



# Dependence of the features of diamondlike carbon films on their synthesis methods, as analyzed by Raman spectroscopy



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## ABSTRACT

The dependence of features of diamondlike carbon (DLC) films on their synthesis methods were clarified by Raman spectroscopy. The DLC films were synthesized by three different methods: photoemission-assisted glow discharge (PAGD), ionized deposition (ID), and unbalanced magnetron sputtering (UBMS). The main difference among these methods was the influence of ions on film formation. Raman analysis in conjunction with the  $sp^2$  cluster model led to the elucidation of each film structure. The DLC film synthesized in PAGD with efficient ion assist consisted of dispersed, small, and unstrained  $sp^2$  clusters surrounded by a dielectric matrix of  $sp^3$  carbon. The clusters were aliphatic, which reflects the methane gas source; however, hydrogen atoms were etched away to some extent because of bond rearrangement caused by the ion assist. The  $sp^2$  clusters synthesized by ID were well-grown aromatic clusters, which reflect the benzene gas source; however, the clusters contained certain amounts of defects, and sufficient electrical isolation occurred among the clusters. The well-grown  $sp^2$  clusters caused weak internal strain of the film. In UBMS without the ion assist, strongly strained  $sp^2$  clusters that included numerous defects from damaged graphite (polyaromatic) radicals by sputtering were created. The density of the clusters was high, and the film was conductive. The defects were removed by introducing methane as a second hydrocarbon source during the synthesis. However, the strain was enhanced further in conjunction with the defect removal.

## 1. Introduction

Carbonaceous materials consist of various structures and bond networks. The constituents are infinite aliphatic chains and polyaromatic rings composed of  $\pi$ -conjugated  $sp^2$ -carbon bonds, dielectric  $sp^3$ -carbon bonds, and hybrid bonds of both. The combination of  $sp^2$  carbon,  $sp^3$  carbon, and other elements is versatile. To resolve such an entanglement is surely difficult but is an attractive objective for enhancing our understanding of these materials.

Diamondlike carbon (DLC) is a nearly ideal specimen because it is composed entirely of  $sp^2$  carbon,  $sp^3$  carbon, and hydrogen atoms [1,2]. Because DLC is amorphous, it possibly contains a combination of bonds and network structures. DLC has been mainly used as a coating material with very low friction and excellent bio-compatibility for industrial and medical products [3,4]. However, the relationship between such application characteristics and the ratio of the three components (i.e.,  $sp^2$

carbon,  $sp^3$  carbon, and hydrogen) is not always clear, and each DLC film is still synthesized empirically. One of the reasons for this lack of clarity is that the film growth mechanism to which the three components contribute is complicated; another reason is that analysis of the amorphous structure is difficult [2].

Raman spectroscopy is a nondestructive method capable of detecting characteristic carbon solid-state structures and is one of the most popular methods for DLC analysis [5,6]. We have recently analyzed DLC films by Raman spectroscopy and have clarified their structure using our  $sp^2$  cluster model [7]. In the present work, we analyze DLC films synthesized by different methods and clarify the relationship between their structural features and their synthesis method.

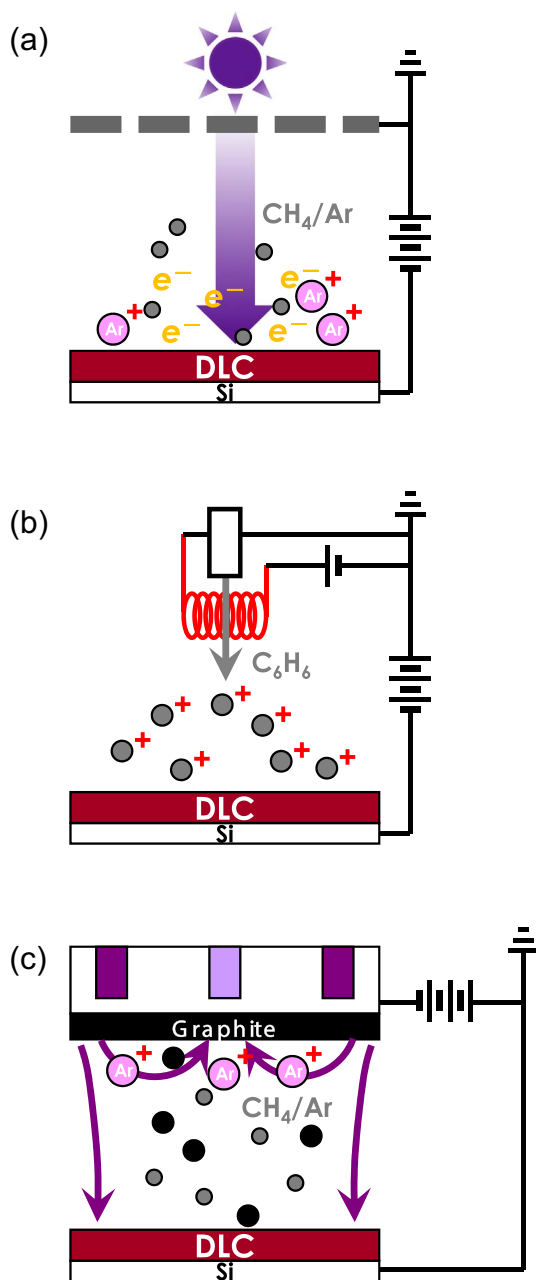
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**Fig. 1.** Schematics of the synthesis methods: (a) PAGD, (b) ID, and (c) UBMS. Gray balls indicate carbon sources: radicals in (a) and (c) and ions in (b). In (a), a UV light source is positioned over the anode, which has a duckboard-like structure to pass UV irradiation to the silicon substrate. In (b), the filament anode (red) is located above the gas outlet. In (c), strong magnets (deep purple) are placed at the both sides under the cathode with a graphite target, and a weak magnet (light purple) is placed at the center. Purple lines indicate the magnetic field. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

