Structural and Optical Characterization of Polymer based TiO$_2$ films for Photovoltaic Applications

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Abstract

The demand for energy worldwide is rising almost on a daily basis. There is need to research on new materials and ways to provide energy. In this preliminary study, we explore the properties of polymer based TiO$_2$ films for possible photovoltaic applications. TiO$_2$ films incorporating Polyvinylidene Fluoride-Co-Hexa fluoropropylene (PVDF-HFP) as the structure directing polymer and using Titanium Isopropoxide as the precursor were deposited by both dipping and spin coating techniques. The films were optimized with respect to solution concentration, and spin coater speeds as well as dip coating with drawl speed. X-Ray diffraction (XRD) structural, as well as transmittance studies were carried out. XRD spectra showed crystalline anatase films with crystal sizes of about 18-24 nm after annealing at about 430±50 ℃ for 30 minutes. The as deposited films were amorphous. For spin coated films, the films uniformity became better with spin speed. However, the optimum speed that ensures uniformity and lack of pin holes was found to be about 3000 RPM. The transmittance of the films decreased with the coater speed. As for the dip coated films the concentration of the solution and the withdrawal speed affect the film thickness and therefore the transmittance of the films. Thicker films were obtained from more concentrated solutions. Decrease in concentration of the solution tended to produce a minimum thickness at some withdrawal speed. It was found that higher withdrawal speeds led to lower transmittance due to thicker films.

Key words: TiO$_2$, Anatase, Polymer, Dip coating, spin coating, transmittance, thickness, structural, Optical, photovoltaic

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1.0 Introduction

With almost no exception, the current generation has assumed a lifestyle of using gadgets that need to be powered. Current estimates for the power needs of the roughly 7 Billion people worldwide are as high as 13 Terrawatts (TW) and it is estimated that in less than half a century, the demand will peak to about 23 Terrawatts (TW) (Kalyanasundaram, 2010). There is, therefore concerted effort in search for alternative energy sources to supplement the current sources. Fossil fuels, nuclear power and renewable energy (solar, wind, hydro etc.) are the key options. Of the three options, renewable energy based on solar resource could be the most appealing and promising since it is free, abundant and free from pollution.

Since the break through work on the possibility of generating electricity by applying the photosynthesis principle, a lot of research has gone in to this area due to its potential to offer cheaper power compared to conventional solar cell (Brain O'Regan and Michael Gratzel, 1991). This type of solar cell device is referred to as the Dye Sensitized Solar Cell (DSSC). In brief, a DSSC is composed of a nanocrystalline

semiconducting film sand winched between two photo electrodes; a photo electrode and a counter electrode. The nanocrystalline semiconducting film has a monolayer of a dye to enhance the absorption of incident photons. On illumination, the absorption of the radiation excites an electron from the dye which is conducted through the back contact of the photo electrode and regenerated through the counter electrode which is usually coated with an electron regeneration catalyst like platinic acid. The electron generated by irradiation on the dye is finally recovered at the counter electrode. Therefore, there is no electron loss.

The DSSC technology however has to overcome a number of bottlenecks before it is competitive enough with the conventional solar cell technology-the p-n junction. Research is ongoing to overcome shortcomings like electron loss through the back contact (Petra and Peter 2003; Waita et al., 2007), improving on the dyes (Kohjiro H. and Nagatoshi K., 2009), increasing porosity of the semi conducting film, (Waita et al., 2006, 2007, Kiema et al., 2005), use of other counter electrodes (Kim et al., 2012) among other approaches.

