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Characterization and Ammonia Sensing Property of Spray Deposited Nanocrystallite ZnO Thin Films.

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ABSTRACT

Thin films of zinc oxide were prepared on a glass substrate using spray pyrolysis technique. The recorded powder XRD pattern shows that the film is polycrystalline in nature with hexagonal (wurtzite) crystal structure. By theoretical calculations, the crystallite size and strain was found to be 46 nm and 2.40 x 10^{-4} respectively. The SEM pattern clearly shows the uniform distribution of particles with spherical structure. The elemental composition of the thin film between Zn and O was found to be 52.12 and 47.79 at% respectively. The film shows a strong absorbance in the UV region and is almost transparent in the entire visible region. By Tacu's plot, the optical band gap of the film was estimated to be 3.2 eV. The response and recovery time of the ZnO film for 10 and 50 ppm ammonia gas is found to be 15 and 6 seconds, 30 and 400 seconds respectively. The mechanism involved in the ammonia gas sensing was briefly elaborate.

Keywords: Spray pyrolysis, ZnO, ammonia gas, SEM, Optical absorption, nanocrystallite

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INTRODUCTION

Different materials in the form of crystal, thin film, powder and gel were being prepared for various technological applications. Devices or components made in thin film forms have advantages over the bulk materials because of extreme compactness and corresponding reduction in size and weight along with low power consumption. Hence materials in thin film forms are preferred much for fabricating devices. Also, there has been an increasing interest in the preparation of nanocrystalline thin film materials owing to their electrical, optical, and mechanical properties being superior to those of conventional coarse granular structures [1]. The surface to bulk ratio for a nanocrystalline material is much greater than for a material with large grains, and hence the nano crystalline material yields a large interface between the solid and a gaseous medium, increasing the gas sensitivity [2].

Thin films can be prepared from many methods, and each method has its own characteristic merits and demerits in producing homogeneous and defect free materials. Among many methods available, spray pyrolysis is simple, inexpensive and the film thickness can be controlled over a wide range. Zinc oxide (ZnO) is one of the most significant II-VI oxide semiconductors having hexagonal wurtzite structure. It has attracted considerable attention due to its excellent optical and electrical properties, and hence has potential applications in various fields such as photocatalysis [3], solar cell [4,5], superhydrophobic surface [6], gas sensors [7,8] etc. Techniques such as spray pyrolysis [9], sol-gel [10], dip coating [11], SILAR [12], etc., are reported to obtain nanostructured ZnO thin films.

Ammonia is used in automotive and chemical industries and is toxic in nature. The OSHA (Occupational Safety and Health Administration, USA) sets the limit for maximum exposure as 35 ppm for a period of 15 minutes [13]. Hence detection of ammonia in environment is of importance for safety and human health. Un-doped and doped ZnO thin films operating from room temperature to 300^{o}C has been previously reported [14,15] towards detecting ammonia. The performance of the sensors depends on nanostructure size and shape [16]. In the present work, ZnO thin film was prepared using spray pyrolysis technique and its structural, morphological, optical and ammonia sensing properties were studied and reported.

Experimental details

Zinc Oxide thin films was prepared by spray pyrolysis technique on glass substrate using aqueous solution of 0.1M zinc acetate [$Zn(CH_3COO)_2.2H_2O$] dissolved in deionised water. The spray pyrolysis system was home built as reported [17] and plate heater was used to heat the substrate. The solution was sprayed at an angle of 45˚ onto preheated glass substrate kept at different temperature. Prior to deposition, the substrates was cleaned acetate and rinsed with deionised water. Compressed dry air at a pressure of 2 kg/cm^2 from an air compressor via an air filter-cum regulator was used as the carrier gas and spray rate of the solution was maintained at 3 ml/min. To avoid excessive cooling of substrates, successive spraying process was used with time period of 15 seconds between successive bursts. Substrate temperature was controlled by a chrome-nickel thermocouple fed to a micro controller with an accuracy of ±1˚C. The temperature on top side of the substrate is measured by placing thermocouple on a reference glass substrate kept nearer to the coating substrate so as to measure the exact temperature.

