Properties of Nanolayered Carbon Films Deposited by Unbalanced Magnetron Sputtering Deposition[2]

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Abstract – Extended cylindrical magnetron sputtering system with rotating graphite cathode has been used for deposition of hard amorphous carbon (a-C) films. Two kinds of configurations of magnetic system ("balanced" one and "unbalanced" one) were used. For the "balanced" system the hardest (13 GPa) and well-adherent film was deposited at high-voltage pulsed negative substrate bias (with voltage of 3.4 kV, pulse width of 40 μs and repetition rate of 1 kHz, correspondingly) synchronized with the magnetron discharge. Meanwhile, for the "unbalanced" system two-fold increase in hardness (up to 26 GPa) was obtained with low-voltage and high-frequency negative substrate bias (with voltage 400 V, pulse width of 10 μs and repetition rate of 20 kHz, correspondingly) non-synchronized with discharge pulses. In the latter case an acceptable film adhesion and thickness were attained by deposition of nanolayered film consisted of alternate hard and soft layers. Probably, the film characteristics can be improved even more after further optimization of the film structure and the layers parameters.

1. Introduction

Hard amorphous carbon (a-C) films are known for their excellent tribological properties [1] such as high hardness and low friction coefficient that leads to sufficient increase in wear-resistance and life time of coated parts. However, one needs low-cost and highly-productive a-C films deposition technology for successful industrial application of the coatings. Another problem to be solved is deposition of relatively thick (1–2 μm) a-C coatings. It is associated with a weak adhesion of a-C films because of specific high intrinsic stresses in the coatings.

Among all methods of physical vapor deposition (PVD) of a-C films only magnetron sputtering [2] meets these requirements because it allows coating of large-area substrates with acceptable film growth rate. But it normally can be applied only for deposition of moderately hard a-C films with a low percentage of tetrahedral bonds. It is necessary to increase 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 [3, 4]. But it leads to decrease in sputtering rate of a cathode because of redistribution of plasma in a cathode-substrate region. Another way is using of pulsed magnetron sputtering since increase in discharge current during the pulse time allows dense plasma generation [5]. 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. Besides the magnetron discharge characteristics, the properties of a-C films are determined by characteristics of substrate bias voltage.

Thus, the purpose of the work was to investigate extensively properties of a-C films deposited by pulsed magnetron sputtering under various experimental conditions (magnetron construction, discharge parameters, characteristics of substrate bias voltage, etc.). Final goal is to develop technology for deposition of relatively thick (~ 1–2 μm) well-adherent and hard (20–30 GPa) carbon films on large-area (~ 1 m^2) substrates with acceptable (~ 1 μm per hour) growth rate.

2. Experimental

A cylindrical magnetron with a rotating graphite cathode developed in IHCE SB RAS (Tomsk, Russia) was used in the experiments (Fig. 1). The magnetron construction allows extremely high degree of target material utilization (up to 80%) and highly uniform films deposition (with thickness deviation of $< \pm 2\%$) [6]. The graphite cathode was made of a 900-mm-long tube (1) with 90-mm outer and 75-mm inner diameters, which was tightly glued to an inserted stainless steel tube (2). Both "balanced" and "unbalanced" configurations of the magnetron were used. In the first case inside the tube three rows of permanent magnets (3) were mounted, while in the second case external magnets (4) were also added. The magnetron was vertically mounted in a vacuum chamber of $1\times1\times1$ m^3 size and permanently rotated at a speed of 30 rpm during the experiments. Both for "balanced" and "unbalanced" configurations parameters of pulsed magnetron discharge (current of 10–60 A, voltage of 660 V, pulse width of 400 μs, and pulse repetition rate of 1 kHz,

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argon pressure of 0.2 Pa) were the same (Fig. 2). One can see rectangular voltage pulses, while current pulses had rather long rise-time of approximately 100 μs. The reason of this fact could be slow generation of plasma near the magnetron cathode and in the chamber.

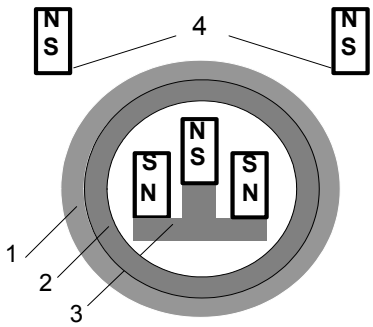


Fig. 1. Cross-section of the magnetron: 1 – graphite tube, 2 – stainless steel tube, 3 – inner permanent magnets, 4 – outer permanent magnets

