

In Situ N₂-Doping of SiC Films Grown on Si(111) by Chemical Vapor Deposition from Organosilanes

J. Chen, A. J. Steckl,^{a,*} and M. J. Loboda^{b,*}

^aNanoelectronics Laboratory, University of Cincinnati, Cincinnati, Ohio 45221-0030, USA

^bDow Corning Corporation, Midland, Michigan 48686-0994, USA

In situ N₂-doping of 3C-SiC films during growth by chemical vapor deposition on Si(111) substrates using single organosilane precursors [trimethylsilane (SiC₃H₉) and silacyclobutane (SiC₃H₈)] was investigated by Hall effect measurements, secondary-ion mass spectrometry (SIMS), and reflection Fourier transform infrared spectroscopy (FTIRS). The electron concentration in SiC films grown from trimethylsilane can be readily controlled by the N₂ flow rate. Reflection FTIRS study of the N₂-doping efficiency yielded results consistent with those from Hall effect and SIMS measurements. The doping efficiency in SiC films grown with silacyclobutane is much lower than that for films grown from trimethylsilane. The electrical properties of the n-type 3C-SiC films were investigated by Hall effect measurements from 80 to ~400 K. The highest electron mobilities at 83 and 300 K are 2115 and 333 cm²/V s, respectively. The corresponding carrier concentrations are 1 × 10¹⁶ and 4 × 10¹⁶ cm⁻³.
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SiC has many superior properties for high power and high frequency electronic devices, such as wide bandgap, high breakdown field, high saturation velocity, and high thermal conductivity. In addition, its high Young's modulus and its toughness, chemical inertness, and radiation resistance make it an excellent material for the fabrication of microelectromechanical systems sensors and controllers operating in extreme environments such as those in turbine engines and nuclear reactors.

Among more than 170 SiC polytypes, 6H-, 4H-, and 3C-SiC are the three most commonly used polytypes in the microfabrication of devices. 6H- and 4H-SiC are the best polytypes for power electronic devices due to the rapid improvement in both size and quality of the substrates. 3C-SiC has its own unique features, such as highest electron mobility, isotropy in both mechanical and electrical properties, and no micropipe defects. The major hurdle of 3C-SiC development is the lack of sizable substrate. However, 3C-SiC can be heteroepitaxially grown on Si substrates, which provides a low cost alternative method for obtaining SiC. Currently, chemical vapor deposition (CVD) is widely employed to grow epitaxial SiC on Si. SiC CVD growth normally takes place at relatively high temperatures (~1350°C) with an SiH₄/C₃H₈/H₂ gas system. The hazardous nature of these gases requires special handling. We have been pursuing the use of the novel organosilane precursors silacyclobutane (SCB-SiC₃H₈) and trimethylsilane (3MS-SiC₃H₉) as alternative Si and C sources for the growth of 3C-SiC.¹⁻⁵ SCB has a strained four-member ring and 3MS has a sterically hindered structure. These features make them easier to pyrolyze, with a high growth rate. Furthermore, these precursors are nonpyrophoric and noncorrosive, making them safer to handle than silane. Films grown by CVD using SCB or 3MS^{3,5} show that crystalline SiC can be obtained on Si(111) at growth temperatures below 1200°C. Our previous results show that the chemical and structural properties of SiC films using 3MS or SCB are similar to those grown at higher temperatures using the SiH₄/C₃H₈/H₂ gas system.

In this work, the electrical transport properties of *in situ* N₂-doped 3C-SiC films grown on Si(111) using SCB or 3MS are investigated by Hall effect measurements and reflection-mode Fourier transform infrared spectroscopy (FTIRS). The electron carrier density and mobility are measured as a function of N₂ flow rate. Reflection-mode FTIRS and secondary-ion mass spectrometry (SIMS) also were utilized to support Hall effect measurements. The relationship between the Hall mobility and the carrier concentration at 300 K also is presented and compared to previously published data.

