Room temperature ferromagnetism in anatase $Ti_{0.95}Cr_{0.05}O_2$ thin films: Clusters or not?

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Laser ablated Cr-doped TiO_2 thin films grown on $LaAlO_3$ substrates are single phased anatase and room temperature ferromagnetic. The magnetic moment of Cr-doped TiO_2 films is rather large, and it is consistent with the theoretical predictions. Magnetic force microscopy measurements certainly suggested that the strong ferromagnetism at high temperature in Cr-doped TiO_2 films is intrinsic, and it must originate from the diluted magnetic matrix but not from any form of clusters. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1841457]

Recently, study on ferromagnetic semiconductors with a Curie temperature (T_C) well beyond room temperature has become an attractive topic for many research groups due to the promising potential of those materials for spintronics applications. One of the biggest interests is the search for high T_C ferromagnetism (FM) in oxides such as ZnO, TiO_2, or SnO_2 doped with transition metals.[1–7]

Besides the quest for materials with a high T_C along with having large magnetic moments, it is of utmost importance to find doped compounds which have great homogeneities, where the dopant atoms could be well dissolved into the oxide host to be "really diluted" and the resulted FM indeed originates from the doped matrices.

Theoretical work has predicted that doping Cr may induce FM in ZnO crystal.[8,9] In this letter, we report about room temperature FM in Cr-doped TiO_2 thin films.

270-nm-thick $Ti_{0.95}Cr_{0.05}O_2$ films were grown on (001) $LaAlO_3$ substrate by using the pulsed laser deposition method from a $Ti_{0.95}Cr_{0.05}O$ ceramic target (KrF laser with $\lambda = 248$ nm). The repetition rate was 5 Hz and the energy density was 2 J/cm^2. The substrate temperature was either 700 or 650 °C. During deposition, the oxygen partial pressure (P_{O_2}) was kept as 10^{-6} Torr, and after deposition, films were cooled down slowly to room temperature under a P_{O_2} of 20 mTorr. The structural study was done by x-ray diffraction (XRD) using a Seifert XRD 3000P. The magnetization measurements were performed by a Quantum Design superconducting quantum interference device system from 0 up to 0.5 T under a range of temperatures from 400 K down to 5 K. The magnetic force microscopy measurements using Solver LS (NT-MDT) were performed at room temperature in zero field. The chemical composition was determined by a Rutherford backscattering spectroscope (RBS).

The Cr content in Cr:TiO_2 films was determined from RBS data to be 5% and it is almost the same as the Cr content in the synthesized target (the error of RBS is of 4%). XRD data showed that all Cr:TiO_2 film are single phased anatase, well *c*-axis oriented and neither peak of Cr metal nor CrO_2 phase is seen (see an example in Fig. 1). However, the films which were fabricated at 650 °C seem to be better crystallized (XRD peaks are sharper with a larger intensity) and from magnetization data shown later, it is also obvious that those films are more strongly ferromagnetic, and thus, there must be some correlation between the structural and magnetic properties. This is similar to what was observed in Co:TiO_2 films on LAO and STO as well as Fe:TiO_2 films on Si.[10,11] The out-of-plane lattice parameter as $c = 9.493$ Å is deviated a bit from that of the nondoped anatase TiO_2 as of 9.523 Å.

The magnetization versus temperature (taken at 0.2 T) and versus magnetic field (taken at 300 K) for Cr:TiO_2 films are shown in Fig. 2. Figure 2(a) shows that all films have Curie temperature (T_C) around 400 K (while the magnetic moment remains almost constant in the whole range of temperature below T_C, and starts falling down while approaching 400 K). The saturation magnetization (M_s) of Cr:TiO_2 films is rather large, indicating a very strong FM in those films. A well-defined hysteresis loop which could be seen clearly from the $M-H$ curves [Fig. 2(b)] taken at room temperature for Cr:TiO_2 films ensured the observation for room tempera-

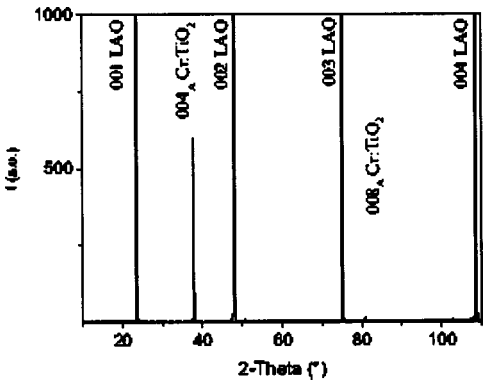

FIG. 1. XRD patterns of a film of $Ti_{0.95}Cr_{0.05}O_2$ fabricated at 650 °C. Anatase peaks are marked by "A."

