Ferromagnetism in transition-metal-doped TiO_2 thin films

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V, Cr, Fe, Co, and Ni had been chosen to substitute partially for Ti in TiO_2. By applying appropriate conditions, transition-metal-doped TiO_2 thin films deposited on $LaAlO_3$ substrates by laser ablation which show a good crystallinity and ferromagnetism above room temperature, could be obtained. The tendency of the dependence of magnetization versus element seems to be in accord with what theories have predicted. Among all the dopants, V appears to be the most promising candidate since its doping results in semiconducting films with a giant magnetic moment. Films are free of dopant particles or clusters. Structural and magnetic measurements have revealed that the room temperature ferromagnetism in V/Cr/Fe/Co/Ni-doped thin films must originate from the transition-metal-doped TiO_2 matrices.

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I. INTRODUCTION

Diluted magnetic semiconductors (DMSs) recently have attracted a lot of attentions due to their great potential for applications in spintronics. A big issue which has been discussed controversially at the moment is the nature of room temperature ferromagnetism (FM) in these systems. The original idea of doping transition metals (TM) for Ti or Zn in TiO_2 or ZnO is to introduce interaction between magnetic atoms (e.g., Mn, Co, etc.) so that as the consequences, FM can be induced in the oxide host materials. However, the question whether the FM observed in TM-doped TiO_2 or ZnO really comes from the doped matrix or not, is still debated in this research field.

Among hole-doped DMSs which have been studied so far, $Co:TiO_2$ and $Fe:TiO_2$ thin films have showed the highest Curie temperature (T_C).[1,2] While Chamber *et al.* claimed that in their $Co:TiO_2$ films which were fabricated by oxygen plasma assisted molecular-beam epitaxy, FM should be intrinsic,[3] Shinde *et al.* suggested that the FM in their laser ablated Co/TiO_2 thin films arises from Co nanoclusters.[4]

Even though Co-doped ZnO or TiO_2 thin films have been fabricated by various techniques,[1,3,5,6] not much work has been done on V/Cr/Fe/Ni-doped ZnO or TiO_2 films. So far, no evidence of FM has been reported for Fe:ZnO films,[7,8] and for Ni:ZnO films, FM was found only at very low temperature.[9] As regards to TiO_2 host, there have been very few reports on Fe and Ni dopings. While Bally *et al.* did not find FM in $Fe:TiO_2$ thin films,[10] Wang *et al.* obtained high T_C ferromagnetic $Fe:TiO_2$ films only on sapphire substrates.[2] Among all of those potential dopants, V was calculated to be the most promising candidate to dope for ZnO in order to obtain a strong FM, because in this case, the energy difference between the ferromagnetic state and the antiferromagnetic state is the largest.[11] However, so far, there has been only one report about V:ZnO thin films[12] 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.[12]

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 of utmost importance. In other words, it is necessary to get the right phase in the films. In order to achieve this, the method of making the targets and the choice of growth conditions must be appropriate. We tried to fabricate $TM:TiO_2$ (TM = V, Cr, Fe, Co, and Ni) thin films by laser ablation from ceramic targets under various conditions. Structural and magnetic properties have been investigated thoroughly in order to illustrate the nature of FM in these materials. Among all the elements of the TM group, only Mn is excluded in our study because, according to some recent theoretical work on doped ZnO, doping Mn alone without additional carriers was supposed not to result in room temperature FM,[13] therefore, also there may be not much hope to obtain high T_C FM in Mn-doped TiO_2. Since the theoretical work suggested that FM is the ground state of V/Cr/Fe/Co/Ni-doped ZnO,[11] experimentally we expected to obtain a high T_C FM also in V/Cr/Fe/Co/Ni-doped TiO_2 thin films.

