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CHARGE CARRIER CONDUCTIVITY MECHANISM FOR ACTIVATED TETRACENE LAYERS

The activation process and the transport process for electrons in the tetracene layers is considered. Obtained results may suggest the hopping transport through the localized states near the Fermi level as a dominant kind of transport. Observed dependence of the conductivity on the vapor concentration of the activator molecules may suggest some ability to utilize.

Keywords: polycrystalline, tetracene films, activation process, electron mobility, carrier transport.

1. INTRODUCTION

Polycrystalline tetracene is representative for n-acene ring low molecular weight compounds. Due to the sp^2 -hybridization of carbon atoms, the molecules are flat. Dense packing herringbone structure of the coordination inside the grains is a compromise between attractive van der Waals forces and repulsive forces emerged from the Pauli exclusion. While van der Waals forces prefer molecules to arrange parallel, the repulsive forces try to minimize the interaction by a perpendicular arrangement of the molecules. Interactions between the molecules determines the number of π connections between them. The number of this connections determine conduction of electrons. The nature of overlap is a crucial feature of the properties of conductivity for molecular materials. Directionality of π orbitals and planarity of molecular framework are necessary for delocalised π - bonding. Knowledge of the conductivity originated from a delicate balance between competing intra- and intermolecular forces is the base sense to explore studies on those materials in different phases crystalline and

amorphous and on modulation of their electric phenomena. The complex nature of the relations between inner structure and charge transport in the external electric field makes uncertainty in determining theoretical model of the conductivity. In the room temperatures is impossible to say obvious if the working model is band model or the dominant are models with localized states. Low molecular weight organic compounds normally are the low-conducting materials. This is both due to their wide forbidden gap resulting in low concentration of charge carriers in the conduction band and due to low drift mobility of charge carriers.

In the room temperatures monocrystals of such organics have got the drift mobility close to $1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at room temperature [1, 2, 3]. The temperature dependence of drift mobility is usually given by: $\mu \propto T^n$, where n changes in the range $0 > n > 2$. However, such a trapping – independent drift mobility may be found only in exceptionally perfect and pure monocrystals [4, 5, 6, 7].

The acene rings easy undergo to polarization and even small amount of chemical impurities (of the order of 1 ppm) [3] or structural imperfections [2, 3] strongly influences the equilibrium between the inner electronic arrangement of the aromatic molecule and the molecules in the vicinity and this is reflected in the charge transport which results in significant decrease in the mobility value [2, 4, 5, 8]. In this case the charge transport may be controlled by multiple trapping.

In heavily doped (or unpurified) and disordered polycrystalline structures the charge mobilities are of the order of $10^{-5} \div 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ [9, 10, 11, 20, 21]. It has been suggested that the charge transport in these cases may be interpreted in terms of hopping transport between localized states [9, 10, 11, 20, 21]. The mayor difference between charge transport in the conduction band controlled by trapping and the hopping transport visible in experiment is the dependence on concentrations of traps (or localized states).

In the case of transport in the conduction band controlled by traps the drift mobility decreases with increasing trap concentration because the probability of trapping and retrapping increases. However, in the case of hopping transport among localized states the drift mobility increases with increasing concentration of the states because the probability of jumps increases with decreasing average distance among the localized states. Also the molecular crystals, among them the simple aromatic hydrocarbons, such as: acenes and p – phenyls, can give evidence of conductivity increase resulted from activation process [12-18].

1.1. Ambient atmosphere activation process

Molecular crystals differentiate from other crystals, for example ionic, in that point, that the intramolecular interactions which are existing inwardly are stronger than 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 them.

Above-mentioned reasons can make them as interesting material from a point of molecular electronics view. There are a lot of agents activating superficially (or by volume) organic solid state. From a point of view of interactions stability and of possibility of probable expectation of electrical properties, the basic agents are so-called Lewis's compounds. They introduce a definite number of donor or acceptor states to organic solid state. Here, we have to do with chemisorptions and diffusion phenomenon. The activator molecules are going to be built in among the molecules of activated material. The charge transferred to the molecule of host material is compensated with the charge transferred to the activator molecule. Interchain or interplanar interactions tend to enlarge distances, with keeping structural identity of sizes for chains or for planes of activated material. Lewis's bases are the molecules with a free pair of electrons in the atoms, and so we are able to take in a number, the molecules of unsaturated and aromatic hydrocarbons which have mobile electrons π .

