한국표면공학회지
J. Kor. Inst. Surf. Eng.
Vol. 36, No. 2, 2003.
<연구논문>

Pulsed Magnetron Sputtering Deposition of DLC Films

Part II: High-voltage Bias-assisted Deposition

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(Received 8 August 2002 ; accepted 23 December 2002)

Abstract

Short (τ=40 μs) and high-voltage (U_{sub}=2~8 kV) negative substrate bias pulses were used to assist pulsed magnetron sputtering DLC films deposition. Space- and time-resolved probe measurements of the plasma characteristics have been performed. It was shown that in case of high-voltage substrate bias spatial non-uniformity of the magnetron discharge plasma density greatly affected DLC deposition process. By Raman spectroscopy it was found that maximum percentage of sp^3-bonded carbon atoms (40~50%) in the coating was attained at energy E_C~700 eV per deposited carbon atom. Despite rather low diamond-like phase content these coatings are characterized by good adhesion due to ion mixing promoted by high acceleration voltage. Short duration of the bias pulses is also important to prevent electric breakdowns of insulating DLC film during its growth.

Keywords : *Diamond-like carbon; Graphite; Pulsed magnetron sputtering; High-voltage bias*

1. INTRODUCTION

For deposition of DLC films it is principally important to create thermodynamically non-equilibrium conditions at the substrate, which supply formation and conservation of the metastable diamond-like carbon phase. This is attained, for instance, by argon ion bombardment of the growing film. So, according to the calculations performed by Seitz and Koehler[1)], an ion with energy of about 100 eV impinging a carbon surface causes a short-term (7×10^{-11} s) local (in a region of about 1 nm in size) increase in temperature (up to 3823 K) and pressure (up to 1.3×10^{10} Pa). Potentially, this can promote the formation of a diamond-like nucleus and its conservation due to quenching. Aisenberg[2)] suggested that Ar^+ ions might efficiently transfer energy to carbon atoms both in the plasma and on the film surface. Such a knocking-on process promotes penetration of carbon atoms into the subsurface region, leading to the growth of diamond nuclei by subplantation mechanism. Both lack of energy per deposited carbon atom (< 30 eV) and its excess (> 1,000 eV) result in growth of graphite-like carbon film.

Thus, in order to produce a high-quality DLC film, it is necessary to control the energy of the bombarding ions and to provide a high-density ion current onto the surface. In our previous paper[3)] it was demonstrated that pulsed magnetron sputtering of graphite target synchronized with low-voltage (up to 500 V) and rather long (160 μs) pulsed substrate bias satisfied the

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above conditions. This technique allowed to deposit DLC coatings with rather high percentage (50-60%) of sp^3-bonded carbon atoms on large-area substrates. However, adhesion of the films was not sufficient for wear-resistant applications due to absence of ion mixing at the film-substrate interface and, probably, because of electrical breakdowns of the growing DLC film. We supposed that for deposition of highly-adherent DLC it is necessary to use short (< 60 ㎲) high-voltage (> 1 kV) bias pulses[3]. Experimental verification of this supposition was the main goal of the work.

2. EXPERIMENTAL

Installation for high-voltage bias assisted pulsed magnetron sputtering deposition of DLC films presented in Fig. 1. We used the same set-up as for low-voltage bias assisted DLC deposition[3] except substrate bias voltage pulsed power supply. The latter produced high-voltage (up to 10 kV) short (40 ㎲) negative bias pulses,

