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The kinetics of photoelectric processes near interfaces of C_{60}/liquid crystals

O.P. BOIKO, YA. I. VERTSIMAKHA[*]

Institute of Physics, National Academy of Sciences of Ukraine,
Prospekt Nauki 46, 252022, Kyiv, Ukraine

The interface between vacuum deposited C_{60} fullerene films and layers of nematic liquid crystals (LC), such as pentylcyanobiphenyl (5CB) or the BL055 mixture has been studied. In order to understand the processes of barrier formation at the C_{60}/LC interface, the kinetics of the dark current, short-circuit photocurrent and photovoltage caused by short pulses of light (~60 sec, $h\nu = 1.88$ eV) were investigated. Initial barrier height at the C_{60}/LC interface and its increase caused by ion diffusion to electrodes under the action of an internal electric field or light are determined. A fast component of the short-circuit photocurrent and photovoltage was observed. This component was probably due to the presence of a partly filled acceptor-like deep electron level associated with an interaction between C_{60} molecules and oxygen. The occupancy of the local states depends on molecular interactions at the interface. Their effect on the processes of ionic polarization and depolarization is discussed.

Key words: *fullerene C_{60}; liquid crystal; interface; photocurrent*

1. Introduction

Heterostructures (HS) formed by fullerenes and liquid crystals (LC), with a potential barrier at their interface, represent a new type of systems that can be applied in optical devices such as spatial light modulators [1]. To make their application possible, the mechanism of formation and properties of the potential barrier at the fullerene-LC interface has to be known.

The formation of potential barriers at interfaces between liquid crystals and organic or inorganic media, in contrast to solid-state structures, depends on the material properties of the photosensitive layer, on effects of ionic polarization and on the diffusion and deposition of ions on the electrode and photosensitive film surfaces. Due to all these factors, simple measurements of steady-state (time-averaged) characteris-

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[*] Corresponding author, e-mail: yavertsi@iop.kiev.ua.

tics of heterostructures do not allow one to separate nor analyze these different contributions.

In order to determine the mechanism and features of potential barrier formation near the interfaces, we have studied the kinetics of dark current (I), short-circuit photocurrent (I_{sc}) and photovoltage (V) in HS consisting of C_{60} and nematic LC (5CB and BL055) under irradiation with pulses of a red LED ($h\nu = 1.88$ eV).

2. Experimental

Films of C_{60} were prepared by thermal vacuum deposition (10^{-3} Pa) onto glass substrates, coated with conductive (180 Ohm/cm^2) and transparent (80%) SnO_2 layers deposited by the pyrolytic technique. The substrate temperature was 300 K. The resulting C_{60} layers consisted of hexagonal crystallites with Wurtzite structure in which the *C*-axis was oriented perpendicular to the substrate. The thickness of the C_{60} films was controlled by an actuator and was equal to 400 nm.

Structures containing undoped LC and LC doped with C_{60} with symmetrical ohmic SnO_2 electrodes were also prepared for comparison. Dielectric spacers ten microns thick set the thickness of the LC layers.

Measurements of the time evolution of I, I_{sc} and V were carried out with an electrometric DC amplifier, their values being recorded by a computer every 250 ms. The amplifier allows both I_{sc} measurements (time constant < 1 ms) and V measurements (time constant < 0.5 s) to be carried out. An external voltage was supplied with a calibrated voltage source. In order to study the processes of depolarization (trapping and recombination of charge carriers) after the illumination of the sample or after a voltage pulse (duration of ca. 60 s), the sample was connected directly to the amplifier input and the kinetics of current decay and depolarization voltage were measured.

3. Results and discussion

3.1. Dark current kinetics and C–V characteristics

It should be first noted that to diminish the influence of charge carrier injection [2] and conventional currents [3] which are usually observed for voltages higher than 3–6 V [2, 3], the measurements were carried out in the voltage range up to 2 V. The contribution of potential barriers is usually maximal in this voltage range; at higher voltages, the barriers are compensated by an external electric field.

