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Description	

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HTML ABSTRACT + LINKS

Ferromagnetism at room temperature with a large magnetic moment in anatase V-doped TiO_2 thin films

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V-doped TiO_2 thin films were grown by laser ablation on $LaAlO_3$ substrates. In the chosen range of the growth conditions, all V:TiO_2 films have an anatase structure and exhibit semiconducting and ferromagnetic behaviors at room temperature. V:TiO_2 films have a giant magnetic moment and they seem to be far better ferromagnetic than Co/Fe/Ni-doped TiO_2 films. This study has proved that a few percent of V substituting for Ti in TiO_2 can result in a potential diluted magnetic semiconductor.
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Since magnetic semiconductors with Curie temperature (T_C) as high as possible are greatly demanding for the development of spintronic devices, diluted magnetic semiconductors (DMSs) and wide gap oxide semiconductors have attracted many research groups. Among hole-doped DMSs which have been studied so far, Co:TiO_2 and Fe:TiO_2 thin films have showed the highest T_C.[1,2] Besides Co and Fe, other dopants such as V, Cr, and Ni were predicted theoretically to be able to introduce ferromagnetic ordering into an oxide semiconductor host such as ZnO via the double exchange mechanism. Among all of those potential candidates, V was calculated to be the most promising dopant for ZnO in order to obtain a strong ferromagnetism (FM) due to the fact that the energy difference between the ferromagnetic state and the antiferromagnetic state is largest in this case.[3] However, so far, there has been only one report about V:ZnO thin films[4] and no experimental study has been done on V:TiO_2 thin films, no matter what the type of film fabrication technique. Saeki *et al.* reported that in their V:ZnO films, even if room temperature FM was found, only metallic samples are magnetic, therefore, the nature of FM must be due to V metal clusters or so.[4] In this letter, we report on room temperature ferromagnetic, semiconducting V-doped TiO_2 thin films fabricated by laser ablation on $LaAlO_3$ substrates.

A $Ti_{0.95}V_{0.05}O_2$ target was made by a sol-gel method. 200-nm-thick V:TiO_2 films were grown by the pulsed laser deposition technique using KrF laser ($\lambda=248$ nm) on (001) $LaAlO_3$ (LAO) substrates. The repetition rate was 5 Hz and the energy density was 2 J/cm^2. Films were fabricated at 700, 650, and 600 °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 investigations were done by x-ray diffraction (XRD) using a Seifert XRD 3000P. The resistance of all samples was measured by the two-probe method using a resistance meter which could detect the resistance up to 10^{16} Ω. 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 down to 5 K. The chemical compositions were determined by both the energy dispersive x-ray method and the Rutherford backscattering spectroscopy method whose parameters were mentioned elsewhere.[5]

The V content in all the fabricated films is almost 5%, and it does not change much while changing the growth conditions. A typical XRD pattern for V:TiO_2 films is shown in Fig. 1. The V:TiO_2 films are pure anatase, well epitaxial and c-axis oriented (with $c=9.517$ Å, in comparison with c of TiO_2 anatase as of 9.513 Å). No peak of either V metal or vanadium oxides has been found in the spectra. The lattice

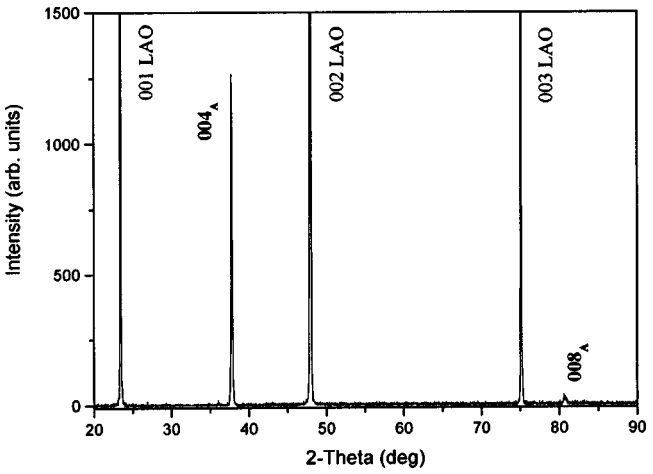

FIG. 1. XRD patterns for the $Ti_{0.95}V_{0.05}O_2$ film fabricated at 700 °C under a P_{O_2} of 2×10^{-6} Torr and a fluence of 2 J/cm^2. Note that only very sharp anatase peaks (marked by A) appeared in the spectra and the film is c-axis oriented.

