Magnetic structure of $V:TiO_2$ and $Cr:TiO_2$ thin films from magnetic force microscopy measurements

Nguyen Hoa Hong,[a] Antoine Ruyter, and François Gervais
Laboratoire LEMA, UMR 6157 CNRS/CEA, Faculté des Sciences et Techniques, Université F. Rabelais, Parc de Grandmont, 37200 Tours, France

W. Prellier
Laboratoire CRISMAT, UMR 6508 CNRS, ENSICAEN, 6 Bd du Maréchal Juin, 14050 Caen, France

Joe Sakai
School of Materials Science, JAIST, Asahidai 1-1, Tatsunokuchi-machi, Ishikawa 923-1292, Japan

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Ferromagnetic V-doped TiO_2 and Cr-doped TiO_2 films were fabricated by the pulsed laser deposition technique on $LaAlO_3$ substrates. All $V/Cr:TiO_2$ films are single phased anatase, well epitaxial, *c*-axis oriented, and strongly ferromagnetic at room temperature. Besides giving evidences for a great flatness and magnetic homogeneities of those films, magnetic force microscopy measurements implied that the V/Cr-doped TiO_2 films seem to have a diluted magnetic structure with the ferrmagnetism originated from the doped matrix rather than any type of magnetic clusters. The size of the ferromagnetic domains was assumed to be 5–10 μm. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1854072]

Over the last few years, diluted magnetic semiconductors (DMS) have attracted many attentions due to their promising potential for applications in spintronics. Many research groups have doped transition metals (TM) for Ti or Zn in TiO_2 or ZnO in order to introduce ferromagnetic ordering oxide hosts. However, the question whether the ferromagnetism (FM) observed in TM-doped semiconducting oxides really comes from the doped matrix or not is still debated in this research field. Even though Co-doped TiO_2 or ZnO thin films have been fabricated by various techniques,[1–4] not much work has been done on V/Cr/Fe/Ni-doped ZnO or TiO_2 films. Among all of those potential dopants, V was predicted to be the most promising candidate to dope for ZnO in order to obtain a strong FM.[5] However, so far, there has been only one report about V:ZnO thin films[6] and no experimental study has been done on $V:TiO_2$ thin films. Saeki *et al.* reported that in their V:ZnO films, only metallic samples are magnetic, therefore, the nature of the observed FM in their films must originate from V metal clusters or so.[6]

It appears that the nature of FM in $TM:TiO_2$ films is still not clear. Therefore, how to obtain good DMS films with room temperature FM arising from the doped matrix is very crucial indeed. $TM:TiO_2$ (TM=V, Cr, Fe, Co, and Ni) thin films were fabricated by laser ablation from ceramic targets under various conditions. Structural and magnetic properties have been investigated thoroughly. Among all of our $TM:TiO_2$ films, $V:TiO_2$ and $Cr:TiO_2$ films have rather large magnetic moments along with an extremely flat surface. Thus, we undertook magnetic force microscope studies on $V/Cr:TiO_2$ films to clarify the nature of FM since they could be good representatives for the $TM:TiO_2$ family.

2700 Å thick films of $V:TiO_2$ and $Cr:TiO_2$ were deposited from $(V \text{ or } Cr)_{0.05}Ti_{0.95}O_2$ ceramic targets by the pulsed laser deposition (PLD) technique (248 nm KrF excimer laser, pulses of 5 Hz) on (001) $LaAlO_3$ (LAO) substrates. The partial oxygen pressure P_{O_2} was 10^{-6} Torr and the energy density was about 2 J/cm^2. The substrate temperature was 650 °C. After deposition, all films were cooled down to room temperature under a P_{O_2} of 20 mTorr. The magnetic measurements were performed by a Quantum Design superconducting quantum interference device system under a magnetic field from 0 to 0.5 T in the range of temperature from 400 K down to 5 K and the magnetic force microscopy (MFM) measurements using Solver LS (NT-MDT) were performed at room temperature in zero field. As for the $Cr:TiO_2$ film, we used a cantilever whose the radius of curvature is less than 90 nm and it 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. As for the $V:TiO_2$ films, we used a tip which was coated by two layers of Co and Cr for measurement at small scales and another tip which was coated by an alloy of FeCoNi for large scales (25×25 μm^2 or 40×40 μm^2) to examine magnetic domains without inducing any modification of the magnetic structure. The tip was magnetized parallel to the film plane (the same as the direction of the applied field in magnetization measurements).

