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Magnetism and structure of anatase $(Ti_{1-x}V_x)O_2$ films

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Anatase TiO_2 is known as a promising host material for a wide-gap ferromagnetic semiconductor as it is a good solvent for numerous transition-metal elements. We report on the structural and magnetic properties of epitaxially grown anatase $(Ti_{1-x}V_x)O_2$ layers where x covers the whole range of solubility of V atoms in anatase TiO_2 and beyond the solubility limit of 21%. We measured an average magnetic moment per vanadium as high as 1 μ_B with a magnetic percolation threshold of less than 6% which agrees with recent theoretical predictions. Interestingly, our results show a decrease of the average V magnetic moment as x increases throughout the solubility range. Anatase $(Ti_{1-x}V_x)O_2$ is no longer present beyond the solubility limit, where the nonmagnetic VO_2 phase forms and destroys the net magnetization. © *2012 American Institute of Physics*. [doi:10.1063/1.3679434]

I. INTRODUCTION

Carrier-mediated ferromagnetism[1] has attracted significant attention during the past decade as it could enable the fabrication of room-temperature ferromagnetic (FM) semiconductors by doping nonmagnetic semiconductors with transition-metal (TM) elements. However, it has turned out that it is a challenging experimental problem, especially to unambiguously exclude the presence of a secondary phase. In TM-doped oxides, unique features like the orbital-moment anisotropy were revealed[2] but the origin of room-temperature ferromagnetism remains highly controversial and the lattice defects are found to play a key role.[3,4] In particular, an indirect double exchange via oxygen vacancies (v_O) is often involved.[5] Nevertheless, Yamada *et al.* have recently given an experimental evidence of carrier-mediated ferromagnetism in anatase $(Ti_{0.90}Co_{0.10})O_2$.[6] In its pure state, anatase TiO_2 (a-TiO_2) is nonmagnetic and insulating with a bandgap of 3.2 eV.[7] It is a good solvent for numerous TM dopants and therefore considered as a potent host material for diluted magnetic semiconductors. Appropriate doping can lead to carrier densities of 10^{21} cm^{-3} (Refs. 8 and 9) and ferromagnetism persisting up to 400 K (Ref. 10). $(Ti_{1-x}V_x)O_2$ is predicted to fulfill the requirements of a FM semiconductor as (i) the V atoms carry a magnetic moment of 1 μ_B when substituting for Ti and (ii) the large solubility of the V atoms in a-TiO_2 of $x_l = 0.21$ exceeds the percolation threshold of the FM interaction x_p of 0.056.[8] Average magnetic moment (μ_V) as high as 4.2 μ_B was reported and attributed to an unquenched orbital moment on the V sites.[11] Our focus is on the magnetism of highly crystalline a-$(Ti_{1-x}V_x)O_2$ (001) films, obtained by sequential deposition of V and TiO_2. x varied from 0 to 0.31, which exceeds the reported solubility limit x_l. Throughout the solubility range the crystal structure is only moderately affected by the V dopants. It is demonstrated that diluted V dopants induce ferromagnetism in a-TiO_2, as expected for partial substitution of Ti by V with μ_V of up to 1 μ_B.

