Properties of CuInS$_2$ free surface and the effect of conductive polymer layers on these properties

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Abstract. The influence of thin conductive polymer layers on the surface photovoltage of CuInS$_2$ (CIS) layers prepared using the so-called CISCuT method was studied. The deposition of poly(3,4-ethylenedioxythiophene) films on the free surface of CIS resulted in a small decrease in the height of the potential energetic barrier and in an increase in the efficiency of charge carriers transport through the CIS/polymer interface. The change of photovoltaic properties resulting from the polymer deposition on the free surface of CIS was also analysed for the carbazole polymers. Our results confirm the possibility of using the conductive polymer films as organic buffer layers in complete cell structures for photovoltaic cells based on the inorganic photoabsorber CIS.

Key words: CuInS$_2$, photovoltaic structure, conductive polymer, interface.

INTRODUCTION

For thin-film solar cells based on CdS and CuInS$_2$ (CIS) or CdS and CuInSe$_2$ (CISe) heterostructures, the efficiency of a solar illumination transformation exceeding 17% was obtained at good radiation stability [1, 2]. However, the presence of toxic cadmium in these heterostructures stimulates a search for CdS substitution.

Prospective materials for CdS substitution are conductive polymers and photosensitive organic semiconductors. The idea of using these materials is supported by the fact that no torn covalent bonds exist in the surface of organic
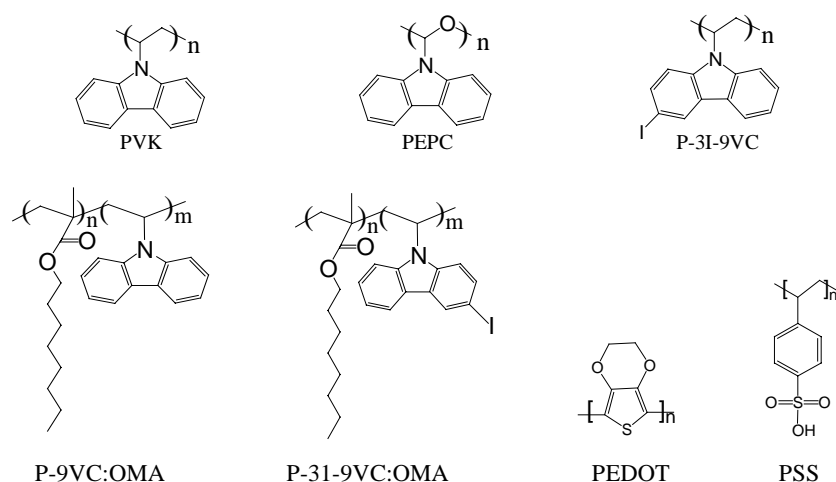
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semiconductors and they should not create additional centres of trapping and recombination at the interface with CIS (CISe). Furthermore, large dimensions of organic molecules should strongly limit the efficiency of their diffusion in CIS layers and the formation of new impurity centres. It should be noted that vinyl polymers containing carbazole, and especially their octylmetacrylate copolymers, are stable to photooxidation and photodestruction compounds [3].

Therefore, the purpose of the present work was to study the properties of the CIS free surface and their change after the thin polymer layer deposition and to search for materials necessary for creating an enhanced barrier with CIS films as well as for protecting CIS from humidity and oxidation.

EXPERIMENTAL

We used the following polymers: polyvinylcarbazole (PVK), polyepoxy-propylcarbazole (PEPC), poly(3-iodine-9-vinylcarbazole) (P-3I-9VC), poly(9-vinylcarbazole co-octyl methacrylate) (P-9VC:OMA), poly(3-iodo-9-vinylcarba-zole co-octyl methacrylate) (P-3I-9VC:OMA), and poly(3,4-ethylenedioxy-thiophene) (PEDOT) doped with polystyrene parasulphonic acid (PSS). Formulas of the polymers studied are presented in Scheme 1.

Scheme 1. Structural formulas of the used polymers.

CIS film deposition on a copper tape (CIS Cu Tape, so-called CISCuT) by an electrodeposition method with successive sulphurization and vacuum annealing was described in [4], and the procedure of Cu/CISCuT/Au and Cu/CISCuT/PEDOT:PSS/Au structure preparation was reported in [5, 6]. Aqueous suspension of 1.5% PEDOT:PSS was purchased from Aldrich and

appropriate mixture for spin-coating was prepared as described in [5]. The layers of carbazole polymers were deposited on the CISCuT films by spin-coating from dichloroethane solution.

