

Heteroepitaxial Growth of SiC on Si(100) and (111) by Chemical Vapor Deposition Using Trimethylsilane

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Heteroepitaxial growth of 3C-SiC on Si by chemical vapor deposition has been investigated using the precursor trimethylsilane. To optimize the growth process and to obtain high growth rates, we have investigated the effect of temperature and precursor flow rate on on-axis Si(100) and off-axis Si(111) substrates. High growth rates, in excess of 30 $\mu\text{m/h}$, have been obtained. Growth on carbonized Si(111) substrates produces a smoother surface morphology compared to films grown on noncarbonized substrates. Growth of thicker SiC films was carried out on carbonized off-axis Si(111) substrates with a growth rate of $\sim 20 \mu\text{m/h}$ at 1200°C and 10 sccm of trimethylsilane. The resulting SiC films were 6-7 μm thick, crack-free, and highly crystalline. This reveals the possibility for the application of these SiC films as "pseudosubstrates" and also for SiC-on-Si microelectromechanical structures which can withstand high temperature and corrosive environments.

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There has been a recent surge in activity in wide-bandgap semiconductor (WBGs) materials because of an increasing need for electronic devices capable of operating at high temperatures, high frequencies, and high power levels. The properties of silicon carbide (SiC) (e.g., wide bandgap, high breakdown electric field strength, high saturated electron drift velocity, and high thermal conductivity) make the material suitable for electronic devices operating under extreme conditions of power and temperature. One of the factors that has inhibited development of SiC device technology is the absence of low-cost SiC substrates. The motivation for the heteroepitaxial growth of SiC-on-Si has been to provide relatively inexpensive and large-area substrates of SiC for electronic devices, X-ray masks, etc.

The heteroepitaxial growth of SiC on Si has been extensively investigated over the last few years. Initial work was done by chemical vapor deposition (CVD) using separate precursors for Si and C. Powell et al.¹ used SiH_4 and propane to grow single-crystalline SiC on Si at 1360°C at growth rates of 2.5 $\mu\text{m/h}$. Nagasawa and Yamaguchi² have reported growth of 3C-SiC on Si(111) using SiH_2Cl_2 and C_2H_2 by low-pressure CVD (LPCVD) at a temperature of 1000°C. An alternative approach has been to use a single precursor containing both Si and C atoms. Steckl et al.³ have successfully investigated the growth of 3C-SiC on Si(100) using silacyclobutane (SCB) at temperatures as low as 800°C. Kunstmann et al.^{4,5} have reported growth of 3C-SiC films of thickness up to 7.5 μm using methyltrichlorosilane (CH_3SiCl_3) and methyltribromosilane at temperatures around 1200°C. Nordell et al.⁶ have studied the growth of 3C-SiC using hexamethyldisilane, while Seo et al.⁷ have utilized tetramethylsilane.

We have previously reported⁸ that the use of the precursor trimethylsilane (3MS) can produce thick SiC films on Si(111) substrates. 3MS is a colorless, noncorrosive, nonpyrophoric organosilane gas. The gas used in this work has been synthesized by Dow Corning Corporation (DC part no. X9-5170). This material is specifically designed to meet the safety, simplicity, and purity requirements of the semiconductor industry. 3MS available in high purity comparable to other VLSI-grade (very large-scale integrated) silanes has been established in the growth of dielectric films by plasma-enhanced CVD.^{9,10} The nonpyrophoric nature of the gas makes it much safer to use as compared to silane. In this paper we report in detail on the growth of SiC with 3MS on carbonized and noncarbonized Si(100) and (111) substrates.

Experimental

The deposition experiments were carried out in a computer-controlled rapid thermal (RT) CVD system, the operation of which has

been previously described¹¹ in detail. Growth runs have been carried out on both Si(100) and Si(111) wafers. Before being transferred to the deposition chamber, the substrates were cleaned by dipping in 1% buffer HF solution for 1 min. In situ cleaning was carried out at 1200°C in a hydrogen atmosphere for 1 min at atmospheric pressure. The deposition experiments were performed at various precursor flow rates (1.5-12.5 sccm 3MS), different substrate temperatures (1000-1200°C), and with and without prior carbonization with propane. The carbonization conditions were 1300°C, 10 sccm C_3H_8 , 1.0 L/min H_2 , and 760 Torr growth pressure. All growth runs were performed for a period of 3 min at low pressure (3.2 Torr) with 1.0 L/min H_2 flow rate. For ease of comparison, the period of growth, growth pressure, and carrier gas flow rate have been kept constant for all experiments. Figure 1 shows a time-temperature schematic diagram of a typical run used for the deposition process.

The SiC films were characterized using several techniques. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to study the surface morphology of the grown films. Cross-sectional SEM was used to study the SiC/Si interface and to measure the thickness of the films. The crystallinity and orientation of the grown films was determined by X-ray diffraction (XRD). Secondary ion mass spectrometry (SIMS) measurements were performed to obtain the depth profiles of the elemental composition of the film.

Results and Discussion

The growth runs were performed with on-axis Si(100) and off-axis Si(111) wafers. The effect of temperature, precursor flow rate, substrate orientation, and carbonization on growth rate, crystallinity, and surface morphology were studied.

