Sensors and Actuators B 133 (2008) 705–716

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Review

High temperature field effect hydrogen and hydrocarbon gas sensors based on SiC MOS devices

Adrian Trinchi[a,*], Sasikaran Kandasamy[b], Wojtek Wlodarski[b]

[a] CSIRO Division of Materials Science and Engineering, P.O. Box 56 (Graham Road), Highett 3169, Victoria, Australia
[b] RMIT University, School of Electrical and Computer Engineering, Victoria, Australia

ARTICLE INFO

Article history:
Received 25 October 2007
Received in revised form 11 March 2008
Accepted 13 March 2008
Available online 21 March 2008

Keywords:
Schottky diode
Transistor
FET
Capacitor
Silicon carbide
Metal oxide semiconductor
MOSFET
Gas
Sensor
Sensing
Review

ABSTRACT

The growing need for reliable, efficient, high temperature hydrogen and hydrocarbon monitoring has fueled research into novel structures for gas sensing. Metal oxide semiconductor (MOS) devices employing a catalytic metal layer have emerged as one of the leading sensing platforms for such applications, owing to their high sensitivity and inherent capability for signal amplification. The limited operating temperature of such devices employing silicon as the semiconductor has led research efforts to focus on replacing them with devices based on silicon carbide (SiC). More recently, MOS devices having different oxide layers exhibiting improved sensing performance have emerged. Considering the amount of research that has been carried out in this area in recent times, it is important to elucidate the new findings and the gas interaction mechanisms that have been ascribed to such devices, and bring together several theories proposed by different research groups. In this paper we first highlight the needs which have driven research into SiC based field effect hydrogen and hydrocarbon sensors, illustrate the various structures being investigated, and describe the device evolution and current status. We provide several sensing examples of devices that make use of different oxide layers and demonstrate how their electrical properties change in the presence of the gases, as well as presenting the hydrogen gas interaction mechanisms of these sensors.

Contents

1. Introduction

1.1. Need for high temperature hydrogen and hydrocarbon sensing

Today hydrogen has many important applications such as its use in the processes of many industries that include chemical, petroleum, food and semiconductor. Furthermore, the negative

* Corresponding author. Tel.: +61 3 9252 6442; fax: +61 3 9252 6253.
E-mail address: avt@ieee.org (A. Trinchi).

0925-4005/$ – see front matter
doi:10.1016/j.snb.2008.03.011

environmental impacts of burning fossil fuels, coupled with rising oil prices, have lead to renewed interest in clean energy technologies, especially those involving hydrogen. Hydrogen sensors would form an integral part of any such systems incorporating hydrogen as a fuel.

Lingering doubts about hydrogen's safety have prevented it from fulfilling its potential as a fuel source. Its low mass and high diffusivity makes it difficult to store. It is highly flammable in concentrations ranging from 4% to 90% by volume, with its lowest explosion limit being 4.1% [1], making the need for placing hydrogen sensors near high concentration storage facilities essential. Hydrogen is also a major cause of corrosion whereby it degrades the mechanical properties (strength and durability) of metals. This is especially significant at elevated temperatures, where it is termed high temperature hydrogen attack (HTHA) and results in embrittlement. For example, the tensile strength of steel alloy 4140 can be reduced by as much as 67% when exposed to hydrogen at a pressure of 41 MPa and a temperature of 300 K [2].

Hydrocarbons are widely used as fuels and as starting materials for numerous products that range from pesticides, solvents, and plastics. They are also commonly found in exhaust gases, largely due to incomplete combustion, predominantly from automobiles. They react in the atmosphere to form ground-level ozone, a major component of smog and also contribute to the formation of green house gases. Hydrocarbons may also pose several health risks, with short-term exposure possibly resulting in dizziness, intoxication, irritations, and anesthesia. Thus monitoring hydrocarbons not only provides a route for process control monitoring, but is also an effective tool towards current stringent pollution control.

Therefore, vital to the utilization of hydrogen and hydrocarbons is the development of efficient and reliable sensors for process monitoring and leak detection applications. Direct monitoring of processes that incorporate them may require the sensors to be placed in environments where temperatures may exceed 500 °C. Hence materials and sensing structures capable of withstanding such conditions are being exhaustively investigated.

