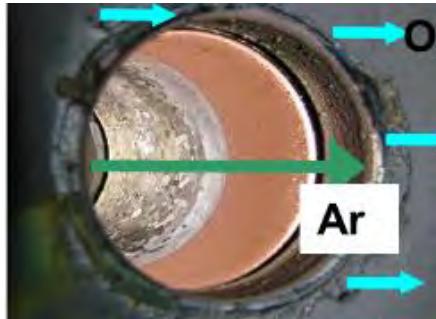


Material und Prozessinnovationen in der industriellen Schicht- und Oberflächentechnik für die kostengünstige Bereitstellung erneuerbarer Energien

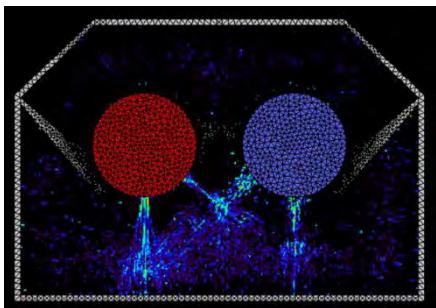


Bernd Szyszka

TU Berlin und PVcomB



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Tel.: +49 160 90672689



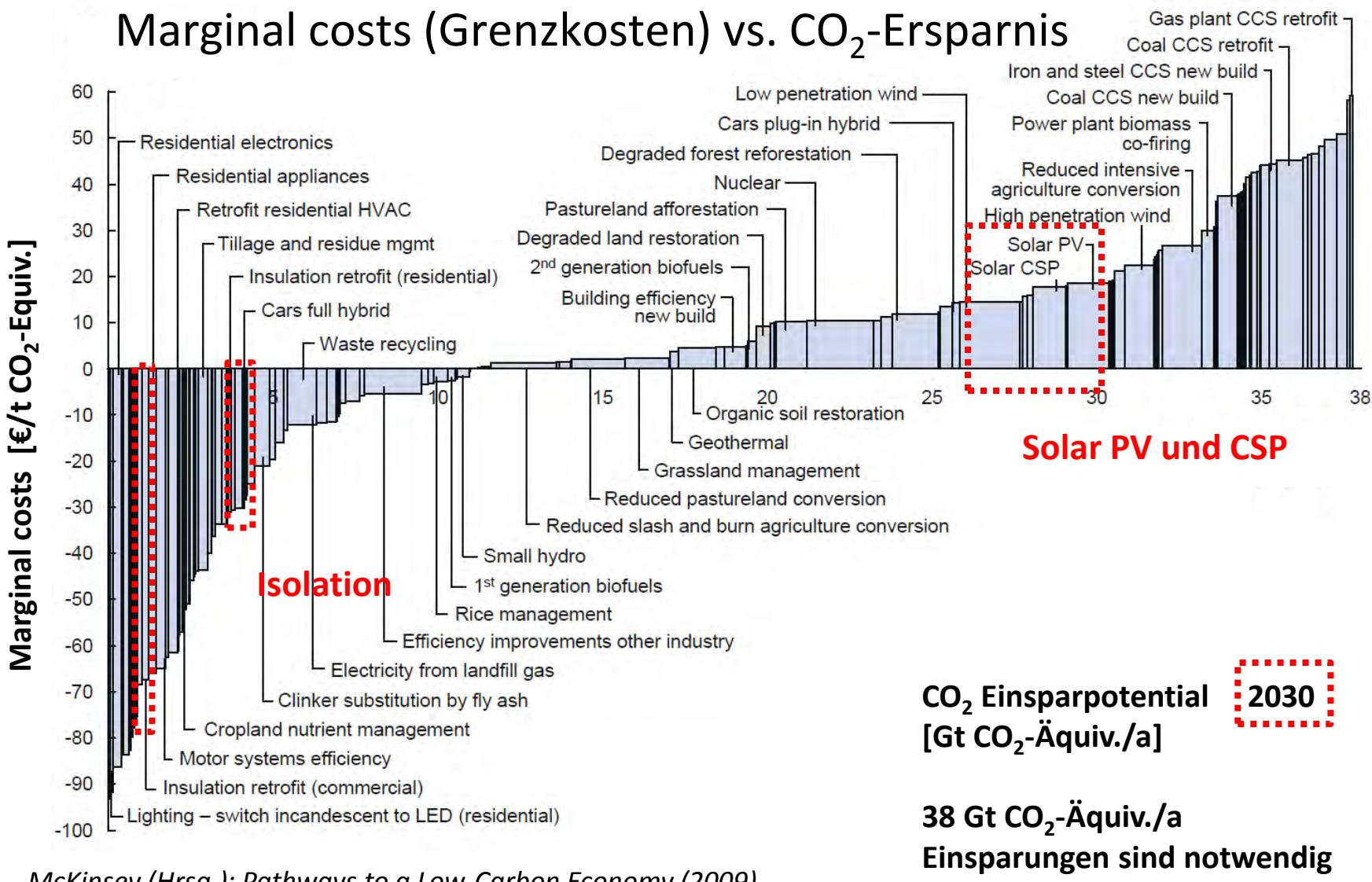
Oben: Hohlkatoden-Gasflusssputtern | Mitte: OPV Slot Dye Coating | Unten: Modellbasierte Prozessentwicklung

Gliederung

- 1 Einleitung
 - Erneuerbare Energien und Beschichtungstechnik
 - Einige Fakten
- 2 Technologien
 - Nanokomposite mittels Gasflusssputtern und ALD
 - Organische Photovoltaik
 - CVD vs. PECVD
 - Multiskalen-Modellierung
- 3 TU Berlin und PVcomB
 - Konzepte & Technologien
- 4 Zusammenfassung & Ausblick

1 Maßnahmen zur Verminderung der CO₂-Emission

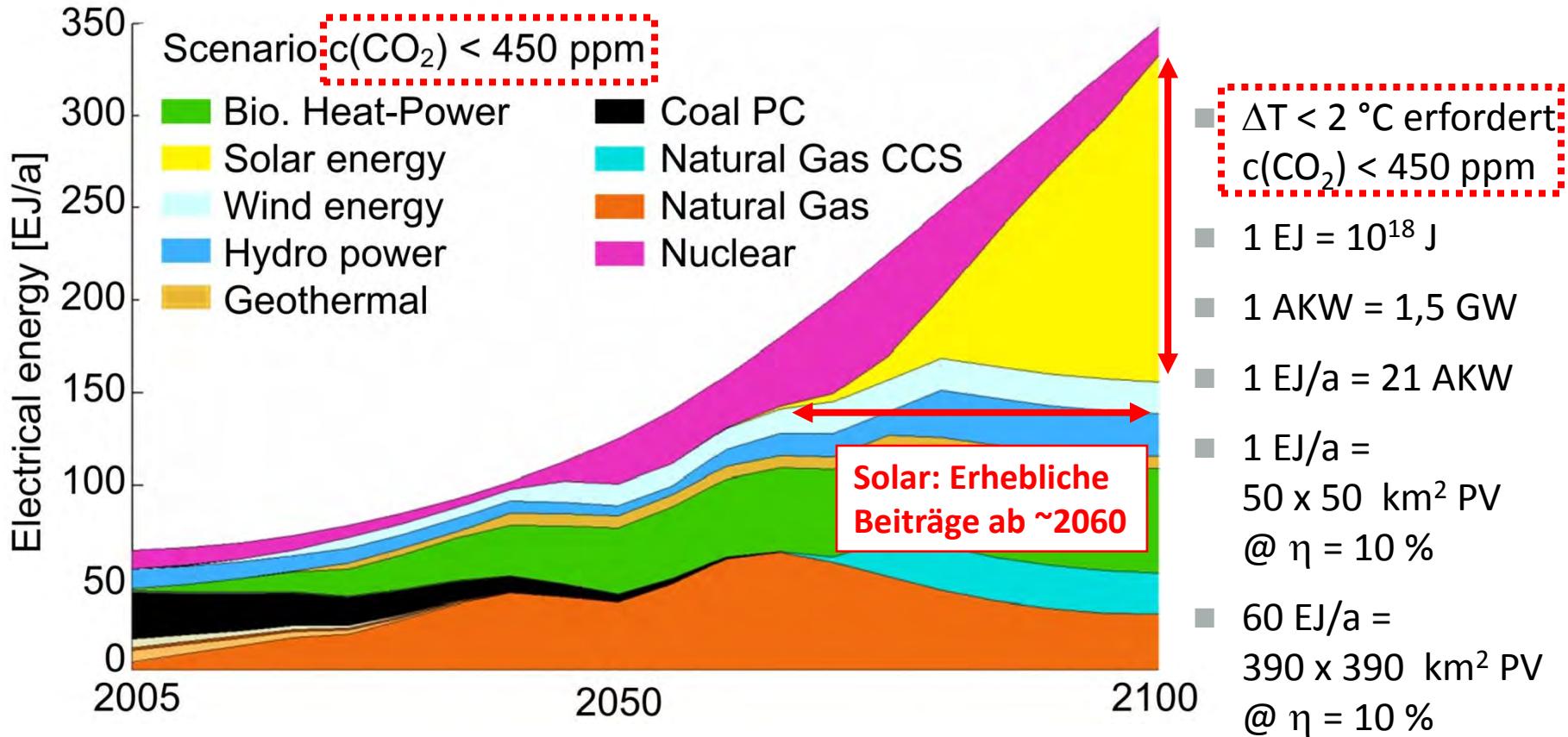
Marginal costs (Grenzkosten) vs. CO₂-Ersparnis



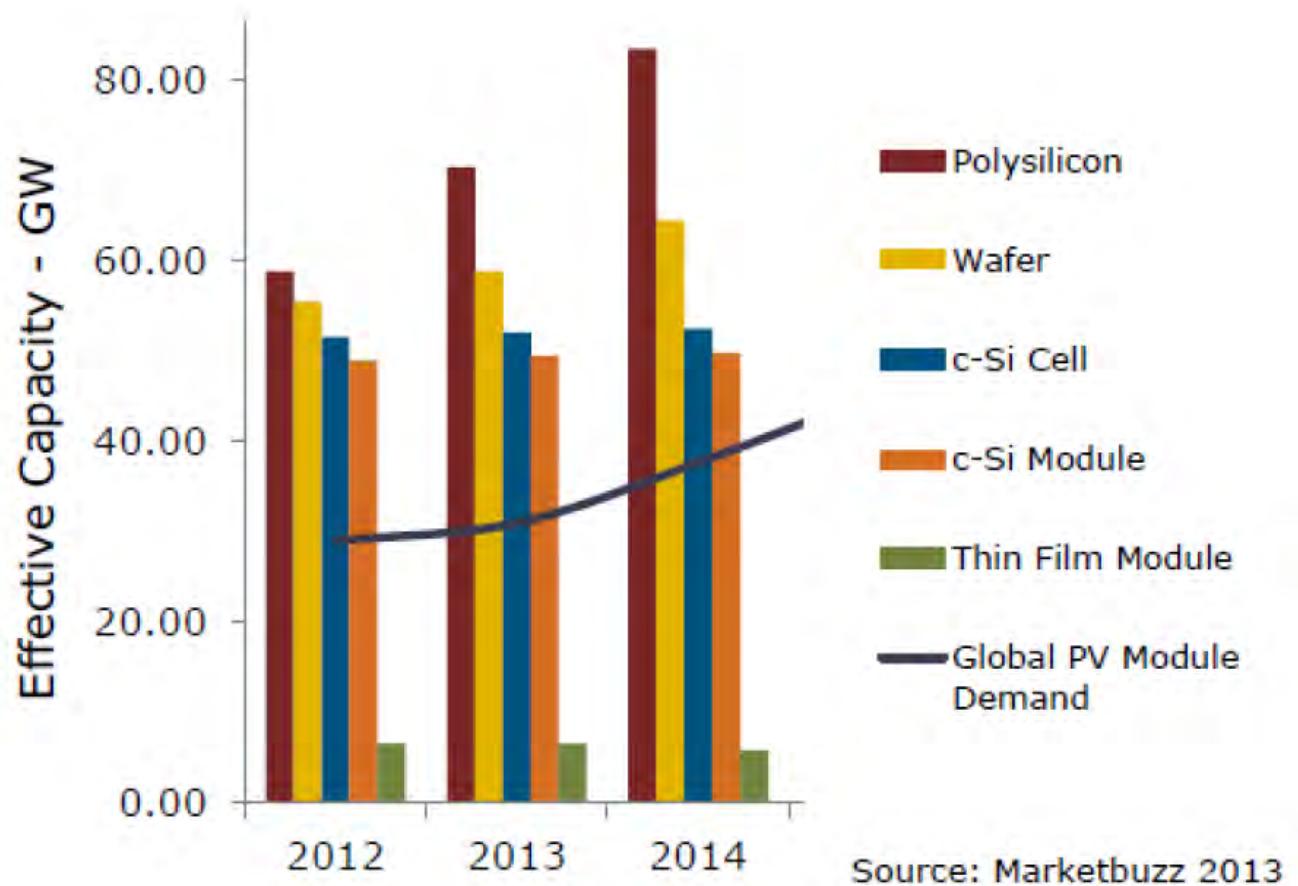
McKinsey (Hrsg.): Pathways to a Low-Carbon Economy (2009)

1 Entwicklung des weltweiten Bedarfs an elektrischer Energie

Szenario für $c(\text{O}_2) < 450 \text{ ppm}$ | $\Delta T < 2^\circ\text{C}$ | Reduktion AKWs



1 PV Überkapazität – Produktionskapazität vs. Installationen



- Immer noch deutliche Überkapazität, daher schlechtes Investitionsklima

F. Wessendorf (VDMA), 5. Thin Film Week 2013

1 Preisentwicklung am Spot-Markt

• PV Spot Prices

	Q1-11	Q1-12	Q1-13	
Residential systems, Germany (\$/W)	3.5	2.7 (-23% YoY)	2.1 (-22% YoY)	1,61 €/W
a-Si modules (\$/W)	1.15	0.73 (-37% YoY)	0.50 (-32% YoY)	0,38 €/W
c-Si modules (\$/W)	1.58	0.87 (-45% YoY)	0.66 (-24% YoY)	0,50 €/W
Cells (\$/W)	1.20	0.50 (-58% YoY)	0.36 (-28% YoY)	0,28 €/W
Wafers (\$/W)	0.89	0.33 (-63% YoY)	0.21 (-36% YoY)	0,16 €/W
Polysilicon (\$/kg)	79	28 (-65% YoY)	17 (-39% YoY)	13 €/kg

- Extremer Kostendruck!
- Spot-Preis für a-Si Module in der Größenordnung bzw. unterhalb der Herstellungskosten
 - Vgl. Prognose von Tokyo Elektron in 2012: Produktion in China für 0,35 €/Wp
Produkt: Mikromorphe Module, 154 W_p, entsprechend $\eta = 10,8\%$
 - Hiesige Hersteller sind von diesen Kosten weit entfernt!

