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Crystalline Molybdenum Oxide Layers as Efficient and Stable Hole Contacts in Organic Photovoltaic Devices

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KEYWORDS

Molybdenum oxide layers; organic photovoltaics; reactive sputtering; OPV device stability; interfacial layers; crystalline metal oxides; low-energy electron microscopy (LEEM); X-ray photoelectron spectroscopy (XPS).

Abstract

High work function metal oxides such as molybdenum oxide (MoO₃ₓ) have demonstrated good hole contact properties in organic photovoltaic (OPV) devices in the past years, and have replaced the otherwise conventionally used PEDOT:PSS. In this work, we introduce new crystalline MoOₓ layers that outperform the otherwise commonly used thermally grown MoOₓ layers in OPV devices. These hole contact layers are developed from super-oxidized MoO₃₂ films grown by reactive sputtering, followed by post-annealing in high vacuum to induce crystallization of the otherwise amorphous MoOₓ films. Standard configuration organic solar cell devices based on DBP as electron donor and C₇₀ as electron acceptor were developed on top of the sputtered MoOₓ, and a large increase in power conversion efficiency as a function of the MoOₓ annealing temperature was observed, which is in clear contrast to devices grown on thermally deposited MoOₓ. The crystallization of the sputtered MoOₓ at elevated temperatures is
shown to lead to high work function films with improved conductivity, resulting in the appealing
device properties. Importantly, long-term stability investigations revealed that devices based on
these crystalline MoO$_x$ films exhibit superior stability as compared to devices based on thermally
grown MoO$_x$. These characteristics show that crystalline MoO$_x$ prepared by post-annealing
sputter deposited films forms a superior hole contact layer material for future air-stable organic
optoelectronic devices.

**Introduction**

High work function transition metal oxides such as molybdenum oxide (MoO$_3$), nickel oxide
(NiO), vanadium oxide (V$_2$O$_5$) and tungsten oxide (WO$_3$) have often been used in the past as
hole extraction/injection layers in organic,\textsuperscript{1} inorganic\textsuperscript{2} and hybrid\textsuperscript{3} optoelectronic devices. Among these metal oxides, MoO$_3$ shows one of the largest work functions,\textsuperscript{1,4,5} combined with relatively low deposition temperatures,\textsuperscript{6} which makes it an attractive material for device integration. In addition, as in the case for other transition metal oxides, the electrical,\textsuperscript{7} optical\textsuperscript{6} and physical properties\textsuperscript{8} of MoO$_x$ can be tuned over wide ranges via defect engineering, making MoO$_x$ particularly interesting for various optoelectronic device applications.

The research focus on organic photovoltaics (OPV) in the past decades has led to a 6-fold rise in device efficiencies over the last 15 years, reaching 17\% power conversion efficiency (PCE).\textsuperscript{9–13} This focus was stimulated by the appealing properties of OPV including light weight, low cost, semitransparency and mechanical flexibility, offering radically new integration schemes compared to commercially available photovoltaic technologies. For successful commercialization of OPV, a further improvement of device stability is considered to be critical, as this is considered a limitation of the technology. Although photochemical reactions between the active organic materials and water and/or oxygen under light illumination is a prominent
cause for device degradation over time,\textsuperscript{14,15} effects arising from interfacial instabilities are also important in OPV technology.\textsuperscript{16–18} Many stability improvements through the introduction of more stable metal oxide interface layers in OPV devices have been reported in the past.\textsuperscript{19,20} The benefits of improved contact layers are also device configuration dependent, e.g., using MoO\textsubscript{x} as hole transport layer in standard configured devices have been demonstrated to positively affect the device stability,\textsuperscript{21} whereas in inverted configuration devices, the conventional PEDOT:PSS has shown relatively higher stability.\textsuperscript{22} The stability improvements seen for specific device configurations arise both due an improved stability of the metal oxide layer itself, an improved stability of the interface between the metal oxide layer and the electrode, and potentially also due to the encapsulating properties of the metal oxide interlayer, protecting the active layer from ingress of water and oxygen.\textsuperscript{23}

