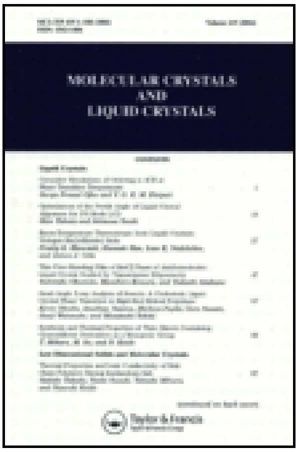

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High Conductivity of the Interface Between Two Dielectric Polymer Films

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The possibility of creating a two-dimensional region with anomalously high conductivity at the interface between two dielectric polymers has been demonstrated. It is established that the conductivity of such a boundary layer is several orders of magnitude higher than the surface conductivity of an individual film. The analysis of the results makes it possible to hypothesize that a layer with a quasi-two-dimensional electron gas is formed in the interface region between two dielectric polymer films. It is shown that, on the basis of this interface, it is possible to create chemical sensors and, in fact, sensors for the relative humidity of air and pH readings.

Keywords Conductivity; interface; polymer film; sensor

Introduction

The properties of a near-surface region in films are usually different from those in bulk. This difference is related to several factors, including the excess free Gibbs energy of the surface and a decrease in the entropy. The mutual influence of contacting layers takes place at their interface (boundary) and involves both the structure of a transition layer and its electron properties. Changes in the electron properties can be traced by measuring the transport characteristics of the resulting two-dimensional (2D) structures. However, the study of the electron transport properties of boundary layers is frequently complicated by a relatively high intrinsic conductivity of the initial polymers, which masks the conductivity of the boundary layer. Therefore, for the experimental investigation of such systems, it is expedient to select polymers with minimum intrinsic conductivity (e.g., dielectrics), so as to minimize the current component passing through the volume of polymers and to study a change in the conductivity along the contacting layers.

Recently, it was reported on the interface between two insulators $LaAlO_3$ and $SrTiO_3$ with anomalous electronic properties, in particular, the charge carrier mobility $\mu = 10^4\,cm^2V^{-1}s^{-1}$ was measured [1]. Later on [2], superconductivity and giant magnetoresistance were revealed in such structures. These phenomena were explained in the framework of a hypothesis that a two-dimensional electron gas is

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formed in the transient layer between two insulators. The mechanism of formation of this electron gas is not clearly understood, but the active studies made it possible to reveal many interesting properties of this interface including the superconductivity at 200 nK, magnetoresistance, ferromagnetic ordering of electrons [3], field control [4], and many other properties [5] inherent in a two-dimensional electron gas. In 2008, similar results were obtained in [6,7], where the transient layer was formed at the interface between two organic insulators – tetrathiafulvalene (TTF) and 7,7,8,8, tetracyanoquinodimethane (TCNQ). The mobility in these structures was about several $cm^2V^{-1}s^{-1}$, and the metal conductivity was revealed. At the same time, the anomalously high conductivity at the interface between two identical polymer layers of poly(difenylenephthalide) (PDP) has been demonstrated [8].

This paper presents the results of further investigations of the charge transport along the boundary of two organic layers of PDP. It is expected that the bending of energy levels in this region leads to the increased local charge concentration and, hence, modifies the transport properties of the 2D structure under consideration. In particular, the electric conductivity of the interface layer must be several orders of magnitude larger than the bulk one. In this connection, it seems important to study the electronic properties of the interface between two dielectric polymer films. The objective of this work was to form a polymer–polymer interface and to investigate its electrophysical properties including the sensory ones.

Experimental

We used poly(diphenylenephthalide)s of the polyheteroarylene polymer class as the objects of investigation. These polymers are highly soluble in organic solvents and possess high film-forming properties [9]. In our experiments, polymer films were obtained by the spin coating of solutions of the polymer in cyclohexanon of various concentrations. The film thickness varied from 30 nm to 1 μm. Metallic copper electrodes were prepared by the vacuum thermal-diffusion sputtering. The current–voltage (*I–V*) characteristics of the samples were measured, by using the standard technique. Temperature measurements were performed in the interval 90–300 K, by using a cryostat with a Dewar vessel. The system under investigation was placed in the Dewar vessel, and the temperature was varied by changing the position of the sample relative to the nitrogen surface. The temperature was monitored with the help of a thermocouple.

