Zinc oxide thin film gas sensor for detection of acetone

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In recent years, studies on zinc oxide (ZnO) films have drawn considerable interest because of their good electrical and optical properties, in combination with their wide bandgap, abundance in nature, and absence of toxicity. The assorted physical properties such as electro-optical, acousto-optical, piezoelectrical and luminescence characteristics, render the thin films of zinc oxide a liable material for a variety of applications. Zinc oxide with a direct bandgap of 3.3 eV at room temperature, is transparent to most of the solar spectrum. ZnO thin films have attracted interest as a window material for solar cells, a low-cost alternative to ITO, optical waveguides, light modulators, gas sensors, and etc. [1–6].

Various techniques have been used to prepare doped or undoped ZnO films. These include magnetron sputtering, plasma enhanced chemical vapour deposition (PECVD), spray pyrolysis, pulse laser deposition, sol–gel process, vacuum evaporation, etc. [7–11]. In the present investigation, the author has used spray pyrolysis technique to prepare thin films of ZnO because this technique is simple and involves low cost equipments. In this paper, the author reports a study on the sensing behaviour of ZnO thin films towards acetone vapour. Although exposure to acetone vapour to human beings is harmful, it has not been one of the extensively studied gases for thin-film gas sensors.

The films were prepared on cleaned glass substrates (40 mm×25 mm×1 mm) which were mounted on a steel plate kept on an electric heater. A particular temperature could be achieved by supplying a suitable power to the heater through a variac. The spraying solution used was of 0.1 M concentration of high purity zinc acetate dehydrate (Merck, India) prepared in distilled water. The solution was sprayed onto the heated substrates using a conventional spray gun. The atomization of the solution into a spray of fine droplets was affected by the spray nozzle with the help of compressed air as carrier gas. During the course of spray, the substrate temperature was monitored using a chromel–alumel thermocouple with the help of a Motwane digital multimeter (Model: 454), and was maintained at about (420 ± 15) °C.

The thickness of the films was determined by weighing method and found to be about ∼50 nm. For making ohmic contacts at both the ends of the film, high conducting silver paste was used. The film was mounted on a 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 acetone using a Keithley System Electrometer (Model: 6514). The sensing behaviour of the film under different concentration levels of acetone were studied in the temperature range between 250 and 375 °C.

The sensitivity has been defined as the percentage change of the film resistance in presence of acetone, and is given by $[((R_a - R_g)/R_a) \times 100\%]$. Here, R_a is the electrical resistance of the film in air and R_g is the resistance after exposure to acetone. After getting response to acetone, the film resistance becomes static and the sensitivity then calculated has been termed as saturation sensitivity.

Fig. 1 shows the effect of working temperature on the saturation sensitivity of ZnO film towards acetone vapour. It is obvious from the figure that working temperature plays a vital role in determining the sensitivity of the film. For a particular concentration of acetone, say 1000 ppm, the sensitivity first increases from 6.8% to 29.5% as the temperature is raised from 250 to 325 °C, and then decreases to 22.7% when the temperature is further raised to 375 °C. In general, there exists an optimum working temperature of a sensor to achieve the maximum sensitivity to a gas of interest, the temperature being dependent upon the kind of gases, i.e., the mechanism of dissociation and further chemisorption of a gas on the particular sensor surface.

The sensing mechanism of the film to acetone may be described as follows. At first, oxygen is adsorbed 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 in the temperature range used, only O^- species which are the most stable ones, will react with acetone. The reaction kinematics is as follows [12]:

$$O_2\ (\text{gas}) <=> O_2(\text{absorbed})$$
$$O_2\ (\text{absorbed}) + e^- <=> O_2^-$$
$$O_2^- + e^- <=> 2\ O^-$$

The reaction mechanism between acetone and ionic oxygen species may take place by two different ways having different rate constants (k) depending upon the temperature [13–15]:

$$CH_3COCH_3\ (\text{gas}) + O^- \rightarrow CH_3C\overset{+}{O}CH_2 + OH^- + e^-;\ k = 1.0 \times 10^{12} \exp(-21000/RT)\ [\text{cm}^3/\text{mol s}]$$

$$CH_3COCH_3\ (\text{gas}) + OH^- \rightarrow CH_3CHO + CH_3O^-;\ k = 2.0\times10^{12} \exp(-63000/RT)\ [\text{cm}^3/\text{mol s}]$$

