

Local electronic states in carbon diamond-like films

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Received August 2, 2024

Revised October 29, 2024

Accepted November 3, 2024

The volt-ampere dependences obtained by scanning the surface of carbon diamond-like thin films in the tunnel current mode are analyzed. Volt-ampere dependences are characterized by pronounced nonlinearity, consisting in the presence of a „zero“ current section on them. In addition, hysteresis can be noted when changing the direction of voltage change and strong current fluctuations at the ends of the volt-ampere dependencies, significantly exceeding the noise level. Spectral analysis of the fluctuation component of the volt-ampere dependencies indicates the frequency of occurrence of current fluctuations. The frequency range ranges from 0.04 to 0.8 V. In the range of dispersion of the maximum of the spectral density distribution, there are several low-amplitude maxima, which may be due to the presence of low-energy states in the energy spectrum of electrons.

Keywords: carbon films, volt-ampere dependencies, sp^2 - and sp^3 -bonds, local electronic states.

DOI: 10.61011/TPL.2025.03.60714.20082

According to the cluster model of carbon films [1,2], carbon atoms with sp^2 -bonds are arranged into hexagonal wafers of about 15 nm in size, linked by π -bonds into stacks — graphite clusters. These clusters are immersed in a matrix made of carbon atoms representing various configurations of sp^2 - and sp^3 -bonds. However, it has been found that in carbon diamond-like films formed by condensation of carbon from the vapor-gas phase obtained by direct evaporation of graphite targets using defocused laser irradiation, the regions with sp^2 - and sp^3 -bonds are arranged into tetragonal (diamond-like) and hexagonal (graphite-like) clusters [3]. In fact, it is a cluster composite of diamond-like and graphite-like clusters [4], linked by both sp^2 and sp^3 -bonds.

The presence of covalently bound sp^2 and sp^3 -clusters creates localized electronic states in the bandgap that control the optical properties of [5]. It should be noted that in diamond-like films there is a high density of localized states in the bandgap, up to its being complete full [5]. The existence in crystals of two types of electronic states (zone and localized, where the nature of localization of electrons is due to their interaction) has been theoretically analyzed [6]. Another mechanism responsible for the appearance of localized states is considered to be the presence of various types of structural defects, primarily defects such as broken bonds [5,7].

Scanning tunneling spectroscopy allows studying the local electronic structure of diamond-like films in areas smaller than the characteristic size of sp^2 and sp^3 -clusters in carbon diamond-like films [8]. Transitions of electrons between localized states, as well as between localized and delocalized states determine a wide range of phenomena: recombination, transfer, absorption of electromagnetic radiation, etc. [8]. In particular, specific features are observed in the

tunneling of electrons in films ta -C (tetrahedral amorphous carbon) and ta -C:H hybridized carbon containing up to 87% sp^3 -hybridized carbon, in the form of regular peaks on the differential conductivity. These features, clearly visible in the differentiation of the volt-ampere dependencies [8], are associated with fluctuations in the density of electronic states in the bandgap and valence bands of amorphous carbon (sp^2 and sp^3 -clusters in our interpretation of the structure [3,4]). Nonlinear volt-ampere dependencies [9] reveal the presence of localized electronic states (traps) in the bandgap of sp^3 -clusters.

Since the publications discussed herein lack information on the quantitative parameters of the peaks in the differential volt-ampere dependencies, this paper performs a Fourier analysis of current fluctuations and discusses the nature of these current fluctuations in the volt-ampere dependencies obtained during tunneling scanning of the surface of carbon diamond-like films.

Carbon diamond-like films were obtained by condensation of carbon on glass substrates with a copper sublayer from the vapor-gas phase obtained by evaporation of a graphite target by defocused laser irradiation in vacuum (residual pressure 10^{-5}). Radiation from a powerful NTS 300 laser with a wavelength of 1064 nm and energy in the range of 4–7 J was introduced into the vacuum volume through a focusing lens, which simultaneously served as a vacuum gate. The structural state of carbon diamond-like films and local volt-ampere dependencies were obtained using a Solver Next scanning probe microscope.