X-ray diffraction (XRD) data (Fig. 1) showed that $V/Cr:TiO_2$ films are single phased anatase, *c*-axis oriented, and no peak of impurity was seen. It appears that V and Cr seem to be dissolved well into TiO_2 structure. Both $V:TiO_2$ and $Cr:TiO_2$ films are room temperature ferromagnetic (with the Curie temperature above 400 K) with very large magnetic moments as of about $4.2\mu_B$ per V atom and $2.6\mu_B$ per Cr atom, respectively [see the $M(H)$ curves taken at 300 K in Fig. 2 as well as the inset for $M(T)$ curves taken at 0.2 T. Note that in these measurements, the magnetic field was applied parallel to the film plane].[7,8] It is known that an isolated

[a]Electronic mail: hoahong@delphi.phys.univ-tours.fr

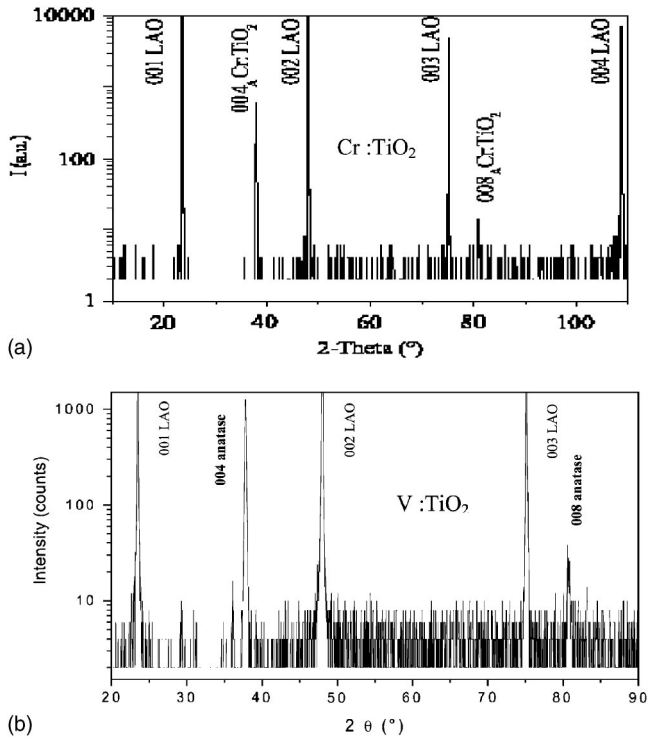

FIG. 1. XRD patterns for $Cr:TiO_2$ and $V:TiO_2$ films.

V atom has a permanent magnetic moment of $3\mu_B$ while bulk V is paramagnetic. The giant magnetic moment as of about $4\mu_B/V$ in $V:TiO_2$ films does not come from V clusters, because, according to a theoretical work calculated for small V clusters, the magnetic moment is the largest (as of $1\mu_B$) when the size of V clusters is 2 atoms, and it decreases as the cluster size increases, then vanishes for V_{15} ($M=0.03\mu_B$).[9] The large value as of $2.6\mu_B/Cr$ of $Cr:TiO_2$ films also could not be resulted from Cr metal clusters because Cr metal is known as paramagnetic at high temperature and antiferromagnetic below 308 K.[10]

As mentioned earlier, from XRD, no peak of impurity was observed since if nanometersized clusters would exist, they might not be detected due to the detection limit of XRD of less than 5%. To ensure whether there are small magnetic clusters or not, as well as to clarify the homogeneity of the films, at first, we performed MFM measurements with a very small scaling.

