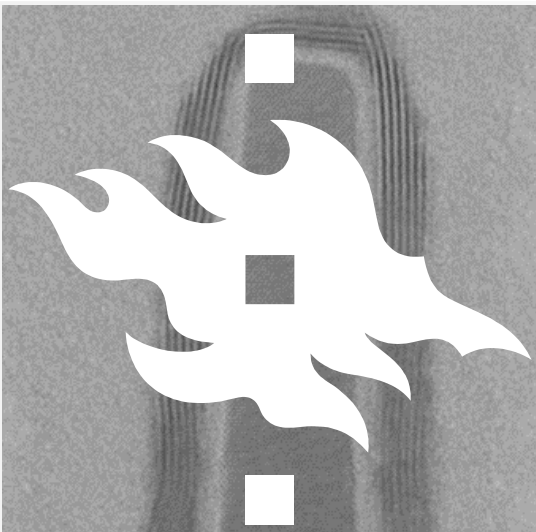
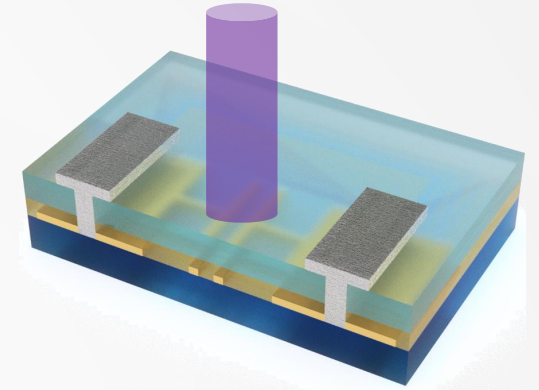
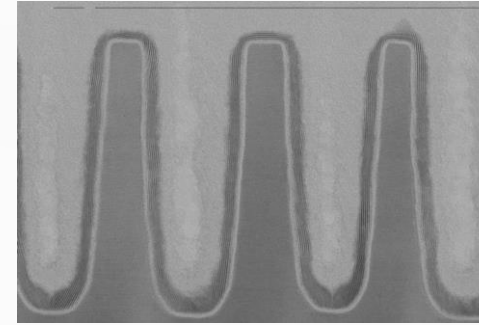
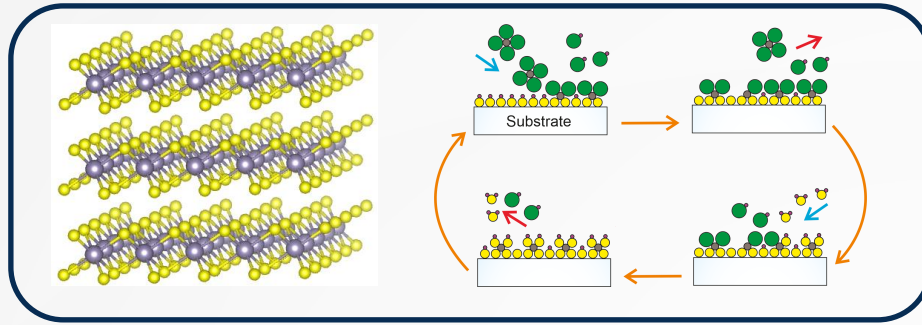




Atomic Layer Deposition of 2D Materials for Electronics and Energy

Miika Mattinen
University of Helsinki, Finland



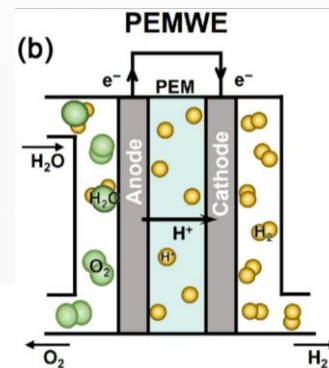
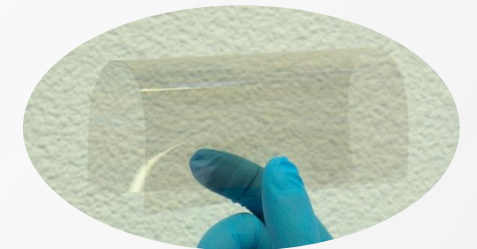
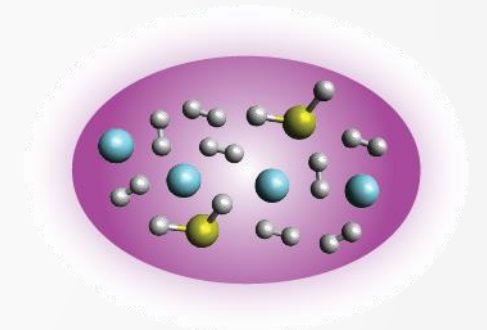
I. What is 2D? TMDC? ALD?

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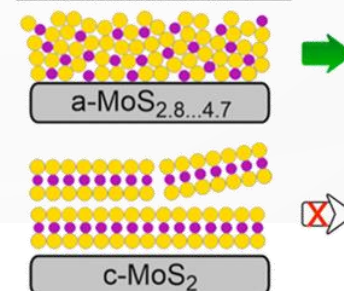
III. 100 °C deposition by plasma ALD compatible with plastics

IV. Tailoring ALD MoS_x for HER

V. Wrapping up



Tailored ALD MoS_x

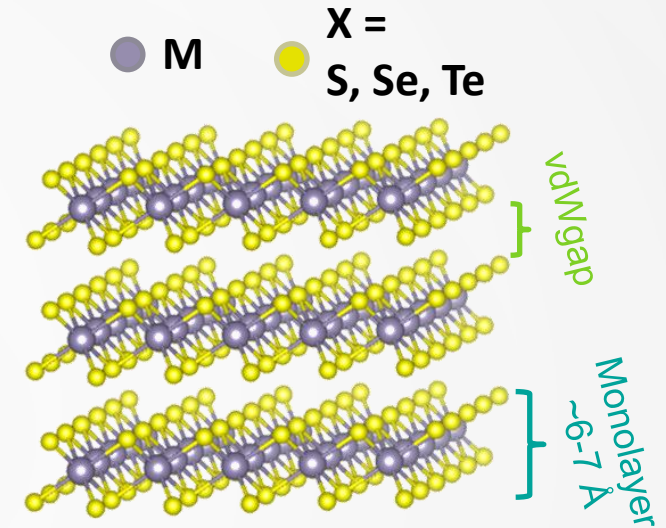


Transition metal dichalcogenides (TMDCs)

MX_2 stoichiometry, layered (2D) structure : 30+ materials

→ Unique properties: electronic, optical, chemical...

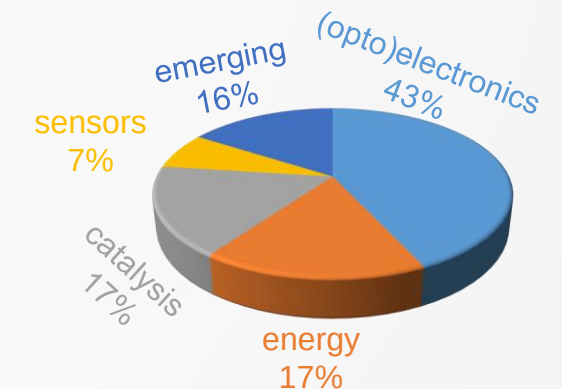
→ Vast application potential



Periodic table of TMDC sulfides

H																		He
Li	Be																	
Na	Mg																	
		Group:	4	5	6	7	8	9	10									
K	Ca	Sc	TiS ₂	VS ₂	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	S	Cl	Ar	
Rb	Sr	Y	ZrS ₂	NbS ₂	MoS ₂	TcS ₂	Ru	Rh	PdS ₂	Ag	Cd	In	SnS ₂	Sb	Te	I	Xe	
Cs	Ba	La-Lu	HfS ₂	TaS ₂	WS ₂	ReS ₂	Os	Ir	PtS ₂	Au	Hg	Tl	Pb	Bi	Po	At	Rn	

