

A Comparative Study of Tin and Indium Oxide Gas Sensors Based on Seebeck Effect

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A comparative study on the response of tin and indium oxide thin sputtered films to different reducing gases is presented. The operation of the sensors is based on the Seebeck effect. Platinum has been deposited on half of the films; thus as the rates of gas reaction on the two halves of the films are expected to be different (inducing a temperature gradient), a Seebeck voltage is developed as the response signal. Different responses experimentally observed for tin and indium oxide sensors are qualitatively explained with the aid of the well established theory of chemisorption of reducing gases on metal oxides and the different electronic properties of tin and indium oxide films. The target gases used were 2000 ppm CO, 10,000 ppm CH₄ and 26 ppm C₂H₅OH diluted in zero-grade air (ZGA).

1. Introduction

Thermal sensors based on the Seebeck effect have been studied^(1,2) and Seebeck coefficients of a variety of metals and semiconductors have been investigated by several researchers.⁽³⁻⁵⁾ Additionally, tin oxide pellets have been used in the past in the fabrication of hydrogen sensitive sensors based on the Seebeck effect.⁽⁶⁾ The behavior of tin oxide reactively sputtered thin films doped with palladium or platinum on half of their surface has been studied in a previous paper.⁽⁷⁾

In this work, simple structures composed of tin and indium oxide reactively sputtered thin films, surface-doped with platinum (on half of their surface) have been considered for sensing CO, CH₄ and C₂H₅OH. It is known^(8,9) that the addition of noble metals as catalysts on the surface of metal-oxide semiconductors has a large influence on the chemisorption

kinetics of reducing gases on their surface. Relying on the difference in the chemisorption behaviors of the plain and the covered film, a Seebeck voltage is expected to appear at the two halves of the film when it is exposed to ambient air. This would happen because oxygen from the atmosphere adsorbs on the film and the heat of adsorption on the two halves of the film is expected to be different due to the catalytic activity of the noble metal. The positive terminal of the sensor is the "hot" half and the negative one the "cold" half (n-type semiconductors). For example, if platinum acts catalytically during oxygen adsorption, the half with platinum must be the positive terminal. If the sensor is exposed to another reacting gas, this Seebeck voltage is expected to change. This voltage change provides an electrical signal related to gas composition.

2. Materials and Methods

SnO_x and InO_x films were deposited by reactive magnetron sputtering on alumina (96%) substrates with an area of 12×26 mm. Oxygen flow during sputtering was controlled using a plasma emission monitoring apparatus, which provided controllable stoichiometry of the deposited film and reproducible films. Oxide thickness was 1,000 nm after a 10-min sputtering time. Platinum was electron-beam evaporated at ambient temperature on half of the film to an average thickness of 5–8 nm. Gold contacts were subsequently thermally evaporated on the two edges of the substrate. The structure of the sensors is shown in Fig. 1.

A sensor characterization setup was designed to measure the steady-state and transient response voltage of the sensors, testing them at a constant temperature (provided by an external heater) and in the presence of different gases. Sensors were tested at 2,000 ppm CO, 10,000 ppm CH_4 and 26 ppm $\text{C}_2\text{H}_5\text{OH}$ diluted in zero-grade air (ZGA). The sensors were kept at an elevated temperature using an external heater, in order for the chemisorption reactions necessary for sensor operation to take place.

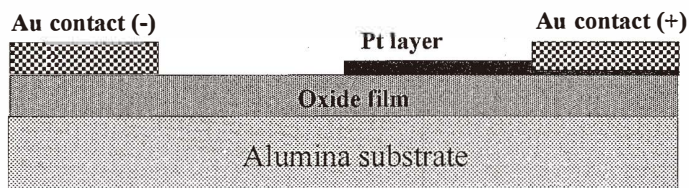


Fig. 1. Sensor architecture.

3. Experimental Results and Discussion

Figure 2 shows the response of the platinum-doped tin oxide sensor to CO, CH₄ and C₂H₅OH. The sensor was kept at 400°C ($\pm 0.1^\circ\text{C}$) during the measurements. Figure 3 shows the response of the platinum-doped InO_x sensor to the same test gases. The sensor was kept at 330°C ($\pm 0.1^\circ\text{C}$) during the measurements. Sensors must operate at elevated temperatures, in order for the test gases (especially CH₄) to dissociate on the sensor surface. The tin oxide sensor was operated at a higher temperature than the indium oxide one because of its higher resistivity, which leads to unreliable results. Note that in the absence of a reducing gas (in ZGA), a voltage of 4–5 millivolts is present (tin oxide sensor, Fig. 2), due to the different oxygen adsorption rates on the two halves. This voltage increases in the presence of reducing gases. A positive voltage denotes that the half doped with platinum is the hot one.

