Formation of Nano-crystalline SiC Films by Laser CVD at Low Temperature

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Abstract

The formation of crystalline SiC film by ArF excimer laser chemical vapor deposition (CVD) has been studied at 298-623K using Si_2H_6 and C_2H_2 as source gases. Transmission electron microscopy (TEM) and X-ray photon spectroscopy (XPS) results indicated that nano-crystalline β-SiC film with a grain size of 10-50 nm was formed with the perpendicular beam even at 294K while only amorphous SiC film was obtained at 294-714K using the parallel beam. The formation rate linearly depended on Si_2H_6 pressure. The photo-absorption measurement showed that crystalline SiC film with a band gap between 1.9-2.5 eV can be easily formed even at room temperature by using a excimer laser CVD.

1. Introduction

SiC is an attractive material for the use of heat-resisting coatings and semiconductors from its prominent properties at high temperatures. Several methods such as sputtering, ion plating, and chemical vapor deposition (CVD) are applied to preparation of SiC thin films. Among the processes, photo-CVD has an advantage of a soft processing resulting in introducing smaller amounts of defects and impurities into the films compared to sputtering and plasma CVD. Recently, photo-CVD using mercury lamp or excimer laser has been carried out to make SiC films for semiconductor devices(1),(2). However, only amorphous SiC has been reported to be formed in these processes.

In the present paper, the synthesis of crystalline SiC film has been studied by photo-CVD using ArF excimer laser.

2. Experimental

Carbon films with a thickness of 15nm supported by a copper micro-grid disk of 3mmϕ, and sheets of copper, molybdenum, graphite and quartz cut into a size of 17x17x1mm were used as substrates. The substrate was placed inside the reaction chamber so that the surface was aligned parallel and perpendicular to the laser beam direction. The chamber was evacuated up to 1×10^{-5}Pa before the reaction. The sources of SiC were 10 vol% disilane and 10 vol% acetylene gases diluted with argon gas. ArF excimer laser with a wave length of 193 nm was irradiated at 75mJ/cm^2 and at a repetition of 25Hz. The pulse width was about 15ns. The photon flux corresponded was 4×10^{16} photons/cm^2/pulse. During the experiment, the window of the chamber introducing the laser beam was sprayed with Ar gas so that the reaction product did not deposit on it.

The flow rate of disilane and acetylene were set at 2-4 and 0-20 standard cm^3 per minute (SCCM), respectively. The total pressure was kept at a constant pressure of 1.33Pa-2.66kPa . The temperature of the substrate was controlled by heating with a halogen lamp from the back side of the substrate and was kept at a constant temperature of 298-623K. After the reaction, the films deposited on the micro-grids were directly observed and identified with TEM (JEM-2000FX and 4000EX). SiC films deposited on copper sheets were removed by dissolving the substrates in 1N HNO_3 solution and after being rinsed with water and methanol, the films were examined with TEM. The films formed on graphite and Mo sheets were analyzed with X-ray photon spectroscopy (XPS). The surface morphology was observed with secondary electron microscopy (SEM). Film thickness was measured with a step height profile-meter.

3. Results and Discussion

3.1 Identification of films

3.1.1 SEM and TEM observation

Figure 1 shows a typical surface morphology of deposited film. The film was made on Mo at 5.5Pa of Si_2H_6 and 27.7Pa of C_2H_2 by the perpendicular beam. The film thickness is about 600 nm. It is seen that the film is composed of small particles with 100-200 nm diameters. The grain size was rather smaller for the parallel beam. However, it was not affected

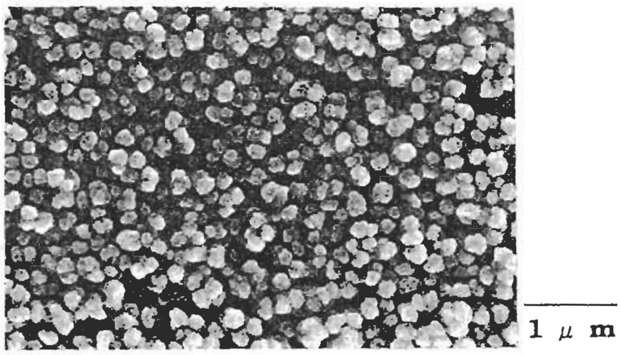

Fig. 1 Surface microstructure of photo-CVD. SiC film was formed at 518K.

by the gas composition and temperature.

