한국표면공학회지
J. Kor. Inst. Surf. Eng.
Vol. 36, No. 1, 2003.
<연구논문>

Pulsed Magnetron Sputtering Deposition of DLC Films
Part I : Low-Voltage Bias-Assisted Deposition

Konstantin V. Oskomov[a], Hui-Gon Chun[b*], Yong-Zoo You[b], Jing-Hyuk Lee[b]
Kwang-Bok Kim[b], Tong-Yul Cho Nikolay S. Sochogov[a], Alexender N. Zakharov[a]

[a]Inst. of High Current Electronics, Siberian Div. of RAS,
4 Akademichesky Ave. 634055, Tomsk, Russia
[b]School of Materials Science and Engineering, ReMM,
University of Ulsan, San 29, Mugue-dong, Nam-gu, Ulsan 680-749, Korea.

(Received 8 August 2002 ; accepted 20 December 2002)

Abstract

Pulsed magnetron sputtering of graphite target was employed for deposition of diamond-like carbon (DLC) films. Time-resolved probe measurements of magnetron discharge plasma have been performed. It was shown that the pulsed magnetron discharge plasma density ($\sim 10^{17}$ m^{-3}) is close to that of vacuum arc cathode sputtering of graphite. Raman spectroscopy was used to examine DLC films produced at low (U_{sub} < 1 kV) pulsed bias voltages applied to the substrate. It has been shown that maximum content of diamond-like carbon in the coating (50 - 60%) is achieved at energy per deposited carbon atom of $E_C = 100$ eV. In spite of rather high percentage of sp^3-bonded carbon atoms and good scratch-resistance, the films showed poor adhesion because of absence of ion mixing between the film and the substrates. Electric breakdowns occurring during the deposition of the insulating DLC film.also thought to decrease its adhesion.

Keywords : Diamond-like carbon, Graphite, Pulsed magnetron sputtering, Low-voltage bias

1. INTRODUCTION

Magnetron sputtering systems (or magnetrons) are widely used for deposition of various films on large-area surfaces (up to 2×2 m^2). An additional advantage of magnetrons is the absence of a droplet fraction in the sputtered, mainly atomic, flow. However, using conventional DC magnetrons for deposition of DLC films is limited because of the low energy of sputtered carbon atoms and the low degree of plasma ionization near the substrate[2)]. Several modifications of DC magnetron sputtering deposition techniques have been employed for production of DLC films, e.g. hollow cathode enhanced[3)] or unbalanced[4)] magnetron sputtering deposition, including ion-assisted one[5)]. In the first case, the energy of sputtered carbon atoms in the vicinity of the substrate increases due to the collisionless transport of these atoms at pressure of 0.01 Pa. However, under these conditions, graphitization of DLC films occurs because of the high electron temperature (~5 eV). In the second case, redistribution of the plasma by a

---

* Corresponding author. E-mail : hgchun@mail.ulsan.ac.kr

magnetic field increases the Ar^+ ion density and the ionization degree (up to 70-80%) near the substrate. This makes it possible to produce DLC films using bias voltage applied to a substrate[5] or its self-biasing[4].

Using pulsed magnetron sputtering instead of DC it is possible to attain the required plasma parameters. It has been shown by Mozgrin et. al. that peak current of pulsed diffuse magnetron discharge can reach 250 A[6]. It leads to increase of plasma density in the substrate zone up to 10^{17} - 10^{19} m^{-3} [6], which approaches the plasma density of cathodic-arc[7] or pulsed laser sputtering[8]. In contrast to unbalanced magnetron sputtering, besides high density, the plasma is characterized by high percentage of target material ions (>30%)[6]. All these features are favorable for the formation of a high-quality DLC film by ion-assisted pulsed magnetron sputtering deposition.

Naturally, properties of DLC films produced by pulsed magnetron sputtering of graphite should depend primarily on the plasma characteristics and on the bias voltage applied to a substrate. So, the purpose of the work was to investigate influence of these factors on the DLC films characteristics.

2. EXPERIMENTAL

The experimental set-up for pulsed-magnetron sputtering deposition of DLC films is shown schematically in Fig. 1. The vacuum chamber (1) with dimensions of 600×600×600 mm^3 is evacuated by a diffusion pump (2). Inside the chamber, a cylindrical magnetron (3) with a graphite target is mounted. The graphite cathode is a 50-cm-long tube of diameter 50 mm; the chamber walls are used as an anode. Permanent magnets located inside the tube create the magnetic field of 50 mT at the surface of the graphite target. The target material is pyrolytic poreless graphite of density 2.2 g/cm^3 and purity 99.997 %.

