

Nanostructured photocatalytic $\text{TiO}_{2-2x}\text{N}_x$ thin films prepared by magnetron sputtering

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ABSTRACT

Nitrogen-doped titania thin films prepared by rf magnetron sputtering in a mixed oxygen-nitrogen atmosphere are characterized here by X-ray absorption and photoemission spectroscopies. Results are given concerning the nitrogen dopant concentration, film stoichiometry, Ti ionization state and local structure of the films. Films properties are correlated with the observed reduced bandgap values.

Keywords: titania, photocatalysts, EXAFS, XANES, XPS

1 INTRODUCTION

Increasing interest is observed during the last decade to doped titania films, owing to the possibility of bandgap narrowing and to charge carrier recombination inhibition for increasing photocatalytic efficiency in visible range. Here we present an X-ray absorption and photoemission (XAFS and XPS) study of nitrogen-doped titania prepared by magnetron sputtering. The films exhibit superhydrophilicity, promising optical properties, and low recombination rates of the charge carriers at the surface [1].

2 EXPERIMENTAL

Pure and nitrogen-doped TiO_2 films, 250 nm thick, were grown in the Plasma Laboratory of the University "A.I. Cuza" Iasi by rf sputtering (13.56 MHz, 150W) in a planar magnetron facility. A sintered ceramic TiO_2 disk (99.99% purity) was used as a sputtering target. The base pressure was 1.3×10^{-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. The nitrogen-doped titania films were deposited with N_2 partial pressure ratio ranging between 0.00 and 0.27 Pa. The samples were deposited on Si(111) substrates.

X-ray absorption fine structure (XAFS) experiments consisting in X-ray absorption near edge spectroscopy (XANES) and Extended X-ray absorption fine structure (EXAFS) were performed at the Hasylab synchrotron radiation facility, beamline A1 (EXAFS I) with a double crystal Si(111) monochromator. The spectra were recorded using a 7-pixel SiGe fluorescence detector.

XPS measurements were performed at the National Institute of Materials Physics Bucharest-Magurele using a VG MkII ESCA setup operating in 10^{-8} Pa pressure range. XPS plots were measured using $\text{Al K}\alpha$ radiation (1486.7 eV) with 50 eV analyzer pass energy. An electron flood gun (3 V/0.1 mA) was used to compensate for surface charging. Sputtering inside the vacuum chamber was avoided, since this process was shown to affect surface stoichiometry [2].

Complementary information was derived from UV-VIS spectroscopy, X-ray diffraction (XRD), atomic force microscopy (AFM), and contact angle data. Some of these measurements have been reported previously [1,3]. From these experiments the structure of the films was found to be mainly rutile with traces of anatase, the bandgap is considerably lower than the anatase one (3.01 eV compared with 3.2 eV), the film rms rugosity is around 3 nm and they are superhydrophilic [1,3].

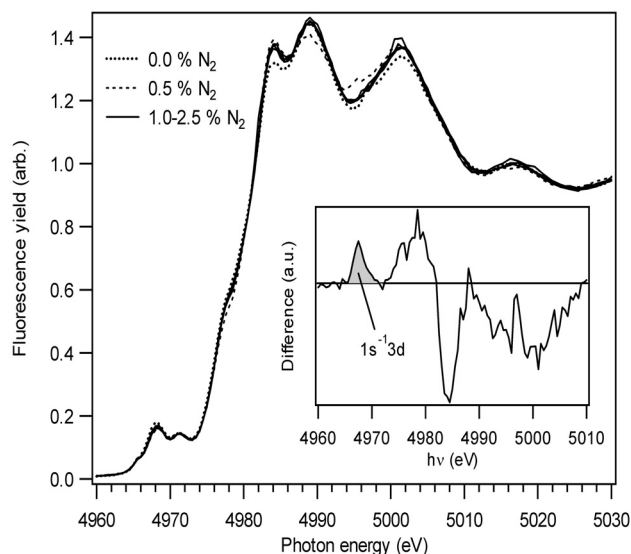


Figure 1: X-ray absorption near-edge structure at the titanium K-edge in undoped and nitrogen-doped samples.

