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CONDUCTIVITY DUE TO ACTIVE COLLISIONS CHANNEL OF ADSORPTION OF ETHANOL TO THIN LAYER OF ACENES

The activation process and the transport process for electrons in the tetracene layers and holes in the p-quaterphenyl layers is considered.. Observed dependence of the conductivity on the vapor concentration of the activator molecules may suggests influence of collisions as a source of injection of the charge through surface potential barrier of adsorption.

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

1. INTRODUCTION

Deep modulation of the conductivity due to the influence of organic vapour on the surface is the reason to make possibility to use thin film material for homogenic sensors [1]. Such a behaviour represents thin layers of polycrystalline tetracene and p-quatephenyl, the two representative for n-acenes and n-phenyl ring compounds in the experiment on adsorption in the atmosphere of vapour ethanol. There is interested fact that electric conductivity of such a layer can increase in such experiment 10^3 times or more [2]. Earlier works [3, 4] were reveal the growth of conductivity in the layers of tetracene and p-quaterphenyl in the presence of external atmosphere of O₂ and of steam H₂O. Such a process with one order rise of the dark current was recognized as a surface activation of the layer due to the chemisorptions of oxygen or steam. The similar effect but considerably stronger, was observed in earlier works [2, 5, 6] for activation of those layers

with ethanol. In this study we make an deeper analysis of the problem of the nature of the adsorption enhanced conductivity of the thin layers of polycrystalline tetracene and p-quatephenyl.

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. 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 0.6 cm^2 of the active surface. Before vaporization the samples were outgassed in the vacuum. The vapour pressure was $p = 10^{-2}$ Torr. Experimental set-up and experimental procedure was the same as reported in [7, 8].

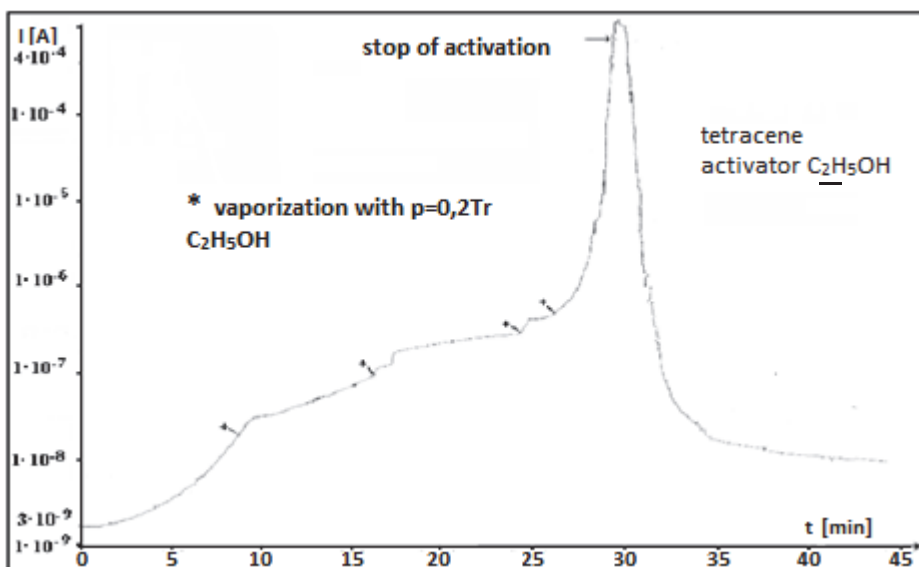


Fig. 1. Saturation effect for the tetracene layer.

Observed kinetics for anthracene and p-querterphenyl layers are presented in Figs. 1 and 2.

The observed increase of the current with saturation effect is very disturbed problem. In difference to explanation used for the common theory for vapour sensors where characteristics of the current -time curves get the saturation effect with the increase of concentration of the active vapour in the situation under study was observed saturation without increase of the pressure of the vapour.

We think that here is a different reason of this increase – changing o portions of the vapour of ethanol in the reaction container. In the Fig. 1 the moments of vaporisation are signed with asterisk. It should be mentioned that the vaporisation without increase in concentration itself plays a very small role. But it was disturbing fact that we have observed an increase of the current after every act of vaporisation.

