Study of N-doped TiO$_2$ thin films for photoelectrochemical hydrogen generation from water

Abstract: The present work deals with nitrogen-doped stoichiometric TiO$_{2}$N and non-stoichiometric TiO$_{2-x}$N thin films deposited by means of dc-pulsed reactive sputtering for application as photoanodes for hydrogen generation from water, using solar energy. Stoichiometric thin films of TiO$_2$ crystallize as a mixture of anatase and rutile while rutile phase predominates in TiO$_{2}$N at higher nitrogen flow rates as shown by X-ray diffraction at grazing incidence, XRD GID. Lack of bulk nitridation of stoichiometric TiO$_2$:N is indicated by valence-to-core X-ray emission spectroscopy, XES, analysis. The energy band gap as well as flat band potential remain almost unaffected by increasing nitrogen flow rate in this case. In contrast to that, non-stoichiometric thin films of TiO$_{2-x}$N demonstrate systematic evolution of the structural, morphological, optical and photoelectrochemical properties upon increasing level of nitrogen doping. Pronounced changes in the growth pattern of non-stoichiometric TiO$_{2-x}$N upon varied nitrogen flow rate, demonstrated by scanning electron microscopy, SEM, can be easily correlated with the crystallographic properties studied by XRD GID. Relative positions of Kβ'' XES lines of the TiO$_{2-x}$N thin films, which depend strongly on the nature of the ligands and their local coordination, change with the increasing nitrogen flow. Doping of nonstoichiometric titanium dioxide with nitrogen shifts the absorption spectrum towards the visible range and increases considerably the flat band potential which is beneficial for water photolysis.

Keywords: nitrogen doped TiO$_2$, thin films, optical properties, flat band potential, XES

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1 Introduction

Replacement of fossil fuels by renewable energy sources, so much anticipated for at least two decades, still remains the biggest challenge for scientists working in the area of “clean” energy. The strategies that rely on solar energy seem to be the most promising as demonstrated by successes of photovoltaics. However, photodecomposition of water, present abundantly on Earth, is still an attractive but largely unexploited scenario [1,2] for generation of pure hydrogen - a fuel of the future. Moreover, due to low efficiency of the process, this approach requires some fundamental breakthrough especially in the field of nanomaterials for photoanodes.

Photoelectrolysis of water is conducted in a photoelectrochemical cell, PEC, the key component of which is a semiconductor photoelectrode. To achieve high solar conversion efficiency of PEC, the photoelectrode material has to fulfil several requirements among which the most important are the efficient absorption of the light and fast charge transfer. Two parameters of the electronic structure: forbidden band gap energy, $E_g$ and the flat band potential, $V_{fb}$, are of a paramount importance for photocatalytic semiconductor. The forbidden band gap decides about the absorption spectrum of the photoanode, whereas the flat band potential determines the recombination rate of the photoexcited electrons and holes [3].
Titanium dioxide, TiO$_2$, is considered as one of the most suitable candidates for the photoanode material in photoelectrochemical cells [4]. However, it is far from being a perfect solution due to its wide band gap (3.0 eV for rutile and 3.2 eV for anatase) that prevents efficient use of visible radiation. Taking into account the energy difference of 1.23 eV between the redox levels H$_2$O/H$_2$ and O$_2$/H$_2$O required for water splitting, the overvoltage losses and the excess of energy needed in order to drive the process at a reasonable rate, the value of band gap energy of an efficiently working semiconductor photoanode should be at least within the range of 1.7-1.9 eV [3].

In order to extend its absorption spectrum towards longer wavelengths, various modifications of TiO$_2$ have been proposed [3-17] but with a limited success.

Undoped TiO$_2$ can be modified by reduction in order to produce nonstoichiometry which plays a special role in the case of nanomaterials. Doping of anionic or cationic sublattices of TiO$_2$ has been shown to narrow the band gap and, thus, alter the optical properties of TiO$_2$. Modification of cationic and anionic sublattices can be achieved by metal type doping (W, Cr, Fe, Nb, Ta, Mn) [10,18] or non-metal (N, S, C) type doping [19-23].

Since the pioneering work of Asahi [13], nitrogen incorporation into the anionic sublattice of titanium dioxide has been expected to bring significant improvement in the photocatalytic and photoelectrochemical behaviour in comparison with the unmodified TiO$_2$ [14-17, 24-28].

