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VOLUME CONDUCTIVITY OF POLYCRYSTALLINE TETRACENE AND P-QUATERPHENYL LAYERS MODIFIED UNDER INFLUENCE OF THE SURFACE ADSORPTION

Volume conductivity of thin organic layers in contact with the ambient atmosphere depends on the volume properties and on the adsorption processes on the free surface of the layer. In order to clarify the role of the surface, experiments were carried out at a temperature close to 293 K to determine the influence of the adsorption dynamics on the change of characteristic relationships observed for the transport of electric charge in vacuum, in the ambient atmosphere and in the controlled atmosphere of the ethyl alcohol vapors. The investigations were carried out for two linear tetracyclic molecular structures, i.e. p-tetraphenyl and tetracene. These molecular systems differ in organization of the rings. The results show an increase in conductivity measured for both compounds when there are the molecules capable of adsorbing to the surface and to transfer or receive charge carriers connected with the process of diffusion or drift transport in the volume of the layer. The nature of the observed increase in conductivity proves that the hopping mechanism is present in the case of conductivity of both tested materials.

Keywords: adsorption, p-quaterphenyl, tetracene, organic semiconductors.

1. INTRODUCTION

Remarkable interest in the recognizing the nature of influence of gas environment on conductivity of the layers of oligoacene's and oligophenylenes is not only in the scope of basic sciences but emerges from a strictly specified demands of the electronic industry. Usability of this materials to production of solar cells, organic electroluminescence diodes (OLEDs) and organic field effect transistors (OFETs) is related to stability of electric properties of thin layers made of these materials under the conditions of contact with air oxygen, moisture or organic solvent. Functionalized derivatives of this compounds are used to produce devices such as gas sensors, specific chemical field-effect transistors (ChemFET) and ion-sensitive field effect transistors (ISFET) [1].

Recently, it was emerged the possibility to use this materials to produce molecular controlled semiconductor resistors (MOCSER) [2]. The presence of surface states activated by the interactions with gas-phase ambient molecules may be the origin of controlling electronic transport processes in such devices. Material characterization opens the possibility for developing such devices.

There is a need to determine the durability of changes caused by surface processes in correlation with the dynamic parameters determining the electric conductivity of theses layers. High resistance, low charge concentration and relatively low mobility of charge carriers are the reasons that the time constants for the changes of electric parameters modulated by the presence of adsorbing molecules are in the magnitude of seconds or even minutes [3] and the maximum values of the carrier mobility captured for linear polycyclic materials in the monocrystalline form are in the order of 1 cm^2/Vs [4]. There is a common knowledge that the electric properties of organic materials are susceptible to influence of the ambient atmosphere. This effect is usually associated with the phenomenon of generation surface states due to adsorption and with transfer of the charge due to the diffusion of the absorber molecules across the interface. Therefore, our studies are the attempt to describe the effect of interactions of different gas molecules with thin layer of polycyclic hydrocarbon on the electric properties of the layer. Two low weight compounds, tetracene and p-quatephenyl, built from four linearly arranged benzene rings were chosen for the study. Tetracene molecules are built of the rigid skeleton, but p-quaterphenyl moiety is built of the benzene rings which can rotate. What is more, both of the studied compounds show the similar crystal packing with the “herring bone” arrangement.

Tetracene with chemical formula $C_{18}H_{12}$ and molecular weight 228.29 g mol^{-1}, crystalizes in triclinic crystal system P1, (which actually is pseudo-monoclinic P21/a): $a = 7.98\pm0{,}02$ Å, $b = 6{,}14\pm0.02$ Å, $c = 13.57\pm0.04$ Å, $\alpha = 101.3\pm0.5°$, $\beta = 113.2\pm0.5°$, $\gamma = 87.5\pm0.5°$ [5], and its thermodynamical parameters [6]: melting point 630 K, enthalpy of fusion $\Delta_{fus}H_m(T_{fus}) = 35.9 \pm 6.7$ $kJmol^{-1}$ which clearly indicates durability of the layers made of the tetracene under conditions of typical usage of electronic devices using multi-layered structures [7].

P-quaterphenyl with chemical formula $C_{24}H_{18}$ and molecular weight 306.40 g mol^{-1}, crystalizes in monoclinic structure P21/a, $a = 8.110 \pm 0.006$ Å, $b = 5.610 \pm 0.004$ Å, $c = 17.910 \pm 0.010$ Å, $\beta = 95.80 \pm 0.06°$ [8,9], and its thermodynamical parameters including melting point 593-594 K and enthalpy of fusion $\Delta_{fus}H_m(T_{fus}) = 57.6 \pm 0.9$ kJ mol^{-1} and the enthalpy of vaporization $\Delta_{vap}H_m(298\ K) = 136.1 \pm 3.2$ kJ mol^{-1} [6] indicates its stability in the room temperatures when the layers are prepared. During deposition on the Au electrode, the molecules of p-qauaterphenyl do not show desorption properties up to 360 K [10]. Both selected compounds have very similar crystalline characteristics such as packing density and coordination number; they differ only in the rigidity of the molecule skeleton.

