

Incorporation of N in the TiO₂ Lattice Versus Oxidation of TiN: Influence of the Deposition Method on the Energy Gap of N-Doped TiO₂ Deposited by Reactive Magnetron Sputtering

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N-doped TiO₂ can be deposited by reactive magnetron sputtering by two methods: incorporation of nitrogen particles in the TiO₂ lattice or incorporation of oxygen particles in the TiN lattice (oxidation). This paper investigates both procedures by experimental and numerical methods in order to establish the best way for incorporation of substitutional nitrogen in the TiO₂ lattice. Films were deposited with different oxygen and nitrogen flow rates for fixed values of argon flow rate, working pressure, DC power, film thickness and target-to-substrate distance. After deposition, samples were characterized by optical spectrophotometry to calculate the energy gaps. The mechanism for incorporation of substitutional nitrogen was investigated by a numerical model based on Berg model, where data were faced to experimental data in order to validate the growing mechanism. Results indicate that the deposition with oxygen flow rates lower than that set for nitrogen decreases the energy gap due to the incorporation of substitutional nitrogen in the film lattice and depositions with high oxygen flow rates decrease the amount of nitrogen in the film lattice due to the fast oxidation of the nitride layers caused by the high sticking coefficient of the oxygen particles.

Keywords: TiO₂, nitrogen, doping, magnetron sputtering, modeling

1. Introduction

Titanium dioxide is a functional semiconductor used in several technological applications due to its chemical and physical characteristics¹⁻⁷. Among the alternatives for improving the catalytic and photovoltaic properties of this material, doping and self-doping are the most suggested^{8,9}. Both procedures incorporate mid-gap states in the film lattice that are responsible by absorption of visible and near-infrared radiation. Doping embeds electronic states above VBM (valence band maximum) or below/inside CBM (conduction band minimum) where nitrogen was found as one of the most efficient for TiO₂ due to the narrowing of the band-gap caused by incorporation of N2p states above VBM⁸. Self-doping (TiO₂ with oxygen vacancies) induce energy states between 0.75 and 1.18 eV below CBM due to the incorporation of active Ti³⁺ states¹⁰.

Several plasma-based methods are commonly used for deposition of N-doped TiO₂^{8,11-17} among which the reactive sputtering is one of the most important due to the possibility for controlling a wide range of properties in thin films technology¹⁸. Based on papers published in the past, films of N-doped TiO₂ is commonly deposited by sputtering of a metallic titanium target with the reactive gas mixture composed by argon, nitrogen and oxygen, where the amount

of substitutional nitrogen in the film lattice was found to be very sensitive to the amount of oxygen in the gas phase. This is caused by oxidation of the nitride layers and high sticking coefficient of the oxygen on Ti and TiN; thus, the effective incorporation of substitutional nitrogen is observed only for cases where the nitrogen flow rate is higher than that used for oxygen during film growth^{11,16,17,19}. Otherwise, interstitial nitrogen becomes favored²⁰ and may desorb when the film structure is subject to annealing conditions²¹.

According to previous studies^{11,19,22}, oxidation of the nitride layers is one of the main reactions responsible by embedding of substitutional nitrogen in TiO₂ during deposition with continuous gas flow rate feeding (see the pulsed case in ref.²³). For nitrogen flow rate at 10 sccm and oxygen flow rate below 1.0 sccm, the incorporation of nitrogen, as substitutional particle, follows four well-defined steps¹¹: (i) chemisorption of nitrogen and oxygen on the titanium surface for compound formation; (ii) decrease of the chemisorption rate due to the filling of the available sites on the titanium surface; (iii) oxidation of the nitride layers and generation of suboxides; (iv) balance of the reactions. In the third step the oxygen concentration in the lattice increases suddenly and the film structure undergoes a transition from nitride to oxide. During the oxidation process, nitrogen may be incorporated as substitutional particle by chemisorption on suboxides, such as Ti₂O₃ and TiO.

