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Version: Version of Record

Link(s) to article on publisher’s website:
http://dx.doi.org/doi:10.1002/adfm.201802893

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Fabrication of Copper Window Electrodes with $\approx 10^8$ Apertures cm$^{-2}$ for Organic Photovoltaics

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A powerful approach to increasing the far-field transparency of copper film window electrodes which simultaneously reduces intraband absorption losses for wavelengths <550 nm and suppresses reflective losses for wavelengths >550 nm is reported. The approach is based on incorporation of a random array of $\approx 100$ million circular apertures per cm$^2$ into an optically thin copper film, with a mean aperture diameter of $\approx 500$ nm. A method for the fabrication of these electrodes is described that exploits a binary polymer blend mask that self-organizes at room temperature from a single solution, and so is simple to implement. Additionally all of the materials used in electrode fabrication are low cost, low toxicity, and widely available. It is shown that these nanostructured copper electrodes offer an average far-field transparency of $\geq 80\%$ and sheet resistance of $\leq 10\, \Omega \cdot \text{sq}^{-1}$ when used in conjunction with a conventional solution processed ZnO electron transport layer and their utility in inverted organic photovoltaic devices is demonstrated.

1. Introduction

Optically thin metal films with a thickness of $<10$ nm are attracting growing attention as window electrodes for a variety of emerging applications\cite{1–3} including thin film photovoltaics\cite{4–6} and displays\cite{7,8} because they are compatible with flexible substrates\cite{9–15} and can be deposited using simple vacuum evaporation. Roll-to-roll vacuum evaporation is attractive as a method for metal electrode deposition for organic optoelectronics\cite{3,11} because it is a proven industrial process for the manufacture of low cost food packaging and insulation foils based on very thin metal films, offering excellent control over metal thickness and uniformity. Indeed for the large-scale manufacture of organic photovoltaics (OPVs) vacuum deposition of the metal electrode is expected to be a tiny percentage of the total cost of a solution processed OPV.\cite{16} To date, silver has been the metal of choice for window electrode applications\cite{9,17} because it offers the highest electrical conductivity and lowest optical losses\cite{18} over the visible and near infrared spectrum. To maximize transparency the thin silver film is typically sandwiched between two wide bandgap inorganic oxides or organic semiconductor layers to form a triple layer electrode architecture.\cite{19} For price-sensitive applications such as OPVs copper is an attractive alternative to silver because it offers comparable electrical conductivity\cite{18} at one hundredth of the cost.\cite{20,21} To date there have been three recent reports of high performance OPVs, using a copper-based window electrode that exhibits performance close to that achieved using an indium-tin oxide (ITO) electrode: Hutter et al. used an 8 nm thick thermally evaporated copper film and a WO$_3$ over layer which serves both as an antireflecting layer and hole-extraction layer.\cite{22} Zhao et al.\cite{23,24} have demonstrated a high performance window electrode based on a partially oxidized copper film sandwiched between ZnO layers, which proved to be remarkably stable towards air oxidation. However, in the latter case both the metal and oxide metal layers were deposited by the process of sputtering,\cite{23,24} the slowness and complexity of which partially offsets the benefit of using a low-cost metal. A different approach for the passivation of optically thin copper film electrodes, that is compatible with vacuum evaporation, is the use of a sub-1 nm aluminum over layer which also serves to reduce the electrode work function so that it can be used as the electron-extracting electrode in OPVs.\cite{25}

For window electrode applications the primary disadvantage of copper as compared to silver is its lower far-field transparency for wavelengths below $\approx 550$ nm, which stems from intraband absorptions\cite{26,27} that do not occur in silver. For wavelengths above $\approx 550$ nm the transparency is reduced due to reflection similar to the case of silver. Ebner et al.\cite{28} and Zhao et al.\cite{24} have shown that absorption losses in optically thin copper films can be reduced to an acceptable level by reducing the thickness of the copper film, with a thickness of 6.5 nm proving to be most effective. Whilst losses due to reflection can be suppressed using a wide bandgap semiconducting layer of specific thickness, there is a compromise to be struck between the optimal thickness to suppress reflection and the thickness needed for optimal electronic functionality.