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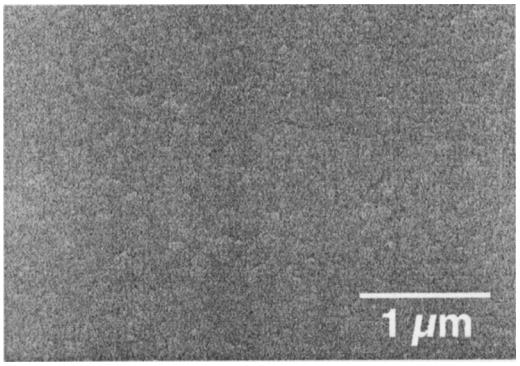

FIG. 2. SEM picture for the $Ti_{0.95}V_{0.05}O_2$ film fabricated at 700 °C under a P_{O_2} of 2×10^{-6} Torr and a fluence of 2 J/cm^2 on a Si substrate.

parameters differ from those of the TiO_2 host, indicating that V really "got into" the structure upon doping. However, it is not able to say definitely that there is no possibility for V particles to exist if they are below the detection limit of the XRD.

Because both the V:TiO_2 film and the LAO substrate are insulating, it is impossible to observe a clear image by a scanning electron microscope (SEM) for V:TiO_2 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 V:TiO_2 films grown on silicon substrates which were fabricated simultaneously with the V:TiO_2 films on LAO in one run. From Fig. 2, one can see that the V:TiO_2 film has a very smooth surface, with no particles/clusters on it. The morphology of V:TiO_2 films is much better than that of Co:TiO_2 films whose alien parts appeared on the surface indicating some sort of outgrowths.[5] Based on the acceptable accuracy of SEM system, we can say that V:TiO_2 films on LAO must have a morphology which is similar to that of V:TiO_2 film on Si. This observation enforced the assumption that V was dissolved well into TiO_2 and did not cause any precipitation.

All of our V:TiO_2 films are semiconductors with the resistivity at room temperature as of about 10^7 Ω cm (note that due to the two-probe method, the resistance of two contacts are included) and it rises up quickly as the temperature increases to reach about 4.5×10^7 Ω cm at about 200 K and

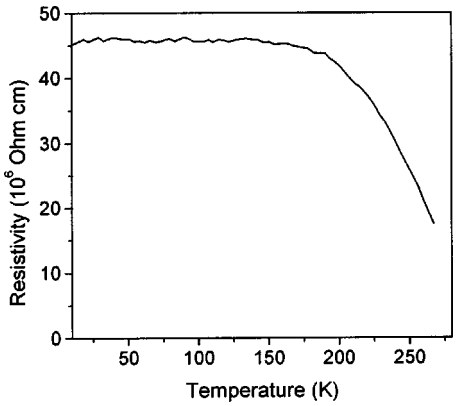

FIG. 3. The temperature dependence of resistivity measure by the two-probe method for the $Ti_{0.95}V_{0.05}O_2$ film fabricated at 650 °C under a P_{O_2} of 2×10^{-6} Torr and a fluence of 2 J/cm^2. Note that the distance between two contacts is 500 μm, the cross section of the sample is 5000 μm×0.2 μm and the applied voltage is 20 V.

