Journal of Non-Crystalline Solids xxx (2010) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Photovoltaic effect in hybrid heterojunction formed from cadmium telluride and zinc perfluorophthalocyanine layers

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ARTICLE INFO

Article history:
Received 26 May 2010
Available online xxxx

Keywords:
Photovoltaic effect;
Hybrid heterojunctions;
Cadmium telluride;
Zinc perfluorophthalocyanine;
Thin layers

ABSTRACT

The results of the research on the photovoltaic effect in a planar system formed from the following layers: ITO, CdTe, zinc perfulorophthalocyanine, bathocuproine and Ag (ITO/CdTe/F_{16}ZnPc/BCP/Ag) are presented. The system exhibited strong current rectification in the dark. A photogeneration of charge carriers in the CdTe layer and at the CdTe/F_{16}ZnPc junction was observed under illumination. The short-circuit current and open-circuit voltage versus light intensity can be explained as a result of a trap-assisted recombination process operating within the heterojunction. The current is limited by space charge for higher values of forward bias.

1. Introduction

Hybrid heterojunctions formed from organic and inorganic materials have recently attracted a great deal of attention due to their likely application in optoelectronic devices, and in solar cells in particular. Titanium dioxide (TiO_2) is most often used in such systems as an inorganic material, while polymers or phthalocyanines are applied as an organic material [1–5]. Intensive researches have been also conducted on bulk heterojunctions consisting of polymers and nanocrystals of other inorganic semiconductors such as CdS, CdSe, $CuInS_2$, ZnO, PbS, PbSe, Si [6–15] and CdTe [16,17].

This work presents the results of research on the photovoltaic effect in a system with planar heterojunction of CdTe/zinc perfluorophthalocyanine (F_{16}ZnPc). This heterojunction type has not been investigated yet. Both materials forming the junction have interesting photovoltaic properties. Cadmium telluride is a semiconductor widely applied in inorganic thin-film solar cells as a good absorber of sunlight [18–21]. Zinc perfluorophthalocyanine is an organic dye with good thermal stability, strong light absorption up to 900 nm and relatively high electron mobility [22,23].

The subject of investigation is a planar heterostructure formed from CdTe, F_{16}ZnPc, bathocuproine (BCP) and Ag subsequently evaporated in high vacuum onto a glass/ITO substrate. The system is abbreviated hereafter as ITO/CdTe/F_{16}ZnPc/BCP/Ag. The BCP plays the role of a buffer layer which acts as a carrier blocking layer, prevents the organic material from damage during Ag deposition and reduces resistance of contact [23,24]. When investigating the photovoltaic effect in the ITO/CdTe/F_{16}ZnPc/BCP/Ag system particular attention was paid to the electronic processes occurring at the CdTe/F_{16}ZnPc interface.

2. Experimental details

The samples were made on glass substrates covered in a half by indium tin oxide (ITO, 40 Ω/square from PGO). The substrates of glass/ITO after purification (ultrasonic baths in acetone and in isopropanol) were placed into a vacuum system ($3 \cdot 10^{-4}$ Pa, Auto 306 Turbo, Edwards) and layers of CdTe (thickness 60 nm), F_{16}ZnPc (thickness 100 nm), BCP (thickness 15 nm) and Ag (thickness 40 nm) were subsequently evaporated using thermal sublimation with an average rate equal to 0.2 Å/s. CdTe (99.99%), F_{16}ZnPc and BCP were purchased from Aldrich. Both organic materials were purified by sublimation in advance. Four samples were produced in a single cycle. Each of them had a 6 mm^2 active surface of electrodes. Additionally, the system without a CdTe layer (i.e. ITO/F_{16}ZnPc/BCP/Ag), but with the same thicknesses of F_{16}ZnPc, BCP and Ag layers as in the ITO/CdTe/F_{16}ZnPc/BCP/Ag system, was made. The measurements were performed under ambient air at room temperature using the apparatus described in the work [3]. The samples were illuminated through the ITO.

