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Sensitivity of SnO_2 Semiconductor Gas Sensors to CO in the Presence of High Concentrations of Water Vapour

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Abstract

Amongst future uses of semiconductor gas sensors, one important application could be the measurement of emission gases for the control of combustion processes. In such measurements, water vapour is always present as a factor that can cause interference. Combustion gases, depending on the fuel, can contain up to 20% by volume of water vapour. Therefore, it is important to elucidate the influence exercised by water vapour on the sensor. In this study, the sensitivities of SnO_2*-based gas sensors to CO and water vapour were investigated in the laboratory. The concentration of water vapour was varied in the range of 0 to 19·9% by volume. The sensors tested were thick film sensors prepared in the laboratory as well as commercial TGS 812 sensors. Water vapour and CO were found to have a synergistic effect on the conductance of TGS sensor but not on the conductance of the thick film sensor. Due to the absence of the synergistic effect between CO and water vapour the thick film sensor is much less sensitive to the variation of the concentration of water vapour in the range of a few percent to 20% by volume than the TGS 812 sensor.*

Eine wichtige zukünftige Anwendung halbleitender Gassensoren könnte die Analyse von Abgasen zur Steuerung von Verbrennungsprozessen sein. Bei derartigen Messungen muß Wasserdampf als mögliche Störquelle immer in Betracht gezogen werden. Verbrennungsgase können in Abhängigkeit des verwendeten Brennstoffs bis zu 20 Vol.% Wasserdampf enthalten. Deswegen ist es unumgänglich, den Einfluß des Wasserdampfes auf den Sensor zu untersuchen. In dieser Arbeit wurde die Empfindlichkeit von SnO_2 *Sensoren gegenüber CO und Wasserdampf labormäßig untersucht. Der Gehalt an Wasserdampf lag im Bereich 0–19·9 Vol.%. Die untersuchten Sensoren waren zum einen im Labor hergestellte Dickfilmsensoren als auch komerzielle TGS 812 Sensoren. Dabei zeigte sich, daß Wasserdampf und CO eine synergetische Wirkung auf die Leitfähigkeit des TGS Sensors, jedoch nicht auf die Leitfähigkeit des Dickfilmsensors hatten. Durch das Fehlen dieser synergetischen Wirkung zwischen CO und Wasserdampf ist der Dickfilmsensor im Bereich einiger Prozent bis 20 Vol.% viel unempfindlicher gegenüber Konzentrationsschwankungen als der TGS 812 Sensor.*

Parmi les utilisations futures des détecteurs à gaz semi-conducteurs, une application importante pourrait être la mesure des gaz d'émission pour le contrôle du procédé de combustion. Lors de telles mesures, la vapeur d'eau est toujours un facteur provoquant des perturbations. Les gaz de combustion peuvent, selon la nature du combustible, contenir jusqu'à 20% volumiques de vapeur d'eau. Pour cette raison, il est important d'éclaircir le rôle exercé par la vapeur d'eau sur le détecteur. On a étudié la sensibilité de détecteurs à gaz à base de SnO_2 *envers le CO et la vapeur d'eau. La concentration en vapeur d'eau était comprise entre 0 et 19·9% volumiques. Les détecteurs testés étaient des capteurs de gaz en couche épaisse préparés en laboratoire ou bien des détecteurs commerciaux de type TGS 812. On a établi que la vapeur d'eau et le CO ont un effet synergétique sur la conductibilité des détecteurs TGS mais pas sur celle des capteurs en couche épaisse. Du fait de l'absence d'effet synergétique entre la vapeur d'eau et le CO, le capteur en couche épaisse est bien moins sensible que le TGS 812 à une*

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variation de la concentration en vapeur d'eau s'échelonnant de quelques pourcent à 20% volumiques.

1 Introduction

Semiconductor gas sensors are widely used for alarm purposes to detect poisonous or explosive gases such as CO. However, because of their sensitivity to many other gases, one of which is water vapour, their use in analytical instrumentation thus far has been limited. Water vapour is a constituent which is practically always present when concentrations of gases are being measured, as, for example, in industrial process gas or pollution control measurements. It is also a gas, the concentration of which can vary within wide limits in common environments where gases are measured.

