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Study of Annealing Temperature Effect on the Performance of ZnO Nanostructure Based DSSC Fabricated by Simple Chemical Bath Deposition Technique

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ABSTRACT: *ZnO nanostructures were grown on FTO coated conducting glass substrates using simple Chemical Bath Deposition (CBD) technique. The prepared samples were annealed at different temperatures namely 200°C, 300°C, 400°C, 500°Cand used as photoanodes in the Dye Sensitized Solar Cells (DSSC). The Solar Cells were fabricated with Eosin Y as Dye, Iodine/Iodide based electrolyte and Graphite coated FTO as counter electrode.The crystal structure, morphology and optical properties were studied for the photoanodes annealed at different temperatures. The degree of crystal orientation of ZnO nanoparticles were determined by X-ray diffraction (XRD) spectrum. The average grain sizes of the ZnO nanostructures was calculated using Scherrer formula and the average grain size were found to increase with the increasing annealing temperature. The hexagonal rod like nanostructures were obtained from Scanning Electron Microscopy (SEM) for the photo anode annealed at 500°C. The direct band gap energies were obtained from UV – Visible absorption spectrum. The conversion performance of the cells was studied with the variation in annealing temperature of ZnO thin films.*
Keywords: *Annealing, CBD Technique, Dye-sensitized solar cell, Photo electrode, ZnO*

I. INTRODUCTION

The need for effective renewable energy is becoming very important to overcome therapidly increasing fossil fuel consumption and excessive greenhouse gas emissions. When the non-renewable resources are consumed, they are not available for future generation and it takes a longer time period for nature to create it again. Nuclear power plant gives a large amount of energy but is extremely hazardous due to its radioactive waste. While, nuclear fusion process is still in experimental stage and is difficult to contain the reaction in a solid container at that temperature of Sun. In India, around 70% of the electricity is generated by thermal power plants [1]. O'Regan and Grätzel developed Dye Sensitized Solar Cells which plays an important role in solar energy harvesting and is cost effective compared to the conventional Silicon solar cells [2].

DSSCs are third generation photovoltaic cells that convert light energy to electrical energy.A DSSC in general consists of a semiconductor (e.g. TiO_2, ZnO and SnO_2) thin film as a photo-anode that is coated or grown on a conductive substrate, a sensitizer (i.e. dye; e.g. N719, N3 or natural dyes from pomegranate, berries etc.,)[3, 4, 5], an electrolyte (redox couples) injected between the sensitizer and counter electrode, and a counter electrode (e.g. Pt and carbon materials) deposited on another conductive substrate[6, 7]. When the photo-anode is exposed to light radiations it causes photo-excitation of the absorbed dye molecules. Thus generated excited electrons are subsequently injected into the conduction band of the semiconductor and thus an electric current flow from photo anode to conductive substrate and to external circuit. The dye is subsequently restored to its original state by electron donation from the redox electrolyte. Thecounter electrode returns charge from the external circuit backto the cycling circuit in the cell [8].

DSSCs fabricated using ZnO nanostructures as photoanode are researched more in the present decade due to its direct wide band gap (3.3 eV), large exciton binding energy (60 meV),high infrared reflectivity, high electrochemical stability, excellent electronic properties and cost effectiveness compared to TiO_2 as photoanode [7]. In this research study, ZnO nanostructures grown on FTO coated conducting glass substrates using simple Chemical Bath Deposition (CBD) technique are used as photoanodes in the Dye Sensitized Solar Cells (DSSC). The effect of annealing of photoanodes on the conversion efficiencies of the fabricated DSSCs is studied.

II. EXPERIMENTAL METHOD

2.1 Materials Used

Fluorine doped tin-oxide (FTO) with a resistance 13 Ω/sq.(Dyesol-TCO) measuring 2x2 cm^2 are used as TCO substrate.Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and Hexamine ($(CH_2)_6N_4$) (Merck make) were used as precursors for ZnO coating and were used as purchased without further purification.The ZnO coating on FTO substrates were carried out in constant temperature water bath and the post annealing of coated samples were done using the muffle furnace.

