TiO_2 Microstructures Synthesized Via Solgel Process for Dye-Sensitized Solar Cell Applications

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Abstract. The titania (TiO_2) was synthesized by means of sol-gel process and the synthesized TiO_2 is coated on quartz substrates by using spin coating technique, the aqueous solution of titanium tetra isopropoxide is used as a precursor. X-ray diffraction and FESEM techniques have been utilized to study the chemical and physical changes in the procedure of sol-gel method.Powder-XRD was used for identification of crystal structures lattice parameter and crystal orientation. The diffraction peaks (101) (004) (200) (105) (211) and corresponding full width at half maximum (FWHM) areidentified to calculate the average crystallite size by making use the Debye-Scherrer'sequation and it is found that 33-40 nm,and confirms $TiO_2$is in anatase phase by standard JCPDS. The product of Tio_2 anatase phase are sharper peaks and peak intensities increased by changing the rotation period. UV–Visible spectrophotometer measurements, the highly transmit area of UV spectrum can be clearly states preparedTiO_2 thin films are semiconducting nature. The optical band gap energy for various rotational speed of TiO_2 thin films are found 3.17- 3.13 eV. These variations in the value of energy band gap strongly recommended for the fabrication in solar cells materials.

INTRODUCTION

The anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic) are the different forms of TiO_2. In nature, rutile is the most widely usage crystal form while brookite form is rarely found.The Rutile phase of crystals are highly steady for the temperature range above 800°C, while brookite and anatase are intermediate state and these are easily changed to rutile at higher temperature [1]. Because of its band gap value these materials insensitive when expose to visible light, it absorb light only in ultraviolet region [2,3]. TiO_2 broadly used in vast range of industrial and marketing goods such as treatment of various surfaces [4]. These materials has a different significant applications, electrochromic systems,anti-reflect coating, solar cells, photocatalytic and gas sensors, [5-6].In this work we used solgel method[7-9], which is proved as one of most efficient and the simplest method in terms of low cost, ecofriendly and quality for the preparing the different thicknessTiO_2 films. In this study, we report the effect of the rotation speed (2000, 1600 and 1200 rpm) on different optical properties of the thin film using spin coating methodwith titanium tetra isopropoxide (TTIP) as starting material of nano-coatings on quartz substrate.

MATERIALS AND METHODS

By various thickness of TiO_2 films are prepared by the step by step, TiO_2 solution, spin coating, dried and finally calcinated at 400^o C. Preparing the solution of TiO_2, by dissolving 0.7 ml $C_{12}H_{28}O_4Ti$ (titanium tetra-isopropoxide) in 8.6ml $CH_3CHOHCH_3$ (isopropyl alcohol). Further 25µl of HCl(Hydrochloric acid) was added to avoid fast hydrolysis process of the precursor.The TiO_2 solution was stirrer under magnetic stirrer for 5hrs to check homogeneous solution, and solution was aging for 10 hrs at 27^o C temperature. The product of cleared solution was spin coated on quartz plate at different rotation speed for 60 sec and then sample was dried using a hotplate at 120° C for 10 min. Before deposition of the film on quartz substrate cleaned the quartz substrate by keeping the substrate in piranha (3:1 proportion of H_2SO_4:H_2O_2) solution to remove the oxide present in the substrate and dried with nitrogen gas. The solution is coated on quartz substrate and are annealed at 400° C for 4 hours in furnace to get a pure TiO_2 thin films.

Characterization of TiO_2 thin film.

The crystal structures, morphologies, particle sizes and phase identification of TiO_2 microstructures were characterized / investigated using XRD (X-Ray Diffraction) executed using Rigaku diffractometer (Cu-Kα radiation with 40 KV (λ=1.54Å)). The diffraction patterns were found with the 2θ range of 20°≤ 2θ ≤ 80° with scanning speed of 1.0°/minute. The morphology of the surface thin film samples was studied by a FESEM (Field Emission Scanning Electron Microscopy) TESCAN-MIRA 3 LMH 2014. The absorption spectra of the TiO_2 films were studied by UV–Vis spectrophotometer (SIMADZU-UV-1800 in the range of 190-1000 nm) equipped with an integrating sphere.

RESULTS AND DISCUSSION

Powder X-Ray Diffraction (PXRD) Analysis.

The XRD patterns of TiO_2 films, at different rotation speed are shown in Fig 1. By matching the obtained peak position and standard JCPDS card (No. 21-1272) it confirms that $TiO_2$is in anatase phase [10].

