

Alcohol sensing of tin oxide thin film prepared by sol–gel process

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Abstract. The present paper describes the alcohol sensing characteristics of spin coated SnO₂ thin film deposited by using sol–gel process. The sensitivity of the film was measured at different temperatures and different concentrations of alcohol at ppm level. Alcohol detection result shows peak sensitivity at 623 K. The variation of sensitivity and ethanol concentration has shown a linear relationship up to 1150 ppm and after that it saturates. The response time measurement of the sensor was also observed and it was found that the response time is 30 sec. The results obtained favour the sol–gel process as a low cost method for the preparation of thin films with a high sensing characteristic.

Keywords. Sol–gel; SnO₂; sensitivity; response time; spin-coating method.

1. Introduction

Over the past few decades, tin oxide based films are widely used as gas sensors due to their high sensitivity in the presence of small amounts of some gases of interest viz. carbon monoxide, ethanol, methane etc. Allied to this advantage is the simple design, robustness, fast response and the possibility of miniaturization of these devices (Dutaive *et al* 1995).

When a SnO₂ semiconductor film is exposed to air, physisorbed oxygen molecules receive electrons from the conduction band of the film and change to O⁻ ads or O²⁻ ads species. These adsorbed molecules form an electron depletion layer just below the surface of SnO₂ particles and forms a potential barrier between particles; consequently the SnO₂ film becomes highly resistive (Coultts *et al* 1984, 1990; Gardener *et al* 1991). The lowering of the potential barrier takes place when the adsorbed oxygen species are exposed to the reducing gases, resulting in the increased conductance of the sensitive film. The variation of the conductance measured under specific gases depends on many parameters such as intrinsic resistance, grain size (Lalweze and Pizolat 1984), grain boundary barriers, detection temperature etc.

Tin oxide films have been prepared by a number of techniques including spray pyrolysis (Tarey and Raju 1985; Lane *et al* 1992), sputtering (Kulkarni and Knickerbocker 1992; Karasawa and Miyata 1993), chemical vapour deposition (CVD) (Park *et al* 1995) and evaporation (Brinker *et al* 1990). Recently the sol–gel

process has been proposed as a new technique for preparing gas sensor devices. This deposition technique seems to be promising because of its many advantages: (i) it is simple and cheap, (ii) it is easy to control the morphology, (iii) it is easy to modify the composition with uniformly dispersed dopants and modifiers, and (iv) it produces both thick and thin films with a high porosity area that improves the efficiency of the sensor in mechanism dominated by surface phenomenon.

Ethanol vapour has been one of the most extensively studied gases for metal oxide gas sensors, particularly due to the need for small practical devices to detect alcohol on the human breath or even to detect leaks in industrial distribution lines. In the present work, we describe a study on the sensing behaviour of SnO₂ thin film towards the ethanol vapour. The sensitive layers were deposited in the form of thin films by sol–gel process. SnO₂ thin film was prepared by spin coating method and its gas sensing properties studied.

2. Experimental

The coating solution used was prepared from an anhydrous SnCl₄ by process. Pure SnO₂ sols were prepared starting from anhydrous SnCl₄, water, propanol, (C₃H₇OH), and isopropanol (2-C₃H₇OH) in the following molar ratio: SnCl₄ : H₂O : C₃H₇OH : 2-C₃H₇OH :: 1 : 9 : 9 : 6. At first SnCl₄ was dropped into two-third of the total amount of propanol. Then one-third of the total water dissolved in the remaining C₃H₇OH was added for pre-hydrolysis of the tin precursor. It was stirred for 1 h and after that the previously prepared sol was mixed with the

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solution of the remaining amount of H₂O dissolved in the prescribed amount of 2-C₃H₇OH. It was again stirred for 1 h. With this procedure, clear and homogeneous sols were prepared.

Prior to the deposition of film on the glass substrate, the substrate was first cleaned with a liquid detergent used for glass cleaning and then it was cleaned with de-ionized water. It was cleaned ultrasonically in methanol and de-ionized water alternatively for three times.

The film was deposited by spin coating at different rpm. After deposition the film was dried for 1 h at 353 K. After that the dried film was fired at 873 K for 1 h at the ambient.

The sensitivity tests were carried out in a homemade testing chamber that measures the surface resistance of the samples (figure 1). Before the measurement, the sample was pre-heated by heating it to 723 K and cooling it to 523 K. This step was repeated three times before starting film characterization in order to clean the sample from water vapour.

