NEW TECHNOLOGIES OF MATRIX COMPOSITE POLYMER PHOTOVOLTAIC AND PHOTORESISTIVE MATERIALS

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ABSTRACT

The goal of the paper is development of more effective technology formation photovoltaic and photoresistive elements based on the polar and nonpolar polymers dispersed by CdS, ZnS, CdSe and CdTl particles. It was established that:

1. **The interphase interaction in photoelectric composites on the interphase boundary is considerably depended on particle size of inorganic phase;**
2. **Polymer matrix is not passive phase in photoelectric composites, but defines a value of $R_{dark\ resistance}/R_{light\ resistance}$ parameter and value of photo-emf;**
3. **3. Plasma crystallization of photoelectric composites is accompanied by formation of local levels with high concentration and activation energy in quasi-forbidden band of polymer matrix;**
4. **Doping of ferroelectric component with domain structure into photoelectric composite of polymer-CdS leads to increasing concentration of centers of local electric fields promoted division of photoinduced charges.**

Keywords: Photovoltaic elements , Photoresistive elements, Polymer composites, Heterogeneous structures

INTRODUCTION

Polymer composites with photosensitive semiconductor particles possess photoelectric, photovoltaic, electro- and photoluminescent, high physical-mechanical properties and combine characteristics phase of semiconductor (disperser) and polymer matrix (dispersion phase) [1-4]. So, for example, polymer-CdS and polymer-ZnS composites are investigated for formation photosensitive, photovoltaic and electro- and photoluminescent elements [4-8]. Existing inorganic semiconductor microparticles in polymer matrix lead to formation new phase on the polymer-semiconductor boundary [8-10] and principal new effects. So, composites of polymer-photosensitive semiconductor particle are investigated as optical, electrophotographic, photovoltaic and photoresistive materials with improved properties. But, on some properties the existing photosensitive composite materials are worse than semiconductor photosensitive elements. Due to wide range of variation of disperser particles concentration in composites of polymer - (CdS, ZnS) semiconductor particle there is a possibility purposeful change photoelectric properties and investigate related photoelectric effects caused by photon interaction with CdS and ZnS particles, and, also with macromolecules chain of polymer phase.

It is very interesting, in point of view of the theory of charge carriers transfer and generation effect in heterogeneous structures, there is an investigation of photoelectrets related effects in composites on the base of various polymers and light-sensitive semiconductors [1,2,3]. Besides, one of the ways of creation of new photoactive materials on the base of more simple technology, particularly large surface photovoltaic elements, is development of polymer-photoconductor type composites. It is necessary to note, that one of main demands for photovoltaic elements is high ration of output power to element weight. So, composite matrix photovoltaic elements have a much prospect.

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Carried out our primary experimental investigation show that composite based on the polar and nonpolar polymers and CdS, ZnS can be used as high effective photovoltaic materials [7]. It was demonstrated there is jump conductivity in composite photoresistors for defined range of compounds.

It was established that near of percolation threshold there is an effect of high photosensitive of polyolefin-CdS [11,12]. But physical and technological peculiarities of photoelectrets effect formation in composite of polymer-lighsensitive semiconductor is practically not been studied.

It is necessary to note that photoelectric effects have been studied intensively also in pure organic materials [5,11-13]. But the attractiveness of these materials as electrets and photovoltaic elements is reduced due to instability studied organic materials and difficulty of obtaining technology.

It is known that one of main factors of photovoltaic effect formation in materials is a division of charges initiated under a light action. For this it is necessary a presence of microfields in range of photocharges formation or near their. This process was strengthened by doping ferropiezoparticles with polydomain structure as third phase. Polydomain structure of ferropiezoparticles allows forming microfields in composite and, consequently, effective division of photocharges carriers.

The goal of given work is development of more effective technologies of formation of photovoltaic and photoresistive elements based on the polar and nonpolar polymers dispersed by CdS, ZnS, CdSe and CdTl particles.

