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ATOMIC STRUCTURE AND MAGNETISM OF PLD DEPOSITED Tio$_2$:Fe

R. M. COSTESCU, G. A. LUNGU[*], G. SOCOL[a], N. G. GHEORGHE, D. MACOVEI, C. C. NEGRILĂ, C. LOGOFĂTU, M. A. HUŞANU, D. G. POPESCU, C. A. TACHE, C. M. TEODORESCU

National Institute of Materials Physics, Atomistilor 105b, P.O. Box MG-7, Bucharest-Magurele, Ilfov, 077125, Romania

[a]National Institute of Lasers, Plasma and Radiation Physics, P.O. Box MG-36, Bucharest-Magurele, Ilfov, 077125, Romania

TiO_2:Fe thin films prepared by pulsed laser deposition exhibit in some case light dependent saturation magnetization, as determined from Kerr magnetometry measurements performed in dark or by illuminating the sample. This phenomenon is studied in correlation with local atomic structure investigated by extended X-ray absorption fine structure, composition and chemical state analyzed by X-ray photoelectron spectroscopy and by X-ray absorption near-edge structure. It is found that light-controllable magnetism is a property of a mixture of Fe and oxidized Fe clusters embedded in the anatase TiO_2 matrix.

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1. Introduction

Transition metal doped titania has been revealed as a promising diluted magnetic semiconductor (DMS) material [1]. One of the main features of such materials is the fact that ferromagnetism occurs due to indirect exchange between localized magnetic moments *via* the free carriers in the semiconductors, an interaction proposed four decades ago by Ruderman, Kittel, Kasuya and Yosida (RKKY) [2]. Hence, possibility of ferromagnetism control is offered, by modulating the carrier density *via* electrical or optical injection [3]. However, the magnetic properties are strongly dependent on the preparation method employed: electrochemistry, sol-gel, magnetron sputtering, molecular beam epitaxy, pulsed laser deposition (PLD). The latter method has been revealed to be amongst the most appropriate for the synthesis of such materials, mainly because of the reproducibility and the possibility of controlling several parameters during deposition: laser fluence and wavelength, atmosphere composition, substrate temperature. In this Contribution we report on the synthesis of TiO_2:Fe and of mixed Ti and Fe oxides by PLD using a KrF excimer laser. The obtained layers were analyzed by X-ray photoelectron spectroscopy (XPS), X-ray absorption fine structure (XAFS: Extended X-ray absorption fine structure, EXAFS; X-ray absorption near-edge structure, XANES) at the Fe K-edge, and magneto-optical Kerr effect (MOKE). The latter measurements were performed in dark or by irradiating optically the sample, in order to check any possibility for optical control of magnetism.

2. Experimental

Samples were prepared on silicon and fused silica substrates by pulsed laser deposition (PLD). An excimer (KrF) laser was used, with pulses of 9 J/cm^2 and repetition rate of 10 Hz, in

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[*] Corresponding author: adrian.lungu@infim.ro

vacuum or in oxygen-containing controlled atmosphere. The targets were prepared by pressing and sintering anatase TiO_2 and iron metal powders. During deposition, the substrates were heated, in order to avoid droplet formation on the surface and for improving the crystallinity. The preparation conditions are given in Table 1.

XPS was employed to derive the elemental composition and chemical states, by using a VG ESCA Mk-II installation, upgraded with a Specs X-ray gun and a Specs electron flood gun for sample neutralization. The Mg K_α unmonochromatized radiation was used for excitation. Photoelectrons were collected at a takeoff angle of 50°. The magnetic characteristics have been inferred from MOKE hysteresis loops (AMACC Anderberg & Modéer Accelerator instrument) with the magnetic field lines parallel to sample surface. MOKE measurements were performed in dark or by illuminating the sample with a standard light bulb of 100 W power placed at 10 cm from the sample.

X-ray absorption fine structure spectroscopy (XAFS) measurements were performed at the Hasylab storage ring facility in Hamburg, Germany, on the beamline E4 (EXAFS II). X-rays produced by a bending magnet were pre-focused by an Au-coated toroidal mirror and then passed through a double-crystal Si(111) monochromator. Fluorescence yield of the Fe-doped titania thin films was measured by recording the Fe K_α fluorescence using a Si(Li) detector, while scanning the excitation photon energy. The reference samples were Fe metal foils (7 μm thickness) or Fe_2O_3, Fe_3O_4, TiO_2 and TiO powders (about 20 mg) pressed in pellets with cellulose. The reference samples were measured in transmission mode by recording the incident and transmitted X-ray intensities with ionization chambers.

