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EFFECT OF ANNEALING TEMPERATURE ON THE REFRACTIVE INDEX OF TITANIUM DIOXIDE (TIO_2) THIN FILMS DEPOSITED BY THERMAL EVAPORATION TECHNIQUE

A. S. Ba-Sabiah*, N. H. Alhardan, S. A. Tawfiq***

**** Department of Physics, Faculty of Education, Hadramout University, Ssieyoun ,9256, YEMEN.***

***** Department of Physics, Faculty of Education, Al Anabar University, Iraq***

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Titanium dioxide (TiO_2) has attracted much attention in the past decades. TiO_2 thin films were prepared using vacuum thermal evaporation technique and then heat treated at different annealing temperatures. An optical characterization method, based only on the transmission spectra at normal incidence of uniform thin films, was used to obtain the refractive index *n*. The dispersion of *n* is discussed in terms of the single-oscillator Wemple and DiDomenico model. The dispersion parameters, E_0 and E_d decreases after annealing at different temperatures for 3h. The obtained results were discussed in terms of an increasing the packing density of the deposited films after annealing treatment.

Keyword: *Thin films; Oxide semiconductor; Titanium dioxide; Refractive index*

1. Introduction

Titanium dioxide (TiO_2) thin films have attracted a lot of interests for its wide uses in photovoltaic devices [1,2], photo catalysts [3], wave guiding [4], and semiconductor [5,6], TiO_2 is a commonly used photo-catalyst because of its stability in UV light and water. However, the need of an ultraviolet (UV) excitation source restricts its technological utility for limited applications.

TiO_2 photo-catalyst effective in solar light or light from visible region of the solar spectrum required a development as future generation photo-catalytic material. TiO_2 absorbs only 5% energy of the solar spectrum hence numerous studies have been performed to extend the photo-response and photo-catalytic activity by modifying its surface structure, surface properties and composition [7–9].

Using conventional methods, TiO_2 films have been prepared in several ways: such as sol–gel method [10], pulsed laser deposition [11], chemical vapor deposition [12], spray pyrolysis [13] and sputtering techniques [14–16].

The present paper deals with the preparation of TiO_2 thin film by thermal evaporation technique. The influence of annealing temperature on the refractive index of TiO_2 thin films has been discussed.

2. Experimental methods

TiO_2 thin films were prepared on a carefully cleaned (in an ultrasonic water bath cleaner and then in absolute ethanol) glass substrates by the thermal evaporation technique of high purity TiO_2 powder (BDH Chemicals Ltd. 99.95%) using an Edward E 306 coating system operated at a vacuum of 4×10^{-5} Torr with the deposition rate maintained at 0.2 nm s^{-1}. The film thickness and deposition rates were controlled by quartz crystal monitor. To investigate the influence of the annealing temperature the samples were post annealed at 300, 400, 500 and 600 ^{0}C for 3 hours in dry air. The optical transmittance $T(\lambda)$ for the as-prepared and annealed thin films were measured in the wavelength range of 400 to 1100 nm using Shimadzu 2101 UV–VIS double beam spectrophotometer at room temperature.

3. Results and discussion

3.1. Calculation of refractive index

A lot of approaches have been used to determine the refractive index (n) and extinction coefficient (k) of a thin film. In the present study, the envelope method proposed by Swanepoel [17] was applied to determine the optical parameters from transmittance spectra. Fig. 1 represents schematic illustration of a thin weakly absorbing inhomogeneous film deposited on a thick finite transparent substrate. Supposing the film have thickness and complex refractive index d and (n - ik), respectively. The n_a and n_b are the refractive indices of the film at the vacuum side and substrate side, respectively. The refractive index of the substrate (n_s) assumed to be known. The thickness of the substrate is several orders of magnitude larger than d, which means that the optical interference effect of the substrate can be neglected. The expression for the transmittance of a weakly absorbing inhomogeneous film on a transparent substrate at normal incidence can be expressed as: [18]

$$T = \frac{Ax}{B - Cx\cos\theta + Dx^2} \tag{1}$$

Where

$A = 16 n_o n_a n_b n_s$; $B = (n_a + n_o)^2 (n_b + n_o)(n_o n_b + n_s^2)$; $C = 2n_o (n_a^2 - n_o^2)(n_b^2 - n_s^2)$

