

RUB

22nd EuroCVD - 16th Baltic ALD | 2019 | Luxembourg

A new MOCVD process for SnO₂ using an amino functionalised tin alkyl precursor: Tuning surface morphology for sensor related applications

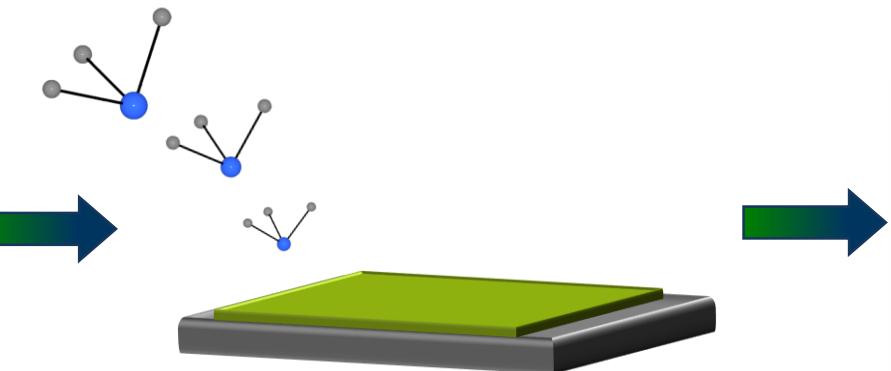
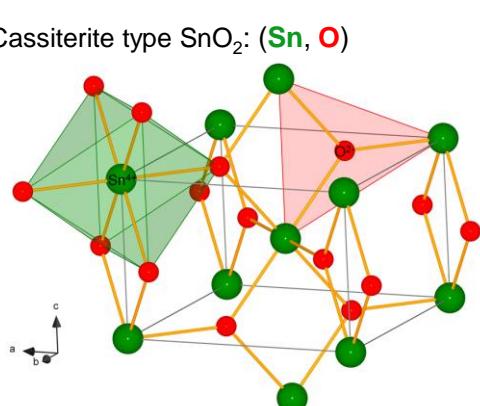
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² Experimental Condensed Matter Physics, Heinrich-Heine University, 40225 Düsseldorf, Germany

SnO_2 : Semiconductor with interesting surface

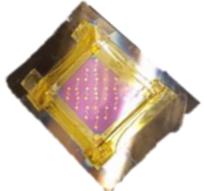
Cassiterite type SnO_2 : (Sn , O)



- Transparent n-type semiconducting oxide (3.6 eV band gap)
- Appealing charge carrier densities and mobilities for TFT applications

➤ Oxygen deficient surfaces!

Red-ox reactions at surface /
gas phase interface



- Conductivity depends on presence or absence of adsorbed surface species



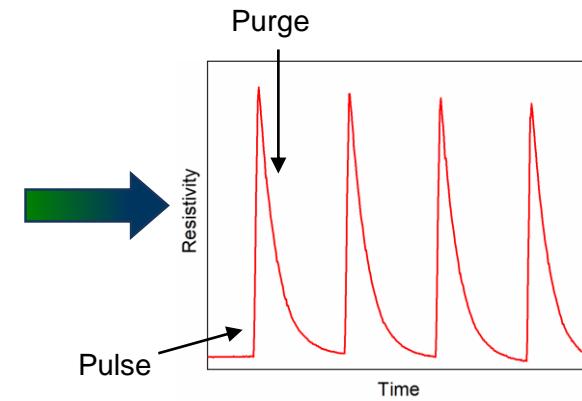
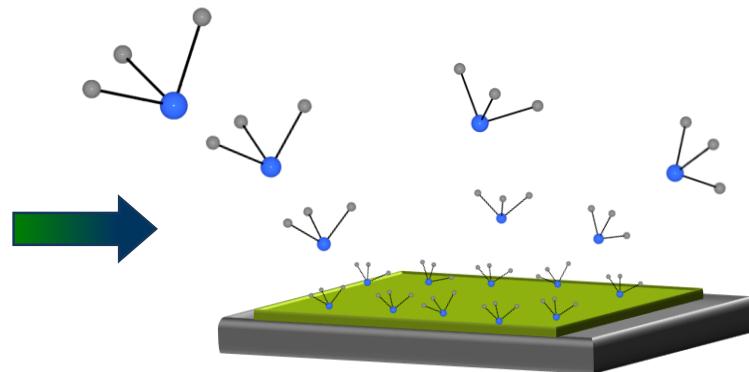
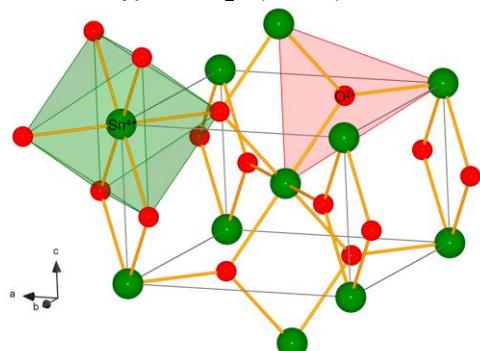
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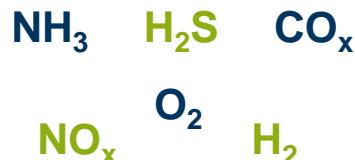
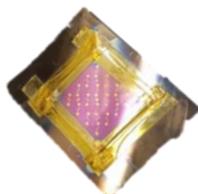
<https://store.ncd.io/product/mq-4-methane-natural-gas-sensor-adc121c-12-bit-adc-i2c-mini-module/>

