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Synthesis And Characterization Of ZnO Thin Film By Spray Pyrolysis Technique

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Abstract
In this paper I reported zinc oxide (ZnO) thin film, deposited on to glass substrate by spray pyrolysis technique. Deposition parameters were optimized. The film was characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), scanning Electron Microscope (SEM) and UV-VIS spectrophotometer. The XRD analysis shows ZnO thin film has hexagonal wurtzite structure; SEM and AFM micrograph shows uniform deposition on to glass substrate and optical band gap was found to be 3.48 eV. The results of structural, surface morphological and optical investigation show that, the film is suitable for gas sensing application.
Keyword: *spray pyrolysis technique; ZnO; gas sensor; thin film; semiconductor*

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I. Introduction

Zinc oxide (ZnO) is a II-VI compound semiconductor material having wurtize structure, wide bandgap energy (3.37 eV at room temperature) and large excitation binding energy (≈ 60 meV) [1]. ZnO exhibits high electrical, optical, and piezoelectric performance. Due to all these properties Zinc oxide can be used in nano-electronic and optoelectronic applications. ZnO is a biocompitable; biosafe and it can be used for biomedical applications without coating.

Thin films of zinc oxide have attracted much technological importance due to its unique properties and as a result of n-type semiconducting material property. It is used in various fields such as solar cells [2], gas sensors [3, 4], varistors [5] surface acoustic wave devices [6]. Many reports were devoted to prepare zinc oxide thin films. High quality ZnO thin films were produced by magnetron sputtering [7,8], laser ablation [9,10], metal organic chemical vapor deposition [11], laser molecular beam epitaxy [12], thermal evaporation [13], sol-gel [14,15], successive ion layer adsorption and reaction (SILAR) [16], Chemical Bath Deposition (CBD) [17, 18], and spray pyrolysis [19-21].

The spray pyrolysis technique is a low-cost technique for creating thin films, ceramic coatings, and powders by spraying a solution of chemical precursors onto a heated substrate, where the heat causes the solvent and volatile byproducts to evaporate and the remaining components to react and form a solid coating. This versatile and scalable process is used to deposit a variety of materials, including metal oxides, semiconductors, and luminous compounds, with deposition parameters like substrate temperature and solution concentration being key to controlling the quality and morphology of the final product.

In the present investigation results of the work on the preparation of zinc oxide thin films by spray pyrolysis technique using precursor solution containing zinc acetate dissolved in deionized water and methanol are described. The preparative parameters such as substrate temperature, concentration of solution spray rate, spray time, pH, and substrate to nozzle distance are optimized to get good quality adherent and uniform thin films. These films are characterized by various characterization techniques for their structural, surface morphological, optical and electrical properties and the effect of thickness was studied.

II. Experimental

For the deposition of zinc oxide (ZnO) thin film the solution of zinc acetate Zn $(CH_3COO)_2$ $2H_2O$ dissolved in deionized water and methanol respectively was used. The appropriate volumes of zinc acetate dissolved in deionized water and methanol were mixed in a beaker, then pour this mixed solution in the tube of spray gun. The cleaned glass substrate was placed in the uniform temperature region of the hot plate. For the motion of spray gun with the help of rotor and electronic speed controller switch on the power supply of concerned circuit. The desired temperature was obtained and controlled with the help of temperature controller. Spraying of precursor solution was started on heated glass substrate, so that heater automatically maintains substrate temperature constant. It is necessary to optimize the process parameters to get good quality uniform, adherent and pinhole free thin films. Finally, as deposited thin film was kept for post thermal heating at 468^0 K for one hour. The film obtained was uniform, transparent, well adherent, and colorless.

