Technical Physics, 2024, Vol. 69, No. 5

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Electrophysical properties of carbon diamond-like and graphite-like thin films

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Received June 1, 2023
Revised March 22, 2024
Accepted March 22, 2024

Measurements of local volt-ampere dependences in carbon diamond-like and graphite-like thin films have been carried out. The analysis of these dependencies allows us to conclude that there is tunneling of charge carriers between conjugated graphite-like clusters through a dielectric layer formed by diamond-like clusters. The structure of a graphite-like cluster, which is a collection of 1 to 3 hexagonal planes shifted relative to each other in positions different from their position in an ideal graphite crystal, allows us to consider their electrophysical properties similar to those of a minimal set of graphene planes. It can be assumed that the revealed features of local volt-ampere dependencies in carbon diamond-like and graphite-like films are related to these electrophysical properties.

Keywords: diamond-like films, graphite-like films, diamond-like clusters, graphite-like clusters, sp^2-, sp^3-bonds, volt-ampere dependence, local electrical conductivity.

DOI: 10.61011/TP.2024.05.58524.141-23

Introduction

According to cluster model of carbon films [1,2] the basic structural component of films are graphite clusters, in which carbon atoms with sp^2-bonds are arranged in plates with size about 15 nm comprising hexagonal rings bonded by π-bonds in stacks — graphite clusters. These clusters are loaded in the matrix of carbon atoms presented different configurations of sp^2- and sp^3-bonds. The graphite clusters monitor the electric properties, the matrix monitors mechanical properties. This model implies the heterogeneity of the film structure — alternation of regions with sp^2- and sp^3-bonds. But recent studies [3] showed that in structure of carbon diamond-like films obtained by laser method the diamond-like clusters prevail, and graphite clusters (more precisely graphite-like), detected by Raman spectroscopy, cover lower fraction and are distributed occasionally among the diamond-like clusters. It is significant that such structure is not an analogue of polycrystalline aggregate, i.e. it does not contain pronounced interfaces. The diamond-like and graphite-like clusters, which size is in range 0.5−1.0 nm, are combined into cluster unit using sp^2- and sp^3-bonds [4].

Variety of structures and unique properties of diamond-like carbon films is due to, first of all, sp^3- and sp^2-bonds of carbon atoms. Such films comprise tetrahedral amorphous carbon [5], so called ta-C, where diamond sp^3-bonds prevail [6,7]. Content of sp^3-bonds in carbon ta-C films can reach 87% [8–10]. Exactly the high content of sp^3-bonds in films ta-C determines high hardness, chemical resistance, low coefficient of friction, thermal stability and high electrical resistance [11–14].

Due to predominance in diamond-like films of tetrahedral clusters formed using sp^3-bonds, the electrical conductivity of such films as macro-objects is close to zero. But, as it was shown by surface scanning of diamond-like carbon film in mode of tunnel current in probe microscope, over its surface the local point conductive channels are distributed [15]. It is evident, that these channels are connected by graphite clusters (more precisely, with chains of graphite-like clusters that form current channels), their concentration in structure of diamond-like film is lower than concentration of diamond-like clusters.

Study of electrophysical properties of natural nanostructured carbon material — schungite — showed that dependence of ground current on voltage applied between the conductive probe and sample surface has non-linear view [16]. Nonlinearity of volt-ampere dependences upon voltage change from −4 to +4 V is either ground current jump about 60 nA at zero potential, or presence of section of „zero“ current in some range of voltage from −1 to +1 V. Discussing the nature of this effect the author of publication [16] states that in schungite the nanoscale units of primary carbon particles present, they form the contact electrical conductive paths. Dielectric admixtures distributed in the carbon matrix in amount of 2−4 at.%, block part of conductive paths, i.e. charge transfer is performed by electrons tunneling upon contact absence between graphite-like particles. So, we can state that schungite conductivity is determined by both contact electrical conductive channels, and by electron tunneling via gaps between graphite particles.

Effect of electrons tunneling via the dielectric interlayer in carbon films, modified by copper, is basic reason of nonlinearity of volt-ampere dependences [17]. The nonlinearity of volt-ampere dependences means presence of current step (publication terms) or section with „zero“

current (in out terms) in some range of voltages. Thickness of the dielectric layer, through which electron tunneling is provided, is 2−4 nm.

In carbon films the graphite clusters formed due to sp^2-bonds determine also optical properties which depend on width of optical band gap. Measurements of optical band gap in carbon films identified that its value inversely proportional to the size of the graphite cluster [1,18]. Considering this ratio it was determined that diamond-like carbon films mainly comprise disordered graphite clusters with dimensions up to 1.5 nm, and diamond phase plays secondary role in optical properties.

