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INFLUENCE OF REACTION CHAMBER TEMPERATURE ON OPTICAL PROPERTIES OF ZNO THIN FILMS PREPARED BY SPRAY CVD TECHNIQUE RELATIVELY AT LOW SUBSTRATE TEMPERATURE

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ABSTRACT
Uniform & homogeneous Zinc Oxide thin films (ZnO) were deposited on cleaned glass substrates by spray CVD technique. Zinc acetate dehydrate and methanol were used as a starting material and solvent. The effect of deposition parameters on structural, optical & electrical properties of the ZnO thin films was investigated. Thermogravimetric analysis (TGA) of the Zinc acetate showed that weight loss continued until 330°C. Structural characterization confirmed polycrystalline nature possessing hexagonal wurtzite structure with crystallite size varying between 100.7 and 268.6 nm. The electrical studies established that the films deposited at 330°C reveal enhancing electrical conduction in ZnO thin films and beyond that the distortion caused in the lattice causes to lower the conductivity. The optical absorption studies reveal that the transition is direct band gap energy. The films also exhibited distinct changes in their optical properties, including a red shift of bandgap.

KEYWORDS: ZnO thin film, spray CVD technique, optical properties, Optical band gap.

INTRODUCTION

ZnO thin film is one of the II-VI compound semiconductors of hexagonal wurtzite crystal structure. It is one of the promising materials in the field of thin film technology due to its versatile applications generated by the particular properties. Recently, the studies to synthesize metal-oxide based nanoprticles of controlled size have gain momentum. Among the various nanomaterials ZnO, with direct wide band gap energy of 3.37eV and a large exciton binding energy (60meV), has become one of the most important functional materials with unique properties of near-ultraviolet emission, optical transparency, electric conductivity and piezoelectricity (B. D. Cullity 1956, Chao-Te Liu et al. 2012, C. M. Lampkin 1979, C. Klingshirn 2007, H. P. Klug et al. 1954). The different keystone properties of ZnO are:-i) a semiconductor- an important functional oxide ii) Wide band gap (3.37eV)- applied for short wavelength optoelectronic applications including laser development iii) High exciton binding energy (60meV). It allows efficient excitonic emission at room temperature . It opens the prospect of fabricating semiconductor lasers in uv spectral region. iv)The non-centrosymmetric characteristic in the wurtzite structure. It results in strong piezoelectric and pyroelectric properties and used in electromechanical coupled sensors and transducers.

Technological progress of modern society depends on the material science and engineering community's ability to conceive the novel materials with extraordinary combination of physical and mechanical properties. Modern technology requires thin films for different applications. Now days, the focus is moving on to the synthesis of ZnO nanostructures. The techniques used for synthesizing ZnO nanostructures mainly include spray pyrolysis, sputtering, sol-gel spin coating, pulsed laser deposition (PLD), chemical vapor deposition (CVD) etc (Huiyong Liu et al. 2010, M. D. Uplane et al. 2000, M. de la L. Olvera, et al. 2001, M. de la L. Olveraet al. 2002). However, these methods require high temperature, expensive substrates, high cost & tedious procedures, sophisticated equipment’s and rigorous experimental conditions. Hence it is necessary to find out a simple and low cost method to synthesize ZnO nanostructures to tackle the problems. In view of this, we followed a simple, inexpensive, environmentally benign, solution-based method with some modification to produce ZnO nanoparticles without templates and catalysts.

In the present work we had explored synthesis of ZnO nanoparticles by spray CVD technique and reported influence of reaction chamber variation on the structural, morphological and optical properties.

ISSN: 2348 – 604X (p); 2348 – 6058 (e)

MATERIALS AND METHODS

Shewale et.al. (2010), reported the schematic experimental set up of spray CVD technique] Rajan *et al.*,(2001) used for synthesis of undoped ZnO thin films. It mainly consists of a spray nozzle assembly, reaction chamber, substrate heater, Chromel-Aluminium thermocouples and PID temperature controllers. ZnO thin film deposition were carried out by using 200ml non-aqueous solution of methanol with 0.075M concentration of high purity zinc acetate [Zn $(CH_3COO)_2 \cdot 2H_2O$] (Thomas Baker, India) dissolved in it. The solution was sprayed through a glass nozzle onto the ultrasonically cleaned glass substrates. The distance between spray nozzle and glass substrate is kept 40cm constant for total length of experiment. The optimized spray rate of ~6 ml min^{-1} is regulated by using compressed air at a pressure of 10 LPM. The different preparative parameters such as solution quantity, concentration, and spray rate were optimized in order to obtain low resistive and highly transparent undoped ZnO thin films.

