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Electrophysical properties of multilayer DLC films with different sp^3 -phase contents

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The resistivity, dielectric constant and breakdown field of diamond-like carbon multilayer films with different contents of the sp^3 -phase obtained in inductively coupled methane plasma have been investigated. The films resistivity appeared to be strongly dependent on the deposition parameters, while the dielectric constant was almost the same for all the samples. As a result of measuring electric current versus temperature and voltage, the hopping type of conductivity was established, and the average hop length and activation energy were determined. When voltage is higher than 1 V, a continuous increase in current up to breakdown takes place due to modification of the film internal structure.

Keywords: diamond-like carbon, multilayer films, electrophysical properties, hopping conduction mechanism.

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Due to the development of diamond microelectronics, interest in studying films based on diamond-like (DLC) carbon has recently increased significantly. The DLC chemical composition and properties are similar to those of diamond; in addition, it is much cheaper in manufacturing, and the range of its possible applications is quite wide: from sensor protective coatings [1] to memristive memory elements [2] and insulating layers [3]. Of particular interest are multisystems consisting of several DLC layers of different compositions. Such composites are primarily used as tribological wear-resistant and mechanically strong coatings [4–6] which are in many respects superior to single-layer DLC films. For instance, paper [4] shows that four-layer and eight-layer N-DLC/DLC systems possess higher resistance to polishing than their constituent monolayers, while resistivity of these multistuctures is 2–2.5 times less than that of an undoped DLC film.

It is known that properties of diamond-like carbon (including dielectric characteristics) depend on the composition: contents of hydrogen [7,8] and sp^3 -hybridized carbon [8,9]. An increase in hydrogen concentration leads to an increase in the film resistivity (ρ) because of an increase in the band gap width. The same effect is provided by an increase in the tetrahedral carbon fraction. Therefore, an idea has arisen of using multilayer DLC films in fabricating high-switching-speed memristors by creating between the layers a gradient of H and sp^3 -C concentrations as in the case of transition metal oxides [10,11]. However, to this end it is necessary to study at the initial stage general electrophysical properties of multilayer films with different contents of the sp^3 carbon phase and to establish their conduction

mechanism. This is just what this work is devoted to.

The study was performed by using facilities of the IPM RAS Common Use Center „Physics and technology of micro— and nanostructures“. DLC films were obtained by plasma-chemical deposition on silicon in an inductively coupled plasma reactor (with the generator frequency of 13.56 MHz) of the Oxford Plasmalab 80 setup. The chemical source of the plasma was gaseous methane fed to the chamber through a gas distribution ring. Substrates made from p -type boron-doped silicon silicon (0.001–0.005 Ω) were preliminary washed from the oxide layer with hydrofluoric acid. The deposited samples were multilayer periodic structures consisting of alternating layers A and B (Table 1) with different sp^3 -carbon contents and the number of periods equal to five. Conditions for depositing individual layers are described in [12]. Their thicknesses (l_A and l_B), as well as the total film thickness (d), were determined with a Bruker D8 Discover diffractometer by small-angle X-ray reflectometry (XRD).

To study electrophysical properties of multilayer DLC films by photolithography (exposure setup SUSS MJB4) and electron beam deposition (setup Amod 206), aluminum metal contacts were formed on the sample surfaces. The ohmic contact to the conductive substrate was made by burning-in indium. The DLC current-voltage characteristics (I-V characteristics) were measured with a Keithley 4200A-SCS parametric analyzer, while to measure capacitance-voltage characteristics (C-V characteristics) a precision Agilent E4980A LCR-meter was used. Based on the C-V characteristics, the dielectric constant (ϵ) was determined within the flat capacitor model via formula

$$C = \epsilon_0 \epsilon S / d, \quad (1)$$

Table 1. Deposition parameters of multilayer DLC films

Sample	Layer A No. [12]	Layer B No. [12]	t_A , s	t_B , s	d , nm (± 0.5)	l_A , nm (± 0.5)	l_B , nm (± 0.5)
DLC-1	6	2	50	120	100	8	12
DLC-2	3	2	120	120	95	8	11
DLC-3	Reference	2	90	120	90	6	12

Note. t_A and t_B are the deposition times of layers A and B, respectively. Hydrogen concentration in the films is $30 \pm 10\%$ [12].

Table 2. Electrophysical characteristics of multilayer DLC films

Sample	ρ , $10^{13} \Omega \cdot \text{cm}$ ($\pm 1\%$)		E_{br} , 10^6 V/cm ($\pm 5\%$)	ϵ ($\pm 5\%$)	l , nm ($\pm 20\%$)	E_a , meV ($\pm 2\%$)
	Prior to heating	After heating				
DLC-1	0.161	0.217	3.6	4.3	12.6	508
DLC-2	2.51	6.04	4.0	4.1	15.5	553
DLC-3	0.00869	0.00861	3.0	4.5	11.8	433

where C is the capacitance, d is the film thickness, S is the contact area, ϵ_0 is the electrical constant. The obtained dielectric constants are averaged values describing the layered structure as a whole.

