

Ethanol and LPG sensing characteristics of SnO₂ activated Cr₂O₃ thick film sensor

RAVI CHAND SINGH*, NIPIN KOHLI, MANMEET PAL SINGH[†] and ONKAR SINGH

Department of Physics, Guru Nanak Dev University, Amritsar 143 005, India

[†]Khalsa College of Engineering and Technology, Ranjit Avenue, Amritsar 143 001, India

MS received 2 April 2009; revised 28 August 2009

Abstract. The sensing response of pure and SnO₂ activated Cr₂O₃ to ethanol vapours and liquefied petroleum gas (LPG) has been investigated. Fine particles of commercial chromium oxide powder were selected and deposited as thick film to act as a gas sensor. The sensor surface has been activated by tin dioxide, on surface oxidation of tin chloride. The concentration of tin chloride solution, used as activator, was varied from 0 to 5% and its effect on gas response, selectivity and operating temperature has been studied. It was found that response to ethanol vapours significantly improved, whereas response to LPG remained unaffected. Moreover, operating temperature remains unchanged both for LPG and ethanol vapours.

Keywords. Gas sensor; chromium oxide; activation energy.

1. Introduction

Gas sensors based on semiconducting metal oxides are the most investigated group of gas sensors. These sensors show conductance change upon exposure to toxic and hazardous gases (Morrison 1987; Yamazoe *et al* 1991; Moseley 1997). So far research has been concentrated on improving the gas sensing behaviour of *n*-type semiconductor such as SnO₂ (Li and Kawi 1998; Singh *et al* 2007), ZnO (Nunes *et al* 1999; Roy and Basu 2002; Singh *et al* 2008) etc. The corresponding gas sensing mechanisms are now well established. By contrast, Cr₂O₃ gas sensors with *p*-type semiconducting behaviour have scarcely been investigated, although a few studies have reported gas sensing characteristics of Cr₂O₃ (Miremadi *et al* 1994; Dawson *et al* 1995; Jayaraman *et al* 1999; Chabanis *et al* 2001; Pokhrel and Nagaraja 2003; Naisbitt *et al* 2006; Pokhrel *et al* 2007; Suryawanshi *et al* 2008). In the present investigation, the surface of Cr₂O₃ sensor has been activated by SnO₂ and its effect on sensor response to ethanol vapours and liquefied petroleum gas (LPG) has been studied.

2. Experimental

2.1 Powder preparation

A commercially available chromium oxide powder, which has wide range of particle size distribution, was

utilized in the present study. To select the finer particles with a more uniform particle size, a suspension of as received Cr₂O₃ powder in water was prepared and ultrasonicated for a few minutes. Ammonium hydroxide was added and the mixture was left undisturbed for the larger particles to settle. The remaining suspension that contained finer particles was separated. These fine particles were dried at 120°C for 1 h and then sintered at 350°C for 2 h. The sintered powder was further ground before its application on the substrate.

2.2 Sensor preparation and testing method

To fabricate thick film sensors, a paste was prepared by mixing a proper amount of sintered powder with distilled water. The thick film of paste was then painted onto an alumina substrate (12 × 5 mm) having gold electrical contacts 2 mm apart. No material as a binder was used since fine particles of chromium oxide were self binding very well. The sensor design is shown in figure 1. Six identical

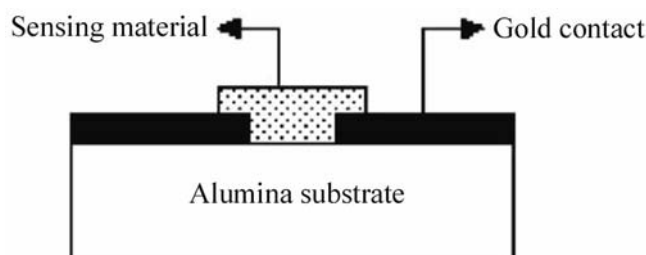


Figure 1. Schematic of gas sensor.

