Fabrication of Amorphous Silicon Carbide Films from Decomposition of Tetramethylsilane using ECR plasma of Ar

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Abstract. Mechanically-hard hydrogenated amorphous silicon carbide (a-SiCₓ:H) films were formed from the decomposition of Si(CH₃)₄ using the electron-cyclotron resonance plasma flow of Ar. An external radio-frequency (RF) voltage was applied to the substrate with the negative self-bias voltage (−V₀RF) of 0-100 V. Compositional analysis was made with a combination of Rutherford backscattering and elastic recoil detection analysis. The C/Si ratios of films were 2.2-2.7. Film hardness was measured with a nano-indentation testing equipment. Chemical bonding was analyzed using carbon-K near edge X-ray absorption fine structure (C-K NEXAFS) spectroscopy using an accelerator NewSUBARU. The peak-fitting analysis of the C-K NEXAFS spectra yielded the sp²/(sp³+sp³) ratios, being fully correlated with film hardness. With supported by the IR and Raman spectroscopic measurements, the change of the chemical structure induced by −V₀RF was discussed.

1. Introduction

Thin films of amorphous silicon carbides (a-SiCₓ) and hydrogenated a-SiCₓ (a-SiCₓ:H) have attracted much attention as potential candidates for mechanical, electronic, and biomedical applications [1]. For the synthesis of these materials, plasma decomposition of tetramethylsilane (Si(CH₃)₄, TMS) has been frequently used. The method of decomposition of TMS applied so far has been mainly the radio-
frequency (RF) discharge where a DC bias voltage is applied to the substrate in order to obtain high mechanical hardness [2-4]. Mechanically-hard a-SiC\textsubscript{x}:H films have also been synthesized using the dissociation reaction of TMS with microwave (MW) discharge flow of Ar where an external RF bias voltage is applied [5,6]. When an RF voltage is applied to the substrate, a negative self-bias voltage, \(-V_{\text{RF}}\), is generated according to a high mobility of free electrons. Positive ions are attracted by \(-V_{\text{RF}}\), causing ion bombardment of the film surface to change the bonding nature [7]. The present study reports on the fabrication of a-SiC\textsubscript{x}:H films using the decomposition of TMS in the electron-cyclotron-resonance (ECR) plasma flow of Ar and on the structural change of films by the application of an RF bias voltage. The hardness of films was measured as a function of \(-V_{\text{RF}}\). As for the mechanical hardness of the carbon-related thin films such as a-SiC\textsubscript{x}:H, the fraction of the sp\textsuperscript{3}-hybridized state of C atoms is the chemical structure of the central importance [7]. The most precise and direct method to evaluate this fraction is the carbon-K near edge X-ray absorption fine structure (C-K NEXAFS) analysis using synchrotron radiation [8,9]. Atomic compositions including hydrogen content were evaluated by the combination of Rutherford backscattering (RBS) and the elastic recoil detection analysis (ERDA). The bonding nature of films was studied on the basis of infrared (IR) absorption and Raman spectroscopic methods. The film properties obtained in this study were compared with those reported previously using MW-discharge flow system [5,6].

2. Experiments

Figure 1 shows a schematic of the ECR-plasma flow apparatus used in the present study. It consisted of a stainless-steel chamber and an ECR discharge source (Irie Koken RBG-152L) which were evacuated to 10\textsuperscript{-3} Pa using turbomolecular (80 L/s) and oil-rotary (180 L/min) pumps. Ar (99.9999\%) was introduced into the discharge section through a needle valve. Microwaves (2.45 GHz, 120 W) were introduced through a coaxial cable and an antenna (A). An external magnetic field was applied using permanent magnets arranged in the vicinity of the upper part of the ECR-discharge source. A stainless-steel nozzle (N) with the inner diameter of 1 mm was set downstream of the discharge section from which TMS (> 95\% purity) was introduced through a Teflon needle valve. The partial pressures of Ar and TMS were 0.40 Pa and 0.13 Pa, respectively. A substrate holder (S) insulated from the wall of the chamber was set \(\approx 5\) mm downstream of the nozzle tip. Pressure was monitored using an ionization gauge. Both Ar and TMS were passed through desiccants (P\textsubscript{2}O\textsubscript{5}). H\textsubscript{2}O molecules adsorbed on the substrate surface and the wall of the chamber were removed by discharging Ar for 1.5 h. An external bias voltage was applied to S using an RF generator (13.56 MHz) through a matching box (MB), and was monitored through a filter circuit (F). Films were formed onto Si substrates of \(\approx 10\) mm\textsuperscript{2} set on S. The deposition time was in the range of 45-90 min.

