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Mechanically Hard SiC_x:H Films in Amorphous Phase

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Amorphous hydrogenated silicon carbide (a-SiC_x:H) films were deposited onto Si substrates by using the decomposition reaction of tetramethylsilane with the microwave discharged products of Ar. The contamination of H_2O molecules was avoided by passing the starting materials through a desiccant (P_2O_5). A negative bias voltage ($-V_{RF}$ = 0-100 V) was applied to the substrate by using an external radio-frequency source to induce Ar-ion bombardment of the film surface. The pressure of Ar was 0.1 Torr. Film thickness was 1-5 μm under the deposition time of 30 min. Hardness of films under the condition of $-V_{RF}$ = 0 V was ≈1 GPa. Under the condition of $-V_{RF}$ = 100 V, the hardness was 42±27 GPa; the maximum hardness was 69 GPa. The observed hardness was comparable to or even higher than the hardness of SiC in crystal phase (20-24 GPa). According to the XPS measurements, the x value was 1.06-1.73. The IR intensities of the hydrogen termination structures were prominent under the low $-V_{RF}$ conditions, whereas they reduced at higher $-V_{RF}$. The Raman spectra showed significant fluorescence signal at low $-V_{RF}$ with negligibly weak scattering signal. At higher $-V_{RF}$, the fluorescence signal was reduced, and the G (graphitic) band appeared. From the above measurements, $-V_{RF}$ induces a structural change from one-dimensional to two- or three-dimensional structures following hydrogen-removal from the film surface.

Keywords: microwave plasma CVD, silicon carbide, thin film, amorphous, hardness, IR spectrum, Raman spectrum, nanoindentation

1. Introduction

Thin films of amorphous carbons and related materials have attracted much attention since they are expected as the potential candidates for the mechanical, electronic, and biomedical applications [1,2]. Among them, amorphous silicon carbides (a-SiC_x) and hydrogenated a-SiC_x (a-SiC_x:H) have been known to possess high mechanical hardness and good adhesion property onto the substrate materials. For the synthesis of a-SiC_x, the sputtering of sintered SiC target has been the most widely used [3-5]. In the early stage of the investigations on the plasma enhanced chemical vapor deposition (PECVD) to synthesize a-SiC_x and a-SiC_x:H, the mixed gases of SiH_4 and organic materials such as CH_4 and C_2H_2 have been used [6-8]. Recently, tetramethylsilane ($Si(CH_3)_4$, TMS) has become widely used as the starting material of PECVD, where a DC bias voltage is applied to the substrate in order to obtain high mechanical hardness [9-11]. The mechanical hardness obtained in these studies has reached ≈ 30 GPa, being in the same magnitude as or even slightly higher than the hardness of the bulk SiC crystal, 20-24 GPa [12].

Ito and co-workers have synthesized the thin films of amorphous carbon nitride (a-CN_y). In these studies, mechanically hard a-CN_y films can be formed when H_2O molecules are removed from the reaction system *and* the radio-frequency (RF) bias voltage is applied to the substrate [13-16]. When H_2O molecules are incorporated into the film, they may form hydrogen bonds in the vicinity of the cluster boundaries, leading to the lowering of the mechanical hardness. Therefore, the contamination of H_2O molecules should be avoided as much as possible. Generally, the effect of applying the bias voltage is the structural modification of film surface induced by the bombardment of ions accelerated in the sheath region surrounding the substrate electrode. The reported method of application of the bias voltage seems, however, to be predominantly limited to DC in the PECVD of a-SiC_x. Since a-SiC_x is insulator, a DC bias voltage may be insufficient to induce the ion bombardment of the film surface. When an RF bias voltage is applied to the substrate, a negative self-bias voltage, $-V_{RF}$, is generated according to a high mobility of free electrons. Positive ions are attracted by $-V_{RF}$, causing ion bombardment of the film surface to induce the change of the bonding nature [17]

The present study reports on the formation of mechanically-hard a-SiC_x:H thin films by using the decomposition reaction of TMS with the microwave (MW) discharge flow of Ar, where H_2O molecules are fully removed from the reaction system and an RF bias voltage is applied. The hardness of films is measured as a function of $-V_{RF}$. The bonding nature of films is studied on the basis of infrared (IR) absorption and Raman spectroscopic methods. From these measurements, the effect of ion bombardment of the film surface and the mechanism of film hardening are discussed.

