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# Ferromagnetism and structural defects in V-doped titanium dioxide

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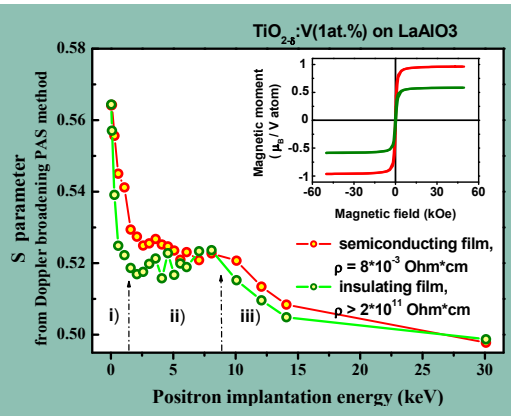
We report recent experimental results about influence of negatively charged structural defects on room-temperature ferromagnetism in V-doped $TiO_{2-\delta}$ thin films with different electric conductivities. Films were prepared on $LaAlO_3$ (001) substrates by RF magnetron sputtering in reduced argon-oxygen atmosphere, while the V to Ti metal ratio was fixed at 1 at.%. The ferromagnetic order at room temperature (RT) was confirmed by SQUID magnetometry. Positron annihilation spectroscopy (PAS) was applied to check the presence of open-volume defects in the $TiO_{2-\delta}$ matrix. The relation between ferromagnetic properties and amount of negatively charged defects in the studied films was established. The collection of structural, magnetometry, magnetotransport, magneto-optic and PAS data hints towards the defect-induced model of ferromagnetism in 1 at.% V-doped $TiO_{2-\delta}$ thin films.




PAS and magnetometry results for V-doped $TiO_{2-\delta}$



**1 Introduction** The interest on doped titanium dioxide thin films as candidates for dilute magnetic semiconductors (DMS) was initiated by the pioneering paper of Matsumoto *et al.* in 2001 [1]. Since then, the number of publications on $TiO_2$ films doped by different 3d impurities, such as cobalt, iron, vanadium or manganese, is steadily increasing. Up to now it was widely believed that the origin of long-range magnetic order in these systems does not depend on the type of 3d dopant.

A number of models of long-range ferromagnetic order in different DMS systems are reported in the literature (see e.g. [2] and references therein): carrier-mediated ferromagnetism, magnetic polarons, superexchange, charge-transfer ferromagnetism of Stoner-type in the impurity band and magnetism of dangling bonds. Nevertheless, each of these models has serious difficulties in explanation of all published experimental data. Furthermore, high Curie temperatures, large magnetic moments per impurity atom and specific features in magnetic, transport and magneto-optical properties are still far from being well understood. In the case of 3d doped titanium dioxide the most popular but competitive points of view on origin of ferromagnetism at RT are carrier-mediated and defect-induced models.

For V-doped titanium dioxide only several controversial results can be found in the literature [3-5]. In our report, combined studies of magnetic and structural properties of $TiO_{2-\delta}$:V(1 at.%) samples (denoted below as $Ti_{0.99}V_{0.01}O_{2-\delta}$) are presented. The relation between room temperature ferromagnetic order and the presence of structural defects in the host matrix is discussed.

**2 Sample preparation** Oxygen deficient $Ti_{0.99}V_{0.01}O_{2-\delta}$ thin films of 600 nm thickness were prepared by reactive RF magnetron sputtering from a metallic $Ti_{0.99}V_{0.01}$ alloy target in argon-oxygen atmosphere at total pressure of $1.2 \times 10^{-2}$ Torr. The $LaAlO_3$ (001) substrates were kept at 650 ºC during film deposition. By variation of the oxygen fraction in the chamber atmosphere, conducting, semiconducting ($\rho \sim 0.008$ Ωcm) or insulating ($\rho > 200$ GΩcm) films have been prepared. Kept in air, as-grown films with metallic conductivity transform into semiconductors and therefore they are not considered in this study.

## 3 Results

**3.1 Structural and EDX analysis** Standard XRD 2θ-θ analysis (not shown) revealed a mixture of anatase and rutile phases for all prepared V-doped $TiO_{2-\delta}$ films with no evidence of V based secondary phases. In addition, element-selective spectroscopy with linear polarized X-rays (XANES) has been applied in soft- and hard X-ray ranges at the $L_{2,3}$ and K absorption edges of titanium for structural characterization, which confirmed the presence of rutile phases in the films. Nevertheless, XANES spectra at the vanadium $L_{2,3}$ absorption edges have not been detected. The most obvious explanation of this fact is the strong background signal from titanium atoms in the film and lanthanum atoms in the substrate since all these fluorescent lines are not well enough resolved.

