Study of structure and defects in Pd films and Pd-Mg multi-layers loaded with hydrogen

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Hydrogen in Pd and Mg

**Palladium**
- High density: 12.023 g/cm³
- Low hydrogen capacity: 0.94 wt.%
- Fast hydrogen absorption: 0.02 bar H₂ / 20°C

**Magnesium**
- Low density: 1.738 g/cm³
- High hydrogen capacity: 7.66 wt.%
- Slow hydrogen absorption: 1 bar H₂ / 300°C

1. **Pd thin films**
   - Hydrogen absorption in Pd films
   - Formation of hydrogen-induced defects

2. **Pd-Mg multi-layers**
   - Hydrogen distribution via Pd
   - Interaction of Pd and Mg atoms
   - Nanocrystalline to epitaxial structure
   - Pd/Mg composition control
RF magnetron sputtering

Pd films
- thickness ~1.4 μm
- single-crystalline substrates
  - sapphire (0001)
  - Si (100)
- deposition temperature
  - 20°C
  - 500°C
- single-layer deposition

Pd-Mg multi-layers
- thickness ~1.3 μm
- amorphous substrates
  - fused silica (FS)
- deposition temperature
  - 20°C
- multi-layer deposition

- base pressure 10^{-5} Pa
- deposition pressure 3 Pa (Ar atmosphere)
- 4 magnetron targets
Slow positron beam SPONSOR

SPONSOR in HZDR
- $^{22}$Na source with W moderator
- 0.03 – 35 keV positron energies
- S and W line-shape parameters
- 2D-coincidence measurement

VEPFIT modelling
- S(E) curves fitting
- linear parameters
  - S parameter of a layer
- non-linear parameters
  - diffusion length $L_+$
  - layer thickness

CDB
- single positron energy measurement
- resolution function with 1.8 keV FWHM
- CDB ratio curves
Pd films

- Pd (111) texture
- deposition at room temperature → nanocrystalline film
- deposition at elevated temperature → oriented polycrystalline film → Pd$_2$Si phase precipitation

nanocrystalline Pd sapphire substrate, RT

nanocrystalline Pd Si substrate, RT

oriented polycrystalline Pd sapphire substrate, 500°C
Virgin Pd films

2-layer VEPFIT model
- Pd film + substrate
  - S parameter of the Pd layer
  - positron diffusion length $L_+$

### nanocrystalline Pd
- positron trapping at grain boundaries
- smaller grains $\rightarrow$ shorter positron diffusion length

### oriented polycrystalline Pd
- positron trapping at misfit dislocations
- increase of positron diffusion length
- decrease of the S parameter

### nanocrystalline Pd + Pd$_2$Si precipitates
- positron trapping at grain boundaries
- larger grains $\rightarrow$ longer positron diffusion length
- enhanced S parameter $\rightarrow$ Pd$_2$Si precipitates
- uniform distribution of Pd$_2$Si particles

<table>
<thead>
<tr>
<th>temperature</th>
<th>substrate</th>
<th>S</th>
<th>$L_+$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>sapphire</td>
<td>0.5382(1)</td>
<td>16.2(3)</td>
</tr>
<tr>
<td>RT</td>
<td>Si</td>
<td>0.5429(2)</td>
<td>29.9(6)</td>
</tr>
<tr>
<td>500°C</td>
<td>sapphire</td>
<td>0.5167(2)</td>
<td>71.6(7)</td>
</tr>
<tr>
<td>500°C</td>
<td>Si</td>
<td>0.5577(2)</td>
<td>32.5(9)</td>
</tr>
<tr>
<td>1000°C / 2 h</td>
<td>bulk Pd</td>
<td>0.49807</td>
<td>151</td>
</tr>
</tbody>
</table>
Hydrogen gas loading of Pd films

- **Hydrogen loading**: 60 kPa H\(_2\) for 12 h, RT
- **Loading cycle**
- **Hydrogen unloading**: 10\(^{-4}\) Pa vacuum for 12 h, RT

\[ \alpha\text{-Pd to } \alpha'\text{-PdH phase transformation} \]
\[ \text{lattice expansion and plastic deformation} \]
\[ \text{formation and movement of dislocations} \]
\[ \text{anisotropic expansion of Pd films} \]
\[ \text{stress accumulation in the film} \]
\[ \text{buckling and detachment of the film} \]

**Ex-situ measurement**

- **Virgin Pd films vs 1 loading cycle vs 10 loading cycles**

- **Pd05 (500°C)**: sapphire Si

- **Buckling already after 1 loading cycle**
- **Adhesion improvement by Pd\(_2\)Si phase**
Hydrogen-loaded Pd films (RT deposited)

- **nanocrystalline films** – 2 competitive processes:
  - **hydrogen trapping at open volume defects** → S parameter decreased
  - **formation of hydrogen-induced dislocations** → S parameter increased

- **additional processes:**
  - artificial prolongation of diffusion length due to non-uniform distribution of defects → dislocation glide during buckling
  - 1 loading-unloading cycle → buckling
  - 10 loading-unloading cycles → detachment
Hydrogen-loaded Pd films (500°C deposited)

- Oriented polycrystalline film
  - 1 loading cycle
    → formation of H-induced dislocations
    → S parameter increased, L+ decreased
  - 10 loading cycles
    → H trapping in dislocations
    → S parameter unchanged, L+ decreased

- Nanocrystalline film + Pd2Si precipitates
  - Same behavior as for nanocrystalline films
    → H trapping at open volumes
    → H-induced dislocations
  - Film adhesion improved
    → Film attached after 10 loading cycles
Pd-Mg multi-layers

