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High-Performance Transparent Copper Grid Electrodes Fabricated by Microcontact Lithography for Organic Photovoltaics

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Abstract

We report high-performance transparent copper grid electrodes on glass and plastic substrates that offer a higher Haacke figure-of-merit than conventional indium-tin oxide electrodes, and are well-matched to the requirements for organic photovoltaics (OPVs). The electrode is fabricated using micro-contact lithography with a combination of molecular resist and low toxicity etchant: namely, hexadecanethiol and aqueous ammonium persulfate. This approach to electrode fabrication is much faster than conventional lithography, because it takes < 2 seconds to print the molecular resist layer and tens of seconds to etch the copper film, with both processes performed in ambient air. The grid linewidth achieved is > 20 times narrower than is possible using conventional metal printing methods and so a grid pitch < 30 µm is easily achieved without increasing metal coverage.
The very small grid-line spacing relaxes the requirement to use highly conductive films to span the gaps between grid lines, reducing parasitic absorption losses. This is demonstrated using an extremely thin (10 nm) poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) layer. Additionally, we present evidence that it is not always necessarily to embed the metal grid into the substrate, or to planarize with a charge transport layer, to avoid leakage current across the OPV device.

**Keywords**

Transparent Electrode, Copper, Microcontact Printing, OPV, Metal Grid

**Introduction**

The power conversion efficiency of organic photovoltaics (OPVs) has now exceeded 15% in the laboratory and there is good reason to expect that the long term stability needed for practical applications is within reach.$^{[1,2]}$ However, there is currently no transparent substrate electrode available that will enable OPVs to realize their full cost-advantage and functional-advantages (e.g. flexibility, light weight, color tuneability) over other types of thin-film photovoltaics, which is limiting for commercial exploitation.$^{[3]}$ For practical application in photovoltaic modules the basic requirement for a transparency $\geq 80\%$, over the wavelength range 400-900 nm, must be matched with an electrode sheet resistance well below $10 \ \Omega \ \text{sq}^{-1}$. The latter requirement is essential to minimise ohmic losses and recombination losses when device dimensions are $\geq 1 \ \text{cm}$, which is the relevant scale for practical application.$^{[4,5]}$ Additionally, the electrode must be robust, compatible with flexible plastic substrates to enable high throughput roll-to-roll processing, and be made using low-cost sustainable materials.$^{[6]}$ Conventional transparent conductive oxides such
as indium tin oxide (ITO) are unsuitable because, as well as the high cost of indium, they are inherently brittle and require post-deposition annealing at $> 300^\circ C$ to achieve optimal performance, making them poorly compatible with flexible plastic substrates.$^{[7,8]}$ Electrodes based on spray coated silver nanowires are inherently costly because of the high cost of silver and the relatively high cost of nanowire synthesis, and also often suffer from poor contact stability at the junctions between nanowires.$^{[9]}$ Whilst optically-thin metal films sandwiched between two impedance matching amorphous oxide layers are compatible with flexible substrates, a very high degree of control over the thickness of each layer is needed to achieve high performance which can only be achieved using a slow metal and oxide deposition process.$^{[3,10–13]}$

To date electrodes based on metal grids with the gaps between grid lines spanned by a conducting polymer offer the highest performance transparent electrodes.$^{[14]}$ However, metal grid electrodes are ordinarily fabricated using photolithography which is an inherently high-cost fabrication method because of the time taken to fabricate the mask on top of the metal and remove the mask after metal etching.$^{[15–17]}$ The photoresist layer also has a typical thickness of 0.5-5 $\mu$m and so its deposition and removal requires relatively large volumes of organic solvent if the electrode is to be scaled for OPVs, which is limiting both from a sustainability and cost perspective.