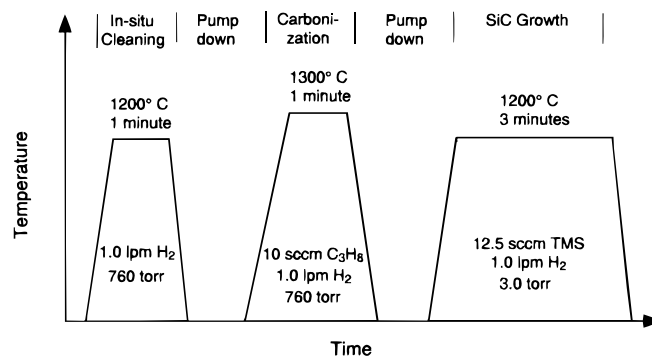


Figure 1. Schematic diagram of typical time-temperature profile used for SiC growth.

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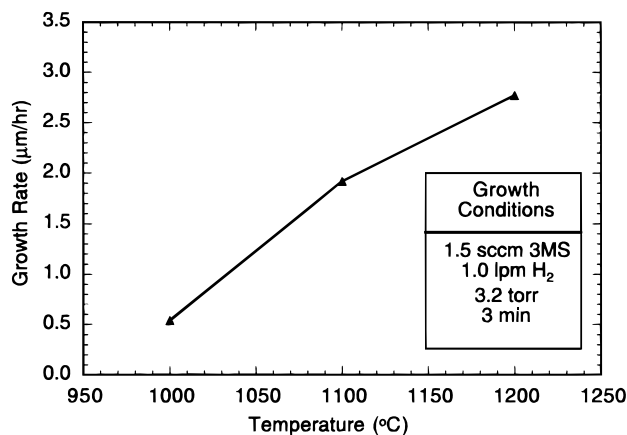


Figure 2. SiC growth rate as a function of growth temperature on noncarbonized Si(100) substrates.

The effect of temperature on the SiC growth rate at a relatively low 3MS flow rate of 1.5 sccm on Si(100) is shown in Fig. 2. The SiC growth rate increased from 0.54 $\mu\text{m/h}$ at 1000°C to 2.77 $\mu\text{m/h}$ at 1200°C. The XRD spectra shown in Fig. 3 for SiC films grown at several temperatures indicate a significant increase in the SiC(200) peak with increasing growth temperature. The increase in XRD peak intensity normalized to film thickness and a corresponding decrease in peak full width at half-maximum (fwhm) with temperature, as shown in Fig. 4, indicate an improvement in crystallinity at higher temperatures. No other XRD peaks were observed, indicating that the material was deposited with a single-crystal orientation. The SiC films were also characterized by Fourier transform infrared (FTIR) spectroscopy. A strong absorption peak was observed at 793 cm^{-1} , corresponding to the Si-C bond. The FTIR transmission spectrum of the film grown at 1200°C is shown in Fig. 5. The fwhm of the FTIR peak is 25 cm^{-1} , which is comparable to values reported in the literature¹⁰ for high-quality SiC films grown by other single precursors.

The growth temperature was observed to also have a significant effect on the growth rate at high precursor flow rates. Figure 6 shows the temperature variation of the growth rate on Si(111) wafers at a 3MS flow rate of 12.5 sccm. Crystalline films of SiC(111) were obtained at temperatures as low as 1000°C. Growth experiments at 900°C under the same conditions revealed no continuous SiC film deposition, probably because of insignificant degree of 3MS decomposition at such low temperatures. Though the growth rate reported by SCB is greater than 10 $\mu\text{m/h}$ at 900°C,¹² at high temperatures the growth rate obtained with 3MS is higher than 32 $\mu\text{m/h}$. This is significantly higher than that obtained using other single precursors such as methyltrichlorosilane and methyltribromosilane,⁴ or the combination of silane and propane.¹ High growth rates also resulted

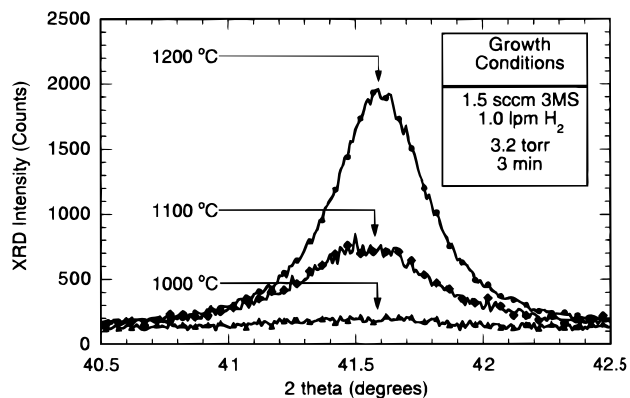


Figure 3. SiC XRD spectra for films grown at several temperatures on noncarbonized Si(100).