$D = (n_a - n_0)^2 (n_b - n_0)(n_o n_b - n_s^2)$; $\theta = \dfrac{4\pi \bar{n} d}{\lambda}$; $x = \exp(-\alpha d)$; $\alpha = \dfrac{4\pi \bar{k}}{\lambda}$

For $n_b > n_s$, at the quarter-wave points where the optical thickness of the film is a multiple of the quarter-wave length, the extreme of the transmittance can be written as [19]:

$$T_M = \frac{Ax}{B - Cx + Dx^2} \tag{2}$$

$$T_m = \frac{Ax}{B + Cx + Dx^2} \tag{3}$$

Where T_M and T_m represents the maxima and minimum transmittance. In the following calculation, both T_M and T_m are the correspondence in the identical optical thickness, which can be gained by the envelopes of the extreme point at a particular wavelength.

Substituting Eq. (2) into Eq. (3) yields:

$$\left(\frac{1}{T_m} - \frac{1}{T_M}\right) = \frac{2C}{A} = \frac{\left(n_a^2 - 1\right)\left(n_b^2 - n_s^2\right)}{4 n_a n_b n_s} \tag{4}$$

In order to get an innermost refractive index, we assume that $n_a = n_b$, and solving Eq. (4) which gives:

$$n_b = \left[N + \sqrt{N^2 - n_s^2}\right] \tag{5}$$

Where:

$$N = 2n_s \frac{T_M - T_m}{T_M T_m} + \frac{\left(n_s^2 + 1\right)}{2} \tag{6}$$

n_s is the refractive index of the glass substrate which was found to be nearly frequency independent [20] and equal to 1.51.

The optical transmittance of the films annealed at various temperatures from 300 to 700 °C, at wavelengths range from 300–1100 nm, was shown in Fig.2. The spectra exhibit interference peaks with an average transmittance in the visible region between 70–88%.

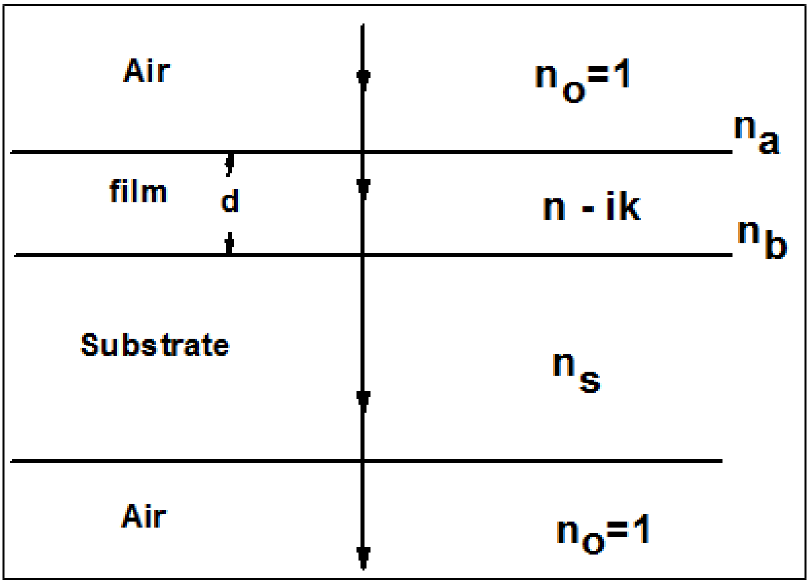

Fig. 1. Schematic illustration of a thin weakly absorbing inhomogeneous film on a thick finite transparent substrate.