When a semiconductor is exposed to a temperature gradient, the free carrier (electron in the case of n-type material) concentration is increased at the hot half rather than at the cold one. Using a solid-state physics approach, when a temperature gradient δT is present the Fermi energy of the semiconductor (proportional to the carrier density) exhibits a constant slope from the hot to the cold half and a voltage difference appears at the two halves of the semiconductor. For an n-type semiconductor the hot half is the positive terminal while the cold one is the negative terminal (the polarity is reversed in the case of p-type material).

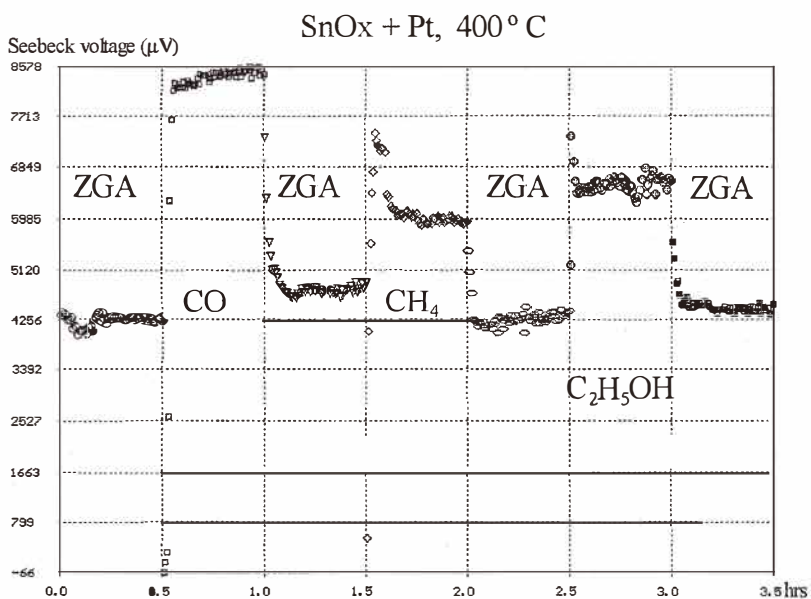


Fig. 2. Seebeck voltage of the SnO_x sensor doped with platinum at half its surface, kept at around 400°C.

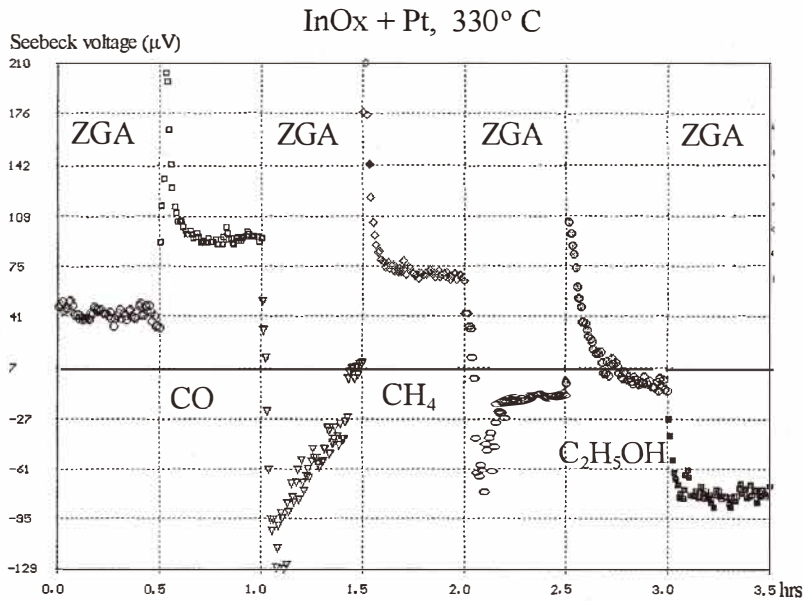


Fig. 3. Seebeck voltage of an InO_x sensor doped with platinum at half its surface, kept at around 330°C.

