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Diamond-Like Carbon Films Deposited by Pulsed Magnetron Sputtering System with Rotating Cathode

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Abstract

Extended cylindrical magnetron sputtering system with rotating 600-mm long and 90-mm diameter graphite cathode and pulsed power supply voltage generator were devel oped and fabricated. Time-dependent Langmuir probe characteristics as well as carbon films thickness were measured. It was shown that ratio of ions flux to carbon atoms flux for pulsed magnetron discharge mode was equal to $\Phi_i/\Phi_C = 0.2$. It did not depend on the discharge current in the range of $I_d = 10\text{~}60$ A since both the plasma density and the film deposition rate were found approximately proportional to the discharge current. In spite of this fact carbon film structure was found to be strongly dependent on the discharge current. Grain size increased from 100 nm at $I_d = 10\text{~}20$ A to 500 nm at $I_d = 40\text{~}60$ A. To deposit fine-grained hard nanocrystalline or amorphous carbon coating current regime with $I_d = 20$ A was chosen. Pulsed negative bias voltage ($\tau = 40$ μs, $U_b = 0\text{~}10$ kV) synchronized with magnetron discharge pulses was applied to a substrate and voltage of U_b = 3.4 kV was shown to be optimum for a hard carbon film deposition. Lower voltages were not sufficient for amorphization of a growing graphite film, while higher voltages led to excessive ion bombardment and effects of recrystalization and graphitization.

Keywords : Pulsed magnetron sputtering, Probe measurements, DLC films deposition

1. INTRODUCTION

There are several methods of physical vapor deposition (PVD) of hard amorphous carbon (a-C) films which are known for their excellent tribological properties[1]. There are vacuum cathode arc evaporation[2], laser ablation[3], ion sputtering[4] and magnetron sputtering[5]. The most hard a-C (up to 80~90 GPa) films with the highest (80~90%) sp^3/sp^2 carbon bonds ratio are deposited by vacuum cathode arc PVD due to a high plasma density created in a substrate vicinity. The rest methods can be applied only for deposition of moderately hard a-C films with a low percentage of tetrahedral bonds. Among all PVD methods only magnetron sputtering allows coating deposition on large-area substrates, but it needs increase of plasma density produced to improve a-C films quality. The most popular approach to increase a plasma density near a substrate in the case of magnetron sputtering is "unbalancing" of a magnetron[6]. But it leads to decrease of sputtering rate of a cathode because of redistribution of plasma in a cathode-substrate region. Another way is to use pulsed magnetron sputtering since increase of discharge current during the pulse time allows dense plasma generation[7]. Up to present time there are no enough experimental data on pulsed magnetron sputtering of graphite, including both plasma characteristics and a-C film properties. Thus, the purpose of the work was to investigate the pulsed magnetron discharge plasma parameters and a-C film properties under various experimental conditions.

2. EXPERIMENTAL

A cylindrical magnetron with a rotating graphite cathode was used in the experiments. The graphite cathode was made of a 600-mm-long tube (1) with 90-mm outer and 75-mm inner diameters, which was

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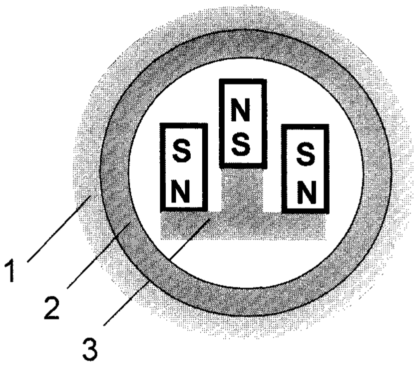

Fig. 1. Schematic of the magnetron: 1 - graphite tube, 2 - stainless steel tube, 3 - permanent magnets.

tightly glued to a stainless steel tube (2) inserted (Fig. 1). Inside the tube three rows of permanent magnets (3) were mounted creating an arc-like magnetic field at the cathode surface. The magnetron was vertically mounted in a vacuum chamber of $0.6 \times 0.6 \times 0.6$ m^3 size and permanently rotated at a speed of 30 rpm during the experiments. Before deposition the chamber was evacuated till 5×10^{-3} Pa and then filled with argon at pressure of 0.25 Pa. Pulsed power supply was based on IGBT transistor and generated rectangular voltage pulses of $U = 900$ V amplitude and $\tau = 400$ μs width, while current pulses had rather long rise-time of approximately 100 μs (Fig. 2). The reason of this fact could be slow generation of plasma near the magnetron cathode and in the chamber. Pulsed current of the magnetron discharge could be varied in the range of 10~60 A.

