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# Amorphous hydrogenated carbon films deposited by a closed-drift ion source

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**Abstract**

The general possibility of the extended (~30 cm) closed-drift ion source application for deposition of wear-resistant amorphous hydrogenated carbon (a-C:H) films on large-area dielectric substrates, in particular, on carbon-fiber plastic, is shown. Parameters of the "ion" and the "plasma" regimes of the ion source operation in argon and methane are defined. It is shown that the ion current nonuniformity is in the range of ±5–15% depending on the operation mode. Optimum conditions for the substrate precleaning in argon and hard, well-adhered a-C:H films deposition from methane are determined. The films are characterized by high hardness (~11 GPa) and low surface roughness (~0.13 nm) that leads to a several times lower friction coefficient (0.05) and wear rate (0.001 $\mu m^3 m^{-1} N^{-1}$) compared to glass and carbon-fiber plastic substrates.

**Keywords:** a-C:H films; Closed-drift ion source; Plastic substrates; Wear resistance

## 1. INTRODUCTION

Hard amorphous hydrogenated carbon (a-C:H) films have many potential applications due to the unique combination of their properties, such as high hardness, low friction coefficient, partial transparency in the infrared and visible spectral ranges, biocompatibility, chemical inertness, and so forth (Deshpandey & Bunshah, 1989). In particular, the films are used as wear-resistant and protective coatings on soft plastics (Grill, 1999). For deposition of hard a-C:H films it is principally important to create thermodynamically nonequilibrium conditions at the substrate, which supply formation and conservation of the metastable diamondlike carbon (DLC) phase. These processes can be induced by thermal spikes (Weissmantel *et al.*, 1980), subplantation (Lifshitz *et al.*, 1994), and stress (McKenzie *et al.*, 1991), which occur in the case of ion-assisted plasma deposition of DLC films.

Despite the variety of ion- and plasma-based techniques for DLC growth, there are not so many examples of their commercial application. For low-cost mass production it is necessary to employ technology which allows production of coatings with a high deposition rate on large-area substrates. Thus, creation of large volumes or extended flows of plasma are required. As was demonstrated by Wood *et al.* (1995), large-scale plasma-immersion deposition can be successfully applied for mass production of wear-resistant a-C:H films on metal substrates. Pulsed magnetron sputtering of an extended graphite target can also be potentially commercialized (Bugaev & Sochugov, 2000). However, these methods employ bias voltage applied to the substrate, and thus cannot be used in the case of dielectric substrates.

In this article, we suggest the use of an extended closed-drift ion source for deposition of a-C:H films on large-area dielectric substrates. Depending on the pressure, this device can produce either an ion beam or both plasma and ion beams (Zhurin *et al.*, 1999). The first regime is suitable for predeposition cleaning and activation of the substrate surface, while the second one is more suitable for deposition of a-C:H films. On the one hand, it allows the bombarding of growing a-C:H film; on the other hand, one can avoid charging of insulating substrates. Thus, the purpose of the article is to investigate the ion source operation regimes and to show the possibility of the deposition of wear-resistant and well-adhered a-C:H coatings on large-area plastic substrates.

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## 2. EXPERIMENTAL

A cross section of the extended (30-cm-long) closed-drift ion source developed at the High Current Electronics Institute (Tomsk, Russia) and used in the experiments is presented in Figure 1. This ion source consists of the anode (1) placed inside the case (cathode; 2) that is connected to the vacuum chamber wall (3) and grounded. In the cathode gap (4) the magnetic field of approximately 1300 G is created by permanent magnets (5). Methane was introduced into the chamber through the ion source. A direct current power supply (6) was connected to the anode in series with ballast resistance of 500 Ω. Depending on the pressure either an ion beam or both an ion beam and glow discharge plasma (7) existed in the chamber. To simulate deposition on large-area substrates, glass and fiber-carbon-plastic pieces of $2 \times 2$ cm$^2$ (8) were mounted on the scanning holder situated in front of the cathode gap at a distance of 10 cm. In our experiments, the scanning distance was 5 cm. Substrate precleaning and a-C:H film deposition conditions are presented in Table 1.

