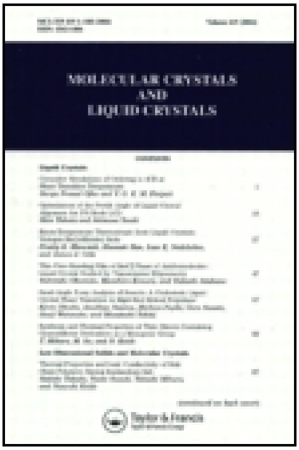

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ANISOTROPIC ORGANIC SYSTEMS AS MOLECULAR MATERIALS FOR ELECTRONICS

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Abstract The review of our results related to some types of molecular organic systems is reported. Some aspects of application of an organic molecular system anisotropy is discussed.

INTRODUCTION

A lot of new developments in micro-, bio- and optoelectronics are based on using anisotropic organic media as functional materials. In a number of problems the organic materials serve as detectors of radiations. These molecular materials are luminescent, and in electronic devices they are employed in pairs with photodetectors.[1,2] According to their application, experimental samples of such materials have a different composition, state and dimension. Nevertheless, they are molecular systems, and thus the corresponding energies of their intermolecular and intramolecular interactions are about 10^{-3} eV and 10^{0} eV. The generation of charge states causes the intermolecular interaction energy increase up to 10^{-1} eV.[3] For such systems the efficiency of the processes of charge carrier as well as excitation energy transfer increases with improvement of a system structure perfection.[4]

This paper is devoted to some aspects of application of different types of anisotropy of the organic molecular luminescence systems in electronic devices.

THE RADIOLUMINESCENCE TECHNIQUE FOR STUDY AN ORGANIC MOLECULAR SOLID

The radioluminescence of organic materials is being investigated for a long time.[2] It is used in various electronic devices for radiation monitoring, nuclear science, astronomy, radiobiology, medicine, etc. By contrast to a photoluminescence process a radioluminescence one include additional stages of charge carrier generation, migration and recombination. The latter results in an electronic excitation of molecules. We have shown [4] that, owing to characteristic properties of the process of a charge carrier energy exchange in organic molecular solids the shape of radioluminescence pulse is sensitive to features of their structure. Hence, the study of the radioluminescence pulse shape can be used for the diagnostics of structure unperfections of a luminescent molecular solid. Irrespective of a future application of a molecular solid the results of such an analysis are useful because they show its semiconducting and luminescent properties.

The shape of the fast component of a radioluminescence pulse of an organic molecular solid is described by the function [4]:

$$i(t) \sim f(t) * \exp(-t/\tau) \equiv \int_0^t f(t-\beta)\exp(-\beta/\tau)\,d\beta \quad (1)$$

$$f(t) \sim \exp(-(t-3\sigma)^2/2\sigma^2) \quad (2)$$

and the shape of its slow component decay (for $t > 50$ ns) is described by function [5]:

$$i(t) \sim (1 + t/t_D)^{-k}, \quad (3)$$

where t is the time after excitation, τ is decay time constant, σ and t_D are the time constants, k is the constant, which is determined by the type of ionizing radiation. For radiations with a high ($\geq 10^1$ MeV/ cm) and low ($\leq 10^{-1}$ MeV/ cm) specific energy loss $k = 1.0$ and $k = 1.5$, respectively. The presence of charge carrier shallow traps (≤ 0.2 eV in depth) has an effect on a σ-value (Eq.(2)). A type and concentration of charge carrier deep traps (> 1.0 eV in depth) produce the main effect on the t_D-value (Eq.(3)). The additional information can be obtained from correlation between the changes in the t_D - value and radioluminescence spectrum.[6]

ORGANIC SINGLE CRYSTALS WITH CONTROLED STRUCTURE PERFECTION

Organic single crystals are used in many electronic devices. We have developed the method which allows to grow organic molecular crystals with controlled structure perfection.[6,7] According to this method, crystals are grown from the melt by Bridgmann process. Doping the melt with electron - seeking addition agents (ESAA) of a high electron affinity allows to control the growth rate of the crystal as well as its structure perfection by changing the concentration C of ESAA in the melt. The latter is manifested in changes in root - mean - square random orientation σ_c of the molecular crystal mosaic structure and was accompanied with a change in concentration of charge carrier (~ 1.2 - 1.4 eV) and exciton (~ 0.24 eV) deep traps. The latter has been obtained by using the aforecited radioluminescence technique. Such deep traps in organic crystals may be explained by the generation of aggregations and ensembles of dislocations in the process of crystal growth.[6] Adding ESAA in concentration $C = C_0 = 0.1$ mol.% to the melt results in the highest structural perfection of the grown crystals, i.e. results in minimizing σ_c-value.

