ISSN : 0974 - 7494 Volume 8 Issue 8

Nano Science and Nano Technology
An Indian Journal

Full Paper

NSNTAIJ, 8(8), 2014 [320-327]

Optical study of titanium dioxide thin films prepared by vacuum evaporation technique

Saad Farhan Oboudi[1], Nadir Fadhil Habubi[2]*, Ali Hussein Ni'ma[3], Sami Salmann Chiad[2]

[1]Baghdad University, College of Science, Physics Department, Baghdad, (IRAQ)

[2]Al_Mustansiriyah University, College of Education, Physics Department, Baghdad, (IRAQ)

[3]Ministry of Higher Education and Scientific Research, Scholarships and Cultural Relations, Baghdad, (IRAQ)

E-mail : nadirf61@gmail.com

ABSTRACT

In this investigation, TiO_2 thin films were synthesized by vacuum evaporation technique on glass substrates at room temperature. The films were then annealed at 200 and 250ºC in air for a period of 1 hour. The optical characterizations of the as deposited and annealed films were carried out using UV–VIS transmittance spectroscopy in the wavelength range 300–900 nm in order to calculate the optical constants such as refractive index, extinction coefficient, real and imaginary parts of dielectric constant. Results illustrate that refractive index, extinction coefficient, both the real and imaginary parts of dielectric constant and the optical conductivity of the films are increasing with increasing annealing temperature, on the other hand, the value of the skin depth is found to be decreases as the annealing temperature increased to 250ºC, so the skin depth is a transmittance related.

KEYWORDS

TCOs;
Titanium dioxide;
Optical constants;
Vacuum evaporation technique.

INTRODUCTION

Considerable interest has been generated in recent years, researchers and engineers paid special attention to TiO_2 thin films, which have many applications in catalysis, photocatalysis and solar cells[1-6]. TiO_2 is a wide band gap semiconductor (3.03 eV for rutile and 3.18 for anatase) and can only absorb about 5% of sunlight in the ultraviolet light region, which largely limits its practical applications because of the lower utility of sunlight and quantum yield. Various researchers started to investigate ways of immobilizing TiO_2 particles, for example in thin film form[7,8]. Actually thin film technique is becoming a standard for preparation of TiO_2-based photocatalysts. One of the advantages of thin film photocatalysts is that the catalyst layer may be connected to an external power source to reduce the recombination of UV-activated electrons and holes and thus, the efficiency of the catalyst is increased.

Formation of a particular phase depends on the nature of the starting material, its composition, deposition method, and annealing temperatures. Many deposition methods have been used to prepare TiO_2 films, including thermal[9], Plasma spray[10], anodic[11], ion beam[12], sol–gel method[13], chemical vapor deposition[14], spray pyrolysis[15], plasma-enhanced chemical vapor deposition[16], pulsed laser deposition[17], and RF sputtering method[18], evaporation[19]. Each one of these methods has its own benefits which can be used to obtain films with specific characterizations.

Many researches have been devoted to study the fabrication and characterization of TiO_2 thin films[20-25]. In this study, the optical characteristics of TiO_2 films deposited by vacuum evaporation technique on glass substrates are reported. The optical constants of the films were examined and the effect of annealing temperature upon the optical properties of the films was investigated.

EXPERIMENTAL PROCEDURE

TiO_2 thin films were prepared by vacuum evaporation technique onto glass substrates at room temperature under vacuum $10^{-}5$mbar. Ti metal (99.99% purity) provided by (Fluka chemicals Germany). Film thickness was checked by an interferometric method[26], and it was found to be 300nm. The oxide was then formed by thermal oxidation at 500C for 45min. Optical transmittance was recorded with a double beam Shimadzu UV-VIS spectrophotometer in the wavelength range 300–900 nm. The effect of annealing temperatures on the optical properties was investigated.

RESULTS AND DISCUSSIONS

Information concerning optical transmittance is important in evaluating the optical performance of conductive oxide films. The spectral dependences of T and R of the as-prepared TiO_2 films and the films after anneal to 200 and 250ºC are shown in Figures 1 and 2 respectively. The results indicate that T increases with the increasing of the incident photons wavelength λ, and decreases with the increasing of annealing temperature. One can notice that the spectral dependences of both T and R of all films as a function of λ in the high absorption region (λ < 1000 nm) is characterized by drastic change of both T and R as a function of λ in which T+R<1 where the optical constants were determined. Figure 1 announces that the percentage of transmission is approximately 45% in the visible region consequently; the transmittance inferred that spin coated TiO_2 films could be used for optical coating applications. The wavelength of the film absorption edge is 290 nm approximately. These results were in a good agreement with that obtained by El-Nahass et al.[27].

Figure 2 shows that in the visible region, the reflectance values were observed between 0.38% and 0.45%. The reflectance of all films had a common tendency that the values increased with the increase of the wavelength. It is seen that the reflectance is limited only by the surface reflectance of about 40% in the visible region.