Among several different deposition methods available to fabricate MoO\textsubscript{x} thin-films, including spray pyrolysis,\textsuperscript{24} electrodeposition,\textsuperscript{25} physical vapor deposition\textsuperscript{26} and sol-gel\textsuperscript{27} deposition, reactive sputtering stands out in terms of extensive control over the deposition parameters, providing broad composition tuning possibilities of the resulting films.\textsuperscript{28} Moreover, as demonstrated in our recent studies on crystallization of MoO\textsubscript{x} thin films,\textsuperscript{29,30} vacuum annealing of reactive sputtered films can lead to a large degree of control over film structure and electronic properties, particularly the work function of the films, making these fabrication processes particularly interesting for optoelectronic device applications. In this communication we report on integration of crystalline MoO\textsubscript{x} hole transport layers, formed from super-oxidized reactive sputtered MoO\textsubscript{3.2} films, in small molecule organic photovoltaic devices based on tetraphenyldibenzoperiflanthen (DBP) and fullerene (C\textsubscript{70}).\textsuperscript{13,31,32} The properties of these devices are assessed and compared to reference devices that incorporate standard thermally grown MoO\textsubscript{x}
films (x~3.0). We demonstrate that the long-term stability of the OPV devices based on the micro-crystalline MoO_x thin-films is dramatically improved: PCE of non-encapsulated devices remains within around 80% of their initial performance after 240 hours of light soaking under 1 sun (1000W/m^2) at ~60°C. In comparison, under the same conditions the PCE of devices based on evaporated MoO_x contact layers dropped below 50% of the initial performance in a fraction of the time. These results show that significant stability advantages arise from integration of micro-crystalline thin-film as hole transport layers in standard configuration OPV devices. In order to characterize the MoO_x films, we assessed the composition of the reactive sputtered films by X-ray photoelectron spectroscopy (XPS), the morphology of the films by atomic force microscopy (AFM), the optical transmittance of the films by UV-visible-NIR spectroscopy, the structure of the films from X-ray diffraction (XRD) analysis, and the surface morphology and work function by low-energy electron microscopy (LEEM).