Ethanol was injected by a micro syringe into the test chamber and the sensing characteristics of the sensor were then observed by measuring the electrical resistance change of sensor when the latter was exposed to ethanol. A typical injection of 0.4 ml of ethanol corresponds to a gas concentration of about 10 ppm (Shurmer 1990). Under the exposure of reducing gas such as alcohol (in the present study), its resistance decreases. Its sensitivity is defined as

$$S = R_{\text{air}}/R_{\text{gas}},$$

where R_{gas} is the resistance of the sensor under gas exposure and R_{air} the resistance of the sensor under air. For the sensitivity measurement, the sample was heated at a temperature range of 353 K–723 K. The resistances of samples were measured at different temperatures and different concentration levels of ethanol. For the response time measurement, the variation of resistance was recorded as a function of time, starting from the moment when the ethanol vapour was injected into the chamber. In this case, the ethanol concentration was set at 500 ppm and temperature at 673 K. The time taken by the sensor for

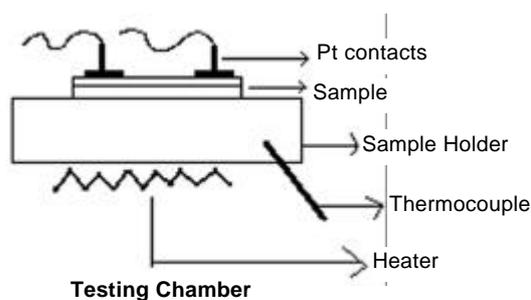
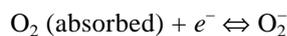
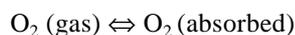


Figure 1. Schematic diagram of the testing chamber used for sensor characteristics measurement.

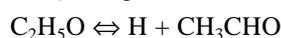
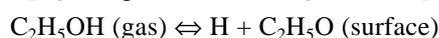
fall of its resistance by 90% was taken as the sensor response time.

3. Principle of ethanol detection

The mechanism of the ethanol detection by tin oxide films can be described as follows: At first oxygen is adsorbed on the tin oxide layer when the sensitive film is heated at ambient at a temperature of 473–723 K. The adsorption of the oxygen forms ionic species such as O²⁻, O₂⁻ and O⁻. These oxygen species when desorbed (desorption of O²⁻, O₂⁻ and O⁻ take place at 323 K, 373 K and 723 K, respectively), result in the increase or decrease of the conductance of SnO₂ layer depending on the nature of gas. Its conductivity increases when the incoming gas is reducing type and decreases when it is oxidizing type. At the higher temperature range only O⁻ species will react with the contaminant gas. The reaction kinematics will proceed like this:



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



4. Results and discussion

Figure 2 shows the dependence of ethanol gas sensitivity to the SnO₂ film at different temperatures. It was

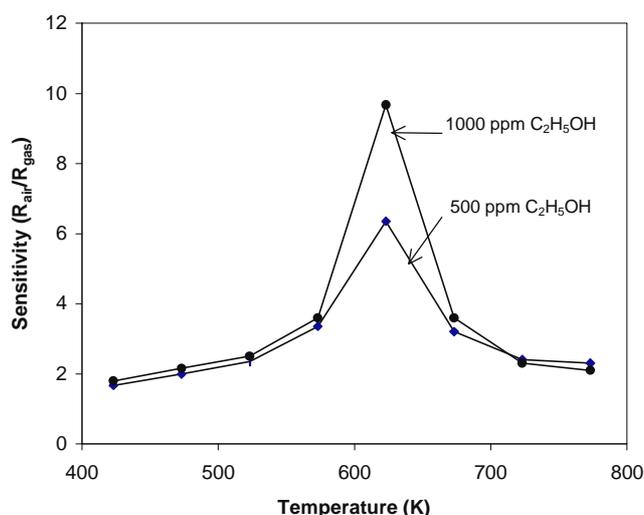


Figure 2. Variation of sensitivity of tin oxide layer with temperature at different ethanol concentrations.

