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SPRAY PYROLYSIS DEPOSITED ZnO NANOSTRUCTURES AS TRANSPARANT WINDOW LAYER FOR PHOTOVOLTAIC APPLICATION

Research

KEYWORDS : Nanostructured ZnO, Spray pyrolysis deposition, XRD, TEM, UV-Vis spectra

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ABSTRACT

Zinc Oxide nanostructures (ZnONS) have been synthesized by spray pyrolysis technique. The prepared samples were characterized by X-ray diffraction (XRD), Scanning electron microscope (SEM), and Transmission electron microscope (TEM). XRD pattern of the prepared sample shows preferential orientation along (002) crystallographic plane and can be indexed to wurtzite structure (JCPDS 36-1451). The X-ray diffraction patterns and transmission electron microscopy for the film showed that the ZnO exibit hexagonal wurtzite crystal structure. Also XRD confirmed that the ZnONS are polycrystalline in nature and no additional peaks were present showing the formation of pure ZnO nanoparticles (ZnONPL). The UV-Vis spectra showed absorbance peaks in the 300-800nm region. Optical transmittance spectra gives excellent transmittance (>85%) and a sharp cut off edge at 385nm. From the spectra, direct band gap of ZnO is determined which is 3.37eV at room temperature that makes ZnO useful for optoelectronic devices such as solar cell, photonic crystals, photodiodes, etc.

INTRODUCTION

Nanostructured zinc oxide has attracted attention of researchers and scientist as transparent conducting oxides (TCOs). It has potential applications in optoelectronic devices due to its wide direct band gap (3.3eV) [1-3]. It also has some unique and interesting physical and chemical properties such as, large exciton binding energy (60meV) [4-5], chemical [6] and thermal stability [7], radiation hardness [8], piezoelectricity and photoelectricity [9], high conductivity, etc. It has abundant in nature and nontoxic. Due to such intriguing properties zinc oxide became a most attractive semiconducting material for the applications in photo-detector [10], gas sensor [11], LED's [12], solar cells [13], photonic crystals [14], UV-protectors filters [15], chemical sensors [16] and photodiodes [17]. Zinc oxide thin films have been prepared by a verity of thin film deposition techniques such as Chemical Vapor Deposition (CVD) [18], Magnetron sputtering [19], spray pyrolysis [20-21], Pulsed Laser Deposition (PLD) [22], sol-gel method [23-24], electron beam evaporation [25]. Among these methods, the spray pyrolysis method is one of the most important method and widely used for the preparation of metal oxide nanostructures. This is an attractive technique for fabricating uniform thin films due to the homogeneity of precursor, a large-area deposition and low cost fabrication.

In this study, ZnO thin films were prepared using spray pyrolysis method using glass substrate at 380^{0}C temperature. Uniformly deposited thin films of ZnO were subjected for different characterizations. Structural and morphological characterizations of the samples are performed using XRD, SEM and TEM respectively. Optical characterization is carried out by UV-Visible spectroscopy. Structural and optical properties of ZnO_{NS} are discussed in this paper.

EXPERIMENTAL DETAILS

The ZnO_{NS} were deposited by spray pyrolysis technique using zinc nitrate solution. This technique is most suitable for the deposition of metal oxide thin films. The ZnO were deposited in O^2 at growth temperature of 400^{0}C using zinc nitrate hexahydrate $Zn(NO_3)_2.6H_2O$ precursor solution. Ultrasonicated glass substrates were used to get uniform thin films. Different deposition parameters were maintained like spray rate, deposition time and concentration of precursor. Methanol is used as a solvent; the volume of spray solution was 30ml. The concentration of zinc nitrate in the spray solution was kept constant at 0.5 mol/L. the pH of the solution is maintained at 5 by adding ammonium hydroxide. The 30 ml solution was sprayed by spray rate 2.5ml/min. Harvested thin films were dried and sintered in an oven 500^{0}C for 5h.

