Stability issues in Pd/B_4C multilayers

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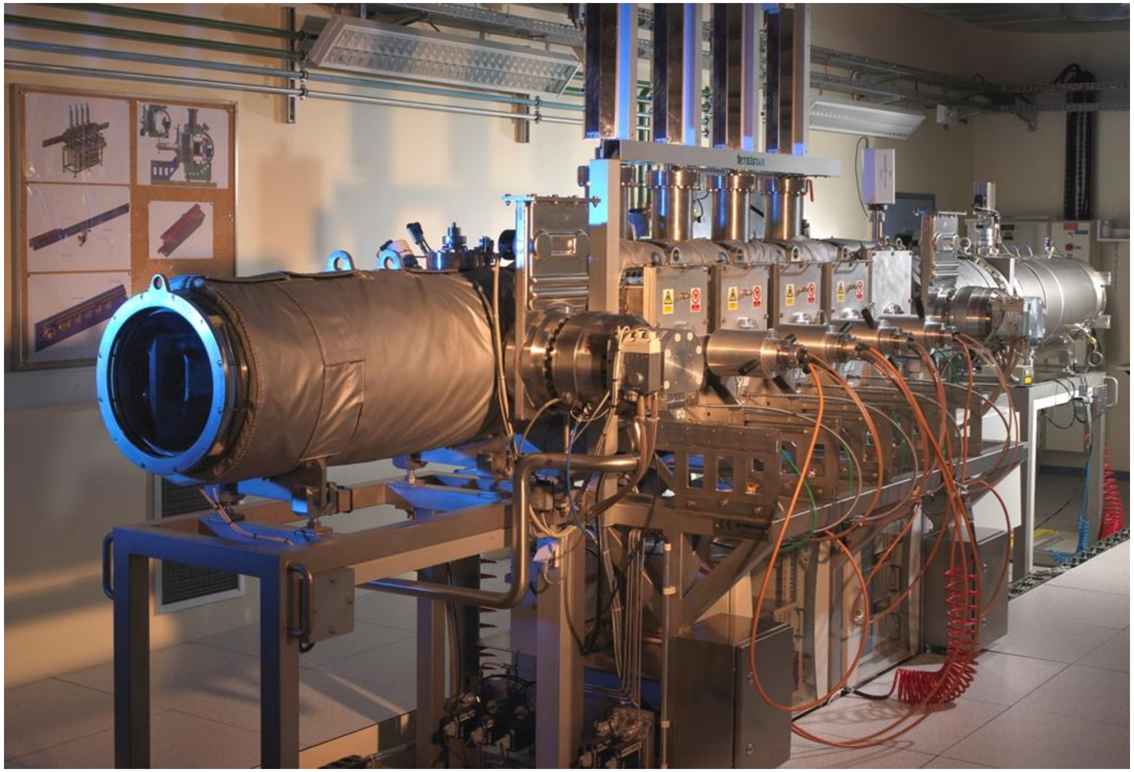
Outline

- Introduction
- ML fabrication
- Experimental techniques
- X-ray studies
- SEM + TEM studies
- Soft X-ray PEEM
- Summary + Outlook



ACKNOWLEDGEMENTS

Support:

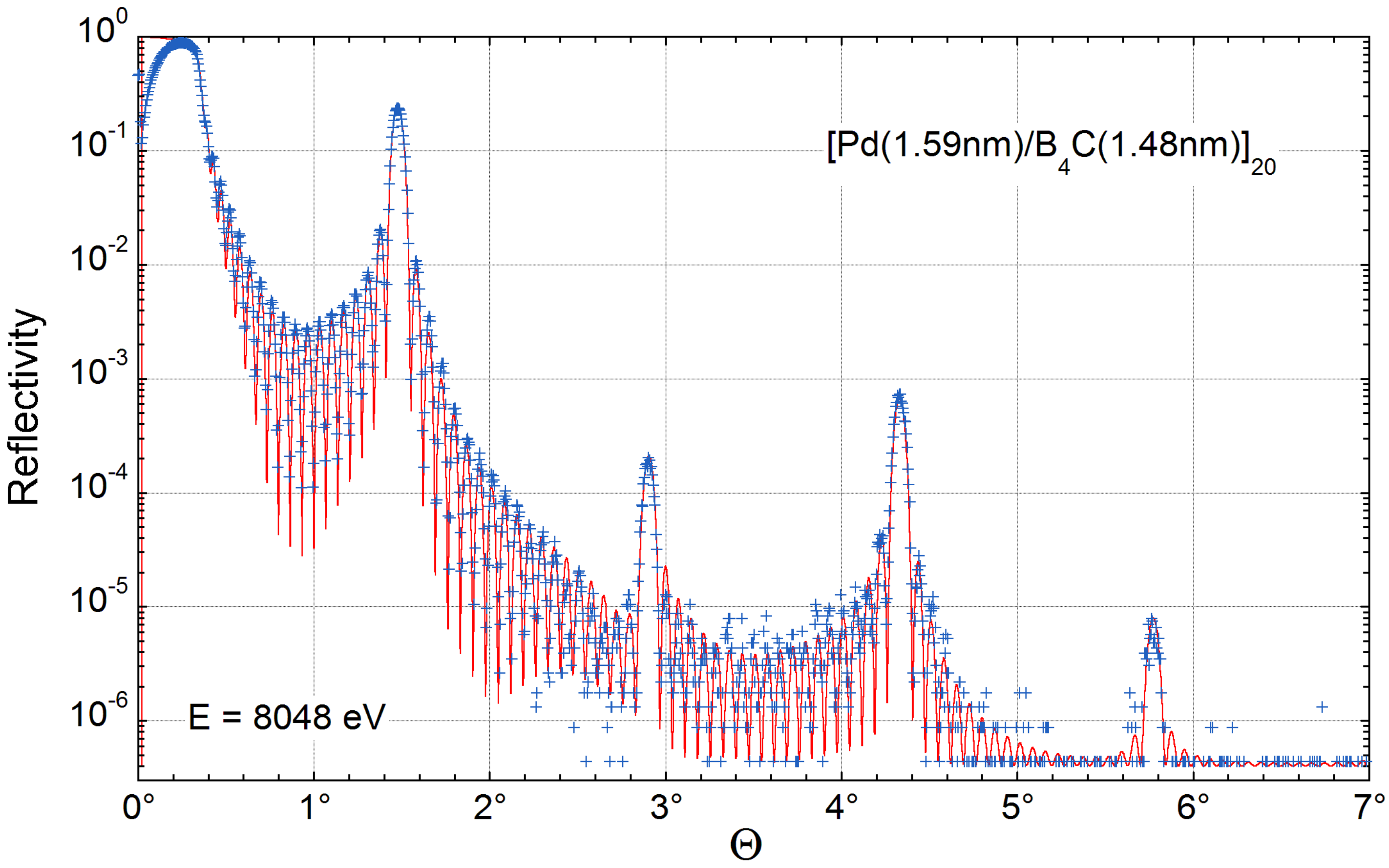
- R. Barrett, A. Vivo (X-ray Optics Group, ESRF, France)
- T. Bigault (Neutron Optics Service, ILL)
- I. Snigireva (Micro-imaging Laboratory, ESRF, France)
- H. Nakajima, S. Rattanasuporn, P. Photonkam, N. Jearanaikoon, W. Busayaporn (BL3.2, SLRI, Thailand)

References:

- Thin Solid Films 588 (2015) 1-10
  Ch. Morawe, R. Supruangnet, J-Ch. Peffen
- Applied Surface Science 367 (2016) 347-353
  R. Supruangnet, Ch. Morawe, J-Ch. Peffen, H. Nakajima, S. Rattanasuporn, P. Photongkam, N. Jearanaikoon
  W. Busayaporn

