New vacuum coating technologies for metal strips and foils

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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

Cost: 1 – 5 €-Cent/m²
2 Vacuum in-line pre-treatment by hollow cathode sputter etching

Dynamic etching rate of Cu strip

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
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.
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 \( (1 \times 10^{-4} \text{ mbar}) \) 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.
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

transient a-C:H:Si:O coating deposited onto a stationary steel sheet, precursor HMDSO
4 PECVD process for metal strips

Examples for coatings on metal strips

<table>
<thead>
<tr>
<th>Coating</th>
<th>Precursor</th>
<th>Dep. Rate</th>
<th>Thickness</th>
<th>Hardness</th>
<th>EDX</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-C:H</td>
<td>C(_2)H(_2)</td>
<td>110 nm/s</td>
<td>0.9 µm</td>
<td>40 GPa</td>
<td></td>
</tr>
<tr>
<td>a-C:H:Si:O</td>
<td>HMDSO</td>
<td>50 nm/s</td>
<td>0.7 µm</td>
<td>13 GPa</td>
<td>O/Si 1.0</td>
</tr>
<tr>
<td>a-Si:H</td>
<td>SiH(_4)</td>
<td>3 nm/s</td>
<td>1.6 µm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5 Plasma activated high-rate electron beam PVD
Spotless arc Activated Deposition (SAD process)
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, TiO₂, 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)
5 Plasma activated high-rate electron beam PVD
Hollow cathode arc Activated Deposition (HAD process)
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$_2$O$_3$, TiO$_2$, TiN, CrN, ...) and
C containing hard coatings

- high deposition rates onto large areas
e.g.:
  50 ... 100 nm/s for Al$_2$O$_3$
  100 ... 1 000 nm/s for SiO$_x$

- high ion current density at the substrate
  (10 – 50 mA/cm$^2$)

- 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 (TiO₂)

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

- **Estimated deposition cost 0.1 - 1 €/m²**
  (layer thickness about 10 – 100 nm)
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
- Estimated deposition cost 1 - 20 €/m² (layer thickness about 1 µm)
6 Application: Silicon oxide layers for transparent abrasion and corrosion resistance

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

- High layer hardness (up to 15 GPa) caused by high degree of ionization in vapor and enhanced substrate temperature (Si-rich SiOₓ layers made by combination of PVD and CVD) The layer hardness is higher than hardness of bulk SiO₂ material (10 GPa).

- High hardness caused by special nano composite material structure (nano crystalline Si could be detected in amorphous SiO₂ matrix by XRD)

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

- Good corrosion protection due to dense layer structure.

- Estimation of deposition cost about 10 €/m² for 2 µm thick layers in pilot production (5 €/m² can be estimated for production process.)
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)

- Plasma activated high-rate electron beam deposition (HAD process)

- Successful organic modification to reduce stress
  by introduction of a monomer in the plasma => combination of HAD + PECVD

- In-line SiO$_x$ high-rate deposition at large areas up to 100 nm/s

- Isolating properties depend strongly from excellent surface quality
  - low roughness
  - extremely low surface defect density

- Estimated deposition cost: 3 – 5 Euro / m$^2$ for:
  - 1 m Coating width
  - 1 … 2 µm layer thickness
  - 50 … 100 nm/s stationary deposition rate
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

<table>
<thead>
<tr>
<th></th>
<th>static rate</th>
<th>10</th>
<th>20</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>dynamic rate</td>
<td>nm$^*$m/min</td>
<td>400</td>
<td>800</td>
<td>2000</td>
</tr>
<tr>
<td>micro hardness</td>
<td>GPa</td>
<td>6</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>refractive index</td>
<td>n @ 550 nm</td>
<td>1.50</td>
<td>1.49</td>
<td>1.48</td>
</tr>
<tr>
<td>absorption</td>
<td>k @ 550 nm</td>
<td>$1 \times 10^{-3}$</td>
<td>$5 \times 10^{-4}$</td>
<td>$5 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
6 Application: Zirconium oxide coatings for fuel cells

Principle of a High-temperature solid oxide fuel cell (SOFC)
type: electrical conduction by oxygen ions

Operation temperature: 600 … 1000°C
6 Application: Zirconium oxide coatings for fuel cells

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

Deposition of Yttrium stabilized Zirconium Oxide by plasma activated high-rate electron beam evaporation on thin stainless steel foil

• Deposition rate 30 - 40 nm/s
• HAD process with ceramic evaporation material or reactive SAD process with metallic evaporation material possible
• Additional plasma enhancement by pulsed Bias voltage
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
Electron beam power: 15 kW
Deposition rate: 40 nm/s
Pulsed Bias: - 120 V
Yttrium content: 5.2 at-%

SAD process
Electron beam power: 32 kW
Deposition rate: 30 nm/s
Pulsed Bias: - 120 V
Yttrium content: 5.4 at-%
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
6 Application: Mo layers for photo voltaic application

Deposition of molybdenum layers with plasma activated electron beam evaporation (SAD process) allows optimized layer structures at high rates up to 250 nm/s
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
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
- Estimated deposition cost 5 - 10 €/m² (layer thickness about 1.5 μm)
6 Application: Decorative coloured coatings

- Interference layers, transparent oxide layers based on TiO₂, Cr₂O₃, ZrO₂, ...
- 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
- Estimated deposition cost 2 - 10 €/m² (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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FEP equipment - “MAXI”
In-line Vacuum Deposition Equipment for Sheets and Metal Strips
8 Summary

Overview of FEP’s research and development work, products and services

• Feasibility studies, reflection on economical aspects

• Technology developments, product developments, scaling up and pre-production qualifications in close cooperation with our partners

• Pilot production in nearly industrial scale

• Support for the realization of industrial and research coating lines e.g. key components for research and production; consisting of hardware, technology and know-how transfer

• Key components for advanced coating systems

• After sales service, spare parts, as well as on going process consulting
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
New vacuum coating technologies for metal strips and foils

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

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