

Article

The Effect of Local Doping of the Polymer–Polymer Interface Using Cu₂O Particles

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Abstract: Electrically conductive polymer materials are increasingly being used as electronic materials, for example, in thin-film transistors. However, the low mobility of charge carriers limits their use. One of the ways to increase the mobility of charge carriers can be the use of interface conductivity along the regions separating the two polymer films. It is important that it could be realized with non-conjugated polymers. There is no direct experimental evidence that the transport of charge carriers occurs along such an interface. It is impossible to deny the possibility of transport on the surfaces of polymer films. The purpose of this work is to study the current flow path in a multilayer sample by marking the polymer–polymer interface with a doping nanolayer of a Cu₂O island film. Spectral methods in the field of electronic absorption of copper oxide were used to control the island film. The electronic parameters of the polymer–polymer interface were studied using injection methods and volt-ampere characteristics. Atomic force microscopy was used to control the thickness and uniformity of the samples. It was found that the doping of the polymer–polymer interface using Cu₂O particles strongly affects the transport of charge carriers; in particular, the conductivity of the structure increases. It is established that this is due to an increase in the mobility of the charge carriers and a decrease in the height of the potential barrier at the 3D metal–2D interface area. Thus, it is established that the transport of charge carriers occurs along the polymer–polymer interface at the structure parameters specified in this work.

Keywords: thin films; interface; polydiphenylenephthalide; non-conjugated polymer; copper oxide; Cu₂O; charge carrier transport; charge carrier concentration; charge carrier mobility; potential barrier



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1. Introduction

Conjugated polymer materials are an important object for the development of electronics and, in particular, organic electronics. They are of scientific interest from the point of view of the synthesis of new compounds with unique properties and the development of new unique applications, including spintronics, optoelectronics, light-emitting diodes and many more [1,2].

It was established that a two-dimensional region with electronic properties different from the volume can occur (or form) along the interface of two organic dielectrics [3,4].

Explanations of anomalous electronic properties (high conductivity and high mobility of charge carriers) were given on the basis of the quasi-two-dimensional (q2DEG) electron gas model. However, the reasons for the appearance of new electronic properties along the interface of two organic dielectrics, [3] and [4], are still debatable. In particular, in [3] it is assumed that a two-dimensional region is formed because of its analogy to semiconductor heterostructures and due to the contact phenomena resulting from the difference in the spectrum of the electronic states, tetrathiofulvalene (TTF) and 7,7,8,8-tetracyanoquinodimethane (TCNQ). In [4], such an explanation was impossible, since the contact of two dielectric polymer films with the same electron spectrum from the class of polyarylene phthalides—polydiphenylene phthalide (PDPh) was used. PDPh is not a conjugated polymer, unlike most electrically conductive polymers. The monomeric link of its structure contains a skeletal part consisting of alternating biphenyl fragments (Figure 1a). The biphenyl fragments are separated by phthalide groups (PGs). PGs are parts of a polymer monomer due to the lack of bonding of valence π electrons along the polymer chain. PGs are large molecular groups with a relatively large dipole moiety. In this regard, phthalide groups on the surface of the films form brushes when forming films from PDPh [5]. This is a well-known thermodynamic effect, which is often used to impart the desired properties to a poly-dimensional surface [6].

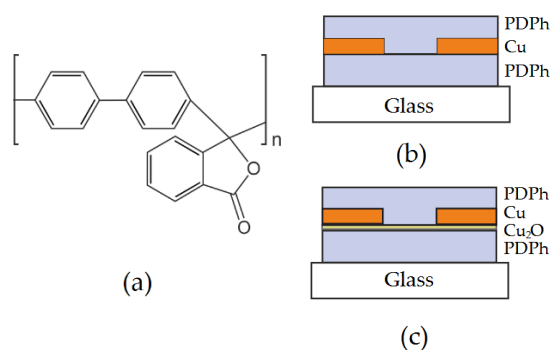


Figure 1. (a) Structural formula of PDPh. Schematic representation of the experimental structure of (b) PDPh/PDPh and (c) PDPh/Cu₂O/PDPh.

