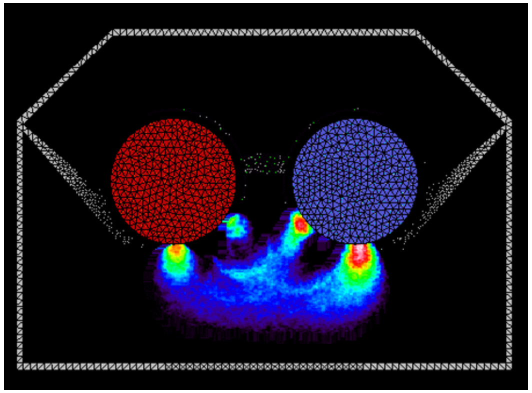

Recent Achievements in Serial Co-Sputtering (SCS) and TCOs for CIGS

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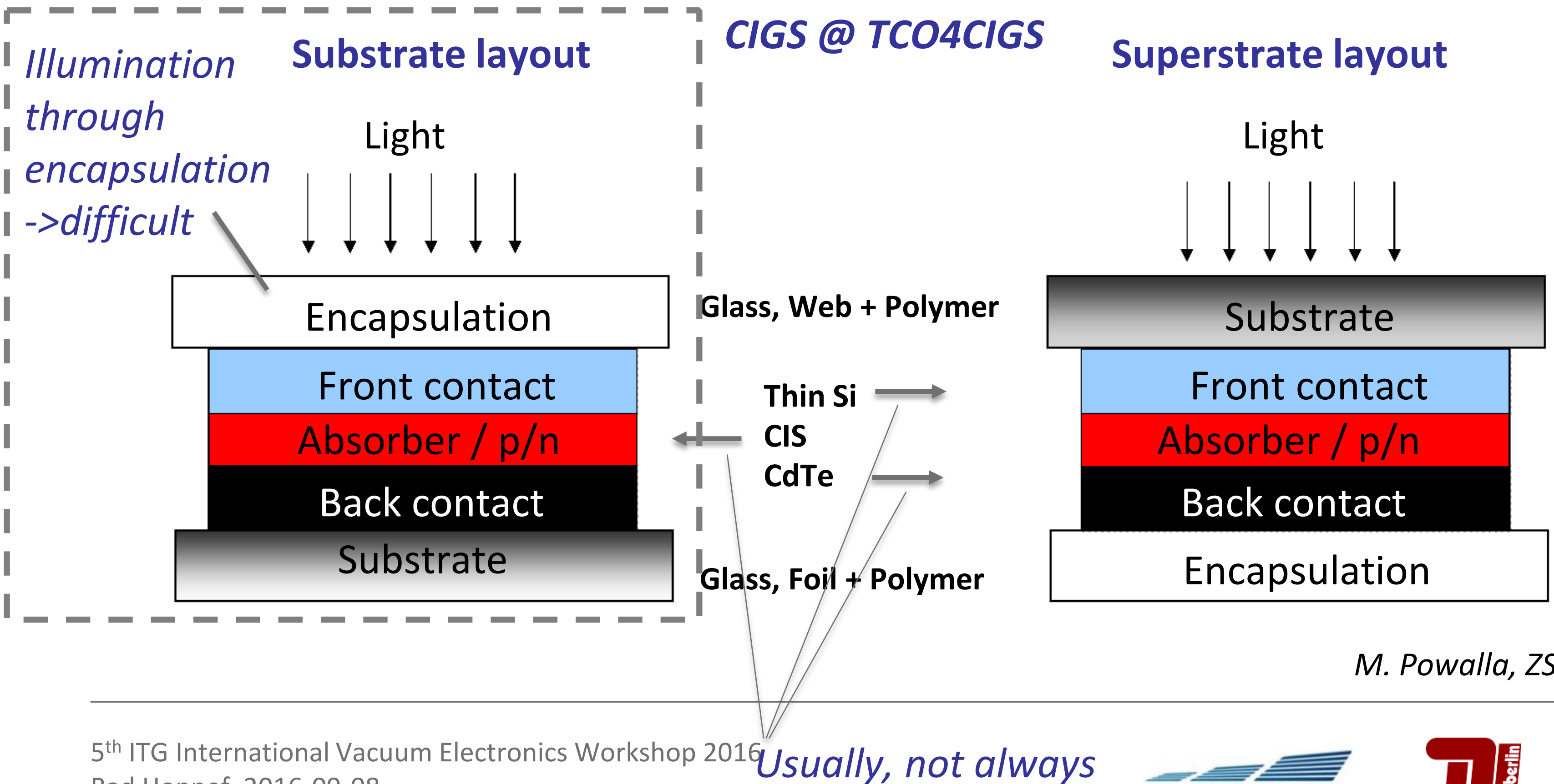
Top: Plasma simulation dual rotatable magnetron | Bottom: SCS set-up with pressure separation

Outline

1 Introduction: Our institute
2 Demands for high mobility TCOs for CIGS
3 In_2O_3:H (IOH) and In-free TCO concepts
4 Serial Co-Sputtering
5 Device results
6 Summary

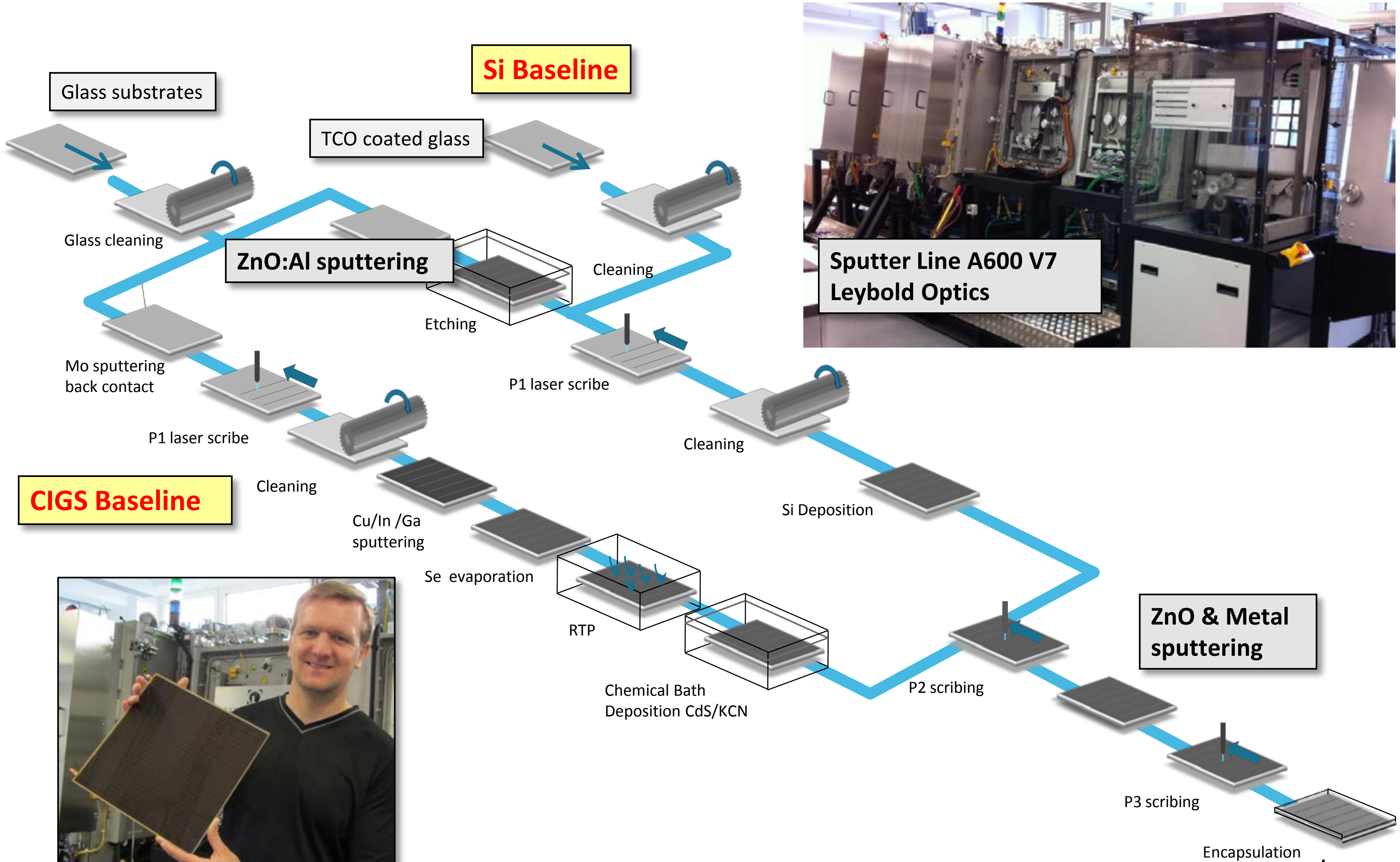
The idea of thin film photovoltaics

"The primary idea is a tiny amount of expensive material (1 µm or so) and lots of cheap glass and wire and metal and plastic"
Ken Zweibel, NREL, 2004



M. Powalla, ZSW

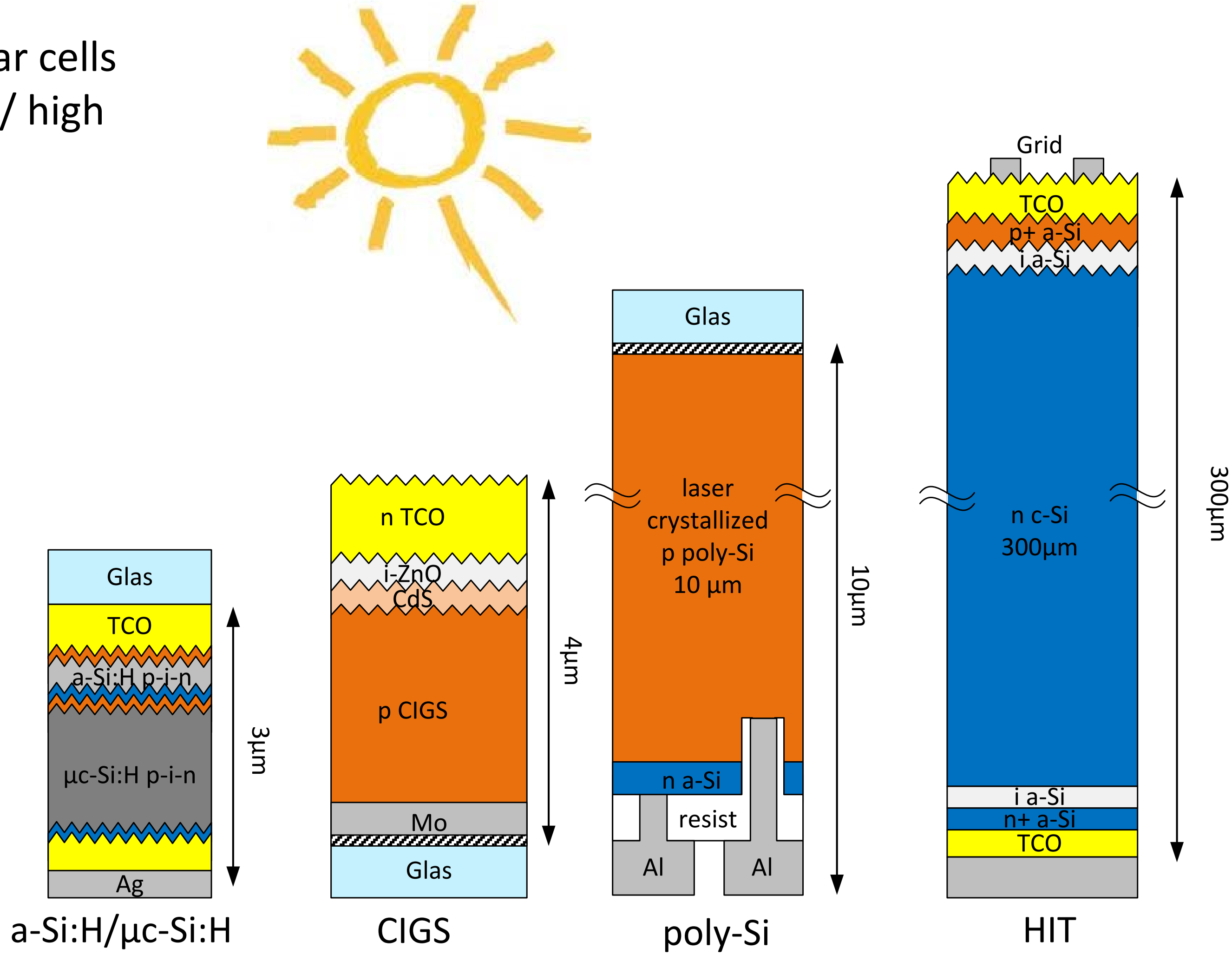
30 x 30 cm² CIGS and Thin-Film Silicon baselines @ PVcomB



www.pvcomb.com

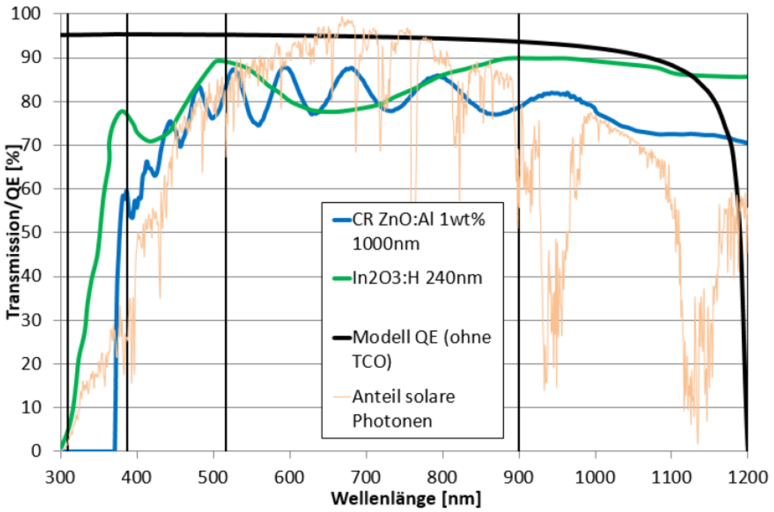
TCOs in Thin Film Solar Cells at PVcomB

- Thin Film solar cells need Low-T_S / high mobility TCO



Motivation: High mobility TCOs for CIGS: The TCO4CIGS project (BMU funded, Oct. ’14 – Sept. ’17)

