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TRANSPORT PROCESSES IN THIN FILMS INDUCED WITH ABSORPTION FOR TWO AROMATIC HYDROCARBONS

Transport processes enhanced by absorption of the volatile ethanol on the tetracene and p-quaterphenyl films are considered. Obtained results may suggest injection of the charge during chemisorptions. There was observed a deep modulation of conductivity due to absorption of ethanol, this dependence suggests some ability to utilize.

Keywords: thin films, tetracene films, p-quaterphenyl films, activation process, electron mobility, carrier transport.

1. INTRODUCTION

Deep modulation of the conductivity during influence of ambient molecules is the reason to make a possibility to use thin film material for homogenic sensors. The advantage of the aromatic hydrocarbons as a future electronic materials are the low melting point and the fact that their properties are good characterised, and as organic materials are processed at low temperatures compared to Si or other covalent semiconductors, cheap polymeric substrates can be used. The well known fact is that for the surfaces of high temperature melting point semiconductors [1,2,3] and for some metals or metal oxides [4, 5] there is observed dissociation of the absorbing molecule for ethanol or other volatile agent. For silicon that fact is connected with strong covalent bonds dangling nearly perpendicular to the surface. These strong bonds make a possibility of the bond cleavage for the covalent bonds in the ethanol, and after that to chemisorbs the rest radicals. There is a question for the ring hydrocarbons

if such similar process is possible. For application use the process should be reversible that means the chemisorptions with possibility for fast desorption process should be present. Two linear different examined ring hydrocarbons one with rigid structure and other with rotating rings fulfil this requirement. For high depth of modulation the mobility is the key performance criterion both for application and for scientific characterisation. During absorption stimulated conductivity mobility depends on several static and dynamical factors. Charge transport can be divided in two parts, first introducing the charge carriers to the surface and second moving charge carriers in the film body. Introduction the charge carriers to the surface is realized by a special kind of "chemical doping". Injected carries, in described experiment, are transported in the electric field induced the biasing voltage.

1.1. Ambient atmosphere adsorption process.

Molecular solids differentiate from other covalently bonded inorganic materials, for example silicon, in that point, that the intramolecular interactions which are existing inwardly are stronger then the intermolecular ones and in that, that they are subjected to strong microscopic polarization in the area related to excess electric charge or dopant charge or to "defect" with permanent dipole moment, and that is because of existence some number of easy polarizing electrons π in the molecule.

Theoretical calculation for ethanol adsorption on tetracene and p-quaterphenyl surfaces must necessarily have a rather approximate character. Experimental information about the reaction paths and the bonding of individual ethanol molecules to the surface is under developing. There is some evidence vote for the meaning that ethanol absorption on organics can be localized, with hydrogen bonding interactions [3,6]. For such chemisorptions the local properties of surface geometry are more important.

2. EXPERIMENTAL

Thin films of tetracene ($C_{18}H_{12}$) and of p-quaterphenyl ($C_{24}H_{18}$) made as a sample a "sandwich" type with Au-Al electrodes were prepared with vacuum deposition method. The polycrystalline samples were obtained by evaporation in vacuum under the pressure of the order of 10^{-5} Torr on glass plates covered with metal film. The substrate temperature was about 300 K and the evaporation rate was changed in the range 20-30 Å/s. Structural examination of the obtained