Why Pd/B_4C ? – Initial observations

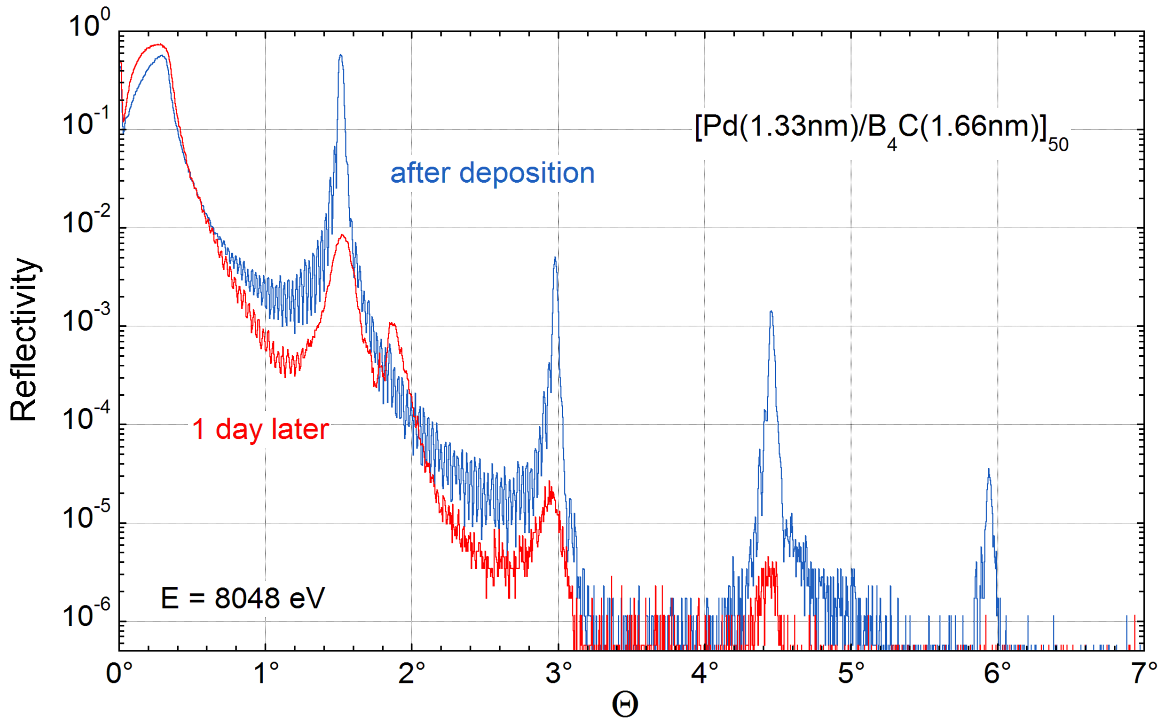
- Attractive optical properties of Pd at E ≤ 24 keV
- Strong materials contrast, sharp interfaces σ = 0.21…0.25 nm

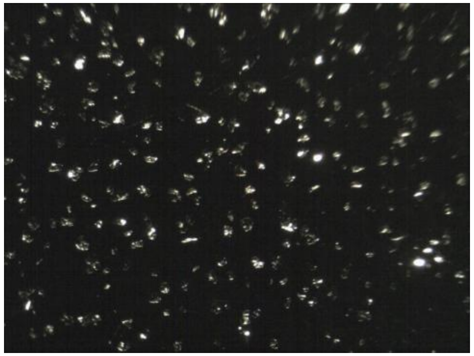


Further observations

- Alteration for d-spacings < 4 nm
- Rapid formation of stains + particles on surface → disappear later !
- Significant reflectance loss + peak shift after 1 day in air !

→ What happened ? Why ? Possible ways out ?





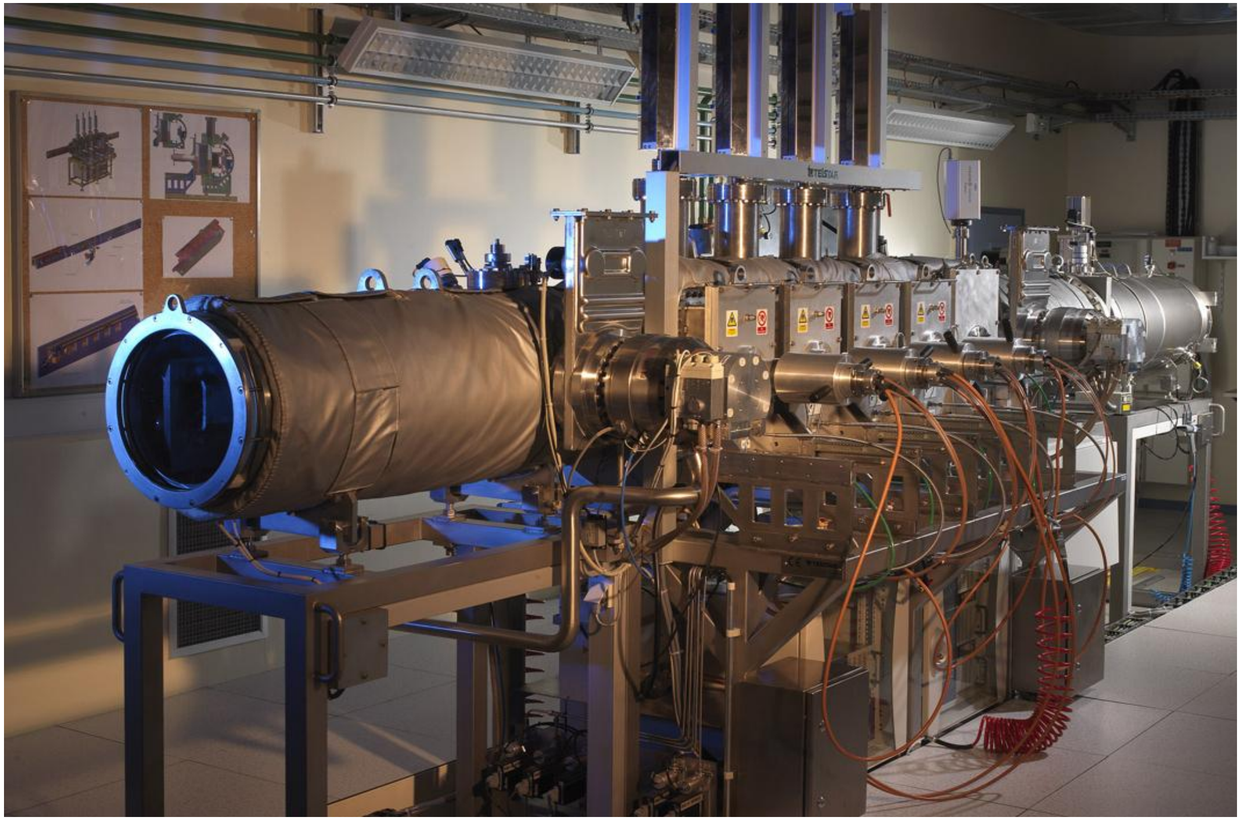
ESRF multilayer deposition facility

- DC sputtering on Si(100) wafers near room temperature
- Horizontal particle flux
- Static or dynamic mode

- D = 67 mm
- p(Ar) = 0.1 Pa

- P(Pd) = 50 W
- P(B_4C) = 500 W

- R(Pd) = 0.4 nm/s
- R(B_4C) = 0.2 nm/s



X-ray reflectivity

- Cu Kα1 micro-focus source (Incoatec IμS, 30 W)
- Montel ML collimator + Ge(111) monochromator

