

Application of Ion Beam Induced Chemical Vapor Deposition for SiC Film Formation on Si Substrates using Methylsilane*

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We propose an experimental methodology for producing silicon carbide (SiC) films on Si substrates using an ion beam induced chemical vapor deposition (IBICVD) technique with methylsilane (SiH_3CH_3) as a gas source. Both methylsilane gas (1.2 sccm) and Ar ion beam (100 eV, 5 μA) were simultaneously introduced onto Si(100) substrates. Temperatures of Si substrates were set at 600, 700, or 800°C. A SiC thin film was formed by the simultaneous introduction of methylsilane and Ar ions onto the Si substrate when the substrate temperature was 600°C. On the other hand, in the cases of 700 and 800°C, SiC films were formed by methylsilane gas alone and SiC film deposition rates by methylsilane gas with the Ar ion beam were approximately identical with those obtained without the Ar ion beam. We therefore conclude that the IBICVD technique with methylsilane is useful for SiC film formation on Si at relatively low substrate temperatures. [DOI: 10.1380/ejssnt.2015.174]

Keywords: Methylsilane; Argon; Ion bombardment; Silicon carbide; Silicon; Chemical vapor deposition; Epitaxy

I. INTRODUCTION

Silicon carbide (SiC) has attracted much attention regarding its application for electronics [1, 2]. In most cases, the successful epitaxial growth of SiC films has been carried out by chemical vapor deposition (CVD) technique using silane, propane, and hydrogen [3]. Golecki *et al.* first reported that a CVD technology using methylsilane (CH_3SiH_3) was useful for the growth of SiC on Si [4]. Subsequent various studies [5–17] also succeeded in producing SiC films on Si using various deposition methods with methylsilane. In those studies [4–17], methylsilane was selected as a gas source because the methylsilane molecule has a Si-C bond and its stoichiometric composition (atomic concentration ratio of Si to C) is the same as that of SiC. On the other hand, Xu *et al.* reported that the dissociative adsorption of methylsilane onto the Si surface broke the Si-C bond [18]. It is conceivable, however, that even when Si-C bond had been cleaved on the surface, Si and C would recombine and the deposition of SiC would proceed in the case when both cleaved Si and C were closely located with each other.

An ion beam induced chemical vapor deposition (IBICVD) technique has been shown to be available for three-dimensional nanostructure fabrication [19] and depositions of ferromagnetic materials [20]. Matsutani *et al.* [21] recently employed hexamethyldisilane

$[(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_3]$ as a gas source for their IBICVD experiments, and reported that the introduction of both hexamethyldisilane and Ar ions onto a Si substrate produced a SiC film on the substrate, concluding that this was due to the dissociation of hexamethyldisilane by the Ar ion impact. However, the infrared spectra of their films suggested that an absorption band of the $-\text{CH}_2-$ wagging mode in Si- CH_2 -Si coexisted with that of the Si-C stretching mode. In addition, the quality of Ar ion beam (*i.e.*, mass and energy spectra) has not been determined in their experiments.

Methylsilane seems to be more suitable as a gas source for SiC film formation by IBICVD than hexamethyldisilane because of the reasons mentioned above. Nevertheless, SiC film deposition experiments by IBICVD with methylsilane have not been carried out yet.

In this paper, we propose an experimental methodology for producing SiC films on Si substrates by means of IBICVD technique using methylsilane as a gas source. We examined the mass and energy distributions of the ion beam prior to the IBICVD film deposition experiments, and after the IBICVD experiments, we assessed deposited films by X-ray diffraction (XRD), Raman spectroscopy, and Fourier transform infrared (FTIR) spectroscopy respectively.

