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Epitaxial growth of 3C-SiC (111) on Si via laser CVD carbonization

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ABSTRACT

A qualitative and quantitative study was performed on the carbonization temperature (T_C) and carbonization time (t_C) with respect to the microstructure and growth rate (R_g) of a 3C-SiC epitaxial layer on Si (111) substrates by carbonization via laser chemical vapor deposition (LCVD). The results showed that the density and size of the voids depended strongly on T_C . The voids were sealed, and thin films were formed continuously and uniformly after a carbonization time of 6 min at $T_C = 1200$ °C. R_g was also dependent on T_C , and increased from 0.43 to 1.35 $\mu\text{m}\cdot\text{h}^{-1}$ with increases in T_C from 1000 to 1200 °C. These deposition rates were 10 to 100 times greater than those of observed for conventional CVD methods.

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LCVD; 3C-SiC; carbonization; morphology; void

1. Introduction

A wide bandgap semiconductor, e.g., cubic 3C-SiC [1,2] has been demonstrated to be a reliable substrate on which to grow high-quality graphene [3]. Growth of 3C-SiC epitaxial film on a Si single crystalline substrate has attracted much attention in recent decades due to the low temperature, low cost and large area growth of the process [4]. 3C-SiC(111) epitaxial thin films have usually been grown on Si by the chemical vapor deposition (CVD) method using carbon (CH_4 or C_3H_8) and silicon (SiH_4 or SiCl_4) precursors in a hydrogen flow. Due to its self-ignitability, flammability and toxicity, however, the use of silane gas sources requires strict safety controls [5–7]. To date, 3C-SiC epitaxial films have been grown by carbonization via the thermal CVD and molecular beam epitaxy (MBE) methods [8,9]; however, in growth rates were less than 0.1 $\mu\text{m}/\text{h}$, which is insufficient for industrial applications [10].

We have developed a laser CVD (LCVD) method to prepare many kinds of epitaxial films at significantly high growth rates at relative lower growth temperatures [11–13]. In this study, 3C-SiC film was constituted by carbonizing a Si (111) single crystal using single propane (C_3H_8) via the LCVD method. The effects of the carbonization temperature (T_C) and carbonization time (t_C) on the growth rate (R_g) and microstructure were investigated.

2. Experimental procedures

Si (111) single crystalline substrates were carbonized by the laser CVD system using a mixture of H_2 (Wuhan Xiangyun Chemical Industry Co., Ltd., 99.99%) and C_3H_8 (Guangzhou HUATE GAS Co., Ltd., China, 99.999%). Si(111) substrates (10 × 10 × 0.5 mm) of [111] orientation (Hefei Kejing Materials Technology Co., Ltd., China) were used. After cleaning with a diluted HF solution (Sinopharm Chemical Reagent Co., Ltd., China, HF ≥ 40%), the substrate was placed in the reaction chamber (vacuated to 1 Pa). Ar gas was filled into the chamber and the total pressure was fixed at 1000 Pa. The substrate was wholly irradiated by an InGaAlAs multimode diode laser (wavelength: 1060 nm). The laser beam was introduced directly into the chamber through a quartz-glass window and expanded by optical lens to about 15 mm in diameter. The carbonization temperature (T_C) was 1000 to 1200 °C, measured with a thermocouple and a pyrometer (Optris, CTlaser 2MH, temperature range: 385 ~ 1600 °C). The flow rate of propane (f_{CH}) was controlled at 1 sccm by a mass flow controller (D07-7, Beijing Sevenstar Electronics Co., Ltd). The carbonization time (t_C) was 2 to 10 min. More details of the experiments and LCVD apparatus are available in our previous works [11,14].

The crystal phases and pole figures were examined by X-ray diffraction (θ - 2θ) with Cu-K α radiation (XRD; Ultima III with a multipurpose attachment, Rigaku, Tokyo, Japan, operating at 40 kV and 40 mA).

Scanning electron microscopy (SEM; Quanta-250, FEI, Houston, TX, at 20 kV) was used to study the surface morphology and conduct a statistical study. The surface topography evaluation was performed using atomic force microscopy [AFM; Bruker (America), Multimode 8]. Transmission Electron Microscopy (TEM; JEM-2100F, JEOL, Japan, at 200 kV) of cross-sections was used to analyze the nature of defects in the thin SiC layers, the heterointerfaces between the

SiC and Si, and the effects of the carbonization process on the Si substrate.

