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SiC-based MIS gas sensor for CO detection in very high water vapor environments

O. Casals[1], Th. Becker[2], P. Godignon[3], A. Romano-Rodriguez[1]
[1] Universitat de Barcelona (UB), MIND-IN[2]UB-Department of Electronics, c/Martí i Franquès 1, 8028 Barcelona, Spain. ocasals@el.ub.es
[2] EADS Innovation Works, Nesspriel 1, 21129 Hamburg, Germany.
[3] Institut de Microelectrònica de Barcelona, IMB-CNM-CSIC, Campus UAB, E-08193 Bellaterra, Spain.

Abstract:
Due to their feasibility to operate at high temperature in environments with extremely high concentrations of water vapor (up to 45% by volume ratio to nitrogen), SiC-based MIS (Metal-Insulator-Semiconductor) capacitors are good candidates to monitor the presence of CO in the exhaust gases of hydrogen- or hydrocarbon-based fuel cells. In this work, we show that these devices are able to detect down to 2 ppm of CO and that their response is hardly affected by the presence of high concentrations of CO_2 or by extremely high water vapor concentrations in pure nitrogen.

Key words: *MIS* (*Metal-Insulator-Semiconductor*), sensor, *CO, water vapor,CO_2, hydrogen- or hydrocarbons-based fuel cells.*

Introduction

Amongst the different types of solid-state gas sensors, field-effect based sensors have shown to be suitable devices to detect hydrogen and hydrocarbons if a catalytic metal layer is used as a gate. Since Lundström et al. [1] reported on hydrogen-sensitive Pd-MOS (Metal-Oxide-Semiconductor) transistors fabricated on conventional silicon substrates, in 1975, field-effect based sensors has experienced significant advances. On the one hand, the use of wide band gap semiconductor such as SiC, group-III nitrides (AlN, GaN and AlGaN) and diamond, allows this kind of sensors to work at higher temperatures than Si-based devices. The higher operation temperature results in a larger responses to hydrogen and hydrocarbons as well as in better response and recovery times [2]. Additionally, these devices withstand the exposure to hazardous gases, which are usually produced in high temperature conditions. On the other hand, the use of a porous and/or discontinue catalytic gate has widened the range of gases to which these devices respond to non-hydrogen-containing species such CO [3,4].

According to the most accepted model for MIS (Metal-Insulator-Semiconductor) sensors, the sensing mechanism to hydrogen or hydrocarbons can be attributed to the formation of H-induced dipole layer at the metal-insulator interface [1]. However, the studies on the sensitivity of MIS devices towards non-hydrogen-containing species such CO have been relatively scarce and the sensing mechanism requires further investigation [5,6].

Recently, we have demonstrated that $Pt/TaO_x/SiO_2/SiC$ MIS capacitors can operate not only at high temperature, but also, in the presence of extremely high water vapor concentrations gases (up to 45% by volume) [7]. In these harsh conditions, these devices are still able to detect hydrogen and hydrocarbons in concentrations far below the legal permissible exposure limits [8,9] or the requirements for hydrogen safety sensors [10]. This fact makes $Pt/TaO_x/SiO_2/SiC$ MIS capacitors suitable to monitor the proper operation of devices such as hydrogen or hydrocarbon-based fuel cells, whose exhaust gases contain extremely high concentrations of water vapor and CO_2 but can also contain remains of the fuel, oxygen and byproducts of the catalytic reaction, such as CO, if the combustion is incomplete.

In this work, the performance of $Pt/TaO_x/SiO_2/SiC$ MIS capacitors operating as CO sensors in atmospheres with extremely high water vapor concentrations and in presence of CO_2 is investigated. The suitability of these sensors to monitor CO in the exhaust of devices such as hydrogen- or hydrocarbon-based fuel cells is discussed. Under the light of the here-reported experimental results a critical

review of the CO sensing mechanisms in MIS devices is also presented.

Experimental

$Pt/TaO_x/SiO_2/SiC$ MIS capacitors have been fabricated on n-type (0001) Si-face 4H-SiC substrates with a 10-μm epitaxial layer (doping level $10^{16}cm^{-3}$) grown on heavily doped substrate (0.021Ω) purchased from CREE Inc. A detailed description of the fabrication process can be found elsewhere [7,11]. After their fabrication, the devices were annealed in alternating reducing and oxidizing atmospheres at temperatures above 600ºC for at least 2 hours in order to obtain a porous gate layer with stable electrical properties [3]. The final layered structure of the MIS capacitors is sketched in Fig. 1.

The MIS capacitor response to gases was measured as the gate voltage change ($\Delta V=V_G(gas)-V_G(N_2)$) under constant capacitance conditions. Water vapor concentrations ranging from 3% (equivalent to 80% relative humidity at room temperature -25°C- and 1 atm) to 45% by volume ratio to gas were obtained by mixing ultrapure water with the gas flux in a Bronkhorst controlled evaporator and mixer (CEM) at 200°C and atmospheric pressure. Water vapor condensation was avoided by thermalizing the gas test chamber and all the pipes at 200ºC.

