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

P. Hruška[1,2], J. Čížek[1], O. Melikhova[1], F. Lukáč[1,3],
C. Correa[1,2], M.O. Liedke[4], W. Anwand[4], L. Fekete[2] and J. Bulíř[2]

FACULTY OF MATHEMATICS AND PHYSICS
Charles University

FZÚ

IPP AS CR

HZDR
HELMHOLTZ ZENTRUM DRESDEN ROSSENDORF

18th International Conference on Positron Annihilation

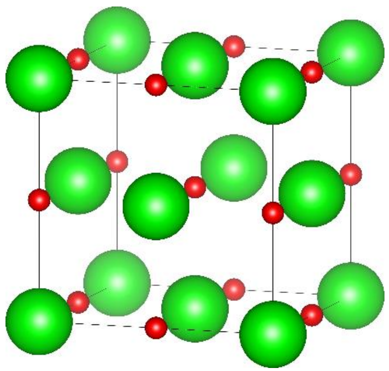
August 23, 2018, Orlando, Florida, USA

# Hydrogen in Pd and Mg

## Palladium

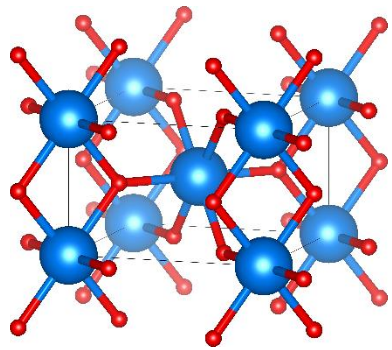
| | | |
|---|---|---|
| – | high density<br>low hydrogen capacity | 12.023 g/cm$^3$<br>0.94 wt.% |
| + | fast hydrogen absorption | 0.02 bar $H_2$ / 20°C |

PdH



## Magnesium

| | | |
|---|---|---|
| + | low density<br>high hydrogen capacity | 1.738 g/cm$^3$<br>7.66 wt.% |
| – | slow hydrogen absorption | 1 bar $H_2$ / 300°C |



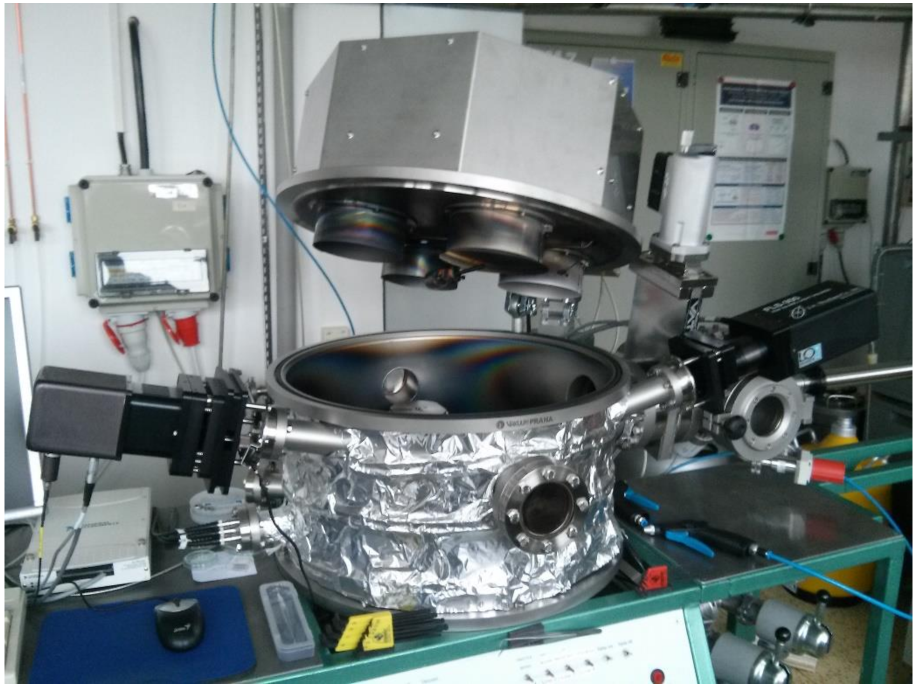
$MgH_2$

1. Pd thin films
   → hydrogen absorption in Pd films
   → formation of hydrogen-induced defects

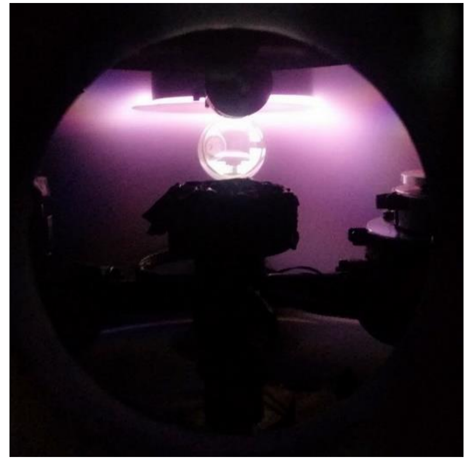
2. Pd-Mg multi-layers
   → hydrogen distribution via Pd
   → interaction of Pd and Mg atoms

thin films
→ nanocrystalline to epitaxial structure
→ Pd/Mg composition control

# RF magnetron sputtering



- base pressure $10^{-5}$ Pa
- deposition pressure 3 Pa (Ar atmosphere)
- 4 magnetron targets



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

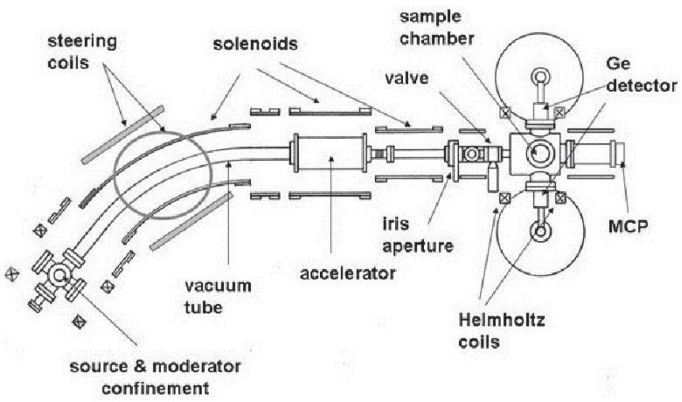
- thickness ~1.3 μm
- amorphous substrates
  → fused silica (FS)
- deposition temperature
  → 20°C
- multi-layer deposition