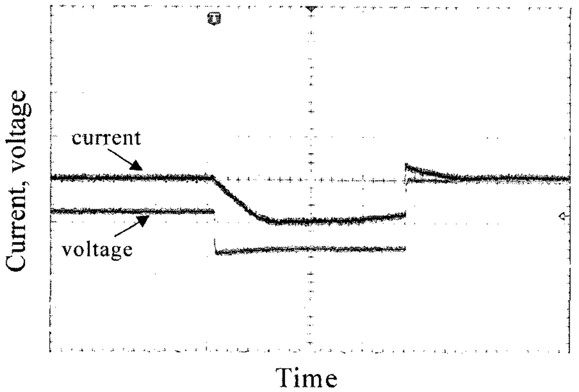

Fig. 2. Voltage and current waveforms for the pulsed magnetron discharge (for the current 1 div = 20 A, for the voltage 1 div = 500 V, for time 1 div = 100 μs).

Silicon substrates were placed at water-cooled holder situated 10 cm apart from the cathode. Thickness of the deposited coatings was measured by an *MII-4* interferometer (*LOMO*, Russia). Flux of carbon atoms directed to the substrate was calculated from a thickness of carbon film deposited in the absence of a substrate bias:

$$\Phi_c = \rho d/m_c t \tau f, \quad (1)$$

where $\rho \approx 2$ g/cm^3 is a film density, d is a film thickness, m_c - carbon atom mass, t - deposition time, τ - discharge current pulse width, f - discharge current pulse frequency. Although we did not measure the film density, here we suppose it to be approximately equal to 2 g/cm^3 because of the following reasons. On the one hand, according to flotation measurements the film is heavier than CCl_4 (ρ = 1.6 g/cm^3), on the other hand, the film density cannot be higher than 2.25 g/cm^3 (i.e. the density of crystalline graphite). So, the film density can be roughly estimated as 2 g/cm^3 that is usual for graphite-like films deposited by magnetron sputtering$^{8)}$.

Plasma characteristics at the substrate position were determined from electrical measurements using a flat 12-mm-diamater Langmuir probe with a guarding ring. The probe current was registered simultaneously with the magnetron current by a *Tektronix TDS 3000* oscilloscope (*Tektronix*, USA). Flux of ions bombarding the substrate was calculated from the measured ion current density:

$$\Phi_i = j/e, \quad (2)$$

where j is ion current density to the probe, e is electron charge.

For investigation of the surface morphology, *Solver P47* atomic-force microscope (*NT-MDT*, Russia) was used and contact mode of surface imaging was applied. To investigate the hardness and elastic modulus of the coating surface layer, a *NanoTest 600* nanoindenter (*MicroMaterials*, Great Britain) was used. The maximum load was 1 mN; the indenter penetration depth did not exceed 5~10% of the film thickness. Dependences of the penetration depth of the diamond Berkovich indenter into the coating on the applied force in the loading and unloading stages were analyzed by the Oliver and Pharr method$^{9)}$. The final values of the hardness and elastic modulus were obtained by averaging the results of ten measurements.

