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Influence of Reaction Chamber Temperature Variation on H_2S Gas Sensing Properties of Zinc Oxide Thin Films Prepared by Novel Spray CVD Technique

Abstract

ZnO thin films were prepared by a facile spray CVD technique using non-aqueous solution of zinc acetate $[Zn(CH_3COO)_2]$ as a precursor. Reaction chamber temperature of novel, spray CVD technique was varied from 300°C to 360°C. The crystal structure, morphology and the gas sensing properties were investigated by using XRD, FESEM, AFM and gas sensing unit. All the films are polycrystalline in nature with hexagonal wurtzite crystal structure oriented along c-axis, perpendicular to substrate. The crystallite size calculated from Scherrer formula was in the range 20-30nm sized grains. Their response towards H_2S gas was measured at different concentrations for different temperatures of reaction chamber. It exhibits fast response as well as fast recovery time. The gas response strongly depends on surface morphology of thin films.

Keywords: Spray CVD Technique, Reaction Chamber. H_2S Gas Sensing, Response Time, Recovery Time

Sunanda C. Yadav
Head
Deptt. of Physics,
Miraj Mahavidyalaya,
Miraj

Mahadev D. Uplane
Deptt. of Instrumentation Science
University of Pune,
Pune.

Introduction

ZnO is one of most studied material in the last seven years due to very interesting properties for optoelectronics [1], gas sensing applications [2] as well as in nano range synthesis[3]. It has respectable value in gas sensor technology as its physical and chemical properties can be easily tailored by using different growth parameters. In view of this aspect we have done an innovative attempt to develop thin films by a novel, newly fabricated, homemade spray CVD technique [4]. This method has the potential in the deposition of metal oxide thin film [5], gas tight coatings [6] at conventionally low temperatures. It is a simple and low cost technique for ceramic thin film deposition at nm- size. More significantly, detection of toxic, harmful pollutant gases like H_2S is subject of growing importance for both domestic and industrial environment. Hence it is ongoing need of society to develop H_2S gas sensors with high sensitivity. In view of this in the present work, we report simple approach that variation of deposition parameters significantly affects the gas sensing properties and also discussed the effect of H_2S gas concentration variation.

Experimental

ZnO thin film deposition was carried out with novel, homemade spray CVD technique by using 200ml non aqueous solution of zinc acetate as a starting solution. By keeping all other preparative parameters such as substrate temperature (200°C), solution quantity, concentration, and spray rate, distance between spray nozzle and glass substrate, as constant the effects of variation of reaction chamber temperature (core temperature) from 300°C to 360°C in stage of 30°C were studied. As deposited films have been characterized by various techniques such as structural investigations were carried out using a Bruker AXS X-ray diffractometer, films surface morphology was studied with the Field emission scanning electron micrographs etc. It's performance towards harmful, toxic gases like H_2S have been tested by using homemade gas sensing unit. Further, variation of resistance as a function of time when sensing element is exposed to reducing gas is used to evaluate the sensitivity of thin films. It can be defined as,

$$S = \frac{(Ra - Rg)}{Ra} \times 100 \ldots\ldots\ldots\ldots \quad (1)$$

Here Ra is the sample resistance measured at ambient environment while Rg is that under the test gas.

Results and Discussion

The main goal of this study is to provide insight into the synthesis of ZnO thin films by newly fabricated spray CVD technique. The first stage of optimization of the growth of ZnO thin films was to study the dependence of their crystallinity as a function of core temperature. For this purpose a set of undoped ZnO thin films were deposited at different temperatures in the range of 300^{0}C to 360^{0}C in steps of 30^{0}C on glass substrate.

Structural Properties

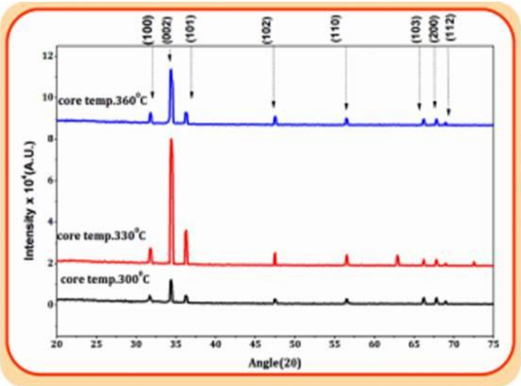

Fig.1 XRD pattern of ZnO thin films

X-ray diffraction analysis of the film confirm that as deposited thin films are polycrystalline in nature possessing hexagonal wurtzite crystal structure. It shows that the structural properties of ZnO thin films largely depend on core temperature with preferential growth orientation along C-axis. Three well-defined peaks, identified as the (100), (002), and (101) diffraction planes of ZnO, are clearly observed in figure1, 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. The films deposited for core temperature 330°C shows higher crystalline quality. The behavior is confirmed by TGA-DTA analysis of zinc acetate. It is well recognized that in spray CVD technique zinc acetate group decomposes at 330°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. The average crystallite size calculated using Debye Scherrer formula changes from 20nm to 30nm. The amount of the defects in the as deposited film was resolved by evaluating the dislocation density (δ) using the simple approach of Williamson and Smallman.