II. EXPERIMENTAL SETUP

Our study was carried out with a low-energy mass-selected ion beam system (ULVAC) [22]. This system has a Freeman-type ion source, where ions are produced from a gas source (pure Ar gas in this study). Ions extracted

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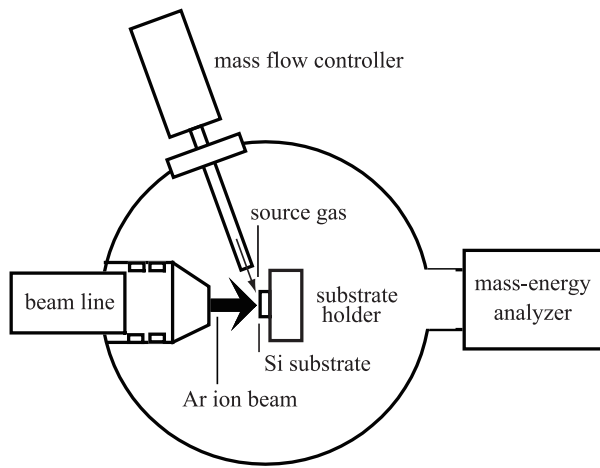


FIG. 1. A schematic drawing of the process chamber of mass-selected ion beam system.

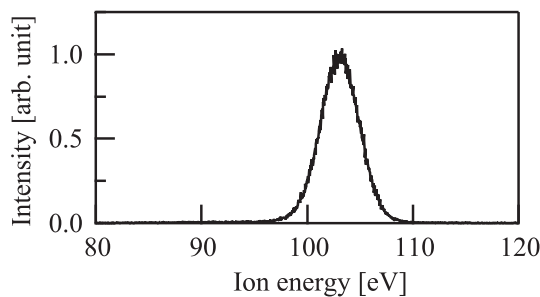


FIG. 2. The energy distribution of ion beam used in this study.

from the ion source are accelerated by a high voltage of -15 kV and mass-selected by a magnetic coil. The mass-selected energetic Ar ion beam is finally decelerated to a desired kinetic energy level prior to its reaching the substrate in the process chamber. The base pressure in the process chamber is approximately 1×10^{-6} Pa. The quality of the ion beam can be determined by a mass-energy analyzer PPM-421 (BALZERS).

A schematic diagram of IBICVD equipment in the process chamber of the ion beam system is shown in Fig. 1. A Si(100) substrate (15×15 mm) was set on the substrate holder in the process chamber. Ar ion energy in this study was set at a relatively low level to avoid significant surface damages by the ion injection. The Ar ion beam current was about $5 \mu\text{A}$. The incident angle of ion beam was set to be normal to the substrate surface. The methylsilane gas was introduced onto the substrate surface at a flow rate of 1.2 sccm through a stainless-steel tube connected to a mass flow controller. The methylsilane gas pressure in the process chamber was 7×10^{-3} Pa during the deposition experiment. The duration of deposition experiments was 30-60 min. For the preparation of Si(100) clean surface, the substrate was temporarily heated to more than 1000°C and the natural oxide layer was then removed before the deposition experiment. The temperatures of Si(100) substrates during the deposition experiment were set at 600 , 700 , or 800°C .

After the IBICVD experiments, we assessed deposited films by XRD, Raman spectroscopy, and FTIR spec-

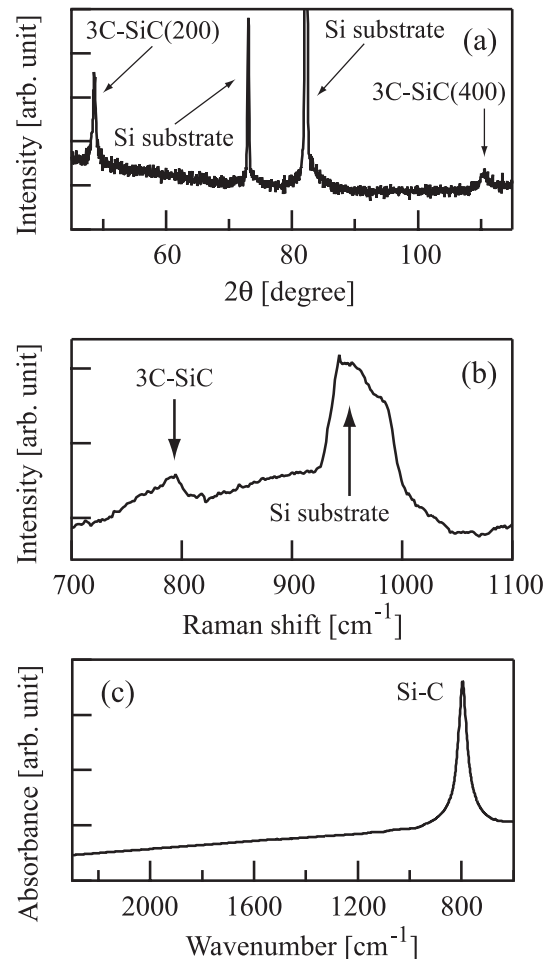


FIG. 3. X-ray diffraction spectrum (a), Raman spectrum (b), and Fourier transform infrared spectrum (c) of a film deposited when assessed with Ar ion beam injections. Substrate temperature during the deposition experiment was 800°C .