EXPERIMENT

The investigations of photovoltaic and photoresistive effects in composites were conducted under atmospheric conditions at room temperature on automated set described in our previously works [7]. The light intensity varied in the range of (0,2-2,5) W/m^2. The intensity of external electric field varied in the range of (0,1-1,2)·10^4 V/m.

Composites based on the high density polyethylene (HDPE)-CdS, low density polyethylene (LDPE)-CdS and polyvinylidene fluoride (PVDF)-CdS are selected as studied object. The volume content (Φ) of CdS in composites varied in the range of (30-40)% vol. Beyond of this range the investigations are not interesting in point of view photovoltaic and photoresistive effects.

The volume content of third ferroelectric phase was chosen from 5% to 20%.

RESULTS AND DISCUSSION

Figure 1 shows the photo-emf ε_{ph} dependence for composites of HDPE-CdS and LDPE-CdS on CdS volume content. The size of CdS particles is 6 mkm, the thickness of sample is 10 mkm. It is seen that with increasing volume content of CdS phase the photo-emf increases and starting from Φ=25% vol. the dependence ε ( ) tends to saturation. The value of ε ( ) depends on the properties of polymer matrix. At other equal conditions composites of HDPE-CdS generate more photo-emf than PVDF-CdS composites.
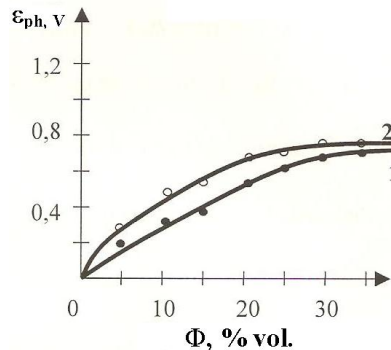

Figure 1. Photo-emf ε_{ph} dependence in composites of HDPE-CdS (1) and LDPE-CdS (2) on CdS volume content. The size of CdS particles is 6 mkm, the thickness of sample is 10 mkm.

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Figure 2 shows ε   dependence for composites of PVDF-CdS- PZT -5   (a) and HDPE-CdS-PZT-5   (b) on volume content of PZT-5   piezoceramic. It is seen that this dependence is appeared as a curve with the maximum. There is a maximum value of ε at volume content of 10% piezoceramic phase. Experiments have shown that the characteristics of photovoltaic cell for composites of polymer-photoconductor are more depended on size of photoconductor particles, thickness of photoelements and formation conditions.
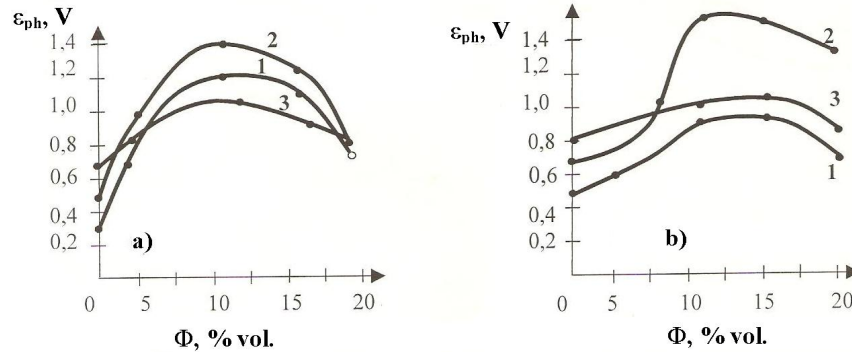

Figure 2. Photo-emf dependence for composites of PVDF+CdS+PZT-5 (**a**) and HDPE+CdS+PZT+5 (**b**) on volume content of PZT-5   piezoceramic. **1** - 10% vol. CdS; **2** - 20% vol. CdS; **3** - 30% vol. CdS.

Figure 3 shows dependence photo-emf value of studied composites on sizes of photoconductor particles. It is seen that the photo-emf of photoconductor noticeable increases when the sizes of photoconductor particles decreases. Apparently, this is conditioned by growth of integral boundary of polymer matrix with photoconductor particles.