Comparison AZO and IOH (Lit. Koida)



- Similar R_{Sh} for 1000 nm AZO and 240 nm IOH, but improved optics for high mobility IOH
- Potential j_{sc} gain: from ~36 to ~40 mA/cm^2
- Worth the effort, even with respect to In-based TCOs

- TCO4CIGS consortium:
  - **Avancis**
  - MAGPULS
  - Sentech Instruments
  - Solayer
  - Fraunhofer IST
  - HZB
  - TU Berlin
  - ZSW

IOH: T. Koida et al., TSF 518 (2010) 2930

Outline

1 Introduction: Our institute

2 Demands for high mobility TCOs for CIGS

3 In_2O_3:H (IOH) and In-free TCO concepts

4 Serial Co-Sputtering

5 Device results

6 Summary

Demands on the window layer

Light management: n(λ), T(λ) →	High optical transmittance
Passivation CIGS / Buffer →	No generation of defects & proper band alignment
Front electrode: R_{Sh} →	Proper matching of sheet resistance and transmittance
Serial connection: TCO/Mo →	Small contact resistance

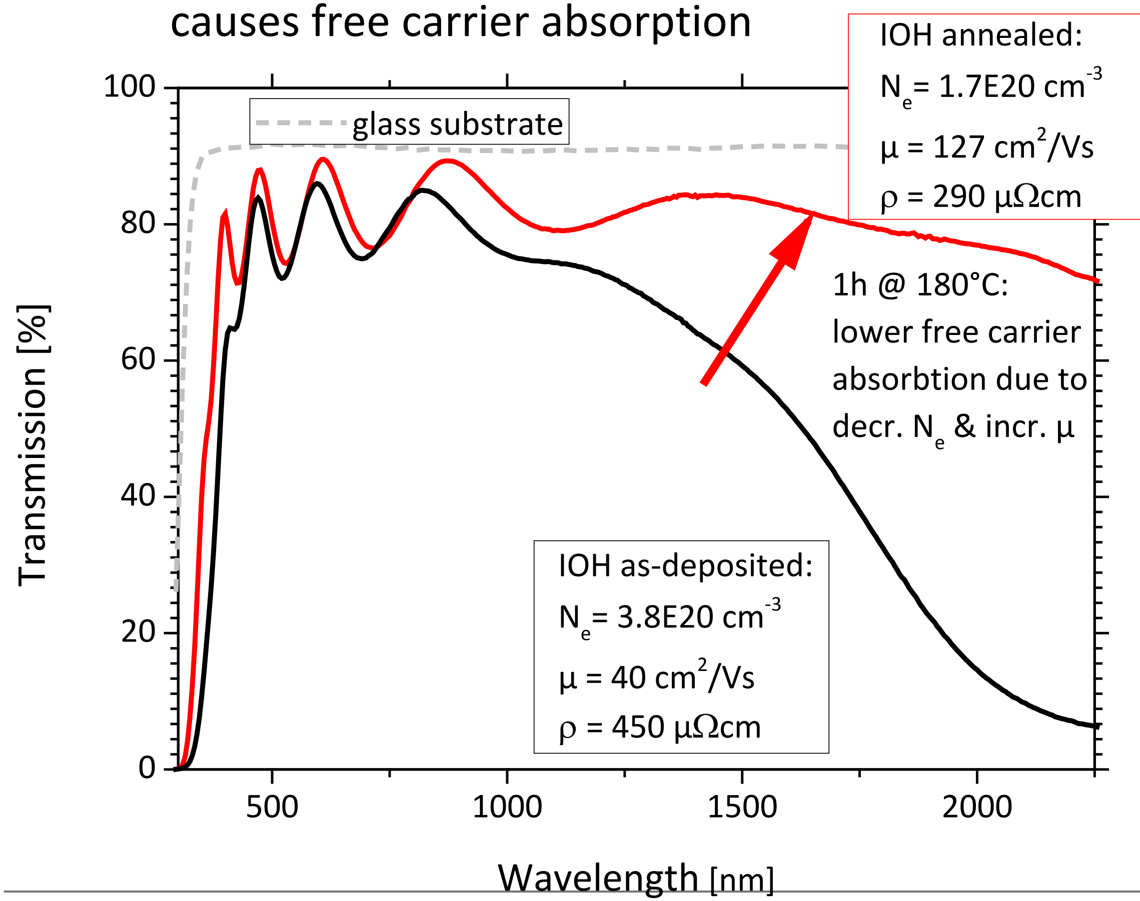
Optimizing the TCO layer

$$\sigma = e \cdot Ne \cdot \mu$$

μ → must be as high as possible

Ne → causes free carrier absorption

σ	Conductivity
e	electron charge
N_e	charge carrier density
μ	carrier mobility



Annealing 1h @ 180 °C in vacuum:
→ μ x 3
→ N_e / 2

Outline

Overview Indium-based TCOs

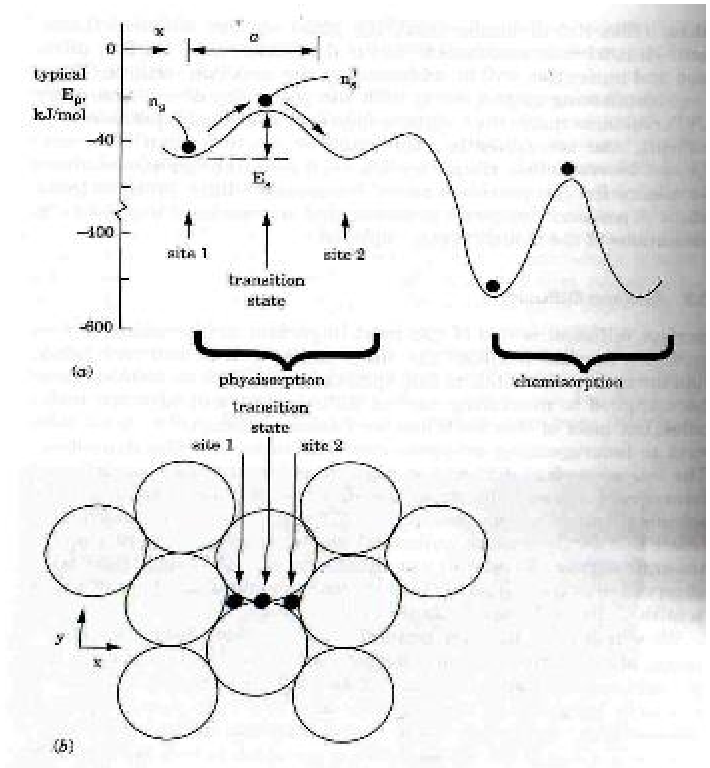
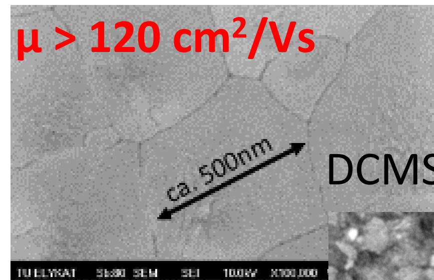


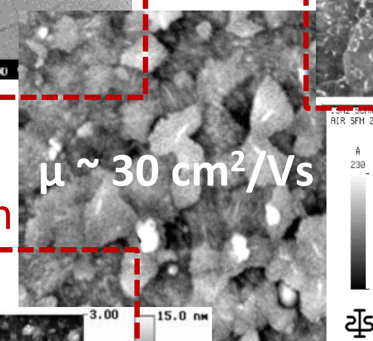
Figure 5.4 Surface diffusion: (a) potential energy vs. position x along the surface, and (b) typical adsorption sites on a surface lattice.

