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ABSORBTION ENHANCED CURRENTS IN THIN LAYERS OF LOW DIMENSION ORGANICS

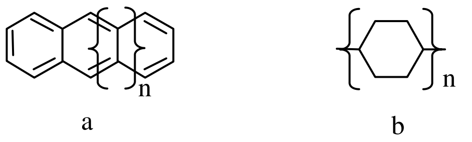
Transport processes enhanced by absorption of the volatile ethanol on the tetracene and p-quaterphenyl films are considered. Obtained results may approve chemisorption's mechanism with hydrogen bonding.

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

1. INTRODUCTION

Deep modulation of the conductivity enhanced influence of ambient molecules is the reason to make a possibility to use thin film material for homogenic sensors. In our observations we have observed a large increase of the conductivity of the thin layer of low dimension organics exposed to the ethanol vapour in the order of 10^4-10^5 without decomposition of the layer. So great increase of conductivity sensors in the range of 10^2-10^3 was reported for dendritic redox polymer when exposed to water vapour or to organic vapour and in the order of 10^4-10^5 for plasticised polyaniline films [1].

There is obvious that absorption of the gases can take big influence on the time dependent electrical habits of the layer when the continuous stream of the absorbate can goes into contact with the active points of the surface. There is a situation where the absorption can make a greater impact on the conductivity, then the adsorbtion. Simply physical adsorption processes do not induce charge transfer. In the conditions of described experiment there is possible transfer of the charge between the adsorbate and the sample. Such a mechanism of the charge transfer is observed primary in the cases when the surface chemisorption process occurred. But with simple chemisorptions should be observed a poisoning of the active surface points with absorbate molecules. Process controlled by chemisorbtion should be rapid and the influence on the conductivity should be exists after ending vaporization. That habit is not observed. The situation needs more complicated model with hydrogen bonding. During absorption stimulated conductivity depends on several static and dynamical factors. Charge transport can be divided in two parts, first introducing the charge carriers to the surface and the second moving charge carriers into the film body. Introduction the surface to the charge carriers is realized by a special kind of "chemical doping". Injected carries, in described experiment, are transported through the layer with the electric field induced by stabilized biasing voltage. For absorbtion experiments there were chosen two low dimensional representatives of organic families, that is tetracene from oligo-acenes and p-quaterphenyl from oligo-phenylenes. Both of the examined substances crystallize in herring-bone arrangement.



a b n = 1,2,3, …

Fig. 1. Structure of oligo-acenes (a) and oligo-phenylenes (b)

2. EXPERIMENTAL

Thin films of tetracene ($C_{18}H_{12}$) and of p-quaterphenyl ($C_{24}H_{18}$) were made as a "sandwich" type with Au – Al electrodes. The polycrystalline samples were obtained by evaporation in vacuum under the pressure of the order of 10^{-5} Torr on glass plates covered with gold film. The substrate temperature was about 300 K and the evaporation rate was changed in the range 20-30 Å/s. Structural examinations of the obtained layers were 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°. 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 μm with the 0.5 cm^2 of the active surface. Before vaporization the samples were outgassed in the vacuum ($p = 10^{-2}$ Torr) in the glass vacuum 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 [2, 3] 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. 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 (20°C). The saturated vapour pressure (Torr) was calculated using the following formula [4]:

$$\log_{10} p = A - \frac{B}{T + C}$$

where: *p*- is the saturated vapour pressure (Torr), *T* is the temperature in degrees Celsius, and *A*, *B* and *C* are constants defined by adsorbate, and for ethanol (271-373 K), A = 8,32109, B = 1718,10, C = 237,52. In the conditions of the experiment maximum pressure for ethanol in the vessel did not exceed 44 Torr. The number of ethanol molecules striking the wall in the vessel was [5]:

$$v = 3.513 \cdot 10^{22} \cdot \frac{p}{\sqrt{MT}}$$

where: v in $cm^{-2}s^{-1}$, *p* in Torr, *M*-molecular weight in g/mol, *T* in Kelvin.
Calculated from that equation number of the ethanol molecules striking in a second the surface of a sample is $6{,}7 \cdot 10^{21}$, and such a number is four times the whole number of all the vapour molecules in the vessel ($1.5 \cdot 10^{21}$). Under assumption that each of ethanol molecule was transported charge of one electron to the surface of the sample [6], the whole potential number of charges in the vessel was $2.3 \cdot 10^{3}$C. Total number of the charge transported via the sample do not exceed $3 \cdot 10^{-2}$C with the vaporisation repeatedly carried during the experiment. Comparison of the numbers presented above may approve the assumption on the absorbtion enhanced currents in thin layers of low dimension organics.

