Investigation of plasma ion composition generated by high-power impulse magnetron sputtering (HiPIMS) of graphite

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Abstract. High-power impulse magnetron sputtering (HiPIMS) of graphite is used to increase the density of the plasma (up to $10^{13}$ cm$^{-3}$) and the fraction of ionization of carbon (up to 70%). It makes possible to increase the ion bombardment of the growing film by applying a negative high-frequency (HF) bias potential to the substrate, which allows deposition of diamond-like (DLC) coatings obtained by subplantation mechanism. The purpose of this research was to measure the ion composition of plasma during HiPIMS of graphite by time-of-flight spectrometer depending on discharge parameters (current, pressure, pulse-width). For any pulse-width (up to 250 $\mu$s) increase of discharge current leaded to growth of C$^+$ fraction (up to 60% for 70 A) that results from more intense sputtering of the graphite cathode. Decrease of argon pressure down to $3 \times 10^{-4}$ Torr leaded to reduction of C$^+$ fraction down to 13%, which is related to less intense sputtering. It can be seen that as the argon pressure in the vacuum chamber increases, the percentage of carbon ions in the flow increases (up to 75%), which may due to the “cooling” of electrons with increasing pressure - they no longer have enough energy to ionize argon (15 eV), but enough energy to ionize carbon (3.6 eV). Thus, using of time-of-flight analyzing of plasma ion composition generated by HiPIMS of graphite one can choose optimum discharge pressure and current – both of them should be maximized.

1. Introduction
Amorphous carbon diamond-like (DLC) films are characterized by a high content of diamond-like C-C bonds (70–90%) that explains their high hardness (up to 50 GPa), high IR transparency (up to 90%) and other properties [1]. The process of creating a metastable, dense phase of sp$^3$-hybridized diamond-like carbon is called ion subplantation [2]. Ions with significant energy penetrate into the depth of the growing film, occupy interstitial positions and increase the local density. The optimum energy is about 100 eV per carbon atom, embedded in the film [3], therefore, in the case of a dense (~ $10^{13}$ cm$^{-3}$) carbon plasma (consisting mainly of singly charged C$^+$ ions), a negative HF bias voltage of -100 V can be applied to the substrate. Diamond-like coatings are deposited by vacuum-arc cathode sputtering, pulsed laser deposition, deposition from an ion beam (i.e. by methods creating high-density carbon ions flow), but all these methods do not allow the deposition of DLC films on large-area substrates. In the case of magnetron sputtering of graphite, it is possible to deposit DLC coatings on large-area substrates, however, the plasma produced in this case has a low (less than 10%) degree of ionization, and the resulting films have a low hardness (5–10 GPa) even with a negative voltage bias applied to the substrate [4]. Increase of the plasma degree of ionization was achieved using inductively coupled plasma (ICP) superimposed on a magnetron plasma, using a hollow-cathode magnetron and using an
external ion source [5, 6]. But all these methods do not allow the deposition of DLC films on large-area substrates, contrary to high-power impulse magnetron sputtering (HiPIMS) of graphite. HiPIMS was used to increase the density of the plasma produced in this case (up to $10^{15}$ cm$^{-3}$) and the fraction of ionization of sputtered material – carbon (up to 70%) [7]. It makes possible to increase the ion bombardment of the growing film by applying a negative bias HF potential to the substrate, which allows deposition of DLC coatings. Parameters of plasma, generated by HiPIMS of graphite, depend on properties of magnetron discharge. In [8] using optical emission spectroscopy, an increase in the number of carbon ions in a plasma with an increase in the current of a short-pulse (5.5 $\mu$s) HiPIMS graphite discharge from 30 A (discharge voltage 1200 V) to 70 A (discharge voltage 1600 V) is shown. In [9] it was shown, that self-sputtering of graphite characterized by abrupt increase of discharge current. It can be related to change in the plasma ion composition: carbon ions should be the majority. The purpose of this research was to measure the ion composition of plasma during HiPIMS of graphite.