3. Results and discussion

Figure 1(a) shows the XRD patterns of deposits fabricated at different temperatures. No peaks of silicon carbide were observed at $T_C = 1000$ °C. At $T_C \geq 1050$ °C, only the (111) peak at $2\theta = 35.6^\circ$ was identified,

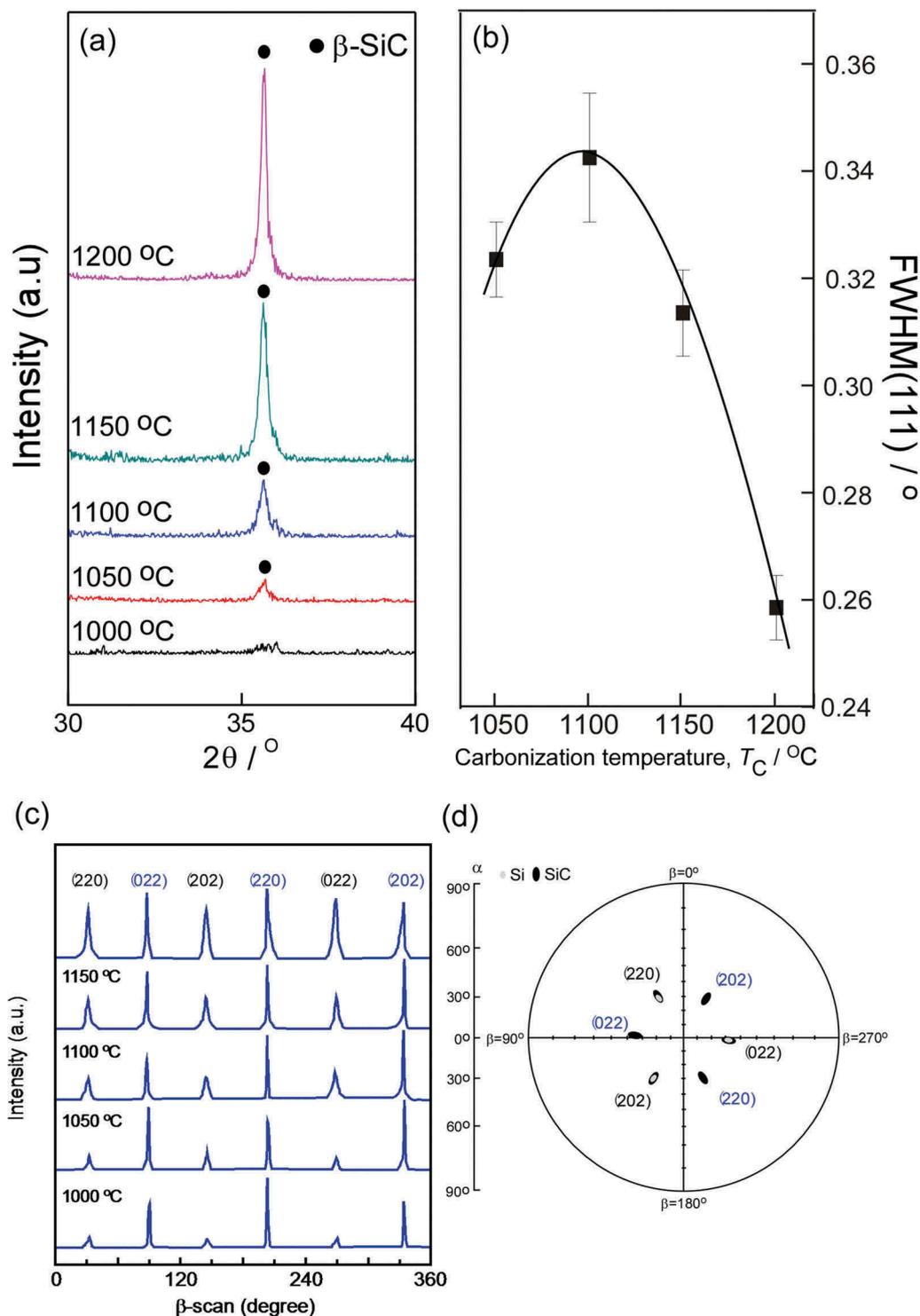


Figure 1. (a) XRD patterns of deposits, (b) full width at half maximum (FWHM) of the 3C-SiC (111) peak, (c) β scanning patterns, and (d) pole figures of the film at $T_C = 1200$ °C and $t_C = 10$ min.

indicating a (111) orientation. The relative intensity of the (111) peak increased with increases in T_C . Figure 1 (b) shows the full width at half maximum (FWHM) values of 3C-SiC (111). FWHM (111) decreased from 0.396° to 0.258° with increases in T_C from 1050 to 1200 °C, indicating that the crystallinity of the SiC film was improved. Grain sizes calculated using the Scherrer formula (Figure 2) and observed by SEM (Figure 3) showed the same trend. However, the calculation results (45 ~ 60 nm) were somewhat smaller from the observation results (58 ~ 97 nm) (Figure 2). Pujar and Cawly investigated the effects of stacking faults on the XRD patterns of 3C-SiC experimentally and by simulation [15–17]. They supposed that the presence of stacking faults and twins led to changes in the diffraction peaks which could provide misleading results when these features were used for crystallite size determinations. The β scanning patterns and poles of 3C-SiC and Si are shown in Figure 1(c,d), respectively. The pole figures for the {220} reflections of 3C-SiC films and Si substrate are both shown at $\alpha = 35^\circ$, which means the 3C-SiC film possesses an epitaxial nature with the Si substrate. In this study, 3C-SiC (111) film displayed six-fold diffraction poles, namely, two sets each of 3C-SiC (220), (022), and (202) poles. The presence of a double positional boundary (DPB) contributed to this phenomenon [18].

