Transient effects of tin oxide CO sensors in the presence of water vapor

D. S. Vlachos, P. D. Skafidas and J. N. Avaritsiotis

View Online   Export Citation

ARTICLES YOU MAY BE INTERESTED IN

Chemiresistive gas sensors employing solution-processed metal oxide quantum dot films
Applied Physics Letters **105**, 163104 (2014); https://doi.org/10.1063/1.4900405

Room-temperature semiconductor gas sensor based on nonstoichiometric tungsten oxide nanorod film
Applied Physics Letters **86**, 213105 (2005); https://doi.org/10.1063/1.1929872

Fabrication and ethanol sensing characteristics of ZnO nanowire gas sensors
Applied Physics Letters **84**, 3654 (2004); https://doi.org/10.1063/1.1738932

Transient effects of tin oxide CO sensors in the presence of water vapor

D. S. Vlachos, P. D. Skafidas, and J. N. Avaritsiotis
National Technical University of Athens, Electrical Engineering Department, Division of Computer Engineering, 157 73 Zographou, Athens, Greece

During the experimental study of CO sensitivity of SnO_2 resistive-type gas sensors in the presence of water vapor, a transient effect was observed which elucidates the CO sensing mechanism in tin oxide. More precisely, after the removal of CO, an increase of the measured conductance was observed, depending on substrate temperature. An explanation of this phenomenon is proposed, which is based on the conductance modulation due to three different mechanisms: Formate desorption, occupation of lattice sites by oxygen molecules, and diffusion of lattice oxygen vacancies to sensor's bulk.

Tin dioxide based thick film gas sensors for CO were printed with dimensions 3×3 cm^2, from thick film pastes which were produced according to a similar method reported by Fuller and Warwick.[1] These sensors showed *n*-type conductivity.[2] Annealing for one week at 600 °C was required in order to make their response reproducible and stable.

All sensors have been tested according to the following experimental procedure:

(a) The temperature of DUTs was raised at 350 °C and it was kept at this level for about an hour.

(b) The temperature was decreased to the required level for the experiment and it was kept there for one hour before water vapor was introduced into the chamber.

(c) Water vapor was introduced in a controllable manner by adjusting the zero grade air flow through a bubbler.

(d) CO was introduced into the chamber when a humidity sensor was giving a stable reading.

All experiments were made with CO at 1000 ppm and zero grade air in a continuous total flow of 300 ml/min in a chamber of about 920 cm^3 with the method described above, and results like the ones showed in Fig. 1 were obtained. From these, it is apparent that undershoot of the resistance in the presence of 40% relative humidity after the removal of CO is typical in these samples. Figure 1 also shows the response of the same samples at different substrates temperatures, where the undershoot is eliminated with increasing temperature.

It is well established that oxygen chemisorption on the tin oxide surface may have an enormous effect on electrical conductivity. This is caused by the acceptorlike nature of oxygen adatoms on an *n*-type adsorbent,[3] like tin oxide. The charge transfer from surface to oxygen adatoms produces a depletion layer, which is very efficient near the grain boundaries.[3,4] Moreover, surface oxygen vacancies may be filled by adsorbed oxygen atoms which decreases the conductivity.[4]

Reducing gases have been found to react with oxygen species on the tin oxide surface with a rate which is a function of the structure of the surface, the temperature, and the nature of the reacting species. In the case of CO, it has been found that the reaction rate with adsorbed oxygen molecules at the surface is at least one order of magnitude smaller than with oxygen adatoms.[5] The aforementioned two reactions immediately cause an increase of sensor's conductivity by charge transfer.

However, in the case of oxygen lattice atoms, CO reacts with them, creating vacancies which do not affect the conductivity. A theoretical model[6] has been proposed assuming that these vacancies act as donors, only after their diffusion into the bulk. This is a very slow mechanism for two reasons: First because the reaction of CO with lattice oxygen is slow[4] and second because there is a time delay before these vacancies act as electron donors.

The presence of water vapor may dominate the behavior of tin oxide based sensors.[3,4,7] Water molecules are physisorbed and they reduce the active sites on surface, or they may dissociate giving hydroxyl species,[4] which may create oxygen vacancies. Introducing CO intermediates, like formate species, are formed, which modify the sensitivity and the response time of the sensor. Moreover, the desorption of these intermediates affect the conductivity. Formate has been found to desorb, giving CO_2 and H_2.[4] Thus, the removal of hydrogen atoms from the surface decrease the conductivity. This is caused because hydrogen atoms act as electrons donors. On the other hand, there is no evidence that formate species act as electron acceptors.[4] So, formate alters the conductance of the sensor only when it desorbs, inducing a decrease of conductivity.
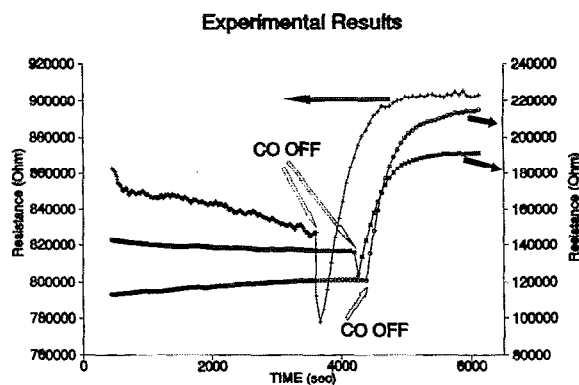
Experimental Results

FIG. 1. Experimental results showing the undershoot of the measured resistance in the presence of 40% relative humidity after CO removal for different substrate temperatures. Two axes were used with same length in order to compare the undershoots. + 150 °C (referred to left axis), * 250 °C, and O 300 °C (referred to right axis).