Zhu et al. [25] studied photoelectrochemical and optical properties of N-doped TiO$_2$ thin films prepared by oxidation of sputtered TiN films. They showed that N-doped samples revealed a shift in the photoresponse towards visible range of electromagnetic spectrum and improved photocurrent density under visible radiation. Babu et al. [26] reported that N-TiO$_2$ prepared by electrospinning followed by the annealing at high temperatures exhibited reduced band gap energy and improved photoconversion efficiency (0.8%) as compared to that of pure TiO$_2$ nanostructures (0.09%). Wang et al. [27] discussed efficient hydrogen generation by photocatalytic water splitting using N-doped TiO$_2$ thin films deposited by r.f reactive magnetron sputtering. Their experimental results demonstrated that the substitutional nitrogen doping narrowed the optical band gap to 2.65 eV. The production rate of hydrogen for N-doped TiO$_2$ film was about 601 μmol g$^{-1}$ h$^{-1}$, which was higher than that of the undoped TiO$_2$ film and even about 50 times higher than that of a dispersive P25 powder treated as a standard for photocatalysis [27].

It has been recently realized that, in order get insight into the mechanism of nitrogen incorporation into TiO$_2$, studies of the electronic and local structure by X-ray spectroscopic methods such as X-ray Absorption Spectroscopy, XAS and X-ray Emission Spectroscopy, XES are necessary [22,23,29,30]. Chen et al. [29] measured O 1s and Ti 2p XAS and XES for pure and N-doped TiO$_2$ nanoparticles. On the basis of spectra comparison (O1s XAS and XES were almost unaffected by nitrogen doping, while Ti 2p spectra were found to be slightly sensitive to nitrogen presence) they concluded that only Ti states were modified by nitrogen doping, due to the difference in coupling between the O and N orbitals with Ti orbitals.

Possible correlation between oxygen NEXAFS spectra (Near-edge X-ray Absorption Fine Structure) and photocatalytic properties of TiO$_2$:N constituted an objective of the work of Braun et al. [30]. They claimed that a significant change in the pre-edge structure as well as shifts of oxygen and Ti edges to lower photon energies followed an improved photocatalytic performance of TiO$_2$:N.

In our previous paper [17] it has been demonstrated that modification of oxygen sublattice of stoichiometric TiO$_2$:N thin films by substitutional nitrogen doping is difficult. As shown by XPS spectra [17] there was no influence of increasing nitrogen flow rate on the relative content of nitrogen built in. However, in the case of non-stoichiometric TiO$_2$:N thin films an increase in N/Ti atomic ratio was accompanied by a decrease in O/Ti ratio. This observation let us to believe that the non-stoichiometry in the oxygen sublattice of TiO$_2$:N thin films creates more favourable conditions for accommodation of a larger amount of nitrogen.

In this work, properties of stoichiometric TiO$_2$:N and non-stoichiometric TiO$_{2x}$:N thin films have been compared with respect to electronic structure and photodecomposition of water. The films were deposited by dc magnetron sputtering from Ti target in a reactive Ar+O$_2$+N$_2$ atmosphere as described before [22]. The ultimate aim is to produce titanium dioxide thin films doped with nitrogen, capable to extend the efficiency range of the photocatalytic processes to the visible region of the electromagnetic spectrum.

In earlier studies, the influence of departure from stoichiometric composition in TiO$_{2x}$ on the photoelectrochemical properties was investigated [6,8]. It was shown that small oxygen deficit in the case of a polycrystalline anode shifted the fundamental absorption edge towards lower photon energies [6,8]. However, for highly non-stoichiometric samples an
enhancement of absorption of light and a shift of the fundamental absorption edge back to UV range could be seen. Even though faster electronic transfer through the photoanode-electrolyte interface as compared with stoichiometric compositions was observed, the photocurrent values decreased with the increasing departure from stoichiometry [8].

Here, the focus is put on the importance of the flat band potential and band gap energy for application of stoichiometric TiO$_2$:N and non-stoichiometric TiO$_{2-x}$:N thin films in the water photolysis. It will be pointed out that these parameters are very sensitive to the changes in the film microstructure and morphology. The aim of this work is to show how nitrogen incorporated into stoichiometric and non-stoichiometric titanium dioxide affects both the flat band potential and the forbidden band gap. The influence of these parameters on the photoelectrolysis will be presented.

