A Pt/Ga_2O_3-ZnO/SiC Schottky Diode-Based Hydrocarbon Gas Sensor

Adrian Trinchi, K. Galatsis, W. Wlodarski, and Y. X. Li

***Abstract*—In this paper, a novel metal-reactive insulator-silicon carbide device with a catalytic layer for hydrocarbon gas-sensing is presented. This structure, employed as a Schottky diode, utilizes sol-gel prepared Ga_2O_3–ZnO layer as the reactive insulator. The sensor has been exposed to propene gas, which lowers the barrier height of the diode. The responses were stable and repeatable at operating temperatures between 300 and 600 °C. The response to propene in different ambients was examined. The effect of diode bias has been investigated by analyzing the sensors response to various propene concentrations when held at constant currents of 2 and 8 mA.**

***Index Terms*—Ga_2O_3, propene, Schottky diode, silicon carbide (SiC), zinc oxide (ZnO).**

I. INTRODUCTION

SINCE the first report of the sensitivity toward hydrogen and ammonia of the Pd metal-oxide-demiconductor (MOS)-based structure by Lundström *et al.* [1] over 25 years ago, research in the development of gas-sensitive MOSFETs, MOS capacitors and Schottky diodes has increased dramatically. Many of such devices are based on silicon substrates whose operating temperature is limited to temperatures below 250 °C [2], rendering them incapable of being used for gas-sensing applications in harsh environments.

Wide band-gap semiconductors, such as diamond [3] and silicon carbide [4], are more suitable for high temperature gas-sensing applications. Silicon carbide (SiC) has many favorable properties for harsh environment hydrocarbon sensing. These include a band gap of 3.02 eV (as compared to 1.1 eV for silicon), a high breakdown electric field and a strong affinity to hydrocarbons [5]. Schottky diode gas sensors based on SiC can provide rapid detection of low gas concentrations (less than 5 ppm) and can operate at temperatures as high as 900 °C.

By employing high temperature (> 500 °C) sensors, combustion processes can be directly and more accurately monitored. This places great demands on the sensors, having to withstand high temperatures and rough environments over long periods. For instance, automotive exhaust sensors for cylinder specific combustion engine control should be capable of operating at 700 °C for at least 4000 h. Sensors currently used for these applications are lambda sensors, which monitor oxygen concentrations. These sensors are based on conductivity changes of semiconducting metal oxides like zirconium dioxide and titanium dioxide [6].

Schottky diodes are advantageous for gas-sensing applications due to the simple electrical circuitry required to operate them. The simplest SiC Schottky diode-based gas sensor is one that consists of a catalytic metal deposited on the semiconducting SiC. The hydrogen and hydrocarbon gases dissociate on the catalytic metal surface and diffuse through the metal/semiconductor interface. This results in a dipole layer that changes the Schottky diode's electrical properties in proportion to the concentration of gas [7].

The current focus of SiC-based Schottky diode gas sensors are metal-reactive insulator-SiC (MRISiC) devices. A reactive insulator (typically a metal oxide layer) is selected for its reactivity to the target gas. The metal oxide reactive insulator layer is deposited between the SiC and catalytic metal. Such devices can offer increased sensitivity, selectivity, and stability [8].

The binary metal oxide of Ga_2O_3–ZnO was chosen as the reactive insulator material. Ga_2O_3 has been reported for monitoring hydrocarbons and hydrogen at operating temperatures above 700 °C [9]. The addition of the ZnO reduces the working temperature of the semiconducting Ga_2O_3.[10] Furthermore, Kalantar-zadeh *et al.* [11] reported the gas-sensing properties of ZnO toward hydrocarbons, whereby it was found that the material proved to be highly sensitive to concentrations of propane below 100 ppm.

The catalytic metal selected was platinum, which chemically adsorbs the hydrogen or hydrocarbons on to the surface. Once there, the hydrogen splits into separate H atoms chemically bound to the platinum contact [12].

In this paper, we investigate the propene (C_3H_6) gas-sensing performance of Pt/Ga_2O_3-ZnO/SiC Schottky diodes. Their electrical response has been measured at operating temperatures from 300 °C to 600 °C under different forward bias conditions and in different ambient gases.