According to the most frequently cited sensing mechanism for semiconductor gas sensors, the response behaviour of these sensors is based on ionosorption of oxygen from the ambient atmosphere causing the formation of a depletion layer on the surfaces of the porous sensing material.[1] Electrons moving from one particle to another experience the hindering effect of potential energy barriers formed in the depleted areas. Both ionosorbed molecular O_2^- and atomic O^- have been observed on the surfaces.[2,3] When a reducing gas, such as CO, is introduced into the ambient atmosphere, the amount of ionosorbed oxygen types are decreased by catalytic reactions taking place at the surface of the sensor material. The potential energy barriers are consequently lowered, which is observed as an increase in the conductance of the sensor. With which forms of oxygen the reducing gases react is still, to some extent, an open question. The ionosorbed forms of oxygen are most often referred to as the reactive forms.[4] On the other hand, Clifford, when developing his theory for the sensing mechanism of semiconductor gas sensors, assumed that the reducing gases react with the physisorbed molecular oxygen.[5] His equation for the response of the semiconductor gas sensor to a single reducing gas, as expressed through the conductance, was

$$G = G_0(1 + K_j[G_j]^{n_j})\beta \quad (1)$$

where G is the conductance, G_0 is a constant depending on the partial pressure of oxygen, K_j is the sensitivity coefficient, $[G_j]$ is the concentration of the reducing gas, n_j is an integer or a fractional number, and β is normally a non-fractional number between 0·25 and 0·5. A good fit between the experimental results and eqn (1) has been obtqined, for example, in the case of the methane response of a TGS 812 sensor.[6,7]

Similarly to reducing gases, water vapour is known to increase the conductance of semiconductor gas sensors.[6] In a study of SnO_2 surfaces, performed using infrared methods, both molecular water and hydroxyl groups were observed at temperatures lower than 200°C, but only hydroxyl groups at higher temperatures.[8] Two peaks were also observed in temperature-programmed desorption chromatograms of water vapour, recorded from SnO_2.[9] One of these peaks, occurring at the lower temperature, was assigned to molecular water and the other to the hydroxyl groups. It was also concluded that molecular water had only a slight effect on the conductance of SnO_2.[9] In the case of most ceramic semiconductors, it is unlikely that a water molecule will capture or inject electrons, as it is unlikely that water vapour will chemically combine with oxygen.[1] To explain the observed increase in the conductance caused by water vapour Morrison has suggested a model based on the barrier theory.[1] According to this model, surface fields are neutralized by the physically adsorbed water, consequently changing the surface state energy of oxygen and leading to a lower surface coverage of ionosorbed oxygen. In the case of the TGS 812 sensor, a response of the power law form has been observed for water vapour.[6,7]

Clifford has also studied the simultaneous effect of CO and water vapour on the response behaviour of the TGS 812 sensor.[6] A good fit of the results with the equation

$$G = G_0(1 + K_{H_2O}[H_2O] + K_{CO}[H_2O][CO] + K'_{CO}[H_2O][CO]^2)^\beta \quad (2)$$

was obtained. In the above equation, K_{H_2O}, K_{CO} and K'_{CO} are constants and [CO] and $[H_2O]$ are the concentrations of CO and water vapour, respectively. A noticeable feature of eqn (2) is that CO and water vapour can enhance the effect of each other, i.e. have a synergistic effect. In Clifford's studies, the concentration of water vapour was restricted to that normally observed in the ambient atmosphere or lower.

High concentrations of water vapour are encountered, for example, in combustion gases, from which it is of interest to detect the concentration of CO, as this can be used as an indication of the completion of the burning process. The operation of semiconductor gas sensors in actual exhaust gases has been tested earlier with different types of fuels.[10–12] In this study, the simultaneous effect of CO and a large concentration of water vapour on SnO_2-based thick film sensors and commercial TGS 812 sensors was investigated in the laboratory environment.