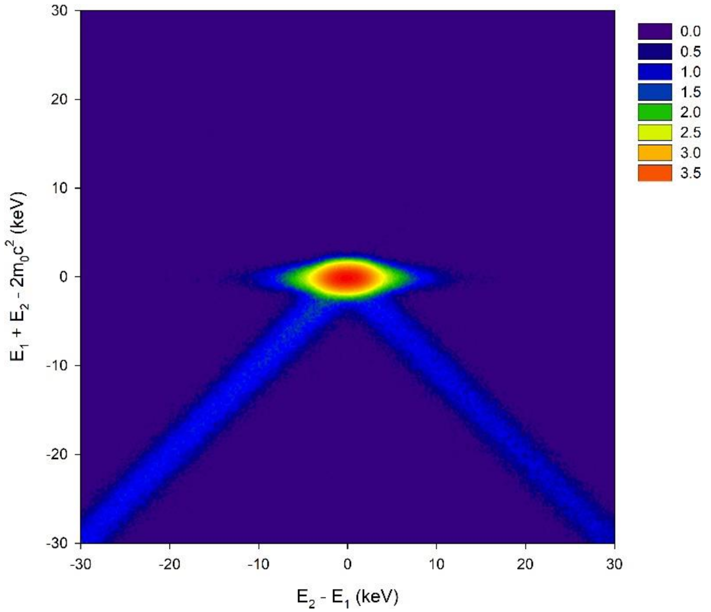
# Slow positron beam SPONSOR

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

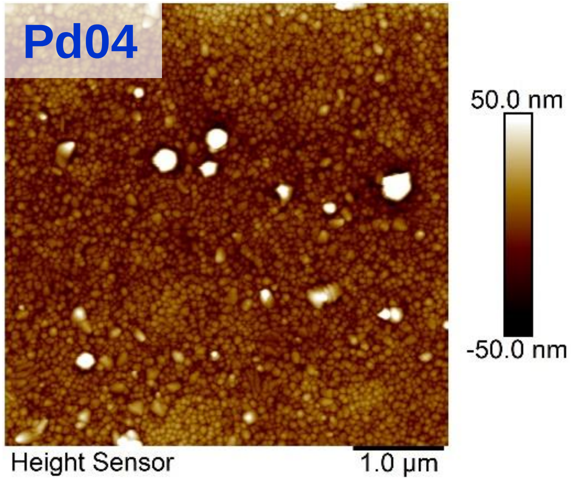
CDB

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

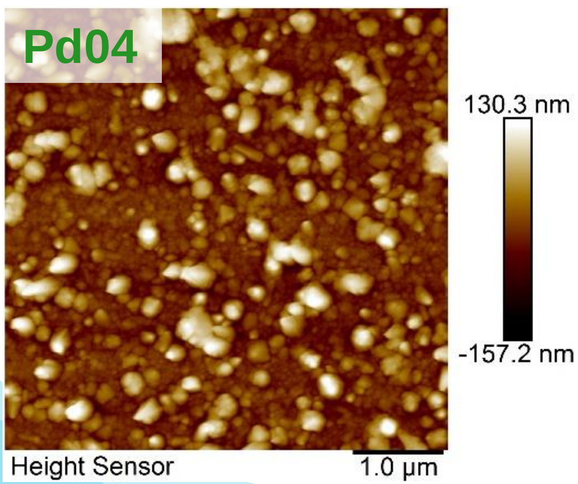
# Pd films

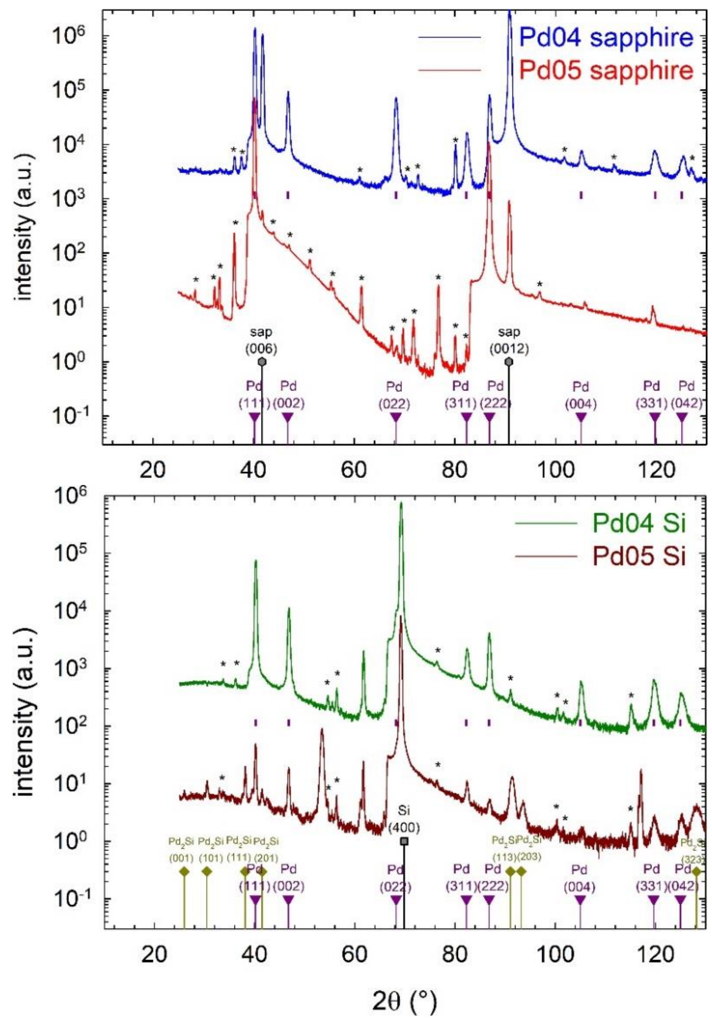
- Pd (111) texture
- deposition at **room temperature**
  → nanocrystalline film
- deposition at **elevated temperature**
  → oriented polycrystalline film
  → $Pd_2Si$ phase precipitation

