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ADSORPTION INDUCED HOLE TRANSPORT IN THIN LAYERS OF NON-ORDERED TETRACENE

Additional disorder induced by adsorption processes by the molecule of ambient are responsible for deep modulation of conductivity. Observations confirmed the dominated role of the increase of the free carrier concentration due to the increase the shallow trap concentration, for modulation of the conductivity.

Keywords: tetracene films, p-quaterphenyl films, adsorption, electron transfer reactions.

1. INTRODUCTION

Cross conductivity of thin layers made of planar tetracene molecules is dependent on the volume and gas adsorption on the surface [1]. To clarify the role of adsorption processes in hole conductivity we compared findings from earlier experiments made in vacuum [2, 3, 4] with conductivity measurements in ambient atmosphere and in the presence of controlled environment composed of ethanol vapour [5].

This features are not only the basic science and may be interested from the engineering science searching the possibilities to meet a problem of ageing and stability of electrical properties of thin layers of tetracene. An efficient application for organic materials requires good understanding of the dynamic interactions of the solid surface with the molecules of ambient vapour. It may be noticed that conductivity enhanced with adsorption process may become similar to the catalysis. The surface of the organic material under study has very little

dangling bonds and is built as a rigid cyclic structures made of atoms connected one to another with strong molecular bonds.

2. EXPERIMENTAL

The measurements reported here were made to verify whether it is indeed the difference in the mobility of holes when the experiment is made in air atmosphere not in the vacuum.

The measuring samples of polycrystalline tetracene ($C_{18}H_{12}$) made as a planar capacitor with Au – Al electrodes were prepared with vacuum deposition method under the pressure of the order of 10^{-5} Torr on glass. Evaporation evaporation rates were kept in the range 20-30 $\text{\AA}/\text{s}$ The substrate temperatures were about 300 K. Disordered layers of tetracene were in the range of 6-10 μm .

Effect of adsorption on the electrical properties of the organic material layers was conducted according the following scheme. Conductivity studies were made in ambient atmosphere with the sample positioning inside a “Faraday cup” (Fig. 1). In the first stage there was measured drift mobility with time of

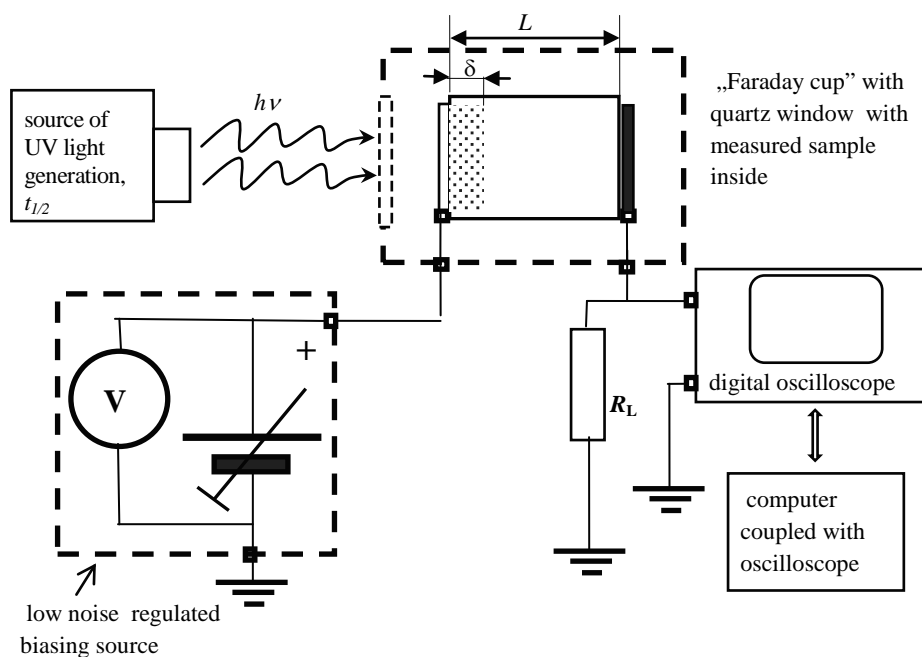


Fig. 1. Measuring set up for TOF measurements

flight method (TOF) with set-up presented in Fig. 1. In the second stage there were made dark U-I measurements at room temperature in the air atmosphere. In the third stage the whole set of findings was numerically processed. The drift mobility, μ , obtained from TOF was a batch quantity essential for processing direct current measurements in the purpose to obtain trap concentration, N_t , and free carrier concentration n_f , values dependent on quasi-Fermi level, E_F .