2. EXPERIMENT

The measurements were carried out in turn in vacuum, in air and in the controlled atmosphere of ethanol (C_2H_5OH). Comparison of the data collected in the vacuum and in the air allowed to indicate the role of adsorption and diffusion of oxygen and H_2O molecules as factors influencing electrical transport in the layers.

1.1. Adsorbates

The molecule of water in the adsorption processes characterizes with the small amount of dispersive forces and with high polarity of the molecule [11] leading to a small interaction energy of H_2O molecules with the surface of adsorbent. The choice of ethanol as the model factor for activating surface of the layer is related to its properties, that is, to the size of the molecule which practically prevents the possibility of diffusion inside the volume and to the presence of carboxyl (COOH) group determining its chemical activity. Ethanol molecule in the adsorption processes is characterized with high adsorption energy to the surface [12] and the large potential energy of dispersive forces, which in turn is proportional to the polarizability and the size of the adsorbate molecules. Ethanol molecule in comparison to the H_2O molecule possesses larger polarizability and is significantly larger. The presence of the active carboxyl group is the reason of high asymmetry of the molecule what is seen in the dipole moment $\mu = 1.7$ D (in the gas phase). The liquid ethanol possesses the significant dielectric constant, $\varepsilon \approx 24$. Alcohol molecule is characterized with non-uniform distribution of the electron density, and that is the reason for possibility of existence of the big participation of the electrostatic interactions, that is inductive and orientational besides the dispersive forces. It should be noted that alcoholes are often used in the technology of organic electronic, and therefore the time constant of the changes of the electrical transport associated with the interactions of the gases with the surface and the volume of the layers is important information. The conductivity and mobility of the layers in the vacuum were measured to determine the basic intrinsic conduction mechanism for both compounds. All the studied layers were made with vacuum thermal deposition method, which provided the measurements made in the vacuum on the undoped layers without the impact of solvents. The vacuum evaporation method further provided that layers of the same quality were used for all measurement steps. This way of making layers has given us the opportunity to compare the properties of electrical transport of the pure materials in the vacuum conditions with the materials under controllable impact of external factors.

1.2. Measuring procedure

The measured samples of polycrystalline tetracene and p-quaterphenyl were prepared with vacuum deposition method under the pressure of the order of 10^{-5} Torr on glass plates supplied with Au electrode.

Evaporation rates were kept in the range 2–3 nm/s, and the thickness of obtained layers were in the range of 14–20 μm for p-quaterphenyl and 16.5 - 20 μm for tetracene. The substrate temperatures during evaporation were maintained near 300 K. The quality of the obtained structures were valuated with use of the X-ray diffractometric method. In order to measure the transport properties of the layers as a top electrode an Al contact was used, which was deposited in the vacuum of 10^{-5} Tr.

Examinations of the effect of adsorption on electrical properties of the organic layers was realized with the measurement scheme described as follows. Preliminary examinations of the hole conduction for organic material were made sequentially in vacuum and in the air, when the measuring cell was placed in the measuring jar supplied with quartz window and acting as “Faraday cage”, what prevents the obtained values of measurements from electromagnetic noise. The choice of the hole conduction measurements was forced by the fact that the intermediate states in the form of the radical-carbanion, susceptible of oxidation when exposed to the air were formed due to the electron transport. This fact was also proved by results of our quantum-mechanical calculations. The calculated HOMO level at $+(0.17\pm0.05)$ eV in the anion form of p-quaterphenyl was non-bonding but in opposite in the cation form the HOMO level is strongly bonded and is in the level of $-(9.24\pm0.50)$ eV.

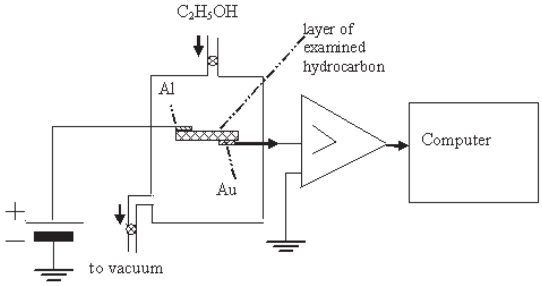

Fig. 1. Scheme of the measuring apparatus.

The vacuum measurements of direct current I-t characteristics were made by measuring apparatus shown in Fig.1 with presence of the C_2H_5OH vapor. The transient currents measurements were made in the dynamic vacuum conditions 10^{-3} Tr - 10^{-4} Tr. It is obvious that in such vacuum there is no possibility to avoid surface adsorption from the residual gases. However, such a procedure in great extent lowers the diffusion pressure on the surface of the layer which comes from the existence of ambient atmosphere, which in accordance to the Fick law, lowers the rate of diffusive flow of the gases into the layer. Preferred are only the places of the surface adsorption with the long surface life time and that's which are immobilized.

In turn, the measurements of the hole conductivity of the layers treated with the influence of the ambient in the pressure 10^5 hPa were executed under the conditions favoring adsorption and diffusion inside the layer, of the oxygen and water molecules which are always present in the air (the relative humidity of the air was 60–70%).

