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Influence of Annealing Temperature on Photoelectrochemical Performance of Zno Thin Films Prepared By Low Temperature Aqueous Chemical Reflux Technique

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Abstract

Transparent crystalline nanostructured zinc oxide (ZnO) thin films were grown by simple low temperature (78 □ C) aqueous chemical reflux technique on a glass substrate using zinc acetate dihydrate and hexametylene tetra amine as the precursors. The effect of annealing on the morphology and the photoelectrochemical (PEC) performance of thin films were examined. The optical, compositional, morphological, and electrochemical properties are investigated. Optical spectra showed strong light absorption in UV region. The XRD spectra examination demonstrated pure wurtzite phase hexagonal ZnO nanorods. The SEM images confirm uniform, compact and well aligned nanorods were grown on the overall substrate surfaces of both samples. The EDS results indicate that the deposited films contain Zn and O with an atomic ratio of 1: 1. PEC study shows that photoconversion efficiency (ɳ) is 1.84 % without annealing and it increases to 2.74 % on annealing.

Keywords- *Single crystalline, Nanocomposite architecture, Photoconversion efficiency.*

Introduction:

Zinc oxide (ZnO) is an important semiconducting material used for variety of technological applications due to its wide band gap (3.37 eV) and high excitonic energy (60MeV), environmental friendly and low cost material [1-2]. To date ZnO has variety of applications such as solar cells, nanolasers, transparent conductors, optics, photocatalysts, optoelectronics, biological sciences, energy storage, gas sensors and biosensors, photodegradation of organic pollutants, hydrogen generation, paintings, self cleaning coatings, supercapacitors, electronic components, chemical catalysis, medicines, bactericides etc [3-4]. Nowadays various methods have been successfully used to fabricate nanostructured ZnO thin films including, chemical bath deposition (CBD), vapors transport process, chemical vapor deposition, pulsed laser deposition, thermal evaporation method, molecular beam epitaxy, RF magnetron sputtering, electro deposition etc. All these methods require sophisticated instrumentations so need to develop new low cost method for deposition of ZnO thin films [5-6].

In the present investigation, we deposited ZnO nanorod thin films at low temperature using simple aqueous chemical reflux technique. The present technique offers several potential advantages over other solution based techniques and it is simple, low cost process which allows precise control over film thickness and morphology. This technique can be easily applied on a large scale by modifying existing industrial deposition procedures [7]. Most importantly, highly crystalline ZnO thin films can be deposited at relatively low temperatures (78°C).

Method and materials:

For the deposition of ZnO thin films zinc acetate dihydrate ($Zn(CH_3COO)_2 2H_2O$), diethanolamine (DEA) ($HN(CH_2CH_2OH)_2$, ethanol and hexamethylenetetraamine (HMTA) $(CH_2)_6N_4$); these analytical reagent (AR) grade chemicals were used without further purification. The solutions were prepared in double distilled water. The glass substrates were ultrasonically cleaned using detergent, acetone and double distilled water.

Thin film synthesis:

For deposition of seed layer Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), complexed with diethanolamine (DEA) in ethanol solvent. The ultrasonically cleaned glass substrates were dipped in seed solution for 10 sec. then slowly removed and overnight dried at room temperature. The seeded films were annealed at 300 □ C for 10 minute and used for deposition. In a typical synthesis, zinc acetate dihydrate and HMTA solutions were prepared in double distilled water. These two solutions were mixed and stirred for 10 minutes. The seeded substrates were dipped in the solution and refluxed to deposit ZnO thin films. Finally, the substrates were washed with double distilled water, dried at room temperature and used for characterization as Z_1 sample and annealed at 400 □C for 1 hour used as Z_2 sample.

Results and discussion

Growth mechanism:

Initially, zinc acetate dissociates in aqueous medium as,

$$Zn(CH_3COOH)_2 + 2H_2O \longrightarrow Zn^{++} + 2CH_3COOH + 2OH^-$$

The HMTA reacts with water and form formaldehyde and ammonia. Ammonia formed in this reaction helps for the formation of zinc hydroxide and to adjust pH of the solution,

$$(CH_2)_6N_4 + 6H_2O \longrightarrow 6HCHO + 4NH_3$$

$$NH_3 + H_2O \longrightarrow NH_4 + OH$$ □

The hydroxide ions formed in above reaction react with Zn^{2+} ions to formed zinc hydroxide,

$$Zn^{2+} + 2\ OH \text{ □} \longrightarrow Zn(OH)_2$$

During the reflux at 77 ±2 °C for 5 hours zinc hydroxide deposited on the substrate loses water molecules and form ZnO, as per following reaction [8-9],

$$Zn(OH)_2 \longrightarrow ZnO(s) + H_2O$$

Optical absorbance study:

UV-Vis-NIR absorption spectra of the deposited ZnO films were recorded in the range of 300-800 nm is shown in Fig.1(a).

