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Iron-doped diamond-like carbon films: technology and nonlinear electron transport

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A technology has been developed to synthesize films of iron-doped diamond-like carbon (DLC) using sputtering of an Fe cathode and plasma-chemical deposition of DLC in a hollow-cathode discharge. At a temperature of 373 K, we studied the dependences of the transverse current on time and applied voltage in W/DLC/W samples with DLC thicknesses of 50 and 100 nm and Fe concentrations of 20 atomic %. In these samples, Fe stimulates changes under the action of an electric field due to the hybridization type in high-resistance sp^3 areas that separate low-resistance sp^2 regions (nanoclusters). Between these regions, hopping transfer of charge carriers occurs. The nonlinearity of the electronic properties of the studied DLC(Fe) films in fields greater than or equal to 10^5 V/cm is associated with $sp^3 \to sp^2$ transitions in sp^3 areas and with field effects under the conditions of hopping conductivity in mesoscopic disordered electronic systems.

Keywords: diamond-like carbon, plasma-chemical synthesis, hopping electron transport, hollow-cathode discharge.

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Diamond-like carbon (DLC) is a metastable form of amorphous carbon with its electronic structure being a mixture of chaotically distributed sp^2 and sp^3 bonds [1–4]. Carbon atoms bound by sp^3-hybridized orbitals form insulating „diamond“ regions, while carbon atoms bound by sp^2 orbitals form conducting „graphene“ regions [5,6]. Initiating a structural rearrangement, the electrical field may induce a redistribution between conducting (sp^2) and insulating (sp^3) regions and, consequently, nonlinearity of electron transport in DLC. It was noted in [7,8] that impurity iron in DLC reduces the activation energy of $sp^3 \to sp^2$ transitions, but these effects have not been studied in sufficient detail. This present study is focused on the nonlinearity of electron transport in DLC:Fe layers induced by the electrical field.

Plasma-chemical deposition of iron-doped DLC films was performed in a hollow-cathode discharge (HCD) from a mixture of reaction gas (propane) and plasma-forming gas (argon) with simultaneous sputtering of the iron cathode surface [9]. Raman spectra of the obtained films feature characteristic D and L peaks at $\lambda \sim 1300$ and $1600\,\mathrm{cm}^{-1}$, respectively (see, e.g., [10]); thus, the films should be considered diamond-like.

DLC:Fe layers with a thickness of 50–100 nm were synthesized using a vacuum setup with a volume of 5 l evacuated to a maximum residual pressure of 10^{-3} Pa by rotary vane forevacuum and diffusion pumps. The limit residual pressure and partial pressure of the reaction gas (propane) were measured by a PMI-2 ionization vacuum gauge, and the pressure of the working gas mixture (propane and argon) was measured with a Thyracont VCC200VF4 capacitive sensor.

The HCD electrode system included a cylindrical iron cathode with an internal diameter of 18 mm, a length of 35 mm, and a wall thickness of 1 mm mounted on a movable Wilson inlet, which was used to set the distance (40 mm) between the cathode and the substrate, and an anode (the vacuum chamber wall). Layers were synthesized at a discharge voltage of 500 V and a current of 200 mA. The total pressure of the working gas mixture (propane and argon) was 65 Pa. The impurity iron concentration in DLC (from 40 to 10 at.%) was set by the partial pressure of propane that varied within the 0.03–0.1 Pa range. The iron concentration was monitored in the process of deposition in an HPC by energy-dispersive spectroscopy (EDS). Numerical modeling of characteristic radiation spectra of film components under the influence of an electron beam was carried out for this purpose in Casino 2.4 with account for the film thickness and the substrate material, and concentrations of carbon and impurity iron were selected so as to fit the obtained relative radiation intensities to the experimental EDS spectra; this technique has already been used in [9]. Characteristic radiation spectra were measured for several electron beam energies (6, 9, and 15 keV) using an INCA X-Act (Oxford Instruments) EDS spectrometer in assembly with a Tescan Vega scanning electron microscope. The thickness and composition of films were determined by combining profilometry and non-destructive quantitative electron probe microanalysis [11] based on EDS. Oxidized Si(100) wafers with a 500-nm-thick deposited tungsten layer (lower electrode) were used as substrates [11].

The dependences of transverse current I on time t and applied voltage V were investigated at room temperature.