II. EXPERIMENTAL PROCEDURE

A. Sample Preparation

The Pt/Ga_2O_3-ZnO/SiC MRISiC devices were fabricated on nitrogen-doped ($1.56 \times 10^{18}/\mathrm{cm}^3$) n-type 6H-SiC wafers (Sterling Semiconductor, USA). The wafers were 254-μm thick and had a resistivity of 0.07 $\Omega \cdot$ cm.

Manuscript received October 17, 2002; revised June 3, 2003. This work was supported by the Cooperative Research Centre (CRC) for Microtechnology, PO Box 218, Hawthorn, VIC 3122, Australia. The associate editor coordinating the review of this paper and approving it for publication was Dr. Lina Sarro.

A. Trinchi, K. Galatsis, and W. Wlodarski are with the School of Electrical and Computer Engineering, RMIT University, Melbourne, Australia (e-mail: avt@ieee.org).

Y. X. Li is with the School of Electrical and Computer Engineering, RMIT University, Melbourne, Australia, and also with the State Key Lab of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Shanghai, China.

Digital Object Identifier 10.1109/JSEN.2003.817670

1530-437X/03$17.00 © 2003 IEEE

The cleaning procedure commenced with an initial washing of the wafers in acetone for 5 min to remove any dust particles from the surface. This was followed immediately by copious rinsing in *iso*-propanol and deionized (DI) water. The native oxide on the wafer was removed by etching in HF (40%) $+H_2O$, 1 : 1, for 5 min. Thereafter the wafer was rinsed in DI water, and then blown dry in nitrogen at room temperature.

B. Device Fabrication

An Oohmic contact was formed on the unpolished side of the SiC wafer by photolithography employing the lift-off technique. The contact consisted of 850 Å of Ti, 250 Å of Pt, and 1000 Å of Au, deposited by e-beam evaporation. The 250-Å layer of platinum forms a diffusion barrier between Ti and Au, preventing them from forming an alloy during the annealing process. The contact was then annealed in nitrogen for 30 min at 450 °C in a similar procedure to that in [13]. The contact test structure was employed to characterize the contact, which proved to be Ohmic above 700 °C.

To realize the reactive insulator Ga_2O_3-ZnO thin films, the sol-gel process was employed. Precursor solutions of gallium *iso*-propoxide ($Ga(OC_3H_7^i)_3$, Chemat Technology, Inc., USA) and zinc acetyleacetonate hydrate ($[CH_3COCH = COCH_3]_2Zn \cdot H_2O$, Sigma-Aldrich, USA) were mixed to achieve solutions of gallium and zinc oxide. The solutions were prepared under a nitrogen atmosphere and were then spun onto the polished side of the SiC at 3000 rpm for 30 s. The thin films were then annealed at 600 °C for 1 hour in air. The film thickness, measured by ellipsometry, was approximately 90 nm.

Following the deposition of the Ga_2O_3-ZnO reactive insulator, a circular pad of platinum was deposited on the thin film by electron beam evaporation. This platinum layer forms the Schottky contact. The pads had a diameter of 1.5 mm and a thickness of 700 Å. A schematic drawing of the device is shown in Fig. 1 below.

C. Film Surface Characterization

An Escalab MkII (VG Scientific), equipped with a five-channeltron detection system and a standard Al $K\alpha_1$ excitation source ($hv = 1486.6$ eV) was employed for the X-ray photoelectron spectroscopy (XPS) experiments. Furthermore, selected-area depth profiles were acquired by using a 2.0-keV energy Ar^+ beam, rastered over an area of the window in the Au mask. In selected-area mode, the photoelectrons were collected from the sample area of diameter 1 mm. The secondary electron images were obtained by using a Cambridge Instruments 360 scanning electron microscope (SEM).

D. Electrical Measurements

The sensors were placed in a multi-channel gas calibration system. This system allows gases to be mixed and different concentration ratios of analyte gases to be exposed to the sensors. The sensors were mounted in a small Teflon chamber sealed with a quartz lid. A stainless steel foil was used for the back contact of the sensor, while the Pt surface was contacted with a needle probe. Forming a contact to the catalytic Pt layer proved difficult, since surface welding of Pt ribbons were found not to be strong enough and the welding easily damaged the surface of the diode. An alumina micro heater was placed beneath the sensor to control the operating temperature. This heater was controlled by a regulated dc power supply. The heater temperature could be varied between room temperature and 600 °C.