The overall reaction process can be expressed as heat decomposition of zinc acetate to form zinc oxide in presence of water as

$$Zn(CH_3COO)_2.2H_2O_{(aq)} \longrightarrow ZnO_{(s)} + CH_3COCH_{3(g)} + CO_{2(g)} + 2H_2O_{(g)}$$

The as grown films were subjected to study further characterization. Film thickness was estimated by weight loss method and verified with cross sectional view of SEM image. To investigate the microstructural detail of the film, PANalytical X-ray diffractometer (Model D/MAX ULTIMA III) using Ni-filtered CuKα X-radiation (λ = 1.54056Å), was employed with generator setting of 30mA and 40kV. Continuous scanning was applied with a speed of 10˚/min. A range of 2θ from 10˚ to 100˚ was scanned from a fixed slit type, so that all possible diffraction peaks could be detected. X-ray line broadening technique was adopted to study microstructural details. Optical measurements were carried out at room temperature using UV-Vis Spectrophotometer (Elico SL159). The vapour sensing property of the film was studied by chemiresistive method using home built gas sensor test chamber.

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RESULTS AND DISCUSSION

Structural and Morphological analysis

Figure 1 shows the XRD pattern of as-deposited ZnO films on glass substrate prepared from 0.1M solution concentration at 250°C. The obtained XRD patterns agree with standard JCPDS card [36-1451] indicating polycrystalline nature with hexagonal (wurtzite) crystal structure. The planes are indexed as (1 0 0), (0 0 2) and (1 0 1) with respect to standard card. XRD peaks are /shows broadened in their shape when compared with standard JCPDS line. These effects can be classified into instrument and specimen broadening. Instrument broadening originates from the non-ideal optical effects of the diffractometer and from the wavelength distribution of the radiation. In the present work, instrumental broadening was corrected by using a standard defect free silicon sample. The specimen broadening arises due to small crystallites and strains in the film. In thin films, strains originate due to lattice mismatch between polycrystalline film and amorphous substrate or difference in coefficients of thermal expansion of the film and the substrate. The following well known Scherrer's formula is utilized to determine crystallite size and microstrain

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad \text{and} \quad \varepsilon_{hkl} = \frac{\beta}{4\tan\theta} \text{ ----------(1)}$$

Where D is the size of the crystallite in the direction perpendicular to the reflecting planes, θ is the diffraction angle, K is the shape factor and is equal to 0.89 for spherical shape, λ is the wavelength of X-ray and β the full width at half maximum of prominent peaks in radian and ε_{hkl} is microstrain. The crystallite size and strain was found to be 46 nm and 2.40 x 10^{-4} unit respectively. The observed crystallite size agrees with the observed scanning electron micrograph shown in fig.2 The SEM also indicates the uniform distribution of crystallite. Analysis of the EDAX spectrum of ZnO thin film coated on glass substrates reveals the presence of Zinc and Oxygen in the film. The composition between Zn and O was found to be nearly stoichiometric (52.12 : 47.79 at%) with oxygen deficient. The presence of excess Zn in the film indicate n-type semiconductor due to electron donor of zinc metal.

Optical studies

Optical absorption measurements were carried out in the wavelength region 300 to 1100nm. Figure 3 show optical absorbance and transmittance of ZnO film and a smooth increase in absorbance above 400nm was observed. This smooth increase is due to crystalline nature of the prepared film. The absorption coefficient α was calculated from Lamberts law (α= (2.303 A) / t) ,where 'A 'is optical absorbance and 't' is the film thickness. Optical band gap E_g and absorption coefficient is related as

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

where A is a constant, exponent p is the transition probability. For p = ½ the transition is direct and allowed, p=2 indirect and allowed and p =3/2 for direct forbidden. To determine the direct allowed band gap, a graph between $(\alpha h\nu)^2$ and hν is plotted and is shown in figure 4. The straight portion of the graph is extrapolated to energy axis to give E_g value and the value is found to be 3.2eV irrespective of deposition temperature.

