

# A technique for suppressing ethanol interference employing Seebeck effect devices with carrier concentration modulation

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## Abstract

Thin sputtered indium oxide films with an additive deposited on the half of their surface are considered as Seebeck effect devices for sensing of methane and ethanol. The electron concentration of the oxide film is controlled with an applied voltage perpendicular to the film with the use of a buried gate under it, in the same way the channel conductance in a MOS device is controlled by the gate voltage. Due to the different chemisorption mechanisms of methane and ethanol, a gate voltage modulating the free electron concentration of the oxide film enhances sensitivity to methane, whereas it does not influence sensitivity to ethanol. © 1997 Elsevier Science S.A.

*Keywords:* Ethanol interference; Seebeck; MOS

## 1. Introduction

The conductance of conventional metal oxide gas sensors in the presence of ethanol is nearly two orders of magnitude higher than the one in the presence of other desirable gases, causing interference problems. On the other hand, Seebeck effect devices based on thin metal oxide films have shown promising results [1,2]. The gas sensing principle of such devices consists of the different heat of adsorption delivered at the two halves of the film, if one half is covered with a catalyst. Induced temperature gradients (a few degrees Celsius) produce measurable Seebeck voltages, even in the range of a few millivolts (depending on the Seebeck coefficient). The Seebeck coefficient of a Seebeck device is proportional to the resistance of the film [3], implying that the response of a Seebeck effect based sensor to ethanol may be suppressed with respect to its response to other gases like CO or CH<sub>4</sub>, which do not induce a large conductance increase, although their heat of adsorption may be high enough. Consequently, the resistance decrease induced by ethanol adsorption may reduce the sensitivity of a Seebeck effect device by

modulating the Seebeck coefficient.

Going one step further, an electrode may be added under the metal oxide sensing film, defined here as gate. The gate voltage will induce and control a depletion or accumulation layer at the oxide, depending on its polarity. The free electron concentration of the semiconducting metal oxide controls the density of surface oxygen atoms and consequently plays an important role in the detection mechanism of reducing gases like CO or CH<sub>4</sub>, which tend to adsorb on oxygen atoms of the sensor surface. The detection mechanism of ethanol is different, i.e. ethanol adsorbs on metal (indium) atoms of the surface and acts as an electron donor [4]. Thus, the free electron concentration modulation technique described above is shown to have a large effect in the case of methane, whereas it has negligible effect in the case of ethanol.

## 2. Experimental techniques

The structure of the device described above is shown in Fig. 1. The gate electrode was deposited by thermal evaporation of gold. The insulating layer was deposited onto the gold gate by thermal evaporation of SiO and subsequent oxidation for the formation of SiO<sub>2</sub>. The

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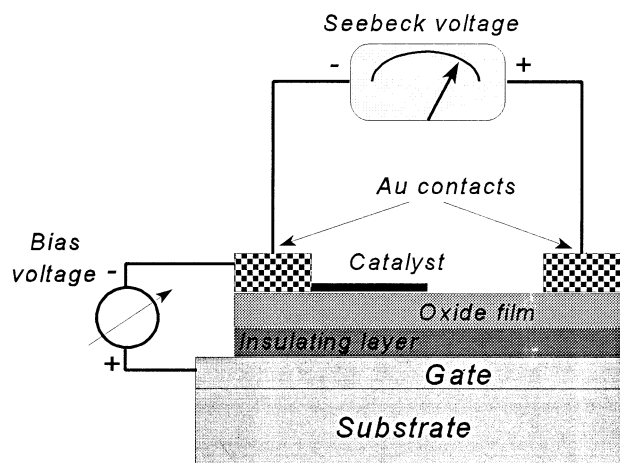


Fig. 1. Structure of the device (not in scale).

thickness of the  $\text{SiO}_2$  layer was around 100 nm. The indium oxide film was deposited onto the insulating  $\text{SiO}_2$  layer by reactive magnetron sputtering of an indium target in  $\text{Ar-O}_2$  mixture. The thickness of the  $\text{InO}_x$  film was around 1000 nm. The stoichiometry of the film was controlled with a Plasma Emission Monitoring technique, which has been found adequate for the fabrication of films with reproducible stoichiometry. Subsequently, palladium was e-beam evaporated onto half of the indium oxide film with the use of a contact mask, to achieve different reaction rates at the two halves of the film in order to measure a Seebeck voltage. Details concerning the fabrication and physical properties of both the oxide film and the catalytic layer can be found elsewhere [5]. Gold ohmic contacts were thermally evaporated at the two edges of the sensor, as the electrodes for measurement of the Seebeck voltage. Fig. 2 shows the  $I-V$  characteristics for this device as a function of the applied voltage at the gate. These characteristics imply a typical MIS behavior in triode (ohmic) region.

