

# AN XPS STUDY OF RF SPUTTERED $Ti_{1-x}Fe_xO_{2-\delta}$ THIN FILMS

Dumitru Luca, Radu Apetrei, Marius Dobromir, Vasile Dascalescu, Cristian-Mihail Teodorescu

## Abstract:

Introduction of small amounts of dopant Fe cations in titania was mainly intended for improving the oxidative power of the host  $TiO_2$  surface, by shifting the absorption edge of the material towards the blue side of the visible range. Apart from this, other possible applications of Fe-containing  $TiO_2$  materials have been foreseen in the field of diluted ferromagnetic semiconductors for spintronics. As a general remark, while pristine and/or low-level doped titania materials remained a hot subject in basic research, and environment- and energy related applications, reports on  $Ti_{1-x}Fe_xO_2$  materials ( $x > 0.1$ ) scarcely occurred in literature. We have initiated recently an investigation of heavily doped titania thin films within a wider iron composition range. Here, we report on the result of an XPS study of the RF sputtered oxygen-deficient  $Ti_{1-x}Fe_xO_{2-\delta}$  thin films ( $x = 0.15 - 0.62$ ) and discuss the connection of the results with the macroscopic properties of the materials.

**Keywords:**  $Ti_{1-x}Fe_xO_{2-\delta}$  thin films, XPS, AFM,  $Fe_2O_3$ , hematite, magnetite.

## 1. Introduction

Pristine and doped  $TiO_2$  materials have been under intensive research for decades, leading to well-documented applications in environment- and energy-related fields [1]-[3]. High efficiency titania materials based on anatase  $TiO_2$  are nowadays utilized as photocatalytic, bactericidal and super-hydrophilic materials, or as key components in gas sensors and dye-sensitized solar cells. On the other hand, diluted magnetic semiconductors prepared by doping titania with small amounts of ferromagnetic impurities (Co, Fe) are now under intensive research for possible applications in spintronics [4]. While the information in the literature is mainly concerned with the effect of low-level substitutional Fe doping of the titania thin films, here we extend our approach towards full characterization of  $Ti_{1-x}Fe_xO_2$  materials in relation with their nano-structure, optical and electric properties.

## 2. Experimental details

300 nm thick films of  $Ti_{1-x}Fe_xO_{2-\delta}$  (TFO) have been grown on soda lime glass and Si(100) substrates in a home-built RF magnetron sputtering facility (13.56 MHz,  $2.5 \times 10^{-5}$  mbar base pressure) [5] under the conditions of constant forward RF power (80 W) and Ar gas discharge pressure ( $5.5 \times 10^{-3}$  mbar). A 7.62 cm diameter ceramic  $TiO_2$  disk target (K. J. Lesker) was used to grow the reference film ( $x = 0$ ). In all the deposition experiments, the film substrates were kept at 250°C. To fabricate TFO

films, 1 to 4 sintered pellets of  $Fe_2O_3$ , 2 mm in diameter, 1 mm thick, were placed in successive deposition runs on top of the facing-up  $TiO_2$  target, within the intensive sputtering area.

Film surface morphology was evaluated from the AFM images taken using a NT-MDT Solver Pro 7 atomic force microscope, operated in tapping mode.

X-ray Photoelectron Spectroscopy (XPS) measurements have been done to derive surface elemental composition and chemical state of O, Ti and Fe. The measurements have been done in a Physical Electronics PHI-5000 VersaProbe XPS system using the mono-chromated  $Al K_{\alpha}$  radiation ( $h\nu = 1486.6$  eV). The take-off angle of the photoelectrons was 45°. All the XPS peak positions in the survey spectra were calibrated with respect to the C 1s peak at 284.6 eV. Information on the films structure was derived from XRD patterns (Dron 2 diffractometer using  $Cu K_{\alpha}$  radiation,  $\lambda = 1.540$  Å). The band gap values were calculated from transmittance data (Perkin Elmer) using the standard procedure [6].

## 3. Results and Discussion

The 200 nm thick film samples have been labeled as  $Fe0$ , and  $Fe1$  to  $Fe4$ , in accordance with the number of  $Fe_2O_3$  pellets used for film preparation, as described in the previous section. The main characteristics of the samples are shown in Table 1. A  $1 \mu m \times 1 \mu m$  detail in the AFM surface picture of the  $Fe3$  sample is shown in Fig. 1, as relevant example. Small grains spread within a rather smooth surface occur in all the investigated samples. The AFM images showed that the surface roughness gradually diminished by introduction of iron in the films.

