

Synthesis and Characterisation of TiO₂ thin film prepared by Spin Coating Technique

R.A.Wagh¹, S.P.Roy², R. S. Patil³

Assistant Professor, Department of Applied Science, Sanghavi College of Engineering, Nasik, Maharashtra, India¹

Associate Professor, Department of Physics, H.P.T Arts and R.Y.K. Science College, Nashik, Maharashtra, India²

Professor, Department of Physics, P. S. G. V. P. Mandal's Arts, Commerce and Science College, Shahada, Nandurbar, Maharashtra, India³.

ABSTRACT: In this paper, we report the uniform deposition of TiO₂ nanocrystalline thin films by using a spin coating technique by preparing TiO₂ gel using P-25 TiO₂, ethanol, acetyl acetone and p-hydroxybenzoic acid. XRD, FE-SEM, UV-VIS, two probe resistivity measurement techniques have been used to investigate the physical properties of the obtained TiO₂ films. The results obtained shows that the TiO₂ thin films are polycrystalline with anatase (tetragonal) phase and dense granular morphology. The average crystallite size of TiO₂ thin film was found to be 20nm. The optical properties are studied by UV-VIS-NIR spectrophotometer, and the results revealed that the optical band gap of the TiO₂ film deposited on the glass substrate is 3.14 eV. The electrical resistivity is of the order of 10⁴ Ω.cm.

KEYWORDS: Titanium dioxide, Spin coating method, XRD, FE-SEM, Nanocrystalline thin film.

I. INTRODUCTION

Titanium dioxide (TiO₂) is one of the most widely studied transition metal oxide semiconductors due to its nontoxic nature, chemical stability and commercial availability at a low cost, robust and general reactivity. During the past decades, TiO₂ thin films have attracted much interest because it has a wide range of promising energy and environmental applications such as hydrogen generation by water splitting [1], photocatalytic water purification [2], dye-sensitized solar cells [3], gas sensor [4], electrodes in solar cell [5] and antireflection coatings [6] etc.

Titanium dioxide occurs in three crystalline polymorphs: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). TiO₂ is wide band gap semiconductor [7] with interesting electrical and optical property [8, 9]. TiO₂ is the promising material as semiconductor having high photochemical stability and low cost [10]. Having wide band gap, the anatase phase of TiO₂ absorbs radiation in ultraviolet region. The anatase phase nanoparticles of TiO₂ provide large surface for absorption resulting in enhanced efficiencies and have large band gap in the form of thin films compared to bulk value. Apart from solar cell application, these thin films with high transparency may also find application as optical filters in spectrometers. [9, 11].

Different methods have been studied for preparation of thin films of TiO₂. One of the simple methods is spin coating method. In this an excess amount of solution is placed on substrate. The substrate is then rotated at a high speed in order to spread the fluid by centrifugal force. The rotation is continued for some time, with fluid being spun off the edges of the substrate until the desired film thickness is achieved. The solvent is usually volatile providing for its simultaneous evaporation.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 1, January 2017

II. RELATED WORK

The Spin coating method has emerged as promising route for synthesis of TiO₂ thin film among other methods such as sputtering[12], chemical vapour deposition[13], evaporation[14] etc due to low temperature process, covers large area[16], low equipment cost [18] etc. TiO₂ has been used to study for its structural, morphological and optical properties by Mohd Said N. D et al[15]. The film annealed at temperature between 350-400°C has anatase phase as reported by Lili Hu et al [16].

III. MATERIALS AND METHODS

A. PREPARATION OF TiO₂

For this P-25 TiO₂ (Degussa, Germany), Analytical reagent grade ethanol, analytical reagent grade acetyl acetone (sigma Aldrich, Germany) and p-hydroxybenzoic acid is used. The TiO₂ film was deposited by using spin coating technique by preparing TiO₂ gel. This gel was prepared by mixing 2gm of P-25(Degussa P-25) with mixture of ethanol and acetyl acetone with 1gm of p-hydroxybenzoic acid.

B. PREPARATION OF THIN FILM

TiO₂ film was prepared on glass substrate. The resultant solution is stirred for 8 hours and probe sonicated with the frequency of 20 KHz for 30min. Now, 1 ml of prepared TiO₂ gel was deposited on centre of glass substrate (Size 1 inch x 1inch) surface. The substrate was accelerated with the different r.p.m. with different time and finally a uniform film was obtained. The synthesized films were annealed at 400°C for 60mins; this removes the impurity and gives porous TiO₂ thin film.

