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Fabrication and characterization of spray deposited ZnO thin films for solar cell application

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ABSTRACT

Semiconducting materials in thin film form are of great interest due to their distinctive physico-chemical properties towards optical and optoelectronic device applications. Zinc oxide (ZnO) is one of the well-known II-VI group wide-band gap semiconductor which shows the wide range of applications such as optical filters, short wavelength emission, transparent conducting, laser diodes and intense luminescence applications etc.,. In the present work the ZnO thin film was fabricated on well cleaned glass substrates by spray pyrolysis technique and the structural, surface and optical properties were investigated by powder X-ray diffraction, scanning electron microscopy and UV-vis spectroscopy at room temperature. Structural parameters such as crystallite size, microstrain and dislocation density were calculated by using Scherrer's formula. The applicability of the spray deposited ZnO thin film towards window material in solar cell application are presented and discussed in the present work.

Introduction

Nanoscale low dimensional semiconducting (LDS) materials are of great interest due to their distinctive physic chemical, optical and optoelectronic properties. Zinc oxide (ZnO) is a wide-band gap semiconductor of the II-VI semiconductor group and having the band gap energy of 3.2 to 3.36 eV at room temperature. One can alter the band gap energy of ZnO by tuning the particle size and ZnO predominantly exist in the hexagonal (wurtzite) crystalline structure which are also naturally exist in the cubic zinc blende and rock salt structures. ZnO shows the hexagonal lattice type with the lattice parameters of a = 3.24 Å and c =5.16 Å) with space group $P6_3mc$ is characterized by two interconnecting sub lattices of Zn^{2+} and O^{2-} ,such that each Zn ion is surrounded by O with tetragonal coordination. Because of this arrangements ZnO nanomaterial possessing the following properties viz. piezoelectricity and spontaneous polarization, and is a key factor in crystal growth and defect generation.

ZnO in thin film form have been widely used in transparent electrodes, surface acoustic wave devices, field effect transistors and display devices. It can be a cheaper alternative to GaN for optoelectronic applications in the blue and UV regions. Because of its tunable and wider band gap the ZnO thin films were effectively utilized as a buffer and window material in solar cells. Nano crystalline high surface area ZnO with porous structures finds applications in chemical sensors and solar cells [1-3]. Thin films of pure and metal ions doped ZnO can be obtained by various techniques such as sol–gel process, spray pyrolysis, organometallic chemical vapour deposition (OCVD) and pulsed laser deposition (PLD), sputtering.

Photo electro chemical (PEC) cells convert solar energy into storable chemical energy as hydrogen through the photoelectrolysis of water. Semiconducting materials were used as photoelectrode in PEC cell and the utilizing semiconductor must be chemically stable with an appropriate bandgap of ~ 1· 8 eV which actually absorb the visible wavelength part of solar radiations [4-5]. Oxide semiconductors such as Tin oxide (SnO_2), Titanium dioxide, (TiO_2), and BaTiO3, investigated as alternative photoelectrodes but these oxide materials have relatively high bandgap energy and cannot absorb large portion of visible light specially ultra violet region [6-8].

On the other hand, from the reported literatures one can understand the low bandgap energy materials such as Gallium arsenide (GaAs) [9], silicon (Si) [10] and indium phosphide (InP) [11] get easily corroded when we make the contact with the electrolyte. ZnO in thin film form is an attractive material for PEC splitting of water mainly due to its high electrochemical stability. The energy levels and bandgap energy of ZnO are quite similar to TiO_2, which is the first material reported for PEC splitting of water. The present research work deals with the fabrication and characterization of ZnO thin films by spray pyrolysis technique. The observed optical, structural and morphological properties were discussed in detail.

Experimental

In the typical synthesis procedure, a spray pyrolysis technique was employed for the synthesis of zinc oxide thin films onto the glass substrates by spray pyrolysis technique from zinc acetate precursor solution (0.1 M). The zinc acetate precursor is dissolved into the double distilled water. The deposition of the ZnO thin films was taken at substrate

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temperature (400 °C). The thermocouples and heating elements are connected with a temperature controller.