3. RESULTS AND DISCUSSION

Typical waveforms of the magnetron discharge current and corresponding probe current are presented in Fig. 3. It can be seen that an increase of plasma

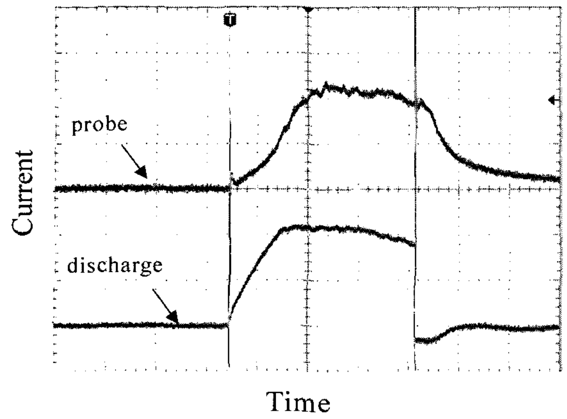

Fig. 3. Probe and discharge currents waveforms for the pulsed magnetron discharge (for the probe current 1 div = 1 mA, for the discharge current 1 div = 10 A, for time 1 div = 100 μs).

density is definitely lower compared to an increase of the discharge current, and maximum of plasma density in substrate vicinity is attained approximately in 100 μs after maximum of discharge current. The delay could be explained by limited rate of plasma generation, but this issue needs further investigations. Nevertheless, one can conclude that, in order to supply an ion bombardment of the growing film effectively, it is necessary to use rather long (~400 μs) discharge pulses. Plasma density and electron temperature values for various regimes of the magnetron discharge are presented in Table 1. As it can be seen, the measured plasma density and ion flux to the substrate calculated accordingly (2) are proportional to the discharge current. But atom flux to the substrate (1) is also approximately proportional to the discharge current. Thus, ratio of the ion and atom fluxes, and, consequently, energy per deposited carbon atom does not depend on the discharge current and it is approximately equal to 0.2 (Table 2). Nevertheless, the carbon film structure depends on the discharge current. In Fig. 4 AFM

Table 1. Pulsed magnetron discharge plasma parameters

I_m (A)	T_e (eV)	j (mA)	n (m^{-3})
10	3	1	$3.7\cdot10^{16}$
20	3	2	$7.5\cdot10^{16}$
40	3	4	$1.5\cdot10^{17}$
60	3	6	$3.0\cdot10^{17}$

where I_m is discharge current, T_e is electron temperature, j is ion probe current density, and n is plasma density.

Table 2. Parameters of pulsed magnetron graphite sputtering

I_m(A)	Φ_i (cm^{-2}s^{-1})	Φ_c (cm^{-2}s^{-1})	Φ_i/Φ_c
10	$5.7\cdot10^{15}$	$2.8\cdot10^{16}$	0.20
20	$1.1\cdot10^{16}$	$6.0\cdot10^{16}$	0.18
40	$2.2\cdot10^{16}$	$1.2\cdot10^{17}$	0.18
60	$3.4\cdot10^{16}$	$1.5\cdot10^{17}$	0.23

where I_m is discharge current, and Φ_i and Φ_c are ion and atom fluxes to a substrate, respectively.

