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Improved zinc oxide film for gas sensor applications

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Abstract. Zinc oxide (ZnO) is a versatile material for different commercial applications such as transparent electrodes, piezoelectric devices, varistors, SAW devices etc because of its high piezoelectric coupling, greater stability of its hexagonal phase and its pyroelectric property. In fact, ZnO is a potential material for gas sensor applications. Good quality ZnO films were deposited on glass and quartz substrates by a novel CVD technique using zinc acetate as the starting solution. X-ray diffraction confirmed the crystallinity of the zinc oxide film and SEM study revealed uniform deposition of fine grains. Undoped ZnO films were used for detection of dimethylamine (DMA) and H_2 at different temperatures by recording the change in resistivity of the film in presence of the test gases. The response was faster and the sensitivity was higher compared to the earlier reported ZnO based sensors developed in our laboratory. The main objective of this work was to study the selectivity of the ZnO film for a particular gas in presence of the others. The operating temperature was found to play a key role in the selectivity of such sensors.

Keywords. Zinc oxide film; dimethylamine; gas sensor.

1. Introduction

Zinc oxide (ZnO) is an important multifunctional material with applications such as varistors, gas sensors, SAW devices, transparent electrodes, catalysts etc. The various applications of ZnO are due to the specific chemical, surface and microstructural properties of this material. The microstructural and physical properties of ZnO can be modified by introducing changes into the procedure of its chemical synthesis. Especially for the application of ZnO as gas sensors porous microstructure of the materials with controlled pore size is preferred. The sensitivity and response time of ZnO based sensors strongly depend on the porosity of the material. The grain size of the polycrystalline zinc oxide material also has noticeable effect on its gas sensing properties. It has been experimentally observed (Xu *et al* 2000) that the gas sensitivity of the ZnO sensors decreases with the increase of its mean grain size.

One of the techniques to deposit ZnO films is spray-pyrolysis. In this method spray droplets strike the heated substrate directly in the form of atomized liquids yielding non-uniformity on the surface of the oxide films. This paper deals with the deposition of ZnO films by an indigenously developed technique, called modified-CVD, in which the deposition takes place in the vapour phase of the precursors. This method is cost effective as compared to the other CVD techniques, simultaneously yielding reasonably good quality films for sensor applications. The deposited films were confirmed to be polycrystalline zinc oxide by XRD analysis. The change in electrical resistance of the films was measured while exposing those to the different concentrations of DMA vapour diluted in argon gas. The effect of the operating temperature on the sensing properties of the ZnO films was studied and the selectivity was observed in presence of hydrogen gas.

2. Experimental

Thin films of ZnO were deposited on 5 × 5 mm glass or quartz substrates by modified-CVD technique. In an attempt to improve the quality of the film by controlling different growth parameters more precisely this indigenously developed system (Dutta and Basu 1993) has been automated with electronic control circuitry.

The deposited films were studied by XRD and confirmed to be polycrystalline ZnO. The SEM micrographs revealed irregular shaped particles with the formation of clusters and pores distributed throughout the film surface. These pores are considered to play a vital role in the process of gas adsorption and hence influence the sensitivity of the oxide films.

The sensor studies were performed in a closed quartz chamber inserted coaxially inside a wire resistance furnace. The relative concentration of the DMA vapour (or H_2 gas) was measured using pre-calibrated gas flow meters. The change in film resistance was noted in different concentrations of the test gas at several temperatures. The sensitivity $[(R_{air}–R_{gas})/R_{air}]$ defined as the percentage change of the film resistance in presence of the test gas was calculated for each temperature and concentration of the test gas. The sensor response and recovery

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times were determined from the transient response characteristics.

3. Results and discussion

After carrying out several number of depositions of the oxide films using the modified-CVD system and subsequent morphological and electrical studies of the deposited films the following optimized conditions have been obtained. (i) Optimum substrate temperature: 350°C, (ii) concentration of the zinc acetate solution (spraying solution): 0·5 M, (iii) nozzle to substrate distance: 14·5 cm, (iv) spray pressure: 0·2 kg/cm^2, (v) single spray time: 5 s, (vi) interval: 60 s and (vii) substrate rotation speed: 20 rpm.