SnO_2 : Semiconductor with interesting surface

Cassiterite type SnO_2 : (Sn, O)

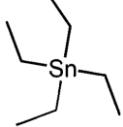


- Transparent n-type semiconducting oxide (3.6 eV band gap)
- Appealing charge carrier densities and mobilities for TFT applications
- Oxygen deficient surfaces!
- Conductivity depends on presence or absence of adsorbed surface species

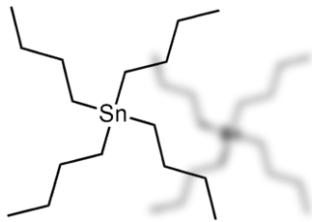


Knowledge on parameters
that affect conductivity of
CVD grown SnO_2 films
highly desirable

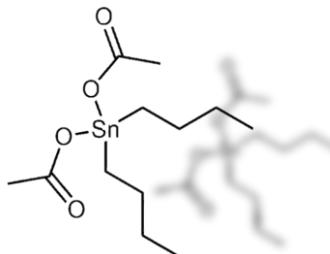
SnO_2 : CVD precursors and primary focus

**TET****Tetraethyl tin(IV)** $T_{\text{Dep.}} = 320 - 420 \text{ }^{\circ}\text{C}$

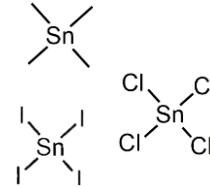
M. Amjoud et al. Ann. Chim. Sci. Mat. 1998, 23, 355.

**TBT****Tetrabutyl tin(IV)** $T_{\text{Dep.}} = 600 - 640 \text{ }^{\circ}\text{C}$

R. Korotkov et al. Thin Solid Films, 2006, 502, 79.

**DBTDA****Dibutyl tin(IV) diacetate** $T_{\text{Dep.}} = 600 - 640 \text{ }^{\circ}\text{C}$

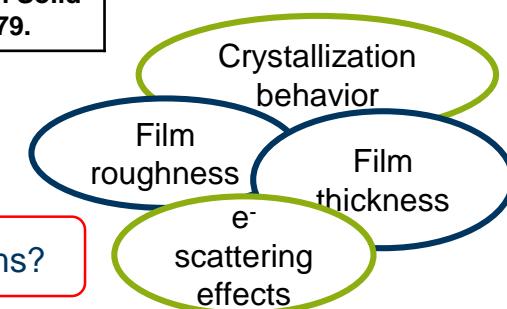
R. Korotkov et al. Thin Solid Films, 2006, 502, 79.



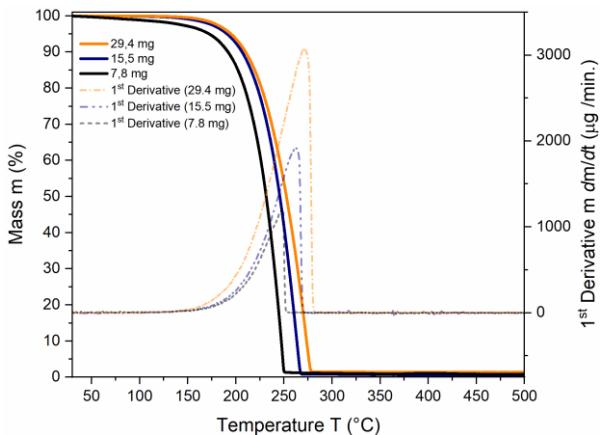
- Typically Sn alkyls and halogenides used as precursors

- For 400 nm - 1200 nm thick films: Influence of morphology & different predominant crystal growth orientations on conductivity thoroughly studied
- Films << 100 nm?

Influence of aspects of “initial” CVD growth on electrical performance of SnO_2 thin films?