2 Materials and experimental methods

Thin films of stoichiometric TiO$_2$:N and non-stoichiometric TiO$_{2-x}$:N were deposited by dc pulsed reactive magnetron sputtering from Ti target onto amorphous silica, Si wafers and Ti foil substrates in a gas atmosphere composed of argon, oxygen and nitrogen as described previously [22]. In order to control the level of non-stoichiometry x in TiO$_{2-x}$:N thin films, optical emission spectroscopy was applied, the idea of which is explained, e.g., in [5,31]. The controllable technological parameter I/I$_0$ related to Ti target sputtering rate, where I denotes the intensity of Ti plasma emission line at $\lambda=500$ nm in reactive gas mixture and I$_0$ is the intensity of the same line at 100% Ar, is a direct measure of departure from stoichiometry x. Low value of the I/I$_0$ parameter results in slow sputtering of oxidized titanium target that yields stoichiometric, transparent metal oxide films. High value of I/I$_0$ corresponds to the fast sputtering of the metallic target surface in oxygen-deficient atmosphere thus non-stoichiometric thin films are formed. Non-stoichiometric titanium dioxide, TiO$_{2-x}$:N thin films were obtained at a constant $I/I_0=0.3$ while stoichiometric TiO$_2$:N layers at $I/I_0=0.13$ which was based on previous experience [17]. Nitrogen was introduced during deposition in a controllable way by measuring and adjusting its flow rate $\eta_{N_2}$.

In order to determine the crystal structure and phase content, X-ray diffraction at grazing incidence, XRD GID was performed on Philips X’Pert MPD diffractometer with Cu Kα radiation. Surface morphology was investigated by scanning electron microscopy SEM (Hitachi Su-70) at the Institute of Physics, Polish Academy of Sciences, Warsaw.

Resonant X-ray Emission Spectra (RXES) were carried out under ambient conditions at Super XAS (X10DA) beamline of Swiss Light Source, Villigen, Switzerland. Spectra were collected using the high-resolution von Hamos bent crystal spectrometer [32]. Details of performed measurements as well as a method of the emission energy scale calibration were described previously [23,33]. In the course of experiments, Kβ XES spectra of titanium were recorded for stoichiometric and non-stoichiometric nitrogen doped titanium dioxide thin films as well as reference samples of TiO$_2$ (P25) and TiN.

Perkin-Elmer Lambda 19 double beam spectrophotometer equipped with a 150 mm integration sphere as a special detector working over a wide wavelength range from 250 to 2500 nm served to acquire optical transmittance and reflectance spectra.

Photoelectrochemical experiments were performed in a custom-made three-electrode system presented in detail in [8]. Photoelectrochemical cell, PEC contained a TiO$_2$ photoanode, a cathode made of Pt foil covered with Pt black and SCE (Saturated Calomel Electrode) as a reference electrode, all immersed in a aqueous solution of Na$_2$SO$_4$ of pH=7. The PEC was illuminated with a white light provided by a 450W Xe lamp. The average power density of light at the photoanode was controlled and amounted to 85 kW m$^{-2}$. ANKO potentiostat provided us with a constant potential difference during the measurements of current versus voltage (I–V) characteristics.

3 Results and discussion

X-ray diffraction patterns of stoichiometric TiO$_2$:N thin films shown in Fig. 1 differ substantially from those of their non-stoichiometric TiO$_{2-x}$:N counterparts as clearly seen in Fig. 2. The non-stoichiometric, undoped TiO$_{2-x}$ films deposited at $I/I_0=0.3$ and $\eta_{N_2}=0$ sccm (Fig. 2), similarly to stoichiometric undoped TiO$_2$ obtained at $I/I_0=0.13$ and $\eta_{N_2}=0$ sccm (Fig. 1) contain a mixture of anatase and rutile polymorphic forms. Anatase predominates as a majority phase, however the relative contribution of rutile is higher for the films obtained at $I/I_0=0.3$ than those at $I/I_0=0.13$. These results remain in agreement with the previous studies [8] dealing with the influence of the deviation from stoichiometry controlled by the technological parameter $I/I_0$ on a relative contribution of anatase and rutile polymorphic forms in titanium dioxide TiO$_{2-x}$. 
It has been demonstrated [8] that low values of $I/I_0$ led to deposition of anatase-rich TiO$_2$ films whereas an increase in $I/I_0$ yielded amorphous films with finely dispersed rutile grains. Anatase dominated films seemed to be a result of specific growth conditions such as a low sputtering rate of the oxidized target surface whereas sputtering performed from the metallic-like target surface at high rates and lower oxygen content created conditions more favourable for the rutile formation [8].

