

## Chemical Vapor Deposition of Silicon Carbide Thin Films Using the Single Precursor 1,3-Disilabutane

Kyung-Won Lee, Jin-Hyo Boo, Kyu-Sang Yu and Yunsoo Kim

Korea Research Institute of Chemical Technology Yusong P.O.Box 107, Taejeon 305-600, Korea  
(Received November 5, 1996)

Epitaxial films of cubic silicon carbide ( $3C\text{-SiC}$ ,  $\beta\text{-SiC}$ ) have been grown on Si(001) and Si(111) substrates by high vacuum chemical vapor deposition using the single precursor 1,3-disilabutane,  $\text{H}_3\text{SiCH}_2\text{SiH}_2\text{CH}_3$ , at temperatures 900~100°C. The advantage of using the single precursor over the conventional chemical vapor deposition is evident in that the source chemical is safe to handle, carbonization of the substrates is not necessary, accurate stoichiometry of the silicon carbide films is easily achieved, and the deposition temperature is much lowered. The films were characterized by XPS, XRD, SEM, RHEED, RBS, AES, and TED.

**Key words :** High vacuum chemical vapor deposition, Single precursor, Accurate stoichiometry

### I. Introduction

As a related compound to diamond, silicon carbide has been shown to form at the interface between the silicon substrate and the diamond film during the diamond growth in microwave plasma chemical vapor deposition.<sup>1)</sup> Some investigators have employed silicon carbide buffer layers to grow diamond films epitaxially.<sup>2)</sup> Silicon carbide, however, is a very important semiconductor material in its own right.

Silicon carbide has been gaining popularity as a compound semiconductor material for applications such as high power, high frequency, and high temperature electronic devices.<sup>3)</sup> Heteroepitaxial growth of thin films of  $\beta\text{-SiC}$  on silicon is usually carried out by chemical vapor deposition using separate sources of silicon and carbon, namely silane and propane (or methane).<sup>4)</sup> This process usually requires high deposition temperatures often exceeding 1300°C. The source chemical silane is quite pyrophoric and therefore extreme caution is needed in its handling. The use of separate sources for silicon and carbon generally requires carbonization of the silicon substrate surface prior to the growth of the silicon carbide films. After carbonization, precise control of the flow rates of source chemicals is necessary in order to obtain accurate stoichiometry. All of these cause difficulties in growing silicon carbide films. The single precursor 1,3-disilabutane,<sup>5)</sup>  $\text{H}_3\text{SiCH}_2\text{SiH}_2\text{CH}_3$ , has two silicon atoms bonded alternately to two carbon atoms, and therefore can be a good single source for the deposition of silicon carbide.<sup>6)</sup> It is a liquid at ambient temperature, has a reasonably high vapor pressure, and most importantly, is stable in air. Chemical vapor deposition of cubic silicon carbide using this precursor turned out to be quite

promising, judging from its simple CVD conditions and the various characteristics of the films produced.

### II. Experimental Procedure

Initially, a simple CVD apparatus consisting of a Pyrex-quartz vertical reactor and a diffusion pumping system was used for low pressure CVD. A carrier gas was not necessary for the delivery of the precursor, since it was readily vaporized upon pumping. The silicon substrates, Si(001) and Si(111), were cleaned by the usual wet cleaning method of using a 20% HF solution in air. Heating of the substrates was achieved by flowing a direct current through them using a power supply. CVD experiments were carried out with the substrates at 650~900°C. The pressure of the CVD chamber was maintained at 25~55 Pa throughout each CVD experiment. As can be seen in the Results and Discussion section, these conditions produced only polycrystalline silicon carbide films.

To achieve epitaxial growth, CVD was now carried out in an ultrahigh vacuum chamber (base pressure  $< 7 \times 10^{-7}$  Pa) equipped with a reflection high energy electron diffraction (RHEED) apparatus and a residual gas analyzer (RGA). Atomically clean surfaces of substrates were prepared by treating them according to the method of Ishizaka and Shiraki.<sup>7)</sup> CVD processes were carried out at the precursor pressure of  $6.7 \times 10^{-4}$ ~ $2.0 \times 10^{-3}$  Pa. The temperatures of the substrates were 900~1000°C, and the duration of deposition was 4~8 h. Carbonization, when performed, was carried out by gas source molecular beam epitaxy (GSMBE) developed by Matsunami.<sup>8)</sup> The films produced by low pressure CVD were characterized by X-ray photoelectron spectroscopy, X-ray diffraction, and

scanning electron microscopy. For films obtained by high vacuum CVD, in addition to these techniques, *in situ* RHEED, Rutherford backscattering spectrometry, Auger electron spectroscopy, and transmission electron diffraction were used.

