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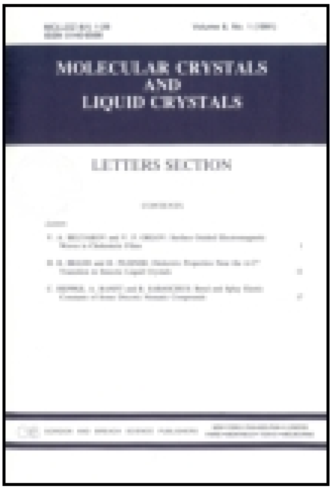

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Published online: 28 Mar 2014.

To cite this article: Ya. Vertsimakha (2014) Gas Sensors Made of Organic Barrier Structures, Molecular Crystals and Liquid Crystals, 589:1, 141-146, DOI: 10.1080/15421406.2013.872413

To link to this article: http://dx.doi.org/10.1080/15421406.2013.872413

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Mol. Cryst. Liq. Cryst., Vol. 589: pp. 141–146, 2014
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.872413

Gas Sensors Made of Organic Barrier Structures

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The consideration of available gas-analyzers and materials for their fabrication has shown that they are not efficient for ecological control. In the fabrication of sensors, inorganic and organic semiconductors and biological membranes are used. Sensors made of inorganic semiconductors have high service life, but low selectivity. Biosensors have high selectivity, but low service life. Organic semiconductor sensors have high selectivity and fair service life, but high inertia. The effect of the film thickness, polymorphic modification, and barriers on the parameters of gas-sensitive organic structures is analyzed.

Keywords Gas sensors; organic barrier structures

1. Relevance of the Problem

At the present time, several millions of devices of about one thousand of different types are produced for the analysis of gases. However, they satisfy the needs of the industry and the economy only by half.

The main part of gas-analyzers is stationary devices of the laboratory type. The majority of them register only a single component of the gas mixture mainly due to a low selectivity and a high inertia. For example, the duration τ of a measurement can be as high as 2–8 min. As the exception, we mention the magnetic gas-analyzers of oxygen, for which $\tau = 16$–50 s, and the optico-acoustic gas-analyzers of CO, CO_2, and CH_4 with $\tau = 30$-60 s [1, 2].

Therefore, the most promising new-generation gas-analyzers are based on the use of adsorptive semiconducting elements, including organic and electrochemical (made of solid electrolytes) ones. Their production involves most widely the sensor elements made of inorganic semiconductors, films of organic semiconductors, and biological membranes. The sensors based on inorganic semiconductors (mainly, on the oxides of metals [3], Ge, Si [4]) possess a high service life, but a low selectivity, except for the sensors of hydrogen and its compounds. For them, $\tau = 50$–100 s. On the contrary, the biosensors have a high selectivity, but a very low service life (hours) [5].

The available sensors based on films of organic semiconductors have, as a rule, a high selectivity and a suitable service life, but a high inertia (τ reaches about 10 min) [2]. Such high inertia is caused by the circumstance that the registration of gases uses a change of their bulk properties (photoconductivity, electroconductivity, magnetic properties), which is determined by the duration of the diffusion of a gas through the film (to the lower electrode).

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Thus, one of the actual problems is the design of selective sensors of gases with small response time (fast-response ones) for a continuous control over technological processes and for the solution of ecological problems. Therefore, we will consider below only the potentialities and the perspectives of a design of selective and fast-response gas-analyzers.

2. Influence of Polymorphic Modifications on the Properties of Sensor Structures "Organic Film/Metal"

The analysis of the influence of gases on properties of various materials showed that the response duration depends not only on the nature (class) of used materials, but also on the properties that are used at the registration of gases [6, 7]. As early as in 1982, it was first proposed for the registration of gases to use a change of properties that are determined by the parameters of a potential barrier near the boundary between an organic film and metals or films of inorganic or organic photoconductors with opposite type of conductivity. In this case, a change of properties of such structures will be determined by the duration of the diffusion of molecules of a gas into the near-surface region with space charge, whose thickness is at most 30–50 nm in organic layers [2, 7]. It was experimentally found in 1989 that the parameters of the organic semiconductors / metal interface (e.g., barrier structures (BS) on the basis of lead phthalocyanine PbPc) are changed rapidly (less 1–2 s) and essentially under the action of oxygen. This process is invertible if the barrier is formed with the use of a metal electrode, which is not oxidized (e.g., a Ni one [6, 7]) and injects no major charge carriers. It was shown in the subsequent works [6–7] that the sensitivity to the action of oxygen depends strongly on the polymorphic modification (PM) of PbPc films.

