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Correlation between crystallinity and magnetism in a series of laser-ablated anatase $Ti_{1-x}Co_xO_2$ thin films

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Abstract

We report on ferromagnetic Co-doped TiO_2 films grown by laser ablation on $LaAlO_3$ and $SrTiO_3$ substrates. Films on both types of substrate are highly crystallized, very well epitaxial, single-phased anatase and show ferromagnetism far beyond room temperature. Due to the smaller lattice mismatch in the case of $LaAlO_3$ substrates, films on $LaAlO_3$ substrates are more oriented than films on $SrTiO_3$ substrates, and therefore have better quality with a larger saturation magnetic moment. Besides x-ray diffraction data, our magnetic force microscopy results also suggest that the ferromagnetism in Co-doped TiO_2 films probably does not stem from either Co-enriched TiO_2 clusters or Co segregations.

One of the recent trends in the field of spintronics is an exploration of magnetic semiconductors with Curie temperature (T_C) higher than room temperature [1, 2]. Theory predicted that the introduction of Mn/Fe/Ni/Co/V/Cr into materials such as GaN, GaP, ZnO and TiO_2 under the right conditions would be found to produce ferromagnetism (FM) near or above room temperature [1, 2]. Growth of these diluted magnetic semiconductors (DMSs) by thin film techniques, such as molecular beam epitaxy (MBE) or pulsed laser deposition (PLD), provides an excellent control of the dopant concentration and the ability to grow single-layer films [1–4].

Since the discovery of Matsumoto *et al* [5], Co:TiO_2 ($Ti_{1-x}Co_xO_2$) thin films have attracted many research groups due to their exhibition of very T_C. However, so far, Co:TiO_2 films have mostly been fabricated from two targets, Ti and Co or TiO_2 and Co:TiO_2 with a very high concentration of Co in order to get very few per cent of Co incorporated in the films, by using combinatorial laser ablation, MBE laser ablation, oxygen plasma-assisted MBE or

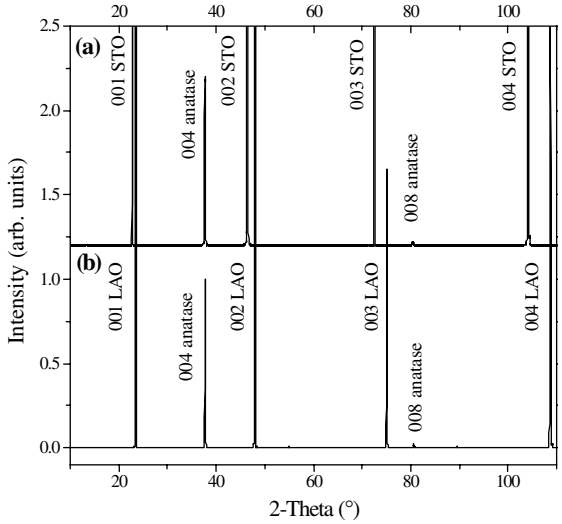

Figure 1. X-ray diffraction pattern (a) for a Co:TiO_2 film on STO under oxygen pressure of 1×10^{-5} Torr and fluence of 3 J cm^{-2} and (b) for a Co:TiO_2 film on LAO under oxygen pressure of 1×10^{-6} Torr and fluence of 1.5 J cm^{-2}.

co-sputtering [5–8]. Some papers reported on films which were laser ablated from a ceramic target but as a result Co did not get into the structure but remained as Co metal [9, 10]. In this work, we report on Co-doped TiO_2 films grown from a ceramic target on $LaAlO_3$ (LAO) and $SrTiO_3$ (STO) substrates by using a conventional PLD system. Structural and magnetic properties of those films as well as substrate effects on them will be focally investigated.

A $Ti_{0.88}Co_{0.12}O_2$ target was synthesized by a sol–gel method. $Ti_{1-x}Co_xO_2$ films were deposited by the PLD technique ($\lambda = 248$ nm KrF laser, 5 Hz repetition rate) on (001) LAO and (001) STO substrates. The oxygen partial pressure was kept in the range from 1×10^{-6} to 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 to room temperature under an oxygen pressure of 20 mTorr. The typical thickness of the films was 2300 Å. The structural study was done by x-ray diffraction (XRD). The magnetic measurements were performed by a Quantum Design superconducting quantum interference device (SQUID) system (in the range of temperature from 400 to 5 K, under magnetic field from 0 to 0.5 T) and a magnetic force microscope (Nanoscope IIIA MFM operated at room temperature in zero field). The chemical composition was examined by a Rutherford backscattering spectroscopy (RBS) method.