The optical properties of TiO_2 thin films by means of optical absorption in the UV-VIS region of (300–

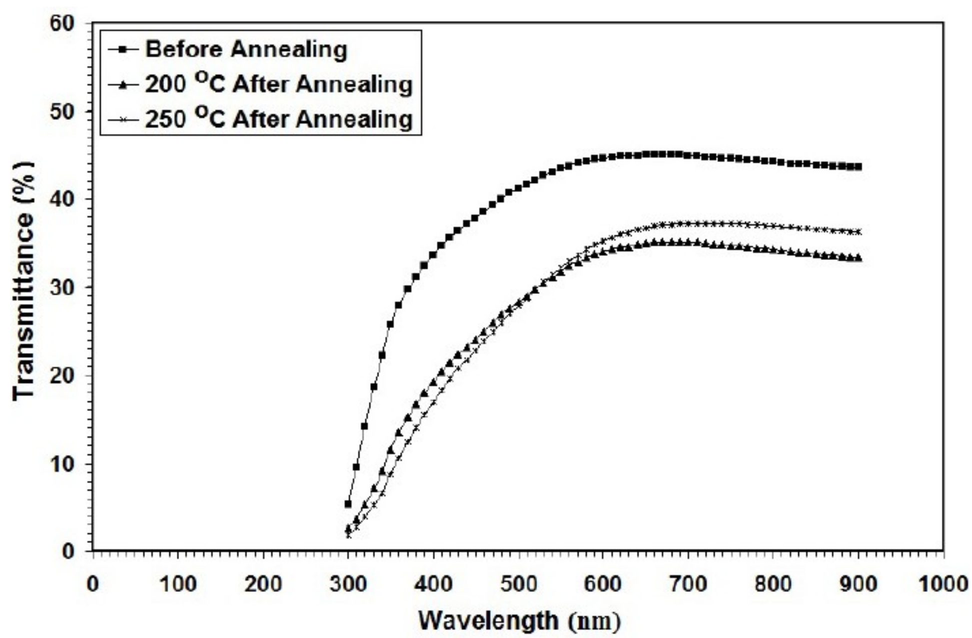

Figure 1 : Transmittance versus wavelength for as deposited and annealed TiO_2 thin films

Full Paper

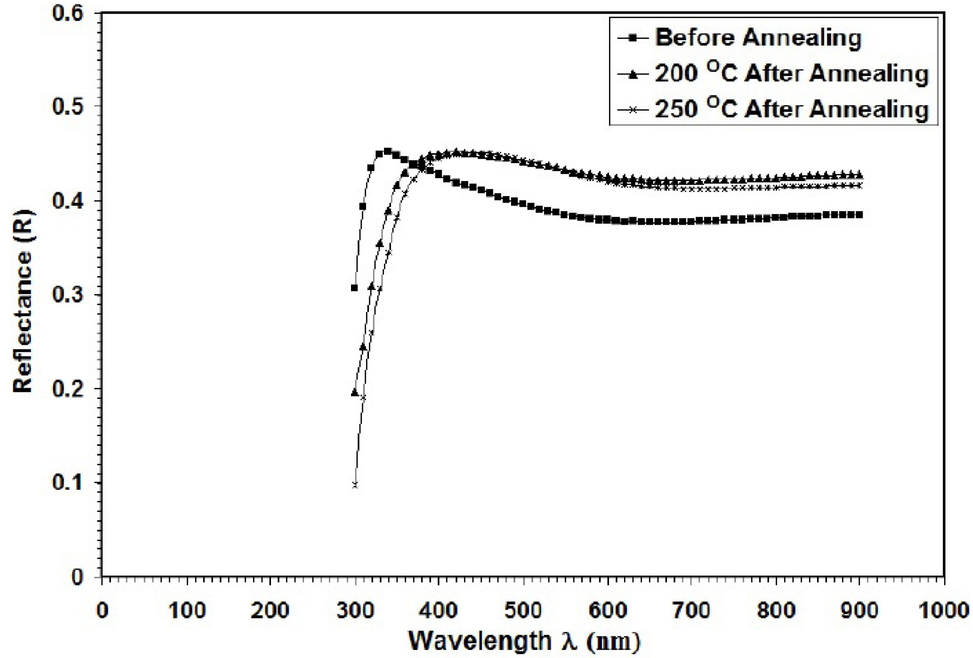

Figure 2 : Reflectance versus wavelength for as deposited and annealed TiO_2 thin films

900) nm have been investigated. The absorption coefficient (α) could be calculated using the following relation[28]:

$$\alpha = \frac{2.303A}{t} \qquad \textbf{(1)}$$

Where (A) is the absorption and (t) is the film thickness. Figure 3 shows the dependence of the absorption coefficient (α) of TiO_2 thin films on the wavelength at two annealing temperatures 200 and 250ºC. It is seen that with increasing annealing temperature the absorption edge shifts to the higher wavelength direction. This result proves that upon increasing the annealing temperature, the absorption edge of TiO_2 films moves to visible spectrum range, which indicates that the films are sensitive to visible light. The blue shift in the absorption band edge has been claimed as a consequence of exciton confinement with decrease particle size (the so-called quantum-size effect) in TiO_2[29]. Serpone et. al.[30] indicated that the blue-shifted absorption thresholds in TiO_2 small particles are direct transition in an