Figure 3 shows surface and sectional SEM and AFM images of deposits prepared at different temperatures for 10 min. The grain size increased from 58 to 97 nm with increases in T_C from 1050 to 1200 °C. The

morphology of the surface grains transformed from triangular into hexagonal. The hexagonal grains were formed by two sets of triangular grains extending over each other face to face. The hexagonal structure is the typical morphology of the <111> orientation in *fcc* films, which is reportedly attributable to TB (twin boundary) growth. Meanwhile, the six-fold structure may be caused by DPB growth corresponding to the pole figure analysis [19]. The average surface roughness (R_a) evaluated by AFM is displayed in Figure 4. R_a decreased significantly from 1000 to 1050 °C with increases in T_C , and then increased with T_C . The minimum R_a was 15.6 nm at $T_C = 1100$ °C.

The preparation of SiC by carbonization, the appearance of voids is usually difficult to avoid. The reason for the voids is occurring Si defects during the film's growth due to Si atoms on the surface of the substrate taking part in the reaction. The loss of Si atoms on the surface is compensated by migration of Si atoms from the Si substrate. Because of the Kirkendall effect [20], it is then possible that the Si vacancies coalesce and form a small void beneath the SiC film at the layer/substrate interface. Figure 5(a,b) show the plan-view SEM of thin SiC film grown on a Si (111) substrate at a substrate temperature of 1150°C. The dark triangular and hexagonal features are voids in the substrate. Corresponding structural models of triangular and hexagonal voids are shown in Figure 5 (c,d). These void facets are the energetically favorable {111} planes: the {111} planes are the faces with the lowest surface energy (the free surface energy of

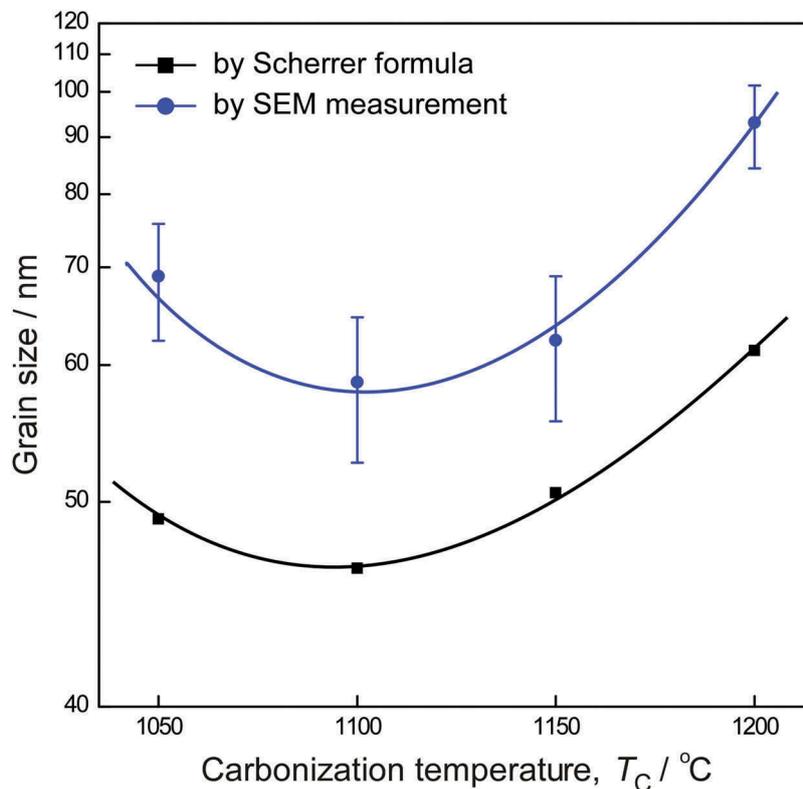


Figure 2. Calculation and observation results for grain sizes.