Post treatment

High mobility IOH*

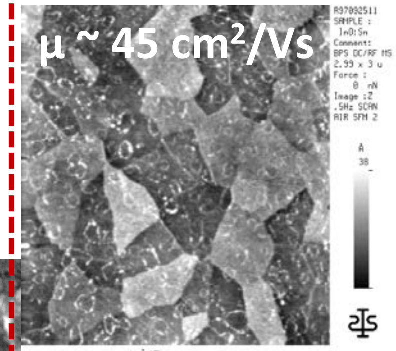


DCMS ITO



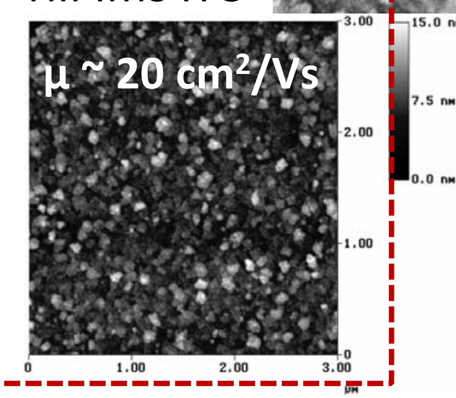
Layer-by-layer growth

RFDCMS ITO

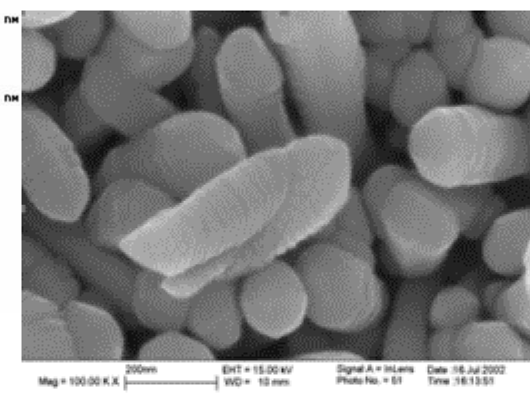


Island growth

HIPIMS ITO

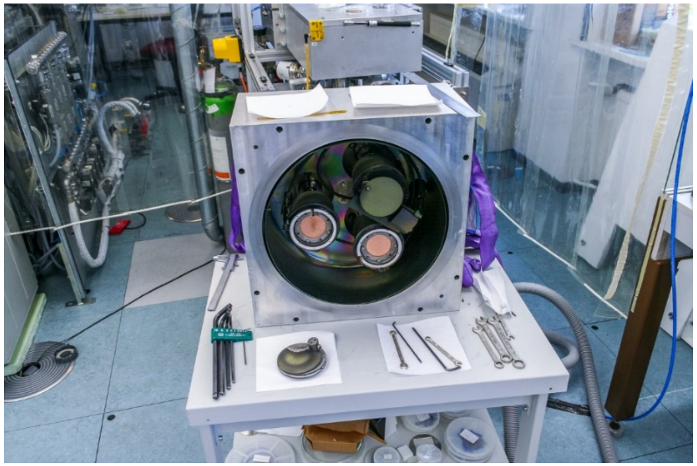


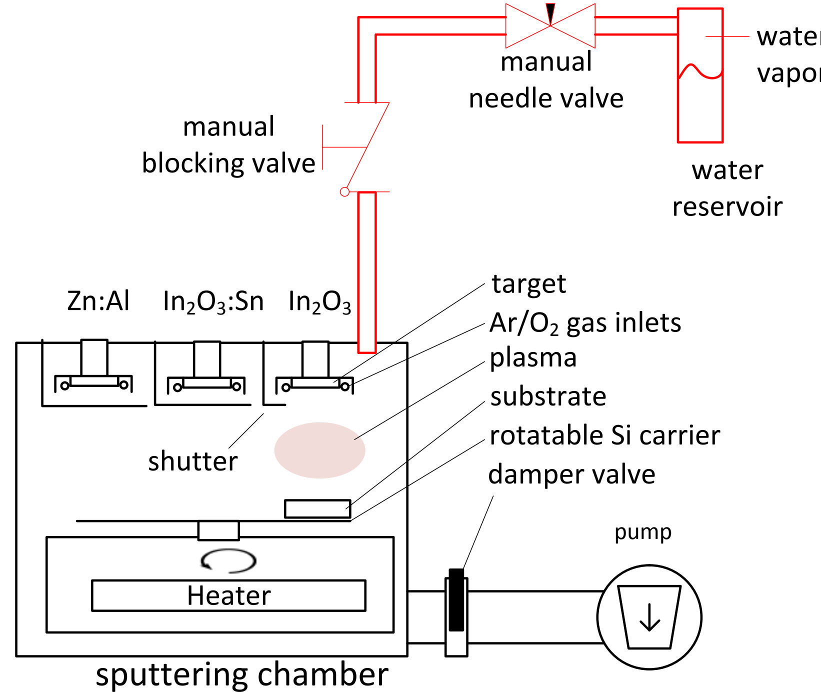
Scaffold ITO



*Smith 1995 | *PhD work of Harald Scherg-Kurmes, TU Berlin 2015*

Synthesis of the IOH layer



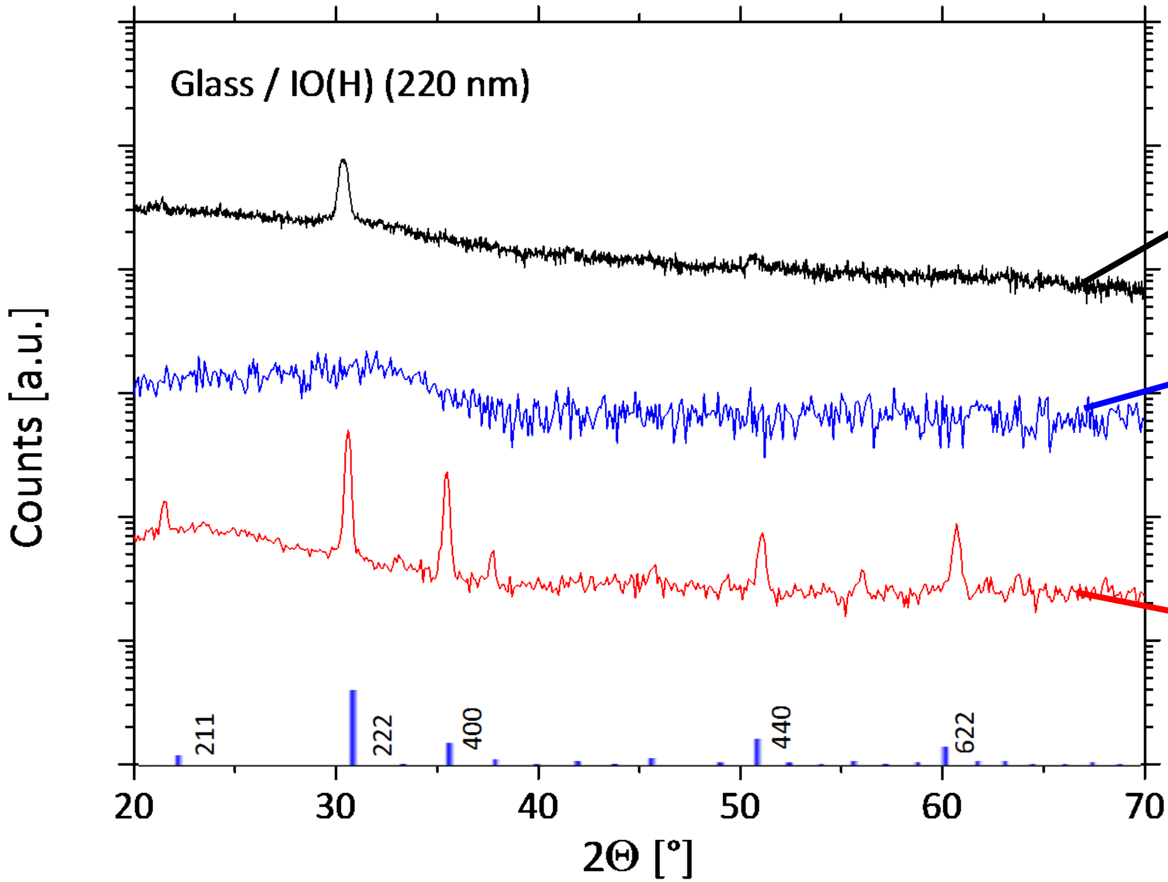


- RF Magnetron sputtering from 2 inch ceramic In_2O_3 target
- Water vapor introduction into sputtering chamber through needle
- Annealing in sputtering chamber under vacuum at 180 °C

- Process parameters:
  - p_{tot} = 1 … 6 x 10^{-3} mbar
  - $p(H_2O)$ = 1.6 x 10^{-6} mbar
  - $p(O_2)$ = 0.32 %
  - P_{RF} = 70 W

H. Scherg-Kurmes et al., Proceedings ICCG 10 (2014), Dresden

Crystallization process during annealing



undoped In_2O_3 as prepared polycrystalline film

Hydrogen-doped In_2O_3:H a. p. X-ray amorphous film

Hydrogen-doped In_2O_3:H p. a. (vacuum annealed at 180 °C)
-> Crystallization
-> μ = 130 cm^2/Vs

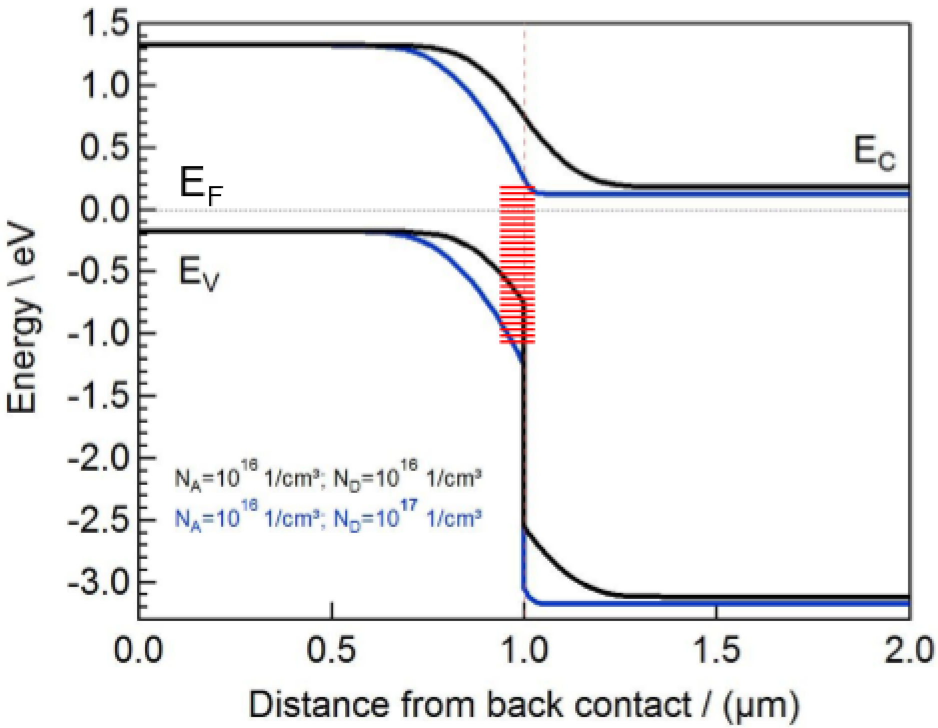
- **Conclusion: H-doping -> a-IOH growth & low temperature crystallization**

H. Scherg-Kurmes et al., Proceedings ICCG 10 (2014), Dresden

Tailoring TCO film properties by Serial Co-Sputtering

- Towards In-free TCOs
  - Amorphous TCOs (Zn-Sn-O, In-Zn-O)
  - TiO_x based TCOs
  - ZnO doping optimization
- Band alignment
  - High n-doping at the interface p-CIGS / n-Window may allow for shifting the junction inside the low defect density CIGS.

CIGS Interface optimization
(TCO4CIGS band structure modeling @ PVcomB)



	S (cm/s)	Voc (mV)	Jsc (mA/cm²)
$N_A=N_D$	0	948	26.9
	$2x10^6$	**627**	26.5
$N_A>N_D$	0	961	26.2
	$2x10^6$	726	17.3
$N_A<N_D$	0	940	27.1
	$2x10^6$	880	26.6

- **Conclusion: E_F close to E_C: The interface of the p-type absorber becomes inverted**

Outline

Problems during sputtering with conventional cathodes

Target poisoning

- Unwanted reactions at the target: Rate ↘ Stability ↘ Film properties ↘

Target composition

- Target composition is fixed & limited due to manufacturing constrains.

Coupling of process parameters

- ZnO:Al: Change of $p(O_2)$ or T_S yields change of c(Al). How to separate?

In-situ control of deposition rate

- Complex optical monitoring. Implementation! Maintenance!

Low sputter yield

- Low deposition rate, costly machinery, waste of energy.

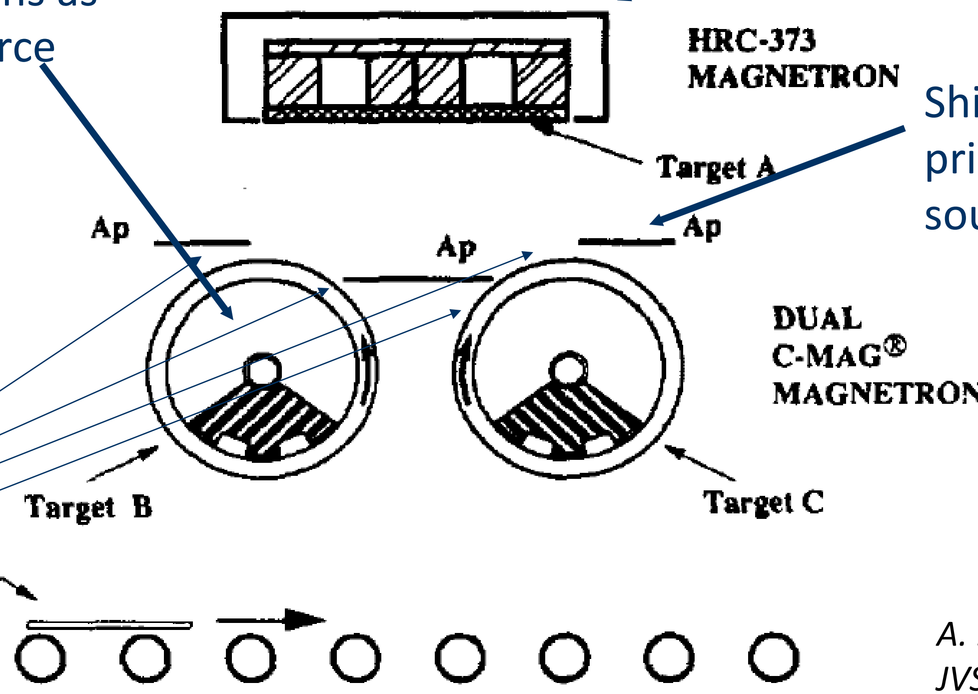
B. Szyszka et al., ICCG 2010 Braunschweig

A solution for these problems:

Planar magnetron as assisting source

Rotatable magnetrons as primary sputter source

Shielding to separate primary and assisting source



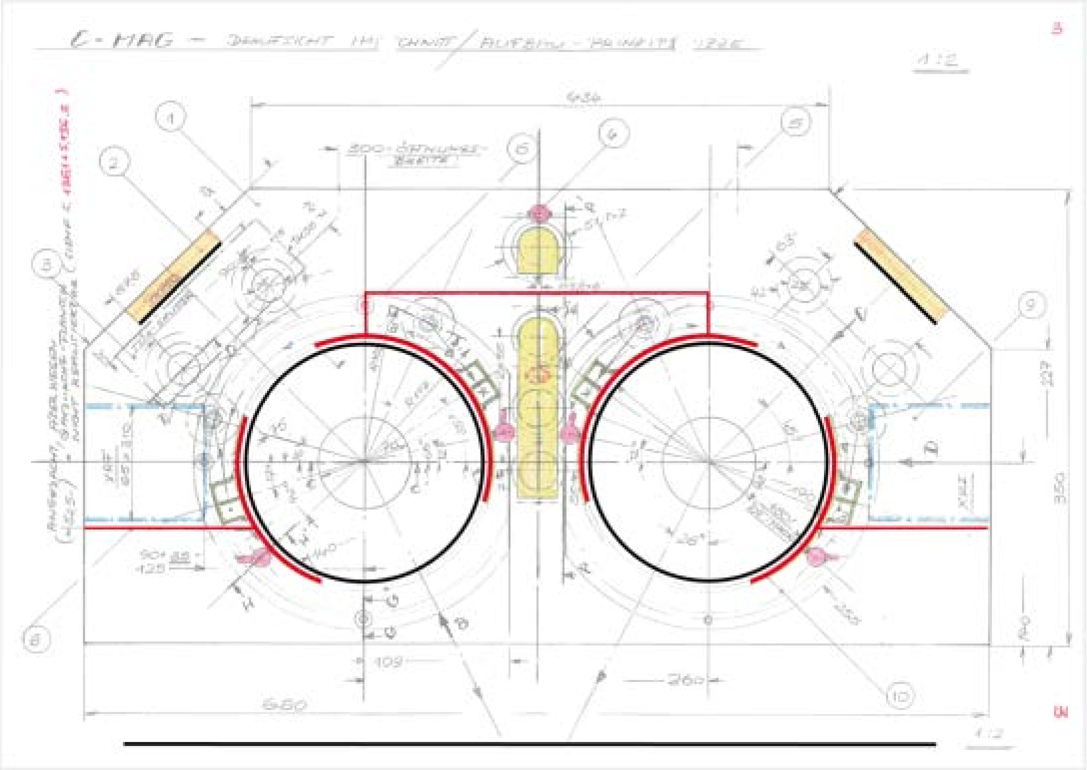
No pressure separation between primary and assisting source!

A. Belkind et al., JVSTA 11 (1993) 314

- Target composition of the primary target can be modified.
- Setup allows for sputter yield amplification for metallic targets.

Experimental realization of the Serial Co-Sputtering with pressure separation (Ferchau Innovation price 2011)

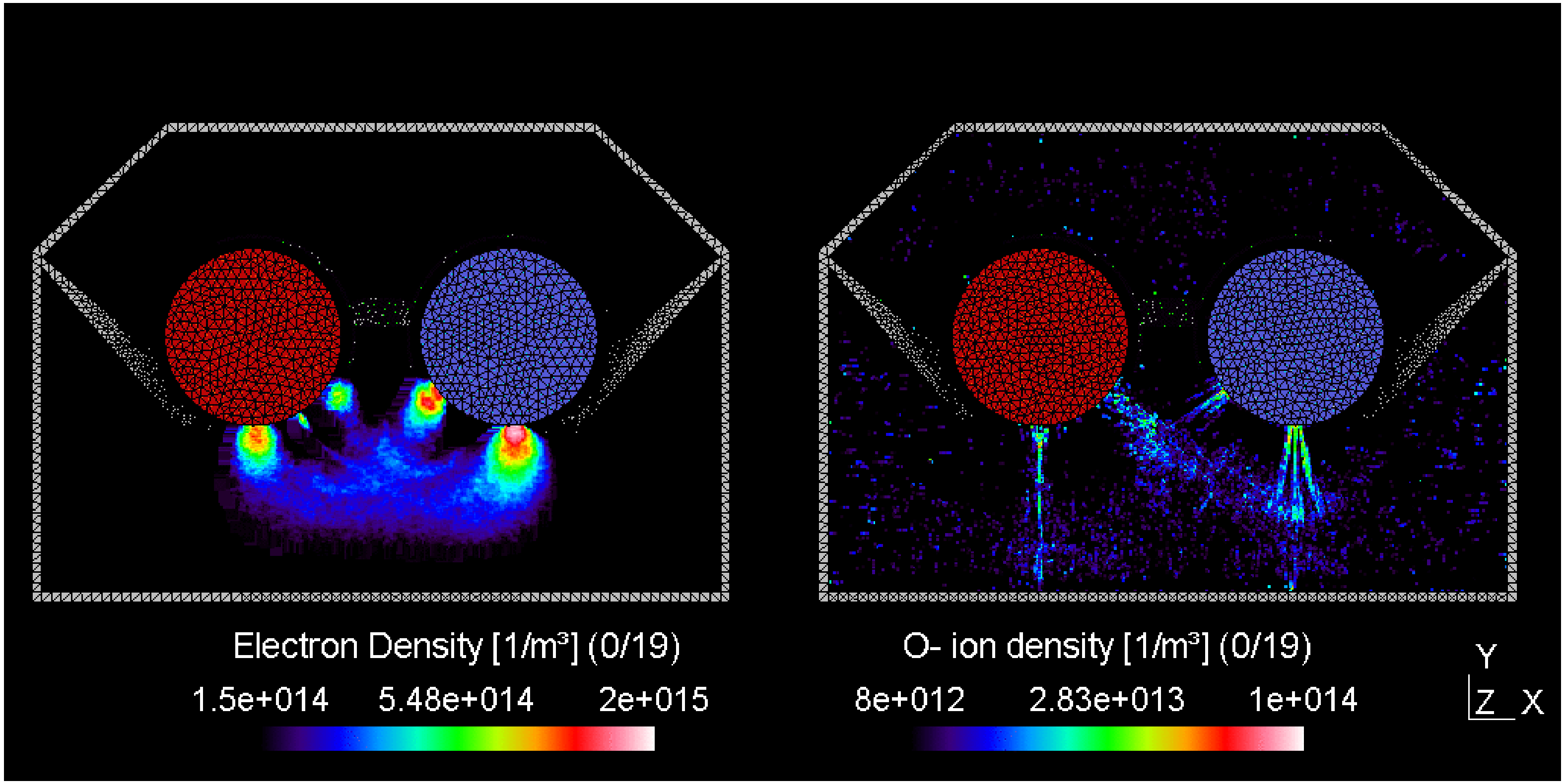
ZnO:Al
$SnZnO_x$
TiO_x:Nb
In-Ga-Zn-O
CIGS
TiO_2:X



