MOCVD of transition metal dichalcogenides: Hydrogen evolution reaction studies on MoS_2 and WS_2

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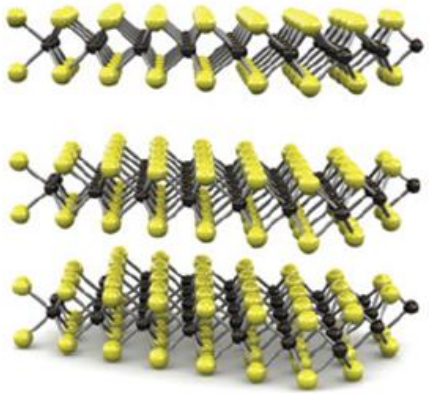
Transition Metal Dichalcogenides (TMDs) – Properties & Applications



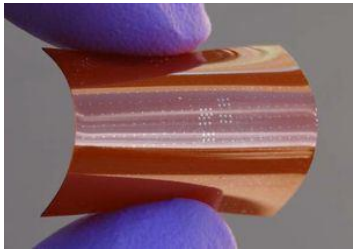
B. Radisavljevic, *et al.*, *Nature Nanotechnology* **2011**, *6*, 147.

Structure

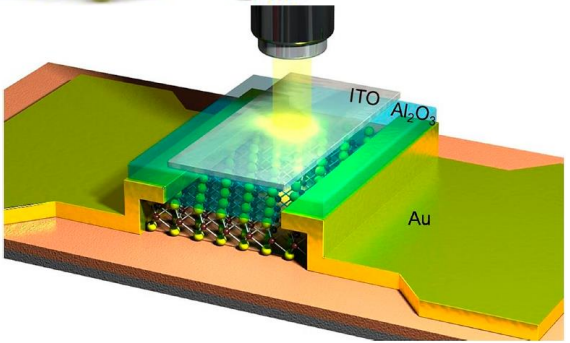
- S-M-S triple layers **stacked through vdW interactions**
- **2H**, 3R, **(1T)** polytypes

Properties

- As bulk (2H): indirect band gaps of 1.29 eV (MoS_2) and 1.3 eV (WS_2) → **n-type semiconductors**
- Indirect band gap → direct band gap of 1.8 eV (MoS_2) and 2.1 eV (WS_2) for monolayers
- Increased photoluminescence and absorption (NIR)
- **Flexible sheets** → 11 % deformation possible

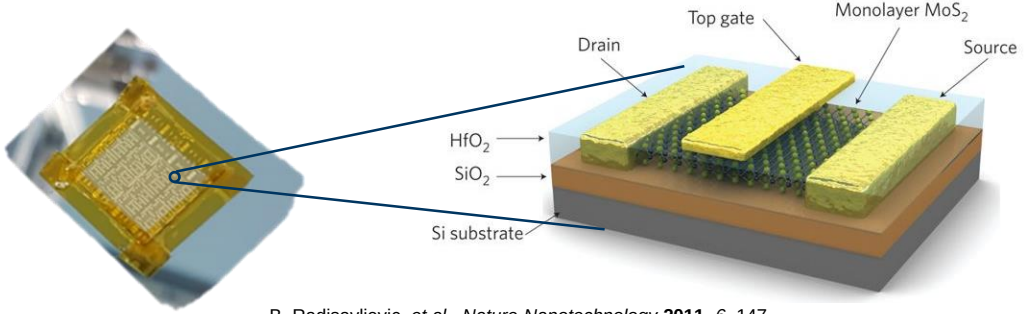


https://www.scienceandtechnologyresearchnews.com/wp-content/uploads/2014/10/MoS2-flexible-circuit_thmb.jpg.



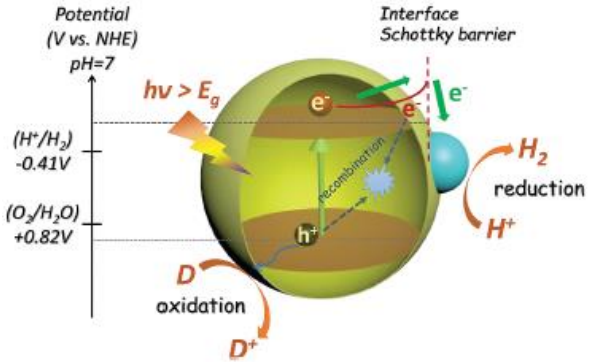
H. S. Lee, *et al.*, *Nano Lett.* **2012**, *12*, 3695.