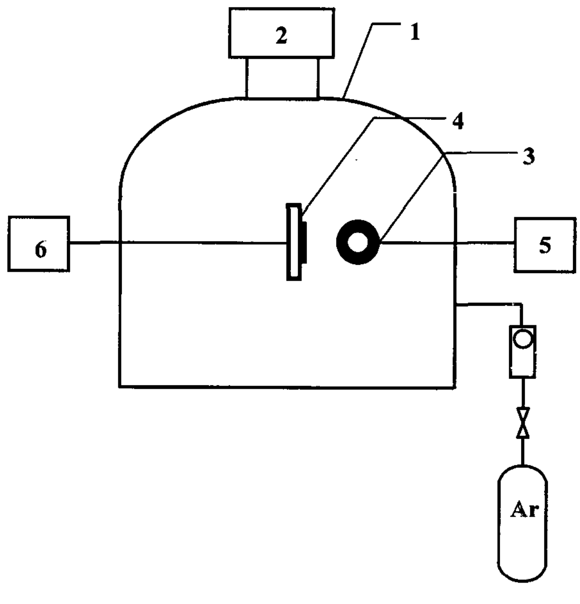

Fig. 1. Schematic of the experimental set-up: 1-vacuum chamber, 2-diffusion pump, 3-magnetron, 4-substrate holder, 5-magnetron power supply, 6-high-voltage substrate bias power supply.

Table 1. Plasma parameters at various distances to the substrate

d (mm)	$n_i (m^{-3})$	T_e(eV)	J_I(Ma/cm^2)
0	2.2 × 10	3.1	5.4
5	2.5 × 10	3.0	6.2
10	4.2 × 10	2.8	9.6
15	5.7 × 10	2.7	13.3

where d is distance to the substrate, n_i is plasma density, T_e is electron temperature, j_i is calaulated ion current density at the substrate

which were synchronized with magnetron discharge pulses, but delayed for 60 ㎲ with respect to their beginning, as it is shown in Fig. 2.

Figure 2(b) presents oscillograms of a high bias voltage U_{sub} and the current J_{sup} onto the substrate. Slight decrease in bias voltage during the pulse is caused by the discharging of the capacitor in the primary circuit of the high-voltage pulse generator. The waveform of the substrate current depends on the state of the plasma in the gap between the magnetron cathode and the substrate. The time it takes for a stable plasma boundary to form is 5~7 ㎲. Thereafter the substrate current J_{sup} remains almost constant until the end of the voltage pulse (Fig. 2 (b)).

Pulsed magnetron discharge parameters (Fig. 2(a)) were also the same as in[3] (i. e. argon pressure P=0.7 Pa, voltage U=800 V, current I=52 A, pulse width τ=100 ㎲ and pulse repetition rate f=250 Hz). Polished Si, Ti and stainless steel plates were used as substrates. Conditions of DLC deposition experiments are given in Table 2.

Compared to lowvoltage bias assisted DLC deposition[3], in this case it is necessary to perform time-resolved probe measurements of plasma density and electron temperature not only in substrate vicinity, but also at the distances of 5~15 mm from the substrate. It is explained by the fact that at high bias voltage plasma sheath at the substrate is rather thick (up to 15 mm), and substrate ion current densi-