In this regard, the authors proposed an interpretation of the results of the study of electronic properties along the polymer–polymer boundary based on the “polar catastrophe” model previously proposed for the contacts of two inorganic dielectrics from the class of LaAlO₃/SrTiO₃ perovskites [7]. This choice was due to the fact that these compounds included side phthalide groups of atoms with a large dipole moment, which is a necessary condition for the applicability of this model. Subsequently, in [8–10], the “polar catastrophe” model proved itself in explaining electrophysical phenomena occurring at the interface of two organic films with a wide band gap.

Previous studies [4,8–10] have shown that if the technology of manufacturing multi-layer polymer structures is followed, a transition layer localized within several monomolecular layers can be formed between two films of organic dielectrics. Unlike perovskite films, polymer films were made via centrifugation from a polymer solution. It is obvious that the electrophysical parameters of this region should strongly depend on the conditions of preparation of a two-layer film (solvent, concentration of solutions, rotation speed of the centrifuge, annealing temperature, ambient atmosphere, humidity, etc.).

In addition, it is always necessary to take into account the possibility of current leakage through the surface of the upper film, along the interface of the polymer film/substrate and directly through the polymer. All these current flow paths are difficult to control experimentally. Thus, it requires a large number of additional experiments with various sample configurations [8].

In this regard, it seems important to be able to indicate the paths of current flow between two electrodes in contact with the polymer–polymer interface. The idea of the ex-

periment implemented in this paper is to place an ultra-thin nanometer layer of “electronic indicator” (EI) along the interface between the two polymer layers. This layer should affect the transport of charge carriers along the polymer–polymer interface depending on the state of the EI. The level of influence of EI on the transport of charge carriers will indicate the implementation of the quasi-two-dimensional transport of charge carriers.

Conclusions about the localization of the charge carrier transport region along the interface have been based on non-direct measurements until now, for example by comparing the values of resistances measured along the interface and along two other interfaces of the structure: the surface of a two-layer film and the polymer film–substrate interface [11]. In the work of [12], the doping of polymer films with organic low molecular weight dopants with large dipole moments was used. This allowed us to establish the effect of doping on the increase in conductivity in the studied structure.

In this regard, the purpose of this work was to study the effect of surface doping of polymer films on the electrophysical properties of a two-dimensional region formed along the polymer–polymer interface.

2. Materials and Methods

A polymer with polar side functional groups, polydiphenylenephthalide, was chosen as an organic dielectric [4,8,9]. Anomalous electronic properties of the interface between two dielectric polymer films were previously observed in poly-N-phenyldiphenylenephthalimide, polydiphenyleneoxidephthalide, polydiphenylenesulfidephthalide and polytherphenylenephthalide [8]. Additionally, it was shown in [13] that similar properties can be observed along the interface of the well-known commercial organic dielectric polymethylmethacrylate. Historically, the first report of the abnormally high conductivity of the polymer–polymer interface was made using the example of the polydiphenylentalide/polydiphenylentalide interface. Various studies of the electronic properties of the interface between two polymer dielectrics were carried out on such a structure and numerous experimental results were accumulated. In this regard, polydiphenylenephthalide was chosen as the object of research.

The structural formula of PDPh is shown in Figure 1a. The synthesis of this polymer is described in detail in the work of Salazkin S.N. et al. [14]. PDPh is distinguished by high chemical and heat resistance. The temperature of the beginning of softening in air is ~ 420 °C, the temperature of the beginning of decomposition ≥ 440 °C. It is soluble in traditional organic solvents: chloroform, methylene dichloride, cyclohexanone, etc. In the normal state, PDPh is a dielectric and is characterized by the following parameters: a band gap width of ~ 4.3 eV, electron affinity of ~ 2 eV and first ionization potential of ~ 6.2 eV [15]. An island film of copper oxide (I) was chosen as the EI. Among the thin films of oxide semiconductors, copper oxide can be produced by the simplest, inexpensive and fastest method of thermal evaporation of Cu and annealing in air [16–19]. Metallic copper is easily oxidized at relatively low temperatures (≥ 200 °C). Cu_2O is a p-type semiconductor with a band gap of 2.04–2.71 eV [20,21]. Cu_2O is an oxide with fully filled d-orbitals. These oxides are usually semiconductors due to the gap between the d-band and the next largest energy band (usually obtained from the s-orbitals of the metal). These oxides tend to behave like their own p-type semiconductors, where the Fermi level is closer to the valence band than to the conduction band; however, the mobility of holes for these materials is quite low [20,22–27]. The character of the Cu_2O p-type is explained by the presence of negatively charged copper vacancies, which introduce an acceptor level approximately 0.3 eV above the valence band [27].

