Sprayed ZnO thin films for ethanol sensors

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Published online: 08 July 2005

The electrical characteristics of ZnO thin films prepared by spray pyrolysis, have been studied for ethanol sensors. The sensitivities of the films are measured at various temperatures and concentrations of ethanol. It is observed that the sensitivity increases with increasing working temperature. At higher ethanol concentrations, the sensitivity increases more rapidly with increasing temperature. Further, the films show fast response and recovery times at higher working temperatures. The sensing mechanism of the films towards ethanol vapour has been explained.

1. Introduction

Zinc oxide (ZnO) is a technologically important material. Thin films of ZnO find many promising applications such as transparent electrodes, gas sensors, surface acoustic wave devices, heat mirrors etc. [1–4]. Several deposition techniques have been used to grow undoped and doped ZnO thin films. These include sputtering, spray pyrolysis, sol-gel process, pulse laser deposition, plasma enhanced chemical vapour deposition, vacuum evaporation etc. [5–9]. In the present investigation, thin films of ZnO have been prepared by using spray pyrolysis technique because this technique is very simple and involves low cost equipments. The technique consists of spraying a solution containing a soluble salt of the cation of interest onto a heated substrate.

In this paper we report on the details of preparing of ZnO thin films by spray pyrolysis and the sensing behaviour of the films to ethanol.

2. Experimental details

The films were prepared on cleaned glass substrates having size about 40 × 25 mm, which were placed on a metallic plate kept on an electric heater and heated to the desired temperature with the help of a variac. The substrate temperature was monitored using a chromel-alumel thermocouple with the help of a Motwane digital multimeter (Model: 454). Before spraying, the glass substrates were cleaned with freshly prepared chromic acid, detergent solution and distilled water. The spraying solution used was of 0.1 M concentration of high purity zinc acetate dihydrate (Merck, India) prepared in distilled water. The solution was sprayed onto the heated substrates using a conventional spray gun with a high air to solution ratio. The spray was applied several times in few second bursts and allowed the substrates to recover their temperatures after each burst. During the course of spray, the substrates temperature was maintained at about (420 ± 15)°C. The spray nozzle was not kept away just above the heated substrates surface to make sure that big drops of solution should not fall directly on the substrates. Further, the spray nozzle was put obliquely to the substrates surface at about 50 cm away from it.

Film thickness was determined by weighing using an electronic precision balance (Citizen, Model: CY 204) and found to be about ∼20 nm. For electrical measurements, high conducting silver paste was applied on both the ends of the sprayed film for making ohmic contacts. The film was mounted on a home-made two-probe assembly placed inside a silica tube which was inserted coaxially inside a resistance-heated furnace. The electrical resistance of the film was measured before and after exposure to ethanol using a Keithley System Electrometer (Model: 6514). The sensing characteristics of the film under different concentration levels of ethanol were studied in the temperature range between 140 and 360°C. To study sensing characteristics of the film, required volume of ethanol was injected into the closed silica tube maintained at various temperatures.

3. Results and discussion

The sensitivity $[((R_a - R_g)/R_a) \times 100\%]$ defined as the percentage change of the film resistance in presence of ethanol, was calculated for each temperature and concentration of ethanol. Here, R_a is the electrical resistance of the film in air and R_g is the resistance after exposure to ethanol.

During the course of experiment it was found that the films prepared on glass substrate at a temperature greater than 470°C did not respond at all to ethanol, indicating thereby that the sensing characteristics of the films are strongly dependent upon the substrate

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DOI: 10.1007/s10853-005-0519-9

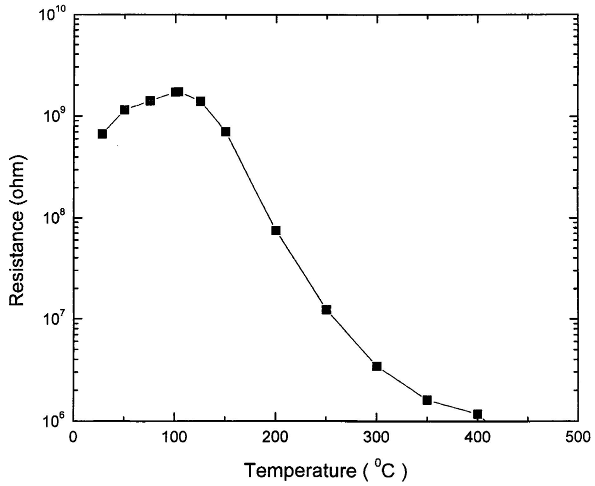

Figure 1 Electrical resistance of a particular ZnO film as a function of temperature.

temperature. While heating the sprayed films in air for sensor studies, it was observed that the electrical resistance first increases up to the temperature about (100 ± 10)°C for different films and then begins to decrease with the rise of temperature. Fig. 1 represents the electrical resistance of a particular such film as a function of temperature. The increase in resistance is attributed to the chemisorption of oxygen on the film surface, causing decrease in the carrier concentration. This is consistent with the adsorption of oxygen on the surface of polycrystalline ZnO films as reported by other researchers [10, 11] The decrease in resistance above 103°C is related to the increase in carrier concentration resulting from the activation of deep donors which may arise due to native defects such as interstitial zinc atoms and oxygen vacancies [12].

Fig. 2 shows the saturation sensitivity characteristics of a particular film for ethanol at different working temperatures. It is obvious from the figure that the sensitivity increases with increasing working temperature. At higher ethanol concentration, the sensitivity increases rapidly with increasing working temperature. This behavior is attributed to the enhancement of adsorption of atmospheric oxygen on the film surface at higher working temperature.

