Indium-free multilayer semi-transparent electrodes for polymer solar cells

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**Abstract**

We have explored the fabrication of indium-free electrodes for use in a PCDTBT:PC\(_{70}\)BM organic photovoltaic (OPV) device, and compare different multilayer electrodes as the device anode. Two oxide/metal/oxide structures were investigated that consisted of MoO\(_3\)/Ag/MoO\(_3\) (MAM) and TeO\(_2\)/Ag/MoO\(_3\) (TAM) multilayers. Using scanning electron microscopy measurements, we find that the electrode utilising a TeO\(_2\) seed layer encouraged the growth of a more continuous silver layer at low film thickness relative to an MoO\(_3\) seed layer, and thus combines enhanced optical transmission (by around 7%) with lower sheet resistance (14 \(\Omega/\square\)). This enhanced optical transmittance results in an increased short-circuit current in photovoltaic cells, with TAM-based devices having a power conversion efficiency around 6% higher than those fabricated using a comparable MAM electrode.

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1. Introduction

In the decade to the end of 2014, world primary-energy consumption grew on average by 2.1% per year [1]. Against this background there is increasing concern about climate change, resource constraints and the security of energy supply, leading to great interest in renewable energy generation. Photovoltaics are expected to play a major role in this sector, and whilst silicon based systems currently dominates the market [2], organic photovoltaics (OPVs) are a promising route to lowering the cost of solar power. The solution processed nature of the photoactive layer allows for the possibility of high throughput production via roll-to-roll techniques such as spray coating or printing [3,4], and in addition OPVs can be fabricated on flexible, lightweight substrates such as PET - [5-7] or even metal foils [8,9].

Due to its combination of high transmittance and good conductivity, indium tin oxide (ITO) is currently the ubiquitous material used as the transparent front electrode in OPVs. There are, however, concerns about the cost and scarcity of indium [7,10] and the embodied energy of the ITO layer [11,12]. Furthermore, high quality ITO is not easily compatible with the cheap, flexible polymer substrates that facilitate roll-to-roll production processes, as the brittle-nature of ITO results in a significant increase in sheet resistance after repeated bending [13,14]. Furthermore, such polymer substrates cannot tolerate the high temperatures that are commonly used in the deposition of highly conductive ITO. This second limitation leads to the sheet resistance of ITO on PET being around five times higher than that of similar ITO layers on glass [5,15-17].

There has thus been significant interest in the development of alternative materials for use as transparent conductive electrodes in OPVs. Here, possible replacements include the highly conductive polymer PEDOT:PSS in combination with metal grids [18,19], carbon nanosheets [20], silver nanowires [21-23] and oxide/metal/oxide stacks. In such oxide/metal/oxide multilayer electrodes, the initial oxide layer acts as a ‘seed layer’ for the subsequent growth of an ultrathin metal film. When used in an OPV, the metal film provides high lateral conductivity ensuring a suitably low series resistance, with the second oxide layer facilitating charge extraction or charge-blocking from the device [24,25]. In addition to their electronic functionality, such oxide layers also suppress reflection from the metal film and maximise optical transmittance [26-29].

In this paper, we explore two different oxide/metal/oxide stacks as the hole extracting electrode in an OPV device based on the polymer:fullerene blend PCDTBT:PC\(_{70}\)BM. Whilst MoO\(_3\)/Ag/ MoO\(_3\) (MAM) electrodes have previously been investigated for use...
in OPVs [30–33], TeO₂/Ag/MoO₃ (TAM) electrodes have not. One study which investigated a TeO₂/Ag/PEDOT:PSS electrode [34] suggested that a tellurium dioxide seed layer should lead to an enhanced short circuit current ($J_{SC}$) in comparison with an equivalent MoO₃/Ag/PEDOT:PSS structure, resulting from the larger (real-part) refractive index of TeO₂ [27]. Whilst the devices fabricated using such electrodes achieved a promising performance, the expected enhancement in $J_{SC}$ resulting from the use of TeO₂ was not verified experimentally. Here we find that replacement of the MoO₃ seed layer by TeO₂ leads to significantly higher transmittance at low silver thickness, attributable to the formation of a more continuous silver layer, as observed by scanning electron microscopy (SEM). When applied as the window electrode in PCDTBT:PC₇₀BM polymer solar cells the improved transmittance of the TAM electrode results in an increased $J_{SC}$ in comparison to devices based on a MAM electrode.

