Effect of Film Thickness on H_2S Gas Sensing Properties of Boron Doped Zinc oxide Nanocrystalline Films

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Abstract. Novel, homemade spray CVD technique was used to deposit boron doped zinc oxide thin films. Thickness of these thin films was varied by varying volume of initial solution. X ray diffraction and Field emission scanning electron microscopy were used to study structure and surface morphology of the thin films. H_2S gas sensing properties of the films were investigated by using homemade gas sensing unit. The dependence of H_2S gas detection on the thickness of boron doped zinc oxide film was studied at 300°C. It is observed that response and recovery time increase with increase in film thickness. It is further seen that improvement in crystallanity and surface morphology with increase in film thickness does not assist to improve the gas detection properties of boron doped zinc oxide film.

Keywords: spray CVD technique, Nano-crystalline films, X-ray diffraction and Field emission scanning electron microscopy, thin films, zinc oxide

INTRODUCTION

For safety of human health and to protect the environment from hazardous gases is an important research issue. Among these gases H_2S gas is badly harmful to human being. Hence, monitor and control of such hazardous gas has become extremely important. Different oxide semiconductors such as ZnO, In_2O_3, and SnO_2 [1–3] are used in solid state gas sensors. However, ZnO-based thin films are widely used in gas sensing to test the suitability as gas sensors. Because of their good chemical sensitivity to different adsorbed gases, high chemical stability, non toxicity, and low cost. Various dopants such as Sn, Al, In, B, Pd, Cu, Fe, Ru, and Ga have been added in ZnO to explore their properties as gas sensors. In this work, we report the correlation between structures, morphology, and thickness of boron doping zinc oxide thin films with gas response properties.

EXPERIMENTAL

Boron doped zinc oxide (B:ZnO) thin films were deposited by using spray CVD technique reported elsewhere [4]. It consists of a reaction chamber, substrate holder along with substrate heater, temperature controllers and nozzle assembly. A cylindrical furnace fixed on metal stand with substrate heater placed at the top and glass nozzle placed at lower side of cylindrical furnace. PID temperature controllers were used to control the reaction chamber temperature and substrate temperature. The ultrasonically cleaned amorphous micro slides were used as substrates. These substrates were kept at 200°C. During deposition, the atomization's of solution into fine droplets were carried out by spray nozzle with the help of compressed air as carrier gas.

The spraying solution of 0.075 M zinc acetate dehydrate (Zn $(CH_3COO)_2$, $2H_2O$) in methanol (A.R. grade) was used as initial ingredient. 2M solution of boric acid in methanol with 0.8at wt% concentration was used as a source of dopant. The solution was sprayed onto hot glass substrates using compressed air as a carrier gas. By changing the volume of spraying solution from 100 to 500ml in steps of 100ml corresponding thickness variation was studied. The average thickness of the film was measured with AMBIOS-XP-1 surface profiler. To study H_2S sensing behavior ZnO resistance is measured in presence of gas as a function of time. The steady- state resistance were investigated at 300^0C temperature for 20 ppm H_2S in air.

Results and Discussion

Fig.1 depicts the X-ray diffraction patterns of the B:ZnO thin films for thicknesses 102 nm, 261nm and

426nm. All the peaks are correspond to the hexagonal wurtzite structure of ZnO. They are indexed according to the JCPDS 80-0075. The preferential orientation along (002) plane improves with increase in film thickness. The mean grain size of the film was estimated by using standard Scherrer formula [5]. The calculated grain size is tabulated in Table 1.

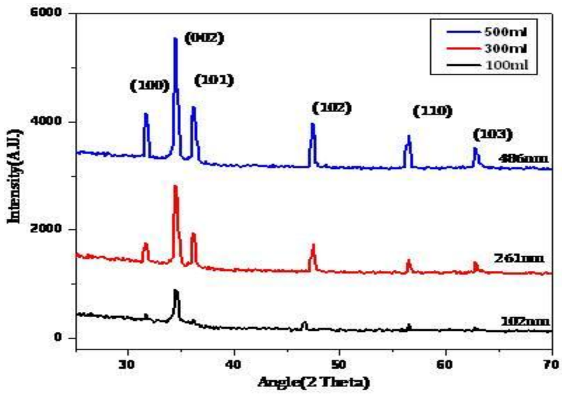

FIGURE 1 X-ray diffraction pattern of B:ZnO thin films

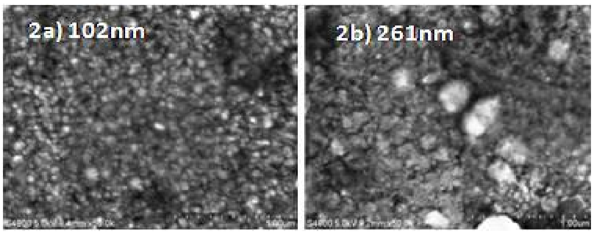

Figure 2 FESEM images of B:ZnO thin films

Figure 2a and 2b are the typical planer FESEM images of the as deposited boron doped ZnO thin films. It is seen that films are composed of circular grains and grain size increase with increase in film thickness. These results support the observations made in XRD studies.

Gas sensing properties

The gas response of B: ZnO nano-crystallites to lower concentration of 20 ppm H_2S gas (do not show remarkable difference for 10ppm) was investigated from 200 to 300^0C operating temperature. and the results are shown in Fig. 4. The sensitivity and fast response is observed at 300°C operating temperature. The resistance response of this sensor structure was transformed into a sensitivity value using commonly used formula for the gases:

$$S = \frac{(R_a - R_g)}{R_a} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where; all terms have their usual meaning. Table 1 shows H_2S gas response for B: ZnO thin films at various thicknesses. The sensitivity of gas sensor was increased with decrease in film thickness and exhibits shortest response and recovery time. It indicates that the smaller grain size provides greater surface area for the materials, which causes stronger interaction between the adsorbed gases and the sensor surface. The dependence of sensitivity on grain size (D) is explained by Xu et al. [6]. Similar to others we also found that films thickness exhibits great role in gas sensing properties.

TABLE 1. B: ZnO Thickness varied H_2S Gas Sensitivity

Thick-ness (nm)	Grain size (nm)	Sheet Res. (KΩ/cm^2)	Response time (sec.)	Recovery time(sec.)	Sensi tivity (%)
102	19	11	7	24	29
182	20	5	9	36	21
261	20	3	14	60	19
381	21	1	18	18	16
486	21	0.8	163	163	14

Conclusions

The uniform thin films of B: ZnO with different film thicknesses were deposited by spray CVD technique. It is clear that the gas response of sensor increases with decrease in the grain size. It provides a larger surface to volume ratio. More specifically the 0.8 at wt% B : ZnO thin films with 102nm film thickness show uniform particle size and exhibits high sensitivity towards hydrogen sulfide gas with rapid response. The good recovery time was obtained for the thinner film. This exhibits that the nano sized B: ZnO thin films deposited by spray CVD technique have a potential to become a good H_2S gas sensing material.

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