Electronic Supplementary Information

Reliable high work-function molybdenum dioxide synthesis via template-effect-utilizing atomic layer deposition for next-generation electrode application

*Ye Won Kim,[1] Ae Jin Lee,[1] Dong Hee Han,[1] Dae Cheol Lee,[1] Ji Hyeon Hwang,[1] Youngjin Kim,[1] Songyi Moon,[2] Taewon Youn,[2] Minyung Lee,[2] and Woojin Jeon[1]**

[1]Department of Advanced Materials Engineering for Information and Electronics, and Integrated Education Program for Frontier Science & Technology (BK21 Four), Kyung Hee University, Yongin, Gyeonggi 17104, Korea

[2]SK Hynix, Inc., Icheon, Gyeonggi 17336, Korea

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Electrical characteristics of deposited MoO_2 thin-film electrodes

The electrical characteristics of the deposited MoO_x thin films were evaluated to apply MoO_x as an electrode material. The resistivities of the MoO_x films deposited using O_3 on the TiN substrate were investigated for various film thicknesses (**Figure S7a**). In the MoO_x films up to 7.5 nm thick, wherein the crystal structure consisted of only the original MoO_2 phase, the resistivity was 1.3×10^{-3} Ω·cm. The increased resistivity of the 10-nm-thick MoO_x thin film was attributed to crystallized-MoO_3-induced film degradation because crystallized MoO_3 is an electrical insulator. The surface morphology was examined using atomic force microscopy (AFM) (Figure S7b). The root-mean-square roughness (R_{rms}) of all the samples was less than 1.98 nm without any extrusion, which can induce severe leakage current degradation in MIM capacitors. These results show that MoO_x deposited using O_3 on the TiN substrate exhibited electrical properties comparable to those of pure TiN as an alternative electrode material for application to MIM capacitors. However, MoO_x thin films are not just electrically comparable to TiN. As an MIM capacitor electrode, a higher-work-function conductor must also be favorable to suppress leakage current conduction. The MIM capacitor fabricated using the ALD TiN electrode exhibited a work function of 4.2 eV. However, the MoO_x/TiN work function was considerably higher (5.5 eV, Figure 5c), which is the highest work function among all the ALD electrode materials (Table I). Moreover, even the 3.5-nm-thick ALD MoO_2 film exhibited a work function as high as 5.4 eV.

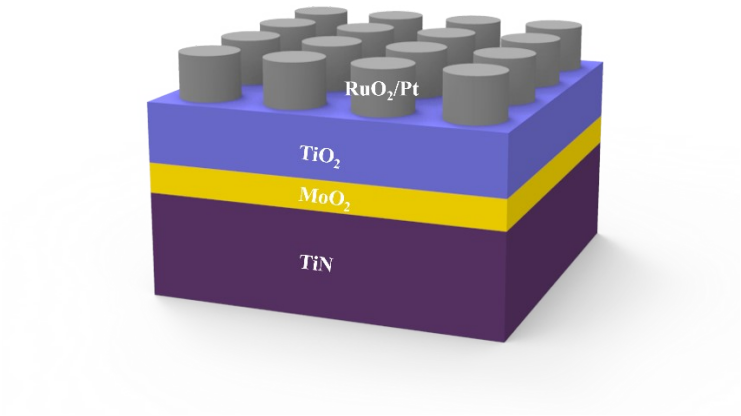

Figure S1. Schematic of the fabricated metal-insulator-metal structure.

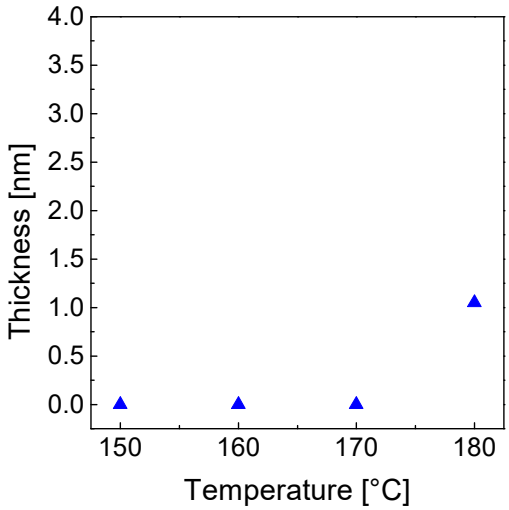

Figure S2. Thicknesses of MoO_x films deposited at different substrate temperatures.