C. CHARACTERIZATION OF TiO₂

The as-deposited thin films of TiO₂ were characterized for structural, optical and surface morphological properties. The TiO₂ films thickness was measured by profilometer.

The X-ray diffraction (XRD) pattern were recorded in the scanning angle 20° to 60° with a Rigaku Rotaflex RO-200B diffractometer using CuKα1 (λ = 1.5418 Å). The surface morphological studies were performed by using scanning electron microscope (SEM) unit. The optical absorption spectra were recorded (between 350nm to 900nm wavelength ranges) by UV-Vis spectrophotometer (Shimadzu model-1601).

IV. RESULT AND DISCUSSION

Fig. 1 shows the X.R.D pattern of porous TiO₂ thin film prepared by spin coating method on glass substrate at optimized parameter. The diffraction pattern shown was recorded in the range of 20° to 80° for glass/TiO₂. From the pattern it is observed that most intense diffraction peak at 2θ=25.33° corresponding to (101) plane. Also some addition small peaks at 37.89°, 48.09° appeared which corresponds to (004) and (200) planes. The XRD diffractogram of the TiO₂ shows tetragonal structure with anatase phase which was confirmed from JCPDS file 894921. The lattice parameters obtained from XRD peaks corresponds to a = 3.777 Å and c = 9.501 Å for the thin film.

The average crystal size of TiO₂ was calculated by using well known Debye-Scherrer's formula

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

Where D= Crystal Size, β= full width at half maxima of the peak (FWHM) in radians and λ = X-ray wavelength (1.5406 Å). The crystal size is calculated and found to be 20.45nm.

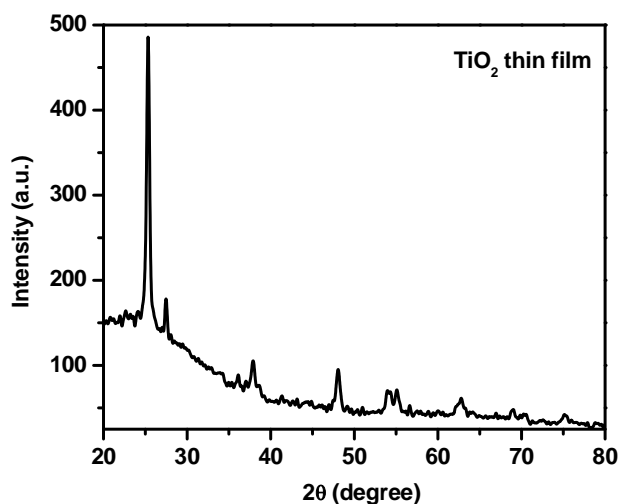


Fig. 1. XRD pattern of TiO₂ thin film

SEM CHARACTERIZATION

The surface morphology of the TiO₂ film deposited on glass substrate by spin coating technique was studied using scanning electron microscope (SEM). The scale bar length was 1.0μm. From the SEM micrograph, it is evident that TiO₂ film is homogeneous having granules like structure. The film is well –covered, adherent, pinholes, without cracks and smooth surface.

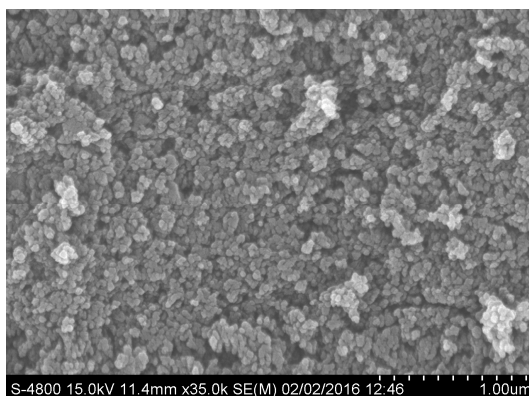


Fig. 2. SEM of TiO₂ thin film

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 1, January 2017

UV VIS CHARACTERISTICS

The optical absorption spectrum of as deposited film of TiO₂ has been recorded at room temperature with considering losses due to reflection and transmission. Fig.3 shows the plot of absorption coefficient versus wavelength for TiO₂ thin film prepared by Spin Coating method. The absorption spectra of TiO₂ thin film deposited on glass substrate was studied in the wavelength range 350nm-900nm. This graph shows that film is highly absorptive.