The choice of the polymer material was dictated by the following considerations. The analysis of electron transport properties of the boundary layers proper is complicated, since conducting polymer materials possess a high intrinsic conductivity, which may shunt the conduction of the boundary layer. In this connection, measuring conditions must be chosen to be such that the conductivity along the interface be higher than the bulk conductivity of the material. Consequently, for our experiments, we took polymers with a low intrinsic conductivity. The optical thickness of the band gap of the polymers used is 3.9–4.2 eV, and the electron work function is approximately 4 eV. Obviously, such polymers are poor conductors in the initial state. For this reason, any insignificant improvement of their transport properties can easily be monitored.

The experimental samples were the multilayer structures presented schematically in Figure 1a. The sample was prepared by consecutive operations as follows. The polymer film was deposited on the surface of a purified polished glass substrate

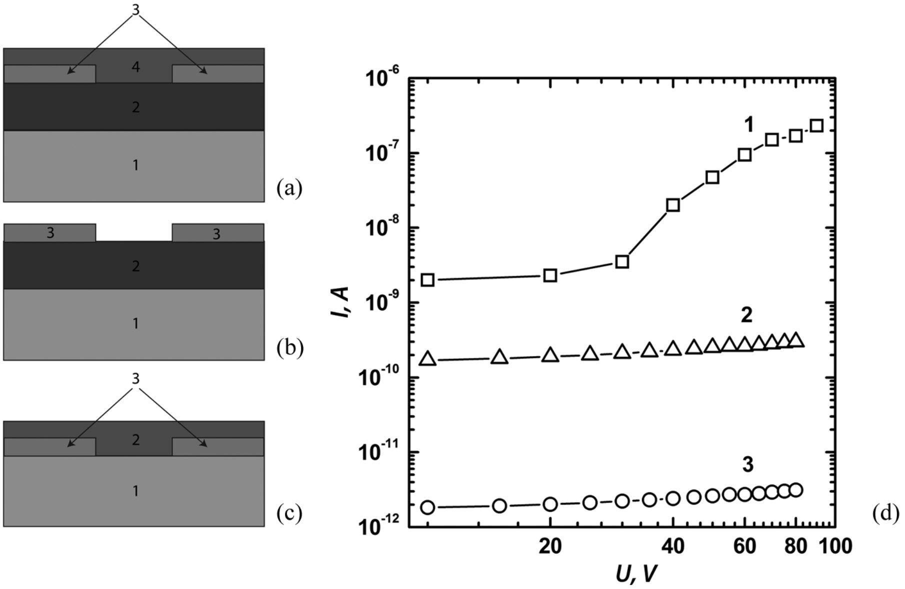


Figure 1. Structures of the experimental samples with (a) two polymer layers, (b) one polymer layer and the electrodes on the polymer surface, (c) one polymer layer and the electrodes under the polymer film: 1 - substrate, 2 - polymer layer, 3 - metal electrodes, 4 - polymer layer, and (d) current–voltage characteristics for samples: (1) - a, (2) - b, and (3) - c.

by the spin coating from a PDP solution. The solvent residuals were removed from the film by the successive drying first in air at room temperature for 30 min and then at 150°C for 40 min. Then, the metal electrodes were deposited on the polymer film surface by the vacuum thermal diffusion sputtering through a shadow mask. The final stage was the deposition of the second polymer layer adhering the entire sequence of technological operations described above. Each layer was about 300 nm thick. The thickness of polymer films and the state of the surface were monitored by a SMM-2000 T atomic force microscope. The electrodes were made of copper. The distance between the electrodes was varied from 30 to 60 μm.

Results and Discussion

In the preparation of the sample, the resistivity was controlled by the two-probe method. As soon as the electrodes were deposited on the first film surface (see Fig. 1b), the resistivity was $\rho \sim 10^7\,\Omega\cdot\text{cm}$ (Fig. 1d, curve 2) and decreased down to $\rho \sim 10^3\,\Omega\cdot\text{cm}$ when the second layer was deposited (see Fig. 1d, curve 1). To refine the possible contribution of the charge carrier transport along the polymer–substrate interface, the samples with the electrode on the glass substrate surface were additionally prepared (see Fig. 1c). In this case, the resistivity was $\rho \sim 10^8\,\Omega\cdot\text{cm}$ (see Fig. 1d, curve 3). The analysis of the current–voltage characteristic obtained in the measurement of the charge carrier transport along the polymer–polymer interface (see Fig. 1d, curve 1) demonstrated that it is well approximated by a function of the form $I = kU^n$. Such dependences can be interpreted in the injection model. This conclusion does not contradict the results of the earlier studies of the electron transport properties of the metal–poly(diphenylphthalide)–metal system [10]. Two regions with different exponents n are clearly seen on the current–voltage characteristic: $n = 1$ at low voltages, and the current–voltage characteristic at higher voltages is superlinear with $n \sim 2$. The voltage, at which the transition from the linear to the superlinear region occurs, corresponds to the situation where the concentration of thermally generated equilibrium free charges becomes comparable with that of injected charges [11]. This balance of concentrations allows us to estimate the electron mobility

