

# Changes of chemical structure of hydrogenated amorphous silicon carbide films with the application of radio-frequency bias voltages during chemical vapor deposition

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## ABSTRACT

Hydrogenated amorphous silicon carbide films were fabricated using the decomposition of  $\text{Si}(\text{CH}_3)_4$  with the microwave discharge flow of Ar. The changes of the chemical structure and the mechanical hardness of films were investigated upon the application of the radio-frequency bias voltages ( $-V_{\text{RF}}$ ) to the substrate. The analysis was based on a combination of Rutherford backscattering and elastic-recoil detection analysis, the X-ray photoelectron spectroscopy, the glow discharge optical emission spectroscopy, the nano-indentation measurements, and Fourier-transformed infrared spectroscopy. The fraction of the C–Si bonding state has a positive dependence on  $-V_{\text{RF}}$ , whereas that of the C–C bonds in the  $\text{sp}^3$  hybridized state is negligible. In addition, hydrogen terminations were removed effectively under the low  $-V_{\text{RF}}$  conditions of 0–20 V. The films show the penetration of O atoms from the atmospheric origin into the bulk region. The mechanical hardness of the present films is the result of the balance among these factors.

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## 1. Introduction

Thin films of amorphous carbons and related materials have attracted much attention, since they are the potential candidates for the mechanical, electronic, and biomedical applications [1–4]. Among these materials, silicon carbides in the amorphous phase (a-SiC<sub>x</sub>) and hydrogenated a-SiC<sub>x</sub> (a-SiC<sub>x</sub>:H) have been expected for protective coatings [5–9], solar cells [10,11], low-friction [12], and biocompatibility [13]. The most-widely used method of synthesis of these materials has been the sputtering of sintered SiC target [14,15]. These materials have been fabricated also by using the plasma enhanced chemical vapor deposition (PECVD). In the early stage, the gas mixtures of SiH<sub>4</sub> and organic materials such as CH<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> have been used [5,10,11]. Recently, tetramethylsilane ( $\text{Si}(\text{CH}_3)_4$ , TMS) has become widely used as the starting material of PECVD [7–9,16–18] because of the safety and easiness of handling.

In the synthesis of mechanically-hard thin films, the bombardment of positive ions onto the film surface induced by the application of the negative bias voltages has been frequently utilized. In the previous reports on the synthesis of a-SiC<sub>x</sub> and a-SiC<sub>x</sub>:H, the negative DC bias voltages have been applied to obtain mechanical hardness [7–9,16,19]. We

have synthesized a-SiC<sub>x</sub>:H films using the dissociation of TMS induced by the reaction with the microwave (MW) discharged products of Ar where the radio-frequency (RF) bias voltages have been applied to the substrate which induces the negative self-bias voltage,  $-V_{\text{RF}}$ , to synthesize mechanically-hard a-SiC<sub>x</sub>:H films [20,21]. However, our previous investigations on the physical property and chemical structure of films upon the application of  $-V_{\text{RF}}$  have been inadequate as described below.

The first problem is the atomic compositions of films. They have been obtained from the X-ray photoelectron (XPS) spectroscopy [20, 21]. This analysis monitors the atomic compositions near the film surface, since the escape depth of photoelectrons in the XPS measurements is limited to  $\leq 5$  nm from the surface. It is frequently encountered that the atomic compositions near the film surface are different from those in the bulk region. In addition, H atoms cannot be detected by XPS. These atoms have been detected using the elastic recoil detection analysis (ERDA), but the quantitative discussion has not been carried out [21]. In this study, the atomic compositions in the bulk region of films including H atoms are analyzed quantitatively by using the combination of Rutherford backscattering (RBS) and ERDA (hereafter referred as RBS/ERDA). The difference of the atomic compositions in the bulk and surface regions can be monitored with the glow-discharge optical emission spectroscopy (GD-OES) [22]. The first purpose of this study is to discuss the atomic compositions of films and their changes upon the application of  $-V_{\text{RF}}$  based on the RBS/ERDA, XPS, and GD-OES measurements.