Herein we demonstrate a different approach to simultaneously reducing intraband absorption losses in optically thin copper films for wavelengths below $\approx 550$ nm and dramatically reducing
suppressing reflection for wavelengths above \( \approx 550 \) nm, which is based on incorporating into the metal film \( \approx 100 \) million circular apertures per cm\(^2\) with a mean diameter of \( \approx 500 \) nm. The size of the apertures is selected to be large enough to ensure that short wavelength light can pass through unhindered, whilst being small enough to ensure that, in the context of an OPV, photogenerated free charge carriers formed in the light harvesting semiconductor adjacent to apertures in the metal electrode can still be extracted by the electrode without the need for a highly conducting charge extracting layer such as heavily doped poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) to span the gaps in the electrode, as is the case for metal nanowire and metal grid electrodes.\(^{[29,30]}\)

This approach to metal window electrode design is applicable to thicker metal films than the optimal of 6.5 nm thickness reported previously,\(^{[24]}\) which are likely to prove more practical to deposit over large areas. Conventional lithographic techniques for fabricating arrays of apertures of this size over large areas are prohibitively costly. One potentially low cost approach is to use micrometer-sized polymer nanoparticles as a shadow mask, deposited directly from a colloidal solution, which has been widely used,\(^{[29,31–33]}\) or formed by polymer blend lithography\(^{[34,35]}\) followed by mask and metal lift-off. To our knowledge the work of Huang et al.\(^{[35]}\) is the only literature pertaining to the use of polymer blend lithography as a mask to pattern metal films. Inspired by the latter, the electrode fabrication process reported herein is based on a simplified method of forming a dense array of apertures in metal films based on copolymer blend lithography that has the advantage that it does not require a metal lift-off step. We show that these electrodes are also easily combined with a widely used, solution processed, electron transport semiconductor that also serves as an antireflecting layer, to realize window electrodes suitable for use in OPVs. The advantage of this approach to copper window electrode fabrication is the technological simplicity that results from the use of metal deposition by simple vacuum evaporation combined with a mask that self-organizes from a single solution, instead of having to synthesize the mask prior to deposition onto the substrate to be etched, as is the case for conventional microsphere lithography. Also, all the solution-based steps use widely available low-cost chemicals, based on earth-abundant elements, and there is no requirement to control humidity or for post-deposition annealing of the polymer blend. When this electrode is used in conjunction with the solution processed wide bandgap n-type semiconductor ZnO, which is very widely used as an electron transport layer in OPVs, a dramatic \( \approx 66\% \) reduction in electrode sheet resistance occurs due to low temperature diffusion of Cu into the adjacent ZnO layer, which greatly increases its performance as a transparent electrode for OPVs.

2. Results and Discussion

Figure 1 depicts the processes of electrode fabrication developed in this study. Copper films were thermally evaporated onto glass substrates modified with a mixed molecular layer of 3-mercaptopropyltrimethoxysilane (MPTMS) and 3-aminopropyltrimethoxysilane (APTMS). We have previously shown that this class of adhesion layer can be applied to both glass and plastic substrates to realize robust copper films without contributing to light absorption.\(^{[29,36]}\) A blend of the immiscible polymers, polystyrene (PS) and poly(methyl) methacrylate (PMMA) in 2-butanone was spin cast directly onto the copper film (Figure 1, step 1), whereupon spontaneous phase separation into well-defined isolated spherical PS domains in a PMMA matrix occurs. Crucially the PS domains protrude from the PMMA surface and extend through most, or all, of the film thickness. Selective removal of PS using cyclohexane (Figure 1, step 2) leaves behind a layer of PMMA with circular holes, which serves as a mask to etch copper (Figure S1, Supporting Information).

