https://doi.org/10.30799/jtfr.004.17010105 J. Thin Films Res. - Volume 1 Issue 1 (2017) 17–19

ISSN: 2581-3811

Share Your Innovations through JACS Directory

Journal of Thin Films Research

Visit Journal at http://www.jacsdirectory.com/jtfr

Effect of Al Doping on Thickness, Optical, Morphological and Structural Properties of TiO_2 Thin Film Prepared by Spin Coating Method

Md. Shamimur Rahman, Md. Abdul Kaiyum*, Md. Aminul Islam

Department of Glass and Ceramic Engineering, Rajshahi University of Engineering & Technology, Rajshahi – 6204, Bangladesh.

ARTICLE DETAILS

Article history:
Received 24 July 2017
Accepted 10 August 2017
Available online 08 September 2017

Keywords:
Spin Coating
Thin Film
Optical Properties
Surface Roughness

ABSTRACT

Pure TiO_2 thin films and Al doped TiO_2 thin films have been prepared by spin coating method. This work is carried out to determine the effect of Al on TiO_2 thin film. Because of Al doping thickness, optical properties, band gap, surface morphology, and structural properties of TiO_2 thin film changes. X-ray diffraction (XRD), Atomic Force Microscopy (AFM), Gravimetric Analysis, and UV-vis. Spectroscopy were carried out to find out the micro-structure, surface morphology, surface roughness, thickness and optical properties of the thin films. 0.5 M TiO_2 thin film shows 473 nm thicknesses where it changes with Al doping. Al also changes the crystal structure and the surface roughness of the film and both of them are carried out by using XRD analysis and AFM analysis. The surface roughness of the films was 12.239 nm for undoped TiO_2 thin film and for 6% Al doped the roughness increases to 85 nm which were calculated by using AFM analysis. The grain size of Al doped TiO_2 thin film was 19.51 nm and 26.95 nm were measured by XRD analysis.

1. Introduction

Titanium dioxide (TiO_2) thin film is a most popular semiconducting material. When it is doped with metallic dopants is properties changes. TiO_2 has also application in pigments and photo-catalytic activity [1]. The novel properties of TiO_2 were published in 1970 [2]. Since then various types of research works are carried out. Because of the electron transport properties of TiO_2, optical and electrical properties are varies and it works very efficiently [3, 4]. There exist various route of preparing TiO_2 and its thin film [5]. Fujishima and Honda first determined the photo-catalytic properties of TiO_2 in 1972 [6]. Now-a-days the properties can be changed by using various types of dopants like Al. DSSC solar cell was developed by O'Regan and Graetzel and influenced by the properties of oxide compound [7].

The properties of the thin films depend on its fabrication method. Sol-gel, sputtering, spin coating, dip coating etc. methods have been used to prepare TiO_2 film [8]. Spin coating method is a low cost method for thin film preparation [9]. In this work, spin coating method was used to prepare thin films. The films were deposited on normal seedless glass slide. The rotation was about 2000 rpm. Optical, and morphological, thickness and structural characterizations were carried out by UV-Vis spectrometer, SEM, AFM, and XRD techniques.

2. Experimental Methods

Pure TiO_2 thin film and Al doped TiO_2 thin films were deposited on glass substrates using spin coating method. Titania (TiO_2 powder) and Al nitrate were used to prepare thin film. Precursors were prepared using TiO_2 solution of 0.5 M and then doped with Al. Al solutions also made in a separate beaker. Then both of the solutions were mixed for preparing thin film forming precursor of different concentration.

The seedless glass slides were cleaned with distilled water, ethanol and ultrasonic bath respectively. Then the films were prepared using homemade spin coater. Each film was prepared from 0.3ml of precursor solution. The size of the glass slide was 15 mm × 15 mm × 1 mm. The slide was spun in air for 60s at 2000 rpm. Finally the prepared films were annealed in a muffle furnace at 15 °C/min heating rate up to 450 °C and soaking time was 30 minutes.

