

SYLWESTER KANIA<sup>1,2</sup>, JANUSZ KULIŃSKI<sup>2</sup>

<sup>1</sup> Institute of Physics, Technical University of Łódź, Wólczańska 219  
90-924, Łódź, Poland

<sup>2</sup> Center of Mathematics and Physics Technical University of Łódź  
Al. Politechniki 11, 90-924 Łódź, Poland

## ACTIVATION PROCESSES FOR TWO CHOSEN AROMATIC HYDROCARBON MATERIALS

*The activation process and the transport process for electrons in the tetracene layers and holes in the p-quaterphenyl layers is considered. Obtained results may suggests the hopping transport through the localized states near the Fermi level as a dominant kind of transport. Observed dependence of the conductivity on the vapor concentration of the activator molecules may suggest that tetracene is better for utilization as a vapour sensors.*

**Keywords:** polycrystalline, tetracene films, p-quaterphenyl films, activation process, electron mobility, hole mobility, carrier transport.

### 1. INTRODUCTION

Weak hydrogen bonds and great variety of adsorption points make possibility of deep modulation of outer molecular orbitals of aromatic hydrocarbons due to variable concentration of adsorbates. This reason can make them a future material from a point of molecular electronics view and make the possibility to use the aromatics for homogenic sensors.

There is a very interesting to compare two representative aromatic hydrocarbons with very similar crystallization properties such as density of packing, or coordination number but with different molecule construction in experiments reveals theirs absorption potentiality.

Acenes are with flat 2D molecules with stiff coupled rings, but n-phenyls are 1D molecules with rotating rings. For both types of aromatics, inner bonds

are directional covalent, but the intermolecular are induced by hydrogen bondings. Tetracene and p-quaterphenyl have the same number of carbon rings for a molecule, so their molecular weight is above 200 g/mol with the overall length between 12-16 Å. The little, 8-10 times shorter, activator molecule of ethanol has a head similar to the water molecule in a shape of the C-O weakly bonded with H atom via oxygen. The weight of this head is two times more than the weight of the non-reactive tail built from CH<sub>3</sub> so this head is decisive for absorption habits. If we make an assumption that the adsorption is caused in relation with hydrogen bonding between adsorbate C<sub>2</sub>H<sub>5</sub>OH and the C-C or C=C bond in hydrocarbon then it can be recognized active points for two types of molecules under examination for adsorption. The shape of isolated molecule possesses an ability to absorb in first coordination sphere about 16 ethanol molecules for tetracene and about 22 ethanol molecules for p-quaterphenyl. It is evident that the molecule built in crystal structure has a small number of free active points.

Ethanol is not conductive, but during absorption process, its like "water" dipole moment can make a distortion of the adsorbing molecule orbitals, what allows to dissociate the head of ethanol and to hydrolyze the hydrocarbon bonds with OH<sup>-</sup> group or with the H<sup>+</sup> ion. Above mentioned processes conduct to physisorption or to chemisorption and conduct to change the electronic states of adsorbing molecule. These interactions and hydrogen bonds are weak, so the additionally created conducting bands must be narrow.

Protons between two molecules, polarize them and attract them by means of induced dipoles, the hydrogen binding energy between ethanol and hydrocarbon is about 40 kJ/mol (0.4 eV/bond) [22]. Such a bond may be a cross-linking for conduction between two neighbouring molecules. The net of such linkings may produce the percolation paths for conduction.

All of these interactions violate the symmetry molecule Hamiltonian.

The broken symmetry of electron Hamiltonian originated from presents of new distortions must conduct to the new electronic eigenvalue states.

Hamiltonian,  $H$ , of a system of crystalline aromatics with adsorbate activator can be described with the equation:

$$\hat{H} = \hat{H}_1 + \hat{H}_2 \quad (1)$$

where:  $H_1$  – Hamiltonian of conducting electron in tetracene or of conducting hole in the p-quaterphenyl,

$H_2(C)$  – Hamiltonian of disturbance as a function of the adsorption  $C$ .

The probability of transition of the molecule from the absorbing state to the new one state with changed absorption concentration, from  $C$  to  $C'$ , is:

$$P(C \rightarrow C') = A \cdot \exp - \left[ \frac{\Delta H_2}{kT} \right] \quad (2)$$

where  $A$  – normalization constant,  $\Delta H_2$  – eigenvalue of Hamiltonian of disturbance,  $k$  – Boltzmann constant,  $T$  – temperature in Kelvin's.

Well known fact is that absorption is easier when the molecule has large number of free absorbing points. When the places are full filled then the probability  $P(C \rightarrow C')$  collapse. Such a fact conduct to the conclusion that with the great vapour concentration,  $\Delta H_2$  can change more slowly. What does it means. Simply, when concentration of the vapour rise then the split between neighbouring states vanishes. As a consequence this fact appears as a origin of a new band, band for additional conduction. This fact may explain the growing raise of the current with the rise of the vapour concentration.

The additional density of states originated from adsorption will be

$$N(C) = \frac{C}{N_A \int_0^C d(\Delta H_2)} \quad (3)$$

where  $N_A$  – Avogadro constant.

In the rigid structure of tetracene molecule the additional violate of symmetry in the Hamiltonian connected with conformation dependent on addition of new absorbing activator molecule will be less than for the rotating rings of p-quaterphenyl, where such a process evidently change the rotational frequency. This fact makes the conclusion that the energetic split  $\Delta H_2(C \rightarrow C')$  from addition of the same concentration of adsorbates to phenyls may be greater than for acenes. So when we have the same concentration of adsorbate on the surface then the density of additional conducting states in p-quaterphenyl will be less than in tetracene. That fact may be a guidelines for searching new sensitive organic materials.

