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Properties of SiC_x Film Prepared with Plasma-based Ion Implantation and Deposition

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SiC_x films were prepared by a hybrid process of plasma-based ion implantation and deposition using hexamethyldisiloxane (HMDSO) gas including silicon. The SiC_x was composed of carbon, silicon, oxygen, and hydrogen. The Si/C in film is 0.34 without negative pulsed voltage, but Si/C is increased with increasing the negative pulsed voltage to 0.56. The hydrogen of 20 - 30 at.% was included in the SiC_x film. The residual stress of SiC_x film was decreased with increasing ion implantation voltage from 0.2 GPa (compressive stress) to -0.2 GPa (tensile stress). The Vickers hardness of SiC_x film was increased from 900 HV with -5 kV of ion implantation voltage to 1800 HV with -20 kV. A SiC_x interlayer of 10 μm in thickness was produced between the DLC film of 1 μm in thickness and the aluminum alloy (A5052) substrate. Adhesion strength of DLC/SiC_x/A5052 system was improved considerably.

Key words: plasma-based ion implantation and deposition, PBIID, SiC_x film, residual stress, tribological property, RBS

1. INTRODUCTION

In plasma-based ion implantation (PBII) technique [1] negative high-voltage pulses are applied to a substrate immersed in the plasma, so that plasma ions are accelerated by the sheath potential formed around the substrate. As a result, uniform ion implantation is realized onto three-dimensional targets with complicated shapes. Use of metal plasmas leads to the deposition as well as implantation on the substrate [2], which process is called a plasma-based ion implantation and deposition (PBIID). In recent years, PBIID process using hydrocarbon gas has studied for the preparation of diamond-like carbon (DLC) coatings. Carbon ion implantation prior to DLC deposition was useful to improve the adhesion of DLC films [3-5]. Carbon ion implantation to the DLC film itself during deposition resulted in considerably reduction of compressive residual stress in DLC film [6,7]. The reduction of residual stress allowed the improvement of adhesion and also the preparation of supra-thick films of 400 μm or more [8]. The PBIID process is a promising technique for the preparation of other ceramic films using different organic gases. However, studies on hard coating ceramic films except DLC are seldom performed yet.

In this paper SiC_x films are prepared with the PBIID process with the superimposed RF and high-voltage pulses [9]. The properties of SiC_x film will be shown and the possibility as a SiC_x interlayer for the hybrid DLC film on aluminum alloy substrates will be also discussed.

2. EXPERIMENTAL

SiC_x films were prepared with the PBIID process using superimposed RF and negative high-voltage pulses as shown in Fig. 1. In this process, the RF pulse (frequency 13.56 MHz, peak power 300 W, duration 50 μs and repetition rate 1 kHz) for initial plasma generation and the negative high-voltage pulse (voltage 0 ~ -20 kV, duration 5 μs and repetition rate 1 kHz) for ion implantation are supplied to the substrate through a single electrical feed-through. The uniform initial plasma along the shape of the substrate was generated because the substrate itself was worked as an RF antenna. Therefore, uniform DLC films were prepared on three-dimensional targets without rotation of targets [10,11]. When the negative high-voltage pulse was supplied to the substrate at the moment of 50 μs later after each RF pulse-off, ions accelerated by the ion sheath potential formed around the substrate were implanted to the substrate. At the same time, the secondary electrons emitted by the ion impact were accelerated to ionize or dissociate atoms and molecules close to the substrate [12]. As a result, lots of ions and radicals were generated around the substrate to form the deposited film on the substrate [13].

A cross-section of vacuum chamber was horseshoe shape (cross-section 420 × 420 mm and height 420 mm). A hexagonal sample holder (dimension of each face: 6 cm in width and 17 cm in height) was installed in the center of a chamber. SiC_x films were prepared after sputter-cleaning using argon plasma for 30 minutes. The precursor gas for SiC_x film was hexamethyldisiloxane (HMDSO) including silicon.