The initial cause of all aforementioned effects is the formation of charge transfer complexes (melt molecule-

molecule of ESAA). It is a very effective process which accompanies melting. It is possible to describe such a complex as an electric dipole with dipole moment $d \sim 2.5D$. Melt molecules orient themselves with respect to a complex electric field within the distance $r_p \sim 0.4 - 0.5$ nm. Thus a local anisotropy of melt properties appears. With the probability of 0.99 molecules of ESAA do not enter the perfect single crystal. The complexes have a very high probability of the breakdown during their entry into the growing crystal layer. For $C < C_0$ the formation of single complexes is the process of primary importance. For $C > C_0$ when the mean distance between complexes has already become equal 6 nm, the formation of supercomplexes in the shape of stacks containing $n_{AD} > 1$ single complexes becomes the most probable process. The C - value growth for $C > C_0$ doesn't cause the change of the total sum of complexes, it only results in the n_{AD} mean value increase.

The formation of orientated melt parts, i.e "partial melt ordering" causes the aftermath of two types. First, it results in an increase in growth rate and structure perfection improvement of the growing crystal due to the decrease of drawing heat with the increase of the melt "ordering". Second, the polarized surroundings of a complex, i.e. a group of mutually orientated melt molecules, having entered into the growing crystal layer may become a crystallization center, which results in the increase of a growth rate. For $C > C_0$, with the C increase the positive effect of those processes on the crystal growth decreases due to increase of n_{AD} value, i.e. the decrease of the ratio C_{AD}/C, where C_{AD} is concentration of complexes in a melt. (For $C < C_0$ $C_{AD} = C$, and for $C > C_0$ $C_{AD} < C$). From the point of view of getting a structure perfect crystal a mean n_{AD} value growth (with C increase) gives the negative effect. Entering of complexes with $n_{AD} > 1$ and products of their breakdown in a crystal grown layer results in the increase of the number of the crystal lattice defects, and for very high C (and n_{AD} values) leads to the formation of nucleation centers, which compete with each other in the crystal growth process.

It should be noted that in the aforementioned experiments the complexes were distributed evenly in the melt volume and only a local anisotropy of the properties of melt parts appears. The same results have been achieved when the "surface" effects were produced too.[7] The structure perfect crystals were growing from the melts when the seed inorganic crystal were used. The seed crystal orientates melt molecules by its electrically active point cleavage surface defects. The crystals of stilbene, anthracene and p-terphenyl were grown. The inorganic crystals of KCl, Al_2O_3, $CdWO_4$, as well as mica ones had been cleaved and then used to seed an organic crystal melt.

LANGMUIR - BLODGETT FILMS

The process of the electron excitation transfer in mono- and multimolecular Langmuir-Blodgett (LB) films is of great interest because of their application possibilities in the field of molecular electronics, biosensors, nano- and biotechnologies. Using molecules containing fluorescent units for LB-films extends their scope. LB - films as selective detectors of ionizing radiation typifies such an application. The ratio of the probabilities of LB-film excitation by long-range radiation and short-range one is negligible. Therefore an alpha-particle detector based on LB-film (or short-range beta-radiation one) practically doesn't detect background radiations. Alternating LB-films with different luminescence decay times in a detector which has a form of stack, one can study the process of energy exchange in various cross-sections of a particle track. The anisotropy of luminescence decay time along such a detector allows to distinguish the information.

LIGHT-CONVERTERS FOR SOLAR ENERGETICS.

The main problem in design of solar energy converters is to increase their conversion efficiency. The solar spectrum and absorption spectra of photodetectors are not the same. Using plastic which contains luminescent molecules with absorption that corresponds to the solar spectrum, one can convert solar light to the range of the photodetector absorption spectrum. A large area plastic allows to detect a lot of solar light photons. The question arises: how to collect converted light on a photodetector of minimal area? Figure 1 demonstrates the answer on this question. Owing to anisotropy in light collection process and reabsorption, light with peak wavelengths λ_2 is effectively collected on the photodetector.

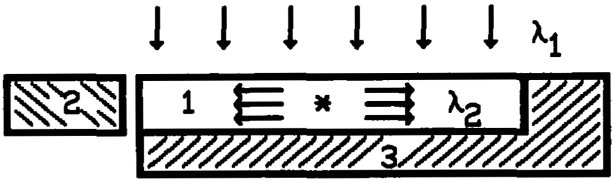

FIGURE 1 Schematic representation of light - converter part of a device for solar energetics.
1 is a plastic with λ_1 and λ_2 peak wavelengths of an absorption and luminescence spectrum ; 2 is a photodetector; 3 is a light - reflection coating.

Doping the plastic based on methyl methacrylate with naphthylamide, naphthoyl benzimidazole and 3,4,9,10 - perylenetetracarboxylic acid derivatives allows to develop an effective light converter working with a silicon photodiode. The plastic area is 50 times as large as photodiode one. Using of such a plastic increases the system power two times.

CONCLUSIONS

Above-mentioned examples in which organic molecular luminescent systems are used for detection of light and ionizing radiation show that well - known applications of molecular systems in electronics doesn't cover the scope for their suitability. Molecular materials allow to develop the effective detectors for environmental monitoring and solar energetics, nuclear science and medicine.

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