Tunability of MoO₃ Thin-Film Properties Due to Annealing in Situ Monitored by Hard X-ray Photoemission

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Supporting Information

ABSTRACT: The chemical and electronic structure of MoO₃ thin films is monitored by synchrotron-based hard X-ray photoelectron spectroscopy while annealing from room temperature to 310 °C. Color-coded 2D intensity maps of the Mo 3d and O 1s and valence band maximum (VBM) spectra show the evolution of the annealing-induced changes. Broadening of the Mo 3d and O 1s spectra indicate the reduction of MoO₃. At moderate temperatures (120–200 °C), we find spectral evidence for the formation of Mo⁵⁺ and at higher temperatures (>165 °C) also of Mo⁴⁺ states. These states can be related to the spectral intensity above the VBM attributed to O vacancy induced gap states caused by partial filling of initially unoccupied Mo 4d-derived states. A clear relation between annealing temperature and the induced changes in the chemical and electronic structure suggests this approach as a route for deliberate tuning of MoO₃ thin-film properties.

INTRODUCTION

It has been demonstrated that molybdenum trioxide (MoO₃) is an excellent (inorganic) hole transport material (HTM) in optoelectronic devices, such as solar cells and/or organic light-emitting diodes (OLEDs). Due to its large work function, MoO₃ generally has a favorable energy level alignment with the active materials and the anode in these devices. For example, in organic solar cells (OSCs), after replacing the (organic) HTM PEDOT:PSS with inorganic MoO₃, mainly to improve long-term stability, the efficiency remained unchanged or was even improved. However, for perovskite-based photovoltaic devices, it has been suggested that the deep valence band of MoO₃ blocks the hole transport. One proposed solution to overcome this problem is to create states within the band gap above the valence band maximum (VBM), also called gap states. Gap states in MoO₃ generally have a favorable energy level alignment with the electronic structure and the composition of MoO₃ films and reported the improvements of OSCs and OLEDs performance upon creating oxygen vacancies or inserting hydrogen atoms into the employed MoO₃. A more favorable energy level alignment was suggested as an explanation, reducing voltage loss and facilitating barrier-free hole extraction. Sample annealing treatments are a common way to introduce oxygen vacancies to tune the electronic structure of metal oxides. With increasing annealing temperature, defect states are proposed to form due to oxygen escaping from the sample (surface); this process in principle allows deliberate modification of the material's electronic structure. Dasgupta et al. reported a MoO₃ annealing temperature of 250 °C in the N₂ atmosphere to be ideal, resulting in an improved charge transport yielding a 50% solar cell performance enhancement. In contrast, Lee et al. demonstrated that an annealing-induced reduction of MoO₃ is detrimental: They reported a reduced OSC efficiency independent of whether the MoO₃ was annealed in N₂, mixed H₂/N₂ atmosphere, or ambient air at 200 or 400 °C, compared to using as-prepared MoO₃ films. It was suggested that for the as-prepared MoO₃, in this particular case, the intrinsic oxygen vacancies and, thus, the already present gap states provided sufficient hole transport, while annealing led to further reduction and detrimental metallic behavior. Note that
in this case, the (surface) stoichiometry can be expected to significantly deviate from the nominal \([O] : [Mo] = 3 : 1\) composition. These seemingly inconsistent results might be attributed to the different initial (i.e., as-prepared) states of the studied MoO3 materials in terms of oxygen vacancy/gap state density.

In order to systematically study the impact of annealing on the \([O] : [Mo]\) composition and the presence and density of gap states, we have in situ monitored the changes in the chemical and electronic structure of MoO3 thin films by hard X-ray photoelectron spectroscopy (HAXPES) while annealing in vacuum. This will establish a sound base for the deliberate tuning of the gap states density via the \([O] : [Mo]\) composition.

### RESULTS AND DISCUSSION

The survey spectra of the as-prepared and annealed MoO3 films (i.e., before and after in situ annealing, respectively) are shown in the Supporting Information (see Figure S1). All expected core level lines of Mo and O atoms are detected. In addition, a small C 1s peak can be observed that might indicate the presence of surface contaminants formed on the sample during sample transport (in inert gas) and/or sample mounting (in ambient conditions). Note that the incorporation of (some) carbon in the MoO3 material during PVD processing (in ambient conditions). Note that the incorporation of (some) carbon in the MoO3 material during PVD processing under high vacuum conditions can also not be excluded. At first sight, the spectra are very similar before and after annealing, for a more detailed discussion of the annealing-induced changes, we will focus on the detail spectra in the following.