Energy-Dispersive X-ray (EDX) spectra of the as-prepared $Ti_{0.99}V_{0.01}O_{2-\delta}$ films showed the absence of the $K_{\alpha,\beta}$ fluorescent lines of iron or cobalt contaminations (6÷7 keV). Instead, La, Al, Ti, O and V lines were observed (see Fig. 1). Due to the low V concentration only the $K_\alpha$ line of vanadium (4.95 keV) is rather well resolved while the $K_\beta$ line (5.43 keV) has a non-detectable intensity. Consequently, the quantitative determination of V concentrations is not possible with sufficient precision.

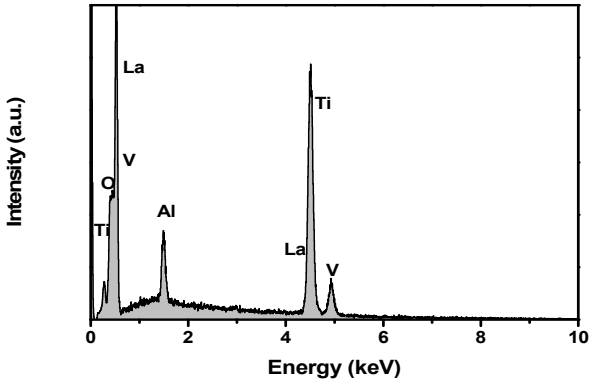



**Figure 1** EDX spectrum of insulating $Ti_{0.99}V_{0.01}O_{2-\delta}$ thin film with mixed structure.

**3.2 Magnetometry and transport studies** A clear magnetic behaviour with pronounced hysteresis at RT was found for semiconducting and insulating $Ti_{0.99}V_{0.01}O_{2-\delta}$ films (Fig. 2). The coercive field of about 300 Oe is rather typical for $TiO_{2-\delta}$:Co systems with different concentrations of impurities and was also previously found for $TiO_{2-\delta}$:V films grown on rutile [6]. Zero field cooling / field cooling (ZFC/FC) curves measurements did not reveal superparamagnetic behaviour. The saturation magnetization for the semiconducting and insulating film corresponds to ~ 0.90 and ~ 0.63 $\mu_B$ per vanadium atom, respectively. These values differ from the results obtained by Hong *et al.* in [3] and our preliminary results [5], where for higher V doping level a larger magnetic moment per vanadium impurity was found.

Temperature dependent charge transport measurements revealed n-type conductivity with $d\rho/dT < 0$ for the semiconducting film in the temperature range from 90 K to 300 K (Fig. 3). Hall resistivity curves (not shown) showed linear dependence on the magnetic field with no signature of anomalous Hall effect contribution.

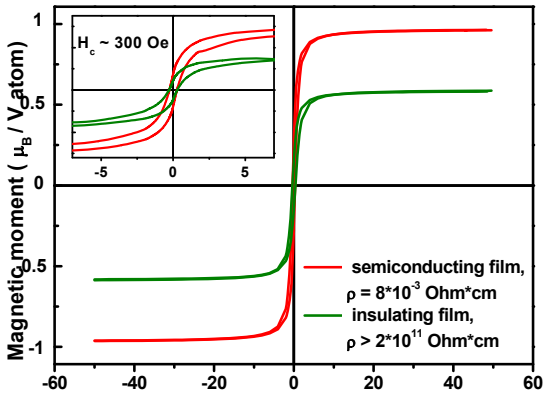



**Figure 2** SQUID magnetometry data measured for semiconducting and insulating $Ti_{0.99}V_{0.01}O_{2-\delta}$ films at RT.

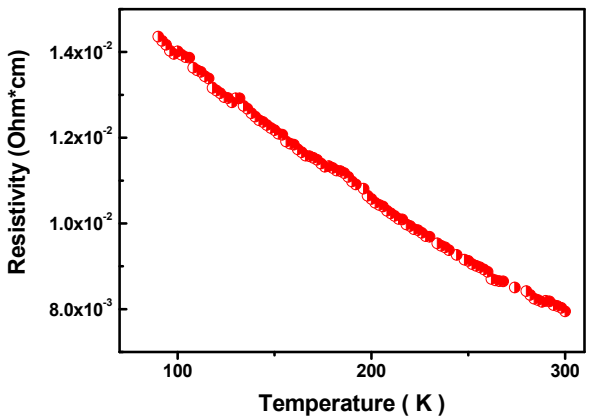



**Figure 3** Temperature dependence of electrical resistivity for semiconducting $Ti_{0.99}V_{0.01}O_{2-\delta}$ film.

Previously, RT ferromagnetism was found for insulating $TiO_{2-\delta}$:Co [7] and $TiO_{2-\delta}$:V [5] with a higher doping level. In the current report, ferromagnetism was observed for either semiconducting or insulating $Ti_{0.99}V_{0.01}O_{2-\delta}$ films and in spite of huge difference in resistivity (~ $10^{13}$ times), the saturation magnetization of the insulating film is only about one and half times lower than for the semiconducting one.

