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Characterization of Diamond-like Carbon Films Prepared by Magnetron Plasma Chemical Vapor Deposition

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Thin films of diamond-like carbon (DLC) can be successfully deposited by using a magnetron plasma chemical vapor deposition (CVD) method with an *rf* (13.56 MHz) plasma of C_3H_8. Plasma characteristics are analyzed as a function of the magnetic field. As the magnetic field increases, both electron temperature (T_e) and density (n_e) increase, but the negative dc self-bias voltage ($-V_{sb}$) decreases, irrespective of gas pressures in the range of 1~7 mTorr. High deposition rates have been obtained even at low gas pressures, which may be attributed to the increased mean free path of electrons in the magentron plasma Effects of *rf* power and additive gas on the structural properties of DLC films aer also examined by using various techniques, namely, TED (transmissio electron diffraction) microanalysis, FTIR, and Raman spectroscopies

Key words : Diamond-like carbon (DLC), Magnetron plasma CVD, Plasma diagnosis, Structural properties

I. Introcuction

The hard forms of amorphous carbon (*a*-C) and hydrogenated amorphous carbon (*a*-C:H) have recently aroused considerable interest due to their mechanical hardness, optical transparency, and chemical inertness. These carbons contain both sp^3 (diamond) and sp^2 (graphite) bonding sites. Their desirable properties arise from the sp^3 component of their bonding and these carbons are frequently called diamond-like carbon (DLC). In general, such carbons can be considered as fully amorphous or contain in crystalline inclusions.[1-3]

A variety of methods (i.e., ion beam, vacuum arc, laser ablation, sputtering, plasma)[4-6] employ energetic species to deposit DLC films. Common to all these methods is the deposition of DLC from particles whose energy is within the range of about 100 eV up to several keV. In addition, it appears that carbon films with diamond-like properties only form under high energy impact.[7]

In this paper we shall report on DLC films deposited from a hydrocarbon gas (C_3H_8) in an *rf* (13.56 MHz) magnetron plasma. This method offers an interesting application potential since a high rate of film growth can be achieved even at low gas pressures. Effects of the magnetic field on plasma characteristics have been examined and the growth mechanism will be discussed. The structural properties of DLC films prepared are systematically investigated using various methods as a function of the deposition conditions.

II. Experimentals

The parallel-type *rf* magnetron plasma CVD system used is schematically shown in Fig 1. The vacuum system consists of the vacuum chamber with an *rf* electrode, magnets, and power supplies. The powered electrode is subjected to a negative dc self bias ($-V_{sb}$). The permanent magnet of 700 Gauss/each placed on each side of the cathode produces a uniform magnetic field over the substrate.

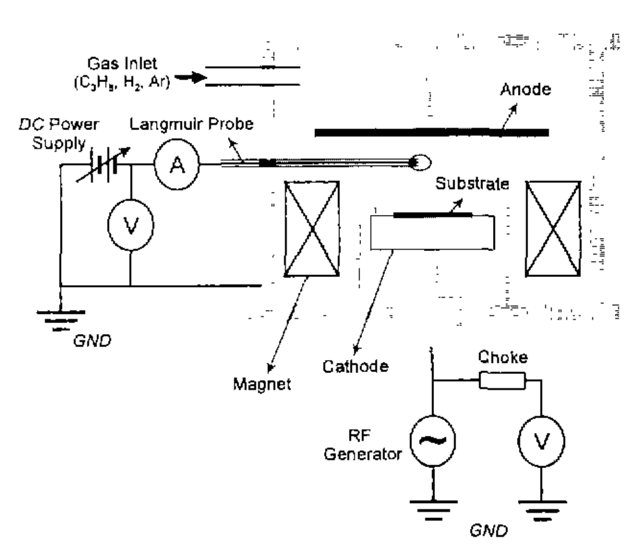

Fig. 1. Schematic diagram of a magnetron plasma CVD system.

Table. 1. Deposition Conditions to Prepare DLC Films

base pressure	$<10^{-6}$ Torr
working pressure	1.8, 6.3 mTorr
rf power	0~300 W
magnetic field	92 Gauss
substrate temperature	room temperature

The minimum magnetic field intensity required for electronic resonance to occur can be estimated from a theoretical expression[8] given by $f=eB/2m_e$ where f and B refer to the resonance frequency and the magnetic field intensity, respectively. Electrostatic Langmuir probe[9] measurement was used to analyze the plasma characteristics under a magnetic field. The probe bias and magnetic field were varied in the ranges of -100~250 V and 45~92 Gauss, respectively. The Ar gas was used as a discharge gas.