2. Experimental

The TAM and MAM devices explored were deposited upon 1.1 mm thick quartz-glass substrates. As a control, identical devices
consisting of a MoO₃ hole-extraction layer deposited on an ITO electrode were also fabricated. Both quartz-glass substrates and pre-patterned ITO films were purchased from Ossila Limited. To prepare the quartz-substrates, they were initially cleaned by sequential sonication in warm Helmanex solution, IPA and deionised water for 5 min before being dried with compressed nitrogen and transferred to a nitrogen glovebox connected to a thermal evaporator. All subsequent thin-film evaporations were performed at a base pressure of $<5 \times 10^{-6}$ mbar through a shadow mask. Evaporation of molybdenum oxide pellets (99.95%, Testbourne), tellurium dioxide powder (99.995% trace metals basis, Sigma-Aldrich) and silver shot ($\geq$ 99.99% trace metals basis, Sigma-Aldrich) were performed at rates of 0.3, 0.3 and 5.0 Å/s–1 respectively. Transmittance spectra were measured using a Horiba FluoroMax-4 and are referenced to air. Sheet resistance was measured using a 4 point probe. SEM images were recorded using an FEI Nova NanoSEM 450 scanning electron microscope. A solid-state backscatter detector was used with a 3 kV primary beam, 5 mm working distance and a $-4$ kV beam deceleration field applied. Atomic force microscopy measurements were obtained using a Veeco Dimension 3100 with tips from Budget Sensors (300G-Al). Data analysis was performed using the Gwyddion software package.

The active layer of the OPV device was based on a blend of the polymer PCDTBT with the fullerene acceptor PC$_{70}$BM. The PCDTBT solution was prepared by adding the dry polymer to chlorobenzene, after which it was stirred at 70 °C for 24 h before being added to PC$_{70}$BM to produce a 1:4 blend of PCDTBT:PC$_{70}$BM at a concentration of 20 mg/ml. The solution was then heated to 70 °C and stirred for a further 24 h to fully solubilise both materials. This solution was cooled to room-temperature, filtered with a 0.45 μm PTFE filter and spin-coated onto the anode at a spin speed between 600 and 2000 rpm, producing a layer having a thickness between 50 and 105 nm (as measured using a Dektak surface profilometer). A top cathode layer was then deposited onto the active layer by a sequential thermal evaporation of 6.5 nm calcium followed by 100 nm aluminium. In all cases, devices thus had a layer structure of glass/anode/PCDTBT:PC$_{70}$BM/Ca/Al. Finished devices were encapsulated using a glass slide and a UV epoxy (Ossila Ltd.) that was cured under a UV lamp for 30 min before being removed from the glovebox for testing. OPV devices were tested using a Newport 92251A–1000 solar simulator (AM1.5 spectrum at an intensity of 1000 W/m$^2$) through a 0.025 cm$^2$ aperture mask used to define the illuminated area. The data presented represents an average over 16 devices from 4 separate substrates for each type of anode tested. We only report the efficiency of the best 50% of devices, thus excluding pixels containing a significant defect, whilst avoiding the use of a statistical method that is open to user bias.

The optical properties of electrodes and OPV devices were modelled using a freely available program based on the transfer matrix method [35]. The optical constants for ITO, Ag, Al and Ca were taken from the library associated with this model, whilst those for MoO₃, TeO$_2$ and the photoactive blend were determined using an M2000v J.A. Woollam Co. spectroscopic ellipsometer.