Based on I-V curves (the linear region near zero voltage V), contact resistivity of the films (ρ_{cont}) was calculated. The measurements were performed for contacts of different diameters (from 50 to 500 μm). At the final stage, the breakdown voltage (U_{br}) was measured. The data is listed in Table 2. The table presents the values of resistivity and breakdown field (E_{br}) derived from ρ_{cont} and U_{br} normalized to the film thickness.

The grown coatings turned out to have similar dielectric constants. This is due to similar chemical compositions of the films. At the same time, values of the sample resistivity are significantly different. The highest was resistivity of the DLC-2 sample grown entirely in inductively coupled plasma. The ρ value of the DLC-1 film obtained under the conditions of a high methane flow and high pressure was an order of magnitude lower. The DLC-3 sample had the lowest resistance (three orders of magnitude lower than that of DLC-2).

The current-versus-voltage dependences were measured in the temperature range of 27 to 150°C. Fig. 1 presents the I-V curves for the contact 50 μm in diameter of the DLC-1 sample, as well as C-V curves (for other samples, the I-V and C-V curves are similar in shape).

After heating and cooling to room temperature, resistivity of the films increased; the higher was the initial resistivity, the more significant was the increase. Thus, there was observed an increase in ρ by 2.4 times for sample DLC-2 and by 1.3 times for DLC-1; resistivity of the DLC-3 sample remained almost unchanged (Table 2). Since, as established by secondary ion mass spectrometry [13], no variations in the DLC film structural composition is

observed at low annealing temperatures; the increase in ρ is associated, in the authors' opinion, with internal migration of hydrogen.

Based on the measured current density (J) dependences on voltage and temperature, it was established that the film conductivity is of the hopping nature and proceeds via charge transfer between graphite clusters through chains of carbon sp^3 -bonds [2]. In the case of such a conduction mechanism, the following formula is valid:

$$J = qNlv_0 \exp(-q\phi_T/kT) \exp(qIV/2dkT), \quad (2)$$

where V is the voltage, T is the temperature, q is the charge, N is the space charge density, l is the mean hop length, ϕ_T is the barrier height, v_0 is the natural oscillation frequency, d is the film thickness, k is the Boltzmann constant.

Formula (2) implies that, starting from a certain voltage value, the current logarithm (I) dependence on V is linear, as well as the $\ln I$ dependence on T^{-1} (Fig. 2).

From relation (2), the hop activation energy (E_a) was determined by approximating the experimental current dependences on temperature at $V = 1 \text{ V}$; in its physical sense, the hop activation energy is the barrier height at zero voltage. The l value was also calculated via (2) by approximating the room-temperature I-V curves. The average hop length in the samples turned out to range from 11 to 16 nm; these values are comparable to the layer thicknesses previously determined by SAXS (Table 1). Probably, in the DLC films under study there takes place a charge transfer through individual layers, whose calculated activation energy is about 500 meV. This is almost 5 times higher than E_a of a single-layer carbon film given in [2].

At voltages of 1 V and higher, the modification of the films begins, which leads to irreversible variations in the I-V characteristic (Fig. 3). This modification is associated