To date literature reports pertaining to phase separation in PS/PMMA blends have emphasized that the size of the PS domains in the PMMA matrix can be controlled by varying the polymer molecular mass combination,\(^{[34]}\) or weight ratio,\(^{[35,37,38]}\) or the humidity of the atmosphere in which the film is deposited,\(^{[34]}\) or with post-deposition annealing.\(^{[38]}\) The deposition protocol reported herein is distinct from these earlier works in that the molecular mass and weight ratio of the two polymers is held constant and the PS domain size is controlled only by adjustment of the overall concentration of the polymer blend solution: A higher concentration yields larger PS domains suitable for transparent electrodes, whilst low concentrations give

![Figure 1. Schematic of electrode fabrication process.](image)
very small island sizes that couple strongly with incident light (Figure S2, Supporting Information). Crucially this process does not require control over humidity or the need for post-deposition annealing, and so is more amenable to upscaling.

An important step in the electrode fabrication processes is the brief UV/O3 treatment to remove PMMA at the bottom of the holes formed by PS removal; Figure 1, step 3. PMMA is uniformly etched under exposure to UV radiation\(^{39,40}\) and so this treatment ensures the holes in the PMMA film extend all the way through to the underlying copper film, as evidenced by the cross-sections of atomic force microscopy (AFM) images (Figure 2: Figure S1g, Supporting Information), forming a clear pathway for the etchant to travel to the surface of metal film. This step is necessary to achieve a high density and uniform distribution of holes in the copper film, without which a significant proportion of holes formed by removal of PS do not extend down to the underlying copper (Figure S1f, Supporting Information).

Etching of the copper film through the PMMA mask (Figure 1, step 4) is achieved by dipping the substrate for 15–20 s into the low-cost etchant ammonium persulphate, which is a common oxidizing and bleaching agent. The etching process is very rapid because the metal thickness is very low, although it can be further speeded up by increasing the concentration of the etchant.

The PMMA mask is removed by ultrasonic agitation in toluene, followed by glacial acetic acid. Glacial acetic acid simultaneously dissolves residual PMMA and any oxide layer at the surface of the copper film that may have formed if the etching processing is performed in air. Glacial acetic acid is known to preferentially remove copper oxides from the surface of copper leaving the metal surface residue free.\(^{27,41}\) Notably, for PMMA layers that are \(\leq 25\) nm thick acetic acid treatment alone is sufficient\(^{41}\) to completely remove the PMMA layer. Together the process illustrated in Figure 1 enables the fabrication of copper electrodes with a random distribution of \(\approx 100\) million circular apertures \(\text{cm}^{-2}\), the average size of which can be altered by changing the concentration of the polymer blend, which enables control within the diameter range of 50–1000 nm (Figure S2, Supporting Information).

For OPV device applications the sheet resistance of the window electrode is a key determinant of device performance and in practice cannot exceed 20 \(\text{Ω sq}^{-1}\) without incurring unacceptable electrical losses.\(^{42–44}\) To determine the thickness needed to achieve the highest far-field transparency, whilst retaining a sheet resistance below 20 \(\text{Ω sq}^{-1}\), different thicknesses of copper films ranging from 9 to 17 nm were used to fabricate electrodes with the same aperture size distribution shown in Figure 2a. The total transmittance and reflectance (i.e., specular and scattered combined) is shown in Figure 3 for films with and without apertures. As expected the transmittance is highest for the thinnest film and the reflectance is greatest for the thickest film. The transmittance is increased by \(\geq 20\)% in absolute terms when apertures are introduced into the film, across the wavelength range of 400–850 nm. For wavelengths below \(\approx 550\) nm the transmittance is increased by 20–25% for all metal thicknesses, which can be rationalized primarily in terms of a reduction in absorption, since the aperture density and size distribution shown in Figure 2 corresponds to removal of one quarter (24 \(\pm 1\)% of the metal electrode. For wavelengths above \(\approx 550\) nm it is evident that the total reflectance is dramatically reduced upon incorporation of apertures, although this does not entirely translate into a commensurate increase in transparency. For example, for an 11 nm thick film the reflectance at 850 nm is reduced from \(\approx 45\)% to \(\approx 12\)% , a decrease of 33%, whilst the transparency increases from 50% to 75%; an increase of only 25%. The \(\approx 8\)% difference is attributed to parasitic absorption due to surface plasmon excitation in the copper electrode\(^{14,45,46}\) which, as shown in the subsequent section, can be largely mitigated by appropriate selection of the adjacent charge transport layer.

