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Growth and properties of multifunctional spray deposited ZnO thin films for vapor sensor application

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ABSTRACT

Simple and economical spray pyrolysis technique (SPT) was employed for the synthesis of multifunctional Zinc Oxide (ZnO) thin film onto glass substrates. The synthesized material was polycrystalline nature as confirmed from X-ray diffraction (XRD). Atomic force microscopy (AFM) image revealed the uniform distribution of roughness 5.8-47 nm. The deposited film was highly transparent with average transmittance of about 75%. The optical transmittance spectrum shows sharp band edge at 310 nm. The gas sensing performance of the spray deposited ZnO films toward to reducing gas like ammonia was also studied.

KEY WORDS: Multifunctional, spray, sensor.

1. INTRODUCTION

For sensor applications, metal oxide semiconductors like SnO_2, ZnO and TiO_2 have been investigated for several decades. Most of them are expected to be excellent candidates to fabricate gas sensors for detecting harmful target gases. As a typical n-type metal oxide semiconductor, ZnO, with a wide band gap (3.37 eV), shows good morphology, tailoring properties, high electron mobility, good chemical stability and low production cost, which are all desirable characteristics for gas sensor. Previous reports have demonstrated that ZnO exhibits good response characteristics to many toxic gases like H_2S, NO_2 and CO, especially for the nanostructures. Due to high specific surface-to-volume ratio, one-dimensional ZnO nanostructures like nanowires, nanotube and nanobelts have been widely adopted to fabricate gas sensor.

In this present work, ZnO thin films were deposited on the glass substrate by using Spray Pyrolysis technique. Structural, morphological and optical studies were carried out to analyze the properties various quantities of precursor solution. Also, the ammonia vapor sensing performance of the sample was studied at 70 ml quantity of precursor solution.

2. EXPERIMENTAL TECHNIQUE

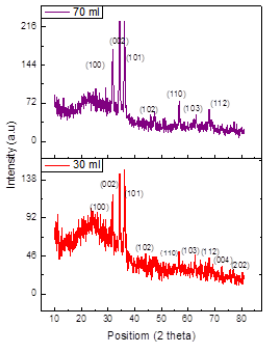
In recent years, the formation of nanostructures and the properties of the metal – oxide thin films depend on the method of synthesis. Over such competing methods, Spray pyrolysis plays a vital role in the synthesis of quality thin films with different nanostructures. It is a modest and inexpensive method used for large area depositions with good uniformity and porosity in films and yields oxide films of high quality at rather low costs when properly controlled. To prepare ZnO thin films, aqueous solution of analytical grade Zinc acetate [$Zn(CH_3COO)_2.2H_2O$] of various quantities of solution is sprayed on glass substrate by masking method. The reaction is given in equation (1).

$$Zn(CH_3COO)_2.2H_2O_{(aq)} \longrightarrow Zn(CH_3COO)_2 + H_2O$$
$$Zn(CH_3COO)_{2(s)} \longrightarrow ZnO_{(s)} + CH_3COCH_{3(g)} + CO_{2(g)} \quad \text{(Equation.1)}$$

3. RESULTS

3.1. Structural properties: The crystal structures of the ZnO nanofilms were characterized via XRD (as shown in Fig. 1). It can be found that all the characteristic peaks of the ZnO nanofilms match well with the diffraction pattern of typical hexagonal wurtzite ZnO structure (JCPDS Card No. 36-1451) and no peaks are observed for other impurities such as $Zn(CH_3COO)_2$ and zinc, indicating the growth of pure ZnO nanofilms and further annealing process is not needed .

The surface topography of the films were observed by atomic force microscopy (AFM) in the tapping mode. Fig. 2(a) and (b) shows the AFM images of ZnO films scanned over an area of 1 cm × 1 cm. It shows that hexagonally faceted columnar grains play a dominant role in the surface morphology. It can be observed that with an increase in quantity of solution, the surface roughness of the films increased. For the quantity of solution (30 ml) the root mean square (RMS) roughness was 5.8 nm. With an increase quantity of solution (70 ml), the RMS roughness has gradually increased to 47 nm. The increase of RMS roughness with the increase of quantity of solution is due to the larger grains formation as well as an increase in the porosity of the films.



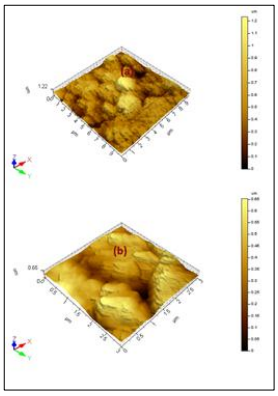


Fig.1.XRD patterns and **Fig.2. AFM images of (a) 30 ml (b) 70ml of ZnO thin film**

3.2. Optical properties: Transmittance of ZnO films was measured in the wavelength range from 300 to 1100 nm. Fig. 3 (a) and (b) shows that the absorbance and transmittance curves of ZnO films with different quantities of solution. All the samples showed good transparency higher than 70%. With increasing quantity of solution, the transmittance of the films decreased. In contrast, absorbance of the films increased. The optical transmittance spectrum shows sharp band edge at 310 nm, corresponding to band gap energy of 3.25 eV.