Saturation of diamond-like film with carbon ions results in increase in concentration of graphite π-clusters, and diamond phase forms the tunnel barrier between them [18]. These structural features has significant effect on electrophysical properties — density of states of π-electrons and value of tunneling parameter (radius of electron localization). For carbon films width of optical band gap in initial state is 1.2 eV and quickly decreases upon increase in concentration of graphite-like clusters to 0.42 eV, tunneling parameter is $\alpha^{-1} = 1.2$ nm [18].

So, we can conclude that electrophysical properties of carbon films can significantly vary from natural for wide-bandgap semiconductors to those typical for the population of graphite-like clusters with close to metals electrical conductivity, and conductive channels are chains of carbon clusters with anisotropy of conductivity 10^4 [19]. It is characteristic that the conductivity of carbon films can be caused by electron tunneling between graphite-like π-clusters, width of barrier layer between them can be about 1.5−2.0 nm [18–20].

Note that in cited papers not all volt-ampere dependences, observed in diamond-like and graphite-like carbon films, are reviewed and discussed. In this relation the present paper shows experimental results on relationship of volt-ampere dependences of diamond-like and graphite-like carbon films and their structural state. Nature of nonlinearity of volt-ampere dependences is discussed.

1. Experimental procedure

To obtain diamond-like carbon films the method of direct evaporation of a graphite target under action of laser radiation of neodymium laser NTS-300 with further condensation of carbon atoms on amorphous substrate made of silicate glass. Direct evaporation of graphite target is possible if laser beam is defocused. The laser radiation was introduced into the vacuum chamber of unit (residual pressure at least 10^{-5} Torr) with installed the graphite targets and substrates of silicate glass with preliminary applied aluminium or copper layer to create the conductive electrode. The initial temperature of substrates and targets was about 300 K. on the graphite target with diameter of 5 mm and thickness about 2 mm the defocused laser beam, which energy was about 4−6 J, created spot with diameter about 3 mm. Exposure time — about 5 min. The obtained flow of evaporated carbon was deposited on substrates, arranged along circle with diameter about 20 cm at distance about 10 cm from target and at angle about 30° to axis of vapor-gas torch, forming a carbon film.

The graphite-like films were obtained by deposition of the graphite nanoparticles from two-phase torch obtained by dispersion of the carbon target with focused laser radiation (ablation method). Part of the carbon target during its dispersion formed the vapor-gas phase, i.e. simultaneously on the substrate carbon condensation was also performed. Energy of laser radiation changed in range 4−6 J both in case of dispersion, and in case of carbon target evaporation. Films thickness in experiments was 200−300 nm.

The surface structure and conductivity of the films were studied using Solver Next scanning probe microscope in the tunnel current mode, followed by Fourier analysis of the structure using the tools of the image processing program „Image Analysis 9.0“. Local electrophysical properties were measured using spreading resistance imaging and electric power spectroscopy methods. Measurements were performed at sections of surface with globular structure with high conductivity. For more contrast identification of sections with heterogeneous conductivity of shift voltage applied during scanning between the conductive probe and ample surface, varied from 0.1 to 10 V. Current level 0.3 nA was assumed as sufficient to register the conductive properties of surface on noise background.

2. Experimental results

Fig. 1 shows the volt-ampere dependences of ground current of local section of diamond-like carbon films. Same volt-ampere dependences are obtained also for graphite-like films. Image of surface structure obtained by scanning of conductive probe in power mode, is given in right and is population of islands. Here localization point for volt-ampere dependences measurement is specified, it is linked with separate island. Same structure of surface is natural also for the graphite-like films. The only difference is concentration of graphite-like clusters: in graphite-like carbon films their concentration is significantly higher then in diamond-like.

From data in Fog. 1 it follows that two types of volt-ampere dependences of ground current are observed: monotonic change of current from −15 to +15 nA in voltage rage from −10 to +10 V, especially evident in voltage range from −3 to +3 V, and volt-ampere dependence with section of „zero“ current in voltage range from −3 to +3 V. Note also that voltage return to initial value does not result in hysteresis in dependence of ground current on voltage in Fig. 1, *a*, at the same time in dependence with section of „zero“ current (Fig. 1, *b*) the small hysteresis is observed. Note that, as in the cited publication [17], noticeable current fluctuations are observed at the edges of nonlinear sections (Fig. 1, *b*).