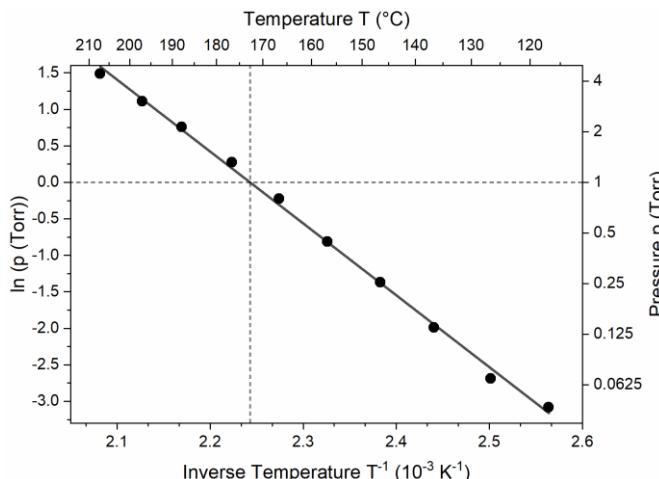


$\text{Sn}(\text{DMP})_4^*$ - Liquid precursor of choice



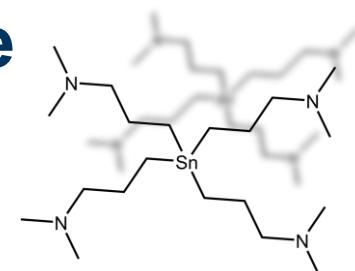
- Clean one-step evaporation & high thermal robustness
- Absence of secondary peaks in TG derivative curves
- Residual masses < 1.5 %

Vapor pressure estimation via stepped
isothermal TG & Langmuir equation



➤ 1 Torr vap. pres. at $(172.7 \pm 2.0)^\circ\text{C}$

$$\ln(p) = -9844.6 T^{-1} + 22.08 \quad (p \text{ in Torr}, T \text{ in K})$$

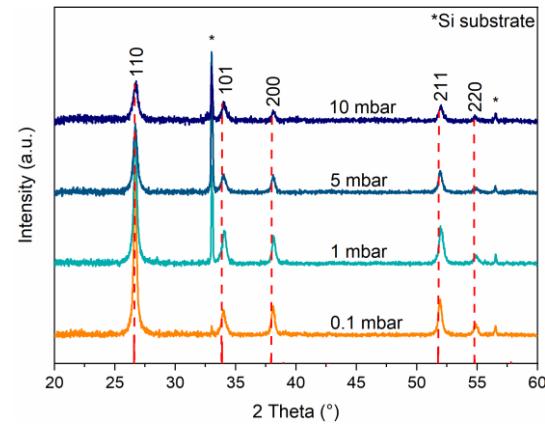
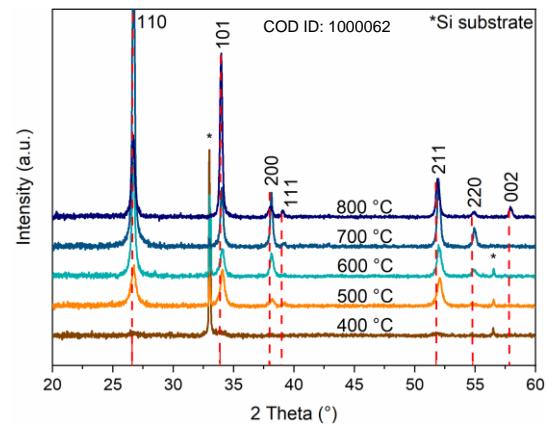
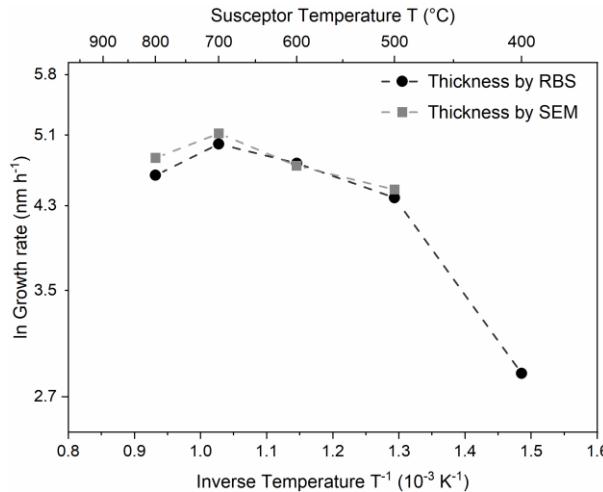


A. Zickgraf et. al. *Inorg. Chim. Acta* 1998, 275-276, 203

DMP = 3-(N,N-dimethylamino)propyl

- No notable degradation upon air exposure at RT
- Precipitation of gel-like substance when mixed with water
- Long-term stability in solution (¹H-NMR study)*