SEM analysis

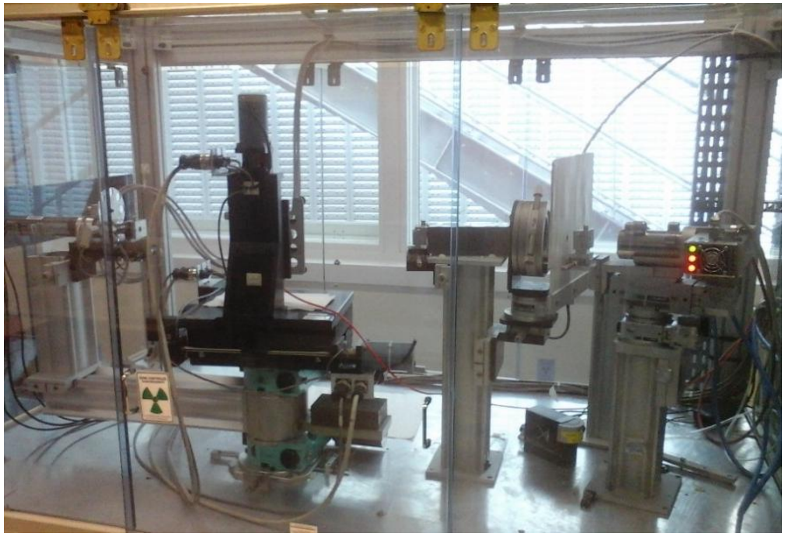
- ESRF Micro-imaging Laboratory (LEO 1530)

TEM analysis

- Serma Technologies (FEI Tecnai G2 F20)

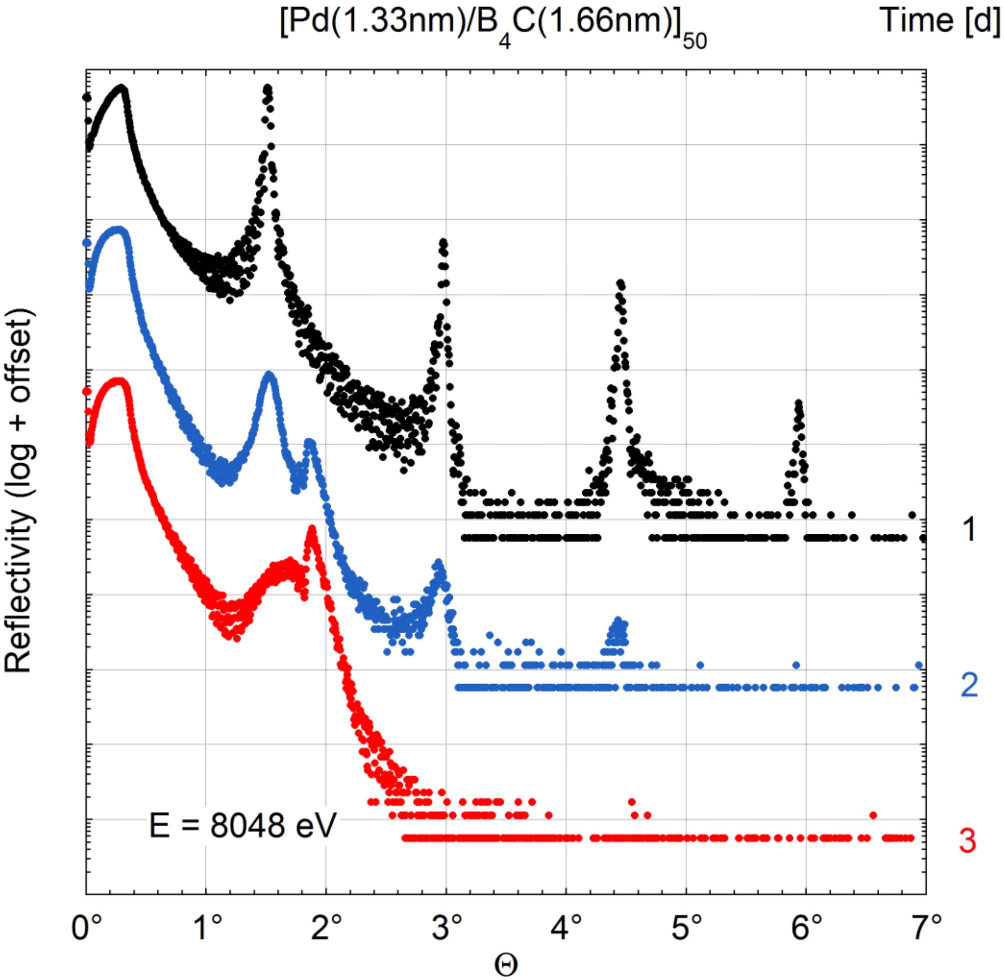
Photoemission electron microscopy (PEEM)

- BL3.2Ub (SLRI – Thailand) at B K-edge
- LEEM III imaging analyzer (ELMITEC)