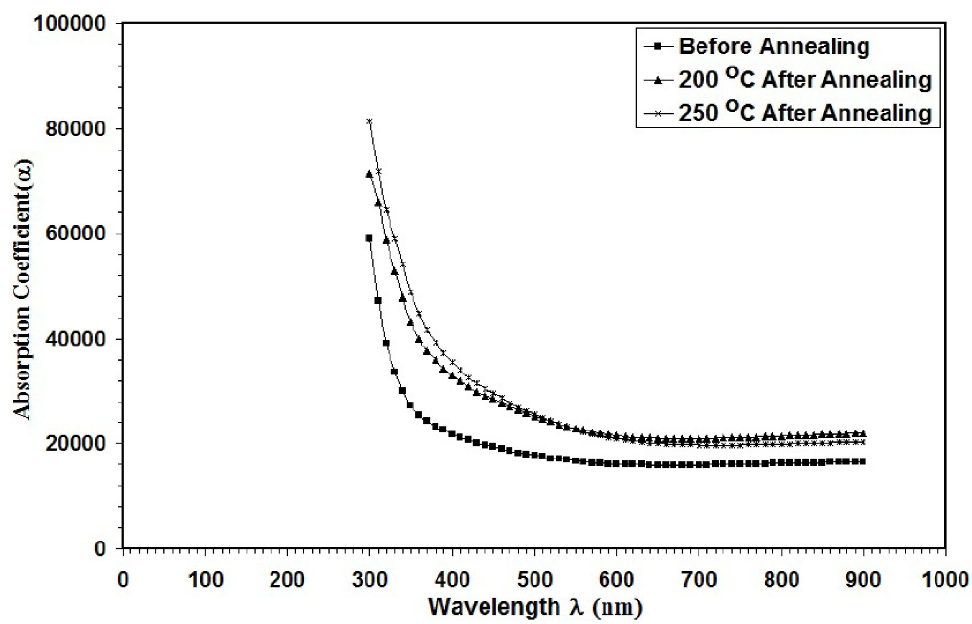

Figure 3 : Absorption coefficient versus wavelength for TiO_2 thin films

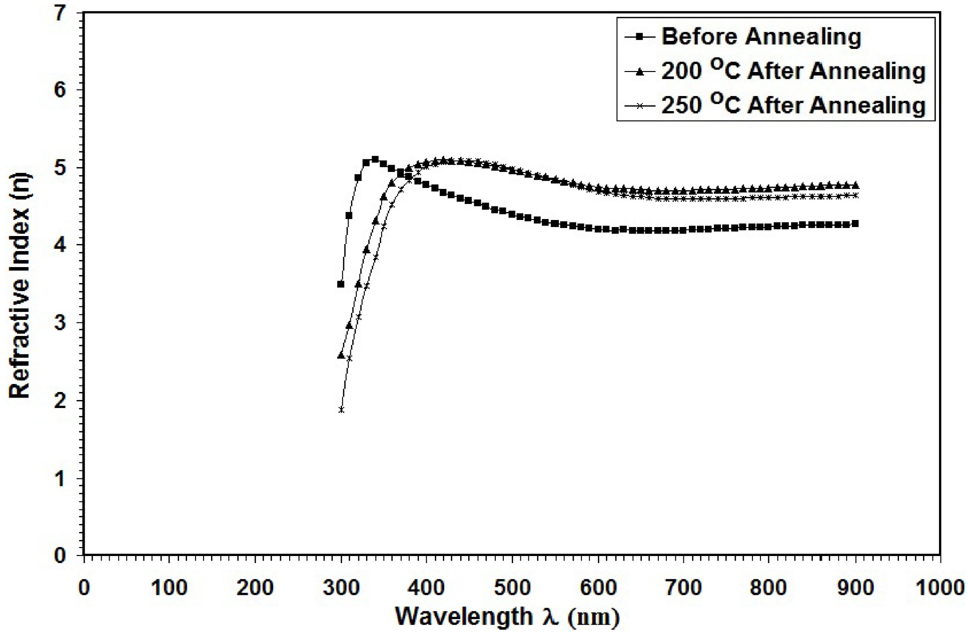

Figure 4 : Refractive index versus wavelength for as deposited and annealed TiO_2 thin films

otherwise indirect band gap semiconductor instead of quantum-size effect. Deloach et. al.[31] recently reported that the blue shift of optical energy gap is due to the change of the energy gap of the disorder crystal in TiO_2 films. The optical energy gaps of the films decrease from 3.25 to 2.95eV when the annealing temperature increases to 250°C. From the result, it is believed that the blue shift of absorption band edge might due to the change of the energy gap of the disorder crystal in TiO_2 films.