CVD Growth Characteristics*



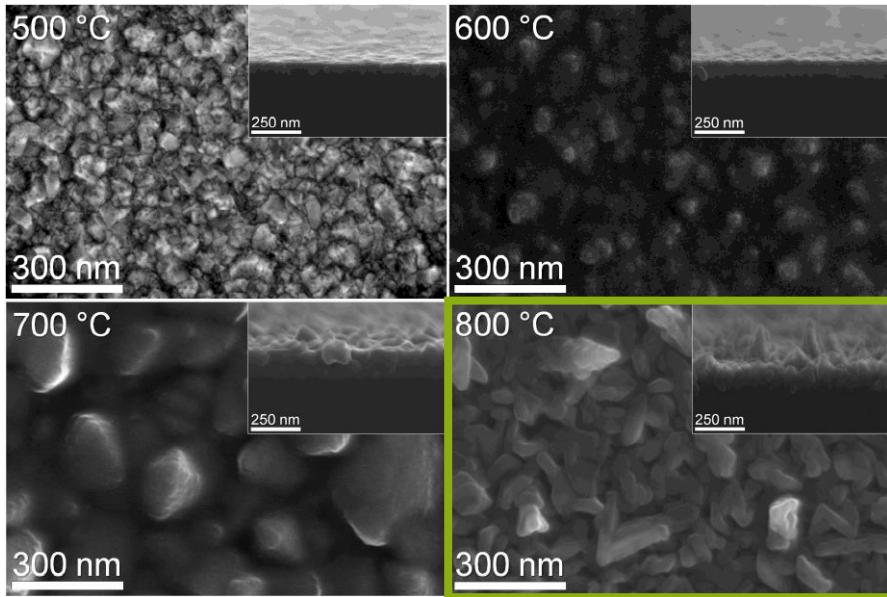
XRD reflections match cassiterite type SnO_2

- (110) orientation preferred between 500 - 700 °C
 - 800 °C change of preferential orientation: (110)↓ vs. (101)↑
 - Between 0.1 - 10 mbar no notable change at $T_{\text{Dep.}} = 600 \text{ °C}$
- Change of CVD growth mechanism indicated

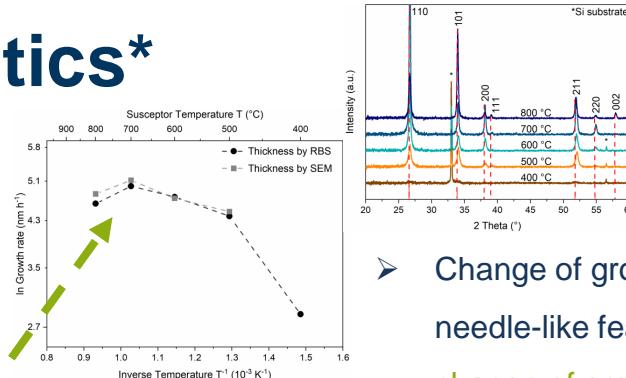
Film growth on Si(100)			
$t_{\text{Dep.}}$ (min)	$T_{\text{prec.}}$ (°C)	Flow _{Prec.} (sccm)	Flow _{Ox.} (sccm)
60	90	50	50

- ~ 400 - 500 °C >> kinetically/reactivity limited
- ~ 500 - 700 °C >> mass transport controlled
- ~ 700 - 800 °C >> thermodynamics controlled?

CVD Growth Characteristics*

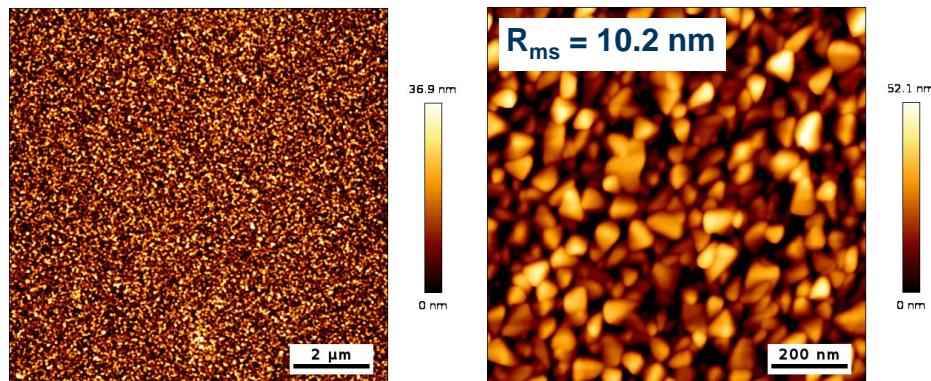


- 700 °C: further enlargement of granular features & distinct size variation visible from cross-section
- 800 °C: Intertwined elongated needles 50 - 200 nm & comparably porous deposit



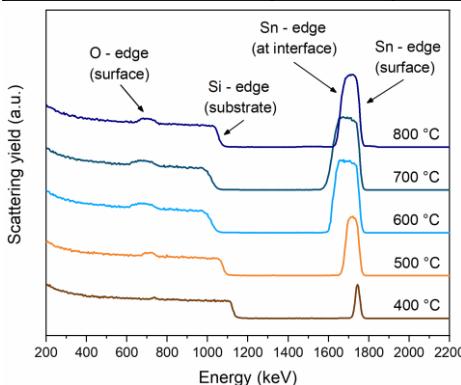
➤ Change of growth from granular to needle-like features ➔ change of preferential orientation

AFM of SnO₂ film deposited at 600 °C



Compositional analysis: “Bulk” vs. Surface

RBS / NRA					
Temperature (°C)	Concentration (at. %) and O to Sn ratio				
	C	N	O	Sn	O/Sn
400	4.2	1.9	63.2	30.7	2.06
500	0.5	n.d.	67.8	31.7	2.14
600	0.9	0.1	66.8	32.2	2.07
700	1.8	0.2	66.1	31.9	2.07
800	n.d.	0.3	68.2	31.4	2.17



- Overall low C and N contaminant levels
- All thin films are slightly oxygen rich in film “bulk”

VS.