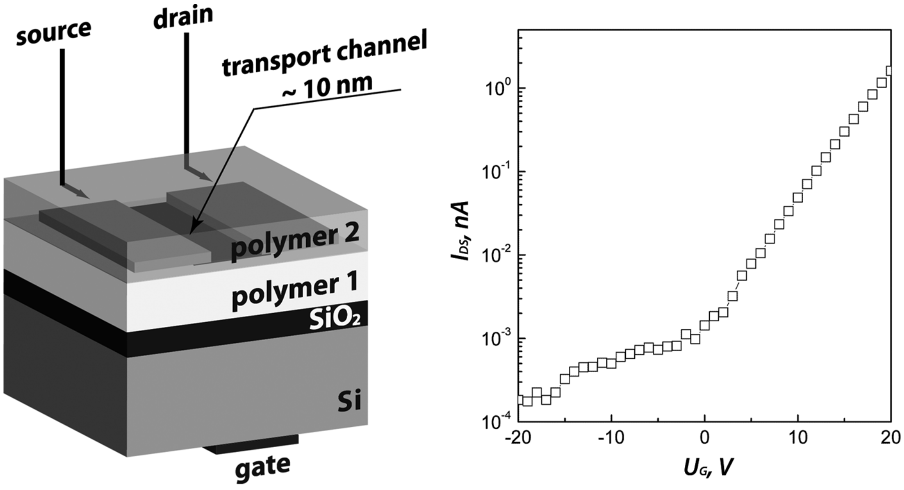
$$\mu = \frac{JL^3}{\theta \varepsilon \varepsilon_0 U_1^2}.$$

The current density J was estimated in terms of the current and the surface area, through which the current was flowing, and which, in turn, was calculated in terms of the electrode thickness d_1 and the transport layer thickness d_2; θ is defined as the ratio of the maximum and minimum currents of the limiting trap filling region. According to the AFM recording, the transport layer thickness was set equal to 10 nm, and U_1 is the voltage at the point of the transition from the linear to the square law. The charge carrier mobility calculated by formula (1) was $3.76 \cdot 10^{-2}\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. It is very high for such materials and is almost five orders of magnitude higher than the bulk mobility $\mu \sim 10^{-6}\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ [12] measured by the time-of-light method. The value obtained is close to the maximum charge carrier mobilities in organic materials, in particular, in organometallic compounds such as phthalocyanines ($\mu \sim 0.4 \div 1\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}$).

It is well known that the bulk conductivity of the polymers studied here is of the hole type. At the same time, the formation of a highly conducting state is associated with the electron conduction [12]. The question arises about the type of charge carriers ensuring an elevated conduction of the boundary transport layer. The answer to this question can be obtained from the analysis of the transport characteristics of transistor structures. Thus, we consider the results of measurements of the I–V curves for samples prepared on silicon plates with an arrangement of electrodes similar to the configuration of a field transistor (see Fig. 2a). Samples with polymer films on silicon plates with an oxide layer were prepared using an analogous technique. The substrates for the transistor structures were $n{+}{+}{-}$Si plates with an ohmic electrode on one side of the plate and a SiO_2 layer (100 nm in thickness) formed by the thermal oxidation on its other side.

We measured the dependence of the current between the drain and the source (lateral electrodes) on the potential supplied to the gate (lower ohmic electrode on the silicon plate) (Fig. 2b). The measured dependence is referred to as the transfer characteristic which shows that the current increases by about five orders of magnitude as compared with the structure of a one-layer polymer film (in this case, the currents are small and amount to less than 10 fA). The shape of the resultant curve indicates that it is electrons that are carriers responsible for the charge transport. Indeed, an increase in the current is observed for positive values of the potential across a shutter.