3. Results and Discussion

3.1 Thickness Measurement

Thickness depends on electrical and optical properties of thin film. The thickness of solid films was measured by Thomson [10]. In thin film experiments, thickness measurement is an important parameter. We used gravimetric analysis for determining thickness of thin film. The thickness of the film can be expressed by Eq.(1).

The thickness t of the thin film is given by

$$t = \frac{m}{A\rho} \qquad (1)$$

where ρ= density, A= area of the film and m= mass of the film. According to different concentrations of different films, resultant thicknesses are shown in the following Table 1.

Table 1 Thickness of undoped and Al doped thin film

Concentration	Avg. Thickness (nm)
0.5M TiO_2	473
2% Al doped	473
4% Al doped	476
6% Al doped	479

Due to varying concentration thickness varies which is shown in Table 1. With 2% Al doped doesn't change thickness due to interstitial position of Al. after that concentration the thickness increases. Thickness changes with concentration within a certain limit. Most of the thesis work and research related to thin film shows the optimum thickness for thin film is below 500 nm in some special cases it is about below 1 micrometer. Our resultant films fulfill the standard condition of thickness of thin film.

3.2 Optical Transmittance

Optical transmittance was determined using UV-Vis. single beam spectrophotometer (Halo SB-10). Transmittance was 80% (max.) for 0.5 M TiO_2 without dopant. When the doping concentration (Fig. 1) reaches at higher amount 2%, 4% and 6%, the absorbance shows a significant increment in the visible region.

---

*Corresponding Author: a.kaiyum.ruet11@gmail.com (Md. Abdul Kaiyum)

https://doi.org/10.30799/jtfr.004.17010105

Cite this Article as: Md. Shamimur Rahman, Md. Abdul Kaiyum, Md. Aminul Islam, Effect of Al doping on thickness, optical, morphological and structural properties of TiO_2 thin film prepared by spin coating method, J. Thin Films Res. 1(1) (2017) 17–19.

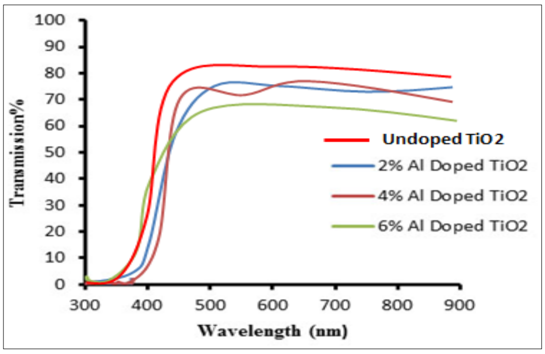


Fig. 1 Optical Transmittance

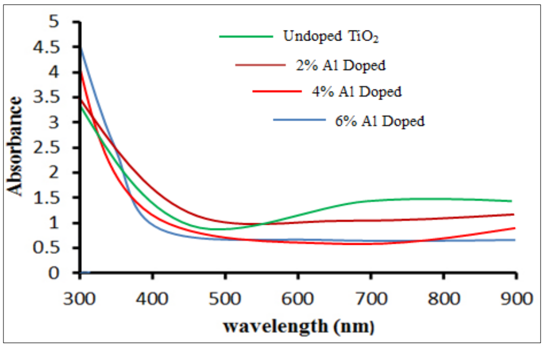


Fig. 2 Absorbance spectra of prepared films

Al dopant increases the absorbance spectrum of TiO_2. Metal creates a new energy level as a result the amount of more energy needed to excite an electron, so the absorbance increases. Maximum absorbance is observed by 6% Al doping. The absorbance spectra are shown in Fig. 2.

3.3 Band Gap

The absorbance coefficient (α) of the undoped thin film and with dopant films was calculated using Eq.(2),

$$\alpha = \frac{1}{t} \ln \frac{1}{T} \qquad (2)$$

where, t is the films thickness calculated (using eqn-1) and T is the transmission of the films. Finally $(\alpha h\nu)^2$ was determined from the optical data analysis. The band gap curve is shown in the following Fig. 3.