The aforementioned three different mechanisms that affect sensor conductance in the presence of CO and water vapor are considered to have an exponential time dependence and a corresponding time constant. When CO is switched off, the adsorption of oxygen atoms is a two stage reaction:

$$O_{2gas} + S + e^- \rightarrow O_{2s}^- + S + e^- \rightarrow 2O_s^- \qquad (1)$$
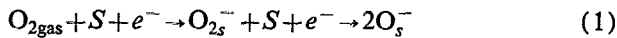
with a time constant τ_1.

Although CO has been turned off, the remaining vacancies still contribute to sensor's resistance with a time constant τ_2. This is the time constant of diffusion of lattice oxygen vacancies to the bulk, which depends strongly on temperature.

The remaining formate species are desorbed very fast giving a time constant τ_3 according to reaction (2). So, the transient sensor resistance after CO removal may be

$$S\text{-COOH} + H^+ + e^- \rightarrow S + CO_2 + H_2 \qquad (2)$$
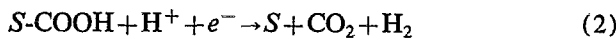
given by

$$R = R_0 - R_1 \exp(-t/\tau_1) - R_2 \exp(-t/\tau_2)$$

$$+ R_3 \exp(-t/\tau_3), \qquad (3)$$

where R_1, R_2, and R_3 are the steady-state contributions of the aforementioned mechanisms, which are considered to be of the same order of magnitude.

Figure 2(a) shows the calculated resistance, using Eq. (3), after CO removal, with $\tau_2 \gg \tau_1$ and $\tau_2 \gg \tau_3$. It is clear from this figure that the undershoot of the resistance is caused solely by oxygen vacancies. More specifically, although both formate and chemisorbed oxygen mechanisms are ceased soon after CO removal, oxygen vacancies continue to contribute to the conductivity during their diffusion to the bulk, because $\tau_2 \gg \tau_1$ and τ_3. Increasing the sensor temperature, the time constant τ_2 of the diffusion is expected to decrease and thus the undershoot is eliminated, as shown in Fig. 2(b), where the resistance is calculated assuming that the oxygen vacancies diffusion time constant ($> \tau_2$) is of the same order of magnitude as the time constants of the other two reactions (τ_1 and τ_3).

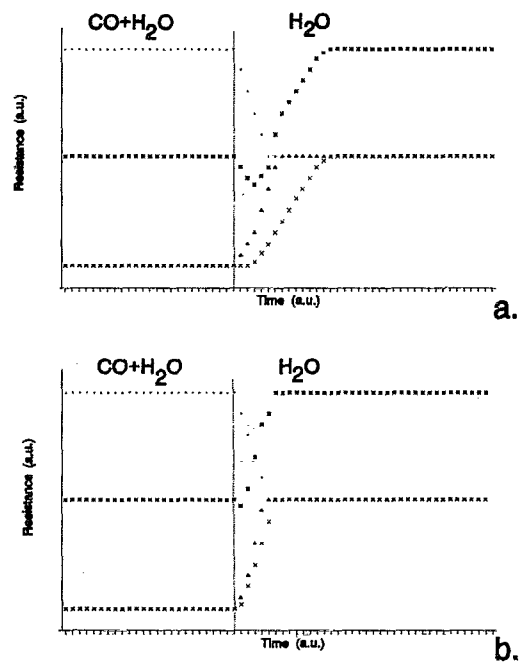Concluding, it has been shown that after CO removal in a humid ambient, the positive contribution of the for-

FIG. 2. Theoretical results showing the sensor's resistance with the different contributions in low (a) and high (b) temperature. * is the calculated resistance, ■ contribution from formate desorption, ▲ contribution from oxygen chemisorption, and x contribution from oxygen vacancies.

mate species is ceasing very fast and the contribution of oxygen vacancies may produce an undershoot of the sensor's resistance. These results support the assumption made by other researchers that oxygen vacancies at the surface of tin oxide do not act as electron donors unless they diffuse into the bulk.

[1] M. J. Fuller and M. E. Warwick, J. Catalysis 29, 441 (1973).
[2] N. Barsan and R. Ionescu, Sensors and Actuators B 12, 71 (1993).
[3] P. T. Moseley, J. O. W. Norris, and D. E. Williams, in Techniques and Mechanisms in Gas Sensing (IOP, Bristol, 1991).
[4] D. Kohl, Sensors and Actuators 18, 71 (1989).
[5] V. Lantto and P. Romppainen, Surf. Sci. 192, 243 (1987).
[6] S. Munnix and M. Schmeits, J. Vac. Sci. Technol. A 5, 910 (1987).
[7] J. Tamaki, M. Nagaishi, Y. Teraoka, N. Miura, and N. Yamazoe, Surf. Sci. 221, 183 (1989).