

## USE OF SINGLE PRECURSORS FOR THE PREPARATION OF SILICON CARBIDE FILMS

Kyunf Won Lee, Kyu-Sang Yu, and Yunsoo Kim\*

*Korea Research Institute of Chemical Technology, Yusong P. O. Box 107, Taejeon 305-600, KOREA*

### ABSTRACT

Heteroepitaxial growth of cubic silicon carbide films on Si(001) and Si(111) substrates at temperatures 900–1000°C has been achieved by high vacuum chemical vapor deposition using the single precursor 1,3-disilabutane without carrying out the carbonization process of the substrate surfaces. The deposition temperature range is much lowered compared with conventional chemical vapor deposition where separate sources for silicon and carbon are employed. The deposition procedure is quite simple and safe. The qualities of the films were found to be very good judging from the results obtained by various characterization techniques including reflection high energy electron diffraction, X-ray diffraction, X-ray pole figure analysis, Rutherford backscattering spectrometry, Auger depth profiling, and transmission electron diffraction.

### INTRODUCTION

Silicon carbide is a promising compound semiconductor that is finding such applications as high frequency, high temperature, and high power devices<sup>[1]</sup>. For these applications it is necessary to make thin films of silicon carbide, and therefore many researchers have investigated the preparation of silicon carbide films employing various source chemicals, substrates, and deposition methods. Traditionally, silicon carbide films have been obtained using separate sources for silicon and carbon such as silane and propane (or other gaseous hydrocarbons) diluted in hydrogen. Silane, although an important chemical, is an extremely pyrophoric compound that requires safety measures. For deposition of silicon car-

bide on silicon using these separate sources for silicon and carbon, due probably to the differences in the affinity of the silicon surface toward silane and propane and to the large lattice mismatch of about 20% between silicon and silicon carbide<sup>[2]</sup>, it is considered necessary to carbonize the silicon substrate surface prior to chemical vapor deposition. Recently, however, chemical vapor deposition using single sources is increasingly studied. These sources include 1,2-bis(silyl)ethane,  $H_3SiCH_2CH_2SiH_3$ <sup>[3]</sup>, diethylsilane,  $(C_2H_5)_2SiH_2$ <sup>[4]</sup>, dimethylisopropylsilane,  $(CH_3)_2CHSiH(CH_3)_2$ <sup>[5]</sup>, 1,3-disilabutane,  $H_3SiCH_2SiH_2CH_3$ <sup>[6]</sup>, 1,3-disilacyclobutane,  $C_2H_6Si_2$ <sup>[7]</sup>, hexamethyldisilane,  $(CH_3)_6Si_2$ <sup>[8]</sup>, methylsilane,  $CH_3SiH_3$ <sup>[9,10]</sup>, silacyclobutane,  $c-C_3H_6SiH_2$ <sup>[11]</sup>, tetramethylsilane,  $(CH_3)_4Si$ <sup>[4]</sup>, and tripropylsilane,  $(C_3H_7)_3SiH$ <sup>[4]</sup>.

Among these, tetramethylsilane is probably the oldest single precursor that is still employed for growing silicon carbide film. In favorable cases carbonization of the silicon substrate surface was reported not necessary<sup>[10]</sup>. In this research we have concentrated on preparing cubic silicon carbide films on silicon substrates by thermal chemical vapor deposition using single sources (precursors) that contain both silicon and carbon atoms. In particular, the use of the single source 1,3-disilabutane is dealt with in detail for the preparation of thin epitaxial films of cubic silicon carbide on Si(001) and Si(111) substrates without carrying out carbonization of the substrate surfaces.

