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Sensors and Actuators B 129 (2008) 200–210
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Hydrogen monitoring for power plant applications using SiC sensors

Reza Loloee [a,*], Benjamin Chorpening [b], Steve Beer [b], Ruby N. Ghosh [a,*]

[a] *Department of Physics and Astronomy, Michigan State University, E. Lansing, MI 48824, USA*
[b] *US DOE-National Energy Technology Laboratory, Morgantown, WV 26505, USA*

Received 11 July 2006; received in revised form 26 July 2007; accepted 26 July 2007
Available online 2 August 2007

Abstract

We have developed a high-temperature gas sensing system for the detection of combustion products under harsh conditions, such as an energy plant. The sensor, based on the wide band gap semiconductor silicon carbide (SiC), is a catalytic gate field-effect device (Pt–SiO_2–SiC) that can detect hydrogen-containing species in chemically reactive, high-temperature environments. The hydrogen response of the device in an industrially robust module was determined under both laboratory and industrial conditions (1000 sccm of 350 °C gas) from 52 ppm to 50% H_2, with the sensor held at 620 °C. From our data we find that the hydrogen adsorption kinetics at the catalyst–oxide interface are well fitted by the linearized Langmuir adsorption isotherm. For hydrogen monitoring in a coal gasification application, we investigated the effect of common interferants on the device response to a 20% H_2 gas stream. Within our signal to noise ratio, 40% CO and 5% CH_4 had no measurable effect and a 2000 ppm pulse of H_2S did not poison the Pt sensing film. We have demonstrated the long-term reliability of our SiC sensor and the robustness of the sensor packaging techniques, as all the data are from a single device, obtained during 5 days of industrial measurements in addition to ∼480 continuous hours of operation under laboratory conditions.

Keywords: Sensors; Hydrogen; SiC; Combustion; High temperature; Coal gasification

1. Introduction

The economic and security impact of limited natural gas supplies has reinvigorated interest in the advancement of cost-effective, clean electricity production from coal. Gasification, or the production of synthesis gas (syngas), is the first step in an advanced, minimally polluting process for production of electricity from coal known as the integrated gasification combined cycle (IGCC) power plant. An IGCC plant produces syngas from coal, cleans the syngas and supplies it as fuel to a gas turbine operated in combination with a steam turbine to maximize thermal efficiency. Future power generation systems may include fuel cells as well to achieve higher power generation efficiencies. The gasification process uses steam reforming or partial oxidation of a hydrocarbon (or a combination of the two) to produce syngas, a mixture composed mostly of hydrogen, carbon monoxide, water vapor and carbon dioxide. For optimal operation, the use of syngas in advanced power production will require online monitoring of the syngas composition via an online gas sensing system that is reliable and can survive the harsh and chemically corrosive operating conditions within the coal gasifier. The desired gas sensors must function at temperatures up to 800 °C in the presence of gases containing significant amounts of hydrogen, carbon monoxide, carbon dioxide, methane, water vapor and hydrogen sulfide. Sensitivity, selectivity, response time for real-time monitoring and long-term stability are additional essential factors for the sensing system.

The wide bandgap semiconductor silicon carbide (SiC) is an attractive candidate for these applications due to the possibility of device operation up to at least 900 °C, high thermal conductivity (4.9 W/cm K), resistance to acidic and basic species, and the maturity of the SiC device fabrication technology [1,2]. Over the past decade SiC sensors have been shown to be sensitive to automobile exhaust and flue gases, including hydrogen, hydrocarbons, CO and NO_x [3–6]. Depending on the application various authors have used different semiconductor device structures such as capacitors, Schottky diodes, p–n diodes and field-effect transistors [1,2,7,8]. We have chosen to use an n-type metal–oxide–semiconductor (MOS) capacitive device on SiC as the high-temperature gas sensor. The sensor is a cat-

* Corresponding authors.
E-mail addresses: loloee@pa.msu.edu (R. Loloee), ghosh@pa.msu.edu (R.N. Ghosh).

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doi:10.1016/j.snb.2007.07.118

alytic gate field-effect device (Pt–SiO_2–SiC) that can detect hydrogen-containing species with ms resolution at 620 °C [9].

This paper is divided into two sections. First we present the result from our sensors operating under laboratory conditions with a sensor temperature of 620 °C and a room temperature gas flow. These measurements were made in a test bench at Michigan State University. We used five different concentrations of hydrogen gas (10.1%, 0.984%, 0.201%, 508 and 52.1 ppm, all with N_2 balance) as the reducers and 1.01% oxygen as the oxidizer (with N_2 balance). In the second part, we tested the performance of the sensor system in an industrial environment, with conditions nearer to those in a syngas facility. These measurements were made in the high performance reactor (HPR) facility at the Dept. of Energy's National Energy Technology Laboratory (DOE-NETL) in Morgantown, WV. We examined the response and selectivity of the sensor in a wide range of syngas composition, including a range of H_2 gas concentration (up to 50%) and common interferant gases such as CO, CO_2, CH_4 and H_2S. In this case the gas temperature was about 350 °C with a 1000 sccm gas flow rate. The sensor temperature was maintained at 620 °C, as in the laboratory experiments. The sensor was self-heated to a temperature far above that of the gas under interrogation for two reasons: first, to ensure that the sensor response would not be affected by fluctuations in the gas temperature and second to obtain a fast (ms) response to changes in flow composition.

