RESEARCH ARTICLE

FABRICATION OF DYE-SENSITIZED SOLAR CELLS BASED ON STRUCTURAL AND OPTICAL PROPERTIES OF ZNO NANORODS

*Ravikumar S[1], Venkatachalam V[1], Saroja M[1], Gowthaman P[2], Thamarai Selvan P[2] and Shankar S[1]

[1]Department of Electronics, Sengunthar Arts and Science College, Tiruchengode, India
[1]Thin film Centre, Department of Electronics, Erode Arts and Science College, Erode, India
[2]Department of Electronics & Comm, Selvamm Arts & Science College, Namakkal, India

ABSTRACT

Thin films form a fair share in the ever growing solar cell research and also in the market. One of the most versatile materials grown as thin films today are from derivatives of pure and doped Zinc Oxide. A combination of dip coating and hydrothermal technique is a powerful tool in order to achieve good quality ZnO thin films. The initial run is made by dip coating process where a supersaturated solution of the material to be coated is taken in a beaker. A glass substrate is dipped into the supersaturated solution and dried for an optimal amount of time. Multi layered thin film coatings are formed and dried consequently before each individual dipping to enhance uniformity. Pure thin films of Zinc Oxide are initially grown by hydrothermal method with thickness varying so as to reach the optimal solar cell quality. These ZnO thin films are investigated for their structural and optical properties to fabricate dye sensitized solar cells. The prepared ZnO ruthenium based DSSC reached a total IPCE of 3.03%.

INTRODUCTION

ZnO is an important semiconductor with direct band-gap of 3.37 eV and high exciton binding energy of 60 meV . Thus, zinc oxide can be a promising candidate for novel applications such as UV detectors (Safa *et al* , 2014), field emission devices (Zhu *et al* ,2003) Efficient field emission from ZnO nano needle arrays. Applied), high sensitivity gas sensors (Shishiyanu *et al* , 2007) , biosensors (Zhang *et al* , 2004) , dye-sensitized solar cells (Repins *et al* , 2008) , photo luminescent materials (Lawrie *et al* , 2009) , photocatalytic degradation of pollutants (Gowthaman *et al* , 2011) and antibacterial purposes (Akhavan *et al* , 2011). One of the key properties of ZnO is that when it is exposed to light, photo excited electron-hole pairs will be generated. Thus, the ZnO nanostructure with narrower band is usually preferred.

Obviously, the size of ZnO nanorods play important role in optimizing the optical properties of ZnO nanorod array films. In this paper, ZnO nanorod films were prepared by hydrothermal method at the low temperature of 90°C. Effect of the growth temperature of ZnO nanorod films structure and morphology properties were investigated by XRD and SEM. A dip coating method was applied to deposit ZnO films on the glass as a seed layers. The grown ZnO nanorods were studied in detail. ZnO has nearly the same band gap and electron affinity as TiO2, making it a possible candidate as an effective DSSC semiconductor. ZnO nano particle DSSCs have shown the second highest efficiencies after TiO2. (Keis *et al* , 2002) Additionally, there is a wealth of information regarding the processing and properties of ZnO nanorods and a large variety of morphologies that are accessible by either vapor deposition (Park *et al* , 2002 ; Huang *et al* , 2001) or solution growth methods (Vayssieres *et al* , 2003 ; Greene *et al* , 2003 ; Peterson *et al* , 2004).

In this article, we report the growth of ZnO nanorods with wurtzite hexagonal structure and the use of these nanorods as the wide band gap semiconductor in DSSCs. Our objective is to introduce and demonstrate new possibilities in designing the semiconductor morphology in DSSCs. While we focus on ZnO, similar strategies can be used with TiO2 and the possibilities are only limited by availability of synthesis methods to produce the appropriate nanostructures.

