

Deposition of Diamond-Like α -C:H Coatings by Decomposition of Acetylene in Nonself-Sustained Plasma Cathode Discharge¹

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Abstract – A method for deposition of amorphous carbon coatings using a nonself-sustained pulse-periodic hollow cathode discharge is proposed and studied. The discharge is maintained by the emission from a grid-stabilized plasma cathode based on a DC hollow-cathode glow discharge and having an expanded anode section. In this method it is possible to considerably vary the discharge gap conditions and the nonself-sustained discharge parameters; hence, properties of the deposited coating can be optimized and the coating can be deposited in a single cycle with preliminary ion sputtering of the surface of the samples and the plasma immersion ion implantation necessary for formation of the interface layer and better adhesion of the deposited coating.

The experiments were performed at the controlled plasma cathode current of 0.2–0.5 A, the amplitude of the nonself-sustained discharge current pulses equal to 0.4–2 A, the pulse repetition rate of 50 kHz, and the pulse length of 10 μ s. The temperature of the uncooled steel, titanium, aluminum and hard-alloy samples was 100 to 200 °C. Coatings up to 10 μ m thick were deposited by acetylene (C₂H₂) decomposition. It was analyzed how the total pressure of the argon and acetylene mixture (0.06–0.6 Pa), the partial acetylene pressure (0.04–0.3 Pa) and the energy of ions (50–400 eV) bombarding the coating influenced the deposition rate (1–8 μ m/h), the coating microhardness (17–40 GPa) and the fraction of sp^3 bonds in the coating (20–70%).

1. Introduction

Properties of α -C:H coatings made by decomposition of hydrocarbon gases in a gas-discharge plasma (the PACVD method) are determined to a large extent by parameters of the plasma and conditions in the discharge gap, which influence the dissociation and the excitation of the plasma particles, the density and the composition of the flux of particles forming the coating, and the energy of ions in the flux. The basic parameters characterizing α -C:H coatings are the fraction of sp^3 bonds in the coatings, the average size of sp^2 clusters, and the concentration of hydrogen atoms in the coatings [1]. As the fraction of sp^3 bonds increases to 70% and the H concentration decreases to

25%, mechanical properties of α -C:H coatings are improved [2]. Such coatings are called diamond-like coatings (DLCs). Since DLCs possess dielectric properties, they generally are made using high-frequency, microwave and pulse discharges. Discharges that present interest for industrial technologies are those producing large volumes of dense homogeneous plasma, which allows deposition of the coatings on large surfaces. It is known that such properties are inherent in a nonself-sustained hollow-cathode discharge maintained by the emission from a grid-stabilized plasma cathode [3]. This discharge remains stable whatever the independent broad variation of the gas pressure, the discharge current and the discharge voltage, which determines the energy of ions bombarding the coating. However, so far this nonself-sustained pulsed discharge has been realized and studied only with the pulse excitation of the discharge in the plasma cathode and a limited pulse repetition rate.

The present study deals with a high-frequency (50 kHz) nonself-sustained discharge, which is realized using a grid-stabilized plasma cathode with a DC discharge. Specific features of the operation of this discharge during deposition of nonconducting films on the surface of electrodes are analyzed. Results of the investigation into the microstructure and the properties of α -C:H coatings made in this discharge are described.

2. Experiment

The electrode system of the gas-discharge device is shown schematically in Fig. 1.

