

Fast Chemical Sensors for Emission Control

by Anita Lloyd Spetz, Peter Tobias, Lars-Gunnar Ekedahl, Per Mårtensson, and Ingemar Lundström

Consideration of environmental issues is constantly growing. This brings about a potential market for more sophisticated control of emissions from automobiles and more advanced on-board diagnosis. There is also a growing interest in zero emission power plants and in stricter regulation of other emission sources in industry. One of the important prerequisites for this development is the existence of reliable chemical sensors for combustion control.

Chemical sensors operating at high temperatures that are fast enough to follow millisecond changes between an oxidizing and reducing ambient can be used for cylinder-specific monitoring of petrol car engines. A high operating temperature also enables monitoring in other aggressive environments like flue gases. Metal oxide sensors based on TiO_2 ¹ or ZrO_2 are today successfully used for combustion engine control. Thin film metal oxide sensors based on SrTiO_3 have been shown to be fast enough for cylinder-specific monitoring.² The metal oxide sensor response is due to a change in the oxygen concentration on the sensor surface and diffusion of oxygen into the bulk of the sensor material. Gas molecules that react with oxygen on the sensor surface, like carbon monoxide, will thus lower the sensor signal; while nitric oxide when decomposing will increase the amount of oxygen on the surface and thus, increase the sensor signal.

Gas-sensitive field-effect devices based on silicon with a catalytic gate of palladium were first reported in 1975 by Lundström et al.³ These sensors can be operated to about 250°C and are employed in commercially-available leak detectors⁴ and so called "electronic noses."⁵ Field-effect devices based on silicon carbide with a platinum or palladium gate were made in 1992^{6,7} and have been operated to 1000°C.⁸ The detection principle for metal oxide silicon carbide capacitors and Schottky diodes (MISiC sensors for short) is based on hydrogen atoms delivered from the decomposition of gas molecules on the surface of the catalytic metal, as schematically shown in Fig. 1. The hydrogen atoms diffuse in less than a few microseconds through the metal and give rise to a polarized layer at the metal insulator interface. The polarization changes the position of the capacitance-voltage (CV) curve of a capacitor to a lower flat band potential. Similarly, for a Schottky diode the current-voltage (I-V) curve changes toward a lower threshold voltage in a reducing environment (see Fig. 2). Water and carbon dioxide are produced through chemical reactions on the sensor surface, which make the sensor response reversible. The large reaction rates at high temperatures and the short desorption time constants for hydrogen at the metal insulator interface are the reasons for a gas response in the millisecond range. The efficient combustion of gases on the catalytic metal also makes the sensors self-cleaning, and thus, highly resistant to poisoning.

Both 4H and 6H SiC materials have been used for the processing of capacitors and Schottky diodes.⁸ The sensors had gates of 100 nm Pt on top of either 10 nm TaSi_x or 1 nm Ta, as shown in Fig. 2. The Schottky diodes were mounted on

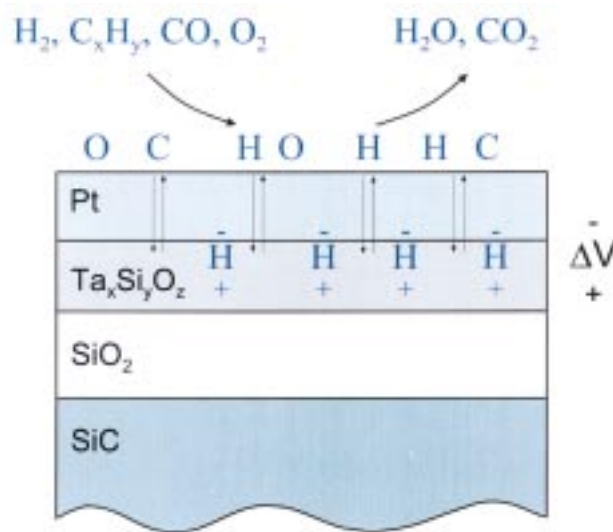


Fig. 1. Schematic drawing of a MISiC sensor. Capacitors have an insulator of about 100 nm and Schottky diodes have a native oxide of about 1 nm thick. The buffer layer of tantalum silicide oxidizes partly during operation.