- Synthesis of new materials and control of doping levels **-> n-TCO for PV applications, n-ASO for TFT application**
- Available for retrofit by Fraunhofer IST / Solayer / Interpane

EP1697555B1: Method and device for magnetron sputtering

Experimental realization of the Serial Co-Sputtering: 2D Plasma-Simulation of electron density and O^- ion density



- 2D Plasma-Simulation incl. negative oxygen ions:
  (Simulation time: t = 50 ... 60 µs), Modeling: A. Pflug, M. Siemers, Fraunhofer IST

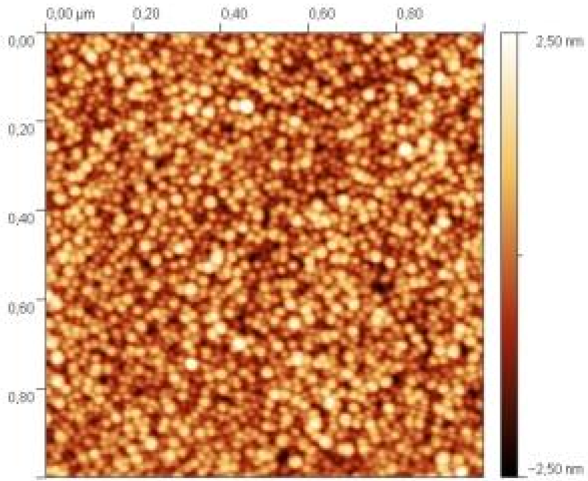
Experimental realization of the Serial Co-Sputtering process with pressure separation

a) Serial Co-Sputtering source (model)

b) First plasma in June 2010

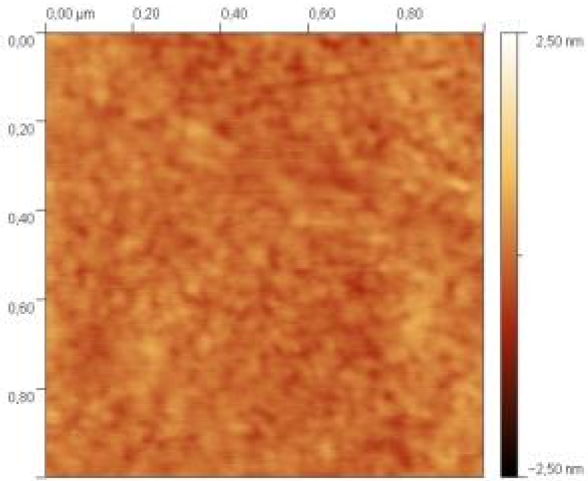
Example: Bi-doping of TiO_2: Improvement of morphology and deposition rate by means of sputter yield amplification

a) TiO_2 @ **18.9 nm m/min**



R_q = 0.81 nm, R_a = 0.65 nm
d = 210 nm

b) TiO_2:3.8 at.%Bi @ **29.4 nm m/min**

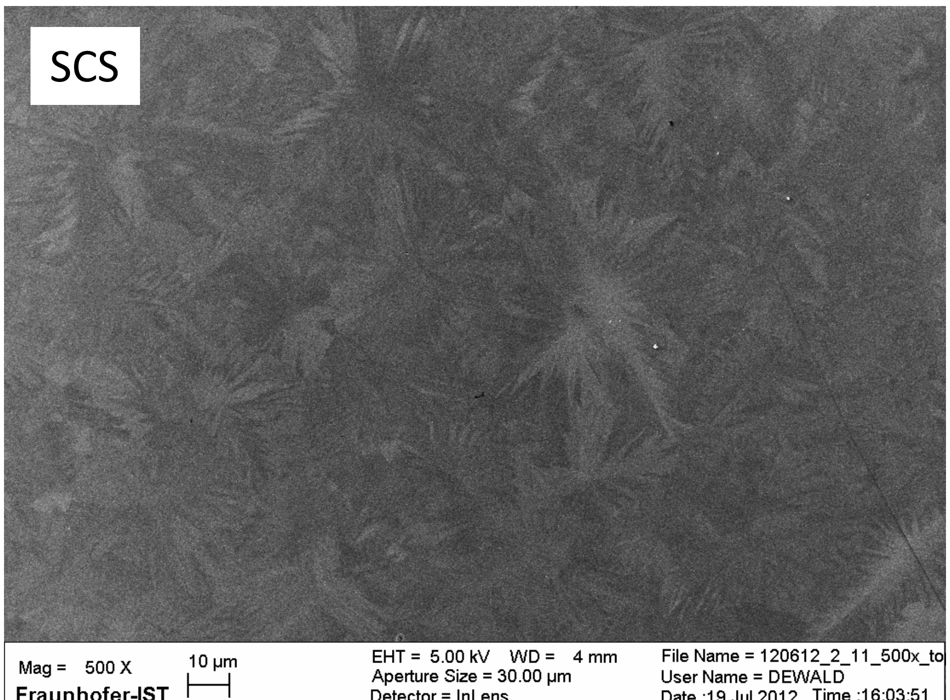


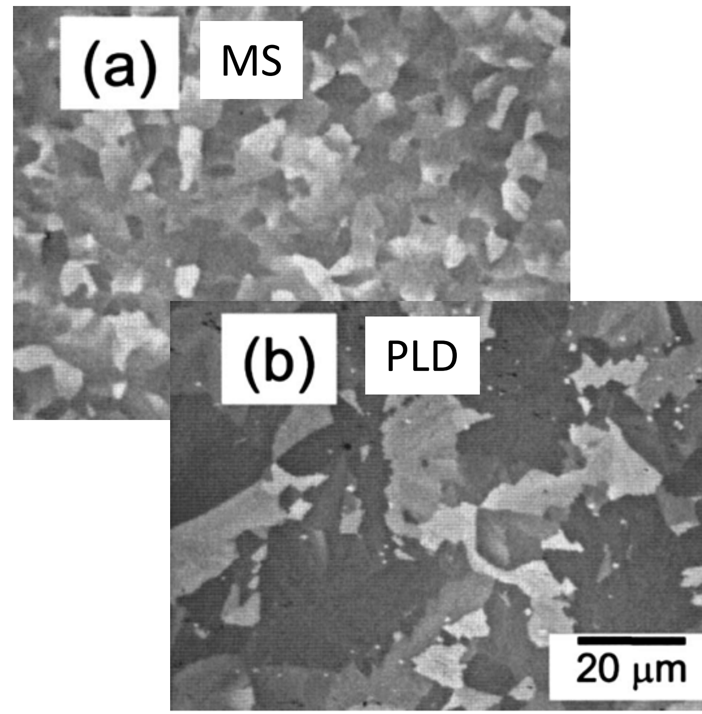
R_q = 0.21 nm, R_a = 0.17 nm
d = 326 nm

- AFM reveals fine grain size for both films.
- Substantial decrease of surface roughness for TiO_2:Bi.
- TiO_x:BiO_x targets are not available due to metallurgical reasons.

Example: Nb-doping of TiO_2
Synthesis of TiO_2 based TCOs by SCS sputtering

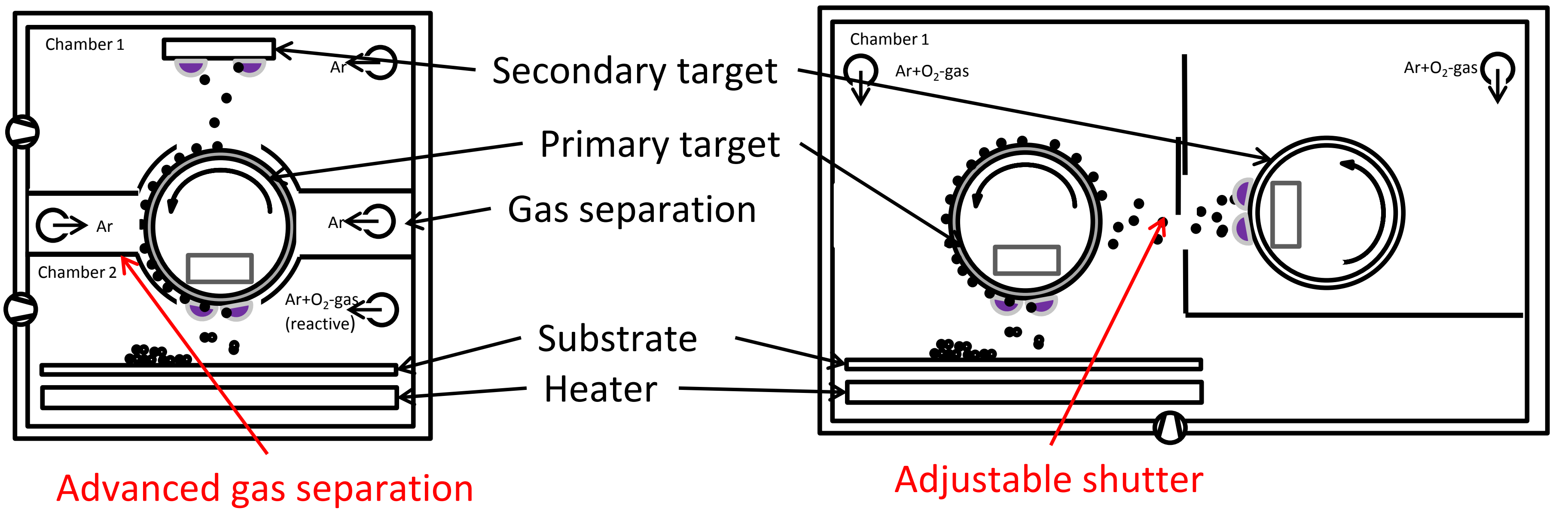
- 2 x 1 kW with TiO_2 rotatable, 2x 200 W with Nb planar targets
- Annealing at 350° in vacuum for 1h -> large anatase grains > 10 µm
- d = 211 nm, R_{sh} = 99.8 Ω , ρ = 2100 µΩcm, T_v = 67.6%, n = 2.45





a, b: T. Hitosugi et al., JVSTA 26 (2008) 1027

Serial co-sputtering (SCS) of TCOs within TCO4CIGS

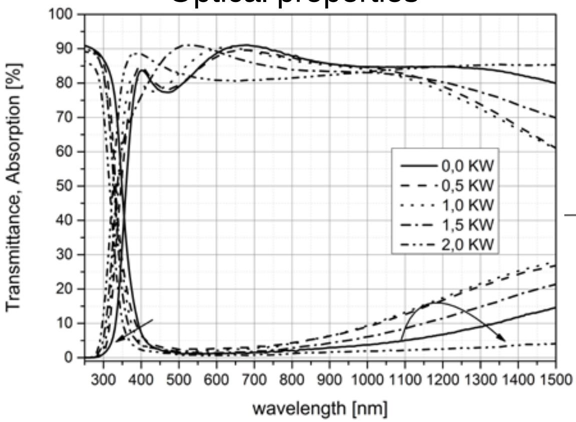


- \+ Separation of reactive gas
- \+ Different partial pressures at main / assisting target
- \+ Large variety of material combinations
- – More complex process and parameter

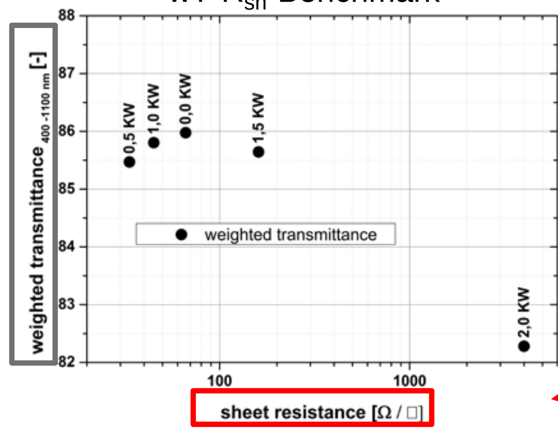
- \+ Easy integration of shielding wall for SCS process
- \+ 2nd target power as process parameter
- – No pressure separation
- – Metallic targets oxidize
- – Shutter needed for low plasma power
- – Magnets has to be rotated

1^{st} results of non-optimized AZO films deposited on soda lime glass by SCS process at PVcomB