### III. Results and Discussion

Figure 1 shows the C 1s high resolution X-ray photoelectron spectrum of the film deposited on Si(001) at 650°C in comparison with a similar spectrum of a sintered piece of  $\beta$ -SiC which contained graphite as a binder. The sintered  $\beta$ -SiC shows two C 1s peaks corresponding to graphitic and carbidic carbons. The lower binding energy peak (carbidic carbon) at 282.1 eV closely matches the C 1s peak at 282.3 eV observed for the film. It clearly indicates that the film is a carbide. The C 1s area was compared with that of Si 2s or Si 2p peak from a high resolution Si spectrum (not shown), giving the ratio of carbon to silicon quite close to 1:1. To confirm the formation of the  $\beta$ -SiC phase, an X-ray diffraction pattern of the film was obtained and compared with a standard powder pattern of  $\beta$ -SiC (Fig. 2). The XRD patterns of the two match very well demonstrating the formation of

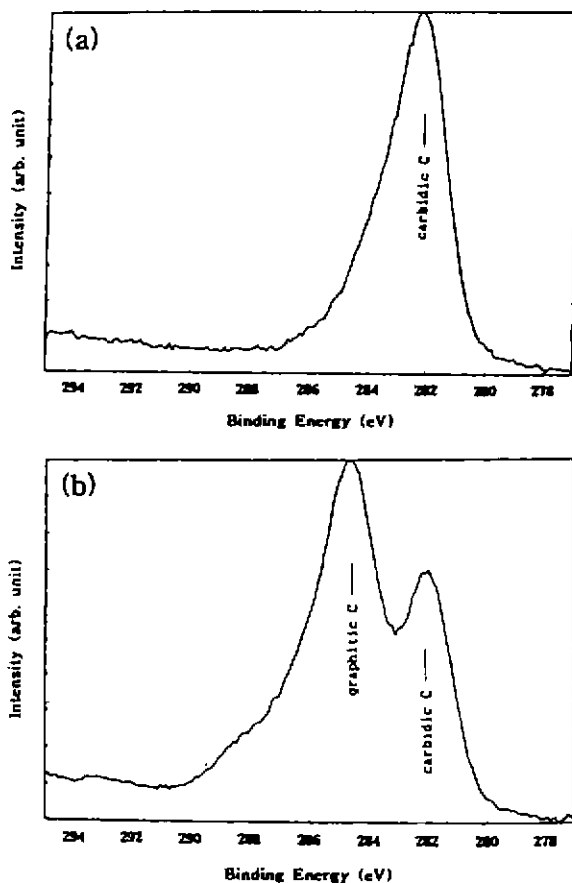


Fig. 1. C 1s high resolution spectra of (a) the film deposited on a Si(001) substrate at 650°C and (b) the sintered body of  $\beta$ -SiC.

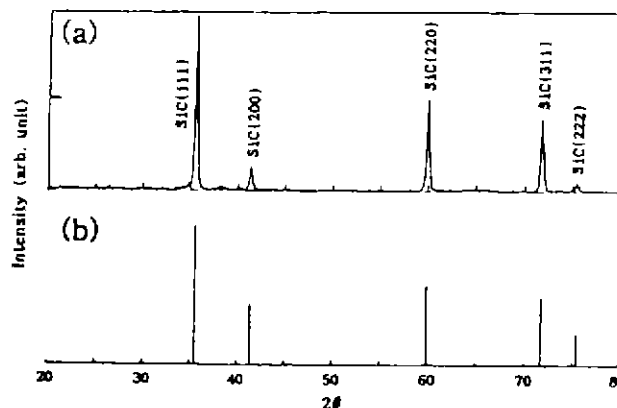


Fig. 2. X-ray diffraction patterns of (a) the film deposited on a Si(001) substrate at 650°C and (b) the  $\beta$ -SiC powders.

the cubic phase. Attempts to grow epitaxial films of silicon carbide failed.

Since it is a general practice to carbonize the silicon substrates prior to chemical vapor deposition, we decided to do carbonization. It was also decided that atomically clean silicon surfaces should be prepared for carbonization and then chemical vapor deposition should be carried out *in situ* under high vacuum conditions to avoid possible contamination of the substrates and the films.

