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Optical and photoelectrical properties of the tetrathiotetracene-fullerene (TTTC₆₀) film heterostructures

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Abstract. The optical and photoelectrical properties of heterostructures (HS) SnO₂TTTC₆₀Ag are investigated. The additional absorption of HS TTT and C₆₀ is revealed in comparison with those for their components, which testifies to the formation of complexes between the TTT and C₆₀ molecules near the TTT-C₆₀ interface. Current-voltage characteristics (J-V) of a dark current is symmetric, as well as corresponds to the Ohm law for the voltages of 0 to 0.4 V. In the voltage range of 0.4 to 1.0 V, the branch of J-V at the positive polarity (I_+) goes above that at the negative polarity (I_-) at a SnO₂-electrode. Thus, in the double logarithmic scale, I_+ and I_- are described by direct lines with the angular factors 1.77 and 1.37, accordingly, and exponents in the half-logarithmic coordinates ($\log I-U$). The open-circuit voltage V_{oc} has a positive polarity at the SnO₂-electrode irrespective of the illumination direction of a sample. Photovoltage is caused by antiblocking bends of bands for holes and electrons near the SnO₂- and Ag-electrodes of TTT and C₆₀ films, accordingly. The dark effective specific resistance of the HS SnO₂TTTC₆₀Ag is equal to $5 \cdot 10^7$ Ohm-cm.

Keywords: fullerene, thin film, optical and photoelectrical properties, absorption spectra.

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1. Introduction

The prospects for using the organic materials as converters of a solar energy into electric one has been shown even more than 20 years ago [1, 2]. But the most intensive period of researches of organic solar cells (OSC) began only for the recent years [3-5]. This process has coincided with a fast development of nanotechnologies [6, 7].

In spite of the achieved progress in the OSC development (especially for the thin plastic OSC), up to date rather important problem is the formation of the photo-injecting electrode.

From our viewpoint, the method of the problem decision may be the use of more conducting (than the basic material) organic materials. It is possible to deposit this organic material film on the transparent layer. Because of its rather great conductivity, this film will not influence the electric characteristics of OSC. A presence of the conducting film can significantly expand the spectral region of OSC on account of, for example, photo-

injection of charge carriers. To check this idea, we have created HS TTTC₆₀. TTT and C₆₀ are the organic semiconductors of hole and electronic types with the specific resistance 10^4 [8] and 10^6 - 10^8 [9] Ohm-cm, respectively.

The aim of this work is to study the formation conditions of photo-injecting electrode basing on the analysis of optical and photoelectrical properties of HS TTTC₆₀.

2. Experimental

Thin films C₆₀, TTT and TTTC₆₀ were produced using the thermal deposition in 6.5 mPa vacuum onto silica substrates. Thicknesses of these films were measured with an interference layer thickness meter МИИ-4. Absorption spectra of the films were obtained using a spectrophotometer Perkin Elmer Lambda 25 UV/VIS at a slit spectral width of 1 nm and at the room temperature.

Current-voltage characteristics (J-V) of a dark current of sandwich structures SnO₂TTTC₆₀Ag were

measured at the setup that consisted of a source of the stabilized constant voltage, a measuring cell with a sample, and the amplifier of direct current Y5-9 with a recorder or the digital voltmeter at the output.

Spectral dependences of a short-circuit current I_{sc} were measured as follows. Light from an iodine incandescent lamp with a capacity of 120 W got onto a monochromator МДР-4 (JIOMO) through a focusing system of two quartz lenses, a modulator (modulation frequency 80 Hz) and a corresponding optical filter.

Then the monochromatic light was focused on a window of the measuring cell, in the center of which a sample was placed. The voltage on a loading resistance, or V_{oc} , was measured with a lock-in nanovoltmeter of the model Unipan-232B with a high-resistance preamplifier of the model 233-7 of the same firm. For synchronous detecting, we used the reference signal from a photon-coupled pair of the light-emitting diode – photodiode placed on the modulator. From the nanovoltmeter output, the signal was come to a computer through the interface card (ET-1050). Spectral distribution of a lamp intensity was measured using a pyrodetector that was placed instead of the sample, and the measured spectra I_{sc} were normalized for the equal quantities of incident quanta of light.

