roughness of the thin films was in

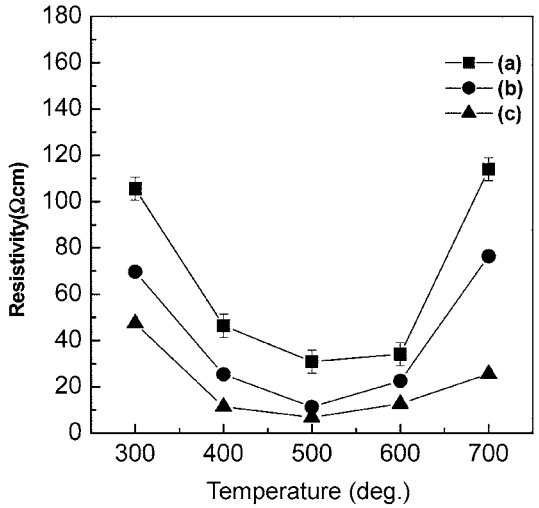

Fig. 3. Resistivity of the $Co_xTi_{1-x}O_2$ films as a function of Si substrate temperature at a working pressure 0.13×10^{-5} MPa using an oxygen flow rate of 50 sccm: (a) x=3 a/o, (b) x=5 a/o, and (c) x=7 a/o.

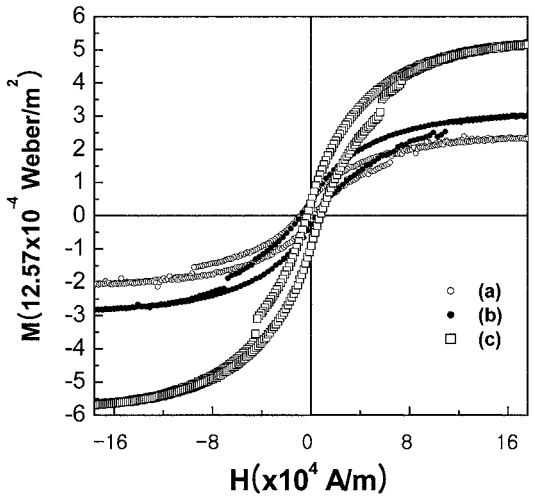

Fig. 5. Representative hysteresis loops for the $Co_xTi_{1-x}O_2$ thin films with Co concentration (x=3-7%) obtained with magnetic fields applied parallel to the plane of the films at room temperature by AGM: (a) x=3 a/o, (b) x=5 a/o, and (c) x=7 a/o.

the range of 10-20 nm.

Figure 3 shows the electrical resistivity of the $Co_xTi_{1-x}O_2$ thin films (x = 3, 5, 7 at %) as a function of Si(100) substrate temperature at a working pressure 0.13×10^{-5} MPa using an oxygen flow rate of 50 sccm. We found that resistivity in the $Co_xTi_{1-x}O_2$ thin films decreases as the Co content increases, regardless of the substrate temperature. This may be due to formation of oxygen vacancies in the anatase TiO_2 structure. Minimum resistivity for the $Co_xTi_{1-x}O_2$ thin films was found when the substrate temperature was 500 °C, at which the maximum magnetic moment was obtained. We found from the XRD results that the less-crystallized anatase phase causes the high resistivity below 500 °C. However, we also found from an atomic force microscopy (AFM) study that the surface roughness of the films increases as the substrate temperature is higher than 500 °C, indicating that the resistivity in the films depends upon the surface morphology. The higher the working pressure, the higher the resistivity of the films, as shown in Fig. 4. This can be also explained by the crystal phase development in the films according to XRD data.

