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Fe-doped TiO₂ thin films

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Abstract

The reactive sputtering technique was used to obtain undoped and Fe-doped TiO₂ thin films deposited on glass substrates. At 250 °C substrate temperature, undoped TiO₂ films crystallize in a mixed rutile/anatase phase, while Fe-doped films exhibit the rutile phase only. Presence of Fe³⁺ ions into the TiO₂ lattice is suggested by the intensity variation of forbidden 1s → 3d transitions between the Ti and Fe K-edges. Ti K-edge EXAFS data are assessed to a mixture of the two kinds of surroundings, a rutile-like crystalline phase, identified also by X-ray diffraction, and a nanosized or amorphous anatase-like surrounding. The local atomic order about Fe atoms is quite different and could be related also to an amorphous phase. The Swanepoel method is used to obtain the dispersion of the refractive index below the interband absorption edge. The dispersion energy, the single-oscillator energy and the coordination number of the Ti atoms are evaluated using the single-oscillator model (Wemple–DiDomenico).

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1. Introduction

Titanium is a 3d transition metal, whose oxides, in thin films, show attractive properties: high transmittance in the visible spectral range, high refractive index, high chemical and thermal durability in hostile environments, etc. Therefore, TiO₂ films have a high potential for device applications. One way of controlling its properties is by doping with different atoms. In our previous papers [1–4] we have reported the influence of doping with Ce, Nb Cr or Fe on the structure, microstructure and, as a consequence, on the optical and electrical properties of titanium oxide films. In this paper we focused on the influence of Fe-doping on the structural properties, local atomic environment, and optical constants of titanium dioxide films.

2. Experimental

Titanium oxide films were prepared by reactive radio-frequency (RF) sputtering in a conventional 13.56 MHz setup (Huettinger, model PFG 300RF). The films were deposited onto glass substrates, at 250 °C. Fe-doping was achieved using a mosaic structure of Ti and Fe₂O₃. Oxygen (99.998%) was used as reactive gas and argon (99.9997%) as sputtering gas. The total pressure of the Ar + O₂ mixture gas during deposition was set at 0.10 Pa, the partial pressure of O₂ being of 0.03 Pa.

For determining the phase composition of the films, X-ray diffraction (XRD) measurements were performed at grazing incidence (4°) using CuK_α radiation ($\lambda = 1.54178$ Å).

Extended X-ray absorption fine structure (EXAFS) measurements at the Ti and Fe K-edges were performed on beamline E4 (station EXAFS II) at the Doris storage ring facility in Hasylab, Hamburg. Measurements were recorded in fluorescence mode, by scanning the photon energy and recording the fluorescence emitted by the

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absorbing atom of interest (Ti or Fe), using a standard liquid nitrogen cooled Ge detector.

The optical transmittance of the films was measured in the visible region using a SPECORD UV–VIS double-beam spectrophotometer, Carl Zeiss Jena.

3. Results and discussion

XRD studies performed on several sets of undoped and Fe-doped TiO_2 samples deposited onto glass substrates, reveal that a phase transformation (anatase to rutile) take place by iron doping films [3,5]. The weight percentage of the rutile phase among the total crystallized phase (i.e. by excluding amorphous contributions which do not reflect in XRD), as calculated using a formula proposed by Spurr and Myers [6], increases by doping from 30% to 100% [5].

Based on EDX measurements [5], the chemical formula of Fe-doped sample may be approximated as $\text{Fe}_{0.01}\text{Ti}_{0.99}\text{O}_2$.

We denote by S and S.Fe the undoped and Fe-doped sample, respectively. The anatase average grain size, obtained from A(101) peak via Scherrer's formula, is about 16 nm, while the rutile peak R(110) is wide for both samples, indicating that rutile grain size is about 7 nm.

Fig. 1 shows the X-ray absorption spectra recorded for Fe-doped sample, S.Fe, at the Ti K-edge (a) and at the Fe K-edge (b). Inserts in both figures present the pre-edge region and the near-edge absorption structure (XANES) at the corresponding edges.

The pre-edge peaks A (Fig. 1) are ascribed to dipole forbidden transitions on 4s and mainly 3d states and their aspect is different for absorbing atoms in different coordination [7]. At the same time, the Fe K-edge XANES shows a pre-edge peak of considerable less intensity. The same peak of less intensity occurs also in the Fe K-edge spectrum of hematite Fe_2O_3 , which was measured as a standard by using the same experimental setup. Its reduced intensity is also a sign of the reduced number of 3d vacancies on which one may excite the core electron (as compared with this value for Ti). We estimated the sole integral (calculated in [arbitrary units of absorption $\times$ eV]) of each pre-edge peak, normalized to the intensity of the absorption jump (in [arbitrary units of absorption]). The obtained values are 0.42 eV for Ti K-edge in TiO_2 , 0.20 eV for both Fe K-edge in hematite and for Fe K-edge in $\text{TiO}_2\text{:Fe}$. By comparison of the integral intensity between Fe and Ti pre-edge peaks and by considering only dipole forbidden transitions on 3d states, with $3d^0$ configuration for Ti^{4+} in titania, one may infer a configuration close to $3d^5$ for Fe in both hematite and in $\text{TiO}_2\text{:Fe}$. This means that iron atoms in the sample of interest $\text{TiO}_2\text{:Fe}$ are in a $3+$ ionization state. The similarity of these two iron states is also supported by the similitude of the overall aspects of the corresponding XANES spectra.

