Slow positron annihilation studies of Pd-Mg multilayers

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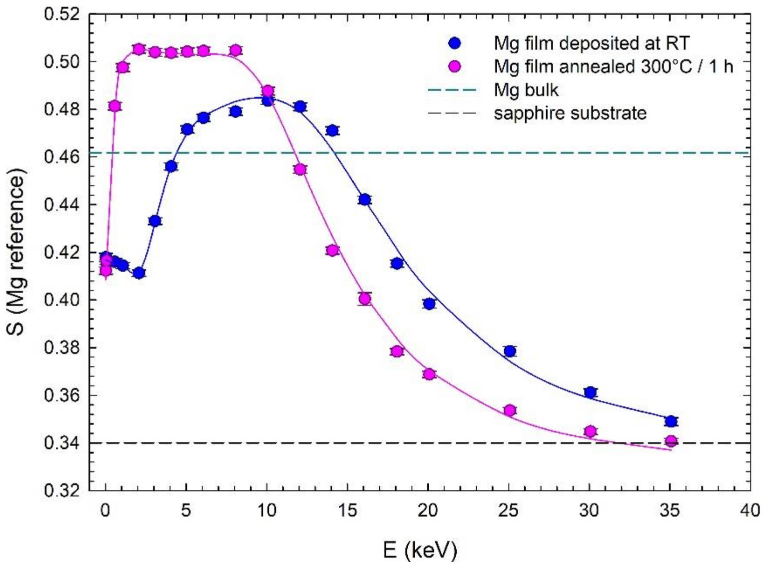
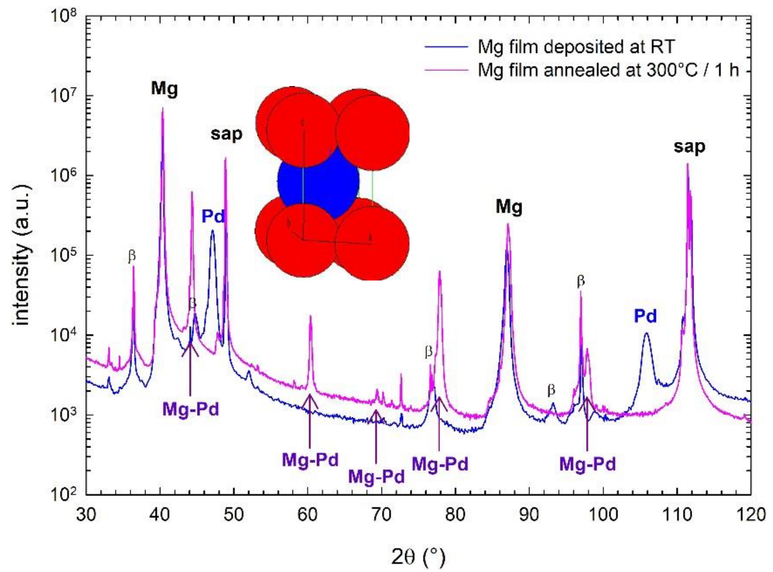
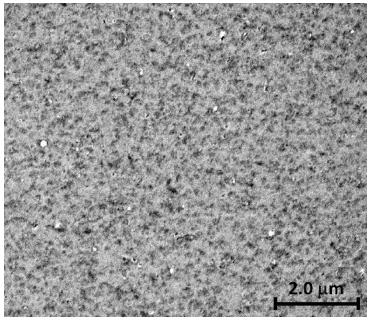
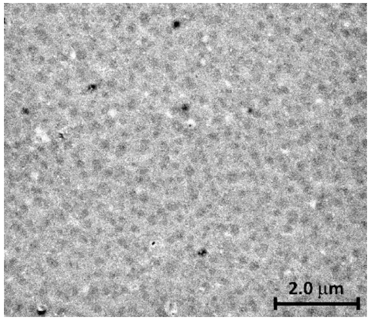
Previous study – Pd capped Mg films







Mg + 20 nm Pd cap
RT deposition



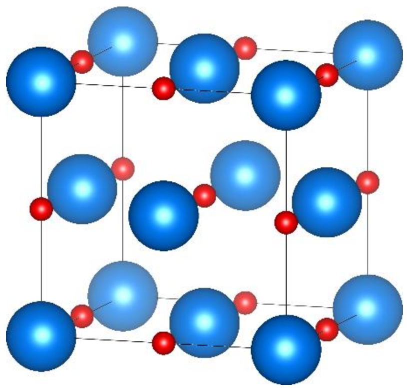
annealed at
300 °C / 1 h

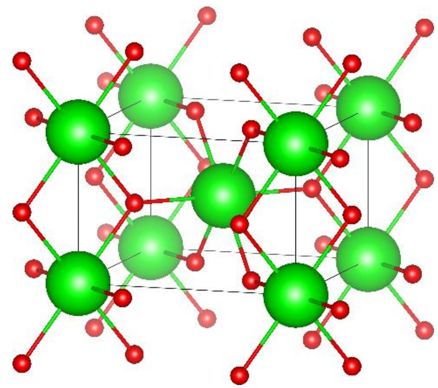
- diffusion of Pd into Mg layer
- metastable Mg-Pd intermetallic phase was formed
- S-parameter enhanced
- positron diffusion length L_+ shortened
- defect structure changed

Hruška P., Čížek J., et al., J. Phys.: Conf. Ser. 674 (2016) 012024
Hruška P., Čížek J., et al., J. Phys.: Conf. Ser. 505 (2014) 012024

Hydrogen storage in Pd and Mg

Palladium			Magnesium		
−	density	12.023 g/cm^3	+	density	1.738 g/cm^3
	hydrogen capacity	0.94 wt. %		hydrogen capacity	7.66 wt. %





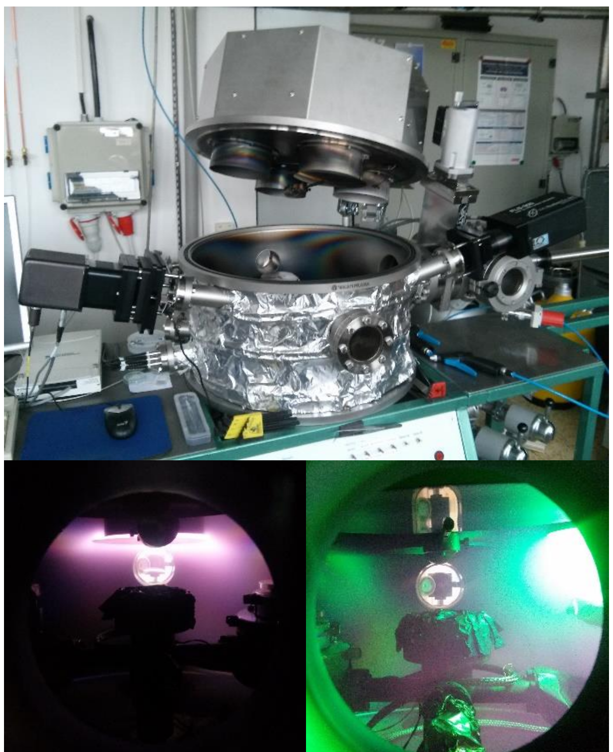
+	hydrogen absorption	0.02 bar / 20°C	−	hydrogen absorption	1 bar / 300°C

Option 1: Structure refinement of Mg down to nanoscale $\rightarrow$ H absorption enhancement

Option 2: Combining Mg and Pd on nanoscale level $\rightarrow$ H distribution via Pd channels

