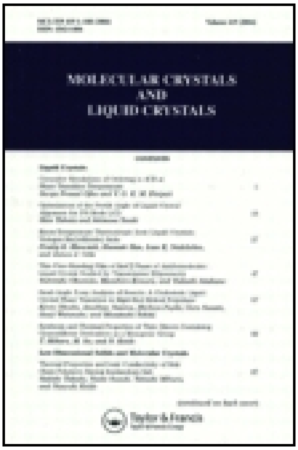

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Lateral Semiconductive and Polymer Conductive Nanolayered Structures: Preparation, Properties, and Application

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Lateral Semiconductive and Polymer Conductive Nanolayered Structures: Preparation, Properties, and Application

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Heterophase nanostructures with alternate semiconductor and electrolytic seams are received. It is shown that the insertion of a polymer composition into the van der Waals gap of crystals causes the additional potential barriers in them. A non-monotone change of the resistance of the obtained structure under applied potential, as well as the strong low-frequency dispersion, has been found out, which can be due to the polarization of double electric layers.

Keywords: GaSe; heterophase nanostructures; hopping transfer; InSe; interculant; spectral photoresponse

INTRODUCTION

Today's state of the environment stimulates the search for a new technological solution for the creation of highly effective, cheap, and, at the same time, reliable sensors and power sources which would enable us to minimize the construction. One of ways of solving this problem is related to the combination of functional properties of non-organic and organic semiconductors by means of the creation of hybrid organo-mineral nanostructures and composites. The successes attained nowadays cannot be considered to be impressive. However, in the decisive trend, i.e., in the creation of multilayer ($\approx 10^6$ layers per mm) nanostructures with alternating mineral-organic interlayers, the interesting photodielectric and photogalvanic phenomena should be expected. On this basis, new phonon nanocrystals and nanophotogenerators can be formed. It is known that structures with alternating nanointerlayers of a semiconductor and a polymer [1,2] which are

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created according to such a principle have shown unique properties which enabled us to recommend them as highly effective capacitors for ac current circuits. The main laws of physical processes running in such structures are not thoroughly studied.

The aim of this work is an attempt to fill, to some extent, the gap in this field.

CONCEPTUAL BASES AND EXPERIMENTAL TECHNIQUE

In our experiments, we used GaSe and InSe layered semiconductors as the initial material. Such crystals are characterized by the presence of the so-called guest-positions oriented perpendicularly to the crystallographic *c*-axis in the regions of action of weak van der Waals forces [3,4]. The insertion of foreign ions, atoms, or molecules into intercrystal gaps is known as the intercalation phenomenon [5].

Peculiarities of the crystalline structure of this type require no precise mechanical and chemical processing of the surface. These crystals are of increased inertness to the adsorption of foreign atoms and molecules. The absence of dangling bonds on the surfaces of these materials ensures a very low rate of surface recombination. In addition, they are of high photosensitivity in the visible and near-infrared regions of the spectrum.

As an electrolyte-polymer photosensitive composition (PC), we used a 0.1 M phenyl acetylene solution in 0.1 M LiBF4 in propylene carbonate, which can be applied to obtaining electroactive polymer materials, in particular, for chemical sources of current [6,7]. This composition cannot be inserted into the structure of a crystal directly; therefore, we applied the three-stage scheme (Fig. 1) to form $\mathrm{GaSe}\langle\mathrm{PC}\rangle$ – and $\mathrm{InSe}\langle\mathrm{PC}\rangle$ intercalated structures.

At the first stage, $NaNO_2$ was inserted into the initial matrix (GaSe, InSe) by means of the direct exposure in its melted substance (300°C) during 5 and 15 min for GaSe and InSe, respectively; by means of this procedure, we essentially increased the distance between layers.

The next stage was the deintercalation of $NaNO_2$ from the crystal by means of the extraction in distillated water during five 24-h cycles and by drying it at a temperature of 110°C and at a decreased pressure. The deintercalated matrix became suitable for the insertion of PC with weakened van der Waals bonds and modified intercrystal force fields.

Therefore, at the third stage, the intercalation of PC into the widened crystal lattice of the obtained deintercalated matrix was carried out by the direct exposure method at room temperature in the mentioned composite for 1 h.