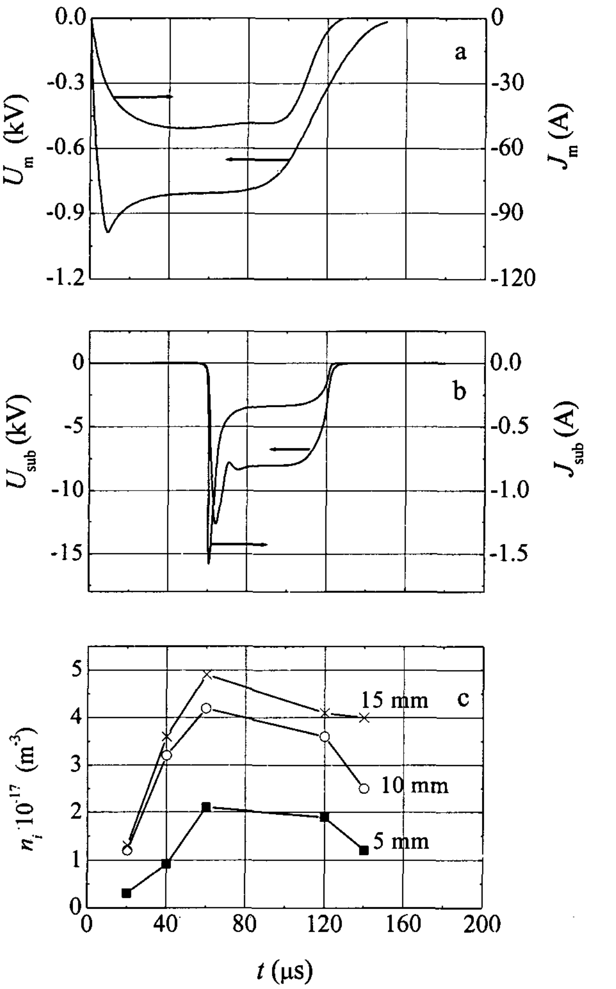

Fig. 2. Time-dependent parameters of the process of ta-C coating deposition: a-voltage U_m and current J_m pulses of the magnetron discharge, b-highvoltage substrate bias U_{sub} and corresponding current J_{sup} pulses, c-the magnetron discharge plasma density n_i taken at various distances from the substrate.

ty is determined by plasma density at the sheath boundary. Results of plasma parameters measurements are given in Table 1. The time dependences of the plasma density, taken at various distances from the substrate, are plotted in Fig. 2(c).

Using the plasma parameters, the ion current density $j_i(s)$ at the plasma boundary was determined by the formula

$$j_i(s)=0.31en_i(s)\sqrt{2kT_e(s)/M_i}, \quad (1)$$

where e is the electron charge, $n_i(s)$ is the plasma density at the plasma boundary, k is Boltzman constant, $T_e(s)$ is the electron temperature, M_i is the ion mass, and s is the width of the plasma sheath formed at the substrate when negative bias voltage is applied. The width is determined by the formula

$$s=\sqrt{\frac{4}{9}\varepsilon_0\left(\frac{2e}{M_i}\right)^{1/2}\frac{U_{sub}^{3/2}}{j_i(s)}}, \quad (2)$$

where ε_0 is the electrical permittivity of vacuum and U_{sub} is the bias voltage at the substrate.

The energy E_C per deposited carbon atom was determined as

$$E_C=eU_{sub}\Phi_i/\Phi_C, \quad (3)$$

where Φ_C is the carbon atom flux and Φ_i is the ion flux onto the surface. The carbon atom flux was estimated by the formula

$$\Phi_C=\rho v/m_C, \quad (4)$$

where ρ is the mass density of the film, v is the rate of growth of the film, and m_C is the mass of a carbon atom. In the previous paper it was shown that the film density can be roughly estimated as 2 g/cm^3 [33]. For steadystate conditions, the ion flux onto the surface can be found as

$$\Phi_i=j_i(s)\tau_{sub}f/e, \quad (5)$$

Table 2. Experimental conditions of high-voltage bias assisted pulsed magnetron sputtering deposition of DLC films

#	U_{sub}(kV)	j_i(mA/cm^2)	Φ_i(cm^{-2}s^{-1})	v(nm/s)	E_C(eV)
1	2	5.9	$3.7\cdot10^{14}$	0.11	240
2	5	7.1	$4.4\cdot10^{14}$	0.10	710
3	7.5	8.2	$5.1\cdot10^{14}$	0.06	1230

where τ_{sub} is the width of the current pulse and f is the pulse repetition rate.

Deposited DLC coatings were investigated by Raman spectroscopy, which experimental details described in[3]. The hardness and adherence of the coatings were determined qualitatively using a rubber with SiO_2 abrasive particles moved reciprocally with an applied load of around 1 kg. The results of the sand-rubber test (scratches and/or delamination) were examined by optical microscope.

