

Heteroepitaxial Growth of SiC on Si by Gas Source MBE with Silacyclobutane

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Abstract 3C-SiC films have been grown by MBE on Si(100) and Si(111) from the organosilane precursor silacyclobutane at temperatures of 800 to 1000°C and pressures of 1 to 5×10^{-6} Torr. The chemical composition of the grown films provided by SIMS indicates a Si to C atomic ratio of about 1. The chemical structure of SiC was confirmed by FTIR. The surface morphology and crystallinity of SiC films were studied by SEM and RHEED. X-ray diffraction reveals that SiC films grown on Si(111) with the presence of native oxide exhibit better crystallinity than those grown on Si(111) surfaces from which the oxide is removed in-situ prior to growth.

1. Introduction

Since bulk crystals of 3C-SiC are not commercially available, heteroepitaxial growth on Si substrate has become an alternative method for obtaining 3C-SiC. Due to the large mismatch in lattice constant and thermal expansion coefficient between 3C-SiC and Si, considerable effort was devoted to improving the film quality. This was normally achieved with a 2-step growth method consisting of carbonization of the Si surface by reaction with a hydrocarbon gas followed by SiC deposition from the reaction of Si- and C-containing gases. Currently, CVD is widely employed to grow epitaxial 3C-SiC films on Si. Since the high CVD growth temperature can cause deterioration of the film quality, reduction of growth temperatures must be realized in order to fabricate the SiC device with suitable properties. In this paper, we report on the growth of 3C-SiC films at lower temperatures utilizing gas source MBE with novel precursors.

2. Experimental Conditions

All 3C-SiC films were deposited on Si substrates in a Riber GSMBE 32 system. The growth chamber was pumped down to a base pressure of less than 5×10^{-11} Torr by a cryogenic pump with a Ti sublimation pump. A residual gas analyzer and a 35 keV reflection high-energy electron diffraction (RHEED) apparatus with an image capture system were mounted on the growth chamber for gas and surface analysis, respectively. The Si substrate was transferred into the growth chamber through a load lock chamber, which was pumped by an ion pump and Ti sublimation pump to a base pressure of 4×10^{-10} Torr. The substrate was heated from the rear by radiative heating from a hot Ta filament which was controlled by a PID controller through a thermocouple. The substrate temperature measured by the thermocouple located at the back of heater was calibrated against a front mounted optical pyrometer, which measured the emission from the heated substrate.

The precursor for SiC growth was silacyclobutane (SCB), which is a liquid at room temperature with a vapor pressure of ~ 400 Torr. SCB is a cyclic molecule with one Si atom in a four-member ring. The strained molecular ring is easier to pyrolyze than the alkylsilanes. The SCB purity is > 99.5%, as determined by gas chromatography and mass spectrometry. SCB was introduced into the growth chamber through a pressure controller. Two inch diameter Si wafers oriented (100) \pm 0.5° ("on-axis") and (111) 2° - 3° off toward (110) ("off-axis") were used as substrates. The MBE growth generally consisted of the following steps: (a) loading of the Si into the load lock chamber and transfer to growth chamber; (b) ramping of substrate temperature to 700°C at a rate of

60°C/min in UHV; (c) SCB introduction into the growth chamber at a pressure of $(1-5) \times 10^{-6}$ Torr; (d) ramping the temperature to the final growth condition at a rate of 20°C/min. Unless otherwise specified, the last step before introducing the Si samples into the MBE was dipping in 1% HF for 60 sec to remove the native oxide. Prior to growth, these samples were heated at 700°C until the Si(100) (2×1) or Si(111) (7×7) RHEED pattern was obtained. For several Si samples, the native oxide removal step was omitted.

The composition-depth profile of SiC films was obtained by SIMS using Cs⁺ bombardment with positive ion detection. Elements monitored in SIMS were C, Si, N and B. Relative sensitivity factors derived from a SiC standard were used to convert ion counts to atomic concentrations. The chemical bonding of the film constituents was investigated by FT-IR. The film crystallinity, surface structure and morphology were characterized by X-ray diffraction, RHEED, and SEM.

3. Results and Discussion

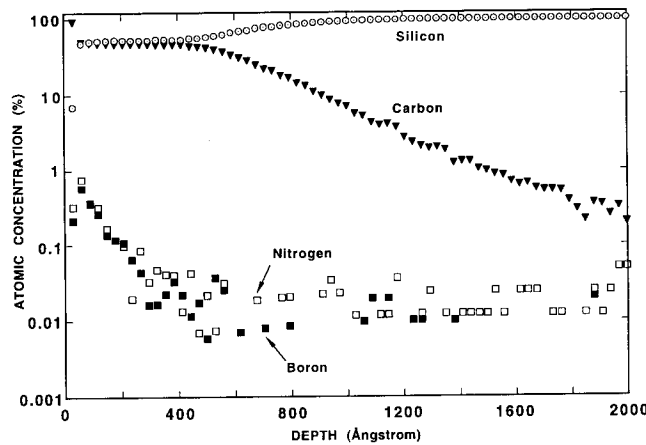


Fig. 1 SIMS depth profile of SiC film grown on Si(100) at 800°C and a pressure of 2.5×10^{-6} Torr.