2.2 Procedure

2.2.1Photo-anode fabrication

ZnO nanoparticles were prepared by Chemical bath deposition (CBD) technique. An aqueous solution was prepared by dissolving 2.4g of Zinc nitrate hexahydrate, 0.12g of Hexamine in 80mL of single distilledwater. This solution was stirred at room temperature for 1 hour in magnetic stirrer. The FTO substrates were immersed vertically in this prepared solution at a temperature of 80°C maintained in the constant temperature water bath for 4 hours. ZnO coated FTO substrates was then removed from the solution and washed many times with distilled water and ethanol and dried. Each of the dried samples wasthen annealed in a muffle furnace for 1 hour at temperatures namely 200°C, 300°C, 400°C and 500°C.

2.2.2 Dye Sensitization

Eosin Y ($C_{20}H_6Br_4Na_2O_5$) is used as a dye. 1mM of Eosin Y is dissolved in 20mL of Ethanol. The dye solution is stirred at room temperature for 30 minutes in magnetic stirrer. The ZnO coated FTO substrates were soaked in the dye solution for 15 min. The dye sensitized electrode was prepared for all the samples by this method.

2.2.3Electrolyte preparation

Iodide/Iodine electrolyte was freshly prepared and used for every assemble DSSC. Iodine (I_2), Potassium Iodide (KI),and Ethylene Glycol were bought from commercial sources. 0.127g of Iodine (I_2) was dissolved in 10mL of Ethylene Glycol and 0.83g of Potassium Iodide (KI) was added and stirred until the solution is completely dissolved[9].

2.2.4 Assembling the DSSC

FTO substrates were cleaned by acetone and isopropyl alcohol and ZnO nanostructures were grown on it by CBD technique. The dye sensitized ZnO coated photoanode is sandwiched with the Graphite counter electrode using the binder clips. A drop of electrolyte was added in between the FTO substrates by using the capillary action of binder clips until the electrolyte was filled. Assembled DSSC is shown in Fig. 1

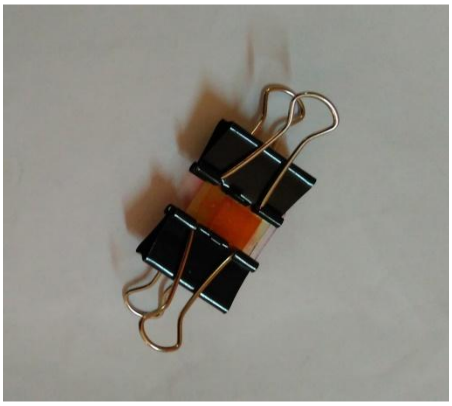

Fig.1. Assembled DSSC

2.3 DSSC Characterization

The crystal orientation of nanoparticles was recorded by XRD (GE X-ray diffraction system-XRD 3003 TT with CuKα radiationof wavelength 1.5406 Å). The morphologies of the photoanode were characterized by using SEM (FEI Quanta FEG 200-High Resolution Scanning Electron Microscope (SEM)). To analyse the light absorption of ZnO photoanodes, UV-Vis-NIR (Cary 5E UV-VIS-NIR instrument) was used. DSSCs were illuminated under a standard solar simulator (1000W/m^2) with current-voltage (I-V) characteristics acquired by a Keithley 2400 sourcemeter (2400 SourceMeter SMUInstrument).

III. RESULTS AND DISCUSSIONS

3.1 Crystal structure - XRD Analysis

The crystalline nature of the ZnO nano/micro structure was studied using X- ray diffraction (XRD). XRD pattern for all the samples have been shown in Fig.2.All the XRD peaks matched well with the JCPDS file no.79-0205of ZnO and indexed accordingly.No new peaks were detected in the XRD. Intensityof the peaks was found to depend on the annealing temperatures of the samples. XRD results show that the films have preferential orientations along (002), (101) and (102) direction, but when the annealing temperature is increased above 400°C, the films show (002) to be more dominant. Particularly, the XRD pattern obtained for the ZnO substrate annealed at 500°C, the intensity of the peak assigned to the (002) plane of wurtzite ZnO was high compared to the rest of the planes. This shows the ZnO nanostructures growth with preferential *c*-axis orientation perpendicularly to the substrate. The average grain sizes of the ZnO nanostructures calculated using Scherrer formula were found to increase with the increasing annealing temperature.

