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SiC-Based MIS Gas Sensor for High Water Vapor Environments

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Abstract

In this work we will prove that SiC-based MIS capacitors can work as efficient gas sensors in environments with extremely high concentrations of water vapour, still being sensitive to hydrogen, CO and hydrocarbons. This makes these devices suitable for long term and efficient operation in harsh environments, such as the exhaust gas atmosphere of hydrogen or hydrocarbon-based fuel cells.

Keywords: gas sensor; water vapor; metal-insulator-semiconductor; MIS; SiC; hydrogen; CO; ethane; ethene; fuel cell

1. Introduction

As results of the combustion of a fuel like hydrogen or hydrocarbons in oxygen, water and carbon dioxide are produced. However, if the reaction is incomplete, the exhausts could contain: rest of the fuel or byproducts of the catalytic reaction, such as smaller hydrocarbons, carbon monoxide (CO) and nitrogen oxide (NO_X), if nitrogen is also present. Besides, the quantity of water vapor produced in the case of hydrogen or hydrocarbon-based fuel cells is extraordinarily large. The control of the emission to the atmosphere of hazardous gases has substantially stimulated the research and development in the field of gas sensors in the last decades. Different types of solid-state gas sensors have been developed to monitor these gases, among them metal-insulator-semiconductor (MIS) field effect devices have the advantage of being the most compatible with the most widespread electronic technology, that of the silicon (Si).

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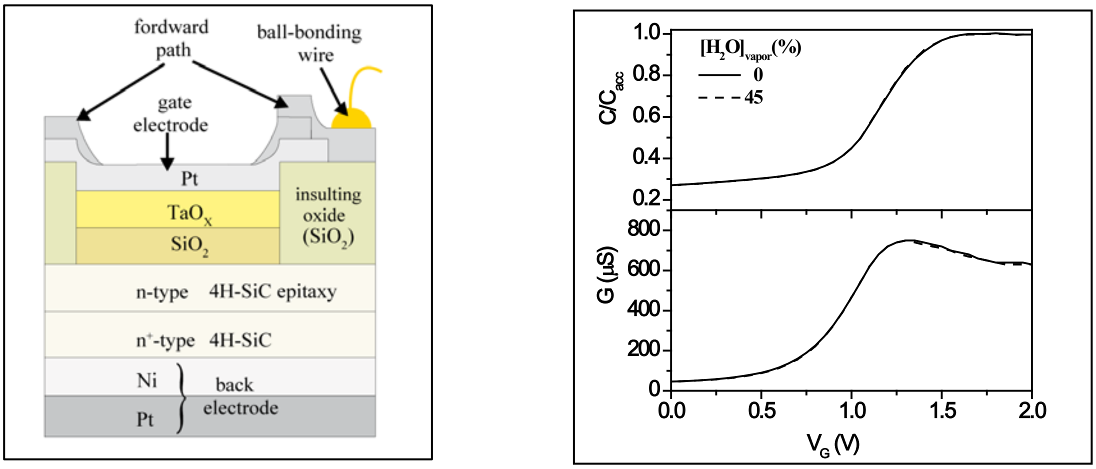
The electric characteristics of a field effect device can be made gas sensitive by using a layer of a catalytic metal, such as palladium (Pd) or platinum (Pt), as gate electrode. The pioneer in the use of metal-oxide-semiconductor (MOS) structures as gas sensor was Lundström in 1975 [1], who reported a hydrogen-sensitive Pd-MOS transistor fabricated on conventional silicon (Si) substrate. Later, the introduction of wide bandgap semiconductors, such as silicon carbide (SiC), group-III nitrides and diamond, has allowed the increase of the devices' operating temperature above the operating temperature of Si [2]. The higher operating temperature results, as compared to the first results, in an increase of the response to hydrogen and a decrease in the response time [3]. Among the wide bandgap semiconductors, SiC is the more suitable for harsh environmental applications due to its high chemical inertness, its physical resistance, its high thermal conductivity, its high breakdown voltage, a significantly more developed technology and, above all, its ability to grown as a good quality of thermal oxide [4].

