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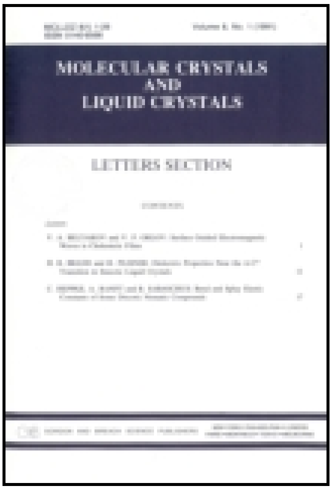

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Donor Oligomer Based Film Heterostructures Doped with Squarilium Organic Dye and their Photoelectric Properties

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Donor Oligomer Based Film Heterostructures Doped with Squarilium Organic Dye and their Photoelectric Properties

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The new heterostructures comprising a squarylium dye (SQ) film deposited onto a oligo-N-epoxypropylcarbazole (OGC) film have been created, and their photoconducting, photodielectric, and photovoltaic properties have been studied. The OGC/SQ heterostructures exhibit the photodiode properties. It is concluded that the p–n junction in these heterostructures is ensured by the hole character of conductivity in the oligomer and the bipolar conductivity of the deposited dye film.

Keywords Organic heterostructures; oligo-N-epoxypropylcarbazole; squarilium dye; charge photogeneration; photovoltaic effect; "memory" effect

Introduction

In recent years, new photovoltaic devices for solar energy converters have been created based on heterostructures involving inorganic and organic materials [1–8]. Centers of light absorption and charge carrier generation in these systems can be represented by organic dye molecules, which possess high extinction coefficients in a broad spectral range and are capable of both accepting and donating electrons in interaction with adjacent donors and acceptors [9–11]. These organic dyes include squaryliums. However, the photoelectric properties of these heterostructures are still insufficiently studied. This work presents the results of an investigation of the photoconductive, photovoltaic and photodielectric characteristics of film heterostructures comprising a photoconducting oligomer film and a squarylium dye layer.

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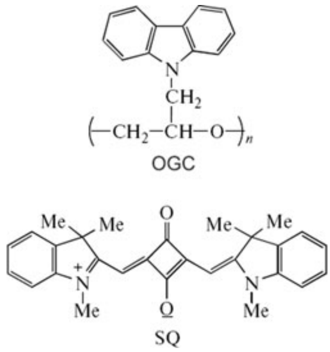

Scheme 1. Molecular structure of studied materials.

Samples and Experimental Methods

The samples were prepared from oligo-N-epoxypropylcarbazole (OGC) and a squarylium dye (SQ):

The samples had the form of (glass substrate)-ITO-OGC/SQ-Al sandwich structures, where ITO is the electrically conducting layer of indium tin oxide (SnO_2:In_2O_3) and Al is the aluminum contact. The OGC/SQ heterostructures were obtained by sequentially depositing OGC and SQ layers. First, the OGC layer was deposited from toluene solutions onto a glass substrate covered with an ITO layer, which was followed by drying at 80°C for 24 h. Then, the SQ layer was deposited onto the OGC film surface in vacuum. Finally, an Al layer was deposited onto the surface of a OGC/SQ structure. The thicknesses (L) of layers, measured with an MII-4 interference microscope, did not exceed 2 μm. The samples of heterostructures were characterized by measuring the (i) optical density (D) as a function of light wavelength (λ), (ii) densities of dark current (j_d) and photocurrent (j_{PH}) as dependent on the magnitude and polarity of the voltage (U) applied to the contacts (and, hence, on electric field strength $E = U/L$ and the direction of field lines in the sample), and (iii) photovoltage magnitude (V_{PH}). The photovoltage was measured using an electrometric amplifier. The j_{PH} and V_{PH} variation with time t during the exposure and after switching off the light source was measured using a digital storage oscilloscope Tektronix TDS1001B and a digital voltmeter Fluke 124. The samples were also characterized by the dielectric loss tangent (tanδ) and electric capacitance (C), which were measured in the dark and on exposure using a sinusoidal alternating voltage with an effective magnitude of 8 V and frequencies within $f = 50$–10^4 Hz. The results of these measurements were used to calculate the values of $\Delta\tan\delta = (\tan\delta_{PH} - \tan\delta_0)/\tan\delta_0$ and $\Delta C = (C_{PH} - C_0)/C_0$, where $\tan\delta_{PH}$, C_{PH}, and $\tan\delta_0$, C_0 are the loss tangent and capacitance after and before switching on the light. The photodielectrical measurements were carried out using a dielectric coefficient and loss factor testing set of the TR-9701 type (based on Schering bridge scheme), external sinus signal generator G3-33 as the alternating voltage source and F-582 null-indicator according to [12, 13].

