AIP | Applied Physics Letters

Electronic depiction of magnetic origin in undoped and Fe doped TiO2−d epitaxial thin films

Komal Bapna, R. J. Choudhary, S. K. Pandey, D. M. Phase, S. K. Sharma et al.

Citation: Appl. Phys. Lett. **99**, 112502 (2011); doi: 10.1063/1.3640212

View online: http://dx.doi.org/10.1063/1.3640212

View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v99/i11

Published by the AIP Publishing LLC.

Additional information on Appl. Phys. Lett.

Journal Homepage: http://apl.aip.org/

Journal Information: http://apl.aip.org/about/about_the_journal

Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: http://apl.aip.org/authors

APPLIED PHYSICS LETTERS **99**, 112502 (2011)

Electronic depiction of magnetic origin in undoped and Fe doped TiO_{2-d} epitaxial thin films

Komal Bapna,[1] R. J. Choudhary,[1,a)] S. K. Pandey,[1] D. M. Phase,[1] S. K. Sharma,[2]
and M. Knobel[2]
[1]*UGC DAE Consortium for Scientific Research, Khandwa Road, Indore 01, India*
[2]*Instituto de Fisica Gleb Wataghin, Universidade Estadual de Campinas (UNICAMP), Campinas 13.083-970, SP, Brazil*

(Received 17 August 2011; accepted 23 August 2011; published online 15 September 2011)

We have investigated the electronic and magnetic properties of the pulsed laser deposited epitaxial thin films of undoped and Fe doped (4 at. %) anatase TiO_{2-d} by photoemission, magnetization measurements, and *ab-initio* band structure calculations. These films show room temperature magnetic ordering. It is observed that Fe ions hybridize with the oxygen vacancy induced Ti^{3+} defect states. Our study reveals the formation of local magnetic moment at Ti and Fe sites to be responsible for magnetic ordering. A finite density of states at the Fermi level in both undoped and Fe doped films is also observed, suggesting their degenerate semiconducting nature. © *2011 American Institute of Physics*. [doi:10.1063/1.3640212]

For the last several years, TiO_2 has been at the center of research activity among the condensed matter community owing to its wide range of applications in optoelectronic devices, transparent conductors, gas sensors, variastors, photocatalytic devices, etc.[1,2] In recent years, efforts are going on to dope transition metal (TM) in TiO_2 for diluted magnetic semiconductors (DMS) based spintronic applications.[3–7] It is expected that doping of TM will induce magnetization, mediated via charge carriers, in an otherwise non magnetic host oxide semiconductor. Another way to induce magnetization in such non magnetic systems is through manipulating either cation vacancy or anion vacancy.[6,8–10] There are various models proposed to explain the observed magnetism in DMS materials such as Ruderman-Kittel-Kasuya-Yosida (RKKY) model,[11] bound magnetic polaron (BMP) model,[12] and Stoner type model.[13] However, the real mechanism is not clear yet now; still one common feature in all these models is the vital role played by the coupling between the charge carriers and the magnetic moments, which decisively formulate the electrical and magnetic properties of these materials.

To better understand the effect of TM doping or presence of defects on the electrical and magnetic properties, it is crucial to realize modification in TiO_2's electronic properties due to TM doping, hybridization of TM ion with oxygen vacancy (O_V) induced defect, and the properties of surface configuration in doped TiO_2 films. These properties are very crucial to unravel many fundamental questions concerning the experimental results, either for photocatalytic or for DMS applications. To understand the modification in electronic properties due to TM doping and hybridization of TM ion with cation, we study the valence band spectra (VBS) of pulsed laser deposited undoped and Fe doped (4 at. %) epitaxial TiO_{2-d} thin films and its consequences on magnetic properties. Our experimental and calculated VBS studies[14] of these films reveal that Ti and Fe form localized states with local magnetic moments. These films show room temperature magnetic ordering. Resonant photoemission studies suggest the hybridization between oxygen vacancy induced Ti 3 d defect states and Fe 3 d derived states, revealing the role of cation defects in the occurrence of magnetization.