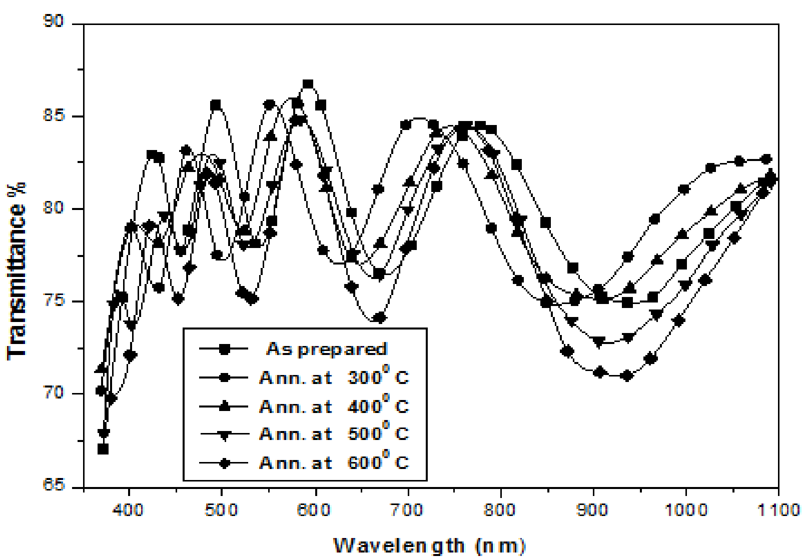

Fig. 2. Transmittance spectrum for as-deposited and annealed (TiO_2) films.

The refractive index (n) of thin films can be evaluated from transmittance data using Swanepoel's method which is based on the idea of Manifacier *et. al*. [21]. The required conditions for this study is that the transparent substrates must be thicker than the investigated film, The application of this method entails, as a first step, the calculation of the maximum T_M and minimum T_m transmittance envelope curves by parabolic interpolation to the experimentally determined positions of peaks and valleys using the OriginLab version 7 program., as shown in Fig. 3.

Using the calculated values of T_M and T_m, the dispersion of the refractive index as a function of wavelength for (TiO_2) thin films annealed at various temperatures is illustrated in Fig. 4. We also found that the refractive index increases with increasing the annealing temperature, being equal to 1.95 for the as prepared films at wavelength of 550 nm as shown in Table 1**.** The higher annealing temperature not only increases the mobility of atoms or molecules of the films, but the calculated refractive index from the transmittance reveal a direct relationship between the film density and the changes of the average grain size. Accordingly, the average grain size and density of the films will increase with increasing annealing temperatures. The change in refractive index is mostly due to changes in electronic structure, associated with the larger lattice parameter and perhaps some variations in atomic co-ordination [22].