■ Semiconductors
■ Borderline semiconductors/semimetals
■ (Semi)metals



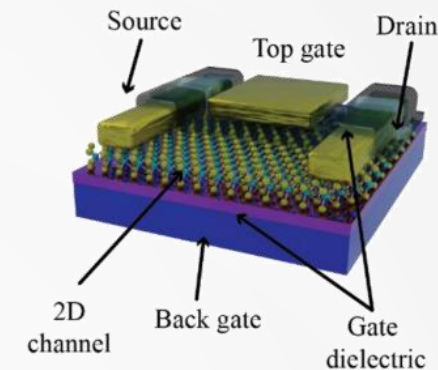
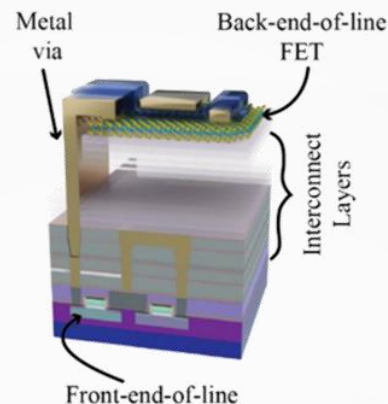
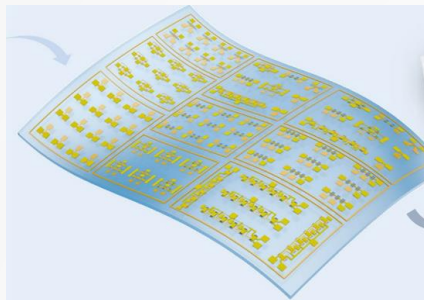
Samadi et al., *Nanoscale Horiz.*, **3**, 2018, 90

Perovskite devices

Dye-sensitized
solar cells

Li-S batteries

Etc.



Flexible ~200 °C

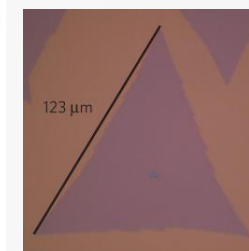
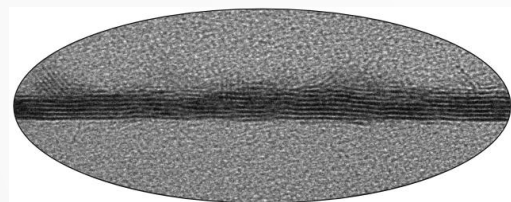
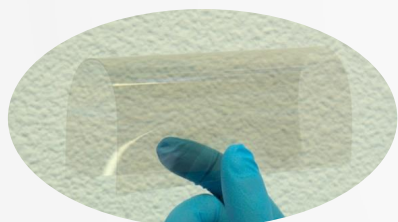
BEOL ~450 °C

FEOL ~900 °C

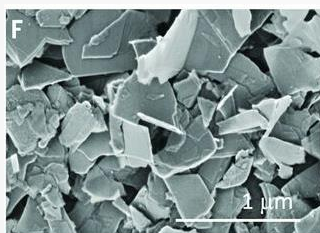
Plasma ALD

ALD

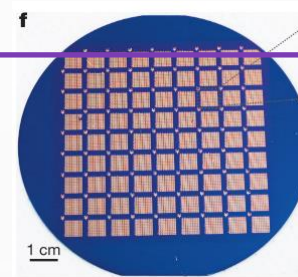
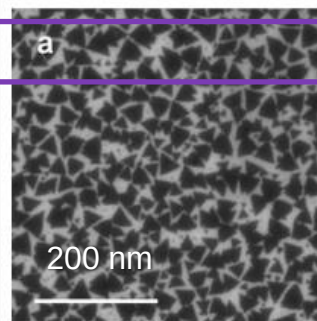
Powder CVD



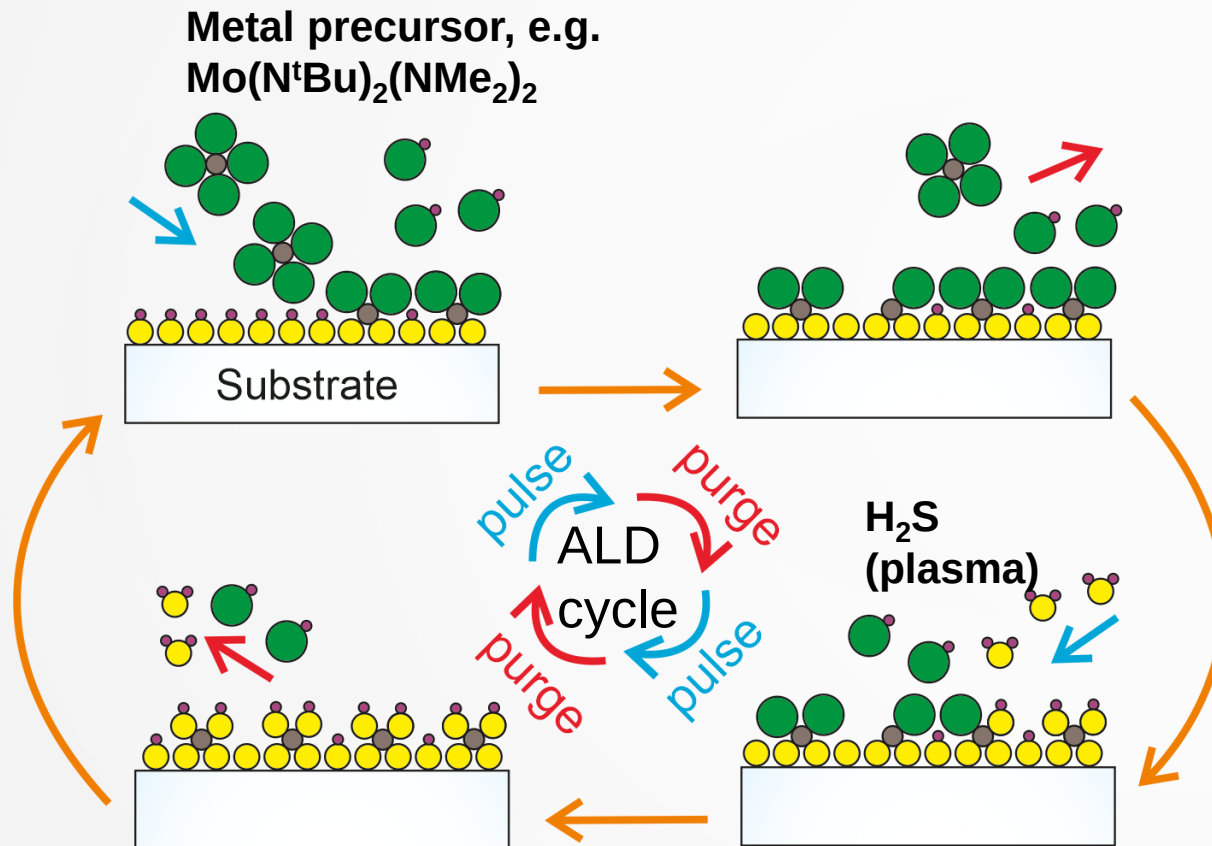
Liquid phase,
printing,
transfer...



