TITANIUM OXYNITRIDE DEPOSITION BY REACTIVE GAS PULSING TECHNIQUE AIMING TO APPLICATION IN GRÄTZEL SOLAR CELLS

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1. Introduction

The increase of worldwide population together with a constant need for new technologies that facilitate our lives, the energy demands has also increased all over the world. Once the non-renewable energies are exhaustible and highly polluting, the scientific community concentrates its efforts to develop more efficient and low cost energy producing from sources, such as, solar cells, wind energy, biomass and nuclear energy (Mills, 2004; Şen, 2004).

The nuclear sources have been widely employed in many countries as primary source for generation of electrical energy because its elevated conversion efficiency (Bela and Juergen, 1997). However, it is not a secure form to power generation as shown in the recent nuclear accident at the Fukushima Daiichi Nuclear Power Plant. This disaster has caused serious consequences for the worldwide population, and after this event, the need for renewable energy sources became even more evident.

Among several renewable alternatives, the solar radiation is the form of energy most abundant in the planet. One way to obtain solar energy is by the absorption of solar radiation using flat panels that directly convert the absorbed in electrical energy through the photoelectric effect (Avrutin et al. 2011, Bhubaneswari et al. 2011, Adolf et al. 1998). Currently, p-n junction is the most common solar cells used worldwide due to its high conversion efficiency compared with other solar cells.

However, besides the traditional solar cells based on p-n junction, Grätzel (2003) has shown an alternative and efficient way to convert solar radiation into electrical energy by means of organic solar cells using, for example, titanium dioxide (TiO_2). Titanium dioxide is an inorganic semiconductor widely used in several technological applications due to its high photocatalytic activity under ultraviolet radiation. On the other hand, the photocatalytic efficiency of pure titanium dioxide after solar irradiation is quite low because the ultraviolet region corresponds only to approximately 5% of the solar spectrum (Stranak et al., 2010). One solution to solve this problem was found in the work conducted by O'Regan and Grätzel (O'Regan and Grätzel, 1991) in which TiO_2 was sensitized covering it with a thin film of organic ruthenium-based dyes. However, these organic dyes are expensive and may detach from the surface when employed in aqueous solutions, and moreover, the long-term stability of cells using different dyes can be questioned (Lindgren et al. 2003). For that reason, many efforts have been done in order to find an alternative way to activate the photocatalytic activity of titanium dioxide by visible light. In 2001, Asahi et al. reported a theoretical study in which they have doped titanium dioxide with several transition metals and non-metal anions and the substitutional nitrogen doping was found to be more effective in decreasing the energy gap of titanium dioxide because the N 2p states contributed to band-gap narrowing by mixing with O 2p states. This study was of great importance to explain the experimental good results obtained by Shinri Sato in 1986 (Sato, 1986) and other researchers that have reported this technique as an reliable way to red-shift the titanium dioxide absorption band (Hěrman et al. (2006) and (Chappé et al. (2004)).

One of the most traditional techniques used to grow titanium dioxide doped with substitutional nitrogen is the reactive magnetron sputtering. However, the reactive sputter deposition at constant gas flow rate not always is the better choice due to the high instability of the deposition process caused by the target poisoning. One alternative to overcame this problem was given by Martin et al. (2007a), that have developed the reactive gas pulsing technique in which the reactive gas flow, like oxygen, is periodically pulsed into the vacuum chamber with the other gas flows at constant rate.

In this paper, titanium oxynitride thin films (TiO_xN_y) were deposited by reactive magnetron sputtering using the reactive gas pulsing technique varying the pulsing time for oxygen flow rate with fixed argon and nitrogen flow rates. The chemical composition, optical and structural properties of the films were analyzed and correlated.

2. Experimental

Titanium oxynitride thin film were deposited on glass and Si (100) substrates using a 34 mm in diameter high purity titanium target (99.6%) in gas mixtures of $Ar+N_2+O_2$ without external substrate heating source. All fixed parameters used in the reactive sputtering process are shown in Table 1. The partial pressures of nitrogen and argon were kept, respectively, at 0.2 Pa and 0.4 Pa while the oxygen flow rate were pulsed at different duty cycles (α = 20, 40, 60, 70 and 80%) by using a rectangular waveform (see Figure 1). The films were analyzed by perfilometry (Tencor Instruments Alpha-Step 500), spectrophotometry (JASCO V570), RBS (Pelletron-tandem model 5SHD) and XRD (Philips X'Pert) techniques.