II. EXPERIMENTAL PROCEDURES

a-TiO_2 ($I4_1/amd$) is tetragonal with $a = 0.3785$ nm and $c = 0.9514$ nm.[9] An atomically clean and flat $LaAlO_3$ (LAO) substrate is indispensable for the growth of high-quality TiO_2 layers. Figures 1(a) and 1(b) show the surface morphology of the substrate. An almost perfect single-terminated surface with straight terrace edges was obtained after annealing at 1150 °C for 2 h in air. The small lattice mismatch between a-TiO_2 and LAO of 0.2% allows an epitaxial growth of a-TiO_2 (001) on LAO (100). a-$(Ti_{1-x}V_x)O_2$ films were grown by pulsed laser deposition, sequentially depositing TiO_2 and V layers. We used a KrF laser of 248 nm wavelength with pulses of 5 J/cm^2. a-TiO_2 was deposited from a sintered TiO_2 target with 1 Hz pulses, under a pure O_2 pressure of 1 mTorr in order to limit the creation of v_O that are usually found to mediate the FM order. V was deposited from a pure V target with 15 Hz pulses. Deposition rates were 6 and 13 pm/s, respectively. Note that TiO_2 undergoes an irreversible phase transition at 577 °C (Ref. 12) from anatase to rutile (r-). Although it was observed that the heteroepitaxial growth allows the formation of anatase beyond this transition, X-ray diffraction (XRD) results showed traces of rutile in the films grown at 600 °C. During the growth, the substrate temperature was 500 °C. In order to promote the diffusion of V atoms in the a-TiO_2, the film was kept at 500 °C for 1 h under 1 mTorr of pure O_2. The samples were then cooled to room temperature in the same atmosphere. Figure 1(c) shows a schematic of the multilayer (ML) and the corresponding depth profile for different diffusion stages. Here we present results obtained for a-TiO_2(9 nm)/V(2 nm)/a-TiO_2(9 nm) and $\{TiO_2/V\}_{30}/TiO_2$ MLs, in which the nominal thickness of a-TiO_2 was set to 5 nm while the thickness of V layers varied from 0 to 0.7 nm ($0 \le x \le 0.31$). The

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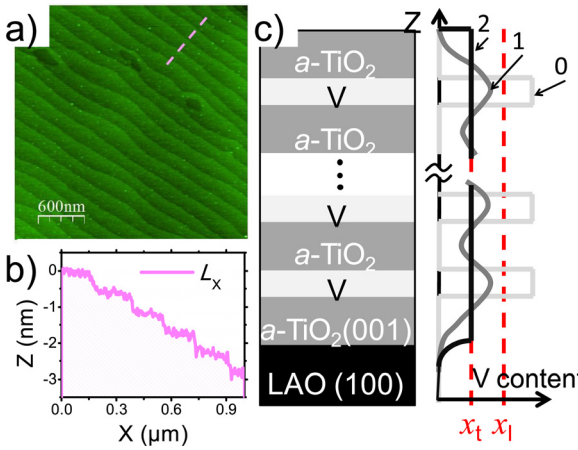

FIG. 1. (Color online) Surface morphology of the processed LAO substrate measured by AFM (a). The dashed line indicates the trace of the surface profile displayed in (b). Schematic depth profile of the ML (c) with a total V content x_t at different stages of the V-dopant diffusion process: not diffused (0), partially diffused leading to a modulated structure (1) and fully dissolved (2).

structure was analyzed by XRD with Cu K_α radiation. The overall film composition was verified by energy-dispersive X-ray spectroscopy. The magnetization was measured using a commercial superconducting quantum interference device (SQUID) magnetometer.

III. RESULTS AND ANALYSIS

Figure 2 shows the XRD pattern of an undoped a-TiO_2 layer of 90 nm thickness. The only observed Bragg-reflections from the film are the a-TiO_2 $\{00l\}$ ($l = 4n$, n an integer) lines which confirms the [001] orientation of the growth. The corresponding rocking curves have a full width at half maximum (FWHM) as small as 0.4°.

The question of the V-dopant distribution is of crucial importance in order to understand the magnetic properties. A complete diffusion of the V dopants could be expected since the sample is kept at 500 °C during the deposition (15 h) and the subsequent annealing (1 h). Let us first consider the case of an a-TiO_2/V/a-TiO_2 trilayer, where the V layer thickness is chosen to give an overall trilayer composition at the solubility limit of V in a-TiO_2 ($x_t = x_l$). A non-homogenous distribution along the growth direction would then inevitably lead to two TiO_2 layers separated by an interlayer with a V-rich phase. Figure 3 shows a θ-2θ scan measured on such trilayer around the 2θ position of the a-$(Ti_{1-x}V_x)O_2$ (004) Bragg-reflection. The presence of Laue fringes is not only the sign of a good crystallinity and flat interfaces but their period gives an accurate value of the crystallite size along

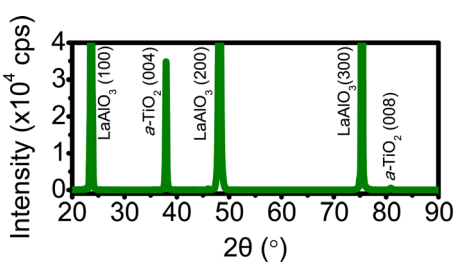

FIG. 2. (Color online) XRD pattern of an undoped a-TiO_2 layer of 90 nm.

