INVESTIGATION OF PHOTO-GENERATION PROCESSES IN SEMICONDUCTIVE POLYMERS

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In article the perspective of researches semi-conductor polymers for creation of photo-electric converters is considered. The processes of photo-generation of charge carriers in a molecular solid state are investigated. The role of the weak intermolecular interaction causing process of photo-generation of charge carriers through a status of the coulomb connected pair is shown. The first results of semi-conductor polymers-silicon systems investigations were reported. Such as of polymer composite materials we have used oligohydroguinone, oligo-α-naphthol, oligo-β-naphthol, oligo-amino-phenylen. Current-voltage characteristics of these polymer-silicon heterojunctions were investigated. The structural regularities of change of the photoeffect quantum efficiency in semiconductive polymers and their molecular complexes are investigated.

1. Introduction

Photo-electric converters on the basis of solid-state semi-conductor elements (Si, CdTe, etc.) have received a wide spreading all over the world. However the basic lack of these converters - high cost of received electric energy. Therefore, recently scientists began to study in more detail applied aspects of perspective semi-conductor polymers with the purpose of reception of cheap energy [1,2,3].

Photosensitive polymeric semiconductors due to combination protosemiconductive properties with thermostability, mechanical and other specific properties of polymers became irreplaceable at creation photovoltaic elements for converters of a solar energy. Scopes of photosensitive polymers are caused by features of intermolecular interaction and an opportunity of formation in them donor-acceptor (DA) complexes with of charge transfer (CCT). Ability to complexing and effective transfer of a charge in molecules of complexes results in their polarizability under action of light and, hence, photopolarization of medium, and also caused by it photovoltaic and to nonlinear-optical properties.

The developed principles of achievement of high quantum efficiency η of photophysical processes, in particular photo-generation of the charge carriers and creation on their basis high-resolution molecular medium with high photosensitivity $S \propto \alpha \cdot \eta$ (α is a factor of absorption) in visible spectrum can be used at a choice and synthesis of materials with components CCT for converters of a solar energy. Development of photosensitive polymers is carried out in two directions: synthesis of polymers with the polyconnected system and creation of systems on the basis of formation in polymers of complexes with charge transfer. The last can be formed as in polymers monomeric part of which are a complex, and at of introduction in polymer of low-molecular substances (for example, dye). They interact with polymer and results as in increase in value of its photosensitivity, and to expansion of spectral region of absorption and sensitivity.

2. Mechanisms of photo-generation of charge carriers

Let's consider features of molecular medium and photophysical processes in them. Molecular medium (both organic crystals, and polymers and a films, containing molecules of CCT) are solid-state systems which are formed due to intermolecular interaction. Intermolecular structure of the covalently connected atoms in a molecule (crystal) or structure CCT, formed due to DA interactions (in solid solutions of polymeric complexes), practically do not change at formation of a solid. Depending on electronic structure of a molecule and the parameters connected to it (polarizability, the dipole moments, DA properties) energy of intermolecular interaction can change over a wide range - from 10^{-3} eV (for Van der Waals interactions) up to units eV (in a case DA connections) [4].

Now we shall consider features of the mechanism of photo-generation of charge carriers. Weak intermolecular interaction in a solid results in strongly defined localization of charge carriers on separate molecules (time of localization $\tau_{loc}=10^{-12}\div10^{-14}$ s) [4]. It causes electronic polarization of a lattice by the charge carrier (time of polarization $\tau_{pol}=10^{-15}\div10^{-16}$ s), time of the carrier transfer between the adjacent located states (time of carrier hop $\tau_{hop}=10^{-12}$ s). In result

$$\tau_{hop} > \tau_{loc} > \tau_{pol}$$

and the carriers transfer is described of not coherent jumps between the located states.

The following formula describing the rate of transitions between two jumps centers with distance of r_{ij} and a difference of connection energy of electron of $\Delta_{ij}E$ [5] is put in a basis of phenomenological model of jump mobility:

$$\Gamma_{ij}=\Gamma_0\exp[-2\gamma r_{ij}-(\Delta_{ij}E/kT)\Theta(\Delta_{ij}E)]$$

Here: γ is a constant of attenuation of wave function of located electron which is accepted as spherically symmetric; $\Theta(x)$ is a unit stepped function). If the spatial arrangement the jump centers and the type of distribution of connection energy are set then we have a problem about casual wanderings of electron on a spatial lattice of the low-energy centers. This problem is known in the literature as a problem *r-E*-lattice percolation.