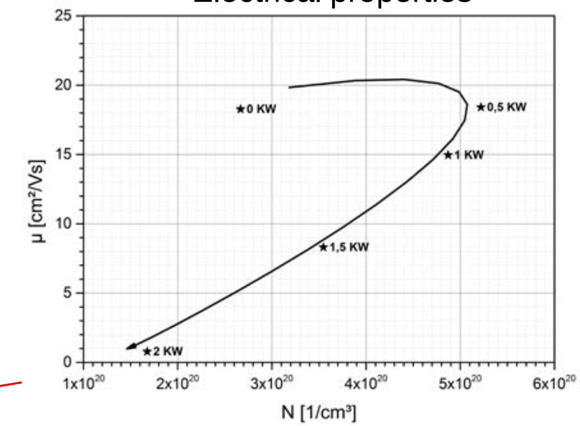
Optical properties



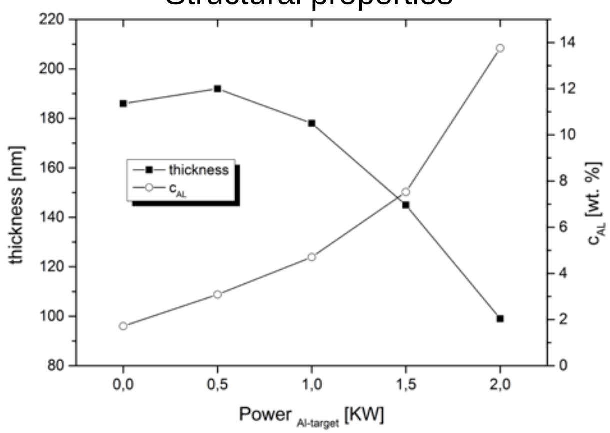
wT-R_{sh}-Benchmark



Electrical properties



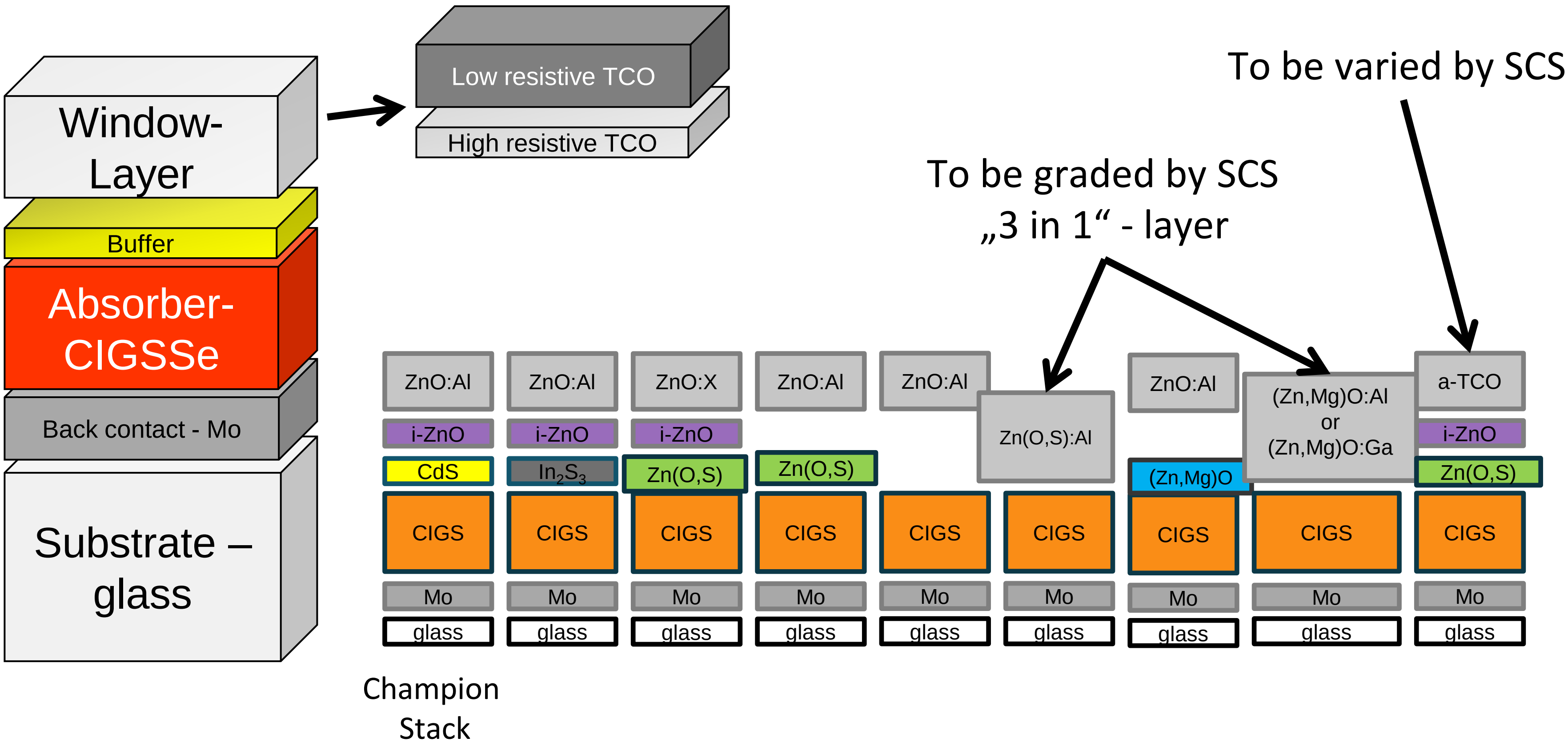
Structural properties



- Increase of power of secondary target P_{AL} leads to:
  - Increase of Al content in AZO films
  - Decrease of deposition rate for higher powers
- ρ passes through a minimum at 0.5 KW
- Transmittance is effected by carrier density as function of P_{AL}
- wT-R_{sh}-Benchmark shows: P_{AL} 0<x<1 KW are beneficial for given parameter

S. Körner, ICCG-11, Braunschweig, June 2016

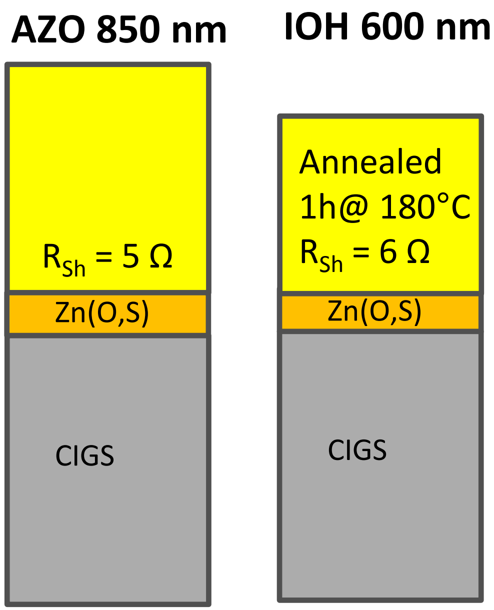
Scheme of CIGS stacks on glass/Mo with alternative buffer layer systems in comparison to the commonly used CdS/i-ZnO*



**adapetd from Witte, W.; Spiering, S. & Hariskos, D. , Substitution of the CdS buffer layer in CIGS thin-film solar cells, in Vakuum in Forschung und Praxis, 2014, 26, 23-7*

Outline

IOH as front contact for CIGS thin film solar cells
Zn(O, S) Buffer

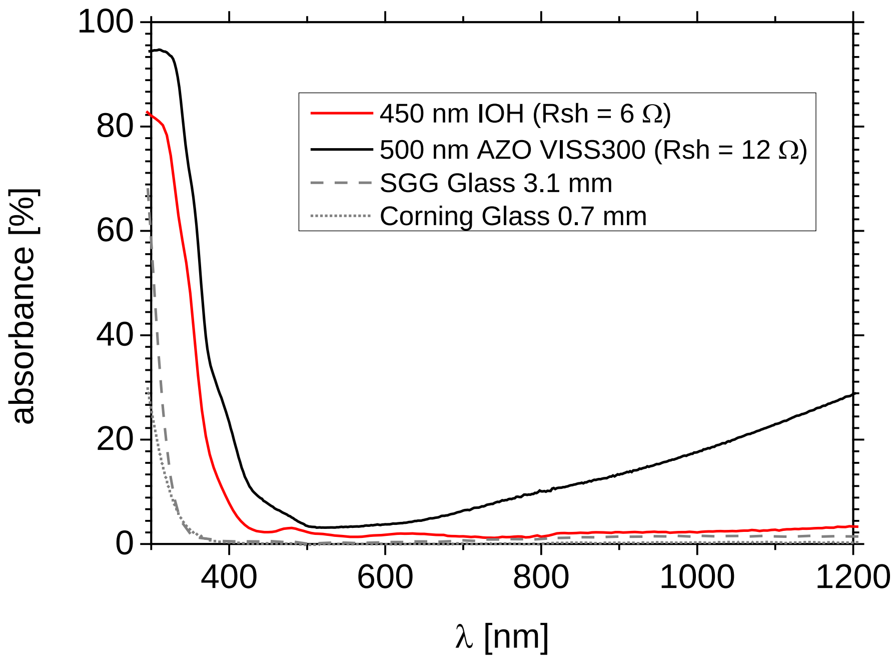


- Thick TCO replaces metal front grid
- IOH has lower free carrier absorption than AZO
- Higher transparency should lead to higher j_{sc} for cell with IOH front contact

TCO Process parameters:

- AZO
  - VISS300 Inline Sputtering System
  - Deposition at T_S ~ 180 °C, RF Process
  - AZO Ceramic Target, 2 wt. % Al_2O_3
  - no post-deposition annealing
- IOH
  - Process parameters described above
  - Deposition at room temperature
  - post deposition annealing:
    1h @ 180 °C in vacuum

IOH as front contact for CIGS thin film solar cells
Zn(O, S) Buffer

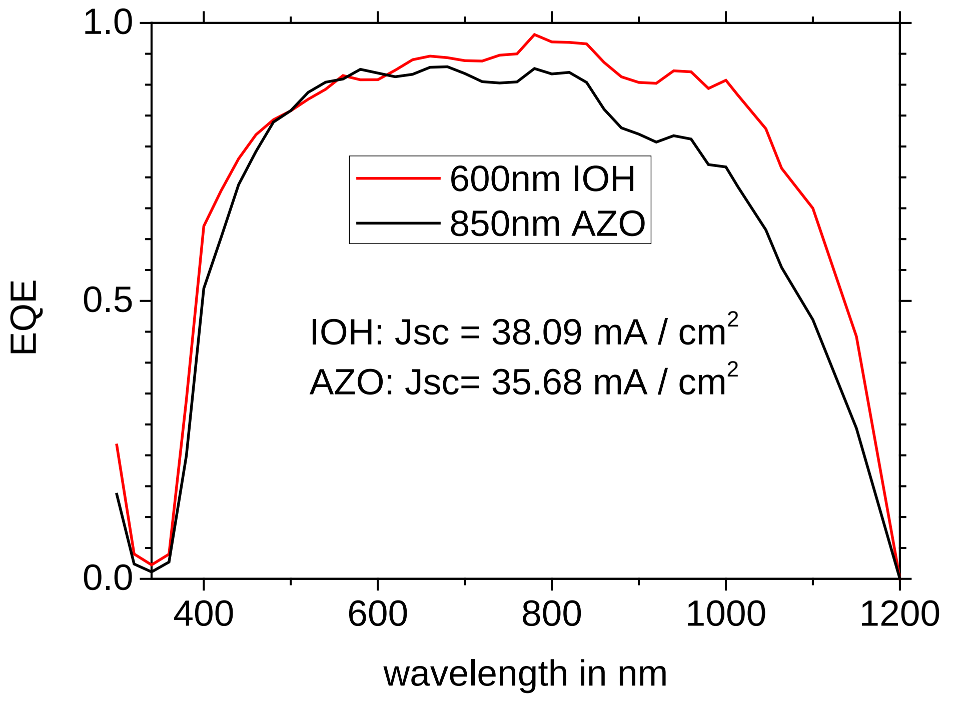


- Absorbance was measured via 100-R-T
- AZO has a higher optical absorption than IOH due to a higher carrier concentration and a smaller bandgap

	Ne	µ	rho
	cm^{-3}	cm²/Vs	µOhm*cm
AZO (deposited @ 180 °C)	4.38E+20	23.0	618
IOH (annealed 1h@ 180°C in vacuum)	1.70E+20	126.6	290

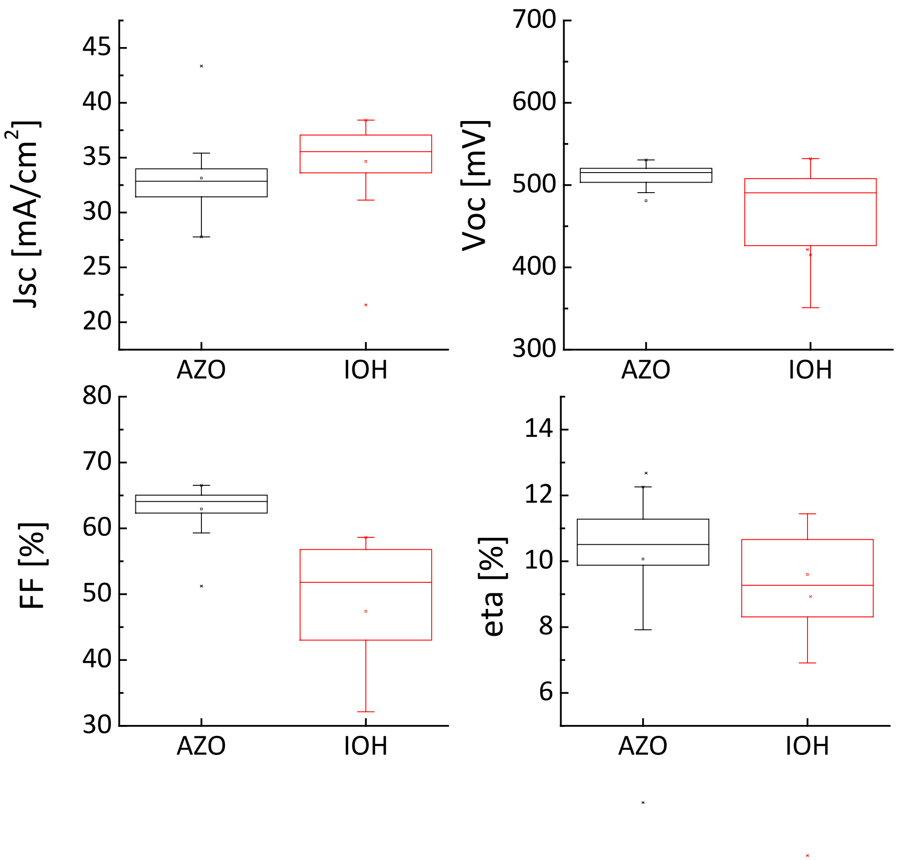
- AZO has a lower mobility than IOH
- Resistivity of AZO is higher