The measurements of RBS/ERDA were carried out using a Tandem-type accelerator (Nisshin High Voltage, NT-1700HS) equipped at Extreme Energy-Density Research Institute of Nagaoka University of Technology. In order to make precise measurements of ERDA, the thickness of films were set \(\approx 300\) nm by adjusting the deposition time appropriately. Films were irradiated by a He\textsuperscript{+} beam accelerated to
25 MeV. In the RBS measurement, scattered He$^+$ beam was detected by a solid-state detector (SSD). The irradiation and detection angles of He$^+$ beam were 18° and 78°, respectively, from the film surface. In the ERDA measurement, recoiled H atoms were detected with SSD positioned at an angle of 168° from the film surface.

The a-SiC$_x$:H film hardness was measured using a nano-indentation testing equipment (Fischer MZT-500) with Vickers indenter. The maximum load and the loading step were set to 1 mN and ~0.05 mN s$^{-1}$, respectively. The hardness of Si substrate was observed as (6.9±0.3) GPa under this condition.

The C-K NEXAFS measurements were carried out at the beamline-9 of NewSUBARU located at Laboratory of Advanced Science and Technology for Industry, University of Hyogo [10,11]. Synchrotron radiation provided from the 10.8-m long undulator was extracted using a Hetttrick-Underwood mount type monochromator with a varied line spacing plane grating of 1200 lines/mm. The energy resolution was estimated to be less than 0.5 eV full width at half maximum (FWHM). The reading of the monochromator was calibrated against the pre-edge resonance corresponding to the $\pi^*$ transition of carbon atoms that appeared at 285.38 eV in the NEXAFS spectrum of graphite [12]. The monochromatized beam in the range of 275-340 eV irradiated the sample at the incident angle of 54.7°, and the absorption spectrum was obtained in the total electron yield mode. The signals from sample films were calibrated against the incident beam intensity measured with a gold grid.

The structural analysis of films was performed using a Raman spectrometer (Jobin Yvon, Model Labram Infinity) and a Fourier Transform Infrared (FTIR) Spectrophotometer (Nicolet IMPACT-410). Raman spectra were obtained in the backscattering mode using an Ar$^+$ laser operating at a wavelength of 514.5 nm and a power of 100 mW. The wavelength resolution was 1 cm$^{-1}$, and the spatial resolution was $\leq$ 1 μm. Scattering signal was detected by using a CCD detector. IR spectra were measured in the Right AEM-Main mode with a MCT/A detector and a resolution of 4 cm$^{-1}$.

3. Results and discussions
Table 1 lists the atomic compositions of films measured using RBS/ERDA. As expected, Si, C, and H atoms were detected. The [C]/[Si] ratios (2.2-2.7) and the H atomic density were observed to be independent of $-V_{RF}$, because the atomic compositions measured in RBS/ERDA may have uncertainties of $\approx$20%.

$$\begin{array}{cccccc}
- V_{RF} & [\text{Si}] & [\text{C}] & [\text{H}] & [\text{C}]/[\text{Si}] \\
0 & 19 & 52 & 29 & 2.7 \\
50 & 22 & 48 & 30 & 2.2 \\
\end{array}$$

Figure 2 shows the indentation hardness of films. The maximum indentation depths of the present measurements were $<0.06$ μm, being $<10\%$ of the film thickness (0.6-2.0 μm). Therefore, the measured hardness was free from the influence from the Si substrates. Under the condition of $-V_{RF}=0$ V, films showed mechanical hardness of 5.5±0.5 GPa, and the hardness was increased slowly to 7.8±0.6 GPa as $-V_{RF}$ increased to 50 V. This observed tendency of mechanical hardness has contrast to our previous study using MW-discharge flow where the film hardness increased rapidly from 2.4±1.1 GPa at $-V_{RF}=0$ V to 8.0±0.6 GPa at $-V_{RF}=20$ V [5,6].

