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Sensors and Actuators B 24-25 (1995) 491-494

SENSORS
AND
ACTUATORS
B
CHEMICAL

The effect of humidity on tin-oxide thick-film gas sensors in the presence of reducing and combustible gases

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Abstract

The effect of humidity on tin-oxide thick-film gas sensors has been studied in the case of carbon monoxide, methanol, butane and propane. The results are qualitatively explained under the assumption that water molecules dissociate on the tin-oxide surface and produce hydroxyl species capable of acting as electron donors. Moreover, palladium and vanadium when used as additives, affect the overall behaviour of sensors in the presence of water vapour. To reduce the effect of humidity, thin organometallic films have been deposited on top of thick tin-oxide-based sensors in order to act as filters. The results show that both the sensitivity of these sensors and the effect of humidity are decreased.

Keywords: Gas sensors; Humidity effects; Tin oxide; Thick films

1. Introduction

Water vapour is a constituent that is almost always present in situations in which information on the concentration of a specific gas is required. The concentration of water vapour can vary within wide limits, covering, for example, a range of more than two orders of magnitude in the ambient atmosphere. Similar to reducing gases, water vapour is known to increase the conductance of semiconductor gas sensors [1-4].

When chemisorbed on a tin-oxide surface, water molecules influence the conductivity in two ways. The first is that the molecules dissociate [2,5] into hydroxyl species, which act as electron donors. These electrons cause a direct increase in the sensor's conductivity. The second mechanism is that hydrogen atoms produced from the water molecule dissociation may react with oxygen lattice atoms by creating vacancies. These vacancies then diffuse to the bulk, where they act as electron donors. This mechanism has a larger time constant than the first one and reduces the tin-oxide surface. If this is true, one would expect that at low temperatures (i.e., about 200 °C), where the filling of oxygen vacancies is a very slow process, in an experiment on supplying and then removing water vapour, the sensor's resistance could not reach its initial value. This has been verified experimentally [5].

In the case of CO, the main mechanism that modifies the conductivity is the removal of chemisorbed oxygen atoms [2,6]. But in the case of hydrocarbons, like methane, propane and butane, the main mechanism is the production of hydrogen atoms by dissociation of the adsorbed molecule on lattice oxygen [2]. It is obvious that the longer the chain of the hydrocarbon, the easier the dissociation is. Finally, in the case of alcohols like ethanol, the main mechanism is similar to the water mechanism described above.

2. Experimental results and discussion

Tin-oxide-based thick-film gas sensors were fabricated according to a method similar to the one reported by Fuller and Warwick [6]. More precisely, SnO₂ was prepared from SnCl₄·5H₂O. An aqueous solution of SnCl₄·5H₂O was neutralized with an aqueous ammonium solution (25%). The resulting precipitate (stannic acid) was washed thoroughly with deionized water to remove Cl⁻ ions, dried at 100 °C for 24 h and then crushed in an agate mortar. The crushed powder was calcinated at 600 °C for 6 h and then crushed again for 1 h. In order to obtain the thick-film paste, an aqueous solution of organic binder was used. Finally, dopants were added producing pastes containing 1 wt.% palladium and past with 0.08 wt.% vanadium.

The sensor characterization set-up was designed to measure the steady-state and transient responses of the samples, testing them at different temperatures and under different ambient gases. The testing conditions are rigorously controlled via a fully automated computer-controlled system. All sensors have been characterized according to the following experimental procedure:

(i) The samples were heated to 450 °C and cooled back to 150 °C in zero-grade air. This step was repeated three times before starting film characterization, in order to clean water vapour remains from the samples.

(ii) The samples were heated to 450 °C in zero-grade air. Then the gas of interest was introduced into the chamber with a predefined concentration (i.e., 1000 ppm for CO, 1000 ppm for methane, 7000 ppm for butane and propane and 30 ppm for ethanol). The samples were cooled back to 150 °C.

Step (ii) is repeated in both wet and dry atmospheres. More precisely, it is repeated three times, once in zero-grade air, once with 22% relative humidity and finally with 60% relative humidity. During the forementioned measuring cycles, the resistance of the samples was recorded at 5 °C intervals as the samples were cooled from 450 to 150 °C. The cooling speed was 10 °C min⁻¹. Given that the response time of the thick-film sensors used is less than 5 s at temperatures above 250 °C as reported in Ref. [7], we believe that this cooling speed is adequate to ensure that no significant transient effects have been recorded, since in the time interval of 5 s, the temperature change is only 0.8 °C.