The influence of domain structure of third phase of ferropiezoceramic material has much importance on value of composite photo-emf. Except PZT-5A (rhombohedral structure) as piezoceramic we have used PZT (tetragonal structure) too.
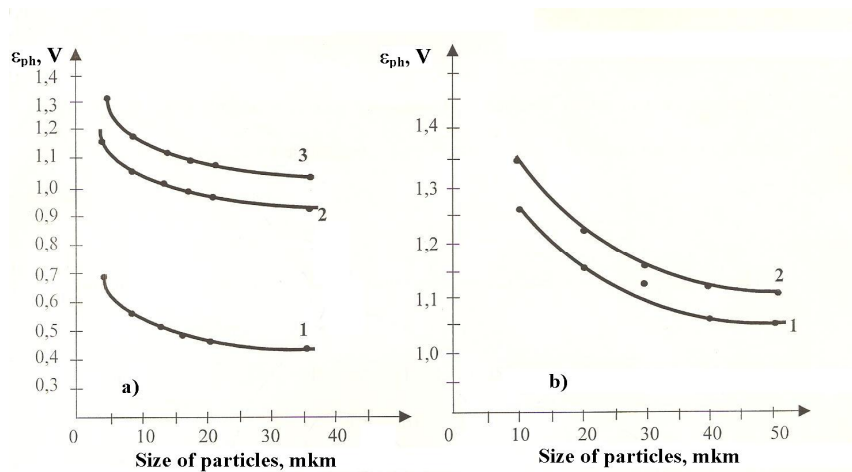

Figure 3 **a**) Photo-emf dependence for composites on sizes of CdS particles. **1**- PVDF+CdS (80:20); **2**- PVDF+CdS +PZT (70:20:10) **3**. PVDF+CdS +PZT-5A (70:20:10).
   b) Photo-emf dependence for composites on thickness of sample. 1- PVDF+CdS + PZT (70:20:10); **2**- PVDF+CdS +PZT-5A (70:20:10). There are volume ratios of composite components in brackets.

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It is known that PZT-5A piezoceramic has domains with sizes more than PZT [12]. On the other hand the less domain sizes the more probability of formation of local electric fields. And in turn, it leads to that the probability of photocharges division in polymer- PZT +CdS composites is more (Table 1).

Table 1. The values of photo-emf of CdS:PZT:PVDF composite for various volume content of components

CdS: PZT: PVDF	ε_ϕ, mV	CdS: PZT: PVDF	ε_ϕ, mV
5:0:95	200	20:0:80	510
5:5:90	235	20:5:75	1150
5:10:85	300	20:10:70	1300
5:15:80	280	20:15:65	1070
5:20:75	230	20:20:60	620
10:0:90	300	25:0:75	600
10:5:85	720	25:5:70	1000
10:10:80	1100	25:10:65	1150
10:15:75	1050	25:15:60	1200
10:20:70	600	25:20:55	600
15:0:85	400	30:0:70	700
15:5:80	820	30:3:65	790
15:10:75	1300	30:10:60	880
15:15:70	1050	30:15:55	880
15:20:65	660	30:20:50	650

So, the piezoceramic doping into polymer-CdS photocomposite leads to noticeable increasing of photo-emf. Photovoltaic effect in composites can be explained by increasing of concentration and charge carriers lifetime under the light action. Photoeffect, photoelectrons formation and division mechanism in composite structures of polymer-photosentive semiconductor filler is unknown while.

Four mechanisms of photovoltaic effect formation in composite are proposed.