Pd-Mg multilayers

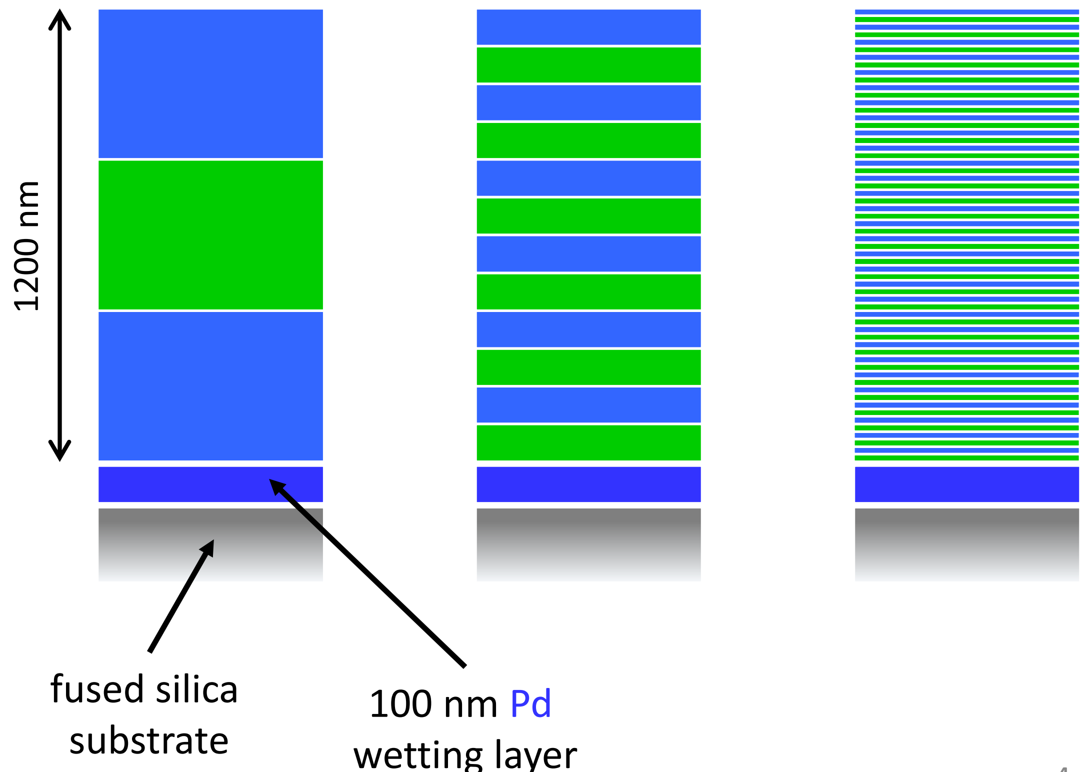
RF magnetron sputtering
room temperature deposition
base pressure 10^{-5} Pa
Ar deposition pressure 3 Pa
total thickness 1300 nm



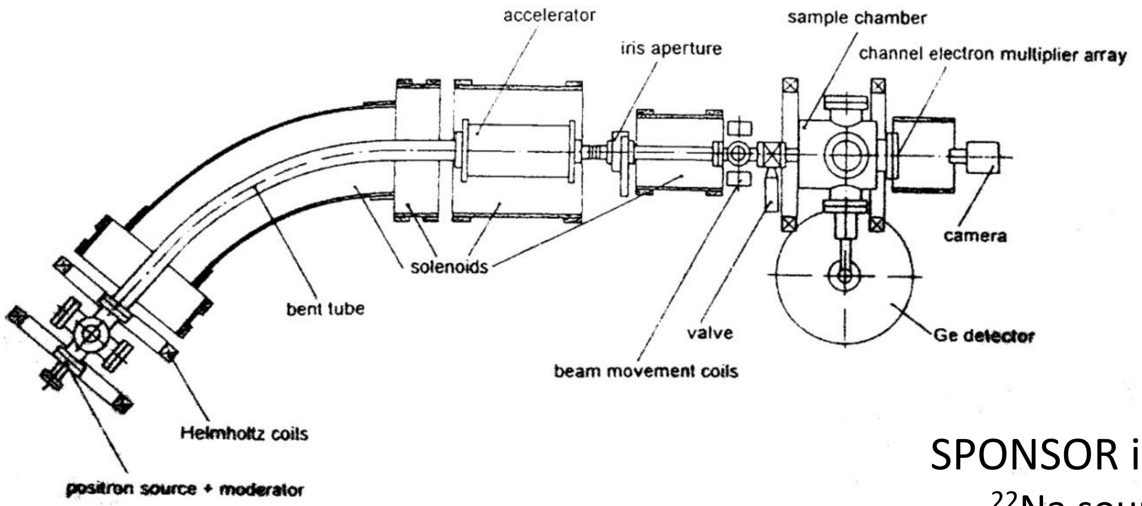
PdMg1
3 layers (400 nm)
2 × Pd + 1 × Mg
Mg/Pd ratio = 0.32

PdMg2
12 layers (100 nm)
6 × Pd + 6 × Mg
Mg/Pd ratio = 0.63

PdMg3
60 layers (20 nm)
30 × Pd + 30 × Mg
Mg/Pd ratio = 0.63

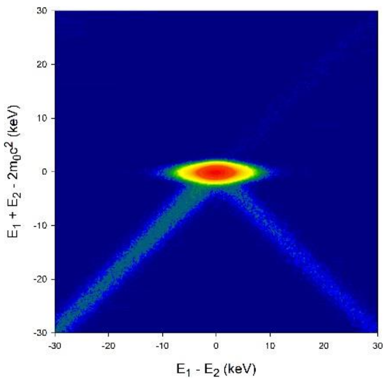


Slow positron beam SPONSOR

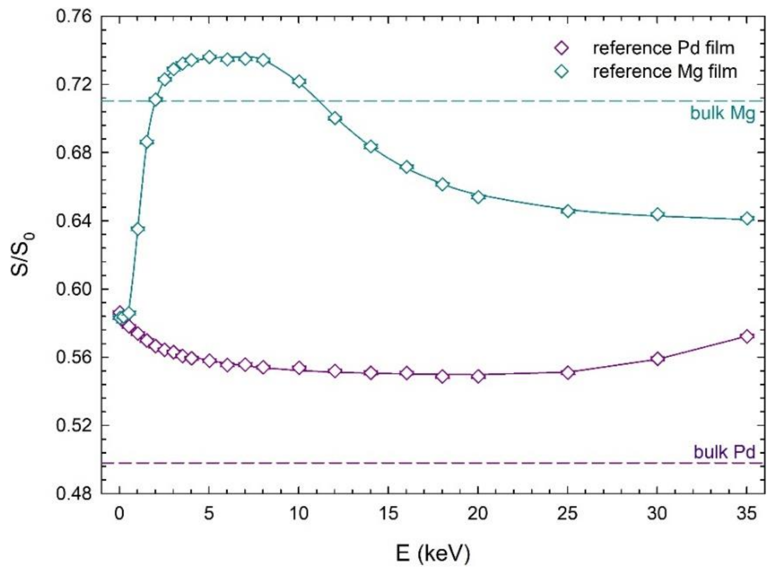


SPONSOR in HZDR
- ^{22}Na source with W moderator
- positron energies from 30 eV to 35 keV
- Doppler broadening measurement
- S and W shape parameters
- Coincidence Doppler broadening

VEPFIT analysis
- S(E) and W(E) curves
- positron diffusion length L_+
- S parameter of each layer