The component of SiC_x films prepared on aluminum alloy (A5052) was measured by RBS (NT-1700HS, Nisshin-High Voltage). The density was determined from the area density measured by RBS and the film thickness. The hydrogen content was measured by

ERDA (NT-1700HS, Nisshin-High Voltage). The residual stress σ of SiC$_x$ films was determined from the curvature and thickness of SiC$_x$ films using Stoney's equation as follows:

$$\sigma = \frac{Eb^2}{3(1-\nu)l^2 d}\delta$$

where E is Young's modulus, ν Poisson's ratio, b and d are the substrate and film thickness, respectively, l the scanning distance, δ the displacement magnitude of substrate. The curvature and thickness were measured by stylus profilometer (Dektak3, ULVAC). The deposition rate of SiC$_x$ film was estimated with the film thickness and the deposition time. The hardness was measured by Vickers hardness meter (HM-124, Akashi). Adhesion strength of hybrid film (DLC/SiC$_x$/A5052 system) was evaluated by the scratch-testing equipment (REVTEST, CSEM). The damaged region along the scratch track was observed with a CCD microscope (VH-8000, KEYENCE).

3. RESULTS AND DISCUSSION

3.1 Deposition rate

The deposition rate of SiC$_x$ film was determined with the film thickness and the processing time. Figure 2 shows the deposition rate as a function of negative pulsed voltage V_b, where the processing time was 2 hours. As seen in Fig. 2, the deposition rate of SiC$_x$ films is about 0.3 μm/h at $V_b = 0$. On the other hand, the deposition rate increases approximately twice with increasing negative pulsed voltage and reaches the maximum deposition rate approximately 0.6 μm/h at $V_b = -10$ kV. The deposition rate is decreased with increasing negative pulsed voltage exceeding $V_b > -10$ kV. The decrease of deposition rate at the higher negative pulsed voltage should be ascribed to sputtering of deposited DLC film by carbon ion implantation.

3.2 Residual stress

Figure 3 shows the residual stress of SiC$_x$ films as a function of negative pulsed voltage, where the positive value of residual stress indicates the compressive stress and the negative value the tensile stress. As shown in Fig. 3, the residual stress of SiC$_x$ films is approximately 0.14 GPa at $V_b = 0$, but the residual stress is increased slightly with increasing negative pulsed voltage at the region of $V_b < -3$ kV. However,with increasing negative pulsed voltage at $V_b > -5$ kV, the residual stress was transferred from the compressive stress to the tensile stress. This transformation in stress should be ascribed to the thermal spike effect by ion implantation.

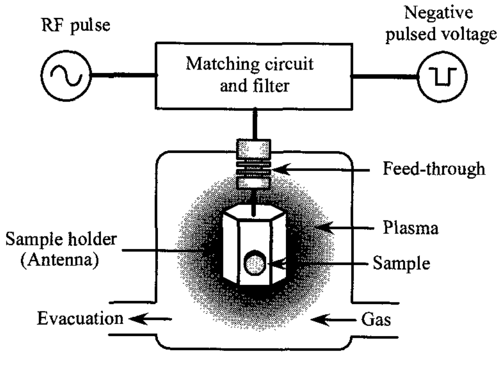

Fig. 1. Schematic of a hybrid process of plasma-based ion implantation and deposition (PBIID) using superimposed RF and high-voltage pulses.

3.3 Density

SiC$_x$ films (0.5 μm in thickness) for the measurement of density were prepared on silicon wafer with various negative pulsed voltages of 0, -5, -10, and -20 kV. Figure 4 shows the density of SiC$_x$ film as a function of negative pulsed voltage, where the density was determined from the area density measured by RBS and the film thickness measured by stylus profilometer. As seen in Fig. 4, the density is about 1.3 g/cm^3 without negative pulsed voltage. The density increases at about 1.9 g/cm^3 at $V_b = -5$ kV. At $V_b > -10$ kV, the density is saturated at about 2.0 g/cm^3. The observed increase in density by ion implantation should be ascribed to the deposition of implanted ions. It is found that the density of SiC$_x$ films prepared in the present experiment is lower than one of SiC (3.2 g/cm^3).