Figure 2 shows the bright-field image (a), dark-field image of [111] direction of β SiC (b) and diffraction pattern (c) for the film prepared by the perpendicular laser beam to the substrate. Fig.2-(d) shows a diffraction pattern from the film formed with the parallel laser beam to the substrate. Clear diffraction spots of β-SiC was obtained for the perpendicular beam. Each single crystal of β-SiC has a size of 5-50 nm as shown in the dark-field image of [111] diffraction beam. The crystalline SiC was formed even at room temperature and its size did not change in the present temperature range. On the other hand, no evident diffraction spot was observed for the films formed by the parallel beam.

Figure 3 shows the HRTEM of the film formed at 518K by the perpendicular beam. The crystalline with a size of 10 nm in the center of this photograph indicates the lattice image from the [110] direction.

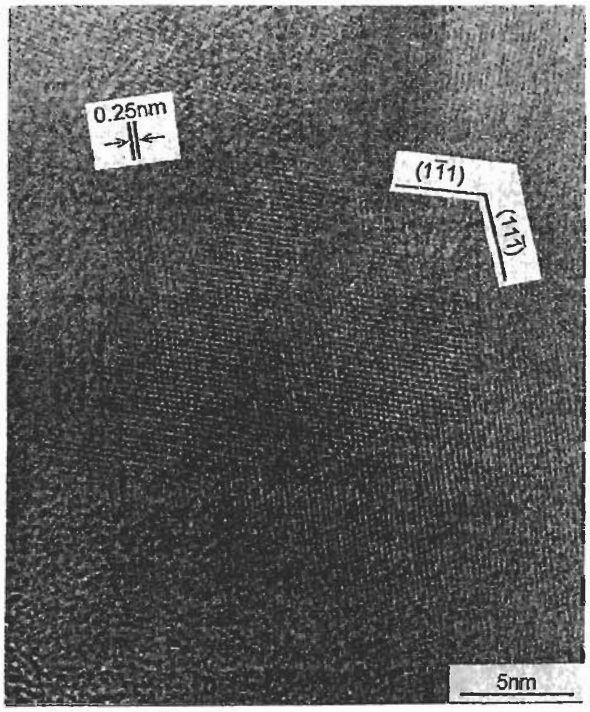

Fig.3 HRTEM of crystalline β SiC film.