MOCVD

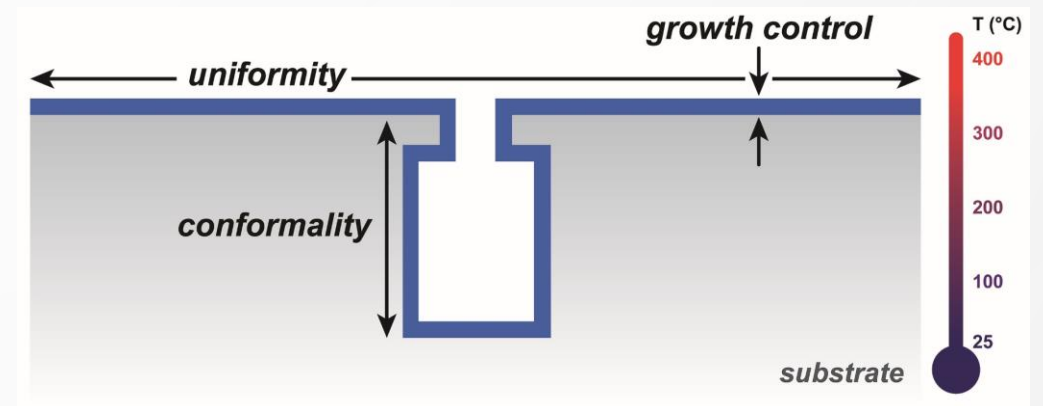


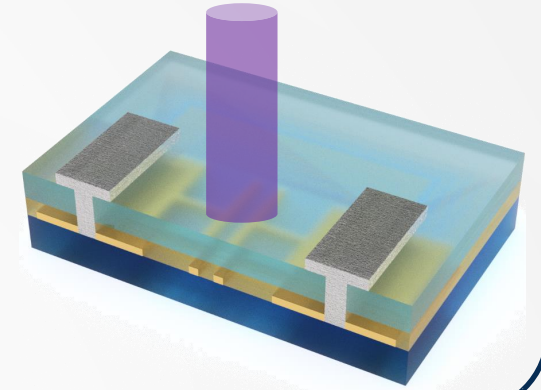
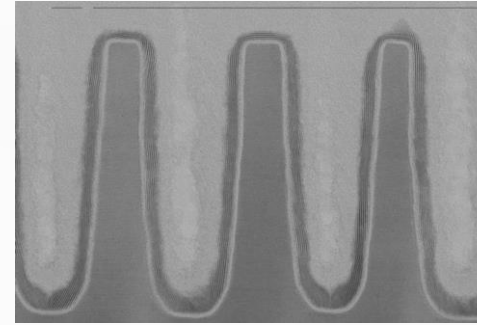
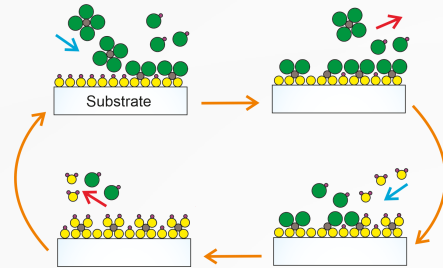
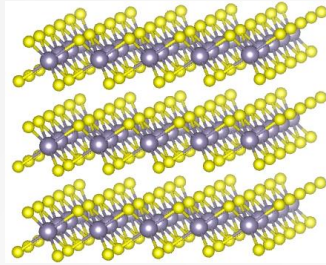
How does ALD work?



Cyclic, **surface-controlled** vapor phase deposition with unbeatable

- Thickness control (sub-ML)
 - Uniformity (also 3D)
 - Low-T deposition
- & industrial use (semicon, solar...)





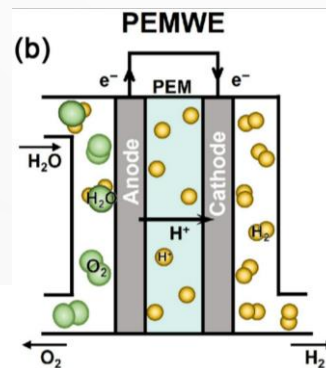
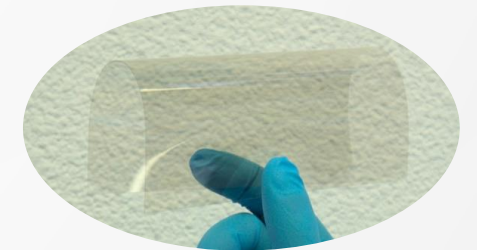
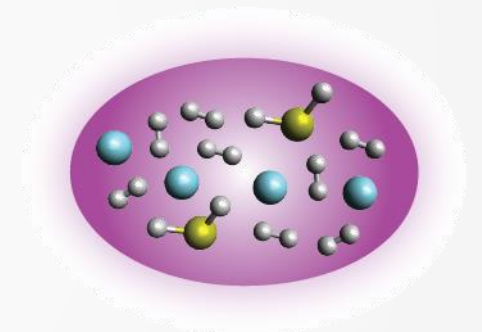
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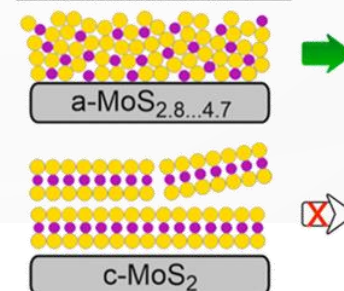
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Tailored ALD MoS_x



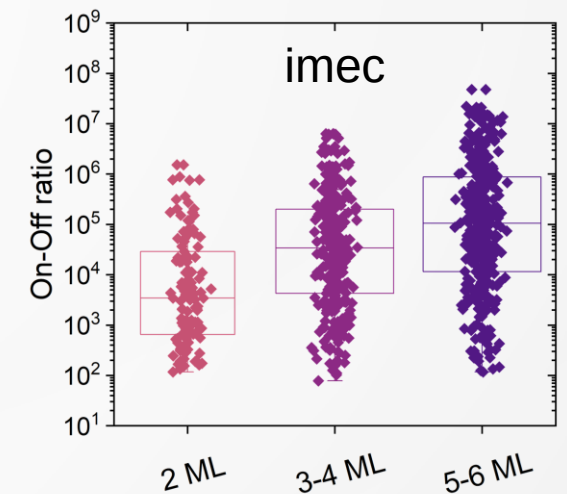
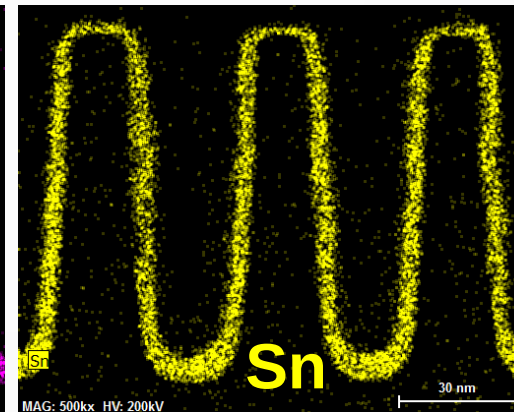
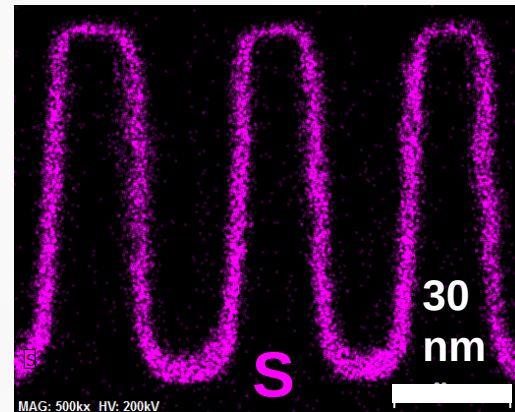
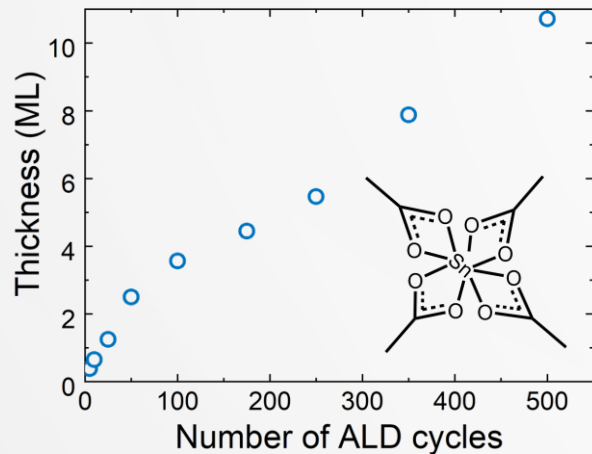
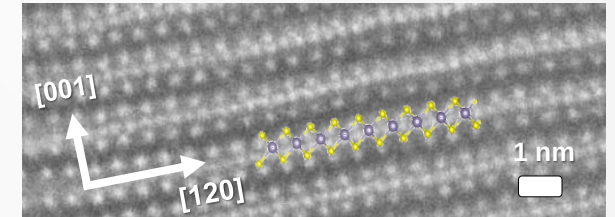
SnS₂ for energy-efficient devices processed at low-T