## 2. Experimental

Five kinds of DLC films were synthesized by three methods: one by photoemission-assisted glow discharge (PAGD) [8], one by ionized deposition (ID) [9,10], and three by unbalanced magnetron sputtering (UBMS) [11,12]. Fig. 1 shows schematics of these methods.

The PAGD is a glow discharge of photoemission-assisted plasma-enhanced chemical vapor deposition (PA-PECVD). An advantage of PA-PECVD over conventional PECVD systems is that, instead of a few accidental electrons, numerous photoelectrons are emitted from the substrate under UV irradiation and function as initial electrons. The UV

light source is located over the anode, which has a duckboard-like structure to pass UV radiation to the substrate. With the aid of numerous photoelectrons, the discharge can be regularly controlled. PA-PECVD has two discharge modes: PAGD and photoemission-assisted Townsend discharge (PATD) [13–15]. In the former mode, an ion sheath is formed via a strong electric field at the substrate cathode and the growth rate is sufficiently high for coating applications (on the order of 100 nm/min) [16]. In the present experiment, a DLC film was synthesized on a silicon substrate in PAGD under an atmosphere of methane/argon = 20/100 sccm at 300 Pa and room temperature [16]. This DLC film was designated as a “PA-DLC” film.

ID is a traditional method for DLC synthesis. The source gas is ionized by thermoelectrons emitted from the filament anode located over the gas outlet. The ions are accelerated by an appropriate negative DC bias voltage to reach the substrate cathode, where a DLC film is formed. In the present experiment, the DLC film was synthesized on a silicon substrate with a DC voltage of  $-2.0$  kV in an atmosphere containing benzene at  $200$  °C [17,18]. The obtained film was designated as an “ID-DLC” film.

UBMS is an improved magnetron sputtering method involving an unbalanced magnetic field. Strong magnets are placed at both sides under the cathode with a target material, and a weak counter magnet is placed at the center. The unbalanced magnetic field from the cathode reaches the substrate anode to affect film formation process. In the present experiment, the film source was fragmented polyaromatic radicals from the graphite target sputtered by argon ions. To tune the film characteristics further, a certain amount of methane was added to each synthesis atmosphere as a second hydrocarbon source [19]. The DLC films (UBMS-DLC films) were synthesized in atmospheres with methane/argon ratios of 0/100, 6/100, and 12/100; the obtained films were designated as “UBMS-0-DLC,” “UBMS-6-DLC,” and “UBMS-12-DLC” films, respectively.

After growth, Raman spectra of all the DLC films were collected in air and at room temperature using a system consisting of a spectrometer (SPEX 500M, HORIBA–Jobin Yvon) and an argon-ion laser with an output power of 0.3 W and an emission wavelength of 488 nm.

## 3. Results and discussion

Fig. 2(a) shows the Raman spectra of the PA-DLC, ID-DLC, and UBMS-12-DLC films. The background intensity of each spectrum was subtracted by a straight line connecting the edges of the spectrum, and the spectral intensity was then normalized to the height. Every spectrum includes a peak at approximately  $1550$   $\text{cm}^{-1}$ , where the G band is typically located. However, a slight shift is observed among the spectra. Their shoulder lineshapes in the region near  $1350$   $\text{cm}^{-1}$ , where the D band is typically located, obviously differ.

Fig. 2(b) shows the Raman spectra of three types of UBMS-DLC films. The spectrum of the UBMS-12-DLC film is identical to that in Fig. 2(a). The D band shoulder becomes increasingly prominent with decreasing amount of methane added to the synthesis atmosphere as a second carbon source. Moreover, the spectra become asymmetric. This variation implies that a new band emerges between the D and G bands.

Fig. 3 shows the background slopes of the aforementioned Raman spectra. Adamopoulos et al. reported [20] a positive correlation between the hydrogen content in DLC films and the slope of the background line of their Raman spectrum. When the hydrogen content in a DLC film increases, hydrogen atoms terminate trap sites or tail states of the optical gap, which enhances the photoluminescence [21,22]. In the present work, the maximum slope is obtained for the ID-DLC film, demonstrating that the film contains a large amount of hydrogen; this result is attributed to the reactants being benzene ions and its fragmented ions. The source used for the PA-DLC film was methane, whose 4:1 hydrogen-to-carbon atomic ratio is substantially greater than the 1:1 ratio of benzene but whose resultant slope is small. This result is attributed to the influence of argon ions accelerated in the sheath

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