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Microstructure and growth of SiC film by excimer laser chemical vapour deposition at low temperatures

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The formation of SiC film by photo-chemical vapour deposition (CVD) using ArF excimer laser with a wavelength of 193 nm has been studied to establish a low-temperature and mild synthetic process for ceramic films. Photo-CVD was conducted using Si_2H_6 and C_2H_2 as source gases on quartz glass, molybdenum and graphite substrates at 508–623 K. The pressure ratio of Si_2H_6 to C_2H_2 was changed from 0.06 to 1.2. The laser was irradiated at 50 mJ cm^{-2} at 25 Hz. The films were identified using transmission electron microscopy and infrared spectrometry, and the chemical composition was determined using Auger electron specroscopy. The growth rate of SiC was measured with a step-height profilometer. β-SiC, with almost stoichiometric composition, was formed in the pressure ratio range, Si_2H_6/C_2H_2, of 0.06–1.2 at 508–623 K. Crystallization of the SiC film was observed with increasing Si_2H_6/C_2H_2 ratio. The film growth rate linearly depended on Si_2H_6 pressure but was independent of C_2H_2 pressure. The rate-determining step of film formation is assumed to be photolysis of Si_2H_6. The cross-section of photolysis calculated from the film growth rate was about 10^{-18} cm^2 for the ArF laser.

1. Introduction

SiC film is attractive for use in heat-resistant coatings and semiconductors owing to its prominent properties such as mechanical strength, thermal conductivity, irradiation resistivity at high temperatures.

Several methods, such as sputtering, ion plating, and chemical vapour deposition (CVD) may be applied to prepare SiC thin films. Among these processes, photo-CVD has the advantage of soft processing, resulting in the introduction of lower amounts of defects and impurities into the films compared to sputtering and plasma CVD. Recently, photo-CVD using a mercury lamp or excimer laser has been carried out to produce amorphous SiC films for semiconductor devices [1, 2]. However, formation conditions and the film growth mechanism have not been clarified.

In the present paper, microstructures and growth kinetics of SiC film prepared with photo-CVD were studied using an ArF excimer at low temperatures.

2. Experimental procedure

Copper, graphite, and quartz sheets of sizes 17 mm × 17 mm × 0.05 mm and 17 mm × 17 mm × 1 mm, respectively, were used as substrates. The substrate was placed inside the reaction chamber so that the surface was perpendicularly aligned towards the laser beam direction. The chamber was evacuated to 1×10^{-5} Pa before the reaction. The SiC sources were 10 vol % disilane and 10 vol % acetylene gases diluted with hydrogen gas. ArF excimer laser with a wavelength of 193 nm was irradiated at 50 mJ cm^{-2} and at a repetition of 25 Hz. The pulse width was about 15 ns. The beam was adjusted to become square in shape with 10 mm × 10 mm on the specimen. The corresponding photon flux was 4×10^{16} photons cm^{-2} pulse^{-1}. During the experiment, the window of the chamber through which the laser beam was introduced, was flushed with argon gas at a constant flow rate of 30 standard cm^3 min^{-1} to avoid the deposition on it of reaction products.

The partial pressures of disilane and acetylene were respectively set at 5–65 and 0–260 Pa. The total pressure was kept constant at 1.331 Pa–2.66 kPa. The temperature of the specimen was controlled by heating with a halogen lamp from the rear side and was kept at 508–623 K. After the reaction, the films deposited on copper sheets were removed by dissolving the substrates in 1N HNO_3 solution and then rinsed with water and methanol; the films were then examined with TEM (JEM-2000FX). The composition of films was determined with Auger electron spectroscopy. The films formed on graphite sheets were also analysed using an infrared spectrometer (JIR-100 FT–IR). The surface morphology was observed using SEM (JEM-840F). Film thickness was measured with a step-height profilometer (Kosaka Laboratories Ltd).