Polycrystalline tetracene and p-quaterphenyl are representative for n-acene and n-phenyl ring low molecular weight compounds. Tetracene molecules due to the  $sp^2$ -hybridization of carbon atoms are flat. Phenyls in opposite have ability to make different crystalline phases due to rotation of rings. The structure inside the grains is a compromise between attractive van der Waals forces and repulsive forces emerged from the Pauli exclusion. Interactions between the molecules determines the number of  $\pi$  connections between them, and is decisive for appearing additional percolation path for carriers. Charge transport is dominated by the comparatively weak short –range intermolecular forces. In theoretical description it force to use the perturbation theory in the sense of

enabling a single molecule to preserve its individuality to some extent and treatise all the influences as a violation of symmetry. The complex nature of the relations between inner structure and charge transport induced in the external drift electric field makes uncertainty in determining theoretical model of the conductivity. In the room temperatures it is impossible to say obvious if the working model is band model or the dominant are models with localized states. Such behaviour is the base sense to explore studies on those materials in different phases to modulate their electric phenomena.

In the room temperatures monocrystals of such organics have got the drift mobility close to  $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  [1-3]. The temperature dependence of drift mobility is usually given by:  $\mu \propto T^n$ , where  $n$  changes in the range  $0 > n > 2$ . However, such a trapping – independent drift mobility may be found only in exceptionally perfect and pure monocrystals [4-7].

The acene and phenyl rings easy undergo to polarization and even small amount of chemical impurities (of the order of 1 ppm) [3] or structural imperfections [2, 3] strongly influences the equilibrium between the inner electronic arrangement of the aromatic molecule and the molecules in the vicinity and this is reflected in the charge transport which results in significant decrease in the mobility value [2, 4, 5, 8]. In this case the charge transport may be controlled by multiple trapping.

In heavily doped (or unpurified) and disordered polycrystalline structures the charge mobilities are of the order of  $10^{-5} \div 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  for tetracene and for p-quaterphenyl are of the order of  $10^{-5} \div 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  [9, 10, 11, 20, 21]. It has been suggested that the charge transport in these cases may be interpreted in terms of hopping transport between localized states [9, 10, 11, 12-18, 20, 21]. The mayor difference between charge transport in the conduction band controlled by trapping and the hopping transport visible in experiment is the dependence on concentrations of traps (or localized states).

Transport in the conduction band controlled by traps makes the drift mobility decreases with increasing trap concentration because the probability of trapping and retrapping increases slow down the speed of carriers. However, in the case of hopping transport among localized states the drift mobility increases with increasing concentration of the states because the probability of jumps increases with decreasing average distance among the localized states.

### 1.1. Activation process

Molecular crystals differentiate from other crystals, for example ionic, in that point, that the intramolecular interactions are directional covalent and stronger than the intermolecular van der Waals or hydrogen, which can be easily modulated by excess dopant charge or with permanent dipole moment. This is because of the existence of some number of easily polarizing electrons  $\pi$  in them. There are a lot of agents activating superficially (or by volume) organics in solid state. From one point of view of interactions stability and of possibility of probable expectation of electrical properties, the basic agents which can be recognized by hydrocarbons are so-called Lewis's compounds, with their behavior to dissociate. In this paper as such an activator, an ethanol ( $C_2H_5OH$ ) is used.

When one activates the organic system then the oxidation of the unsaturated  $sp^2$  system leads to carbon-carbon double-bond cleavage and then to generate the defected  $sp^3$  bond. When it runs through the transition states then it is similar with the chemisorptions phenomenon (with synchronous charge transfer), and then comes to the diffusion in the interchain or interplanar area. If there is no following stabilization for such transition stages then that process is reversible. In the case of strong activators, there is present an entire disjunction of the  $\pi$ -electron system and system come next to shaping itself as a system with saturated  $sp^3$  bonds.

It is known that some atmosphere molecules give rise to additional localized states in typical simple aromatic hydrocarbons. If the states were to be traps controlling the charge transport in the conduction band, this should cause the drift mobility to decrease when measured in the atmosphere. In case of domination of hopping transport among localized states the drift mobility may be expected to increase in the atmosphere. The process of surface activation of organic materials usually leads to modification of their electrical characteristics. This modification manifests itself with the increase of the dark conductivity and the photoconductivity, and with the change of the value of the activation energy, the value of the charge mobility and the dielectric loss. For acenes the electric conductivity can increase, for example  $10^3$  times or much more due to nature of the activator and mobility of the rings. Similarly the activity interaction response time for the sample is dependent on the time stability of obtained effect and on its reversibility. Usually there is a change of the character of the carrier mobility transport, and become to be a visible depressive transport due to manifestation of the deep trapping states. Activation process for acenes leads to the variation in the energy structure of the energy gap, what demonstrates among other things in the photoluminescence effect. It appears subsequent to wavelength shift of the emission to the states accessible in the visible range.

The basic goal of the presented investigations is to find the influence of precipitate activator molecules on charge transport of polycrystalline: tetracene and p-quaterphenyl and to judge those ability to utilize.

