

Deposition and doping of silicon carbide by gas-source molecular beam epitaxy

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Thin films of silicon carbide (SiC) have been deposited at 1400–1450 °C on vicinal and on-axis 6H-SiC(0001) substrates by gas-source molecular beam epitaxy using the SiH₄-C₂H₄-H₂ gas system. Polytype control (6H- or 3C-SiC) was established by utilizing substrates of particular orientations. Residual, unintentionally incorporated nitrogen impurity levels were affected by changing the SiH₄/C₂H₄ gas flow ratio, in agreement with the “site-competition epitaxy” model. *In situ* doping was achieved by intentional introduction of nitrogen and aluminum into the growing crystal. © 1997 American Institute of Physics. [S0003-6951(97)01836-6]

The extremes in the thermal and electronic properties of wide-band-gap semiconductors make possible many current and conceivable applications. Silicon carbide is one of the most studied of these materials. About 250 different polytypes have been reported.¹ The sole cubic (zinc-blende) structure (β - or 3C-SiC) has a room-temperature energy band gap of 2.3 eV. Among the hexagonal and rhombohedral polytypes (α -SiC) the most common is 6H-SiC with a room-temperature band gap of ≈ 3.0 eV. Single-crystal epilayers of 3C- and 6H-SiC can be homoepitaxially deposited via various vapor phase epitaxial growth procedures.

Previous SiC film growth studies via molecular beam epitaxy (MBE) on 6H-SiC substrates at growth temperatures which were lower (< 1200 °C) than those typically used in chemical vapor deposition (CVD) reportedly did not result in homoepitaxial reproduction of the 6H substrate. Recently, we have reported² the first deposition of 6H-SiC(0001) epilayers by gas-source MBE (GSMBE) at $T \geq 1350$ °C using SiH₄-C₂H₄-H₂. The only previous report of SiC doping by MBE was performed by Kaneda *et al.*³ who deposited B-doped films of 3C-SiC(111) on on-axis 6H-SiC{0001} at 1150–1400 °C. *p-n* junction diodes between *p*-type ($p = 1 \times 10^{18} \text{ cm}^{-3}$) 3C-SiC(111) and *n*-type ($n = 5.6 \times 10^{16} \text{ cm}^{-3}$) 6H-SiC(0001) exhibited breakdown fields of $6.7 \times 10^5 \text{ V cm}^{-1}$.

In this work, a previously described⁴ GSMBE system was employed to deposit and dope 3C- and 6H-SiC. The base pressure of the system was $\approx 10^{-9}$ Torr and the operating pressure was approximately $(1-4) \times 10^{-4}$ Torr silane (SiH₄), ethylene (C₂H₄), and hydrogen (H₂) were used to grow the SiC at temperatures between 1400 and 1450 °C. Films were doped *n*-type using N atoms introduced from either NH₃ (300 ppm in H₂) or molecular N₂. *p*-type conductivity was achieved by incorporating Al evaporated from a standard MBE effusion cell. Table I lists the growth conditions.

Since previous studies by CVD⁵⁻⁸ have demonstrated the advantage of using 6H-SiC(0001) crystals cut off-axis to assist in the homoepitaxial growth of the 6H polytype,

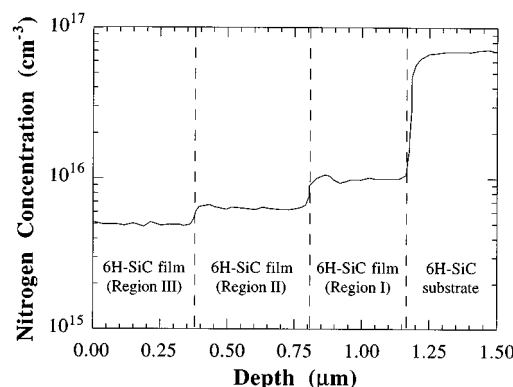


FIG. 1. SIMS profile of a 6H-SiC(0001) films grown at 1400 °C with 0.75 sccm SiH₄, 5 sccm H₂, and a variable C₂H₄ flow: 0.375 sccm in Region I, 0.5 sccm in Region II, and 0.75 in Region III. Note the changes in the nitrogen incorporation that resulted from changing the C₂H₄ input due to site-competition epitaxy between C and N.

α (6H)-SiC(0001) substrates cut $3.5 \pm 0.5^\circ$ toward $[1\bar{1}20]$ were the most common substrates used. On-axis α (6H)-SiC(0001) were also used, in cases where β (3C)-SiC(111) was desired. Substrates were dipped in a 10% HF solution, loaded immediately into the growth chamber and cleaned *in situ* using a SiH₄ exposure and UHV anneal.⁹

The epilayers were characterized using reflection high-energy electron diffraction (RHEED), secondary ion mass

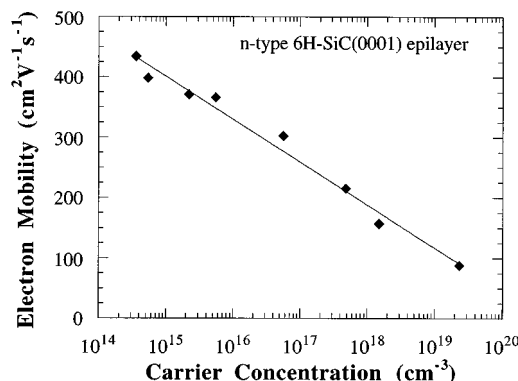


FIG. 2. Electron mobility vs carrier concentration for *n*-type 6H-SiC(0001) epilayers. Measurements were performed at room temperature. The solid line is a guide for the eye.

