

## FORMATION FEATURES OF THE PIEZORESISTIVE EFFECT IN THE POLYMERS-SEMICONDUCTOR COMPOSITES

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Formation features of the piezoresistive effect in the polymer-semiconductor composites are investigated on the basis of analysis of relationships of their piezoresistive properties with electrophysical parameters of the semiconductive filler and the structure of the polymer matrix.

The simple model of the composite allowing an explanation of the change of the conduction of the polymer-semiconductor composite under a stress is suggested. It is regarded that a stress leads to the change of the probability of the charge tunneling through the barrier on the polymer-semiconductor phase boundary. The magnitude of the potential barrier is calculated on the basis of analysis of the steady-state current-time-voltage-temperature characteristics.

It is shown that piezoresistive properties are determined mainly by concentrations and traps depth of occurrence determining of the magnitude of the potential barrier on the phase boundary, and a charge transport features through thin polymer interlayers between semiconductor particles.

It was shown before that the formation of the potential barrier on the phase boundary causes the formation of the piezoresistive effect in two and multiphase composites [1,2]. Parameters of the potential barrier and consequently piezoresistive properties of composite components are a polymer and a semiconductor.

In this paper formation features of the piezoresistive effect in the polymer-semiconductor composites are investigated on the basis of analysis of relationship of piezoresistive properties with electrophysical parameters of the filler and a structure of a polymer matrix.

Powder polymers of high-density polyethylene (HDPE), polypropylene (PP) and polyvinylidene fluoride (PVDF) are used as a matrix of composites. Semiconductor materials of silicium (Si) and germanium (Ge) as a powder are used as a filler. The choice of this fillers is due to reason that their electrophysical characteristics (conductance, concentration, mobility of charge carries) might be regulated in a wide range. Composites are obtained by hot pressing method [1].

In Fig.1 (a,b) the dependences of  $\lg \rho$  on the pressure (P) for composites on the basis of HDPE (1), PP (2) and PVDF (3) with Si and Ge are quoted. It is seen that the resistivity of composites decreases with the increase of the pressure and the degree of the decrease of the resistivity depends on properties of a polymer and a filler. The pressure sensitivity largely depends on the filler content in composites (see Fig.2, a). A degree of a resistivity change along with the pressure can be determined with the ex-

pression of  $\lg \frac{\rho_0}{\rho}$ , where  $\rho_0$  and  $\rho$  - a resistivity of com-

posites at the normal pressure (it is taken as the zero) and the final pressure (in this case it is equal to 4 MPa). Can be assumed that with the increase of the filler content a conduction mechanism of composites is gradually changed: in the filler contents (to the maximum of the dependence of  $\lg(\rho_0/\rho) = f(C)$ ) the conduction mainly is determined by a tunnel transport of carries through a polymer interlayers between filler particles, and at