RBS data showed that, depending on growth conditions, Co content is slightly deviated from that of the target and might vary from 6.9% to 11.6%, but in all cases Co atoms are localized mostly near the surface (Co content could be 30% in the 400 Å thick layer taken from the surface but only 6% in deeper layers) [11]. Note that Co distribution in our films is completely different from that of Co:TiO_2 films fabricated by laser MBE under a similar range of oxygen pressure [12] (according to this report, Co nanoclusters were localized mainly at the interface between the film and the substrate).

X-ray measurements showed that Co:TiO_2 films on both types of substrate are single-phased anatase, (001) oriented, with only anatase peaks appearing in the spectra. No peaks of cobalt or cobalt oxide are found (see figure 1). The out-of-plane lattice parameter calculated from the 004 reflection is found to be $\approx$9.52 Å. The in-plane lattice parameter is obtained from the 105 reflection and equal to $\approx$3.77 Å in agreement with the values of bulk anatase [13].

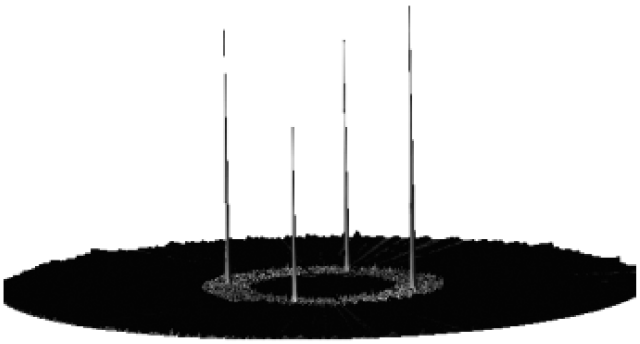

Figure 2. An x-ray pole figure recorded around the {105} reflection of a Co:TiO_2 film ($x = 6.9\%$) on STO. Note the four diffractions peaks separated by 90° indicating a fourfold symmetry.

Note that the values are substrate independent, indicating that the mismatch of the film does not affect its structure. Films grown on both types of substrate are well epitaxial and highly oriented (see the rocking curve data shown later). Figure 2 is an example of a pole figure measurement performed around the 105 reflection, on the film grown on STO under the oxygen pressure of 1×10^{-5} Torr and the fluence of 3 J cm^{-2}. We can see four peaks separated by 90° indicating fourfold symmetry with in-plane alignment of the film with respect to the substrate (cube over cube), i.e. the epitaxial relationships as follow: $[100]_F \parallel [100]_S$ and $[010]_F \parallel [010]_S$ (where subscripts S and F refer respectively to the substrate and the film). So far, no Co:TiO_2 films fabricated by a conventional PLD and from a ceramic target show such a pure phase of anatase and such a good orientation. Good anatase Co:TiO_2 films were fabricated by a combinatorial library PLD from two targets [5] while films fabricated by a conventional PLD and one ceramic target did not show good qualities (Co:TiO_2 films on STO were mixed by anatase and rutile phases [9]; moreover, in all films, FM was claimed to be caused by Co segregations [9, 10] or along with presented Co nanoclusters, films were metallic near room temperature [12]). Besides the good crystallinity and the obvious semiconducting behaviours[4], magnetic measurements also showed that our films are room temperature ferromagnetic and the FM seems to originate from the Co-embedded TiO_2 matrix rather than any type of cluster.

In spite of the difference in growth conditions, the magnetic properties do not differ much from one film to the others. One example of MFM images is shown in figure 3 for the film with the highest Co content (11.6%) on LAO. From the MFM image (figure 3(b)), we can see parts with a different brightness. By noting that, in comparison with the corresponding topography (figure 3(a)), the spots which appear dark in the MFM image do not match the dark spots in the topography, we can confirm that the obtained response (the contrast) is due to the magnetism of the film and not due to the surface effect. On the other hand, at room temperature, no intrinsic domain structure was seen, showing that the film is very homogeneous. According to the RBS data, Co atoms are situated more densely near the surface where MFM is surely sensitive enough to detect whether ferromagnetic clusters exist. Besides, MFM was performed on an area of 2.5×2.5 μm^2 so nanometre-sized clusters must be observed if available, but no trace of them was seen. Measurements on the same sample with a larger scale were also performed. From figure 4, one can see both the topography and MFM images recorded in the area of 20×20 μm^2. From the topography image (figure 4(a)), it is obvious that the grain distribution is rather uniform (also see the zoom for a smaller area of 5×5 μm^2 in

[4] Private data: all Co:TiO_2 films on LAO and STO have resistivity at room temperature of about 1 Ω cm and it rises quickly with decreasing temperature as for typical semiconductors.