In the first stage of this work, the effects of variation of reaction chamber temperature (core temperature) from 300^0C to 360^0C in stage of 30^0C were studied by keeping substrate temperature constant at 200^0C. In the next stage of this work, the effects of substrate temperature variation from 190^0C to 220^0C in stage of 20^0C have been studied for optimized core temperature of 330^0C (which is same as obtained from decomposition temperature of ZnO by TGA-DTA analysis). Throughout the experimentation, the both the substrate and core temperature were controlled using electronic temperature controllers. Hazardous gases evolved during the thermal decomposition were expelled out by using exhaust fans.

Characterization Techniques for Synthesis of ZnO Thin films

The structural investigations of ZnO thin films were carried out using a Bruker AXS X-ray diffractometer (German make Bruker axs D-8 Advance Model) using Cu–Kα (λ = 1.54 Å) as radiation source operating at 40 kV and 30 mA and step size of 0.11. The diffraction angle '2θ' was varied from 20^0 to100^0 with a step of 0.02^0/min. The films thickness and roughness was measured by surface profilometer model Ambios XP-1. The electrical resistivity studies were carried out using the home made two-probe resistivity unit for temperature range of 300–500K. The films surface morphology was studied with the Field emission scanning electron micrographs (FESEM) from Centre for Materials for Electronics Technology, Pune at 50,000× magnification. The transmission spectrum (normal incidence) measurements were made at room temperature in the spectral range of 290–1100 nm using a UV–VIS spectrophotometer (Shimatzu1800model). Measurements of room temperature transport properties like resistivity (ρ), conductivity (σ), sheet resistance (R_s), carrier concentration (n), and mobility(μ) were carried out by the Van der Pauw technique[14] and Hall effect set up, supplied by Scientific Equipment's, Rookie, India. Colloidal silver paste was used for ohmic contacts. Photoluminescence spectra of the samples were recorded with a spectrofluorimeter JASCO, model–F.P.-750, Japan using a 260nm line of an ultraviolet lamp as an excitation source. The three dimensional morphology of the growth was examined by using atomic force microscopy (AFM), Nanoscope instruments, USA in contact mode, with V shape silicon nitride cantilever of length 100μm and spring constant 0.58N/m.

RESULTS AND DISCUSSION

To prepare the metal oxide films, the precursor solution is sprayed through the nozzle; when it enters the reaction chamber, it pyrolytically decomposes into metal oxide particles. These particles are pushed upward by the atomized air and reach the preheated substrates. The substrate heater offers the initial nucleation centres onto the preheated substrates for the growth of film and provides average kinetic energy for the even distribution of the deposits. After the initial nucleation process at the respective substrate temperature, the agglomeration of the grains may tend to form large clusters. Thus, deposition occurs in two steps, namely requisite chemical pyrolysis and nucleation/growth. Hence, this novel method is the amalgamation of chemical vapour deposition and conventional spray pyrolysis technique.

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Characterization of ZnO thin films by X ray diffraction Technique

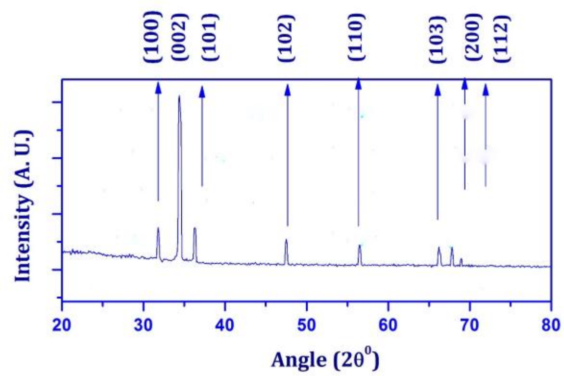

Figure 1. A typical X-ray diffraction pattern for 330^{0}C

X-ray diffraction pattern is helpful in studying synthesis of different morphologies of ZnO micro tubes with the crystallite size, structure and phase formation. Fig.1 reveals that the structural properties of the ZnO films largely depend on core temperature. All the three films show preferential orientation along (002) plane perpendicular to substrate i.e. along C-axis. Similar texturing of the films has also been observed by other groups (M. J. Buerger (1942). Three well-defined peaks, identified as the (100), (002), and (101) diffraction planes of ZnO, are clearly observed in diagrams, along with less intense peaks (102), (110), (103), (200), (112) indicating the polycrystalline wurzite structure of ZnO. The d values of thin films were in good agreement with those reported in the PDF for ZnO (JCPDS card file No: 80-0075, a = 3:24982 and c = 5.20661 Å). It is evident from this figure that structural properties of the ZnO films are strongly depend on core temperature. The films deposited for core temperature 330^{0}C shows higher crystalline quality. The behavior is confirmed by TGA-DTA analysis of zinc acetate in section 3.2.2. It is well recognized that in spray CVD technique zinc acetate group decomposes at 330^{0}C temperature at which thermal decomposition in the reaction chamber takes place followed by the nucleation around scattered centers causing the subsequent growth in different forms.

