Supporting Information

Synthesis of Large Area two-dimensional MoS_2 films by Sulfurization of Atomic Layer Deposited MoO_3 Thin Film for Nanoelectronic applications

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General process schematic (synthesis/fabrication)

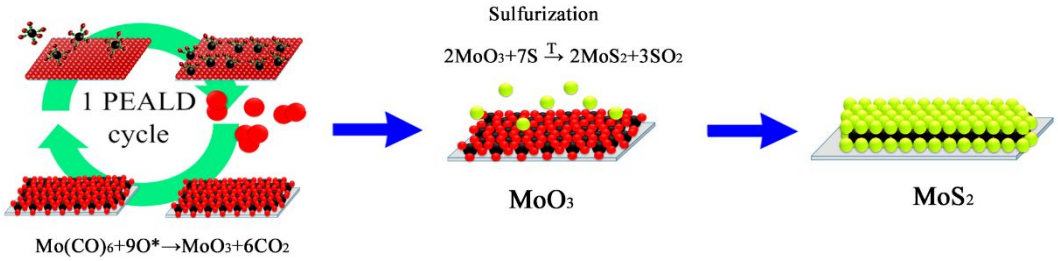

Figure S1. Process schematic for the thin MoS_2 film fabrication by the MoO_3 sulfurization from a chemistry perspective

Development of the ALD process for MoO_3 growth

Thin MoO_3 films were deposited in a commercially available hot-wall Picosun R200adv reactor equipped with a remote RF inductively coupled plasma source, operated at a power of 2500 W using $Mo(CO)_6$ (molybdenum hexacarbonyl 99.9% from Sigma Aldrich) and O_2-plasma as the Mo-precursor and oxygen source, respectively. Nitrogen (99.999%) was used both as carrier and purge gas, while Ar (99.9999%) was used as a carrier in plasma source. Solid-State $Mo(CO)_6$ source was kept at 40°C during the ALD process to produce an adequate vapor pressure. The $Mo(CO)_6$ and O_2-plasma exposure times were fixed at 1.6 and 21.0 s, respectively. After each reactant exposure, the reactor was purged by 8.0 s. The substrate temperature was maintained at 165°C. The specific characteristics of the utilized equipment are extremely long (≈ 60 cm) distance from the plasma source to the substrate and high working pressure (~ 1.0 mbar). Under such conditions, the kinetic energy of charged particles reaching the substrate is evaluated to be negligibly low, which was confirmed by additional measurements carried out directly on the described equipment.

At the described conditions the MoO_3 film growth rate was found to be ~0.45 Å/cycle which is comparable to the existing literature data. The utilized ALD process allowed obtaining thin MoO_3 films with a good uniformity ($1\sigma \approx 3.5\%$) on a 4" silicon wafers with 10 nm-thick Al_2O_3 seed layer (Figure S2).

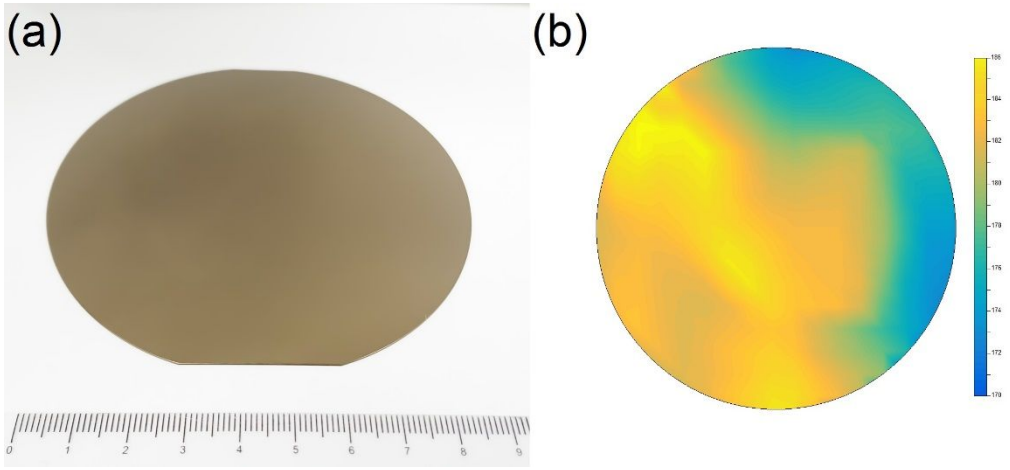

Figure S2. Photograph of the 4” silicon wafer with the ALD-grown MoO_3 film (400 ALD cycles) (a) and MoO_3 film thickness distribution across the wafer area, measured by spectral ellipsometry (b)

