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Conductivity of sandwich-structures based on dye-doped photoconducting and non-photoconducting polymer films

N.A. Davidenko¹, N.A. Derevyanko², L.I. Fenenko³, A.A. Ishchenko²,
G.P. Olkhovik³, P.S. Smertenko³

¹ Taras Shevchenko Kyiv National University, 64 Volodymyrs'ka str., 01033 Kyiv, Ukraine
Phone (044) 220 5057

² Institute of Organic Chemistry NASU, 5 Murmanska str., 02094 Kyiv, Ukraine
Phone (044) 551 0682

³ Institute of Semiconductor Physics NASU, 45 prospekt Nauki, 03028, Kyiv, Ukraine
Phone (044) 265 6477, e-mail: fenenko@class.semicond.kiev.ua

Abstract. Electroconducting properties of sandwich-structure samples with films based on photoconducting polymer poly-*N*-epoxypropylcarbazole and non-photoconducting polyvinylethylal, doped by cationic, anionic, neutral and intraionic organic dyes are researched. It is revealed that, in thin polymer films with considerable dye concentration, the conductivity of organocomplexes, contrary to ionic and neutral dyes, changes the mechanism, is increased by some orders and weakly depends on polymer nature. Their conductivity is comparable to the analogous value of a sandwich-structure based on polyphenilenevinylene.

Keywords: photoconducting films, poly-*N*-epoxypropylcarbazole, organic dyes, electroconductivity, thermofield generation.

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1. Introduction

Sandwich-structures based on polymers doped by organic dyes can possess considerable electrical conductivity (EC) and photoconductivity (PC). Therefore, they are the perspective materials for electroluminescent devices [1,2]. Photoconducting films based on poly-*N*-epoxypropylcarbazole (PEPC) are applied as reversible registering medium in electrography and holography [3]. Such media possess also the electroluminescent effect [4]. These properties are determined by a capability of dye-doped polymer to photogeneration and transport of charge carriers [1, 3]. Undoped polyvinylethylal (PVE) films possess low EC, but PVE itself has good film-forming properties and can be used as a film-forming base for molecular doped compositions.

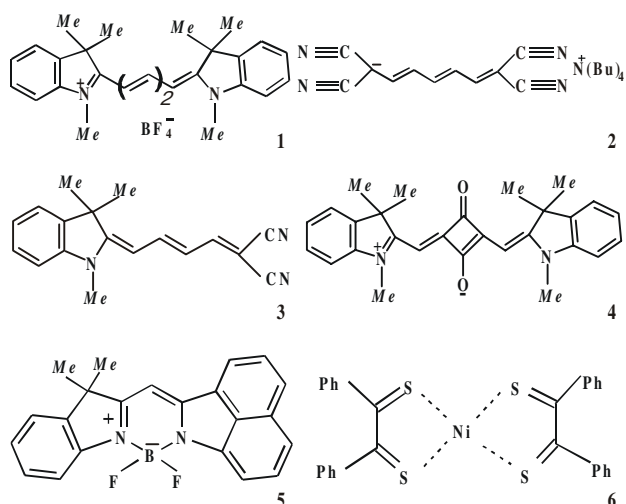
The purpose of this work was to research the EC peculiarities of the sandwich-structures based on PEPC and PVE films doped by organic dyes of various ionic ability. For comparison EC of polyphenilenevinylene (PPV) films, which is widely applied in electroluminescent devices based on organic polymer films [10] were examined, also.

2. Samples and experimental

The following dyes were studied as dopants: cationic (1), anionic (2), neutral (3), and intraionic (4-6) [5].

The investigations of EC were made on sandwich-structures Me-(polymer + *N* mass. % of 1-6 dyes)-SnO₂:In₂O₃, where the metal cathode Me (In, Al, Cu) pads were pressed to the surface of polymer film deposited on a glass substrate with SnO₂:In₂O₃ (ITO) layer, and *N* was the dye concentration. In our experiments value *N* was varied from 0 to 50 mass. %. The area of Me contact was 1 mm². The films of dye-doped polymers were fabricated by drying up of poured solutions of polymer with the dye in 1,2-dichlorethane on the surface of glass substrates with ITO. A PPV films were prepared using the method described in [6]. The film thickness (*L*) was between 0.3–5 μm.

