

# A new ammonia sensor

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**Abstract** - Ammonia gas (NH<sub>3</sub>) detection is widely used, from air conditioning to searching for life on mars, and in many situations there is an increasing demand for cheap and reliable NH<sub>3</sub> sensors. When used as the dielectric in a capacitive sensing arrangement, porous SiC has been found to be extremely sensitive to the presence of NH<sub>3</sub> gas. The exact sensing method is still not clear, but NH<sub>3</sub> levels lower than ~0.5ppm could be detected. We report the fabrication and preliminary characterisation of NH<sub>3</sub> sensors based on porous SiC. SiC is a very durable material and should be good for sensors in harsh environments. So far the only NH<sub>3</sub> sensors using SiC have been FET based, and the SiC was not porous. In our devices, SiC was deposited by PECVD on standard p-type single-crystal Si and was then made porous by electrochemical etching in 73% HF using anodisation current-densities of 1-50mA/cm<sup>2</sup>. Preliminary data is given for our devices response to NH<sub>3</sub> in the range 0-10ppm NH<sub>3</sub> in dry N<sub>2</sub> carrier gas, as well as the response to relative humidity between 10%RH and 90%RH.

**Keywords** - Porous SiC, ammonia sensor

## I Introduction

There are many situations where monitoring of ammonia (NH<sub>3</sub>) gas is required, the most common being leak-detection in the compressor rooms of air-conditioning systems [1], sensing of trace amounts of ambient NH<sub>3</sub> in air for environmental analysis [2], breath analysis for medical diagnoses [3], animal housing [2], explosives and fertilizer manufacturing [4]. Even on Mars, ammonia detection is regarded as a possible key to identifying life; recently the ESA Mars Express satellite has 'tentatively' identified the presence of NH<sub>3</sub> in the Martian atmosphere [5].

Generally, because it is toxic (but yet biodegradable – not a greenhouse gas), it is required to be able to sense low levels (~ppb-ppm) of NH<sub>3</sub>, but detectors should also be sensitive to much higher levels. NH<sub>3</sub> gas is a very

corrosive gas, often causing current NH<sub>3</sub> sensors to suffer from drift and have short lifetimes.

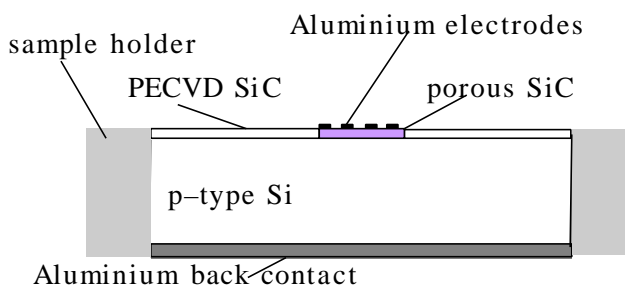
SiC, with its well known ability to withstand harsh chemical environments, has been demonstrated to be a very favour-able material for sensors operating in aggressive environments such as chemical plants, car exhausts and in elevated temperatures.

Membrane or thin film structures have also been demonstrated, which is a big advantage as regards ease of integration with standard processing, due to greater flexibility in choice of doping type and concentration.

We found porous SiC, when used as the dielectric in a capacitive sensing arrangement to be extremely sensitive to the presence of NH<sub>3</sub> gas. Compared to existing FET NH<sub>3</sub> sensors [6], our devices are much more simple to fabricate and achieve similar sensitivities.

We have made sensors using porous SiC, made porous by electrochemical anodisation in HF [7]. Earlier work on relative humidity sensors showed how the sensitivity to RH could be controlled by porosity, the pore size distribution, and the porous morphology. For humidity sensing the requirements are to have a pore size distribution with pore sizes 1-100nm and a random porous structure. In other words, pores larger than ~100nm, are not useful for RH sensing. We have tried to utilise this fact to realise gas sensors which would be insensitive to RH. Cross-sensitivity, or rather lack of, to other gases is a very important issue for gas sensors, but another often overlooked parameter is sensitivity to water vapour (humidity).