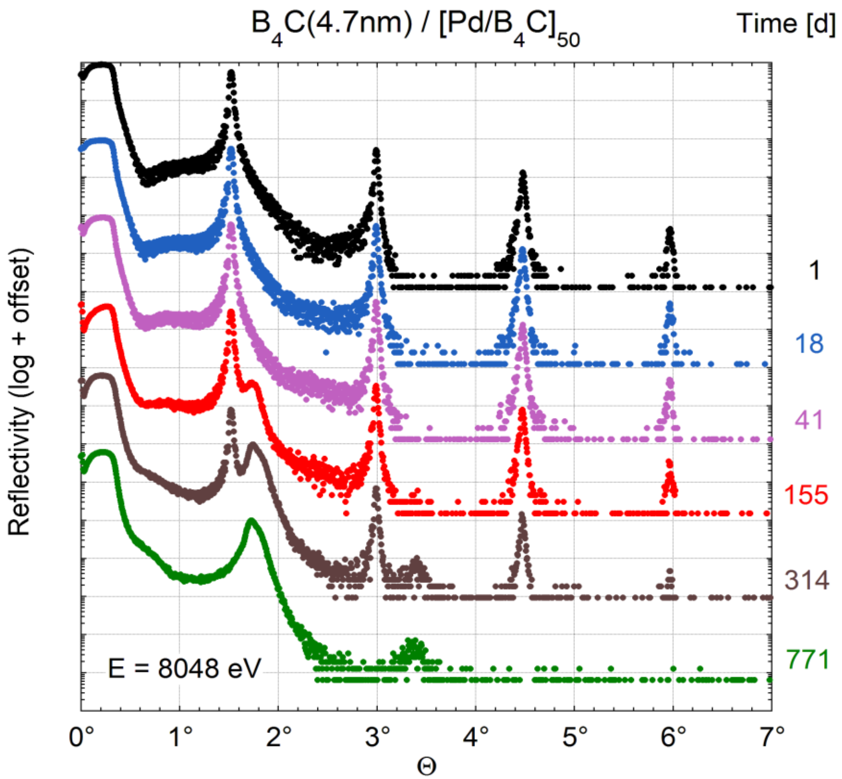
X-ray reflectivity

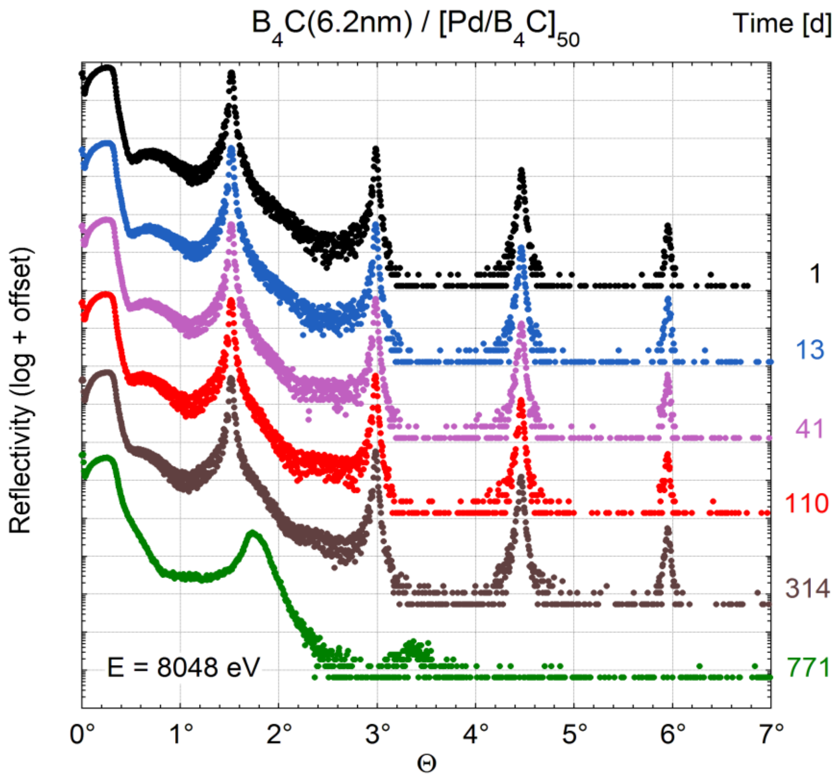
- Unprotected Pd/B_4C MLs
- $[Pd(1.33nm)/B_4C(1.65nm)]_{50}$
- Stored in air at RT
- Immediate and fast degradation
- Original ML structure disappears
- New peak at higher angles
- No further evolution after a few days



X-ray reflectivity

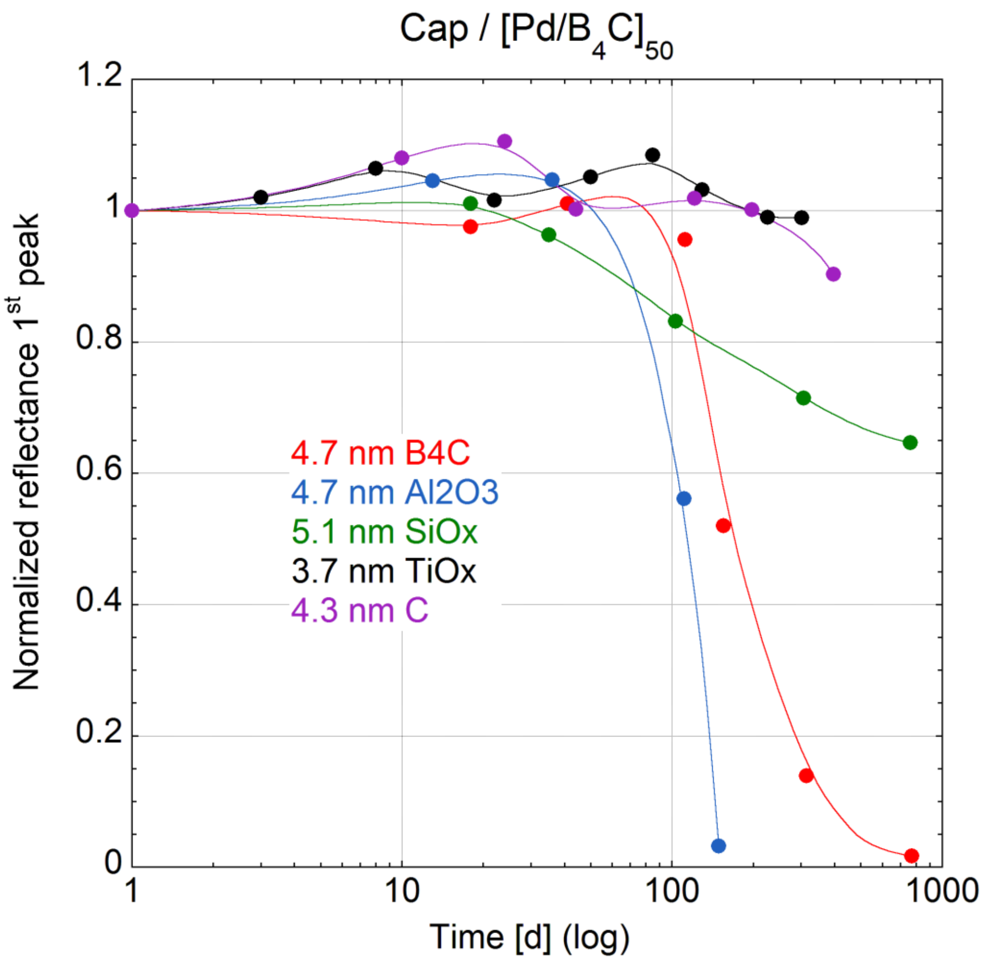
- ML sample series with cap layer: B_4C(var)/[Pd(1.35nm)/B_4C(1.65nm)]$_{50}$
- Degradation slowed down (>1y), but not stopped
- ML period reduction from 3.0 nm to 2.3 nm
- Old peak sharp, new peak broad → co-existence of laterally separated phases





