Physics of the Solid State, 2023, Vol. 65, No. 1

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Transport properties of layered heterostructures based on conducting polymer

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Received September 29, 2022
Revised September 29, 2022
Accepted October 1, 2022

Polydiphenylenephthalide (PDP) belongs to the class of organic dielectrics, which exhibit electric conductive properties when an external electrostatic field and/or mechanical stress are applied. In this work, the transport properties of thin-film layered lead—PDP—lead structures were experimental-ly studied in a wide temperature range. At sufficiently high temperatures, the volt-ampere depend-ences are satisfactorily described in terms of the injection model of currents limited by the space charge. At temperatures below $\sim 7.5\,\mathrm{K}$, a number of samples exhibit features that can be explained by the effect of induced superconductivity in a thin film of a conducting polymer enclosed between two massive superconductors (lead).

Keywords: thin films, conducting polymer, superconductivity.

DOI: 10.21883/PSS.2023.01.54989.490

1. Introduction

Most polymers can be classified as organic dielectrics. However, a number of reports have appeared relatively recently that under the influence of external parameters such as mechanical voltage and/or electrostatic field, a number of polymers exhibit high electrical conductivity [1]. The effect was interpreted as stimulating the metallic state of [2]. The purpose of this work was to study this interesting phenomenon in a wide temperature range: from 4.2 K to the room temperatures.

The films of the most studied polymer from the class of polyarylene phthalides — polydiphenylene phthalide (PDF) [3,4] were selected as objects of research. PDF — is a carbocyclic polymer with high chemical stability and heat resistance, transparency in the visible range of the spectrum and high mechanical strength. PDF has an amorphous structure with a degree of crystallinity not exceeding 15%, a glass transition temperature of 420°C, a temperature of the beginning of decomposition in air of 440°C, a coke number of 75—76 in the formation of durable transparent coke, oxygen index 42—43. It is characterized by an unusually high chemical resistance. Conditions for the selective production of polydiphenylene phthalide with a molecular weight of more than $(50-60)\cdot 10^3$ are found without gelfraction formation. Under normal conditions, the PDF is a wide-band dielectric and is characterized by the following parameters: the band gap width $\sim 4.3\,\mathrm{eV}$, electronic output operation $\sim 4.2\,\mathrm{eV}$, electron affinity energy $\sim 2\,\mathrm{eV}$, first ionization potential $\sim 6.2\,\mathrm{eV}$. A model image of the structural unit of the PDF polymer is shown in Fig. 1, *a*.

Polymers of this class are soluble in organic solvents and have exceptional film-forming properties [5,6]. According to these results, continuous homogeneous films can be obtained by centrifugation from a solution in cyclohexanone on a metal surface with a thickness of up to several nanometers. The uniformity and defect-free surface on nanoscopic scales has been repeatedly confirmed by various methods, including scanning tunneling and atomic force microscopy. In some cases, it was possible to observe areas with a surface macromolecular (quasi-crystalline) ordering [7].

The excellent operational properties, as well as the sensitivity of electrical and optical properties to external