2. Experimental setup and methods of measurements
Figure 1 presents a schematic representation of the time-of-flight spectrometer, which is described in more detail in [10]. The graphite cathode of the magnetron (1, figure 1) is supplied with a pulsed voltage from a power source, as a result a high-current pulsed discharge (HiPIMS) lights up. The power source allowed to apply voltage pulses with a duration of 3–250 $\mu$s, voltage of 100–1000 V, current up to 1000 A and frequency of 0.1–15 kHz to the cathode. Thickness of the cathode was 8 mm, it was pressed from pyrolytic conductive dense PPG-8 graphite particles. The magnetron was equipped with NdFeB permanent magnets. At a distance of 8 cm from the cathode of the magnetron, an anode accelerating ions was placed (2, figure 1), to which a voltage of +15 kV was applied and a cathode that blocked electrons (3, figure 1), to which a voltage of -300 V was applied. A diaphragm with a diameter of 2 mm was situated in the center of the anode. As a result, in the discharge area (where argon was supplied) the pressure was 0.2 Pa, and in the working part of the spectrometer (where the turbo-molecular pump with a capacity of 900 l/s$^{-1}$ was located) – 0.05 Pa.

![Figure 1. Schematic diagram of the experimental set-up: 1 – magnetron sputtering system with graphite cathode; 2 – accelerating anode; 3 – accelerating-closing cathode.](image-url)
To get the plasma from the discharge, a shutter is used, located at a distance of 50 cm from the cathode (figure 1) and made as a set of two groups of alternating concentric rings located in a plane parallel to the cathode. One of the groups is grounded. The ion detector is located on the spectrometer axis at an ion-drift distance of $L = 1.2$ m from the shutter plane and is shielded from the maximum current by a disk in the center, which simultaneously serves to monitor the level of ion current. A deflection voltage pulse of -2 kV and duration of 150 ns is applied between the groups of rings. It should be noted that the angle of deflection does not depend on the type of particles and is about several degrees for accelerating voltage of $U_{acc} = +15$ kV. The ions from the plasma input the photomultiplier and induce its current, which is registered by an oscilloscope. The time corresponding to the appearance of peaks $t$ is used to calculate the mass-charge ratio $Q/A$ and determine the type of particles according to (1):

$$\frac{Q}{A} = \frac{mL^2}{2eU_{acc}t^2},$$

where $Q$ is the charge quantity and $A$ is the mass quantity of the ion, $m$ is the nucleon mass, $L$ is the ion-drift distance, $e$ is the electron charge, $U_{acc}$ is the accelerating voltage, $t$ is the time of appearance of a peak. The dependence of current of photo-multiplier on time is presented on figure 2 (the opening time of the shutter corresponds to the noise at the beginning of the oscillogram). An area under the curve is corresponding to quantity of the certain ions, so we can calculate the ion composition of the plasma.

![Dependence of photo-multiplier current on time and calculated plasma ion composition for argon pressure of $5\times10^{-4}$ Torr and pulse discharge current of 28 µs duration and 50 A amplitude.](image)

**Figure 2.** Dependence of photo-multiplier current on time and calculated plasma ion composition for argon pressure of $5\times10^{-4}$ Torr and pulse discharge current of 28 µs duration and 50 A amplitude.

### 3. Results and discussion

The characteristic currents of the photo-multiplier (see figure 2) were obtained, then the plasma ion composition was calculated and the percentage of singly-charged carbon ions for different pressures (figure 3), currents (figure 4), and pulse durations were shown (figure 5) and at different times during a long (250 µs) pulse (figure 6).
Figure 3. Dependence of $C^+$ ions percentage in plasma of HiPIMS of graphite on discharge pressure for pulse discharge current of 30 µs duration and 60 A amplitude.