3 RESULTS AND DISCUSSIONS

3.1. X-ray absorption fine structure

Fig. 1 depicts the Ti K-edge XANES of undoped and doped samples. The absorption signal was normalized to unity absorption jump. The spectra are rather similar, only

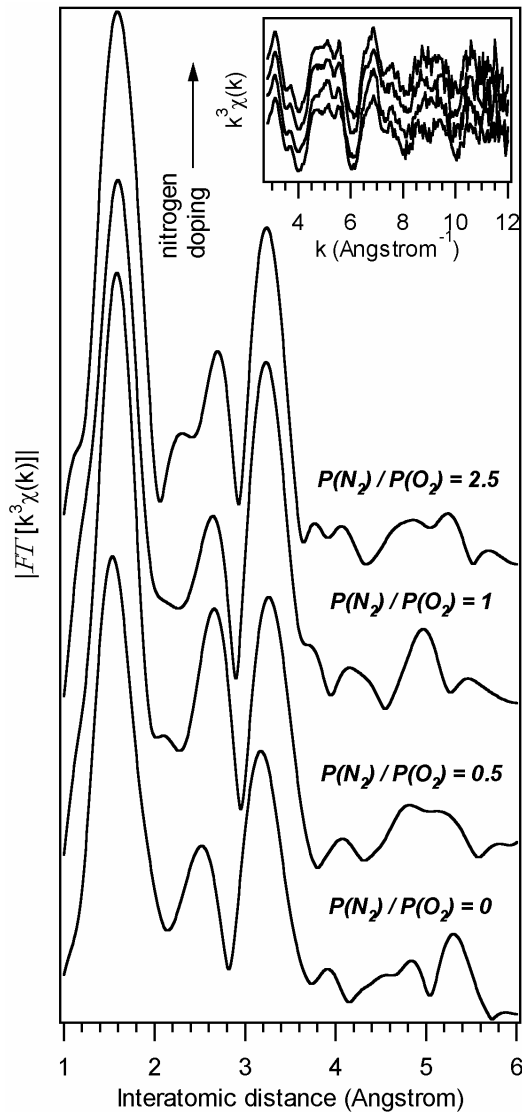


Figure 2: Fourier transforms of the X-ray absorption near-edge structure (EXAFS) at the titanium K-edge. In inset: k^3 -weighted EXAFS functions.

the undoped sample and the lowest nitrogen-content sample showing distinct features. These spectra are represented with dashed lines in Fig. 1. The most important remark here is the decrease of the pre-edge peak (4968-4975 eV) when doping with nitrogen, a fact which can be ascribed to "dipole-forbidden" $1s \rightarrow 3d$ one-electron transitions [4]. The integral amplitude of the pre-edge peak is, within a first approximation, proportional to the number of $3d$ vacancies per Ti atom [$n_v(3d)$]. If one considers Ti^{4+} in pure TiO_2 , with $n_v(3d) = 10$, the computed variation of the peak integral in doped samples results in an enrichment of the Ti $3d$ population by $\approx 0.6e$. This is in contrast with the intuitive assertion that N in titania acts as p -type impurity. In fact, changes in the magnetron plasma dynamics due to the presence of nitrogen stabilizes titania suboxides with deficit of oxygen such that, globally, the grown films are n -doped. The oxygen deficit was evidenced