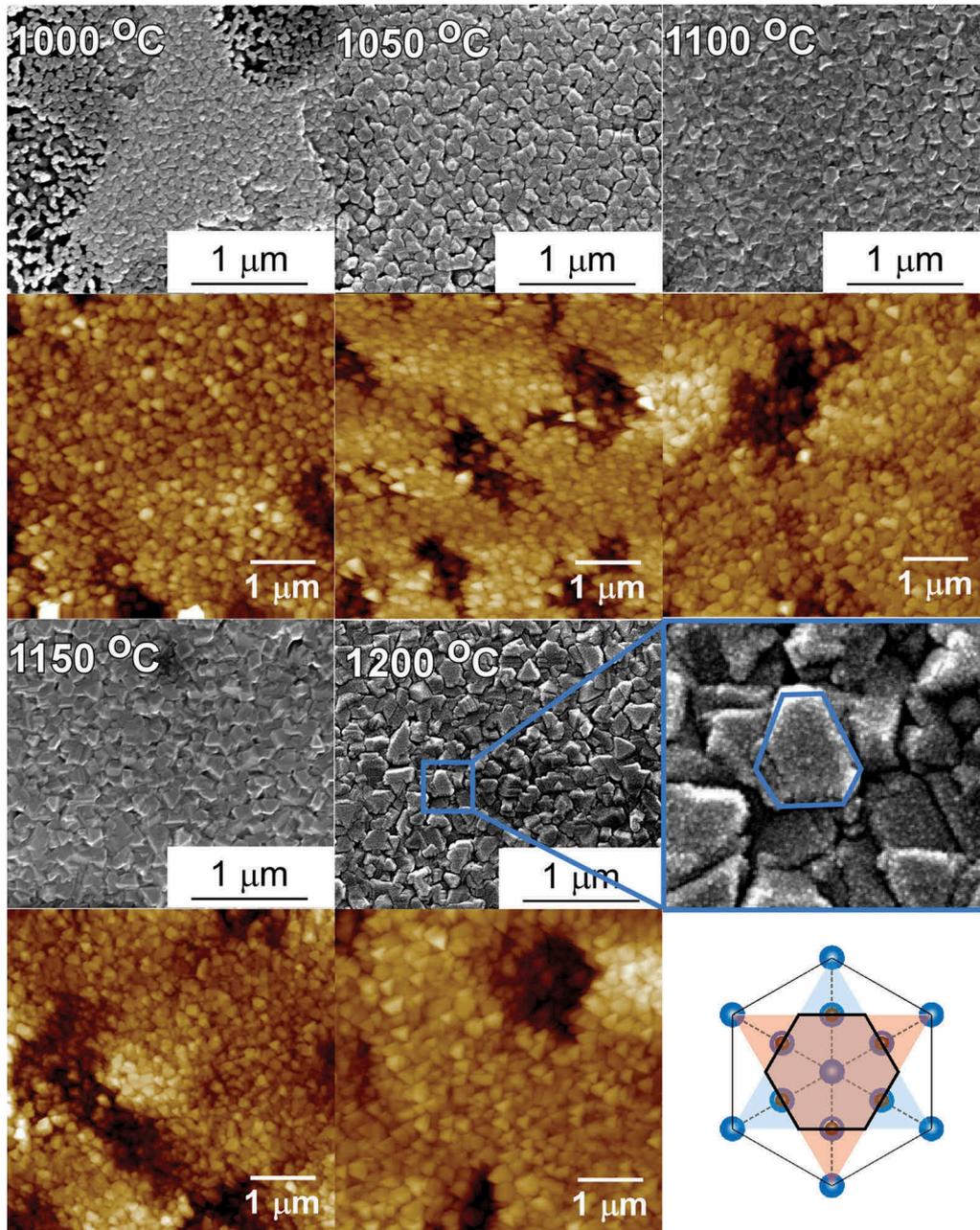


Figure 3. Surface SEM and AFM images of films prepared at $T_C = 1000$ to 1200 °C and $t_C = 10$ min; the inset is an enlarged view of the designated region that depicts the hexagon growth of 3C-SiC (111) films.

Si: $\gamma(111) = 1.23 \text{ J m}^{-2}$ [21]. The hexagonal void shown in Figure 5(d) can be seen as a truncated octahedron obtained by cutting off a solid with eight faces [22]. (In the new solid, the corners are transformed into squares and the triangular faces of the octahedron turn into regular hexagons). Figure 6, the size of the voids increases with increases in the carbonization temperature, whereas the density of the voids decreases (Figure 6). At $T_C = 1000$ °C, while the average void size is small (less than $2.0 \mu\text{m}$), the void density is extremely high due to large numbers of small nucleating voids on the surface. At $T_C = 1200$ °C, the average void size increase to about $4.0 \mu\text{m}$, while the void density is reduced by an order of 1. In Figure 4, the films deposits show a relatively lower

surface roughness because of a combination of relatively lower size and density of the voids.

Figure 7 presents the Arrhenius plots of the T_C and R_g of 3C-SiC films formed by laser CVD and conventional growth processes [23,24]. R_g increased from 0.43 to $1.35 \mu\text{m}\cdot\text{h}^{-1}$ with increases in T_C from 1000 to 1200 °C. These deposition rates are 10 to 100 times greater than those of conventional CVD methods. The growth rate of films is often correlated with the kinetic controlling mechanisms of the deposition process [i.e., either the mass transfer regime (MTR) or the chemical reaction regime (CRR)] [25,26]. The transition from CRR to MTR is usually led by an increase in temperature [26]. Loumagne et al. [25,26] found that a process