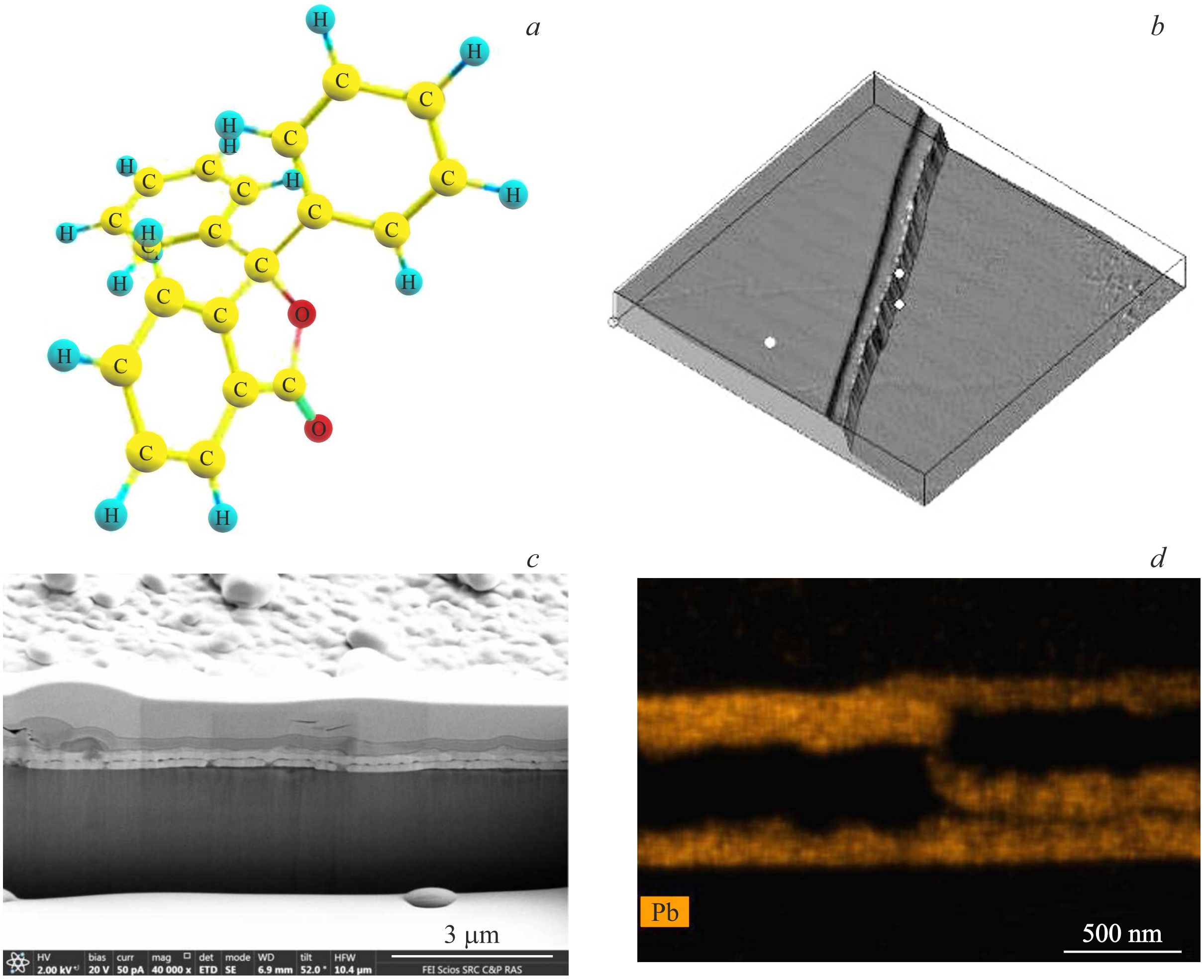

Figure 1. (*a*) Model image of a polymer structural unit PDF. (*b*) Three-dimensional image of the edge of a polymer film chip on a dielectric substrate obtained by atomic force microscopy. The step height is about 390 nm. (*c*) Micrograph of the edge of the heterostructure on glass Pb–PDF–Pb–0,4_GLASS obtained by scanning electron microscopy. The cut is made by a focused beam of gallium ions. Two upper layers — epoxy resin and sputtered platinum, necessary for the needs of electron microscopy. Sandwich thickness lead–PDF–lead ~ 470 nm. (*d*) Micrograph of the distribution of lead (light tone) on a cut of the Pb–PDF–Pb–0.2_GLASS heterostructure obtained by transmission electron microscopy.

influences (temperature, pressure, various types of radiation, electric and magnetic fields, etc.) make PDF a promising material for applications in organic electronics devices [2].

2. Samples

Layered heterostructures lead–PDF–lead were manufactured in a glove box in a nitrogen atmosphere with minimal moisture and oxygen content without exposure to the room atmosphere between cycles of formation of various layers. Glass or oxidized silicon were used as substrates. The substrates were previously cleaned in ethyl alcohol, and then — in distilled water using ultrasonic treatment. Hydrophilization of the surfaces was carried out by treating the substrates with cyclohexanone immediately before applying the polymer solution. The electrodes were two mutually perpendicular strips of lead with a width of ~ 1 mm, between which a polymer film was located (Fig. 2, *a*). Lead was chosen as a fairly low-melting metal exhibiting superconducting properties. The production of thin-film lead electrodes with a thickness from 50 to 200 nm was carried out by thermal evaporation in vacuum. The critical temperature of massive lead $T_c(\text{Pb\_3D}) = 7.2$ K. However, in the form of a thin film, the critical temperature of the superconductor may differ significantly from the tabulated value of [8,9]. In our samples, the critical temperature of lead electrodes varied $7.8\,\text{K} < T_c(\text{Pb\_film}) < 8.2\,\text{K}$.