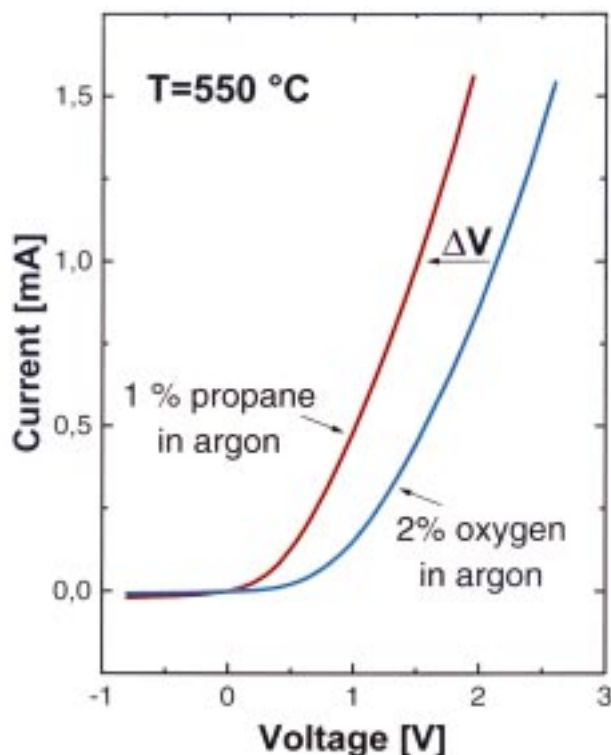


Fig. 2. I-V curve of a Schottky diode in two different ambients. The voltage at a constant current is monitored as the time-resolved sensor signal. The voltage change, ΔV , at a constant current gives the response to the reducing gases.

heated ceramic rods to enable direct monitoring, for example in exhaust gases, as shown in the photo in Fig. 3. The capacitors were mounted in a heated furnace in a quartz tube on a platinum foil and contacted by a platinum probe. A Boonton bridge at 1 MHz was used for the capacitance measurements, while the current measurements of Schottky diodes were performed with very simple electronics. The voltage at a constant capacitance, or at a constant current, gives a time-resolved sensor signal. The gas response, ΔV , is defined as the differ-

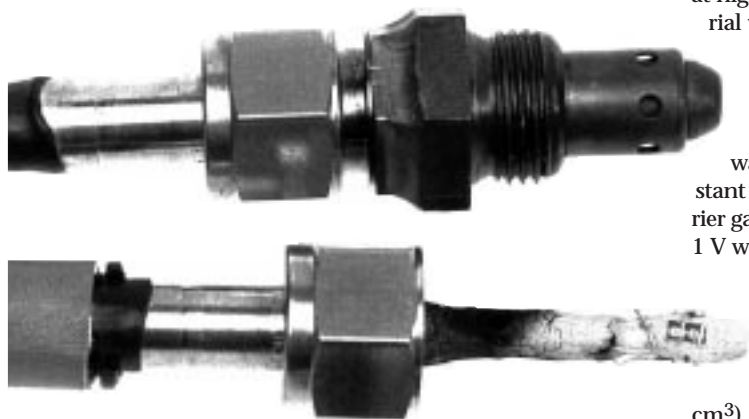


FIG. 3. Photo of a ceramic rod with two sensors glued at the tip. The top picture shows the shielding used to protect the sensor.

