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BIPOLAR TRANSPORT OF CHARGE CARRIERS IN THIN FILMS OF 9,10-DIMETHYLANTHRACENE AND 1-ACENAPHTHENOL

The current-voltage (I-U) characteristics we have been measured for thin films of 1-acenaphthenol and 9,10-dimethyl-anthracene prepared from their commercially available materials as products with purity ≥ 10^{-3} mass %. Using the method of differential processing of the characteristics, charge transport mechanism in these films was assessed.

Keywords: 1-acenaphthenol, 9,10-dimethylanthracene, conductivity, electric characterization.

1. INTRODUCTION

Recently one can observe constantly increasing interest to thermally stable low molecular derivatives of polycyclic aromatic hydrocarbons (PAHs) to which the title 1-acenaphthenol (1-Acol) and 9,10-dimethylanthracene (9,10-DMA) (their known crystal structures were redetermined by one of us [1, 2]), also belong. The interest is mainly connected with a very interesting optical and opto-electrical properties of this group of compounds, and especially the charge and energy transport properties owing to which they are now treated as one of the most promising active materials for a new generation of low-cost, flexible

electronic and opto-electronic devices. The most intensively studied prototypes of these devices, in which a number of different PAH derivatives in the form of technologically preferred thin films are tested as active materials, are organic light emitting diodes (OLEDs), organic field-effect transistors (OFETs) and photovoltaic and solar cells [3-8]. In the case of such weakly bonded organic active materials, the charge and energy transport properties are, however, very sensitive not only to physical imperfection of their films but, first of all, to chemical impurities contained in them, even if their concentration is on ppm or sub-ppm scale [9-11]. Therefore, high purity is of extreme importance for obtaining meaningful results for all questions, which are connected with energy and charge transfer.

In our previous paper [12], the preliminary results of electric characterization of both aforementioned materials were interpreted on the basis of the classic theory of space charge limited currents (SCLC) [13]. As a result, it has been found that in the case of 1-Acol, the concentration of the traps lies in the range of $2 \cdot 10^{11} \div 1 \cdot 10^{14}$ cm^{-3}, while for 9,10-DMA this concentration reaches a value of $9 \cdot 10^{14}$ cm^{-3}. It has also been observed that the measured *I-U* characteristics became fully stable only when the field strength reached the values from the range of $2 \cdot 10^{6}$ V/m to $2 \cdot 10^{7}$ V/m. Simultaneously resistivity of the layers were on the levels of $1.0 \cdot 10^{11} \div 9.0 \cdot 10^{12}$ and $6 \cdot 10^{11} \div 1.4 \cdot 10^{12}$ Ωm for 1-Acol and 9,10-DMA, respectively.

In this paper, based on the experimental results obtained in the frame of work cited above, and using the method proposed by Manfredotti at al. [14, 15], charge transport mechanism in these films was assessed.

2. EXPERIMENTAL

2.1. Materials

The starting materials were commercially available 1-Acol (purity -99%) and 9,10-DMA (pure), purchased from Aldrich and Fluka respectively. The materials were recrystalized from distilled benzene and from anhydrous ethyl alcohol, then, they were chromatographed on columns filled with Al_2O_3, and dried under vacuum. The gas chromatographic (a Hewlett Packard 5890 series II gas chromatograph equipped with a mass spectrometry detector) analysis of such purified materials has shown that the total impurity content in them is $\leq 10^{-3}$ mass %.

2.2. Measurements

The thin films of 1-Acol and 9,10-DMA were deposited in the vacuum of order of 10^{-5} Tr on an Au layer (bottom electrode) deposited earlier on the quartz glass substrate. In the same manner was also prepared the top aluminum electrode using an appropriate mask. In this way the measuring cell (see Fig. 1a) in the form of planar capacitor with the plates area of about 0.5 cm^2 was made. For such constructed capacitor the capacitance was measured (Semi-Automatic RLC Bridge type E314), in order to evaluate the thicknesses (L) of the investigated films. These thicknesses were 18.5 and 16 μm for 9,10-DMA and 1-Acol, respectively. During measurements the measuring cell was placed in the Faraday Cage (see Fig. 1b) for eliminating the electromagnetic noise. Current-voltage characteristics were obtained for the field strengths from $2 \cdot 10^5$ V/m to $2 \cdot 10^7$ V/m; an appropriate range of the biasing voltages was 3-280 V. The above characteristics were determined in the ambient atmosphere at the temperature of 300 K.