For the manufacture of submicron PDF films, the method of centrifugation of a polymer from a solution in cyclohexanone on a solid substrate was used. When preparing the solution, the polymer was first soaked in a small amount of solvent until completely dissolved, then

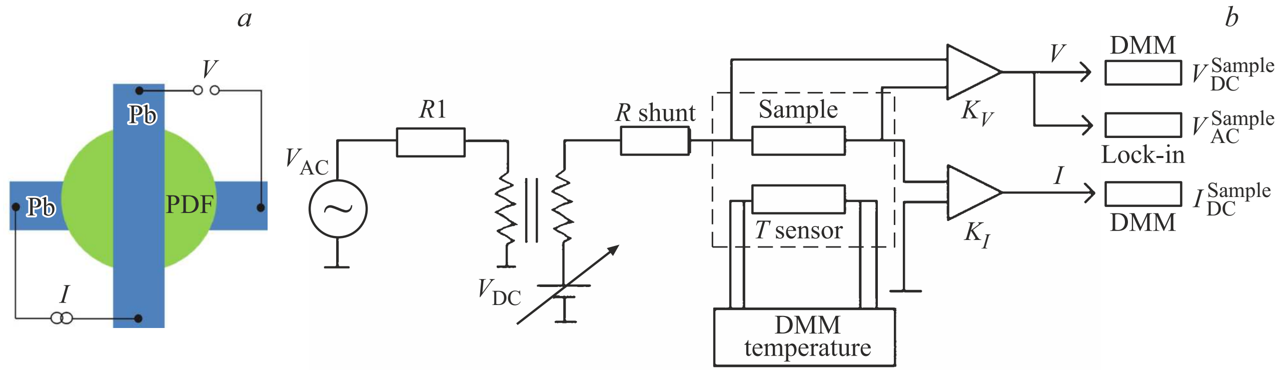

Figure 2. (a) The schematic representation of the heterostructure and configuration of contacts. (b) Schematic diagram of measurements of $V(I)$ and $R(T)$ characteristics.

the solvent was added in the required amount and the solution was kept for another day in the dark. Polymer solutions in cyclohexanone with concentrations of $0.1-15$ by weight % were used for the manufacture of films of various thicknesses. A polymer solution of the selected concentration was applied to a substrate mounted on a centrifuge holder. The rotation speed was, as a rule, 2000 rpm. The resulting polymer film about 45–60 min was dried in air at room temperature. Then the final drying was performed to remove the solvent residues at a temperature of 150–200°C for 45 min. Depending on the concentration of solutions, it was possible to obtain films of various thicknesses from several nm to several mkm. The formation of films from dilute solutions occurs by the mechanism of linear or loop adsorption, when the macromolecules at the interface of the phases are fully or partially elongated. Also, film formation at such low concentrations strongly depends on the energy interaction of macromolecules with the substrate surface, which is reflected in the weak dependence of the thickness of the films on the concentration of the solution. With increasing concentration, tangles and associates of macromolecules are formed in the solution, as well as the influence of adhesion processes decreases, but the cohesion forces increase. In the entire thickness range from 3 nm to 1 mkm, films are obtained solid, without significant defects and through holes. It was found that at a given centrifuge speed (2000 rpm for 20 s), the thickness of the films is determined by a close to linear dependence on the weight concentration of the polymer in solution. The surface roughness of the PDF polymer measured by an atomic force microscope (Fig. 1, b), as a rule, was several nm. With an increase in the thickness of the polymer film, the influence of heterogeneities of the substrate surface decreases to minimum values of the order of 0.4 nm.