In the control cells consisting of undoped LC and symmetrical SnO_2 electrodes, after an external voltage impulse U is applied the dark current I rises rapidly to a value I_0 and then, due to polarisation processes (the motion of ions to electrodes), slowly (30–60 s) approaches a steady-state value I_s (Fig. 1, curve 1), as observed earlier

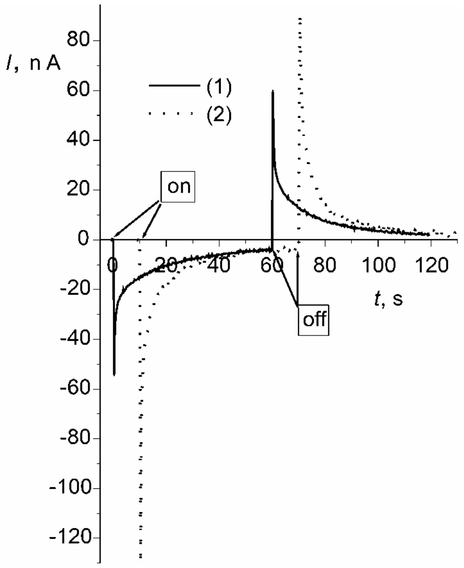

Fig. 1. Kinetics of the dark current in symmetrical 5CB LC cells (1) and C_{60} solution in 5CB (<0.17 wt. %) (2) under applied voltage of 0.4 V

[4, 5]. The half-time of the decay was ca. 4 sec for cells with 5CB, and ca. 3 sec for those with BL055. The dependence of I_0 on voltage is practically linear for these cells (Fig. 2a, curve 1), i.e. no observable potential barriers form on the SnO_2/LC interfaces.

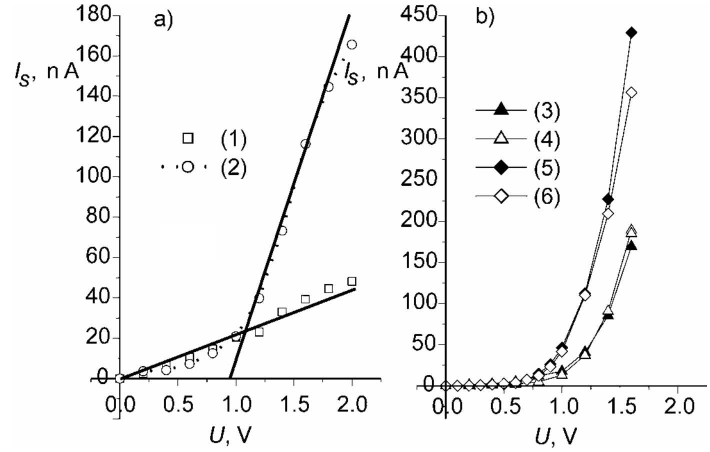

Fig. 2. Steady-state dark current–voltage characteristics in: a) symmetrical LC cells with 5CB (1) and C_{60} solution in 5CB (<0.17 wt. %) (2); b) heterostructures C_{60}/5CB (3, 4) and C_{60}/BL055 (5, 6) for positive (3, 5) and negative (4, 6) polarity on LC

The dark current kinetics of C_{60}/LC HS is generally similar to the kinetics of LC cells with ohmic SnO_2 electrodes, although both the initial (I_0) and steady-state (I_s)

currents, and also their relaxation times, depend on the value of U and its polarity. For voltages up to 1.5 V of both polarities the dependence $I_0(U)$ has a poorly expressed exponential character, being almost symmetrical (weakly depending on the polarity of U). It is similar to characteristics of two counter-connected equivalent diodes with a large series resistance r_s. At voltages between 1.5 and 2.0 V, $I_0(U)$ becomes almost linear, allowing r_s to be estimated. For the structures studied, $r_s \cong$ (10–40) MOhm. An extrapolation of the linear part of $I_0(U)$ gives a cut-off voltage of 0.35± 0.05 V for HS with BL055 and ca. 0.2 V for HS with 5CB. One may thus estimate the initial band bending (initial barrier height, Y_0) to be in the range of (0.2–0.4) eV.

The voltage dependences of steady-state current (I_s) are clearly exponential in HS of both 5CB and BL055 (Fig. 2b). Extrapolation of the linear parts of $I_s(U)$ dependences yields cut-off voltages of 1.03 ('+' on LC) and 1.07 V ('–' on LC) for C_{60}/BL055 HS, and 1.10 and 1.15 V for C_{60}/5CB HS. The obtained cut-off values are probably approximately equal to the sum of the barrier heights in these HS. This is equal to a first approximation to the sum of the initial barrier height in the darkness before supplying external voltage Y_0 and an additional band bending Y_p. The latter are formed due to the diffusion and adsorption of ions on the electrodes, usually called as the polarization process [4]. The total barrier in C_{60}/LC is more than 3 times higher than that obtained for CdSSe/BL055 HS [5].