TOF method makes it possible to obtain the values of drift mobility without disturbing mass diffusion process (connected with adsorption of gases) within studied layers. These feature creates the possibility of separation of the conductivity component associated with modification of electrical properties of the layer caused by the diffusion of the adsorbed gas particles inside the layer, when compared with findings obtained in the vacuum conditions. All measurements were made in the interval of the field strength from $8 \cdot 10^5$ V/m to $2.5 \cdot 10^7$ V/m, greater strengths caused the higher current flow above $1,4 \cdot 10^{-5}$ A/cm² with tendency to damage the layer.

TOF measurements have been made in the set-up shown in Fig. 1. As a light source for the charge carrier generation, an ORIEL 6426 xenon flash-lamp (with $\lambda > 280$ nm, pulse width 1.6 μ s, with maximal pulse power of 0.32 J). The UV pulse was absorbed in the narrow layer (δ) near Al semitransparent electrode. The hole pulse was then driven to the opposite Au electrode by the electric field induced by biasing potential. Typical pulse registered in the computer coupled with digital oscilloscope DS100CA is shown in the Fig. 2.

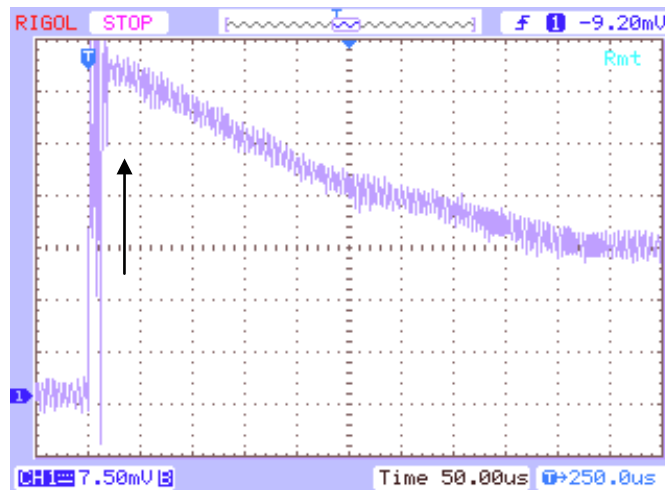


Fig. 2. Typical oscillogram for tetracene layer: $L = 8,5 \mu\text{m}$, $U = 2.84$ V, arrow indicate the time of flight (t_f)

The direct determination of the hole drift mobility, μ , for the carrier transit across the layer width L in the presence of biasing potential U gives [6, 7]

$$\mu = \frac{L^2}{U \cdot t_r} \quad (1)$$

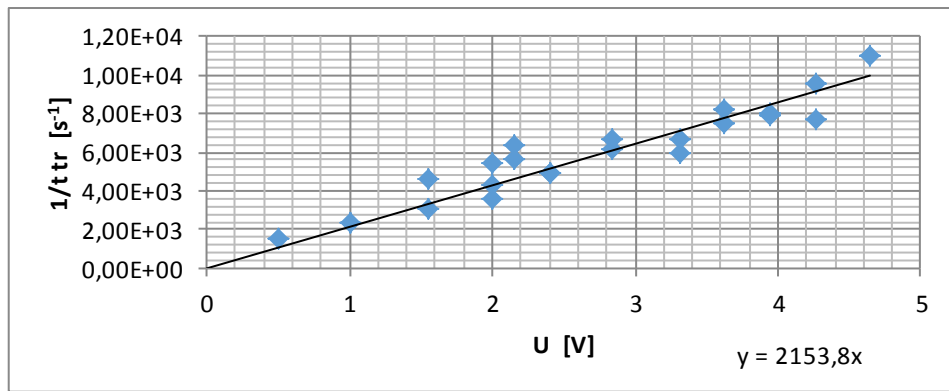


Fig. 3. The inverse transit time of hole TOF pulses vs. applied voltage estimated at 294 K showing a linear dependence ($L = 8,5 \mu\text{m}$)

The linear dependence of inverse transit time vs. biasing potential (see Fig. 3) appears as an evidence proved applicability of TOF method [7]. The resulted drift mobility for holes is $\mu = (1.6 \pm 0,9) \cdot 10^{-3} \text{ cm}^2/\text{Vs}$.