3. Results

3.1. Microstructures of films

Fig. 1 shows the typical surface morphology of the film deposited on copper at 518 K. The film was

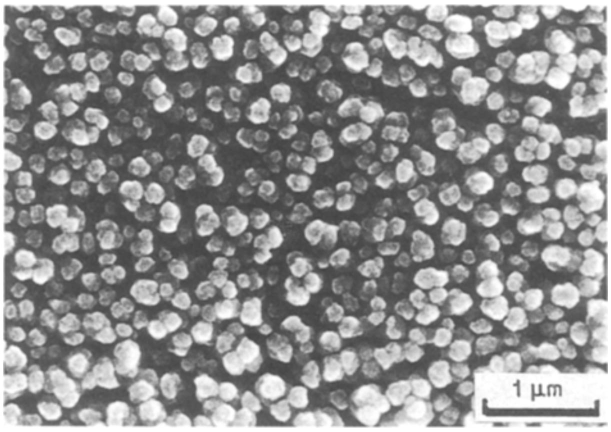

Figure 1 Surface microstructure of SiC film formed at a pressure ratio, Si_2H_6/C_2H_2, of 0.12 at 518 K.

produced at 8.1 Pa Si_2H_6 and 65 Pa C_2H_2, with a film thickness of about 0.6 µm. The film was covered with small particles, around 0.1–0.2 µm diameter. The surface morphology was almost same, independent of gas composition and substrate temperature under the present conditions.

Fig. 2 shows changes of microstructure and electron diffraction patterns of the films with increasing silane gas pressure. Films were produced at 518 K for 600 s. After removal from the copper substrates, films were observed with the TEM. Under excess acetylene pressure conditions, the film had a uniform structure and diffraction patterns showed amorphous SiC. With increasing silane gas pressure, island-like deposition occurred, as seen in Fig. 2e and, simultaneously, diffraction spots of crystalline β-SiC appeared.