## 2. EXPERIMENTAL

Thin films of polycrystalline tetracene ( $C_{18}H_{12}$ ) or of p-quaterphenyl ( $C_{24}H_{18}$ ) made as the sample a “sandwich” type with Au – Al electrodes were prepared with vacuum deposition method evaporation in vacuum under the pressure of the order of  $10^{-5}$  Torr on glass plates covered with metal electrode. The substrate temperature was about 300 K and the evaporation rate was changed in the range 20-30 Å/s. X-ray diffraction structural examinations of the obtained layers were made using automatic diffractometer DAR in the  $2\theta$  range from  $5^\circ$  to  $80^\circ$  with measuring step  $0,05^\circ$ .

Typical diffraction pattern for the polycrystalline tetracene films is described with Fig. 1a. and for p-quaterphenyl with Fig. 1b.

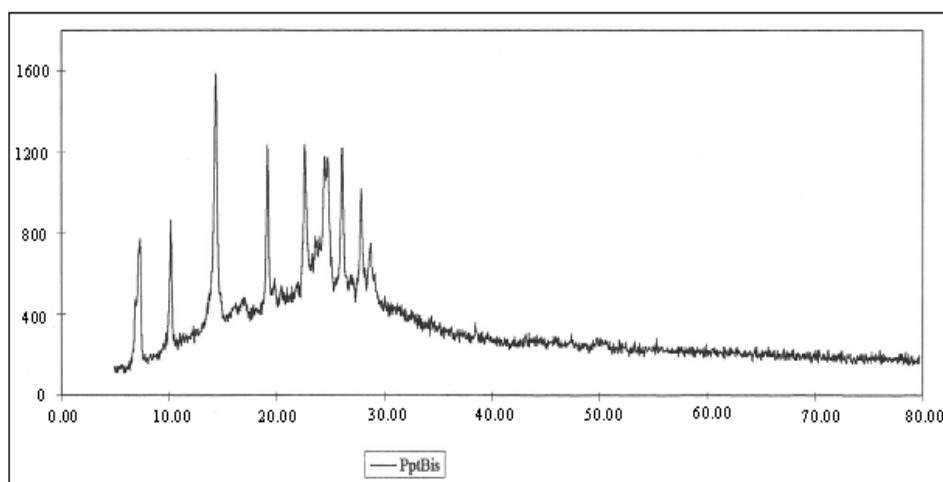


Fig. 1a. Diffractogram of the tetracene polycrystalline film. Plot of the intensity of X-ray diffraction lines in function of the angle  $2\theta$

The microscopic observations evidence reveals the sizes of the surface's grains in the order of one micrometer. The thickness of the obtained films were

from about 15  $\mu\text{m}$  to 20  $\mu\text{m}$ . Such layers were fixed upon the vacuum of the order  $10^{-2}$  Torr and then they were subjected to the action of the vapour activator -  $\text{C}_2\text{H}_5\text{OH}$ .

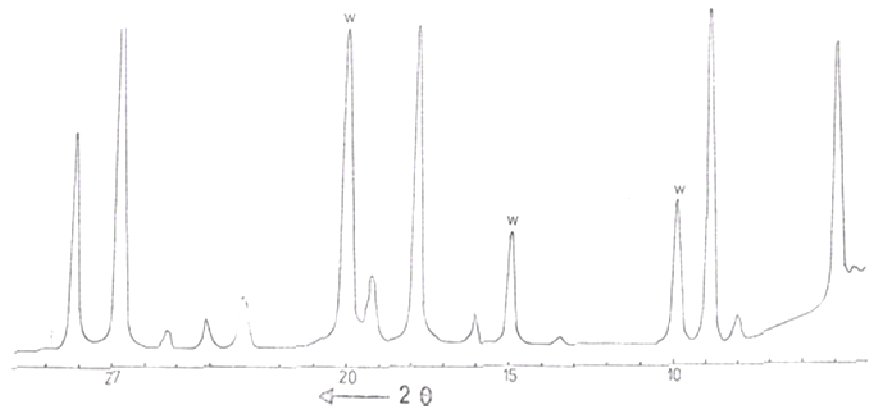


Fig. 1b. Diffractogram of the p-quaterphenyl polycrystalline film. Plot of the intensity of X ray diffraction lines in function of the angle  $2\theta$

That activator has been chosen because its high polarity (with permanent dipole momentum 1.7 D dependent on appearance OH group) what make possible attachment in physic sorption process. During chemisorption process the head of molecule, C-O-H, acts like water molecule dissociating to  $\text{O-H}^-$  and  $\text{H}^+$ . The ethyl cation ( $\text{C}_2\text{H}_5^+$ ) displays hyperconjugation effect enables to interact via proton ( $\text{H}^+$ ) binding with the  $\pi$  centers of hydrocarbons, eg. the double (C=C), and  $\sigma$  centers – (C-C) bonds [22].

### 2.1. The influence of the atmosphere on conductivity of the tetracene and p-quaterphenyl

The experimental set – up, Fig. 2, consists of the current source and electronic recorder  $X(t)$  and  $Y(t)$  allows to take measurements and registration of changes of a dark current flow through the studying sample during the action of activator. It was observed here a clear growth of the direct current conductivity even for five orders due to rise of the molecular concentrations of the  $\text{C}_2\text{H}_5\text{OH}$ , what can be evidently seen in the Figs. 3 and 4. With the larger concentrations of molecules  $\text{C}_2\text{H}_5\text{OH}$  and with sufficiently long times above 200 s, for tetracene layers with the thickness approx. 15  $\mu\text{m}$  there were observed irreversible damages of the layer after growth of the current above the level of  $5 \cdot 10^{-4}$  A.

