

SUPPLEMENTAL INFORMATION

Tunability Of MoO₃ Thin-Film Properties Due To Annealing – In-Situ Monitored By Hard X-Ray Photoemission

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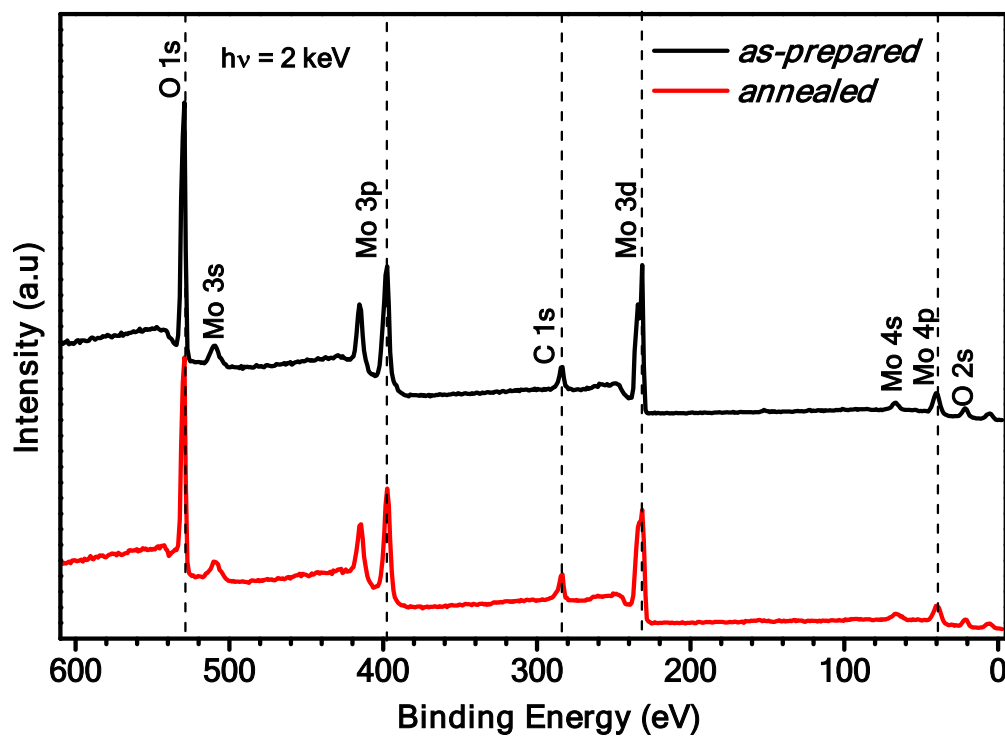


Figure S1 Survey spectra of the *as-prepared* and *annealed* MoO₃ thin films. The spectra have been offset for clarity.

