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Optimizing the Annealing Rates of Titanium Dioxide as a Photoanode of a Dye Sensitized Solar Cell

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ABSTRACT: Titanium dioxide thin films were grown on fluorine-doped tin oxide (SnO₂: F) layer which has been deposited on glass substrate using a doctor blade technique. The transmittance spectra and optical images of as deposited and thermally treated thin films at different rates (one-step annealing, 1°C/min and 2°C/min) were taken using UV-Vis spectroscopy and optical microscope respectively. All samples exhibited high transmittance, > 80%, for wavelength range ~420 nm to 800 nm and low transmittance of less than 30 % at shorter wavelength below 380 nm. All samples show high absorbance of above 2.0 % at wavelength of 420 nm, and low at longer λ . Band gap energy changes with annealing rates, 3.38, 3.30, 3.28 and 3.28 eV for as deposited, one step, 1°C/min and 2°C/min respectively. Plots of grayscale values against position on the images generate step like profile –high elevations (picks) and low elevations (valleys) depicting rough surface of TiO₂. The efficiency of the solar cells was studied using solar simulator at an intensity of 100mWcm⁻². Samples annealed at 1°C/min with high band gap of 3.28 and improved surface roughness for greater surface area for dye adsorption show the best incident photon to current efficiency of 3.31% which is relatively higher than that of 2°C/min, which is 3.11%, thus annealing rates affects the conversion efficiency of the DSSC.

KEYWORDS: Annealing rates, Dye sensitized solar cell, Titanium dioxide, Efficiency.

I. INTRODUCTION

Currently dye sensitized solar cells have attracted great attention since its invention by Michael Gratzel in 1991 [1]. DSSC comprises of three main components: photoanode, redox couple electrolyte, and counter electrode. In DSSCs, photogenerated charge carriers from dye molecules are collected by photoanode and counter-electrode material which transfer these charge carriers (electrons) to the outer circuit [2–4].

Mesoporous titanium dioxide is mostly used oxide materials as photoanode of a DSSC due to unique properties such as wide bandgap, stability and versatility. It also gives the highest photo-conversion efficiency and is an abundant in nature. The surface area of the TiO₂ plays an important role in increasing the efficiency of the solar cell as a large area means more adsorbed dye. Annealing process enhances the electron transportation in semiconductor materials [5]. The low-temperature films have low level of crystallization of interconnection between particles comparing with high-temperature film [6,7]. Titanium dioxide is an excellent semi-conductor which crystallizes in three different crystalline structures: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic) [8, 9]. Anatase is more photoactive, has a greater band gap, higher refractive index, and higher electron diffusion coefficient than that of rutile [10]. TiO₂ thin films can be prepared by a wide variety of techniques in chemical route such as chemical vapor deposition, aerosol pyrolysis [11], electrochemical deposition [12], and sol-gel method [13-17].

In this study, we demonstrate the preparation of anatase TiO₂ thin films on glass substrate by sol-gel method using the titanium tetraisopropoxide as Ti-precursor. Here we also discuss the effects of annealing temperatures rates on the surface roughness and optical properties of the TiO₂ thin films and overall effect on the performance of a DSSC.

II. METHODOLOGY

TiO₂ thin films were prepared through sol-gel technique. FTO SnO₂: F, sheet resistance, 7 Ω /sq, Solaronix, Switzerland) substrate were cleaned using acetone (99.9 %), ethanol (99.5 %) and deionized water subsequently for 5 minutes in each step. FTO glass substrates were then dried using pressured air. The adhesive tapes were then placed on the edges of the FTO glass substrates to form guide for spreading the Titanium nanoxide T/sp (18% wt, 15-20 nm, solaronix Switzerland). The films were subjected to room temperature for 30 minutes. Prepared TiO₂ thin films were then subjected to different annealing conditions. Some samples were left to dry at room temperature and they were