![Figure 2](image-url)

**Figure 2.** a) SEM showing the morphology of 11 nm thick copper films with apertures. Inset: a photograph of an 11 nm thick copper electrode with (right) and without (left) apertures. b) Cross-section taken from an AFM image of the same sample as in (a) showing the depth of the apertures. c) Histogram showing the size distribution of apertures computed for a \(20 \times 20 \mu\text{m}^2\) AFM image.
The data in Figure 3 show that the highest transparency is achieved using the thinnest copper film. However, since sheet resistance increases with decreasing film thickness, as shown in Figure 4a, a compromise must be struck between these properties for optimal performance as a window electrode in OPVs. It is evident from Figure 4a that incorporation of apertures increases the sheet resistance for all metal thicknesses, consistent with scattering of electrons at the aperture edges. The sheet resistance of films with apertures is only below 20 Ω sq⁻¹ for a metal thickness above 14 nm. However, for application in OPVs the window electrode is invariably buried beneath a wide bandgap charge transport layer such as ZnO or PEDOT:PSS, which both require annealing at low temperature (100–200 °C) for optimal performance. In this study a solution processable ZnO electron extraction layer was used, which can be processed using a variety of deposition methods including screen printing and doctor blading. The ZnO annealing step was initially performed at 120 °C which, for an 11 nm thick copper film with apertures, resulted in a notable reduction in the sheet resistance of the electrode from 29.8 ± 0.7 to 24.2 ± 0.7 Ω sq⁻¹. Increasing the annealing temperature to 180 °C resulted in a larger reduction in sheet resistance to 17.9 ± 0.4 Ω sq⁻¹. Remarkably the sheet resistance continued to decrease upon long term storage in a glove box, reaching ≈9.6 Ω sq⁻¹ after five months storage. Over the same period there is a small reduction in the far-field transparency of ≈2.6% across the visible spectrum (Figure S3, Supporting Information), although in terms of the electrode Haacke figure of merit (FoM), which is widely used to compare the performance of window materials, the benefit of the large reduction in sheet resistance far outweighs the detrimental effect of the small reduction in transparency: The FoM increases from 0.0099 to 0.0135 Ω⁻¹. To our knowledge, for a Cu-based window electrode, this FoM has only been exceeded by electrodes.
with a more complex triple layer oxide–metal–oxide structure fabricated by sputtering deposition (see Table S1, Supporting Information). X-ray diffraction analysis (Figure S4, Supporting Information) reveals that this ≈66% total reduction in sheet resistance cannot be attributed to a change in crystallinity of the copper film\cite{a14} since the intensity of the reflections from Cu crystal planes does not change, consistent with the very high surface melting temperature of copper (\(>400^\circ\)C).\cite{a52,a53} An alternative explanation is that the intrinsic conductivity of the ZnO film is increased when annealed at the higher temperature of 180 °C and/or the conductivity is increased due to doping of the ZnO by Cu that diffuses from the underlying Cu film. To test this hypothesis conductive atomic force microscopy (C-AFM) analysis was performed on nanoaperture Cu electrodes covered with a 62 nm thick ZnO overlayer annealed at 120 and 180 °C. It is evident from the C-AFM images and the corresponding cross-sections given in Figure 5, that the current drop across the aperture when annealed at 120 °C is very abrupt and distinct (indicated by green arrows), and so the boundary of the aperture in the underlying Cu layer is well-defined. Conversely, the electrode annealed at a higher temperature of 180 °C shows a more gradual drop in current as the probe moves over the site of an aperture in the underlying Cu film and has a minimum at the centre of the aperture, so the boundaries of the apertures appear more diffuse in the current map. These spatially resolved electrical measurements are compelling evidence for an increase in the conductivity of ZnO in the plane of the oxide close to the metal film, which is consistent with the reduction in measured sheet resistance. Notably however, the applied voltage for the electrode annealed at 180 °C is twice that needed to achieve the same current as compared to the film annealed at 120 °C (8 vs 4 V), which seems to contradict the conclusion that the conductivity of the ZnO layer is increased in the sample annealed at 180 °C. It is however important to note that C-AFM measures the conductance normal to the plane of the film surface, and so it is sensitive to variations in the conductivity of the uppermost surface of the oxide as compared to the bulk, which may have become more resistive due to higher barriers to charge extraction/injection and transport at higher annealing temperature.\cite{a54}