The effect of nitrogen upon evolution of XRD patterns is significantly different in the case of stoichiometric (Fig. 1) and non-stoichiometric titanium dioxide films (Fig. 2). In contrast to stoichiometric TiO$_2$ thin films, the non-stoichiometric TiO$_{2-x}$N layers quickly lose their crystallinity upon nitrogen doping (Fig. 2) and become almost completely amorphous at the nitrogen flow rate $\eta_{N_2}$ of about 0.27 sccm. Then, at $\eta_{N_2}$ of about 1.06 sccm titanium nitride phase starts growing (Fig. 2). For stoichiometric TiO$_2$:N films, the relative contribution of anatase and rutile forms changes with the increasing nitrogen flow rate $\eta_{N_2}$ (Fig. 1). Fraction of rutile increases systematically with the increasing $\eta_{N_2}$. No dramatic amorphisation is observed as in the case of TiO$_{2-x}$N (Fig. 2) thus it can be concluded that nitrogen probably could not incorporate into stoichiometric TiO$_2$ lattice.

Fig. 3 presents the SEM images of non-stoichiometric TiO$_{2-x}$:N thin films deposited under different nitrogen flow rates $\eta_{N_2}$ at $I/I_0$ = 0.3. The pronounced changes in the films morphology with the increasing nitrogen flow rate $\eta_{N_2}$ can be observed. Corroborating the results of XRD, it is evident that the sample obtained at $\eta_{N_2}$ = 0 sccm is well crystallized. Two kinds of nanosized grains can be distinguished in this SEM top-surface image (Fig. 3a), one of 26 nm for smaller features and the other of about 90 nm for bigger protrusions. In the cross-sectional views, a columnar growth of a film deposited at $\eta_{N_2}$ = 0 sccm is pronounced. Columns grow perpendicularly to the surface whereas some of them are wider and are ended with a cap. Upon nitrogen doping of the non-stoichiometric TiO$_{2-x}$:N the columnar growth is no longer seen (Fig. 3b). Cross-section of thin films obtained at $\eta_{N_2}$ = 0.27 sccm indicates dense and uniform, non-columnar growth. This result is consistent with XRD analysis which shows that the sample deposited at $\eta_{N_2}$ = 0.27 sccm loses its crystallinity and becomes fully amorphous (Fig. 2). As the nitrogen flow rate $\eta_{N_2}$ increases further, the growth...
mode changes to columnar again. SEM images indicate thin and regular fibres for films obtained at \( \eta_{N_2}=0.53 \) sccm, 0.67 sccm, 0.8 sccm (Figs. 3c,d,e, respectively). For the films obtained at \( \eta_{N_2}=0.53 \) sccm and \( \eta_{N_2}=0.67 \) sccm orientation of fibres is similar and approximately perpendicular to the surface. The top surface images of the films deposited at \( \eta_{N_2}=0.53 \) sccm, \( \eta_{N_2}=0.67 \) sccm and \( \eta_{N_2}=0.8 \) sccm show that the average feature size decreases with the increasing nitrogen flow rate from about 27 nm for a film obtained at \( \eta_{N_2}=0.53 \) sccm to 17 nm for a film deposited at \( \eta_{N_2}=0.8 \) sccm. The crystallites are closely packed together without any trapped pin-holes at the surface. For the sample deposited under \( \eta_{N_2}=0.8 \) sccm the fibers tend to grow oriented with respect to the normal to the surface.