labelled as-deposited samples. Some samples were annealed at temperature ramp $1^{\circ}/\text{min}$ from room temperature to 175°C , and then sintered at 450°C for 30 min in a furnace. Some were annealed at temperature ramp $2^{\circ}\text{C}/\text{min}$, then sintered at 450°C for 30 mins other samples were annealed and sintered at 450°C for 30 mins were left to cool in furnace. The transmittance spectra for the prepared samples in each category of annealing process were obtained using UV-Vis spectrophotometer for optical analysis. An optical microscope, Zeiss Axio Zoom V16, in reflection mode was used to obtain optical images of the films at magnifications 16, 100 and 260X. The incident light ($400 \leq \lambda \leq 800 \text{nm}$) emitted by LEDs mounted on the sides of the stage of the microscope was reflected by the TiO_2 films, passed through a 1mm aperture into the lens and finally by an AxioCam Mrc5 high resolution CCD camera (pixel size: $3.4 \times 3.4 \mu\text{m}$) interfaced with PC. The CCD was used to acquire 8-bit images at 2584×1936 (5Mpixel) resolution. Optical images were then analysed using image j software. Prepared samples then dye- sensitized through immersing them in 0.5 mM cis-diisothiocyanato-bis (2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) bis (tetrabutylammonium), the so called N719 dye for 24 hours to maximize dye loading.

In preparation of counter electrodes, the FTO glass substrates were first cleaned in acetone (99.5 %) for 6 minutes using cotton swaps then soaked in ethanol (99.5 %) for 5 minutes. Finally, they were rinsed with deionized water for 6 minutes then dried using pressurized air. The adhesive tapes were placed on the edges to form guide in spreading the platinum precursor paste (platisol T/sp pore size, 15-20 nm, solaronix Switzerland) through the doctor blade procedure. The prepared samples were heated at temperature ramp of $5^{\circ}/\text{min}$ upto 175°C , then sintered at 450°C for 30 mins to activate the platinum films.

A dye-sensitized solar cell was assembled by sealing the dye-coated TiO_2 electrode with the platinum-coated FTO counter electrode using a dupont surlyn (meltonix 1170-25 solaronix) leaving a small space for the electrolyte introduction. The redox couple, iodine/triiodide, (Iodolyte HI-30, Solaronix, Switzerland) was then introduced into the space between the electrodes and later sealed. The fabricated solar cell was then characterized by analysing the I-V characteristics obtained through applying an external bias on the cell in a dark room. A 450 W halogen lamp adjusted to an intensity of $100 \text{mW}/\text{cm}^2$ was used. The irradiance on the DSSCs was maintained at 1 sun, $100 \text{mW}/\text{cm}^2$ with the use of a solar power meter TM206 and single crystal Si photoanode. During characterization, the cells were covered with a black-printed paper with a hole measuring 1cm^2 for the active area. The photovoltaic (PV) parameters, open-circuit voltage (V_{oc}) short-circuit current density, J_{sc} , and the fill factor (FF) were extracted from the I-V curve and used to calculate the DSSC's power conversion efficiency.

III. RESULTS AND DISCUSSION.

Surface roughness

Surface roughness of titanium dioxide treated under different thermal conditions were evaluated by studying the 2D microscopic images with image j software. Figure 1 shows 2D optical image of TiO_2 deposited on FTO obtained at magnification of 16, 100 and 260x. The variations in contrast regions indicates variations in surface topographies of films. Thin films annealed at $1^{\circ}\text{C}/\text{min}$ and $2^{\circ}\text{C}/\text{min}$ are relatively uniform and have minimal cracks unlike one step annealed samples.

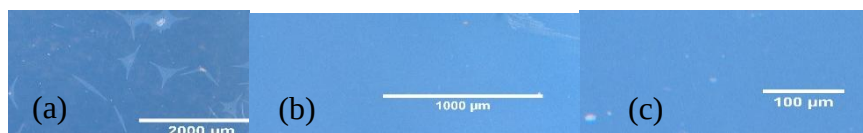


Figure 1: TiO_2 films deposited on FTO glass annealed at $1^{\circ}\text{C}/\text{min}$ obtained at (a) 16x, (b) 100x and (c) 260x magnifications.

The surface roughness was analysed by plotting line profiles at different positions on the image spanning the whole area and average Gray values recorded. The variation of Gray values with distance along the region of interest on the images is shown in figure 2. All curves show similar trend on the variation of pixel intensity with the position.