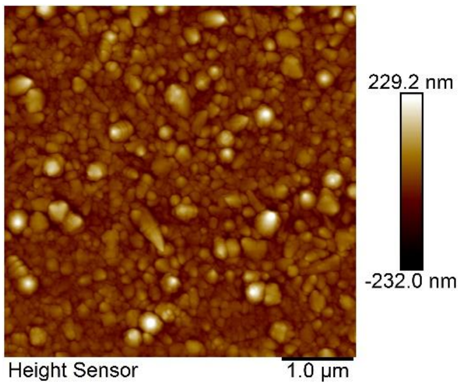
Pd and Mg reference films



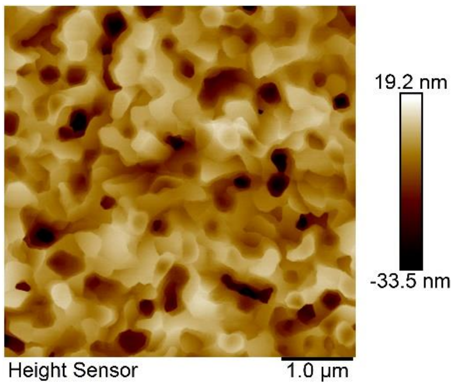
	S/S_0	L_+ (nm)
Pd film	0.5493(2)	57(2)
Mg film	0.7369(3)	11(2)
FS substrate	0.6326(2)	22(1)

nanocrystalline structure
→ positron trapping at grain boundaries
nanocrystalline Pd and Mg references
→ initial guesses for VEPFIT

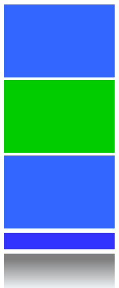
Pd reference film
1300 nm Pd
FS substrate

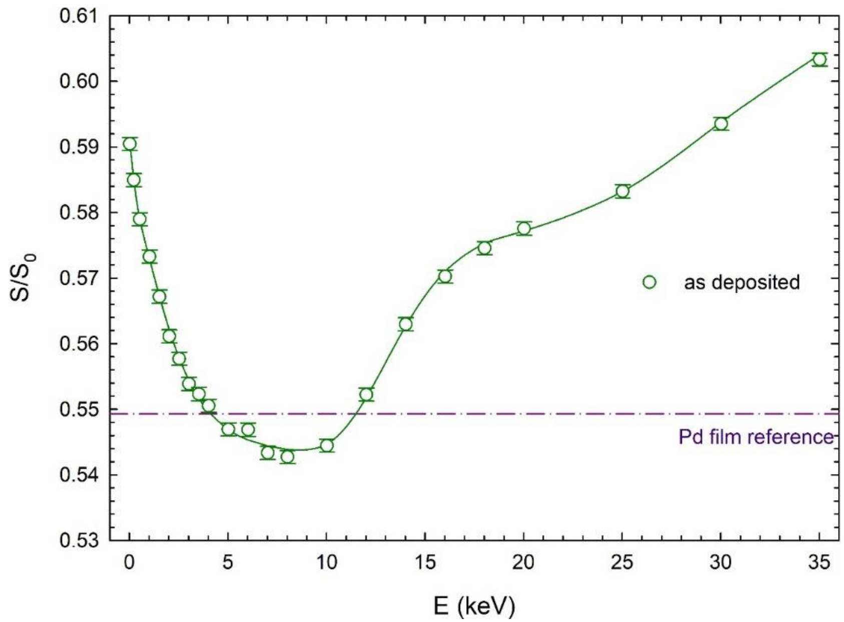


Mg reference film
20 nm Pd cap
1300 nm
FS substrate

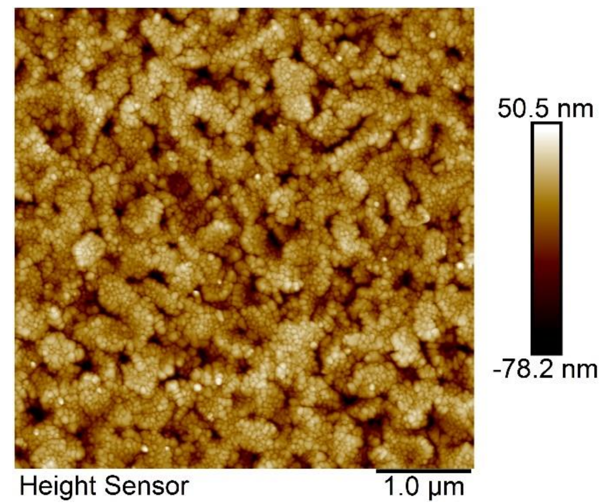


PdMg1 – as deposited

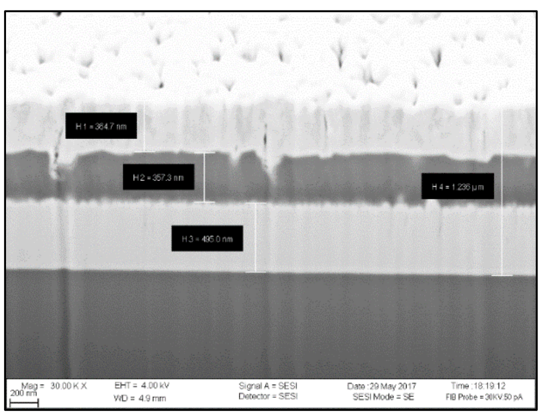


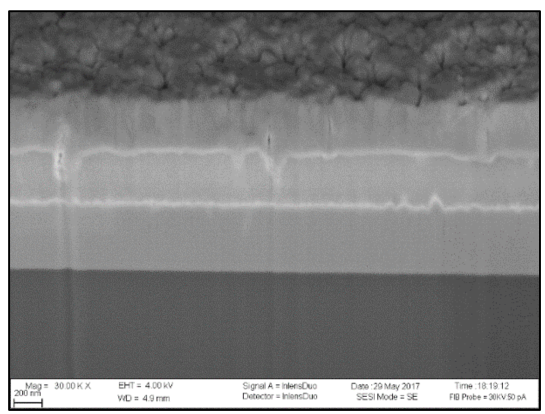


AFM - surface



SEM - cross section



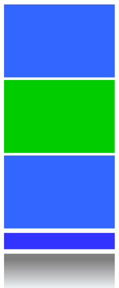


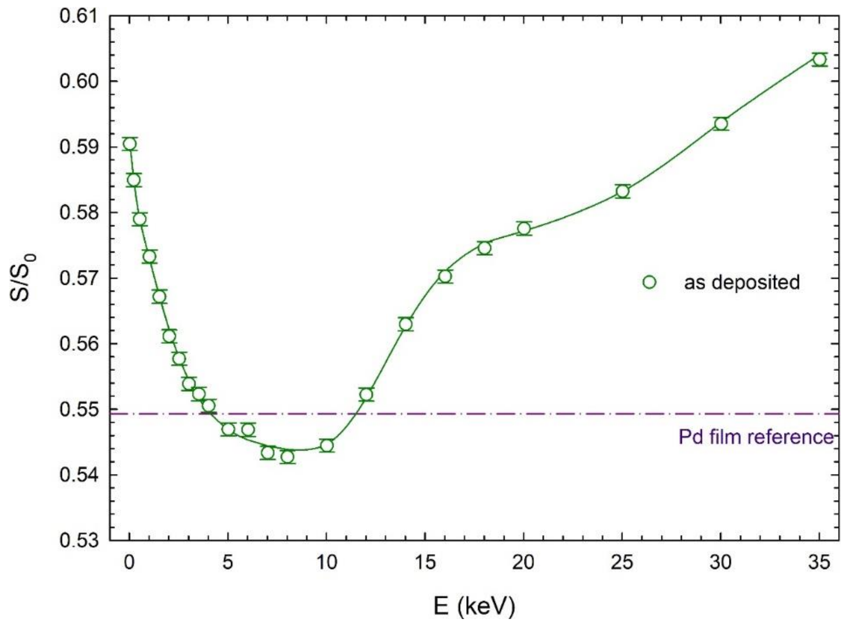
nanocrystalline structure
~ 10 - 100 nm

VEPFIT layers

1. Pd top
2. Mg middle
3. Pd bottom
4. FS substrate

PdMg1 – as deposited





as deposited	S/S_0	L_+ (nm)
Pd top	0.5427(4)	14.3(5)
Mg middle	0.719(7)	21(6)
Pd bottom	0.550(2)	68(11)

*FS substrate fixed parameters

Higher positron affinity in Mg compared to Pd leading to effective broadening of Mg layer.