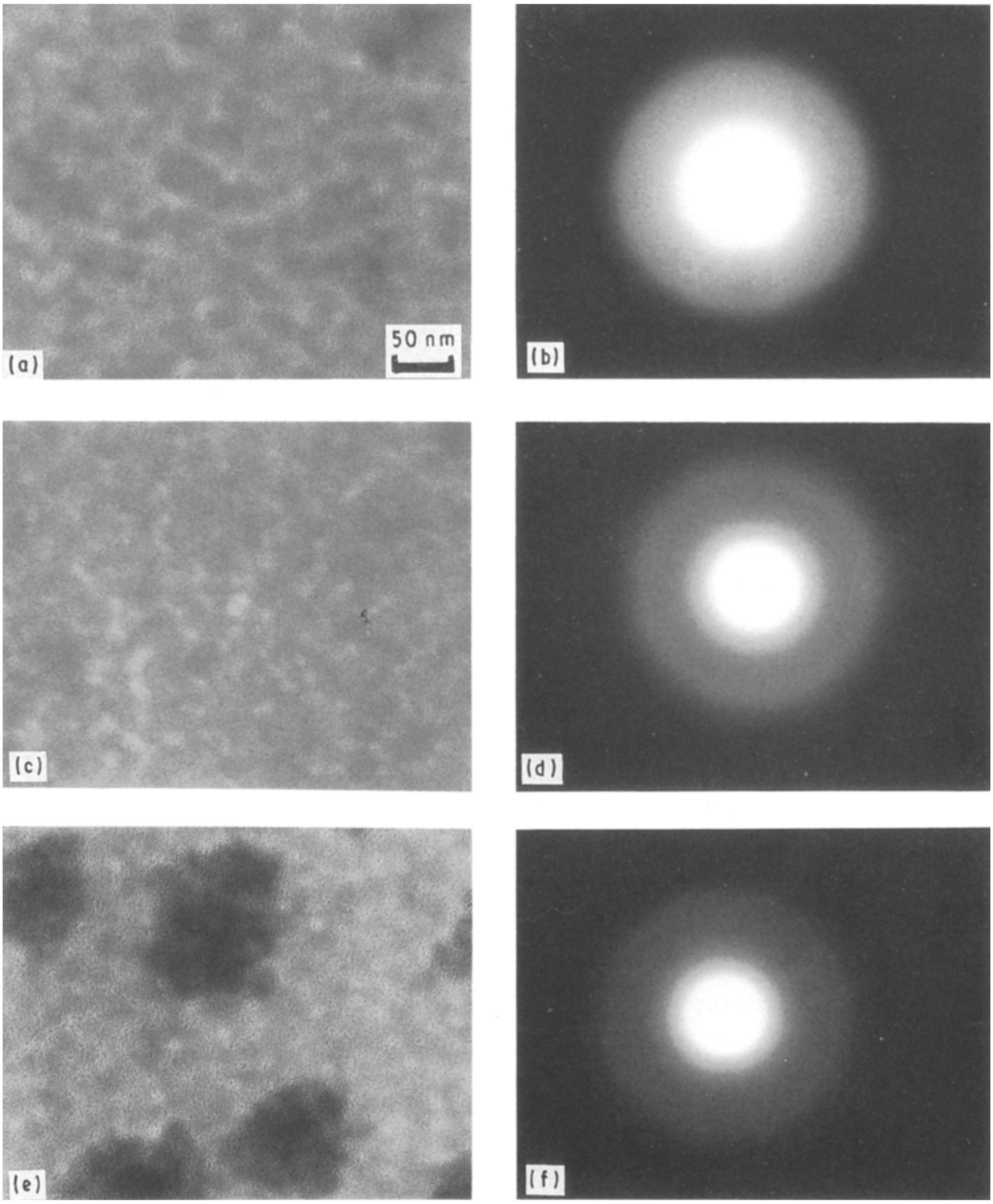

Figure 2 Transmission electron micrograph of photo-CVD films formed at pressure ratios of Si_2H_6/C_2H_2 of (a, b) 0.06, (c, d) 0.12, (e, f) 0.24, and (g, h) 0.60 at 518 K. (a, c, e, g) Bright-field images, (b, d, f, h) diffraction patterns.

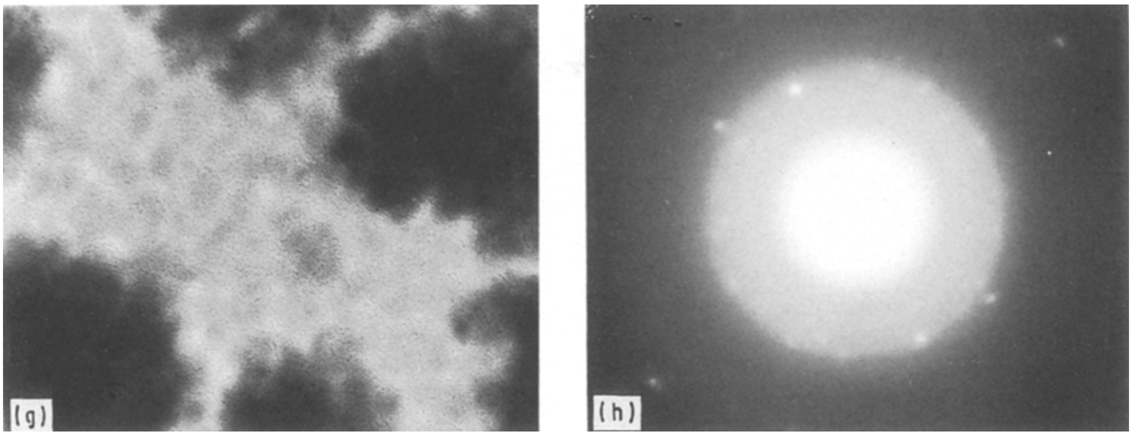

Figure 2 (Continued)