When one activates the organic system then the oxidation of the unsaturated sp^2 system leads to carbon – carbon double-bond cleavage and then to generate the defected sp^3 bond. When it runs through the transition states then it is similar with the chemisorptions phenomenon (with synchronous charge transfer), and then comes to the diffusion in the interchain or interplanar area. If there is no following stabilization for such transition stages then that process is reversible. In the case of strong activators, there is present an entire disjunction of the π - electron system and system come next to shaping itself as a system with saturated sp^3 bonds.

It is known that some atmosphere molecules give rise to additional localized states in typical simple aromatic hydrocarbons. If the states were to be traps controlling the charge transport in the conduction band, this should cause the drift mobility to decrease when measured in the atmosphere. In case of domination of hopping transport among localized states the drift mobility may be expected to increase in the atmosphere. The process of superficial activation of organic materials usually conduct to modification their electrical characteristics. This modification manifests itself with the increase of the dark conductivity and the photoconductivity, and with the change of the value of the

activation energy, the value of the charge mobility and the dielectric loss. For acenes the electric conductivity can increase, for example 10^3 times or much more due to nature of the activator. Similarly the activity interaction response time for the sample is dependent on the time stability of obtained effect and on its reversibility. Usually there is a change of the character of the carrier mobility transport, and become to be a visible depressive transport due to manifestation of the deep trapping states. Activation process for acenes leads to the variation in the energy structure of the energy gap, what demonstrates among other things in the photoluminescence effect. It appears subsequent to wavelength shift of the emission to the states accessible in the visible range.

The basic goal of the presented investigations is to find the influence of precipitate activator molecules on charge transport of polycrystalline tetracene.

2. EXPERIMENTAL

Thin films of tetracene ($C_{18}H_{12}$) made as the sample a “sandwich” type with Au – Al electrodes were prepared with vacuum deposition method. The tetracene 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 $0,05^\circ$.

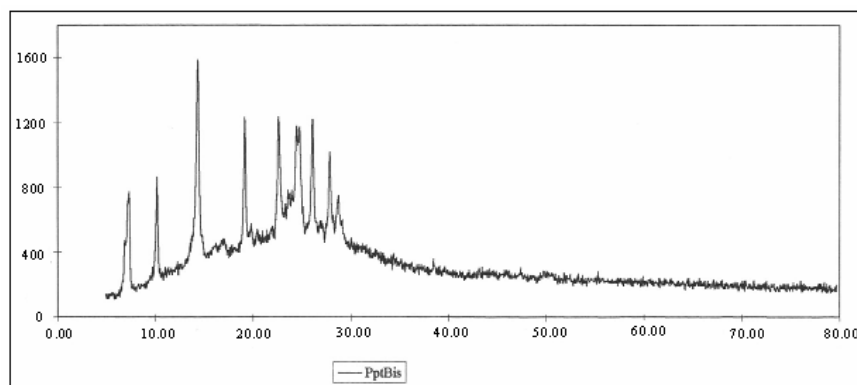


Fig. 1. Diffractogram of the tetracene polycrystalline film. Plot of the intensity of X ray diffraction lines in function of the angle 2θ

Typical diffraction pattern for the polycrystalline tetracene films is described with Fig. 1.

The microscopic observations evidence tells that the sizes of the surface's crystallites for such films are in the order of the micrometer. The thickness of the obtained films were about 15 μm or above. Such layers were fixed upon the vacuum of the order 10^{-2} Torr and then they were subjected to the action of the vapour activator - $\text{C}_2\text{H}_5\text{OH}$. That activator has been chosen because its high polarity (molecule $\text{C}_2\text{H}_5\text{OH}$ has a permanent dipole momentum 1.7 D dependent on appearance OH group).

Used experimental set – up [17,18] consists of the current source and electronic recorder X(t) and Y(t) and allows to take measurements and registration of changes of a dark current flow through the studying sample during the action of activator. It was observed here a clear growth of the direct current conductivity even for five orders due to rise of the molecular concentrations of the $\text{C}_2\text{H}_5\text{OH}$, what is evidently seen in the Figs. 2, 3.

Progress of conductivity was dependent on the time of activation and on the concentration of the activator vapour.

For lower concentrations of activator it was observed the saturation of the current flowing through the sample after times greater then 600 s. Moreover with graduated rise in the concentration of activator vapour, the conductivity of measuring sample increased and conductivity saturation occurs on higher level (Fig. 3).