In the work samples were 2 types: a pure polymer–polymer interface (Figure 1b) and an interface with an embedded thin layer of EI (Figure 1c). The samples of the first type were a two-layer PDPh–PDPh polymer film with electrodes embedded in the interface. The samples of the second type were with an island Cu_2O film placed along the polymer–polymer interface.

Slide glasses with a size of 15×15 mm were used as substrates. The substrates were cleaned in an ultrasonic bath. Cleaning was carried out sequentially in acetone, ethanol, deionized water, followed by drying at a temperature of 100°C . Each stage of cleaning was carried out for at least 10 min. The first polymer layer was deposited to the cleaned substrate via centrifugation of 5 wt.% polymer solution in cyclohexanone at 3000 rpm for 1 min. Then, the samples were dried for 45 min in air at room temperature. To remove solvent residues, the sample was annealed under pre-vacuum conditions at a temperature of 150°C for 1 h. It is known that PDPh films produced by this technology are continuous and homogeneous up to thicknesses of several nanometers [28].

The next stage was the deposition of metal electrodes to the surface of the polymer layer via the thermal vacuum evaporation of Cu (99.99%, Sigma-Aldrich) at 10^{-6} Pa through shadow masks. The gap between the electrodes was $30\ \mu\text{m}$, thickness ~ 100 nm and width 4 mm. The thickness of the deposited metal layer was calculated according to the formula

$$d = \frac{m}{4\pi r^2 \rho} \quad (1)$$

where m is the deposited metal mass, ρ is the density and r is the distance from the sample surface to the evaporator.

In the case of the second type of the structure, the EI layer was formed before metal electrodes deposition. The procedure consisted of the deposition of an island layer of copper with a thickness of ~ 5 nm on the polymer surface, followed by its oxidation to Cu_2O . The thickness of 5 nm was the maximum thickness when the surface conductivity of the copper film had an activation character typical of island films. Oxidation was carried out in an oxygen atmosphere at 200°C for 40 min. This method is sufficient for complete oxidation of the copper film to single-phase Cu_2O [16–19].

The second polymer layer was formed on the surface of the first film with deposited electrodes. Polymer solution of 5 wt.% in cyclohexanone were used according to a similar procedure for the first polymer layer.

The surface morphology and thickness films at all stages of the production of the multilayer structure were controlled using an atomic force microscope NTEGRA II (NT-MDT Spectrum Instruments, Moscow, Russia) adopting an Au-coated silicon probe with a nominal 35-nm tip curvature radius and a typical force constant of 0.1 N. The AFM images were obtained in contact mode. Before and after each measurement the noise level was 0.01 nm.

The quality of the manufactured layers was estimated according to two criteria: root-mean-square (RMS) surface roughness and thickness. The numerical value of RMS was obtained from a series of AFM images from different parts of the sample surface with the same dimensions of $5 \times 5\ \mu\text{m}$. The thickness was estimated using the height difference between the layers. In the case of a Cu_2O layer and copper electrodes, the transition boundary was created using a tightly pressed shadow mask. For polymer films, a stump was formed using a copper cutter, since the layers were made via the method of centrifugation over the entire surface of the sample from a PDPh solution.

The morphology of the surface of each layer is shown in Figure 2. The surfaces of the polymer films are smooth and flat (Figure 2a,d). The RMS surface roughness deduced from the AFM topography images is ~ 1 nm. Figure 2e,f shows the topography of the surface and a 3D image of the lower polymer layer with a slice section. The film is homogeneous in thickness except for the small section along the cut. This indicates good film-forming properties of PDPh. This fact has been repeatedly confirmed in our previous works [8–10,28].