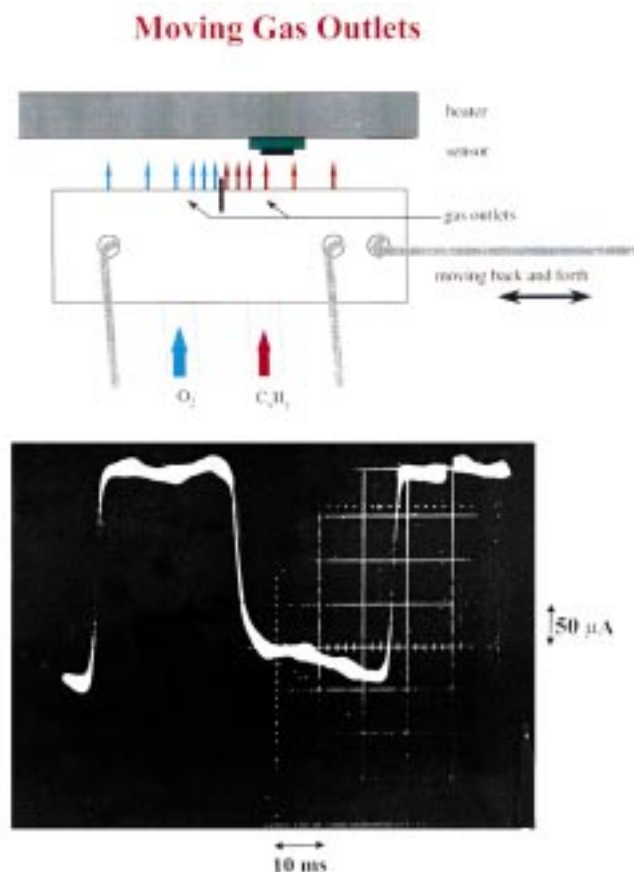


FIG. 4. (top) Schematics of the moving gas outlets. The spacing of the arrows indicates that the gas flows were larger toward the center of the moving outlets; (bottom) the sensor signal obtained when the gas ambient is changed with moving gas outlets. In this measurement the current at a constant voltage is observed on an oscilloscope. An ambient of 3% butane in Ar gives a larger current than 5% oxygen in Ar. Sensor temperature, about 550°C.

ence between the signal in oxygen and the signal in a reducing ambient, as indicated in Fig. 2.

The processing technology in silicon carbide is still not mature enough for the fabrication of high-temperature field-effect transistors, which probably would be an even better sensor device.

Fast Speed of Response at High Temperature

We have observed that capacitors can generally be operated at higher temperatures than Schottky diodes. The 4H SiC material with a band gap of 3.2 eV allows a higher operating temperature than the 6H material with a band gap of 2.9 eV. We have used 4H SiC for capacitors, where the epilayer was grown in a hot wall CVD reactor.⁹ For these devices the CV characteristics could be measured at 1000°C.⁸ It was also possible to measure the voltage change at a constant capacitance when propane pulses were mixed into a carrier gas of oxygen in argon. The response to propane was about 1 V with time constants below 100 ms.

It is important to accurately determine the time constants for these devices. Standard valves that would switch the gas mixture in the order of milliseconds are not available. By using automotive injection valves in front of a small heated chamber (volume of 6 cm³), response times, t_{90} , below 10 ms were estimated for SrTiO₃ devices.² Another approach is to use moving gas outlets to rapidly change the gas atmosphere over the sensor surface. The sensor is exposed to gases from two outlets, one with a reducing and one with an oxidizing mixture, respectively, as shown in Fig. 4.¹⁰ The outlets are moved back and forth below the sample, typically at a frequency of 15 Hz. The sensor signal, in this case measured as the current change at a constant applied voltage, is recorded on an oscilloscope. Time constants for the gas response of a few milliseconds can be estimated from results like that in Fig. 4.