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2. Experiments

Fig. 1 shows the schematic diagram of the MWCVD apparatus used in the present study. Ar (≥99.9999% purity) was introduced into the discharge tube made of Pyrex glass with the outer diameter of 15 mmϕ through a stainless steel needle valve and P_2O_5 (98.0% purity) as a desiccant. The tip of the discharge tube was reduced to ≈3 mmϕ. The pressure of Ar was 0.1 Torr measured inside the chamber. The Ar plasma flow was produced by microwave (MW) discharge (2.45 GHz, 100 W). TMS was introduced into the chamber from the nozzle through a Teflon needle valve and P_2O_5. The partial pressure of TMS was approximately 5 mTorr. H_2O molecules adsorbed onto the wall of the chamber or included in the starting materials were effectively eliminated with monitoring the OH($A^2\Sigma^+$-$X^2\Pi$) emission intensity reduced to ≤3%. The RF bias voltage was applied to the substrate stage (S) by using the RF generator (13.56 MHz, denoted as RF) through a matching box (MB), and monitored through a filter circuit (F). Since the partial pressure of Ar is much higher than that of TMS, the ions that bombard the film surface are predominantly Ar^+. Inside the stage, cooling water was circulated. Films were deposited onto single-crystal Si substrates with 10 mm×10 mm in size. The deposition time was 30 min.

The film thickness was measured using a one-dimensional surface roughness tester (Tokyo Seimitsu, Surfcom 550A) by masking a part of the substrate with aluminum foil. Compositional analyses for the films prepared under the conditions of $-V_{RF}$ = 0 and 100 V were made by use of the X-ray photoelectron spectroscopy (XPS) (JEOL JPS-9010) before and after Ar^+ etching. The etching time was 300 s with the Ar^+ energy of 800 eV. The etching depth was not measured. Films prepared under the condition of $-V_{RF}$ = 100 V were analyzed by using X-ray diffraction (XRD) (MacScience, M03XHF MXP3) with the sampling interval of 0.05 deg and with the scan speed of 4.00 deg min^{-1}.

The indentation hardness was measured using a Fischer H-100 ultralow-load microhardness indenter where a Berkovitch indenter was used. The maximum load applied was 7 mN. The load-displacement curves were measured under the condition described in detail in ref. [13].

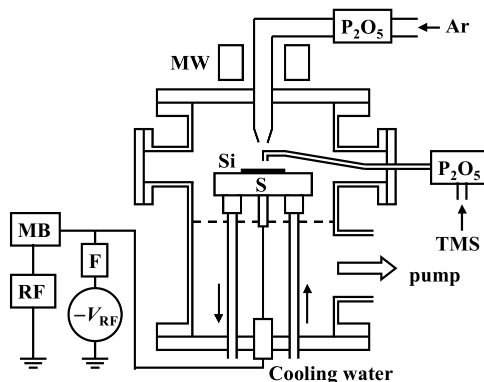

Fig. 1 Microwave plasma CVD apparatus.

The scratch test using diamond indenter (RHESCA CSR-02F) was carried out to investigate the adhesion property of a-SiC_x:H films onto Si substrate. The maximum load applicable was 1 N. The load of 89.3 mN was needed to peel the film prepared under the condition of $-V_{RF}$ = 0 V off the substrate. For the films prepared under the conditions of $-V_{RF}$ ≥ 20 V, the films did not peel off.

The structural analysis of the sample was performed using a Fourier Transform Infrared (FTIR) Spectrophotometer (Nicolet IMPACT-410) and a Raman spectrometer (Jobin Yvon, Model Labram Infinity). IR spectra were measured in the Right AEM-Main mode with a MCT/A detector and a resolution of 4 cm^{-1}. 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 ≤1 μm. Scattering signal was detected by using a CCD detector.

3. Results and Discussion

Fig. 2 shows the example of the observed Si2p and C1s peaks of XPS around 153 eV and 285 eV, respectively. In addition, O1s peak was observed at 532 eV being, presumably, the atmospheric origin (see the

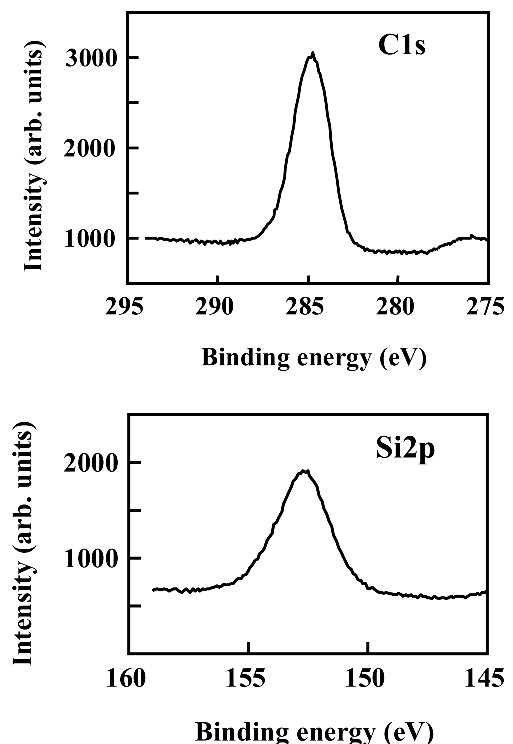

Fig. 2 XPS spectra of a-SiC_x:H film prepared under the condition of $-V_{RF}$ = 0 V. The Ar-ion etching was not carried out