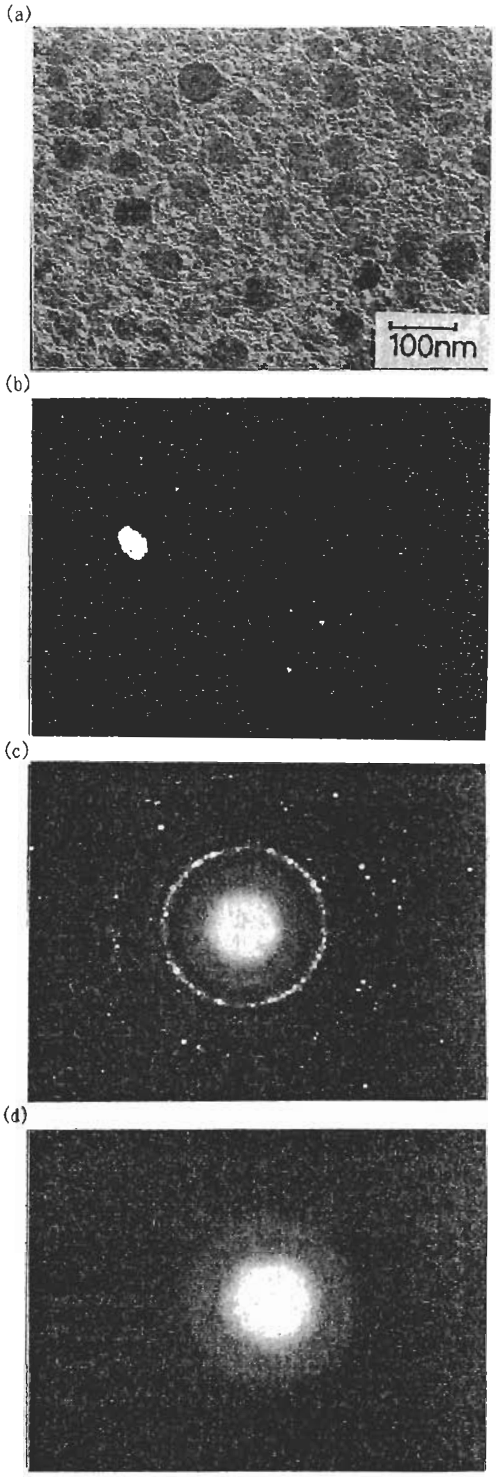

Fig. 2 TEM of SiC films formed with the perpendicular laser beam to the substrate (a-c) and parallel beam (d) at 518K. (a) bright-field image, (b) dark-field image for the [111] diffraction beam, (c) and (d) diffraction patterns.

3.1.2 XPS analyses

Figure 4 shows the XPS spectra for the C(1s) region. Thermal CVD SiC and IG-110U were used as SiC and graphite standards, respectively. By curve-fitting the spectra with coupled Gaussian and Lorentzian peaks, the binding energy of C(1s) for each material was obtained. As seen in this figure, the data fit with 2 or 3 peaks. Peak (1) with a binding energy of 283.4 eV is assigned to C(1s) of the β-SiC standard, which is in good agreement with the reference SiC. In SiC films formed with both parallel and perpendicular beams, the existence of Si-C bonding is confirmed.

Peak (2) with a binding energy of 284.4-284.8 eV appearing in the films fits with C(1s) of graphite. Furthermore, peak (3) at around 285 eV observed in all samples is considered to be due to hydrocarbon in the matrix or the C-O bond caused by CO or oxygen adsorption on the surface. The results in Fig.1 indicate that the film formed using the parallel beam contains fair amounts of graphite compared to the film by the perpendicular beam. For hydrocarbon, it is assumed that H-C bonds exist in SiC since the SiC film was synthesized with Si_2H_6 and C_2H_2.

Si-C bonding was also examined in Si(2p). The XPS spectra of Si(2p) for the films are shown in fig. 5. In this figure, the spectra from the Si(100) single crystal (peak(1)) and thermal CVD β-SiC (peak(2)) are indicated for reference. The Si-C peak for films formed with both perpendicular and parallel beams coincides with that of standard thermal CVD β-SiC of 100.4 eV, and is different from peak (1), which is found at 99.1 eV from the Si crystal. There is another small peak at 101.5 eV. This peak does not fit with Si from SiO_2 (103.1 eV) but fits with the Si-O bond (101.9-102.2 eV) caused by CO or oxygen adsorption. Although

