

Effect of carbonization on the growth of 3C-SiC on Si (111) by silacyclobutane

C. Yuan and A. J. Steckl

Nanoelectronics Laboratory, Department of Electrical and Computer Engineering, University of Cincinnati, Cincinnati, Ohio 45221-0030

M. J. Loboda

Dow Corning Corporation, Midland, Michigan 48686-0994

(Received 1 December 1993; accepted for publication 9 March 1994)

Chemical vapor deposition of SiC on Si (111) from silacyclobutane ($c\text{-C}_3\text{H}_6\text{SiH}_2$, SCB) has been carried out on propane carbonized and on virgin Si substrates. The carbonization was performed at 760 Torr and the SiC growth at 5 Torr. Transmission electron diffraction (TED) and x-ray diffraction were used to determine the crystallinity of the resulting films. The minimum temperature for obtaining crystalline films, as indicated by a TED pattern consisting of sharp spots with (111) SiC crystal hexagonal symmetry, was lower with carbonization ($\sim 800\text{--}900^\circ\text{C}$) than without ($\sim 1000^\circ\text{C}$). However, the carbonization process creates voids in the Si just below the SiC/Si interface, while SCB growth without carbonization produces a very smooth and void-free interface. Fourier-transform infrared measurements of SiC films grown at 1200°C without carbonization exhibit a sharp (full width at half-maximum = 30 cm^{-1}) Si-C absorption peak at 794 cm^{-1} .

The superior physical properties¹ of 3C-SiC translate into a potentially very useful semiconductor material for various electron devices² requiring a wide band-gap energy, high breakdown electric field, high thermal conductivity, etc. An exciting, but challenging, objective is to develop a SiC technology which integrates SiC thin films with Si substrates. This approach takes advantage of the cost, size, quality, and availability of Si wafers. It also allows the exploration of the integration of SiC device with Si technology. Most previously reported deposition of crystalline SiC on Si has utilized chemical vapor deposition (CVD) with separate C- and Si-bearing precursors,³⁻⁸ which requires independent flow control of each precursor since the optimum mixture varies with temperature, pressure, etc. Molecular beam epitaxy (MBE) with gas and solid sources has also been successfully used⁹ to grow crystalline SiC films on Si.

Single source precursors,¹⁰ containing directly bonded Si and C atoms, have the advantage of a simpler CVD process and of the possibility of a more efficient deposition with fragments containing intact Si-C bonds.¹¹⁻¹⁶ Silacyclobutane molecules, which have a four-member ring structure containing Si atoms bonded to C atoms, have been recently investigated for thin film growth of SiC.¹⁷⁻²² Monosilacyclobutane ($c\text{-C}_3\text{H}_6\text{SiH}_2$, SCB) which is a liquid at room temperature, has been previously utilized²⁰ for the deposition of crystalline SiC films at temperatures ranging from 900 to 1200°C by rapid thermal CVD (RTCVD) on Si (100) and (111) substrates, which had been *in situ* carbonized to provide a SiC starting layer.²¹ In this letter, the deposition of SiC on carbonized Si (111) is extended to lower temperatures ($700\text{--}900^\circ\text{C}$) and the deposition of SiC films on Si (111) without carbonization is investigated at 900 to 1200°C .

The deposition experiments were carried out in a computer-controlled RTCVD system equipped with a quartz growth chamber, two groups of IR lamps, a molecular drag pumping system, etc. The system has been successfully

used^{21,22} to grow crystalline SiC-on-Si at high temperature ($1100\text{--}1350^\circ\text{C}$) utilizing a variety of hydrocarbon gases either by themselves (carbonization) or in conjunction with silane, as well as growth at reduced temperatures ($900\text{--}1200^\circ\text{C}$) with SCB.²⁰ The SCB, of purity $>99.5\%$ (impurities are by-products of the reaction, primarily propylsilane and toluene) was connected directly to the growth system through a mass flow controller.

In preparation for SiC growth, the Si substrates undergo *ex situ* cleaning by HF dip. This is followed by *in situ* cleaning in an HCl/H₂ atmosphere at 1200°C . Next is the carbonization of the Si with propane (diluted to 5% in H₂ in cylinder) at 1300°C and atmospheric pressure. A propane flow of 9 sccm and H₂ flow of 0.9 l/min in the reactor is used to produce a $\sim 250\text{-\AA}$ layer of SiC in 1 min. Finally, SiC films are grown by SCB pyrolysis at temperatures from 700 to 1200°C . While SCB is flowing, the temperature is ramped up to a rate of 180°C/s . Reaction times of 1 to 10 min are normally chosen for the SCB growth. For SiC growth without carbonization the intermediate step was omitted. Growth of SiC films with SCB takes place at 5 Torr under flow conditions of 1.9 l/min H_2 and either 1 or 0.2 sccm SCB corresponding to growth with or without carbonization, respectively. A schematic diagram of the SiC growth process is shown in Fig. 1.