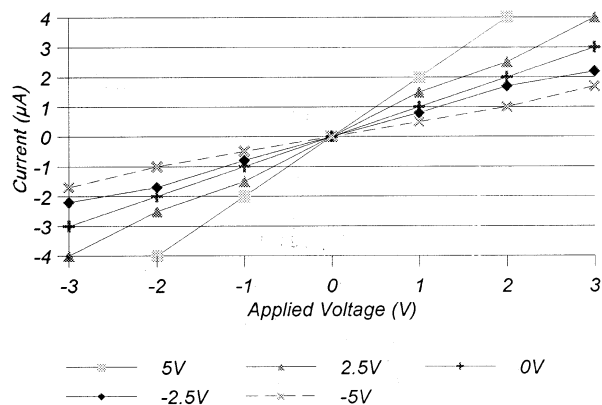


Fig. 2.  $I-V$  characteristics of the device showing a typical MIS behaviour in triode (ohmic) region.

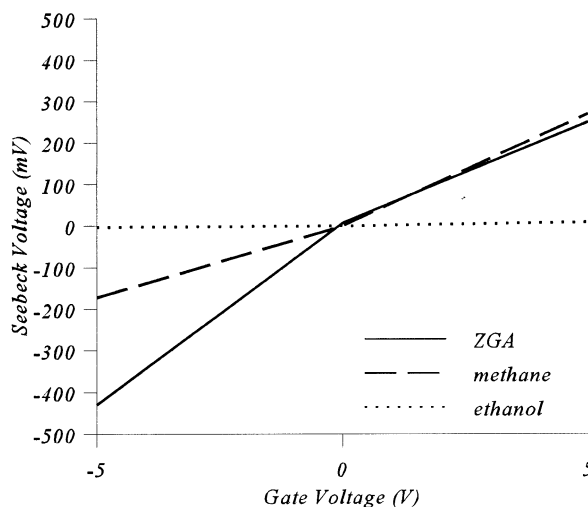


Fig. 3. Output signal of the device as a function of gate voltage.

The sensor characterisation set up was designed to measure the steady-state response of the samples, testing them at a constant temperature of  $400^\circ\text{C}$  and under different gas compositions. The sensors were operated at an elevated temperature because target gases do not adsorb on oxide surface at low temperatures. The testing conditions were rigorously controlled via a fully-automated computer-controlled system. The sensor was exposed to zero grade air (ZGA, purified mixture of 80%  $\text{N}_2$  and 20%  $\text{O}_2$ ), to 1%  $\text{CH}_4$  diluted in ZGA and to 30 ppm  $\text{C}_2\text{H}_5\text{OH}$  diluted again in ZGA. The gate voltage was set at  $-5$ ,  $0$  and  $+5$  V. After the sensor was left for 20 min at the specified gate voltage and under the specified gas composition both the voltage across the gold contacts (Fig. 1) and the resistance of the film were recorded. This procedure was followed nine times, for every gate voltage and test gas composition.

### 3. Experimental results and discussion

Although the concentration of methane is three orders of magnitude higher than the one of ethanol, the resistance change induced in the presence of methane is over one order of magnitude lower than the one induced in the presence of ethanol. More specifically, with zero gate voltage the resistance of the sensor is nearly  $10\text{ M}\Omega$  in the absence of reducing gases, and it falls to around  $300\text{ k}\Omega$  in the presence of 1% methane, whereas a fall down to  $70\text{ k}\Omega$  is observed in the presence of 30 ppm ethanol; in other words a resistance change has been observed which is 3200% for 1% methane and 14200% for 30 ppm ethanol.

Fig. 3 shows the Seebeck voltage of the sensor in the presence of ZGA, methane and ethanol. From Fig. 2 it

is obvious that the dependence of Seebeck voltage on gate voltage in the presence of ethanol is negligible compared to the one both in the presence of methane and in the absence of any reducing gas (i.e. in the presence of ZGA only). More specifically, the Seebeck voltage in the presence of ethanol varies from  $-3$  mV with  $-5$  V gate voltage to  $10$  mV with  $+5$  V gate voltage. These values are very low to be observed in Fig. 2. However, the Seebeck voltage recorded in the presence of methane or ZGA was two orders of magnitude higher, if a gate voltage was applied. In the presence of ZGA (i.e. in a partial pressure 0.2 atm of oxygen) the Seebeck voltage of the device was  $250$  mV for a gate voltage of  $5$  V,  $7$  mV for zero gate voltage and  $-430$  mV for gate voltage  $-5$  V. In the presence of 1% methane these values were slightly altered ( $270$  mV at  $5$  V,  $5$  mV at  $0$  V and  $-170$  mV at  $-5$  V), but they were by far larger than the ones observed for ethanol. This is explained in the following.