S. de Haan, 5. Thin Film Week April 2013 | T. Eisenhammer, IWTSSC-4, März 2012

1 Kostenlage bei der Herstellung von CIS Solarzellen

Abschätzung 180 MWp Fab, Grenzebach, Standort D

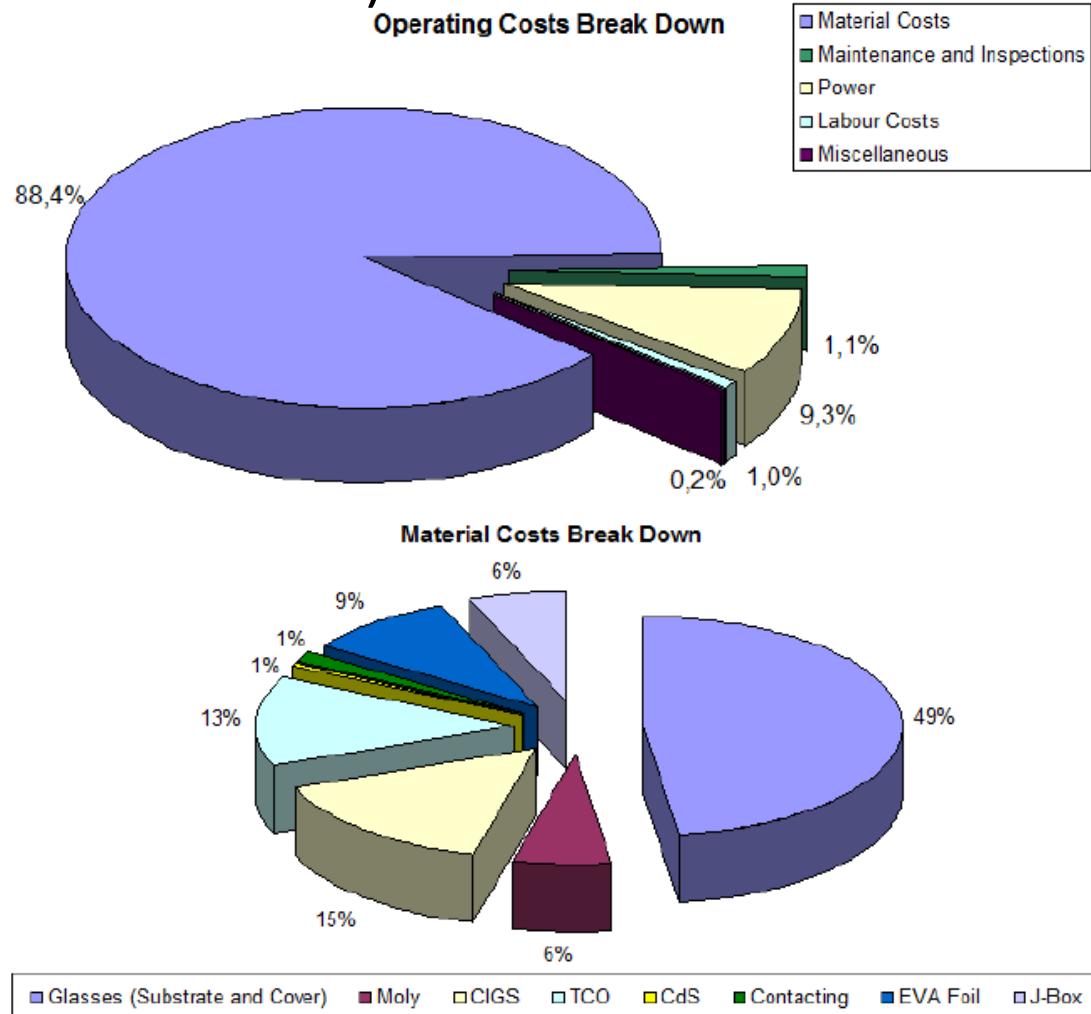
- 180 MWp Fab für
185 Mio € Invest
- 113 Mio €/a
Betriebskosten
- $\eta = 12\%$, 270 W
Module
- Abschreibung 7 a
- TOC: 0,78 €/W_p
- Zellaufbau:
G / Mo (400 nm) /
CIGS (1,9 μm) /
CdS (50 nm) /
i-ZnO (50 nm)
ZnO:Al (1000 nm)

Total Cost of Ownership						
regarding VDMA norm 34160						
Project Number		0				
Project Version		0				
Summary Total Cost of Ownership						
E	Costing Setup	184.965.245 €	0 €	184.965.245 €	184.965.245 €	Details
E1	Purchasing	169.215.245 €		169.215.245 €		
E2	Infrastructure	15.750.000 €		15.750.000 €		
E3	Miscellaneous	0 €		0 €		
B	Operating Costs Duration	791.530.008 €	0 €	791.530.008 €	791.530.008 €	
B1	Operating Costs / Year	113.075.715 €	0 €	113.075.715 €		
	IH1 Maintenance and Inspections	632.592 €		632.592 €		
	IH2 Scheduled Repairs	443.087 €		443.087 €		
	IH3 Unscheduled Repairs	206.187 €		206.187 €		
	RK1 Occupancy Costs	278.588 €		278.588 €		
	MK1 Material Costs	68.810.847 €		68.810.847 €		
	EK1 Costs for Electric Power	20.553.396 €		20.553.396 €		
	EK2 Costs for Compressed Air	963.434 €		963.434 €		
	HB1 Operating Supplies	72.270 €		72.270 €		
	EN1 Disposal Costs	1.051 €		1.051 €		
	PK1 Personnel Costs	21.107.921 €		21.107.921 €		
	WK1 Tooling Costs	6.342 €		6.342 €		
	RU1 Set-up Costs	0 €		0 €		
	LK1 Storage Costs	0 €		0 €		
	SO1 Miscellaneous	0 €		0 €		
V	Elimination	4.171.636 €	0 €	4.171.636 €	4.171.636 €	
V1	Dismantling	5.493.630 €		5.493.630 €		
V2	Declining Balance	-1.321.994 €		-1.321.994 €		
V3	Miscellaneous	0 €		0 €		
	Total Cost of Ownership					
	Total Cost of Ownership / Watt					0,7783 € / Watt

E. Wenninger (Grenzebach), Otti Glas und Solar 2011

1 Aufteilung der Betriebskosten (welche 81 % der TCO ausmachen)

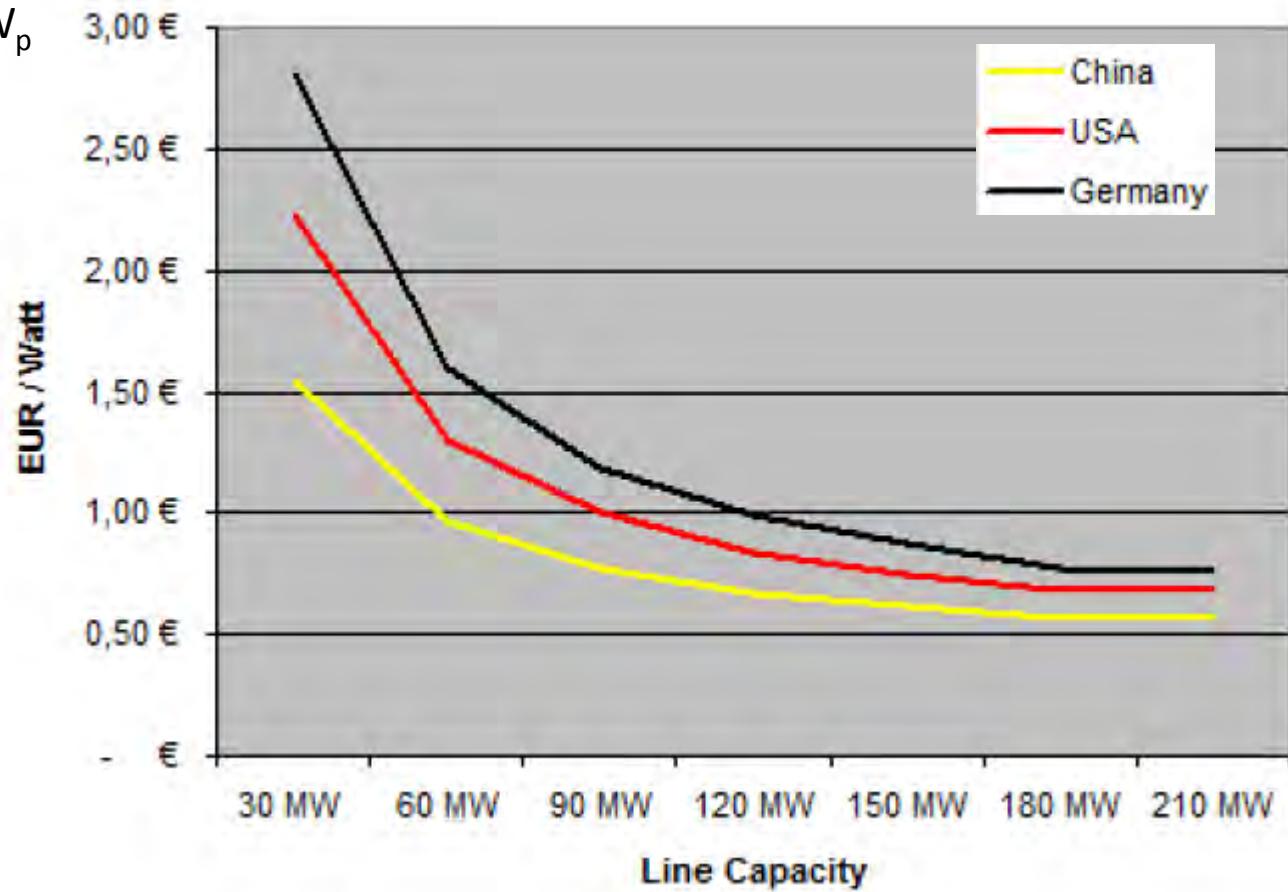
- Die Materialkosten sind der bei weitem größte Kostenfaktor
- Und von den Materialien trägt Glas ganz wesentlich bei!
- Die Kosten für CIS & CdS (16 %) sind niedriger als die Kosten für TCO & Mo (19 %)



E. Wenninger (Grenzebach), Otti Glas und Solar 2011

1 Standortvergleich und Skaleneffekte

- Kapazität > 100 MW_p anzustreben
- Ca. 20 % Kostenvorteil bei Fertigung in China gegenüber Deutschland



E. Wenninger (Grenzebach), Otti Glas und Solar 2011

1 Investitionskosten vs. Betriebskosten

für einen Betrieb der Anlage über 7 Jahre

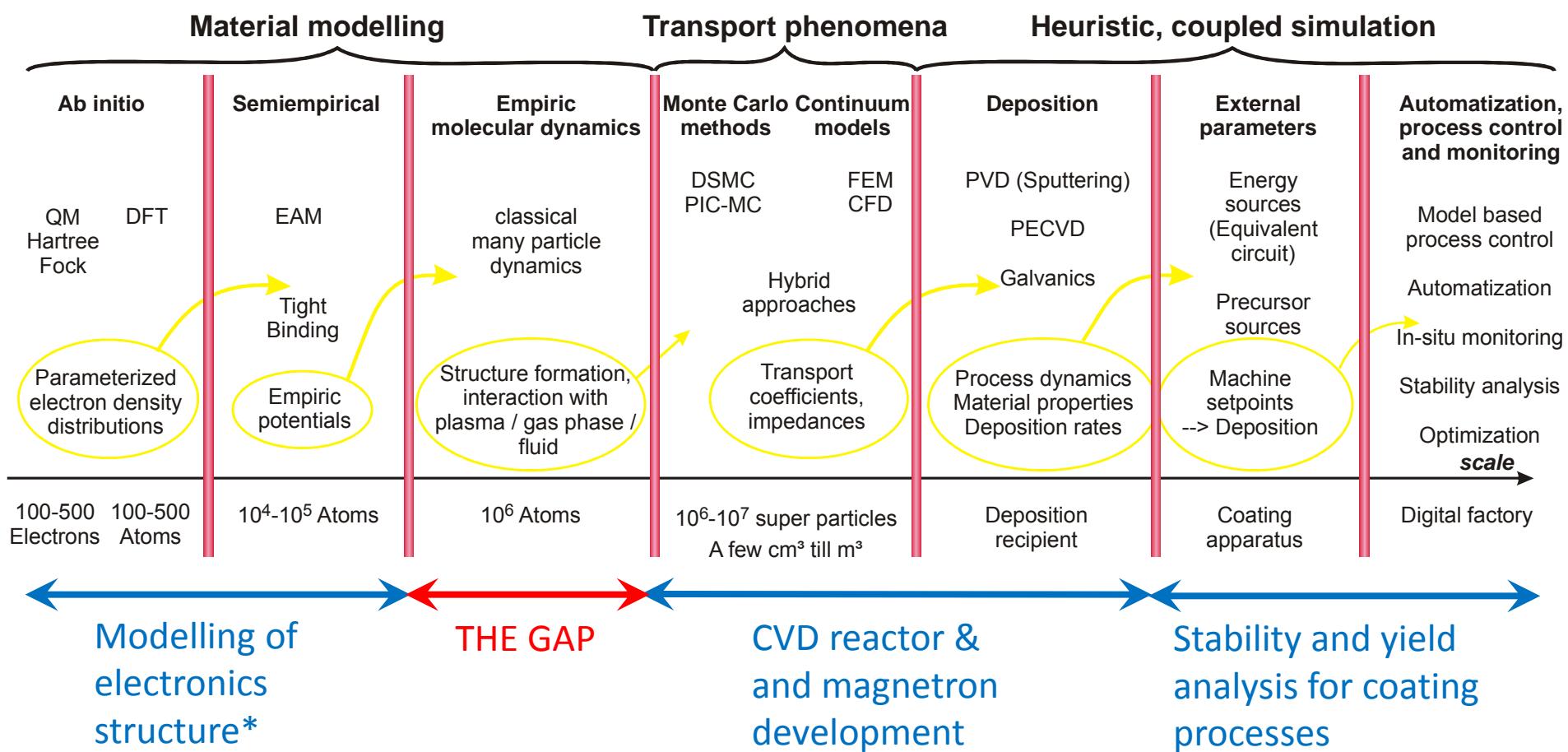
- Investitionskosten: 185 Mio €
- Betriebskosten: 791 Mio €
- Konsequenz für TCO:
0,775 € / Wp
mit 19 % Anteil Investitionskosten
und 81 % Anteil Betriebskosten

- Konsequenz:
 - Geringer Impact bei Substitution bestehender Beschichtungslösungen (Hochvakuumtechnik) durch kostengünstigere Lösungen (Atmosphärendruckbeschichtung)
 - Starker Impact für: (i) Wirkungsgradsteigerung und (ii) Minimierung der Materialkosten, hier sind die Glaskosten ganz wesentlich

2 Technologie

- Modellierung
 - Multiskalen-Modellierung für die digitale Fabrik
 - DFT / DSMC / PIC-MC Rechnungen
- Vakuumverfahren
 - MEGATRON™ Sputtern
 - Hohlkatoden-Gasflusssputtern
- Technologisch neue Ansätze
 - OPV Bandbeschichtung mittels Slot Dye Coating