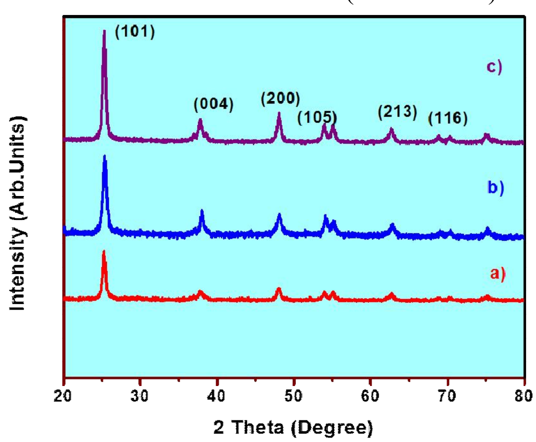

FIGURE 1.XRD pattern for the TiO2 thin film a)1200 rpm b) 1600rpm and c) 2000 rpm for 60 sec.

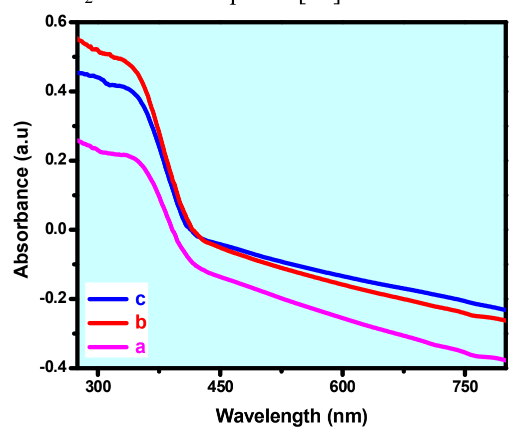

FIGURE 2.UV-Visible absorption spectra and Optical band gap for the TiO2 thin film a)1200 rpm b) 1600rpm and c) 2000 rpm for 60 sec.

The TiO_2 anatase formed was confirmed when the sample were dried at 100° C for 10 minutes. These peaks are sharp and intensity increases with the different rotation period. From Fig. 1, peak at 2θ =25.24° which is attributed to the plane (101) TiO_2anatase phase. The diffraction peaks are identified to determine the average crystallite size by making use of Debye-Scherrer's equation and it is found that 33-40 nm (Table 1). As noted from the XRD, small amount of peak intensity is decreases by different rotation speed of the film thickness. The product of the anatase phase is a metastable phase and is thermodynamically steady. The results are well matches with the in literature [11]. In this paper we report polycrystalline anatase phase of titanium oxide is prepared at 1200, 1500, and 2000 rpm for 60 sec.

UV-Visible Spectra Analysis and Optical energy band gap

Fig. 2 shows the UV / Vis. absorption spectra of different thickness of TiO_2 films were recorded in the wavelength range of 280 to 750 nm. From the spectrum there are two cleared areas; region around <320 nm is solid absorptionarea and solid transmittance locale >409 nm. For all different films have approximately acomparable absorption edges at 338 nm. This absorption edges determine the growth from VB (valance band) to CB(conduction band) [12]. The film has establishedmaximum transmittance (83%) in the visible region. The typical transmittance spectra of TiO_2 thin film, representing the solid reduction of transmittance in the UV region for all prepared samples. The transmittance in the UV area of spectrum can be clearly states semiconducting nature of TiO_2 films since the existence of energy band gap [11]. Hence TiO_2 films emphatically absorb ultraviolet radiations and transmit visible light, accordingly these could be used to confirm that potential opto-electronic gadgets for UV radiations.

TABLE 1. Rotation speed, Peak position of the TiO2 thin films annealing at 400° C for 2hours.

Rotation Speed (rpm)	Thickness of the Film	2 θ (Peak Position)			Lattice constant		Crystal Size (nm)	Optical Band gap (eV)
		(101)	(004)	(200)	a=b (Å)	C (Å)		
1200	1.26μm	25.24	37.84	48.06	3.786	9.512	40.30	3.13
1600	492 nm	25. 26	37.86	48.08	3.787	9.515	34.56	3.13
2000	460 nm	25.26	37.86	48.08	3.787	9.515	33.23	3.17

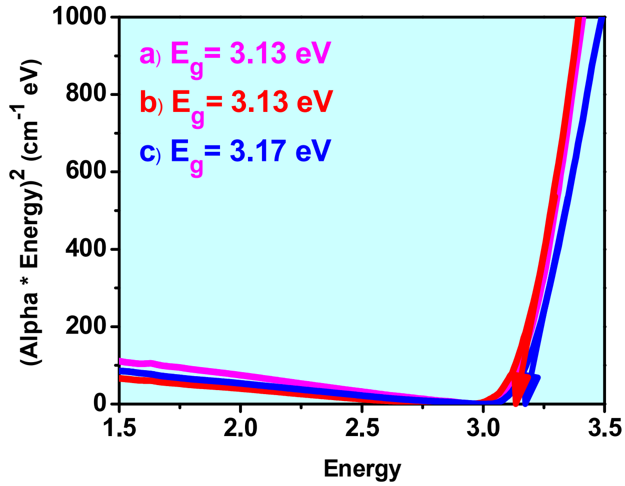

FIGURE 3. Energy band gap of the TiO2 thin film a)1200 rpm b) 1600rpm and c) 2000 rpm for 60 sec.