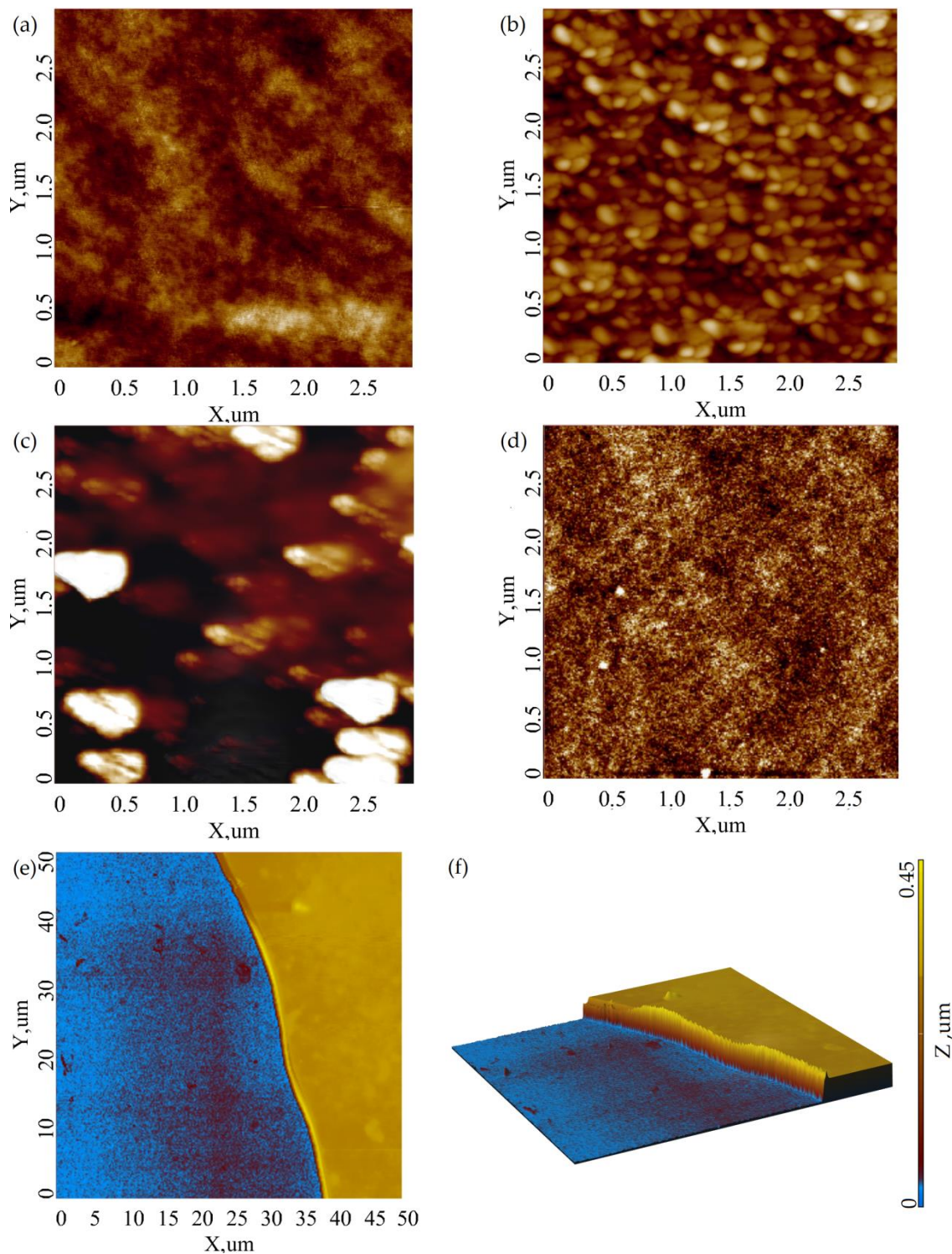


Figure 2. AFM image of the surface of (a) the lower PDPh layer; (b) the Cu_2O oxide layer; (c) the copper electrode; (d) the upper PDPh layer; (e,f) the surface topography and 3D image of the lower polymer layer with a slice section.