Whilst solid state diffusion of Cu into the ZnO layer would be expected to be accelerated by thermal annealing, diffusion of Cu into oxides at very low temperature is also known,\cite{a22,a55,a56} and so electrical doping of the ZnO layer by Cu also offers an explanation for the reduction in electrode sheet resistance upon annealing. Direct evidence for Cu diffusion from the underlying Cu film into the ZnO layer is provided by XPS analysis of a Cu electrode buried beneath a 62 nm thick ZnO layer annealed at 120 and 180 °C (see Figure S5 and Table S2, Supporting Information). The escape depth of Cu 2p photoelectrons is limited to less than 10 nm and so the presence of clearly defined Cu 2p peaks in the spectrum for the film annealed at 180 °C, confirms that Cu has diffused through the entire thickness of the ZnO layer and the process is thermally accelerated. Based on this XPS analysis the elemental composition at the ZnO surface is estimated to be <1% Cu. Evidence for Cu-doping of the ZnO film at the sites above apertures in the Cu film is provided using spatially resolved energy dispersive X-ray spectroscopy (EDXS) (see Figure S6 and Table S3, Supporting Information) although, unlike XPS, EDXS probes the elemental composition of the entire ZnO thickness. It is clear from the composition derived from the EDXS analysis (Table S3, Supporting Information),

**Figure 5.** C-AFM images showing the current profiles obtained by applying a bias of 4 and 8 V, respectively, for Cu nanohole electrodes with 62 nm ZnO annealed at a)120 °C and b)180 °C. c,d) The cross-sections of (a) and (b) respectively along the lines shown.
Information) that the proportion of Cu in ZnO regions adjacent to the underlying Cu is very much higher than 1%, which evidences very extensive Cu diffusion into the ZnO overlayer. The large difference between the Cu concentration derived from XPS and EDXs measurements provides compelling evidence that the Cu concentration in the ZnO film normal to the plane of the film is not homogenous, but concentrated in the region nearest the Cu film. This gradient in Cu concentration offers a plausible explanation for the apparent reduction in conductivity of the ZnO film measured using C-AFM, since the conductivity of Cu doped ZnO is known to depend strongly on Cu concentration.\cite{57,58} ZnO is known to exhibit n-type conductivity\cite{59,60} and it has been shown that at low concentrations (<1%) Cu dopants act as deep acceptors, which reduce the n-type character by acting as a compensating center.\cite{61} Conversely at higher concentrations of >3% the conductivity is increased due to accumulation of metallic Cu at the grain boundaries, which reduces the contact resistance between the ZnO crystallites.\cite{57}

The high concentration of Cu dopant nearest the Cu film could therefore give rise to the observed reduction in the electrode sheet resistance. At the same time the low concentration of Cu dopant at the uppermost surface of the 62 nm ZnO film would reduce the n-type character of the oxide thus increasing the barrier to electron injection into the conduction band, which would manifest as an apparent reduction in the conductivity normal to the plane of oxide film. To confirm that an increase in the conductivity of the ZnO overlayer is the reason for the reduction in the large electrode sheet resistance, the ZnO layer on five month old electrodes with a sheet resistance of 9 $\Omega$ sq$^{-1}$ was selectively removed by etching with acetic acid (Figure S7, Supporting Information).\cite{27,41} After this treatment the sheet resistance increases to $\approx 40$ $\Omega$ sq$^{-1}$, which confirms that the doped ZnO overlayer is the reason for the reduction in sheet resistance. Notably, $\approx 40$ $\Omega$ sq$^{-1}$ is $\approx 10$ $\Omega$ sq$^{-1}$ higher than that of freshly etched Cu electrodes; 29.8 $\pm$ 0.7 $\Omega$ sq$^{-1}$. Such an increase is however not unexpected since: (i) the Cu that has diffused into the ZnO layer (and is thus removed upon etching) has reduced the thickness of the metal film; (ii) at the interface between the Cu film and the ZnO overlayer it is plausible that the Cu has been partially oxidized, forming a thin Cu oxide interlayer which would be readily etched by acetic acid,\cite{27,41} and so this would also reduce the Cu metal thickness.