Experimental

The SiC films were grown on 3 in. Si(111) substrates (p-type, 150-300 Ω-cm, off-axis) using SCB or 3MS at 1200°C and 4 Torr. Prior to CVD growth, a thin buffer layer was formed using propane at 1300°C and 1 atm to reduce the effects of large lattice mismatch and thermal expansion coefficient difference between SiC and Si(111). The flow rate was 10 sccm for propane and 40 sccm for SCB or 3MS. H₂ and N₂ were used as carrier gas and dopant, respectively. The H₂ flow rate was always 2 slm (standard liters per minute) during carbonization and 1 slm during growth. The N₂ flow rate ranged from 0.1 to 100 sccm and was the same for both carbonization and growth. The SiC growth rates of approximately 0.3 μm/min for 3MS and 1 μm/min for SCB are much higher than those typically obtained from the SiH₄/C₃H₈/H₂ gas system at the same growth temperature. The SiC film thickness of samples used for Hall measurements ranged from 0.5 to 1.5 μm as measured by cross-sectional scanning electron microscopy (SEM). Prior to Hall effect measurements, the surface morphology was measured by SEM and the film crystallinity was checked by X-ray diffraction.

Electrical properties of grown SiC films were measured in a variable temperature MMR Corp. Hall effect measurement system with a magnetic field up to 1.2 T. The samples were usually cut into a square shape of 1 × 1 cm. The Si substrate was not removed. Ohmic contacts of nickel silicide were formed by annealing deposited Ni at 900°C in forming gas for 10 min. Electrical connections were made by placing silver epoxy dots on ohmic contacts at the four corners of the sample and curing at 100°C overnight. The quality of the electrical contacts was evaluated by checking the linearity of their current-voltage (I-V) relation. The samples were cooled in a small Joule-Thomson refrigerator, and a Si diode was used to measure the temperature. The magnetic field was set at 1 T (10,000 Gauss) for all Hall effect measurements.

The atomic concentration of N atoms and the bonding of N atoms in the SiC lattice were investigated by SIMS and reflection-mode FTIRS, respectively. For reflection FTIRS measurements, the angle of incidence was 85°, and a polished Si(100) surface was used for the reference signal. Baseline distortion due to optical interference and dispersion was removed.

Results and Discussion

Figure 1 shows the electron carrier concentration of SiC films grown with 3MS as a function of N₂ flow rate. By varying the N₂ flow rate from 0.1 to 20 sccm, we increased the net electron concentration from just above 1 × 10¹⁷ to nearly 1 × 10²⁰ cm⁻³. The N₂-doping efficiency during SiC growth with 3MS is similar to that obtained with SiH₄/C₃H₈ in the same C:Si ratio of 3 on Si substrates⁶

* Electrochemical Society Active Member.

^z E-mail: a.steckl@uc.edu

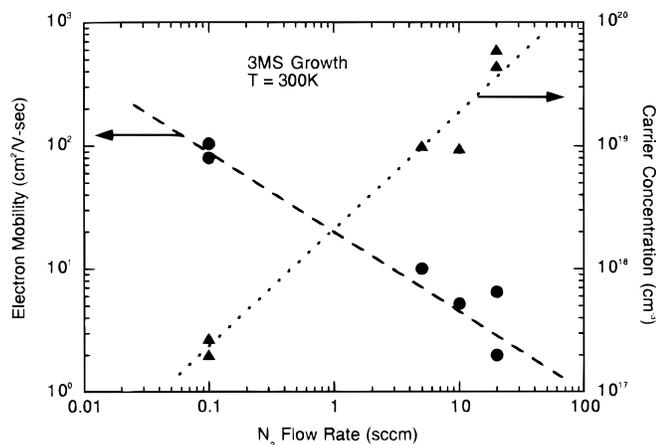


Figure 1. Effect of N_2 flow rate during SiC growth with 3MS on electron carrier concentration and Hall electron mobility.

and 6H-SiC substrates.⁷ The simultaneous effect of the N_2 flow rate on the mobility also is shown in Fig. 1. As expected, increasing the doping level decreases the mobility, from $104 \text{ cm}^2/\text{V s}$ for a N_2 flow rate of 0.1 sccm to $2 \text{ cm}^2/\text{V s}$ when the N_2 flow rate is 20 sccm .