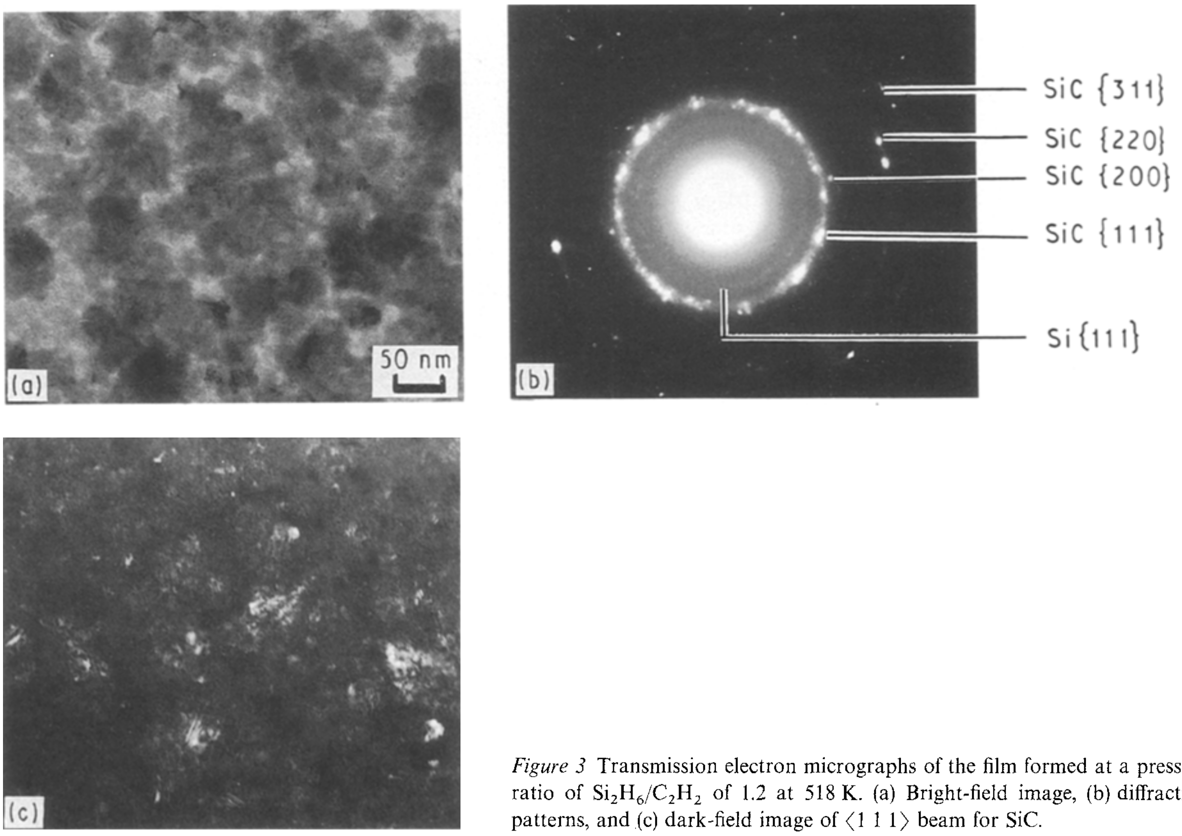

Figure 3 Transmission electron micrographs of the film formed at a pressure ratio of Si_2H_6/C_2H_2 of 1.2 at 518 K. (a) Bright-field image, (b) diffraction patterns, and (c) dark-field image of $\langle 1\ 1\ 1\rangle$ beam for SiC.

Fig. 3 shows the result of TEM observation for the film formed at a pressure ratio of Si_2H_6 to C_2H_2 of 1.2. Fig. 3a shows the bright-field image, (b) the diffraction patterns, and (c) the dark-field image for $\langle 1\ 1\ 1\rangle$ diffraction beam of β-SiC. As seen in these photographs, island-like deposits with a size of around 0.2 μm are composed of crystalline β-SiC. Figs 2 and 3 indicate that SiC films crystallize easily with increasing pressure ratio of Si_2H_6 to C_2H_2. In Fig. 3b, a weak diffraction ring corresponding to $\{1\ 1\ 1\}$ of silicon is observed. Trace amounts of silicon, therefore, are also deposited together with SiC formation at this pressure ratio.

Infrared absorption analyses also indicated the formation of SiC film, using ultraviolet laser CVD. Fig. 4 shows infrared absorption spectra for the film formed on a graphite substrate at the pressure ratio of 0.12 and for β-SiC crystals as a reference. Reference SiC was prepared with a thermal CVD. The spectra are close to that of SiC crystal. The strong absorption at around 850 cm^{-1} is attributable to Si–C stretching. In the spectra for the film, there seems to be several peaks based on Si–H [3] between 800 and 1000 cm^{-1} compared to SiC formed by thermal CVD. It is considered that the present SiC film prepared by photo-CVD at room temperature contains large amounts of hydrogen.