After preparing an oxide layer on the substrate surface as devised by Shiraki *et al.*, the substrate was introduced into the CVD chamber, and the oxide layer was removed by heating the substrate at 900~950°C. Gas source molecular beam epitaxy using propane was performed at 750°C for carbonization. The carbonization process was carried out in 60~90 min and the resulting RHEED pattern was confirmed. Chemical vapor deposition was then executed around 950°C for 4 h with the initial pressure of 1,3-disilabutane at  $1.1 \times 10^{-3}$  Pa. The chamber pressure increased to  $1.3 \times 10^{-3}$  Pa by the time the CVD process was finished. The silicon carbide film produced in this process displayed properties quite similar to those of the films obtained on uncarbonized silicon substrates. Therefore the experimental results obtained using carbonized silicon substrates are not discussed any further.

In his paper on carbonization of Si(001) surface by GSMBE,<sup>5</sup> Matsunami noted that carbonization of silicon substrate is necessary to overcome the difficulties in heteroepitaxial growth of silicon carbide such as the large lattice mismatch of about 20% between silicon and silicon carbide, and the strong affinity of the silicon surface to hydrocarbon species. With single sources that contain both silicon and carbon atoms, carbonization does not seem to be a prerequisite process. Several investigators have reported on the successful growth of cubic silicon carbide films using single precursors such as methylsilane,<sup>9</sup> hexamethyldisilane,<sup>10</sup> and silacyclobutane.<sup>11</sup> In particular, the precursor methylsilane and our precursor

1,3-disilabutane are quite noteworthy in that they both have the desirable 1:1 ratio of carbon and silicon atoms. CVD by these precursors is expected to yield stoichiometric silicon carbide films.

The precursor 1,3-disilabutane employed in this work is a liquid (colorless) around room temperature and has a vapor pressure of about 3.6 kPa at 28°C. Its vapor was introduced into the vacuum chamber through a variable leak valve and discharged from a nozzle located 5 cm above the silicon substrate maintained at 930°C. This temperature has been optimized for the growth of silicon carbide on Si(001) and is lower than the temperatures of the usual CVD of using separate sources for silicon and carbon by more than 300°C. The silicon substrates were cleaned as described previously and their atomic cleanliness was confirmed by RHEED. The RHEED patterns showed a  $2 \times 1$  structure for Si(001) and a  $7 \times 7$  structure for Si(111).

Figure 3 shows the RHEED pattern of the silicon carbide film deposited on a Si(001) substrate. This pattern shows heteroepitaxial relationship of the  $\beta$ -SiC film with the substrates. Similar result was obtained from the film grown on a Si(111) substrate.

Figure 4 shows the XRD patterns of the films grown on Si(001) and Si(111). On Si(001), only the 3C-SiC(200) and 3C-SiC(400) peaks are seen except the substrate peak Si(400). Likewise, on Si(111) the two peaks 3C-SiC(111) and 3C-SiC(222) are observed with the substrate peaks Si(111) and Si(222). This figure corroborates the results of the RHEED observations.

To obtain compositional information of these SiC films, Rutherford backscattering spectrometric analysis was employed. In Fig. 5, RBS result is shown for the film deposited on Si(001). From this spectrum, the ratio of carbon to silicon atoms for this film was calculated to be 1.00 indicating that stoichiometric silicon carbide was deposited in our CVD. Auger depth profiling (Fig. 6) also reveals that the stoichiometric composition is maintained along the depth of the film. Analogous results were obtained for the film grown on a Si(111) substrate. It is rather surprising that accurate stoichiometry was not



Fig. 3. RHEED pattern of the film deposited on a Si(001) substrate at 930°C.

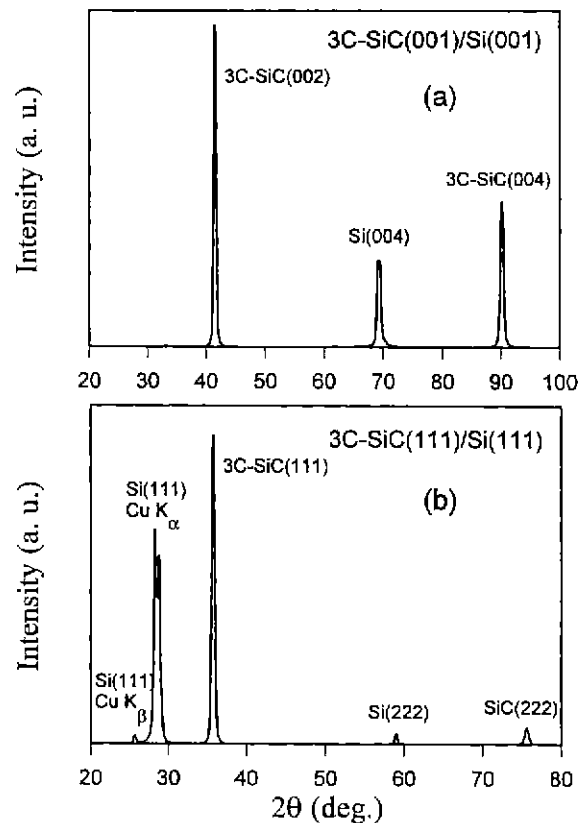


Fig. 4. XRD patterns of the films deposited on (a) Si(001) and (b) Si(111) substrates.

easily obtained with either methylsilane or sila-cyclobutane.<sup>12</sup> The reason for this is not yet known. Scanning electron microscopy images of the films (not shown) revealed locally flat surfaces with steps of different heights.