Cu_2O has a granular structure with a surface roughness of about 4 nm. This corresponds to approximately 80% of the nominal thickness of the oxide layer. A high surface roughness value indicates the presence of isolated islands instead of solid films.

The surface of the copper electrodes has a structure with large grains with a surface roughness of 10 nm. The formation of grains, apparently, is a consequence of the pro-

cesses of recrystallization and agglomeration during the deposition of copper atoms on the substrate.

The study of the electronic properties of Cu₂O films was carried out via optical methods using a Shimadzu UV-1800 spectrophotometer (Shimadzu Corporation, Kyoto, Japan). For this purpose, the Cu₂O films on a quartz substrate were made in parallel with the formation of island films on polymer. The thickness of the film and the manufacturing method were the same.

The spectra of the UV-visible region were recorded in the wavelength range of 250–800 nm in air at room temperature (Figure 3a). It is revealed that Cu₂O films are characterized by high transparency in most of the visible range.

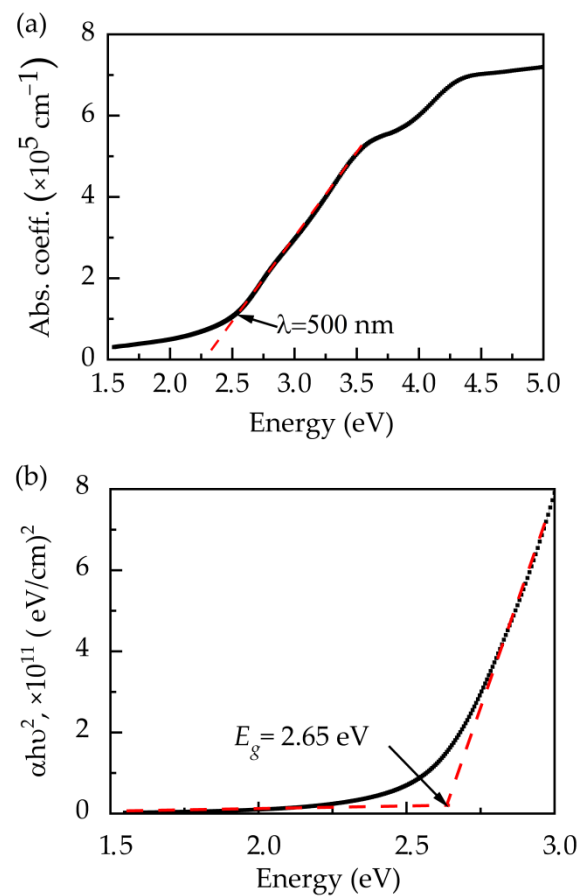


Figure 3. (a) Absorption coefficient α with photon energy and (b) Tauc's plot of thin copper oxide film.

The optical width of the band gap is estimated according to the absorption coefficient. The band gap energy is the energy difference between the bound state (valence band) and the free state (conduction band). The minimum energy required to excite an electron from a bound state to a free state and to participate in the conduction process must be at least equal to the width of the band gap. The band gap width of the copper oxide film was determined using Tauc's method from the optical absorption spectrum [29] using the equation:

$$\alpha h\nu = B(h\nu - E_g)^n, \quad (2)$$

where B is the Tauc's constant, h is the photon energy, E_g is the optical band gap of the material, α is the absorption coefficient and the value of $n = \frac{1}{2}$ or 2 for direct and indirect allowed transitions, respectively.

The absorption coefficient α is calculated from the transmission spectrum data according to the Beer–Lambert law (3):

$$\alpha(\lambda) = -\frac{1}{d} \ln\left(\frac{T}{100}\right) \quad (3)$$

where T is the transmittance in % at the wavelength λ and d is the film thickness.