The compressed air was allowed to atomize the solution containing the precursor compounds through a nozzle on to the heated glass substrate. The motion of the nozzle was controlled by stepper motor, which is connected to the electronic kit. The harmful fumes evolved during the deposition were expelled out using external exhaust system. The deposited ZnO films were further used to investigate the structural and optical properties. The structural characterizations were carried out using Philips PW 3710 X-ray diffractometer with CuKα radiation (wavelength 1.5405Å). The optical properties were analyzed by UV-Vis Systronics-119 spectrophotometer in the wavelength range 350 to 850 nm.

Results and discussion

Structural properties

The X-ray diffraction (XRD) pattern recorded over the 2θ values between 10°-100° for the ZnO sample deposited onto the glass substrate from 0.1 M solution concentration and substrate temperature (400 °C) is shown in Fig. 1. The deposited ZnO film shows polycrystalline and matches well with the hexagonal crystal structure. All the observed diffraction peaks can be well assigned to the hexagonal-phase, reported in the literature [12]. From XRD pattern, it is noticed that deposited optimized ZnO film has preferred orientation along (002) plane. Other orientations corresponding to (100), (101) and (004) planes are also present with low relative intensities as compared to that of (002) plane, indicating the preferred growth along c-axis orientation.

The crystallite size was calculated by using the Debye-Scherrer's formula:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad \text{------------------ (1)}$$

where, λ is the wavelength (1.5406 Å) and β is full width in radian at half maximum of the peak and θ is the Bragg's angle of the XRD peak. The calculated crystallite size was found to be 40 nm for the optimized ZnO thin film.

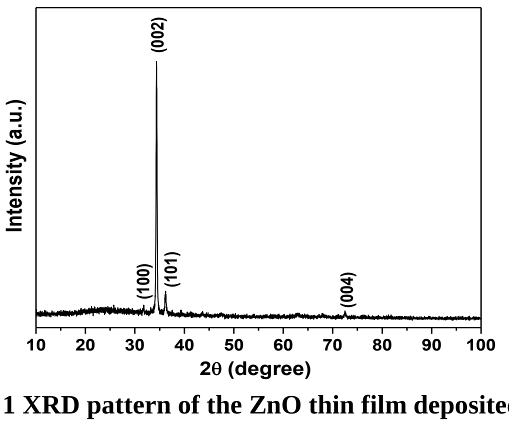

Fig. 1 XRD pattern of the ZnO thin film deposited at optimized condition.

SEM analysis

Surface features of the deposited ZnO thin film was analyzed by scanning electron microscopy at room temperature. The observed SEM image of the spray deposited ZnO shows the nanorod like morphology with porous surface texture. The length of the nanorod was in the order of 1µm and the thickness of the nanorods was in the order of nm. The observed SEM image shows the ZnO nanorods having higher growth in one direction where as other dimension was strongly confined. Few ZnO nanorods having needle shape and the bottom side having predominant growth and the growth ratio decreasing abruptly and finally reach the needle shape and was shown in the fig 2.

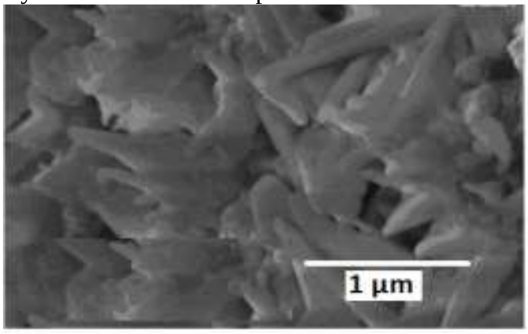

Fig 2. The SEM image of the deposited ZnO thin film

Optical properties

The optical absorption spectrum of the ZnO thin film recorded in the wavelength range 350 nm to 850 nm and is shown in Fig. 3. Band gap energy (E_g) can be estimated from the optical absorption measurement. The plot of $(\alpha h\nu)^2$ with photon energy (hν) is shown in the Fig. 4.