Fig. 1 shows the experimental results of the effect of humidity on the CO sensitivity. At temperatures below 300 °C the sensitivity to CO increases as the relative humidity is increased. The reason for this is that water vapour increases the electron concentration of tin oxide as explained in section 1. Thus, the oxygen adatoms are increased [3]. Since CO is sensed by the

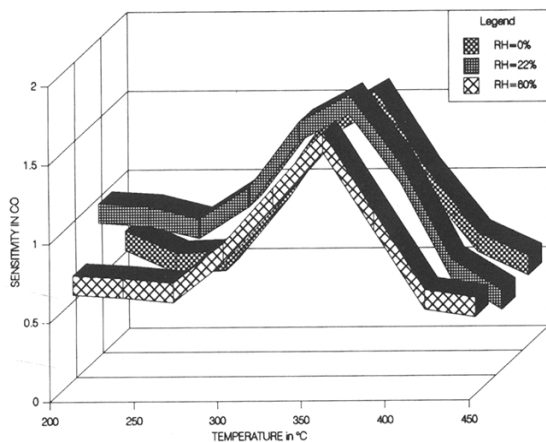


Fig. 1. Sensitivity in CO under different levels of relative humidity vs. temperature.

removal of these adatoms, the higher the amount of these adatoms, the higher the sensitivity is. On further increasing the relative humidity, the sensitivity starts to decrease. This behaviour is due to a synergetic effect between CO and water vapour, according to which adsorbed hydroxyl species may react with CO forming formate species ($-\text{COOH}^-$), as has been explained in detail elsewhere [4].

However, the effect of humidity on the CO sensitivity is negligible at temperatures where the maximum sensitivity has been recorded.

In Fig. 2, the interference of water vapour in the case of hydrocarbons is shown. In Fig. 2(a) the change in sensitivity under different levels of relative humidity in butane is shown; the behaviour in propane is almost identical to that in butane.

The fast decrease in sensitivity with increasing water vapour concentration can be explained by the reduction of the tin-oxide surface caused by water molecules, which decreases the butane and propane dissociation rates given that the active site (oxygen lattice atoms) density has been decreased.

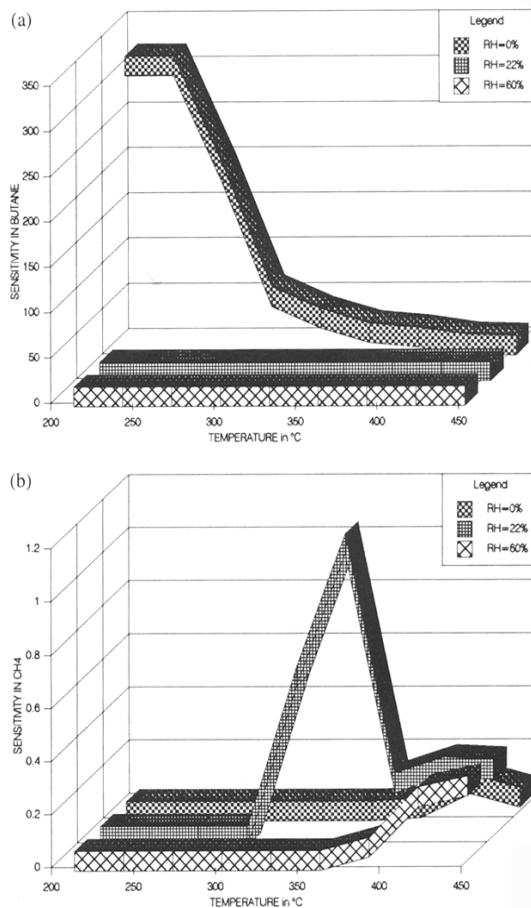


Fig. 2. Experimental results for the sensitivity in butane (a) and methane (b) under different levels of relative humidity vs. temperature.

Antithetically, in the case of methane, as shown in Fig. 2(b), the effect of humidity seems random. This is because, at the temperatures under consideration, the dissociation rate of methane is lower than those of propane and butane.

In the case of ethanol, the experimental results are shown in Fig. 3. Here a similar behaviour to that in CO is observed, but the mechanism is different. Initially, the increase of electron concentration caused by water molecules helps the dissociation of ethanol and thus increases the sensitivity. This is attributed to the increase of oxygen vacancies due to the presence of water, which makes tin atoms more attractive to ethanol [2]. As the relative humidity increases, the contribution of water molecules to the conductivity of the tin-oxide film (through the hydrogen atoms attached to oxygen lattice atoms) is greater than that of ethanol and consequently the ethanol sensitivity decreases. However, the exact mechanisms are not known and further investigations are required.