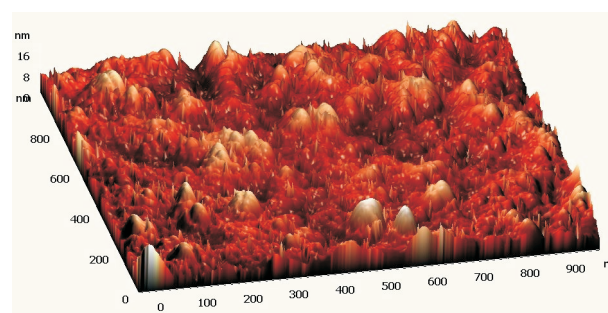


Fig. 1. A 3-D AFM image of the  $Fe3$  film surface.

A peak value of 13 nm was found for the average surface roughness of the reference sample ( $Fe0$ ). The TFO films' average roughness remains below this value, fluctuating between 5 and 8 nm, upon increasing Fe concentration in the films (see Table 1).

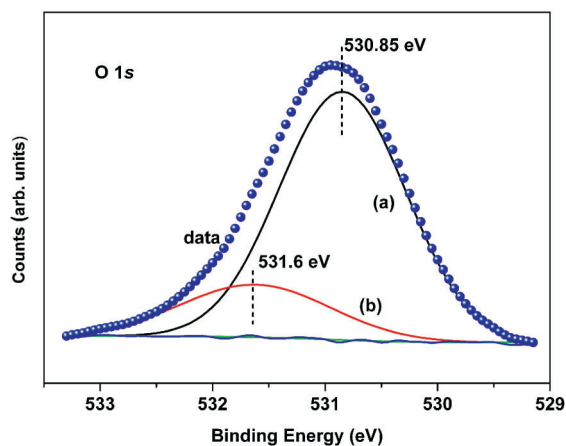


Fig. 2. High resolution scan of the O 1s peak (sample Fe3).

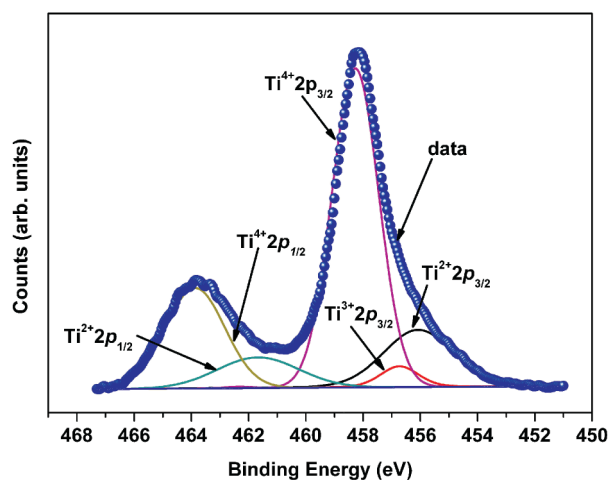


Fig. 3. High resolution scan of the Ti 2p peak (sample Fe3).

The XPS data showed that the Fe/Ti atomic ratio of the as-prepared films increased monotonically by increasing the number of the  $\text{Fe}_2\text{O}_3$  pellets (samples Fe0 to Fe4) as shown in Table 1. All the samples were oxygen deficient, as no  $\text{O}_2$  was introduced in the discharge gas during deposition to compensate for oxygen depletion [7]. Even in the reference sample (FeO),  $\delta$  is 0.66. As seen in Table 1, the O/(Ti+Fe) atomic ratio diminishes gradually up to a value of 0.82 in the highest iron content TFO films.

The Fe/Ti atomic concentration ratio increases monotonically from 0.00 to 1.60 under the same conditions (see Table 1).

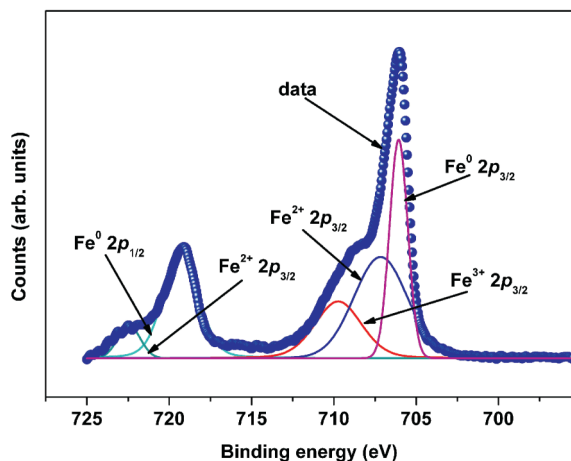


Fig. 4. High resolution scan of the Fe 2p peak (sample Fe3).

The position and the shape of the O 1s core level peak remain practically unchanged in all the investigated samples. This peak can be deconvoluted into: (a) a main component, located at BE = 530.8 eV, related to the O-Ti<sup>2+</sup> bonding and (b) a weaker one (BE = 531.6 eV), shifted with 0.5 eV towards higher binding energies, compared with BE = 531.1 eV, specific to the O-Ti<sup>3+</sup> bonding [2] (see Fig. 2). This shift is related to additional effect of the so-called surface component, reported in ref. [3] due to adsorbed OH- radicals in the surface.

