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HOLE DRIFT MOBILITY IN ANTHRONE AND ANTRACHINONE LAYERS WITH DIFFERENT STRUCTURE

The hole drift mobilities were measured with use of time of flight method (TOF) for layers of antrachinone and anthrone with different structural orders. The differences in the values of mobility for anthrone and anthrachinone are explained as an effect of different permanent dipole moment for these molecules.

Keywords: polycrystalline films, quasi amorphous films, amorphous films, anthrone, antrachinone, hole drift mobility, carrier transport.

1. INTRODUCTION

This paper analysis hole transport in the case of two organic materials which differ with the molecular dipole moment. There is a lack of the first-principles analytic theory explaining charge carrier mobility for condensed organic semiconducting materials over a wide range of physical material parameters, such as presence of the molecular dipole moment. Understanding the role of charge localization and energetic disorder connected with the presence or absence of the molecular dipole moment in the charge transport through these materials is crucial to enable rational design for applications of organic devices. Polycrystalline and amorphous materials posses defects at boundaries between crystalline grains. But the fundamental nature of the condensed organic materials, made of isolated, independent molecules held

together by weak van der Waals bonds, makes the presence of non-periodicity introduced by the limits of grains negligible. Such a phenomenon is possible due to the fact that molecular condensed materials are made of the atomically ordered nearly individual units-molecules, and there are no-dangling covalent bonds. The presence of the of the weak dipole and quadrupole interactions may act to localise electronic states.

This article concerns the problem of the presence of the molecular dipole moment as a source of the differences in the hole transport for the thin layers of acenes. This was the reason for whose research has been undertaken on the layers of a different arrangements of the molecules that is polycrystalline, quasi-amorphous and amorphous. The study focused on two compounds, antrachinone and anthrone, each of which has a different dipole moment, but both compounds condensed with nearly identical crystalline structure.

2. EXPERIMENTAL AND RESULTS

The measurements were made in the ambient atmosphere in room temperature using time of flight (TOF) spectroscopy [1]. The samples were made in the planar layered structure (named "sandwich" structure). There were taken *I-t* current characteristics forced with photoexcitation of electron-hole carriers near the semitransparent electrode in the presence of biasing electrical field.

2.1. Structures of antrachinone and anthrone

The parameters of nearly the same structures of antrachinone, $C_{14}H_8O_2$, and anthrone, $C_{14}H_{10}O$ [2] are presented in Table 1.

Table 1

compound	Space group	Lattice constant, [Å]	Lattice angle β [degree, min]	Dipole moment, [D]
Antrachinone ($C_{14}H_8O_2$)	C_{2h}^5(P2$_1$/a)	$a_0 = 15,8$, $b_0 = 3,94 - 3,99$, $c_0 = 7,865(10)$	102°″43′(2′)	0,6 (in benzene)
Anthrone ($C_{14}H_{10}O$)	C_{2h}^5(P2$_1$/a)	$a_0 = (15.80\pm0.03)$, $b_0=(3.998\pm0.005)$, $c_0 = (7.86\pm0.16)$	101°″40′(10′)	3,66 (in benzene)

2.2. Sample preparation

Methods for preparation of the layers are described in [3, 4]. The exemplary X-diffractograms of the layers under investigation are presented in Figs. 1 and 2.
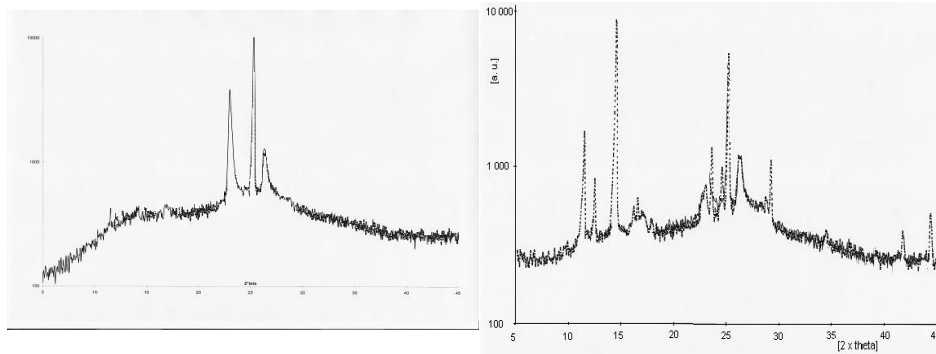

Fig. 1. Diffraction pattern (X ray) for quasi-amorphous (left) and polycrystalline (right) anthrone layers
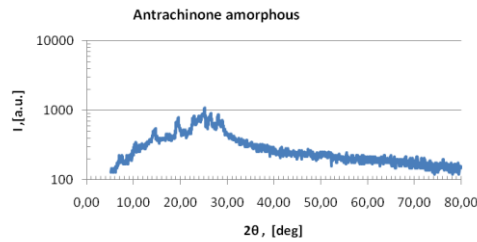

