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On the mechanism of formation of the photoelectret state in 4-nitro-4′-aminodiphenyl thin films*

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The mechanism of photoelectret formation in organic polycyclic compounds is discussed on the example of 4-nitro-4′-aminodiphenyl. It is established that the magnitude of photoelectret field is associated with the magnitudes of the external electric field and the pyroelectric field. Photogenerated and injected holes are the main source of photoelectret charge in these materials. The magnitude and kinetics of photoelectret state depend on the polarity of illuminated electrodes.

Key words: *photoelectret state; organic semiconductors; trapping centres; pyroeffect*

1. Introduction

It is known that photoelectret state is formed in photosensitive high-resistant semiconductors in the presence of deep trapping levels for majority carriers and of electrode barriers [1]. The generation of non-equilibrium carriers in inorganic and organic semiconductors is difficult in some details but the mechanism of photoelectret state (PhES) formation is the same: inhomogeneous distribution of charge carriers in trapping centres along the electric field. PhES in inorganic semiconductors has been investigated in detail but it did not find a wide practical application. A search for new photoelectrets among organic semiconductors gave positive results. For example, photoconductivity, PhES and pyroeffect, independent of external electric field, successfully combine in 4-nitro-4′-aminodiphenyl (NADPh). This opens new perspectives for practical application of the above material in optical memory, optical transmission, etc. [2]. The material was also selected due to an overlap of photoconductivity and pyroeffect in some spectral regions that

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permits the PhES investigations in the presence and absence of pyroelectric field in the function of wavelength.

2. Experimental

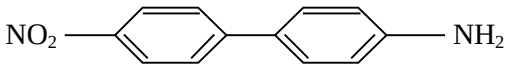
NADPh thin-film samples were manufactured in the form of sandwich-cells, which were obtained by consecutive application of the bottom aluminium electrode, organic material and the top aluminium electrode on the substrate (quartz, glass ceramic, polymer film) by the thermal deposition in vacuum. The working area of the samples corresponded to the overlapping area of lower and upper electrodes and was equal to 25×10^{-8}–16×10^{-6} m^2, while the thickness of the photosensitive pyroelectric (photopyroelectric) amounted to 0.5–1.0 μm. Purity of the organic materials was ensured by the recrystallization and controlled by a stability of the melting temperature.

Irradiation of photopyroelectric sensitive elements was carried out using a xenon-krypton lamp, blackbody and monochromator. Pyroeffect and PhES kinetics were investigated with an electrometric amplifier and oscillograph.

Thermally stimulated currents were measured using the photopolarization method described in details previously [1].

3. Results and discussion

The molecule of NADPh contains two heterogroups: a strong acceptor group – NO_2 and a donor one – NH_2:



Polycrystalline NADPh consists of conglomerates of small single crystals [3]. The organic film is deposited in such a manner (the substrate is heated during the deposition) that the spontaneous orientation of these conglomerates occurs and they possess a dipole moment distinct from zero. NADPh molecule has dipole moment of 6.4 D in the ground state increasing to nearly 20 D in the first excited singlet state [4], due to the transfer of one of the nitrogen lone-pair (lp) electrons of amino group to the nitro group possessing strong acceptor properties.

NADPh thin films exhibit strong absorption in UV spectral region (Fig. 1). The long-wavelength shift of the absorption edge, in comparison with the spectrum of non-substituted diphenyl, is caused by the introduction of a heterogroup.

The photoconductivity spectrum to some extent follows the absorption spectrum with the exception of the long-wavelength region. The polarity of illuminated electrode has the essential influence on the spectral characteristic of photoconductivity. Under the

illumination of positive electrode, the photoconductivity maximum at 375 nm is much higher than under the illumination of negatively biased electrode. The reverse picture is observed for the maximum at 540 nm. The photoconductivity measurements confirm that the holes are the majority carriers in NADPh [5].

Experimental data point to PhES formation during the photocurrent flow. The PhES field is directed oppositely to the biasing field direction. The PhES magnitude depends on the sign of the potential of the illuminated electrode, the light intensity and the magnitude of external electric field. Investigations of spectral dependencies of the photoelectromotive force showed that symmetric barriers, assisting the PhES formation, are formed on both contacts.