In order to better follow the changes of the Mo 3d and O 1s detail spectra during in situ annealing, the individual spectra are summarized as 2D maps in Figure 1a,b, respectively. The x axis shows the BE region of the spectra; the color code indicates the spectral intensity (normalized to the intensity in the BE range of 227.5-228.5 eV for Mo 3d and 524-525 eV for O 1s to exclude intensity variations due to fluctuating photon flux); and the y axis represents the annealing temperature (and thus also annealing time). The 2D maps (in particular of the Mo 3d line) clearly show a redistribution of spectral intensity indicating annealing-induced changes of the MoO3 chemical structure. However, also distinct spectral changes in the O 1s line (i.e., emergence of peak at BE ~533.1 eV) induced by the annealing treatment are observed. The top panels in Figure 1 show respective (a) Mo 3d and (b) O 1s sum spectra derived by adding individual spectra in the temperature ranges of 30−100 °C and 240−310 °C.

From RT to around 100 °C (i.e., the temperature range highlighted by the blue box and represented by the blue spectrum in the top panel of Figure 1a), little or no change is detected in the Mo 3d 2D map. Increasing the annealing temperature from 100 °C to around 240 °C, in contrast, causes obvious changes of the Mo 3d spectra. The 3d_{3/2} and 3d_{5/2} peaks undergo significant asymmetric broadening, and the peaks gradually shift to lower BE values. A further increase of the annealing temperature to 310 °C seems to result only in comparatively minor additional peak broadening. This is somewhat different to what can be observed for the O 1s spectra, here the most pronounced change, indicated by an asymmetric narrowing of the main peak and a broadening of the minor contribution toward high BE values, can be observed for temperatures below 100 °C and above 200 °C, respectively, with only minor changes in the intermediate temperature regime. Overall, the spectral changes are less pronounced for the O 1s, compared to the Mo 3d spectra, but can clearly be observed in the top panel of Figure 1b.

MoO3 is known to suffer X-ray beam-induced changes, however, measurement parameters have been optimized at the beginning of the experiment to minimize these effects. In fact, after this optimization, no indication of beam damage was observed before and after the measurement sequence (see Figure S2) and thus, we clearly attribute the observed redistribution of spectral intensity to the annealing (and not due to X-ray irradiation).

To quantitatively analyze the annealing-induced changes, the individual spectra have been fitted (see Supporting Information for details and Figure S3 for selected fit spectra). For the as-prepared MoO3 film, the spectrum can be reasonably fit by a single spin-orbit doublet (Mo 3d_{5/2} located at BE: 232.5 ± 0.05 eV). Thus, the main oxidation state of molybdenum in

![Figure 1. Evolution of the (a) Mo 3d and (b) O 1s spectra upon in situ annealing in vacuum presented in 2D intensity maps, where the x axis represents the binding energy region of the spectra, the y axis shows the annealing temperature (and thus also annealing time), and the color code indicates the normalized spectral intensity. The upper panels show respective sum spectra recorded in the stated temperature regime.](image-url)
our sample is +6$^{15,23}$ which is in line with a stoichiometric MoO$_3$ film. However, the nonzero residuum of the fit (see top left panel of Figure S3) suggests that the presence of a small amount of lower oxidation state Mo cannot be excluded, in accordance with refs 18 and 22. At 120 °C, an additional doublet located at lower BE (Mo 3d$_{3/2}$ at BE: 231.6 ± 0.05 eV, see Figure S3) appears, which increases in intensity with annealing temperature. This doublet is ascribed to the +5 oxidation state of Mo.$^{15}$ For annealing temperatures above approximately 200 °C, a third doublet (again at a lower Mo 3d$_{3/2}$ at BE: 230.7 ± 0.05 eV, see Figure S3) is required to properly fit the Mo 3d line, which is ascribed to the Mo oxidation state +4.$^{23}$ In Figure S3, it can be observed that the Mo 3d contributions that represent high Mo oxidation states gradually shift to higher BE values with increasing annealing temperature, likely due to the gradual appearance of the additional low oxidation state contributions at lower BE values. At the same time, the spectral intensity of the low oxidation state (i.e., Mo$^{5+}$ and Mo$^{6+}$) contributions increases at the expense of the high oxidation state (i.e., Mo$^{6+}$) components. The most common explanation for the appearance of low Mo oxidation states is the creation of oxygen vacancies and a related charge transfer upon vacuum annealing.$^{16}$