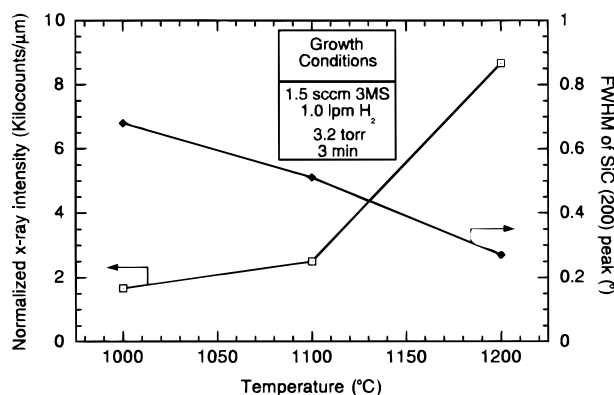


Figure 4. SiC XRD peak intensity (normalized to film thickness) and peak fwhm vs. growth temperature for films on noncarbonized Si(100).

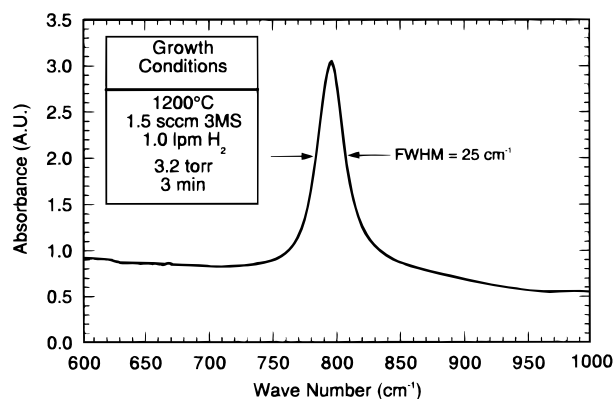


Figure 5. FTIR transmission spectrum of SiC film grown on noncarbonized Si(100) substrate.

in nonuniform growth across the wafers at high temperatures. Additional growth experiments at different temperatures are required to accurately predict the activation energy for the process.

The XRD spectra for films grown under the conditions of Fig. 6 are shown in Fig. 7. A significant increase in SiC XRD signal with growth temperature is observed. The uncorrected value of fwhm of the SiC(111) peak for the film grown at 1200°C is 0.244°. The fwhm value obtained after stripping the $K\alpha_2$ peak but not corrected for the system broadening is 0.208°, which is comparable to values reported in the literature.¹¹ The XRD peak signal normalized to the film thickness, as shown in Fig. 8, clearly indicates a corresponding improvement in crystallinity at higher growth temperatures.

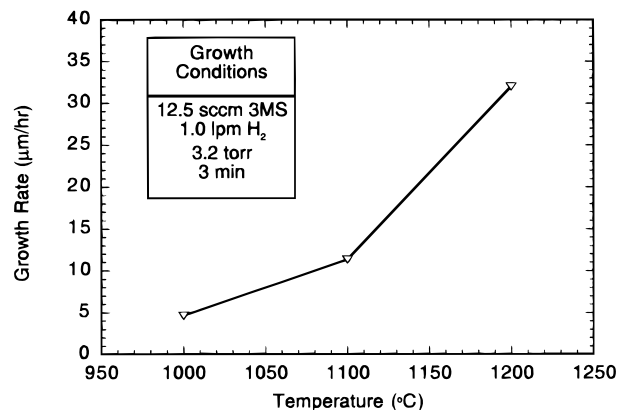


Figure 6. SiC growth rate as a function of growth temperature on noncarbonized Si(111) substrate.

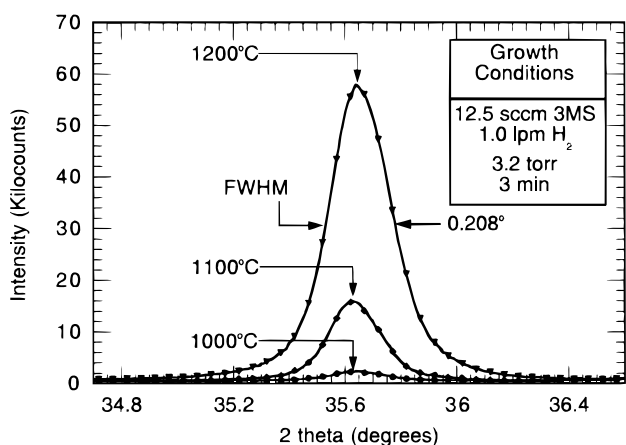


Figure 7. SiC XRD spectra for films grown at several temperatures on non-carbonized Si(111).

The effect of precursor flow rate has been studied on both Si(100) and Si(111) wafers at a growth temperature of 1200°C. Figure 9 shows the variation of growth rate with 3MS flow rate on Si(100) and Si(111) wafers. Growth rates of 5-10 $\mu\text{m/h}$ are obtained at lower 3MS flow rates, while a growth rate as high as 32 $\mu\text{m/h}$ are obtained at the highest flow rate of 12.5 sccm. However, at the highest flow rate the color of the films obtained is relatively dark, probably due to excess carbon incorporation. Under high-flow-rate conditions, the cleanliness of the growth chamber also deteriorates rapidly. This is because of deposition of a carbon-rich film on the chamber walls, which progressively increases with time. This in turn converts the process into a “warm” wall process because of absorption of heat by the material deposited on the walls of the chamber.

