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Selectivity and stability of a tin dioxide sensor for methane

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Abstract

The selectivity and long-term stability of a screen-printed tin dioxide sensor for methane are discussed in this paper. A dependence of the sensitivity to ethanol on the thickness of the sensor is highlighted and can be exploited to improve the sensor's selectivity. A further enhancement of the selectivity can be brought about by the use of specially devised screen-printed filters. The long-term behaviour of the sensor is found to improve as the annealing temperature is raised in the range 750–950 °C. Based on the literature, a tentative explanation of the experimental findings is given.

Keywords: Methane sensors; Tin dioxide

1. Introduction

Semiconductor gas sensors are used as domestic gas detectors to produce an alarm at a given gas concentration as prevention measure against gas explosion hazards. Such sensors should have selectivity and long-term stability of the alarm threshold.

The gas-sensing properties of semiconducting oxide films, namely ZnO and SnO_2, have been studied for a long time [1,2] and SnO_2 gas sensors have been available for more than 20 years. The basic mechanism that brings about the sensitivity of these oxides to reducing gases is well known: the reduction of their surface makes electrons available for electrical conduction and causes the electrical resistance of the oxide to decrease. Yet gas sensors are generally compounded from a mixture of SnO_2 and electrically inert oxides such as Al_2O_3 and SiO_2, with some noble metal acting as a catalyst. It is therefore very difficult to achieve a thorough understanding of the gas-sensing process because the properties of gas sensors depend very strongly on their composition and preparation conditions. The effect of different noble metals on sensitivity has been discussed [3,4] and it has to be exploited to obtain selectivity towards the desired gas. The grain size and dispersion of the noble metal catalyst, grain size of the SnO_2 crystallites and the concentration of hydroxyls on the oxide's surface are only some of the many factors that affect the sensitivity and the stability of gas sensors [5–7]. The dependence of the selectivity and of the long-term stability of a methane gas sensor on the preparation conditions is addressed by this paper.

2. Experimental

Gas-sensitive films were screen printed on alumina substrates. In operation the sensors were kept at their working temperature by a screen-printed platinum heater that had been previously deposited on the other side of the alumina substrate. The films were polycrystalline and their composition was approximately SnO_2 70 wt.%, Al_2O_3 29.5 wt.%, Pd (or Pt) 0.5 wt.%.

The mean grain size of SnO_2 was of the order of 300 nm. The mean grain size of Al_2O_3 was below 1000 nm. The Pd particles were so finely dispersed that they were not detected by SEM analysis and it is inferred that their size was below 10 nm.

Films between 10 and 200 μm thick were tested to investigate the effect of thickness. Annealing followed deposition: temperatures between 750 and 950 °C were used. Surface layers based on Al_2O_3 were studied in order to increase the sensor's selectivity.

Each sensor was connected in series with a load resistor and a d.c. source applied a constant voltage continuously when the sensor was in operation. The sensor's resistance was calculated from the voltage drop at the ends of the load resistor.

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The water content of test-gas mixtures was 50% relative humidity at 22 °C, except where otherwise stated. The pressure in the measurement chamber was 1 atm. The oxygen partial pressure was about 0.21 atm in all the tests because the sensor was meant to operate in air.

3. Results and discussion

Our attention was focused on two features of methane gas sensors: selectivity and stability. It is generally accepted that the strongest interference in the detection of methane comes from ethanol in domestic alarm systems. The lower explosion limit of methane in air is 5% and the alarm is usually set between 0.3 and 1%. On the other hand, the threshold limit value of ethanol is 0.1%. Because of this a sensor can be regarded as selective if its sensitivity to 0.2% ethanol in air is lower than that to 1% methane in air. The stability requirement demands that sensitivity to methane and selectivity be maintained at least over several months.

The sensitivity to a certain gas mixture was defined as follows:

$$S=(R_a-R_g)/R_g$$

where R_a is the resistance in air and R_g is the resistance in the given gas mixture.