It was observed a growth of the direct current conductivity for five orders for tetracene and for p-quaterphenyl due to rise of the molecular concentration of the C_2H_5OH, what is presented in the Figs. 2, 3. After interruption of the vaporization exhausting reactor with vacuum pump the conductivity rapidly decays to the level of one order of magnitude above the original level.

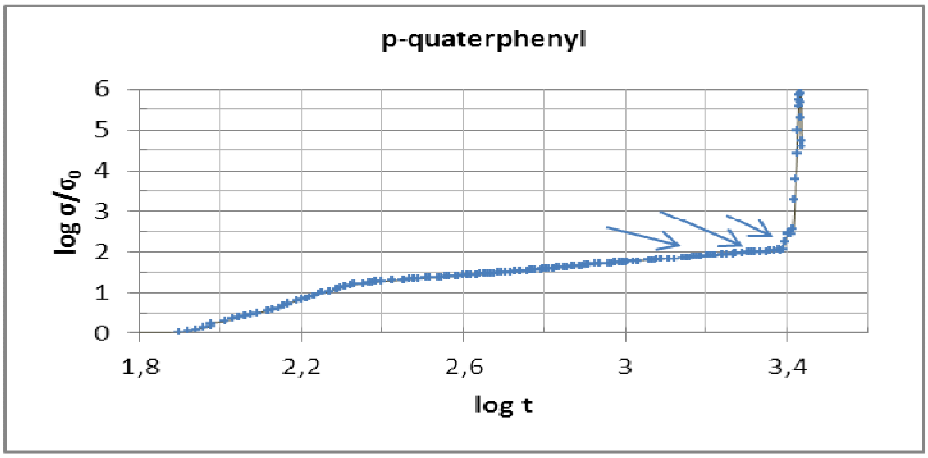


Fig. 2. Dependence of the dark conductivity for the p-quaterphenyl film in the function of the vaporization time (activator – C_2H_5OH). Arrows point the moments of the increase of the vapour concentration, σ_0-dark conductivity of the film in the vacuum

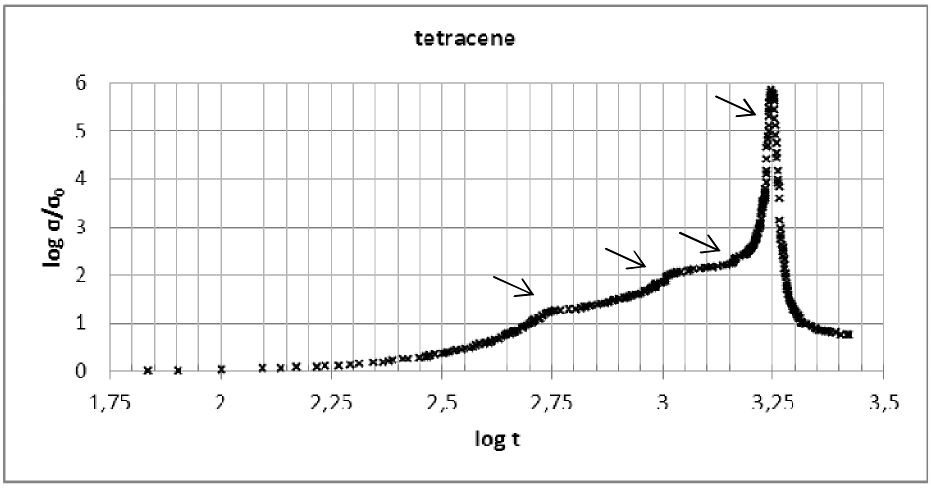


Fig. 3. Dependence of the dark conductivity for the tetracene film in the function of the activation time (activator – C_2H_5OH). Arrows point the vaporization moments, σ_0-dark conductivity of the film in the vacuum

3. RESULTS AND DISCUSSION

The alcohol molecules in the vessel have a speed of the order 400 m/s, and the kinetic energy G, of the order: $G = 6/2kT \approx 0.1\ eV$.
From the *virial* theorem we have, that a condition for alcohol molecule to create stable system must be in the manner:

$$2 \cdot G + V < 0$$

(where: V – energy of attractive potential, (always negative)) what imply the numerical condition:

$$V < -2 \cdot G \approx -0{,}2\ eV.$$

The hydrogen bonding with the binding energy of the order 0.1-0.5 eV [7] fulfils that condition. That partial chemisorbtion process is connected with concentrating the electron charge in the space near the hydrogen atom [8]. This process may be responsible for the transfer of charges between adsorbate molecule and the layer [9, 10, 11]. After each of vaporization moments it was observed that the kinetics were accelerated (see Figs. 2, 3). It is connected with refreshing of the adsorbate layer. The possible explanations are the active collisions between adsorbate protonated ethanol cluster ions and non-ionized ethanol molecule making stable dimer [12] in the manner:
$\{(C_2H_5OH)_2 \cdot H^+ - (C_2H_5OH)\}$ with the binding energy 0.95 eV
or $\{(C_2H_5OH) \cdot H^+ - (C_2H_5OH)\}$ with the binding energy 1,6 eV.
Such a dimer when creates has a kinetic energy (without vibrational modes):