3. Results and discussion

Fig. 1 presents the MOKE loops obtained on the four samples, in dark (blue curves) and by optical irradiation (red curves). Samples TF5 and TF6 exhibited negligible magnetism, whereas samples TF3 and TF4 showed superparamagnetic properties [5]; nevertheless, the magnetization is about 3-4 times larger in TF3 than in TF4.

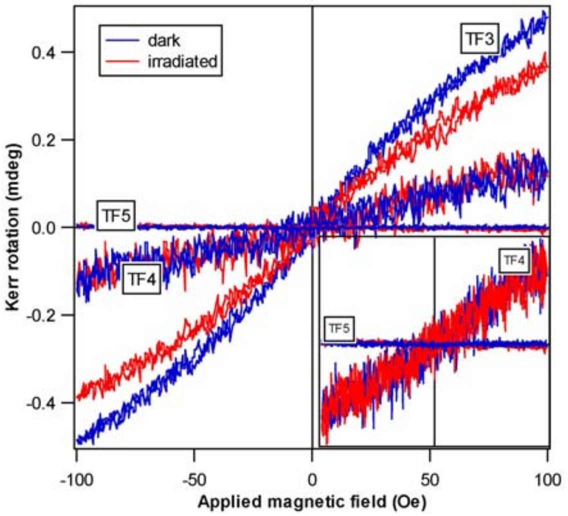


Fig. 1. Magneto-optical Kerr effect (MOKE) loops for various samples. Blue curves: measurements performed in dark, red curves: measurements while irradiating the samples in the optical range.

Additionally, TF3 exhibited quite different magnetization curves for measurements performed in dark or by irradiating the sample. A similar behavior was reported in Ref. [6], namely a decrese in the coercitive field was observed for a specific ferromagnetic sample of (In,Mn)As. Nevertheless, the actual data are the first observation of such behavior for an oxide-based DMS. As may be seen from Table 1, the only difference between TF3 and TF4 is the substrate temperature during the PLD process. It is clear that the occurence of the light-dependent magnetism in TF3 needs to be investigated in more detail.

Fig. 2 presents X-ray photoelectron spectroscopy data for Ti 2*p* (a); O 1*s* (b); Fe 2*p* (c). The samples were measured as introduced, without Ar$^+$ sputtering, since it has been shown that this process results in oxygen depletion near the surface [4]. Hence, the O 1*s* electron distribution curve (EDC) contains a major contribution from the inherent contamination layer (oxygen in O=O, O=C, HO-C coordinations [7], see Fig. 2b). Therefore, in deriving the sample compositions from Table 1, these components were subtracted from the O 1s EDC. The sample composition was infered by using Wagner's atomic sensitivity factors [8]. XPS data suggest two situations: (i) for depositions performed in vacuum, a higher Fe concentration is obtained and the sample stoichiometry is strongly affected; (ii) for depositions performed in oxygen atmosphere, a few Fe at. percents are obtained (5-8 %), embedded in TiO$_2$ with unaffected stoichiometry. The Ti 2*p* EDC aspect (Fig. 2a) confirms this supposition [4]. One may suppose that "peroxides" formed in case (i), such as Fe$_2$Ti$_5$O$_{17}$ or Fe$_2$Ti$_4$O$_{15}$ form superparamagnetic (SP) nano-particles.

