Preparation of Ferromagnetic Cobalt Substituted TiO_2 (Anatase) Thin Films by Electrochemical Deposition

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Dilute magnetic semiconductors (DMS), also known as semi-magnetic semiconductors,[1] have stimulated considerable interest in recent years.[2,3] Their combined ferromagnetic and semiconducting character is of particular interest for spintronics.[2] However, most DMS cannot be used as room-temperature ferromagnets in practical spintronics applications because they possess low Curie temperatures.[4,5]

Recently, Matsumoto et al.[6] reported that Co-doped anatase thin films, produced by laser ablation in high vacuum, display room-temperature ferromagnetism (RTF). According to this report, when the concentration of Co in the film is between 0 and 8 atom %, the film shows ferromagnetic long-range ordering. The magnetic moment of saturated Co was reported to be 0.32 μ_B, and the film exhibited a positive magnetoresistance (MR) up to 60% at 2 K in an 8 T field. The reason that Co-doped anatase films have RTF characteristics, however, is still unclear. Some researchers[7,8] have suggested that the observed ferromagnetic behavior is caused by Co cations substituted into the anatase lattice, which is similar to the local structure environment of Co in $CoTiO_3$. Others believed that clusters of Co *metal* in these films generated the observed RTF properties.[9,10] More recently, a model based on oxygen vacancies was reported by Liu et al.[11]

Synthesis of Co-doped thin films has been achieved by a variety of methods including spray pyrolysis,[12] oxygen-plasma-assisted molecular-beam epitaxy (OPA-MBE),[7] and reactive co-sputtering[10] and the RTF properties of these films were confirmed. In this study we demonstrate the formation of ferromagnetic Co-doped anatase TiO_2 films by a solution-based process. Cathodic electrolytic deposition (CELD)[13] has been defined as a process in which film deposition is achieved via the hydrolysis of a metal salt solution using an electrogenerated base such as OH^- to form oxides, hydroxides, or peroxides on a cathodic electrode. Hydroxides and peroxides are then converted to oxides by thermal treatment. This method has previously been used successfully to deposit ceramic oxide films such as TiO_2, ZrO_2, and $ZrTiO_4$.[14] In comparison with the other methods electrochemical routes offer several advantages: they are a low-temperature synthesis technique, the procedure is simple and relatively inexpensive, and the film can be controlled through varying the cell parameters (potential or current) or by the composition of the bath. Considering the benefits of the CELD method, we report here on the successful growth of Co-doped anatase films on Ti and Si substrates using electrolytic deposition. The postannealed films are transparent and nanocrystalline and show ferromagnetic behavior at room temperature with no evidence for the formation of Co metal clusters.

The preparation of TiO_2-based films from aqueous solution requires the stabilization of the Ti^{4+} cation in solution; here a peroxo-complex was used (eq 1). On application of a cathodic current to the substrate material, locally generated OH^- reacts with this complex resulting in the precipitation of a Ti−hydroxy film (eq 2).

$$Ti^{4+} + H_2O_2 + (n-2)H_2O \rightarrow [Ti(O_2)(OH)_{(n-2)}]^{(4-n)+} + nH^+ \quad (1)$$

$$[Ti(O_2)(OH)_{(n-2)}]^{(4-n)+} + nOH^- + kH_2O \rightarrow TiO_3\cdot(H_2O)x \quad (2)$$

With the addition of Co^{2+} to the electrolyte this becomes

$$(1-y)[Ti(O_2)(OH)_{(n-2)}]^{(4-n)+} + nOH^- + kH_2O + yCo^{2+} \rightarrow Ti_{(1-y)}Co_yO_3\cdot(H_2O)x \quad (3)$$

The as-deposited material is gel-like (amorphous and hydrated). The Co cation is incorporated into this gel as it deposits onto the surface (eq 3) in approximately equivalent concentrations as the molar fraction in solution, as confirmed by energy dispersive X-ray spectroscopy (EDS). The total film thickness after 45 min deposition is ∼500 nm (measured in cross section in the scanning electron microscope) indicating an average deposition rate of around 0.2 nm·s^{-1}.