Studies of the effect of surface adsorption on the activation of the conductivity of the above-described layers were carried out in a glass vacuum chamber using polar solvent-ethyl alcohol as activator. All the measurements were accomplished in the temperature near 293 K.

1.2.1. Transport measurements in vacuum and in ambient

The transient current studies on the influence of the adsorption made in the vacuum and in the ambient on charge carriers mobility were carried out using the time of flight method (TOF) [4]. This method gives the possibility to get the value of drift mobility separately for the electrons and the holes, without disturbing the processes of mass diffusion within the volume of the layer. So this creates an opportunity of separating the component associated with the modification of the electric properties of the layer caused with the diffusion of the mobile particles of the adsorbate gases into the depth of the layer independently of the presence of the surface states. The nitrogen laser, λ=337.1 nm light pulses werte used in the experimental set-up for generation of the electron-hole pairs in the proximity of the top electrode. Intensity and time of the light pulse duration were accordingly 5 μJ and 8 ns. Biasing voltage extort the thin sheet of the generated positive charge of the holes in the direction of cathode, and the negative electrons were collected by a anode. Transient current pulses of the holes, generated in this manner, were registered by the digital oscilloscope DSO-5804 and then were subjected the digital processing with use of computer. Drift mobility was calculated from the kink point of the *I-t* transient characteristics transformed to the double logarithmic axes, log *I*-log *t*, with use of the formula:

$$\mu = \frac{v}{F} = \frac{L^2}{t_t U} \quad , \tag{1}$$

where v is drift velocity of the holes, F the value of the field inside the sample, L is a sample thickness, t_t is a time of flight and U is a bias voltage.

According to the Mott-Davies model describing the hopping transport in the narrow band of trap states near the Fermi level it is possibility to obtain the temperature dependence of the drift mobility in the form of [13]:

$$\mu = \frac{1}{6}\frac{eR^2}{kT}\nu_{ph}\exp(-2\alpha R)\exp\left(\frac{-\Delta E}{kT}\right) \tag{2}$$

where R is the mean distance between localized states, e – electron charge, k – Boltzmann constant ($1.38\cdot10^{-23}$ J/K), ν_{ph} – photon frequency, α – the decay constant for the wave function of the localized state (usually assumed to be α^{-1}, comparable to the mean distance among the molecules), ΔE – effective width of the narrow band of localized states through which transport takes place and T –temperature in the Kelvin scale.

1.2.2. Measurements on the influence of surface adsorption kinetics on the electric transport

Studies on the influence of the surface adsorption kinetics of the ethanol vapour on the conductivity of the layers made of organic material that is for tetracene and p-quaterphenyl were made in the glass vacuum chamber placed in the grid made of the Cu which isolated from the electromagnetic noise.

The measuring scheme was in the following order:

1. Preliminary pumping of the glass chamber which contained measured layer to the high vacuum in the order of 10^{-5} Tr, and then after vacuum was stabilized, outgassing to maintain the dynamic vacuum in the level of 10^{-2} Tr.
2. Bringing into the chamber with measured layer a saturated ethanol vapour from the reservoir of the ethanol alcohol being in the thermodynamic equilibrium with its vapour. The process was executed in the room temperature when the vacuum pump was cut off from the measuring chamber. Biasing voltage during the whole time of the experiment was assured by stabilized supplier.
3. When the saturation of the volume current passing through the layer was observed, then the chamber with the sample was brought once more to the contact with the reservoir of the equilibrium ethanol vapour. Such process was repeated until obtaining the situation when current passing through remarkably grown (to the order of 10^{-5} A).
4. When the above procedure scheme was finished then the biased sample was pumped again to the high vacuum. The measurements were ended when the low sample current was established.

3. RESULTS AND DISCUSSION

3.1. Electric transport in vacuum and in the ambient

The drift mobility values were obtained for both studied compounds in the vacuum as well as in the ambient atmosphere. Activation energy values were also determined, when the time of flight was measured in the temperature range *T* from 290 K to 340 K and the evidence was handling in accordance with Eqs. (1) and (2). Obtained values of mobility and activation energy for hole conductivity are presented in Table 1.

Table 1

Mobilities determined in vcacuum and in ambient.

compound	in vacuum	in ambient
	mobility, (cm^2/Vs)	activation energy, (eV)
tetracene	$(1.6\pm0.2)\cdot10^{-3}$	(0.03 ± 0.01)
p-quaterphenyl	$(2.0\pm0.2)\cdot10^{-4}$	(0.03 ± 0.01)

3.2. Conductivity modulation due to the effect of controlled adsorption of ethanol vapour

Adsorption kinetics of the ethanol vapours in the contact with the layers of both examined materials exhibit complex character (Fig. 2 and Fig. 3). The layers after preliminary pumped to the high vacuum, and then kept in the dynamic vacuum of the order of 10^{-2}–10^{-3} Tr show no increase in the current during the first 60 s after being exposed to alcohol vapour. Noticeable increase in current is seen only after this activation time.