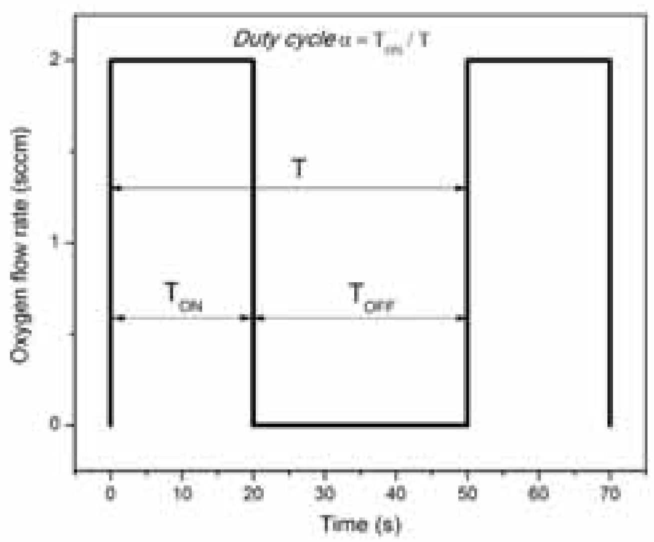

Fig. 1: Rectangular waveform used to the pulsing of oxygen flow rate.

The results from perfilometry and spectrophotometry were used to calculate the deposition rate and optical band gap of the films. RBS data were used to calculate the overall film concentration and the XRD data, obtained from grazing incidence angle, were used to study the influence of the oxygen pulsing duty cycle on the formation of the film structures.

Table 1: Deposition parameters.

Parameter	Value
Target-to-substrate distance	40 mm
Power supply	dc, 130W
Partial pressure of argon	0.4 Pa
Partial pressure of nitrogen	0.2 Pa
Partial pressure of oxygen	0.09 Pa
Deposition time	30 minutes
T (total period of one cycle)	50 s

3. Results and discussions

3.1. Perfilometry

The deposition rate and film thickness as function of the oxygen pulsing duty cycle are shown in Figure 2. Results indicate an important decrease of the deposition rate as the oxygen pulsing duty cycle is increased from 20 to 80%. This effect is the well-known mechanism called "target poisoning" that is caused by the formation of oxide compounds at the target surface, which contributes considerably to decrease of the sputter yield of the compound and, consequently the deposition rate decreases. A more accentuated decrease of the deposition rate can be observed between α = 40 and 60%, which probably is related with the transition between the nitride mode and oxide mode.

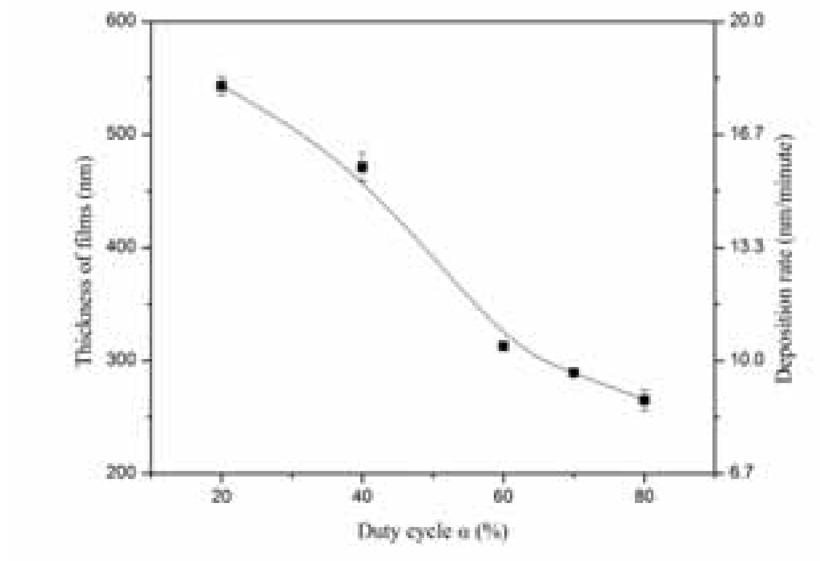

Fig. 2: Deposition rate and thickness of the films as function of oxygen pulsing duty cycle.