II. EXPERIMENT

$Ti_{1-x}TM_xO_2$ targets (TM: V, Cr, Fe, Co, and Ni) where $x = 5\%$, 5%, 8%, 12%, and 8%, respectively, were prepared

by a gel method which was derived from the citrate gel processes.[14] The dopant content was chosen differently for different compounds in order to avoid segregations in each case. Basically the sol-gel method allows us to maintain the nominal composition with a high density in spite of chemical phase segregations, therefore, it gives an opportunity to have an uniform distribution of elements. 2700-Å-thick-$TM:TiO_2$ films were deposited 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 600, 650, or 700 °C. After deposition, all films were cooled down to room temperature under a P_{O_2} of 20 mTorr. All films were deposited on substrates with the same size (5 mm × 5 mm) to be able to compare quantitative values directly. The structural analysis was done by x-ray diffraction (XRD) with Cu $K\alpha$ radiation. The resistivity was measured by a two-probe method using a resistance meter which could detect the resistance up to 10^{16} Ω. 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 a magnetic force microscope (Nanoscope IIIA MFM operated at room temperature in zero field). The film morphology was checked by a scanning electron microscope (SEM). The chemical composition was determined by a Rutherford backscattering spectroscope (RBS).

III. RESULTS AND DISCUSSIONS

From RBS measurements, the V, Cr, Fe, Co, and Ni contents in V/Cr/Fe/Co/Ni-doped TiO_2 films are determined to be 5%, 5%, 8.1%, 10%, and 4.3%, respectively. XRD spectra [Fig. 1(a)] in log scale showed that all films are well *c*-axis oriented, pure anatase (no peak of any impurity could be seen, at least from the XRD measurements with the detection limit as of less than 5%). Despite the difference in concentration, the out-of-plane parameters of V/Cr/Fe/Co/Ni are not very different from each other, and are just a bit shortened compared to that of the non-doped TiO_2. From this very small difference, we may say that the dopants were really substituted for Ti in TiO_2 host matrix and we have obtained solid solutions. The SEM and MFM data shown later in this letter may also enforce the assumption that there is no possibility for dopant particles/clusters to exist.

Since basically both our $TM:TiO_2$ film and the LAO substrate are insulating, it is impossible to observe a clear image by a scanning electron microscope (SEM) for $TM:TiO_2$ thin films on LAO without using a Pt–Pd coating. Therefore, in order to judge the morphology of the films, instead, we observed SEM images for $TM:TiO_2$ films grown on silicon substrates which were fabricated simultaneously with the $TM:TiO_2$ films on LAO in one run. In Fig. 2, the SEM image of one film of $Fe:TiO_2$ on Si is shown (this $Fe:TiO_2$ film is chosen to show as a typical representative because the Fe content in the film is rather large, and large enough to reveal some outgrowths or excess dopant clusters if they may exist). One can see that the $Fe:TiO_2$ film has a very smooth