MATERIALS AND MEHODS

Seed layers were deposited on the glass substrates by dip coating method. All the reagents used in the experiment were analytically pure and used without further purification. Prior to

---

*Corresponding author: **Ravi kumar S**
Department of Electronics, Sengunthar Arts and Science College, Tiruchengode, India

deposition, the glass substrates were cleaned with de-ionized water, acetone, chromic acid solution, sodium hydroxide solution, 2- propanol, ultrasonic agitator and finally dried in a hot air oven at 70°C for 10 minutes. 0.1 mol of zinc acetate was dissolved into 10ml of ethanol, wherein white floccules immediately appeared as soon as they were mixed. Then 0.25ml of distilled water was introduced drop by drop through syringe. Under stirring, the solution was transferred into a clear and homogeneous solution. The above solution was stirred continuously for 2 hours at room temperature. The seed solution was deposited on well cleaned glass substrates for five times at regular intervals of one minute at 70°C temperature. The five layer films were annealed in a muffle furnace at 200°C for 1 hour.

ZnO nano rods were grown on seed layer deposited glass substrates by hydrothermal method for 5 hours at 80°C, 90°C, and 100°C growth temperatures. Zinc nitrate hexa hydrate Zn $(NO3)2.6H20$ and hexamethylenetetramine (HMT) $C6H12N4$, were employed as precursors. The molar concentration of the precursors was taken in the ratio of 1:10 with 0.02 mol of zinc nitrate and 0.2 mol of HMT. The above solution was mixed through magnetic stirrer for 2 hours. In the growth process, the ZnO seed coated glass substrates were immersed in solution. The solution was heated with a hot air oven and maintained at different growth temperatures of 80°C, 90°C, and 100°C for 5 hours. At the end of the growth period, the substrates were removed from the solution and rinsed immediately with deionized water to remove the residuals from the surface and dried in air. Then the above films were annealed in muffle furnace at 500°C for 1 hour. The crystal structure and morphology of ZnO nano rods were investigated by X-ray diffraction (XRD) and Scanning Electron Microscope (SEM). The absorbance spectra have been recorded using a spectrophotometer JASCO V-570. The photoluminescence spectra of the prepared ZnO nanorods have been recorded using a HORIBA JOBIN YVON- Fluorolog at an excitation wavelength of 350 nm.

To prepare ZnO thin films for dye sensitized solar cell; the paste was prepared by mixing 2.0 g of synthesized ZnO powders with a mixture consisting of 5.0 g of -terpineol, 0.5 g of cellulose, and 20 ml of ethanol, which was sonicated for 24 hrs at 1200 Wcm^{-2}.(Senthil *et al* , 2014). By using the prepared paste ZnO thin films were prepared by coating the paste on a FTO conducting glass plate (Hartford FTO,~30 cm^{-2}, 80% transmittance in visible region) using the doctor blade technique. The prepared films were annealed at 450°C for 30 min.

In cell assembly section, to prepare dye sensitized solar cells, the prepared thin film electrodes were immersed in a 3.0×10^{-4} Mole, N719 [RuL$_2$(NCS)$_2$]:2TBA, (L=2,2'-bipyridyl-4,4'-dicarboxylic acid; TBA=tetra-n-butylammonium) dye solution at room temperature for 24hrs, after that period the film was rinsed with anhydrous ethanol, and dried. The structure of the dye is shown in figure 1.

A platinum coated FTO electrode was then placed over the dye adsorbed electrode, and the edges of the cell were sealed with a sealing sheet (PECHM-1, Mitsui-Dupont Polychemical) by heating with hot plate at 100°C for 2 minutes. A redox electrolyte consisting of 0.5M KI, 0.05M I$_2$, and 0.5M 4-tertbutylpyridine was used as a solvent and a drop of electrolyte solution was injected into the drilled hole in the counter electrode and was driven into the cell. Finally, the hole was sealed using additional cello tape and the size of the electrodes used was 0.4 cm. Thickness of the films has been determined using gravimetric method and confirmed using stylus profilometer. The thickness of the deposited ZnO films has been found to lie in the range of 800-850 nm.
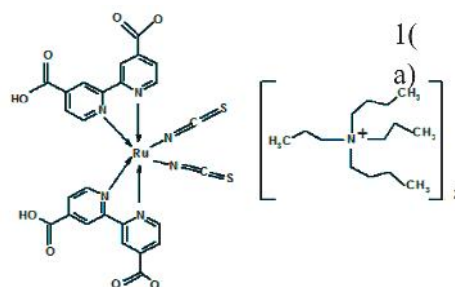

Fig 1 The structure of Ruthenium (N719) dye.

