Synthesis of diamond-like hydrocarbon films by atmospheric pressure filamentary dielectric barrier discharge

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Abstract. Diamond-like hydrocarbon (DLHC, a-C:H) films were synthesized under atmospheric pressure filamentary by dielectric discharge (FDBD) to improve their mechanical properties compared to the films synthesized by glow dielectric barrier discharge (GDBD). GDBD is generally used for atmospheric pressure-plasma-enhanced chemical vapour deposition. The discharge form transitioned from GDBD to FDBD by increasing the gap between electrodes from 1 to 4 mm. The hardness of the films increased from 3.7 to 11.9 GPa by using FDBD. The results indicate that hard DLHC films can be synthesized at room temperature and on a large area under atmospheric pressure using FDBD.

1. Introduction

Amorphous carbon films were widely employed in various fields of industrial applications due to their excellent chemical and mechanical properties; high hardness, high abrasion resistance, gas barrier properties [1-2]. Among them, hydrogenated amorphous carbons (a-C:H) are called Diamond-like hydrocarbons (DLHCs), and synthesized by the easily accessible deposition processes such as plasma enhanced chemical vapor deposition (PECVD) at vacuum condition [3]. However, in case of various industrial applications, the vacuum process has several drawbacks, such as high costs and limited coating area associated with vacuum equipment. Generating low temperature plasma under atmospheric pressure (AP) condition is one of the solutions to solve the above problems. The stabilization of atmospheric pressure glow plasma using dielectric barrier discharge (DBD) was reported in 1990 [4-5]. AP-PECVD using DBD has been actively studied for synthesizing low-cost, highly-functional films [6–8]. DBD is classified into glow DBD (GDBD), glow-like DBD, Townsend DBD, and filamentary DBD (FDBD) [9]. The GDBD is conventionally used for the AP-PECVD process. The plasma generated by GDBD uniformly covers the surface and synthesizes smooth films while inhibiting powder formation unlike those generated by other discharges. However, the ion density and the electron density in GDBD are not sufficient to deposit hard DLHC films compared to low-pressure CVD (LPCVD), and only soft DLHC films with higher hydrogen content have been synthesized by GDBD [10-12]. In contrast to GDBD, FDBD consists of many filamentary discharges (streamers) that have significantly higher ion density and electron density. However, the synthesis process using FDBD has several problems; the discharge with high plasma density can damage the substrate, and deposit films with non-uniformity due to a state where the streamers are retained at the same points. In this work, we present the results on synthesis of hard DLHC films at room temperature using FDBD. To generate FDBD with a large number of streamers between the electrodes of DBD equipment, we employed substrates with various levels of surface resistivity and investigated their

effects on the film synthesis. The DLHC films were produced using FDBD with various electrodes gaps, and we evaluated the characteristics of the films [13].

2. Materials and Methods

A schematic diagram of the AP-PECVD apparatus used in this study is shown in Figure 1. The plasma was maintained between the parallel copper electrodes: the upper electrode, 100×10 mm^2 in size, was connected to a high-frequency pulsed power supply (SPD1PGU1, SK Medical Electronics Co., Ltd., Japan) and overlaid with a alumina dielectric plate (1mm in thickness), and the lower electrode, 200×300 mm2 in size, was grounded. 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, and hardness. The boron-doped Si substrates were cut into small pieces of 30 mm length × 70 mm width. The surface resistivity of the Si substrates was 47.2 Ω /sq.. as measured by a four-point probe apparatus. To evaluate the effect of the surface conductivity, 50 μm thick polyethylene terephthalate (PET) films coated with transparent conductive polymer using poly (3,4-ethylenedioxythiophene) (PEDOT) were used. The surface resistivity of the un-coated PET film was 109 Ω /sq.., and those of the conductive polymer coated PET films were 150, 200 and 530 Ω /sq..
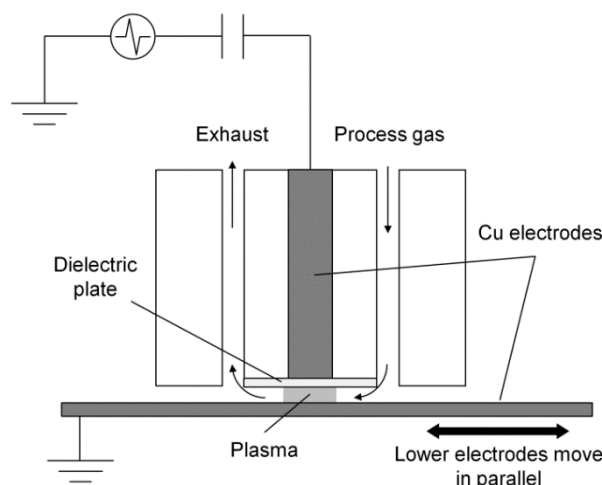

Figure 1. Schematic presentation of the AP-PECVD apparatus.