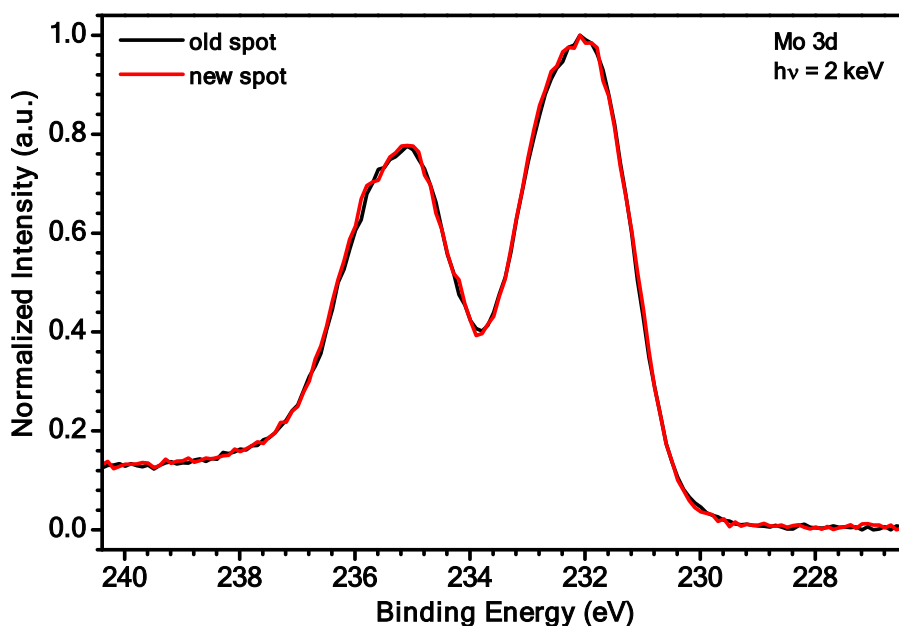


Figure S2 Mo 3d spectra of the MoO₃ thin film after annealing of an “old spot” (i.e., the sample region that was irradiated by x-rays during the in-situ annealing) and a “new spot” (i.e., a sample region that was not irradiated by x-rays before this measurement).

X-ray beam induced changes during spectroscopic measurement of MoO₃ thin films cannot be excluded and thus have to be considered. When using, e.g., a commercially available lab-based non-monochromatized Mg K_α excitation source, the measurement time of MoO₃ film on one spot should be limited to 2 hours if x-ray beam induced changes should be kept in an acceptable range.¹ For synchrotron-based hard x-ray spectroscopy measurements of this study, we also tested for x-ray beam induced changes. As shown in Figure S2, the Mo 3d spectra of an “old spot” (hard x-ray irradiation time around 2.5 h) and a “new spot” (without preexisting hard x-ray irradiation) of a MoO₃ thin film using optimized measurement parameters overlap. This suggests that there are negligible x-ray beam induced changes occurring during the time frame of the HAXPES measurements and that the changes we observe can mainly be attributed to the vacuum annealing.

