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CORRELATED NETWORKS IN THE ADSORPTIONENHANCED CURRENTS

Injection of carriers into thin layers of acenes due to adsorption of ethanol activator molecules is considered as a electron transfer reaction between two phases. Complexity of the processes may be diminished with applying electron transfer theory in the meaning of Marcus.

Keywords: tetracene films, p-quaterphenyl films, adsorption, electron transfer reactions.

1. INTRODUCTION

Organic thin layers made of the acenes have broad applications in many fields of modern microelectronics. Especially, the deep modulation of the conductivity due to the adsorption-induced electron transfer processes at the interface between organic solid state layer and gaseous activator is under great interest of gas sensor technology. An efficient application for organic materials requires very good understanding of the dynamic interactions of the solid surface with the molecules of ambient vapour. It may be noticed that conductivity enhanced adsorption process becomes similar to the catalysis. In our experiments the reactants exchange the charge with the solid phase and then they are transformed into the substrates (molecules or ions), but the molecules belonged to the solid phase are subjected to the reversible transformations in the run of the carriers forced by the electromotive force (EFM) existing in the measuring circuit. For the reason of electronic phenomena all the described process can be compared to the principle of operation for the bipolar transistor where the active absorbing surface acts as a basis injected carriers.

Consequently, interesting reactions are that which conduct to the short range interactions with excitons or other forms for transferring the charge existing on the surface of the solid phase connected with possibility of transferring this charge into the volume of the layer. Such a description of the process of enhancing current due to adsorption was presented in [1], and then developed [2] in connection with new conceptual theory of abrupt transition in the structural formation of interconnected networks [3, 4]. There is a some number of reports devoted to independent transfer of the small molecules to the absorbing solid organic surface with the energetic disorder and structural roughness (for example [5]) with use of Monte Carlo simulations, but these papers do not touch problem of injection of charges during adsorption.

Absorption of the ethanol and other alcohols on the hydrocarbon films carbonized at high temperature was examined with use of infra-red spectroscopy [6]. Such a methodology allows to establish which atoms or group of atoms of adsorbate and absorbent react mutually in the process of adsorption. In the result of this explorations it was found that the adsorbed molecules had been formed the wide band of the stretching oscillations O-H (3550 cm^{-1}), which widening is connected with creation of H bonds. Apolar group of adsorbed ethanol forms the stretching bands C-H in the region of 2990 and 2820 cm^{-1}. Forming the band at 1480 cm^{-1} (not existing for the gas molecule) points out that a fraction of ethanol is absorbed with cooperation of apolar group C_2H_5 to the weakly oxidized surface. Above data indicate the multichannel adsorption process, so in that reason point to the coexistence of several competitive processes, and only part of them leads to the interactions with the layer molecules connected with transfer of the carriers. Complexity of the whole problem allows however use the simplifying concept of Marcus'es electron transfer reactions theory [7,8]. This observation coincides with our proposed model in that and earlier papers [9-12].

2. EXPERIMENTAL

Thin films of polycrystalline tetracene ($C_{18}H_{12}$) and of p-quaterphenyl ($C_{24}H_{18}$) made as a measuring cells of "sandwich" type with Au – Al electrodes were prepared with vacuum deposition method under the pressure of the order of 10^{-5} Torr on glass plates covered with metal film. During evaporation the evaporation rates were kept in the range $20 \div 30$ Å/s. The substrate temperatures were about 300 K and obtained layers were in the thickness range from 15 μm to 17 μm. Structural examinations of the obtained layers were made using X-ray diffraction with an automatic diffractometer DAR in the 2θ range from $5°$ to $80°$ with measuring step $0.05°$. Direct measurements of the current response for the

