

Photovoltaic Properties of Tetracene and Pentacene Layers

Ryszard Signerski, Grażyna Jarosz, Jan Godlewski*

Gdansk University of Technology, G. Narutowicza 11/12, 80-952 Gdansk, Poland
E-mail: zofia@mif.pg.gda.pl

Summary: Photovoltaic phenomenon in tetracene and pentacene layers evaporated under the same conditions onto a glass substrate and provided with the same couple of electrodes is investigated. Comparison of the results obtained for both organic materials makes it possible to conclude that in spite of differences in mechanisms of charge carrier generation, the values of photovoltaic parameters are very similar.

Keywords: charge transport; photovoltaic effect; tetracene; pentacene; thin films

Introduction

Tetracene and pentacene are materials which have been examined for many years and therefore they can be treated as model organic materials^[1,2]. One can find many works on photovoltaic phenomenon in tetracene published hitherto (e.g. ^[3-6]) and lately also in pentacene ^[7,8]. The objective of our study is to compare photovoltaic properties of pentacene and tetracene layers evaporated under the same conditions (pressure, substrate temperature and evaporation velocity) and provided with the same couple of electrodes, Au and Al. It is a typical set of electrodes used in the metal-organic layer-metal sandwich systems. The Au electrode (its work function is about 5 eV) effectively injects holes into both materials, while Al (its work function is about 4.2 eV) forms a contact of a barrier with properties similar to Schottky barrier and limits the hole injection.

Experimental

Tetracene and pentacene (Aldrich) powder were purified by vacuum sublimation before they were used in the investigations. Samples were obtained by vacuum evaporation (Auto306 Edwards with a turbomolecular pump, 10^{-3} Pa) of the following layers onto a glass substrate (room temperature): Au, tetracene (Tc) or pentacene (Pn), Al with adequate thicknesses: 10 nm, 400 nm,

15 nm, and with common surface of 0.1 cm^2 . The average evaporation velocity of organic layers was about 0.1 nm/s . Samples were made in a series of five cells. We have examined 11 samples with Pn and 9 samples with Tc.

Our experimental research involves spectra of photovoltaic short-circuit currents for illumination through either Al or Au, dependences of short-circuit currents on the light intensity and current-voltage dependences of illuminated or unilluminated samples. All investigations were carried out in air and at room temperature. In spectral measurements, a constant value of flux of photons penetrating into the organic layer was kept for the whole range of wavelengths.

Results and Discussion

Figures 1 and 2 show spectral characteristics of cells with Tc and Pn under illumination through Al or Au and absorption spectra of organic layers. In all cases photovoltaic current flows through organic layers from Al to Au.

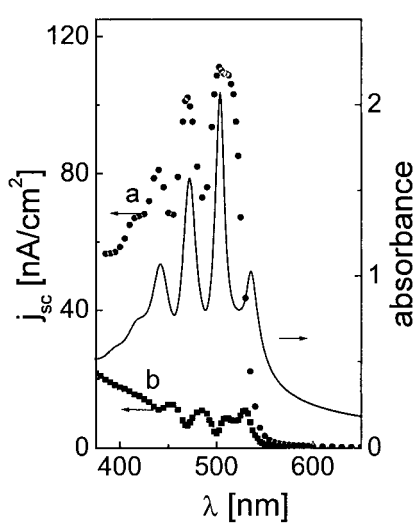


Figure 1. Short-circuit current spectrum for Al/Tc/Au cell illuminated through Al (a) or Au (b) (light intensity $I_0 = 10^{13}\text{ photons}/(\text{cm}^2\text{s})$) and absorption spectrum of the Tc layer (solid line).

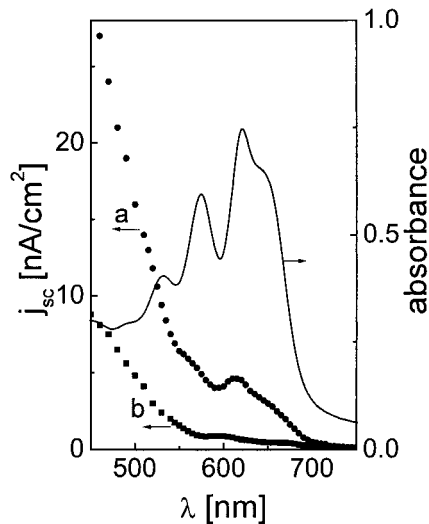


Figure 2. Short-circuit current spectrum for Al/Pn/Au cell illuminated through Al (a) or Au (b) (light intensity $I_0 = 10^{13}\text{ photons}/(\text{cm}^2\text{s})$) and absorption spectrum of the Pn layer (solid line).