It consists of a grid-stabilized glow-discharge plasma cathode with an expanded anode section and a plasma chamber for excitation of the nonself-sustained discharge and deposition of α -C:H coatings on samples. The electrode system of the plasma cathode with a coarse grid is analogous to the system described in [4] and includes trigger electrode 1, hollow cathode 2 with the exit aperture of diameter 6 mm, and anode grid 3 of diameter 80 mm with holes 1×1 mm in size. The round plasma chamber with a volume of ~ 3 l is formed by cathode electrode 4, which is electrically connected to anode grid 3. Rod anode 5 and samples 6 are placed in the cathode cavity. Argon is fed to the discharge system of the plasma cathode and acetylene

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(C₂H₂) is leaked into the plasma chamber. According to [5], acetylene is more suitable for making of DLCs with high mechanical properties because the smaller ratio of the hydrogen and carbon atoms H/C reduces the probability of the polymerization process in the plasma, favors the acceleration of the deposition rate, and is conducive to the smaller concentration of H atoms in the coating. A self-sustained DC (0.2–0.5 A) glow discharge at the operating voltage of 350–450 V is ignited in the electrode system. When a pulse voltage is applied to the plasma chamber electrodes (10 μs, 50 kHz) with an adjustable amplitude (100–600 V), a nonself-sustained discharge, whose current amplitude in the anode circuit increases with growing emission current of the plasma cathode, applied voltage and gas pressure, is ignited in the chamber.

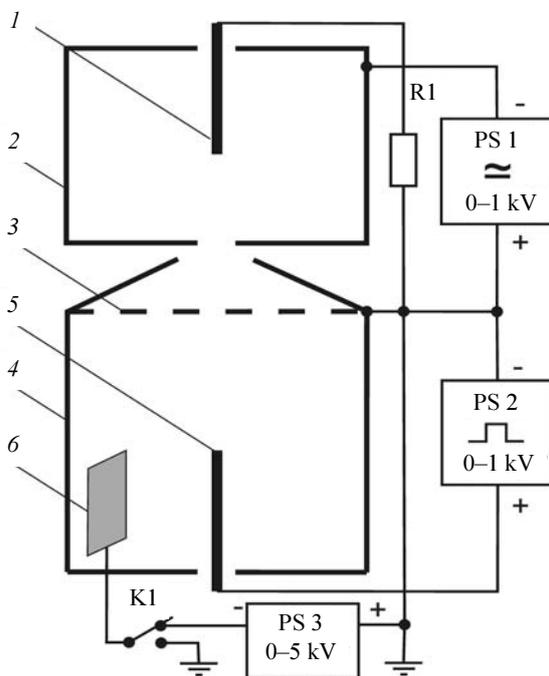


Fig. 1. Diagram of the gas-discharge device

Since DLCs are characterized by high internal stresses, particular emphasis was placed on the preparation of the surface of the samples. Before placing the samples in the chamber, they were cleaned in an ultrasound bath with a solvent. The surface of the samples was sputtered by argon ions in the plasma chamber. Subsequent to ion sputtering, acetylene was leaked into the plasma chamber, a constant negative potential of 3 kV was applied to the samples, and the plasma immersion ion implantation was realized in the pulsed discharge plasma for an interface formation.

This pretreatment excluded peeling of the coatings on stainless steel, titanium, tungsten carbide with 8% cobalt (BK8) hard alloy and aluminum substrates, the maximum thickness of the coatings (2–10 μm) was almost inversely proportional to their microhardness. It is known [6] that the increase in the substrate tem-

perature during deposition leads to graphitization of the coating. Check experiments including measurements of the temperature of uncooled samples showed that at the maximum amplitude of the nonself-sustained discharge current pulses equal to 2 A the temperature of the samples during deposition of the coatings was not over 200 °C. The experiments were performed taking different values of the total pressure of the gas mixture Ar + C₂H₂ (0.06–0.6 Pa), the acetylene partial pressure (0.04–0.3 Pa) and the voltage U_2 applied to the electrode of the plasma chamber (50–600 eV). As a first approximation, this voltage determines the energy of ions bombarding the coating. The estimates demonstrate that the change of the potential at the coating surface because of its charging with the ion flux is not more than ~10 V at the ion current density and the current pulse length used in the experiment.