The IR absorbance of Si-N bonds in the SiC lattice has a linear relationship with the electron carrier concentration, since each incorporated N forms four Si-N bonds and generates one free electron. However, the Si-N and Si-C stretching vibration absorption bands in transmission-mode FTIRS are overlapped. Transmission-mode FTIRS of SiC/Si₃N₄/Si(100) and Si₃N₄/Si(100) structures was performed. The transmission FTIR spectra of SiC/Si₃N₄ and SiC shown in Fig. 2 were obtained by using Si and Si₃N₄/Si as references, respectively. The absorption band at 800 cm^{-1} and the broad band centered at 850 cm^{-1} are from Si-C and Si-N stretching vibrations, respectively. However, in reflection-mode FTIRS, Si-C and Si-N vibration bands shift in opposite directions due to the dispersion in SiC refractive index and polarization of reflective light^{8,9} and thus can be clearly identified. Figure 3 shows the identification of these absorption bands. In spectra (a) and (b), the peaks at $\sim 785 \text{ cm}^{-1}$ are due to the Si-C stretching vibration. The peak at $\sim 1159 \text{ cm}^{-1}$ in spectrum (c) is assigned to Si-N bond vibration in the Si₃N₄ layer, as is the peak at $\sim 1128 \text{ cm}^{-1}$ in spectrum (a). The peaks at $980\text{--}990 \text{ cm}^{-1}$ in spectra (a) and (b) can be reasonably assigned to Si-N bonds formed by N atoms occupying C vacancy sites in the C sublattice. This possibility is much more likely than that of N atoms

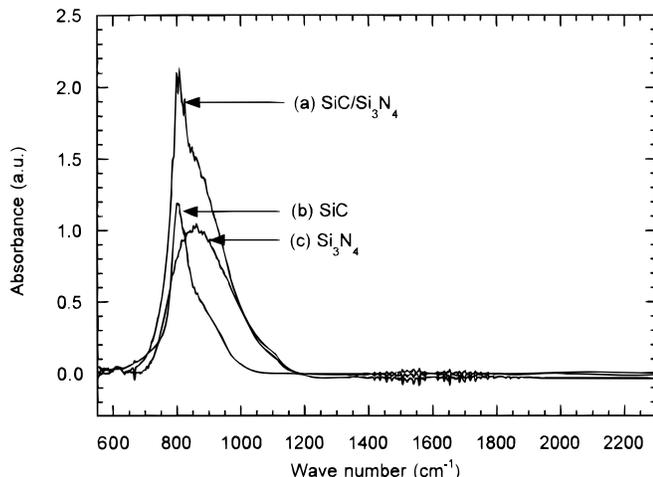


Figure 2. Transmission-mode FTIR spectra for SiC/Si₃N₄/Si structure with Si (curve a) and Si₃N₄/Si (curve b) as background. Also shown is the spectrum of an Si₃N₄/Si structure with Si(100) as background (curve c).

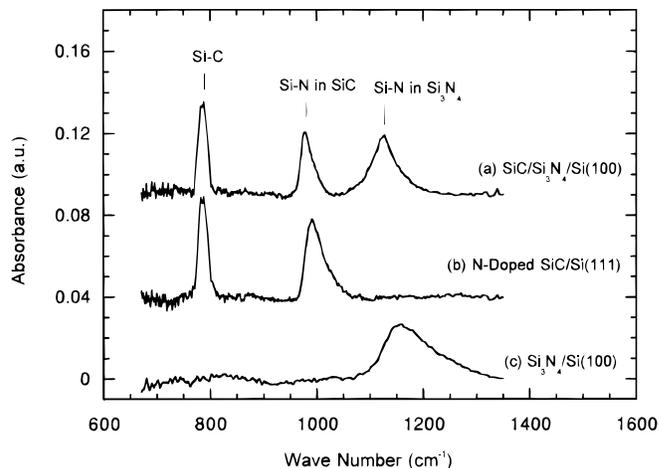


Figure 3. Reflection-mode FTIR spectra of (a) SiC/Si₃N₄/Si(100), (b) N-doped SiC/Si(111), and (c) Si₃N₄/Si(100). Polished Si(100) surface was used as reflection plate for (a) and (c), Si(111) surface for (b).

occupying Si sites and forming C-N bonds, due to the large size difference of N and Si atomic radii. This assignment is supported by the C-N bond vibration peaks reported at ~ 1350 and $\sim 2800 \text{ cm}^{-1}$ in tertiary amine.¹⁰

