Fabrication of Dye Sensitized Solar Cell Using Nanocrystalline TiO$_2$ and Optical Characterization of Photo-Anode

K. Usha$^1$, B. Mondal$^{2,*}$, D. Sengupta$^{2,3}$, P. Das$^{2,3}$, K. Mukherjee$^2$, P. Kumbhakar$^4$

$^1$Department of Engineering Physics, Bengal College of Engineering & Technology, Durgapur, India
$^2$Centre for Advanced Materials Processing, CSIR-Central Mechanical Engineering Research Institute, Durgapur, India
$^3$AcSIR Research Fellow, Centre for Advanced Materials Processing
CSIR-Central Mechanical Engineering Research Institute, Durgapur, India
$^4$Department of Physics, National Institute of Technology, Mahatma Gandhi Avenue, Durgapur, India

*Corresponding Author: bnmondal@cmeri.res.in

Abstract

Anatase phase containing nano-crystalline TiO$_2$ thin film is prepared by the peptization of modified Ti-isopropoxide sol using HNO$_3$ as peptizing agent. The resulting sol is concentrated in a rotary evaporator bath. TiO$_2$ film is deposited on ITO substrate by spin coating process. The compact film is annealed at 450˚C and 500˚C for optical studies. The subsequently it is modified as photo-anodes in dye sensitized solar cells. The prepared materials are characterized by X-ray diffraction (XRD), UV-Vis absorption spectroscopy and high resolution transmission electron microscopy (HRTEM). The colloidal particles are 6-8nm in average size while the grain growth of the particles are in the order of 13-20nm after annealing of the thin film. The obtained lattice constants of the TiO$_2$ nanocrystals are $a=3.79\,\text{Å}$ and $c=9.48\,\text{Å}$ from XRD data as compared to JCPDS data of $a=3.79\,\text{Å}$ and $c=9.52\,\text{Å}$. The photo conversion efficiency of assembled dye sensitized solar cells comprising of ~5µm thickness of the film are determined to be of the order of 6.77%.

Keywords

TiO$_2$ Thin Films, Annealing, Photo-Anodes, Optical Constants, Band Gap, Photo-Conversion Efficiency

1. Introduction

In recent years nanosized materials have attracted the technological world due to their high surface to volume ratio which makes a dramatic change in physical and chemical properties as compared to the bulk material. Specifically in semiconductors, the band gap is size dependent due to quantum confinement effect. Thin n-TiO$_2$ coatings have wide range of applications in self-cleaning, gas sensing, electronic devices and photovoltaic [1-4]. TiO$_2$ films of 15-20 micron thickness made from particles of 25nm-50nm in size are used as electrodes in dye sensitized solar cells [1, 5]. Homogeneous TiO$_2$ thin films with good adherence to the substrate could be obtained by adopting several techniques like chemical vapor deposition, physical vapor deposition, electron-beam evaporation, magnetron sputtering, sol-gel etc [5, 6]. The sol-gel based thin film deposition using different techniques like spin / dip coating and screen printing may be suitable for the cost effective production of futuristic dye sensitized solar cells with promising solar to electric conversion efficiency.

The morphology and optical properties of TiO$_2$ depend appreciably on the precursor type, synthesis procedure, deposition method and annealing temperatures [7-9]. In this paper, the physical properties of thin films deposited by spin coating technique are studied using acetyl acetone (Acac) modified colloidal sols of titanium isopropoxide. Highly transparent films of TiO$_2$ with good adhesion to the glass substrate are prepared via sol gel synthesis. The electronic band gap of thin film annealed at moderately low temperature is found large. The thickness of the layer has been increased by coating the sol repeatedly. In order to develop the photo electrodes, the thin film of titania sol is annealed at 450-500˚C. The TiO$_2$ film is prepared from colloidal particles of TiO$_2$ using TritonX 100 as surfactant and terpineol as binder. The sol is used for spin coating on indium doped tin oxide (ITO) based conducting glass substrate for making suitable thin films. The surface morphology of the TiO$_2$ thin film is investigated using scanning electron microscope (SEM). The optical properties are measured by varying thickness of the film. Counter electrode is prepared by coating platinum paste on ITO glass substrate followed by annealing at 450˚C which is used as cathode. Popular ruthenium based dye (N719) is used as photo-sensitizer and I$_{-}$/I$_{3}^{-}$ is used as electrolyte to prepare sandwiched type solar cell. The photo-voltaic characteristic of the prepared solar cell is measured under simulated solar light (100 mW/cm$^2$).
2. Materials and Methods