A number of techniques have been used in depositing the semiconducting film: Sputtering (Waita et al., 2007; J. Rodri´guez et al., 2000; M. Go´mez , et al., 2000), Screen printing (S. Burnside et al., 2000), Spray pyrolysis (A.Conde-Gallardo et al., 2005,),hydrolysis of TiCL4 (Kristel Möldre, et al., 2015), and sol-gel dip coating (Jan Prochazka et al., 2013). In their work, Jan Prochazka et al., (2013) incorporated the use of a polymer (poly (Hexafluorobutyl Methacrylate)) as the structure directing agent and titanium ethoxide as the precursor using the dip coating techniques. The films were found to be dense and promoted thixotropic properties. We would like, in this work try a different polymer and determine the properties of the film so obtained. Furthermore, we use two deposition techniques and compare the film properties.

In this paper therefore, we report the structural and optical properties of TiO_2 films that use Titanium Isopropoxide as the precursor and incorporating Polyvinylidene Fluoride-Co-Hexa fluoropropylene (PVDF-HFP) as the structure directing polymer deposited by the dipping and spin coating techniques.

2.0 Experimental Techniques

2.1 Solution Preparation

Two solutions, herein referred to as solution 1 and 2 were separately prepared at room temperature and then mixed together under magnetic stirring. Solution 1 was made by mixing ≈2.2 ml of Hydrochloric Acid (HCl) (Aq) (Aldrich) (37%) and ≈2.55 g of Titanium Isopropoxide (Aq) (Aldrich) with magnetic stirring and stirred until the solution was homogeneous (≈ 30 minutes). This formed the precursor solution. Solution 2 was also made under stirring and composed of ≈ 0.55 g (11-12 pellets) of Polyvinylidene Fluoride-Co-Hexa fluoropropylene (PVDF-HFP) (Aldrich) in a mixture of Acetone and N-Methyl-2-Pyrrolidone (NMP) (Aldrich) in the ratio of 2:3, Acetone to NMP, total volume of mixture, 60 ml. Magnetic Stirring was done until all polymer was dissolved (≈ 90 minutes). Solution 1 was then mixed with solution 2 under constant stirring which continued until the solution became homogeneous (≈ 2 hrs). All solutions were prepared at room temperature and kept covered thereafter.

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2.2 Substrate cleaning

Both plain glass and Fluorine Doped Tin Oxide (FT0) (15 Ω/m^2) (Hartford) substrates were used for film deposition after cleaning. The substrates were cleaned by ultra-sonicating (about 30 minutes) in deionized soapy water, then in pure deionized water for about 10 minutes. Thereafter, the substrates were ultrasonically cleaned in ethanol which had 2-3 drops Hydrochloric Acid (HCl) added for about 30 minutes followed by 30 minutes in Acetone and 30 minutes in Ethanol. Finally, the substrates were rinsed with deionized water and dried by blowing with nitrogen gas.

2.3 Film deposition for Structural studies

Two films (4(a) and 4 (b)) were deposited on FTO glass substrates and allowed to dry at room temperature. 4(a) was used as deposited while 4 (b) was heat treated in a programmable oven (Nabertherm) for $\approx$ 30 mins at $\approx$ 430 ±50 ℃ and allowed to cool down to room temperature.

2.3 Film deposition and heat treatment

Pre-cleaned Flourine Doped Tin Oxide (FTO) glass substrates where used as substrates and the films were coated by simple hand dipping. For each solution, two films were made: 4a and 4b. 4a deposited and allowed to dry at room temperature (as deposited) while 4b was heat treated in open air for $\approx$ 30 minutes at $\approx$ 430 ±50 ℃ after coating and allowed to cool down to room temperature.

2.4 Thickness optimization

The amounts of Acetone and NMP were varied in order to vary the film thickness. The solution with concentration 1 (conc 1) was, 12 ml of Acetone and 18 ml of NMP. Two more dilute solutions were made: concentration 2 and 3 (conc 2 and conc 3). These concentrations were made by reducing the amount of polymer in the solvent in conc 1 while maintaining all else constant. The film thickness was measured using a Dektak 3 surface profilometer (Sloan Technology).

