Materials Science-Poland, *Vol. 27*, *No. 3*, *2009*

Photoelectric properties of WO_3/tetracene heterojunctions*

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Photoelectric properties of ITO/tetracene (Tc)/Ag and ITO/WO_3/Tc/Ag sandwich systems have been reported. The system containing the WO_3/Tc heterojunction exhibits a higher current rectification in the dark and a stronger photovoltaic effect. Values of the open-circuit voltage exceeding 800 mV have been observed. The obtained results can be elucidated on the assumption that a downward band bending or an interface dipole at the WO_3/Tc heterojunction occurs.

Key words*: hybrid heterojunction; tetracene; tungsten trioxide*

1. Introduction

Hybrid heterojunctions, formed from inorganic semiconductor transporting electrons and organic dye or semiconductor applied as a material which both absorbs light and transports holes, presently attract a great deal of attention due to their potential applications in electronic devices, particularly in solar cells. In such heterojunctions, mostly TiO_2, CdS and CdSe are used as inorganic semiconductors, while polymers [1, 2], porphyrins and phthalocyanines are used as organic materials [3, 4].

The results of our research on the photoelectric properties of a planar heterojunction formed from WO_3/tetracene (Tc) are presented in this work. Tungsten trioxide (WO_3) is a wide band-gap (E_g = 3.3 eV) n-type semiconductor which attracts a great deal of attention due to possible application in electrochromic devices, gas sensors and as a photoanode material for photochromical hydrogen production [5, 6]. In organic systems, thin layers of WO_3 were applied as hole-injecting layers or as interlayers in tandem devices [7, 8]. Tetracene is also a wide band-gap semiconductor (E_g = 3.1 eV), however, its electric and photoelectric properties are mainly related to the transport of

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*The paper presented at the 11th International Conference on Electrical and Related Properties of Organic Solids (ERPOS-11), July 13–17, 2008, Piechowice, Poland.

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holes. The processes of injection, photogeneration and transport of charge carriers as well as photovoltaic and photoconductive properties of single crystals and polycrystalline tetracene layers, have been discussed in many works (e.g., [9–18]). On the other hand, only a few papers have been published dealing with heterojunction structures based on tetracene [19–21]. This work presents the results of research performed on the ITO/WO_3/Tc/Ag system which have been compared with the results obtained on the ITO/Tc/Ag systems.

2. Experimental

The investigated systems were obtained by vacuum evaporation (3×10^{-4} Pa, Auto 306 Turbo, Edwards) of the following materials: WO_3 (thickness 6 nm), Tc (thickness 455 nm) and Ag (thickness 40 nm), on a glass/ITO substrate (100 Ω/square, AWAT). The active surface of electrodes was equal to 6 mm^2. The average deposition rate was 0.1 nm/s. The apparatus applied for measurements was described in detail elsewhere [4].

The samples were illuminated through the ITO electrode. Measurements of current–voltage curves in the dark and under illumination as well as of the short-circuit current (j_{sc}) and the open-circuit voltage (U_{oc}) against wavelength (λ) and light intensity (I_0) were performed.

3. Results and discussion

Dark current–voltage curves of the investigated systems are presented in Fig. 1. Positive voltage refers to the higher potential on the ITO electrode.

