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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 \(\mu_B\) 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 \((\nu_O)\) is often involved.\(^5\) Nevertheless, Yamada et al. have recently given an experimental evidence of carrier-mediated ferromagnetism in anatase (Ti\(_{0.99}Co_{0.01}\))O\(_2\).\(^6\) In its pure state, anatase TiO\(_2\) \((a\text{-}TiO}_2\) 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 \(\mu_B\) when substituting for Ti and (ii) the large solubility of the V atoms in \(a\text{-}TiO}_2\) of \(x = 0.21\) exceeds the percolation threshold of the FM interaction \(x_p\) of 0.056.\(^8\) Average magnetic moment \((\mu_v)\) as high as 4.2 \(\mu_B\) was reported and attributed to an unquenched orbital moment on the V sites.\(^9\) Our focus is on the magnetism of highly crystalline \(a\text{-}(Ti_{1-x}V_x)O_2\) (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 \(a\text{-}TiO}_2\), as expected for partial substitution of Ti by V with \(\mu_v\) of up to 1 \(\mu_B\).

II. EXPERIMENTAL PROCEDURES

\(a\text{-}TiO}_2\) \((I4/mmd)\) 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 \(a\text{-}TiO}_2\) and LAO of 0.2% allows an epitaxial growth of \(a\text{-}TiO}_2\) (001) on LAO (100). \(a\text{-}(Ti_{1-x}V_x)O_2\) 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\(^2\). \(a\text{-}TiO}_2\) 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 \(\nu_O\) 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 \((r\text{-})\). Although it was observed that the heteropitaxial 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 \(a\text{-}TiO}_2\), 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 \(a\text{-}TiO}_2(9 \text{ nm})/N(2 \text{ nm})/a\text{-}TiO}_2(9 \text{ nm})\) and \((TiO}_2/V)_{30}TiO_2\) MLs, in which the nominal thickness of \(a\text{-}TiO}_2\) was set to 5 nm while the thickness of V layers varied from 0 to 0.7 nm (0 ≤ \(x ≤ 0.31\)). The

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structure was analyzed by XRD with Cu $K_x$ 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 confirm the [001] orientation of the growth. The corresponding rocking curves have a full width at half maximum (FWHM) as small as 0.4\(^\circ\).

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\(^\circ\)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 $a$-$TiO_2$ \((x_t = x_i)\). 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 \(\theta-2\theta\) scan measured on such a trilayer around the \(2\theta\) position of the \(a\)-(Ti\(_{1-x}\),V\(_x\))O\(_2\) 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 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 \(2\theta\) position of the \(a\)-TiO\(_2\) \(\langle 004\rangle\) Bragg-reflection. The crystalline structure is only moderately affected by the V dopants as the FWHM of the rocking curve reflection for a TiO\(_2\)/V/TiO\(_2\) trilayer. The solid line is the simulated pattern around the \(2\theta\) position of a TiO\(_2\)/V/TiO\(_2\) trilayer. The solid line is the simulated pattern of a single layer of 20 nm.
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$_x$)$_2$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 $3 \mu_B$. 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, the inset shows the 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 $\mu_B$.

FIG. 5. (Color online) Magnetization of $\{\text{TiO}_2/V\}_{30}/\text{TiO}_2$ MLs with $x$ of 0.06, 0.12, 0.18, and 0.31, measured at 10 K. The inset shows the 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 $\mu_B$.

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. On the other hand, a theoretical work calculated that in V clusters, the V magnetic moment decreases as the cluster size increases, from 1 $\mu_B$ (2 atoms) to 0.03 $\mu_B$ (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$_{11}$ atoms in $a$-TiO$_2$, the non-magnetic VO$_2$ phase forms that reduces the value of $\mu_V$.

IV. CONCLUSION

In summary, we have studied the structural and magnetic properties of highly crystalline $a$-(Ti$_{1-x}$V$_x$)$_2$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 $\mu_B$ 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$_x$)$_2$O$_2$ phase forms which leads to a negligible magnetization.

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