Ammonia sensing studies

To study ammonia sensing property of ZnO thin film, a glass test chamber was home built as reported [18]. It consists of (i) 1.5L glass chamber (ii) plate heater with thermostat to maintain ZnO film at different temperature (ii) outlet valve connected to vacuum pump and (iii) inlet port to inject target vapour in the form of liquid through chromatographic syringe. The level of ammonia inside the chamber is calculated in ppm unit and varied from 10 to 50 ppm. First the electrical contacts were made on the film using thin copper wire and silver paste. The terminals were connected to data acquisition system to record the resistance change. ZnO film resistance was measured under air and in ammonia atmosphere at room temperature.

When ZnO film is exposed to air atmosphere, oxygen molecule traps electrons from conduction band of the film and adsorbed as molecular oxygen ion on the surface as given in the equation (1). This leads to an

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increase in ZnO film resistance. As such, desired concentration of ammonia was injected in the chamber at room temperature. The ammonia vapour reacts with the molecular oxygen ion and releases electron through oxidation process as given in equation (2).

$$O_2 + e^- \longrightarrow O_{2(ads)}^- \quad \text{---------- (1)}$$

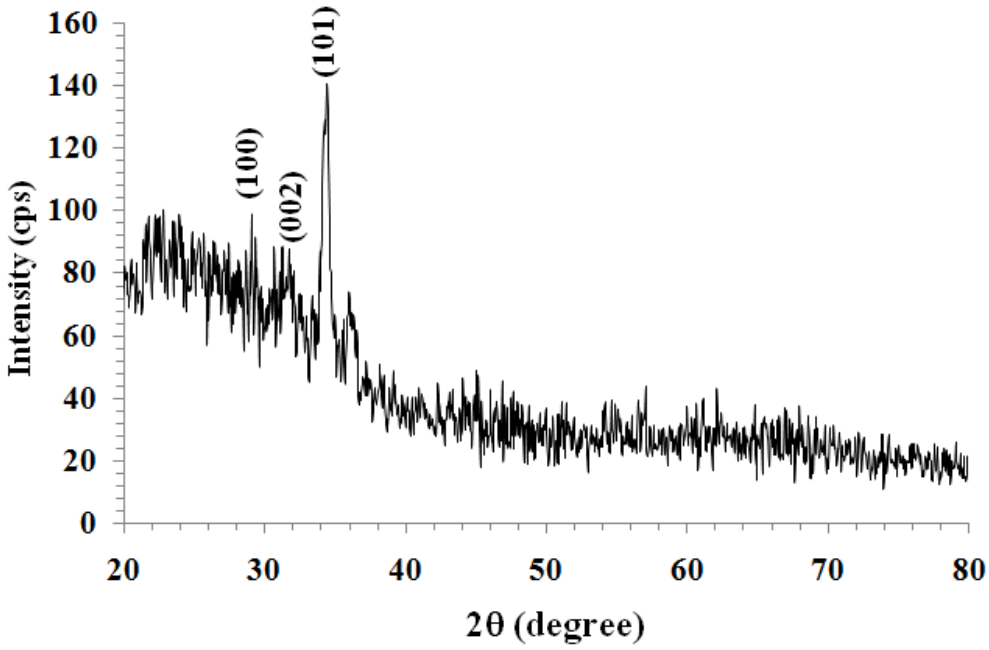
$$4NH_3 + 3O_{2(ads)}^- \longrightarrow 2N_2 + 6H_2O + 3e^- \quad \text{---------- (2)}$$

Thus, the electrons released from the surface reaction are transferred back into the conduction band and result in the decrease of ZnO film resistance. The response of the film for different ammonia level was studied and calculated using the relation

$$S = (R_{air} - R_{ammonia}) / R_{ammonia}.$$

where R_{air} and $R_{ammonia}$ is the resistance of ZnO film in air and ammonia atmosphere. Figure 5 shows the transient plot of ZnO film for 10 and 50 ppm of concentrations. The time required for the film to reach a 90% decrease from the baseline resistance after injecting ammonia was taken as the response time and was found to be 15 and 6 sec for 10 and 50 ppm respectively. Similarly the time required for the film to reach 90% of the baseline was taken as the recovery time and was found to be 30 and 400 sec for 10 and 50 ppm of ammonia respectively. The fast response and recovery time is due to nanocrystallite of the prepared ZnO thin film.