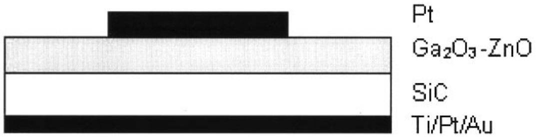


Fig. 1. Schematic diagram of the Pt/Ga_2O_3-ZnO/SiC Schottky diode-based hydrocarbon sensor.

TABLE I
XPS COMPOSITIONAL ANALYSIS (AT. %) OF THE Ga_2O_3-ZNO THIN FILMS ANNEALED AT 600 °C

Ga 2p^3	Zn 2p^1	O 1s (Ga)	O 1s (Zn)	C 1s
21.7	13.2	35.1	17.5	12.6

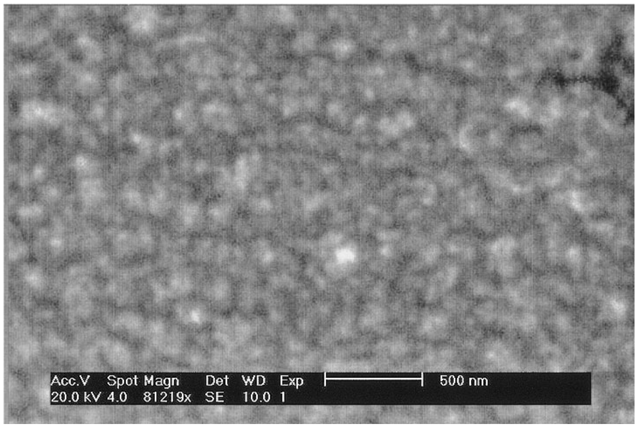


Fig. 2. SEM micrograph of Ga_2O_3-ZnO thin film annealed at 700 °C.

Gases were supplied to the gas chamber through a Teflon tube 3 mm in diameter. A computer-controlled gas mixing system was used for the supply of gases. The total gas flow was 0.4 l/min, and the gas pressure over the sensor was approximately one atmosphere. Certified N_2, O_2, C_3H_6 gas bottles balanced with dry N_2 with a purity of 99.99% or better were used for the gas-sensing measurements.

A Hewlett Packard 34 401 A multimeter and a Keithley 485 picoammeter were used for measuring the voltage and current respectively. The response was recorded as the shift of the I–V curve at constant currents of 2 and 8 mA.

III. RESULTS

A. Microstructure Analysis (XPS and SEM)

XPS analysis was carried out on the Ga_2O_3-ZnO thin films. These results are highlighted in Table I, which shows a summary of the thin films chemical composition.

The results showed that the films consist of stoichiometric Ga_2O_3 and ZnO. The presence of C could result from the SiC substrate as well as organic impurities from the precursor solutions. Additionally, there was a small content of SiC due to the

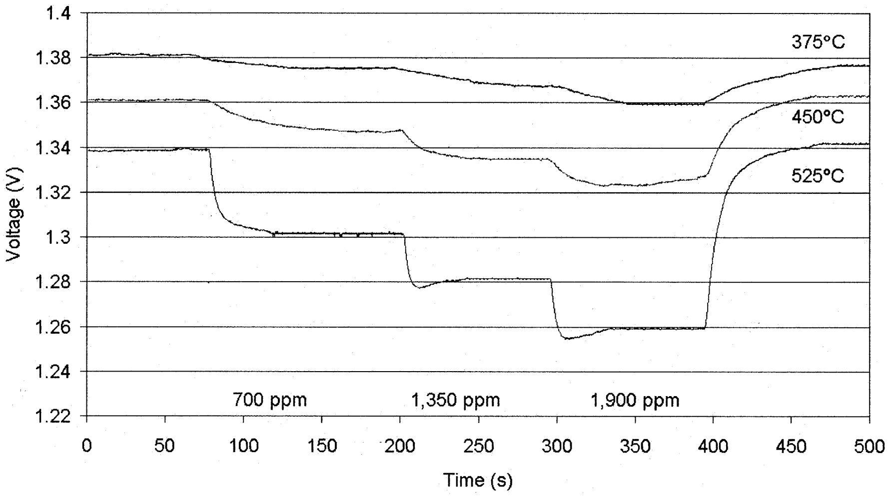


Fig. 3. Gas response of Schottky diode-based sensor to 700, 1350, and 1900 ppm of propene in an ambient of air, with a forward bias current of 2 mA.