The morphology of the obtained thin films is closely related to the deposition conditions such as pressure and substrate temperature, which determine the mode of growth of the films as described by Thornton [34]. Depending on the ratio of substrate temperature to the melting point of a metal as well as a gas pressure, the nucleation and growth mechanism changes. According to Thornton [34], it is possible to obtain porous layers with rough surfaces (zone 1); dense, columnar grains from top to bottom (zone 2); crystallized, not necessarily columnar grains (zone 3) and dense fibre-like grains in which grain outlines are difficult to identify (transition zone). The growth of non-stoichiometric TiO\(_{2-x}\):N thin films can be accounted for some extent by Thornton model. It can be concluded that thin film deposited at \( \eta_{N_2}=0 \) sccm (Fig. 3a) belongs to zone 1, whereas sample obtained at \( \eta_{N_2}=0.53 \) sccm (Fig. 3c) to the transition zone. Thin films deposited at \( \eta_{N_2}=0.67 \) sccm (Fig. 3d) and \( \eta_{N_2}=0.8 \) sccm (Fig. 3e) with regular, narrow fibres fit in zone 3.

Analysis of valence-to-core X-ray emission lines, of stoichiometric TiO\(_2\):N, non-stoichiometric TiO\(_{2-x}\):N thin films and those of reference samples (TiO\(_2\) P25, TiN) are shown in Figs. 4-5. The X-ray emission spectra mainly consist of two dominant features called K\(\beta\) main lines and K\(\beta\) satellite lines. K\(\beta\) main line arises from a core-to-core 3p-1s transition and consists of two features: K\(\beta_1\),\(3\) peak and a low energy K\(\beta_1\) shoulder due to (3p,3d) exchange interactions. K\(\beta\) main lines of non-stoichiometric TiO\(_{2-x}\):N thin films were discussed previously by Kollbek et al. [22]. It was shown [22] that the intensity/width of the area normalized K\(\beta\) emission line and the energy position of K\(\beta_1\),\(3\) line slightly evolved with the increasing nitrogen flow rate \( \eta_{N_2} \) while the overall shape of Ti K\(\beta\) XES spectra was similar for all the nitrogen-doped TiO\(_{2-x}\):N samples. This effect could be attributed to slight, systematic variation of the effective density of the Ti 3d electrons [22]. The effective density of d electrons around the Ti ion (derived from K\(\beta\) main emission lines using IAD (Integrated Absolute Difference) method [22]) was found to be correlated with the energy shift of the respective K absorption edges. The absorption edge was displaced to lower photon energies with the increased nitrogen flow rate \( \eta_{N_2} \), due to enhanced effective density of d electrons.

In the present work, detailed analysis of K\(\beta\) valence-to-core X-ray emission lines is carried out (Figs. 4-5). The K\(\beta\) satellite region is divided into the K\(\beta_1\)'' (cross-over) features and the K\(\beta_{2,3}\) peak directly below the Fermi level (Fig. 4). It is known that valence-to-core X-ray emission lines are sensitive to the local environment of 3d metals.
and probe the structure of short-range order in the system under study [35, 36]. For chemical compounds of 3d metals and elements with similar atomic number such as O and N, relative distances between Kβ” and Kβ2.5 lines depend almost linearly on the energy position of 2s-atomic levels of the metal ligands [37]. Kβ satellite lines of stoichiometric TiO2:N and non-stoichiometric TiO2-x:N thin films are included in Fig. 4a and Fig. 4b, respectively. One can see that all the spectra have a pronounced Kβ” peak. For stoichiometric TiO2:N thin films no differences between spectra shape and peak positions can be seen in Fig. 4a. For non-stoichiometric TiO2-x:N thin films (Fig. 4b) spectral shapes vary significantly. A shift of Kβ2.5 line towards lower energy upon increasing nitrogen doping is observed. The energy position of the Kβ2.5 peak shifts by about 2.6 eV in the case of ηN2=1.06 sccm in comparison with the energy

Figure 4: The Kβ satellite lines of valence-to-core XES spectra for thin films of a) stoichiometric TiO2:N (I/I0=0.13) and b) non-stoichiometric TiO2-x:N (I/I0=0.3); spectra of reference samples TiO2 P25, TiN are shown for comparison.

Figure 5: Background-subtracted valence-to-core XES spectra for thin films of a) stoichiometric TiO2:N (I/I0=0.13) and b) non-stoichiometric TiO2-x:N (I/I0=0.3) along with spectra of reference samples TiO2 P25, TiN. All the valence-to-core XES spectra are off-set in energy to the maximum position of Kβ2.5 feature of TiO2 P25 reference sample.
position of the Kβ2.5 peak of TiO2:P25 reference sample. The energy position of the Kβ2.5 emission peak for the sample obtained at \( \eta_{N2}=1.06 \) sccm, i.e. 4961.3(1) eV, is close to that of the Kβ2.5 emission peak for the TiN reference sample, 4960.7(1) eV. Hence, the relative positions of the Kβ2.5 and Kβ” peaks of the film deposited at \( \eta_{N2}=1.06 \) sccm clearly indicate the presence of nitrogen as the nearest neighbour of titanium in the structure and, thus, prove the incorporation of a considerable amount of nitrogen into the crystal structure of non-stoichiometric TiO2-x.

