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## Magnetism of Co-doped titania thin films prepared by spray pyrolysis

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Co-doped TiO<sub>2</sub> (anatase) films prepared by spray pyrolysis at 500 °C are investigated for the possible existence of room temperature ferromagnetism (RTF). These films were characterized by x-ray diffraction, Raman spectroscopy, and x-ray photoelectron spectroscopy at room temperature, followed by studies of the temperature and magnetic field dependence of the magnetization by squid magnetometry. For Co doping of upto 10 at. %, no phase other than anatase could be detected, and there is no RTF in these films. Instead, the magnetic susceptibility  $\chi$  fits the modified Curie–Weiss law  $\chi = \chi_0 + C/(T + \theta)$ , with  $\theta \approx 5$  K and magnitude of  $C$  consistent with Co<sup>2+</sup> paramagnetism in Ti<sub>1-x</sub>Co<sub>x</sub>O<sub>2-x</sub>. Only for  $T \leq 5$  K, a hysteresis loop with coercivity  $H_c = 200$  Oe is observed. These observations suggest Co<sup>2+</sup> paramagnetism, with exchange interaction becoming important for  $T \leq 5$  K in the case of 10% Co/TiO<sub>2</sub> films. © 2003 American Institute of Physics.  
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Because of the increasing demand of the information technology field for faster data processing and larger charge storage capacity, the field of spintronics is growing rapidly.<sup>1</sup> For this purpose, metal–ferromagnetic–semiconductor based heterostructures have been studied extensively. However, it remains difficult to transfer electron spin across the ferromagnetic–semiconductor interfaces mainly due to their dissimilar electronic conductivities.<sup>2–4</sup> Another promising approach is to integrate ferromagnetic semiconductors with existing semiconductors.<sup>5–6</sup> For example, for Mn-doped GaAs coherent transfer of electron spins has been demonstrated.<sup>5</sup> The Curie temperatures  $T_C$  of most of these materials are however below RT requiring additional research to increase  $T_C$  above RT.<sup>7</sup> Matsumoto *et al.* reported the room-temperature ferromagnetism (RTF) properties in epitaxially grown Co-doped TiO<sub>2</sub> thin films using pulsed laser deposition.<sup>8</sup> The RTF behavior was also confirmed in Co-doped TiO<sub>2</sub> thin films prepared by oxygen plasma assisted molecular beam epitaxy,<sup>9</sup> and reactive cosputtering techniques.<sup>10</sup> The origin of RTF of these films, however, remains poorly understood. For example, Matsumoto *et al.*<sup>8</sup> commented that precipitated magnetic Co clusters in TiO<sub>2</sub> matrix could be responsible for the observed RTF although no evidence for Co clusters was confirmed from the x-ray diffraction (XRD) or transmission electron microscopy (TEM) measurements. This possibility was also raised by Park *et al.* who in a recent study have provided evidence for the presence of Co clusters from magnetic study.<sup>10</sup> The presence of such clusters has also been reported by Mitani *et al.*<sup>11</sup> Both Matsumoto *et al.* and Park *et al.* claimed that Co doping (up to 12 at. %) systematically dissolves in TiO<sub>2</sub> lattice. Chambers *et al.*,<sup>9</sup> on the other hand, ruled out the possibility of Co inclusion in anatase TiO<sub>2</sub> lattice and concluded that the local coordination of Co in Ti<sub>1-x</sub>Co<sub>x</sub>O<sub>2</sub> films

is similar to that in CoTiO<sub>3</sub>. The RTF properties were observed in those films where the local coordination of Co was similar to that in CoTiO<sub>3</sub>. On the other hand, films with substantial Co outdiffusion to the near-surface regions [with Co valence state +2 or +3 as revealed by x-ray photoelectron spectroscopy (XPS) analysis] were essentially nonferromagnetic.

In this work, we have synthesized a series of Co-doped TiO<sub>2</sub> thin films (up to 10 at. % Co content) on commercial glass substrates by spray pyrolysis.<sup>12</sup> We do not observe RTF behavior in these films which apparently is in contradiction to the earlier-mentioned studies. It is argued that the possible reason for this contradiction could be due to the nature of Co substitution in host TiO<sub>2</sub> lattice.