Angle-resolved XPS analysis for MoO_3 film thickness determination

Mo3d and Al2p XPS spectra collected from *as-grown* MoO_3 film at different electron emission angles (25, 45 and 65°) are presented in Figure S3.

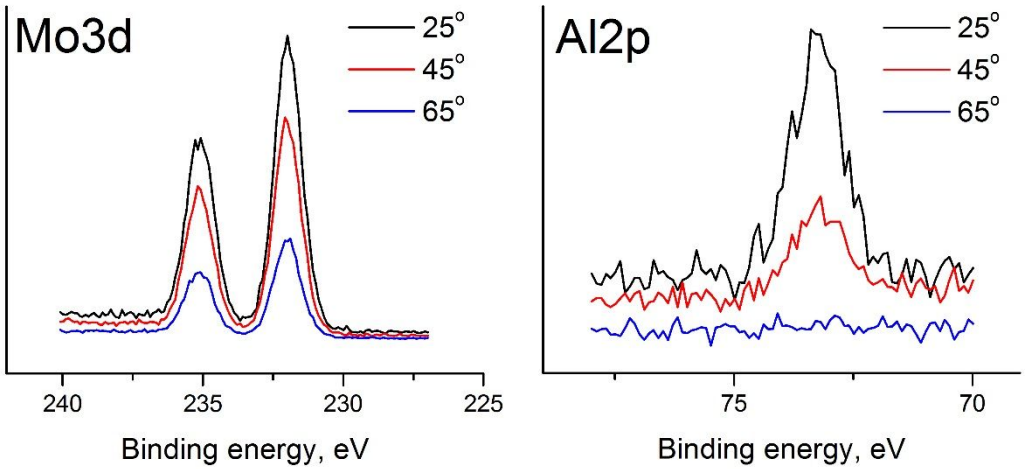

Figure S3. Angle-resolved XPS spectra collected from *as-grown* thin MoO_3 film on sapphire

It becomes obvious that a MoO_3 film with a notable thickness was achieved since the Mo3d/Al2p ratio monotonically increased with the rise of collection angle (θ) while the Al2p signal completely vanished at θ=65°. The following equations were used for the film thickness (*h*) and continuity factor (*f*) determination:

$$I_{Mo} = I^0_{Mo} \times f \times \cos(\theta) \times \left(1 - exp\left(-\frac{h}{\lambda^{MoO3}_{Mo3d} \times \cos(\theta)}\right)\right)$$

$$I_{Al} = I^0_{Al} \times (1 - f) \times \cos(\theta) \times exp\left(-\frac{h}{\lambda^{MoO3}_{Al2p} \times \cos(\theta)}\right)$$

Here λ denotes the inelastic mean free path while I^0 denotes the signal from the uncovered thick (XPS non-transparent) layer for a given material. The λ values were calculated by the TPP-2M method (MoO_3 density was given as 4,69 g/cm^3 and bandgap E_g as 2,88 eV) with the following result: $\lambda^{MoO3}_{Mo3d} = 20{,}2$ Å and $\lambda^{MoO3}_{Al2p} = 22{,}5$ Å. Next, the experimental I_{Mo}/I_{Al} values were fitted by the described model and the completely continuous film (*f*=1) was found in all cases while its thickness depended on ALD cycles number.