nanocrystalline Pd
**sapphire** substrate, **RT**

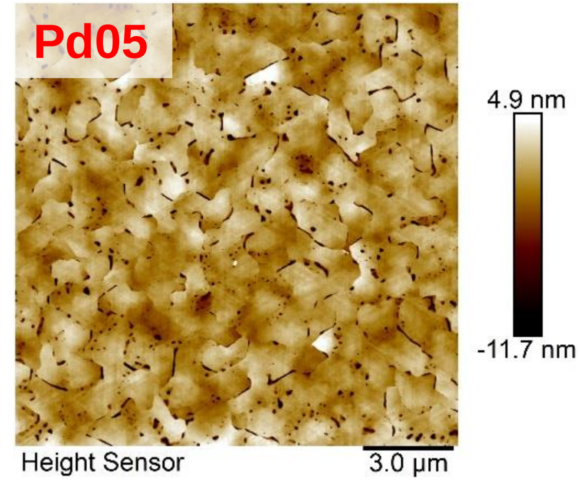



nanocrystalline Pd
**Si** substrate, **RT**

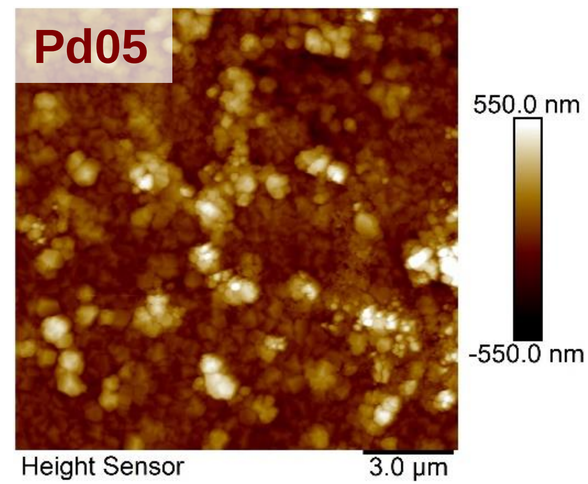


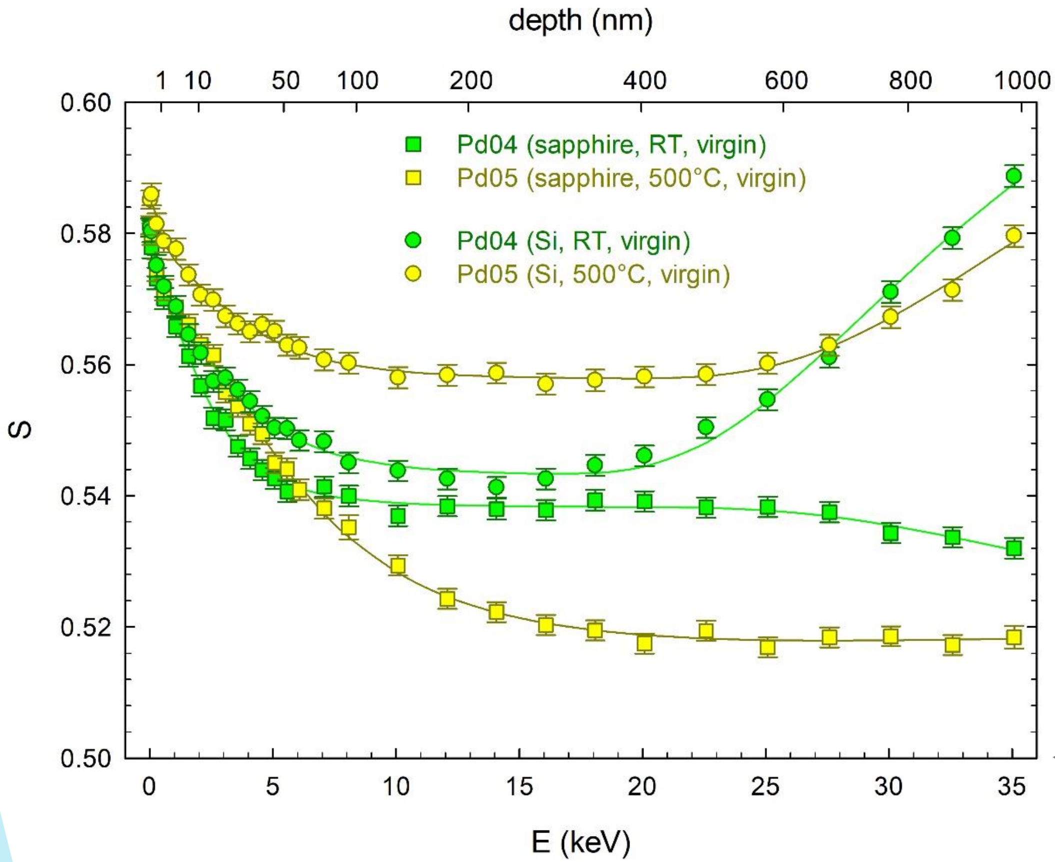

oriented polycrystalline Pd
**sapphire** substrate, **500°C**




nanocrystalline Pd + $Pd_2Si$
**Si** 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** (green square, green circle)
- positron trapping at grain boundaries
- smaller grains → shorter positron diffusion length

**oriented polycrystalline Pd** (yellow square)
- positron trapping at misfit dislocations
- increase of positron diffusion length
- decrease of the S parameter

**nanocrystalline Pd + $Pd_2Si$ precipitates** (yellow circle)
- positron trapping at grain boundaries
- larger grains → longer positron diffusion length
- enhanced S parameter → $Pd_2Si$ precipitates
- uniform distribution of $Pd_2Si$ particles

| | temperature | substrate | S | $L_+$ (nm) |
|---|---|---|---|---|
| green square | RT | sapphire | 0.5382(1) | 16.2(3) |
| green circle | RT | Si | 0.5429(2) | 29.9(6) |
| yellow square | 500°C | sapphire | 0.5167(2) | 71.6(7) |
| yellow circle | 500°C | Si | 0.5577(2) | 32.5(9) |
| | 1000°C / 2 h | bulk Pd | 0.49807 | 151 |

# Hydrogen gas loading of Pd films

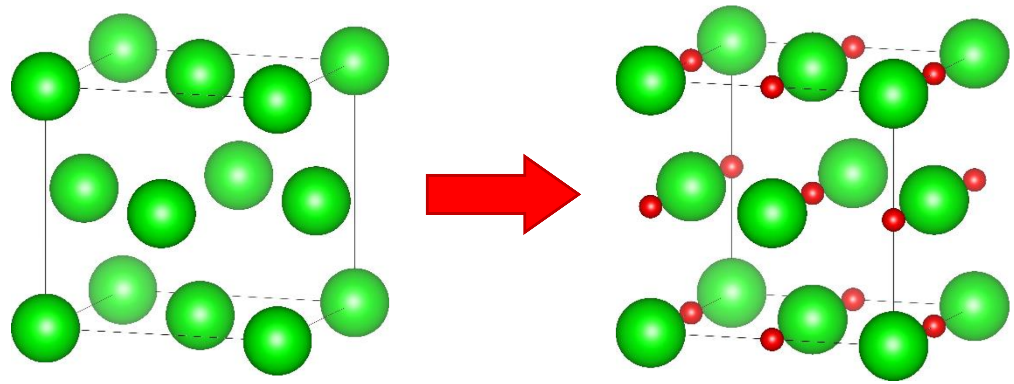
**hydrogen loading**
60 kPa $H_2$ for 12 h, RT

**loading cycle**

**hydrogen unloading**
$10^{-4}$ Pa vacuum for 12 h, RT

hydrogen loading
↓
α-Pd to α'-PdH phase transformation
↓
lattice expansion and plastic deformation
↓
formation and movement of dislocations
↓
anisotropic expansion of Pd films
↓
stress accumulation in the film
↓
buckling and detachment of the film

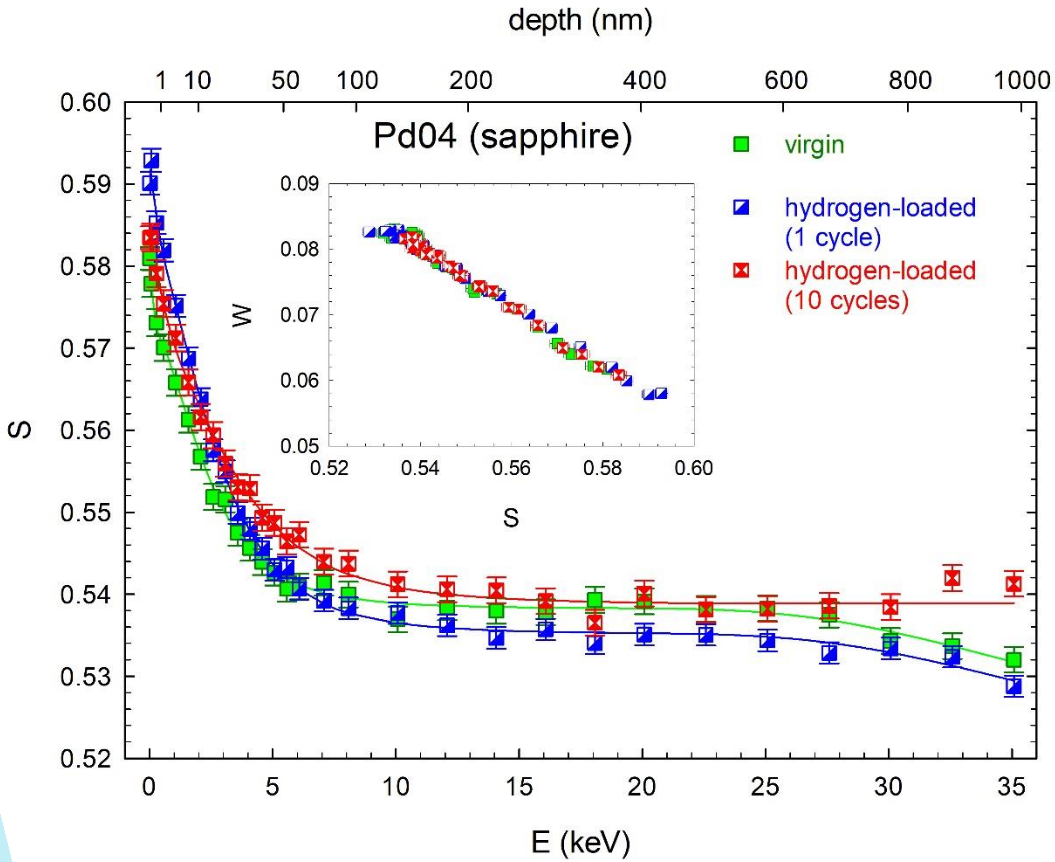
ex-situ measurement
**virgin** Pd films vs **1 loading cycle** vs **10 loading cycles**