For Tc illuminated through Al we observe good correlation between spectra of the photovoltaic current and absorption (we should note that the peak of absorption spectrum at 535 nm is not associated with an excited state but originates from diffraction-interference effects ^[9]). This relation, called symbatic, results from the dissociation of excitons at the Al electrode and the injection of holes into Tc. If the cell is illuminated through Au, the filtration action of Tc leads to antibatic relation between spectra of the current and absorption (the hole injection by Al which is now a back-electrode) ^[10]. Similar characteristics can be obtained also if the photogeneration of charge carriers occurs in strong electric field of a barrier formed by a metal of low work function and a p-type semiconductor (Schottky barrier). We cannot entirely exclude this case for the Al/Tc interface. The role of acceptor impurities can be played by oxygen centres ^[5].

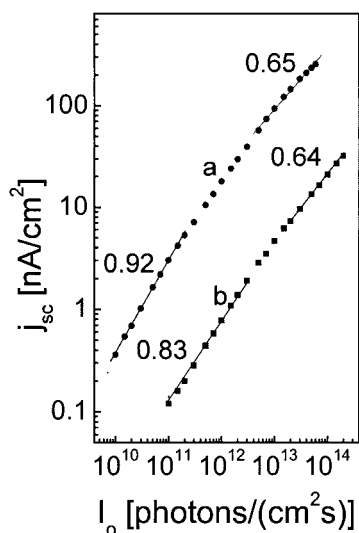


Figure 3. Light intensity characteristics of short-circuit current for Al/Tc/Au cell illuminated through Al by monochromatic light of $\lambda = 505$ nm (a) and for Al/Pn/Au cell illuminated through Al by monochromatic light of $\lambda = 615$ nm (b).

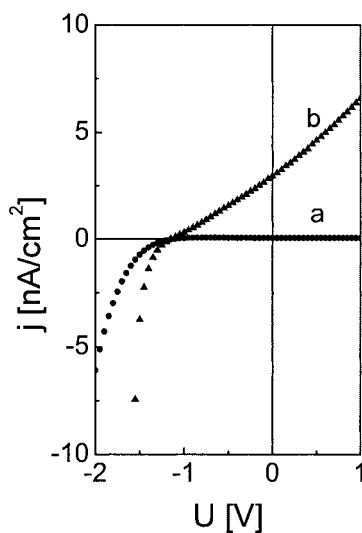


Figure 4. Voltage characteristics of dark current (a) and photocurrent under illumination with monochromatic light ($\lambda = 615$ nm, $I_o = 10^{13}$ photons/(cm² s)) through Al (b) for Al/Pn/Au cell.

Noticeable smaller differences between spectral characteristics of short-circuit currents obtained for both directions of illumination are observed for the cell with Pn (Fig. 2). Now the structure of current characteristics is determined also by bulk processes of the photogeneration or by the exciton release of charge carriers from traps. The range for $\lambda < 550$ nm corresponds to intrinsic generation. Charge carriers in this range are produced by either dissociation of mixed states of CT and Frenkel or autoionization of molecular excited states ^[2,11]. At $\lambda > 550$ nm, free charge carriers (holes) can be produced in extrinsic processes such as interactions of excitons with oxygen centres near the Al electrode, trapped charge carriers or with the Al electrode ^[1,12,13].

Taking into account Figs. 1 and 2, we can calculate the incident-photon-to-current-efficiency: $IPCE = j_{sc}/eI_0$ (where e is the elementary charge), which is 0.7 % for Tc ($\lambda = 505$ nm) and 0.3 % for Pn ($\lambda = 615$ nm). For $\lambda < 550$ nm, IPCE values for Pn are greater than for Tc.

Dependences of a short-circuit current on the light intensity for the Al/Tc/Au and Al/Pn/Au cells illuminated through Al are presented in Figure 3. These characteristics are not linear but they can be approached in sections by the relation of the type $j_{sc} \sim I_0^n$ with values of n written over the characteristics. Values of $n < 1$ indicate the existence of trapping processes ^[14] or the charge carrier recombination ^[1].

Figure 4 shows voltage dependences of both dark current and photocurrent (corresponding to the photovoltaic range) for illumination through Al obtained for the Pn cell. The sign of the voltage denotes polarization of the Al electrode. The obtained open-circuit voltage U_{oc} amounts to -1.15 V and is the same for illuminated and unilluminated sample. Therefore it is not photovoltage. We observed also a small "battery effect", e.g. the short-circuit current in the dark $j_{sc, dark} \approx 10^{-12}$ A/cm². This effect can result from corrosion of the Al electrode ^[15]. From the voltage dependence of the photocurrent, we can estimate power conversion efficiency: $\eta = P_{out max}/P_{input} \approx 0.025$ %.