After the measurements, a number of heterostructures were sent for analysis by high-resolution transmission electron microscopy and/or scanning electron microscopy (Fig. 1, c). None of the studied samples found systematic „sticking of" lead electrodes through the polymer thickness. However, a number of photos show some defects in the form of short circuits. The origin of these artifacts is not entirely clear: they could initially be present in heterostructures, or appear during the preparation of a sample for electron microscopy.

3. Results and discussion

The experiment was carried out in a four-contact configuration with direct or alternating currents (Fig. 2, b). Both $R(T)$ and $V(I)$ sandwich dependencies Pb–PDF–Pb could be measured, as shown in Fig. 2, a, and the transport characteristics of each lead electrode separately. To remove the differential characteristics of $dI/dV(V)$, a modulation technique and phase-sensitive detection were used. To suppress the negative influence of spurious electromagnetic interference, a multi-stage system of RLC filters [10] was used.

For $R(T)$ measurements in the region of cryogenic temperatures, the current value from 0.1 to 100 mkA was chosen in such a way that its increase by an order of magnitude did not lead to a noticeable offset in the temperature of the superconducting phase transition. All experiments were carried out in a direct pumping cryostat ^{4}He. Thermometers were calibrated by vapor pressure ^{4}He and by reference points of superconducting transitions of pure massive superconductors (Al, In, Sn, Pb). The resulting absolute error in determining the temperature was ~ 10 mK, while the relative — less than 1 mK. Repeated measurements of T_c of the same sample coincided with an accuracy of several mK. The degradation of the samples over time was analyzed. The difference between two measurements of the same sample was 3 months, while the shift of the beginning of the phase transition was minimal $\delta T_c \approx 0.01$ K.

Volt-ampere characteristics (VAC) measured in a wide temperature range from room to $T = 10$ K for Pb–PDF–Pb sandwiches demonstrate a significantly nonlinear dependence with hysteresis (Fig. 3). At the same time, for small voltage offsets V, a decrease in the differential resistance dV/dI $(V, T = \text{const})$ is observed, followed by an increase at large voltage values.