In this case, the character of a change of short circuit current, I_{sc}, (ΔI_{sc}) at the filling of a measuring chamber by oxygen at the excitation of I_{sc} by modulated or unmodulated emission of light-diodes is the same, but the signal/noise (drift) ratio under unmodulated emission of light-diodes is several times less than that under the analogous modulated illumination. The use of modulated light of light-diodes allows one to choose the optimum registration frequency, i.e., to enhance the sensitivity and the selectivity of a sensor element, since the maximum effect of other gases is observed at different modulation frequencies. Therefore, in what follows, we present only the results on the influence of oxygen on I_{sc} at the excitation by modulated light.

For Au/PbPc/Ni BS, it was confirmed that a change of I_{sc} at the injection of oxygen is significantly larger at the illumination of the upper barrier electrode than that of the ohmic Au-electrode. This is especially manifested at the illumination of the structure by light of a red light-diode, whose emission is strongly absorbed. In this case, the principal maximum in the region 400–500 Hz and two inflections (hidden maxima) near 1000 and 5000 Hz are observed on the frequency dependences of I_{sc} at two different pressures and the illumination of the Ni-electrode. All three maxima are clearly seen on the frequency dependences of the ratio I_2/I_1 (Fig. 1). It is established that the sign and the magnitude of a change in I_{sc} at the adsorption of an acceptor gas depend essentially on the crystal structure (PM). The least changes in I_{sc} (slight decrease) during the adsorption of oxygen were observed for films of a quasiamorphous modification (x-PM), and the highest one (significant increase in I_{sc}) was registered for films with the triclinic modification. Such strong dependence of the change in I_{sc} on the type of a polymorphous modification is explained by the dependence of parameters of the potential barrier on the metal – organic semiconductor interface on the crystal structure.

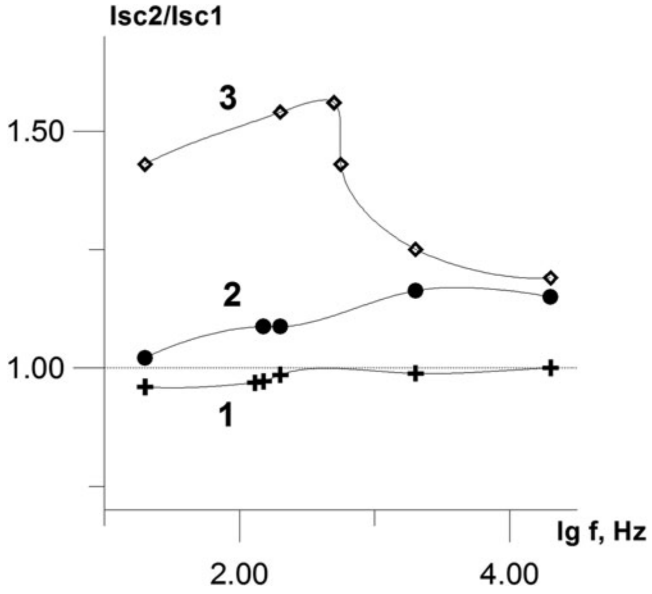

Figure 1. Frequency dependences of the ratio I_{sc2} / I_{sc1} at two different pressures of oxygen for the quasiamorphous (X) (1), monoclinic (2) and triclinic (3) modifications of Au/PbPc/Ni under the illumination of a Ni-electrode.

Their frequency position is practically independent of the pressure of oxygen. It was shown that they are caused by the creation of two charge-transfer (CT) complexes of the acceptor type $PbPc^{\delta+} \ldots O_2{}^{\delta-}$ in the space charge region near the boundary with the Ni-electrode and of a single complex in the quasineutral region. In order to confirm this assertion, we have performed the measurement of $I_{sc}(f)$ on control structures with two ohmic electrodes, where the main contribution to the creation of I_{sc} must be given only by CT-complexes located in the bulk of a film. In the structures with both ohmic electrodes, the maximum on the $I_{sc}(f)$ curve is observed only at 5 kHz, and the ratio I_2/I_1 in the region of low frequencies is less by one order and is independent of f. This confirms that the "fast states" with relaxation times of about 0.2 μs are localized in the quasineutral bulk of a film.

The content of a semiconducting material in PbPc films was set by the temperature of a substrate (T_s) in the process of thermal sputtering in vacuum. We have obtained the films of mainly the quasiamorphous modification at $T_s < 310$ K and ones of the stable triclinic modification at $T_s > 430$ K. At $T_s = 340$–380 K, the highest content of the monoclinic PM was observed [8].