The C-K NEXAFS spectra of a-SiC$_x$:H films are shown in Figure 3 where the NEXAFS spectrum of graphite is also shown. The narrow peaks appearing in 285.3 eV were assigned to the transitions from C1s core level to the unoccupied $\pi^*$ levels of sp$^2$ (C=C) and sp (C≡C) sites [8]. The broad feature observed in the range of >288 eV was assigned to the $\pi^*$$\rightarrow$C1s transitions of sp$^2$(C=C) and sp$^3$(C-C) bonds [12,13] and the $\pi^*$$\rightarrow$C1s transitions of Si-C bond [14,15] overlapped with the direct ionization.

In order to evaluate the intensities of the $\pi^*$$\rightarrow$C1s peaks, the simulation analysis of the observed NEXAFS spectra was made as follows [9]. The profile of a $\pi^*$$\rightarrow$C1s peak was assumed to be a single
Gaussian function. The broad feature in the region of >288 eV was represented by the superposition of six Gaussian functions as listed in Table 2 and additional Gaussian functions in the high-energy side to reproduce the profile due to direct ionization [16]. In addition, a linear baseline was assumed. The observed C-K NEXAFS spectra were fitted with the peak heights and widths of the above Gaussian functions as the parameters. Figure 3 shows the result of this analysis. Table 2 lists the height, $H$, and the width, $W$, for each Gaussian profile. From this analysis, the $sp^2/(sp^2+sp^3)$ ratio of a-SiC$_x$H films were estimated as

$$\frac{sp^2}{sp^2+sp^3} = \left(\frac{I_{sp}^{all} / I_{VRF}^{all}}{I_{sp}^{all} / I_{VRF}^{all}}\right).$$

In eq. (1), $I_{sp}^{all}$ and $I_{VRF}^{all}$ represent the areal intensities of the $\pi^*\leftrightarrow C$-1s peaks of a-SiC$_x$H films and graphite, respectively, and $I_{VRF}^{all}$ and $I_{VRF}^{all}$ represent the areas of the total profiles of the NEXAFS spectra of a-SiC$_x$H films and graphite, respectively, evaluated from the numerical integrations of the observed spectra. The $sp^2/(sp^2+sp^3)$ ratios obtained from the above procedure are shown in Figure 4 as a function of $-V_{RF}$. Figure 5 shows the correlation between the $sp^2/(sp^2+sp^3)$ ratios and the hardness of films where films fabricated in this study (open circles) and those obtained in our previous study (closed circles) [6] are compared. The decline for the present films is steeper than that for the previous films. This difference will be discussed later in this section.

Figure 6 shows the IR spectra of films, where the normalization with their film thickness was not carried out. Following vibrational bands were observed; 670-760 cm$^{-1}$ (Si-C stretching), $\approx$1000 cm$^{-1}$ (bending vibration modes of Si-CH$_3$ and Si-(CH$_2$)$_n$Si), $\approx$1250 cm$^{-1}$ (Si-CH$_3$ symmetric bending), 2100 cm$^{-1}$ (Si-H stretching), and 2700-3000 cm$^{-1}$ (C-H stretching) [17]. As inferred from Figure 6, the intensities of the Si-CH$_3$, Si-(CH$_2$)$_n$Si, Si-H, and C-H vibration modes remain unquenched with the application of $-V_{RF}$. This tendency is contrast to the previous result of a-SiC$_x$H films fabricated in the

Table 2 Analysis of C-K NEXAFS spectra.\textsuperscript{a1}

| Energy [eV] | Assignment | $-V_{RF}=0$ V | $-V_{RF}=20$ V | $-V_{RF}=50$ V |
|------------|------------|---------------|---------------|---------------|
|            | $H$ | $W$ | $H$ | $W$ | $H$ | $W$ |
| 285.3      | $\pi^*\leftrightarrow 1s$ (C=C) | 0.827 | 1.91 | 0.359 | 1.94 | 0.226 | 1.75 |
| 286.8      | $\pi^*\leftrightarrow 1s$ (C=O) | 0.947 | 0.78 |
| 287.8      | $\sigma^*\leftrightarrow 1s$ (C-H) | 0.453 | 1.84 | 0.200 | 1.58 | 0.138 | 1.59 |
| 288.8      | $\sigma^*\leftrightarrow 1s$ (e. p.)\textsuperscript{b} | 0.718 | 3.07 | 0.335 | 2.48 | 0.142 | 2.30 |
| 290.2      | $\sigma^*\leftrightarrow 1s$ (C-Si) | 1.34 | 6.27 | 0.440 | 4.06 | 0.295 | 4.47 |
| 293        | $\sigma^*\leftrightarrow 1s$ (C-C) | 0.947 | 8.25 | 0.479 | 6.96 | 0.384 | 3.99 |
| 300        | $\sigma^*\leftrightarrow 1s$ (C-C) | 0.920 | 11.9 | 0.405 | 11.3 | 0.306 | 16.3 |
| 309        | | 0.755 | 18.7 | 0.179 | 18.9 | | |
| 327        | | 0.828 | 29.4 | 0.563 | 47.6 | 0.424 | 39.8 |