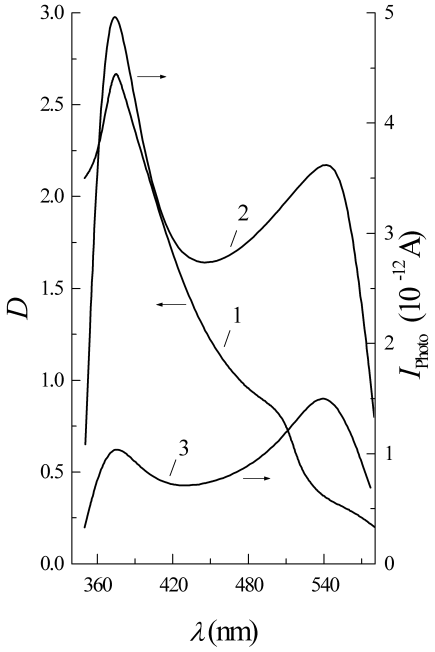


Fig. 1. Spectra of optical absorption (1) (sample thickness – 0,15 μm) and photoconductivity at the irradiation of positive (2) and negative (3) electrodes for thin film of 4-nitro-4′-aminodiphenyl (sample thickness – 0,15 μm and ~1 μm)

After achieving its maximal value, the photocurrent relaxes to a certain level. On repeated illumination, the photocurrent does not reach the maximal value but initially increases exponentially with following saturation to some stationary value. This feature indicates that the formation of PhES results in a decrease of the total electric field in the sample. The magnitude of the PhES field is approximately one order of magnitude lower than that of the biasing field.

Under the influence of external electric field, which is much higher than pyroelectric one, non-equilibrium carriers, both formed under the illumination and injected from the electrodes, move towards electrodes. The dynamics of PhES field formation is determined by the drift of holes, which are the majority charge carriers in NADPh, to the negatively biased electrode.

Barriers of approximately 1 eV high, hindering a free exchange of carriers between the organic material and electrode, exist at the interfaces between organic material and the aluminium electrodes [6]. Due to the presence of these barriers, the charge carriers are trapped with high probability in near-electrode region, creating an additional charge at the interfaces. It is possible that a part of trapped carriers will be released from traps under the influence of light, temperature, electric field, etc.

The depth of trapping centres responsible for the PhES can be determined, as a rule, by thermally stimulated current method in photoelectret regime. In the case of NADPh samples, the investigation of thermally stimulated currents [7] yield the trap depths

amounting to 0.3 and 0.6 eV. On the other hand, the depths 0.3 and 0.7 eV were obtained from the temperature dependencies of photocapacitance for investigated sandwich cells [8]. Thus, two types of trapping centres with the depths of 0.3 and 0.7±0.1 eV take part in the PhES formation processes.

Despite the fact that photoelectret charge decays with time (Fig. 2) due to detrapping process, the residual charge after the saturation at ~10^4 s is sufficient for effective application of PhES phenomenon in this material.

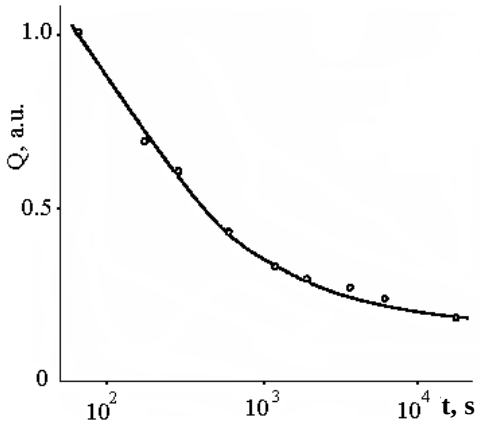


Fig. 2. Kinetics of PhES decaying
in NADPh thin films in darkness at 300 K

The regularities of PhES formation and disappearance for inorganic semiconductors can be used for the description of processes in NADPh. For example, the dependencies of PhES field on the biasing electric field (Fig. 3) and on the intensity of polarizing field (Fig. 4) have a similar character. It is clear that the saturation of PhES field in both cases is connected with filling traps. At the same time, some PhES peculiarities associated with the differences between inorganic and organic semiconductors occur.

An efficient process of PhES formation occurs, in analogy to inorganic semiconductors, at the wavelength corresponding to photoconductivity maxima. The presence of electrode barriers, strong optical absorption in UV region as well as different origin of photoconductivity maxima require a detailed consideration of PhES formation mechanism in 375 nm and 540 nm regions.

At 375 nm practically all light is absorbed in the contact region where the generation of electron–hole pairs takes place. Under the illumination of the positive electrode, the holes drift into the material bulk towards the non-illuminated electrode, where the trapping occurs. The electrons located near the illuminated electrode cannot form a sufficient heterocharge because due to optical excitation and hole injection from aluminium electrode. Thus, the space charge is formed, mainly, near the negatively charged electrode.

Hole injection from illuminated electrode is absent during the illumination of negatively charged electrode by 375 nm light. So, only carriers generated by the light in organic material make contribution into the photoconductivity. The holes drift to illuminated electrode, where part of them is trapped in the trapping centres. Because the area where the positive space charge is formed is permanently under illumination, the process of PhES formation is accompanied by a partial release of this charge. The region of the space charge is formed near the non-illuminated electrode.