**Results and Discussion**

The device structure used in this work is sketched in figure 1A. Following growth of the MoO_x layers on top of indium tin oxide (ITO) substrates, post-annealing experiments were carried out in a device fabrication cluster tool under ultrahigh vacuum (10^-9 mbar). The J-V characteristics (figure 1B) demonstrate that devices based on the sputtered MoO_x show significant improvements in device performance with post-annealing temperature of the MoO_x layer, going from the very poor performance of devices based on non-annealed sputtered MoO_x films to J-V characteristics that resemble those of devices based on thermally grown MoO_x films. Figure 2A shows the PCE performance as a function of post-annealing temperature for the DBP/C_{70} based OPV devices employing 30 nm hole transport layers of thermally deposited (MoO_{Th}) and reactive sputtered (MoO_{Sp}) MoO_x. Clearly, devices using as-deposited MoO_{Sp} show very poor
performance, which could be explained by a low electrical conductivity and/or a low work function for these non-annealed sputtered MoO\textsubscript{x} films, as previously reported. In this device configuration, efficient hole extraction at the anode contact requires that the work function of the MoO\textsubscript{x} layer should be equal to or larger than the HOMO energy level of DBP (5.5 eV). Devices made from post-growth annealed MoO\textsubscript{Sp} show promising characteristics, and films annealed to 350°C reach similar PCE values as the as-deposited MoO\textsubscript{Th} films. Table 1 summarizes the electrical performance results for devices based on both types of hole transport layers as a function of the post-growth annealing temperature. As it can be seen from Table 1, the average current density of the devices based on the 350°C vacuum annealed MoO\textsubscript{Sp} is comparable to that of the as-deposited MoO\textsubscript{Th}, which is also confirmed from the measured external quantum efficiency (EQE) spectra (figure S3). The improvement of device performance with annealing temperature is only observed for the MoO\textsubscript{Sp} films, whereas the opposite trend is seen for MoO\textsubscript{Th} films, showing a consistent performance drop with increasing annealing temperature. In order to shed further light on the electrical properties of these MoO\textsubscript{Th} and MoO\textsubscript{Sp} films, a conductivity analysis of the films was carried out (figure 2B). By increasing the annealing temperature of the sputtered films to 350°C, the conductivity of the MoO\textsubscript{Sp} films improves significantly, by close-to a factor 3 compared to the as-deposited films. The electrical analyses of the as-deposited MoO\textsubscript{Th} films show comparable properties to the sputtered films, consistent with the similar device parameters observed for these films. For the MoO\textsubscript{Th} films annealed at 350°C, a further rise in the conductivity of the films is observed. As reported in Table 1 this conductivity rise does not lead to improved device performance. This suggests that either the morphology or composition of the films plays an important role in these properties, which motivates the following microstructural investigations and surface analyses.
XPS measurements were conducted to shed light on the differences in the composition of the films upon the post-growth annealing, which was investigated for annealing temperatures up to 500°C. As seen in figure S1B and table S1 (and in supplementary note#1), a stronger reduction of the oxide is observed for the thermally grown MoO$_x$ in comparison to the sputtered MoO$_x$. For annealing at 200°C, the formation of Mo$^{5+}$ oxidation states is seen for MoO$_{Th}$, while only Mo$^{6+}$ states appear in the MoO$_{Sp}$ surface up to this temperature range. For MoO$_x$/ITO samples annealed up to 350°C, Mo$^{4+}$ species start to appear for MoO$_{Th}$, while this is not the case for the less reduced MoO$_{Sp}$ surface (figure S2). These chemical changes are also correlated with changes of the optical transmittance of the films, displayed in figure S4, which shows that annealing MoO$_{Th}$ films induces a reduction in optical transmittance. In contrast, annealing affects optical transmittance much less in the MoO$_{Sp}$ films. Taken together, the stability of optical transmittance and the decreased oxide reduction observed by XPS corroborate the improved thermal stability of the MoO$_{Sp}$ films upon post-growth annealing (figure S4A, table S1 and supplementary note#1). The stronger oxide reduction of the MoO$_{Th}$ upon annealing can also explain the increase in conductivity seen for these films, as shown in figure 2B.\textsuperscript{27} In addition, as reduced MoO$_x$ is n-doped, occupied gap states during illumination lead to an upward shift of the Fermi level and thus to decreased work function values.\textsuperscript{1} In addition to the effect of reduced optical transmittance, such a decrease in work function could explain the drop in device performance seen for the MoO$_{Th}$ films annealed at 350°C, although further analysis is needed to understand the relative importance of these effects. The general tendency of metal-oxides to lose oxygen under ultrahigh vacuum annealing is well known,\textsuperscript{34} and as the thermally deposited MoO$_x$ forms slightly sub-stoichiometric films,\textsuperscript{35} the surfaces of these films are likely to be reduced more strongly, compared to the super-oxidized films formed with oxygen excess in the sputter
process. In this interpretation, the oxygen excess in MoO$_{Sp}$ films may allow for nearly stoichiometric crystalline arrangements to form during the ultrahigh vacuum annealing, while such crystallization is suppressed in MoO$_{Th}$ films that are initially less oxygen rich.

AFM analysis of the MoO$_{Sp}$ and MoO$_{Th}$ films annealed at 200°C and 350°C was conducted to study their morphology on ITO substrates (figure 3A-D). It should be noted that no considerable difference in film morphology for neither of the films was observed upon annealing at temperature up to 200°C. As the post-annealing temperature reaches 350°C, however, substantial changes in the surface morphology are seen for the sputtered films. In recent studies, we have shown that annealing MoO$_x$ films with oxygen rich surfaces leads to a higher surface corrugation on silicon surfaces, as oxygen excess lowers the activation energy for nucleation.$^{30}$ A similar trend is seen in the AFM results presented in figure 3. Specifically, post-annealing the less oxygen rich MoO$_{Th}$ films at 350°C induces formation of relatively small clusters, as depicted in figure 3B. Post-annealing beyond 350°C, the surface morphology presents high aspect ratio needle-like structures, which have been reported by several groups.$^{36,37}$ In this work, an increase in cluster size for both oxides was also observed at annealing temperatures up to 500°C. We therefore suggest that the large MoO$_x$ clusters grown at high temperatures lead to the short circuits in the thin film devices, as seen in figure 2 and Table 1.

