PHOTORESISTIVE EFFECT IN THE COMPOSITIES CONSISTING OF ORGANIC AND INORGANIC PHOTOSENSITIVE SEMICONDUCTORS

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The results on photoconductivity effect in the composites consisting of polymer matrix and photosensitive semiconductor phase are presented. The effect of R_d/R_{ph} parameters of photosensitive semiconductor phase on photoconductivity is studied. It is shown that, there is no direct contact between the composites' photoconductivity and the appropriate parameter of its photosensitive semiconductor phase.

1. Introduction

At present, the creation of the materials exhibiting photosensitivity property and allowing to convert energy of light to electricity are carried out in the following directions [1-10]: 1) creation of the new photosensitive materials on the base of available semiconductors [3-5]; 2) creation of the new organic photoelectric materials on the base of multifunctional polar polymers [1,3,4]; 3) creation of the composites based on organic matrices (polymers) and photosensitive semiconductor phases [2-6]; 4) fabrication of nanostructured composites consisting of photosensitive inorganic nanosized particles and various matrices (polymer, semiconductor, ceramics) [1,5,7,9]. Analysis of the recently achieved results show that, at present, there is an increased interest on study of photosensitive polymer composites as well as nanocomposites with various components (phases) and the heterogeneous structures. The main reason of such an increased interest is the existence of a number of semiconductors and polymers with various properties and further possibility of fabrication of new composites with photoelectric properties. In addition, simplicity of fabrication technology of photosensitive composites increases the importance of this topic. A lot of experimental results exhibit that the main parameters of the fabricated light-sensitive polymer matrix composites are greater than sum of the similar parameters of the separate components forming the composite which means that synergetic effect can be formed in such heterogeneous systems [1,5,6,15,16]. At same time, we need to note that observed effects in photocomposites, including synergetic effect, are directly related with electron-ion processes appeared inter hase bounds [11-14]. Therefore, interphase interaction in the polymer matrix photocomposites, both physical and chemical structures of each of the components of composites, surface activity, electrical properties and appropriate variation of the electrical change state within the interphase border have great advantage on the fabrication of the photoelectric materials with various functionality properties. Properties of any active composites are directly related to characteristics of their inorganic phases (ZnS, CdS). Therefore, in order to study any effect, including photoelectric effect in the composite materials, one need to start from selection of the inorganic phase in initial stage. At present paper, it is appropriate to use simple photosensitive semiconductors (Se, Te), $A^{II}B^{VI}$ and $A^{III}B^{V}$ compounds as active phase for study of photoresistive,

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photovoltaic and photoelectret effects [7-14]. Bandgap of these photosensitive materials increases similarly ZnS is the material that has highest bandgap value. Selection of photosensitive phase by such a way allows to change efficiently parameters of formed potential barrier between polymer and semiconductor in the composite material. Parameters of potential barrier formed as a result of electron exchange in the polymer-semiconductor border obtain highest value in the Se(Te)-polymer composites. Its main reason is that bandgap of Se is lower than bandgap of polymer. At same time, lowest interphase potential barrier will appear in the border of ZnS-polymer. This means, that ZnS is most efficient photoelectric composite for photoresistors.

The aim of current paper is fabrication of CdS and ZnS composite materials and determination of formation mechanism of their photoconductivity effect.
In order to achieve above mentioned aim, solution of the following problems are planned:

- the study of the photoresistivity effect in the CdS, ZnS and as well as composites with polar or nonpolar polymer phases;
- the study of C-V characteristics of polymer-ZnS composites;
- influence of electrophysics (ε, ρ_v) properties fluorine-containing polymers to the properties of the composites fabricated on their bases.

2. Research objects and methods

The following composites are selected as research objects:
- composites consisting of CdS, ZnS semiconductor phase (dispergator) - polar and non - polar polymers (matrix) with photoresistive properties;
- polar and non-polar polymers - Polyvinylidene fluoride (PVDF), F42, Polyvinylidene chloride (PVDC), High-density polyethylene (HDPE), Low-density polyethylene (LDPE).

3. Analysis and discussion of the experimental results

First, based on the photoelectric effect, let justify the selection of the second phase for described polymer matrix composites:

a) At first approximation, we assume that R_d/R_{ph} characteristics for photoresistive composites should be higher;

b) Photosensitive semiconductors with various I_d/I_{ph} characteristics should be used as second phase;

c) Photosensitive photoconductors with lower I_d/I_{ph} characteristics should be used as second phase;

d) A lot of semiconductors with various photoelectrical characteristics should be used as second phase.

It is necessary to note that selection of the polymer phase for photoconductive composites is also important stage. Due to that bandgap of the composite polymer is higher ($\geq 10eV$), the following factors determinate generation of its charge carriers:

- electron transfer from valence to conductive zone;
- electron transfer from local, by other words, from energy states of bandgap zone to conductive zone;
- electron transfer from valence zone to empty levels located in the quasi-bandgap zone;
- appearance of excitons and their participance in the electrical conductivity of the material after dissosiation or ionization.

