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# Plasma chemical deposition of hydrogenated DLC films with different hydrogen and $sp^3$-hybrid carbon content

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The influence of methane plasma parameters on the deposition rate and on the content of the hydrogen and the $sp^3$-carbon fraction in hydrogenated diamond-like carbon films (DLC) was investigated. It was shown that the proportion of the $sp^3$-carbon fraction mainly depends on the inductive power and the argon addition to the plasma; the latter also contributes to a decrease of hydrogen in the films.

**Keywords:** diamond-like carbon, plasma chemical deposition, $sp^2$-, $sp^3$-hybridization, Raman spectroscopy, secondary-ion mass spectrometry.

## 1. Introduction

Diamond-like carbon (DLC) is a material that consists of carbon atoms with $sp^3$- and $sp^2$-hybrid orbitals, which is widely used as protective coatings [1], in microoptomechanic systems [2,3], and as memristor memory cells [4]. Properties of DLC materials are highly dependent on the content of „diamond" and „graphite" fractions in them. Depending on the composition, DLC can be either a material with high hardness and dielectric properties, or a material with a low coefficient of friction combined with conductivity. The degree of carbon hybridization in these films can be controlled by varying the deposition conditions. Specifically, in [5] the authors have demonstrated that an increase in the Ne fraction in the composition of sputtering gas in the case of impulse magnetron deposition of composite DLC films results in an increase in the $sp^3$-fraction of carbon along with an increase in hardness and wear resistance of the resulted coatings. In [6], non-hydrogenated diamond-like carbon has been produced with varying bias voltage in the process of deposition. It has been found that a higher bias voltage promotes better sputtering of the graphite target and improvement of the etching effect and, as a consequence, an increase in „diamond" bonds in the DLC. As a result, the adhesive and tribological properties of coatings change significantly.

In this study, the method of low-temperature deposition in inductively coupled methane plasma is used to control the composition of DLC films. It will be shown that by varying the process parameters (including the type of gas discharge), it is possible to produce films with different contents of the $sp^3$-fraction of carbon. To analyze deposited coatings, a unique developed technique is used to identify carbon phases based on the intensity ratio of secondary cluster ions $CsC_8/CsC_4$ [7]. This technique makes it possible to unambiguously identify the obtained samples as DLC, and also provides information about the distribution of „graphite" bonds over the film thickness.

## 2. Experimental

Common Research Center Physics and technology of micro- and nanostructures of the Institute for Physics of Microstructures of Russian Academy of Sciences. The DLC films were produced by plasma-enhanced chemical-vapor deposition using an Oxford Plasmalab 80 Plus setup. The plasma was driven by a generator with a frequency of 13.56 MHz. For the substrates, we used KDB (100)-oriented silicon (0.001−0.005 Ohm) pre-cleaned from the oxide layer by washing in HF. The thickness of the films was measured by small-angle X-ray reflectometry (using a „D8 Discover" X-ray diffractometer). The elemental composition (Figure 1) was established by secondary-ion mass spectrometry (using a „TOF.SIMS-5/100" mass spectrometer). The percentages of hydrogen and the fraction of $sp^3$-hybridized carbon were determined by Raman spectroscopy (using a Renishaw inVia confocal Raman microscope). To calculate the content of hydrogen in films ($X_{\mathrm{H}}$), we used a technique based on the ratio between the slope of the fitted linear background $L$ (Figure 2) and the intensity of the $G$-peak [8]. The content of $sp^3$-hybridized carbon ($X_{\mathrm{sp3}}$) was calculated on the basis of the position of the $G$-peak [9]. Methane flowrate ($f$), pressure ($p$), capacitive power ($RF_p$) and inductive power ($ICP_p$), as well as composition of the plasma (argon addition) were varying parameters. The data are tabularized. Sample 1 was chosen as a reference for comparison; it has been grown with $f = 10\,\mathrm{cm^3/min}$, $p = 10\,\mathrm{mTorr}$, $RF_p = 75\,\mathrm{W}$, $ICP_p = 0\,\mathrm{W}$.