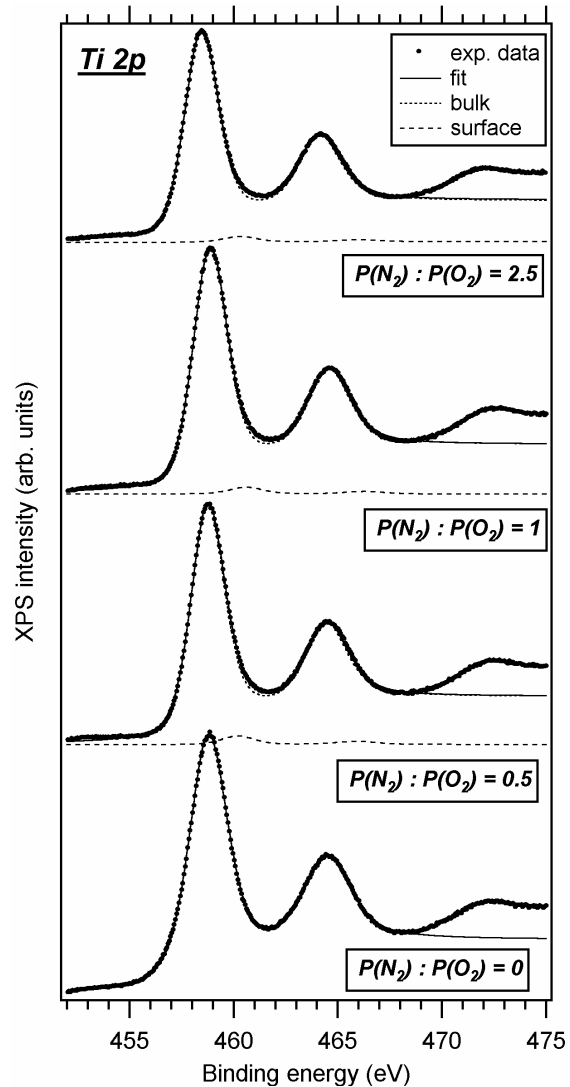


Figure 3: X-ray photoelectron spectra of Ti $2p$, with deconvolutions into one spin-orbit splitted doublets for the undoped sample, and in two doublets for the doped samples.

by X-ray diffraction: following mild annealing, suboxides, such as Ti_4O_7 occurred [1]. In our case, by considering O^{2-} anions, an average ionization state of $Ti^{3.5+}$ is inferred, which implies an enrichment of the titanium $3d$ population by roughly $0.5e$ per atom. Therefore, XANES estimates of the $3d$ electron population increase agree with XRD data.

The Fourier transforms of the k^3 -weighted extended X-ray absorption fine structure spectra (EXAFS) functions are represented in Fig. 2, whereas the k^3 -weighted EXAFS signals are represented in the inset of Fig. 2 (k being the photoelectron's wavevector). As expected, there are no major differences between the EXAFS spectra. Note, however, visible changes in the second coordination shell, located initially (in the undoped sample) at 2.52 Å, where a splitting of this shell occurs gradually into two subshells at 2.29 Å and 2.69 Å. The position of the first coordination shell also evolves from 1.53 Å to 1.57-1.58 Å.

X-ray diffraction data evidenced also an increase in the anatase (101) peak area by nitrogen doping. While the evolution of the first coordination shell can be attributed to the relative increase of anatase content (anatase first shell distances are slightly smaller as compared to rutile), 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 (undetected in the XRD patterns) could be inferred from the EXAFS spectra. We suggest that 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 electron and hole are in tail states [5].

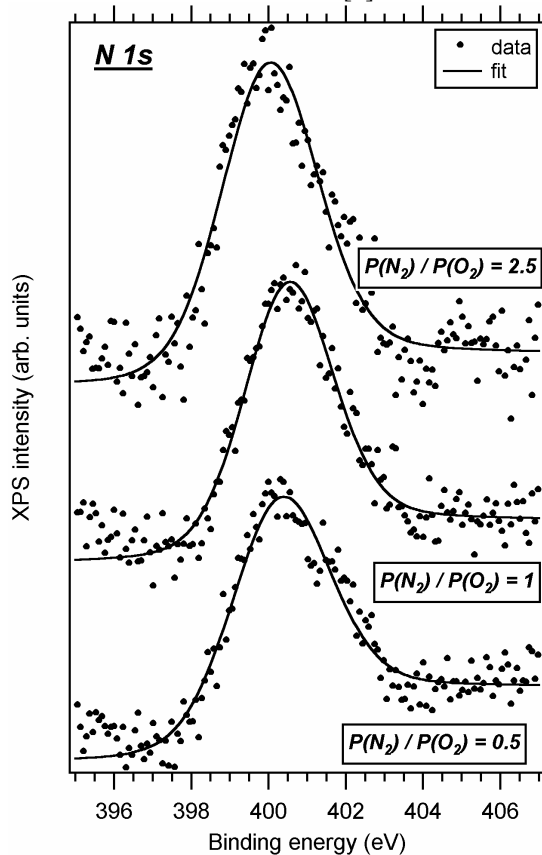


Figure 4: X-ray photoelectron spectra of N 1s, with deconvolution with one Voigt line and the associated integral background.