**PdMg1** (3 layers)
Pd (500 nm) + Mg (400 nm) + Pd (400 nm)

**PdMg2** (13 layers)
7 x Pd (100 nm) + 6 x Mg (100 nm)

**PdMg3** (34 layers)
Pd (100 nm) + 18 x Mg (20 nm) + 15 x Pd (20 nm)

- Pd (111) and Mg (0001) texture
- Nanocrystalline columnar structure
Virgin Pd-Mg multi-layers

- Pd and Mg reference
  - bulk Pd and Mg
  - nanocrystalline Pd and Mg film

  bare FS substrate measurement

  2 linear dependences in S-W plot
  - Pd surface + Pd layer (a)
  - Pd/Mg layers (+ FS substrate) (b) + (c)

3 positron states superpositions
a) annihilation on Pd surface and in the top Pd layer
b) annihilation in Pd and Mg inner layers
c) annihilation in Pd/Mg layers and in FS substrate
Virgin Pd-Mg multi-layers

4-layer VEPFIT model

<table>
<thead>
<tr>
<th>sample</th>
<th>layer</th>
<th>S</th>
<th>L+ (nm)</th>
<th>thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdMg1</td>
<td>Mg middle</td>
<td>0.719(7)</td>
<td>21(6)</td>
<td>395(10)</td>
</tr>
<tr>
<td></td>
<td>Pd bottom</td>
<td>0.550(2)</td>
<td>68(11)</td>
<td>530(60)</td>
</tr>
<tr>
<td></td>
<td>Pd top</td>
<td>0.5326(7)</td>
<td>6.3(2)</td>
<td>44.1(9)</td>
</tr>
<tr>
<td>PdMg2</td>
<td>Mg sub-top</td>
<td>0.618(3)</td>
<td>30(5)</td>
<td>180(20)</td>
</tr>
<tr>
<td></td>
<td>Pd/Mg mixed</td>
<td>0.5842(4)</td>
<td>3(17)</td>
<td>1070(30)</td>
</tr>
<tr>
<td>PdMg3</td>
<td>Mg sub-top</td>
<td>0.596(2)</td>
<td>10(20)</td>
<td>40(40)</td>
</tr>
<tr>
<td></td>
<td>Pd/Mg mixed</td>
<td>0.6225(3)</td>
<td>17(2)</td>
<td>1300(100)</td>
</tr>
</tbody>
</table>

*FS parameters fixed from bare FS measurement

- positron trapping at grain boundaries → enhanced S parameter → shorter diffusion length
- higher fraction of GBs in Pd compared to Mg
- larger grains in bottom Pd compared to top Pd
- effective narrowing of Pd layer due to higher positron affinity of Mg compared to Pd
- decrease of S parameter of Mg layer due to annihilations with Pd
- lower S parameter near substrate due to different grain sizes
Hydrogen loaded Pd-Mg multi-layers

**hydrogen loading**
4 kPa H$_2$ for 2 h, RT

**hydrogen unloading**
10$^{-3}$ Pa vacuum for 2 h, RT

- moderate loading conditions
- phase transformation $\alpha$-Pd to $\alpha'$-PdH
- top Pd layer transformed into hydride
- Mg layers and inner Pd layers not transformed

- buckling of all multi-layers
  $\rightarrow$ dislocations in all Pd/Mg layers
  $\rightarrow$ stress released by dislocation movement

- adhesion properties
  $\rightarrow$ strong Pd – Mg adhesion
  $\rightarrow$ weak Pd – FS adhesion
Hydrogen loaded Pd-Mg multi-layers

• S parameter increased in all layers
  → formation of hydrogen-induced dislocations in the whole volume
• top Pd layer hydrogenated
  → hydrogen trapping at open volumes (lower S)
  → hydrogen-induced dislocations (lower $L_+$)
• reduced density of dislocations in near substrate layers
  → decreased S parameter
  → artificially prolonged diffusion length
  → glide of dislocations to the “bottom surface”
• layer thicknesses same as in virgin multi-layers
• same 2 linear dependences in S-W plot
CDB measurement

- **PdMg3 multi-layers**
  - virgin
  - hydrogen-loaded
  - annealed up to 450°C
- measurement at 9 keV positron energy
- 10 – 12 Pd/Mg layers covered
- 200 nm implantation, 250 nm FWHM

- dominant annihilations with Pd electrons
- open-volume defects decorated with Pd → improvement of hydrogen absorption???
- annealing of multi-layer → diffusion of Pd into Mg layers

<table>
<thead>
<tr>
<th>Fraction of Pd</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>uniform Pd distribution</td>
<td>0.61</td>
</tr>
<tr>
<td>virgin sample</td>
<td>0.76</td>
</tr>
<tr>
<td>hydrogen-loaded sample</td>
<td>0.76</td>
</tr>
<tr>
<td>annealed sample (up to 450°C)</td>
<td>0.85</td>
</tr>
</tbody>
</table>
Conclusions

**Pd films**

- nanocrystalline Pd → positron trapping at grain boundaries
- oriented polycrystalline Pd → positron trapping at misfit dislocations
- hydrogen loading → formation of H-induced dislocations
  → H trapping at open volumes
  → dislocation glide during buckling

- Pd$_2$Si precipitates → uniform distribution in the film
  → improved adhesion to the substrate

**Pd-Mg multi-layers**

- nanocrystalline structure → positron trapping at grain boundaries
- hydrogen loading → top Pd layer transformed into hydride
  → H-induced dislocations in the whole volume
  → dislocation glide during buckling
  → strong Pd-Mg adhesion
- annihilation sites → open volumes decorated with Pd atoms
  ⇒ improved H absorption???
  → diffusion of Pd into Mg layers by annealing
Thank you for your attention.