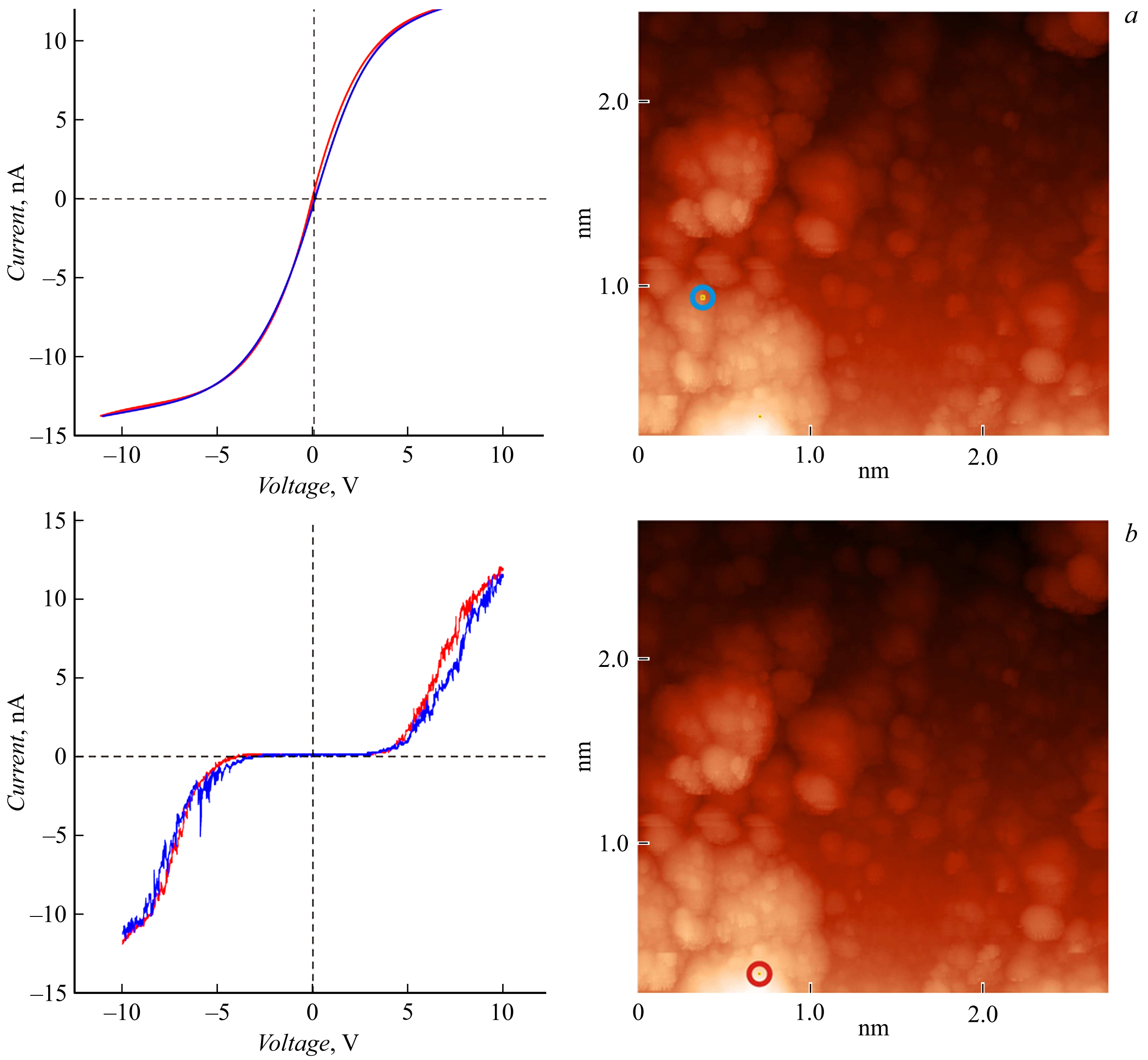

Figure 1. Local nonlinear volt-ampere dependences in carbon film: *a* — Linear section in range of voltages from -3 to $+3$ V; *b* — Dependence with section of „zero“ current in voltage range from -3 to about $+3$ V. The island structure of the carbon film with the localization of the point of measurement of the volt-ampere dependence is shown on the right.

When measuring in mode of the tunnel current (conductive probe is at some distance from the carbon film surface) the volt-ampere dependence with section of „zero“ current (Fig. 2) is observed with well expressed hysteresis and current fluctuations.