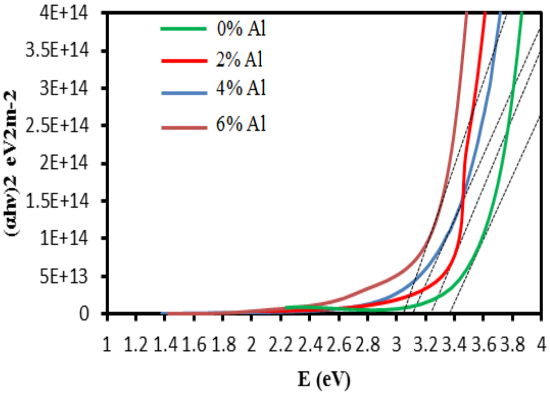
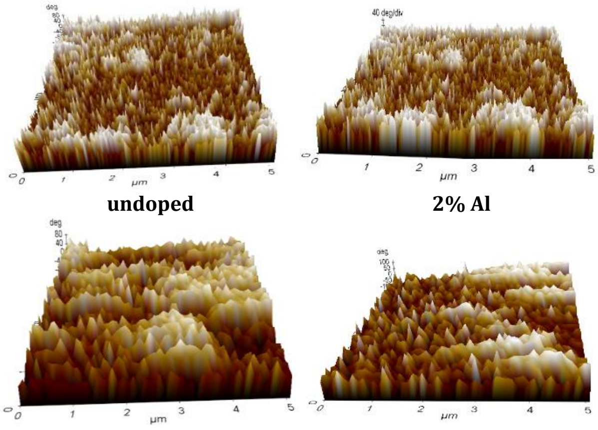


Fig. 3 Optical band gap of undoped and Al doped thin film

The optical band gap of the films, obtained with single run spin coating, exhibited direct bang gap energy was about 3.35 eV for undoped thin film and decreases with increasing dopant is shown in the Fig. 3.

3.4 AFM Analysis

The surface morphology of the film was carried out by using Atomic Force Microscopy (AFM). The surface morphology of undoped TiO_2 and the morphology of Al doped thin films are shown in the Fig. 4. With increasing the amount of Al doping the size of the crystal become broader.



undoped **2% Al**

4% Al **6% Al**

Fig. 4 AFM images of undoped and Al doped thin film

We have calculated the value of surface roughness by using XEI-70. The value of surface roughness increases with increasing concentration of Al dopant. The surface roughness is given in Table 2.

Table 2 Surface roughness of undoped and Al doped thin film

Amount of Al doping (%)	Surface Roughness, Rq (nm)
Undoped	12.23
2% Al	41.10
4% Al	67.35
6% Al	85.15

3.5 XRD Analysis

For determining the crystal structure of thin films XRD was carried out with a radiation source of Cu Kα and the wavelength was λ = 1.54 Å . The method of Full Width at Half Maxima (FWHM) was used to determine the exact 2θ positions. The grain size of the films was measured by using the Scherrer's formula from XRD patterns [11].

The Fig. 5 shows the X-ray diffraction patterns prepared by spin coating method. The films are spun at 2000 rpm and annealed at 450 °C. All the prepared films are shown anatase phase. Increase in the Al concentration the peak become sharper.

$$D = \frac{0.9 \times \lambda}{B\ Cos\theta} \qquad (3)$$

The crystal structure of thin film depends on the amount of concentration of dopants. It is found that diffraction peak located at 2θ=25.258° (A)(101). By using the Eq.(3) the grain size was calculated. The peak of pure TiO_2 decreases at 6% it shows a massive change in the pattern than pure TiO_2. The calculated grain size is given in Table 3.

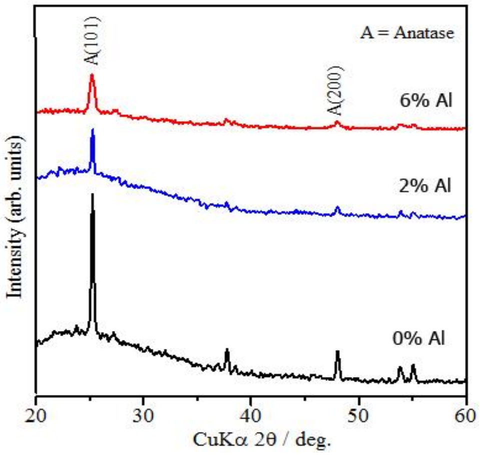


Fig. 5 XRD patterns of undoped and Al doped thin film

Table 3 Grain sizes of undoped and Al doped thin film

Name	Bragg's Angle (degree)	Grain size (nm)
Undoped TiO_2	12.61	13.46
Al doped (2%)	12.632	19.51
Al doped (6%)	12.629	26.95