PVK polymers were synthesized by thermoinitiated radical polymerization from 9-vinylcarbazole in isopropyl alcohol medium at 82 °C. The time of polymerization was 1 h.

Both copolymers and homopolymer P-3I-9VC were synthesized by thermoinitiated radical polymerization from respective monomers (3-iodo-9-vinylcarbazole and octyl methacrylate (Aldrich) for P-3I-9VC:OMA, 9-vinylcarbazole (Aldrich) and octyl methacrylate for P-9VC:OMA and 3-iodium-9-vinylcarbazole for P-3I-9VC) in isopropyl alcohol medium at 82 °C. As the initiator of all these processes 4,4-azo-bis-isobutironitrile (Aldrich) was used. The time of polymerization was 2 h for both copolymers and 0.5 h for P-3I-9VC. After polymerization all polymers were purified by precipitating twice from benzene to methanol.

In the case of copolymers the values of copolymerization ratios r_1 and r_2 for different pairs of comonomers were determined by the method of crossing curves with using Mayo–Lewis differential equation (for yields <10%). These values are: $r_1 = 0.28 \pm 0.02$, $r_2 = 1.73 \pm 0.04$ for the pair of comonomers 3-iodium-9-vinylcarbazole with octyl methacrylate and $r_1 = 1.01 \pm 0.05$, $r_2 = 0.99 \pm 0.07$ for the pair of comonomers 9-vinylcarbazole and octyl methacrylate [3].

PEPC polymer was produced by the "Azot" plant (Severodonetsk, Ukraine). The average molecular weights of polymers and co-polymers are the following: PVK 10000–20000, PEPC 900–1000, P-3I-9VC 1000–10000, both P-9VC:OMA and P-3I-9VC:OMA 5000–7000. The contents of 9-VC monomer and 3I-9VC monomer in copolymers were 48 mol % and 70 mol %, respectively.

Photovoltage was measured by the Bergman method improved by Akimov [7]. According to this technique, a sample is isolated from the other electrode (ITO layer deposited on a polished quartz substrate) with a 10–20-μ thick transparent dielectric film. Illumination of such cells by the light pulses of t_l duration will lead to differences in the potentials of "capacitor" photovoltage between the illuminated and the dark surfaces of the cell. Alternate voltage on the loading resistance was measured by an experimental setup.

The measurement setup consisted of the following parts: 120 W iodine tungsten lamp (Hitachi), systems of quartz lenses, chopper (frequency of modulation 80 Hz), and the monochromator MDR-4 (LOMO). Monochromatic light was then focused onto a window of an electrically screened measurement cell in the centre of the sample. Photovoltage was measured by a lock-in nanovoltmeter Unipan-232B with a preamplifier Unipan-233-7. The signal from an optronic pair mounted on the chopper was used as a reference for the lock-in. The experimental data were collected in a PC by an ET-1050 interface card.

After each series of measurements, the spectral distribution of the lamp was measured by a calibrated pyroelement and photovoltage spectra were normalized on the equal number of incident photons.

RESULTS AND DISCUSSION

Figure 1 shows the spectral dependence of the surface photovoltage (V_s) of the CISCuT film and the absorption coefficient k of CIS n-type films prepared by electrodeposition [8].

An approximation of the long wavelength edge of the spectral dependence of $V_s^2(h\nu)$ gives a band gap value $E_g = 1.46 \pm 0.02$ eV.

It should be noted that V_s reaches its maximal value already at $k = 2 \times 10^3$ cm^{-1} ($h\nu = 1.6$ eV), and at a further increase of $h\nu$ and k (for two orders), V_s decreases. It is particularly obvious on V_s dependence on k (Fig. 2).

A similar dependence of V_s on k was observed in bipolar semiconductors with a small length of the carrier diffusion for hydrogenized amorphous silicon [9] and CdP$_2$ [10]. For such semiconductors, the calculation of the surface photovoltage is complicated, and unfortunately, we were unable to obtain a simple analytical expression.

