

Fabrication and characterization of nano-structured ferromagnetic $\text{Ti}_{1-x}\text{Fe}_x\text{O}_2$ thin films

R. Apetrei¹, C. Negri², D. Macovei², V. Dascalescu¹, D. Luca¹, and C.M. Teodorescu²

¹"Alexandru Ioan Cuza" University Iasi, King Carol I No. 11, 700506 Iasi, Romania

²National Institute of Materials Physics Bucharest, 105 bis Atomistilor St. 077125-Magurele, Romania

Nanostructured intrinsic and doped titanium oxide materials have been subject to both basic and applied research in photocatalytics, photovoltaics, or superhydrophilicity/hydrophobicity related systems [1-3]. Diluted magnetic semiconductors based on titania materials have also been extensively studied during last years in connection with promising applications in spintronic devices. The results reported here are related to this latter class of applications, based on the Coey model of ferromagnetic coupling *via* the electrons trapped in oxygen vacancies in TiO₂ materials [4]. The characterization of heavily Fe-doped RF-sputtered TiO₂ thin films has been done here in terms of elemental composition, surface morphology, atomic ordering, structure, room-temperature magnetic and optical properties.

The samples have been prepared in an RF sputtering facility (13.56 MHz, 80 W) according to the procedure described in more detail in ref. [3], using a ceramic TiO₂ disk target and 1 to 3 Fe₂O₃ sintered pellets, placed on the high-rate sputtering area. The morphology, structure, elemental composition, and the band gap values have been derived from the AFM (NT-MDT Solver), XRD (Bruker D8), XPS (Phi-UlvacVersaProbe 5000), and spectro-photometry (Perkin Elmer) data, respectively. The magnetic characteristics have been inferred from MOKE loops (AMACC Anderberg & Mod er Accelerator). X-ray absorption fine structure (XAFS) measurements were performed at the Hasylab storage ring facility in Hamburg, Germany, on the beamline E4 (EXAFS II). Monochromatic photons were used in all experiments, along with standards of powder materials and reference metals (Fe or Ti) for scale standards, in the transmission mode. The fluorescence spectra (Ti and Fe K_α) of the Ti_{1-x}Fe_xO₂ films were recorded with a Si(Li) detector, while scanning the incident photon energy.

The evolution of the Fe signal in the XPS spectra, for different Fe content in the films ($x = 0$ to $x = 0.6$) is shown in Fig. 1. An AFM surface view of Ti_{0.4}Fe_{0.6}O₂ sample is shown in Fig. 2. Smooth surface film (mean roughness values ranged between 5 to 9 nm) were observed, within the above-mentioned Fe content values. The grazing angle XRD patterns (not shown here) showed the existence of nanometer-sized anatase ordered domains spread with an amorphous matrix. The effect of increasing the Fe content in the films was reflected in the shift of the absorption edge in the optical transmittance data from 394 nm to 515 nm (spectra not shown here, due to room limitation).

The evolution of the hysteresis loops with Fe content is shown in Fig. 3, while the X-ray absorption near-edge structure at the Ti and Fe K-edge are shown in Figs. 4 and 5. The oxygen-depletion in the magnetron plasma stabilizes titania suboxides in the films with oxygen deficit that finally result in *n*-doped films [3]. These results will be fully discussed in the final paper, taking into account the chemical reactivity and the alterations in the electronic structure of the materials. As demonstrated by MOKE and the EXAFS data (Figs. 3 and 6, respectively), there is a close correlation between the activation of the oxygen vacancy processes with the anatase-ordered domains and the ferromagnetic properties of the films.

Acknowledgements: This work was granted by the Romanian National Authority for Scientific Research through Contract No. 71-063/2007. Support from Dr. Dariusz Zajac at the E4 beamline is gratefully acknowledged.

References:

- [1] T. L. Thompson, J. T. Yates Jr., Chem. Rev. **106**, 4428 (2006).
- [2] K. Seki, M. Tachiya, J. Phys. Chem. **B 108**, 4806 (2004).
- [3] D.Luca, C.M.Teodorescu, R.Apetrei, D.Macovei, D.Mardare, Thin Solid Films **515**, 8605 (2007).
- [4] J.M.D. Coey, A.P. Douvalis, C.B. Fitzgerald, M. Venkatesan, Appl. Phys. Lett. **84**, 1332 (2004).

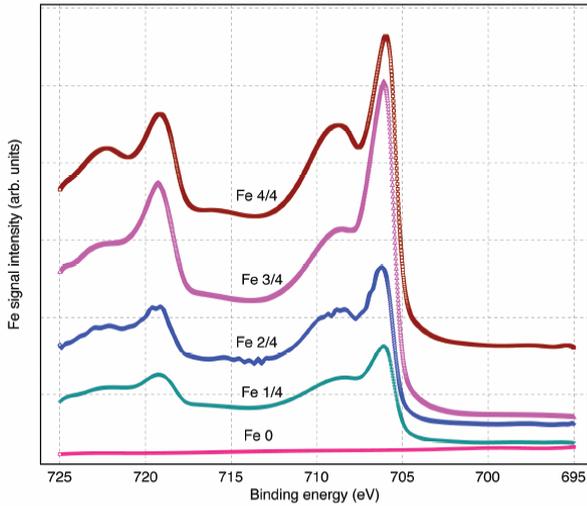


Figure 1: The Fe signal evolution in the XPS spectra.