As we already noted, in order to clarify formation mechanism of photoresistive effect in the composites, it is necessary to study effects, which formation mechanisms in polymer-semiconductor composites are close or complementary to each other. In our opinion, photovoltaic effect can be as an example for such an effect. In figures 1 and 2, we present C-V characteristics of PVDF-ZnS composite.
One need to clarify that the following parameters are optimized during study of the C-V characteristics of the composites:

- the volume rate of light-sensitive ZnS in composite (Φ,%);
- polarization time of composite (t_p,sec.);
- voltage applied during the polarization of the composite (U_p,V);
- the intensity of the light falling on the surface of the sample during the polarization (E_l, mVt/cm^2).

Parameters listed above are optimized based on analysis of a lot of experimental results[1,5,6,15,16]: Φ=(30 − 60)% vol.; t_p=(0,25 − 0,5) hours; U_p=(20 − 150)V; E_l=(200 − 400) mVt/cm^2. Here, experimental measurements of E_l and Φ parameters are very important. I_{ph}/I_d= f(E_l) dependence is presented under influence of light in order to obtain C-V characteristics and to select its intensity. In figure 3, the dependence of I_{ph}/I_d ratio of composites from E_l is presented. As one observes, at initial state the I_{ph}/I_d ratio increases sharply, then starting from $E_l \geq 400$ mVt/cm^2 it becomes stabile in dependence on the phase.
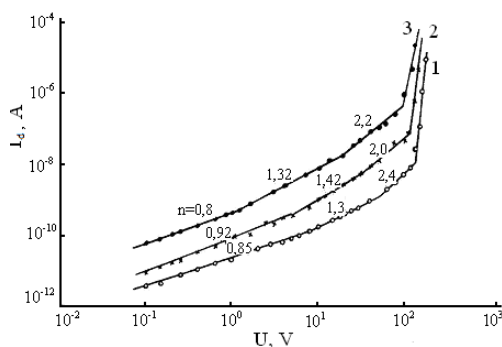

Fig. 1. C-V characteristics of PVDF – ZnS composite under the dark media.
1. PVDF - 20% volume ZnS; 2. PVDF - 40% volume ZnS; 3. PVDF - 60% volume ZnS.
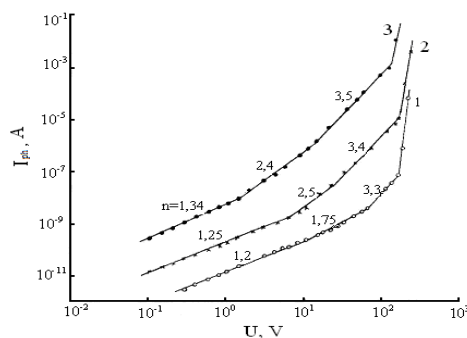

Fig. 2. C-V characteristics of PVDF – ZnS composite under the influence of light with
400 mVt/cm^2 intensity. 1. PVDF - 20% volume ZnS; 2. PVDF - 40% volume ZnS;
3. PVDF - 60% volume ZnS.

Therefore, value of E_l was taken being equal to 400mVt/cm^2 during study of photoconductivity effect in composites. I_{ph}/I_d=f(Φ) dependence was taken into account during selection of optimal volume ratio of photosensitive phases in composites (CdS, ZnS). Obtained results show that, optimal value of Φ changes in 30 − 60% volume range for photocomposites PVDF - ZnS. Similar experiments were pefromed also for PVDF-CdS [2]. Obtained results show that, optimal volume ratio of CdS in composite is 40 - 70%.
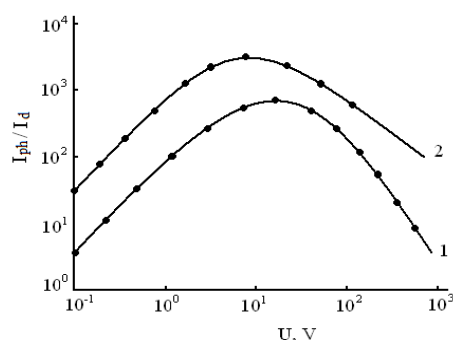
Fig. 3. $I_{ph}/I_d = f(U)$. 1. F42 – 50% volume CdS; 2. F42 – 50% volume ZnS; $E_l=400$ mVt/cm^2.