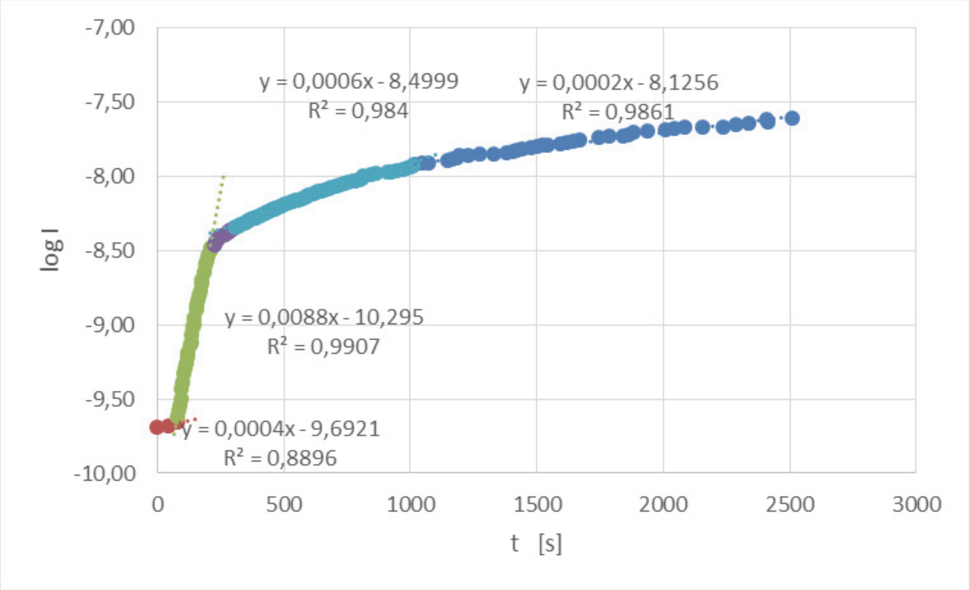

Fig. 2. dependence of dark current as a function of time of contact with alcohol vapour for the layer of p-quaterphenyl.

The characteristic for p-quaterphenyl is continued in three stages. The first stage characterizes with time constant of the current rise, $\tau = (0.11\pm0.03)\cdot10^3$ s, and after the time of $1.5\cdot10^2$ s it goes into the slower growth period of $7.0\cdot10^2$ s, characterized with life time $\tau = (1.7\pm0.3)\cdot10^3$ s, which in turn goes into slower section of growth with time constant of $\tau = (4.7\pm1.2)\cdot10^3$ s. The process of desorption of alcohol from the p-quaterphenyl surface during pumping with vacuum pump proceeds for several seconds and the current value returns to the initial value which was before starting the controllable adsorption of alcohol vapour. In turn, the process of adsorption the alcohol vapour on the tetracene surface has another character. After the activation time, when there is absence of the noticeable current rise, the time constant for the current growth gradually decreases from the value of $\tau = (0.91\pm0.19)\cdot10^3$ s for the first stage (the duration of this stage is $1.5\cdot10^2$ s), through $\tau = 0.45\cdot10^3$ s (duration of this stage is $1.7\cdot10^2$ s) to $\tau = (0.25\pm0.07)\cdot10^3$ s (time duration of this fragment is $1.3\cdot10^2$ s). Feeding with new portions of the equilibrium vapour from the container with alcohol again makes slowdown of the rate of the rising current, and after that emerges the stage with the time constant for current rise $\tau = (1.0\pm0.3)\cdot10^3$ s.

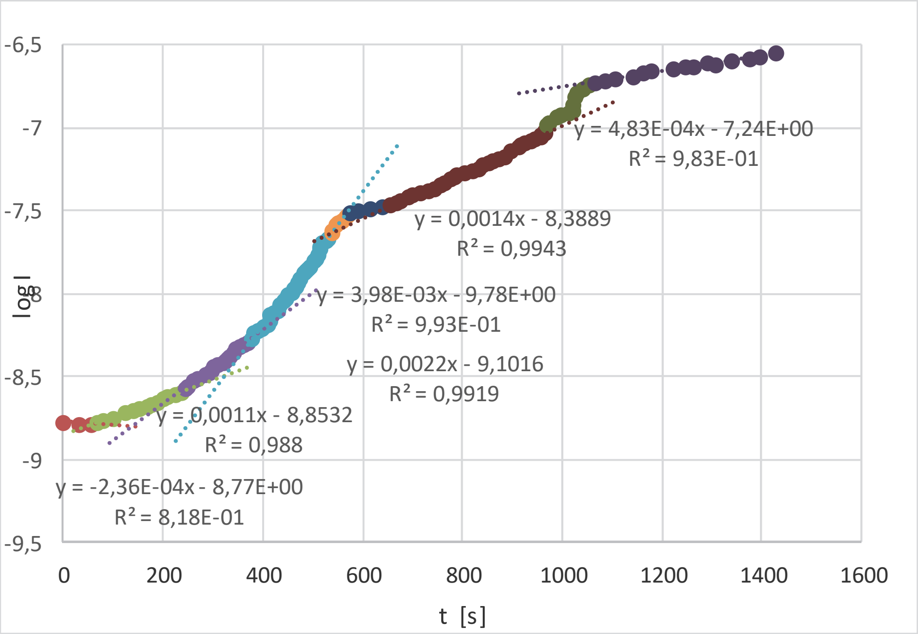

Fig. 3. Dark current as a function of time of contact with alcohol vapour for the layer of tetracene.

