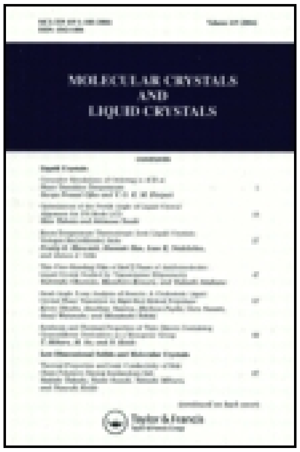

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Peculiarities Of Electronic Processes At Organic Photosensitive Films Interface And Prospectives Of Their Practical Application

Ya. I. Vertsimakha [a]

[a] Institute of Physics of NASU, Prosp. Nauki 46, 252028, Kyiv, Ukraine

To cite this article: Ya. I. Vertsimakha (1998): Peculiarities Of Electronic Processes At Organic Photosensitive Films Interface And Prospectives Of Their Practical Application, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 324:1, 57-64

To link to this article: http://dx.doi.org/10.1080/10587259808047134

Mol. Cryst. Liq. Cryst., Vol. 324, pp. 57–64
Reprints available directly from the publisher
Photocopying permitted by license only

Peculiarities Of Electronic Processes At Organic Photosensitive Films Interface And Prospectives Of Their Practical Application

YA.I.VERTSIMAKHA
Institute of Physics of NASU, Prosp.Nauki 46, 252028 Kyiv,
Ukraine

The peculiarities of potential barrier formation at the interface of organic photosensitive films (OPF) with metals and inorganic semiconductors (IS) are analyzed. The basic attention is given to the effect of an adsorption of oxygen, polymorphic modifications and processes of polarization arising due to the caption of nonequilibrium charge carriers in contact area of a space charge. In view of this the basic reasons for low efficiency of a solar energy conversion and possibility of their practical use are analyzed.

Gas detection by change of properties which depend on the parameters of the interface between OPF and metal or IS, allows one to improve the time of response and selectivity of sensors. The use of IS of CdS, CdSe type for creating a blocking barrier at the OPF interface allows one to increase the height of the barrier and sensitivity to gases several times.

Keywords: interface, organic photoconductors, potential barriers, photovoltaic properties, solar cells, molecular gas sensors.

Organic photosensitive films (OPF) are widely used for the development of solar cells (SC) [1], electrographic structures [2], gas sensors [3] and non-linear optical elements [4]. The progress in these areas is impossible without understanding the processes of barrier formation near OPF interface.

The absence of broken covalent bonds at OPF surface allowed us to hope that when gases adsorbed on their surface are absent, the formation of potential barriers at their interface with metals (M) will be defined by the difference in electron energies . However, the studies of dark current - voltage characteristics (C-V) for sandwich-structures (SS) obtained in high vacuum and measured under the same conditions have shown the absence of a space charge region (SCR) at the interface with metals [1]. The presence of oxide layers at the interface in the same conditions does not influence dark electrical properties of structures and does not result in SCR appearance[1].

However after the contact of these structures with air, and / or on measuring them in an atmosphere, C-V gain diode character, i.e. at interface the potential barriers are formed, which parameters are defined by thickness distribution of ionized impurity centers stipulated by the interaction of active adsorbed gases (mainly, oxygen) with organic molecules. The parameters of these potential barriers are different at upper and lower electrodes, that results in SC parameter distribution dependence on the lightening direction [5-7]. Under these conditions the presence of an oxide layer at the interface leads to capturing non-equilibrium charge carriers in the near surface region by «oxygen» centers and creating an internal electrical field directed towards the electric field which existed before illumination, near the electrode. It results in a significant (for SS with Al electrode) diminution of a stationary value of photovoltaic short-circuit current (Isc) under the nonmodulated illumination and most clearly it is observed on studying photovoltaic effects kinetics and Isc dependence on frequency modulation of exciting light [7]. The effect is exhibited most strongly in SS with blocking upper electrode from easy oxidized M (Al, Pb, Sn). It is one of the principal reasons of small efficiency of light transformation in electrical energy (η) by developed SC based on OPF, in which for creating a barrier, an easy oxidized Al-electrode is used. Even with using for creating at the barrier of the upper electrode from inoxidized Ni, the significant amount of trap non-deep centers of capturing nonequilibrum carriers noticeably reducing Isc is created, especially with high light intensities [6, 7]. The Schottky barrier with small concentration of such capture centers [6, 7] is formed only when the lower Ni-electrode is used. This limits a choice of metal electrodes for creating organic SC . Therefore for increasing potential barrier height it is expediently to use thin IS films, at which surface broken covalent connections fixing Fermi level are absent at near surface region (for example, A_2B_6)) [8]. Their principal virtue is a small rate of a recombination in SCR at interface[8].

