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HOLE DRIFT MOBILITY IN ANTHRONE AND ANTRACHINONE LAYERS

Drift mobility of holes in antrachinone and anthrone polycrystalline thin films evaporated in the vacuum of the order of 10^{-5} Torr was measured with time-of-flight- method. The one order difference in mobility values for both –four ring acenes purified with zone melting before vaporization and identical in crystallization structure but with different molecule symmetry may have the origin in the presence of the difference in permanent dipole moment for both molecules.

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

1. INTRODUCTION

Organic molecular crystals in the type of thin films and aggregates are technologically very attractive materials in the electronic meaning. Their usefulness relies to a large extent on their photoconductivity, light absorption, non linear polarizability etc., what does it means to the properties immediately related to the electronic structure of these materials. A rigorous quantum mechanical treatment of a crystal requires determination of its band structure within periodic boundary conditions. Such a calculation for the crystals built up of the large sized molecules is very difficult and sometimes is not possible without the coarsened approximations.

One of the possible path for omit this problem is to limit the quantum mechanical treatment to an individual molecule and then to consider the intermolecular interactions in terms of the self consistent reaction field. The basic molecular properties can be used as the input parameters in calculations of

solid state properties, such an energetic structure of the forbidden gap and can be verified by an experiment [1, 2].

Molecular electrostatic potential is formed by contribution from atomic charges, dipoles, the higher multipole moments vanished by symmetry [3]. If molecular crystal is formed only by the van der Waals interactions, the shortest intermolecular separations C...H and C...C are as follows 2.8-2.9 Å and 3.3-3.4 Å [4]. At the distances of this range, the contributions from atomic quadrupole moments can be neglected and for calculations of the crystalline electrostatic potential so only atomic point charges and point dipoles should be used.

In some molecular crystals the effect of the crystal structure exceeds the effect of hydrogen bonding and is directed oppositely to it; thus the total effect of crystalline electrostatic potential reduces the molecular dipole moment [5]. There were taken here tests to check how the dipole moment of the molecules of the molecular crystal or its absence affects the mechanism of the charge carriers transport. For this reason there were chosen two molecular crystals with nearly identical crystalline structure. The first was the anthracene, with molecules possessing the nearly zero dipole moment. The second was the anthrone, which molecules are characterised with the specific dipole moment. The experiments yield the different values of the carrier mobility for both compounds.

2. EXPERIMENTAL AND RESULTS

2.1. Properties of anthracene and anthrone

The structure of anthracene, $C_{14}H_{10}$, has been repeatedly investigated, most recently at room temperature. Its crystals are monoclinic with a bimolecular unit of the dimensions (in room temperature): $a_0 = 15.810(15)$ Å, $b_0 = 3.942(5)$ Å, $c_0 = 7.865(10)$ Å, $\beta = 102^\circ 43(2)'$ [7, 12]. The space group $C_{2h}^5(P2_1/a)$ places its atoms in the positions: $(4e) \pm(xyz; x+1/2, 1/2 y, z)$.

The crystals of anthrone, $C_{14}H_{10}O$, are monoclinic with a bimolecular unit of the dimensions (in room temperature): $a = (15.80 \pm 0.03)$ Å, $b = (3.998 \pm 0.005)$ Å, $c = (7.86 \pm 0.16)$ Å and $\beta = 101^\circ 40'$ [7, 12]. The space group $C_{2h}^5(P2_1/a)$ places its atoms in the positions: $\pm(xyz; x+1/2, 1/2 - y, z)$ with oxygens distributed statistically over half of these positions.

Planar, centrosymmetric molecules of anthracene have the bond dimensions with the distances C-H lying between 1.00 and 1.04 Å. The anthracene molecule possesses a natural dipole moment measured in benzene 0.6 D ($2.00 \cdot 10^{30}$ Cm) [5],

but computed from the Chyperchem programme the worth is 0.00079 D (it means that practically equals zero). The anthrone molecule possess a greater natural dipole moment measured in benzene 3.66 D ($1.22 \cdot 10^{29}$ Cm) [5].