The next bringing into contact with new portion of equilibrium vapour results in lengthen the life time of the current rise to the value of $\tau = (2.1\pm0.7)\cdot10^3$ s. Kinetics of desorption in the case of tetracene layers consists of two stages (Fig. 4), the first with duration of 1.3 10^2 s and characterized with time constant

τ = (0.031±0.011)·10^3 and the second longer stage with time constant τ = (1.7±0.3)·10^3 s.

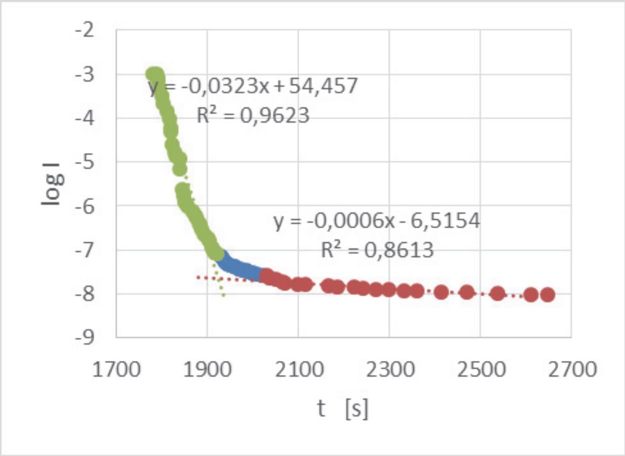

Fig. 4. Decay of current in the tetracene layer after vacuum pumping.

3.3. Discussion

Diffractometric X-ray examinations, XRD, have shown that the obtained layers were polycrystalline. Their comparison indicates a noticeable increase in drift mobility when measured in vacuum and in ambient conditions. The low value of activation energy of the order of kT and increase of the conductivity in the conditions of larger amount of the localized states indicate the emergence of the conductivity mechanism connected with existence of the transport involving the local states, the so-called hopping conductivity. This indicates also the appearance of the transport band.

The drift mobility in the examined tetracene layers under the ambient conditions in the room temperature was $\mu = (2.5\pm0.5)\cdot10^{-3}$ cm²/Vs, and the estimated density of states in the Fermi level for the air measurements was $(6\pm1)\cdot10^{20}$ cm^{-3}/eV. Analogous values for p-quaterphenyl layers were $(9\pm2)\cdot10^{-4}$ cm²/Vs and $(6.0\pm1.2)\cdot10^{20}$ cm^{-3}/eV. Such values are typical for non-crystalline materials characterized with hopping conductivity. If we assume that this kind of transport is realized through the localized states near the quasi-Fermi level for holes, then the drift mobility in the scope of Mott-Davies model [13] can be expressed by Eq. (2). The use of this dependence enabled to obtain the value of activation energy from the slope of the characteristics lnμ vs 1/*T*. Using Eq. (2) for determining the mobility of charge carriers, with assumption of the isotropic distribution represented in the phase space of density of the states, one can estimate the geometric density of states using the following dependence [14,15]:

$$N(E_F) = (3/4\pi)\cdot(1/R^3\Delta E) \tag{3}$$

The use of the Eqs. (2-3) allows to obtain the estimation of the average distance *R*, between localized states for holes transport and to estimate the average density of localized states $N(E_F)$ at the Fermi level. Assuming, that for tetracene α^{-1} value is of (1.2±0.3) nm, it can be obtained, that R = (2,5±0.5) nm and $N(E_F)$ =(5.8±2.3)·10^{20} cm^{-3}eV^{-1}, in turn for p-quaterphenyl α^{-1} is of (1.6±0.4) nm, which leads to the following values, R = (2.3±0.4) nm and $N(E_F)$ =(3.0±1.8)·10^{19} cm^{-3}eV^{-1}.

The measurements for p-quaterphenyl layers were made in the biasing range of the measuring cell from 1.1·10^4 V/cm to 1.9 10^5 V/cm.