3. Results and discussion

3.1. Optical and electrical properties of TeO$_2$ and MoO$_3$ based electrodes

To explore the effect of the structure of the oxide/metal/oxide multilayers on their optical properties, we fabricated a series of structures in which the thickness of the metal (silver) film was varied. The thickness of all films was determined by the film thickness monitor in the evaporation chamber. Note that such thicknesses should be considered as an average value, as the films are highly structured at nanometre length-scales (vide infra). In Fig. 1(a) and (b) we plot transmittance spectra for multilayer MAM electrodes as the silver-film thickness was varied between 4 and 10 nm (part (a)) and 10 and 16 nm (part (b)). In Fig. 1(c) and (d), we similarly show transmittance spectra for the TAM electrodes as the thickness of the silver was varied between 4 and 8 nm (part (c)) and 8 and 16 nm (part (d)). In all cases, the thickness of the oxide films (both MoO$_3$ and TeO$_2$) was fixed at 10 nm. In line with other reports on oxide/metal/oxide structures, we find that (counter-intuitively) the transmittance of the film initially increases with increasing thickness of the silver layer, before reaching a maximum at a thickness termed the percolation threshold. Above this thickness, the transmittance of the multilayer reduces, an effect particularly pronounced at longer wavelengths as a result of the silver film acting as a mirror. It can be seen that for our MAM electrodes the maximum transmittance occurs at a silver thickness of 10 nm; a result comparable to other literature values for the percolation threshold of Ag on MoO$_3$ (being between 10 and 11 nm [30–32]). For the TAM electrodes, the maximum transmittance occurs at a reduced silver thickness of 8 nm. We summarise the average transmittance of the MAM and TAM electrodes over the wavelength-range 350–700 nm in Fig. 1(e), where it can be seen that over the Ag thickness range 4–8 nm average transmittance rises from 62–67% for the MAM structure and 71–76% for the TAM structure.

We have also measured the sheet resistance of the films as a function of the thickness of the silver layer, with data presented in Fig. 1f. It can be seen that for both the MAM and TAM electrodes there is a rapid decrease in sheet resistance as the thickness of the silver layer increases, however this decrease saturates as the film thickness exceeds the percolation threshold.

In Fig. 2, we illustrate the potential benefits of the use of the TAM structure as a transparent front electrode in an OPV, by plotting the relative transmission of the MAM and TAM electrodes at their percolation threshold (point of maximum optical transmittance). We find that the TAM electrode having an 8 nm thick silver layer has a maximum transmittance of 81.3%, an average transmittance (between 350 and 700 nm) of 76.3% and a sheet resistance of 13.9 Ω/s–1. In contrast a MAM electrode having a 10 nm thick silver layer has reduced maximum transmittance of 78.2% and an average transmittance (350–700 nm) of only 70.9%, with the sheet resistance being slightly lower at 8.3 Ω/s–1. For comparison, the reference ITO electrode (150 nm) coated with a 10 nm thick MoO$_3$ layer has a maximum transmittance of 89.8%, an
average transmittance (350–700 nm) of 83.8% and a sheet resistance of 15.9 Ω/□. Figs. 1e and f clearly show that for low thickness of the silver film, the TAM electrode has a significantly higher transmittance and somewhat lower sheet resistance than the corresponding MAM electrode. As the thickness of the silver increases, the relative improvement in transmittance afforded by the use of a TAM structure is reduced, with the transmission of the TAM electrode being only slightly greater than that of the MAM electrode at and above the percolation threshold. Above an Ag thickness of 8 nm, the sheet resistances of the TAM and MAM electrodes are similar.