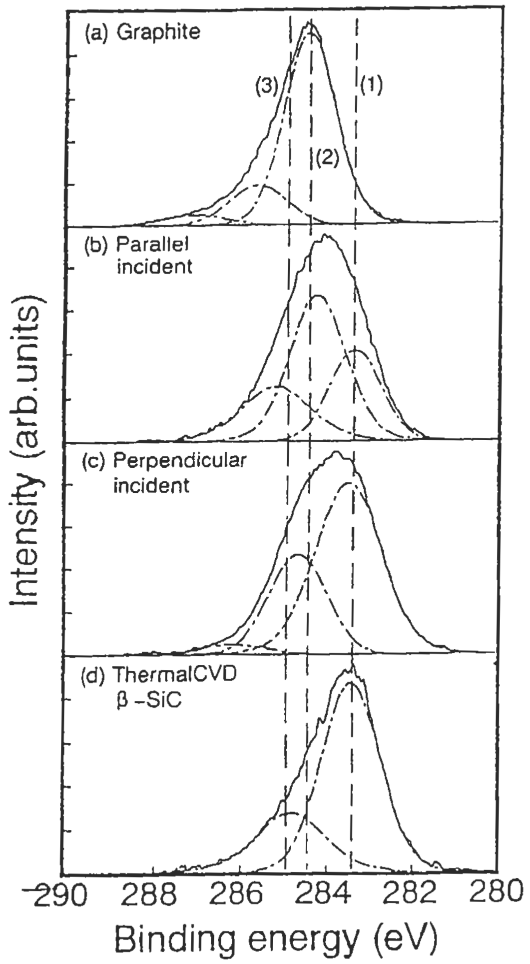

Fig.4 C(1s) XPS spectra from graphite (a), SiC film formed by parallel (b), and perpendicular (c) incident beams to substrates, and thermal CVD β SiC (d).

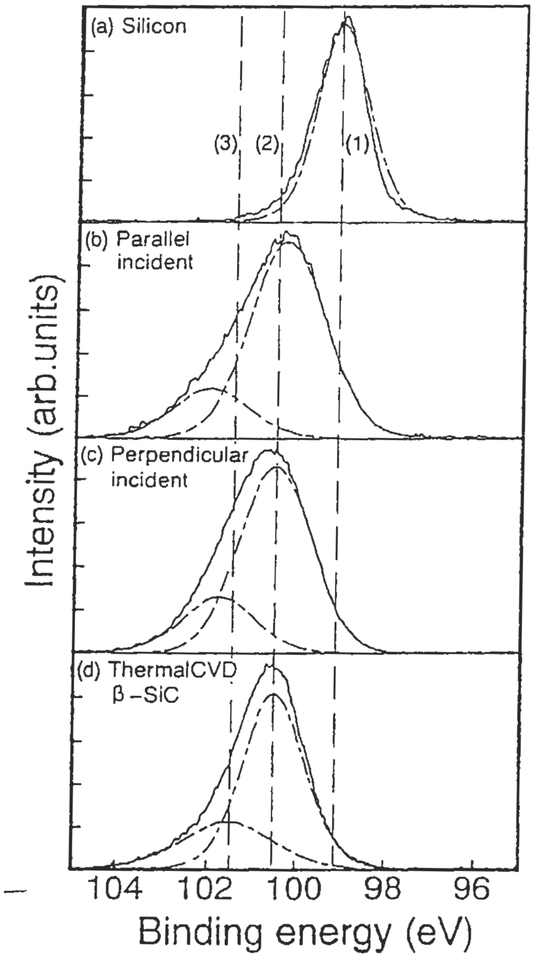

Fig.5 Si(2p) XPS spectra from (100) Si (a), SiC film formed by parallel (b), and perpendicular (c) incident beams to substrates, and thermal CVD β SiC (d).

Ar sputtering was performed before the XPS analyses, it is likely that some CO or oxygen still remained on the surface of specimens, with the exception of the reference Si sample having a smooth surface, because of the microscale roughness, as seen in Fig. 1.

From the XPS analyses, the film formed with perpendicular beam is considered to be mainly composed of SiC, while the film with the parallel beam includes a fair amount of carbon and hydrocarbon.

The compositional change of films formed for various pressure ratios of C_2H_2 to Si_2H_6 + C_2H_2 were examined based on the XPS results.