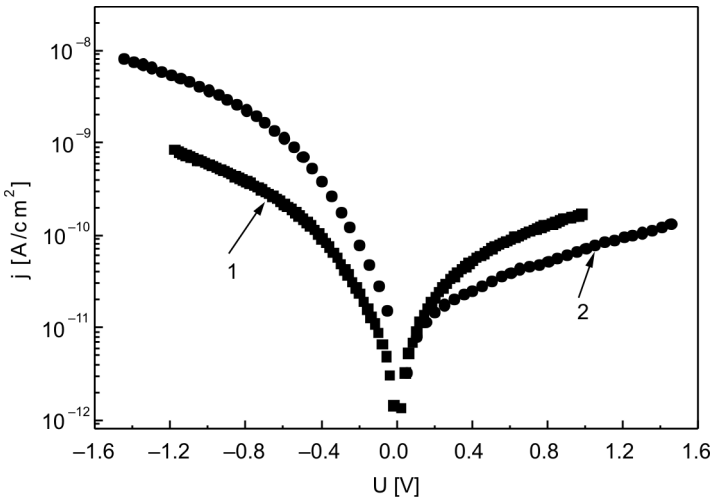

Fig. 1. Dark current–voltage curves of the investigated systems: curve 1 – ITO/Tc/Ag, curve 2 – ITO/WO_3/Tc/Ag

Curve 1 (the ITO/Tc/Ag system) exhibits little current rectification. The ratio of rectification is 3.3 at U = 1 V. As the work functions of ITO and Ag electrodes are high (higher than 4 eV) and the ionization energy and energy gap of tetracene equal 5.3 eV and 3.1 eV, respectively [10], we can notice that the electrode barriers for hole injection are much higher than for electron injection. Therefore, we can assume that the current flowing through Tc in the ITO/Tc/Ag system is a hole current, flowing independently of bias direction.

Curve 2 was obtained for the ITO/WO_3/Tc/Ag system. As the thickness of WO_3 in this system was merely 6 nm, we can presume that the applied voltage was equal to the voltage across the Tc layer (455 nm thick). The ITO/WO_3/Tc/Ag system exhibits a stronger current rectification: the ratio of rectification yields 50 at 1 V. This rectification can be interpreted on the assumption that the energy level shift resulting from transfer of electrons from Tc into WO_3 forms at the WO_3/Tc interface. It is either a downward band bending, formed by space charge, or an interface dipole layer. In the presence of such an energy level shift, the barrier for hole injection from ITO into Tc is higher, while the barrier for electron injection is lower. This enables us to elucidate why, at the +ITO/–Ag polarization we observed a smaller hole current in the ITO/WO_3/Tc/Ag than in the ITO/Tc/Ag. On the other hand, the current flowing through the ITO/WO_3/Tc/Ag system at the –ITO/+Ag polarization is a sum of a hole current injected by Ag and an electron current injected by ITO/WO_3.

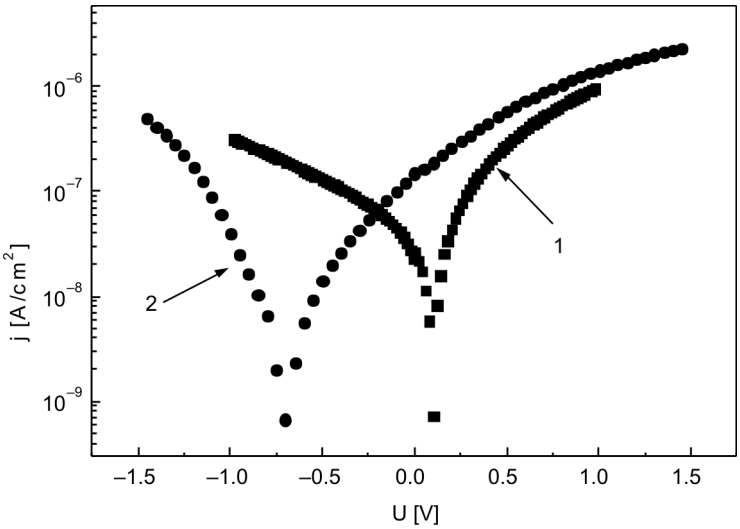

Fig. 2. Photocurrent–voltage curves of the ITO/Tc/Ag illuminated with light of 530 nm (curve 1) and of the ITO/WO_3/Tc/Ag illuminated with light of 515 nm (curve 2); $I_0 = 10^{15}$ ph/(cm^2·s)