Plan-view and cross-sectional transmission electron dif-

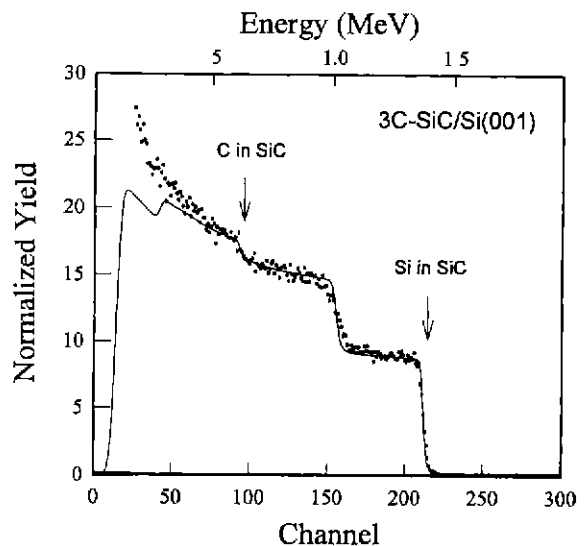


Fig. 5. Rutherford backscattering spectrum of the film deposited on a Si(001) substrate.

fraction (TED) patterns of the films deposited on Si(001) (at 950°C) and Si(111) (at 980°C) are shown in Fig. 7 and Fig. 8, respectively. The selected-area TED pattern of

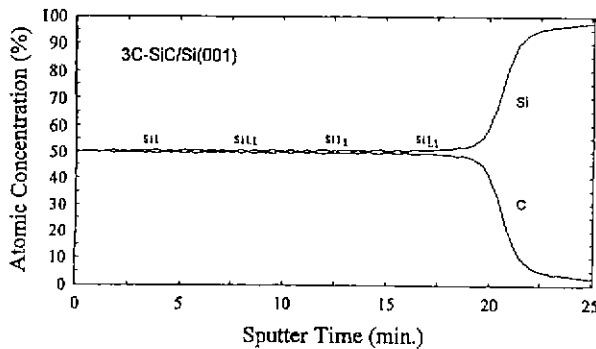


Fig. 6. Auger depth profiling of the film deposited on a Si (001) substrate.

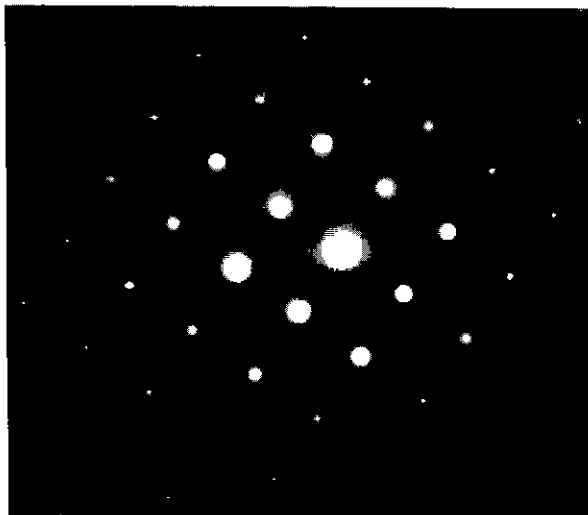


Fig. 7. A plan-view transmission electron diffraction pattern of the free-standing film deposited on a Si(001) substrate.

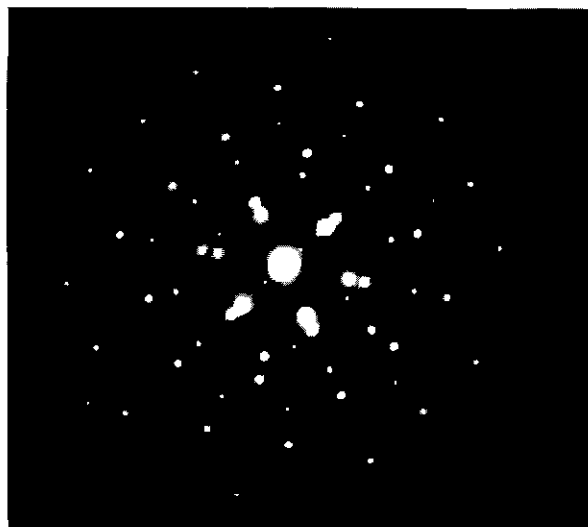


Fig. 8. A cross-sectional transmission electron diffraction pattern of the film deposited on a Si(111) substrate.

