AIMS Materials Science, 3(2): 349-356.
DOI: 10.3934/matersci.2016.2.349
Received: 26 January 2016
Accepted: 15 March 2016
Published: 17 March 2016

http://www.aimspress.com/journal/Materials

Research article

Synthesis and characterization of ZnO thin film by low cost modified SILAR technique

Haridas D. Dhaygude [1], Surendra K. Shinde [1], Ninad B. Velhal [2], G.M. Lohar [1], and Vijay J. Fulari [1,*]

[1] Holography and Material Research Laboratory, Department of Physics, Shivaji University, Kolhapur-416004 (MH), India
[2] Thick and Thin Film Device Laboratory, Department of Physics, Shivaji University, Kolhapur-416004 (MH), India

***Correspondence**: Email: vijayfulari@gmail.com; Tel: +91-231-2609224; Fax: +91-231-2690533.

Abstract: The ZnO thin film is prepared on Fluorine Tin Oxide (FTO) coated glass substrate by using SILAR deposition technique containing $ZnSO_4.7H_2O$ and NaOH as precursor solution with 150 deeping cycles at 70 °C temperature. Nanocrystalline diamond like ZnO thin film is characterized by different characterization techniques such as X-ray diffraction (XRD), Fourier transform (FT) Raman spectrometer, Field Emission Scanning Electron Microscopy (FE-SEM) with Energy dispersive X-Ray Analysis (EDAX), optical absorption, surface wettability and photoelectrochemical cell performance measurement. The X-ray diffraction analysis shows that the ZnO thin film is polycrystalline in nature having hexagonal crystal structure. The FT-Raman scattering exhibits a sharp and strong mode at 383 cm^{-1} which confirms hexagonal ZnO nanostructure. The surface morphology study reveals that deposited ZnO film consists of nanocrystalline diamond like morphology all over the substrate. The synthesized thin film exhibited absorption wavelength around 309 nm. Optical study predicted the direct band gap and band gap energy of this film is found to be 3.66 eV. The photoelectrochemical cell (PEC) parameter measurement study shows that ZnO sample confirmed the highest values of, short circuit current (I_{sc} - 629 μAcm^{-2}), open circuit voltage (V_{oc} - 878 mV), fill factor (FF - 0.48), and maximum efficiency (η - 0.89%), respectively.

Keywords: zinc oxide thin film; XRD; (FE-SEM); optical; photoelectrochemical cell

1. Introduction

Zinc oxide (ZnO) is an II-VI group semiconductor having wide band gap energy (Eg~3.3–3.4 eV at 300 K) [1,2,3].

Zinc oxide (ZnO) thin films have been fruitfully incorporated in the transparent conducting oxides used in modern solid state technologies such as, optoelectronic devices, Solar cells, sensors, heat reflecting mirrors etc. [4].

In the recent years, various techniques are used for the preparation of ZnO thin films such as, chemical vapor deposition (CVD), RF magnetron sputtering ,Pulsed laser deposition, Photo-atomic layer deposition, spray pyrolysis, Metal oxide chemical vapor deposition (MOCVD, Electrodeposition, Sol-gel process, Successive Ionic Layer Adsorption and Reaction (SILAR), Chemical bath deposition (CBD) etc.

The SILAR technique has many advantages such as effectiveness, simplicity, easily controlled deposition rate, deposition parameters, and thickness of the film. For synthesis of ZnO thin films, the basic building blocks are ions instead of atoms and thus, the preparative parameters can be easily controlled.

The SILAR technique is also known to be a modified version of chemical bath deposition. Apart from effectiveness and simplicity, there are another advantages to convenient for large scale deposition mainly: i) the process can be approved on any kind of substrate, ii) It does not require high quality substrates, also not require vacuum at any stage, iii) By changing the deposition cycles, the deposition rate ,thickness of the film can be easily controlled, also it operates at low temperature. This SILAR technique is totally based on the adsorption and reaction of the ions from the solutions.

In this work, the ZnO diamond like nanostructure is prepared by SILAR technique and characterized by using XRD, FE-SEM, and UV-vis absorption study.