2.1 Model based development: Filling the gap from 1st principle DFT modeling up to the digital factory

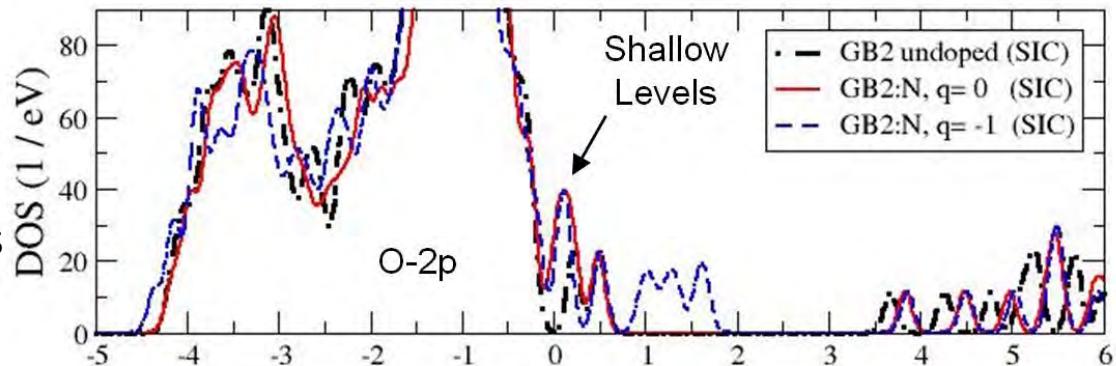


K. Roths et al., *Forschungsagenda Oberfläche*, DFO Service 2006, ISBN-10: 3834912301

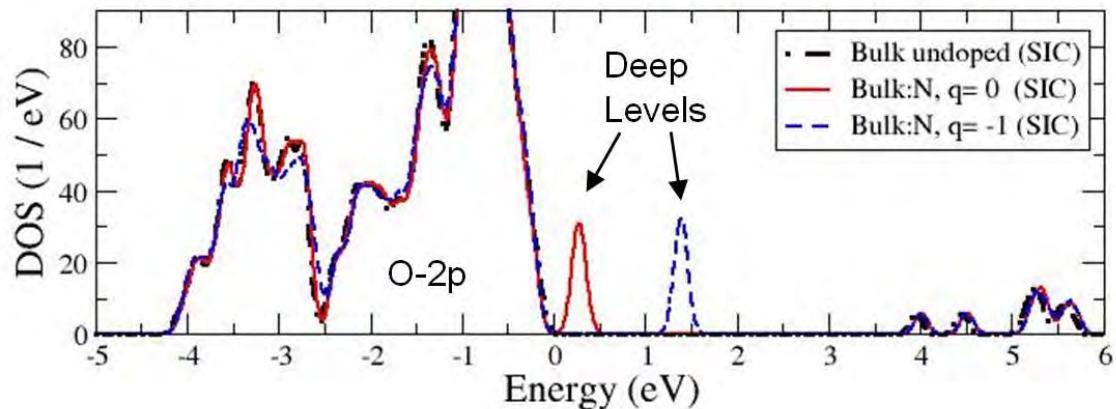
* W. Körner, C. Elsässer, *Physical Review B* 81 (2010) 85324

2.1 Beispiel: Diskussion grundlegender Materialfragen mittels Density-Functional-Theory (DFT): Zustandsdichte ZnO:N

- Dotierung Korngrenzen
 - Flache Zustände nahe am Valenzband
 - Bilden Akzeptor-Niveaus aus



- Dotierung Einkristall
 - N-Dotierung liefert tief liegende Zustände
 - Als Akzeptor-Niveaus ungeeignet



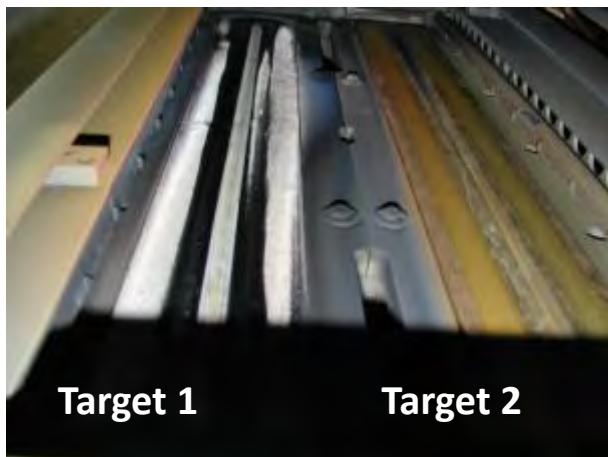
- Fazit: An experimentelle Daten (Bandlücke) angepasste DFT unter Einbeziehen von Defekten (Korngrenzen) als praktisches Werkzeug für das Materialdesign!

B. Szyszka et al., *Thin Solid Films* 518 (2010) 3109

2.1 Exp. to model: 2D Simulation of a magnetron discharge

Geometric decomposition of a reactor chamber

Empirical geometry



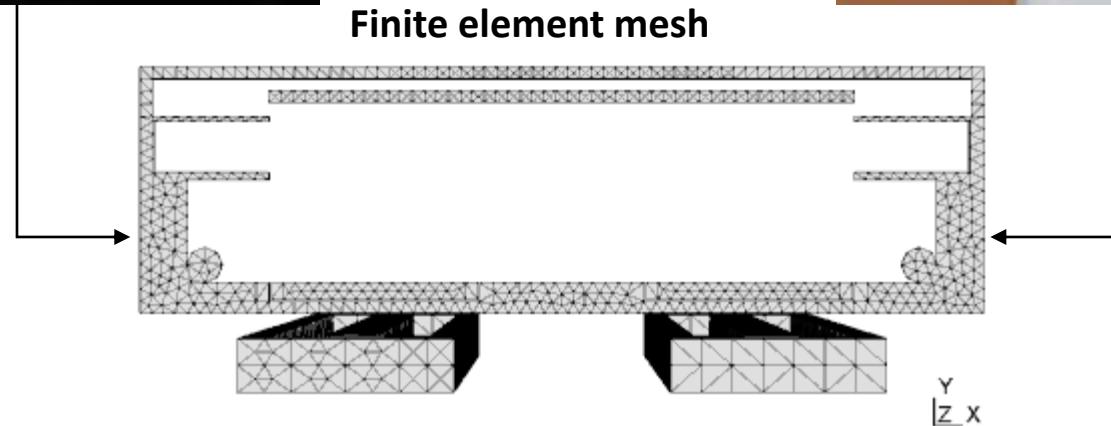
CAD drawing (file format: IGES, STEP, etc...)



Available as...

Finite element mesh

Abstraction
with GMSH



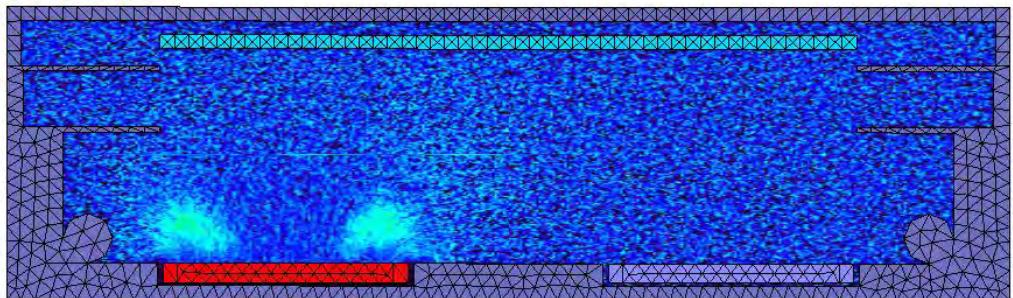
A. Pflug et al., Proc. SVC 52 (2009) 364

2.1 2D Simulation of magnetron discharges

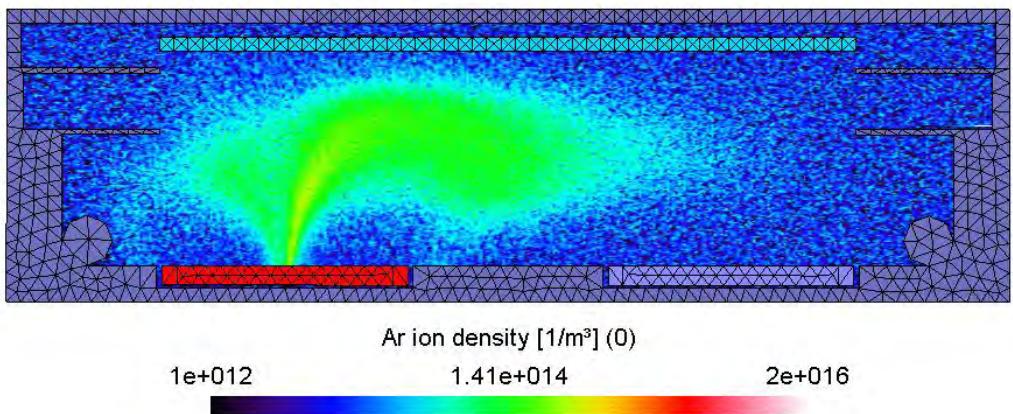
Difference between DC and pulsed mode

- Features in RF mode different to DC mode
 - Plasma density in bulk significantly increased
 - Strongly enlarged positive plasma potential
 - Ar⁺ / O₂⁺ ions escape in every direction
 - High ion flux and ion energy on substrate

DC power, 1.0 Pa, 50 W/m, 40 % O₂ in Ar



RF power, 13.56 MHz



A. Pflug et al., Materials Technology 26 (2011) 10

2.2 Model -> Experiment: Serial Co-Sputtering

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 constraints.

💣 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

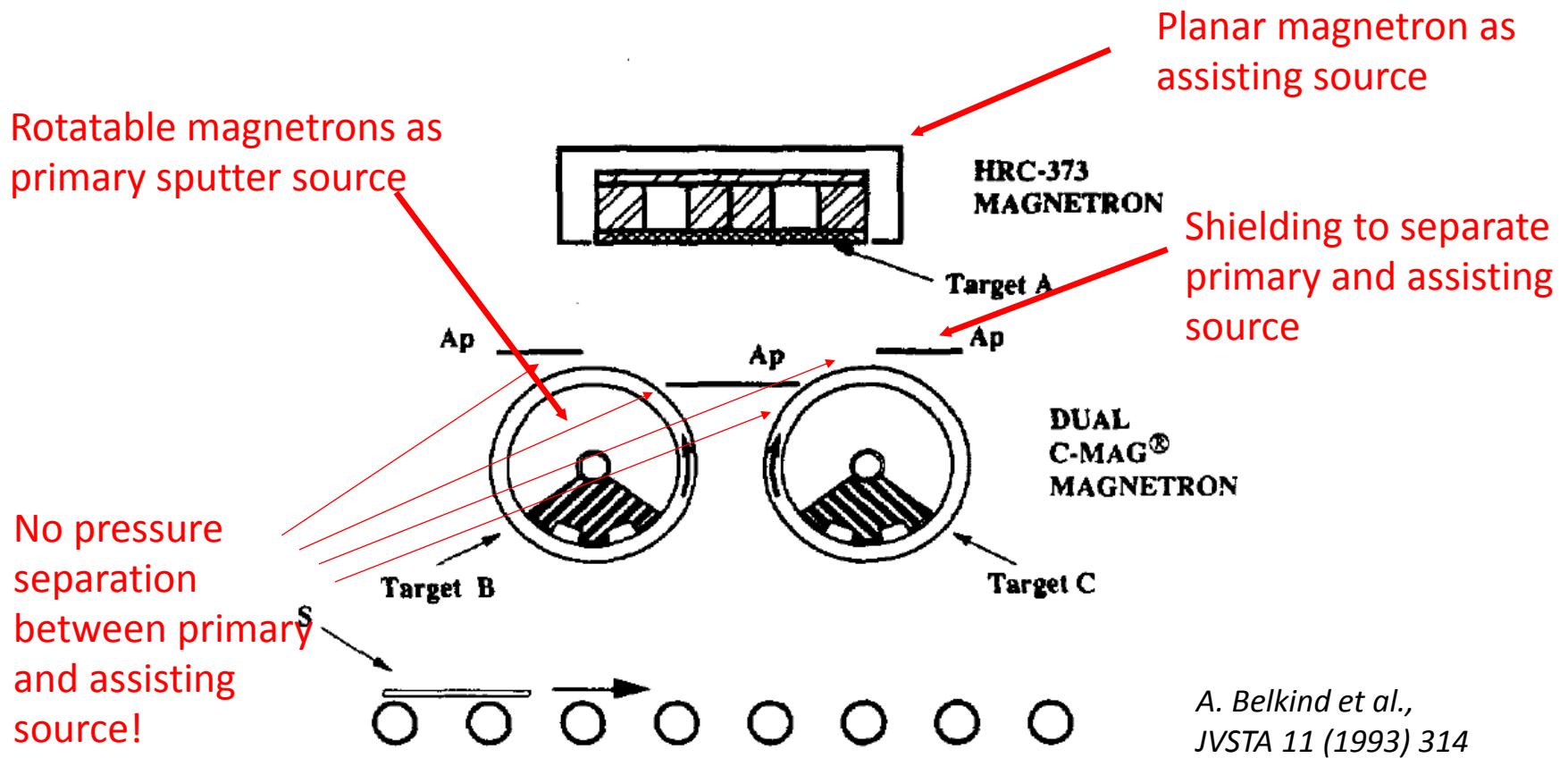
- Complex optical monitoring. Implementation! Maintenance!



Low sputter yield

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

2.2 A solution for these problems:

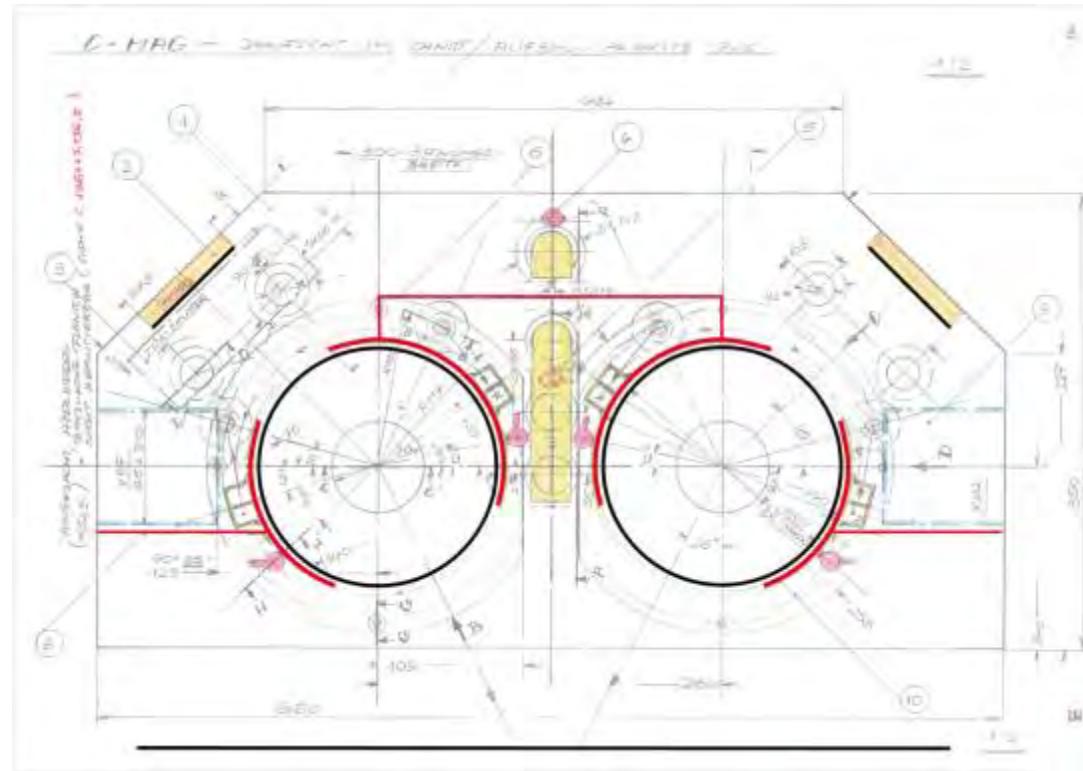


- Target composition of the primary target can be modified.
- Setup allows for sputter yield amplification for metallic targets.