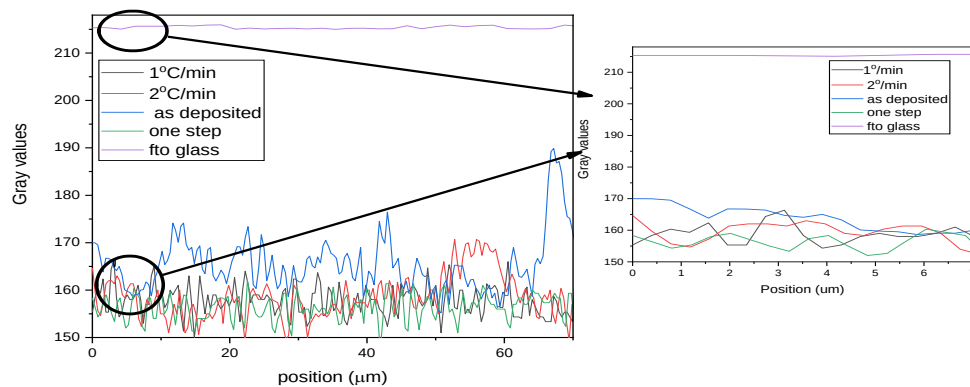


Fig 2. Profile of contrast (gray values) as a function of position obtained along the line drawn on images .

The plots present regions of high elevations (picks) and lower elevation (valleys) with increase in distance along the straight line plotted on the images. As can be seen variation in pixel intensity (Gray values) is highly dependent on surface roughness, with 1°C/min samples showing a lower variation of 9.74 and one step annealed samples being the highest with 11.17 as shown in table 1. Variation in pixel intensity seem to reduce with lowering of annealing rates with improved surface roughness. Thin films given one step annealing at 450°C for 30 mins, are characterized by defects such as cracks and agglomerations, thus showing a higher variation in pixel intensity with position depicting a high surface roughness.

Annealing rates	Gray value		
	Average minimum ± 0.01	Average maximum ± 0.01	Range ± 0.01
1°C/min	154.50	164.24	9.74
2°C/min	153.45	164.10	10.65
As deposited	170.10	165.00	5.10
One step	154.20	165.37	11.17
Blank FTO	206.10	206.10	0.00

Table 1: variation of Gray values with annealing rates.

The variation in roughness is attributed to the growth of small globules of TiO_2 with some areas agglomerated on the glass substrate. Lowering of annealing rate i.e 1°C/min and 2°C/min, the surface roughness reduces and improved, causing more growth of TiO_2 particles on the substrate and less agglomeration. The high surface roughness on one-step annealed films is attributed to the film being mainly amorphous and thus begins to crystallize into anatase phase after annealing at 400°C [18]. Tian et al. [19] observed that low annealing rate enhances both the mobility of molecules as the particle crystallization simultaneously takes place. The enhanced mobility of molecules makes the surface of TiO_2 smooth, that is, crystallization granulate the surface. Thus, the mobility of molecules played a primary role in the change of morphology (as observed in the 1°C/min and 2°C/min annealing rates) and as a result, the surface roughness decreased as the films became more homogeneous. Low annealing rates gives the atoms activation energy for them to nucleate hence improving the film quality which results to a decrease in grain boundaries [20, 21]. Improvement in the annealing rate, crystallization occurred leading to granulation [22].

Optical properties

The transmittance and absorbance spectra were obtained using UV-Visible spectrophotometer in the range of (280-800) nm. From figure 3 (a), it can be observed that the transmittance of the TiO_2 thin film decreases with increasing annealing temperature and lowering of annealing rates, this is attributed to the increase in film homogeneity, with the improvement of the surface roughness promoting the increase of the surface scattering of the light by increasing the

columnar growth with needle and rod like shape [23,24]. In addition, the transmittance increases with increasing wavelength for all prepared thin films.

The absorbance is found to be maximum at wavelength ~ 400 nm for all the samples with $1^\circ\text{C}/\text{min}$ and $2^\circ\text{C}/\text{min}$ having the highest and as deposited samples having a slightly lower absorbance. At wavelength shorter than 400 nm, the absorbance is almost the same for all the samples, however, at the wavelength longer than 430 nm, the absorbance decreases and approaches zero towards 800 nm as shown in figure 3 (b).

