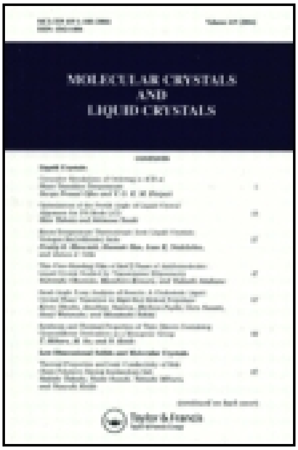

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Photoelectrical Processes Near Interface of Molecular Crystals and Liquid Crystals

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Photoelectrical Processes Near Interface of Molecular Crystals and Liquid Crystals

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Photoelectric properties of heterostructures consisting of deposited films of an inorganic semiconductor (IS) – CdSSe or molecular crystals (MC) with different molecular structure (phthalocyanines of Pb, ClAlCl) and nematic liquid crystal BL055 have been studied.

The main attention was given to the effect of MC molecular structure on the creation of potential barriers at MC/LC interface in heterostructures and effect of them on processes of polarization by strong absorbed light excitation and external constant electric field of different polarity.

Keywords: interface; heterostructure; phthalocyanines; C-V characteristics; polarization

INTRODUCTION

The interest to the investigation of heterostructures (HS) of photosensitive inorganic semiconductors (IS) and molecular crystals (MC) with liquid crystals (LC) is caused by necessity to understand features of the creation of potential barriers on their interface and use of them for the operation of parameters of spatial photomodulators [1].

The analysis of the literature data has shown, that formation of barriers on such interface both energy structure of IS and MC ,and an ionic polarization, changes of orientation of LC molecules director under the action internal and external electric fields, processes of diffusion and deposition of ions on a surface of an electrode and photosensitive film, play an important role. The efficiency of the diffusion processes in LC is much higher than that in solids.

Therefore the purpose of this study was to research features of effects of ionic polarization in IS (MC) - LC HS by photoelectric methods.

EXPERIMENTAL

Photosensitive HS layers were prepared by vacuum deposition of CdSSe, ClAlClPc, PbPc (at 10^{-3} Pa) on glass substrates pyrolytically coated by conductive (180 Ohm / cm^2) and transparent (80 %) SnO_2 layers. Temperature of substrate was 570 K during CdSSe deposition for obtaining the stable and well oriented layers, and for ClAlClPc and PbPc layers corresponding temperature was 300 and 393 K. A contents of S in CdSSe was nearly 0,6. Obtained CdSSe layers consist of hexagonal crystallites with orientation of an axis C perpendicularly substrate. For increase of a photosensitivity of CdSSe layers they quenched in $CdCl_2$+$CuSO_4$ vapours at 770 K during one hour, and ClAlClPc, PbPc in air at 370 K during 3 hours. It has allowed simultaneously to decrease speed of surface recombination of charge carriers on a free surface of CdSSe [2].

LC layer thickness was set by 10 microns teflon spacers.

The kinetics of a short-circuit photocurrent (I_{sc}) and kinetics of a photovoltage (V) of IS (MC) – LC HS was researched at excitation from different sides by the impulse of strong absorbed the light diode with hv=1,88 eV. The measurements I_{sc} and V were provided with the help of an electrometer with recorder. Electrometer in different modes measures a short-circuit current ($R < 100R_{gs}$) and measurement of V ($R > 100R_{gs}$), at time constant τ=0.1 sec.

The study of kinetics of dark current for HS and LC sample with symmetric SnO_2 ohmic electrodes was conducted by the external field impulse of the different value and polarity, for the determination of parameters of the interface and processes of the polarization. The field was supplied from the source (range of the source 0.01-300 V with step of digitization 0.01 V). The kinetics of a dark current was measured by the mentioned above electrometer and recorder. The field was supplied with impulse by duration of 60 sec then the sample short-circuited and the kinetics of the current of depolarization was measured.