3. Experimental data

Dependences of the optical density $D(E)$ in the spectral region of 1.24 to 6.0 eV for films of C_{60} , TTT and $TTTC_{60}$ are resulted in Fig. 1. The film C_{60} with the thickness of 200 nm strongly absorbs in UV region 4.14 to 6.0 eV (curve 1). It was not possible to determine a peak position of this absorption, as their peak intensities $D_{max} > 3$ and exceed the maximum permissible optical density that the device can measure. The longwave part of the film C_{60} consists of three bands with the peaks at 2.00, 2.61 and 3.50 eV.

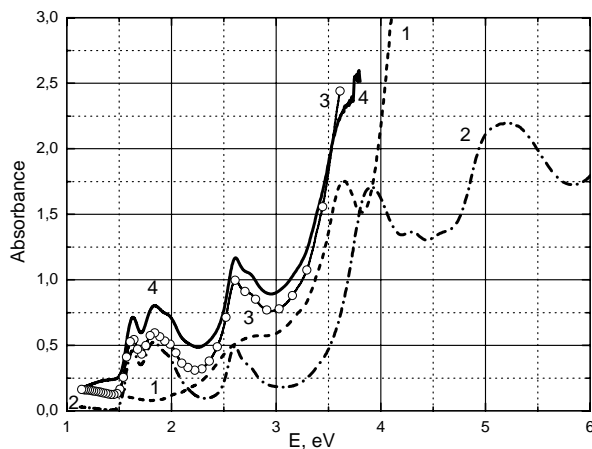


Fig. 1. Spectral dependence of the optical density: C_{60} (1); TTT (2); C_{60} + TTT (3) and $TTTC_{60}$ (4).

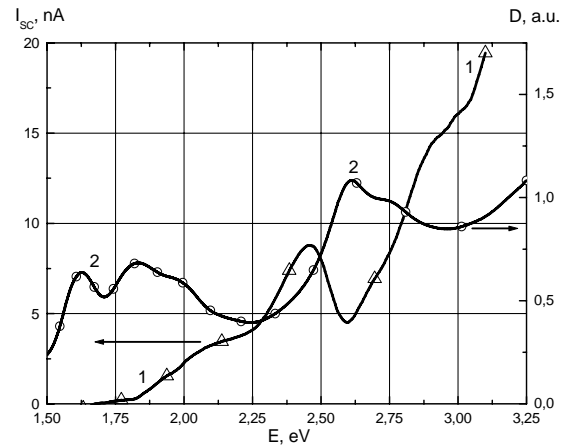


Fig. 2. Spectral dependences of the short-circuit photocurrent (I) and optical density (2) for the HS $TTTC_{60}$.

In the absorption spectrum of TTT films with the thickness of 200 nm, five bands at 1.64, 2.61, 2.88, 4.32, and 5.28 eV are observed (curve 2). Two longwave structural bands at 1.64 and 2.61 eV have vibrational peaks with the frequency 1410 cm^{-1} [10].

Curve 3 corresponds to the sum of curves 1 and 2 concerning the straight line $D = 0.68$ (the least value D for the film C_{60}), and curve 4 – to the spectrum absorption of $TTTC_{60}$.

The spectrum I_{sc} when illuminating the sandwich structure $\text{SnO}_2\text{TTTC}_{60}\text{Ag}$ through a SnO_2 -electrode by the modulated light is resulted in Fig. 2 (curve 1). It is visible that the photoresponse is observed at the photon energy of $E \geq 1.77 \text{ eV}$. Here, I_{sc} strongly grows within the range of 2.60 to 3.10 eV. At the longwave edge, two bands I_{sc} are observed at 2.07 and 2.46 eV. The band 2.46 eV is shifted into the longwave part relatively to the absorption band of HS $TTTC_{60}$ at 2.61 eV (curve 2). In the region of 2.26 to 2.76 eV, the I_{sc} spectra and absorption of HS $TTTC_{60}$ anticorrelate. It was not possible to measure I_{sc} spectra at illumination of HS $TTTC_{60}$ from the Ag-electrode owing to small transparency of this electrode.

Table summarizes the data on the values I_{sc} normalized on a power unit of modulated light for the sandwich structures $\text{SnO}_2\text{TTTC}_{60}\text{Ag}$ at their illumination by the modulated radiation of various photodiodes without taking into account the transparency of SnO_2 - and Ag-electrodes.

