

Study of Spin Coated Titanium Dioxide Films

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Abstract— The titanium dioxide (TiO₂) films have been obtained for different spin speeds using spin coating technique on to the glass substrates kept at 350 °C. The conditions have been optimized to obtain quality films. The films so obtained have been studied for their structural characterization through XRD analysis. Optical absorption studies to find optical band gap of the films have been made through UV-Visible spectroscopy in the spectral range 300 -1100 nm. Effect of spin speed on the surface morphology and optical properties of these films has been studied. Results show that both the surface morphology and optical properties get modify by varying spin speed.

Index Terms—Spin coating, TiO₂, surface morphology, optical properties

I. INTRODUCTION

Titanium dioxide (TiO₂) has been studied widely for its remarkable electronic, optical properties and for its stability in the adverse environment. TiO₂ films have been used for a variety of applications such as optics industry [1], solar cells [2], dye sensitized solar cells [3], electrochromic displays [4] dielectric applications [5], self cleaning purposes [6] optical filters [7] and photocatalytic layers [8]. TiO₂ antireflection coatings [9-12] have been used for increasing the visible transmittance in heat mirrors [13]. Titanium dioxide have been found to exist in three crystalline phases: rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic) and the phase existing in thin film form depends upon the conditions and parameters of the fabrication method [14]. The refractive index at 500 nm for rutile and anatase bulk titania is about 2.7 and 2.5 respectively [15]. Various deposition methods have been employed to get TiO₂ in thin film form, such as plasma enhanced chemical vapor deposition [5], sol-gel methods [16, 17], chemical vapor deposition [18] and DC reactive magnetron sputtering [8], RF reactive magnetron sputtering [3, 19], electron-beam evaporation [20], ion-beam assisted deposition [21].

Spin coating has been widely used technique for deposition of TiO₂ films on glass substrate using precursor solutions of titanium isopropoxide (C₁₂H₂₈O₄Ti) with a suitable molar ratio

of different components of solution [22] with the advantage of relatively low cost for large-scale production of thin films.

The effect of solution concentration and the number of coating layers on structural, optical and electrical properties of sol-gel derived TiO₂ films have studied [23].

In this paper, we present a study of the structural and optical properties of spin coated titanium dioxide films on glass substrates using acetylacetonate stabilized titanium isopropoxide precursor. The effect of spin speed on these properties has been investigated.

II. EXPERIMENTAL DETAILS

Chemically and thermally stable films of titanium dioxide have been prepared using the spin coating method. Microscope glass slides have been used as the substrate for films. The glass slides were sequentially cleaned in an ultrasonic bath with acetone and ethanol before deposition. Finally they were rinsed with distilled water and were properly dried. The precursor solution was prepared by mixing 1.2 ml Titanium (IV) isopropoxide, 0.83 ml of acetylacetone and 17.97 ml of ethanol. The solution so obtained was stirred at room temperature for half hour in an air tight container. About 2.5 μl of this spreading solution was dispensed on to the substrate from a distance of 5 mm above the substrate and spinner (Apex system model NXG M1) was employed to spin the substrate at different speeds ranging from 1500 to 4500 rpm with spin time 30 sec. for each film. The films so obtained were heated in air at 350 °C for fifteen minutes. The films were then cooled down to room temperature in open air. This process was repeated 7 times for each film. The crystalline properties of the TiO₂ films were analyzed by an X-ray diffractometer (Model-D5000, Siemens) using CuK_α radiations (λ=0.15406 nm) and operating at an accelerating voltage of 40 kV and an emission current of 30 mA. Data were acquired over the range of 2θ from 15 to 70° at scanning speed of 5° min⁻¹. The XRD method was used to study the change of crystalline structure. The UV-visible-IR optical transmission spectra of TiO₂ thin films were recorded by a double-beam spectrophotometer in the range of 300-800 nm. The measurements were taken at a normal incidence using a reference blank substrate. From the transmittance and absorbance spectra, Swanepoel [24] methods were used to calculate the optical constants, absorption coefficient and optical band gap of the films. The thickness of the thin films were estimated 301nm, 182 nm and 127 nm for films obtained at spinning speed of 1500, 3000 and 4500 rpm respectively using max-min method, using the formula:

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$t = \lambda_1 \lambda_2 / 4n (\lambda_2 - \lambda_1)$, Where 't' is the thickness of the film, λ_1 and λ_2 are the wavelengths which corresponds to the maxima and minima of the transmittance spectra and 'n' is the refractive index to TiO₂.

III. RESULTS AND DISCUSSION

A. Structure:

The X-ray diffractogram of TiO₂ films grown at different spin speeds has been shown in figure 1 (a-c).