The experimental background-subtracted valence-to-core XES spectra of stoichiometric TiO2:N and non-stoichiometric TiO2-x:N thin films are given in Fig. 5a and 5b, respectively. In order to perform a deeper analysis of XES profiles, the Kβ main line was fitted by Lorentz function and then subtracted as a background from XES data. In addition, all the valence-to-core XES spectra were off-set in energy to the position of Kβ2.5 peak of the TiO2 P25 reference sample. In Fig. 5a neither shift nor splitting of Kβ” line is observed, which indicates a lack of bulk nitridation of stoichiometric TiO2 thin films. The relative positions of Kβ” lines of the non-stoichiometric TiO2-x:N films, which depend strongly on the nature of the ligands and their local coordination, change with the increasing nitrogen flow (Fig. 5b). Substitution of nitrogen for oxygen in the TiO2-x:N structures leads to the appearance of shoulders on the right side of Kβ” lines at the relative energy close to the position of Kβ” lines of TiN. Also the intensity of the Kβ” peak changes significantly upon increasing nitrogen doping. The feature of Kβ” peak characteristic for the presence of oxygen in the first coordination shell of titanium decreases, whereas the intensity of feature corresponding to nitrogen-titanium chemical bonds increases. Results of the analysis of valence-to-core X-ray emission lines correlate well with those of the X-ray photoelectron spectroscopy [17] as well as with conclusions drawn from X-ray diffraction and imply that the non-stoichiometry in the oxygen sublattice of TiO2-x thin films creates more favourable conditions for nitrogen accommodation.

The effect of varied nitrogen flow rate \( \eta_{N2} \) during deposition on the optical properties of stoichiometric and non-stoichiometric titanium dioxide thin films can be discussed on the basis of complete information obtained from spectrophotometric measurements included in Figs. 6-7. As one can see, there is no big change in the shape of transmittance and reflectance spectra (Figs. 6a, 7a) for stoichiometric TiO2:N thin films sputtered at different \( \eta_{N2} \). All stoichiometric samples are transparent over the visible range while there is no significant shift of the fundamental absorption edge towards lower energies (Fig. 6a). On the contrary, transmittance spectra for non-stoichiometric TiO2-x:N films are strongly modified by the increasing nitrogen flow rate (Fig. 6b). Periodic oscillations of the transmittance and reflectance coefficient with wavelength, due to the interference effect, at photon energies below the fundamental absorption edge, can be seen at \( \eta_{N2}=0 \) and \( \eta_{N2}=0.27 \) sccm, only. This is characteristic for transparent titanium dioxide thin films. Upon increasing nitrogen flow rate to \( \eta_{N2}=0.53 \) sccm and \( \eta_{N2}=1.06 \) sccm, the oscillations become strongly attenuated, absorption of light increases and the fundamental absorption edge is shifted towards visible range. The reflectance spectra for non-stoichiometric TiO2-x:N films obtained at \( \eta_{N2}=0 \) sccm and \( \eta_{N2}=0.27 \) sccm are similar (Fig. 7b). As the nitrogen flow rate \( \eta_{N2} \) is raised, the optical absorption systematically increases hence the interference is destroyed. For the film deposited at \( \eta_{N2}=1.06 \) sccm that crystallizes in TiN structure, the plasma reflection edge at about 2.0 eV can be seen which remains related to an increase in the photon absorption at the free carriers. Occurrence of the plasma reflection edge within the visible range of spectrum is held responsible for a golden tint of the deposited thin films, similarly to the case of films with large deviation from stoichiometry as shown in [33].