\textsuperscript{a1} $H$ and $W$ are the spectral height in arbitrary units and the width in units of eV, respectively.
\textsuperscript{b} Abbreviation of excitonic process.
MW-discharge flow system where the IR intensities of the above absorption bands quenched effectively with the application of \(-V_{RF}\) [5].

Figure 7 shows the Raman spectra of films. G (graphitic) band (\(\approx 1450\ \text{cm}^{-1}\)) was observed accompanied by weak D (disordered) band (\(\approx 1300\ \text{cm}^{-1}\)). These bands were very weak at \(-V_{RF}=0\ \text{V}\), whereas they became prominent as \(-V_{RF}\) increased. The observed Raman shifts of the G- and D-bands were 50-100 cm\(^{-1}\) lower than those of amorphous carbons [18], being attributable to the lowering of the C=C vibrational frequency induced by the substitution of Si atoms [19]. In addition, background signals toward higher Raman shift were observed which is attributable to the fluorescence due to the one-dimensional conjugated structures of carbons containing hydrogen terminations [20].

In the following, the difference of the film-hardening mechanism between the present films and those fabricated in the previous MW-discharge flow system is discussed. In general, film hardness may have positive correlations with the fractions of the C atoms in the sp\(^3\)-hybridized state, whereas have negative correlations with the densities of the hydrogen terminations [21]. In the case of the MW-discharge flow, films fabricated without RF bias include hydrogen terminations and Si-Si bonds [6]; they decrease under the RF-biased conditions, and instead, the C-Si bonds increase to cause the increase of the film hardness. This mechanism may be consistent with the literature [4]. The structural change observed in the present films may be somewhat different from the case of MW-discharge flow. The relative density of the C atoms in the sp\(^3\) state has a positive dependence on \(-V_{RF}\) from the analysis of the C-K NEXAFS spectra. The [C]/[Si] ratios of the present films (\(\approx 2.5\)) are higher than those in the previous study (\(\approx 1.0\)) [5,6]. Therefore, the decline shown in Fig. 5 may be caused by the increase of the density of the sp\(^3\)-hybridized C-C bonds as well as the Si-C bonds. Films fabricated under the condition of \(-V_{RF}=0\ \text{V}\) showed lower sp\(^3\)/(sp\(^2\)+sp\(^3\)) ratio than those under the same condition in the MW-discharge flow system as shown in Figure 5, and both films contain hydrogen terminations. These observations are consistent with higher mechanical hardness of the present films of \(-V_{RF}=0\ \text{V}\). On the other hand, films formed under the RF-biased conditions include more significant amount of hydrogen terminations than those fabricated previously. Therefore, hardness of the present films may
be suppressed to be lower than the previous films even under the same $sp^2/(sp^2+sp^3)$ ratio (see Fig. 5).

4. Conclusions
Mechanically-hard a-SiC$_x$:H films were fabricated using the decomposition of TMS in the ECR plasma flow of Ar. An external RF voltage was applied to the substrate. C-K NEXAFS spectra were observed, and the $sp^2/(sp^2+sp^3)$ ratios were obtained. These ratios were found to be correlated well with the film hardness. The C/Si ratios were 2.2-2.7. Significant increase of the density of $sp^3$(C-C) bonds may be induced by the bombardment of positive ions (mainly Ar$^+$) induced by $-V_{RF}$. Mechanical hardness of the present films is explicable in terms of the fraction of the $sp^3$ component of C atoms and the amount of hydrogen terminations.

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