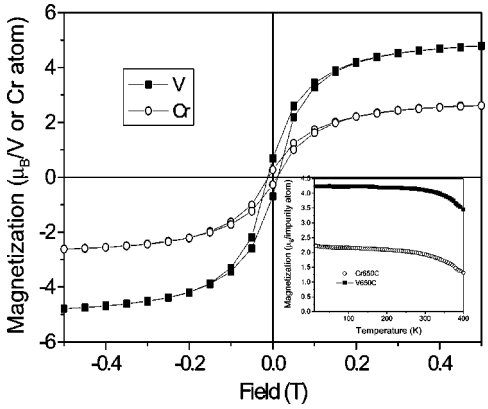

FIG. 2. Magnetization vs magnetic field at 300 K for $Cr:TiO_2$ and $V:TiO_2$ films. The inset shows *M-T* curves taken at 0.2 T.

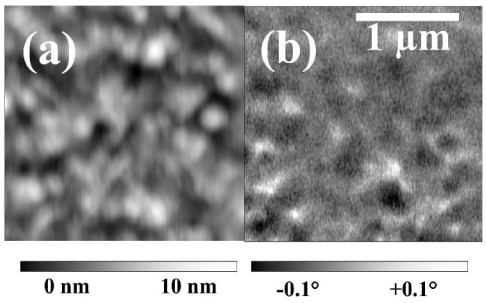

FIG. 3. Topography image (a) and the corresponding MFM image (b) of the same area of 2×2 μm^2 for the $Ti_{0.95}Cr_{0.05}O_2$ film. The tip was magnetized perpendicular to the film plane.

The $Cr:TiO_2$ film gave clear magnetic signals at room temperature and revealed a smooth surface. Five topography measurements gave an estimation of the roughness of the $Cr:TiO_2$ film as of only 1.26 nm. Figure 3(a) shows the topography image of the area of 2×2 μm^2. The corresponding phase of MFM (recorded with a lift height of 52 nm) is shown in Fig. 3(b). Note that several dark spots in the MFM images do not match dark spots in the topography images, therefore the recorded magnetic signals are real, and not due to the surface effect. Magnetic signals detected at room temperature confirmed the strong FM which was observed from magnetization measurements. We also can notice that the different brightness showing only a small variation of the MFM response and it is not in favor of any magnetic cluster. According to Ref. 11, magnetic clusters must give a very strong magnetic response and a very clear contrast, because, 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. In contrast, what we observed is only a small difference in magnitude of magnetic signals and it seems to reflect a diluted magnetic structure. The white regions that one may see in contrast with the black regions are only the reflections due to the stray field at the edge of the grains (interpreted from the comparison with the grain size which could be seen from the topography image). Thus, the observed contrast was caused by the limitation of the grain morphology, but not by any real domain structure.

Similarly, the diluted magnetic structure was observed in $V:TiO_2$ films. The film gave strong signals at room temperature. Figure 4(a) shows a topography image taken on the area of 2.5×2.5 μm^2 and Fig. 4(b) is the corresponding MFM image. The topography image taken in this small scale confirms the film flatness with the local roughness of 2 nm. If the sample is not very flat, the detected signal for the topography image is mainly due to the roughness of the film. On the contrary, when the sample has a great flatness, the magnetic signals would show up at the same time, thus, they could be also detected. In the topography image [Fig. 4(a)], we can also observe the magnetic signals, therefore, it is for sure that the film has an extremely flat surface.

By comparing Figs. 4(a) and 4(b), one can see that the MFM image is completely different from the topography one, thus, the strong signals detected at room temperature are due to the real magnetic responses but not the surface effect. On the other hand, the little difference in brightness of the