That is a difficult to judge if it has been caused by a firm joint of the  $C_2H_5OH$  molecules to the layer and with the transition of the tetracene to the state of high conductivity connected with creation of new states in scope of the bond theory or with inducing the new percolation paths. It is nearly obvious that in both channels the dielectric should have brought to the high conductivity state inside small grains with simultaneous high resistance of the interlayer between grains. Such a mechanism may cause non uniformity of the field in the layer and may be responsible for the damages of the electric contacts in the places of meeting metal electrode with dielectric due to the dissipation of the energy. In such a model there is possible locally to overheat the points of interfaces to the temperature in the proximity of the Tamman temperature ( $2/3$  of the melting point) which is for both studying materials under ca. 400 K. In this temperature there is possible the reaction in solid state, so in the case of consideration there is real possibility for occurrence of chemisorption process.

Progress of conductivity was dependent on the time of activation and on the concentration of the activator vapour. The time constant for the absorption start were: 30.8 s for tetracene, and 51,0 s for p-quaterphenyl for the ethanol pressure in order of 2 Pa.

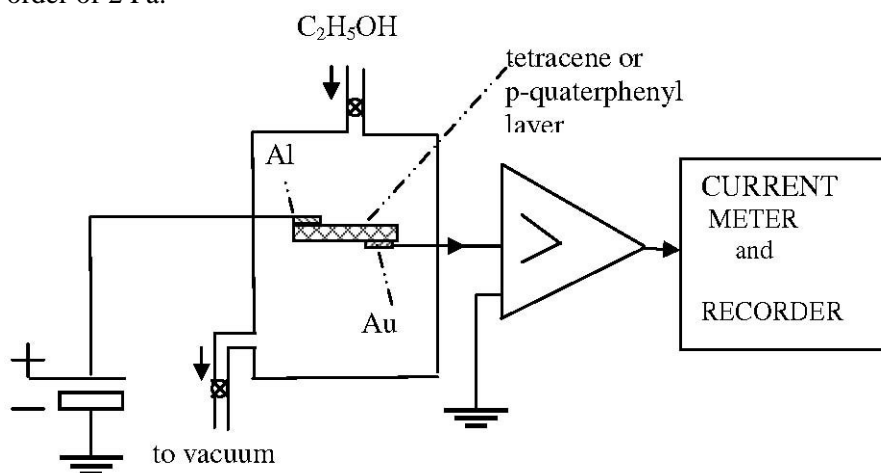


Fig. 2. Schematic diagram for the measuring apparatus for activating films and for register the variations of the dark current due to activation processes

The sample "response" time due to the activator molecules is dependent on theirs concentration and is shorter for higher concentrations. The time-constants for saturation were above 1000 s for both hydrocarbons. Process is not fully



reversible, for tetracene layer time-constant of desorption was only 11.3 s. The steady value of a current after sequence activation and desorption is higher than were on the start in vacuum. The kinetics of the process persuade to the conclusion, that at the beginning of the activation process occurs physisorption with addition of the chemisorptions of the  $C_2H_5OH$  molecules on the tetracene and p-quaterphenyl surface. transition from physisorption to the chemisorptions must be connected with the diffusion process which enables recovering process for the surface or for rebuilding of the volume. It means, that at the start the conductivity value is determined by the surface of the film, and then also with the bulk processes.

The activation process leads among others to the increase of the number of the surface states, what develops in the energetic structure of energy gap as presence the additional energy states with the concentration determined with equation (3). The measurements were fulfilled in 300 K, when the If the concentration of the activator molecules is sufficient, then the states those (in the structural sense) may be filled with  $C_2H_5OH$  molecules on the surface will be populated and then adequately those ones connected with the bulk of the film as well. Then appear the additional states related to the bulk of the film and the volume states may be responsible for non reversible level of the current before and after whole measuring procedure. In such 3D model the chemisorptions is not necessary to explain the irreversibility.

It seems, that in the discussed process the decisive part plays the molecular polarizability and chemisorptions induced in the places of overheating, it means the deformation of the electron shells in the tetracene or p-quaterphenyl microcrystals influenced with electric field of the  $C_2H_5OH$  molecules or by reaction with  $C_2H_5^+$  ion with participation of proton.

The activation process is not fully reversible. If we do not treat the conditions of damage (in the electric sense hazards) then we can consider the process of the activation of the layer as the reversible process with the occurrence of the small „memory” effect (i.e., that outputs level of current near the same voltage should be somewhat higher than it was on a first stage). The similar phenomenon as described above was observed for different aromatic low-molecular hydrocarbons.

If we assume that covering of the surface  $\sigma$ , is proportional to the molecule time of adhesion  $\tau$ , and to the molecular flux of vapour  $F$ :

$$\sigma = \tau \cdot F \quad (4)$$

where:  $F = \frac{N_A p}{\sqrt{2\pi m T R}}$  then we obtain:

$$\sigma = \frac{N_A p}{\sqrt{2\pi m R}} \tau_0 \exp\left[\frac{\Delta H_{\text{abs}}}{RT}\right] \quad (5)$$

where:  $p$  – pressure,  $N_A$  – Avogadro constant,  $m$  – gram-molecular weight,  $R$  – gas constant,  $T$  – temperature and  $\Delta H_{\text{ads}}$  – heat of adsorption, and typical value  $\tau_0 = 10^{-13}$  s.