RESULTS AND DISCUSSION

Fig. 2 shows the XRD patterns of the prepared thin films with growth solution Zinc nitrate and Hexamethylenetetramine (HMT), with different growth temperatures of 80°C, 90°C and 100°C for 5 hours. All the diffraction peaks can be indexed within experimental error as hexagonal ZnO phase (Wurtzite - structure) which matches with the JCPDS card no: 036-1451.
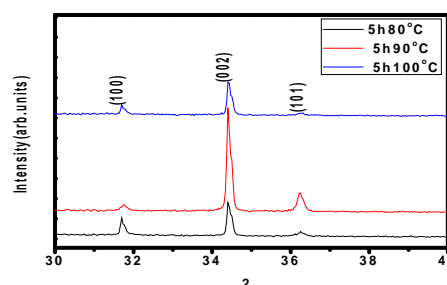

Fig 2 XRD pattern of ZnO thin films at 80°C, 90°C, and 100°C for 5 hours.

The strong and narrow diffraction peaks indicate that the material has a good crystallinity. The XRD patterns of the films at growth temperature of 80°C and 100°C for 5 hours annealed at 500°C shows that, it has a moderate (002) peak, weak (101) and (100) peak. The XRD pattern growth temperature of 90°C for 5 hours annealed at 500°C has a very strong (002) peak and weak (100) and (101) peak. From the above XRD patterns it is clearly seen that, at the growth temperature of 90°C the diffraction peaks were oriented strongly along the (002) peak. This implies that the grown nanorods show perfect c-axis orientation which is in accordance with SEM images. The average size of the ZnO particle is calculated using Debye Scherer formula,

$$davg = 0.9 \ / \ Cos$$

where *davg* = average crystal size,   = Wavelength of incident beam (1.5406A) ,   = FWHM in radians and   = scattering angle in degree. The grain size of the nano particles are found to be 108.88nm, 109.709nm and 113.137nm for growth temperatures of 80°C, 90°C, and 100°C respectively. This implies that growth temperature influences the particle size.

The SEM images of the products are given in Fig.3(a), Fig.3(b) and Fig.3(c). Many rod-like hexagonal structures can be clearly seen. The sizes of the products are homogeneous and the mean size is about 100 - 300 nm. The images can be indexed as hexagonal Wurtzite-structural ZnO, which is very consistent with the analysis of XRD. As stated in the XRD patterns, the SEM images of the ZnO nano rods indicates that the length of the ZnO nano rods is maximum when the growth temperature is at 90°C. It indicates that the samples grown in same solution experienced different growth rate of nano rods at 80°C and 100°C.
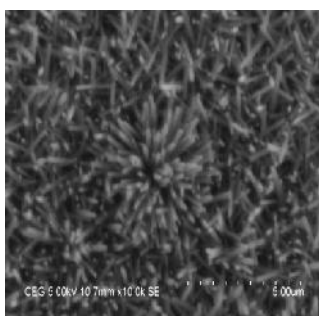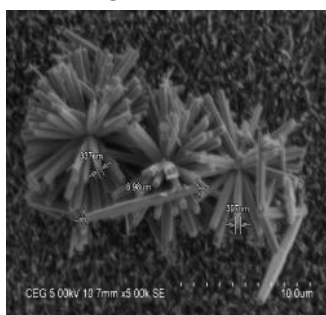