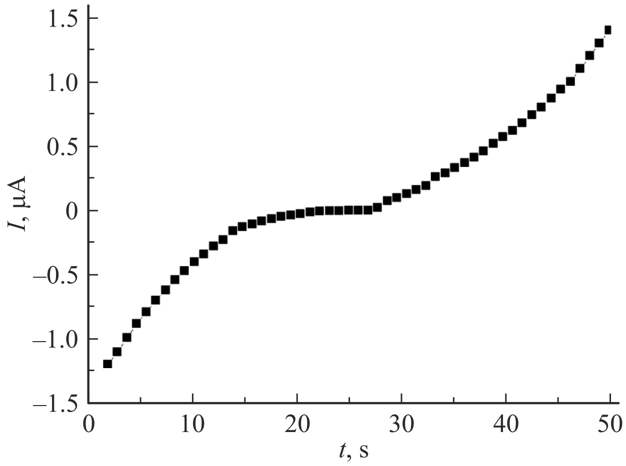

Figure 1. Time dependence of the transverse current for DLC : Fe with a thickness of 50 nm and a Fe concentration of 20 at.% at a linear voltage sweep rate of 0.4 V/s.

Tungsten contact pads with a diameter of 3 mm and a thickness of 200 nm were deposited onto the DLC surface for measurements. A Tektronix AFG3252 sawtooth voltage generator was used to set transverse voltage V in measurements of current-voltage curves (CVCs) of DLC : Fe films. This voltage was measured by a 16-bit analog-to-digital converter in an ICP-DAS ET-7026 input/output module. The sweep frequency was 10 mHz, and the voltage amplitude varied from 1 to 10 V. The current was measured with a Keithley 6485 picoammeter.

Figure 1 shows the dependence of I on t for a 50-nm-thick DLC : Fe film with a Fe concentration of 20 at.% measured with a linear V sweep at a constant rate of 0.4 V/s within the range from -10 to $+10$ V. It is easy to plot the CVC of a film when the voltage sweep rate is known. Dependence $I(t)$ is nonlinear at $t < 20$ s and $t > 28$ s (i.e., in fields $> 3 \cdot 10^5$ V/cm).

Figure 2, *a* illustrates the dependence of I on t for a 100-nm-thick DLC : Fe film with a Fe concentration of 20 at.% at cyclic sawtooth variation of V at a rate of 0.4 V/s. Figure 2, *b* shows the dependence of I on t in the region of maxima marked in Fig. 2, *a* by arrows (the numbering of curves corresponds to the numbers of arrows). These dependences reveal a sharp increase in current in fields $\geqslant 2 \cdot 10^5$ V/cm.

The nonlinearity of electronic properties of DLC is related to a change in the type of hybridization in its local regions with $sp^3 \rightarrow sp^2$ transitions under the influence of electrical fields $\geqslant 10^5$ V/cm [8]. It is believed that DLC is an ensemble of low-resistance inclusions of sp^2 regions (nanoclusters) in an insulating sp^3 matrix with the defect density in it depending on the synthesis conditions [8,11]. Separated by insulating sp^3 gaps, these inclusions form chains along which hopping carrier transport proceeds. Nonlinear behavior of CVCs associated with a change in the type of hybridization has already been observed in undoped DLC layers, although the fields in these experiments were stronger ($\sim 10^6$ V/cm) [12].

Note that the CVC nonlinearity may have a different nature in the case of hopping transport. The transverse hopping conductivity of thin films is largely determined by mesoscopic effects: the formation of percolation chains from centers with the narrowest intercenter (in the present case, intercluster) potential barriers [13–15] wherein the electrical field is maximized. Electron transport in the non-ohmic regime with percolation conductivity was examined in [16]. Specifically, it was demonstrated that a transition to an exponential $I(V)$ dependence occurs in relatively strong fields $eFa > k_\text{B}T(k_\text{B}T/eV_0)^\nu$. The CVC then takes the form similar to the Poole–Frenkel law: $I \propto \exp(C\alpha F^{1/2}/k_\text{B}T)$, where $\alpha = e(aV_0)^{1/2}$, F is the electric field strength; e is the elementary charge; k_B is the Boltzmann constant; T is temperature; V_0 and a are the amplitude and the characteristic spatial scale of potential fluctuations, respectively; C is a numerical coefficient ($C \approx 0.3$ [17]); and ν is the critical index of the percolation theory ($\nu \approx 1$). In the present case, the fluctuation potential is naturally associated with the chaotic distribution of charge localized at electrically active defects

