Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information Material to

Molybdenum Precursor Delivery Approaches in Atomic Layer Deposition of α-MoO_3

Daniela Lorenzo[§], David M. Tobaldi[§,*], Vittorianna Tasco[§,*], Marco Esposito[§], Adriana Passaseo[§], Massimo Cuscunà[§]

[§] CNR NANOTEC Institute of Nanotechnology, Via Monteroni, Lecce 73100, Italy

Corresponding Authors

*E-mail: david.tobaldi@nanotec.cnr.it.

*E-mail: vittorianna.tasco@nanotec.cnr.it

Twitter: **@D14MT** (DM Tobaldi)

Twitter: **@VittoriannaT** (V Tasco)

S1. FILM DEPOSITION

A conventional time-sequenced growth of thin films by ALD consists of 4 consecutive steps: dosing, purging, plasma exposure, purging.[S1] However, for the growth of MoO_x thin films, the employment of $(N^tBu)_2(NMe_2)_2Mo$ as molybdenum metalorganic precursor, given its low vapour pressure of 0.2 Torr at 55 °C,[S2,S3] although particularly advantageous for high temperature growth,[S4] required the use of a long dosing/bubbling step of 6-8 seconds.[S4]

Conversely, aiming to obtain oriented $\alpha-MoO_3$ with short cycle time, the implemented boosting method follows the steps reported in the table of Figure S1a. In detail, we have added, at the beginning of the ALD cycle, an injection step of 1 s, when N_2 is pulsed at the bottom of the Mo precursor cylinder by means of an injection valve (V_I) (see Figure S2a), whilst keeping closed the bubbling valve (V_B) (Figure S2b). Figure S1a (bottom panel) reports the reactor pressure over a few ALD cycles, showing a pressure drop during the injection step: actually, the N_2 was completely conveyed into the precursor cylinder by contemporary closing the bubbling and purging (V_{P1}) valves (see Figure S2). After increasing the pressure in the headspace of the cylinder, the $(N^tBu)_2(NMe_2)_2Mo$ vapour space was pulsed for 1.5 s into the process chamber during the dosing step (Figure S1a, bottom panel). A pressure gradient of about 3 Pa was generated in the reactor owing to the combination of the precursor vapour and the carrier gas (N_2). The growth cycle is then completed with the standard steps of precursor purge (2 s), plasma exposure (2 s of O_2 plasma) and reactant purge (2.5 s). The chosen plasma exposure time (2 s) is sufficient to obtain a complete combustion of ligands and prevent the incorporation of carbon-based impurities in the films.