Several analysis and characterization techniques were utilized to study the SiC films. X-ray diffraction (XRD) and plan-view transmission electron diffraction (TED) were performed to determine the crystallinity of the SiC films. The TED was obtained after the Si substrate was removed by etching. The surface morphology was investigated by optical microscopy, scanning electron microscopy (SEM), and plan-view transmission electron microscopy (TEM). The SiC/Si interface and the SiC film thickness were evaluated by cross-sectional SEM. Fourier-transform infrared absorption (FTIR)

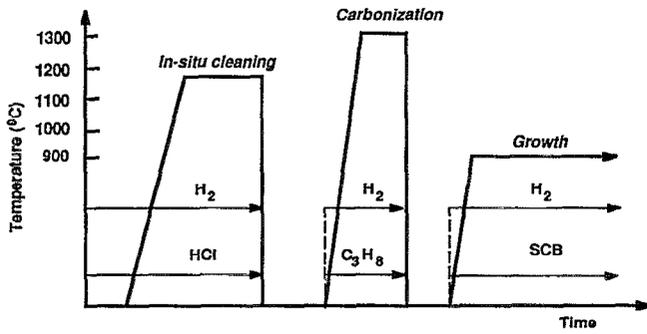


FIG. 1. SiC growth process schematic indicating the temperature and gas flow as a function of time.

was applied to identify the bonding and, hence, the chemical nature of the films.

The growth rate with SCB on carbonized substrates is shown in Fig. 2 as a function of reaction temperature in the lower temperature range of 700 to 900 °C. A log-linear relation holds in this temperature range, presumably given by a surface-reaction-rate limited process. At the top of Fig. 2 are the corresponding TED patterns from the SiC films. The sharp dot patterns signify that well-ordered (crystalline) SiC film growth does occur even at temperatures as low as 700 °C. The activation energy (E_a) of the growth rate in the region shown in Fig. 2 is calculated to be 1.03 eV/molecule. By comparison, SiC growth with the single precursor hexamethyldisilane¹⁵ (at 760 Torr) has an activation energy of 3.24 eV/molecule. Since the strain in a four-member carbosilane ring with a single Si atom was calculated²³ to be 0.73 eV/molecule, it is apparent that the ring strain in SCB results in a significant decrease in the activation energy for SiC thin film growth.

XRD spectra are presented in Fig. 3 for SiC films grown on carbonized Si (111) at 700 and 800 °C, along with corresponding plan-view TEM and TED of each film. The XRD of each film shows only the SiC (111) peak at $2\theta=35.63^\circ$,

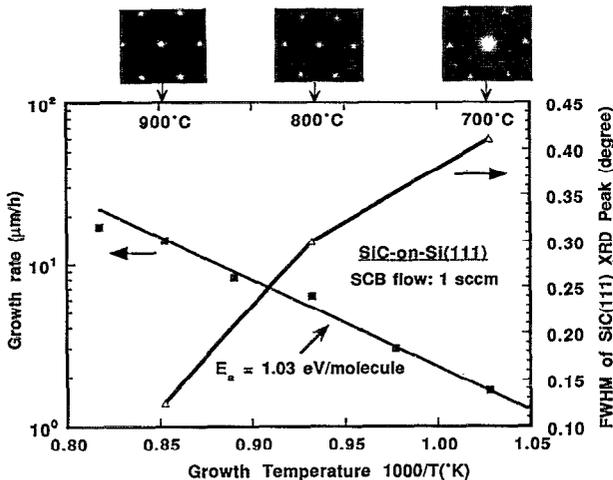


FIG. 2. Effect of growth temperature on SiC growth rate and on the FWHM of the (111) XRD peak of films grown with precarbonization.

