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Charge Carriers Transport Mechanism in a-TNF Thin Layers

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The development of modern photocopying machines, the search for cheap, efficient and reliable solar cells, the search for new conducting materials and molecular storage systems has motivated experimental and theoretical work on organic materials such as molecular crystals, polymers and low-dimensional organic compounds. The organic electron acceptor 2,4,7-trinitro-fluorenone is used as sensitizer of photosensitive polymers, to extend the spectral range of their photosensitivity through the formation of charge-transfer complexes. Also, the thin films of TNF, depending on conditions of samples preparation, can be obtained in amorphous, polycrystalline and crystalline forms and, therefore, this material can be useful to investigate the effect of structure of organic materials on their electrical and photoelectrical properties.

The effect of trapping centres on the conductivity of amorphous 2,4,7-Trinitro-Nine-Fluorenone (a-TNF) is investigated by Space Charge Limited Current (SCLC), Thermally Stimulated Currents (TSC, TSD) and Transient photoconductivity methods. It is found that electron traps in a-TNF have a smoothly varying distribution centered at about $E_t = 0.29 \pm 0.04$ eV with a dispersion parameter $\sigma = 0.11 \pm 0.02$ eV. The true activation energy at room temperature is $E_a = 0.45 \pm 0.03$ eV. The zero-field extrapolated activation energy is $E_{ao} = 0.65 \pm 0.02$ eV. It was suggested that the transport of charge carriers in a-TNF is controlled by traps. Concentration of traps and drift mobility of electrons were evaluated.

Key words and phrases: amorphous solids, electronic transport, charge traps, transient photoconductivity, space charge, thermally stimulated current, activation energy.

1. Introduction

The amorphous organic electron acceptor 2,4,7-Trinitro-9-Fluorenone (a-TNF) is an aromatic solid whose electronic property enables it to be a candidate in a wide areas of application; as a photoconductor [1], as a transport layer for electrons in multilayer photoreceivers [2, 3], as sensitizer of polymers which form charge-transfer complexes with it [4, 5].

The reported data provide important information on electronic properties of a-TNF layers but it is still incomplete and insufficient to understand the electronic transport in amorphous TNF and the effect of electron trapping centres on the conductivity of a-TNF.

This work is devoted to studying the Space Charge Limited Current (SCLC), the Thermally Stimulated Currents (TSC, TSD), and the transient photoconductivity in a-TNF.

2. Results and Discussion

In SCLC experiments it was found that regardless of electrodes materials the electric current through the thin films of a-TNF was the non-linear function of the electric field across a sample. The typical current-voltage characteristic (CVC) of a sandwich-type amorphous TNF sample plotted in log-log scale is shown in Fig. 1 (curve 1). The dots in this graph denote the experimental results and the solid line is the computer simulation of a CVC. As it can be seen at low injecting level, the space charge limited current shows a quadratic dependence on the applied voltage and superquadratic, at higher injecting levels. The dependence of the slope of the CVC is

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given by $n = \mathrm{d}(\lg J)/\mathrm{d}(\lg V)$ and shown in Fig. 1 (curve 2). The quadratic dependence of the current density J on applied voltage V in thin films of a-TNF shows the realization of SCLC conditions in our experiments. The observed dependence of the slope of the CVC on the applied voltage cannot be explained on the assumption of the discrete or exponential distribution of charge trapping states in a-TNF samples.

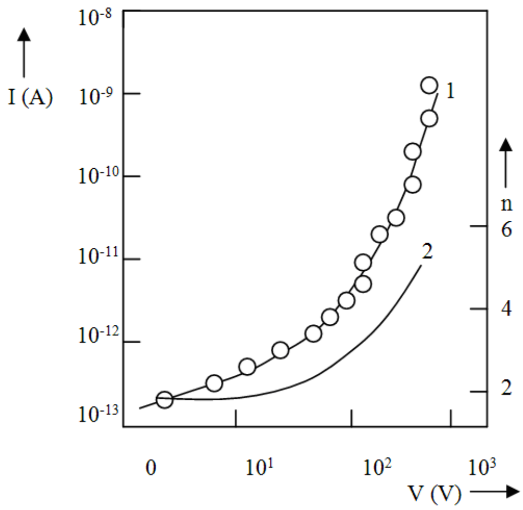

Figure 1. CVC of the Al-a-TNF-Al type sample, sample thickness $d = 8\mu$m. Solid line (curve 1) is the calculated curve approximating the experimental points. Curve 2 is $n = f(V)$

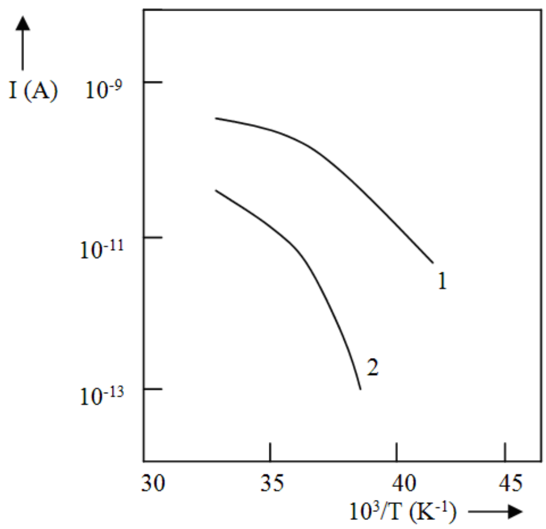

Figure 2. Temperature dependence of SCLC with voltage as variable parameter. Curve 1–300 V and curve 2–50 V

