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HOLE DRIFT MOBILITY FOR DIFFERENT STRUCTURES OF ANTHRONE AND ANTRACHINONE LAYERS

Drift mobility of holes in antrachinone and anthrone thin films evaporated in the vacuum of the order of 10^{-5} Tr was determined with time of flight method (TOF). The layers had different structural order due to the temperature of vaporized substrates. The results show almost lack of the mobility dependence due to the structural order. One order of difference in mobility values for antrachinone and anthrone may have origin in the presence of the difference in permanent dipole moment of the molecules.

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

1. INTRODUCTION

The paper concern the problem of the origin of the differences in the hole transport for the thin layers of acenes. For this reason we have studied layers with different crystal order, that is polycrystalline, quasi-amorphous and amorphous for two compounds with different molecular dipole moment but with nearly identical crystalline structure, that is for antrachinone and anthrone.

Antrachinone and anthrone are the promising materials for thin layer organic electronics. The organic layers are the compromise between strong

coupling forces in the molecule in the sense of the covalent bonds and intermolecular forces dependent on the weak hydrogen or van der Waals bonds in the range of $10^{-3} \div 7 \cdot 10^{-2}$ eV. The energy of the dipol-dipol interactions between molecules with permanent dipole moment is with some approximation described by the formula:

$$U_{d-d} = -\frac{2c}{3kT} \frac{\mu_a^2 \mu_b^2}{r^6}$$

where r – is a distance between centres of dipoles, μ – dipole moment, k –Boltzmann constant ($1{,}38 \cdot 10^{-23}$ JK^{-1}) and T – thermodynamic temperature.

In the case of antrachinone 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}-10^{-6} eV, what does mean three orders of magnitude less than the van der Waals potential. Anthrone molecules possess a greater natural dipole moment, which for example when measured in benzene is of 3,66 D ($1{,}22 \cdot 10^{-29}$ Cm) [1] and the energy of dipol-dipol interaction can be estimated in the order of 10^{-2}-10^{-3} eV, comparable to the van der Waals potential. The additional dipol-dipol energy present for anthrone structures can lead to broadening of the bands in the case of layer of ordered state, or can lead to the higher overlapping of the wave functions for the charge carriers conducting via localized states.

2. EXPERIMENTAL AND RESULTS

2.1. Properties of antrachinone and anthrone

The structures of antrachinone, $C_{14}H_8O_2$, and anthrone, $C_{14}H_{10}O$ are nearly the same, monoclinic with space group C_{2h}^5(P2$_1$/a) with bimolecular unit of the dimensions (at room temperature) $a_0 = 15{,}8$ Å, $b_0 = 3{,}94 - 3{,}99$ Å, $c_0 = 7{,}865(10)$ Å, $\beta = 102°43(2)$' for antrachinone, and $a_0 = (15.80\pm0.03)$ Å, $b_0 = (3.998\pm0.005)$ Å, $c_0 = (7.86\pm0.16)$ Å, $\beta = 101° 40'$ for anthrone [2, 3]. The main difference essential for the reason of this paper is the fact that the antrachinone molecules posses negligible dipole moment, opposite to the anthrone molecules which are characterised by large dipole moment of 3,6 D.

2.2. Sample preparation

The spectral grade antrachinone and anthrone (purified with zone melting) were used for obtaining thin film samples by evaporation in vacuum under the pressure of the order of 10^{-5} Torr on glass plates supplied with gold electrode.

The substrates temperatures during evaporation for polycrystalline layers were kept near 300 K, and for quasi amorphous layers were kept in the range of 170-200 K using a proper evaporation rate. Structural examination of the antrachinone and anthrone layers were made using automatic X-ray diffractometer DAR [4, 5]. The exemplary X-diffractograms are presented in Figs. 1 and 2.
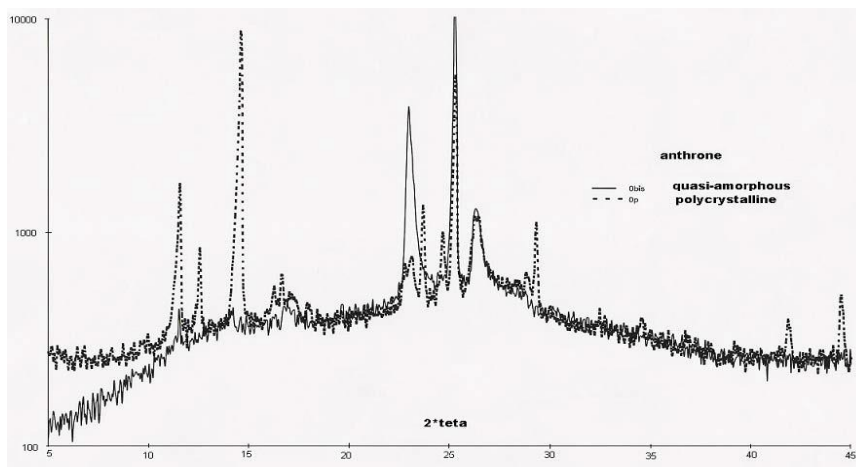

