Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 252 (2006) 7473–7486
applied surface science
www.elsevier.com/locate/apsusc

The influence of catalytic activity on the phase transition governed binary switch point of MISiC-FET lambda sensors

Helena Wingbrant *, Anita Lloyd Spetz

S-SENCE and Applied Physics, Linköping University, SE-581 83 Linköping, Sweden

Received 16 February 2005; received in revised form 1 September 2005; accepted 1 September 2005
Available online 28 October 2005

Abstract

A metal insulator silicon carbide field effect transistor (MISiC-FET) sensor with a catalytic metal gate is currently under development for detecting the lambda value, or air-to-fuel ratio, of gasoline exhausts. It has been noticed that a change from a low to a high signal level of the sensor occurs at a lambda value above 1.00, which is an oxidizing atmosphere. The exact location of the switch point depends both on the kind of gas and gas concentrations chosen to obtain a specific lambda value. The switch point would rather have been expected at 1.00, which is at stoichiometry, irrespective of the composition of the gas mixture. The origin of this phenomenon is studied here by exposing the sensor to lambda stairs while changing different operating parameters. An increase in catalytic activity has been observed to move the switch point of the device towards a lambda value of 1.00. A similar effect is achieved when decreasing the flow or increasing the temperature of operation of the device. The behavior is explained through the introduction of mass transport limitations in the measurement cell, and the difference in diffusion constants and sticking coefficients among the gases when reaction limitation prevails.

Keywords: MISiC-FET; Catalytic activity; Binary switch point; Phase transition; Lambda

1. Introduction

Since the introduction of the catalytic converter in the 1970s it has been of large importance to develop sensors that can measure the lambda value, or the air-to-fuel ratio, of the gasoline engine exhausts. The reason for this is that the catalytic converter does not reach its optimum efficiency unless the gas mixture is kept at stoichiometric conditions. The lambda value is defined as the air-to-fuel mass ratio in the exhausts before the catalytic converter divided by the air-to-fuel mass ratio at stoichiometry (Eq. (1)). Thus, the lambda

* Corresponding author. Tel.: +46 13 28 1710;
fax: +4613 28 8969.
E-mail address: helwi@ifm.liu.se (H. Wingbrant).

0169-4332/$ – see front matter
doi:10.1016/j.apsusc.2005.09.003

value in the exhausts equals 1.00 at stoichiometric conditions [1]:

$$\lambda = \frac{(m_{\text{air}}/m_{\text{fuel}})_{\text{real}}}{(m_{\text{air}}/m_{\text{fuel}})_{\text{stoich}}} \quad (1)$$

By utilizing a sensor that can detect lambda the composition of the exhaust gases can be controlled. A stoichiometric value of lambda is achieved through closed loop control. The lambda value is kept in an oscillating mode close to one, to increase the long-term stability of the catalytic converter.

Different types of sensors have been developed for this purpose throughout the years. The most commonly used lambda sensor in modern cars is ZrO_2-based and measures the O_2 concentration in the exhausts by means of oxygen conductivity through the material [2]. However, due to limitations in the speed of response and the sensitivity to thermo shock, the ZrO_2-based sensor cannot be used for cylinder-specific measurements or immediately at cold start. The problem at cold start arises from the fact that water from the combustion condenses on the cold exhaust pipe walls, and these droplets may be carried downstream and hit the fragile lambda sensor if it is heated to its operating temperature. All in all, these problems motivate the development of other types of lambda sensors that are faster and more robust. Such a sensor can be realized by using the $SrTiO_3$-based metal oxide sensor, developed by Siemens, which has been demonstrated to respond fast enough to changes in the composition of exhaust gases to be used for cylinder-specific measurements [3]. Another alternative is to use the field effect sensor with a catalytic metal gate and a wide bandgap material such as SiC [4–12] or GaN [13] as the semiconducting substrate material. Only the SiC-based field effect device will be treated in this publication.

The sensitivity of a metal insulator silicon carbide (MISiC) capacitor field effect device to lambda was first reported by Baranzahi et al. [4]. Since then both SiC-based Schottky diode devices, demonstrated e.g. by Hunter et al. [14], and transistor type SiC-based devices, first tested by Svenningstorp et al. [15], have been developed. The sensor has been shown to have a short response time [5,6,16] and has been used for cylinder-specific measurements [7,8]. Since it is based on silicon carbide, which is a robust material, it is suitable for cold start lambda sensing, and its ability to work as a cold start lambda sensor has been studied earlier [9]. The MISiC field effect device has been observed to give either a binary [4–7] or a linear [8,9] response to lambda depending on the measurement circumstances, e.g. the temperature of operation or the catalytic activity in the measurement cell [10]. This makes it possible to choose whether to use the sensor as a binary or a linear device. In most cases a sensor with a linear response to lambda is desired for closed loop control, since it gives a more precise control of the lambda value.

When the sensor was tested for the cold start application it was observed that the binary or linear behavior also depended to a large extent on the pre-treatment of the device [11]. The change from a binary to a linear behavior was correlated to the restructuring and the following decrease in catalytic activity of the gas-sensitive gate metal surface when exposing the sensor to a harsh environment. This was in accordance with earlier findings presented by Baranzahi et al. [10] regarding the influence of catalytic activity in the measurement cell on the sensing characteristics. During laboratory measurements it was also observed that the sensors, when being exposed to lambda stairs, had a binary shift at a lambda value of 1.08 [9,11]. This was rather expected at 1.00, that is, at stoichiometry, since there is a large change in the composition of the gas species in the ambient at this lambda value. Moreover, it was noticed that the lambda value where the switch point occurred depended on the individual gas components and concentrations used to achieve the different values in the lambda stairs. In engine measurements the switch point also occurred at a lambda value above 1.00, but closer to stoichiometry than in the laboratory experiments [9]. Baranzahi et al. [10] observed that the binary switch point can be moved from stoichiometry by either lowering the operating temperature or decreasing the catalytic metal area in the measurement cell, which indicates that a switch point that deviates from a lambda value of 1.00 is due to the catalytic activity in the measurement cell not being high enough. However, during the experiments performed by Baranzahi et al. [10] a dependence of the gas composition used for achieving a certain lambda value had not been seen, although it was tested, and the binary switch point of the devices was most often