Along with the main TiO<sub>2</sub> oxide component, smaller amounts of TiO and Ti<sub>2</sub>O<sub>3</sub> are present in the films. This conclusion is evident from the core level Ti 2p<sub>3/2</sub> XPS spectra (an example of the deconvolution is shown in Fig. 3). The normalized peak areas of the Ti<sup>2+</sup> and Ti<sup>3+</sup> signals with respect to the Ti<sup>4+</sup> main peak vary from 0.68:0.40:1.00 for x = 0.15; to 0.21:0.30:1.00 for x = 0.29 to 0.13:0.11:1.00 for x = 0.46 and 0.07:0.13:1.00 when x = 0.62.

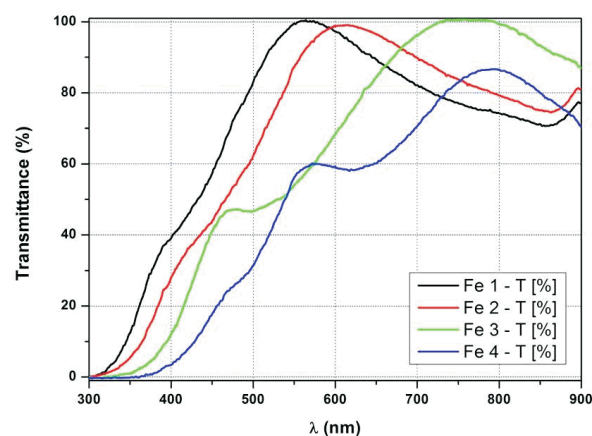


Fig. 5. The transmittance spectra of the TFO films.

The peak area of the core level Fe 2 p<sub>3/2</sub> peak increases by a factor of slightly larger than 4 after increasing the number of Fe<sub>2</sub>O<sub>3</sub> pellets. In all the Fe-containing films, the Fe 2p peak could be deconvoluted into three components: (a) the Fe<sup>0</sup> non-reacted component, whose weight fluctuates around 32% from the total amount of Fe in the sample; (b) the Fe<sup>2+</sup> component weighting approx. 24% of the total amount of Fe, and (c) the Fe<sup>3+</sup> component - the balance. An example of the de-convolution of the 2p<sub>3/2</sub> peak of the Fe3 sample is shown in Fig. 4.

Previously, Fe K - edge XANES measurements have been done on lower iron - content Ti<sub>1-x</sub>Fe<sub>x</sub>O<sub>2</sub> films (x ranging between 0 and 0.15) [8]. The results for nearest-neighbour configuration showed that both magnetite and metal Fe co-exist in the samples with x = 0.15, while the EXAFS spectra at the same edge showed the existence of hematite. This is so, since the Fourier transforms rely on a (distorted) second coordination shell (due to the presence of Ti cations), similar to the 2<sup>nd</sup> coordination shell of hematite.

Weak anatase A(101) and A(004) diffraction peaks occurred in the XRD patterns of the FeO reference film, exclusively (not shown here), while the diffraction features of the TFO samples remained below the detection limit of the diffraction instrument.

Increasing the iron content results in dramatic alteration of the optical parameters of the films. The transmit-

tance spectra (Fig. 5) of the films show that the threshold,  $\alpha$ , of the fundamental absorption of the  $Ti_{1-x}Fe_xO_2$  films could be described by the expression:  $\alpha = A(E-E_g)^2$ , where  $A$  is a constant,  $E$  and  $E_g$  are the optical band gap of the ferromagnetic film and pure anatase  $TiO_2$ , respectively. The value of the exponent is a characteristic for the indirect allowed transition dominating over the optical absorption [6]. The optical band gap values, derived according to the procedure by Sreemany and Sen [6], are listed in Table 1. The corresponding shifts in the absorption edge of the TFO materials are equivalent to a shift in the absorption edge in terms of wavelength from 413 nm (sample Fe0) to 564 nm (sample Fe4).

Table 1. Sample main data.

Sample	x	R(nm)	O/(Ti+Fe) atomic ratio	Fe/Ti atomic ratio	$E_g$ (eV)
Fe0	0.00	13	1.34	0.0	3.0
Fe1	0.15	8	1.22	0.34	2.7
Fe2	0.29	5	1.10	0.54	2.5
Fe3	0.49	5	0.79	1.33	2.3
Fe4	0.62	8	0.82	1.60	2.2

#### 4. Conclusion

300 nm thick, amorphous  $Ti_{1-x}Fe_xO_{2-\delta}$  films (with  $0 < x < 0.62$  and  $0.66 < \delta < 1.18$ ) have been fabricated by RF magnetron sputtering of a titania sintered target. The iron content in the sample has been adjusted using a mosaic configuration, by placing a variable number of  $Fe_2O_3$  sintered pellets on the magnetron surface in the high-rate sputtering area.