The absorption coefficient α lies in the range from 10^4 to 10^5 cm^{-1} (Figure 3a). The absorption region is at a wavelength less than 500 nm. It is known that a value showing $\alpha > 10^4 \text{ cm}^{-1}$ indicates the presence of direct electronic transitions [30,31] occurring from dipole-resolved blue and indigo transitions. A direct band gap is typical for thin films, whereas transitions with an indirect band gap are usually detected for relatively thick films [32]. In this case, the energy of the forbidden zone (E_g) was estimated under the assumption of a permitted forward transition ($n = \frac{1}{2}$). The value of the band gap width is located at the intersection of the linear approximation of the edge of the main absorption (Figure 3b) and the spectrum below the main absorption [29]. Thus, the E_g value of the Cu_2O film is 2.65 eV. It may seem that this value is somewhat overstated. However, it is known that with a decrease in the thickness of the amorphous Cu_2O film, the band gap increases [21]. For example, in [33] it was found that a decrease in the size of Cu_2O nanoparticles from 3.2 to 2.1 nm leads to an increase in the band gap of 2.15 to 2.71 eV due to the effect of dimensional quantization. Therefore, an increase in E_g in our case may be evidence that the Cu_2O film is an island, which is in close agreement with other experimental results [21,33].

Electrophysical measurements were carried out using the Keysight B2902A precision parametric analyzer (Keysight Technologies, Santa Rosa, CA, USA) in the atmosphere under normal conditions.

3. Results and Discussion

Figure 4 shows typical volt-ampere characteristics (VAC) of two types of experimental structures measured along the polymer–polymer interface. The difference between these VAC is that curve two corresponds to a sample with an insular copper oxide film along the interface, and that curve two corresponds to a sample without an insular copper oxide film. It is clearly seen that the introduction of an insular layer of Cu_2O along the polymer–polymer interface leads to an increase in the current flowing through the sample (Figure 4a, red curve) compared to the sample in which there is no insular layer (Figure 4a, black curve). Both dependences have a nonlinear character, which is often observed when injecting charge carriers into organic semiconductors and dielectrics. Usually, such dependence can be approximated by a function of the form

$$I \sim U^n, \quad (4)$$

where I is the current and U is the voltage.

The conversion of the VAC in logarithmic coordinates allows us to estimate some parameters of the injection model. Figure 4b shows the VAC in logarithmic coordinates. It is clearly seen that in different ranges of applied voltage, the functional dependence $I = f(U)$ is different. Both dependences have a nonlinear character. This is often observed when charge carriers are injected into organic semiconductors and dielectrics.

The insertion of an island layer of Cu_2O along the polymer–polymer interface leads to an increase in the current through the sample (Figure 4a, red curve) compared to the sample with no island layer (Figure 4a, black curve). For the volt-ampere characteristics, two areas of dependence are well distinguished: Ohmic at low voltages and superlinear at high voltages.