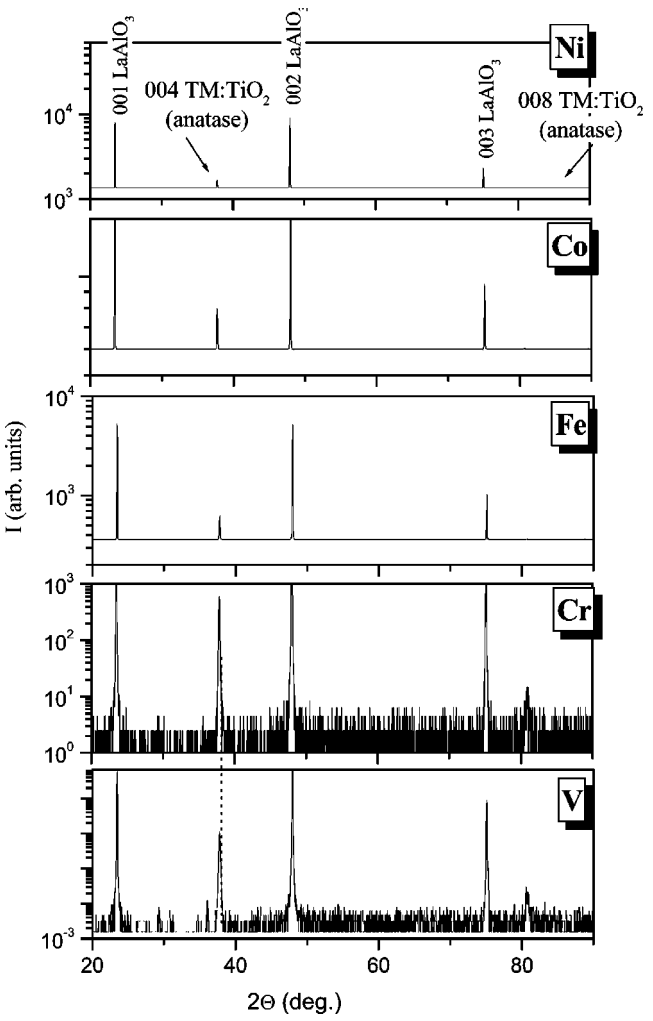

FIG. 1. XRD diffraction patterns of V/Fe/Co/Ni-doped TiO_2 films fabricated at 700 °C and of the $Cr:TiO_2$ film fabricated at 650 °C.

surface, with no particles/clusters on it. A similar image was obtained for all other $TM:TiO_2$ films on Si.[15,16] Based on the acceptable accuracy of SEM system, we can say that $TM:TiO_2$ films on LAO must have a morphology which is similar to that of $TM:TiO_2$ film on Si (in fact, due to a much

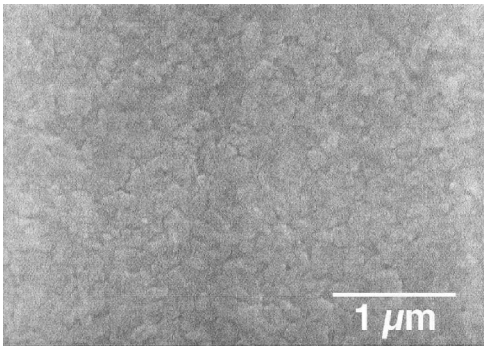

FIG. 2. SEM image of the $Fe:TiO_2$ film fabricated at 700 °C on Si substrate (note that this film was deposited simultaneously in the same run with the $Fe:TiO_2$ film on $LaAlO_3$ substrate).

larger mismatch in the case of Si compare to LAO, films on Si used to be crystallized in several orientations while films on LAO grown under the same conditions usually have a much better crystallinity and all are *c*-axis oriented. Thus, SEM images of films on LAO are expected to be better. Note that the resolution of SEM is less than 10 nm).[15–17] This observation enforced the assumption that V, Cr, Fe, Co, and Ni were dissolved rather well into TiO_2. Later in this report, we will discuss more details about the origin of FM in our films, either from an indirect evidence based on the temperature dependence of resistivity or other direct evidences from MFM data, to reinforce our assumption of having no clusters on our $TM:TiO_2$ films.

Under our chosen range of growth conditions, all of $TM:TiO_2$ films are room temperature ferromagnetic [Figs. 3(a) and 3(b) show $M(T)$ curves taken at 0.2 T for $TM:TiO_2$ films fabricated at 700 °C]. All films have T_C above 300 K (basically T_C is determined from the inflection point of $[M(T)]$ curves measure at 0.2 T). One can see that the $[M(T)]$ curves just start falling down when they approach 400 K, therefore T_C is considered to be a bit higher. Room temperature ferromagnetism is confirmed by magnetization data versus magnetic field taken at 300 K. All $[M(H)]$ curves show a well-defined hysteresis loop (a typical example is shown in Fig. 3(c)) [note that the shape of $[M(H)]$ curves taken at 300 and 5 K are quite similar indicating that the samples are certainly in a ferromagnetic state over a wide range of temperature].