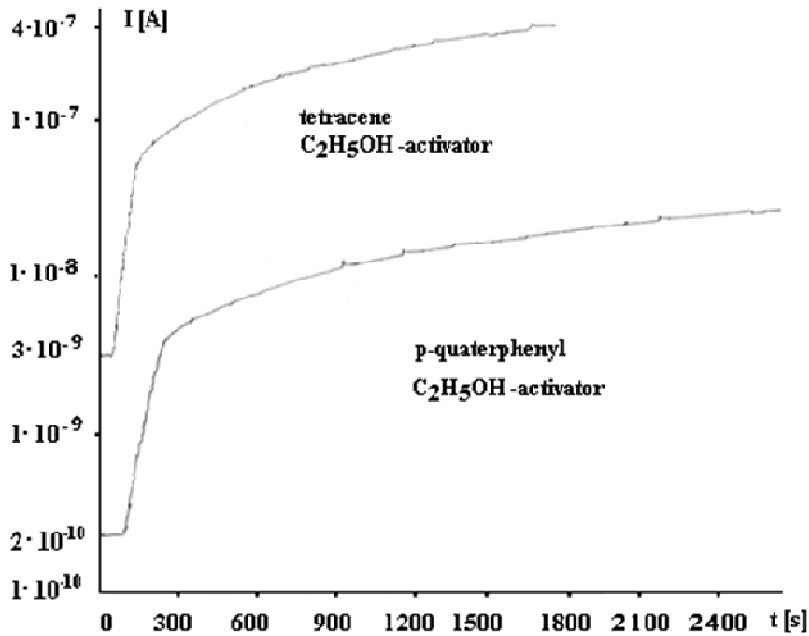


Fig. 3. Dependence of the dark current flow through the film in the function of the activation time for tetracene and p-quaterphenyl films with activator –  $C_2H_5OH$

Assumed that the rise of the current over initial value  $I_0$ , is proportional to the covering of the surface, then the enthalpy determined from the slope of  $C_2H_5OH$  absorption line (from Fig. 4) is identical for tetracene and for p-quaterphenyl. Based on it we can suggest nearly identical mechanism of adsorption influence on the electron structure of adsorbing molecule for both studied substances.

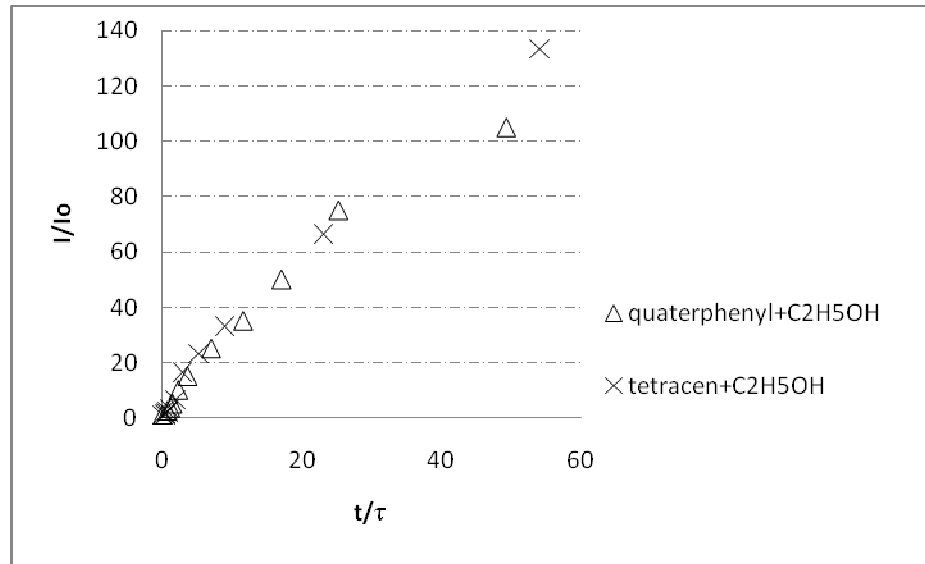


Fig. 4. Dependence of normalized dark current flow through the film in the function of the normalized activation time

Sorption introduce a definite number of donor or acceptor states to organic solid state. Kinetics of the current have to one to make a conclusion that here there is a case of physic sorption with addition of proper ratio of chemisorption. It is obvious that diffusion phenomena must be present in conditions of 300 K temperature. The activator molecules are going to built in to the specific places of the molecules of activated material. The charge transferred to the molecule of host material is compensated with the charge transferred to the activator molecule. Interchain or interplanar interactions tend to change distances, with keeping structural identity of sizes for chains or for planes of activated material. Lewis's bases are the molecules with a free pairs of electrons in the atoms, and so there is a number of the molecules of unsaturated and aromatic hydrocarbons which have additional mobile electrons  $\pi$ .

If we do not treat the conditions of damage (in the electric sense hazards) then we can consider the process of the activation of the layer as the reversible process with the occurrence of the small „memory” effect (i.e., that outputs level of current near the same voltage should be somewhat higher than it was on a first stage). The similar phenomenon as described above was observed for different aromatic low-molecular hydrocarbons.

Precise description of the shape of the current – voltage characteristic for acenes with discrete trapping levels is impossible. Approximate equation should be in the form of:

$$J = \varepsilon\varepsilon_0\mu\theta\alpha^2\beta(V^2/L^3), \quad (6)$$

where:  $1 < \alpha < 2$ ,  $1/2 < \beta < 1$ ,  $\mu$  – mobility of carriers,  $\varepsilon$  – relative dielectric permittivity,  $\varepsilon_0$  – vacuum permittivity,  $V$  – applied voltage,  $L$  – the sample thickness,  $\theta(T) = n/n_t$ ,  $n$  – the total density of free charge carriers,  $n_t$  – the density of the trapped carriers.