The chemical composition of SiC films at various pressure ratios of silane to acetylene was measured using Auger electron spectroscopy. In Fig. 5, the atomic concentration of silicon in the films is plotted against the gas pressure ratio. As may be seen, the silicon content of the films is almost 0.5 and the composition does not deviate widely from the stoi-

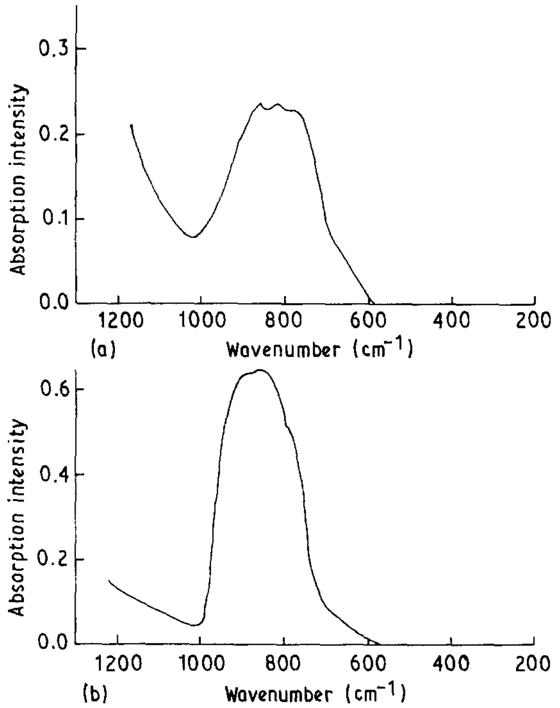

Figure 4 Infrared absorption spectra for (a) film formed by photo-CVD, and (b) β-SiC with an average grain size of 100 μm prepared by thermal CVD. The film was prepared at a pressure ratio, Si_2H_6/C_2H_2, of 0.12 at 518 K.

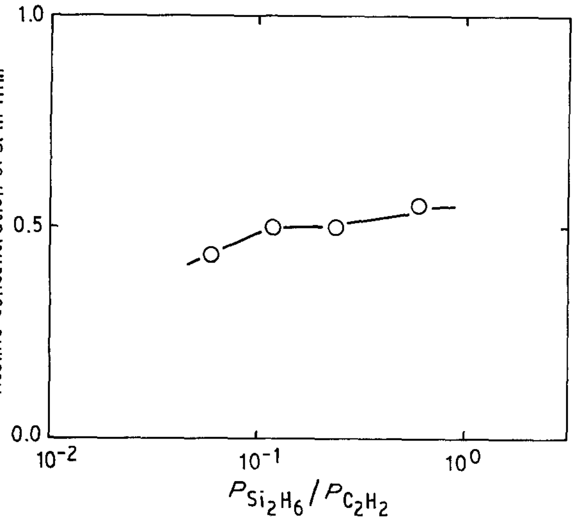

Figure 5 Atomic concentration of silicon in the film measured using AES as a function of pressure ratio of Si_2H_6/C_2H_2 at 518 K.

chiometric composition of SiC in the Si_2H_6/C_2H_2 ratio range of 0.1–1.0.

In the present study, no product was formed on the substrates, except for in a C_2H_2 gas environment at 508–623 K.

3.2. SiC film growth

The growth rates of SiC film on silica glass were measured under various pressures and temperatures.

Fig. 6 shows the change in film thickness with time at 518 K. Partial pressures of Si_2H_6 and C_2H_2 were kept at 39 and 118 Pa, respectively. The thickness increases linearly with time of laser irradiation. Identical linear time dependencies of thickness as in Fig. 6 were observed at different pressures and temperatures. The slope of the curves as shown in Fig. 6 will then give the film growth rate.