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TABLE I. Range of growth parameters used in the course of this study.

	undoped	<i>n</i> -type doped	<i>p</i> -type doped
Substrate	6H-SiC(0001)	6H-SiC(0001)	6H-SiC(0001)
Deposition pressure (Torr)	$\approx 2 \times 10^{-4}$	$\approx 2 \times 10^{-4}$	$\approx 2 \times 10^{-4}$
Deposition temperature (°C)	1400	1400	1450
SiH ₄ flow rate (sccm)	0.75	0.75	0.75
C ₂ H ₄ flow rate (sccm)	0.375, 0.5, 0.75	0.375	0.75
H ₂ flow rate (sccm) ^a	5	0–5	5
Al cell temperature (°C)	N/A	N/A	770–1010
NH ₃ :H ₂ flow rate (sccm) ^{a,b}	N/A	0–5	N/A
N ₂ flow rate (sccm) ^b	N/A	0–5	N/A

^aThe total H₂+NH₃H₂ flow rate was maintained at 5 sccm.^b*n*-type doping was performed with either NH₃ or N₂.

spectroscopy (SIMS), mercury-probe capacitance-voltage (*C*–*V*) analysis, and room-temperature Van der Pauw–Hall-effect measurements. Special contact pads,⁹ produced by depositing heavily doped ($\approx 10^{18}$ cm⁻³) SiC through a shadow mask, were used to create ohmic contacts on undoped and lightly doped samples. All doped samples (≈ 1 μm in thickness) were grown on substrates of the opposite doping type in order to minimize parallel conduction phenomena.

Since even the most pure SiC grown from the vapor phase contains some quantity of N, it was not surprising that the major contaminant in these films was N. The presence of the N impurity is particularly significant, because it is the most shallow donor impurity in SiC. Consequently, it was the agent responsible for the *n*-type character of unintentionally doped SiC films. Although the growth rate measured at the temperatures and ambient conditions studied here was not observed to change when the C₂H₄ flow rate was modulated between 0.375 and 0.75 sccm at a constant SiH₄ flow rate (0.75 sccm) considerable differences in the background atomic nitrogen and electron concentrations in the SiC films was measured. The background level of N was in accordance with the “site-competition epitaxy” model arguments^{10–13} based on the principle of competition between C and N for the C sites, and Al and Si for the Si sites in the SiC crystals. Thus, the N contamination level was significantly decreased by increasing the amount of C (C₂H₄) delivered in the gas phase.

Figure 1 shows a depth profiled 6H-SiC(0001) film grown at 1400 °C using 0.75 sccm SiH₄ and a variable C₂H₄ flow. The C₂H₄ flow was varied according to: 0.375 sccm for 3 hr (Region I), 0.5 sccm for 3 h (Region II), and 0.75 sccm for 3 h (Region III). The change in N content with C source supply is very apparent from the abrupt changes that occur in the N depth profile. A flow of 0.75 sccm C₂H₄ resulted in the incorporation of N at the detection limit for N ($\approx 5 \times 10^{15}$ cm⁻³) in the SIMS system.

Several films of both 6H-SiC (grown on vicinal 6H-SiC)

and 3C-SiC (grown on on-axis 6H-SiC) were also grown at 1400 °C using the three different C₂H₄ flow rates noted above. The carrier concentration and mobility results from *C*–*V* and Hall-effect characterization are listed in Tables II and III. The increase in the impurity and electron concentrations with decreasing C₂H₄ input confirmed the “site-competition model” for N incorporation by MBE.

Despite the fact that unintentionally doped SiC films were *n*-type as grown, *n*-type doping was studied in order to establish a controllable electron population within the grown films. In order to perform this study, N was introduced into the SiC lattice during growth of the SiC epilayers. Since the quantity of N incorporated into the SiC lattice from residual gas molecules in the growth reactor was not a concern when *n*-type doping was performed, the reactant mixture with the lowest total input of source gases (0.75 sccm SiH₄, 0.375 sccm C₂H₄, and 5 sccm H₂) was chosen. Donor doping was performed *in situ* at 1400 °C on monocrystalline 6H- and 3C-SiC using both the H₂-diluted NH₃ and pure N₂. Doping between 5×10^{15} and 8×10^{17} cm⁻³ was achieved using the NH₃/H₂ mixture; 1×10^{18} – 4×10^{19} cm⁻³ with the N₂ additions. Figures 2 and 3 show the electron mobility as a function of electron concentration in the close-packed plane for 6H-SiC(0001) and 3C-SiC(111) at room temperature for both undoped and doped films.