Normal θ-2θ XRD patterns of the doped and undoped films (Fig. 1(a)) reveal that the films have anatase structure with growth along c-axis. In plane ϕ scan measurement confirmed the epitaxial nature of the films on the $LaAlO_3$ (LAO) substrate (not shown here). The x-ray photoelectron spectroscopy (XPS) measurements for Ti 2 p and Fe 2 p core levels are shown in Fig. 1(b). Features of Ti $2p_{3/2}$ core level spectrum were fitted with combined Gaussian-Lorentzian functions, revealing 3+ and 4+ states of Ti.[15] Fe $2p_{3/2}$

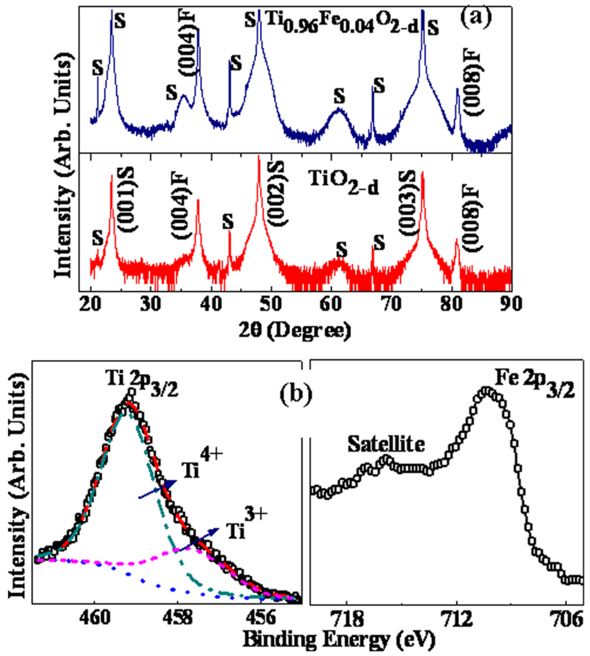

FIG. 1. (Color online) (a) XRD patterns (normal θ-2θ scan) of TiO_{2-d} and 4% Fe doped TiO_{2-d} films, S and F stand for LAO substrate and film, respectively, and (b) left panel Ti $2p_{3/2}$ core level and right panel Fe $2p_{3/2}$ core level x-ray photoelectron spectrum of the Fe doped film.

[a)] Author to whom correspondence should be addressed. Electronic mail: ram@csr.res.in.

spectrum shows one main peak along-with a satellite. The position of the main peak is at ~710 eV, which is ~4 eV more than that corresponding to the metallic Fe clusters.[16] We have performed depth profile analysis also and it turns out that the spectra remain same, ruling out the possibility of formation of Fe clusters in TiO_2 matrix either at surface or in the bulk of it and suggests the incorporation of Fe in the host matrix with valence state between 2+ and 3+.

In order to understand the modifications in electronic structure of TiO_{2-d} due to Fe doping, the VBS of both the samples, lying within 3 eV of binding energy, are recorded at incident photon energy (PE) PE of 50 eV as shown in Fig. 2(a). Interestingly, the VBS of these films reveal a non-zero finite density of states (DOS) close to Fermi level (E_F) indicating their degenerate semiconducting nature, which is suggested to occur due to overlap of the O_V induced shallow donor defect band with the conduction band.[5] In undoped sample, we observe a peak at binding energy position 0.9 eV (feature A), whereas in Fe doped sample, we observe another peak at 2 eV (feature B) besides the peak at 0.9 eV. The appearance of feature A is in accordance with the previous reports on oxygen deficient TiO_2 films and is attributed to the localized 3 d states.[15,17] To understand the VBS of these films, we have calculated the DOS corresponding to ferromagnetic solutions of $Ti_{0.75}Fe_{0.25}O_{1.75}$. The convoluted DOS of this compound is shown in the Fig. 2(b). On comparing the experimental spectra with the convoluted DOS, we can say that feature A corresponds to defect induced Ti 3 d symmetric states and feature B corresponds to Fe 3 d states. These features, being quite away from the Fermi level (E_F) and arising due to inclusion of U, can be considered as a signature of localized Ti 3 d and Fe 3 d states. These states are responsible for formation of net magnetic moments at Ti and Fe ions, as discussed in the later part of the paper.