The most accepted model attributes the sensing mechanism of MIS hydrogen sensors to the formation of H-induced dipole layer at the metal-oxide interface. The hydrogen gas molecules are dissociative absorbed at the surface of the catalytic gate and then the atomic hydrogen diffuses quickly towards the metal-oxide interface through the dense metallic layer. The use of a porous and/or discontinue catalytic gate has widened the range of gases to which these devices respond [5]. Thus, non-hydrogen-containing species, like CO, can be detected by MIS devices with a porous and/or discontinuous gate, which implies the direct interaction of the gas with metal-oxide interface or with the layer/s under the metallic layer.

In this work, we propose, for the first time to our knowledge, the use of $Pt/TaO_X/SiO_2/SiC$ MIS capacitors to monitor the exhaust gases of hydrogen or hydrocarbon-based fuel cells, that is, to detect hydrogen, CO and hydrocarbons in atmospheres with extremely high concentrations of water vapor (up to 45% by volume ratio to nitrogen) and temperatures above 200˚C.



(a) (b)

Fig. 1. (a) Schematic diagram of the layers that comprise the MIS capatitors; (b) Admittance versus gate voltage curves (C-V_G and G-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.

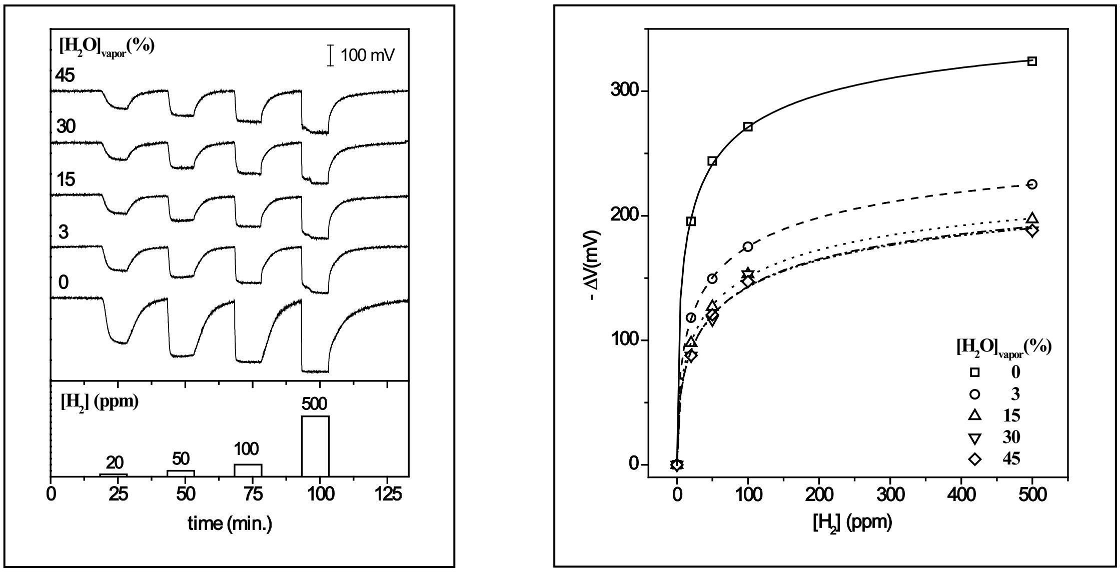
2. Experimental

MIS capacitors were fabricated on n-type (0001) Si-face 4H-SiC substrates with a 10-nm epitaxial layer ($10^{16}cm^{-3}$ of doping level) grown on heavily doped substrate (0.021Ω) purchased from CREE Inc. The 20-nm-thick silicon oxide (SiO_2) layer has been grown by dry oxidation and subsequently annealing in 50% N_2O/Ar atmosphere in order to improve the electrical performance of this layer at high temperatures. The catalytic gate was formed by sputtering a 100-nm-layer of metallic platinum (Pt) on a 20-nm.thick buffer layer of $TaSi_X$ deposited also by sputtering on the SiO_2 prior the Pt deposition. The back contact of the devices was formed by sequentially sputtering nickel layers on the substrates. The MIS devices as obtained when fabricated are quite sensitive to hydrogen but their gas response and electrical characteristics are instable at the usual operating temperatures. Besides, the as-fabricated devices show a poor o null response to the concentrations of CO or of hydrocarbons required for the present application. Thus, the devices were annealing in alternating reducing and oxidizing atmospheres at temperatures above 600ºC for some hours in order to obtain a porous gate layer and stable electrical characteristics. This treatment produces the oxidation of the deposited $TaSi_X$ layer to Ta_2O_5 and tantalum sub-oxides (TaO_X) and to a small quantity of SiO_X. The final layer structure of the MIS capacitors is schematized in Fig.1. A detailed description of the process of fabrication of the MIS capacitors has been published elsewhere [6].