2.5 Film deposition by spin coater

The spin coater used was a KW-4A Model (CHETMAT Technology) and was first calibrated to create a correlation between the knob setting and the digital display. Film deposition using the spin coater was done on pre cleaned glass substrates masked at one end using a scotch tape to create a step for thickness measurements. The substrates were kept fixed on the coater using a double sided tape. About 500 µl of the solution was then carefully spread on the substrate using a calibrated pipette. Depositions were done at various digital speeds.

2.6 Film deposition by Dip coating

Dip coating was done using an automated, computer controlled Dip coater Robot (R & K Germany). Two solutions were made and added together making a total volume of 60 ml and were used immediately after preparation (concentration 1, (conc 1) . Different coatings on plain glass substrates were deposited by varying the withdrawal speed of the substrate. After deposition, the films were kept at room temperature until they were dry before heat treatment at $\approx$ 450 ℃ for $\approx$ 30 minutes in a programmable furnace.

2.7 Structural studies

X-ray diffraction (XRD) of the deposited films was done using a computer controlled Siemens Diffractometer at a voltage of 45 KV and current 40 mA. The diffraction angle was varied from 20º to 60º.

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2.8 Optical measurements

Optical measurements were done using both a computer controlled single beam UV-VIS-NIR High Resolution Spectacular HR 2000 Light Source Spectrometer (Ocean Optics Inc.) which was equipped with Halogen and Deuterium lamps..

3.0 Results and Discussion

3.1 Structural characterization of the coated films

The XRD patterns for the films is displayed in fig 1 below. Film 4a was found to be amorphous while 4b was found to be crystalline with Anatase phase. The average crystal size estimated from Scherer's formula was ~ 18-24 nm. The crystal size is critical in photovoltaics for it affects both the electron mobility as well as light harvesting. Small crystal sizes (< 20 nm) reduce the space charge area leading to electron recombination due to lack of electron /electron interface energy barrier as well as low conduction (Zaban et al., 2000, Gratzel, 2000). On the hand, large crystals create large surface area for more dye anchoring increasing electron generation rate, faster electron transport as well as slower recombination rate (S. Nakade et al., 2003).
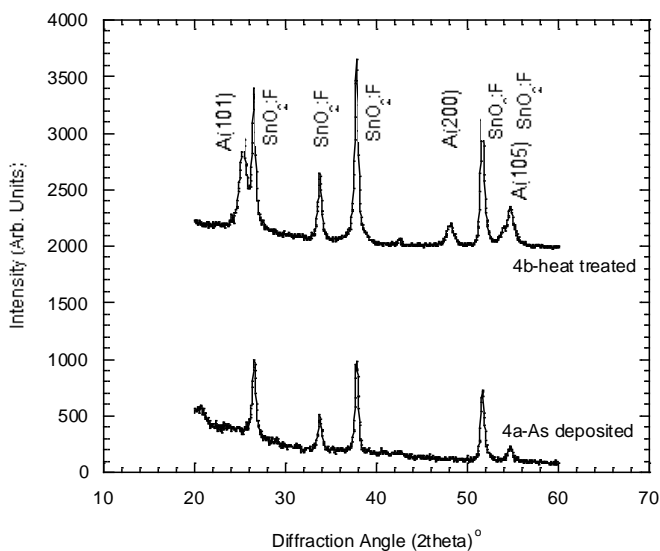

