

# Hybrid solar cells based on CuInS<sub>2</sub> and organic buffer–sensitizer layers

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## Abstract

Hybrid solar cells on the basis of CuInS<sub>2</sub> (CIS) photoabsorber on Cu-tape (CISCuT) in combination with organic buffer layers of Zn-phthalocyanine (ZnPc), ZnPc:fullerene (ZnPc:C<sub>60</sub>) composite and conductive polymer buffer layers of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with polystyrenesulfonate (PSS) were prepared using vacuum evaporation and spin-casting techniques. To prepare solar cells with an active area of 2 cm<sup>2</sup>, the appropriate deposition parameters and thickness of ZnPc, ZnPc:C<sub>60</sub> and PEDOT-PSS layers were selected experimentally. For preparation of semitransparent contact-window layers, chromium and gold were evaporated on the surface of ZnPc, ZnPc:C<sub>60</sub> and PEDOT-PSS films. It was found that an intermediate chromium layer improves PV properties of the structures with organic buffer layers. The photosensitivity at small illumination intensities of complete structures with ZnPc and ZnPc:C<sub>60</sub> layers increased more than one order of magnitude in comparison with the structures where the PEDOT-PSS buffer layer was deposited. The presence of C<sub>60</sub> in the composite-buffer layer results in increased photoconductivity. The best structure with composite ZnPc:C<sub>60</sub> buffer layer showed an open-circuit voltage of 560 mV, a short-circuit current density of around 10 mA/cm<sup>2</sup> and a photoconversion efficiency of around 3.3% under the light illumination with an intensity of 100 mW/cm<sup>2</sup> from a tungsten–halogen lamp. The low transmission of the semitransparent chromium–gold window layer is the reason for relatively low current density.

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**Keywords:** CuInS<sub>2</sub>; PEDOT; Solar cell; Buffer layer

## 1. Introduction

More than 95% of the solar cells in use today are made of crystalline silicon (c-Si); the average cost of the electricity generated is \$0.3/kW h. By comparison, in most parts of the United States, electricity costs about \$0.06/kW h. Thus, costs are approximately five times as much for electricity from solar cells. If the cost of producing solar cells could be reduced by a factor of 10, solar energy would be not only environmentally, but also economically favorable [1].

In the field of research and development of low-cost solar energy converters, hybrid organic–inorganic solar cells in an all thin-film configuration deserve a serious investigation. For example, prospective materials for substitution of inorganic semiconductors in solar cells can be conductive polymers and

photosensitive organic semiconductors [2–8]. The idea of using these materials is supported by the fact that no dangling bonds exist on the surface of organic semiconductors and they should not create additional centres of trapping and recombination at the interface with an inorganic photoabsorber. Furthermore, the large dimensions of organic molecules should strongly limit the rate of their diffusion in inorganic layers and the formation of new impurity centres.

CuInS<sub>2</sub> (CIS) is a photoabsorbing semiconductor with a direct band gap close to 1.5 eV. It exhibits a high light absorption coefficient in the visible spectral range and stability. In our investigations, Cu/CIS structures were used, fabricated at Institut für Solartechnologien (Frankfurt (Oder), Germany). The so-called CISCuT deposition method was used to form a polycrystalline CIS absorber layer on a copper tape [8]. The idea of this method is a fast roll-to-roll sulfurization in S<sub>x</sub>+N<sub>2</sub> gas atmosphere at 500–600 °C. The precursor is indium electrodeposited onto the copper tape substrate. The Cu/CIS

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structures (manufactured in 2004), which were used for the studies presented here, have shown efficiencies up to 7% ( $V_{oc}$  was around 600 mV) in the usual production cycle (CuI buffer deposited by spray process).

It should be noted, that roll-to-roll process is a prospective technique for preparing low-cost solar cells to be directly incorporated into roofing materials, thus reducing installation costs. On the other hand, organic semiconductors that can be dissolved in common solvents and coated onto various substrates are promising candidates for this application.

In the present study, a number of new hybrid solar cells based on Cu/CIS substrate/absorber and organic buffer layers of Zn-phthalocyanine (ZnPc), ZnPc:C<sub>60</sub> composite, and conductive polymer buffer layer of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with polystyrenesulfonate (PSS) was prepared and investigated. In this approach, the organic layer is considered as an alternative for the traditional buffer layer in the conventional cell structure [7].