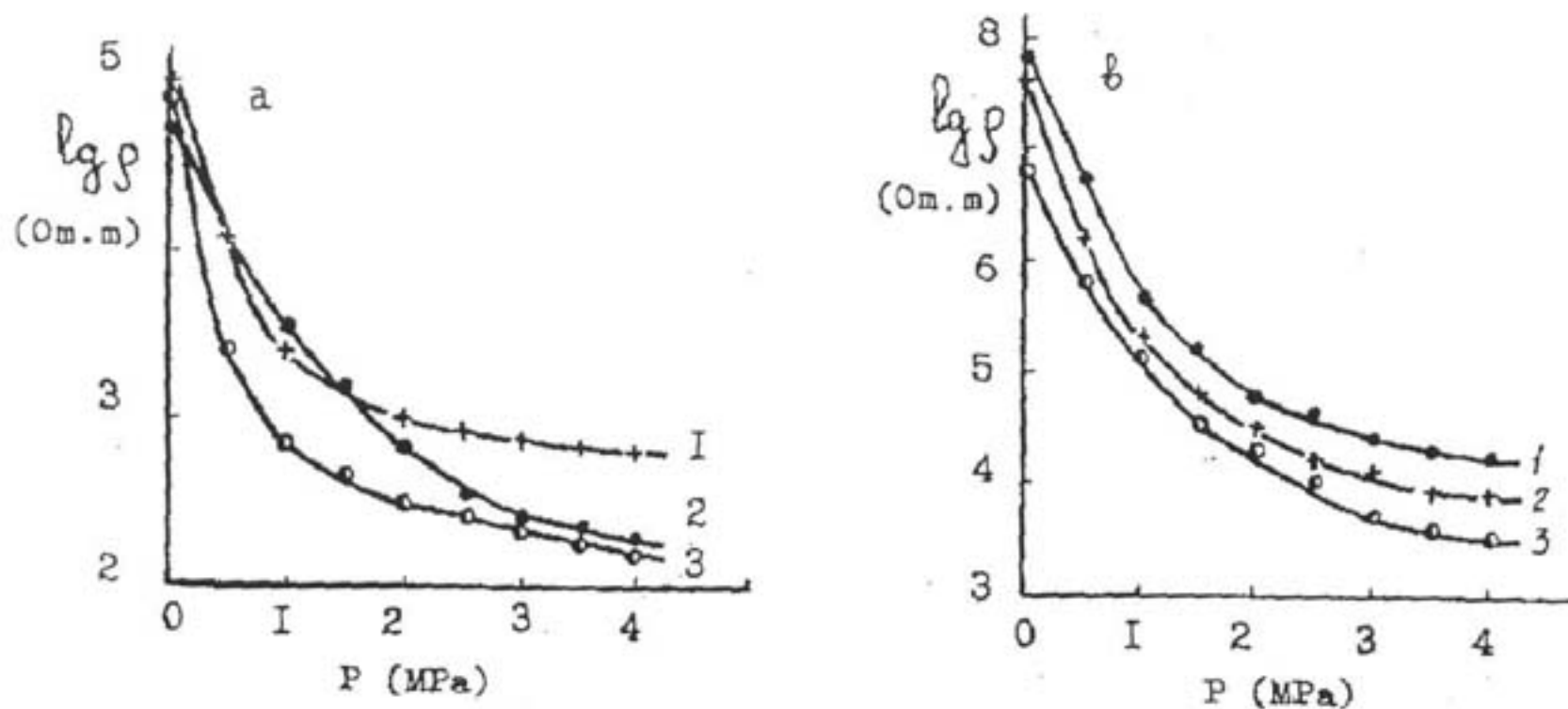


Fig. 1. Dependences of specific resistivity on pressure for composites: 1- HDPE+Si; 2 - PP+Si; 3 - PVDF+Si (a), 1- HDPE+Ge; 2 - PP+Ge; 3 - PVDF+Ge (b).  $C=50\%$  mass. Si and Ge are n-type semiconductors.