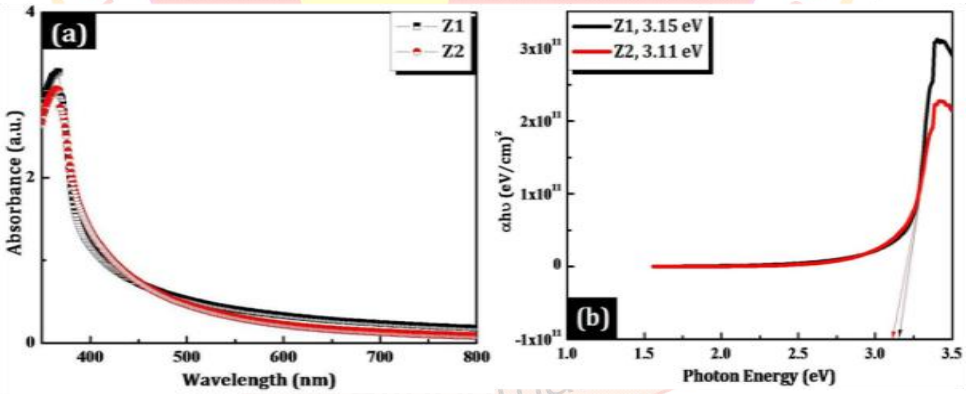

Fig.1a. Plots of Absorbance Vs wavelength **Fig.1b** shows plot of $(\alpha h\upsilon)^2$ Vs. hυ.

Using the absorption edge value, band gap was calculated according to the Tauc relation, i.e. $(\alpha h\nu)^2$ Vs. hν. The plot of $(\alpha h\nu)^2$ vs. hν gives straight line Fig.1(b) at higher energies indicating direct type of transitions [10]. The band gap of Z_1 and Z_2 samples were found 3.15 and 3.11 eV respectively.

Structural study:

The XRD patterns of the deposited ZnO thin films were shown in Fig.2. All the obtained peaks well match with the hexagonal wurtzite crystal structure of ZnO (JCPDS 80-0078). No other major impurity peaks were observed in XRD pattern indicating ZnO nanorods having pure hexagonal wurtzite crystal structure.

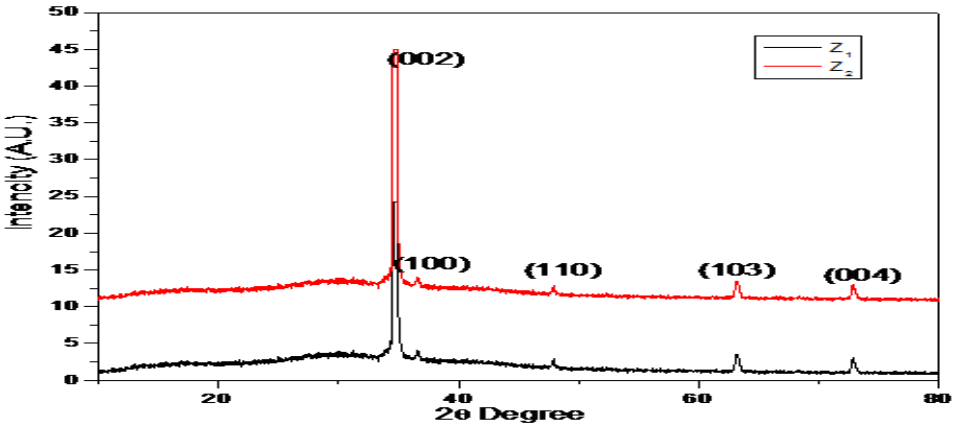

Fig. 2 X-ray diffraction patterns of deposited ZnO thin films.

Applying the Debye Scherrer's formula to the prominent diffraction peak (002) of spectrum, which is unique for hexagonal wurtzite crystal structure of ZnO and the crystallite size is found 30 nm [11].