Properties & Applications



B. Radisavljevic, *et al.*, *Nature Nanotechnology* **2011**, *6*, 147.

https://www.extox.de/de/produkte/83-transmitter/145-transmitter-exsens



K. Chang, *et al.*, *Adv. Energy Mater.* **2016**, *6*, 1502555.

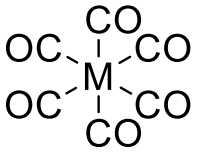
Applications

- Electronics on TFT basis (2H)
- HER (co-catalyst)
- Sensors

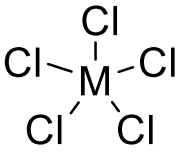
https://www.robotshop.com/de/de/mq-135-gassensor.html

→ **CVD and ALD necessary for large-area, high uniformity and precise thickness control**

Precursor



N. Imanishi, *J. Electrochem. Soc.* **1992**, *139*, 2082.

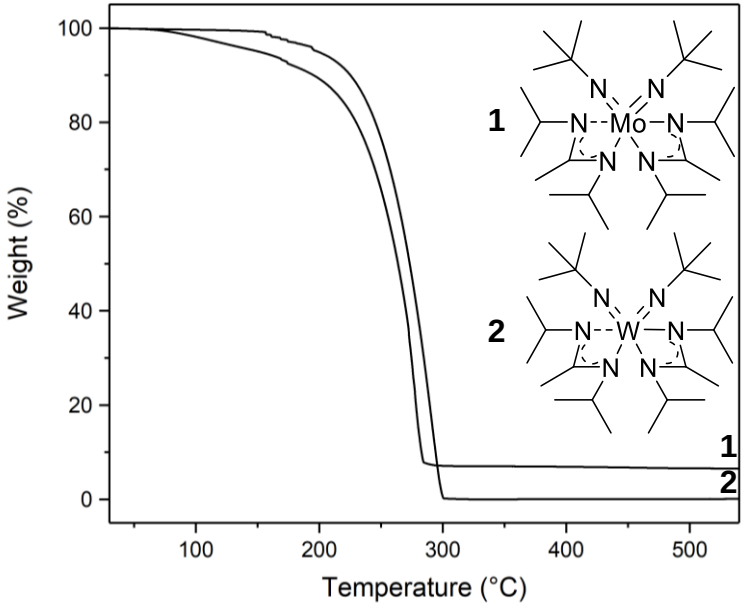


W. K. Hofmann, *J Mater Sci* **1988**, *23*, 3981.

- \+ Highly uniform films
- \- Halide incorporation
- \- Toxic by-products
- \- Usage of toxic H_2S as co-reactant

Improved

Precursors

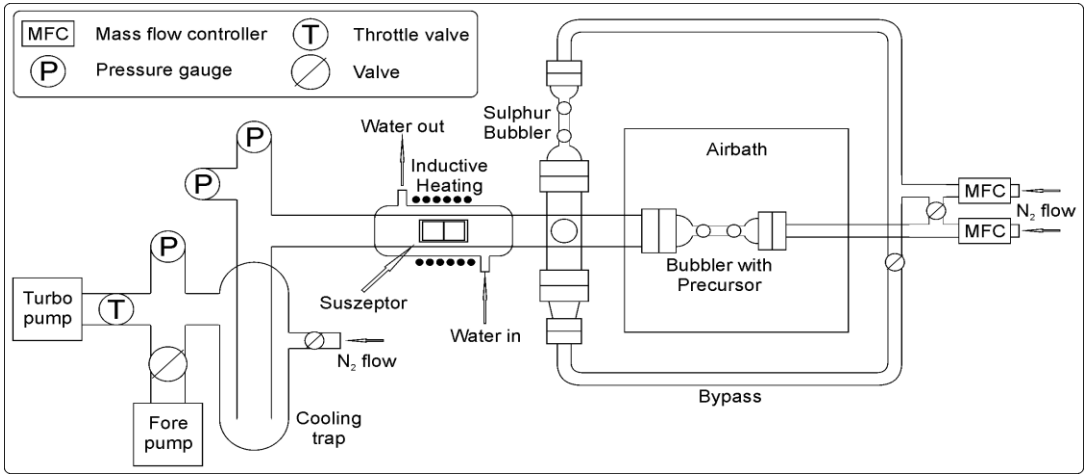


- Volatile and thermally stable
- One-step evaporation
- **Onset: 90 - 100 °C** (1 % mass loss)
- Residual masses < 10 wt.%

→ **Thermal properties of the precursors promising for application in MOCVD**

MOCVD of MoS_2 & WS_2

Reactor setup

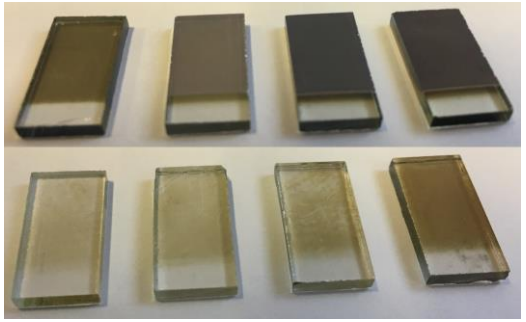


Process parameters

- $T_{evap.}$ = 80 °C (precursor), $T_{evap.}$ = 130 °C (sulfur)
- $T_{dep.}$ varied from 600 to 800 °C, p = 1 mbar
- **Direct growth of TMDs** without post deposition treatment