To shed more light on the AFM results, where significant surface aggregation is seen for the MoO$_{Sp}$ films annealed at 350°C, XRD analysis of both oxides was carried out and presented in figure 3E. The XRD analysis clearly supports that crystallization of the MoO$_{Sp}$ films on the ITO surfaces takes place at elevated temperatures, as seen for the layers annealed at 350°C, which shows a preferred orientation of the crystallites with the (100) plane parallel to the substrate surface. No crystallization was seen (in the detection limit of the XRD) for the MoO$_{Th}$ films
annealed up to 350°C. Crystallization of nearly stoichiometric MoO$_{Sp}$ films on silicon surfaces has been shown to be followed by large work function increases, from around 4.8 eV for as-deposited films to around 6.3 eV (on average) for films annealed at 500°C. In order to probe the work function of the super-oxidized and annealed MoO$_{Sp}$ films formed on ITO surfaces in this study, LEEM measurements of the films annealed at 350°C were conducted, as shown in figure 4. LEEM imaging and work function mapping shows that after annealing at 350°C the surface of the 30 nm MoO$_{Sp}$ is dominated by micro-aggregates featuring high work function exceeding 6 eV, about 0.3 eV higher compared to the matrix between the aggregates. We believe that the micro-aggregates seen in the bright-field LEEM images at 4.5V (figure 4A), as also seen for super-oxidized films on silicon surfaces, correspond to the MoO$_3$ phase observed during the XRD analysis. The crystallization process can therefore explain the increase in device performance seen with annealing temperature for the MoO$_{Sp}$ based devices, as an increase in both conductivity and work function is seen as a result of crystallization.

The fact that the crystalline MoO$_{Sp}$ films show more resilience towards oxygen reduction could have important implications for the stability of the devices built with them. Light soaking of thermally evaporated MoO$_{Th}$ was previously shown to result in the formation of Mo$^{5+}$ species, in a similar manner as heat treatment of MoO$_{Th}$ leads to formation of Mo$^{5+}$ species in the experiments reported here. As a consequence of oxide reduction in MoO$_{Th}$ over time, a decrease in work function values and a resulting loss in device performance has been reported. In order to test the stability of the devices developed in this study, we performed ISOS3-L2 degradation tests under 1 sun illumination for non-encapsulated devices. The results of tracking device performance parameters over time are shown in figure 5. The initial PCE of the MoO$_{Sp}$ device was 3.83%, whereas it was 3.67% for the MoO$_{Th}$ device. The devices based on MoO$_{Sp}$
clearly show a superior air stability compared to those developed from the MoO$_{Th}$ films, and an impressive 80% of the initial PCE for the MoO$_{Sp}$ devices is maintained after 240 hours of light soaking under 1000W/m$^2$ irradiation at ~60°C. This is in strong contrast to the MoO$_{Th}$ devices, which at best (for 10 nm MoO$_x$ film thickness) maintain just below 50% device performance after the same testing duration. Stability results for devices based on post-annealed MoO$_{Th}$ films are summarized in figure S5, and these show no further stability improvement compared to the as-deposited MoO$_{Th}$. In addition, figure S6 show the stability of devices based on 30nm MoO$_{Th}$ deposited at room temperature, demonstrating that the MoO$_{Th}$ device stability only drop further when a similar MoO$_x$ thickness as in the MoO$_{Sp}$ based devices are employed. Since the reduction of the oxide over time is reported as a significant cause of degradation for these layers in devices, we assume that it is the strong resilience of the crystalline MoO$_{Sp}$ layers towards oxygen reduction that is causing this pronounced device stability and significantly increased device lifetimes. This interpretation is supported by the evolution of the optical transmittance of the MoO$_x$ films upon light-soaking, as shown in figure S4C-D: an improved stability of the MoO$_{Sp}$ films is seen compared to the MoO$_{Th}$ films, consistent with our hypothesis of reduced oxygen vacancy light absorption upon light degradation. Clearly, film changes take place in the initial light-soaking phase of the MoO$_{Sp}$ based devices, which results in an initial PCE drop followed by a recovery process. This has also been reported for standard configuration MoO$_x$ OPV devices in the past,$^{38}$ and can be assigned to photo-induced transformations taking place in the MoO$_3$ films.