2. Materials and Method

ZnO thin film is deposited on FTO coated glass substrate by means of Successive Ionic Layer Adsorption and Reaction (SILAR) technique. Zinc sulphate ($ZnSO_4$) and sodium hydroxide (NaOH) are used as the precursors for the synthesis of ZnO thin film. The cationic precursor of required concentration for 0.1 M ZnO is prepared by mixing zinc sulphate powder (used as the complexing agent) in 100 ml deionized water solution. The pH of the cationic solution is ~6. For the deposition of ZnO thin film; the substrate is immersed in cationic precursor solution at about 20 seconds in which the zinc ions are absorbed by FTO substrate and then substrate is rinsed in deionized water about 5 seconds. Thereafter, the substrate is immersed in the anionic precursor solution 0.1 M (NaOH) for 20 seconds, NaOH solution is kept at constant temperature bath (about 70 °C); the oxygen ions reacted with the adsorbed Zn^{+2} ions on the substrate. Finally, the substrate is immersed in deionized water for 5 seconds to remove the loosely bound ions. This completes one SILAR cycle for deposition of ZnO thin film. For 150 SILAR cycles, we have to obtain deposition of ZnO thin film of beloved thickness.

The structural characterization of ZnO diamond like nanostructure is carried out by X-ray diffractometer under Cu–K_α copper target from a Bruker D2 phaser model. Surface morphology of ZnO nanostructure is studied using field emission scanning electron microscope (FE-SEM) of Hitachi (S-4200 model. Absorption spectrum is recorded at room temperature with UV–Vis

spectrophotometer (1800 Shimadzu, Japan). Raman scattering experiment is performed in at room temperature with Raman system from Bruker AXE Analytical Instruments PVT, Germany. The Raman spectrum excited with Nd: YAG laser source at wavelength1064 nm having Raman shift 500 to 1200 cm^{-1} having Ge detector is also used. Keithley 4200-SCS model is used to measure the photoelectrochemical cell parameters of ZnO tin film.

3. Results and Discussion

Figure 1 shows the distinctive XRD pattern of ZnO thin film. XRD pattern of ZnO sample shows the polycrystalline nature having hexagonal crystal structure. The reflection peaks are to be observed at (101), (1020 and (200), which can be perfectly matched with JCPDS Card No. 00- 036-1451 [5,6]. The intense diffraction peak is observed at (102) then by using the Scherer's formula [7], we have to calculate the crystallite size of the peak (102) and found to be 113 nm.

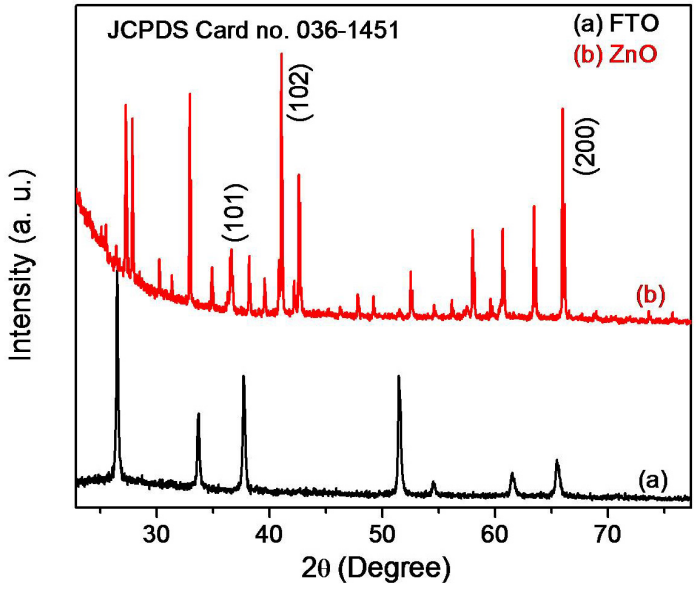

Figure 1. XRD pattern of (a) FTO (b) ZnO thin film.

Figure 2 represent the FT-Raman spectrum of ZnO thin film. The Nd: YAG laser having 1064 nm wavelength of source of light is used. The Raman signals are usually very sensitive to detect the unknown crystal structure as well as to verify the defects in the crystal structure. The sharp intense peak is observed at 383 cm^{-1} (known as Raman active optical phonon mode), which confirms hexagonal phase of ZnO compound. All these peaks (101, 318, 361, 383 cm^{-1}) well matched with literature values [8,9,10].