In OPF structures photogeneration takes place in the SCR, thickness of which is very small (20-60 nм) [1, 9], and η strongly depends on a type of polymorphic modification (PM), which contents in most studies of OPF were not controlled. It is shown for CdSSe/Pentacene heterostructures that optimum thickness of OPF layer is equal to SPR thickness whereas optimum thickness of IS is equal to diffusion length of non-equilibrium carriers [8] . These two singularities of OPF as a rule were not taken into account with manufacturing organic SC and this is the main reason of small η and difference in the value of η for the same OPF in different papers.

Our estimations have shown, that by using optimum thickness of the most photosensitive PM of known OPF for SC preparation it is possible to achieve in the near future η→ 5 % with illumination AMO-2. However the possibility of their practical use will depend on effectiveness of the development of minimization methods of organic SC parameter degradation and monitoring of OPF O_2 doping level. The investigation of photovoltage., Isc and resistance dependences of the upper electrode R for unprotected and protected HS on time of storage in darkness shows great Isc increase and low V increase at small times and further V decrease [10]. The decrease of Isc and V, which is amplified by a strong rise of R, predominates with solar light illumination [10]. The observed degradation of the organic SC parameters is caused mainly by photochemical processes at the upper electrode, instead of bulk properties, as it was supposed earlier (under the same conditions the change of an absorption OPF fails to be registered). The presence of maxima on Isc (t) is caused by the existence of an optimum doping O_2 level. These processes in organic SC are rarely investigated nowadays.

In most cases different bulk property changes are used for gas registration though the time of their response for concentration of gas change is large [3,11], that is mainly defined by gas diffusion time through a film. Therefore for enhancement of the molecular sensor (MS) velocity rate it is necessary to reduce a thickness of a film [11] or to use, for gas detection, the change of properties stipulated by the presence of a potential barrier at the upper electrode organic SS [3].

It is shown experimentally that the diminution of a thickness of LB-films up to one monolayer (4 nm) allows one to reduce the time of the response to 10 s [12], and the time of changing the properties depending on parameters of interface metal / OS with O_2 adsorption of the order of 1s already for thickness OS 400 nм. The use of interface is still more prospective because with the use for Isc excitation of the modulated illumination it is possible, by a selection of frequency modulation, to increase selectivity and signal / noise ratio since frequency dependences of Isc on an air and in vacuum differ significantly. [13].

For optimization of MS operation the influence on Isc change of the material of the upper electrodes, PM, energies of quanta, frequency modulation of light , Y value on interface M / OPF (OPF/IS) during O_2 adsorption was investigated[13-14]. PM OS was set by the temperature of a substrate (Ts) during thermal deposition in vacuum and controlled with absorption spectra.

The analysis of our and literature data shows that during O_2 adsorption in polyacenes and phthalocyanines weak complexes with charge transfer (CTC) are formed that leads to the creation in them no less than two centers of a carrier capture with different depth and different times of relaxation. The processes connected with a «fast» center are completely reversible [3, 7].

The efficiency of CTC formation during O_2 adsorption depends both on a molecular structure OPF (for example, nature of central Pc atom), and on PM type. PM essentially influences the parameters (especially Y) of formed potential barriers in near elecrode region [14-16]. It was experimentally confirmed on an example of lead Pc (PbPc) SS that the PM change reduces in Y change in 6 times and even can change a zone bend direction near the surface. For quasiamorphous PM with a small Isc a change was observed under illumination of both light diodes. In SS triclinic PM the p increase results in essential increasing Isc, and the sensitivity of Isc for monoclinic PM is noticeably less and varies a character of dependence's. The maximum Isc sensitivity is observed for SS triclinic PM under IR illumination modulated with frequency 400-500 Hz by light. The same dependence on PM is observed and with excitation by a similar non-modulated radiation, however, an absolute value of Isc increasing in this case several times (for triclinic PM 4 times) is less than that of a maximum change under the modulated illumination [16].

The value of Y on the interface Ni/PbPc is of the order 0.3 eV [3]. For sensitivity enhancement of such fast MS O_2 it is necessary to increase Y. It is difficult to do it by substituting electrode material since the metals, which can form the greater potential barrier with OS are oxidized [9]. Therefore for creating MS O_2 with better parameters, than at SS Ni/PbPc we have proposed using anisotype HS from IS and OS. As a model for researches we selected HS from ClAlClPc and CdS_xSe_{1-x} on which interface the value of Y achieves 0.72 eV [9], i.e. is more significant, than on the interface Ni/PbPc [5-7]. Thus, not only the spectral area of excitation (practically all visible and near IR region) extends, but also it is possible to separate the contributions to processes IS and OS since ClAlClPc absorbs light in the region of a transparency CdS_xSe_{1-x}.