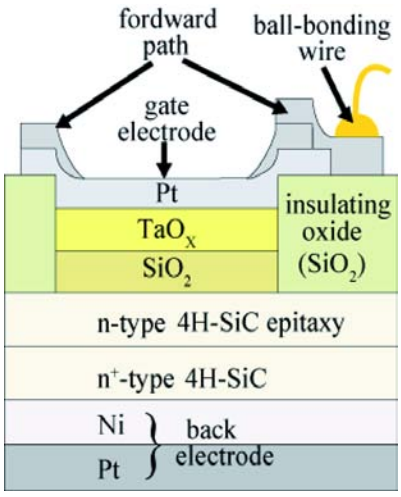

Fig. 1 Schematic diagram of the layers that comprise the MIS capacitors. Reprinted from [7], with permission from Elsevier.

Results and discussion

In nitrogen atmosphere, the presence of water vapor (up to 45% concentrations) at temperatures ranging from 200 to 400ºC did not produce any significant change in the admittance curves (Fig. 2). No degradation of the electrical performance of the devices was observed after days of working under these water vapor rich conditions. This remarkable insensitivity and stability can be explained by 1) the fact that the water vapor dissociation on Pt surfaces, which could lead to H atoms that could reach the metal-insulator interface, is unlikely at the temperatures used in this work [12]; and 2) the interaction between water vapor molecules and the surface of the TaO_X layer exposed through the Pt porous gate does not produce any electrically measurable effect.

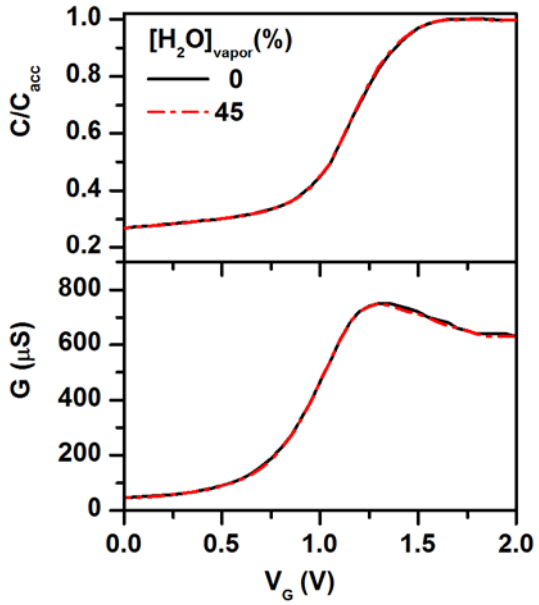

Fig. 2 Admittance versus gate voltage curves ($C\text{-}V_G$ and $G\text{-}V_G$) of a $Pt/TaO_x/SiO_2/SiC$ MIS capacitor operating at 250°C in dry nitrogen and in the presence of 45% of water vapor. Reprinted from [7], with permission from Elsevier.

The dynamic response of a $Pt/TaO_x/SiO_2/SiC$ MIS capacitor to pulses of CO from 1 to 20 ppm in different water vapor concentrations is shown in Fig. 3. The detection limit to CO of these MIS capacitors at any water vapor content is around 2 ppm, since the response to 1 ppm is just in the limit of experimental error (10mV). This performance is suitable to monitor the more restrictive permissible exposure limits (8.6 ppm for 8 hours TWA according to WHO [13]). It is noteworthy that the water vapor changes in the gas mixture hardly have any effect neither on the sensor's response nor on the response and recovery times. This result hints that CO and water vapor molecules neither compete for the same adsorption sites nor interact between them at the sensor's surface.

The influence of CO_2 on the sensor's ability to detect CO has also been studied. Fig. 4 shows that the introduction of 1% CO_2 in the test chamber hardly interferes in the MIS capacitors' response to CO. Likewise, the device did not show any significant response to CO_2 in the range of temperatures studied neither.

All these results demonstrate that the here-presented MIS sensors are suitable to target CO detection in water vapor and CO_2 rich atmospheres.

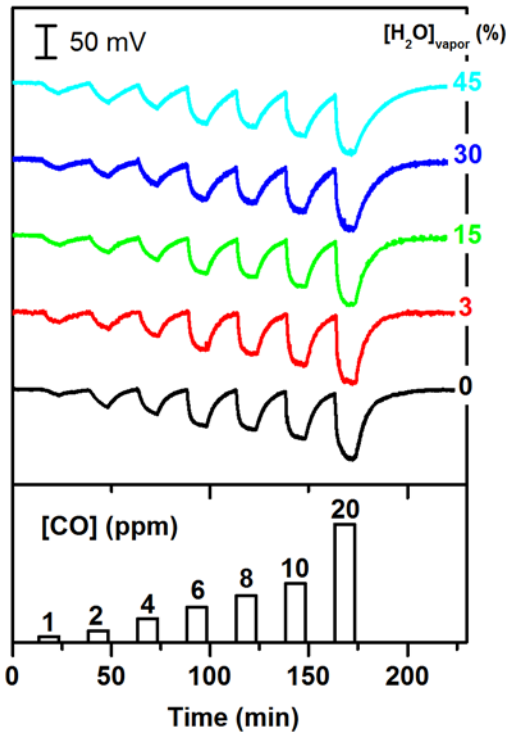

Fig. 3 Dynamic response of a Pt/TaO_x/SiO_2/SiC MIS capacitor a) to pulses of CO in different vapor containing atmospheres at 300 ºC.