3. Discussion

Family of volt-ampere dependences shown in Fig. 1 coincides with same dependences of natural nanostructured carbon material [16], local electric conductivity of which is linked with units of graphite-like clusters, forming the current channels, and type of volt-ampere dependences is determined by intercalated impurity elements along the boundaries of graphene layers of schungite, blocking part of the ground current channels. In fact, the current channels are blocked by dielectric clusters formed by impurity elements. Comparing volt-ampere dependences of schungite and our carbon films, note that dependence in Fig. 1, *a* coincides with volt-ampere dependence of schungite most purified from impurity atoms, they concentrate along boundaries into independent clusters.

volt-ampere dependences in Fig. 1, *b* and 2 with sections of „zero“ current are similar to same dependences in schungite. In cited paper [16] the specified features of volt-ampere dependences are determined by both formation of contact conductive channels, and by electrons tunneling upon absence of ohmic contact between particles, i.e. upon presence of interparticle gaps, which width satisfies the tunneling conditions. So, our diamond-like and graphite-

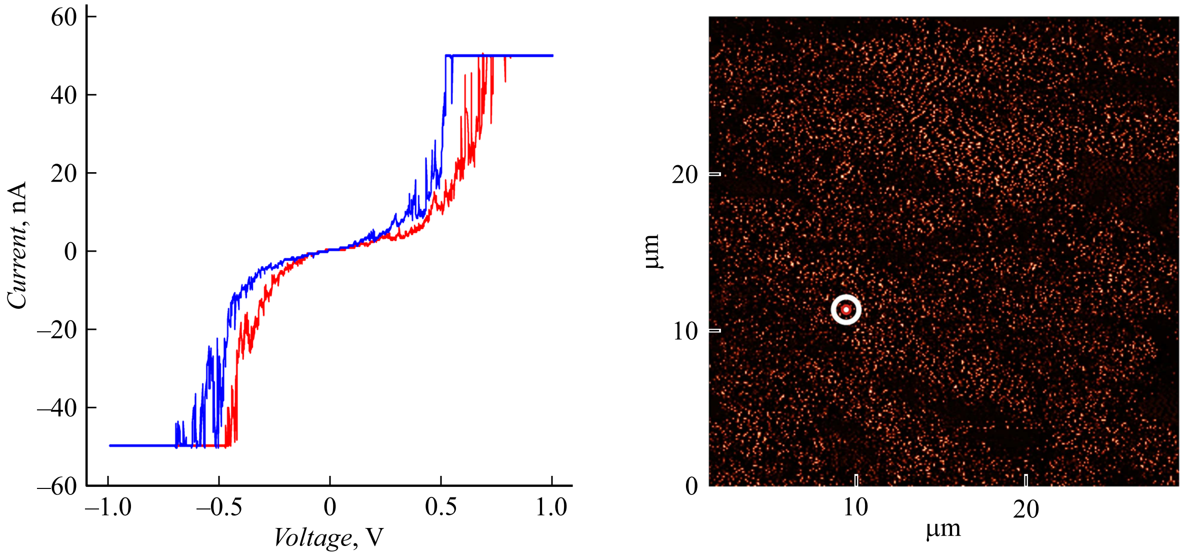

Figure 2. Local volt-ampere dependence with section of „zero current“, obtained in tunneling current mode; structure of current channels with localization of point of measurement of volt-ampere dependence is shown on the right.

like carbon films, as schungite represent a composite of conductive graphite-like clusters and dielectric interlayers (in our case the role of dielectric interlayer is played by diamond-like clusters, which size is in range of 0.5 to 1.0 nm [3,4]). But in any variant, as in publication [17], the diamond-like phase forms the tunnel barrier between graphite-like π-clusters.

The hysteresis observed in volt-ampere dependences (Fig. 1, *b*, 2), possibly is linked with processes of polarization of dielectric component of the nanocomposite conductor–dielectric [16]. On the other hand, hysteresis can be caused by the presence of localized states (traps) in the band gap of the composite dielectric conductor-dielectric and conductivity caused by charge carriers from different traps [21]. Actually, in structure of diamond-like — graphite-like composite the clusters are combined into the cluster unit using sp^2- and sp^3-bonds [4], i.e. presence of sp^2-bond between carbon atoms in tetragonal group and carbon atoms of hexagon group, presumably, is equivalent to occurrence of localized electron states in band gap of diamond-like cluster and features on volt-ampere dependences. More detail data on localization of π-electrons in ta-C films are given in publication [22].

To implement the effect of electrons tunneling via dielectric layer some limit conditions shall be met: tummeling parameter and thickness of dielectric layer are equal to 0.45 nm and 1.5–2.0 nm respectively [17,18]. According to data of publication [4], the diamond-like cluster comprising atoms of first and second coordination spheres, has at least 17 atoms and size 0.35 nm. If at least half of the atoms of the third coordination sphere participate in the cluster formation, the cluster size will be about 0.5 nm. Evaluated size of diamond cluster is about 0.5–1.0 nm [4].