The coating thickness was evaluated from the weight increment of the sample; in doing so, the density of the coating was taken equal to 2 g/cm³ [2]. The coating microhardness was measured by the Vickers method at a load of 0.2–2 N using a PMT-3M microtester. Microhardness values measured for Ti substrates, which were 3 GPa hard, were processed by a method [7] taking into account the effect of the soft substrate. Coatings ~1 μm thick deposited on the substrate of the BK8 hard alloy were studied by the nanoindentation method on a Nanotest 600 device (Micro Materials Ltd.) using a Berkovich diamond pyramid. The load was applied with the automatic control of the indentation depth (0.1–1 μm). The “loading-unloading” cycle was 40 s long. Values of the coating hardness were calculated by the Oliver–Pharr method [8].

The effect of the coating deposition conditions on the *sp*³ fraction in the coating was determined quantitatively using the Raman spectroscopy by a method based on measurements of the spectrum band (*G* and *D*) parameters. Laser radiation in the visible light spectrum with the wavelength of 514.5 nm was used for resonance excitation.

The microstructure of the coatings and their thickness were examined in a LEO 982 scanning electron microscope.

3. Results

Figure 2 presents the rate of the α-C:H coating deposition vs. the acetylene partial pressure in a mixture of Ar and C₂H₂ gases at a constant total pressure of the mixture equal to 0.26 Pa, an average density of the ion current equal to 0.4 mA/cm² and a voltage of 200 V. The surface area, on which the coating was deposited, was equal to the sum of the surface areas of the plasma chamber and the samples, i.e., ~10³ cm². The deposition rate increased with growing partial pressure of acetylene and gas discharge current.

The evolution of the Raman spectra with varying potential difference between the electrodes of the non-

self-sustained discharge and different gas pressures is shown in Fig. 3.

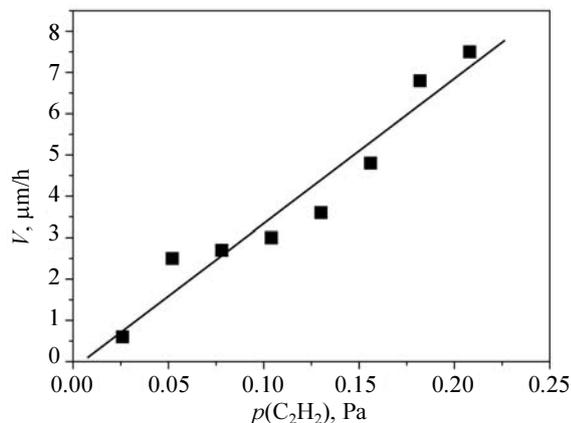


Fig. 2. The deposition rate of α -C:H coatings vs. the acetylene partial pressure at the pressure of the Ar + C₂H₂ gas mixture equal to 0.26 Pa

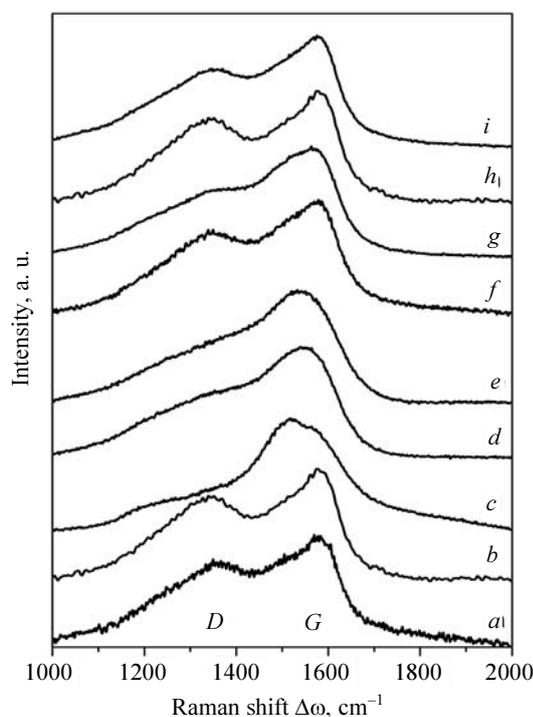


Fig. 3. Visible Raman spectra of the films deposited at different discharge voltages: 100 (a); 200 (b, f-i); 300 (c); 400 (d); 600 V (e); and different $p(\text{C}_2\text{H}_2)$: 0.06 (f); 0.10 (g); 0.16 (a-e, h); 0.21 Pa (i)