3.2. Origin of enhanced transmittance in TeO2 based electrodes

The trends observed in transmittance and sheet resistance as the silver layer thickness increases result from the growth characteristics of the metal film. As silver is deposited, it initially forms isolated islands and chains (so-called Volmer–Weber growth), resulting in poor lateral conductivity due to a lack of continuous conduction pathways. As the film thickness increases, the silver particles coalesce to form an increasingly uniform and continuous layer. The formation of continuous conduction pathways then results in a rapid reduction in sheet resistance, a process that slows once a uniform and well-connected film has been created. Whilst a number of studies have observed these same trends for a variety of oxide/metal/oxide structures, there is some disagreement as to the exact source of the initial increase in transmittance as the layer is deposited. Some studies attribute it simply to light scattering by the unconnected islands, with this scattering effect being reduced as the layer becomes more uniform [36–38]. Others attribute it to surface plasmon resonance at the optimum thickness, with excitation of the surface plasmon only being achieved effectively for the structure which obtains maximum transmittance (due to the different sizes and spacing of metallic chains in films with different thickness) [39–41]. One recent study observed that as the film thickness increased, the film structure changed from one characterised by narrow cracks between metal islands and chains (usually unconnected) to a continuous structure with a random collection of nanoholes. It was proposed that the nanoholes allow for the formation of surface plasmon polaritons which propagate through the holes, with light then being re-radiated, thus increasing transmission. At higher thicknesses, such nanoholes become covered by the silver layer, and transmittance again drops [42].

We propose that our results can be explained by the formation of a more continuous silver layer at low thickness on a tellurium dioxide seed layer in comparison to silver films grown on a molybdenum oxide seed layer. The formation of a more continuous Ag layer on TeO2 is consistent with the observed improvement in transmittance due to reduced scatter from unconnected islands, whilst the reduced sheet resistance at low silver thickness is similarly explained by the more continuous silver film. Overall, this effect allows the optimised TAM electrode to have a notably higher transmittance than can be obtained using a MAM electrode. This proposal is also consistent with the percolation threshold being reached at a comparatively reduced silver thickness on the TeO2 seed layer compared to that observed on the MoO3 seed layer (8 nm and 10 nm respectively). Clearly for Ag

![Graphs and images](image-url)
thicknesses above the percolation threshold for both types of electrode, the silver films formed are quasi-continuous and no large differences in transmittance are observed. The formation of a more continuous silver film on TeO$_2$ is commensurate with previous work in which liquid Ag was found to have a slightly lower contact angle on TeO$_2$ than on MoO$_3$ [43]. This is indicative of stronger interactions between the silver and the TeO$_2$, which will increase the energetic favourability of silver atoms becoming positioned on the metal oxide layer rather than aggregating into disconnected clusters. A lower contact angle will thus assist in the formation of a more continuous silver layer by encouraging growth to occur in a layer-by-layer manner (Frank–van der Merwe growth) and reducing the favourability of island formation. The lower contact angle on a TeO$_2$ seed layer can be thought of as showing the improved wettability of liquid Ag on TeO$_2$, which enhances the uniformity of the silver film. We note that modification of the seed layer to achieve a higher surface energy (giving stronger substrate–silver interactions) has previously been found to lead to the formation of a more continuous silver film in MAM electrodes [44].

We have modelled the optical properties of the multilayer stacks using a Transfer-Matrix model to explore whether differences in the refractive index (real and imaginary) of the seed layers play a significant role in modifying the optical transmission of the electrodes Fig. 4.

**Fig. 4.** SEM images of MoO$_3$/Ag and TeO$_2$/Ag bilayers in which the oxide thickness is fixed at 10 nm. Parts (a) and (c) show MoO$_3$/Ag bilayer for a silver thickness 6 nm and 8 nm respectively. Parts (b) and (d) similarly show a TeO$_2$/Ag bilayer again utilising a silver layer having a thickness of 6 nm and 8 nm respectively. Blue scale bars correspond to 500 nm. In each case, we show a magnified image of the film surface in which the length of the (red) scale bar is set at 200 nm.
The model assumes that all layers are uniform and continuous, and thus does not take into account the reduction in transmittance which occurs at silver film thickness below the percolation threshold for an oxide/metal/oxide structure. As input into this model, we have established \( n \) and \( k \) for TeO\(_2\) and MoO\(_3\) using spectroscopic ellipsometry as shown in Fig. 3(a) and (b) respectively. The calculated transmittance of MAM and TAM multilayer electrodes, (both having layer thickness of 10–8–10 nm) are shown in Fig. 3(c). It can be seen that our model suggests that over the wavelength region 380–800 nm, the MAM and TAM electrodes have an average transmittance of 81.2\% and 82.1\% respectively. The small enhancement in transmittance predicted for the TAM electrode results from the lower extinction coefficient of TeO\(_2\) compared to MoO\(_3\), as well as its favourable refractive index (higher at longer wavelengths, lower at shorter wavelengths – see Fig. 3(a)). This result strongly suggests that the enhancements in transmittance in the TAM structures observed for silver thickness less than 10 nm can be attributed to the formation of a more continuous silver film rather than any optical effects resulting from the differing seed layer materials themselves, with the slightly increased transmission for the TAM structures compared to the MAM structures for thicker Ag films attributable to the favourable optical properties of TeO\(_2\).