3. RESULTS AND DISCUSSION

The time dependences of the plasma density, taken at various distances from the substrate, are plotted in Fig. 2(c). As it follows, the density of the magnetron discharge plasma is maximum and almost stable in the interval between the 60th and the 120th microsecond from the beginning of the pulse. Therefore, in the experiment on deposition of DLC films, the high-voltage pulsed bias was applied to the substrate with a delay of 60 μs relative to the magnetron discharge pulse (see Fig. 2). As it can be seen from Fig. 2(b), in this case the substrate current remains approximately constant after the formation of the cathode plasma sheath, thus Eqs. (1) - (2) are valid.

As mentioned above, spatial nonuniformity is characteristics of the pulsed magnetron discharge plasma. Plasma density n_i measured at various distances from substrate is presented in Table 1. Besides, measured electron temperature T_e and calculated substrate ion current density j_i are given for the 60th microsecond after magnetron discharge pulse start. Fig. 3 presents the plasma density spatial distribution at the 60th and the 120th microsecond from the beginning of the discharge pulse. The coincidence of these two curves also proves temporal stability of the plasma characteristics within the mentioned time interval.

Accordingly Eqs. (1) and (2), the ion current density $j(s)$ in the case of magnetron sputtering is not a constant, unlike the case of a uniform plasma, but depends on the plasma sheath width s qt the substrate. The reason for this is the spatial nonuniformity of the plasma density $n_i(s)$ and electron temperature $T_e(s)$ resulting from the cylindrical geometry of the magnetron sputtering system. Thus, dependences of the ion current density and the substrate plasma sheath width on the substrate bias voltage can be found by solving the system of Eqs. (1) and (2) using results of plasma measurements (Table 1). As it follows from Fig. 3, dependence of plasma density on distance to the substrate can be approximated as:

$$n_i(s) = 2.2 + 0.016\, s^3, \quad (6)$$

where s and $n_i(s)$ are given in mm and 10^{17} m^{-3} correspondingly. Assuming electron temperature equal approximately to 3 eV and independent

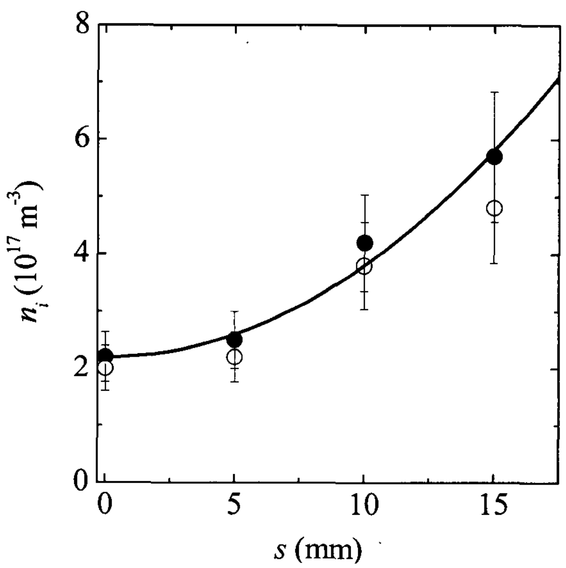

Fig. 3. Measured plasma density n_i vs. distance to substrate for various time intervals (points - experimental data, line - approximation), ● — 60 μs from the beginning of the magnetron discharge pulse, ○ — 120 μs from the beginning of the magnetron discharge pulse.

on s (see Table 1), accordingly to (1) and (6) we can deduce ion current density vs sheath thickness as:

$$j_i(s) = 5.4 + 0.039\,s^2 \qquad (7)$$

where s and $j_i(s)$ are given in mm and mA/cm^2 correspondingly. Substituting ion current density in (2) by (7) we can derive $s(U_{sub})$ and then $j_i(U_{sub})$ as functions of substrate bias voltage:

$$s(U_{sub}) = 8.32\sqrt{\sqrt{1+0.15U_{sub}^{3/2}} - 1}, \qquad (8)$$

$$j_i(U_{sub}) = 2.7(\sqrt{1+0.15U_{sub}^{3/2}} + 1) \qquad (9)$$

where s, $j_i(s)$ and U_{sub} are given in mm, mA/cm^2 and kilovolts correspondingly.