2 Experimental Procedure

The schematic diagram of the measuring system is shown in Fig. 1. Carrier gas (90 vol.% Ar, 5 vol.% CO_2 and 5 vol.% O_2) and a gas containing CO (3 vol.% CO in N_2) were mixed in a gas blender (Signal model 850). The carrier gas composition was chosen because of its ready availability from a commercial gas supplier. Comparison was later made with a gas in which nitrogen was the main component instead of argon. No significant differences in the results were observed.

The flow rate of the dry gas was 5 $dm^3\,min^{-1}$ and the volume of the test chamber was 1·7 dm^3. A CrNi–Ni thermocouple was used to measure the temperature inside the chamber. Measurements were carried out at temperatures ranging from 300 to 500°C. The values of the conductances of the sensors were determined by measuring the voltages over 100 kΩ resistors, connected in series with the sensors to be studied and a 10 V DC voltage source.

Water vapour was introduced into the measuring chamber by using a small pump (Ventur Alitea C 1-V) that supplied water through a spiral steel tube placed inside a furnace. The temperature of the furnace was about 350°C. The dry gas mixture was preheated in the same furnace before leading it into the test chamber. The gas and water vapour tubes merged before entry into the chamber.

The concentration of CO was varied between 0 and 1000 ppm and the concentration of water vapour between 0 and 19·9% by volume (0 to 199 000 ppm). The percentage of water vapour was calculated on the basis of the amount of water consumed.

In studies with CO and water vapour simultaneously, the settings of the gas blender were the same as with dry gas. When humid gas was used, the concentration of CO at the same dial settings was lower due to the dilution by water vapour added to the gas flow.

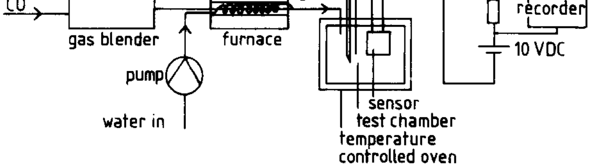

Fig. 1. Schematic diagram of the measuring system.

When the amount of water vapour was less than 10 vol.% of the total gas flow, the feed of water was pulsating, causing oscillations in the sensor response. In this case, the results were averaged over a longer period of time.

Four thick film gas sensors of the type tested earlier in actual exhaust gas measurements[11] and two commercial Taguchi gas sensors (TGS 812) were tested simultaneously. The TGS sensors were removed from their plastic cases and mounted on alumina substrates, having two gold stripes, with drops of fritless gold paste. In both sensor types SnO_2 was the basic gas-sensing material. In the TGS sensor the gas-sensitive layer of about 110 μm in thickness has been plated on a hollow alumina cylinder having two gold electrodes. According to EDS studies, the gas-sensitive layer also contains aluminium oxide and silicon dioxide. The purity of SnO_2 is not known and in EDS studies no metal catalysts have been observed. In the thick film sensors, gold was used as the electrode material. The gas-sensitive layer of about 30 μm in thickness which was fired at 950°C is composed of high purity SnO_2 mixed with 10 wt% of aluminium oxide and 3 wt% of silicon dioxide.

The drift in the conductance values of the thick film sensors appeared to be strong during the first ten days of the experimental period and the conductances decreased by 40% from the initial values. The measurements were carried out after this period of stabilization. No drift was observed in the conductance values of the TGS sensors. The results given in this study are those for one sensor of each group, and are typical of all the sensors of the group.

3 Results and Discussion

3.1 Sensitivity of the sensors to CO in dry gas

Sensitivities of the sensors to CO in dry gas were determined before water vapour was let into the test chamber. Results of these experiments are shown in Fig. 2 for the thick film and the TGS sensor at the temperatures of 350 and 500°C. G_{CO}/G_0 is the ratio of the conductances, G_{CO} and G_0, as measured in a gas containing CO and in the carrier gas alone, respectively. Thus, the value of the ordinate of each response curve is one when there is no CO in the gas.

