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ADSORPTION OF ETHANOL TO THIN LAYER OF ACENES AS A PROCESS OF INTERCONNECTED NETWORKS

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 charge through the surface potential barrier of adsorption. Applied model of two-body interactions in the interface of adsorption is approved on the basis of theory of area law for entanglement from exponential decay of correlations. Quantum description of adsorption of small hydrocarbon to the solid acenes involve only diagonal elements of the interaction matrix.

Keywords: tetracene films, p-quaterphenyl films, adsorption, interconnected networks.

1. INTRODUCTION

Organic semiconductor gas sensors are very appropriate for vapour detection, because they change their conductivity when exposed to vapours. The changes can be correlated quantitatively to the vapours concentration. The interactions of the gas molecules with organic layer can be considered as a kind of injection of the carriers.

This work explores the influence of the adsorption of the volatile ethanol molecules to the surface of polycrystalline tetracene or p-quaterphenyl. The electrical response measured when the layer is exposed to ethanol vapour shows a deep decrease of the resistance of the film. We have noticed that the presented sensor layers exhibits attractive performances, good sensitivity to the ethanol, deep modulation of the current up to current density of 10^{-5} A/cm^2. These features suggest possibility of some application. In this paper we try to describe and explain some processes related to the structure of the surface with contact of the vaporized ethanol. We also try to describe the features present in the layer in dependence on the charge transfer through the surface layer. We employ the concept of the quantum transition theory matched with the model of interconnected networks. For this reason, the Hamiltonian was constructed, which takes into account the particles interacted with solid surface originated from gas in the ensemble of the adsorbing layer as well as the ensemble of interacting skin layer of the solid. The Hamiltonian obtained in the course of such description ought to be noticed as the sum of the terms for two-particle interactions. Such interpretation leads to the model of independent conductivity channels.

2. EXPERIMENTAL

Thin films of tetracene ($C_{18}H_{12}$) and of p-quaterphenyl ($C_{24}H_{18}$) made as a sample of “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 layers was made using X-ray diffraction with an automatic diffractometer DAR. Diffraction studies were made in the 2θ range from 5º to 80º with measuring step 0.05º. Experimental setup [1,2] consisted of the current source and electronic recorder and allowed to take measurements and registration of changes of a dark current flow through the sample during the action of activator. Once the system was vaporized with ethanol, the current continued to increase and it saturated between every step of vaporization. The kinetics of the current for tetracene and p-quaterphenyl films vaporized with C_2H_5OH are presented in Fig. 1.

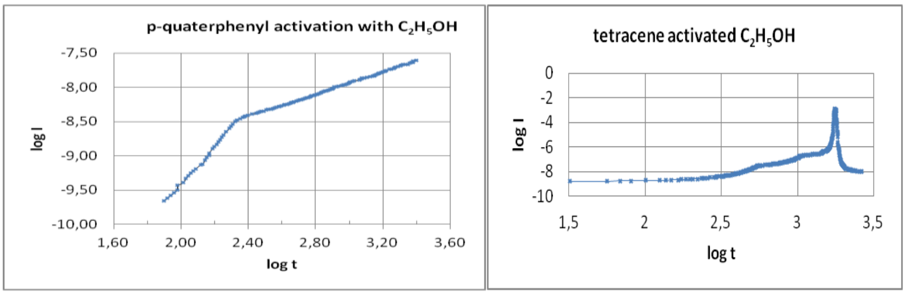

Fig. 1. Kinetics of the current for tetracene and p-quaterphenyl films vaporized with C_2H_5OH

3. MODEL

In previous papers we have recognised conduction due to the absorption of the ethanol to the tetracene or p-quatephenyl as the variety of the transition state reactions [3, 4]. If we want to describe dynamic properties of adsorption layer in interaction with surface we must separate the thermodynamic subsystem of interacting molecules [5,6] and determine the directivity of interactions. In the papers [6-8], we have characterized the phenomenological structural model of the interacting surface and we have developed a perturbed Hamiltonian for such system. The important feature of quantum many-body states is amount of entanglements in the state. Taking into account the fact that the adsorption layer decay in the conditions of vacuum may have width of few angstroms we can adopt the theory of an area law for entanglement from exponential decay of correlations [9]. In the scope of this model using the second quantization for a given bipartite-mixed quantum state ρ_{XY}, we can quantify the correlation between X and Y. Correlation function generalizes two point correlation functions, in the condensed-matter physics, in which both X and Y are composed of a single sites, (Fig. 2). In accordance with the concept of abrupt transition in the structural formation of interconnected networks [9,10] 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 $|\psi>_{1,\dots,n}$ composed of n qubits defined on a finite dimensional lattice has ξ-exponential decay of correlations if for every two regions X and Y separated by l sites

$$Cor\left(X:Y\right) \leq 2^{-l/\xi} \tag{1}$$

Here ξ – is the correlation length of the state.