Fig.1 XRD pattern of ZnO films



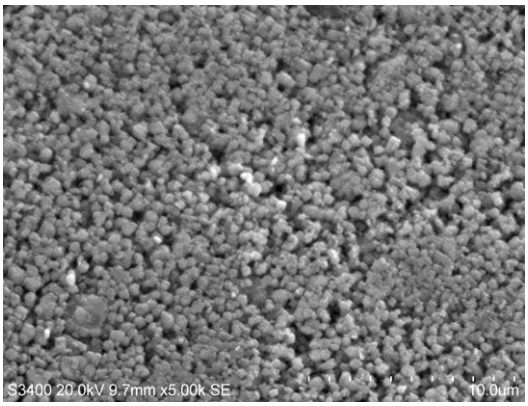


Fig.2 SEM image for ZnO films

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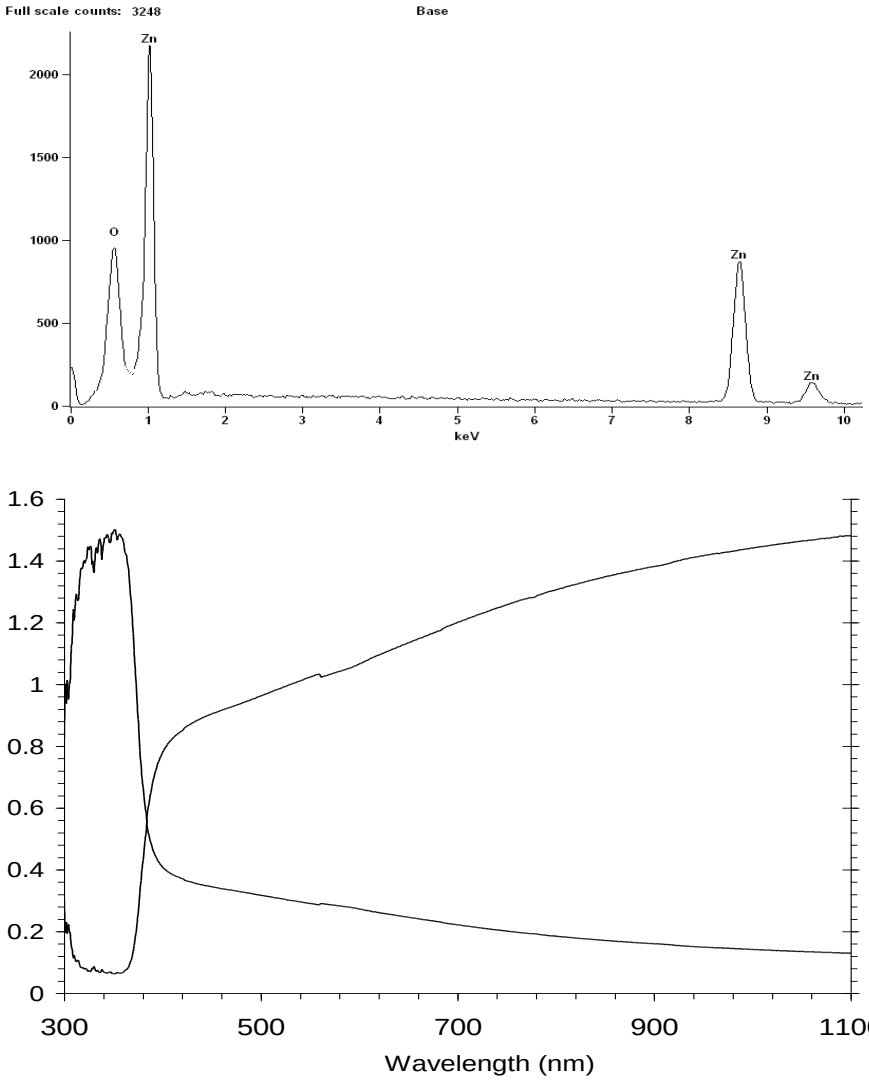