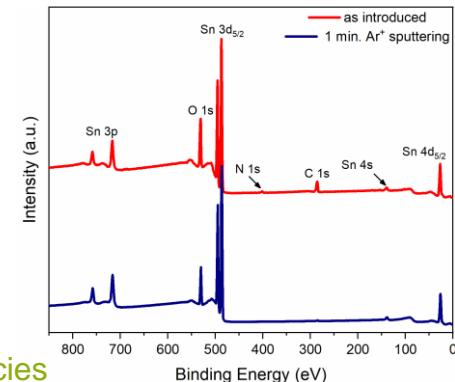
	a.i.	1 min. Ar ⁺ (2 kV)
O/Sn	1.55	1.08
C (at.%)	25.3	2.5
N (at.%)	0.5	0.3

- Notably oxygen deficient Sn/O ratio on the surface

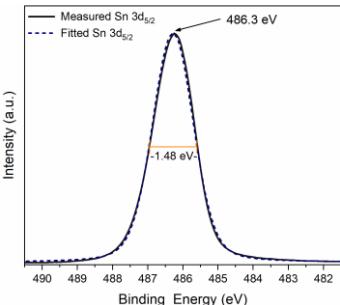
- Preferential oxygen sputtering

High temperatures facilitate surface reconstructions*

→ Sn²⁺ point defects and O vacancies



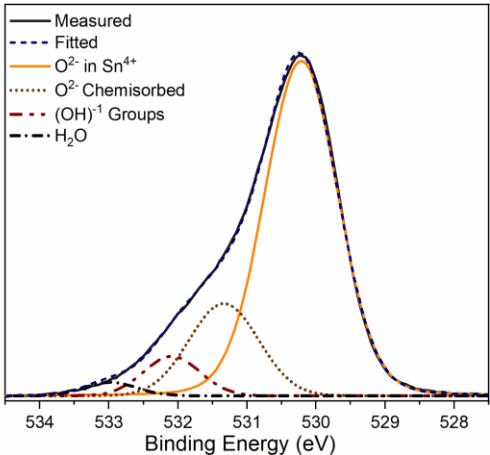
Compositional analysis: Surface species



Sn 3d_{5/2} and O 1s core level spectra investigated for as deposited SnO₂ thin film

- In Sn 3d_{5/2} no pronounced lower energy shoulder or asymmetry indicating distinct Sn²⁺ phase

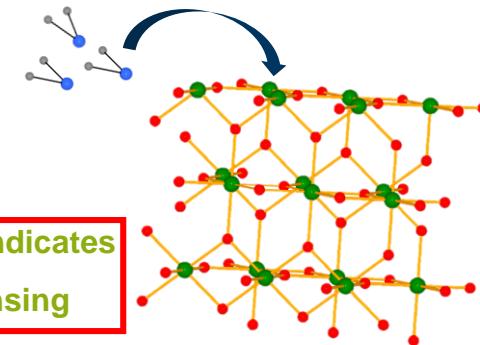
- Broad FWHM of 1.48 eV may reflect point defects (Sn²⁺ and O²⁻ vacancies)



- Surmised Sn²⁺ point defects / oxygen vacancies facilitate adsorption of various species

High concentration level of chemisorbed O²⁻ indicates potentially high selectivity for chemical sensing

XPS (Sample T _{Dep.} = 600 °C)		
Oxygen species	Binding Energy (eV)	Integral (%)
O ²⁻ bonded to Sn ⁴⁺	530.2	73.2
O ²⁻ chemisorbed	531.3	18.4
O ²⁻ (OH ⁻)	532.1	6.4
O ²⁻ (H ₂ O)	532.9	2.0