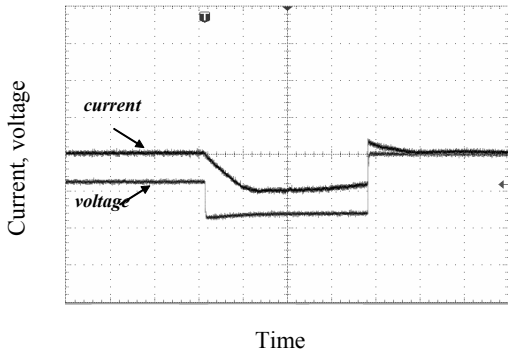


Fig. 2. Voltage and current waveforms for the pulsed magnetron discharge (for the current 1 div = 20 A, for the voltage 1 div = 500 V, for time 1 div = 100 μs)

Two kinds of substrate bias voltage have been used in the experiments, high-voltage one (with voltage of 0–10 kV, pulse width of 40 μs and repetition rate of 1 kHz, correspondingly) and low-voltage one (with voltage of 0–1000 V, pulse width of 10 μs and repetition rate of 20 kHz, correspondingly). In the former case the bias pulses were synchronized with magnetron discharge one, and in the latter case they were not.

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 thickness and density of carbon film deposited in the absence of a substrate bias. 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. 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 [7]. The final values of the hardness and elastic modulus were obtained by averaging the results of ten measurements.

3. Results and Discussion

Current from Langmuir probe situated 10 cm apart the magnetron shows that an increase of plasma density is even 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 (Fig. 3). The delay could be explained also 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.

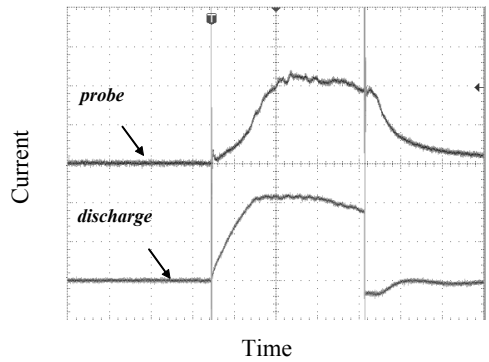


Fig. 3. Probe and discharge currents waveforms for the pulsed magnetron discharge (for the probe current 1 div = 1 mA, for the discharge current 1 div = 10 A, for time 1 div = 100 μs)

From Langmuir probe data and films deposition rate measurements it was found that both ions and atoms fluxes to the substrate are approximately proportional to the discharge current. Thus, ratio of the fluxes, and, consequently, energy per deposited carbon atom in the case of substrate biasing did not depend on the discharge current (for “balanced” and “unbalanced” configurations the ratio is about 0.2 and 1, correspondingly). So, for further experiments the pulse current of 20 A was chosen mainly because of

easier technological realization of the pulsed power supply for the magnetron.

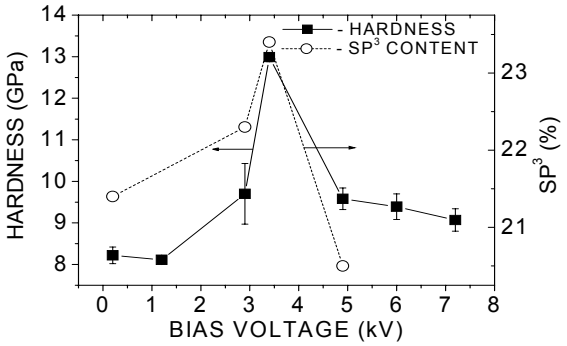
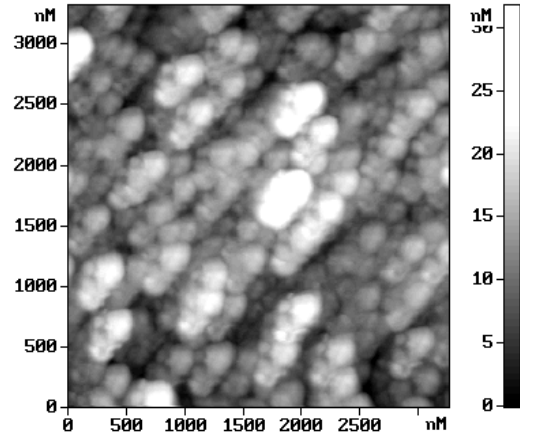


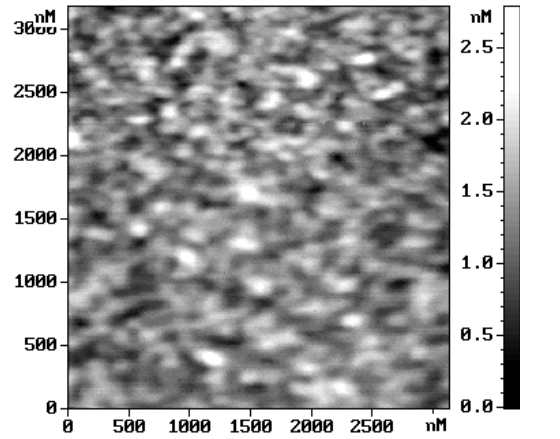
Fig. 4. Hardness and sp^3-bonded carbon content vs. voltage for a-C films deposited by pulsed magnetron sputtering assisted by pulsed high-voltage substrate bias