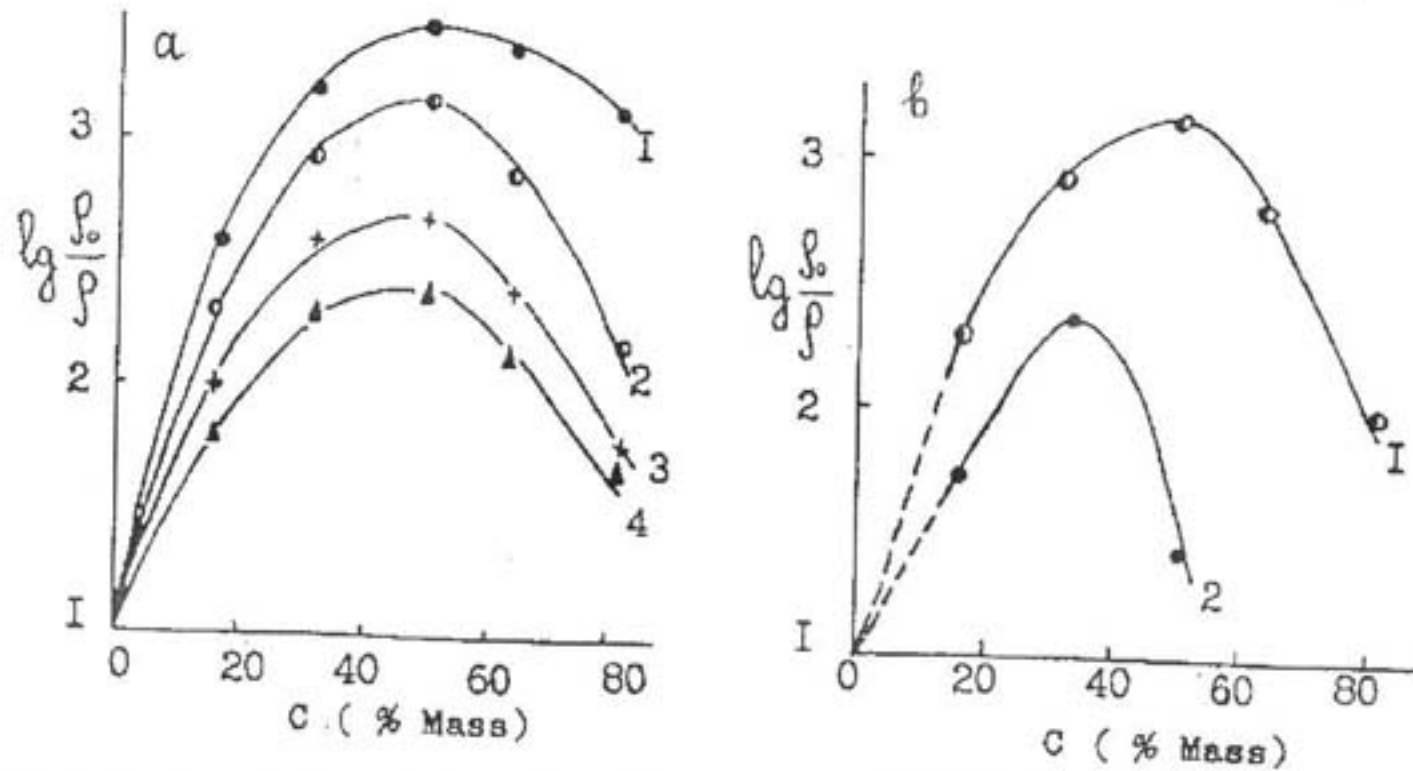


Fig. 2. a) Dependences of  $lg(\rho_0/\rho)$  on filler content ( $C$ ) for composites: 1 - PVDF+Si; 2 - HDPE+Si; 3 - PVDF+Ge; 4 - HDPE+Ge. b) Dependences of  $lg(\rho_0/\rho)$  on  $C$  for HDPE+Si composite. 1 and 2 - for rapidly and slowly cooled composites, accordingly.

high contents, the conduction mainly is due to the direct contacts between particles and a formation of conducting chains. Therefore,  $lg \frac{\rho_0}{\rho}$  of composites with the increase of the filler content at first rapidly increases up certain value of  $C$  and then starts to decrease.

While considering the mechanism conduction of piezoresistor composites we proceeded the possibility of charge carriers tunneling over the barrier on the polymer-semiconductor boundary [1,2]. Taking into consideration this a simple model of the composite allowing an explanation of a change of a conduction of the polymer-semiconductor composite by the action of a stress is shown on the Fig.3. During the contact of phases forming the composite, charge exchange occurs between them which causes to the establishment of a thermodynamical equilibrium on the phase boundary. In this case the Fermi level in both phases is equaled. We can assumed that charges move from the semiconductor (for example n-type Si) to a polymer phase and stabilize in various boundary traps. A positive charge is equal to magnitude of its is formed in a semiconductor phases. Positive and negative charges will distribute in corresponding phases in a certain band near the phase boundary depending on the charge concentration in the semiconductor particle and traps in a polymer matrix on the phase boundary. It is obvious that in this case the barrier height is equal to a difference in work function of a polymer between a semiconductor or an electron affinity of phases. The barrier width depends on the concentration and distribution of traps in a polymer on the phase boundary. Due to an abrupt distinct of the concentration and distribution of charges localization centers in phases the potential barrier will have an unsymmetrical form. Let's note that an indicated parameters of a barrier in a composite can be a bit different depending on a polymer interlayers thickness between semiconductor particles which in their turn depends on a diameter and a semiconductor filler volume

content. The polymer interlayers thickness between particles is decreased with the increase of the filler