## EXPERIMENTAL PROCEDURE

The single precursor 1,3-disilabutane was synthesized according to the method of Jung, *et al*<sup>[11]</sup>. It is a colorless liquid at ambient temperature with reasonably high vapor pressure (3.6 kPa at 28°C), stable in air, and has an odor similar to usual solvents. The molecule has two silicon atoms bonded alternately to two carbon atoms. All other atoms are hydrogens. It therefore has a 1 : 1 ratio of silicon to carbon atoms. It was thought that stoichiometric films of silicon carbide would be produced by using this precursor, and consequently it was employed in this research. The silicon substrates were Si(001) and Si(111). Each substrate was treated by the method of Ishizaka and Shiraki<sup>[13]</sup> to make a thin protective oxide film on the surface. This was then transferred to an ultrahigh vacuum chamber (base pressure  $< 7 \times 10^{-7}$  Pa) to remove the oxide layer by heating (at 900–950

°C) *in situ* and to subsequently deposit silicon carbide on it by high vacuum chemical vapor deposition. The chamber pressure during the CVD process was maintained at  $1.1\text{--}1.3 \times 10^{-3}$  Pa by the vapor of 1,3-disilabutane alone. A carrier gas was not necessary since the vapor pressure of the precursor was high enough for carrying out high vacuum CVD. The cleanliness of the substrate surfaces was confirmed by reflection high energy electron diffraction (RHEED) and the structures of the films formed were also examined by RHEED. Each CVD experiment was usually performed for about 4 h.

After this, the sample was taken out of the chamber to characterize the deposited film with X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), X-ray pole figure analysis, Rutherford backscattering spectrometry (RBS), Auger depth profiling, and transmission electron diffraction (TED).

## RESULTS AND DISCUSSION

Each of the CVD experiments was performed after the cleanliness of the substrates was confirmed *by in situ* RHEED. A  $2 \times 1$  RHEED pattern and a  $7 \times 7$  RHEED pattern were obtained from clean Si(001) and Si(111) substrates, respectively. Figure 1 is a RHEED pattern (taken with the electron beam in the [110] direction) of a film deposited on a Si(001) substrate at 930°C. It shows a well-developed spot pattern of cubic silicon carbide film with streaks connecting the spots perpendicularly. Sometimes extra spots appear around the main ones when the substrate temperature was rapidly raised up to the deposition temperature in the presence of the

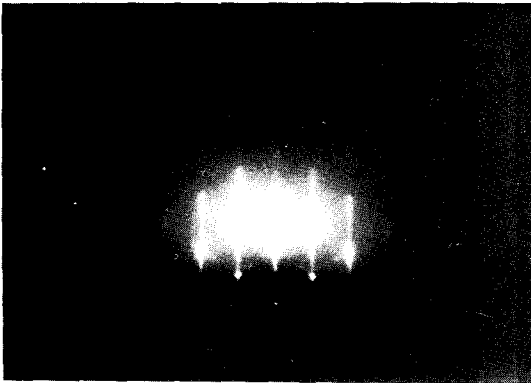


Fig. 1 RHEED pattern of a film deposited on a Si(001) substrate at 930°C

precursor. The important point here is that the  $1 \times 1$  RHEED pattern was obtained as soon as the temperature of the substrate reached about 750°C at which deposition of silicon carbide became appreciable. With separate sources, for example silane and propane, it is considered that this pattern should be obtained first by carbonization of the silicon substrate using propane or other hydrocarbon sources before the deposition of silicon carbide is carried out in earnest. Therefore our result indicates that carbonization process is not needed when 1,3-disilabutane is employed as the source material. The RHEED pattern (not shown) obtained from a film deposited on Si(111) at 980°C showed a similar but somewhat skewed structure of diffraction spots as expected<sup>[14]</sup>. In Figure 2a is shown the X-ray diffraction pattern of the film deposited on Si(001). It clearly shows that other than the Si(004) peak due to the substrate, only the peaks due to 3C-SiC(002) and 3C-SiC(004) appear indicating that phases different from the cubic phase were not formed and the film is apparently epitaxial. Likewise, the XRD pattern (Figure 2b)

of the film formed on a Si(111) substrate shows only the 3C-SiC(111) and 3C-SiC(222) peaks other than the substrate peaks, Si(111) and Si(222). Pole figure analyses of the films deposited on Si(001) and Si(111), shown in Figure 3, verify that they were grown epitaxially. Figure 3a shows four {111} pole density maxima with a fourfold symmetry and the angle from the surface normal of 54.7°. Figure 3b shows three {110} pole density maxima with a threefold symmetry and the angle from the surface normal of 35.3°. These pole figures are much alike to the corresponding pole figures (not shown) of