Refractive index of the films is an important parameter for optoelectronic devices design. In order to calculate the optical constant refractive index (n) and the extinction coefficient (k) of the films at different wavelengths, we can use the following relations[32]:

$$n = [1 + R/1 - R] + [4R / (1-R)^2 - k^2]^{1/2} \quad (2)$$

$$k = \alpha\lambda/4\pi \quad (3)$$

Where (α) is the absorption coefficient and λ is the wavelength. The refractive index of the films was cal-

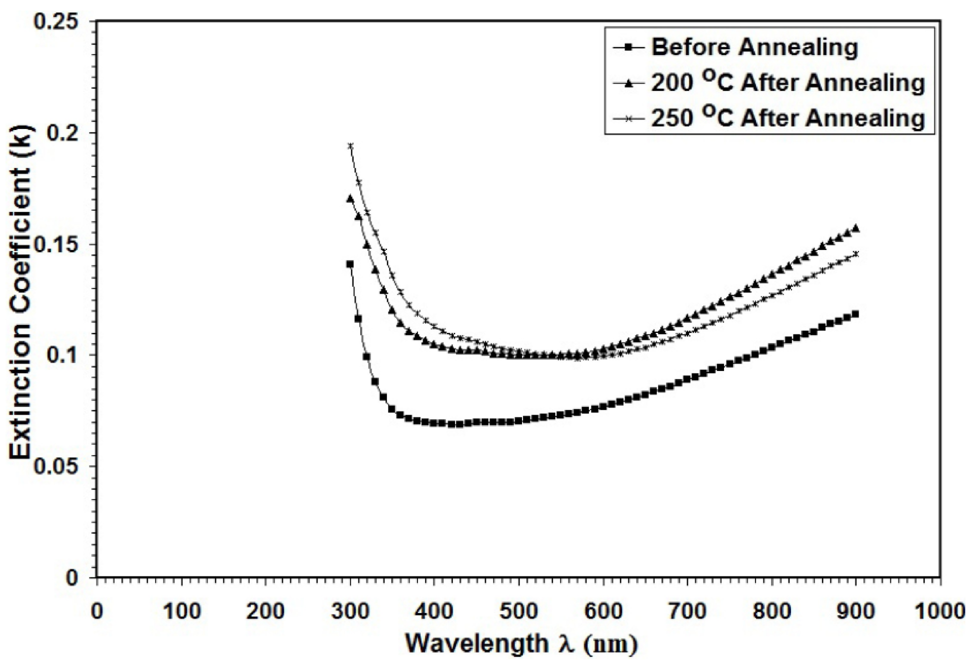

Figure 5 : Extension coefficient versus wavelength for as deposited and annealed TiO_2 thin films

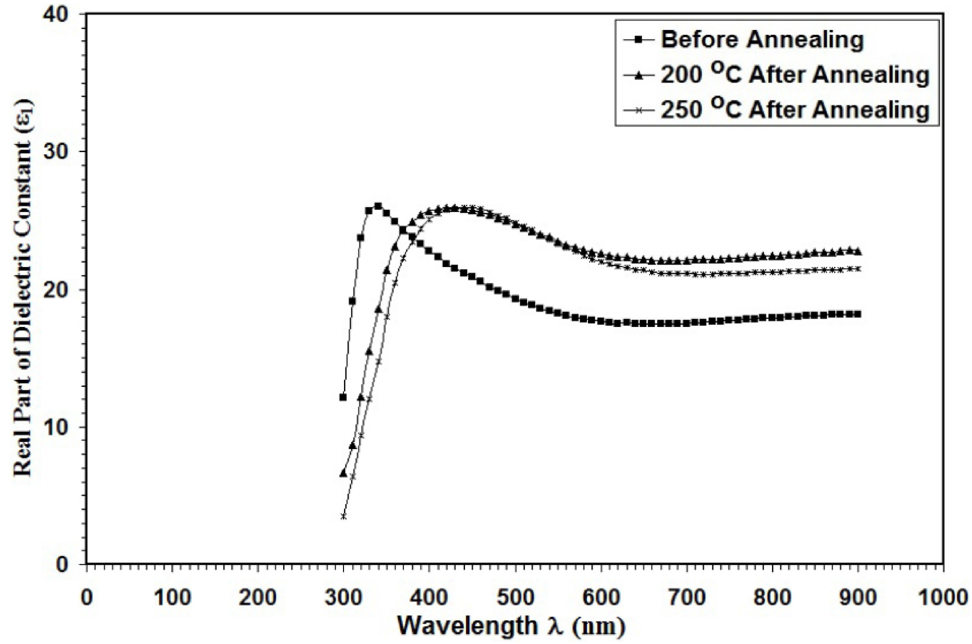

Figure 6 : Real part of the dielectric constant for as deposited and annealed TiO_2 films

culated by using Eq. (1) and the variation of refractive index with wavelength for the films is shown in Figure 4. All films showed similar behavior in refractive index spectra which is a gradually decreases with increasing wavelength. It can be noticed that the refractive index of the films that annealed to 200 and 250ºC is increased. This increase may be attributed to higher packing density and change in crystalline structure, Many researchers reported that annealing treatment caused refractive index to increase due to the enhancement of crystallization[33-35]. Refractive index values of the samples have varied between (4.2–4.8) at long wavelengths.