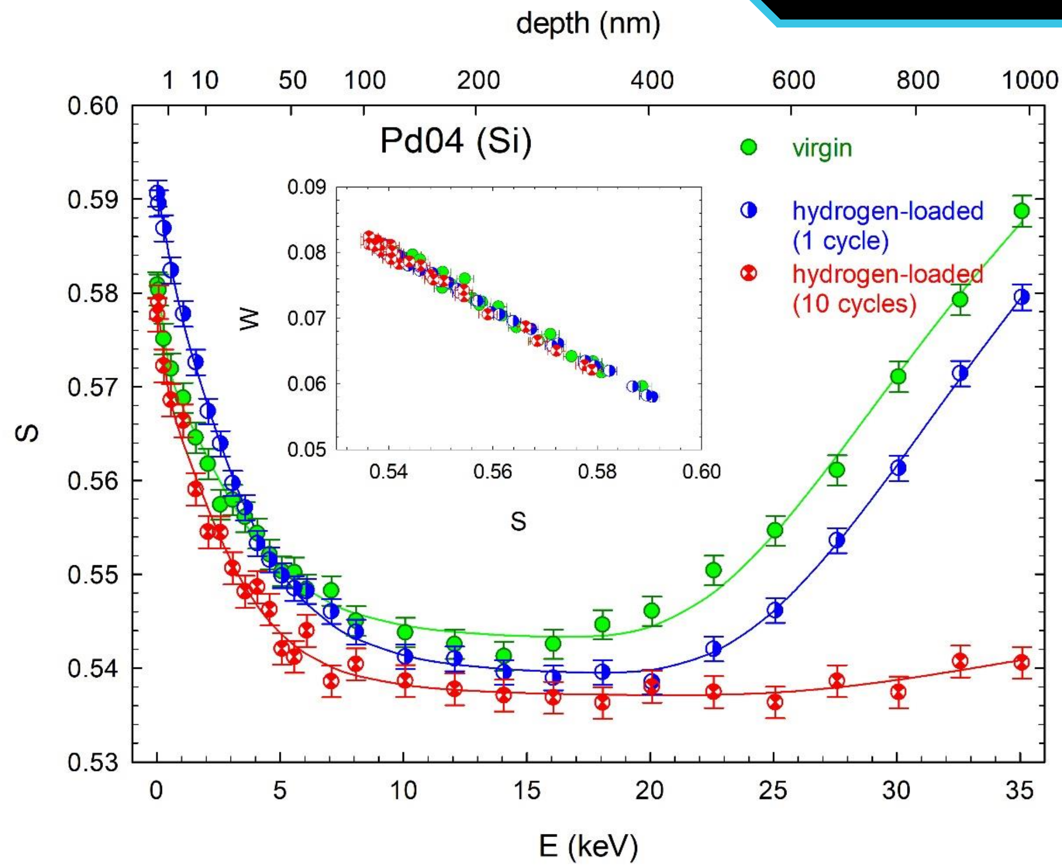


α-Pd α'-PdH


- buckling already after 1 loading cycle
- adhesion improvement by $Pd_2Si$ phase

# Hydrogen-loaded Pd films (RT deposited)



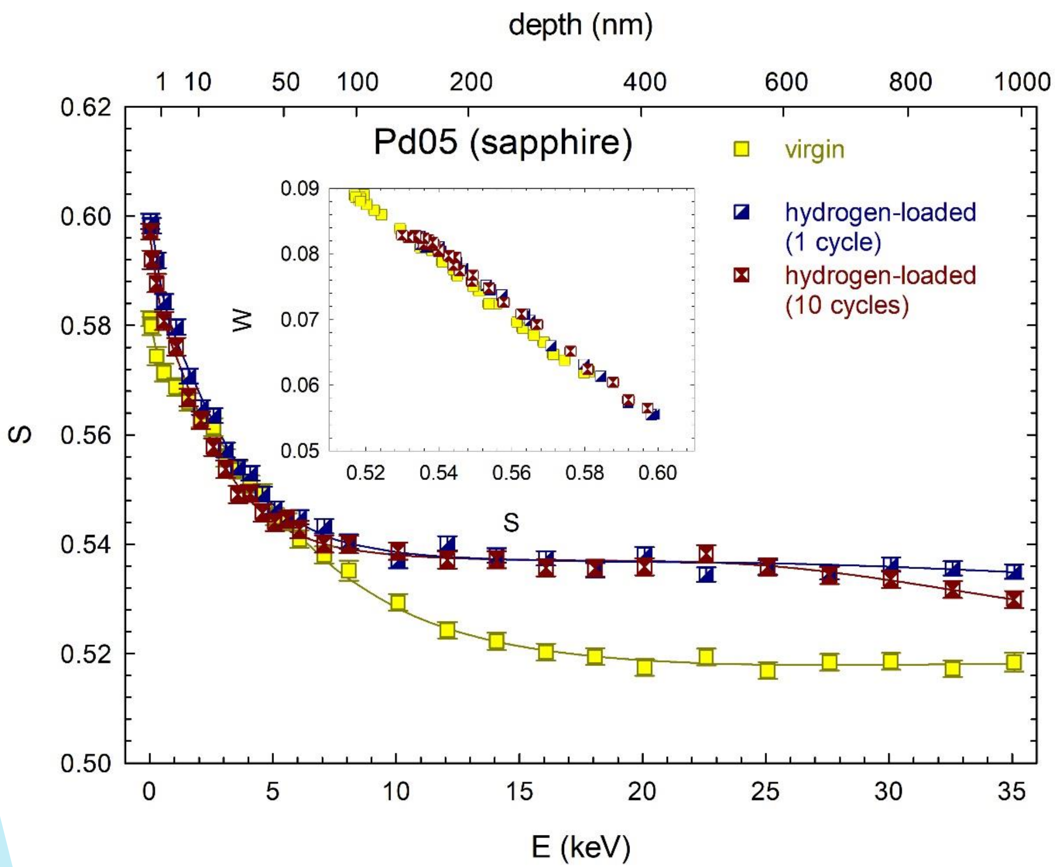

nanocrystalline films – 2 competitive processes:

- **hydrogen trapping at open volume defects**
  → S parameter decreased
- **formation of hydrogen-induced dislocations**
  → S parameter increased

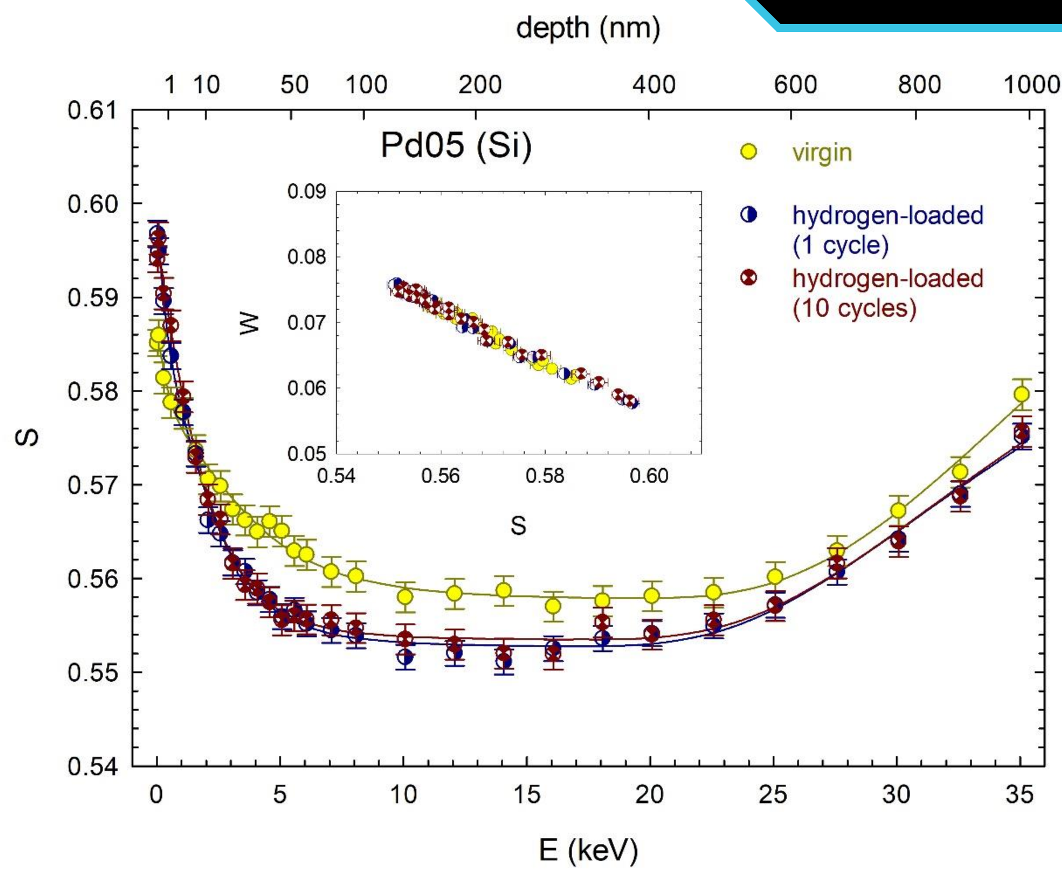
additional processes:

- 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




nanocrystalline film + $Pd_2Si$ precipitates

- 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

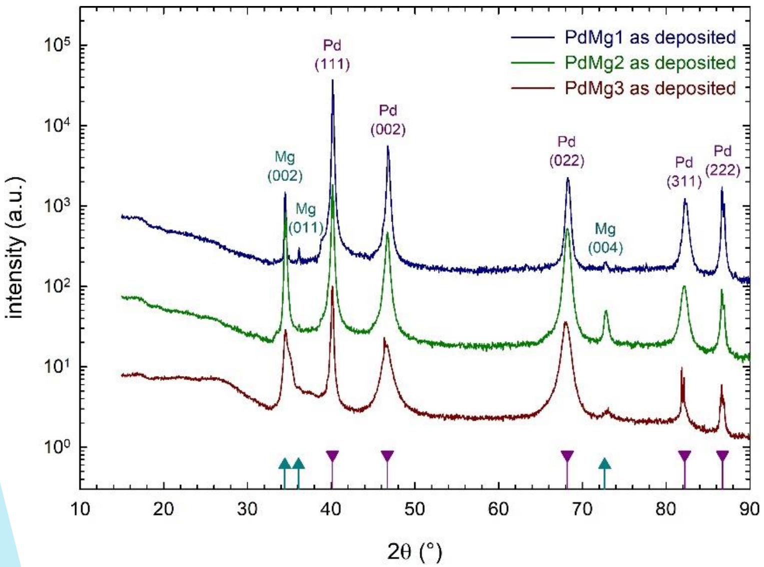
- same behavior as for nanocrystalline films
  - → H trapping at open volumes
  - → H-induced dislocations
- film adhesion improved
  - → film attached after 10 loading cycles

# Pd-Mg multi-layers

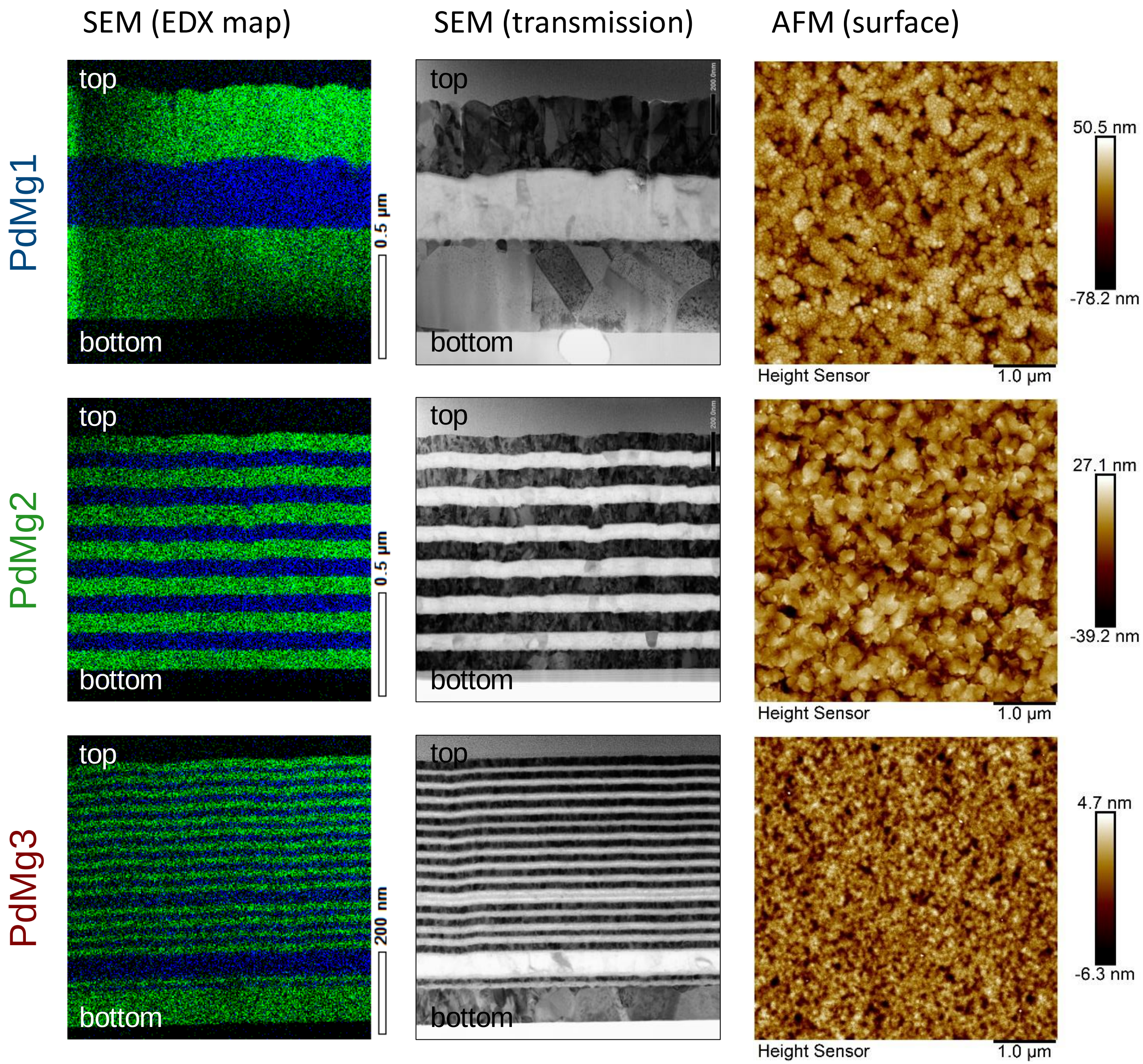
## PdMg1 (3 layers)
Pd (500 nm) + Mg (400 nm) + Pd (400 nm)