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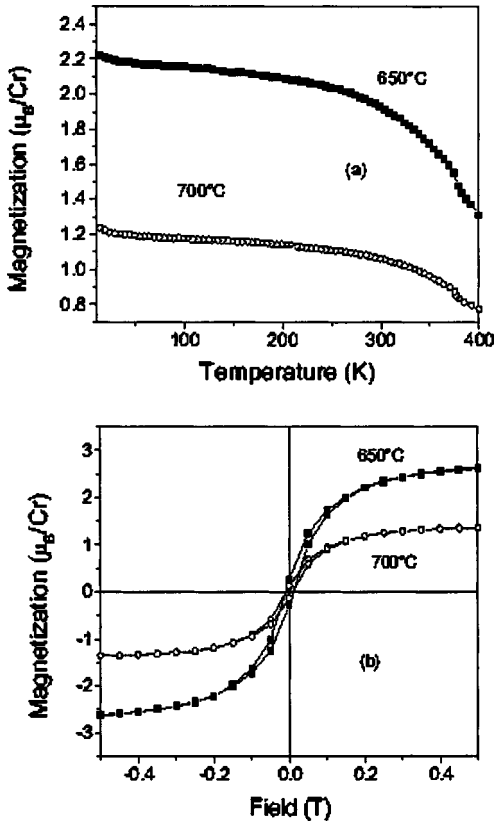

FIG. 2. Magnetization of $Ti_{0.95}Cr_{0.05}O_2$ films fabricated at 650 and 700 °C vs (a) temperature under 0.2 T and (b) magnetic field at 300 K.

ture FM mentioned earlier. Certainly all $Cr:TiO_2$ films are ferromagnetic even beyond room temperature. Note that different growth conditions could result in a large difference in the magnitude of saturation magnetization (M_s) (it is 1.3 μ_B/Cr for films fabricated at 700 °C and 2.6 μ_B/Cr for films fabricated at 650 °C). Measurements for four films fabricated under the same growth conditions showed that those results are reproducible.

The large magnetic moment as of 2.6 μ_B/Cr is in accord with the prediction of the theory that, as regards the magnitude of magnetic moment, Cr doping results in a value about half of that of V doping but surpasses that of Fe doping (in comparison with the values as of 4.2 μ_B/V for $V:TiO_2$ films and 1.5 μ_B/Fe for $Fe:TiO_2$ film which were grown under the same conditions).[8,4,12] This value could not result from Cr metal clusters because Cr metal is known as paramagnetic at high temperature and antiferromagnetic below 308 K. Both the T_C and M_s values of $Cr:TiO_2$ films (at larger than 400 K and 2.6 μ_B/Cr, respectively) do not match those values of CrO_2 either (CrO_2 has T_C as of 386 K and $M_s = 2.03$ μ_B/Cr),[13] thus it is impossible to presume that FM in the film comes from CrO_2 clusters (also recall the XRD data with no peak of CrO_2).

Our $Cr:TiO_2$ films have a very high resistivity (about 10^7 Ω cm at room temperature and keeps oscillating in the same order in the whole range of temperatures and just rises up slightly at very low temperatures) and certainly it is semiconductors. Since the films do not have metallic behavior, there are two assumptions: One is that our $Cr:TiO_2$ films appear to be cluster-free. Another is that films may have clusters which are not connected to one another, therefore, no conductive flow. Theoretically, Sheng *et al.*[14] calculated for