The typical local volt-ampere dependence of the tunneling current and the distribution of current channels on the surface of the diamond-like film are shown in Fig. 1.

The volt-ampere dependencies shown in Fig. 1 contain a section of „zero“ current and clearly pronounced fluc-

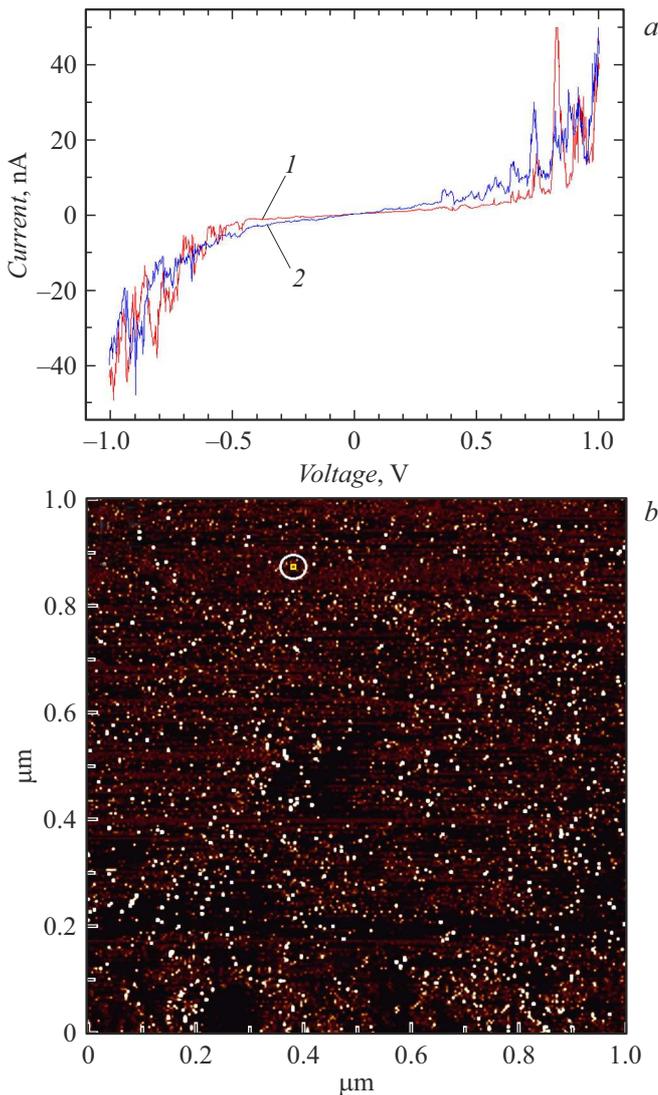


Figure 1. *a* — local volt-ampere dependences in a carbon diamond-like film with a „region of „zero“ current in the voltage range from approximately -0.3 and $+0.3$ V. *1* — voltage change from -0.3 and $+0.3$ V, *2* — voltage change from $+1.0$ to -1.0 V. *b* — distribution of localized tunneling current channels across the film surface with a highlighted measurement point of the volt-ampere dependence.

tuations of the tunnel current, the magnitude of which exceeds the noise level. To reveal the periodicity of these current fluctuations, we should perform a spectral analysis of the fluctuation component of the volt-ampere dependence, having previously isolated it from the experimental dependence (Fig. 1, *a*) by subtracting „smooth“ dependence, representing, for example, an approximating polynomial of the third degree of type

$$f(x) = ax^3 + bx^2 + cx + d,$$

where $f(x)$ — current value, x — voltage, a, b, c, d — adjustable coefficients. For a given volt-ampere dependence

(Fig. 1), the polynomial has the following form

$$f(x) = 48.13x^3 - 4.0x^2 + 0.76x + 1.06.$$

Fig. 2 shows the resulting dependence, which represents one current fluctuations in the voltage range from -1.0 and to $+1.0$ V. We shall single out two sections from this fluctuation current dependence in the voltage range from -1.0 to 0 V and from 0 to $+1.0$ V and perform a spectral analysis of each section of the fluctuation current-voltage dependence (Fig. 3). Similar actions were performed with the volt-ampere dependence at reverse voltage change from $+1.0$ to -1.0 V.