The calculated values of extinction coefficient, k versus λ for TiO_2 films are illustrated in Figure 5. It could be noticed that k values increases with increasing the wavelength and also increased as the films annealed to 200 and 250ºC, such results was also confirmed by Hasan et. al.[36].

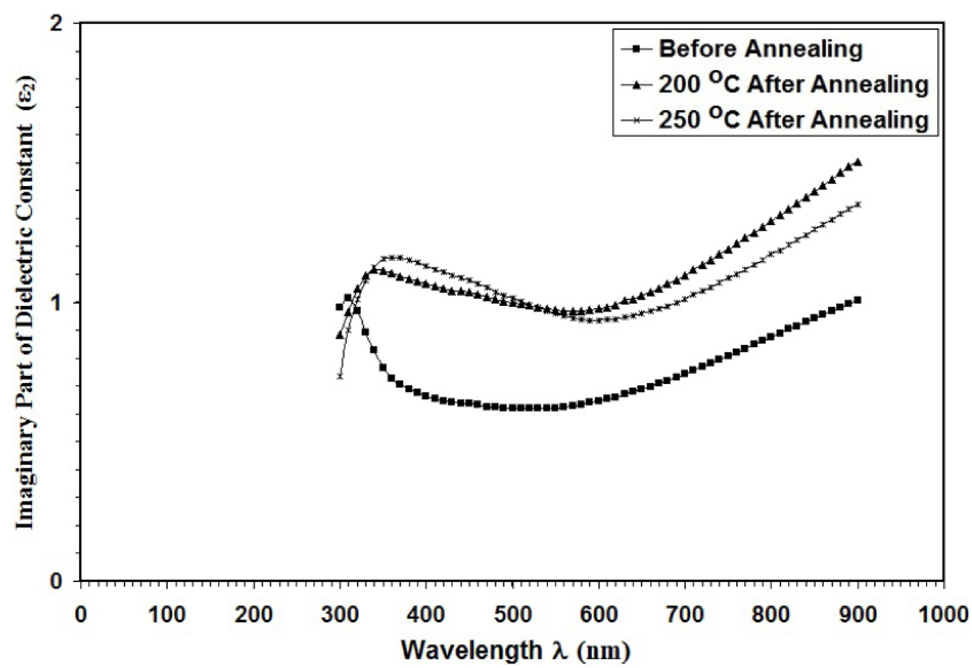

Figure 7 : Imaginary part of the dielectric constant for as deposited and annealed TiO_2 films

The obtained values of *n* and *k* were used to calculate both ε_1 and imaginary ε_2 parts of the dielectric constant and they were obtained using the formulas[37]:

$$\varepsilon_1 = n^2 - k^2 \quad (4)$$

$$\varepsilon_2 = 2nk \quad (5)$$

Where ε_1 determines the maximum energy that can be stored in the material, ε_2 also is called the relative loss factor and represents the absorption of electrical energy by a dielectric material that is subjected to an alternating electromagnetic field. The variation of both real ε_1 and imaginary ε_2 parts of the dielectric constant for all TiO_2 films (before and after annealing) as a function of wavelength are shown in Figures 6 and 7. It can be noticed that the values of the real part are higher than those of the imaginary part. The ε_1 increase forward as the wavelength increases and display a maximum starting around 340nm which corresponds to di-