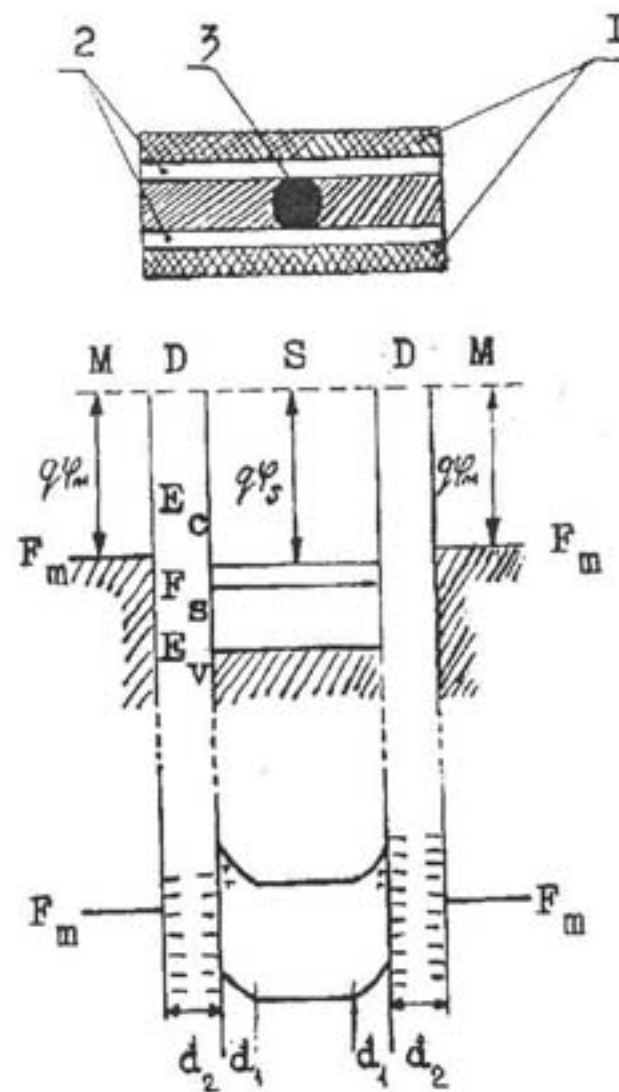


Fig. 3. Simple model of composite and energy band diagram of metal-polymer-semiconductor-polymer-metal. 1 - metal electrodes; 2 - polymer interlayers; 3 - semiconductor particle;  $\phi_m$  and  $\phi_s$  - work function of a metal and a semiconductor, accordingly;  $E_m$  and  $E_s$  - the Fermi level of metal and semiconductor;  $d_2$  - polymer interlayer thickness;  $d_1$  - depletion layer width in semiconductor particle.



content and therefore, a number of ionized (charged) traps is decreased due to the increase of the electrostatic (Coulomb) repulsion between two boundary layers of a polymer matrix (Fig.3) abutting on two neighbour particles or an electrode and a particle. Therefore the decrease of the composite conductivity with the increase of the content in particular is connected to the decrease of the depletion layer width and the potential barrier height on the phase boundary. From this point of view one may explain the piezoresistive effect in the polymer-semiconductor composite. The polymer interlayers thickness is decreased by the action of a stress and this leads to release of charge carriers from ionized traps on the polymer-particle boundary due to the increase of the electrostatic repulsion. If an energy of released charge carriers from traps of polymer interlayers will not be enough to raise to the conduction band then the jump mechanism of conduction is realized. In accordance with a space and energy distances between separate traps a deformation of polymer interlayers and an activation of charge carriers under a stress may lead to the charge tunneling from one trap to another.

The potential barrier on the polymer-semiconductor phase boundary is calculated. The volt-ampere characteristics were used for this and the steady-state current-time-voltage-temperature characteristics were analysed. It is found that for investigated composites the value of the potential barrier ( $\phi$ ) changes from 0,2 to 0,6 eV at various content of semiconductor fillers. After the determination of the potential barrier height one may determine the barrier width on the phase boundary. We specify for definiteness  $\phi=0,4$  eV. The value of  $\epsilon$  for composites on the base of polyolefins changes from 2 to 5 and for composites on the base of PVDF - from 12 to 13. The concentration of charge carriers ( $N$ ), which can be accepted as equal to the doping level ( $N_d$ ), approximately changes from  $10^{15}$  to  $10^{20}$  cm<sup>-3</sup> in conditions of our experiments. Suppose  $N=10^{20}$  cm<sup>-3</sup>. Let's imagine that the barrier potential of  $\phi=0,4$  eV exists between the phase boundary and a

point in the polymer matrix or in the semiconductor particle, where the field goes to zero. This means that there is the potential difference between these points of  $U=\phi/e$ , where  $e$  - is electronic charge. This condition is enough to determine as a first approximation of the barrier width on phase boundary by formula

