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

A S Grenadyorov¹, V O Oskirko¹, K V Oskomov¹,² and V A Semenov¹

¹Institute of High Current Electronics SB RAS, 2/3 Akademichesky Ave., Tomsk, 634055, Russia
²National Research Tomsk State University, 36 Lenin Ave., Tomsk, 634050, Russia

E-mail: oskomov@yandex.ru

Abstract. High-power impulse magnetron sputtering (HiPIMS) of graphite is used for deposition of hard and wear-resistant amorphous carbon films, because tetragonal diamond-like carbon (DLC) bonds produced under subplantation mechanism at negative substrate bias voltage more intensive in the case of high-density plasma. In scientific literature one can find the fact that DLC films are more hard (37 GPa) in the case of short (7 µs) magnetron discharge pulses comparing to long (50 µs) ones (17 GPa) in HiPIMS of graphite. Likely, it is connected with denser plasma and more effective carbon subplantation in the case of short discharge pulses compared to long ones. To confirm this, it is necessary to investigate dependencies of plasma parameters (ion concentration, electron temperature, plasma and floating potentials) generated by HiPIMS of graphite on discharge pulse width. It was shown that electron temperature increased from 5.34 to 10.27 eV, and plasma density increased from $1.2 \times 10^{10}$ to $2.2 \times 10^{10}$ cm$^{-3}$ while pulse width decreased from 100 to 15 µs. It can be explained by increase of plasma disequilibrium since pulse current and power density increased to 250 A and 39.4 W/cm$^2$, respectively.

1. Introduction

The preparation of amorphous carbon diamond-like (DLC) films with a hardness of up to 50 GPa and a diamond-like carbon content of 70-90% on large-area substrates is still an urgent problem [1]. Such films are produced by vacuum-arc cathode sputtering, pulsed laser deposition, deposition from an ion beam, but all these methods do not allow the deposition of a-C films on large-area substrates. In the case of magnetron sputtering of graphite, it is possible to deposit a-C 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 small hardness (5-10 GPa) even with a negative voltage bias applied to the substrate [2]. High-power impulse magnetron sputtering (HiPIMS) is used to increase the density of the plasma produced in this case (up to $10^{13}$ cm$^{-3}$) and the degree of its ionization (up to 30-50%). This makes it possible to increase the ion bombardment of the growing film by applying a negative bias potential to the substrate, which allows deposition of DLC coatings.

In [3], pulsed high-current magnetron sputtering of graphite with increasing pulse width up to 200 µs, voltage amplitude up to 700 V and current density up to 4 A/cm$^2$ became an arc discharge without forming a cathode spot. The hardness of the diamond-like a-C coating deposited by supplying a negative bias potential of −100 V to the substrate reaches 34.5 GPa. In [4], the pulse duration of a high-current magnetron discharge during HiPIMS of graphite was small (7 µs), so to maintain an
independent discharge to the cathode, it was necessary to apply high-voltage pulses of 2200 V, with a current density of 0.4 A/cm². The hardness of a diamond-like a-C coating, deposited at negative bias potential of –80 V on the substrate, reaches 37 GPa. The authors of [5] studied the plasma produced by HiPIMS of graphite by optical emission spectroscopy. It is shown that when the discharge pulse duration is reduced to 5.5 μs and the discharge voltage is increased to 2200 V, the concentration of ions of the sputtered material – carbon is growing (in comparison with the discharge pulse duration is 30 μs and the discharge voltage is 1200 V). Thus, the properties of the plasma produced by HiPIMS current magnetron sputtering of graphite depend on the duration of the discharge pulse.

2. Experimental setup and methods of measurements

Measuring of plasma parameters (its density, potential, electron temperature) depending on discharge pulse width was the main goal of the research. In figure 1 is a schematic diagram of the experimental setup. Research were carried out in a vacuum chamber made of 600×600×600 mm³ stainless steel, the walls of which were an anode of a magnetron discharge. The magnetron was attached to the chamber, the main components of which are a graphite cathode sprayed (disk 100 mm in diameter and 5 mm thick), as well as a system of permanent magnets made of NdFeB alloy. The graphite cathode was made by sintering from the powder of pyrolytic dense electrically conductive graphite of PPG-8 grade. The working gas was argon, the pressure in the chamber was maintained at 0.2 Pa. In this paper, we investigated the properties of a plasma produced by pulsed high-current magnetron sputtering of graphite as a function of the duration of the discharge pulse. The power supply made it possible to apply voltage pulses with duration of 3-250 μs, voltage of 100-1000 V, current up to 1000 A and a frequency of 0.1-15 kHz per cathode. The plasma parameters were measured with a Langmuir probe made of nichrome wire with a diameter of 1 mm and a length of 4 mm. The probe was located at a distance of 100 mm from the cathode along the center. It was supplied with a constant voltage from the source from –40 V to +40 V with steps of 2 V step for interval from –10 V to 10 V and 10 V for others. The current to the probe, discharge current and discharge voltage were registered by an oscilloscope.