3.2. Spectrophotometry

The optical band gap was determined from the Tauc relation (Hěrman et al., 2006):

$$\alpha_A h\upsilon = B\left(h\upsilon - E_g\right)^r \qquad \text{(eq. 1)}$$

where, α_A the absorption coefficient, hv the energy of the incident photons, B a constant and E_g the energy gap. The power r characterizes the transition process (0.5 for direct and 2 for indirect). Titanium oxynitride is considered as semiconductor with indirect transition (Kumar et al. 2000) and we have used r = 2. The absorption coefficient was calculated from the following equation (Lindgren et al., 2003):

$$\alpha_A d = -ln\left(\frac{T}{1-R}\right) \qquad \text{(eq. 2)}$$

where d the film thickness, T and R the transmittance and reflectance, respectively. Figure 3 shows the transmittance data obtained for films deposited at different oxygen pulsing duty cycles (α = 20, 40, 60, 70 and 80%). Films deposited at α = 20 and 40% are opaque, which is typical from titanium nitride structure. Increasing the oxygen pulsing duty cycle to 60% films become slightly transparent and at higher duty cycles (70 and 80%) the films become entirely transparent, which are in good agreement with the results obtained by other researches (see Hěrman et al., (2006) and Chappé et al., (2003)).

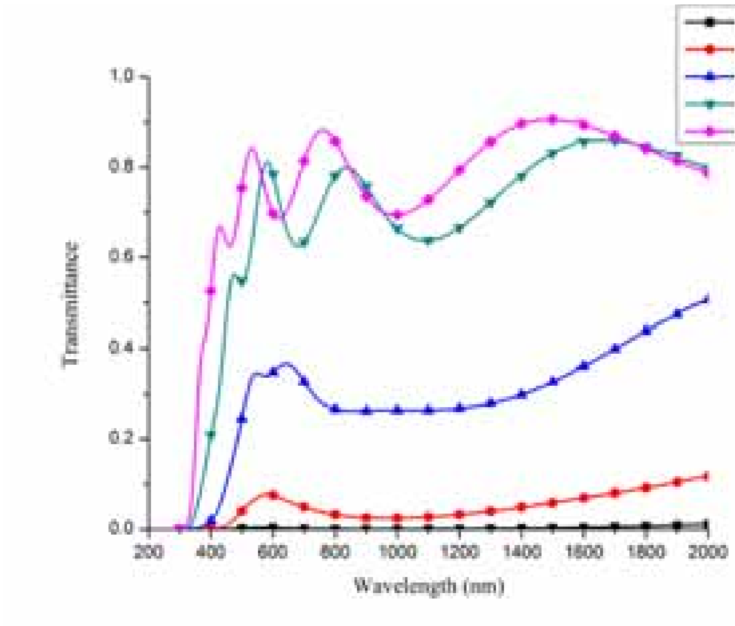

Fig. 3: Transmittance spectra of titanium nitride, titanium oxynitride and titanium dioxide films as function of the photon wavelength.

The optical band gap obtained from the transmittance and reflectance spectra using the Tauc relation (see Fig. 4), indicates that the film deposited at oxygen pulsing duty cycle of 60% has the lowest energy gap (1.91 eV) and increasing the pulsing duty cycle, the substrate is gradually covered by oxide compound so that this effect contributes to increase the optical band gap up to 3.26 eV (α = 80%), which is the typical energy gap of the titanium dioxide structure (see Table 2).

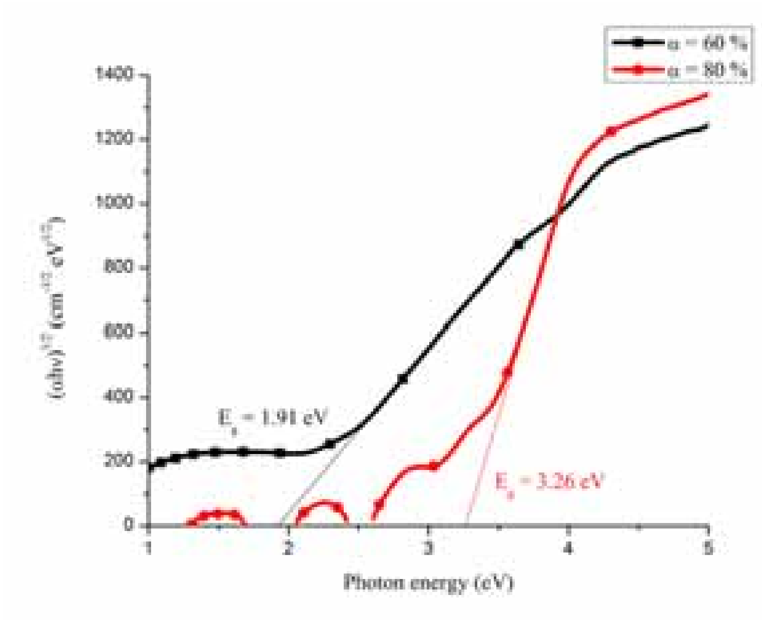

Fig. 4: Optical band gap E_g of titanium oxynitride and titanium dioxide evaluated from the transmittance and reflectance spectra using the Tauc relation.