Based on the Mo 3d fits, the Mo$^{5+}$/Mo$_{total}$ intensity ratios are derived. As shown in Figure 2a, the Mo oxidation state +6 Mo oxidation state +5 contributions start to plateau at 240 °C, while the slope of the Mo oxidation state +6 contribution decrease is rather constant, indicates that in this temperature region, the reduction process is dominated by the direct +6 → +4 oxidation state conversion or the dynamic balance between the conversion of +6 → +5 and + 5 → +4 oxidation states. Our finding is in agreement with previous reports on MoO$_3$ films annealed in the N$_2$ atmosphere.$^{23}$ The degree of reduction can be expressed by the [O]:[Mo] (surface) composition. The [O]:[Mo] ratio derivation is based on the oxidation state contributions to the Mo 3d spectra assuming a [O]:[Mo] = 3 for the oxidation state +6 (i.e., MoO$_3$), [O]:[Mo] = 2.5 for the oxidation state +5 (i.e., MoO$_2$), and [O]:[Mo] = 2 for the oxidation state +4 (i.e., MoO$_2$). From RT to 240 °C, the [O]:[Mo] ratio changes from 3.0 (stoichiometric MoO$_3$) to 2.7 (see blue line in Figure 2a). Note that a similar loss (∼10%) of oxygen is derived when the O 1s (Figure S4) and Mo 3d (Figure S3) lines are used for quantification and that our result is similar to that reported by Zhang et al. for annealing in N$_2$. They found that the [O]:[Mo] ratio also decreases from 3.0 to 2.7 when raising the annealing temperature from RT to 250 °C.$^{23}$ It is observed that below 100 °C (see Figure 2a), neither the [O]:[Mo] ratio nor the predominant Mo oxidation state +6 changes significantly; most likely because the thermal energy (even in combination with vacuum conditions) is insufficient to break O–Mo bonds.

For the curve fit analysis of the O 1s spectra (see Supporting Information, Figure S4), at low annealing temperature, two spectral components are sufficient to get a reasonable fit. The dominant peak at 530.54 ± 0.05 eV is in the BE range that generally can be attributed to metal oxides, that is, MoO$_3$. The smaller high binding energy contribution O1 at 531.69 ± 0.05 eV is in a BE range that is usually ascribed to (surface) −OH groups.$^{15,24}$ As the temperature increases from RT to approximately 100 °C, it can be observed that the high binding energy contribution gets smaller (see Figure S4 and also indicated by the narrowing of the O 1s peak visible in the 2D map in Figure 1b). Increasing the temperature further, starting from approximately 200 °C, a third contribution (O2) at 533.09 ± 0.05 eV is required for a reasonable fit and component O1 increases again. This is accompanied by a widening of the O 1s peak (see 2D map in Figure 1b). While the initial decrease of component O1 with increasing temperature agrees with the attribution to −OH groups (due to annealing-induced dehydration or desorption of surface −OH groups), the subsequent O1 increase at higher temperatures indicates oxygen in another chemical environment. Indeed O 1s contributions of molybdenum oxide in this BE range are also often related to oxygen present in molybdenum suboxides and the related distorted chemical environment due to oxygen vacancies.$^{15}$ The spectral fraction of all oxygen components as derived from the spectra in Figure 1b are displayed in Figure 2b. While the O-metal contribution to the O 1s line continuously decreases with annealing temperature, the spectral fraction of O1 shows a shallow minimum around 100 °C and a slight but steady increase at higher temperatures. Thus, at low temperature, we suggest the O1 component of the O 1s line to be mainly due to −OH groups, which dehydrate or desorb with increasing temperature. The increase of the O1 spectral fraction can then be explained by an enhanced presence of molybdenum suboxides (or oxygen vacancies) increasingly formed at temperatures >100 °C. This model is corroborated by the finding of