Growth experiments were also conducted on carbonized substrates. The carbonization process using propane and hydrogen is used to grow an initial SiC buffer layer followed by the growth of a thicker SiC layer using 3MS. The effect of the buffer layer on the subsequent SiC growth rate, crystallinity, and morphology was studied. The carbonization conditions were optimized and hence were kept constant for all runs (1300°C, 10 sccm C_3H_8 , 1.0 L/min H_2 , and 760 Torr). Figure 10 compares the variation of SiC growth rate with 3 MS flow rate on noncarbonized and carbonized Si(111) substrates. Though the growth rate obtained on noncarbonized substrates is relatively higher, the films grown on carbonized substrates exhibit a much better crystallinity, as seen in the plot of normalized XRD intensity as a function of flow rate shown in Fig. 11.

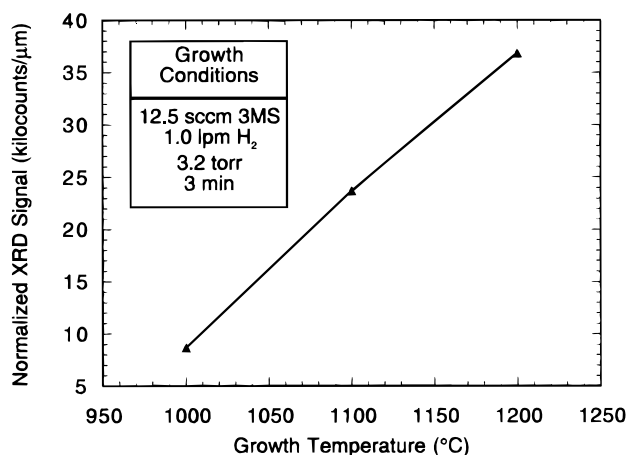


Figure 8. SiC XRD peak intensity (normalized to film thickness) and peak fwhm vs. growth temperature for films on noncarbonized Si(111).

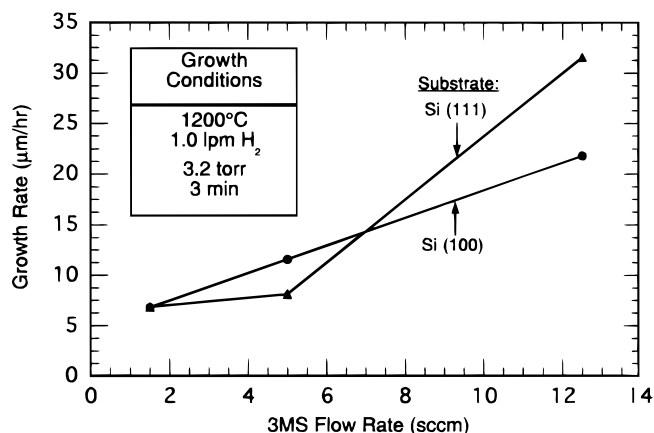


Figure 9. Variation of SiC growth rate with 3MS flow rate on Si(111) and Si(100) substrates.

The effect of carbonization on the morphology of SiC grown on Si(111) can be seen in the SEM photographs shown in Fig. 12. The surface of the film grown on the noncarbonized substrate is quite rough. The carbonized films reveal large triangular pits at the SiC/Si interface, formed during the carbonization process, due to the outward diffusion of Si. On the noncarbonized substrates, the SiC/Si interface shown in Fig. 13 reveals much smaller pit size and density. This is

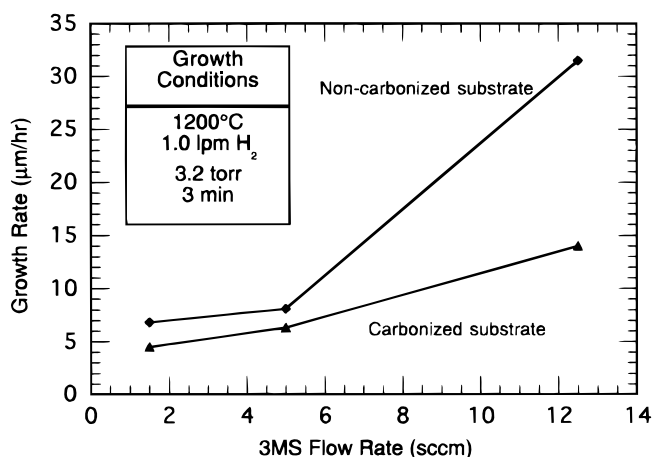


Figure 10. SiC growth rate as a function of 3MS flow rate on carbonized and noncarbonized Si(111) substrates.