SEM Analysis:

The SEM images of the deposited ZnO thin films were shown in Fig.3. SEM images clearly show the formation of uniform ZnO nanorods on the overall substrate surface. Average length and diameter of ZnO nanorods is found to be 50 nm and 10 nm respectively.

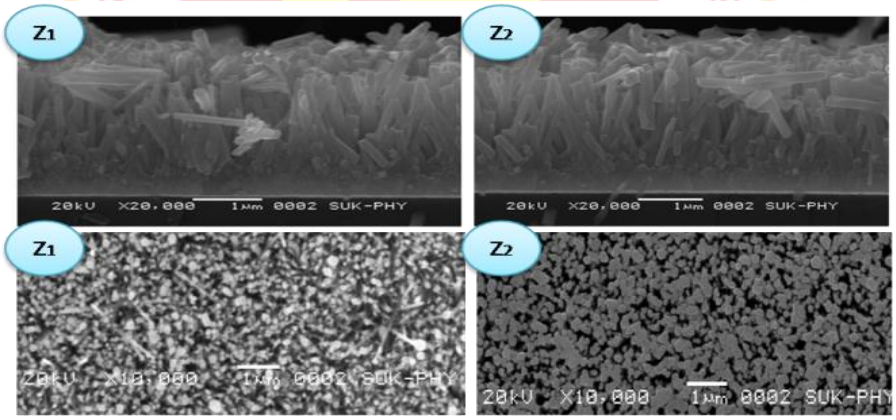

Fig.3: SEM cross section and top views of sample Z_1 and Z_2.

The annealed sample shows more regular arrangement of nanorods which can provide the faster conduction pathway for charge transport and the electron transfer time from carrier generation to the collection electrode is significantly reduced results in better PEC performance [12].

Compositional Analysis:

An elemental composition of ZnO thin films was analyzed by EDS as shown in Fig.4**.**

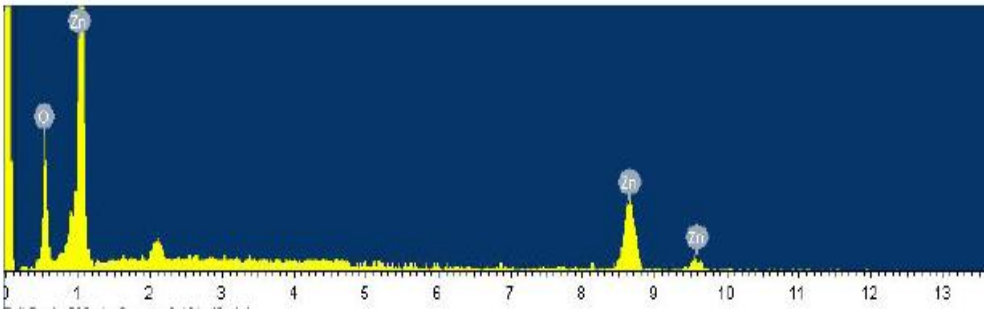

Fig. 4: Energy Dispersive X-ray (EDX) spectrum of Z_2 sample.

There is no trace of any other impurities could be seen within the detection limit of the EDS as presented in Fig.4. The EDS results indicate that the deposited films mainly consist of Zn and O with an approximate atomic ratio of 1: 1 which is in consistent with the stoichiometry of ZnO. Hence EDS analysis confirms the formation of pure ZnO thin films [13].

PEC Performance:

The metal oxide semiconductors can absorb large amount of light radiation to form photogenerated electron–hole pair. The photogenerated electrons can transport directly through crystallites and compact layers to the conducting substrates with minimum loss. This photogenerated electrons travel through the external load and completes the circuit by entering back through the counter electrode [14]. The J-V characteristic curve of ZnO nanorod thin film samples Z_1 and Z_2 under UV illumination in light and dark is shown in Fig. 4. It was found that with annealing the sample PEC efficiency increases from 1.84 to 2.74%. The low PEC efficiency for without annealed sample (sample Z_1) is due to irregular arrangement of nanorods results in spreading of light photons and decreases the light photon absorption efficiency. While on annealing nanorods regularly arranged on the substrate surface increases the light photon absorption efficiency results in increase in the PEC efficiency to 2.74 %. [15]. The PEC solar cell device fabrication and PEC output parameters are as follows,

