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Synthesis and Characterization Zinc Oxide Thin Films Prepared by Chemical Bath Deposition

C. V. Chanmal*[1], S. S. Bandgar[1], C. D. Mungamode[2], S. G. Pawar[1], R. N. Mulik[1]
*[1]Department of Physics, D. B. F. Dayanand College of Arts & Science, Solapur, Maharashtra, India
[2]Department of Physics, Mahatma Gandhi College, Armori, Maharashtra, India

ABSTRACT
In the present work, zinc oxide thin films were prepared by simple chemical bath deposition (CBD) method. The deposition conditions such as pH and temperature were optimized to obtain well adherent uniform thin films. The prepared zinc oxide thin films were characterized for structural and morphological studies. The structural characterization was carried out by using X-ray diffraction (XRD) and Fourier transform Infra Red (FTIR) spectroscopy. The structural characterization indicates the uniform deposition of zinc oxide thin films onto glass substrate. The X-ray diffraction pattern of chemical bath deposited zinc oxide shows all the characteristic peaks related to wurtzite phase of zinc oxide. Further, structural characterization was carried out using FTIR spectroscopy which also confirms the deposition of zinc oxide thin films. The morphology study of zinc oxide thin film was carried out using scanning electron microscopy (SEM). The SEM micrograph show granular structural morphology of zinc oxide thin films. In conclusion, zinc oxide thin films were successfully prepared by chemical bath deposition technique and the films shows uniform well adherent morphology.
Keywords : Zinc Oxide, Thin Films, Chemical Bath Deposition, Structure, Morphology

I. INTRODUCTION

Semiconductor nanoparticles have attracted significant research interest in recent years due to its novel optical, electrical and mechanicals properties. [1-2] These interesting properties of nanoparticles results from quantum confinement effects due to nano dimensions as compared with their bulk counterparts. Among various semiconductor nanoparticles, nano sized zinc oxide (ZnO) particles is studied extensively as its structure and properties can be easily tailored by choosing various synthesis methods. [3-5] Zinc oxide is a semiconductor with a wide band gap of 3.37 eV and large exciton binding energy of 60 meV. Till date, numerous application of ZnO nanoparticles have been explored in number of different fields such as in dye sensitized solar cell, gas sensors and light emitting diodes. [6-8] Zinc oxide is one of the most important nanomaterials for integration in microsystems and biotechnology. Furthermore, the optical properties of zinc oxide make it useful in the application of transparent conducting anode in photovoltaic cells.[9] Additionally, the structure of zinc oxide has non-centrosymmetric characteristics which exhibit piezoelectric properties useful in electromechanical coupled sensors and transducers property.[10]

To explore the full potential of nanomaterials for various applications, it is highly desirable to prepare the semiconductor in the form of thin films by using simple fabrication method. Ultimately, the properties of semiconductor thin film depend upon the method of preparation. To date, various techniques have been used for the deposition of ZnO thin films namely pulsed laser deposition, magnetron sputtering, spray pyrolysis, molecular beam epitaxy. [11-17] However, the above mentioned techniques require precise control over process parameter to obtain thin films with desired properties. The ZnO thin films deposited from the above techniques were also found to have low resistivity and high transparency in the visible region which becomes hindrance to the solar cell applications. The complexity of processing method also brings the lot of variation in the obtained results. Therefore, there is a need to understand the structure property relation and develop simple fabrication method for thin films which can be used in various nanotechnology applications such as sensors and molecular electronics for next generation's high performance nano-devices. In the present work, we adopt a simple chemical bath deposition technique to deposit thin films of Zinc oxide. The chemical bath deposition is a simple, cost effective technique to fabricate the thin films of ZnO. The structure and morphology study of prepared thin films of zinc oxide were reported.

II. METHODS AND MATERIAL

Materials and synthesis method

AR grade Zinc acetate ($Zn(CH_3COO)_2.2H_2O$), Sodium Hydroxide (NaOH) and Triethylamine were used as precursor materials. The ZnO thin films were grown onto glass substrate from solutions containing zinc acetate $Zn(CH_3COO)_2.2H_2O$ (0.5 M) and one drop triethylamine of analytical reagent grade. A hot plate with a magnetic stirrer was used to heat and stir the bath solution. The pH of the final bath was raised by the addition of a small quantity of base (0.5 M NaOH) to maintain pH in the range of 10-11. The reaction mixture was maintained at a temperature of 80 °C along with continuous stirring. The glass substrates were cleaned with acetone before immersing into the reaction bath. Substrates were taken out of reaction bath after 90 minutes of reaction time and then washed with distilled water. Finally, the substrate with deposition were dried at temperature of 100 °C and annealed at 290 °C for 30 minutes in a muffle furnace to get ZnO thin film.

Characterization details

Thin films were characterized by X-ray diffraction technique (XRD) for its structural analysis. A X-ray diffractometer with Cu Kα radiation (λ = 1.54 A°) Philips PW-3710 was used for this purpose. The diffraction pattern is recorded with 2θ angle ranging from 20° to 80°. Nicolet iN5 FTIR microscope in the range of 500 cm^{-1} to 5000 cm^{-1} was recorded for IR spectrum of prepared sample. The SEM (JEOL JSM 6360) operating at 20 kV is used for surface morphology studies of the thin films.