**Conclusions**

We studied the morphological, structural and electrical properties of reactive sputtered super-oxidized molybdenum oxide layers along with their use as hole transport layer in small molecule
based OPV devices. We have demonstrated that the performance of OPV devices based on sputtered MoO$_x$ hole transport layers is increased when these MoO$_{Sp}$ films are post-growth annealed in vacuum. In contrast, we find that on commonly used thermally evaporated MoO$_{Th}$ layers post-growth annealing has the opposite effect, reducing device performance. We show that increased device performance is correlated with the formation of micro-crystalline MoO$_3$ in super-oxidized MoO$_{Sp}$ layers on ITO substrates upon vacuum annealing at 350°C. The crystallization process leads to a formation of high work function MoO$_3$ micro-aggregates at the film surfaces. The thermal stability of the MoO$_x$ layers was determined from XPS studies, showing that the crystalline MoO$_{Sp}$ films maintain large amounts of oxygen even after ultrahigh vacuum annealing at temperature as high as ~500°C; this finding suggests a path towards further optimization of high-stability MoO$_x$ thin-films. The stability of OPV devices using both MoO$_{Sp}$ and MoO$_{Th}$ hole transport layers was evaluated from ISOS3-L2 long-term degradation studies, where it is shown that non-encapsulated OPV devices employing micro-crystalline MoO$_{Sp}$ hole transport layers maintain 80% of their initial power conversion efficiency over 240 hour tests, compared to efficiency decline to below 50% seen for the MoO$_{Th}$ based devices. We thus believe that crystallization of sputtered metal-oxide interfacial layers is a promising route for the development of organic photovoltaic devices with improved device stability.

**Experimental**

Molybdenum oxide films were formed by DC sputtering (20°C substrate temperature) from a molybdenum target (99.95% purity from Kurt Lesker) under $10^{-3}$ mbar deposition pressure using argon plasma in combination with oxygen to form super-oxidized MoO$_{3.2}$. Deposition of MoO$_x$ was done on plain ITO samples for optical analysis and on pre-patterned ITO samples to investigate the electrical properties and surface morphology. The substrates were pre-cleaned in
acetone followed by isopropanol alcohol in an ultra-sonic bath, and subsequently blow dried with nitrogen. Following growth, samples were immediately transferred to a nitrogen glovebox connected to a cluster deposition tool for subsequent device development.

For thermally evaporated MoO\(_x\), commercially available molybdenum oxide powder (Sigma Aldrich, 99.99\%) was thermally evaporated in the device cluster tool, and directly transferred to the process chamber under ultra-high vacuum (10\(^{-9}\)mbar) for further processing. The thickness of the MoO\(_x\) films was measured by a quartz crystal microbalance and confirmed with AFM and XRD measurements.

For device fabrication, DBP (above 99.5\% purity) from Luminescence technology, C\(_{70}\) (> 99.5\% purity) from Solenne BV and BCP (99.5\% purity) from Sigma Aldrich were thermally evaporated in the cluster deposition tool and were transferred in vacuum to the organic process chamber. The thicknesses of the layers were: DBP 20nm (rate of 0.03nm/s), C\(_{70}\) 30nm (rate of 0.04nm/s) and BCP 10nm (rate of 0.03nm/s). All organic layers were deposited consecutively under ultrahigh vacuum of 10\(^{-8}\)mbar, while the samples were kept at room temperature. The active area of each cell is 10 mm\(^2\) as defined by a shadow mask of the top electrode. 100nm silver (purity of 99.99\%) was thermally evaporated on top of the BCP layer at a rate of 0.5nm/s to complete the devices.

EQE measurements were performed by irradiating the samples with a 150W Xe lamp through a monochromator (VIS-NIR Newport Cornerstone 1/4m) fiber coupled into a Mitutoyo FS-70 microscope. The external quantum efficiency measurements were carried out in air at 300K using the same conditions aforementioned. A calibrated Si photodiode (Hamamatsu S2386-44 K) was used to measure the incident power.
AFM was performed in tapping mode using a Veeco Dimension 3100 microscope. MoO$_x$ 30nm films were annealed at elevated temperature for 30 min (for each temperature step) under ultra-high vacuum. After annealing, the samples were kept in the vacuum chamber until they cooled to 50°C, and subsequently transferred for AFM analysis.

For the optical transmittance measurements, samples were encapsulated in a glovebox using encapsulation glue (UV-VIS curable glue, DELO LP655) with BK7 glass windows. The measurements were performed using a Shimadzu UV-2700 spectrophotometer.

Standard J-V analysis was performed under 1 sun illumination (100mW/cm$^2$) using an AAA solar simulator from Abet Technologies and a Keithley 2400 source-meter. Stability studies were done under 1 sun illumination of continuous light exposure from an Infinity PV ISOSun solar simulator, and characterized using the AAA simulator. The sample holder’s optical window was based on fused silica glass that had more than 90% transmittance above 270 nm. We introduced no compensation factor for the 10% loss in our analysis. The sample holder does not provide any barrier against oxygen, humidity and temperature. The samples were continuously light-soaked for 5 consecutive days. The temperature inside the setup was 60°C.