Whitesides et al. have shown that an alkanethiol layer only one small molecule in thickness (1-2 nm) printed using the soft lithographic process of microcontact printing ($\mu$-CP) is sufficient to serve as an etch mask for patterning films of gold (Au), silver (Ag) and copper (Cu) when used in conjunction with a thiosulfate/ferricyanide etchant.$^{[18, 22]}$ $\mu$-CP is compatible with roll-to-roll processing and so that pioneering work opened the door to the possibility of patterning these highly conductive metals with sub-micron resolution over large area using tiny amounts of resist,$^{[19]}$ without complex metal mesh transfer, photolithographic or electrochemical deposition steps.$^{[14]}$
However, to date the use of this approach to fabricate transparent grid electrodes suitable for photovoltaic devices has been sparsely explored. To our knowledge there has been only one literature report relating to the use of μ-CP to fabricate transparent electrodes based on a metal grid: Zou et al. have shown that silver grids with a line width of ≥ 7 µm and line-spacing of 50 µm on glass can be fabricated using μ-CP printed resist layers of 11-mercaptoundecanoic acid and a thiourea/ferric nitrate silver etchant.[21] In addition to the high cost of silver, the performance of those electrodes was limited by the large gaps between the grid lines, which compromised the fill-factor of the OPV devices.[21]

Here we report the fabrication of high performance Cu grid electrodes on both glass and plastic substrates by μ-CP, using a hexadecanethiol (HDT) monolayer resist together with the low-cost, low-toxicity and single-component etchant ammonium persulfate (APS).[23] Cu is the metal of choice because it is ~100 times lower cost than Ag with comparable electrical conductivity, and has a work function of 4.6 - 4.9 eV which is comparable to that of ITO glass (~ 4.9 eV).[25, 26]

Using this new resist-etchant combination we show that excellent selectivity and edge resolution can be achieved on Cu without the need for additional additives, enabling the fabrication of Cu grids with line-widths < 2 µm and line spacing < 30 µm. When combined with an extremely thin poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) layer to span the gaps between grid lines, these grid electrodes can be used as the transparent electrode in OPVs as a viable alternative to ITO glass, without the complexity of having to embed them into the substrate.

Results and Discussion

Electrode fabrication
Cu films with a thickness of 40-500 nm (depending on the desired sheet resistance) are deposited onto glass and polyethylene terephthalate (PET) substrates by vacuum evaporation. A polydimethylsiloxane (PDMS) stamp patterned with relief structures and dosed with HDT is then brought into intimate contact with the Cu coated substrates for ~2 seconds to deposit the HDT self-assembled monolayer (SAM) mask. The film with patterned HDT monolayer is then submerged in an aqueous solution of APS to etch those areas not functionalized with the HDT monolayer. Persulfate ions decompose in contact with Cu metal, forming Cu\(^{2+}\) and SO\(_4^{2-}\) ions respectively (Equation 1) and the resultant copper is recoverable from solution as copper sulfate.[24]

\[
S_2O_8^{2-} + Cu \rightarrow 2SO_4^{2-} + Cu^{2+}
\]

This process is schematically illustrated in Figure 1.
Figure 1. Schematic of the Cu grid fabrication process. The fabrication of the PDMS stamp is detailed additionally in SI Figure S1.

A dense monolayer of HDT with few defects is formed with contact times < 2 seconds, which hinders the approach of the aqueous persulfate ions to the Cu metal. The efficient removal of the Cu metal not covered by the HDT monolayer is found to be possible with a wide range of etchant concentrations (4 - 50 mM) and metal thicknesses (40 - 500 nm), with etch times of the order of tens of seconds. As a result of the low metal thickness as compared to the metal line-width (> 1000 nm), undercutting of the metal film by the etchant is not observed. This process yields high quality square Cu grids with line-widths of 1.0 - 3.0 μm for metal thicknesses of 40-500 nm. The quality of the grid electrodes is found to be independent of whether the HDT monolayer was stamped in a nitrogen atmosphere or ambient air. By varying the grid pitch between 27.3 and 150 μm, whilst maintaining a line width of 1.4 μm, the far-field transparency is increased from 80 to 92% without exceeding 10 Ω sq⁻¹ sheet resistance: Figure 2.
Figure 2. Optoelectronic performance for a range of Cu grids of pitches from 27.3 μm to 150 μm, denoted $p$, and fixed metal thickness 120 nm. Data for the fitted line is given in Table S1. (Inset) An optical microscope image of an example Cu grid.

