



# Synthesis of diamond-like carbon films on Si substrates by photoemission-assisted plasma-enhanced chemical vapor deposition

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## ABSTRACT

Diamond-like carbon (DLC) films grown by photoemission-assisted plasma-enhanced chemical vapor deposition (PA-PECVD) have attracted attention as a gate insulator for graphene-channel field effect transistors (GFETs). In this study, the possibility of using PA-PECVD to grow insulating DLC films for GFETs is explored by focusing on the growth rate and uniformity of DLC films on Si substrates. Initially, the DLC films were formed at a constant rate but the growth rate decreased rapidly when the thickness reached approximately 400 nm. This is because of a decrease in photoelectron emissions from the Si substrates as they are covered by DLC films which absorb UV photons. However, the DLC films formed uniformly at thicknesses less than 16%. This result indicates that PA-PECVD is a promising method for growing DLC films as the gate dielectric layer of GFETs.

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## 1. Introduction

Because of its high electron mobility [1], graphene is a suitable substance for use in graphene-channel field effect transistors (GFETs) [2,3]. Currently, both top-gate transistors, made by the formation of gate dielectric films on graphene [2,4], and back-gate transistors, made by the transfer of graphene to insulator films such as SiO<sub>2</sub> [3,5], have been proposed. From a practical viewpoint, top-gate GFETs have an advantage over back-gate GFETs because the transfer process is not necessary. Recently, top-gate GFETs using HfO<sub>2</sub> [6] and Al<sub>2</sub>O<sub>3</sub> [7,8] as the gate dielectric films have been reported. However, these GFETs have not yet utilized the high carrier mobility of graphene because oxygen atoms in the dielectric films break the  $\pi$  bonds of graphene. To solve this problem, oxygen-free insulating materials should be used for GFET gate dielectric films. One such candidate is diamond-like carbon (DLC) [9]. DLC is composed of only carbon and hydrogen, and its band gap can be changed by changing the concentration of hydrogen from 1 to 4 eV [10,11]. DLC is one of the most suitable materials for use as the gate dielectric film for GFETs.

There are two methods for growing DLC: chemical vapor deposition (CVD) [12] and physical vapor deposition (PVD) [13]. However, a large amount of soot is generated in the PVD process. Consequently, PVD is not appropriate for the formation of gate DLC films in a clean room. Furthermore, the traditional plasma-enhanced CVD method is also not applicable for growing gate DLC. In the traditional plasma process, such as RF- and microwave-excited plasmas, the plasma is generated throughout

the chamber, which leads to soot being deposited on the chamber wall. In addition, high-power RF- and microwave-excited plasmas break graphene channels. To solve these problems, a plasma-enhanced CVD process which causes limited damage to the graphene channels and generates plasma localized near the substrate to avoid soot deposition on the chamber wall is required. Photoemission-assisted plasma-enhanced CVD (PA-PECVD) [14–16] can satisfy these demands. Photoemission-assisted (PA) plasma, which is a DC discharge plasma combined with UV irradiation, can only be generated near the substrate. UV irradiation causes photoemission from the substrate. Photoelectrons are accelerated by an electric field between the counter electrode and the substrate, leading to the dissociation of gases. Films grow after the dissociated radical species reach the substrate. Furthermore, the plasma can be generated with low bias voltage (under 200 V) and low power consumption (typically under 5 W) [14], leading to the low kinetic energy and flux of positive ions which reduces the amount of ion damage; hence, the plasma damage to graphene is smaller than that from other plasmas. We have used the PA-PECVD method to grow DLC for GFET gate dielectric films [9].

However, when an insulating DLC film is grown on a substrate, it is expected that PA-plasma will not be maintained on the substrate because photoemission from an insulating DLC film is much smaller than that from a conductive substrate. In case of thin DLC films, photoelectrons can be emitted from the substrate through DLC by the tunnel effect. However, it is not clear how thick DLC films can be grown using PA-PECVD. In this study, experiments for observing DLC growth on Si substrates were performed. The thickness limit for insulating DLC films grown by PA-PECVD was obtained from the thickness dependence of growth time. Based on these experimental results, the possibility of DLC growth for gate dielectric films using PA-PECVD was demonstrated.