Linear uniformity of the ion beam current was measured by a flat strip-like ($15 \times 1$ cm$^2$) probe that was moved along the ion source parallel to its slot at a distance of ~10 cm. The probe was negatively biased at −30 V to reflect the electrons. Measurements of ion energy were made using a three-grid retarding electrostatic analyzer. The first plasma-confining grid was under floating potential, the second electron-reflecting grid was under negative potential (−30 V), while potential of the third ion-retarding grid was varied to allow only the ions with energies higher than the retarding potential to reach the collector. Finally, plasma parameters were measured by a plane Langmuir probe with a guard ring and the area of the collecting surface was equal to 1 cm$^2$.

For investigation of the surface morphology, an atomic-force microscope Solver P47 (NT-MDT, Zelenograd, Russia) was used, and contact mode of imaging was applied.

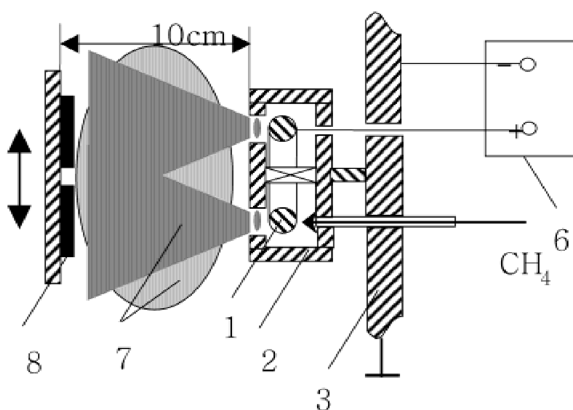


**Fig. 1.** Schematic draft of experimental setup for deposition of a-C:H films from the ion–plasma flow generated by the closed-drift Hall–current ion source: 1: anode of the ion-source, 2: cathode (case) of the ion source, 3: vacuum chamber wall, 4: cathode gap, 5: permanent magnets, 6: power supply, 7: ion–plasma flow, 8: substrates.

**Table 1.** *Substrate precleaning and a-C:H films deposition conditions*

| Process | No. | $P$ (Pa) | $U$ (V) | $I_d$ (mA) | $I_i$ (mA) | $v$ (nm/s) |
|---|---|---|---|---|---|---|
| Precleaning | IS1–IS3 | 0.03 | 1100 | 0 | 30 | — |
| Deposition | IS1 | 0.1 | 800 | 800 | 30 | 0.28 |
| | IS2 | 0.08 | 900 | 500 | 30 | 0.12 |
| | IS3 | 0.08 | 700 | 350 | 30 | 0.07 |

$P$ is the pressure, $U$ is the discharge voltage, $I_d$ is the discharge current, $I_i$ is the ion beam current, and $v$ is the film growth rate.

The a-C:H films deposited onto the glass were investigated; in all cases the coating thickness was about 2 $\mu$m. Thickness of the a-C:H films was measured by an optical microscope/interferometer MII-4 (LOMO, St. Petersburg, Russia). For investigation of the hardness and elastic modulus of the a-C:H coating surface layer a nanoindenter NanoTest 600 (MicroMaterials, Wrexam, UK) was used. Here, 2-$\mu$m-thick a-C:H films deposited onto glass were analyzed. The maximum load was 5 mN and the load rate was 0.25 mN/s; the indenter penetration depth did not exceed 5–10% of the film thickness. Dependences of the penetration depth of the diamond Berkovich indenter in the coating on the applied force in the loading and unloading stages were analyzed by the Oliver and Pharr (1992) method. The final value of the hardness and elastic modulus was obtained by averaging 10 measurements. For wear and friction coefficient measurements, a pin-on-flat homemade wear machine was used. Made of a WC-Co ball of 3 mm diameter was used as a counterpart. It was loaded to 3 N and moved reciprocally at a 4 mm distance and 15 mm/s speed. The adherence of the coatings was determined qualitatively using a rubber with $SiO_2$ abrasive particles moved reciprocally with an applied load of ~10 N. The results of the sand-rubber test (delamination) were examined by the optical microscope/interferometer MII-4.