2.2 Experimental realization of the MEGATRON™ process

Serial co-sputtering with pressure separation

$ZnO:Al$
 $SnZnO_x$
 $TiO_x:Nb$
 $In-Ga-Zn-O$
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 / Interpane

B. Szyszka et al. Cur. Appl. Phys. 12 (2012) S2 | EP1697555B1: Method and device for magnetron sputtering

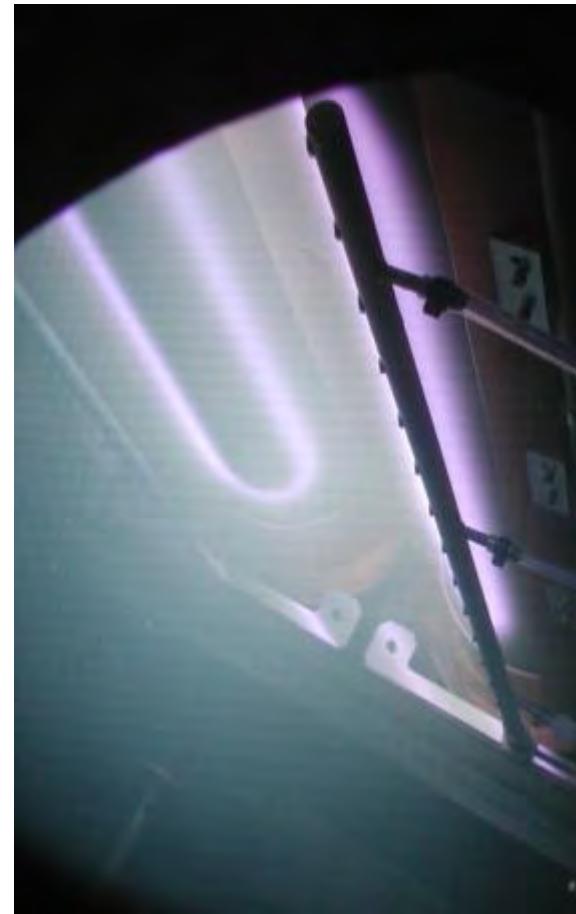
2.2 Experimental realization of the MEGATRON™ process

Serial co-sputtering with pressure separation

a) Serial co-sputtering source (model)



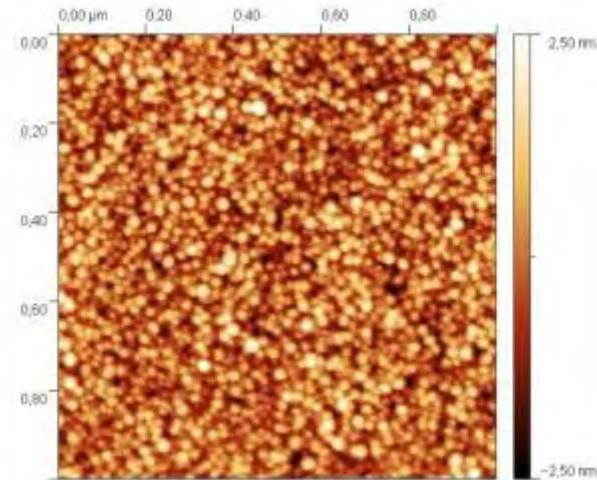
b) First plasma in June 2010



2.2 Example: Bi-doping of TiO₂

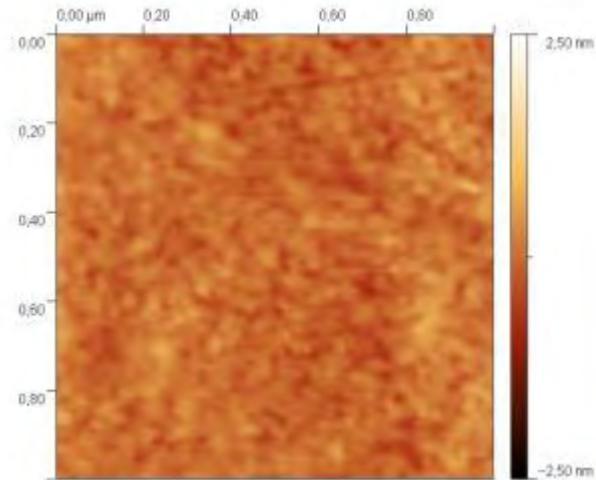
Improvement of morphology and enhancement of rate

a) TiO₂ @ 18.9 nm m/min



$R_q = 0.81 \text{ nm}$, $R_a = 0.65 \text{ nm}$
 $d = 210 \text{ nm}$

b) TiO₂:3.8 at.%Bi @ 29.4 nm m/min



$R_q = 0.21 \text{ nm}$, $R_a = 0.17 \text{ nm}$
 $d = 326 \text{ nm}$

- AFM reveals fine grain size for both films
- Substantial decrease of surface roughness for TiO₂:Bi
- TiO_x:BiO_x targets are not available due to metallurgical reasons

2.2 Summary MEGATRON™

Ferchau Innovation Price 2011

Rotatable magnetron sputter source for serial co-sputtering at Fraunhofer IST

- For the 1st time, we've realized a magnetron coating module based on DSMC gas flow simulation and PIC-MC plasma simulation.
- Shielding tube allows for proper gas separation & increase of ion energy.

Serial co-sputtering of TiO₂:Bi

- Ceramic TiO₂ tube sputtering: Rate enhancement by 35 % due to serial cosputtering using Bi.
- Deposition rate of 34.2 nm m/min @ 18 kW for TiO₂:Bi (corresponds to 90 kW for 3.75 m cathode): Increase of dep. rate by 35 %.
- Excellent film properties:
 - Improved smoothness due to Bi-doping
 - No change of optical properties (550 nm: $k < 2 \times 10^{-3}$, $n > 2.45$)
 - Dense films, glass like morphology, moderate stress (~ -200 MPa)

2.2 Summary MEGATRON™

Serial co-sputtering of TiO₂:W

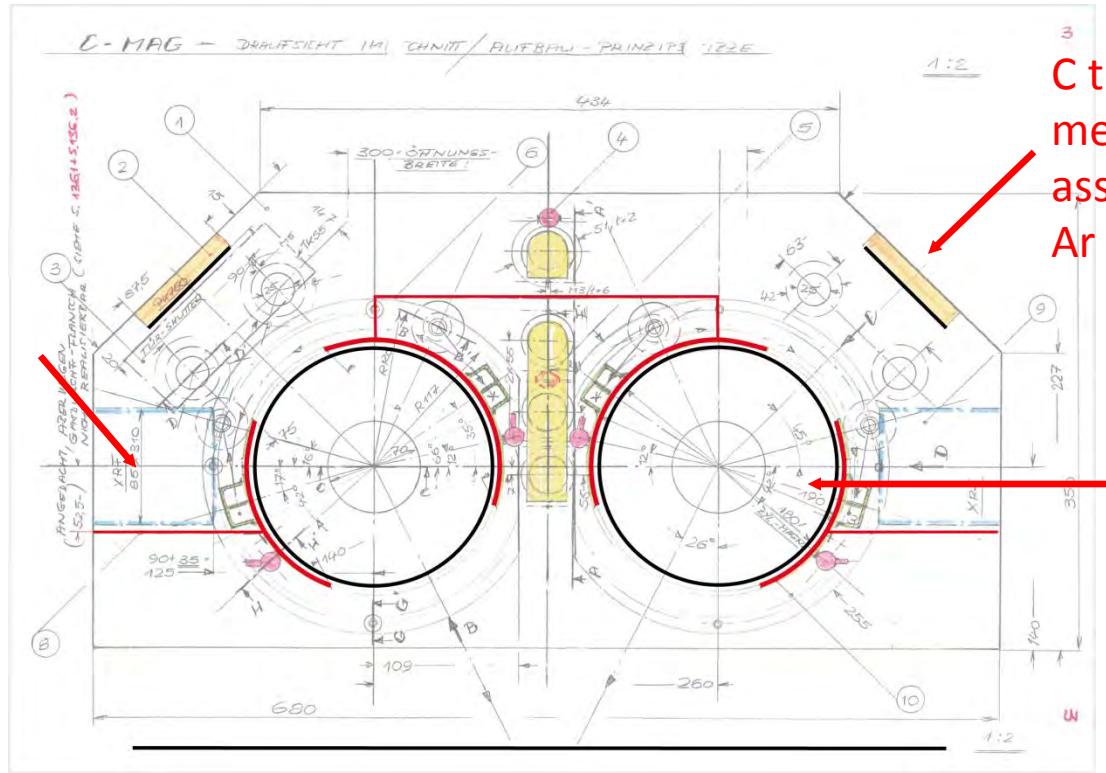
- Ceramic TiO₂ tube sputtering: Rate enhancement > 100 % due to serial cosputtering using W.
- Limit: Performance of the shielding: Onset of unwanted increase of p(O₂) at highest growth rate conditions.
- Deposition rate of 55 nm m/min achieved: Increase of dep. rate by 100 %.

Serial co-sputtering of TiO₂:Nb

- Pathway for the control of Nb-doting.
- Preliminary results: $\rho = 2100 \mu\Omega\text{cm}$ for 210 nm thick film after annealing at 350 °C for 1 h in vacuum (large grain size anatase film)

2.2 Outlook: Further operation modes of the MEGATRON

XRF unit for measurement of target stoichiometry

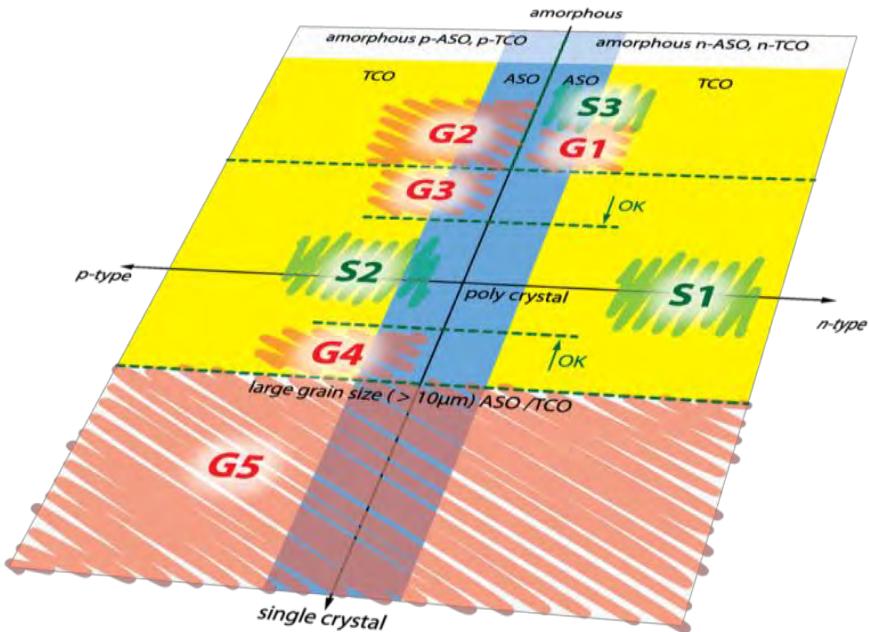


C tubes are metallized by assistant sources in Ar plasma.

C targets: Will produce only CO₂ in Ar / O₂

- XRF: Measurement of target stoichiometry @ known Bi metallization: Allows for calculation of deposition rate.
- C tubes: Metallization is oxidized at the substrate, transfer of the precision of Ar sputtering to oxide film growth, similar to Meta Mode.