interface adsorption process were fulfilled in the set up shown in the Figure 1. The measuring cell was fixed in the vacuum flask with controllable ethanol vapour flux getting out from the source with the vapour pressure of 10^{-2} Tr. The first and the another doses of the vapour were controlled with precision gas-inlet valve. New dose of vapour makes the current to continue the increase and the saturation was realized in the higher level. The characteristic kinetics of the current for tetracene film vaporized with C_2H_5OH is presented in Fig. 2.
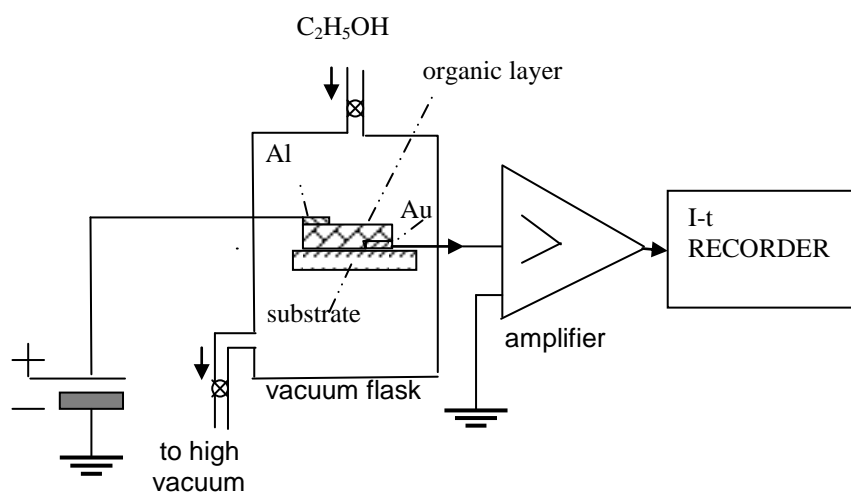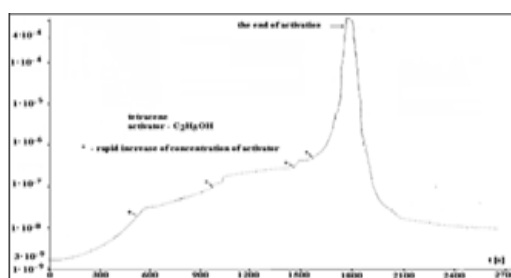

Fig. 1 Experimental setup

Fig. 2. Effect of added ethanol on absorption-current in the anthacene layer (thickness 15 μm, active surface area 0,5 cm^2)

3. DISCUSSION

Discussion is divided into two kinetics problems, first is the nature of kinetics of the adsorption, and second is how the adsorption process influence the kinetics of the electron transfer in the interface. The adsorption process is studied in the vacuum where the competition of different kinds of molecules is eliminated. But even in such defined case the competition of decomposition products originated from the ethanol vapour exists. Ethanol at 300 K slightly decomposes, and the main decomposition products appeared in the equilibrium conditions [13] are acetaldehyde – CH_3CHO (2%) and H_2O (6%) and intact ethanol (92%). At 300 K other decomposition products as C_2H_4, CO_2, C_2H_6 may be produced. The mixture entered to the reactor flask will be under influence of the disrupting potential [14] existing between dangling vicinal rings of the layer molecules. Such an interaction in the range of 0.5 eV is able to make additional decomposition of the vapour molecules. In the low temperature conditions ethanol gas undergoes dehydration step so acetaldehyde may be present in the reactor. The absorbed hydrogen atoms are able to mediate to transfer electrons to the dangling rings of the molecules placed in the irregularities of the layer [5]. The probable sequence of reactions can be expressed as follows:

$$CH_3CH_2OH \rightarrow CH_3CHO + 2H_{ads} + 2e^-.$$

The O-H bound of hydroxyl group of ethanol is already activated resulting with the oxygen atom bonding to the surface:

$$OH + OH \rightarrow H_2O + O_{ads}.$$
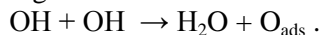
Oxygen atom absorbed at surface can absorb an electron from layer molecule creating a new transport charge – hole. This process is possible because in the equilibrium the mixture may contain H_2O. Adsorbed oxygen can enhance the chemisorptions of ethanol [6]. Such a mechanism is consistent with the earlier works [15] where it was revealed growth of conductivity in the layers of tetracene and p quaterphenyl in the presence of external atmosphere of O_2, H_2O.

Treating the whole process as a reaction of the electron transfer, the adsorption enhanced current may be considered as the charge flow between molecules of ethanol in vapour phase to the molecules of condensed layer. And in the set-up presented in Fig. 1 the measured characteristics can be considered as resulting from injection of electrons into the film.