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## 2. Experimental methods

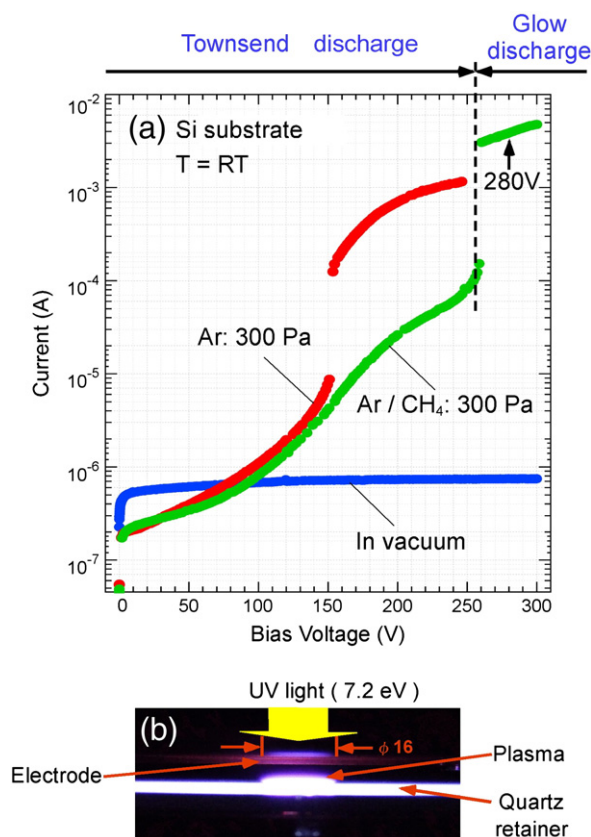
DLC growth experiments were performed using a PA plasma apparatus [14–16]. The wavelength of UV light for photoemission is 172 nm. In order to prevent photoemission from a substrate holder, the sample was retained using a torus-shaped quartz retainer, which allowed the plasma to be generated only on the substrate. The diameter of the inner hole of the quartz retainer was 16 mm. The substrate for DLC growth was a high As-doped low-resistivity Si(001) wafer, with an area of  $25 \times 25 \text{ mm}^2$ . These Si substrates were treated by a simple RCA cleaning method [17] before being introduced into the CVD chamber. After the substrate was introduced, it was irradiated by Ar plasma to remove contaminants. The Ar plasma condition is as follows: bias voltage  $V_B = 250 \text{ V}$ , Ar pressure = 200 Pa, and maximum discharge current = 250  $\mu\text{A}$ . After cleaning using the Ar plasma, DLC was grown on the substrate using Ar-diluted  $\text{CH}_4$ . The flow rates of Ar and  $\text{CH}_4$  were 50 and 10 sccm, respectively, and the total pressure was 300 Pa. No heating of the substrate was performed. The growth period was changed from 5 to 600 s to investigate the DLC growth rate.

The chemical configuration of DLC was evaluated using microscopic laser Raman spectroscopy (SPEX 500M, HORIBA Jobin Yvon). The observations were conducted with an excitation light of 488 nm from an  $\text{Ar}^+$  ion laser at an output power of 0.3 W. The thickness of the DLC films was measured using a stylus profilometer (DEKTA 3030 ST, Sloan) and atomic force microscopy (NPX200, SII). The AFM measurements were performed in the contact mode using an exclusive cantilever (NPX1CTP003) whose spring constant is 4 N/m.

