Cul as versatile hole-selective contact for organic solar cell based on anthracene-containing PPE–PPV

Shaimaa A. Mohamed, Jacek Gasiorowski, Kurt Hingerl, Dietrich R.T. Zahn, Markus C. Scharber, Salah S.A. Obayya, Mabrouk K. El-Mansy, Niyazi S. Sariciftci, Daniel A.M. Egbe, Philipp Stadler

Technische Universität Chemnitz, Semiconductor Physics, 09107 Chemnitz, Germany
edepartment of Physics, Faculty of Science, Benha University, Stadium Street, 13518 Benha, Egypt
bCenter for Photonic and Smart Materials (CPSM), Zewail City of Science and Technology, Sheikh Zayed District, 6th of October City, 12588, Giza, Egypt
cDepartment of Physics, Faculty of Science, Benha University, Stadium Street, 13518 Benha, Egypt
dInstitute for Surface- and Nanoanalytics, Johannes Kepler University Linz, Altenberger Str. 69, 4020 Linz, Austria

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An important issue in construction of organic photovoltaic cells concerns the selective contacts. Here, especially the modification of the hole-extraction is challenging, as energy levels have to match the polymer’s highest occupied molecular orbital (HOMO). We took the view to the mutual anode interface and we sought for a solution-based alternative for commonly PEDOT:PSS – with an eye on improving the hole-extraction with an inorganic interlayer. We present copper iodide (Cul) as a versatile inorganic p-type semiconductor that meets the requirements for enhanced charge extraction in donor polymers. We applied two types of anthracene-containing PPE–PPV block–copolymers that recently gained attention as efficient active absorbers in bulk heterojunction photovoltaic cells. We report on the advantages using Cul as hole-selective contact and show an improvement of the power conversion efficiency in polymer-based solar cells.

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1. Introduction

Thin film organic photovoltaic cells (OPVs) employ various organic conductive polymers as a donor absorber-part in bulk heterojunction type solar cells. They attract attention for their solution processibility and are suggested as powerful option for the photovoltaic market due to their flexibility, lightness and moderate cost as well as low environmental impact [1–6]. One significant concern discussed in all-solution based bulk heterojunction solar cells is the contact interface [7–10]. In order to achieve efficient charge extraction, selective contacts have to be applied between the active layer and electrodes to tune the work function by preventing the exciton quenching at the electrode surface and recombination of the photogenerated carriers [11,12]. Various types of interlayer materials are available to match the corresponding active layer’s energy levels, however, when strictly following a solution-based route, the portfolio of available materials becomes limited. On the electron-selective side, for instance, polyethyleneimine-based interlayers (PEI) have recently gained attention to form excellent band-matching to the active layers [13]. Calcinated ZnO and In$_2$S$_3$ derived from sol–gel processing shows similar results [14,15]. On the hole-selective side, solution-cast options are rare [16]. Predominantly most device structures rely on PEDOT:PSS [17,18]. Taking into consideration various reports on interface-problems related to the use of PEDOT:PSS and the necessity to find additional useful options consequently [19,10]. The variety of conjugated polymer–fullerene systems used as the active layers leads to very individual demands on the hole-contact side, which cannot be covered by PEDOT:PSS alone [20–22]. This argument applies in particular for the non-thiophene-based polymers that use p-phenylene-ethylbenylene and p-phenylene-vinylene (PPE–PPV) backbones as an example [23–27]. Here the interface matching with PEDOT:PSS can suffer from detrimental energy level offsets and/or degradation effects attributed to residual water, ionic species and the layer’s acidity [28,10]. In order to overcome barriers and improve the mutual interface between the polymer’s HOMO and the electrode, thin films of the copper (I) iodide have been applied in various photovoltaic devices earlier [29–32]. In this work, we demonstrate the capability of using solution-processed Cul as a hole selective contact (HSC) in the conjugated systems based on the non-thiophene polymer. Specifically, we use high molecular weight anthracene-containing...
poly (p-phenylene-ethynylene)-alt-poly (p-phenylene-vinylene) (PPE–PPV) with and without statistical distribution of octyloxy and 2-ethylhexyloxy side chains as active layers in combination with PCBM (see Fig. 1a) [23–27]. CuI as an interfacial layer is sandwiched between the active matrix and the final contact on the anode-side. For a complementary study of the interface, we conducted experiments with and without CuI as selective contact and discuss its role serving as a useful solution-processible alternative to PEDOT:PSS and as add-on contact layer in combination with PEDOT:PSS. Finally, we report on an increase in the power conversion efficiency by including CuI as a hole-selective contact (HSC) layer.