In spite of the fact that electronic properties of N-doped TiO2 have been systematically investigated using theoretical as well as experimental methods, proper description of electronic levels is still necessary. Asahi et al. [13] assumed that band gap narrowing caused by N substitution for O is due to the mixing of N 2p with O 2p orbitals in the valence band. Contrary to that, Irie et al. [38] proposed that visible-light response in N-doped titanium dioxide may be due to N 2p states located above the valence band maximum. Di Valentin et al. [14,39,40] have noticed a profound difference between the influence of nitrogen doping upon the electronic structure of anatase and rutile polymorphic forms of TiO2. For the rutile TiO2 polymorph, the top of the valence band is lowered by 0.4 eV upon N-doping as compared with undoped TiO2. As a consequence, the N 2p states localized just above the valence band are slightly below those that are formed analogously in anatase, due to the fact that the top of valence band in anatase remains unaffected by N-doping. This argument was used to account for the absence of red-shift of the absorption edge upon nitrogen doping in rutile [14].

Nakano et al. [41] studied incorporation of nitrogen in TiO2 films deposited by reactive magnetron sputtering and subsequently crystallized by annealing at 550°C in flowing N2 gas. Deep-level optical spectroscopy
measurements revealed two characteristic levels located at \( \sim 1.18 \) and \( \sim 2.48 \) eV below the conduction band. Nakano et al. [41] suggested that 1.18 eV level should be attributed to the O vacancy state and could be active as an efficient generation-recombination centre. The role of oxygen vacancies following substitution of nitrogen for oxygen has recently become more and more appreciated. Chan and Lu [42] attributed the red-shift of absorption edge in substitutionally doped nitrogen \( \text{TiO}_2-N \) films to presence of the oxygen vacancies.

The band gap energy \( E_g \) derived in a standard way [31,43,44] from the optical transmittance and reflectance

\[ E_g = \text{hv} - E_{\text{conduction}} - E_{\text{valence}} \]

Figure 6: Transmittance spectra for thin films of (a) stoichiometric \( \text{TiO}_2:N (I/I_0=0.13) \) and (b) non-stoichiometric \( \text{TiO}_2-x:N (I/I_0=0.3) \) deposited onto amorphous silica substrates; \( \text{hv} \) – photon energy.

Figure 7: Reflectance spectra for thin films of (a) stoichiometric \( \text{TiO}_2:N (I/I_0=0.13) \) and (b) non-stoichiometric \( \text{TiO}_2-x:N (I/I_0=0.3) \) deposited onto amorphous silica substrates; \( \text{hv} \) – photon energy.
spectra shown in Figs. 6-7 is plotted against the nitrogen flow rate $\eta_{N_2}$ in Fig. 8. The value of $E_g$ is read from the linear fit of $(\alpha h\nu)^{1/m}$ vs. photon energy $h\nu$, where $\alpha$ is the absorption coefficient, as a point at which $\alpha=0$. The power coefficient $m$ takes a value of $1/2$ for direct allowed and $m=2$ for indirect allowed optical transitions. The type of the electronic transition was determined in the previous experimental and theoretical studies that indicated TiO$_2$ as a material with direct and indirect allowed transitions [45,46].

As it can be concluded from Fig. 8a, for stoichiometric TiO$_2$:N thin films there is no influence of nitrogen doping on the calculated band gap energy, $E_g$. For both, direct allowed and indirect allowed transitions, $E_g$ is almost unaffected by nitrogen flow rate.

In the case of non-stoichiometric TiO$_{2-x}$:N thin films, $E_g$ was estimated only for samples obtained at $\eta_{N_2}=0$ sccm, $\eta_{N_2}=0.27$ sccm and $\eta_{N_2}=0.53$ sccm (Fig. 8b). Optical absorption for the thin film deposited at $\eta_{N_2}=1.06$ sccm is very high and no fundamental absorption edge can be seen which remains in accordance with TiN formation confirmed by XRD. The energy band gap determined for non-stoichiometric TiO$_{2-x}$:N thin films varies quite significantly upon nitrogen doping. This result is independent of the assumed electronic transitions. We cannot conclude which one: direct or indirect predominates. However, the values of $E_g$ obtained for direct allowed transitions overestimate the values of band gap usually reported for TiO$_2$ [47,48].