For dielectric with uniform continuous distribution of traps

$$\rho(E) = \rho_0 = \text{const} \quad (7)$$

(in the limits from  $E_i$  to  $E_l$ ) where  $E_l > E_i$  (Fig. 5a) the current – voltage characteristic may be described with formula:

$$I = eN_c\mu(V/L)\exp(-E_l/kT)\exp(bV/\rho_0kT), \quad (8)$$

where:  $b = \varepsilon\varepsilon_0\alpha\beta/eL^3$ ,  $1/2 < \alpha < 2$ ,  $1/2 < \beta < 1$ ,  $N_t$  – the quantity of the localized states per volume unit, and  $N_c$  – the number of states in the conductivity band,  $\rho_0$  – density of trap distribution.

For the more complicated expansion of states in the forbidden gap, expressions describing the size of the current rise have more elucidated figure and for example of the exponential expansion decreasing with the growth of energy:

$$\rho(E) = \rho_0\exp(-(E_l - E_i)/kT_c), \quad (9)$$

formula is

$$I = (bN_c\mu e/LN_t) \cdot V^{1+T_c/T} \cdot [\exp(-E_l/kT)], \quad (10)$$

where:  $b = \varepsilon\varepsilon_0\alpha\beta/eL^3$ ,  $1 < \alpha < 2$ ,  $1/2 < \beta < 1$ ,  $N_t$  – the quantity of the localized states per volume unit, and  $N_c$  – the quantity of states in the band,  $T_c$  – characteristic temperature. If we activate the layer then the density of localized states should clearly increase. For the dielectric with either continuous or complex distribution of traps, what is true for polycrystalline layers, it is impossible to show analytic formula describing the current – voltage characteristic due to the complexity of the problem.

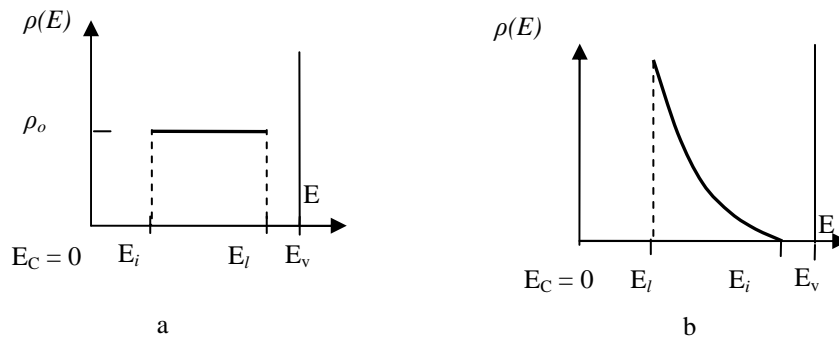


Fig. 5. The pattern of the energetic expansion of the states situated between the levels of energy  $E_i$  and  $E_l$ : a) continuous expansion of the states, b) the expansion of the states decrease exponentially with energy

For the dielectric with both continuous and complex distribution of traps what is true for polycrystalline layers it is impossible to show analytic formula describing the current – voltage characteristic due to the complexity of the problem. Nevertheless the growth of the quantity of the localized states, within the scope of this model should lead to decrease of the value of the current. Unless, the real growth of the carrier mobility should have been occurred, and so great then it can exceed the velocity of growth of the localized states density, or if the localized states would tends to stay such a states through them the conductivity may occur, what is possible in the condition when the hopping transport is the dominant mechanism of conductivity. Verification of such hypothesis would be easy and right, if one could directly measure the mobility value during the process of activation of the studied layer. Unfortunately such measurement from technical regards could not be made.

It succeed only to make the measurements of the drift mobility for the tetracene and p-quaterphenyl layers in the vacuum of  $10^{-5}$  Tor and in the air with moisture approx. 60-70%, that is in the presence of the polar molecules of the aqueous steam ( $H_2O$ ) and the molecules of oxygen ( $O_2$ ). The mechanism of sorption should have to be the same as for the “head” of ethanol. Obtained TOF (Time Of Flight) impulses possess the kink point allowing directly to mark the mobility of carriers in described layers. For electrons in tetracene layers in vacuum was obtained drift mobility  $\mu = 4 \cdot 10^{-4} \text{ cm}^2/\text{Vs}$  with activation energy 0.04 eV, but in ambient atmosphere the drift mobility was  $\mu = 9.5 \cdot 10^{-4} \text{ cm}^2/\text{Vs}$ .

There were obtained for holes in p quaterphenyl layers in vacuum drift mobility of value  $\mu = 2.0 \cdot 10^{-5} \text{ cm}^2/\text{Vs}$  with activation energy 0.04 eV, and in atmosphere the drift mobility  $\mu = 9.0 \cdot 10^{-5} \text{ cm}^2/\text{Vs}$ .

The low value of the drift mobility for both hydrocarbons, below  $10^{-2} \text{ cm}^2/\text{Vs}$ , and its low activation energy in the order of  $kT$  suggests that the hopping charge transport takes place in a narrow band of localised states.