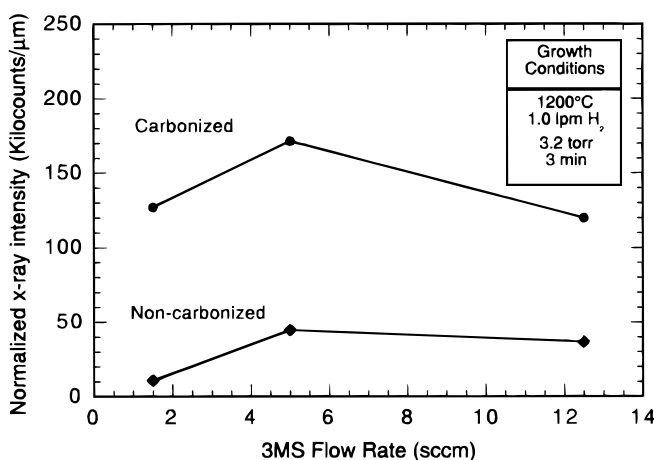
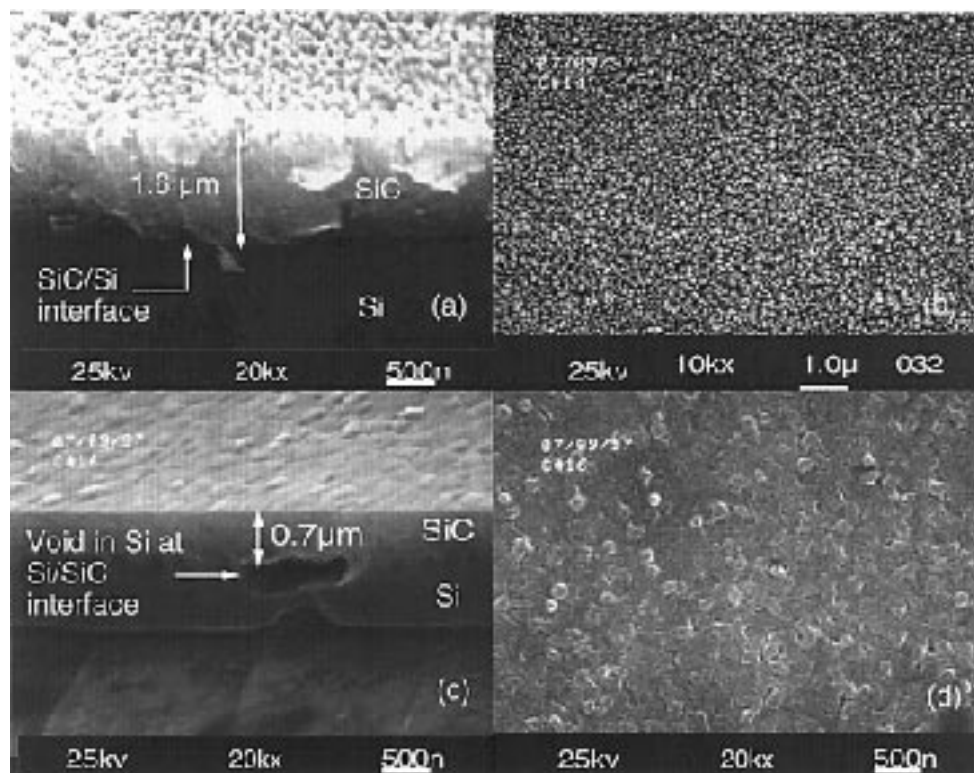


Figure 11. SiC XRD peak intensity (normalized to film thickness) vs. 3MS flow rate for films on carbonized and noncarbonized Si(111) substrates.

Figure 12. SEM microphotographs of SiC films grown on Si(111): (a) and (b) non-carbonized sample; (c) and (d) carbonized sample. Growth conditions: 1200°C, 3.2 Torr, 12.5 sccm 3MS, and 1.0 L/min H₂.



probably because the primary source of Si at the SiC/Si interface is from the precursor and not from the Si substrate. The surface morphologies of these films was also studied by AFM. The average roughness (R_a) of the carbonized film obtained from a 10 μm line scan is 2.05 nm as compared to 6.29 nm for a noncarbonized film. The higher roughness of the noncarbonized films is probably due to higher growth rates than in the case of the carbonized substrates. Figure 14 shows the surface topography of the SiC films grown on carbonized and noncarbonized Si(111) as obtained by AFM.

The composition of SiC grown on various substrates was obtained by SIMS measurements. In general, the SiC grown on carbonized substrates exhibits much better stoichiometry as compared

to the noncarbonized film. Relatively lower growth rates coupled with growth on a highly crystalline buffer layer could be possible reasons for better stoichiometry obtained for growth on carbonized films. SIMS depth profiles of SiC films grown on carbonized and noncarbonized Si(111) substrates are shown in Fig. 15. Figure 16 shows the depth profiles of B in these SiC films grown on heavily doped ($\rho = 0.009 \Omega \text{ cm}$) Si(111) substrates. Very little if any B autodoping occurs in SiC films grown on either carbonized or noncarbonized substrates. The B level in the SiC is at the noise level of the measurement.

Using the high-growth-rate capability of 3MS, we also investigated the growth of thicker SiC films. There are several reasons for pursuing the growth of thicker SiC films on Si. These include the fabrication of self-supporting SiC layers ("pseudosubstrates") and for SiC-on-Si microelectromechanical structures (MEMS) which can withstand high temperature and corrosive environments. Since the growth on carbonized substrates yielded better surface morphology, the substrate was carbonized prior to the thick film growth. The SiC growth was done at 1200°C, 3.2 Torr, 1.0 L/min H₂, and 10 sccm 3MS for a period of 20 min.