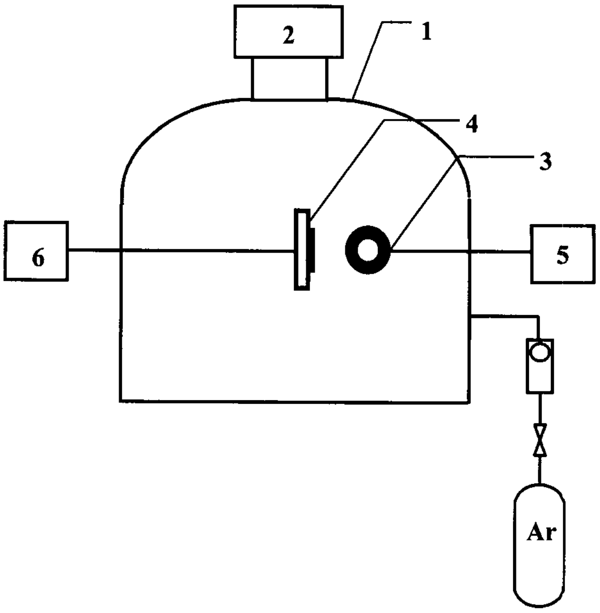

Fig. 1. Schematic of the experimental set-up: 1 - vacuum chamber, 2 - diffusion pump, 3 - magnetron, 4 - substrate holder, 5 - magnetron power supply, 6 - low-voltage substrate bias power supply, 7 - high-voltage substrate bias power supply.

At argon pressure of P=0.7 Pa pulsed magnetron discharge of voltage U=800 V, peak current I=52 A, pulse width τ=100 μs (Fig. 2 (a)), and pulse repetition rate f=250 Hz was ignited in the chamber by magnetron pulsed power supply (5). In front of the magnetron, at the distance of 50 mm, a substrate holder (4) was placed. Polished silicon, titanium and stainless steel plates were used as substrates. Low-voltage (up to 500 V) negative bias pulses of duration τ=160 μs (Fig. 2(b)) synchronized

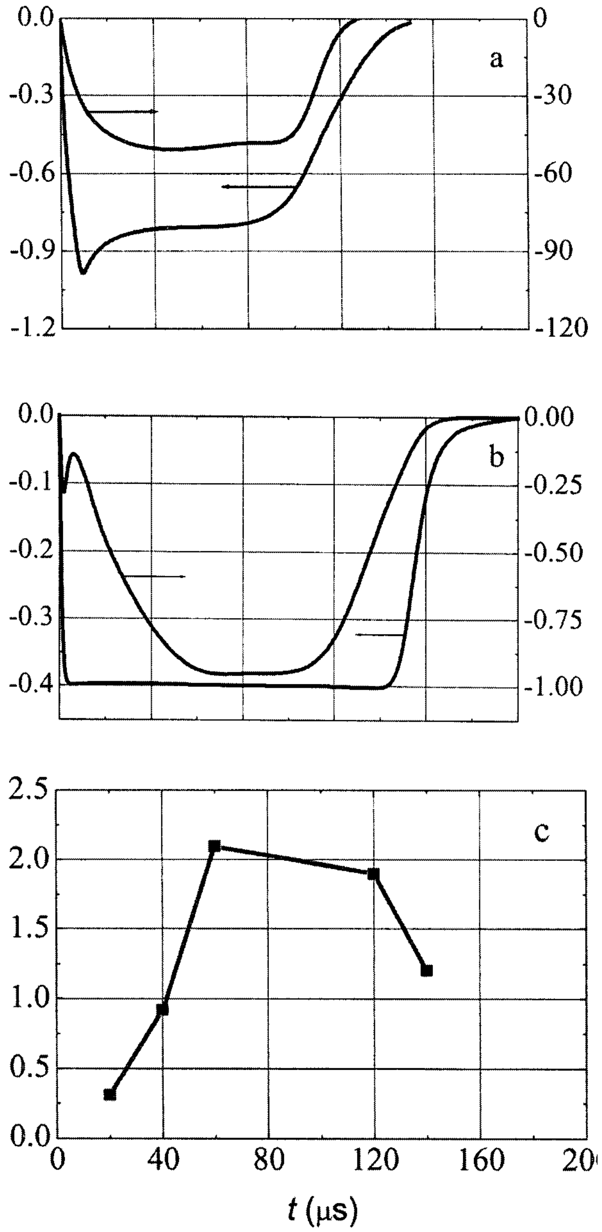

Fig. 2. Time-dependent parameters of the DLC coating deposition: a-voltage U_m and current J_m pulses of the magnetron discharge, b-low-voltage substrate bias U_{sub} and corresponding current Jsub pulses, c-the magnetron discharge plasma density n_i taken at the substrate vicinity.

with magnetron discharge pulses were applied to the substrate holder from pulsed bias power supply (6). Conditions of DLC deposition experiments are given in Table 2.