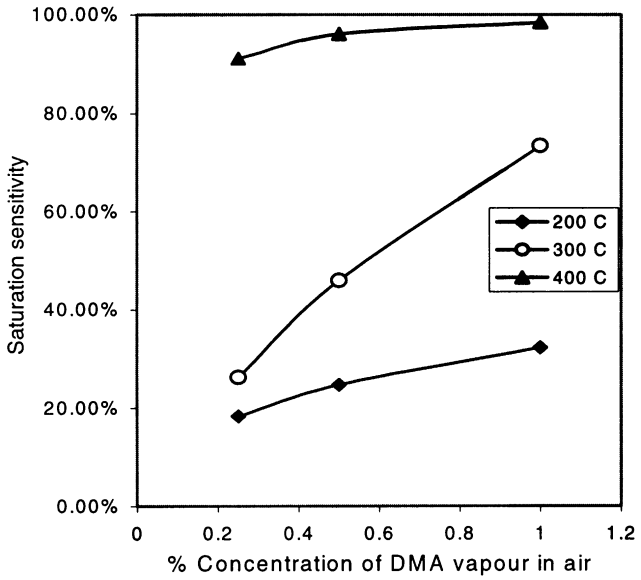

Figure 1. Effect of operating temperature on saturation sensitivity.

The peaks in the obtained XRD plots were identified by comparing the lattice parameters reported in the JCPDS file. Thus the deposited film was confirmed to be polycrystalline ZnO with the peak corresponding to the (101) plane being the strongest one. The crystallite sizes were estimated using the Scherrer formula

$$D = 0{\cdot}9\ l/b\ (\cos q), \tag{1}$$

where l is the X-ray wavelength, q the Bragg's angle, b the full width of the diffraction line at half of the maximum intensity. For ZnO film deposited at 350°C the corresponding crystallite size of ~ 15 nm was measured. The annealing of this film in O_2 ambient at 500°C for 15 min resulted in an increase in crystallite size (~ 25 nm). Probably a fresh layer of ZnO formed by the reaction of the interstitial zinc with oxygen chemisorbed on the surface thereby increasing the lattice order in the film (Pizzini *et al* 1987). On the other hand annealing the as-deposited ZnO film in the reducing ambient resulted in a decrease in the crystallite size down to ~ 12 nm. From the gas sensing point of view the diminishing grain size of the sensor material is considered to be facilitating, as it is well known that the sensing mechanism of ZnO belongs to the surface controlled type. The smaller the grain size, higher is the specific surface area and sensitivity. Xu *et al* (2000) reported that when the grain size was > 40 nm the gas sensitivity decreased quickly. So the grain size (~ 12–15 nm) of the ZnO film deposited by the modified CVD method exhibited excellent sensitivity even without any surface modification by catalytic metals. The effect of operating temperature was found to play a vital role in determining the sensitivity of the ZnO film sensors to dimethylamine (DMA). For a particular concentration of DMA, say 0·25%, the sensitivity increased from 18·3% to 91% as the temperature was raised from 200°C to 400°C. In general there exists an optimum operating temperature of a sensor to achieve the maxi-