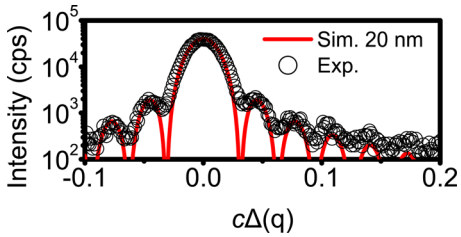

FIG. 3. (Color online) θ-2θ pattern around the a-$(Ti_{1-x}V_x)O_2$ (004) Bragg-reflection for a TiO_2/V/TiO_2 trilayer. The solid line is the simulated pattern of a single layer of 20 nm.

the direction perpendicular to the film plane. The period perfectly matches with the total thickness of the film which rules out the case of a subsisting V-rich interlayer. Note however that if that supports the idea of a complete diffusion of the V dopants and a homogenous distribution of them in the direction perpendicular to the substrate plane, it is not sufficient to discard the hypothesis of partial V clustering. Therefore, in the following discussion on the magnetic properties, both the homogeneous distribution and the partial clustering hypotheses are considered.

Figure 4 displays XRD patterns of a-$(Ti_{1-x}V_x)O_2$ ML films around the 2θ position of the a-TiO_2 (004) Bragg-reflection. The crystalline structure is only moderately affected by the V dopants as the FWHM of the rocking curve of a-$(Ti_{1-x}V_x)O_2$ (004) Bragg-reflections broadened from 0.4° to 0.6° when x increases from 0 to 0.25, as expected for cation substitution by $V^{4+}(V_{Ti})$. This result agrees with earlier theoretical and experimental works showing that V impurities are well-dissolved in a-TiO_2.[11,13]

$(Ti_{1-x}V_x)O_2$ was found to undergo a phase modification around x_l, as the 2θ position of the most intense peak shifts from 37.7° (a-TiO_2 (004)) to 39.7° which matches with the position of r-VO_2 (200) when x increases from 0.25 to 0.31. The VO_2 phase observed at $x = 0.31$ is highly crystalline and oriented with a measured rocking curve width of 0.5°. The presence of VO_2 in this film was unambiguously confirmed by measuring the temperature dependence of the electrical resistivity between 300 and 400 K. Indeed VO_2 undergoes a metal-to-insulator transition at 338 K which accompanies a phase transition from high- temperature rutile ($P4_2/mnm$) to low-temperature monoclinic structure ($P2_1/c$). A sharp

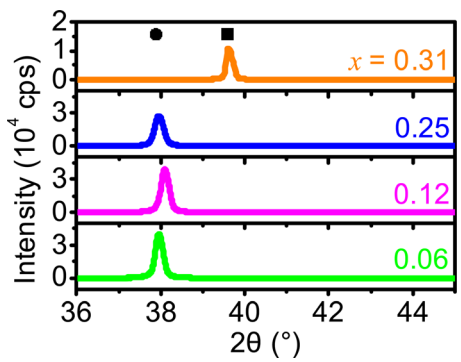

FIG. 4. (Color online) XRD pattern of a-$(Ti_{1-x}V_x)O_2$ films with x of 0.06, 0.12, 0.25, and 0.31. The circle indicates the 2θ position of a-TiO_2 (004) and the square the 2θ position of r-VO_2 (200).

