New vacuum coating technologies for metal strips and foils

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Content

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1 Introduction

- Growing interest for metal strips and foils with special surface functions
- Call for very thin substrate materials for light-weight applications and saving resources
- Complex layer systems with special and high-quality properties needed
- Requirement for low cost coating technologies onto large areas
- Motivation to use PVD/PECVD processes:
  - Variety of layer materials available for deposition (metals, alloys, compounds, …)
  - Very precise coating
  - Outstanding environmental compatibility of processes
  - Promising R&D results and first industrial applications
- Demands for new processes:
  - High-rate deposition but with excellent layer properties -> plasma assistance
  - adapted pre-treatment processes
  - active substrate cooling in vacuum during coating
- First industrial application in development, especially in the field of energy

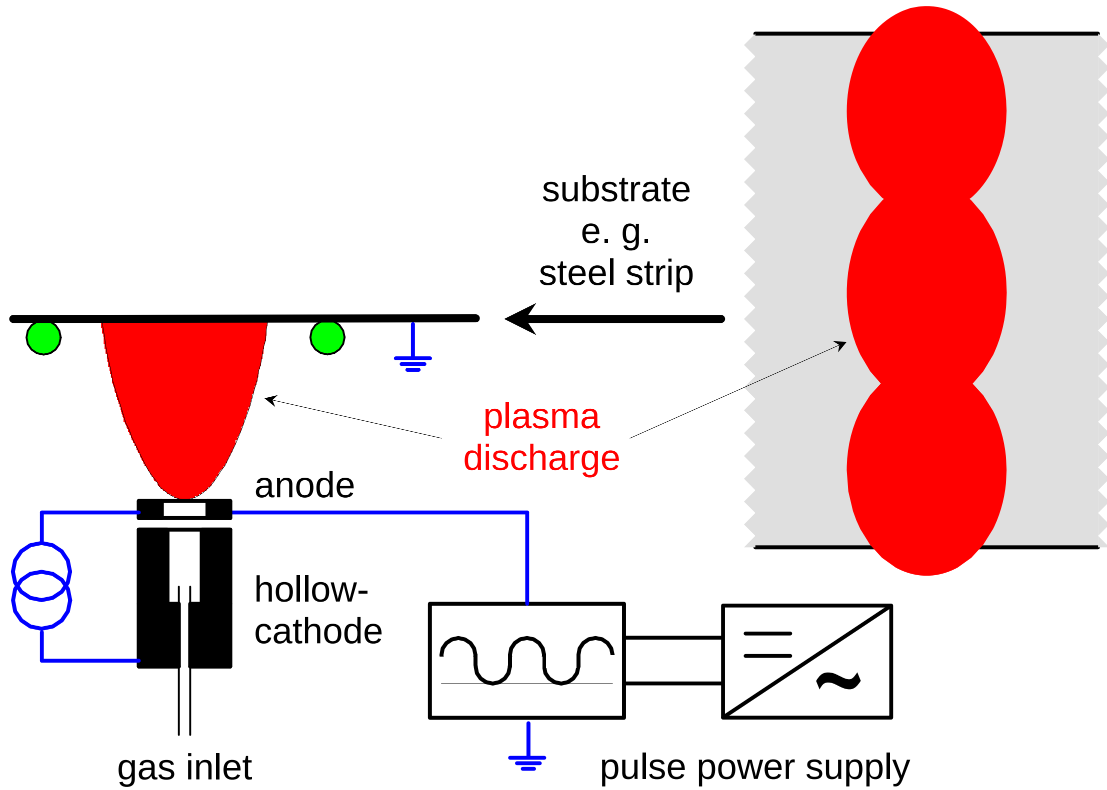
2 Vacuum in-line pre-treatment by hollow cathode sputter etching

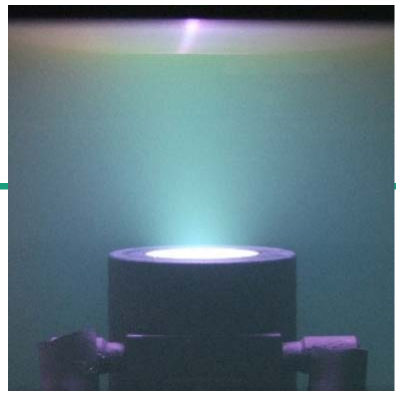
Parameter
for one etching station

Power: 50 kW with 5 hollow cathodes per 1 meter strip width

Etching rate: 5 nm at 1 m/s strip speed; higher removal by arranging some stations

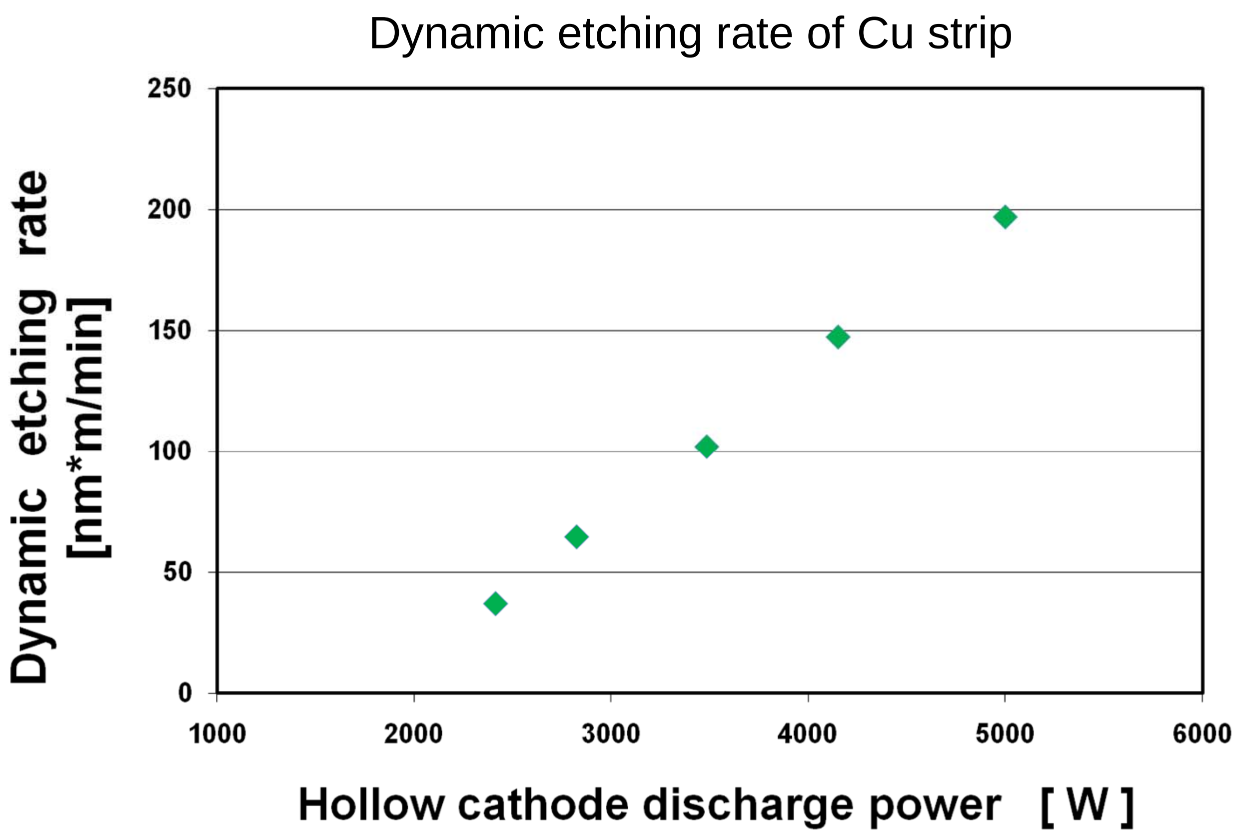
Frequency: 20 – 50 kHz (sine wave) for arc depression





non magnetic and ferror-magnetic metal strips with arbitrary thickness

2 Vacuum in-line pre-treatment by hollow cathode sputter etching



Etching rate depends on
- realized power in hollow cathode (discharge current × discharge voltage) and
- Bias Voltage (pulse power supply, about 400 – 600 V)