In the case of Fe/Co/Ni, the saturation magnetization (M_s) is still rather modest, and these small values, in addition to the T_C just around 400 K, ruled out the assumption if the FM in those films comes from Fe, Co, or Ni metal particles/clusters.[6,15,17] Note also that the $[M(T)]$ curves of our $TM:TiO_2$ films remain constant in a wide range of temperature below T_C and they are not of samples with metallic clusters, because in the later case, usually there is an anomalous temperature dependence of magnetic moment which must be observed clearly in the $[M(T)]$ characteristics.[18]

In the case that the substrate temperature was 650 °C, we obtained the much larger values of M_s for all the films of $TM:TiO_2$ and the maximal value obtained is 4.23 μ_B for the $V:TiO_2$ films [see Fig. 4 for $M(H)$ curves taken at 300 K and a typical $[M(T)]$ curve taken at 0.2 T]. The giant magnetic moment as of 4.23 μ_B in $V:TiO_2$ films is rather significant. It is known that an isolated V atom has a permanent magnetic moment of 3 μ_B while bulk V is paramagnetic. No possibility for V clusters to exist in those films, because, according to the experimental work of Douglass *et al.*[19] and Liu *et al.*,[20] the upper limits of magnetic moment for V_9 and V_{99} clusters are 0.59 and 0.18 μ_B only, respectively, while a rather careful theoretical work calculated for small V clusters showed that the magnetic moment is the largest (as of 1 μ_B) when the size of V clusters is two atoms, and it decreases as the cluster size increases, then vanishes for V_{15} ($M = 0.03$ μ_B) and meanwhile exhibits some oscillations.[21] Most probably, such a giant magnetic moment observed in $V:TiO_2$ films is due to unquenched orbital contributions which were similarly found in $Co:SnO_2$ thin films (i.e., the orbital moment of vanadium remains unquenched since the atoms surrounding the vanadium atoms have gained a moment via electronic effects).[22]

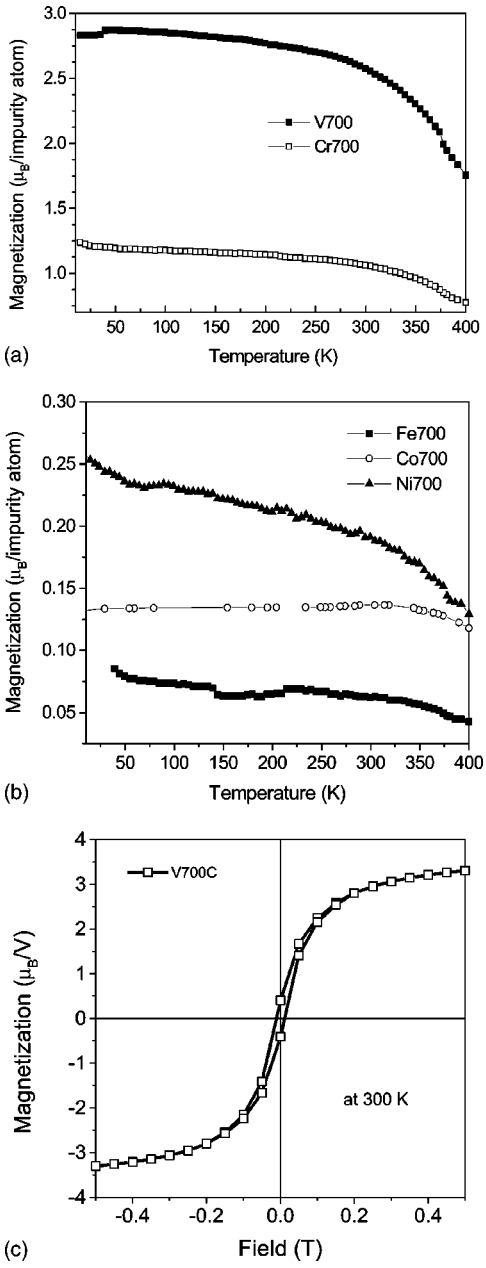

FIG. 3. Magnetization (a) and (b) vs temperature taken at 0.2 T for $TM:TiO_2$ films fabricated at 700 °C, and (c) vs magnetic field at 300 K for the $V:TiO_2$ film fabricated at 700 °C.