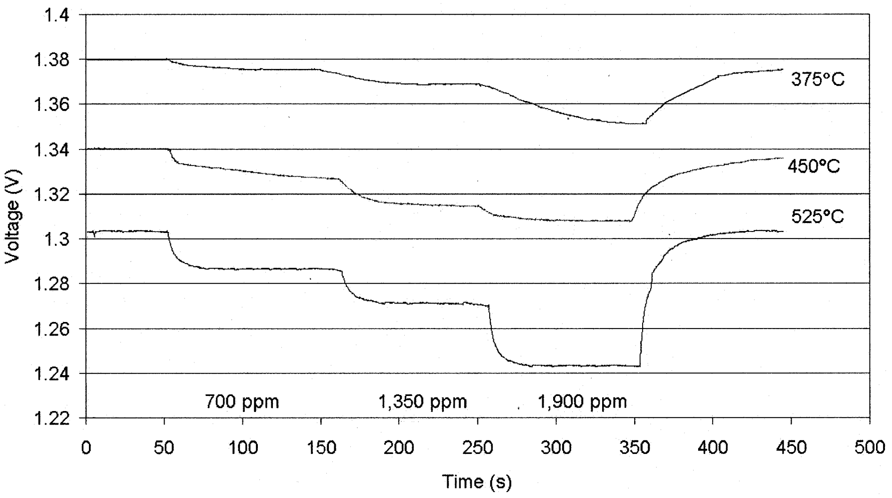


Fig. 4. Gas response of Schottky diode-based sensor to 700, 1350, and 1900 ppm of propene in an ambient of 5% O_2 in N_2, with a forward bias current of 2 mA.

presence of possible pinholes and cracks in the film, which may have occurred during the fabrication of the films.

Fig. 2 shows a secondary electron image of the Ga_2O_3-ZnO thin films annealed at 700 °C. The surface is very smooth with no visible cracks or defects. The structure is homogenous and compact. When inspected under higher magnification, the nano-sized grains are seen.

B. Gas-Sensing Characterization

The sensors responses to propene gas were investigated over the temperature range 30 °C-600 °C in ambients of 5% O_2 in N_2 and air. The gas concentration of propene was varied from 700 to 1,900 ppm. The current-voltage curves of the of the Pt/Ga_2O_3-ZnO/SiC gas sensor show a distinct characteristic shift when the ambient gas is changed from air to that containing propene gas.

Fig. 3 shows the response of the sensor from 375 °C to 525 °C for three concentrations of propene in air when the forward bias current is 2 mA. The first observation is that the magnitude of the response increases with temperature and that the change in output voltage is directly proportional to the change in propene concentration. At 375 °C a voltage change of approximately 6 mV was measured when the sensor was exposed to 700 ppm of propene and 21 mV for 1900 ppm. When the operating temperature was increased to 450 °C, the sensors baseline became more stable, straying from its mean value of 1.361 V by ± 0.495 mV, as opposed to ± 0.581 mV at 375 °C. Furthermore, the response increased by 14, 12, and 12 mV, respectively, for each of the three propene gas concentrations investigated at 450 °C.

Fig. 4 illustrates the sensors response when the ambient gas was changed from air to 5% O_2 in N_2. A comparison of Figs. 3 and 4 show that the change in output voltage of the sensors in an ambient of 5% O_2 in N_2 gas were considerably lower than those in air. This result is consistent over all operating temperatures. However, the base voltage in air is higher in the air ambient than in that with 5% oxygen in nitrogen.

Additionally, it was observed that with less oxygen content in the ambient gas, the response time of the sensors increased substantially. This is especially evident at an operating temperature of 450 °C and a propene concentration of 1900 ppm where the

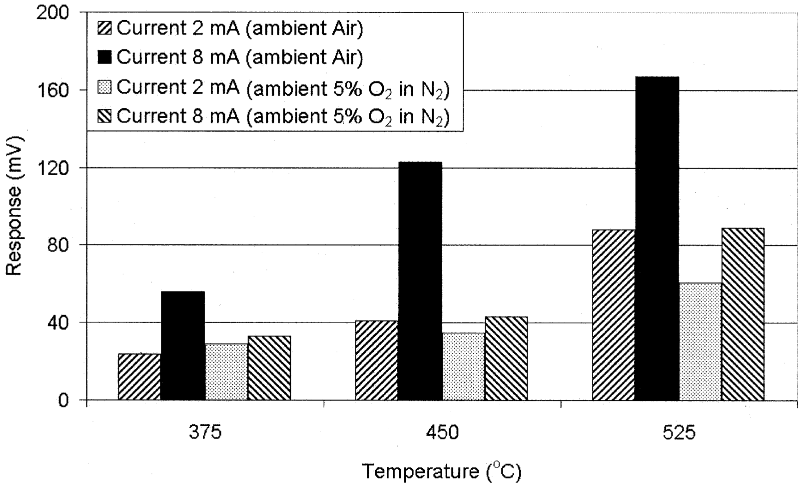


Fig. 5. Response versus temperature for 1900 ppm propene at forward bias currents of 2 and 8 mA in ambients of air and 5% O_2 in N_2.