![Figure 2](image-url) (a) Mo$^{5+}$/Mo$_{total}$ ratios (left y axis) and the [O]:[Mo] ratio (right y axis) and (b) relative contribution to the O 1s line of the studied MoO$_3$ thin films as function of annealing temperature as derived from the data in Figure 1.
increased Mo$^{4+}$ at annealing temperatures of 100 °C and higher (see Figure 2a). The onset of increased O2 component intensity of the O 1s line and the appearance of Mo$^{5+}$ in the Mo 3d spectra coincide (see Figure 2a,b), and so, we speculate that the O 1s component O2 can be ascribed to (another) chemical oxygen environment distorted by an even higher amount of oxygen vacancies. The presence of different chemical oxygen environments that appear at different concentrations of oxygen vacancies can be explained as being due to the differing coordination of the oxygen atoms at a molybdenum oxide surface. According to Tokarz-Sobieraj et al.,$^{2,5}$ three types of oxygen exist at the surface of a molybdenum oxide: singly, doubly, and triply coordinated oxygen. The limited surface sensitivity of our HAXPES measurements and relaxation processes at the molybdenum oxide surface upon formation of oxygen vacancies (as suggested in ref 28) can lead to scenarios that would be in agreement with the observed behavior.

The valence band (VB) region (Figure S5) was recorded during the in situ annealing experiment. Due to the low photoionization cross section of the VB states, the data has a significantly lower signal-to-noise ratio than the 2D intensity maps of the Mo 3d and O 1s lines in Figure 1. At first sight, no distinct spectral changes with annealing temperature can be observed. However, close inspection of summations of spectra derived by adding individual spectra in the temperature ranges of 30–100 °C and 240–310 °C depicted as blue and red spectra, respectively, in the top panel of Figure S5, reveals small but significant differences. In the above-VBM region between 0 and 2.8 eV BE, increased spectral intensity can be observed in the high-temperature sum spectrum (red spectrum) compared to the low-temperature sum spectrum (blue spectrum). A detailed evolution of these above-VBM (or gap) states is presented in Figure S6 (left panel). Despite the low signal-to-noise ratio, it seems that these states are not present until the annealing temperature exceeds 165 °C, confirmed by the quantified spectral intensity in the region between 3 and −2 eV (Figure S6, right panel), for which an increase can be identified in spite of considerable variation. At approximately this temperature, we start to find evidence for the presence of Mo in an oxidation state of +4 (see Figure 2a). However, due to the insufficient signal-to-noise ratio (in particular in the above-VBM region) of the data acquired in the fast in situ measurement mode, it is not possible to exclude the presence of above-VBM spectral intensity also for lower annealing temperatures (see discussion below).

High-quality VB spectra of the as-prepared and annealed MoO$_3$ film recorded before and after the in situ experiment are shown in Figure 3. The individual regions in these spectra are discussed in detail in our previous publication.$^{20}$ The majority of the spectral intensity (in particular between BEs of 10 and 2.5 eV) has O 2p character. Under both conditions, the VBM position as derived by linear approximation of the leading edge is determined to be 3.00 ± 0.10 eV below $E_f$ independent of annealing, which is in agreement with VBM values reported for (nearly) stoichiometric MoO$_3$ films.$^{15}$ Above-VBM (defect) states in the band gap are detectable but very weak in the as-prepared MoO$_3$ film. Greiner et al. suggested that, from a thermodynamics perspective, even stoichiometric MoO$_3$ can contain some defect concentration.$^{31}$ After annealing, two pronounced above-VBM features with local maxima at BE of ~0.8 and ~1.8 eV are detected (indicated by the blue arrows). In transition metal oxides, these (defect) states can generally be attributed to the partially filled metal d band (in our case, the usually unoccupied Mo 4d-derived states). However, the origin of these defect states is still under debate. Many studies suggest that oxygen vacancies are the main reason for these defect gap states. Greiner et al.,$^{16}$ for example, differentiate between dilute (i.e., low) and nondilute (i.e., very high) O vacancy defect concentration scenarios and attribute $d^1$ and $d^2$ to singly and doubly occupied d bands of Mo$^{5+}$ and Mo$^{4+}$ cations, respectively. While our data of the annealed MoO$_3$ sample seems to agree with the nondilute O vacancy defect concentration scenario, close inspection of the above-VBM region of the as-prepared MoO$_3$ on a magnified (×10) scale in Figure 3, showing spectral intensity in the d$^2$ region, however, contradicts the corresponding dilute O vacancy defect concentration scenario. This points to a more complex explanation. The defect states in MoO$_3$/organic material structures, for example, are typically explained by the charge transfer from the organic materials to the MoO$_3$ film or by interface states, rather than by the intrinsic property of MoO$_3$. Additional high-quality spectra of particularly the above-VBM region as a function of O vacancy defect concentration (i.e., Mo$^{4+}$/Mo$_{total}$ ratio) would be required to ultimately resolve this issue, in the future.