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Besides the oxidation of TiN layers, nitrogen can also be embedded in the pre-deposited TiO₂ film; however, this method requires high energy procedures, such as, ion implantation²⁴ or nitridation of the TiO₂ under oxygen-free conditions²⁵. Other methods include the reactive sputter deposition of TiO₂ by feeding the reactive gas mixture with small quantities of nitrogen in the gas phase^{26,27}.

In this paper, we reproduced the deposition of N-doped TiO₂ by reactive magnetron sputtering by two methods: setting the nitrogen flow rate higher than that for oxygen and vice-versa. The purpose is to investigate the best condition for decreasing the energy gap of the films and understand the growth mechanisms during deposition. Studies were conducted by experimental and numerical methods.

2. Experimental

Films of N-doped TiO₂ were deposited on grounded and unheated glass substrates (borosilicate) by DC reactive magnetron sputtering using a planar magnetron with a titanium disk (99.6%) of 34 mm in diameter as target. Film thickness were fixed at 2 μm (controlled by deposition rate). Studies were conducted in two particular conditions: (i) nitrogen flow rate higher than that set for oxygen and (ii) nitrogen flow rate lower than that set for oxygen. In the first condition, the argon flow rate, nitrogen flow rate, DC power, target-to-substrate distance and working pressure were fixed at 10 sccm, 10 sccm, 150 W, 30 mm and 5.0 mTorr, respectively. Depositions were made with oxygen flow rates of 0.2, 0.6 and 3.5 sccm. Films (3 samples) were semi-transparent (dark and yellow) at low oxygen flow rate (0.2 and 0.6 sccm) and transparent at high oxygen flow rate (3.5 sccm). In the second condition, argon flow rate, oxygen flow rate, DC power, target-to-substrate distance and working pressure were fixed at 10 sccm, 3.5 sccm, 150 W, 30 mm and 5.0 mTorr, respectively, and depositions were made with nitrogen flow rates of 0, 0.5, 1.0, 1.5 and 2.0 sccm. Films (5 samples) were transparent. The working pressure was adjusted by the throttle valve of the diffusion pump in all depositions. The base pressure was kept at 10⁻⁶ Torr and experimental conditions are summarized in Table 1.

Samples were investigated by optical spectrophotometry (JASCO V570) and data of transmittance and reflectance (measured in the 300-2000 nm range) were used to calculate the energy gaps by Tauc plots where the absorption coefficients were calculated with equation given in ref.²⁶. The growth mechanisms were evaluated with a numerical model based on Berg model described in refs.^{11,19,28}. This model is a set of ODEs that describe the temporal evolution of the chemical composition of the films that were assumed as a mixture of several compounds, such as, TiO, Ti₂O₃, TiO₂, TiN and substitutional nitrogen (O-Ti-N). The numerical data were used to investigate the compound fraction on the substrate (fraction of compound covering the substrate

Table 1. Experimental conditions.

Parameter	First condition	Second condition
DC power (W)	150	150
Target-to-substrate distance (mm)	30	30
Working pressure (mTorr)	5.0	5.0
Argon flow rate (sccm)	10	10
Nitrogen flow rate (sccm)	10	0
		0.5
		1.0
		1.5
		2.0
Oxygen flow rate (sccm)	0.2	3.5
		0.6
		3.5
Thickness of the films (μm)	2	2

surface) as function of the deposition time and calculate the percentage of substitutional nitrogen in the film lattice. This latter parameter was given by the fraction of O-Ti-N in the steady state condition.

3. Results and Discussions

Figure 1 shows the energy gap of the films deposited in the first condition. For oxygen flow rate of 0.2 sccm, film shows double electronic transition: one related to the excitation of N2p states (2.2 eV)⁸ and other to the excitation of Ti³⁺ states (0.6 eV)¹⁰. For oxygen flow rate of 0.6 sccm, the electronic structure shows single transition at 2.5 eV that is related to N2p states⁸. At high oxygen flow rate (3.5 sccm), the energy gap increases toward to the normal value of undoped anatase TiO₂ (3.2 eV). The two latter films are crystalline, according to results show in ref.¹¹; thus, among these three conditions, the oxygen flow rate of 0.6 sccm was the best condition for deposition of crystalline N-doped TiO₂.