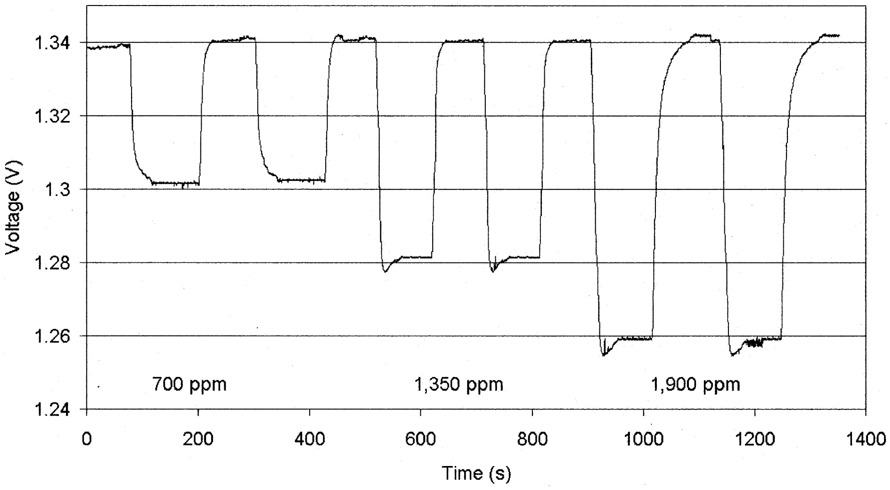


Fig. 6. Response of sensor at 525 °C in ambient of air.

response time was approximately 50 s as opposed to 36 s in an ambient of air.

Fig. 5 shows the response of Schottky diode-based gas sensor to 1900 ppm of propene gas in ambients of air and 5% O_2 in N_2 as a function of operating temperature. By examining this figure, it is clear that the reduced forward bias current results in a much smaller response. When the ambient gas was air, the response at 2 mA was approximately half of that at 8 mA. However, due to the nature of the I–V relationship of the Schottky diode, the base voltage for the forward current of 2 mA is less than that at 8 mA. Furthermore, the change in bias current did not affect the response time of the diodes.

An important aspect of sensor performance is stability and repeatability. Fig. 6 shows the Schottky diode's response to consecutive pulses of different propene gas concentrations in an ambient of air at an operating temperature of 525 °C. It is observed that the responses are stable and reproducible, returning to the base voltage.

C. Discussion

Lundström and coworkers first reported a model for the gas-sensing mechanism of metal-insulator-SiC (MISiC) structure in which they suggested hydrogen atoms from the hydrogen molecules that are dissociated at the catalytic metal surface, diffuse through the metal film, and form an electrically polarized layer at the metal-insulator interface [14]. The hydrogen atoms at the metal-insulator interface decrease the barrier height of the Schottky barrier, resulting in a voltage drop across the forward biased diode. This results in a shift along the voltage axis of the diodes I–V curve. Such a case is evident from the response of the diodes observed in the previous section.

Our results suggest that the increased oxygen content of the ambient gas mixture provides a higher propene gas response due to the increased number of active oxygen sites in the metal-oxide layer. This is in agreement with Jacobsen *et al.* [15] who investigated Pt/CeO_2/SiC Schottky diodes. According to them, the diffusion of oxygen into the semiconducting CeO_2 surface creates more sites for hydrogen atoms. It is known that oxygen ions diffuse through Ga_2O_3 and ZnO at temperatures above 300 °C and the results presented in Figs. 4 and 6 confirm this.