XPS analysis of as-grown MoO_3 film

The completely oxidized Mo^{6+} state in as-grown MoO_3 film is clearly seen in Figure S4:

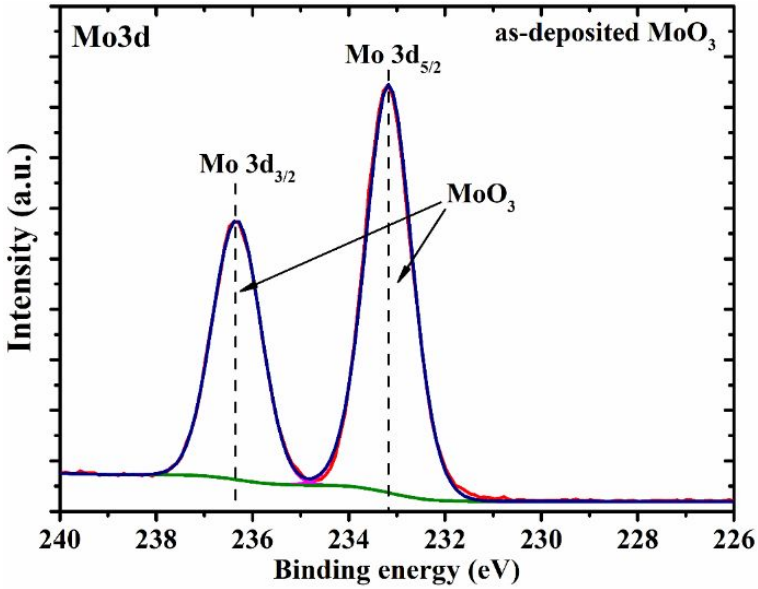

Figure S4. XPS Mo*3d* spectra for the as-deposited MoO_3 film. The blue line represents the raw spectra, and other color lines represent the deconvoluted peaks, and the green line represents the background.

Raman spectra deconvolution

The result of the Raman spectra deconvolution for the films, sulfurized at different temperatures are presented in the table below:

Table 1. Raman spectra deconvolution parameters

mode	500°C			700°C			900°C			1000°C		
	k, (cm^{-1})	Γ, (cm^{-1})	A (a.u.)	k, (cm^{-1})	Γ, (cm^{-1})	A (a.u.)	k, (cm^{-1})	Γ, (cm^{-1})	A (a.u.)	k, (cm^{-1})	Γ, (cm^{-1})	A (a.u.)
A_{1g}-LA(M)	**181,9**	**36,5**	**2623**	**178,1**	**15,5**	**2320**	**177,8**	**10,3**	**2257**	**177,0**	**10,9**	**4282**
TA(K)	188,7	6,3	391	188,3	6,2	555	188,2	9,8	877	188,0	13,2	2031
-	217,6	21,2	1438	212,4	30,5	1847	208,7	20,4	938	212,3	27,7	2833
LA(M)	**229,5**	**13,2**	**2315**	**227,8**	**13,6**	**1811**	**228,2**	**22,5**	**1984**	**228,4**	**14,4**	**2389**
TO(M)	349,7	40,8	2085	348,9	51,6	2000	346,6	49,8	2203	344,7	49,3	2241
LO(M)	377,5	17,0	2271	279,1	9,5	1992	377,9	8,2	1991	376,7	8,8	2325
E_{2g}^1	**383,2**	**7,6**	**714**	**383,2**	**6,2**	**1716**	**383,3**	**5,5**	**2934**	**383,3**	**4,7**	**4370**
B_{1u}	404,1	5,1	372	404,2	5,4	908	403,8	6,3	1421	404,1	6,3	2637
A_{1g}	**407,8**	**6,2**	**1025**	**407,7**	**4,5**	**1094**	**407,8**	**4,7**	**1134**	**407,7**	**4,8**	**1880**
b	**416,6**	**23,6**	**2881**	**417,2**	**18,9**	**6684**	**418,9**	**13,8**	**5298**	**419,0**	**13,4**	**9146**
2LA(M)	**450,6**	**28,4**	**2451**	**453,1**	**21,7**	**11266**	**456,6**	**17,1**	**9081**	**456,4**	**20,0**	**19956**
A_{2u}	**463,2**	**18,2**	**1726**	**464,7**	**10,2**	**2729**	**466,8**	**8,6**	**4620**	**467,0**	**8,3**	**6775**
-							445,9	29,0	6219	444,6	40,0	10779

SAED images

In addition to the presented in the manuscript SAED images, similar ones were also collected with a smaller aperture size (200 nm), allowed to collect information from less number of grains (Figure S5).