The far-field average transparency is only marginally reduced as grid thickness increases from 40 to 120 and 500 nm; 83.3%, 80.3% and 77.2%: SI Figure S2. This small decrease in transparency, when going from a metal thickness of 40 to 120 nm, can be understood in terms of the loss in transparency of the Cu grid lines themselves because at a thickness of 40 nm Cu films are semi-transparent.

The advantage of using very narrow grid line-widths is that the gaps between lines can be smaller for the same metal coverage of the transparent supporting substrate. This is important for application as the transparent electrode in OPVs because, due to the low conductivity of organic semiconductors, the gaps between grid lines invariably need to be spanned with a thick (50 -100 nm) conducting layer of PEDOT:PSS to ensure efficient charge extraction.\textsuperscript{[14]} The larger the spacing between the grid lines the more conductive this layer must be to avoid excessive recombination and ohmic losses, which degrade PV device fill-factor.\textsuperscript{[5]} However, increasing the conductivity of the layer spanning the gaps between grid lines inevitably results in more parasitic light absorption by it due to the higher free charge carrier density.\textsuperscript{[27, 28]} Due to the very small line separation used herein, a PEDOT:PSS layer with a thickness of only 10 nm is used, which absorbs an insignificant portion of the incident light: SI Figure S2. The thickness of this layer is verified by atomic force microscope (AFM) scoring analysis: SI Figure S3. The Haacke figure-of-merit ($T_{550\text{nm}}^{10} / R_{sh}$)\textsuperscript{[14]} - a metric commonly used to compare the performance of different types of transparent electrodes - is 0.031 with 120 nm grid thickness and 27.3 μm pitch, which increases
to 0.048 upon storage at ambient temperature due to a reduction of sheet resistance from 3.2 to 2.4 Ω sq⁻¹. This reduction in electrode sheet resistance upon storage time can be accelerated by low temperature (120°C) thermal annealing and so is attributed to an increase in the crystallinity of the Cu grid with time. To our knowledge, this is the highest Haacke figure-of-merit reported for a metal-oxide free, non-embedded metal grid suitable for OPVs,[1⁴] and is higher that of conventional ITO glass coated electrodes (0.040): Supporting information Table S2. Indeed, if the average transmittance across the wavelength range 400-800 nm is used instead of the transmittance at 550 nm the Haacke figure-of-merit for all of the Cu grid designs fabricated in this work far exceeds that of ITO glass: Supporting Information Table S2. The very low sheet resistance (2.4 Ω sq⁻¹), which is a factor 4-5 times lower than ITO on glass (15 Ω sq⁻¹), is particularly enabling for OPV module design because it allows for the width of individual devices to be increased beyond 1 cm, reducing scribe area without significant ohmic losses.[⁴]

**OPV device studies**

For OPV device applications the Cu grids are briefly UV/O₃ treated to oxidize the HDT monolayer and then rinsed with acetic acid to remove oxidized Cu. This process improved wetting between the substrate/grid and the PEDOT:PSS layer. The utility of these electrodes in OPV devices is demonstrated using the device architecture: Electrode | zinc oxide nanoparticles (ZnO) | PBDB-T/ITIC | MoO₃ | Al. In the current context the conductive PEDOT:PSS (PH1000) layer covers the copper grid lines as well as the gaps between them, so it is the PEDOT:PSS that determines the energetics at the interface with the ZnO electron transport layer. In the first instance a device area typical of that reported in the literature; 6 mm², was used together with a Cu grid thickness of 40 nm which has a sheet resistance of 15 Ω sq⁻¹. This sheet resistance is comparable to that of the
commercial ITO coated glass reference electrodes used in this study. Within error the open-circuit $(V_{oc})$ and fill-factor $(FF)$ of OPV devices is comparable for devices using ITO and Cu grid electrodes, but the short-circuit current density $(J_{sc})$ is $\sim 13\%$ lower in the latter consistent with the lower far-field transparency of the Cu grid with 27.3 $\mu$m pitch; Figure 2 and SI Table S3. However, by increasing the grid pitch the average transparency can be increased to a level equal to that of ITO glass (Figure 2), which reduces the gap in $J_{sc}$: Supporting Information Table S4 and Figure S4.

