

Conference Proceeding on Nanomaterials and Nanochemistry Hard Carbon and Silica based Films Synthesized under Atmospheric Pressure

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Abstract

Atmospheric pressure-plasma enhanced chemical vapor deposition (AP-PECVD) method using a dielectric barrier discharge (DBD) is a cost-effective process because of no need of vacuum process. In this study, we synthesized silica-based films (SiO:CH) and hydrogenated amorphous carbon films (a-C:H) by AP-PECVD method. We synthesized SiO:CH films from tetramethoxysilane (TMOS) and O₂ diluted with N₂ and investigated the effect of the substrate temperature and the TMOS flow rate on hardness of the films. The hardness increased from 4.0 to 6.9 GPa as the substrate temperature increased from 80 to 300°C. To synthesize a-C:H films, filamentary DBD (FDBD) was used to improve the hardness compared to the films synthesized by glow DBD (GDBD), which is generally used for APCVD. The hardness of the films increased from 3.7 to 11.9 GPa by using FDBD.

Keywords: amorphous carbon films; silica-based films; atmospheric pressure, plasma, chemical vapor deposition, hardness

Introduction

Both amorphous carbon films (e.g., a-C and a-C:H) and silica-based films (e.g., SiO_x and SiO:CH) have been actively studied for industrial applications because of their excellent characteristics such as high hardness, high abrasion resistance and high gas barrier properties [1-3]. These films have attracted much interest as protective layers for transparent polymeric materials used as substitute for glass [4]. They are generally synthesized at low pressure, typically below 100 Pa by chemical vapor deposition (CVD) [5]. However, the vacuum technique takes a lot of costs because of the expensive pumping equipment and the time-consuming vacuum process. The atmospheric pressure-plasma enhanced chemical vapor deposition (AP-PECVD) process using dielectric barrier discharge (DBD) is one of the approaches to overcoming the cost problems. Around 1990, a homogeneous dielectric barrier discharge (DBD) generating atmospheric pressure glow discharge (APGD) was reported [6-9]. SiO:CH were synthesized using DBD in helium or in nitrogen with an admixture of organosilicon compounds, such as hexamethyldisiloxane (HMDSO) or tetraethoxysilane (TEOS) [10,11]. However, the films deposited by AP-PECVD are generally inferior to those synthesized at low pressure in hardness due to high content of carbon-related bonds [12].

In this study, SiO:CH films were synthesized from tetramethoxysilane (TMOS), which has a low content of carbon atoms per molecule

compared to HMDSO or TEOS, and O₂ diluted with N₂ by the AP-PECVD process using DBD. We prepared the films with varying substrate temperature and process gas flow rate and investigated film characteristics such as hardness, abrasion resistance, and chemical bonding structure [13].

Like SiO:CH films, hydrogenated amorphous carbon (a-C:H) films deposited by the AP-PECVD method are generally polymer-like and soft with a high content of hydrogen [14]. The properties of a-C:H primarily depend on the energy of the ionic species in film deposition [15]. High ion energies give a-C:H films with a mixture of sp³ and sp² sites which have the diamond-like properties of high hardness, high wear resistance and high refractive index. Conversely, a-C:H deposited with few, low energy ions consists of a loosely bonded network which is polymer-like and mechanically soft.

Dielectric barrier discharges (DBDs) are classified into glow DBD (GDBD), glow-like DBD (GLDBD), Townsend DBD (TDBD) and filamentary DBD (FDBD), according to the discharge mechanism [16]. The GDBD is commonly used for synthesis of a-C:H films since the plasma generated by GDBD uniformly covers the surface and synthesizes smooth films while suppressing powder formation unlike that generated by the other discharges. However, the ion density and the electron density in GDBD is not sufficient to synthesize hard a-C:H films compared to low pressure CVD, and only soft a-C:H films have been synthesized by GDBD [17,18]. In contrast to GDBD, FDBD consists of a lot of filamentary discharges (streamers) and the streamers have high ion density and electron density. The

synthesis process using FDBD has problems of the damage caused to the substrate by the discharge with high plasma density and deposition nonuniformity due to a state where the streamers retain at the same points.

In this study, we synthesized hard a-C:H films at room temperature using FDBD as a new synthesis process. To avoid powder formation in FDBD, we used CH₄ which consists of single bonds to reduce gas phase reaction unlike C₂H₂. To generate FDBD with a large number of streamers between the electrodes of DBD equipment, we employed the substrates with low surface resistivity. The a-C:H films were synthesized by FDBD with various electrodes gaps. We investigated the characteristics of the films such as hardness and chemical bonding structure [19].