To prepare these films, calculated amounts of titanium acetylacetonate and cobalt nitrate, codissolved in ethanol, were sprayed over the glass substrates kept at 400 °C using nitrogen gas. These films were then annealed at 500 °C for 3 h in air for organic removal as well as crystallization. The deposited films had a thickness in the range of 80–190 nm. The nature of phase formation and structural properties of these films were analyzed by x-ray diffraction in conjunction with the micro-Raman spectroscopy. Magnetic measurements on these films were carried out in the range of 1.7–300 K using a commercial superconducting quantum interference device magnetometer. The surface composition and the chemical states of the constituent elements were analyzed using a XPS.

As revealed by XRD, all the films were polycrystalline and crystallized into the anatase crystal structure with no significant shift of the Bragg lines with Co doping. No metallic Co precipitation or any other Co–Ti phase(s) were detected in XRD upto 10 at. % Co doping. The ionic radius of Co<sup>2+</sup> is close to that of Ti<sup>4+</sup> ions with equivalent coordination number. Therefore, the lattice spacing does not change significantly even if Co dissolves in TiO<sub>2</sub> lattice and forms

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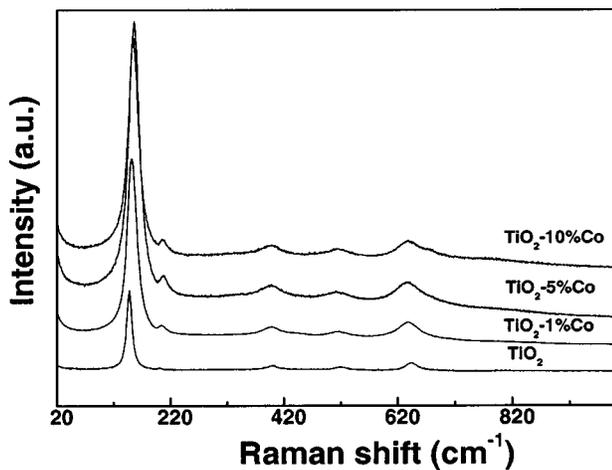


FIG. 1. Micro-Raman spectra of (a) 0.0 (undoped), (b) 1.0, (c) 5.0, and (d) 10.0 at. % Co-doped TiO<sub>2</sub> thin films.

solid solution without any secondary phase precipitation (at least within the detection limit of XRD). The local Co induced structural modification of TiO<sub>2</sub> host was also analyzed by micro-Raman spectroscopy. Figure 1 shows the micro-Raman spectra of TiO<sub>2</sub> thin films with various Co content. All the observed bands are identified from the tetragonal anatase phase. The presence of any other vibration mode/(s) from secondary phase/(s) (e.g., metallic Co or various Co-Ti oxide species) were not detected in any of these spectra.

Our XPS studies showed the core levels of Ti 2p<sub>1/2</sub> and Ti 2p<sub>3/2</sub> to be approximately at 463.90 and 458.44 eV (after carbon correction), respectively, which are assigned to the Ti<sup>4+</sup> in anatase TiO<sub>2</sub>, assuming the 0.76 eV shift (in Ref. 13, the Ti 2p<sub>3/2</sub> position is reported at 459.2 eV) could be due to the retained strain in thin films. Figure 2 shows the Co 2p level core spectra of 10 at. % Co-doped TiO<sub>2</sub> thin film, the Co 2p<sub>3/2</sub> and 2p<sub>1/2</sub> peaks being at 780.85 and 796.78 eV, respectively, with a peak separation of 15.93 eV. Comparing with results in Ref. 13, it is ruled out that in our films Co is in metallic state in anatase TiO<sub>2</sub> (metallic Co 2p<sub>3/2</sub> has a peak position at 778.3 eV). Instead our result indicates that Co is in +2 valence state and not bonded to oxygen as CoO since Co 2p<sub>3/2</sub> in CoO has a peak position at 780.4 eV and the observed peak in the present study appeared at 780.85