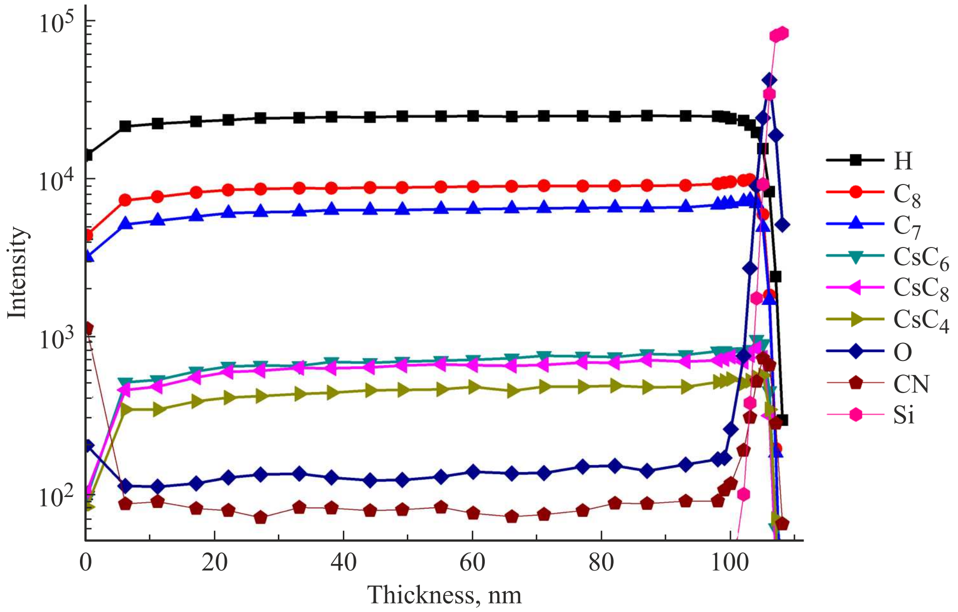

**Figure 1.** Distribution of secondary ions of chemical elements over depth in the DLC film (sample 7) plotted in a semi-logarithmic scale.

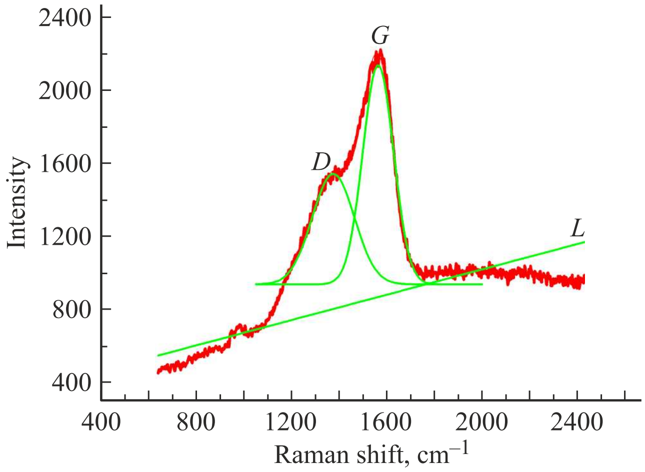

**Figure 2.** Spectrum of Raman scattering in a DLC film (sample 2) recorded at a laser wavelength of 515 nm: red line — 5-point smoothed spectral line, green lines — approximation of the spectrum by Gaussian functions plotted in the range from 950 to 2000 $cm^{-1}$, and the fitted linear background. (The colored version of the figure is available on-line).

## 3. Results and discussion

The produced films were homogeneous, smooth (Figure 3), with a good adhesion to silicon. It turned out that they had a high content of hydrogen, which is typical for the method of plasma-enhanced chemical deposition of DLC [10]. Also, the samples had traces of oxygen and nitrogen that have entered there from reactor walls. The peak of the intensities of CN and oxygen secondary ions at the interface with the substrate is due to the short-term high-power ignition of the plasma at the initial moment of growth. The $CsC_8/CsC_4 > 1$ ratio makes DLC films unambiguously distinguishable from graphite with the deposition of films occurred uniformly over the entire thickness with retention of the same content of the $sp^2$-fraction of carbon.

The presence of hydrogen in the films is responsible for the slope of Raman spectra of DLC because of the phenomenon of photoluminescence of C–H-bonds [8]. The spectra had peaks typical for diamond-like films — *D* and *G*. The *D*-peak was observed near 1315–1380 $cm^{-1}$ and was due to the presence of some graphite domains with different sizes. The *G*-peak is related directly to the vibration of double bonds of carbon inside graphite rings. It was observed at 1520–1560 $cm^{-1}$.