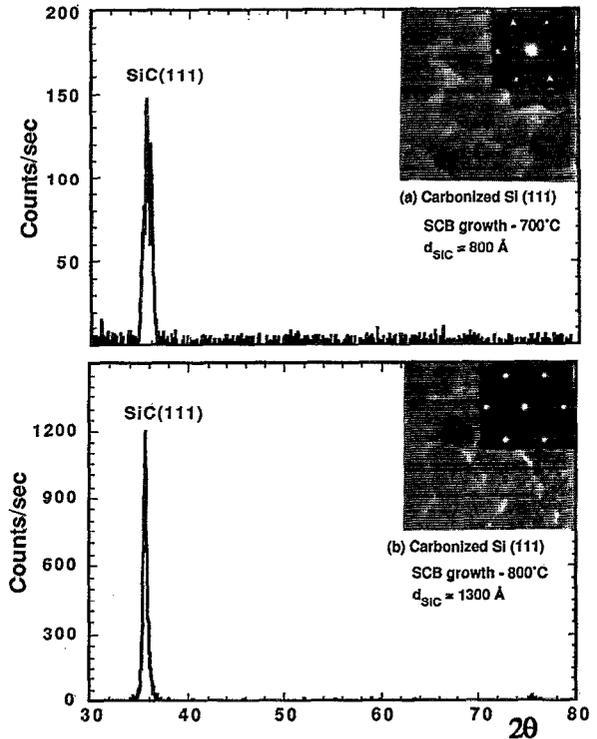


FIG. 3. XRD and TEM/TED of SiC films obtained with precarbonization and SCB growth at (a) 700 °C and (b) 800 °C.

while the TED data exhibit the spot pattern of the SiC (111) structure, which indicates the formation of the cubic SiC structure. The film grown at 800 °C displays excellent structural properties in terms of the XRD peak intensity (1200 counts per second for a film thickness of only 1300 Å) and full width at half-maximum (FWHM) of 0.30° (corrected for system broadening of 0.08°). The TED for the film grown at 700 °C shows a very faint ring diffraction pattern in addition to the spot pattern, which indicates a well-ordered polycrystalline SiC. As shown in Fig. 2, increasing the growth temperature over the 700 to 900 °C results in certain improvements: increasing growth rate and decreasing FWHM of the SiC (111) XRD peak.

A comparison of the morphology of SiC films grown with and without the carbonization process is shown in Fig. 4. SiC growth at 800 °C following carbonization at 1300 °C is compared to growth at 1000 °C without precarbonization. The optical microscopy photo in Fig. 4(a) exhibits the triangular features characteristic of void formation during the carbonization process in the Si (111) substrate just below the SiC/Si interface. On the other hand, no such features are visible in the optical microscopy photograph [see Fig. 4(b)] of the SiC film grown without precarbonization. The TED patterns indicate monocrystalline film formation in both cases. The SEM cross-sectional view of Fig. 4(d) shows that a highly adherent SiC layer is grown on the Si substrate even without the carbonization layer.

The SiC-on-Si deposited by using SCB was evaluated by FTIR transmission spectroscopy in the range from 400 to 4000 cm^{-1} . The absorption spectra of SiC films grown without carbonization at 1000 and 1200 °C are shown in Fig. 5.

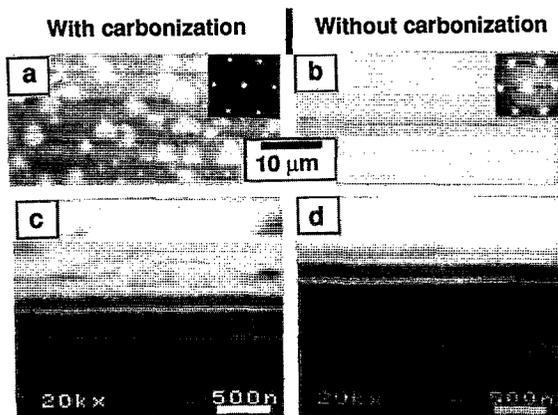


FIG. 4. Comparison of SiC films grown on precarbonized layer at 800 °C (a), (c) and without carbonization at 1000 °C (b), (d): (a), (b) optical microscopy and TED pattern—plan view and (c), (d) SEM cross section.

An intense absorption peak corresponding to the stretching vibration of the Si–C bond is observed at 794 cm^{-1} . No Si–H, C–C, or C–H bonds were detected within the scanned range. The insert in Fig. 4 shows the 794 cm^{-1} peak of the SiC film grown at 1000 °C on an expanded scale, indicating an FWHM of 50 cm^{-1} . The FWHM of the same peak for 1200 °C grown film is 30 cm^{-1} . These values are comparable to those observed by gas source (MBE)⁹ with C_2H_2 and Si solid source.

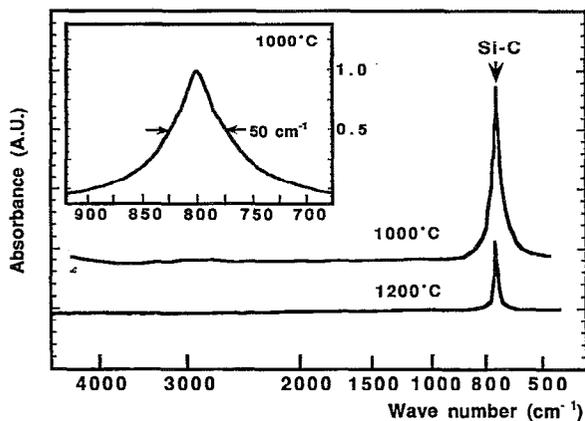


FIG. 5. FTIR transmission spectrum for SiC films grown at 1000 and 1200 °C without carbonization.