2.2. Sample preparation

The thin film samples with spectral grade antrachinone and anthrone (purified with zone melting) were obtained by evaporation in vacuum under the pressure of the order of 10^5 Torr on glass plates. The substrate temperature for polycrystalline layers was about 300 K with a proper evaporation rate. Structural examination of obtained antrachinone layers was made using X – ray diffraction.

2.3. Measurements

Free pairs of electron-hole were generated by a nitrogen laser, with the pulse intensity of 5 μ J 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 was completely described in [7-10, 15, 16].

Typical current pulse obtained for the polycrystalline antrachinone layers is presented in Fig. 1.

The examinations on the hole mobility for the polycrystalline antrachinone layers were made in the limits of the electrical field from $3 \cdot 10^3$ V/cm to $2 \cdot 10^4$ V/cm in the room temperature and the results are presented in Fig. 5. The determination of the activation energy of the mobility for these layers was made in the temperature limits 285-353 K.

Typical current pulse obtained for the polycrystalline anthrone layers is presented in Fig. 2.

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 $4 \cdot 10^4$ V/cm. The investigations were made in the room temperature and the typical results are presented in Fig. 2. The determination of the activation energy of the mobility for these layers was made in the temperature limits 285-353 K. The values of the electric fields have been chosen because of the possibility to avoid too low levels of time of flight signal and the second reason was that the shape of the pulse should have possessed the “kink point” in the linear scale in the I-t characteristics.

