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A new planar device based on Seebeck effect for gas sensing applications

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Abstract

A new planar sensor structure has been developed, which takes advantage of the differential temperature appearing between the two halves of a tin or an indium oxide film, one half of which is covered with a catalyst, in the presence of a combustible gas. Since the rates of reaction of the combustible gas on the two halves of the film are expected to be different, different amounts of heat are delivered at the two halves of the film, resulting in a temperature gradient across the film. According to the Seebeck effect, this temperature gradient produces a voltage difference at the two edges of the film. Different Seebeck voltage values have been recorded when the structure is exposed to various gases, due to the different heat of adsorption or combustion delivered from each gas at the two portions of the film.

Keywords: Seebeck effect; Gas sensing; Planar structure

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 [3–5]. Additionally, tin oxide pellets have been used in the past to successfully provide hydrogen sensitive sensors based on the Seebeck effect [6].

In this work, simple structures using tin and indium oxide reactively sputtered thin films, surface-doped with palladium or platinum (on the half of their surface) have been considered for sensing CO, CH₄ and C₂H₅OH. It is known [7,8] 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 differential chemisorption behaviour of the plain and the covered with a noble metal portions of a film, a Seebeck voltage is expected to appear at the two edges 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 portions of the film is expected to be different due to the catalytic activity of the noble metal. The posi-

tive terminal of the sensor is the 'hot' edge and the negative the 'cold' edge. For example, if platinum is deposited on the half of the film and platinum acts catalytically for oxygen adsorption, the edge with platinum must be the positive terminal. Now, if the sensor is exposed to concentrations of another reacting gas, this Seebeck voltage is expected to change. This voltage change provides an electrical signal related to gas composition.

2. Experimental techniques

SnO_x and InO_x films were deposited with reactive magnetron sputtering on alumina (96%) substrates with dimensions 12 × 26 mm. Oxygen flow during sputtering was controlled with a plasma emission monitoring apparatus, providing controllable stoichiometry of the deposited film and reproducible films. Oxide thickness was 1000 nm after a 10 min sputtering time. Palladium or platinum was electron-beam evaporated at ambient temperature on the half of the film with an average thickness of a few nanometers. Gold contacts were subsequently thermally evaporated on the two edges of the substrate. It is known that ultra thin evaporated metal films are discontinuous, consisting of discrete islands (clusters), with average dimension around 3–8 nm [9]. The structure of the sensors is shown in Fig. 1.

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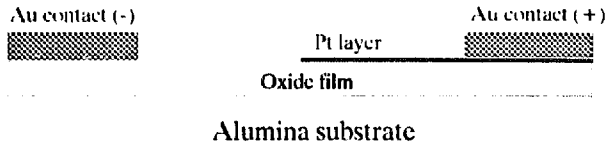


Fig. 1. Sensor architecture.

The sensor characterization setup was designed to measure the steady-state and transient response voltage of the sensors, testing them at constant temperature (provided by an external heater) and under different gases. Sensors were tested at 2000 ppm CO, 10 000 ppm CH₄ and 26 ppm C₂H₅OH diluted in zero grade air (ZGA, artificial, purified mixture of 80% nitrogen and 20% oxygen).

3. Experimental results and discussion

Palladium covered sensors, either tin or indium oxide based, did not show remarkable sensitivity to any of the test gases. On the contrary, platinum covered sensors exhibit remarkable responses to most test gases. Fig. 2 shows the response of a platinum covered tin oxide sensor to CO, CH₄ and C₂H₅OH, at 360°C. Note that in the absence of a reducing gas (in zero grade air) a voltage of a few millivolts is present, due to the different oxygen adsorption rates on the two halves. This voltage increases in the presence of reducing gases. Fig. 3 shows the response of the same sensor at 390°C. It is interesting to compare the responses to CO and CH₄ with the corresponding responses of Fig. 2. The positive voltage denotes that the edge doped with platinum is the hot terminal.

Fig. 4 shows the response of a platinum doped InO_x sensor to the same test gases. Note the different behaviour of the transient response in the presence of butane and propane. The sensor was kept at 330°C during the measurements.

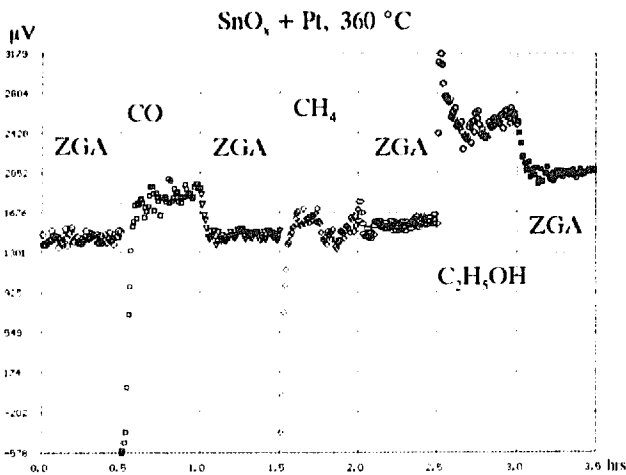


Fig. 2. Seebeck voltage of an SnO_x sensor doped with platinum at its half surface, kept at around 360°C.