Energy dispersive X-ray spectrometry analysis:-

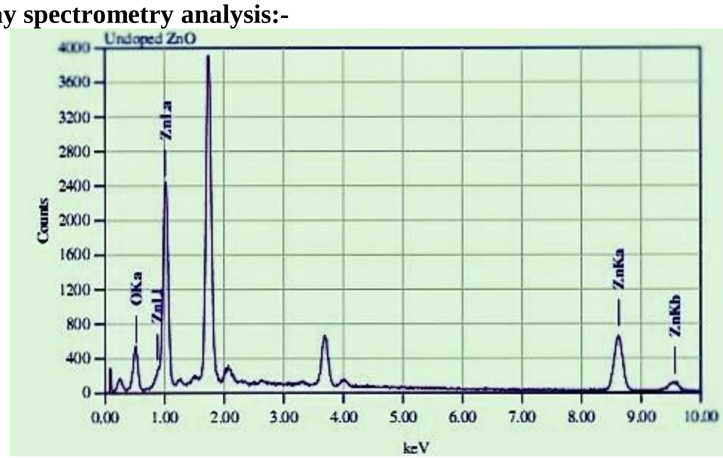

Figure 2. EDAX of ZnO thin film at330^{0}C

To check the composition of the as-grown ZnO thin films, EDX analysis was performed. Figure 2 demonstrates the typical EDX analysis of the as-grown ZnO thin films. It is confirmed from the EDX analysis that the grown ZnO thin film was composed of zinc and oxygen only. The appearance of Si peak in the spectrum is due to the substrate.

Table 1 Element Composition for EDAX of ZnO thin film

Element	Element %	Atomic %
O	22.27	24.81
Zn	46.07	75.19
Total	100.00	100.00

Optical Properties:-

The optical transmission of the ZnO thin films synthesized by spray CVD system on corning glass substrates is as shown in figure 3. The maximum visible average transmission was found to be 90% for core temperature 360^0C. It shows that with increasing reaction chamber temperature results into increased transmittance of thin films and at optimized temperature 330^0C, the films show 83% average transparency.

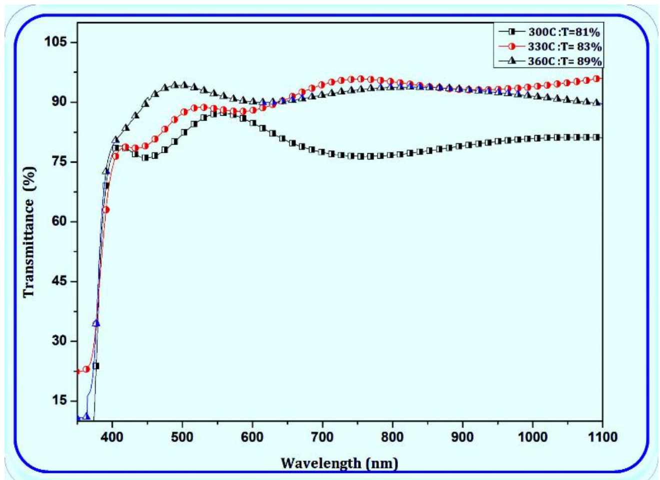

Figure 3. Optical transmission spectra of Zn0 thin films

These transmittance curves with interference fringe pattern between the wave fronts generated at the two interfaces (air and substrate) define the sinusoidal behavior of the curves. This revealed the smooth reflecting surfaces of the film and there was not much scattering/absorption loss at the surface suggesting that it has non uniform distribution of film thickness, refractive index and conductivity. In transparent metal oxides, metal to oxygen ratio decides the percentage of transmittance. A metal rich film usually exhibits less transparency. At lower temperatures, i.e. at 300^0C, relatively lower transmission is due to incomplete decomposition of the sprayed droplets. In general, in the visible region of the spectrum, the transmission is very high (high enough to observe interference fringes). It is due to the fact that the reflectivity is low and there is no (or less) absorption due to transfer of electrons from valence band to conduction band owing to optical interference effects, it is possible to maximize the transmission of thin film at particular region of wavelengths. The uniform and transparent films are formed within temperature range 330^0C

ISSN: 2348 – 604X (p); 2348 – 6058 (e)

to360^{0}C. The smoother surface morphology and less grain boundary density the films has, the higher the transmittance.