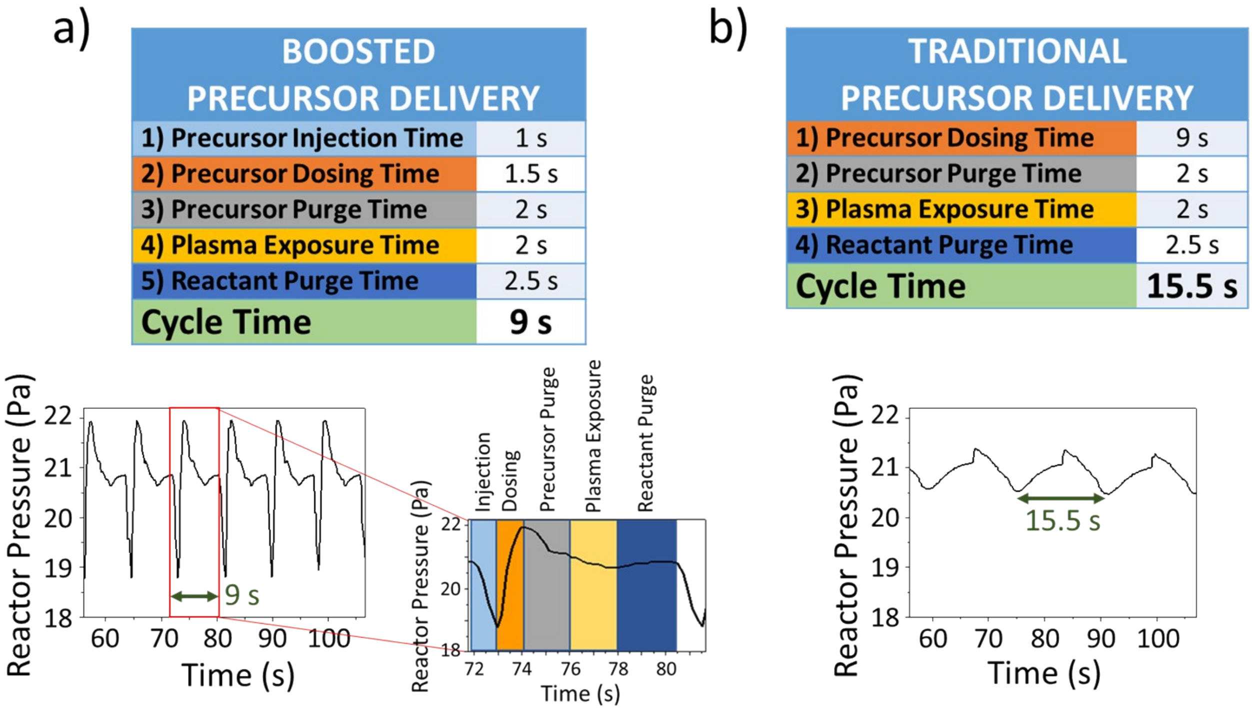


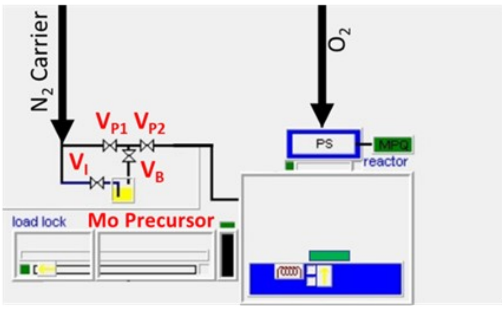
Figure S1. a) Boosted and b) traditional precursor delivery methods for MoO_x growth by ALD along with the reactor pressure over a few cycles. The resulting total time of each ALD cycle in the boosted approach was reduced down to 9 s, that is a reduction of 42% with respect to the traditional precursor injection mode.

The saturation curve for the precursor dose is shown for a deposition temperature of 100 °C (Figure S3); the GPC shows a saturation at a value of about 0.11 nm, after a bubbling valve opening time of 1.5 s. By doubling the injection time (2 s) and keeping the bubbling valve opening time of 1.5 s, the GPC value remains unchanged in the saturation regime. Hence, as the injection and bubbling times of 1 s and 1.5 s, respectively, were chosen as standard, a full ALD cycle with our boosted Mo precursor delivery method lasts 9 s (Figure S1a).

Conversely, a traditional $(N^tBu)_2(NMe_2)_2Mo$ precursor delivery needs to start with a long precursor pulse to work in saturation regime, as reported in Figure S3. As it can be noted, saturation is observed only after a V_B valve opening time of 9 s; N_2 gas is used as a carrier gas during this precursor dosing time. The growth cycle is then completed with the standard steps reported in Figure S1b (top panel). The reactor pressure over a few ALD cycles is also shown, demonstrating as this strategy needs longer dosing time to reach a sufficient reactor overpressure (1 Pa) to get a saturated GPC.

Consequently, the minimum ALD cycle lasts 15.5 s, in agreement with similar approaches in the literature.[S4] Therefore, the resulting total time of each ALD cycle was reduced from 15.5 s down to 9 s with our boosted precursor delivery approach, that means a time reduction of 42%. The growth rate was correspondingly boosted up to 44 nm/hour with respect to the 28 nm/hour. This suggests that the engineered gas supply solution produced an actual increase in the number of deposited Mo atoms per unit of time.

a)



b)

BOOSTED PRECURSOR DELIVERY: DEPOSITION PARAMETERS	
Deposition Temperatures	RT – 50 – 100 – 150 – 200 – 400 °C
Bubbler Temperature	55°C
Delivery Line Temperature	120°C
Base Pressure	10^{-6} mbar
N_2	40 sccm
O_2	150 sccm
Precursor Injection Time	1 s V_I ON, V_B OFF, V_{P1} OFF, V_{P2} ON
Precursor Dosing Time	1.5 s V_I OFF, V_B ON, V_{P1} ON, V_{P2} ON
Precursor Purge Time	2 s V_I OFF, V_B OFF, V_{P1} ON, V_{P2} ON
Plasma Exposure Time	2 s V_I OFF, V_B OFF, V_{P1} ON, V_{P2} ON, PLASMA ON
Reactant Purge Time	2.5 s V_I OFF, V_B OFF, V_{P1} ON, V_{P2} ON
Cycle Time	**9 s**

Figure S2. a) Sketch of the Sentech ALD bubbling system for Mo precursor. b) Deposition parameters and steps related to the developed ALD process, which is featured by a boosted precursor delivery mode.

300 ALD cycles were then repeated for the film growth by using the boosted precursor delivery method with the defined injection and dosing standard times, with a set of substrate temperatures between RT and 400 °C.