Pd top and Mg middle layers

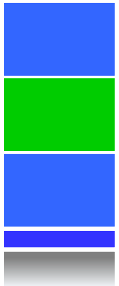
→ growing on metallic layer with Pd(111) and Mg(0001) texture

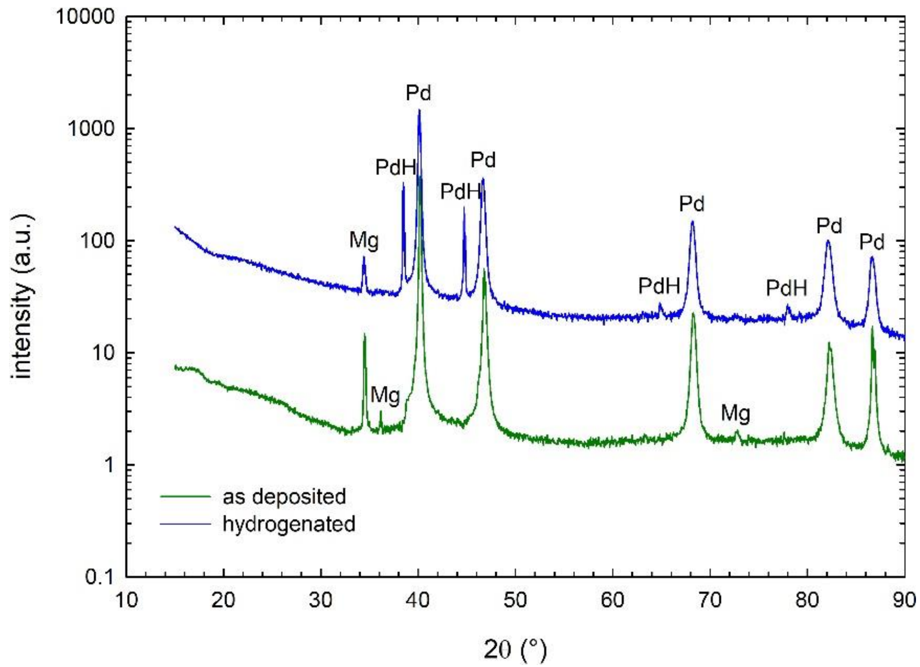
→ lower S parameter compared to the nanocrystalline reference

Pd bottom layer

→ similar to nanocrystalline Pd reference

PdMg1 – H_2 gas loading





as deposited sample (virgin)

- textured Pd and Mg layers

hydrogenated sample

- extra PdH peaks
- no MgH_2 peaks
- Pd and Mg peaks remain

H_2 loading of the Pd top layer. Mg layer not hydrogenated!

Hydrogenation

samples placed in vacuum chamber (10^{-4} Pa)

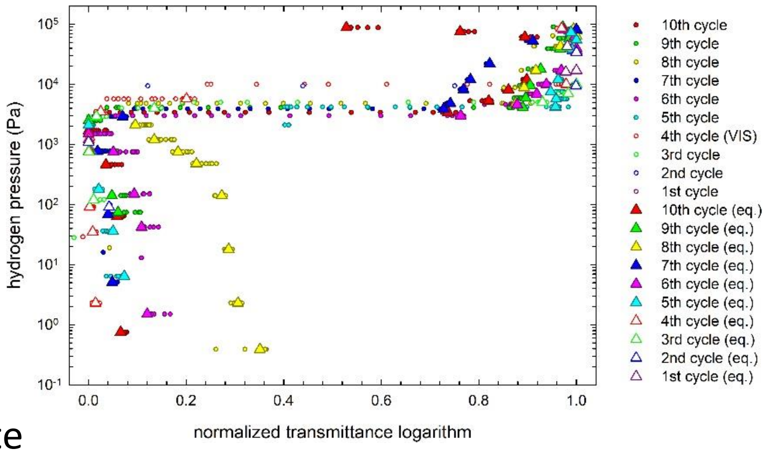
→ H_2 gas loading at 20 °C / 4000 Pa / 2 h

→ phase transformation conditions for 20 nm Pd film

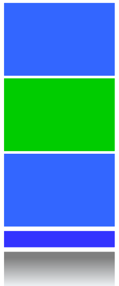
α-Pd → α'-PdH phase transformation

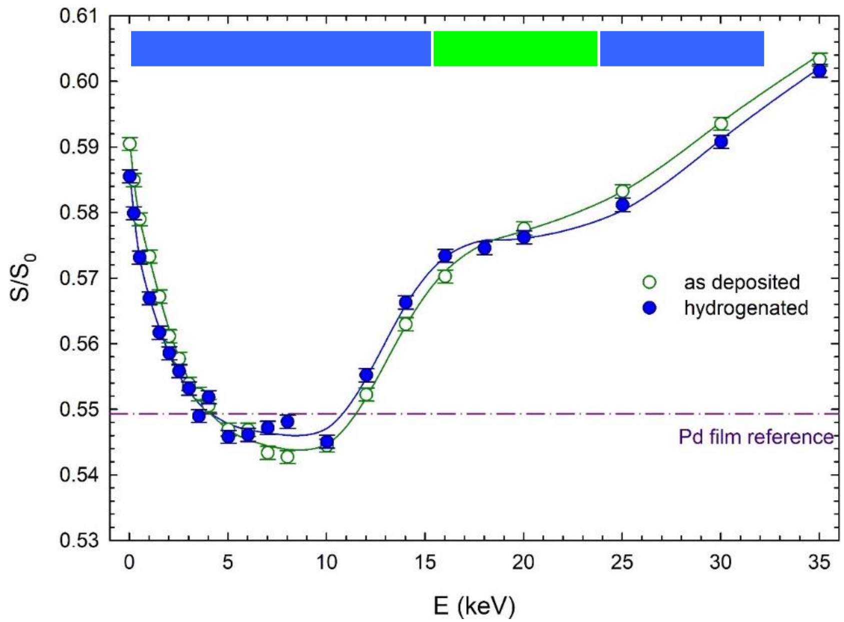
→ plastic deformation of the film

→ buckling of the film and detachment from the substrate



PdMg1 – hydrogenated





as deposited	S/S_0	L_+ (nm)
Pd top	0.5427(4)	14.3(5)
Mg middle	0.719(7)	21(6)
Pd bottom	0.550(2)	68(11)

hydrogenated	S/S_0	L_+ (nm)
Pd top	0.5453(4)	12.3(6)
Mg middle	0.749(7)	24(8)
Pd bottom	0.544(2)	36(10)

