

Preparation of various DLC films by T-shaped filtered arc deposition and the effect of heat treatment on film properties

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ABSTRACT

Keywords:

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Various diamond-like carbon (DLC)

Tetrahedral amorphous carbon (ta-C)

Heat resistance

Different types of diamond-like carbon (DLC) films (ta-C, a-C, ta-C:H and a-C:H) were prepared on super hard alloy (WC-Co) substrate using a T-shape filtered arc deposition (T-FAD) system. At first, the film properties, such as structure, hydrogen content, density, hardness, elastic modulus, were measured. Ta-C prepared with a DC bias of -100 V showed the highest density (3.1 g/cm^3) and hardness ($70\text{--}80 \text{ GPa}$), and the lowest hydrogen content (less than $0.1 \text{ at. \%}$). It was found that the hardness of the DLC film is proportional to approximately the third power of film density. The DLC films were then heated for 60 min in an electric furnace at 550°C in N_2 . Only the ta-C film hardly change its structure, although other films were graphitized. The 200-nm thick ta-C film was then heated for 60 min through the temperature range from 400 to 800°C in N_2 with $2 \text{ vol.\%}$ of O_2 and the film structure found to be stable up to 700°C . The substrate was oxidized at 800°C , indicating the ta-C film had a thermal barrier function up to that temperature.

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1. Introduction

Amorphous carbon, well known as diamond-like carbon (DLC), is an interesting material and has attracted more and more attention recently. Many properties change depending on the sp^2/sp^3 ratio, hydrogen (H) content, and amorphousness. DLC is typically classified into four types: hydrogen-free tetrahedral amorphous carbon (ta-C), hydrogen-free amorphous carbon with lower tetrahedral fraction (a-C), hydrogenated ta-C (ta-C:H), and hydrogenated a-C (a-C:H) [1,2]. For example, ta-C has higher electrical resistivity, although a-C is conductive since it is somewhat graphitized. It is necessary to choose the appropriate type of DLC for the specific application. In recent years, ta-C has especially been the focus in various application fields [2]. One of the applications is utilization at high temperature, such as a protective coating for press molds [3]. Therefore, the high-temperature stability of the film should be investigated.

DLC film can be prepared by a variety of methods, including plasma CVD [4], ion beam plating (hot filament-assisted ionized-gas deposition) [5], balanced and unbalanced magnetron sputters

[6], and cathodic vacuum arc deposition [7]. Cathodic vacuum arc deposition is only one method to prepare four kinds of the DLC mentioned above. However, the problem is that micron and/or sub-micron droplets are emitted from the cathode spot of the vacuum arc discharge and adhere to the film. In order to remove the cathode droplets from the cathodic arc plasma, the filtered arc method [8] has been developed, where the cathodic plasma is magnetically transported through a curved or bent duct. The droplets are trapped at the duct wall, when they are in molten form. However, since the droplets emitted from the graphite cathode are in the solid phase, filtration by the conventional filtered arc system is practically difficult. One of present authors has recently developed the T-shape filtered arc deposition (T-FAD) system [9,10], in which the droplets are separated from the plasma at the 90° -degree bent position. In the present study, different types of DLC films were prepared by T-FAD. The principal properties of the films were analyzed, and the heat resistance of the films was investigated.

2. Preparation of various DLCs and characterization

Fig. 1 depicts the T-FAD system. The carbon plasma was generated between the graphite cathode and stainless steel anode, and clean carbon plasma transferring to the process chamber was

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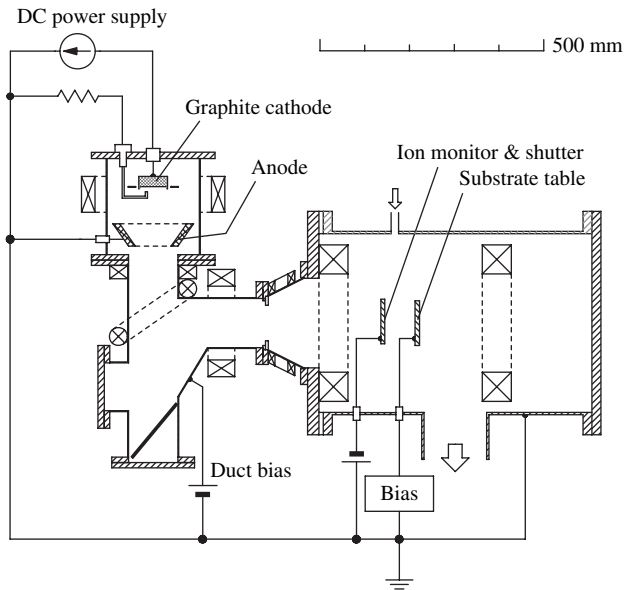


Fig. 1. Schematic diagram of T-FAD system.

obtained through a T-shape duct, where the cathode droplets were removed. Major conditions for preparing different types of DLC films are listed in Table 1. Hard and soft ta-C films were prepared without any gas introduction into the chamber and with DC and pulse bias, respectively. Relatively soft a-C was also prepared without any gas introduced and with pulse bias of higher voltage. Ta-C:H and a-C:H were prepared with hydrogen (H_2) and acetylene (C_2H_2) gases, respectively. The substrate used was super-hard alloy (tungsten carbide (WC containing cobalt (Co) binder), 12.7 mm $\times$ 12.7 mm, 5 mm thickness). All films were prepared at less than 100 °C. Film thickness was 150–400 nm.