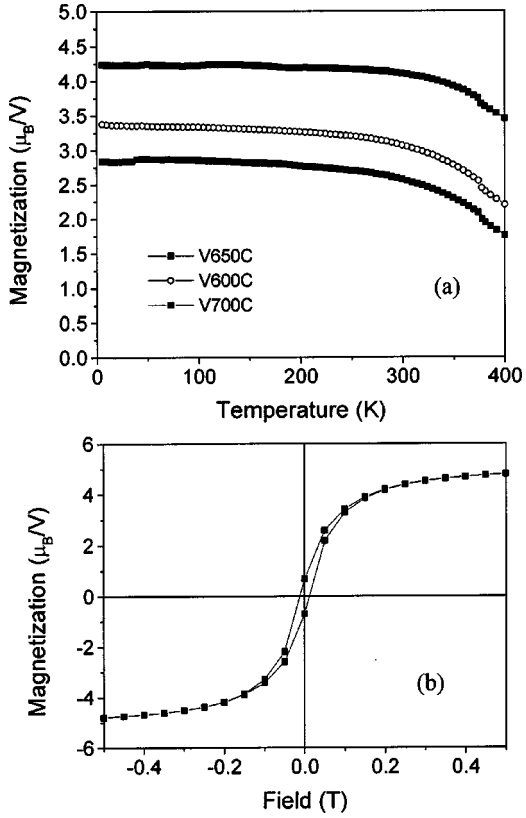

FIG. 4. (a) Magnetization vs temperature under 0.2 T for the $Ti_{0.95}V_{0.05}O_2$ films fabricated at 600, 650, and 700 °C and (b) magnetization vs magnetic field at 300 K for the $Ti_{0.95}V_{0.05}O_2$ film fabricated at 650 °C (2×10^{-6} Torr; 2 J/cm^2).

remains the same for lower temperatures (see Fig. 3). This is important to note, since if the ferromagnetism that we may find is not associated with the semiconductivity, it would be a proof for V to remain as metal clusters or so, instead of being really substituted for Ti in TiO_2 matrix, as in the case of unsuccessful doping reported in Ref. 4 for V:ZnO films or in Ref. 5 for Co:TiO_2 films in which ferromagnetism was based on the formation of dopant clusters, thus the doped TiO_2 films are metallic at room temperature. The magnetization versus temperature (taken at 0.2 T) and versus magnetic field (taken at 300 K) for V:TiO_2 films are shown in Fig. 4. Figure 4(a) shows that all films have Curie temperature (T_C) higher than 400 K (with the magnetic moment remains constant in the whole range of temperature below T_C). The saturation magnetization (M_s) of V:TiO_2 films is rather large, more than one order larger than that in the case of Co, Fe, or Ni doping,[6,7] indicating a very strong FM in those films. A clear hysteresis, which could be observed from $M-H$ curves [Fig. 4(b)] taken at room temperature for V:TiO_2 films, ensured the observation for room temperature FM mentioned earlier. Certainly all V:TiO_2 films are ferromagnetic even far beyond room temperature.

The films fabricated at 650 °C have the largest saturation magnetic moment as of 4.23 μ_B/V. This giant magnetic moment is in accord with the prediction of the theory that, as regards to the magnitude of magnetic moment, V surpasses all other elements of iron group while doping it in ZnO, for example.[3] It is known that an isolated V atom has a permanent magnetic moment of 3 μ_B while bulk V is paramag-

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netic. A large value of magnetic moment of 4.23 μ_B per atom in our films completely rules out the possibility for V clusters to exist, because, for example, according to the experimental work of Douglass *et al.*[8] and Liu *et al.*,[9] the upper limits of magnetic moment for V_9 and V_{99} clusters are 0.59 and 0.18 μ_B only, respectively, while some computational work brought out conflicting results as 2.78 or 0.33 μ_B for the V_9.[10–12] 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.[13] Most probably, such a giant magnetic moment observed in V:TiO_2 films could be explained by 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).[14] This assumption seems to be rather convincing because when the V concentration increases, the magnetic moment decreases[15] due to the enhancement of quenching when the dopant–dopant associations increase.

While considering the saturation magnetic moment versus element of V/Fe/Co/Ni-doped TiO_2 films fabricated under the fluence of 2 J/cm^2 and at 700 °C, we have found that the tendency is almost similar to what the theory drew for transition metal-doped ZnO, where the largest M_s is for V doping, and reduces in the case of Fe, Co, and Ni doping.[3] A slight difference (a plateau stretching from Fe to Ni in comparison to the tendency for rising up in the case of doping in ZnO) can be explained by the differences due to a different host (TiO_2 in our case), the material as films (the theory did not calculate for the concrete materials as films, how thick they are, etc...), and also the growth conditions which are very hard to keep strictly the same for different runs (the dopant concentration in the targets, the plume...).[15]

In summary, V:TiO_2 thin films fabricated by laser ablation on $LaAlO_3$ substrates from a ceramic target showed very good qualities. Besides a very well-established crystallinity, all the films are ferromagnetic semiconductors at room temperature, with no trace of any V particle or cluster. A significant feature is that the V:TiO_2 film have a large magnetic moment. A low doping of V in TiO_2 seems to result in a potential candidate to applications.

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