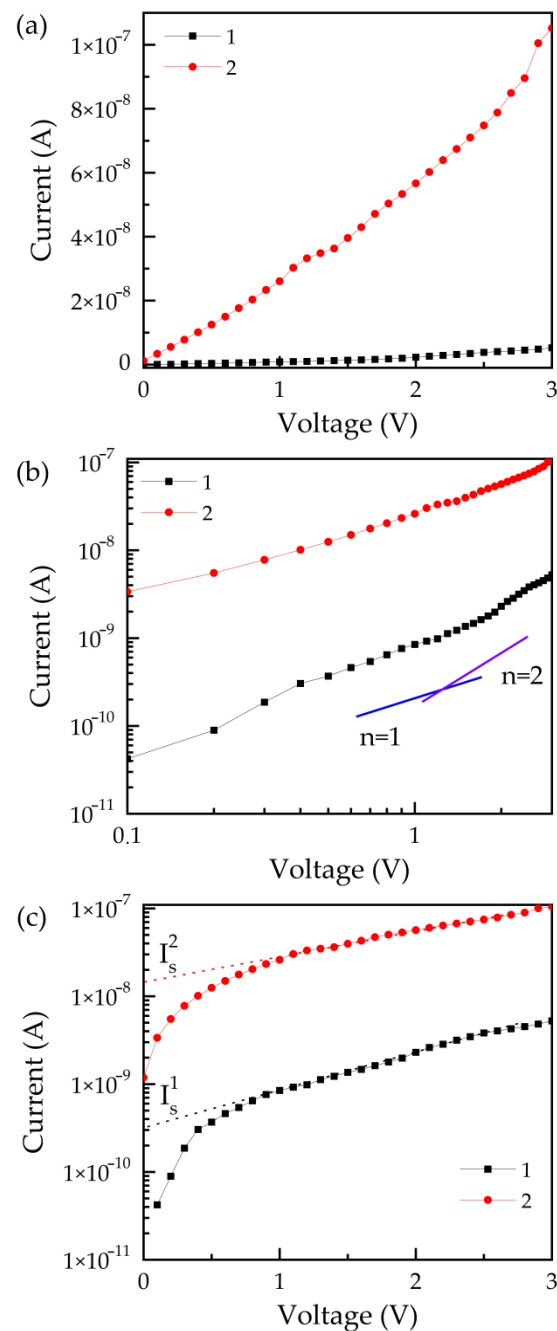


Figure 4. (a) Volt-ampere characteristics measured along the interface of polymer films, (b) in semi-logarithmic and (c) logarithmic coordinates. 1—PDPh-PDPh, 2—PDPh-Cu₂O-PDPh. $I_s^{1,2}$ —are the saturation currents for doped and non-doped samples.

Estimates of the electronic characteristics of experimental structures were carried out within the framework of a theoretical model for space-charge-limited currents [34]. This model has previously been successfully used to study charge transfer in complex multi-layer structures containing metal-polymer interfaces or polymer-polymer boundaries [10]. According to this model, at low voltages, the current is caused by its own charge carriers and therefore the VAC has a linear Ohmic form:

$$j = \frac{en_0\mu U_n}{L}, \quad (5)$$

where j is the current density, L is the distance between the electrodes, U_n is the voltage corresponding to the transition point on the VAC from the linear to the superlinear section, n_0 is the concentration of proper charge carriers, μ is the mobility of charge carriers and e is the elementary electric charge (electron charge).

The current of charge carriers injected from the electrode has a power dependence on the applied voltage:

$$j = \frac{\varepsilon\varepsilon_0\mu U_n^2}{L^3} \quad (6)$$

where $\varepsilon_0 = 8.85 \times 10^{-12} \text{ F}\cdot\text{m}^{-1}$ is the dielectric constant and $\varepsilon = 3$ is the dielectric permittivity of the polymer.

The equality of the currents described using Formulas (5) and (6) corresponds to the transition from a linear section to a superlinear one on the VAC curve. Thus, by equating these currents with each other, it is possible to estimate the concentration of its own charge carriers:

$$n_0 = \frac{\varepsilon\varepsilon_0 U_n}{eL^2}, \quad (7)$$

It is also possible to estimate the effective mobility of the charge carriers:

$$\mu_{eff} = \frac{jL^3}{\varepsilon\varepsilon_0 U_n^2} \quad (8)$$

The parameters of charge carriers calculated according to (7) and (8) are as follows: for the PDPh–PDPh interface, the concentration of charge carriers is $n_0 \approx 1.7 \times 10^{17} \text{ m}^{-3}$ and the mobility of the charge carriers is $\mu_{eff} \approx 1.2 \times 10^{-2} \text{ cm}^2/\text{V}\cdot\text{s}$ for the PDPh–Cu₂O–PDPh interface $n_0 \approx 2.5 \times 10^{17} \text{ m}^{-3}$ and $\mu_{eff} \approx 2.5 \times 10^{-1} \text{ cm}^2/\text{V}\cdot\text{s}$, respectively.

The presented evaluation results showed that the introduction of an island Cu₂O film along the polymer–polymer interface practically does not affect the concentration of charge carriers. At the same time, the island film strongly affects the mobility of charge carriers, increasing it by almost an order of magnitude along the interface.

The potential barrier height at the metal–polymer boundary was estimated based on the Richardson–Dashman equation [35] using the formula:

$$e\varphi_B = kT \ln\left(\frac{SA^{**}T^2}{I_S}\right) \quad (9)$$

where T is the temperature, k is the Boltzmann constant, e is the electron charge, S is the contact area, A^{**} is the Richardson constant and I_S is the saturation current.