The impedance measurements in the direction of the crystallographic *c*-axis are performed in the range of frequencies $10^{-3} \div 10^{5}$ Hz

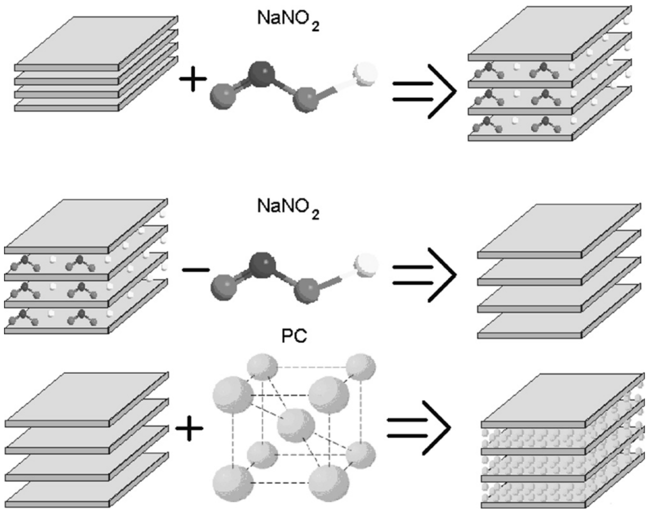


FIGURE 1 Stages of GaSe⟨PC⟩ formation.

at the values of the constant voltage of bias in this direction of 0, 0.2, 0.4, 0.6, 0.8, and 1.0 V with the help of an "AUTOLAB" measuring complex of the "ECOCHEMIE" firm (the Netherlands) equipped with FRA-2 and GPES computer programs. Before inserting PC into them, all the investigated widened samples revealed linear voltage-current characteristics in the range of voltages $-1 \div +1\,\text{V}$. The photoelectric investigations were made with the help of an SF-4 spectrophotometer.

RESULTS AND DISCUSSION

In Figure 2, the frequency dependences of the specific resistance along the direction perpendicular to the layers ($\rho_\perp$) of a monocrystal GaSe with widened deintercalated structure before (a) and after (b) the insertion of the polymer composite at different bias voltages are given. It can be seen that, for a widened matrix, the directly proportional decrease in specific resistance with increase in the bias voltage is observed. This is fairly accounted for by the increase in the transmission through the potential barrier between layers caused by the applied bias voltage. According to Geballe-Pollak's theory [8], the presence of the segments decreasing proportionally to $\sim\omega^{-0.8}$ in the frequency dependences $R(\omega)$ indicates the essential contribution of hopping carriers into the conductance. This is always accompanied by a change in the capacitance of the complete response of localized states and the frequency-dependent impedance. The impedance is