Fig 1. XRD patterns for the deposited films on FTO substrates

3.2 Spin coating

3.2.1 Spin Coater Calibration

The spin coater was calibrated and fig 2 below shows the variation of digital spin coater display with the position of the spin coater knob. As can be observed, there is a direct correlation between the two. This enabled us to determine the speed of the coater at various knob settings.
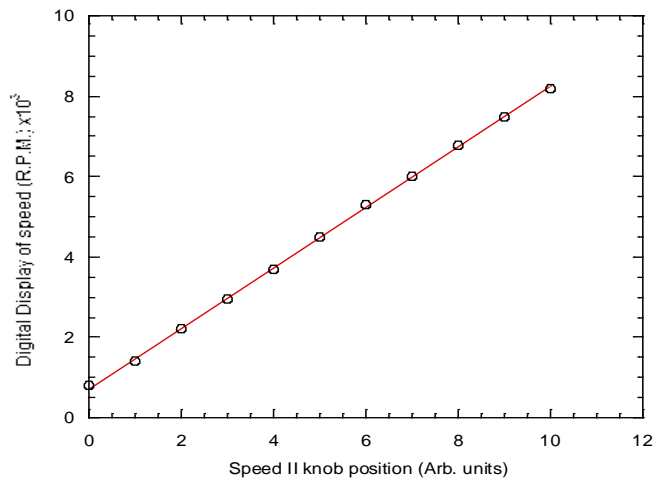
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Fig 2. The spin coater calibration: Digital speed display versus the speed knob position

Fig 3 below shows the variation of film thickness with speed of the spin coater. The film thickness was measured using a Dektak 3 surface profilometer (Sloan Technology). Visual inspection was used to gauge how uniform the films were. The films deposited at 800 and 1400 R.P.M. 470 nm and 297 nm thick respectively (first two data points below)and did not appear very uniform. On the other hand, the films deposited at speeds of about 3000 R.P.M and above appeared uniform with the uniformity getting better with increase in speed but tended to lose continuity as the speed increased. The thickness of the films were measured for the various increasing spin speeds. Pinholes were visible in some of the films. The general trend observed is a decrease of the film thickness with the coater speed. Increased speeds increases also the centrifugal force accelerating the solution to the edges of the substrate. The solution spreads more and the film thickness therefore decreases.
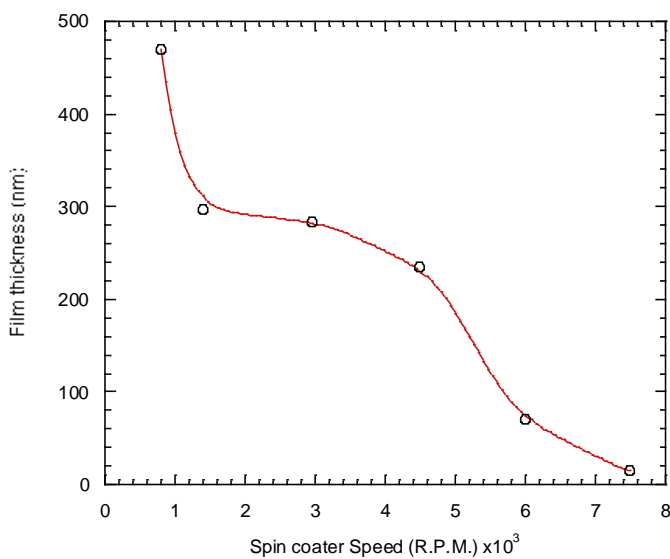

Fig. 3 . The Spin coater calibration: variation of film thickness with spin coater speed