**3.3 Magneto-optical spectroscopy** Magneto-optical (MO) spectra were measured in the transversal Kerr effect geometry in an energy range of 0.5 ÷ 3.5 eV at external magnetic fields up to 3.0 kOe by the highly sensitive dynamical method. These MO spectra allow to draw conclusions about the interband densities of states which characterize the magnetic ion. The shape of the spectra and the magnitude of the transversal Kerr effect can be used to determine the presence of 3d clusters in the sample studied. Surprisingly, none of the measured MO spectra indicates the presence of spin-orbit interaction of vanadium impurities with the $TiO_{2-\delta}$ matrix (Fig. 4) despite the fairly strong magnetic moment per impurity atom was found from the magnetometry data. The absence of the MO signal can be considered not only as an exclusion of the V moment to be the source of the ferromagnetic properties but also as an indirect confirmation of absence of ferromagnetic Fe and Co impurity clusters in the films.

Contrary to the case of Co- doping at the same doping level in $Ti_{0.99}V_{0.01}O_{2-\delta}$ there was no evidence of new spin-polarized states inside the band gap leading to new MO transitions. Thus, jointly with transport measurements, a pure defect-induced nature of ferromagnetism in these films was concluded.

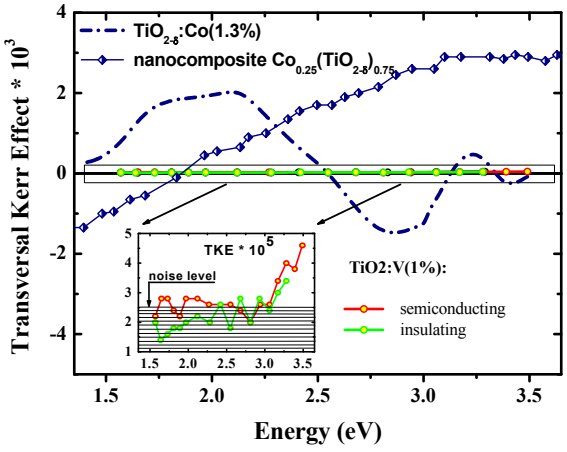



**Figure 4** Magneto-optical spectra for all prepared $Ti_{0.99}V_{0.01}O_{2-\delta}$ films (see inset for detailed view). The spectra of anatase $TiO_{2-\delta}$:Co(1.3at.%) [8] and nanocomposite $Co_{0.25}(TiO_{2-\delta})_{0.75}$ [9] are shown for comparison.

**3.4 Positron annihilation spectroscopy (PAS)** PAS is an efficient tool to probe a depth profile of open-volume defects in thin films: being positively charged, positrons are trapped by negatively charged vacancies or their agglomerations and annihilate with nearest electrons resulting in creation of two photons with opposite *k*-vectors. In the case of V- doped $TiO_{2-\delta}$ films, this spectroscopy could be used effectively to explore either Ti or V vacancies and to distinguish their influence on magnetism from influence of positively charged oxygen vacancies.

PAS measurements were performed at the Slow Positron System of Rossendorf (SPONSOR) [10] by depth-resolving Doppler broadening method. Positrons of predetermined energies ranging from 27 eV up to 30 keV penetrate into the sample up to several micrometres depth with the highest energies reaching the $LaAlO_3$ substrate. The motion of positron-electron pairs during annihilation at negative vacancy causes a Doppler broadening of the 511 keV full-energy peak which was recorded by two opposite Ge detectors with an energy resolution of 1.09 ± 0.01 keV at the annihilation line.

As a measure of open-volume defects the so-called S-parameter could be used: S-parameter is the ratio of the central part of the measured photo-peak (within ± 0.92 keV) to the total peak area. Thus, the S-parameter represents the annihilation with slow valence electrons [11].

The dependencies of S-parameter on energy of implanted positrons for studied films are shown in Fig. 5. As follows from the figure, each curve has three characteristic regions: (i) below 2 keV, which represents the surface region of the $TiO_{2-\delta}$ film, (ii) 2 ÷ 9 keV, which relates to the bulk $TiO_{2-\delta}$ and (iii) above 9 keV, which corresponds to the interface between the film and $LaAlO_3$ substrate.