RESULTS AND DISCUSSION

Dark current kinetics of 50 microns LC cell (0,5 MBBA + 0,5 EBBA nematic mixture) with symmetric SnO_2 electrodes were studied in [3]. After initial fast increase of current up to I_0, current decrease to stationary I_s value was observed. This decrease was explained by bulk charge creation and caused by ionic polarization voltage with value $U_p \approx 1,7$ V (0,37 from value of the initial), which reduces of external field. The part of entrapped charge (0,3) in sample at polarization is released at turn off of external power and reduces in origin of a current of depolarization Id of an opposite polarity. The mechanism of the process of polarization and Up direction were not defined. It is stated the increase of resistance of a sample during polarization, which is characterized by the parameter α [4], defined from the obtained data about transition currents, and was 3,75

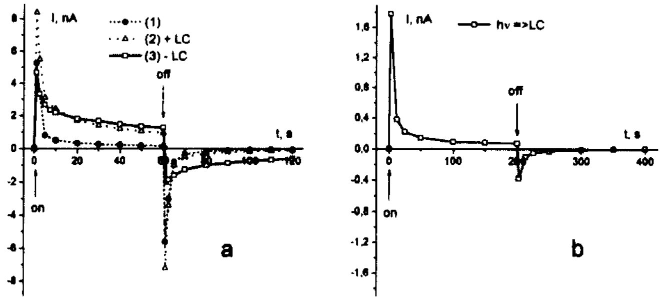

FIGURE 1 Kinetics of dark current for LC sample (1) and under external electric field (U=0.2V) of different polarity (2,3) for CdSSe/LC heterostructure (a) and short -circuit photocurrent kinetics by strong absorbed red light excitation (hv=1.8eV) (b) for above HS.

We observed similar behaviour of dark I for the cell with BL055 nematic mixture independently on polarity of power supplied (Fig. 1a, the curve 1). Determined by the same technique U_p was nearly 0,6 V (0.6 from initial value of supplied field) and $\alpha \approx 1{,}45$, but I_d/I_0-I_s value was sufficiently greater (table 1a). Polarization potential determined by the method not taking into account migration of ions [5] is U_p=0.73V (0.73 from value of supplied field). Therefore, the process of polarization in BL055 has more expressed character, that can be caused by the smaller concentration of unmonitored ions in our cells than used in [3], as the currents, registered by us, were on 3 order less.

The kinetic of dark current in HS is qualitatively similar to its kinetic in LC cell with symmetric SnO_2-electrodes, however the presence of IS or MC layer strongly reduces the dependence as values I_0, I_s and I_d, and times of their relaxation τ_p and τ_d, from polarity of the

TABLE I. Parameters characterized processes of polarization and depolarization for LC cell, IC/LC cell, and MC/LC cell by action of constant current pulse in darkness (a) and under HS illumination (IC, MC excitation) by strong absorbed light (hν=1,8 eV) (b).

a

Structure	LC	CdSSe/LC		ClAlClPc/LC	
Parameters		+ LC	- LC	+ LC	- LC
I_0,nA	4.67	8.40	5.27	21.6	43.5
I_s,nA	1.27	0.95	0.17	6.2	17.5
I_d/I_0-I_s	0.59	0.97	1.10	1.17	0.97
$k_p=I_0-I_s/I_0$	0.73	0.89	0.97	0.71	0.60
$k_p{}^*=I_d/I_d+I_s$	0.61	0.88	0.97	0.75	0.59
α	1.43	1.03	0.91	0.89	1.02
Q_p/Q_0	0.96	0.78	0.90	0.57	0.52
Q_d/Q_p	0.20	0.07	0.07	0.34	0.35
τ_p,sec	34	20	12	34	19
τ_d,sec	39	3	3	19	22

b, (positive value on illuminated electrode)

	hν>LC	hν>SnO_2	hν>LC	hν>SnO_2
I_{s0},nA	1.78	-0.10	0.70	+0.63
I_{ss},nA	0.07	-0.006	0.04	-0.05
$I_{sd}/I_{s0}-I_{ss}$	0,22	0,43	0,79	0,81
$k_p=I_{s0}-I_{ss}/I_{s0}$	0,96	0,94	0,94	0,92
$k_p{}^*=I_{sd}/I_{sd}+I_{ss}$	0.84	0.87	0.93	0.90
α	3.96	2.17	1.25	1.5
Q_p/Q_0	0.90	0.95	0.79	1.09
Q_d/Q_p	0.019	0.026	0.025	0.009
τ_p,sec	33	36	242	109
τ_d,sec	19	16	34	29

* - ions migration taken into account

supplied voltage U. Most strong dependence from polarity U is observed for I_s. This value as a rule is more greater when to supply on LC the power of such polarity, which causes the injection of major charge carriers from IC or MC in LC, i.e. depends on a type of conductivity of semiconducting layer. Therefore the I_s ratio at different polarity U reaches 3 in HS based on ClAlClPc and PbPc, and in HS based on CdSSe - even 6. This leads to Up increase in HS based on IS (table 1a). A current-voltage characteristic of I_s (Fig. 2a, the curve 2) is typical for diodes with great series resistance. The extrapolation of a linear part I_s (U) dependence gives the value V_b=0,4 V of barrier height at CdSSe/LC interface, and V_b < 0,2 V of ClAlClPc/LC interface one. Obtained for CdSSe/LC HS V_b close to V_b value for CdS/MBBA GS.

