Hydrogen sulphide detection in extreme environments

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Abstract. The present paper reports a novel approach to detect hydrogen sulphide (H$_2$S) at high temperatures, using a silicon carbide based MIS capacitor. The leakage current is monitored through the gas sensor and is shown to be described by a trap assisted conduction mechanism. The hydrogen-like response of the sensor when exposed to H$_2$S is observed by lowering the barrier height between the palladium metal gate and the insulator of the device. Reliable low electric field current-voltage characteristics are obtained at 325 ºC and ultimate sensitivities below 50 ppm are reported. The suitability of this technology for the remote monitoring of volcanic emissions is outlined and predictions made for the deployment in other applications, including outer space.

1. Introduction

Silicon Carbide (SiC) based detectors have been demonstrated as the optimal solution for sensing of both gas and radiation in extreme environments. The material has advanced rapidly over the past few years, both in terms of wafer fabrication and process technology, and is now the most mature amongst the wide bandgap semiconductors. Several unique material properties highlight silicon carbide as the preferred material for deployment in hostile environments. The band gap in 4H-SiC (3.26 eV) is almost three times greater than that of silicon and this allows operation at temperatures up to 1000 ºC [1]. The high stability of the carbon – silicon bond gives a high resistance to both chemical and radiation damage [2]. The critical electric field in SiC is eight times higher than in silicon, which allows low loss power electronic devices, which can extend battery life.

The interior of a volcanic vent is one of the harshest places on earth. Many of the world’s volcanoes are active and located close to dense urban conurbations where immediate dangers threaten the surrounding residents. It is estimated that 500 million people worldwide live within the shadow of a volcano, and for example, the three million Neapolitans who live on the flanks of Mt. Vesuvius are under a direct threat of eruption, when magma and ash would deposit over their communities. In nature, hydrogen sulphide (H$_2$S) is one of gas species discharged from volcanoes, prior to eruption and it is commonly found in the volcanic ambient and plumes. With its colourless, flammable and poisonous gas characters, H$_2$S is also considered harmful to the human body. Volcanic lava is considered to be the most devastating and violent scenario of eruption, however discharged ash and cloud is of far greater concern, because of the significant risks to aviation and air pollution. This can potentially impact on the global climate [3], the effects of which could be last for months or even years. Emissions from the fumaroles are composed primarily of H$_2$O, CO$_2$, HF, HCl, SO$_2$ and H$_2$S, often at temperatures exceeding 500 ºC [4]. The prediction of eruptions is linked to the change in the flux of sulphur and carbon containing gases, from changes in the composition of the magma beneath
the surface. In the period prior to the eruption of Mt Pinatubo in the Philippines in 1991, the sulphur emission rate increased by a factor of ten [5].

Conventionally, the surveillance techniques for monitoring the chemical compositions of the gases have been performed by manually collecting gases samples and analysing them in the laboratory [6]. By using compact, low cost and potentially disposable sensors, it will become possible to deploy many hundreds or even thousands in a single installation, which will allow a far higher level of information to be extracted from the environment and hence more accurate eruption predictions than is possible using traditional technologies.

Small and lightweight silicon carbide based gas sensors offer the possibility for operation as high-temperature sensors and electronics for remote monitoring of volcanic and geothermal activities. Remote sensing in harsh environments also requires minimal power consumption in both of the sensor and the wireless communication network. Micro-scaled capacitors with different surface areas can be fabricated as small as 50 $\mu m^2$ for a single device. The weight of the sensor before mounted to the package is less than 1 mg, and the power consumption required for each capacitor is less than 10 $\mu W$. Telemetering this information in real time from the sensors requires the majority of the power whilst transmitting data, where low leakage current condition must be kept in the dispatched devices, to operate at low level signal for sensing. We present a low leakage current technique for gas sensors coupled with the unique properties of silicon carbide, to herald a new era for extreme sensing applications.