Fig. 1 shows a plot of the sensitivity of a 14 μm thick film as a function of temperature. Three gas mixtures were used: 1% methane–air, 0.05% ethanol–air, 0.01% hydrogen–air. The sensitivity of a much thicker film (85 μm) is plotted in Fig. 2. It is apparent that the sensitivity to 0.05% ethanol–air is much higher than that to 1% methane–air for the 14 μm film. On the contrary, Fig. 2 shows that above 400 °C the sensitivity to 0.2% ethanol–air is lower than that to 1% methane–air

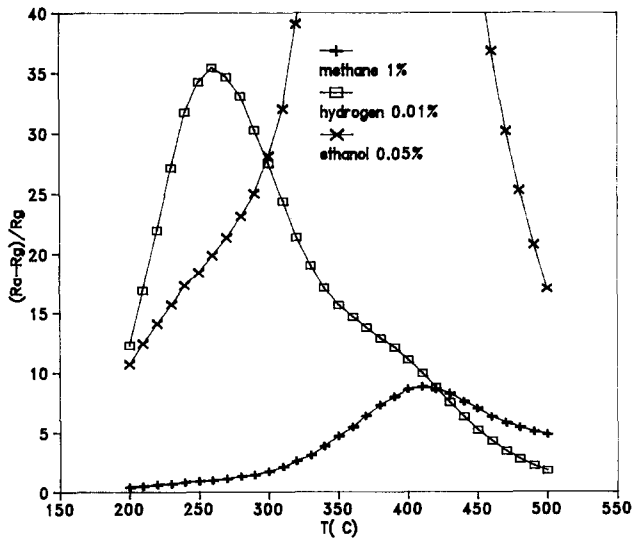

Fig. 1. Sensitivity of a 14 μm thick sensor.

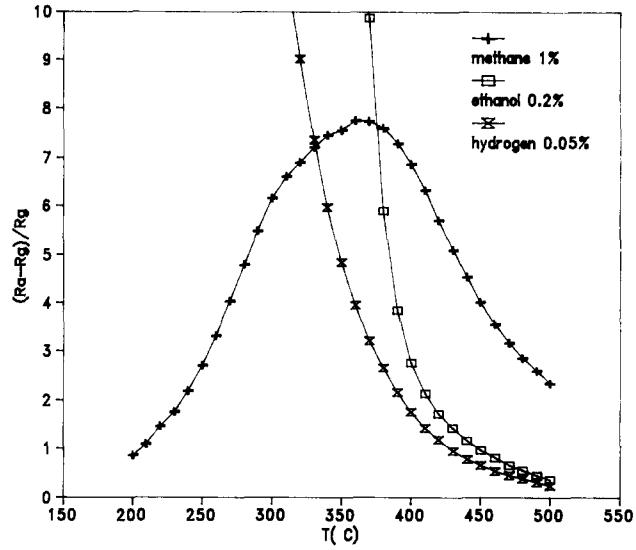

Fig. 2. Sensitivity of an 85 μm thick sensor.

Table 1
Effect of the addition of ethanol to methane–air gas mixtures

	R (ohm) in air	R (ohm) in air + 0.2% ethanol
$p_{CH_4}=0.01$ atm	575	555
$p_{CH_4}=0.0025$ atm	1425	1375

for the 85 μm film. It must be stressed that the sensitivity to ethanol decreases as the film thickness increases, while the sensitivity to methane remains more or less unchanged. Such a dependence of the sensitivity to ethanol on film thickness has already been reported by Komori et al. [8]. It was put down to the fact that ethanol can be oxidized easily on the hot outer surface of the film, whereas methane, which is more stable, is oxidized only through the interaction with SnO_2 and the catalyst. Because of this, the oxidation of ethanol affects only the outer layer of the film, while the oxidation of methane affects the whole film's depth. Thus the thicker the film, the lesser the effect of ethanol.

This behaviour prompted the idea that selective filters could be devised, which could oxidize ethanol but not methane. Filters based on Al_2O_3 were developed and they proved so effective that the sensor's reading in 0.25% methane–air was not significantly affected by the addition of 0.2% ethanol [9]. Table 1 gives the resistance values measured in both methane–air and in methane–0.2% ethanol–air mixtures on a sample fitted with the special filter. One can see that the electrical resistance did not change significantly when ethanol was added. Similar results were found for several samples that had been prepared in different batches.

Before discussing the effect of relative humidity, it is worth pointing out that the electrical resistance was

found to depend on the methane partial pressure after the following relationship in the range 0.001–0.05 atm:

$$R = a(p_{CH_4})^{-b}$$

where b is of the order of 0.5. This kind of dependence made it easy to link the measured resistance values to the corresponding methane partial pressures once the constants a and b had been found experimentally for each sensor.