Powerful plasma sources are needed → Hollow cathode **arc** source

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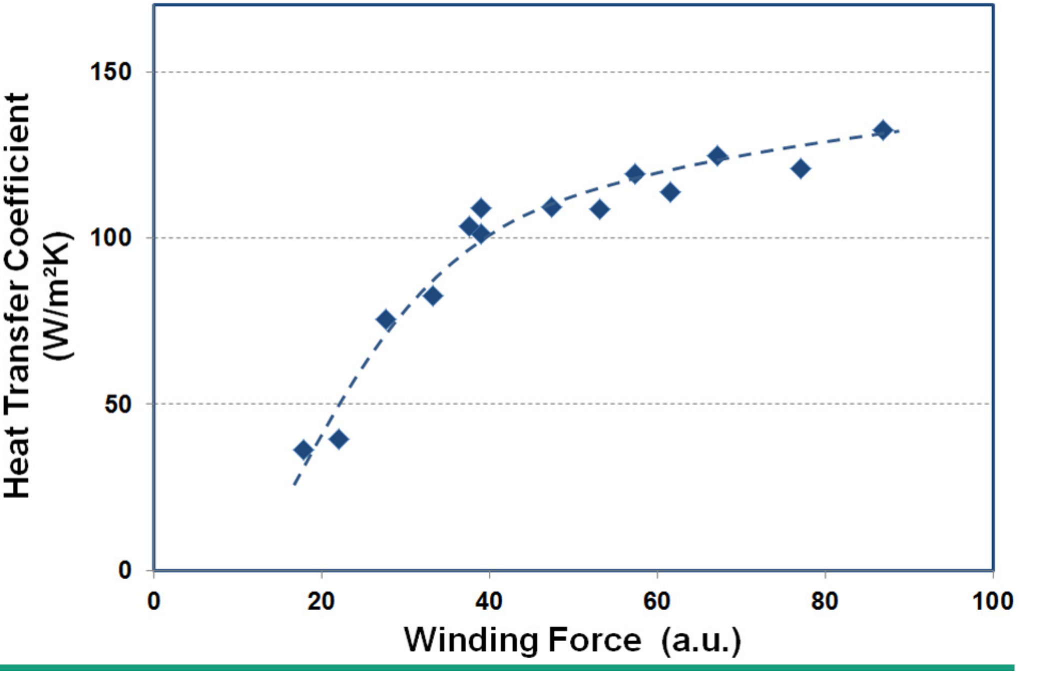
3 Substrate cooling in vacuum – Brush cooling

- Idea: realization of a large number of effective working contact points for heat transportation by brush arrangement
- Heat transmission coefficients of up to 150 W/m²K were reached with a static brush cooling device.



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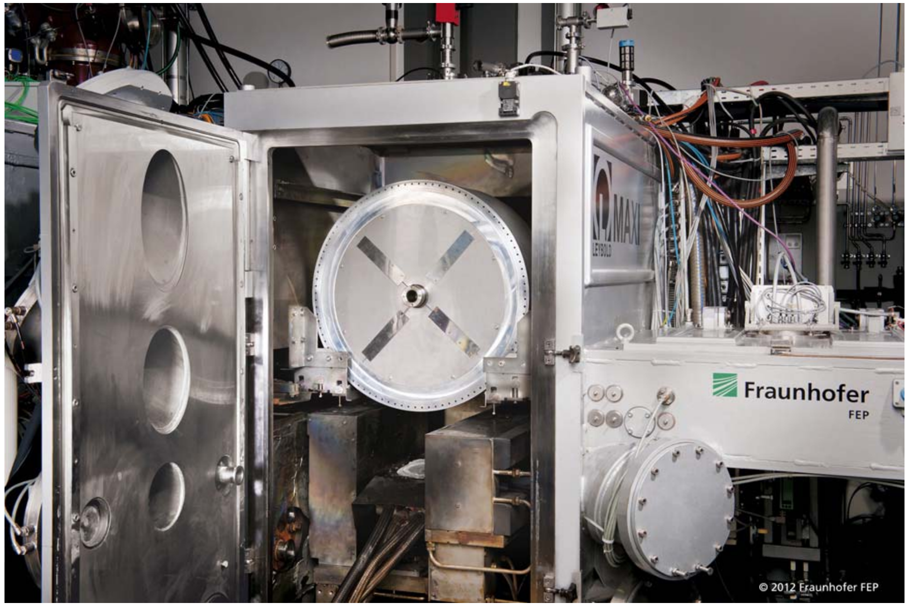
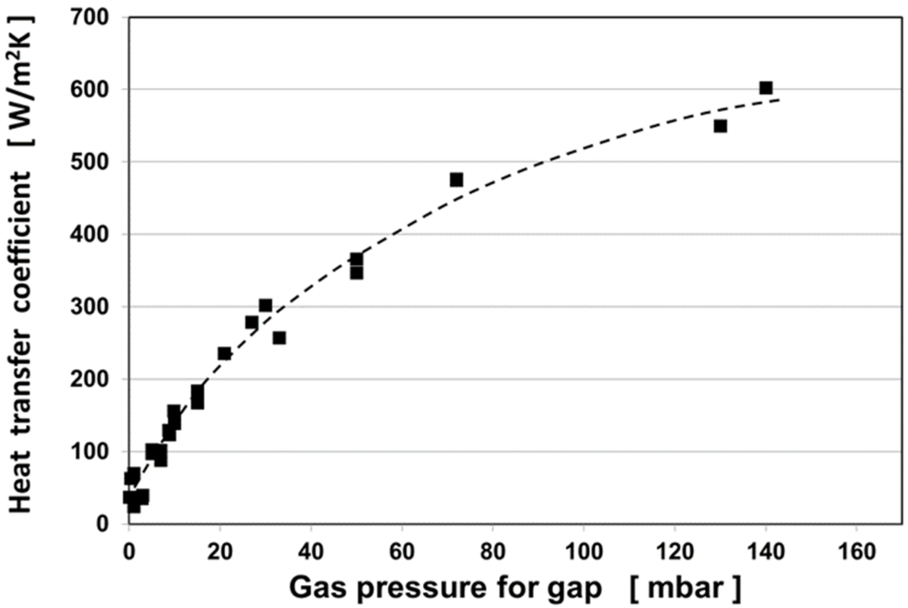
3 Substrate cooling in vacuum – Gas cooling drum

- Idea: realization of gas filled contact area for heat transportation
  between strip and cooling drum,
  meanwhile the requirements on the pressure for vacuum coating ($1 \cdot 10^{-4}$ mbar) were fulfilled.

- Heat transmission coefficients of up to 600 W/m²K were reached
  with a gas cooling drum. There are further potential for increasing of cooling effect.