Also, contrary to the predictions of theories based on the discrete and exponential distribution of traps in energy, the observed temperature dependence of SCLC is non-linear. This dependence with voltage as a variable parameter is shown in Fig. 2, where curve 1 corresponds to the high injection level (300 V) and curve 2 to the low injection level (50 V). Such behaviour of SCLC temperature dependence at different injection levels and, also the non-linear dependence of the slope n of the CVC on applied voltage, witnesses in favour of a Gaussian distribution of local trapping states centred in the forbidden energy gap [6–9]. From the SCLC measurements and computer simulation on the basis of a Gaussian model the effective density states N_c in the conduction band, the density of trapping states N_t, the position of the distribution maximum E_t and the distribution parameter σ were evaluated in a-TNF samples. Values of these parameters are given in Table 1.

Table 1

Values of parameters

Parameters	Methods	
	SCLC	TSC,TSD
N_c (cm^{-3})	(2 ±0.2) x 10^{21}	
N_t (cm^{-3})	(1 ±0.2) x 10^{17}	
E_t (eV)	0.29 ±0.04	0.35 ±0.04
σ (eV)	0.11 ±0.02	

The analysis of the shape of CVC and the temperature dependence of SCLC indicate that electric fields used in experiments were insufficient for the complete filling of trapping states and current through a sample of a-TNF was controlled by charge traps.

In time-of-flight experiments it is found that the majority charge carriers in samples of a-TNF are electrons and transient photocurrent pulse shows a dispersive character.

The typical transient photocurrent pulse plotted in log-log scale is shown in Fig. 3 (on the left), where the solid line is the computer simulation on the basis of the theory of dispersive transport of charge carriers.

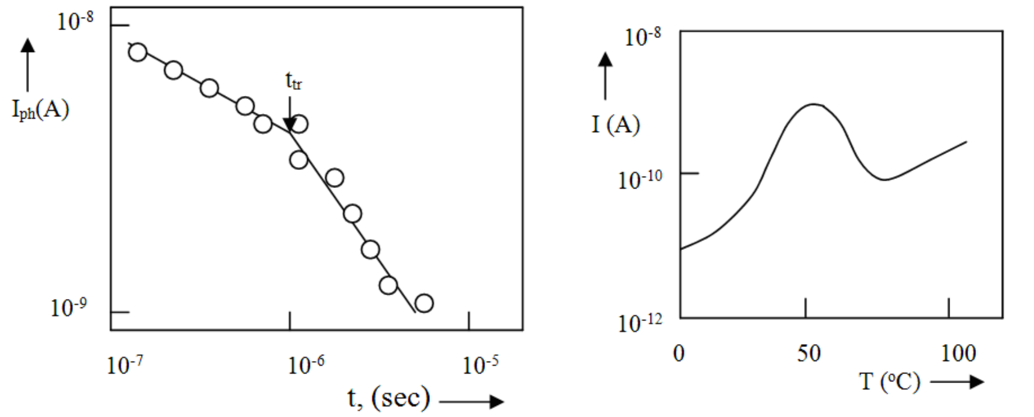

Figure 3. Dependence of the transient photocurrent on time in a-TNF. Solid line is a calculated curve and dots are experimental results (on the left). TSC spectrum for a-TNF. Voltage is 30 V. Heating rate is 5°C/min (on the right)

Time corresponding to the change in the slope of the solid line is the transit time t_{tr}. The drift mobility of electrons in a-TNF was calculated with the use of the conventional relation $\mu = d/Et_{tr}$ (E — the electric field across a sample and d — the sample thickness). It was found that the drift mobility of electrons in thin films of a-TNF depends on temperature and on the sweep field. The temperature dependence of μ reveals the activated nature of electron flow. The computed activation energy at an electric field of 3×10^7 V/m is $E_a = 0.45 \pm 0.03$ eV. The dependence of μ on E in the range of the sweep field used in the experiments is similar to that predicted by Poole-Frenkel theory. The zero-field extrapolated activation energy is $E_{ao} = 0.64 \pm 0.04$ eV.

The trapping states in TSC measurements were filled by applying the voltage ($V = 250$ V) across the samples at room temperature. After two hours the samples were rapidly cooled to -70°C. The thermostimulated current was registered at 30 V across the sample and at steady rate of heating of 5°C/min.

Our study of TSC in a-TNF samples indicates the variation of the thermostimulated current with temperature with a pick value at 50°C (Fig. 3, on the right). The activation energy, calculated from the initial rise of the heating curve is 0.35 ± 0.04 eV.