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

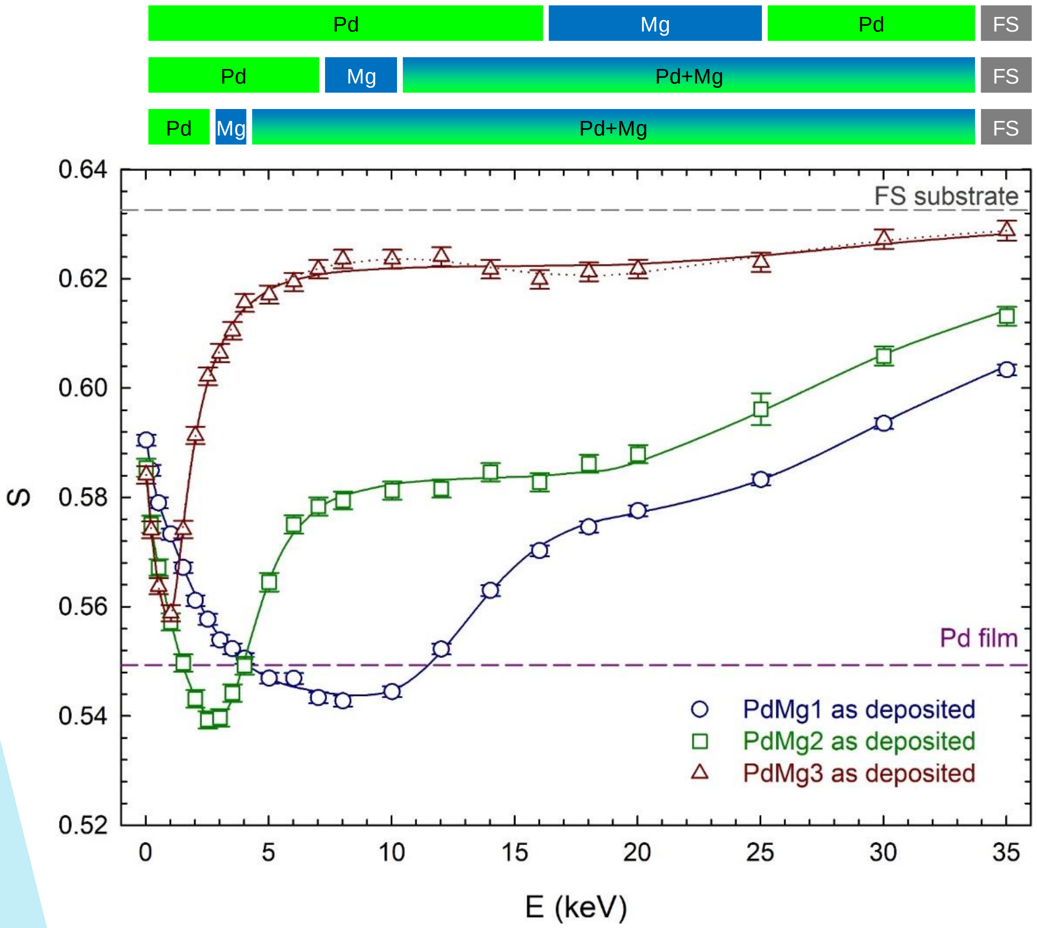
## PdMg3 (34 layers)
Pd (100 nm) + 18 x Mg (20 nm) + 15 x Pd (20 nm)




- Pd (111) and Mg (0001) texture
- nanocrystalline columnar structure



# Virgin Pd-Mg multi-layers



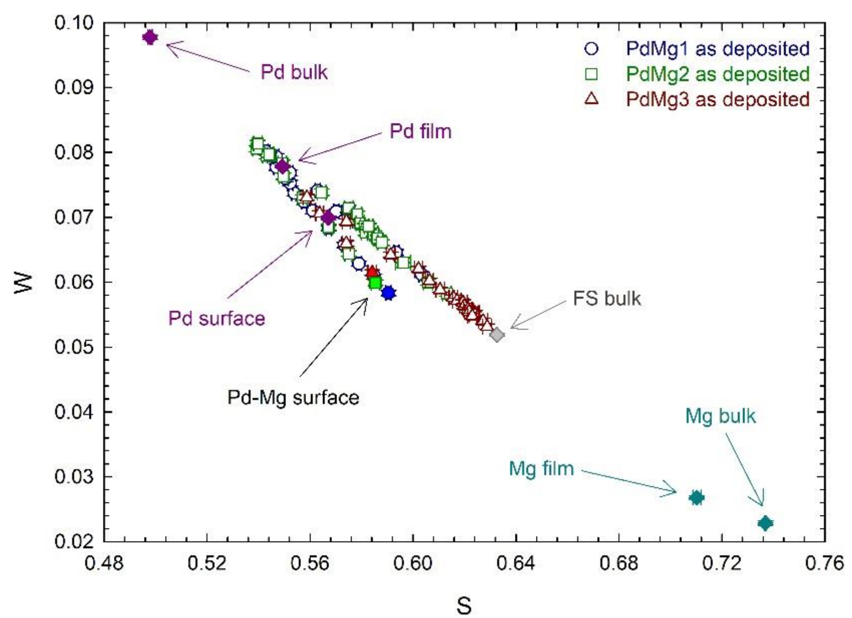

Pd and Mg reference

- bulk Pd and Mg
- nanocrystalline Pd and Mg film

bare FS substrate measurement

2 linear dependences in S-W plot

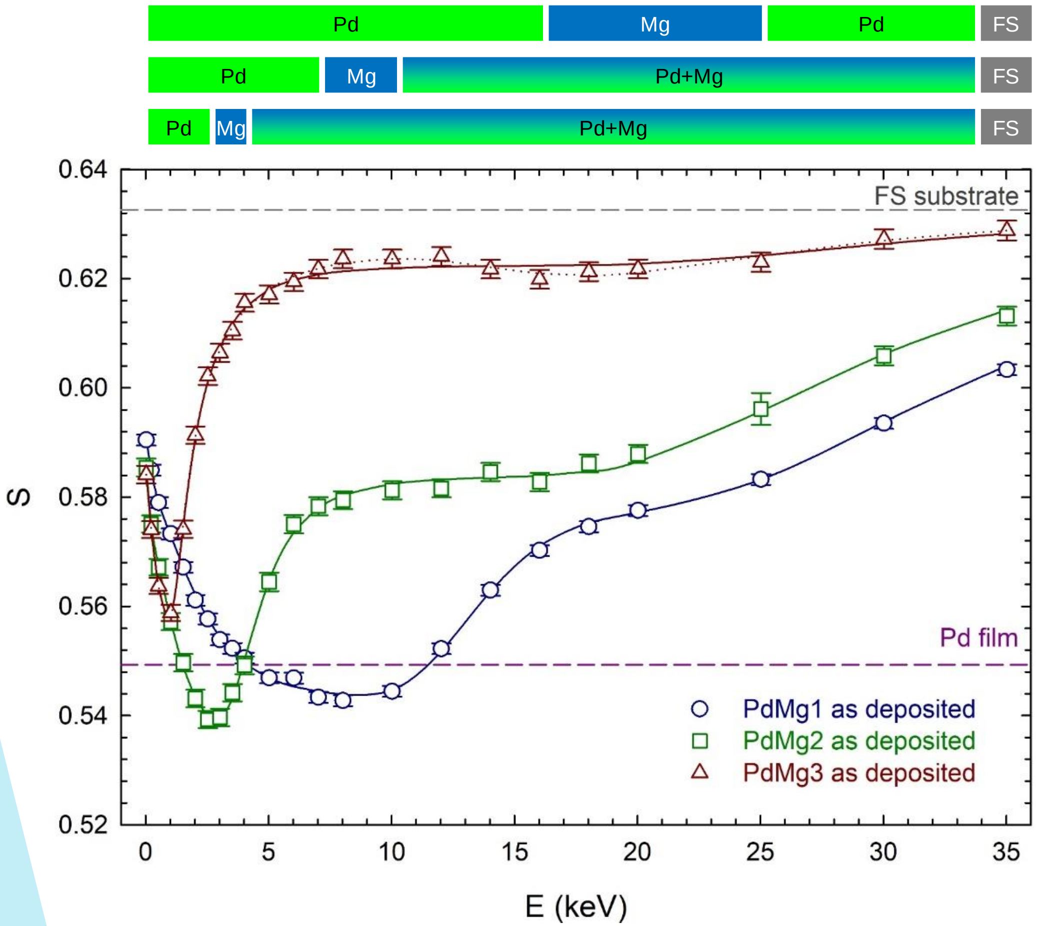
- Pd surface + Pd layer (a)
- Pd/Mg layers (+ FS substrate) (b) + (c)