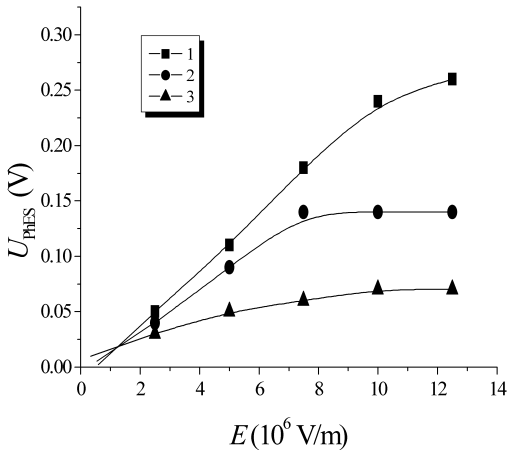


Fig. 3. Dependence of the PhES field on the external electric field in 4-nitro-4′-aminodiphenyl thin film: 1 – at the illumination of negatively charged electrode by 375 nm light; 2 – at the illumination of negatively charged electrode by 540 nm light; 3 – at the illumination of positively charged electrode by 375 nm light

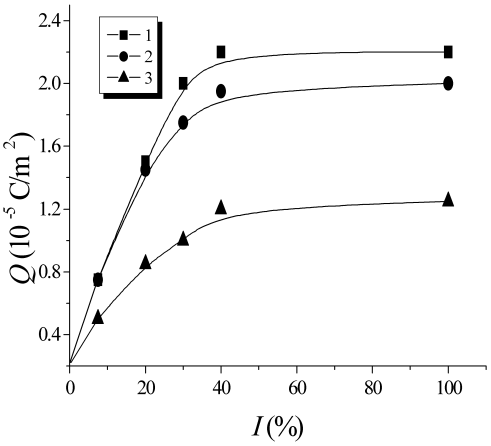


Fig. 4. Dependence of the PhES charge on the light intensity in

4-nitro-4′-aminodiphenyl thin film: 1 – at the illumination of negatively charged electrode by 375 nm light; 2 – at the illumination of negatively charged electrode by 540 nm light; 3 – at the illumination of positively charged electrode by 375 nm light

Though the hole conductance is dominant in NADPh, the electron type of conductance associated with the electron drift due to electron photoinjection from the electrode into the sample body cannot be excluded completely.

The carriers trapped in the NADPh bulk in trapping centres are released due to different processes. The emptying of trapping centres may be due to the thermal detrapping. The probability of such a process is determined by the simple Boltzmann dependence being more probable for the shallow centres than from deep ones. The optical detrapping of carriers is also possible. The absorbed light can release the carriers directly (the phonon is absorbed by the trapped charge carrier) or through the formation of triplet excitons interacting afterwards with the trapped charge carrier [9].

The dark polarization, caused by equilibrium charge carriers, plays a noticeable role in the whole polarization. The electrode injection is so intensive that at the investigation of dark polarization by depolarization method, illuminating the positively charged electrode by 375 nm light in the external circuit we observed the current flowing in the same direction as the dark current. This means that the photoinjection current is larger than the current caused by the dark polarization decay. On increasing the PhES charge, i.e., on increasing the exposition to light during the PhES formation, the photodepolarization current exceeds the photoinjection current.

It must be mentioned that in the above case the PhES field is not completely destroyed, because the positive heterocharge close to the unilluminated elecctrode remains uncharged. This charge can be destroyed by the illumination of whole bulk of the sample, for example, by the 550 nm light. The experimental results confirm that only the light of 550 nm wavelength causes the complete destruction of PhES.

In our conditions, the PhES is destroyed after 20–300 s of the illumination of samples with light from the region of long-wavelength photoconductivity maximum. A nonuniform rise of PhES charge in the initial moment of depolarisation at different polarity of illuminating electrode can be mainly explained by the existence of the pyroeffect. The pyroelectric field assists the PhES formation under the influence of external electric field on illuminating the positive electrode, and prevents this process on illuminating the negative electrode. The heat time constant for investigated films is 0.4 s and the Maxwell relaxation time is 30 s. From this it follows that the influence of pyroelectric charge on PhES becomes apparent only at the initial moment of PhES formation and destruction. The relative importance of this effect decreases with the increasing external electric field.

A slower rise of PhES charge is explained by the accumulation of negative PhES charge, which is partially compensated by the hole injection from the illuminated positively electrode, into the near-electrode layer. Under illumination of negatively biased

electrode during the PhES formation, the hole injection becomes slower and PhES charge creation is mainly due to non-equilibrium carriers.

Conclusions

The investigations of photopolarization and photodepolarization reported in this paper showed that in NADPh thin films the process of PhES formation and destruction is mainly realized due to non-equilibrium holes generated by light in the sample bulk and owing to holes injected from illuminated aluminium electrode. The magnitude of PhES field is determined by the biasing electric field and by pyroelectric field.

Acknowledgements

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