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The second is the bonding states of C atoms. Generally, the hardness of amorphous carbons and related thin films correlates with the fraction of the  $sp^3$ -bonding component of C atoms [1–4]. However,  $a\text{-SiC}_x\text{:H}$  includes not only the C–C bonds but also the C–Si bonds, the latter of which are also composed of C atoms in the  $sp^3$  configuration. It has been suggested by a simulation analysis that the negative DC bias voltages induce the increase of the fraction of the C–C bonds in the  $sp^3$  configuration [7,8]. In our previous studies, we have measured the carbon-K near-edge X-ray absorption fine structure (C–K NEXAFS) spectra of  $a\text{-SiC}_x\text{:H}$  films formed from the decomposition of TMS by a microwave discharge flow [21] and by an electron–cyclotron resonance plasma [23] of Ar. In these studies, we have found that  $sp^2$  component of C atoms reduces upon the application of  $-V_{\text{RF}}$ . It is difficult, however, to distinguish the C–Si and C–C bonding states in the C–K NEXAFS spectrum, because these components appear in a congested region of the spectrum originating from the C( $\sigma^* \leftarrow 1s$ ) transition [21]. These bonding components can be observed rather in a separated way in the high-resolution X-ray photoelectron spectroscopy (XPS). In this study, the XPS spectra of the C1s and Si2p states were measured with high resolution.

The third problem is the measurements of the film hardness and IR-absorption spectroscopy. It has been reported in our previous study that the hardness of  $a\text{-SiC}_x\text{:H}$  films increases steeply from 2.4–8 GPa, and simultaneously, the IR intensities of the hydrogen terminations [ $\text{CH}_n$  ( $n = 1\text{--}3$ ) and SiH] decreases when  $-V_{\text{RF}}$  increases as 0–20 V [20]. Since  $-V_{\text{RF}}$  has been set every 20 V in that study, however, the detailed changes of the film hardness and IR intensities have been ambiguous. More detailed measurements will be necessary to investigate the change of the chemical structures and physical properties particularly in the range of  $-V_{\text{RF}} = 0\text{--}20$  V.

In the course of the present study, the contamination of O atoms from the atmosphere is found to be so serious that the mechanical hardness of films is affected. The effect of O atoms is discussed in detail in this study.

## 2. Experiments

### 2.1. Preparation of $a\text{-SiC}_x\text{:H}$ films

Fig. 1 shows the schematic of the microwave (MW) plasma CVD apparatus used in the present study. The vacuum chamber with an inner diameter of 101.6 mm was evacuated to  $\approx 0.4$  Pa using oil-rotary and

mechanical booster pumps. Ar gas (99.9999% purity) was introduced into the chamber through a quartz discharge tube (15 mm) which was set to the upper part of the chamber, and the plasma flow of Ar was produced by a MW (2.45 GHz, 100 W) discharge. TMS was introduced with the pressure of  $\leq 0.7$  Pa through a stainless-steel nozzle with an inner diameter of 1 mm whose tip was positioned at  $\approx 11$  mm above the Si substrate on the stage (S).  $\text{H}_2\text{O}$  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  $\text{P}_2\text{O}_5$ . A RF electric field of commercially-allowed 13.56 MHz was applied to the substrate stage through a matching box (MB) with  $-V_{\text{RF}}$  being in the range of 0–120 V measured through a filter circuit (F). The application of  $-V_{\text{RF}}$  of  $> 120$  V was avoided to prevent the heating of the coaxial cable between the matching box and the vacuum chamber. Before the film deposition, the MW discharge flow of Ar was generated without introducing TMS under the condition of  $-V_{\text{RF}} = 50$  V for 30 min. By this pre-discharge procedure,  $\text{H}_2\text{O}$  molecules adsorbed onto the inner wall of the chamber and O atoms on the Si substrate were removed effectively (see Sections 3.1 and 3.4). After this procedure, TMS was introduced to deposit the films. The deposition time,  $t_d$ , was set to 30 min. The apparatus shown in Fig. 1 has the structure to introduce cooling water to suppress the increase of the temperature of the substrate during the deposition. Since any difference was observed for the hardness and the chemical structures of films whether the cooling water was introduced or not. Therefore, the data presented in this paper were obtained without cooling water and were independent of the temperature of the substrate.