From figure 2 it was seen that plasma of HiPIMS of graphite contains doubly-charged argon and carbon ions due to high (up to 70 A) pulsed discharge current. Plasma also contains $H^+$ and $^{13}C^+$ ions, because hydrocarbons and carbon $^{13}$C isotope contain in the graphite cathode, as well as oxygen O$^+$ ions from residual atmosphere and argon gas impurity. However, percentage of these ions was small and didn’t affect percentage of singly-charged carbon and argon ions.

From figure 3 it can be seen that as the argon pressure in the vacuum chamber increases, the percentage of carbon ions in the flow increases, which may be associated with more active ionization of argon and more active sputtering of graphite in the process. This may also be due to the "cooling" of electrons with increasing pressure - they no longer have enough energy to ionize argon (15 eV), but enough energy to ionize carbon (3.6 eV) [11]. Therefore, the plasma Ar$^+$ content falls from 88 to 25%, while the C$^+$ content increases from 13 to 75%.

With an increase in the discharge pulse current, the C$^+$ content in the plasma of HiPIMS of graphite constantly increases and reaches 60% at 60 A (figure 4). This trend was observed both for 20 µs and for 30 µs pulse width. This coincides with the published results of [8], where the methods of optical emission spectroscopy showed an increase in the number of carbon ions in a plasma with an increase in the current of short-pulse (5.5 µs) HiPIMS graphite discharge from 30 A (discharge voltage of 1200 V) to 70 A (discharge voltage of 1600 V). In figure 5, the current in the pulse changed differently (not independently, but increased with a decrease in the length of the discharge pulse, since the average discharge current remained constant at 50 mA). The result is the same – as the discharge pulse current increases, the C$^+$ content in the plasma increases (up to 45% at 40 A).
Figure 4. Dependence of C+ ions percentage in plasma of HiPIMS of graphite on discharge current for pulse discharge duration of 22 µs and 10⁻³ Torr argon pressure.

According to [5], the percentage of C⁺ in plasma at HiPIMS should not exceed 20% due to the low sputtering rate of graphite, small cross section and high energy of its ionization. In our case, a high value is obtained due to the fact that the stream of sputtered carbon atoms (which are then ionized by...
electron impact) is directed into the holes in the anode and the accelerating-locking cathode (see figure 1), falling into the region of reduced pressure and accelerating (unlike atoms of the working gas-argon, which are equally likely to be due to stochastic motion).

Figure 6. Dependence of C\(^+\) ions percentage in plasma of HiPIMS of graphite on time in the case of long (250 \(\mu\)s) discharge pulse for 10\(^{-3}\) Torr argon pressure and 60 A pulse discharge amplitude.

In figure 6 you can see how the percentage of C\(^+\) changes over time with HiPIMS graphite in the case of a long (250 \(\mu\)s) discharge pulse. It can be seen that at the beginning of the pulse, the percentage of C\(^+\) in plasma is 0\% (not yet sputtered), then rises to the maximum (50–60\%), then drops to 20\%, which is consistent with [5]. This is associated with complex processes occurring with atoms and ions of the working gas, as well as with atoms and ions of the cathode material (target) in the sputtering process and requires further study.

4. Conclusion
Output signal of the time-of-flight analyzer depends on discharge parameters – argon pressure, discharge current and pulse duration. Increase of discharge current to 70 A leaded to growth of C\(^+\) fraction up to 60 \% that results from more intense sputtering of the graphite cathode. This trend was observed both for 20 \(\mu\)s and for 30 \(\mu\)s pulse width. As the argon pressure in the vacuum chamber increases, the percentage of carbon ions in the flow increases, which may be associated with more active ionization of argon and more active sputtering of graphite in the process. This may also be due to the "cooling" of electrons with increasing pressure – they no longer have enough energy to ionize argon (15 eV), but enough energy to ionize carbon (3.6 eV) Thus, using of time-of-flight analyzing of plasma ion composition generated by HiPIMS of graphite one can choose optimum discharge pressure and current – both of them should be maximized.

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