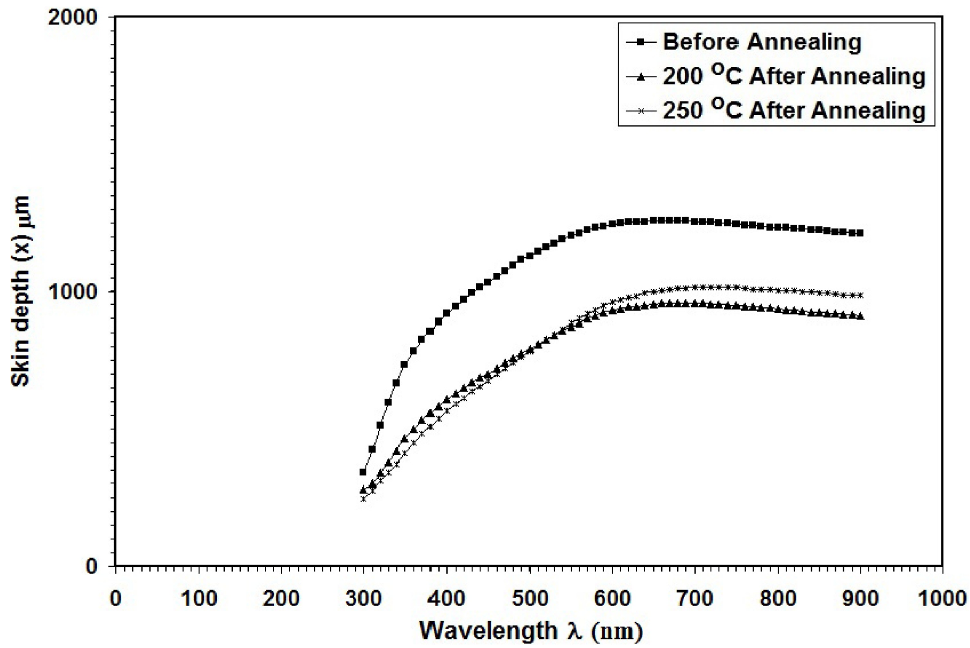

Figure 8 : Skin depth versus wavelength for as deposited and annealed TiO_2 thin films

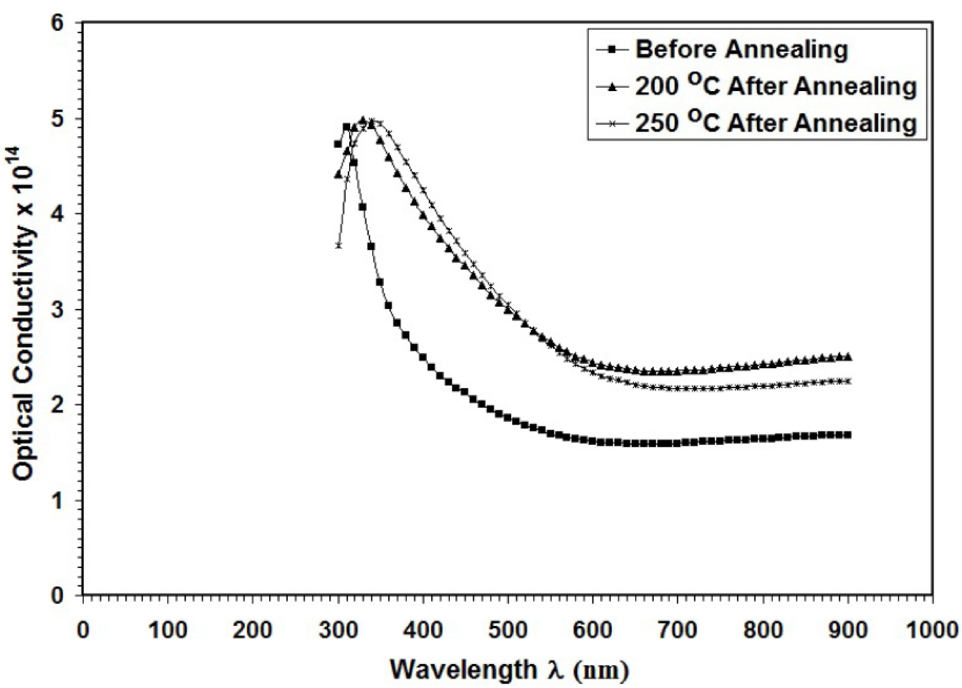

Figure 9 : Optical conductivity versus wavelength for as deposited and annealed TiO_2 films

rect energy gap. Also the values of real and imaginary parts of the dielectric are found to be increases after annealing.

The skin depth could be calculated using the following relation[38]:

$$\chi = \lambda / 2\pi k \quad (6)$$

Where λ is the wavelength of the incident photon, k is the extinction coefficient. Figure 8 show the variation of skin depth as a function of wavelength for all films. It is clear from the figure that the skin depth increase as the wavelength increase, this behavior could be seen in all samples, but the skin depth decreases as the annealing temperature increases to 250ºC, which means that the skin depth is a transmittance related.

The optical conductivity was calculated using the relation[39]:

$$\sigma = \alpha\, n\, c / 4\pi \quad (7)$$

Where (c) is the velocity of light.

Figure 9 shows the variation of optical conductivity with the wavelength. It was observed that the optical conductivity increases with the increasing of annealing temperature. It can be noticed that the optical conductivity for all films increased in the high photon energies region and decreased in the low photon energy region, this decrease is due to the low absorbance of the films in that region. It is seen that the optical conductivity decreases with increasing wavelength, which has drastically increased corresponding to the absorption edge and the optical gap. This suggests that the increase in optical conductivity is due to electrons excited by photon energy. The origin of this increasing may be attributed to some changes in the structure due to the annealing and the charge ordering effect [68].

CONCLUSION

TiO_2 thin films have been successfully deposited onto a glass substrate by vacuum evaporation technique. All samples were optically characterized by using UV-VIS technique and the results were systematically presented. It was found that the transmittance of the TiO_2 films in the visible domain reaches 45% in a large spectral range. Results indicate that the optical parameters are strongly dependent on annealing, as the annealing temperature increases, the energy gap of the TiO_2 films decreases to 2.95eV. The refractive index, the extinction coefficient, the real and imaginary parts of the dielectric constant, and the optical conductivity was calculated and they are tending to decrease with increasing annealing temperature, on the other hand the skin depth increases with increasing annealing temperature. These present observations can help improve the understanding of the optical parameters of TiO_2 thin films.