## 3. Results and discussion

Bias voltage  $V_B$  dependencies of interelectrode current  $I_p$  ( $I_p$ – $V_B$  characteristics) in vacuum, Ar, and Ar-diluted  $\text{CH}_4$  atmospheres under the UV irradiation are shown in Fig. 1(a).  $I_p$  increased rapidly in vacuum with  $V_B$  up to 5 V and then saturated at approximately  $7 \times 10^{-7} \text{ A}$  independent of  $V_B$ . In contrast,  $I_p$  increased exponentially with  $V_B$  in Ar and Ar-diluted  $\text{CH}_4$  atmospheres.  $I_p$  in the Ar atmosphere showed rapid increase when  $V_B$  was increased further, i.e.,  $V_B = 154 \text{ V}$ . This result can be interpreted based on  $\alpha$  and  $\gamma$  regimes. The  $\alpha$  regime is the ionization process by the collisions between free electrons accelerated by electric field and gas atoms/molecules. The secondary electrons are emitted in the ionization process and then the current increases. By increasing  $V_B$ , the amount of positive ion and free electron between electrodes also increases, so that  $I_p$  increases in Fig. 1(a). The rapid increase of  $I_p$  at  $V_B = 154 \text{ V}$  is due to the  $\gamma$  regime. The  $\gamma$  regime [18] is that electrons are emitted from a cathode by impingement of the positive ions with the cathode via Auger exciting process. When the enough amount of positive ions is generated, the self-sustained discharge starts because emitted electrons by the  $\gamma$  regime generate the enough positive ion by the  $\alpha$  regime. This self-sustained discharge is named as “glow discharge”. In the glow discharge, the amount of emitted electron from the cathode by the  $\gamma$  regime is much larger than that by the UV irradiation from Xe excimer lamp, so that  $I_p$  shows rapid increase. In the low  $V_B$  region under  $V_B = 154 \text{ V}$ ,  $I_p$  is smaller than it in the glow discharge mode. Therefore, this discharge manner is “Townsend discharge”. In this region, there are not enough secondary electrons emitted from the cathode by the  $\gamma$  regime for the self-sustained discharge. This exponential increase in  $I_p$  indicates that the  $\alpha$  regime occurs. We named this plasma, maintained by UV irradiation and  $\alpha$  regime, photoemission-assisted Townsend (PAT) discharge plasma. In the traditional DC discharge, Townsend discharge mode has been interpreted as the current increase by an avalanche multiplication. In the PAT discharge region, the electrons increase also by the avalanche multiplication.

The same trend of  $I_p$ – $V_B$  characteristics was observed in the Ar-diluted  $\text{CH}_4$  atmosphere, but the transition voltage from PAT discharge to glow discharge was 255 V, which was larger than that in the Ar atmosphere. This is because of the difference in the degree of ionization. Since Ar has



**Fig. 1.** Bias voltage  $V_B$  dependence of interelectrode current  $I_p$  in vacuum, Ar, and Ar-diluted  $\text{CH}_4$  atmospheres under the UV irradiation. Discharge phase changes from Townsend discharge to glow discharge at 255 V in Ar-diluted  $\text{CH}_4$  atmosphere. (b) Photograph of photoemission-assisted glow discharge plasma in Ar-diluted  $\text{CH}_4$  atmosphere ( $V_B = 280 \text{ V}$ ). Plasma is generated only on the center of the torus-shaped quartz retainer.

no vibrationally and rotationally excited state, the collision that occurred between the Ar atoms and the electrons was primarily elastic. Therefore, the electrons could easily reach kinetic energy levels sufficient for ionization. As a result, the Ar atom is easily ionized even with low  $V_B$ . In contrast, the  $\text{CH}_4$  molecules become not only vibrationally and rotationally excited but also dissociative, such as  $\text{CH}$ ,  $\text{CH}_2$ , and  $\text{CH}_3$  [19]. Therefore, the electrons lose energy through the excitation and dissociation of  $\text{CH}_4$ . Consequently, high  $V_B$  is required for the ionization of the Ar-diluted  $\text{CH}_4$  atmosphere. In addition,  $I_p$  in Ar and Ar/ $\text{CH}_4$  atmospheres is smaller than it in vacuum under the low  $V_B$  region ( $V_B < 80 \text{ V}$ ). This is due to “space charge effect”. The  $\alpha$  regime does not occur at low  $V_B$  less  $V_B = 20 \text{ V}$  because the energy of photoelectron is smaller than ionization energy of Ar. The emitted photoelectrons are accumulated near the substrate by the elastic scattering with Ar atoms. The accumulated electrons prevent photoelectrons from emitting the photoelectrons. This is called “space charge effect”. The cross-section of elastic scattering between electrons and Ar atoms is also large over  $V_B = 20 \text{ V}$  region, however  $I_p$  increases exponentially by the  $\alpha$  regime.

As shown in Fig. 1(b), the PA glow discharge plasma is generated only on the substrate. Without UV light irradiation, the glow discharge occurs not only on the substrate but also below the sample holder. The purpose of this study is to obtain the limit thickness of DLC growth. Therefore, DLC growth was performed using the PA glow discharge ( $V_B = 280 \text{ V}$ ).