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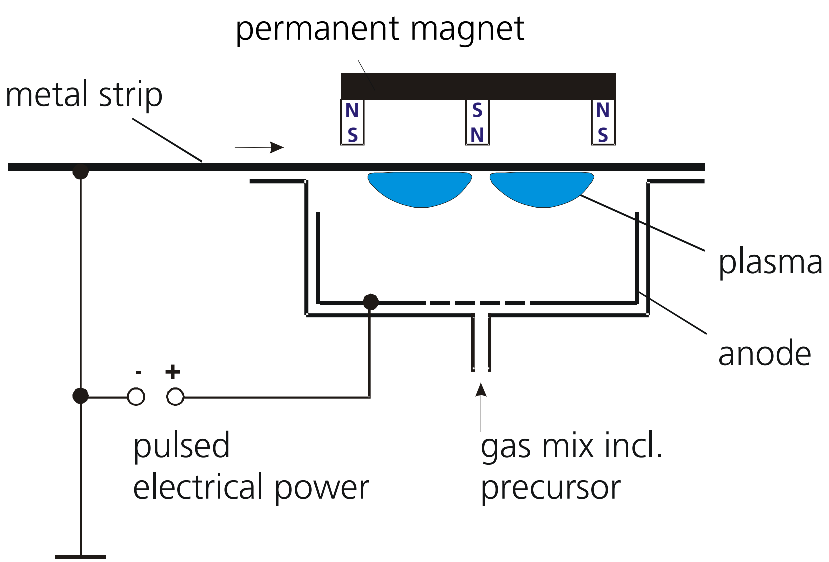
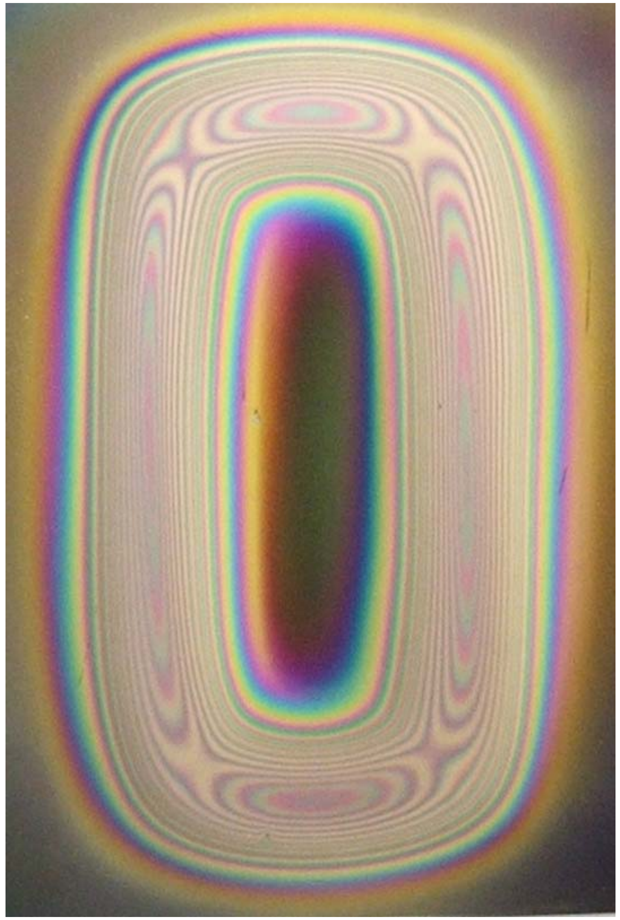
4 PECVD process for metal strips

Principle:

- magnetron discharge burning on the metal strip (= cathode)
- Metal strip at ground potential, encapsulated anode
- MF-pulsed glow discharge



transparent a-C:H:Si:O coating deposited onto a stationary steel sheet, precursor HMDSO



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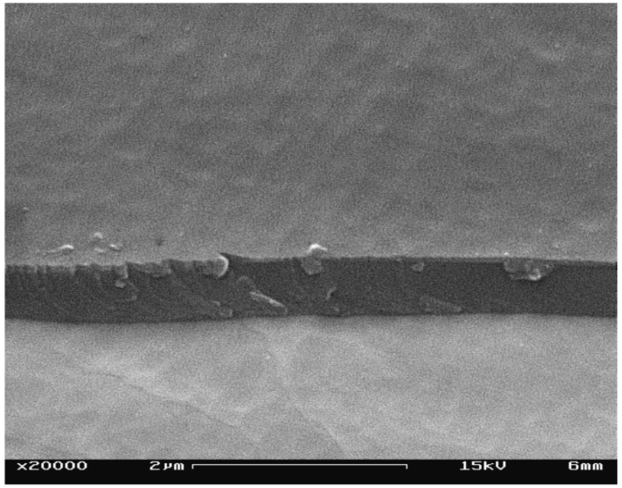
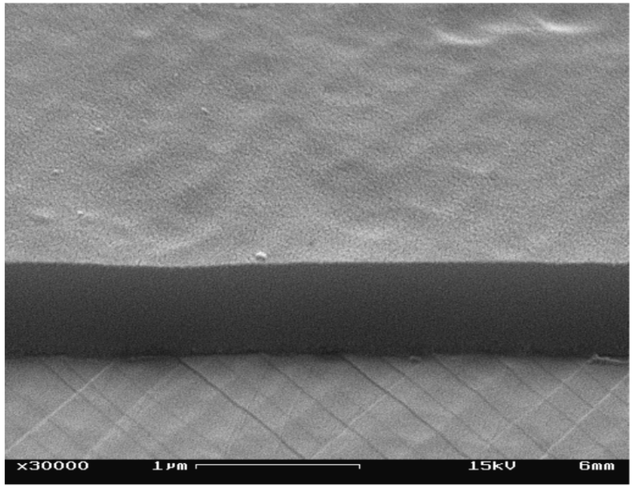
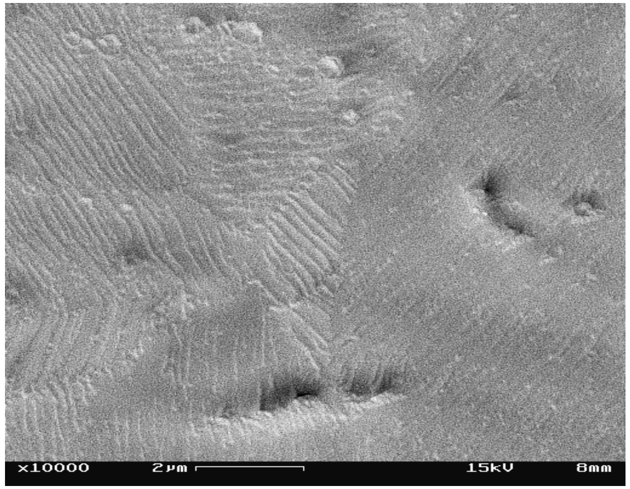
4 PECVD process for metal strips

Examples for coatings on metal strips







<u>a-C:H</u>

precursor:	C_2H_2
dep. rate:	110 nm/s
thickness:	0,9 µm
hardness:	40 GPa

<u>a-C:H:Si:O</u>

precursor:	HMDSO
dep. rate:	50 nm/s
thickness:	0,7 µm
hardness:	13 GPa
EDX:	O/Si 1,0