Fig. 7 shows the relation between the growth rate and Si_2H_6 pressure at a constant pressure of C_2H_2 at 518 K. The pressure dependence of the rate is nearly 1, i.e. the rate of growth is proportional to Si_2H_6 pressure. On the other hand, the growth rate is almost independent of C_2H_2 pressure, as shown in Fig. 8.

Fig. 9 shows plots of the growth rate against the substrate temperature. The temperature dependence of the growth rate is very small in the present temperature range between 518 and 630 K. The estimated activation energy for the growth rate is about 0.17 eV.

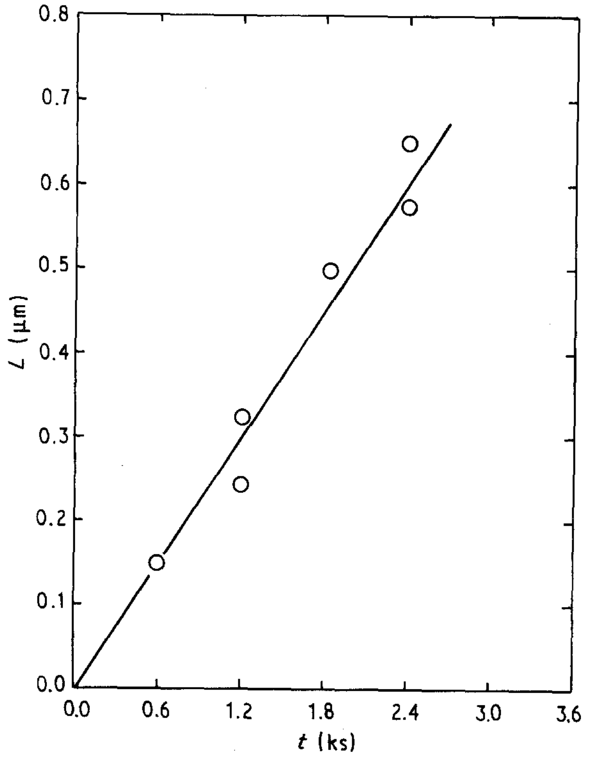

Figure 6 Film thickness as a function of laser irradiation time at a Si_2H_6 pressure of 39 Pa and a C_2H_2 pressure of 118 Pa at 518 K.

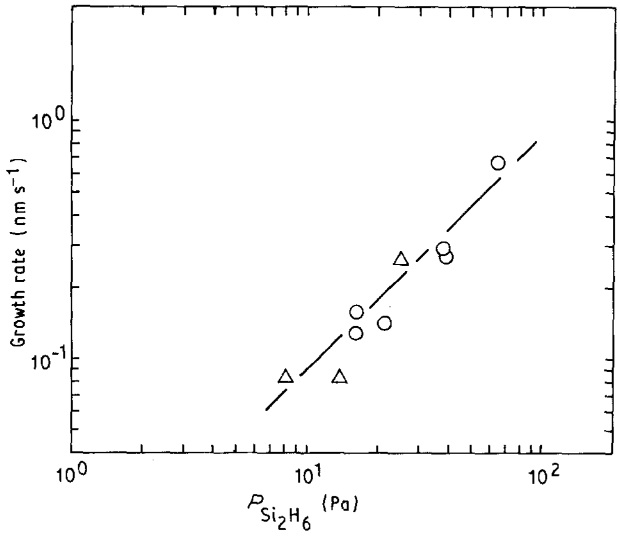

Figure 7 Relation between film growth rate and Si_2H_6 pressure at constant C_2H_2 pressure. $p_{C_2H_2}$: (○) 109–118 Pa, (△) 62–72 Pa, at 518 K.