The substrates were set on the lower electrode moving back and forth for 30 mm range in the direction of plasma length (10 mm) at speeds of 0.1 mm/s. The gap between upper and lower electrodes was set between 1 mm and 4 mm. According to Meek [14], the larger the electrodes gap, the more likely it is to generate streamer discharges because the electron avalanche generated rapidly. The DLHC films were synthesized from CH$_4$/He/Ar mixture. The gas mixture was introduced through a slotted gas outlet located at the center axis of the upper electrode. He has high ionization energy and decomposes CH$_4$ efficiently by Penning ionization. Whereas, the diffusion coefficient of Ar is lower than He, hence Ar can generate streamers easily. The flow rates of He, Ar, CH$_4$ were set at 4 l/min, 1 l/min and 200 ml/min, respectively. The input power was 90 W and the pulse width and the peak negative voltage were set at 5 μs and 7 kV respectively.

The thickness of the DLHC films was measured by a contact-type surface profiler (Dektak 3030, Veeco Instruments Inc., USA). The cross sections of the films were observed by scanning electron microscopy (SEM: S-4700, Hitachi High Technologies Corp., Japan). The hardness of the films was studied using a Nanoindentation Tester (Agilent Nano Indenter G200, Agilent Technologies Inc., USA) with a Berkovich diamond indenter using the Oliver and Pharr method [15]. The structure of the films was studied by Raman spectroscopy (STR300, Seki Technotron Corp., Japan).

3. Results and Discussion

Figure 2 shows the discharge images viewed from the horizontal direction at various electrodes gaps without substrates. The forms of discharge were transitioned from GDBD to FDBD with an increase of the gap between the electrodes. The glow discharge was clearly confirmed at an electrodes gap of 1 mm, and at 2 mm gap, the discharge form was a mixture of FDBD and GDBD. The discharge form completely shifted to FDBD with a large number of 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 CH_4/He/Ar mixed gas using the bare lower electrode.
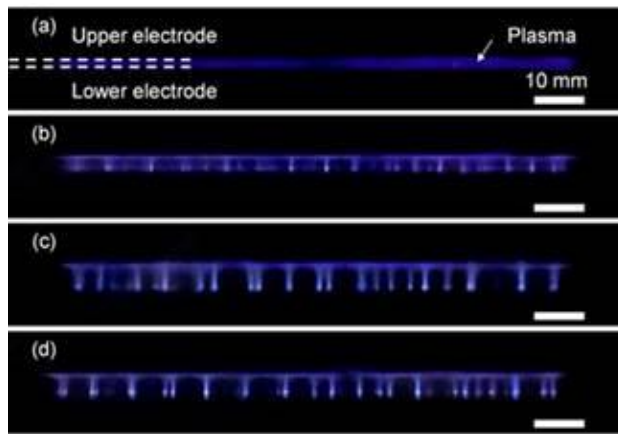
Figure 2. Discharge images without substrates (bare lower electrode). Electrodes gap: (a) 1 mm, (b) 2 mm, (c) 3 mm, (d) 4 mm.

Figure 3 shows the discharge images with the substrates with different surface resistivities. When the surface resistivity increased from 200 to 530 Ω /sq., the discharge form shifted to GDBD due to a decrease in the electric field.
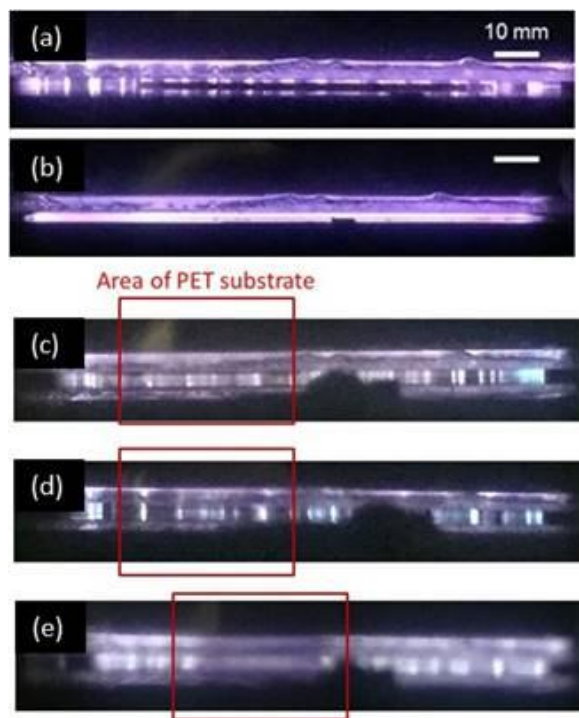
(a) B-doped Si (47.2 Ω/sq.）(FDBD);

(b) PET50 μm (10^9 Ω/sq.）(GDBD)

(c) Conductive polymer-coated PET (150 Ω/sq.）(FDBD);

(d) Conductive polymer-coated PET (200 Ω/sq.）(FDBD);

(e) Conductive polymer-coated PET (530 Ω/sq.）(GDBD).

Figure 3. Discharge images at the electrodes gaps of 4 mm with substrates.

