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Ferromagnetism in nanocrystalline epitaxial Co:TiO₂ thin films

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We report on the observation of remarkable room-temperature ferromagnetism in nanocrystalline epitaxial Co:TiO₂ films grown on sapphire (0001) substrates by a pulsed-laser deposition technique using high-density targets. The films were characterized by x-ray measurements, atomic force microscopy, micro-Raman, electron-paramagnetic resonance, and magnetization studies. The films exhibit three-dimensional islandlike growth that contains nanocrystalline particles. Our experimental results suggest that the remarkable ferromagnetism in Co:TiO₂ films is controlled either by the interstitial Co²⁺ ions or small clusters, which are mainly present at the interface and on the surface of the films. Our work clearly indicates that Co interstitials and nanoclusters cause room-temperature ferromagnetism in Co-doped TiO₂. © 2005 American Institute of Physics. [DOI: 10.1063/1.1944209]

Recent advances in the emerging field of diluted magnetic semiconductors (DMS) have attracted widespread attention due to their potential applications in the rapidly developing field of spintronics.¹⁻⁴ The search for integrating the semiconductors with the magnetic properties in the same material has become a prerequisite for successful fabrication of potential devices of shrinking dimension, such as high-performance read-heads, nonvolatile memories, and other state-of-the-art storage devices.^{5,6} Hence, the discovery of DMS exhibiting room temperature ferromagnetism (FM) has established an important achievement for possible applications of functional spintronics.⁷ Although there have been many advances in incorporating magnetic ions into host semiconductors, particularly wide band gap III-V and II-VI based DMS materials, applications were possible only at low temperatures in such materials due to their low magnetic transition temperature, T_c . Among DMS materials, Co-doped TiO₂ (Co:TiO₂ or CTO) has received interest^{8,9} because it is a transparent semiconductor. However, the origin of the ferromagnetic properties, particularly a possibility arising either from the Co clusters^{9,10} or intrinsic phenomenon¹¹ of Co substitution in Ti lattice, and the ionic state of Co remain ambiguous.

Several techniques have been employed to fabricate epitaxial Co:TiO₂ films using oxide-based substrates, such as SrTiO₃, LaAlO₃ (LAO) for anatase,^{11,12} and Al₂O₃ for rutile phase stabilization,^{13,14} which show ferromagnetism at room temperature. The origin of ferromagnetism in this DMS is still debated due to possibilities of Co clustering as described above, and incorporation of Co atoms in the lattice. How-

ever, one of the most important issues is that Co-doped TiO₂ could contribute significantly to the field of spintronics as a potential DMS, if successfully synthesized, exhibiting dilute magnetic nature. Here we report the growth of Co:TiO₂ films containing nanoparticles ordered to form epitaxial films on Al₂O₃ substrates. The films demonstrate remarkable structural, microscopic, ferromagnetic, and spectroscopic properties at room temperature. The results demonstrate that Co can substitute Ti, and the predominant valence state is Co²⁺.

Co:TiO₂-Sapphire(0001) epitaxial films were grown by the PLD technique (KrF excimer, $\lambda=248$ nm, laser repetition rate of 2–5 Hz) with a pulse energy density of 1 to 2 J/cm² and utilizing both target and substrate rotation facilities. High-density Ti_{1-x}Co_xO (CTO) targets were used. Stoichiometric amount of TiO₂ and CoO (both 99.99% purity) powders were mixed, calcined at 700 °C for 12 h followed by isostatic pressing at 400 MPa, and finally sintered at 1000 °C in order to make high-density target. The films were deposited with a substrate temperature $T_s=700$ –800 °C, keeping oxygen partial pressure $PO_2=1 \times 10^{-5}$ Torr. Clean single crystalline sapphire substrates were loaded to the chamber and heated just after the ultimate base pressure $<4 \times 10^{-8}$ Torr is reached. The film thickness is about 57 nm. The x-ray diffraction (XRD) of the films was done in a Rigaku x-ray diffractometer using Cu K α radiation. The Raman spectra were recorded using a LabRam micro-Raman spectrometer with He-Ne laser excitation (wavelength: 632.8 nm). The ferromagnetic resonance (FMR) experiments were done on a Bruker EMX spectrometer operating at 9.6 GHz microwave frequency. Quantum Design Superconducting Quantum Interference Device (SQUID- MPMS) was used to measure the magnetization of films.

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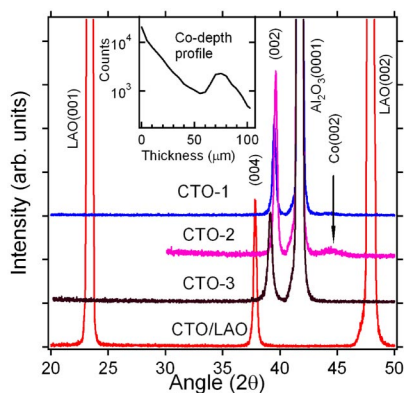


FIG. 1. (Color online) X-ray diffraction pattern of Co:TiO₂ films grown on sapphire and LaAlO₃ substrates using targets containing different concentration of Co. The inset shows the Co depth profile of CTO-2 from secondary ion mass spectroscopy.