## 3. RESULTS AND DISCUSSION

### 3.1. Characteristics of the closed-drift ion source

The ion source has two regimes of operation. The first one is the "ion regime" (high voltage, low current) characterized by the presence of a narrow ion beam in the chamber. As follows from retarding the three-grid analyzer measurements, the mean ion energy is about half of the operating voltage (Fig. 2). Plasma concentration in the vacuum chamber (~$10^9$ cm$^{-3}$) is low (Table 2). This low-pressure ($<8 \times 10^{-2}$ Pa in case of argon and methane) regime is preferred for substrate surface cleaning and etching as sputtering of the cathode is negligible. As can be seen from Figure 3, linear ion current nonuniformity in case of a low-pressure regime is lower than ±5% at 90% of the ion source length.

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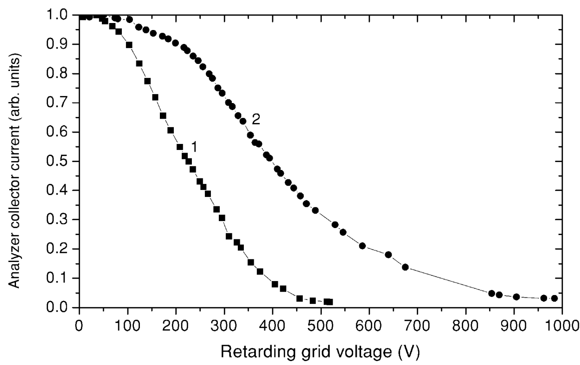


**Fig. 2.** Results of retarding three-grid analyzer measurements of the closed-drift ion source characteristics in the "ion" regime. 1: gas flow rate: 30 sccm, pressure: 0.5 mTorr, voltage: 520 V, current: 12 mA; 2: gas flow rate: 30 sccm, pressure: 0.5 mTorr, voltage: 1000 V, current: 33 mA.

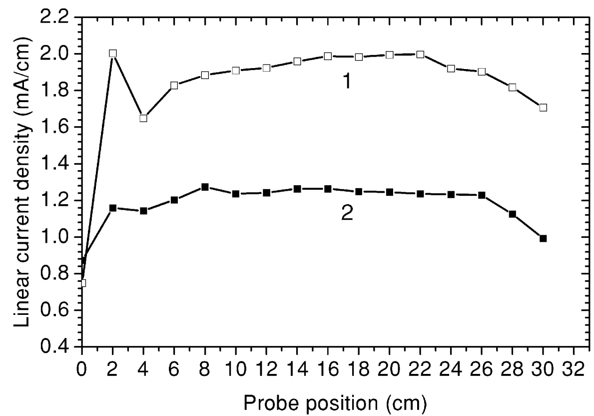


**Fig. 3.** Results of the ion current linear uniformity measurements in the "ion" regime. 1: gas flow rate: 38 sccm, pressure: 0.6 mTorr, voltage: 1100 V, current: 53 mA; 2: gas flow rate: 25 sccm, pressure: 0.4 mTorr, voltage: 1000 V, current: 23 mA.

The ion current distribution is only slightly affected by the chamber geometry or operating conditions.

The second operation mode of the closed-drift ion source is the "plasma regime" (low voltage, high current) characterized by the presence of relatively dense ($\sim 10^{10}$ cm$^{-3}$) plasma in the vacuum chamber (Table 2). This regime is preferred for ion-assisted deposition of a-C:H films under higher gas pressure ($\geq 8 \times 10^{-2}$ Pa). It is not acceptable for cleaning since the cathode sputtering is sufficient in argon atmosphere in this case. In Figure 4 one can see two curves corresponding to the retarding three-grid analyzer located in the ion beam (2) and out of it (1). The abrupt drop of collector current occurs when the ion retarding grid potential becomes higher than the positive plasma potential ($U_p = +300$–400 V). But, when the collector is located in the ion beam (curve 2, Fig. 4), at $U_p > +400$ V there is collector current caused exclusively by the ion beam ions. It can be derived that the mean ion energy in the plasma regime is lower ($\sim$100 eV) than in the ion regime ($\sim$500 eV). It is also necessary to note that the linear ion and plasma nonuniformity is strongly affected by the chamber geometry and can reach $\pm$15% (Fig. 5), but it is acceptable in the case of a-C:H films deposition for tribologic purposes.