SnS₂: Large indirect E_g (2.2-2.6 eV) & low melting point (865 °C vs MoS₂ 1750 °C)

- **2-step ALD process** Sn(OAc)₄ + H₂S (dep 150 °C + anneal 250 °C)

➤ 2-10 ML films on SiO₂, sapphire... (2", limited by reactor size)

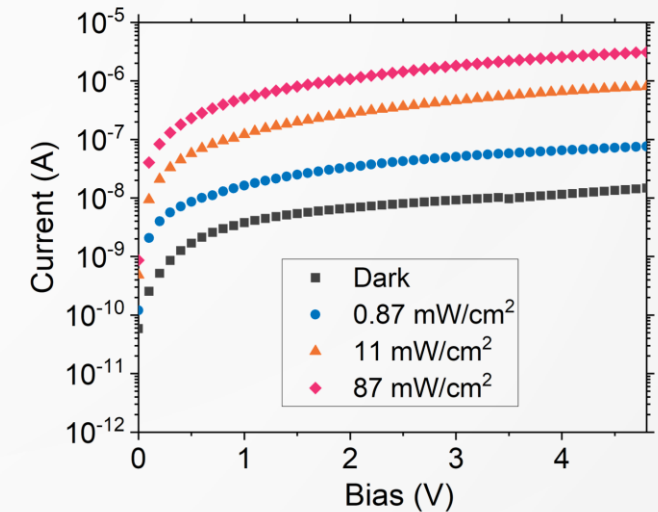
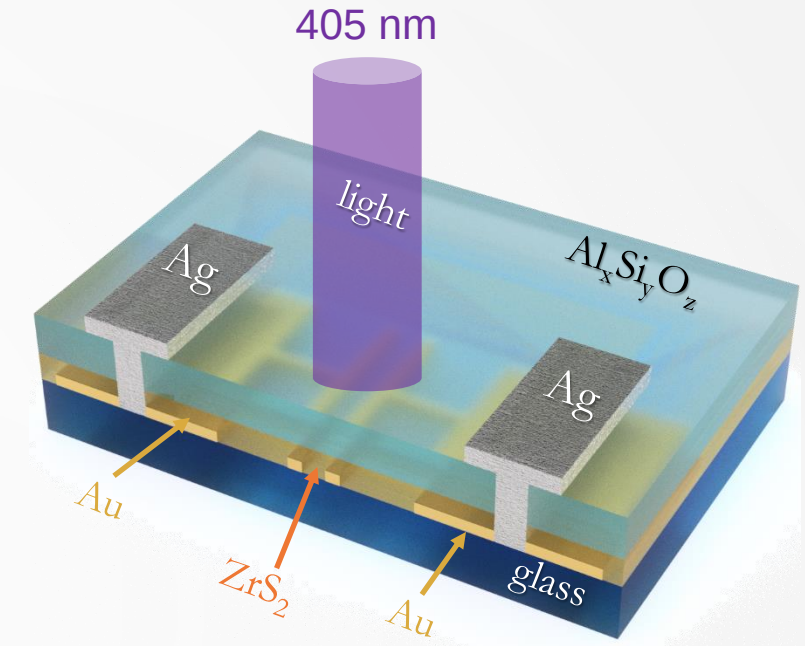
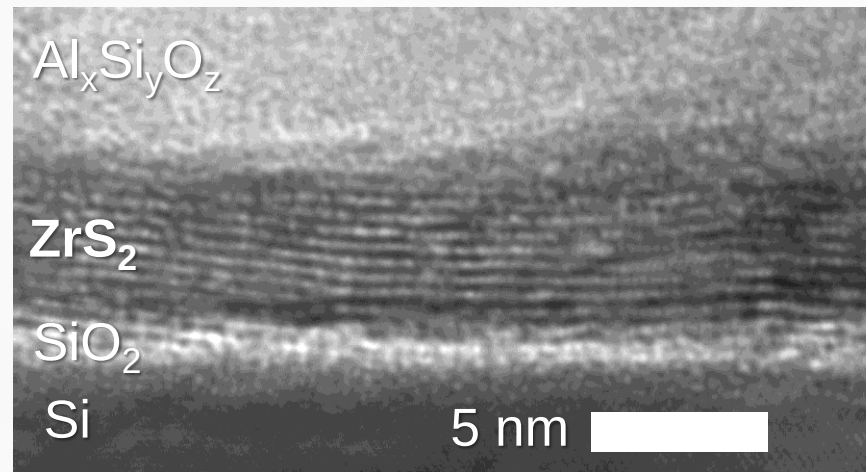
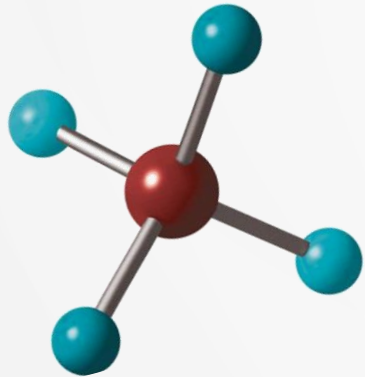
FET: high on/off ratios (processing-related variation)



HfS₂ and ZrS₂ for optoelectronics

$E_g \sim 2$ eV; high theoretical carrier mobilities

- ALD using $\text{MCl}_4 + \text{H}_2\text{S}$ @ 400 °C
- ALD in situ capping to prevent oxidation
- Simple photodetectors fabricated

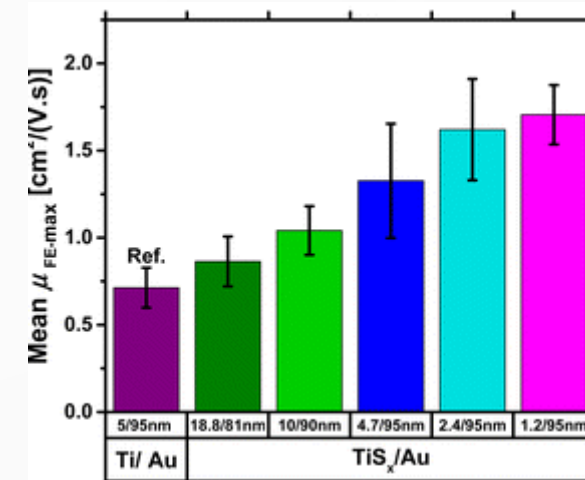
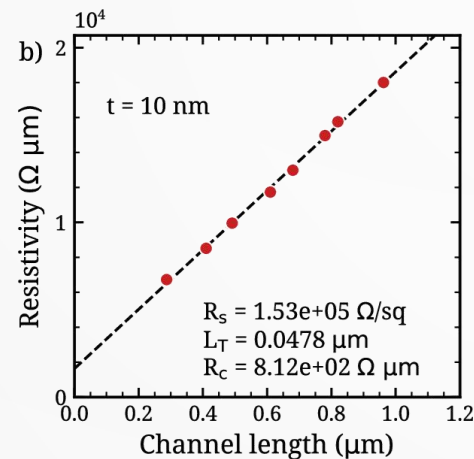
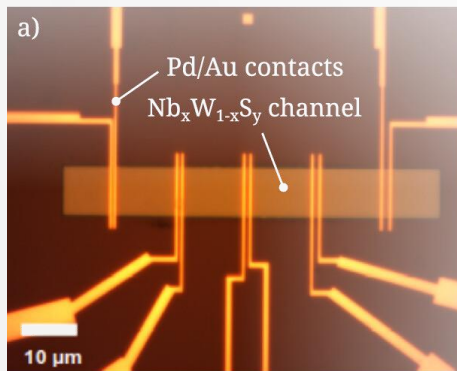