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




- 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

4-layer VEPFIT model

| sample | layer | S | L+ (nm) | thickness (nm) |
|---|---|---|---|---|
| **PdMg1** | Pd top | 0.5427(4) | 14.3(5) | 352(8) |
| | Mg middle | 0.719(7) | 21(6) | 395(10) |
| | Pd bottom | 0.550(2) | 68(11) | 530(60) |
| **PdMg2** | Pd top | 0.5326(7) | 6.3(2) | 44.1(9) |
| | Mg sub-top | 0.618(3) | 30(5) | 180(20) |
| | Pd/Mg mixed | 0.5842(4) | 3(17) | 1070(30) |
| **PdMg3** | Pd top | 0.476(8) | 5.7(3) | 5.8(2) |
| | Mg sub-top | 0.596(2) | 10(20) | 40(40) |
| | Pd/Mg mixed | 0.6225(3) | 17(2) | 1300(100) |

*FS parameters fixed from bare FS measurement

- 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

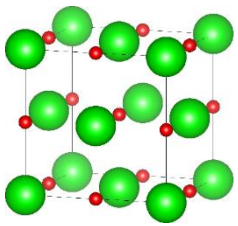
# Hydrogen loaded Pd-Mg multi-layers

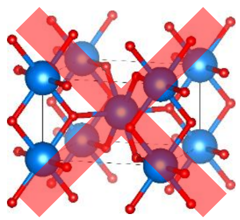
**hydrogen loading**
4 kPa $H_2$ for 2 h, RT

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

- moderate loading conditions
- phase transformation $\alpha$-Pd to $\alpha$'-PdH

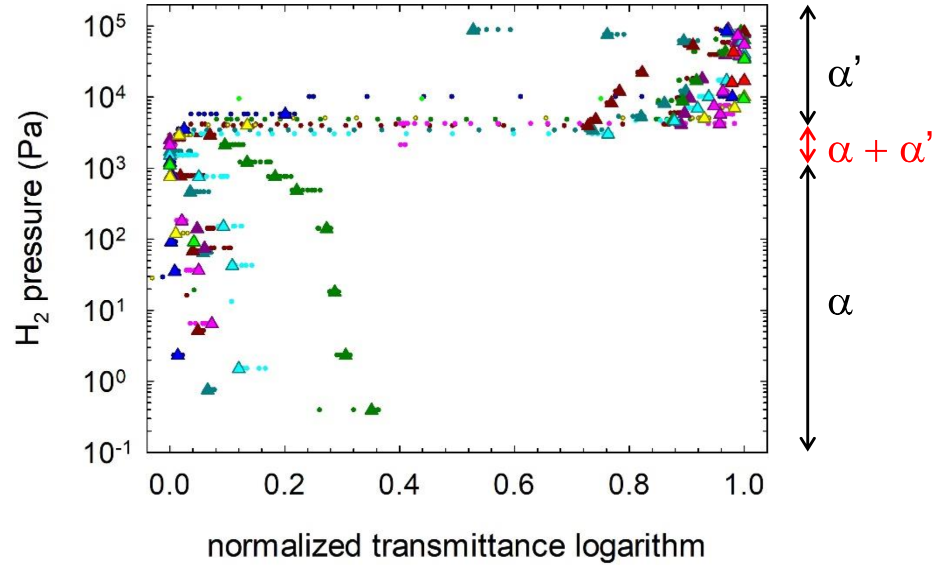
- top Pd layer transformed into hydride
- Mg layers and inner Pd layers not transformed

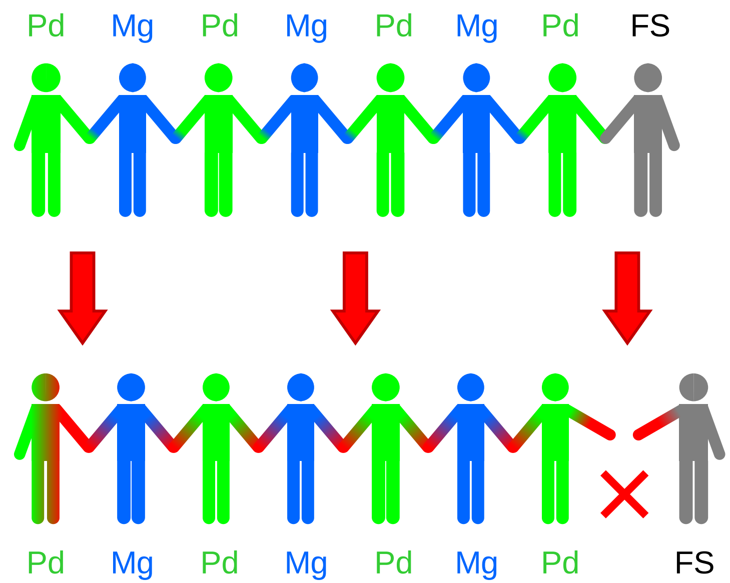




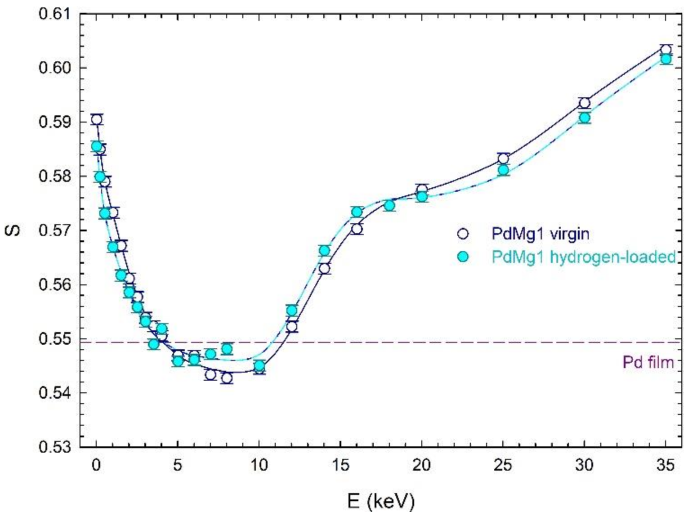
- buckling of all multi-layers
  → dislocations in all Pd/Mg layers
  → stress released by dislocation movement

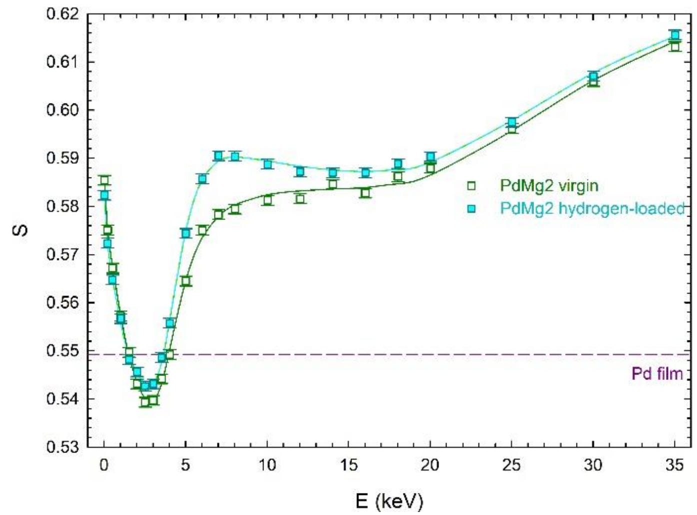
- adhesion properties
  → strong Pd – Mg adhesion
  → weak Pd – FS adhesion