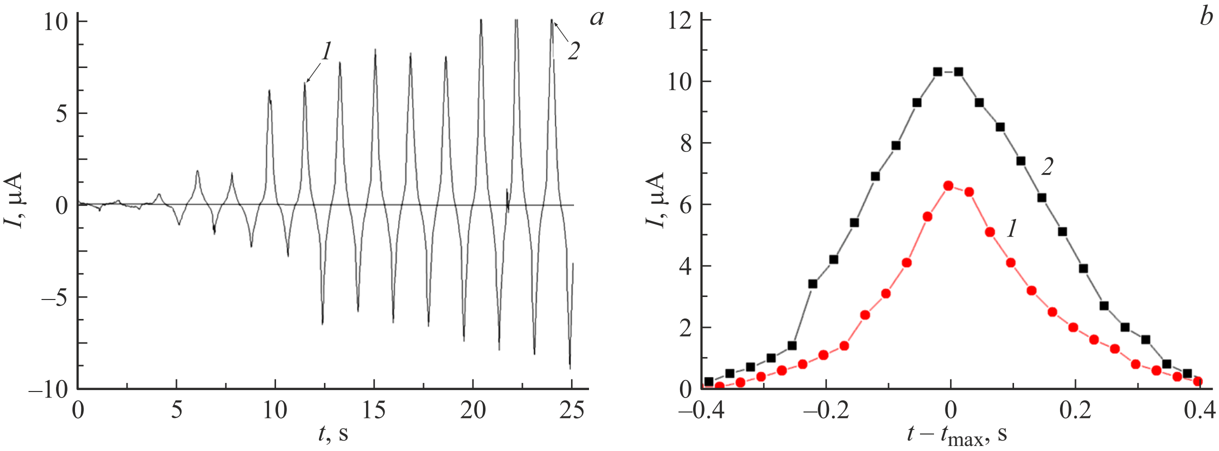

Figure 2. *a* — Time dependence of the transverse current for DLC : Fe with a thickness of 100 nm and a Fe concentration of 20 at.% at a sawtooth voltage sweep rate of 0.4 V/s; *b* — the same dependence in the region of maxima indicated in the left panel.

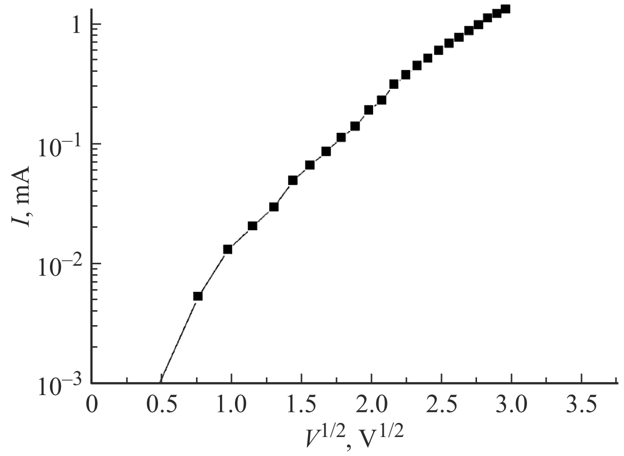

Figure 3. Dependence of current I on $V^{1/2}$ at a DLC : Fe thickness of 50 nm and a Fe concentration of 20 at.%.

in the DLC matrix. The experimental dependence of I on V is linearized in coordinates $\lg I{-}V^{1/2}$ (Fig. 3). Assuming that $\partial F/\partial V \sim 1/d$ (d is the DLC thickness), one may easily estimate the relation between d and correlation radius $L_0 \approx a(eV_0/k_\mathrm{B}T)^\nu \approx a(eV_0/k_\mathrm{B}T)$ of a percolation cluster based on the slope of this dependence in the linear region (at $V > 1\,V$) and experimental values of $\partial \ln(I)/\partial(V^{1/2})$. Taking the above expressions for $I(F)$, α, and $\partial F/\partial V$ into account, we obtain $L_0/d \approx [\partial \ln(I)/\partial(V^{1/2})]^2(k_\mathrm{B}T)/Ce$; the magnitude of this ratio corresponding to the experimental values of slope $\partial \ln(I)/\partial(V^{1/2}) \sim 2.2\,\mathrm{V}^{-1/2}$ (Fig. 3) is on the order of unity. Therefore, the studied systems should be regarded as mesoscopic with hopping transport confined predominantly to individual chains of sp^2 nanoclusters where both the electric field strength and the local current density increase sharply.

Thus, the nonlinearity of electronic properties of the studied DLC : Fe films detected in fields $\geqslant 10^5$ V/cm may be associated both with a change in the type of hybridization in high-resistance sp^3 gaps, which separate low-resistance sp^2 regions (nanoclusters) that support hopping transfer of charge carriers, under the influence of an electric field and with field effects under the conditions of hopping conductivity of mesoscopic disordered electron systems.

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Conflict of interest

The authors declare that they have no conflict of interest.

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