The MIS capacitor response to the presence of the different gases has been measured as the change of the gate voltage needed to maintain constant the value of capacitance of the devices ($\Delta V = V_G(gas) - V_G$). Absolute water vapor concentrations ranging from 3% (equivalent to 80% relative humidity at room temperature and 1 atm) to 45% were obtained by mixing ultrapure water with the gas flux in a Bronkhorst controlled evaporator and mixer (CEM) at 200˚C and at atmospheric pressure.

3. Results

The admittance curves obtained in the presence of water vapor concentrations from 0 to 45% (by volume ratio of water vapor to nitrogen) indicates that the MIS capacitors are almost insensitive to the presence of water vapor in absence of other gases than nitrogen (Fig. 1b). Besides, no degradation of the electrical performance of the devices has been observed after days of working under these high water concentrations atmospheres.



(a) (b)

Fig. 1. (a) MIS capacitor's dynamic response towards four concentrations of hydrogen in different water vapor containing atmospheres; (b) MIS capacitor's response as a function of the hydrogen concentration for different water vapor atmospheres.

Fig. 2a shows the dynamic response of the MIS capacitors to pulses of hydrogen from 20 to 500 ppm in different water vapor atmospheres at 300ºC. As it is seen, the response of the sensor towards hydrogen decreases with increasing amount of water vapor in the gas mixture. However, a saturation is observed above 30%, giving rise to a nearly water vapor independent hydrogen sensing behavior. It is noteworthy that, for all the water vapor concentrations, the response curves towards hydrogen (at atmospheric pressure) are proportional to the Langmuir's isotherm corresponding to the dissociative adsorption of hydrogen at the sensor's surface (eq. 1).

$$\Delta V([H_2])=\Delta V_{max}\cdot\frac{k^{1/2}\cdot[H_2]^{1/2}}{1+k^{1/2}\cdot[H_2]^{1/2}} \qquad (1)$$

The lower values tested for ethane and ethene have been 100 ppm and 20 ppm, respectively. In both cases, MIS capacitors are able to detected these concentrations even in the presence of the highest water vapor concentration studied (45%). The MIS capacitors have shown also a measurable response to concentrations of CO as low as 2 ppm in dry nitrogen and their response have been found to be hardly dependent on the water vapor concentration.

4. Conclusions

In this work, we have show that the electrical characteristics of a Pt/TaO_X/SiO_2/SiC MIS capacitor are not affected by the presence in the atmosphere of water vapor concentrations as higher as 45% (by volume ratio to nitrogen). Besides, the sensors are able to detect down to 1 ppm hydrogen, 2 ppm CO, 100 ppm of ethane and 20 ppm of ethene under these high water vapor conditions. Thus, we can conclude that the Pt/TaO_X/SiO_2/SiC MIS capacitors can be used to monitor the exhaust gases of hydrogen or hydrocarbon-based fuel cells.

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