The direct current measurements of U-I characteristics were made in the set-up built from the elements shown in Fig. 1 and the current was measured with electrometer – 219A with the same samples as for TOF. Description of the results was made with use the theory of differential analysis of space charge limited current (DA-SCLC) [8, 9, 10]. This theory enables evaluation of the electrical parameters of the layer without assumptions about the shape of the density of states (DOS). Obtained U-I characteristic (Fig. 4) was used for calculations DA-SCLC with use the drift mobility value from TOF as a batch value for calculations..

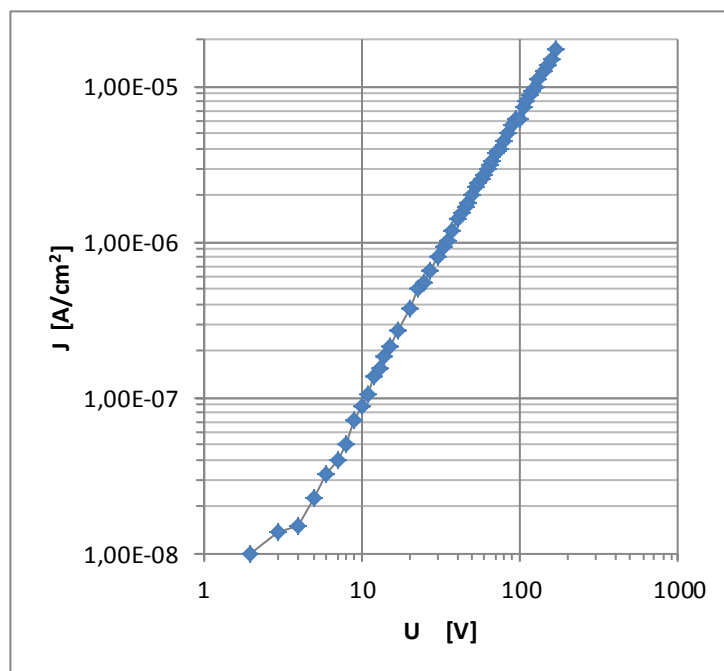


Fig. 4. U-I steady state characteristic for tetracene layer ($L = 8,5\mu\text{m}$)

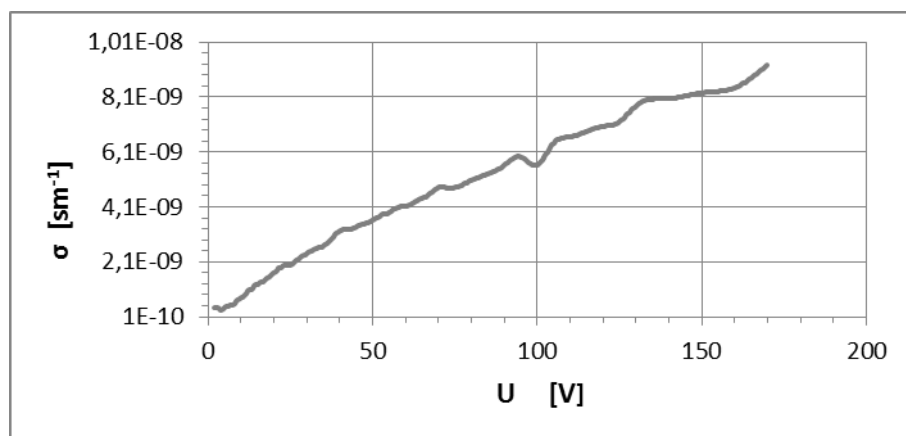


Fig. 5. Conductivity of the tetracene disordered layer slightly dependent on the biasing voltage

Determined total trap density is $N_t = 1,6 \cdot 10^{20} \text{ cm}^{-3}$, and the free carriers concentration, n_f , is dependent on the quasi-Fermi level and is in the range of $8 \cdot 10^9 - 2 \cdot 10^{11} \text{ cm}^{-3}$.