Cylinder Specific Monitoring

The fast speed of response, the sensitivity to reducing gases, and the high operating temperature of the sensors were utilized for cylinder-specific combustion monitoring.¹¹ Schottky diode sensors operated at about 700°C were placed in the manifold of a four cylinder 1.6 liter petrol engine. The engine was mounted on a test bench. The MISiC sensor was positioned about 68 cm downstream from the engine, where the two branches of the manifold are joined. Four reference oxygen sensors (the so-called universal heated exhaust gas oxygen, UHEGO, sensor or λ -sensor) were used for the calibration of each cylinder. In the experiments one of the four cylinders had a deviating air-to-fuel mixture. This cylinder was given a too-rich (excess fuel) or a too-lean (excess air) air-to-fuel ratio, while the other three cylinders were running close to normal. Figure 5 shows four different measurements with cylinder 1, 3, 4, or 2, respectively, running too rich. The sensor signal decreases sharply at the ignition of the deviating cylinder (which is expected when the gas ambient becomes more reducing, as shown in Fig. 2).

The results in Fig. 5 suggest that MISiC devices may be an interesting complement to presently used combustion monitors, since one sensor is capable of separating the exhaust pulses from different cylinders. However more work is needed before the devices are ready for applications in cars, particularly regarding their long term stability and mode of operation in the exhaust of a car.

(continued on next page)

Kinetic Phase Transitions

The fast responses observed in Fig. 5 are associated with a chemical transition on the catalytic metal surface, which goes from being covered with oxygen to hydrogen (and eventually hydrocarbon/carbon) at a given fuel/air (oxygen) ratio. The fast transition between a hydrogen or oxygen-covered surface gives a “binary” signal, which has basically only two levels, a high voltage level in oxygen and a low voltage level in hydrogen. This is due to mass transport limitations of the reactants toward the sensing surface. The switching phenomenon is called a kinetic phase transition.¹² A special case of mass transport limitation occurs when the catalytic combustion in the sensor housing and on the sensor surface is so effective that the whole sensor housing is depleted of one kind of molecule. The transition occurs now when the ratio of reducing to oxidizing molecules in the gas phase is stoichiometric. This condition is called an injection limitation^{13,14} or thermodynamic equilibrium¹⁵ since the condition is equivalent to a situation where the gas mixture is in thermodynamic equilibrium. For a MISiC sensor the signal changes from a large to a small value when the metal surface switches from being oxygen to hydrogen covered. This occurs for example during the cylinder specific monitoring shown in Fig. 5.

Kinetic phase transitions on MISiC sensor surfaces in hydrogen and oxygen mixtures have been studied in some detail.¹⁴ The transition point changes with temperature, since surface reactions are temperature dependent and thus, affect the degree of transport limitations toward the surface. The transition point also changes with flow rate and becomes injection-limited at sufficiently large temperatures and/or low flow rates. The details of the switching behavior depend also on the total amount of catalytic surface exposed in the sample cell.¹⁴ At injection limitation, the sensor signal changes sharply at $\alpha=(H_2/2O_2)=1$ as shown in Fig. 6.

At lower temperatures both diffusion and reaction rate limitations influence the position of the transition point.^{12,14} That is, the signal of this binary sensor changes to its lower level generally at a lower hydrogen concentration than given by $\alpha=1$. The switching behavior is understood from the kinetics of the reactions on the catalytic metal surface where adsorbed hydrogen and oxygen atoms participate in water production reactions, but also block the dissociation of hydrogen and oxygen molecules impinging on the surface.

The fraction of occupied surface sites or the coverage by hydrogen atoms, Θ_H , oxygen atoms, Θ_O , and OH-groups, Θ_{OH} , on the catalytic metal surface is determined by rate equations of the following form:

$$d\Theta_H/dt = 2f_{H_2}(1-\Theta_H-4\Theta_O-4\Theta_{OH}) - r_1\Theta_O\Theta_H - r_2\Theta_{OH}\Theta_H - d_1\Theta_H^2 \quad [1]$$

$$d\Theta_O/dt = 2f_{O_2}(1-\Theta_H-4\Theta_O-4\Theta_{OH})^2 - r_1\Theta_O\Theta_H \quad [2]$$