Table. The values I_{sc} in sandwich structures $\text{SnO}_2\text{TTTC}_{60}\text{Ag}$.

Characteristics of light-emitting diodes			I_{sc} , mA/W	
			Direction of illumination	
Color	Photon energy, eV	Light power, nW	SnO_2	Ag
Dark blue	2.64	750	9.2	4.50
Green	2.18	100	10.0	2.00
Red	1.90	230	4.3	0.86
Infra-red	1.32	1440	0.7	0.06

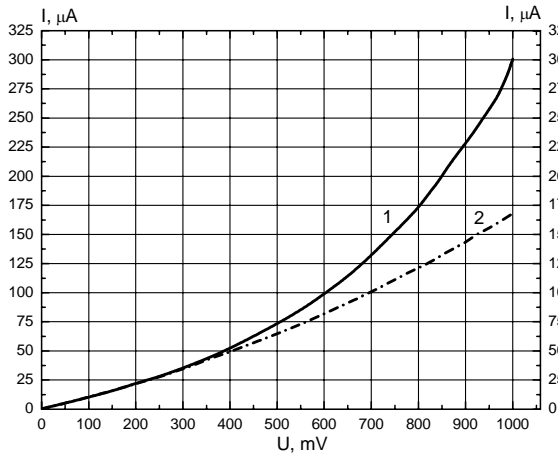


Fig. 3. Current-voltage characteristics of HS TTTC₆₀ for positive (1) and negative (2) polarities at the SnO₂-electrode.

Comparison of the values I_{sc} for red and infrared light-emitting diodes testify that, in the longwave region, the photoresponse is the order less than that for $E > 1.90$ eV.

J-V of the sandwich structure SnO₂TTTC₆₀Ag is shown in Fig. 3. In the voltage range 0.4 to 1.0 V $I_+ > I_-$, where I_+ and I_- – dark currents for positive (curve 1) and negative (curve 2) polarities at the SnO₂-electrode, respectively.

In the double logarithmic scale, the branch I_+ consists of two sections. The initial section with the angular factor $\kappa_1 = 1.0$ corresponds to the Ohm law. It passes into a superlinear section with $\kappa_2 = 1.77$. For I_- $\kappa_1 = 1.0$ and $\kappa_2 = 1.37$. For both branches of the voltage the transitions from ohmic to a superlinear section are identical and equal to 0.4 V. The dark resistance of TTTC₆₀ is determined in the ohmic section. It equals 8 kOhm. When the area of contacts is 25 mm² and HS thickness ≈ 400 nm, the effective specific resistance ρ is equal to $5 \cdot 10^7$ Ohm·cm, which is the same order with that for the film C₆₀ [9].

In the half-logarithmic scale ($\log I-U$) in the voltage range 0.4 to 1.0 V, the experimental points of J-V fit a direct line well. For I_+ its inclination is more than that for I_- . V_{oc} has positive polarity at the SnO₂-electrode and negative polarity at the Ag-electrode irrespective of the direction of illumination.

4. Discussion of experimental data

In the literature [11-13], the C₆₀ weak band of 2.00 eV is identified as a ζ -band ($h_u \rightarrow t_{1u}$ – a transition with the energy of 2.00 eV). Structural absorption of the film C₆₀ in the region 2.43 to 3.03 eV is caused by overlapping of closely-located bands A and B ($h_{1u} \rightarrow t_{1g}$ – transitions with the energies 2.41 and 2.70 eV, accordingly). The nature of the band C observed as a shoulder at 3.2 eV in the spectrum (Fig. 1, curve 1) is not discussed in the literature. The absorption band at 3.65 eV is identified as a D₂-band ($g_g \rightarrow t_{1u}$ – a transition with the energy 3.54 eV). All the

absorption bands of the film C₆₀ within the spectral region 1.24 to 6.20 eV fall into that of the excited states of $\pi\pi^*$ -type. From them, the ζ -, A-, B-bands are caused by transitions of electrons from the level of the most occupied molecular orbital, and all the others – from lower occupied orbitals into the levels of antibinding orbitals [13].