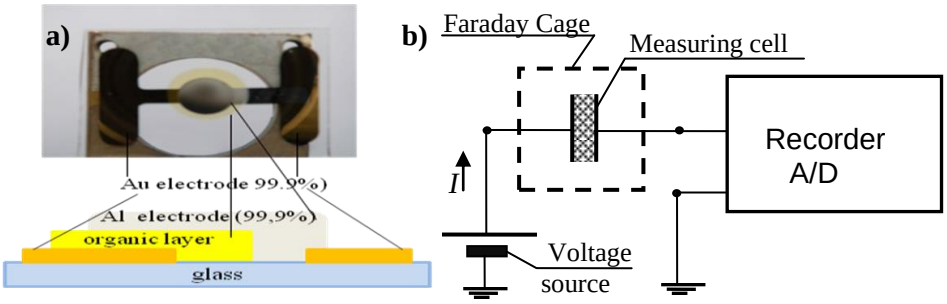

Fig. 1. The schemes of the measuring cell and its picture (a) and the measuring setup used for determination of I-U characteristics (b)

3. RESULTS AND DISCUSSION

As mentioned in the Introduction, the charge transport mechanism (holes and electrons) may be determined from a slope (α) of current-voltage characteristics (i.e. current density (J) *versus* biasing voltage (U)) defined as [14, 15]:

$$\alpha = \frac{d[\ln(J)]}{d[\ln(U)]}. \tag{1}$$

Basing on the α values, the measured *I-U* characteristics may be transformed to the α – *U* ones, which allow obtaining the mean value of charge carrier mobilities.

Figs. 2a) and b) shows *J-U* characteristics in log-log coordinates that were determined on the basis of the *I-U* characteristics measured for thin films of both investigated compounds. Instead the transformed characteristics α – *U* where the values of power exponent α were calculated from the above *J-U* characteristics according to eq. 1, are presented in Figs. 2c) and d). In the calculations, a Logger Pro Vernier Software & Technology program was used.

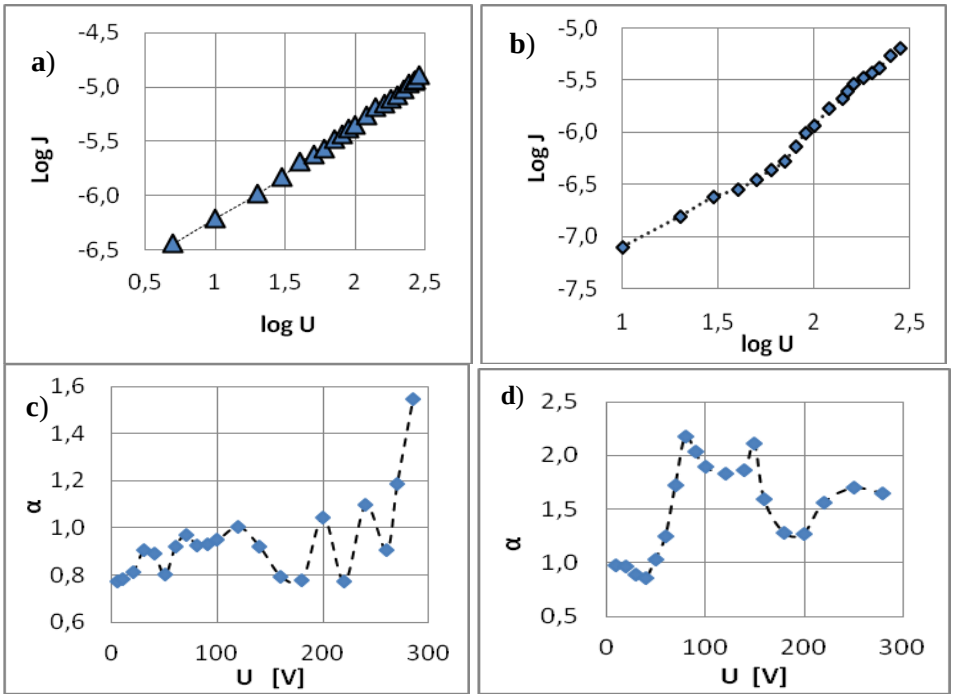

Fig. 2. Characteristics of *J versus U* calculated for 9,10 DMA (*L* = 18.5 μm) **a**) and 1-Acol (*L* = 16 μm) **b**), and their respective characteristics of α *versus U* **c**) and **d**)