troscopy respectively. XRD spectra (θ - 2θ method) were obtained with RINT2000 (RIGAKU) using $\text{K}\alpha_1$ of Co ($\lambda = 1.78892 \text{ \AA}$). Raman spectra were obtained from LABRAM-HR800WH (HORIBA) with 532.19 nm laser as the excitation source. The laser was 0.73 mm in diameter and taken the focus to observe the area of approximately $1 \mu\text{m}$. We obtained FTIR spectra in a transmission method using an FTIR spectrometer FTS3000 (BIO-RAD) equipped with deuterated triglycine sulfate detector.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Before the IBICVD film deposition experiments, the mass spectrum of ion beam was measured by PPM-421. It was found that only a single peak appeared at the mass number of 40, suggesting the presence of pure Ar^+ ions [23]. Then, the energy distribution of Ar ions was measured by PPM-421. The energy spectrum of Ar^+ ion beams (Fig. 2) shows that the peak energy is located at 103 eV , indicating that the ion beams used in this study are monochromatic in energy distribution.

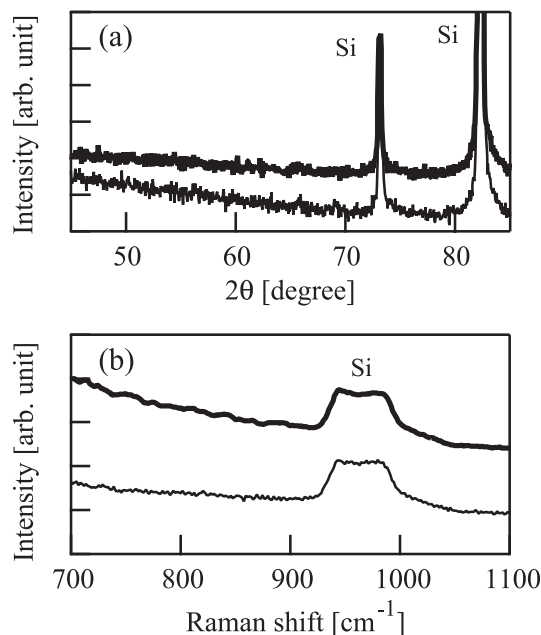


FIG. 4. X-ray diffraction spectrum (a) and Raman spectrum (b) of a film deposited when assessed with Ar ion beam injections are shown by thick lines. Substrate temperature during the deposition experiment was 600°C. In both (a) and (b), X-ray diffraction and Raman spectra of a pristine Si substrate are also shown by thin lines.

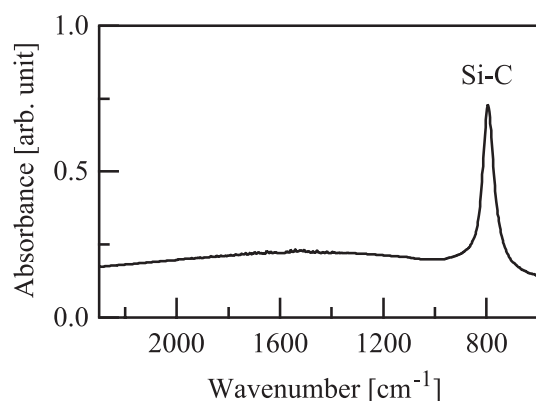


FIG. 5. Fourier transform infrared spectrum of a film deposited when assessed with Ar ion beam injections. Substrate temperature during the deposition experiments was 700°C.