Reaction mechanism

Zinc acetate provides Zn^{2+} ions required for formation of ZnO films and the water molecules in the double distilled water provide O^{2-} ions. The reaction mechanism during this procedure is shown in the following equation. The deposition process mainly consists of the formation of ionic species and transport of these species through the medium and condensation of these species on the substrate. The main principle of chemical bath deposition technique is controlled precipitation of compounds in the solution of its constituent.

The reaction mechanism for the deposition of ZnO by chemical bath deposition method is illustrated below,

$Zn(CH_3COO)_2{\cdot}2H_2O + TEA \rightarrow [Zn(TEA)]^{2+} + 2CH_3COO^-$

$[Zn(TEA)]^{2+} \rightarrow Zn^{2+} + TEA$

$2NaOH \rightarrow 2Na^+ + 2OH^-$

$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2\downarrow$

$Zn(OH)_2 \rightarrow ZnO + H_2O\uparrow$

III. RESULTS AND DISCUSSION

A. XRD results

The XRD pattern of prepared ZnO thin film was studied for its structural properties. The XRD pattern shown in (Figure 1) clearly indicates the formation of hexagonal wurtzite phase of ZnO which is in good agreement with the standard JCPDS Card No. 036-1451. The peak broadening and sharp diffraction peaks in the XRD pattern indicate the presence of small nanocrystals and good crystallinity of the prepared film.

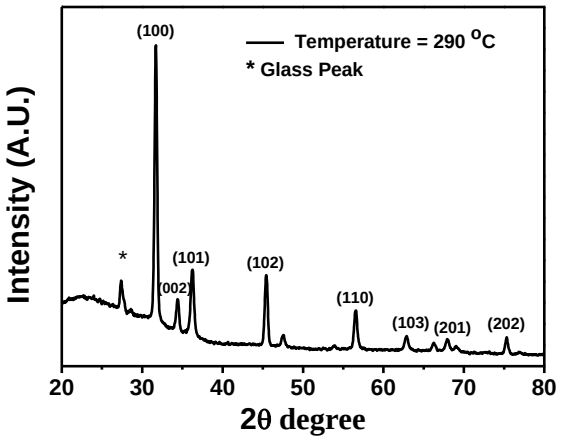

Figure 1. XRD Pattern of ZnO thin film deposited by chemical bath deposition.

The wurtzite phase crystallization of ZnO occurs when the oxygen atoms are arranged in a hexagonal close packed (HCP) type with zinc atoms occupying half the tetrahedral sites. The Zn and O atoms are tetrahedrally coordinated to each other and have its equivalent position. The zinc structure is open with all the octahedral and half the tetrahedral sites empty. [18] According to Bragg's law,

$$2d \sin\theta = n\lambda \qquad (1)$$

Where, n is order of diffraction (usually n = 1), λ is X-ray wavelength and d is the interplanar spacing between planes of given Miller indices h, k and l. In ZnO hexagonal structure, the spacing in d is related to the lattice constants a, c and the Miller indices by the following relation[1].

$$\frac{1}{d_{hkl}^2} = \left[\frac{4}{3}\frac{h^2+hk+k^2}{a^2}\right] + \frac{l^2}{c^2} \qquad (2)$$

The lattice constant a and c are calculated for (100) and (002) plane respectively by following relation[19],

$$a = \frac{\lambda}{\sqrt{3}\sin\theta} \qquad (3)$$

$$c = \frac{\lambda}{\sin\theta} \qquad (4)$$

The lattice constants (a = b = 3.2256 A° and c = 5.1932 A°, c/a = 1.6099) and diffraction peaks corresponding to the planes (100), (002), (101), (102), (110), (103) are obtained from X-ray diffraction data consistent with the JCPDS data of ZnO. The interplanar spacing (d h k l) calculated from XRD is compared with JCPDS data card and corresponding (h k l) planes are summarized in Table 1. The XRD peak profile analysis is a simple and powerful method to evaluate the peak broadening with crystallite size and lattice strain due to dislocation.

In ZnO thin films, the (101) diffraction peak is much stronger than the (002) peak. This indicates that the ZnO nanocrystals have a preferential crystallographic (101) orientation. The average crystallite size was calculated from strongest XRD peak of (101) based on the Debye–Scherrer equation. [20,21]

$$D = \frac{0.89\,\lambda}{\beta\cos\theta} \qquad (5)$$

Where, β is the full width at half maximum (FWHM), λ is the wavelength of the incident X-ray (λ = 0.1540 nm), D is the grain size, and θ is the Bragg angle. The average crystallite size calculated for synthesized ZnO nanoparticles was 17.07 nm. The size of crystallite is assumed to be the size of a coherently diffracting

domain and it is not necessarily the same as particle size.