The film thickness was measured with stylus surface profilers (Veeco, Dektak 3; and Panasonic, UA-3P). A structure and crystallinity analysis was made using a micro Laser Raman spectroscope (JASCO, NRS-1000: laser wavelength, 532 nm; resolution, 0.85 cm^{-1} ; laser spot radius, 4 μm ; laser power, 5 mW) and X-ray diffraction analyzer (XRD; Rigaku, RINT-2500: radiation source, Cu $K\alpha$). The H content in the film was analyzed with Rutherford Back-Scattering Elastic Recoil Detection Analysis (RBS-ERDA; National Electrostatics Corp., Model 5SDH-2 Pelletron Accelerator). The film density was analyzed with an X-ray Reflectometer (XRR; Philips, X'Pert PRO MRD). The hardness and elastic modulus were measured with nanoindenters (Elionix, ENT-2100; and Hysitron, Tribo Indenter).

High-temperature treatment was carried out in a self-developed heating system with an electric furnace, in which the ambient gas was controlled. In the system, the sample was quickly transferred into the heated furnace by a robot arm.

Table 1
Preparation conditions of various DLCs in T-FAD (arc current, 30 A)

Number	DLC category	Introduction gas	Substrate temperature (°C)	Process pressure (Pa)	Substrate bias (V)
1	ta-C(H)	Non	Less than 100	Less than 0.02	DC –100
2	ta-C(S)	Non	Less than 100	Less than 0.02	Pulse –100 ^a
3	a-C	Non	Less than 100	Less than 0.02	Pulse –500 ^a
4	ta-C:H	H_2	Less than 100	0.2	Pulse –100 ^a
5	a-C:H	C_2H_2	Less than 100	0.2	Floating

^a "ta-C(H)" and "ta-C(S)" indicate harder and softer ta-C, respectively.

^a Unipolar pulse, 10 kHz, duty 20%.

3. Properties of as-deposited DLCs

3.1. Deposition rate

The deposition rate, derived from film thickness and deposition time, is shown in Fig. 2. The deposition rate for ta-C:H film was relatively lower, since H_2 gas somewhat interfered with the carbon plasma reaching the substrate. Moreover, the film may be etched by H ion. The a-C:H film showed the highest deposition rate. This was considered to be the result of the PVD–CVD hybrid process [10], as the introduced gas of C_2H_2 was another carbon source. The deposition rates of ta-C and a-C film, which were prepared without any gas introduction, ranged between those of ta-C:H and a-C:H films.

3.2. Raman spectra

Raman spectra of the as-prepared films are shown in Fig. 3. In the figure, G and D represent the average values in general peaks of G-band (1580 cm^{-1}) and D-band (1360 cm^{-1}), respectively. The spectra were the hybrid band between G- and D-bands. These spectral shapes were in agreement with model shapes in the report by Robertson [2], indicating all of the films were amorphous.

3.3. Hydrogen content

The H content in atomic percent in as-prepared film is shown in Fig. 4. Ta-C and a-C film had very low H content. A small amount (1–2 at. %) of hydrogen detected in ta-C and a-C film was considered to have originated from the residual gas and/or water in the chamber, since for ta-C(H) preparation, the chamber was baked at 120 °C for 1 h, but not for ta-C(S) and a-C. This is indicated that it is important to remove the water from the chamber to prepare the DLC film with less hydrogen. The ta-C:H and a-C:H films have a considerable amount of H.

3.4. Density

Film density is shown in Fig. 5. Ta-C film had a considerably high density (3.1 g/cm^3) which is very close to the density of diamond 3.515 g/cm^3 [2]. Ta-C:H film had a lower density than a-C film. The lowest density was found in a-C:H film, as generally expected.

3.5. Hardness

The hardness and elastic modulus are shown in Figs. 6 and 7, respectively. The properties of diamond [2] are also indicated. Ta-C(H) film had the highest hardness, which was very close to the hardness of diamond. Ta-C:H film had a lower hardness than a-C film.

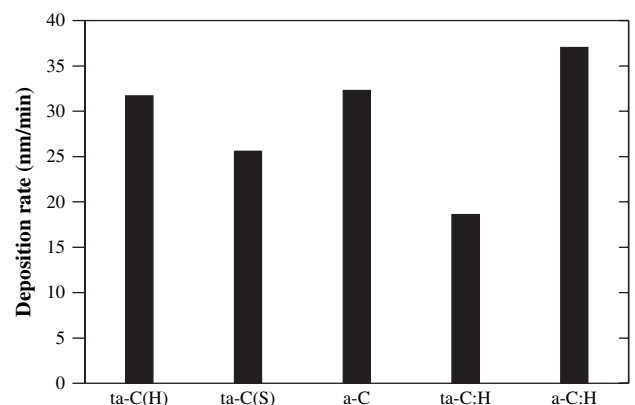


Fig. 2. Deposition rate of various DLC films.

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