Table 1: Optimized parameters

Initial Ingredients	Zinc Acetate Zn $(CH_3COO)_2$ $2H_2O$, Deionized Water (H_2O), Methanol (CH_3OH)
Substrate temperature	648 ^{0}K
Concentration of solution	0.2M
Composition (Volume Ratio)	80:20
Spray Rate	10 mL/min
Nozzle to substrate distance	25 cm
Carrier Gas	Air
Gas flow rate	10 lit/min
Gas Pressure	1 Kg/ m^2

The deposited thin film was characterized by X ray diffraction (XRD), scanning electron microscopy (SEM), and optical absorption spectra. X-ray diffraction pattern was recorded on Bruker AXS D8 advanced X-Ray diffractometer using Cu-Kα radiation wavelength (λ = 1.5405Å) within range from 20^o to 100^o. The SEM micrograph was recorded on JOEL-JSM-5600 SEM instrument model. The optical absorption spectra of the film was measured in the wavelength range of 350–850nm on a Shimadzu UV-2450 spectrophotometer. Film thickness was measured by weight difference method.

III. Results And Discussions

XRD Analysis

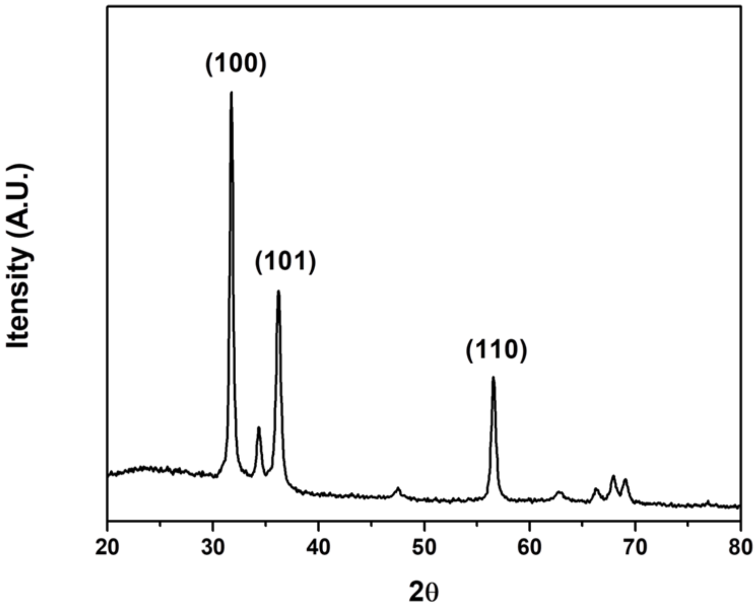

Fig. 1 XRD pattern of ZnO thin film

The structural determination and crystallite size ZnO thin film was carried out by X-ray diffraction (XRD) pattern. Fig. 1 shows X-ray diffraction pattern of ZnO thin film. Six small and three large peaks are observed. More than one XRD peaks indicate that the deposited film is polycrystalline in nature. The 2θ peaks at 31.68°, 36.09° and 56.50° corresponding to (100), (101) and (110) planes. These peaks are compared with the JCPDS file no. 070–2551, confirms the formation of ZnO thin film with hexagonal Wurtzite type structure. The crystallite size (D) was calculated by Scherrer's formula [22] from the full width at half maxima (β) of the peaks expressed in radians.

$$D = \frac{K\lambda}{\beta Cos\theta} \quad (1)$$

where 'K' is constant dependent on crystallite shape (0.89), 'λ' is wavelength of CuKα1 radiation, and 'θ' is angle between the incident and scattered X-rays. The average crystallite size (derived from Fig. 1) is found 30 nm.

Surface Morphology Analysis

Surface morphology of the films was studied by scanning electron microscope (SEM) and atomic force microscopy (AFM) images. Fig. 2 (a) shows SEM image of ZnO thin film. It is observed that the particles were covered on the entire substrate surface.