Materials and Methods

SiO:CH films

Figure 1 shows a schematic view of the AP-PECVD apparatus (Sekisui chemical Co., Ltd., Japan). Plasma is sustained between parallel-plate electrodes covered with alumina dielectric plates. Silica-based films were deposited from a mixture of tetramethoxysilane (Si(OCH₃)₄, TMOS) and O₂. The gas mixture was introduced through a slotted gas outlet located at the center axis of the upper electrode. The gas conditions were; TMOS 0.15, 0.2 and 0.3 g/min, O₂ 8 l/min. The chamber was purged with N₂ gas and the deposition pressure was adjusted to 95 kPa. The deposition was carried out at substrate temperatures of 80, 100, 200 and 300°C. Pulsed power was fixed at 135 W with peak negative voltage of 14 kV and a pulsed frequency was operated at 20 kHz at a pulse width of 10 μs, 8 inch single crystal Si (100) wafers were set as substrates on the lower electrode moving at the speed of 45 mm/min parallel to the upper electrode. The discharge gap between the substrate and upper electrode was set to be 1.5 mm.

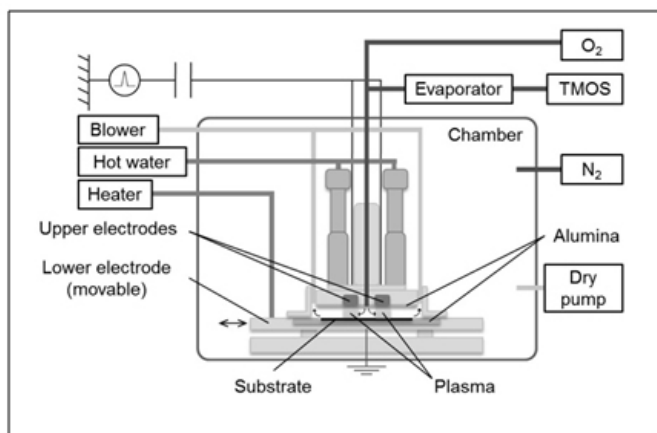


Figure 1: Schematic diagram of the atmospheric pressure plasma CVD apparatus

a-C:H films

The same AP-CVD apparatus (Figure 1) without the alumina dielectric plate for the lower electrode was employed for a-C:H film preparation. Boron doped single crystal Si (100) wafers (KOUJUNDO CHEMICAL LABORATORY CO., LTD) with a thickness of 380 μm were used as substrates to measure thickness, chemical bonding structure, hardness. The boron doped Si substrates were cut to 30 mm length × 70 mm width from the wafers. The surface resistivity of the Si substrates was 47.2 Ω/sq. determined by the four point probe

measurement. To evaluate the effect of the surface conductivity, 50 μm thick polyethylene terephthalate (PET) films coated with transparent conductive polymer. The surface resistivities of PET were, over 10⁹ (uncoated), 150, 200 and 530 Ω/sq.

The substrates were set on the lower electrode moving back and forth at intervals of 30 mm in the direction of plasma length at speeds of 0.1 mm/s in parallel to the upper one. The gap between upper and lower electrodes was varied with 1 mm, 2 mm, 3 mm and 4 mm. According to Meek [20], the larger the electrodes gap, the more likely to generate streamer discharges, because the electron avalanche generated in typical barely spread and rapidly grows.

The a-C:H films were synthesized from a mixture gas of CH₄, He and Ar. The mixture gas was introduced through a slotted gas outlet located at the center axis of the upper electrode. Helium has high ionization energy and it can stably decompose CH₄ by Penning ionization. On the other hand, the diffusion coefficient of Ar is lower than He, thus Ar can generate streamers easily. The He and Ar flow rates were 4 l/min and 1 l/min, respectively. The CH₄ flow rate was set at 200 ml/min. The pulsed power was fixed at 90 W with a peak negative voltage of 7 kV and the pulsed frequency was operated at 30 kHz with a pulse width of 5 μs for plasma source.

Film characterization

The film thickness was measured by a spectroscopic ellipsometer (FE-5000S, Otsuka Electronics Co., Ltd., Japan) for SiO:CH films and a contact-type surface profiler (Veeco Instruments Inc., USA) for a-C:H films. The cross-sectional surfaces of the a-C:H films were observed by scanning electron microscopy (SEM: S-4700, Hitachi High Technologies Corp., Japan) operating at an acceleration voltage of 5 kV. The hardness of the films was measured using nano indentation tester (Agilent Nano Indenter G200, Agilent Technologies Inc., USA) with a Berkovich diamond indenter. The indent load was 1.0 mN and the load-displacement curve was analyzed using the Oliver and Pharr method [21]. The measurements of the hardness were performed at 5 different surface locations. The structure of the films was determined by Raman spectroscopy (STR300, Seki Technontron Corp., Japan). Unpolarized Raman spectra were acquired at 532 nm. The spectral resolution was 0.75 cm⁻¹.