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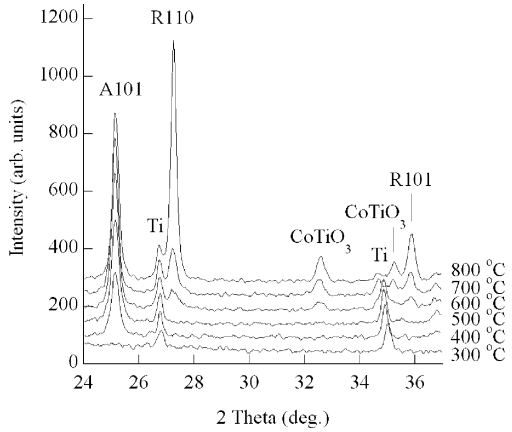

Figure 1. HTXRD pattern of $Ti_{0.95}Co_{0.05}O_2$ film deposited on a Ti substrate, annealed in situ from room temperature to 800 °C. "A" denotes anatase peak positions, and "R" denotes rutile.

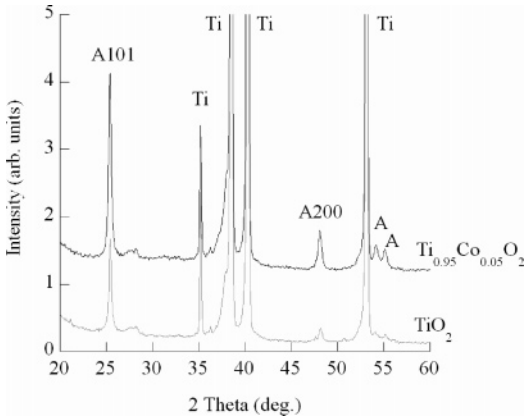

Figure 2. Comparison of the XRD patterns for un-doped and doped ($x = 0.05$) anatase films thermally treated at 400 °C for 1.5 h.

Figure 1 shows the high-temperature X-ray diffraction (HTXRD) pattern of a $Ti_{0.95}Co_{0.05}O_2$ film annealed from room temperature to 800 °C (under an Ar atmosphere to minimize substrate oxidation).

Only peaks attributed to the substrate (Ti) were observed at room temperature which confirms that the as-deposited film was amorphous. When the anneal temperature was increased to 400 °C, peaks corresponding to the anatase phase were observed indicating the crystallization and dehydration of the as-deposited structure (eq 4).

$$2Ti_{(1-y)}Co_yO_3{\cdot}(H_2O)x \rightarrow 2Ti_{(1-y)}Co_yO_2 + 2xH_2O + O_2 \quad (4)$$

Upon further increasing the temperature to 600 °C a transition to the rutile polymorph is observed with simultaneous ejection of $CoTiO_3$ from the lattice. Thus, careful control of the annealing temperature below 600 °C is required for maintained solubility of the Co in the host TiO_2 lattice; below 600 °C the formation of $CoTiO_3$ is completely suppressed. A comparison of the XRD patterns for both the doped and the un-doped anatase films are shown in Figure 2.

From these data the lattice parameters were calculated from a Le Bail extraction of the diffraction data using the GSAS suite of programs[15] (Table 1). The *d*-spacing increased for the doped films in agreement with predictions for a Co-doped anatase matrix. In particular the *c*-axis was found to increase

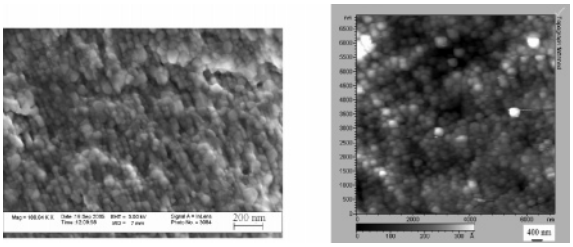

Figure 3. Film morphology for anatase $Ti_{0.95}Co_{0.05}O_2$. (left) FESEM image, (right) AFM image.

Table 1. Lattice Parameters from XRD Data for Un-Doped and Co-Doped Anatase Films Annealed at 400 °C

film	*d* spacing (Å)	lattice parameter (Å)
TiO_2	$d_{101} = 3.501$	$a = 3.7930(9)$
	$d_{200} = 1.888$	$c = 9.008(2)$
$Ti_{0.95}Co_{0.05}O_2$	$d_{101} = 3.505$	$a = 3.7853(8)$
	$d_{200} = 1.890$	$c = 9.468(3)$

markedly from 9.008(2) Å to 9.478(3) Å; these results are consistent with those in the literature for films formed using vacuum techniques.[6,16] In addition there is a clear shift of the diffraction peaks with temperature corresponding to the thermal expansion of the film.