In this work we have attempted to make SiC porous with pores (mostly) larger than 100nm and tested their response to dry NH<sub>3</sub> gas in a nitrogen carrier gas. We also tested the response to relative humidity of our sensors.



**Figure 1.** A schematic of the devices used in this work. The sensing mechanism is capacitive with porous SiC as the sensing dielectric.

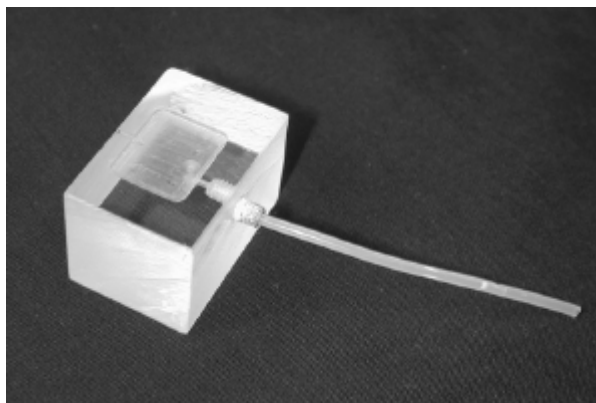
## II Experimental

Thin films of (p-type) SiC were deposited on standard Si wafers, using PECVD, and doped with Boron in-situ. The thickness of the films were  $\sim 5000\text{\AA}$ .

After the thin films were deposited, a SiN mask was deposited on the backside of the wafer as a KOH mask to make membranes. Al electrodes were deposited on the front side. Then Al was evaporated on the backside of the wafer, and the wafers were diced into 10mm x 10mm samples. The samples were then mounted on specially prepared holders for porous formation.

We made porous SiC by electrochemical etching/anodisation using 73% HF (including Triton X100 surfactant), anodisation current densities,  $J_A$ , in the range 1 – 50 mA/cm<sup>2</sup>, and anodisation times,  $t_A$ , between 30 seconds and 10 mins.

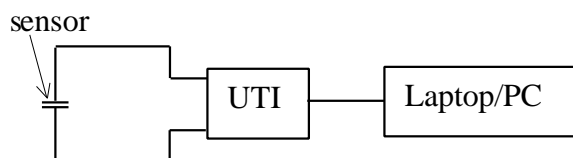
Figure 1 shows a schematic of the devices used in this work. The phase angles of the sensing capacitors were typically  $\sim -85^\circ$ , in dry air, indicating reasonable quality capacitors.



**Figure 2.** Picture of the 180 $\mu$ l ‘mini-chamber’ used to test our sensors response to ammonia.

Electrical contacts were made to the sensors by wire bonding, and their response in the range 0.5 – 10 ppm NH<sub>3</sub> gas was recorded. To do this a miniature ‘chamber’ was fabricated, with a volume of just 180 $\mu$ l – see figure 2. This was necessary as in a bigger chamber the very low concentrations of ammonia caused the sensors to appear to have a very slow response.

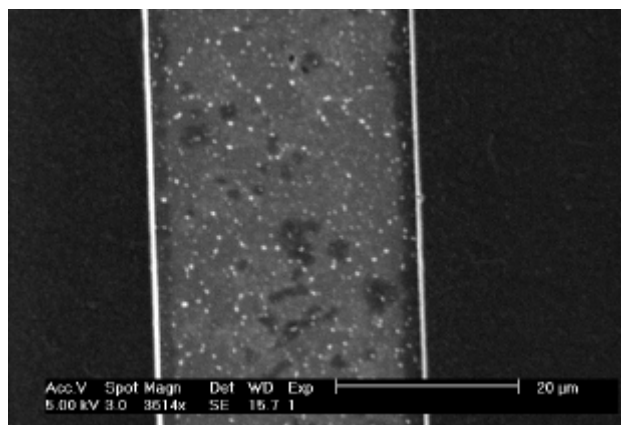
Interfacing to the sensors was via a Universal Transducer Interface (UTI) – from SMARTEK. The UTI can be used instead of an impedance analyser to monitor the capacitive response of our porous SiC sensors. Using the UTI and purpose written software, we can monitor sensors response outside of the laboratory. In fact the whole system can be battery operated and is completely mobile. A schematic of the (mobile) detection system, including sensor, UTI interface and laptop is shown in figure 3.