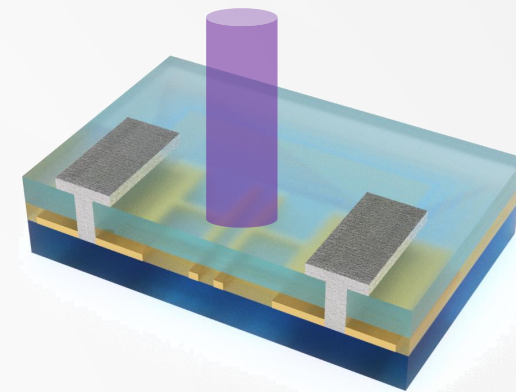
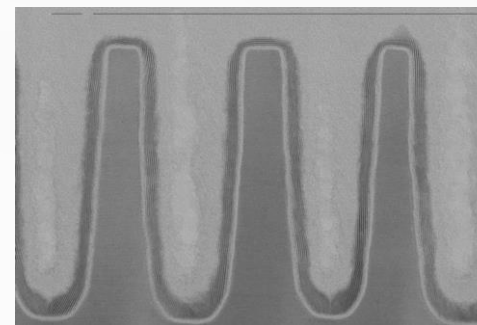
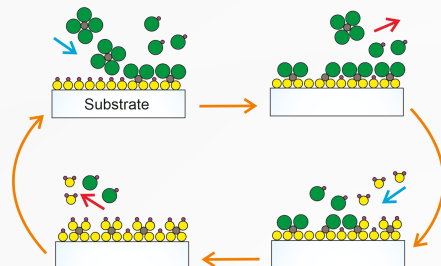
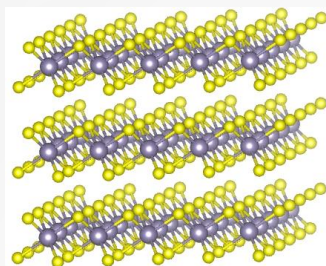
(semi)Metallic TMDCs reducing contact resistance to semiconducting TMDCs

Low **contact resistance** between Pd and $\text{Nb}_x\text{W}_{1-x}\text{S}_y$

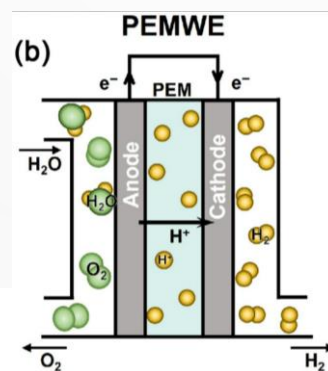
→ can be inserted between TMDC channel and metal contact

FET device: **3x mobility improvement** in MoS_2 channel by replacing Ti contact with TiS_2

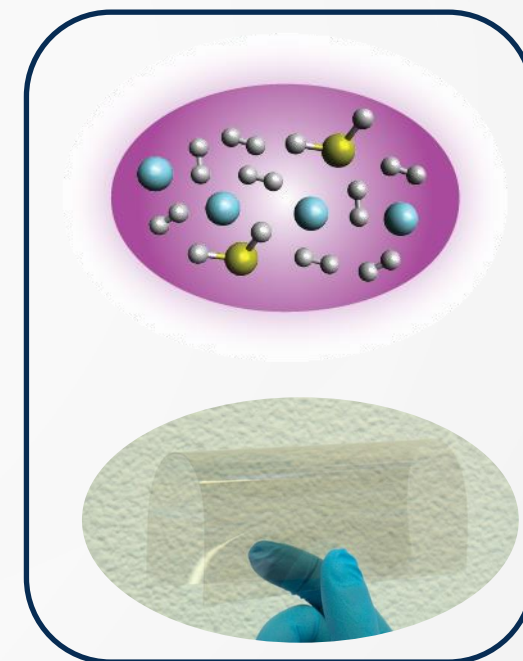
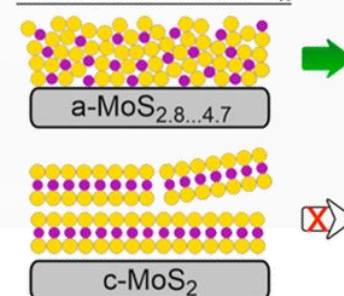




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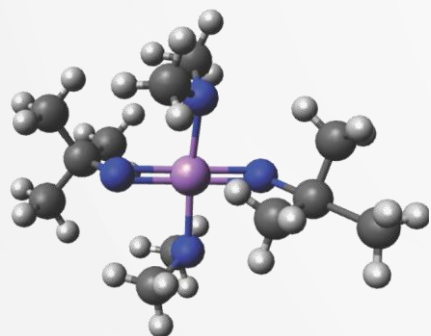
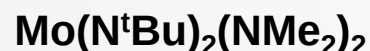
Tailored ALD MoS_x



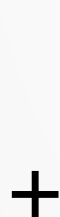
Record-low T_{dep} (100 °C) for MoS_2 , WS_2 , TiS_2 ... using plasma ALD

Key enablers:

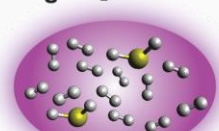
Reactive plasma-generated species
+ control of S stoichiometry with H_2



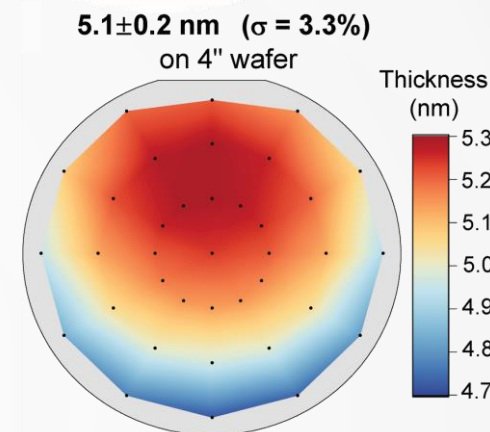
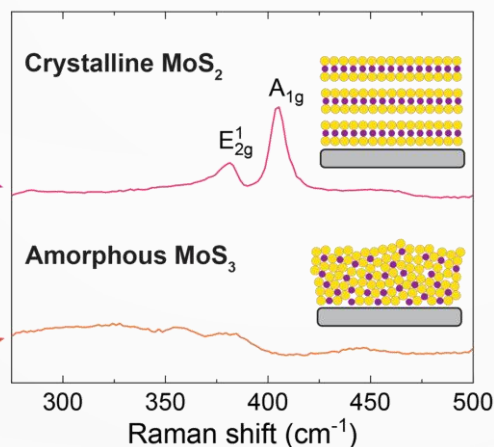
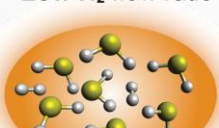
$\text{H}_2\text{S}/\text{H}_2/\text{Ar}$ plasma