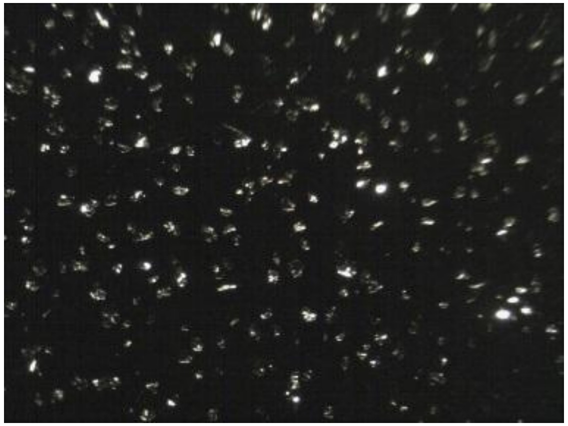
X-ray reflectivity

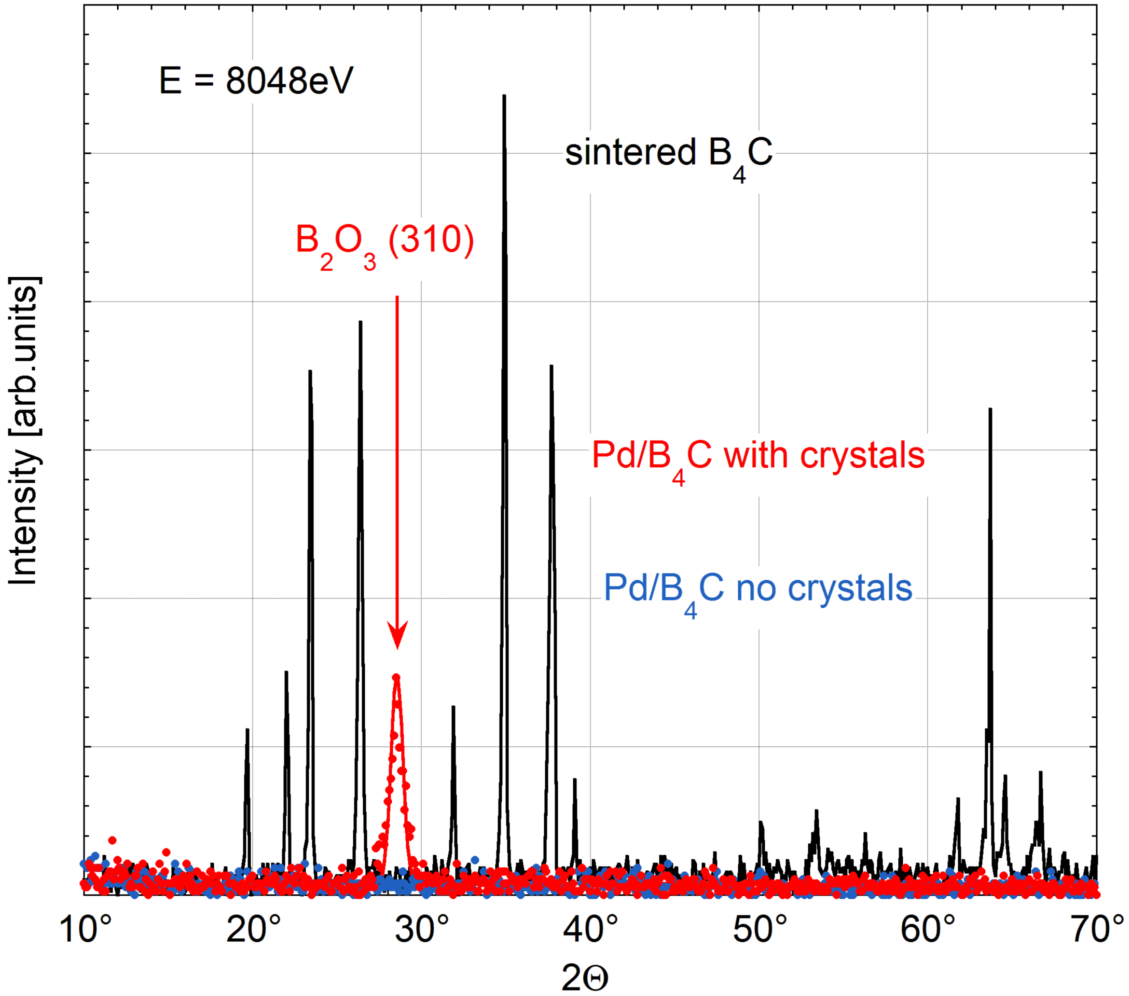
- Further cap layer materials: B_4C, Al_2O_3, $Si(O_x)$, $Ti(O_x)$, C
- Variable cap layer thickness (wedge)
- Similar reflectivity patterns and rapid drop after 100 d for B_4C and Al_2O_3
- Slower decay for $Si(O_x)$
- Moderate reflectance loss for thin (< 4 nm) $Ti(O_x)$ and C cap layers
- No degradation on Pd/B_4C ML in vacuum !



X-ray diffraction

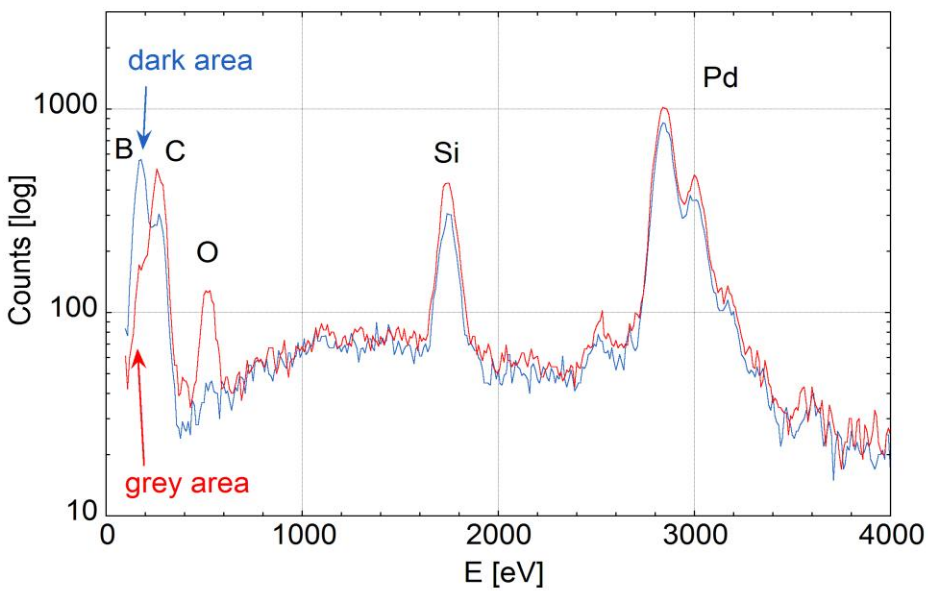
- MLs with surface crystals cause broad peak at B_2O_3(310) position
- No peaks on MLs without crystals
- No B_4C peaks
- Massive oxidation of B_4C ?
- Why do the crystals disappear ?

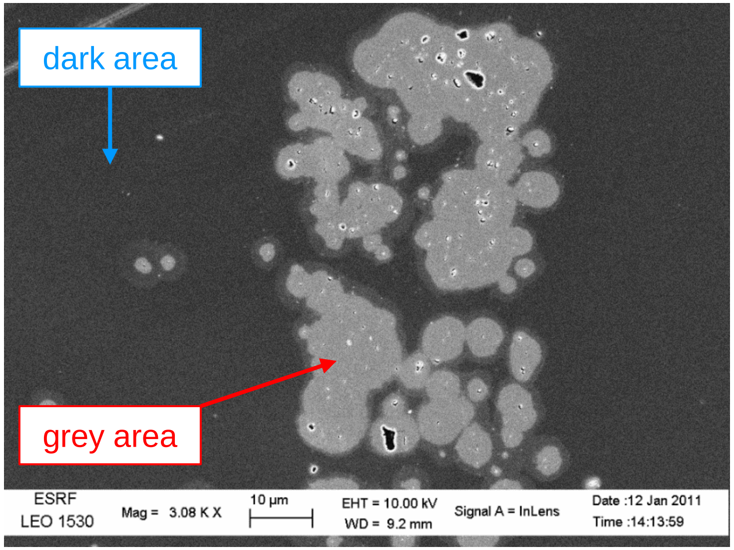


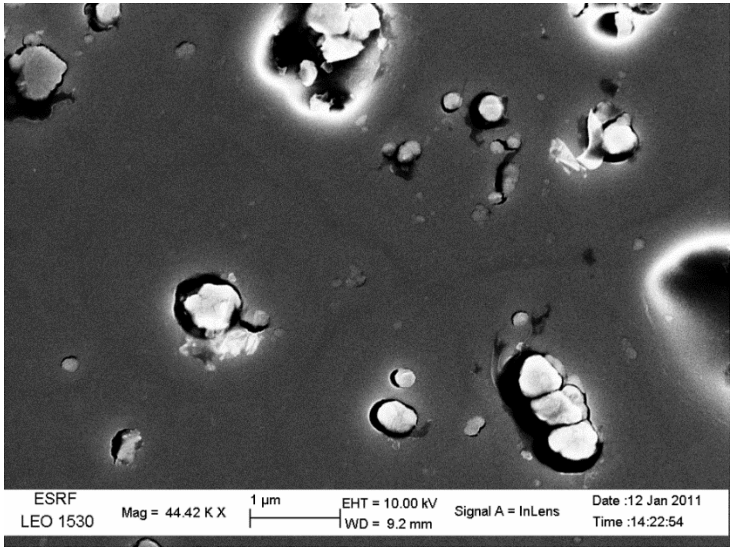


SEM imaging + EDX

- B_4C(5.1nm) / [Pd(1.31nm)/B_4C(1.34nm)]$_{150}$
- 2 months stored in air
- Defects containing particles (or holes)
- Surrounded by grey halos
- B + C in dark zones
- B depletion and O inclusion in grey areas