*Author for correspondence (ravichand.singh@gmail.com)

samples prepared were heated at 350°C for 1 h. To activate the sensors, 4 µl of SnCl₄ solution at different concentrations (0.5%, 1.0%, 2.0%, 3.0%, 5%) was added to the surfaces of five sensors, respectively followed by heating at 350°C for 1 h, leaving one inactivated. For studying the sensing characteristics, a simple home built apparatus was used which consists of a simple potentiometric arrangement, a test chamber of 40 litres volume in which a sample holder, a small temperature controlled (by dimmer stat & thermocouple) oven and a mixing fan were installed. The fabricated sensor was placed in the test chamber oven at suitable temperature, and known quantity of gas species was injected into the test chamber. Variation of voltage signal across a resistance connected in series with sensor was monitored and recorded with a computer. All the sensors were tested following same procedure by varying the temperature from 200 to 400°C. The conductance of pure and activated gas sensors was calculated at 200, 250, 300, 350 and 400°C by measuring voltage drop and current flowing through these.

3. Results and discussion

3.1 Structural analysis

X-ray diffraction analysis of the fabricated sensors was carried out by using D8 Advance Bruker diffractometer. Figure 2 shows the X-ray diffraction pattern of pure and SnO₂ activated Cr₂O₃. The presence of well resolved and sharp lines was compared with standard data at the investigation lab, which indicate the polycrystalline nature of Cr₂O₃ material. In figure 2, diffraction pattern 'f' shows

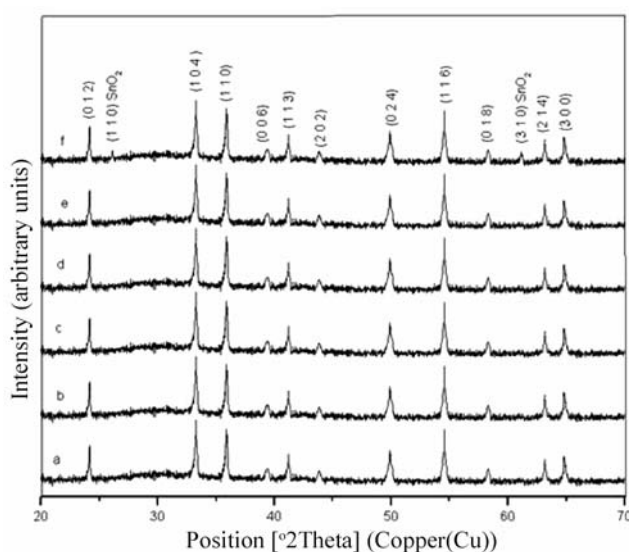


Figure 2. XRD patterns of (a) pure Cr₂O₃, (b) 0.5% SnO₂ activated Cr₂O₃, (c) 1% SnO₂ activated Cr₂O₃, (d) 2% SnO₂ activated Cr₂O₃, (e) 3% SnO₂ activated Cr₂O₃ and (f) 5% SnO₂ activated Cr₂O₃.

small peaks of tin dioxide as well. The average crystallite size D can be determined using Scherrer's formula

$$D = k\lambda/\beta\cos\theta, \quad (1)$$

where λ is X-ray wavelength, β the full width at half maxima (FWHM), θ the diffraction angle and k the Scherrer's constant.

The average crystallite size approximated using this formula was around 48 nm.

The scanning electron microscopy for surface analysis of samples was carried out by using LEO 435 VP instrument. Figure 3 represents SEM microphotographs of six samples of chromium oxide with tin dioxide activation at various concentrations from 0–5%. Clusters and agglomeration are quite clear in the pictures. The effect of SnO₂ on the morphology of the material is not visible in SEM pictures.

3.2 Effect of doping

The height of energy barrier to electron conduction between neighbouring grains in a material is an important factor, which determines sensitivity of the material. The activation energy of semiconductor can be calculated by the equation (Madou and Morrison 1989)

$$G = G_0 \exp(-qV_s/kT), \quad (2)$$

where G_0 is a factor that includes the bulk intergranular conductance, k the Boltzmann's constant, T the absolute temperature, and qV_s the potential energy barrier at the interface between two neighbouring grains. The activation energy was evaluated from a plot between $\ln G$ and $1000/T(K)$ as shown in figure 4 and results are tabulated in table 1.

The activation energy depends upon particle size (Zhang and Liu 2000) and dopant amount (Song *et al* 2007). In our case the change in activation energy has been caused by the addition of SnO₂ and not by particle size because particle size remained unchanged in all the sensors, which is clear from XRD and SEM analyses. The sample activated with 2% SnO₂ shows minimum value of activation energy, which means that to increase the conductivity of sample supply of lesser amount of energy was necessary as compared to other samples.