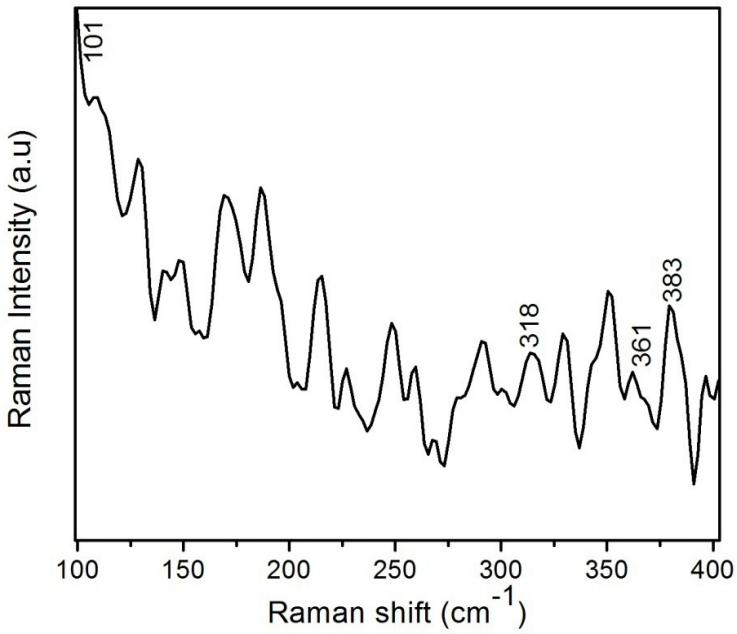

Figure 2. FT-Raman spectrum of ZnO thin film.

Surface morphology is very important tool to investigate nanostructure of thin film. Figure 3a shows the surface morphology of the prepared film. FE-SEM shows the nanocrystalline diamond like morphology, which is useful for semiconductor gas sensor and also demonstrate aggregation of the particles. This aggregation occurred probably during the process of drying reported in the literature [11]. The EDAX spectrum of the prepared ZnO sample is shown in Figure 3b. Thus, the sample contains only Zinc and Oxygen impurity.

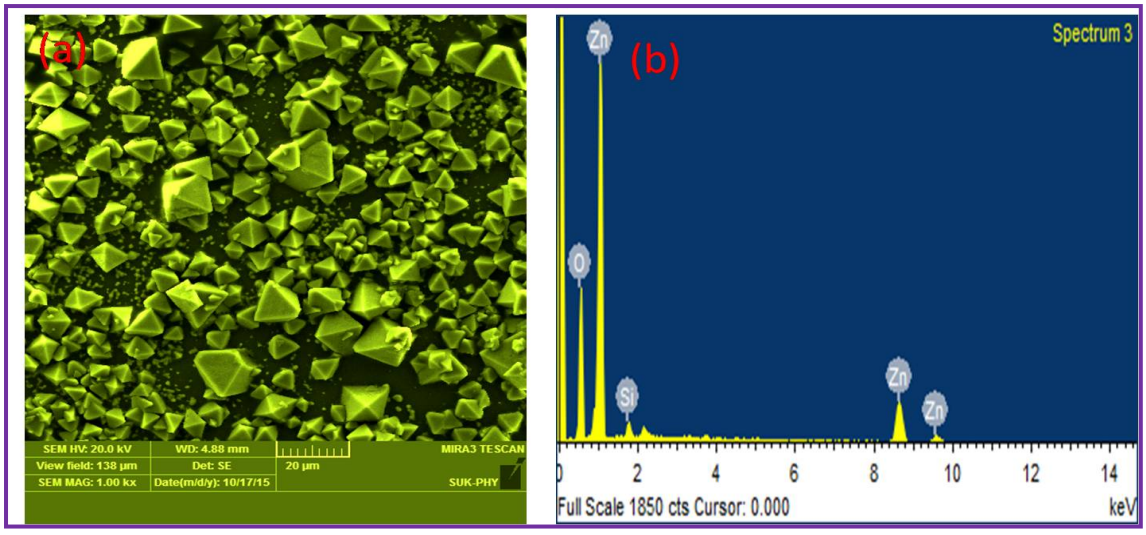

Figure 3. (a) FE-SEM image of prepared ZnO thin film (b) EDAX of ZnO thin film.

Figure 4 shows the absorption spectrum of ZnO thin film. The absorption wavelength is observed at 309 nm in the absorption spectrum. The thickness of the film is measured with the help

of surface profilometer and found to be 274 nm. The optical band gap energy (E_g) of the thin film is calculated from Tauc's plot, as shown in inset of figure 4.