Time-dependent plasma probing was performed in the vicinity of the substrate. The Langmuir probe was made of ϕ 0.6-mm nichrome wire; the length of the charge-collecting part of the probe was 6.0 mm. The measurements were used to determine the main plasma parameters (the plasma density and electron temperature given in Table 1). The time dependence of the plasma density is plotted in Fig. 2(c).

Using the plasma parameters, the steady state (flat top of substrate current oscillogram in Fig. 2(b)) substrate ion current density ji was determined by Bohm's formula

$$j_i = 0.4en_i\sqrt{2kT_e/M_i}], \qquad (1)$$

where e is the electron charge, ni is plasma density at the substrate vicinity in steady state (flat top of graph in Fig. 2(c)), k is Boltzman constant, T_e is electron temperature and M_i is the ion mass.

The energy E_C per deposited carbon atom was determined as

$$E_C = eU_{sub}\Phi_i/\Phi_C,, \qquad (2)$$

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

$$\Phi_C = \rho\nu/m_C, \qquad (3)$$

where ρ is the mass density of the film, ν is the film growth rate, and m_C is the mass of carbon atom. Obviously, the atom flux depends only on the discharge characteristics, and, thus, it can be determined for every sputtering mode in the absence of substrate bias. Glassy carbon-like films were deposited onto a substrate under these conditions. The coating thickness was measured with an optical interferometer. Density of the glassy carbon-like films was evaluated equal to 2 g/cm^3 by floatation experiments. Since the substrate current pulse has trapezium-like shape, the ion flux onto the surface can be found as

$$\Phi_i = j_i \tau_{sub} f/e, \qquad (4)$$

where τ_{sub} sub is the current pulse width at half-height and f is the pulse repetition rate.

The deposited DLC coatings were investigated by Raman spectroscopy. Films of thickness 100 nm and more deposited on crystalline silicon were used as samples for examination. The films were absorbing enough to exclude the influence of the substrate on the measurements. Raman spectra were obtained with a 514-nm Ar$^+$ laser whose radiation was focused into a 50㎛-diameter beam. The energy density in this case was low enough to prevent graphitization of the films during examination. The spectra were recorded in the range 800-1800 cm^{-1} with 1.5-cm^{-1} resolution and then fitted by two Lorentz curves having maxima in the regions 1500 (1600 cm^{-1} (*G*-peak) and 1300-1400 cm^{-1} (*D*-peak). The Raman spectra for the samples deposited in the conditions presented in Table 2 are given in Fig. 3, and their fitting parameters are given in Table 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 ~ 1 kg. The results of the sand-rubber test (scratches and/or detachments) were examined by optical microscopy.

3. RES.ULTS AND DISCUSSION

Plasma characteristics measurements results and calculated accordingly (1) ion current density for pulsed magnetron sputtering of graphite in argon atmosphere are summarized in Table 1. These data correspond to 60-120㎲ from the beginning of the voltage pulse. The probe was placed at the substrate position holder that is 50 mm from the target surface. For comparison, the characteristics of the plasma of the DC magnetron discharge are given. The obtained values of the plasma density (~10^{17} m^{-3}) are close to the plasma parameters attained by cathodic-arc$^{7)}$ or pulsed laser sputtering$^{8)}$ of a graphite target. The time dependence of the plasma density is plotted in Fig. 2(c). It is shown that plasma is almost stable in the interval between the 60th and 120th from THe beginning of the pulse. This is also followed from the substrate current oscillogram (Fig. 2(b)).