3. Conclusion

Electrons are the majority charge carriers in thin films of a-TNF , this fact is proved by the polarity dependence of transient photocurrent in time-of-flight experiments. The bulk electronic current is controlled by shallow traps with Gaussian distribution centred in the forbidden gap at 0.29 ± 0.04 eV below the conduction level. The fact that the activation energy obtained in SCLC experiments is less than that obtained in time-of-flight experiments may support the suggestion that two processes contribute to E_{ao}, the thermally activated transport of electrons and the thermal dissociation of electron-hole pairs into free charges. The effect of the sweep electric field on the value of E_a ($Ea < E_{ao}$) is due to the modulation of depth of charge traps by electric field, according to the Poole–Frenkel effect and also, due to the dependence of the activation energy of photogeneration of charge carriers on the electric field across a sample which is in a good agreement with the prediction of the theory of photogeneration of charge carriers in organic semiconductors [10, 11]. The activation energy obtained from TSC measurements is slightly higher than E_t calculated from SCLC measurements but it is still within the range of experimental errors. This may indicate the fact that the same trapping states control the thermostimulated and space charge limited currents.

References

1. *Mort J.* Polymers and Electronic Materials // Adv. Phys. — 1980. — Vol. 29, No 2. — Pp. 367–408.
2. *Mark H.* Electro- and Photo-Responsive Polymers // J. Polym. Sci. — 1978. — No 62. — Pp. 1–12.
3. *Prister G.* Hopping Transport in Doped Organic Polymers // Phys. Rev. — 1977. — Vol. (b) 47, No 8. — Pp. 3676–3687.
4. *William D. J.* Charge Transport in Polymeric Photoconductors // Amer. Chem. Soc. Polym. Prep. — 1975. — Vol. 16, No 2. — Pp. 215–218.
5. *Melz P. J.* Charge Transport in Polymeric Photoconductors // Amer. Chem. Soc. Polym. Prep. — 1975. — Vol. 16, No 2. — Pp. 219–224.
6. *Bulyshev Y. S., Kashirskiy I. M., Sinitskii V. V.* Photo-Injection of Charge Carriers in Poli-1-Vinil-1,2,4 – Triazole // Phys. Stat. Sol. — 1982. — Vol. (a) 69. — Pp. 139–143.
7. *Gill W. D.* Drift Mobility of Charge Carriers in TNF-PVK // J. Appl. Phys. — 1974. — Vol. 45, No 12. — Pp. 3943–3949.
8. *Bulyshev Y. S., Kashirskiy I. M., Sinitskii V. V.* Trapping Centres in Poli-1-Vinil-1,2,4 – Triazole // Phys. Stat. Sol. — 1982. — Vol. (a) 70. — Pp. 139–143.
9. *Nespurek S., Silinsh E. A.* Space Charge Limited Current Theory for Trapping States // Phys. Stat. Sol. — 1976. — Vol. (a) 34. — Pp. 747–759.
10. *Abdel-Malik T. G., Abdeen A. M.* Photoconductivity of PVK // Phys. Stat. Sol. — 1982. — Vol. (a) 72. — Pp. 99–104.
11. *Onsager L.* Initial Recombination of Ions // Phys. Rev. — 1938. — Vol. 54. — Pp. 554–557.

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Механизм переноса носителей заряда в тонких слоях а-ТНФ

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Для расширения спектральной области фоточувствительности полимеров используется низкомолекулярное органическое соединение 2,4,7-тринитрофлуоренон (ТНФ), который образует со многими полимерами комплексы с переносом заряда. В зависимости от условий приготовления тонкие плёнки ТНФ могут быть получены в аморфном, поликристаллическом и кристаллическом состояниях, что делает это вещество удобным для изучения влияния структуры на его электрофизические свойства.

В тонких слоях аморфного тринитрофлуоренона (а-ТНФ) обнаружены и исследованы токи термостимулированной деполяризации (ТСД), термостимулированной проводимости (ТСП) и токи, ограниченные пространственным зарядом (ТОПЗ). Результаты исследования указывают на электронную природу этих токов. По характеру нарастания ТСП и виду вольтамперных характеристик установлено существование локализованных состояний, обладающих гауссовским распределением по энергии с параметрами: $E_t = 0{,}29 \pm 0{,}04$ эВ (положение центра распределения ловушек) и $\sigma = 0{,}11 \pm 0{,}02$ эВ (дисперсионный параметр). Обнаруженные центры являются ловушками как для неравновесных носителей заряда, генерированных светом, так и для инжектированных из электродов. На основании анализа результатов и в соответствии с теорией ТСД, ТСП и ТОПЗ определены основные параметры центров локализации в изученных образцах: плотность, глубина залегания, дисперсия энергетического распределения, эффективная плотность состояний на уровне проводимости.

Полученные данные обсуждаются с точки зрения механизма зонного переноса неравновесных носителей заряда, контролируемого центрами захвата.

Ключевые слова: аморфные твёрдые тела, перенос электронов, ловушки зарядов, импульсная фотопроводимость, пространственный заряд, термостимулированный ток, энергия активации.