2.2 Transparent conductive oxides



- Plasma damage in DC ceramic target TCO sputtering
- Rotatable target damage modeling
- Prevention of plasma damage by reactive deposition
- Prevention of plasma damage by RF superimposed DC deposition

ASO area



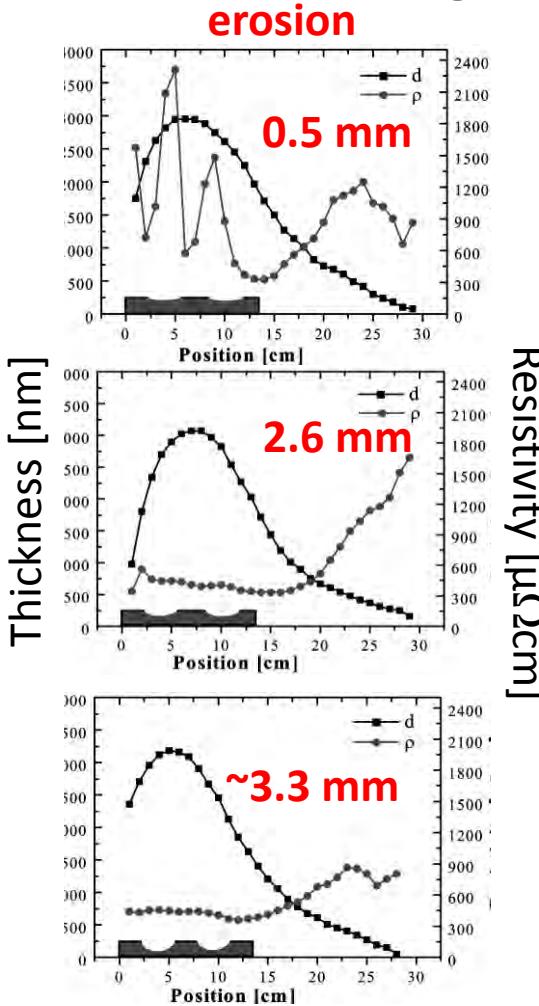
State of the art



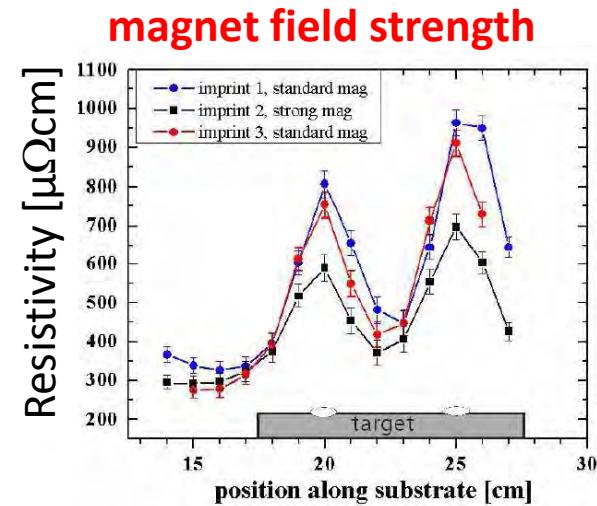
Orama research goals

2.2 Plasma damage and target erosion / magnetic field

Ceramic target ZnO:Al deposition, static deposition



- Resistivity increase at racetrack position
- High energy particles damage on the growing film
- Due to negative oxygen ions, which are accelerated in the cathode sheath
- Strong dependence on target erosion and discharge voltage
- Strong need for low impedance sputter processes
- In particular for rotatable magnetrons

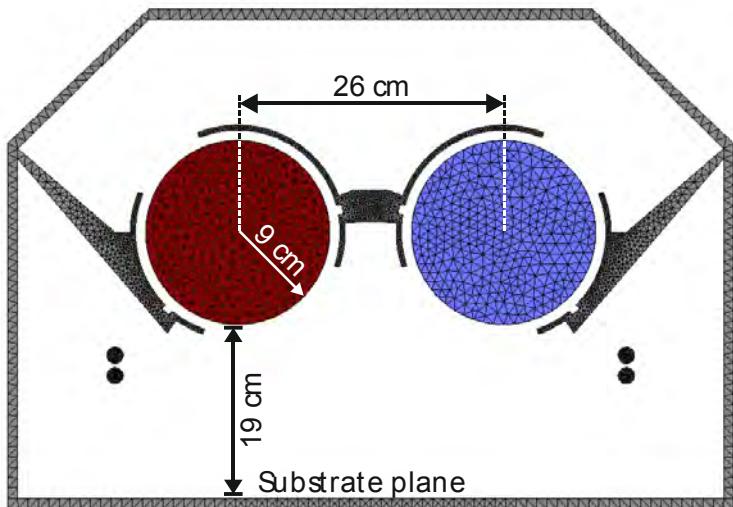


W. Dewald et al., Thin Solid Films 518 (2009) 1085 | W. Dewald et al., Proc. PVSEC 24 (2009) 2824

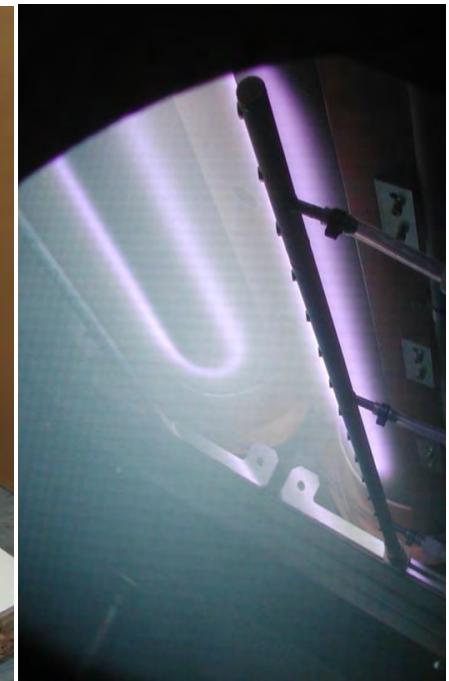
2.2 Modeling of TCO deposition process

Negative oxygen ion issue

- Model geometry



- Corresponding hardware (Fraunhofer IST)



2.2 Modeling of TCO deposition process

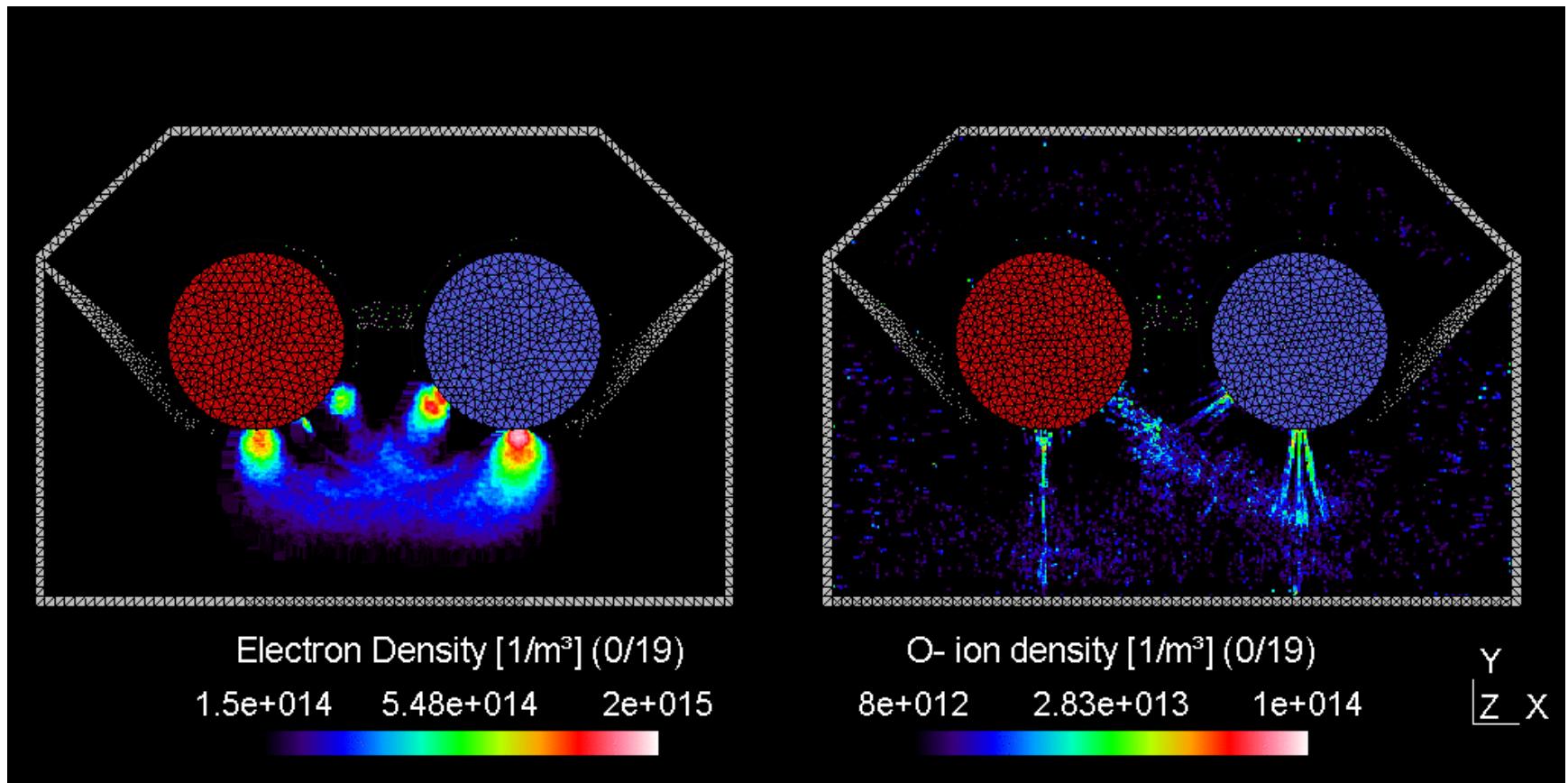
Model features

- Simplified plasma chemistry
 - Species: Ar, O₂, Ar⁺, O₂⁺, O₂⁻, O⁻, e⁻
 - Elastic collisions between electrons, ions and neutrals
 - Charge exchange collisions between ions and neutrals
- Negative O⁻ ions can be created at the target surface upon ion impact
- Parameters
 - Bipolar sine wave voltage ± 250 V, 100 kHz
 - Total pressure = 300 mPa
 - Time step = 10 ps
 - Total physical time interval = 60 μ s ($\rightarrow 6 \times 10^6$ PIC-MC iterations)

2.2 Modeling of TCO deposition process

Visualization of electrons and negative O⁻ ions

- 100 kHz sine wave, time interval between 50...60 µs shown



2.2 ZnSnO_x TCO Beschichtungsprozess

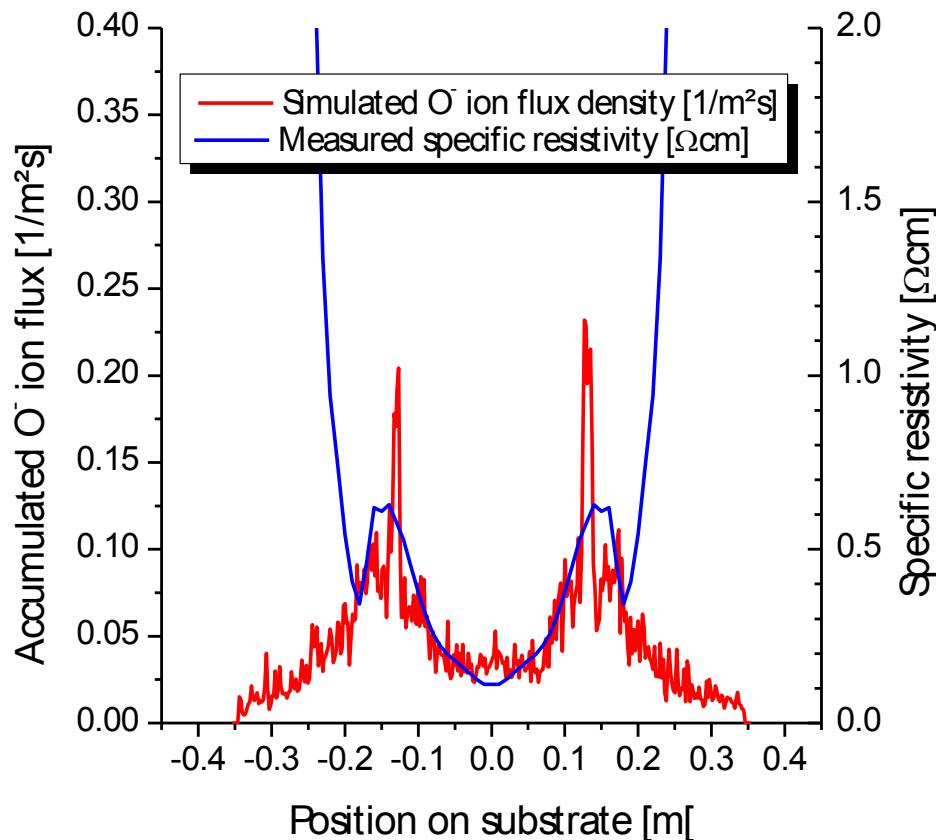
Widerstandsprofil vs. Modellierung des O⁻ Bombardements

■ Experiment:

- Widerstandsüberhöhung vor den Racetracks.

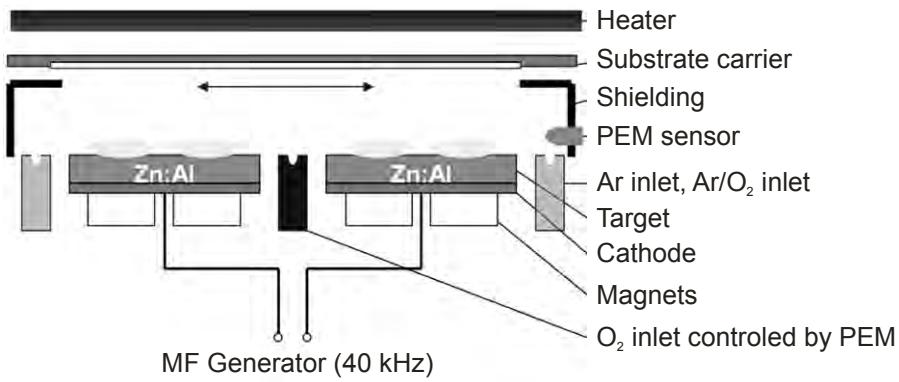
■ Simulation:

- Modellierung der negativen Sauerstoffionen (Erzeugung, Beschleunigung, Transport, Teilchenstrombilanz am Substrat)