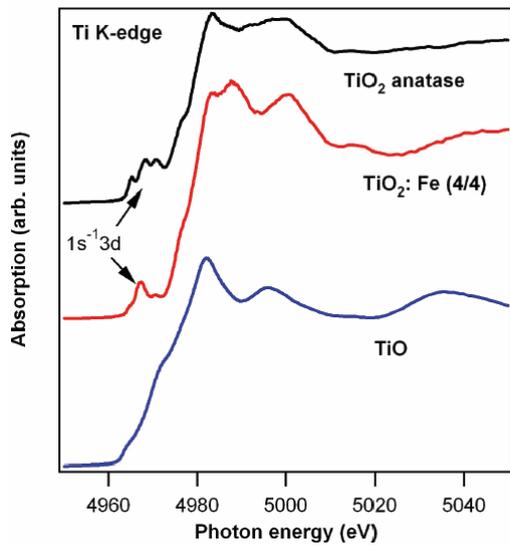


Figure 3: MOKE loops of the samples (the labels 1/4 to 4/4 indicate the values of $x = 0.15, 0.30, 0.45,$ and $0.60,$ respectively).

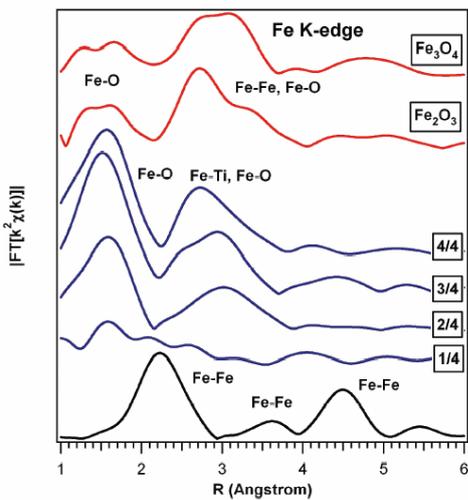


Figure 5: X-ray absorption near-edge structure at the titanium Fe K-edge for the same materials.

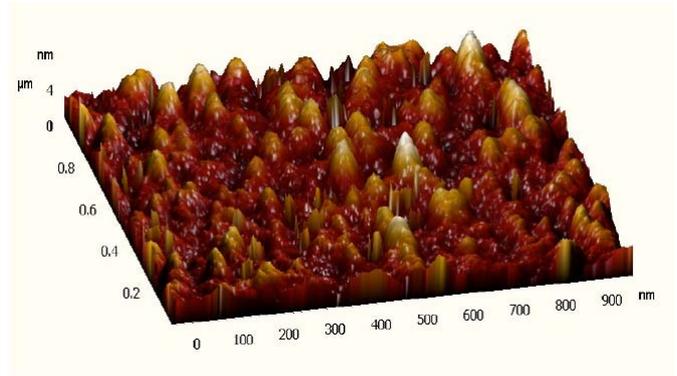


Figure 2: An AFM image of the $Ti_{0.4}Fe_{0.6}O_2$ sample surface.

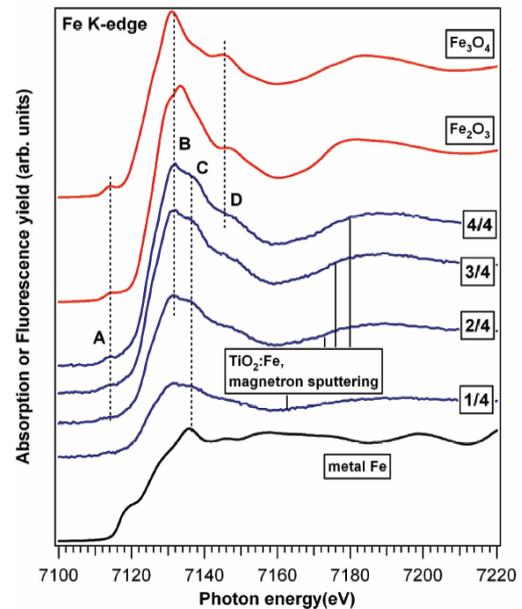


Figure 4: X-ray absorption near-edge structure at the titanium K-edge for various doping conditions.

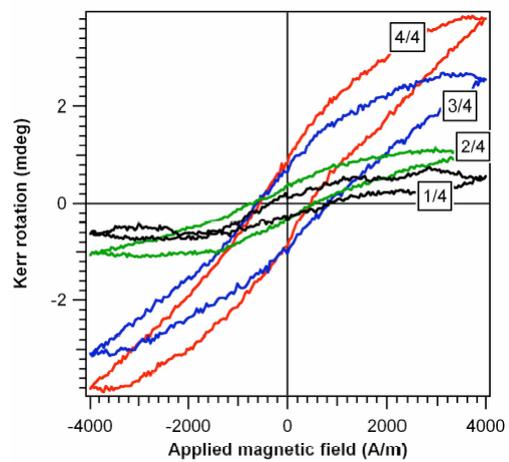


Figure 6: Fourier transforms of the X-ray absorption near-edge structure (EXAFS) at the titanium K-edge.