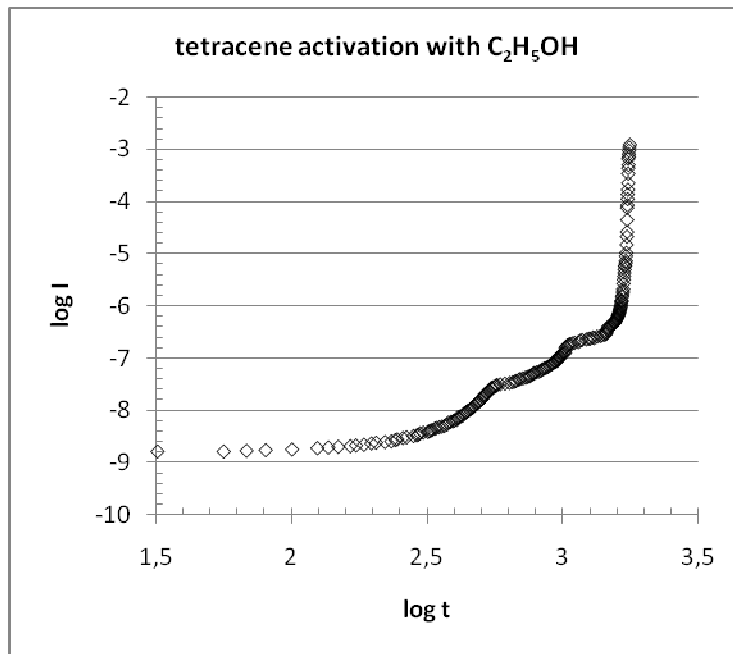
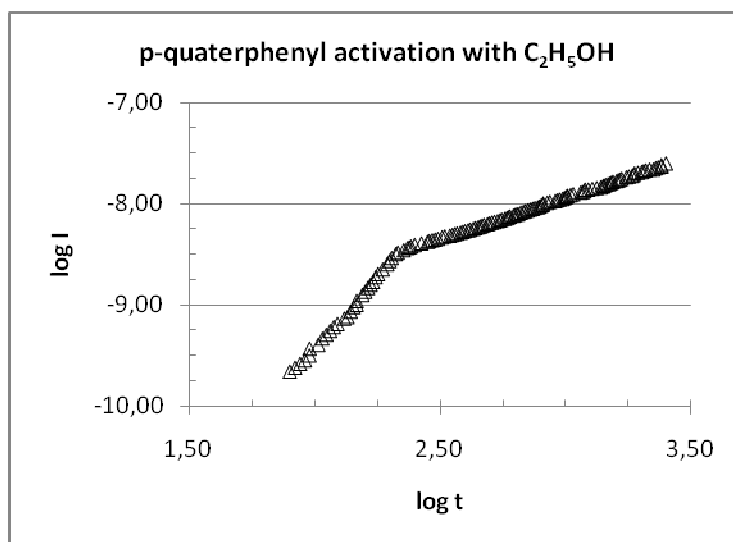
tetracene layers was made using X-ray diffraction. In order to attain that, one employed an automatic diffractometer DAR. Diffraction examinations were made in the 2θ range from 5° to 80° with measuring step $0,05^\circ$.

Tetracene, $C_{14}H_{10}$, build with four ring rigid structure, crystallize with triclinic structure, $P\bar{1}$, with two molecules pro cell, with cell dimentions: $a = 0,791(5)$ nm, $b = 0,6065(2)$ nm, $c = 1,3445(12)$ nm, $\alpha = 101,10(6)^\circ$, $\beta = 113,31(9)^\circ$, $\gamma = 85,91(4)^\circ$ [7]. The crystal structure of solid p-quaterphenyl, $C_{24}H_{18}$, with molecule build from four rotatable rings is monoclinic, $P2_1/a$, with two molecules pro cell. The lattice constants are $a = 0,811$ nm, $b = 0,561$ nm, and $c = 1,791$ nm, and the monoclinic angle is $\beta = 95,80^\circ$ [8]. The p-quaterphenyl molecules form stacked layers with herringbone molecular packing inside each layer. In solid state rotations of the rings are disabled.

The microscopic observations evidence tells that the sizes of the surface's crystallites for such films are in the order of the micrometer. The thicknesses of the obtained films were about $15 \mu\text{m}$. Before activization the samples were outgassed in the vacuum ($p = 10^{-2}$ Torr) in the measured chamber. Then they were subjected to the action of the vapour activator – C_2H_5OH . This activator has been chosen because its high polarity (molecule C_2H_5OH has a permanent dipole momentum 1.7 D dependent on appearance OH group).

Experimental set-up [9,10] consists of the current source and electronic recorder and allows to take measurements and registration of changes of a dark current flow through the studying sample during the action of activator. Once the system was vaporized with ethanol, the current continues to increase. It was observed a growth of the direct current conductivity for five orders for tetracene and for two orders for p-quaterphenyl due to rise of the molecular concentrations of the C_2H_5OH , what is presented in the Figs. 1,2.

Progress of conductivity was dependent on the time of activation. The initial pressure of ethanol was 0.2 Torr and the measurements were performed at room temperature. The equilibrium pressure for ethanol in the room temperature is ca. 44 Torr, and such a value was in container with liquid ethanol.