hydrogenation of Pd top layer

→ hydrogen induced defects

plastic deformation of Mg layer

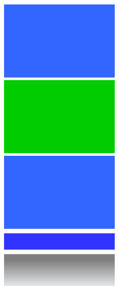
→ deformation induced defects

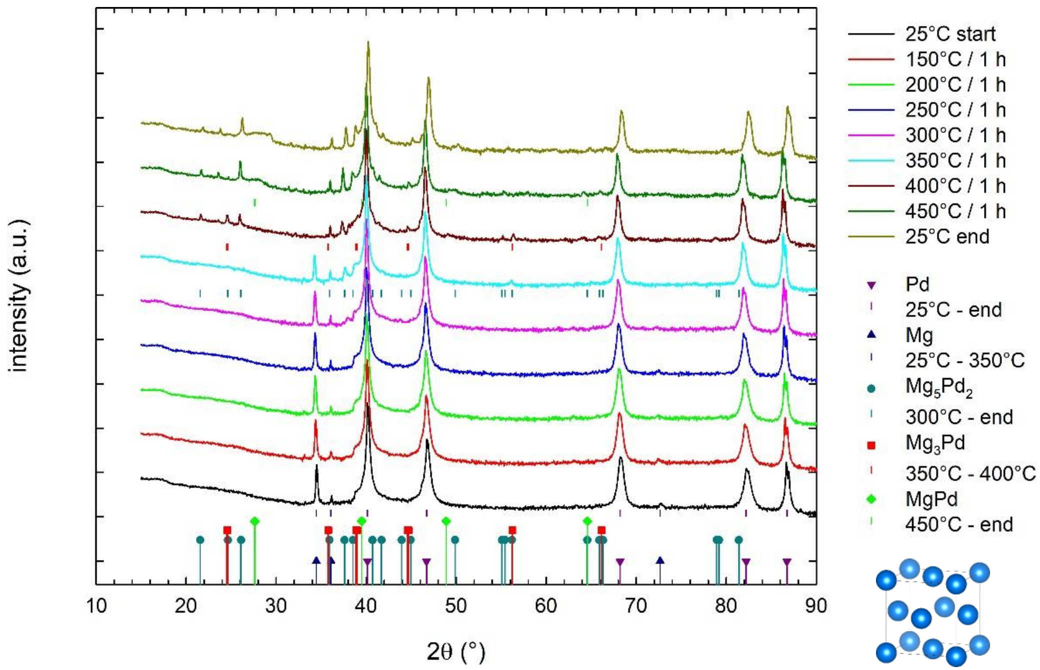
detachment of Pd bottom layer

→ substrate-film misfit dislocations
disappearance due to the stress relaxation

Higher positron affinity in Mg compared to Pd leading to effective broadening of Mg layer.

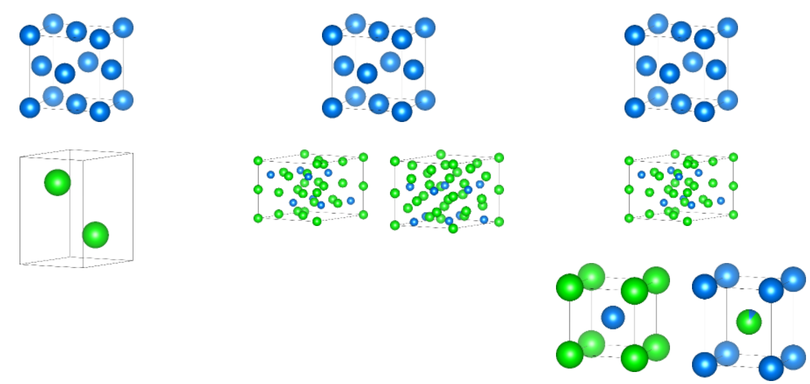
PdMg1 – annealing





Pd	25 °C → 450 °C
Mg	25 °C → 350 °C
Mg_5Pd_2	300 °C → 450 °C
Mg_3Pd	350 °C → 400 °C
MgPd	450 °C
$Mg_{0.9}Pd_{1.1}$	450 °C

average Mg/Pd ratio = 0.32



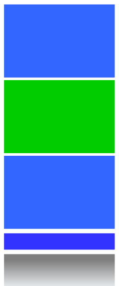
Annealing

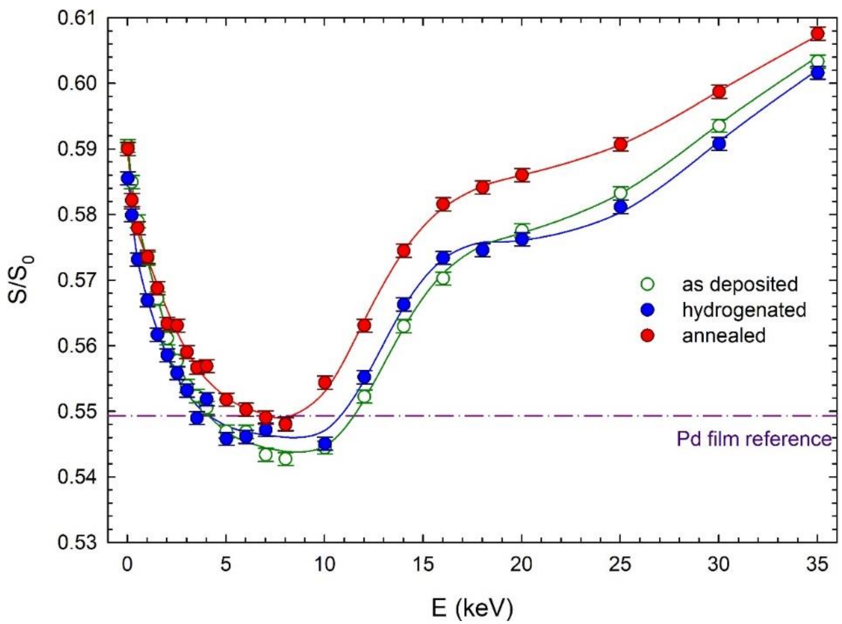
sample placed in vacuum chamber (10^{-4} Pa)
→ annealing under protective Ar atmosphere
→ isothermal annealing 50 °C / 1 h up to 450 °C
→ in-situ XRD measurement

XPS measurement (1st and 2nd atomic layers)
→ 98.8 % Pd + 1.2 % Mg

Diffusion of Pd into Mg layer → formation of Mg-Pd intermetallic phases (Mg-rich and “balanced”).

PdMg1 – annealed





Pd layers enriched with Mg
→ S parameter increase
Pd-Mg middle layer
→ S parameter decrease

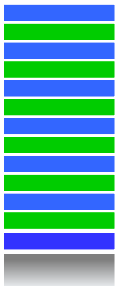
thinner Pd layers due to higher positron affinity in Mg and diffusion of Pd into middle layer

as deposited	S/S_0	L_+ (nm)
Pd top	0.5427(4)	14.3(5)
Mg middle	0.719(7)	21(6)
Pd bottom	0.550(2)	68(11)

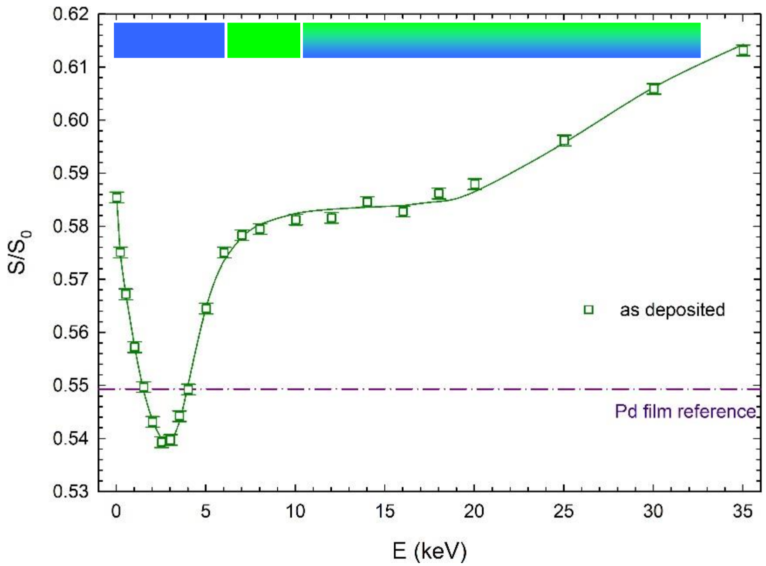
hydrogenated	S/S_0	L_+ (nm)
Pd top	0.5453(4)	12.3(6)
Mg middle	0.749(7)	24(8)
Pd bottom	0.544(2)	36(10)