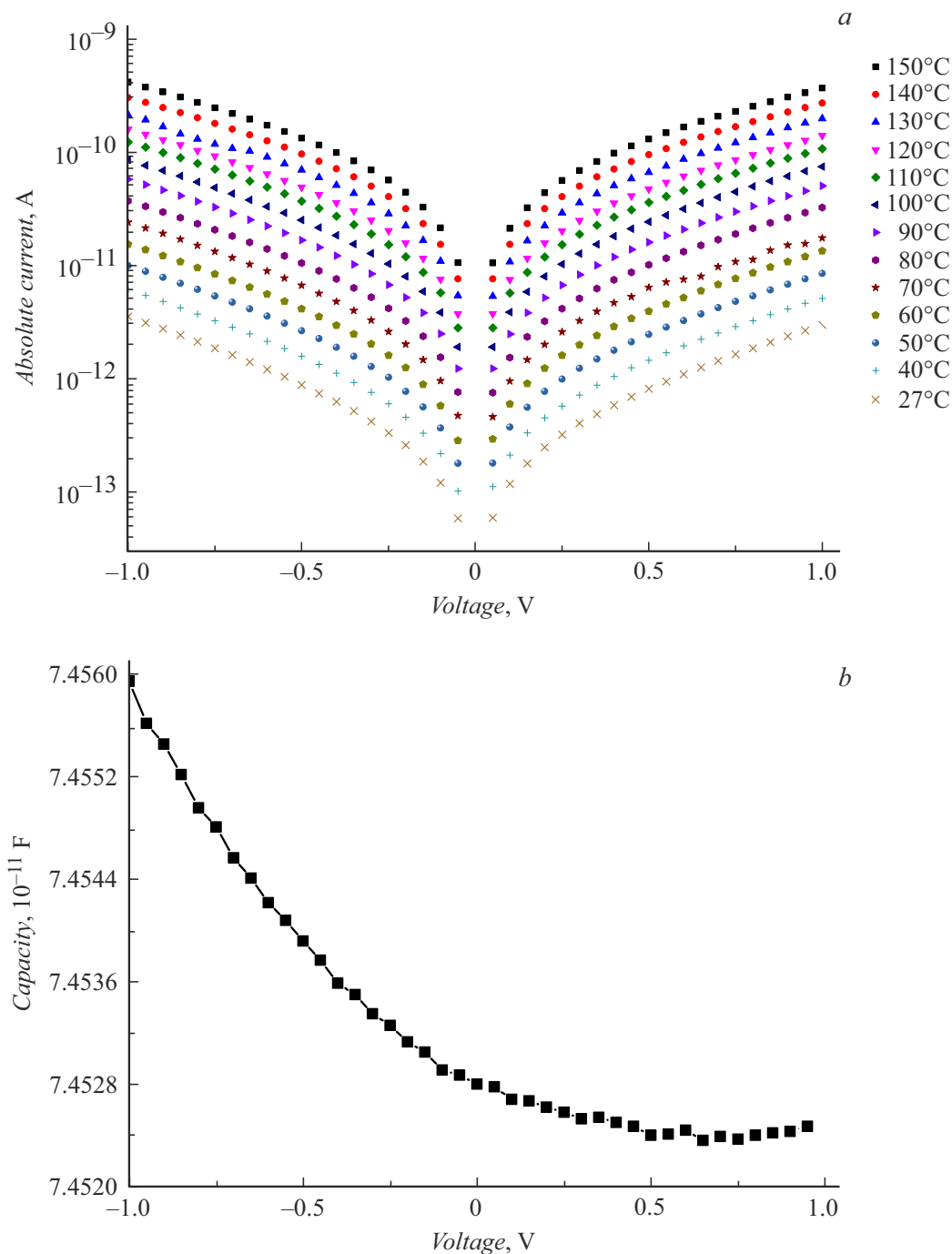


Figure 1. Current versus voltage at different temperatures (a) and C-V characteristics (b) for the multilayer DLC film in the range of -1 to 1 V.

with the graphite clusters rearrangement and concentration, due to which current increases continuously with increasing voltage. This behavior of films distinguishes them from „classical“ dielectrics SiO_2 and SiN_x [14], Al_2O_3 [15], in which the current remains low up to the very breakdown.

Thus, the work has shown that the studied multilayer DLC films are characterized by the hopping conduction mechanism with the average hop length of about 13 nm and activation energy of about 500 meV. Charge is transferred

through individual layers. The film resistivity ranges from $8.7 \cdot 10^{10}$ to $2.5 \cdot 10^{13} \Omega \cdot \text{cm}$ and depends on the deposition parameters: methane flow, pressure, presence of inductively coupled plasma. At the same time, dielectric constants of the samples differ insignificantly. All the films exhibit a quite high breakdown field ($(3-4) \cdot 10^6 \text{ V/cm}$); however, they cannot be used as protective dielectric layers because their internal modification takes place at voltages above ~ 1 V.

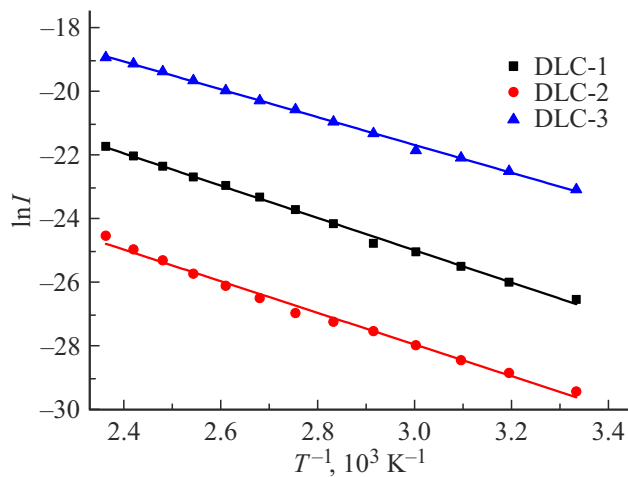


Figure 2. Dependences of $\ln I$ on T^{-1} at the voltage of 1 V for multilayer DLC films.