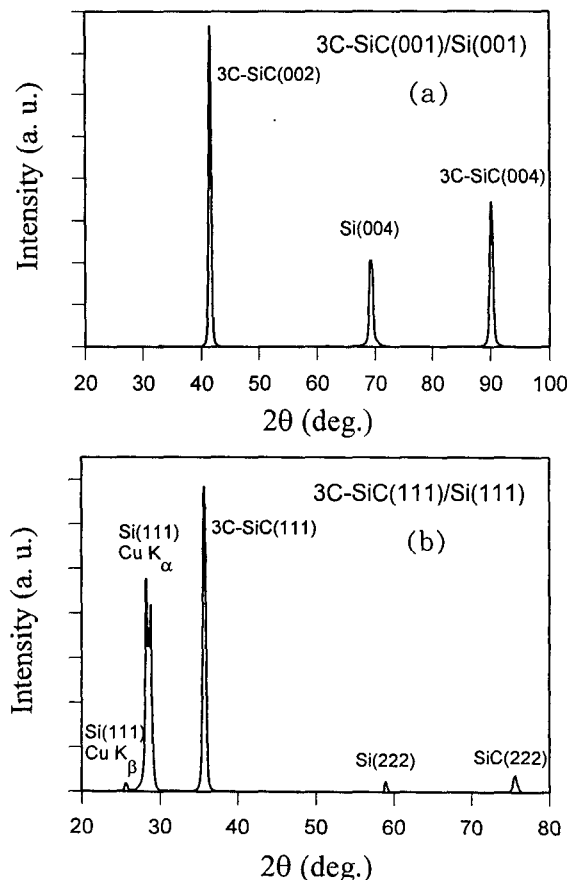


Fig. 2 XRD patterns of (a) the film of Figure 1 and (b) a film grown on a Si(111) substrate at 980°C.

the Si(001) and Si(111) substrates, which clearly demonstrates that the films were epitaxially grown on Si(001) and Si(111) with the heteroepitaxial relationships  $3C\text{-SiC}(001)[110] \parallel \text{Si}(001)[110]$  and  $3C\text{-SiC}(111)[10\bar{1}] \parallel \text{Si}(111)[10\bar{1}]$ , respectively.

The temperature of our chemical vapor deposition is lowered by more than 300°C compared with the usual chemical vapor deposition employing separate sources for silicon and carbon. It is quite interesting that Gole-

cki *et al.* could deposit epitaxial silicon carbide films on silicon at 750°C using the simplest single precursor methylsilane<sup>[10]</sup>. It might be proper at this stage to speculate on the plausible mechanism for the surface reaction during the deposition of cubic silicon carbide on the silicon substrate. Due to the fact that single precursors have constituent atoms directly bonded together or indirectly bonded in close proximity, within distances of at most a few atomic bonds, surface diffusion energy for the molecules adsorbed on the substrate surface may not be greatly needed. Bond breaking and bond formation are not so much prominent as in the case of using separate sources. This conjecture may be justified if we compare the CVD using methylsilane with that using silane and propane. It is also interesting to note that the source chemical tetramethylsilane, although a single precursor, requires much higher deposition temperatures; it has four methyl carbon atoms bonded to a single silicon atom, so more Si-C bonds to break to form SiC films than either methylsilane or 1,3-disilabutane. It is then understandable that 1,3-disilabutane deposits silicon carbide films at higher temperatures (900–1000°C) than methylsilane. In comparison with 1,3-disilabutane, the disadvantage of methylsilane is that it is pyrophoric.