The origin of features A and B is further confirmed by performing resonance photoemission study (RPES), by recording VBS at different incident PE in the range of 40-62 eV, which covers the Ti 3 p → 3 d and Fe 3 p → 3 d photo-absorption region as shown in Fig. 2(c) for 4% Fe doped film. Using these spectra, we plot constant initial states (CIS) intensity of features A and B with respect to incident PE as shown in Fig. 3(a). It is evident from Fig. 3(a) that feature A shows maxima at 45 eV and feature B shows maxima at 57 eV, which happen to be the resonance energy due to localized Ti and Fe derived states, respectively.[17,18] This further confirms that features A and B are due to Ti 3 d and Fe 3 d derived states, respectively. In Fig. 3(b), we have shown the

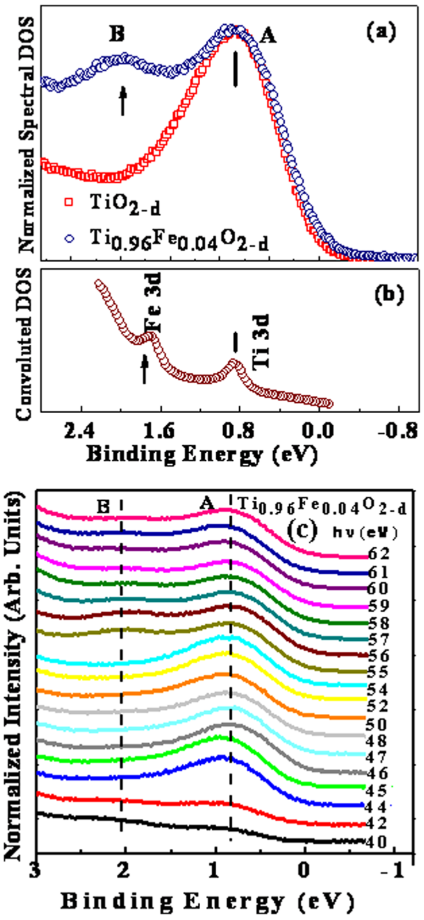

FIG. 2. (Color online) (a) Valence band spectra of Fe doped and undoped TiO_{2-d} films recorded at PE 50 eV; (b) convoluted DOS within GGA+U formulation for Fe doped TiO_{2-d}; and (c) valence band spectra of Fe doped TiO_{2-d} films recorded at different PE in the range of 40-62 eV.

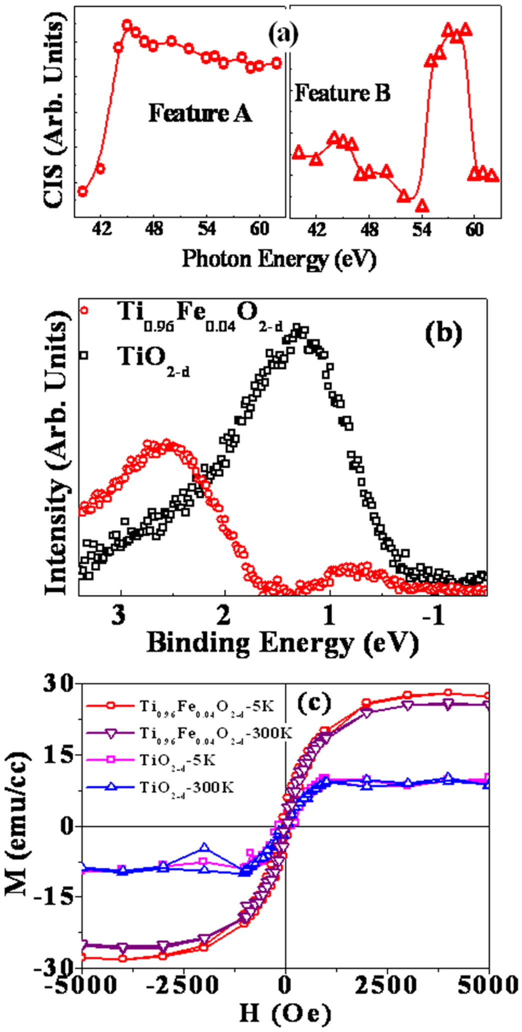

FIG. 3. (Color online) (a) CIS photoemission intensities as a function of PE for feature A of undoped TiO_{2-d} film (left panel) and feature B of 4% Fe doped TiO_{2-d} film (right panel); (b) the difference of spectral DOS recorded at 40 eV and 45 eV for TiO_{2-d} films and the same at 50 eV and 57 eV for Fe doped TiO_{2-d} films; and (c) magnetic hysteresis behaviour of both the films at 300 K and 5 K.