As shown in Fig. 2, both the thick film sensor and the TGS sensor were more sensitive to CO at 350°C than at 500°C. A similar result has also been obtained by other researchers for SnO_2-based sensors.[13,14] The thick film sensors were more sensitive to CO than the TGS sensors at both

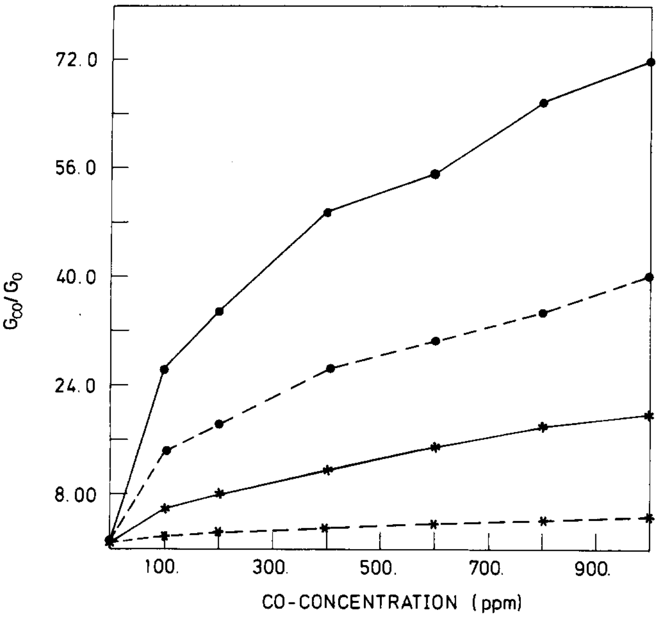

Fig. 2. The ratio of the conductance in a gas containing CO (G_{CO}) and a gas without (G_0) for the sensors at 350°C and at 500°C. *——, thick film sensor at 500°C; ●——, thick film sensor at 350°C; *- - -, TGS 812 sensor at 500°C; ●- - -, TGS 812 sensor at 350°C.

temperatures. The value of G_{CO}/G_0 was 20 for the thick film sensor and 5 for the TGS sensor at 500°C when the concentration of CO was 1000 ppm (Fig. 2).