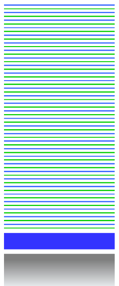
annealed	S/S_0	L_+ (nm)
Pd top	0.5470(7)	18.7(7)
Mg middle	0.698(6)	18(8)
Pd bottom	0.583(1)	26(9)

PdMg2 and PdMg3 – as deposited

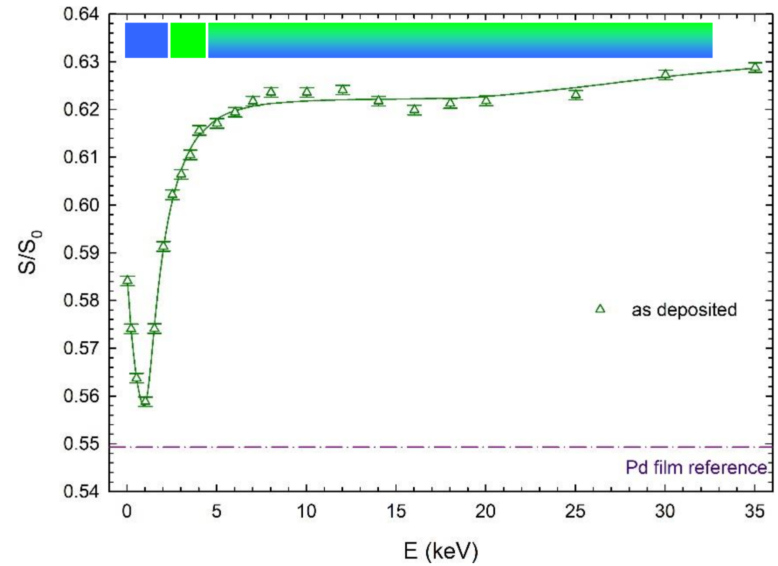


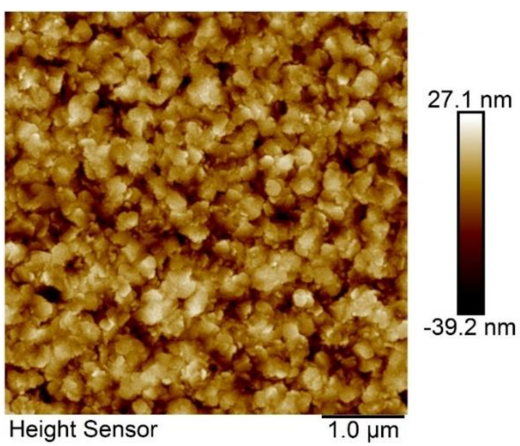
PdMg2





PdMg3

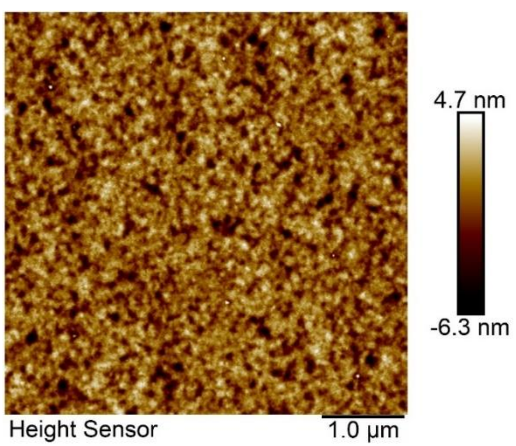




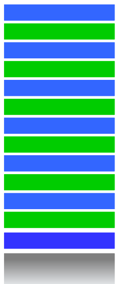
nanocrystalline structure
~ 10 - 100 nm

VEPFIT layers

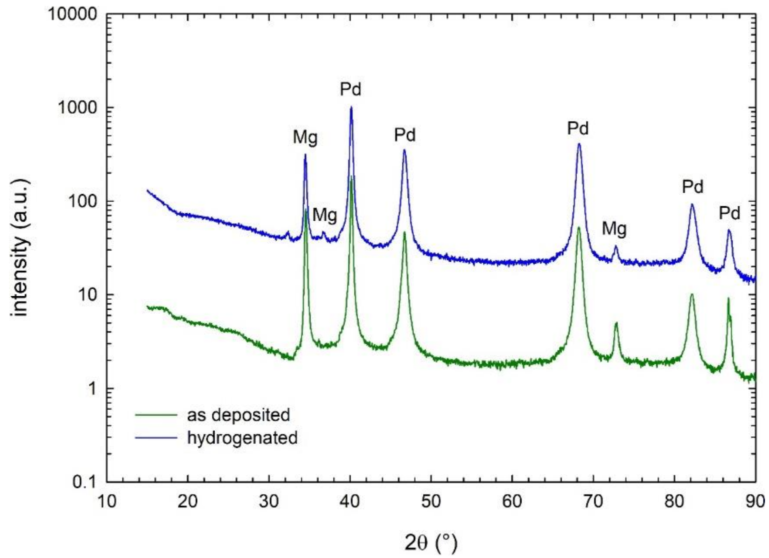
1. Pd 1st
2. Mg 2nd
3. Pd-Mg mixture with average density
4. FS substrate

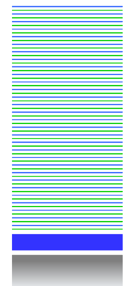


PdMg2 and PdMg3 – H_2 gas loading

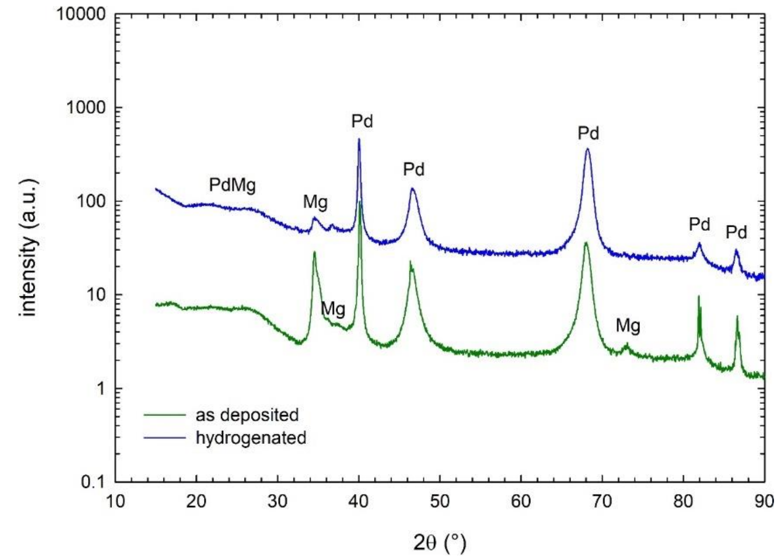


PdMg2





PdMg3



Hydrogenation

same conditions as for PdMg1

buckling of both films
→ films not detached
→ hydrogenation of the top Pd layer

H_2 loading of the Pd top layer only. H did not diffuse through Mg layers (100 nm and 20 nm)!