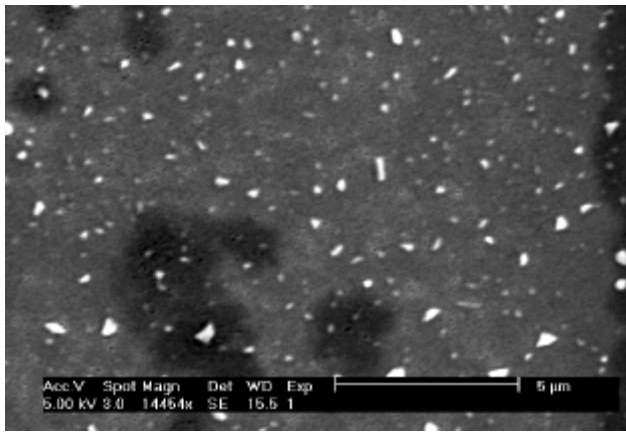
**Figure 3.** Schematic diagram of the measurement setup used to test our sensors response to ammonia. The UTI, which can be battery operated, can also have a wireless output, enabling monitoring in almost all situations.

## III Results

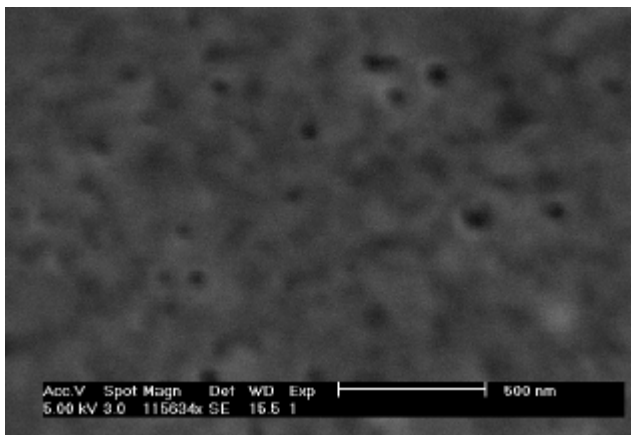
Figures 4(a), (b) and (c) show SEM images of the SiC surface after porous formation.



(a)



(b)



(c)

Figure 4. (a) SEM image showing the electrodes and the porous SiC surface. The darker ‘patches’ of the SiC surface contain larger pores; (b) SEM image showing pores mostly with diameters >100nm; enlargement of a section of (b).

Many pores with dimensions >100nm are visible. There are also pores with dimensions <100nm, which probably cause some RH sensitivity. This is the subject of future work.

Figure 5 shows the response of our sensor to dry NH<sub>3</sub> gas in a nitrogen carrier gas. Known concentrations of ammonia gas, in a nitrogen carrier gas, were passed into a small chamber. We cycled the NH<sub>3</sub> gas concentration from 0.5 ppm NH<sub>3</sub> up to 5ppm NH<sub>3</sub>, then 9.5 ppm NH<sub>3</sub>. The output from the UTI shows almost zero hysteresis and it seems that our sensor may be also sensitive to much lower concentrations of NH<sub>3</sub>.