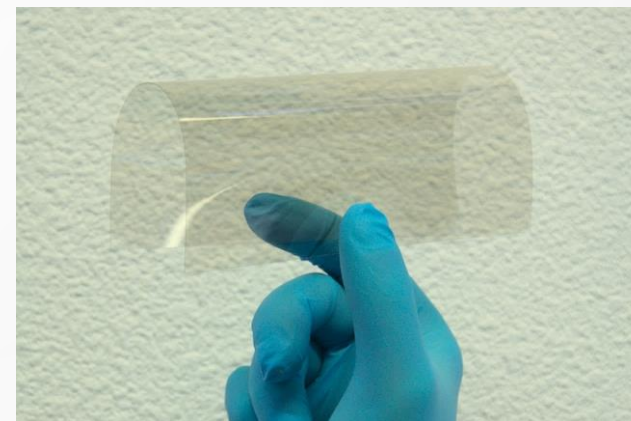
High H_2 flow ratio



Low H_2 flow ratio



~5 nm MoS_2 on $15 \times 15 \text{ cm}^2$ PET foil @ 100 °C

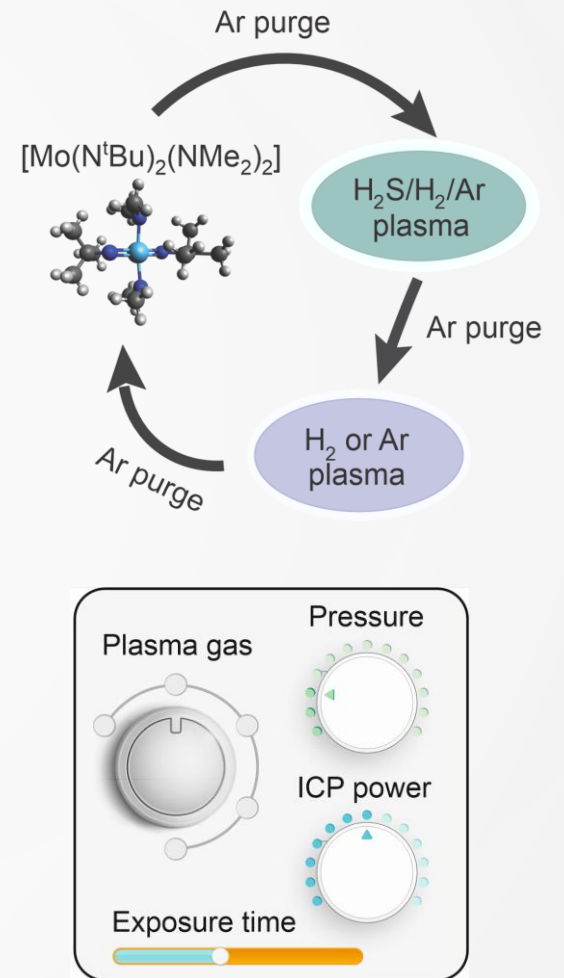


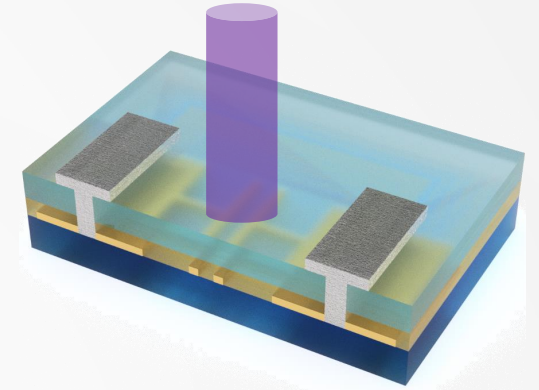
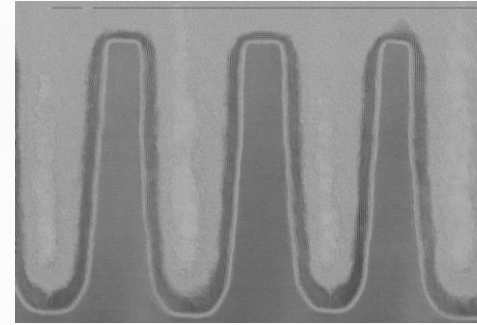
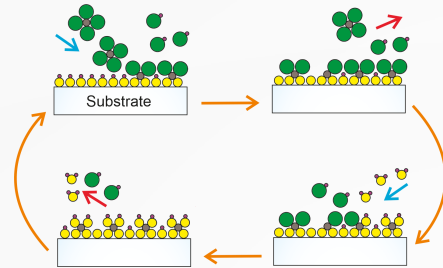
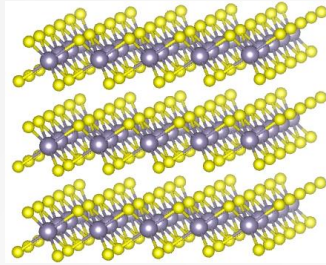
Advanced ALD process design for improved electrical performance

Three-step process (two plasmas) & plasma parameter control

➤ Tailoring MoS₂ properties @ 150 °C

	H ₂ plasma 3-step	Ar plasma 3-step	High H ₂ 2-step
H impurity (at-%)	9	2	22
O impurity (at-%)	1.4	1.2	6
μ (cm ² V ⁻¹ s ⁻¹)	0.3	0.3	0.02
n (cm ⁻³)	10 ¹⁸	10 ¹⁶	10 ²¹





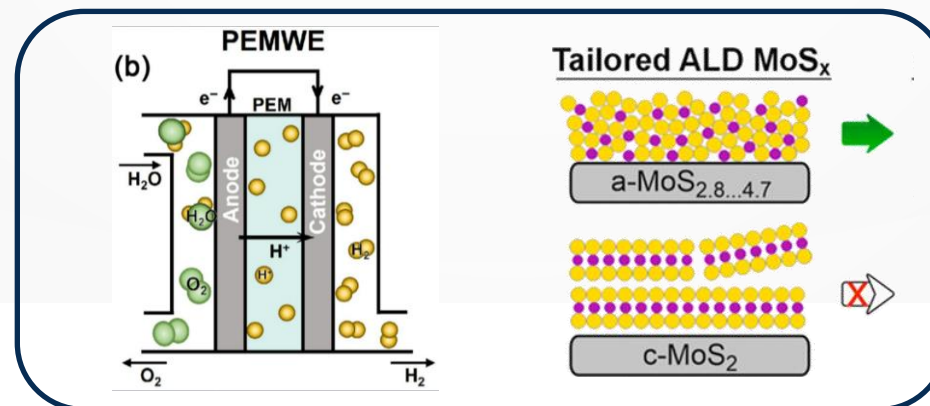
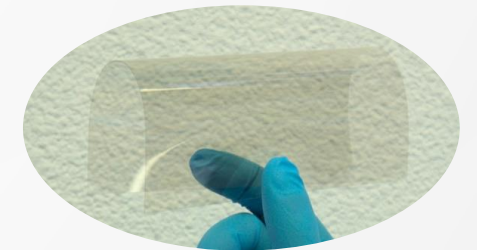
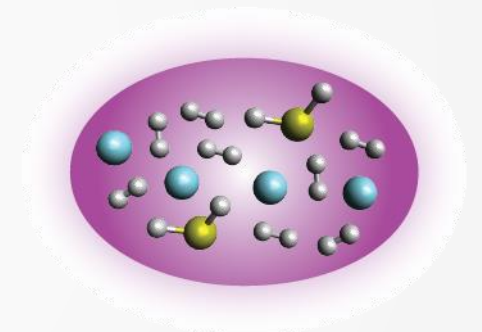
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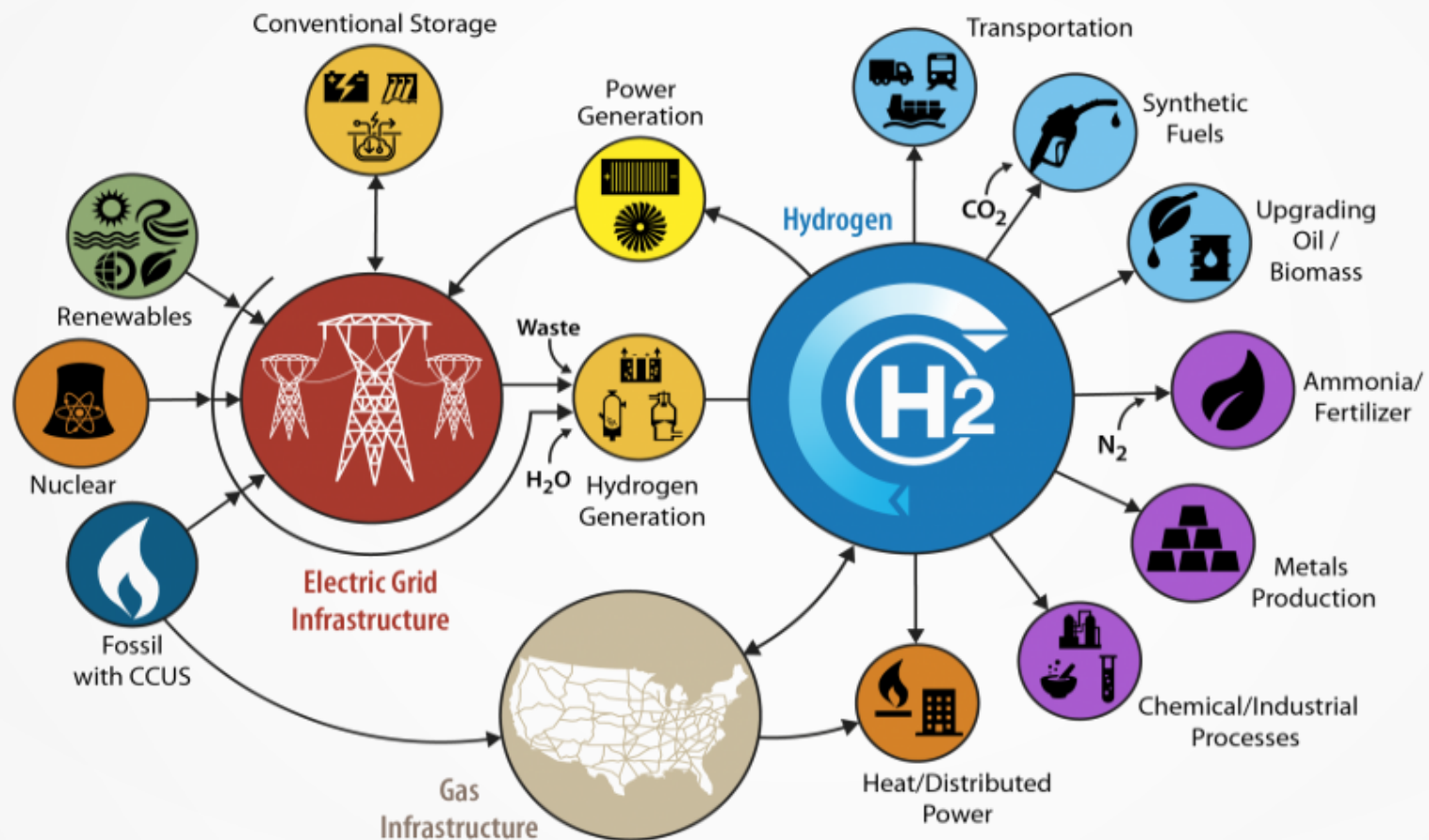
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Electrocatalysis in the center of H₂ economy