In Fig. 4, the experimental results for three different samples, one pure tin oxide, a second doped with palladium and a third one doped with vanadium, are shown. The interference is plotted for different levels of relative humidity at the temperature of the maximum sensitivity. We define interference here as the change in sensitivity caused by the presence of water vapour over the sensitivity in dry air. It is clear from the Figure that palladium decreases the interference compared to the pure tin-oxide film. On the other hand, vanadium seems to decrease drastically the effect of water vapour in the case of ethanol, but has no effect in the case of methane.

Finally, a method is proposed that can decrease the effect of water vapour in tin-oxide-based gas sensors. A thin metallorganic film is deposited over the thick-film gas sensor. The paste consists of an active material and a thickening agent. The active material is prepared

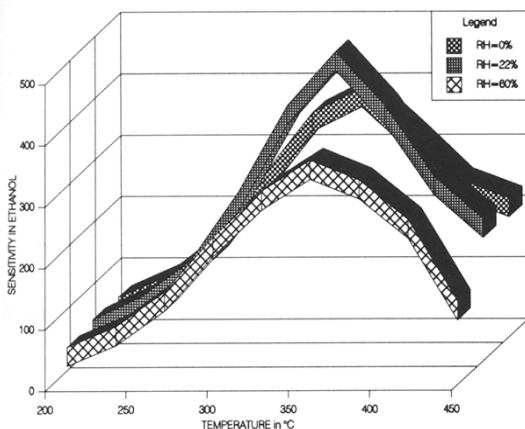


Fig. 3. Experimental for the sensitivity in ethanol under different levels of relative humidity vs. temperature.

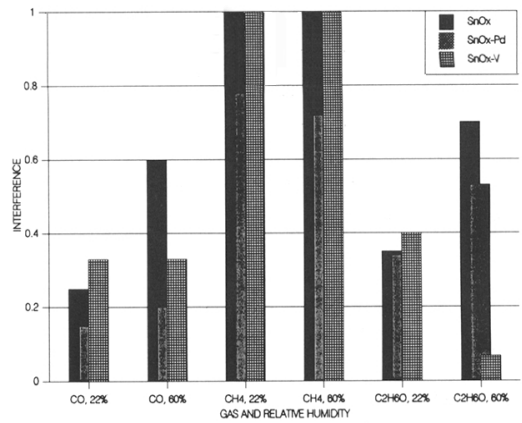


Fig. 4. Experimental results for the interference of water vapour in the case of three samples, one pure tin oxide, one doped with Pd 1 wt.% and one doped with V 0.08 wt.%.

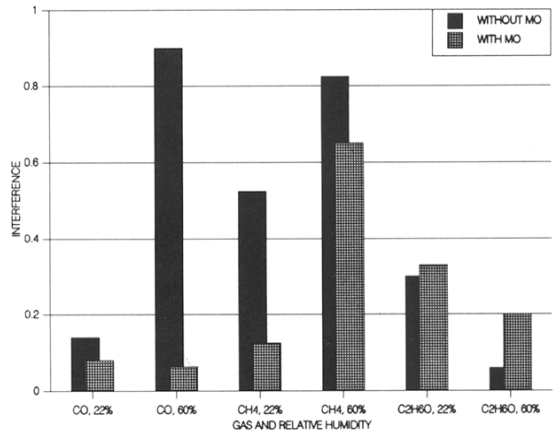


Fig. 5. Experimental results showing the water vapour interference in simple thick films and in a thick film with a thin metallorganic film deposited over it.

starting from tin(II) 2-ethylhexanoate. Mixing with a polymer solution of ethylhexyl alcohol results in a paste with a viscosity of approximately 30 Pa s, which is stable up to 4% Sn. After studying the films printed from this paste, it was found that they have very small conductivity and almost negligible sensitivity to most gases of interest. Thus, on printing these pastes over the thick film, the sensing material remains the same. But these thin films may act as filters to some gases. In Fig. 5, the experimental results from these devices are compared to those for simple thick-film sensors. In the case of both CO and methane, it seems that a very significant decrease of interference is obtained. But in the case of ethanol, the interference is increased. This may be caused by the similar mechanisms of ethanol and water vapour, as mentioned in Section 1.

3. Conclusions

The effect of humidity on the sensitivity of the sensors studied depends on the amount of water vapour in the air, the type of gas analyte and the type of dopant introduced in the thick-film gas sensor.

Moreover, the incorporation of a metallorganic filter by screen printing on the top of the tin-oxide thick film dramatically reduces the humidity effect in the case of carbon monoxide.

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