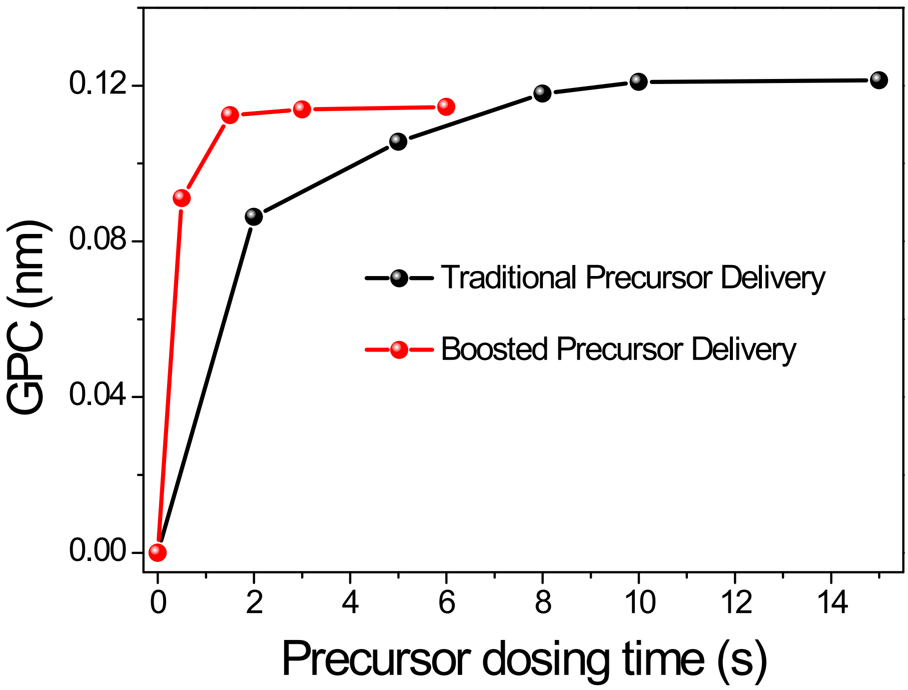


Figure S3. Precursor saturation curve showing the GPC as a function of precursor dosing time for both traditional and boosted precursor $[(N^{t}Bu)_2(NMe_2)_2Mo]$ delivery approaches. A constant O_2 plasma exposure time of 2 s was set, whilst the substrate temperature was set at 100 °C.

S2. MORPHOLOGICAL, STRUCTURAL AND OPTICAL ANALYSIS

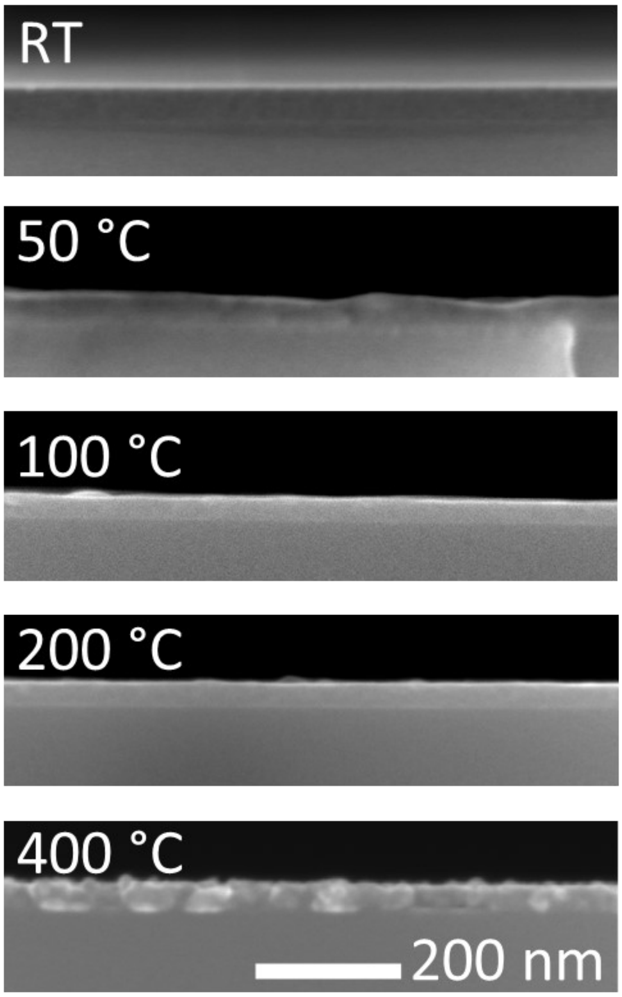


Figure S4. Cross-view SEM images of MoO_x thin films deposited by means of the boosted precursor injection method (300 ALD cycles) on silicon substrate with native oxide on top at different temperatures.

The thickness of MoO_x films deposited at different temperatures was also measured by cross-sectional SEM (Figure S4). The values of about 50 and 38 nm are measured for the deposition temperatures of RT, and both 50 and 400 °C, respectively. For the intermediate temperatures (100, 150 and 200 °C) we measured a thickness in the range 33-34 nm. Such results are in good agreement with the thicknesses retrieved by ellipsometry investigation. Therefore, the Cauchy model used for fitting the ellipsometry measurements is a good approximation.