Fig. 1. Kinetics of the current for tetracene film vaporized with C₂H₅OHFig. 2. Kinetics of the current for p-quaterphenyl vaporized with C₂H₅OH

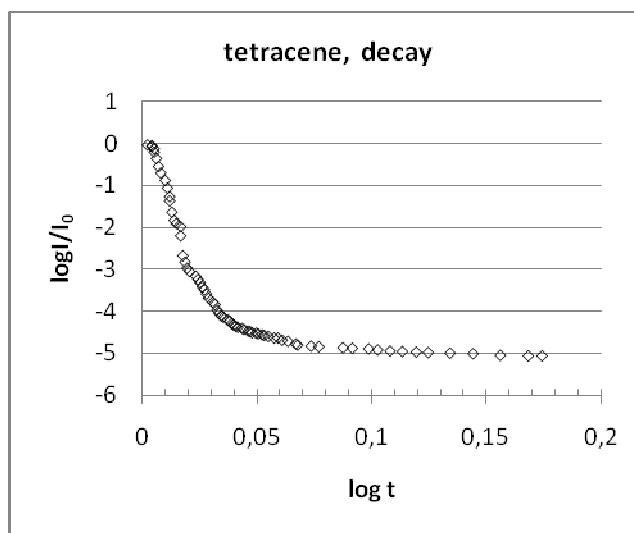


Fig. 3. Kinetics of the decay current for the tetracene

There was observed jumps of the current during refreshing ambient atmosphere connecting to the reactor the vapour from container with liquid activator. But the total characteristic maintained its character.

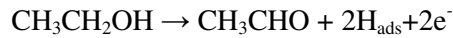
After interruption of the vaporization exhausting reactor with vacuum pump the current rapidly decays to the level of one order of magnitude above the original level.

2. RESULTS AND DISCUSSION

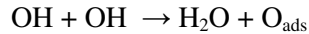
Presented problem can be classified as absorption with low kinetic energies of the adsorbate molecules. This kinetic energy, of the order of 26 meV is too low to overcome potential barriers on the adsorbing surface. Instead, the high sticking probability is caused by steering effect that means by the probability to enter the molecular chemisorption state. All ethanol molecules that find their way to the molecular chemisorption state at low kinetic energies do in fact remain trapped.

Ethanol slightly decomposes and at 300 K, the major decomposition products of ethanol in blank reactor [11] are acetaldehyde – CH_3CHO (2%) and H_2O (6%) and intact ethanol (92%). Below 300 K other decomposition products

as C₂H₄, CO₂, C₂H₆ are practically absent. The mixture coming to the reactor may decompose in the disrupting potential [6] between dangling vicinal rings of the layer molecules. In the low temperature ethanol gas undergoes dehydration step, acetaldehyde is observed as the major intermediate form of ethanol forming an absorbed hydrogen atom. The absorbed hydrogen atoms then can loose electrons to the dangling ring [6] of the layer molecule which can be expressed as:



The O-H bond of hydroxyl group of ethanol is already activated resulting with the oxygen atom bonding to the surface [1].



The absorbed oxygen atom can absorb an electron from layer creating a new transport charge – hole.

This process is possible because in the equilibrium the mixture contains 6% of H₂O. Adsorbed oxygen can enhance the chemisorptions of ethanol.

Such a mechanism is consistent with the earlier works [10,12-17] where it was revealed growth of conductivity in the layers of tetracene and p-quaterphenyl in the presence of external atmosphere of O₂, H₂O (Table 1) and with [18,19] where was described vaporization with ethanol.

Table 1
Growth of the mobility due to O₂ and H₂O absorption

Material	carriers	in vacuum		in ambient
		Mobility [cm ² /Vs]	Activation energy [eV]	Mobility [cm ² /Vs]
tetracene	electrons	4,0·10 ⁻⁴	0,03	7,0·10 ⁻⁴
p-quaterphenyl	holes	2,0·10 ⁻⁴	0,03	9,0·10 ⁻⁴
	electrons	1,0·10 ⁻⁴	0,03	1,7·10 ⁻⁴

This phenomenon was in contradiction to the work of Bäessler [20] devoted to the non-dispersive and dispersive transport in random organics, where it was concerned that rise of the energetic and spatial dispersion of states tends to the reduction of conductivity value. Such a habit can be explained with assumption that during absorption established injection of the carriers. This process require occurrence of chemisorptions connected in the case of ethanol with its decomposition.

Neutralization of molecules and atoms near surfaces has been modeled quantum mechanically by several authors [21,22,23]. The one electron Hamiltonian can be written as

$$H(z) = \sum_k E_k n_k + E_a(z) n_a + \sum_k [V_{ak}(z) c_a^+ c_k^- + V_{ak}^*(z) c_k^+ c_a^-]$$

Here n -is number of particles operator, E -is energy of the wave function, c^+ and c^- are creation and annihilation operator, z – is the atom or molecule distance, and V_{ak} is the transition matrix element connecting the atomic or molecular states and surface states. Computing the matrix elements $\langle \Psi_a | H | \Psi_k \rangle$ for transition is a complex problem. One of the simplifications useful in the technological calculations is using a method of atom – atom potentials [24].