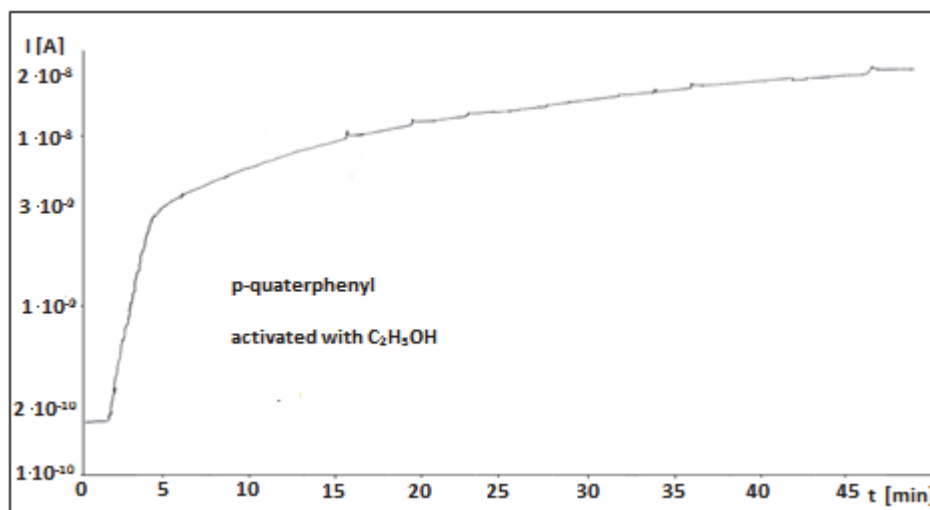


Fig. 2. Kinetics of the the dark current flow through the p-querterphenyl film in the function of the activation time (activator – C₂H₅OH).

The explanation of this fact can be recognised on connection with refreshing of the ambient atmosphere with new portion of a vapour in the equilibrium with the liquid ethanol, with the pressure 10^{-2} Tr.

The possible mechanism of adsorption of ethanol was presented in [7, 8]. In the scope of this model there is present neutralization of absorbed molecules by collisions in layer of absorption. The absorbed hydrogen atoms then can lose electrons to the dangling ring [9] 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 [10].



The absorbed oxygen atom can absorb an electron from layer creating a new transport charge –hole. Adsorbed oxygen can enhance the chemisorptions of ethanol.

2. DISCUSSION

Neutralization and scattering of molecules and ad-atoms near surfaces has been modeled quantum mechanically by several authors [11, 12, 13]. With the assumption that molecules of the volume of the vapour and the absorbed molecules constitutes two- dimensional localized gas, the one electron Hamiltonian can be written as

$$H(z) = \sum_k E_k n_k + E_a(z) n_a + \sum_k \left[V_{ak}(z) c_a^+ c_k^- + V_{ak}^*(z) c_k^+ c_a^- \right] \quad (3)$$

Here n -is number of particles operator, E -is energy of the wave function, c^+ and c^- are creation and annihilation operator for the molecule of gas, 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 $\langle \Psi_a | H | \Psi_a \rangle$ for transition is a complex problem. One of the simplifications useful in the technological calculations is using a method of atom – atom potentials [14, 15].

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 above mentioned matrix element is connected directly with probability of the transfer of the electron to the layer. The average current through the layer increases with an increase in time without increase of concentration of the ethanol. But such a habit needs the average kinetic energy of a vapour molecules to increase, making greater the matrix element $\langle \Psi_a | H | \Psi_a \rangle$ for transition.

It is very surprising that the average kinetic energy increases with an increase in time without increase of concentration. To explain that we must see the fact of refreshing of the molecules during every cycle of vaporisation. With new portion of molecules there is renewed an equilibrium distribution of the energy in coincidence with Maxwell distribution.

Let assume the simple model of the active collisions in the adsorption layer. In the conditions of the experiment we can calculate the number of ethanol molecules collide with surface of the sample as $7 \cdot 10^{21}$ molecules/s. Under assumption that each of ethanol molecule was transported charge of one electron to the surface of the sample, 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 calculated with integration of the I-t curve (Fig. 1) do not exceed $3 \cdot 10^{-2} C$ ($2 \cdot 10^{17}$ electrons) with the vaporisation repeatedly carried during the experiment. That is a question on the kinetic level of the adsorption barrier for injection of the carrier to the layer. Knowing the time of experiment ($t \approx 2 \cdot 10^3$ s) we can obtain the mean current in the order of 10^{14} electron/s. Hence in the reaction must entrance the number of 10^{14} molecules/s what is $1.5 \cdot 10^{-8}$ part of the whole number of ethanol molecules in the reaction vessel. That is a relative number of molecules with energy over threshold energy. If we consider the Maxwell distribution for the velocity of the ethanol molecules then we can suppose that there is a proper figure for the probability P of the existence of the molecules with energy suitable to make an active collision that we can calculate.

For the Maxwell distribution $f(v)$, the probability of a molecule having speed between v_1 and v_2 is

$$P = \int_{v_1}^{v_2} f(v) dv = \left[\operatorname{erf} \left(\sqrt{\frac{m}{kT}} v_2 \right) - \sqrt{\frac{2m}{kT}} v_2 \exp \left(-\frac{mv_2^2}{2kT} \right) \right] - \left[\operatorname{erf} \left(\sqrt{\frac{m}{kT}} v_1 \right) - \sqrt{\frac{2m}{kT}} v_1 \exp \left(-\frac{mv_1^2}{2kT} \right) \right] \quad (4)$$

If we assume $v_2 \rightarrow \infty$, then the first term in (4) is $\operatorname{erf}(0) = 1$.