Importantly, for practical application in OPVs an electrode with a sheet resistance of $15 \, \Omega \, \text{sq}^{-1}$ is too high, because when the device area is increased the fill-factor $(FF)$ decreases precipitously: For example, increasing the device area to only 60 mm$^2$, incurs a 23% reduction in fill-factor (Figure 3 and Table S2). Consequently, for practical application in OPVs ITO glass is not suitable as the transparent electrode unless it used in conjunction with a highly conductive metal grid. A key advantage of transparent electrodes based on metal grid is that it is possible to reduce the sheet resistance without reducing the transparency by increasing the thickness of the grid lines. Increasing the Cu grid thickness by a factor of 3 reduces the sheet resistance of the Cu grid electrode from 15 to $3.2 \, \Omega \, \text{sq}^{-1}$, whilst reducing the transparency by only 3% (Supporting Information Figure S2). When the area of OPV devices using the 120 nm thick Cu grid electrode is increased from 6 to 60 mm$^2$ there is no significant change in the device performance parameters: Figure 3, Table S3.
Figure 3. Champion device characteristics for ITO and Cu grid devices in the structure: Electrode (ITO or Cu Grid & PEDOT:PSS) | ZnO | PBDB-T/ITIC | MoO3 | Al. Solid (dashed) lines refer to measurements under 1 sun light (in the dark).

One factor that has been reported to be problematic for electrodes based on an etched metal film for applications in OPVs is the height of the step at the edge of metallized regions, which results in non-uniform thickness of the organic semiconductor layers and current leakage across the device: For example, Lee et al. have shown that for a random-metal wire electrode based on an etched metal film, OPV device performance and yield dramatically deteriorates when the metal
thickness is increased much beyond 15 nm.\textsuperscript{[29]} Importantly, using the approach reported herein Cu grids with a grid height of 120 nm achieve comparable performance and yield to that of OPV devices fabricated on planar ITO reference electrodes, even though the organic photoactive layer thickness is comparable to the grid height. This result indicates that, either the PEDOT:PSS and ZnO layers planarize the grid or that all layers conformally coat the Cu grid so that there is no significant variation in the thickness of the photoactive organic semiconductor layer. The extent to which each layer conforms to the Cu grid topography was determined using AFM and cross-sectional scanning electron microscopy (SEM): Figure 4. Figure 4 (a) shows that the PEDOT:PSS and ZnO layers together reduce the Cu grid step height by only \( \sim 25\% \), but accumulate at the base of the Cu grid lines smoothing the abrupt step (detailed in Figure 4 (b)).
Figure 4. (a) Atomic force microscope (AFM) images of a Cu grid on glass with a line height of 120 nm: (Black) bare; (Green) with 10 nm PEDOT:PSS overlayer; (Blue) with 25 nm Al-doped ZnO overlayer; (Red) with 10 nm PEDOT:PSS and 25 nm Al-doped ZnO bilayer. (b) Cross-sectional SEM image of an OPV device with the structure: Cu grid electrode (120 nm grid height) | PEDOT:PSS (10 nm) | Al-doped ZnO (25 nm) | PBDB-T / ITIC | MoO$_3$ (6 nm) | Al (150 nm). Further detail is shown in SI Figure S5.