### 3.2. Characteristics of a-C:H films deposited by the closed-drift ion source

It was found by qualitative adhesion tests that before a-C:H film deposition, it is necessary to clean the substrates in the ion mode in argon for 15 min to attain satisfactory adhesion. In this case, we did not observe delamination of the a-C:H films after treatment with rubber with $SiO_2$ particles. Conditions of the ion precleaning are presented in Table 1.

**Table 2.** *Closed-drift ion source plasma parameters*

| Regime | $P$ (Pa) | $I_d$ (mA) | $T_e$ (eV) | $n_i$ (cm$^{-3}$) |
|---|---|---|---|---|
| Ion | 0.06 | 30 | 4 | $10^9$ |
| Ion–plasma | 0.08 | 600 | 4 | $2 \cdot 10^{10}$ |

$P$ is the pressure in the chamber, $I_d$ is the discharge current, $T_e$ is the electron temperature, and $n_i$ is the ion concentration.

As was shown by Atomic Force Microscopy (AFM), the deposited a-C:H films are characterized by a very smooth surface. According to Figure 6 and Table 3, root-mean-square (RMS) roughness of the coatings is less than 0.4 nm. It is natural for DLC films deposited at low pressure (Jun *et al.*, 2000). It is also known that the diamond-like a-C:H film grown under optimum ion bombardment is smoother compared to polymer-like and graphite-like films deposited at lack of and excessive ion treatments, respectively (Jun *et al.*, 2000). It can be noted that ion beam current was constant for all deposition regimes IS1–IS3, while radical flux to the substrate increased with discharge current. Thus, sample IS1 was subjected to minimum ion treatment, while IS3 received maximum treatment. So, the increased RMS roughness for IS1 and IS3 samples can be attributed to their deviation from the diamond-like structure to those of polymer-like and graphite-like, correspondingly.

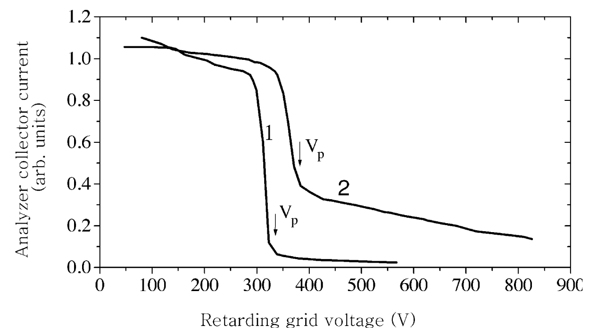


**Fig. 4.** Results of retarding three-grid analyzer measurements of the closed-drift ion source characteristics in the "plasma" regime: 1: the analyzer is situated out of the ion beam, 2: the analyzer is situated in the ion beam.

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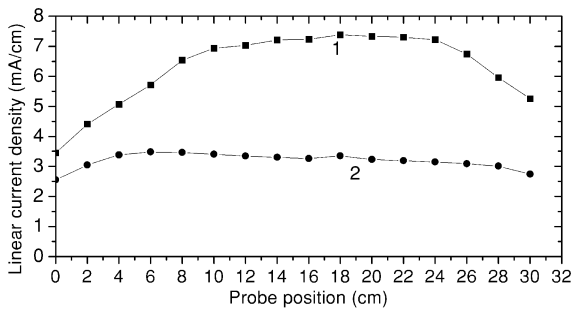


**Fig. 5.** Results of the ion current linear uniformity measurements in the "plasma" regime. 1: gas flow rate: 42 sccm, pressure: 0.7 mTorr, voltage: 400 V, current: 490 mA; 2: gas flow rate: 48 sccm, pressure: 0.8 mTorr, voltage: 460 V, current: 370 mA.