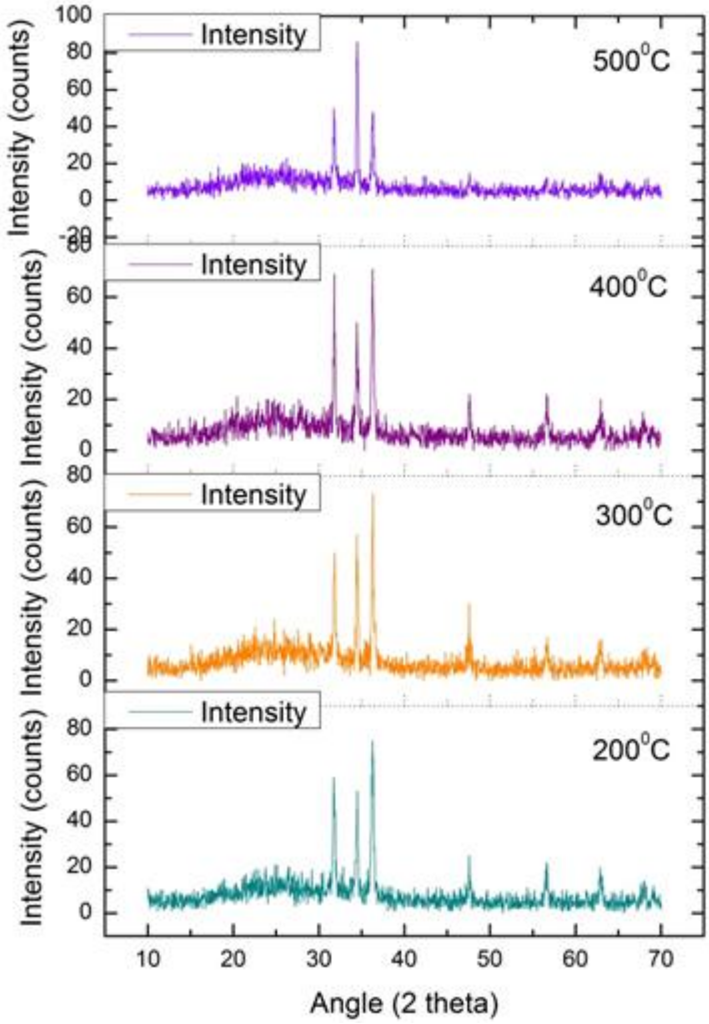

Fig.2 XRD pattern of ZnO at various annealing temperatures

The average grain sizes of the ZnO nanostructures calculated using Scherrer formula (1) were found to increase with the increasing annealing temperature.

$$D = \frac{k\lambda}{\beta cos\theta} \quad (1)$$

The average grain size was calculated for the dominant peak orientations along (100), (002), (101) and is shown in the Table.1 -

Table.1 Average size of samples

Sample annealed at 200°C	Average size (nm)
(100)	23.14
(002)	24.99
(101)	22.38
Sample annealed at 300°C	Average Size (nm)
(100)	25.168
(002)	26.37
(101)	29.89
Sample annealed at 400°C	Average Size (nm)
(100)	27.80
(002)	23.39
(101)	24.05
sample annealed at 500°C	Average Size (nm)
(100)	23.14
(002)	25
(101)	22.38

3.2 Morphology structure – SEM analysis

The SEM images of ZnO nanostructure morphologies for the sample annealed at 500°C are shown in Fig.3.