Fig. 1. Diffraction pattern (X ray) for polycrystalline and quasi-amorphous anthrone layers
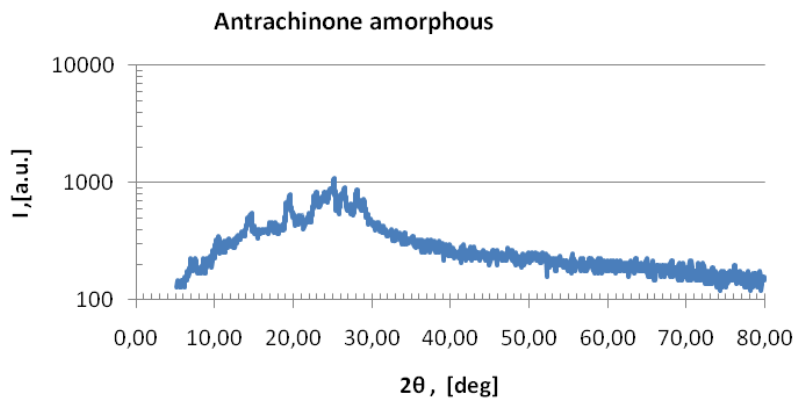

Fig. 2. Diffraction pattern (X-ray) for amorphous antrachinone layers

2.3. Measurements

Free pairs of electron-hole were generated by a nitrogen laser, with the pulse intensity of 5 μJ and with pulse duration width $t_{1/2}$ of 8 ns. Measurements were made using the time of flight set-up working under computer control which enables to control the measurements and to store the data. The time of flight was found from the current signal. The current pulses were measured with digital oscilloscope Hung Chang DSO 5804 and Rigol DS1062CA. The system details were completely described in [6,7]. The examinations of the hole mobility for the polycrystalline antrachinone layers were made at the room temperature biasing with the electrical field in the limits from $3 \cdot 10^3$ V/cm to $2 \cdot 10^4$ V/cm. The determination of the activation energy of the mobility for these layers was made in the temperature limits 285-353 K.
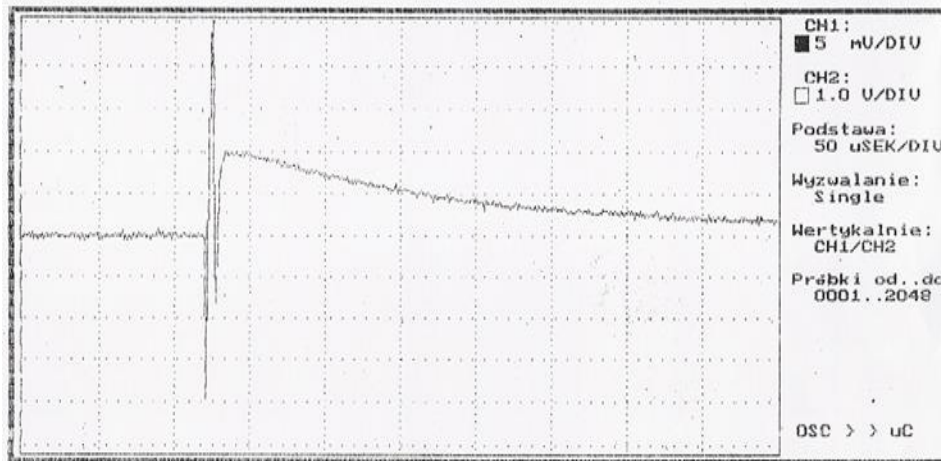

Fig. 3. Typical current pulse for amorphous anthrone layers

The examinations of the hole mobility for the polycrystalline anthrone layers were made in the limits of the electrical field from $1 \cdot 10^3$ V/cm to $2 \cdot 10^4$ V/cm. Measurements for amorphous and quasi amorphous anthrone and antrachinone were made in the limits from $1 \cdot 10^3$ V/cm to $1 \cdot 10^4$ V/cm. All the measurements were made at room temperature. The activation energy of mobility for those layers was determined in the temperature limits 285-353 K. Typical current pulse obtained for the amorphous anthrone layers is presented in Fig. 3. The values of the electric fields applied in the time of flight measurements have been chosen after taking the *U-V* characteristics for which

we had obtained the level when the traps were fulfilled. For this and greater values of the field we have obtained the shape of the pulse which possessed the "kink point" on the *I-t* characteristics plotted in the log-log scale.