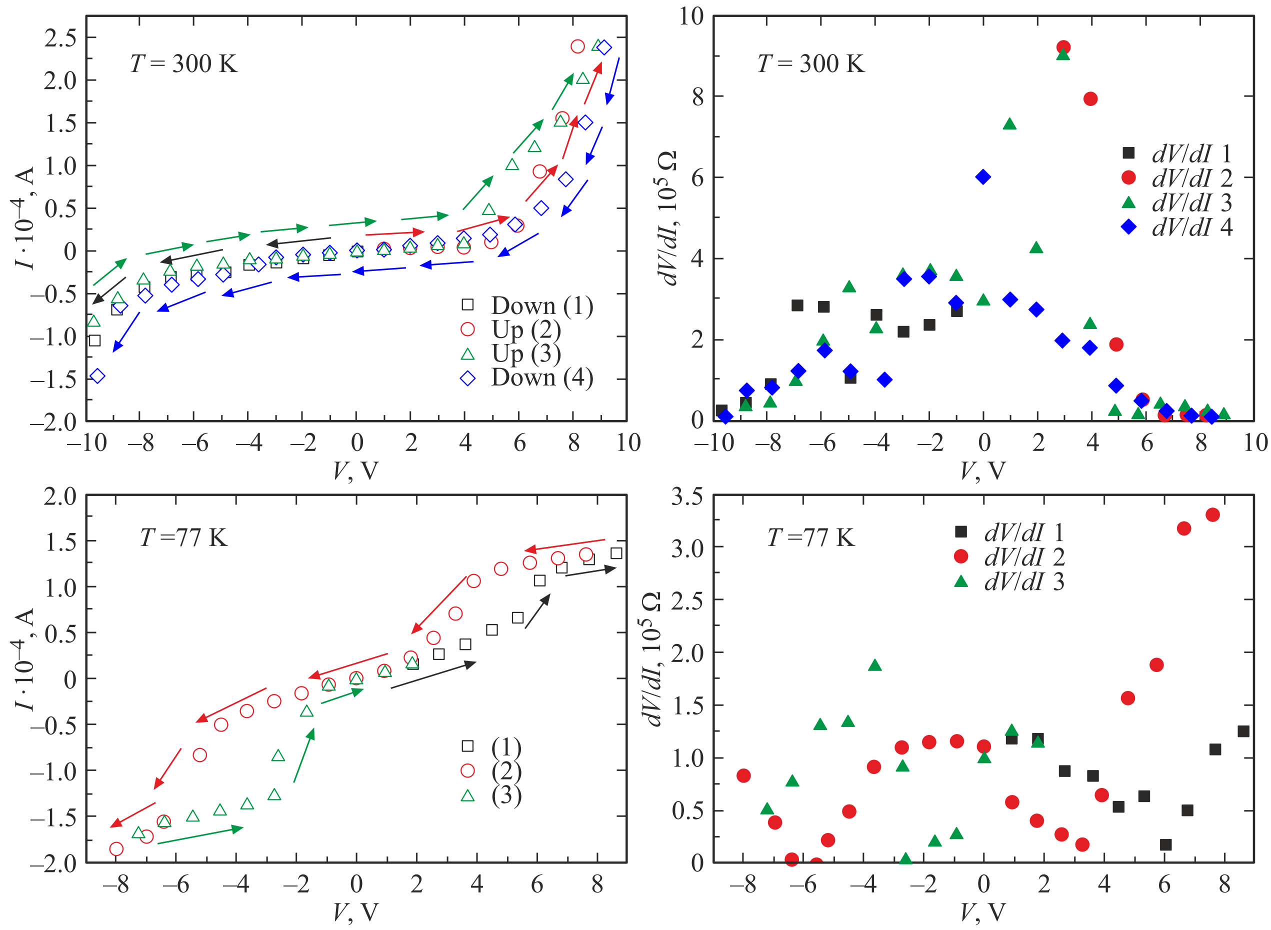

Figure 3. Volt-ampere $I(V)$ (left column) and differential $dV/dI(V)$ (right column) characteristics for the Pb$-$PDF$-$Pb_0.75_Si heterostructure measured at two temperatures: 300 K (top row) and 77 K (bottom row). The arrows show the direction of change of the bias voltage V. The symbols correspond to different measurement cycles.

It is established that in the measured structure Pb$-$PDF$-$Pb, the shape of the volt-ampere characteristics strongly depends on temperature. At 300 K at low voltage values, an ohmic section is observed on the dependence of the current on the applied voltage. For the positive section of the VAC, this dependence is recorded to values of about 4 B, for the negative — up to $-6B$. Further, a nonlinear section of the VAC with a functional dependence of $I \sim kU^n$ is observed. At temperatures 77 K and below, the dependence $I = f(U)$ is also nonlinear, but is significantly different. In particular, with an increase in voltage, there is a tendency to saturation of the current flowing through the heterostructure.

Earlier, [2], it was found that at high temperature, the mechanism of overcoming the barrier at the metal/polymer contact is satisfactorily described within the framework of the injection model of currents limited by a volume charge. At low temperatures, the tunnel mechanism is the predominant mechanism. This conclusion was recently confirmed in the work [11]. The VAC asymmetry relative to the direction of current flow indicates the presence of potential barriers at opposite interfaces of different heights.

The volt-ampere characteristics presented in Fig. 3 do not contradict these conclusions. In this regard, for the analysis of VAC at 300 K, the formalism of the theory of injection currents can be applied, which allows us to estimate the concentration of proper charge carriers (n_0) and their minimum mobility (μ). According to this model, the ohmic behavior of the VAC at low voltages is due to its own charge carriers. If the concentration of injected carriers begins to exceed the concentration of their own, then there is a transition to a straight-line section. The corresponding calculations give the following values: for positive polarity $n_0 = 2.21 \cdot 10^{20}\,\mathrm{m}^{-3}$, $\mu = 2.65 \cdot 10^{-7}\,\mathrm{m}^2/\mathrm{Vs}$;for negative polarity $n_0 = 3.57 \cdot 10^{21}\,\mathrm{m}^{-3}$, $\mu = 8.34 \cdot 10^{-9}\,\mathrm{m}^2/\mathrm{Vs}$.