The next step was to characterize the overall composition of the films by RBS. Figure 4 shows the RBS result of the film grown on Si(001) at 930°C. The spectrum was taken with a 2.44 MeV  $\text{He}^{++}$  beam and the detector placed at a scattering angle of 170°. The high-energy edges centered at 1.38 MeV and 0.62 MeV correspond to Si and C in the film, respectively.

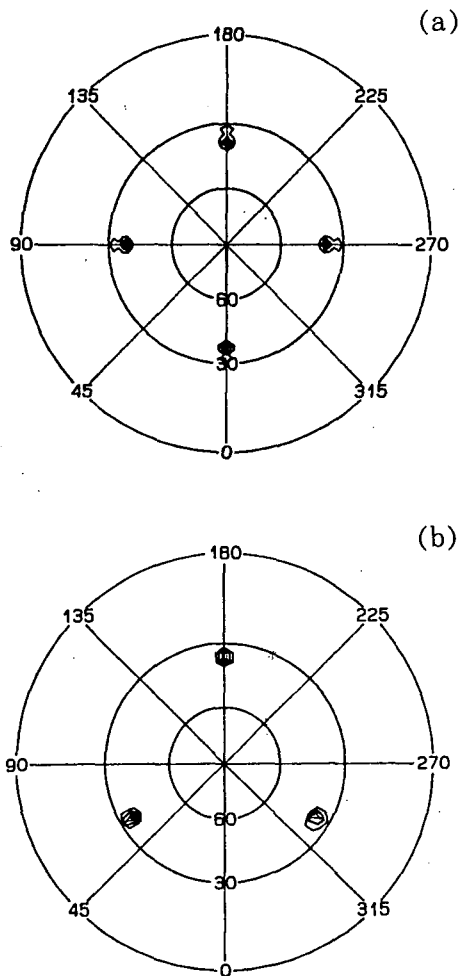


Fig. 3 Pole figures of (a) the film of Figure 1 and (b) the film of Figure 2b.

The peak near 1.04 MeV is attributed to scattering from Si at the SiC–Si interface and the step observed at that point indicates the increase in the Si concentration at the SiC–Si interface. From the spectrum the ratio of carbon to silicon atoms in the film was calculated to be 1.0:1.0 within the limits of accuracy, which demonstrates quite an accurate stoichiometry. Using the theoretical value for the density of cubic SiC and the data from RBS, the thickness of the film was found to be 0.24  $\mu\text{m}$ . Typical growth rate was in the range 0.15–0.4  $\mu\text{m}/\text{h}$  for most of the films, varying depending on the pressure difference between the reservoir of 1,3-disilabutane and the CVD chamber, the pumping conditions, and temperature of the substrates.

The variation of the composition of the film along the perpendicular direction was examined by Auger depth profiling shown in Figure 5. The concentrations of silicon and carbon were normalized using their Auger sensitivity factors. It is clear from the figure that the 1:1 stoichiometric ratio of carbon to silicon is maintained throughout the film thickness. Similar results were obtained for the

films grown on Si(111) substrates. In passing different values for this ratio were obtained for silacyclobutane (1.1 at 900°C approaching 1.0 at 1050°C) and methylsilane (0.8 over the temperature range)<sup>[15]</sup>. Since silacyclobutane has three carbon atoms and one silicon atom, it is probably prone to yield carbon-rich films. Considering the stoichiometric composition of methylsilane, however, it is rather surprising that nonstoichiometric films were obtained from this source.