Field effect hydrogen and hydrocarbon gas sensors based on Si substrates have operating temperatures limited to below 200 °C. High temperature operation, particularly for long periods, places great strain and demands on the sensors. For instance, automotive exhaust sensors for cylinder specific combustion engine control should be capable of operating at 700 °C for at least 4000 h [3]. Consequently, research efforts have intensified in the last decade into materials that not only allow for increased operating temperatures, but which are also compatible with Si fabrication technologies. SiC has emerged as the leading candidate for field effect based sensors [4,5]. In addition to its compatibility with Si, its wide band gap, chemical inertness and stability make it ideal for high temperature operation in harsh/rugged environments.

1.2. Field effect sensors based on SiC

There are many structures that can be employed for hydrogen and hydrocarbon gas sensing applications, for example, single and mixed semiconducting metal oxides (SMOs) [6–13], conductive polymers [14–16], as well as acoustic wave devices [17–20], although acoustic wave and conductive polymer based sensors are not well suited for high temperature applications. The most commonly employed hydrocarbon sensors are catalytic bead/hot bead sensors, which safely "burn" the hydrocarbon molecules that are adsorbed on the surface. Although they are robust and inexpensive, they have low sensitivity and have a high susceptibility towards contamination. Of the many transduction platforms available, field effect devices are highly favorable owing to their high sensitivity, as they exhibit an exponential relationship between current and voltage or impedance and voltage, unlike other types of sensors. This means that slight changes in their input can be amplified in their output, and this can be exploited for sensing applications.

Field effect gas sensors operate by monitoring changes in their electrical field distributions in the presence of an analyte gas species. They consist of junctions of metal, semiconducting and insulating materials. Direct measurements of current, capacitance and conductance are made as a function of bias voltage, and from them numerous parameters (including barrier height, interface state density, etc.) may be determined.

SiC based field effect gas sensors belong to the metal oxide semiconductor (MOS) family of devices. They are layered structures in which a catalytic metal, generally group VIII transition metals such as platinum (Pt) or palladium (Pd), is deposited over an oxide layer, which may be an insulating or semiconducting (usually SiO_2). The metal and oxide layers are in turn deposited onto a SiC substrate. The output signal is generally the change in bias voltage upon exposure to gas, when kept at a constant bias current or capacitance. Their manufacturing processes and packaging technology are the same as for standard integrated circuits. The sensors typically have dimensions measuring less than a few mm^2.

As seen in Fig. 1, SiC based field effect gas sensors can have several different configurations. In each configuration, gas molecules dissociate via a catalytic reaction on the metal surface. The reaction products and intermediary products may polarize and adsorb on the metal surface, or spill over to the uncovered parts of the oxide surface. Hydrogen atoms formed by dissociative reactions of hydrogen or hydrogen-containing species diffuse through the catalytic metal and form dipoles at the metal–insulator interface [21]. A resulting dipole layer alters the electric field distribution within the sensors, causing a shift in either its current–voltage (I–V), capacitance–voltage (C–V) or conductance–voltage (G–V) characteristic. Upon exposure to reducing gases, such as H_2 and hydrocarbons, these characteristic curves will shift towards lower voltages, and vice versa for oxidizing gases such as O_2 and NO_x.

The Schottky diode is a two terminal device in which a potential difference is placed across the metal and SiC, causing a current to flow. In general, the thickness of the oxide is typically several atomic layers, and is referred to as an interfacial layer. Based on the thermionic field emission conduction mechanism of Schottky diodes, the diode current can be expressed by [22]:

$$I(V) = I_{\text{sat}} \exp\left(\frac{qV}{nkT} - 1\right) \tag{1}$$

$$I_{\text{sat}} = SA^{**}T^2 \exp\left(\frac{-q\phi_b}{kT}\right) \tag{2}$$

where V is the voltage, q is the electron charge (1.602×10^{-19} C), n is the ideality factor, k is the Boltzmann constant (1.38×10^{-23} J/K), T is the temperature (K), I_{sat} is the saturation current, S is the area of the contact (cm^2), A^{**} is the effective Richardson's constant (A cm^{-2} K^{-2}) and ϕ_b is the barrier height.

For the capacitor structure, the terminals are also placed on the metal and SiC. However, the oxide layer thickness is typically larger than for the diode's, around 100 nm, which is to prevent tunneling between the metal and semiconductor. Furthermore, this oxide layer must be insulating in order to prevent current conduction and to facilitate the buildup of charge on either of its sides. Changes in the flat-band voltage of the sensor are monitored in the presence of a gas. The total capacitance of the device is the series addition of the oxide and semiconductor capacitances, C_{ox} and C_S, respectively, and is expressed by:

$$C_{\text{total}} = \frac{C_{ox}C_S}{C_{ox} + C_S} \tag{3}$$