In previous paper [25] it was reported that for tetracene and for p-quaterphenyl there are a similar mechanisms of absorption in ethanol atmosphere. It was concluded that the proper mechanism is chemisorption of ethanol to the rings of the layer with hydrogen bonding. Now we can indicate that the presence of thermal decomposition of ethanol leads to the conclusion that even in the clean vacuum system we have to do with multicomponent absorption. This novel insight can connect with the earlier works [9,10 12-17,21.26] into one complete system of observations oriented on the technological aspect of application of low dimension ring organic systems in modern electronics.

Absorption surface processes presented here can be classified as dark injection of the charges originated from adsorbing and diffusing molecules through the whole width of the layer. The concurrent adsorption of several species at the surface of the examined layers is dependent on the distance, r , from the lattice, on which the molecules are positioned reaching the local minimum of energy. Depending on this distance and on interaction strength between adsorbate species and the surface the absorption can be divided in two channels: physisorption (mostly referred to van der Waals forces) and chemisorptions (with hydrogen bonding or with other kind of covalent bonding). Experimentally determined from adsorption kinetics mean binding energy was for tetracene – 0,87 eV, and for p-quaterphenyl was – 0,77 eV. Such value approved the assumption of presence of chemisorptions. For example [26] for a solid benzene rings the cohesive energy between two rings is 480 meV and it is clearly seen that such interaction between surface rings can be an origin of dissociation energy for binding molecules of ethanol and his products from its thermal or stimulated with the surface presence decomposition. From technological point of view for the proper gas sensing based on the studied high ohmic layers under interest are only processes transferring charges inside or outside the layer, giving a modulation of the electronic signal. Due to the scope

of this article, the study must be restricted to the processes of chemisorptions. Let assume a simple Schrödinger equation in the manner presented in [27] with potential centered on the lattice rings $V_{ij}(x_i, y_j, r)$ (where x_i, y_j the surface coordinations of the absorbing ring), $U_{k,k'}$ – interaction potential between different gas molecules (numbered by – k) in the absorbing layer, V_{ck} – the potential centered on the absorbing molecule and U_k – potential energy of the absorbing particles in the absorbing layer:

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

where $\Delta_{i,j} = \partial^2/\partial x_i^2 + \partial^2/\partial y_j^2$. Now the solution will be given as the linear combination of the electron wave function ψ_k of the adsorbate and layers rings $\psi_{i,j}$:

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

where: $|a_{k,i,j}|^2$ – means the probability to find the electron on the k-th gas molecule, and $|a_{i,j}|^2$ – means the probability to find the electron at the i,j-th ring. If the barrier energy towards neighbor lattice rings is larger then the energy between the adsorbate – k-th and its nearest ring, then the wave function reduces to:

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

And the problem separates to the sum of the terms centered on the each of k-th adsorbate particle. What more, with such boundary conditions, the problem of the transport inside the layer can be treated as a sum of the transported carriers originated from different kind of absorbing species. Problem of adsorption time for activated tetracene and p-quaterphenyl layers was described in previous paper [25].

In general, the interaction energy of molecular crystal may be described as:

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

where the 3x3 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. In the molecular crystals, transitions, caused for example by interaction with adsorbing molecules, appears

not only as displacements of centre of gravity, but also as change of orientation of molecules in their distortion or in rotational displacement.

The conductivity enhanced with activation can be described with use of Boltzmann equation for distribution function, what lead to the tensor dependence:

$$\mu_{i,j} = \frac{eD_{i,j}}{kT}$$

where $D_{i,j}$ and $\mu_{i,j}$ – tensor components for diffusion and mobility. This dependence is valid for every independent quantum process passing with own channel of transport.

3. CONCLUSIONS

The outline of this article is as follows:

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 uses in the practice.
2. The large concentration of the vapour is going to short-circuit the layer of tetracene, and it conduct to requirement for suitable thickness of the applied layers. In contrary p-quaterphenyl layers do not short circuit and demonstrate deep modulation of current in two orders of magnitude. Such a habit vote for p-quaterphenyl as a perspective material for chemical sensors.
3. It seems that the described absorbtion process is connected with absorbtion and decomposition of the ethanol on the surface, connected with transfer of the charge to the layer or from the layer. Such situation can be considered as a quantum process passing with several channels of transport.