The sensor's reading was insensitive to variations of the relative humidity in the range 30–80% at room temperature. This was proved by two-step tests: first a calibration curve of the electrical resistance as a function of methane concentration was measured in air with 50% relative humidity, then the sensor's response to 0.25% methane–air was measured for two other relative humidity values: 30 and 80%. The data thus obtained were evaluated with the calibration curve in order to get the corresponding methane concentrations. Table 2 shows the results for five samples: the estimated methane concentrations range from 0.23 to 0.32% as a consequence of the relative humidity variations. This degree of uncertainty in the determination of the methane concentration is acceptable and it was confirmed by several other tests performed on samples prepared in different batches.

These results pertain to sensors that had been annealed at 870 °C, but they apply to the whole range of annealing temperatures that was investigated (750–950 °C). In fact the sensitivity curves do not change appreciably with annealing temperature.

Conversely, the annealing temperature has a strong effect on stability. Figs. 3–5 show that the stability

Table 2
Effect of variations of the relative humidity on the determination of the methane concentration in a 0.25% methane–air mixture

Sample No.	Relative humidity (%)	R (ohm)	CH_4 conc. (%)
1	30	12580	0.32
	50	14660	0.25
	80	13130	0.30
2	30	8186	0.28
	50	8710	0.25
	80	8774	0.25
3	30	7848	0.28
	50	8430	0.25
	80	8437	0.25
4	30	10410	0.28
	50	11000	0.25
	80	11040	0.25
5	30	14630	0.27
	50	15190	0.25
	80	15710	0.23

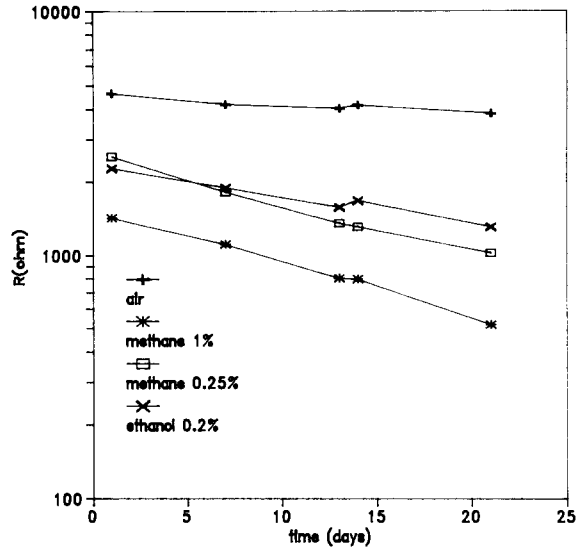

Fig. 3. Behaviour of a sensor annealed at 750 °C.

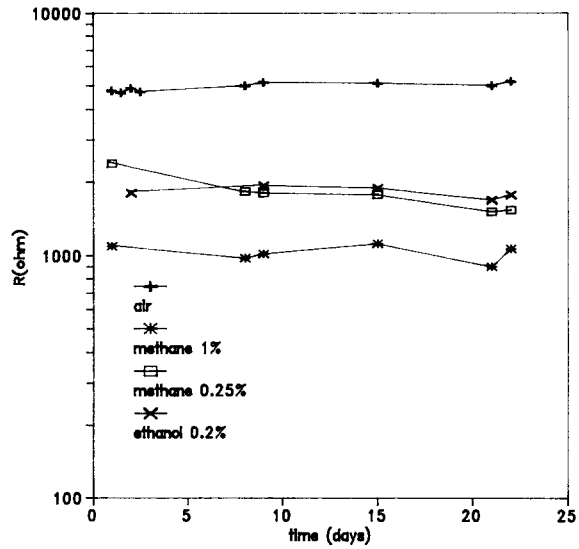

Fig. 4. Behaviour of a sensor annealed at 870 °C.

increased as the annealing temperature was raised from 750 to 870 and 930 °C, respectively. The long-term behaviour of a sensor that had been annealed at 930 °C is shown in Fig. 6. The response to the following gas mixtures was monitored: air, 0.2% ethanol–air, 1% methane–air. The resistance values measured in both ethanol and methane drift appreciably over this 11 month test, but it is worth pointing out that the ranges of values measured in ethanol and in methane do not overlap. This is a definite improvement on the results shown in Figs. 3 and 4. In fact it would be possible to set the alarm level at the resistance value measured in 1% methane–air at the start of such a test and the sensor would maintain selectivity for the following 11 months. The increase in sensitivity to methane would lower the threshold methane concentration from 1 to about 0.1% by the end of the test. Fig. 6 also shows