Table 1. Plasma parameters for various modes of magnetron sputtering of the graphite target in argon

Mode	P_{Ar} (Pa)	PU_m (V)	J_m (A)	τ_m (㎲)	f (Hz)	T_e (eV)	n_i (m^{-3})	j_i (mA/cm^2)
DC	0.6	450	1	–	–	2.7	9.10^{15}	0.2
Pulsed	0.7	800	52	100	250	3.1	2.210^{17}	5.4

where PAr is argon pressure in the chamber, Um and Jm are magnetron discharge voltage and current respectively (pulsed or DC), mis duration of magnetron discharge currentr pulse, f is pulse repetition rate, Te is electron temperature, ni is pasma density, ji is ion current density at the substrate

Deposition conditions of the investigated DLC are presented in the Table 2. During the experiments only bias voltage has been changed. Other parameters of magnetron discharge and bias pulses were constant (see Section 2 of the paper). That is why fluxes of ions $\Phi_i = 1.0 \times 10^{15}$ cm^{-2} s^{-1} and atoms $\Phi_C = 3.1 \times 10^{15} cm^{-2}$ s^{-1} to the substrate calculated accordingly (3) and (4) were also constant. As the bias voltage varied from 0 to 500 V, the calculated according to (2) energy per deposited carbon atom E_C changed from 0 to 160 eV, and the film grow^th^ rate decreased from 0.29 to 0.16 nm/s due to sputtering and densification processes.

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

#	U_{sub} (kV)	ν (nm/s)	E_C(eV)
1	0	0.29	0
2	0.1	0.27	30
3	0.3	0.20	100
4	0.4	0.17	130
5	0.5	0.16	160

where Usub is negative substrate bias voltage, vis film growth rate, EC is energy per deposited carbon atom

The Raman scattering spectra for the deposited DLC films are given in Fig. 3, and their fitting parameters are given in Table 3. It can readily be seen that all spectra can be approximated by the sum of two Lorentz curves having maxima in the regions 1500-1600 cm^{-1} (*G*-peak) and 1300-1400 cm^{-1} (*D*-peak), respectively. The *G*-peak is sharper than the *D*-peak and can be attributed to the scattering by optical zone center phonons of graphite. The *D*-peak is a wide "shoulder" resulting from the scattering by optical zone edge phonons activated by disordering of graphite[9]. The Raman spectra give no possibility to estimate quantitatively the sp^3-to-sp^2 bond ratio; nevertheless, some qualitative information can be extracted from them. So, the increase in the ratio of the integrated intensities of the *D*-peak and the *G*-peak (I_D/I_G) simultaneous with the shift of the *G*-peak toward the region of higher wave numbers, as well as the widening of the *D*-peak and the narrowing of the *G*-peak testify to an increase in sp^2 bond content in the amorphous carbon film[9].

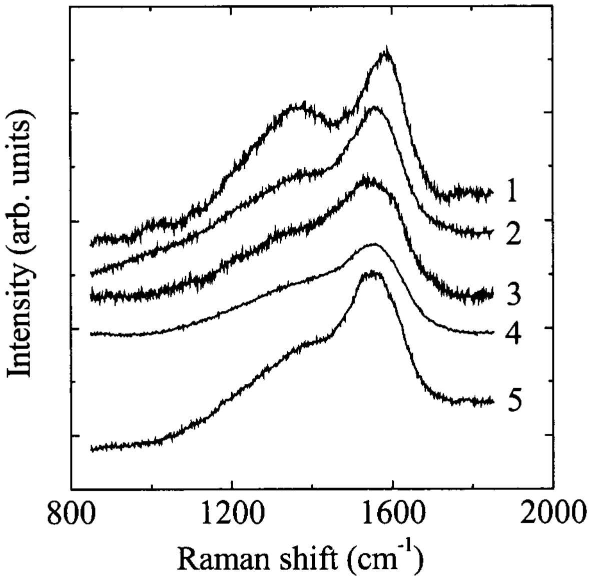

Fig. 3. Raman spectra of the DLC films deposited according to the experimental conditions presented in Table 2.

As it follows from the integrated intensity ratio of the peaks I_D/I_G, the percentage of diamond-like carbon in the DLC films initially abruptly increases, as E_C is increased from zero to 140 eV, and then decreases. This dependence of the diamond-like carbon content in a coating on E_C is in good agreement with the data available in the literature for the DLC films produced by cathodic-arc PVD[7]. These results, as well

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	1577	107	1354	244	1.77
2	1555	125	1365	247	1.13
3	1548	159	1352	257	0.84
4	1552	143	1360	258	1.02
5	1552	135	1358	244	1.14

where Γ_G is G-peak shift, w_G is G-peak width at half-maximum, Γ_D is D-peak shift, w_D is D-peak width at half-maximum

as plasma density measurements, confirm that conditions realized in the case of low-voltage bias assisted pulsed magnetron sputtering PVD are close to those typical of cathodic-arc PVD. Such a behavior can be explained by the formation of diamond-like carbon phase accordingly subplantation theory at E_C > 50 eV, followed by its graphitization as the excessive (E_C > 140 eV) particle energy converts into heat. According to Qian et. al., this I_D/I_G ratio (0.84-1.14) is typical of DLC films containing about 50-60% of sp^3-bonded carbon atoms[10].