### EXPERIMENTAL SECTION

Thin films of 50 nm MoO$_3$ were deposited onto Au (100 nm)/glass substrates by physical vapor deposition (PVD) in high vacuum condition (~10$^{-7}$ mbar) as in our previous study of MoO$_3$.$^{20}$ For the transport to the analysis tool, the MoO$_3$/Au/glass samples were sealed in the N$_2$-purged glovebox directly connected to the PVD system. The HAXPES measurements were conducted at the high kinetic energy photoelectron spectrometer (HiKE) endstation located at the BESSY II KMC-1 beamline at Helmholtz-Zentrum Berlin für Materialien und Energie GmbH (HZB).$^{28,29}$ During the sample mounting and loading into the analysis system, air exposure was limited to <10 min. HiKE is equipped with a Scienta R4000 electron energy analyzer and is operated in ultrahigh vacuum (UHV) conditions: base pressure in the analysis chamber is ~10$^{-7}$ mbar. For the HAXPES measurements, the excitation energy was set to 203

![](image.png)
eV (henceforth simply called “2 keV”). The pass energy and energy step width were 200 eV (500 eV) and 0.1 eV (0.5 eV) for all the core levels (survey) scans, respectively. The binding energy (BE) scales of the HAXPES spectra were calibrated using Au 4f reference measurements of a clean Au foil, setting the Au 4f7/2 core level line to be at 84.00 eV. The total energy resolution of the core level spectra was approximately 0.25 eV.

The inelastic mean free path of the photoelectrons depends on their kinetic energy and is around 3 nm in MoO3 for the considered photoemission lines and excitation energy, that is, the signal contribution exponentially decreases to <5% for 8 nm (for the O 1s line) and 10 nm (for the valence band) from the sample surface for the measurement geometry used here.26,31

First, high-quality HAXPES data were taken on the as-prepared MoO3 film. Then, the O 1s, Mo 3d, shallow core level, and valence band energy regions were measured consecutively in a fast in situ measurement mode while heating the sample at a rate of approximately 2 °C/min in UHV, covering a temperature (pressure) range from 25 °C (～10⁻⁹ mbar) up to 310 °C (～low 10⁻⁷ mbar range) as measured by a type N (Nicrosil-Nisil) thermocouple connected to the sample stage. This in situ annealing was controlled by a resistive heater controller (ZRHCN RHC, Vacuum Generator) unit, which regulates the current applied to the resistive heater below the sample stage based on the thermocouple feedback. For the acquisition of one Mo 3d spectrum, the total measurement time is 36 s. Because the heating rate is rather slow (2 °C/min), we consider the change in temperature over the course of the collection of one spectrum to be negligible. Data acquisition continued after turning off the heater until the sample cooled down to room temperature. Finally, a full set of high-quality HAXPES data of the annealed MoO3 sample was collected. Note that at this point, the [O]:[Mo] composition does significantly deviate from the 3:1 stoichiometry of the as-prepared MoO3. We will nevertheless refer to this sample as “annealed MoO3” in the following.

CONCLUSIONS

In this work, the chemical and electronic structure of MoO3 thin films has been in situ monitored by hard X-ray photoelectron spectroscopy during vacuum annealing. The VBM position was found to be independent of annealing at 3.00 ± 0.10 eV below Ep. However, broadening of the Mo 3d and O 1s spectra with increasing annealing temperature is attributed to the formation of Mo³⁺ and (for >165 °C) Mo⁴⁺ states. At the same time the [O]:[Mo] ratio decreases from 3.0 to 2.7. As a consequence of the significant annealing-induced formation of Mo³⁺ and Mo⁴⁺, an increasing above-VBM spectral intensity can be observed attributed to O vacancy related gap states due to partial filling of (initially unoccupied) Mo ⁴d-derived states. Therefore, vacuum annealing is suggested as a simple approach to deliberately tune the properties of MoO3 thin films.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01027.
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