A kinetic modeling of the hydrogen interaction with a Pd-SiO_2-Si (Pd-MOS) device was reported by Fogelberg *et al.* [16]. They suggested that the interface hydrogen atoms are strongly polarized. Hence, it is the large hydrogen polarization at the Pd/SiO_2 interface and not a large concentration of adsorbed hydrogen atoms, which accounts for the very high sensitivity of a Pd-MOS hydrogen sensor. Other gas-sensing mechanisms have been reported by Zhu *et al.* [17], [18], who investigated Schottky diode gas sensors based on amorphous ferroelectric materials with high dielectric constant. They attribute their responses to the adsorbed hydrogen molecules on the catalytic metal dissociating hydrogen ions, which diffuse through the material under a positive bias. This causes the build up of an interface potential resulting from the accumulation hydrogen ions. This polarization potential causes a change in the output voltage.

The results presented in this paper demonstrate the sensitivity of the Ga_2O_3 MRISiC sensors when operated continuously for three days. The sensors maintained their baseline throughout this testing period. However, when operated at continuously for longer than three days and when the exposure time of a single pulse of propene gas exceeded 1 h, the recovery time was quite slow (several hours), and the baseline drifted to higher voltages. The test chamber required flushing with synthetic air in order to return to the baseline voltage. Additionally, each time the sensors were reset, they returned to the same baseline voltage for the respective operating temperature.

We believe that further investigation and layer modifications of Pt/Ga_2O_3-ZnO/SiC Schottky diodes and MOS capacitors could provide a greater understanding of the gas-sensing mechanism of this device.

IV. CONCLUSION

Novel Pt/Ga_2O_3/SiC Schottky diode hydrocarbon gas sensors have been fabricated. The sol-gel process was employed to prepare the gas selective layer of nano-sized Ga-Zn oxide. The sensors were operated at constant currents of 2 and 8 mA and exposed to various concentrations of propene gas in different ambients.

It was found that when the propene gas was introduced in an ambient of high oxygen concentration, the sensors response increases and the response time decreases. It was observed that the sensor responses were linear when exposed to different concentrations of propene gas. The largest response of the sensors (160 mV) was observed at an operating temperature of 525 °C, for 1900 ppm in an ambient of air when the bias current was 8 mA. The sensor responses were stable and repeatable at all operating temperatures tested, however, at temperatures above 450 °C superior sensing characteristics were observed.

Additionally, by increasing the forward bias current, the sensor's response increased. The sensors are currently being calibrated toward other hydrocarbons including methane, propane as well as toward hydrogen sulfide and hydrogen gas. A comparison of the device's performance under different annealing conditions could also provide valuable information

ACKNOWLEDGMENT

The authors would like to thank Prof G. Reeves for his assistance in forming the Ohmic contacts.

REFERENCES

[1] Lundström, S. Shivaraman, C. Svensson, and L. Lundkvist, "Hydrogen sensitive MOS field-effect transistor," *Appl. Phys. Lett.*, vol. 26, no. 2, pp. 55–57, 1975.

[2] G. Muller and G. Krotz, "SiC for sensors and high-temperature electronics," *Sens. Actuators A*, vol. 43, pp. 259–268, 1994.

[3] W. P. Kang, G. Gurbuz, J. L. Davidson, and D. V. Kerns, "A new hydrogen sensor using a polycrystalline diamond-based Schottky diode," *J. Electrochem. Soc.*, vol. 141, pp. 2231–2234, 1994.

[4] J. B. Casady and R. W. Johnson, "Status of silicon carbide (SiC) as a wide-bandgap semiconductor for high-temperature applications: A review," *Solid State Electron.*, vol. 39, pp. 1409–1422, 1996.

[5] A. Arbab, A. Spetz, and I. Lundstom, "Gas sensors for high temperature based on metal-oxide-silicon carbide (MOSiC) devices," *Sens. Actuators B*, vol. 15–16, pp. 19–23, 1993.

[6] D. Manno, G. Micocci, R. Rella, A. Serra, A. Taurino, and A. Tepore, "Titanium oxide thin films for NH_3 monitoring: Structural and physical characterizations," *J. Appl. Phys.*, vol. 82, pp. 54–61, 1997.

[7] L. G. Ekedahl and M. Eriksson, "Hydrogen sensing mechanisms of metal insulator interfaces," *Acc. Chem. Res.*, vol. 31, pp. 249–256, 1998.