REFERENCES

[1] P.S.Shinde, H.P.Deshmukh, S.H.Mujawar, A.I.Inamdar, P.S.Patil; Spray deposited titanium oxide thin ûlms as passive counter electrodes, Electrochimica Acta, **52**, 3114–3120 **(2007)**.
[2] K.S.Kim, M.A.Barteau; Structure and Composition Requirements for Deoxygenation, Dehydration, and Ketonization Reactions of Carboxylic Acids on TiO_2 (001) Single Crystal Surfaces, J.Catal., **125**, 353-375 **(1990)**.
[3] D.G.Cahill, T.H.Allen; Thermal conductivity of sputtered and evaporated SiO_2 and TiO_2 optical coatings, Appl.Phys.Lett., http://dx.doi.org/10.1063/1.112355, **65**, 309 **(1994)**.
[4] B.O'Regan, M.GraÈtzel; A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films, Nature, **353**, 737-740 **(1991)**.
[5] S.Ben Amor, G.Baud, J.P.Besse, M.Jacquet; Structural and Optical Properties of Sputtered Titanium Films, Mater.Sci.Eng.B, **47**, 110-118 **(1997)**.
[6] P.Babelon, A.S.Dequiedt, H.Moste Âsa-Sba, S.Bourgeois, P.Sibillot, M.Sacilotti; SEM and XPS studies of titanium dioxide thin films grown by MOCVD, Thin Solid Films, **322**, 63-67 **(1998)**.
[7] R.W.Mattews; Photooxidation of organic impurities in water using thin films of titanium dioxide, J.Phys.Chem., **91**, 3328-3333 **(1987)**.
[8] A.Fujishima, T.N.Rao, D.A.Tryk; Titanium dioxide photocatalysis, Journal of Photochemistry and Photobiology - C: Photochemistry Reviews, **1**, 1-21 **(2000)**.
[9] B.Morris Henry; Method of depositing titanium dioxide (rutile) as a gate dielectric for MIS device fabrication, US Patent, 4, 200, 474 **(1978)**.
[10] Atin Sharma, Andrew Gouldstone, Sanjay Sampath, Richard J.Gambino; Anisotropic electrical conduction from heterogeneous oxidation states in plasma sprayed TiO_2 Coatings, J.Appl.Phys., http://dx.doi.org/10.1063/1.2382456, **100**, 114906 **(2006)**.
[11] M.R.Kozlowski, P.S.Tyler, W.H.Smyrl, R.T.Atanasoki; Anodic TiO_2 Thin Films Photoelectrochemical, Electrochemical, and Structural Study of Heat-Treated and RuO2Modified Films, J.Electrochem.Soc., **136**, 442-450 **(1989)**.
[12] Chen Yang, Huiqing Fan, Yingxue Xi, Jin Chen, Zhuo

Li; Effects of depositing temperatures on structure and optical properties of TiO_2 film deposited by ion beam assisted electron beam evaporation, Applied Surface Science, **254**, 2685–2689 **(2008)**.

[13] Jin Young Kim, Dong-Wan Kim, Hyun Suk Jung, Kug Sun Hong; Influence of Anatase–Rutile Phase Transformation on Dielectric Properties of Sol–Gel Derived TiO_2 Thin Films, Jpn.J.Appl.Phys., **44**, 6148-6151 **(2005)**.

[14] V.G.Besserguenev, R.J.F.Pereira, M.C.Mateus, I.V.Khmelinskii, R.C.Nicula, E.Burkel; TiO_2 thin film synthesis from complex precursors by CVD, its physical and photocatalytic properties, International Journal of Photoenergy, **5**, 99-105 **(2003)**.

[15] H.P.Deshmukh, P.S.Shinde, P.S.Patil; Structural, optical and electrical characterization of spray-deposited TiO_2 Thin Films, Materials Science and Engineering: B, **130(1-3)**, 220–227 **(2006)**.

[16] Wenli Yang, Colin A.Wolden; Plasma-enhanced chemical vapor deposition of TiO_2 thin films for dielectric applications, Thin Solid Films, **515**, 1708–1713 **(2006)**.

[17] Narumi Inoue; Hiromitsu Yuasa, Masayuki Okoshi; TiO_2 thin films prepared by PLD for photocatalytic applications, Applied Surface Science, **197–198**, 393–397 **(2002)**.

[18] Cheol Ho Heo, Soon-Bo Lee, Jin-Hyo Boo; Deposition of TiO_2 thin films using RF magnetron sputtering method and study of their surface characteristics, Thin Solid Films, **475**, 183–188 **(2005)**.

[19] H.Pulker, G.Paesold, E.Ritter; Refractive indices of TiO_2 films produced by reactive evaporation of various titanium-oxygen phases, Appl.Opt., http://dx.doi.org/10.1364/AO.15.002986, **15**, 2986-2991 **(1976)**.