The results obtained from the thick-film experiment are very encouraging. The crystallinity of the films was measured by XRD. Because the very strong intensity of the SiC (111) peak saturated the detector, Al filters were placed in the path of the diffracted X-ray beam. Figure 17 contains an XRD spectrum of the SiC/Si(111) thick-film structure. The uncorrected fwhm values of the SiC(111) and the Si(111) peaks are 0.187 and 0.116°, respectively. The corrected values obtained by stripping the $K\alpha_2$ peak are 0.141 and 0.10° for SiC and Si, respectively. The fwhm of 0.1° for the Si peak represents effectively the resolution of the XRD system. The finding that the SiC peak fwhm is comparable to that of Si is indicative of the highly crystalline nature of the SiC film. Figure 18 shows a cross-sectional SEM photograph of the SiC/Si(111) thick-film structure. The thickness of the SiC film as obtained by cross-sectional SEM is 6.3 μm , which translates to a growth rate of $\sim 19 \mu\text{m/h}$. The SiC film was continuous and there were no cracks observed on the SiC surface. Though the surface was rough, it was highly uniform, indicating that the morphology could be improved by polishing.

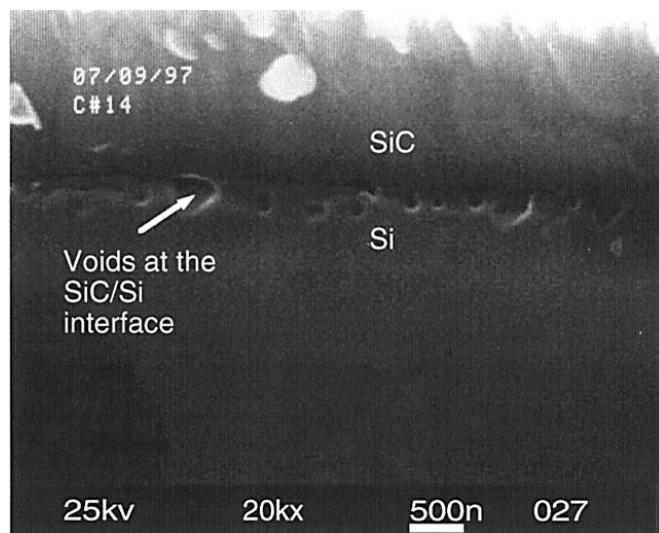


Figure 13. The SiC/Si interface as seen by cross-sectional SEM (60°C tilt) on sample grown on noncarbonized Si(111). Growth conditions: 1200°C, 3.2 Torr, 12.5 sccm 3MS, and 1.0 L/min H₂.

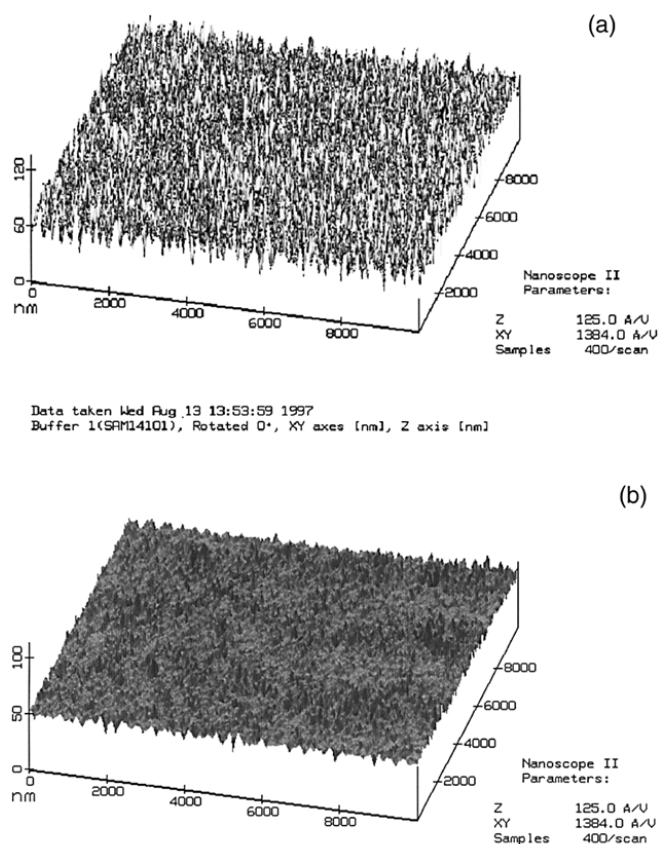


Figure 14. Surface topography of SiC on Si(111) obtained by AFM: (a) non-carbonized and (b) carbonized substrate.