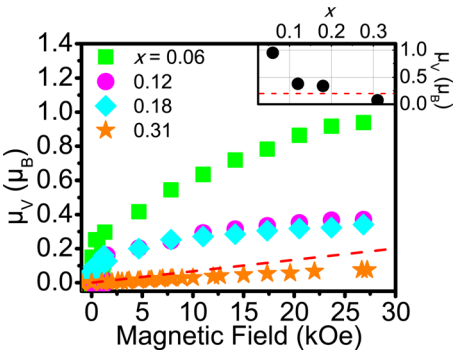

FIG. 5. (Color online) Magnetization of $\{TiO_2/V\}_{30}/TiO_2$ MLs with x of 0.06, 0.12, 0.18, and 0.31, measured at 10 K. The inset shows the x dependence of the magnetization at 3 T. The dashed lines correspond to the calculated magnetization expected for isolated V atoms with a magnetic moment of 3 μ_B.

decrease of the resistivity was measured at around 350 K in the film with $x = 0.31$. No trace of pure Ti was detected by XRD. We note that r-TiO_2 and r-VO_2 have similar lattice parameters. The mismatch along the in-plane directions, that is, [010] and [001] would be 0.8% and 3%, respectively. The stabilized phase at $x = 0.31$ values would thus correspond to r-$(Ti_{1-x}V_x)O_2$.

We measured negligible magnetic moment in the TiO_2 film alone. In the following, we assume that the magnetic moment is carried by V atoms. Bulk V is paramagnetic and the permanent magnetic moment of vanadium is 3 μ_B. The magnetization originating from isolated V atoms can be calculated using the Langevin function. At 10 K and under a magnetic field of 3 T, it leads to 0.2 μ_B per vanadium atom.

The following magnetic measurements correspond to the $\{TiO_2/V\}_{30}/TiO_2$ MLs. In Fig. 5 we compare the magnetization of four $(Ti_{1-x}V_x)O_2$ films with x of 0.06, 0.12, 0.18, and 0.31. Throughout the solubility range, μ_V remains larger than the calculated moment for isolated V atoms which shows that (i) the V-V pairs are magnetically coupled with $\mu_V \approx 1$ μ_B and (ii) the magnetic percolation threshold is less than 0.06 (fifth neighbor in the a-TiO_2 structure).[8] However, μ_V is found to decrease when x increases. According to calculations,[13] a ground state with antiferromagnetic (AFM) coupling is favored for V-V nearest neighbors and is highly sensitive to the V-V distance, which agrees with the work of Moodera *et al.*[14] on thin (less than 1 atomic layer thick) V films. On the other hand, V-O-V exchange is generally found to be FM. As the amount of V dopants increases, one could then expect that AFM interaction settles between the nearest V-V pairs while FM would be favored in the other configurations. Magnetic frustration and partial AFM interaction would then lead to an overall decrease of the average V magnetic moment. At $x = 0.25$, the μ_V decrease would be triggered by 60% of compensated V^{4+} spins.

As mentioned above, we cannot exclude the hypothesis of partial V clustering. Indeed, it was previously calculated that the energy of the nearest-neighbors configuration is the lowest which favors V-dopants clustering.[13] On the other hand, a theoretical work calculated that in V clusters, the V magnetic moment decreases as the cluster size increases, from 1 μB (2 atoms) to 0.03 μB (15 atoms). Thus, one could expect that increasing the amount of dopants (x), the formation of larger V clusters embedded in the a-TiO_2 matrix leads to a decrease of the average magnetic moment.

Finally, our XRD results show that as x increases beyond the solubility limit of V_{Ti} atoms in a-TiO_2, the nonmagnetic VO_2 phase forms that reduces the value of μ_V.

IV. CONCLUSION

In summary, we have studied the structural and magnetic properties of highly crystalline a-$(Ti_{1-x}V_x)O_2$ films throughout the solubility range and beyond. Our results agree with recent calculation on an average magnetic moment of V atoms of 1 μ_B and a magnetic percolation threshold of less than 6%. Increasing the dopant concentration is found to decrease the average V magnetic moment, which can be explain by (i) competing AFM and FM interaction and (ii) partial V clustering. Beyond the solubility limit a nonmagnetic rutile $(Ti_{1-x}V_x)O_2$ phase forms which leads to a negligible magnetization.

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