

## Bi-layer functionally gradient thick film semiconducting methane sensors

A BANERJEE, A K HALDAR, J MONDAL, A SEN\* and H S MAITI

Electroceramics Section, Central Glass and Ceramic Research Institute, Kolkata 700 032, India

**Abstract.** Gas sensors based on metal oxide semiconductors like tin dioxide are widely used for the detection of toxic and combustible gases like carbon monoxide, methane and LPG. One of the problems of such sensors is their lack of sensitivity, which to some extent, can be circumvented by using different catalysts. However, highly reactive volatile organic compounds (VOC) coming from different industrial and domestic products (e.g. paints, lacquers, varnishes etc) can play havoc on such sensors and can give rise to false alarms. Any attempt to adsorb such VOCs (e.g. by using activated charcoal) results in sorption of the detecting gases (e.g. methane) too. To get round the problem, bi-layer sensors have been developed. Such tin oxide based functionally gradient bi-layer sensors have different compositions at the top and bottom layers. Here, instead of adsorbing the VOCs, they are allowed to interact and are consumed on the top layer of the sensors and a combustible gas like methane being less reactive, penetrates the top layer and interacts with the bottom layer. By modifying the chemical compositions of the top and bottom layers and by designing the electrode-lead wire arrangement properly, the top layer can be kept electrically shunted from the bottom layer and the electrical signal generated at the bottom layer from the combustible gas is collected. Such functionally gradient sensors, being very reliable, can find applications in domestic, industrial and strategic sectors.

**Keywords.** Sensor; semiconductor; tin dioxide; functionally gradient.

### 1. Introduction

Gas sensors using metal oxide semiconductors were first proposed by Seiyama *et al* (1962) and Taguchi (1962). The recent concern over environmental pollution and efficiency in a variety of combustion processes and of increased awareness over the need to monitor potentially hazardous gases have stimulated substantial research and development in the field of gas sensors. Such sensors are primarily based on *n*-type semiconductors like SnO<sub>2</sub>, where loss of oxygen on heating results in the generation of oxygen vacancies (balanced by the reduction of some of the Sn<sup>4+</sup> ions to Sn<sup>2+</sup> ions) leading to electron donor states. In the first reaction, atmospheric oxygen becomes chemisorbed to the surface, consuming the electron as given below



As the free electrons are consumed, the conductivity decreases. Any reducing gas, present in the ambient, produces a counter reaction where, the reducing gas removes the chemisorbed oxygen, frees the bound electrons and increases the conductivity of the semiconducting gas sensors thus generating a signal. However, such sensors respond to different reducing gases and to impart selectivity, normally the following three methods (Roy Morrison

1987) are tried. They are (i) the use of catalysts and promoters, (ii) modification of the operating temperature and (iii) the use of filters. Normally palladium is used as a catalyst (Kohl 1990; Gopal and Schierbaum 1995) and is an indispensable component in SnO<sub>2</sub> sensors, especially for the oxidation of hydrocarbons. Incidentally, highly reactive volatile organic compounds (VOC) emanating from different industrial and domestic products like paints, lacquers, varnishes can strongly influence (Schweizer-Berberich 1999) such sensors and can give rise to false alarms even in the absence of detecting gases like methane. These VOCs are highly reactive and so far, two techniques have been attempted to circumvent the problem. One is the use of charcoal filter (Schweizer-Berberich *et al* 1999). The disadvantage of this method lies in the fact that charcoal filters also adsorb most of the combustible gases and hence cannot be used to detect satisfactorily the combustible gases like methane, propane, LPG etc in presence of VOCs. The other alternative (Papadopoulos *et al* 1996) is to use uncoated/coated (Pt, Pd) filters of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, WO<sub>3</sub> etc on SnO<sub>2</sub>. However, the second method gives protection primarily against alcohol cross-sensitivity, whereas VOCs, in general, are either not affected by such filters, or the overall sensitivity of the sensors dramatically goes down.

In the present work, a novel bi-layer functionally gradient sensor has been developed to get round the problem. Here, instead of adsorbing the VOCs, they are allowed to interact and are consumed on the top layer of the sensors

\*Author for correspondence

and the combustible gases like LPG, methane being less reactive penetrate the porous top layer and interact with the bottom layer to generate the desired signal.

## 2. Experimental

Batches containing tin dioxide and antimony (0–1 wt.% as  $\text{Sb}_2\text{O}_3$ ); tin dioxide, palladium (0–2 wt.% as  $\text{Pd}^0$ ) and antimony (0–1 wt.% as  $\text{Sb}_2\text{O}_3$ ) were prepared by simultaneous precipitation technique. In this technique, stannous chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ) solution was made in water containing a very small amount of hydrochloric acid (1–2%). Antimony oxide ( $\text{Sb}_2\text{O}_3$ ) was dissolved as antimony chloride in hydrochloric acid (50%) and  $\text{PdCl}_2$  was dissolved as  $\text{Pd}(\text{NO}_3)_2$  in hot nitric acid (~20%). The above solutions were added to ammonium hydroxide solution (pH above 10 and under stirring) so that all the hydroxides were precipitated simultaneously. The precipitates were washed, made chloride free and finally calcined at  $900^\circ\text{C}$  (2 h) to get the oxide powders. The phase identification of the calcined powders was carried out by X-ray diffraction (Philips, PW 1710). Particle morphology of the powders was observed in a scanning electron microscope (Leo, 30i).

