Substrate effects on the room-temperature ferromagnetism in Co-doped TiO_2 thin films grown by pulsed laser deposition

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$Co:TiO_2$ films were fabricated by laser ablation on Si, $LaAlO_3$ (LAO), and $SrTiO_3$ (STO) substrates from a ceramic target. Films on all types of substrates have Curie temperature (T_C) above 400 K. All films are highly crystallized with different structures. While films on Si substrates are rutile, films on LAO and STO substrates are single phased anatase. Due to the different lattice mismatch, films grown under the same growth conditions on Si, LAO, and STO substrates have different saturation magnetization and coercivity. While Co atoms are mostly localized near the surface of the films, magnetic measurements suggested that the ferromagnetism unlikely originates from Co clusters. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1669111]

After the discovery of Matsumoto *et al.*,[1] $Co:TiO_2$ thin films have attracted many research groups due to their exhibition of room temperature ferromagnetism (FM). Growth of this diluted magnetic semiconductor by thin film techniques provides excellent control of the dopant concentration. So far, $Co:TiO_2$ films were basically fabricated from two targets, Ti and Co metal targets, or TiO_2 and $Co:TiO_2$ with a very high concentration of Co in order to get a very small percent of Co incorporated into the films.[1–4] A big issue in the field at the moment is that whether the high temperature FM in $Co:TiO_2$ films comes from Co metal/clusters or not. In this work, we have fabricated $Co:TiO_2$ films on silicon, $LaAlO_3$ (LAO) and $SrTiO_3$ (STO) substrates. Effects of the substrates on structural and magnetic properties of $Co:TiO_2$ films will be discussed in detail.

A $Ti_{0.88}Co_{0.12}O_2$ target was synthesized by a sol–gel method. 2300-Å-thick $Co:TiO_2$ films were deposited by the pulsed laser deposition (PLD) techniques (248 nm KrF laser, 5 Hz repetition rate) on unetched (100) Si, (001) LAO, and (001) STO substrates. The oxygen pressure (P_{O2}) was either 1×10^{-6} or 1×10^{-5} Torr, and the energy density was either 1.5 or 3 J/cm^2. The substrate temperature was 700 °C. After deposition, films were cooled down slowly to room temperature under the P_{O2} of 20 mTorr. The crystalline structure was studied by x-ray diffraction (XRD). The magnetization measurements were performed by a Quantum Design superconducting quantum interference device (SQUID) system from 0 to 0.5 T and from 400 K down to 5 K. The magnetic force images were observed by Nanoscope IIIA magnetic force microscopy (MFM) operated at room temperature under zero field. The chemical composition was determined by the Rutherford backscattering spectroscopy (RBS) method.

It is clearly found that the type of substrates certainly defines the structure of $Co:TiO_2$ films. With our chosen growth conditions, all $Co:TiO_2$ films on Si are rutile, while films grown on LAO and STO are anatase (Fig. 1). From Fig. 1(a), one can see that the film grown on Si is single phased rutile and highly epitaxial with the *c* axis of the rutile (around 2.96 Å) perpendicular to the substrate plane. Neither Co peak nor cobalt oxide peak was found in the spectra. Films on Si substrates are mostly *c* axis oriented but other diffraction peaks indexing on the basis of the rutile phase are also present, indicating that the film grows with several orientations (probably due to the large lattice mismatch). Other additional measurements such as the Φ scan recorded around the {110} family planes shows 90° separated peaks that gives evidence of in-plane texture of the rutile phase and similar scans taken on the {220} family planes of Si proved that the TiO_2 rutile layer grows epitaxially on Si substrates.[5] Rutile $Co:TiO_2/Si$ films were fabricated by co-sputtering from Co and Ti targets,[6] while in the present study they were grown by the PLD from one ceramic target. $Co:TiO_2$ films on both LAO and STO are not rutile but pure anatase, (001) oriented, with only anatase peaks appearing in the spectra. No peak of any impurity appeared in the XRD patterns. The out-of-plane lattice parameter calculated from the 004 reflection is about 9.52 Å and the in-plane lattice parameter obtained from the 105 reflection is about 3.77 Å and they are consistent with the values of bulk anatase.[7] Those parameters are almost the

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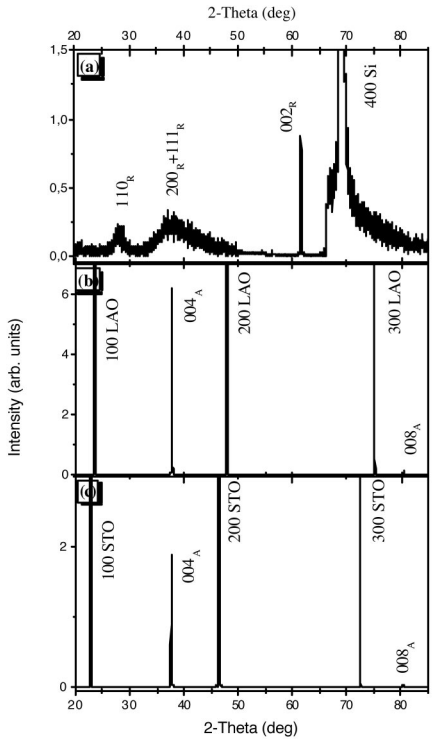