Custom-built CVD reactor

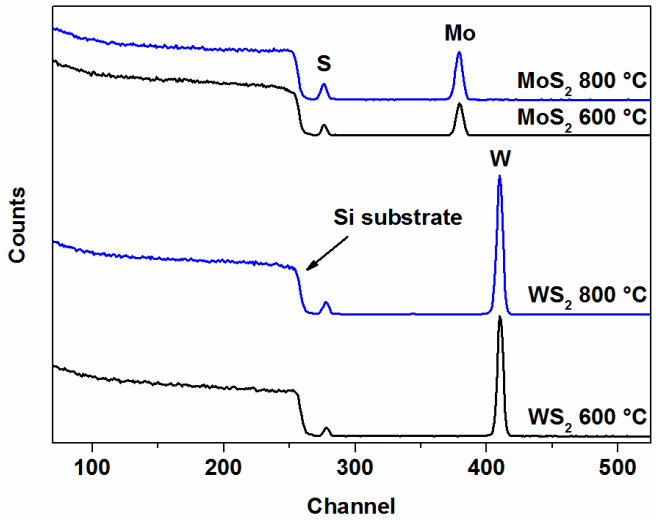
Optical appearance of Mo and W films on quartz substrates



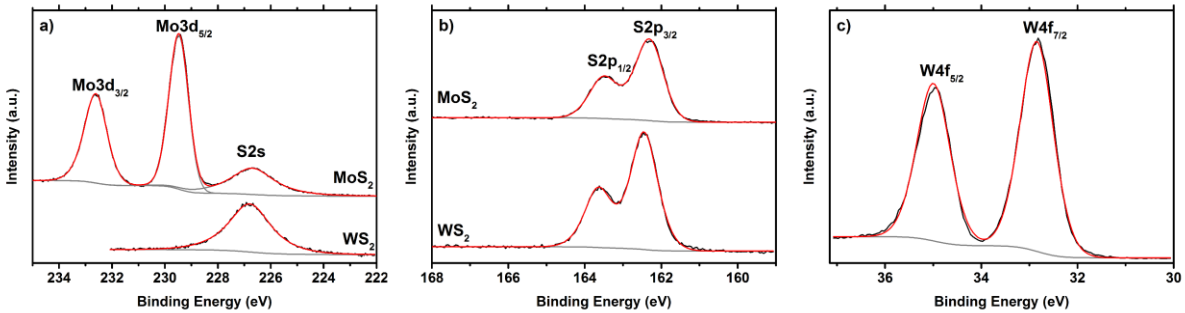
Compositional Analysis

	M (at. %)	S (at. %)	O (at. %)	N (at. %)	C (at. %)	M/S ratio
WS_2 (600 °C)	29.4	46.6	0.1	17.8	6.1	0.63
WS_2 (800 °C)	24.3	50.1	4.0	5.2	16.5	0.48
MoS_2 (600 °C)	30.2	63.2	0.1	2.9	3.6	0.48
MoS_2 (800 °C)	30.9	60.7	3.3	0.6	4.5	0.51

RBS



XPS



- **RBS/NRA and XPS** reveal M/S ratio of around 0.5 at 800 °C
- Mo precursor highly reactive towards elemental sulfur under adopted process conditions
- Thickness 20 nm

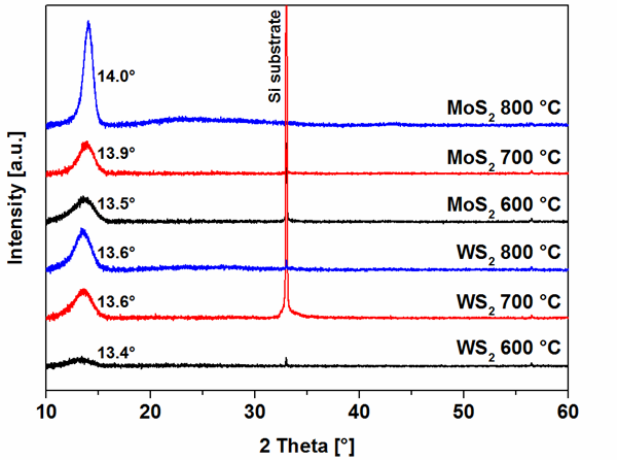
Structural Analysis

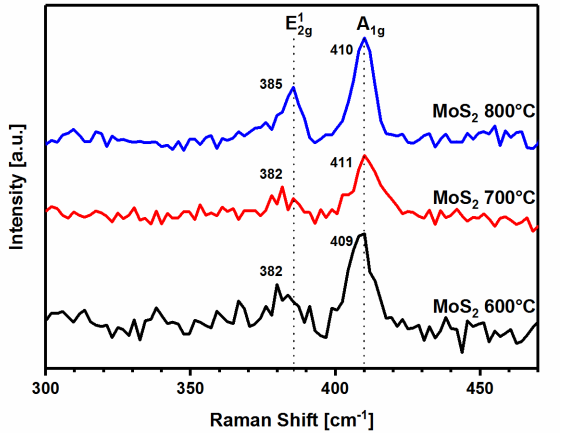
XRD (ICSD 95570 + ICSD 202366)