The energy band diagram of the metal gate-insulator-semiconductor-metal contact structure, along with the

electric field distribution, is shown in Fig. 4. Fig. 4 refers to the case of a large negative applied gate voltage, where the bending of the semiconductor near the surface is fully controlled by the applied voltage (the depletion depth is larger than the semiconductor thickness). The surface states at the insulator–semiconductor interface have been neglected, while the surface states at the semiconductor surface have been taken into account as it is shown by the step in the electric field in Fig. 3b, at  $x = W$ . After detailed calculations and assuming that (a) all temperature gradients due to gas adsorption are linear and (b) the electron relaxation time of the semiconductor is proportional to  $E^{-1/2}$ , where  $E$  is the electron energy, the following expression for the seebeck voltage was obtained:

$$V_{\text{seeb}} = \frac{2}{q} \frac{\delta T}{T_1} (y_R + F) \quad (1)$$

where  $y_R$  is the depletion width induced by gate voltage at the surface of the semiconductor (Fig. 3a),  $F$  is the distance of conduction band from Fermi level at flat-band conditions (without gate voltage),  $\delta T$  is the temperature gradient due to the differential heat of gas adsorption at the two halves of the film,  $T_1$  is the temperature of the semiconductor ( $400^\circ\text{C}$ ) and  $q$  the electron charge. The quantity  $y_R + F$  is the distance of conduction band from Fermi level at the surface of the semiconductor with applied gate voltage that depletes the semiconductor (Fig. 3a). Extracting the dependence of  $y_R$  on the applied voltage from Fig. 3a, we obtain the seebeck voltage as a function of the applied voltage:

$$\frac{dV_{\text{seeb}}}{dV} \sim qD_s V \quad (2)$$

where  $D_s$  is the density of surface states per unit area and eV. This equation is valid in the case of a negative gate voltage, which leads to depletion of the semiconductor and explains the different slope of the Seebeck voltage in the presence of ZGA and methane: methane removes oxygen adatoms and lowers the density of surface states. In the case of a positive gate voltage, the accumulation of electrons in the semiconductor leads to strong oxygen adsorption, given that the number of oxygen adatoms removed by methane becomes negligible. Thus, the differential heat of adsorption controls the measured Seebeck voltage.

In the case of ethanol, the band bending is fully controlled by the donor-like surface states induced by ethanol decomposition, eliminating the effect of the applied gate voltage. Moreover, as has been mentioned above, the large resistance decrease in the presence of ethanol leads to a small Seebeck voltage, since Seebeck voltage is known [3] to be proportional to semiconducting film resistance.

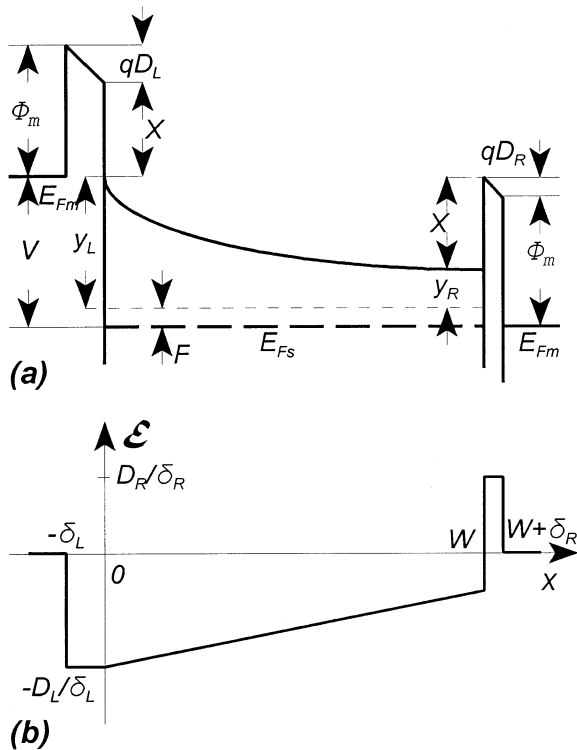


Fig. 4. (a) Energy band diagram of the gate-metal oxide-gold contact structure, (b) Electric field distribution.  $\Phi_m$  is the metal work function (gate or contacts),  $X$  is the electron affinity of the semiconductor,  $V$  is the applied gate voltage,  $y_L$  and  $y_R$  are the depletion widths induced by the gate voltage at the bottom and the surface of the semiconductor respectively,  $D_L$  and  $D_R$  are the voltage drops across the gate and surface insulating layers respectively,  $F$  is the distance of the conduction band from the Fermi level at flat band conditions and  $\delta_L$  and  $\delta_R$  are the thicknesses of the interfacial insulating layers at semiconductor–gate interface and semiconductor surface respectively.

#### 4. Conclusions

The free electron concentration modulation technique described above may be used to eliminate ethanol response in Seebeck effect gas sensors. Operating the sensor at a gate voltage which increases the depletion layer the response to methane is enhanced, whereas the response to ethanol remains unaffected.

Furthermore, the Seebeck effect type gas sensors based on n-type semiconducting indium oxide are recommended for the detection of combustible gases, like methane, which induce relatively small resistance changes of the film oxide.

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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 produc-

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