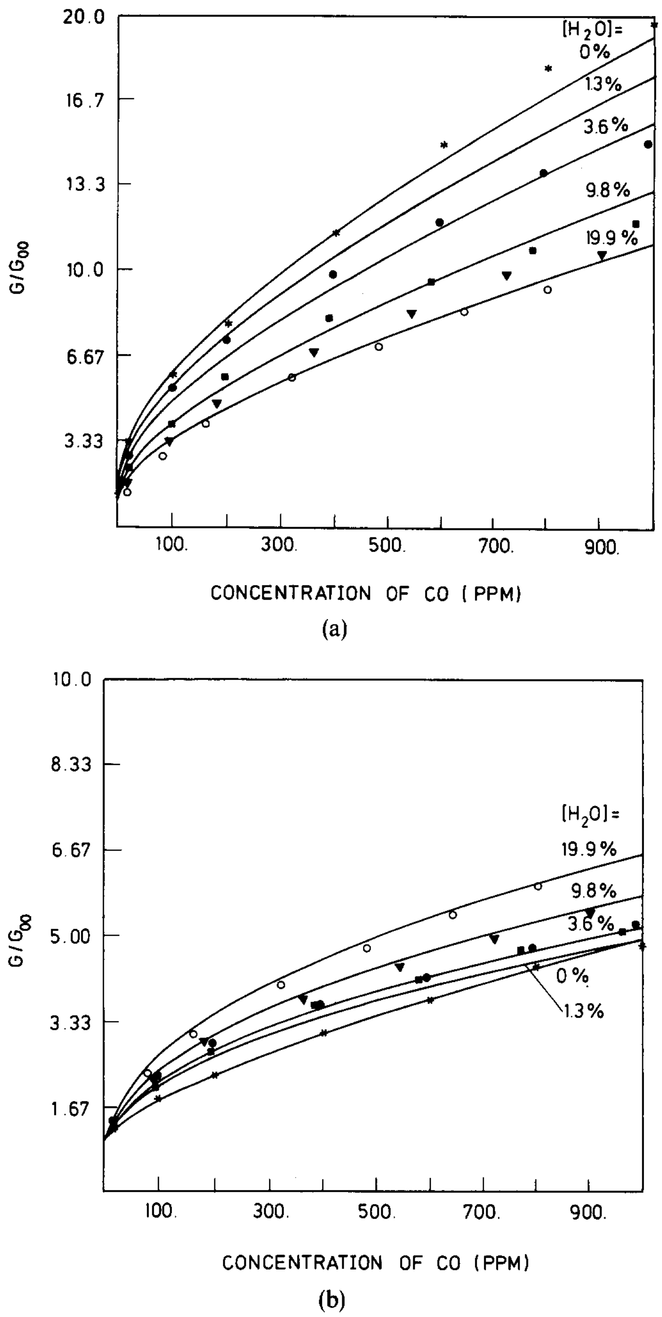

Fig. 3. The ratio of the conductance in a gas containing CO and water vapour (G) and water vapour alone (G_{00}) for (a) the thick film sensor and (b) the TGS 812 sensor, when the concentration of water vapour in the gas was 0%(*), 1·3%(●), 3·6%(■), 9·8%(▼) and 19·9%(○), at the temperature of 500°C. Curves were calculated by fitting experimental results of eqns (3a), (3b) and (4).

3.2 Sensitivity of the sensors to water vapour and CO

To examine the simultaneous effect of water vapour and CO on the conductance of semiconductor gas sensors, the results of the measurements carried out at 500°C are shown in Fig. 3(a) and (b) using normalized values of the conductance. The normalization was accomplished by dividing the value of the conductance, obtained with both CO and water vapour in the ambient atmosphere, by the value with the same concentration of water vapour but without CO. One interesting feature in these figures is that, for the TGS sensor, the conductance ratio increases slightly with increasing concentration of water vapour, whereas for the thick film sensor, this ratio decreases considerably. If eqn (2) is considered and G, measured in a gas containing both CO and water vapour, divided by G_{00}, measured in a gas containing only water vapour, an approximately constant value is obtained at each concentration of CO, irrespective of the concentration of water vapour. This is similar to the behaviour shown by the TGS sensor in Fig. 3(b). Thus, an approximately constant ratio G/G_{00} would be indicative of the synergistic effect of CO and water vapour on the conductance of a semiconductor gas sensor. Various expressions of the type shown by eqn (2) were fitted to the values of G/G_{00} obtained experimentally. The best fit was obtained with

$$G = G_0(1 + K_1[H_2O] + K_2[CO] + K_3[CO]^2 + K_4[H_2O][CO] + K_5[H_2O]^2[CO])^\beta \tag{3a}$$

and

$$G_{00} = G_0(1 + K_1[H_2O])^\beta \tag{3b}$$

In eqn (3a) the response behaviour in a dry gas is also included. In the fit, represented in Fig. 3(b) as solid lines, the following values were used for the parameters:

$K_1 = 0{\cdot}0093\ \text{ppm}^{-1}$
$K_2 = 0{\cdot}0323\ \text{ppm}^{-1}$
$K_3 = 2{\cdot}72 \times 10^{-5}\ \text{ppm}^{-2}$
$K_4 = 5{\cdot}0 \times 10^{-4}\ \text{ppm}^{-2}$
$K_5 = 3{\cdot}57 \times 10^{-9}\ \text{ppm}^{-3}$
$\beta = 0{\cdot}384$

The most significant difference between eqn (3a) and eqn (2) is the second-order term for water vapour concentration included in eqn (3a) and the lack of the synergistic second-order term for CO concentration.