Figs. 2c) and d) show that on the plots of transformed characteristics a few clear maxima (α_{max}) occur. According to the suggestion of Bagratishvilli et. al. [16], Tagyev et. al. [17] and Mikhelashivi et. al. [18] the values of α_{max} may be used for evaluation of the discrimination coefficients Q_{max} and Q_{am} defined by eq. 2 and eq. 3, respectively.

$$Q_{\max} = \frac{(2\alpha_{\max} - 1)^2 (\alpha_{\max} - 1)}{(\alpha_{\max} + 1)^2} \tag{2}$$

$$Q_{am} = \frac{(2\alpha_{\max} - 1)(\alpha_{\max} - 1)}{(\alpha_{\max})^3} \frac{\varepsilon\mu}{L^3} \frac{U_m}{J_m} \tag{3}$$

Here, U_m, J_m, ε and μ are: the voltage, the current density, the dielectric constant and the mobility in the limits of SCLC current, respectively; all these quantities correspond to α_{max}. For the calculations the values of ε were assumed to be equal 3.1 for both materials, because of similar values of polarization energy for two and three ring acenes being in the range of 1.6 eV [19], and μ was estimated from the Child's law for the SCLC currents [18].

The values of Q_{max} and Q_{am} calculated for both materials are presented in Table 1 together with the value of $4\alpha_{max}$ which is valid as a discrimination criterion for the condition for for appears field ionization (proposed in the papers [16, 18], i.e. $Q_{max}<4\alpha_{max}$).

Table 1

No.	compound	Q_{max}	Q_{am}	$4\alpha_{max}$
1	1-acenaphthenol	1.32	0.51	4.383
2	9,10-dimethylanthracene	0.031	0.23·	8.716

In the Table 2 mobilities and recombination mobilities determined from transformed current -voltage characteristics are compared with the time of flight (TOF) mean drift mobility obtained earlier by us (non-published data) for the same layers. The condition for appears field ionization i.e. $Q_{max}<4\alpha_{max}$, is fulfilled for both materials. (see Table 2).

Table 2

No.	compound	carrier mobility [cm^2/Vs]	recombination mobility [cm^2/Vs]	TOF mean drift mobility [cm^2/Vs]
1	1-acenaphthenol	4.8	1.9	1.1
2	9,10-dimethylanthracene	0.91	0.25·	0.14

For 1-Acol we obtained the condition $Q_{max}>1$, what can denotes monopolar injection. This result is in accordance with our earlier TOF measurements, where the life time for electrons was immeasurable. However, obtained Q_{am} value being on the order of one may stand for one of the three possibilities: the injection of free carriers (with recombination limited current) or field ionization of trap levels or trap free SCLC currents. For 9,10- DMA the both values of Q_{max}

and Q_{am} are clearly less than one. Therefore, this fact may be treated as an unambiguous case of double injection of free carriers.

4. CONCLUSIONS

- Basing on the results of our investigations it may be concluded that the use of obtained high purity materials has excluded the impact of impurities on the electrical characteristics. The impact of high purity is seen in high conductivities for both materials: 1-Acol and 9,10-DMA.
- For 1-Acol it was obtained more possible the unipolar mechanism of current flow but for 9,10-DMA the bipolar conductivity was unambiguously confirmed.
- The method of differential processing of current voltage used for recognition of charge flow mechanism approved its effectiveness, it was justified by comparison of the conductivity measurements with TOF method.
- It is noteworthy that phenomenon of bipolar transport is of great significance for possibility for its use in ambipolar OFETs, which are the basic element in the organic circuits such as inverters, oscillators and even recently in organic light emitting transistors.
- High bipolar conductivity for 9,10-DMA and high values of the mobilities for electrons and for holes allows us to conclude that it has a great potential for applications in organic electronics.

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TRANSPORT BIPOLARNY W CIENKICH WARSTWACH 9,10-DIMETYLOANTRACENU I 1-ACENAFTOLU

Streszczenie

Stosując kryteria dyskryminujące zasięg występowania mechanizmów przewodzenia można postawić hipotezę, że prądy płynące przez warstwy 9,10 dimetyloantracenu są bipolarne, zaś w przypadku 1-acenaftolu prądy mogą być monopolarne lub bipolarne. Wysokie wartości ruchliwości dla obu materiałów wskazują na ich duży potencjał do potrzeb elektroniki organicznej. Bipolarność prądów płynących przez 9,10 dimetyloantracen w połączeniu ze stabilnością chemiczną i mechaniczną uzyskiwanych z niego warstw pozwala traktować ten materiał jako wysoce przydatny dla potrzeb optoelektroniki.