A Cu film thickness of 11 nm was chosen to demonstrate utility of this electrode and the window electrode in an OPV device. In OPVs the ZnO layer serves primarily as a charge extraction layer although, like other wide bandgap charge extraction materials, can also serve as an antireflecting layer when used in conjunction with metal film window electrodes: Figure S8 of the Supporting Information shows how the transparency of an 11 nm copper film (without apertures) is improved as a function of the ZnO layer thickness (20–96 nm). The average transparency of the copper electrode (400–800 nm) with apertures is increased from 75.9% to 84.1% using the optimized ZnO thickness of $\approx 6$ nm (Figure 4b), which is comparable to that achieved using thinner copper films without apertures reported previously (Table S1, Supporting Information).\cite{22,24,28}

Importantly, the inclusion of ZnO does not complicate the process of electrode fabrication, since wide bandgap charge extraction layers are an essential component of high performance OPVs regardless of the choice of electrodes. To demonstrate these electrodes as window electrodes in OPVs, devices were fabricated with the architecture: Cu (11 nm)/ZnO ($x$ nm)/MoO$_3$ (10 nm)/Ag (80 nm), where $x = 20$–62 nm. Whilst the highest electrode transmittance was achieved using a ZnO thickness of 62 nm, the efficiency of an OPV device depends on a complex interplay of optical and electrical factors,\cite{53,62,64} and so devices with different thicknesses of ZnO ranging from 20 to 62 nm were tested (Table S3 and Figure S9, Supporting Information). The device power conversion efficiency is maximized when the thickness of ZnO is 33 nm. Champion devices achieved a power conversion efficiency of 4.9 and 6.8% for devices using an 11 nm thick copper electrode without and with apertures, respectively. The large difference in power conversion efficiency results from a $\approx 35$% improvement in short-circuit current density ($J_{sc}$) in devices using the electrode with apertures as shown in Figure 6, which is consistent with more light entering the device. Crucially, there is no significant difference in open-circuit voltage ($V_{oc}$) or device fill-factor (FF), which is consistent with the expectation that the apertures in the copper film electrode are sufficiently small not to require the use of a highly conducting polymer to span the apertures.

### 3. Conclusion

In summary, we have demonstrated a novel approach to simultaneously reducing intraband absorption losses in optically thin copper films for wavelengths below $\approx 550$ nm and dramatically suppressing reflection for wavelengths above $\approx 550$ nm, which is based on incorporation of $\approx 100$ million
circular apertures per cm² into the copper film with a mean aperture diameter of ~500 nm. Additionally, we have described a method for the realization of such an electrode that could be applied to other thin metal films. The advantage of this method is that the mask self-organizes at room temperature from a single solution, the metal is deposited by simple vacuum evaporation, and all subsequent steps are solution-based processes using widely available low-cost chemicals based on earth abundant elements, without the need to control humidity or for post-deposition annealing. Consequently, there is considerable potential for scaling these electrodes for OPV applications. Remarkably, when this electrode is constrained beneath a solution processed ZnO layer, widely used as an electron transport layer in OPVs, brief thermal annealing at only 180 °C dramatically improves the electrode conductivity due to spontaneous diffusion of Cu into the ZnO over layer. This process is particularly important for improving the conductivity across those regions above apertures in the Cu film, which ensures that the device fill-factor is not degraded as compared to that achieved using an electrode without apertures in the Cu film. Notably, in the current study the Cu electrodes are supported on glass for ease of handling. However, we have previously demonstrated that unpatterned optically thin Cu films of the same thickness have identical properties on glass and plastic substrates when using the metal deposition protocol used in the current work. Since the approach reported herein for the formation of apertures in Cu films is compatible with plastic substrates, there is no barrier to translating this approach to plastic substrates for the realization of flexible OPVs.