The response versus the CO concentration curve was found to follow eq. (1),

$$\Delta V([CO]) = \Delta V_{\max} \cdot \frac{k \cdot [CO]}{1 + k \cdot [CO]} \quad (1)$$

where ΔV_{max} and k are constants dependent on the temperature. This equation is based on the Langmuir's isotherm for non-dissociative adsorption and implies the assumption that the sensor's response is proportional to the amount of CO molecules adsorbed at the sensor's surface. Hence, ΔV_{max} is the voltage change measured when all the available CO adsorption sites of the sensor's surface are occupied. The agreement with our experimental data demonstrates that CO molecules are non-dissociatively adsorbed on Pt. This fact is also supported by surface science [12] and in situ drift studies of the Pt-gate surfaces of similar devices [5,6]. However, MIS devices with a dense hardly respond to CO and, therefore, the molecular adsorption on the Pt surface alone cannot explain the sensitivity of MIS devices to this gas. Moreover, CO adsorbates lead to a positive change in the work function, like in the case of O_2, whereas the sign of the MIS sensors' response to these gases is just the opposite.

In order to explain this behavior, it has been suggested that the CO sensing mechanism for this kind of devices could be related to the modulation of the magnitude or the quantity of remaining hydrogen dipoles at the metal-oxide interface by the CO adsorption at the Pt surface [14]. Alternatively, it has also been proposed that the sensor signal is produced by the removal of oxygen from partially oxidized Pt, which was directly observed on the surface of similar devices [3,5]. However, both theories fail to explain the lack of response to CO molecules in dense-gate devices or the reversibility of the CO effects on the devices in pure nitrogen atmospheres.

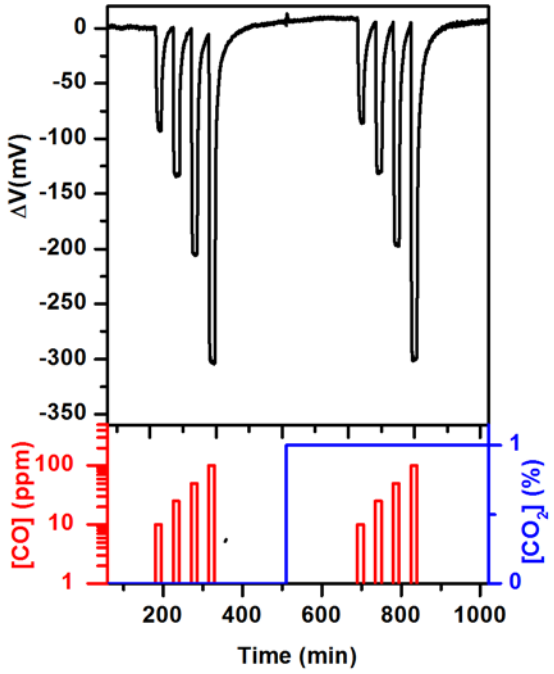

Fig. 4 Dynamic response of a Pt/TaO_x/SiO_2/SiC MIS capacitor to pulses of CO in presence and absence of 1% of CO_2 at 260 ºC.

The CO spillover phenomenon (interphase diffusion of adsorbed atoms or molecules), which is common metal-assisted catalysis on mixed oxides [15-17], could provide a more consistent explanation. According to this, the sensor's response to CO could be attributed to CO molecules that, after being adsorbed at the Pt near the bare patches of TaO_x, migrate to this oxide via spillover [3,18]. Thus, the response signal would be modulated by the molecular adsorption of CO on the Pt surface of the devices, which is consistent with the experimental results. Likewise, the recovery of the sensor baseline signal after the removal of CO from the gas mixtures can be explained by the reverse spillover phenomenon. At the same

time, the direct adsorption of the CO molecules at the surface of the exposed TaO_x areas of the porous Pt electrode is also possible and it would also explain the lack of response in dense-gate devices. In any case, whatever is the way that drives the CO molecules to the TaO_x it leads to a modulation of the surface dipole layer in the exposed patches of this oxide by the formation of dipoles.

Conclusions

MIS capacitors are suitable to detect CO in challenging conditions, such is the ones found in the exhaust gases of hydrogen or hydrocarbons based fuel cells. The no cross-sensitivity between water vapor (even at 45% by volume) and CO indicates that water vapor molecules do not compete with CO molecules for the adsorption sites. Likewise, the sensors are non-responsive to CO_2 and its presence in the gas mixture hardly interferes in the capacitors' response to CO. In these harsh measuring conditions, the devices are able to detect CO concentrations down to 2 ppm.

Under light of the here-presented results, the commonly proposed mechanism of the CO detection in this kind of devices seems to be the rather simplistic. Other mechanisms, such as spillover phenomenon are necessary to successfully explain all the experimental evidences.

Acknowledgements

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