Figure 2 shows the photocurrent–voltage curves of the samples illuminated with monochromatic light of the intensity of 10^{15} ph/(cm^2·s) and of the wavelength corresponding to maxima of photocurrent spectra presented in Fig. 3. The system of

ITO/Tc/Ag (curve 1) exhibits rather a small value of the open-circuit voltage (U_{oc} = 80 mV) whereas quite a high value of U_{oc} was observed for the system with the WO_3 layer, and it has the opposite direction (U_{oc} = –700 mV, curve 2). It can be explained if the energy level shift is assumed to occur at the WO_3/Tc interface. This energy level shift, Δ, has to fulfil the following condition: $\Delta \geq \Delta W + eU_{oc\max}$, where ΔW is the difference between the work functions of the ITO and Ag electrodes.

The values of the photocurrent obtained for the highest applied voltages are several orders of magnitude higher than for dark current (cf. Fig. 1) and, with the increase of voltage, they tend towards saturation. The flux of excitons dissociating at the positively biased electrode determines the saturation photocurrent. Holes are injected into tetracene as a result of exciton dissociation [9, 13, 17]. This mechanism of photogeneration of charge carriers is confirmed by the spectrum of short-circuit current shown in Fig. 3.

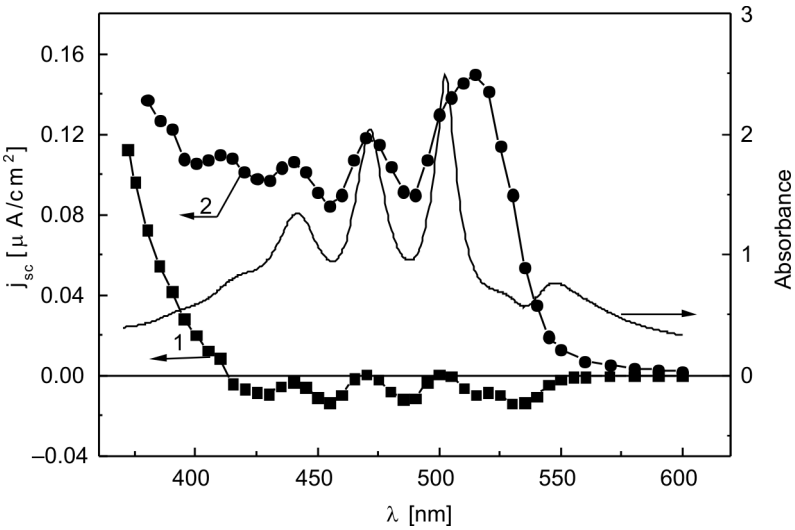

Fig. 3. Spectra of short-circuit current of the investigated systems (curve 1 – ITO/Tc/Ag, curve 2 – ITO/WO_3/Tc/Ag) and the absorbance spectrum of the Tc layer; $I_0 = 10^{15}$ ph/(cm^2·s)

In the ITO/Tc/Ag system, the short-circuit current flows through the Tc layer from Ag to ITO (therefore we note that $j_{sc} < 0$) and is determined by the difference in fluxes of holes injected by excitons dissociating at both electrodes. The direction of short-circuit current is in agreement with the direction of the inner electric field resulting from the difference between the work functions of the electrodes ($W_{Ag} < W_{ITO}$). The current spectrum (curve 1) is antibatic to the absorption spectrum of the Tc layer [9, 13, 17]. It should be noticed that the absorption spectrum of the Tc layer 455 nm thick does not correlate well with the real absorption for λ > 500 nm. In particular, a single component of the Davydov splitting, which has the maximum at λ = 520 nm, is weakly noticeable in measurements of unpolarized light transmission. On the other

hand, the maximum of the absorption spectrum observed at 545 nm derives from the diffraction effect occurring in polycrystalline layers of Tc [22].