Figure 6 shows the relation between carbon concentration in the SiC film and the pressure rate of C_2H_2. The carbon concentration increased with C_2H_2 rate and the stoichiometric value of SiC was obtained at around 0.6 of the C_2H_2 rate.

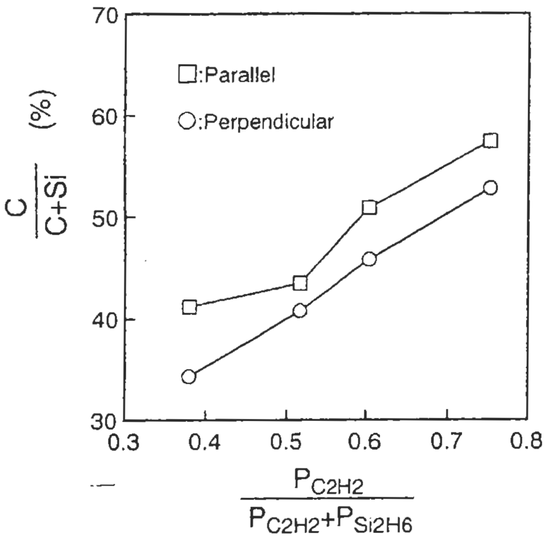

Fig.6 Carbon concentration in the film, C/(Si+C), as a function of acetylene pressure ratio in the reactant gas, $P_{C2H2}/(P_{C2H2}+P_{Si2H6})$.

3.2 SiC film growth

The growth rates of SiC film on silica glass under the perpendicular excimer laser irradiation were measured.

The thickness increased linearly with time. Then the growth rate were plotted against a pressure of the reactant. In fig. 7, the relations between the rate of growth and the Si_2H_6 pressure at different pressures of C_2H_2 are shown. The rate of growth is proportional to Si_2H_6 pressure, but was almost independent on C_2H_2 pressure. The temperature dependence of the growth rate was very small in the temperature range between 518 and 630K. The estimated activation energy for the growth rate was about 0.17 eV. This indicates that the film growth rate process does not seem to be controlled by a thermal activation process.

From the above results, the growth rate of the SiC film is expressed as

$$dL/dt = k\sigma v_p[Si_2H_6] \qquad (1)$$

where L is the thickness, k the constant, 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. The estimated value of σ from the experimental result was 1×10^{18} cm^2 which is very close to the absorption cross-section of Si_2H_6 at 190 nm(3).

In Fig. 7, the irradiation time of the laser is 15ns x 25Hz in a second. If the film grows during the irradiation, the real growth rates shown in Fig. 7 are made about by 3×10^6 times. It is therefore clear that laser CVD is a extremely high-speed film production process.

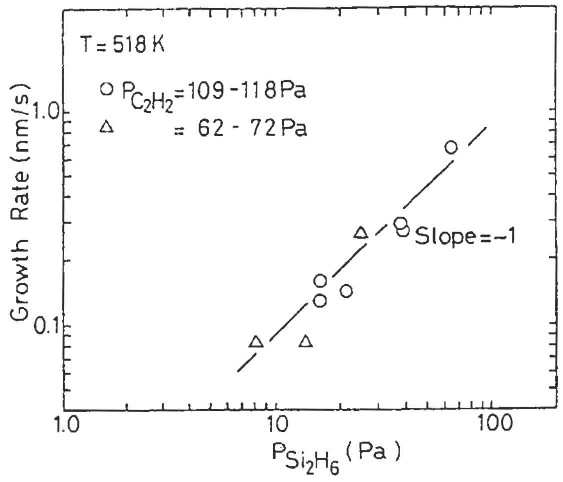

Fig.7 Relation between film growth rate and Si_2H_6 pressure at constant C_2H_2 pressure. P_{C2H2}: (○) 109-118Pa, (△) 62-72 Pa, at 518K.