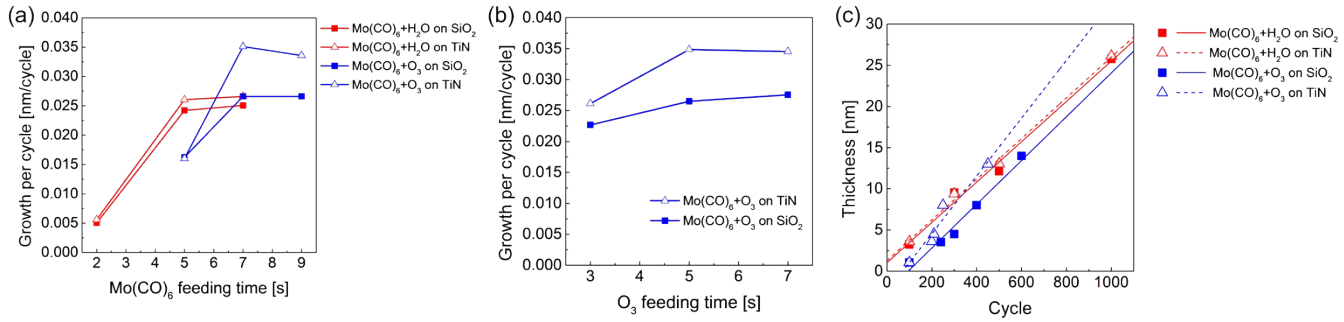

Figure S3. Growth per cycle plotted as functions of (a) $Mo(CO)_6$ feeding time and (b) O_3 feeding time. (c) Thickness of deposited MoO_x thin films plotted as functions of number of cycles for various process conditions and substrates.

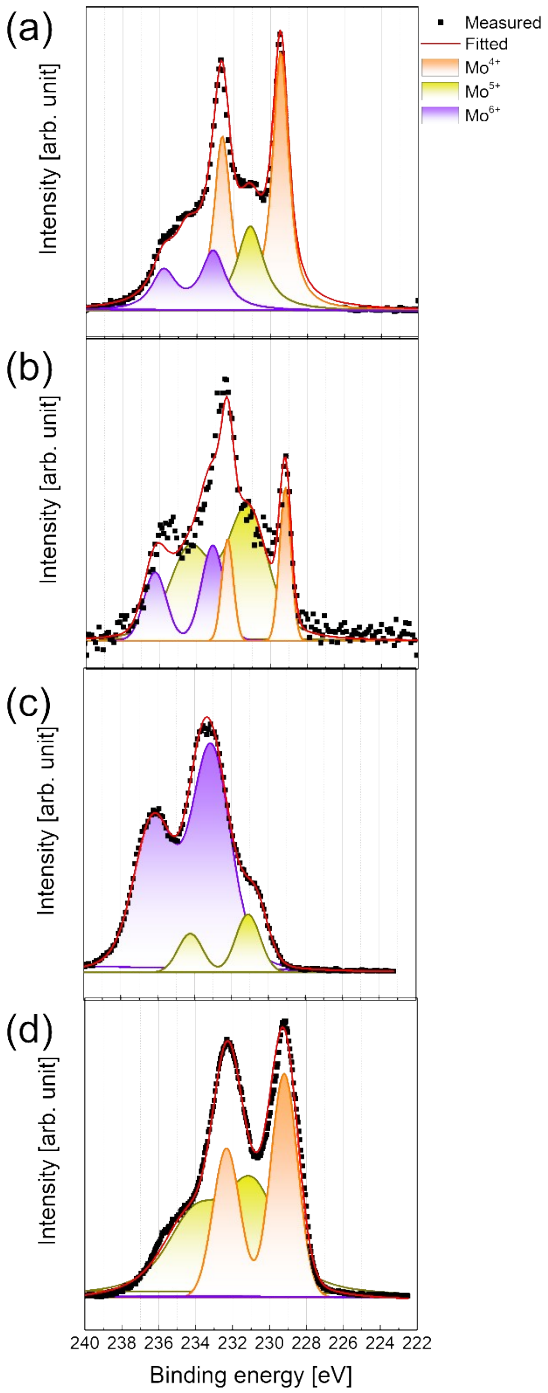

Figure S4. XPS Mo 3*d* spectra of (a) $Mo(CO)_6$+O_3 and (b) $Mo(CO)_6$+H_2O thin films deposited on TiN and (c) $Mo(CO)_6$+O_3 and (d) $Mo(CO)_6$+H_2O thin films deposited on SiO_2.