The numerical calculation of V_s (k) at different values of the Debye length of screening L_d, the length of the diffusion of the minority carriers of charge (electron defects) L_p, the velocity of a surface recombination S, the adhesion coefficient of holes αp and electrons αn has shown that a V_s decrease with a k
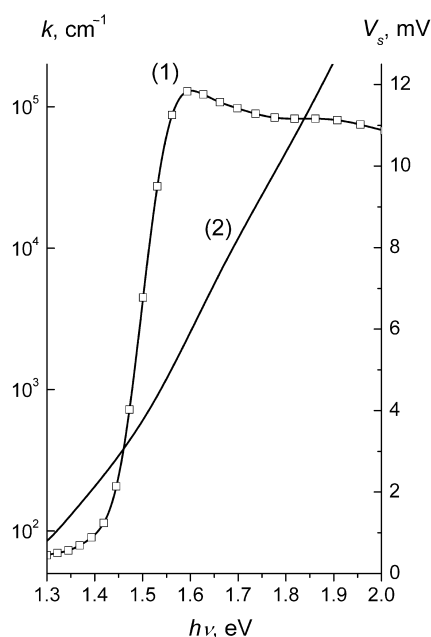

Fig. 1. Spectral dependences of surface photovoltage V_s of CISCuT film (1) and absorption coefficient k for CIS n-type films prepared by electrodeposition (2) [8].
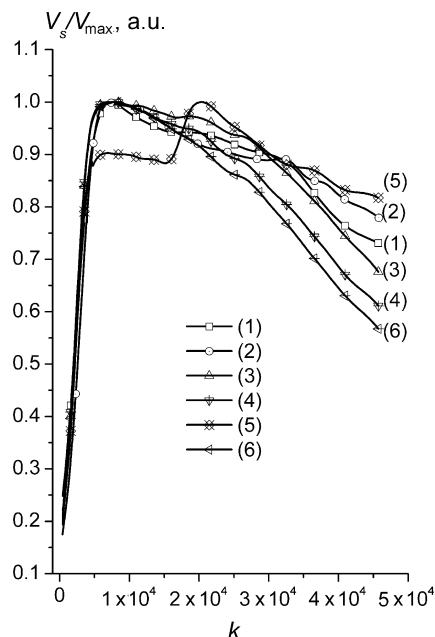
Fig. 2. The dependence of photovoltage V_s on the absorption coefficient k for CISCuT before (1) and after deposition of carbazole polymers (2–6): P-3I-9VC : OMA – curve (2); PVK – curve (3); P-9VC : OMA – curve (4); P-3I-9VC – curve (5); PEPC – curve (6).

rise in the short-wave region of the spectrum should be observed at $L_p < L_d$, $S \gg 1$ and at small values of the adhesion coefficient of both types of charge carriers on a surface αp, $\alpha n \approx 0$ [9] or at $\alpha p \gg 1$ and $S \gg 1$ [10]. In both cases, the maximum dependence of V_s on k is observed at $kL_d \approx 1$, and the slope of the short-wavelength decrease of V_s increases at the magnification of S [9, 10]. This is explained by the overflow of the rate of surface recombination above the velocity of carriers flow from volume to the surface, thus $V_s(k)$ dependences are similar. Therefore, to identify the main reasons of the above considerations, we carried out measurements of V_s dependence at a constant external voltage and a stationary value of low-absorbed illumination ($h\nu > E_g$).

The small (less than 10%) influence of an external electric field on V_s, caused by the strongly absorbed light ($h\nu = 1.9$ eV), proves the formation on the CISCuT free surface of a major concentration of the surface trap and recombination centres, which screen the activity of the external electric field.

Figure 3 shows the dependence of V_s excited by the modulated strongly absorbed illumination light of a red light-emitting diode ($h\nu = 1.9$ eV) on the energy of the quanta of a stationary value of low-absorbed monochromatic illumination with $h\nu < E_g$. It can be seen that at irradiating a free surface CIS, minimum values are observed at 1.22 and 1.36 eV, i.e. at those energies of quanta where minimization of the filling degree of surface levels occurs. Hence, the acceptor levels located apart about 0.1 and 0.2 eV higher of the edge of the CISCuT valence band make a contribution to the barrier formation at a free surface of the CISCuT layers studied.