The temporal evolution of the simulated compound fraction on the substrate for the films deposited with oxygen flow rates of 0.2, 0.6 and 3.5 sccm is shown in Figure 2. According to the numerical model, particles of nitrogen and oxygen are first adsorbed on the titanium surface for compound formation. Then, oxygen particles oxidize the TiN layers and, as consequence, the fraction of TiN decreases and the amount of TiO₂ increases faster. Note that due to the higher amount of nitrogen in the gas phase, the TiN formation rate is higher than that for oxide layers. These steps are observed for all conditions where the concentration of substitutional nitrogen (fraction of O-Ti-N) decreases as the oxygen flow rate increases. This effect may be caused by decreasing of the suboxides in the film lattice during oxidation¹¹. The estimated percentage of substitutional nitrogen (fraction of O-Ti-N in the steady state condition shown in Figure 2) for

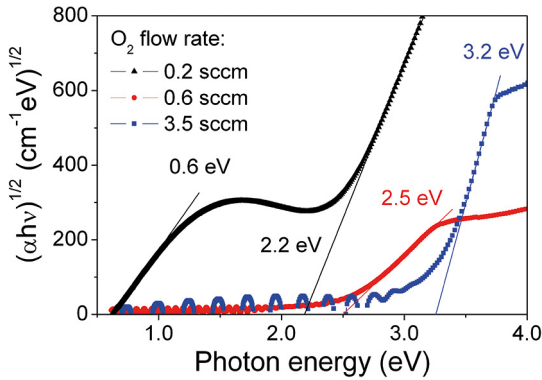


Figure 1. Energy gap of the films deposited with 10 sccm of nitrogen flow rate and different oxygen flow rates.

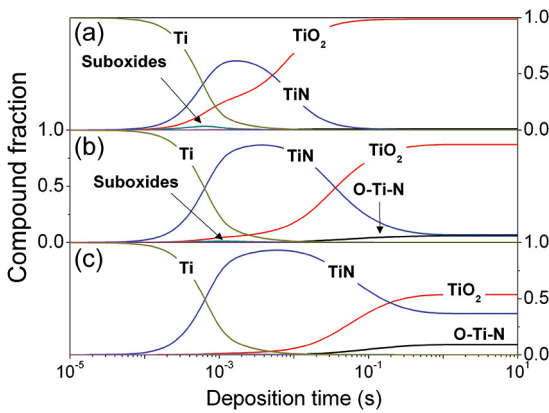


Figure 2. Simulated compound fraction on the substrate as function of the deposition time for N-doped TiO₂ deposited with nitrogen flow rate of 10 sccm and oxygen flow rates of (a) 3.5, (b) 0.6 and (c) 0.2 sccm (fraction = 1: full coverage of the substrate, fraction = 0: no compound formation).

films deposited with oxygen flow rates of 0.2, 0.6 and 3.5 sccm are 9, 6 and 1%, respectively. The transition region (between pure titanium surface and steady state condition) gets wider as the oxygen flow rate decreases. This is caused by decreasing of the oxidation rate due to decrease of the oxygen partial pressure on the film surface, which enables the incorporation of substitutional nitrogen in the film lattice to expressive values in the steady state condition. Otherwise, the surface is fully oxidized. The overall results of experimental studies about the chemical composition of films deposited in the same conditions are in agreement with the results presented in this paper^{11,19}. However, the modeled concentration of suboxides in the steady state condition does not match with XPS data (chemical composition on the film surface) presented in ref.¹¹. This may be related with the natural loss of oxygen in the titanium oxide surface¹, which was not employed into the numerical model. On the other hand, RBS data (chemical composition of the film bulk) are in agreement with modeled data.