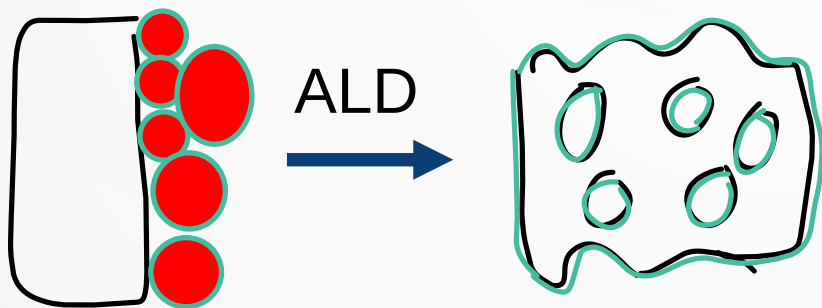
MoS_x for HER in acid

Promising **PGM-free alternatives** for PEM electrolyzers

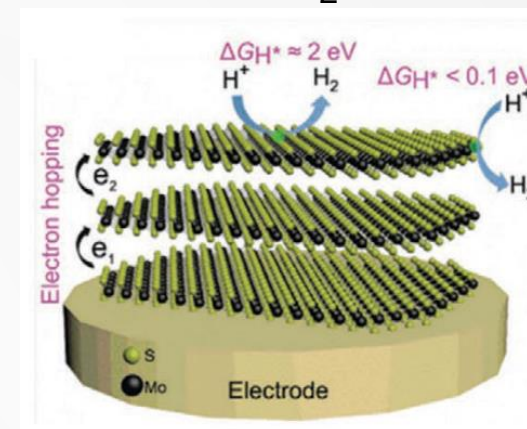
- Crystalline, 2D MoS₂ (c-MoS₂)
- Amorphous MoS₂...MoS₆ (a-MoS_{2+x})

Controlled catalysts by ALD to understand effects of MoS₂ composition and structure

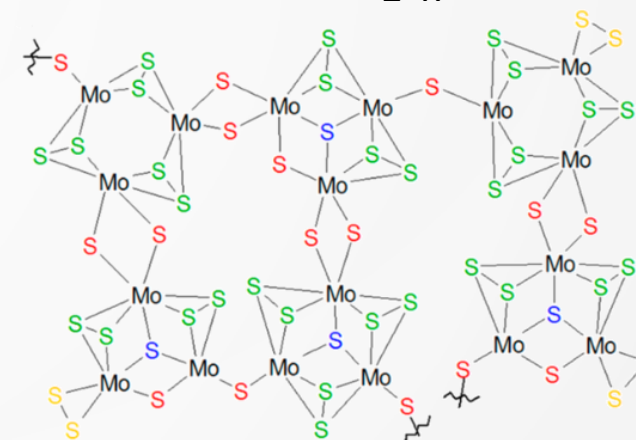
ALD also interesting for **electrolyzers** (loading↓, new designs)



c-MoS₂



a-MoS_{2+x}



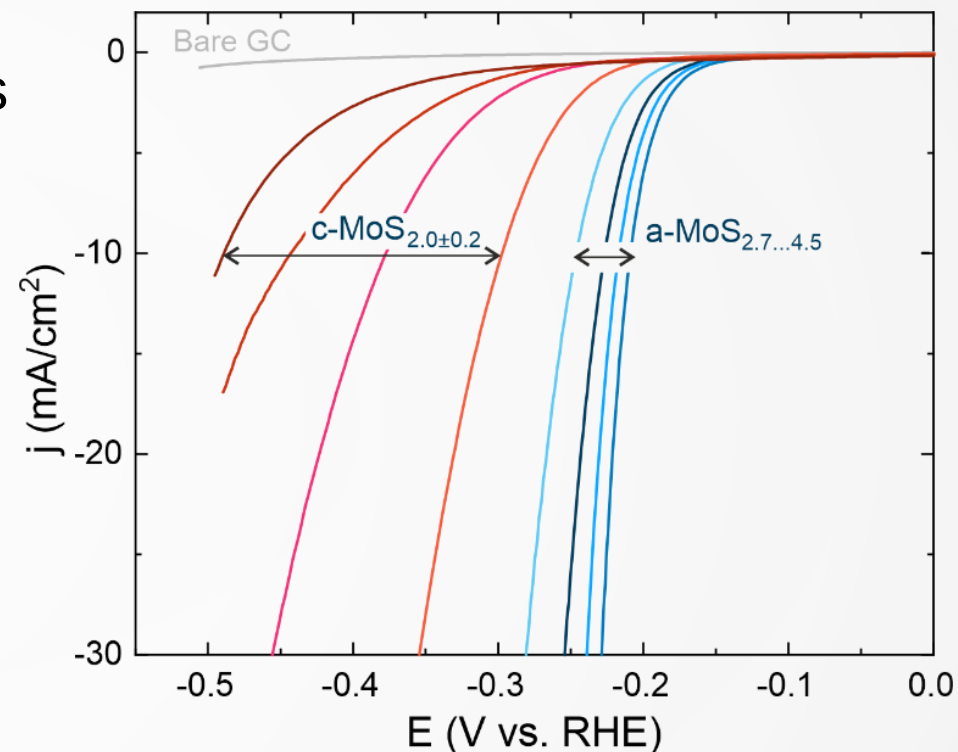
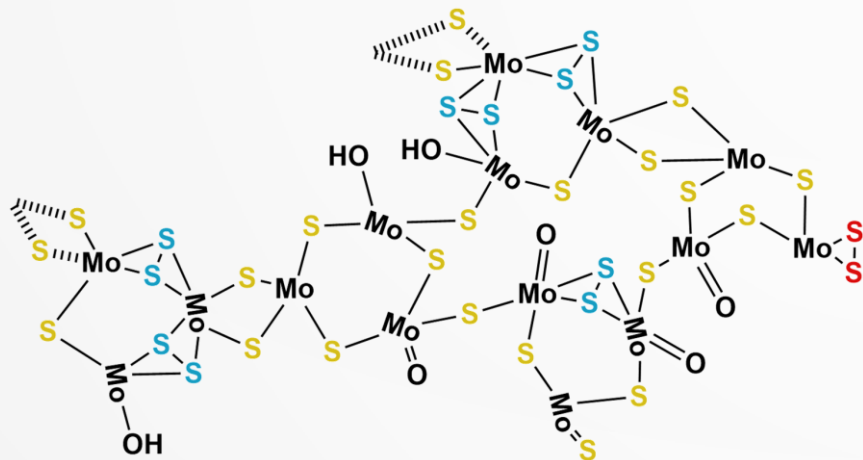
a-MoS_{2+x} is more active for HER than c-MoS₂