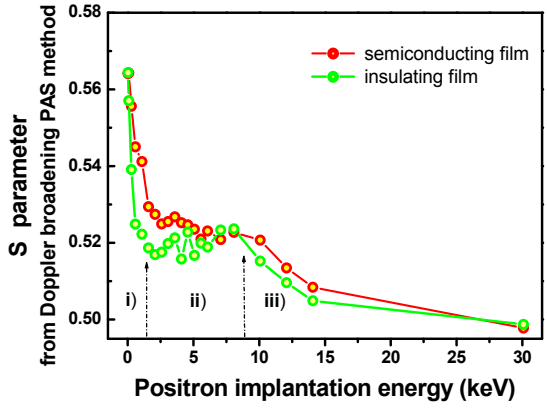



**Figure 5** Energy dependence of S-parameter obtained for $Ti_{0.99}V_{0.01}O_{2-\delta}$ films by PAS method.

The main interest is focused at the first and the second regions. Compared to the semiconducting sample, the insulating film shows a steeper slope of this dependency in the first region followed by a well pronounced plateau with the visibly smaller S-parameter, which refers to more perfect and uniform structure of bulk insulating film with a lower defect concentration. The absence of a plateau and a higher S-parameter within the second region in the case of semi-

conducting sample indicates a higher concentration of open-volume defects across the whole volume of the film. The decrease of S-parameter in the third region reflects the transition from the defective films to the highly perfect single crystalline $LaAlO_3$ substrate.

Thus, we observed that the semiconducting $Ti_{0.99}V_{0.01}O_{2-\delta}$ film reveals more negatively charged structural defects contrary to the insulating film. Also it is possible to estimate a ratio of the defect concentrations in both films taking into account the S-parameter of the single crystal rutile $TiO_2$ (0.5004 +/- 0.0008) and the S-parameter for saturation trapping. This estimation results in the defect concentration ratio of 0.67 between the insulating and the semiconducting film and correlates well with a ratio of the saturation magnetization in these films which is equal to 0.7.

**4 Conclusions** In this work, the results of structural, magnetic, transport, magneto-optical and positron annihilation studies of $Ti_{0.99}V_{0.01}O_{2-\delta}$ thin films have been presented. Room temperature ferromagnetism was observed in films with significantly different conductivities. Combining all obtained results, the following conclusions can be drawn:

(i) the "pure" carrier-mediated model of RT ferromagnetism is not applicable to $Ti_{0.99}V_{0.01}O_{2-\delta}$ since both semiconducting and insulating films with a resistivity difference of about 13 orders of magnitude exhibit a ferromagnetic hysteresis while the saturation magnetization differs only by a factor of 1.5;

(ii) the higher saturation magnetization of the semiconducting sample is found to correlate well with a higher density of negatively charged structural defects as probed by PAS. Possible candidates for these defects are Ti vacancies [12] or defect complexes involving $Ti^{3+}$ [13]. Therefore, it is proposed that these types of defects (and their agglomerations) should be taken into account when considering room temperature ferromagnetism in V- doped $TiO_{2-\delta}$ in addition to the influence of positively charged oxygen vacancies and their complexes;

(iii) the negligible magneto-optical transversal Kerr effect response and the absence of the anomalous Hall effect supports the assumption of defect-induced origin of magnetism in studied $Ti_{0.99}V_{0.01}O_{2-\delta}$ films without involvement of free charge carriers or the local magnetic moment of the V ion.

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## References

[1] Y. Matsumoto, M. Murakami, T. Shono et al., Science **291**, 854 (2001).
[2] J. M. D. Coey, M. Venkatesan, and C. B. Fitzgerald, Nature **4**, 173 (2005).
[3] N. H. Hong, J. Sakai, and A. Hassini, Appl. Phys. Lett. **84**, 2606 (2004).
[4] N. H. Hong, J. Sakai, W. Prellier et al., Phys. Rev. B **70,** 195204 (2004).
[5] A. F. Orlov, L. A. Balagurov, I. V. Kulemanov et al., SPIN **2**, 1250011 (2012).
[6] A. S. Semisalova, Yu. O. Mikhailovskiy, A. Smekhova et al., Solid State Commun., submitted.
[7] K. A. Griffin, A. B. Pakhomov, C. M. Wang et al., Phys. Rev. Lett. **94**, 157204 (2005).
[8] A. Granovsky, A. Orlov, N. Perov et al., JNN **12**, 7540 (2012).
[9] E. A. Gan'shina, A. B. Granovsky, A. F. Orlov et al., J. Magn. Magn. Mater. **321**, 723 (2009).
[10] W. Anwand, G. Brauer, M. Butterling, H. R. Kissener, and A. Wagner, Defect Diffusion Forum **331**, 25 (2012).
[11] D. W. Gidley, H.-G. Peng, and R. S. Vallery, Annu. Rev. Mater. Res. **36**, 49 (2006).
[12] J. O. Guillen, S. Lany, and A. Zunger, Phys. Rev. Lett. **100**, 036601 (2008).
[13] B. J. Morgan, D. O. Scanlon, and G. W. Watson, J. Mater. Chem. **19**, 5175 (2009).