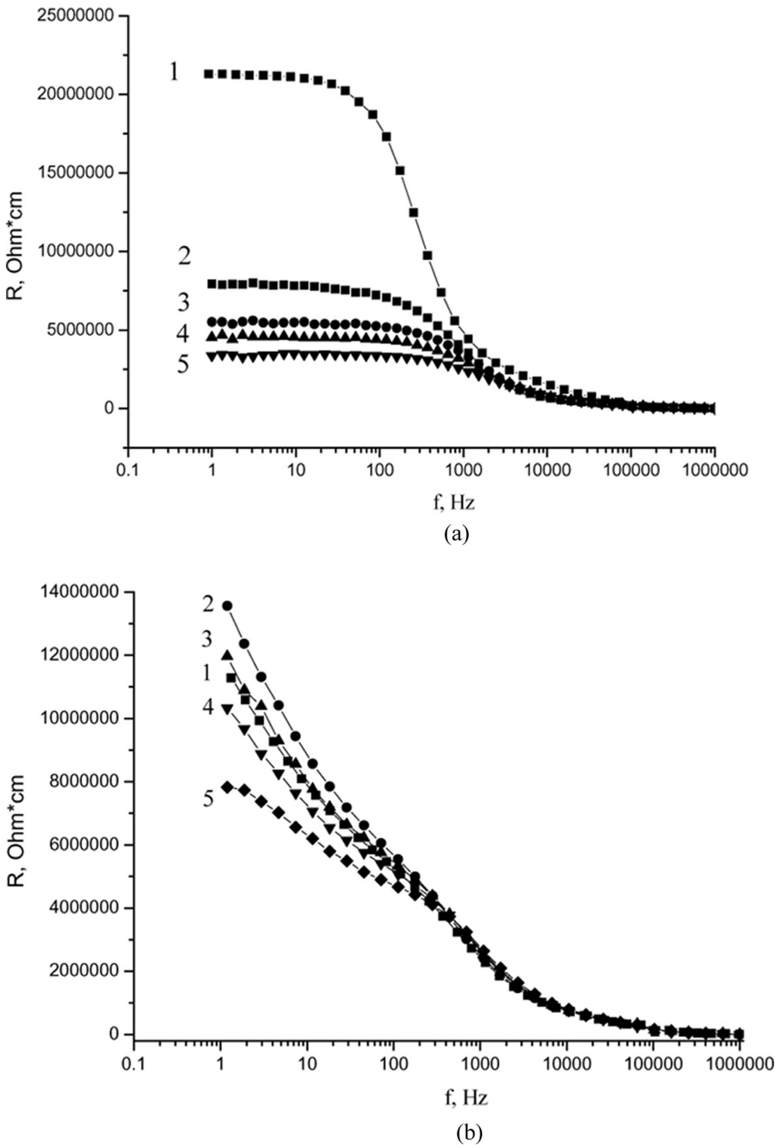


FIGURE 2 Frequency dependences of the specific resistance of monocrystalline GaSe with extended deintercalated structure in the direction perpendicular to layers ($\rho_{\perp}$). (a) Sample before and (b) after the polymer composition insertion under applied potentials: 0 V – (1); 0.2 V – (2); 0.4 V – (3); 0.6 V – (4); 1.0 V – (5).

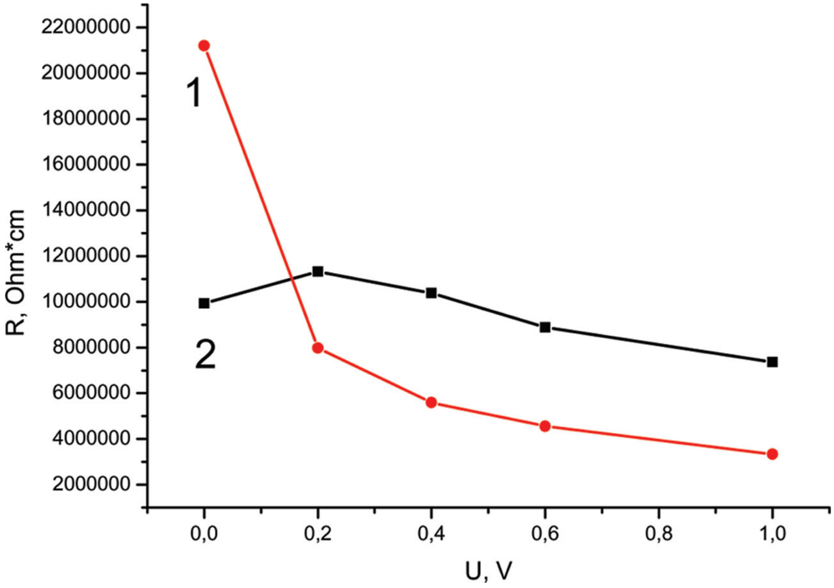
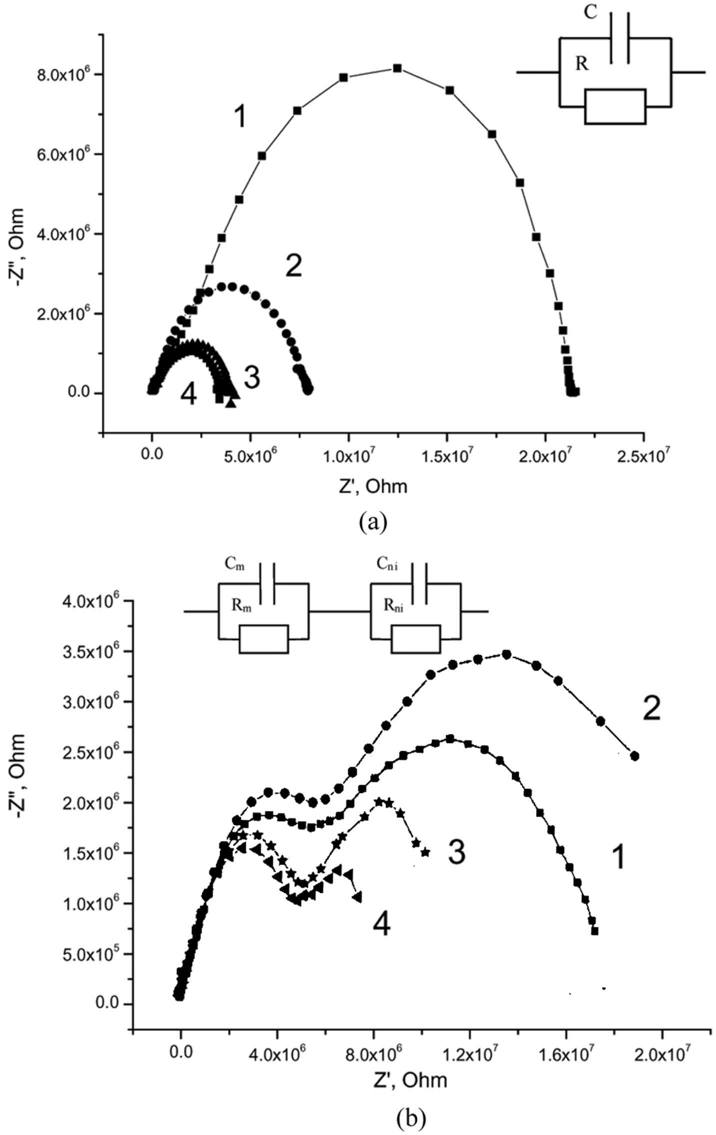