Fig. 4 presents the dependences of the ion current density at the plasma boundary and the substrate sheath thickness on the substrate bias voltage. It can be seen that for these sputtering modes the width of the substrate plasma sheath is small compared to the characteristic dimensions of the substrate holder throughout the range of bias voltages, which were applied to the substrate in our experiments. So, we can neglect the difference between the ion current densities at the substrate and at the plasma boundary and use the $j_i(U_{sub})$ values from Fig. 4 to calculate E_C from Eqs. (3) - (5).

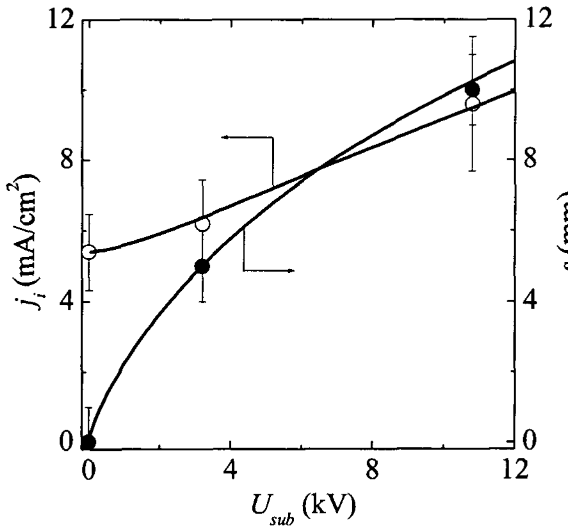

Fig. 4. Calculated ion current density j_i and thickness s of the substrate plasma sheath vs. the substrate bias voltage U_{sub} (points - experimental data, lines - approximations), ○ - ion current density at the substrate, ● - substrate plasma sheath thickness.

Conditions of DLC deposition are described in Section 2 of the paper and given in Table 2, and results of their examination by Raman scattering are presented in Fig. 5 and in Table 3. During the experiments only bias voltage has been changed. Other parameters of magnetron discharge and bias pulses were constant. That is why fluxes atoms $\Phi_C = 3.1 \times 10^{15}$ cm^{-2} s^{-1} to the substrate calculated accordingly (3) was constant. But the ion flux Φ_i was increased as the bias voltage changed from 2 to 7.5 kV due to increase in substrate ion current (see Fig. 4) density. At the same time energy per deposited carbon atom E_C is changed from 240 to 1,230 eV, and the film growth rate decreased from 0.11 to 0.06 nm/s. These growth rates are several times lower than in case of low-voltage bias[3] due to more intensive film sputtering caused by higher ion energy.

As it can be concluded from the Raman spectroscopy data, the sample with E_C=710 eV shows the best combination of parameters (the

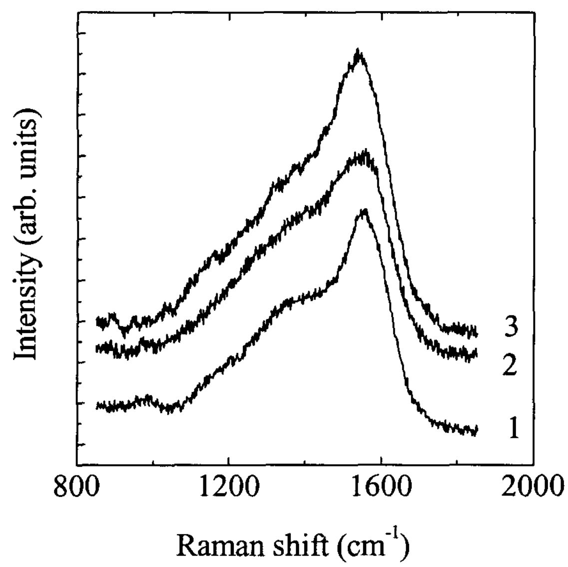

Fig. 5. Raman spectra of the DLC films deposited according to the experimental conditions presented in Table 2.