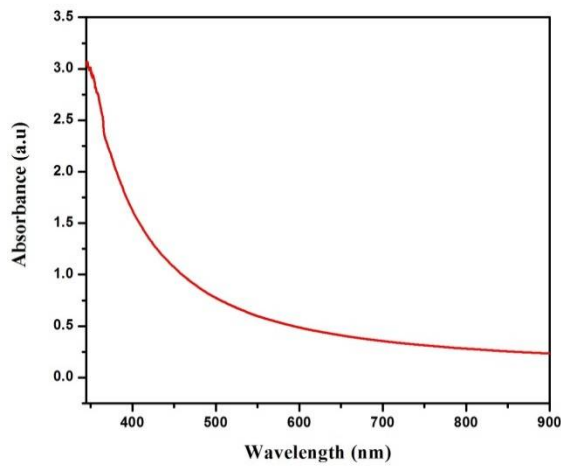


Fig. 3. The optical spectra of TiO₂ thin film

BAND GAP MEASUREMENT

The band gap, E_g, for TiO₂ film was determined by plotting $(\alpha h\nu)^2$ (eV/cm²) versus photon energy, hν (eV) graphs. Extra plotting the straight-line part of the curve in fig.4 to the energy axis, gives the value of band gap, E_g, for TiO₂ thin film. The band gap for TiO₂ was found to be 3.14 eV which is comparable to the bulk value (3.14eV) as reported by Kim J. etal [17].

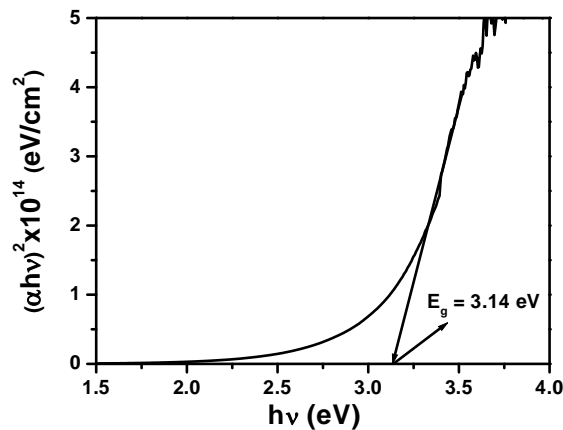


Fig. 4. Estimation of bandgap of TiO₂ thin film

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 1, January 2017

ELECTRICAL RESISTIVITY

The resistance of as deposited nanocrystalline TiO₂ thin film deposited on glass substrate is found to be $4.71 \times 10^8 \Omega$ at particular value of voltage. Fig.5 shows variation of $\ln \rho$ with inverse of absolute temperature for titanium dioxide

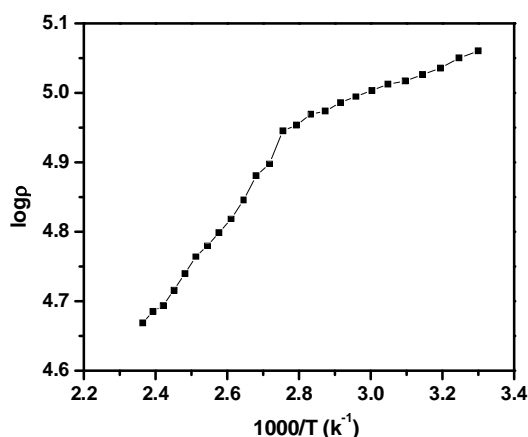


Fig.5.Variation of $\log \rho$ with inverse of absolute temperature

The resistivity of the TiO₂ is calculated using the value of R and are found to be $1.601 \times 10^4 \Omega\text{-cm}$ respectively. Both the values are obtained by applying two probe techniques. The resistivity of TiO₂ film decreases with increase in temperature, showing the semiconducting nature of the as-deposited film.

V. CONCLUSION

In this work TiO₂ thin film were prepared by spin coating technique by using p-hydroxybenzoic acid, ethanol, acetyl acetone and P-25 TiO₂ (Degussa) powder. The film is annealing at 400 °C. The phase of annealed thin film is found to be of pure anatase in nature. The crystal size is found to be 20.45nm. The energy band gap for the TiO₂ thin films was found to be 3.14eV. Sharpe increase in absorption spectra at short wavelength (380nm) for TiO₂ represents that it strongly absorbs shorter wavelength (UV) light. The resistivity of the TiO₂ is found to be $1.601 \times 10^4 \Omega\text{-cm}$ respectively.