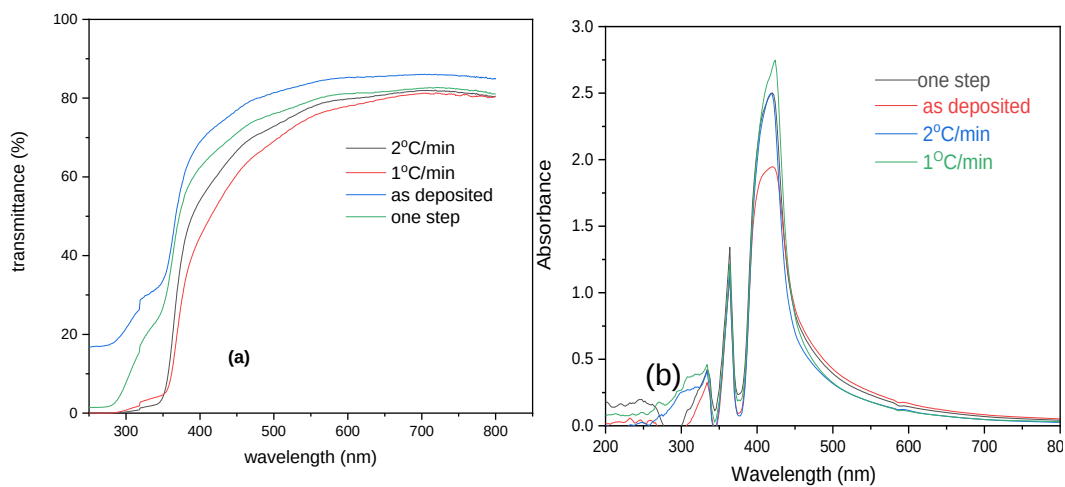


Fig. 3: UV-Vis transmittance (a) and absorbance (b) spectra of TiO₂ thin films deposited on FTO annealed at different rates.

Band gap energy (E_g) of the films annealed with different rates are obtained by using the Tauc equation 3 [25, 26].

$$(\alpha h\nu)^{\frac{1}{2}} = A(h\nu - E_g) \quad \dots \dots \dots 3$$

Where, α = absorption coefficient, A = constant independent of photon energy and $h\nu$ (eV) = energy of excitation. The value of E_g is obtained by extrapolating the straight-line portion of the plot to zero absorption edge in graph of $(\alpha h\nu)^2$ versus energy axes ($h\nu$) i.e. $(\alpha h\nu)^2 = 0$, the evaluated band gap of titanium dioxide thin film is shown in fig.4.

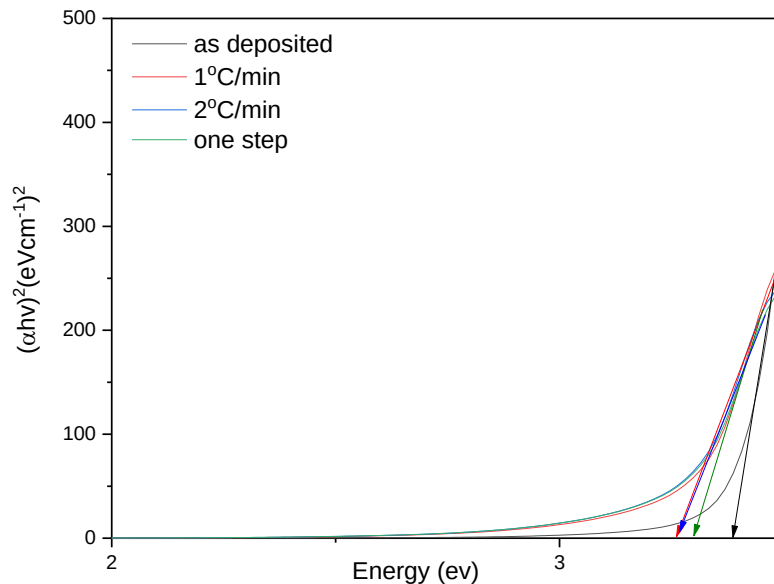


Fig.4: Tauc plot for indirect transition for a TiO₂ thin films annealed at different rates.

The values of E_g are found to be 3.38, 3.30, 3.28 and 3.28 eV for the films annealed at; as deposited, one step, 1°C/min and 2°C/min respectively. As deposited TiO₂ thin film is having the highest energy band gap of 3.38 eV and the thin films annealed at 2°C/min and 1°C/min is having slightly lower value of 3.28 eV. This may be due to the improvement of crystallinity and change in the morphology of the film on annealing. Annealing of TiO₂ thin films leads to increased levels of localized near valence band and these levels are ready to receive electrons and generate tails in the optical energy gap and tail is working toward reducing the energy gap, or can be attributed to increased size particles in the films [27]. The observed change in the energy band gap E_g with annealing agrees with reported work [28]. The energy gap value depends on the film's deposition conditions and its preparation method which influences the crystalline structure.