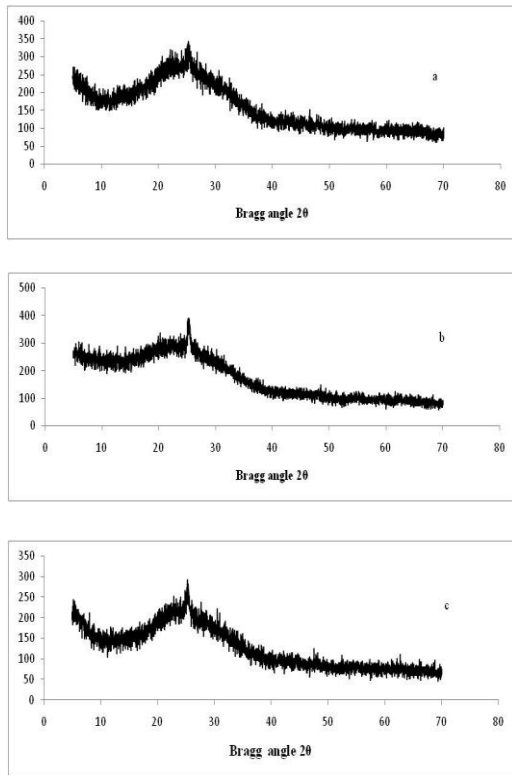


Fig. 1 (a,b,c) : XRD pattern for titanium dioxide films grown at (a) 1500 rpm (b) 3000 rpm and (c) 4500 rpm

The d values of the films are compared with the literature data to confirm the structure of TiO₂ and found to be in good agreement thus confirming the formation of TiO₂ film on the substrate. The films are observed to have a preferential crystallographic texture in the [101] direction corresponding to the Bragg angle $2\theta = 25.2^\circ$. However, X-ray diffractogram shows the presence of weak intensity peaks with orientation [200] with $2\theta = 48.1^\circ$ that is also in agreement with the previously reported values. The films deposited at higher spin speed show comparatively intense peaks. Also the decrease in full width measured at half maxima (FWHM) of diffraction peaks has been noticed, thus suggesting a high degree of crystallinity with increase in spin speed.

B. Optical Properties:

The absorption coefficient of TiO₂ films deposited on glass has been determined over the energy range 1.1-2.4 eV, which correspond to an absorption edge in the lower energy

region of the transmittance spectra of the films taken over 300-1100 nm range. This absorption edge of the TiO₂ has been examined in terms of a direct transition using the equation of Bardeen et al [25], stating that : $\alpha hv = B(hv - E_g)^n$, where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the optical band gap, B is a constant which does not depend on photon energy and n has four numeric values (1/2 for allowed direct, 2 for allowed indirect, 3 for forbidden direct and 3/2 for forbidden indirect optical transitions). In this work, direct and indirect band gap was determined by plotting $(\alpha hv)^2$ vs. $h\nu$ and $(\alpha hv)^{1/2}$ vs. $h\nu$ curves respectively, with the extrapolation of the linear region to energy axis. The direct and indirect band gap energy of TiO₂ films deposited on glass substrate for different spin speeds have been plotted in figs 2 and 3 respectively and has been listed in table 1.

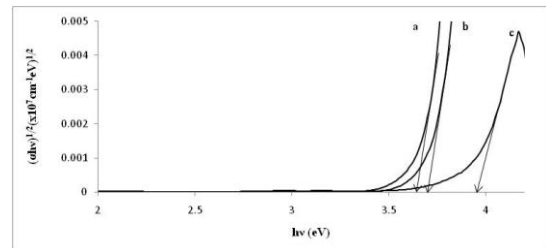


Fig. 2 : $(\alpha hv)^{1/2}$ vs. $h\nu$ for the titanium dioxide films

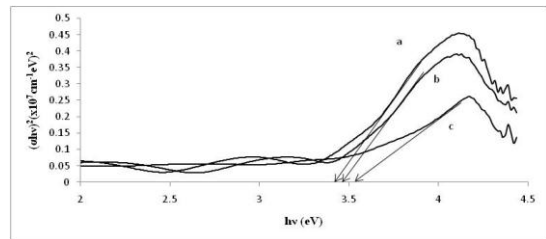


Fig. 3 : $(\alpha hv)^2$ vs. $h\nu$ for the titanium dioxide films

Table 1: Band gap energy of TiO₂ films deposited on glass substrate at different spin speeds and annealed at 350 °C.

