System for deposition of diamond like $a$-C:H films in Ar-C$_2$H$_2$ plasma with ion beam assistance

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Abstract. The paper presents a system which comprises a gas plasma source and an ion source and allows surface treatment of dielectrics due to ion charge compensation by plasma electrons. The ion energy corresponds to the discharge voltage of the ion source. The hardness of a-C:H coatings deposited by the method is up to 40–45 GPa.

1. Introduction
The high wear resistance, high hardness, and low friction coefficient of diamond-like carbon (DLC) coatings make them promising for deposition on cutting tools. DLC coatings can be formed by physical vapor deposition, e.g., vacuum arc [1] or magnetron sputtering [2], and by plasma-enhanced chemical vapor deposition in different discharges, e.g., rf discharge [3] or glow discharge [4]. The formation of carbon and hydrocarbon films with desired parameters depends strongly on the ion energy delivered to the surface of a growing film. In pulsed vacuum arc deposition, this energy is specified by the parameters of the discharge and plasma filtering system, and in rf plasmas, by the self-bias of a substrate. Such methods of controlling the ion energy severely limit the operating conditions of discharges, which produce carbon-containing plasmas, and narrow the range of operating parameters. Often, a bias is applied to a substrate with a growing DLC film [4], making it possible to vary the ion energy independently of the plasma generation conditions. However, DLC coatings are non-conducting, and the bias pulse should thus be short (up to tens of microseconds), which limits the coatings thickness. Another shortcoming of such systems is the impossibility to treat dielectric materials. In this context, ion beam technologies appear promising for the formation of DLC coatings [5, 6]. In these technologies, the energy to the surface of a growing film is delivered by ions which are accelerated by a separate device with independently controlled parameters. The use of only ion beams for the formation of dielectric coatings is problematic because of the necessity to remove the positive charge from the surface of a growing film. Therefore, it is reasonable and promising to use an ion beam jointly with a plasma whose electrons can compensate the ion charge at the surface of a coating. The main discharge plasma present in the region of substrates can serve not only as a carbon ion source but also as an electron source to provide the operation of an auxiliary non-self-sustained discharge. The auxiliary discharge can serve as a source of accelerated ions which deliver a desired energy to a coating.
The non-self-sustained mode of auxiliary discharges allows one to control the discharge parameters and hence the energy and current density of ions over a wide range.

Here we propose a system based on a hollow-cathode non-self-sustained glow discharge for the generation of an ion beam and present research data on its capabilities for depositing DLC coatings.

2. Experimental

In our experiments, we used a system with a vacuum chamber of dimensions 600×600×600 mm (figure 1) preliminary pumped by a turbomolecular pump to a pressure of no worse than $5 \times 10^{-2}$ Pa at a rate of 500 l/s. In the chamber, an gas arc discharge was ignited by a PINK plasma generator with a thermionic and hollow tungsten cathodes [7]. At the outlet of its cathode cavity, a diaphragm of diameter 20 mm was located; the gas supplied to the cathode cavity was argon. The diaphragm allowed us to reduce the arrival of acetylene from the working chamber to the region of the hot cathode, precluding its fast chemical erosion. At the same time, the operation of the main discharge was impeded, and conditions were provided for electron acceleration in the diaphragm region. The acceleration of electrons at the cathode cavity outlet enhanced the ionization efficiency of acetylene in the vacuum chamber, and it was required to increase the discharge voltage to 120–130 V (against standard 35–60 V). The discharge was powered by a specially designed (homemade) power supply with an output current of 120–50 A and operating voltage of 60–200 V, respectively. The power supply was equipped with an arc quenching system. The water-cooled inner walls of the vacuum chamber and the heat-insulated emission grid electrode of the ion source were at the potential of the main discharge anode.

During the operation with plasma-forming hydrocarbon gases, the water-cooled walls of the vacuum chamber were covered with a non-conducting hydrocarbon film within several minutes. Under such conditions, the main discharge current took the path exclusively to the emission grid electrode, as the hydrocarbon films on its hot surface were graphitized and became conducting. The ion source represented a water-cooled casing which was electrically insulated from the chamber walls and contained a cylindrical cathode cup of inner diameter 100 mm and height 50 mm on the inside. The emission electrode was fixed on the side flange of the vacuum chamber such that its hole was fully overlapped. In the emission electrode, there was a window of diameter 100 mm covered with a braided fine grid (0.5×0.5 mm) having a geometric transparency of $\approx 45\%$. The cathode cup and the emission electrode were coaxially fixed at 25 mm from each other and were placed at the potential of the vacuum chamber, forming a hollow cathode with a ring gap which opposed an axially located heat-insulated ring anode of dimensions $\Omega$150×30 mm. The system operated as follows. The electrons from the main discharge plasma penetrated through the grid of the emission electrode to the hollow cathode of the ion source and oscillated there, ionizing the gas supplied through the gas inlet of the ion source casing. The ions from the auxiliary discharge plasma were accelerated in the cathode layer near the emission electrode and injected back to the vacuum chamber through the emission grid. The design has the advantage that all electrodes are heated to temperatures at which hydrocarbon films on their surface are graphitized and become conducting, and this allows long-term operation (for more than 2 h) with no cathode and anode spots. The non-self-sustained glow discharge was powered by a pulsed source with an output voltage of up to 1 kV, average current of up to 10 A, and frequency of up to 50 kHz at a pulse duty factor of 10–80%.