All $TM:TiO_2$ films have the resistivity in the range of semiconductors and have a semiconducting temperature dependence. A typical example can be seen in Fig. 5 for a $V:TiO_2$ film. In the case of having metal clusters in the films, normally the film should show a metallic behavior, but it is not the case of our $TM:TiO_2$ films (see the inset). On the other hand, according to both a theoretical work 30 years ago of Sheng *et al.*[23] for hopping transport of metallic clusters, and an experimental work recently on $Co:TiO_2$ films with an existence of Co clusters confirming the correctness of the earlier one,[24] samples having multiphases or in other words, clusters, should have the relationship with temperature that

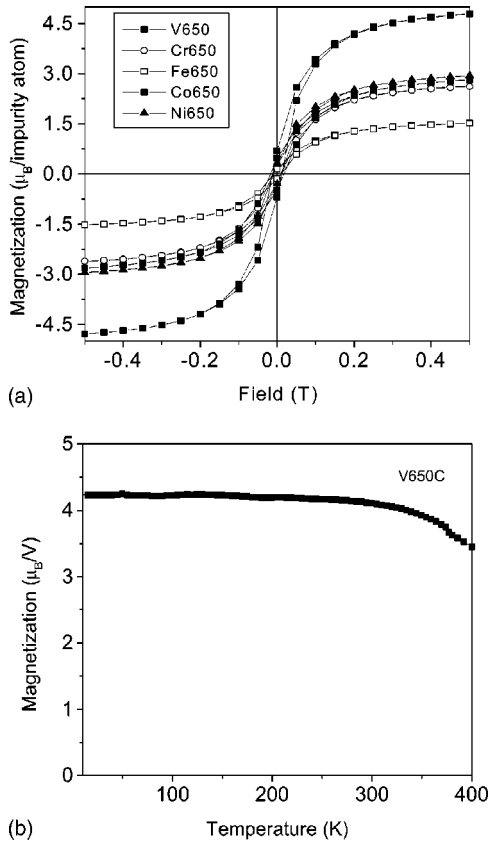

FIG. 4. Magnetization (a) vs magnetic field taken at 300 K for the $TM:TiO_2$ films fabricated at 650 °C and (b) vs temperature for the $V:TiO_2$ film fabricated at 650 °C.

obeys the law of $\log R \propto T^{-1/2}$. Figure 5 shows that in our films, $\log R$ vs $T^{-1/2}$ is not linear, so that it can be considered as an indirect evidence to prove that there are no clusters in our films.

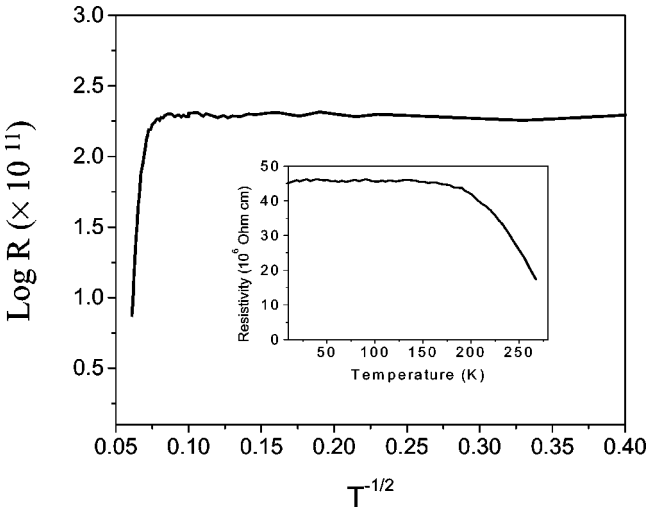

FIG. 5. Log R as a function of $T^{-1/2}$ for the $V:TiO_2$ film fabricated at 650 °C. The inset show the standard $\rho(T)$ curve. Note that the distance between two contacts is 500 μm, the cross section of the sample is 5000 $\mu m \times 0.2$ μm and the applied voltage is 20 V.