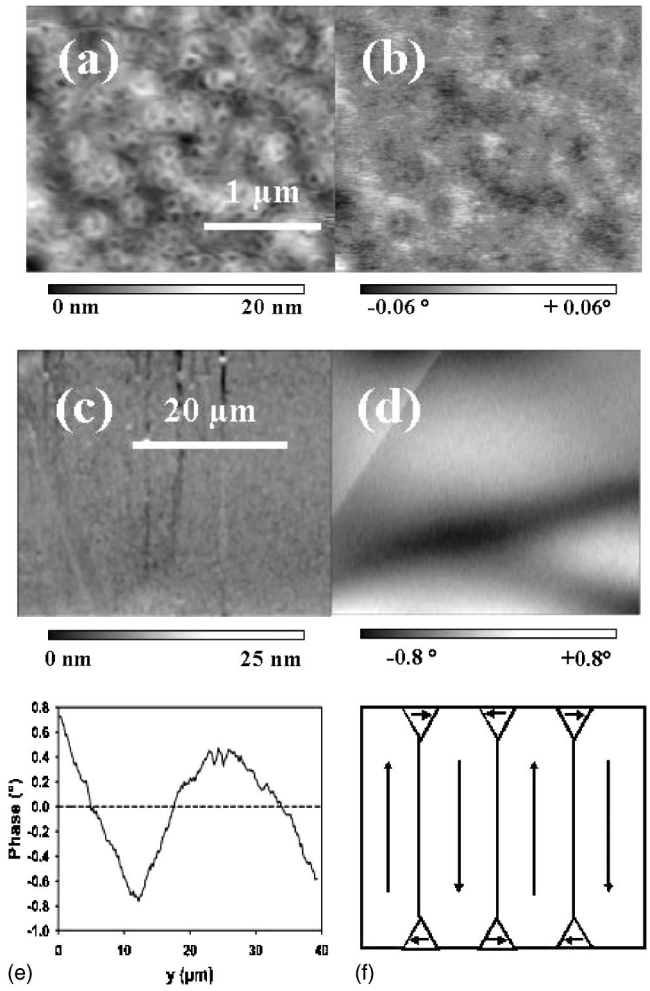

FIG. 4. For the $Ti_{0.95}Vr_{0.05}O_2$ film: (a) and (b) Topography image and the corresponding MFM image of the same area of 2.5×2.5 μm^2, (c) and (d) topography image and the corresponding MFM image of the same area of 40×40 μm^2. The tip was magnetized parallel to the film plane (e) The profile of phase values corresponding to the image (d) taken vertically and (f) a schematic for a domain structure.

relative MFM responses (see a small variation in magnetic phase changing only in between very small values of −0.06° and 0.06°) confirms the absence of any magnetic cluster. The MFM image of $V:TiO_2$ film reveals a real diluted magnetic structure with a great magnetic homogeneity. No domain wall was observed suggesting that the size of ferromagnetic domains must be larger than the scale that we performed these measurements.

Intentionally, in order to determine the domain size of the $V:TiO_2$ ferromagnet, MFM measurements were performed on the area of 40×40 μm^2 (see Fig. 4(c) for the topography image and Fig. 4(d) for the corresponding MFM image). In this large scale, the roughness of the films was determined averagely as of 14 nm. No clue of clusters was seen (if clusters are observed in this big scale, then correspondingly, we must observe some peak of alien phases from XRD also, but it is not the case, consistently). The difference in absolute values of phase is large, going from −0.8° to 0.8° as indicated in Fig. 4(d), and it confirms the real signals of a strong FM at room temperature. The white slide at the corner must be due to the constrains of the substrate (i.e., the twinning of $LaAlO_3$) which was confirmed by finding no difference on the surface when checking the signals crossing over it. Apart from it, we can see clearly some straight separations between white regions and black regions indicating a domain structure that we have been searching. From the profile of phase sweeping through the cross section vertically, one can see that the magnetic phase changes from a positive value (highest +0.8°) for the white region to a negative value (lowest −0.8°) for the black region and turns to a positive one again for the next white region [Fig. 4(e)]. It is likely that, in this film, there is a ferromagnetic domain structure where the directions of magnetization of the two nearest neighbor domains are opposite to each other [in order to easily imagine, see the schematic plotted in Fig. 4(f)]. The size of those ferromagnetic domains is big: according to what we can see from Fig. 4(d), as for the white regions, it is probably larger than 10 μm, and as for the black ones, the size is about 4–5 μm. Those two are comparable, so that it is not possible to interpret the black gaps as domain walls but they are domains themselves. The domain walls should be those straight lines which separate white and black parts.

In conclusion, we obtained laser ablated $Ti_{0.95}Cr_{0.05}O_2$ and $Ti_{0.95}V_{0.05}O_2$ thin films on $LaAlO_3$ substrates as strong ferromagnets with a single phased anatase structure. MFM measurements confirmed the strong FM at room temperature of those films, and more importantly, suggested that the V/Cr-doped TiO_2 films likely have a diluted magnetic structure with the FM originated from the doped matrix rather than any type of magnetic clusters. The size of the ferromagnetic domains was supposed to be 5–10 μm.

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