The saturation levels of the currents after every vaporization are important because they are directly correlated with the rate of electron transfer at the interface and may be considered as proportional to the number of electrons which cross the interface existing at the surface of the layer. The rate of electron-transfer can be calculated easily by integration the *I-t* curve. Similar shape of dependence for absorption of ethanol was observed in [6] in the function

of relative pressure (relative to the pressure of saturated vapour-$p_0 \approx 44$ Tr). The process was rapid and linear with the growth of a pressure for low relative pressures (in the order of $0,1p/p_0$) what can be explained as a confirmation for the high energy of adsorption interactions with organic solids for this alcohol. Making an assumption that an excited acene molecules at the surface are produced by direct electron injection at the solid surface array or by exciton migration from interior of the crystal to the surface we can consider the whole process as a reaction with reaction cross section σ_e for the p-quaterphenyl (anthracene) – ethanol system. In that limits the following estimation can be valid roughly:

$$\sigma_e = \sigma_g \cdot Q_{ex} \cdot \frac{1}{\tau \cdot N_v} , \qquad (1)$$

where σ_g is geometrical cross section of a site of surface lattice with acene molecule of the film, Q_{ex} is the reaction yield per exciton reached at the surface, τ is approximated by exciton lifetime in the bulk layer, N_v – number of collisions of adsorbate in the interface layer. Substituting the numerical values $\sigma_g = 50$ Å^2, $Q_{ex} = 1$, $N_v = 1,5 \cdot 10^{14}$ cm^{-2}s^{-1}, $\tau = 4 \cdot 10^{-9}$ s, σ_e is roughly equal to $2 \cdot 10^{-6} \cdot \sigma_g$. It conduct to the conclusion that the reaction was limited the number of collisions in the interface.

For observed systems the time dependence of desorption current and obtained value of entropy for sorption, for tetracene $\Delta H = 84$ kJ/mol and for p-quaterphenyl $\Delta H = 77$ kJ/mol, may points out that two mechanisms are present: physic sorption and weak chemisorption.

In the previous paper [2] we have discussed the phenomenon of adsorption in the scope of the model of abrupt transitions in the structural formation of two undirected interconnected networks with the same number of nodes [3,4] and developed in [16] and in the scope of this model is needed a description using the Hamiltonian in the manner of sum of terms centered on the active lattice nodes of the layer.

4. CONCLUSIONS

If we consider 2-D localized gas layer at the interface interacted with molecules of condensed layer then we can in terms of semi-classical Marcus's theory charge transfer rate may be interpreted as reaction rate for change ionization states between adjacent molecules. The decisive parameter for charge transport between molecules in the interlayer is intermolecular transfer integral J_{ij}, that express the possibility of transfer of charges between interacting

molecules. For adjacent molecules the transfer integral may be evaluated from Schrödinger equation. Making use of Fermi golden rule for describing the resonant transition from initial state |i> located in the 2-D gas layer in the interface to a final manifold of discrete states |α> with energies E_α located in the solid layer under the influence of a time- independent perturbation, the transfer rate between initial state *i* and a final states *α* is given by [7]:

$$k_{i\alpha} = \sum_\alpha k_{i\alpha} = \frac{2\pi}{\hbar} \sum |J_{i\alpha}|^2 \delta(E_i - E_\alpha) \qquad (2)$$

where: $J_{i\alpha} = <i|U|\alpha>$ is a perturbation matrix element between the initial state and one of the final states, and δ function ensures energy conservation during the transition between the initial and final states.

In the high temperature limit, the transfer rate for a charge to hop from a site i to a manifold of final sites α is [8]:

$$k_{i\alpha} = \frac{2\pi}{\hbar} \frac{J_{i\alpha}^2}{\sqrt{4\pi\lambda_{i\alpha} k_B T}} \exp\left[-\frac{\left(\Delta E_{ij} - \lambda_{i\alpha}\right)^2}{4\lambda_{i\alpha} k_B T} \right], \qquad (4)$$

where T is temperature, $\lambda_{i\alpha} = \lambda_{i\alpha}^{int} + \lambda_{i\alpha}^{out}$ is the reorganization energy, which is a sum of intra- and intermolecular (outersphere) contributions, $\Delta E_{i\alpha}$ is the site-energy difference, and $U_{i\alpha}$ is the electronic coupling element.

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SKORELOWANE SIECI W PRĄDACH WZMOCNIONYCH ADSORPCJĄ

Streszczenie

Badano proces aktywacji i proces transportu elektronów w warstwach tetracenu i p-kwaterfenylu. Złożoność procesów towarzyszących przepływowi prądu wzmacnianego adsorpcją wymaga modeli upraszczających. Możliwość zastosowania modelu gwałtownych przemian w tworzeniu strukturalnym oddziałujących wzajemnie sieci prowadzi do możliwości zastosowania hamiltonianu będącego sumą hamiltonianów dla każdego z kanałów transferu ładunku. Stwarza to możliwość zastosowania koncepcji szybkości transferu ładunków na bazie teorii Marcusa reakcji z transferem elektronów.