Films deposited in the second condition presents the typical energy gap of undoped anatase TiO₂ (3.2 eV), as shows Figure 3. The temporal evolution of the simulated compound fraction, depicted in Figure 4, indicates that the mechanism for film growth is similar to that observed previously; however, the film surface is fully oxidized and it is caused by combination of the lower amount of nitrogen in the gas mixture and higher sticking coefficient of the oxygen particles¹⁹. Then, the probability for an oxygen atom occupies an oxygen vacancy is higher than that for a nitrogen atom, where the majority of nitrogen bindings are broken by the high density of oxygen particles on the film surface. Therefore, the substitutional nitrogen is not incorporated in the film lattice; it is released back to the gas phase. The increase of the nitrogen flow rate from 0 to 2.0 sccm only increases the amount of TiN layers in the transition region, which are fastly oxidized, giving a negligible amount of O-Ti-N in the steady state condition. Note that the time required for the system reach the steady state condition is lower in the second condition. This is caused by decreasing

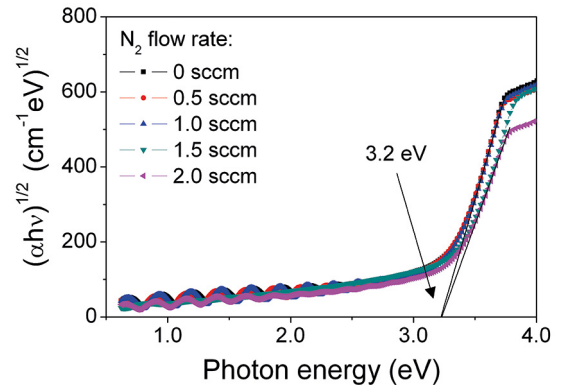


Figure 3. Energy gaps of the films deposited with 3.5 sccm of oxygen flow rate and different nitrogen flow rates.

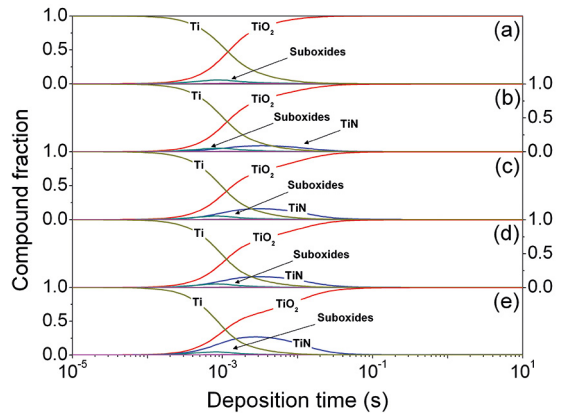


Figure 4. Simulated compound fraction on the substrate as function of the deposition time for N-doped TiO₂ deposited with oxygen flow rate of 3.5 sccm and nitrogen flow rates of (a) 0, (b) 0.5, (c) 1.0, (d) 1.5 and (e) 2.0 sccm (fraction = 1: full coverage of the substrate, fraction = 0: no compound formation).

of the competing reactions between oxygen and nitrogen due to decreasing of the nitrogen working pressure. It also explains the later beginning of the reactions in the second condition (after 10^{-4} s) in comparison to the beginning of the reactions in the first condition (before 10^{-4} s).