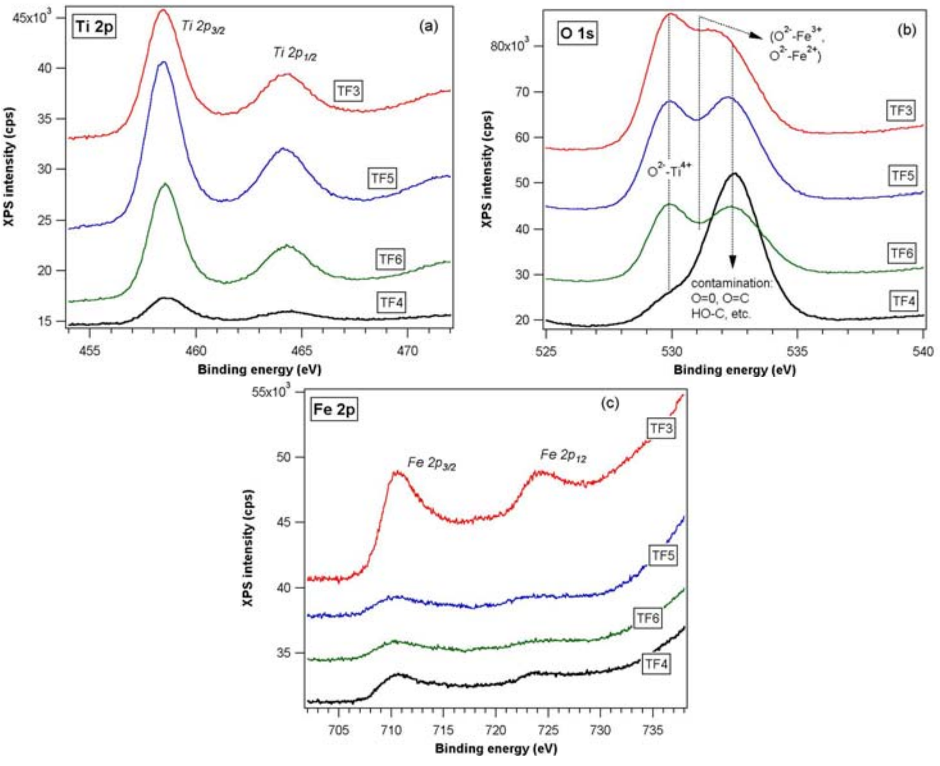


Fig. 2. Electron distribution curves (EDC) obtained by X-ray photoelectron spectroscopy of the Ti 2p levels (a); O 1s levels (b); Fe 2p levels (c).

Fig. 3 presents Fe K-edge XAFS from the investigated samples, compared with spectra of references hematite, magnetite, and Fe metal. It is clear that the TF4 spectrum is quite similar to the spectrum of Fe metal; this observation, correlated with the superparamagnetic properties evidenced by MOKE magnetometry (Fig. 1), allows to infer that sample TF4 is composed by Fe metal nanoparticles. This observation does not contradict the approximate peroxide stoichiometry inferred by XPS (Table 1); simply the XPS technique investigates only the 1-2 nm of the sample surface, owing to the limited photoelectron escape depth [9], while X-ray absorption probes the whole film thickness. Also, the TF5-6 XAFS spectra ressemble the hematite Fe$_2$O$_3$ spectrum, although the XPS data suggest Fe$_x$Ti$_{1-x}$O$_2$ compounds.