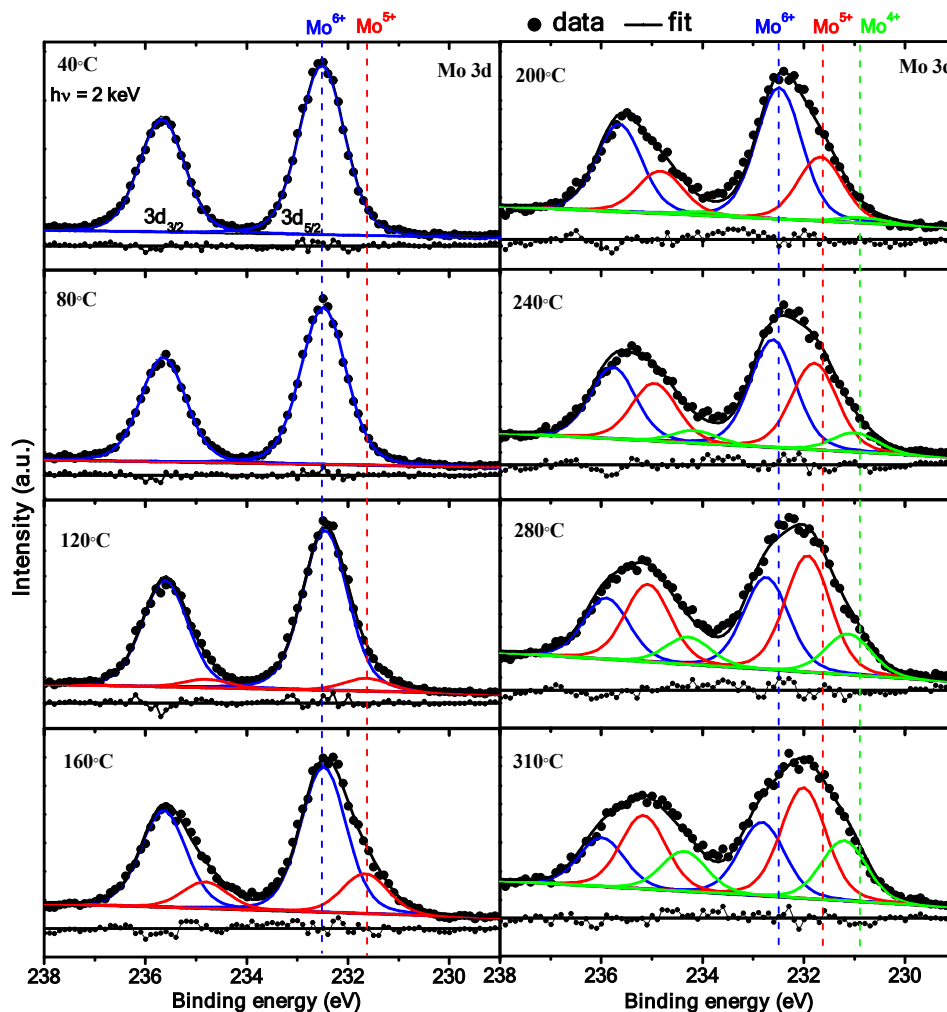


Figure S3 Mo 3d spectra of the MoO₃ thin film at different annealing temperatures including curve fit analysis results (for details see below).

All spectra were fit simultaneously. For the curve fit analysis a linear background and two (> 160°C: three) linked Voigt peak pairs with same width and shape (per Mo species) are required to get reasonable fits. For the Mo 3d Voigt peak pairs the spin-orbit split is fixed at 3.16 eV³ and the 3d_{5/2}:3d_{3/2} ratio is – according to the 2j+1 multiplicity – fixed at 3:2.

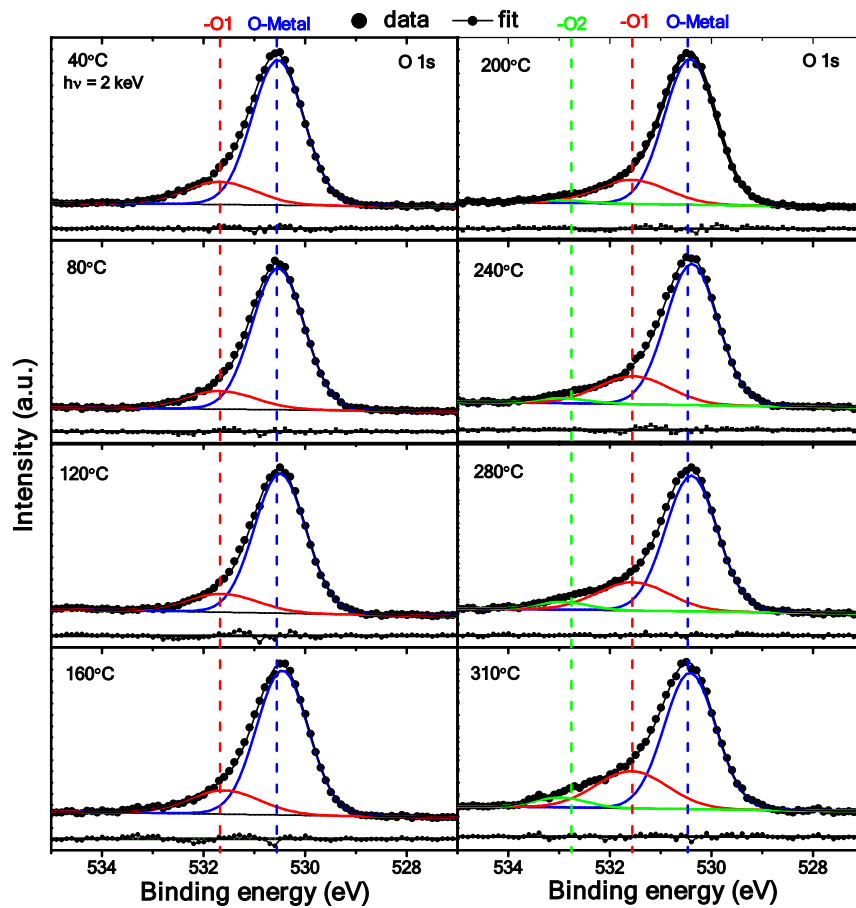


Figure S4 O 1s spectra of the MoO₃ thin film at different annealing temperatures including curve fit analysis results (for details see below).

All spectra were fit simultaneously. For the curve fit analysis a linear background and two ($> 160^{\circ}\text{C}$: three) Voigt peaks are required to get to reasonable fits. Considering the different oxygen environments with probably different bond angles and distances (in particular for the presumably amorphous $-\text{OH}$ contribution), a different spectral shape for the O1 species was used for the fit, while the same shape was employed for the O-metal and O2 contribution.