Fig. 2. Diffraction pattern (X-ray) for amorphous antrachinone layer

2.3. Measurements

Measuring procedures used for obtaining TOF transients are described in [5]. Exemplary shape of the transient *I-t* is presented in the Fig. 3. It is seen that such a shape allows the direct determination of the mobility.
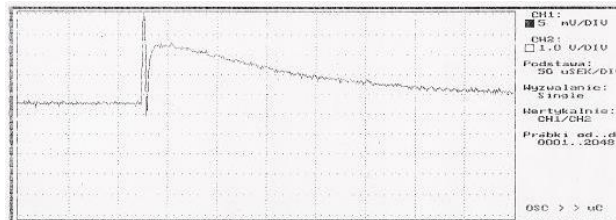

Fig. 3. Typical current pulse for amorphous antrachinone layers ($U = 240$ V, $L = 29$ μm)

2.4. Results

Obtained TOF captures of current-time pulses, allowed estimation the value for the time of flight (t_t) for measuring samples. For the more precision determination of the t_t value, obtained transients were transformed into log-log scale. All the obtained results are summarized in Table 2, where μ is drift mobility, and E_a is activation energy.

Table 2

Compound	structure	μ, [cm^2/Vs]	E_a, [eV]
antrachinone	polycrystalline	$(8 \pm 2) \cdot 10^{-4}$	0,03
	quasi-amorphous	$(3 - 7) \cdot 10^{-4}$	0,03
	amorphous	$(0,9 - 6,0) \cdot 10^{-4}$	0,03
anthrone	polycrystalline	$(7 \pm 2) \cdot 10^{-3}$	0,03
	quasi-amorphous	$(3 - 7) \cdot 10^{-3}$	0,03
	amorphous	$(0,6 - 4,0) \cdot 10^{-3}$	0,03

The low value of drift mobility for both molecular compounds and low activation energy suggest that the hopping charge transport takes place in the narrow band of localised states at the Fermi level.

3. CONCLUSIONS

From obtained results is seen (Table 2) that for the polycrystalline and quasi amorphous layers the values of hole mobility for anthrone ($\mu = 3,6$ D) is of one order of magnitude higher than for antrachinone ($\mu = 0,6$ D). For the amorphous layers high dispersion of results was obtained. However the trend line indicate a slightly higher value for anthrone layers. High dispersion of the mobility values for the amorphous layers should be caused by the partial layer's recrystallization process during measuring experiment. It was impossible to univocally evidence this recrystalization. Perhaps this results were under impact of the conditions of the execution of the experiment, that is in the ambient atmosphere and under influence of air composition. The impact of such conditions on evidence was recognized in the [1]. Based on the obtained results it could be built the hypothesis, that for the increased mobility of anthrone layers is responsible the presence of the considerable value of dipole moment, in comparison to its lack for the antrachinone layers.

The choice of the Hamiltonian in the situation described in this article is connected with the fact that nuclear dynamics is much slower than the dynamics of charge carriers and the fact that electronic coupling is weak. Hamiltonian for charge transport should be connected with static disorder, based on the

assumption on the electronic density of states and on the hopping rates between localized states.

For low density materials one-electron Hamiltonian is convenient for presentation the different kinds of charge carriers motion [7]:

$$H = H_0 + H_1 + H_2 + H_3 + H_4 \qquad (1)$$

where:

$$H_0 = \sum_n \varepsilon a_n^+ a_n + \sum_\lambda \hbar\omega_\lambda \left(b_\lambda^+ b_\lambda + \frac{1}{2} \right),$$

$$H_1 = \sum_n \sum_m J_{nm} a_n^+ a_m,$$

$$H_2 = \sum_\lambda \sum_n g_{n\lambda}^2 \hbar\omega_\lambda a_n^+ a_n \left(b_\lambda + b_{-\lambda}^+ \right),$$

$$H_3 = \sum_n \sum_{\substack{m \\ n \neq m}} \sum_\lambda f_{nm\lambda}^2 \hbar\omega_\lambda a_n^+ a_m \left(b_\lambda + b_{-\lambda}^+ \right),$$

$$H_4 = \sum_n \delta\varepsilon_n a_n^+ a_n + \sum_n \sum_{\substack{m \\ n \neq m}} \delta J_{nm} a_n^+ a_m.$$

Hamiltonian H_0 represents the full energy of the system, theirs molecules and the lattice are in the excited state, but without taking into account inter-interactions. Energy of excited state of a molecule in the defined lattice site is described with ε, its variations are described with $\delta\varepsilon_n$. The variation of ε is connected with non-phonon dispersion of energy states (diagonal elements H_{nn} of the Hamiltonian matrix). Non-diagonal elements δJ_{nm} (nm-element in the Hamiltonian matrix), represents the non-diagonal disorder of the force of interactions between two lattice nodes, but without presence of phonons (for example connected with disorder due to dipol-dipol orientation). a_n^+, a_n are followingly the operators of creation and annihilation of excited electron with energy ε in the node n., and b_n^+, b_n are followingly the operators of normal oscillations with energy $\hbar\omega_\lambda$ interact with electron in the state n and $g_{n\lambda}$ is non-dimensional coupling constant for this interaction. Transfer Hamiltonian H_1 describes electron transfer from node (n) to node (m) with overlapping energy J_{nm}. Terms H_2 and H_3 are described the impact of the lattice vibrations on the electron flow. The last H_4 is divided into two disorder terms, first one is responsible for statistical diagonal disorder and the second one for statistical non-diagonal disorder.