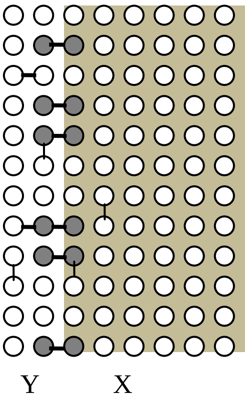

Fig. 2. Model of adsorption layer as a system of entangled pairs X and Y. Shaded square denotes region of solid layer. Pairs crossing the boundary (dark) contribute to the entropy of the region inside the layer [7]

Tetracene and p-quaterphenyl molecules have length between 12 and16 Å, and the molecules of activator - ethanol are 8-10 times shorter. Aromatic rings act as hydrogen bond acceptors [11], with bonding proton at a distance of 1 Å from the centre of benzene ring, and 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 (see the Fig. 2), we can estimate l as 12 Å, and ξ as 4,2 Å, then from equation (1) we can obtain:

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

This result confirms the assumption of low width of the adsorption layer and gives entanglement E of X and Y (in our case: ethanol - solid layer) as a function of reduced density matrix of $|\psi>_{X,Y}$ dependent only on one of the regions, for example X. Obtained in this manner von Neumann entropy H is proportional to its boundary not to the volume of the system [9]:

$$E\left(|\psi\rangle_{XY}\right) = H\left(\rho_X\right) = -tr\left(\rho_X \cdot \log \rho_X\right) \tag{2}$$

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

There can be underlined the fact that the value of correlation we have obtained is without any assumptions about the shape of the potential. In [9], the theorem is proven, that such model can be applied to the disordered Hamiltonians exhibiting many-body localization or mobility gap always fulfill an area law. In our case we have constant area of active nodes in the surface layer (all surface molecules are made of benzene rings) and if we recognize them as a X sites in equation (2) then in the scope of this model a description using the

Hamiltonian in the manner of sum of terms centered on the active nodes is approved. This leads to the conclusion that simple Schrödinger equation in the manner presented in [6] with potential centered on the lattice rings: $V_{ij}(x_i,y_j,r)$ [4] (where x_i and y_j denote the surface coordinates of the absorbing ring), and with $U_{k,k'}$ – 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 is good approximation for adsorption of shorter molecules of ethanol at the rings of acenes. The Schrödinger equation will be of the shape:

$$H\psi = \left[-\frac{\hbar^2}{2m}\sum_{i,j}\Delta_{i,j} + \sum_{i,j} V_{i,j}\left(x_i, y_j, r_k\right) + \sum_{i,j}\left(V_{ck}\right)_{i,j} + \sum_{k} U_k + \sum_{k,k'} U_{k,k'} \right]\psi \qquad (3)$$

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

On the basis of the theory considered above, the solution may be given as the linear combination of the electron wave function ψ_k of the absorbate gas and rings of the solid layer $\psi_{i,j}$:

$$\psi_{i,j} = a_{k,i,j}\psi_k + \sum_{i,j} a_{i,j}\psi_{i,j} \qquad (4)$$

where: $|a_{k,i,j}|^2$ denotes the probability to find the electron on the k-th absorbing molecule, and $|a_{i,j}|^2$ denotes the probability to find the electron at the i,j-th ring. The correlation value we have obtained above in the scope of model of abrupt transitions in structural formation of interconnected networks approve reduction of this wave function to the function centered only on layer rings (or equivalently on the nodes of the (imagine) network made for adsorbing gas molecules:

$$\psi_{i,j} = a_k\psi_k + a_{i,j}\psi_{i,j} \qquad (5)$$

If we separate problem to the sum of the terms centered on the each of k-th adsorbate particle then the result may approve the concept of multichannel mechanism of conduction in the region of the layer of adsorption. 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 permeating number of interconnected networks [10].

3. CONCLUSIONS

1. The kinetics of conductivity obtained during ethanol adsorption to the tetracene and p-quaterphenyl films are in coincidence with the two body collision mechanism.
2. Theorem of area interactions on the basis of theory of entanglement from exponential decay of correlations approved the picture with Hamiltonian described as a sum of interactions. The wave functions can be centered only at the nodes of one of interacting phases.
3. Modulation conductivity is probably connected with surface activation not with the diffusion of ethanol inside the layer.

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ADSORPCJA ETANOLU DO CIENKICH WARSTW ACENÓW JAKO PROCES WZAJEMNEGO ODDZIAŁYWANIA SIECI

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. Słuszność takiego modelu uzasadnia twierdzenie o powierzchniowym charakterze oddziaływań wynikającym z teorii eksponencjalnego zaniku korelacji [9]. Teoretyczna analiza procesu adsorpcji węglowodoru na powierzchni pierścieniowego acenu nie wymaga znajomości wyrazów mieszanych macierzy przejścia. Powinno to prowadzić do znacznego uproszczenia procedury obliczania parametrów modelu oddziaływań.