To clarify the influence of the polymeric layers on the properties of the surface CIS, we conducted measurements of V_{xx} spectral dependences (Fig. 4) and short circuit photocurrent I_{sc} (Fig. 5) of structures Cu/n–CIS/Au with a barrier of a Schottky type at the CIS/Au interface and Cu/n–CIS/PEDOT–PSS/Au heterostructures, at which CIS and Au layers were prepared under the same conditions, at irradiating through a semitransparent Au-electrode.

The structure and electrical properties of these structures are described in [5]. It is obvious that after the deposition of this conductive polymer layer, V_{xx} (Fig. 4) is slightly decreased and I_{sc} (Fig. 5), on the contrary, is strongly magnified. Simultaneously, the rate of the short-wavelength drop is reduced both for V_{xx} and I_{sc} in the range of 1.6–3.0 eV. Accordingly, the decrease of V_{xx} and the rate of the short-wave drop testify the minimization of the efficiency of the charge carrier capture and/or recombination at the CIS/PEDOT-PSS interface (and/or concentrations of trap centres), caused by the interaction between the molecules of a polymeric compound and those on the surface of a CIS film. The increase of I_{sc} testifies that because of the interactions there is an increase in the efficiency of charge carriers transfer on the electrode. Qualitatively, the same result was observed at the irradiation of these structures by AMO-2 [5]. This is a typical effect; however, a possible mechanism is still unknown. Apparently, it will depend on the strength of the interaction of the molecules of a polymeric compound and CIS, i.e. on the molecular structure of organic molecules.
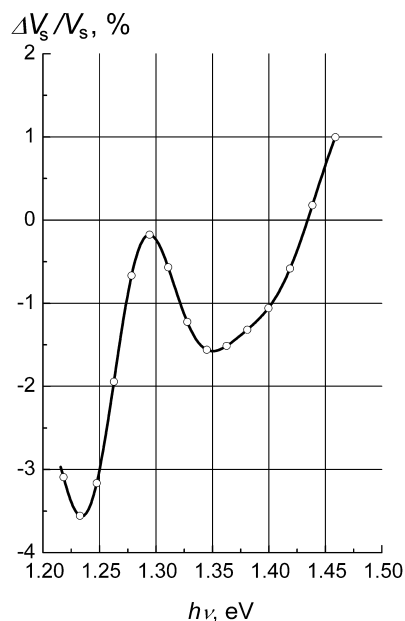
Fig. 3. Effect of low-absorbed IR illumination on CISCuT film photovoltage excited by red light emitting diode (LED).
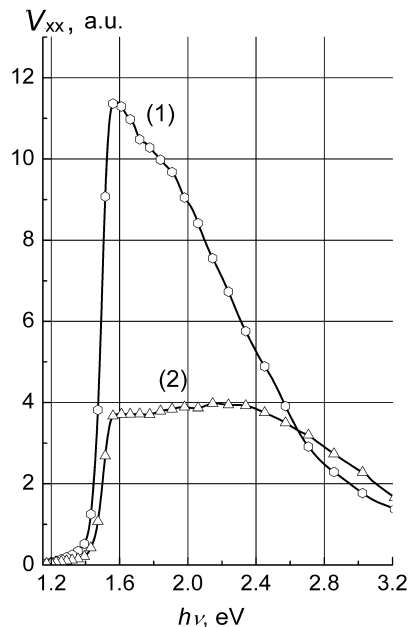
Fig. 4. Spectra of photovoltage V_{xx} for CISCuT/Au (1) and CISCuT/PEDOT-PSS/Au (2) structures normalized on equal numbers of incident photons.

In addition, the effect of the polymer molecular structure on the photovoltage of CIS at deposition on a free surface of a thin layer of carbazole polymers was studied. The results of measurements of V_s spectral dependences are summarized in Fig. 6. It can be seen that after depositing the polymeric layer of PVK on a free surface of CISCuT, a small decrease in the absolute value of V_s (height of a potential barrier) occurs, with some change in the high energetic part of the spectrum in the case of iodine-containing polymers and copolymers (Fig. 6). Namely at the deposition of P-3I-9VC and P-3I-9VC:OMA, the increase of photovoltage is in the range 2.3–3.2 eV, accompanied with good homogeneity, especially in the case of P-3I-9VC:OMA.