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3.2.2 Optical measurements

The variation of transmittance and spin coater speed is displayed in figure 4 below. The transmittance of the films tend to increase with the spin coater speed. This observation is in agreement with the observation discussed above on speed variation with film thickness. This is because as the film thickness decreases due to higher speeds, the film will become more transparent. From our data, it appears that speeds of about 3000 and above would give us films with above 60 % transmittance for most of the wavelength and the film thickness can be carefully monitored so that it does not become too thin to create pin hole and no uniformity. Lower speeds produced films that seem to compromise the film's transmittance.It is also noted that at higher speeds, transmittance of the coated films and that of the plain glass tend to be close, a possible indication of pinholes in the coated films. However, we did not do further study to confirm this although it is needed.
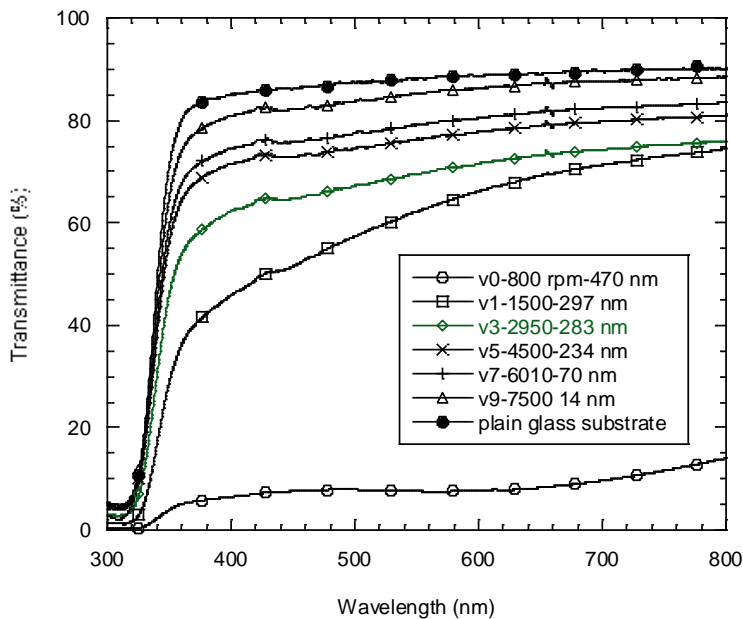

Fig 4. Transmittance of the films deposited at various spin coater speeds

3.3 DIP COATING

3.3.1 Film thickness variation with withdrawal speed

A plot of film thickness against withdrawal speed for the three concentrations is as displayed below in figure 5. The spectra for concentration 1 (conc 1) appears like a smooth tick/right ($\surd$) changing shape to more of a bowel as the solution concentration reduces. Thus, as the solution concentration reduces, the film thickness variation at low and high speeds becomes less significant. In other words, the withdrawal speed does not lead to large differences in the film thickness at low and high with drawal speeds. We explain the observation as follows: At low withdrawal speeds, evaporation as well as convection effects determine the film deposition rate. Due to the slow withdrawal speeds, these two effects create a low film deposition rate leading to thin films. As the withdrawal speed increases, gravity related viscous drag force dominates leading to increase in film thickness. This effect seems to become more prominent as the concentration of the solution increase. According to David Grosso (2011), the dip coating technique has three regimes: Capillary at low withdrawal speeds, draining at high withdrawal speeds and Intermediate which is an overlap of the two regimes and his observation of dip coating concurs with ours.
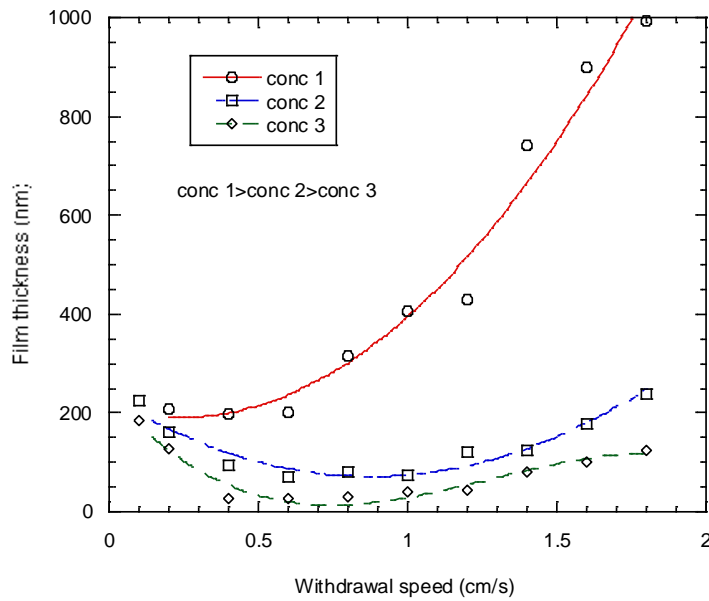
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Fig 5. Film thickness variation with withdrawal speed for various concentrations of the solution