### 2.2. RBS/ERDA

The atomic compositions were obtained using RBS/ERDA. The measurements 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. Films were deposited onto the Si substrates of  $\approx 100$  mm<sup>2</sup>. In order to make precise measurements of ERDA, the thickness of films were set  $\approx 300$  nm by adjusting the deposition time appropriately. In the measurements, the films were irradiated by the  $\text{He}^+$  beam accelerated to 2.5 MeV. In the RBS measurement, the scattered  $\text{He}^+$  beam was detected by a solid-state detector (SSD). The irradiation and detection angles of  $\text{He}^+$  beam were  $18^\circ$  and  $78^\circ$ , respectively, from the film surface. In the ERDA measurement, recoiled H atoms were detected with SSD positioned at an angle of  $168^\circ$  from the film surface.

### 2.3. XPS

Analyses of compositions and bonding states of films were made by use of XPS (JEOL JPS-9010) equipped at Analysis and Instrumentation Center of Nagaoka University of Technology. Films deposited onto Si substrates of  $\approx 7$  mm<sup>2</sup> were used as the samples, and the XPS measurements were carried out under the condition of  $2.0 \times 10^{-7}$  Pa using a Mg  $K_{\alpha}$  source. For the compositional analysis, the energy resolution of the XPS spectrometer was set to 1 eV. First, the XPS survey-scan spectra were observed for the as-deposited films under the conditions of  $-V_{\text{RF}} = 0, 10, 20, 40,$  and  $100$  V. Then, films were etched by using  $\text{Ar}^+$  sputtering where the kinetic energy of  $\text{Ar}^+$  was 700 eV, and the scans were repeated. The etching depth was estimated to  $\approx 10$  nm which corresponds to that of  $\text{SiO}_2$  under the same energy of  $\text{Ar}^+$ . The areas of the XPS profiles of Si, C, and O atomic peaks were measured, being converted to the atomic percent by multiplying appropriate factors. In our previous study, the compositional analysis by XPS has been carried out for the films fabricated at  $-V_{\text{RF}} = 0, 60,$  and  $100$  V without the  $\text{Ar}^+$  etching [21]. Therefore, the present compositional analysis is more detail than our previous analysis. For the analysis of the chemical bonding, a higher energy resolution of 0.1 eV was applied. In this experiment, films prepared under the conditions of  $-V_{\text{RF}} = 0, 10, 20,$  and  $100$  V were

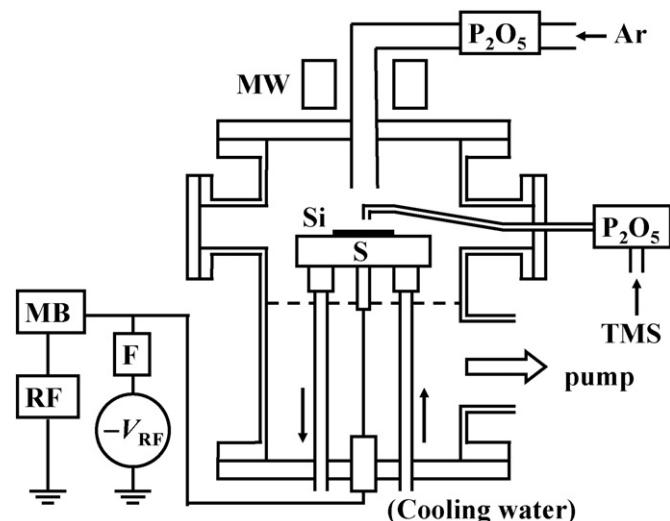


Fig. 1. Experimental apparatus.

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