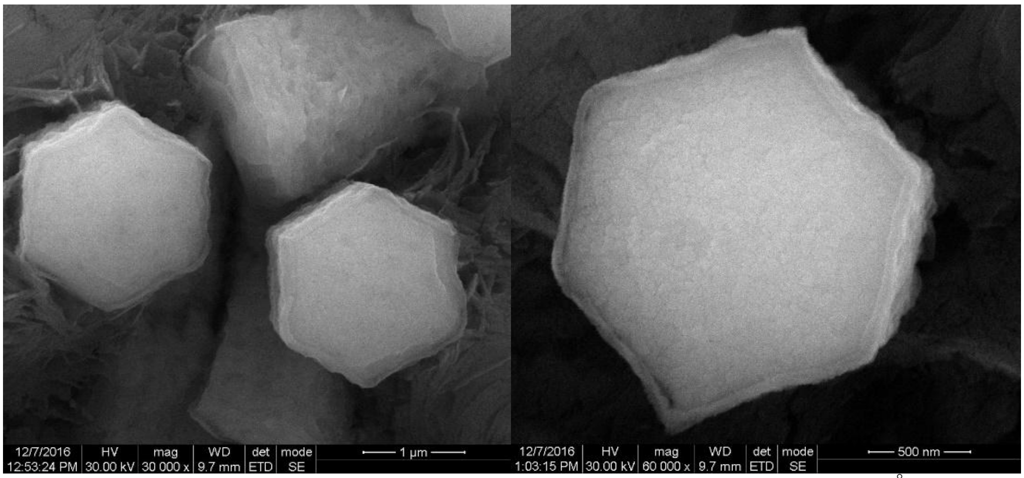

Fig.3 SEM images of ZnO particles using CBD technique annealed at 500°C

Hexagon shapednanorod growthwas obtained from SEM images for ZnO photoanode annealed at 500°C.The imagesreveal porous nanostructures on the surface with a nano/micro rod growth perpendicular to the plane of the substrtqate. This provides a direct path for the electron transfer from photoanode to the conducting surfdace. This leads to much higher electron mobility and decreases the time for electron to travel to the electrode. The dye molecules get attached to the ZnO photoanode and thus act as a sensitizer for efficient light harvesting [10, 11]. Light absorption of the DSSC can be increased without affecting the efficient electron transport. This gives an increase in the performance of DSSCs.

3.3 Optical Properties – UV-Vis Absorption Spectroscopy

The UV-Visible absorption spectrum of ZnO nanostructures annealed at temperatures 200°C, 300°C, 400°C and 500°C are shown in Fig.4. The characteristic absorption of ZnO nanostructures in the UV region from 200 to 370nm is observed in all samples. The spectra also revealed that the ZnO thin film has a low absorbance in visible region (400-690nm).

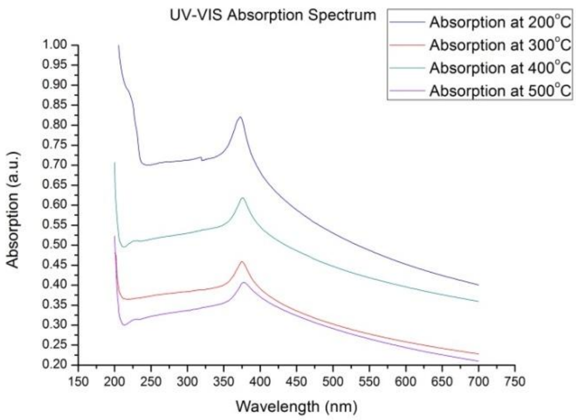

Fig.4. UV-Visible absorption spectrum at various annealing temperatures

In the absorption spectra,peak shift from 373nm, 375nm, 376nm, 377nm was detected for the samples annealed from 200°C, 300°C, 400°C, and 500°C.This shift may be due to the change in the size of the particles. The corresponding band gap of ZnO were calculated as 3.32eV, 3.3eV, 3.29eV, 3.289eV annealed from 200°C, 300°C, 400°C and 500°C.

3.4 J-V Characteristics

The performance of the DSSC was analyzed by calculating the fill factor and efficiency for each DSSCs.