2. Experimental

For the photovoltaic cells as an active matrix we employed anthracene-containing poly (p-phenylene-ethynylene)-alt-poly (p-phenylene-vinylene) (PPE–PPV) with and without statistical distribution of octyloxy and 2-ethylhexyloxy side chains and respectively donated AnE-PVstat and AnE-PVab for the donor part. Both polymers have the same band gap 2.1 eV but different characteristics. We add the standard deviation $\sigma$ for all parameters per batch (20 samples). The spectral photocurrent external quantum efficiency (EQE) is measured using an optical fiber monochromatized Xenon-lamp with a typical illumination density of 5–10 W, connected to a ACTON Spectra Pro150 monochromator and EG&G 7260 DSP Lock-in amplifier to measure the photocurrent response. The short circuit current $I_{sc}$ values are derived by integrating spectral EQEs and corrected in all $J–V$ plots and tables accordingly. For the optical characterization transmission measurements are carried out at room temperature using a PerkinElmer T80 UV/VIS Spectrophotometer with a wavelength range between 400 and 900 nm. A Woollam M-2000 (rotating compensator) ellipsometer covering an energy range from 1.1 to 5 eV is used for gaining the dielectric function and absorption coefficient of Cu respectively. For this thin films on glass are characterized at 6 different angles (variable angle spectroscopic ellipsometry, VASE). The optical data (real and imaginary part of the dielectric function $\epsilon_1$, $\epsilon_2$) are derived from an optical model fit. The morphology of the thin-films is characterized using an atomic force microscope (AFM, Digital Instruments DIMENSION 3100, and tapping mode). A Bruker Dektak profilometer was used to verify thin films thicknesses.

3. Results and discussion

In order to elucidate the impact of Cul as hole-selective contact (HSC), we present photovoltaic devices using both AnE-PVstat and AnE-PVab. The corresponding chemical structures of the polymers, the energy and device diagram are depicted in Fig. 1. We highlight the hole-selective part of the cell and our strategy to improve the interface between the donor polymer’s HOMO and the work function of the contact electrode (in this case indium tin oxide ITO).

A major motivation in this work has been finding an alternative for PEDOT:PSS – as mentioned earlier various detrimental effects are associated with the polymer composite. Hence we pursue a device study for implementation of solution-cast Cul as a possible candidate. The first subject, we have been interested in, is the optical properties. Different to similar inorganic selective contacts as molybdenum(‘)oxide Cul’s absorption (optical band gap 400 nm, peak absorption) critically overlaps with the active layer. For application in a solar cell we therefore sought for an optical
crosscheck. We derive the dielectric function, absorption coefficient and the transmission using variable angle spectroscopic ellipsometry (VASE) and in a separate experiment UV-VIS transmission of solution-cast thin-film CuI. We denote that earlier studies covered predominantly vacuum-deposited CuI films [36,37].

The response of a 34 nm solution-cast thin-film reflects an absorption feature at 400 nm (α = 0.5 cm⁻¹). The optical model fitting the experimental values Ψ(ω) and Δ(ω) at six incident angles yield the dielectric function (ε₁, ε₂) of the material and the calculated absorption coefficient α using Eq. (1):