https://doi.org/10.30799/jtfr.004.17010105

Cite this Article as: Md. Shamimur Rahman, Md. Abdul Kaiyum, Md. Aminul Islam, Effect of Al doping on thickness, optical, morphological and structural properties of TiO_2 thin film prepared by spin coating method, J. Thin Films Res. 1(1) (2017) 17–19.

4. Conclusion

Thickness of the film increases within increases concentration up to a certain limit. If we increase the concentration the films become thick. The optical band gap decreases with Al impurities into the thin film. AFM analysis proves there is no crack on the film surface and the roughness increases with dopant. Al doping has a great impact on the grain sizes of the film and the grains become larger due to Al doping compared to undoped thin film.

Acknowledgement

Authors would like to thank Md. Abdullah Al Mahmood (Assistant professor), Tasmia Zaman (Assistant professor), and Mst. Sharmin Mostari (Lecturer) dept. of Glass and Ceramic Engineering (GCE), RUET and also like to thank Dr. Md. Faruk Hossain (Professor, EEE, RUET) for giving them suggestions about this work and providing them equipment and instruments.

References

[1] E. Pelizzetti, C. Minero, Mechanism of the photo-oxidative degradation of organic pollutants over TiO_2 particles, Elecrochim. Acta 38 (1993) 47-55.

[2] A. Fujishima, K. Honda, S. Kikunchi, Photosensitized electrolytic oxidation on semiconducting n-type TiO_2 electrode, Kogyo Kagaku Zasshi 72 (1969) 108-113.

[3] C.O. Robichaud, A.E. Uyar, M.R. Darby, L.G. Zucker, M.R. Wiesner, Estimates of upper bounds and trends in nano-TiO_2 production as a basis for exposure assessment, Environ. Sci. Technol. 43(12) (2009) 4227-4233.

[4] U. Sirimahachai, S. Phongpaichit, S. Wongnawa, Evaluation of bacterial activity of TiO_2 photocatalysts: A comparative study of laboratory made and commercial TiO_2 samples, Songklanakarin Jour. Sci. Technol. 31(5) (2009) 517-525.

[5] N.T. Nolan, Sol-Gel Synthesis and characterization of novel metal oxide nano-materials for photo-catalytic applications, Ph.D. thesis, Dublin Institute of Technology, Ireland, 2002.

[6] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, Nature 238 (1972) 37-38.

[7] B. O'Regan, M. Graetzel, ARTICLE TITLE, Nature 353 (1991) 737–740.

[8] K. Bouabid, A. Ihlal, Y. Amir, A. Sdaq, A. Assabbane, Y. Ait-Ichou, et al., Optical study of TiO_2 thin films prepared by solígel, J. Ferroelect. 372 (2008) 69-75.

[9] C. Rath, P. Mohanty, V. Pandey, N.C. Mishra, Oxygen vacancy induced structural phase transformation in TiO_2 nanoparticles, J. Phys. D 42 (2009) 205101.

[10] D.A.H. Hanaor, G. Triani, C.C. Sorrell, Morphology and photocatalytic activity of highly oriented mixed phase titanium dioxide thin film, Surf. Coat. Technol. 205(12) (2011) 3658-3664.

[11] B.D. Cullity, Elements of X-ray diffraction, Addision-Wesley Pub, USA, 1956.

https://doi.org/10.30799/jtfr.004.17010105

Cite this Article as: Md. Shamimur Rahman, Md. Abdul Kaiyum, Md. Aminul Islam, Effect of Al doping on thickness, optical, morphological and structural properties of TiO_2 thin film prepared by spin coating method, J. Thin Films Res. 1(1) (2017) 17–19.