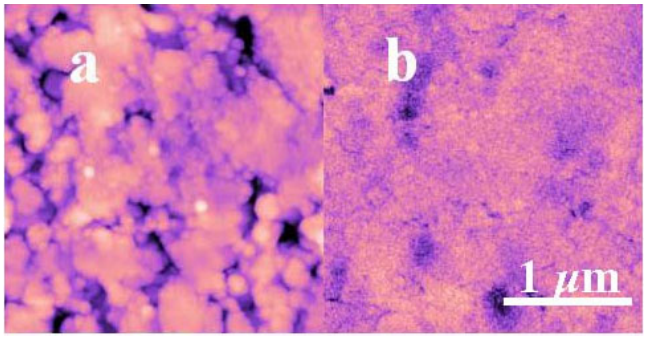

Figure 3. Magnetic force micrographs taken at room temperature and zero field for the Co:TiO_2 film with Co content of 11.6% on LAO: (a) topography image and (b) MFM image. To observe the magnetic region of the film, a hard Co-alloy-coated silicon tip, which was magnetized along the tip axis, was applied perpendicular to the film surface with a lift height of 250 Å. Both topography image (a) and MFM image (b) were recorded on the same area of 2.5 × 2.5 μm^2.

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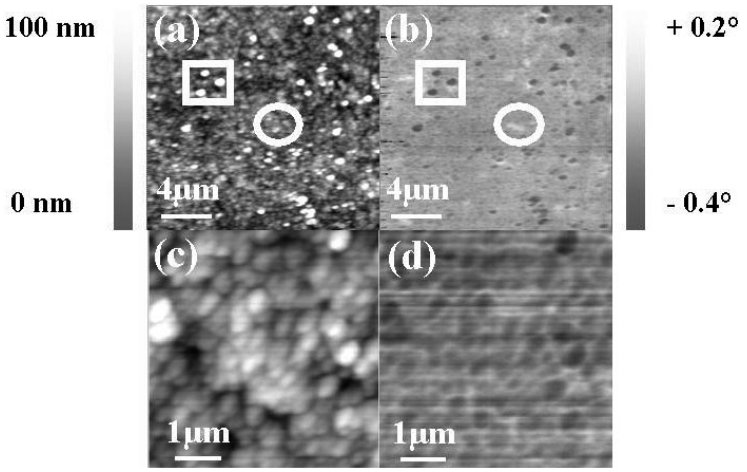

Figure 4. Magnetic force micrographs taken at room temperature and zero field for the Co: TiO_2 film with Co content of 11.6% on LAO: (a) topography image and (b) MFM image. Both topography image (a) and MFM image (b) were recorded on the same area of 20 × 20 μm^2. The squares and circles are only guides for the eyes. Zooms of an area of 5 × 5 μm^2 are shown in (c) and (d) for both topography and MFM images, to see more clearly the magnetic structure.

figure 4(c)). Comparing with the topography image, in figure 4(b), one can see that apart from the dark spots matching the white spots in figure 4(a) which is due to the surface effect while the tip is touching the surface (marked by squares as examples), in other places (marked by circles as examples) there is no corresponding contrast between the topography and the MFM images and the observed signals must be due to the real magnetic responses, in fact rather strong. Figure 4(b) shows a domain structure which is very uniform (see also figure 4(d) for a zoom for an area of 5 × 5 μm^2), with a similar appearance at the boundaries in between one and the other. However, the size of each is exactly the same as the size of the grain that we can see from the topography image (figure 4(b) and/or figure 4(c)), and we must say that the observed domains are induced by the limitation of grain boundaries and morphology rather

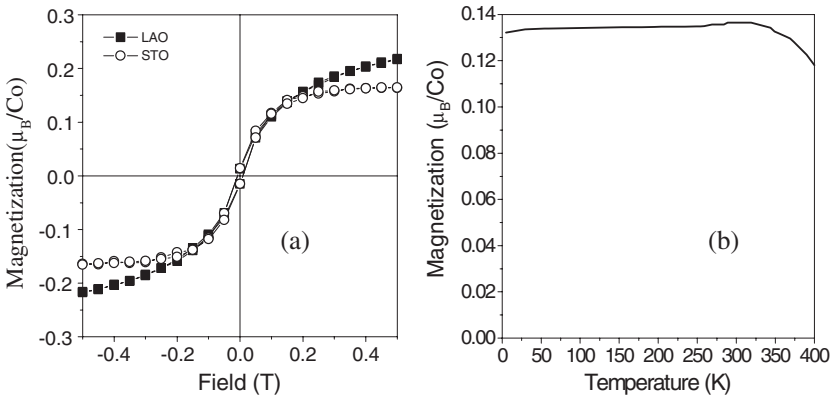

Figure 5. Magnetization versus (a) magnetic field taken at 300 K and (b) temperature under 0.2 T for the Co:TiO_2 films with $x = 10\%$ on LAO and STO.