2. Silicon carbide based MIS sensor fabrication and structure

2.1 Sample preparation
Research grade N-type 4H-SiC wafers of 10 $\mu m$ thick epilayer doped with $3 \times 10^{15}$ cm$^{-3}$ were used to fabricate silicon carbide based metal-insulator-semiconductor (MISiC) capacitors. The 4H-SiC wafers were cleaned using trichloroethylene (TCE), acetone, isopropyl alcohol (IPA) followed by rinsing in deionised (DI) water. After that a conventional RCA clean was carried out, and then the wafers were dipped in to a diluted HF solution to remove native oxide on the SiC surface prior to oxidation. Thermal oxides of 25 nm thickness were grown at 1150°C in dry O$_2$ ambient prior to titanium (Ti) deposition. Titanium films of 50 nm thickness were deposited on SiO$_2$/SiC stack layers using a thermal evaporation system at the base pressure of $5 \times 10^{-6}$ torr. Ti-films were then oxidized in dry O$_2$ ambient at temperature 800 °C to form 75 nm thick TiO$_2$ layers. Subsequently, 50 nm palladium (Pd) layers were deposited and patterned as a gate electrode of different areas to fabricate MISiC capacitors. The schematic structure of the sensor is illustrated in figure 1 and a reflected light micrograph in figure 2.

2.2 Measurements
Electrical properties of the Pd/TiO$_2$/SiO$_2$/SiC gate dielectric stack over a temperature range of 25 to 600 °C were determined by current-voltage ($I$-$V$) characteristics using a Keithley 487 picoammeter in conjunction with a computer controlled hot plate. The device is mounted on to a ceramic dual in line (DIL) package using solvent-less silver epoxy. The sensors are tested in gas rig in vacuum, Hydrogen Sulphide (H$_2$S) and Nitrogen (N$_2$) gas as synthetic air.
3. Result and discussion

The current-voltage characteristics of the sensor have been measured between 25 and 600 °C. Results for temperatures above 325 °C are shown in figure 3. Lower temperature data sets are limited by the noise floor of the picoammeter and show a leakage current of $1 \times 10^{-11}$ A. These results show that the sensor is thermodynamically stable over this temperature range, with no sudden changes in the characteristics observed. The leakage current through the device is linear with a strong temperature dependence, which suggests a hopping or trap assisted conduction mechanism is responsible. The results shown in figure 3 can be modelled using the trap assisted conduction model developed in [7] using equation (1)

$$J_L = C_1 E \exp \left( \frac{-q\phi_A}{kT} \right)$$

Where $C_1$ is the density of trapping states in the bulk of the dielectric, $E$ is the electric field in the dielectric stack and $\phi_A$ is the barrier height of the palladium / TiO$_2$ junction, as shown in figure 4. Fits to the data gave $\phi_A = 0.46$ eV and $C_1 = 1 \times 10^{-8}$ cm$^{-1}$Ω$^{-1}$.

The catalytic metal gate contact dissociates the H$_2$S to form hydrogen atoms, which then diffuse through metal gate to form a dipole layer at Pd/TiO$_2$ interface which results in the change of electrical...
response of the device [8]. At temperatures below 600 ºC, this decomposition is not total and some of the hydrogen may be contained in molecules, which do not give a measurable signal on the sensor. Figure 5 shows the current voltage characteristics of the sensor in the presence of H$_2$S gas with concentrations ranging from 0 to 1800 parts per million (ppm) at a temperature of 325 ºC. The figure shows the same characteristic behaviour as the data shown in figure 3, indicating that the leakage current is dominated by the trap assisted conduction mechanism. The stepped response to increases in H$_2$S concentration is also observed. As mentioned above, reduced power consumption is one of key advantages to deploy remote sensing in harsh environment. This obvious change in current indicates the ability of MISiC sensor to operate at the very low electric fields (corresponding to a maximum Electric Field of 50 kV/cm) hence minimal power consumption can be achieved by operating the device in this regime. The sensitivity can therefore be calculated by monitoring leakage current upon exposure to the designated gas species. The response of the gas sensor in hydrogen sulphide (I$_{H2S}$) and in pure nitrogen (I$_o$) was measured and the gas sensitivity (S) can be defined as

\[
Sensitivity = \frac{\Delta I}{I_o} = \frac{I_{H2S} - I_o}{I_o}
\]  

Extracted values at each of the test voltage confirm the sensitivity is independent of the applied low electric field, which is illustrated in the experimental data shown in figure 6. This is in agreement with the calculated sensitivities using equation (2), which yields values between 1.5 and 11.5. In addition, the extracted sensitivity in this study is amongst few groups who have reported H$_2$S sensing by metal insulator semiconductor structures, as well as an improved sensitivity in comparison to other detection methods [9].