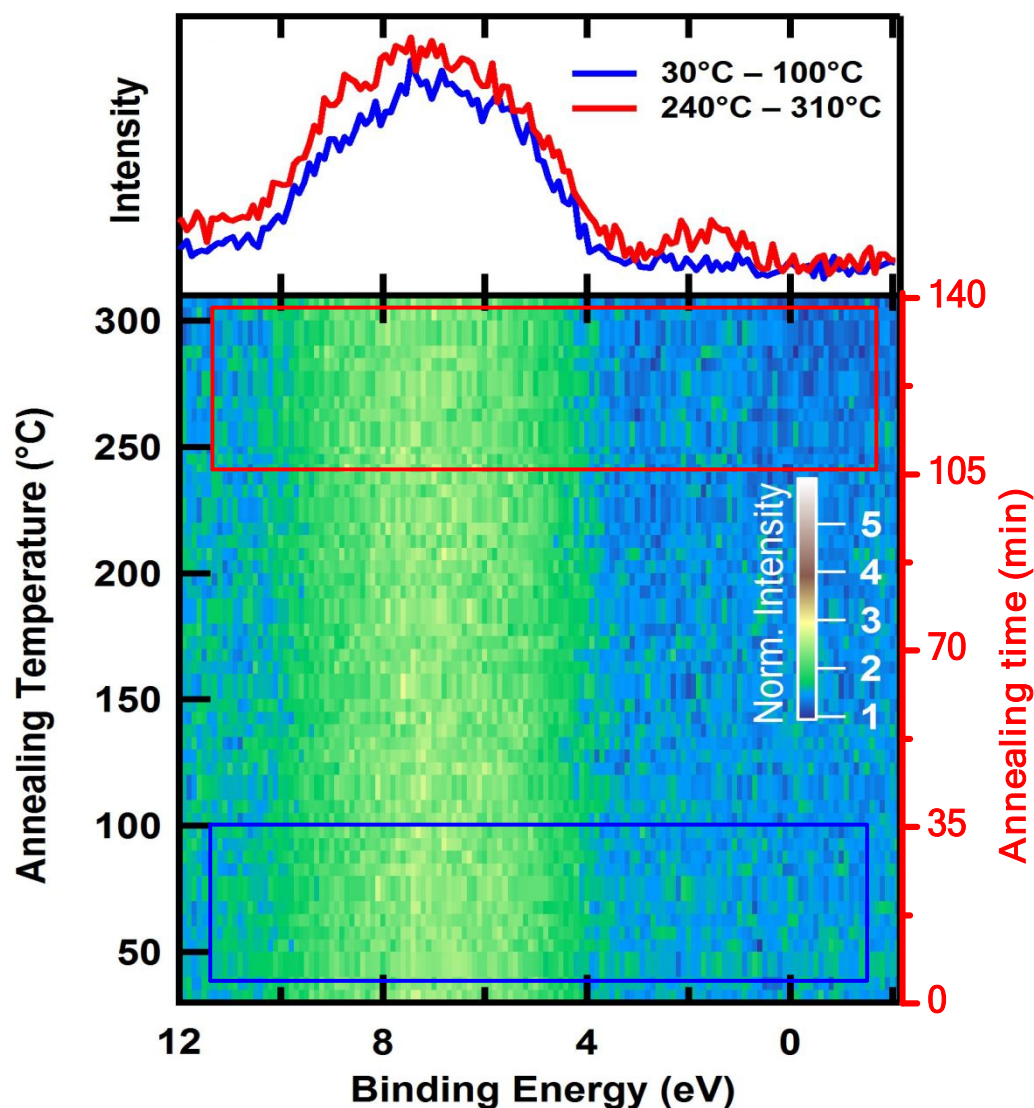


Figure S5 Evolution of the HAXPES spectra around the valence band maximum upon in-situ annealing in vacuum presented in a 2D intensity map, where the x-axis represents the binding energy region of the spectra, the y-axis shows the annealing temperature (and thus also annealing time) and the color code indicates the normalized spectral intensity. The upper panel shows respective sum spectra recorded in the stated temperature regime.