For film deposition, the system is first evacuated to a pressure less than 10^{-6} Torr by the diffusion pump and then a 15-min Ar discharge (100 W, 4.5 mTorr) is started in order to sputter clean the boron-doped Si (100) substrate. Subsequently, a hydrocarbon gas (C_3H_8) is leaked into the system via a mass flow controller. Other detailed deposition conditions used to prepare DLC films are summarized in Table 1.

The film thickness was measured using a surface profilometer (Esaki SR 3000) and the film desity was estimated by comparing the weight of Si before and after film deposition. The structural properties such as sp^3 fraction and the C-H bonding of DLC films were analyzed as a function of deposition conditions by measuring the Raman and FTIR spectra in the ranges of 100~1700 cm^{-1} and 400~4000 cm^{-1}, respectively. The effect of additive Ar gas during film deposition on the microscopic structure of DLC films is also examined by measuring TED (transmission electron microscopy) patterns.

III. Results and Discussion

A typical I-V characteristic of Langmuir probe is shown in Fig. 2. The saturated currents of electrons ($I_{e,sat}$) and ions ($I_{i,sat}$) increase as the magnetic field increases. This may be due to the fact that increasing magnetic field enhances the probability of collisions between gas molecules and electrons, thus increasing the number of electrons and ions.

The probe current consists of two components contributed by electrons and ions. The electronic current can be given[10] by

$$I_{probe}(V) = I_e(V) + I_i(V) \tag{1}$$

$$I_e(V) = I_{e\,sat}\exp(-eV/kT_e) \tag{2}$$

$$I_{e\,sat} = 0.25eN_eS\,(8kT_e/m_e)^{1/2} \tag{3}$$

From (3), S is the area of probe. The electron temperature (T_e) can be obtained from the slope of ln $[I_{probe}(V) - I_i(V)]$ vs. V plot, hence leading to the estimation of electron density (N_e). The estimated values of plasma parameters are summarized in Table 2 as a function of the magnetic field. It is clearly seen that both electron density and temperature substantially increase with the increasing magnetic field.

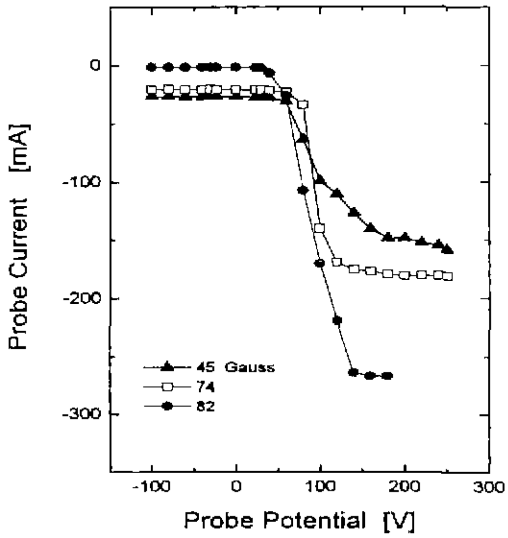

Fig. 2. Langmuir probe I-V characteristics as a function of magnetic field.

The most important parameter to deposit films using *rf* glow discharge is the sheath potential (V_s) between plasma and powered electrode. Neglecting the very small contribution of the plasma potential (V_p), V_s may be given by the negative dc self-bias (V_{sb}) and expressed[11] by (4) where V_{rf} is the magnitude of the *rf* bias.

$$V_{sb} = -V_{rf} + \frac{kT_e}{2e}\ln\left(\frac{2\pi eV_{rf}}{kT_e}\right) \tag{4}$$

To examine the effect of magnetic field on the deposition characteristics of DLC films, changes of the negative self-bias (V_{sb}), cathodic ion current (I_{cat}), and deposition rate have been measured as a function of magnetic strength. The results are shown in Fig. 3. At a fixed *rf* power, as the magnetic field increase both V_{sb} and I_{cat} substantially decrease, however, the growth rate monotonously increases.