$$G_D \approx 2 \cdot (6/2)kT = 6\ kT \approx 0{,}2\ eV$$

and the probability to destroy hydrogen bonding is large. During quenching hydrogen bonding may be realized the injection of the charge to the layer. All of these interactions violate the symmetry of Hamiltonian of the system. The broken symmetry of electron Hamiltonian must conduct to the new electronic eigenvalue states. Hamiltonian, H, of a system of solid layer of organic with absorbate activator can be described with the equation:

$$\hat{H} = \hat{H}_0 + \hat{H}_1(\varphi),$$

where: H_0 – unperturbated electron Hamiltonian of the layer without absorbate, $H_2(\varphi)$ – perturbation Hamiltonian as a function of the covering of the surface (φ).
The equilibrium covering of the surface is:

$$\varphi_0 = p\left[N_A / (2\pi MkT)\right]^{1/2} \tau_0 \exp\left(\varDelta H_{ads} / (kT)\right),$$

where: p – pressure, N_A – Avogadro constant, M – molecular weight, k – Boltzmann constant, T – temperature, ΔH_{ads} – heat of adsorption for one adsorbate molecule, and $\tau_o = 10^{-13}$ s. With assumption that the increase of the conductivity σ, is proportional to the covering of the surface φ, the enthalpies of adsorption [10], are for tetracene and for p-quaterphenyl: 84,4 kJ/mol and 77,4 kJ/mol respectively.

The probability of transition of the molecule from the absorbing state to the new one state with changed covering of the surface, from t φ o φ′, is:

$$P(\varphi \rightarrow \varphi') = A \cdot \exp\left[-\Delta H_1 \big/ kT\right],$$

where: A – normalization constant, ΔH_1 – eigenvalue of Hamiltonian of disturbation, k – Boltzmann constant, T – temperature in Kelvin's.

The absorption is easier when the impinging molecule has large number of free absorbing points. When the places are occupied then the probability $P(\varphi \rightarrow \varphi')$ should decrease. That makes us to conclude that when concentration of the vapour rise then the split between neighbouring states vanishes. As a consequence this fact appears as an 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. But the concurred process is poisoning the active points with immobile molecules trapped with hydrogen bonds.

Neutralization of molecules and atoms near surfaces has been modeled quantum mechanically by several authors [13, 14, 15]. The one electron Hamiltonian can be written as:

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

Here n-is a 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 $<\Psi_a|H|\Psi_a>$ for transition is a complex problem. One of the simplifications useful in the technological calculations is using a method of atom – atom potentials [15].

Due to the scope of this article restricted to the processes of chemisorptions, let assume a simple Schrödinger equation in the manner presented in [16] with potential centered on the lattice rings $V_{ij}(x_i,y_j,r)$ (where x_i, y_j the surface coordination 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 :

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

$\Delta_{i,j} = \partial^2 \big/ \partial x_i^2 + \partial^2 \big/ \partial y_j^2$. Now the solution will be given as the linear combination of the electron wave function ψ_k of the absorbate 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 absorbate – 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 adsorbtion time for activated tetracene and p-quaterphenyl layers was described in previous paper [17]. 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 a change of orientation of molecules in theirs distortion or in rotational displacement.

4. CONCLUSIONS

1. The kinetics of conductivity obtained during ethanol adsorption to the tetracene and p-quaterphenyl films are in coincidence with hydrogen bonding mechanism.
2. Formation of dimers should be possible mechanism of refreshing the surface.
3. Obtained kinetics approved the assumption that the process of modulation conductivity is connected with surface activation not with the diffusion of ethanol inside the layer.

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PRĄDY WZMOCNIONE WPŁYWEM ABSORBCJI W CIENKICH WARSTWACH NISKOWYMIAROWYCH ZWIĄZKÓW ORGANICZNYCH

Streszczenie

Kinetyka aktywacji etanolem cienkich warstw dwu niskowymiarowych przedstawicieli aligo-acenów i oligo-fenylenów (tetracen i p-kwaterfenyl) wskazuje, jako dominujący mechanizm modulacji przewodnictwa warstw, mechanizm absorbcji powierzchniowej. Zderzenia aktywne molekuł alkoholu z adsorbowanymi jonami alkoholu mogą powodować odświeżenie powierzchni absorbującej i zwiększenie szybkości kinetyki.