EQE measurements of CIGS cells



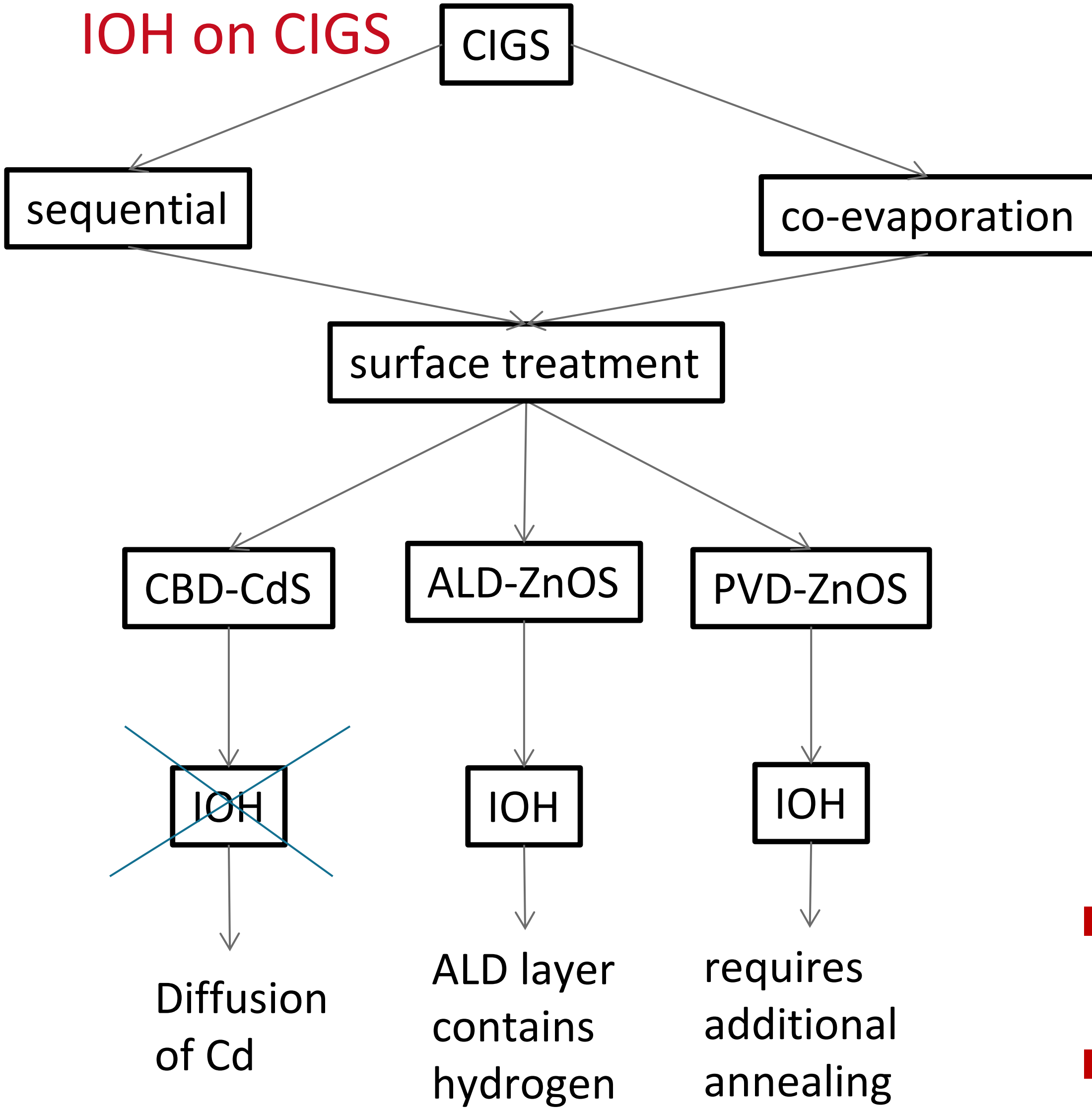
- EQE is higher for IOH than for AZO
- Higher IOH transmittance leads to higher EQE values in the blue and the NIR spectrum
- integrated EQE current corresponds to light-IV measurements

Light-IV measurements of CIGS cells



- Higher Jsc for IOH front-contact due to higher transparency
- Voc is a little lower for IOH, possible due to annealing process in vacuum
- FF is lower for IOH. Band alignment optimization between IOH and Zn(O,S) might solve this.
- eta of both cells almost similar (higher inhomogeneity for IOH due to smaller sputtering target)

IOH on CIGS



First results on sequentially prepared CIGS with CdS and ALD-ZnOS:

Spezifi-kation	Jsc [mA/cm²]	Voc [mA]	FF [%]	Eta [%]
ALD/AZO	38,1	457	64,4	11,2
ALD/IOH as depo	36,6	442	63,3	10,2
ALD/IOH vacuum	38,4	439	63,6	10,7
CdS/AZO	37,5	437	62,3	10,2
CdS/IOH as depo	35,6	430	61,7	9,4
CdS/IOH vacuum	28,5	435	60,2	7,5

- Results for in-house CIGS, sequential process
- Best results for ALD ZnOxSy and IOH vacuum annealed

Outline

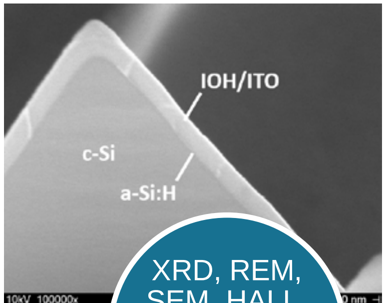
Summary

- SCS – What?
  - Doping of targets, e. g. of rotatable targets, by means of sputtering on them with a 2nd source
- SCS – Why?
  - To tailor doping levels
  - To modify structure and morphology, e. g. ultra smooth TiO_2:Bi films with properties similar to ion-beam sputtered films
  - To increase deposition rate by means of sputter yield amplification effect
- SCS – How?
  - Model based source design for pressure separation
  - Industrial scalable technology with standard rotatables

Summary

- TCO4CIGS
  - Novel TCO In_2O_3:H with mobility up to 130 cm^2/Vs at $T_S < 200$ °C
  - Contact layer for Thin Film Solar Cells (CIGS, HIT, a-Si/µc-Si)
  - Device results: CIGS cells with IOH contacts reveal:
  - (i) improved Jsc -> elimination of free carrier absorption
  - (ii) decrease of FF -> improvement of band alignment to Zn(O, S) buffer necessary
  - Serial co-sputtering for tailored doping and gradients in TCOs
- Next steps
  - Optimization of band alignment to increase FF and thus eta
  - Up-scaling towards 30 x 30 cm^2 dynamic deposition, DC pulse sputtering
  - Set-up of serial co-sputtering for tailored doping to achieve highly doped interface for improved band alignment

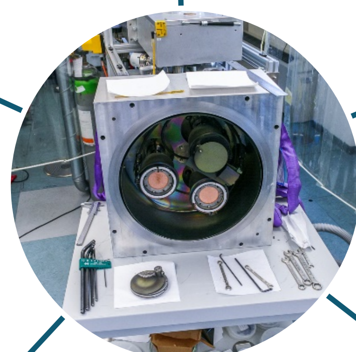
R&D Approach



XRD, REM, SEM, HALL, Optics, Hall, EPMA, SIMS

Bessy, XPS, UPS

TCO4CIGS Bosch / Avancis



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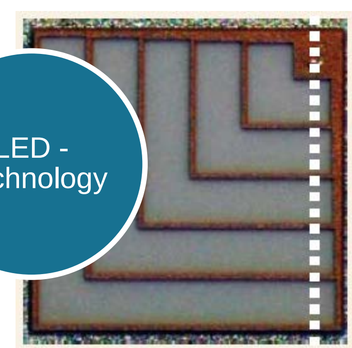
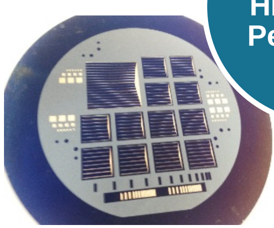


LED - Technology



Device HIT, CIGS, Perovskite

Acknowledgements

Federal Ministry for the Environment, Nature Conservation and Nuclear Safety

Federal Ministry of Education and Research

Orama project funded under contract NMP3-LA-2010-246334 by the European Commission

ORAMA

Project “Spitzenforschung und Innvation in den neuen Ländern” funded by BMBF and SENBWF under grant no. 03IS2151

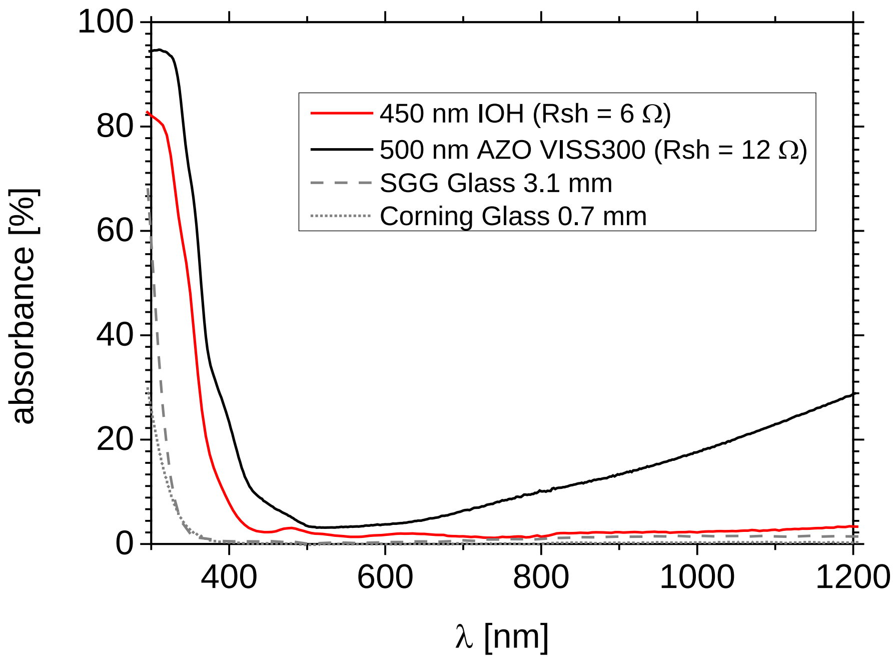
Project TCO4CIGS funded by BMU under grant. no. 0325762

Crystals are like people, it is the defects in them which tend to make them interesting!

Prof. John Ziman
(solid state physicist and humanist,
born1925, died 2005)

Thank you very much for your attention

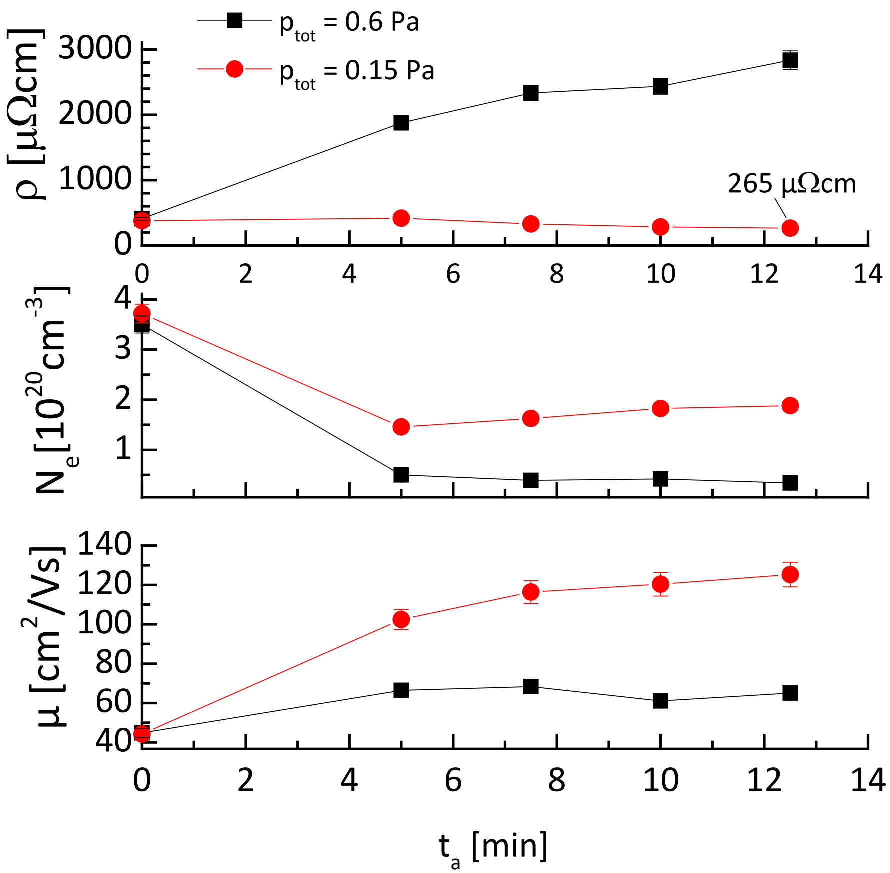
IOH as front contact for CIGS thin film solar cells
Zn(O, S) Buffer