The composition of the SiC films was determined by SIMS depth profiling. A typical depth profile of a SiC film on Si(100) is shown in Fig. 1. This film was grown at ~ 800 °C. The film composition of Si and C is fairly uniform for a depth of ~ 400 Å. A long carbon tail into the Si substrate is observed, which could be caused by: (a) carbon atoms diffusing into the Si during growth; (b) non-uniform film thickness resulting in certain locations where the SiC layer is removed sooner during SIMS profiling. The SIMS data also show that N and B impurities are present in a concentration of 0.01-1% in the SiC film. The growth rate is ~ 6 Å/min, which is in the range reported for SiC growth rate by GSMBE [1-4].

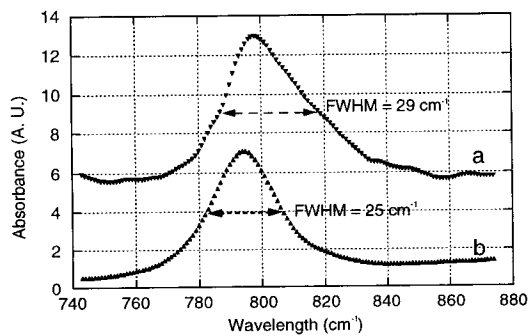


Fig. 2

FTIR spectra of SiC films grown at 1000 °C with SCB on: (a) Si(111) off-axis; (b) Si(100) on-axis. The peak wavenumbers are 794 cm^{-1} for (a) and 795 cm^{-1} for (b).

The chemical bonding of the MBE grown SiC films from SCB was studied by transmission mode FT-IR. FT-IR peaks of SiC films on Si(111) and Si(100) substrates are shown in Fig. 2. Only the Si-C stretching vibration at about 794 cm^{-1} was observed. The FWHM of the Si-C peaks obtained from SiC films grown on Si(100) and Si(111) are $\sim 25\text{ cm}^{-1}$ and $\sim 29\text{ cm}^{-1}$, respectively. These values are comparable to that obtained from SiC grown by CVD with SCB [5] at 1200°C and is one half of the value obtained for a CVD film grown at 1000°C . The FWHM of the Si-C FTIR peak reported for SiC films grown by MBE with the 2-step, 2-gas process [1,6] is similar to the value we have obtained with our 1-step, 1-gas process.

RHEED patterns from SiC films grown on Si without native oxide, shown in Fig. 3, indicate that the SiC crystal orientation follows that of the Si (100) or (111) substrate. SiC films start to grow when the substrate temperature reaches $\sim 750^\circ\text{C}$. The RHEED patterns of SiC films grown between ~ 750 and $\sim 850^\circ\text{C}$ are composed of both rings and spots. At a growth temperature of 900°C , there are still some faint rings observed in the RHEED patterns, as seen in Figs. 3a and 3c. When the growth temperature reaches 1000°C , a crystalline SiC surface was observed, as shown in Figs. 3b and 3d. The RHEED images and related surface quality are similar to that of previous reports [7,8] on SiC MBE which utilized the more complicated two step method. The twin spots clearly visible in the SiC(111) RHEED pattern are believed to be caused by anti-phase domains [9].

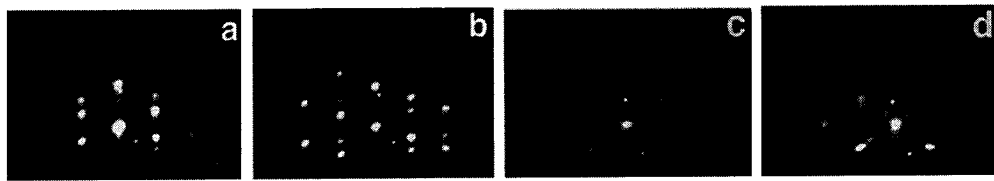


Fig. 3 RHEED images of SiC films grown on: (a) Si (111) at 900°C ; (b) Si (111) at 1000°C ; (c) Si (100) at 900°C ; (d) Si (100) at 1000°C . The primary beam is on $\langle 110 \rangle$ azimuth.

Since RHEED can only provide structural information of the top several monolayers of the surface, XRD was also used to study crystallinity of the SiC films. The XRD of SiC films grown on Si(111) with an SCB partial pressure of 4.7×10^{-6} Torr exhibits a single SiC peak at $2\theta \approx 35.7^\circ$ from (111) planes. This observation indicates that oriented SiC films were obtained.