Thus, we can conclude that an optimal mixture of reactive gases is given when oxygen pulsing duty cycle around 60%. Films deposited at that condition can absorb photons with wavelength below about 640 nm, *i.e.* more than a half of the visible spectrum, while films deposited at α = 70 and 80% can only absorb photons from the ultraviolet spectrum region.

Table 2: Calculated optical gap

Duty cycle α (%)	Optical gap (eV)	Appearance
20	-	Opaque
40	-	Opaque
60	1.91 ± 0.02	Dark greenish
70	3.01 ± 0.01	Yellowish
80	3.26 ± 0.05	Transparent

3.3. Rutherford Backscattering Spectroscopy (RBS)

The overall composition of the films as function of the oxygen pulsing duty cycle is shown in Figure 5. Results indicate that the films are free of impurities and the modification on the pulsing duty cycle significantly changes their chemical composition. As described in section 3.2, the film deposited at α = 20% is opaque and the RBS analysis confirms our hypothesis, showing predominantly a titanium nitride chemical composition nitrogen (33%) and oxygen (26%). Increasing the oxygen pulsing duty cycle, films become more oxide although the partial pressure of nitrogen is approximately twice of the oxygen partial pressure. This effect is caused due to the higher sticking coefficient of oxygen in relation to nitrogen (Harra, 1976). Despite the low amount of nitrogen in the films (about 5%) deposited with α = 70 and 80%, the measured energy gap present typical values obtained for rutile and anatase phases. This indicates that nitrogen do not substitute the oxygen position but occupies interstitial sites on the film lattice.

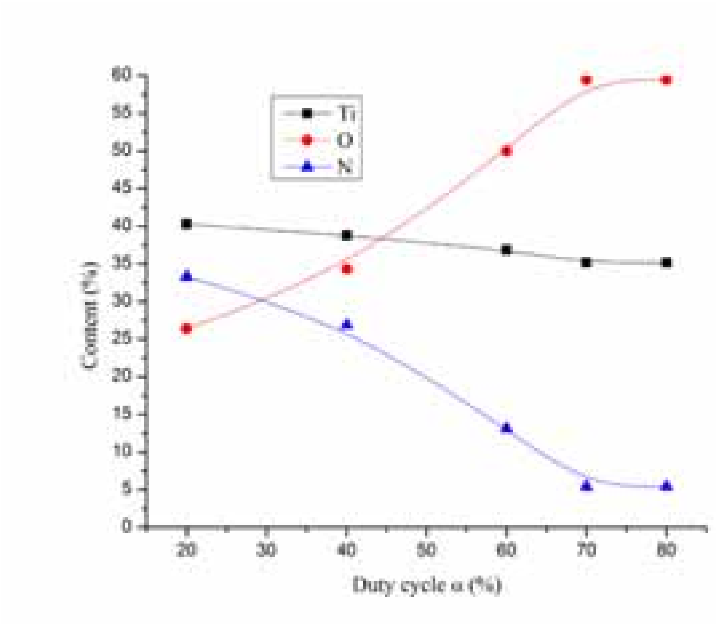

Fig. 5: Chemical composition of the films as function of the oxygen pulsing duty cycle.

3.4. X-ray Diffraction (XRD)

The XRD patterns are shown in Figure 6 at different oxygen pulsing duty cycles. As mentioned in the last sections, films deposited at α = 20 and 40% are opaque, which is typical from the titanium nitride structure. These films show the most common crystallographic orientation for titanium nitride, *i.e.* (111) and (200). The film that has the lowest optical band gap, deposited at α = 60%, is amorphous and this is in agreement with other studies (Hĕrman et al. 2006). For films deposited at α = 70 and 80%, it is observed a slight crystallization of the rutile and anatase phase which are in agreement with the calculations of the energy gap and the data from RBS.

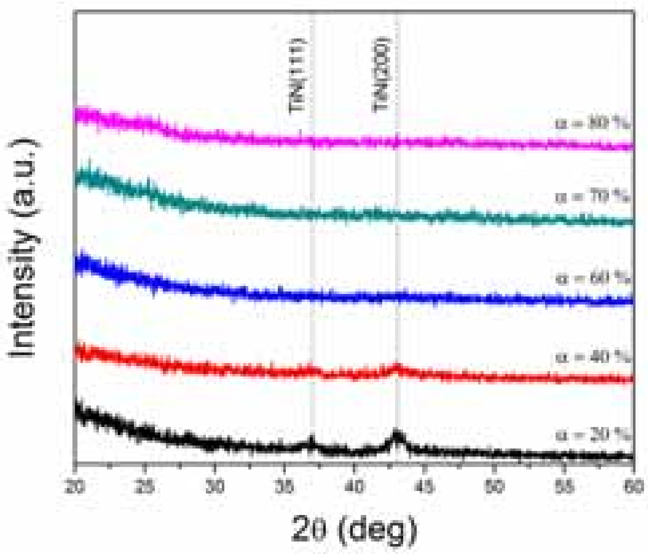

Fig. 6: XRD patterns to the films deposited at different oxygen pulsing duty cycles.