Table 3. Parameters of Raman spectra of the DLC films

#	Γ_G(cm^{-1})	w_G(cm^{-1})	Γ_D(cm^{-1})	w_D(cm^{-1})	I_D/I_G
1	1,546	142	1,360	263	1.13
2	1,540	14	1,350	291	1.09
3	1,555	125	1,365	247	1.28

lowest integrated intensity ratio for the D-peak and the G-peak, the greatest halfwidth of the G-peak, and the greatest shift of the G-peak toward small wave numbers)[4]. The graphite-like phase content in the film is higher for lower E_C values (240 eV) and, especially, for higher E_C values (1,230 eV). In the first case, this is caused by lack of the energy promoting the formation of a dense diamond-like phase, while in the second one, this is a consequence of its excess, which converts into heat and causes graphitization of metastable carbon. In our opinion, this substantial difference in optimum E_C for high-voltage and low-voltage bias[3] might be due to (1) a decrease in the ratio of the ion-to-neutral flux onto the film surface, resulting from a shortening of the bias pulse; and (2) deposition of graphite-like carbon without bias at the substrate, i.e., at the beginning and at the end of the magnetron sputtering pulse. So, considerable part of the ion energy is spent for resputtering and etching of nondiamond-like carbon from the surface of the growing film, and for ion-induced mixing. These deposition conditions are close to those of ion beam assisted PVD, for which optimal E_C values are 300-1,000 eV[5-6]. However, even disregarding the above considerations, the obtained range of optimal E_C values is in agreement with the data reported by Lifshitz et. al.[7-8]. Furthermore, Lacerda et. al. noted that, although some increase in the content of sp^2 carbon in the films with increasing E_C up to 1,000 eV is observed, the hardness of the films decreases insignificantly compared to the abrupt decrease in the intensity of the internal stresses and the enhancement of their adhesion[9,10].

The I_D/I_G values for the Raman spectra of the DLC films deposited at a high-voltage substrate bias (1.09～1.28) are higher than those obtained with a low-voltage one (0.84～1.14)[3]. This corresponds to a lower percentage (40～50 %) of tetrahedrally bonded carbon in the coatings[11]. Despite this, adhesion of these films to metals is considerably higher than in the case of a low-voltage bias applied to the substrate[3] and no scratches and delamination were observed for the DLC films after the sand-rubber test. The improvement may be caused by ion-induced mixing between the film and the substrate and between neighboring layers in the film, as well as by relaxation of internal stresses in the film under the high-energy ion bombardment. Besides, as it was observed by optical microscope, insulating DLC film is not subject to breakdowns because of the shortening of the bias pulse, that is also favorable to its quality.

4. CONCLUSIONS

Pulsed magnetron sputtering of graphite synchronized with high-voltage (～5 kV) and short (～40 ㎲) pulsed substrate bias voltage makes it possible to produce DLC films with moderate percentage (40～50%) of sp^3-bonded carbon atoms and rather low growth rates (～300 nm per hour) compared to low-voltage bias assisted deposited DLC. In spite of this fact, these films are characterized by reasonable scratch resistance and high adhesion. It can be supposed that the improvement of the coating adhesion is caused by high-energy ion bombardment leading to ion mixing at the film-substrate interface. Besides, short voltage pulses help to avoid electric breakdowns of the insulating DLC film.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. M. D. Efremov (Institute of Semiconductors Physics, Novosibirsk, Russia) for the performance of Raman analysis of samples and to Professor A. V. Kozyrev (Institute of High Current Electronics, Tomsk, Russia) for fruitful discussions. This work was supported in part by the Korea Science and Engineering Foundation (KOSEF) through the Research Center for Machine Parts and Materials Processing (ReMM) at the University of Ulsan, Korea.

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