Uniform and good quality thin films were obtained and subjected for different characterizations. Structural analysis is done using Rigaku, Ultima IV diffractometer with Cu-Kα radiation (λ=0.15456nm) as x-ray source at 40Kv and 40mA in the scanning angle (2θ) from 20-90^0. Morphology of the samples was studied using JEOL 200cx TEM. TEM micrograph is used to verify particle size and structure. JEOL JSM-6360 SEM is also used to investigate surface morphology of the film. UV-Visible studies are performed using Shimadzu UV-Vis spectrometer.

RESULTS AND DISCUSSION

3.1. X-ray diffraction studies:

The XRD pattern of ZnO was used to find out phase purity and structural parameters. The XRD patterns of pure ZnO were recorded at 500^{0}C temperatures is as shown in Fig.1. The film exhibits some characteristic peaks for (100), (002) and (101) planes indicating the polycrystalline nature of the film. Recorded XRD data is found to match with JCPDS reference pattern (file:361451) of ZnO. The analysis of diffraction peaks has revealed the hexagonal wurtzite structure of ZnO [26].

The crystallite size D is determined using the Debye-Scherrer formula [27].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where, λ is wavelength of X-ray in nm, β is the FWHM in radians

The grain size value is found to be 65nm.

Lattice parameters and volume of ZnO primitive cell can be calculated by using Le-Bail and Pawley refinement method,

$$a = \sqrt{\frac{1}{3}}\left(\frac{\lambda}{\sin\theta}\right) \quad (2)$$

$$b = \frac{\lambda}{\sin\theta} \quad (3)$$

$$v = 0.866a^2c \quad (4)$$

Where, a, b and c are lattice parameters.

We also determined bond distance between Zn-O by using Eq (5) [28].

$$l = \sqrt{\left[\frac{a^2}{3} + \left(\frac{3}{4} - \frac{a^2}{3c^2}\right)^2 c^2\right]} \quad (5)$$

It is found to be bond length Zn-O is approximately 2Å. All the calculated values are tabulated in Table1.

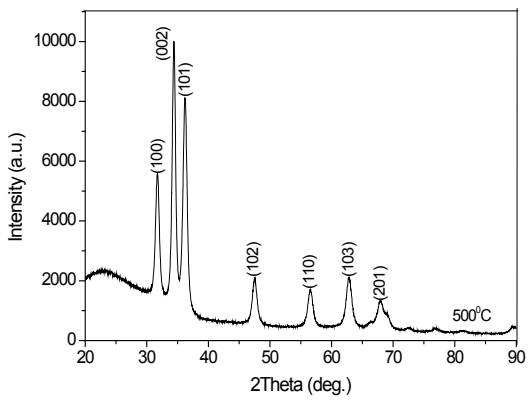

Figure 1: X-ray diffraction pattern of ZnO_{NS}

3.2. Morphological studies:

Figure 2(a) shows SEM picture of ZnO_{NS} film prepared by spray pyrolysis method. It can be seen that the microstructure of the films is highly porous and homogeneous. SEM micrograph shows mesh like texture formed by spherical grains. The preferential growth orientation (002) is observed for this sample.

The TEM micrograph for ZnO nanocrystals is as shown in figure 4 (b). The crystallites have polycrystalline hexagonal wurtzite morphology. It has been shown that the average size of synthesized ZnO particles is about 50nm. TEM image strongly support XRD spectrum that indicating the hexagonal shape of ZnO_{NS}. By clearly showing hexagonal grains it confirms the formation of ZnO_{NPL}.

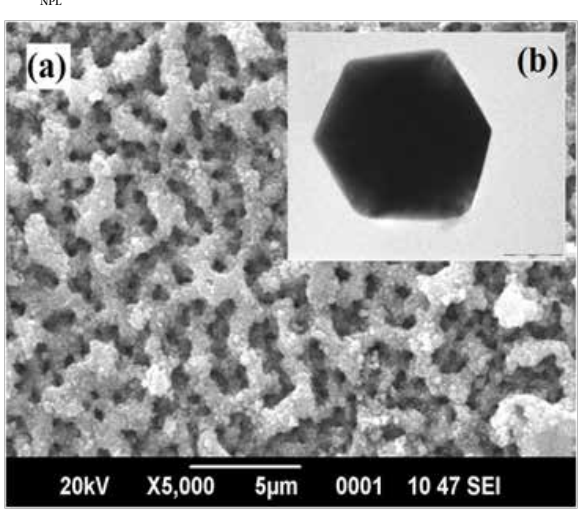

Figure 2: (a) SEM micrograph (b) TEM micrograph showing hexagonal wurtzite structure of ZnO