	Ne	μ	rho
	cm^{-3}	cm²/Vs	μOhm*cm
AZO (deposited @ 180 °C)	4.38E+20	23.0	618
IOH (annealed 1h@ 180°C in vacuum)	1.70E+20	126.6	290

- AZO has a lower mobility than IOH
- Resistivity of AZO is higher

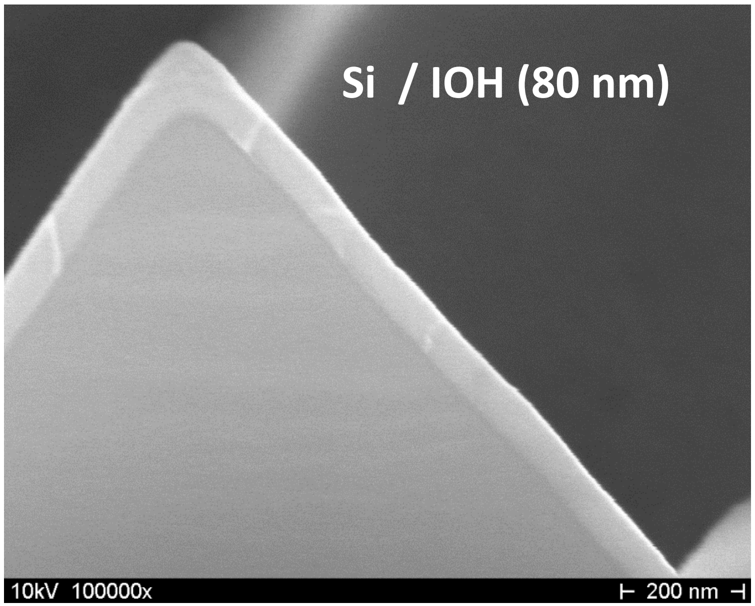
Optimization of IOH annealing process in air @ 200 °C



- Up to now: Complicated vacuum annealing:
  - Technically complex
  - Limits device performance (e. g. for a-Si/c-Si heterojunction cells)
- IOH annealing behavior in air can be controlled by deposition parameters, e. g. pressure
  - High p_{tot}: Low μ and high resistivity after annealing in air because of oxygen diffusion
  - Low p_{tot}: μ = 130 cm^2/Vs, ρ < 300 μΩcm. Same results as after annealing in vacuum.
- **Conclusion: low deposition pressure enables air annealing**

IOH properties on rough substrates

a) Film growth: annealed IOH on patterned Si wafer



- Dense growth on structured Si wafer
- No indication for columnar growth

b) Electrical properties: annealed IOH on textured soda lime glass (vacuum annealed at 180 °C)

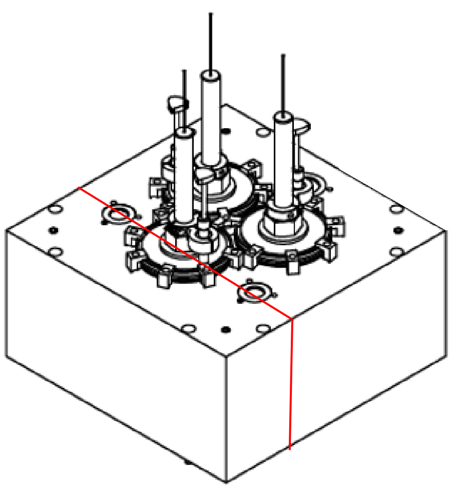
Sample	N_e [10^{20} cm^{-3}]	μ [cm^2/Vs]	ρ [Ωcm]
as deposited	3.76	30.5	4.60E-4
p. a. 30 min	1.21	60.7	8.50E-4
p. a. 1 h	1.71	80.7	4.53E-4

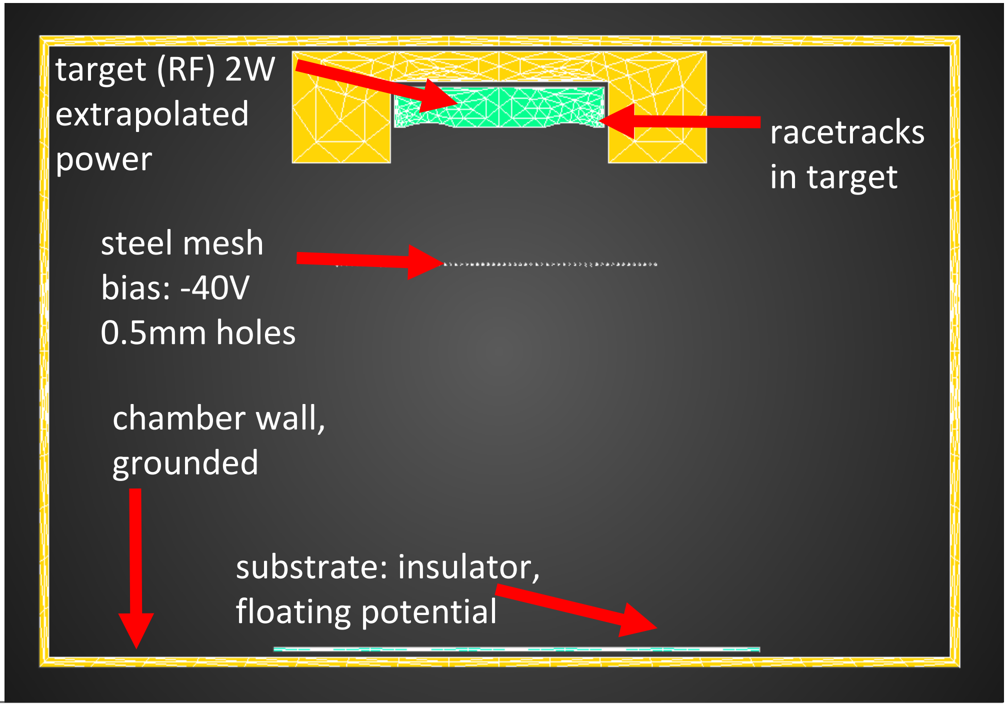
- Some limitation on mobility due to rough substrate

Outline

Monte Carlo Simulation of the sputtering process

- Analysis of energetic particles inside the plasma for the optimization growth process
- 2-dimensional CAD-model of sputtering chamber, Particle-In-Cell Monte Carlo-Calculation on TFD-Linux-Cluster
- Example: How does introduction of neg. biased mesh influence O- ions during sputtering?

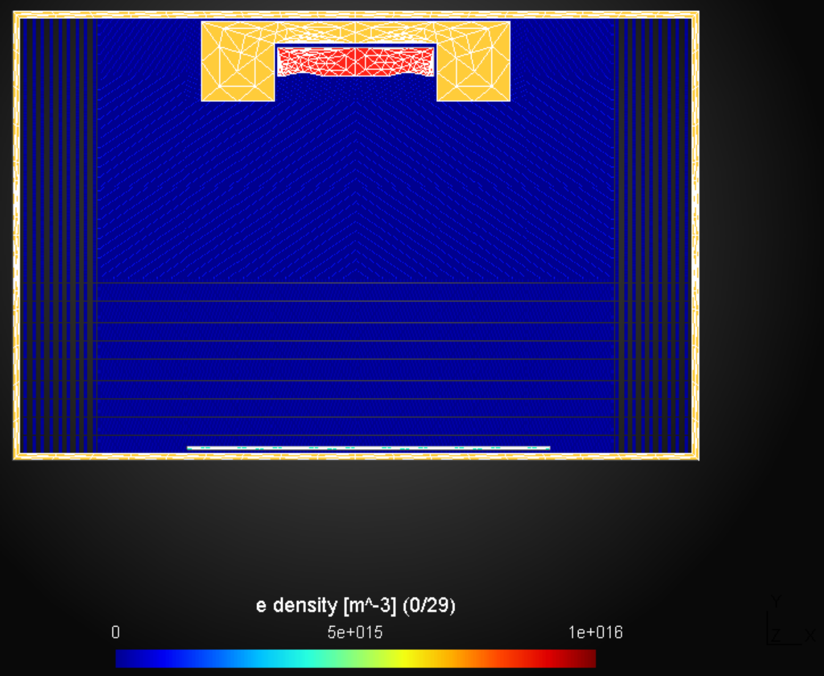


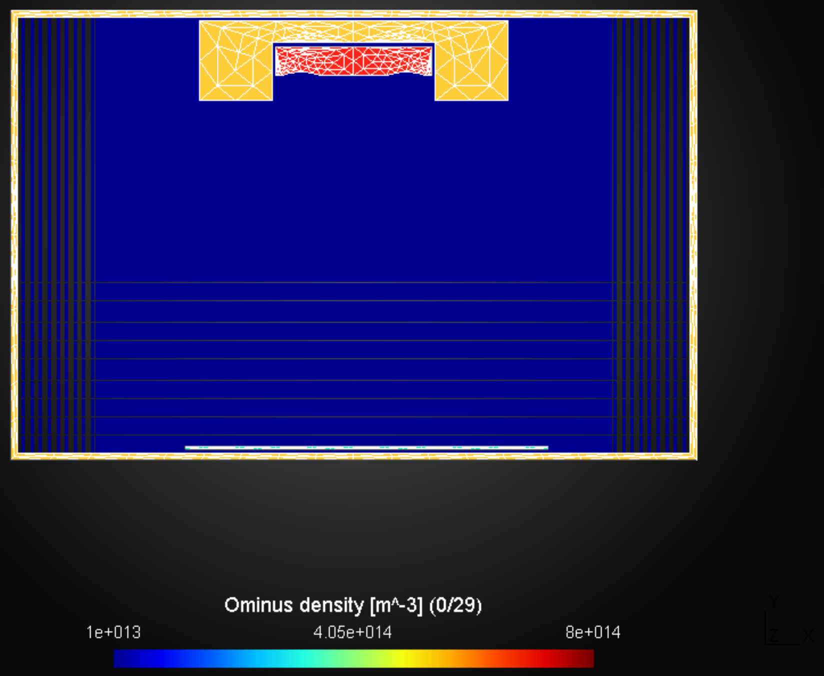


A. Pflug et al., SCT 260 (2014) 411

Monte Carlo Simulation of the sputtering process

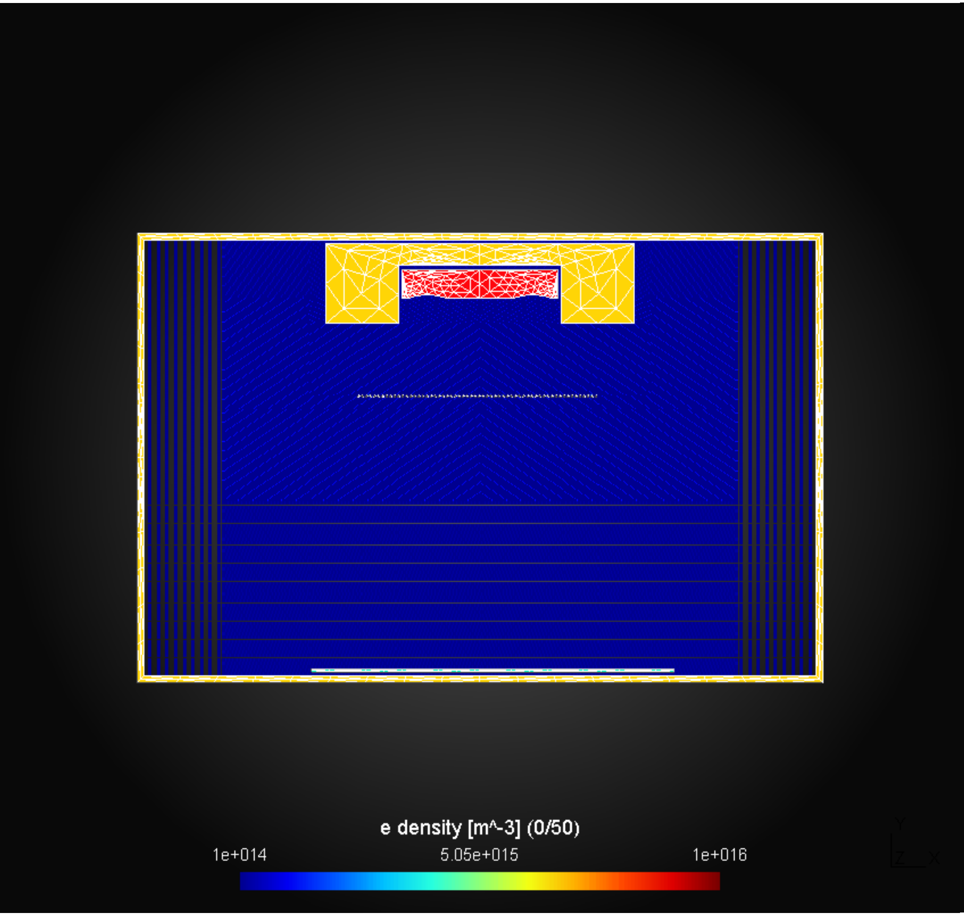
- Plasma ignition process is shown
- O- Ions are generated at target surface
- O- Ions are accelerated towards substrate (Energy: ~ 150 eV) and damage the growing film