Table 1 Results of the compositional analysis

(a) before etching

$-V_{RF}$ (V)	Si	C	O	x
0	37.0	48.9	14.1	1.32
100	31.4	54.2	14.4	1.73

(b) after etching

$-V_{RF}$ (V)	Si	C	O	x
0	43.5	46.0	10.5	1.06
100	34.0	42.8	23.2	1.26

discussion on the IR spectra). Table 1 lists the result of the compositional analysis based on XPS. The x values before etching were 1.32 and 1.73 for the films prepared under $-V_{RF}$ = 0 and 100 V, respectively. Those after etching were 1.06 and 1.26. Therefore, a carbon-enriched layer is formed near the surface of films. In particular, the carbon content of the surface layer in the films formed under the RF-biased condition was found to be significantly high.

Fig. 3 shows the examples of the experimental results of indentation measurements of the a-SiC_x:H films prepared under the conditions of (a) $-V_{RF}$ = 0 V, (b) $-V_{RF}$ = 50 V, and (c) $-V_{RF}$ = 100 V. The loading and unloading curves are indicated by squares and lozenges, respectively. The maximum indentation depths at the applied load of 7 mN were (a) 409 nm, (b) 112 nm, and (c) 62 nm, corresponding to the maximum hardnesses of (a) 1.6 GPa, (b) 21 GPa, and (c) 69 GPa, respectively. The above depth values are at most 1/3 of the film thickness (1-5 μm). Therefore, the influence of the Si substrate is negligible. The film hardness was measured for 2-5 points for a sample. In particular, measurements were repeated for several samples under the conditions of $-V_{RF}$ = 80 and 100 V to check the reproducibility. Fig. 4 shows the observed hardness plotted against $-V_{RF}$. As indicated in Fig. 4, the errors of the observed hardnesses were within 5 GPa for 0 V ≤ $-V_{RF}$ ≤ 60 V, whereas the errors under the conditions of $-V_{RF}$ = 80 and 100 V are large, evaluated as 10 and 27 GPa, respectively. The maximum hardness increased monotonically, indicating the effectiveness of the Ar^+ bombardment of the film surface. Since any diffraction signal was observed in the XRD measurement, films prepared in this study are amorphous.

Fig. 5 shows the IR spectra of a-SiC_x:H films prepared under the conditions of (a) $-V_{RF}$ = 0 V, (b) $-V_{RF}$ = 50 V, and (c) $-V_{RF}$ = 100 V. As indicated in Fig. 5, the following vibrational bands were observed: 670 - 760 cm^{-1} (Si-C stretching), ≈1000 cm^{-1} (bending vibration modes of Si-CH_3 and Si-$(CH_2)_n$-Si), ≈1250 cm^{-1} (Si-CH_3 symmetric bending), 2100 cm^{-1} (Si-H stretching), and 2700 - 3000 cm^{-1} (C-H stretching) [11]. As the $-V_{RF}$ value increased, the intensities of the Si-CH_3, Si-$(CH_2)_n$-Si, Si-H, and C-H vibration modes decreased. This observation indicates that hydrogen atoms in the films are preferentially removed by the Ar^+ bombardment. Since the OH and SiO stretching vibration modes were not observed, the contamination of O atoms is negligible. This observation indicates that the starting materials are fully desiccated and SiO_2 particles originating from the glass discharge tube are negligible. Therefore, O1s peak observed in the XPS measurement is attributable to the atmospheric H_2O molecules that contaminate into the films during the waiting time (several days) of XPS measurement.

Fig. 6 shows the Raman spectra of a-SiC_x:H films prepared under the conditions of (a) $-V_{RF}$ = 0 V, (b) $-V_{RF}$ = 50 V, and (c) $-V_{RF}$ = 100 V. The Raman spectrum of (a) shows any scattering signal; instead, a strong background signal toward higher Raman shift (i.e. longer wavelength) is observed. This background signal is attributed to the fluorescence due to the one-dimensional conjugated structures that contain amount of hydrogen termination structure [18]. On the other hand, the Raman spectra of (b) and (c) show the G (graphitic) band around 1450 cm^{-1} with negligible intensity of the background fluorescence signal. The observed G-band wavenumber is ≈100 cm^{-1} lower than that of the amorphous carbon materials [19]. This lowering can be attributed to the substitution of the Si atoms into the six-membered rings of the graphitic