<u>a-Si:H</u>

precursor:	SiH_4
dep. rate:	3 nm/s
thickness:	1,6 µm

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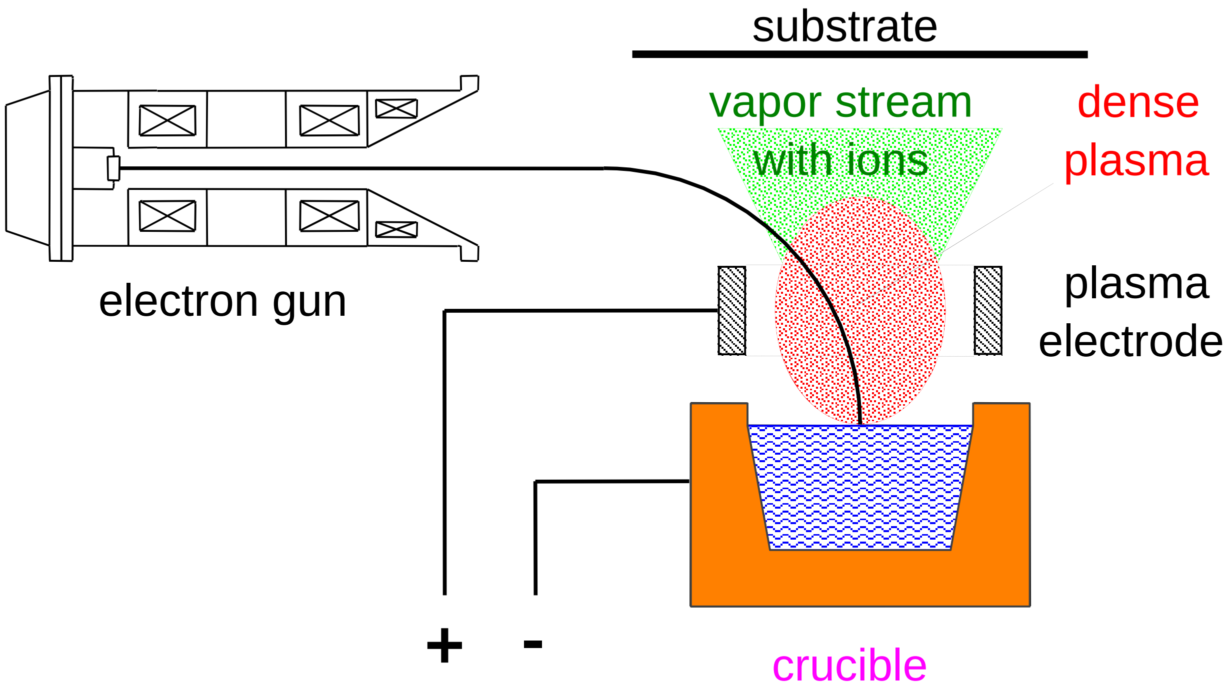
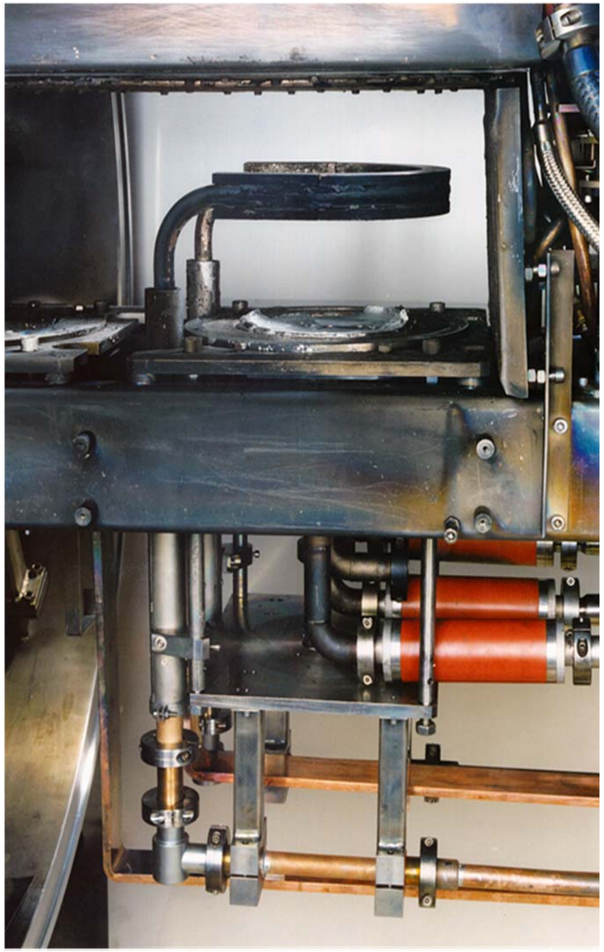
5 Plasma activated high-rate electron beam PVD Spotless arc Activated Deposition (SAD process)





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5 Plasma activated high-rate electron beam PVD Spotless arc Activated Deposition (SAD process)

- Plasma activated deposition of high melting metals (Ti, Zr, Cr, W, Mo, …), alloys and compounds (Nitrides, Oxides, Carbides) e.g. TiN, TiC, TiO_2, WC, ZrN, …
- High deposition rates onto large areas up to 2 µm/s for metals and alloys up to 200 nm/s for compounds
- High ion current density at the substrate (100 – 300 mA/cm²)
- Pure metal plasma (ionisation degree up to 60%)
- Dense layers without droplets
- Arrangement for large deposition width by deflection of electron beam and spotless arc (approved up to 600 mm)

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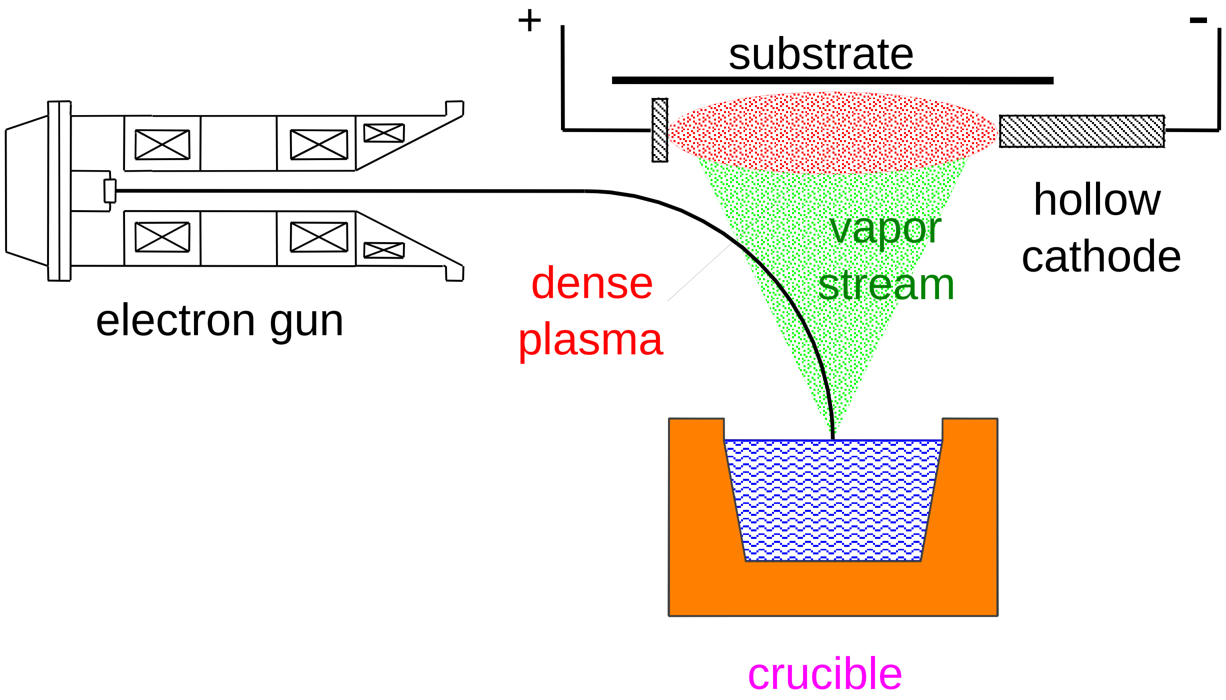
5 Plasma activated high-rate electron beam PVD
Hollow cathode arc Activated Deposition (HAD process)



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5 Plasma activated high-rate electron beam PVD
Hollow cathode arc Activated Deposition (HAD process)

- plasma activation for high-rate electron beam evaporation, especially of insulating and other compounds (SiO_X, Al_2O_3, TiO_2, TiN, CrN, ...) and C containing hard coatings