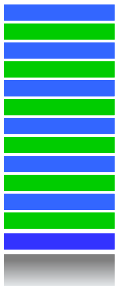
as deposited samples (virgin)

- Pd and Mg texture similar to PdMg1
- MgPd and $Mg_{0.9}Pd_{1.1}$ phases in PdMg3 at RT

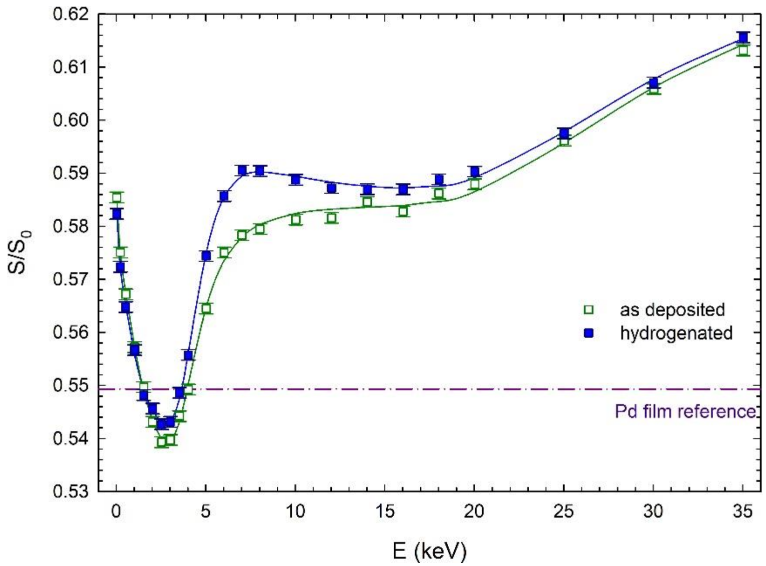
hydrogenated samples

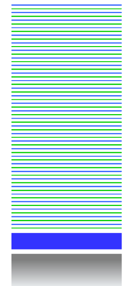
- no MgH_2 or PdH peaks
- other Mg and Pd layers not hydrogenated

PdMg2 and PdMg3 - hydrogenated

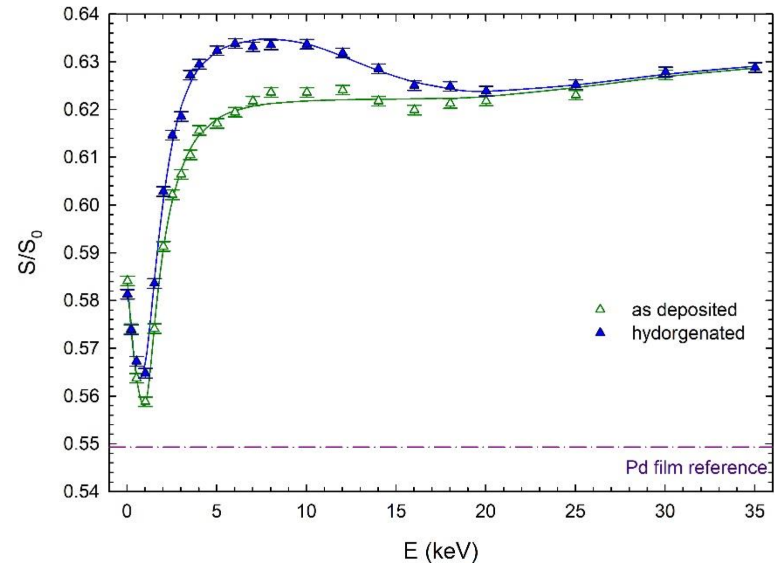


PdMg2





PdMg3



Pd 1st layer

→ plastic deformation due to phase transformation α-Pd → α′-PdH

→ hydrogen induced defects formation

Mg 2nd layer

→ plastic deformation of Pd 1st layer

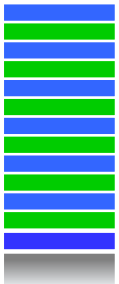
→ increase of S parameter of Mg layer

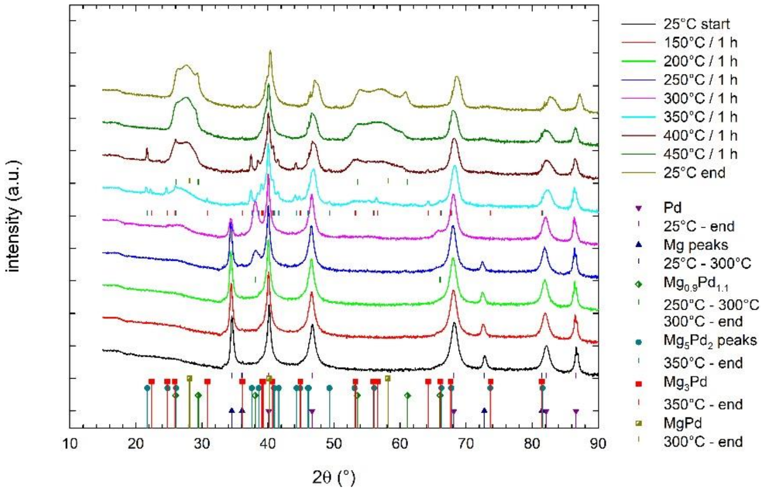
Pd-Mg bottom layers

→ near-substrate layers with similar parameters as virgin sample

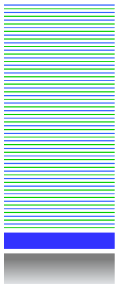
PdMg2 and PdMg3 - annealing

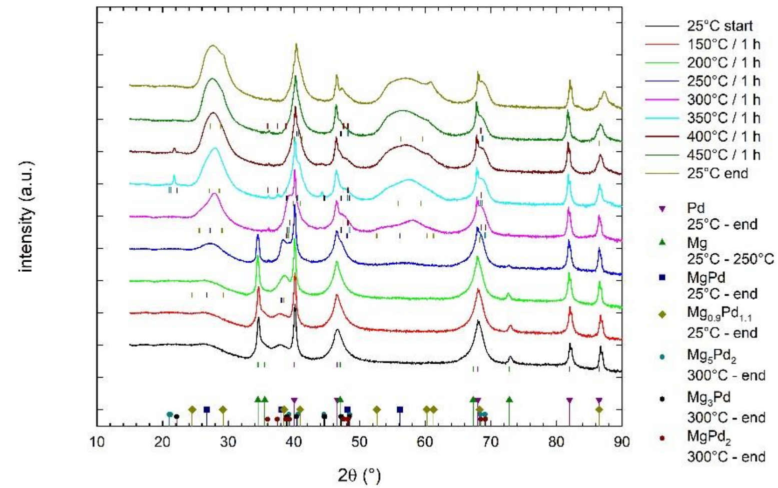
PdMg2





PdMg3



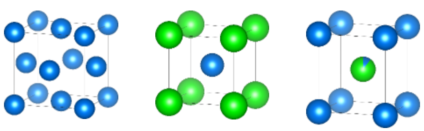


Annealing
same conditions as for PdMg1
average Mg/Pd ratio = 0.63

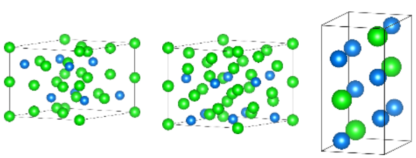
XPS measurement (1st and 2nd atomic layers)
→ 74.1 % Pd + 25.9 % Mg in PdMg2
→ 50.8 % Pd + 49.2 % Mg in PdMg3

Pd and Mg mixing → stable MgPd and $Mg_{0.9}Pd_{1.1}$ phases formed.