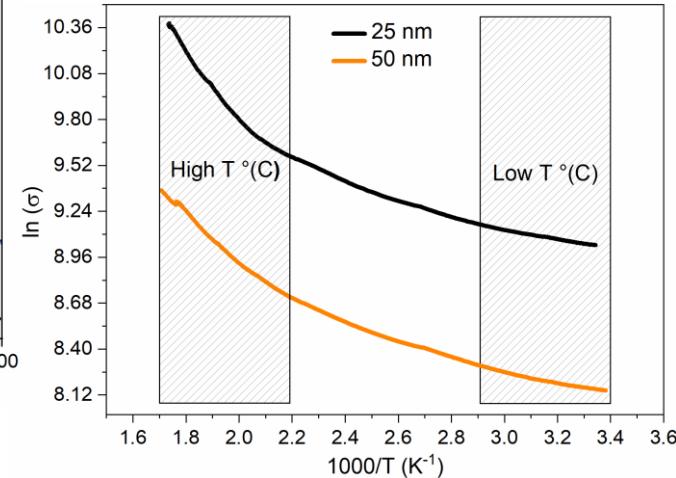
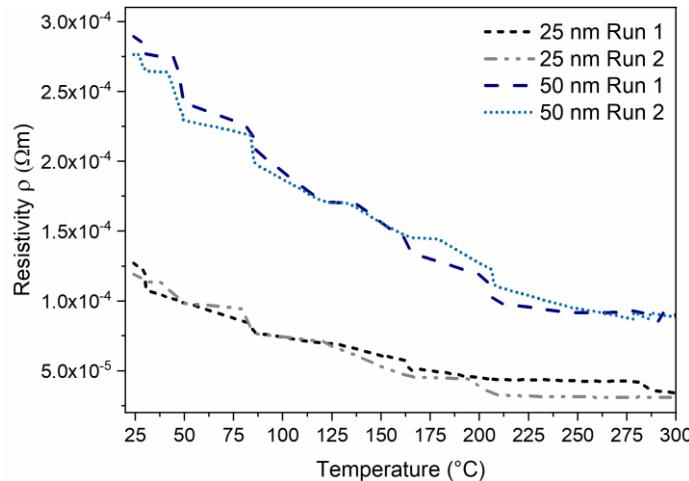


SnO_2 thin film Resistivity Performance

Temperature varied van der Pauw
(4-point probe) of thin films grown
at 600 °C

- Reversible electrical resistivity in 3 consecutive runs & absence of hysteresis

Thinner CVD deposited film provides lower resistivity



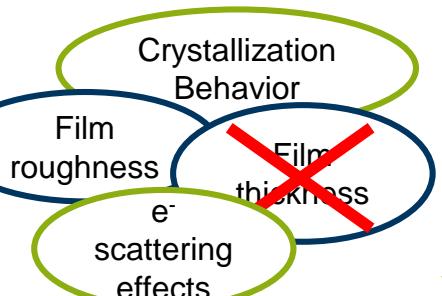
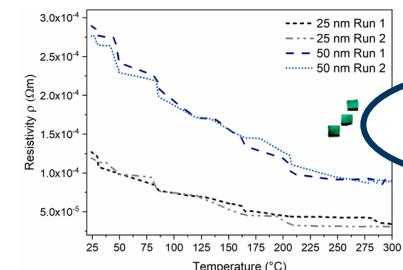
- Natural logarithm of electrical conductivity ($\ln \sigma$) as function of temperature:

Smooth transition from extrinsic (Low T) to intrinsic (High T) conduction

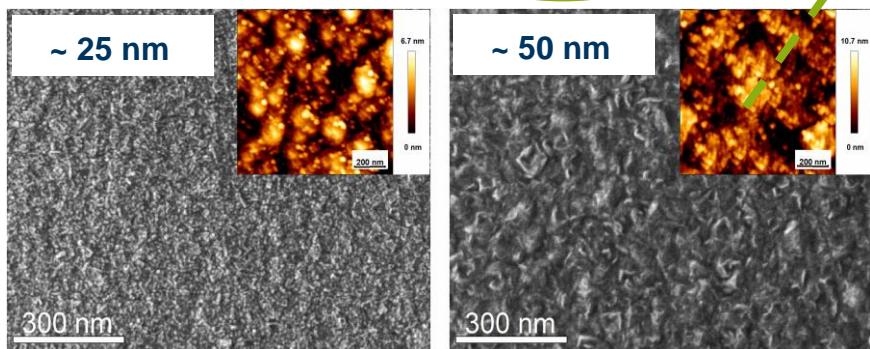
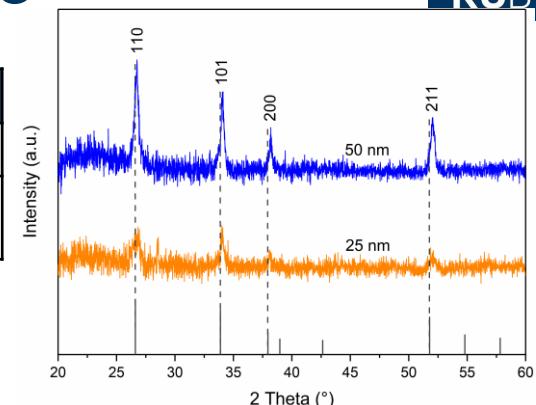
Continuous contribution of extrinsic region (Oxygen vacancies + desorption of $\text{H}_2\text{O}/\text{OH}/\text{O}^{2-}_{\text{chemisorbed}}$)

Why???