FIGURE 3 Dependence of the specific resistance of the extended deintercalated structure on the applied potential measured at 3 Hz. (a) Sample before and (b) after the polymer composition insertion.

determined by the jumps of charge carriers from one localized state to another one close to the Fermi level or by the processes of trapping and excitation of charge carriers into the tails of bands or into the bands of non-localized states. Indeed, the ideal or deformed semicircle in the complex impedance plane which is characteristic of such cases has different values of its radius depending of the bias voltage (Fig. 4a). The simplest equivalent electric circuit which models such a character of Nyquist plots is the link of a resistor and a capacitor connected in parallel.

After the insertion of PC into the widened crystal lattice of GaSe, the specific resistance for the direct current which flows perpendicularly to the layers decreases according to the law represented in Figure 2b. The application of a constant bias leads to an increase in *R* and to the disappearance of the frequency-independent interval; in addition, the dependence of the specific resistance on the applied bias is not monotonous (Fig. 3). But, for the widened matrix, we previously obtained a monotonous dependence. The Nyquist plots immediately responds to this: it transforms its shape from the one-arc into the two-arc one (Fig. 4b). In this case, the equivalent electric circuit contains the connection of two parallel RC links in series (Cm||Rm and Cip||Rip) which model



(a)

(b)

FIGURE 4 Nyquist plots of monocrystalline GaSe with the extended deintercalated structure. (a) Sample before and (b) after the polymer composition insertion at applied potentials: 0 V – (1); 0.2 V – (2); 0.8 V – (3); 1.0 V – (4).

TABLE 1 Parameters of Elements of the Electric Equivalent Circuit Before and After the Polymer Composition Insertion at Different Applied Potentials

GaSe with extended deintercalated structure			GaSe⟨PC⟩				
Applied potential, V	R, Ohm	C, F	Applied potential, V	R_{m}, Ohm	C_{m}, F	R_{ni}, Ohm	C_{ni}, F
0	6.89E+06	1.20E–11	0	2.47E+06	2.47E−11	4.26E+06	3.21E−08
0.2	2.26E+06	1.03E−11	0.2	2.51E+06	1.18E−11	4.82E+06	2.16E−08
0.4	1.67E+06	1.11E−11	0.4	2.31E+06	1.20E−11	3.75E+06	2.37E−08
0.6	1.42E+06	1.23E−11	0.6	2.21E+06	1.39E−11	3.22E+06	3.11E−08
0.8	1.22E+06	9.97E−12	0.8	2.18E+06	1.15E−11	2.02E+06	4.97E−08
1.0	1.09E+06	1.22E−11	1.0	1.96E+06	1.62E−11	1.75E+06	2.61E−08

the processes of electric charge transfer through the matrix material and the matrix-PC interface, respectively (see the insert in Fig 4b). The second low-frequency link models the emergence of an additional barrier for the hopping transfer (Table 1). A vivid evidence of this is the transformation of the *I-V* characteristic from the linear to the diode character as a result of the insertion of PC.