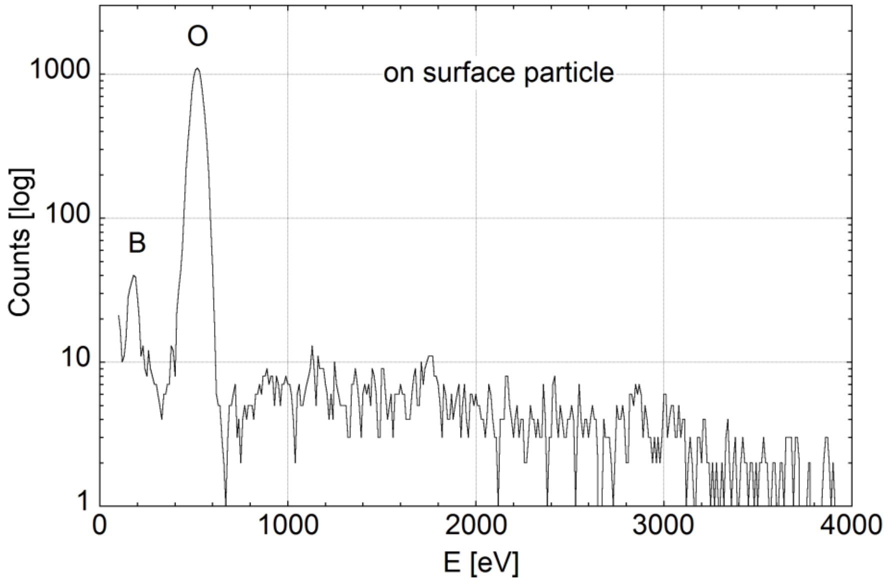


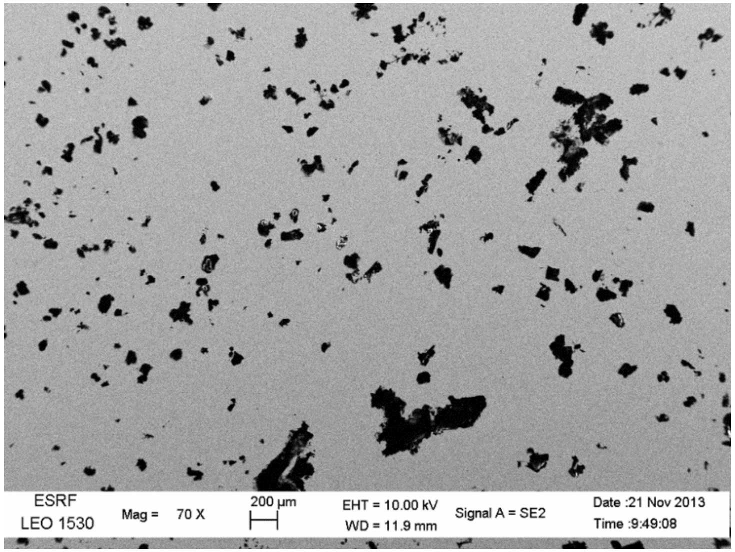


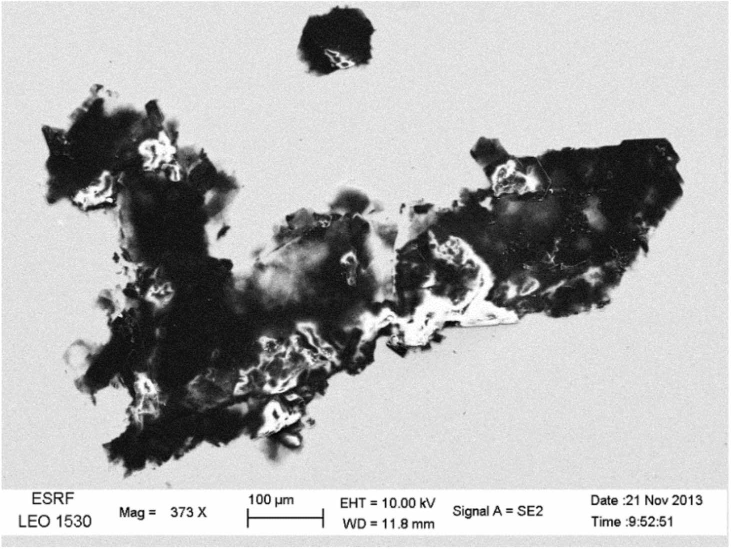


SEM imaging + EDX

- B_4C(2.4nm) / [Pd(1.33nm)/B_4C(1.66nm)]$_{50}$
- 2 months stored in air
- Large insulating surface particles
- Spectra on particle
- B and O signals only
- Evidence for B_2O_3 crystals

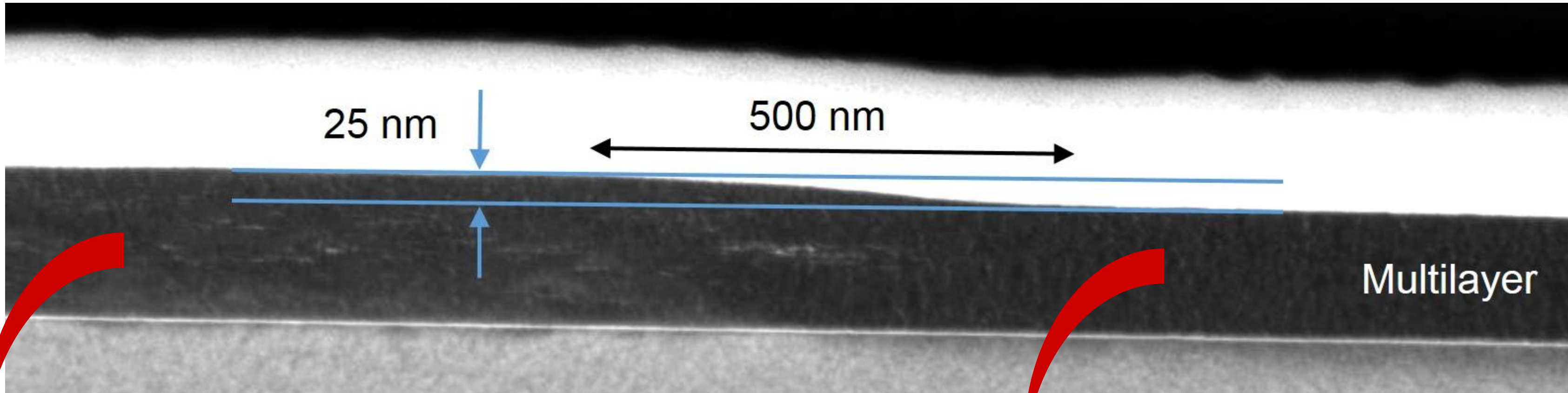


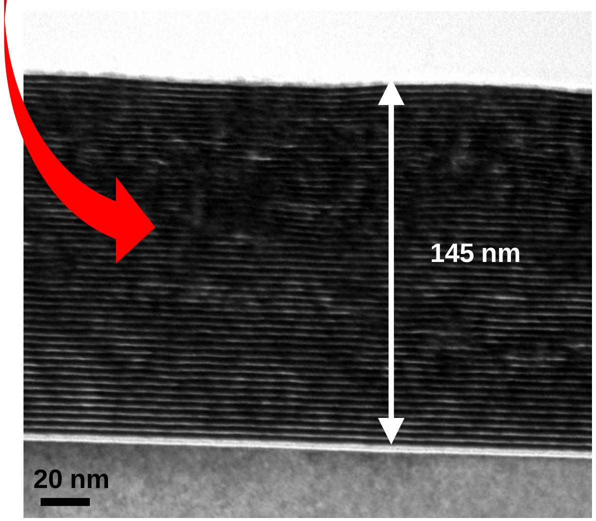


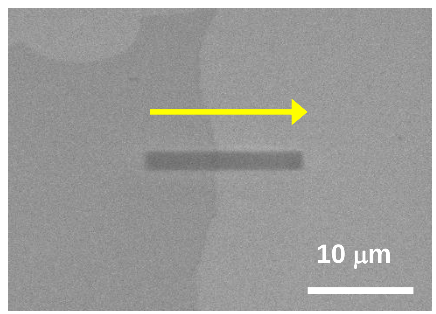


TEM STUDIES

- B_4C(4.2nm) / [Pd(1.33nm)/B_4C(1.65nm)]$_{50}$ (6 months stored in air)