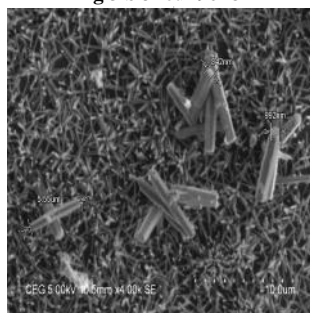**Fig 3 a** 5hour 80°C

Fig 3 b 5hour 90°C

Fig 3 c 5hour 100°C

ZnO nanorods

The growth rate is defined along with growing length per growth temperature. Fig.3a and Fig.3c shows SEM images of ZnO nanorods grown at 80°C and 100°C in which rods have grown in all directions in a flower like pattern, which reveals the XRD patterns, where all three peaks are moderately reflected. Fig.3b shows SEM image of ZnO nanorod grown at 90°C. These rods show hexagonal structure with increase in

diameter and its length towards c-axis orientation. This result relates with the peaks as indicated in the XRD pattern.
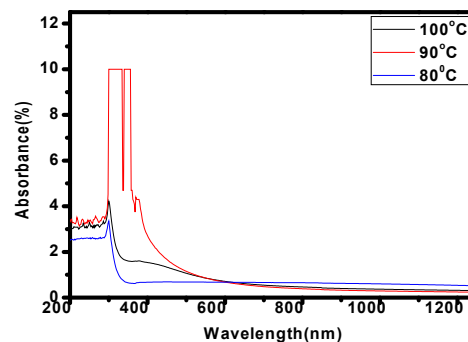

Fig 4 UV-Vis absorption spectra of ZnO at three different growth temperatures

The optical absorption in the UV region and corresponding photo efficiency influences the use of ZnO nanorods for photo catalytic and solar cell activities (Wilson *et al* , 1996). Fig.4 shows the absorption spectra of ZnO nanorods. The optical absorption edge has a tendency to shift to an upper wavelength with increase in growth temperature. It is well identified that the optical absorption determines the optical band gap of ZnO films which has a direct band gap. The optical band gap of ZnO films at growth time of 5 hours for 80°C, 90°C and 100°C growth temperature was found to be 3.40 eV, 3.23 eV and 3.25 eV respectively. With the increase of growth temperature from 80°C to 90°C, the band gap decreases from 3.40 eV to 3.23 eV. Considering the results, it is clearly indicated that as growth temperature increases the band gap decreases. The decrease in band gap of ZnO films may be attributed to the improvement in the crystalline quality of the films along with the reduction in porosity and increase in grain size.
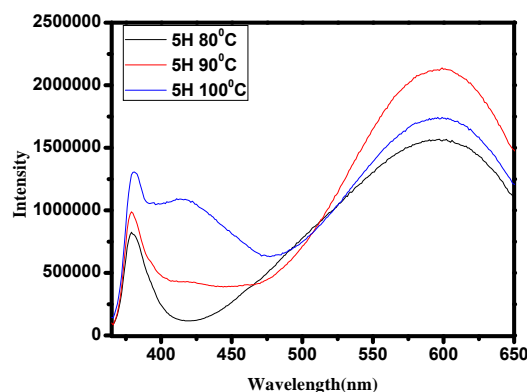

Fig.5 Room temperature Photoluminescence spectra obtained at three different growth temperatures

The Room temperature Photoluminescence spectra of ZnO samples obtained with an excitation wavelength of 350nm for three different growth temperatures of 80°C, 90°C and 100°C is shown in the fig.5. The Ultraviolet (UV) emission peak in the range of 340-380 nm shows the PL spectra, with moderate intensity of peaks. The UV emission also called the near band edge emission (NBE) may originate from free excitonic emission in the ZnO materials as ZnO has a high exciton binding energy of 60meV at room temperature. Besides the

medium UV emission peak, PL spectrum covers the surface related strong visible PL emission peaks which dominates all PL spectra in the wavelength range of 550-650nm. The intensity of this broad visible PL emission is highly sensitive to the environment and mainly depends on the surface to volume ratio of the nano particles (Ghosh *et al* , 2008).