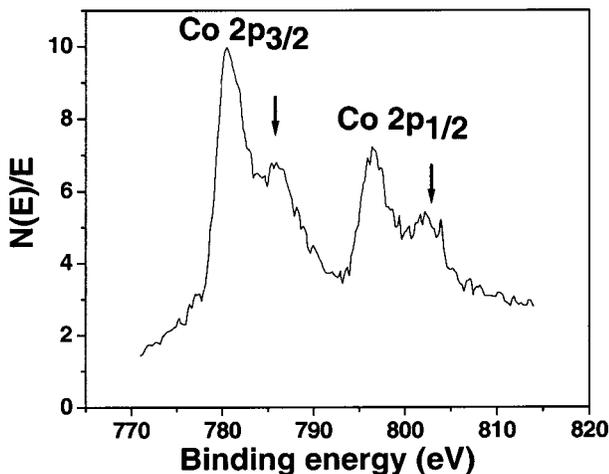


FIG. 2. XPS spectra of Co 2p peaks from 10 at. % Co-doped titania, see text for arrows.

TABLE I. Composition of undoped and Co-doped TiO<sub>2</sub> films.

Film composition	O:Ti (nominal)	O:Ti (expt.)	Co:Ti (nominal)	Co:Ti (expt.)
TiO <sub>2</sub>	2:1	2.6:1	...	...
Ti <sub>0.9</sub> Co <sub>0.1</sub> O <sub>1.9</sub>	2.1:1	2.85:1	0.11:1	0.10:1

eV. The shift of 0.45 eV indicates that there is indeed an inclusion of Co in TiO<sub>2</sub> lattice forming solid solution of composition Ti<sub>1-x</sub>Co<sub>x</sub>O<sub>2-x</sub>. The splitting of Co 2p<sub>3/2</sub> and 2p<sub>1/2</sub> peaks (marked by arrows) could be due to the Ar sputtering done for surface cleaning prior to the XPS measurement. The oxygen 1s band for undoped TiO<sub>2</sub> films is observed at about 529.3 eV, (not shown) which corresponds to oxygen in TiO<sub>2</sub>.<sup>12</sup> The shoulder at the higher binding energy (~532 eV) corresponds to oxygen in either adsorbed water molecule or OH group at the film surface (not shown).

As shown in Table I, the atomic content ratio of O:Ti is higher than the nominal composition due to the presence of adsorbed water and the Co:Ti ratio is quite close to the expected nominal composition. This is in contrast to the observation made by Chambers *et al.*<sup>9</sup> who have reported Co affluence at the surface of their films.

The results of our magnetic studies on the 10% Co-doped TiO<sub>2</sub> sample are shown in Figs. 3 and 4. In order to avoid the background signal from the glass plate, the thin-film material was carefully scrapped-off the glass plate and the magnetic data measured is shown in Figs. 3 and 4. Prior to scrapping-off the material, the magnetic studies on the thin films was also done and the data were similar to those in Figs. 3 and 4 except for the background diamagnetic signal from the glass plate. The temperature variation of the magnetic susceptibility  $\chi$  in zero field cooled (ZFC) and field cooled (FC) cases showed some bifurcation of the data below about 6 K (Fig. 3). The solid line in Fig. 3 is fit to the modified Curie-Weiss law:  $\chi = \chi_0 + C/(T + \theta)$  with  $\chi_0 = 1.2(0.1) \times 10^{-5}$  emu/g Oe,  $C = 1.4(0.1) \times 10^{-3}$  emu K/g Oe, and  $\theta = 5(1)$  K. Using  $C = N\mu^2/3k_B$ , with  $N$

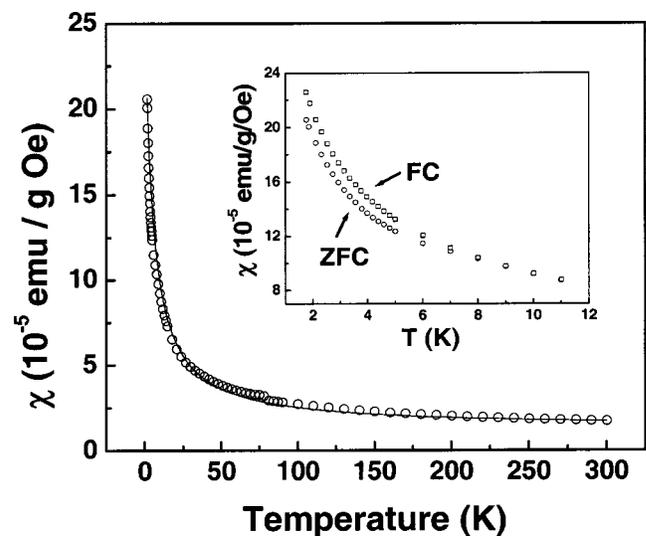


FIG. 3. Temperature variation of the magnetic susceptibility  $\chi$  for the 10% Co-doped film for FC and ZFC cases in  $H = 2000$  Oe. The solid line is fit to the equation  $\chi = \chi_0 + C/(T + \theta)$ . The inset shows the data for the low temperature region.