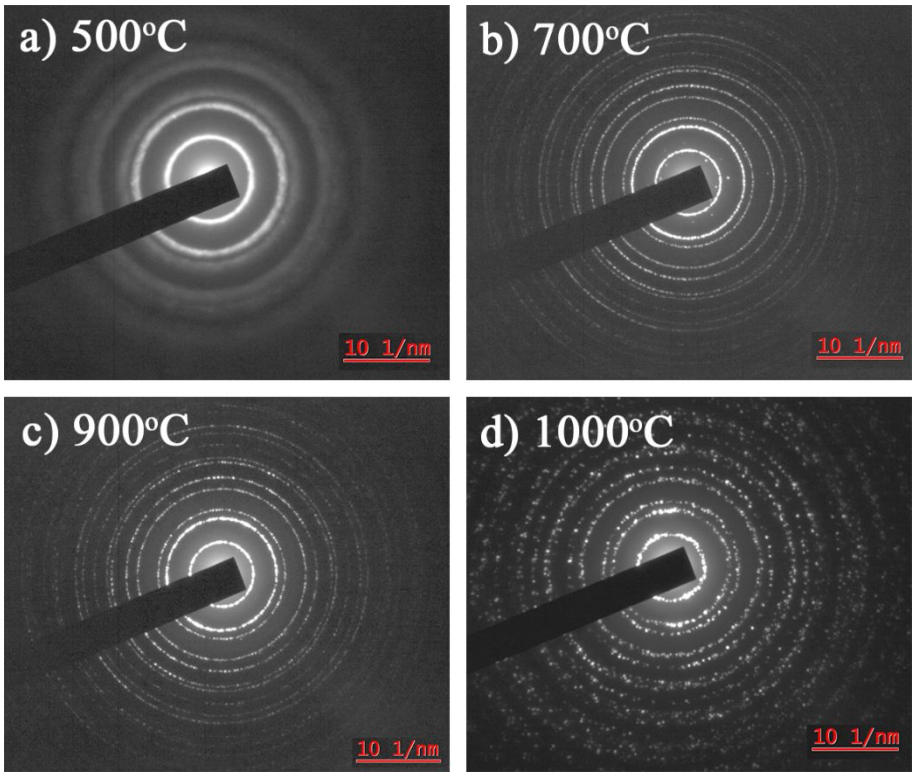

Figure S5. SAED patterns collected with an aperture diameter of 0.2 μm

One can see that sulfurization temperature increase resulted not only in the crystalline size growth but also improvement of their quality since the diffraction rings firstly become sharper (700 °C) and, finally, look-like a finite spotty pattern (1000 °C).

Rocking curve analysis

The observed variation in the preferred crystallographic orientation of the grains after the sulfurization at the two temperatures (900 and 1000 °C) was confirmed by the X-ray rocking curve analysis (Figure S6):

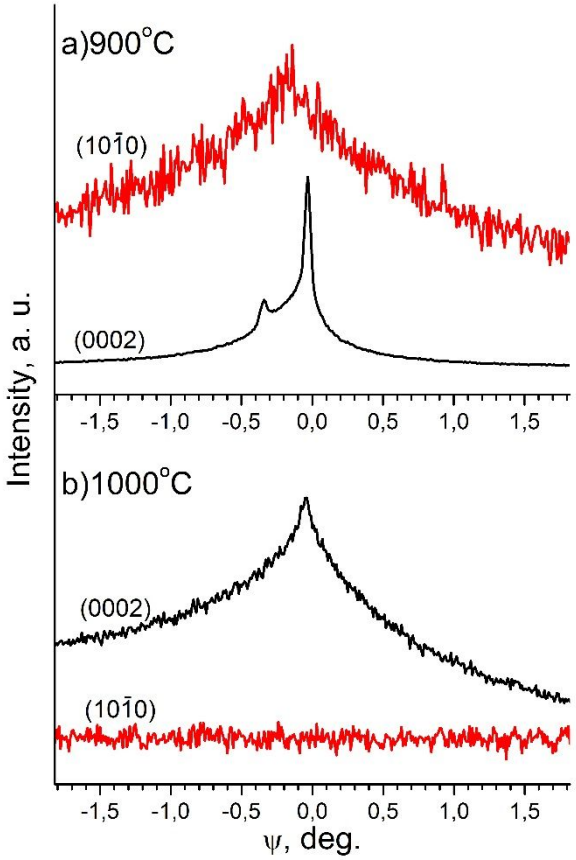

Figure S6. (0002) and rocking curve collected from the 10-nm-thick MoS_2 films sulfurized at 900°C (a) and 1000°C (b), respectively