The temperature dependences of the conductivity were measured for two different experimental configurations. Using the two-probe method, we obtain that the conductivity increases with the temperature. This behavior of the current–voltage characteristic can be attributed to the charge carrier injection from the metal



(a) (b)

Figure 2. Organic field-effect transistor based on the interface of two polymer films as a transport layer (a) and its transfer characteristic (b).

electrodes into the polymer film limited by a Schottky barrier. This conclusion agrees with the above analysis of the current–voltage characteristics [8]. This means that the two-electrode method does not allow one to estimate the true electric conductivity along the interface between two polymer films. In view of this circumstance, the four-probe measurement of the conductivity was realized. As the temperature increases, the electric conductivity decreases, possibly indicating its metal type. We note that a similar difference in the conductivity-*versus*-temperature curves measured by the two- and four-probe methods was observed in the investigation of the properties of the quasi-two-dimensional electron gas formed along the $LaAlO_3$–$SrTiO_3$ and TTF–TCNQ interfaces [6].

The next stage of the work was the development of an acting model of a sensor for the air relative humidity (see Fig. 3a). The current–voltage characteristics of the structures obtained were measured with different amounts of the atmospheric humidity. A dependence of the conductivity on the relative humidity r was constructed on the basis of measured curves, and it is presented in Figure 3b. As follows from Figure 3b, an increase in the humidity affects an increase in the specimen conductivity. It is possible to separate three sections on the curve in different ranges of humidity values. At relatively low humidities (25–40%), there was a little increase in the conductivity. The next range (40–50%) corresponds to a sharp increase in the conductivity. With a further increase in the humidity (50–70%), there is an insignificant increase in the conductivity with subsequent saturation. Rapid response sensors for the relative humidity were studied. It follows from experiments that the response time is not more than 5 sec. Most often, this time corresponds to the diffusion leveling with the rapid opening of a cover, beneath which there is a sensor with increased humidity of 80%, with 20% humidity for the surrounding air. Using the substances, whose molecules do not contain a hydroxyl group, as dopants has demonstrated that, in this case, there is no change in the conductivity. Thereby, the selectivity has been demonstrated for the interface between polymer films to substances with hydroxyl groups. By using this

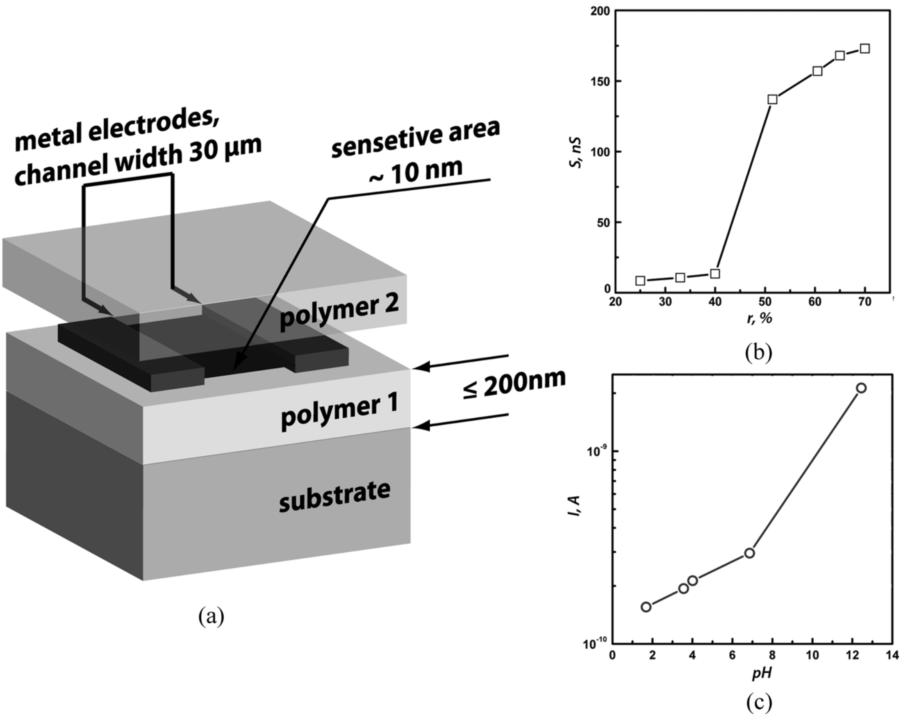
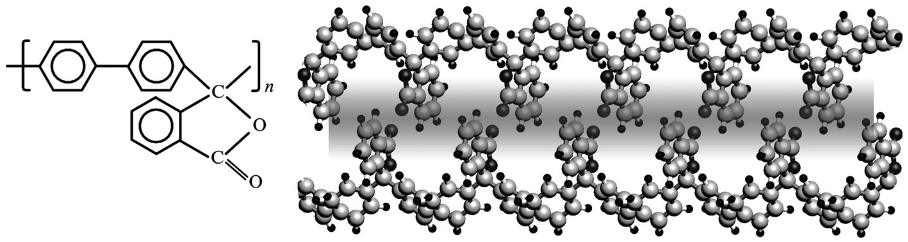