The previous conditions were investigated for particularized flows. In order to investigate the amount of nitrides or oxides in the film structure for several experimental conditions, the chemical composition was modeled as function of different combinations of oxygen and nitrogen flow rates in the steady state condition. Data are summarized in the chemical composition maps, detailed in Figures 5 and 6. Figure 5 show that the film is initially composed by stoichiometric TiN for depositions without oxygen in the plasma atmosphere and nitrogen flow rates above 1.0 sccm. This condition is valid for a very restrict range of the oxygen flow, indicating that the deposited nitride layers are very sensible to tiny changes of oxygen in the gas discharge. When the oxygen particles are added at quantities below 0.5 sccm, they oxidize the TiN layers and the O/Ti ratio

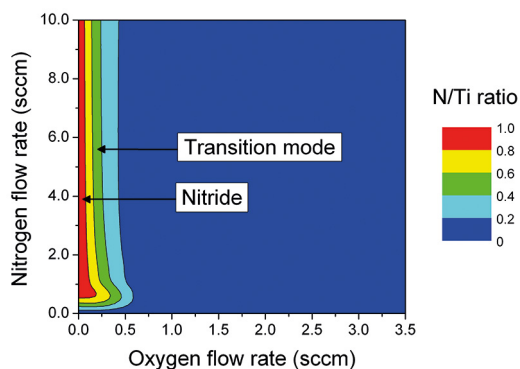


Figure 5. Simulation of the N/Ti ratio on the substrate as function of different combinations of oxygen and nitrogen flow rates (chemical composition map). The nitride region is mostly composed by stoichiometric TiN ($N/Ti \approx 1$).

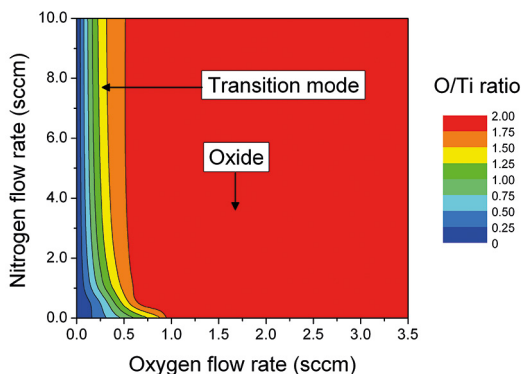


Figure 6. Simulation of the O/Ti rate on the substrate as function of different combinations of oxygen and nitrogen flow rates (chemical composition map). The oxide region is composed by stoichiometries between $TiO_{1.75}$ and TiO_2 . At oxygen flow rate of 3.5 sccm, the film coverage is mostly composed by TiO_2 ($O/Ti \approx 2$).

starts to increase towards to the full coverage of the substrate with stoichiometric TiO_2 . See Figure 6. The N/Ti ratio decreases to inexpressive values after 0.75 sccm of oxygen and remains unaltered when the amount of oxygen is constant for a wide range of nitrogen flow rate. Note in Figure 6 that higher oxygen flows are required to increase the O/Ti ratio when the plasma is nitrogen-free, indicating that the oxidation of the nitride layers increases the surface oxidation rate²².

The concentration of substitutional nitrogen for different combinations of oxygen and nitrogen flow rates is shown in the doping zone map, illustrated in Figure 7 for the steady state condition. The increase of the oxygen flow rate increases the suboxide formation; thus, substitutional nitrogen is incorporated into the film lattice where the maximum value ($\sim 9\%$) is obtained around to 0.2 sccm of oxygen (red zone). The increase of the O_2 flow rate decreases the concentration of substitutional nitrogen due to the oxidation processes. At 0.6 sccm of oxygen, the film is transparent with the yellowish appearance, where this is caused by the higher concentration of oxide layers mixed with TiN clusters. In addition, a large combination of oxygen and nitrogen flow rates may be set to obtain the same concentration of substitutional nitrogen (yellow/green zone). At 3.5 sccm of oxygen (blue zone), there is no practical value for the nitrogen flow rate in which the incorporation of substitutional nitrogen is possible, which is in agreement with our experiments.

Keeping the oxygen flow rate around to 0.6 sccm (best condition for deposition of crystalline N-TiO₂) and increasing the nitrogen flow rate, it is also possible to increase the concentration of substitutional nitrogen in the film lattice (vertical transition from green zone to the yellow/red zone); however, increasing the nitrogen flow rate to high values leads to the increase of the working pressure and decreasing of the mean free path and particles energy, which may be detrimental for several film properties, such as, crystallinity, roughness and thickness. These characteristics are fundamental for applications of this material in solar cells and water splitting^{2,5,6}.