2.1. Synthesis of n-TiO₂ Colloidal Sol

Colloidal sol consisting of nanocrystalline TiO₂ particles is synthesized from titanium iso-propoxide as the precursor by using wet chemical route. Titanium iso-propoxide is highly hygroscopic and hydrolyses readily in exposure to moisture. In order to control the rate of hydrolysis, the precursor is modified with acetyl acetone (in the molar ratio of 1:3). Such chemical modification generates exothermic reaction resulting dark yellow colour. The modified precursor is then added to 0.1M HNO₃ under continuous stirring. The obtained sol is stable for several days and suitable for coating [10, 11]. The obtained sol is then heated in a rotary evaporator bath with a controlled heating at 80°C for 2 hrs and is ready for deposition as thin film on ITO glass substrate through spin coating process [5].

2.2. Thin Film Deposition

The concentrated colloidal sol is spin coated with single layer (which is referred as TF-1 here after) annealed at 450°C for 45 mins. The thickness of the layer has been increased by successive spin coating of 3-layers (which is referred as TF-2 here after). After the spin coating is done at an increasing rate of 50 rotations/sec and maintains ~3000 rpm for a period of 3 mins. Finally, the film is annealed at 450-500°C to remove the organic binders and obtain good adhesion to the substrate. In case of TF-2, since the thin film is made by repetitive spin coating of the TiO₂, the growth of the grains over the films is controlled by preheating at 250°C and finally the film is annealed at 450-500°C.

In order to develop the photo-anode of the solar cell, the TiO₂ paste is further spin coated on as-obtained TiO₂ thin film (TF-2) of ITO glass substrate. The TiO₂ paste is prepared using distilled water, organic binders of PEG 300, TritonX 100 and TiO₂ powders which are obtained from the dried sol of TiO₂. The photo-anode is finally annealed at 450°C for 45mins. The obtained titanium dioxide film on ITO glass substrate is soaked in N719 dye overnight. The platinum paste coated on ITO glass substrate which is annealed at 350°C, 20 mins is used as counter electrode. The photo-anode and counter electrode are sandwiched together using a sealant. A drop of I-/I₃- redox couple as electrolyte is inserted through a small hole that is left during sealing. The assembled solar cell is ready for I-V measurement.

2.3. Characterization

The morphology of colloidal particles is investigated by TEM (Model: Hitachi S-530) analysis. The TGA and DTA measurements are carried out in a thermal analyzer (NETZSCH STA 449 F3 Jupiter). The XRD pattern of the thin films are collected by PAN analytical diffractometer fitted with CuKα radiation tube (λ = 1.54Å), UV-Vis-NIR studies are carried out using Schimadzu UV-3600 spectrophotometer. The morphology of the photoanode is studied by SEM (Model: Hitachi S-530) I-V characterization under illumination is done using Scinception Integrated Photovoltaic testing system which is equipped with 150W xenon lamp as the light source. To measure the photovoltaic performance of the assembled solar cell, integrated photovoltaic system from Scinception Instruments, Canada is used. This system has 150W Xenon lamp as light source and Kithely 2400 SMU to measure the I-V characteristics of the solar cell. The input voltage and current supply to the source lamp can be controlled. A separate luxmeter is used to check and compare the brightness of the source with that of Sunlight. By measuring the luminosity of the Sun in broad day light when the Sun is at its zenith and comparing the brightness with that of the source lamp, the position of the cell holder is calibrated for different illuminations.