To estimate thickness of di.electric layer between graphite-like clusters we analyze distribution of current channels in structure of carbon films [15]. The Fourier analysis of structural data of surfaces given in Fig. 1, 2, including analysis of maximum and minimum value of periodicity parameter of the radial distribution function of spectral power (actually distance between two neighboring current channels), indicates (see Table) that upon change in energy of laser radiation from 4.0 to 6.0 J the minimum value of parameter changes from 4.7 to 2.8 nm for diamond-like films and from 4.9 to 2.4 nm for graphite-like films.

So, minimum value of periodicity parameter in distribution of current channels in carbon thin films and presence of „zero“ current in some voltage range (Fig. 1, *b* and 2) confirm that condition is met of electrons tunneling between graphite-like clusters via the isolating layer of diamond-like clusters in films during current channel formation [20].

Note that according to cluster model in carbon thin films the graphite-like clusters are set of hexagonal plates bonded by π-bonds in stacks — graphite clusters [1], but in graphite-like cluster these plates occupy positions not corresponding to their position in graphite crystal [4,23]. X-ray studies [24] say that in the graphite-like clusters the tree-dimensional periodicity natural for the graphite crystal in location of graphene layer is absent, the graphene layers are shifted and turned relative each other. Due to small size of clusters, size does not exceed 1 nm [4], and considering interplanar spacing equal to 3.36 Å, in our graphite-like clusters from 1 to 3 disoriented hexagonal plates are arranged, which is associated with occurrence of large mechanical stresses [25].

Heavy distortion and defectiveness of the structure of the graphite-like cluster is confirmed by the Raman spectra (Fig. 3).

Minimum and maximum value of parameter of periodicity

Energy of laser radiation, J	Carbon films	Value of periodicity parameter	
		Minimum, nm	Maximum, nm
4.4	Diamond-like	4.7	430
	Graphite-like	4.9	427
5.0	Diamond-like	4.8	284
	Graphite-like	4.9	427
6.0	Diamond-like	2.8	433
	Graphite-like	2.4	428

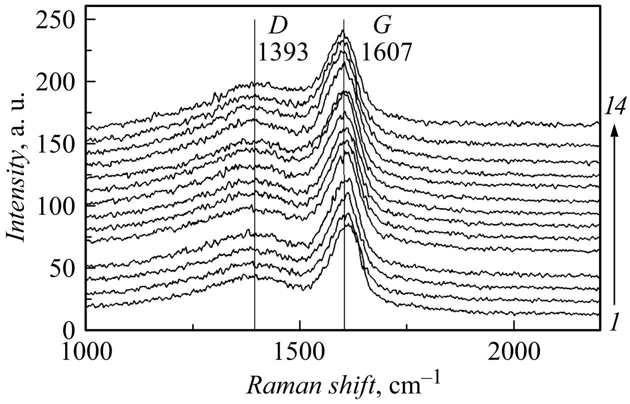

Figure 3. Spectra of Raman scattering obtained by excitation of laser radiation with wavelength 325 nm in14 points along diamond-like carbon film.

Presence of wide *D*-band with maximum at about $1393\,\text{cm}^{-1}$, together with spectral *G*-line near $1610\,\text{cm}^{-1}$, natural for ideal crystal of graphite confirm the presence of graphite-like clusters with rather distorted structure. Shift of *G*-line to high frequency region (its general location for graphite — $1580\,\text{cm}^{-1}$) is due to small size of stacks of graphene layers. In this relation we can suppose that conductivity of current channels in diamond-like and graphite-like carbon films is due to state of subsystem of π-electrons, natural for individual graphene plane, or their minimal set, which is in stressed and highly distorted state and turned relative to each other.

Conclusion

Analysis of volt-ampere dependences in diamond-like and graphite-like carbon thin films ensures the conclusion that presented features are due to charge carrier tunneling between graphite-like clusters via the isolating layer formed by diamond-like clusters. Local conductivity in carbon films, apparently, is due to features of structural state of graphite-like clusters, and associated with these features state of π-electrons. Firstly, these features are due to the small size of the cluster (less than 1 nm), due to which graphite-like clusters are formed by limited number of graphene planes from 1 to 3. Secondly, position of hexagonal graphene plates of the cluster is characterized by rather disordered stacking of hexagonal planes as compared with their position in graphite crystal. In this relation the graphite-like clusters, which size is about 1 nm, are structures which electrophysical properties correspond to properties of minimum set of graphene planes.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by I.Mazurov