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Citation: *Appl. Phys. Lett.* **102**, 183303 (2013); doi: 10.1063/1.4804294

View online: <http://dx.doi.org/10.1063/1.4804294>

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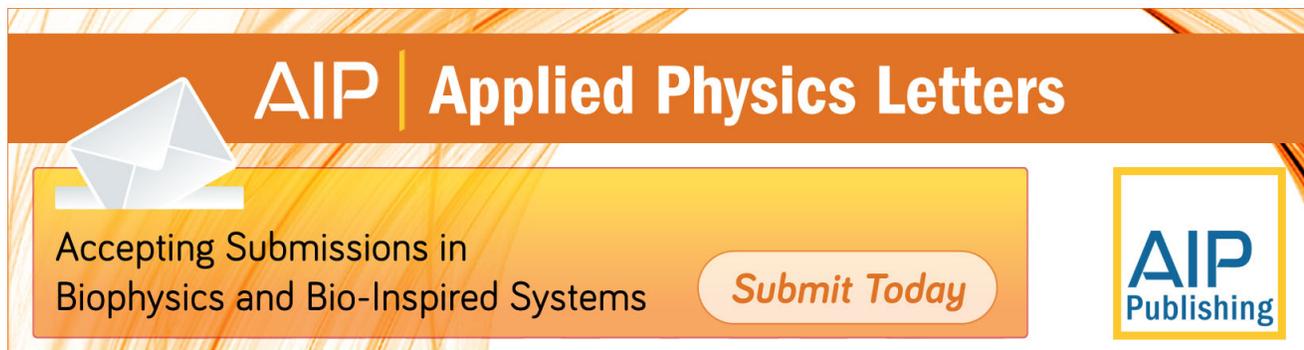
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Air processed organic photovoltaic devices incorporating a MoOx anode buffer layer

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(Received 17 December 2012; accepted 12 April 2013; published online 9 May 2013)

Molybdenum oxide (MoOx) has been shown to act as an efficient hole extraction layer in organic photovoltaic (OPV) devices. However, exposing MoOx films to air is problematic as it is hygroscopic; the uptake of moisture having a negative impact on its electronic properties. Here, we use spectroscopic ellipsometry to characterise the uptake of water, and fabricate PCDTBT:PC₇₀BM based OPVs to determine its effects on device performance. We then show that thermally annealing MoOx reduces its hygroscopicity, permitting it to be processed in air. Using this process, we create air-processed OPVs having PCEs (power conversion efficiencies) of up to 5.36%. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4804294>]

Organic photovoltaic devices (OPVs) have made great progress towards commercialisation. The objectives of 10% power conversion efficiency under AM1.5 illumination coupled with 10 yr operational lifetime now appear to be within reach, with efficiency in excess of 10% for tandem polymer:fullerene systems¹ and evaporated small molecule systems.² Operational lifetimes of several thousand hours have also been demonstrated using robust encapsulation techniques,³ with further improvements expected on the basis of sustained improvements in organic light emitting diode lifetimes which now approach 100 000 h.⁴ However, there still remain manufacturing challenges to be addressed before OPV technology can approach widespread commercial production.

Recent improvements in polymer:fullerene solar cell efficiency and stability have largely come from the synthesis of new polymers that have lower lying HOMO levels and reduced energy gap. A lower lying HOMO level has the twin benefit of allowing more of the energy of each photon to be harvested due to better energy alignment to PCBM,⁵ while also improving the stability of the material by making oxidation more difficult. As such, there has been a recent trend for high efficiency OPVs to utilise polymers with HOMO levels in the region of -5.1 eV to -5.5 eV, including PTB7 (Ref. 6) (-5.15 eV) and PCDTBT⁷ (-5.5 eV). These materials contrast with more well-established polymer electron-donors such as P3HT⁸ and MEH-PPV⁹ that have HOMO levels of around -5.0 eV. It has also been shown that PCDTBT¹⁰ and PCBM¹¹ both have promising stability under ambient conditions.