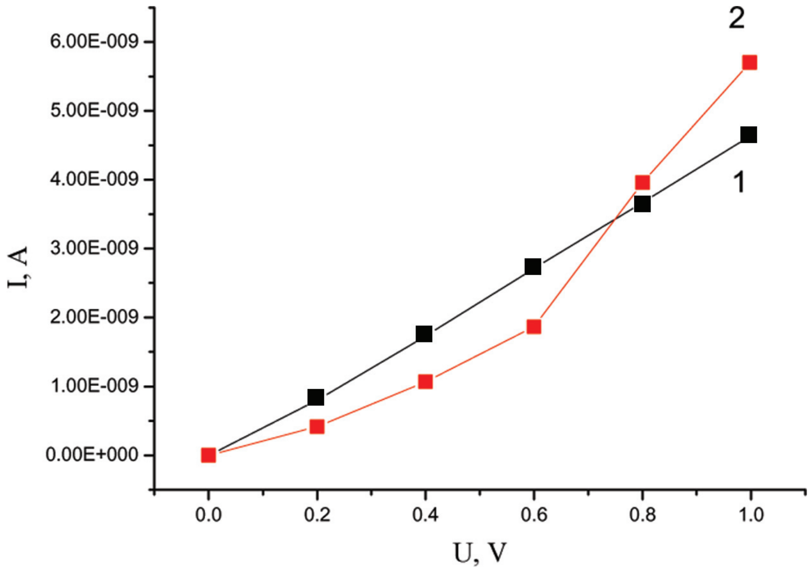
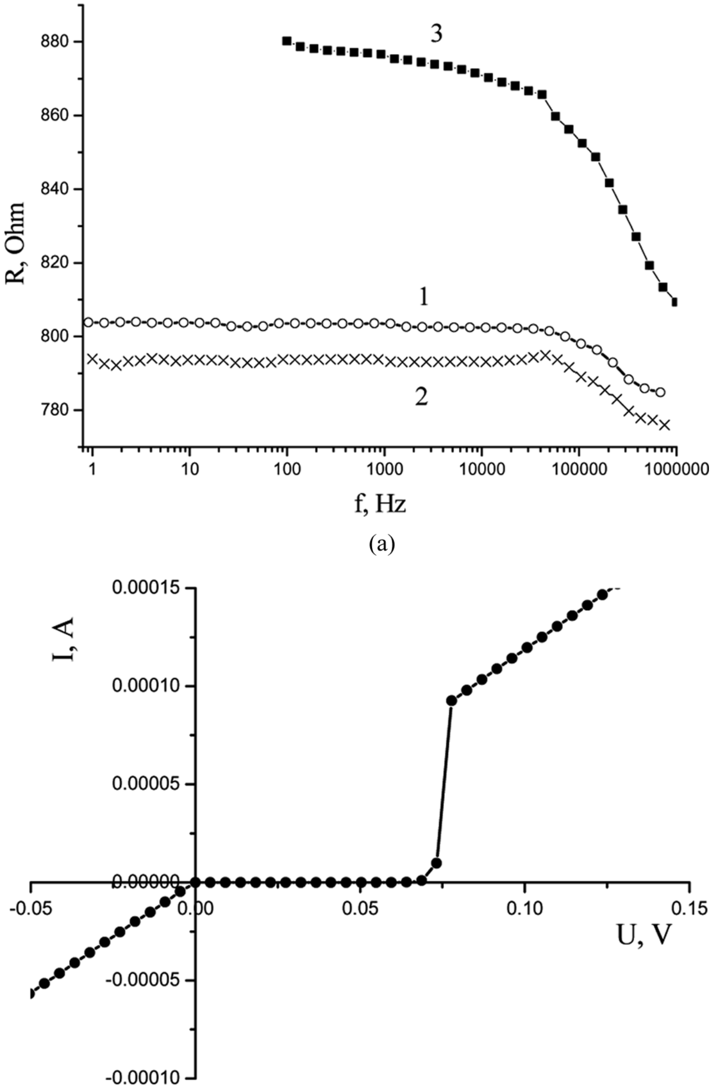


FIGURE 5 Voltammetric curves of the bulk material (1) and the nanostructure interface (2).