Figure 1 shows the XRD patterns of CTO–Sapphire (0001) films at a constant PO_2 using three different targets with Co concentration varying from 6 to 12 at. % designated 6 at. % as CTO-1, 10 at. % as CTO-2, and 12 at. % as CTO-3. The XRD patterns for all films grown on sapphire (0001) reveal one dominating plane (002) of the rutile phase, illustrating the epitaxial nature of the film and rutile phase stabilization. This undoubtedly indicates the preferential orientation of the crystal plane in parallel with the substrate surface. The rocking curves for the epitaxial growth of the films show that the full-width half-maximum (FWHM) calculated from x-ray (200) line broadening increase from 0.3° to 0.35° with increasing Co concentration in the target at the same growth conditions, illustrating the poor crystalline quality of the film for higher concentration Co. It is interesting to note that the peak position for the higher concentration of Co shifts to lower angle. However, interestingly, a small but discernable peak at about 44.5° was observed, particularly in CTO-2 film. This is certainly due to Co (002) reflection preferably oriented in the plane (c axis) either in a small cluster form or as interstitials. On the other hand, the film grown on LAO substrate exhibits only one dominating peak (004), illustrating the presence of only anatase phase. No evidence of Co clusters or Co intermetallic compounds was observed in films deposited on LAO substrate. The c axis parameter of anatase as deduced from the (004) reflection is about 0.9500 nm for CTO–LAO, which suggests that Co ions have been incorporated into the anatase structure substituting Ti ions in the lattice. Furthermore, the unit-cell elongation along the c axis strongly suggests that mostly Co is in +2 state whose atomic radius (0.072 nm) is larger than Ti^{4+} , which is in agreement with a recent report.¹⁵ In view of the above, the slight shift of rutile (002) peak in CTO–sapphire to higher angle indicates the fact that the substitutional effect is also present in CTO–sapphire when grown using targets containing different concentration of Co.

In order to study the variation of Co density as a function of film thickness (co-depth profile), we carried out secondary mass ion spectroscopy in CTO-2 and the Co depth profile is presented in the inset of Fig. 1. It is clear that the density of Co is much higher at the surface and decreases as the film thickness decreases. However, surprisingly, the Co density suddenly increases at the interface (~ 57 nm) where a sharp jump in Al depth profile starts, illustrating that Co diffuses into the substrates and probably acts as a nucleation

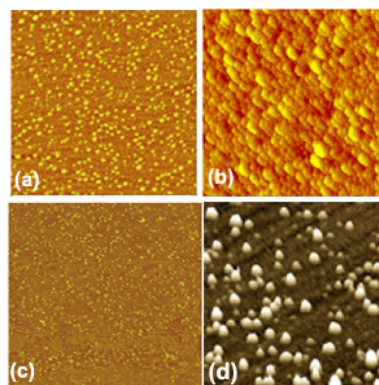


FIG. 2. (Color online) AFM pictures of as-grown Co:TiO₂ films from targets containing (a) 6 at. %, (b) 10 at. %, (c) 12 at. %, and (d) 6 at. % of Co. All scans from (a) to (c) are $2\ \mu\text{m} \times 2\ \mu\text{m}$ in dimension. The image in (d) shows the 3D image over $1.5\ \mu\text{m} \times 1.5\ \mu\text{m}$ area.

center for the formation Co clusters. On the other hand, it is noted that the x-ray mapping of CTO–sapphire films over $20\ \mu\text{m} \times 20\ \mu\text{m}$ area on the surface of the film clearly illustrates that Co is uniformly distributed in the TiO₂ matrix.

The atomic force microscopy (AFM) images of as-grown Co:TiO₂ films are shown in Figs. 2(a)–2(d). The AFM images show remarkable nanocrystalline features in Figs. 2(a) and 2(c) for CTO-1 and 2, respectively. The particles are very uniform in size in both films. The particle size decreases from 25 nm to less than 20 nm with increasing Co concentration. However, it is interesting to note the self-assembly of CTO oriented nanocrystals of size 35 nm for CTO-2 film as shown in Fig. 2(b). On the other hand, CTO-1 grown with a slightly higher repetition rate (7 Hz) shows a distinct three-dimensional (3D) islandlike growth feature with average particle size of 50 nm as shown in Fig. 2(d) over a $1.5\ \mu\text{m} \times 1.5\ \mu\text{m}$ area. The above results show that the Co concentration in the target affects the microstructure of the film, although other growth parameters, which are kept constant for the present experiment, may also have an effect on this.