difference of VBS recorded at 40 and 45 eV for TiO_{2-d} film as well as 50 and 57 eV for $Ti_{0.96}Fe_{0.04}O_{2-d}$ film. As discussed earlier, 45 eV and 57 eV PE happen to be the on-resonance energy for Ti and Fe derived states in the VBS, respectively, whereas 40 and 50 eV are the off-resonance state for Ti and Fe, respectively. Therefore, the difference spectra would reveal the contribution of Ti derived state and Fe derived states in different parts of the VBS. From the difference spectra, we note that Fe 3 d and Ti 3 d states overlap considerably over a wide range of binding energy, suggesting these states are well hybridized. A hump at 45 eV in the CIS plot of Fe derived feature B is consistent with this observation. We also notice a non-zero value of the difference spectra close to E_F in both the difference spectra, indicating that close to E_F, DOS is due to Fe and Ti derived states.

In Fig. 3(c), we show room temperature and 5 K magnetic hysteresis plots for the undoped and Fe doped films, measured using 7T SQUID magnetometer in the reciprocating sample option mode. The observed data reveal saturation magnetic moment of 7 emu/cc and 22 emu/cc in the undoped and Fe doped films, respectively. The observed magnetic ordering in undoped TiO_{2-d} is consistent with the observed incoherent feature A corresponding to the Ti 3 d states in experimental VBS and our theoretical calculation. In our calculation on Ti_4O_7, O_V induced a local magnetic moment of about 0.4 μ_B and 0.25 μ_B at neighbouring Ti sites. However, the moments at these Ti ions are aligned antiparallel to each other giving rise to ferrimagnetic arrangement with net magnetic moment of about 0.15 μ_B per unit cell. The result is qualitatively in agreement with the previous report by Yang *et al.*,[19] where they have shown antiferromagnetic ordering of two Ti^{3+} ions close to the O_V sites. They interpreted that the two electrons associated with the O_V will convert neighbouring Ti^{4+} ions into Ti^{3+} ions, which would induce an equal local magnetic moment of 1 μ_B at these sites. In such a situation, insulating behavior is expected. However, in our case, we observe a finite DOS at E_F in both the films. In this condition, there could be another possibility, viz., one of the two electrons associated with the O_V would convert neighbouring Ti^{4+} ion into Ti^{3+} ion and another would be delocalized in TiO_2, yielding unequal redistribution of charges at the neighbouring Ti ions. Hence induced local magnetic moments at these Ti ions would be different leading to ferrimagnetic arrangement.

In another theoretical report by Kim *et al.*,[20] a weak magnetic moment of 0.06 μ_B in Ti atom due to O_V was observed. Hong *et al.*[9] observed finite magnetic moment in undoped anatase TiO_{2-d}, while Yoon *et al.*[21] observed that magnetization of the undoped anatase TiO_{2-d} films scaled with the conductivity, which could be controlled by varying oxygen partial pressure during deposition. Conversely, Coey *et al.*[13] did not get any ferromagnetic signal in undoped TiO_2 films. Thus, these ambiguities in the various results suggest that the magnetic properties of these samples are highly dependent on the charge redistribution created by O_V. For Fe doped sample ($Ti_{0.75}Fe_{0.25}O_{1.75}$), our calculation suggests magnetic moment of 3.5 μ_B per Fe site, which is close to the value reported by Park *et al.*[4] However, this value is 1.2 μ_B more than experimentally observed moment in Fe doped film. The experimentally observed less magnetic moment suggests that not only magnetic impurity but other magnetic effects like the coupling between the Fe ions and Ti^{3+} defect state (as per the BMP model and also revealed in the CIS plot of feature B as shown in Fig. 3(a)) and interaction between charge carriers and Fe ions (as revealed by DOS at E_F to be due to Fe and Ti derived states and shown in Fig. 3(b)) could also be responsible for the overall magnetic properties of these materials. The interaction between Fe ions and Ti^{3+} could be antiferromagnetic since $Fe^{3+/2+}$ ions are either just or more than half filled state. Thus, our results unambiguously establish the formation of localized moments at Ti and Fe sites which may have deeper consequences in the magnetic and electrical transport properties of the compounds.