The spectra were processed by resolving them into two Gaussian components G and D . Figure 4 shows the ratio of the peak amplitudes I_D/I_G , the location of the peak G on the frequency scale $\omega(G)$ and its full width at half-maximum $\text{FWHM}(G)$, the microhardness H and the sp^3 fraction as a function of the voltage U_2 for coatings deposited at the total pressure of the gas mixture equal to 0.26 Pa and the acetylene partial pressure of 0.16 Pa.

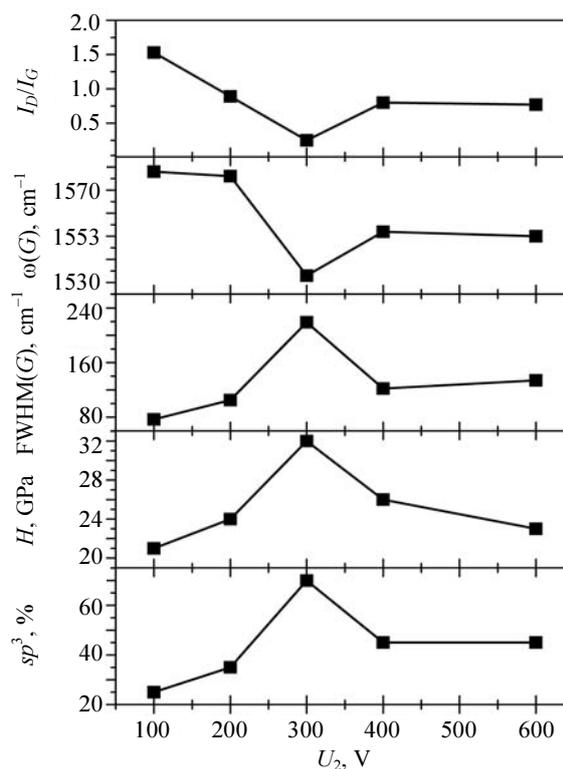


Fig. 4. The I_D/I_G ratio, the location of G , $\text{FWHM}(G)$, the microhardness H and the sp^3 fraction vs. the discharge voltage U_2

The fraction of sp^3 bonds was estimated by a method [1] based on the variation of this quantity from I_D/I_G and $\omega(G)$.

The maximum fraction of sp^3 bonds corresponded to the minimum of the ratio between the peak amplitudes of the Raman spectrum I_D/I_G and the maximum displacement of the peak G to the region of shorter wavelengths. A spectrum with these parameters was obtained for a coating deposited at a voltage of 300 V. The width of the peak G was directly proportional to the density and the Young modulus of the coating [2], which, in turn, correlated with the value of the coating microhardness. The maximum microhardness of the coating deposited at a discharge voltage of 300 V was ~ 32 GPa, which is close to the upper limit of this parameter for α -C:H coatings quoted in the literature known to the authors. The dependence of the coating hardness values measured by the nanoindentation method on the indenter penetration depth δ is shown in Fig. 5. When the penetration depth was equal to the coating thickness, the measured values approached those of the substrate hardness. The data obtained at $\delta = 300$ nm are in satisfactory agreement with the values measured with a PMT-3 microtester.

Maximum hardness values measured by the nanoindentation method were obtained for coatings deposited at $U_2 = 400$ V (Fig. 6), the total pressure of the gas mixture equal to 0.23 Pa and the acetylene partial pressure 0.13 Pa. They weakly depend on the acetylene partial pressure and the total pressure of the

gas mixture and are equal to 100, 48, and 40 GPa at the indenter penetration depth of 100, 200, and 300 nm respectively.

