

Hydrogen gas sensors using 3C-SiC/Si epitaxial layers

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Abstract. A hydrogen gas sensor consisting of planar electrical NiCr contacts formed on the surface of a 3C-SiC epitaxial layer grown on Si(001) has been fabricated and tested. The n-type, 4 μm thick 3C-SiC epi layer was grown under low-pressure conditions with an approximate doping density of 10^{18} cm^{-3} . This sensor demonstrates a two-fold repeatable improvement in stability and sensitivity in comparison to an n-type Si sensor of the same type also fabricated and tested under the same conditions. Both the 3C-SiC/Si and Si sensors operated up to 250 °C; however, the 3C-SiC/Si sensor was able to detect hydrogen at concentrations far exceeding that of the Si sensor. The 3C-SiC/Si device detected hydrogen at concentrations ranging from 0.333% to 100% in Ar while the Si sensor could only detect hydrogen at concentrations ranging from 2% to 100% in Ar. Based on this preliminary data, it has been shown that 3C-SiC/Si hydrogen sensors of this type have a larger dynamic range and higher sensitivity to hydrogen than Si sensors, thus allowing for harsh environmental applications.

Introduction

High temperature extreme environment solid-state gas sensing is of great interest to the automotive, aerospace and chemical processing industries [1,2]. The wide bandgap, high thermal conductivity and thermal and chemical stability make silicon carbide (SiC) an ideal solid-state gas sensing material for operation under “harsh” conditions [3,4]. According to literature, a silicon (Si) gas sensor reportedly failed between 200°C and 250°C because of its relatively small bandgap of 1.1 eV [4-6]. This gives a 3C-SiC gas sensor (bandgap = 2.36 eV), the potential to operate at far greater temperatures. The 3C-SiC polytype was chosen because of its high electron mobility ($\sim 10^3 \text{ cm}^2/\text{V}\cdot\text{sec}$) and ability to be epitaxially grown on Si, thus greatly decreasing the cost of wafers in comparison to bulk 3C-, 4H- or 6H-SiC substrates [7].

Epitaxial growth of 3C-SiC on Si(001)

In this work, a 3C-SiC epi layer was grown on Si(001) in a low-pressure horizontal cold-wall CVD reactor [8]. The process involves three main steps. First, a native oxide H_2 etch of the silicon wafer was performed. This was followed by a carbonization step, which converts the Si surface to SiC. The final step is the growth of the 3C-SiC epi layer on the carbonized surface. Prior to growth, the Si wafer was RCA cleaned and placed on a graphite susceptor, which was inserted into the reaction tube. Purified hydrogen, with a flow of 9 SLM, was introduced at a pressure of 150 Torr. The susceptor and Si wafer were then heated by radio frequency (RF) induction to 1000°C and hydrogen etched in this manner for 10 min. The RF generator was then switched off for 5 minutes. Propane was then added to the hydrogen stream at a partial pressure of 0.03 Torr. After 60 sec, the RF generator was switched back on until the growth temperature of 1380°C was reached. After 90 sec SiH_4 and C_3H_8 were introduced at partial pressures of 0.035 and 0.035 Torr respectively. 3C-SiC growth was then conducted for 120 min after which the RF generator was turned off and the sample

was cooled under an Ar flow to ambient temperature. A growth rate of $\sim 2\mu\text{m}/\text{hour}$ is typical for this process thus resulting in a $4\mu\text{m}$ film for subsequent gas sensor fabrication.