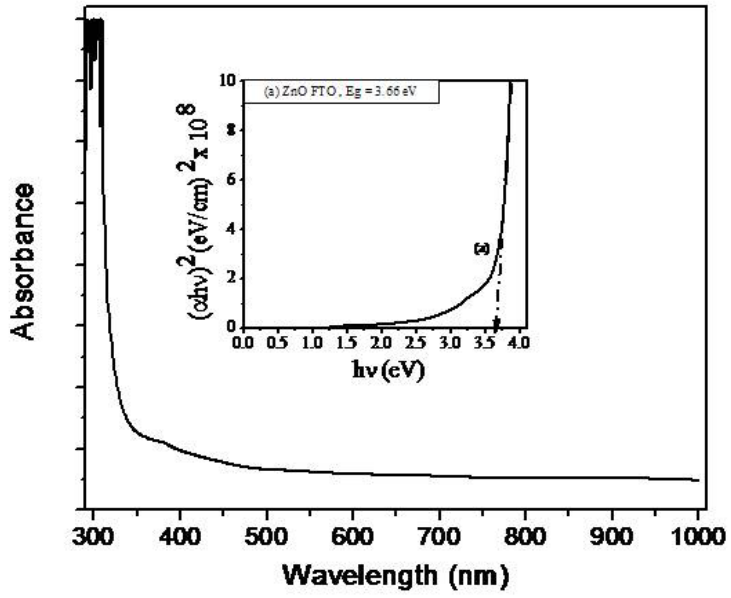

Figure 4. Absorption spectrum of ZnO thin film (Inset of fig. Band gap of ZnO thin film).

The plot suggests that the film have direct allowed transition. For such transition, we have

$$(\alpha h\vartheta)^2 = A(h\vartheta - E_g)^n \tag{1}$$

Where, α be an absorption coefficient, hν is photon energy, E_g is optical band gap, n = 1, for direct allowed transition & A is a constant. The band gap value of ZnO thin film is found to be 3.66 eV. This value is in good agreement with the value reported earlier [12].

The quantitative valuation of the wetting property of a solid with a liquid is expressed in terms of the contact angle θ. Figure 5 shows the schematic diagram of the contact angle and the interfacial surface tension. The most important relation regarding the contact angle is Young's equation [13] that relates the contact angle θ, solid-vapor surface tension γ_{sv}, liquid-vapor surface tension γ_{lv}, and solid-liquid surface tension γ_{sl} as expressed as,

$$\gamma_{l_v} \cos\theta = \gamma_{sv} - \gamma_{sl} \tag{2}$$

The contact angle of the water drop on the thin film is measured using a contact angle goniometer. The image of the drop is analyzed with the standard software to compute contact angle and found to be 75° which is hydrophilic having surface tension 39 dyne/cm.

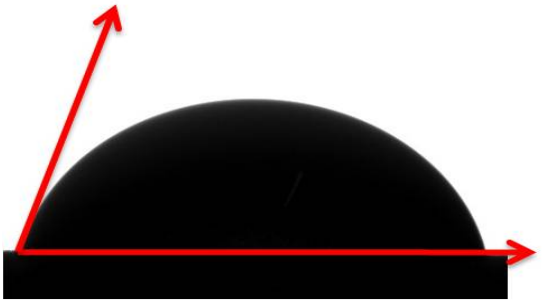

Figure 5. Water droplet contact angle on ZnO thin film.

The PEC is the most reliable technique, for conversion of the solar energy into the electrical energy. The PEC solar cell have wide applications due to low fabrication cost, high through put and easily to form the junction in an electrolyte [14,15]. Moreover, the photovoltaic activity of ZnO film is studied by forming the photoelectrochemical cell having ZnO/0.5 M (Na_2SO_4)/C cell configuration. Figure 6 shows the I–V characteristics of the ZnO thin film in the dark and under illumination having input power is 30mW/cm^2 respectively. For ZnO thin film, the preparative parameters such as open circuit voltage (V_{oc}), short circuit current density (I_{sc}), fill factor (FF) and efficiency (η%) are presented in Table 1.

Table 1. I–V parameters of ZnO thin film in the dark and under illumination condition.

Sr. no.	Sample	I_{sc} (μA)	V_{oc} (mV)	I_{max}	V_{max}	FF	η %
1.	ZnO	629	878	614	435	0.48	0.89

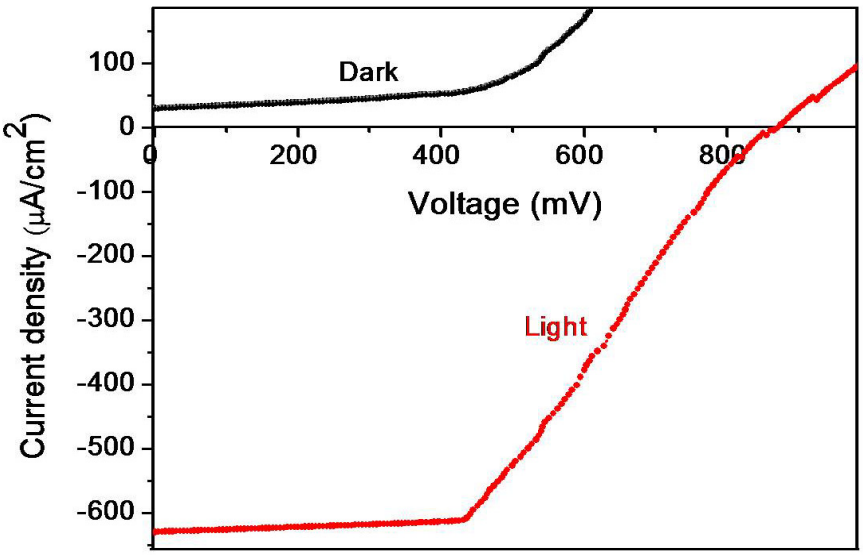

Figure 6. Photocurrent against voltage curve in the dark and under visible light of ZnO thin film.