Despite high concentration of sp^3-bonded carbon, the deposited DLC can not be used as protective or wear-resistive coatings. No scratches were observed after the sand-rubber test, but film delamination was obvious. To produce hard and highly-adhesive DLC coatings, besides the required energy per carbon atom (~100 eV), it is important to provide bombardment of the substrate and growing film by high-energy ions to activate mixing at the film-substrate interface and between the film layers.

The deterioration of adherence might be caused by electric breakdowns of the insulating DLC coating occurred as the coating was charged to a critical voltage (there were spot-like defects observed on the surface of the films) during the comparatively long (160 ㎲) bias voltage pulse. Let us use the electrical characteristics of typical DLC films given in[11] (the breakdown electric field lying in the range 10^8 - 10^{12} V/m and the dielectric constant varying from 4 to 9) and put the current density at the substrate equal approximately to 60 A/m^2 (see Table 1). We then obtain that in these conditions a DLC film can be charged to a critical voltage within 60 ㎲, i.e., before the end of the bias pulse at the substrate. Thus, to produce DLC coatings of higher quality, it is necessary to apply to the substrate high-voltage bias (several kV) and short (< 60 ㎲) pulses synchronized with the magnetron discharge pulses. Experimental demonstration of validity of this statement is yet to be done.

4. CONCLUSION

1) Pulsed magnetron sputtering of graphite synchronized with a high pulsed bias voltage applied to the substrate makes it possible to produce high-quality DLC films with high growth rates (up to 1 ㎛/h) and rather high percentage (50-60%) of sp^3-bonded carbon atoms. This is possible due to denser plasma generated by pulsed magnetron sputtering of graphite (10^{17} - 10^{18} m^{-3}) compared to dc magnetron sputtering (~10^{16} m^{-3}).

2) Despite high concentration of sp^3-bonded carbon, the deposited DLC showed poor adhesion. Possible reason is absence bombardment of the substrate and growing film by high-energy ions activating mixing at the film (substrate interface and between the film layers.

Deterioration of adherence might be caused also by electric breakdowns of the insulating DLC coating that occurred as the coating was charged to a critical voltage during the comparatively long (160 ㎲) bias voltage pulse. Thus, to produce DLC coatings of higher quality, it is necessary to apply to the substrate high-voltage bias (several kV) and short (< 60 ㎲) pulses synchronized with the magnetron discharge pulses. Experimental demonstration of validity of this statement is yet to be done.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. M. D. Efremov (Inst. of Semiconductors Physics, Novosibirsk, Russia) for the performance of Raman analysis of samples and to Professor A. V. Kozyrev (Inst. 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.

REFERENCES

1. S. P. Bugaev, N. S. Sochugov, Surf. Coat. Technol., 131 (2000) 474.
2. L. G. Jacobsohn, F. L. Freire Jr., J. Vac. Sci. Technol., A 17 (1999) 2841.
3. S. M. Rossnagel, M. A. Russak, J. J. Cuomo, J. Vac. Sci. Technol., A 5 (1987) 2150.
4. N. Savvides, J. Appl. Phys., 59 (1986) 4133.
5. E. Mounier, Y. Pauleau, Diamond Relat. Mat., 6 (1997) 1182.
6. D. V. Mozgrin, I. K. Fetisov, G. V. Khodachenko, Fizika Plazmy, 21 (1995) 422.
7. M. M. M. Bilek, M. Chhowalla, W. I. Milne, Appl. Phys. Lett., 71 (1997) 1777.
8. A. A. Voevodin, S. J. P. Laube, S. D. Walck et al., J. Appl. Phys., 78 (1995) 4123.
9. R. Vuppuladhadium, H. E. Jackson, R. L. C. Wu, J. Appl. Phys., 77 (1995) 2714.
10. F. Qian, R. K. Singh, S. K. Dutta, P. P. Pronko, Appl. Phys. Lett., 67 (1995) 3120.
11. C. V. Deshpandey, R. F. Bunshah, J. Vac. Sci. Technol., A7 (1989) 2294.