As follows from Fig. 3, the spectral density of fluctuations contains maxima, indicating the periodicity of the appearance of fluctuations in the volt-ampere dependences (Fig. 1, *a*). In addition to the main maximum, the spectrum contains three or four more maxima of much smaller amplitude, but exceeding the noise component of the spectrum. The generalized data of the spectrum analysis are summarized in the table.

From the given data, in addition to fluctuations of the tunnel current, we can note the presence of the „section of zero“ current and hysteresis of the volt-ampere dependences when changing the direction of change of the applied bias voltage. It is believed that the presence of the „section of zero“ current (current step in terms of [10]) is caused by the tunneling of electrons in the current channel, which is a chain of graphite-like and diamond-like clusters in carbon films. At differentiation of volt-ampere dependences allocate the region in the vicinity of zero voltage, which allows determining the bandgap width, the position of the Fermi level and peaks of differential conductivity in carbon diamond-like films [5,11].

The presence of localized states (traps [9]) in the bandgap is the main cause of nonlinearity, as well as hysteresis of the volt-ampere dependences, which is due to the different

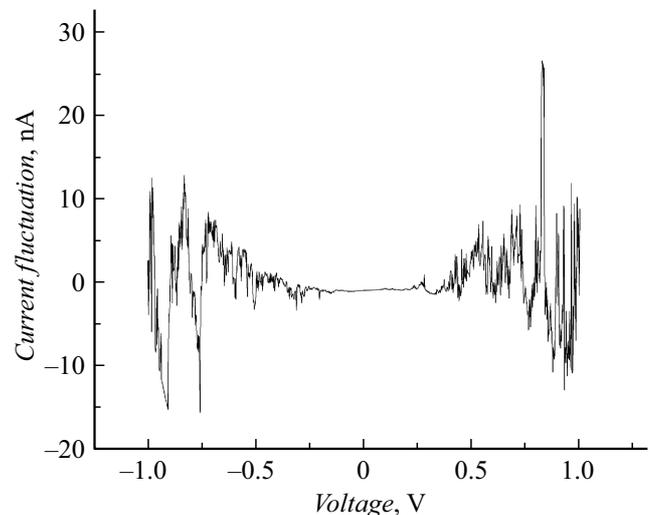


Figure 2. The fluctuation component of the current of the volt-ampere dependence in the voltage range from -1.0 to $+1.0$ V.

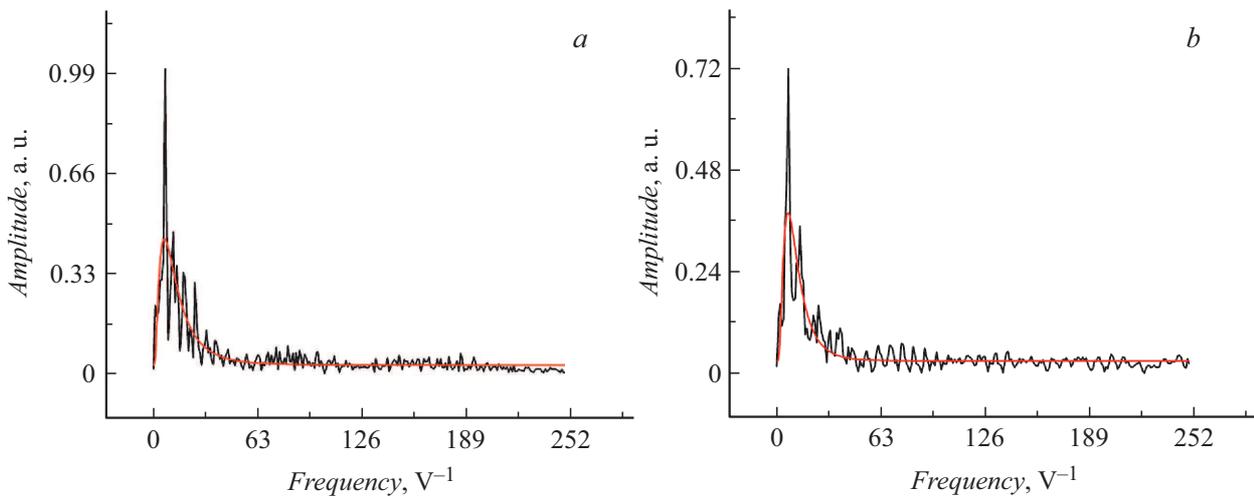


Figure 3. The spectral power density of the current fluctuations of the volt-ampere dependence in the voltage range from -1.0 to 0 V (a) and from 0 to $+1.0$ V (b).