One of the important characteristics of gas gages is a range of measurement of the concentration of a gas that is determined by the dependence of the measured parameter on the partial pressure (p) of the gas under study. In [8, 9], it was shown that the dependence of I_{sc} on p of oxygen for the barrier structures PbPc/ Ni in a wide range of pressures is well described by the formula $\Delta I_{sc} = Ap^{0.5}/1 + bp^{0.5}$, where A and b are constants, which characterize the probability of the direct and reverse processes, respectively. At low $\boldsymbol{p}$, the above expression coincides practically with the Freundlich empiric formula, which is experimentally corroborated for the oxides of metals [8]. This testifies to a wide range of registration of oxygen by fast-response barrier sensors.

It is established that the most fast-response and selective sensor elements are presented by the optoelectronic couple “red light diode – organic barrier structure” on the basis of films made of lead phthalocyanine in the triclinic modification with the upper cut-off metal electrode (Ni), which is weakly oxidized.

The height of a potential barrier on the boundary Ni/PbPc is equal to 0.3 eV [6]. It is obvious that, in order to improve the parameters of such fast-response sensor of oxygen, we must increase the height of a potential barrier. But it is difficult to practically realize such increase by changing the electrode material, because the metals forming a high potential with PbPc are easily oxidized, which leads to the creation of slow capture centers and to the recombination in the oxidized layer [7].

3. Perspectives of Sensor Structures on the Basis of Hybrid Heterostructures

The above consideration implies that one of the means to enhance the sensitivity of barrier gas-sensitive elements is to increase the height of the barrier near the interface of a heterostructure (HS).

Therefore, in order to produce a sensor of oxygen with parameters, which are better than those of the Ni/PbPc barrier structures, it was proposed in [10] to use anisotype heterostructures made of inorganic and organic semiconductors and called “hybrid” ones in the literature. As a model structure for the study, we chose a HS made of cadmium sulfoselenide (CSS) and chloroaluminumchlorophthalocyanine (ClAlClPc), for which the potential barrier height on the boundary attains 0.72 eV [10], i.e., it is significantly more than that on the Ni/PbPc boundary [6]. In addition, the spectral region of excitation of such HS is wide (practically, the entire visible and near-IR regions). In this case, we have possibility to separate the contributions from the processes running in inorganic and organic semiconductors, because CSS absorbs in the transparency region of ClAlClPc, and ClAlClPc absorbs in the transparency region of CSS

For the experimental verification of this proposal, we have used the structures obtained by thermal sputtering on substrates with different temperatures (CdS_xSe_{1-x} - 580 K, ClAlClPc - 350 K, CuI - 300 K). The thicknesses of layers of CdS_xSe_{1-x}, ClAlClPc, and CuI were equal to 310, 290, and 40 nm, respectively. The measurements of the influence of oxygen on I_{sc} were performed at the illumination by modulated (with different modulation frequencies) emission of a green light-diode (it excites only the CdS_xSe_{1-x} layer) and an IR light-diode (it excites only the ClAlClPc layer) from both sides. These measurements have confirmed that, at the illumination with an IR light-diode through the upper CuI electrode (i.e., at the excitation of only the organic layer), the increase of I_{sc} with the partial pressure of oxygen for the HS by 11 times more than that for control structures ITO/ClAlClPc/CuJ. However, changes in I_{sc} are insignificant at the excitation of the layer of CdS_xSe_{1-x}, i.e., the adsorption of oxygen changes mainly the properties of the organic layer, whereas the role of the layer of CdS_xSe_{1-x} is only reduced to the creation of a potential barrier.

Maximum changes in I_{sc} at a variation of the partial pressure of oxygen were observed at modulation frequencies of 400–500 Hz. This testifies that, at the adsorption of oxygen near the interface of the HS, the concentration of centers (charge-transfer complexes) in the organic layer with a relaxation time of 2–4 ms significantly increases.

4. Influence of Donor Gases

We note that the processes caused by the action of acceptor gases are well studied, whereas few data on the influence of donor gases are available, and they are contradictory. For

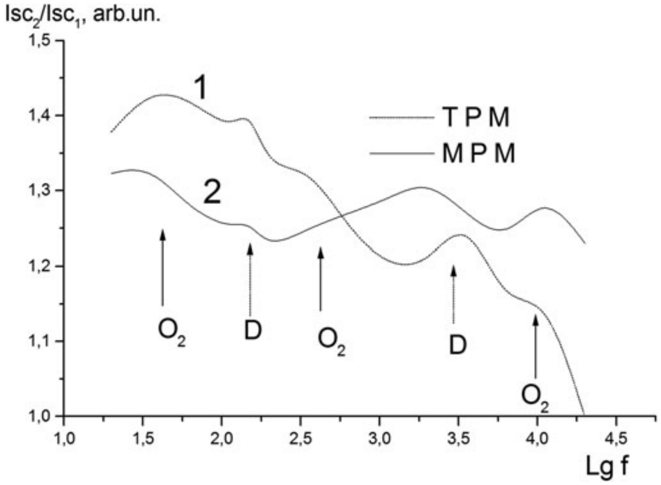

Figure 2. Frequency dependences of I_{sc2} / I_{sc1} for different PMs - triclinic (1) and monoclinic (2) modifications.