The flat band potential is responsible for separation of charge carriers by the electric field. For good and efficient photoanode, the flat band potential should be negative and significantly different from zero [3, 8]. The flat band potential has been determined from the photocurrent measurements in the PEC with different photoanodes (TiO$_2$, TiO$_2$:N, TiO$_{2-x}$:N). Fig. 9 presents the typical current–voltage characteristics in the dark and under illumination for stoichiometric thin film TiO$_2$:N photoanodes deposited at $\eta_{N_2}=0$ sccm and $\eta_{N_2}=0.2$ sccm in the buffer solution (pH=7). The dark current and the photocurrent are affected by the magnitude and sign of the applied external potential $V_B$. Dark current is low when the photoanode is biased positive of the $V_B$. Upon illumination of the photoanode through the electrolyte, a large photocurrent appears. The photocurrent is significant owing to minority carriers participation in the interfacial charge transfer. When the applied potential approaches the flat band potential $V_{FB}$ the magnitude of the photocurrent decreases. The flat band potential $V_{FB}$ can be measured as a threshold of photocurrent at $V_B = V_{ON}$. As long as an applied external potential $V_B$ is higher than the flat band potential $V_{FB}$, the semiconductor electrode works as a photoanode in the PEC and water photolysis takes place; photocurrent is significantly higher than the dark current (Fig. 9). In contrast to that, at $V_B < V_{FB}$ many larger dark current flows and the system cannot work as a photoelectrolyzer any longer.

Influence of the nitrogen flow rate $\eta_{N_2}$ on the flat band potential $V_{FB}$ for nitrogen doped stoichiometric and non-stoichiometric titanium dioxide thin films as well as influence of technological parameter $I/I_0$ on $V_{FB}$ of undoped non-stoichiometric TiO$_{2-x}$ thin films are presented in Fig. 10. For TiO$_{2-x}$ thin films obtained with no nitrogen introduced, the absolute value of $V_{FB}$ decreases with the

Figure 8: Energy band gap $E_g$ determined from optical transmittance and reflectance spectra shown in Figs. 6-7 as a function of nitrogen flow rate $\eta_{N_2}$ for thin films of a) stoichiometric TiO$_2$:N ($I/I_0=0.13$) and b) non-stoichiometric TiO$_{2-x}$:N ($I/I_0=0.3$); energies of direct and indirect allowed optical transitions are shown.
increasing value of the parameter I/I_o, which means that at higher oxygen deficit, the recombination rate is enhanced [8]. For nitrogen doped stoichiometric TiO_2:N films there are no systematic changes in V_{FB} upon increasing nitrogen flow rate ηN_2. The value of flat band potential is within the range of -0.47 V and -0.37 V. On the contrary, the absolute value of the flat band potential for the non-stoichiometric TiO_{2−x}:N thin films increases, i.e., V_{FB} shifts towards more negative values, upon the increase in the nitrogen flow rate ηN_2.

4 Conclusions

Differences and similarities in the structural, optical and photoelectrochemical properties as well as in the electronic structure were observed for thin films of nitrogen-doped stoichiometric TiO_2:N and non-stoichiometric TiO_{2−x}:N films deposited by means of dc-pulsed reactive sputtering from Ti metallic target onto amorphous silica, Si wafers and Ti foil substrates.

It was found that stoichiometric TiO_2:N thin films crystallized as an anatase and rutile mixture. Relative content of these two polymorphic forms changes with the nitrogen flow. XRD measurements of non-stoichiometric TiO_{2−x}:N thin films revealed dramatic changes in the crystallographic structure with the increasing nitrogen flow rate ηN_2 from crystallized anatase-rutile mixture, through the amorphous state, up to TiN.

The SEM images of non-stoichiometric titanium dioxide thin films doped with nitrogen corroborate the XRD results.

Substitution of nitrogen for oxygen in the TiO_{2−x}:N structures leads to the appearance of shoulders on the high energy side of Kβ" lines, close to the position of Kβ" lines of TiN. For stoichiometric TiO_2:N thin films neither shift nor splitting of Kβ" line is observed, which indicates a lack of bulk nitridation of titanium dioxide. XES analysis proves that non-stoichiometry in the oxygen sublattice creates conditions more favorable for nitrogen incorporation into the crystal structure of TiO_2.

The observed shift of the optical absorption edge towards the visible range of the light spectrum (red-shift) with the increasing nitrogen flow rate is quite pronounced for TiO_{2−x}:N.

In the case of non-stoichiometric TiO_{2−x}:N thin films the band gap energy E_g decreases and the flat band potential V_{FB} shifts towards more negative values upon the increasing nitrogen flow rate which should be beneficial to the process of photoelectrolysis and hydrogen generation.

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