For XPS analysis, the as-deposited films grown on ITO or n-type Silicon wafers were exposed to the environment and then transferred into an ultrahigh vacuum chamber with a base pressure of 5x10$^{-10}$ mbar, where X-ray photoelectron spectroscopy (XPS) was carried out on a SPECS PHOIBOS 100-1DLD photoelectron spectrometer. XPS was conducted at 5x10$^{-10}$ mbar using a monochromatic Al Kα source (h=1486.7 eV). The spectrometer was calibrated using the Ag 3d5/2 peak at 368.21 eV and the Ag 3d3/2 peak at 374.21 eV after sputter cleaning the surface. In situ post-annealing experiments were conducted followed by further XPS experiments. The samples were annealed for 30 min at 90°C, 30 min at 150°C and 30 min at 200°C. The
temperature measurements are within ±10° C. Additionally, a flash annealing was performed at 500°C for 5 min. XPS spectra were recorded following each step after sample cool down to about ~40°C.

Specular X-Ray diffraction (XRD) studies were performed on a PANalytical Empyrean System using radiation from a sealed copper tube. The incident beam was conditioned with a 0.02 rad Soller slit and a 1/8° divergence slit and a 10 mm beam mask. The diffracted beam was detected via a 0.02 rad Soller slit and a bent graphite monochromator using a one-dimensional PIXEL detector for counting. For the MoO$_3$ crystal structure, the following data was used as a reference: a= 13.867, b = 3.697 and c = 3.964, space group Pnma (orthorhombic).$^{39}$

LEEM experiments were performed in the spin-polarized LEEM system at the National Center for Electron Microscopy, Molecular Foundry at Lawrence Berkeley National Laboratory under a base pressure of 5x10$^{-11}$ mbar, while the post-growth processing of the MoO$_x$ samples was performed in a connected preparation chamber at 2x10$^{-9}$ mbar. The work function of the cathode was previously calibrated by measuring the vacuum level of a clean surface of highly oriented pyrolytic graphite (HOPG) using the same experimental conditions. By taking the HOPG work function from the literature,$^{40,41}$ we can determine the work function of the LEEM electron source (cathode) to be about $\Phi(Cathode) = \Phi(HOPG) - \varphi \sim 1.4 \pm 0.1 \, eV$.

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Supporting information. See additional supplemental material information about thermal stability studies of MoO$_x$ thin-films measured by x-ray photoelectron spectroscopy, in addition to optoelectronic properties and device stability of organic solar cell devices based on MoO$_x$ thin-films with different thicknesses and annealing conditions.
Figure 1. A) Sketch of OPV stack using 30nm of sputtered (MoO$_{Sp}$) or thermally evaporated (MoO$_{Th}$) molybdenum oxide hole transport layers on top of the ITO electrode in standard configuration small molecule devices, B) Representative JV characteristics of devices based on the MoO$_{Sp}$ and the MoO$_{Th}$ hole transport layers.
Figure 2. A) Device mean PCE using 30nm of MoO$_{Sp}$ and MoO$_{Th}$ hole transport layers post-growth annealed at different temperatures in vacuum. B) Conductivity of the MoO$_x$ hole transport layers measured in an ITO/MoO$_x$/Ag device stack using 30nm thick MoO$_{Sp}$ and MoO$_{Th}$ layers annealed at different temperatures.
Table 1. Device performance data

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<th>Hole transport layer</th>
<th>Annealing Temp. (°C)</th>
<th>PCE (%)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>$V_{oc}$ (V)</th>
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<td>MoO$_{Th}$</td>
<td>30</td>
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</tbody>
</table>