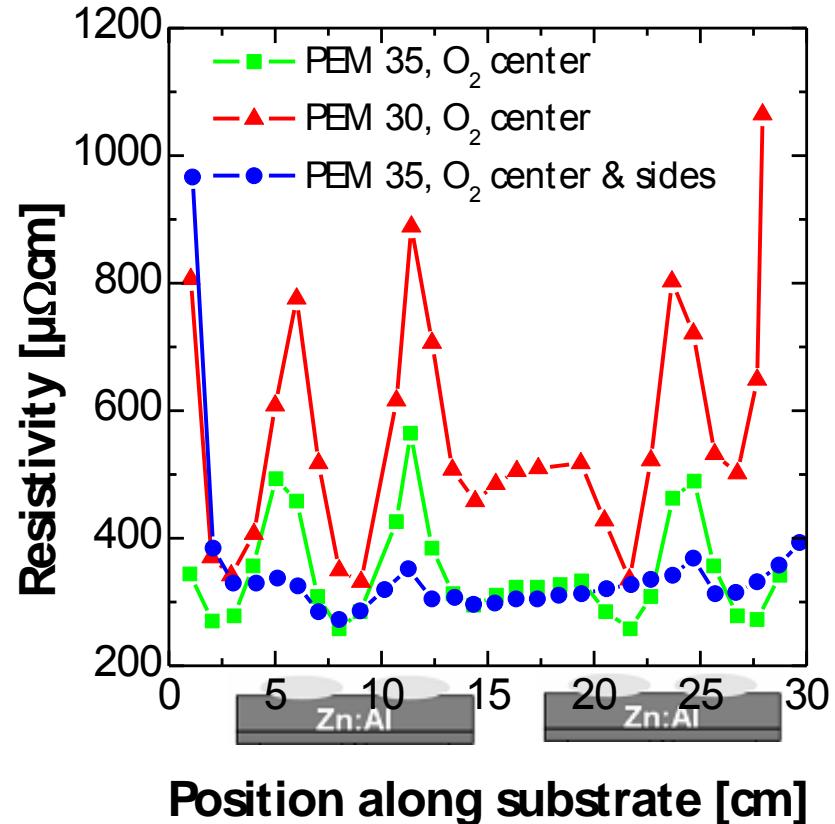


2 Properties of reactive MF sputtered ZnO:Al films

Static deposition



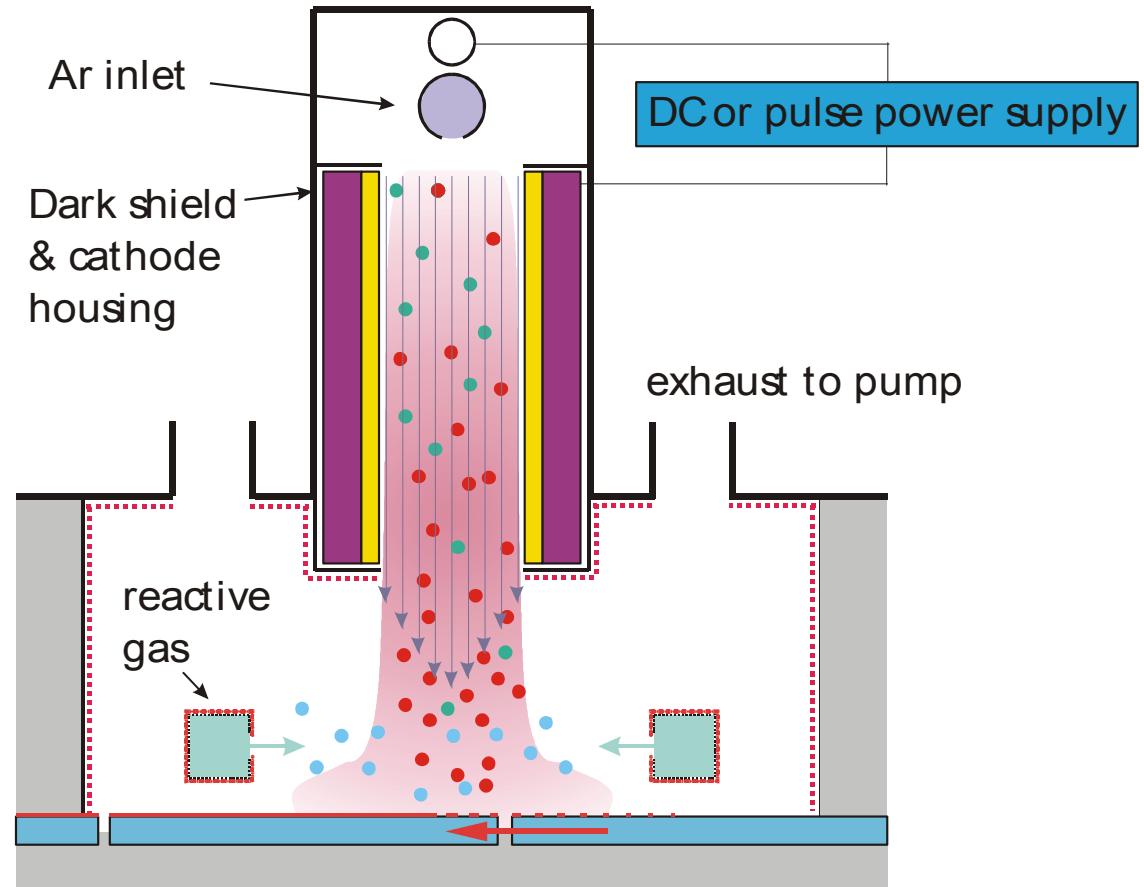
- Dependence of plasma damage on gas inlet system
- Formation of negative ions *can* be suppressed in reactive sputtering.



S. Calnan et al., *Thin Solid Films* 516 (2008) 1242

2 Hohlkatoden-Gasflusssputtern (GFS Prozess)

- $p_{\text{tot}} = 0.1 \dots 1 \text{ mbar}$
- Keine Targetvergiftung
- Beschichtung mit sehr hoher Rate
- Hohe Plasmadichte
- Niederenergetische Beschichtung
- Targetausnutzung > 80 %
- Die GFS-Technologie wurde in den 1980er Jahren in Adlershof entwickelt.*

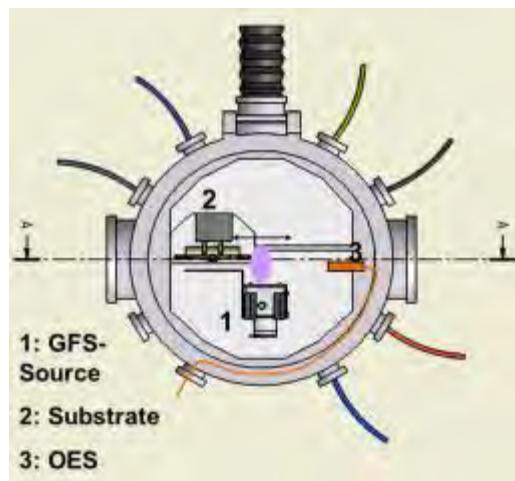


* Akademie der Wissenschaften, Zentralinstitut für Elektronenphysik, Rudower Chaussee 5

T. Jung et al., Mat. Sci. Eng. A140 (1991) 528

2 Material development using hollow cathode gas flow sputtering (GFS)

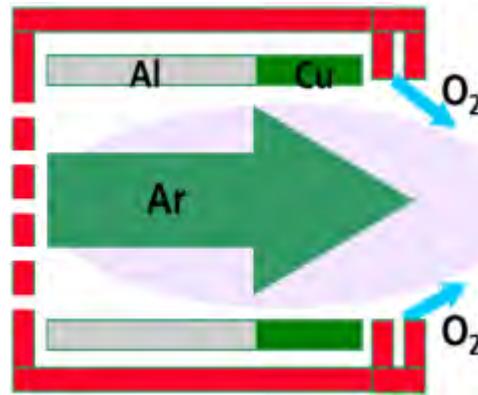
Hollow Cathodes Gas Flow Sputter System



- Scale-able system up to 1m, offered by FhG-IST
- More than 20 units installed

► Simple and rugged, no turbo

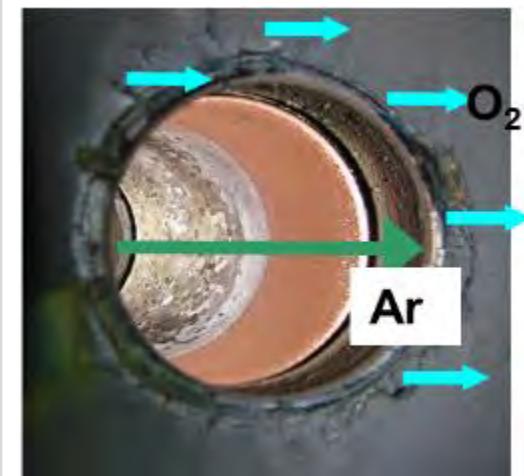
GFS Co-sputter process for Delafossite



- Remote process, no arcing due to purge gas
- Dense plasma / low energy, mbar, high rate

► Soft growth DC sputtering

Experiment



- Sputtering of Cu and Cr ring segments
- Control by OES and / or pressure

► Adjustable composition

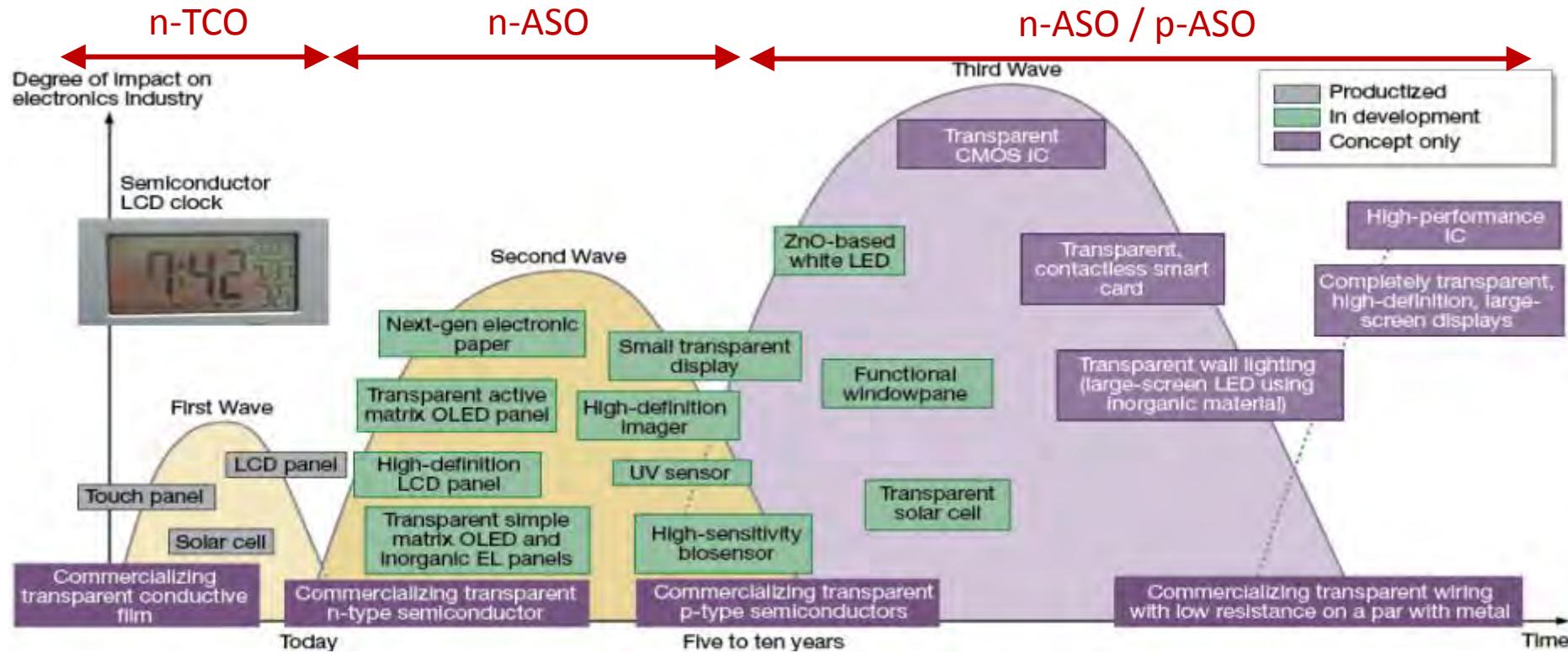
T. Jung et al., Surf. Coat. Technol. 86-87 (1996) 218 | B. Szyszka et al., Thin Solid Films 518 (2010) 3109

2 Potential of the GFS technology

- Recent results
 - ZTO layers with mobility exceeding $50 \text{ cm}^2/\text{Vs}$
 - $\text{TiO}_2:\text{W}$ layers capable for visible light induced decomposition of fatty acids
 - p-type delafossite films using reactive GFS
 - UV-protection of polycarbonate with organic modified ZnO capable for more than 4 000 h global radiation.

- Industrialization
 - Pilot lines for 3D parts are being installed in industrial scale at Fraunhofer IST currently

2 Road map for oxide based, transparent electronics

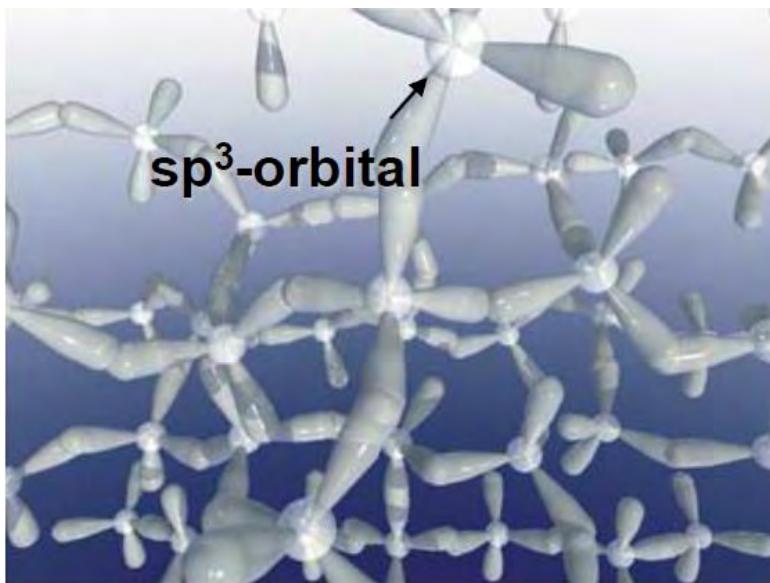


- **1st wave: n-TCOs as transparent conductors**
- **2nd wave: n-ASOs for oxide TFTs and related products**
- **3rd wave: oxide p-n junctions for oxide LEDs and oxide μ-electronics**

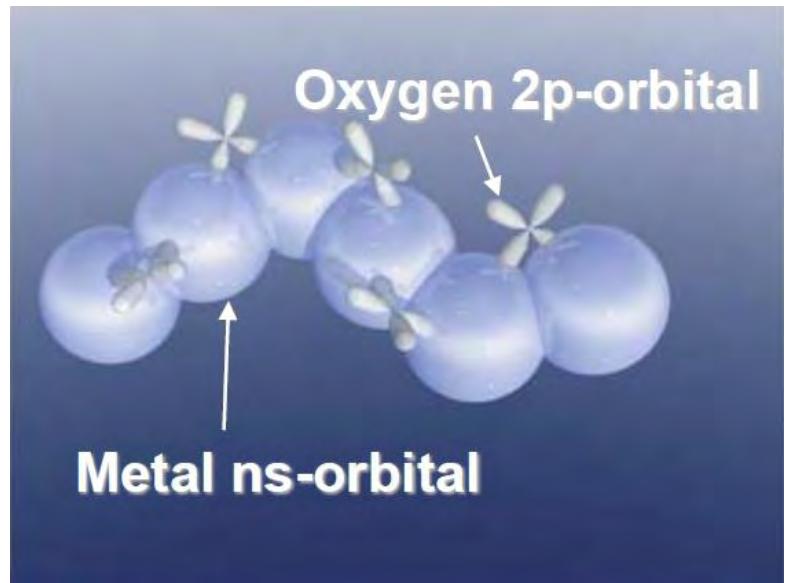
Nikkei Electronics Asia November 2007 – Transparent electronic products soon a reality

2 Amorphous oxides as high quality semiconductive materials

a) Covalent amorphous semiconductor (e.g. a-Si:H)