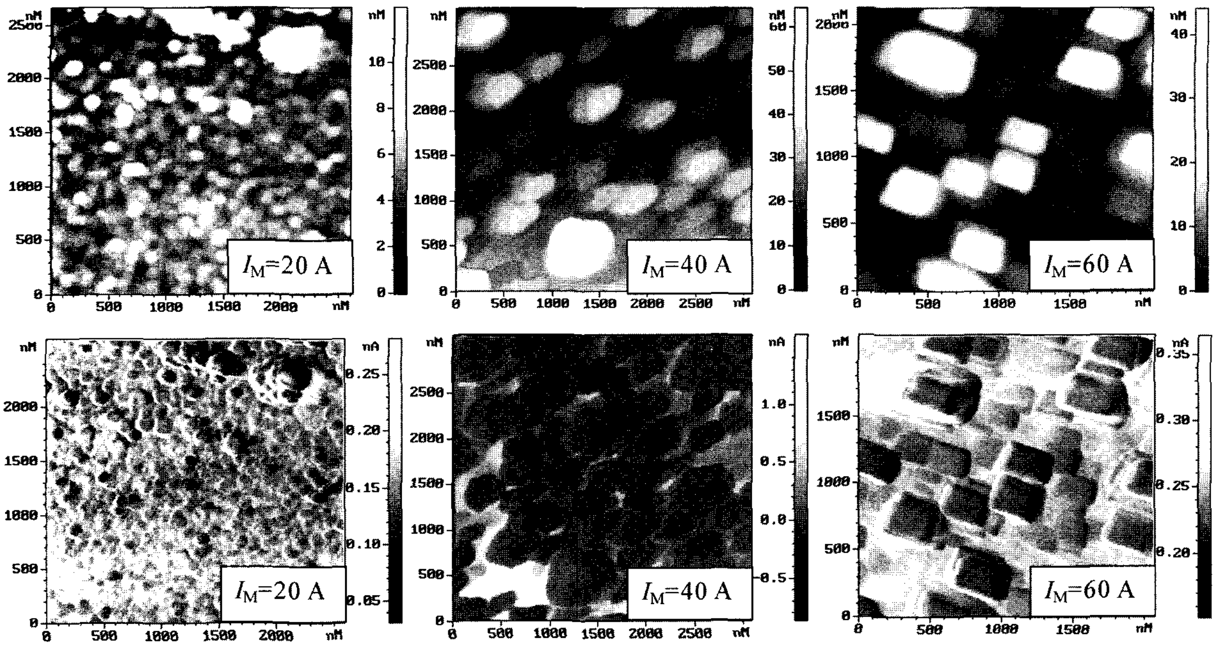

Fig. 4. Surface (top row) and lateral force (bottom row) AFM images of coatings deposited at various magnetron discharge currents without substrate bias.

images of graphite coatings deposited without substrate bias are presented. It is clearly seen that grain size in the films increases from 100 nm to 500 nm. It is known that only fine-grain nanocrystalline or amorphous carbon films are usually hard[1]. Formation of such kind of films (not only carbon ones) during ion-assisted deposition can be explained by increase of nucleation sites density due to defects induced by ions[10]. Obviously, a graphite film with smaller grains (100 nm) already have higher nucleation sites density and it can be easier turned into nanocrystalline or amorphous phase under ion bombardment compared to the film with larger grains. That is why pulsed magnetron discharge with the current of 20 A was chosen for hard carbon film deposition.

Dependencies of hardness and reduced elastic modulus on substrate bias voltage for carbon films deposited at pulsed discharge current of 20 A are presented in Fig. 5. One can see that maximum hardness (13 GPa) and elastic modulus (154 GPa) correspond to substrate bias of 3.4 kV. At lower or higher substrate bias voltages both hardness and elastic modulus drop. In the first case it can be explained by the lack of ion bombardment during the deposition that does not allow to transform graphite carbon phase into hard diamond-like one. In the second case the reason is excessive ion bombardment that also leads to graphitization of the coating.

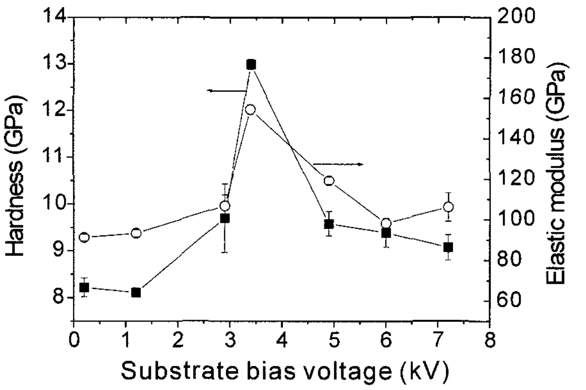

Fig. 5. Dependencies of hardness and elastic modulus on substrate bias voltage for carbon films deposited at magnetron discharge current of 20 A.

Investigations of the films surface by atomic-force microscopy support this conclusion. As it can be seen from Fig. 6, a carbon film deposited at substrate bias voltage of 0.2 kV consists of well-formed agglomerated grains of about 100 nm and roughness of 3.8 nm. Such a structure is characteristic of polycrystalline graphite films deposited without substrate bias. The film deposited at 3.4 kV substrate bias voltage is characterized by much lower roughness (0.3 nm) and almost not resolved crystalline structure that is natural for hard carbon coatings[11]. At last, the film deposited at 7.2 kV substrate bias voltage again is characterized by more pronounced structure and higher roughness