Table 2

Density of states (DOS) and mean distance between localized states (R) determined in vcacuum and in ambient.

compound	In vacuum		In ambient	
	Density of states, (cm^{-3}/eV)	Mean distance between localized states, (Å)	Density of states, (cm^{-3}/eV)	Mean distance between localized states, (Å)
tetracene	(5.8±2.3)·10^{20}	(25±5)	(6±1)·10^{20}	(25±5)
p-quaterphenyl	(3.0±1.8)·10^{19}	(23±4)	(6.0±1.8)·10^{20}	(9±2)

Fast desorption of the ethanol vapour from the surface of the layers of both examined compounds demonstrates the obvious lack of diffusion processes into the volume. Therefore, the process of rising current in the presence of ethanol vapour is a surface process, the effect of which is seen in measurements and can be explained as the process of exchange the charge on the surface, which allows for increased flow of the charge through the layer. It may be assumed that in the conditions of the contact of the alcohol molecules with the surface the whole process can be treated as the electron transfer between the gas molecules of ethanol and hydrocarbon molecules forming surface. The rate of that charge transfer can be determined by integration of the *I-t* dependence. Therefore the excitation of the molecules forming the surface, which must be present in the occurrence of charge transport processes, should be connected with direct injection of electrons into the net of localized surface states or with the exciton migration from the volume of the layer to the surface. Making the assumption that for such a process in the p-quaterphenyl (anthracene) – ethanol system, the reaction cross section is σ_e, then the following estimation can be accepted:

$$\sigma_e = \sigma_g \cdot Q_{ex} \cdot \frac{1}{\tau_{ex} \cdot N_v}, \tag{4}$$

where σ_g is geometrical cross section of a site of surface lattice filled with arene molecule which form film, Q_{ex} is the reaction yield per exciton reached at the surface, τ_{ex} is a mean exciton lifetime and N_v is the number of collisions of adsorbate with the layer. Substituting the numerical values, appropriate in our case, $\sigma_g = 50$ Å^2, $Q_{ex} = 1$, $N_v = 1.5 \cdot 10^{14}$ cm^{-2}s^{-1}, $\tau = 4 \cdot 10^{-9}$ s, we get the estimation for σ_e as $2 \cdot 10^{-6} \cdot \sigma_g$. This conducts to the conclusion that the reaction was limited with the number of collisions in the interface. It should be noted that the electric measurements were carried for the dark currents, without use of the additional sources of excitation of ethanol molecules, i.e. without using radiation exposure absorbed in the whole system, without changing vapour pressure and without changing temperature. The only reason for the increase in current flow through the layer was the exchange of ethanol vapour molecules between the reservoir where the presence of liquid ethanol forced the existence of the saturated ethanol vapour and the chamber with examined layer inside. An additional thermodynamic force was a voltage-stabilized current flow through the layer. Observed variability of the electrical conductivity associated with surface adsorption process can be considered as the injection of dark currents induced by the transfer of the charge from (or to) molecules which were adsorbed on the surface and diffused across the surface of adsorbent. All of the adsorbate molecules compete one each other which leads them to occupy the positions with energy near the minimum local configuration energy. On the other hand, depending on the distance and the interaction between the absorption molecules and the absorber surface, the sorption process can be classified as two-way, physical sorption (mainly associated with van der Waals forces and London dispersive forces) and chemisorption (with binding hydrogen or related to the type of covalent bonding force). Obtained mean binding energy value from adsorption kinetic was (0.87±0.25) eV for tetracene and (0,77±0.23) eV for p-quaterphenyl. Such values are appropriate for weak chemisorption. For example for benzene rings, the cohesion energy between the two ring surfaces is 0.48 eV [16]. It is easy to see that such strong repelling interactions between the rings in the surface of the layer can be a source of strong electrostatic potential gradients, which can cause dissociation of ethanol molecules adsorbed on the surface and products of its disintegration.

Such a surface process can be simulated with quantum-mechanical calculations [16-19]. A description of the dynamics of such interaction of the adsorption layer with the adsorbing surface can be obtained by considering the division of the system into two thermodynamic subsystems of interacting molecules [16] and determining the directionality of the interactions of the interacting molecules. An important element of many-body interactions is the degree of entanglement of quantum states. Considering that the adsorption layer under vacuum conditions disappears at the thickness of several angstroms, we can adopt the theory of an area law for entanglement produced at exponential decay of correlations [20]. In the scope of this model for a given biparticle-mixed quantum state ρ_{XY}, one can quantify the correlation between two interacted subsystems X and Y, composed of a single site. Correlation function generalizes two-point correlation functions, in the condensed-matter physics, in which both X and Y are composed of a single site (Fig. 5).

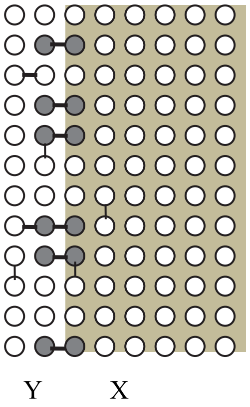

Fig. 5. Model of adsorption layer as a system of entangled pairs X and Y. Shaded square – means region of solid layer. Pairs crossing the boundary (dark) contribute to the entropy of the region inside the layer [20].