## 2. Experimental

Aqueous suspension of 1.5% PEDOT-PSS was purchased from Aldrich and an appropriate mixture for spin-coating was prepared as described in a previous paper [7]. The mixture was spin-coated on Cu/CIS substrates and dried at 40 °C in vacuum for 3 h. The average thickness of PEDOT-PSS films was about 50 nm. Thin films of ZnPc and ZnPc:C<sub>60</sub> composite (1:1) with a thickness of 20 nm were thermally evaporated in high vacuum about  $10^{-7}$  Torr onto the CIS surface. The substrates do not need to be heated in this procedure.

All investigated photovoltaic structures were fabricated in sandwich configurations Cu/CIS/ZnPc/Cr/Au, Cu/CIS/ZnPc:C<sub>60</sub>/Cr/Au and Cu/CIS/PEDOT-PSS/Cr/Au as shown in Fig. 1. For preparation of semitransparent chromium–gold contact-window layers, chromium and gold were evaporated on the surface of the PEDOT-PSS, ZnPc and ZnPc:C<sub>60</sub> composite films using LEYBOLD LH evaporator integrated with the glove box MBRAUN MB 150 B-G. The lux–voltage measurements were performed

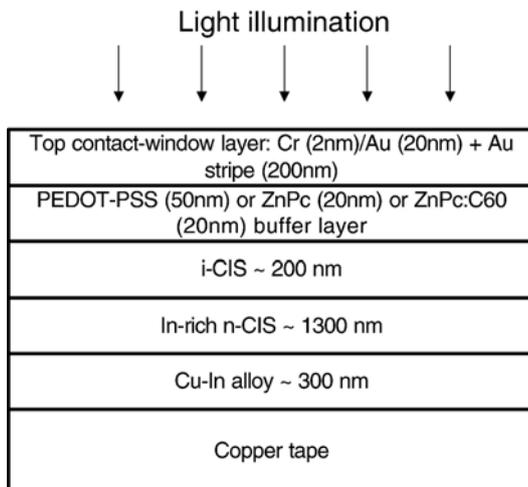


Fig. 1. Schematic drawing of complete PV structures based on CISCuT photoabsorber and PEDOT-PSS, ZnPc and ZnPc:C<sub>60</sub> composite-buffer layers.

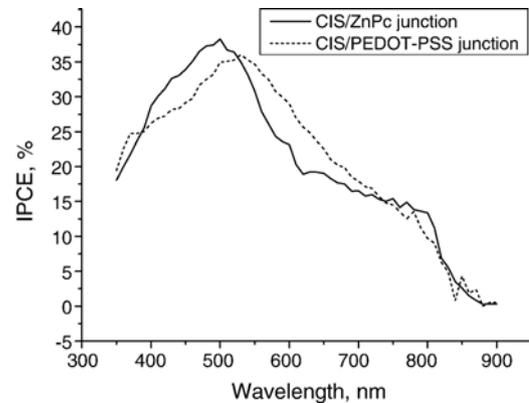


Fig. 2. The incident photon to current conversion efficiency (IPCE) spectrum for representative CIS/PEDOT-PSS and CIS/ZnPc PV junctions.

using grey light filters of various optical densities and TES 1323 Digital Lux Meter. Current–voltage characteristics were measured using Autolab PGSTAT 30 potentiostat/galvanostat. The light with an intensity of 100 mW/cm<sup>2</sup> from a tungsten–halogen lamp was used for irradiation. The active area of the junctions CIS/ZnPc, CIS/ZnPc:C<sub>60</sub> and CIS/PEDOT-PSS was 2 cm<sup>2</sup>.

## 3. Results and discussion

According to our approach, a photovoltaic p–i–n structure is formed between the intermediate buried layer of In-rich CIS, low-doped or undoped CIS at the surface of the absorber and PEDOT-PSS or ZnPc buffer layer (Fig. 1). The physical concept of operation of solar cells based on CISCuT photoabsorber with p-type buffer layer was presented in the paper [9] in more detail. As it was proposed in previous studies [8], the deposition of PEDOT-PSS and phthalocyanine films on the surface of CISCuT layers gives a small decrease of the potential energetic barrier and an increase in the efficiency of hole collection through the CISCuT–organic hole conductor interface.