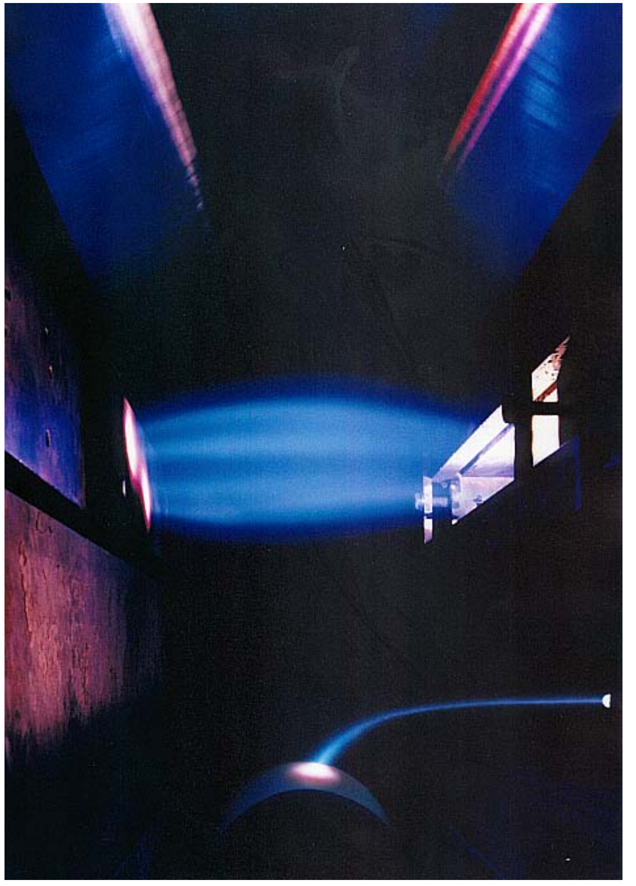
- high deposition rates onto large areas
  e.g.:
  50 ... 100 nm/s for Al_2O_3
  100 ... 1 000 nm/s for SiO_X

- high ion current density at the substrate (10 – 50 mA/cm²)

- ionisation degree of the vapour up to 50%

- dense layers without droplets

- arrangement for large deposition width (proven up to 2 850 mm)



6 Application: Photo catalysis and photo wettability (TiO_2)

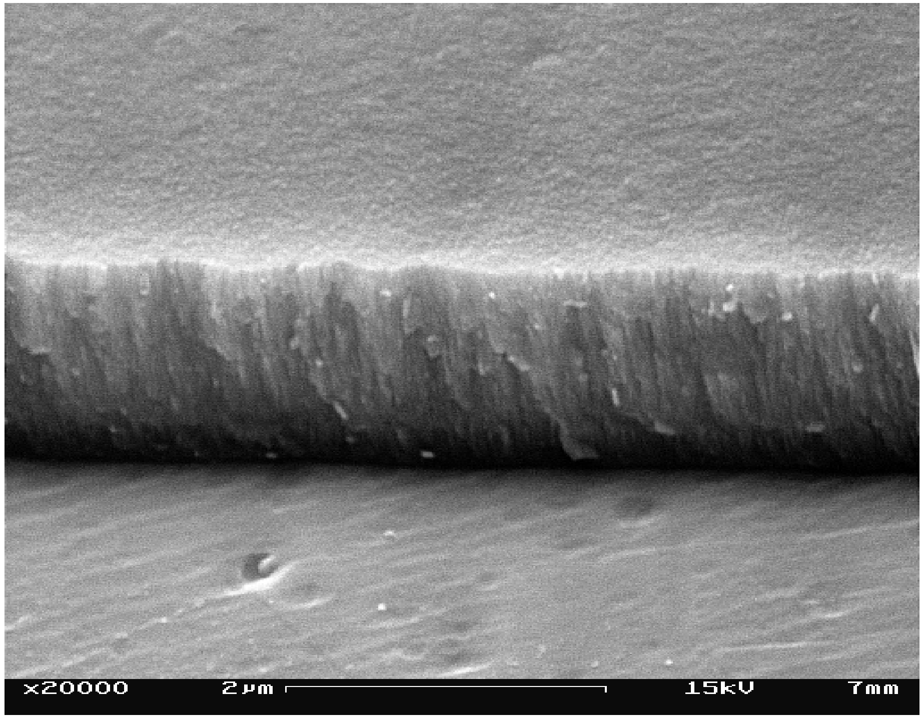
Crystalline (anatas) titanium dioxide shows special properties:

- Photo catalysis
  - Stimulation of oxidation and reduction processes after activation of the coating (Exposure with UV-A or sunlight)
  - Decomposition of organic and inorganic substances on the surface
- Photo wettability / hydrophilicity
  - degradation of the contact angle against water to below 10° after activation of the layer
  - formation of a closed water film on the surface
- High deposition rates up to 100 nm/s
- Dense layer structure and high hardness by plasma activated deposition

6 Application: Hard coatings (TiC / WC)

Reactive Deposition of TiC and WC onto large areas by SAD process:

- Electron beam evaporation of Ti or W in carbon containing atmosphere
- Deposition of TiC:
  - deposition rate up to 100 nm/s
  - hardness up to 33 GPa
- Deposition of WC:
  - deposition rate up to 200 nm/s
  - hardness up to 30 GPa
- Good layer adhesion



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6 Application: Silicon oxide layers for transparent abrasion and corrosion resistance

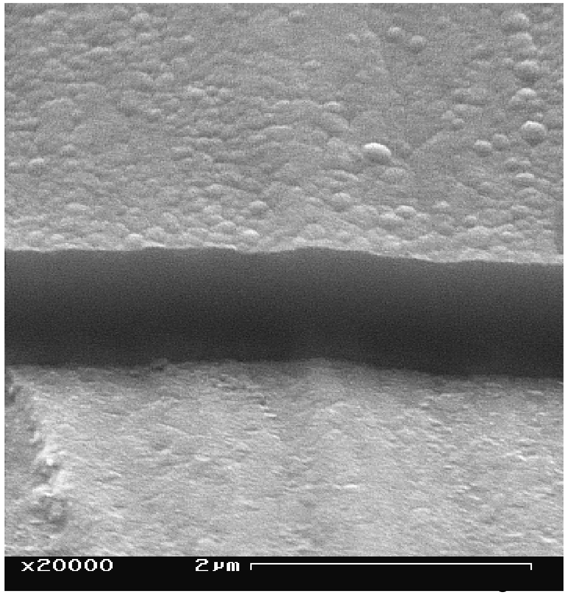
- Deposition rate up to <u>150 nm/s</u>
  by plasma activated high-rate electron beam deposition (HAD process)

- High layer hardness (up to <u>15 GPa</u>)
  caused by high degree of ionization in vapor and enhanced substrate temperature
  (Si-rich SiO_X layers made by combination of PVD and CVD)
  The layer hardness is higher than hardness of bulk SiO_2 material (10 GPa).

- High hardness caused by special nano composite material structure (<u>nano crystalline Si</u> could be detected in amorphous SiO_2 matrix by XRD)

- Low absorption (<u>k< 0.01</u> @ 550 nm)
  in the total hardness range from 5 to 15 GPa

- Good corrosion protection due to <u>dense layer structure</u>.