- *First*, photoeffect is formed by volume excitation of electrons from valent zone of conductor into conduction zone of dielectric (polymer matrix) when overcomes potential barrier of trapeziform form on the division boundary of polymer-photoconductor.
- *Second*, photoeffect is formed by charge release from boundary relatively deep traps and umklapp process in conduction zone of polymer.
- *Third*, photoeffect is formed by charge release from boundary deep traps and umklapp process on high concentration shallow levels in quasi-forbidden zone of polymer.
- *Fourth*, photoeffect is formed by excitation of electrons from valent zone of conductor and transfer on high concentration shallow levels in quasi-forbidden zone of polymer.

There is traps ionization before illumination as result charges exchange between phases owing to difference of work function of electrons from semiconductor and polymer. For benefit of third and fourth assumptions there are experimental results obtained for spectral dependence of photocurrent on volume content of semiconductor filler in composite (Figure 4).

We can conclude from Figure 4: 1) the maximums of spectral sensitivity of CdS and composite based on it don¢t coincide; 2) the maximums of spectral sensitivity of composites shift in range of large λ, that is low energy of light quantums, when volume content of CdS increases. It is possible to explain the role of shallow traps in photovoltaic effect formation in composites if we base on fundamental conception of physics of semiconductors and dielectric, that is all changes of physical and chemical structures are accompanied formation and growth of traps concentration in quasi-forbidden zone. The maximums shift of relative spectral sensitivity of CdS and PVDF-CdS composite

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with various volume content CdS, on our opinion, enough testify about the role of shallow traps in process division and transfer of charges and, consequently, in formation of photovoltaic effect in composites. For the benefit of this assumption there are experimental results obtained for composites components of which modified in conditions of plasma electric discharge action in electronegative gases (air medium).
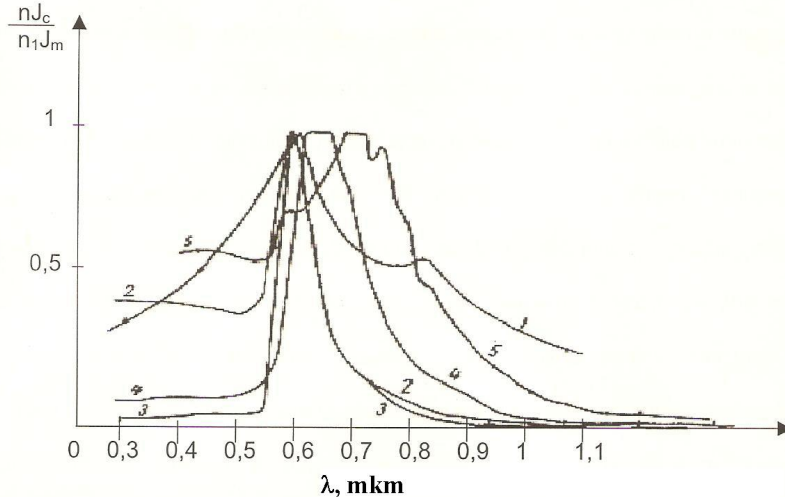

Figure 4 Relative spectral sensitive of CdS and PVDF+CdS composite. **1**- CdS; 2- PVDF +20% vol. CdS; **3**- PVDF +40% vol. CdS; **4**- PVDF +60% vol. CdS; **5**- PVDF +80% vol. CdS.

Electrodischarge crystallization was carried out on next way. After short time pressing of composite at melting temperature upper die was separated from sample surface and connected with special discharge cell. This cell allows initiating various intensity electric discharges in air. Discharges formed in air with thickness of 1 mm between glass barrier and sample of composite. The cell was under electric voltage of 10 kV with frequency of 50 Hz. At this, composite is crystallized under simultaneous application of temperature, electric discharge and discharge radiation beginning with melting temperature.

Composites have obtained by method of hot pressing and variation of temperature-time and temperature-pressure regimes of crystallization at simultaneous action of electric discharge plasma. Changing of crystallization temperature was stepwise carrying out at the beginning stage of cooling and then with rate 0,25-2 K/min till room temperature. Structure changing was controlling by method of IR spectroscopy of polymer phase of composite at small volume content of semiconductor phase.