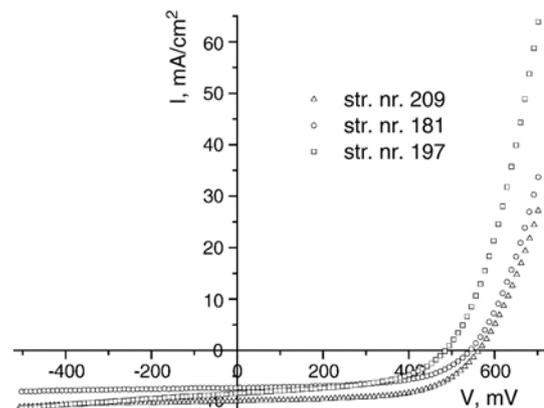


Fig. 3.  $I$ – $V$  characteristics of complete PV structures based on CISCuT photoabsorber and PEDOT-PSS, ZnPc and ZnPc:C<sub>60</sub> composite-buffer layers: str. nr. 209 — Cu/CIS/ZnPc:C<sub>60</sub>(20 nm)/Cr(2 nm)/Au(20 nm)/Au stripe (200 nm); str. nr. 181 — Cu/CIS/ZnPc(20 nm)/Cr(2 nm)/Au(20 nm)/Au stripe (200 nm); str. nr. 197 — Cu/CIS/PEDOT-PSS(50 nm)/Cr(2 nm)/Au(20 nm)/Au stripe (200 nm).

Table 1  
PV parameters of prepared hybrid structures under light illumination with an intensity of 100 mW/cm<sup>2</sup> from a tungsten–halogen lamp

Structure number <sup>a</sup>	Open-circuit voltage $V_{oc}$ , mV	Short-circuit current density $I_{sc}$ , mA/cm <sup>2</sup>	Fill-factor FF	Active area $S_{act}$ , cm <sup>2</sup>	Maximal output power $P_{max}$ , mW	Photoconversion efficiency $\eta$ , %
209	560	9.9	0.60	2	6.6	3.3
181	542	7.3	0.58	2	4.5	2.3
197	485	8.3	0.51	2	4.1	2.1

<sup>a</sup> Structure number 209 — Cu/CIS/ZnPc:C<sub>60</sub>(20 nm)/Cr(2 nm)/Au(20 nm)/Au stripe (200 nm); structure number 181 — Cu/CIS/ZnPc(20 nm)/Cr(2 nm)/Au(20 nm)/Au stripe (200 nm); structure number 197 — Cu/CIS/PEDOT-PSS(50 nm)/Cr(2 nm)/Au(20 nm)/Au stripe (200 nm).

The resulting thickness of PEDOT-PSS buffer, and its morphology depends on the dilution, composition of the solution mixture and on the rotation speed during spin-coating. The best result was obtained by spin-coating of PEDOT-PSS aqueous dispersion which was mixed with glycerin, *N*-methyl-2-pyrrolidone (NMP) and isopropanol as described in the previous paper [7]. In our devices, the optimal thickness of PEDOT-PSS was about 50 nm. In the case of ZnPc and ZnPc:C<sub>60</sub> buffer layers, high quality uniform films with a thickness of 20 nm were obtained by evaporation of ZnPc or co-evaporation of ZnPc with C<sub>60</sub> in high vacuum.

It was found, that the intermediate chromium layer between the gold contact and the buffer layer improves PV properties of prepared structures with organic buffer layers. In our assumption, this phenomenon is related to the suppression of a deep gold penetration into the buffer layer by the chromium intermediate layer. It should be noted, that the active area of the prepared solar cells was increased from 10–20 mm<sup>2</sup> [7] to 2 cm<sup>2</sup> (close to overall size of the sample). It is an important step towards solar cell production.

The incident photon to current conversion efficiency (IPCE, Fig. 2) for a CIS/PEDOT-PSS and CIS/ZnPc PV junctions reveals that the light absorbed by CIS leads to a photocurrent in a wide spectral range. In the graphs, the contribution of CIS to the photocurrent can be easily recognized in the range of visible light as a broad peak typical for photoabsorbers based on copper indium chalcogenides. Even though ZnPc is widely used as a photoactive material in solar cells [10], it does not contribute strongly to the photocurrent generated by the CIS/CuT/ZnPc solar

cell. Our data show, that the IPCE of ZnPc-cells is comparatively lower in the range where ZnPc is absorbing (around 600 nm of the wavelength value).