In the case of the thick film sensor, a considerable decrease in the ratio G/G_{00} is seen to occur at increasing concentrations of water vapour. If eqn (2) is considered, it is possible to conclude that, in order to describe the response behaviour, the synergistic terms have to be omitted. Various expressions were thus fitted to the experimentally obtained values of G/G_{00} shown in Fig. 3(a). The best fit, in this case, was obtained with

$$G = G_0(1 + K_1[H_2O] + K_2[CO] + K_3[CO]^2)^{\beta} \qquad (4)$$

in which equation no synergistic effect between CO and water vapour is suggested. The fit shown in Fig. 3(a) as solid lines was obtained by employing the following parameter values:

$K_1 = 2{\cdot}38 \times 10^{-5}\ \text{ppm}^{-1}$
$K_2 = 1{\cdot}8726\ \text{ppm}^{-1}$
$K_3 = 7{\cdot}88 \times 10^{-3}\ \text{ppm}^{-2}$
$\beta = 0{\cdot}32$

Due to the levelling of the conductance at high concentrations of water vapour, the fit is not good in the whole range of concentrations of water vapour.

The data shown in Fig. 3(a) and (b) has been replotted in Fig. 4(a) and (b). The concentration of CO has now been taken as a parameter and the absolute humidity as a variable. To consider the effect of temperature similar graphs are shown in Fig. 5(a) and (b) for the thick film sensor and the TGS sensor at the temperatures of 300°C, respectively. The points shown were obtained by the interpolation of the experimental results. As can be seen from Fig. 4(a) and (b), the synergistic effect of CO and water vapour in the TGS sensor, as compared with the thick film sensor, appears as a stronger increase in the conductance as a function of absolute humidity. By comparing Fig. 5(a) with Fig. 4(a), and Fig. 5(b) with Fig. 4(b), it can be concluded that the synergistic effect also prevails in the TGS sensor at 300°C, whereas in the thick film sensor no such effect appears. The results of measurements carried out at 400°C were also in agreement with the above observation.

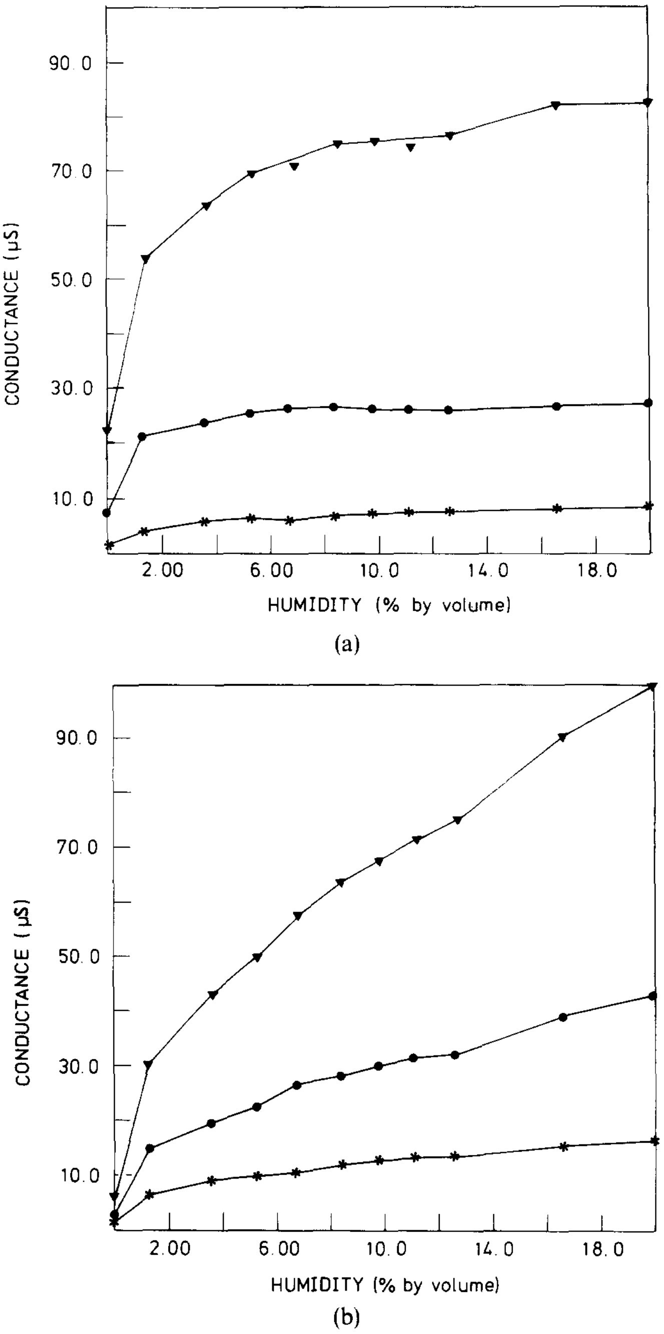

Fig. 4. The conductance response of (a) the thick film sensor and (b) the TGS 812 sensor to water vapour when the concentration of CO in the gas was 0 ppm (*), 110 ppm (●) and 800 ppm (▼), at the temperature of 500°C.