The ion beam energy was measured with a single-grid energy analyzer. The analyzer is a collector to which a variable bias was applied, precluding the arrival of ions with an energy lower than its potential to its surface. At a distance of 1 mm upstream of the collector, there was a grid with a mesh size of 0.4×0.4 mm, diameter of 16 mm, and geometric transparency of 40% fixed on the stainless steel casing. No electrons from the main discharge plasma arrived at the collector because a negative bias of 250 V was applied to the grid of the energy analyzer, and its value was sufficient for the formation of a cathode layer in the main discharge plasma. The collector was placed coaxially to the window of the emission electrode at a distance of 50 mm.
The instantaneous values of the potential and collector current were measured using an automated digital recording system. The beam energy characteristics were measured at an Ar pressure in the vacuum chamber of 0.3 Pa with no gas supply to the ion source and with the main discharge current chosen to provide an auxiliary discharge current of 5 A.

![Schematic of experimental arrangement.](image)

**Figure 1.** Schematic of experimental arrangement.

The substrate material for depositing a-C:H films was tungsten carbide (VK8 grade). The substrates were polished and were fixed on a holder kept at floating potential in the center of the chamber. The temperature of the holder was measured with a thermocouple. Directly before deposition, the substrates were exposed to ion cleaning and heating to 130 °C with an Ar ion beam. The deposition time was 40 min. The temperature of the holder at the end of the process was no greater than 170 °C.

The operating pressure in the chamber was measured using an ionization gauge. The system operates such that during the discharge operation in an acetylene-containing atmosphere, the pressure readings decrease 5–6 times, depending on the parameters of the main and auxiliary discharges. This is likely because acetylene is dissociated with the release of a large amount of hydrogen, and the relative sensitivity of the used pressure gauge to hydrogen differs greatly from its sensitivity to argon and acetylene. To avoid measurement errors, the acetylene flow during deposition was controlled with an RRG-10 flow meter, and the pressure in the chamber was measured with the discharges off. All coatings were deposited at a partial acetylene pressure of 1.2 Pa, which corresponds to a flow rate of 18 l/min, and at a partial argon pressure of $6 \times 10^{-2}$ Pa. The partial pressure ratio was $\text{Ar/C}_2\text{H}_2 = 1/20$.

The coating microhardness was measured with a PMT-3M device, and the nanohardness with a Nanotest 600 device (Micro Materials).
3. Results and discussion

Our measurements of the ion energy (figure 2) show that at a pressure of 0.3 Pa, the maximum ion energy corresponds to the auxiliary discharge operating voltage with an accuracy of several volts. By estimates, the maximum range of ion energies is 60–70 V. Here, it should be taken into account that the range of ion beam energies depends strongly on the operating pressure, distance from the emission grid, and form factor of the emission and energy analyzer grids. The maximum ion beam density (accounting for the geometric transparency of the analyzer grid) is 1.25 mA/cm² and increases somewhat if the grid form factor is allowed for. The current density of plasma ions (to the right of the ordinate) is 0.5 mA/cm².

The coatings were deposited at constant average main and auxiliary discharge currents of 10 and 3.5 A, respectively. The discharge operating voltage in the ion source was varied from 300 V to 700 V. The auxiliary discharge current was controlled by varying the pulse duty factor from 65 to 40%.

According to microhardness measurements at an indenter load of 50 g, the coating microhardness increases from 25–35 GPa at an auxiliary discharge voltage of 300 V to 40–45 GPa at 625–700 V. The wide microhardness spread occurs because the coatings during deposition were partially separated and were thus discontinuous and nonuniform in thickness. The poor coating adhesion is due to insufficient ion cleaning of the surface from cobalt. The maximum coating thickness is 5.7 μm, and the film growth rate is thus ≈ 8.5 μm/h. According to nanohardness measurements at a load of 2–20 mN, the nanohardness of all specimens increases from 12–16 to 19–24 GPa with increasing the load. Such a behavior of the nanohardness and its considerable difference from the microhardness can be explained by the presence of a thin surface layer (tens of nanometers) with modified properties due to chemical reactions with atmospheric air.

Figure 2. Collector current versus its voltage at auxiliary discharge voltages equal to 100 V (a), 250 V (b), and 600 V (c).
4. Conclusion
Thus, the ion-plasma system based on a non-self-sustained glow discharge provides the generation of a plasma and an ion beam of energy gradually variable in the range of hundred electron-volts in a carbon-containing gas atmosphere. The system allows the deposition of diamond-like $a$-C:H films with a thickness of several micrometers and microhardness of up to 40 GPa. The preliminary ion cleaning of VK8 alloy substrates in the system is insufficient for satisfactory adhesion of the diamond-like coatings, and additional experiments are needed for its improvement.

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