Results and Discussion

SiO:CH films

Figure 2 shows the hardness of the SiOC(-H) films as a function of the substrate temperature. The hardness of the films increased as the substrate temperature increased. The hardness of the film deposited at 80°C was measured to be 4.0 GPa. Further increase in the substrate temperature to 300°C resulted in an increase in the hardness up to 6.9 GPa.

Silica-based films were synthesized at 80°C with varying TMOS flow rates, aimed at deposition to heat-sensitive polymeric materials. Figure 3 shows the deposition rate and hardness of the films as a function of the TMOS flow rate. As the TMOS flow rate increased from 0.15 g/min to 0.3 g/min, the deposition rate increased from 0.55 nm/s to 1.5 nm/s and the hardness slightly decreased from 4.3 GPa to 3.3 GPa. The hardness of the silica-based films deposited at low temperature, 80°C was relatively hard ranging from 3.3 GPa to 4.3 GPa, which is more than ten times harder than polymeric materials. This result indicates the applicability of the AP-PECVD method for synthesizing hard films on heat-sensitive materials such

as commodity polymers; PC or polypropylene.

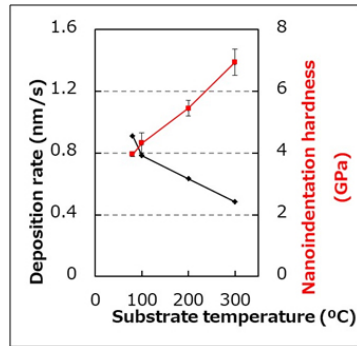


Figure 2: Deposition rate and Hardness of the SiOC(-H) films as a function of the substrate temperature. TMOS flow rate : 0.2 g/min

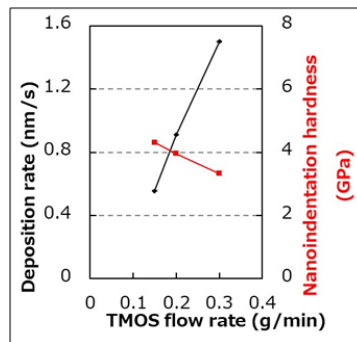


Figure 3: Deposition rate and Hardness of the SiOC(-H) films as a function of TMOS flow rate Substrate temperature.: 80°C

a-C:H films

Figure 4 shows the discharge images observed from the horizontal direction at various electrodes gaps without substrate using the bare lower electrode. The discharge form was transitioned from GDBD to FDBD with increasing the electrodes gap. The glow discharge was clearly formed at an electrode gap of 1 mm. At 2 mm, the discharge form was a mixture of streamers and glow discharges. The discharge form completely shifted to FDBD with many streamers when the gap was at 3 mm and 4 mm. The results showed that FDBD can be easily generated by increasing the electrodes gap using CH₄/He/Ar mixed gas using the bare lower electrode.

Figure 5 shows the discharge images with the substrates with various surface resistivities. As shown in Figure 5, when the surface resistivity was higher than 530 Ω/sq, FDBD was not generated due to a decrease of the electric field.

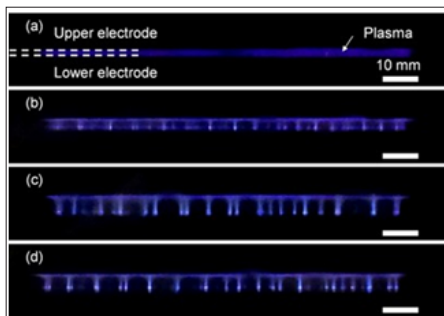


Figure 4: Discharge images without substrates (bare lower electrode) at electrodes gaps of:

(a) 1mm, (b) 2mm, (c) 3mm, (d) 4mm

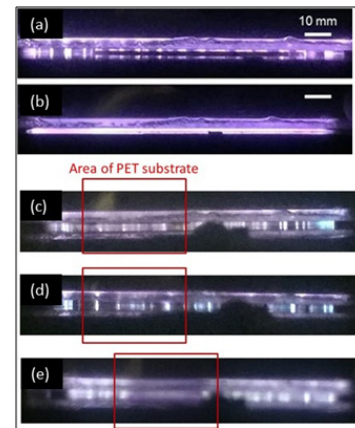


Figure 5: Discharge images at electrodes gaps of 4 mm with substrates having different surface resistivity:

- (a) B-doped Si (47.2 Ω/sq) (FDBD)
- (b) PET50 μm (109 Ω/sq) (GDBD)
- (c) PET (150 Ω/sq) (FDBD)
- (d) PET (200 Ω/sq) (FDBD)
- (e) GDBD : PET (530 Ω/sq) (GDBD)

Figure 6 shows the cross-sectional SEM images of the a-C:H films synthesized with 1 mm and 4 mm of electrodes gaps. The thickness of the a-C:H films was unified at about 500 nm by changing the deposition time based on the deposition rate. A smooth surface without the powder formation was confirmed on the a-C:H films synthesized using both GDBD and FDBD. The thickness of the film synthesized using FDBD was about 540 nm ± 20 nm at all points, indicating a-C:H films were uniformly synthesized. The reason is considered that the streamers shifting from higher resistivity point to lower resistivity point on the surface according to deposition of insulating a-C:H, the a-C:H films were uniformly synthesized on the substrates.

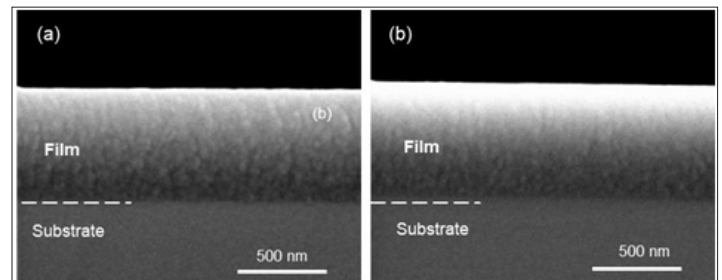


Figure 6: Cross-sectional SEM images of DLC thin films synthesized with electrodes gap (a) 1 mm and (b) 4 mm

Figure 7 shows the deposition rate of the a-C:H films as a function of the electrodes gap. As the electrodes gap increased from 1 mm to 4 mm, the deposition rate increased from 1.1 nm/s to 1.9 nm/s. Figure 6 shows the hardness of the a-C:H films as a function of the electrodes gaps. The hardness of the films increased from 3.7 GPa to 11.9 GPa with increasing the electrodes gap from 1 mm to 3 mm. The hardness became constant when the electrodes gap was increased to 4 mm. These results indicate that the a-C:H films synthesized by FDBD are harder than those synthesized by GDBD. The hardness of a-C:H films using GDBD is reported to be achieved at 3 GPa. [22,23]. The Raman spectra (not shown) of the a-C:H films with various electrode gaps showed that higher background intensity of the photoluminescence due to the polymeric structure

with high content of hydrogen for the electrode gaps of 1mm and 2mm. In contrast, when the electrode gap increased to 3 or 4mm, the background intensity was greatly reduced that indicated high energy of FDBD make hydrogen abstraction from C-H bond.

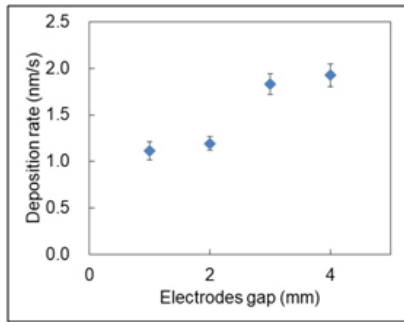


Figure 7: Deposition rate of the a-C:H films as a function of the electrode gap

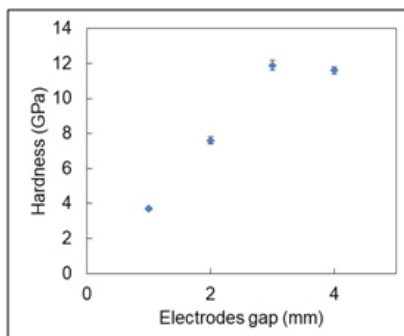


Figure 8: Hardness of the a-C:H films as a function of the electrode gap

Conclusion

we synthesized SiO₂CH films by AP-PECVD method and investigated the effect of the substrate temperature on the hardness of the films. As the substrate temperature increased from 80 to 300°C, the hardness increased from 4.0 to 6.9 GPa. Also, the hardness slightly increased with decreasing the TMOS flow rate. The films which are comparable to the hardness of those deposited by LP-PECVD or conventional soda glass were obtained.

We synthesized hard a-C:H films at room temperature using FDBD with various electrodes gaps at atmospheric pressure. The discharge form was transitioned from GDBD to FDBD with increasing the electrodes gap to 3 mm or over when the surface resistivity of substrates was lower than 530 Ω/sq. and mixture of He and Ar were used as a dilution gas. the hardness of the films increased from 3.7 GPa to 11.9 GPa with increasing the electrodes gap from 1 mm to 3 mm. These results indicate that hard a-C:H films were synthesized at low temperature by FDBD.

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