3.3. Optical absorption study

UV-Vis spectrum is used to determine the optical band gap of nanomaterials. The optical absorption spectrum of ZnO thin film was recorded in the region ranging from 300 to 800nm using UV-Vis spectrometer (Fig.3 (a)). The stoichiometric semiconducting compound shows sharp transmission edge at that photon energy which corresponds to the forbidden energy gap. Assuming a direct transition between the edge of the valence and the conduction band, the variation of the absorption coefficient with the photon energy can be described by the following equation [29]:

$$\alpha h\nu = A\left(h\nu - E_g\right)^{1/2} \quad (6)$$

Where α be the absorption coefficient, $h\nu$ is incident photon energy, E_g is the optical band gap, for allowed direct transition and A is a characteristic parameter, independent of photon energy.

The optical band gap energy is determined by extrapolation of the linear part of $(\alpha h\nu)^2$ vs. $h\nu$ to $\alpha \cdot h \cdot \nu \rightarrow 0$. Using this procedure, the values of energy band gap corresponding to investigated ZnO films were determined

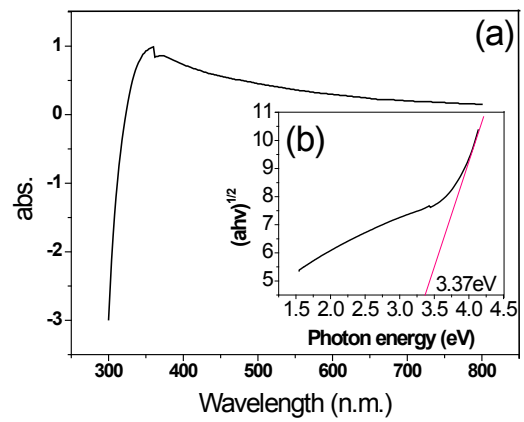

Figure 3: (a) UV-Vis absorption spectra (b) $(\alpha h\nu)^{1/2}$ versus photonic energy hν plot of ZnO calcined at 500^{0}C

For the optical device fabrication, the thin film should be highly transparent and conductive. The absorbance of the ZnO film is low in the visible wavelength; while high transmission (>80%) obtained in the same region. There is sharp cut off edge near 380nm due to inter-band transitions. This sharp edge indicates a good structural quality of the synthesized film and makes it a potential candidate for optical device fabrication.

The band gap energy (Eg) of the ZnO can be determined by Tau plot of versus photon energy hν (eV). The band gap obtained is found to be 3.37eV as shown in Figure 3(b). This value agrees well with the reported value (3.2-3.4eV) of the bulk band gap of ZnO films [30].

Table 1: Calculated data of ZnO nanomaterials

Properties	ZnO
a(nm)	0.3229
c(nm)	0.5186
lande' g factor	1.959
Grain size (nm)	50
Volume (nm3)	0.0468
X-density(g/cm3)	17.38
Density(g/m3)	5.47×10-6
APF(%)	0.7525
Eg Optical bandgap (eV)	3.37
c/a ratio	1.6060
Molecular wt (g mol-1)	81.4
Bond length Zn-O(Å)	2.089

CONCLUSIONS

In our research work, we have successfully obtained ZnO_{NS} thin films using spray pyrolysis technique. Structural, morphological and optical properties of post-heated ZnO thin films at 500^0C temperature have been studied. XRD pattern reveals that, the synthesized material exhibit hexagonal crystal structure with preferential orientation along (002) crystallographic plane. The structural analysis confirms the polycrystalline nature of ZnO. The morphological study through SEM micrograph shows mesh-like pattern of ZnO_{NS}. TEM picture clearly shows hexagonal shape of ZnO_{NPL} and strongly support XRD pattern. The optical band gap of ZnO material is obtained by UV-Visible study and is found to be 3.37eV. UV-Visible study shows ZnO films are applicable for optoelectronic applications.

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