If we use the approximation:

$$\operatorname{erf}(x) \approx \frac{\exp(-x^2)}{\sqrt{\pi}} \cdot \frac{1}{x} \quad (5)$$

Then for $P = 1.5 \cdot 10^{-8}$ we obtain from (5) $x = 4$. This figure means that threshold kinetic energy (E_k) of ethanol molecule is in order of:

$$E_k = \frac{4}{2} kT = 2kT = 2E_{mp} \quad (6)$$

Where E_{mp} is the kinetic energy for the most probably speed. For the room temperature we obtain threshold value: $E_k = 2 \cdot 26 \text{ meV} = 52 \text{ meV}$. This value is with good coincidence with the earlier works [3, 4] where the recognized activation energy in tetracene for conduction of electrons was 0.04 eV with mobility of $4.0 \cdot 10^{-4} \text{ cm}^2/\text{Vs}$.

With this value of mobility the concentration of the carriers in the volume of the layer should be in the order of $n = 5 \cdot 10^{16} \text{ cm}^{-3}$.

This results may prove the assumption of two body direct interactions activating the conduction in the layer via injection of the carrier from adsorbing molecule.

Such small activation energy may explain the growth of the current after every vaporization, as a expansion of refreshed molecules with energy over the most probably energy. As a result, the number of effective collisions between reactant molecules also increases. For reactions in the absorption layer, the amount of kinetic energy of ethanol molecule available at room temperature is only slightly less than the activation energy for the reaction. By adding only a small amount of energy, it is obtained big increase in reaction rate (visible as increase of the current value) because adding that last little bit of energy required to make the reaction proceed.

The above approve the assumption that refreshing of Maxwell distribution is the major factor for increase in the fraction of molecules which can cross the energy barrier after refreshing.

Under assumption of a kinetic collisions we can assume one dimensional movement of the particles during collision. In such a situation we can use a simple Schrödinger equation very similar to 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 :

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

where
$$\Delta_{i,j} = \partial^2 / \partial x_i^2 + \partial^2 / \partial y_j^2 \quad (8)$$

The solution will be given as the linear combination of the electron wave function ψ_k of the absorbate and layers rings of acenes $\psi_{i,j}$:

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

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. So we can consider the problem of conductivity as multichannel problem with every channel activated in the two body interactions in the manner of simple collisions with transferring kinetic energy of impact ethanol directly into energy of activation of conduction.

3. CONCLUSIONS

1. The kinetics of conductivity obtained during ethanol adsorption to the tetracene and p-quaterphenyl films are in coincidence with two body collision mechanism.
2. Vaporisation without changing pressure gives the rise of the current due to refreshing the number of the molecules. with higher then mean energy
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.
4. Obtained values of activation energy are with good coincidence with values obtained in the hopping model of conduction [3, 4].

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REFERENCES

- [1] Svetlicic V., Schmidt A.J., Miller L.L., Chem. Mater., **10** (1998) 3305.
- [2] Kania S., Sci. Bull. Techn. Univ. Lodz, Physics, **22** (2002) 31.
- [3] Kania S., Kondrasiuk J., Bąk G.W., Eur. Phys. J. E., **15** (2004) 439.
- [4] Kania S., Kondrasiuk J., Bąk G.W., Mol. Phys. Reports., **25** (1999) 93.
- [5] Kania S., Kuliński J., Sci. Bull. Techn. Univ. Lodz, Physics, **30** (2009) 47.
- [6] Kania S., Kuliński J., Sci. Bull. Techn. Univ. Lodz, Physics, **29** (2008) 45.
- [7] Kania S., Kuliński J., Chem. Met. Alloys, **4** (2011) 31.
- [8] Kania S., Kuliński J., Sci. Bull. Techn. Univ. Lodz, Physics, **32** (2011) 23.

- [9] Levitt M., Perutz M.F., *J. Mol. Biol.*, **201** (1988) 751.
[10] Cho H.C., *Chinese J. Phys.*, **33** (1995) 91.
[11] Brako R., Newns D.M., *Rep. Prog. Phys.*, **52** (1989) 655.
[12] Los J., Geerlings J.J.C., *Phys. Rep.*, **190** (1990) 133.
[13] Kitaigorodsky A.I., *Molecular Crystals and Molecules*, Academic Press, New York, 1973.
[14] Sonderrmann U., Kutoglu A., Bäessler H., *J. Phys. Chem.*, **89** (1985) 1735.
[15] Delugeard Y., Desuche J., Baudour J.L., *Acta Cryst.*, **B32** (1976) 702.
[16] Velasco-Velez J.J., Kunze U., Haas T., *Phys. Status Solidi A.*, **207** (2010) 924.

PRZEWODNICTWO ZALEŻNE OD KANŁU ZDERZEŃ AKTYWNYCH W ADSORPCJI ETANOLU DO CIENKICH WARSTW ACENÓW

Streszczenie

Badano proces aktywacji i proces transportu elektronów w warstwach tetracenu i p-kwaterfenylu. Zależność procesów przewodnictwa od chwilowej wartości stężenia par aktywatora sugeruje wzrost natężenia prądu związanego z adsorpcją jako wynik procesów dwuciałowych zderzeń z wstrzykiwaniem nośników ładunku do warstwy. Uzyskane wartości potwierdzają wyniki dla badanych związków uzyskane przy założeniu hoppingowego mechanizmu przewodzenia opisanego w [3, 4].