2.4. Results

For the polycrystalline layers of antrachinone and anthrone the mobilities for holes were in the range $(8\pm2)\cdot10^{-4}$ cm^2/Vs and $(7\pm2)\cdot10^{-3}$ cm^2/Vs. Temperature dependences of the mobility μ in cm^2/Vs were given by formulae

$$\ln\mu = -\frac{3365}{T} - 3{,}643$$

for antrachinone and

$$\ln\mu = -\frac{3896}{T} - 5{,}622$$

for anthrone polycrystalline layers. These results indicate the activation energy of the order 0,03 eV, which is close to *kT* (0,026 eV). Additionally the shape of those dependences presented in log-log scale with "kink point" may approve the assumption that the hopping transport is present in the layers for both studied materials and that the activation energy for hopping is of the order of 0,03 eV [8, 9].

The measurements of the hole mobility were made within limits of the electrical field from $1\cdot10^3$ V/cm to $1\cdot10^5$ V/cm. The investigations were made in the room temperature and the results are presented in the Table 1.

Table 1

compound	ordering	hole mobility μ [cm^2/Vs] (T = 300 K)	activation energy E_a [eV]	applied electric field [V/cm]
antrachinone	polycrystalline	$(8 \pm 2)\cdot10^{-4}$	0,03	$3\cdot10^3$ to $2\cdot10^4$
antrachinone	quasi-amorphous	$(3-7)\cdot10^{-4}$	0,03	$3\cdot10^3$ to $2\cdot10^4$
antrachinone	amorphous	$(0,9-6,0)\cdot10^{-4}$	0,03	$3\cdot10^3$ to $2\cdot10^4$
anthrone	polycrystalline	$(7\pm2)\cdot10^{-3}$	0,03	$1\cdot10^3$ to $1\cdot10^5$
anthrone	quasi-amorphous	$(3-7)\cdot10^{-3}$	0,03	$1\cdot10^3$ to $1\cdot10^5$
anthrone	amorphous	$(0,6-4,0)\cdot10^{-3}$	0,03	$1\cdot10^3$ to $1\cdot10^5$

For both molecular crystals the 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.

3. CONCLUSIONS

Findings of investigations demonstrate that the conductivity of both exercised spectral grade compounds does not exhibit the explicit dependence on the structure of the layer. For the antrachinone layers with perturbed crystal order, the value of holes mobility was smaller than $1 \cdot 10^{-3}$ cm^2/Vs at room temperature, which is typical for acenes, whereas for anthrone layers the mobility of the holes was almost one order of magnitude greater.

Measurements of the drift mobility in the discussed range of temperature for both of the acenes gives nearly identical character of the temperature dependence of this mobility, $\mu_d = \mu(T)$. In the range of error, it has an activated character with small activation energy of the order of kT.

The methodology of the experiment excludes influence of coordination of the molecule and influence of short-range and long-range ordering on observed differences in the conductivity for both compounds. Therefore the differences in the measured mobility may be attributed to the differences in permanent dipole moment for both examined molecules.

The carrier mobility values and activation energy suggest that we can meet here with two possibilities: the band transport with participation of traps [10] or with hopping transport [10, 11]. The more precise determination needs further studies on the influence of the structural disorder on the mobility value.

Acknowledgements

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DRYFTOWA RUCHLIWOŚĆ DZIUR W WARSTWACH ANTRONU I ANTRACHINONU O RÓŻNEJ STRUKTURZE

Streszczenie

Badano proces transportu dziur w polikrystalicznych, quasi-amorficznych i amorficznych warstwach antronu i antrachinonu. Do naparowania warstw w próżni 10^{-5} Tr użyto materiałów o czystości spektralnej. Pomiary ruchliwości wykonano metodą TOF. Obydwa związki z punktu widzenia krystalograficznego posiadają prawie jednakową strukturę układu jednoskośnego o prawie identycznych stałych sieciowych i prawie identycznym kącie β. Przebadano trzy rodzaje warstw, to jest o strukturze polikrystalicznej, quasi-amorficznej i amorficznej. 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. Dla obu związków uzyskano w temperaturze pokojowej wartości ruchliwości mniejsze niż 10^{-2} cm^2/Vs z energią aktywacji ruchliwości rzędu 0.03 eV. Uzyskane wartości przemawiają za transportem hoppingowym. Na podstawie badań wydaje się, że moment dipolowy cząsteczek może mieć istotny wpływ na wielkość ruchliwości nośników ładunku.