The deposition rate of the DLHC films as a function of the electrodes gap is shown in Figure 4. 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.
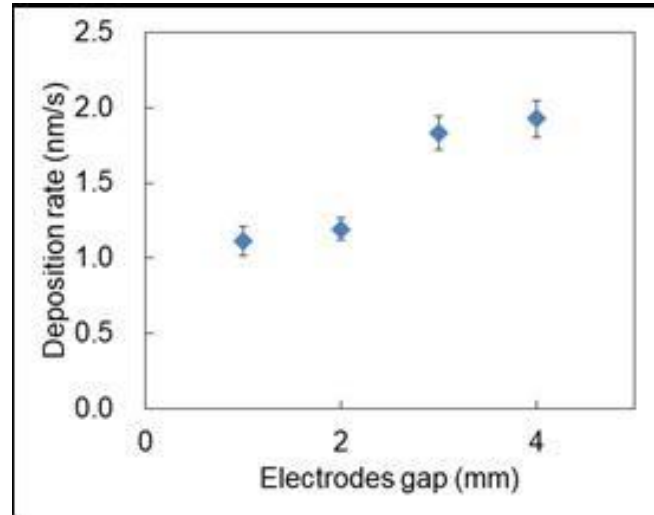
Figure 4. Relationship between deposition rate and electrodes gap of DLHC films.

Figure 5 shows SEM micrographs of the cross-section of the DLHC films synthesized with 1 mm and 4 mm of electrode gaps. The thicknesses of the DLHC films were coordinated to ca. 500 nm by adjusting the time of deposition. A smooth surface without the powder formation was confirmed on the DLHC 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 DLHC films were uniformity produced. This is because the streamers shift from a higher resistivity point to a lower resistivity point on the surface in accord with the deposition of insulating DLHC.
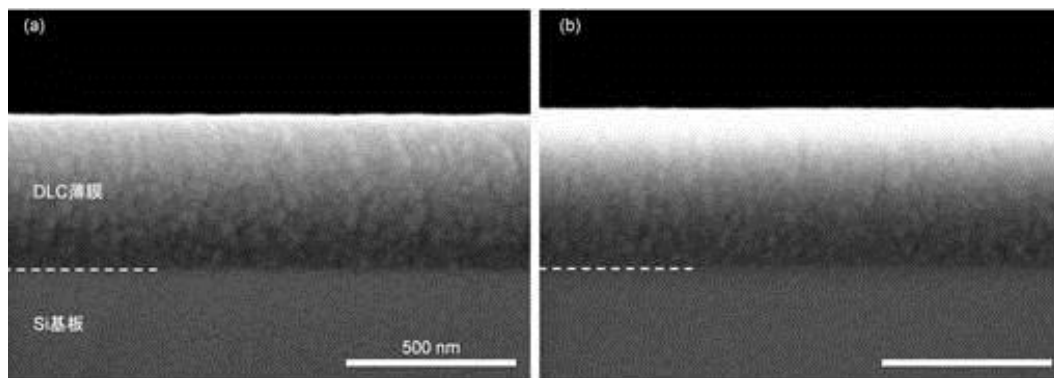

Figure 5. SEM images of cross-section of DLHC films.

Electrodes gap: (a) 1 mm; (b) 4 mm.

The hardness of the DLHC films as a function of the electrodes gaps is shown in Figure 6. When the electrodes gap increased from 1 mm to 3 mm the hardness of the films increased from 3.7 GPa to 11.9 GPa. The hardness became constant when the electrodes gap was increased to 4 mm. These results indicate that the DLHC films deposited by FDBD are harder than those deposited by GDBD.

The hardness of DLHC films using GDBD is reported to be achieved at 3 GPa[16-17]. The Raman spectra (not shown) of the DLHC films with various electrodes gaps showed that higher background intensity of the photoluminescence due to the polymeric structure with high content of hydrogen for the electrodes gaps of 1mm and 2mm. In contrast, when the electrodes 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.
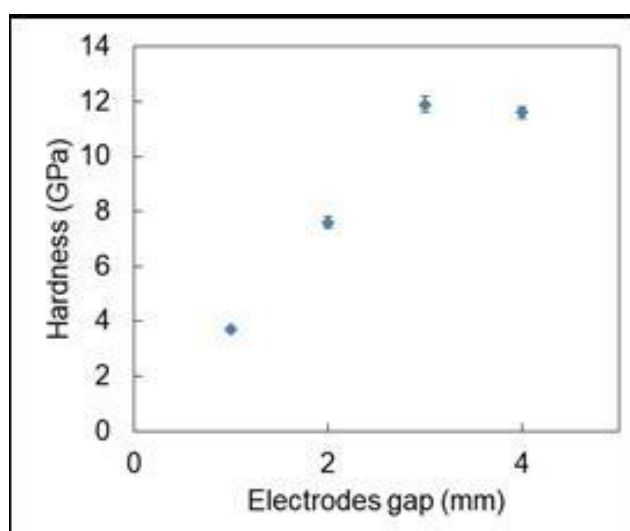
Figure 6. Relationship between hardness of the DLHC films and electrodes gap.

4. Conclusions

Hard DLHC films were synthesized at room temperature using FDBD with various electrodes gaps under atmospheric pressure. The form of discharge was transitioned from GDBD to FDBD with an increase of 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 DLHC films increased from 3.7 GPa to 11.9 GPa with increasing the electrodes gap from 1 mm to 3 mm.

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