The concentration of non-equilibrium electrical charge (Q), which appeared in the bulk of the film heterostructures after illumination without applying an external voltage was also measured for these samples. The procedure for measuring Q and determining the dependence of Q on the illumination time (t_1) and the time after switching off light (t_2) is shown by diagrams in Fig. 1.

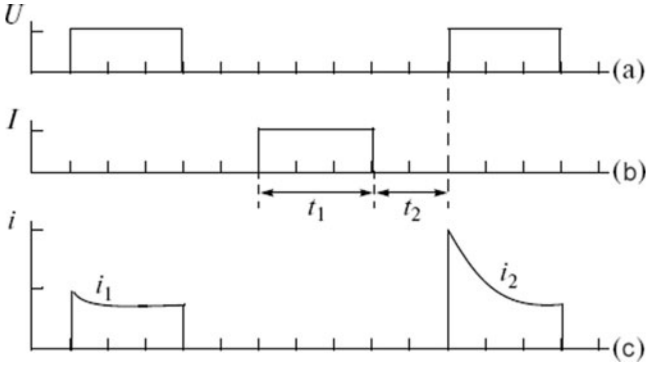

Figure 1. Profiles showing the sequence of voltage (a) and light switching on (b), and conduction current measurement (c) in ITO-OGC/SQ-Al samples.

First, a voltage (U) was applied to the sample in the dark, and the kinetics of the conduction current (i_1) was recorded using a storage oscilloscope. Then the electrical contacts were shorted, the sample was irradiated with the light for the time t_1, the light was switched off, the electrical contacts were disconnected after the time t_2, the voltage U was applied to the sample, and the kinetics of current (i_2) was recorded. From these measurements, the buildup and decay kinetics of Q were determined using the relationship:

$$Q = \int (i_2(t) - i_1(t))dt/eSL,$$

where e is the electron charge and S is the area of the sandwiched sample.

The light sources for measuring j_{PH}, V_{PH} and Q were represented by red light-emitting diodes (with a light intensity of 3 mW) with maximum emission intensities at $\lambda = 650$ nm respectively. The samples were illuminated on the side of the ITO layer. All measurements were performed at room temperature.

Results and Discussion

Since OGC does not exhibit intrinsic optical absorption in the visible spectral range, the spectrum of OGC/SQ heterostructures is determined by the absorption in the SQ layer deposited onto the OGC film (Fig. 2, curve 1). The absorption band of SQ-dye in its solid film is considerably broadened as compared to that of SQ molecules in solutions and oligomeric matrices of photoconducting OGC (Fig. 2, curve 2).

The absorption band shapes for the film and solution are also significantly different. These significant differences in the widths and shapes of the absorption bands of SQ in the solid state and in solution are related to a strong interaction that arises between SQ dye molecules in the former case due to their very close proximity. This intermolecular interaction in a solid film with fixed chaotic arrangement of dye molecules is predominantly responsible for the observed inhomogeneous broadening and deformation of the absorption band contour.

Figure 3 (curve 1) shows the dependences of j_{PH} on the magnitude and polarity of the applied (to the electric contacts of the samples) electric voltage.

The curves 2 and 3 in Figure 3 present plots of j_{PH} versus t measured on exposure to light and after switching off the light source. It was established that the photocurrent density jph growth and relaxation kinetics at a negative voltage on the ITO electrode is significantly

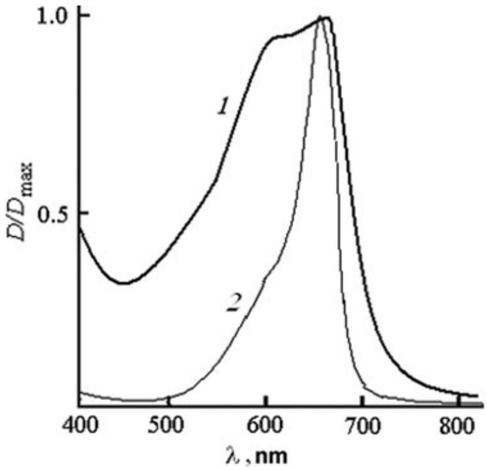

Figure 2. Optical absorption spectra of OGC/SQ heterostructure (1) and the OGC based film doped with 1 wt.% of SQ (2).