Most surprising for us was the fact that $I_s(U)$ was almost symmetrical, although the C_{60} layer was deposited onto one electrode only. It was thus supposed that $I_s(U)$ would be asymmetrical, as earlier observed for CdSSe/LC HS [5]. An analysis of possible reasons for this feature has shown that it was most probably caused by a poor solubility of C_{60} in LC, which we were unable to observe earlier. After the cell preparation, a part of the C_{60} molecules diffused from the film to the LC and then precipitated on the opposite 'clean' SnO_2 electrode (on which we did not deposit any C_{60} layer). Naturally, the precipitation process would occur only when there is no quasi-stationary equilibrium. Before this equilibrium established, part of the molecules in the LC layer formed ions or charged complexes consisting of C_{60} and LC molecules. This model seems to be confirmed by an increase of I_0 (in the cells containing LC doped with 0.17 wt. % of C_{60} it is 2.4 times larger than in those containing undoped LC – cf. Fig. 1, curve 1).

Since C_{60} molecules are strong acceptors (trap centres for electrons) [6], it is reasonable to assume that the concentration of negative ions will increase in the LC layer. Therefore, potential barriers of practically identical height but of opposite polarities are formed at both electrodes of HS.

To check experimentally our hypothesis, we measured $I_s(U)$ characteristics in a cell with two symmetrical SnO_2 electrodes, between which LC doped with <0.17 wt. % of C_{60} (maximum solubility at 300 K) was placed. The measured $I_s(U)$ dependence for such a cell, presented in Fig. 2a (curve 2), is almost symmetrical and has an exponential character, which confirms our suggestion. The cut-off voltage for this dependence $Y \cong 0.95$ V, i.e. is only 8–15% smaller than the cut-off for the HS in which the C_{60}

layer is deposited by thermal vacuum evaporation. The difference may be caused by differences between the structures of a layer deposited by vacuum evaporation and formed as a result of C_{60} precipitation onto the surface of SnO_2 electrodes.

4. Photovoltaic properties

The main attention in the present study was given to measurements of current kinetics, since the time constant of the measuring device is small in this mode (<1 ms) and transitional processes can be recorded more clearly.

A typical I_{sc} kinetics measured in a C_{60}/LC HS under the excitation with a pulse of 'red' LED ($h\nu$ = 1.88 eV) is shown in Fig. 3a, b. I_{sc} kinetics for CdSSe/BL055 HS are also shown for comparison (Fig. 3c).

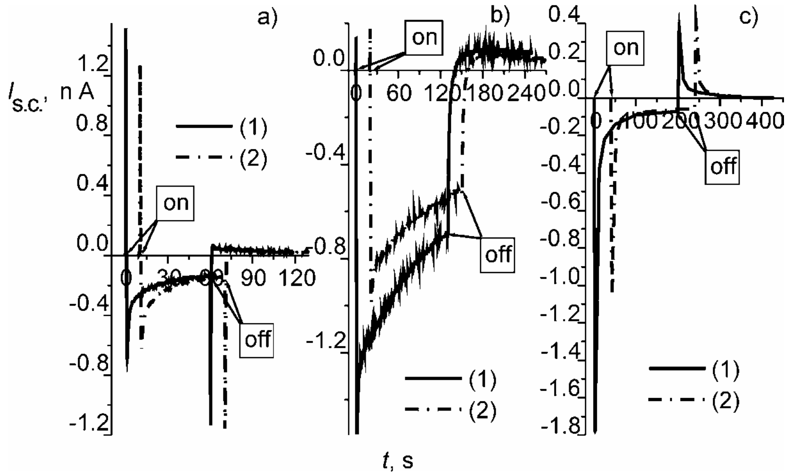

Fig. 3. Kinetics of the photocurrent in heterostructures C_{60}/BL055 (a), C_{60}/5CB (b) and CdSSe/BL055 (c) under illumination ($h\nu$ = 1.88 eV) through LC (1), C_{60} or CdSSe (2)

It can be seen that the presence of an I_{sc} peak with a '–' on the illuminated surface (independent of the illumination direction) and the following slow decrease with the decay time of 20 sec (for HS with BL055) and 100 sec (for HS with 5CB) is common to all these HS. We were not able to record I_{sc} for the structure with symmetrical SnO_2 electrodes, since LC does not absorb this light.