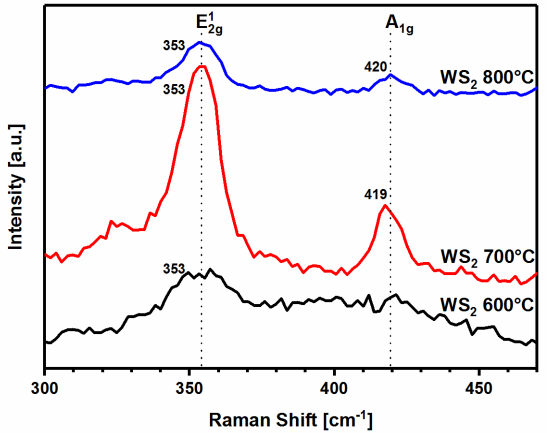
- **Hexagonal (2H) MoS_2 and WS_2 (P63/mmc)**
- Widths of reflexes decrease with higher T → Larger crystallite size
- Reflex shift at lower T → Strain effects

Raman spectroscopy

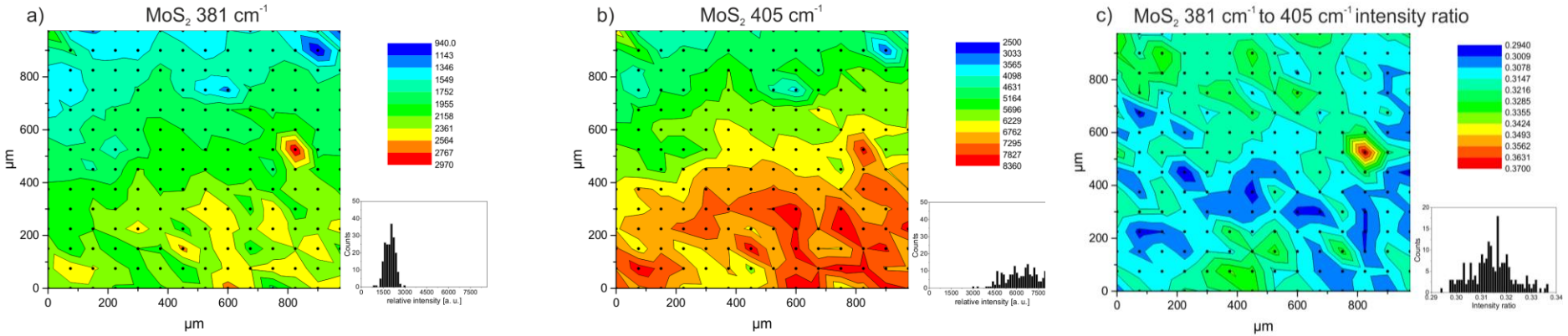
- In-plane and out-of plane vibration appear
- Frequency difference as indicator for No. of layers (<20 ML for 25 cm^{-1})
- Increases for thicker films