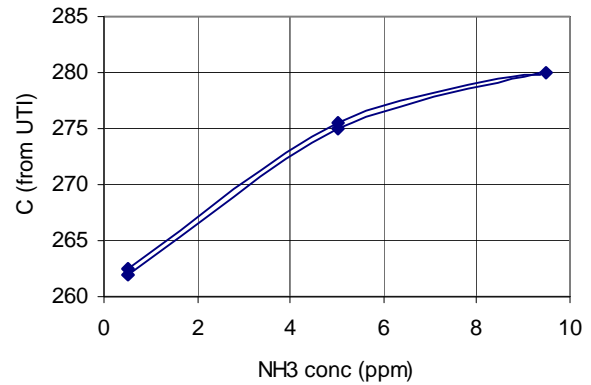


Figure 5. The response of our porous SiC capacitance sensor to dry NH<sub>3</sub> gas. Interfacing to a laptop pc was by the Universal Transducer Interface (UTI) from SMARTEK. The points were repeated several times and almost no hysteresis was evident. Measurements were taken approximately 10 mins after changing the NH<sub>3</sub> concentration.

We also tested this particular sensors response to RH between 10% and 90% RH. The normalised capacitance response is shown in figure 6. As can be seen, the response to up to 50%RH is very small. We attribute this to an absence, or at least very small amounts of pores with diameters <100nm – see figure 4(c). With more optimum pore morphology we hope to decrease this response, and also in-crease the response to NH<sub>3</sub>.

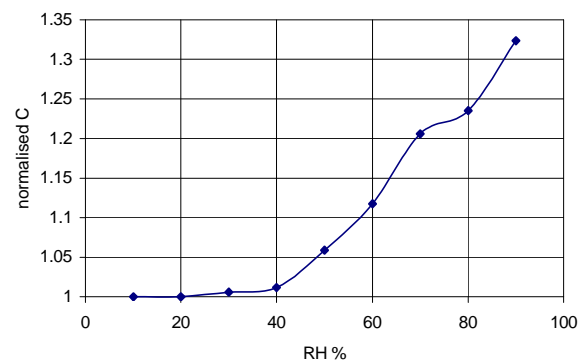


Figure 6. The response of our porous SiC capacitance sensor to relative humidity (10%-90%RH).

## IV Discussion

We have used Al electrodes in this work because initially we were developing relative humidity sensors with the view to eliminating cross-sensitivity to ambient gases. However, as reported in this paper, we noticed a high sensitivity to  $\text{NH}_3$  during our experiments. Therefore, we adopted the route of trying to decrease the sensitivity to humidity while maintaining the sensitivity to ammonia by having (as much as possible) a porous SiC structure with pores  $>100\text{nm}$  diameter. However, as discussed,  $\text{NH}_3$  is corrosive, and so the next step in developing our  $\text{NH}_3$  sensors would be to change the electrodes to another metal, possibly Au.

As regards the response to  $\text{NH}_3$  gas from our porous SiC sensors, it seems that the sensors can detect a change in ammonia gas concentration of  $\sim 1\text{-}2\text{ppm}$ . It is not yet clear exactly what the sensing mechanism is, but possibly, due to a small voltage applied during capacitance measurements, a thin depletion layer is formed on the surface of the SiC. Ammonia molecules passing over this depletion layer might be decomposed, and subsequently, hydrogen atoms adsorb onto this depletion layer, thus changing the junction capacitance. This is then interpreted by the UTI as a change in total capacitance.

Also, it is possible that the sensors are sensitive to  $\text{NH}_3$  over a much wider concentration range – the shape of the curve of figure 5 for the lower concentrations indicates that it may be sensitive to much lower concentrations than  $0.5\text{ppm}$   $\text{NH}_3$ .

With more optimised pore morphology we anticipate an improvement in its sensitivity to  $\text{NH}_3$  and also a decrease in sensitivity to RH. With different electrodes (e.g. Au), we will also be investigating the effects of different anodisation conditions (HF concentration, anodisation time etc) on the response to  $\text{NH}_3$  as well as other gases.

## Acknowledgements

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