Figure 3. Sensor on the base of the interface of two polymer films (a) and its characteristics: dependence of the conductivity on the air relative humidity *r* (b), dependence of the current with a fixed voltage on the pH index (c).

unique feature of a transport layer, the experimental specimens obtained may be used as multiphase sensors for determining the hydrogen index (pH-meter), and this has been done by experiment. Compositions with a known pH value were added successively to a specimen. Then the current–voltage characteristics were measured. The results obtained are shown in Figure 3c as the current at the same fixed voltage *versus* the pH value. It follows from Figure 3c that there is an increase in the conductivity with a reduction in the acidity. This confirms the assumption made about the selective sensitivity toward a hydroxyl group. The use of new polymer materials opens extensive possibilities for creating chemical nano-sized sensors for different substances.

To explain the high conductivity over the interface between organic materials [6–8], various physical models were proposed. In [13], the conductivity is due to a rather high surface density of geminate pairs formed at the interface. Conditions are established, wherein the transitions of a significant portion of charge carriers between molecules require no thermal activation or tunneling.

We can assume that the structure of the interface between two polymer layers differs from the equilibrium structure in the bulk of the sample. The experiments described in [14] show that the polymers with side functional groups must orient themselves toward the interface between these groups. The latter may lead to the selective ordering of these groups at the surface and to an increase in their local concentration due to the close stacking. In the polymers studied here, the phthalide group that can be appropriately oriented relative to the film surface plays the role



(a) (b)

Figure 4. Structural formula of poly(diphenylenephthalide)'s monomer (a) and a three-dimensional model image of the interface of two polymer films (b).

of the side group (see Fig. 4). In principle, this conclusion does not contradict the assumption about a possibility of the formation of localized levels of the transient layer with the participation of side phthalide groups of polymer molecules, which are electron traps according to [15].

In the framework of one of the models previously proposed in [16–18], it was assumed that, in order to form a two-dimensional electron gas at the interface between two insulators, dipole groups should be present on at least one of the surfaces in contact. From this point of view, it seems possible to use materials having functional groups with a high dipole moment. Polymers can be taken as such materials. It is well known that the side functional groups of polymers are predominantly oriented along the normal to the polymer–air interface [19]. A similar orientation should occur when one polymer film is formed on the surface of another one. As a result, a nanolayer can appear in the near interface region, which is formed by the side groups of polymer molecules.

Conclusions

The sharp increase (by three to five orders of magnitude) in the conductivity of the samples after the deposition of the second polymer layer can be explained as follows. A thin transition layer with a structure differing from the bulk structure is apparently formed at the interface between the two polymers. We can assume that the interface between polymer films facilitates the preferred antiparallel orientation of phthalide side fragments with an appreciable dipole moment [20]. Such an orientation increases the local "2D" concentration of electron traps (phthalide side groups), which does not contradict the results obtained in [14]. The trapping of the excess charge injected from the electrodes to phthalide groups of poly(diphenylenephthalide) leads to the emergence of deep localized states in the polymer band gap [20,21]. These states ensure a higher conductivity level and modifies the shape of I–V curves upon the passage of a current. Thus, our studies lead to the conclusion on a possibility of the formation of a transport layer at the interface of two polymer films which possesses an elevated conductivity.

To summarize, we have shown that the interface between two dielectric polymer films has an anomalously high conductivity and a charge carrier mobility. The investigation data such as the presence of a pronounced interface between the polymer films, the metal type of the conductivity, and the presence of the field effect suggest the presence of a quasi-two-dimensional electron gas at the interface between the polymer insulators. However, this statement requires additional investigations, first of all, at low temperatures. It is interesting that the values of charge carrier parameters at room temperature were relatively lower than the parameters of interfaces prepared with the use of inorganic materials [1–6]. Probably, this is attributed to the high defect content of the polymer–polymer interface due to the imperfect technology used in this interface preparation. Although the technology should be improved, the advantages of polymer organic interfaces in the manufacture of the electronic materials with unique electronic properties are apparent.

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