3. Results and discussion

Fig. 1 shows the short-circuit current versus wavelength ($I_{sc}(\lambda)$) obtained under constant flux of photons ($I_o = 10^{15}$ ph/(cm^2 s)) and absorption spectra of CdTe and F_{16}ZnPc layers. The short-circuit current flows through the system from the Ag electrode to the ITO electrode. Comparing the $I_{sc}(\lambda)$ curve with the absorption spectra it can be noticed that the short-circuit current is determined by photons

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0022-3093/$ – see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.jnoncrysol.2010.05.073

Please cite this article as: R. Signerski, et al., Photovoltaic effect in hybrid heterojunction formed from cadmium telluride and zinc perfluorophthalocyanine layers, J. Non-Cryst. Solids (2010), doi:10.1016/j.jnoncrysol.2010.05.073

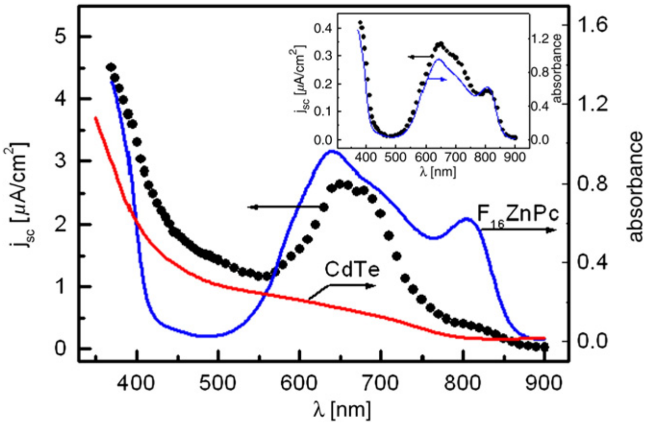

Fig. 1. Spectral dependence of short-circuit current of ITO/CdTe/F_{16}ZnPc/BCP/Ag system and absorption spectra of CdTe and F_{16}ZnPc layers. Inset: spectrum of short-circuit current of ITO/F_{16}ZnPc/BCP/Ag system and absorption spectrum of F_{16}ZnPc layer. The systems were illuminated with a light of constant flux of photons equal to 10^{15} ph/(cm^2 s).

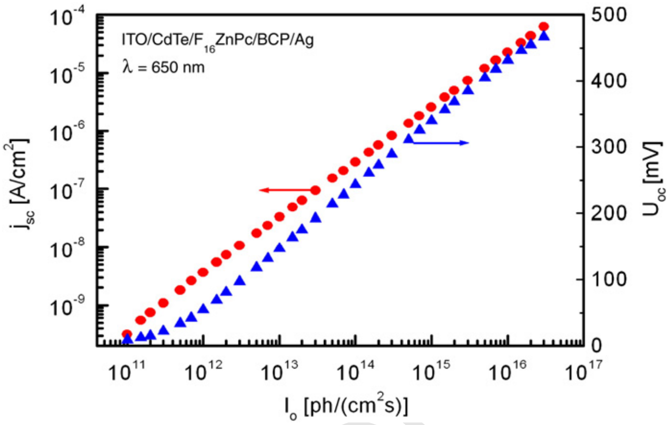

Fig. 2. Light intensity dependence of short-circuit current and open-circuit voltage for system when illuminated with monochromatic light of 650 nm.

absorbed in the CdTe layer as well as in the F_{16}ZnPc layer. When λ>550 nm the photogeneration of charge carriers via dissociation of excitons generated in the F_{16}ZnPc layer close to the interface of CdTe/F_{16}ZnPc is noticeable in I_{sc}(λ). This dissociation results in injection of a hole into a valence band of CdTe, while an electron moves towards the Ag electrode. The transfer of the hole to the layer of CdTe is possible, since the ionization energy of CdTe (5.8 eV [18]) is smaller than the ionization energy of F_{16}ZnPc (about 6.5 eV [25]). Within the range where λ<550 nm the I_{sc} (λ) curve correlates quite well with the absorption spectrum of CdTe and it indicates that photogeneration of charge carriers in CdTe dominates. The electrons generated as a result of band to band excitation are injected into F_{16}ZnPc, while holes move to the ITO electrode. In this case the transfer of electrons to F_{16}ZnPc is possible due to the fact that the electron affinity of CdTe (4.3 eV [18]) is smaller than the electron affinity of F_{16}ZnPc (about 4.6 eV [25]). In the short-circuit mode the transport of charge carriers through the system is determined by both their diffusion and drift in an inner electric field. The electric field appears as a result of alignment of the Fermi levels of electrodes and layers forming the system. It can be anticipated that the inner field in the considered system is directed from Ag to ITO due to the fact that the work function of ITO (4.7 eV [7]) is greater than the work function of Ag (4.3 eV [26]). This is also the direction of the short-circuit current in our system.