A significant photovoltage and photocurrent of the fabricated solar cells have been observed under tungsten–halogen light illumination with an intensity of 100 mW/cm<sup>2</sup>. Fig. 3 shows  $I$ – $V$  characteristics of the best obtained structures having an active area of 2 cm<sup>2</sup> with PEDOT-PSS and ZnPc or ZnPc:C<sub>60</sub> composite-buffer layers. The best obtained hybrid PV structure Cu/CIS/ZnPc:C<sub>60</sub>/Cr/Au has reached an efficiency of around 3.3% (Table 1). Doping of the ZnPc layer by C<sub>60</sub> results in a higher photoconductivity because of a photoinduced electron transfer from the ZnPc to the fullerene [11], thus decreasing the series resistance in the device and improving the fill-factor and current in the device. The lux–voltage measurements (Fig. 4) show that the structures with ZnPc buffer layer were much more sensitive at low illumination intensity in comparison with PEDOT-PSS based cells. According to our assumption, use of organic photoabsorber ZnPc reduces the shunt resistance of the structure and therefore increases the sensitivity at low illumination intensity conditions.

Fig. 5 shows the optical transmission spectrum through the Cr(2 nm)/Au(20 nm) top contact-window layer. It should be noted, that parasitic absorption of light in the semitransparent top layer decreases the photovoltage/photocurrent in the prepared cells. On the other hand, a too thin Cr/Au layer increases the series resistance of the structure, even though a narrow (2 mm) bus bar of thick gold was applied to channel the current to the contact point. Further studies will have to include the deposition of a more transparent electrode with good contact properties on top of the organic buffer layer.

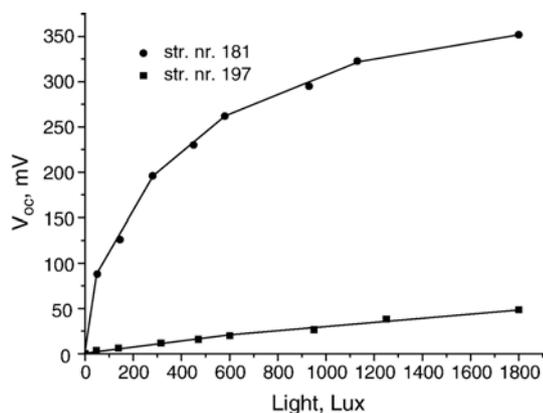


Fig. 4. Lux–voltage characteristics of complete PV structures based on CIS/CuT photoabsorber and PEDOT-PSS or ZnPc buffer layers: str. nr. 181 — Cu/CIS/ZnPc(20 nm)/Cr(2 nm)/Au(20 nm)/Au stripe (200 nm); str. nr. 197 — Cu/CIS/PEDOT-PSS(50 nm)/Cr(2 nm)/Au(20 nm)/Au stripe (200 nm).

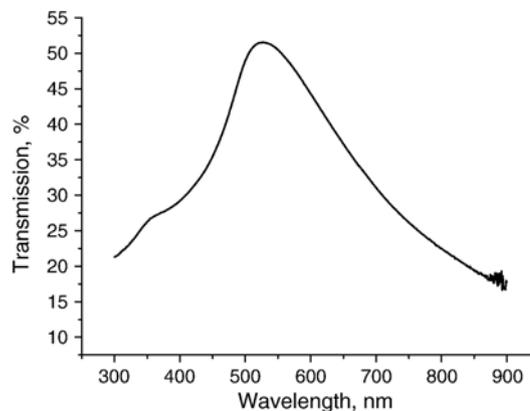


Fig. 5. Light transmission spectrum through Cr(2 nm)/Au(20 nm) top contact-window layer.

#### 4. Conclusions

Flexible hybrid solar cells based on the CISCuT material and utilizing thin-film buffer layers of the conductive polymer PEDOT-PSS and the organic photoabsorber ZnPc or a ZnPc:C<sub>60</sub> composite were prepared and characterized. Special attention was paid to the preparation of a semitransparent Cr/Au top-window layer with the aim to prevent Au penetration into the structure. The best structure with the ZnPc:C<sub>60</sub> composite-buffer-sensitizer layer so far showed a photoconversion efficiency of around 3.3% under tungsten–halogen lamp light illumination of 100 mW/cm<sup>2</sup> intensity. It should be noted, that cells with ZnPc buffer–sensitizer layer are much more photosensitive at low illumination intensity in comparison with cells with a conductive polymer buffer layer, making these structures highly interesting for indoor applications as studied in the Euro-PSB project. We have shown that our deposition technique gives us a way to prepare flexible hybrid solar cells using relatively simple step-by-step methods.

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