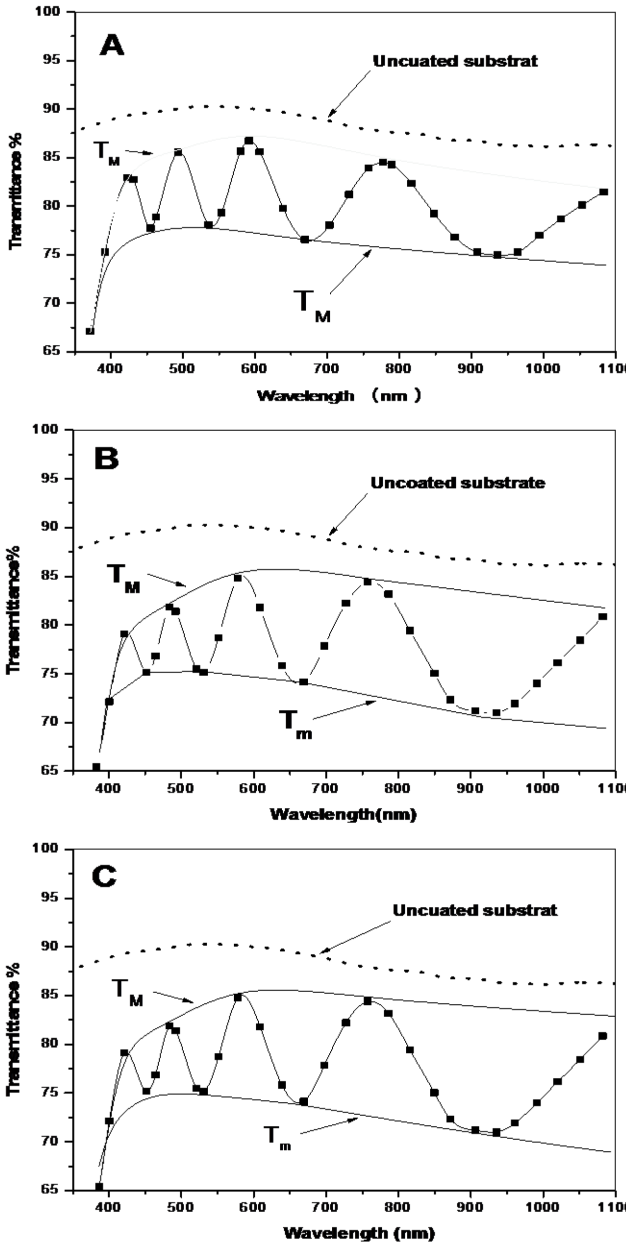

Fig. 3. Transmittance spectrum for the as-deposited and annealed (TiO_2) films, including the maximum (T_M) and minimum (T_m) transmittance envelope curves, (A) As prepared (B) Annealed at 400 °C and (C) Annealed at 600 °C.

3.2. Analysis of the optical dispersion based on the single-oscillator model

The dispersion of the refractive-index The refractive-index dispersion n(hν), of crystalline and amorphous materials can be fitted by the Wemple - DiDomenico relationship [23,24]:

$$\left(n^2-1\right)=\frac{E_d E_0}{E_0^2-\left(h\nu\right)^2} \tag{7}$$

Where E_0 and E_d are the single-oscillator fitting constants, which measure the oscillator energy and strength, respectively. By plotting $\left(n^2-1\right)^{-1}$ as function of $\left(h\nu\right)^2$ and fitting a straight line as shown in Fig. 5**,** E_0 and E_d can be determined directly from the slope, $\left(E_d E_0\right)^{-1}$, and the intercept on the vertical axis, $\left(E_0/E_d\right)$, respectively. The obtained values of E_0 and E_d which calculated from the straight plots shown in Fig. 5, are listed in **Table 1**. It is clear that the values of dispersion parameters, E_0 and E_d are decreased by increasing annealing temperatures, this behavior can be attributed to an increasing in the packing density after annealing treatment [25].

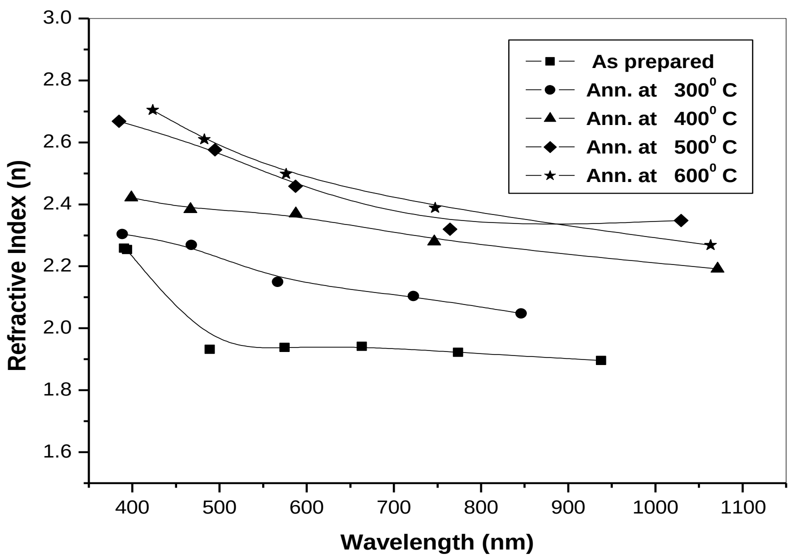

Fig. 4. Variation of refractive index *n* versus the wavelength for the as-deposited and annealed (TiO_2) films.