The rate of decrease in the short wavelength for these polymers is minimal (Fig. 2, curves 2 and 5), but V_s (k) dependences have a more complicated shape. This may be caused by the more complex character of the interaction between iodine-containing polymers and CIS layers. Also, we can conclude that the efficiency of the interaction of carbazole polymer compound with the molecules of CIS is less intensive than with the molecules of PEDOT.

It should be noted that the P-9VC:OMA copolymer forms the most homogeneous films on CIS layers and their deposition causes a decrease in the photovoltage, although neither the value nor the spectral dependence of photovoltage (as well as for PVK) will change significantly, i.e. P-9VC:OMA and PVK layers
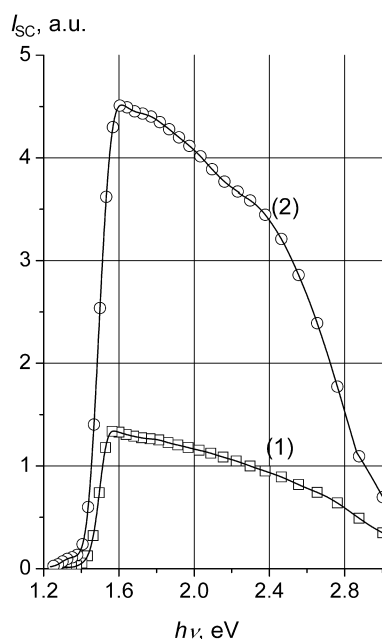
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Fig. 5. Spectra of short-circuit photo-current I_{sc} for CISCuT/Au (1) and CISCuT/PEDOT-PSS/Au (2) structures normalized on equal numbers of incident photons.
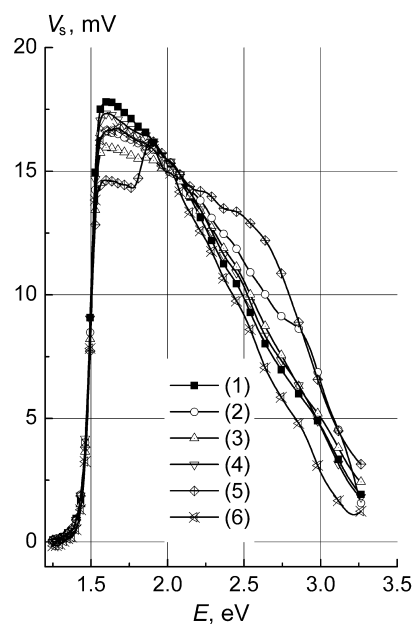
Fig. 6. Spectral dependences of surface photovoltage V_s of CISCuT before (1) and after deposition on the surface of carbazole polymers (2–6): P-3I-9VC:OMA – curve (2); PVK – curve (3); P-9VC:OMA – curve (4); P-3I-9VC – curve (5); PEPC – curve (6).

are mostly "neutral". The OMA copolymers have enhanced mechanical properties, including flexibility and plasticity due to the presence of flexible octyl groups. Also, these polymers are more stable to photooxidation and in aggressive media in comparison with PVK [3].

The deposition of the PEPC layer leads to the most significant decrease in photovoltage in the range 2.0–3.2 eV due to the increase of the rate of trapping and surface recombination of charge carriers near the PEPC/CIS interface. Therefore, it can be seen that the P-3I-9VC:OMA copolymer layer deposition on CIS leads to some widening of the spectral range of photosensitivity, while the P-9VC:OMA copolymer is most promising for creating a "neutral" protective layer for CIS films.

CONCLUSIONS

The CISCuT layers studied have a high photosensitivity in the range 1.5–3.2 eV. The approximation of the long-wavelength edge of the spectral dependence of the surface photovoltage yields the value of band gap $E_g = 1.46 \pm 0.02$ eV. The weak (<10%) influence of the electric field on the surface photovoltage created by

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strongly absorbed light ($h\nu = 1.9$ eV) and the decreasing photovoltage at $h\nu$ increase in the range 1.55–3.2 eV ($\alpha > 2 \times 10^3$ cm^{-1}) prove that a strong concentration of surface trap centers and the recombination of charge carriers are formed on the free surface of CISCuT layers. The basic contribution to the barrier formation at the free surface of CISCuT layers is made by the acceptor levels located about 0.1 and 0.22 eV higher than the edge of the valence band of CISCuT.