The observed X-ray rocking curve maximum at the non-zero Ψ angle indicates the presence of the grains along the direction deviated from the normal direction to the substrate surface by the Ψ angle. First, the significant intensity in the rocking curve near the 2θ ~32.7° coincides with the θ-2θ result indicating the presence of the grains along the out-of-plane direction with a relatively large variation in their out-of-plane direction orientation for the case of the sulfurization at 900 °C (Figure S6). Another notable finding is that the [0001]-oriented grains have misoriented grains with a particular misorientation angle of ~0.3 °, in addition to the main precisely [0001]-oriented grains. These two findings suggest that the crystallographic alignment of the grain in this film is less perfect, compared to the MoS_2 film sulfurized at 1000 °C, which did not show any peculiarity in the [0001]-oriented grains and involvement of the (10-10)-oriented grains (Figure S6).

The volume ratio of fractions with different orientations (for the 10 nm MoO_3 film sulfurized at 900 °C) could be calculated using a simple uniaxial texture model (March-Dollase) and rocking curve maxima comparison:

Table 2. Volume ratio of fractions with different orientations

Fraction	$[0001]_{MoS2}$ ↑↑ $[0001]_{Al2O3}$	$[0001]_{MoS2}$ ⊥ $[0001]_{Al2O3}$	Misoriented ($\angle_{MoS2/Al2O3} \approx 0.3°$)
Volume ratio	1	0.05	0.12

The model for the MoO_3 to MoS_2 conversion

According to the presented in the main manuscript experimental data, the following model can be suggested for the MoO_3 to MoS_2 conversion:

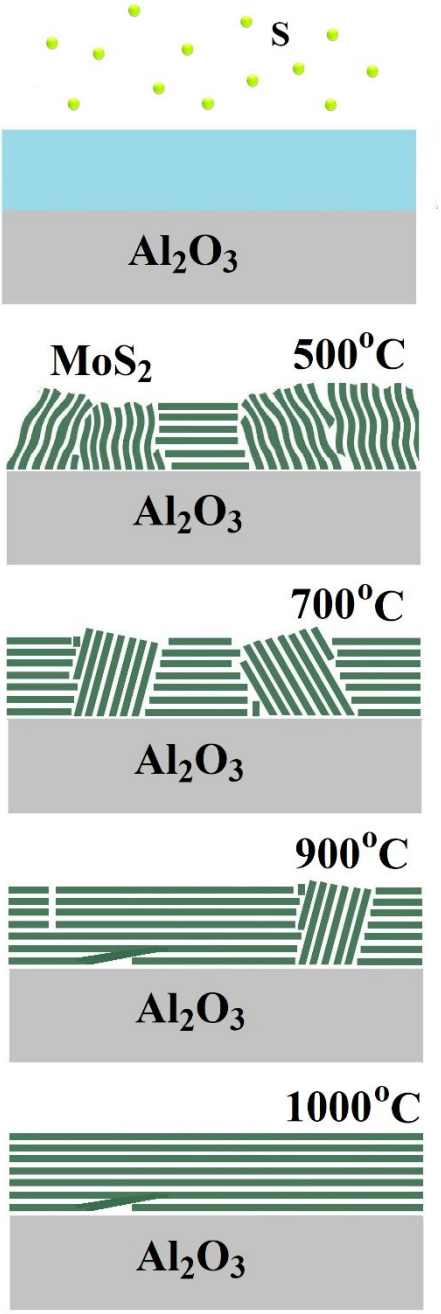

Figure S7. The possible model of MoO_3 to MoS_2 conversion at different temperatures.