Table 1: The Refractive index n, dispersion energy E_d, oscillator energy E_0 for TiO_2 films at different annealing temperatures.

Ann, Temp. [^oC]	n	E_d [eV]	E_0 [eV]
As prepared	1.95	0.20	0.08
300	2.12	0.17	0.06
400	2.32	0.15	0.04
500	2.47	0.18	0.04
600	2.51	0.18	0.05

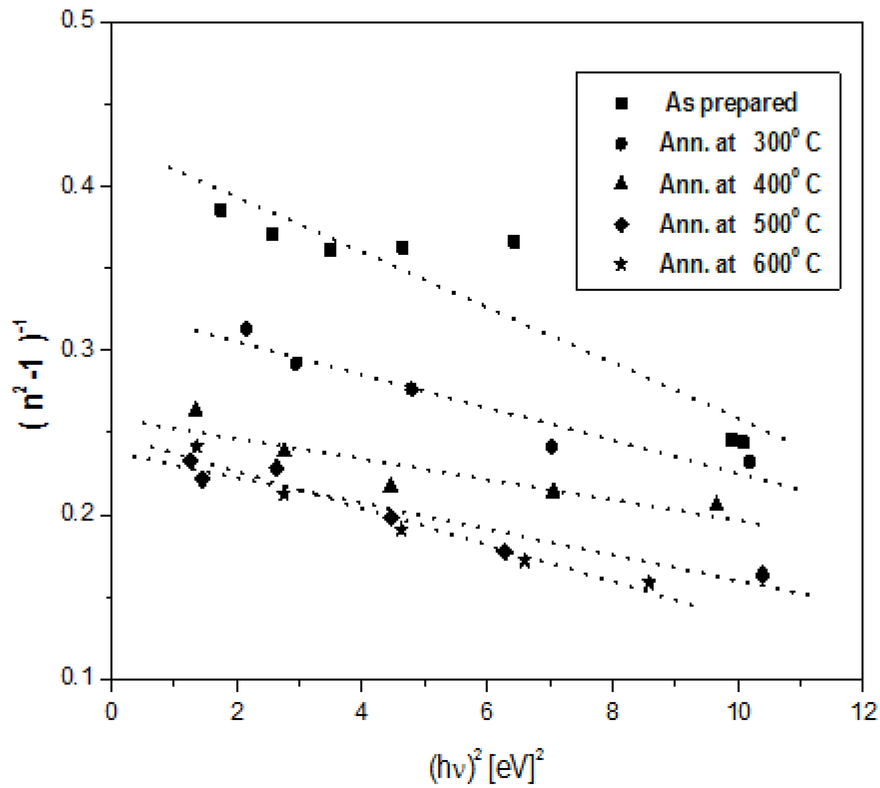

Fig. 5. The refractive-index factor $(n^2-1)^{-1}$ versus $(h\nu)^2$ for the as-deposited and annealed (TiO_2) films.

5. Conclusions

Thermal annealing of the as-deposited Titanium dioxide (TiO_2) films at different temperatures induces changes in their optical transmittance. Increasing the value of refractive index of 1.95 for the as prepared film was obtained with increasing the annealing temperature. Furthermore, the values of dispersion parameters, E_0 and E_d are also decreased by increasing annealing temperatures, this behavior can be attributed to the increasing in the packing density after annealing treatment.

References

[1] B.A. Perkinson, M.T. Spitlet, *Electrochem. Acta* 37 (1992) 943.

[2] A. Haggfeldt, U. Bjorksten, S.-E. Lindquist, *Solar Energy Mater. Solar Cells* 27 (1992) 293.

[3] S. Tokita, N. Tanaka, H. Saitoh, *Jpn. J. Appl. Phys.* 39 (2000) L169.

[4] A. Bahtat, M. Bouderbala, M. Bahtat, M. Bouazaoui, J. Mugnier, M. Druetta, *Thin Solid Films* 323 (1998) 59.

[5] H. Fukuda, S. Namioka, M. Miura, Y. Ishikawa, M. Yoshino, S. Nomura, *Jpn. J. Appl. Phys.* 38 (1999) 6034.