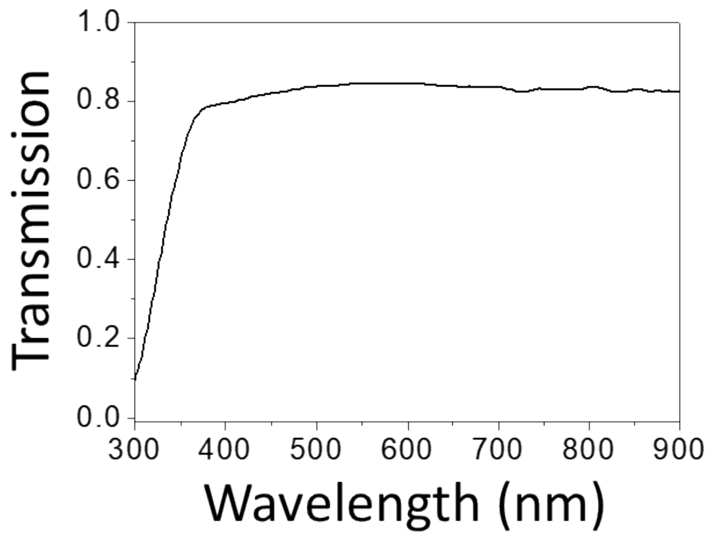


Figure S5. Transmission spectrum of the MoO_3 film deposited at 400 °C (by boosted precursor delivery, 300 ALD cycles), thickness of about 38 nm as measured by cross-sectional SEM.

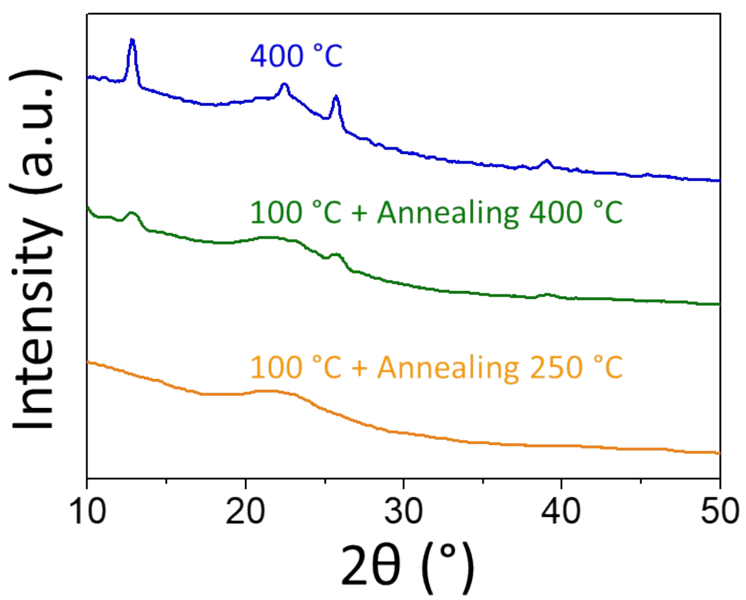


Figure S6. Grazing incidence X-ray diffractograms of MoO_x film deposited at 100 °C (by boosted precursor delivery) and post-annealed in a furnace at 250 °C and 400 °C in N_2 for 3 hours. The diffractogram of the film deposited at 400 °C by means of the boosted precursor delivery approach was also reported for comparison.

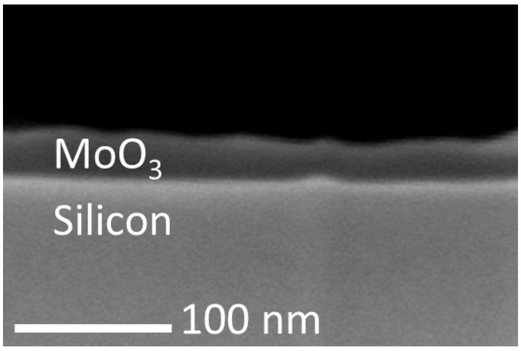


Figure S7. Cross-view SEM image of MoO_3 film deposited at 100 °C and post-annealed in a furnace at 400 °C in N_2 for 3 hours.

SUPPORTING INFORMATION REFERENCES

S1 S. M. George, *Chem. Rev.*, 2010, 110, 111–131.

S2 A. Bertuch, G. Sundaram, M. Saly, D. Moser and R. Kanjolia, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 2014, 32, 01A119.

S3 J. Ziegler, M. Mews, K. Kaufmann, T. Schneider, A. N. Sprafke, L. Korte and R. B. Wehrspohn, *Appl. Phys. A*, 2015, 120, 811–816.

S4 M. F. J. Vos, B. Macco, N. F. W. Thissen, A. A. Bol and W. M. M. (Erwin) Kessels, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 2016, 34, 01A103.