The reflection-mode FTIRS data was obtained for a set of SiC films grown as a function of N_2 flow rate. The SiC films were grown on carbonized Si(111) at 1200°C using 3MS. The N_2 flow rate was varied from 0.1 to 20 sccm during growth. The resulting spectra are shown in Fig. 4. The measured absorbance was normalized by the SiC film thickness to allow comparison of the FTIR peak heights. The Si-C absorption peak at 980 cm^{-1} increases monotonically with increasing N_2 flow rate. This indicates an increasing number of N atoms incorporated into the C sublattice with increasing flow rate. These results are consistent with both Hall effect and SIMS measurements. Figure 5 shows the comparison of electron carrier concentration, N atomic density and normalized Si-N bond IR absorbance measured by Hall effect, SIMS, and reflection FTIRS, respectively. The three measurements show the same increasing trend with increasing N_2 flow rate and thus support each other.

The temperature dependence of the electron carrier concentration is shown in Fig. 6 for both 3MS- and SCB-grown SiC films. The electron carrier concentration exhibits an Arrhenius-type behavior over the ~ 175 to 350 K temperature range. Over this range, the doping compensation model fits the Hall effect data reasonably well.

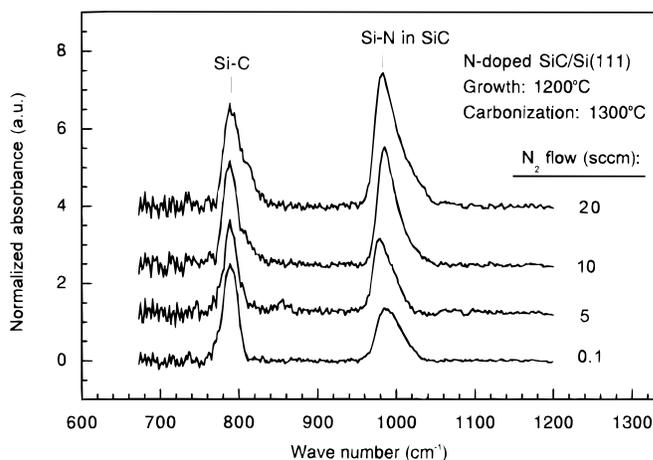


Figure 4. Reflection-mode FTIR spectra of N-doped SiC/Si(111) grown at 1200°C with 3MS and N_2 flow rate from 0.1 to 20 sccm . Polished Si(111) surface was used as reflection plate.

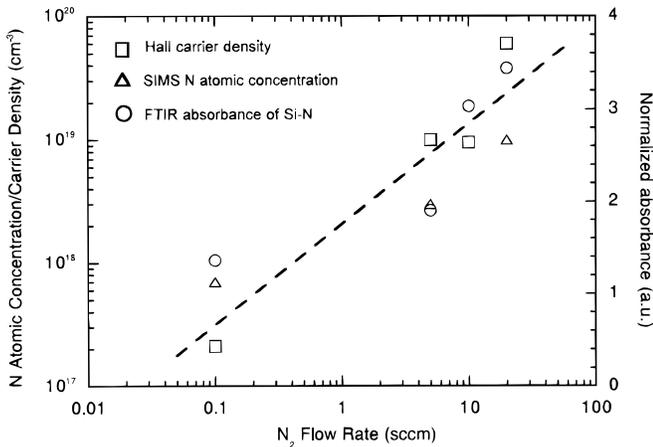


Figure 5. N₂ flow rate dependence of electron carrier concentration measured by Hall effect, N atomic density obtained by SIMS, and normalized Si-N absorbance from reflection FTIRS.

Using the simplified version of the compensation model, the temperature dependence of the carrier concentration [$n \sim \exp(-E_d/k_bT)$]¹¹ results in a N ionization energy (E_d) estimated at ~52 and ~62 meV for SCB- and 3MS-grown films, respectively. These values are larger than the 34-37 meV energy reported by Suzuki *et al.*⁶ for N₂-doped 3C-SiC and obtained from Hall effect measurements over a similar temperature range. However, our values match fairly well with the 53-55 meV nitrogen-bound exciton energy reported by Dean *et al.*¹² from optical measurements.

