A NEW AMMONIA SENSOR BASED ON A POROUS SIC MEMBRANE

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Summary: *Porous SiC has been found to be extremely sensitive to the presence of ammonia (NH_3) gas. We report the fabrication and preliminary characterisation of NH_3 sensors based on porous SiC and Al electrodes. The idea of the SiC is that it is a very durable material and that it should be good for sensors in harsh environments. Until now the only NH_3 sensors using SiC have been FET based, and the SiC was not porous. The SiC was deposited by PECVD on standard p-type single-crystal Si and was made porous by electrochemical etching in 73% HF and anodisation current-densities of 1-50mA/cm^2. Because the etch-rate of Al in 73% HF is very low, we can use Al electrodes instead of Au. This also facilitates our sensor fabrication, as Al is more cleanroom friendly than Au. Preliminary data is given for our devices response to NH_3 in the range 0-10ppm NH_3 in dry N_2 carrier gas.*

Keywords: *NH_3 sensor, porous SiC, Al electrodes*

INTRODUCTION

Ammonia sensors find applications in many areas including leak-detection in air-conditioning systems [1], environmental sensing of trace amounts ambient NH_3 in air [2], breath analysis for medical diagnoses [3], animal housing [2], and more. Generally, because it is toxic, it is required to be able to sense low levels (~ppm) of NH_3, but it should also be sensitive to much higher levels. NH_3 gas can be quiet corrosive, often causing NH_3 sensors to have short lifetimes. SiC with its well known ability to withstand harsh chemical environments, should in principle be a better material for sensors in such environments. 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_3 gas. Compared to existing FET NH_3 sensors [5], 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 [6]. Earlier work on humidity sensors showed how the sensitivity to RH can 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, or smaller than ~1nm, are not useful for RH sensing. We have tried to utilize this fact to realise gas sensors which could be insensitive to RH. In this work we have made sensors with pores larger than 100nm and tested their response to dry NH_3 gas in a nitrogen carrier gas. We also tested the response to RH of our sensors.

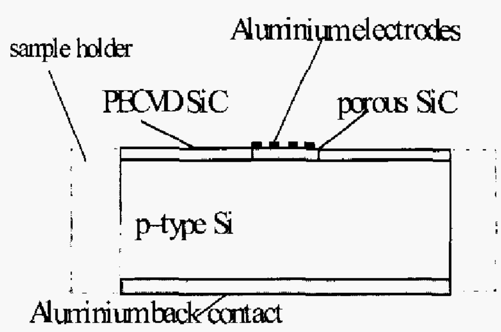

Fig. 1. A schematic of the devices used in this work. The sensing mechanism is capacitive with porous SiC as the sensing dielectric.

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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 ~5000Å.

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^2, 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 ~ - 85°, in dry air, indicating reasonable quality capacitors.

Electrical contacts were made to the sensors by wire bonding, and their response in the range 0.5 – 10 ppm NH_3 gas was recorded. To do this a miniature 'chamber' was fabricated, with a volume of just 180µl – 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.

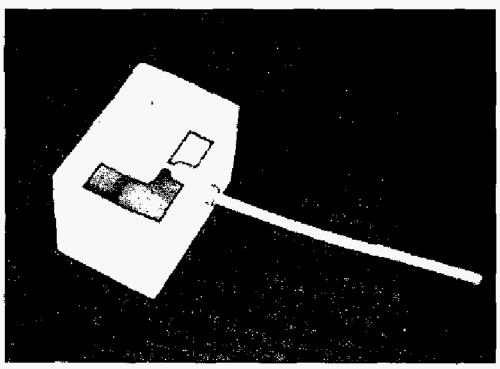

Fig 2. Picture of the 'mini-chamber' used to test out sensors response to ammonia.

Interfacing to the sensors was via a Universal Transducer Interface (UTI) – from Smartec. The UTI can be used instead of an impedance analyser to monitor the response of our porous SiC sensors. Using the UTI and purpose written software, we can monitor sensors response outside of the lab. In fact the whole system can be battery operated and is completely mobile.

RESULTS

Figures 3(a)&(b) show SEM images of the SiC surface after porous formation. 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 4 shows the response of our sensor to dry NH_3 gas in a nitrogen carrier gas.