3.3 Gas sensing behaviour

The sensor response magnitude, S , was determined as G_a/G_g ratio, where G_a is the conductance in air ambience and G_g conductance in air–gas mixture. Though not a measurable quantity, selectivity is defined as the ability of a sensor to respond to a certain gas in the presence of other gases.

The operable temperature of sensors, fabricated from activated and pure materials was found and it is observed

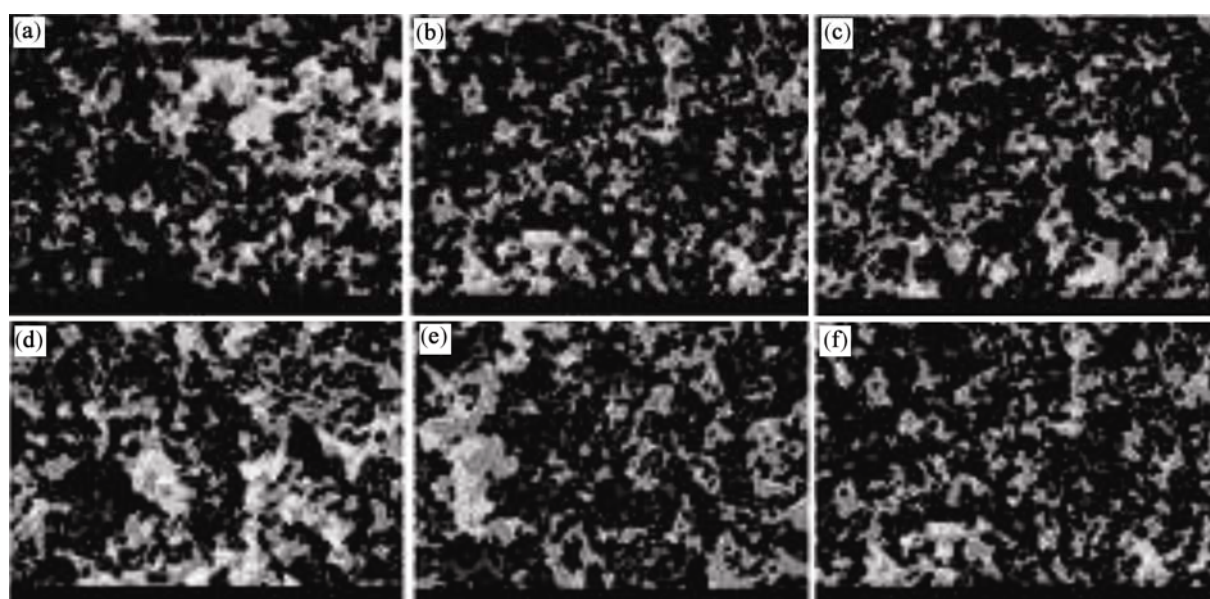


Figure 3. SEM micrographs: (a) pure Cr₂O₃, (b) 0.5% SnO₂ activated Cr₂O₃, (c) 1% SnO₂ activated Cr₂O₃, (d) 2% SnO₂ activated Cr₂O₃, (e) 3% SnO₂ activated Cr₂O₃ and (f) 5% SnO₂ activated Cr₂O₃.

Table 1. Activation energy of pure and activated Cr₂O₃ sensors.

Sl. No.	Cr ₂ O ₃ activated with wt.% tin chloride solution	Conductance at 300°C (Ω^{-1})	Activation energy (eV)
1.	0%	60.6×10^{-8}	1.027
2.	0.5%	72.72×10^{-8}	0.922
3.	1%	84.84×10^{-8}	0.803
4.	2%	107×10^{-8}	0.694
5.	3%	92.11×10^{-8}	0.837
6.	5%	83.02×10^{-8}	0.743

that all the sensors gave best response at 300°C to ethanol and LPG as shown in figure 5. Gas species to be detected require certain amount of thermal energy to cross the potential barrier and combine with the adsorbed oxygen. At optimum operable temperature, maximum number of gas molecules possesses required energy and react with adsorbed oxygen resulting in large change in conductance of sensing element. Above 300°C the sensor response decreases because amount of adsorbed oxygen available at the sensing site on the sensor surface reduces to react with gas molecules leading to small change in conductance. To find optimum doping, the response of sensors, activated with various wt.% concentrations of tin chloride solution, was investigated. It is clear from figure 5(a–f) that at 300°C, response of the sensor increases gradually to ethanol vapours as a function of solution concentration of tin chloride and optimized at 2 wt.%. There is no effect of SnO₂ activation on LPG detection (figure 5g). With further increase of doping sensor response decreased (figure 5b). It is interesting to note that the sample with optimum activation of tin dioxide has minimum value of activation energy as shown in table 1.