[20] K.Bouabid, A.Ihlal, Y.Amir, A.Sdaq, A.Assabbane, Y.Ait-Ichou, A.Outzourhit, E.L.Ameziane, G.Nouet; Optical study of TiO_2 thin films prepared by solgel, Ferroelectrics, **372**, 69-75 **(2008)**.

[21] S.Wang, G.Xia, H.He, K.Yi, J.Shao; Structural and optical properties of nanostructured TiO_2 thin films fabricated by glancing angle deposition, J.Alloys and Compounds, **431**, 287-291 **(2007)**.

[22] H.Y.Ha, S.W.Nam, T.H.Lim, I.H.Oh, S.A.Hong; Properties of the TiO_2 membranes prepared by CVD of titanium tetraisopropoxide, J.Membr.Sci., **111**, 81-92 **(1996)**.

[23] Liu Pei-Sheng, Cai Wei-Ping, Wan Li-Xi, Shi Ming-Da, Luo Xiang-Dong, Jing Wei-Ping; Fabrication and characteristics of rutile TiO_2 nano particles induced by laser ablation [J]. Transactions of Nonferrous Metals Society of China, **19**, s743-s747 **(2009)**.

[24] S.N.Karthick, K.Prabakar, A.Subramania, J.J.Jang, Kim Hce-Je; Formation of anatase TiO2 nanoparticles by simple polymer gel technique and their properties, J.Powder.Technol., **205**, 36-41 **(2011)**.

[25] C.Rath, P.Mohanty, V.Pandey, C.Mishran; Oxygen vacancy induced structural phase transformation in TiO_2 nanoparticles. J.Phys.D, **42**, 205101 **(2009)**.

[26] M.Hernandez, A.Juárez, R.Hernandez; Interferometric thickness determination of thin metallic films, Superficies y Vacío, **9**, 283-285 **(1999)**.

[27] M.M.El-nahass, M.H.Ali, A.El-Denglawey; Structural and optical properties of nano-spin coated sol gel porous TiO_2 films, Trans.Nonferrous Met.Soc.China, **22**, 3003-3011 **(2012)**.

[28] Z.S.El Mandouh, M.S.Selim; Physical properties of vanadium pentoxide sol gel films, Thin Solid Films, **371**, 259-263 **(2002)**.

[29] G.H.Li, L.Yang, Y.X.Jin, L.D.Zhang; Structural and optical properties of TiO_2 thin film and TiO_2 + 2 wt.% ZnFe2O4 composite film prepared by r.f. sputtering, Thin Solid Films, **368**, 163-167 **(2000)**.

[30] N.Serpone, D.Lawless, R.Khairutdinov; Size Effects on the Photophysical Properties of Colloidal Anatase TiO2 Particles: Size Quantization versus Direct Transitions in This Indirect Semiconductor, J.Phys.Chem., **99**, 16646-16654 **(1995)**.

[31] J.D.Deloach, G.Scarel, C.R.Aita; Correlation between titanium film structure and near ultraviolet optical absorption, J.Appl.Phys., **85**, 2377-2384 **(1999)**.

[32] Mandeep Singh, Dinesh Pathak, Aman Mahajan, R.K.Bedi; Sol gel spin coated TiO2 films for transparent window Applications, Journal of Optoelectronics and Advanced Materials, **14(7-8)**, 624–629 **(2012)**.

[33] Q.Ye, P.Y.Liu, Z.F.Tang, L.Zhai; Hydrophilic properties of nano- TiO_2 thin films deposited by RF magnetron sputtering, Vacuum, **81**, 627-631 **(2007)**.

[34] C.Yang, H.Fan, Y.Xi, J.Chen, Z.Li; Effects of depositing temperatures on structure and optical properties of TiO_2 film deposited by ion beam assisted electron beam evaporation, Applied Surface Science, **254**, 2685-2689 **(2008)**.

[35] Y.Q.Hou, D.M.Zhuang, G.Zhang, M.Zhao, M.S.Wu; Influence of annealing temperature on the properties of titanium oxide thin Film, Applied Surface Science, **218**, 98-106 **(2003)**.

[36] M.M.Hasan, A.S.M.A.Haseeb, R.Saidur, H.H.Masjuki; Effects of Annealing Treatment on Optical Properties of Anatase TiO2 Thin Films, International Journal of Chemical and Biological Engineering, **1(2)**, 92-96 **(2008)**.

[37] F.Buet, J.Olivier-Fourcade, Y.Bensimon, P.Belougne; Complex Impedance Study of Chalcogenide Glasses, Solid State Communications, **77**, 29-32 **(1991)**.

[38] J.F.Eloy; Power Lasers, National School of Physics, Grenoble, France, John Wiley and Sons, **59**, **(1984)**.

[39] J.I.Pankove; Optical processes in semiconductors, Dover Publications, Inc. New York, 91 **(1975)**.