(b)

FIGURE 6 Frequency dependences of the specific resistance of monocrystalline GaSe with the extended deintercalated structure in the direction perpendicular to layers ($\rho_{\perp}$). (1) The sample before and (2) after the polymer composition insertion under the applied potential: 1.0 V – (3).

A non-trivial result was the strong low-frequency dispersion of the resistance after the application of the bias voltage, which is caused, probably, by the polarization of double electric layers (DEL) of the crystal-PC interface. The aforesaid polarization is accompanied by an increase in the Q-factor of DEL. This, in its turn, causes an essential contribution of bias currents into the total current. Just on the ground of these facts, it can be unambiguously explained that the high-frequency arc at different values of the bias is practically unchangeable; and the simultaneous decrease in ImZ for equal frequencies of the second arc can be also explained.

The *I-V* characteristic of the bulk of the material (Fig. 5) is well approximated by a linear law ($I \sim U$), and the interface of phases by a quadratic law ($I \sim U^2$).

The analogous results are also obtained for InSe (Fig. 6a). The only difference is that the change is less because of both the lower electric resistance of initial samples and the less ability to split under the action of $NaNO_2$. However, in this case, the fact of the emergence of a step in the *I-V* characteristic after the insertion of PC (Fig. 6b) turned to be extraordinary; the cause for this is not known surely yet. However, it can be assumed that this can be related to the Coulomb blockade of a charge carried from the semiconductor to polymer layers. The illumination of GaSe⟨PC⟩ with 60-W integrated light leads to the emergence of a photo e.m.f. of 0.1 V in the direction

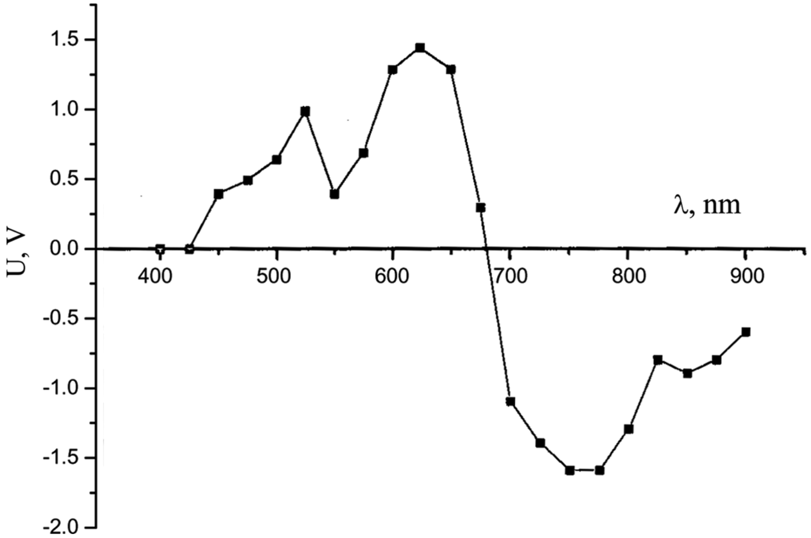


FIGURE 7 Wavelength dependence of the open circuit potential of GaSe⟨PC⟩.

perpendicular to nanolayers. The magnitude of this e.m.f. varies with the duration of the illumination, and the behavior of the photo e.m.f. indicates the formation of a photoelectret state [9]. Indeed, the form of the spectral photoresponse (Fig. 7) resembles the relaxation of a photoelectret state caused by the relaxation of a homocharge due to the fact that trap centers become charge free because of both the action of photons with energy from 1.84 to 2.91 eV and the relaxation of a heterocharge with energy from 1.38 to 1.77 eV. So, the thin structure of the spectrum indicates a complicated character of the distribution of trap centers in the forbidden band.

CONCLUSION

The experimental results presented in this work have convincingly shown that the insertion of polymer composition into intercrystalline gaps changes the potential relief of the matrix. It has been found that the variation of the resistance of the obtained structure is not monotonous with a change in the bias voltage. This resistance is found to possess the strong low-frequency dispersion, which is caused, probably, by the polarization of electric double layers.

The illumination of such heterophase nanostructure with 60-W integrated light leads to the emergence of a photo e.m.f. of 0.1 V in the direction perpendicular to the nanointerlayers. The mechanism of this emergence of the photo e.m.f. is related to the absorption caused by the presence of impurities.

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