$$d\Theta_{OH}/dt = r_1\Theta_O\Theta_H - r_2\Theta_{OH}\Theta_H \quad [3]$$

The last term in Eq. 3 is the water formation rate. The f 's are the reactive normalized molecular fluxes toward the metal surface, i.e., the number of molecules which are dissociated per second per surface site. The difference in the order of the blocking of hydrogen and oxygen dissociation, respectively, is due to a difference in the mobility of hydrogen and oxygen atoms on the surface.^{12,14} Rate constants are r_1 , r_2 and d_1 , where d_1 describes the spontaneous formation of hydrogen molecules on the metal surface. The factor four in the equations originates from the assumption that one adsorbed oxygen atom (or OH group) blocks four surface sites. The

details of the water production reactions may differ from those described by the equations above.¹⁶ Furthermore, we may neglect the spontaneous formation of hydrogen molecules at the transition point where in principle all dissociated hydrogen and oxygen molecules end up in water molecules. The coverage of Θ_O , Θ_{OH} , and Θ_H are small at the transition point, which then occurs at: $2f_{O_2} \approx f_{H_2}$. Without mass transport limitations the reactive molecular flux, at a given temperature, is proportional to $Cs/M^{1/2}$ where C is the concentration of the molecules in the gas phase, M the molecular mass and s the dissociation probability (i.e., reactive sticking coefficient). During conditions of mass transport limitation, the concentration of the molecules varies to the distance to the surface. The molecular flux toward the surface is (at the transition point) controlled either by diffusion of molecules to the sensing surface and/or injection of molecules into the sample cell. In the last case the transition occurs at the stoichiometric ratio, since the fluxes become proportional

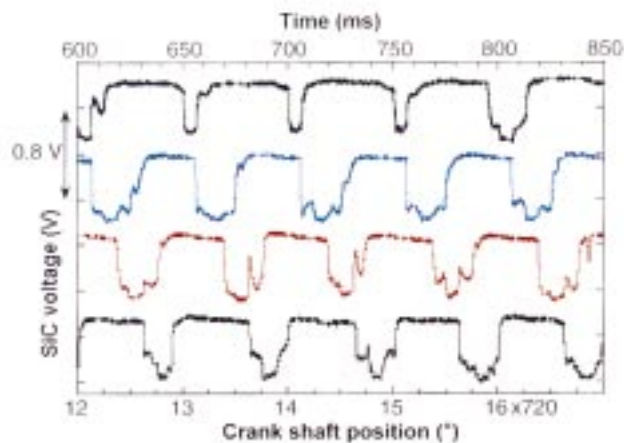


Fig. 5. Four measurement sequences for one MISiC sensor at 700°C positioned in the exhaust manifold of a 4 cylinder 1.6 liter petrol engine. One cylinder is rich (excess fuel), and the other three are running normally. From top to bottom: The rich cylinder is 1,3,4,2 respectively. Engine speed is 2400 rpm. The four curves are obtained sequentially in time, but are plotted displaced and related to the crank shaft position to illustrate that the rapid change in the sensor response occurs when the rich cylinder ignites.¹¹

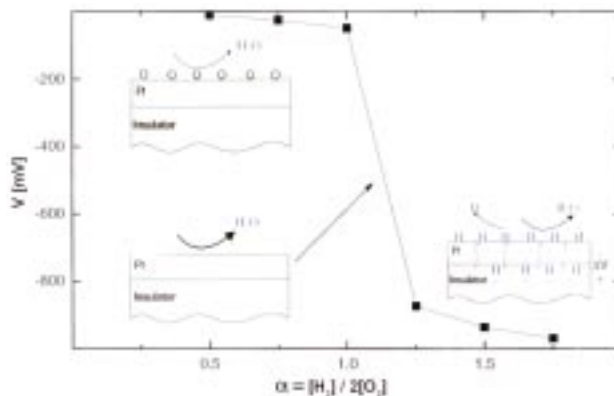


Fig. 6. The signal of a MISiC capacitor at 665°C to an increasing hydrogen concentration in a mixture of 1% oxygen in argon. The sensor signal in 20% oxygen is set to 0V. Gate composition: 100 nm Pt - 10 nm TaSix - 100 nm SiO₂. The curve was based on data in Ref. 14. The inserts show schematically the coverages and water production rates on the platinum surface for different regions of the hydrogen to oxygen ratio. The water production rate is at a maximum at the transition point. The hydrogen covered surface gives a large decrease in signal compared to the oxygen covered surface, that is a large sensor response.