The peculiarity of C_{60}/LC is the presence of a fast short circuit component of opposite sign (I_{scb}). The rise and fall times of I_{scb} are both approximately 1 sec. The peak I_{scb} value for C_{60}/BL055 HS (Fig. 3a) is almost 5 times greater than for C_{60}/5CB HS (Fig. 3b), i.e. I_{scb} strongly depends on the LC material.

The presence of I_{scb} in C_{60}/LC HS may be caused by the formation of acceptor-like deep electron levels (filled in the darkness) in C_{60} (near the C_{60}/LC or SnO_2/C_{60} interface), which according to [6] (Fig. 4) are situated at 0.8 eV under the conduction band

and are probably due to interactions of C_{60} molecules with oxygen. Upon illuminating the C_{60} layer carriers are released from these centres. Consequently the concentration of trapped electrons decreases and therefore the I_{scb} signal decreases. A decrease in the occupancy of this impurity level will naturally cause a shift of the quasi-Fermi level resulting in a fast increase of Y_0. Naturally, the position of the Fermi level at the C_{60}/LC interface will depend on the interaction of LC with the C_{60} film surface and even its small shift will strongly change the occupancy of this level and consequently the peak value of I_{scb}. This may explain the smaller value of I_{scb} in C_{60}/5CB HS (Fig. 3b). This acceptor-like level is probably localized near the C_{60}/LC interface, since oxygen is adsorbed on the film surface after its preparation. Consequently, the concentration of adsorbed oxygen molecules and their complexes with C_{60} molecules will be larger on the free surface of C_{60} film.

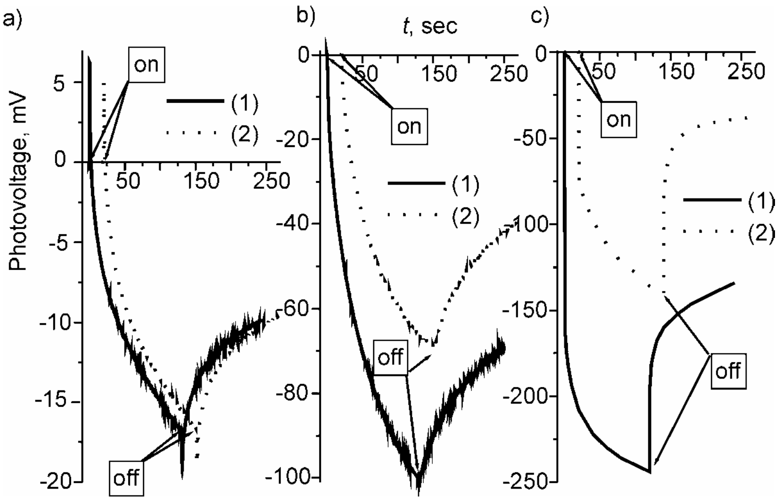

Fig. 4. Kinetics of the photovoltage in heterostructures C_{60}/BL055 (a), C_{60}/5CB (b) and CdSSe/BL055 (c) under illumination ($h\nu$ = 1.91 eV) through LC (1), C_{60} or CdSSe (2)

To verify whether such an impurity level is indeed formed in our structures, we carried out measurements of the surface conductivity of C_{60} layers in vacuum and in the ambient atmosphere. The specific resistance of the layers in the darkness in vacuum is of the order of 10^{10} Ohm·cm. In the air, due to oxygen adsorption on the free surface of films, their resistance slowly increases by more than 2 orders of magnitude, and the photocurrent decreases, in agreement with the literature data [6]. After air is pumped out, only a partial reversibility of dark resistance and photocurrent is observed, i.e. deep trapping centres (probably charge transfer complexes between C_{60} molecules and oxygen) remain. This result confirms that the formation of acceptor-like levels acting as deep trapping centres on the surface of the investigated C_{60} films can indeed take place.

As was shown in the previous sections, it follows from the analysis of $I(U)$ dependences that blocking barriers are formed near both electrodes in the studied C_{60}/LC HS and the measured structures are similar to two counter-connected diodes. In this case, I_{sc} recorded by the meter is:

$$I_{sc} = A(d_1 - \gamma_1 d_2) \tag{1}$$

where A is a constant proportional to the quantum efficiency of the charge carrier photogeneration and to absorbance (practically equal for deposited and precipitated layers), d_1 is the thickness of the illuminated layer, d_2 – the thickness of the layer near the opposite electrode, and γ_1 – the coefficient of the decrease in light intensity on the opposite electrode due to its absorption in the first layer and scattering in the LC layer.