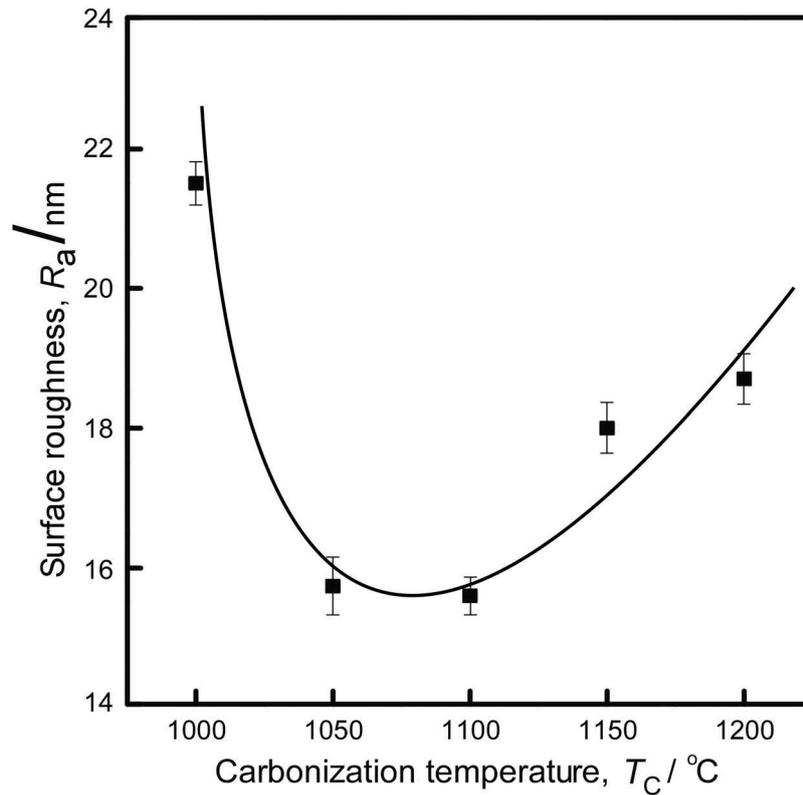


Figure 4. Surface roughness (R_a) of SiC films.

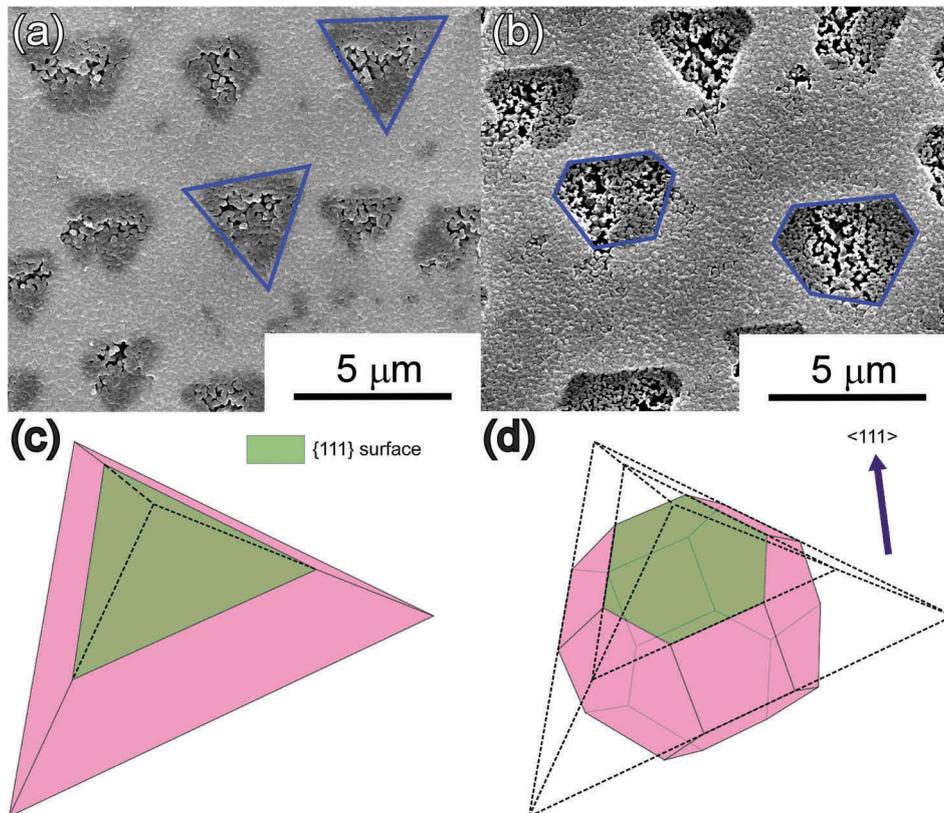


Figure 5. (a) Triangular and (b) hexagonal voids observed by surface SEM of a SiC layer grown at 1150 °C. Structure model of (c) triangular and (d) hexagonal voids.

exhibiting relatively lower activation energy indicates the MTR domain. Considering the kinetics, the activation energy for our processes has been calculated from Figure 7, showing ~80 kJ/mol in

the temperature range of 1000 to 1200 °C, which is much lower than that reported in our previous works [11,27], indicating that films growth in the LCVD processes pertains to the MTR domain.