Figure 5 shows optic density changing of anew formed (- - ; = ,) strips in IR spectrum of polymer matrix of PVDF+5% vol. CdS composite. Obtained results demonstrate that even during short time of plasma crystallization the structure of polymer matrix is subjected intensity changing, that is, there is an increasing heterogeneity of polymer phase structure.

Really, the generation of (- - ; = ,) groups in IR spectrums indicates about changing of chemical structures of macromolecules (heterogeneous), strengthening of intermolecular interactions owing to much polarity of these groups and formation - - bridges between molecules. Undoubtedly, as it was shown above these chemical changes are accompanied by changing of crystallization conditions and, consequently, of physical structure of polymer phase of composite: the interface interaction on boundary of polymer-semiconductor changes, the density of local levels in forbidden zone of polymer increases, the parameters of potential barrier on interphase boundary and energy distribution of traps change.

As it was noted above, photovoltaic, photoresistive and photoelectrets effects are related. The investigation of formation mechanism of one of these effects promotes understanding of formation nature of other effects.
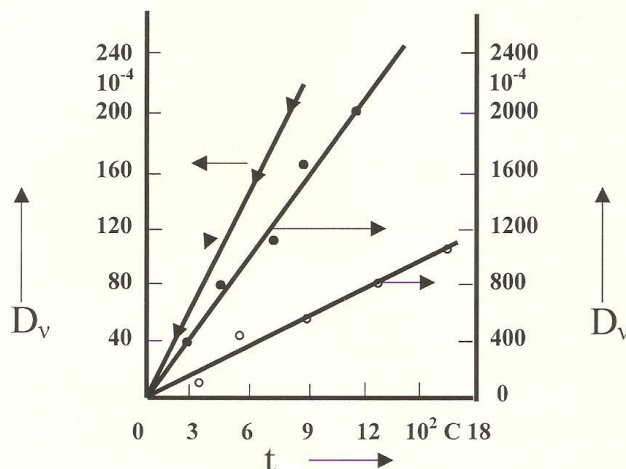
Figure 5 Change of optical density of D_v strips appeared in IR spectrums of polymer phase of PVDF+5% vol. CdS composite at electrothermodischarge crystallization. The rate of cooling is $V_{cool.}=2^0C/min$; the voltage applied to testing cell is U=16 kV; the breakdown voltage in gas phase in cell is $U_{bv}=11,8$ V; energy of microdischarges is $\Delta W=1,4 \cdot 10^{-6}$ J; **1** - $\nu = 3380($ $)sm^{-1}$; **2** - $\nu = 1735$ (= $)sm^{-1}$; **3** - $\nu = 1280$ (- - $)sm^{-1}$.

There are photoconductivities of composites obtained on the base of PVDF and various photosensitive CdS, CdSe, CdTe, GaSe semiconductors (doped by rare earth elements) in Table 2.

Table 2. Photoconductivity of composites on the base of PVDF and various photosensitive CdS, CdSe, CdTe, GaSe semiconductors

Semiconductors	R_d/R_l	Composites crystallized by cooling	R_d/R_l	Composites crystallized by cooling at simultaneous discharge action	R_d/R_l
CdS	10^2-10^3	PVDF -CdS	10^2-10^4	PVDF -CdS	10^3-10^5
CdSe	20	PVDF -CdSe	5	PVDF -CdSe	$(0,5-2)10^2$
CdTe	3-6	PVDF -CdTe	5	PVDF -CdTe	$(0,2-0.5)10^2$
GaSe	10^2-10^3	PVDF -GaSe	2-5	PVDF -GaSe	10^2-10^4

Obtained results are concerned to 2 types of crystallization regimes. It is observed, that photosensitivity defined as R_d/R_l ($R_{dark\ resistance}/R_{light\ resistance}$) are noticeable differenced. The composites crystallized under simultaneous action of electric discharge plasma and temperature have high R_d/R_l.