A stage of transfer, and also processes of photons absorption by molecules of complexes usually describe by concept of a state with of a charge transfer (CT–charge

transfer states) - excitations of neutral states of complexes in which (as opposed to excitons where electron and hole are located on one molecule with distance between them independent of time) excited electron passes to the molecule nearest or following it, but remains coulomb connected with the hole. Energy E^{i}_{CT} and E_{CP} (CP-charge pair) of these ionic states are below of conductivity zone. At absorption of a photon by a molecule of a solid occurs or autoionization (Franck-Condon transition from the basic state in one of excited), or direct excitation of CT- states therefore the status of the coulomb connected pair (a so-called CP-state) and then there can be free charge carriers are formed.

3. Mathematical models of photo-generation of charges carriers

Photo-generation of charge carriers in medium with weak intermolecular interaction occurs through a state of the coulomb connected pair carriers of an opposite sign. Process of charge separation of such pair in external electric field ε includes two stages: a stage thermalization of a charge carrier connected in a pair and a stage of thermal-field dissociation of the connected pair charges. On the first stage connected electron loses the excess of kinetic energy, coming in balance with phonons on some distance between the charges, called of radius carrier thermalization r_t. This stage is characterized by a quantum efficiency of connected pairs formation η_0. On the stage of thermal-field dissociation the thermalized connected pairs are separated owing to interaction with phonons. фононами, This stage is described by probability of dissociation $f_d(r,d,E_f)$. From here

$$\eta = \eta_0 f_d(r,\theta,E_f) g(r,\theta) dr^3 , \qquad (1)$$

Here: $g(r,\theta)$ is a function of pairs on value of radiuses r and their orientations relative to a direction of field E_f, θ is a corner between vectors r and E. At $r < 10^{-8}$ m $g(r,\theta)=\delta(r - r_t)$ and expression (1) passes in $\eta = \eta_0 f_d(r_t,E_f)$.

In a stationary state of isotropic system of the noninteracting pairs which are in balance with medium with constant dielectric permeability ε and at constant temperature T, the probability of dissociation of the pairs charges $f_d(r_t,E_f)$ is defined by three-dimensional Onsager model [6]:

$$f_d = \left(1 - \frac{kT}{eE_f r_t}\right) \sum_j \frac{eE_f r_c}{kT} I_c\left(\frac{e^2}{\varepsilon r_t kT}\right),$$

Here: e is the electron charge;

$$I_j(x) = I_{j-1}(x) - \frac{x_j}{j! e^x}, j > 1 \quad I_0(x) = 1 - e^{-x} .$$

This Onsager model most correctly reflects physics of process for thermalized pairs.

Thus, the features of molecular mediums are connected to weak intermolecular interaction in them, resulting, first, to molecular character of light absorption and the photo-generation of charge carriers following it through a state a coulomb connected pair; second, to localization of charge carriers on separate charges and their low mobility (in comparison with semiconductors, where $\mu \approx 1 \text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$). Weak intermolecular interaction and strong localization of charge carriers on separate molecules in a solid cause process of photo-generation of charge carriers through a state of the coulomb connected pair, formed as a result of molecular absorption of a photon with possible direct excitation of CT-states.

4. Physical models of photo-generation of charges carriers

Physical models of photo-generation differ with the processes resulting to separate of pairs on distance r_t. In various jump models [7,8] such process is a jump of the carrier from the excited molecule of a complex on the next intermediate state. In dissociation-jump models [9] these are jumps on the located states with dissociation on model of the Pool - Frenkel [10].

In molecular crystals (homomolecular mediums) 3 models was development: “optical transitions” [11], "ballistic" [12] and "eximer" [13]. For polyvinyl-carbazole PVC it is shown, that in the region of singlet absorption band the quantum efficiency η grows in discrete steps with growth of radiation energy $\hbar\omega$ so, that in each strip η and r_t are constant. For crystals of polyacen, in near-threshold region of absorption with growth of number of aromatic rings η grows from 10^{-3} up to 5.