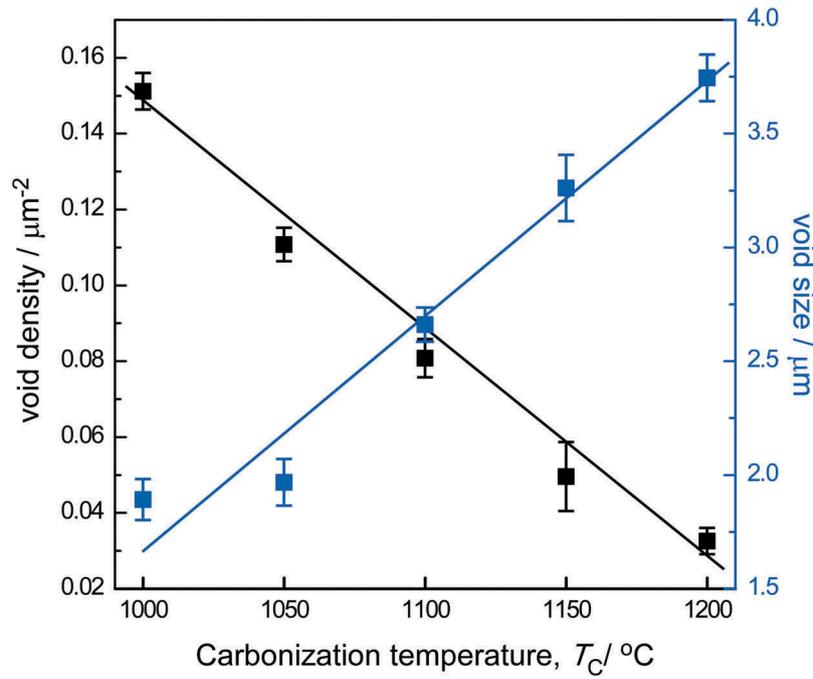


Figure 6. The effects of T_C on the size and density of voids.

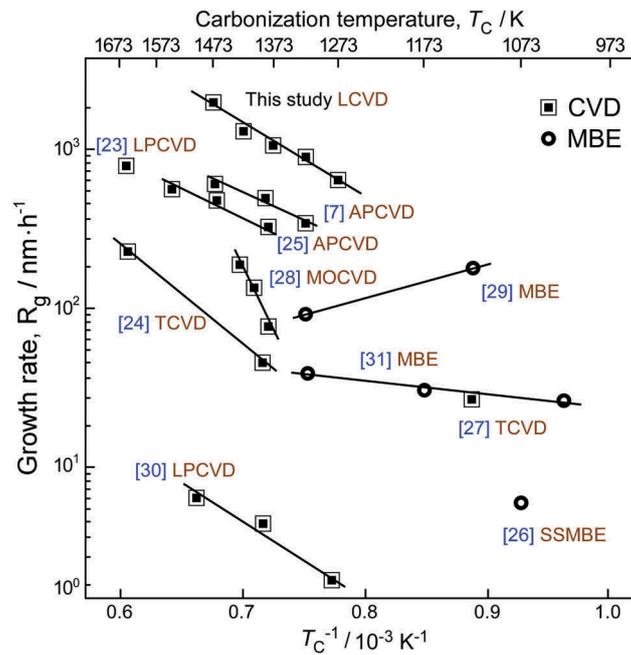


Figure 7. Effect of T_C on R_g .

Figure 8 shows surface SEM and AFM images of 3C-SiC films prepared at 1200 °C for different carbonization times (t_C). The density of the voids was almost constant, but the size of voids increased slightly. Although the size of the voids increases slightly after 6 min (Figure 9), R_a reached the maximum at $t_C = 6$, min as shown as Figure 10, because there was insufficient time to permit a uniform layer to seal over the void within 6 min. This phenomenon also was detected in a previous study³⁵. The growth rate was also reduced with increases in the carbonization time, because the carbon and silicon

atoms in the reactant gases seal the voids to form uniform thin films (Figure 10).

Figure 11 shows cross-sectional TEM images of thin films deposited at $T_C = 1200$ °C and $t_C = 4$ to 10 min. Cross-sectional TEM analysis is helpful in the detection of voids in SiC layers, as well as providing accurate measurements of thickness and interfacial roughness. In Figure 11(a,b), where the interface between Si and SiC for carbonization at $t_C = 4$ to 6 min is shown, voids extending deep into the substrate are easily observable. At $t_C = 8$ min, as shown in Figure 11(c), a longer