Position of the maxima of the power spectral density spectra and voltage periodicity of the current fluctuations of the volt-ampere dependence

Voltage interval	$F1, V^{-1}$	$F2, V^{-1}$	$F3, V^{-1}$	$F4, V^{-1}$	$\Delta U1, V$	$\Delta U2, V$	$\Delta U3, V$	$\Delta U4, V$
from -1.0 to 0 V	6.99	11.99	13.98	17.98	0.14	0.083	0.072	0.06
from 0 to $+1.0$ V	1.99	6.74	13.98	24.97	0.50	0.15	0.07	0.04
from $+1.0$ to 0 V	1.37	3.994	5.99		0.73	0.34	0.17	
from 0 to -1.0 V	1.27	5.99	15.36	17.48	0.79	0.17	0.065	0.07

Note. The main maxima of the spectrum of current fluctuations of the volt-ampere dependences are highlighted in bold.

concentration of electrons in localized states in the bandgap of the dielectric [12,13]. A sharp increase in the measured current (current fluctuation in our terms) is observed when a certain limiting voltage is reached, at which all traps are filled with carriers [9]. Peaks of differential conductivity [11] are also associated with localized states.

The spectral power density of the current fluctuations, shown in Fig. 3 and in the table, indicates that the periodicity voltage for the direct dependence corresponds to the main maxima of the spectral density — 0.14 and 0.15 V, for the reverse volt-ampere dependence — from 0.17 and 0.173 V. In addition to the main maxima of the spectral density and therefore the periodicity voltages, we can note the range of periodicity voltages corresponding to the low-amplitude maxima of the spectral density: for the direct volt-ampere dependence, this range lies in the range of voltages from 0.04 to 0.5 V, for the reverse — from 0.065 to 0.79 V. These intervals of periodicity of current fluctuations in the volt-ampere dependences in our films roughly coincide with the period of oscillations for two-dimensionally ordered linear-chain carbon with thicknesses of 50 and 500 nm, falling in the range of 0.135 – 0.383 V [14], and with a quasiperiodicity period of value 0.2 – 0.4 V in copper-modified amorphous carbon films [10]. It may be noted that [11] also revealed regularities with an interval of 0.4 V on the differential conductivity. The presence of

fluctuations with lower voltage periodicity in the range of 0.04 – 0.1 V may correspond to the existence of low-energy electronic states, the filling or release of which by carriers [9] responsible for the appearance of such current fluctuations.

In carbon condensate (in our case between diamond-like and graphite-like clusters) there is a strong covalent-type interaction due to sp^2 and sp^3 -bonds [3]. Such interaction, as in [15], leads to a change in the electronic structure of both clusters, i.e. electrons of the π - sp^2 -fragment of the graphite-like graphene cluster appear to be localized inside the tetragonal clusters (hybridized carbon matrix sp^3 [16]). The same situation, indicating the appearance of localized states in the interaction of the graphene layer with the dielectric MnO substrate, is discussed in [15].

Thus, the study of tunneling volt-ampere current fluctuations using Fourier analysis in carbon diamond-like films shows that the volt-ampere current fluctuations are characterized by periodicity with a voltage ranging from 0.04 to 0.79 V. Such fluctuations of current volt-ampere dependences are caused by localized electronic states, the filling or release of which at voltage changes leads to current jumps. The formation of such states is caused by covalent sp^2 and sp^3 -bonds between tetragonal (diamond-like) and hexagonal (graphite-like) clusters. The scattering of oscillation periodicity values indicates the presence of

localized states in a wide range of energies, in fact low and high energy values differ by an order of magnitude.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by J.Savelyeva