There is more interesting result of absence of direct dependence between photosensitivity of composites and analogous parameters of semiconductor phase. For example, photosensitivities of CdS and GaSe are changed in range of 10^2-10^5. But, composites based on their have noticeable different relations of R_d/R_l. In the first approximation, we can say that the cause of these effects there is differences of interface interactions on interphase boundary, shapes and parameters of potential barrier and consequently, density of local levels in quasiforbidden zone of polymer phase. All of these reasons are directly connected with disorder of composite structure.

All this indicate that polymer matrix is not passive phase in photoelectric composites. For benefit of this assumption there is increasing photosensitivity of composites crystallized under the action of plasma of electric discharge (Table 2). Crystallizing under the action of plasma of electric

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discharge polymer phase has high concentration and activation energy of local levels in quasiforbidden zone in comparison with polymer phase under the action only temperature.

CONCLUSION

So, in result of investigations we can make next conclusions:

1. The interphase interaction in photoelectric composites on the interphase boundary is considerably depended on particle size of inorganic phase;
2. Polymer matrix is not passive phase in photoelectric composites, but defines a value of R_d/R_l parameter and value of photo-emf;
3. Plasma crystallization of photoelectric composites is accompanied by formation of local levels with high concentration and activation energy in quasi-forbidden band of polymer matrix;
4. Doping of ferroelectric component with domain structure into photoelectric composite of polymer-CdS leads to increasing concentration of centers of local electric fields promoted division of photoinduced charges.

REFERENCES

1. I.N.Orudjev, . . urbanov, . . rimov, . . medov ,Photosensiyivity composites based on the PVDF+CdS. *Fizika,* 1999, v.5, 3, pp.60-63.
2. M.K.Kerimov, M.A.Kurbanov, A.A.Bayramov, A.I.Mamedov ,Matrix Active Micro- and Nanocomposites Based on the Polymer, Semiconductive and Ferropiezoceramic Materials. *Nanocomposites and Polymers with Analytical Methods* / Book 3. Book edited by: John Cuppoletti, 2011, INTECH Open Access Publisher. pp.375-404
3. . . rimov, Molecular mechanisms of electrostimulated processes in polymers. *ScDr Thesis*, Baku, Physics Institute, 1987.
4. .V.Vannikov, .D.Grishina ,Photochemistry of polymer donor-acceptor complexes. , *Nauka*, 1984.
5. Ludwik Badian, Investigation of effects caused with space charge in dielectrics. *J. Electrostatics,* 8(1975), pp.1-11
6. Arghya Narayan Banerjee, The design, Fabrication and photocatalytic utility of nanostructed semiconductors: focus on TiO_2-based nanostructures. *Nanotechnology, Science and Application.* 2011, 4, 35-65.
7. N.Minanin, K.Sasaci, K.Tsido, Improvement of the performance of particulate phthalacyamina photovoltaic cells by the use of polar polymer. *J.Appl. Physics* 34, 1983, 11, 6764-6766.
8. Navneet, P.K.C. Pillai, A study of the photoconducting properties of HgS/Cd(S,Se):Cu mixed pigment-resin system. *J. Electrostatics* 1984, 1, 21-31/
9. M.Ieda ,Electrical conduction and carrier traps in polymer materials. *IEEE Trans. Elect. Insulat.* 1988.
10. J.Mort, D.M. Pai ,Photoconductivity and related phenomena. *Amsterdam: Elsevier*, 1976, 502p.
11. A.Shik, H.Ruda, E.H.Sargent, Photoelectric phenomena in polymer-based composites. J. *Appl.Physics*, 2000 v.88 6 p.115-118.
12. K.Yoshimo, J.Kyokane, T.Nishitani, Y.Jnuishi ,Electron-induced Conduction in Polyethylene. *J. Appl. Phys*. 1978, v.49, 9, 4849-4853.
13. V.S. ilnicov, Photoconductivity of polymers. *L., Chemistry*, 1990, p.240.