The VBM 2D map is normalized to the background in the BE range of -0.5 to -1.5 eV to account for intensity variations due to photon flux fluctuations. Due to the low photoionization cross section of the states deriving the VB, the data has a significantly lower signal-to-noise ratio than the 2D intensity maps of the Mo 3d and O 1s line in Figure 1. A detailed evolution of these above-VBM (or gap) states is presented in Figure S6 (left panel) by means of spectra summed up in the stated temperature intervals.

Despite the still low signal-to-noise ratio it seems that these states cannot be observed until the annealing temperature exceeds 165°C, confirmed by the integrated spectral intensity in the region between 3 and -2 eV (Figure S6, right panel) for which an increase can be identified in spite of significant variation.

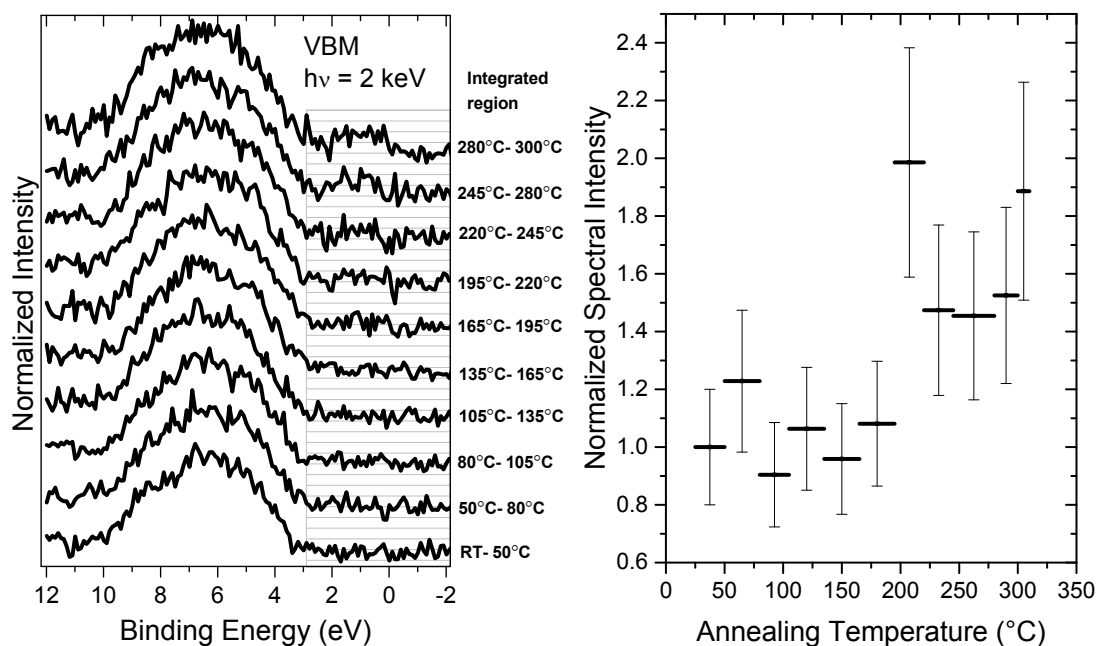


Figure S6 (left panel) Sum spectra of the valence band maximum from the 2D intensity map shown in Figure S5 in the stated temperature intervals. (right panel) Spectral intensity integrated in the energy region between 3 and -2 eV of the sum spectra shown in the left panel as a function of mean annealing temperature of the respective annealing temperature interval.

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2. Trzhaskovskaya, M. B.; Nefedov, V. I.; Yarzhemsky, V. G., Photoelectron Angular Distribution Parameters for Elements $Z=1$ to $Z=54$ in the Photoelectron Energy Range 100–5000 Ev. *Atomic Data and Nuclear Data Tables* **2001**, *77*, 97-159.
3. Meyer, J.; Hamwi, S.; Kröger, M.; Kowalsky, W.; Riedl, T.; Kahn, A., Transition Metal Oxides for Organic Electronics: Energetics, Device Physics and Applications. *Advanced Materials* **2012**, *24*, 5408-5427.