Spin speed (rpm)	Direct Band Gap(eV)	Indirect Band Gap(eV)
1500	3.64	3.42
3000	3.70	3.45
4500	3.95	3.52

It has been observed that the band gap energy increases with the increase in spin speed. This may be attributed to the fact that higher spin speed causes uniform spreading of precursor solution on substrate exhibiting more ordered structure by lowering the number of defects and that ultimately causes comparatively less contribution to the absorption [26]. Results are in good agreement with the findings of Amor et. al. [19], Habibi et. al. [20] and Yang et. al. [21].

IV. CONCLUSIONS

The anatase phase titanium dioxide thin films have been produced by spin coating method on glass substrates for different spin speeds. XRD analysis shows the improvement in crystallinity with the increase in spin speed. It is observed that the allowed direct and indirect optical band gap of the films increases with the increase of spinning speed.

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References

- [1] H. K. Pulker; Coatings on Glass, Elsevier, Amsterdam, **1999**.
- [2] S. Ito, T. Kitamura, Y. Wada, S. Yanagia, *Solar Energy Mater. Solar Cells*, **2003**, 76, 3.
- [3] Y. M. Sung, H. J. Kim, *Thin Solid Films*, **2007**, 515, 4996.
- [4] A. E. Aliev, H. W. Shin, *Displays*, **2002**, 23, 239.
- [5] W. Yang, C. A. Wolden, *Thin Solid Films*, **2006**, 515, 1708.
- [6] C. Euvananont, C. Junin, K. Inpor, P. Limthongkul, C. Thanachayanont, *Ceramics International*, **2008**, 34, 1067.
- [7] K. Kannan, R. Balasubrahmaniam, *Thin Solid Films*, **1988**, 109, 59.
- [8] C. J. Tavares, J. Vieira, L. Rebouta, G. Hungerford, P. Coutinho, V. Teixeira, J.O. Carneiro, A.J. Fernandes, *Mater. Sci. Eng., B*, **2007**, 138, 139.
- [9] H. Kawasaki, T. Ohshima, Y. Yagyu, Y. Suda, S. I. Khartsev, A. M. Grishin, *J. Phys.: Conf. Series*, **2008**, 100, 012038.
- [10] S. Ray, U. Dutta, R. Das, P. Chatterjee, *J. Phys. D: Appl. Phys.*, **2007**, 40, 2445.
- [11] Z. Wang, Q. Chen, X. Cai, *Applied Surface Science*, **2005**, 239, 262.
- [12] P. Jin, L. Miao, S. Tanemura, G. Xu, M. Tazawa, K. Yoshimura, *Applied Surface Science*, **2003**, 212-213, 775.
- [13] M. Okada, M. Tazawa, P. Jin, Y. Yamada, K. Yoshimura, *Vacuum*, **2006**, 80, 732.
- [14] S. M. Tracey, S. N. B. Hodgson, A. K. Ray, Z. Ghassemlooy, *J. Mater. Proc. Technol.*, **1998**, 77, 86.
- [15] Q. Ye, P. Y. Liu, Z. F. Tang, L. Zhai, *Vacuum*, **2007**, 81, 627.
- [16] M. S. Ghamsari, A. R. Bahramian, *Materials Letters*, **2008**, 62, 361.
- [17] Z. Wang, U. Helmersson, P. O. Käll, *Thin Solid Films*, **2002**, 405, 50.
- [18] H. Sun, C. Wang, S. Pang, X. Li, Y. Tao, H. Tang, M. Liu, *J. Non-Cryst. Solids*, **2008**, 354, 1440.
- [19] S. B. Amor, G. Baud, M. Jacquet, N. Pichon, *Surf. Coat. Technol.*, **1998**, 102, 63.
- [20] M. H. Habibi, N. Talebian, J. H. Choi, *Dyes and Pigments*, **2007**, 73, 103.
- [21] C. Yang, H. Fan, Y. Xi, J. Chen, Z. Li, *Applied Surface Science*, **2008**, 254, 2685.
- [22] A. K. Hassan, N. B. Chaure, A. K. Ray, A. V. Nabok, S. Habesch, *J. Phys. D: Appl. Phys.*, **2003**, 36, 1120.
- [23] U. Selvaraj, A. V. Prasadarao, S. Komarneni, R. Roy, *J. Am. Ceram. Soc.*, **1992**, 75(5), 1167.
- [24] R. Sawanepoel, *J. Phys. E: Sci. Instrum.*, **1983**, 16, 1214.
- [25] J. Bardeen, F. J. Blatt and L.H. Hall, Photoconductivity Conf., Ed. R. Breckenridge, B. Russel and T. Hahn, John-Weiley, New York (1956).
- [26] S. Badrinarayann, A.B. Mandale, *J. Mater. Res.*, **1995**, 10, 1091.