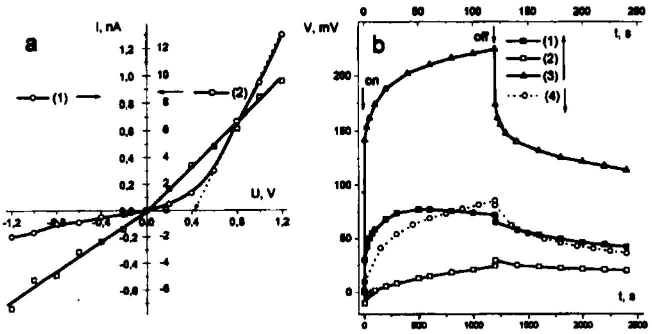

FIGURE 2 C-V characteristics for peak (1) and stationary (2) values of current (a) and photovoltage V kinetics for ClAlClPc/LC (1,2), CdSSe/LC (3) and PbPc/Lc(4) heterostructures by strong absorbed red light excitation (hv=1.8eV) through LC layer (2,3,4) and SnO_2 electrode(1) (b).

I_{sc} kinetics under illumination of HS by the impulse of strong absorbed light (Fig 1b,curves 3) is similar to the kinetics for constant U impulse (Fig. 1b, curves 1,2). However I_0, I_s and I_d values strongly depend on the direction of illumination (table 1b). Since light practically can not transmit through a photosensitive layer to the opposite side of IC or MC film, the Isc value under HS illumination from the side LC will be defined by the height of barrier at the CdSSe (ClAlClPc) /LC interface (SnO_2/CdSSe (ClAlClPc) – for opposite side illumination).SnO_2-electrodes form ohmic contact with CdSSe [5], and form small barrier with PbPc and ClAlClPc (Vb=0,1 eV) [5]. Therefore observable I_{sc} ratio under the illumination from different sides is 17,6 for HS based on CdSSe and only 1,5-2 for HS based on phthalocyanines. The obtained values well correlate with the V_b value, estimated from I_s (U)dependence.

The V kinetic in HS researched (Fig. 2b) differs from I_{sc} kinetic (Fig. 1b),- after an initial jump the smooth increase is observed in all cases. At turn off of light, V of the opposite sign is not observed, and there are fast and then slow components of drop. The V kinetics is similar to kinetics of an electric moment of polarization in dielectrics [4].

The different character of V and I_{sc} kinetics testifies, that the direction of internal electric field and the fields of polarization in researched HS IS, MC/LC coincide. Therefore decrease I and I_{sc} by the action of constant external electric field or light impulses is caused mainly by increase of resistance of structures due to the probable formation of depletion layer at the creation of space charge during polarization.

Comparison of parameters of polarization and depolarization in LC and HS under constant electric field and light action (Table 1a and b) displays, that both deceleration of processes of ionic polarization and the decrease depolarized charge part occur at illumination by light. This can be caused by the decrease of the efficiency of nonequilibrium carriers of current trapping by deep centers.

CONCLUSIONS

Potential barriers with 0.2-0.4 eV height are formed at IS, MC interface with LC. Their height depend on the energy structure of inorganic photoconductors and molecular crystals.

The presence of internal fields at the interface of photoconductor with LC leads to strong dependence of an ionic polarization on polarity of external field and its amplification for that polarity, at which there is an injection of major charge carriers from semiconductors in LC.

The opposite view of kinetics of photoelectric of short-circuit and photovoltage testifies that directions of internal electric fields and field of polarization in researched HS are equal independently on type of semiconductor (p or n).

I and I_{sc} decrease under impulses of external electric field or light are due to mainly increase of the resistance of structures because of a formation of depletion layer at creation of space charge region during polarization.

The deceleration of processes of polarization and decrease of the part of depolarized charge occur at excitation by the impulses of strong absorbed light.

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