3C-SiC/Si Gas Sensor Fabrication and Testing

The gas sensing device was fabricated by evaporating NiCr (2000 \AA) equipotential contacts on the 3C-SiC face of the structure. The device was then annealed at 950°C for 2 minutes in an Ar atmosphere to produce ohmic contacts. Figure 1 shows a schematic drawing of the 3C-SiC/Si gas sensor. An n-type Si(001) sensor was also fabricated in the same manner and simultaneously tested for comparison. Both sensors were approximately $1\text{cm} \times 1\text{cm}$, with 2.5mm wide contacts with an 5mm wide gap between the contacts. The initial resistances of the 3C-SiC/Si and Si devices were approximately $13\ \Omega$ and $16.6\ \Omega$ respectively. The two sensors were placed in a gas sensor test bed, shown in figure 2. Both sensors were biased with 2V using a Hewlett-Packard model 6626A quad programmable power supply. The sensors were exposed to UHP H_2 to determine sensor response at varying concentrations (0.333% to 100%) of H_2 in Ar with pure Ar flows in between each H_2 concentration to allow for complete desorption. The temperature of the test bed was varied from 50°C to 250°C in 50°C increments. The current flowing through each sensor was measured by a Keithley model 2700 Digital Multimeter (DMM) equipped with a Keithley model 7700 20-Ch. Multiplexer.

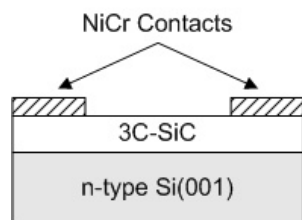


Fig. 1. Schematic drawing of 3C-SiC/Si gas sensor. The 3C-SiC film is $4\mu\text{m}$ thick.

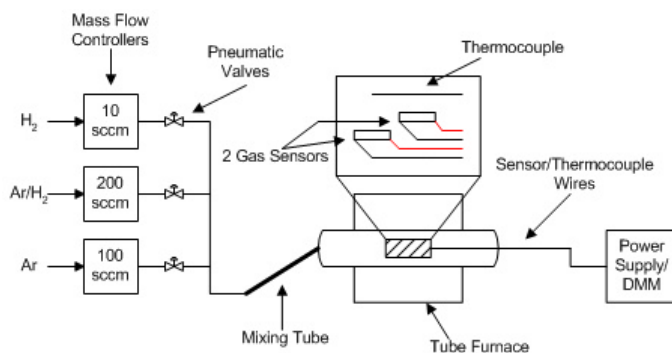


Fig. 2. Gas sensor test bed.

Results and Discussion

The 3C-SiC/Si sensor was observed to be a great deal more sensitive to H_2 concentration than the Si sensor throughout the temperature range tested in this work. The gas sensor response in figures 3-6 (? I) is the change in current of each device relative to the current in 100% Ar (0% H_2). Figure 3 illustrates the sensor response to various H_2 concentrations (10% to 100% in 10% increments) at 50°C with an Ar purge between H_2 events to allow for desorption. It can be clearly seen that at 10% H_2 , the 3C-SiC/Si sensor gave an approximately two-fold greater response than the Si sensor; while at 100% H_2 , the 3C-SiC/Si sensor showed approximately 3.5 times the response of the Si sensor. The Si sensor also saturated at about 40% H_2 in Ar, thus not allowing for reliable detection beyond this concentration. Figures 4 and 5 show the 3C-SiC/Si and n-type Si(001) gas sensor response respectively to various concentrations of H_2 at various temperatures. Both sensors show a decrease in response, indicating a loss of sensitivity, as temperature increases. An empirical least squares fit to the relation between 3C-SiC/Si gas sensor response and H_2 concentration shown in figure 4 is shown in table 1.

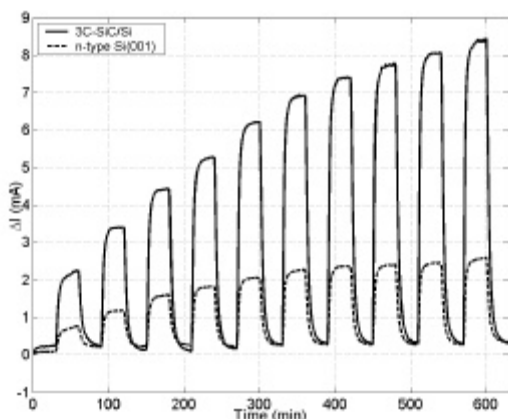


Fig. 3. Gas sensor response at 50°C to various concentrations of H₂ (10% to 100% with 10% steps). Solid line denotes 3C-SiC/Si response, dashed line Si response.