than of the real ferromagnetic domains of a ferromagnet. The ferromagnetic domains which may exist must have a size bigger than the size of the grain. On the other hand, note that the roughness of the film is 14.2 nm, showing that the film has a rather flat surface. From the uniform distribution of the grain, as well as from the value of magnetization which will be discussed below, it is hard to assume that the FM in the film is due to Co particles/clusters.

A well defined hysteresis loop was observed in all films, showing that they are ferromagnetic even at room temperature. With different growth conditions, the saturation magnetization (M_s) and the coercivity (H_C) of films are different, but all have T_C above 400 K (see a typical example in figure 5). The highest M_s we can obtain is 0.23 μ_B/Co for the film on LAO with Co content x of 10% (this film was deposited under the lowest applied oxygen pressure and the lowest fluence. Similarly, among all films grown on STO, the film grown under the same conditions also has the highest M_s). From x-ray analysis, only a small difference in lattice parameters versus Co content is recognized. $M(H)$ curves (figure 5(a)) for two films with the same fabrication conditions (therefore, the same Co content x), one on LAO and one on STO, show that the film on LAO has a larger M_s and a stronger FM. The better magnetic properties obtained in films on LAO substrates can be explained from the viewpoint of the structural analysis. From rocking curve measurements which were recorded around the 004 diffraction peak of anatase, for four pairs of films with the same growth conditions but different substrates (one example for the film with Co content of 6.9% is shown in figure 6), it is found 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°). These values are close to the reported value of Kim *et al* (0.66°) [12] and Shinde *et al* (0.3°) [10]. Such a difference between LAO and STO substrates can be mainly explained by the lattice mismatch between the film and the substrate as observed by Stampe *et al* [9] where the FWHM is significantly larger on STO. 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).

The saturation magnetic moment of Co metal is known as 1.7 μ_B/Co and it was found in Co:TiO_2 films with Co clusters [9]. If the FM comes from Co-enriched TiO_2 clusters, it should be about 1.2 μ_B/Co [8]. Such a modest value of M_s of 0.23 μ_B/Co or smaller in our films, and the T_C just around 400 K (which is much lower than the value of above 1000 K of Co metal clusters) as well as the magnetic homogeneity observed by MFM (magnetic signals were detected while no domain wall was present), suggest that the room temperature FM in our films seems to originate from Co-embedded TiO_2 matrix.

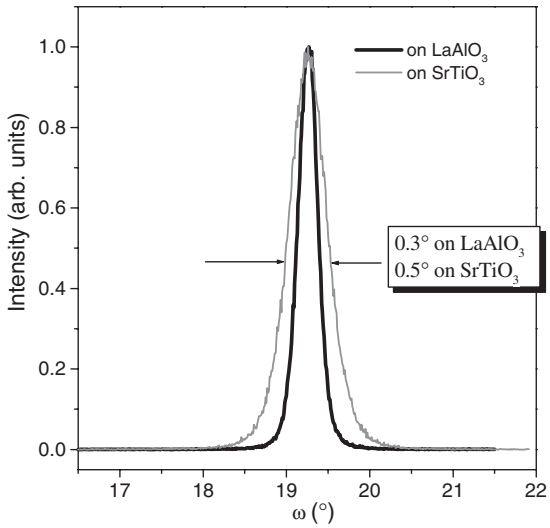

Figure 6. Rocking curves (ω scan) recorded around the 004 reflection of two films with $x = 6.9\%$ on both LAO and STO substrates. Note the smaller value of the FWHM on LAO.

In summary, we have obtained pure anatase Co:TiO_2 films on LAO and STO substrates. Films with various conditions are all ferromagnetic far beyond room temperature. All grown films are highly crystallized, very well epitaxial and single-phased anatase. Due to the smaller lattice mismatch in the case of LAO, films on LAO are somewhat more oriented than films on STO, and therefore have better quality with a larger saturation magnetization. Our results enforce the assumption that the room temperature FM in our Co:TiO_2 films seemingly stems from the Co:TiO_2 matrix rather than any type of cluster.

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