The studies of O_2 influence on Isc were carried out under green modulated illumination (excites CdS_xSe_{1-x} layer) and IR (excites only ClAlClPc layer) light diodes from different sides. The absolute Isc change with O_2 adsorption increase for HS by two orders is more than for control SS, and the relative increase is 11 times [15]. The absolute increase of Isc is maximum for frequency modulation of 400 - 500 Hz. With O_2 adsorption near HS interface concentration of CTC with relaxation times of 0.01 - 0.1 s will mainly increase . The formation of such centers in SCR OPF specifies that relative increase of Isc with IS excitation is not only less significant but also has an opposite sign with excitation of CdS_xSe_{1-x} layer by a radiation green light diode and ClAlClPc layer - by radiation of IR. light diode. The opposite sign of Isc change with IS excitation and OPF can be stipulated by different direction of the displacement in them of the Fermi quasilevel, with an O_2 adsorption. It is connected with the fact that the investigated HS semiconductors _with a different type of conductivity were used.

Thus it is shown that:

1. The capture of non-equilibrium carriers of charge in near surface region especially in an oxide layer by «oxygen» centers results in the creation of an internal electrical field near to an electrode directed towards to existing one before illumination, and thus in a diminution of a stationary value Isc and essentially limits possibilities of a choice of metals for increasing the height of a potential barrier at electrodes.

2. The structures with a blocking barrier near the top electrode are more promising for manufacturing organic photoconvertors (SC).

3. For increase of potential barrier height at interface OPF it is expedient to use thin films IS, in which broken covalent bonds are absent at the surfaces fixing the Fermi level on a surface (for example, A_2B_6). Their principal advantage is a small velocity of a recombination in SCR at the interface.

4. The possibilities of organic SC application will be defined by the efficiency of searching the methods of minimizing the degradation of their parameters stimulated by photochemical processes at interface.

5. The use of organic barrier structures with Ni upper electrode for sensors allows one to increase essentially gas sensor velocity rate.

6. By selection of frequency modulation of light it is possible to increase selectivity and sensitivity of MS.

7. Basic paths of OPF MS parameter improvement are the choice of optimum polymorphic modification, diminution of OPF thickness up to the thickness of SCR and the use of A_2B_6 for the barrier creation.

References

[1]. J.Simon, J.-J.Andre, *Molecular Semiconductors*, Springer-Verlag, Berlin Heidelberg (1985).

[2].. K.Arishima, H.Hiratsuka, A.Tate, T.Okada, *Appl. Phys. Lett.*, **40**, 279 (1982).

[3]. Ya. I.Vertsimakha, A.V.Kovalchuk, M.V.Kurik, *Sov. J.Phys. Chem.*, **63**, 1662 (1989).

[4]. M.Hosoda, T.Wada, A.Yamada, A.F.Garito, H.Sasabe, *Jap. J.Appl. Phys.*, **30**, L1486 (1991).

[5]. Verzimacha Ja. I., Kovalchuk A.V., M.V.Kurik, C.Hamann, A.Mrwa. *Phys.Stat.Sol. (A),* **74**, .K109, (1982)

[6]. Verzimacha Ja. I., Kovalchuk A.V., Kurik M.V. et al. *Phys.Stat.Sol. (A),* **82**, K111 (1984)

[7]. Ya. I.Vertsimakha, A.V.Kovalchuk, C.Hamann, M.Muller, *Ukr. Phys. J.* **29**, 1370 (1984).

[8]. Vertzimacha Ja. I., Timofeev S.V., Trofimov V. I., Tsizh B.R., Sov.J.Appl. Spectr., 53, 685, (1990)

[9]. Ya. I.Vertsimakha , A.V.Koval'chuk, *Organic semiconductor materials*, **7**, 25, (1984)

[10]. Ya. I.Vertsimakha, Yu.M.Osipov, G.P.Shaposhnikov, B.R.Tsizh, *Organic semiconductor materials*, **10**, 23 (1988).

[11] Ya. I.Vertsimakha., *Organic semiconducor materials* **5**, 102 (1982).

[12]. R.A.Collins, K.A.Mohammed, J.Phys. D., **21** (2), 154 (1988).

[13]. A.B.Verbitsky, Ya. I.Vertsimakha, D.V.Korbutyak, *Optoelectronics and Semiconductor Technics,* **28**, 57 (1995).

[14]. A.B.Verbitsky, Ya. I.Vertsimakha, D.V.Korbutyak, *Functional Materials,* **4**, 57 (1997).

[15]. D.R.Tsizh, A.B.Verbitsky, Ya. I.Vertsimakha, *Functional Materials*, **4**, 61 (1997).

[16]. Ya. I.Vertsimakha, A.B.Verbitsky, *Theoretical and Experimental Chemistry*, **33**, 239 (1997)