Current-voltage characteristics of investigated samples were measured by automated tester 14-TKS-100 and processed by PC. The value of applied electric field (*E*) was varied in the range of (1–20)×10⁷ V/m. The absorption and photoluminescence spectra of polymer films were measured within the range from 400 nm to 1100 nm. In



this range PEPC and PVE absorption is absent and there is the absorption of long wavelength π - π^* electronic transitions of 1–6 compounds. All measurements were made at the room temperature ($T = 293$ K).

3. Results and discussion

Absorption and fluorescence spectra of 1–6 dyes in liquid solvent have the clearly expressed vibration structure [5]. Such structure takes place also in the polymer film even at rather high N . However, with an increase N the vibration structure is considerably smoothed out, and the absorption band is broaden and shifted to long-wavelength range. The concentration effects in dyes spectra testify about an existence of intermolecular interactions in a dye-dye system, which lead to formation of the dyes aggregates [5].

In samples with PEPC films without dopants the current value I depends on polarity of applied electric field at $L < 1 \mu\text{m}$. At negative potential on Me contact, it can

be 1–2 order more than at the positive one. In samples with $L > 1 \mu\text{m}$ the I value does not depend on polarity of the applied electric field and at the constant E value it increases rectilinearly with an increase L . In the range $E = (3-20) \times 10^7$ V/m dependence plot of the I versus E is rectilinear in coordinates $\lg(I) \sim E^{1/2}$. These results are agreed with ones obtained previously [3], where, using thermostimulated current technique, ascertained was the fact that for temperatures $T > 273$ K the EC of undoped PEPC films with $L > 1 \mu\text{m}$ is determined by two components: thermofield generation of holes from impurity centres in the film bulk and ion conductivity. As for PEPC films with $L < 1 \mu\text{m}$ dependence on the polarity of the applied electric field is appeared and I value increases with decrease of L . It is necessary to consider that in EC of investigated samples deposit contribution of the hole injection current from contacts occurs. Therefore contribution of third component of EC determined by thermofield carriers injection from the contacts is necessary to be taken into account for the samples with $L < 1 \mu\text{m}$.

In samples with PVE without dopants the current value is one order less than in samples with PEPC. For any L the I value does not depend on polarity of applied electric field and increases rectilinearly with an increase L at a constant E .

Dye doping of polymer films leads to an increase of their EC. The dependence plot of I versus E in coordinates $\lg(I) \sim E^{1/2}$ for the samples with 50 mass. % of 1–6 dyes in thick films is represented in Fig.1. Fig.2 shows similar dependencies but for thin films. At the positive potential of electric field on ITO contact the I value in samples with 1,3–6 dyes is more than at the negative potential on this contact. The opposite picture is observed in samples with two-anionic dye.

The obtained results indicate that in investigated samples the thermofield generation of charge carriers from dye molecules gives essential contribution into EC. At

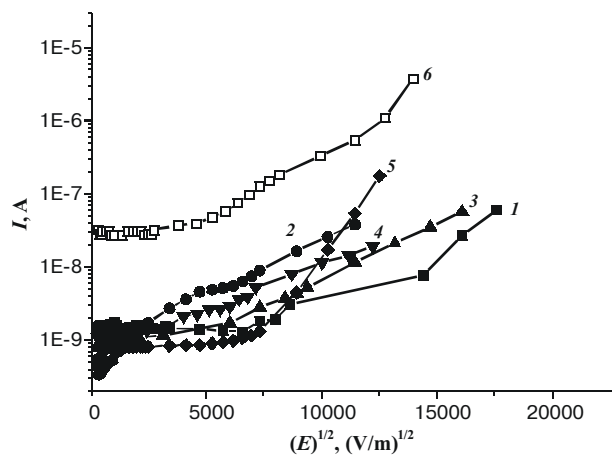


Fig. 1. The dependence plots of I versus E in samples of In-(PEPC+50 mass. % 1-6 dyes)-ITO, $L \geq 1 \mu\text{m}$. Numbers of curves correspond to dyes numbers in the article.