The analysis of the VAC in the framework of the Schottky barrier model allows us to estimate the height of potential barriers at the metal/polymer interface. As a rule, the Richardson ratio is used for this. To do this, it is important to determine the saturation current by the semi-logarithmic dependence of the current on the applied voltage. This is the so-called current at zero voltage. In addition, it is necessary to take into account the coefficient of non-continuity of the barrier. We selected

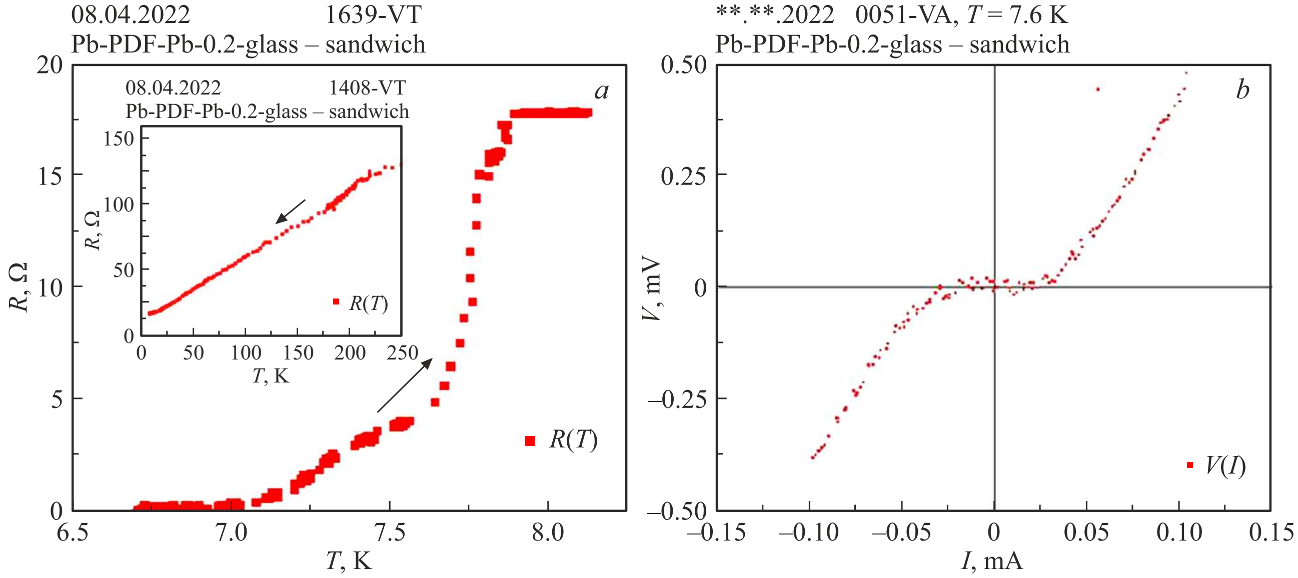

Figure 4. (a) Dependence of resistance on temperature $R(T)$ for the sandwich Pb$-$PDF$-$Pb$-$0.2$-$GLASS with a polymer thickness of about 300 nm. A blurred superconducting transition is traced, starting at a temperature of $\sim$ 7.8 K, correlating with the critical temperature of the lead electrode. The insert shows data in a wide temperature range. The arrows show the direction of temperature change. (b) $V(I)$ dependence at temperature $T = 7.6$ K can be interpreted as the presence of an overcurrent: zero potential difference at finite current.

the value of the latter from the previously performed measurements. As a result, the following values of potential barriers were obtained: for positive polarity +0.46 eV; for negative polarity −0.47 eV. Unexpectedly close values of the heights of potential barriers may be associated with a limited range of stresses, since the nonlinear section is shifted to the boundary of this range. The latter makes it difficult to correctly interpolate the current saturation region on the ordinate axis. The hysteresis of the VAC in Fig. 3 is apparently due to the presence of a volumetric charge, the concentration and energy distribution of which in the band gap of the polymer depends on the rate of charge injection. Therefore, there is a dependence of the VAC shape on the direction of voltage change. With an increase in voltage (the rate of injection of excess charge from the electrodes), the charge traps are filled. In the reverse course, a change in charge transfer occurs in the presence of filled electronic states, which changes the shape of the VAC.