3.2. X-ray photoelectron spectroscopy

Fig. 3 shows the Ti 2p electron distribution curves (EDCs), together with their deconvolution with a Voigt spin-orbit split doublet (VSOD) with inelastic background [6]. The spectrum of the undoped sample can be well deconvoluted into a single doublet, with different Lorentzian widths for the 2p_{3/2} and 2p_{1/2} lines, a phenomenon which was ascribed to Coster-Kronig decay of the later state [7]. The spectrum of doped samples can be

deconvoluted into two VSODs, ascribed to bulk and surface Ti, respectively.

Fig. 4 displays the N 1s EDCs for doped samples, with the deconvolution into a Voigt line and background (VLB). By using tabulated atomic sensitivity factors (ASF) [8], one derives the nitrogen content in the samples, which is shown in Fig. 5. The derived nitrogen content ranges from 2.6 % to 4.1 % in the investigated samples.

Fig. 6 shows the O 1s EDCs, along with their deconvolutions using up to three VLB. The spectrum of the undoped sample is well deconvoluted into two VLB, one for the bulk oxygen (binding energy $BE \approx 530$ eV) and the other for the hydrocarbons of surface contamination layer ($BE \approx 531.3$ eV). For doped samples, an additional component at higher binding energy ($BE \approx 533$ eV) occurs, due to oxygen in a more neutral state, possibly not coordinated with titanium nor with carbon in the surface.

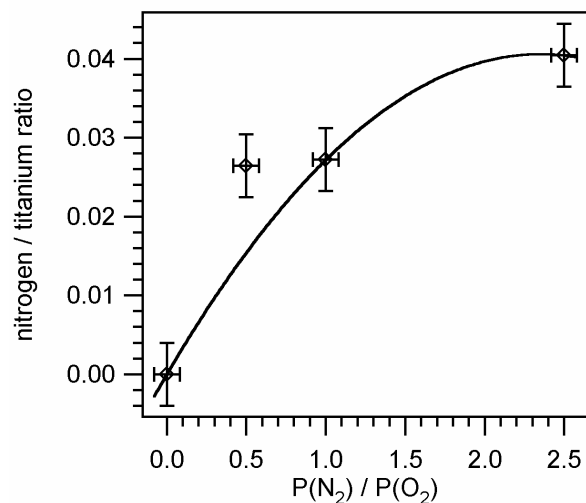


Figure 5: Nitrogen atomic concentration, obtained from the analysis of the deconvoluted XPS data. The line is just a guide for the eye.

The inelastic background amplitude for both "surface" components is almost zero (although allowed to vary in the simulation), which implies that these components are indeed related to surface atoms. The same is valid for the surface component of Ti in the doped samples (Fig. 3).

Fig. 7 shows the oxygen stoichiometry derived from the Ti 2p (Fig. 3) and O 1s (Fig. 6) peaks. The undoped sample has a stoichiometry of TiO_{1.98}, close to titania, whereas for doped samples the oxygen content seems to increase. Nevertheless, this result is not physical, since (i) suboxides were evidenced by X-ray diffraction [1]; (ii) analysis of the pre-edge XANES peak (Fig. 1) evidenced titanium in a less positive ionization state; (iii) the evolution of O 1s binding energy (Fig. 8) for both bulk and sample-related surface component shows oxygen in a less negative ionization state. Consequently, we conjecture that part of the bulk O 1s signal for the doped samples is originating in somewhere else (e.g. limited oxygen enrichment near the first atomic layers of titania) and draw the "corrected" curve of oxygen stoichiometry in Fig. 7. The obtained oxygen composition