Glass-FTO/ZnO/0.1 M Na_2SO_4/Graphite

	V_{oc}	V_{max}	J_{sc}	J_{max}	FF	η %
Z_1	720	325	0.27	0.16	0.274	1.84
Z_2	825	433	0.52	0.32	0.32	2.74

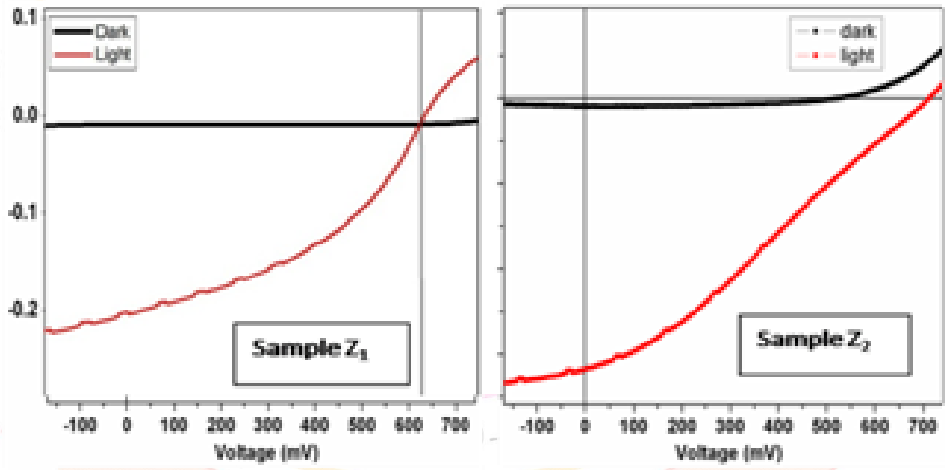

Fig.4: J-V characteristic curve of thin film samples Z_2 and Z_1.

Conclusions:

The well aligned, uniform and compact ZnO nanorods can be deposited on overall substrate surface using simple low temperature chemical reflux technique. The absorption spectrum of samples showed the strong absorption in UV region and the band gap were found 3.15 eV and 3.11 eV. The SEM study showed uniform, compact arranged and well aligned nanorods on overall substrate surface. Compositional analysis confirms the formation of ZnO samples. PEC study showed that photoconversion efficiency 1.84 % for as deposited sample increases to 2.74% for annealed sample.

References:

1. Mali S. S., Kim H, Shim C, Patil P. S, Kim , J. H, Hong C K., Sci. Rep.,(2013), 3; 3004.
2. Chate P. A, Sathe D J, Hankare P P, J Mat. Sci. Mater Electro, (2011), 22;111.
3. Bouraiou A., Aida M.S., Tomasella, E. Attaf N. J. Mater. Sci. (2009), 44, 1241-1244.
4. Kharade S. D., Ghanwat V. B., Mali S.S., Bae W. R., Patil P. S., Hong C. K., Kim J. H.
5. Bhosale P. N., New J. Chem., (2013), 37, 2821.
6. Mahato S., Kaur A. K., Journal of Electroanal. Chem., (2015), 742, 23.
7. Jagadale S.K., Bhosale P. N., Mane R.K., IJSR, 5(10) (2016), 419-422
8. Das V., Selvaraj S.,J., Solid State Commu., (1998), 108, 873-877.
9. Hosseinmardi A., Shojaee, N., Rad, T. Ceramics Intern. (2012), 38 1975–1980.
10. Shinde D. B., Jagadale S. K., Mane R. K., Mane R. M., Mali S.S., Hong C. K and Bhosale
11. P. N. J. Nanomed. Nanotech. (2015), S7:004, 2157-7439.
12. Patil, N. S., Sargar A. M., Mane S. R., Bhosale P. N. J.Appl.Surf. Sci. (2008), 254, 5265.
13. Mane R. K., Ajalkar B. D.,Bhosale, P. N. J. Mate. Chem. Phys., (2003), 82,534-537.
14. Agilan S.,Mangalaraj D.,Narayandas, S. K. Mohan R.G., Physica B. (2005), 365, 93-101.
15. Kharade R.R., Patil S.P., Mane R.M, Patil P.S, Bhosale P.N. J. Opt.Mater.(2011),34, 322.
16. Anand, K. Kumar P. and Thangaraj, P. J. Optoelectron. Adv. Mater., (2011),13, 702-706.
17. Ali A. I., Ammar A. H., Moez A. A., J. Superlat. and Microstr. (2014), 65, 285–298.