Creation of electrical charges, their transfer in the high heterogeneous structured polymer matrix and stabilization in the interphase border is main problem of the formation of photoresistive effect in the polymer-photosensitive semiconductor composites. Thereby, photoconductivity, C-V characteristics of polymer-$A^{II}B^{VI}$ composites are studied in dependence from photosensitive inorganic volume ratio and their initial photoelectric properties. As we noted already, in general, photoresistive composites consist of polar, non-polar polymers, photosensitive and exhibiting higher R_d/R_{ph} factor $A^{II}B^{VI}$ semiconductor materials. In table 1, R_d/R_{ph} ratio of $A^{II}B^{VI}$ semiconductors and composites with PVDF matrices fabricated on their bases is presented [3].

Table 1. Photoconductivity properties of photosensitive semiconductor materials and composites [3]

Semicon-ductors: $A^{II}B^{VI}$	R_d/R_{ph} (20 mVt/cm^2)	Crystallized composites under normal cooling conditions	R_d/R_{ph}	Crystallized composites under joint influence of electric gas discharge plasma and temperature	R_d/R_{ph}
CdS	10^2-10^5	PVDF – CdS[3]	10^2-10^4	PVDF – CdS[3]	10^3-10^5
CdSe	20	PVDF – CdSe	5-10	PVDF – CdSe	$0{,}5 \cdot 10^2$-10^2
CdTe	3-6	PVDF – CdTe	5-10	PVDF – CdTe	$(0{,}2$-$0{,}5)10^2$
GaSe	10^2-10^4	PVDF – GaSe	2-10	PVDF – GaSe	10^2-10^4
ZnS	$10^2 – 10^4$	PVDF – ZnS	$\sim10^4$	PVDF - ZnS	$10^3 – 10^5$

As one observes from table 1, semiconductors with higher photoconductivity can not preserve their sensitivity in the polymer phase. For example, if R_d/R_{ph} factor of CdSe is equal to 20 in initial state, then, the similar factor is $0{,}5 \cdot 10^2$ - 10^2 for PVDF-CdSe. R_d/R_{ph} factor of CdSe is equal to 3-6. At same time, this factor is 5-10 for PVDF-CdTe. If R_d/R_{ph} factor of GaSe is equal to 10^2 - 10^4, then, the similar factor is 2 – 10 for PVDF-GaSe. Obtained a lot of experimental results show that at given inorganic phase, R_d/R_{ph} parameter of the semiconductor is not proportional to the similar parameter of the composite obtained in its base.This interesting and complicated effect from the formation mechanism viewpoint requires performance of more detailed experimental analysis. Another factor, that one need take into account, arises from the results obtained for crystallized samples of the photoelectrical conductivity of the composites in case of their electrical qas discharge and under the joint influence of the temperature (Table 1). It is clear from this table that crystallization of the composites under the electrical gas discharge and the joint influence of the temperature shaprly influences to their R_d/R_{ph} parameter. At same time, one need to note that if composites consisting of inorganic photosensitive semiconductors and polymers are crystallized under the influence of the temperature, then, photoconductive characteristics of the composite materials don't differ sharply. It high lights important of polymer phase that is as important and complex as formation effect. In our work, we study photoelectric, photoresistive and photoelectret

effects in the ZnS phase composites with high bandgap ($\leq$ 3,6eV) in order to clarify the existence of the possible connection between the photoresistive and photoelectret effects in $A^{II}B^{VI}$ – polymer composites. Table 1 presents one result that has practical importance: ZnS phase composites are photoresistors with higher R_d/R_{ph} ratio. One can change expediently quasi-bandgap of the polymer phase (or make closer Fermi level to the conducting level) by the use of extrernal factors in order to clarify formation mechanism in composites.

Crystallization of the composite under the electrical gas discharge plasma is one of the external factors example. Crystallization process leads to the oxydation of the polymer chain [6,15,16]. It is known that any variation of the arbitrary dielectric structure follows to creation of the local levels and icrease of Fermi level in its quasi-bandgap [10]. Then, quasi-bandgap of the modified polymer under the electric gas discharge plasma influence becomes close to the similar parameter of inorganic phase CdS, ZnS and as a result it provides increase of the photoconductivity. One can clarify more mentioned above statement via the suggested by us models for composites. Study of the influence of the polymer phase to the phenomena in the semiconductor phase during the study of photoresistivity effect in composites (polymer-photosensitive semiconductor) will allows us to clarify mechanism of the photoresistivity effect. For this aim, first, let's to consider formation stages of the photoresistivity effect in the polymer-ZnS composites. Therefore, we consider electrical charge carriers transfer in the separately taken phases of the photocomposite under the influence of the light (Figure 4).