The peak B is a sign also of octahedral ionic cage, whereas peak C can be regarded as a resonance connected to excitation with charge transfer on second-order cationic neighbors, at least for zincblende structure [8]. The pres-

Fig. 1. Absorption spectra (including pre-edge, XANES and EXAFS regions) at Ti K-edge (a) and Fe K-edge (b) in iron-doped titania. Inserts: the pre-edge and XANES regions of the two spectra. In the insert of (b) also the Fe K-edge XANES of pure hematite (Fe_2O_3), recorded in the same experimental setup, is shown.

ence of peak B and the considerable decreased intensity of peak C in the Fe XANES may be viewed as a sign of a less defined long-range order in the Fe environment. It may be possible that a strong distortion of the octahedral lattice, as derived from peak B, to be accompanied by a less effective mechanisms of excitation with charge transfer (peak C).

Peak D is a multiple scattering XANES resonance in titania [8,9] and its absence at the Fe edge may also be viewed as a sign of local amorphisation around the Fe ions.

When analyzing Ti K-edge EXAFS data, we could infer that the local atomic order around Ti atoms is not similar to pure rutile nor to pure anatase, but rather to a mixture of the two kinds of surroundings (Ti1 and Ti2). The first Ti neighbouring is assessed by taking into account that X-ray

diffraction has identified rutile crystals (Ti1); consequently by comparison with the Ti K-edge EXAFS data, the occurrence of another amorphous or nanosized phase with anatase-like surrounding (Ti2) is proposed. Dopant segregation was pushed back, since the EXAFS spectrum of such segregated structures is quite different [10]. Concerning the Fe K-edge EXAFS data, this is more similar to the anatase-like environment [9], so we infer that Fe atoms occupy sites which are quite similar to the amorphous or nanosized anatase-like environment of Ti2, in a phase which did not exhibit long-range ordering.

The recorded EXAFS spectra, after standard data treatment [11] are represented in Fig. 2. For computation of the photoelectron wavevector, edge energies before the onset of the pre-edge peak (4965 eV for Ti, 7109.5 eV for Fe) have been considered instead of inflection points of the main edge. This choice leads to a much better match between the recorded EXAFS spectra and the simulated EXAFS by using the anatase or rutile structure. The simulations are also shown in Fig. 2. In computing these simulations, the complete anatase and rutile structures have been considered, together with values of the Debye–Waller factors of 0.15 Å and the inelastic mean free path dependence obtained from [12]. The backscattering amplitudes, backscattering phase shifts and absorbing atom phase shifts were taken from Ref. [11]. The obtained simulated spectra are similar to the measured spectra reported recently in [13];

the discrepancies can be related to multiple scattering effects [9]. Also, in the insert of Fig. 2 we have represented the Fourier transform of the EXAFS spectra, both at Ti and Fe K-edges.

A direct comparison between the measured Ti EXAFS spectra and the simulated ones can be used as an evidence of co-existence of rutile and anatase-like surrounding in the sample. A least square fit refinement of the first features led to a relative contribution of $62 \pm 8\%$ anatase-like to the total spectrum. We cannot speculate more on this aspect since it seems that titania phases with strongly distorted octahedral structures are present in the EXAFS spectrum. Taking into account X-ray diffraction data, these phases are amorphous. Note also, when speaking about anatase-like environment that the Fourier transform of the spectrum is not quite similar to the anatase one [13], especially concerning local atomic environment at the 3rd and 4th coordination shell. A further refinement of the EXAFS spectra is a complicated work and efforts are in course to extract maximum of information from these spectra.

The EXAFS at the Fe K-edge is considerably different from the EXAFS at the Ti K-edge. From the Fourier transform of the EXAFS spectrum at the Fe K-edge (insert in Fig. 2) one may infer the presence of two well defined coordination shells at low interatomic distances about the Fe atoms, whereas in the local environment of Ti contributions from several shells with slightly different interatomic distances are merged into the first peak of the Fourier transform. For larger interatomic distances, the radial distribution function about the Fe atoms decrease drastically, which can be seen as a sign of a lower long-range order about these atoms.

The wavelength dependency of the films refractive index, $n(\lambda)$, has been examined by using the Swanepoel method [14]. This method needs the optical transmittance spectra for the studied thin films. TiO_2 films are transparent in the visible region [3] and its transparency exhibits a sharp decrease in the UV region. The fluctuations on these spectra are connected with the film thickness and consequently with the interference in the layer. The number of the available fringes gives the accuracy of this method [14]. The refractive index of the substrate in the region of weak absorption was determined by means of transmission spectrum for the clean substrate alone and it was found to be 1.47. The curves $n(\lambda)$, presented in Fig. 3, show a Sellmeier dispersion type dependence as reported in literature [4] for the visible spectral range, where TiO_2 films are transparent.