It is obvious from (4) that the main reason for a significant decrease of V_{sb}-reduction, however, the growth

Table 2. Variations of Plasma Parameters as a Function of Magnetic Field

B (Gauss)	45	74	82
$\lvert I_{i,sat}\rvert$ (mA)	18.7	14.5	1.6
$\lvert I_{i,sat}\rvert$ (mA)	158	181	267
T_e (eV)	9.0	10.0	13.5
N_e ($\times 10^{10}$, 1/cm^3)	3.2	4.2	11 3

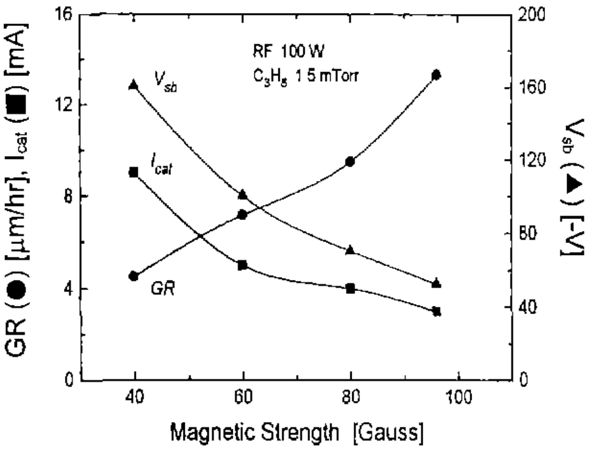

Fig. 3. Variations of self bias (V_{sb}), cathodic ion current (I_{cat}), and growth rate (*GR*) as a function of magnetic field.

rate increase with the magnetic field. This may be due to the fact that higher density of electrons and ions can be obtained when a higher magnetic field is applied. It is also interesting to note that a dense magnetron plasma renders the *rf* discharge stablility and the film growth even at a low gas pressure of about 1.5 mTorr.

Fig. 4 shows the variation of self bias, growth rate, and film densit as a function of *rf* power which varies from 20 W to 200 W. The dc self bias, as expected, increases with increasing rf power. A larger V_{sb} is observed at a higher pressure, which is not in the case of a conventional plasma. It may be conjectured that the chamber pressure used to grow DLC films in this experiment is low enough for gas molecules to be fully ionized within the sheath.

The growth rate and density of DLC films first increase, but they are saturated or decreased when the *rf* power exceeds 140 W. This may be accounted due to the sputtering effect[12] on the deposited film surface of the bombardment of high-energy ions, which results in the removal of the bonded hydrogen. The highest growth rate and film density schieved under nominal conditions are about 4.8 μm/hr and 2.45 g/cm^3, respectively.

Fig. 5 shows Raman spectra of DLC films prepared under different *rf* powers and gas pressures. Two noticeable Raman bands are observed at around 1580 cm^{-1} (denoted by 'G-band') and 1350 cm^{-1} (denoted by 'D-band'), respectively. Although the exact correlation between Raman bands and microstructure of DLC films is not clear, it has been concluded in the literature[13] that the above two Raman bands originate from carbon clusters with and sp^2 (graphite-like) configuration. The results show that the intensity of 'D-band' is increased by increasing the *rf* power (200 W) and pressure (6.3 mTorr). This indicates that the carbon network in the DLC film becomes increasingly disordered and graphitized. Dehydrogenation due to either the effect of sputtering or that of local-heating by ion bombardment is believed to be responsible for the above result.

Reduction of hydrogen content at high *rf* power was also observed in FTIR spectra of those films. Typical C-H infrared absorptions of stretching mode in DLC films reported in the literature[13] are as follows; sp^3 CH_3