If, in Figs 4 and 5, the value of the conductance obtained at a certain concentration of water vapour and a certain concentration of CO is compared with the value at the same concentration of CO and the zero concentration of water vapour, it is seen that both sensors are more sensitive to water vapour at 300°C. The results of measurements carried out at 400°C were intermediate with respect to results of

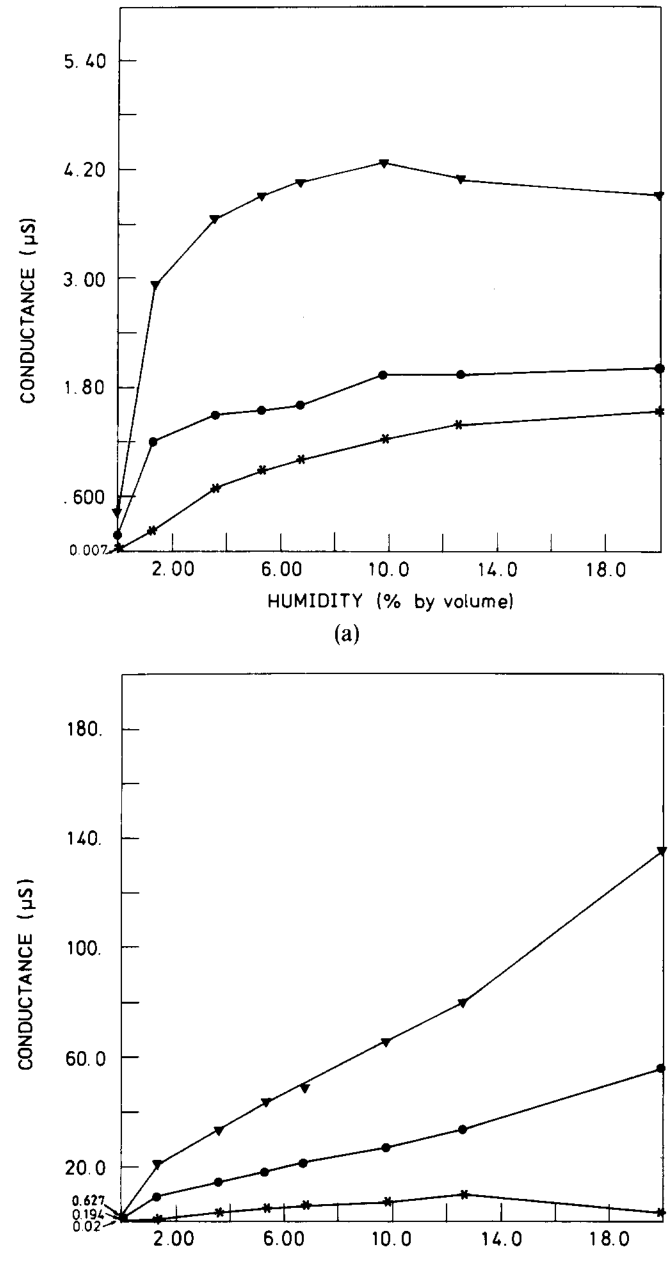

Fig. 5. The conductance response of (a) the thick film sensor and (b) the TGS 812 sensor to water vapour when the concentration of CO in the gas was 0 ppm (*), 100 ppm (●) and 800 ppm (▼), at the temperature of 300°C.

measurements carried out at 300 and 500°C. This would favour higher operating temperatures for the sensors. However, zero concentration of water vapour is never met in practical situations. For example, the saturated pressure of water vapour at −20°C corresponds to a concentration of 1000 ppm. In combustion gases the concentration of water vapour varies typically from a few percent to 20% by volume. As can be seen, for example from Fig. 4(a) and (b), in this range of concentrations, the thick film sensor is much less sensitive to the variation of the concentration of water vapour than the TGS sensor.