Applying the concept of abrupt transition in the structural formation of interconnected networks [20,21] we can apply this model to the gas molecules in the adsorption layer as well as to the nodes in the solid surface. The quantum state $|\psi\rangle_{1,\dots,n}$ composed of n qubits defined on a finite dimensional lattice has ξ-exponential decay of correlations $Cor(X,Y)$ between the net of region X and Y determined with formula:

$$Cor\left(X:Y\right)\le 2^{-l/\xi} \tag{5}$$

where ξ is correlation length for one of the regions, for example the region X, while l is the length of the entanglement between the nodes of these two regions. Tetracene and p-quaterphenyl molecules possess a length between 12-16 Å, and the molecules of activator - ethanol are 8-10 times shorter. Aromatic rings act as hydrogen bond acceptors [22], when proton participated in the hydrogen bond is in a distance of 1 Å from the center of benzene ring, then the total length of the hydrogen bond does not exceed 4.2 Å. In the reason of the model of adsorption layer as a system of entangled pairs (where the nodes are from X and Y regions), we can estimate l of 12 Å, and ξ of 4.2 Å, then from Eq. (5) we can obtain:

$$Cor\left(X:Y\right)\le 2^{-4{,}2/12}=0{,}785$$

This correlation value, confirm the assumption that the adsorption layer with low width gives the entangled states. Entanglement entropy E for X and Y (in our case: X- ethanol, Y- solid layer) as a function of reduced density matrix of $|\psi>_{X,Y}$ is dependent only on one of the regions, for example X. The von Neumann entropy H obtained in this manner is proportional to entropy of the boundary not to the entropy of the volume of the whole system [20]:

$$E\left(\left|\psi\right\rangle_{XY}\right)=H\left(\rho_X\right)=-tr\left(\rho_X\cdot\log\rho_X\right) \tag{6}$$

where ρ_X is reduced density matrix of $|\psi>_{XY}$ in the region X.

Assuming that in the case of strong physic sorption, the structure of Hamiltonian of the system is similar to that presented in [19] with the potential $V_{ij}(x_i,y_j,r)$ centered on the ring in the layer, where x_i, y_j are the surface coordination's of the ring binding the absorbate molecule, and $U_{k,k'}$ – interaction potential between different gas molecules (numbered by k) in the absorbing layer, V_{ck} – the potential centered on the molecule of absorbate and U_k – potential energy of the absorbate molecule in the absorbing layer then the Schrödinger equation will be:

$$H\psi=\left[-\frac{\hbar^2}{2m}\sum_{i,j}\Delta_{i,j}+\sum_{i,j}V_{i,j}\left(x_i,y_j,r_k\right)+\sum_{i,j}\left(V_{ck}\right)_{i,j}+\sum_{k}U_k+\sum_{k,k'}U_{k,k'}\right]\psi \tag{7}$$

where $\Delta_{i,j}=\partial^2/\partial x_i^2+\partial^2/\partial y_j^2$.

When strong physic sorption is present then interactions between the electron donating molecule and the electron withdrawing molecule are stronger than the dispersion type forces between neutral molecules. This situation is presented in Fig. 5 where pairs crossing the boundary (dark) contribute to the entropy of the region inside the layer [20] and lead to the formation of charge transfer complexes. Such resonance forces of charge transfer can be considered by means of wave functions created a new functions of ground state ψ_k for absorbate and for rings in the layer $\psi_{i,j}$:

$$\psi_{i,j} = a_{k,i,j}\psi_k + \sum_{i,j} a_{i,j}\psi_{i,j} \ , \tag{8}$$

where $|a_{k,i,j}|^2$ denotes the probability to find the electron on the k-th molecule of adsorbate gas, and $|a_{i,j}|^2$ denotes the probability to find the electron at the i, j-th ring.

If the barrier between the adjacent rings is greater than the energy present between the k-th absorbate molecule and the ring closest to this the molecule (because the rings represent solid phase and k-th adsorbate molecule is belonged to gas phase), then the wave function describing the charge transfer is reduced to the interaction with the two closest molecules from gase and from solid:

$$\psi_{i,j} = a_k\psi_k + a_{i,j}\psi_{i,j} \tag{9}$$

In this case, the problem of the whole surface interactions can be separated into the sum of the factors centered on each of the adsorbate molecules numbered by the k index. Moreover, under such boundary conditions, the problem of transport inside the layer may be considered as a simple sum of the terms assigned to the transported charge carriers. Each of them comes from different types of molecules accomplished adsorption. In general, the energy of the molecular crystal can be written as:

$$E(a) = E^{(2)}(a) + \sum_{n\geq 3} E^{(n)}(a) + \Delta E_{ZPE}(a) \tag{10}$$

where the 3×3 matrix a represents lattice parameters, $E^{(2)}$ is pairwise additive, two-body term, $\sum_{n \geq 3} E^{(n)}$ represents the sum of many-body non additive terms, and ΔE_{ZPE} is zero-point-energy correction. The direction of charge transfer and the stability of the associated interaction are related to the asymmetry of the properties of the interacting phases. Asymmetry in our case means that the excess of electrons is on the side of the adsorbate atoms relative to the ring of the layer ($a_k >> a_{i,j}$). Then applying the second order perturbation theory one can obtain the E_G energy of the new basic state ($\psi_{Gi,j}$) given as:

$$E_G = E_0 - (H_{01} - SE_0)^2 / (E_1 - E_0) \tag{11}$$

where E_1, is the energy of the state described by wave function $\psi_{i,j}$ with Hamiltonian

$$H_{01} = \int \psi_k H \psi_{i,j} dv, \tag{12}$$

and overlap integral:

$$S = \int \psi_k \psi_{i,j} dv \tag{13}$$

The weight of this expression should be high when the final term of the sum $[(H_{01} - SE_0)^2 / (E_1 - E_0)]$ is high. In such a case $(E_1 - E_0)$ should be low, i.e. transfer energy for relocation the electron from gas molecule to the ring should be small.