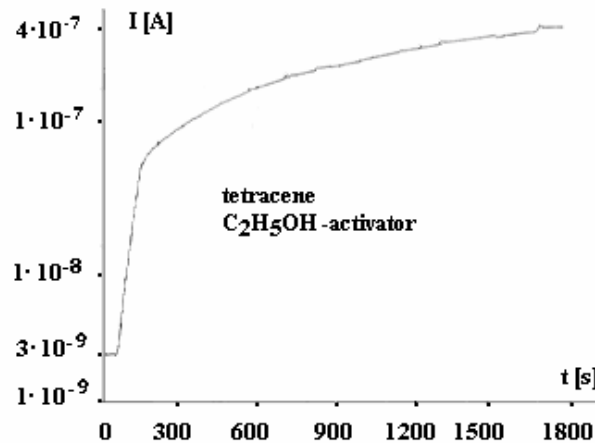


Fig. 2. Dependence of the dark current flow through the film in the function of the activation time (tetracene film, activator – $\text{C}_2\text{H}_5\text{OH}$)

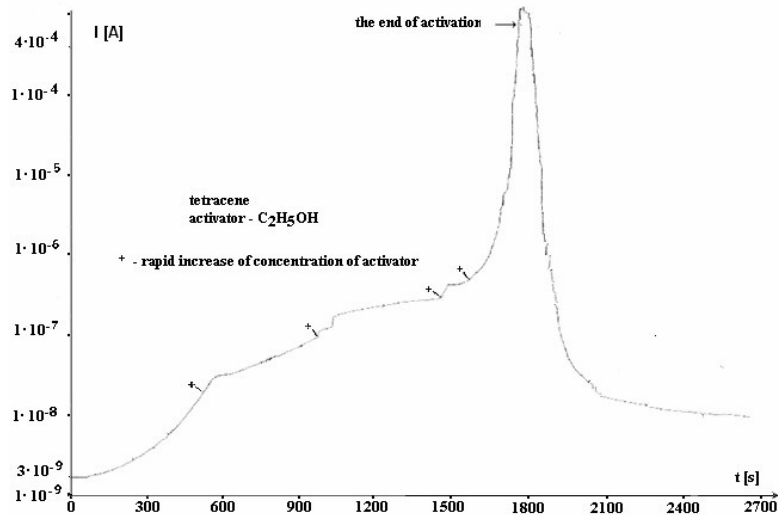


Fig. 3. Dependence of the dark current flow through the film in the function of the vapour concentration, and time

2.1. The influence of the activator on conductivity of the tetracene

With the larger concentrations of molecules C_2H_5OH and with sufficiently long times above 200 s, for layers with the thickness approx. $15 \mu m$ was observed that after growth of the current above the worth of $5 \cdot 10^{-4}$ appeared irreversible damage of the layer. that is a difficult to judge if it has been caused by a firm joint of the C_2H_5OH molecules to the layer and has been related to transition of the tetracene to the state of high conductivity, what should bring to the high conductivity state of the dielectric. In such a process it is likely that there were present space no uniformity of the field in the layer or there were the damages of the electric contacts in the places of meeting metal electrode with dielectric due to the dissipation of the energy.

If we do not treat the conditions of damage (in the electric sense hazards) then we can consider the process of the activation of the layer as the reversible process with the occurrence of the small „memory” effect (i.e., that outputs level of current near the same voltage should be somewhat higher than it was on a first stage). The similar phenomenon as described above was observed for different aromatic low-molecular hydrocarbons.

Precise description of the shape of the current – voltage characteristic for acenes with discrete trapping levels is impossible. Approximate equation should be in the form of:

$$J = \varepsilon\varepsilon_0\mu\vartheta\alpha^2\beta(V^2/L^3) , \quad (1)$$

where: $1 < \alpha < 2$, $1/2 < \beta < 1$, μ – mobility of carriers, ε – relative dielectric permittivity, ε_0 – vacuum permittivity, V – applied voltage, L – the sample thickness, $\vartheta(T) = n/n_t$, n – the total density of free charge carriers, n_t – the density of the trapped carriers.

For dielectric with uniform continuous distribution of traps

$$\rho(E) = \rho_0 = \text{const} \quad (2)$$

(in the limits from E_i to E_l) where $E_l > E_i$ (Fig. 5a) the current – voltage characteristic may be described with formula:

$$I = eN_c\mu\left(\frac{V}{L}\right)\exp\left(-\frac{E_l}{kT}\right)\exp\left(\frac{bV}{\rho_0kT}\right), \quad (3)$$

where: $b = \varepsilon\varepsilon_0\alpha\beta/eL^3$, $1/2 < \alpha < 2$, $1/2 < \beta < 1$, N_t – the quantity of the localized states per volume unit, and N_c – the number of states in the conductivity band, ρ_0 – density of trap distribution.