For "balanced" magnetron configuration it was found that low-voltage biasing is not effective for deposition of hard a-C films. Most probably, it is connected with insufficient ion bombardment during the film deposition that is caused, in turn, by low ion-to-atom ratio for the "balanced" magnetron configuration. In Fig. 4 one can see dependence of hardness and sp^3/sp^2 carbon ration on amplitude of the high-voltage bias pulses. One can see only fairly increase in these parameters at optimum voltage (3.4 kV) up to 13 GPa and 23.4%, correspondingly, compared to 8 GPa and 21.4%, correspondingly, at zero voltage. It means that there is no change of phase from graphite-like to diamond-like one since the ions energies are excessive for it, and hardening of the film is caused by decrease in grain size in graphite film under high-energy ion bombardment. It is clearly seen from AFM images (Fig. 5). Such findings correlate with mechanism proposed by Brottman et. al. [8] after extensive study of a-C films deposited by DC magnetron sputtering. Nevertheless, the films posses enough hardness (13 GPa) for low- and medium-load tribological applications. Moreover, because of their graphitic nature, they have good lubricant properties and absence of intrinsic stresses. The latter allows deposition of relatively thick protective a-C films.

The next series of experiments have been performed with use of "unbalanced" magnetron configuration. In this case low-voltage bias was found to be appropriate for deposition of hard a-C films. The hardest coating (26 GPa) was deposited at the substrate bias amplitude of –400 V, and its elastic modulus was equal to 333 GPa that is similar to those of diamond-like carbon films widely presented in literature (Fig. 6). Growth rate of the coating was about 1 micron per hour. It is necessary to note that mechanical characteristics of the coatings are close to those of a-C films deposited by laser ablation [9] only ta-C films deposited by filtered vacuum cathode arc are characterized by higher hardness and elastic modulus, as a rule [10].



U_{sub} = 0.2 kV



U_{sub} = 3.4 kV

Fig. 5. Surface AFM images of a-C coatings deposited at various substrate bias voltages for high-voltage bias assisted pulsed magnetron sputtering

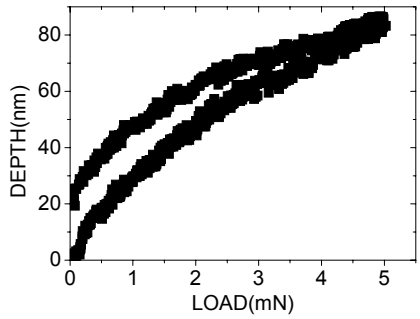


Fig. 6. Nanoindentation curve for nanolayered a-C film deposited by low-voltage bias assisted pulsed unbalanced magnetron sputtering

Most probably, in this case we have true change in phase from graphite-like one to diamond-like one. In order to clarify it we need additional XPS investigation of the films. This supposition is supported by poor adhesion of thick films to substrates that is caused by high intrinsic stresses which are inherent for diamond-like films. In order to prevent this effect and attain 1–2-μm-thick film we deposited nanolayered films consisted of alternate 30–40-nm-thick hard and soft carbon layers. Such kind of technique to relief the

film intrinsic stress has been proposed by many research groups [11, 12]. Obviously, a-C films deposited with "unbalanced" magnetron configuration are more promising than ones deposited with "balanced" magnetron configuration. However, the quality of the former films can be even improved after further investigation of their properties and optimization of their structure and deposition process.

4. Conclusions

Two kinds of configurations of magnetic system ("balanced" one and "unbalanced" one) of an extended cylindrical magnetron sputtering system with rotating graphite cathode were used for experiments on deposition of hard carbon films on large-area substrates. For both cases plasma density and sputtering rate of graphite for a pulsed magnetron discharge with a current of 10–60 A were found to be approximately proportional to the current. Thus, ratio of ion and atom fluxes at a substrate did not depend on the discharge current (~ 0.2 for "balanced" configuration and ~ 1.0 for "unbalanced" one). For the "balanced" system the hardest (13 GPa) and well-adherent film was deposited at high-voltage pulsed negative substrate bias (with voltage of 3.4 kV, pulse width of 40 μs and repetition rate of 1 kHz, correspondingly) synchronized with the magnetron discharge. Meanwhile, for the "unbalanced" system two-fold increase in hardness (up to 26 GPa) were obtained with low-voltage and high-frequency negative substrate bias (with voltage 400 V, pulse width of 10 μs and repetition rate of 20 kHz, correspondingly) non-synchronized with discharge pulses. In the latter case an acceptable film adhesion and thickness was attained by deposition of nanolayered film consisted of 30-40-nm-thick alternate hard and soft layers.

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