The obtained PL results of the samples indicate that the visible PL emission is enhanced while the UV emission is suppressed as growth temperature increases and particularly at 90°C, due to large competition from the defect emission and increase in both the oxygen vacancies and zinc interstitials (Tian *et al* , 2009).
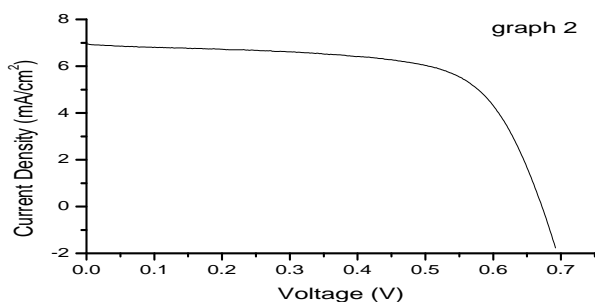

Fig 6 IV graph of the solar cell.

Fig.6 shows the current – voltage (I-V) characteristics for DSSCs constructed using Ruthenium dye (N719) and measured under a stimulated illumination with a light intensity of 100mW / cm2. The fill factor (FF) DSSC was calculated using the equation,

$$FF = I_{max} V_{max} / I_{sc} V_{sc}$$

and the incident photon – to – current (IPCE) efficiency ( ) was calculated using the equation

$$(\%) = I_{max} V_{max} / P_{inc} . A$$

where I_{max} and V_{max} are the current and voltage obtained at the maximum power point on the photovoltaic power output curve and P_{inc} is the intensity of the incident radiation and A is the area of illumination respectively. In the present work the incident illumination was 100 mW / cm^2 and the area of illumination was 0.5 cm x 0.5 cm. In principle, the maximum I_{sc} of a dye-sensitized solar cell is determined by how well the absorption window of the dye overlaps with the solar spectrum. The solar cell parameters are given in table 1.

Table 1 Solar cell parameters

Sentizer	J_{SC}(mA/cm2) x10^{-3}	Voc(V)	Jmax (mW x10^{-3})	FF	%
Ruthenium (N719)	6.762	0.6735	1.212	6.653	3.030

CONCLUSION

ZnO nano rods had been successfully synthesized in a hydrothermal method at low growth temperature of 90°C for 5 hours and annealed at 500°C. The prepared ZnO nanorods were characterized by XRD, SEM, UV and PL. From the XRD results, it is clearly seen that, at the growth temperature of 90°C the diffraction peaks were oriented strongly along the (002) peak. The grain size of the nano particles are found to be increasing as growth temperature increases. SEM results

clearly show that nanorods grown at 90°C have hexagonal structure with increase in diameter and length towards c-axis orientation when compared to 80°C and 100°C. The UV-Vis Absorption spectra show that band gap of the grown rods decreases from 3.40 eV to 3.23 eV as growth temperature increases. The PL spectrum shows two emission bands, near band edge emission in the UV region and high intensity broad emission in the visible region. From the results it is shown that the high quality ZnO nano rods can be grown using hydrothermal process and one can apply these high quality ZnO nano rods on the electrode of dye-sensitized solar cell to increase the contact area between ZnO and dye, follow-on in the enhancement of efficiency for dye-sensitized solar cell. These ZnO nanorods were used for the preparation of DSSC with ruthenium dye (N719). ZnO nanorod based dye sensitized solar cells have been fabricated using a liquid electrolyte and organic dyes. Due to the improved Isc and FF, the ruthenium based DSSC reached a total IPCE of 3.03%.

References

1. B. J. Lawrie, R. F. Haglund, R. Mu. (2009) Enhancement of ZnO photoluminescence by localized and propagating surface plasmons. Opt. Express, Vol. 17, No. 4, 2009, pp. 2565-2572.

2. E.Wilson, (1996), Enhanced visible light photocatalysis through fast crystallization of zinc oxide nanorods , Chem.Eng.News, 74,29-33.

3. F. Zhang, Xiaoli Wang, Shiyun Ai,Zhengdong Sun, Qiao Wan, Ziqiang Zhu,Yuezhong Xian, Litong Jin, KatsunobuYamamoto. (2004) Immobilization of uricase on ZnO nanorods for a reagentless uric acid biosensor. Analytica Chimica Acta, Vol.519, No. 2, pp. 155-160.