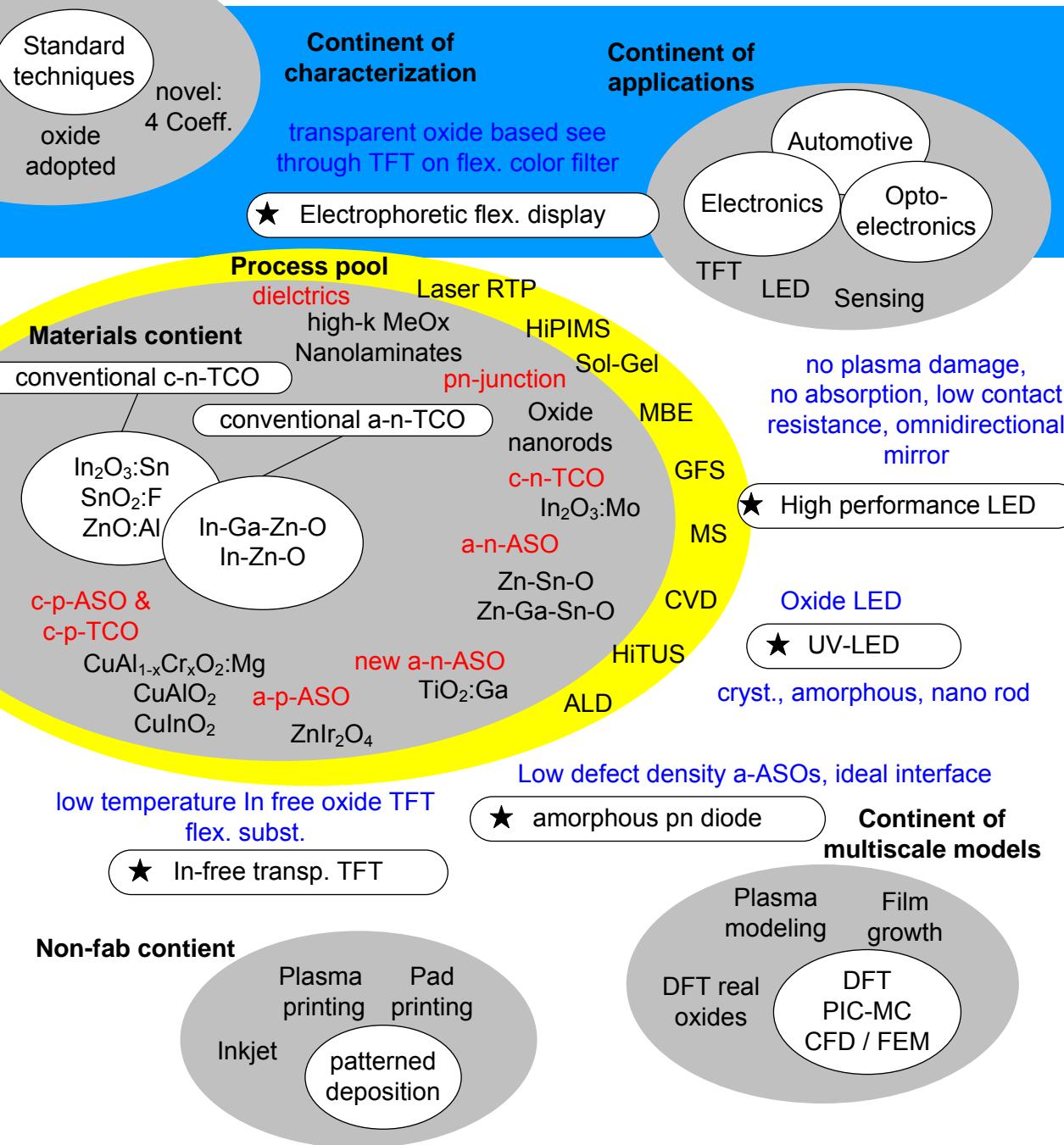
b) Amorphous metal oxide (with (n-1)d¹⁰s⁰ (n ≥ 4), e.g. InO_x)



→ sp³-overlap (cryst. ordering)
important for high mobility

→ Spherical ns-orbitals overlap in
a-MeO_x
→ High mobility, even in amorphous state.

K. Nomura et al., Nature 432 (2005) 488 | H. Hosono et al., J. Non Cryst. Sol. 198-200 (1996) 165

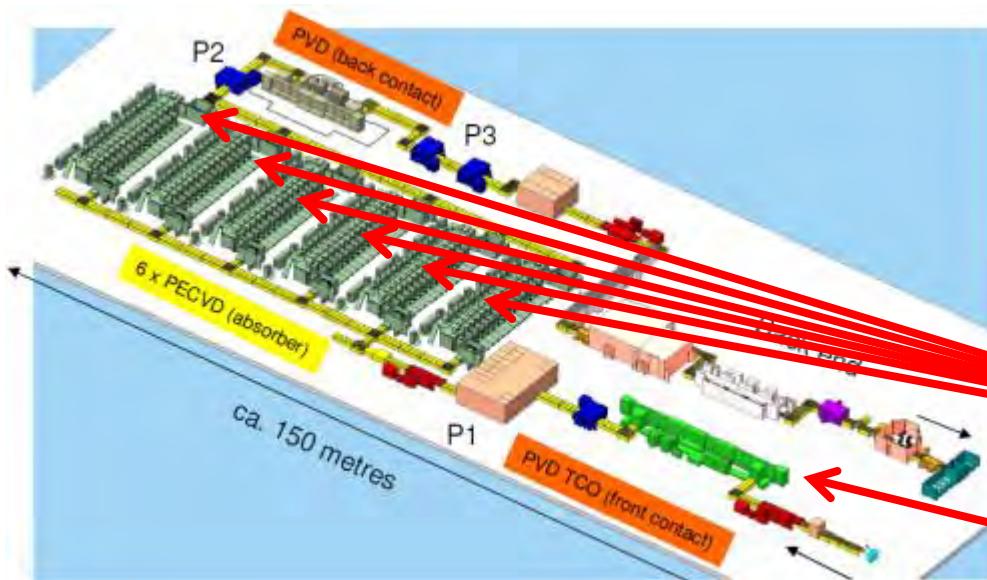


Oxide electronics: the unknown sea map

**ORAMA FP7
R&D topics**

2.2 Conventional a-Si:H / μc-Si:H 50 MWp plant

More challenging than expected...but a story to be continued



- 50 MWp production
- Cycle time: 70 s
- Status 2009: $\eta = 8.5 \%$
- Status 2012: $\eta = \sim 10.5 \%$

... feeds them all!

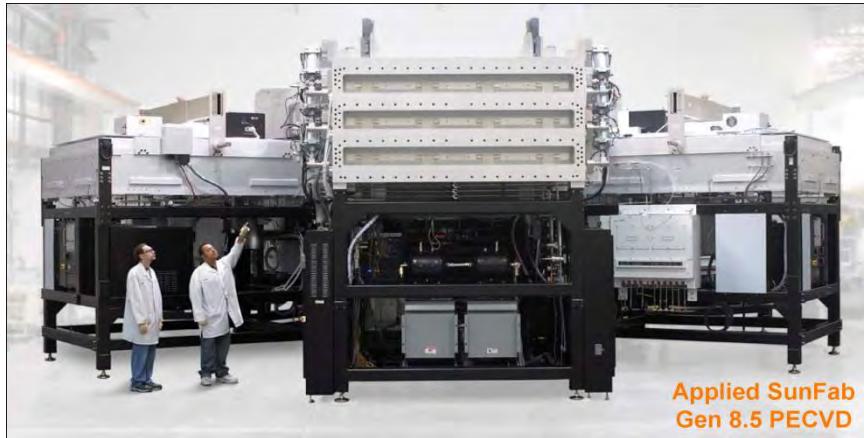
One TCO coater

- Cost driver #1:
Low efficiency
- 2014: DEMO 14 project,
14 % cell efficiency,
12 % module (stable)
- Cost driver #2:
Large area PECVD
(6 RF or VHF cluster
tools!)
- Cost driver #3: TCO
Ceramic target
 $ZnO:Al$, insufficient
light management

M. Liehr et al. (Leybold Optics), Presentation V2009 (Dresden, Oct. 2009)

2.2 Substitution of PECVD by novel processes

Hot wire CVD (CAT CVD)

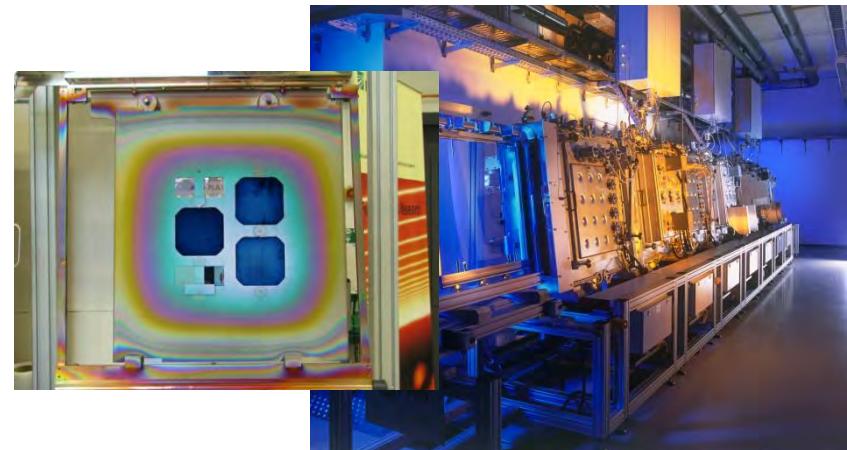


a) State of the art: Large Area PECVD

- ▶ AMAT SunFab: Gen. 8.5 ($5,7 \text{ m}^2$)
Oerlikon KAI 1200: Gen 5 ($1,5 \text{ m}^2$)
- ▶ Low rate (< 1 nm/s)
- ▶ Poor material utilization
- ▶ Complex technology
- ▶ Adopted from flat panel display

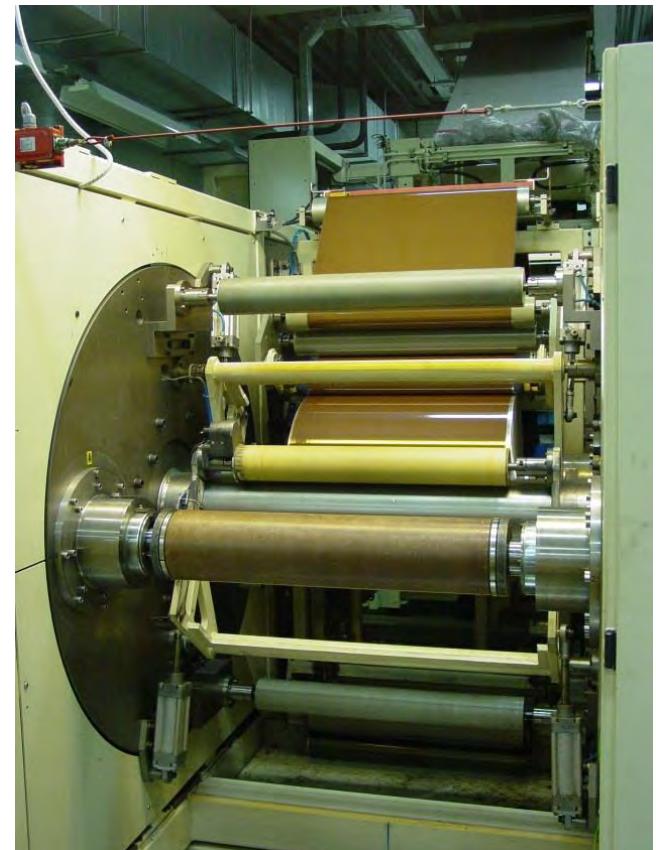
b) Hot-wire CVD

- ▶ Activation of SiH_4 at the hot wire
- ▶ Simple, robust, in-line compatible
- ▶ Lab: $a > 1.5 \text{ nm/s}$ achieved
- ▶ Scaling: $50 \times 60 \text{ cm}^2$ @ FhG-IST
- ▶ Material utilization > 80 %



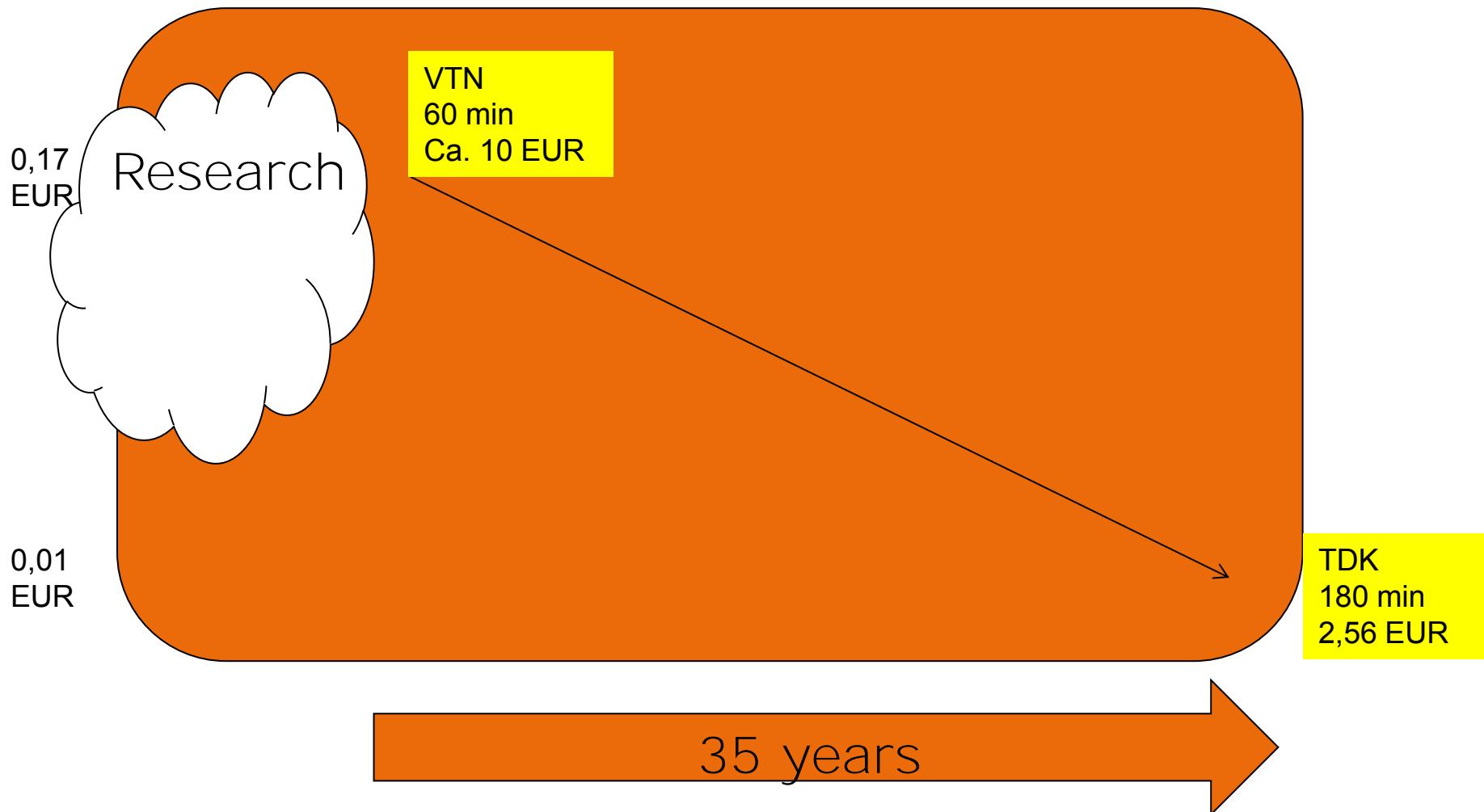
2.3 Rückblick: Herstellung von Videoband mittels Slot-Dye-Coating