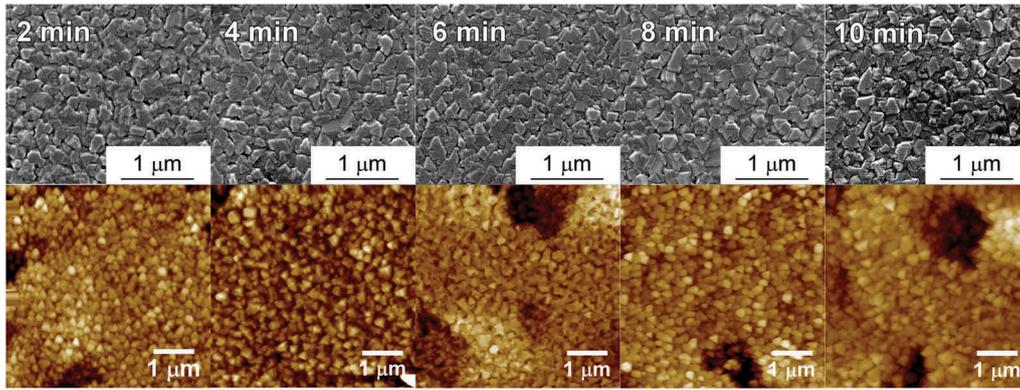


Figure 8. The surface SEM and AFM images of 3C-SiC films prepared at $t_c = 2$ to 10 min and 1200 °C.

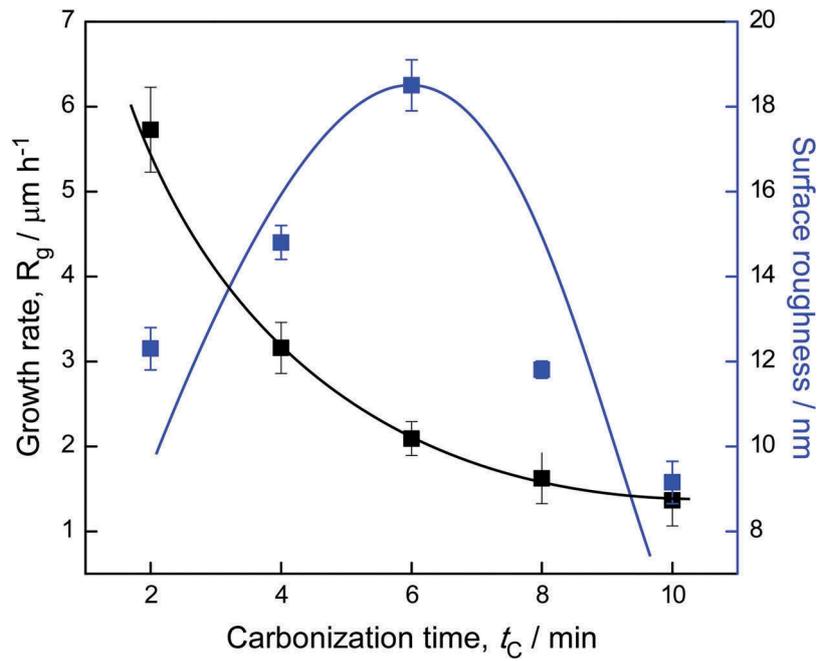


Figure 9. The sizes and densities of voids at $t_c = 2$ to 10 min and 1200 °C.

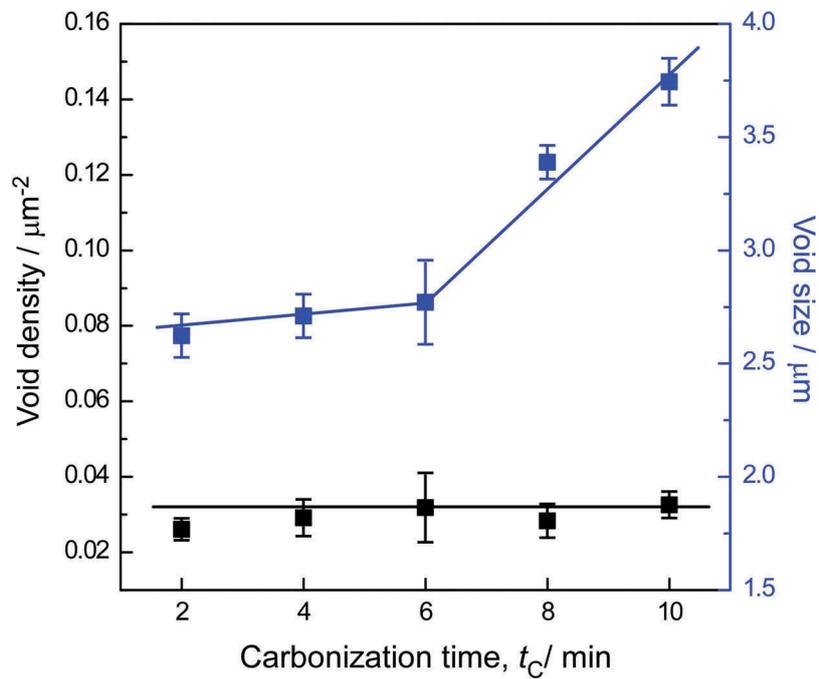


Figure 10. R_g and R_a at $t_c = 2$ to 10 min.