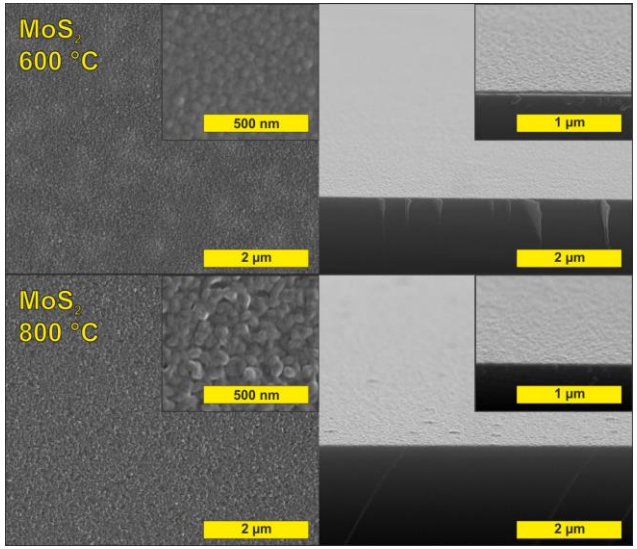
Raman Mapping

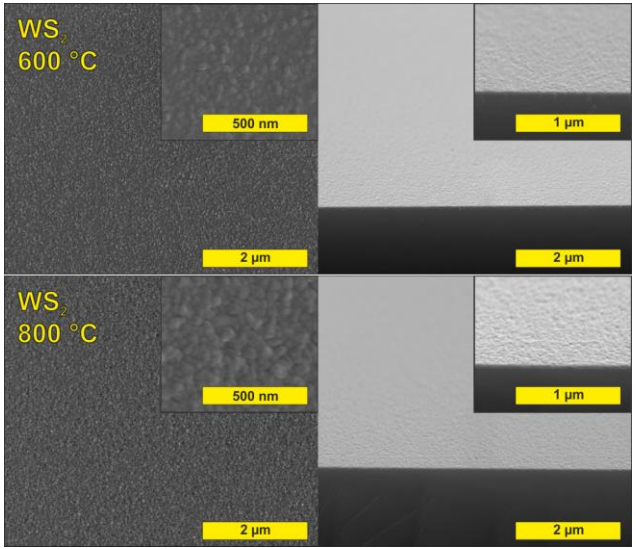


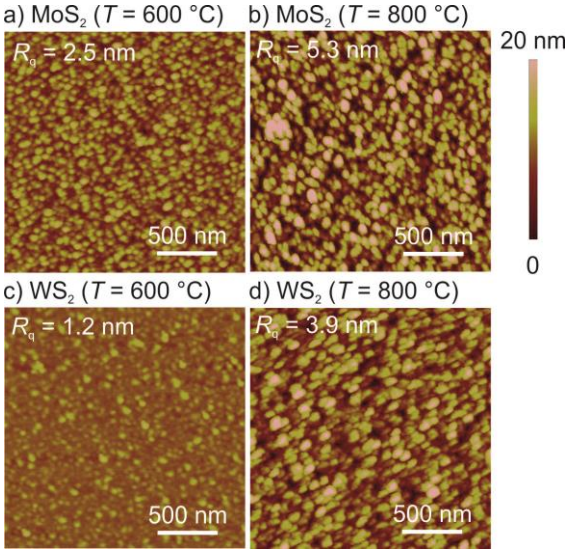
- (1 x 1) mm^2 samples (step size 75 µm) of 10 nm MoS_2 on Si
- Intensity of the two characteristic Raman peaks mapped (381 cm^{-1} and 405 cm^{-1})
- Narrow signals intensity ratio → **large-area uniformity**

→ **XRD and Raman Mapping revealed successful fabrication of 2H structures with large area uniformity**

Surface Morphology

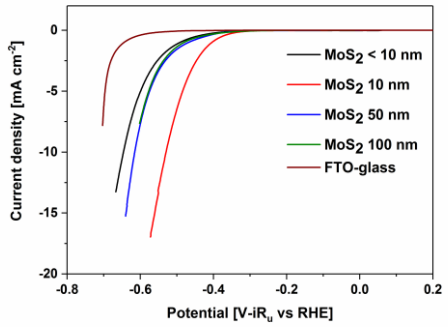


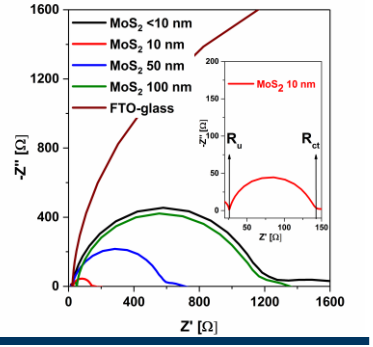


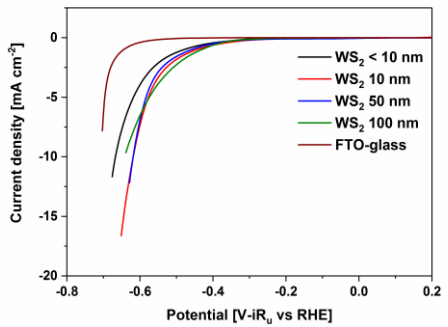


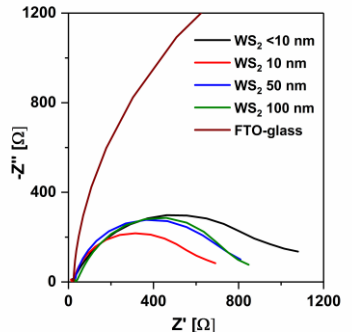
- Large-area coverage over whole temperature range
- T-dependent crystallite formation (higher roughness of 800 °C film)
- Growth rates from cross-sections 2 nm min^{-1} (600 °C and 800 °C) and 3 nm min^{-1} (700 °C)

Hydrogen Evolution Reaction (HER) Studies







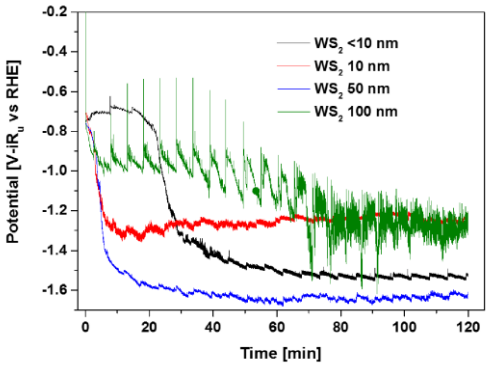


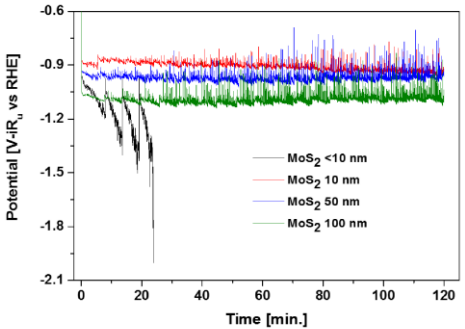
- MoS_2 as promising electrocatalyst for HER
- Electrocat. activity of films on FTO-glass in 0.5 M H_2SO_4
- Polarization curves from LSV
- -0.48 V overpotential vs. RHE for 10 nm film (-5 mA cm^{-2} current density)
- Best performing film also with lowest charge transfer resistance (Nyquist plot)
- Anisotropic activity (edge and basal planes)