Device performance results in terms of power conversion efficiency (PCE), short-circuit current density ($J_{sc}$), fill factor (FF) and open-circuit voltage ($V_{oc}$) from DBP/C$_{70}$ organic photovoltaic devices employing 30 nm MoO$_{Th}$ and 30nm MoO$_{Sp}$ hole transport layers, respectively. The MoO$_x$ layers are post-growth annealed at different temperatures in vacuum before finalizing the OPV device fabrication.
Figure 3. AFM images of 30nm Molybdenum oxide films on ITO post-growth annealed at different temperatures in vacuum: A) MoO\textsubscript{Th} at 200°C (R\textsubscript{RMS} = 4.8 nm), B) MoO\textsubscript{Th} at 350°C (R\textsubscript{RMS} = 8.7 nm), C) MoO\textsubscript{Sp} at 200°C (R\textsubscript{RMS} = 4.9 nm), and D) MoO\textsubscript{Sp} at 350°C (R\textsubscript{RMS} = 11.6 nm). E) Specular X-ray diffraction of 30nm Molybdenum oxide films deposited on ITO and post-growth annealed at different temperatures. The curves are vertically shifted. The background of the ITO substrate is displayed for comparison. Only the sputtered molybdenum oxide post-growth annealed at 350°C shows a clear crystallization of the layer with a preferred orientation of the crystallites with the (100) plane parallel to the substrate surface (black solid line).
**Figure 4.** LEEM analysis of the surface of the sputtered MoO$_x$ oxide post-growth annealed at 350°C. A) Bright-field image at 4.5 V of the surface shows higher electron reflectivity of high-work function micro-aggregates (brighter) on the surface of the oxide. B) Electron reflectivity as a function of electron landing energy (including cathode offset), $I-V$ LEEM spectroscopic information of the crystalline MoO$_{Sp}$ on ITO. The micro-aggregates (red line) and the matrix between aggregates (blue line) show a difference of 0.3 eV in work functions, ~6.2 eV for the surface aggregates and ~5.9 eV for the matrix. IV curves show an average of around thousands of pixels for each case. C) 2D work function map rendered in color according to color bar (right) highlights micro-grains with 0.3 eV higher work function (red color) compared to the matrix (blue color). FOV for both A and C is ~10 µm.
Figure 5. Normalized PCE of the non-encapsulated organic photovoltaic devices based on MoO$_x$ hole transport layers. Red line depicts device performance from the 30 nm sputtered oxide post-growth annealed at 350$^\circ$C, while the black line shows the PCE versus operation hours for devices using 30 nm thermally grown oxide (as-deposited at room temperature). Devices based on the sputtered MoO$_x$ show an impressive $\sim$80% of its initial PCE value after 240 hours of ISOS3-L2 degradation. Plots represent best performing devices in both cases.
References


(36) Mohamed, S. H.; Venkataram, S. Thermal Stability of Amorphous Molybdenum Trioxide


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![Graph showing current density vs. voltage for different materials and temperatures.]

- 30nm MoOSp@30°C
- 30nm MoOSp@350°C
- 30nm MoOTh@30°C

Materials layers:
- Ag
- 10nm BCP
- 30nm C_{70}
- 20nm DBP
- MoO_{x}
- ITO
**A)**

- **Graph A**: Mean PCE (%) vs. Temperature (°C)
  - **MoO\textsubscript{Sp}**: Black line with square markers
  - **MoO\textsubscript{Th}**: Red line with circle markers

**B)**

- **Graph B**: Current Density (mA/cm\textsuperscript{2}) vs. Voltage (V)
  - **Mo\textsubscript{Sp} @30°C**: Black line with square markers
  - **Mo\textsubscript{Sp} @350°C**: Red line with circle markers
  - **Mo\textsubscript{Th} @30°C**: Blue line with triangle markers
  - **Mo\textsubscript{Th} @350°C**: Pink line with triangle markers
Mean $= 6.0041 \text{ eV}$

A) 

B) 

2$\mu$m

C) 

Electron Reflectivity

Landing Energy + $\Phi_{\text{Cathode}}$ (eV)
Normalized Intensity / counts s⁻¹ vs. Binding Energy / eV

A) Mo⁺⁶
Mo⁺⁵
Mo⁺⁴

B) 500°C
Mo⁺⁶
Mo⁺⁵
Mo⁺⁴

200°C
Mo⁺⁶
Mo⁺⁵
Mo⁺⁴

RT
Mo⁺⁶
Mo⁺⁵
Mo⁺⁴

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A

B

C

D

Transmittance (%)

MoO$_{sp}$ @ 350°C (Fresh)

MoO$_{sp}$ @ 350°C (Degraded)

MoO$_{th}$ @ 30°C (Fresh)

MoO$_{th}$ @ 30°C (Degraded)

Wavelength (nm)

Transmittance (%)

MoO$_{sp}$

MoO$_{th}$

540nm

830nm

Day

ACS Paragon Plus Environment