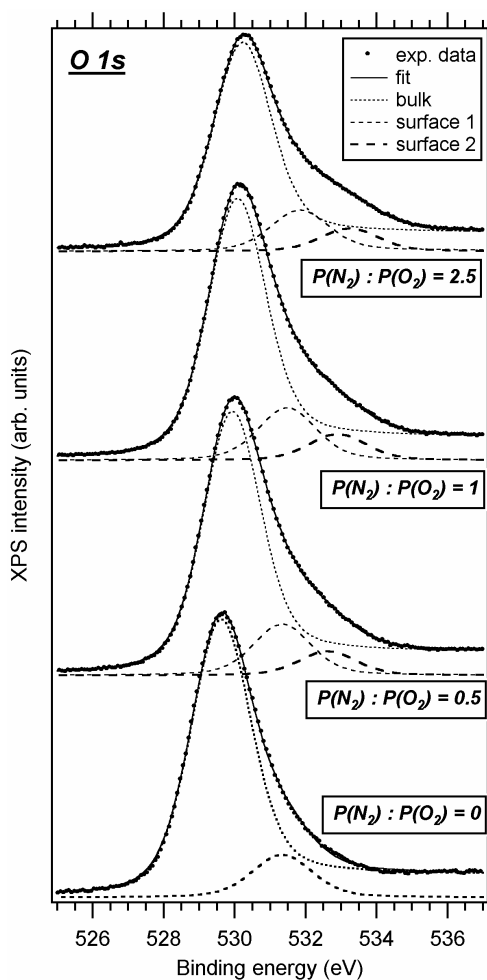


Figure 6: Deconvolution of O 1s spectra with two Voigt lines and associated backgrounds for the undoped sample, and with three Voigt lines + backgrounds for the doped samples. See text for more comments.

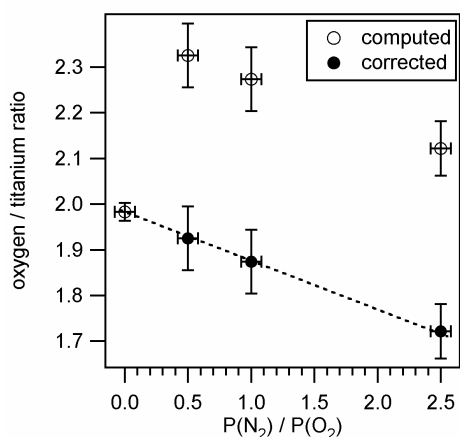


Figure 7: O stoichiometry in the samples, as derived from XPS data. Open circles depict the values computed from the raw data, closed circles are corrected values taking into account an additional O 1s component, whose binding energy (BE) is close to the one of bulk O 1s.

for the most doped samples is approximately $\text{TiO}_{1.72}\text{N}_{0.04}$, composition which agrees with the observed Ti_4O_7 in X-ray diffraction and with the $\approx + 3.4$ charge state of titanium inferred from XANES. The observed splitting in EXAFS of the second coordination shell (Fig. 2), along with the bandgap lowering [1] can be related to the presence of titanium suboxides.

4 CONCLUSION

XPS and XANES data evidenced the presence of titania suboxides, which are formed in the films when the gas composition during deposition is enriched in nitrogen. The nitrogen content of the samples was accurately determined, sample composition varying from $\text{TiO}_{1.98}$ to $\text{TiO}_{1.72}\text{N}_{0.04}$, with O-enrichment near the film surface. Local structure changes (evidenced by EXAFS) and stoichiometry alteration, result in the (previously reported) improved photocatalytic properties of the films.

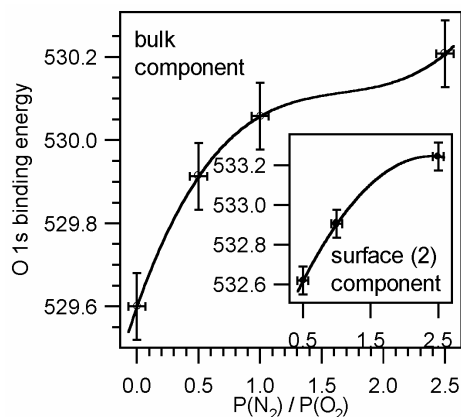


Figure 8: The evolution of the oxygen binding energy of the bulk component with the nitrogen doping. Insert: the evolution of the binding energy of the surface component.

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