Since the subsequent device layers also coat conformally, the grid pattern is also found on the surface of a completed OPV devices: SI Figure S6. This result shows that whether or not a metal grid line thickness can be tolerated in an OPV device depends not only the metal thickness, but
also on how the charge transport layer(s) at the interface between the grid and the photoactive layer conform to the grid, particularly at the base of the grid lines. The data show that for grids with a height comparable to the thickness of the bulk-heterojunction layer in OPVs it is not always necessary to embed the Cu grid into the underlying substrate, or to use a very thick interfacial layer.

Finally, translating the Cu grid electrode to flexible PET substrates has no adverse effect on electrode or OPV device performance: The power conversion efficiency is 6.0 ± 0.8 % on glass and 5.8 ± 0.6 % on PET (SI Table 2 and Figure S7). Additionally, unlike ITO films on plastic substrates, these Cu grid structures do not deteriorate when repeatedly bent through a small radius of curvature rendering them compatible with roll-to-roll processing: Figure S8. It is also possible to ensure that the Cu grid is resistant to aggressive cleaning procedures such as ultra-sonic agitation in solvents by functionalizing the substrate with organic-silane derivatives using our previously developed protocol for attaching evaporated Cu films to PET (Figure S9),[30] although this was not necessary for OPV devices reported herein.

Whilst the long-term stability of the Cu electrodes is not the subject of the current study, it is notable that upon exposure to ambient air the Cu grids fabricated in this study oxidized very slowly: After 160 days (> 5 months) the height of a set of Cu grids was measured using AFM as 127.4 ± 1.2 nm (SI, Table S5). The oxide was then selectively removed by rinsing in acetic acid,[31] leaving Cu grids of height 122.8 ± 1.8 nm, which corresponds to a 4.7 nm oxide overlayer, or 2.8 nm of metal converted to the oxide. This very slow rate of oxidation is consistent with the detailed study of the rate of copper film oxidation in ambient air reported by Platzman et al.[32]
Conclusions

In summary we have reported the fabrication of high performance transparent grid electrodes on glass and plastic substrates that meet the requirements for utility in high performance OPVs: namely, ≥80% far-field transparency (over the wavelength range 400 - 900 nm) a sheet resistance < 10 Ohms per square, compatibility with flexible substrates and low cost non-toxic materials. These electrodes have been fabricated using microcontact printing lithography using a combination of etchant and molecular resist that enables the fast fabrication of high quality copper grids without the complexity associated with metal mesh transfer, photolithographic or electrochemical deposition steps. Indeed this approach to electrode fabrication is much faster than conventional lithography, taking < 2 seconds to print the resist layer and tens of seconds to etch the film. This approach to electrode fabrication is sustainable because: (i) it can be performed in ambient air; (ii) it uses tiny quantities of resist; (ii) ammonium persulfate is a low toxicity etchant which can be recycled. A key advantage of this fabrication method over printed metal grids is that the achievable line width is > 20 times narrower which consequently means that a smaller spacing between grid lines is possible, relaxing the conductance requirements for the charge collecting interlayer. Interestingly, we have also found that (depending of OPV device structure) it is not necessarily essential to embed the grid electrode into the substrate or into a thick charge transport layer for utility, which avoids a further processing step.

Experimental

Production of the master/stamps:

Onto a 3” polished Si wafer a photoresist bi-layer consisting of MicroChem polydimethylglutarimide (PMGI) SF11 and MICROPOSIT S1818 was layered and exposed to 130
mJ cm\(^{-2}\) UV light through a chromium mask patterned with the grid lines and developed for 30s in MF-319 developer. 500 nm Al\(_2\)O\(_3\) (99.99%, Kurt J. Lesker) was then evaporated across the wafer before a lift off with acetone, propanol, MF-319 developer and a final rinse with DI water. Through the remaining Al\(_2\)O\(_3\) mask the grid lines were etched using an Inductively Coupled Plasma (ICP) Etcher to a depth of 5.2 μm into the Si wafer. This extreme depth was used to avoid ‘sagging’ of the void during printing. The resultant master was used with the Al\(_2\)O\(_3\) left in place, after silanisation for 1 hr in Trichloro(1H,1H,2H,2H-perfluoroctyl)silane vapour. All electrodes unless stated otherwise were produced using the same polymeric PDMS stamp formed upon this master (reused) with 1.4 μm wide lines and 10% coverage defined with respect to the original master. Differences in current, for example between grids on plastic and glass or 40 and 120 nm high grids are attributed to widening of these lines during printing and can be compensated for by stamp design.