to the injected concentration of the molecules and an equivalent injection drift velocity, which is equal for all types of molecules. Thus the MISiC sensors, when used for combustion engine control, should be operated in the injection-controlled regime.

Calculations with reasonable values of the rate constants for the surface reactions, injection velocities into the sample cell and for the hydrogen adsorption sites at the Pt-insulator interface show that submillisecond response times are possible. The sensor response above and below the transition point is determined by the details of the chemical reactions on the metal surface and also depends strongly on the temperature, which can be utilized to give more detailed information about exhaust gases as described below.

Exhaust Diagnosis

The difference in concentrations between oxidizing and reducing species in a gas mixture can be defined by a lambda factor (λ).¹⁷ The gas mixture contains excess reducing species when $\lambda < 1$ and contains excess oxidizing species for $\lambda > 1$. Close to one, λ can be approximated by

$$\lambda = 1 + (2[O_2] + [NO] - \sum_{i=1}^n (2x+y/2)[C_xH_y] - [CO] - [H_2])/20 \quad [4]$$

where the gas concentrations are given in percent. During combustion at the stoichiometric ratio ($\lambda=1$) where the reducing

species matches the oxidizing species, the gas mixture is ideally converted to only water, nitrogen, and carbon dioxide.

A two-level experimental design¹⁸ was used to investigate the influence of the different components in synthetic exhausts on the sensor signal. Capacitor devices placed on a 2x3 cm² platinum foil in a furnace were used for these measurements. The sensors were exposed to mixtures containing propane (C₃H₆), carbon monoxide, hydrogen, oxygen, nitric oxide, water, as well as gases that are supposed to be inert, nitrogen and carbon dioxide. (For typical gas concentrations see Ref. 19.) The concentration of CO, NO, H₂, and C₃H₆ was either at a high or a low level. In this way the sensors were exposed to 16 (2⁴) different gas mixtures, which were randomly and repeatedly generated. The λ value was kept constant by adjusting the oxygen concentration. The effect of a single gas component is calculated as the difference between the average of the sensor signals for all mixtures where the concentration of this component is high, and the average of the signals where the concentration of this component is low. This gives the effect of this component in all possible variations of the four gases.

Figure 7a shows an example of the effect of a single gas component in the synthetic exhaust gas at one temperature (500°C) for five different λ -values calculated according to Eq. 4. In summary, the following observations are made at different temperatures, some of which are further illustrated in Fig. 7b. At 300°C, only hydrogen shows an effect. This means that the sensor signal significantly decreases when the hydrogen concentration is changed from a low to a high level (at a constant λ), but not when the other concentration levels are changed between the low and high concentration levels. This is valid for all λ values, regardless of whether the oxidizing species or the reducing species are in excess. At 400°C, the effects are overall rather small; only carbon monoxide has a small effect on the lean side. At 500°C, hydrocarbons and NO significantly decrease the sensor signal, but again only on the lean side. The impact of hydrocarbons at the higher temperature is probably due to the fact that the hydrogen splitting from the molecules becomes more effective at this temperature. The negative sign of the effect of NO indicates that it is a less effective oxidizing agent than oxygen. At 600°C, no significant influence of the gas composition could be identified, as expected from the more effective combustion on the sensor surface at this temperature. The sensor just shows a binary signal, low in excess reducing gases ($\lambda < 1$) and high in excess oxidizing species ($\lambda > 1$).