Using the same analysis used for the vacuum data given above, we have extracted the barrier height and bulk trap density from the data, as shown by the fits in figure 7. The barrier height is extracted by applying the trap assisted conduction model to the results acquired in the sensing system. Whilst the trap density remains unchanged, with $C_1$=1.0x$10^{-8}$ cm$\Omega^{-1}$, the value of the barrier height reduces, from 0.46 to 0.327 eV, as the H$_2$S concentration increases from 0 to 1800 ppm respectively. This indicates the increased leakage current is due to barrier height lowering upon exposure to hydrogen sulphide. As a consequence the barrier height of H$_2$S is observed to give a hydrogen-like behaviour, as has been demonstrated in our in our previous work [10].
4. Conclusion
In the present work the suitability of MISiC sensors for the detection of volcanic emissions has been investigated. The gas response is observed by monitoring the change in the gate current through a dielectric stack with catalytic Pd metal surface. The sensing mechanism, which is described by a trap assisted conduction model, provides reliable gas response in the low electric field region. We show that the barrier height ($\phi_A$) reduces with increasing gas concentration, because of the formation of a dipole charge layer under the metal gate. The observed lowering in barrier height is similar to that seen on exposure to hydrogen, suggesting that the catalytic contact is decomposing the hydrogen sulphide to form hydrogen atoms.

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References
[1] Lloyd Spetz A et al. 2001 SiC Based Field Effect Gas Sensors for Industrial Applications Phys. Stat. Sol. (a) 185 15-25
[2] Metzger S, Henschel S, Köhn O and Lennartz W 2002 Silicon Carbide Radiation Detector for Harsh Environments IEEE Transactions on Nuclear Science 49 1351
[3] McGonigle A J S 2005 Volcano remote sensing with ground based spectroscopy Phil. Trans. R. Soc. A 363 2915–2929
[4] Symonds R B, Rose W I, Bluth G and Gerlach T M 1994 Volcanic gas studies: methods, results, and applications, in Carroll M R and Holloway J R, eds., Volatiles in Magmas: Mineralogical Society of America Reviews in Mineralogy, 30 1-66
[5] Dagg A S, Tubianosa B S, Newhall C G, Tungol N M, Javier D, Dolan M T, Delos Reyes P J, Arboleda R A, Martinez M M A and Regalado M T M 1996 Monitoring sulphur dioxide emission at Mt Pinatubo, in Newhall C G and Punongbayan R S, ‘Fire and Mud - Eruptions and Lahars of Mount Pinatubo, Philippines’ University of Washington Press Seattle WA 409-414
[6] Symonds R B, Rose W I, Bluth G J S and Gerlach T M 1994 Volcanic-gas studies: methods, results and applications Reviews in Mineralogy and Geochemistry 30 1–66
[7] Fiorenza P, Lo Nigro R, Raineri V, Lombardo S, Toro R G, Malandrino G and Fragalà I L 2005 From micro- to nanotransport properties in Pr$_2$O$_3$-based thin layers J. Appl. Phys. 98 044312

[8] Ekedahl L G, Erikson M and Lundström I 1998 Hydrogen Sensing Mechanisms of Metal-Insulator Interfaces Acc. Chem. Res. 31 249

[9] Baranzahi A, Lloyd Spetz A, Glavmo M, Carlsson C, Nytoft J, Salomonsson P, Håggendal B, Mårtensson P and Lundström I 1997 Response of metal-oxide-silicon carbide sensors to simulated and real exhaust gases Sens. Actuators B, 43 52–59

[10] Weng M H, Horsfall A B, Mahapatra R and Wright N G 2006 First observation of hydrogen sensing by trap assisted conduction current in Pd/TiO$_2$/SiC capacitors at high temperature Proceedings of IEEE Sensors Conference Deagu Korea