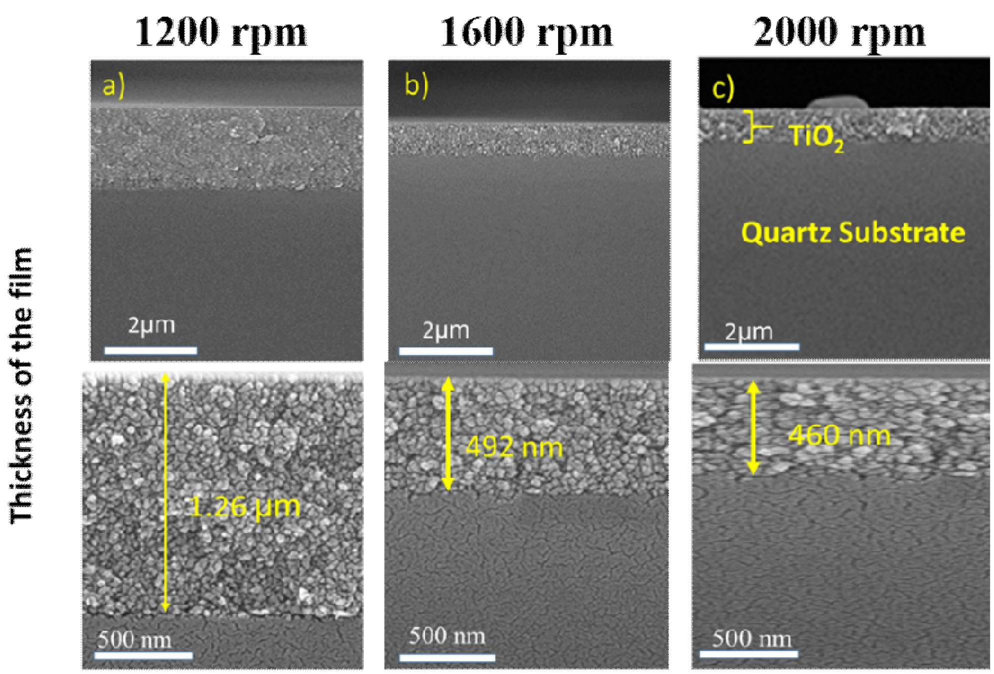

FIGURE 4. Cross sectional FESEM images of the TiO_2thin film a)1200 rpm b) 1600rpm and c) 2000 rpm for 60 sec.

Fig. 3, displays the optical energy band gap of different rotation speed with different thickness of TiO_2 films and these are calculated by usingTauc'sequation $(\alpha h C) = (h\vartheta - E_g)^n$, where, 'h' is photon energy,'n' is corresponding to 0.5 and 2 for direct and indirect band gap semiconductor, α is the absorption coefficient and calculated from, $\alpha = A/t_{film}$, where A is the measured absorbance and $t_{film}$is the film thickness[12]. The linear line of hC versus$(\alpha h C)^2$ at the absorption edge, these plots shows the semiconducting nature of the material [13]. By extrapolating the straight line of the plot to zero absorption coefficient (x-axis) gives the optical band gap (E_g) of TiO_2 films. The optical energy band gap for various rotational speed of TiO_2 thin films are found 3.13 eV, 3.13 eV and 3.17 eV, respectively. The band gap value decreases because of increase in grain size value of TiO_2 films (different thickness). Additional reason may be defect levels in the forbidden band of TiO_2 sub-bands decreasing the energy band gap [11]. These variations in the value of energy band gap strongly recommended for the fabrication of solar cells materials [14].

Field Emission Scanning Electron Microscopy (FESEM) Analysis

Fig. 4 displays the cross-sectional view of FESEM pictures for all samples. From the figure, the thickness of TiO_2 film decreases with increasing the rotational speed. The thickness spin coated sample for 2000, 1600 and 1200 rpm were found to be 460 nm, 492 nm and 1.26 µmcorrespondingly and tabulated in Table 1.

CONCLUSIONS

The thickness of TiO_2 films influences the properties of the energy band gap with TiO_2film by changing with rotation speed which has been studiedcoating on the quartz plates. The diffraction peaks are identified to determine the average crystallite size by making use of Debye-Scherrer'sequation and it is found that 33-40 nm. As noted from the XRD, small amount of peak intensity is decreases by different rotation speed of the film thickness. The transmittance in the UV area of spectrum can be clearly states semiconducting nature of TiO_2 thin films for the reason that of the existence of energy band gap. The optical energy band gap for different rotational spin speed of TiO_2 thin films are found 3.13 eV, 3.13 eV and 3.17 eV, respectively. The band gap value decreases because of increase in grain size value of TiO_2 films (different thickness). Hence TiO_2 films emphatically absorb ultraviolet radiations and transmit visible light, accordingly these can be developed to potential opto-electronic gadgets for UV radiations.

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