4. Experimental Section

Substrate Cleaning: Glass substrates of the required dimension (12 × 12 mm for OPV devices and 26 × 26 mm for electrode characterization) were cut from 1.2 mm thick glass microscope slides (Academy) and 12 × 12 mm glass substrates with an 8 mm wide ITO strip were purchased from Thin Film Devices Inc. with an ITO stated thickness of 145 nm ± 10 nm and a sheet resistance of 15 ± 3 Ω sq⁻¹. Both types of substrates were cleaned by ultrasonic agitation in a diluted solution of surfactant, deionized water, acetone, and IPA for 30 min each followed by drying with a stream of nitrogen and UV/O₃ treatment for 15 min.

Mixed Monolayer Deposition: For glass substrates, a mixed monolayer was deposited prior to evaporation of Cu by exposing the substrates to vapors of MPTMS (Sigma-Aldrich) and APTMS (Sigma-Aldrich) at 50 mbar for 4 h immediately after UV/O₃ treatment.

All electrode and device fabrication were carried out in a nitrogen filled glove box with an O₂ level <1 ppm unless otherwise stated. Evaporation of metals and metal oxides was carried out with a CreaPhys Organic Molecular evaporator colocated in the same glove box. The thickness of deposited layers was monitored using a carefully calibrated quartz-crystal microbalance mounted adjacent to the substrate. All metals were thermally evaporated from tungsten boats. MoO₃ was thermally evaporated from a powder of MoO₃, it is known that during vacuum evaporation it is necessary to anneal both the substrate in the etchant for 15 min to fabricate the ETL. The enhanced device performance obtained by incorporating an ultrathin layer of PEI or poly-(ethyleneimine)-ethoxylated has already been reported. Therefore, a thin layer of PEI was spun on top of ZnO as a capping layer following the annealing process to maximize device performance. PCE10 (poly(4,8-bis-[5-(2-ethylhexyl)thiophen-2-yl]benzo[1,2-b;4,5-b’]dithiophene-2,6-diyi-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]-thiophene-2-carboxylate-2-6-diyi)]) and PC71BM [(6,6)-Phenyl-C₆₁-butryc acid methyl ester] were mixed in 2:3 mass ratio to make a 35 mg mL⁻¹ solution in chlorobenzene (97%) and 1,8-diiodooctane (3%) and deposited by spin-coating from a static start at 3000 rpm for 120 s to form the photoactive layer. These slides were left inside the evaporator overnight and MoO₂ (10 nm at 0.1–0.2 Å s⁻¹) was deposited as the HTL followed by Ag (80 nm at 1.0–1.2 Å s⁻¹). Notably, whilst the molybdenum oxide layer is deposited from a powder of MoO₂, it is known that during vacuum evaporation it is expected to be partially reduced to MoO₂₋ₓ, where x < 0.3. Ag was deposited through a shadow mask to give an electrode area of 0.06 cm².

Characterization of OPV Devices: Current density–voltage testing was performed in the dark and under 1 sun simulated solar illumination...
using a Keithley 2400 source measurement unit and a custom Labview interface using an ABET technologies Sun 2000 Solar Simulator. The intensity was set to 100 mW cm\(^{-2}\) over the AM 1.5G solar spectrum. The light source was calibrated using a calibrated silicon diode. OPV devices were measured through a mask having a pixel area of 0.013 cm\(^2\). EQE measurements were done using a white light xenon arc lamp (Scientech SF150), monochromator (Photon Technology International), focusing and splitting lenses, current–voltage amplifier (Femto DHPCA-100), lock-in amplifier (Stanford Research SR830 DSP), and a custom Labview interface.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors would like to thank the United Kingdom Engineering and Physical Sciences Research Council (EPSRC) for funding (Grant No. EP/N009096/1) and the University of Warwick for the award of a Chancellor’s International Scholarship to H.J.P. All data supporting this study are provided as supplementary information accompanying this paper.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

copper, photovoltaics, polymer blend lithography, solar cells, transparent electrodes

Received: April 27, 2018
Revised: June 25, 2018
Published online: July 23, 2018