It is clear from this model that non-equilibrium electrical charge carriers created by light thanks to the internal photo effect are concentrated in the border of ZnS – polymer due to electrical field applied to the composite. Movements of the electrons in the semiconductor particles with microscopic size satisfy laws of quantum mechanics. One observes from the model that tunneling of electrical charge carriers concentrated in the border from the borders potential barrier should be transferred in the polymer phase unless they reach electrodes, i.e. charge conservation principle should be satisfied. Rapidity of the free electrons tunneled through the potential barrier depends on supra molecular structure, density and trap number of the polymer phase with specific electrical resistivity.
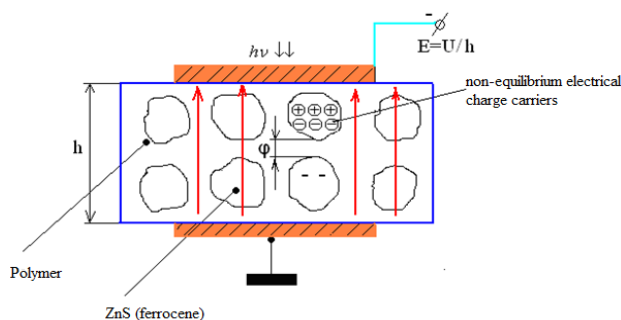

Fig. 4. Model of the electrical charge transfer in single phases of the photocomposite

Therefore, some of the electrical charge carriers tunneled through the potential barrier becomes stabile in the local levels and do not participate in the formation of the electrical current. This exhibits itself in the formation of the photoresistive, photovoltaic and photoelectret effects in the polymer-light sensitive composites in the various levels. For example, in the composites under study, existence of the local levels (with polymer phase) with high concentration and activation energy in the formation of the photovoltaic and photoelectret effect is mandatory. However, existence of such local levels for increase of the efficient (I_d/I_{ph}) of the composite photoresistors is not mandatory. Concentration of the local levels in the bandgap of the polymer phase from the interphase border depends at first from the bulk density of the semiconductor phase. The following effects play main role in case of increase of the bulk density of the semiconductor phase:

Thickness of the polymer layer between the photosensitive semiconductor particles decreases and probability of the electron transfer from particle to particle increases (percolation effect);

During increase of the specific capacity of the semiconductor phase, concentration of the structure defects increases in the polymer matrix, i.e. concentration of the local levels increases in the quasi-bandgap of the polymer. As a final result, electrophysical properties as well as efficient electrical conductivity of the composite will be changed. Efficient conductivity of the polymer-semiconductor composites is defined by conductivity of the semiconductor-polymer-semiconductor chain. During increase of the concentration of the semiconductor phase, number of such chains will be increased, too and width of the potential barrier will be decreased in the interphase border

$$\varphi = \frac{e^2 N_i d}{2\pi\varepsilon\varepsilon_0}$$

Here, e is charge of the electron, N is concentration of the local levels, d is the width of the excess layer in the border of polymer and semiconductor, ε is the permitivity of the transition layer, ε_o is the dielectric constant. The structure of the polymer matrix will be formed under the completein fluence of the surface of the semiconductor phase. At $\Phi=0,4-0,6$ values of the semiconducting phase, efficient electrical conductivity (σ_0) of the composite in fact will be equal to interparticle contact conductivity of the semiconductor, i.e. $\sigma\approx\sigma_k$ (σ_0 is efficient conductivity of the composite, σ_k is interparticle contact conductivity). It is necessary to note that, at present, computing methods of the efficient electrical conductivity of the models and polymers dispersed with the semiconductor particles, which would completely describe influence both of the composites efficient electrical conductivity and size of the particles of the inorganic phase (taking into account nanosizes) to the contact conductivity of the semiconductor-polymer-semiconductor system. Case of tunneling of the electrons through the interparticle polymer layer has been considered during determination of the contact electrical conductivity between the particles of the inorganic phase. For determination of the contact conductivity between two particles, one need to take into account electrostatic force effect in case of tunneling of the electrons through interparticles contact zone, i.e.

$$\sigma_k = 2e^2\sigma_f\sigma_p/\pi R\varepsilon\varepsilon_0\varphi_m$$

here, φ_m is the tunneling force of the electrons from semiconductor, e is the charge of the electrons, ε is relative permitivity of contacts, ε_0 is permitivity, R is the radius of the particle, σ_f is the electrical conductivity of the semiconducting particle and σ_p is the conductivity of the polymer layer. Taking into account mentioned above statements, let's consider possible mechanisms of the photoresistive and photovoltaic effects in the polymer-ZnS systems, based on the models of the composite photoresistors and photovoltaic elements.

4. Conclusions

Main reason of formation of photoresistive effect in the photosensitive composites consisting of poliolefin, fluorine contained polymer matrix and CdS, ZnS is transfer of electric charge carriers under the jointly applied electric field and interphase border potential as a result of internal photoeffect.

It is experimentally determined that there is no any proportionality between R_d/R_{ph} parameter and similar parameter of the composite formed on its base. It is shown that suitable change of photoresistor properties of the composites as a cusequence of the their crystallization under the influence of the electrical gas discharge is possible.

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