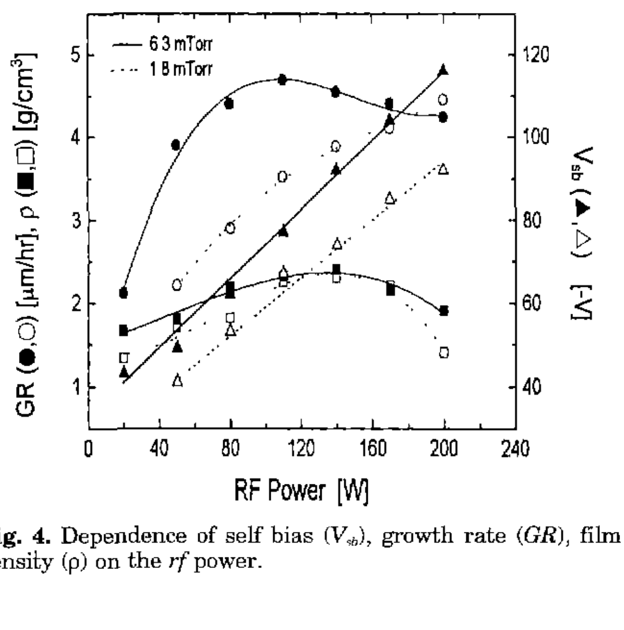

Fig. 4. Dependence of self bias (V_{sb}), growth rate (*GR*), film density (ρ) on the *rf* power.

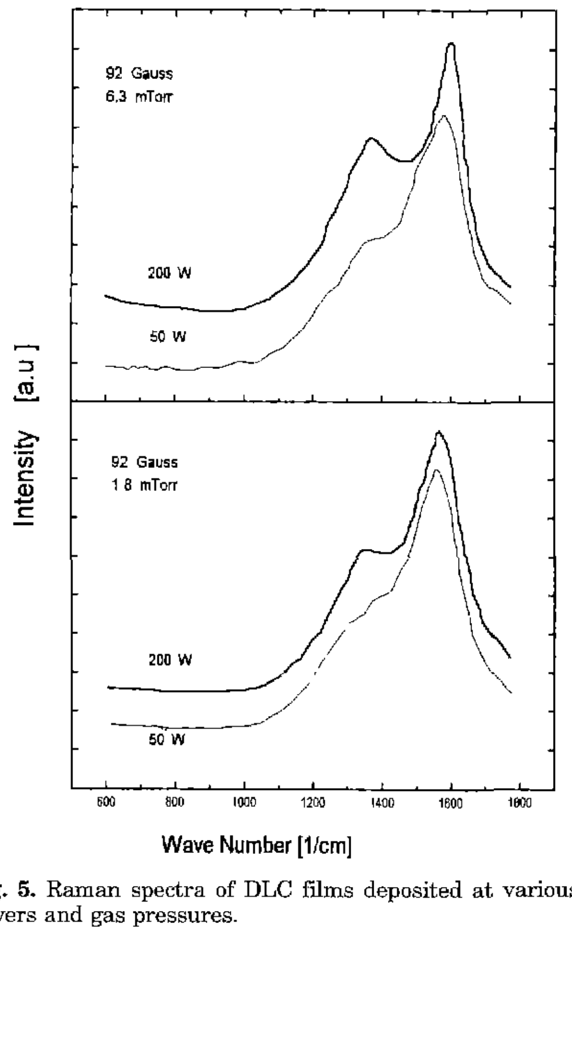

Fig. 5. Raman spectra of DLC films deposited at various *rf* powers and gas pressures.

(symmetric) at 2875 cm^{-1}, sp^3 CH_2 (asymmetric) at 2929 cm^{-1}, sp^3 CH_3 (asymmetric) at 2960 cm^{-1}, sp^2 CH_2 (olefinic) at 3025 cm^{-1}, and sp^3 CH (aromatic) at 2875 cm^{-1}. In general, the relative fraction of sp^3 configuration can be estimated by measuring the relative magnitude of absorption areas of peaks below 3000 cm^{-1} over those of peaks above 3000 cm^{-1}.

In addition, the bonded hydrogen content in the DLC films is determined by measuring the area of peaks between 2800~3100 cm^{-1}. The results shown in Fig. 6 indicate that most of DLC films prepared in this work have a sp^3 configuration. It is alsol found that the hydrogen content decreases with increasing *rf* power and gas pressure.

Several samples were prepared by injecting an Ar gas in addition to C_3H_8 gas during film deposition, in order to investigate the efect of additive gas on the microstructure of DLC films. For samples deposited either with Ar gas (C_3H_8/Ar=0.15) or without, transmission electron diffraction (TED) patterns were measured.

The gas pressure and *rf* power were kept at 6.3 mTorr and 200 W, respectively. Two TED patterns of those films are compared in Fig. 7. As seen in the photos, adding the Ar gas makes the area of bright center nearrower and the diffraction rings more obvious.