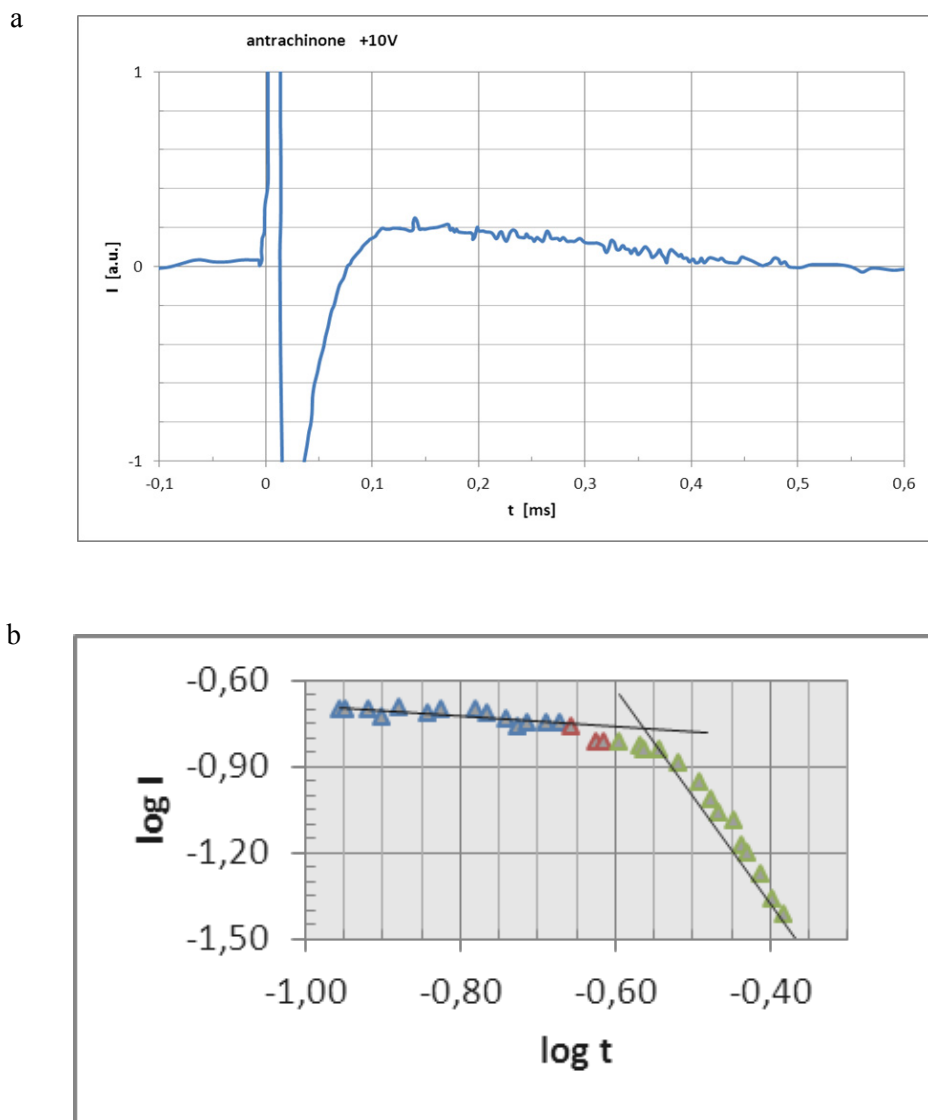


Fig. 1. a) Exemplary I-t characteristics for antrachinone layer (the image obtained from oscilloscope), b) the same in double logarithmic scale. The arrow shows t_r – time of flight.

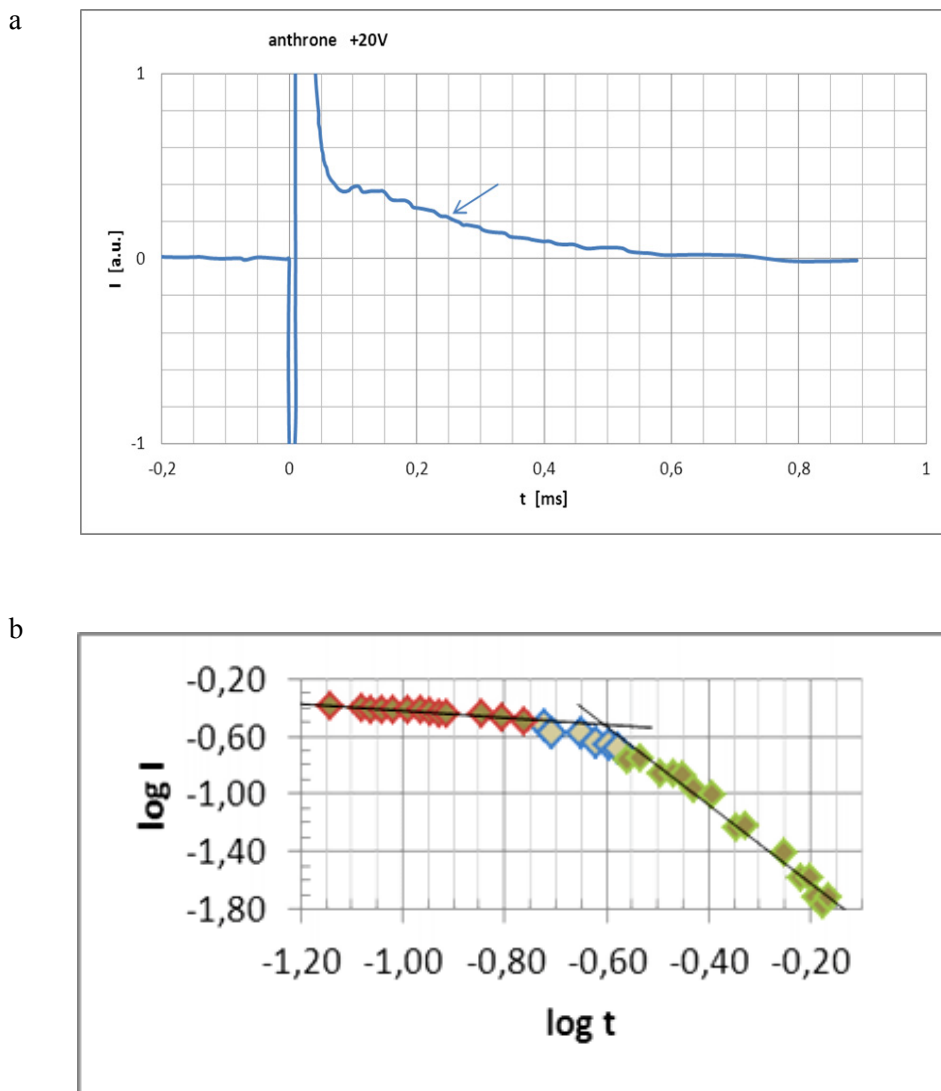


Fig. 2. a) Exemplary I-t characteristics for anthrone layer (the image obtained from oscilloscope), b) the same in double logarithmic scale. The arrow shows t_f – time of flight.