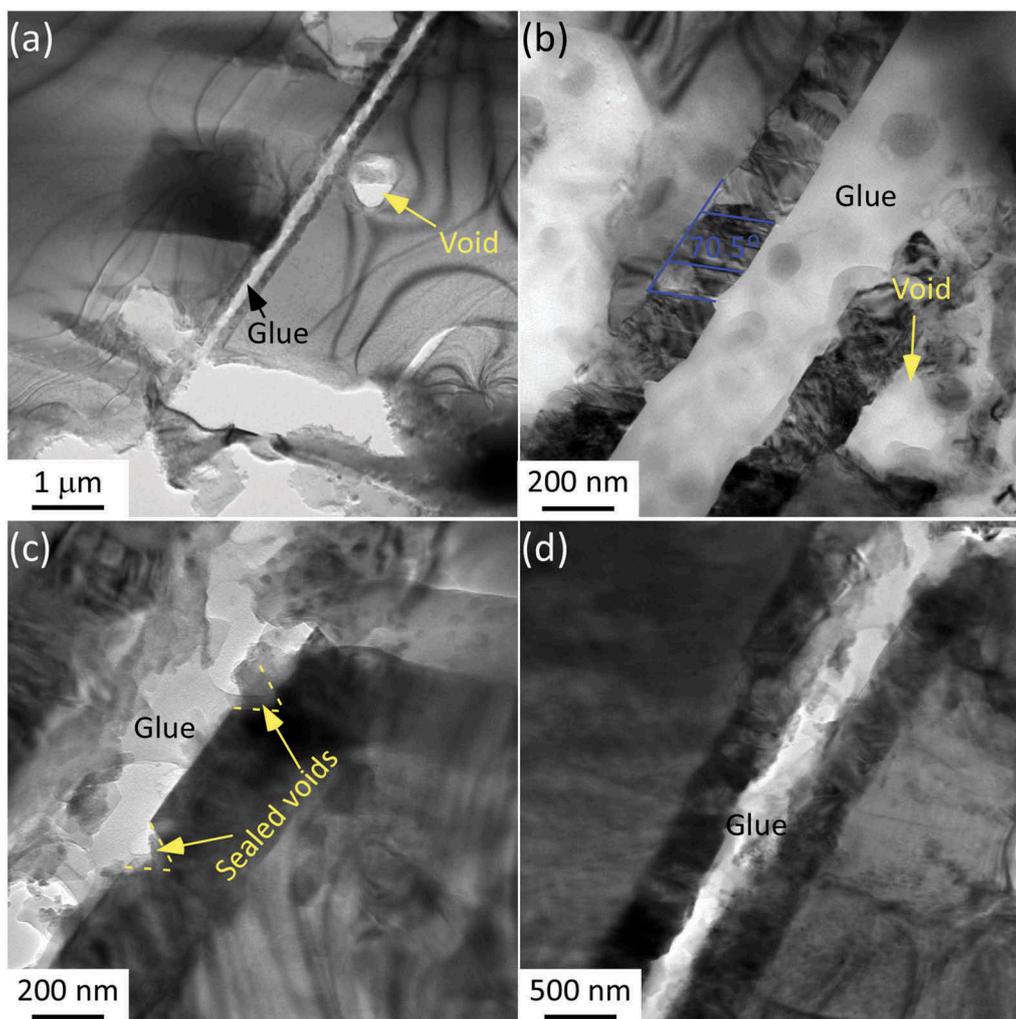


Figure 11. Cross-sectional TEM analysis of thin films deposited at $T_C = 1200\text{ }^\circ\text{C}$ and $t_C =$ (a) 4 min, (b) 6 min, (c) 8 min, and (d) 10 min.

carbonization time led to a continuous thin film sealing over the voids. The heterointerface of a sample carbonized for 10 min, shown in Figure 11(c), is continuous, with minimal roughness and without voids in the substrate. Dark striations tilted 70.5° in the growth direction $\langle 111 \rangle$ can be observed in the cross-section images, moreover seen in Figure 11(b). Those striations are stacking faults (SF), such as twins that developed also happened along the $\langle 111 \rangle$ direction, as mentioned in the discussion of the XRD simulation results.

4. Conclusions

Epitaxial SiC layers were grown on (111)-Si surfaces by carbonization via LCVD using C_3H_8 as the carbon source. The effects of the carbonization temperature (T_C) and carbonization time on the microstructure and growth rate were investigated by XRD, AFM, SEM, and TEM analysis techniques. We found that the density and size of the voids was strongly dependent on T_C , with a positive correlation. The voids were sealed, and continuous and uniform thin films were formed after a carbonization time of 6 min at $T_C = 1200\text{ }^\circ\text{C}$. R_g was also dependent on T_C

increasing from 0.43 to $1.35\text{ }\mu\text{m}\cdot\text{h}^{-1}$ with increases in T_C from 1000 to $1200\text{ }^\circ\text{C}$. These deposition rates are 10 to 100 times greater than those achieved by the former CVD methods.

Disclosure statement

No potential conflict of interest was reported by the authors.

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