example, some authors observed a decrease in the electroconductivity and the photoconductivity at the injection of a donor gas, whereas the other ones found an increase in these quantities. In work [8, 9], it was first shown that such specific feature of the action of donor gases is caused by a complicated mechanism of their interaction with OH and by the strong dependence of the processes on a PM of Pc, whose properties essentially differ and were not controlled by the other authors. This is essentially manifested in the study of the frequency dependences of I_{sc} for sensor structures (SS) with different PMs. For example, Fig. 2 presents the frequency dependences of I_{sc} for SS of PbPc with triclinic polymorphic modification (TPM) and monoclinic polymorphic one (MPM) in a mixture of oxygen and ammonia, the latter being a strong donor with respect to PbPc. The influences of other donor gases on I_{sc}(f) are similar.

This is well seen in Fig. 2, where the frequency dependences of the ratio I_{sc2}/I_{sc1} (I_{sc1} is the value of I_{sc} at $p = 20$ Pa, and I_{sc2} is the value of I_{sc} after the injection of ammonia mixed with air) are shown. The continuous arrows show the positions of the maxima caused by CT-complexes of the acceptor type. The dotted arrows indicate the maxima caused by the injection of ammonia with donor property. The intensity of these maxima increases with the concentration of ammonia and also depends strongly on PM. For the quasiamorphous (X) PM, such changes are slight and are omitted in Fig. 2.

The presented data are explained with a mechanism that includes two main processes running simultaneously: the neutralization of charge-transfer complexes formed by oxygen by molecules of a donor gas and the creation of charge-transfer complexes of the donor type with creation of a free electron.

The first process will cause only a decrease in the concentration of adsorbed molecules of oxygen and, hence, a decrease in I_{sc} without significant shift of the positions of maxima. The second process will lead to the appearance of new maxima (inflections) on the frequency dependence of I_{sc} and, as a result, to a shift of the position of the main maximum. The dominance of one of the processes determines the character of the influence of a donor gas on I_{sc}. In this case, the second process dominates. The formation of such complexes is characteristic of zinc phthalocyanine, where Zn^{2+} ion is inclined to the sp^3-hybridization. The same hybridization is characteristic of Pb^{2+} ion.

Thus, these studies have shown that the position of the maximum on the dependence of I_{sc} on the modulation frequency of the emission of a light-diode depends on the nature of a gas. In other words, the selectivity can be increased due to the choice of the registration frequency. In addition, at the measurement of the frequency dependence of I_{sc}, it is also possible to determine the presence of active (donor) gases in air. Thus, it is possible to produce a matrix sensor that will allow one to determine the concentrations of several gases with a single element by means of the change of the modulation frequency of the emission of a light-diode.

5. Conclusions, Ways to a Further Improvement of the Sensitivity, and Perspectives of Barrier Organic Sensors

Thus, the above-described barrier sensors have significant advantages as compared with all available sensor elements by the fast response and the selectivity at the present time. The former allow one to fabricate also transportable fast-response gas-analyzers, because the sizes, prices, and feed power for serial light-diodes and other elements of the scheme are small.

From the technical viewpoint, the most optimal construction of a sensor for the registration of oxygen is the optoelectronic couple formed by an IR light-diode and the organic barrier structure PbPc/Ni or CdS_xSe_{1-x}/ClAlClPc. The use of the modulated emission of light-diodes allows one not only to enhance the sensitivity and the selectivity of such sensors, but also to develop a matrix gas-analyzer, which will determine the concentrations of several gases by measuring the signals at several frequencies characteristic of these gases.

As is known, the photogeneration of charge carriers in organic semiconductors occurs mainly in the space charge region, whose typical thickness is about 30–50 nm. The thickness of organic films of the gas-sensitive barrier structures under study is essentially larger than that of the space charge region, which has led, of course, to a decrease in the efficiency of the photogeneration of charge carriers and, hence, ΔI_{sc}. Therefore, the simple ways to improve the parameters of such sensors of oxygen are the optimization of the thickness of an organic film and the use of new more photo- and gas-sensitive OS.

To enhance the selectivity of matrix gas-analyzers, especially their sensitivity to donor gases, the anisotypical structures produced from two organic semiconductors can be used, but this will require the additional studies and the optimization of the choice of organic components.

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