The magnetic behavior for the $Co_xTi_{1-x}O_2$ thin films grown on Si (100) has been studied as a function of Co content at room temperature. In Fig. 5, are shown representative hysteresis loops for the $Co_xTi_{1-x}O_2$ thin films with Co concentrations (x=3-7%) obtained with magnetic fields applied parallel to the plane of the films at room temperature by AGM. Obviously, the hysteresis loops are indicative of ferromagnetic ordering at room temperature for all the samples with Co concentrations in the range 3-7%. The saturation mag-

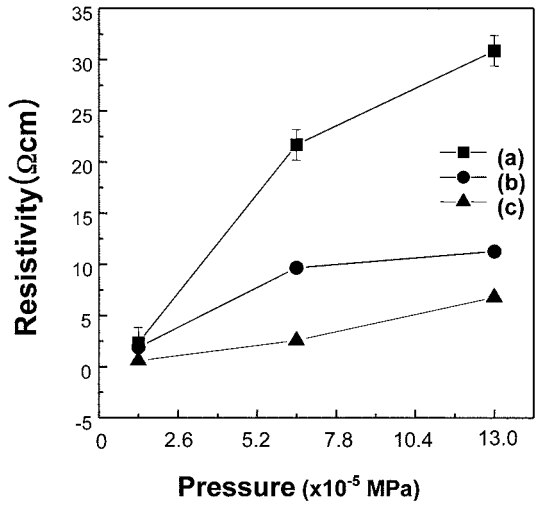

Fig. 4. Resistivity of the $Co_xTi_{1-x}O_2$ films (x=3, 5, 7 at %) as a function of working pressure.

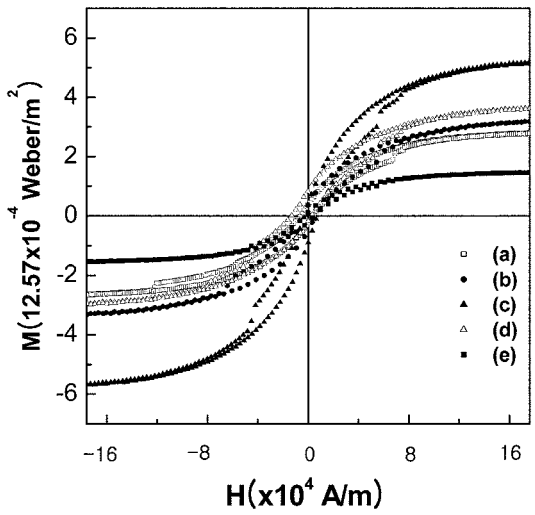

Fig. 6. Si substrate temperature-dependent hysteresis loops for the $Co_xTi_{1-x}O_2$ thin films with x=7%; (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, and (e) 700 °C

netization (M_s) increases with increasing Co concentration. In particular, the $Co_xTi_{1-x}O_2$ film with x=7% exhibits M_s=5.31 × 10^7 C/m^3 and H_c=7,365 A/m. Clearly, the $Co_xTi_{1-x}O_2$ films do not exhibit a superparamagnetic behavior, illustrating that the ferromagnetism in the $Co_xTi_{1-x}O_2$ films originates from Co nanoclusters as a secondary phase [9]. Figure 6 displays substrate temperature-dependent hysteresis loops for the $Co_xTi_{1-x}O_2$ thin films. As mentioned above, the highest value of the magnetic moment was obtained at 500 °C, indicating that the magnetic moment in the films is related to the resistivity. It is inferred that the magnetic moment of the $Co_xTi_{1-x}O_2$ thin films is likely to depend upon the extent of crystallization of the anatase phase. We found that the magnetic moment in the $Co_{0.07}Ti_{0.93}O_2$ on a $LaAlO_3$(100) substrate is higher than that with $Co_{0.07}Ti_{0.93}O_2$ on a Si substrate, which can be due to the smaller lattice mismatch.

Conclusion

We have investigated the crystal structure and magnetic properties of $Co_xTi_{1-x}O_2$ thin films $0.03 \leq x \leq 0.07$), grown on Si(100) substrates by a pulsed laser deposition (PLD). We found that the crystal structure exhibiting ferromagnetism at room temperature originates from the anatase phase in the films. We also found that the magnetic moment in the films is dependent upon the extent of crystallization of the anatase phase, which is associated with the resistivity of the films.

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