The oscillator energy and strength and the optical bandgap can be determined by applying the Wemple–DiDomenico relation [15]

$$n^2(\nu) = 1 + \frac{E_o E_d}{E_o^2 - (h\nu)^2} \quad (1)$$

where E_o and E_d represent the oscillator energy and dispersion energy (the strength of interband optical transitions) respectively and $h\nu$ is the photon energy.

Fig. 2. Extracted Ti K-edge and Fe K-edge EXAFS spectra from absorption spectra given in Fig. 1 together with simulated anatase and rutile EXAFS spectra (see text for details). Insert: Fourier transforms of the experimental EXAFS spectra.

Fig. 3. The refractive index n versus wavelength λ , in the visible range, for undoped and Fe-doped TiO_2 films.

By putting the relation (1) in the form

$$\frac{1}{n^2 - 1} = \frac{E_o}{E_d} - \frac{(h\nu)^2}{E_o E_d} \quad (2)$$

and representing $(n^2 - 1)^{-1}$ versus $(h\nu)^2$, a linear behavior is obtained (Fig. 4) having correlation coefficients very close to 1 (0.999). The slope of the linear dependence is $(E_o E_d)^{-1}$, and the intercept with the vertical axis, E_o/E_d . The oscillator energy, E_o , is an “average” energy gap, as specified in the literature [15,16]. For the undoped film, the calculated values of E_d and E_o are 16.72 eV and 6.67 eV, respectively, while for the Fe-doped film these values are 15.85 eV and 6.64 eV, respectively.

Wemple has established an empirical relation for the dispersion energy

$$E_d = \beta N_c N_e Z_a \quad (3)$$

where N_c is the coordination number of the cation that is the nearest neighbor to the anion, N_e is the effective num-

Fig. 4. $(n^2 - 1)^{-1}$ versus $(h\nu)^2$, in the visible range, for undoped (sample S) and Fe-doped (sample S.Fe) TiO_2 films. The dash lines represent the fitting straight-lines.

ber of valence electrons per anion, β is a constant and Z_a is the formal chemical valence of the anion. For TiO_2 , $\beta \cong 0.22$ [15], N_e has the value 8, as already specified in Ref. [4] and $Z_a = 2$. From relation (3), the values of N_c are 4.75 and 4.5 for S and S.Fe, respectively.

A rutile sample (S.Fe) is expected to be more dense than the mixed anatase/rutile sample (S) and to have higher refractive indices. The calculated n values presented in Fig. 3 do not confirm this observation. In a qualitative sense, the refractive index is the “optical density” of a material and the mentioned discrepancies can be related to the fact that the doped sample may have a porosity that would lower the refractive index [3]. Here, not only the phase composition brings its contribution, but also the fact that the sample S.Fe has nanosized grains [5]. The values of $n(633 \text{ nm})$ (1.93 in the undoped sample and 1.90 in Fe-doped sample), much smaller than the average n values of rutile and anatase single crystals (2.75 and 2.52, respectively [17]), prove a high void content ($>5\%$) in the films. Consequently, the structural differences together with the microstructural ones, explain why the Fe-doped TiO_2 films, with a rutile phase spread in an amorphous phase, exhibit lower n values, as compared to the undoped TiO_2 film (Fig. 4). According to Ref. [4], an XRD amorphous sample is characterized by lower refractive indices than the polycrystalline ones and it has also lower dispersion energy and coordination number of the cation. Here, for the nanostructured sample S.Fe we reach to the same conclusion.

4. Conclusions

Reactive RF sputtering was utilized to deposit undoped and Fe-doped TiO_2 thin films onto glass substrates. When deposited onto heated substrates, the films present polycrystalline structures. By doping with low concentrations of Fe, the structure changes from mixed anatase/rutile to pure rutile.

From Fe K-edge extended X-ray absorption fine structure, some general conclusions may be summarized as follows: (i) Fe atoms are in 3+ ionization states; (ii) the long-range order about the Fe atoms is considerably affected, as compared with that around the Ti atoms (from both XANES and EXAFS data); (iii) the Ti EXAFS spectrum reveals a mixture of rutile phase (Ti1) and of an amorphous phase where Ti atoms are in locally distorted anatase-like environment (Ti2), but with no long-range ordering visible by X-ray diffraction; (iv) the edge energy had to be chosen just at the onset of the pre-edge peak instead of on the main edge for both Fe and Ti.

The dispersion of the refractive index below the interband absorption edge was obtained by applying the Swanepoel method to optical transmittance spectra. The dispersion energy and the single-oscillator energy in the undoped film are 16.72 eV and 6.67 eV, respectively, while in the Fe-doped film these values are 15.85 eV and 6.64 eV, respectively. The structural differences together with the microstructural ones, explain why the Fe-doped TiO_2 films,

with a single rutile phase spread in an amorphous phase, exhibit lower n values, and also lower values for the coordination number compared to the undoped TiO₂ film.

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