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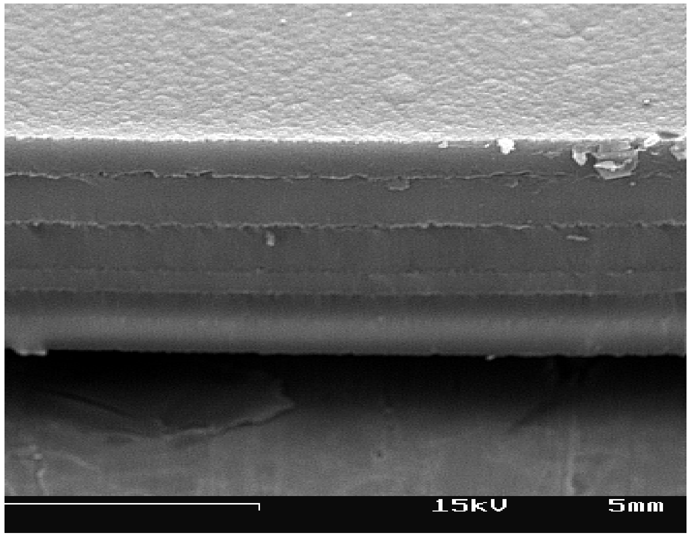
6 Application: Silicon oxide layers for isolating properties

- Deposition of SiO_X based electrically insulating layers on metal strips and foils
  - layer thickness about 10 µm without delaminating
  - brake down voltage of about a few 100 V (> 10 µm)
- Successful organic modification to reduce stress
  by introduction of a monomer in the plasma => combination of HAD + PECVD
- Isolating properties depend strongly from excellent surface quality of the substrate:
  - low roughness
  - extremely low surface defect density



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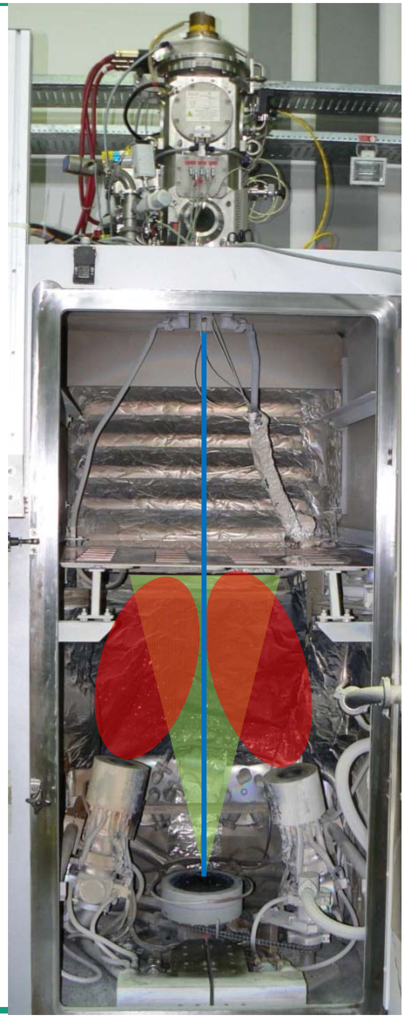
6 Application: Silicon oxide layers in optical layer quality

- Plasma-activated electron beam evaporation (HAD process)
  - electron beam evaporation of Silicon Dioxide
  - hollow cathode arc discharge in vapor/argon atmosphere
  - reactive processing in oxygen atmosphere
  - large distance between crucible and substrate (about **1 m**) for excellent layer homogeneity
- Substrate: aluminum strip
  - strip width 300 mm
  - surface quality mirror finished
- Characteristic parameters for SiO_X layers deposited with large crucible-substrate distance

static rate	nm/s	10	20	50
dynamic rate	nm*m/min	400	800	2000
micro hardness	GPa	6	5	4
refractive index	n @ 550 nm	1.50	1.49	1.48
absorption	k @ 550 nm	1×10^{-3}	5×10^{-4}	5×10^{-4}



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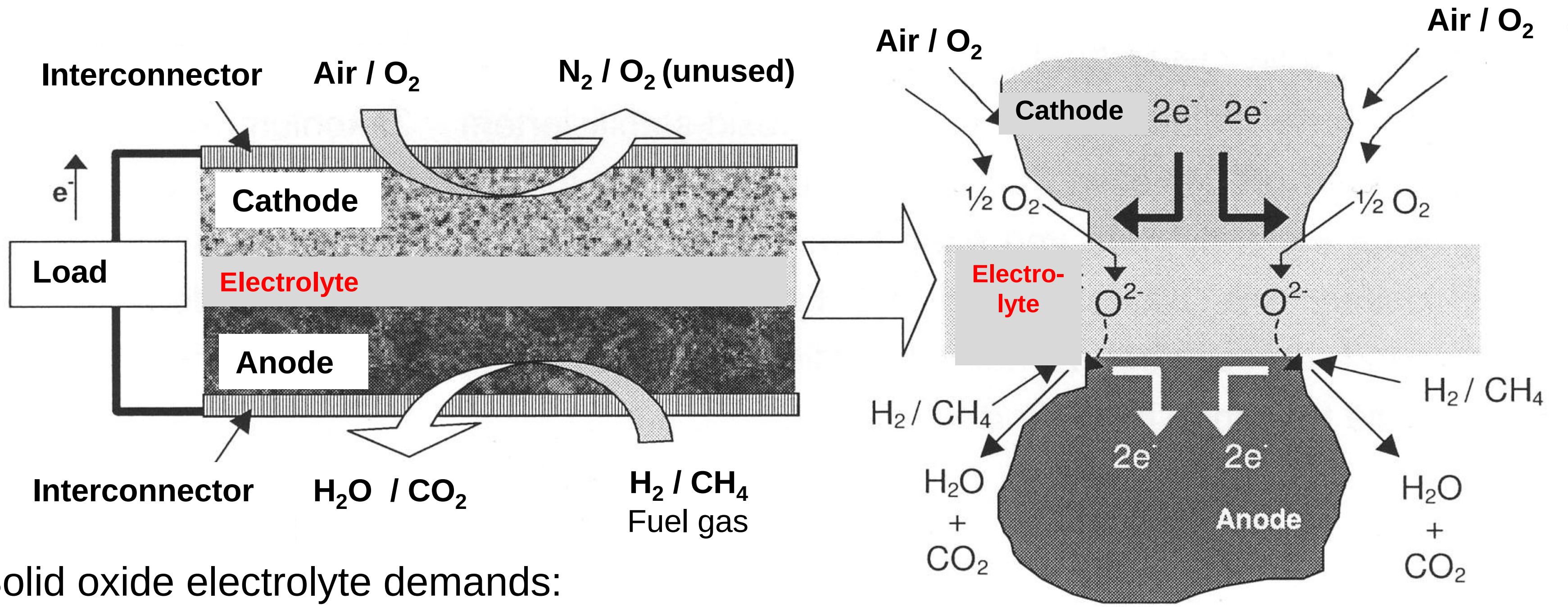
6 Application: Zirconium oxide coatings for fuel cells

Principle of a High-temperature (600 … 1 000°C) solid oxide fuel cell (SOFC)



Solid oxide electrolyte demands:

- High electrical conductivity for oxygen ions
- Low electrical conductivity for electrons
- Long-term stability for high-temperature operation
- Tightness for the non-ionized gases
- Chemical stability in contact with electrode materials and working gases
- Reliability, ageing resistance, thermal cyclability

Graphics: Forschungszentrum Jülich GmbH, Institut für Energieforschung

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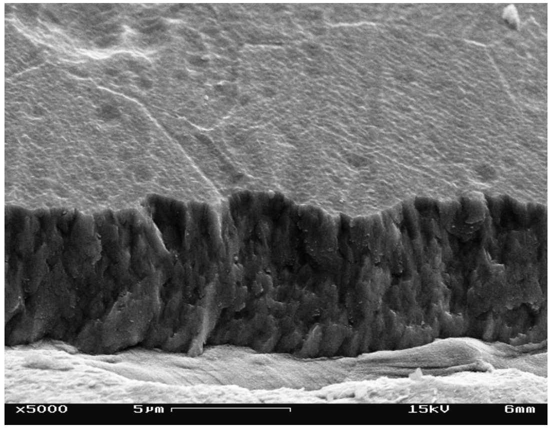
6 Application: Zirconium oxide coatings for fuel cells

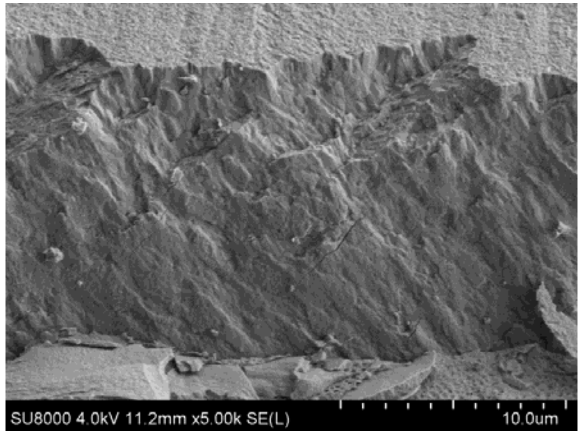
Results:

- Strong influence of plasma activation on the microstructure
- Cubic phase with (111), (100) or (311) texture
- Additional effect on microstructure caused by pulsed bias
- Dense coatings, barrier properties for gases are promising
- High-rate PVD processes are available for dense YSZ



HAD process from ceramic

Electron beam power:	15 kW
Deposition rate:	40 nm/s
Pulsed Bias:	- 120 V
Yttrium content:	5.2 at-%



SAD process from metals

Electron beam power:	32 kW
Deposition rate:	30 nm/s
Pulsed Bias:	- 120 V
Yttrium content:	5.4 at-%

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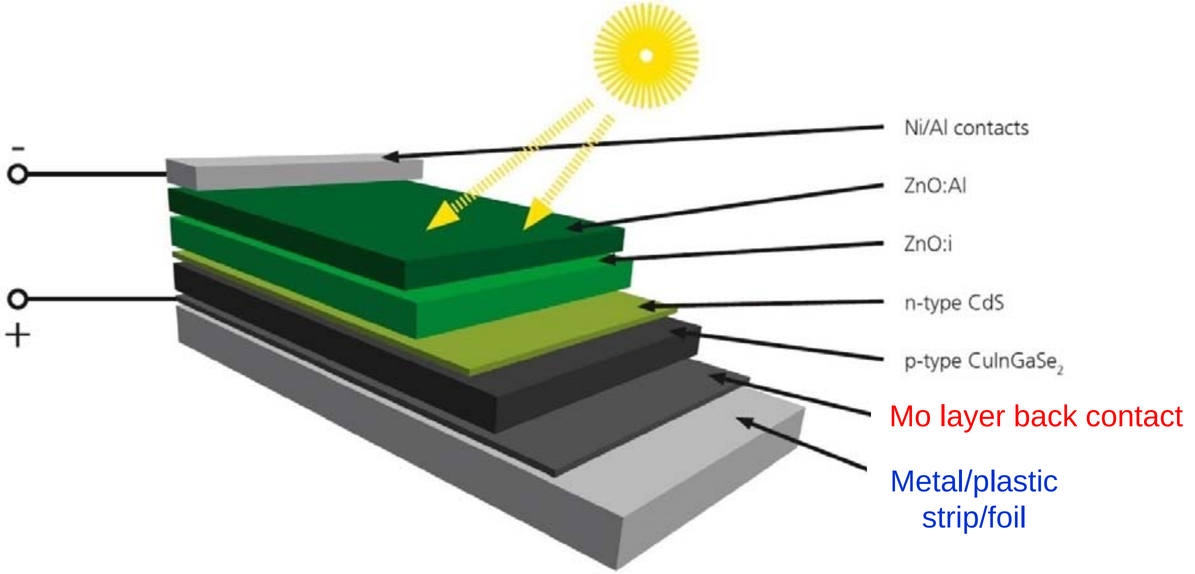
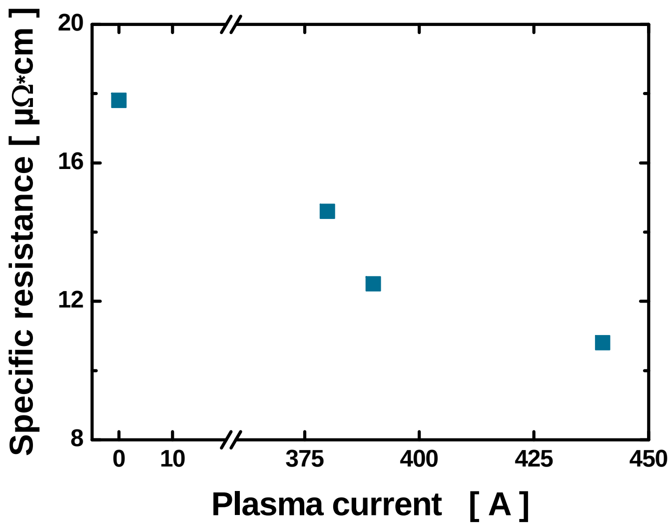
6 Application: Mo layers for photo voltaic application

Application:

- Electrical back contact for CIS-/CIGS solar cells
- Molybdenum coatings guarantee therefore the needed chemical stability, the barrier against diffusion of impurities into the absorbing layer and the low ohmic resistance
- During processing of CIS-/CIGS solar cells temperatures of 500 – 600°C are needed
- Deposition of Mo layers with plasma activated electron beam evaporation (SAD process)





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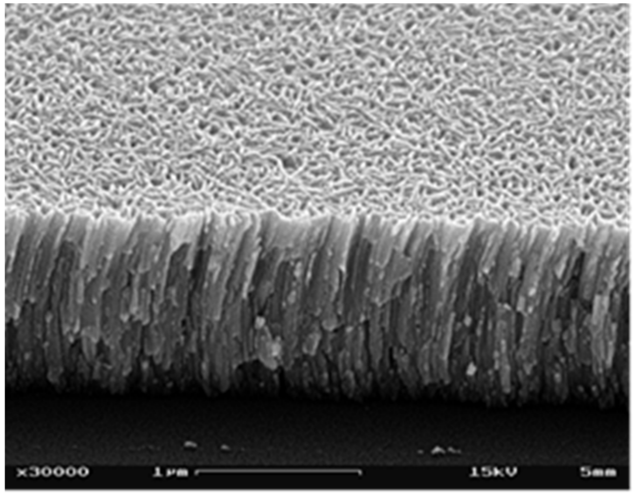
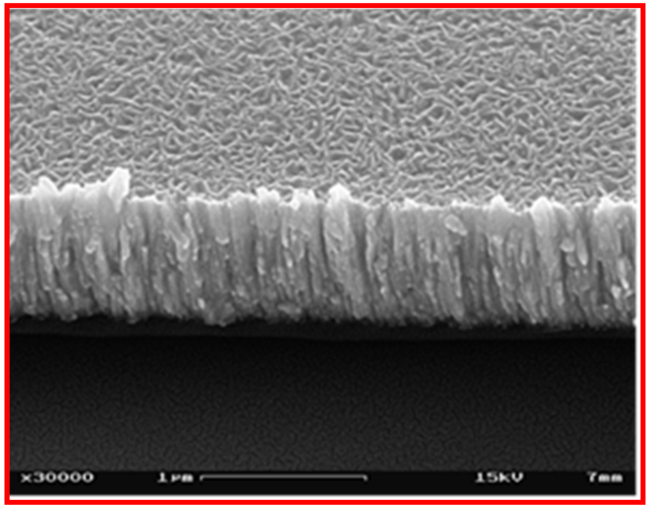
6 Application: Mo layers for photo voltaic application

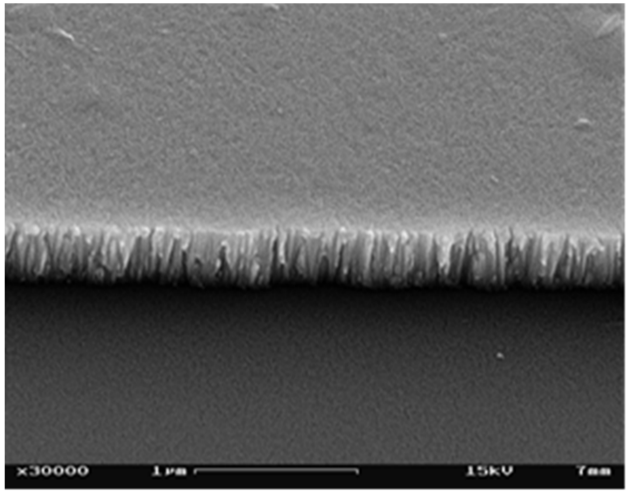
SEM pictures of different molybdenum layers, deposited by various PVD methods



Electron beam evaporation without plasma activation (rates up to 240 nm/s were investigated)



Electron beam evaporation with plasma activation (SAD process) (actually rates up to 60 nm/s were investigated, higher rates possible)



Magnetron sputtering (reference) (typical rate 7 nm/s)

The deposited molybdenum layers on low sodium content glasses show the identical cell efficiency like standard layers.