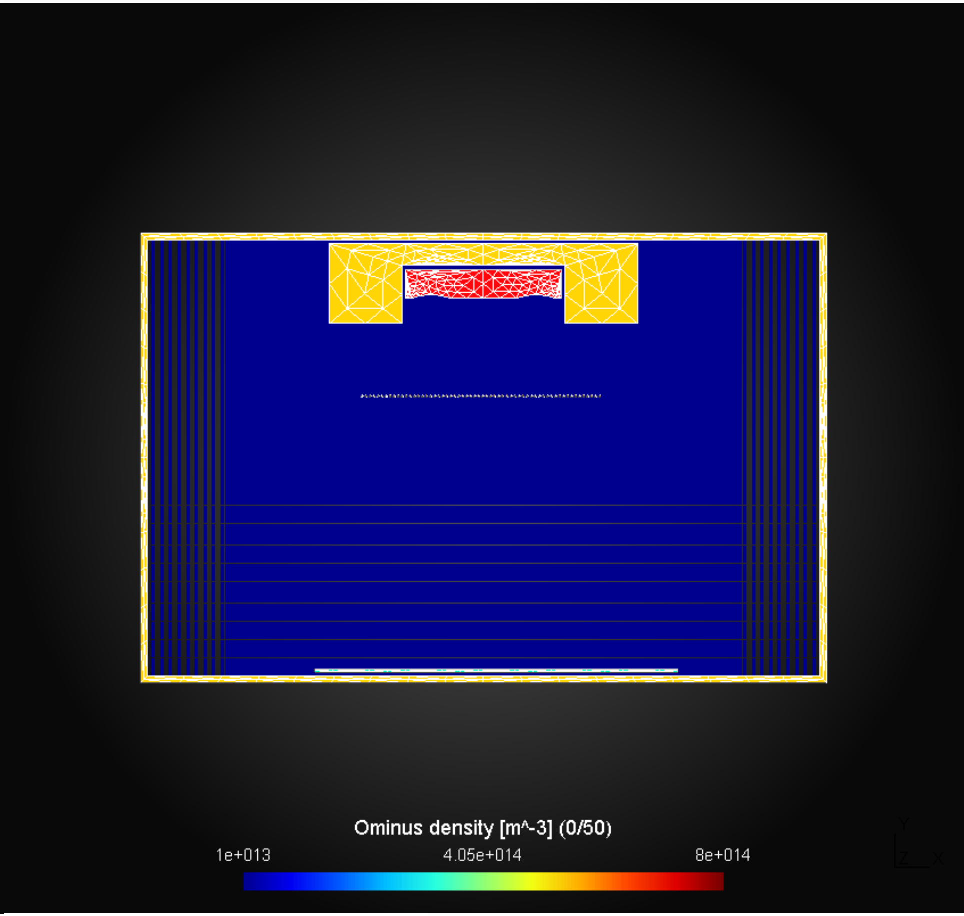




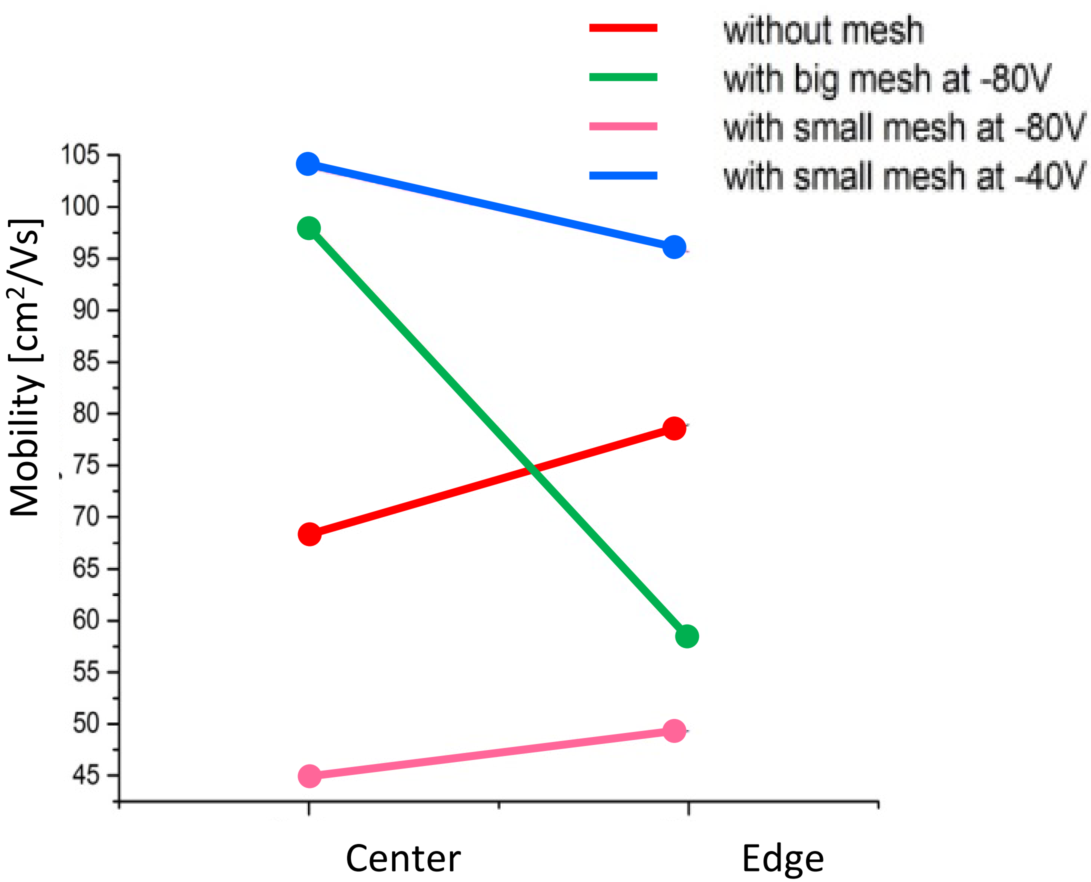
Monte Carlo Simulation of the sputtering process

- Mesh @ -40V, 0.5 mm holes
- O- Ions are decelerated by mesh
- Mesh decreased O^- density by factor 4
- Better growth conditions for TCO





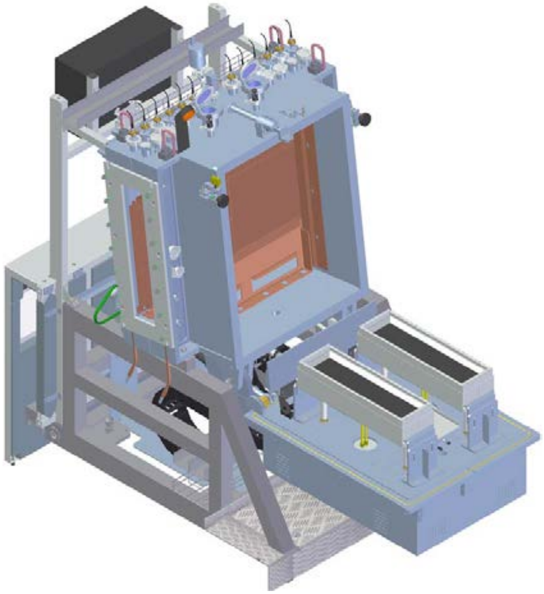
IOH results
(post annealed, on glass)



- Plasma damage due to fast O- ions has been reduced due to introduction of biased grid. Ref. ZnO: Yasui
- More homogenous IOH has been grown.
- Results still preliminary.
- However: Indication for need for soft growth conditions is clear, e. g.:
  - Hollow cathode GFS
  - RF-DC MS
  - MW enhanced MS
  - Low-voltage DC MS

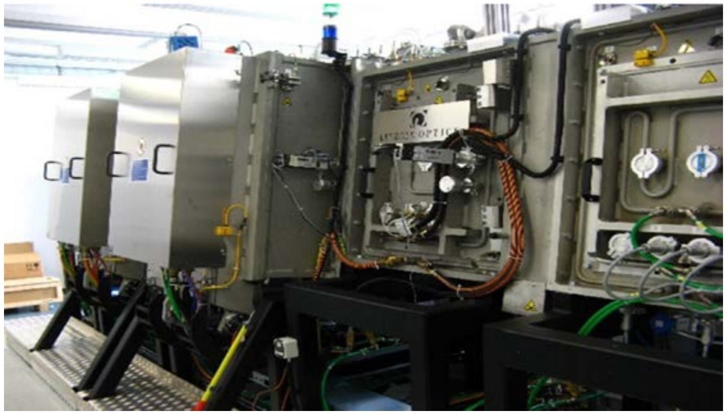
A. Hafez, Master Thesis TU Berlin, 2014 | K. Yasui et al. MSE-B 148 (2008) 26

Ongoing up-scaling: In-line coater Leybold Optics in-line coater A600V7- „LOS-1“

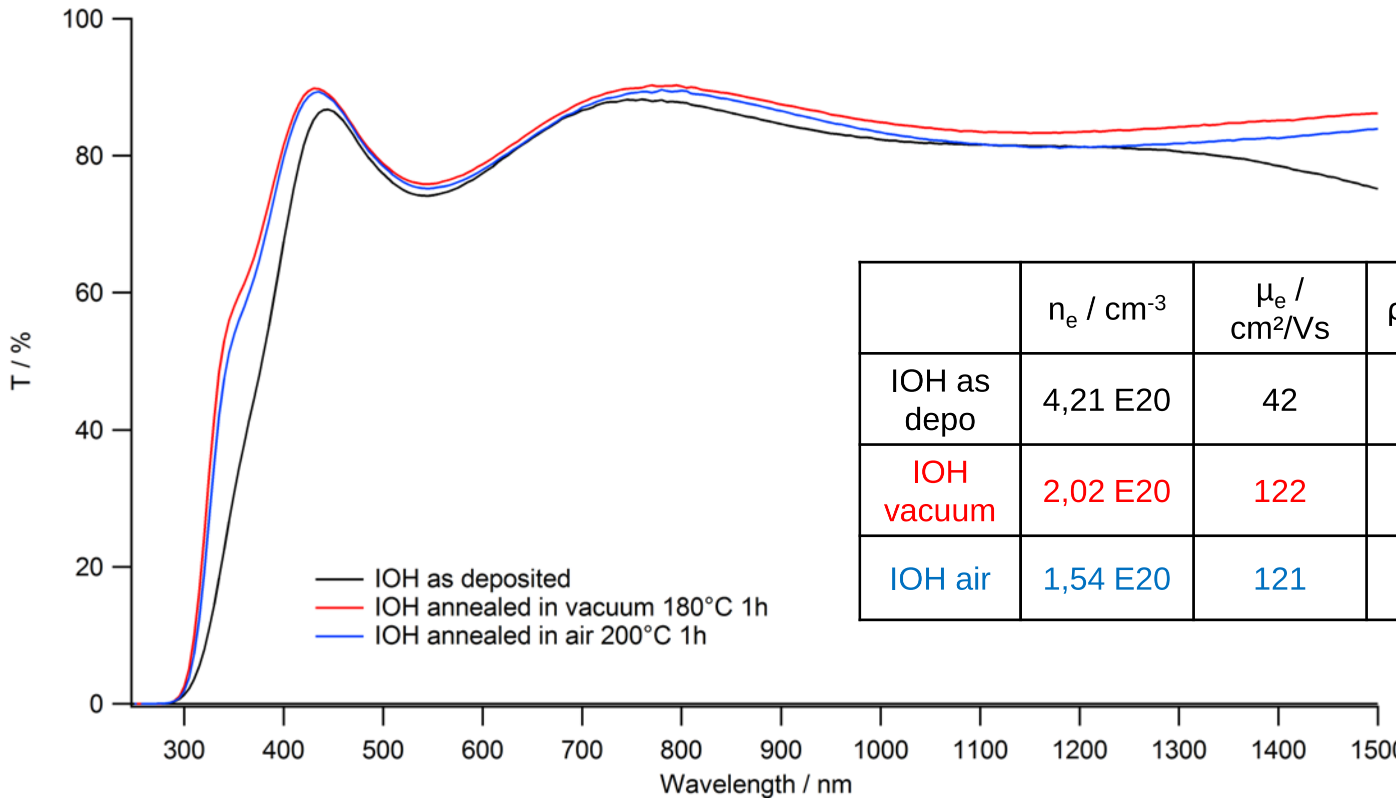


- Vertical in-line coater, 7 ° concept
- Substrate dimension 300 x 300 mm^2
- 600 mm target length (rotatable and planar magnetron sputter modules)
- Substrate temperature up to 300 °C
- DC, DC bipolar pulsed
- Serial co-sputtering

- IOH: Planar target DC magnetron sputtering



Ongoing up-scaling: Vertical in-line DC pulse magnetron sputtering of IOH

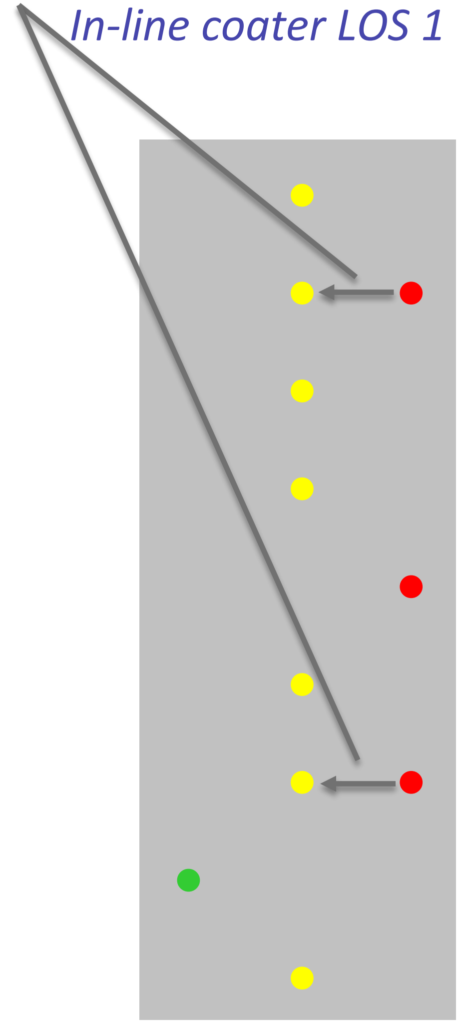


	n_e / cm^{-3}	μ_e / cm^2/Vs	ρ / µΩcm
IOH as depo	4,21 E20	42	355
IOH vacuum	2,02 E20	122	254
IOH air	1,54 E20	121	335

D. Erfurt, details to be presented at the upcoming TCM in Crete

IOH from a production viewpoint

Planar InOx target DC sputtering
In-line coater LOS 1



1.) Layer stack with proper functionality

2.) Sputter source

3.) Depostion process

4.) Substrate pretreatment / cleaning

5.) Proof of concept for scaling & long term issues

6.) Cost analysis

7.) Production coater

8.) Quality control

9.) Production chain integration

G. Bräuer, Oberflächenbeschichtung: Beschreibung von Produktionsprozessen, 2002