Surface Morphology

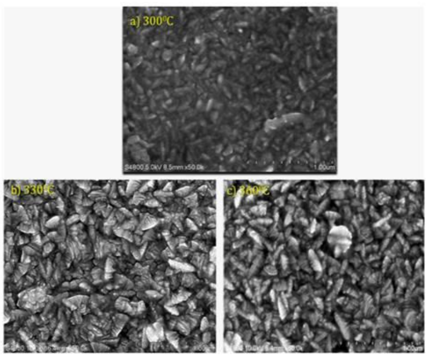

Fig.2 FESEM micrographs of ZnO thin film

In the lower temperature environment at 300°C, a large quantity of micro tubes of length 1µm and width 50nm are formed. At pyrolytic decomposition temperature, of 330°C the system leads to the formation of huge, pyramidal shaped and large number of regular micro crystals, of length 4 µm and height 2 µm (fig.2). With further increasing reaction chamber temperature, causes to decrease the size of micro crystals and morphology changes into micro tubes of length edge 3 µm and diameter 1µm. These agglomerates are composed of many grains with sizes somewhat bigger than crystallite sizes as measured from X-ray diffraction patterns.

Atomic Force Micrograph (AFM)

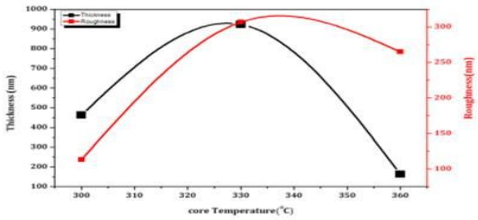

Fig.3. Thickness, roughness variation

It shows well covered surfaces with pyramidal shaped grains structure. The apparent size of the grains from the surface images is higher than the values calculated from the XRD measurements, indicating that these grains are probably an aggregation of crystallites. Due to the pyramidal shaped grains, the surface roughness of thin film increases (Fig. 3).

Electrical Conductivity

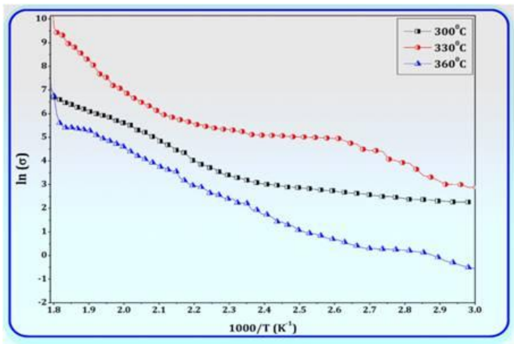

Fig. 4 Variation of ln (ρ) with (1000/T)

The dc conductivity of as deposited thin films is studied over a temperature range from 60°C to 300°C with respect to their core temperature variations by conventional d. c. two-probe resistivity unit. Figure 4 indicates Arrhenius plots of conduction showing the variation of ln(σ) with 1000/T. It is clearly seen from the plot that the films show two types of conduction mechanism. In the lower temperature region low slope indicating semiconducting behavior which transfers to metallic with increase in temperature.

H_2S gas sensing properties

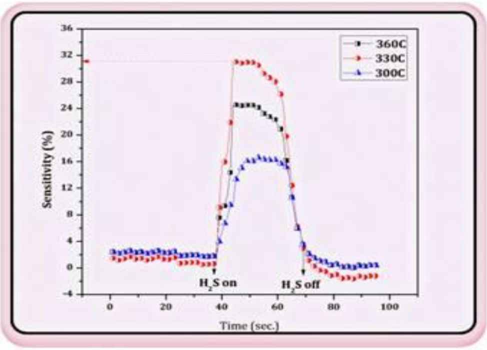

Fig.5 H_2S gas sensitivity

Figure 5 indicates response behavior of 20ppm H_2S gas for operating temperature 300°C. The sensitivity of these films (Fig 5) exhibits highest response for 330°C reaction chamber temperature. From all above observations it is seen that maximum sensitivity with quick response (2 sec) and fast recovery (10 sec) for sensing H_2S gas is observed at 330°C. It indicates 330°C as the optimized reaction chamber temperature to sense H_2S gas for undoped ZnO thin films.

It is well known that the gas sensing mechanism is based on surface morphology, grain size where the oxygen adsorbates play the major role. The atmospheric oxygen gets adsorbed on the surface of thin film causing to reduce the conductivity. At optimized reaction chamber temperature 330°C the conductivity of ZnO thin film increases, as a result more oxygen adsorbates formed on surface of thin film. The reducing gas reacts with these species and releases the electron back to the conduction band causing to decrease the resistivity of sensing element. The effect of concentration variation of reduced gas on sensitivity is as shown in figure 6. It indicates that the sensitivity increases linearly with increasing concentration of reducing gas (H_2S).

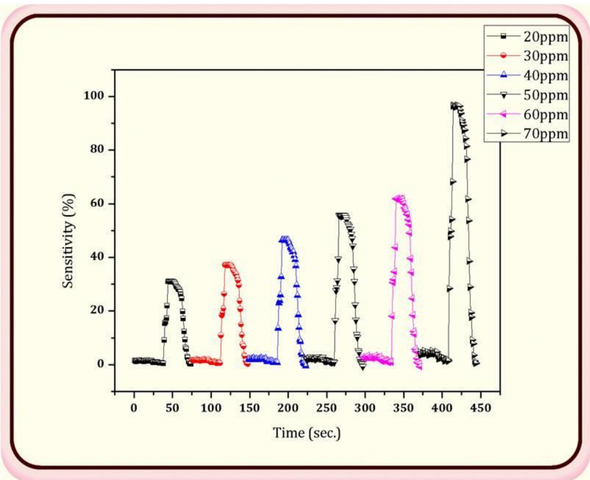

Fig.6 Sensitivity variation with H_2S gas concentration

Conclusion

ZnO thin films have been successfully deposited by using novel spray CVD technique. XRD studies reveal that all films are polycrystalline in nature indicating enhanced crystallinity for 330°C reaction chamber temperature. FESEM morphology supports this result. Compared to all range of reaction temperature variation, 330°C offers maximum response towards H_2S gas sensing properties with fast response and recovery time.

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