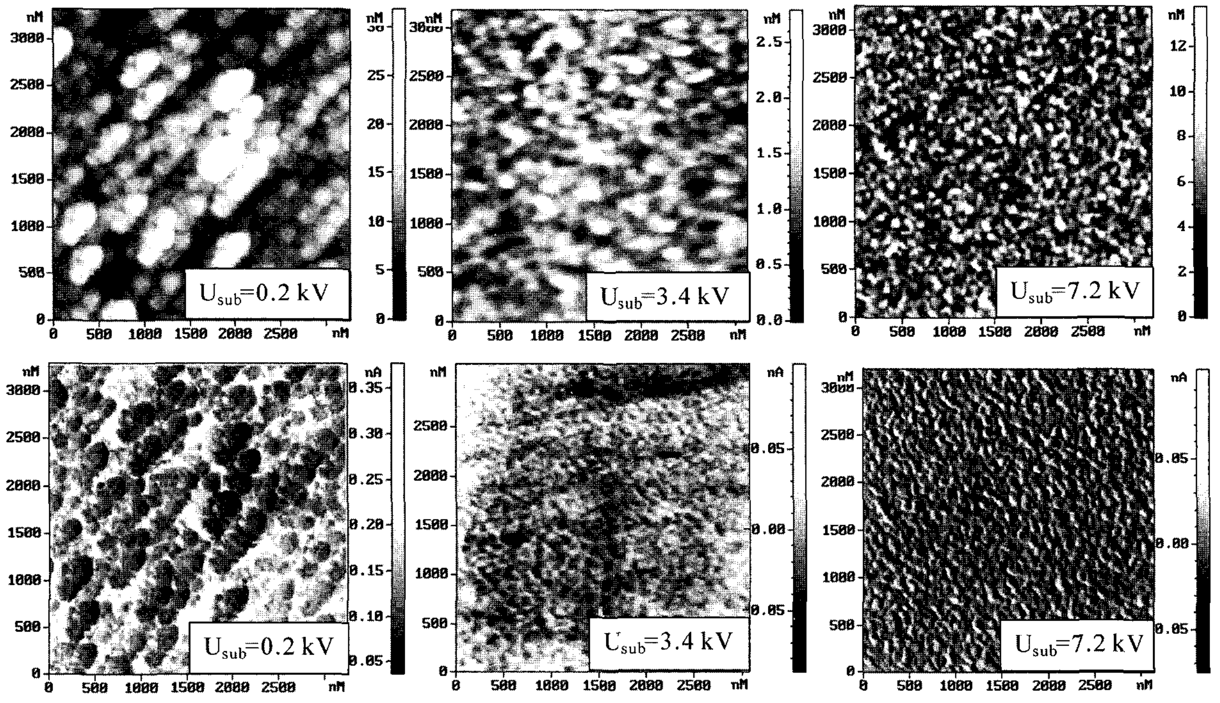

Fig. 6. Surface (top row) and lateral force (bottom row) AFM images of coatings deposited at various substrate bias voltages and magnetron discharge current of 20 A.

(1.6 nm). Probably, this is consequence of recrystalization process initiated by excessive ion bombardment.

4. CONCLUSION

Plasma density and sputtering rate of graphite for a pulsed magnetron discharge with a current of 10-60 A are found to be approximately proportional to the current. Thus, ratio of ion and atom fluxes at a substrate is about 0.2 and it does not depend on the discharge current. Nevertheless, the magnetron discharge current affects a grain size in the carbon films - the grain size increases from 100 nm to 500 nm while the discharge current increases from 10 to 60 A. Thus, in order to deposit hard fine-grained nanocrystalline or amorphous carbon films the low-current (20 A) mode of pulsed magnetron sputtering synchronized with negative substrate bias voltage was used. It is shown that carbon film deposited at 3.4 kV substrate bias voltage is characterized by maximum hardness (13 GPa) and elastic modulus (154 GPa), as well as by the lowest roughness (0.3 nm) that is natural for hard carbon films. Carbon films deposited at lower or higher substrate bias voltages are softer and rougher due to lack or excess of ion bombardment during their growth.

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