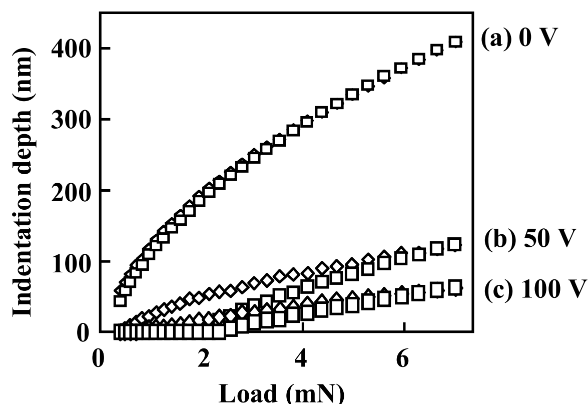

Fig. 3 Load-displacement curves for a-SiC_x:H films.

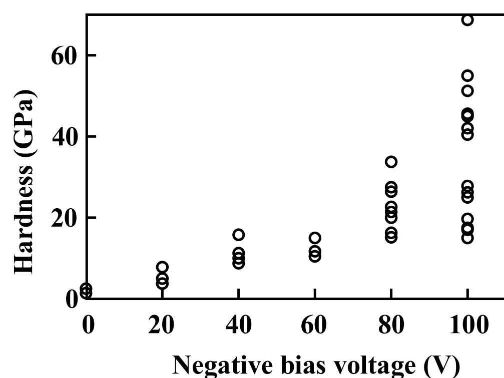

Fig. 4 Hardness of a-SiC_x:H films.

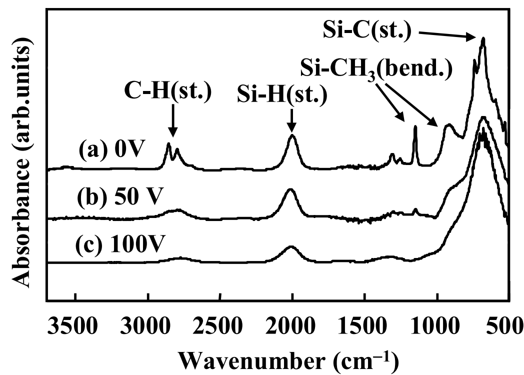

Fig. 5 IR-absorption spectra of a-SiC_x:H films.

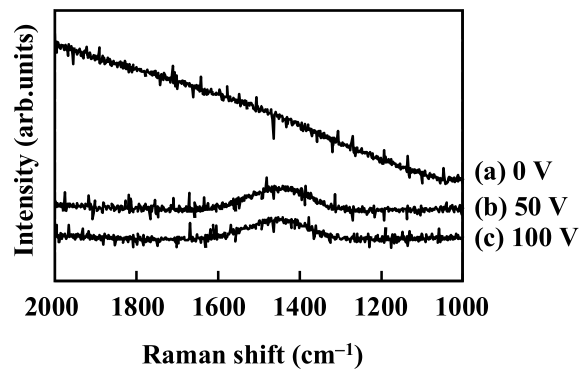

Fig. 6 Raman-scattering spectra of a-SiC_x:H films.

network [5].

From the XPS, IR, and Raman observations, the following mechanism of film hardening is suggested. When Ar^+ bombards the film surface, H atoms are removed preferentially as supported by the IR spectra (see Fig. 5). After the removal of H atoms, dangling bonds may be generated to recombine to induce the change from one-dimensional to two- or three-dimensional Si-C and C-C structures. The formation of the two-dimensional Si-C bonds is evidenced by the appearance of the G-band in the Raman spectra (see Fig. 6). The formation of the C-C bonds can be inferred from the production of the carbon-enriched layer near the film surface under the RF-biased condition (see Table 1). The recombine process may induce the increase of the size of clusters and simultaneous decrease of number density of the cluster boundaries, and may also include the formation of the three-dimensional structures. These effects induced by the Ar^+ bombardment may lead toward higher hardness [1,2].

4. Conclusion

A-SiC_x:H films were deposited onto Si substrates by using the decomposition reaction of TMS with the MW discharged products of Ar. The contamination of H_2O molecules is avoided by passing the starting materials through P_2O_5. A negative RF-bias voltage was applied to the substrate to induce Ar^+ bombardment of the film surface. Hardness of films under the condition of $-V_{RF} = 0$ V was ≈1 GPa. Under the condition of $-V_{RF} = 100$ V, films showed the hardness of 42±27 GPa; the maximum hardness was 69 GPa. This hardness is comparable to or even higher than that of bulk SiC (20-24 GPa). The compositional, IR-spectroscopic, and Raman-scattering analyses showed that the bombardment of Ar^+ induced by the RF bias to the film surface induces the removal of hydrogen atoms from the film surface, causing the structural change of the film from one-dimensional to two- or three-dimensional structures.

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