The dislocation density (delta), which represents the amount of defects in the sample is defined as the length of dislocation lines per unit volume of the crystal and is calculated using the following equation. [22]

$$\delta = \frac{1}{D^2} \qquad (6)$$

Where, D is the crystallite size. The dislocation density (d) is 3.4318×10^{-3} $(nm)^{-2}$.

Table 1. Interplanar Spacing (Dhkl) from XRD and JCPDS Data Card for corresponding (hkl) planes.

Plane (hkl)	d_{JCPDS}(A°)	d_{XRD}(A°)
100	2.8143	2.8193
002	2.6033	2.6039
101	2.4759	2.4745
102	1.9111	1.9944
110	1.6247	1.6200
103	1.4771	1.4753
200	1.4072	1.4021
201	1.3583	1.3794
202	1.2380	1.2591

B. FTIR results

FTIR technique is a powerful tool to understand and analyze the structure of thin films of ZnO prepared by chemical bath deposition method. The frequencies at which absorption occurs may indicate the type of functional groups present in the substance. The FTIR spectrum illustrates a series of absorption bands in the range of 500-4000 cm^{-1}. Figure 2 shows the FTIR absorbance spectra of ZnO thin films samples prepared by chemical bath deposition. The small peaks at 917 cm^{-1}, 683 cm^{-1} and 487 cm^{-1} which are attributed to the stretching mode of a ZnO bond.[23-24] The characteristic peaks at 1550 cm^{-1} and 1450 cm^{-1} are attributed to symmetric and asymmetric C=O bonds vibrations respectively.[25] The X-ray diffraction study also indicated successful deposition of ZnO thin films on glass substrate. Thus, the structural characterization done using XRD and FTIR studies indicates stoichiometric deposition of ZnO along with formation of nanocrystallites onto glass substrate. [26]

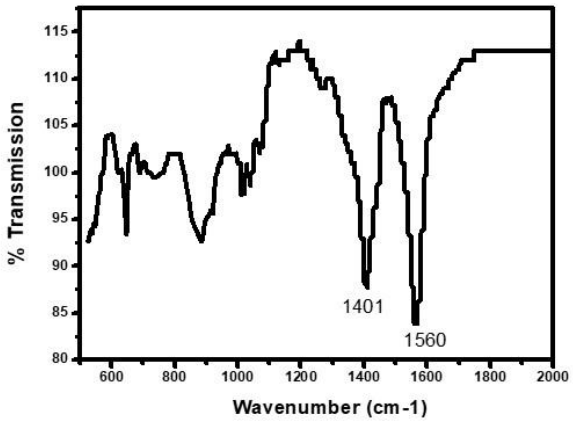

Figure 2. FTIR spectra of zinc oxide (ZnO) thin films.

C. SEM results

The scanning electron micrograph image of zinc oxide (ZnO) thin films deposited by chemical bath deposition is shown in Figure 3. The SEM image shows that zinc oxide has spherical morphology. The film consists of nanocrystalline grains with uniform distribution on the entire substrate surface with randomly oriented morphology. The zinc oxide thin film morphology shows uniform dispersion of nanoparticles with slight agglomeration. The crystallite size of ZnO nanoparticles is in the range of 20 nm. Thus, the SEM analysis of crystallite size shows a good agreement with that results obtained from XRD analysis. [27]

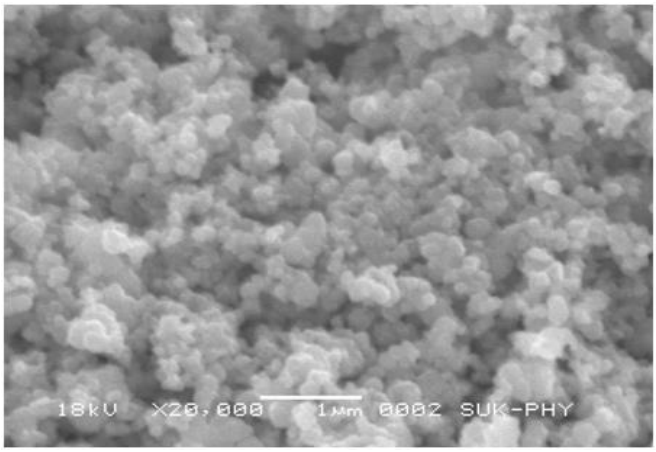

Figure 3. Scanning electron micrograph of zinc oxide (ZnO) thin films.

IV. CONCLUSION

The zinc oxide thin films were successfully prepared by simple chemical bath deposition (CBD) technique. The thin films having uniform morphology were deposited onto glass substrate. The ZnO thin films characterized by structural and morphological study shows the uniform deposition of ZnO thin films onto glass substrate. The X-ray diffraction spectra show all the characteristics peaks of zinc oxide indicating stoichiometric transformation of zinc oxide into thin film. The FTIR results also corroborate the formation of ZnO nanocrystallites onto glass substrate. The SEM image shows that spherical morphology of zinc oxide thin films with uniform dispersion. In conclusion, the zinc oxide thin films deposited by chemical bath deposition method shows excellent structural and morphological properties which can be potentially useful for applications in solar cell.

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