I-V measurement

Current-voltage (I-V) measurement was performed using TiO₂ thin film's structure to determine their electrical properties. The efficiency of DSSCs fabricated from prepared TiO₂ annealed under different annealing rates varies. These efficiencies were obtained from the photocurrent-voltage characteristics shown in figure 5, under a simulated sunlight of 100mW/cm². The efficiency (η) and the fill factor (FF) of the solar cells were computed as given in the Equations (2) and (3) [33].

$$FF = \frac{V_{max} \times J_{max}}{V_{oc} \times J_{sc}} \quad \dots \dots \dots (2)$$

where V_{max} and J_{max} represent the voltage and the current at the maximum output power point respectively.

$$\eta = \frac{V_{oc} \times J_{sc} \times FF \times 100}{P_{in}} \quad \dots \dots \dots (3)$$

where P_{in} = incident light power.

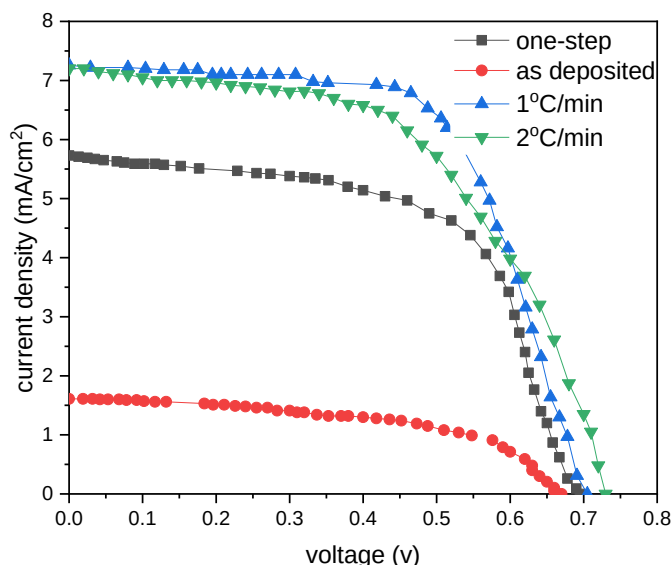


Fig. 5: I-V characteristics for TiO₂ thin films deposited onto FTO with different annealing rates

After the annealing process and fabrication of the cells, the parameters that characterize a solar cell were measured and tabulated in table 2. It can be seen that annealing rate plays a vital role towards the performance of the cell. The current density of solar cells increased with lowering annealing rates along with the conversion efficiency (η). From table 2 the highest current density is 7.33 mA and the lowest being 1.61mA which give the conversion efficiency of 3.31% and 0.53% respectively. Annealing rate also seem to affect the FF in that with the variation of the annealing rate the FF improves. The highest FF is 0.64 which corresponds to annealing rate of 1°C/min and the lowest being 0.49 which is that of as deposited samples.

Poor surface roughness and much agglomeration of one step TiO₂ thin films may lead to reduction of the active surface area for dye adsorption and as a consequence, it will reduce photocurrent. Moreover, this agglomeration, decrease electrical contact, because it reduces the area of interconnection between nanoparticles [29-31]. Therefore, the resistance for charge transfer is increased and charge transporting become lower [32]. Samples left to dry at ambient exhibit poor results because of poor electrical properties due lack of thermal activation, these can lead to poor adhesion of TiO₂ deposition, poor dye adsorption and no electrical network between the particles. Annealing process increases the surface area of the films which will ensure more dye molecules are adsorbed on the film. This will lead to an increase in the number of excited electrons due to increased light harvesting ability of the films as observed in 1°C/min annealed samples. The conversion efficiency will therefore increase.

Sample	V_{OC} (V)	J_{SC} (mA/cm ²)	F.F (%)	η (%)
1°C/min	0.705	7.33	0.64	3.31
2°C/min	0.72	7.2	0.56	3.11
one step	0.695	5.73	0.50	2.4
as deposited	0.67	1.61	0.49	0.53

Table 2: summarized output parameters of DSSCs fabricated from TiO₂ annealed at various

IV. CONCLUSION

TiO₂ thin film is highly transparent in the visible range and annealing treatment causes slight decrease in the visible transmittance with improvement in surface roughness. Annealing titanium dioxide with the rate of 1°C/min and 2°C/min give high absorbance and a wide bandgap. The influence of annealing rate on optical properties of titanium dioxide films on the performance of the DSSCs was studied and found to influence the conversion efficiency of DSSCs, with 1°C/min and 2°C/min giving the highest conversion efficiency of 3.31% and 3.11% respectively.

Improving the annealing rates ($1^{\circ}\text{C}/\text{min}$) improves the electrical property of the TiO_2 and thus improving the performance of the DSSCs.

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