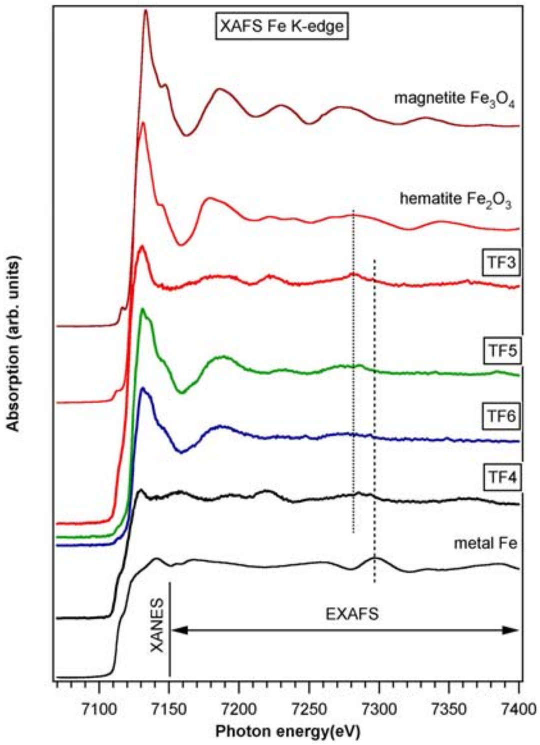


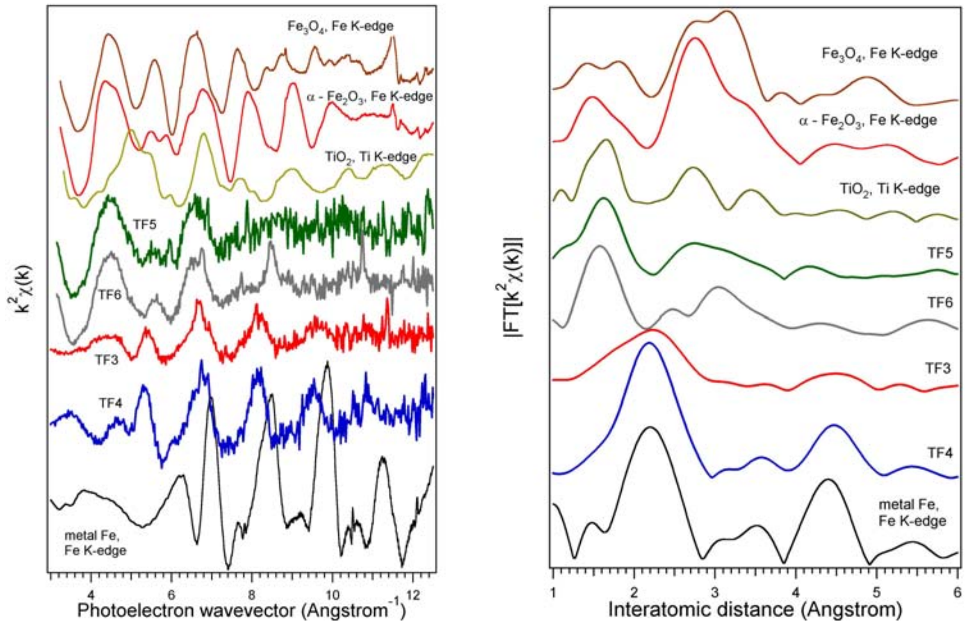
Fig. 3. Fe K-edge X-ray absorption fine structure spectra of samples TF3-6, compared with spectra of reference oxides (hematite Fe_2O_3, magnetite Fe_3O_4) and of metal Fe. The EXAFS and XANES regions are indicated.

For TF3, the sample which is the most interesting in view of its unusual magnetisation decrease with irradiation (Fig. 1), the situation is more complicated. The near-edge structures (Fig. 3) consist in less prononced resonances than for other oxide-base samples. Also, the pre-edge structure presents a shoulder quite similar to the XANES of metal Fe. We may infer that TF3 is composed by Fe in multiple environments: partly metallic, partly oxidized.

The EXAFS oscillations are extracted from the XAFS measurements by using a standard procedure [10] and are represented in Fig. 4a. The Fourier transforms (FT) of the EXAFS function, weighted by the square of the photo-electron wavevector $k = [2m(h\nu - E_0)]^{1/2}/\hbar$ (E_0 being the Fe K absorption threshold energy) and by using a Hanning window [10], are represented in Fig. 4b. Data for the Ti K-edge EXAFS measurements on a reference anatase TiO_2 are also represented in Fig. 4, for comparison.

Table 1. Summary of the relevant parameters for the investigated samples.

Sampl e series	Preparation conditions		Atomic composition				Magnetism
	$P[O_2]$ (Pa)	substrate T (°C)	Fe:Ti	O:Ti	O:(Ti+ Fe)	Approximate surface stoichiometry	
TF3	10^{-3}	450	0.397	3.438	2.461	$Fe^{7+}{}_2Ti^{4+}{}_5O^{2-}{}_{17}$	light-dependent SP
TF4	10^{-3}	600	0.483	3.624	2.444	$Fe^{7+}{}_2Ti^{4+}{}_4O^{2-}{}_{15}$	light-independent SP
TF5	0.1	450	0.054	2.051	1.946	$Fe_xTi_{1-x}O_{2-\delta}$, δ, $x \approx$ 0.05	paramagnetism
TF6	10	450	0.080	2.110	1.954	*ibid.*, $\delta \approx 0.05$, $x \approx$ 0.08	not measurable



a b

Fig. 4. (a) k^2-weighted EXAFS spectra $\Delta\mu/\mu_0$ extracted from the X-ray absorption (Fig. 3); (b) Fourier transforms of the k^2-weighted EXAFS signal.

The analysis of the EXAFS data reveals that the FT for samples TF5-6 are quite similar to that of Ti K-edge, so in this case the Fe local environment is quite similar to that of Ti in anatase. The second and third coordination shell of TF5 resembles also to the hematite case, whereas for TF6 it ressembles to the magnetite case. It seems that these two samples are composed by a mixture of Fe oxide (hematite or magnetite) nanoparticles, with a contribution from Fe placed substitutionally in the anatase TiO_2 lattice.