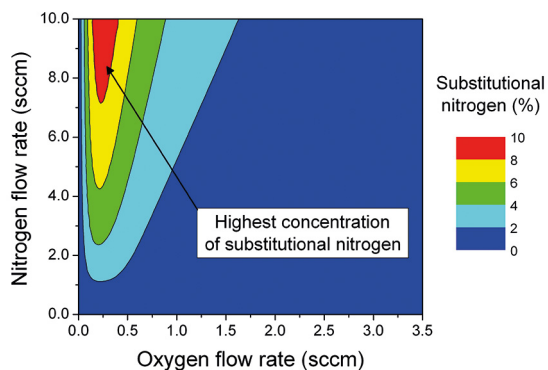


Figure 7. Simulation of the concentration of substitutional nitrogen in the film lattice as function of different combinations of oxygen and nitrogen flow rates (doping zone map).

4. Conclusions

The deposition of N-doped TiO₂ with oxygen flow rate higher than that set for nitrogen avoids the incorporation of nitrogen atoms as substitutional particles in the film lattice due to the fast oxidation of the nitride layers. To reduce the releasing of nitrogen particles back to gas phase, and improve the incorporation of substitutional nitrogen, the nitrogen flow rate must be kept as high as possible while the reactive gas mixture is fed by small quantities of oxygen during film processing.