Mott-Davies model describing the hopping transport in a narrow band of states at the Fermi level the drift mobility is given by:

$$\mu = (1/6)(eR^2/kT) \cdot v_{ph} \cdot \exp(-2\alpha \cdot R) \cdot \exp(-W/kT) \quad (11)$$

where  $R$  – is the average distance between the localized states,  $e$  – is the electron charge,  $k$  – is Boltzmann constant,  $\alpha$  – is the decay of the localized state wave function,  $W$  – is the effective width of the band of localized states,  $T$  – is the temperature. Using the above equation and the geometrical formula  $N(E_F) = (3/4\pi)(1/R^3W)$  one can estimate the average distance between the localised states  $R$  and the density of localised states at the Fermi level  $N(E_F)$ .

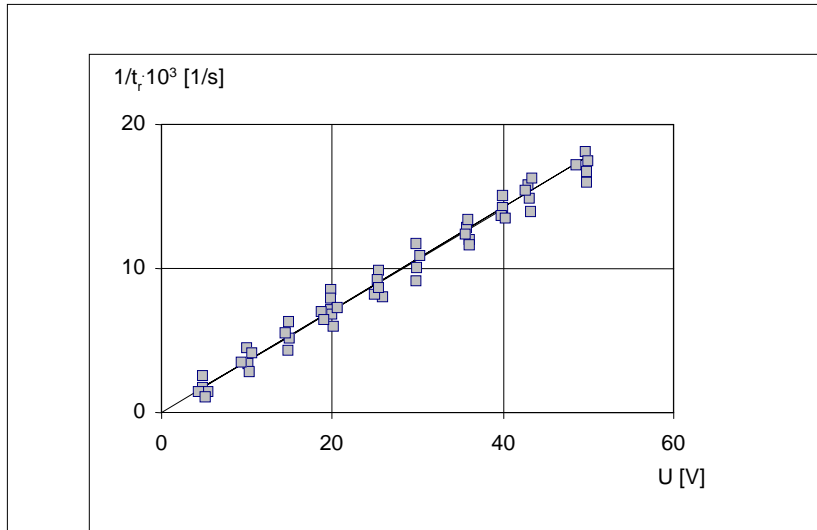


Fig. 6. Diagram of an inverse time-of-flight  $1/t_r$  for electrons in tetracene upon the voltage applied to the film,  $L = 17,5 \mu\text{m}$ ,  $\mu_e = 9,5 \cdot 10^{-4} \text{ cm}^2/\text{Vs}$

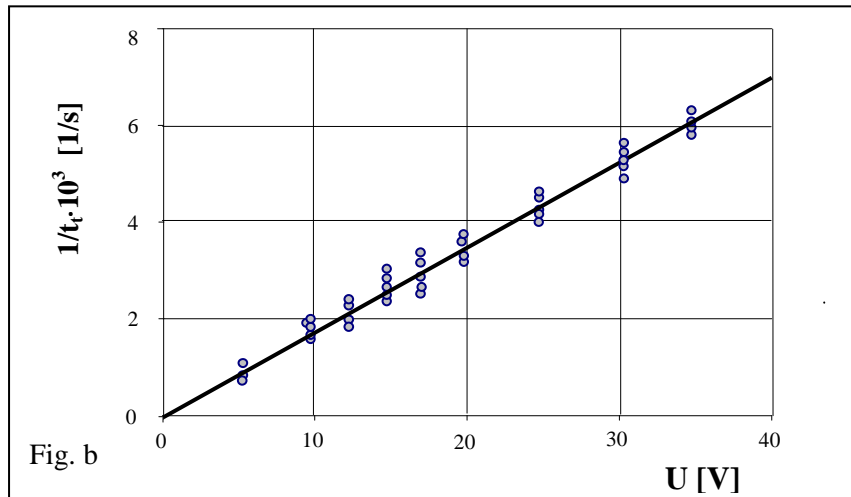
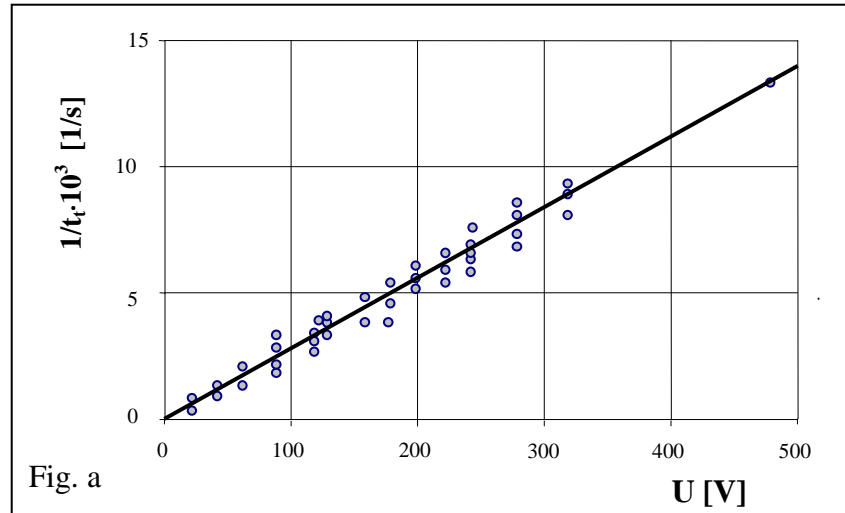


Fig. 7. Examples of relation between transition times of holes and voltage for p – quaterphenyl thin film: a) the measurements carried out in the vacuum. Sample thickness  $L = 18 \mu\text{m}$ , b) the measurements carried out in the air. Sample thickness  $L = 20 \mu\text{m}$

The values of  $N(E_F)$  obtained for the measurements in vacuum are close to  $3 \cdot 10^{19} \text{ cm}^{-3} \text{ eV}^{-1}$  for both hydrocarbons, while for the measurements carried out in the air turns out to be nearly 1 order of magnitude higher, about  $6 \cdot 10^{20} \text{ cm}^{-3} \text{ eV}^{-1}$ . This values of the density of states are typical for many non-crystalline materials and seems to confirm the consistency of the model used.