Figure 1. Schematic diagram of the experimental set-up.
3. Results and discussion
In table 1 one can see parameters of HiPIMS of graphite – discharge pulses width, magnitudes of discharge voltage and current, discharge power density. Pressure of argon in the vacuum chamber and the pulses repetition rate were constant and equal to 0.2 Pa and 2 kHz, respectively. It can be seen that discharge current was as high as 40 A for 100 µs pulse width (for 15 µs it was equal to 250 A). In figure 2 discharge and probe currents are presented. The probe current was changed during the discharge pulse, since parameters of the plasma also were changed. Firstly, it was grown to maximum, then dropped. So, to form the Langmuir probe characteristic, we used the peak value. In figure 3 one can see the Langmuir probe characteristic (probe current vs. probe voltage) for 100-µs discharge pulse. There are ion saturation current (at −20 to −40 V probe voltage) and electron saturation current (at 0 to +40 V probe voltage). Ion saturation current is too small (0.27 mA) for calculation of plasma density by Bohm formula, so we calculated plasma density and electron temperature using probe characteristic fracture point (at −4 V) [6]. It was assumed that the plasma consisted mostly from the argon singly charged ions, since the graphite was not self-sputtering material [7].

![Figure 2](image)

**Figure 2.** Discharge (a) and probe (b) currents for HiPIMS of graphite by 100-µs pulses.

| Pulse width (µs) | Pulse voltage (V) | Pulse current (A) | Power density (W/cm²) |
|------------------|-------------------|-------------------|-----------------------|
| 15               | 825               | 250               | 39.4                  |
| 25               | 720               | 150               | 34.4                  |
| 50               | 635               | 70                | 28.3                  |
| 100              | 595               | 40                | 30.3                  |

**Table 1.** Discharge parameters of HiPIMS of graphite.
The plasma parameters are presented in table 2. In the case of HiPIMS of graphite, the plasma density (~10^{10} \text{ cm}^{-3}) was an order higher than in DC magnetron sputtering of graphite (~10^{9} \text{ cm}^{-3}) [8]. It can be seen that plasma density and electron temperature are slightly higher for shorter pulses. It coincides with [9] and can be explained by higher disequilibrium plasma, discharge current and discharge power density in case of lower duty cycle (shorter pulse duration). Plasma potential (-4 \text{ V}) and floating potential (-20 \text{ V}) are constant. Higher plasma density and electron temperature in the case of lower duty cycle of impulse power plasma supplying (shorter discharge pulses) is theoretically calculated in [9]. But experimental measurements of plasma parameters in HiPIMS of graphite versus duration of discharge pulse were made firstly.

![Figure 3. Probe characteristic for HiPIMS of graphite by100-µs pulses.](image)

| Pulse width (µs) | Plasma density (cm^{-3}) | Electron temperature (eV) | Plasma potential (V) | Floating potential (V) |
|------------------|--------------------------|---------------------------|----------------------|-----------------------|
| 15               | 2.2 \times 10^{10}       | 10.27                     | -4                   | -20                   |
| 25               | 1.7 \times 10^{10}       | 9.54                      | -4                   | -20                   |
| 50               | 1.5 \times 10^{10}       | 6.23                      | -4                   | -20                   |
| 100              | 1.2 \times 10^{10}       | 5.34                      | -4                   | -20                   |

4. Conclusion
Plasma parameters (ion concentration, electron temperature, plasma and floating potentials) generated by HiPIMS of graphite vs. discharge pulse width have been investigated. It was shown that electron temperature increased from 5.34 to 10.27 eV, and plasma density increased from 1.2 \times 10^{10} to 2.2 \times 10^{10} \text{ cm}^{-3}, while pulse width decreased from 100 to 15 \mu s. It can be explained by increase of plasma disequilibrium since pulse current and power density increased to 250 A and 39.4 W/cm^2,
respectively. The plasma density was an order higher than in DC magnetron sputtering of graphite ($\sim 10^9$ cm$^3$). It is positive for producing of tetragonal diamond-like carbon (DLC) bonds under subplantation mechanism at negatively biased substrate.

**Acknowledgements**
This work was performed in terms of the State task of the Institute of High Current Electronics (№ 0366-2016-0010).

**References**
[1] Bewilogua K and Hofmann D 2014 Surface & Coatings Technology **242** 214
[2] Neuville S and Matthews A 2007 *Thin Solid Films* **515** 6619
[3] Mcculloch D, Bilek M, Partridge J and Mckenzie D 2016 *Journal of Applied Physics* **119** 155303
[4] Konishi T, Yukimura K and Takaki K 2015 *Surface & Coatings Technology* **286** 239
[5] Yukimura K, Ogiso H, Nakao S and Takaki K 2013 *IEEE Transactions on Plasma Science* **41** 3012
[6] Chen F 1984 *Introduction to Plasma Physics* (New York: Plenum)
[7] Anders A, Andersson J and Ehiasarian A 2007 *Journal of Applied Physics* **102** 113303
[8] Rossnagel S, Russak M and Cuomo J 1987 *Journal of Vacuum Sciences and Technology A* **5** 2150
[9] Ashida S, Lee C and Lieberman M 1995 *Journal of Vacuum Sciences and Technology A* **13** 2498