To further explore the origin of the improved transmittance of the TAM electrodes at low Ag thickness, we have recorded SEM images of bilayer structures consisting of the metal oxide seed layer and an Ag layer. This is shown in Fig. 4, where we plot images for Ag films having a thickness of 6 nm and 8 nm on 10 nm thick seed layers of TeO\(_2\) and MoO\(_3\). It can be seen that the 6 nm thick silver film deposited on MoO\(_3\) (part (a)) is characterised by a series of thin “chains” having a typical width in the range 10–30 nm. Such structures presumably result in a non-continuous pathway for charge-carrier extraction. In contrast, the 6 nm thick silver film deposited on TeO\(_2\) (part (b)) appears to be more continuous in nature and consists of a series of holes having a diameter of around 5–20 nm. Importantly, such films contain fewer isolated (unconnected) features. When the silver thickness is increased to 8 nm, the film on MoO\(_3\) (part (c)) appears to have formed a more connected structure, whilst the film on TeO\(_2\) (part (d)) exhibits fewer holes than with the 6 nm thick film. In fact, when we compare the magnified images of an 8 nm Ag film on MoO\(_3\) (part (c)) with a 6 nm Ag film on TeO\(_2\) (part (b)) we find that they appear qualitatively similar. This finding is commensurate with our measurements of their optical properties, in which we found that the percolation threshold occurred for Ag films that were 2 nm thinner on a TeO\(_2\) seed layer compared to those on MoO\(_3\). Estimates of the coverage of the silver films from these SEM images also fit with this conclusion (see Table S2).

### 3.3. Indium-free polymer solar cells

In order to demonstrate the practical use of such electrodes, we have fabricated bulk heterojunction polymer solar cells based on a PCDTBT:PC\(_{70}\)BM photoactive layer using MAM, TAM and ITO/MoO\(_3\) anodes. In each case, multilayer electrodes having the maximum transmittance were used; the MAM electrode thus utilised a 10 nm Ag layer whilst the TAM electrode incorporated a slightly thinner 8 nm Ag layer.

Again, we have used Transfer Matrix modelling to predict the optimum thickness of both the oxide layers in the multilayer electrode and the thickness of the PCDTBT:PC\(_{70}\)BM active-layer [35]. The model allows us to predict the short-circuit current of a device by assuming an internal quantum efficiency of 100\% (i.e. ignoring possible charge extraction losses). We term this photocurrent as \( J_{SC\_100\%} \). In our model, we adjust the thickness of the hole-extraction layer (the metal oxide layer placed adjacent to the active layer), the thickness of the seed layer positioned beneath the Ag and the thickness of the active semiconductor layer. We find that for seed layers having a thickness \( \geq 30 \) nm, our model predicts that \( J_{SC\_100\%} \) is maximised, however this photocurrent is only marginally larger than that predicted when using a 5 nm seed layer. In fact, we find that by adjusting the thickness of the active layer, the \( J_{SC\_100\%} \) takes values between 11.50 and 11.59 mA/cm\(^2\) as the seed layer thickness varies from 5 to 40 nm. We note, however, that thicker seed layers require the use of slightly thicker active layers (by around 10 nm) in order to maximise \( J_{SC\_100\%} \). Experimentally, increasing the thickness of the active layer is known to increase loss within the device as a result of increased non-geminate charge recombination. In addition, we found that a thinner seed layer lead to a slight reduction in sheet resistance and a better correspondence to the modelled transmittance (see Figure S1 and Table S1). For this reason, we used a relatively thin (5 nm) seed layer for the MAM and TAM electrodes – an approach that has also been used in other studies [45]. With this seed layer thickness of 5 nm we find that the average transmittance in the 350–700 nm range rises slightly from 70.9\% to 71.7\% for the optimised MAM electrode and from 76.3\% to 77.1\% for the optimised TAM electrode. Our model predicted that both of these electrodes the optimum value of \( J_{SC\_100\%} \) would occur for a metal oxide HTL having a thickness of 10 nm with the active layer having a thickness of 70 nm. Experimentally, however, we found that the optimum device efficiency occurred when the active-layer was slightly thinner (60 nm) than predicted by the model for both types of multilayer electrode. For devices utilising an ITO/MoO\(_3\) electrode, our model similarly predicted an optimum active layer thickness of 85 nm, however experimental measurements determined the highest device efficiency was realised for an active layer thickness 75 nm (see Tables S3, S4 and S5 for details). In both cases, the discrepancy between the results of the model and the experimental device optimisation likely results from imperfect charge extraction through the active layer; an effect not considered by the model.