This voltage is called Seebeck voltage (from the name of its discoverer) and is proportional to the temperature gradient according to eq. (1):

$$\delta V = \alpha_s \delta T \quad (1)$$

where α_s is the Seebeck coefficient expressed in V/K and depends on the material properties and on temperature. The Seebeck coefficient may be expressed as a function of film resistivity, ρ , only, according to the following relation:⁽¹⁾

$$\alpha_s = \frac{mk}{q} \ln \left(\frac{\rho}{\rho_0} \right) \quad (2)$$

where k is the Boltzmann constant, $m \approx 2.6$ and $\rho_0 \approx 5 \cdot 10^{-6} \Omega \cdot m$. (Ref. 1 gives a thorough mathematical treatment.)

Considering the structure of our sensors which is shown in Fig. 1, a temperature gradient between the two halves of the semiconducting film is created due to the different rates of gas chemisorption imposed by the catalytic layer present on half of the film. The edge of the films covered with the catalyst is connected to the positive terminal of the

voltmeter; thus a voltage increase (with respect to the Seebeck voltage measured in the presence of air) means that the catalytic layer increases the combustion rate of the target gas. Conversely the catalytic layer decreases the combustion rate (or the heat of adsorption) of the target gas, with respect to the combustion rate in the absence of the catalyst.

The response of the tin oxide sensor to target gases is shown in Fig. 2, while the response of the indium oxide sensor is shown in Fig. 3. The sensors exhibit interesting transient responses in the case of CO, CH₄ and C₂H₅OH. Note that tin and indium oxide sensors exhibit different transient responses. Note also that different transient responses were observed in the case of CO, CH₄ and C₂H₅OH. These experimental results are explained in the following section.

Platinum has a work function of 5.2 eV, while the electron affinities of tin and indium oxide are 4.8 and 4.45 eV, respectively.⁽¹⁰⁾ As a consequence, a band bending of around 0.4 eV is expected to induce a depletion layer at the part of the tin oxide film covered with platinum, thus resulting in a markedly low concentration of free electrons. The depth of the depletion layer (at the surface of each grain) at the side of the film covered with platinum depends on the free electron concentration of the semiconductor. In the case of the indium oxide film, which has a considerably higher free electron concentration than the tin oxide film, the depletion width is expected to be lower,⁽¹⁰⁾ although it is induced from a higher band bending (0.75 eV). On the other hand, free electrons are needed for oxygen adsorption and formation of oxygen adatoms (O₂⁻ or O⁻); the availability of surface oxygen adatoms favors the adsorption of reducing gases which react with oxygen.⁽¹¹⁾ Reaction of reducing gases with surface oxygen species is expected to provide transient effects until the concentration of this species decreases to a threshold, under which this mechanism becomes secondary.

The tin oxide sensor with platinum has a high sensitivity to CO (see Fig. 2). However, for the first few minutes in which the sensor is exposed to CO, a negative Seebeck voltage is observed implying that the part of the tin oxide film not covered with platinum is the active part. This can be explained if we accept the fact that CO reacts with surface oxygen ions present at a considerably high concentration at the part of the film not covered with platinum. In other words, tin oxide grains at the half of the film covered with platinum are severely depleted of free electrons and, as a consequence, oxygen species cannot be adsorbed at a significant concentration, preventing CO adsorption.

This transient behavior was not observed in the case of the indium oxide sensor (Fig. 3). This can be attributed to the fact that the free carrier density of indium oxide is considerably higher than that of tin oxide. Thus indium oxide grains in the part of the film covered with platinum are depleted of free electrons at a smaller degree, which permits the significant adsorption of oxygen species on the surface. An increase in the concentration of this species enables the reaction with CO to proceed, which prevents the appearance of the transient effects observed in the case of the tin oxide sensor. An overshoot of the Seebeck voltage for the first four minutes (recall that the time interval between consecutive Seebeck voltage measurements in Figs. 2 and 3 is 30 s) after CO introduction in the measuring chamber can be explained by assuming that some time is required for the film resistance to decrease after exposure to CO. During the time interval that the film exhibits a high resistance, a large Seebeck coefficient (eq. (2)) results in a high Seebeck voltage. Note that

this behavior is not observed in the case of the tin oxide sensor, probably because transient effects due to CO in the case of SnO_x films have a relatively shorter response time (recall the lower availability of surface oxygen species attributed to lower electron availability).