The response of the Pt–SiO_2–SiC sensor to hydrogen is a multistep process. Following dissociation of molecular hydrogen at the heated Pt catalytic sensing film, atomic hydrogen diffuses through the catalyst and is adsorbed at the metal–oxide interface creating a dipole layer, which in turn shifts the device potential by an amount, ΔV. For our capacitive structures we fix a capacitance set-point and monitor the chemically induced change in potential as the sensor signal. The kinetics of hydrogen adsorption at the metal–insulator interface has been studied both experimentally and theoretically by a number of groups [10–17]. Standard models of the sensor response, ΔV, invoke an adsorption isotherm to determine the number of occupied adsorption sites. These include the Temkin isotherm [15], which predicts a logarithmic relationship between sensor signal and hydrogen concentration (typically in the 0–10% range) and the Langmuir isotherm [18]. Here we examine the applicability of both isotherms in terms of the hydrogen response of our sensor to a room temperature and 350 °C flowing gas stream.

2. Experimental

2.1. Sensor fabrication, characterization and measurement

The SiC field-effect gas sensors were fabricated on n-type 6H–SiC substrates with a 5 μm epitaxial layer (nominal doping of 2.1×10^{16} N/cm^3), grown on 3.5° miscut, highly doped (5×10^{18} N/cm^3) wafers. The gate oxide (~39 nm) was grown on 1 cm^2 SiC chips via dry oxidation at 1150 °C, followed by a 900 °C Ar anneal and a 2 h 1175 °C post-oxidation NO passivation anneal [19]. The Pt gates (100 nm thick) were sputtered directly onto the SiO_2–SiC chips using a dc magnetron sputtering at a substrate temperature of 350 °C and in a 2.5 m Torr Ar

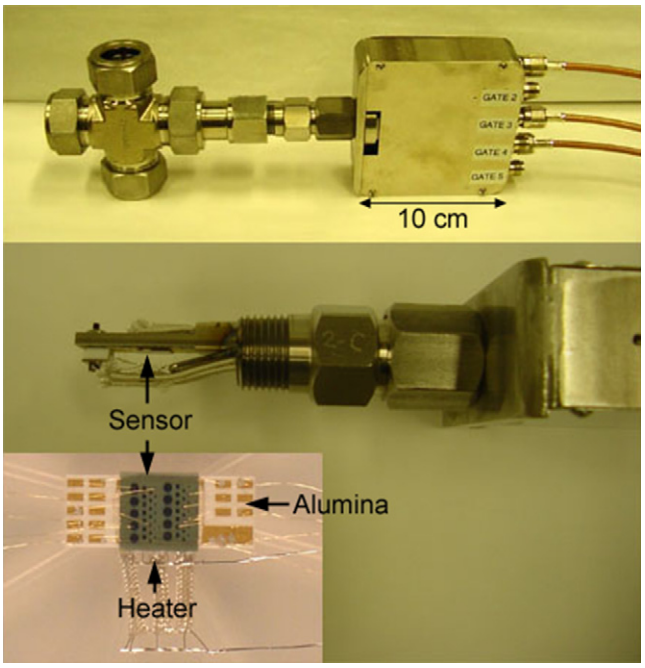

Fig. 1. Photographs of: (i) top panel—sensor test module with the electrical breakout box and (ii) bottom panel—the interior of the test module with a SiC sensor chip. Shown in the insert is the array of 52 sensors on a 1 cm^2 SiC chip mounted on an alumina header with three backside heaters.

atmosphere. Using a mechanical mask, we deposited an array of 52 gates (see Fig. 1 insert) on each chip with nominal diameters ranging from 200 to 1000 μm. Each chip was then glued onto a thermally conducting, electrically insulating alumina header using silver print. After connecting the Pt gates to the gold pads on the alumina header via wire bonding, the whole assembly was mounted inside a high-temperature sensor test module. The mounted chip can be heated up to 670 °C by three microheaters attached to the back of the alumina header.

Each Pt–SiO_2–SiC sensor was characterized via 1 MHz capacitance–voltage spectroscopy at 300–620 °C using a Boonton capacitance-meter (model 7200) with sensitivity of 1 pF. Details of the sample preparation and measurement techniques are in Ref. [20]. The C–V curves were taken under (i) ambient conditions, 99.999% purity mixtures of (ii) 1.01% oxygen in nitrogen and (iii) 10.1% hydrogen in an 80 sccm nitrogen gas stream. Prior to sensing measurements, the Pt catalytic gate was activated [2]. Activation took place by switching back and forth between oxidizing and reducing gases for several hours at a sensor temperature ≥620 °C. This procedure is required to obtain a fast and stable sensor response. All the devices on the 1 cm^2 sensor chip were activated simultaneously by flooding the entire chip with gas.

To use the device as a sensor, we use a feedback circuit to hold the capacitance constant, and monitor the gate bias voltage during gas exchange as the sensor signal [3]. We have developed a sensor control and data acquisition program for sensing measurements at industrial application sites that runs as an executable on any personal computer with a National Instruments GPIB data acquisition card. A graphical user interface allows the operator to choose the (i) sensor set-point or capacitance set-