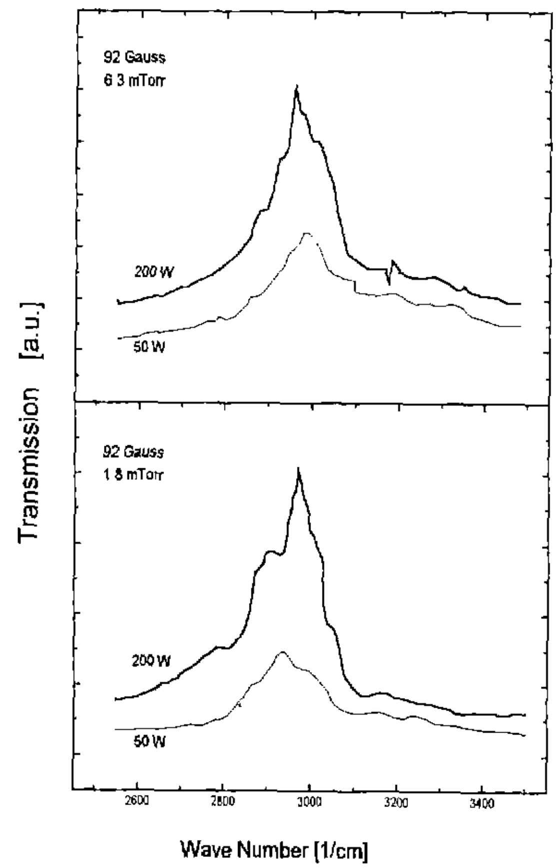

Fig. 6. FTIR spectra of DLC films deposited at various *rf* powers and gas pressures.

(a)
(b)

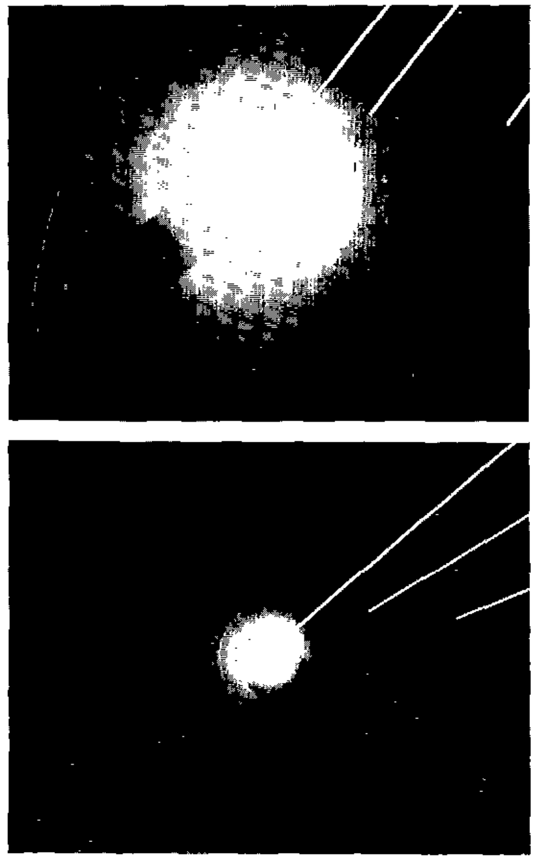

Fig. 7. TED patterns of DLC films deposited (a) without and (b) with Ar gas

This may be explained by the fact that heavy Ar atoms can transfer their momentum to the carbon atoms, rendering the carbon network of DLC film graphite-like nature due to the localheating effect. This result is also in agreement with the Raman shift of the 'G' band towards a higher wave number when the Ar gas is diluted.

Conclusions

Diamond-like carbon films have been successfully deposited by utilizing a magnetron plasma CVD method. Under nominal deposition conditions, the highest growth rate and density of the DLC films achieved were about 4. 8 μm/hr and 2.45 g/cm^3, respectively. when a magnetic field was applied, a denser plasma was obtained, rendering a stable discharge even at a low gas pressure of 1.5 mTorr. It was found that the reduction of a dc self bias with an increasing magnetic field was attributed to a substantial increase of an electron temperature. The carbon network of DLC films became ordered and graphitized with an increasing *rf* power and with the addition of Ar gas. More detailed analysis on the structural properties of DLC films deposited under similar conditions are being performed using an EELS (electron energy loss spectroscopy) method.

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