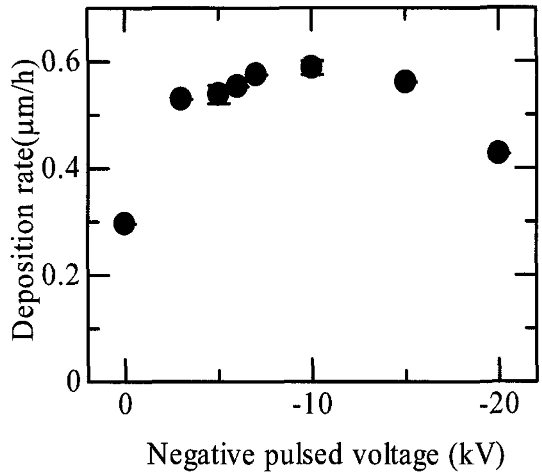

Fig. 2. Deposition rate vs. negative pulsed voltage.

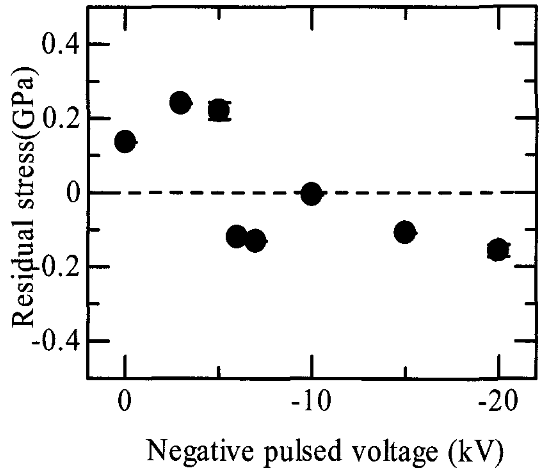

Fig. 3. Residual stress vs. negative pulsed voltage.

3.4 Carbon, silicon and hydrogen content

The elements of SiC_x film were measured by RBS and ERDA. Figure 5 shows the content of carbon, hydrogen and silicon in the film as a function of negative pulsed voltage. Although not shown here, oxygen was also observed in the SiC_x film, but the its exact content was not measured. As seen in Fig. 5, the carbon content is about 50 - 55 at.% that is little dependent on the negative pulsed voltage. The contents of silicon and hydrogen are about 17 at.% and 33 at.%, respectively, without the negative pulsed voltage. When the negative pulsed voltage is increased, the silicon content is increased to about 28 at.% at V_b = -20 kV, while the hydrogen content is decreased to about 20 at.%. The ratio of silicon to carbon, Si/C, is 0.34 at V_b = 0, but Si/C is increased with increasing the negative pulsed voltage and reached to 0.56 at V_b = -20 kV.

3.5 Hardness

Figure 6 shows the hardness of SiC_x films on the aluminum alloy substrate as a function of negative pulsed voltage, where the thickness of SiC_x film was about 10 μm and the maximum load of Vickers intender was 10 g. In the present measurements, the maximum displacement of indenter was less than one-tenth of the thickness of SiC_x films, so that the hardness of film itself could be measured without any effect of substrate hardness. As seen in Fig. 6, the hardness of SiC_x film is about 900 HV at V_b = -5 kV, increases with increasing negative pulsed voltage, and reaches to about 1800 HV at V_b = -20 kV which is larger than that of DLC film prepared with hydrocarbon gas (typically 1300 HV) [14]. The hardness of SiC_x film should be dependent on density, residual stress, hydrogen content, and component. Since the density, residual stress and hydrogen content are almost constant with increasing negative pulsed voltage, an increase in hardness at V_b = -20 kV should be ascribed to the increase in Si/C ratio.