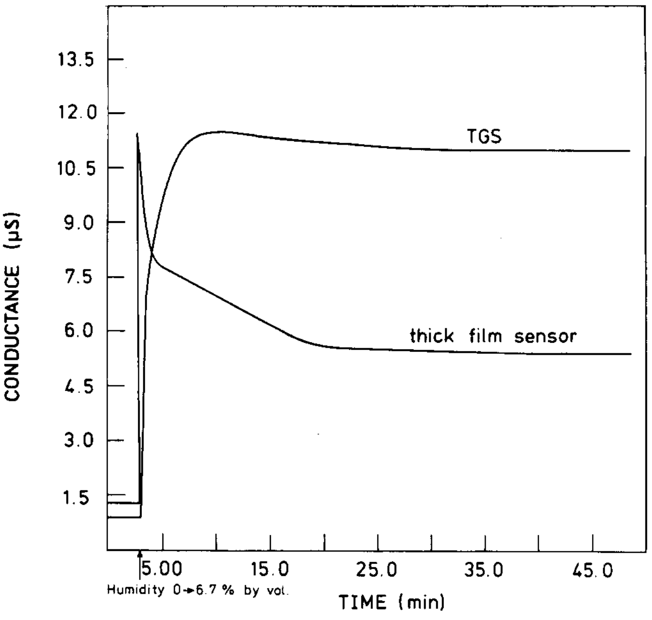

Fig. 6. The conductance response of the thick film sensor and the TGS 812 sensor when the concentration of water vapour was increased from 0 to 6·7% by volume.

Figure 6 shows the response time of the TGS and the thick film sensor obtained by increasing the concentration of water vapour from 0 to 6·7% by volume. In the response of the thick film sensor, a strong peak appears immediately after the change of the concentration of water vapour. The height of this peak is about two times the final value. In the TGS sensor, there is only a slight overshoot in the conductance after the addition of water vapour into dry gas. When more water vapour is added into humid gas, the conductances of both sensors increased smoothly without passing through any maximum values.

The recovery of the sensors after an exposure to a high concentration of water vapour was rather slow. At 500°C, 1 h after an experiment with humid gas, the response of the sensors to CO in dry gas was about 80% of the initial value. The response to CO recovered fully to the original magnitude in 24 h. The response times of the sensors were also longer in humid gas than in dry gas. They were approximately 50 and 10 s at 500°C in humid gas and dry gas, respectively, when the concentration of CO increased from 0 to 20 ppm. These times include the delay time related to the measuring system.

Besides the above difference in the behaviour of the thick film sensors and the TGS sensor used in this study some other differences have also been observed in the behaviour of these sensors. According to the interpretation of the results of Ref. 4, O-species occurring on the surfaces of the TGS sensor are missing from the thick film sensors. Also in measurements in which the temperature of the sensors is pulsed between a lower temperature of about 200°C and an upper temperature of about 400°C the behaviour of the TGS sensor differs from that shown by the thick film sensor. Possible reasons such as difference in the shape of the sensors and difference in their materials and microstructure are not yet well understood.

4 Conclusions

Commercial TGS 812 sensors and the thick film sensors made for the study were found to show different behaviour with respect to their CO response in the presence of high concentration of water vapour at temperatures ranging from 300 to 500°C. This difference in their behaviour could be fairly well described by allowing CO and water vapour to enhance the effect of each other in the TGS sensor, while omitting such description in the behaviour of the thick film sensors. This difference may be related to differences observed in some other measurements such as temperature-pulsed CO measurements. The reason leading to this difference are not yet well understood, however. Due to this lack of synergism in the thick film sensors they are less sensitive to the variation of water vapour content in CO measure than the TGS 812 sensors.

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