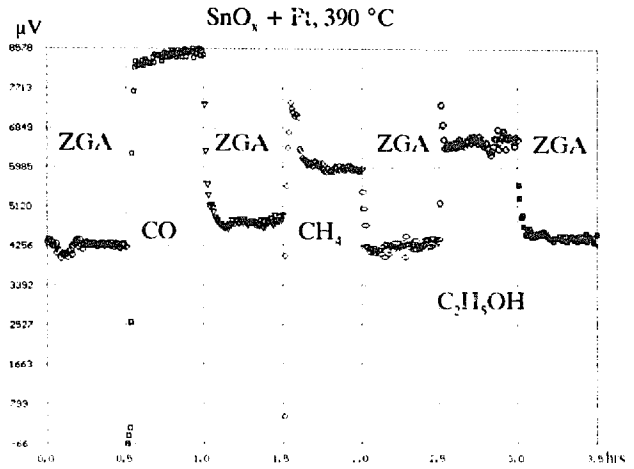


Fig. 3. Seebeck voltage of the SnO_x sensor doped with platinum at its half surface, kept at around 390°C.

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 edge with respect to the cold edge. From a solid-state physics approach, when a temperature gradient δT is present the quasi Fermi energy of the semiconductor (proportional to the carrier density) exhibits a constant slope from the hot to the cold edge and a voltage difference appears at the two edges of the semiconductor. For an n-type semiconductor the hot edge is the positive terminal while the cold is the negative terminal (the polarity is reversed in the case of p-type material). This voltage is called Seebeck voltage (from the name of its discoverer) and is proportional to the temperature gradient according to Eq. (1):

$$\delta V = \alpha_s \delta T$$

where α_s is the Seebeck coefficient expressed in volts/K and depends on the material properties and on temperature. The Seebeck coefficient may be expressed as a

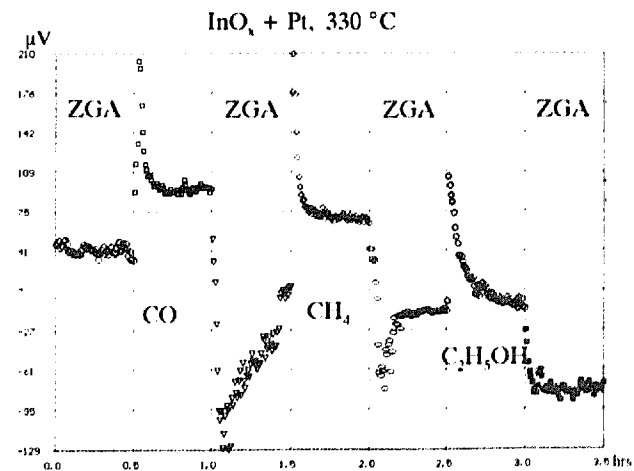


Fig. 4. Seebeck voltage of an InO_x sensor doped with platinum at its half surface, kept at around 330°C.

function of film resistivity, ρ , only according to the following relation [1]:

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

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

Considering the structure of our sensors shown in Fig. 1, the temperature gradient between the two edges of the semiconducting film is created due to the different rates of gas chemisorption imposed from the catalytic layer present on half of the film. The edge of the films 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. In an opposite case the catalytic layer decreases the combustion rate (or the heat of adsorption) of the target gas, with respect to the one achieved without the catalyst.

The response of a platinum covered tin oxide sensor to target gases is shown in Figs. 2 and 3. The sensor exhibits interesting transient responses in the case of carbon monoxide, methane and ethanol. Note that different transient responses were recorded in the case of carbon monoxide, methane and ethanol. These experimental results are being theoretically interpreted and results will be published in a forthcoming paper.

Similar behaviour is observed in the case of InO_x film with platinum catalyst deposited on the half of its surface, as shown in Fig. 4.

4. Conclusions

Tin oxide and indium oxide thin films doped at the half of their surface with an ultrathin layer of a noble metal 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. The explanation of the interesting transient effects observed will be given in a forthcoming paper under preparation.

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Biographies

John Avaritsiotis was born in Greece in 1948. He received his B.Sc. (Hon.) in physics from the Department of Physics of the University of Athens in 1972. His M.Sc. and Ph.D. degrees were obtained from Loughborough University of Technology, UK, in 1974 and 1976, respectively, in the field of thin-film technology and fabrication of thin-film devices. From 1976 to 1979 he was employed as a research fellow in the Thin Film Group of Loughborough University of Technology. From 1980 to 1986 he was appointed lecturer at the Electronics Laboratory of Athens University, and in 1986 he was elected Associate Professor in the Department of Electrical Engineering of the National Technical University of Athens. In 1990 he was elected Professor of microelectronics in the same department. He has worked as a technical consultant to various British and Greek industrial firms for the incorporation of new thin-film deposition techniques in their production processes. He has published over 30 technical articles in various scientific journals, and has presented more than three dozen papers at international conferences. His research activities have been focused in the field of microelectronic materials and thin film deposition techniques for use in the fabrication of semiconductor devices. His present research interests concern study of the electrical properties of thin insulating and semiconducting films deposited by sputtering, on-chip interconnections and MCMs for high speed circuits; design of ASICs, development of fabrication processes for the production of solid-state gas sensors and design and prototyping of smart sensors. Professor Avaritsiotis is a member of the Editorial Advisory Board of the journal *Active and Passive Electronic Components*, a Guest Editor of *IEEE Transactions on Components, Packaging and Manufacturing Technology* and a senior member of IEEE and a member of IOP and ISHM.

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