4. Conclusions

In this paper, titanium oxynitride was successfully deposited by reactive magnetron sputtering using the gas pulsing technique. The overall results indicate that is possible to control the optical properties, chemical composition and structural properties of the films by modifying the duty cycle of the oxygen flow rate. The RBS and spectrophotometry results show that there is an oxygen pulsing duty cycle that favours the growing of the film with the highest doping of substitutional nitrogen (13%) and, as consequence, the lowest energy gap, 1.91 eV. This film absorbs photons with wavelengths below 640 nm, which means the absorption of more than a half of the visible spectrum. Thus, these results make titanium oxynitride a promising technology to substitute the organic dyes commonly used together with pure titanium dioxide in dye-sensitized solar cells.

5. References

Adolf, G., Joachim, K., Bernhard, V., 1998. Crystalline Silicon Solar Cells**,** John Wiley & Sons, New York.

Asahi, R., Morikava, T., Ohwaki, T., Aoki, K., Taga, Y., 2001. Visible-light photocatalysis in nitrogen-doped titanium oxides. Sci. 293, 269-271.

Avrutin, V., Izyumskaya, N., Morkoç, H., 2011. Rev.: Semiconductor solar cells: Recent progress in terrestrial applications. Superlat. and Microst. 49, 337–364.

Bela, J. C., Juergen, K., 1997. Nuclear power applications: Supplying heat for homes and industries. IEAA Bullet. 39, 21-25.

Bhubaneswari, P., Iniyan, S., Goic, R., 2011. A review of solar photovoltaic technologies, Renew. and Sust. En. Rev. 15, 1625–1636.

Chappé, J.-M., Martin, N., Terwagne, G., Lintymer, J., Gavoille, J., Takadoum, J., 2003. Water as reactive gas to prepare titanium oxynitride thin films by reactive sputtering, Thin Sol. Film. 440, 66-73.

Grätzel, M., 2003. Dye-sensitized solar cells. J. Photochem. Photobiol. C: Photochem. Rev. 4, 145-153.

Harra, D. J., 1976. Review of sticking coefficients and sorption capacities of gases on titanium nitride, J. Vac. Sci. Technol. 13, 471-474.

Hĕrman, D., Šícha, J., Musil, J., 2006. Magnetron sputtering of TiO_xN_y films. Vacumm. 81, 285-290.

Lindgren, T., Mwabor, J.M., Avendaño, E., Jonsson, J., Hoel, A., Granqvist, Claes-Göran, Lindquist, Sten-Eric, 2003. Photoelectrochemical and Optical Properties of Nitrogen Doped Titanium Dioxide Films Prepared by Reactive DC Magnetron Sputtering. J. Phys. Chem. B. 107, 5709-5716.

Martin, N., Lintymer, J., Gavoille, J., Chappé, J.M., Sthal, F., Takadoum, J., Vaz, F., Rebouta, L., 2007a. Reactive sputtering of TiO_xN_y by the reactive gas pulsing process. Part I: Pattern and period of pulses. Surf. & Coat. Tech. 201, 7720-7726.

Martin, N., Lintymer, J., Gavoille, J., Chappé, J.M., Sthal, F., Takadoum, J., Vaz, F., Rebouta, L., 2007b. Reactive sputtering of TiO_xN_y by the reactive gas pulsing process. Part II: The role of the duty cycle. Surf. & Coat. Tech. 201, 7727-7732.

Mills, D., 2004. Advances in solar thermal electricity technology. Solar Energ. 76, 19–31.

O'Regan, B., Grätzel, M., 1991. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films, Nature. 353 737-740

Sato, S., 1986. Photocatalytic activity of NO_x-doped TiO_2 in the visible light region, Chem. Phys. Lett. 123 126.

Şen, Z., 2004. Solar energy in progress and future research trends. Progr. in Ener. and Combust. Sci. 30, 367–416.

Stranak, V., Quaas, M., Bogdanowicz, R., Steffen, H., Wulff, H., Hubicka, Z., Tichy, M., Hippler., R., 2010. Effect of nitrogen doping on TiO_xN_y thin film formation at reactive high-power pulsed magnetron sputtering. J. Phys. D: Appl. Phys. 43, 1-7.