These suppositions are confirmed also by wear, friction coefficient, and hardness measurements. As follows from Table 3 and Figure 7, the hardness of the less rough sample IS2 is maximum, which is in agreement with the previous conclusions and with reference data (Jun *et al.*, 2000). The same coating has the lowest friction coefficient and wear rate (Table 3 and Fig. 8), which are several times lower compared to glass and carbon-fiber plastic substrates themselves.

**Table 3.** *a-C:H films characteristics*

| No. | $R_a$ (nm) | $H$ (GPa) | $E_r$ (GPa) | $w$ ($\mu m^3 m^{-1} N^{-1}$) | $\mu$ |
|---|---|---|---|---|---|
| IS1 | 0.35 | 8.84 ± 0.08 | 75.7 ± 0.5 | 0.010 | 0.07 |
| IS2 | 0.13 | 11.19 ± 0.23 | 87.6 ± 1.3 | 0.001 | 0.05 |
| IS3 | 0.16 | 10.19 ± 0.11 | 82.5 ± 1.6 | 0.002 | 0.08 |

$R_a$ is the root-mean-square roughness, $H$ is the nanohardness, $E_r$ is the elastic modulus, $w$ is the wear rate, and $\mu$ is the friction coefficient.

## 4. CONCLUSION

An extended closed-drift ion source potentially can be used for deposition of wear-resistant amorphous hydrogenated carbon films on both dielectric and conductive large-area substrates, since the nonuniformity of ion current along the ion source is no more than 5–15%, which is acceptable for deposition of a-C:H coating intended for tribological applications. The ion source has two distinct operation modes: the "ion" one ($P < 0.08$ Pa, $U = 1000$ V, $I = 30$ mA, only the ion beam exists in the chamber), and the "plasma" one ($P \geq 0.08$ Pa, $U = 700$–$900$ V, $I = 350$–$800$ mA, both the ion beam and the glow discharge plasma exist in the chamber), the parameters are valid for argon and methane. The first mode is convenient for precleaning of substrates in argon, while the second one can be successfully used for deposition of a-C:H films from methane.

In the case of carbon-fiber plastic and glass substrates, the optimum conditions for precleaning and a-C:H film deposi-