To utilise such materials having lower HOMO levels also requires the use of hole extraction contacts having a similarly low lying work-function. A variety of such interface layers have been investigated, such as chlorinated ITO¹² and transition metal oxides such as MoOx,⁸ WOx,¹³ and VOx.¹⁴ In particular, MoOx has been studied due to its low lying conduction band (-6.7 eV (Ref. 15)) and its ease of

deposition via thermal evaporation,¹⁶ sputtering,¹⁷ and solution processing.¹⁸ When used as the hole-extracting anode in an OPV device containing an organic semiconductor having a large ionisation potential, the organic semiconductor close to the MoOx interface has been shown to become *p*-doped as a result of charge-transfer¹⁵ with such interfaces supporting efficient hole-extraction.¹⁹ This has permitted OPVs based on the polymer PCDTBT to be created having power conversion efficiencies (PCEs) of over 7%.¹⁰

It is apparent, however, that whilst MoOx can be utilised to produce high-efficiency OPV devices, its use is not without problems. In particular, MoOx is susceptible to loss of oxygen during evaporation which can result in changes in stoichiometry and electronic energy levels.²⁰ In certain states, it is also hygroscopic and can adsorb water to produce a hydrated crystal within a few Langmuir.²¹ It is believed that water species adsorbed into the MoOx crystal either reside between the MoOx clusters in the bulk of the material, changing the cluster size and, as a result, the band gap,¹⁵ or are weakly bound by Van der Waals forces on the surface.^{22,23} Water adsorption can occur on timescales of a few tens of minutes even in a highly pure nitrogen atmosphere with water levels of less than 1 ppm,²¹ and almost instantaneously in air. This sensitivity suggests that understanding—and stabilising—the oxidation and hydration state of MoOx will be a key requirement in any practical manufacturing process.

In this paper we address this issue, and investigate the water uptake into the bulk of thermally evaporated MoOx films. We then apply a simple thermal anneal process to a MoOx film which helps reduce its up-take of water when exposed to ambient conditions. We then use this process to fabricate PCDTBT:PC₇₀BM bulk heterojunction OPVs having a relatively high PCE (5.36%) using an air-based deposition protocol. Our results demonstrate that high-efficiency OPV devices can be fabricated in air; a result that will be an important component in any low-cost manufacturing process.

Pellets of molybdenum (VI) oxide were purchased from Testbourne Ltd and used as received. MoOx was deposited

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via thermal evaporation under a vacuum of 10^{-6} mbar at a rate of 0.2 \AA s^{-1} using fresh molybdenum (VI) oxide pellets for each evaporation. The vacuum chamber was attached to an inert glovebox ($<1 \text{ ppm O}_2/\text{H}_2\text{O}$) allowing samples to be loaded and unloaded without being exposed to the atmosphere. The glovebox was fitted with a molecular sieve and charcoal scrubber through which the box gas is circulated in order to remove volatile organic compounds. A series of different films were prepared; films for device evaluation were deposited on patterned ITO and had a thickness of 10 nm, whilst films for ellipsometry were prepared on a silicon wafer and had a thickness between 15 and 20 nm. To study the uptake of moisture by MoOx, and the effects of thermal annealing under nitrogen on MoOx, *in situ* ellipsometry was performed using a spectroscopic ellipsometer (M2000v, J.A. Woollam Co., USA) to characterise swelling of thin-films. Here, dynamic reflection data (ψ and Δ) were recorded every 10 s with the thickness of the MoOx film extracted using a Cauchy model.²⁴

Organic photovoltaic devices were fabricated on ITO substrates coated with a MoOx film that had undergone a series of different exposure protocols. The active organic layers were prepared by spin-casting either in a nitrogen filled glovebox ($<1 \text{ ppm O}_2/\text{H}_2\text{O}$), or under a laminar flow-hood in ambient atmosphere. Optimised devices²⁴ were based on a blend of the polymer PCDTBT and the fullerene PC₇₀BM, supplied by Ossila Limited. To fabricate thin films, solutions of a 1:4 blend of PCDTBT:PC₇₀BM dissolved in chlorobenzene and then spin-cast on the ITO/MoOx to form a film having a thickness of around 70 nm. A device cathode consisting of a composite calcium/aluminium film (2.5/100 nm) was then deposited on the PCDTBT:PC₇₀BM via thermal evaporation. Devices were finally encapsulated using a glass cover slip and an inert UV-curable epoxy. The finished devices were measured using a Newport 92251A-1000 AM1.5 solar simulator calibrated against a NREL certified silicon reference cell. The values of *PCE*, *J_{sc}*, *FF*, and *V_{oc}* that we quote represent an average of parameters recorded from 20 pixels defined on five separate substrates in which the worst 25% of pixels had been omitted to account for devices in which there was a gross film defect. The errors quoted are defined by the standard deviation about the mean.