$$\alpha = \frac{\omega \varepsilon_2(\omega)}{C \gamma_0(\omega)}$$

with c being the speed of light, ω the angular frequency and nᵢ the refractive index. The corresponding spectra are plotted in Fig. 2a and b. For full consistency we have included the transmission of CuI and PEDOT besides. Interestingly, the results reflect a higher transmission for CuI in the visible-near infrared regime – except for the mentioned band absorption below 500 nm (Fig. 2c). Because of the absorption band we define layers below 34 nm to suit the requirements in terms of transparency as hole-selective contact on top of glass-ITO. The next step has been now a comparison of CuI’s thin film morphology on ITO (left) and on ITO/PEDOT:PSS (right) by AFM (Fig. 3a). For both cases we report on a homogeneous film formation of as-spun CuI. The root mean square roughness RMS is found slightly increased on bare ITO as compared to PEDOT:PSS coated ITO (Fig. 3a, 3.2 nm and 1.89 nm for CuI on ITO and ITO/PEDOT:PSS respectively). For a complete device study we are also interested, how the active layers are impacted by CuI. We pursue an AFM study elucidating the consecutive active layer’s nanomorphology. Earlier contributions have addressed morphological aspects in the polymer-fullerene blends of AnE-PVstat and AnE-PVab and its impact on the cell performance [25]. Within one active layer system, however, we observe minor morphological changes followed by introduction of CuI (Fig. 3cb). Such consistency rules out a major contribution to nanomorphology consequently, confirm our main statement to assign CuI’s role to improve on interfacial energy level alignment.

To confirm this statement further, we compare photovoltaic devices based on two similar polymers both hole-contacted either by CuI and PEDOT:PSS (control), respectively. The resulting J–V curves of the photovoltaic cells are shown in Fig. 4 including the linear and semi-logarithmic graphs for AnE-PVstat (left) and AnE-PVab (right). We present the results from sets of control devices

Fig. 2. (a) The dielectric function determined in detail by variable angle spectroscopic ellipsometry (VASE) from as-spun CuI layer on top of glass is shown for the UV-visible part of the spectrum. (b) According to the dielectric function the absorption coefficient α is derived. (c) We compare the optical transmittance of 34 nm CuI and ITO/glass with a control layer of PEDOT:PSS on ITO/glass.

Fig. 3. (a) AFM topographies of thin-film CuI on plane ITO and ITO-PEDOT:PSS. The-values vary from nm to nm with PEDOT:PSS acting as a smoothening layer. (b, c) Impact of CuI on the nanomorphology of the bulk-heterojunction. Left-hand the control devices are shown, right-hand side topographies with CuI underneath.
(black, PEDOT:PSS), sets of Cul-based (red) devices and, in addition, sets of combined devices (blue, double layer Cul on PEDOT:PSS). The latter combinatorial strategy (double layer) has been applied, in order to crosscheck for benefits from both HSC-types. It is exactly the most promising approach, as \( V_{OC} \) and \( J_{SC} \) values have improved significantly with respect to the single layer strategies. An overview of all corresponding PV-parameters is presented in Table 1. A detailed look to the \( J-V \) curves shows the control device (black line) with PEDOT:PSS and a PCE of 1.0% and 2.9% for AnE-PV\text{stat} and AnE-PV\text{ab}. By introducing Cul instead, the efficiencies are slightly increased to 1.3% and 3.2% respectively. Using Cul and PEDOT:PSS the PCEs have been improved mainly due to higher \( V_{OC} \) and \( J_{SC} \) respectively. Considering now all insights from optics, morphology and devices we finally evaluate the merit for using solution processed Cul thin-films. Our initial motivation has been mainly driven by the need for alternative solution-based and transparent hole-selective contact electrodes. Taking PEDOT:PSS now as a reference point our complementary study demonstrates Cul as a serious competitor – finally even beneficially improving photovoltaic performances in our photovoltaic system. The optical study reflects the transmission profile with a feature peak at 400 nm. To meet a similar transparency like PEDOT:PSS, we suggest to limit the Cul-thickness to maximum 35 nm. We additionally view to nanomorphology, both Cul itself and its impact to the consecutive active layers. Most important, in the latter we find consistency in the nanomorphologies, which appears independent from the hole-selective contact underneath. Differently, the device performance is indeed impacted: Cul applied as a direct substitute or as add-on layer on PEDOT:PSS serves as excellent hole-selective contact at least equal to the control devices. Our choice for the polymer-fullerene system has been made with care, to work out the role in a particularly interface-sensitive PPV-system. We outline the positive effects of Cul: Although they exhibit poorer serial resistances and, in combination with PEDOT:PSS, also lower fill factors, the \( J_{SC} \)-values improved significantly. The reasons for the enhancement relate to the presence of Cul – different to PEDOT:PSS it is cast from non-aqueous solutions, it is neither acidic nor basic and it offers similar smoothness as PEDOT:PSS. Hence we assign the enhanced performance to an interfacial effect. Furthermore, the spectral EQE measurements indicate no active contribution of Cul to the charge-separation (Fig. 5) – the spectra