Figure 7b suggests how to analyze slightly oxidizing gas mixtures. For example for a mixture with a λ of 1.02, three sensors with temperatures of 300, 400, and 500°C show very different sensitivity profiles. Approximately, the first sensor measures hydrogen, the second CO, and the third hydrocarbons. A sensor operating at 600°C is also needed to keep track of the λ value. This indicates that an array of sensors operating at different temperatures can be used for exhaust diagnosis.

Conclusions

Chemical sensors with catalytic metal gates operated at high temperatures provide new possibilities for emission control. Their operation principle is very simple and is based on phenomena with very small time constants occurring on surfaces and at interfaces, enabling very fast responses. They demonstrate also an interesting combination of material physics, heterogeneous catalysis, and electronic devices. Thus, MISiC sensors are not only applicable as combustion monitors and for emission control, but will also create new knowledge about catalytic reactions at high temperatures at atmospheric pressure. ■

(continued on next page)

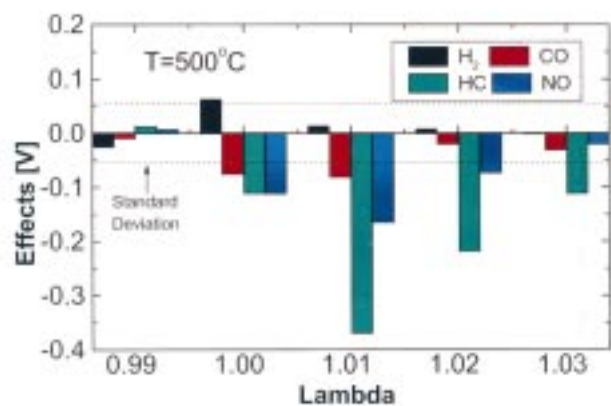


Fig. 7a. The effects on the signal of a MISiC sensor (capacitor with a gate composition of 100 nm Pt - 10 nm TaSi_x - 100 nm SiO₂) of four of the gases in a gas mixture at five λ -values at 500°C. The λ -value of the gas mixture is adjusted by varying the oxygen concentration. The sensor is placed in a furnace.

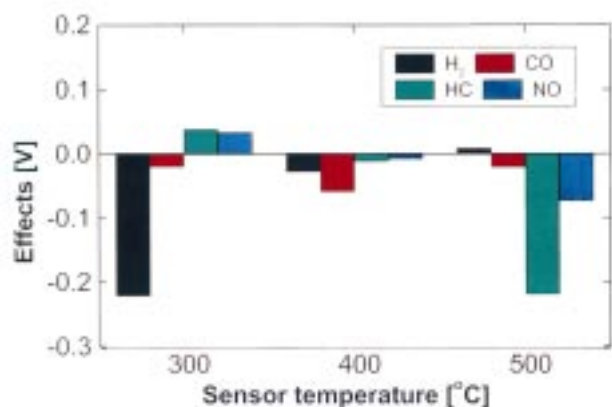


Fig. 7b. Sensitivity profiles of the MISiC sensor at three different temperatures, when the ambient is kept at a constant λ value of 1.02 (excess of oxidizing molecules) by adding the appropriate amount of oxygen.

Acknowledgments

Our research on high temperature chemical sensors based on silicon carbide is supported by grants from the Swedish National Board for Industrial and Technical Development, and Swedish Industry through the center of excellence, S-SENCE, and the Swedish Research Council for Engineering Sciences. The work described was carried out partly at the Laboratory of Applied Physics at AB Volvo Technological Development in Göteborg, Sweden (simulated exhaust measurements) and at Mecel AB in Åmål, Sweden (cylinder specific monitoring). The contribution by Dr. Amir Baranzahi to the results presented in this paper is greatly acknowledged.