For the more complicated expansion of states in the forbidden gap, expressions describing the size of the current rise have more elucidated figure and for example of the exponential expansion decreasing with the growth of energy:

$$\rho(E) = \rho_0\exp\left(-\frac{E_l - E_i}{kT_c}\right), \quad (4)$$

formula is

$$I = \frac{N_c\mu e}{L}\left(\frac{b}{N_t}\right)V^{\left(\frac{T_c}{T}+1\right)}\left[\exp\left(-\frac{E_l}{kT}\right)\right], \quad (5)$$

where: $b = \varepsilon\varepsilon_0\alpha\beta/eL^3$, $1 < \alpha < 2$, $1/2 < \beta < 1$, N_t – the quantity of the localized states per volume unit, and N_c – the quantity of states in the band, T_c – characteristic temperature. If we activate the layer then the density of localized states should clearly increase. For the dielectric with either continuous or complex distribution of traps, what is true for polycrystalline layers, it is impossible to show analytic formula describing the current – voltage characteristic due to the complexity of the problem.

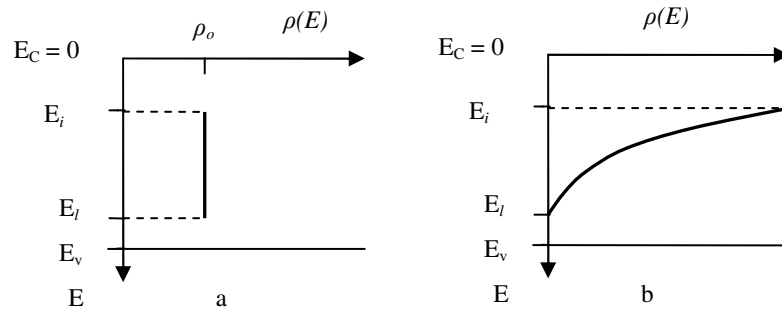


Fig. 4. The pattern of the energetic expansion of the states situated between the levels of energy E_i and E_l . a). continuous expansion of the states, b).the expansion of the states decrease exponentially with energy

For the dielectric with both continuous and complex distribution of traps what is true for polycrystalline layers it is impossible to show analytic formula describing the current – voltage characteristic due to the complexity of the problem. Nevertheless the growth of the quantity of the localized states, within the scope of this model should lead to decrease of the value of the current. Unless, the real growth of the carrier mobility should have been occurred, and so great then it can exceed the velocity of growth of the localized states density, or if the localized states would tends to stay such a states through them the conductivity may occur, what is possible in the condition when the hopping transport is the dominant mechanism of conductivity. Verification of such hypothesis would be easy and right, if one could directly measure the mobility value during the process of activation of the studied layer. Unfortunately such measurement from technical regards could not be made.

It succeed only to make the measurements of the drift mobility for the tetracene layers in the vacuum of 10^{-5} Tor and in the air with moisture approx. 60-70%, that is in the presence of the polar molecules of the aqueous steam (H_2O) and the molecules of oxygen (O_2). For the layers of the tetracene in the arrangement of the sandwich electrodes there were made measurements of the electrons mobility using set – up presented [18,20]. Obtained impulses possess the kink point letting directly to mark the mobility of electrons in described layers. For electrons in tetracene layers in vacuum was obtained drift mobility $\mu = 4 \cdot 10^{-4} \text{ cm}^2/\text{Vs}$ with activation energy 0.04 eV, but in ambient atmosphere the drift mobility was $\mu = 9.5 \cdot 10^{-4} \text{ cm}^2/\text{Vs}$. The low value of the drift mobility, below $10^{-2} \text{ cm}^2/\text{Vs}$, and its low activation energy in the order of kT suggests that the hopping charge transport takes place in a narrow band of localised states.

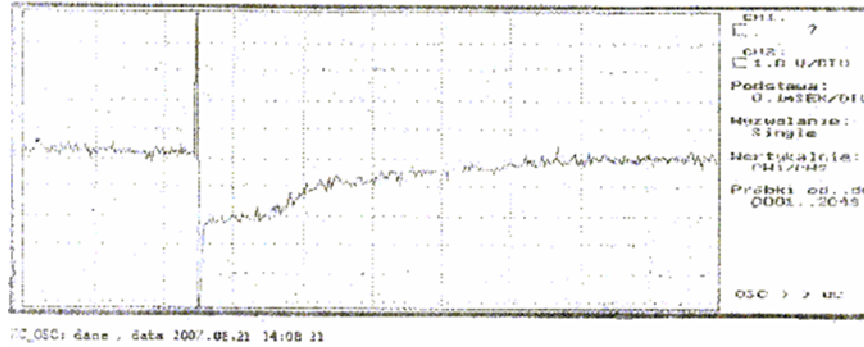


Fig. 5. Typical current pulse for electrons obtained for the polycrystalline tetracene film, thickness $L = 19 \mu\text{m}$, voltage applied to the film $U = 19 \text{ V}$, measured in ambient atmosphere