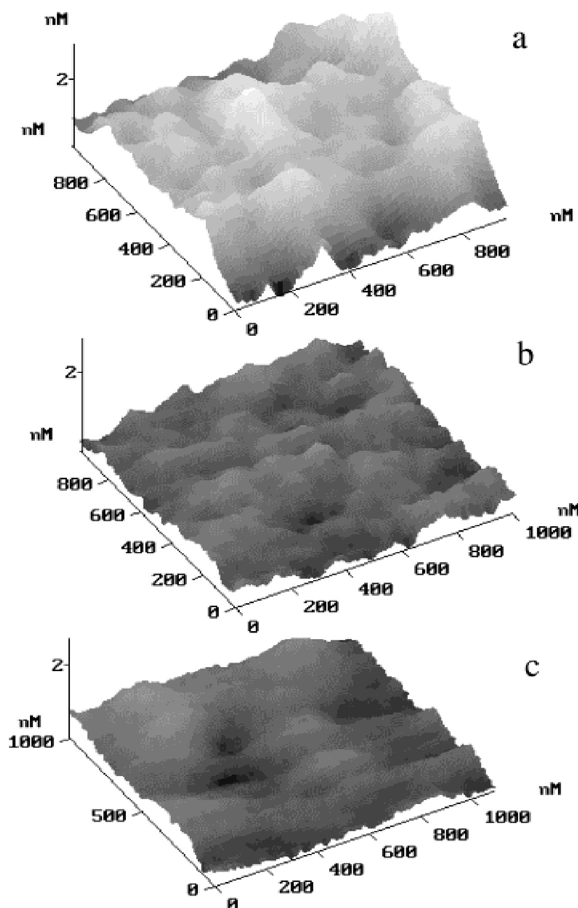


**Fig. 6.** AFM images of a-C:H films deposited on glass in IS1 (a), IS2 (b), and IS3 (c) regimes.

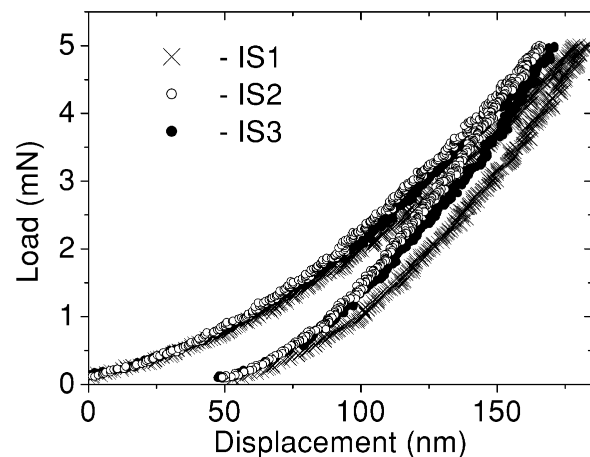


**Fig. 7.** Load versus displacement curves for a-C:H films deposited on glass.

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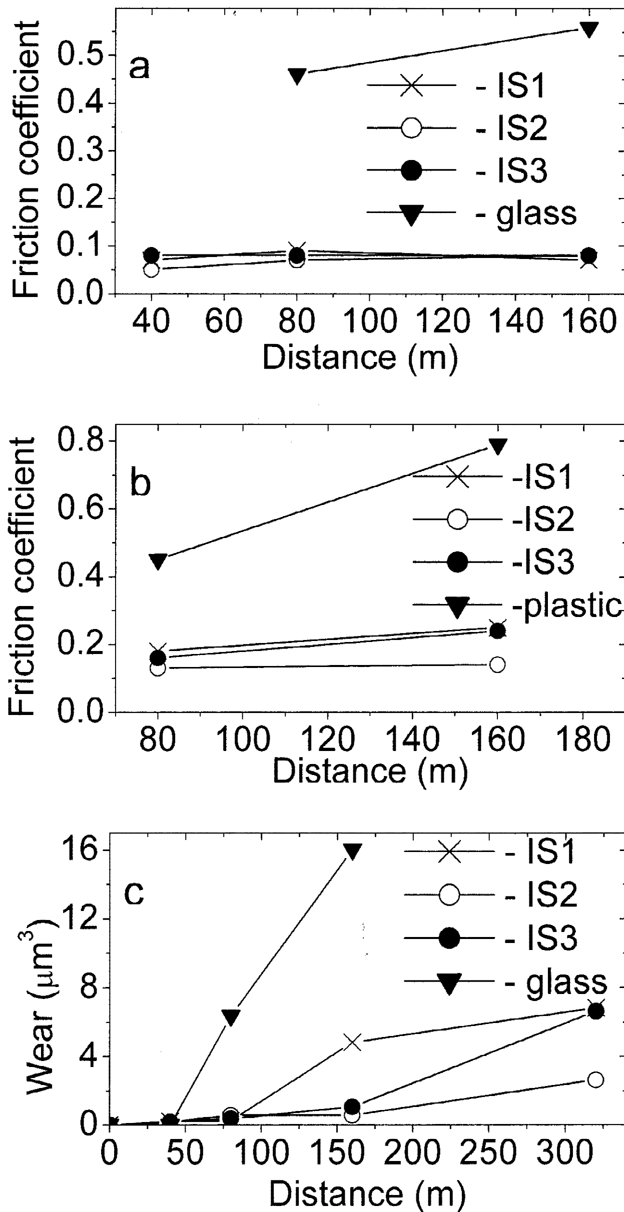


**Fig. 8.** Dependencies of friction coefficient (a, b) and wear (c) of a-C:H films deposited on glass (a, c) and plastic (b).

tion are as follows, respectively: $P_{Ar} = 0.03$ Pa, $U = 1000$ V, $I = 30$ mA and $P_{CH4} = 0.08$ Pa, $U = 900$ V, $I = 500$ mA. The deposited film is characterized by high hardness ($\sim$11 GPa), low roughness ($\sim$0.13 nm), and good adhesion (no delamination after sand–rubber test). It leads to a several times lower friction coefficient (0.05) and wear rate (0.001 $\mu m^3 m^{-1} N^{-1}$) compared to the substrates.

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