This occurs when the ionization energy of the gas molecule (or its dissociation product) in the adsorbed state will be low, but the ring of a molecule in the surface shows a high affinity for electrons. At the same time, this leads to the requirement for value $[(H_{01} - SE_0)^2]$ to be maximized, to ensure greater stability of charge transfer process. This means, that the overlap of ψ_k and $\psi_{i,j}$ should be large, i.e. the orbitals donating the electron and the orbitals withdrawing the electron should be sufficiently close to each other, and more they both should have a similar symmetry. In our case, this refers to the symmetry of the type π derived from ring bonds and the symmetry of the n-type orbital derived from the free electrons of the dissociated gas molecule. In summary, the interaction leading to charge transfer will be stronger between the orbitals of the electron donating molecule characterized with higher energy level and the withdrawing molecule orbitals with low level of energy, while also requiring similarity of symmetry and the possibility of direct physical contact. The similarity of symmetry should be understood in this case as the suitable relative orientation of the electron donating molecule and the electron withdrawing molecule. Therefore, there must be a match between the HOMO orbital of the electron donating molecule and the LUMO orbital of the electron withdrawing molecule. The position of the balance of interacting molecules will also depend on the repulsive forces resulting from Pauli's exclusion principle on electrons and the repulsion of nuclei.

5. CONCLUSIONS

Study of the response of tetracene and p-quaterphenyl layers to the presence of vapor of ethyl alcohol under vacuum conditions allows to isolate phenomena related only to the surface interactions with alcohol vapor. The order of activation energy values obtained at room temperature suggests the existence of the complex of phenomena related to the active uptake of the equilibrated molecules of alcohol vapor by the layer surface in the presence of the surface potential of the tested layer. The effect of these phenomena is an origin of increase of the conductivity of the tested layer. The conductivity activation mechanism may be related to the dissociation of ethanol molecules and the formation of hydrogen bonds, and to the formation of undesired double bonds in the adsorption layer.

Our observations indicate that the adsorption processes described above are characterized by total or partial reversibility when the effects of the activating gas molecules will be omitted. Such reversibility is important for layer applications as gas sensors. In turn, the use of organic materials in the manufacturing of semiconductor devices requires stable properties of the layers, which are related to the occurrence of irreversible transformations, or with the resistance of these layers to external factors.

Based on the above data, the increase in hole mobility can be interpreted as a result of the increase in density of localized states. This means compliance with our earlier suggestion that the increase in conductivity as a result of the activation process can be achieved by increasing the number of localized states, provided that these states are the states through the holes are transported.

It also means that the dominant transport mechanism should be hopping transport.

In addition, observations show that:

1. The activation process leads to an increase in DC current conduction in aromatic hydrocarbons and is a reversible process. This suggests the possibility of application in practice.
2. The discussed phenomenon indirectly seems to confirm the validity of assumption that the hopping transport is dominant here.
3. Surface activation of low molecular weight organic layers may be utilized.

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PRZEWODNICTWO OBJĘTOŚCIOWE WARSTW POLIKRYSTALICZNEGO TETRACENU I POLIKRYSTALICZNEGO P-CZTEROFENYLU MODYFIKOWANE WPŁYWEM ADSORPCJI POWIERZCHNIOWEJ

Streszczenie

Przewodnictwo objętościowe warstw organicznych badane w warunkach kontaktu z atmosferą otoczenia zależy od właściwości objętościowych oraz od procesów adsorpcji cząsteczek aktywatora na powierzchni swobodnej. W celu wyjaśnienia roli powierzchni przeprowadzono w temperaturze bliskiej 293 K eksperymenty nad określeniem wpływu dynamiki adsorpcji na zmianę charakterystycznych zależności obserwowanych dla transportu ładunku elektrycznego w próżni, w atmosferze otoczenia oraz w kontrolowanej atmosferze par alkoholu etylowego. Badania przeprowadzono dla dwu liniowych struktur molekularnych cztero-pierścieniowych, to jest p-czterofenylu i tetracenu. Związki te różnią się organizacją pierścieni. Wyniki wskazują na wzrost przewodnictwa mierzonego dla obu związków, gdy występuje obecność cząsteczek zdolnych do adsorpcji na powierzchni, które mogą przekazać lub odebrać nośniki ładunku zdolne do dyfuzji lub uporządkowanego transportu w objętości warstwy. Charakter obserwowanego wzrostu przewodnictwa świadczy o obecności mechanizmu hoppingowego w przypadku przewodnictwa obu badanych materiałów.