To study the effect of the adsorption of water, we explored the performance of MoOx (on ITO) films that had been exposed to the atmosphere for 5 min before being returned to the glovebox and then used to fabricate OPV devices. This anode is then compared to our “benchmark” device in which the ITO/MoOx is never exposed to the atmosphere. We refer to these devices as “air exposed” and “reference,” respectively. We plot the JV curves from the best performing device from each set of fabrication parameters in Figure 1, and summarise device metrics in Table I. It can be seen that reference devices had an average PCE of $(5.00 \pm 0.09)\%$, with air exposed devices having a lower average PCE of $(4.48 \pm 0.07)\%$. We attribute the reduction in PCE of the air exposed devices to the adsorption of water into the bulk of the MoOx film. Previous measurements have shown that MoOx is hygroscopic and that its work-function is sensitive to exposure to water and can change by up to 1.2 eV within a few Langmuir of contact with moisture in

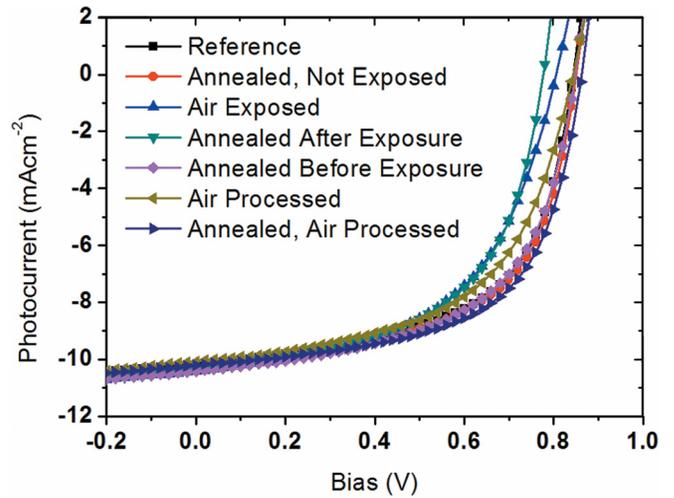


FIG. 1. JV curves under AM1.5 irradiation for best device from each set of fabrication parameters.

the atmosphere.²¹ Other studies have concluded that this results from a change in hydration state,¹⁵ with X-ray scattering used to demonstrate the presence of water molecules adsorbed within the MoOx crystal.²⁵ When used with PCDTBT, the large electron-affinity of MoOx (-6.7 eV) permits charge-transfer doping of the PCDTBT around the MoOx-PCDTBT interface. However the work-function of the hydrated form of MoOx is lower lying by up to 1.5 eV,²¹ with such a reduction in work-function reducing *p*-type doping and thus resulting in internal charge extraction losses as confirmed by a reduction in *V_{oc}* and *FF* as can be seen in Table I.

To explore whether this reduction in device efficiency as a result of air-exposure can be recovered, we have used thermal annealing under an inert atmosphere to remove moisture from the film. Our approach here is based on previous work in which it has been shown that a thermal anneal at temperatures up to 120°C can modify the hydration state of thin film MoOx.²⁵ To test such an approach, we have again exposed ITO/MoOx films to the atmosphere for 5 min; however on return to the glovebox, the ITO/MoOx films were thermally annealed before being used as an OPV anode. A number of different annealing conditions were explored, with data representing optimum processing conditions (120°C for 30 min) shown. The metrics for such devices are shown in Table I and are referred to as “annealed after exposure.” We have also explored applying the same thermal annealing treatment to an ITO/MoOx film *before* it is air exposed (referred to as “annealed before exposure”). Again,

TABLE I. Average OPV device metrics.

	<i>PCE</i> (%)	<i>FF</i>	<i>V_{oc}</i> (V)	<i>J_{sc}</i> (mA/cm ²)
Reference	5.00 ± 0.09	58.1 ± 0.7	0.85	-10.21 ± 0.11
Annealed, not exposed	5.10 ± 0.04	58.7 ± 0.3	0.85	-10.31 ± 0.12
Air exposed	4.48 ± 0.07	53.6 ± 0.8	0.80	-10.45 ± 0.09
Annealed after exposure	4.50 ± 0.07	56.2 ± 0.6	0.78	-10.29 ± 0.09
Annealed before exposure	5.06 ± 0.10	57.0 ± 0.6	0.85	-10.51 ± 0.11
Air processed	4.98 ± 0.12	57.7 ± 1.2	0.85	-10.12 ± 0.09
Annealed, air processed	5.26 ± 0.04	60.2 ± 0.4	0.86	-10.17 ± 0.06

a similar thermal treatment protocol was employed. As a control, we have also applied the same thermal anneal treatment to an ITO/MoO_x film that was not subsequently exposed to the atmosphere. This device is referred to as “annealed, not exposed.”