3. Results and Discussions

3.1. TEM Characterization of the Colloids

TEM is employed to know the crystalline nature, size and phase of the TiO₂ colloidal particles. Though the particles in the TiO₂ colloidal sols show crystalline nature, the particle size is very small due to peptizing treatment. Figures 1(a) and 1(c) show the TEM images of the obtained colloidal particles. TiO₂ colloids are well dispersed with a size of around 6 nm and the shape of the particles is almost spherical with some irregularities as depicted in Fig.1 (c). The crystal planes of the colloids are calculated by analyzing the SAED pattern as shown in Fig. 1(b) by using the formula,

\[ \frac{d_1}{d_2} = \frac{R_2}{R_1} \]

where \( d_1 \) & \( d_2 \) are the inter planar distances of the crystals and \( R_1 \) & \( R_2 \) are the radii of the Ewald spheres obtained from TEM characterization. Ratio of the diameters of the spheres is matched with that of the ratio of the \( d_{\text{hkl}} \) of the anatase phase crystals.

\( \text{Figure 1. (a)TEM, (b) SAED images & Fringe pattern of Green TiO}_2 \) Colloidal Sols modified with Acetylacetone and (d) TEM, (e) SAED Images & (f)HRTEM Fringe pattern of annealed particles peetled from thin films annealed at 450°C
Figures 1(d), Fig. 1(e) and Fig. 1(f) show the TEM image, SAED pattern and lattice fringes respectively of particles obtained from peeling the thin film annealed at 450°C. The planes obtained by calculation of radius of the spheres in the SAED pattern (from Eqn. 1) correspond to the XRD peaks of the diffraction of deposited thin films. The lattice fringe patterns in Fig.1(c) and Fig. 1(f) are used to calculate the lattice spacing $d_{101}$ of the TiO$_2$ crystals. The values of $d_{101}$, $d_{200}$, $d_{004}$ are found to 3.41Å, 1.69Å, 2.25Å, respectively for colloidal sols and 3.56Å, 1.88Å and 2.34Å respectively for nanoparticles annealed at 450°C which corresponds to the JCPDS data for the bulk TiO$_2$ of anatase phase [12-14]. The obtained values are with an average error of 0.8% as compared to that of bulk TiO$_2$ values.

3.2. TG/DTA Characterization of the Dried Titanium Sol

In order to find out the mass loss with temperature thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) studies are carried out at a constant heating rate of 10°C/min over temperature range of 25-800°C using 30-35 mg of dried colloidal sols in a ceramic crucible. The TGA pattern indicates that the thermal decomposition of this substance broadly involves dehydration and organic matter loss through temperature escalation. There are major peaks 40-110°C and ~610°C. This clearly shows the phase change of TiO$_2$ from amorphous to anatase phase at temperatures below 110°C which is also accompanied by loss of solvents as shown in Fig. 2. The peak around 610°C might be due to transition of anatase to rutile phase of TiO$_2$. Though this could not confirmed here, it is found in literature that TiO$_2$ transforms to rutile phase from anatase phase beyond 420°C [1]. But in our case this is seen around 610°C. This may be due to the formation of ligands of organic solvents with precursor during modification.

3.3. X-Ray Diffraction (XRD) of Thin Film

To determine the grain growth and phase of the grains on the annealed thin films, XRD of the grains is studied. The XRD pattern of the annealed thin films is shown in Fig. 3.

It is observed that the film when annealed at 450°C is consisted of anatase phase of TiO$_2$ and the X-ray diffraction patterns match well with the standard diffraction data of anatase JCPDS data (No. 21-1272). In the diffraction pattern, no impurities of phases have been observed. The grain size of the thin films is calculated using Debye-Scherer formula. The calculated grain size of the thin films is about 15.8nm and 20nm for TF1 and TF2 respectively. The obtained values of $d_{101}$, $d_{004}$, and $d_{200}$ from the XRD data are 3.52Å, 1.90Å, and 2.40Å, respectively. The values of lattice parameters obtained from X-ray diffraction pattern and TEM analysis have been compared. The lattice parameters obtained from TEM data are $a = 3.79 Å$, $c = 9.46 Å$ while that from XRD peaks correspond to $a = 3.79 Å$ and $c = 9.48 Å$ for thin film of TF1. The values of the lattice parameters of film TF2 obtained from the XRD data remain same as TF1. Both the values are close to the bulk TiO$_2$ anatase phase of $a = 3.78 Å$ and $c = 9.51 Å$. The ratio of $c/a$ for samples annealed at 450°C is 2.49 for TF1 and 2.50 for TF2 whereas as calculated from XRD peaks the ratio is 2.52. The reported ratio of stress free grains of TiO$_2$ thin films annealed at 450°C is 2.51Å [6, 15].