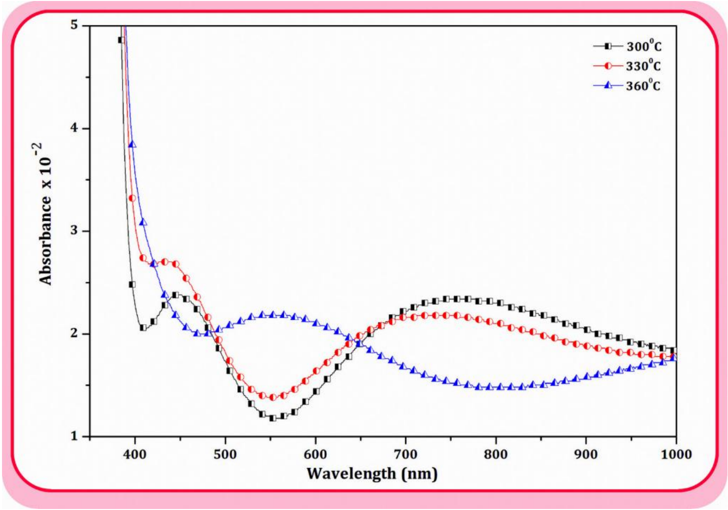

Figure 4. Optical transmission spectra of Zn0 thin films

Figure 4 shows the optical absorption spectrum vs. wavelength. The graph reveals that the absorption in ZnO thin film is low enough to pass most of the light. However, less than 0.1% of absorption occurs in the visible region. The absorption coefficient 'α ' of the films was determined from absorbance measurements.

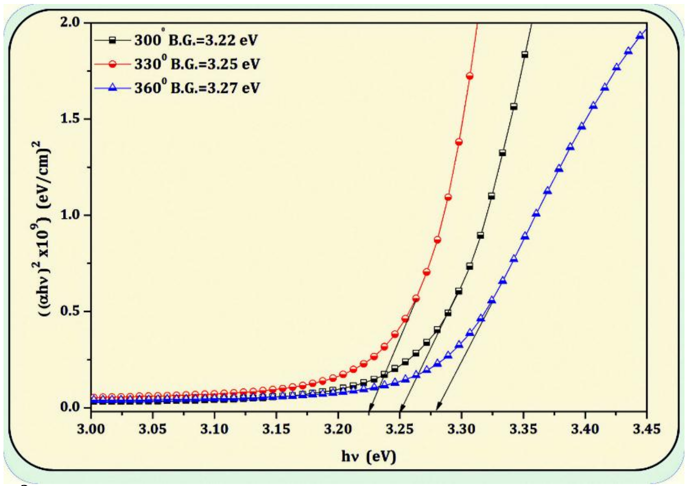

Figure 5. The plot of $(\alpha h\nu)^2$ vs. hν for Zn0 films

The calculation of the absorption coefficient of the film in this region was performed using the following expression:

$$\alpha = \frac{2.303A}{t} \text{ -- (1)}$$

where A is the optical absorbance. The optical absorption edge was analyzed by the following equation,

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \text{ --- (2)}$$

Where A is constant, *h*ν incident photon energy, Eg is the energy band gap.

Figure 5 shows the plot of $(\alpha h\nu)^2$ vs. *h*ν for undoped ZnO thin films synthesized by spray CVD technique. It has been observed that the plot is linear over a wide range of photon energies indicating a direct type of transitions. The intercepts (extrapolations) of these plots (straight lines) on the energy axis reflect the energy band gaps vary between 3.22eV to 3.27eV. It reveals minimum optical band gap value for optimized 330^0C temperature indicating better crystallinity. These observed values of optical band gap are in good agreement with the previous reports by others (Tae Young Ma et al. 2000, Zhong Lin Wang 2004).

CONCLUSION

The intrinsic and microcrystalline properties of ZnO thin films are synthesized with a newly designed, homemade spray CVD technique. The major benefits of this technique are precise stoichiometry and its ability to deposit vapours on a large surface area with a high uniformity of thickness. The commercialization potential is enhanced by the low deposition temperature. During the synthesis of 0.075M pure ZnO thin films in non-aqueous medium (solution quantity- 200ml) by spray CVD technique the substrate temperature is kept constant at 220°C and effect of core temperature variation has been studied in the range 300°C to 360°C in steps of 30°C on glass substrate. XRD analysis reveals that all films show (002) as the preferential orientation perpendicular to substrate with particle size 22nm. Among all the three samples, the films deposited at 330°C show better crystallinity showing highly textured films. The optical transmittance curve indicates the interference fringe pattern showing enhanced optical transmittance with core temperature. The optical absorption curve reveals enough absorption to pass most of the light. Absorption data is used to calculate band gap energy which is found to be minimum for 330°C core temperature. This may be attributed to the better crystallinity and lower defect density near the band edge.

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