In the absorption spectrum of the TTT film (Fig. 1, curve 2), two longwave structural bands are caused by transitions of the valence electrons of sulfur (S) atoms into the first two unoccupied levels ($l_1\pi^*_{1-}$ and $l_1\pi^*_{2-}$ excitations, accordingly). All the other bands belong to the electronic transitions from the lower occupied levels [10].

Comparison of the absorption spectra of HS TTTC₆₀ (Fig. 1, curve 4) and the sums of those for separate TTT and C₆₀ (Fig. 1, curve 3) shows that, in the region of the first and second singlet transitions of TTT, an additional absorption is observed. That points to the interaction of TTT and C₆₀ molecules near the interface of TTT and C₆₀ layers with formation of their complexes.

A source is the photovoltage. The data on the work function A for TTT, C₆₀, SnO₂ and Ag, which are equal 4.47 [14], 4.53 [9], 5.15 and 4.3 eV [15], accordingly, are used to study the nature of the photovoltage.

Energy diagrams of electronic levels at the near-electrode regions and interface TTT-C₆₀ were considered in the band-to-band approximation assuming that $E_g(\text{TTT}) \approx E_g(\text{C}_{60}) = 2.0$ eV [9, 14]. As $A(\text{SnO}_2) > A(\text{TTT})$ and $A(\text{Ag}) < A(\text{C}_{60})$, at the contacts SnO₂-TTT and Ag-C₆₀, bends of TTT and C₆₀ bands are antiblocking for holes and electrons – the basic charge carriers in the films TTT and C₆₀, accordingly. Thus, near the contacts, space charges of equilibrium holes and electrons are formed (Figs 4a and b, respectively).

At the interface $A(\text{TTT}) < A(\text{C}_{60})$, the antiblocking bend of bands for electrons is formed only in the layer C₆₀, if to take into account that $\rho(\text{TTT}) \ll \rho(\text{C}_{60})$ (Fig. 4c). In the TTT films, the bands are flat.

For an estimation of the penetration depth of light into the TTT and C₆₀ films, we used the Lambert-Beer law:

$$I = I_0 e^{-\alpha d}, \quad (1)$$

where I_0 and I – the intensities of falling light near the electrode and at a distance d from the contact; α – the absorption factor.

From the equation (1) we determine the transmission factor of the film T :

$$T = I/I_0 = e^{-\alpha d}. \quad (2)$$

The penetration depth of light may be estimated with taking the logarithm (2), believing that $T \leq 0.1$. After transformations, we obtain

$$d_0 \geq 2.3/\alpha. \quad (3)$$

The value α is determined from the absorption spectra of the TTT and C₆₀ films (Fig. 1, curves 1 and 2) at $E = 2.61$ eV. It is found that $\alpha(\text{TTT}) \approx \alpha(\text{C}_{60}) = 2.5 \cdot 10^4 \text{ cm}^{-1}$ and, according to (3), makes $\sim 10^{-4} \text{ cm} = 1000 \text{ nm}$.

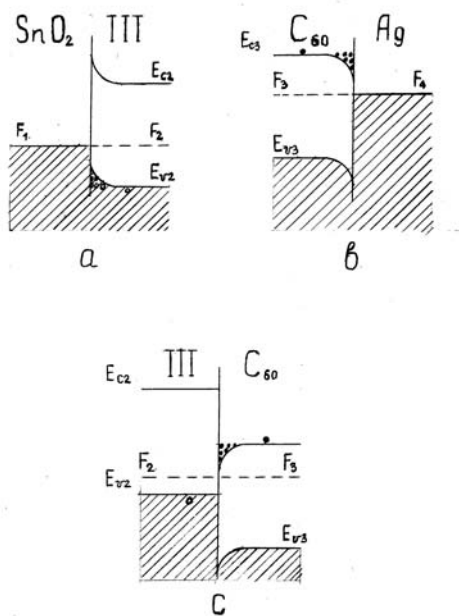


Fig. 4. Energy diagrams of electronic levels of the contacts: SnO₂-TTT (a), Ag-C₆₀ (b), TTT-C₆₀ (c).

What this means is light passes through the transparent SnO₂-electrode up to the opposite electrode. The same isn't true for Ag-electrode, as its transparency is insignificant.

At illumination of an unbiased HS, electron-hole pairs are photogenerated, if $E > E_{ph}$, or carriers of one polarity are photogenerated at $E < E_g$. Nonequilibrium holes diffuse to a SnO₂-electrode, electrons – to an Ag-electrode. For the mode V_{oc} SnO₂ is charged positively, and Ag – negatively, irrespective of the illumination direction, which are in agreement with the experiment.