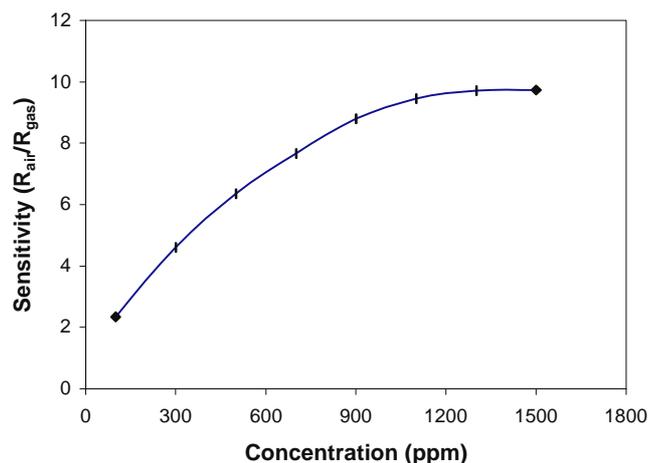


Figure 3. Variation of sensitivity with ethanol concentrations at 623 K.

measured at 1000 ppm and 500 ppm of C_2H_5OH concentration. The highest sensitivity was obtained at 623 K. It shows that at 623 K, most of the adsorbed oxygen species would have reacted with the OH group of ethanol vapour. It is reported that the highly active O^- is the dominant species in case of SnO_2 for temperature between 423 K and 933 K. The major adsorbed species in our films is therefore likely to be O^- . This adsorbed oxygen creates a space charge region near the film surface by extracting electrons from the material. Ethanol, being reducing in nature, removes adsorbed O^- species from the surface and re-injects the electrons back to the material, thereby reducing the resistance. The peak sensitivity at 623 K indicates that the equilibrium density of chemisorbed O^- ions is maximum at this temperature. From the figure, it is also clear that with the increase in the ethanol concentration the sensitivity shows an increasing trend. It seems that due to increase in the concentration, more adsorbed species come into contact with ethanol and hence decreasing the resistance, which resulted in higher sensitivity.

Figure 3 shows the dependence of gas sensitivity of the SnO_2 film on the concentration level of alcohol at 623 K. It is clear from the graph that with the increase in the concentration the sensitivity increases linearly up to 1150 ppm of C_2H_5OH after that it saturates. The graph also indicates that at low concentration sensitivity has a linear relationship with concentration because there may be sufficient number of available surface states to act on ethanol vapour. After 1150 ppm level of C_2H_5OH the curve flattens because there would not be enough ionosorbed oxygen species to contribute to detecting mechanisms. The linear behaviour of the curve may be extended to some extent by taking longer area of the sensor. It also shows that the film is sensitive even at 100 ppm of ethanol vapour. Linearity of sensitivity in the

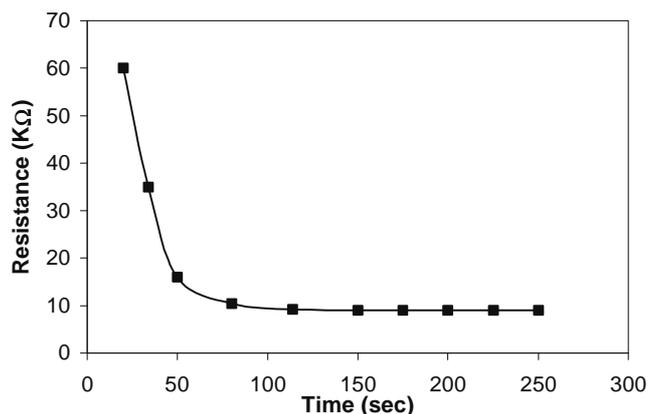


Figure 4. Response time of tin oxide sensor at 500 ppm of ethanol.

low concentration range is properly suited for the use of these films in checking the concentration of ethanol in human breath.

Figure 4 shows the response time of the sensor at 623 K. The response time in this case is ~ 30 sec. It is clear from the figure that the sensor resistance comes to saturation at 100 sec. It suggests that after this time there is no more O^- species left to react with the ethanol vapour. It also indicates that by increasing the surface area i.e. increasing the grain size of the film, one can increase the response time.

4. Conclusions

A study on the alcohol sensing characteristics of spin coated SnO_2 film prepared by sol-gel technique has been carried out. It was observed that the sensitivity of the film was at the peak value at around 623 K, which may be the saturation point of the redox reaction between the ethanol vapour and the adsorbed oxygen gas species. The sensing properties were studied at very low concentration of alcohol and it was found that the gas is sensitive even at 100 ppm of alcohol. The film shows excellent sensing characteristics at 623 K. The response time is also fast. The results obtained by sol-gel technique are promising for the preparation of sensitive and low cost ethanol sensor. Sol-gel technique can be used for the detection of a variety of gases and by adding different dopant to the solution the selectivity of the tin oxide film can be increased. This work is under progress.

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