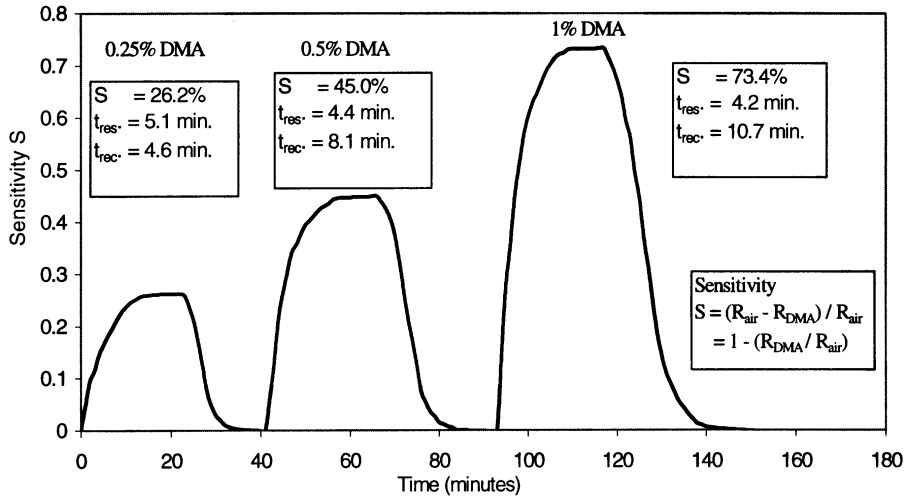

Figure 2. Transient response characteristics in presence of DMA at 300°C.

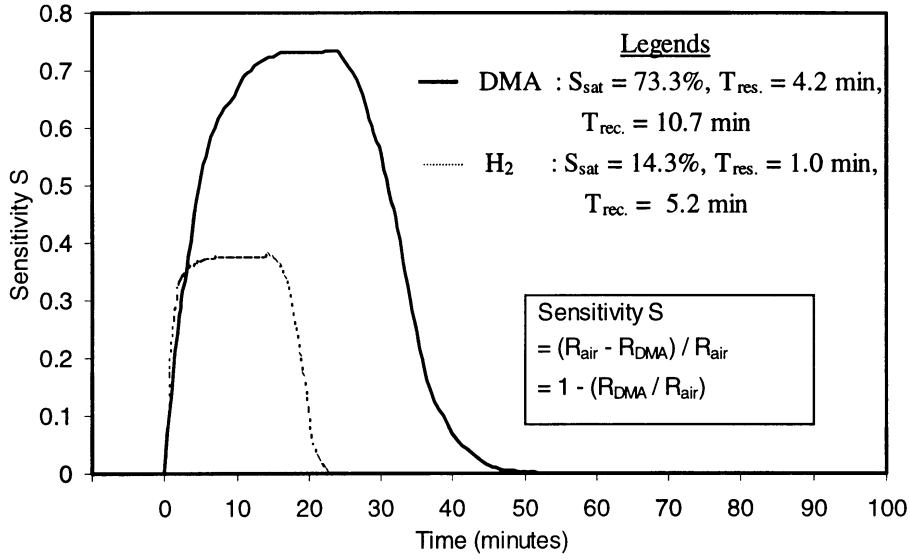

Figure 3. Comparison of transient response characteristics of ZnO at 300°C in presence of 1% DMA and 1% H_2 in air.

mum sensitivity to a gas of interest, the temperature being dependent upon the kind of gases i.e. the mechanism of desorption and dissociation of a gas on the particular sensor surface. The effect of operating temperature on the saturation sensitivity to DMA is presented in figure 1.

In terms of resolution of the ZnO film sensor though the operating temperature of 300°C was found most suitable since at this temperature the sensitivity vs concentration curve showed much stiffer and linear behaviour as compared to 200 and 400°C. A typical transient response of the ZnO films at 300°C with varying concentrations of DMA vapour is shown in figure 2.

The sensitivity was found to increase with concentration of DMA vapour in the test gas. The sensor response time, defined as the time taken by the ZnO film to attain 1/*e* of its saturation sensitivity after exposure to the DMA vapour, was found to decrease with the increasing concentration. Though the recovery time kept on increasing, which indicates a longer time taken by the sensor to revert back to its base-line properties for the next operation.

Figure 3 shows that the sensor exhibited much larger sensitivity for exposure to DMA as compared to that for same concentration (1% in air) of hydrogen gas. This particular observation indicates that at 300°C the ZnO sensor preferentially respond to the DMA vapour though with a larger response and recovery time. The interference of CO with DMA sensitivity is underway.

4. Conclusions

Good quality ZnO thin film, as produced by a modified-CVD technique, developed in our laboratory, showed the performance of a superior DMA sensor at an optimum operating temperature of 300°C. The selectivity for DMA in air, with respect to hydrogen, was also very good.

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