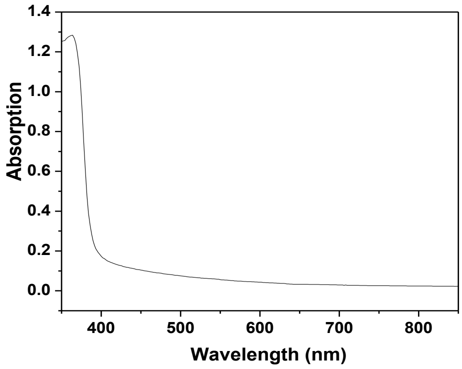

Fig. 3 Optical absorption spectrum of the deposited ZnO thin film

The recorded optical absorption data were analyzed using the equation (2) of optical absorption in semiconductor near band edge.

$$\alpha = \frac{\alpha_0 (h\upsilon - Eg)^n}{h\upsilon} \qquad \text{---------------------------- (2)}$$

where, E_g is the separation gap between bottom of the conduction band and top of the valence band, hν is the photon energy and n is a constant. The value of n depends on the probability of transition; it takes values as 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transition, respectively. If plot of $(\alpha h\nu)^2$ versus (hν) is linear the transition is direct allowed. Extrapolation of the straight-line portion to zero absorption coefficient (α=0), leads to estimation of band gap energy (E_g) value. The value of band gap energy of the ZnO film is found to be 3.25 eV.

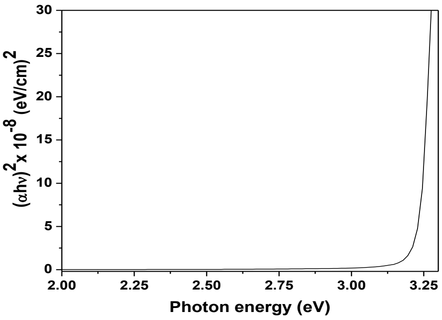

Fig. 4 Plot of $(\alpha h\nu)^2$ vs. hν of the spray deposited ZnO thin film

The optical transmission spectrum of ZnO thin film recorded in the wavelength range 350-850 nm is shown in Fig. 5. The deposited ZnO film is highly transparent in the visible range with an average transmittance reaching values up to 80% and presents a sharp ultraviolet cut-off wavelength approximately at 380 nm. The observed high transmittance of ZnO film can be attributed to the complete decomposition of the precursor at higher temperature (400 °C).

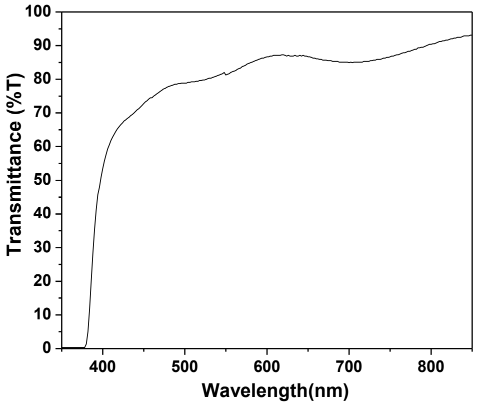

Fig. 5 Transmittance spectrum of the ZnO thin film deposited at optimized condition.

Conclusion

The deposition of the ZnO thin films was conducted at the optimized substrate temperature around 400 °C. The structural characterizations of the spray deposited ZnO thin film was carried out using Philips PW 3710 X-ray diffractometer with CuKα radiation (wavelength 1.5405Å) which shows the optimized ZnO film has preferred orientation along (002) plane. The optical properties were analyzed by UV-Vis Systronics-119 spectrophotometer in the wavelength range 350 to 850 nm. The deposited ZnO thin film exhibits over 80 % transmittance in the visible region and displays the band gap energy of 3.25 eV which is suitable for solar cell window material in solar cell system.

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