As noted above, under normal conditions, PDF exhibits the properties of an organic dielectric. The application of uniaxial pressure and/or an electrostatic field converts the polymer into an electrically conductive state [1,2]. It should be noted that all our layered Pb$-$PDF$-$Pb heterostructures demonstrated a conducting state even at the smallest voltage offsets. Apparently, the effect is explained by the presence of „internal“ mechanical stress already at the stage of formation of the structure itself, sufficient to initiate a conducting state. It cannot be excluded that the difference between the critical temperature of lead electrodes and the tabulated value for a massive material is also a consequence of the tension of the metal film.

As expected, the transport characteristics of thin-film lead electrodes showed metallic behavior: in the normal state, the resistance of the films decreased linearly with a decrease in temperature and the VAC demonstrated ohmic behavior. At temperatures of the order of T_c(Pb_film) $\approx$ 8 K a sharp superconducting transition was observed.

Perhaps the most interesting are the results of transport measurements of Pb$-$PDF$-$Pb sandwiches at temperatures below the critical temperature of the superconducting transition of lead electrodes. In a number of samples with a polymer film thickness of less than 350 nm, features are observed that unequivocally indicate the presence of a superconducting state: a sharp drop in resistance to instrumental zero ($\sim$ 5 nV) and the presence of an overcurrent at VAC (Fig. 4). A trivial explanation may be the occurrence of short circuits between lead plates: either macroscopic „punctures“, or the germination of thin dendrites. The second possibility seems unlikely: neither previous studies, nor selective microscopic analysis of a cut of several samples by scanning and transmission electron microscopy (Fig. 1, *c, d*) not revealed signs of dendrites. At the same time, microphotographs taken by high-resolution transmission electron microscopy occasionally show some macroscopic features such as lead electrode short-circuits through the polymer thickness (Fig. 1, *d*). These defects are — episodic and their nature does not indicate „burning“ of the PDF film during the thermal spraying of lead. Moreover, the temperature of the beginning of decomposition of PDF is 440°C, which is significantly higher than the melting point of lead 327°C. It cannot be excluded that defects of the type „collapse“ of the upper electrode (Fig. 1, *d*) not are „internal“ and could arise only during the preparation of a sample cut for transmission electron microscopy. A sufficiently high critical current (Fig. 4, b) also indicates a significant area of the conducting channel, which does not correspond to the scenario of the occurrence of single point short circuits. The second alternative explanation of the dependencies in Fig. 4 there may be a Josephson effect: the flow of an overcurrent between two superconductors separated by a dielectric barrier. However, the correlation of parameters of the order of two spatially separated superconductors — is a subtle quantum mechanical effect, which in all practically realizable cases is observed at dielectric thicknesses of the order of several nm, while in our case superconductivity in Pb–PDF–Pb sandwiches manifests itself at polymer thicknesses up to 350 nm. Based on the above, we can assume that the dependencies on Fig. 4 can be explained by the effect of induced superconductivity in a thin film of a conductive polymer enclosed between two massive superconductors (lead). The justification of this statement requires additional verification. Experiments on planar heterostructures are planned in the near future, where superconductivity, if observed, cannot be explained by trivial metal short circuits.

4. Conclusion

The dependences of $R(T)$, $V(I)$ and $dV/dI(V)$ of thin-film layered structures lead–PDF–lead in a wide temperature range were experimentally investigated. At sufficiently high temperatures, the volt-ampere dependences are satisfactorily described within the framework of the injection model of currents limited by a volumetric charge. The hysteresis of VAC is apparently due to the presence of a volumetric charge, the concentration and energy distribution of which in the band gap of the polymer depends on the rate of charge injection. At temperatures below $\sim 7.5\,\mathrm{K}$, features are observed in a number of samples that can be explained by the effect of induced superconductivity in a thin film of a conductive polymer enclosed between two massive superconductors (lead).

Acknowledgments

K.A.B.'s work was supported by the Fundamental Research Program of HSE University. K.Y.A., A.R.Yu, D.D.K. and A.N.L. express their gratitude to the cooperation program „Mirror Laboratories“ National Research University „Higher School of Economics“ and Bashkir State Pedagogical University named after M.V. Akmulla.

Conflict of interest

The authors declare that they have no conflict of interest.

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