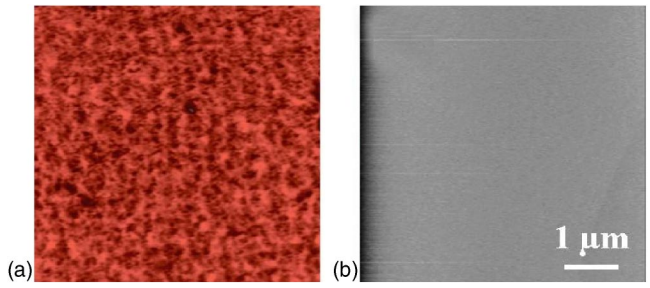

FIG. 6. Topography (a) and corresponding MFM images (b) recorded on the same area of 5×5 μm^2 for the $V:TiO_2$ film fabricated at 650 °C. The tip was magnetized parallel to the film plane.

The remark that the room temperature ferromagnetism in our $TM:TiO_2$ does not come from TM particles/clusters are reinforced directly by MFM measurements. All films showed clear magnetic signals at room temperature and revealed a smooth surface. Surprisingly, among all of $TM:TiO_2$ films, the $V:TiO_2$ film which has the largest magnetic moment showed the best magnetic homogeneity and the MFM image eliminates the doubt of having metal clusters/particles is the film. MFM is a very effective tool for magnetic investigations on submicron scale, but how to have the distinction of the magnetic image from the topography one is a rather delicate problem. In order to solve this, the magnetic measurements were executed by a two-step method. In the first step, the topography was determined and in the second one the cantilever was lifted to different lift heights Δz (100 and 150 nm, to ensure that it is higher than where the Van der Waals forces could exist and cause mixed signals). We used a tip which is sensitive to magnetic forces (i.e., coated with two layers of Co and Cr) and it was magnetized perpendicular to its axis (i.e., parallel to the film plane and the same as the direction of the applied field in magnetization measurements). Figure 6(a) shows a topography image taken on the area of 5×5 μm^2. The corresponding MFM (phase shift) image measured for $\Delta z = 150$ nm can be seen from Fig. 6(b) (for $\Delta z = 100$ and 150 nm, we obtained the same results). The topography image confirms the sample flatness and its low surface roughness of about 4 nm. As seen from Fig. 6, the MFM image is completely different from the topography image, therefore, the strong signals at room temperature that we have detected, surely come from the magnetic response but not the surface effects. (Note that the mean root square of the phase shift over the entire image as of 0.2° is a typical value for these measurements, to ensure that the signals are physical but not topographic.) The absence of contrast on the surface is in favor of a very homogeneous film without any cluster. Very similar images, but with a much better solution can be obtained in measurements with a perpendicular configuration (see Fig. 7). Figure 7(a) shows a topography image taken on the area of 5×5 μm^2. The corresponding MFM image can be seen from Fig. 7(b). As seen from Fig. 7, the MFM image is completely different from the topography one, therefore, the detected signals surely come from the magnetic responses but not from the surface effects. The absence of contrast on the surface is in favor of a greatly homogeneous film. Note that a small variation of the MFM

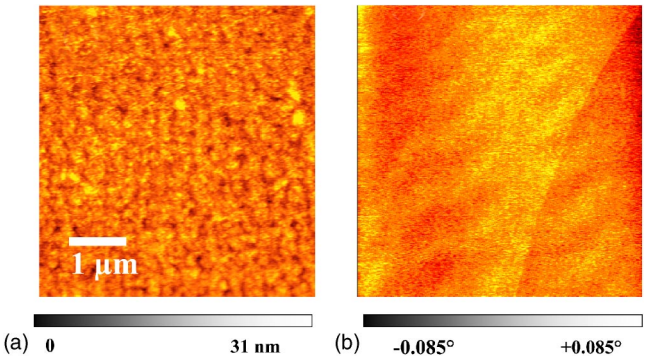

FIG. 7. The topography (a) and the MFM (b) images taken at room temperature on the area of 5×5 μm^2 of the V:TiO_2 film grown on LAO at 650 °C. The tip was magnetized perpendicular to the film plane.

response does not imply a 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 big change like a step).[25] The fluctuation of magnetization that we could observe in the MFM images of TM:TiO_2 films gives a strong, direct evidence for a real diluted magnetic structure (note that no domain wall was observed in this scaling size).

