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Local structural analysis of a-SiC$_x$:H films formed by decomposition of tetramethylsilane in microwave discharge flow of Ar ☆

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ABSTRACT

Hydrogenated amorphous silicon carbide (a-SiC$_x$:H) films were prepared by the decomposition of tetramethylsilane (TMS) with microwave discharge flow of Ar. When radio-frequency (RF) bias voltage ($-V_{RF}$) was applied to the substrate, the film hardness increased as (2.39 ± 1.12)–(9.15 ± 0.55) GPa for $-V_{RF}$ = 0–100 V. The a-SiC$_x$:H films prepared under various $-V_{RF}$ conditions were analyzed by the carbon-K near edge X-ray absorption fine structure (NEXAFS), by the elastic recoil detection analysis (ERDA), and by the X-ray photoelectron spectroscopy (XPS). From a quantitative analysis of NEXAFS, the sp^2/(sp^2 + sp^3) ratios of C atoms were evaluated as 67.9 ± 2.0, 55.4 ± 2.7, and 51.7 ± 0.7% for $-V_{RF}$ = 0, 60, and 100 V, respectively. From ERDA, hydrogen content of the film prepared under the condition of $-V_{RF}$ = 100 V was found to decrease 28% comparing with that under $-V_{RF}$ = 0 V. It is suggested that the cause of the increase of the film hardness when applying $-V_{RF}$ is predominantly the growth of the sp^3-hybridized structure of C atoms accompanied by the decrease of hydrogen terminations.

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1. Introduction

Hydrogenated amorphous silicon carbide (a-SiC$_x$:H) films are promising materials for mechanical protection coatings [1], optical coatings for solar cells [2], and X-ray lithography masks [3]. Generally, a-SiC$_x$:H films can be generated by various methods such as plasma enhanced chemical vapor deposition (PECVD) [4–8]. The PECVD process has many tunable parameters such as discharge power, gas pressure, gas flow rate, substrate temperature, and substrate bias voltage. These parameters have been optimized to obtain various film properties [9–13]. When radio-frequency (RF) voltage is applied to the substrate, a negative self-bias voltage ($-V_{RF}$) is generated due to a large difference between the mobilities of ions and electrons. The generation of $-V_{RF}$ induces the acceleration of positive ions toward the substrate to cause ion bombardment. Therefore, hardness of a-SiC$_x$:H films is variable as a function of $-V_{RF}$. However, the mechanism of film hardening by applying $-V_{RF}$ has not been sufficiently understood.

A number of studies have been reported on the mechanisms of the film hardening of amorphous carbon (a-C) and hydrogenated a-C (a-C:H) films. It has been established that the dominant mechanism is the structural changes around carbon atoms accompanied by the change of hydrogen content [14]. The increase of hardness of a-SiC and a-SiC:H has been induced by a transition from amorphous to crystallized states by annealing at high temperature [15]. However, mechanism of hardening of a-SiC:H films based on the local structure around carbon atoms and the hydrogen content has not been discussed.

In the present study, local structural analysis was carried out based on the carbon-K near edge X-ray absorption fine structure (C-K NEXAFS) analysis using synchrotron radiation. In addition, variation of hydrogen content is studied by using the elastic recoil detection analysis (ERDA). Comparing the sp^2/(sp^2 + sp^3) ratio, hydrogen content, and film hardness, the mechanism of the film hardening of a-SiC$_x$:H by applying $-V_{RF}$ is discussed.

2. Experiments

2.1. Preparation of a-SiC$_x$:H films

Fig. 1 shows the schematic of the microwave (MW) PECVD apparatus used in the present study. The vacuum chamber with an inner diameter of 101.6 mm was evacuated to ~3 × 10^{-3} Torr (~0.4 Pa) using oil-rotary and mechanical-booster pumps. A quartz discharge tube (15 mmϕ) was set to the upper part of the chamber, and Ar gas (99.9999% purity) was introduced into the chamber through the discharge tube. The pressure of Ar was maintained 0.1 Torr (13.3 Pa) during the film deposition. Ar plasma flow was produced by MW (2.45 GHz, 100 W) discharge. Tetramethylsilane (Si(CH$_3$)$_4$: TMS) was introduced through a stainless-steel nozzle with an inner diameter of

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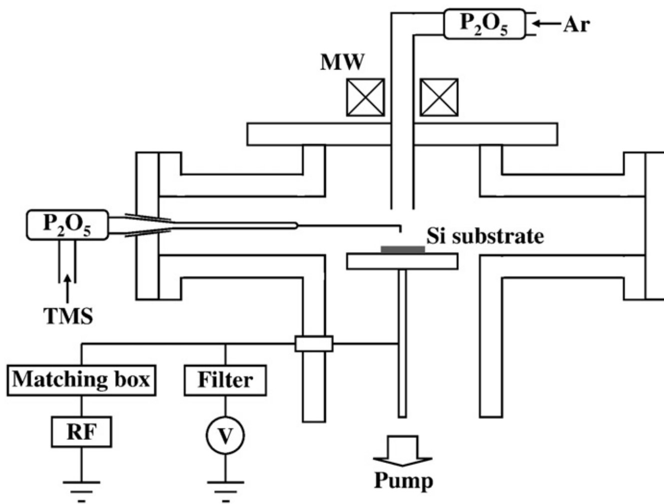

Fig. 1. Schematic of MWCVD apparatus used in the present study.