$$W = \left( \frac{2\epsilon\epsilon_0 U}{eN} \right)^{1/2}$$

When  $\epsilon=12$ ,  $N=10^{20}$  cm<sup>-3</sup> and  $U=0,4$ V we get  $W \approx 3 \cdot 10^{-6}$  cm. It is seen that the barrier width on the phase boundary essentially depends on charge carriers concentration in the semiconductor particle. At a very low values of its the piezoresistive sensitivity will be low, since a charge tunneling occurs mainly by the applied field which is equivalent to decrease of a stress. At high values of  $W$  which is equal to low value of  $N$  a tunneling process is actually difficult and that's why the piezoresistive sensitivity also decreases.

Thus, the obtained experimental results allow to make a conclusion that the piezoresistive properties are determined mainly by a charge transport through thin polymer interlayers between semiconductor particles, electrochemical potential of phases, concentration and traps depth of occurrence on the phase boundary and interphase interactions in polymer-semiconductor contact areas.

A certain confirmation of this assumption is distinct change of the piezoresistive sensitivity  $\lg \frac{\rho_0}{\rho}$  of composites depending on their temperature-time obtaining conditions which influence on the supermolecular structure of the polymer phase (Fig.2, b) and therefore, on parameters and distributions of boundary traps.

[1] M.G. Shakhtakhtinsky, A.I. Mamedov, M.A. Kurbanov, A.A. Garagashov. Articles of AS of Azer. SSR, 1998, № 7, p.44-47.

[2] M.G. Shakhtakhtinsky, A.I. Mamedov, M.A. Kurbanov, A.A. Garagashov. Articles of AS of Azer. SSR, 1987, № 4, p.69-71.

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### POLİMER YARIMKEÇİRİCİ KOMPOZİTLƏRDƏ PİEZOREZİSTOR EFFEKTİNİN FORMALAŞMASININ XÜSUSİYYƏTLƏRİ

Polimer-yarımkeçirici kompozitlərdə piezorezistor effekti onların piezorezistiv xassələrinin yarımkeçiricinin elektrofiziki parametrləri və polimer matrisanın strukturu ilə qarşılıqlı əlaqələrinin analizi əsasında tədqiq edilmişdir.

Mexaniki gərginliyin təsiri altında kompozitlərin elektrik keçiriciliyinin dəyişməsinə izah etməyə imkan verən kompozitin sadə modeli təklif olunmuşdur. Hesab olunur ki, mexaniki gərginlik polimer-yarımkeçirici fazalar sərhəddindəki çəpərdən yüklərin tunnel etməsi ehtimalının dəyişməsinə gətirir. Cərəyan-zaman-gərginlik-temperatur xarakteristikalarının analizi əsasında potensial çəpərin qiyməti hesablanmışdır. Göstərilmişdir ki, piezorezistiv xassələr əsasən fazalar arası sərhəddə potensial çəpərin qiymətini təyin edən tələlərin konsentrasiyası və yerləşmə dərinliyi ilə və yarımkeçirici hissəcikləri arasında nazik polimer təbəqələrdən yüklərin daşınmasının xüsusiyyətləri ilə müəyyən olunur.

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### ОСОБЕННОСТИ ФОРМИРОВАНИЯ ПЬЕЗОРЕЗИСТОРНОГО ЭФФЕКТА В КОМПОЗИТАХ ПОЛИМЕР-ПОЛУПРОВОДНИК

В данной работе исследовались особенности формирования пьезорезисторного эффекта в композитах полимер-полупроводник на основе анализа взаимосвязи их пьезорезистивных свойств с электрофизическими параметрами полупроводникового наполнителя и структуры полимерной матрицы.

Предложена простая модель композита, позволяющая объяснить изменения проводимости композита под действием механического напряжения. Считается, что механическое напряжение приводит к изменению вероятности туннелирования

заряда через барьер на границе раздела фаз полимер-полупроводник. Рассчитана величина потенциального барьера на основе анализа характеристик равновесный ток-время-напряжение-температура.

Показано, что пьезорезистивные свойства, в основном определяется концентрацией и глубиной залегания ловушек, определяющих величину потенциального барьера на границе раздела фаз, и особенностями переноса зарядов через тонкие прослойки полимер между частицами полупроводника.

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