3.4. UV-Vis Absorption Characteristics

The transmittance spectra for the thin films are taken in the wavelength range of 300–800nm. The UV-Vis transmission spectra of both the thin films are shown in Fig.4. The transmittance is greater than 80% for both the films in the wavelengths above 400nm. For films with good transmittance, if $T_m$ and $T_p$ represent the values of minimum and peak transmittance, their thickness can be derived using the envelope method with the following equations:

$$\frac{1}{T_m} - \frac{1}{T_p} = \frac{1}{4} \left( n^2 - 1 \right) \left( n^2 - n_s^2 \right)$$

(2)

From Eqn. (2) $n$ can be found as,

$$n = \sqrt{N + \sqrt{\left( N^2 - n_s^2 \right)}}$$

(3)
The thickness of the thin film is calculated using the formula

$$d = \frac{\lambda_1 \lambda_2}{2(n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1)}$$  \hspace{1cm} (5)$$

Here, $T_P$ and $T_m$ at the required wavelengths are calculated by tracing the envelopes of the peak and minimum transmittances covering the range of data, $n$ represents the refractive index of the thin film and $n_s$ represent the refractive index of the substrate. $\lambda_1$ and $\lambda_2$ refer to the wavelengths of two corresponding maxima or minima. The thickness of the thin films as calculated from the UV-VIS spectra are found to be 792nm and 867nm respectively for TF1 and TF2. This method is quite reliable since the above equations are derived on the basis of interference effects of light on thin film and is employed by other authors in deriving the thickness of various thin films in which few of them showed that the accuracy of this method is quite good and that the error percentage compared to the values obtained by ellipsometry is within 4\% [16-21].

Anatase TiO$_2$ is an indirect band gap semiconductor. The transmittance of the films TF1 and TF2 in the wavelength range 300-800nm is shown in Fig. 4(a). The calculated values of the indirect band gap obtained from the plot of $(\alpha h\nu)^{1/2}$ vs $h\nu$ as shown in Fig. 4(b) for TF1 and TF2 annealed at 450˚C is 3.45 and 3.38eV. The band gap of thin titanium dioxide films is usually in the range of 3.2-3.23eV [6]. There is a rise in band gap which account to a rise of ~4-7\%. There could be two reasons for the rise in band gap, either high dislocation density around grain boundaries over thin films or due to quantum effect if the size of the particles is below Bohr radius (2.35nm for TiO$_2$ particles) [22]. From the TEM pictures of the TiO$_2$ particles annealed at 450˚C (Fig. 1d), it can be seen that the size of the particles is between 8-10nm. Hence the radius of the particles, assuming them to be near spherical as seen from the TEM picture, is larger than the Bohr radius. Therefore quantum effect is not responsible for the increase in band gap. The TiO$_2$ sol is synthesized by modifying the precursor with organic solvents. These solvents form chelating agents and are bound to the TiO$_2$ molecules upto temperatures beyond 450˚C. The presence of these organic bonds may be responsible for the dislocation density around the grains over the thin films resulting in rise in band gap. When TF2 is annealed at 500˚C, the band gap is reduced to 3.18eV. The band gap of bulk anatase phase TiO$_2$ is 3.18eV. The organic compounds completely vanish at temperatures of 500˚C and above. Hence the film TF2 which is annealed at 500˚C show the band gap equal to that of the bulk TiO$_2$. 

![Figure 4.](image-url)
layers the film becomes compact and thicker. The refractive index of the films annealed at higher temperature increases due to compactness and increases the grain size of the film which is evident from Fig. 5.

3.5. Dye Sensitized Solar Cells Characterization

The SEM pictures of green and annealed thin TiO$_2$ films are shown in Fig.6 (a) and Fig.6 (b). The SEM photographs show the morphology of the green and annealed films developed by spin coating TiO$_2$ paste on sol-gel developed TiO$_2$ films. The grain size of the annealed thin films at 450°C is about 13-20nm.