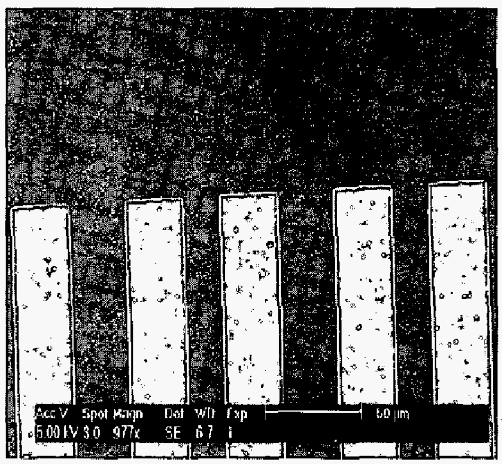

Fig. 3(a). SEM image showing the electrodes and the porous SiC surface. The darker 'patches' of the SiC surface contain larger pores – see figure 3(b)

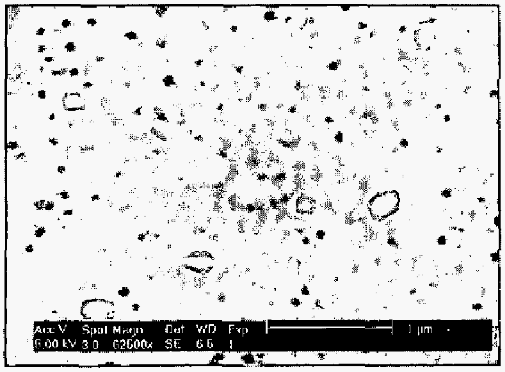

Fig. 3(b). Higher magnification SEM image showing larger (>100nm) pores within the darker regions of the SiC surface

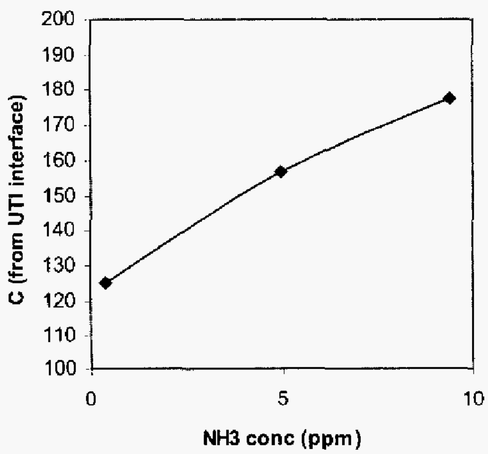

Fig. 4. The response of our porous SiC capacitance sensor to dry NH3 gas Interfacing to a laptop pc was by the Universal Transducer Interface (UTI) from Smartek. The points were repeated several times and almost no hysterisis was evident. Measurements were taken approximately 10 mins after changing the NH3 concentration.

Known concentrations of ammonia gas, in a nitrogen carrier gas, were passed into a small chamber. We cycled the NH_3 gas concentration from 0.5 ppm NH_3 upto 5ppm NH3, then 9.5 ppm NH_3. The output from the UTI shows almost zero hysterisis and it seems that our sensor may be also sensitive to much lower concentrations of NH_3.

We also tested this particular sensors response to RH between 10% and 90% RH. The normalised capacitance response is shown in figure 5. As can be seen, there is a response to RH but it only ~3% between 10% and 90%RH. With more optimum pore morphology we hope to decrease this response, and also increase the response to NH_3.

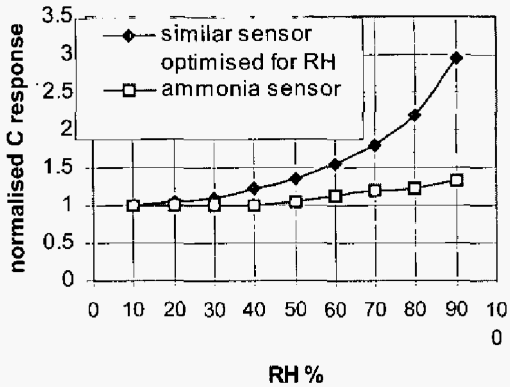

Figure 5. The response of our porous SiCammonia sensor to relative humidity (10%-90%RH). For comparison a similar sensor optimised for RH sensing is also shown.

DISCUSSION

We have tested porous SiC for its response to NH_3 gas. It seems that the sensors can detect a change in ammonia gas conentration of ~1-2ppm.

Also, it is possible that the sensors are sensitive to NH_3 over a much wider concentration range – the shape of the curve of figure 4 for the lower concentrations indicates that it may be sensitive to much lower concentrations than 0.5ppm NH_3.

With more optimised pore morphology we anticipate an improvement in its sensitivity to NH_3 and also a decrease in sensitivity to RH.

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