faster than that in the positive voltage case. From these data, it might be concluded that the samples with OGC/SQ heterostructures exhibit photodiode properties. The latter statement is confirmed by the results of investigations of the photovoltaic characteristics of these samples. It is established that irradiation leads to the generation of photovoltage with a

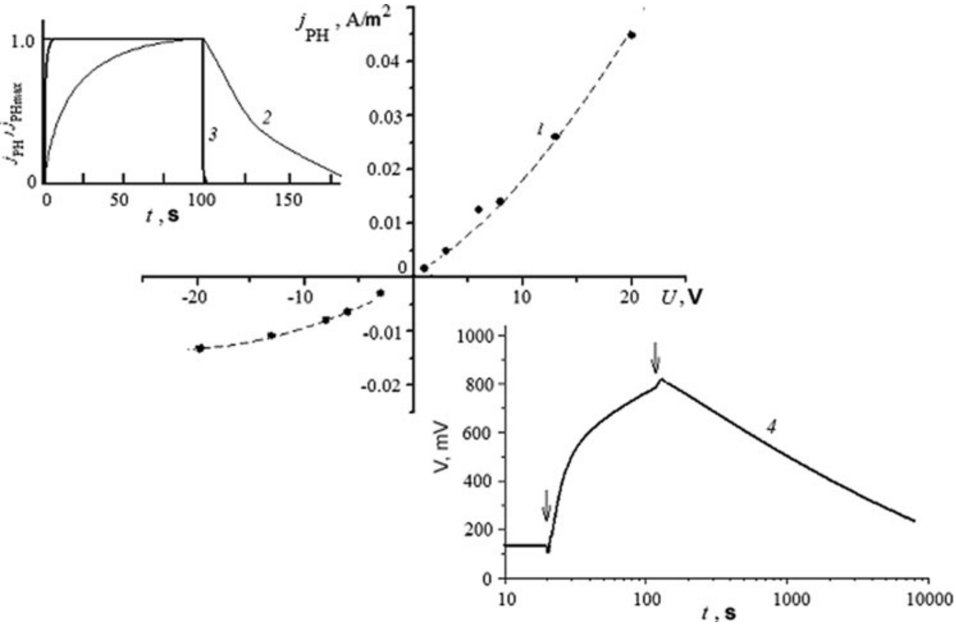

Figure 3. Plots of the photodiode current-voltage characteristics (1) of an ITO-OGC/SQ-Al heterostructure sample; normalized kinetic curves of j_{PH} for positive (2) and negative (3) applied voltage on the ITO electrode, and kinetics of photovoltaic response in this heterostructure irradiated by the light with λ ~ 650 nm (4). Vertical arrows indicate the moments of light being switched on and off.

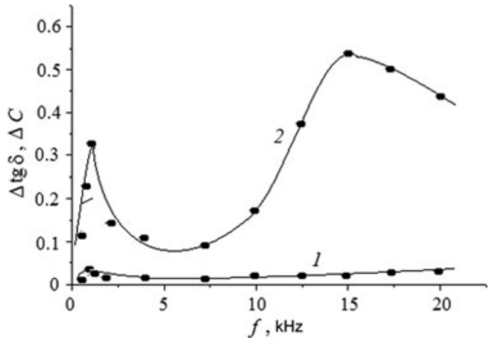

Figure 4. Plots of (1) Δ tanδ and (2) ΔC vs. frequency f for ITO-OGC/SQ-Al heterostructure exposed to the light of a red light emitting diode ($\lambda_{max} \sim 650$ nm).

positive sign on the ITO electrode. The curve 4 in Figure 3 shows the plots of j_{PH} versus t measured on exposure to the light and after switching off the light source.

It is also found that, after switching on the light, (i) the values of both tanδ and C increase in phase with the growth of V_{PH} and (ii) the dielectric characteristics exhibit recovery. However, the Δtanδ and ΔC values significantly depend on frequency f (Fig. 4) and these dependences have two maxima.

It was also observed that non-equilibrium electrical charge is formed in the investigated samples (when their electrical contacts were shorted) during prolonged illumination and it relaxes for a rather long time after switching off the light. This space charge can be leveled by applying an external electrical field. Figure 5 shows the buildup (curve 1) and relaxation (curve 2) kinetics of Q. These kinetics correlate with the kinetics of the corresponding V_{PH} changes (Fig. 3, curve 4).