It can be seen that thermally annealing a film after air exposure results in no improvement of average PCE, with devices having an efficiency of $(4.50 \pm 0.07)\%$ compared with air exposed devices $(4.48 \pm 0.07)\%$. Such a process does not recover the efficiency of the Reference devices $(5.00 \pm 0.09)\%$. It is likely that this failure to recover OPV efficiency results from incomplete removal of adsorbed water in the bulk of the films, resulting in a reduced work-function and poor charge extraction at the MoO_x-active layer interface. The annealing process does not appear to affect the efficiency of the annealed MoO_x film that was not exposed to the atmosphere, as the efficiency of the “annealed, not exposed” OPV devices is $(5.10 \pm 0.04)\%$. If, however, an OPV is made from a MoO_x film that has been thermally annealed in the glovebox before exposure to air, it appears to prevent a significant loss in device efficiency. For example, OPVs having an ITO/MoO_x anode annealed at 120 °C for 30 min before exposure to air had an average PCE of $(5.06 \pm 0.10)\%$; an efficiency comparable to that of the Reference device $(5.00 \pm 0.09)\%$ and larger than that of devices that were air exposed without prior thermal treatment $(4.48 \pm 0.07)\%$. This suggests that annealing promotes a film structure that slows down the adsorption of water.

To test this hypothesis, we have used spectroscopic ellipsometry to explore the rate at which MoO_x films undergo swelling as they are exposed to air. Here, we have studied two nominally identical 20 nm thick MoO_x films deposited on a silicon wafer, with one film initially thermally annealed at 120 °C for 30 min. The results of this experiment are shown in Figure 2(a), where we plot the % change in film thickness as a function of exposure time. It can be seen that the unannealed MoO_x film undergoes an increase in thickness of around 1.30% over the course of the experiment, while the film that was initially thermally annealed undergoes a much smaller increase in thickness (around 0.18%). This process has a time constant of 10s of minutes and is significantly longer than that reported elsewhere on the basis of *in situ* XPS data;²¹ however our ellipsometry measurements probe the bulk of the film rather than being sensitive to the properties of the surface alone, which is likely to undergo much faster changes. Clearly, our findings demonstrate a correlation between the uptake of moisture by a MoO_x film and reduced device efficiency, and confirm our speculation that thermal annealing suppresses the uptake of moisture thereby resulting in a smaller change in work-function and thus improved device performance.

We propose that the thermal annealing process results in a densification of the MoO_x film, thereby reducing its porosity and limiting its ability to adsorb moisture. Such a densification process resulting from thermal annealing has previously been observed in other metal-oxide films.²² To confirm our speculation, we have again used ellipsometry to measure changes in the thickness of a previously unannealed MoO_x film as it annealed at 120 °C for 30 min in a nitrogen atmosphere and then returned to room temperature. The