For further investigations, all the sensors were operated at optimum operating temperature of 300°C. Figure 6 shows sensor response versus time for pure and optimum activated Cr₂O₃ gas sensor to 250 ppm ethanol, and LPG at 300°C. It is clear that sensor is more sensitive to ethanol vapours than LPG.

Though there is no change in the sensor response to LPG, but interestingly the sensing response to ethanol has been doubled (~10) as compared to pure sensor. In other words, the doping has transformed it to a sensor which is more sensitive to ethanol than LPG. Figure 7 shows the variation of sensitivity of optimum activated sensor with concentration of ethanol and LPG, and sensitivity varies almost linearly up to 500 ppm concentration.

The adsorption–desorption of molecules at the sensor surface is the principle mechanism for gas detection. The surface Cr³⁺ ions act as donors, removing holes from the Cr₂O₃. The surface oxygen, O⁻ or O²⁻, forms a donor–acceptor complex with the surface of Cr³⁺, restoring holes in the valence band and increasing the conductivity. In the first place the adsorbed gaseous species at the chromium oxide surface acts as an electron donor, changing

Cr^{4+} to Cr^{3+} and removing holes from the Cr_2O_3 valence band. Ethanol/LPG react with the adsorbed oxygen and the resulting Cr^{3+} donors decrease the conductivity. Therefore, with reducing gas on this p -type sensor, the conductivity drops. Upon removal of reducing species or introduction of air or oxygen, the mechanism is reversed and the conductivity returns to its original state. The adsorption of atmospheric oxygen on the sensor surface forms ionic species such as O_2^- and O^- which acquire electron from the conduction band. The reaction kinetics is as follows (Sahay and Nath 2008)

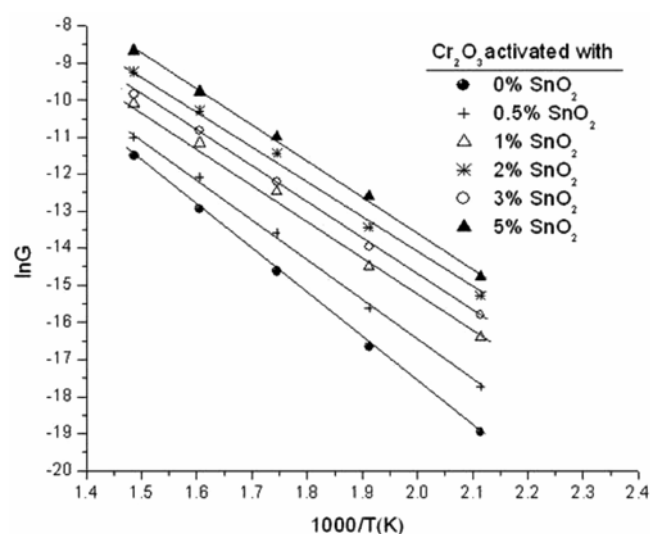


Figure 4. Temperature dependence of conductance of pure and activated Cr_2O_3 sensors.

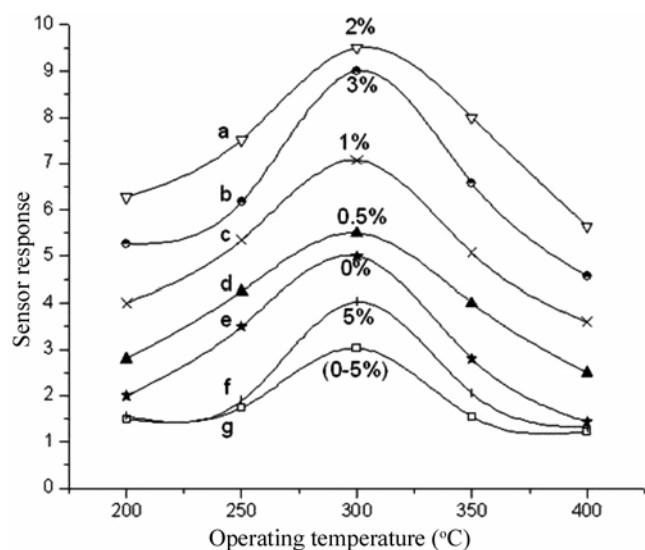
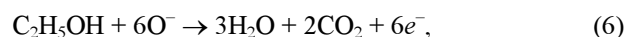


Figure 5. Sensing response to ethanol (a-f) and LPG (g) for different dopant concentrations (0-5%) at different operating temperatures.