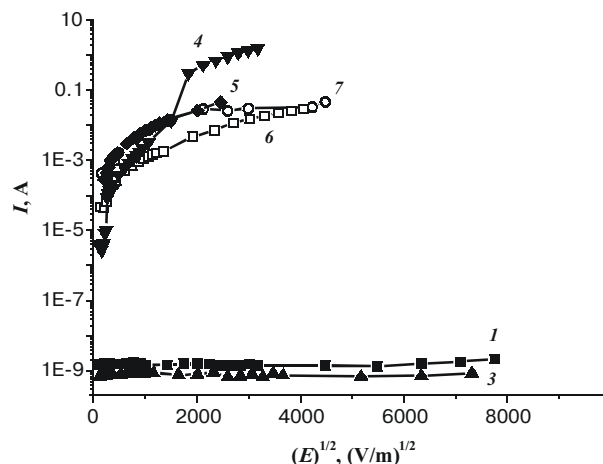


Fig. 2. The dependence plots of I versus E in samples of In-(PEPC+50 mass. % 1-6 dyes)-ITO, In-PPV-ITO $L \leq 1 \mu\text{m}$. Numbers of curves correspond to dyes numbers in the article. Number 7 corresponds to curve for the structure with PPV.

small L , the current of injected carriers from electric contacts influences on EC too. For the samples with thin polymer films the I increase with an increase L for $E < 5 \times 10^7$ V/m and the I decrease with the increase L for $E > 7 \times 10^7$ V/m is typical. For $L < 1 \mu\text{m}$ and $E > 7 \times 10^7$ V/m $\lg(I) \sim E^{1/2}$ dependence becomes superlinear and at considerable dye concentration ($N > 20$) the I values are comparable to conductivity currents in Me-PPV-ITO samples. Therefore, it is possible to assume that the thermo-field charge carrier injection from the contacts gives essential contribution into the current at large E values. This assumption is confirmed by the dependence of I value on the nature of metal electrode. With a decrease of a work function (energy of the Fermi level) of the metal cathode, in the line from Cu to Al, In in the samples with thin polymer films, the value I is increased.

It is possible to characterise the nature of a change of EC of doped polymer films with an increase of dye concentration by the change of an exponent (α) in the $I \sim E^\alpha$ dependence. Earlier such differential method was de-

scribed in [7]. The dependence plots of $\alpha(E)$ in the researched samples are presented in Fig. 3. The greatest exponent values of dependencies $I(E)$ and maximal EC, which is comparable to that of samples Me-PPV-ITO, is observed at considerable concentrations of 4–6 dyes.

Among investigated dyes the intraionic dyes are the most inclined to aggregate. Therefore, it is possible to conclude that the increase of EC of polymer films with an increase N is related to amplification of electron interactions in the dye-dye system. The assumption about high EC of dye aggregates and low conductivity between them is confirmed experimentally using the results of EC investigation of Me-(PVE+N mass. % of dye)-ITO. The investigated samples at small dye concentration do not possess high EC for any L . However, in the samples with $N > 30$ mass. % and $L < 1$, the conductivity can reach values close to one in similar samples of Me-(PEPC+N mass. %)-ITO. With an increase of L in samples with PVE, the conductivity decreases much more considerable than that in samples with PEPC.