[8] Reactive-Insulator SiC-Based Schottky Diodes as Gas Sensors. Lewis Research Center, Cleveland, OH. [Online]. Available: http://www.nasatech.com/Briefs/Jan99/LEW16544.html

[9] M. Fleischer and H. Meisner, "Selective gas detection with high temperature operated metal oxides using catalytic filters," in *Proc. Transducers*, Sendai, Japan, June 7–10, 1999, pp. 136–139.

[10] Y. X. Li, A. Trinchi, W. Wlodarski, K. Galatsis, and K. Kalantar-zadeh, "Investigation of the oxygen gas sensing performance of Ga_2O_3 thin films with different dopants," *Sens. Actuators B*, to be published.

[11] K. Kalantar-zadeh, A. Trinchi, W. Wlodarski, A. Holland, and M. Z. Atashbar, "A novel love mode device with nanocrystalline ZnO film for gas sensing applications," *Proc. 1st IEEE Conf. Nanotechnology*, pp. 556–561, 2001.

[12] P. W. Atkins, *Physical Chemistry*, 6th ed. New York: Freeman, 1999.

[13] C. K. Kim, J. H. Lee, Y. H. Lee, N. I. Cho, and D. J. Kim, "A study on a platinum-silicon carbide Schottky diode as a hydrogen gas sensor," *Sens. Actuators B*, vol. 66, pp. 1116–118, 2000.

[14] I. Lundström, M. Armgarth, and L. G. Petersson, *CRC Crit. Rev. Solid State Mater. Sci.*, vol. 15, pp. 201–210, 1989.

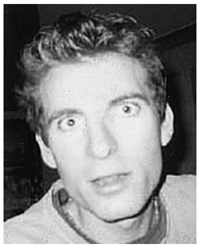
[15] S. Jacobsen, U. Helmersson, L. Ekedahl, I. Lundström, P. Martensson, and A. Lloyd-Spetz, "Pt/CeO_2 SiC Schottky diodes with high response to hydrogen and hydrocarbons," in *Proc. Transducers*, Munich, Germany, June 10–14, 2001, pp. 832–835.

[16] J. Fogelberg, M. Eriksson, H. Dannetun, and L. G. Petersson, "Kinetic modeling of hydrogen adsorption/absorption in thin films on hydrogen-sensitive field-effect devices: Observation of large hydrogen-induced dipoles at the Pd-SiO_2 interface," *J. Appl. Phys.*, vol. 8, pp. 988–992, 1995.

[17] W. Zhu, O. K. Tan, Q. Yan, and J. T. Oh, "Microstructure and hydrogen gas sensitivity of amorphous $(Ba, Sr)TiO_3$ thin film sensors," *Sens. Actuators B*, vol. 65, pp. 366–370, 2000.

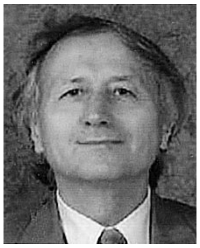
[18] J. Deng, W. Zhu, O. K. Tan, and X. Yao, "Amorphous $Pb(Zr, Ti)O_3$ thin film hydrogen gas sensor," *Sens. Actuators B*, vol. 77, pp. 416–420, 2001.

Adrian Trinchi received the B.S. and B.Eng. degrees (with honors) from the University of Melbourne, Melbourne, Australia in 2000. He is currently pursuing the Ph.D. degree at RMIT University, Melbourne, with his major areas of research being material characterization and the sensing properties of MRISiC and acoustic wave devices.

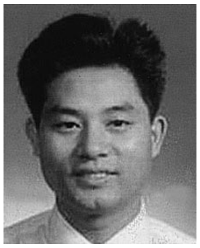


K. Galatsis received the Ph.D. degree from RMIT University, Melbourne, Australia, in 2002.

His research efforts are focused on MoO_3-based MOS gas sensors, the development of gas analyzers, vehicle cabin air quality monitors, and smoke IR backscattering detectors. He is currently working in the U.S.



W. Wlodarski has worked in the areas of sensor technology and instrumentation for over 30 years. He has published four books and monographs, over 250 papers, and holds 28 patents. He is a Professor and Head of the Sensor Technology Laboratory, School of Electrical and Computer Engineering, at RMIT University, Melbourne, Australia.



Y. X. Li received the Ph.D. degree in electronics engineering from Xi'an Jiaotong University, China, in 1991.

He has carried out research in Germany and Australia, and is currently a Professor at the Shanghai Institute of Ceramics, Shanghai, China. His research interests are currently focused on electronic materials and devices. He has published more than 90 papers and holds four patents.