Fig. 2(a) shows the growth time dependence of the DLC thickness. For relatively short growth times, i.e., below 220 s, the thickness was proportional to the growth time. In this timeframe, the growth rate GR was obtained as 1.75 nm/s. However, the growth rate decreased significantly after 220 s and was 0.002 nm/s. The Raman spectra and photographs of the DLC films grown for 20, 60, and 120 s are shown

in Fig. 2(b), (c), and (d), respectively. In the Raman spectra, very broad G and D bands can be observed at  $1360$  and  $1520\text{ cm}^{-1}$ , respectively. These band spectral features are characteristic of DLC films [10,11]. On the other hand, a sharp peak located at  $950\text{ cm}^{-1}$  is harmonic overtone peak due to the Si substrate. Furthermore, the DLC films showed varied colors from blue, green, to red (pictures are not shown). This is the interference colors between the DLC surface and DLC/Si interface. This indicates that grown DLC is optically transparent. From these results, it is determined that DLC films can be grown on Si substrates using PA-PECVD.

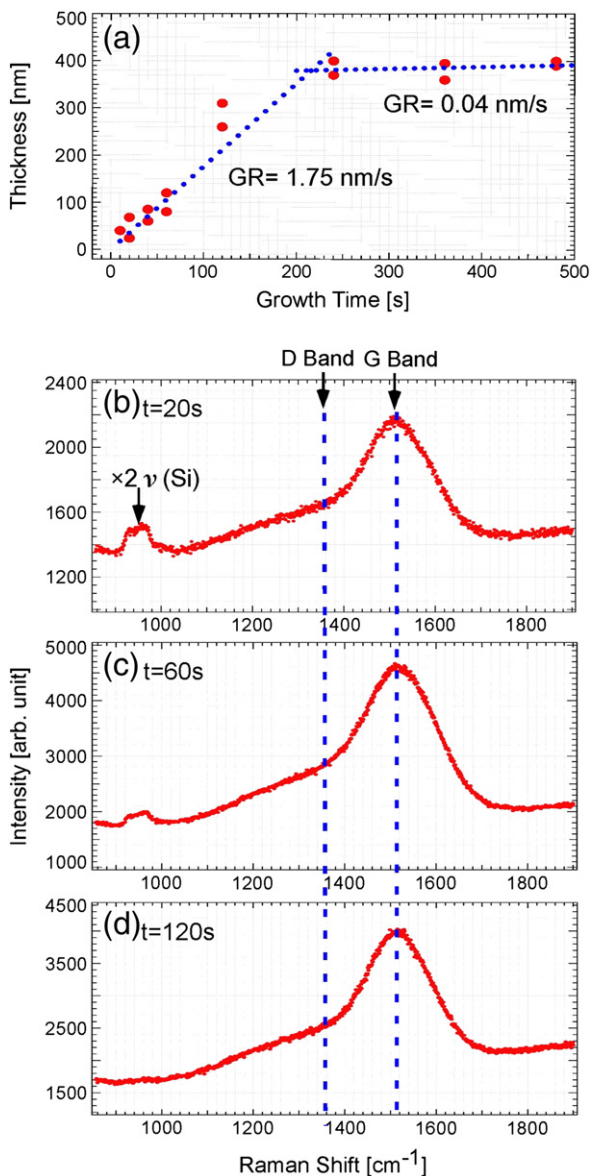
We also investigated the time dependence of  $I_p$  during DLC growth, as shown in Fig. 3(a), in order to clarify the reason for the growth rate decrease shown in Fig. 2(a). Immediately after the CVD growth started,  $I_p$  decreased from  $5 \times 10^{-3}\text{ A}$  relative to the growth time. Then  $I_p$  suddenly decreased to  $1 \times 10^{-4}\text{ A}$  at  $240\text{ s}$ . In order to confirm the correlation between the  $I_p$  and growth rate, the electric charge (integration of  $I_p$  with respect to the growth time) dependence of growth rate is shown in Fig. 3(b). The thickness is proportional to the electric charge, indicating the growth rate should be gradually decelerated with the gradual decrease of  $I_p$ . Therefore, it is found that decrease in  $I_p$  is concurrent

with decrease in growth rate. It is thought that  $I_p$  decrease because the  $\gamma$  coefficient is different. When the thickness of DLC films reaches about  $400\text{ nm}$ ,  $I_p$  decreases suddenly. This decrease of  $I_p$  indicates that the discharge manner changes from PA glow discharge to PAT discharge. Amazingly, the cause of growth rate decrease at about  $400\text{ nm}$  is not charging up of the DLC films, because PA glow discharge plasma can be generated again by the further  $V_B$  increasing ( $V_B = 352\text{ V}$ ). However, the grown DLC films are not conductive, its resistivity cannot be measured using our four-probe measurement system (over  $10^5\text{ }\Omega\text{ cm}$ ). The reason of decrease of the  $\gamma$  coefficient at  $400\text{ nm}$  of thickness has not been cleared yet, but insulating DLC films can be formed using PA-PECVD. Here, we should consider the emission pass of photoelectrons during PA-PECVD growth on the DLC surface. The UV light is absorbed by DLC films and photoelectrons are emitted by DLC surfaces. As the results, DLC takes positive charge because DLC is insulator. When the DLC film is formed on the Si surface, the valence electrons of Si are excited and injected into the conduction band of DLC, leading to the dissolution of the DLC charge up.