Dipole-dipole interactions energy between the dipol ds_1 in the centre of the coordinate system having direction s_1 in the field originated from the network

of point dipoles with directions s_n is shown below in the form of the sum of interactions with all other dipoles [6]:

$$\delta J_{1\alpha} = \frac{d^2}{2} \sum_{n=2}^{\infty} \left[\frac{s_1 s_n}{\left| r_{1n} \right|^3} - \frac{3(s_1 r_{1n})(s_n r_{1n})}{\left| r_{1n} \right|^5} \right], \tag{2}$$

where: s_1, s_n, r_{1n} are wectors, r_{1n} is a position of n-th dipole, α-sign a manifold of the network of point dipoles. This energy may be an element for the second term in the Hamiltonian H_4. In the case of antrachinone, with the molecules with natural dipole moment measured in benzene of 0,6 D ($2,00 \cdot 10^{-30}$ Cm) [1], this energy is in the order of $10^{-5} \div 10^{-6}$ eV, that is in three orders of magnitude less than the van der Waals potential energy (estimated in the range of $10^{-3} \div 7 \cdot 10^{-2}$ eV), but anthrone molecules possess a significant natural dipole moment, when measured in benzene is of 3,66 D ($1,22 \cdot 10^{-29}$ Cm) [1] and in this case the energy of dipol-dipol interaction can be in the order of $10^{-2} \div 10^{-3}$ eV, does it mean the value comparable to the van der Waals potential. These additional dipol-dipol energy present for anthrone structures can lead to broadening of the bands in the condensed form and to the enhanced overlapping of the wave functions for the charge carriers conducting via localized 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]:

$$k_{i\alpha} = \frac{2\pi}{\hbar} \frac{J_{i\alpha}^2}{\sqrt{4\pi \lambda_{i\alpha} k_B T}} \exp\left[-\frac{\left(\Delta E_{ij} - \lambda_{i\alpha} \right)^2}{4\lambda_{i\alpha} k_B T} \right], \tag{3}$$

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

For both molecular compounds in condensed state obtained values of the mobility are below 10^{-2} cm^2/Vs, and the estimated values of the activation energy are the same.

Despite of almost the same crystallization structure (the space group C_{2h}^5(P2$_1$/a) operates for both), clear differences in the magnitude of mobility were observed. For anthrone, with molecule possessing a natural dipole moment, the mobility of holes in the condensed state is almost one order of magnitude greater than that measured for antrachinone this fact can be connected with the higher value of transfer rates taking into account in the term H_4 of Hamiltonian. The more precise determination needs further studies on the influence of the structural disorder on the mobility value.

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REFERENCES

[1] **Kania S., Kondrasiuk J., Bąk G.W.**, Eur. Phys. J. E, **15** (2004) 439.
[2] **Landolt-Börnstein**, Zahlenwerte und Funktionen aus Naturwissenschaften und Technik, Springer Verlag, Berlin, 1971.
[3] **Kania S.**, Sci. Bull. Tech. Univ. Łódź, s. Physics, **28** (2007) 27.
[4] **Kania S.**, Sci. Bull. Tech. Univ. Łódź, s. Physics, **30** (2009) 65.
[5] **Kania S.**, Sci. Bull. Tech. Univ. Łódź, s. Physics, **34** (2013) 19.
[6] **Kitaigorodskii A.I.**, Molecular Crystals and Molecules, Acad. Press, N.Y. 1973.
[7] **Pope. M., Swenberg C.E.**, Electronic processes in organic crystals., Clarendon Press New Yor 1982.
[8] **Rühle V., Lukyanov A., Falk M., Schrader M., Vehoff T., Kirkpatrick J., Baumeier B.** and **Andrienko D.**, J. Chem. Theory Comput., 7 (2011) 3335.

DRYFTOWA RUCHLIWOŚĆ DZIUR W WARSTWACH ANTRONU I ANTRACHINONU O RÓŻNEJ STRUKTURZE

Streszczenie

Poddano analizie wartość ruchliwości dziur w polikrystalicznych, quasi-amorficznych i amorficznych warstwach antronu i antrachinonu. Materiały wyjściowe były o czystości spektralnej. Oba związki krystalizują w identycznej strukturze $C_{2h}^5(P2_1/a)$ krystalograficznej układu skośnego o prawie identycznych stałych sieciowych i prawie identycznym kącie β. Dla warstw antronu, którego cząsteczki posiadają stały moment dipolowy, uzyskano prawie o rząd większą wartość ruchliwości niż dla warstw antrachinonu, niezależnie od stopnia uporządkowania tych warstw. Próbujemy sformułować hipotezę i wykazać jej słuszność, że za prawie o rząd większą ruchliwość dziur w warstwach antronu odpowiada obecność znacznego momentu dipolowego w cząstkach tego związku.