XANES and EXAFS investigations of magnetron sputtered Fe-doped titania thin films

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Titanium oxides, in thin films, show high transmittance in the visible spectral range, high refractive index, high chemical and thermal durability in hostile environments, with high potential for practical applications. Doping with different atoms (Ce, Nb, Cr, Fe) is a common way of controlling the material properties of TiO₂ thin films [1]. In this work we focused on the influence of Fe-doping on the structural properties, local atomic environment, and optical constants of TiO₂ films.

Titanium oxide films were prepared by reactive radio-frequency (RF) sputtering in a conventional 13.56 MHz setup (Hüttinger, 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 (N4.8) was used as reactive gas, mixed with argon (N5.7). The total pressure of the Ar + O₂ mixture gas during deposition was set at 0.10 Pa, and the partial pressure of O₂ was 0.03 Pa. The thin films were first characterized by X-ray diffraction and optical transmittance; synchrotron radiation measurements comprised EXAFS and XANES measurements at the beamline E4 (EXAFS II) of the Doris storage ring in HASYLAB, Hamburg [2].

Fig.1 shows the X-ray absorption spectra recorded for Fe-doped sample 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 are ascribed to dipole forbidden transitions on 4s and mainly 3d states and their aspect is different for absorbing atoms in different coordination [3]. The Fe K-edge XANES shows a pre-edge peak of considerable less intensity, which occurs also in the Fe spectrum of hematite Fe₂O₃, measured in the same experimental setup. The reduced intensity of A is a sign of the reduced number of 3d vacancies. We estimated the integral of peak A, normalized to the intensity of the absorption jump. The obtained values are 0.42 eV for Ti K-edge in TiO₂, 0.20 eV for hematite and for TiO₂:Fe. Considering only dipole forbidden transitions on 3d states, with 3d⁰ configuration for Ti⁴⁺ in titania, one may infer a configuration close to 3d⁵ for Fe in both hematite and in TiO₂:Fe. This means that iron atoms in the sample of interest TiO₂:Fe are in a 3+ ionization state.

The peak B is a sign of octahedral ionic cage, whereas peak C can be regarded as a resonance connected to excitation with charge transfer on second-order cationic neighbors [4]. The presence 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. Peak D is a multiple scattering XANES resonance [4,5] and its absence at the Fe edge is a sign of amorphisation around the Fe ions.

From the Ti K-edge EXAFS data (Fig. 2), it seems 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. Concerning the Fe K-edge EXAFS data (Fig. 2), this is more similar to the anatase-like environment [5], 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. This results also by comparison with simulations of EXAFS spectra by using anatase or rutile-like environments, atomic parameters from [6], inelastic mean free path given by the "universal curve", and Debye-Waller factors of 0.15. The obtained simulated spectra are quite similar to the measured spectra reported recently in [7].
The EXAFS at the Fe K-edge is considerably different from the EXAFS at the Ti K-edge. From the Fourier transforms (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 sub-shells with slightly different interatomic distances are merged into the first peak. For larger interatomic distances, the radial distribution function about the Fe atoms decreases drastically, which is as a sign of a lower long range order about these atoms.

Figure 1: (a) Ti K-edge and (b) Fe K-edge X-ray absorption spectra of a Fe-doped TiO$_2$ thin film. Insert in both figures: the XANES region.

Figure 2: The EXAFS functions at Fe and Ti K-edge, together with simulated spectra of rutile and anatase. Insert: the Fourier transforms of $k^3$-weighted EXAFS functions at both Fe and Ti K-edges.

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