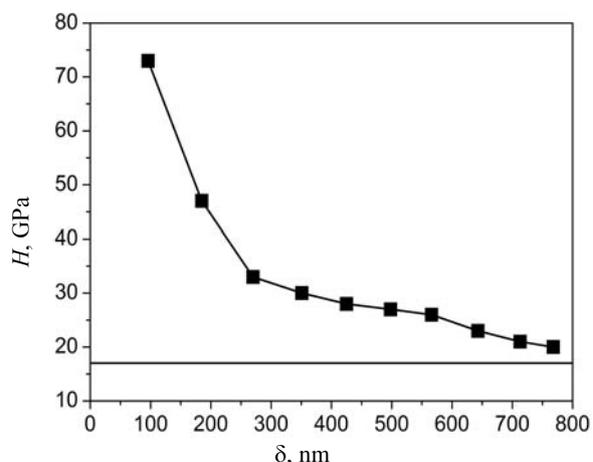


Fig. 5. Nanohardness vs. indenter penetration depth. The horizontal line shows hardness of the hard alloy BK8 substrate (17 GPa)

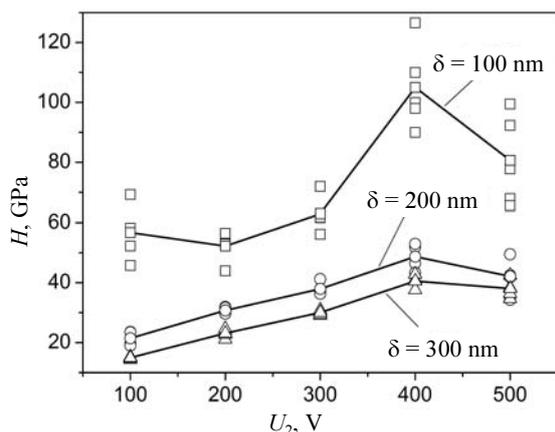


Fig. 6. Nanohardness vs. discharge voltage

Brittle cleavage of an α -C:H coating 1 μm thick having a maximum hardness is shown in Fig. 7. The coating is uniform and amorphous in its cross section and has a constant thickness.

4. Conclusion

A grid-stabilized plasma cathode based on a DC glow discharge maintains a high-frequency (50 kHz) non

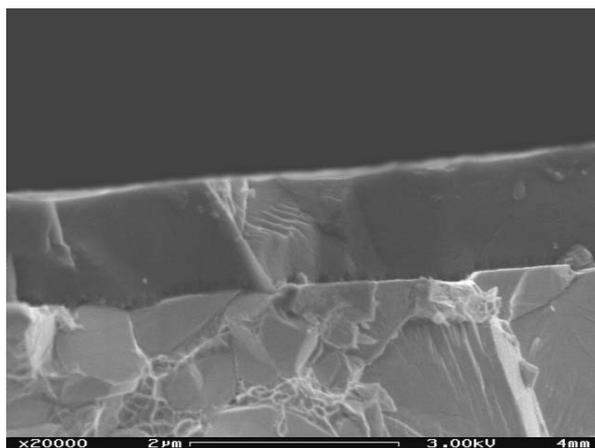


Fig. 7. Cross-sectional SEM image of a diamond-like coating with a brittle cleavage

self-sustained hollow-cathode discharge for generation of large volumes of dense spatially homogeneous plasma. The independent adjustment of the voltage and the current of the pulsed discharge and its stable operation over a wide interval of pressures and gas mixture compositions made it possible to optimize the deposition conditions and achieve a high microhardness of amorphous hydrocarbon coatings (> 30 GPa), a large fraction of sp^3 bonds, and a high rate of the coating deposition equal to (2–8) $\mu\text{m}/\text{h}$.

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