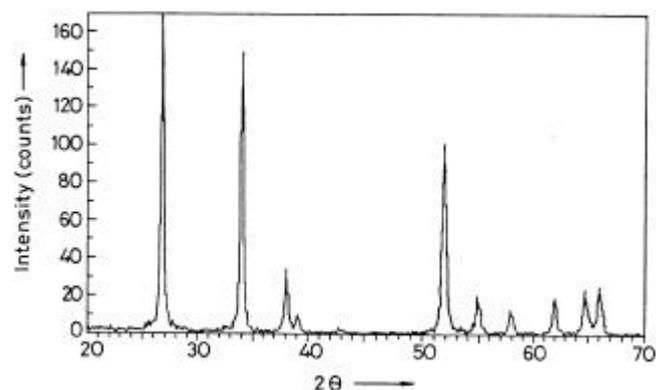
Thick pastes of the powders were prepared in an aqueous medium containing a small amount of ethyl cellulose binder. The pastes were painted on the outer surface of thin alumina tubes (length 3 mm, outer diameter 2 mm and thickness 0.5 mm) with gold electrode and platinum lead wires already attached at the ends (by curing at a high temperature). Kanthal heating coils were placed inside the tubes. The consistency of the pastes and the processing variables were optimized to get final coatings of 50–60  $\mu\text{m}$  thickness. For the functionally gradient bi-layer sensors the bottom layer was a coating of a powder containing tin dioxide, antimony oxide and palladium, whereas the top layer was a coating of tin dioxide, palladium and alumina powder (5–30 wt.%). After applying the bottom coating, the assembly was dried in an oven followed by application of the top coating. Finally, the coated alumina tubes were cured at a temperature in the range of  $600$ – $1000^\circ\text{C}$  for 3 h. The electrical resistance and methane (500 ppm) sensitivity of the coatings were measured at different temperatures (up to  $350^\circ\text{C}$ ) by using a digital multimeter (Solartron), a constant voltage/current source (Keithley 228A) and X–Y recorder (Yokogawa). All the fired samples were initially preheated at  $350^\circ\text{C}$  for 72 h to achieve the desired stability before the measurements.

## 3. Results and discussion

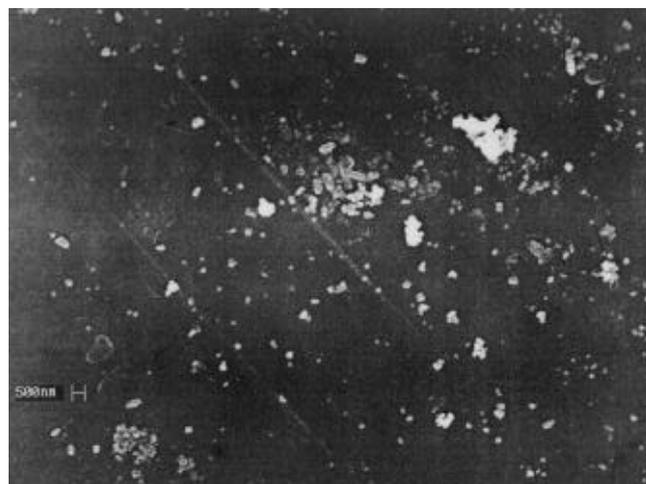
The X-ray diffractogram of calcined tin hydroxide powder is depicted in figure 1, which indicates complete  $\text{SnO}_2$  phase formation after firing at  $900^\circ\text{C}$ . The scanning elec-

tron micrograph of the calcined powders (figure 2) shows particles of the order of 100 nm size. The typical trend of resistance vs temperature (figure 3) of pure  $\text{SnO}_2$  can be understood by considering the competitive adsorption of oxygen and moisture on  $\text{SnO}_2$  surface from the ambient (Saha et al 2001). Incidentally, antimony oxide is often added (Potthast and Schumann 1999) to tin dioxide in real life sensors to enhance their conductivity. On doping with antimony,  $\text{SnO}_2$  shows a decrease in resistivity owing to substitution of  $\text{Sn}^{4+}$  by  $\text{Sb}^{5+}$  ( $\text{Sb}^{5+}$  should be predominant at the firing temperature) leading to an increase in carrier concentration (donor doping) (Rajpure et al 2000). Hence Sb-doped samples show orders of magnitude lower resistance than that of pure  $\text{SnO}_2$ . The effect of Sb-doping on the sensitivity ( $S$ ) of  $\text{SnO}_2$  samples in 500 ppm methane at  $350^\circ\text{C}$  has been depicted in figure 4 where the sensitivity ( $S$ ) is given by

$$S = (R_A - R_G)/R_A \times 100\%, \quad (2)$$



**Figure 1.** X-ray diffractogram of precipitated tin hydroxide powder after calcination at  $900^\circ\text{C}$ .



**Figure 2.** Scanning electron micrograph of a typical calcined powder.