Also important is that while the 3MS-grown film used an N₂ flow rate of 0.1 sccm, the SCB-grown film used 50 sccm of N₂. In spite of the much higher N₂ flow rate, the SCB-grown film exhibited a carrier concentration ~5 times smaller than that obtained with 3MS. For example, at room temperature, the SCB-grown film had an electron carrier concentration of $4 \times 10^{-16} \text{ cm}^{-3}$, while the 3MS-grown film yielded $2 \times 10^{17} \text{ cm}^{-3}$. This difference in doping efficiency cannot be explained on the basis of simple site competition¹³ between N and C atoms, since both 3MS and SCB have the same C:Si ratio of 3. The very high growth rate experienced with SCB is probably an indica-

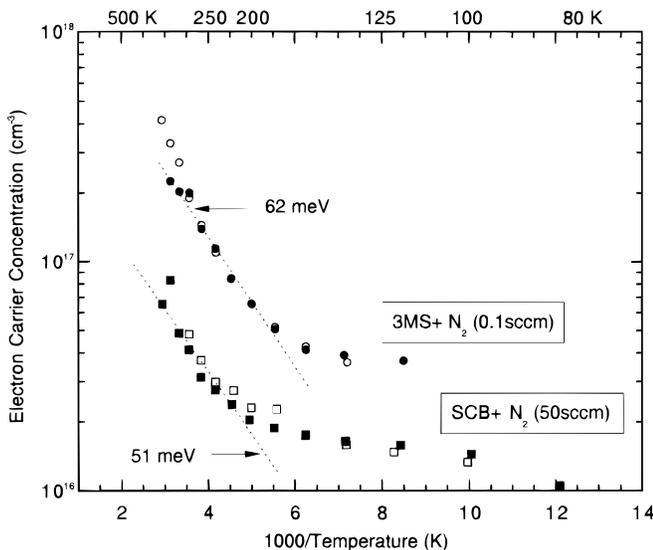


Figure 6. Temperature dependence of carrier concentration of 3C-SiC films grown by SCB and by 3MS with *in situ* N₂-doping (50 sccm for SCB and 0.1 sccm for 3MS). The filled and empty symbols represent separate growth runs.

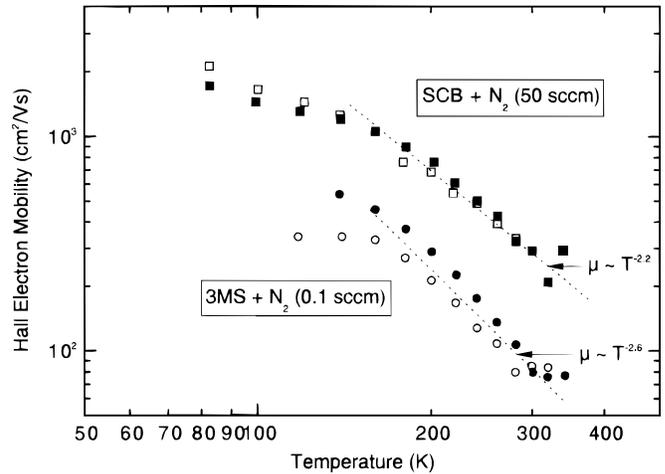


Figure 7. Temperature dependence of electron mobility of 3C-SiC films grown by SCB and by 3MS with *in situ* N₂-doping (50 sccm for SCB and 0.1 sccm for 3MS). The filled and empty symbols represent separate growth runs.

tion that the SCB molecule is very efficient in producing Si-C bonds and thus excluding N atoms from being incorporated in the lattice.

Figure 7 shows the temperature dependence of electron mobility of several SiC films grown with SCB and 3MS. The Hall electron mobility increases monotonically with decreasing temperature over the range measured. At 83 K, the electron mobility of SiC films grown using SCB is as high as 2115 cm²/V s and decreases to 333 cm²/V s at 300 K. The mobility decreases with a T^{-n} dependence, where n is 2.2 for SCB-grown films and 2.6 for 3MS-grown films. This temperature dependence at the higher temperatures is due to lattice scattering. Similar results have been suggested by Suzuki for SiH₄/C₃H₈-grown SiC films, where he measured⁶ a value of $n = 2-2.2$. The mobility leveling off at temperatures below 150 K indicates that ionized impurity scattering starts to play an important role but does not yet dominate the mobility.¹⁴ For measurement temperatures above 400 K, the SiC electron mobility as well as concentration varied dramatically from measurement to measurement, even at the same temperature. This is believed to be due to the effect of the Si substrate. Hall effect measurements on the plain p-Si(111) substrate show that for the temperature range of 80 to ~420 K, the majority carriers are holes with a concentration of 9×10^{13} to $2.6 \times$