4. Conclusion

In this work, ZnO thin film is successfully synthesized through SILAR technique. XRD study reveals that ZnO thin film is polycrystalline nature having hexagonal crystal structure. The FT-Raman spectrum shows that the observed peak at 383 cm^{-1} is due to Raman active mode, which confirms the hexagonal ZnO compound. FE-SEM study reveals that diamond like morphology. EDAX analysis confirms that the sample is composed of Zn and O. The band gap energy is found to be 3.66 eV. In addition, a surface wettability studies show ZnO is hydrophilic in nature. For PEC measurements the ZnO sample shows relatively maximum efficiency ($\eta = 0.89$) under visible light illumination.

Acknowledgement

The authors are thankful to the DST-FIST, DST-PURSE India and PIFC for providing instrumental facilities at department of physics, Shivaji University, Kolhapur.

Conflict of Interest

All authors declare that there is no conflict of interest in this paper.

References

1. Fortunato E, Gonçalves A, Pimentel A, et al. (2009) Zinc oxide, a multifunctional material: from material to device applications. *J Appl Phys A* 96: 197–205.
2. Martins R, Barquinha P, Pimentel A, et al. (2008) Electron transport in single and multicomponent n-type oxide semiconductors. *J Thin Solid Films* 516: 1322–1325.
3. ÖzgürÜ, Alivov YI, Liu C, et al. (2005) A comprehensive review of ZnO materials and devices. *J Appl Phys* 98: 041301–041402.
4. Brien SO, Nolan MG, Çopuroglu M, et al. (2010) Zinc oxide thin films: Characterization and potential applications. *J Thin Solid Films* 518: 4515–4519.
5. Martins R, Fortunato E, Nunes P, et al. (2004) Zinc oxide as an ozone sensor. *J Appl Phys* 96: 1398–1408.
6. Shinde SK, Thombare JV, Dubal DP, et al. (2013) Electrochemical synthesis of photosensitive nano-nest like $CdSe_{0.6}Te_{0.4}$ thin films. *J Appl Surf Sci* 282: 561–565.
7. Lohar GM, Dhaygude HD, Patil RA, et al. (2015) Studies of properties of Fe2+ doped ZnSe nanoneedles for photoelectrochemical cell application. *J Mater Sci Mater Electron* 26: 8904–8914.
8. Haratia M, Love D, LauWM, et al. (2012) Preparation of crystalline zinc oxide films by one-step electrodeposition in Reline. *J Mater Lett* 89: 339–342.
9. Xu XL, Lau SP, Chen JS, et al. (2001) Polycrystalline ZnO thin films on Si (1 0 0) deposited by filtered cathodic vacuum arc. *J Cryst Growth* 223: 201–205.
10. McGuire K, Pan ZW, Wang ZL, et al. (2002), Raman Studies of Semiconducting Oxide Nanobelts. *J Nanosci Nanotechnol* 2: 499–502.

11. Dhaygude HD, Shinde SK, Dubal DP, et al. (2015) Electrosynthesis of nanoflower like-ZnS thin films and its characterization. *J Mater Sci Mater Electron* 26: 8563–8567.
12. Hong RY, Li JH, Chen LL, et al. (2009) Synthesis, surface modification and photocatalytic property of ZnO nanoparticles. *J Powder Technol* 189: 426–432.
13. Kwok DY, Lam CNC, Li A, et al. (1998) Measuring and interpreting contact angles: a complex issue, Colloids and Surf. A: Physicochemical and Engineering Aspects, 142: 219–235
14. Lohar GM, Jadhav ST, Dhaygude HD, et al. (2015) Studies of properties of Fe^{3+} doped ZnSe nanoparticle and hollow spheres for photoelectrochemical cell application. *J Alloy Compd* 653: 22–31.
15. Lohar GM, Jadhav ST, Takale MV, et al. (2015), Photoelectrochemical cell studies of Fe^{2+} doped ZnSe nanorods using the potentiostatic mode of electrodeposition. *J Colloid Interf Sci* 458: 136–146.

AIMS Press