The XPS results showed that a non-reacted  $Fe^0$  component occurs in all the iron-containing as-deposited samples, spread in the amorphous matrix. This is accompanied by a red shift of the absorption edge of approximately 151 nm and a decrease of the band gap from 3.0 to 2.2 eV, in the same range of Fe composition.

The oxygen-depletion in the films is related to the important fraction of the high-valence state of titanium and Fe cations. The XPS results suggest that it is quite probably that magnetite, hematite and metallic Fe nanodomains can be present in the films, as spread out in the amorphous material, as demonstrated for samples with  $x$  below 0.15 [8].

The current results extend the composition range of the TFO materials above the limit value  $x = 0.15$ , which is the maximal value reported in ref. [8] At least for this limit value, where we can compare the results, the current XPS results confirm the former XANES and EXAFS results, i.e.: (a) A predominant  $TiO_2$  phase coexist with significant  $TiO$  and  $Ti_2O_3$  phases (but no metal Ti); (b) magnetite, hematite and metal Fe co-exist with hematite.

Further information on the local order around the cations species and type of Fe incorporation in the range of  $x$  between 0.15 and 0.62 is expected from the last-hour performed XANES and EXAFS measurements at the HASY-LAB synchrotron facility in Hamburg, Germany. The data are now under processing, and the results are scheduled

for publication further on.

#### ACKNOWLEDGMENTS

The financial support from the Romanian Ministry of Education, Research and Innovation, through Grant 71-63/2007 (MAMA-INCOAPE) is acknowledged.

The support from Dr. D. Timpu from the Institute of Macromolecular Chemistry "Petru Poni" in Iasi, Romania, in the AFM measurements is appreciated.

#### AUTHORS

**Dumitru Luca\***, **Radu Apetrei**, **Marius Dobromir**, **Vasile Dascaleanu** - Alexandru Ioan Cuza University of Iasi, 11 Carol I Blvd. 700506-Iasi, Romania. Phones: +40 232 20 1179, +40 232 20 1171, fax: +40 232 20 1150.

E-mails: dumitru.luca@uaic.ro, rapetrei@uaic.ro, marius.dobromir@uaic.ro, dascaleanu@yahoo.com.

**Cristian-Mihail Teodorescu** - National Institute of Materials Physics, Bucharest, 077125 Magurele-Ilfov, Romania. Phone: +40 21 369 0170, fax: +40 21 369 0177. E-mail: teodorescu@infim.ro

\* Corresponding author

#### References

- [1] Thompson T.L., Yates J.T. Jr., „Surface science studies of the photoactivation of  $TiO_2$  new photochemical processes”, *Chem. Rev.*, no. 106, 2006, pp. 4428-4453.
- [2] Luca D., Teodorescu C.M., Apetrei R., Macovei D., Mardare D., „Preparation and characterization of in-created - efficiency photo-catalytic  $TiO_{2-x}N_x$  thin films”, *Thin Solid Films*, no. 515, 2007, pp. 8605-8608.
- [3] Luca D., Macovei D., Teodorescu C.M., „Characterization of titania thin films prepared by reactive pulsed-laser ablation”, *Surf. Sci.*, no. 600, 2006, pp. 4342-4346.
- [4] Coey J.M.D., Douvalis A.P., Fitzgerald C.B., Venkatesan M., „Ferromagnetism in Fe-doped  $SnO_2$  thin films”, *Appl. Phys. Lett.*, no. 84, 2004, pp. 1332-1334.
- [5] Luca D., Mardare D., Iacomi F., Teodorescu C.M., *Appl. Surf. Sci.*, no. 252, 2006, p. 6122 f.
- [6] Sreemany M., Sen S., „A simple spectro-photometric method for determination of the optical constants and band gap energy of multiple layer  $TiO_2$  thin films”, *Mat. Chem. Phys.*, no. 83, 2004, pp. 169-177.
- [7] Mardare D., Iacomi F., Luca D., „Substrate and Fe-doping effects on the hydrophilic properties of  $TiO_2$  thin films”, *Thin Solid Films*, no. 515, 2007, pp. 6474-6478.
- [8] Apetrei R., Negrila C., Macovei D., Dascaleanu V., Teodorescu C.-M., Mardare D., and Luca D., “Fabrication and characterization of nano-structured ferro-magnetic  $Ti_{1-x}Fe_xO_2$  thin films”. In: *Proc. NSTI Nanotech 2009*, www.nsti.org, ISBN 978-1-4398-1782-7, vol. 1, pp. 375-378.