Along with the XRD and MFM data indicating structurally and magnetically single phases in TM:TiO_2 films, both values of M_s and T_C, which are unlikely to be of TM particles and clusters (much smaller in the case of Fe/Co/Ni and much higher in the case of V and Cr), rule out the possibility for TM particles and clusters to exist. On the other hand, the fact that all films have the resistivity at room temperature in the range of semiconductors, supports this remark.[15,16]

A dependence of M_s versus element for TM:TiO_2 films fabricated at 700 and 650 °C is plotted in Fig. 8. {Note that the values of M_s were taken from the saturation magnetic moments which could be pointed out from $[M(H)]$ curves.} It is worth noticing that in TM:TiO_2 films, the largest M_s is obtained for V doping, and it reduces about half in the case of Cr doping and rises up again slightly from Fe to Ni dopings, and it reflects a strong similarity to the chemical trend of TM:ZnO in which, the largest energy difference is found in V, reducing about half in Cr doping, and rising up gradually from Fe thru Co to Ni (it means that once the ferromagnetic phase is established, that state is the most stable in V doping case, less in Cr, etc., and while comparing to other transition-metal element doping cases, one can see that in the case of V doping, it requires more energy to return to antiferromagnetic state, therefore, as consequences, should be stronger. The other comparative trends could be seen directly from the plot).[11] Note that V surpasses all other transition-metal elements to result in a very large magnetic moment. From Fig. 8, about the discrete values of M_s, one can see a slight difference from what Sato and Katayama-Yoshida calculated for TM-doped ZnO (2.5 μ_B/impurity atom for V:ZnO, about 4 μ_B/impurity atom for Fe:ZnO, etc.),[11] but this can be easily explained by the difference of the host (TiO_2 in our case), of the material as films (the theory calculated for single crystals) and of the growth conditions which were hard to keep exactly the same for different runs (the dopant concentration in the targets, the plume, etc.). For example, note that the quantitative values are different for films deposited at different temperatures (see two cases shown for 650 and 700 °C). This plot confirms that in DMS research, experimentally we could obtain the same tendency as theories have predicted.

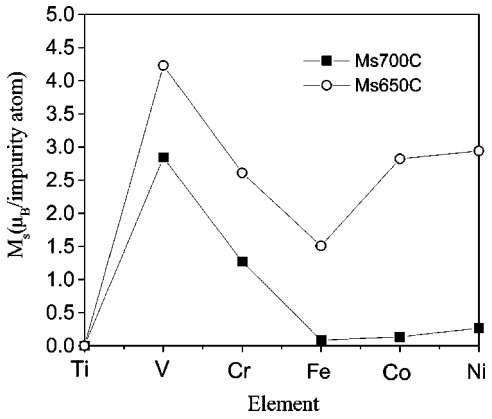

FIG. 8. Saturation magnetization vs element for TM:TiO_2 films fabricated at 700 and 650 °C {quantitative data taken from the saturated magnetic moments deduced from $[M(H)]$ curves measured at 300 K}.

IV. CONCLUSION

V/Cr/Fe/Co/Ni-doped TiO_2 thin films which were deposited on $LaAlO_3$ substrate by ablation laser show a good crystallinity and room temperature ferromagnetism. The tendency of the dependence of magnetization versus elements are well consistent with the theoretical work. Among all the dopants, V appears to be the most promising candidate since its doping results in semiconducting films with a giant magnetic moment. No particles or clusters were observed in the films. Structural and magnetic measurements have shown that the room temperature ferromagnetism in V/Cr/Fe/Co/Ni-doped thin films must originate from the transition-metal-doped TiO_2 matrices.

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