2.4 Results

The results of analysis for these investigations are shown in the Fig. 3 and Fig. 4. For the polycrystalline anthracene layers there were obtained the mobilities for holes in the range $(8\pm 2)\cdot 10^{-4}$ cm²/Vs and the activation energy for mobility on the level of kT , that was 0.03 eV.

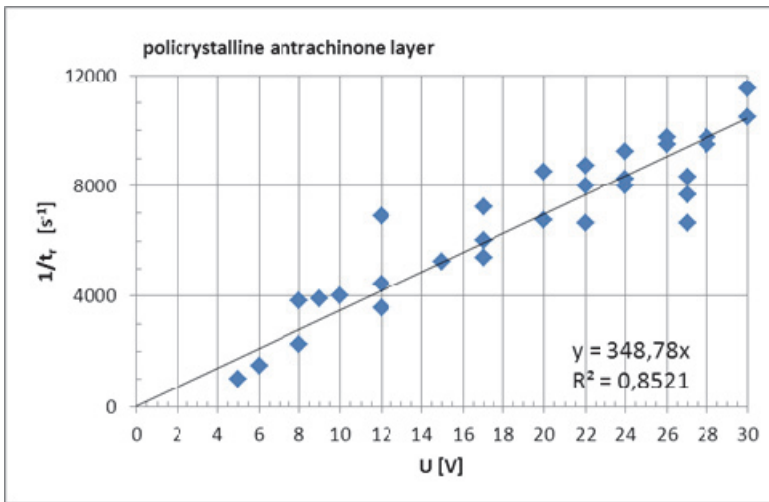


Fig. 3. Exemplary inverse time of flight for holes versus voltage for polycrystalline anthracene layers.

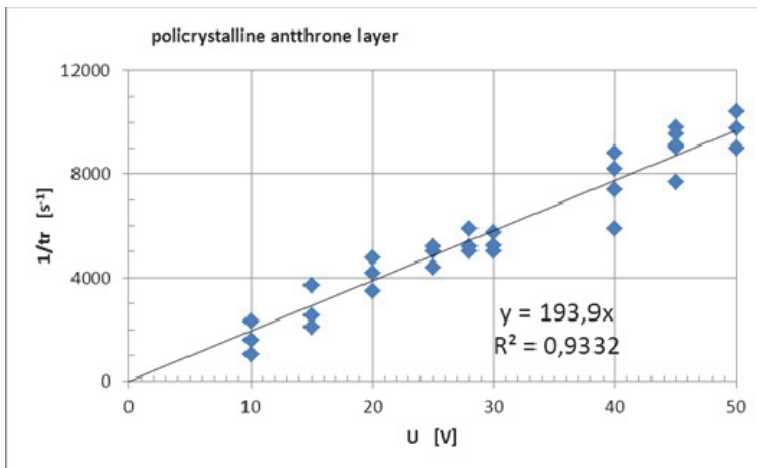


Fig. 4. Exemplary inverse time of flight for holes versus voltage for polycrystalline anthrone layers.

From the comparison of the diffraction pattern for polycrystalline layers of antrachinone and of anthrone – the patterns for anthrone are more complicated what appears to be evidently related to the molecule asymmetry and presence of their dipole momentum. The results of investigations for anthrone are shown in the Fig. 4. There were obtained the mobility value for holes in the range $(7\pm 2)\cdot 10^{-3}$ cm²/Vs and the activation energy for mobility on the level of kT , that is 0.03 eV.