Fig 3. Optical absorbance and transmittance Spectra of ZnO thin films

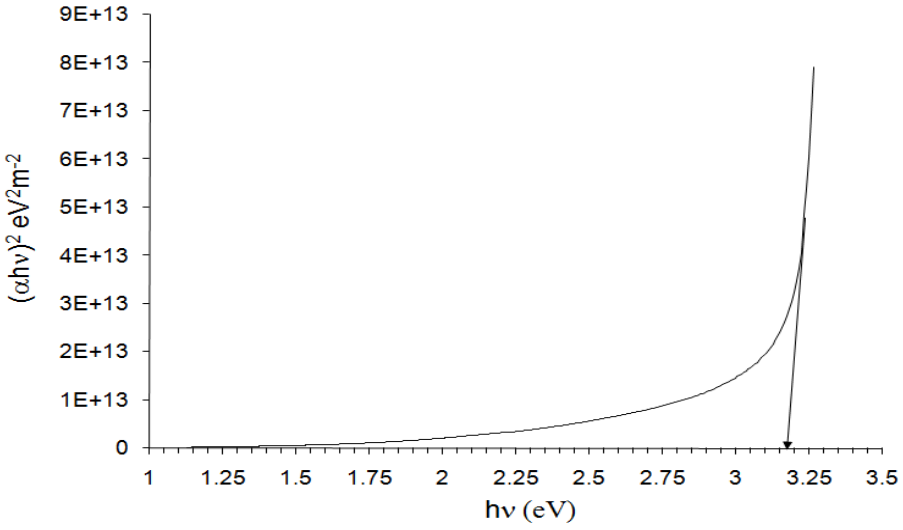

Fig.4 Plots of $(\alpha h\nu)^2$ and (hν) for ZnO thin films

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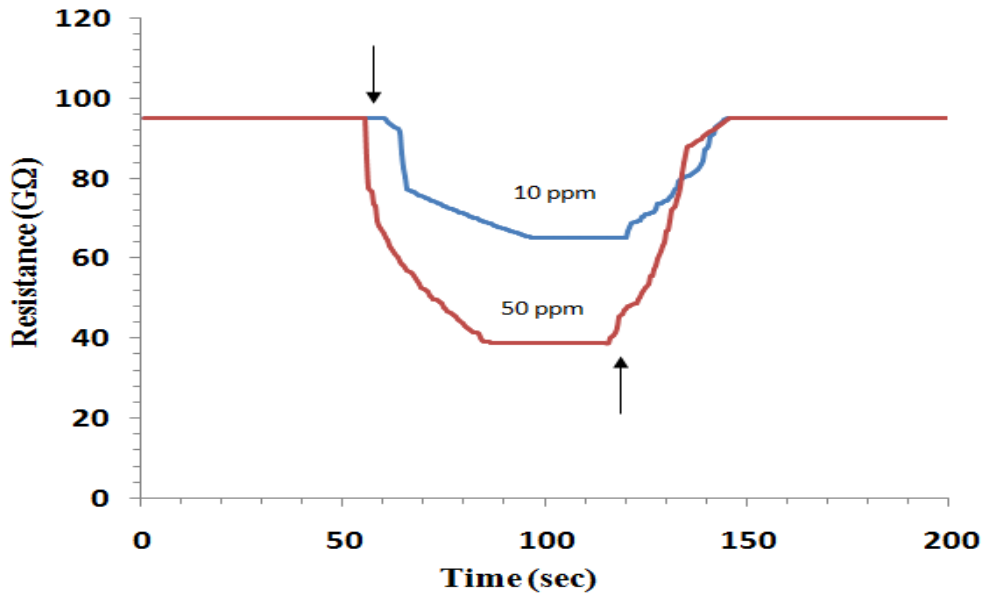

Fig 5.Transient plots of ZnO film for 10 and 50 ppm of concentrations

CONCLUSION

Zinc Oxide thin film was prepared by home built spray pyrolysis unit on glass substrate. XRD results indicates the polycrystalline nature of the film with preferential orientation along (1 0 1) plane. From SEM, the crystalline size was in the order of nanometer. Optical studies revealed the prepared film is of semiconducting type with band gap of 3.20eV. The response of the ZnO film towards ammonia was found to be good with response and recovery time in the order of seconds.

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