Mott-Davies model describing the hopping transport in a narrow band of states at the Fermi level the drift mobility is given by:

$$\mu = \frac{1}{6} \frac{eR^2}{kT} v_{\text{ph}} \exp(-2\alpha) \exp\left(-\frac{W}{kT}\right) \quad (6)$$

where R is the average distance between the localized states, e is the electron charge, k is Boltzmann constant, α is the decay of the localized state wave function, W is the effective width of the band of localized states, T is the temperature. Using the above equation and the geometrical formula $N(E_F) = (3/4\pi)(1/R^3W)$ one can estimate the average distance between the localised states R and the density of localised states at the Fermi level $N(E_F)$. The values of $N(E_F)$ obtained for the measurements in vacuum are close to $3 \cdot 10^{19} \text{ cm}^{-3} \text{ eV}^{-1}$, while for the measurements carried out in the air turns out to be nearly 1 order of magnitude higher, about $6 \cdot 10^{20} \text{ cm}^{-3} \text{ eV}^{-1}$. These values of the density of states are typical for many non-crystalline materials and seems to confirm the consistency of the model used.

The voltage dependence of the time – of – flight $1/t_r$ for the polycrystalline layer is presented in the Fig. 6. Obtained current pulses (Fig. 5) had characteristic kink point which enables direct estimation of the transit time for electrons for polycrystalline layers.

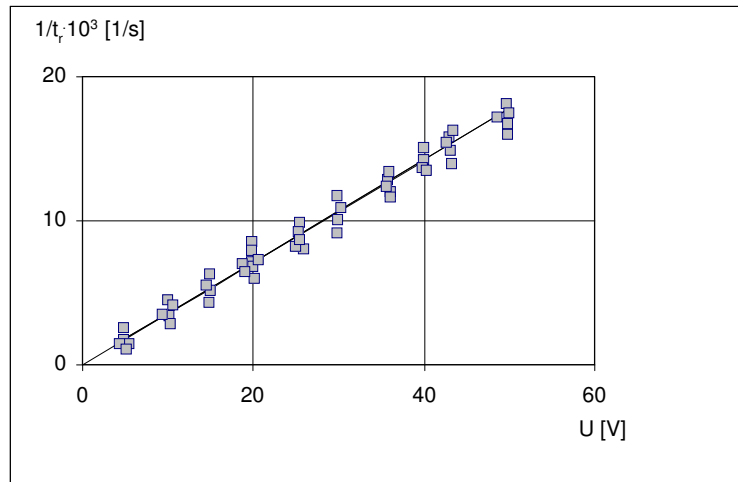


Fig. 6. Diagram of an inverse time-of-flight $1/t_f$ for electrons upon the voltage applied to the film, $L = 17,5 \mu\text{m}$, $\mu_e = 9,5 \cdot 10^{-4} \text{ cm}^2/\text{Vs}$

The fact that the mobility of electrons grows, we can interpret as the growth of the density of localized states. This marks, that our earlier suggestion, that the growth of conductivity occurred in the result of the process of activation can follow through the growth of the quantity of localized states of course it is possible if these states will be the states through the transportation of electrons occurs [19].

So we came into conclusion that the hopping transport should be the predominant mechanism of transport.

3. CONCLUSIONS

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, and it conduct to requirement for proper thickness of the applied layers.
3. It seems, that the described phenomenon in the indirect way seems to confirm the legitimacy of the foundation, that there is hopping transport predominant here.

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MECHANIZM PRZEWODNICTWA ŁADUNKU W AKTYWOWANYCH WARSTWACH TETRACENU

Streszczenie

Badano proces aktywacji i proces transportu elektronów w warstwach tetracenu. Uzyskane wyniki zdają się sugerować, że mamy tu do czynienia, z jako dominującym transportem, z transportem hoppingowym poprzez stany zlokalizowane w pobliżu poziomu Fermiego.

Zależność procesów przewodnictwa od chwilowej wartości stężenia par aktywatora i odwracalność procesu może sugerować pewne możliwości uytylitarne.