Process of photo-generation in molecular crystals progresses through the CT-states formed at absorption of a photon owing to excess oscillatory energy ~ (0,3 ÷ 0,4) eV. This energy is lost on interaction with lattice photons for 80-100 collisions on dependent on a voltage of field $\mathcal{E}$ on distance of $r_t(T) = (6 \div 10) \cdot 10^{-9}$ m [4]. In result the state of the connected pair formed with radius r_t (a so-called CP-state), absorbed additional energy from medium can form free charges carriers. In considered model η and r_t depend on energy of a photon [4]. At large energy a process of autoionization can be occurring.

For molecular mediums on basis of DA complexes besides jump [4] and dissociation-jump [8] models can be selected exciplex [14] at structurally-chemical sensitizing of photoeffect and ion - radical [15] at a spectral sensitization by dyes.

In accordance with exciplex model, photo-generation occurs in process thermal-field dissociation of nonrelaxed state of exciplex Cz^{+}-$(D^{+}A^{-})$**, formed at absorption the photon by a molecule of the donor (carbazole fragment of PVC Cz) [16] or a acceptor molecule (intermolecular CCT) and the subsequent electron thermalization [14]. In the given model radius $r_t = (2 \div 3) \cdot 10^{-9}$ m cannot depend from $\mathcal{E}$ and $\hbar\omega$ in a absorption band as a result of the fast intermolecular relaxation absorbed a photon of a molecule.

At a spectral sensitization of a photoeffect the process of photo-generation is carried out from a state of the connected ion - radical pair ^{1,3} [IPR], arising of exciplex state of the absorbed a photon molecule dye* and carbazole groups of polymer Cz. Primarily formed from of a state (dye-Cz)* the state ^{1,3}[IPR] dissociates on free carriers, and arising in result singlet-triplet conversion with a constant k_{st}, dependent on intensity of a magnetic field [14] state ^{1,3}[IPR] gives neutral products [16,17]:

$$\text{dye}^* + \text{Cz} \overset{\hbar\omega}{\leftrightarrow} (\text{dye-Cz})^* \leftrightarrow {}^{1,3}[\text{IPR}] \overset{kst}{\leftrightarrow} {}^{3,1}[\text{IPR}] \downarrow \eta \quad \text{h} + \text{e}$$

The listed physical models of photo-generation in molecular mediums on basis CCT do not give the dependences connecting value and spectrum η with structure of molecules CCT. For the molecular mediums containing CCT, it was possible to connect parameters of the photophysical processes proceeding after a photon absorption by a molecule, with parameters of chemical structure of molecules of complexes.

For molecular crystals the correlation of η with energy gap width has been found. As opposed to this, the class of mediums on basis CCT is more extensive and in him there is an opportunity to choose series of naturally changeable structures of complexes.

As transport of the photogenerated charge carriers in such mediums is carried out as a result of noncoherent jumps between the located states, the establishment of connection of photo-generation parameters and structure demands methods of measurement η, allowing to take into account or exclude influence of a stage of transport on measured values.

5. Experiment and first results

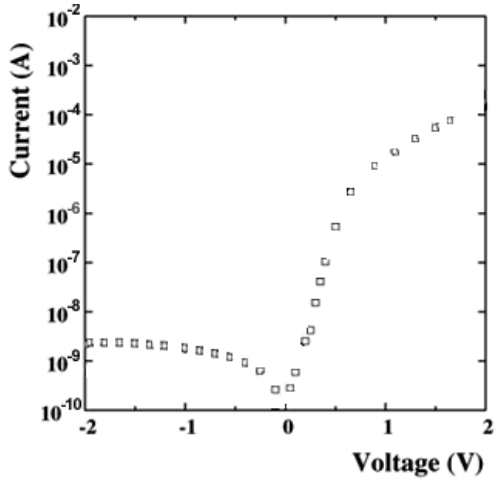

Fig.1. The current-voltage characteristic of the heterojunction silicon-polymer diode.

We have carried out experiments on formation and investigation of semiconductive composite polymers and of silicon-polymer structures. Such as of polymer composite materials we have used oligohydroguinone, oligo-α-naphthol, oligo-β-naphthol, oligo-amino-phenylen. Polymer-silicon heterojunctions were made by electrochemically deposited method. A 40 nm layer of polyaniline was deposited onto a n-type silicon (100) substrate of resistivity of 1 Ω·cm.