The spectral dependence of the short-circuit current of ITO/WO_3/Tc/Ag is presented as curve 2 in Fig. 3. The short-circuit current flows through the Tc layer from the ITO/WO_3 electrode to Ag. This is the hole current generated as a result of exciton dissociation at the WO_3/Tc interface. Its direction correlates with the inner electric field if we take into account the presence of an energy level shift at the WO_3/Tc interface. Values of the short-circuit current are significantly higher than in the system without the WO_3 layer, and curve 2 correlates reasonably well with the absorption spectrum of tetracene (symbatic relation [9, 13, 17]).

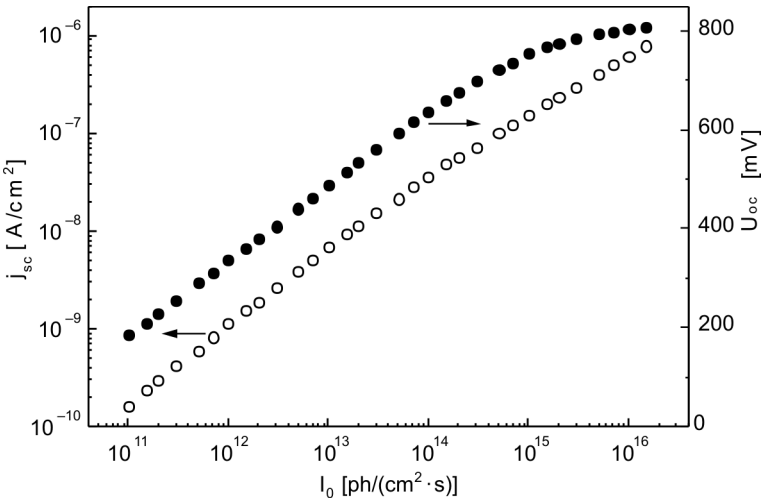

Fig. 4. Short-circuit current and open-circuit voltage against light intensity for the ITO/WO_3/Tc/Ag system illuminated with light of 515 nm

Figure 4 shows the dependences of the short-circuit current and the open-circuit voltage on light intensity for the ITO/WO_3/Tc/Ag system. The system was illuminated with monochromatic light of λ = 515 nm (the wavelength at which j_{sc} reaches its maximum, see Fig. 3). The $j_{sc}(I_0)$ relationship is sublinear and it can be approximated by $j_{sc} \propto I_0^m$, where m = 0.8 for $I_0 < 10^{14}$ ph/(cm^2·s) and m = 0.6 for higher values of light intensity.

The sublinear relation between photocurrent and light intensity has already been observed in other systems with Tc layers [12, 13, 17], and was interpreted as a result of charge carrier trapping or exciton quenching by charge carriers. The influence of these processes increases with the increase in the thickness of the organic layer. From the open circuit voltage–light intensity curve we can notice that U_{oc} increases by 150 mV/decade for $I_0 < 10^{14}$ ph/(cm^2·s) and for higher light intensity it reaches 0.8 V. Such a relation has not been observed for the systems with a Tc layer, according to the published data. Taking into account that $U_{oc\max}$ = 0.8 V and ΔW = 0.3 eV (the differ-

ence between the work functions of the ITO and the Ag electrodes) we can estimate the energy level shift as $\Delta \geq 1.1$ eV.

It is worth emphasizing that in the investigated systems the photogeneration of charge carriers (holes) occurs at the ITO/Tc, WO_3/Tc and Tc/Ag interfaces as a result of exciton dissociation. The ITO/WO_3/Tc/Ag system shows an explicitly stronger photovoltaic effect in comparison with the ITO/Tc/Ag system. The obtained open-circuit voltage exceeded 800 mV. Our experimental results can be explained on the assumption that an energy level shift occurs at the hybrid heterojunction of WO_3/Tc.

Acknowledgement

This work has been supported by the Polish Ministry of Science and Higher Education with a Grant for the years 2006–2009 under the project No. 3T11B06530.

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Received 11 September 2008
Revised 25 February 2009