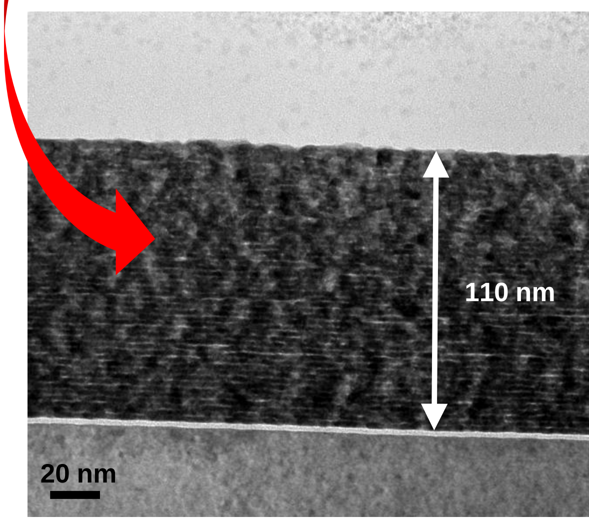






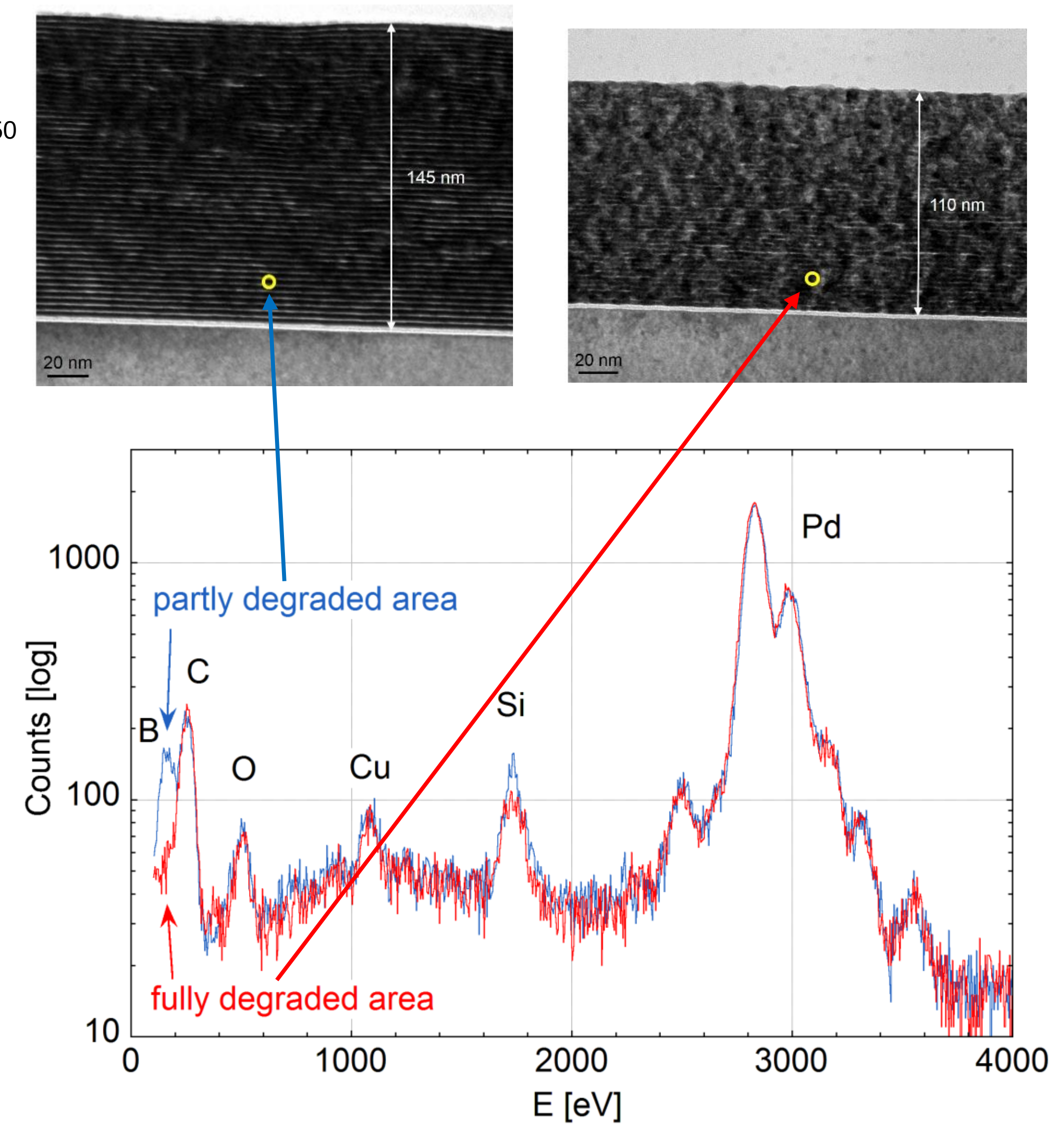
Dark → Grey zone

- Thickness loss of 25%
- ML structure distorted



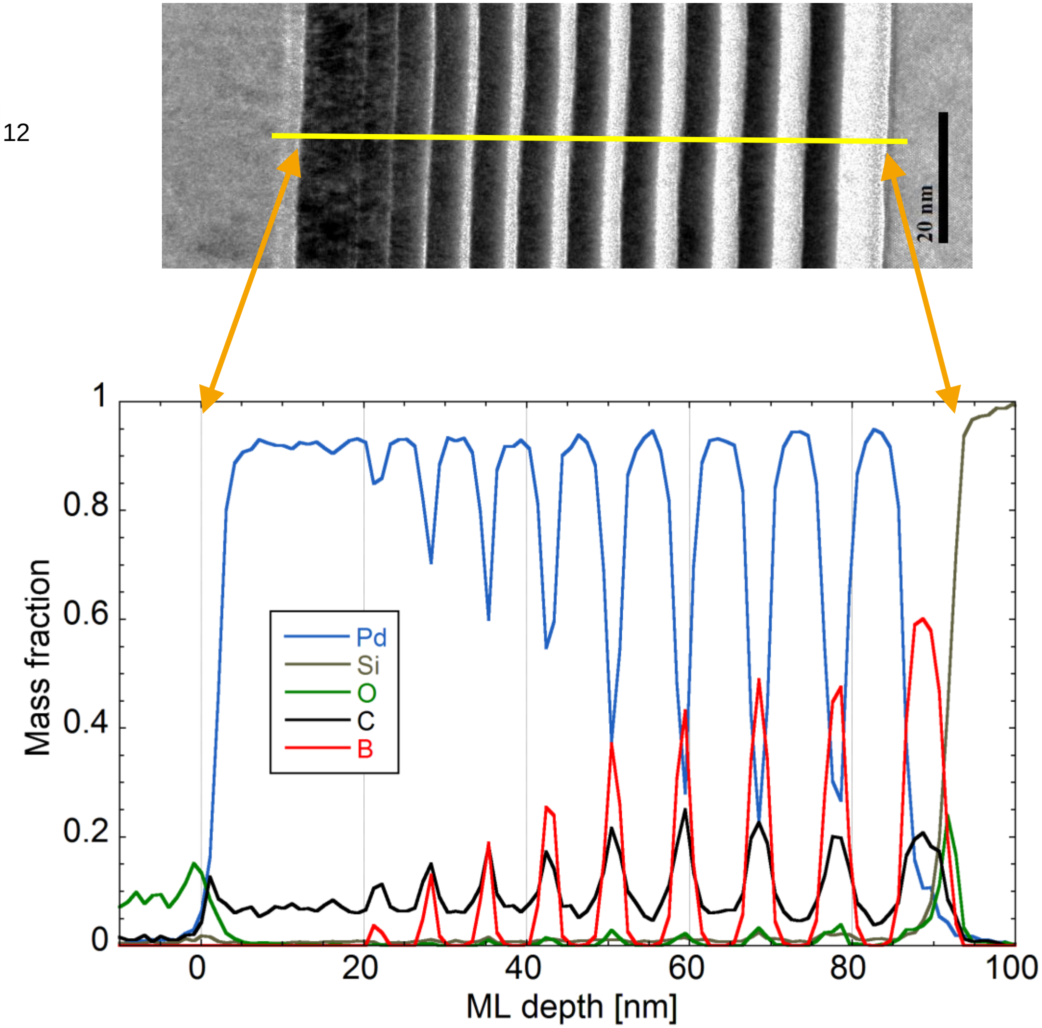
TEM EDX

- $B_4C(4.2nm)$ / $[Pd(1.33nm)/B_4C(1.65nm)]_{50}$
- 6 months stored in air
- Probing local cross section
- B depletion in degraded areas
- Similar spectra compared to SEM data
- Single layers not resolved



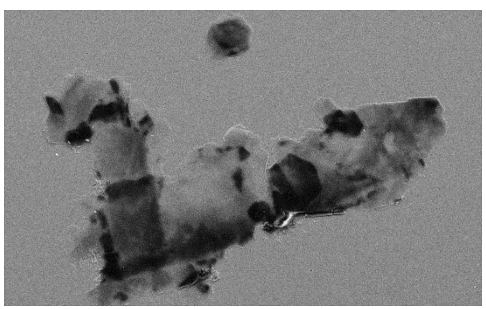
TEM EDX

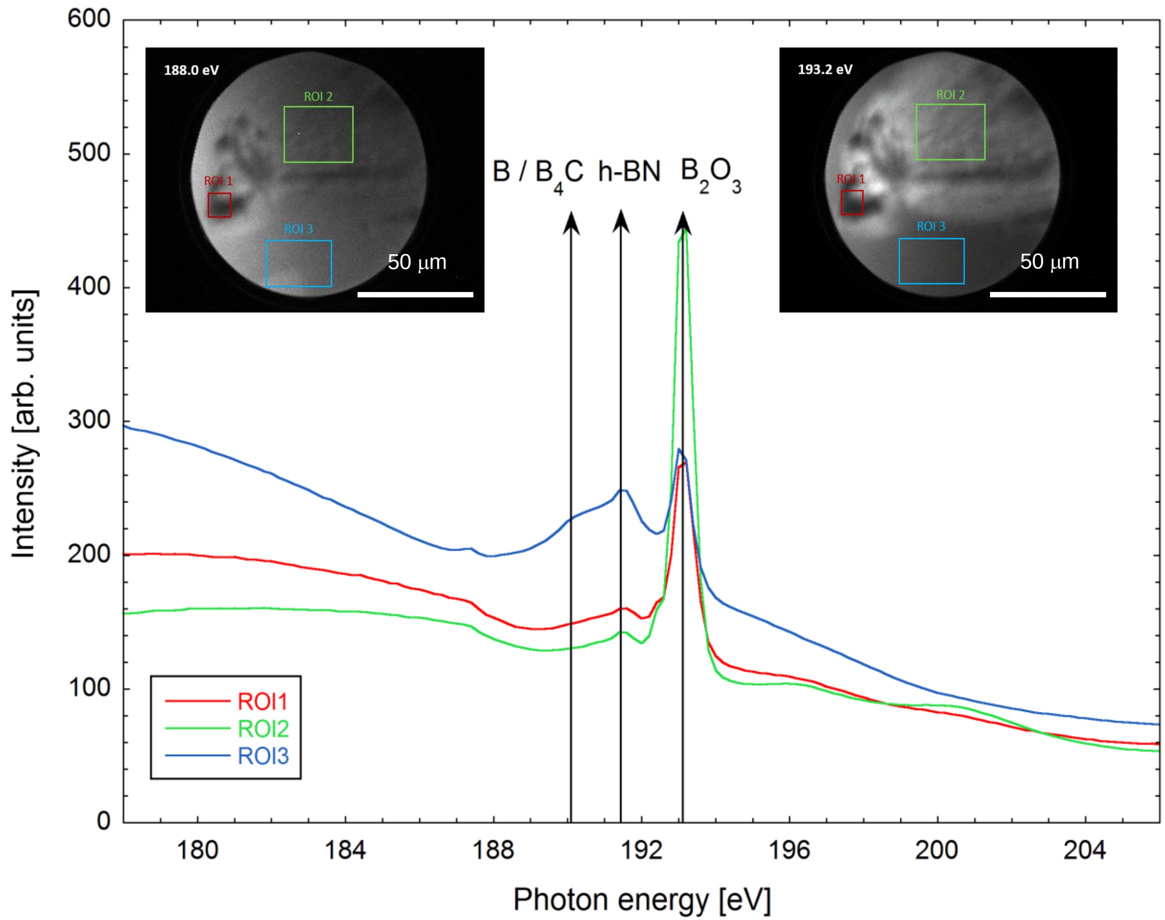
- Non-periodic ML with variable t(B_4C)
- B_4C(0.5nm) / [Pd(4.0nm)/B_4C(6.5-1.0nm)]$_{12}$
- 3 years stored in air
- Scan across ML depth
- Pd signal ≈ deposited quantities
- B signal appears for t(B_4C) > 1.5 nm increases with ML depth down to Si
- C fraction saturates earlier
- O content scales with B signal
- Upper B_4C layers disappeared
- Lower B_4C layers oxidized



PEEM imaging spectroscopy

- B_4C(2.4nm) / [Pd(1.33nm)/B_4C(1.66nm)]$_{50}$
- 5 weeks stored in air
- Showing surface crystals
- Chemical shift of B Kα peaks
- High spatial resolution
- Sensitive to low-Z elements
- B_2O_3 like compounds on crystals
- B / B_4C away from crystals
- Confirms x-ray and EDX data