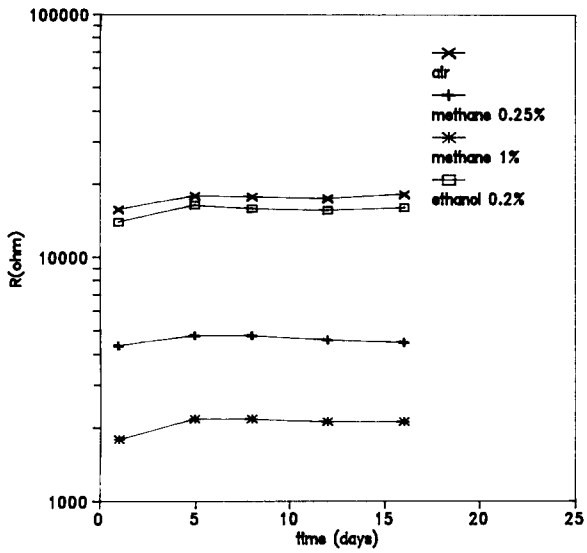

Fig. 5. Behaviour of a sensor annealed at 930 °C.

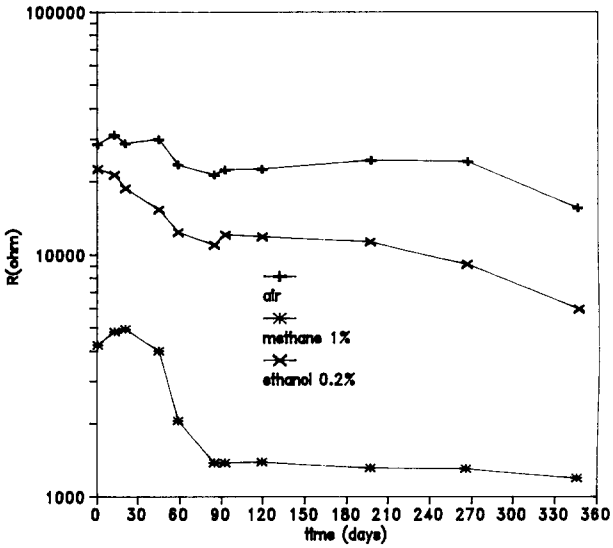

Fig. 6. Long-term behaviour of a sensor annealed at 930 °C.

that the threshold methane concentration would be far more stable if it were set after ageing for three months.

A dependence of stability on annealing conditions was reported by Nakamura et al. [10] and the drift in resistance values was put down to three factors [5,10]: grain growth of SnO_2 particles, decrease in water chemisorption and Pd sintering. In the sensors studied in this paper the mean grain size of SnO_2 particles (300 nm) is far larger than the expected depth of the region that is depleted of charge carriers by oxygen chemisorption, which must be of the order of 5 nm [6,11,12]. Under these conditions the sensor's resistance must depend on the height of the potential barrier between grains ('grain boundary control' according to Refs. [6,11]) and no dependence on grain size is expected. This rules out grain growth as a cause of long-term drift in these sensors. Decrease in water chemisorption and Pd sintering may account for the observed drift and the improvement brought about by increasing the annealing temperature supports this assumption. In fact high-temperature annealing can accelerate these processes and force them to draw closer to equilibrium conditions. The use of such large crystallites deserves one further remark: even though far smaller crystallites would have a higher sensitivity to reducing gases, they would give rise to the grain-growth effect on long-term stability.

4. Conclusions

A methane gas sensor has been developed: it is compounded from large-grain-sized SnO_2, Al_2O_3 and Pd. High selectivity was attained through the deposition of thick layers and it was improved by the development of special filters. It was found that long-term stability was brought about by annealing at high temperature: after such a treatment the sensitivity to methane tended to increase in time, but the sensor maintained its selectivity. In fact even a high concentration of ethanol could not reduce the resistance to the threshold value set for methane in an 11 month test.

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Biographies

Lucio de Angelis was born in 1942. From 1966 to 1970 he was a research member of the Raman spectroscopy group of the Physics Department of Rome University. In 1971 he joined Eniricerche. He has been working in the field of optoelectronic devices using both crystalline and amorphous semiconductors. His current interest is in the study and fabrication of electrochemical and semiconductor-based chemical gas sensors.

Roberto Riva was born in 1961. He received a degree in physics from the University of Milan in 1986. Since then he has worked in the field of solid-state physics. He joined Enirichercherche in 1991.