Epilayers of 6H- and 3C-SiC were doped *p*-type by incorporating Al in the growing epilayers. All growth experiments were performed at 1450 °C using 0.75 sccm SiH₄, 0.75 sccm C₂H₄, and 5 sccm H₂. The higher C₂H₄ flow rate was used to take advantage of the site-competition process which resulted in a decrease in the concentration of background N, a compensating impurity in *p*-type SiC. The higher temperature was used in an attempt to aid in dopant activation. Acceptor doping between 2×10^{15} and 8×10^{18} cm⁻³ was achieved. Figures 4 and 5 show the hole mobility as a function of hole concentration in the close-

TABLE II. Electrical properties of undoped 6H-SiC films.

<i>C</i> – <i>V</i> measurement		Hall measurement	
C ₂ H ₄ flow (sccm)	$N_D - N_A$ (cm ⁻³)	n (cm ⁻³)	μ_n (cm ² V ⁻¹ s ⁻¹)
0.375	4.3×10^{15}	2.2×10^{15}	371
0.5	1.3×10^{15}	5.4×10^{14}	398
0.75	7.1×10^{14}	3.6×10^{14}	434

TABLE III. Electrical properties of undoped 3C-SiC films.

<i>C</i> – <i>V</i> measurement		Hall measurement	
C ₂ H ₄ flow (sccm)	$N_D - N_A$ (cm ⁻³)	n (cm ⁻³)	μ_n (cm ² V ⁻¹ s ⁻¹)
0.375	9.1×10^{15}	5.3×10^{15}	608
0.5	3.7×10^{15}	9.8×10^{14}	681
0.75	9.2×10^{14}	4.6×10^{14}	772

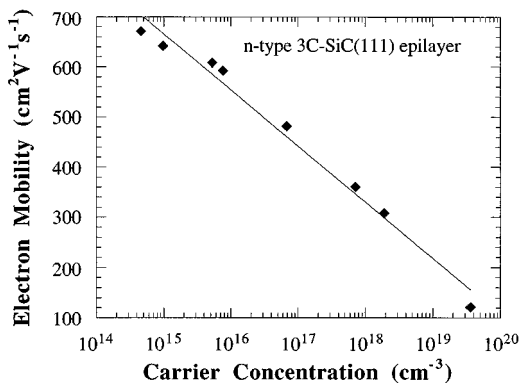


FIG. 3. Electron mobility vs carrier concentration for *n*-type 3C-SiC(111) epilayers. Measurements were performed at room temperature. The solid line is a guide for the eye.

packed plane for 6H-SiC(0001) and 3C-SiC(111) measured at room temperature.

In summary, monocrystalline thin films of 3C- and 6H-SiC have been grown on on-axis and vicinal α (6H)-SiC(0001) substrates, respectively, by GSMBE at 1400–1450 °C using a SiH₄-C₂H₄-H₂ gas mixture. The concentration of N in the epilayers was found to depend directly on the SiH₄/C₂H₄ ratio. An undoped 6H-SiC epilayer with an electron concentration of $3.6 \times 10^{14} \text{ cm}^{-3}$ and mobility of $434 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was produced. This mobility measurement is believed to be the highest reported for this polytype and, perhaps, is an indication of the high purity achieved in 6H-SiC epilayers by GSMBE. Epilayers could be doped *n*- or *p*-type *in situ* by adding N or Al.

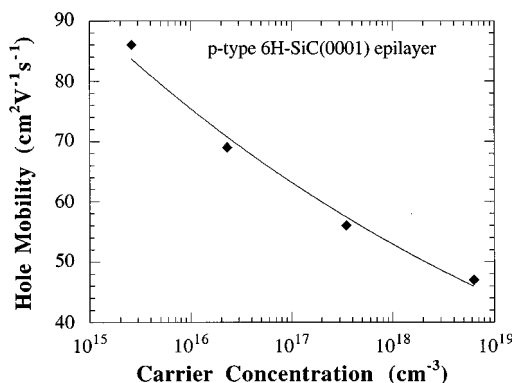


FIG. 4. Electron mobility vs carrier concentration for *p*-type 6H-SiC(0001) epilayers. Measurements were performed at room temperature. The solid line is a guide for the eye.

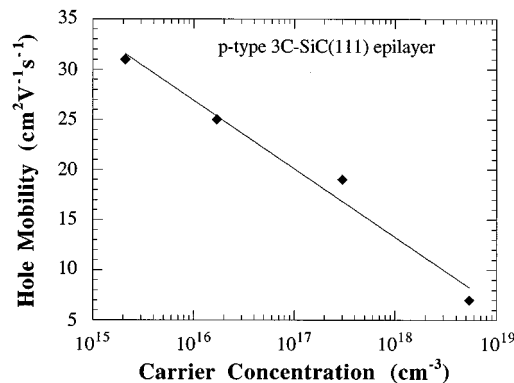


FIG. 5. Electron mobility vs carrier concentration for *p*-type 3C-SiC(111) epilayers. Measurements were performed at room temperature. The solid line is a guide for the eye.

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