Fig. 7 was taken after the substrate was etched away and the film was ion-milled. It shows sharp diffraction spots revealing that the film is single-crystalline SiC with cubic structure.

For the film grown on Si(111), a cross-sectional TED was obtained at the interfacial region between the film and the substrate. In Fig. 8, therefore, diffraction spots from both the SiC film and the Si substrate appear together. Besides the normal diffraction spots due to the cubic SiC structure, extra spots and lines can be seen indicating the existence of microtwins and stacking faults.

## IV. Conclusions

From our CVD work using 1,3-disilabutane, the following conclusions can be drawn:

1. Handling of the source chemical is safe and simple.
2. The deposition temperature is lowered by more than 300°C compared with the conventional CVD process using separate sources for silicon and carbon.
3. Accurate stoichiometry of the silicon carbide film is easily achieved.
4. Carbonization of the silicon substrate is not necessary.
5. Epitaxial growth of cubic silicon carbide is achieved on both Si(001) and Si(111).

## Acknowledgement

The authors thank the Ministry of Information and Communication of Korea for the financial support of this work.

## References

1. B. E. Williams and J. T. Glass, "Characterization of Diamond Thin Films: Diamond Phase Identification, Surface Morphology and Defect Structures," *J. Mater. Res.*, **4**[2], 373-384 (1989).
2. H. Kawarada, T. Suesada and H. Nagasawa, "Hetero-epitaxial Growth of Smooth and Continuous Diamond Thin Films on Silicon Substrates via High Quality Silicon Carbide Buffer Layers," *Appl. Phys. Lett.*, **66**[5], 583-585 (1995).
3. K. Shenai, R. S. Scott and B. J. Baliga, "Optimum Semiconductors for High-Power Electronics," *IEEE Trans. Electron Devices*, **ED-36**[9], 1811-1823 (1989).
4. Y. Fujiwara, E. Sakuma, S. Misawa, K. Endo and S. Yoshida, "Epitaxial Growth of 3C-SiC on Si by Low-pressure Chemical Vapor Deposition," *Appl. Phys. Lett.*, **49**[7], 388-390 (1986).
5. I. N. Jung, G.-H. Lee and C.-H. Song, Korean Patent Appl. No 92-4705, March 1992.
6. J. H. Boo, K.-S. Yu, Y. Kim, S. H. Yeon and I. N. Jung, "Growth of Cubic SiC Films Using 1,3-Disilabutane," *Chem. Mater.* **7**[4], 694-698 (1995).
7. A. Ishizaka and Y. Shiraki, "Low Temperature Surface Cleaning of Silicon and Its Application to Silicon MBE," *J. Electrochem. Soc.*, **133**[4], 666-671 (1986).

8. T. Yoshinobu, H. Mitsui, Y. Tarui, T. Fuyuki and H. Matsunami, "Cracking of Saturated Hydrocarbon Gas Molecular Beam for Carbonization of Si(001) Surface," *Jpn. J. Appl. Phys.*, **31**[11B], L1580-L1582 (1992).
9. I. Golecki, F. Reidinger and J. Marti, "Single-crystalline Epitaxial Cubic SiC Films Grown on (100) Si at 750°C by Chemical Vapor Deposition," *Appl. Phys. Lett.* **60**[14], 1703-1705 (1992).
10. K. Takahashi, S. Nishino and J. Saraie, "Low-Temperature Growth of 3C-SiC on Si Substrate by Chemical Vapor Deposition Using Hexamethyldisilane as a Source Material," *J. Electrochem. Soc.*, **139**[12], 3565-3571 (1992).
11. A. J. Steckl, C. Yuan, J. P. Li and M. J. Loboda, "Growth of Crystalline 3C-SiC on Si at Reduced Temperatures by Chemical Vapor Deposition from Silacyclobutane," *Appl. Phys. Lett.*, **63**[24], 3347-3349 (1993).
12. A. D. Johnson, J. Perrin, J. A. Mucha and D. E. Ibbotson, "Kinetics of SiC CVD: Surface Decomposition of Silacyclobutane and Methylsilane," *J. Phys. Chem.*, **97**[49], 12937-12948 (1993).