FIG. 1. X-ray diffraction pattern for: (a) a Co:TiO_2 film deposited on a Si substrate under an oxygen pressure of 1×10^{-5} Torr and a fluence of 3 J/cm^2; (b) a Co:TiO_2 film deposited on a LAO substrate under an oxygen pressure of 1×10^{-6} Torr and a fluence of 1.5 J/cm^2 and (c) a Co:TiO_2 film deposited on a STO substrate under an oxygen pressure of 1×10^{-5} Torr and a fluence of 3 J/cm^2.

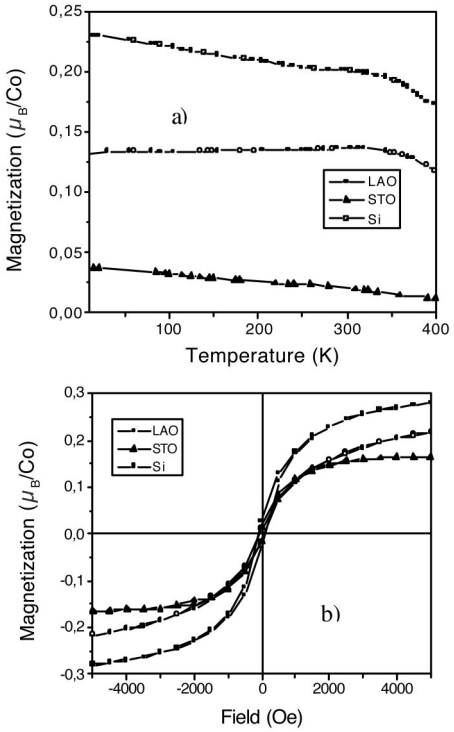

FIG. 2. Magnetization vs: (a) temperature taken at 0. 2 T and (b) magnetic field at 300 K for the Co:TiO_2 films with Co content as of 10% on Si, LAO, and STO substrates.

same for both films on STO and LAO. Films grown on both types of substrates are epitaxial and highly oriented. So far, good anatase Co:TiO_2 films were fabricated by a combinatorial library PLD from two targets,[1] while films fabricated from one ceramic target did not show good qualities (Co:TiO_2 films on STO were mixed by anatase and rutile phases,[8] or in those films, FM came from a Co cluster,[8,9] or besides having Co nanoclusters, Co:TiO_2 films showed metallic behavior).[10,11]

Along with the good crystallinity and the semiconducting behaviors[12] (where the resistivity is about 0.1 Ω cm at room temperature), our Co:TiO_2 films are room temperature ferromagnetic and the FM likely stems from the Co-doped TiO_2 matrix rather than any type of clusters. The RBS data showed that Co content in the film could be slightly deviated from that of the target, and it might vary from 6.9% to 11.6%. However, on the same type of substrate, the magnetic properties do not depend much on Co content. In contrast, with the same Co content, Co:TiO_2 films on different types of substrates clearly showed some differences in their ferromagnetic behavior. Figure 2(a) shows that all films have T_C above 400 K, however, the magnitude of magnetization is largest for the film grown on Si, and smallest for the film grown on STO. From Fig. 2(b), one can see that even though all films are ferromagnetic at room temperature, the saturation magnetization (M_s) and coercivity are different for films on different substrates. The maximum M_s is 0.31 μ_B/Co for films on Si, 0.23 μ_B/Co for films on LAO, and 0.16 μ_B/Co for films on STO. The better ferromagnetic properties obtained in films on LAO compared to those in films on STO can be explained from the viewpoint of the structural analysis. The rocking curve measurements, which were recorded around the 004 diffraction peak of anatase for films with the same growth conditions but different substrates, showed that the full width at half maximum (FWHM) of the film on LAO is smaller (0.3°) than that of the film on STO (0.5°).[13] Such a difference between LAO and STO substrates can be basically explained by the lattice mismatch between the film and the substrate as observed in Ref. 8. Indeed, the in-plane lattice parameter of anatase is 3.7848 Å, therefore the mismatch is smaller on LAO (3.789 Å) and larger on STO (3.905 Å).

Since it is not able to observe a MFM image for films on STO due to their small remanent magnetization (RM), MFM measurements were performed on two films on LAO and Si to confirm the room temperature FM (see Fig. 3). To detect the magnetic signals, a magnetized, hard Co-alloy-coated silicon tip, was applied perpendicular to the film surface with a lift height of 250 Å. Figures 3(a) and 3(b) are the topography image and the phase image (respectively) for the film with the highest Co content (11.6%) on LAO and Figs. 3(c) and 3(d) are the topography image and the phase image (respectively) for the film with the Co content of 10% on Si. For both films, magnetic responses at room temperature were observed. In Fig. 3(b), we can observe parts with a different brightness. Compared to the corresponding topography [Fig. 3(a)], one can see that the spots which appear to be dark in the MFM image do not match the dark spots in the topography, therefore, it is clear that the obtained response is really due to the magnetism of the film but not the surface effect.