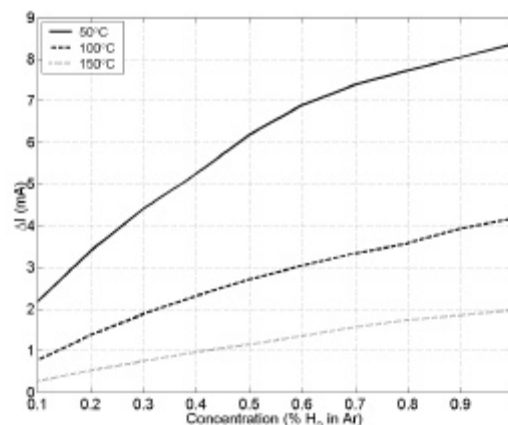


Fig. 4. 3C-SiC/Si gas sensor response vs. H₂ concentration at various temperatures.

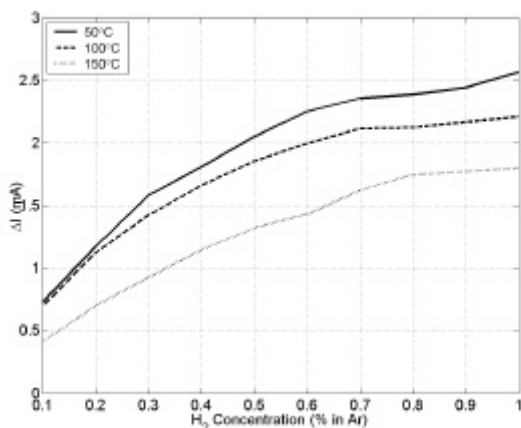


Fig. 5. n-type Si(001) gas sensor response vs. H₂ concentration at various temperatures.

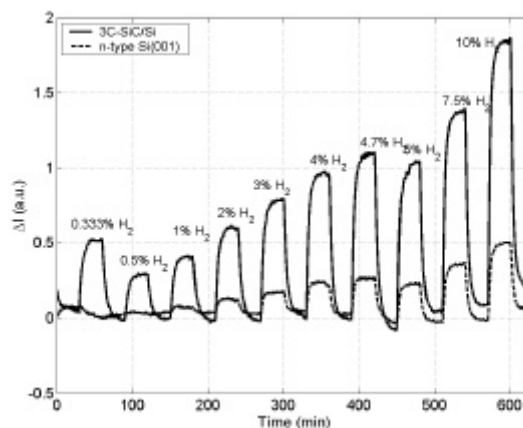


Fig. 6. Gas sensor response at low H₂ concentrations at 50°C.

Table 1. Empirical relationships between 3C-SiC/Si sensor response to H₂ concentration at various temperatures

Temperature	Empirical fit	R ² Correlation Factor
50°C	$\Delta I = -0.0089[C_{H_2}]^2 + 0.017[C_{H_2}]$	0.9842
100°C	$\Delta I = -0.0028[C_{H_2}]^2 + 0.0068[C_{H_2}]$	0.9937
150°C	$\Delta I = -0.0008[C_{H_2}]^2 + 0.0027[C_{H_2}]$	0.9990

Note: ΔI [mA] and C_{H_2} [% H₂ in Ar]

The 3C-SiC/Si sensor showed the ability to detect extremely low concentrations of H₂ in Ar, while the Si sensor was limited in its concentration limits. The sensor response at low concentrations (0.333%, 0.5%, 1%, 2%, 3%, 4%, 4.7%, 5%, 7.5% and 10% H₂ in Ar) is shown in figure 6. The total gas flow for these low concentrations was not kept constant (due to mass flow controller limitations). Thus there is no correlation between gas sensor response amplitude and H₂ concentration. This leads to the conclusion that the adsorption process is mass transfer limited. The 3C-SiC/Si sensor was able to detect H₂ down to 0.333% H₂ in Ar, while the Si sensor was only able to detect down to 2% H₂ in Ar.

Conclusions

The 3C-SiC/Si gas sensor showed to be more sensitive to H₂ concentration than the n-type Si(001) sensor. The empirical relationships shown in table 1 allow for the determination of H₂ concentration by measuring the current relative to 0% H₂. The 3C-SiC/Si gas sensor also showed no H₂ saturation effects allowing for the practical application in real-time H₂ concentration measurements.

Acknowledgements

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