Current-voltage characteristics of these devices were investigated. The size of sensors was 10x10 mm and thickness was 300 microns. The devices present good electrical characteristics, with apparent barrier high of 0,59 V, reverse bias current of 5 nA and rectifying ratio of ~50 at ± 1,0 V. The current voltage characteristic of the heterojunction silicon-polymer diode is shown in fig.1.

6. Conclusion

The established structural regularities of change of quantum efficiency of a photoeffect in polymeric semiconductors and their molecular complexes have shown that existing classes of photosensitive materials now differ with character of interaction in mediums:

- ionic and covalent (energy of interaction E> 1eV) - in molecules of dyes and polymers;
- donor-acceptor (E = 0,05 ÷ 1 eV) - at formation by polymers of molecular complexes with low-molecular additives;
- hydrogen (E = 0,04 ÷ 0,2 eV) - at formation supra-molecular structures.

These regularities have defined requirements to structures of molecules of complexes with high quantum efficiency of photoprocesses: donor fragments or molecules should have low potentials of ionization (<7,4 eV), and acceptor one should have high energy of electron affinity (more than 1,0 eV). The following still requirements are necessary for achievement of higher quantum efficiency of photo-generation:

1) The molecule of the donor with the specified potentials of ionization of aromatic fragments (or an acceptor with the specified electron affinity) should be polymeric with number of fragments not less than 5, and periodically located with distance between them $0{,}7\cdot10^{-9}$ m < l < $1{,}5\cdot10^{-9}$ m;

2) Molecules of the donor and an acceptor, a forming molecular complex, should form polymer with the size of the monomeric link limited in thermalization radius $(1{,}5\div3{,}5)\cdot10^{-9}$ m.

The formulated requirements allow to predict limiting quantum efficiency of photoprocesses and to choose photosensitive components of molecular complexes.

Current-voltage characteristics of semiconductive composite polymers and of silicon-polymer structures were investigated.

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YARIMKEÇİRİCİ POLİMERLƏRDƏ FOTOGENERASİYA PROSESİNİN TƏDQİQİ

Məqalədə fotoelektrik çeviricilərin yaradılması üçün yarımkeçirici polimerlərin tədqiqatı perspektivliyinə baxılır. Molekulyar bərk cisimdə yükdaşıyıcıların fotogenerasiya proseslərinin xüsusiyyətləri tətqiq edilmişdir. Kulon rabitəli cütlərin halı ilə yükdaşıyıcıların fotogenerasiya prosesini səciyyələndirən zəif molekullararası qarşılıqlı əlaqənin rolu göstərilmişdir. Yarımkeçirici polimer-silisium sistemlərin araşdırılmasının birinci nəticələri verilmişdir. Oligohydroguinone, oligo-*α*-naphthol, oligo-*β*-naphthol, oligo-amino-phenylen polimerlər kompozit materiallar kimi istifadə olunmuşdur. Polimer-silisium geterostrukturların cərəyan-gərginlik xarakteristikları tədqiq olunmuşdur. Molekulyar komplekslərdə və polimer yarımkeçiricilərdə fotoeffektin kvant çıxışlarının struktur dəyişməsinin qanunları tətqiq edilmişdir.

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ИССЛЕДОВАНИЕ ПРОЦЕССОВ ФОТОГЕНЕРАЦИИ В ПОЛУПРОВОДНИКОВЫХ ПОЛИМЕРАХ

В статье рассмотрена перспективность исследований полупроводниковых полимеров для создания фотоэлектрических преобразователей. Исследованы процессы фотогенерации в полупроводниковых полимерах, и показаны особенности механизма фотогенерации носителей заряда в молекулярном твердом теле. Показана роль слабого межмолекулярного взаимодействия, обуславливающего процесс фотогенерации носителей заряда через состояние кулоновски связанной пары. Представлены первые результаты исследований систем: полупроводниковый полимер-кремний. В качестве полимерных композитных материалов использованы полимеры oligohydroguinone, oligo-α-naphthol, oligo-β-naphthol, oligo-amino-phenylen. Исследованы вольт-амперные характеристики гетероструктур полимер-кремний. Исследованы структурные закономерности изменения квантовых выходов фотоэффекта в полимерных полупроводниках и их молекулярных комплексах.

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