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REFERENCES

- [1] **Cho H.C.**, Chinese J. Phys. **33**, 1(1995) 91.
- [2] **Gavrilenko A.V., Bonner C.E., Gavrilenko V.I.**, arXiv:0802.1092v1 [physics.comp-ph] (2008) 1.
- [3] **Oliveira B.G., Vasconcellos M.L.A.A, Olinda R.R., Filho E.B.A.**, Stuct. Chem. **20** (2009) 81.
- [4] **Cheong H.W., Lee M.J.**, J. Cer. Proc. Res. vol 7, 3 (2006) 183.
- [5] **Pistonesi C., Juan A., Farkas A.P., Solymosi F.**, Surf. Sci. **602** (2008) 2206.
- [6] **Levitt M., Perutz M.F.**, J. Mol. Biol. **201** (1988) 751.
- [7] **Sondermann U., Kutoglu A., Bäessler H.**, J. Phys. Chem., **89** (1985) 1735.
- [8] **Delugeard Y., Desuche J. and Baudour J.L.**, Acta Cryst., **B32** (1976) 702.
- [9] **Kania S.**, Sci. Bull. Łódź Technical University, 2002, No. 914 Physics, vol. **22**, 31.
- [10] **Kania S., Kondrasiuk J., Bąk G.W.**, Eur. Phys. J. E., **15**, (2004) 439.
- [11] **Cheong H.W., Lee M.J.**, J. Ceram. Proc. Res. vol. **7**, No 3 (2006) 183.
- [12] **Kania S., Kondrasiuk J.**, Sci. Bull. Łódź Technical University, 1996, No. 770 Physics, vol. **16**, 43.
- [13] **Kania S., Kondrasiuk J., Bąk G.W.**, Proc. SPIE. **3179** (1997) 190.
- [14] **Kania S., Kondrasiuk J., Bąk G.W.**, Molecular Physics Reports, **25**, (1999) 93.
- [15] **Kania S.**, Visnyk of Lviv University. Series Physical, **N 40**, 322 (2007).
- [16] **Kania S.**, Sci. Bull. Łódź Technical University, 2007, No 991 Physics, vol. **27**, 23.
- [17] **Kania S., Wiczorek M., Świątek J.**, Visnyk of Lviv University. Series Physical, **N 38**, (2005) 391.
- [18] **Kania S., Kuliński J.**, Sci. Bull. Łódź Technical University, 2008, No. 1030 Physics, vol. **29**, 45.
- [19] **Bäessler H.**, Mol Cryst. Liq. Cryst. **252** (1994) 11.
- [20] **Anderson P.W.**, Phys. Rev. **124** (1961) 41.
- [21] **Brako R., Newns D.M.**, Rep. prog. Phys. **52** (1989) 655.
- [22] **Los J., Geerlings J.J.C.**, Phys. Rep. **190** (1990) 133.
- [23] **Kitaigorodsky A.I.**, Molecular crystals and molecules (Academic Press, New York 1973).
- [24] **Kania S., Kuliński J.**, Sci. Bull. Łódź Technical University, 2009, No. 1057 Physics, vol. **30**, 47-64.
- [25] **Bludsky O., Rubes. M.**, Phys. Rev. Lett. B **77**, 092103 (2008).
- [26] **Velasco-Velez J.J., Kunze U., Haas T.**, Phys. Status Solidi A., **207** (2010) 924.

**TRANSPORT ŁADUNKU W CIENKICH WARSTWACH
INDUKOWANY ABSORBCJĄ DLA DWU
AROMATYCZNYCH WĘGLOWODORÓW****Streszczenie**

Badano proces aktywacji i proces transportu elektronów w warstwach tetracenu i p-quaterphenylu. Uzyskane wyniki zdają się sugerować, że mamy tu do czynienia z chemisorpcją etanolu i produktów jego rozpadu termicznego skojarzoną z transferem elektronów do lub z warstwy. Właściwym do opisu transferu elektronów wydaje się być model kwantowy jednoelektronowy, rozpisany dla każdego rodzaju cząsteczki absorbentu. Wydaje się, że duża głębokość modulacji prądu oraz zależność procesów przewodnictwa od chwilowej wartości stężenia par aktywatora i odwracalność procesu może sugerować pewne możliwości użyteczne.