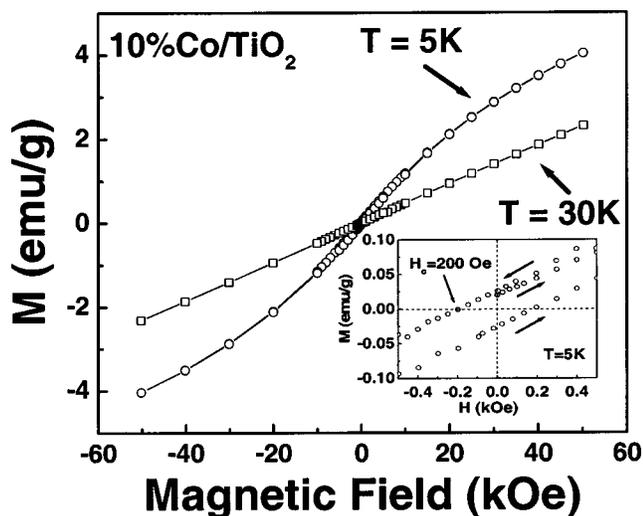


FIG. 4. Magnetization vs magnetic field for 10% Co/TiO<sub>2</sub> at 5 and 30 K. The inset shows the data for the low field regions at 5 K. The lines connecting the data are for visual aid.

= number of magnetic ions/g,  $k_B$  = Boltzmann constant, and  $\mu$  = magnetic moment, yield  $\mu \approx 3.0(0.1) \mu_B$  for the Co<sup>2+</sup> ions substituting for Ti<sup>4+</sup> ions in the anatase unit cell for 10% Co doping, assuming the composition Ti<sub>1-x</sub>Co<sub>x</sub>O<sub>2-x</sub>. This magnitude of  $\mu$  is somewhat lower than the expected value of  $\mu = 3.87 \mu_B$  for 10 at. % Co<sup>2+</sup> with spin  $S = 3/2$  but the difference can easily be explained assuming the actual concentration of Co in the thin film is somewhat less than the nominal 10% value. The Curie–Weiss temperature  $\theta \approx 5$  K represents antiferromagnetic exchange interaction between the Co<sup>2+</sup> ions. The bifurcation of the FC and ZFC data below 6 K may be a manifestation of this interaction.

The field dependence of the magnetization at  $T = 5$  and 30 K (Fig. 4) shows that the hysteresis is not observed at 30 or 300 K (not shown). However, at 5 K,  $M$  vs  $H$  is nonlinear and in the inset of Fig. 4, we have plotted the low-field region of the loop showing coercivity  $H_c \approx 200$  Oe and the remnant magnetization of about 0.02 emu/g.

In conclusion, we have successfully prepared Co:TiO<sub>2</sub> thin films by spray pyrolysis at relatively low temperature (500 °C). In this technique, the phase formation kinetics is expected to be very different from that in the physical vapor deposition techniques since in spray pyrolysis, the constituent elements are mixed at molecular level and also the an-

nealing temperature was kept relatively low to avoid any possible secondary phase segregation even in relatively higher doping content. Films so prepared were characterized by XRD, XPS, and micro-Raman studies in order to establish the solubility of Co in TiO<sub>2</sub> lattice up to 10 at. % Co content. These films were found to be paramagnetic at room temperature but on cooling further the magnetic susceptibility followed a Curie–Weiss law with a very low  $\theta \approx 5$  K. Only for  $T \leq \theta$ , hysteresis loop is observed. The apparent disagreement of our results in the Co:TiO<sub>2</sub> films prepared by spray pyrolysis with other reported results on Co/TiO<sub>2</sub> films prepared by other methods (where RTF has been observed),<sup>8–10</sup> is most likely due to the different nature of incorporation of Co into the anatase lattice.

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