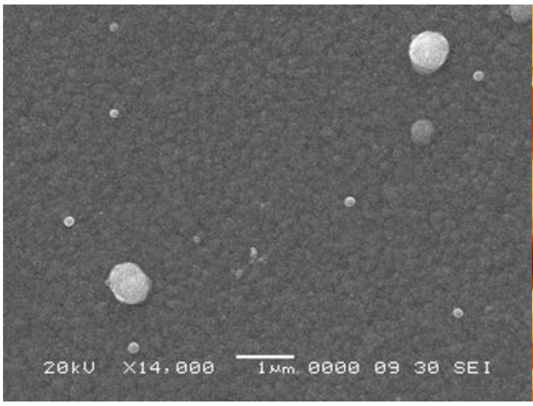

Fig. 2(a) SEM image of as deposited SnO_2 thin film

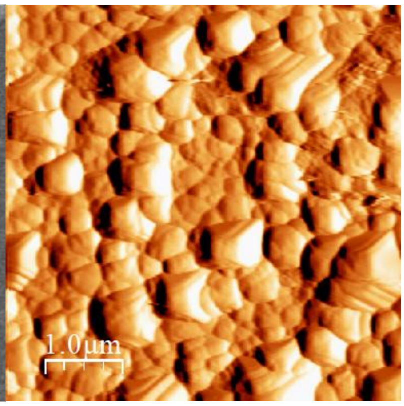

Fig. 2(b) AFM image of as deposited SnO_2 thin film

Fig. 2 (b) shows AFM image of deposited ZO thin film. From the image it is clear that the film is uniform and substrate surface is well covered by fine spherical or elliptical grains. The average cluster size was determined to be 140 nm and average surface roughness was 0.0005 nm. The cluster size and root mean square (rms) surface roughness were determined by using the software which was provided with the microscope.

Optical Analysis

Energy band gap is calculated by using UV-VIS absorbance spectra of spray deposited ZnO thin film. The absorbance spectra were used to study the optical transition in the films, which were studied at room temperature in the wavelength range of 300–1100 nm. The optical absorption studies revealed that the film is highly absorptive and have direct type of transitions, which allowed the determination of optical band gap by the following Urbach relationship

$$\alpha h\nu = A\left(h\nu - E_g\right)^n \qquad (2)$$

where 'A' is the constant; depending upon the transition probability for direct transition, n = 1/2 for direct allowed transition and 'E_g' is the optical band gap of the material.

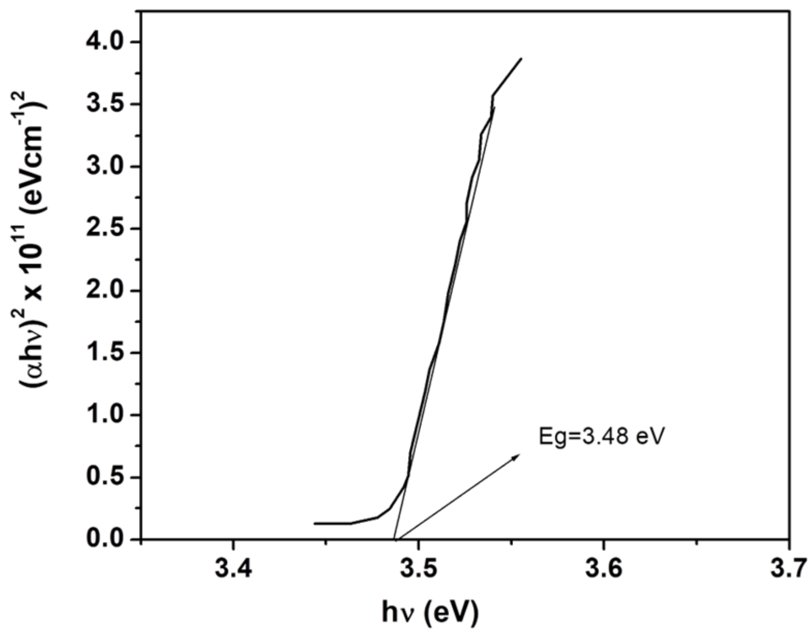

Fig. 3 plot of $(\alpha h\nu)^2$ Vs hν of spray deposited ZnO thin film

Fig. 3 shows the variation of $(\alpha h\nu)^2$ versus hν. Extrapolating the straight-line portion of the plot of $(\alpha h\nu)^2$ versus hν for zero absorption coefficient value gives the band gap energy, which is found to 3.48 eV.

IV. Conclusion

The thin films of ZnO, deposited on to glass substrates by using spray pyrolysis technique. The XRD studies showed that the deposited film has polycrystalline Wurtzite type structure. SEM and AFM images showed uniform deposition of film on to the glass substrate. Optical study showed band gap energy equal to 3.48 eV. All the characteristics show the formation of semiconductor thin film, can be used gas sensing as well as any semiconductor device applications.

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