In summary, SiC thin films have been grown on Si (111) using the cyclic organosilane precursor SCB. Monocrystalline films have been obtained at growth temperatures as low as 800 °C with precarbonization, as well as 1000 °C and higher without carbonization. In the range of 700–900 °C the postcarbonization growth rate has an activation energy of 1.03 eV. Most importantly, in the absence of precarbonization, SiC growth on Si (111) provides a void-free structure, which is required for SiC/Si heterojunction device applications.

The research at Cincinnati was partially supported by the NASA Space Engineering Center. The authors gratefully acknowledge the assistance of A. K. Rai with the TEM investigation, M. Philips and W. Huff with XRD measurements, H. T. Henderson and H. C. Chang with the FTIR measurements.

- ¹J. A. Powell and L. G. Matus, in *Amorphous and Crystalline Silicon Carbide II*, edited by M. M. Rahman, C. Y. Yang, and G. L. Harris (Springer, Berlin, 1989), Vol. 43, p. 14.
- ²R. F. Davis, G. Kelner, M. Shur, J. W. Palmour, and J. A. Edmond, *Proc. IEEE* **79**, 677 (1991).
- ³P. Liaw and R. F. Davis, *J. Electrochem. Soc.* **132**, 642 (1985).
- ⁴S. Nishino, H. Suhara, H. Ono, and H. Matsunami, *J. Appl. Phys.* **61**, 4889 (1987).
- ⁵J. A. Powell, L. G. Matus, and M. A. Kuczumski, *J. Electrochem. Soc.* **134**, 1558 (1987).
- ⁶A. Suzuki, K. Furukawa, Y. Higashigaki, S. Harada, S. Nakajima, and T. Inoguchi, *J. Cryst. Growth* **70**, 287 (1984).
- ⁷Y. Furumura, M. Doki, F. Mieno, T. Eshita, T. Suzuki, and M. Maeda, *J. Electrochem. Soc.* **135**, 12 (1988).
- ⁸Y. Hirabayashi, K. Kobayashi, and S. Karasawa, *J. Cryst. Growth* **99**, 284 (1990).
- ⁹T. Sugii, T. Aoyama, and T. Ito, *J. Electrochem. Soc.* **137**, 989 (1990).
- ¹⁰L. V. Interrante, B. Han, J. B. Hudson, and C. Whitmarsh, *Appl. Surf. Sci.* **46**, 5 (1990).
- ¹¹I. Golecki, F. Reidinger, and J. Marti, *Appl. Phys. Lett.* **60**, 1703 (1992).
- ¹²A. D. Johnson, J. Perrin, J. A. Mucha, and D. E. Ibbotson, *J. Phys. Chem.* **97**, 12948 (1993).
- ¹³S. Nishino and J. Saraie, in *Amorphous and Crystalline Silicon Carbide*, edited by M. M. Rahman, C. Y. Yang, and G. L. Harris (Springer, Berlin, 1989), Vol. 34, p. 45.
- ¹⁴Y. Avigal, M. Schieber, and R. Levin, *J. Cryst. Growth* **24/25**, 188 (1974).
- ¹⁵K. Takahashi, S. Nishino, and J. Saraie, *J. Electrochem. Soc.* **139**, 3565 (1992).
- ¹⁶K. A. Jacobson, *J. Electrochem. Soc.* **118**, 1001 (1971).
- ¹⁷M. J. Loboda, in *Amorphous and Crystalline Silicon Carbide IV*, edited by M. M. Rahman, C. Y. Yang, and G. L. Harris (Springer, Berlin, 1992), Vol. 71, p. 271.
- ¹⁸D. J. Larkin, L. V. Interrante, J. B. Hudson, and B. Han, *Mater. Res. Soc. Symp. Proc.* **204**, 141 (1991).
- ¹⁹D. J. Larkin and L. V. Interrante, in Ref. 17, p. 239.
- ²⁰A. J. Steckl, C. Yuan, and J. P. Li, *Appl. Phys. Lett.* **63**, 3347 (1993).
- ²¹A. J. Steckl and J. P. Li, *IEEE Trans. Electron Devices* **39**, 64 (1992).
- ²²A. J. Steckl and J. P. Li, in Ref. 17, p. 49.
- ²³H. E. O'Neal and M. A. Ring, *J. Organomet. Chem.* **213**, 419 (1981).