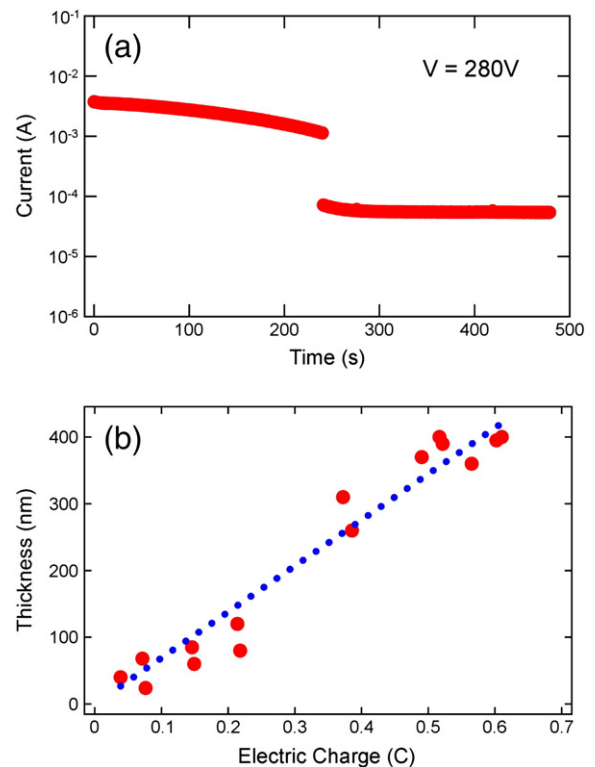
Finally, the cross-sectional line profile of a DLC film grown for  $120\text{ s}$  is shown in Fig. 4. The thickness at the center of the film is approximately  $300\text{ nm}$  and the maximum thickness is approximately  $350\text{ nm}$ . From this result, it is concluded that DLC films can be grown with 16% dispersion of thickness.

#### 4. Conclusion

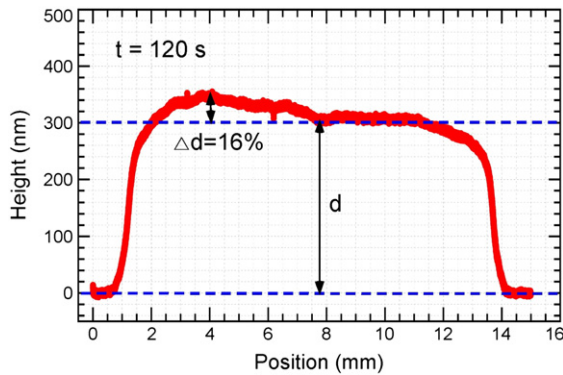
In this study, the possibility of using photoemission-assisted plasma CVD (PA-PECVD) for growing insulating DLC film for GFETs was explored from the viewpoints of growth rate and uniformity of the DLC films on the Si substrates. The PA glow discharge plasma disappears after growing the DLC film on the Si surface, but photoelectrons are emitted from the DLC surface by UV irradiation. The DLC films which have enough thickness can be grown using PA-PECVD. Furthermore, the smallest dispersion of DLC thickness was 16%. Therefore, the PA-PECVD method is applicable



**Fig. 2.** (a) Growth time dependence of DLC thickness. Growth rate (GR) changes from  $1.75\text{ nm/s}$  to  $0.02\text{ nm/s}$  at  $220\text{ s}$ . Raman spectra and photographs of DLC films grown for (b) 20, (c) 60, and (d) 120 s.



**Fig. 3.** (a) Time dependence of discharge current during DLC growth on the Si substrate. (b) Electric charge (integration of  $I_p$  with respect to the growth time) dependence of the film thickness.



**Fig. 4.** Cross-sectional line profile of DLC film grown for 120 s. The thicknesses shown in Fig. 2(a) are the values at the center of the films.

for growing DLC films as gate insulators. This suggests that future work should attempt to decrease dispersion of thickness and investigate the electrical properties of grown DLC films.

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