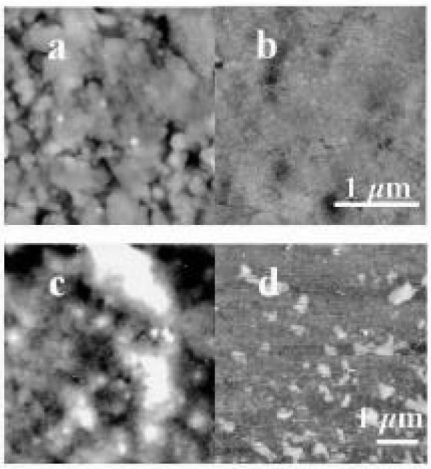

FIG. 3. Topography (A) and (C) and corresponding MFM images (B) and (D) for Co:TiO_2 thin films grown on LAO (Co content as of 11.6%) and on Si (Co content as of 10%), respectively. The topography image and the MFM image were recorded on the same area of $2.5\times2.5\ \mu m^2$ for the film on LAO and $5\times5\ \mu m^2$ for the film on Si.

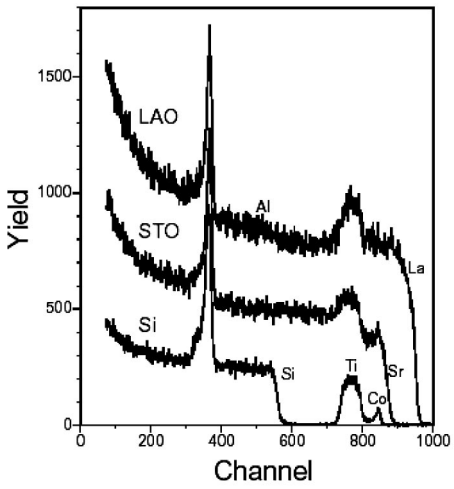

FIG. 4. RBS spectra for Co:TiO_2 films grown on LAO, STO, and Si substrates under an oxygen pressure of 1×10^{-6} Torr and a fluence of 1.5 J/cm^2.

Moreover, at room temperature, no intrinsic domain structure was seen, showing that the film is very homogeneous and has a small RM.

RBS spectra for Co:TiO_2 films are shown in Fig. 4. Because the signals from the LAO and STO completely overlap those from the films, and signal/noise ratio is comparable, it is very difficult to determine Co contents in the films grown on LAO and STO. In the spectrum of Co:TiO_2 grown on the Si substrate, peaks are well separated, and the noise/signal ratio is ignorable, therefore we may say that the compositions which were determined from these data are precise, and basically they can be used for films on LAO and STO, which were deposited in the same run. While the Ti peak has a simple rectangular shape showing that the Ti contribution is uniform over the whole thickness of the film, the Co peak has a larger height on the right hand side (corresponding to the shallower levels taken from the surface) and a smaller height on the left hand side (deeper levels). We can interpret that the Co distribution is not uniform, and Co atoms are localized mostly near the surface of the film. Calculations in this case give the results that Co distribution is richest in the 400 Å thick layer taken from the surface. For this 400 Å thick layer, the MFM is sensitive enough to reflect whether any form of ferromagnetic Co clusters exists. Note that the MFM measurement was performed on the sample with the highest concentration of Co but no trace of any cluster was seen, therefore it is reasonable to assume that the inhomogeneity is less probably found in the films with smaller Co contents. Thus, it is not able to claim that the FM of this film is due to Co clusters. For the Co:TiO_2/Si thin film, bright regions are highly visible [see Fig. 3(d)]. One can see that small domains are embedded in the background. Because the value of the saturation magnetization per Co atom for this sample is 0.31 μ_B (referring to the value in Fig. 2) which is about 1 order lower than that of the Co metal (known as 1.7 μ_B/Co), these small bright regions cannot be ascribed to Co clusters. It is more reasonable to consider them as local variations of the ferromagnetic response due to the nonuniform distribution of Co. The remark about local ferromagnetic phase observed in the Co:TiO_2 film on Si seems to be consistent with the RBS data mentioned earlier. The fact that the Co:TiO_2/LAO film is more magnetically homogeneous than the Co:TiO_2/Si film can be explained from a much bigger lattice mismatch between the film and the substrate in the latter case.

Besides the XRD pattern which showed no trace of any impurity, the modest values of M_s in our films (much smaller than that of Co metal), and the T_C just around 400 K (it must be 1000 K in the case of Co metal clusters) as well as the magnetic response observed by MFM likely ruled out the existence of Co particles and implied that the room temperature FM in our films seems to originate from the Co:TiO_2 matrix.

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