3.3.2 Transmittance of the films

The transmittance of the films deposited using the three different concentrations showed the same trend and behavior. The only difference was the level of transmittance which decreased as the concentration increased. Due to this, we present the transmittance spectra for the films deposited using concentration 1 only, as in figure 6 below. The observation below is that the higher the withdrawal speed, the lower the transmittance. This behavior has a direct correlation to film thickness because concentrated solutions produced thicker films. As a matter of fact, the transmittance of such films would be lower compared to less concentrated solutions. For films meant to have high transparency to radiation in the visible range, low withdrawal speeds are therefore recommended although that has to be balanced with the film thickness required.
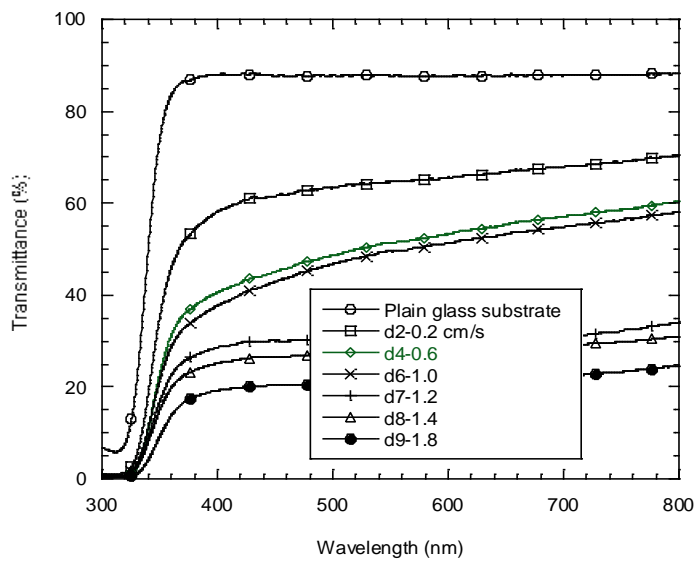
Fig 6. Transmittance versus wavelength for the films deposited at various withdrawal speeds. The films were made through solution of concentration 1 (conc 1).

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3. 4 Conclusion

The structural and transmittance properties of TiO_2 incorporating Polyvinylidene Fluoride-Co-Hexa fluoropropylene (PVDF-HFP) as the structure directing polymer and using Titanium Isopropoxide as the precursor have been deposited by both dipping and spin coating techniques.

XRD structural studies revealed that as deposited films were amorphous but heat treated films at about 450±50 ºC exhibited crystalline nature while revealing the Anatase phase of TiO_2 considered better for photovoltaic application than the other phases of TiO_2. The average crystal size estimated from Scherer's formula was ~ 18-24 nm.

Films deposited by spin coating showed better uniformity of thickness as the speed increased, although at very high spin speeds, the films showed some pin holes. The thickness also decreased with the spin coater speed. The optimum speed that ensures uniformity and lack of pin holes was found to be about 3000 RPM. Since the film thickness decreases with spin coater speed, it is expected that the transmittance of the films decreases with the coater speed. This was confirmed through our measurements.

As for the dip coated films, it was observed that the concentration of the solution as well as the withdrawal speed both affect the film thickness and therefore the transmittance of the films. More concentrated solutions had thicker films. The difference in thickness of the films at low and high speeds was also bigger as the solution concentration increased. Low concentrations had speeds where the film thickness was minimum.

The transmittance of the films deposited using the three different concentrations had the same trend. It was found that higher withdrawal speeds led to lower transmittance due to thicker films.

In order to complete our optimization of the films, we shall, in our next communication report on more optical parameters of the films as well as the performance of the solar cells fabricated using these films.

3.5 Acknowledgement

3.6 References

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