**Forming of grid electrodes:**

40 – 120 nm Cu (99.999%, Kurt J. Lesker) was evaporated at 1 Å s\(^{-1}\) to freshly cleaned and UV/O\(_3\) treated plastic (polyethylene terephthalate, PET) or glass at \(<\ 10^{-6}\) base pressure. These were then immediately taken into air and gentle contact was made with a patterned PDMS stamp inked with 2 mM hexadecanethiol (HDT, 97% dry wt., Alfa Aesar) and dried for 1 minute. Contact was held for \(<\ 2s\) to minimise widening of the fine grid lines. These electrodes were then dipped in an aqueous 4 mM ammonium persulfate solution (APS) at room temperature for 30 – 90s dependent on metal thickness to form the grid lines. The HDT mask was not removed and these electrodes were washed in acetic acid for 10s before use directly in the devices described.
Sheet resistance measurement:

18 × 18 mm patterned Cu grid electrodes were produced as above onto which silver contacts were painted to connect a Keithley 2400 source meter. Resistances were calculated using the Van der Pauw method at an applied voltage of 5 mV. For the sheet resistance evolution electrodes were stored in ambient laboratory air and remeasured periodically. The temperature fluctuated between 18-30°C and the humidity between 15-50%.

Model optoelectronic devices:

To the prepared grid electrodes (on glass or PET) where specified a 10 nm PEDOT:PSS film was spin-cast at 5000 rpm from a filtered solution diluted with 2 parts deionised water and annealed at 120°C in air for 15 minutes. Together with ITO glass reference electrodes (Washed and UV/O3 treated. Glass; Thin Film Devices. PEN; Diamond Coatings) transferred into a N₂ filled glovebox with < 2 ppm O₂ and H₂O, 25 nm of ZnO was deposited by spin coating (Aluminum-doped zinc oxide ink for spin coating/slot-die coating, Sigma Aldrich, 5000 rpm, filtered) followed by the bulk heterojunction. For the PBDB-T/ITIC (Ossila) devices solutions were prepared in anhydrous chlorobenzene and 0.5% 1,8-Diodooctane (DIO) at a 1:1 wt% (20 mg per mL), spin cast at 2500 rpm and annealed at 120°C for 15 minutes. For the PBDB-T-2Cl/ITIC-2F (Ossila) devices solutions were prepared in anhydrous chlorobenzene and 1% 1,8-Diodooctane (DIO) at a 1:1 wt% (26 mg per mL), spin cast at 2500 rpm and annealed at 100°C for 15 minutes. All devices were loaded to the thermal evaporator. 6 nm MoO₃ was then evaporated at 0.2 Å s⁻¹ before the devices were transferred under vacuum to the pixel mask and 150 nm Al was evaporated at 1 Å s⁻¹. Prior to testing, the PBDB-T-2Cl/ITIC-2F devices only were again annealed at 120°C for 15 minutes.
All devices were tested unencapsulated under 1 sun illumination in an N\textsubscript{2} atmosphere (< 2 ppm O\textsubscript{2}, H\textsubscript{2}O) through a calibrated shadow mask for the small area devices.

**Supporting Information**

The following files are available free of charge.

All data supporting this study are provided as supplementary information accompanying this paper, including tabulated device data, SEM images and AFM analysis. (.docx)

**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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**References**


20. -


**Graphic for Manuscript**
Line Width: 1.8 μm
Pitch: < 25 μm
$R_{sq}$: 2.4 Ω sq$^{-1}$