Analogously, the measured value under the illumination of the opposite electrode is:

$$I^*_{sc} = A(d_2 - \gamma_1 d_1) \tag{2}$$

We do not know the thickness of the precipitated layer formed due to diffusion from the LC layer onto the ‘clean’ electrode. To estimate it, we have measured I_{sc} for the cell with two symmetrical SnO_2 electrodes, between which LC doped with <0.17 wt. % of C_{60} was placed, and for which the C–V characteristic is exponential (Fig. 1b). The value of I_{sc} in these structures was more than two orders smaller than that for HS. This is evidence that $d_2 << d_1$ and that the influence of the precipitated layer in I_{sc} formation can be neglected during the further analysis of photovoltaic properties.

A slow decrease of I_{sc} is observed after reaching the peak value (Fig. 3). A similar decrease is observed in the kinetics of dark current (Fig. 1). The decrease of both I_{sc} and dark current can be explained by the diffusion of LC ions towards the electrodes and their separation by the intrinsic field of the initial barrier [4, 5]. It is obvious that the concentration of ions due to their transport to the electrodes will decrease and simultaneously the additional intrinsic electric field near the electrodes will increase. The decrease of ion concentration should lead to an increase in the differential resistance of the structure and a decrease of I_{sc}. To explain $I_s(U)$ dependences, we supposed that the barrier height Y and internal electric field increase due to ion diffusion, which in turn should lead to an increase in I_{sc}. From Fig. 1 it is clear that only a decrease in I_{sc} is observed in the studied HS, i.e. the main contribution to the process comes from an increase in structure resistance. Because of this, determining the direction of the internal electric field is impossible from I_{sc} kinetics alone.

Since the value of V does not depend on structure resistance, we have carried out a measurement of its kinetics to solve this problem (Fig. 4).

It can be seen that in both types of C_{60}/LC HS quasi-steady-state value of V has the same sign (negative at the illuminated surface). A slow increase in V is observed in all structures after reaching the maximal value of I_{sc}, i.e. the directions of the initial and additional electric fields (barriers) are the same.

It is possible to estimate the ratio of the heights of the initial barrier and an additional one, created by ion diffusion (Y_0/Y_p) by measuring the ratio of fast and slow components of V, built up under the illumination through LC layer. The Y_p/Y_0 ratio is 0.7–0.8 for C_{60}/LC HS (for comparison, it amounts to 0.5 for CdSSe/BL055 HS), being in good agreement with the data obtained from an analysis of the dark current –voltage characteristics. This confirms that the contribution of ion diffusion is dominant in the formation of internal electric fields in the studied HS.

5. Depolarization processes

After the sample has been biased with a voltage, a drift of ions initially concentrated near the electrodes towards the middle of the LC layer is initiated. Ions partially recombine with ions of opposite charge drifting in the opposite direction. Due to this, a current in the opposite direction arises (the depolarization current, I_d [4]) with a time constant τ_d close to, but not equal to, the time constant of polarization τ_p. Naturally, the ratio of the charge that is released during the depolarization (Q_d) to that trapped during the polarization (Q_p) cannot exceed unity, although this does not mean that the peak value of I_d cannot be larger than the peak value of the depolarization current $I_p = (I_0 - I_s)$. On the contrary, if $\tau_d < \tau_p$ (as in the case, e.g., of CdSSe/LC HS) then I_d/I_p can be > 1. Therefore, the efficiency of recombination can be correctly estimated if the ratio Q_d/Q_p is known.

Typical kinetics of dark current are shown in Fig. 1. In symmetrical LC structures undoped and doped with C_{60}, both I_d and Q_d are practically independent of the polarity and are proportional to U at $U < 1$ V. They also tend to saturate at higher voltages, while Q_p practically linearly depends on U. I_d and Q_d also tend to saturate at $U > 1.2$ V ($eU > Y$), while Q_p superlinearly depends on U at these voltages. Due to this, the ratios of Q_d/Q_p and I_d/I_p markedly decrease in all structures when U increases in the range $U > 1$ V. Therefore, the efficiencies of polarization and depolarization in the different studied structures can be correctly compared using parameters obtained at $U = 1$ V only. They are presented in Table 1.

It can be deduced from the values of the Q_d/Q_p ratio that 80% of the ions recombine and/or are trapped in deep capture centres during polarization in LC structures with ohmic electrodes and only 20% of them reach the opposite electrode in these structures. Even higher fractions of ions (c.a. 90%) recombine or are trapped by deep capture centres in HS. An observed rise in the efficiency of recombination and trapping of ions in HS can be explained by the presence of intrinsic electric fields.