Chemical characteristics of a film formed by introducing methylsilane gas and Ar ion beam onto a Si substrate at the substrate temperature of 800°C were analyzed by XRD, Raman spectroscopy, and FTIR spectroscopy. Figure 3(a) shows the XRD spectrum. The diffraction peaks of the film can be seen at 48.5 and 110.5 degrees in addition to two Si peaks. The former two peaks correspond to 3C-SiC(200) and 3C-SiC(400), suggesting that an *a*-axis-oriented 3C-SiC film was produced. A Raman spectrum (Fig. 3(b)) shows two peaks at 796 and 950 cm^{-1} . The 796 cm^{-1} peak is the transverse optic phonon peak of 3C-SiC [24] whereas the broad peak at 950 cm^{-1} is associated with the second-order Raman spectra for Si [25]. Figure 3(c) shows an FTIR spectrum. This spectrum has

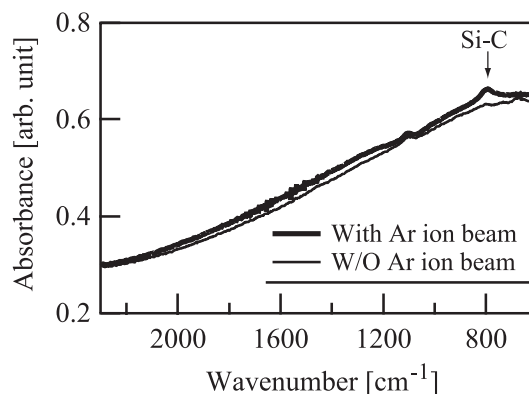


FIG. 6. Fourier transform infrared spectra of films deposited when assessed with (thick line) and without (w/o; thin line) Ar ion beam injections. Substrate temperature during the deposition experiments was 600°C.

only one absorption band at about 790 cm^{-1} , indicating that SiC film was formed on the surface, since the 790 cm^{-1} peak is well known to be associated with SiC [26]. These measurements clearly indicate that the film obtained was pure cubic SiC and epitaxial with respect to the Si(100) substrate.

Then, the films, which had been formed by introducing methylsilane gas and Ar ion beam onto Si at the substrate temperature of 600 and 700°C, were analyzed by XRD and Raman spectroscopy. However, no SiC peaks were observed in both XRD and Raman spectra of these films. In the case of the substrate temperature of 600°C, for example, the XRD (Fig. 4(a)) and Raman spectra (Fig. 4(b)) are shown by thick lines. In Fig. 4(a) and (b), spectra of a pristine Si substrate are also shown by thin lines for comparison.

We then analyzed these films with FTS3000 to determine whether SiC films actually existed on the substrate. Figure 5 shows an FTIR spectrum of the film formed on Si by introducing methylsilane gas with the Ar ion beam at the substrate temperature of 700°C. This spectrum has only one absorption band at about 790 cm^{-1} , clearly indicating that SiC films were actually formed on the surfaces. The SiC film in this case seems to be amorphous, because no clear SiC peaks can be detected in XRD and Raman spectra. In fact, a previous CVD study with methylsilane have revealed that for the epitaxial growth of crystalline SiC films, the substrate temperature was necessary to be 750°C or higher [4].

The FTIR spectrum of a film formed at the substrate temperature of 600°C following the introduction of methylsilane gas with the Ar ion beam is shown by a thick line in Fig. 6. The thick line in Fig. 6 indicates that a Si-C peak appeared at about 790 cm^{-1} . On the other hand, the FTIR spectrum of a film formed at the substrate temperature of 600°C following the insertion of methylsilane gas without the Ar ion beam is shown by a thin line in Fig. 6; the Si-C peak could hardly be seen in this case. These results in Fig. 6 suggest that a SiC film on the Si substrate could be induced by the Ar ion beam injection.