4. K. Keis, E. Magnusson, H. Lindstrom, S.E. Lindquist, A. Hagfeldt, (2002) Dye-Sensitized Solar Cells Using Fresh and Dried Natural Dyes , Sol. Energy Mater. Sol. Cells 73 PP-51.

5. L.E. Greene, M. Law, J. Goldberger, F. Kim, J.C. Johnson, Y.F. Zhang, R.J. Saykally, P.D. Yang,Angew. (2003), High – Performance Integrated ZnO Nanowire UV Sensors in Rigid and Flexible Substrates ,Chem. Int. Ed. 42, 3031.

6. *M. Ghosh, A.K .Raychaudhuri. (2008), Shape transition in ZnO nanostructures and its effect on blue-green photoluminescence ,Nanotechnology 19, 445704.*

7. M.H. Huang, Y.Y. Wu, H. Feick, N. Tran, E. Weber, P.D. Yang, (2001) , One- Dimensional Meso-Structures : The Growth and the Interfaces , Adv. Mater. 13 113.

8. O. Akhavan, R. Azimirad, S. Safa. (2011) Functionalized carbon nano tubes in ZnO thin films for photoinactivation of bacteria ,Materials Chemistry and Physics, Vol. 130,No. 1, 2011, pp. 598-602.

9. P. Gowthaman ,M. Saroja , M. Venkatachalam , J. Deenathayalan , T.S Senthil, (2011) Photo catalytic degradation of methelene blue dye using hydrothermally synthesized ZnO nanorods , Optoelectronics and Advanced materials – rapid communications, Vol. 5(12): pp.1307 – 1311.

10. R.B. Peterson, C.L. Fields, B.A. Gregg, (2004) Epitaxial chemical deposition of ZnO nano columns from NaOH solutions , Langmuir 20 5114.

11. Repins, Miguel A. Contreras, Brian Egaas, Clay DeHart, John Scharf, Craig L. Perkins, Bobby To, Rommel Noufi. (2008) 199%_efficient ZnO/CdS/CuInGaSe2 solarcell with 81 2% fill factor. Progress in Photo voltaics : Research and applications, Vol. 16, No. 3, pp. 235-239.

12. S. Safa, R. Sarraf-Mamoory, R. Azimirad. (2014) Investigation of reduced graphene oxide effects on ultra-violet detection of ZnOth in film. Physica E: Low-dimensional, pp. 155-160.

13. S.T. Shishiyanu, T.S. Shishiyanu and O.L. Lupan, (2007) *Sensing Characteristics of Tin-Doped ZnO Thin Films as NO2 Gas Sensor* , Sensors and Actuators B Chemical, Vol. 107, N°1, pp. 379 – 386,.

14. T.S. Senthil, Dongjin Kim, N. Muthukumarasamy, Misook Kang,(2014) Closely packed dense network

rutile nanorods with gadolinium for efficient dye sensitized solar cells , Applied Surface Science , 313, 858–863

15. Vayssieres, (2003) Growth of Arrayed Nanorods and Nanowires of ZnO from Aqueous Solutions, Adv. Mater. 15 464.

16. W.I. Park, D.H. Kim, S.W. Jung, G.C. Yi, (2002), Metal organic vapor-phase epitaxial growth of vertically well-aligned ZnO nanorods , Appl. Phys. Lett. 80 4232.

17. Y.W. Zhu, H. Z. Zhang, X. C. Sun, S. Q.Feng, J. Xu, Q. Zhao, B. Xiang, R. M.Wang, D. P. Yu. (2003) Efficient field emission from ZnO nano needle arrays. Applied Physics Letters, Vol. 83, No. 1, pp. 144-146.

18. Yu .Tian , Lu Hong-Bing, Liao Lei, Li Jin-Chai, Wu Yun, Fu Qiang, (2009), Controlled growth surface morphology of ZnO hollow microspheres by growth temperature , Physica E 41, 729.

How to cite this article:

****