Deposition rate ($v$) and characteristics of the resulted diamond-like carbon films

| Sample No. | Varying parameter | $v$, nm/min | Thickness, nm | $X_{sp3}$, % | $X_H$, % |
|---|---|---|---|---|---|
| 1 | Reference sample | 9 | 133 | 47 | 24 |
| 2 | $ICP_p = 250$ W | 5 | 75 | 32 | 29 |
| 3 | $ICP_p = 150$ W | 6 | 85 | 40 | 30 |
| 4 | $RF_p = 250$ W | 10 | 146 | 43 | 26 |
| 5 | $p = 50$ mTorr | 14 | 212 | 47 | 24 |
| 6 | $f = 100$ $cm^3$/min,<br>$p = 50$ mTorr | 12 | 182 | 47 | 29 |
| 7 | $f = 100$ $cm^3$/min,<br>$p = 50$ mTorr,<br>$RF_p = 40$ W | 7 | 106 | 51 | 30 |
| 8 | Argon addition,<br>25 $cm^3$/min | 5 | 78 | 46 | 17 |

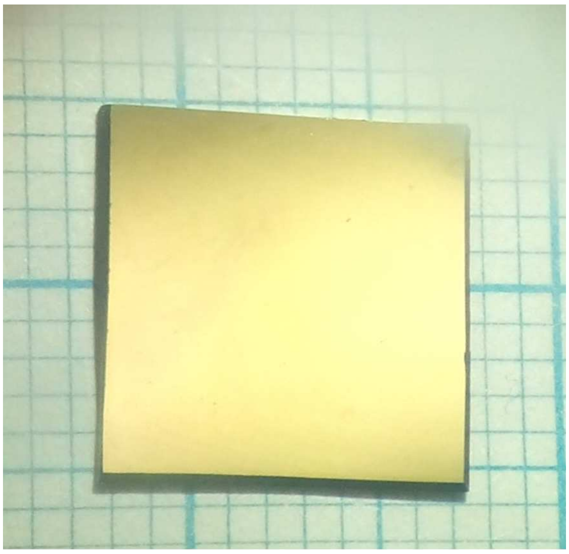

**Figure 3.** Photo of the DLC film deposited onto silicon (sample 1).

Based on the obtained data, a conclusion can be made that the strongest effect on the content of the $sp^3$-fraction of carbon has the inductive power. Turning on the generator of inductively coupled plasma resulted in a decrease in $X_{\mathrm{sp3}}$ by 15% at $ICP_p = 250\,\mathrm{W}$ (the effect was less noticeable at 150 W). This was accompanied by a 1.8 times decrease in the deposition rate. At the same time, the content of hydrogen in films has increased insignificantly. The inductively coupled plasma is characterized by a high density of charged particles as compared to the plasma of capacitive discharge. This results in an increase in the film etching rate and, as a consequence, in a decrease in the DLC deposition rate. Also, the surface of the sample becomes charged. The local electric field holds the carbon layers in two-dimensional configuration [11], which promotes formation of graphite clusters and decrease in the ratio of $sp^3/sp^2$-carbon.

The effect of capacitive power on $X_{\mathrm{sp3}}$ took place as well, however, it was less noticeable than the effect of inductive power. The „graphite“ fraction has decreased by 4% with the use of a capacitive discharge power of 250 W (compared to $RF_p = 75\,\mathrm{W}$). As the $RF_p$ increases, the effect of film etching becomes more noticeable due to the growth of the energy of reaction particles. Intermolecular layers in graphite are bound one to another by weak Van der Waals interaction, therefore they are subjected to more intensive etching than co-valence „diamond bonds“.

It is worth to note that the varying of methane pressure and flowrate did not affect the carbon hybridization degree in DLC. However, the process rate increased significantly (from 9 to 12 nm/min). This is due to the increase in concentration of ions and radicals in the plasma as the operating pressure and flowrate of methane grows.

An addition of argon to the plasma composition has resulted in a decrease in $X_{\mathrm{H}}$, which, with the $X_{\mathrm{sp3}}$ retained at the level of the reference sample, was indicative of an increase in „non-hydrogen“ content of the $sp^3$-fraction of carbon in the film. Such effect of argon is due to the direct destruction of graphite rings by particles of the argon plasma.

## 4. Conclusion

Thus, this study has demonstrated the possibility to control chemical composition of DLC films by varying the parameters of deposition in the reactor of inductively coupled plasma. The transition from capacitive discharge to inductively coupled discharge is accompanied by a decrease in the content of $sp^3$-hybridized carbon in the resulted films due to the effect of surface charging and holding of the carbon layers in two-dimensional configuration by local electric field. The addition of argon during the growth process helps to reduce the content of hydrogen in the DLC and reduce the deposition rate as a result of film etching.

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### Conflict of interest

The authors declare that they have no conflict of interest.

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