### Table 1

<table>
<thead>
<tr>
<th>HSC</th>
<th>PCE (%)</th>
<th>FF</th>
<th>( V_{OC} ) (V)</th>
<th>( J_{SC} ) (mA cm(^{-2}))</th>
<th>( R_s ) (( \Omega ))</th>
<th>( R_{sh} ) (( \Omega ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>AnE-PV\text{ab} PEDOT:PSS</td>
<td>1.0 ± 0.05</td>
<td>57 ± 1.7</td>
<td>0.84 ± 0.02</td>
<td>1.81 ± 0.07</td>
<td>33 ± 2</td>
<td>1945 ± 60</td>
</tr>
<tr>
<td>Cul</td>
<td>1.3 ± 0.06</td>
<td>52 ± 1.6</td>
<td>0.82 ± 0.02</td>
<td>2.42 ± 0.07</td>
<td>34 ± 3</td>
<td>827 ± 27</td>
</tr>
<tr>
<td>Combined</td>
<td>1.5 ± 0.08</td>
<td>57 ± 1.6</td>
<td>0.83 ± 0.03</td>
<td>2.70 ± 0.10</td>
<td>28 ± 3</td>
<td>842 ± 27</td>
</tr>
<tr>
<td>AnE-PV\text{stat} PEDOT:PSS</td>
<td>2.9 ± 0.18</td>
<td>63 ± 1.7</td>
<td>0.79 ± 0.10</td>
<td>4.76 ± 0.30</td>
<td>15.5 ± 1.4</td>
<td>1524 ± 37</td>
</tr>
<tr>
<td>Cul</td>
<td>3.2 ± 0.19</td>
<td>63 ± 1.8</td>
<td>0.76 ± 0.02</td>
<td>5.45 ± 0.17</td>
<td>12.6 ± 1.5</td>
<td>781 ± 27</td>
</tr>
<tr>
<td>Combined</td>
<td>3.5 ± 0.18</td>
<td>51 ± 1.3</td>
<td>0.84 ± 0.02</td>
<td>6.65 ± 0.20</td>
<td>8.7 ± 0.9</td>
<td>788 ± 30</td>
</tr>
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![Fig. 4. The J–V curves (linear, semi-logarithmic) of the glass/ITO/HSC/AnE-PV\text{stat}:PCBM/LiF/Al (left) and glass/ITO/HSC/AnE-PV\text{ab}:PCBM/LiF/Al in dark and under illumination of AM 1.5G at 100 mW cm\(^{-2}\).](image-url)
match the active layer’s absorption shown in the dashed line in the graph. Though the absorption in the 34 nm HSC-layer can lead to reduced fill-factors and reduced serial resistances. Both subjects are reflected in our photovoltaic devices, however they can be resolved by optimizing the device design and layer-thickness in future.

4. Conclusions

Alternative solution-processed hole-selective contacts in polymer solar cells are rare – we took the view on this central front in device research and introduced CuI as inorganic thin-film option. The as-spun p-type semiconductor serves as an excellent contact layer on a level with the predominantly used PEDOT:PSS. We point out the advantages of interfacing non-thiophene based polymers and show in a combinatorial strategy that Cu interlayers help improving the PCE efficiency significantly. We include a detailed characterization of the optical properties of as-spun Cu layers and work out its absorption properties, film-form properties and impact on the active layer’s morphology. Its optical qualities together with its thin-film properties and, in particular, its performance in the device make Cu a versatile hole-selective alternative for organic photovoltaic applications.

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