The EXAFS oscillations for TF4 are quite similar to that of metal Fe, except for a constant phase shift (Fig. 4a). Its FT (Fig. 4b) is also quite similar to the case of Fe metal, therefore strenghtening the belief that this sample is composed by metal Fe (superparamagnetic) nanoparticles.

The case of TF3, which is the most interesting one, is again the most dificult to assess. A high degree of disorder may be infered from its FT (Fig. 4b). The first coordination shell presents a broad maximum, which may arise from Fe both in metallic aggregates and from oxidized Fe, but for the latter actually it is difficult to assess wheter it represents Fe oxides or Fe placed substitutionally in the TiO_2 lattice. A second coordination shell presents a high degree of disorder, whereas a third coordination shell appears at a similar position as in metal Fe. Consequently, this sample seems to be composed partly by Fe nanoparticles and partly by oxidized Fe in an environment difficult to be exactly determined within the actual data. More detailed curve fitting analysis of the EXAFS data are needed to gain more information on this sample, but this procedure is beyond the aim of the present Contribution.

4. Conclusions

Three situations were evidenced in samples obtained by PLD from anatase TiO_2 and metal Fe mixtures: (i) Samples prepared in oxygen atmosphere, where Fe partly substitutes Ti in anatase-like environments, superposed to Fe in oxide-like environments (hematite or magnetite). These samples did not exhibit relevant magnetic properties at room temperature. Therefore, a standard room temperature ferromagnetic DMS was not synthesized, despite the EXAFS evidence for some Fe substituting Ti in TiO_2. (ii) Samples prepared in vacuum at high temperature, where superparamagnetic Fe particles were evidenced by several methods; (iii) Samples synthesized in vacuum at lower temperature, where a superparamagnetic behaviour was evidenced, with a visible decrease in magnetization under optical irradiation. These samples are composed of mixtures of Fe nanoparticles and oxidized Fe, with a high degree of local disorder.

Acknowledgements

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References

[1] K. A. Griffin, A. B. Pakhomov, C. M. Wang, S. M. Heald, K. M. Krishnan, Phys. Rev. Lett. **94**, 157204 (2005); N. H. Hong, J. Magn. Magn. Mater. **303**, 338 (2006); T. C. Kaspar, T. Droubay, V. Shutthanandan, S. M Heald, C. M. Wang, D. E. McCready, S. Thevuthasan, J. D. Bryan, D. R Gamelin, A. J Kellock, M. F. Toney, X. Hong, C. H. Ahn, S. A. Chambers, Phys. Rev. B **73**, 155327 (2006).
[2] M. A. Ruderman, C. Kittel, Phys. Rev. **96**, 99 (1954); T. Kasuya, Progr. Theor. Phys. **16**, 45 (1956); K. Yosida, Phys. Rev. **106**, 896 (1957).
[3] H. Ohno, D. Chiba, F. Matsukura, T. Omiya, E. Abe, T. Dietl, Y. Ohno, K. Ohtani, Nature **408**, 944 (2000); T. Zhao, S. R. Shinde, S. B. Ogale, H. Zheng, T. Venkatesan, R. Ramesh, S. Das Sarma, Phys. Rev. Lett. **94**, 126601 (2005); D. Chiba, M. Sawicki, Y. Nishitani, Y. Nakatani, F. Matsukura, H. Ohno, Nature **455**, 515 (2008).
[4] D. Luca, D. Macovei, C. M. Teodorescu, Surf. Sci. **600**, 4342 (2006).
[5] L. Néel, Ann. Geophys. **7**, 90 (1951).
[6] A. Oiwa, T. Slupinski, H. Munekata, Appl. Phys. Lett. **78**, 518 (2001).
[7] J. F. Moulder, W. F. Stickle, P. E. Sobol, K. Bomben, Handbook of X-ray Photoelectron Spectroscopy 2nd ed. (J. Chastain, editor), Perkin-Elmer Corporation (Physical Electronics), Eden Prairie, MN (1992).
[8] C. D. Wagner, L. E. Davis, M. V. Zeller, J. A. Taylor, R. M. Raymond, L. H. Gale, Surf. Int. Anal. **3**, 211 (1981).
[9] S. Hüfner, Photoelectron Spectroscopy: Principles and applications, 3rd Ed., Springer, Berlin (2003).
[10] B. K. Teo, EXAFS: Basic Principles and Data Analysis, Springer, Berlin (1983).