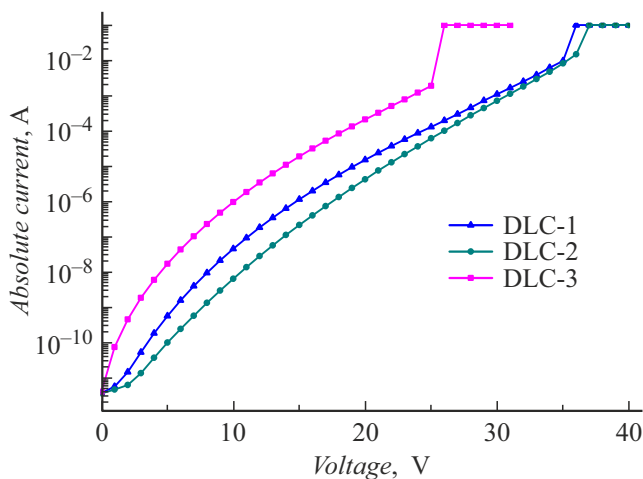


Figure 3. I-V curves of the multilayer DLC films at voltages below 40 V.

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Conflict of interests

The authors declare that they have no conflict of interests.

References

- [1] S.A. Smallwood, K.C. Eapen, S.T. Patton, J.S. Zabinski, *Wear*, **260** (11-12), 1179 (2006). DOI: 10.1016/j.wear.2005.07.019
- [2] Y.-J. Chen, K.-C. Chang, T.-C. Chang, H.-L. Chen, T.-F. Young, T.-M. Tsai, R. Zhang, T.-J. Chu, J.-F. Ciou, J.-C. Lou, K.-H. Chen, J.-H. Chen, J.-C. Zheng, S.M. Sze, *IEEE Electron Dev. Lett.*, **35** (10), 1016 (2014). DOI: 10.1109/LED.2014.2343331
- [3] D. Nakajima, H. Kuwabara, S. Annaka, S. Fujii, Y. Tanaka, K. Hirakuri, *Diam. Relat. Mater.*, **103**, 107731 (2020). DOI: 10.1016/j.diamond.2020.107731
- [4] Y. Lu, G. Huang, L. Xi, *Diam. Relat. Mater.*, **94**, 21 (2019). DOI: 10.1016/j.diamond.2019.02.019
- [5] Y. Iijima, T. Harigai, R. Isono, S. Degai, T. Tanimoto, Y. Suda, H. Takikawa, H. Yasui, S. Kaneko, S. Kunitzugu, M. Kamiya, M. Taki, *AIP Conf. Proc.*, **1929**, 020024 (2018). DOI: 10.1063/1.5021937
- [6] Y. Li, J. Enomoto, Y. Hirata, H. Akasaka, N. Ohtake, *Materials*, **14**, 2300 (2021). DOI: 10.3390/ma14092300
- [7] M. Massi, H.S. Maciel, C. Otani, R.D. Mansano, P. Verdonck, *J. Mater. Sci.: Mater. Electron.*, **12** (4-6), 343 (2001). DOI: 10.1023/A:1011252629646
- [8] Md.K. Hassan, B.K. Pramanik, A. Hatta, *New Diam. Front. Carbon Technol.*, **16** (4), 211 (2006). https://myukk.xsrv.jp/free-journal/download.php?fn=NDFCT518_full.pdf
- [9] E. Staryga, G.W. Bak, M. Dłuńiewski, *Vacuum*, **74** (2), 325 (2004). DOI: 10.1016/j.vacuum.2003.12.150
- [10] S.H. Lee, J. Moon, Y.J. Jeong, J. Lee, X. Li, H. Wu, W.D. Lu, *ACS Appl. Electron. Mater.*, **2** (3), 701 (2020). DOI: 10.1021/acsaem.9b00792
- [11] W. He, H. Sun, Y. Zhou, K. Lu, K. Xue, X. Miao, *Sci. Rep.*, **7**, 10070 (2017). DOI: 10.1038/s41598-017-09413-9
- [12] A.I. Okhapkin, M.N. Drozdov, P.A. Yunin, S.A. Kraev, D.B. Radishev, *Semiconductors*, **57** (5), 303 (2023). <https://journals.ioffe.ru/articles/57145>.
- [13] A.I. Okhapkin, P.A. Yunin, E.A. Arkhipova, S.A. Kraev, S.A. Korolyov, M.N. Drozdov, V.I. Shashkin, *Semiconductors*, **54** (9), 1056 (2020). DOI: 10.1134/S1063782620090213.
- [14] S. Chander, S. Gupta, Ajay, M. Gupta, *Superlatt. Microstruct.*, **120**, 217 (2018). DOI: 10.1016/j.spmi.2018.05.039
- [15] S. Maikap, R. Panja, D. Jana, *Nanoscale Res. Lett.*, **9** (1), 366 (2014). DOI: 10.1186/1556-276X-9-366

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