SUMMARY

Degradation process in Pd/B_4C MLs

- Oxygen enters through defects, drains Boron to form B_2O_3
- B_2O_3 crystallizes at surface, then evaporates or dissolves in air
- Boron depletion and d-spacing reduction in affected areas
- ML order severely disturbed
- Time scale: hours $\rightarrow$ days (unprotected MLs)
- Protection layers: life time $\rightarrow$ years ($\rightarrow$ stable in vacuum)

Why fast degradation in Pd/B_4C MLs ?

- Thermodynamics of Pd/B_4C and other Metal/B_4C MLs
- Enthalpy of formation $\Delta_f H^0$ (solid-solid reactions) [kJ/mol]
- Free energy of formation $\Delta_f G^0$ (solid-gas reactions) [kJ/mol]

Material	B	C	O
B		-71 (B_4C)	-1194 (B_2O_3)
Pd	-26 (Pd_5B_2)		-85 (PdO)
Mo	-121 (Mo_2B)	-46 (Mo_2C)	-668 (MoO_3)
W	-31 (WB)	-20 (WC)	-764 (WO_3)

- B_2O_3 formation favored in Pd/B_4C $\rightarrow$ interface reactions with Pd prohibited
- Competing reactions in Mo/B_4C and W/B_4C $\rightarrow$ protection barrier formation
- Fast kinetics due to large interface

OUTLOOK

- Ongoing follow-up of long term stability
- Test of further barrier layers
- Stress issue in Pd/B_4C
- Test and review other absorber/B_4C or Pd/spacer systems

Thank you !