In summary, we have studied the electronic and magnetic properties of Fe doped and undoped anatase TiO_{2-d} epitaxial thin films by combined experimental and theoretical tools. Experimental and calculated VBS studies reveal incoherent features due to Ti^{3+} defect states (in both the films) as well as Fe derived states with local moment and a finite spectral DOS at E_F. These films show magnetic ordering. Further work is under progress to understand the effect of explicit local magnetic moment on the electrical and magneto-transport properties.

The authors acknowledge Mr. A. Wadiker for his help in RPES measurements at AIPES beamline on INDUS-1.

[1] P. Wang, Z. Liu, F. Lin, G. Zhou, J. Wu, W. Duan, B.-L. Gu, and S. B. Zhang, Phys. Rev. B **82**, 193103 (2010).
[2] S. U. M. Khan, M. Al-Shahry, and W. B. Ingler, Jr., Science **297**, 2243 (2002).
[3] N. H. Hong, W. Prellier, J. Sakai, and A. Hassini, Appl. Phys. Lett. **84**, 2850 (2004).
[4] M. S. Park, S. K. Kwon, and B. I. Min, Phys. Rev. B **65**, 161201(R) (2002).
[5] S. R. Shinde, S. B. Ogale, S. Das Sarma, J. R. Simpson, H. D. Drew, S. E. Lofland, C. Lanci, J. P. Buban, and N. D. Browning, Phys. Rev. B **67**, 115211 (2003).
[6] S. B. Ogale, Adv. Mater. **22**, 3125 (2010).
[7] T. Ohsuki, A. Chainai, R. Eguchi, M. Matsunami, Y. Takata, M. Taguchi, Y. Nishino, K. Tamasaku, M. Yabashi, T. Ishikawa, M. Oura, Y. Senba, H. Ohashi, and S. Shin, Phys. Rev. Lett. **106**, 047602 (2011).
[8] A. Sundaresan, R. Bhargavi, N. Rangarajan, U. Siddesh, and C. N. R. Rao, Phys. Rev. B **74**, 161306 (2006).
[9] N. H. Hong, J. Sakai, N. Poirot, and V. Brizé, Phys. Rev. B **73**, 132404 (2006).
[10] S. K. Pandey and R. J. Choudhary, J. Phys.: Condens. Matter. **23**, 276005 (2011).
[11] Z. Wang, W. Wang, J. Tang, L. D. Tung, L. Spinu, and W. Zhou, Appl. Phys. Lett. **83**, 518 (2003).
[12] J. M. D. Coey, M. Venkatesan, and C. B. Fitzgerald, Nature Mater. **4**, 173 (2005).
[13] J. M. D. Coey, P. Stamenov, R. D. Gunning, M. Venkatesan, and K. Paul, New J. Phys. **12**, 053025 (2010).
[14] See supplementary material at http://dx.doi.org/10.1063/1.3640212 for the experimental and computational details.
[15] R. Sanjines, H. Tang, H. Berger, F. Gozzo, G. Margaritondo, and F. Levy, J. Appl. Phys. **75**, 2945 (1994).
[16] R. Prakash, D. M. Phase, R. J. Choudhary, and R. Kumar, J. Appl. Phys. **103**, 043712 (2008).
[17] Z. Zhang, S.-P. Jeng, and V. E. Henrich, Phys. Rev. B **43**, 12004 (1991).
[18] R. Prakash, R. J. Choudhary, and D. M. Phase, J. Phys.: Condens. Matter **20**, 335225 (2008).
[19] K. Yang, Y. Dai, B. Huang, and Y. P. Feng, Phys. Rev. B **81**, 033202 (2010).
[20] D. Kim, J. Hong, Y. R. Park, and K. J. Kim, J. Phys.: Condens. Matter **21**, 195405 (2009).
[21] S. D. Yoon, Y. Chen, A. Yang, T. L. Goodrich, X. Zuo, D. A. Arena, K. Ziemer, C. Vittoria, and V. G. Harris, J. Phys.: Condens. Matter **18**, L355 (2006).