X-ray absorption (XANES and EXAFS) studies of TiO$_{2-x}$N$_x$ thin films prepared by reactive magnetron sputtering

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Increasing interest was given during the last decade to doped titania films, owing to the possibility of narrowing bandgaps and to charge carrier recombination inhibition for increasing photocatalytic efficiency in visible range. Here we present an X-ray absorption (XAS) study of nitrogen-doped titania prepared by reactive magnetron sputtering. These thin films were shown to prove super-hydrophilicity and promising optical properties, together with low recombination rates of the charge carriers at the surface [1].

Pure and nitrogen-doped TiO$_2$ films, 250 nm thick, were grown by rf sputtering (13.56 MHz, 150W) in a planar magnetron facility. A 2" sintered ceramic TiO$_2$ disk (99.99% purity) was used as a sputtering target. The setup consisted of a stainless steel deposition chamber, with base pressure of $1.3 \times 10^{-5}$ Pa. Ar, O$_2$ and N$_2$ gases were introduced into the deposition chamber via mass flow controllers. The total gas pressure in the discharge was 1.2 Pa in all current experiments, while ensuring a low-content O$_2$ atmosphere (0.11 Pa) to compensate for oxygen depletion in the films [5]. The nitrogen-doped titania films were deposited with N$_2$ partial pressure ratio ranging between 0.0 and 0.27 Pa, the remaining up to 1.2 Pa being Ar. The samples were deposited on Si(111).

XAS experiments were performed at the HASYLAB synchrotron radiation facility, beamline A1 (EXAFS I), by using a 7-pixel fluorescence detector. Other measurements performed on these films include UV-vis. spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and contact angle measurements. From these former experiments the quantity of nitrogen doping in the film was determined (ranging from 2.6 % to 5.1 % for the atomic N/Ti ratio), the structure of the films was found to be mainly rutile with traces of anatase, the bandgap is considerably lower than the anatase one (3.2 eV), reaching even 3.01 eV for the sample with highest nitrogen content, whereas the rugosity of the films is around 3 nm rms [1,2].

X-ray absorption near-edge (XANES) results are plotted in Fig. 2. The spectra are quite similar: only the undoped sample and the lowest content doped nitrogen sample present distinct features. These spectra are represented as dashed lines in Fig. 1. The spectra were normalized to

![Graph](image-url)

**Figure 1:** XANES of undoped (finely dashed line) and nitrogen-doped titania thin films (other lines). Insert: difference between the XANES spectra of undoped and doped samples, respectively.
absorption jump equal to unity. The most important remark here is the decrease of the pre-edge peak Ti$^{4+}$ in pure TiO$_2$, with $n_v(3d) = 10$, the computed variation of the peak integral in doped samples implies an enrichment of the Ti 3d population by $\approx 0.6e$. This is in contrast with the common sense (4968-4975 eV) when doping with nitrogen, which can be ascribed to "dipole-forbidden" 1s $\rightarrow$ (4s, mainly 3d) one-electron transitions. The integral amplitude of the pre-edge peak is, as a first approximation, proportional to the number of 3d vacancies per Ti atom [$n_v(3d)$]. If one considers assertion that N in titania acts as $p$-type impurity. In fact, changes in the magnetron plasma dynamics due to the presence of nitrogen stabilises titania suboxides with deficit of oxygen such that, globally, the grown films become $n$-doped. The oxygen deficit was evidenced by XPS, where stoichiometries such as TiO$_{1.98}$ were put in evidence. In some cases, suboxides such as Ti$_4$O$_7$ were visible in X-ray diffraction. Consequently, XANES confirmed the increase in 3d electron population.

The extended X-ray absorption fine structure spectra are plotted in Fig. 2, weighted by $k^3$, $k$ being the photoelectron’s wavevector. The Fourier transforms of the $k^3$-weighted EXAFS functions are represented in Fig. 3. As expected, there are no major differences between the EXAFS spectra. Note, however, that visible changes in the second shell occur, located initially (in the undoped sample) at 2.52 Å, where gradually a splitting of this shell occurs into two sub-shells at 2.33 Å and 2.69 Å. The position of the first coordination shell also evolves from 1.53 Å in the undoped sample to 1.6 Å in the 1.5 % N sample, then decreases back to 1.57-1.58 Å. X-ray diffraction evidenced also an increase in the anatase (101) peak, reaching a maximum in the 1.5 % N sample, then decreasing. While the evolution of the first coordination shell can be attributed to the relative increase of anatase content, the observed splitting in the first coordination shell cannot be explained simply by the relative interplay between anatase and rutile phase; consequently, a further amorphous or nanosized phase (which do not manifest in the XRD patterns) could be inferred from the EXAFS spectra. Maybe this amorphous phase is the main responsible for the observed increased photocatalytic efficiency, since electron-hole recombination efficiency in amorphous semiconducting materials has been shown to decrease, especially when the electron and the hole are in tail states [3].

References