In the case of the Tc cell, the current-voltage dependence is similar and $U_{oc, dark}$ amounts to -1.05 V, but $U_{oc, photo} = -1.25$ V and $\eta = 0.1$ % for $I_0 = 10^{13}$ photons/(cm²s) and $\lambda = 505$ nm.

Figure 5 shows current-voltage characteristics of cells with Tc and Pn under illumination through Al with white light of 300 W/m² (Xe lamp of 150 W with H₂O and BG 14 filters). η values calculated for these characteristics are almost the same for Tc and Pn, ca. 10^{-4} %. The obtained values are low, because the parameters of our samples (e.g. thickness of layers, the kind of

electrodes and their transmission) have not been optimized.

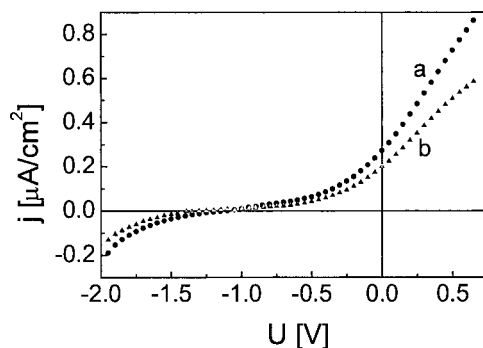


Figure 5. Photocurrent-voltage characteristics for Al/Pn/Au cell (a) and for Al/Tc/Au cell (b) under illumination through Al with white light.

Conclusions

Our investigations were based on a comparison of photovoltaic properties of Al/Tc/Au and Al/Pn/Au cells. We can conclude that the photovoltaic phenomenon for both systems has many features in common but the mechanisms of charge carrier photogeneration can differ. Particularly in the investigated wavelength ranges:

- the photovoltaic short-circuit current in Tc cells results from extrinsic processes of exciton dissociation at the Al electrode or near it,
- the short-circuit current in Pn cells is produced in both intrinsic and extrinsic processes, which occur in a wider region of the sample than in Tc cells,
- the photovoltaic parameter values of Tc and Pn cells obtained under the illumination with white light (of a spectrum similar to solar one) are nearly the same.
-

Acknowledgements

Work was supported by KBN under Program No. 4 T11B 057 22.

- [1] M. Pope, Ch. E. Swenberg, *"Electronic Processes in Organic Crystals and Polymers"* Oxford Sci. Publ., New York-Oxford 1999.
- [2] E. A. Silinsh, V. Capek, *"Organic Molecular Crystals"*, AIP Press, New York 1994.
- [3] L. E. Lyons, O. M. G. Newman, *Aust. J. Chem.* **1971**, *24*, 13.
- [4] A. K. Gosh, T. Feng, *J. Appl. Phys.* **1973**, *44*, 2781.
- [5] A. J. Twarowski, A. C. Albrecht, *J. Chem. Phys.* **1979**, *70*, 2255.
- [6] R. Signerski, J. Kalinowski, I. Koropeczy, S. Nespurek, *Thin Solid Films* **1984**, *121*, 175.
- [7] Ya. Vertsimakha, A. Verbitsky, *Synth. Met.* **2000**, *109*, 2475.
- [8] J. H. Schon, Ch. Kloc, B. Batlogg, *Appl. Phys. Lett.* **2000**, *77*, 2475.
- [9] W. Hofberger, *Phys. Status Solidi A* **1975**, *30*, 271.
- [10] R. Signerski, J. Kalinowski, *Thin Solid Films* **1981**, *75*, 151.
- [11] P. J. Bounds, W. Siebrand, *Chem. Phys. Lett.* **1982**, *85*, 496.
- [12] G. Jarosz, R. Signerski, J. Godlewski, *Adv. Mater. Opt. Electron.* **1996**, *6*, 379.
- [13] G. Jarosz, R. Signerski, J. Godlewski, *Synth. Met.* **2000**, *109*, 161.
- [14] R. Signerski, J. Kalinowski, *Mol. Cryst. Liq. Cryst.* **1993**, *228*, 213.
- [15] K. Murata, S. Ito, K. Takahashi, B. M. Hoffman, *Appl. Phys. Lett.* **1997**, *71*, 674.