The above discussion attempts to explain the different temperature gradients obtained for tin and indium oxide sensors. However film resistivity has a large influence on the Seebeck coefficient (eq. (2)). Since the base resistivity of tin oxide is several orders of magnitude higher than that of indium oxide, Seebeck voltages at least one order of magnitude higher were obtained for the tin oxide sensor.

Analogous transient effects were recorded during the exposure of the tin oxide sensor to CH₄, which can be explained based on the same assumption as that in the case of CO. However, an overshoot of the Seebeck voltage was observed. Recall that according to eq. (2) the Seebeck voltage depends on semiconductor resistance and is expected to decrease when film resistance decreases. At 400°C, after surface oxygen species are removed, CH₄ reacts with surface lattice oxygen atoms. The surface oxygen vacancies produced need some time to diffuse to the bulk and to decrease film resistance. During this time the Seebeck voltage is increased, as shown in Fig. 2.

The negative transient Seebeck voltage attributed to the lower availability of oxygen species at the half of the film covered with platinum (than the one at the half of the film not covered with platinum), has not been observed during the exposure of the indium oxide sensor to CH₄ (Fig. 3). This happens for the same reason as that in the case of CO (i.e., high electron concentration). However, the voltage overshoot after CH₄ introduction, which lasts about two minutes, can be again attributed to the high initial resistance of the sensor, which seems to decrease rapidly in the presence of CH₄, compared to CO.

Ethanol reacts rapidly with tin and indium oxide surfaces, producing oxygen vacancies.⁽¹¹⁾ The transient behavior of the sensors in the presence of C₂H₅OH can be attributed to the increased resistance of the film before the oxygen vacancies produced diffuse to the bulk, in order to act as donors. After oxygen vacancies have diffused to the bulk and film resistance has decreased, according to eq. (2) the Seebeck voltage decreases (Figs. 2 and 3).

It is interesting to note the recovery behavior of the indium oxide sensor in the presence of ZGA, after the removal of CO, CH₄ or C₂H₅OH. An undershoot of the Seebeck voltage was observed, which may be attributed to the low resistance of the film due to exposure to the reducing gas. However, as the resistance of the film increases slowly due to oxygen adsorption, the Seebeck voltage also increases (eq. (2)). Note the large recovery time after CO removal compared to that after CH₄ removal. At 330°C, CO removes oxygen lattice atoms, while CH₄ does not. Oxygen species adsorbed on the film surface need some time to diffuse to the bulk and replenish lattice sites, resulting in a long recovery time. On the other hand, since CH₄ does not produce lattice oxygen vacancies at low temperatures,⁽¹¹⁾ a short recovery time is observed because the resistance of the film increases quickly. Exposure to C₂H₅OH results in surface reduction and the resistance of the film does not return to its initial value.⁽¹¹⁾ Figure 3 shows that the Seebeck voltage after C₂H₅OH removal is slightly lower than that before the sensor was exposed to C₂H₅OH.

Negative voltage values are observed in Fig. 3 in the presence of ZGA. This result is misleading because the Seebeck voltages of the two junctions of the sensor to the metal wires connecting it to the multimeter should be taken into account. A temperature

difference δT between these two junctions produces a small voltage, negligible in the case of the tin oxide sensor. However, since the Seebeck voltage of the indium oxide sensor is very small (in the range of μV), the Seebeck voltage due to the electrical connections of the sensor with the voltmeter is not negligible, producing an offset.

4. Conclusions

Tin oxide and indium oxide thin films doped at half of their surface with an ultrathin platinum layer have been evaluated as sensors for reducing and combustible gases. The Seebeck voltage produced in the presence of different gases has been considered as the output signal of the sensors. Both tin and indium oxide films doped with platinum were found to be very sensitive to most test gases. Interesting transient effects observed have been explained taking into account the well established reactions⁽¹¹⁾ occurring at the surface of tin and indium oxide films in the presence of CO, CH₄ and C₂H₅OH. Differences in the responses of tin and indium oxide sensors have been qualitatively explained taking into account the markedly low resistivity of indium oxide.

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