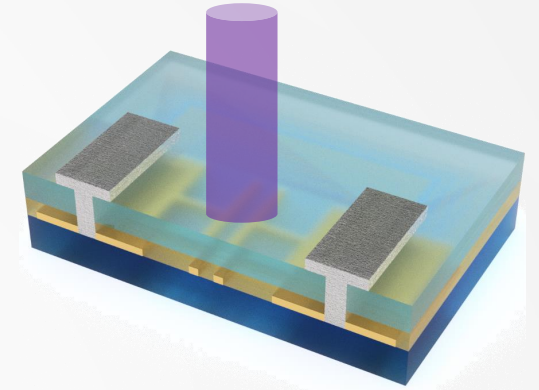
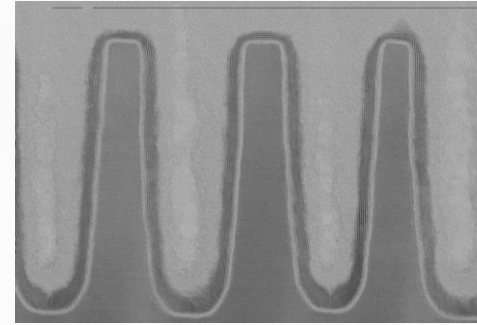
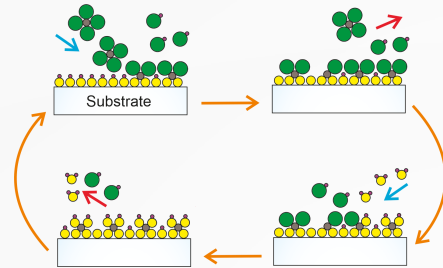
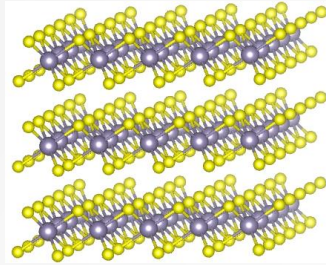
c-MoS₂: (low-ish) activity, depends on dep conditions

➤ No structural or compositional changes

a-MoS_{2+x}: **highly active** at any stoichiometry

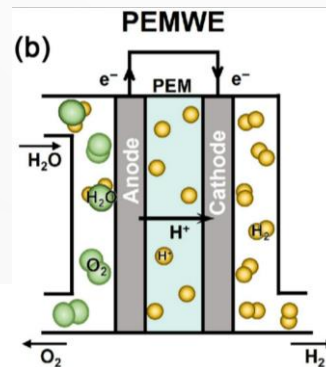
➤ **Transforms** to a-MoS₂O_y



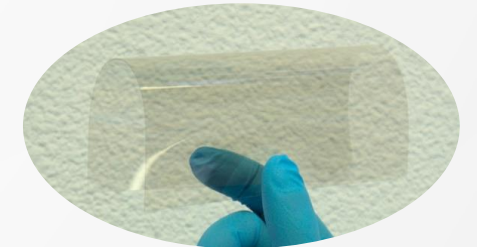
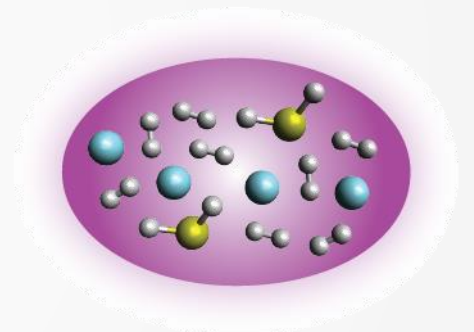
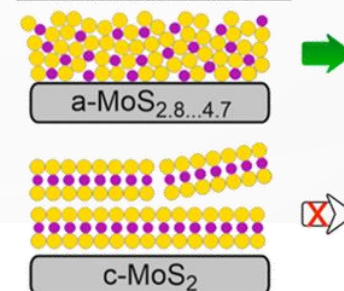


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V. Wrapping up



Tailored ALD MoS_x



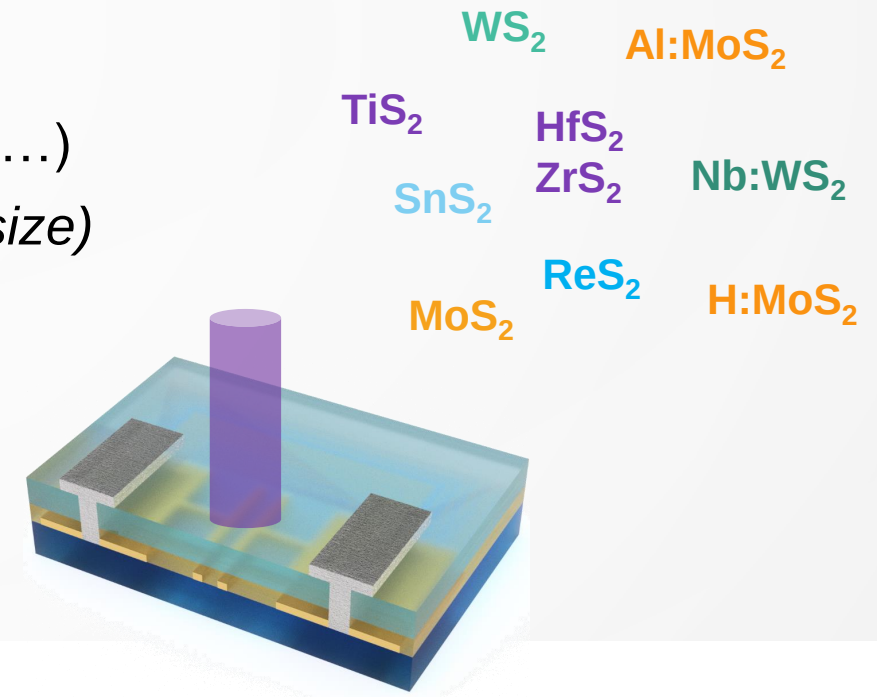
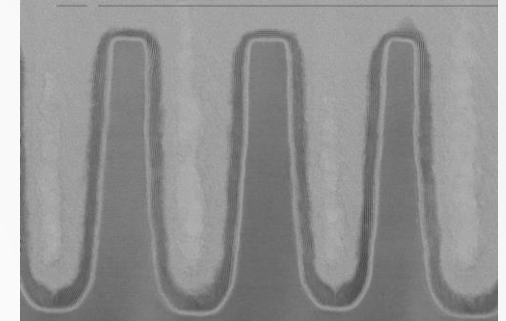
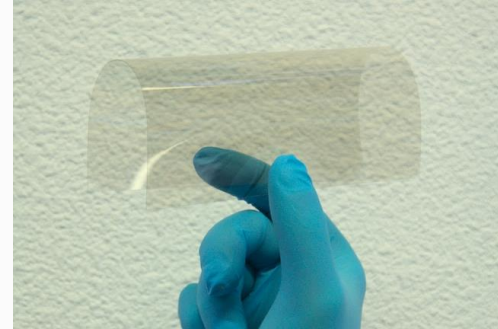
ALD: 2D material via unique self-limiting surface chemistry

ALD TMDCs offers (opto)electronics

- Low thermal budget (esp. Plasma)
 - Uniformity and conformality (3D)
 - Wide material selection (more to come)
 - Already in use (high-k, WF metals, multiple patterning...)
- (May not be the best for: strictly monolayer, large grain size)*

Characteristics also useful for **energy** (electrolysis...)

It's all about deposition chemistry



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