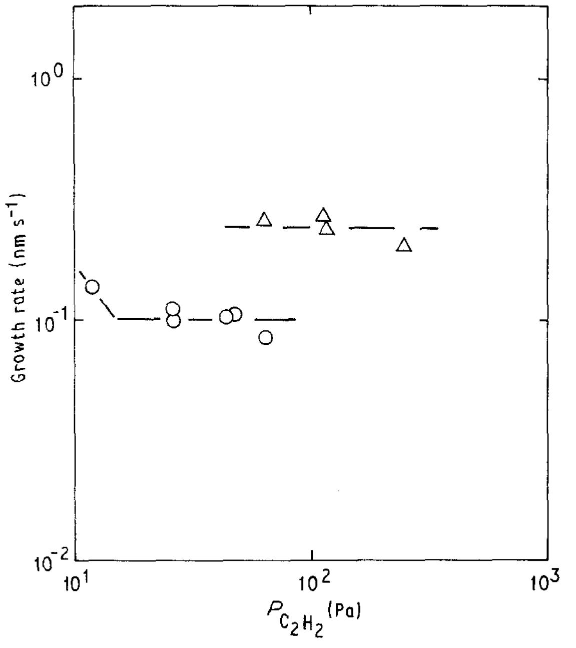

Figure 8 Relation between film growth rate and C_2H_2 pressure at constant Si_2H_6 pressure. $p_{Si_2H_6}$: (○) 5.5–8.1 Pa, (△) 32–39 Pa at 518 K.

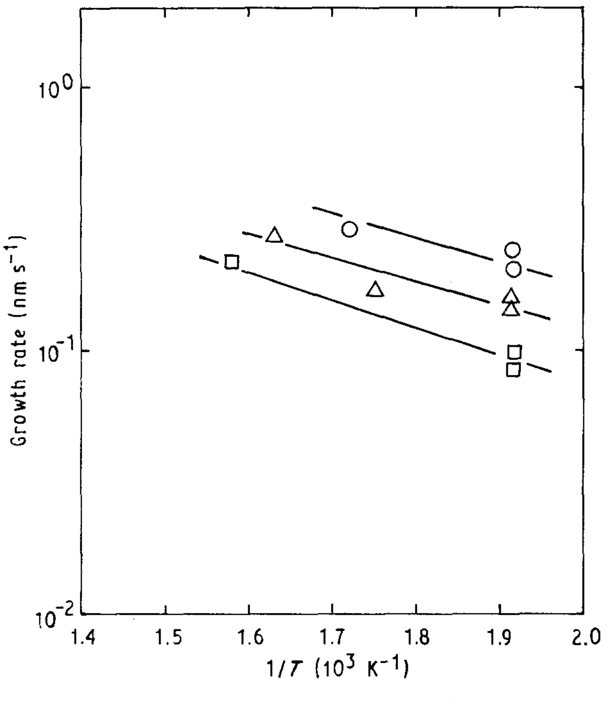

Figure 9 Plots of film growth rate against reciprocal substrate temperature. $p_{Si_2H_6}$: (○) 32–39 Pa, (△) 14–16 Pa, (□) 6.7–7.6 Pa.

The film growth process therefore does not seem to be controlled by a thermal activation process.

4. Discussion

4.1. SiC film formation

From the observation of microstructure of the deposited films by laser CVD and examination of their growth rates, the SiC film formation by photo-CVD can be discussed.

ArF laser has a wavelength of 193 nm, corresponding to a photon energy of 6.41 eV. The binding strengths of C–H and H_3Si–SiH_3 bonds are around 3.51 eV [4]. Therefore, Si_2H_6 and C_2H_2 gases are easily excited by the ArF laser.

The photolysis reactions of these gases are considered to be as follows [5]

$$Si_2H_6 + h\nu \rightarrow SiH_2 + SiH_3 + H \quad (1)$$

$$\rightarrow SiH_3SiH + H \quad (2)$$

$$\rightarrow Si_2H_5 + H \quad (3)$$

$$C_2H_2 + h\nu \rightarrow C_2H + H \quad (4)$$

In the above processes, SiH_3 and Si_2H_5 are major radicals [5]. These react with C_2H to form SiC in the gas phase, or on the substrate during the lifetime of radicals, according to

$$2SiH_3 + C_2H \rightarrow 2SiC + 7/2H_2 \quad (5)$$

$$Si_2H_5 + C_2H \rightarrow 2SiC + 3H_2 \quad (6)$$

In the present study, small amounts of silicon are also deposited together with SiC formation. Thus the direct reaction from silane radicals to silicon is also considered to occur on the substrate