In order to reveal the consequence of the CdTe layer presence to our system we also performed measurements on a system without CdTe (i. e. ITO/F_{16}ZnPc/BCP/Ag). The inset of Fig. 1 shows a spectrum of I_{sc}(λ) obtained on this system and the absorption spectrum of F_{16}ZnPc. A good correlation between both the spectra (symbatic relation) within the whole range means that charge carriers are generated via dissociation of excitons at the ITO electrode: holes transfer to the ITO electrode, whereas electrons move through the system from ITO t[illegible] The short-circuit current direction is here the same as in the ~~layer~~ with CdTe. When comparing the spectra of both systems, explicit differences in I_{sc}(λ) resulting from the presence of the CdTe layer and the CdTe/F_{16}ZnPc interface are noticeable. Moreover, the values of I_{sc} obtained on the system with CdTe are almost one order of magnitude higher than for the[illegible]em without CdTe.

When investigating the system of ITO/CdTe/F_{16}ZnPc/BCP/Ag we also performed measurements of the spectral dependence of open-circuit voltage U_{oc}(λ). This curve exhibited, however, the same features as I_{sc}(λ) and therefore it is not presented here.

Fig. 2 shows short-circuit current (I_{sc}) and open-circuit voltage (U_{oc}) as a function of light intensity (I_o) for a system illuminated with monochromatic light of 650 nm. This wavelength correlates with a peak in the I_{sc}(λ) spectrum. The relationship of I_{sc}(I_o) is almost linear: $I_{sc} \sim I_o^n$ with $n = 0.96$. The linear relation means that either the short-circuit current is not limited by a charge carrier recombination, and so it equals the generation current, or a monomolecular recombination via states trapping charge carriers operates within the junction [27]. We anticipate, however, that it is rather the latter than the former case that occurs in our system. It is suggested at least by the current-voltage relationship for reverse bias (Fig. 3), since I_{sc} does not equal the generation current (no explicit saturation of the reverse current appears).

The U_{oc}(I_o) relation presented in Fig. 2 can be extrapolated within the range from 10^{12} ph/(cm^2 s) to $5 \cdot 10^{15}$ ph/(cm^2 s) as [28]:

$$U_{oc} = \frac{mkT}{e}\ln(\alpha I_o) \tag{1}$$

where kT/e is the thermal potential equal to 25 mV and $\alpha = 3.31 \times 10^{-12}$ cm^2 s, m = 1.68. The values of α and m depend on a model of heterojunction. The case with m>1 is observed when a recombination via trapping states operates in a junction [29,30]. If $I_o > 5 \cdot 10^{15}$ ph/(cm^2 s), the U_{oc}(I_o) relationship tends to saturate and we can estimate the maximum open-circuit voltage value as $U_{ocmax} \approx 0.5 \div 0.6$ V. The maximum open-circuit voltage value in bilayer systems is mainly determined by the difference between the ionization energy of donor (I_D) and the electron affinity of acceptor (A_C): $\Delta = I_D - A_C$. However, the

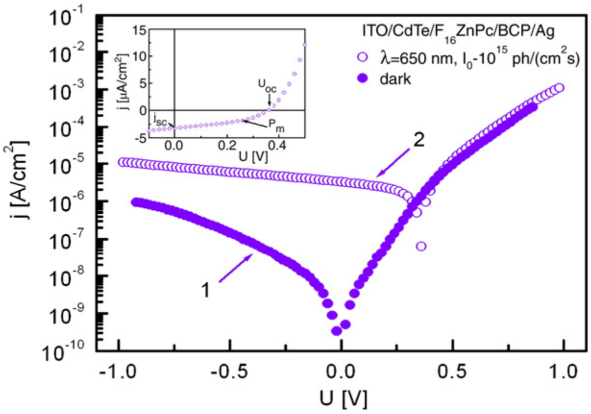

Fig. 3. Current density against applied voltage for system in dark (curve 1) and illuminated with monochromatic light of 650 nm and intensity of $I_o = 10^{15}$ ph/(cm^2 s) (curve 2 and inset). Inset: coordinates of P_m refer to photovoltaic power maximum: $U_m = 0.26$ V and $j_m = 1.84$ μA/cm^2.

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values of U_{ocmax} obtained experimentally are smaller than Δ, usually by tens of eV [31]:

$$eU_{oc\ max} = \Delta - (0.3 \div 0.7)\text{eV} \tag{2}$$

Taking into consideration that I_D of CdTe equals 5.8 eV and the A_C of $F_{16}ZnPc$ is about 4.6 eV we obtain Δ = 1.2 eV. It means that the empirical relation (2) is also fulfilled for our system. On the other hand, when describing the U_{oc} we should additionally take into account the role of the ITO/CdTe contact. Our research performed on ITO/CdTe/Ag confirms this thesis, since the illumination of ITO/CdTe/Ag with the monochromatic light of λ = 650 nm and $I_o = 10^{15}$ ph/(cm^2 s) generates $U_{oc} = 120$ mV and this open-circuit voltage is of the same polarity as in the system considered in this work. We come therefore to the conclusion that U_{oc} of ITO/CdTe/$F_{16}ZnPc$/BCP/Ag is generally a sum of voltages generated on the ITO/CdTe junction and the CdTe/$F_{16}ZnPc$ junction. However, for λ = 650 nm, U_{oc} is mainly dominated by the CdTe/$F_{16}ZnPc$ junction.