Depolarization processes have also been observed in HS after the illumination was switched off, as is well seen in Fig. 3. The decay of the depolarisation current in this case (hereafter denoted I_{sd}) is similar to that of I_d after switching off the voltage. Thus one can formally use the same formalism to characterize the kinetic processes. In the following, we shall employ the same parameters marked additionally with the subscript s.

Table 1. Parameters characterizing processes of polarization and depolarization for LC cell and HS under 1V voltage pulse in dark

Parameters	Structure								
	BL055	CdSSe/BL055		C_{60}/BL055		% 5CB	5CB + 0.1% C_{60}	C_{60}/5CB	
U sign	±	+LC	–LC	+LC	–LC	±	±	+LC	–LC
I_0, nA	4.67	8.40	5.27	290	284	150.8	190	62	57
I_s/I_0	0.27	0.11	0.03	0.16	0.15	0.09	0.08	0.28	0.23
$(I_0 - I_s)/I_0$	0.73	0.89	0.97	0.84	0.85	0.91	0.92	0.71	0.77
Q_p/Q_0	0.96	0.78	0.90	0.76	0.81	0.84	0.81	0.65	0.72
$I_d/(I_0 - I_s)$	0.59	0.97	1.10	1.16	1.23	0.56	1.09	1.12	0.99
Q_d/Q_p	0.20	0.07	0.07	0.05	0.05	0.14	0.17	0.11	0.08

It should be noted that the efficiency of depolarization I_{scb} (current of electrons detrapped from the surface level upon illumination) and I_{sc} (which is mainly ionic current) differ greatly. 85–90% of the photoexcited electrons in C_{60}/BL055 HS are retrapped probably by the same centres (Fig. 3a). The parameters obtained for ion depolarization are presented in Table 2.

Table 2. Parameters characterizing processes of polarization and depolarization for HS under illumination with a red LED ($h\nu = 1.88$ eV)

Structure	CdSSe/BL055		C_{60}/ BL055		C_{60}/ 5CB	
Illuminated side	LC	SnO_2	LC	SnO_2	LC	SnO_2
I_{s0_2}, nA	1.78	0.10	690	624	1541	983
I_{ss}/I_{s0_2}	0.04	0.06	0.19	0.22	0.45	0.51
$k_p = (I_{s0} - I_{ss})/I_{s0}$	0.96	0.94	0.81	0.78	0.55	0.49
Q_p/Q_0	0.90	0.95	0.72	0.66	0.40	0.34
$k_d = I_{d0}/(I_{s0} - I_{ss)}$	0.22	0.43	0.12	0.14	0.10	0.14
Q_d/Q_p	0.019	0.026	0.06	0.08	0.105	0.14

A comparison of ion polarization and depolarization parameters in LC structures and in HS under the action of electric field or light impulses (Tables 1 and 2) reveals that in the latter case, about 90% of ions recombine or become trapped during the depolarization in HS. However, the rate of depolarization in this case is noticeably smaller ($\tau_{ds} > \tau_d$). This effect can be due to the diminution of the capture efficiency of nonequilibrium carriers by trapping centres. This probably stipulates the attenuation of polarization processes (decrease of Q_p/Q_0 ratios) upon excitation by light.

6. Conclusions

The initial bands bending of ca. 0.35 eV exists in C_{60}/LC HS. This value increases up to (1.0–1.1) eV due to ion transport to electrodes after applying an external field. The presence of even a small amount of C_{60}, whose solubility in LC is of the order of ca. 0.1 wt. % in the studied structures, leads to the diffusion of C_{60} from the deposited layer in LC and their precipitation on the opposite SnO_2 electrode. This results in the formation of almost symmetrical HS after cell preparation with almost the same potential barrier heights near both electrodes. Hence the dependences of current on the external voltage in the darkness become exponential and almost symmetrical, and ion concentration in LC increases.

Another peculiarity of C_{60}/LC HS is the appearance of a fast component in the short-circuit photocurrent and photovoltage, caused by a change in the occupancy of acceptor-like deep electron levels, whose presence is due to interactions of C_{60} molecules with oxygen. The occupancy depends on the interaction of LC molecules with C_{60} molecules near the interface.

80% of the charges recombine and/or become trapped in deep levels during the process of depolarization in LC structures with ohmic contacts. The efficiency of this process increases to 90% in HS, practically independently of the excitation method (illumination or external electric field).

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