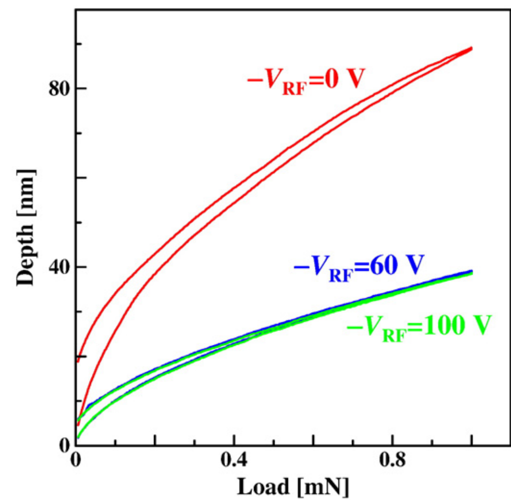

Fig. 2. Indentation-depth curves for a-SiC$_x$:H films.

1 mmϕ, whose tip was positioned at ~11 mm above the Si substrate of the area of ~10×10 mm^2 and the thickness of 0.70 mm. H_2O molecules included in Ar and TMS as impurity and/or adsorbed on the wall of the apparatus were excluded by passing through the cells filled with P_2O_5. The RF (13.56 MHz) bias voltage was applied to the substrate stage through a matching box. A self-bias voltage, $-V_{RF}$, was measured through a filter circuit. In the present study, $-V_{RF}$ was varied in the range of 0–100 V. Under the conditions of higher $-V_{RF}$, the surface roughness of films becomes too large to make precise measurements of hardness. The thickness of a-SiC$_x$:H films deposited under various $-V_{RF}$ conditions was in the range of 2–5 μm.

2.2. Mechanical hardness

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 measurements were carried out both for the loading and unloading directions. The hardness of Si substrate was observed as (6.9±0.3) GPa under the same condition.

2.3. Structural and compositional analyses

The C-K NEXAFS measurements were carried out at the beam-line 9 of NewSUBARU located at Laboratory of Advanced Science and Technology for Industry, University of Hyogo. The details of BL-9 are described in refs. [16,17]. Synchrotron radiation (SR) was extracted from the 11-m undulator and irradiated the sample at the incident angle of 54.7°. The absorption spectrum was obtained in the total electron yield (TEY) mode. The signal from the samples was calibrated against the incident beam intensity measured with a gold grid.

The compositional analyses were carried out with an electrostatic accelerator located at Kobe University [18]. In the Rutherford backscattering (RBS) measurement, the accelerated He^+ ions were irradiated the a-SiC$_x$:H films, and scattered He^+ ions were detected by a solid-state detector (SSD). In the measurement of ERDA, H atoms recoiled from the films were detected with SSD. The measurement of the X-ray photoelectron spectroscopy (XPS) (JEOL JPS-9010TR) was carried out to observe the compositions of a-SiC$_x$:H films prepared under the conditions of $-V_{RF}$=0 and 100 V, where Mg K$_\alpha$ was used as the X-ray source.

3. Results and discussion

Fig. 2 shows the indentation depth curves of a-SiC$_x$:H films prepared under the conditions of $-V_{RF}$=0, 60, and 100 V. The curves of $-V_{RF}$=60 and 100 V were almost identical. The maximum indentation depth in this test was ~90 nm which was ≤4.5% of the film thickness. Therefore, it was confirmed that the a-SiC$_x$:H film hardness was correctly evaluated without influence of the substrate. The hardness of a-SiC$_x$:H films was shown in Fig. 3 as a function of $-V_{RF}$. The hardness increased rapidly from (2.39±1.12) GPa at $-V_{RF}$=0 V to (8.02±0.63) GPa at $-V_{RF}$=20 V. In contrast, the hardness increased slowly as (8.02±0.63)–(9.15±0.55) GPa in the range of $-V_{RF}$=20–100 V. Higher DC or RF bias voltage may often be used for fabrication of mechanically hard a-C and related materials including a-SiC:H [15,19]. According to these reports, the substrate bias voltage makes the film hardness to increase. It is often observed that for a certain bias voltage the hardness saturates and that for higher bias voltage the hardness even decreases [19]. The observed tendency in hardness shown in Fig. 3 is consistent with these reports.

The C-K NEXAFS spectra of a-SiC$_x$:H films deposited under the conditions of $-V_{RF}$=0, 60, and 100 V are shown in Fig. 4. The NEXAFS spectrum of graphite is also shown as a reference. A narrow peak appearing at 285.3 eV was assigned to the transitions from C1s core level to the unoccupied π* levels of sp^2 (C=C) and sp (C≡C) sites [20]. Since the C=C bond dominates in a-C films, these peaks originate predominantly in the sp^2 bonding structure. The intensity of the C1s→π* peak decreased with increasing $-V_{RF}$, indicating that the sp^2/(sp^2+sp^3) ratio in a-SiC$_x$:H films decreased by applying $-V_{RF}$ to

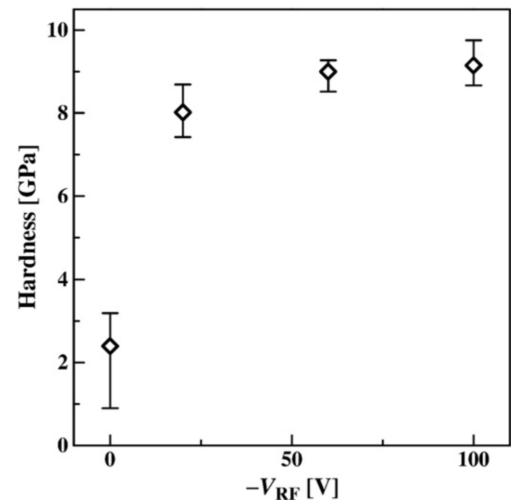

Fig. 3. Mechanical hardness of a-SiC$_x$:H films as a function of $-V_{RF}$.

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