Further growth of SiC device layers on these thick films is only possible if considerable improvement in surface morphology can be reached. Therefore, the films were subjected to a polishing procedure to investigate their use as pseudosubstrates. The films were polished using a 0.1 μm diamond powder lapping film. Figure 19 contains plan-view SEM photographs of the SiC on Si(111) thick-film structure which compare the surface morphologies before (as-grown sample) and after polishing. The surface morphology of the polished surface is a considerable improvement from the as-grown film, suggesting feasibility of such a process. It has been reported¹³ that the dislocation density in thicker films decreases considerably as compared to that present at the SiC/Si interface. Although no regrowth experiments were performed in this study, encouraging results in the thick-film-growth experiments coupled with improved surface morphology obtained after polishing demonstrated the capability of this approach for the fabrication of SiC-on-Si pseudosubstrates for device as well as MEMS applications.

Conclusion

Good-quality crystalline SiC films were grown on Si using 3MS as the single precursor. To the best of our knowledge, this is the first report of the growth of crystalline SiC using 3MS. High growth rates, in excess of 30 $\mu\text{m}/\text{h}$, were obtained. Although lower growth rates were obtained on carbonized substrates, there is considerable improvement in crystallinity and surface morphology using the buffer-layer approach. In general, we conclude that 3MS-grown films on Si substrates are good candidates for various applications, including (i) SiC pseudosubstrates for subsequent epitaxial growth and device fabrication; (ii) lateral and vertical SiC Schottky diodes; and (iii) SiC-on-Si MEMS which can withstand high temperature and corrosive environments.

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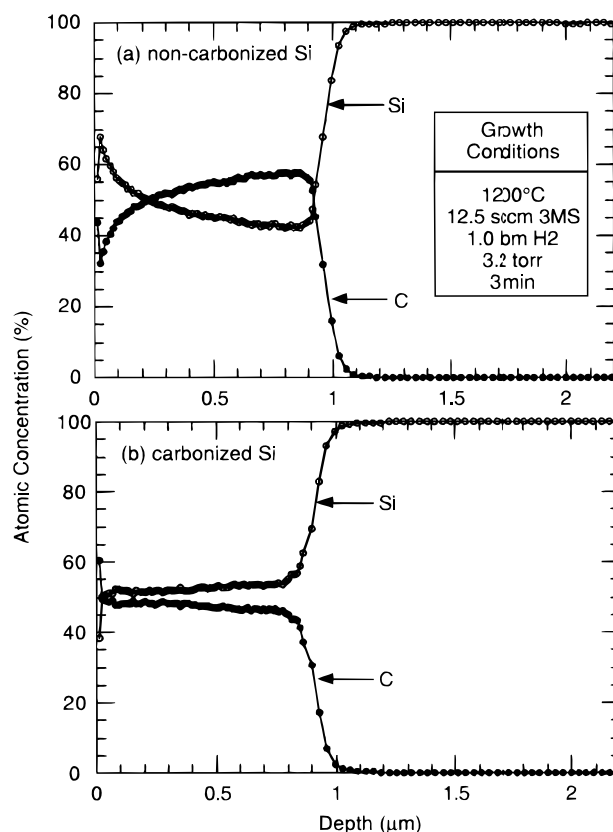


Figure 15. SIMS depth profiles of Si and C atoms in SiC grown on Si(111) using the same conditions on (a) noncarbonized and (b) carbonized substrate.

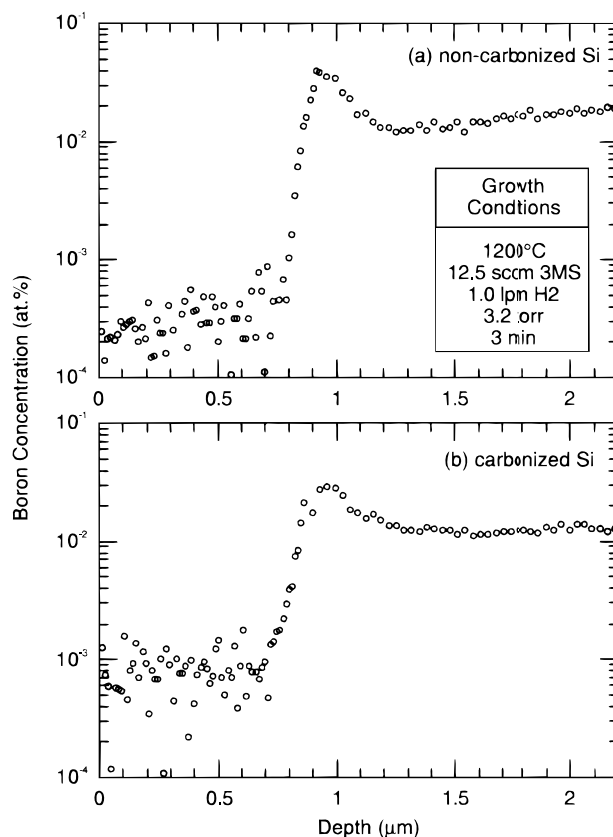


Figure 16. SIMS profiles of boron in SiC grown on p^+ -Si(111) sample using the same growth conditions on (a) noncarbonized and (b) carbonized substrate.