The SiC film thickness was measured by a variable-angle spectroscopic ellipsometer VASE (J.A. Woollam

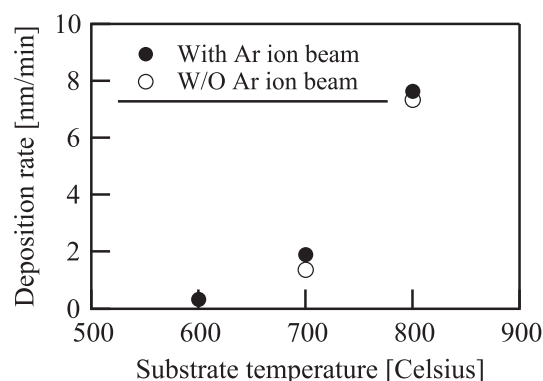


FIG. 7. The deposition rates of SiC films formed by introducing methylsilane gas with and without the Ar ion beams are plotted by closed and open circles, respectively.

Co.). The SiC film deposition rate can thus be determined by the film thickness and the duration of deposition experiment. The deposition rates of SiC films formed by introducing methylsilane gas with the Ar ion beam are plotted by closed circles in the respective cases of 600, 700, and 800°C (Fig. 7). The film thickness in this case seems to be the sum of both IBICVD and usual thermal CVD effects. However, the film thickness at 600°C is certainly due to the IBICVD effect alone because Ar ion beam is essential for SiC film formation and no thermal CVD effect seems to be available at this temperature (Fig. 6). Figure 7 also indicates that at 600°C, the film deposition rate induced by IBICVD could be approximately 0.3 nm/min. Similarly, the deposition rates of SiC films formed following the introduction of methylsilane gas alone are also shown in Fig. 7 by open circles in both cases of 700 and 800°C. In this case, the film thickness is solely ascribed to the thermal CVD effect; the film deposition rates at 700 and 800°C are estimated to be 1.4 and 7.3 nm/min, respectively. These are much larger than that obtained by IBICVD at 600°C. Figure 7 indicates that when the substrate temperatures are 700 and 800°C, the film deposition rates obtained when assessed with the Ar ion beam are almost identical with those obtained without the Ar ion beam. Therefore, significant effects of Ar ion beams on SiC film formation were not found in the cases of both 700 and 800°C; at 700 and 800°C, the degree of film thickness increase induced by IBICVD is much smaller than the film thickness induced by a thermal CVD technique. It is considered therefore that at these temperatures, the IBICVD effect is almost negligible since the thermal CVD effect is more dominant than IBICVD effect in this study.

The mean free path of methylsilane molecules in the process chamber is estimated to be about 1 m, being much

longer than the distance (0.04 m) between the muzzle of ion beam line and the substrate surface. It can be surmised therefore that the interaction between methylsilane gas molecules and injected Ar ions is little or extremely limited before the arrival of Ar ions at the substrate surface. In other words, methylsilane gas dissociation following Ar ion impact cannot occur before the arrival of Ar ions at the substrate surface. It is conceivable, however, that the injected ion beam dissociates the methylsilane gas adsorbed on the substrate surface, or also that newly formed films may degenerate.

The ion beam cross section was an ellipse close to a circle and its approximate diameter was 15 mm. The Ar ion current density was about $3 \mu\text{A}/\text{cm}^2$ and the number of Ar ion fluence onto the substrate surface was estimated to be 2×10^{13} ions/ $\text{cm}^2\cdot\text{s}$. The increase of the Ar ion fluence may be required to enhance the effect of IBICVD on the SiC deposition.

IV. CONCLUSIONS

We have here proposed an experimental methodology which made it possible to deposit SiC films on Si(100) substrates. The methylsilane gas was introduced onto the substrate surface at a flow rate of 1.2 sccm with Ar ion beam injections. The Ar ion energy was approximately 100 eV whereas the Ar ion beam current was about $5 \mu\text{A}$. The temperatures of Si substrates were set at 600, 700, or 800°C. The XRD and Raman spectra showed that 3C-SiC films were grown on Si in the case of substrate temperature of 800°C. When temperature was 700°C, a clear 3C-SiC peak was not observed in both XRD and Raman spectra. Nevertheless, a peak associated with the Si-C bond could be identified in FTIR spectra. Unfortunately, significant effects of Ar ion beams on the SiC film thickness could not be detected in the cases of both 700 and 800°C. At the substrate temperature of 600°C, however, the Si-C peak appeared in FTIR spectrum in the presence of Ar ion beams. Therefore, an Ar ion beam injection induces the formation of SiC thin film when the substrate temperature being 600°C.

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