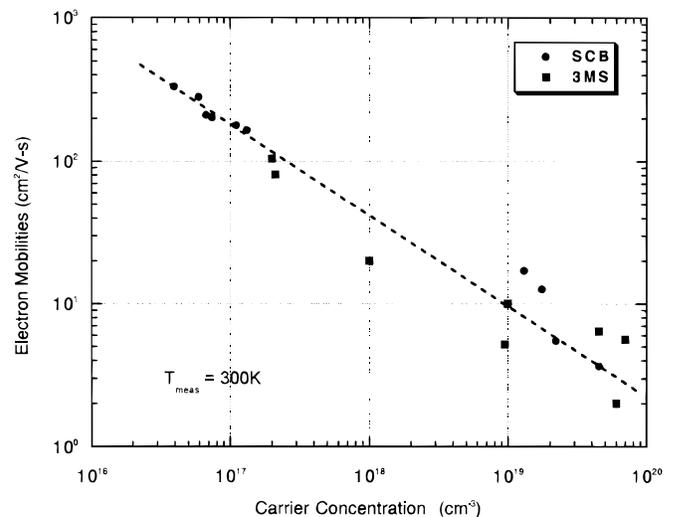


Figure 8. Electron mobility vs. carrier concentration measured from SiC films grown with SCB or 3MS on Si(111).

10^{14} cm^{-3} . Above 440 K, Si becomes intrinsic and conducting, and the Hall voltage became too small to be measured accurately.

Figure 8 shows the relationship between electron mobility and carrier concentration at a fixed temperature of 300 K measured from several SiC films grown by SCB and 3MS with *in situ* N_2 -doping. The well-known trend of increasing electron mobility with decreasing carrier concentration is reproduced for the SiC growth with single organosilanes. The best results come from an SCB-grown film with a mobility of $333 \text{ cm}^2/\text{V s}$ and a carrier concentration of $4 \times 10^{16} \text{ cm}^{-3}$. The mobilities of 3MS-grown films are usually smaller and carrier concentrations higher than those films grown with SCB under very similar conditions. The reason is not quite clear, but it may be related to the different reactivities of SCB and 3MS on the Si and SiC surfaces. Since SCB pyrolyzes more rapidly than 3MS due to its strained ring structure, it would be harder for impurities in the ambient and in the gas source (including the desired impurity: N) to be incorporated into the SiC lattice during growth. Figure 7 also shows that electron mobility decreases monotonically as the carrier concentration increases. Electron mobilities of 3C-SiC grown from organosilanes are comparable to those obtained by Matsunami's group¹⁵ and by Powell *et al.*¹⁶ on 3C-SiC films grown with an $\text{SiH}_4/\text{C}_3\text{H}_8/\text{H}_2$ gas system.

Conclusions

We investigated the structure and electrical properties of N_2 -doped SiC films grown from single-precursor SCB or 3MS by reflection-mode FTIRS and Hall effect measurements. Nitrogen can be effectively doped into 3MS-grown films with various N_2 flow rates during the growth. Reflection-mode FTIRS was used to study N-doping efficiency, and the results are consistent with those from Hall effect and SIMS measurements. SCB growth requires a much higher N_2 flow rate for doping, but has yielded mobilities higher than those obtained with 3MS-grown films. A mobility of $333 \text{ cm}^2/\text{V s}$

was obtained at 300 K from a SiC film grown using SCB. SCB and 3MS are appealing alternatives as precursors for 3C-SiC growth, given their ability to provide a safe and simple fabrication process. Further work is underway to improve SiC high temperature electrical properties by fabricating SiC SOI structure with SiO_2 or Si_3N_4 as an insulating layer between SiC and Si to reduce the substrate effect.

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