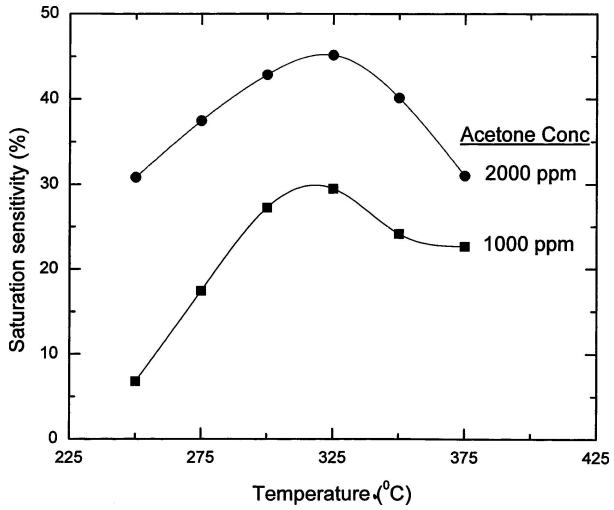

Figure 1 Variation of saturation sensitivity of ZnO film with temperature at different acetone concentrations.

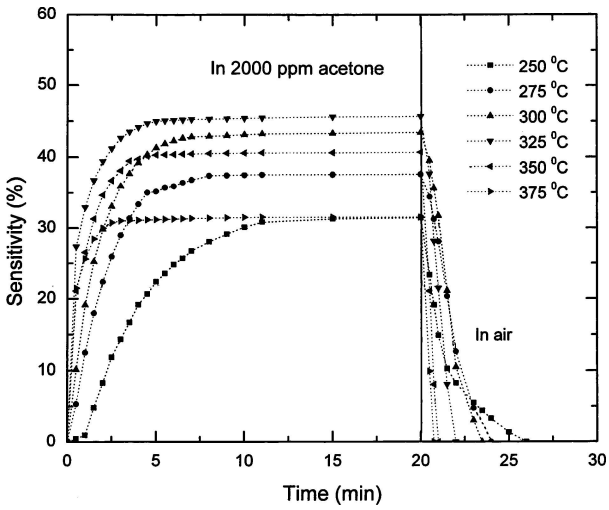

Figure 3 Time dependence of sensitivity of ZnO film exposed in 2000 ppm acetone and air.

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

$$CH_3COCH_3\ (\text{gas}) + O^- \rightarrow CH_3\overset{+}{C}O + CH_3O^- + e^-;$$

$$k = 1.0 \times 10^{12} \exp(-42000/RT)\ [\text{cm}^3/\text{mol s}]$$

$$CH_3\overset{+}{C}O \rightarrow \overset{+}{C}H_3 + CO;\ k = 2.0 \times 10^{11}$$

$$\times \exp(-15000/RT)\ [1/\text{s}]$$

$$CO + O^- \rightarrow CO_2 + e^-$$

Fig. 2 shows plots of saturation sensitivity against concentration of acetone in air at four different temperatures. At 275 °C, the sensitivity increases sharply as the concentration of acetone increases from 1000 to 3000 ppm, and after that it almost saturates. At temperatures 300 and 325 °C, the sensitivity increases with increase in the concentration of acetone up to 3000 ppm, and then further decreases with enhancement of the acetone concentration in air. While at 350 °C, the sensitivity increases with acetone concentration up to 4000 ppm and then decreases. From the figure it is obvious that not only temperature but also the concentration level of acetone plays a role in determining the sensitivity of the film. This is attributed to the result owing to the reaction mechanism of acetone with adsorbed oxygen species on the film surface as well as the availability of such adsorbed species on the surface to react with acetone in the higher concentration region.

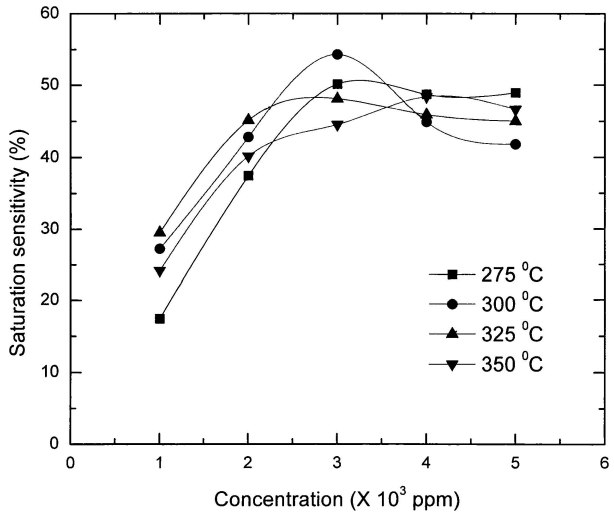

Figure 2 Dependence of saturation sensitivity of ZnO film on acetone concentration at different working temperatures.

Fig. 3 shows time dependence of sensitivity of the film exposed in 2000 ppm acetone and air at different temperatures. To study the transient response of the film, required volume of acetone was injected into the closed silica tube at time $t = 0$. After 20 min, both the ends of the tube were opened. It is found that response time and recovery time are sensitively dependent upon the working temperature. The time for response and recovery becomes shorter with increasing working temperature, especially recovery time.

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