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6. References

- Diebold U. The surface science of titanium dioxide. *Surface Science Reports*. 2003;48(5-8):53-229.
- O'Regan B, Grätzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature*. 1991;353:737-740.
- Burschka J, Pellet N, Moon SJ, Humphry-Baker R, Gao P, Nazeeruddin MK, et al. Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature*. 2013;499:316-319.
- Pessoa RS, Fraga MA, Santos LV, Massi M, Maciel HS. Nanostructured thin films based on TiO₂ and/or SiC for use in photoelectrochemical cells: A review of the material characteristics, synthesis and recent applications. *Materials Science in Semiconductor Processing*. 2015;29:56-68.
- Fujishima A, Rao TN, Tryk DA. Titanium dioxide photocatalysis. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*. 2000;1(1):1-21.
- Fujishima A, Rao TN, Tryk DA. TiO₂ photocatalysts and diamond electrodes. *Electrochimica Acta*. 2000;45(28):4683-4690.
- Kim SK, Kim WD, Kim KM, Hwang CS. High dielectric constant TiO₂ thin films on a Ru electrode grown at 250 °C by atomic-layer deposition. *Applied Physics Letters*. 2004;85:4112.
- Asahi R, Morikawa T, Ohwaki T, Aoki K, Taga Y. Visible-light photocatalysis in nitrogen-doped titanium oxides. *Science*. 2001;293(5528):269-271.
- Xiong LB, Li JL, Yang B, Yu Y. Ti³⁺ in the surface of titanium dioxide: generation, properties and photocatalytic application. *Journal of Nanomaterials*. 2012;2012:831524.
- Nakamura I, Negishi N, Kutsuna S, Ihara T, Sugihara S, Takeuchi K. Role of oxygen vacancy in the plasma-treated TiO₂ photocatalyst with visible light activity for NO removal. *Journal of Molecular Catalysis A: Chemical*. 2000;161(1-2):205-212.
- Duarte DA, Massi M, da Silva Sobrinho AS. Development of dye-sensitized solar cells with sputtered N-doped TiO₂ thin films: from modeling the growth mechanism of the films to fabrication of the solar cells. *International Journal of Photoenergy*. 2014;2014:839757.
- Livraghi S, Paganini MC, Giamello E, Selloni A, Di Valentin C, Pacchioni G. Origin of photoactivity of nitrogen-doped titanium dioxide under visible light. *Journal of the American Chemical Society*. 2006;128(49):15666-15671.
- He G, Zhang LD, Li GH, Liu M, Wang XJ. Structure, composition and evolution of dispersive optical constants of sputtered TiO₂ thin films: effects of nitrogen doping. *Journal of Physics D: Applied Physics*. 2008;41(4):045304.
- Irie H, Watanabe Y, Hashimoto K. Nitrogen-concentration dependence on photocatalytic activity of TiO_{2-x}N_x powders. *Journal of Physical Chemistry B*. 2003;107(23):5483-5486.
- Kosowska B, Mozia S, Morawski AW, Grzmil B, Janus M, Kałucki K. The preparation of TiO₂-nitrogen doped by calcination of TiO₂·xH₂O under ammonia atmosphere for visible light photocatalysis. *Solar Energy Materials and Solar Cells*. 2005;88(3):269-280.
- Stranak V, Quaas M, Bogdanowicz R, Steffen H, Wulff H, Hubicka Z, et al. Effect of nitrogen doping on TiO_xN_y thin film formation at reactive high-power pulsed magnetron sputtering. *Journal of Physics D: Applied Physics*. 2010;43(28):285203.
- Heřman D, Šícha J, Musil J. Magnetron sputtering of TiO_xN_y films. *Vacuum*. 2006;81(3):285-290.
- Smith DL. Thin-Film Technology. In: Smith DL, ed. *Thin-Film Deposition: Principles and Practice*. New York: McGraw-Hill; 1995. p. 1-7.
- Duarte DA, Sagás JC, da Silva Sobrinho AS, Massi M. Modeling the reactive sputter deposition of N-doped TiO₂ for application in dye-sensitized solar cells: effect of the O₂ flow rate on the substitutional N concentration. *Applied Surface Science*. 2013;269:55-59.
- Emeline AV, Kuznetsov VN, Rybchuk VK, Serpone N. Visible-light-active titaniaphotocatalysts: the case of N-doped TiO_{2-x}N_y—properties and some fundamental issues. *International Journal of Phototenergy*. 2008;2008:258394.
- Saha NC, Tompkins HG. Titanium nitride oxidation chemistry: an X-ray photoelectron spectroscopy study. *Journal of Applied Physics*. 1992;72(7):3072.
- Duarte DA, Massi M, Sagás JC, da Silva Sobrinho AS, Irala DR, Fontana LC. Hysteresis-free deposition of TiO_xN_y thin films: effect of the reactive gas mixture and oxidation of the TiN layers on process control. *Vacuum*. 2014;101:200-204.
- Martin N, Sanjinés R, Takadoum J, Lévy F. Enhanced sputtering of titanium oxide, nitride and oxynitride thin films by the reactive gas pulsing technique. *Surface and Coatings Technology*. 2001;142-144:615-620.
- Batzill M, Morales EH, Diebold U. Surface studies of nitrogen implanted TiO₂. *Chemical Physics*. 2007;339(1-3):36-43.

25. Chai JW, Yang M, Chen Q, Pan JS, Zhang Z, Feng YP, et al. Effects of nitrogen incorporation on the electronic structure of rutile-TiO₂. *Journal of Applied Physics*. 2011;109(2):023707.
26. Lindgren T, Mwabora JM, Avendaño E, Jonsson J, Hoel A, Granqvist CG, et al. Photoelectrochemical and optical properties of nitrogen doped titanium dioxide films prepared by reactive DC magnetron sputtering. *Journal of Physical Chemistry B*. 2003;107(24):5709-5716.
27. Irala DD, Maciel HS, Duarte DA, Massi M, da Silva Sobrinho AS. Influence of the nitrogen concentration on the photoinduced hydrophilicity of N-doped titanium dioxide thin films deposited by plasma sputtering. *ECS Transactions*. 2010;31(1):109-115.
28. Berg S, Nyberg T. Fundamental understanding and modeling of reactive sputtering processes. *Thin Solid Films*. 2005;476(2):215-230.