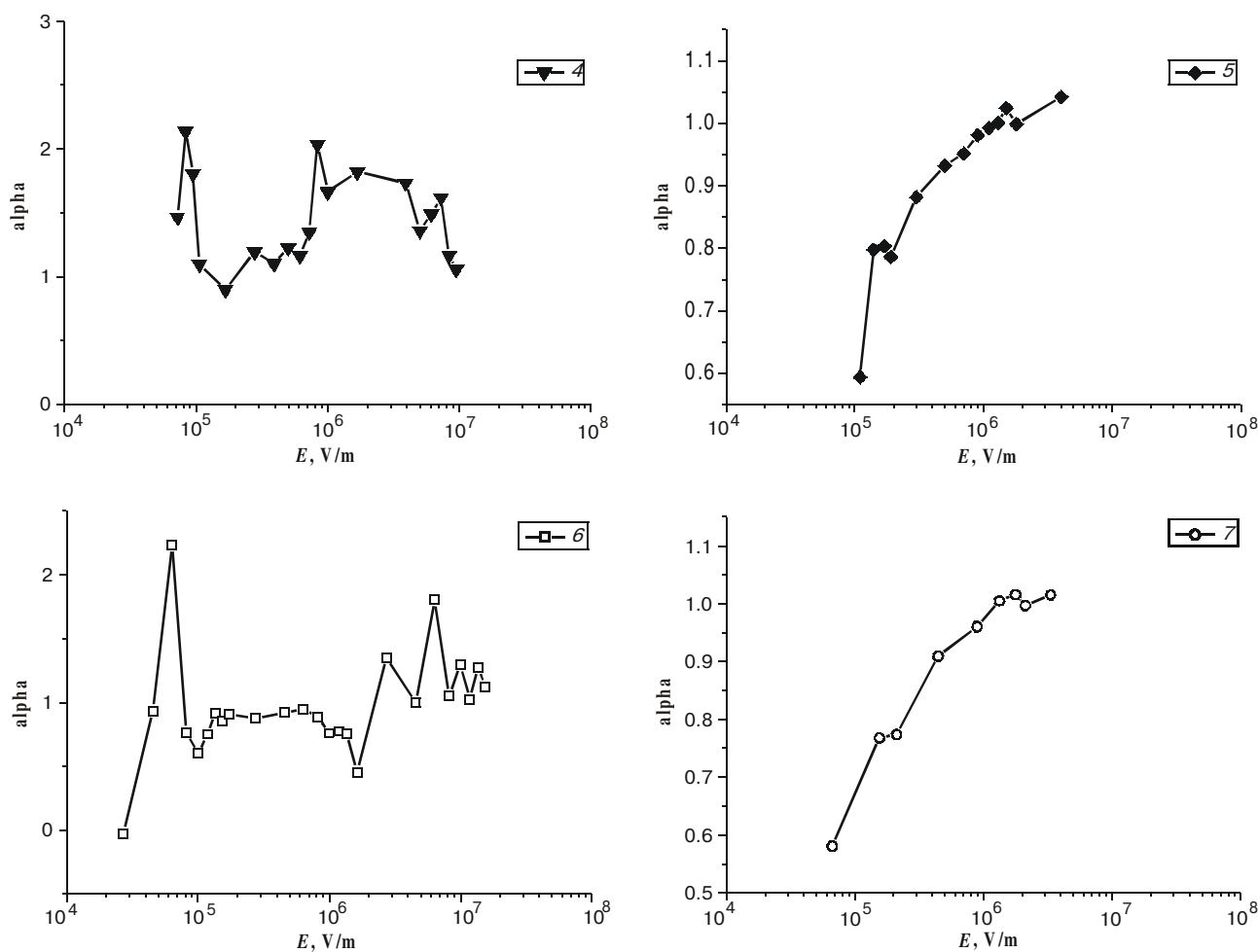


Fig. 3. The dependence plots of $\alpha(E)$ in samples In-(PEPC+N mass. % dyes 1-6)-ITO, In-(PVE+N mass. % dye 1)-ITO, In-PPV-ITO; $L = 0.5 \mu\text{m}$.

4. Conclusion

The high EC of sandwich-structure samples with thin polymer films takes place with an increase of 4–6 dye concentration. The current value of conductivity of such samples is comparable to a current value in similar samples with PPV films. The effect of increase of conductivity is less expressed for sandwich-structures with cationic, or anionic dyes in comparison with the intraionic ones. It is explained by the fact that the ionic dyes are capable to intermolecular electronic exchange of charge carriers of one type (holes or electrons). Even in aggregates of such dyes the conditions for bipolar conductance are not provided.

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