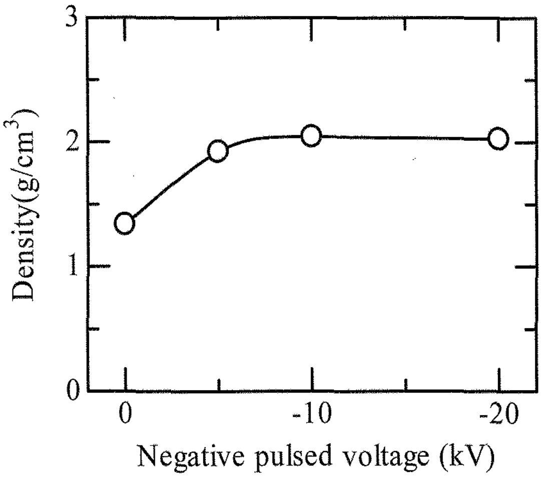

Fig. 4. Density vs. negative pulsed voltage.

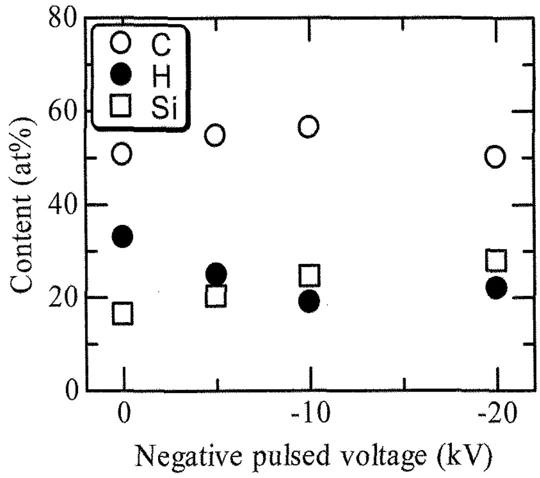

Fig. 5. Composition vs. negative pulsed voltage.

3.6 Friction coefficient

Figure 7 shows the friction coefficients of SiC_x and DLC films on an aluminum alloy (A5052) substrate which was measured by the ball-on-disk friction tester, where the load of ball (SUJ-2 and 5 mm in diameter) was 300 g. As seen in Fig. 7, the friction coefficient of SiC_x film is about 0.2 that is larger than 0.15 of DLC film.

3.7 Scratch test

DLC films, which have excellent tribological characteristics such as great hardness, high wear resistance, and low coefficient of friction, on

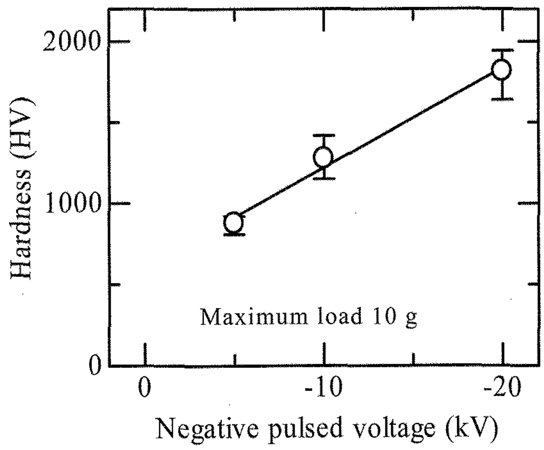

Fig. 6. Hardness vs. negative pulsed voltage.

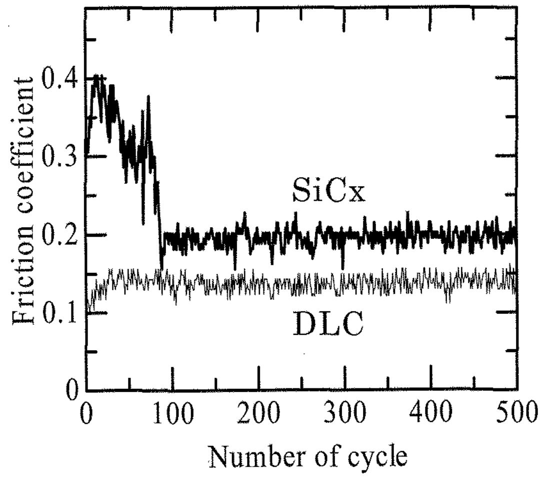

Fig. 7. Friction coefficient of SiC_x and DLC films.