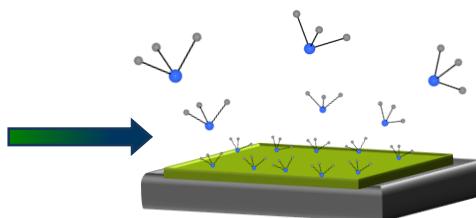
SnO_2 thin film Resistivity Performance



AFM		
Thickness (nm)	~ 25	~ 50
R_{ms} roughness (nm)	1.52	2.31



- More pronounced surface topography with larger grained facets for ~ 50 nm sample

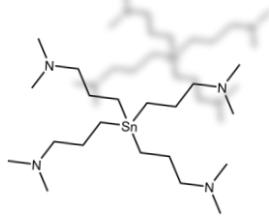
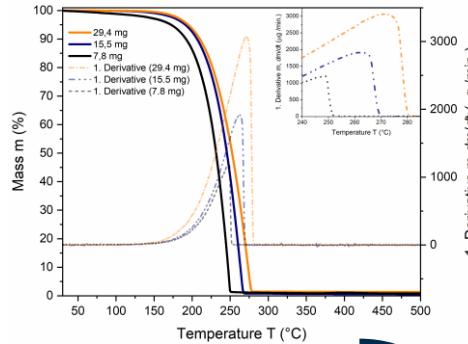


Intrinsic features of initial CVD film growth allow to “tune” SnO_2 film resistivity

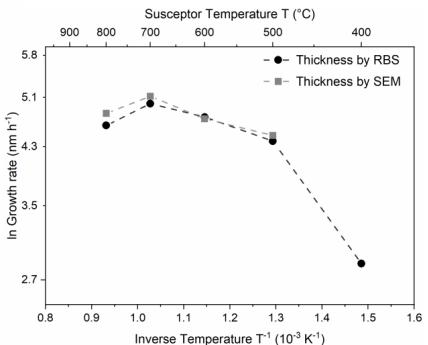
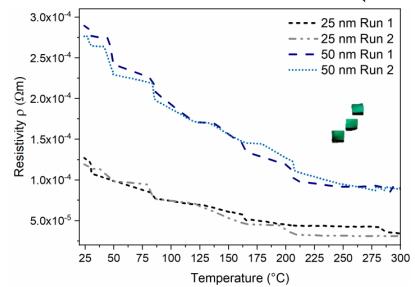
- Impact of crystallinity difficult to assess
 - Different thickness & heat exposure times

Exploring chemical sensor performance (ongoing research)

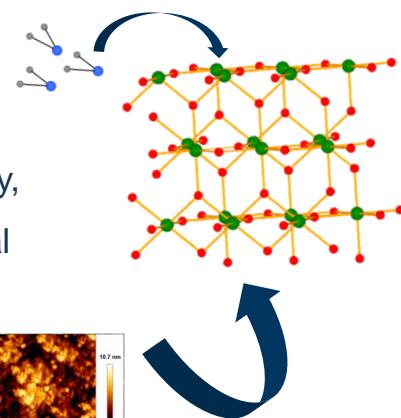
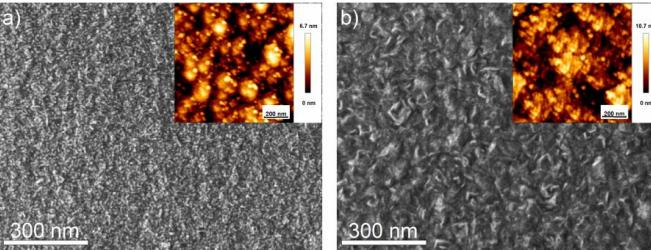
Summary



➤ Employing $\text{Sn}(\text{DMP})_4$ as a new CVD precursor for SnO_2 in combination with O_2



➤ Device quality SnO_2 thin films with tunable surface topography, high purity and preferred crystal orientation



Acknowledgment



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CVD/ALD Papers
(@CVD_ALD_papers)

Surveying and tweeting recent publications featuring
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Investitionen in Wachstum
und Beschäftigung