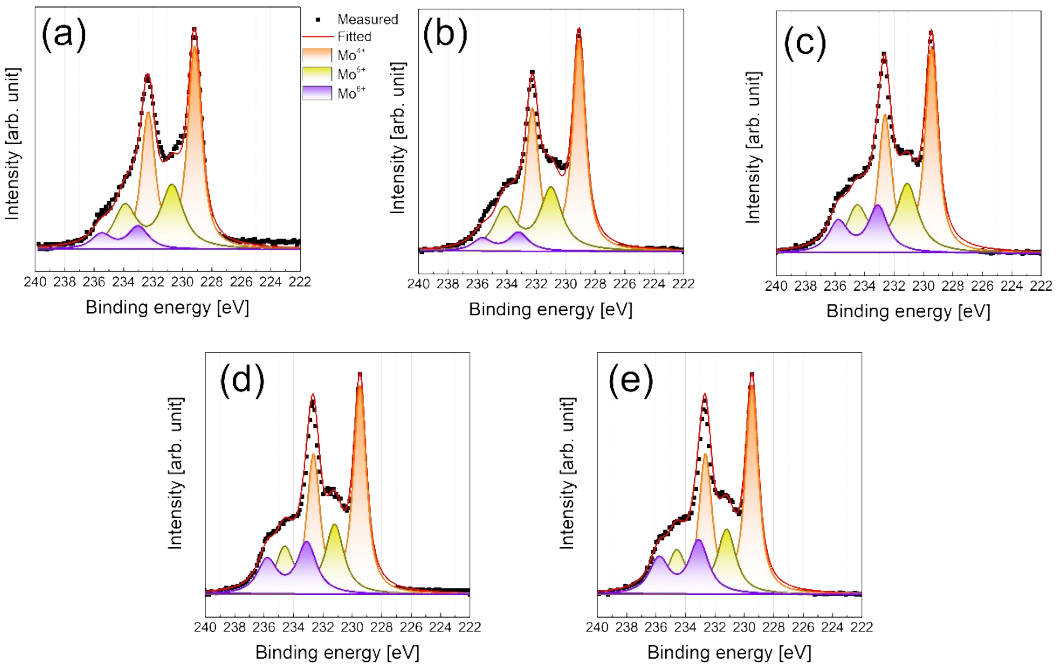

Figure S5. Mo *3d* XPS spectra of (a) 1.2-, (b) 3.6-, (c) 4.1-, (d) 8.0-, and (e) 12.4-nm-thick MoO_2 thin films.

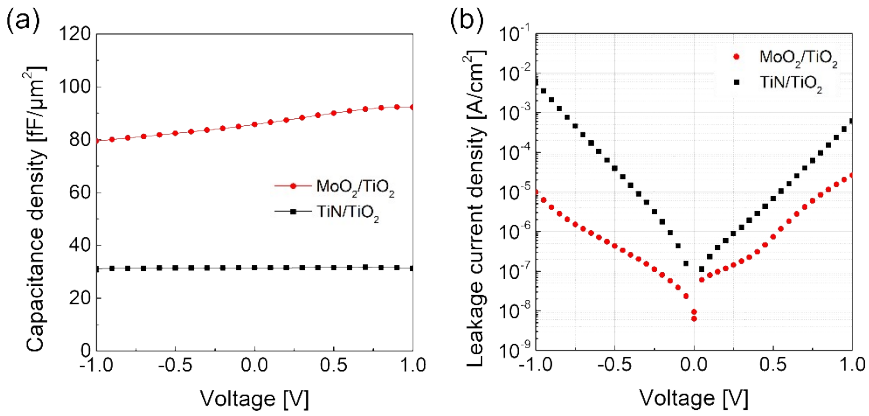

Figure S6. (a) C–V and corresponding (b) J–V curves for 16-nm-thick TiO_2 thin films deposited on MoO_2 and TiN substrates.

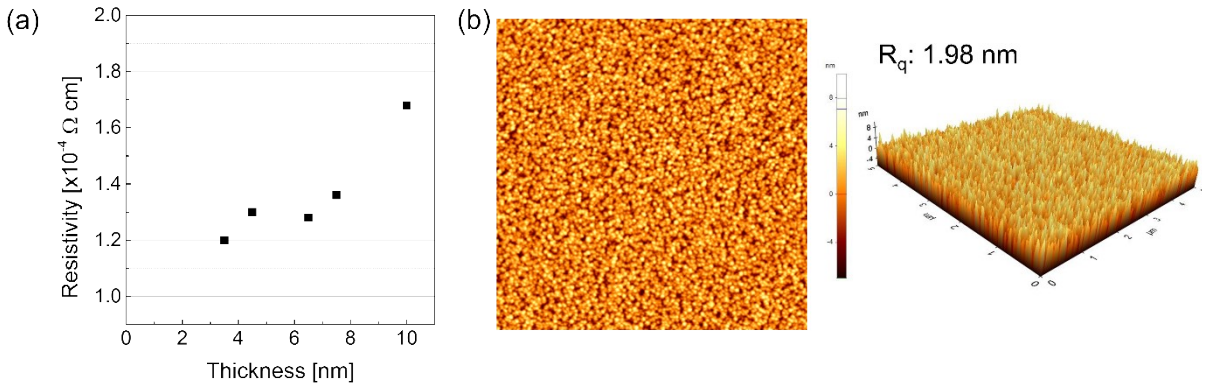

Figure S7. (a) Resistivity of MoO_2 thin films deposited at various thicknesses. (b) AFM image and R_{rms} of 4.5-nm-thick MoO_2 thin film.