The value of the activity energy for mobility was determined only in the small range of temperatures, and it can be supposed in the range of kT . For the polycrystalline materials when the transport is controlled by the traps, the drift mobility can be described with the formula $\mu_d(T) = a T^{-n} \cdot b \exp(-E_t/kT)$, where E_t is the mean depth of the traps. If the second term dominates in this formula, then the mobility dependence should have possess the identical shape as for the hopping transport: $\mu_d(T) \approx \exp(-E_t/kT)$, where E_t is the activation energy for hopping [10, 11].

For both molecular crystals obtained values of the mobility are below 1 cm²/Vs, and measured 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) there were observed clear difference in the mobility magnitude. For anthrone, with molecule possessed a natural dipole moment the mobility of holes in the condensed state is almost one order of magnitude greater then measured for antrachinone.

3. CONCLUSIONS

Charge carrier mobility in organic molecular crystals is very sensitive even with small dopant concentrations (in the order of/less then 1 ppm). Presence of the trap states originated as well from dopants as from structural events determines the lower limit of the temperature when the measurements of the microscope mobility μ_0 should have be impossible to make. Below this temperature the real measurements give the drift mobility μ_d controlled with multitrapping ($\mu_d < \mu_0$) [11]. In antrachinone layers it was obtained typical for – acenes, with perturbed crystal order, the value less then $1\cdot 10^{-3}$ cm²/Vs for holes mobility (in the room temperature). Whereas for polycrystalline anthrone layers the mobility of the holes was almost in order greater.

Measurements of the drift mobility in the discussed range of temperature for both of the acenes gives identical character of the temperature dependence of this mobility, $\mu_d = \mu(T)$. In the range of error it has activate character with small activation energy in the order of kT . Obtained results do not let for unambiguous determination for the transport mechanism.

It is known that for the pure monocrystals there was obtainable independent from the presence of the traps mobility value of the order of $1 \text{ cm}^2/\text{Vs}$ or greater with deactivation character of the dependence of the mobility, $\mu_0 \sim T^{-n}$. Whereas for the disturbed systems, i.e. polycrystalline when transport is controlled with multitrapping, the drift mobility will be considerably smaller and character of its temperature dependence can be described with the another formula:

$$\mu_d(T) = a T^{-n} \cdot b \exp(-E_t/kT),$$

where E_t is the mean depth of the traps. If in this formula the second term dominates, then the mobility dependence has the identical character as for the hopping transport: $\mu_d(T) \approx \exp(-E_{ht}/kT)$, where E_{ht} is the activation energy for hopping [10, 11].

Comparing obtained values of mobility for both –acenes identical in crystallization structure one should think about the origin of the different mobility values and should have to consider the possibility if theirs type of the dependence was connected with the presence of the permanent dipole moment for the anthrone molecules.

The carrier mobility values and activation energy suggest that we can meet here with two possibilities the band transport with participation of traps [14] or with hopping transport [13,14]. The precise determination needs further studies on the influence of the structural disorder on the mobility value.

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DRYFTOWA RUCHLIWOŚĆ DZIUR W WARSTWACH ANTRONU I ANTRACHINONU

Streszczenie

Badano proces transportu dziur w polikrystalicznych warstwach antronu i antrachinonu. Pomiaru 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 . W przypadku antronu, którego cząsteczki posiadają stały moment dipolowy, uzyskano prawie o rząd większą wartość ruchliwości niż dla antrachinonu. Dla obu związków uzyskano wartości ruchliwości mniejsze niż $10^{-2} \text{ cm}^2/\text{Vs}$ z energią aktywacji ruchliwości rzędu kT . Wielkości te mogą przemawiać za transportem hoppingowym, nie mniej dopiero badanie mechanizmu transportu z uwzględnieniem zmiany struktury warstw może w pełni zweryfikować hipotezę. Na podstawie badań wydaje się, że moment dipolowy cząsteczek, mimo identycznej struktury kryształu, może mieć wpływ na wielkość ruchliwości nośników ładunku.