Fill factor (FF)is calculated using this formula,

$$FF = \frac{Jmax \times Vmax}{Jsc \times Voc} \qquad (2)$$

Efficiency(η) is calculated using this formula,

$$\eta = \frac{Voc \times Jsc \times FF}{Pin} \quad (3)$$

The maximum efficiency was obtained to be 0.38% for the DSSC with photoanode annealed at 500°C. The Fig.5 shows the J-V characteristic graph for the photoanode annealed at 500°C.

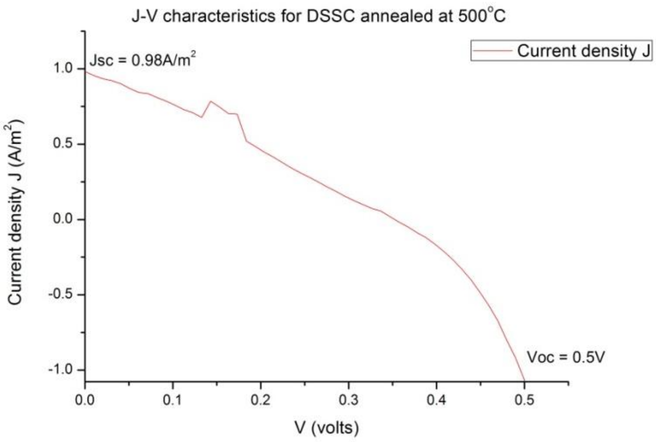

Fig.5. J-V characteristics for DSSC annealed at 500°C

The open circuit voltage was found from Keithley solar source meter and is shown in Table.2.

Table.2 Open circuit voltage of Photoanodes annealed at various temperatures

Annealing Temperature of photoanodes (°C)	Open circuit voltage (V)
200	0.325
300	0.41
400	0.4
500	0.5

The maximum open circuit voltage (Voc) for the DSSC was found to be 0.5V when annealed at 500°C. It is found that the Voc value increased from 0.325 to 0.5 V when the annealing temperature was increased from 200 to 500°C. This is a noticeable 53.8% increase in Voc with increase in annealing temperature.This may be due to the porous nanostructures and micro/nano rod growth and improved crystallinity of the photo anode annealed at 500^0 C, making it possible for more dye adsorption in the sample compared to 200^0 C annealed sample. Thus it is understood that that the morphology of the coated nanostructures play a crucial role in improving the conversion efficiency of the DSSCells.CBD technique adopted here is found to be preferable method of growing ZnO nanostructures on FTO substrates for photoanode, with the ease of preparation, low temperatures involved and cost effectiveness of the method.

IV. CONCLUSION

In this study, ZnO coated DSSC were prepared using CBD technique and annealed at various temperatures and the performance of the DSSC was studied from open circuit voltage.The maximum open circuit voltage (Voc) for the DSSC was found to be 0.5V when annealed at 500°C. It is found that the Voc value increased from 0.325 to 0.5 V when the annealing temperature was increased from 200 to 500°C. This is a noticeable 53.8% increase in Voc. The present study show that the ZnO coated photo anode annealed at 500°C DSSC prepared by the simple cost effective CBD technique was found to be more efficient cells compared to the ZnO based DSSCs annealed at lower temperatures. This might be due the improvement of crystallinity of the sample with the preferential c- axis oriented nano/micro rod growth in the samples annealed at 500°C. CBD technique adopted here is found to be preferable method of growing ZnO nanostructures on FTO substrates for Photo anode, with the ease of preparation, low temperatures involved and cost effectiveness of the method. The performance of DSSC can also be increased by increasing the thickness of ZnO nanoparticles. This can absorb more dye and thus it leads to absorbance of more light photons.

A much more detailed study is also planned in future with the natural dyes in the place of Eosin Y to understand the effectiveness of photoelectron production in ZnO based DSSCs.Thus the study show the noticeable effect of annealing temperature on the performance of ZnO nanostructure based DSSC fabricated by simple Chemical bath deposition technique.

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