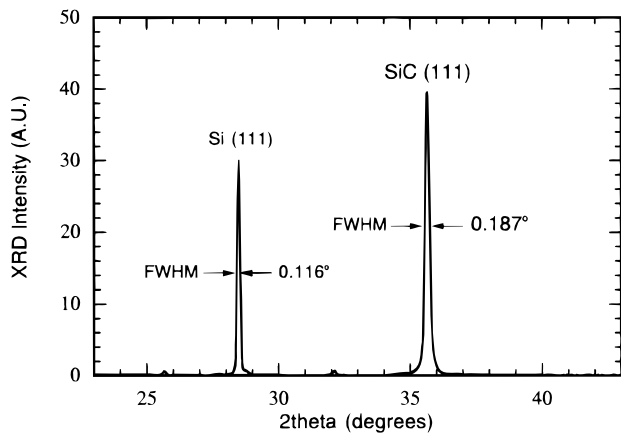


Figure 17. XRD spectra of SiC thick-film structure grown on carbonized Si(111).

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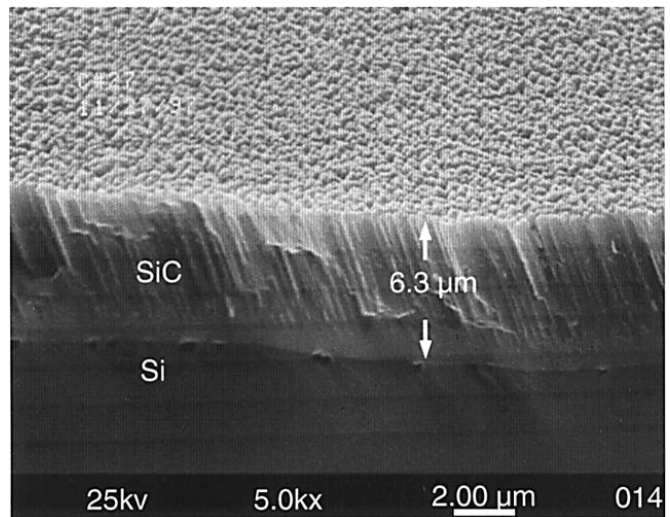


Figure 18. Cross-sectional SEM photograph of SiC/Si(111) thick-film structure.

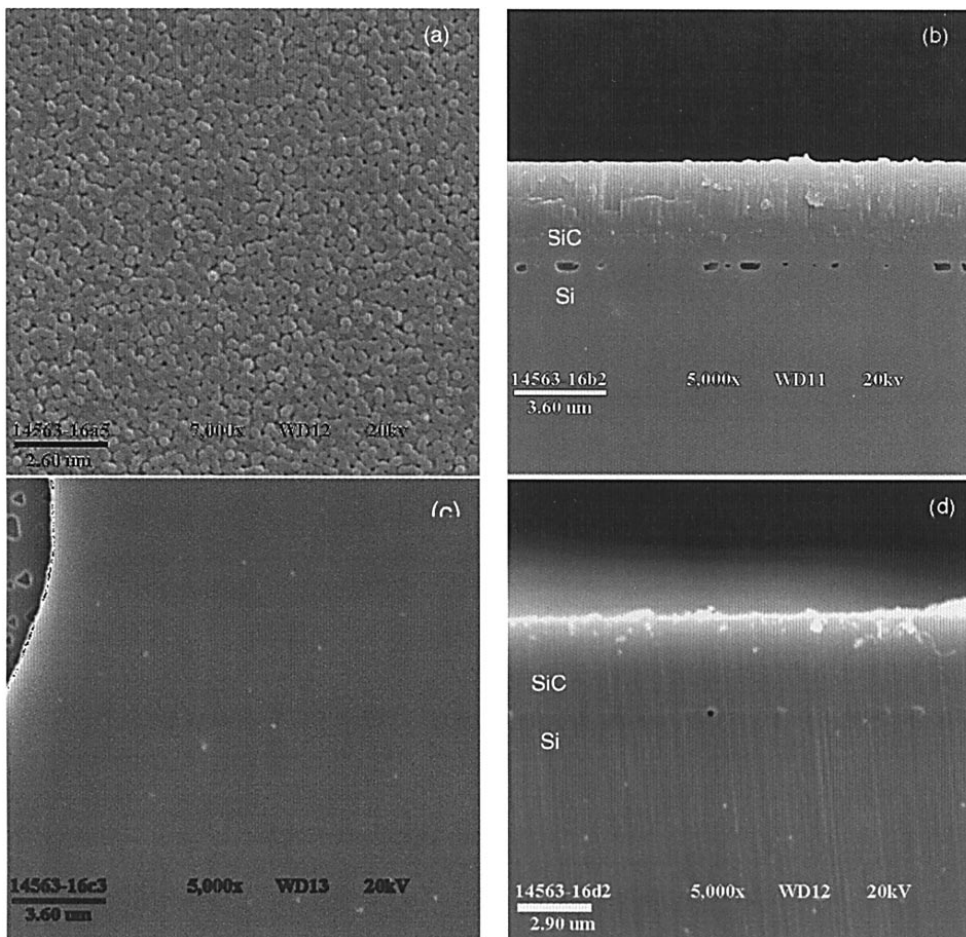


Figure 19. SEM photographs of SiC on Si(111) thick-film structure: (a) and (b) as-grown sample; (c) and (d) polished sample.