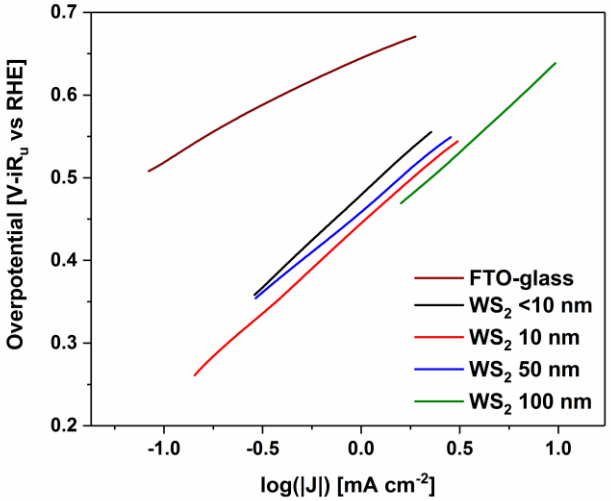
- WS_2 films with poor performance (-0.58 V)
- Instability under reductive conditions visible in long-term galvanostatic tests

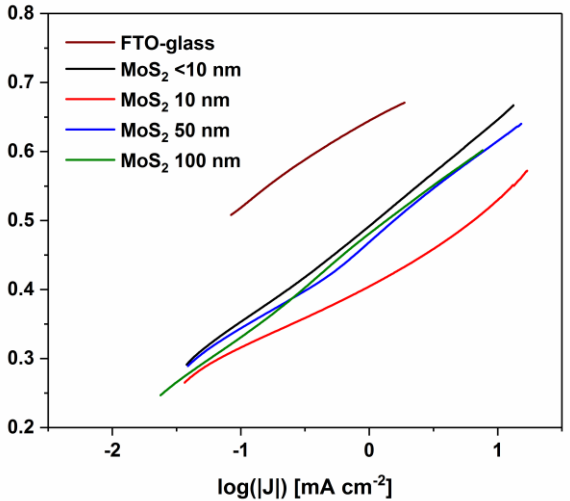
→ **MoS_2 with better performance as co-catalyst**

HER Studies









- Unusual high Tafel slopes of WS_2 films also indicate pronounced reductive processes rather than HER
- 109 mV per decade for best performing MoS_2 film

→ **Primary Volmer reaction step is rate-limiting for the HER**

- Low absorbance above 800 nm also advantageous

Summary & Outlook

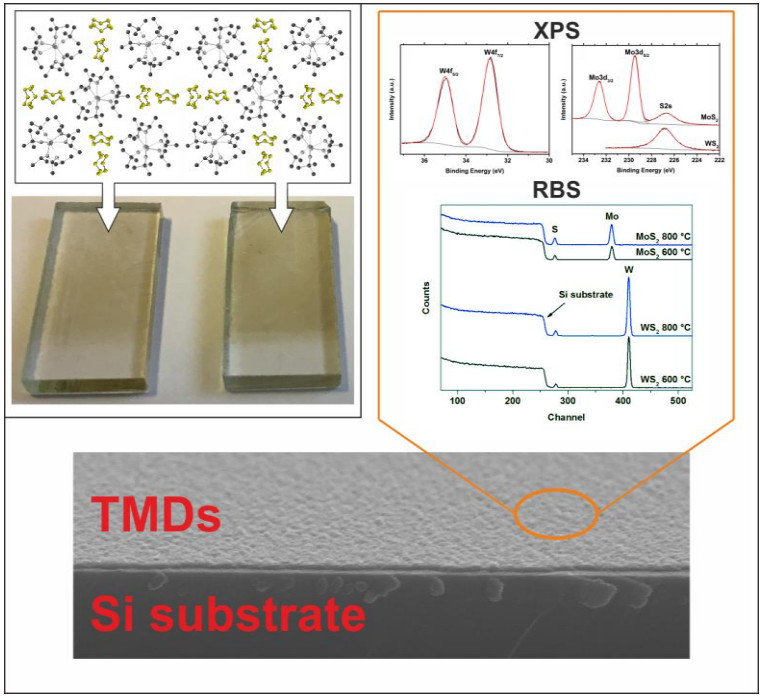
- New route for **direct growth of MoS_2 and WS_2 through MOCVD with elemental sulfur**
- **No post-deposition treatment needed**
- **Large-area uniform films** with low level of impurities
- Promising film quality especially for MoS_2 films
- Good performance in HER activity tests

→ Further precursor screening concerning reactivity towards less harmful sulfur sources like elemental sulfur