In Fig. 3, we show the Raman spectra of CTO films and the sapphire (0001) substrate. Besides the Raman bands at 350, 421, 433, and 583 cm^{-1} , which are due to sapphire substrates, two shoulder signals appeared at 442 and 610 cm^{-1} due to rutile phase. The Raman spectra show that the structure is predominantly rutile and highly crystalline. A broad peak observed at 680 cm^{-1} is believed to be additional fea-

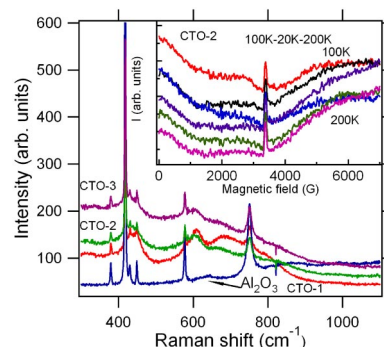


FIG. 3. (Color online) Raman spectra of Co:TiO₂ film synthesized from the target containing different Co concentration. The spectrum for the substrate (sapphire) is also shown. The inset shows the FMR spectra of Co:TiO₂ film synthesized from the target containing 10 at. % of Co at various temperatures.

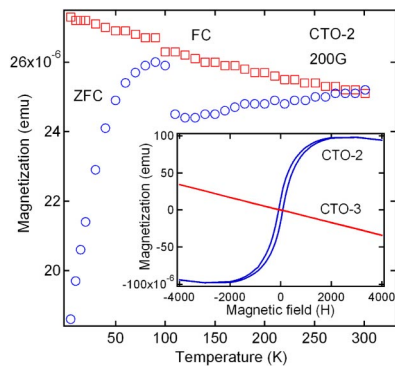


FIG. 4. (Color online) Magnetic field dependence of field-cooled (FC) and zero-field-cooled (ZFC) curves of CTO-2 in a field of 200 G. The inset shows the ferromagnetic hysteresis loops of CTO-2 and CTO-3 films at 300 K.

ture in the rutile structure and may be related to the Co interstitials or small clusters. The intensity of the broad peak is much pronounced for CTO-2. Hence, the coincidence of the presence of this peak and the observed peak due to Co in x-ray reflection illustrate the presence of either interstitials or small clusters due to Co. The most probable presence is either Co interstitials or very small Co clusters of nm scale, which is consistent with the recent observation⁹ of Co nanoclusters of about 10 nm size in the anatase phase from transmission electron microscopy studies.

FMR is one of the sensitive tools to study the presence of magnetic ions. In order to infer the Co charge state, we have studied the FMR spectra of CTO-2 (shown in the inset in Fig. 3) at different temperatures, ranging from 100 to 200 K. The temperature independent electron paramagnetic resonance (EPR) of the EPR cavity is seen at about 3.3 KG. At 100 K, the FMR spectra exhibit pronounced hump at around 2500 G. The hump feature, which is a strong function of temperature, weakens as temperature is raised. This is a clear signature of ferromagnetic Co^{2+} as Co^{3+} does not show up in FMR spectra. The decrease of the FMR signal with increasing temperature may be related to the presence of Co^{3+} ions at higher temperature. This provides strong experimental evidence in favor of the presence of Co^{2+} ionic state which is responsible for the ferromagnetism in CTO films.

Figure 4 shows the field-cooled (FC) and zero-field-cooled (ZFC) magnetization of the CTO-2 film, displaying a ferromagnetic behavior. The FC and ZFC curves show anomalous jump at about 100 K, illustrating a sudden change in the spin structures, which is related to a metastable magnetic state. In order to confirm the ferromagnetic behavior, magnetic field dependence of magnetization (MH) curves are shown at 300 K for two representative CTO films, including CTO-2. The CTO-2 film displays remarkable ferromagnetic behavior at 300 K. The magnetic field at which the maximum in magnetization, H_m (low field to high field) achieved is estimated to be 2 KG at 300 K. However, the room temperature ferromagnetic hysteresis shrinks significantly for CTO-3, which can be attributed due to the poor crystalline quality of these films when synthesized from the target containing higher concentration of Co as discussed earlier. It is noted that the background magnetic contribution due to sapphire substrate has not been corrected. This will further increase the H_m values. However, this may not affect the qualitative effects of on magnetization results.

In view of the above, the origin of the ferromagnetism in CTO films can be attributed to the presence of Co^{2+} ions that are either in the interstitial positions or in the form of a small metal clusters. This is also consistent with the recent report of channeling experiments.¹⁶ However, the ferromagnetic exchange mechanism between $\text{Co}^{2+}-\text{O}-\text{Co}^{3+}$, giving rise to ferromagnetism¹⁵ in this system seems to be totally implausible in the absence of Co^{3+} ions. The dispersed Co clusters or interstitial site occupations show a true diluted magnetic nature and can be a potentially significance to the field of spintronics.

In conclusion, we have demonstrated that the epitaxial Co:TiO₂ films grown on sapphire substrates show remarkable surface morphology comprising of nanocrystalline particles from a 3D islandlike growth. The studies from x-ray, magnetic and spectroscopic measurements suggest that the ferromagnetism observed in Co:TiO₂ film is controlled either by the interstitial Co^{2+} ions or small clusters. The Co depth profile clearly indicates the presence of Co clusters at the interface and on the surface which influence the ferromagnetism significantly. Our results are significantly important for fabricating the Co:TiO₂ films for possible spintronic applications.

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