Complete processing of CIS-cells and investigation of cell efficiency were realized in the ZSW Stuttgart

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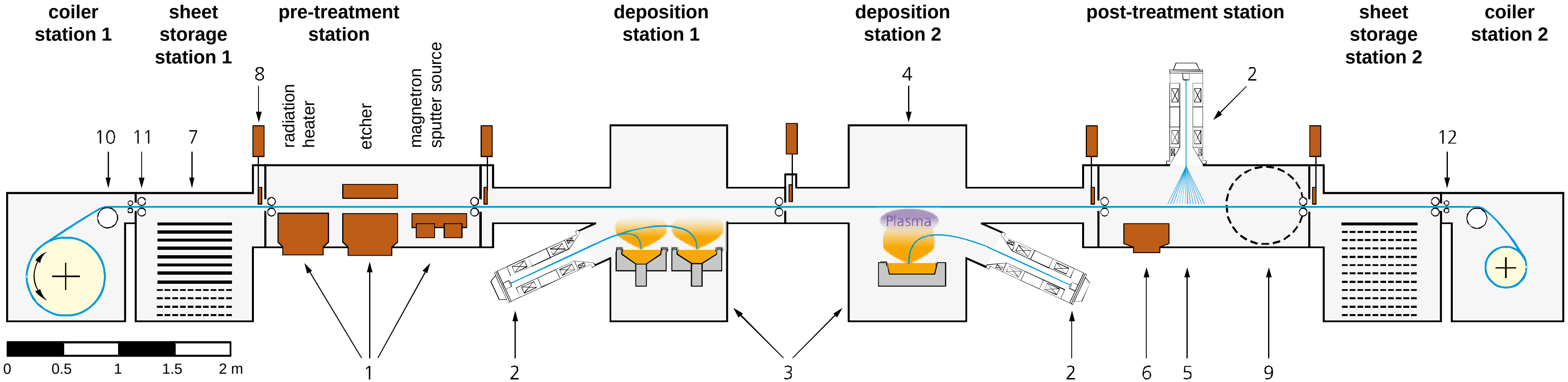
6 Application: Decorative coloured coatings

- Self coloured coatings like TiN
- Corrosion, abrasion and scratch protection
- High deposition rates up to 50 nm/s
- Dense layer structure by plasma activated deposition
- Typical layer thickness about 1.5 µm

6 Application: Decorative coloured coatings

- Interference layers, transparent oxide layers based on TiO_2, Cr_2O_3, ZrO_2, …
- Hard coatings
- Corrosion, abrasion and scratch protection
- High deposition rates up to 3 nm/s
- High layer thickness uniformity (< ± 1.5 %)
- Dense layer structure by pulsed magnetron sputtering
- Adjustable colour as a function of layer thickness
- Typical layer thickness 50 – 300 nm

7 FEP equipment - “MAXI”
In-line Vacuum Deposition Equipment for Sheets and Metal Strips



general
(flexible technological equipment - example)

1...various pre-treatment processes, e.g. heating, etching, deposition of interfacial layers
2...high power electron beam gun
3...various crucibles to evaporate different materials (metals, alloys or compounds)
4...plasma activated deposition process
5...thermal post-treatment, e.g. electron beam heating
6...XRF-thickness-distribution-measurement-system, optical film thickness measurement system by using acromatic light
7...sheets in frames, stacked
8...valves, to decouple pressure
9...turn-over device for double side coating of sheets
10...strip edge control system
11...sealing roll pairs, to decouple pressure
12...squeeze valve, during coil change

sheets

maximum size:	500 mm x 500 mm
maximum weight:	15 kg
speed:	0.001 ... 1.0 m/s

strips

maximum width:	300 mm
minimum thickness:	0.04 mm
maximum thickness:	1.50 mm
speed:	0.001 ... 1.0 m/s

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8 Summary and Outlook

New vacuum coating technologies for metal strips and foils

- Many new coating technologies are on the way
- New plasma processes are developed
- New cooling possibilities developed and proven
- Fundamental research has been performed
- Quality of the deposited layer stacks is promising
- Estimated deposition cost are reasonable
- Some unique large scale laboratory equipment are available at FEP
  e.g. our MAXI line closes the gap between laboratory equipment and industrial plants
- Some new applications are well prepared for upscaling and industrialization
- Main fields of current and future applications:
  Energy (PV, batteries, fuel cells, mirrors, solar thermal, …) and decorative elements

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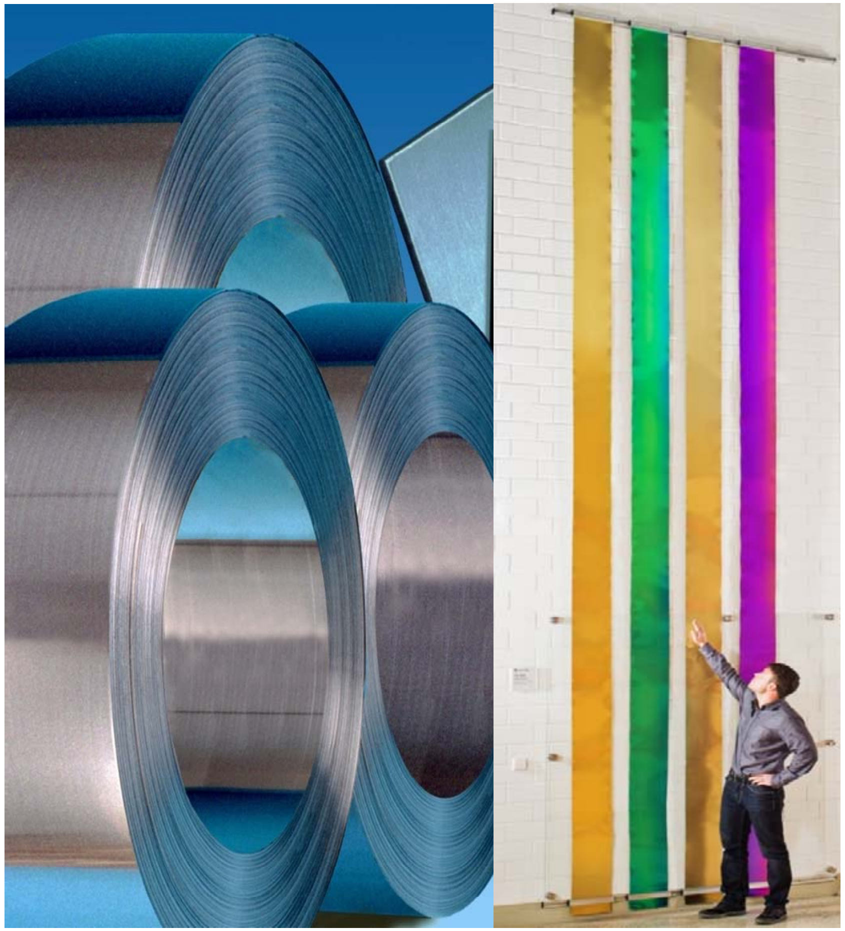
New vacuum coating technologies for metal strips and foils



Ladies and gentlemen
thank you very much
for your kind attention!

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