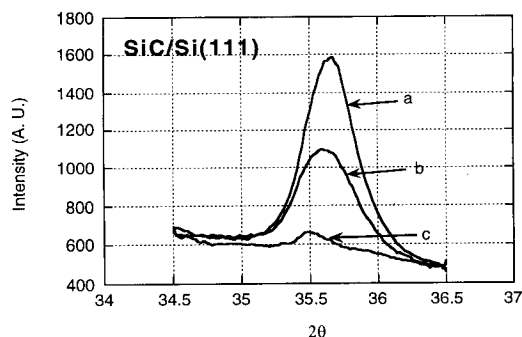


Fig. 4

XRD of SiC films grown on Si(111) at:

- (a) 1000°C , with native oxide, 80 min, FWHM = 0.33° ;
- (b) 800°C , with native oxide, 55 min, FWHM = 0.41° ;
- (c) 1000°C without native oxide, 80 min.

The XRD spectra in Fig. 4 show the effect of not removing the native oxide prior to SCB growth. The chamber pressure was 4.7×10^{-6} Torr during the growth. Clearly, the presence of the native oxide results in a significant improvements in crystallinity. Indeed, even sample "b" grown with native oxide at 800°C produces a much stronger signal than "c" grown at 1000°C without the oxide. The FWHM (0.33°) of sample "a" is actually superior to the values reported for SiC films

grown by MBE with various other processes [1, 2, 6]. A similar observation on the effect of the native oxide has been reported for SiC MBE growth on Si with C_2H_2 [10,11]. A possible explanation for this phenomenon is that Si is very reactive with SCB (and other hydrocarbons), so the presence of the thin native oxide layer can reduce the reaction rate during the nucleation phase.

The SiC surface was in general quite smooth and uniform. The typical SiC growth pits with rectangular geometry for growth on (100) Si and triangular shape on (111) Si are observed. Fig. 5 shows SEM images of the SiC (111) and SiC (100) surfaces. It is interesting to note that the pit density for growth on (100) surface is much larger than for growth on (111), while the opposite is true for pit size. For example, in the insert of Fig. 4a, square pits observed through the SiC (100) surface range in size from 0.5 to 1 μm , whereas the triangular pits shown in Fig. 4b through the SiC (111) surface range from 5 to 10 μm .

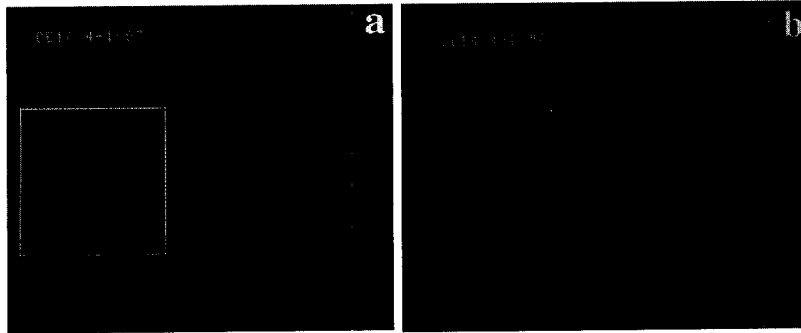


Fig. 5

SiC surfaces grown on:
(a) Si (100) on-axis at 1kx mag, insert at 10.1kx mag;
(b) Si (111) off-axis at 1kx mag.

5. Summary

In summary, RHEED, XRD, SIMS, FTIR and SEM were employed to characterize SiC films MBE-grown from SCB. One-step growth of SiC layers on Si from a single gas precursor at low temperatures by MBE method is proven possible. To our knowledge, this is the first report on the growth of SiC by GSMBE with SCB and the first time SiC has been grown by GSMBE without carbonization. The presence of the native oxide was shown to play a critical role in the growth of crystalline SiC films.

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6. References

- [1] T. Sugii, T. Aoyama and T. Ito, *J. Electrochem. Soc.*, **137**, 989 (1990).
- [2] H. Yamada, *J. Appl. Phys.*, **65**, 2084 (1989).
- [3] S. Motoyama, N. Morikawa, M. Nasu and S. Kaneda, *J. Appl. Phys.*, **68**, 101 (1990).
- [4] S. Tanaka, R. S. Fern and R. F. Davis, *Appl. Phys. Lett.*, **65**, 2851 (1994).
- [5] C. Yuan, A. J. Steckl and M. J. Loboda, *Appl. Phys. Lett.*, **64**, 22 (1994).
- [6] K. Kim, S-D Choi and K. L. Wang, *Thin Solid Films*, **225**, 235 (1993).
- [7] S. Motoyama, N. Morikawa and S. Kaneda, *J. Crystal Growth*, **100**, 615 (1990).
- [8] T. Yoshinobu, H. Mitsui, T. Fuyuki and H. Matsunami, *J. Appl. Phys.*, **72**, 2006 (1992).
- [9] M. Kitabatake, M. Deguchi and T. Hirao, *J. Appl. Phys.*, **74**, 4438 (1993).
- [10] T. Yoshinobu, T. Fukuki and H. Matsunami, *Jpn. J. Appl. Phys.*, **30**, L1086-L1088 (1991).
- [11] T. Yoshinobu, H. Mitsui, Y. Tarui, T. Fukuki and H. Matsunami, *J. Appl. Phys.*, **72**, 2006 (1992).