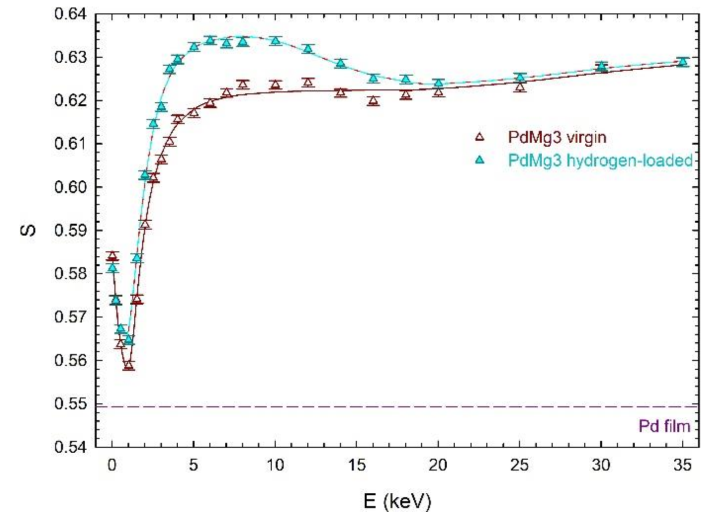


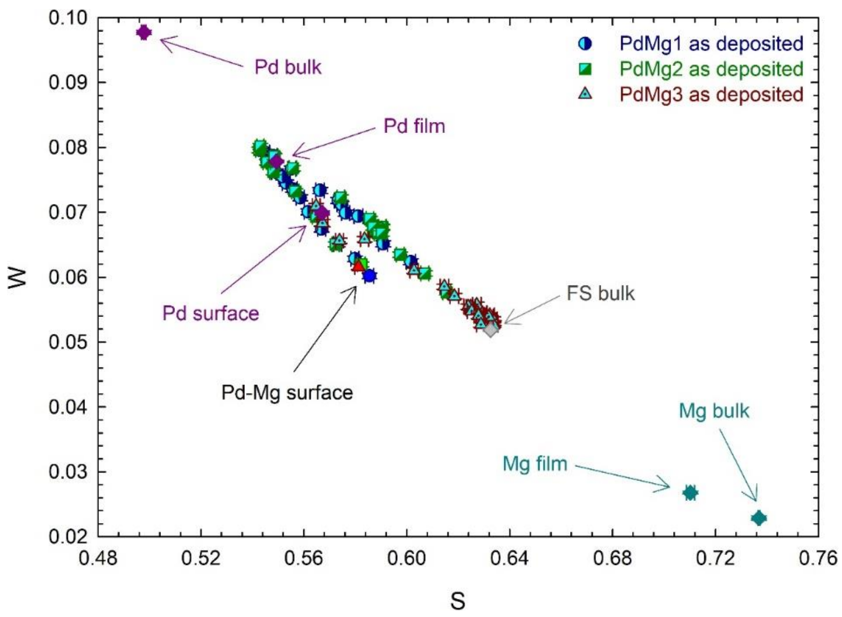
# Hydrogen loaded Pd-Mg multi-layers



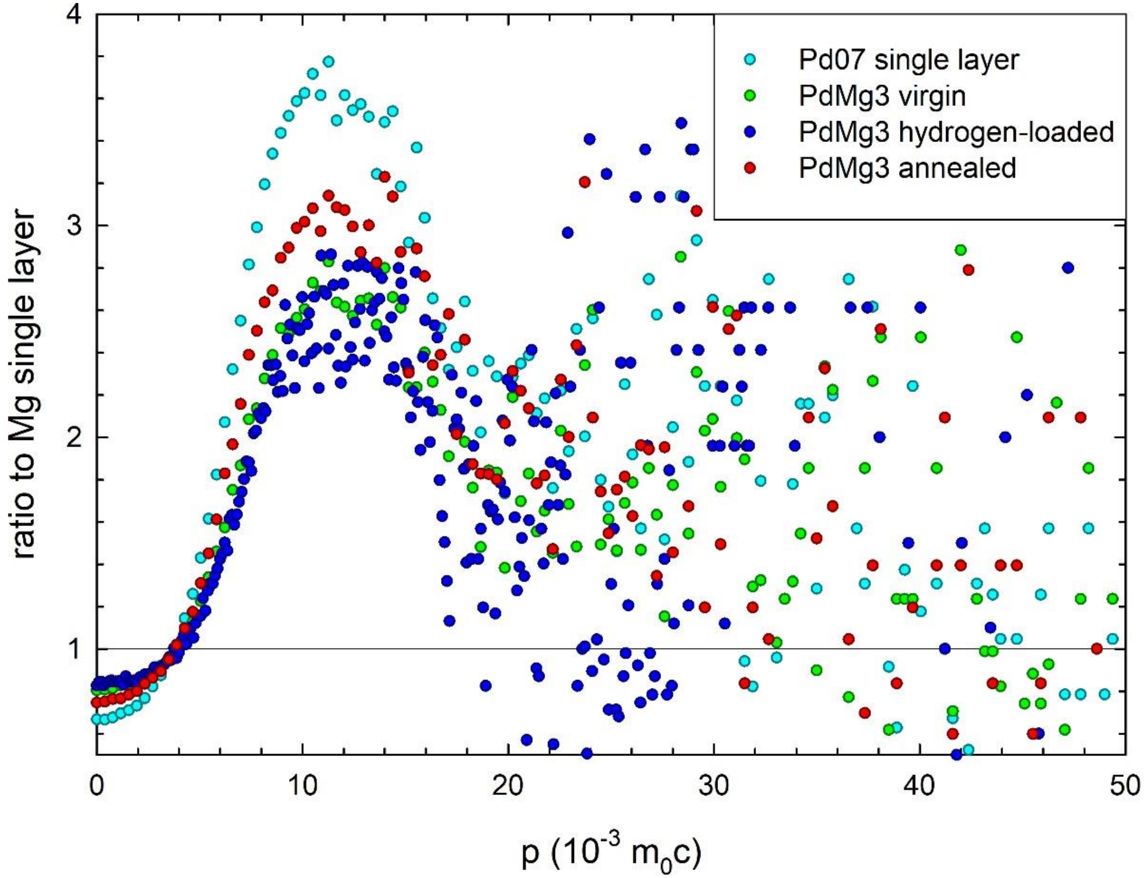




- S parameter increased in all layers
  - → formation of hydrogen-induced dislocations **in the whole volume**
- top Pd layer hydrogenated
  - → hydrogen trapping at open volumes (lower S)
  - → hydrogen-induced dislocations (lower $L_+$)
- **reduced density of dislocations in near substrate layers**
  - → 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

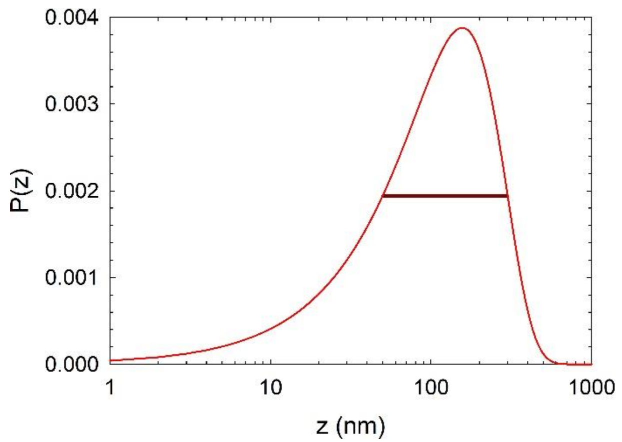


# CDB measurement




- **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

| fraction of Pd | |
|---|---|
| uniform Pd distribution | 0.61 |
| virgin sample | 0.76 |
| hydrogen-loaded sample | 0.76 |
| annealed sample (up to 450°C) | 0.85 |

# 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
- $Pd_2Si$ 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.