3.3 Optical properties

Absorption coefficient were measured at 2 to 4.5 eV of photon energy, E_{ph}, on the films formed on quartz glass. The plot of $(\alpha E_{ph})^{1/2}$ versus E_{ph} obeys the Tauc approximation(4) as shown in Fig. 8 for the films prepared by the perpendicular beam. The linear portions in the figure were extrapolated to zero absorption to give the optical band gaps. Similar plots were obtained for the films formed by parallel beam. Figure 9 shows the optical band gaps, E_0, of the films varying with the carbon concentration. Optical band gaps were in the range from 1.9 to 2.5 eV and the values of the films prepared by the parallel beam are slightly higher than by the perpendicular beam. However, reduction in E_0 was not clear for the crystalline SiC film compared to that for amorphous SiC film because of the fine grains of SiC.

The present results indicates that crystalline SiC film with a band gap between 1.9-2.5 eV can be easily formed even at room temperature by using a excimer laser CVD.

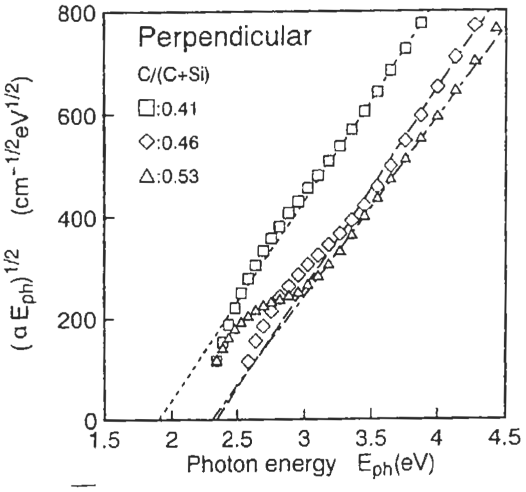

Fig.8 Optical absorption of SiC film with different carbon content prepared with the perpendicular beam irradiation to the substrate.

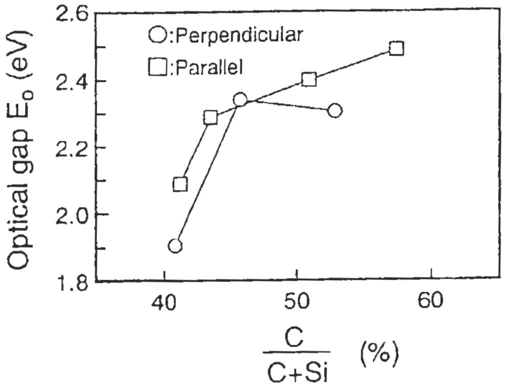

Fig.9 Dependence of optical band gaps on the carbon content in the SiC films.

4. Conclusion

The synthesis of SiC film by ArF excimer laser CVD was examined.

The followings are concluded.

1) Nano-crystalline β SiC film with a crystalline size of 5-50nm was formed at 298-623K using the perpendicular beam to the substrate surface while only amorphous SiC was detected for the parallel beam.

2) Carbon concentration in the SiC film increased with partial pressure of C_2H_2. Stoichiometric composition of SiC was obtained at around 0.6 of the ratio of C_2H_2 to $C_2H_2 + Si_2H_6$.

3) SiC film growth rate linearly depends on Si_2H_6 pressure and is independent on C_2H_2 pressure and temperature between 518-623K.

4) Nano-crystalline SiC film has a optical band gap of 1.9-2.5 which is comparable to amorphous SiC film.

References

1. T.Taguchi,Y.Kameda,H.Kushida,K.Toyoda and S.Tanaka, Rev.Laser Eng.,17, 211(1989).
2. A.Yamada,J.Kenne,M.Konagai and K.Takahashi, Appl.Phys.Lett., 46,272(1985).
3. U.Itoh,Y.Toyoshima,and H.Onuki, J.Chem.Phys., 85,4867(1986).
4. J. Tauc, Amorphous and Liquid Semiconductors, ed. By J.Tauc, Plenum, New York 1974.