Matsumoto et al.[6] reported that only the (004) and (008) peaks corresponding to anatase were observed, indicating a high degree of texture in their films. However, in the current work it is clear that the (101) and (200) peaks of the anatase phase are predominant, indicative of randomly oriented material, as was reported by Punnoose et al.[8] The reason for these differences may be due to different deposition methods, Co contents, or substrate effects.

The morphology of the annealed doped film is shown in Figure 3. Before thermal treatment, the film is amorphous and no crystallites were observed. After annealing at 400 °C for 1.5 h in air, spherical particles can be seen in the field emmision scanning electron microscopy (FESEM) image, Figure 3. The particle size distribution is relatively homogeneous and about 50 nm in diameter.

EDS analysis confirmed that Co is distributed throughout the film with only slight variations in the composition. On average, the Co:Ti ratio is 4%, and this agrees well with the nominal stoichiometry of 5% Co in the solution. According to Matsumoto et al.[6] the maximum solid solubility of Co in TiO_2 is 8%, and above this value $CoTiO_3$ forms. From the current work it is clear that at elevated temperatures (greater than 600 °C) the solubility of Co in TiO_2 is significantly decreased, as evidenced by the ex-solution of $CoTiO_3$. The absence of $CoTiO_3$ at low temperature is consistent with the level of Co suggested in this study and in previous literature reports.

The same grain shape of the doped film is shown more clearly in the atomic force microscopy (AFM) image, Figure 3. Using the XRD measurements the grain size was also calculated using the Scherrer equation (eq 5):

$$t = \frac{0.9\lambda}{B\cos\theta} \quad (5)$$

where t is particle size, λ is the wavelength of Cu Kα, and B is fwhm (full width at half-maximum) of the broadened diffraction line on the 2θ scale (radians). This calculation

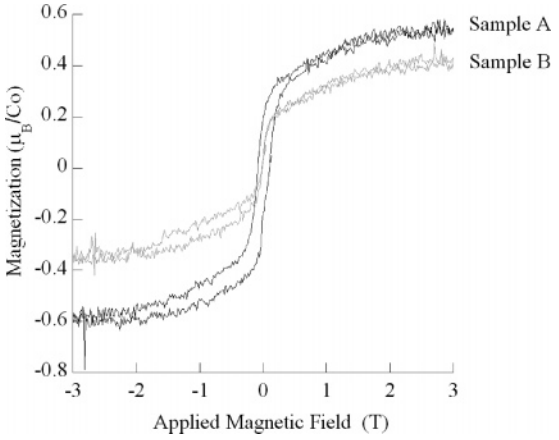

Figure 4. Room temperature in-plane magnetization vs magnetic field for two $Co_{0.05}Ti_{0.95}O_2$ samples (denoted A, B) produced under nominally identical experimental conditions.

gives a value of 50−100 nm, consistent with the FESEM and AFM data.

Finally, the magnetic character of the electrodeposited material is confirmed. Figure 4 shows room temperature in-plane magnetization versus magnetic field for two samples produced with nominally identical experimental conditions (denoted A and B). The difference of the two hysteresis loops may be due to the variation of the Co concentration in the films or due to variation in the volume of the deposited materials. The behavior is clearly ferromagnetic, and the signal is appropriate for a dilute ferromagnetic oxide thin film (0.35−0.6 μ_B/Co) and in agreement with Matsumoto et al.[6] Coupled with the XRD results, we suggest that in these films the magnetic behavior observed is related to Co cations substituted in the TiO_2 structure.

In summary, $Ti_{1-x}Co_xO_{2-\delta}$ films have been successfully prepared using a simple solution-based approach. The composition of the films is directly related to the solution concentration. When the annealing temperature is greater than 600 °C a $CoTiO_3$ impurity phase is formed along with the rutile polymorph. However, when controlling the annealing temperature below 600 °C only single phase anatase is observed, and the lattice parameter is consistent with site-substitution by Co cations. The films annealed at 400 °C show room-temperature ferromagnetic behavior as observed for films grown under vacuum conditions. This approach is an attractive method of producing ferromagnetic material with well-controlled stoichiometry and crystallization behavior.

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Supporting Information Available: Details of deposition conditions and film analyses (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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