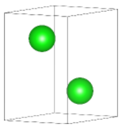
stable phases
Pd, MgPd, $Mg_{0.9}Pd_{1.1}$



metastable phases
Mg_5Pd_2, Mg_3Pd, $MgPd_2$

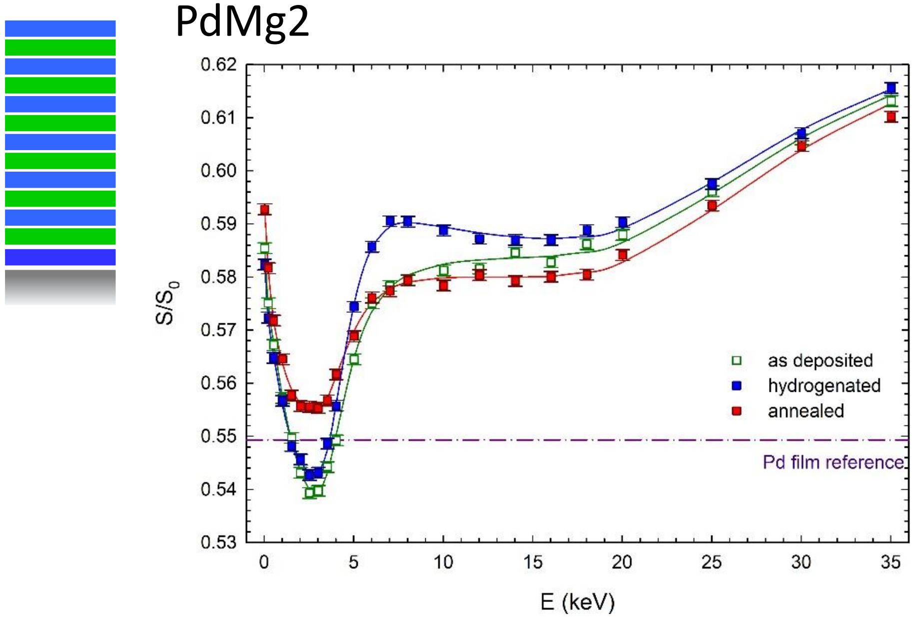


non-stable phases
Mg

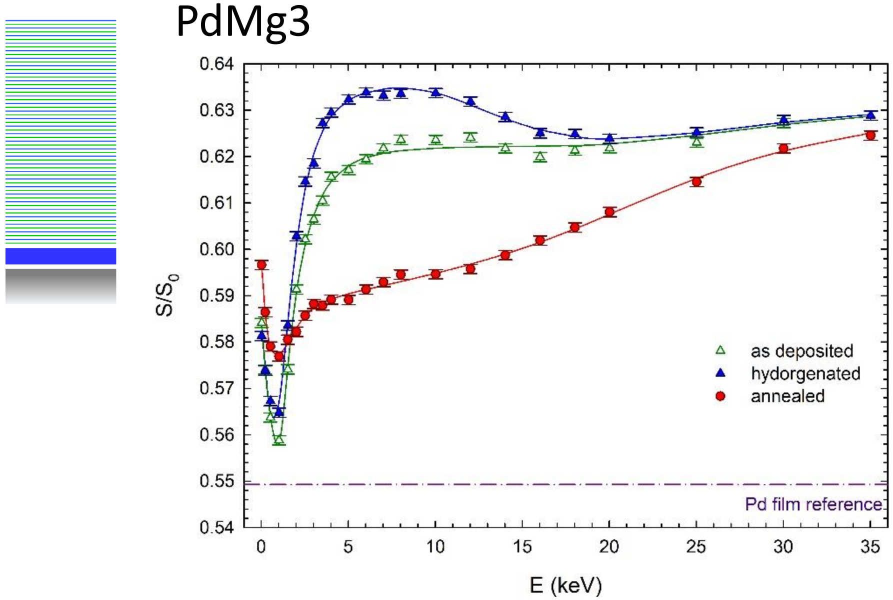


PdMg2 and PdMg3 - annealed

PdMg2



PdMg3



mixing of Pd and Mg layers

→ S parameter of (originally) Pd layer increases

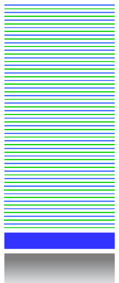
→ S parameter of (originally) Mg layer decreases

layered structure

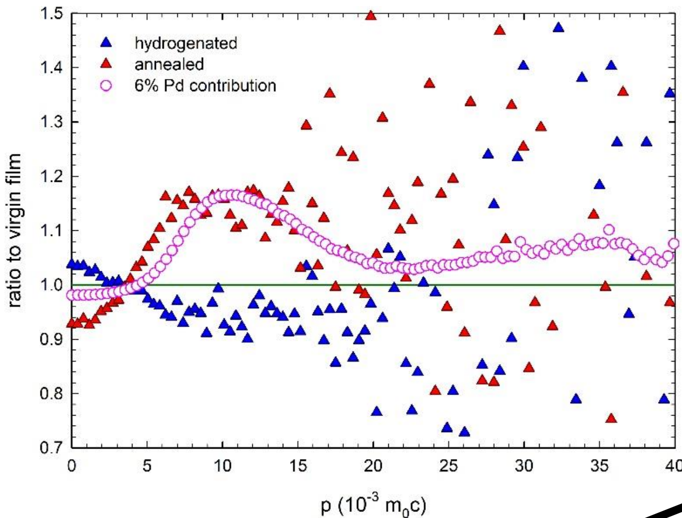
→ conserved for PdMg2 film – incomplete transformation into MgPd and $Mg_{0.9}Pd_{1.1}$

→ blurred for PdMg3 film – complete transformation into MgPd and $Mg_{0.9}Pd_{1.1}$

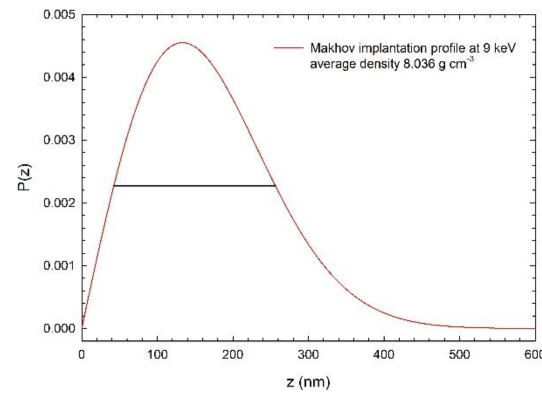
Coincidence Doppler broadening



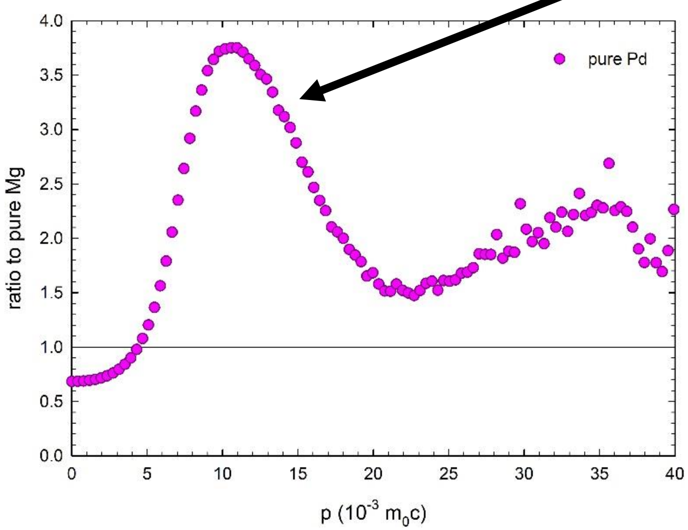
PdMg3



- CDB measurement for 9 keV positron energy
- mean implantation depth = 133 nm
- FWHM of implantation profile = 213 nm
- 10 Pd/Mg layers covered
- balanced probability of positron stopping in Pd and Mg layer



d-electrons contribution



hydrogenated sample

→ enhanced annihilation at hydrogen-induced defects

annealed sample

→ enhanced d-electron contribution coming from annihilations with Pd electrons

Conclusions

1. PdMg films with 3 different types of layered structure were prepared by RF magnetron sputtering.
2. H_2 gas loading led to transformation of top α-Pd layer into α'-PdH phase. This transformation introduce stress which causes buckling of the film. H did not diffuse into Mg layers.
3. Formation of Mg-Pd intermetallic phase was elucidated. Pd diffuse into Mg layers and initially form Mg-rich phases. Further Pd diffusion leads to formation of "balanced" phases MgPd and $Mg_{0.9}Pd_{1.1}$.
4. Positrons predominantly annihilate with Mg-rich environment due to higher positron affinity of Mg compared to Pd.