The assembled solar cell with an effective area of 0.25cm$^2$ is characterized under different illuminations of 0.1Sun, 0.4Sun, 0.6Sun and 1Sun for current voltage measurements.

At different illuminations, there is a very slight change in open circuit voltage of the solar cell while the short circuit current is seen to change linearly with illumination. Fig. 7 shows the current and voltage characterization of the solar cell at different illuminations. The open circuit voltage of assembled cell at 1Sun is found to be 0.72V and short circuit current density is 13.87mA/cm$^2$ as depicted in Fig.8.
The corresponding fill factor and efficiency are found to be 0.68 and 6.77% respectively. For the solar cell assembled with TF3 the inset in Fig.8 shows the trend of I-V characteristics measured under dark while the Fig.8 depicts the I-V characterization of the assembled solar cell under illumination. An equivalent two diode model is used to fit the dark I-V characteristics of the assembled solar cell. From the two diode model, the forward bias characteristics of the solar cells in the dark is given by

\[
I = I_{01}\left(e^{\frac{q(V-IR_s)/kT}{\eta_1 kT}} - 1\right) - \frac{V - IR_s}{R_{sh}}
\]

where \( R_s \) represents series resistance, \( R_{sh} \) represents shunt resistance, \( \eta_2 \) represents diode ideality factor of dye sensitized solar cells, \( I_{01} \) represents diffusion current and \( I_{02} \) represents generation recombination current. For a typical dye sensitized solar cells the diode ideality factor lies between 1 and 2 [5]. For ideal case diode ideality factor should be 1 while in non-ideal case the defects drive the factor upto 2. Externally measured ideality factor is the sum of ideality factors of individual junctions which makes ideality factor >> 2 and varies with the film thickness. The values obtained here are of films with different conductivities, there cannot be any comparison done for these values with that of normal diodes. The accumulation of electrons at the metal semiconductor junction and defects in the semiconductor also increases the ideality factor [16]. Using the above model, the shunt resistance has been obtained by curve fitting for the assembled solar cell under dark and is found to 20KΩ. The decrease in shunt resistance will lead to larger recombination reducing the open circuit voltage. For an ideal cell the shunt resistance in infinity which means that the electrons do not have alternate path to flow. Therefore, dark I-V characterization can be a powerful tool to analyze the performance of solar cells before assembling them into modules.

Figure 8. Current-Voltage Characteristics of the Dye Sensitized Solar Cells Under 1 Sun Illumination And (Inset) I-V Characterization of Assembled Solar Cell Under Dark

4. Conclusions

Highly transparent thin films of n-TiO₂ with good adhesion are obtained using sol gel synthesis followed by spin coating. The prepared films are characterized in terms of their phase formation behavior and morphological characteristics. The lattice constants are \( a = 3.79\,\text{Å} \) and \( c = 9.48\,\text{Å} \) from XRD characterization and \( a = 3.79\,\text{Å}, \ c = 9.46\,\text{Å} \) from TEM characterization. The thin films are found to be of large band gap. The thicknesses of the films are found to be 792nm and 867nm for TF1 and TF2, respectively. The refractive indices for these films are between 2.7 and 2.2 for the wavelength range 370nm to 750nm while the refractive index is higher than 2.4 for wavelengths smaller than 370nm. The values of band gap for both TF1 and TF2 films are 3.45eV and 3.38eV respectively. The band gap of the annealed thin film (TF2 annealed at 550°C) is found to be 3.48eV. The phase of the n-TiO₂ particles on the annealed thin films is found to be anatase phase. The assembled dye sensitized solar cells consisting of modified TiO₂ electrodes has an efficiency of 6.77% with a fill factor of 0.68.
Acknowledgements

The authors would like to express their gratitude to the Director-CSIR-CMERI for his kind permission to publish the paper. The authors are also grateful to CSIR, Govt. of India, for the financial support through networking projects (NWP-0051). The help rendered by our scientific & technical staffs of CAMP, CSIR-CMERI, Durgapur is acknowledged. The authors are also thankful to Indian Association for the Cultivation of Science (IACS), Kolkata and National Institute of Technology (NIT), Durgapur for HRTEM and XRD studies respectively.

REFERENCES