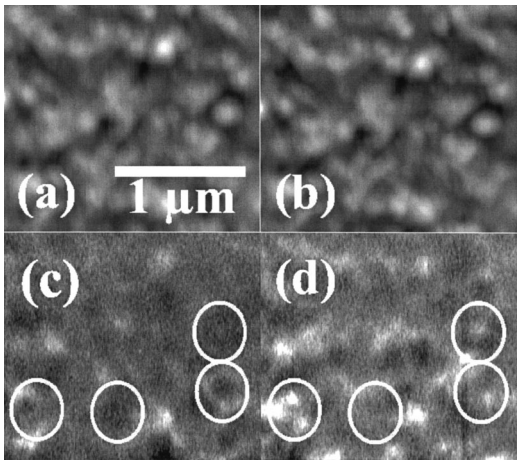

FIG. 3. (a) and (b) Topography images of the same area of 2 μm × 2 μm for the $Ti_{0.95}Cr_{0.05}O_2$ film fabricated at 650 °C. Corresponding phase images recorded using different polarization for the cantilever: Up for (c) and Down for (d). Circles are only guides for eyes.

hopping transport of metallic clusters, and found that samples having clusters should have a relationship with temperature that obeys the law of $\log R \propto T^{-1/2}$ (and experimental work on $Co:TiO_2$ films with the existence of Co clusters also confirmed it).[15] In our films, $\log R$ versus $T^{-1/2}$ is not linear, and definitely it can be considered as a indirect evidence for having no clusters.

In order to confirm the room temperature FM in those films and clarify its magnetic origin, direct observations of local magnetic response from MFM measurements (by using atomic force microscopy in MFM mode) were done. We used a cantilever whose radius of curvature is less than 90 nm and is sensitive to magnetic forces (i.e., it was coated with two layers of Co and Cr), and it was magnetized parallel to its axis. Five topography measurements confirm the flatness of the sample with the roughness estimated as of only 1.26 nm. Figures 3(a) and 3(b) show topography images of the area of 2 μm × 2 μm recorded during two scans using two opposite directions of magnetization of the cantilever (i.e., Up and Down).

The corresponding phase changes MFM, recorded with the same lift height of 52 nm, are shown in Figs. 3(c) and 3(d), respectively. Note that several dark spots in the MFM images do not match dark spots in the topography images [in Figs. 3(a) and 3(b)], then surely the magnetic signals are real, and they are not due to the surface effect. Strong magnetic signals detected confirm the strong FM which was observed from magnetization measurements. Also, we can notice that the different brightness showing only a small variation of the MFM response does not support the presence of any magnetic cluster which should give a very strong magnetic response and a clearer contrast (in principle, the difference in magnetic response when moving from one spot of having no clusters to another spot with clusters must go through a steep rise which is akin to a step).[16] On the contrary, what we observed is only like "a fluctuation" and it is in favor of a real diluted magnetic structure.

The cantilever, which had been magnetized by using a magnetic field of 0.35 T, seems to present a field which is strong enough to tilt the magnetic moments of a few points [see circles in Figs. 3(c) and 3(d)]. Note that, for the image recorded using the Up polarization configuration of the can-

tilever [Fig. 3(c)], the observed contrasts are not totally opposite to those obtained in the image taken with the Down polarization configuration [Fig. 3(d)]. This observation is another proof (besides the comparison between the MFM images and the topography images) to confirm that the detected magnetic signal is real, and the sample is certainly ferromagnetic at room temperature. On the other hand, it shows that the sample has not been demagnetized between these two measurements, so that the magnetic moments aligned with the field in the previous state still remained, therefore the field with the opposite direction applied in the next state was just able to align the magnetic moments in the specimen partially (that is why it could not turn all the spins in the opposite direction to give a completely opposite contrast in MFM measurements).

In conclusion, we obtained laser ablated $Ti_{0.95}Cr_{0.05}O_2$ thin films on $LaAlO_3$ substrates as strong ferromagnets with a single phased anatase structure. The maximum saturation magnetic moment which could be achieved in our films is 2.6 μ_B/Cr, and this value seems to be in accord with the prediction of theories. Moreover, MFM measurements confirm the room temperature FM, and more crucially, also ensures that the Cr-doped TiO_2 films certainly have a diluted magnetic structure with the FM originated from the doped matrix rather than any type of magnetic cluster.

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