A current flow through the structure SnO₂TTTC₆₀Ag may be ascribed as follows. If SnO₂ is biased positively relative to Ag, the injected from SnO₂ and Ag holes and electrons drift accordingly to the TTT / C₆₀ interface and recombine here. At the negative bias on SnO₂, the through current changes direction, and the interface will be again a place of recombination. The observed experimentally inequality $I_+ > I_-$ is caused by that, at the negative bias of SnO₂, the injection of electrons and holes is limited by the small potential barriers: for holes – near an Ag-electrode and electrons – near SnO₂-electrode.

Thus, in this work, the possible mechanisms of a current flow and a photovoltage in the film structures are described. Some additional researches are necessary to understand better the nature of these mechanisms and evaluate how much would the use of these HSs as solar elements be perspective.

5. Conclusions

The additional absorption of HS TTTC₆₀ in comparison with the sum of those for its separate components points

to the formation of the molecule complexes of TTT and C₆₀ near the interface of these layers.

At illumination of the HS TTTC₆₀, I_{sc} is caused by a photovoltage that arises near the SnO₂- and Ag-electrodes owing to the antiblocking bends of bands for the nonequilibrium holes and electrons in the TTT and C₆₀ films, accordingly.

References

1. C.W. Tang, Two-layer organic photovoltaic cell // *Appl. Phys. Lett.* **48**(2), p. 183-185 (1986).
2. J. Simon, J.-J. Andre, *Molecular Semiconductors*. Springer-Verlag, 1985.
3. J.-M. Nunzi, Organic photovoltaic materials and devices // *C.R. Phys.* No. 3, p. 523-542 (2002).
4. B.A. Gregg, M.C. Hanna, Comparing organic to inorganic photovoltaic cells: Theory, experiment, and simulation // *J. Appl. Phys.* **93**(6), p. 3605-3614 (2003).
5. M. Niggemann, B. Zimmermann, J. Haschke, M. Glatthaar, A. Gombert, Organic solar cell modules for specific applications – From energy autonomous systems to large area photovoltaics // *Thin Solid Films* **516**, p. 7181-7187 (2008).
6. R. Saito, R. Dresselhaus, M.S. Dresselhaus, *Physical Properties of Carbon Nanotubes*. Imperial College Press, 1998.
7. *Nanotechnology Research Directions: IWCN Workshop Report*, Ed. by M.C. Rocco. Kluwer Academic Publishers, 2000.
8. D.R. Balode, E.A. Silinsh, L.F. Taure, The mechanisms of conductivity and corrected energy structure of tetrathiotetracene // *Izvestiya AN Latv. SSR. Ser. fiz. tekhn. nauk*, No. 1, p. 35-45 (1978) (in Russian).
9. T.L. Makarova, Electrical and optical properties of pristine and polymerized fullerenes // *Semiconductors* **35** (3), p. 243-278 (2001).
10. M.P. Gorishnyi, Effect of p-n conjugation on the energy structures of tetrathio- and tetraselen-tetracene // *Ukr. fiz. zhurnal* **47**(8), p. 711-714 (2002).
11. Ying Wang, M. Holden, A.M. Rao *et al.*, Interband dielectric function C₆₀ and M₆C₆₀ (M = K, Rb, Cs) // *Phys. Rev. B* **45**(24), p. 14396-14399 (1992).
12. M.K. Kelly, P. Etchegoin, D. Fuchs, W. Krätschmer, and K. Fostiropoulos, Optical transitions of C₆₀ films in the visible and ultraviolet from spectroscopic ellipsometry // *Phys. Rev. B* **46**(8), p. 4963-4968 (1992).
13. J. Hora, P. Panek, K. Navratil, B. Handlivova *et al.*, Optical response of C₆₀ films and solutions // *Phys. Rev. B* **54**(7), p. 5106-5113 (1996).
14. E.A. Silinsh, *Electronic States of Organic Molecular Crystals*. Zinatne, Riga, 1978 (in Russian).
15. V.S. Fomenko, *Emission Properties of Materials*. Naukova dumka, Kiev, 1981 (in Russian).