- Schnelle Beschichtung von Rolle zu Rolle:
 - Atmosphärendruckprozess
 - Schichtdicke ~40 µm
 - 1200 m/min bei 120 cm Breite,
24/7 Betrieb
- Prozessschritte:
 - Lack-Vorbereitung (Suspension herstellen,
mischen, filtern)
 - Band Reinigung
 - Hochgeschwindigkeits-Coating endlos von
Rolle-zu-Rolle
- Aufgabe OPV:
 - Transfer auf OPV Stacks
 - Kontaktierung / Barrieren / Effizienz /
Lebensdauer

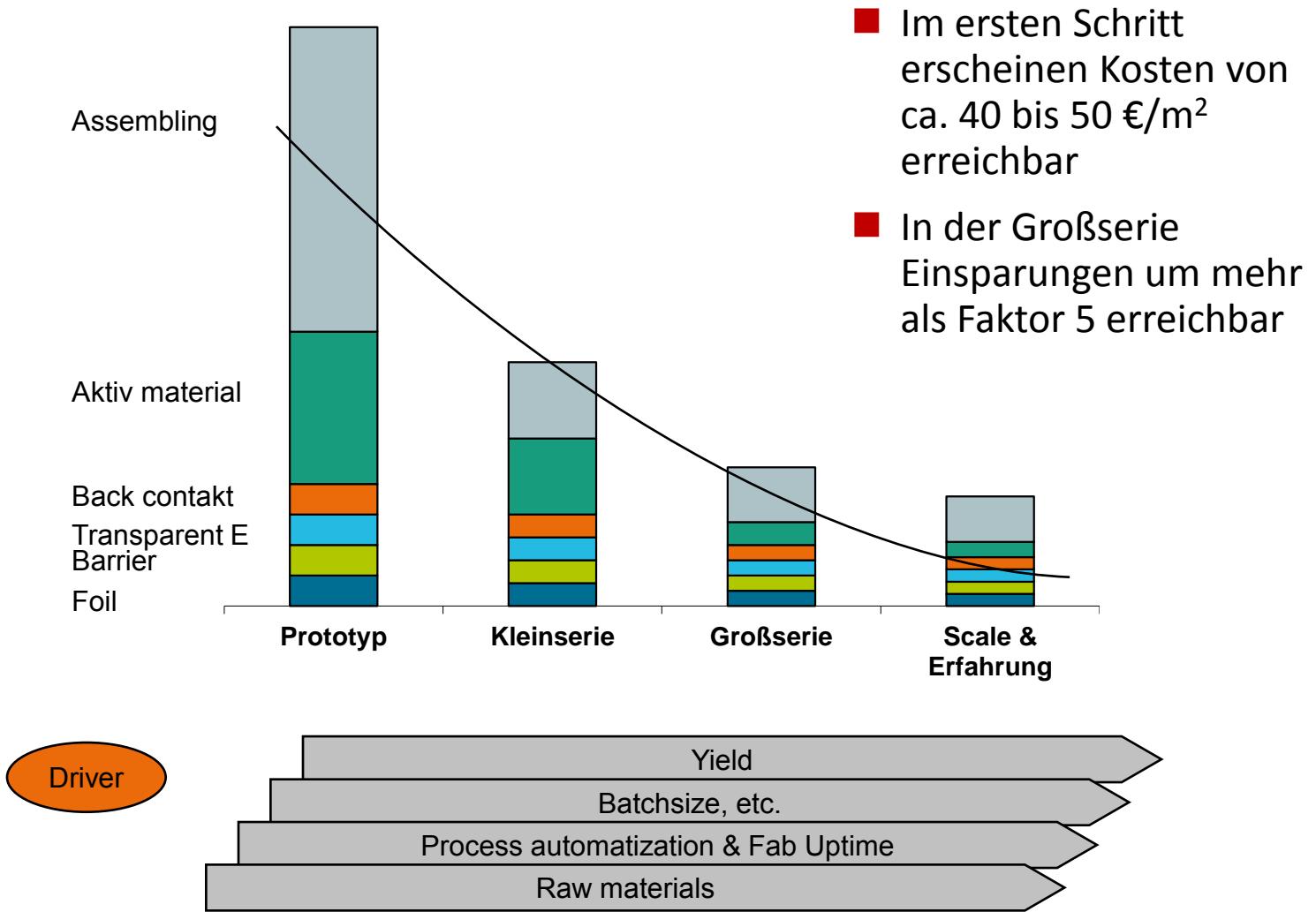


D. Teckhaus, IDTechEx Printed Electronics & Thin Film Week, April 2013

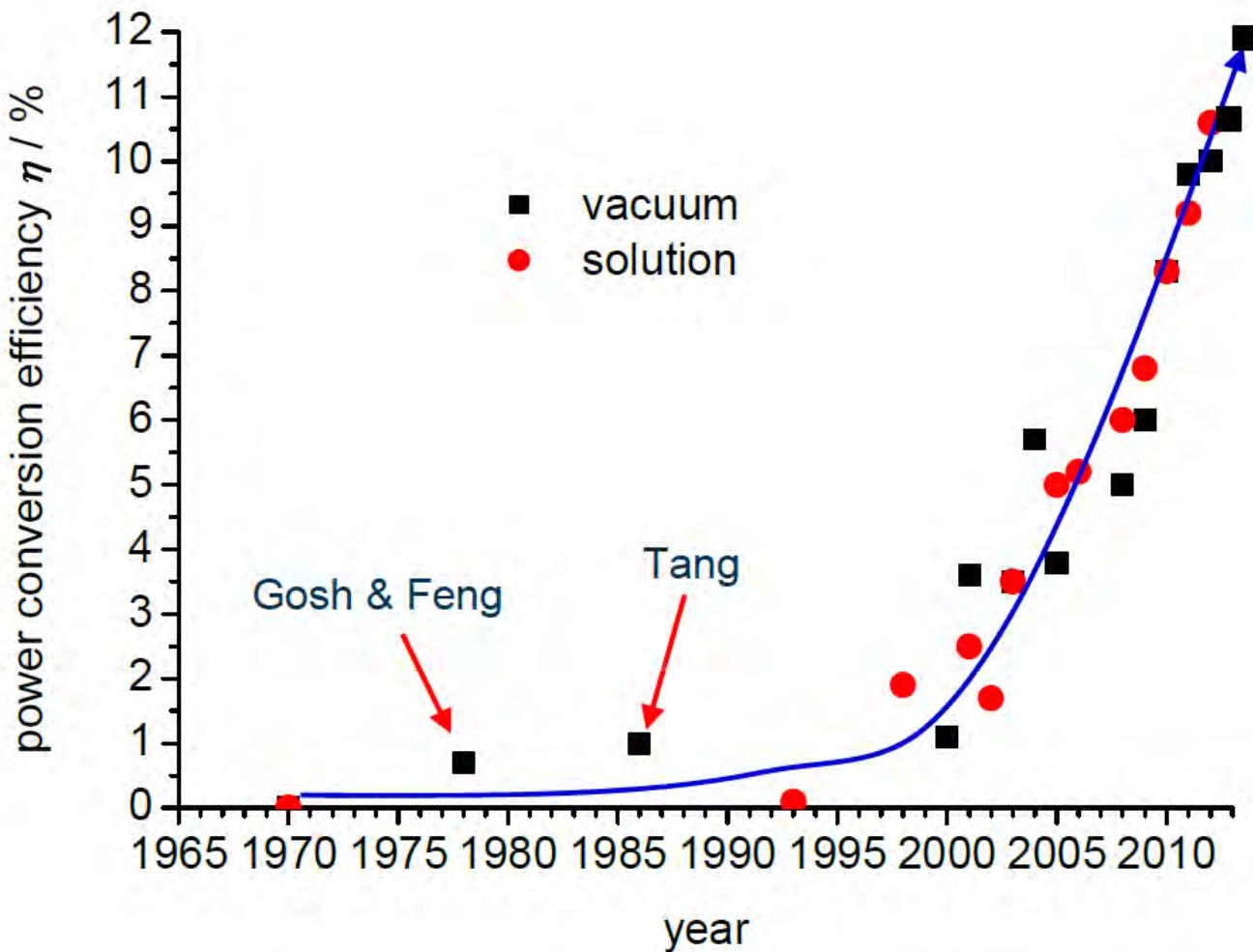
2.3 Entwicklung der Kostensituation bei Videotapes: Faktor 17 in 35 Jahren



2.3 OPV Kostenszenario



2.3 OPV: Vakuumbasierte vs. nasschemische Prozesse



H. Hoppe, IDTechEx Printed Electronics & Thin Film Week, April 2013

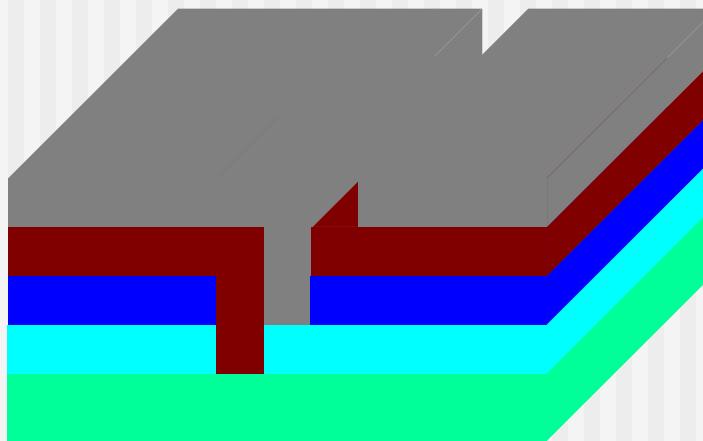
Results PPP-Project R2R OPV System



Gen1 (Starting PPP)



layer	back electrode
process	P3: laser ablation

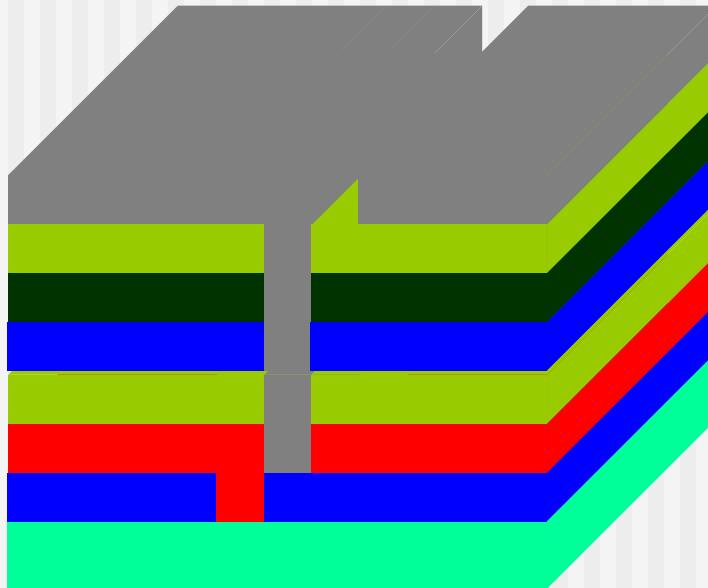


Generation	1
semitransparent electrode	ITO/PEDOT:PSS
active layer	P3HT:PCBM
ETL interlayer	none
back electrode	aluminium
efficiency target	2.5%

Gen4 (planed PAPPA)



layer	back electrode
process	P3: laser ablation



Generation	4
semitransparent electrode	silver grid & PH1000 (ZnO)
active layer 1	to be defined
ETL interlayer	TiO _x
HTL interlayer	PEDOT:PSS
active layer 2	to be defined
ETL interlayer	TiO _x
back electrode	AL (AG or AU)
efficiency target	8-10%

3 Zusammenfassung und Ausblick

- Relevanz des Themas „Beschichtungen für erneuerbare Energien“
 - Schlüsselthema für die Energiewende und für das Erreichen der CO₂-Einsparziele
 - Massiver Ausbau notwendig
- Vakuumverfahren
 - Neue Ebene des Verständnis durch Modellierung
 - Megatron™: Schlüsseltechnologie für PVD
 - Hohlkatoden-Gasflusssputtern: Neue Basistechnologie für die Materialentwicklung
- OPV mittels Slot-Dye Bandbeschichtung
 - Basierend auf der Video-Tape-Fertigung
 - Hoch innovatives und ausbaufähiges Verfahren

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

Prof. John Ziman
(solid state physicist and humanist,
born 1925, died 2005)



Vielen Dank für die Aufmerksamkeit

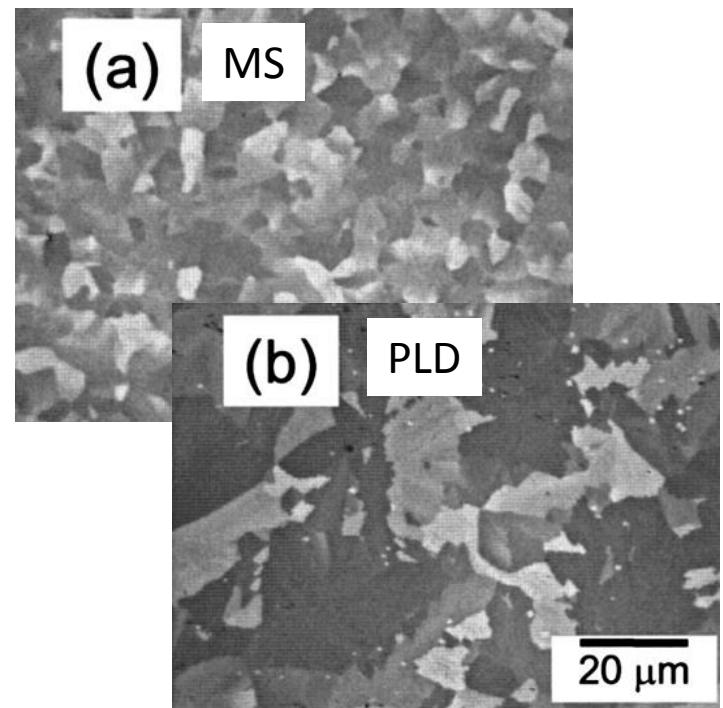
2 Conditions for ZnSnO_x deposition by C-Mag sputtering

Process	Bipolar CMAG 61.5 kHz		
System parameters	Base pressure	P ₀	< 5 x 10 ⁻⁶ mbar
	Cathode		Dual cylindrical cathode (Interpane)
	Generator		AE Crystal
	Target to substrate dist.	d _{ST}	190 mm
	Target material		ZnO:SnO _x (Zn:Sn = 68:32)
Process parameters ZnO:SnO _x deposition	Gas flows	q(MG)	Ar: 190 sccm, Ar+10%O ₂ : 50 sccm
	Total pressure	P _{tot}	≈ 400 mPa
	Power	P	~ 15 kW / bipolar MF @ 61.5 kHz
	Substrates		Float glass
	Carrier speed	v _C	Static, 15 min

2.2 Example: Nb-doping of TiO₂

Synthesis of TiO₂ based TCOs by MEGATRON sputtering

- 2 x 1 kW with TiO₂ rotatable, 2 x 200 W with Nb planar targets
- Annealing at 350 °C in vacuum for 1 h -> 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