The crystal structures of the bulk of the films were investigated with transmission electron diffraction. Figure 6a is a plan-view TED pattern of the film deposited on a Si(001) substrate at 930°C. The film was ion-milled after the substrate was etched away for selected-area TED examination. It shows sharp diffraction spots with a fourfold symmetry revealing that the film is single-crystalline SiC with cubic structure. Figure 6b is a cross-sectional TED pattern of the film deposited on Si(111) at 980°C, at the interfacial region between the film and the substrate. In this figure, therefore, diffraction spots from both the silicon carbide film and the silicon substrate appear together. The figure nicely shows the sixfold symmetry for both the silicon carbide film and the silicon

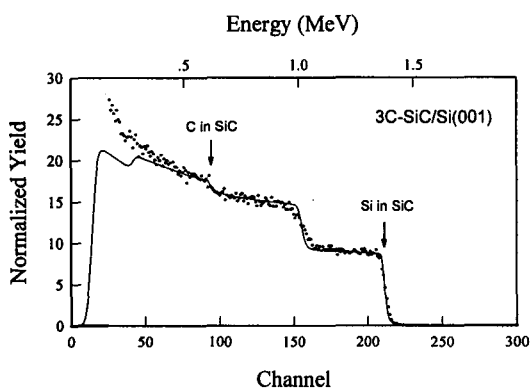


Fig. 4 Rutherford backscattering spectrum of the film of Figure 1.

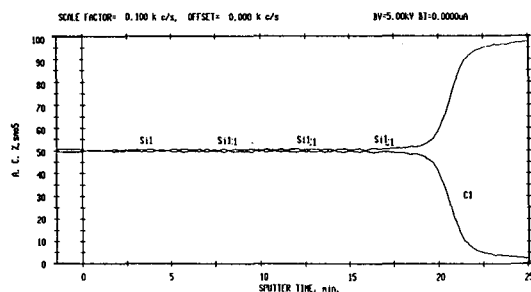


Fig. 5 Auger depth profiling of the film of Figure 1.

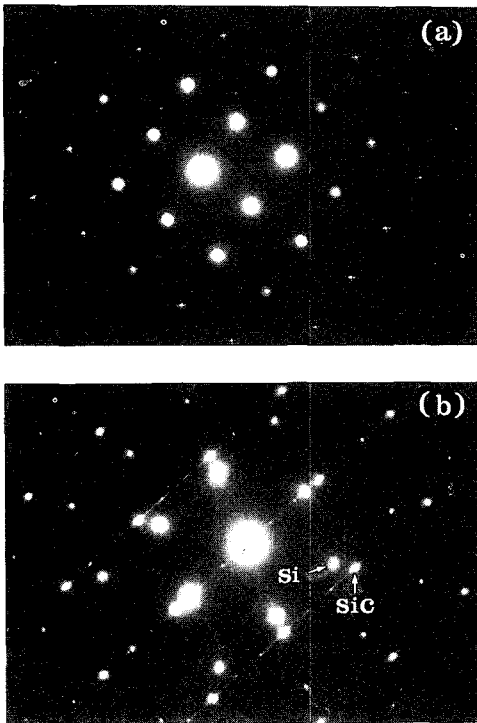


Fig. 6 TED patterns (a) the film of Figure 1 and (b) the film of Figure 2b.

substrate. 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.

In regard to the purity of the films, it is believed that our films are quite pure since a separate elastic recoil detection (ERD) experiment showed only 0.35 atomic % of hydrogen incorporation. This contrasts very well with other experimental data that showed a few atomic % of hydrogen (an order of magnitude higher) incorporation in silicon carbide films produced from different precursors<sup>[15]</sup>. An XPS experiment showed much less amount of surface hydrocarbon species compared to a different group's result<sup>[16]</sup>. This purity aspect of our investigation is now being

pursued and will be reported elsewhere.

## CONCLUSIONS

From the results of our investigation we can draw the following conclusions.

- 1) Heteroepitaxial growth of cubic silicon carbide films on silicon substrates has been achieved using the single precursor 1,3-disilabutane.
- 2) Handling of the source chemical is safe and simple.
- 3) The deposition temperature is lowered by more than 300°C compared with the conventional CVD process using separate sources for silicon and carbon.
- 4) Accurate stoichiometry of the silicon carbide film is easily achieved.
- 5) Carbonization of the silicon substrate is not necessary.

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