3. DISCUSSION

The behaviour of increase the current above the limit of the field strength up from $2,5 \cdot 10^7 \text{ V/m}$, caused the higher current flow above $1,4 \cdot 10^{-5} \text{ A/cm}^2$ with tendency to damage the layer. This situation is very similar to the observation of the increase of the current during the experiments with vaporization of the tetracene layer with ethanol vapour [11]. The mechanism in [11] was directly connected with surface activation process. The magnitude of the ethanol molecule makes unlikely mechanism of diffusion into the body of the layer. And the rapid increase was connected with active collisions between vapour molecules in the space near the tetracene surface led to the dissociation of the molecules in the adsorbing layer and the presence of the hydrogen bonding generating during the collisions. In such a situation the origin of the increased conductivity is not a greater drift mobility but existence of injection of the carriers during surface reactions.

The case described in this article is connected with adsorption of the small molecules the air is consisted of, predominantly most interesting is oxygen. The great density of traps $N_t = 1,6 \cdot 10^{20} \text{ cm}^{-3}$, comparable to the whole density of states $N_v = 3,3 \cdot 10^{21} \text{ cm}^{-3}$, may be connected with diffusion of the mass into the volume of the layer but it is not only possible mechanism. Oxygen atom absorbed at surface can absorb an electron from layer molecule creating a new transport charge-hole. This process is possible because in the equilibrium the ambient may contain H_2O .

Treating the whole process as a reaction of the electron transfer, the adsorption enhanced current may be considered as the charge flow between molecules of gas phase to the molecules of condensed layer.

The saturation levels of the currents during vaporization connected with the current flow forced by biasing voltage is directly correlated with the rate of electron transfer at the interface and may be considered as proportional to the number of electrons which cross the interface existing at the surface of the layer. The rate of electron-transfer can be calculated easily by integration the $I-t$ curve. Making an assumption that an excited tetracene molecules at the surface are produced by direct electron injection at the solid surface array or by exciton migration from interior of the crystal to the surface we can consider the whole

process as a reaction with reaction cross section σ_e for the tetracene system. In that limits the following estimation can be valid roughly

$$\sigma_e = \sigma_g \cdot Q_{ex} \cdot \frac{1}{\tau \cdot N_v}, \quad (2)$$

where: σ_g is geometrical cross section of a site of surface lattice with tetracene molecule of the film, Q_{ex} is the reaction yield per exciton reached at the surface, τ is approximated by exciton lifetime in the bulk layer, N_v – number of collisions of adsorbate in the interface layer.

For observed systems the time dependence of desorption current and obtained value of entropy for sorption, for tetracene $\Delta H = 84$ kJ/mol [1], may points out that two mechanisms are present: physic sorption and weak chemisorption.

If we consider 2-D localized gas layer at the interface interacted with molecules of condensed layer then in terms of semi-classical Marcus's theory charge transfer rate then reaction rate for change ionization states between adjacent molecules i and a final α is given by [12]:

$$k_{i\alpha} = \sum_{\alpha} k_{i\alpha} = \frac{2\pi}{\hbar} \sum |J_{i\alpha}|^2 \delta(E_i - E_{\alpha}) \quad (3)$$

where: $J_{i\alpha} = \langle i|U|\alpha \rangle$ is a perturbation matrix element between the initial state and one of the final states, and δ function ensures energy conservation during the transition between the initial and final states.

The decisive parameter for charge transport between molecules is intermolecular transfer integral J_{ij} , that express the possibility of transfer of charges between interacting molecules. For adjacent molecules the transfer integral may be evaluated from Schrödinger equation.

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TRANSPORT DZIURÓWY WZMOCNIONY ABSORPCJĄ W NIEUPORZĄDKOWANYCH WARSTWACH TETRACENU

Streszczenie

Badano proces aktywacji i proces transportu elektronów w warstwach tetracenu poddanych oddziaływaniu powietrza. Badania przeprowadzone za pomocą metody czasu przelotu (TOF), której wyniki posłużyły jako wsadowe do obliczeń parametrów elektrycznych warstw przy wykorzystaniu metody różniczkowej analizy prądów ograniczonych ładunkiem przestrzennym, wykazały koncentrację pułapek $N_t = 1,6 \cdot 10^{20} \text{ cm}^{-3}$, porównywalną do całkowitej gęstości stanów $N_v = 3,3 \cdot 10^{21} \text{ cm}^{-3}$; może to świadczyć o nasilonej dyfuzji masy w głąb warstwy.