It can be suggested that exposure of OGC/SQ heterostructures to the visible light leads to photogeneration of charge carrier pairs in the SQ layer, with their subsequent dissociation into free carriers responsible for the photoconductivity. The photoconductivity current can be driven by an external voltage source or by a difference in the work functions of ITO and Al electrodes. The asymmetric current–voltage (I–U) characteristic and positive sign

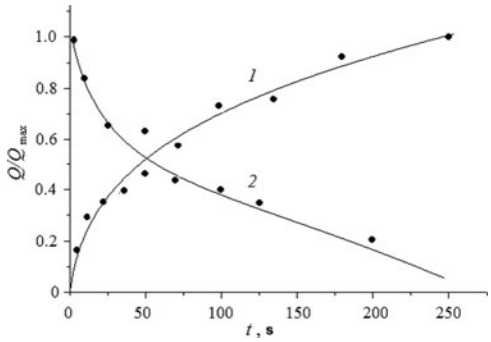

Figure 5. Normalized kinetic curves of buildup (curve 1) and relaxation (curve 2) of Q (where the illumination time $t_1 = t$, the time after switching off light $t_2 = 0$ - in the Q buildup case; and $t_1 = 300$ s = Const, $t_2 = t$ - in the relaxation of Q case according to the procedure for measuring Q described by diagrams in Figure 1, respectively).

of the photovoltaic response on the ITO electrode (Fig. 3) are indicative of the presence of a p–n junction in the investigated structures. This p–n junction occurs at the interface between OGC and SQ layers, since OGC always possesses p-type conductivity, while the SQ layer can exhibit both p- and n-type conductivity. The formation of a photodiode I-U characteristic, fast photocurrent kinetics at negative voltage on the ITO electrode, and the appearance of photovoltage (Fig. 3) can be explained by the transfer of non-equilibrium holes from the SQ to OGC layer with their subsequent transport to the ITO contact and the transport of non-equilibrium electrons in the SQ layer to the Al contact. This mechanism is operative provided that an electron from the highest occupied molecular orbital (HOMO) of carbazole fragments in the OGC layer can pass to the vacant HOMO of an excited dye molecule in the SQ layer. Therefore, non-equilibrium positive charge carriers (holes) responsible for the photoconductivity in OGC can be generated upon light-induced excitation of SQ molecules in the deposited solid film. The growth and relaxation of photovoltaic response V_{PH} upon the light being switched on and off, respectively (Fig. 3), is characterized by slow kinetics with a relaxation time constant, which is more than ten times greater than the time constant of j_{PH} relaxation during the photoconductivity measurements in strong electric fields. This can be explained by a low mobility of non-equilibrium holes in the OGC layer, which is below 10^{-6} cm^2/(V·s) at low field strengths E [14], and increases exponentially with increase in the applied external electric field strengths E. Upon the separation of non-equilibrium charge carriers generated due to the internal photoeffect in the SQ layer, the non-equilibrium holes move with small velocities in the OGC layer. The non-equilibrium electrons can be characterized by different mobility values (probably the electrons have the larger mobility in the SQ layer). This corresponds to the two maxima in the dependences of $\Delta\tan\delta$ and ΔC on frequency f of the applied alternating voltage (Fig. 4). As the frequency increases, the charge carriers accelerate their motion toward one electrode and then return with the same velocity to the opposite electrode. However, at high frequencies f, the mobility of non-equilibrium charge carriers does not follow the electric field changes.

It is interesting to note the existence of the dark voltage V_d ($\sim$180 mV) on the electrical contacts of the investigated heterostructures even without preliminary excited light illumination of samples (Fig. 3, curve 4). This fact can be explained at least by a geometrical ordering of SQ dye molecules in the SQ layer (the SQ molecule has a non-zero dipole moment), or electrical space charge appearance at the interlayer heterostructure interfaces. The last case can be realized by the charge carriers thermogeneration in the SQ layer and their following capture on the deep traps (in particular) at the SQ/OGC interlayer interface. The deep traps existence confirmed by the slow character of photocurrent kinetics (curve 2 in Fig. 3) and non-equilibrium space charge Q appearance under light illumination of the heterostructures (Fig. 5).

Conclusions

The new heterostructures based on SQ dye film deposited onto a OGC film have been created, and their photoconducting, photodielectric, and photovoltaic properties have been studied. The OGC/SQ heterostructures exhibit the photodiode properties. Although the obtained film heterostructures do not exhibit high photovoltage, the OGC/SQ system may serve a prototype for new materials involving organic dyes in charge photogeneration and transport layers and also as model photovoltaic media. The observed effect of "memory" of previous light exposure of the heterostructures samples could be useful for the designing of new materials for information recording media and optoelectronics.

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