[6] M.B. Lee, M. Kawasaki, M. Yoshimoto, B.K. Moon, *Jpn. J. Appl. Phys.* 34 (1995) 808.

[7] M.I. Litter, J.A. Navio, *J. Photochem. Photobiol. A* 98 (1996) 171.

[8] C.C. Wang, Z. Zhang, J.Y. Ying, *Nanostruct. Mater.* 9 (1997) 583.

[9] G.H. Li, L. Yang, Y.X. Jin, L.D. Zhang, *Thin Solid Films* 368 (2000) 168.

[10] J. Yu, X. Zhao, J. Du, W. Chen, *J. Sol–Gel Sci. Technol.* 17 (2000) 163.

[11] J.-H. Kim, S. Lee, H.-S. Im, *Appl. Surf. Sci.* 151 (1999) 6.

[12] J. Hu, R.G. Gordan, *J. Appl. Phys.* 71 (1992) 880.

[13] M.N. Islam, T.B. Ghosh, K.L. Chopra, H.N. Acharya, *Thin Solid Films* 280 (1996) 20.

[14] C.H. Heo, S.B. Lee, J.H. Boo, *Thin Solid Films* 475 (2005) 183.

[15] Z.C. Jin, I. Hamberg, C.G. Granqvist, *J. Appl. Phys.* 64 (1988) 5117.

[16] T. Minami, H. Sato, K. Ohashi, T. Tomofugi, S. Takata, *J. Cryst. Growth* 117 (1992) 370.

[17] R. Swanepoel, *J. Phys. E* 16 (1983) 1214.

[18] Y.Y. Liou, C.C. Lee, C.C. Jaing, C.W. Chu, J.C. Hsu, *Jpn. J. Appl. Phys.* 34 (1995) 1952.

[19] X. Wu, F. Lai, L. Lin, J. Lv, B. Zhuang, Q. Yan and Z. Huang, *Appl. Surf. Sci.* 254 (2008) 6455.

[20] G.A.N. Connnell, A. Lewis, *Phys. Status Solidi (b)* 60 (1973) 1002.

[21] J. C. A Manifacier, J. Gasiot, J. P. Fillar, *J. Phys E* 9 (1976) 291.

[22] M. Wöhlecke, V. Marrello, and A. Onton, *J. Appl. Phys.* 48 (1977) 1748.

[23] S.H. Wemple, M. DiDomenico, *Phys. Rev. B* 3 (1971) 1338.

[24] S.H. Wemple, *Phys. Rev. B* 7 (1972) 3767.

[25] C. Ottermann and K. Vange, *Thin Solid Films* 286 (1996) 32.

تأثير درجة حرارة التلدين على معامل الانكسار لأغشية ثاني أكسيد التاتانيوم (TiO_2) الرقيقة والمحضرة بتقنية التبخير الحراري

عبد الله سعيد عاشور باصبيح* ، نائف حماد الحردان، سعد عبد البارى توفيق***

***جامعة حضر موت، كلية التربية، سيؤن، اليمن**

****جامعة الانبار، كلية التربية، قسم الفيزياء، العراق**

: تم تحضير أغشية رقيقة ذات سمك ثابت من مادة ثاني أكسيد التاتانيوم (TiO_2) بطريقة التبخير الحراري تحت ضغط منخفض علي شرائح زجاجية. تم دراسة تأثير درجة حرارة التلدين على بعض الثوابت الضوئية مثل معامل الانكسار (n) الذي تم حسابه من منحنى النفاذية باستخدام طريقة سوانابول ، كما أمكن تطبيق نموذج المتذبذب الأحادي لإيجاد كل من طاقة المتذبذب الأحادي (E_o) وطاقة التفريق (E_d) ، وقد أظهرت النتائج اعتماد هذه الثوابت على درجة حرارة التلدين حيث تم تفسير النتائج التي تم الحصول عليها أخذاً في الأعتبار ان عملية التلدين أدت إلى زيادة كثافة الرص و زيادة ترتيب الذرات.