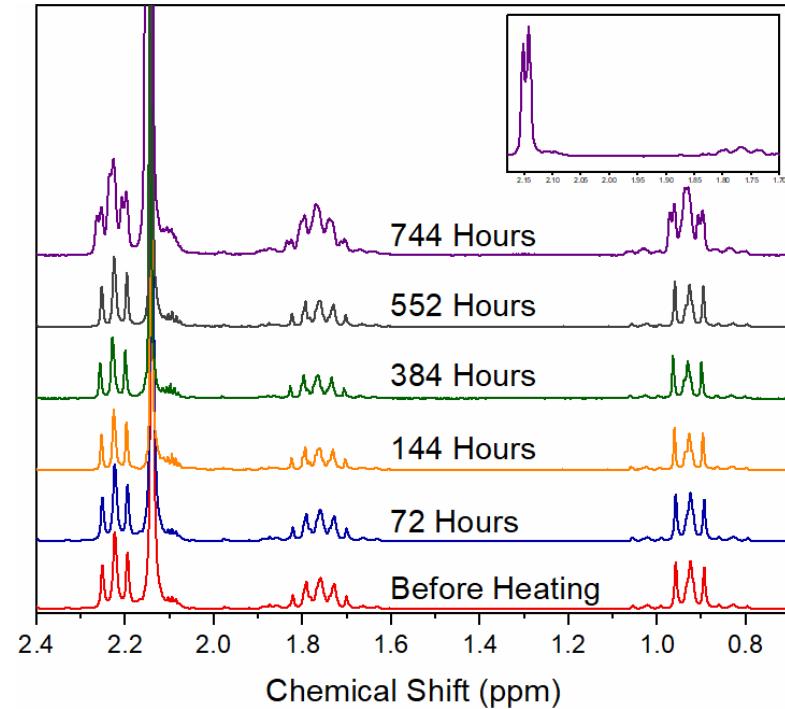
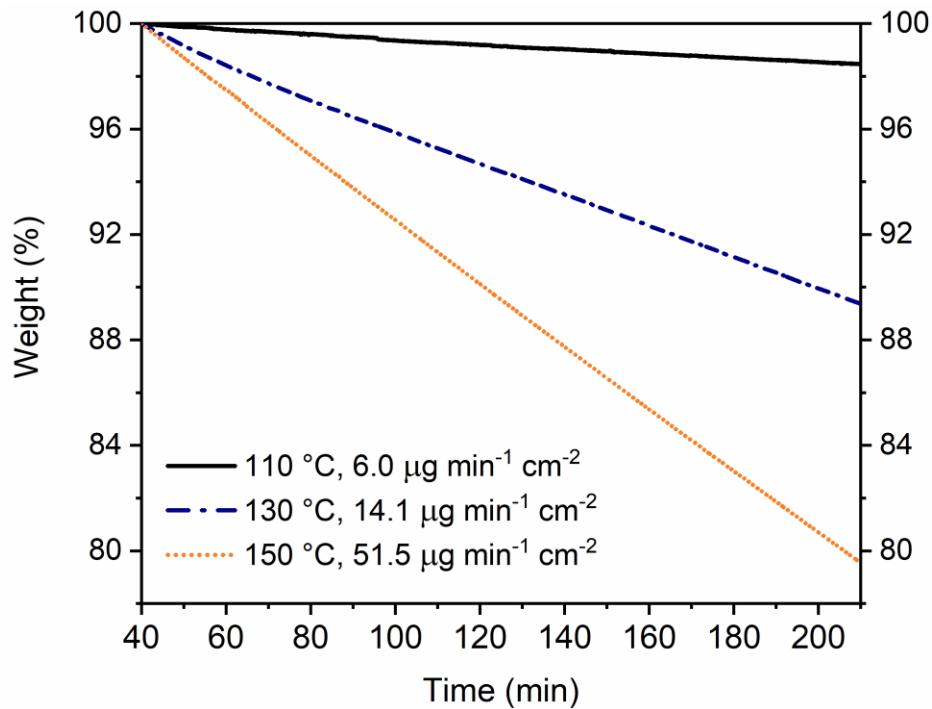


EUROPÄISCHE UNION
Investition in unsere Zukunft
Europäischer Fonds
für regionale Entwicklung

RUBION

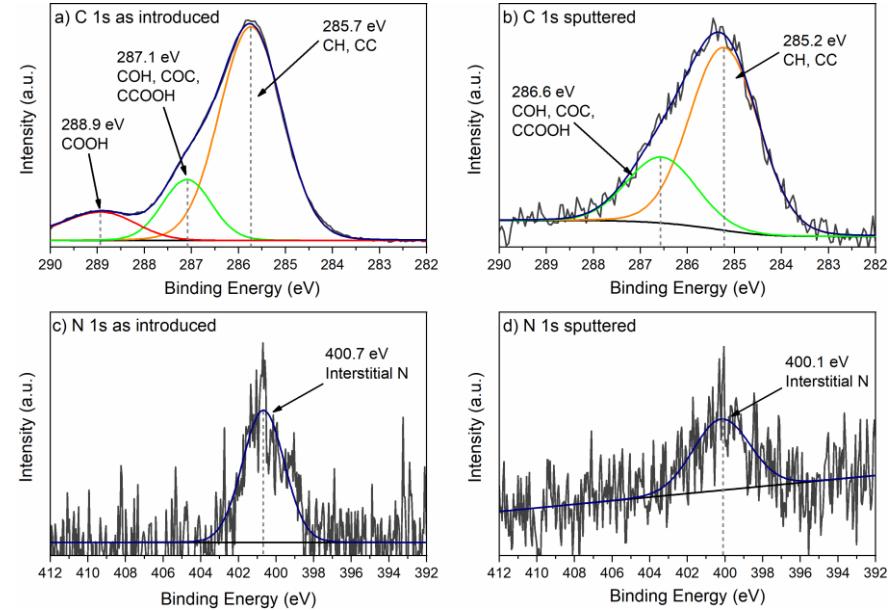
Central Unit for Ionbeams
and Radionuclides

Appendix



Appendix

RBS / NRA					
Pressure (mbar)	Concentration (at. %) and O to Sn ratio				
	C	N	O	Sn	O/Sn
0.1	0.8	0.2	66.9	32.1	2.08
1	0.9	0.1	66.8	32.2	2.07
5	0.2	1.0	67.2	31.6	2.12
10	n.d.	1.4	67.4	31.2	2.16



Appendix