→ Gas sensor tests under preparation

→ Investigation of electric properties and evaluation as channel material in TFTs

→ Transfer to ALD for better thickness control (ML growth)



S. Cwik, *et al.*, *Adv. Mater. Interfaces* **2018**, *5*, 1800140.

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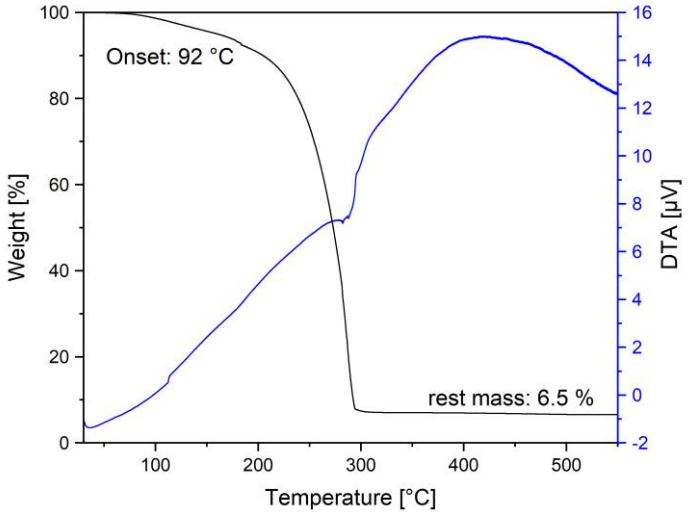
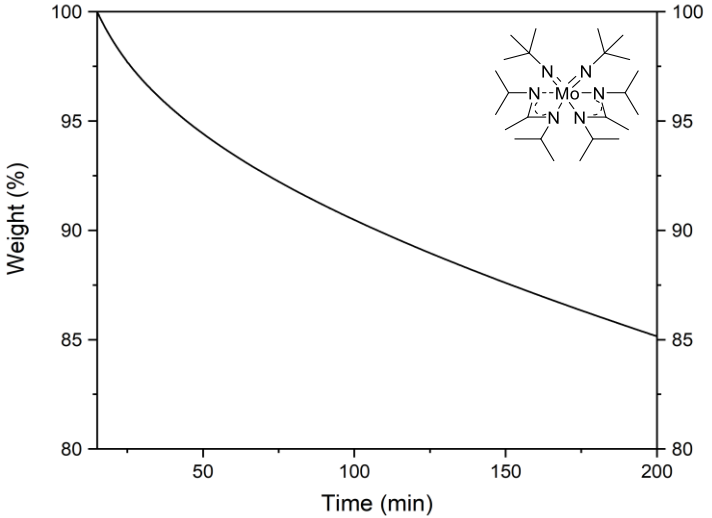
Appendix

DTA and Iso-TG



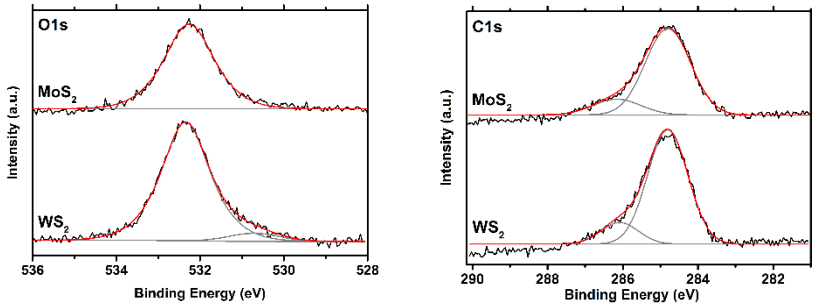


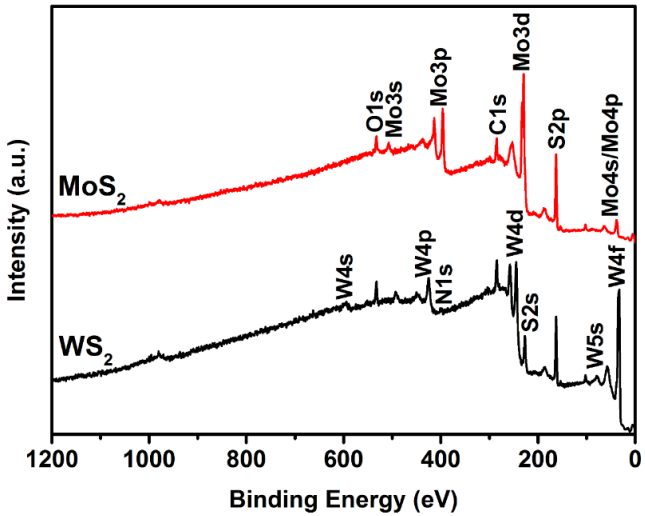
- Iso-TGA at 80 °C, 200 min
- Evaporation rate: 13 µg/min
- Linear evaporation