The saturation current is located from the intersection of the linear approximation of the VAC in semi-logarithmic coordinates ($\ln(I) - U$) with axis $U = 0 \text{ V}$. Thus, in order to estimate the value of I_S , the voltage characteristics shown in Figure 4a were converted in semi-logarithmic coordinates. The corresponding dependencies are shown in Figure 4.

As a result, the following values of the height of the potential barrier were obtained: for the PDPh–PDPh interface— $\varphi_B \approx 0.45 \text{ eV}$; for the PDPh–Cu₂O–PDPh interface— $\varphi_B \approx 0.34 \text{ eV}$.

One can confidently state the change in the transport of charge carriers along the polymer–polymer interface when an island Cu₂O film is placed on it. Apparently, this may be an important confirmation that it is the interface that is the transport layer for charge carriers. Increasing the mobility of charge carriers to values comparable to the parameters of charge carriers in Cu₂O ($2.34 \times 10^{-1} \text{ cm}^2/\text{V}\cdot\text{s}$ [22]) also confirms this conclusion.

Noteworthy is the significant decrease in the height of the potential barrier at the contact of the metal electrode with the quasi-two-dimensional polymer–polymer region. Such a decrease in the potential barrier can be explained on the basis of the 3D/2D contact model considered in [36]. According to this model, the injection of charge carriers into a two-dimensional one occurs by sequentially passing through a potential barrier located under the electrode and a barrier formed at the edge of the metal electrode. There are several assumptions in this model. First of all, it is assumed that a three-dimensional metal

electrode is formed directly on a two-dimensional region. At the same time, there is no strong surface interaction between the metal electrode and the two-dimensional region due to the overlap of orbitals between metal atoms and molecules below the underlying layer.

In the case of metal and polymer surface contact, relatively weak adhesion occurs very often. This may indicate the implementation of the contract at the expense of Van der Waals forces. It can lead to a limitation of the injection current due to a potential barrier of a certain height. In our case $\varphi_B \approx 0.45$ eV.

At the same time, when the interaction between the metal electrode and the two-dimensional region increases, this inevitably leads to a decrease in the potential barrier. It can be assumed that the presence of Cu_2O islands really affects the formation of contact in a similar way. This can explain the detected decrease in the height of the potential barrier.

4. Conclusions

An electronic state with high conductivity is formed along the interface between two films of a polymer dielectric. The conductivity significantly exceeds the bulk conductivity of the polymer. At the same time, the concentration of charge carriers remains low on the order of 10^{-17} m^{-3} . At the same time, the mobility of charge carriers becomes abnormally large and reaches values of $\sim 10^{-1} \text{ cm}^2/\text{Vs}$. This is indeed an abnormally large value, since the mobility measured using the time-of-flight method for the volume of the polymer film [37] gives values of $\sim 10^{-6} \text{ cm}^2/\text{Vs}$. The possibility of somehow influencing the transport of charge carriers by modifying the interface itself can expand the boundaries of the practical application of abnormally high conductivity along the polymer–polymer interface. Additionally, it can answer the fundamental question about the localization of this transport. In this paper, the chosen method of deposition of a nanometer Cu_2O film on the polymer surface allowed for minimizing the diffusion of dopant particles into the film volume.

Doping of the polymer–polymer interface with a Cu_2O island film showed that the electrical conductivity along the interface increases significantly, not by increasing the concentration of charge carriers, but by increasing their mobility. Additionally, the estimates of the concentration of charge carriers give values for their own charge carriers. This means that in both cases we are dealing with the polymer's own charge carriers. The obtained estimates (10^{17} cm^{-3}) are close to the values obtained earlier for the volume of the polymer films [38]. Therefore, at low voltages on the sample, the conductivity along the interface is low.

It was found that the Cu_2O doping of the interface significantly changes the height of the potential barrier, reducing it from 0.45 eV to 0.36 eV. In this way, it is possible to control the contact parameters between a three-dimensional metal electrode and a two-dimensional electrically conductive organic region. Perhaps such an approach to the modification of a quasi-two-dimensional electronic structure can be practically used to purposefully change its electronic properties, which would be useful for developing heterostructures of transistors and sensors.

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