References

1. E. M. Logothetis and W. J. Kaiser, *Sensors and Actuators*, **4**, 333 (1983).
2. H. Meixner, J. Gerblinger, U. Lampe, and M. Fleischer, *Sensors and Actuators B*, **23**, 119 (1995).
3. I. Lundström, M. S. Shivaraman, C. M. Svensson, and L. Lundkvist, *Applied Physics Letters*, **26**, 55 (1975).
4. Sensistor AB, Engelbrektsgratan 13, Box 76, S-581 02 Linköping, Sweden.
5. Nordic Sensor Technologies AB, Teknikringen 6, Mjärdevi Science Park, S-583 30 Linköping, Sweden.
6. A. Spetz, A. Arbab, and I. Lundström, *Book of Abstracts Euroensors VI*, San Sebastian, Spain, October 5-7, 9, (1992).
7. G. W. Hunter, P. G. Neudeck, G. D. Jefferson, G. C. Madzar, C. C. Liu, and Q. H. Wu, *Fourth Annual Space System Health Management Technology Conference, Cincinnati, OH*, NASA Technical Memorandum, **106141** (1992).
8. A. Lloyd Spetz, A. Baranzahi, P. Tobias, and I. Lundström, *Physica Status Solidi (a)*, **162**, 493 (1997).
9. E. Janzén and O. Kordina, in *Silicon Carbide and Related Materials*, Kyoto, Japan, IOP Publishing Ltd., **142**, chapter 4, 653 (1996).
10. P. Tobias, A. Baranzahi, A. Lloyd Spetz, O. Kordina, E. Janzén, and I. Lundström, *IEEE Electr. Dev. Lett.*, **18**, 287 (1996).
11. A. Baranzahi, P. Tobias, A. Lloyd Spetz, I. Lundström, P. Mårtensson, M. Glavmo, A. Göras, J. Nytomt, P. Salomonsson, and H. Larsson, *SAE Technical Paper Series 972940, Combustion and Emission Formation in SI Engines, (SP-1300)*, 231 (1997).
12. V. P. Zhdanov and B. Kasemo, *Surf. Sci. Rep.*, **20**, 111 (1994).
13. M. Rinnemo, Thesis, Gothenburg Studies in Science and Technologies, Sweden, ISBN 91-7197-333-8 (1996).
14. A. Baranzahi, P. Tobias, A. Lloyd Spetz, P. Mårtensson, L.-G. Ekedahl, and I. Lundström, *J. Electrochem. Soc.*, **145**, 3401 (1998).
15. A. D. Brailsford, M. Yussouf, E. M. Logothetis, and M. Shane, *Sensors and Actuators B*, **24-25**, 362 (1995).
16. S. Ljungström, B. Kasemo, A. Rosén, T. Wahnström, and E. Fridell, *Surf. Sci.*, **216**, 63 (1989).
17. E. M. Logothetis, in *Proceedings of the 8th Automotive Materials Conference*, Vol. 1, p. 281, American Ceramics Society, Westerville, OH (1980).
18. G. E. P. Box, W. G. Hunter, and J. S. Hunter, *Statistics for Experimenters*, John Wiley & Sons, New York (1978).
19. P. Tobias, P. Mårtensson, A. Baranzahi, P. Salomonsson, L. Åbom, L. Lundström, and A. Lloyd Spetz, *Sensors and Actuators B*, **47**, 125 (1998).

About the Authors

Anita Lloyd Spetz, Peter Tobias, Lars-Gunnar Ekedahl, Per Mårtensson, and Ingemar Lundström are affiliated with the Division of Applied Physics and the center of excellence, S-Sence (Swedish Sensor Center) at Linköpings University. **Dr. Anita Lloyd Spetz** is the head of the group working on high temperature chemical sensors in which **Peter Tobias** is a PhD student. **Dr. Lars-Gunnar Ekedahl** is a professor of surface chemical physics and head of a research group working in heterogeneous catalysis. **Dr. Per Mårtensson** was until the fall of 1998 the director of S-Sence. He is now the director of research and development of electronic noses at Nordic Sensor Technologies. **Dr. Ingemar Lundström** is professor and head of the Division of Applied Physics.