The deposition of PEDOT : PSS polymeric films on the free surface of CISCuT layers results in a small decrease in the height of the potential energetic barrier (the corresponding shift in the range of the space charge in the polymer layer) and an increase in the efficiency of charge carrier transport through the CISCuT/polymer interface. This is confirmed by the surface photovoltage and an essential (>3 times) increase in the short-circuit photocurrent I_{sc}, practically without a change in the rate of trapping recombination of charge carriers (the slope of the drop in the surface photovoltage at $h\nu$ increase in the range 1.55–3.2 eV).

Among the carbazole polymers studied, P-3I-9VC : OMA copolymer layer deposition on CIS leads to some widening of the spectral range of photosensitivity, while the P-9VC : OMA copolymer is the most prospective for creating a "neutral" protective layer for CIS films.

ACKNOWLEDGEMENTS

REFERENCES

1. Klaer, J., Bruns, J., Henninger, R., Siemer, K., Klenk, R., Ellmer, K. & Bräunig, D. Efficient CuInS$_2$ thin-film solar cells prepared by a sequential process. *Semicond. Sci. Technol.*, 1998, **13**, 1456–1458.
2. Stolt, L., Hodstrom, J., Kessler, J., Ruch, M., Velthaus, K.-O. & Schock, H. W. ZnO/CdS/CuInSe$_2$ thin-film solar cells with improved performance. *Appl. Phys. Lett.*, 1993, **62**, 597–599.
3. Zagdanskaya, N. E., Fedorova, L. N., Kuz′min, R. N. & Pochinok, V. Ya. Polymer photoconductors based on halogen derivatives of vinylcarbazole. *Vest. Kiev Gos. Univ. Khim.*, 1982, **23**, 34–38 (in Russian).
4. Penndorf, J., Winkler, M., Tober, O., Roeser, D. & Jacobs, K. CuInS$_2$ thin film formation on a Cu tape substrate for photovoltaic application. *Sol. Energy Mater. Sol. Cells*, 1998, **53**, 285–298.
5. Bereznev, S., Konovalov, I., Kois, J., Mellikov, E. & Öpik, A. CuInS$_2$/PEDOT photovoltaic structure. *Materials Research Society Symposium Proceedings, Organic and Polymeric Materials and Devices*, 2003, **771**, 243–248.

6. Kois, J., Bereznev, S., Raudoja, J., Mellikov, E. & Öpik, A. Glass/ITO/In(O,S)/CuIn(S,Se)$_2$ solar cell with conductive polymer window layer. *Sol. Energy Mater. Sol. Cells*, 2005, **87**, 657–665.

7. Akimov, I. A. Internal photo-effect studies in semiconductors by capacitor method. *Opt.-mech. promyshl.*, 1966, **5**, 4–13 (in Russian).

8. Martinez, A. M., Arriaga, L. G., Fernandez, A. M. & Cano, U. Band edges determination of CuInS$_2$ thin films prepared by electrodeposition. *Mater. Chem. Phys.*, 2004, **88**, 417–420.

9. Dmitruk, N. L., Kruchenko, Yu. V., Litovchenko, V. G. & Popov, V. G. Surface photovoltage in semiconductors at deviation from quasi-equilibrium. *Poverkhnost' Fiz., khim., mekh.*, 1986, **5**, 56–62 (in Russian).

10. Dmitruk, N. L., Zuev, V. A., Kruchenko, Yu. V. & Stepanova, M. A. Surface photoelectric phenomena in bi-polar semiconductors with low diffusion length. *Optoelectron. poluprovodn. mekh.*, 1992, **23**, 78–83 (in Russian).

Elektrit juhtiva polümeerkile mõju CuInS$_2$ pinna omadustele

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On uuritud EJP-kile mõju CISCuT-meetodil valmistatud CuInS$_2$ (CIS) fotovoltomadustele. On selgunud, et polü(3,4-etüleendioksütiofeen)- (PEDOT-)kile sadestamine CIS-i pinnale alandab CIS/EJP ülemineku potentsiaalibarjääri kõrgust, soodustades laengukandjate liikumist. On uuritud ka CIS-i struktuuri fotovoltomaduste muutust C$_{12}$H$_9$N-i sadestamisel CIS-i pinnale. Töö tulemused kinnitavad EJP-kilede kasutamise võimalikkust "puhverkihina" fotovolthübriidsetes struktuurides koos CIS-i fotoabsorberkihiga.