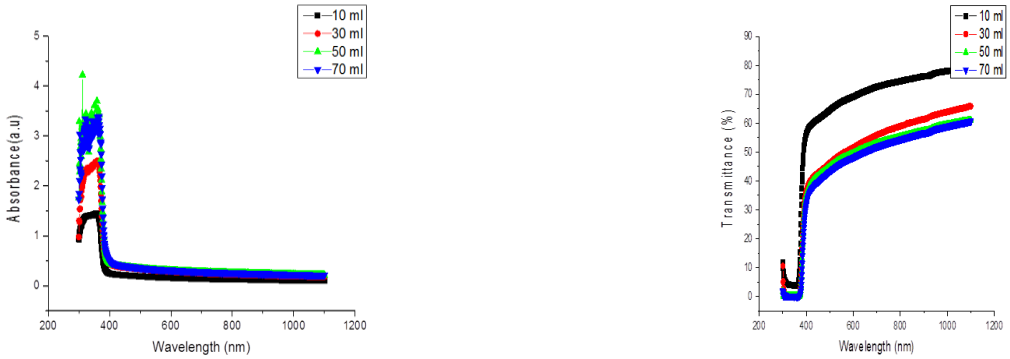


Figure.3(a)absorbance and (b) transmission spectra of various solution quantity of ZnO thin film

3.3. Gas sensing properties: The gas sensitivity measurement of the ZnO sensors was carried out by using a home-made gas sensor system. The temperature of the system was controlled from room temperature to 500^0C ($\pm1^0$C) and the electrical resistance was measured. Conducting silver paste was used to make contacts on both ends of film. The film area was kept constant for the sample prepared for the measurement of gas sensitivity. A known amount of gas was injected into the system and subsequently, the decrease in film resistance was monitored till it became constant. Finally, one end of tube was opened and air was pumped to recover the initial value of resistance in air. The sensor sensitivity was measured at the 5 and 50ppm for ammonia vapor at room temperature. The experiment was repeated twice to check the repeatability of the sensor. The gas sensitivity (S (%)) is calculated using Eq. (2). The output signal from the op-amp is connected to a computer controlled National Instruments–data acquisition board (NI-DAQ 6212) interfaced with Lab VIEW software to record voltage and, then, to convert into electrical resistance of the film by ohms law.

$$S = \frac{Ro - Rg}{Rg} \times 100\% \quad \text{(Equation.2)}$$

Where, Ra is the resistance of the sensor in the presence of air and Rg is the resistance of the sensor in the presence of ammonia. When ZnO film is exposed to air atmosphere, oxygen molecule traps electrons from conduction band of the film and exists as molecular oxygen ion on the surface as given in the equation (3). This leads to an increase in ZnO film resistance. Desired concentration of ammonia is injected in the chamber at room temperature. The ammonia vapor reacts with the molecular oxygen ion and releases electron through oxidation process as given in equation (4). This in turn decreased the width of space charge region and also decreased the resistance of the ZnO film.

$$O_2 + e^- \longrightarrow O_{2\,(ads)}^- \quad \text{(Equation.3)}$$

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

Figure 4 shows the transient plot of ZnO film for 5 and 70 ppm of concentrations. The time required for the film to reach a 90% decrease from the baseline resistance after injecting ammonia is taken as the response time and is found to be 40 and 89 sec for 5 and 70 ppm respectively. Similarly the time required for the film to reach 10% of the baseline is taken as the recovery time and is found to be 56 and 108 sec for 5 and 70 ppm of ammonia respectively.

The fast response and recovery time is due to nanocrystallite of the prepared ZnO thin film (70 ml) for 5 ppm at room temperature.

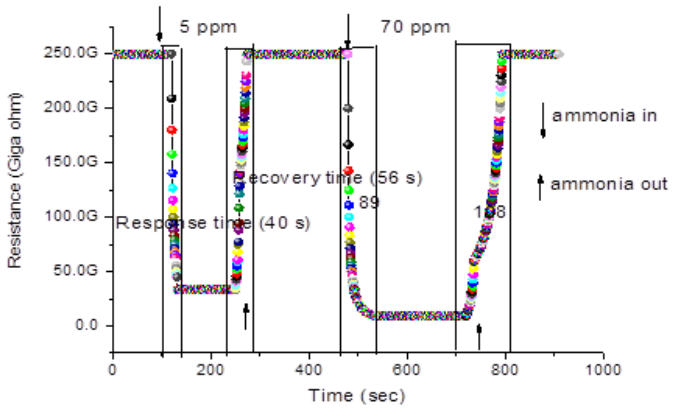


Fig.4.Resistance response of 5 and 70 ppm at room temperature

4. CONCLUSION

The multifunctional ZnO thin films are synthesized by using a simple, low cost SPT onto the glass substrates at 230^0C from 10 to 70 ml aqueous precursor solution of zinc acetate. The sample deposited at optimized conditions is highly transparent with average transmittance 75%. XRD results indicate the polycrystalline nature of the film with preferential orientation along (1 0 1) plane. The response of the ZnO film towards ammonia was found to be good with response and recovery time in minimum vapor concentration at 5 ppm. The low level detection measurement and monitoring of ammonia at room temperature in the atmosphere are extremely important in the field of environmental, automotive, chemical and medical diagnostic industries for human health.

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