→ **Constant evaporation without decomposition at 80 °C**

Appendix

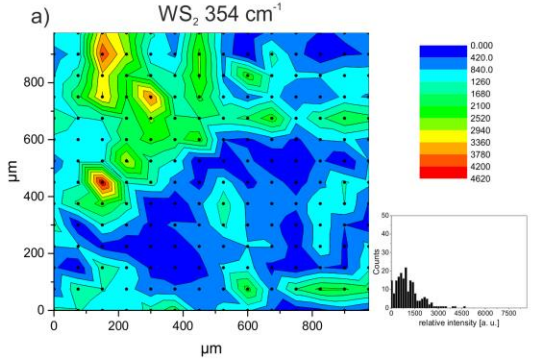
XPS

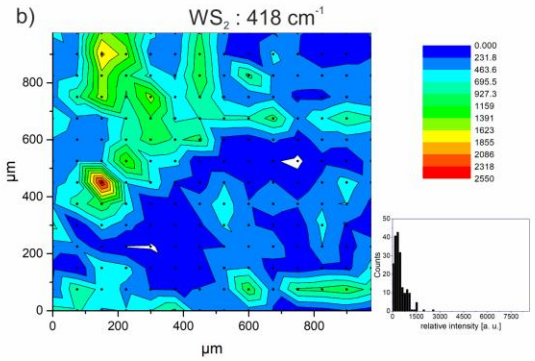


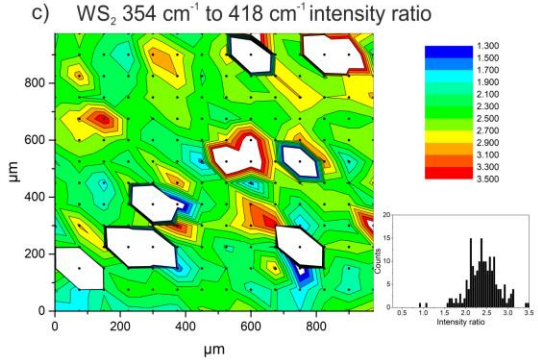


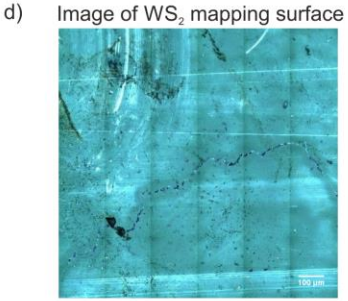
Appendix

Raman Mapping



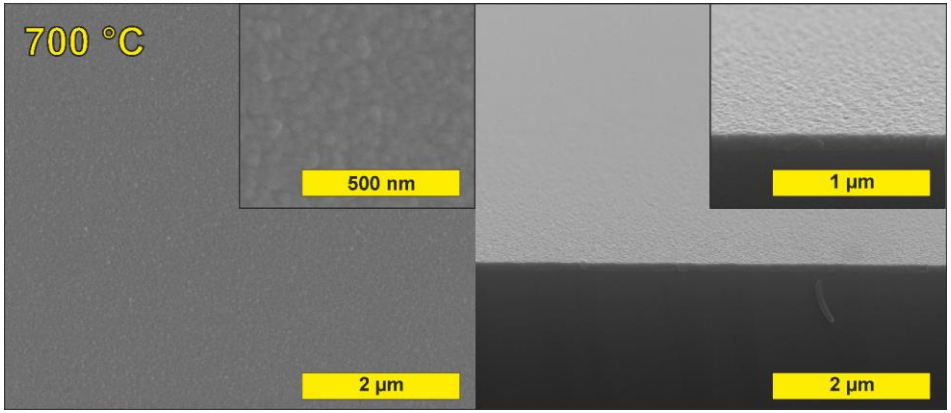


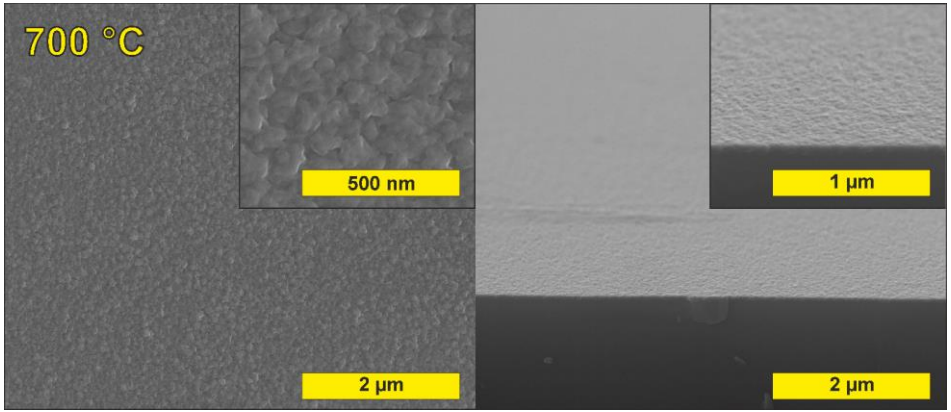




Appendix

SEM





Appendix

Absorbance