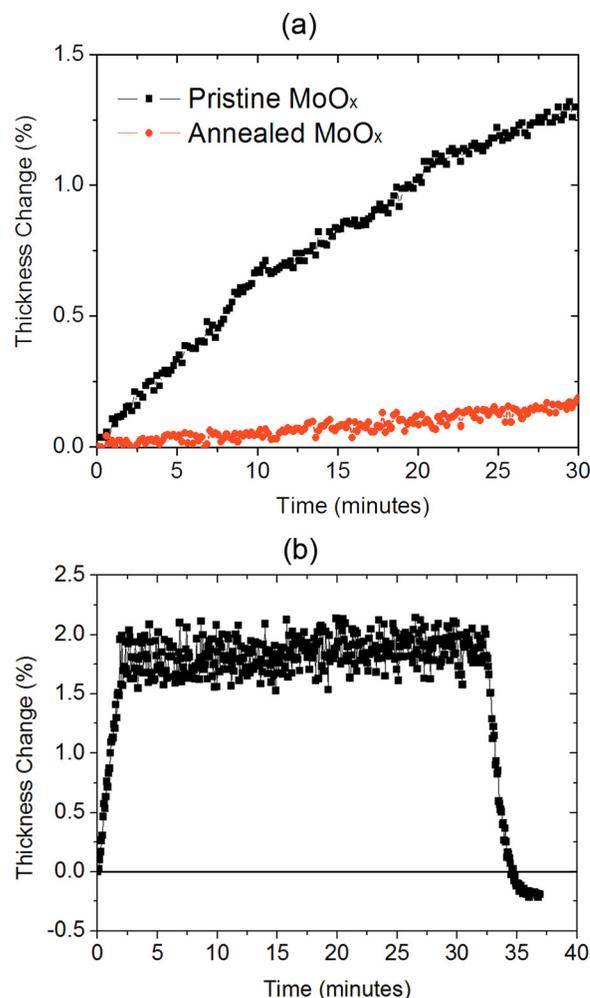


FIG. 2. (a) The thickness of a 20 nm thick MoO_x film as a function of time on exposure to air as measured by ellipsometry. Here, data are plotted for a pristine film and for a film that had initially been annealed at 120 °C for 30 min under nitrogen. (b) The thickness of a 20 nm MoO_x film as a function of time as measured by ellipsometry. Here, data are plotted for a pristine film that is heated to 120 °C for 30 min under nitrogen and then left to cool to room temperature.

results of this experiment are shown in Figure 2(b). It can be seen that on return to room-temperature, the thickness of the film is reduced by 0.19%, suggesting an increase in density of the same order. This increase in film density most likely results from a reduction of the volume of voids between grains in the MoO_x crystal, thereby reducing its ability to adsorb water. We believe that this observation explains the reduced hygroscopicity of the thermally annealed MoO_x film on exposure to air in Figure 2(a). Note, we have also performed wide scan XPS measurements on the MoO_x films to test for the presence of surface contamination. This did not reveal the presence of significant quantities of chlorine or carbon-based species on the MoO_x surface, indicating minimal contamination resulting from solvent exposure within the glovebox.

We can use this enhanced stability of MoO_x to air exposure to explore the processing of the active semiconductor under ambient conditions. We have therefore fabricated OPV devices in which the PCDTBT:PC₇₀BM blend was spin coated in filtered air under a laminar flow workbench before being returned to the glovebox for cathode evaporation and

encapsulation. Here, the active layer was deposited on untreated MoOx films and on MoOx films that had been thermally annealed in a glove-box at 120 °C for 30 min. Such devices are identified as “air processed” and “annealed, air processed.” The *JV* curves of the devices are again shown in Figure 1, with device metrics summarised in Table I. We find that devices processed in air on MoOx films that were not initially thermally annealed ($4.98 \pm 0.12\%$) had efficiencies comparable to the Reference device. Unexpectedly however, we find that the devices in which the MoOx film was initially thermally annealed before air exposure, with the PCDTBT film then deposited *in air* had a slightly higher average efficiency ($5.26 \pm 0.04\%$) (with one device having an efficiency of 5.36%) compared to devices that were thermally annealed and then processed in the glovebox ($5.10 \pm 0.04\%$). This small, but surprising, improvement in efficiency results from improved V_{oc} and FF , indicating that spin coating the active layer in air onto thermally annealed MoOx films is apparently beneficial to charge extraction at the polymer-MoOx interface.

We speculate that this improvement in device efficiency does not result from changes in the active organic layer, as no apparent changes are detected in J_{sc} . Rather, we propose that the improvement could derive from the presence of a thin layer of a water species on the surface of the MoOx film. We believe that such a *surface-bound* layer is not detrimental to device efficiency (as opposed to water adsorbed within the MoOx film that reduces the work-function), as it will result in the formation of a dipole, due to the charged nature of the water species chemically bound to the surface.^{23,26} This improvement is not seen in devices in which the active layer was deposited in the glove box, as the water species on the surface of air exposed MoOx films are likely to be partially removed in the vacuum load-lock on re-entry to the glovebox. We propose that the devices in which the active layer was spun in air show an improvement over devices prepared in the glovebox as water species are still present on the surface of the MoOx when the active layer is deposited.

In summary, we have fabricated PCDTBT:PC₇₀BM based OPVs utilising an ITO/MoOx anode and have explored the effect of selective exposure of the anode to air. As MoOx films are hygroscopic, we show that this exposure results in a swelling of the MoOx that is detrimental to device efficiency. However by applying an initial thermal anneal to the ITO/MoOx film, we show that this uptake of water can be suppressed; a process that results from film densification. We have used this result to fabricate OPV devices based on a blend of PCDTBT:PC₇₀BM, with the active semiconductor layer spin cast in air. Such air-processed devices had an average value for PCE of ($5.26 \pm 0.04\%$); a value

significantly larger than that of devices in which no thermal anneal process was applied that were fabricated inside a nitrogen-filled glovebox ($5.00 \pm 0.09\%$). This promising result suggests that the active layers of a polymer photovoltaic device can be fabricated using an air-based processing route; a result that may be of significant benefit in the development of a low cost, high volume manufacturing process.

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