The voltage dependence of the time-of-flight  $1/t_r$  for the polycrystalline layer is presented in the Figs. 6 and 7. Obtained current pulses had characteristic kink point which enables direct estimation of the transit time for electrons for polycrystalline layers.

The fact that the mobility of electrons in tetracene and holes in p-quaterphenyl increase, we can interpret as the growth of the density of localized states. This marks, that our earlier suggestion, that the growth of conductivity occurred in the result of the process of activation can follow through the growth of the quantity of localized states of course it is possible if these states will be the states through the transportation of carriers occurs [19].

So we came into conclusion that the hopping transport should be the main mechanism of transport.

### 3. CONCLUSIONS

1. The process of activation leads to the growth of the dc conductivity in aromatic hydrocarbons and this is the reversible process. This suggests the possibility of employ them in the sensors.
2. The large concentration of the vapour is going to short-circuit the layer, and it conduct to requirement for proper thickness of the applied layers.
3. It seems, that the described phenomenon in the indirect way seems to confirm the legitimacy of the foundation, that there is hopping transport predominant here.

### ACKNOWLEDGEMENTS

Great thanks to prof. M. Wieczorek for support in structural examinations and to prof. J. Świątek for valuable discussions.



## REFERENCES

- [1] **Silinsh E.A.**, Organic Molecular Crystals, Their Electronic States (Springer-Verlag, Berlin, 1980).
- [2] **Pope M., Swenberg C.E.**, Electronic Processes in Organic Crystals, (Clarendon Press, Oxford, 1982).
- [3] **Silinsh E.A., Capek V.**, Organic Molecular Crystals, Interaction, Localization and Transport Phenomena, (American Institute of Physics, New York, 1994).
- [4] **Karl N.**, J. Crystal Growth **99** (1990) 1009.
- [5] **Karl N., Marktanner J., Stehle R., Warta W.**, Synthetic Metals **41** (1991) 2473.
- [6] **Warta W., Karl N.**, Phys. Rev. B **32** (1985) 1172.
- [7] **Warta W., Stehle R., Karl N.**, Appl. Phys. A **36** (1985) 163.
- [8] **Karl N.**, Organic Semiconductors, in: Landolt-Bornstein, Group III, vol.17 Semiconductors, (Springer, Berlin, 1985) 106-218.
- [9] **Mycielski W.**, J. Non-Cryst. Solids, **37** (1980) 267.
- [10] **Kania S., Kondrasiuk J., Bąk G.W.**, Proc. SPIE. **3179** (1997) 190.
- [11] **Kania S., Kondrasiuk J., Bąk G.W.**, Molecular Physics Reports, **25**, (1999) 93.
- [12] **Emoto N., Kotani M.**, Chem. Phys. Lett., **101** (1983) 386.
- [13] **Wagner G. et. al.**, Mol. Cryst. Liq. Cryst., **118** (1985) 85.
- [14] **Proń A., Billaud D., Lefrant S.**, Wiss. Berichte Ak. Der Wiss. Der DDR, **29** (1984) 27.
- [15] **Kispert L.D., et al.**, Mol. Cryst. Liq. Cryst., **118** (1985) 313.
- [16] **Kania S., Kondrasiuk J.**, Sci. Bull. Łódź Technical University, No. **770** Physics, Vol. **16** (1996) 43.
- [17] **Kania S.**, Sci. Bull. Łódź Technical University, No. **914** Physics, Vol. **22** (2002) 31
- [18] **Kania S., Kondrasiuk J., Bąk G.W.**, Eur. Phys. J. E., **15** (2004) 439.
- [19] **Kania S.** Visnyk of Lviv University. Series Physical, **N 40** (2007) 322.
- [20] **Kania S.**, Sci. Bull. Łódź Technical University, No. **991** Physics, Vol. **27** (2007) 23.
- [21] **Kania S., Wiczorek M., Świątek J.**, Visnyk of Lviv University. Series Physical, **N 38** (2005) 391.
- [22] **Boaz G. Oliveira, et.al.**, Struct Chem, **20** (2009) 81.

## **MECHANIZM PRZEWODNICTWA ŁADUNKU W AKTYWOWANYCH WARSTWACH TETRACENU I P-CZTEROFENYLU**

### **Streszczenie**

Badano proces aktywacji i proces transportu nośników w warstwach tetracenu i czterofenylu. Uzyskane wyniki zdają się sugerować, że mamy tu do czynienia, jako dominującym transportem, z transportem hoppingowym poprzez stany zlokalizowane w pobliżu poziomu Fermiego.

Zależność procesów przewodnictwa od chwilowej wartości stężenia par aktywatora i odwracalność procesu może sugerować pewne możliwości użytkowe. Wydaje się, że większe możliwości zastosowań w technologii cienkowarstwowej ze względu na dużą głębokość modulacji konduktywności i niewystępowania efektu przebiccia ma p-czterofenyl. Tetracenu może mieć zastosowanie jako materiał modulujący swoje przewodnictwo w obecności gazów pod warunkiem zastosowania grubszych warstw.