REFERENCES

- [1] Fujishima, A., and Honda, K., "Electrochemical photolysis of water at a semiconductor electrode", Nature, Vol.238, no. 5358, pp.37–38, 1972.
- [2] Hoffmann, M. R., Martin, S. T., Choi, W., and Bahnemann, D. W., "Environmental applications of semiconductor photocatalysis," Chemical Reviews, Vol. 95, no. 1, pp.69–96, 1995.
- [3] Regan, B. O., and Gratzel, M., "A low-cost, high-efficiency solar cell based on dye sensitized colloidal TiO₂ films", Nature, Vol. 353, no. 6346, pp.737–740, 1991.
- [4] Castaneda L., Alonso J., Ortiz A., Andrade E., Saniger J., and Banuelos J., "Spray pyrolysis deposition and characterization of titanium oxide thin films," Materials Chemistry and Physics, vol. 77, no. 3, pp. 938–944, 2002
- [5] Okuya M., Prokudina N. A., Mushika K. and Kaneko S., "TiO₂ Thin Films Synthesized by the Spray Pyrolysis Deposition (SPD) Technique," Journal of the European Ceramic Society, Vol. 19, No. 6, 1999, pp. 903-906
- [6] Bange K., Ottermann C., Anderson O., Jeschkowski U., Laube M., Feile R., "Investigation of TiO₂ thin film deposited by different technique" Thin Solid Films 197, 279 (1991)
- [7] Valencia, S., Marín J. M., Restrepo, G., "Study of the bandgap of synthesized titanium dioxide nanoparticles using the sol-gel method and a hydrothermal treatment", Open Material Science, J.4:9–14, 2010.
- [8] Wang X., Masumoto H., Someno Y., Chen L., and Hirai T., "Design and preparation of a 33-layer optical reflection filter of TiO₂-SiO₂ system," J. Vac. Sci. Technol. A 18, pp.933–937 2000. 38

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 1, January 2017

- [9] Emadi A., Wu H., Graaf G., Wolffenbuttel R., "Design and implementation of a sub-nm resolution microspectrometer based on a Linear Variable Optical Filter" *opt. Express* 20(2012) 489-507
- [10] Ramakrishna G., Ghosh, H. N., "Optical and photochemical properties of sodium dodecylbenzenesulfonate (DBS)-capped TiO₂ nanoparticles dispersed in nonaqueous solvents", *Langmuir*, Vol.19, pp.505-508, 2003
- [11] Carmo J., Rocha R., Bartek M., Graaf G., Wolffenbuttel R.F., Correia J.H., "A review of visible-range Fabry–Perot microspectrometers in silicon for the industry", *opt. laser technol.* 44(2012), pp.2312-2320.
- [12] Teresa M. R. Viseu, Isabel M C. Ferreira, "Morphological characterization of TiO₂ thin film", *Vacuum* 52, pp.115–120
- [13] Wu J.J., Yu C.C., "Aligned TiO₂ Nanorods and Nanowalls", *J. Phys. Chem. B* vol. 108 (2004) pp.3377
- [14] Habibi M. H., Talebian N., Choi J. H., "The effect of annealing on photocatalytic properties of nanostructured titanium dioxide thin films," *Dyes and Pigments*, vol. 73, 2007, pp. 103-110.
- [15] Mohd Said N. D., Sahdan M. Z. , Senain I. , Bakri A. S , Abdullah S. A. , Mokhter F. , Ahmad A. and Saim H., "Effects of annealing temperature on structural, morphological and optical properties of TiO₂ thin film", *ARPN Journal of Engineering and Applied Sciences*, VOL. 11, No. 8, april 2016
- [16] Hu L., Yoko T., Kozuka H., Sakko S., "Effects of solvent on properties of sol–gel derived TiO₂ coating films", *Thin Solid Films* 219 (1992) 18–23
- [17] Kim, J., and Kang, M., "A Newly Designed a TiO₂-Loaded Spherical ZnS Nano/Micro-Composites for High Hydrogen Production from Methanol/Water Solution Photo-Splitting", *Bull. Korean Chem. Soc.*, Vol.33 No.7, pp.2133-2139, 2012.
- [18] Kajitvichyanukula P., Ananpattarachai J. , Pongpom S., "Sol–gel preparation and properties study of TiO₂ thin film for photocatalytic reduction of chromium(VI) in photocatalysis process" Sol–gel preparation and properties study of TiO₂ thin film for photocatalytic reduction of chromium(VI) in photocatalysis process", *Science and Technology of Advanced Materials* 6 (2005) 352–358.