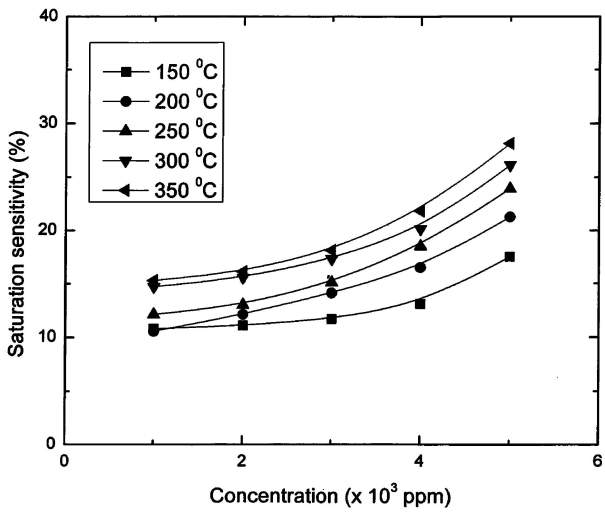

Figure 2 Saturation sensitivity characteristics of the film for ethanol.

The ethanol-sensing mechanism of the film can be explained as follows:

At first, oxygen is absorbed on the zinc oxide surface when the film is heated in air. At lower temperatures, the surface reactions proceed too slowly to be useful. The adsorption of oxygen forms ionic species such as O^{2-}, O_2^- and O^- which have acquired electrons from the conduction band and which desorb from the surface at 80, 130 and 500°C respectively. So at the temperatures on which sensor studies have been carried out, only O^- species will react with ethanol. The reaction kinematics is as follows [13]:

$$O_2\ (\text{gas}) <=> O_2\ (\text{absorbed})$$

$$O_2\ (\text{absorbed}) + e^- <=> O_2^-$$

$$O_2^- + e^- <=> 2O^-$$

The reaction between ethanol and ionic oxygen species can take place by two different ways:

$$C_2H_5OH\ (\text{gas}) + O^- <=> CH_3CHO + H_2O + e^-$$

$$C_2H_5OH\ (\text{gas}) <=> H + C_2H_5O\ (\text{surface})$$

$$C_2H_5O <=> H + CH_3CHO$$

$$CH_3CHO + O\ (\text{bulk}) \rightarrow CH_3COOH + O\ (\text{vacancies})$$

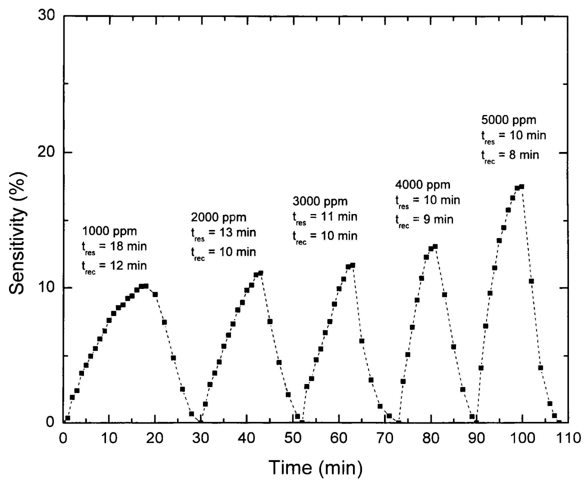

Figure 3 Transient response characteristics of the film for various ethanol concentrations at 150°C.

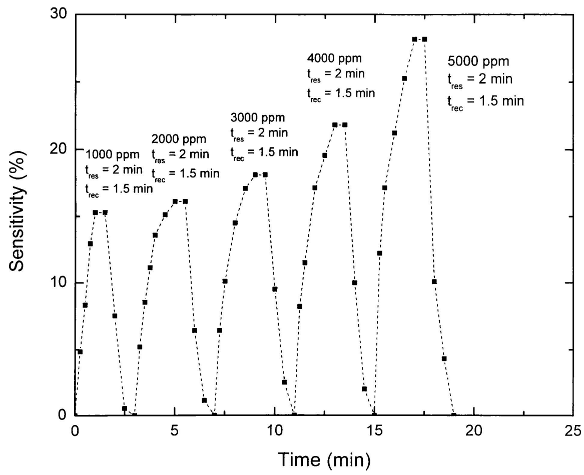

Figure 4 Transient response characteristics of the film for various ethanol concentrations at 350°C.

Figs 3 and 4 represent the transient response characteristics of the film for various ethanol concentrations at 150 and 350°C respectively. To study the reversibility of transient response of the film, both the ends of the silica tube were opened. It is seen that the response time (t_{res}) and recovery time (t_{rec}) decrease significantly at higher working temperature. At lower working temperature, the response time and recovery time decrease with increasing ethanol concentration but at higher working temperature, they do not depend upon the concentration of ethanol.

4. Conclusion

The sprayed ZnO thin films have shown considerable changes in their resistances when exposed to ethanol in the temperature range between 140 and 360°C. The sensitivity is found to increase with increasing working temperature. At higher ethanol concentrations, the sensitivity increases more rapidly with increasing temperature. Response and recovery times are found to be sensitively dependent upon the working temperature.

Acknowledgement

The authors are thankful to the Ministry of Human Resources Development, Govt. of India for sanctioning an R & D project (F.26-4/99 TS.I) under which this work has been carried out.

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Received 30 September 2004
and accepted 15 February 2005