We tabulate average device parameters for solar cells fabricated using the three different types of anodes in Table 1. We find that the optimised devices using a TAM electrode had an average PCE of \((4.22 \pm 0.08)\%\) whilst the optimised MAM-electrode devices had a slightly lower average PCE of \((3.94 \pm 0.12)\%\). The improvement in efficiency for devices incorporating the TAM electrode results from a relative enhancement in \( J_{SC} \) by \((8.70 \pm 0.12)\) mA/cm\(^2\) compared with \((8.11 \pm 0.14)\) A/cm\(^2\); an effect that we attribute to the higher transmittance of the TAM electrode. The optimised ITO/MoO\(_3\) reference device had the highest average PCE of \((4.81 \pm 0.09)\%\), again resulting from an enhanced \( J_{SC} \) of \((9.12 \pm 0.24)\) mA/cm\(^2\). It is
worth noting that ITO/MoO3 devices having an active layer thickness identical to that used in the TAM and MAM devices had a slightly lower PCE of 4.49%, with a comparable yet slightly lower JSC than the TAM devices (8.54 ± 0.23) mA/cm². Current-density against voltage curves for typical solar cells incorporating each different anode are shown in Fig. 5.

It is apparent that the ITO/MoO3 based devices were also characterised by a larger VOC than were the devices utilising a MAM or TAM anode. This effect has been observed previously in both MAM [46,47] and has been attributed to diffusion of Ag through the charge extracting metal oxide layer, although such reductions in VOC are not uniformly reported; it is possible that, for example, variations in substrate temperature during the evaporation could result in differences in Ag diffusion. We note, however, that if such a reduction in VOC could be eliminated, then devices utilising the TAM electrode would outperform those based on ITO in which a comparable thickness of active layer has been used.

4. Conclusion

In conclusion, we have fabricated TeO2/Ag/MoO3 (TAM) multilayer electrodes that have an average transmittance of 77.1% over the wavelength range of 350–700 nm. This transmittance is larger than the widely investigated multilayer system consisting of MoO3/Ag/MoO3 (MAM) that has an average transmittance of only 71.7% over the same wavelength range. When used as the semi-transparent electrode in a polymer solar cell, the improved transmittance of the TAM electrode results in an increased JSC in comparison to devices based on the MAM electrode (8.70 vs 8.11 mA/cm²), leading to a small improvement in power conversion efficiency (4.22 vs 3.94%). We note however that such efficiencies are generally smaller than that of devices based on a conventional ITO electrode that reach an optimised efficiency of 4.81%. We conclude therefore that a TAM multilayer electrode is likely to be a promising candidate as an indium free electrode for polymer solar cells, and that tellurium dioxide acts as an efficient seed layer in a multilayer electrode as it encourages the growth of a smooth and continuous silver film.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.solmat.2015.10.010.

References