Fig. 3 shows the dependence of dark current (curve 1) and photocurrent (curve 2 and inset) on the applied voltage. The positive voltage refers to the higher potential on ITO. The dark curve exhibits a strong current rectification effect. The rectification ratio yields 301 at U = 0.8 V. The reverse dark current seems to be formed by electrons injected from ITO into CdTe, since the estimated height of the barrier limiting this injection (the difference between the work function of ITO and the electron affinity of CdTe) is smaller than the height of the barrier limiting the hole injection from Ag into $F_{16}ZnPc$ (the difference between the ionization energy of $F_{16}ZnPc$ and the work function of Ag). For a forward bias (U>0) we can notice two distinct regions of the dark current–voltage curve. The following relation [28]:

$$j = j_o \exp\left(\frac{e|U|}{rkT}\right) \tag{3}$$

is fulfilled within the range from 0.08 V to 0.30 V with the diode quality factor r equal to 2.08 for kT/e = 25 mV. If the value of r is close to 2, then a current flowing through a system is determined by a recombination of charge carriers with[illegible]unction. When U>0.6 V the power relation of the following form~~s~~:

$$j = AU^p \tag{4}$$

with p = 7.0 is a proper extrapolation of the experimental curve. This relation (i.e. when p>2) is observed in the case of space charge limited current flowing in the presence of traps with depths distributed exponentially [32]. The A factor depends, *inter alia*, on the trap concentration, charge carrier mobility and layer thickness. With respect to the above consideration, we can anticipate that the forward dark current is formed by electrons injected from the Ag electrode and by holes injected from the ITO electrode. The value of this current is limited either by the charge carrier recombination process within the junction or by the space charge. Due to the fact that the electric conductivity of CdTe is much higher than the electric conductivity of $F_{16}ZnPc$ we anticipate that the space charge limiting transport of charge carriers through the system occurs mainly in $F_{16}ZnPc$.

Curve 2 and the inset in Fig. 3 show the photocurrent versus voltage for a system illuminated with monochromatic light of 10^{15} ph/(cm^2 s) and 650 nm. The system exhibits photovoltaic effect with the following parameters: short-circuit current $j_{sc} = 3.3$ μA/cm^2, open-circuit voltage $U_{oc} = 0.36$ V, fill factor $FF = (j_m \cdot U_m)/(j_{sc} \cdot U_{oc}) = 0.41$ (see inset) and power conversion efficiency η = 0.16%. For forward bias, when U>0.6 V the photocurrent, as the dark current, can be extrapolated by the relation (4). Slightly higher values of the photocurrent than of the dark current should be related to the effect of photoconductivity in $F_{16}ZnPc$. The dependence of the photocurrent on voltage, when U<0.1 V, fulfills formally the relation (3), but with r = 32.8. However, such a big value of r does not find any grounds in a simple heterojunction model, and so the relation (3) should be treated as preliminary in an analysis of the reverse photocurrent-voltage dependence of our system.

4. Summary

The work presents the results of the research on the photovoltaic properties of a hybrid planar system formed by ITO/CdTe/$F_{16}ZnPc$/BCP/Ag. Such a system has not been investigated yet. Owing to the spectral dependence of the short-circuit current we can reach a conclusion that charge carriers can be generated both in the CdTe layer (band to band transition) and as a result of exciton dissociation at the CdTe/$F_{16}ZnPc$ interface. On the other hand, the dependence of short-circuit current and open-circuit voltage on light intensity suggests that the trap-assisted recombination process operates in the heterojunction of CdTe/$F_{16}ZnPc$. The system exhibits strong current rectification in the dark. For the forward case the region limited by recombination and the region limited by space charge can be distinguishable in the dark current versus voltage curve. The explanation of the dark current and photocurrent dependence on voltage for a reverse case requires further investigation.

Acknowledgement

This work was supported by the Polish Ministry of Science and Higher Education with a grant for the years 2006–2009 under Program No. 3T11B06530.

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