$$SiH_3 \text{ or } Si_2H_5 \rightarrow Si + nH_2 \quad (7)$$

On the other hand, carbon or graphite deposition was not observed, except under a C_2H_2 environment. The binding energies of H–SiH_3, H–Si, and C–CH are 4.07, 3.10, and 9.95 eV [4], respectively. Therefore, Reaction 7 may occur by absorption of photons, while the triple bond of acetylene is hardly dissociated by the ultraviolet light present, to produce carbon on the substrate. SiC nuclei are probably formed on the substrate through the reactions of silane radicals and acetylene radicals. The chemical composition of the films deposited is almost constant at SiC stoichiometry, independent of the gas concentration ratio, Si_2H_6/C_2H_2. However, the morphologies of the films differ for the different Si_2H_6/C_2H_2 values. Island-like deposits were formed and changed from amorphous to crystalline with increasing Si_2H_6/C_2H_2 value. The crystallization of films is considered to relate to the silicon formation and thermal activation due to the laser heating. Silicon, which is easily crystallized [3] by the ultraviolet laser perpendicularly irradiating the substrates, might have acted as a nucleus for the crystallization of SiC films.

Fairly large amounts of hydrogen are predicted to be included in the film from the infrared spectra. The role of hydrogen in the SiC will be needed to be examined precisely.

4.2. Film growth kinetics

From the examination of growth rates of the films at various Si_2H_6 and C_2H_2 pressures, as shown in Figs 7 and 8, the growth rate may be simply given as

$$\delta L/\delta t = kp_{Si_2H_6} \quad (8)$$

where L is the thickness, k the rate constant and $p_{Si_2H_6}$ the Si_2H_6 pressure. Because the growth rate does not depend on C_2H_2 pressure and the temperature dependence of the substrate was negligibly small, the rate-determining step is considered to be controlled by photo-decomposition of Si_2H_6, expressed as Equations 1–3. The photo-decomposition rate is represented by

$$\delta N/\delta t = \sigma v_p[Si_2H_6] \qquad (9)$$

where N is the number of silicon radicals formed by photolysis, σ the cross-section of photo-decomposition of Si_2H_6, v_p the photon flux, and $[Si_2H_6]$ the concentration of Si_2H_6 in the path length of photons. Assuming that all radicals which reached the substrate contributed to the formation of the film, Equation 8 can be replaced by Equation 9. The lifetime of radicals is about 0.2 ms [6] and the path length about 20 mm at 16 Pa and 518 K [6]. Assuming the silicon concentration accumulated in the film during the actual ultraviolet laser irradiation from the film growth rate, as shown in Fig. 6, σ can be estimated to be about $1 \times 10^{18}\,cm^2$. This value closely coincides with the reported value of $4 \times 10^{-18} cm^2$ for Si_2H_6 at 190 nm [7].

In Figs 6–9 the irradiation time of the laser is 15 ns × 25 Hz per second. If the film grows during irradiation, the real growth rates shown in Figs 7–9 are about 1×10^6 times this value. The apparent growth rate at a silane pressure of 16 Pa at 518 K under the present laser irradiation condition was $0.15\ nm\ s^{-1}$, while the estimated actual value becomes $150\ \mu m\ s^{-1}$. Because SiC film formation by thermal CVD at 1473 K [8] is around $0.2\ \mu m\ s^{-1}$, it is found that laser CVD is an extremely high-speed film-production process if continuous or high repetition irradiation by ultraviolet laser light is realized.

5. Conclusions

The synthesis of SiC film by ArF excimer laser CVD was examined at 508–623 K. The following conclusions were drawn.

1. β-SiC with almost stoichiometric composition was formed in the pressure ratio range, Si_2H_6/C_2H_2 of 0.06–1.2 at 508–623 K.
2. SiC film crystallized with increasing Si_2H_6 pressure.
3. SiC film growth rate linearly depends on Si_2H_6 pressure but is independent of C_2H_2 pressure.
4. The rate-determining step of film formation is assumed to be the photolysis of Si_2H_6.
5. The calculated photo-decomposition cross-section of Si_2H_6 is about $10^{-18}\,cm^2$.

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