softer substrates such as aluminum alloys were easily broken by strong local loads because of deformation of substrate [15]. In order to study the effect of a SiC_x interlayer on adhesion of DLC film, a hybrid DLC film (1 μm in thickness) with a thick SiC_x interlayer (10 μm in thickness) is prepared on the A5052 substrate. Adhesion of hybrid DLC film was evaluated by a scratch tester. Figure 8 shows the optical micrograph of scratch tracks around the starting point for the DLC films with the SiC_x interlayer of different hardnesses ((a)1300 and (b)1800 HV). As seen in Fig. 8 (a), the large initial flaking of DLC film is observed at the point of about 300 μm from the starting point (load is about 3 N). On the other hand, as seen in Fig. 8 (b), the small initial flaking is observed at the point of about 600 μm from the starting point (load is about 6 N). These results show that the interlayer of harder SiC_x film is effective for improvement of adhesion strength and durability.

4. CONCLUSION

SiC_x films were prepared with the PBIID process using HMDSO gas. RBS measurement showed that the composed elements were carbon, silicon, and oxygen. Si/C is 0.34 without negative pulsed voltage, but Si/C is increased with increasing the negative pulsed voltage to 0.56. Besides, it was confirmed by ERDA analysis that hydrogen of 20 - 30 at.% was included in the SiC_x film. The dependence of SiC_x film properties on the negative pulsed voltage for ion implantation was as follows: The residual stress was decreased with increasing negative pulsed voltage from about 0.2 GPa (compressive stress) to about -0.2 GPa (tensile stress). The hardness was increased with increasing negative pulsed voltage from 900 HV to 1800 HV. The density was increased with increasing negative pulsed voltage and was saturated at about 2.0 g/cm^3. The hydrogen content was decreased with increasing negative pulsed voltage and was saturated at about 20 at.%. The interlayer of harder SiC_x film was effective for improvement of adhesion of DLC film on the soft substrate such as aluminum alloys.

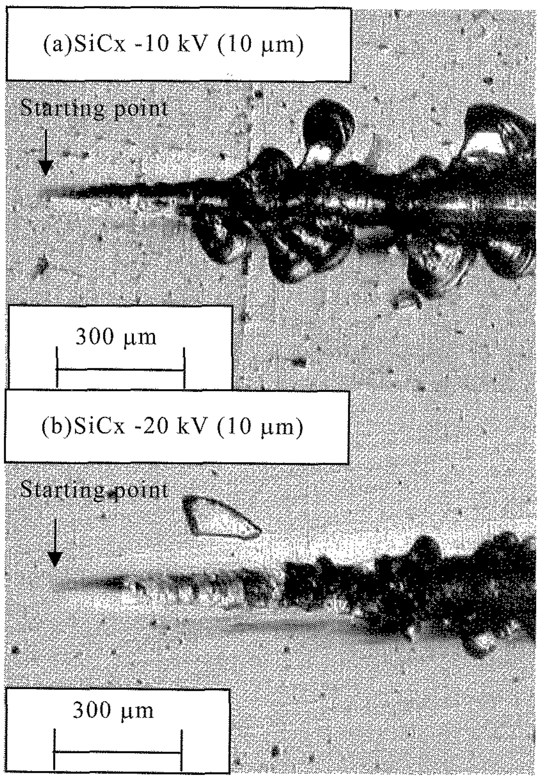

Fig. 7. Optical micrograph of scratch tracks around the starting point for DLC films with different-hardness SiC_x film interlayer ((a)1300 HV and (b)1800 HV) on aluminum alloy (A5052) substrate.

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