The oxygen species react with ethanol (Suryawanshi *et al* 2008) and LPG (Sahay and Nath 2008; Patil and Patil 2009) through complex series of reactions as follows



The above reaction takes place only if gases are completely oxidized on the sensor surface. From the results it seems that LPG does not oxidize completely and may be following the reaction scheme given below (Mishra *et al* 2008)

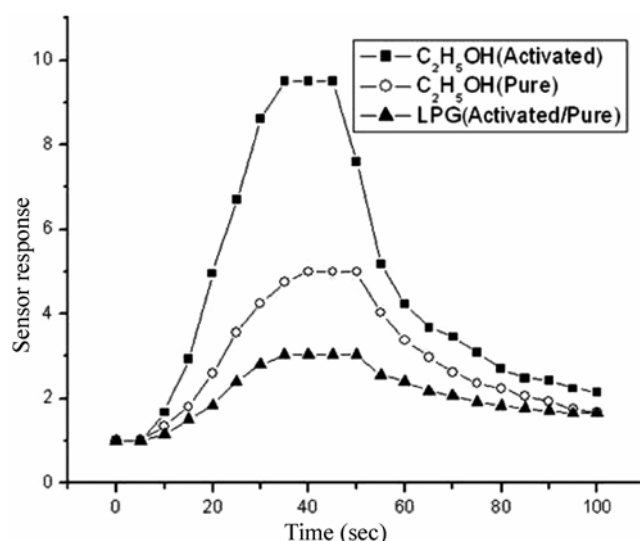
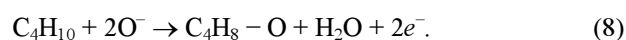


Figure 6. Sensing characteristics of pure and optimum activated Cr_2O_3 gas sensor exposed to 250 ppm gas species at 300°C .

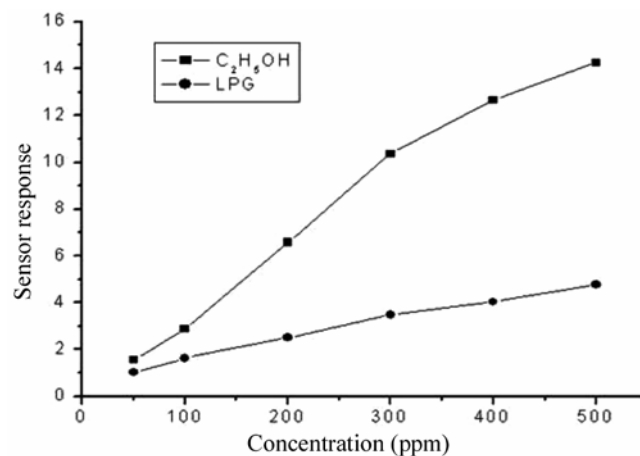


Figure 7. Sensor response of optimum activated Cr_2O_3 gas sensor to different concentrations of gas species at 300°C .

Partially oxidized gases may not change the conductivity of sensor element drastically, which might have happened in present study of LPG sensing.

Another role of additives is that they can modify the microstructure of the base material and introduce donor or acceptor levels, leading to the changes in material resistivity. In the present study the modification in material has reflected in its activation energy variation. The optimum change in the conductance and activation energy has been observed with addition of 2 wt.% tin chloride solution as shown in table 1. The optimum sensor response to ethanol (figure 5) has been observed with a sensor exhibiting minimum activation energy that is sensor activated with 2 wt.% tin chloride solution (table 1). The failure of tin dioxide to improve the sensor response to LPG may be due to the fact that it is not a suitable catalyst for LPG detection.

4. Conclusions

The sensor response of Cr₂O₃ to ethanol vapours can be selectively improved by the surface modification with tin dioxide. Addition of 2 wt.% tin chloride solution on the sensor surface brought maximum reduction in activation energy of base material and led to optimum ethanol sensing response. The results reveal that tin dioxide is not an appropriate catalyst to improve sensing response of Cr₂O₃ to LPG.

Acknowledgements

Authors would like to thank UGC for financial support and IIT Roorkee, for XRD and SEM investigations.

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