

Screening of oxidation resistant capping layers for EUV multilayers

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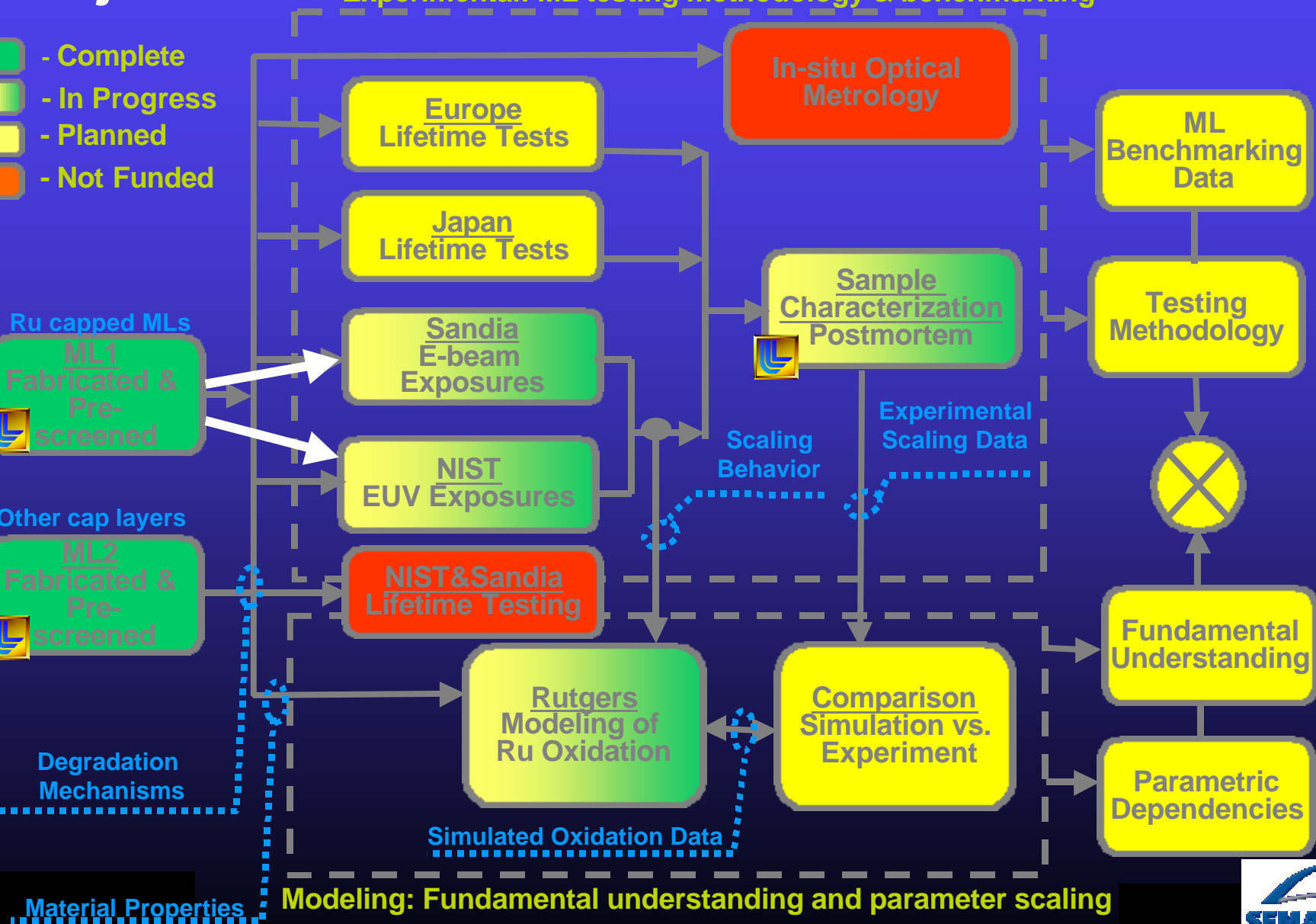
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Project Plan

-  - Complete
-  - In Progress
-  - Planned
-  - Not Funded



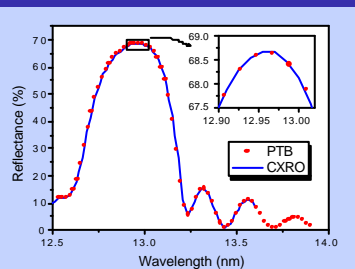
Screening tests overview



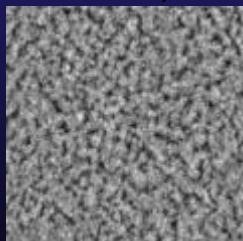
Screening tests

Report to SEMATECH

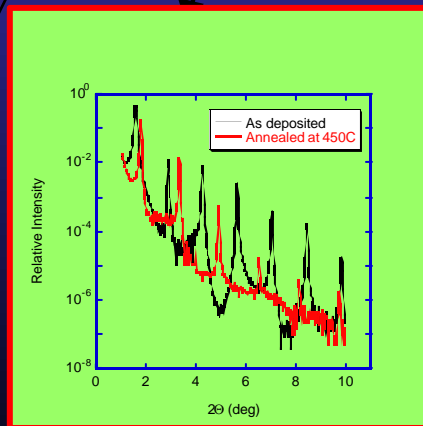
Reflectometry



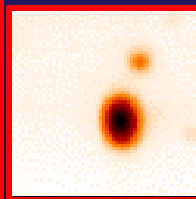
AFM measurements



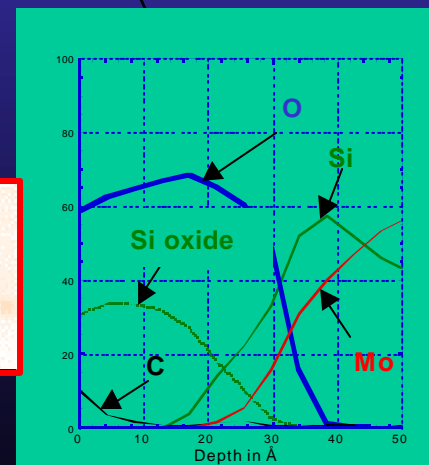
Thermal annealing



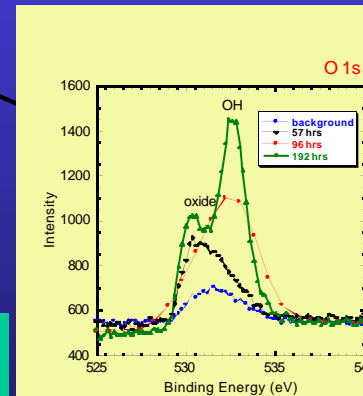
E- beam exposures



Depth profiling



Surface chemistry

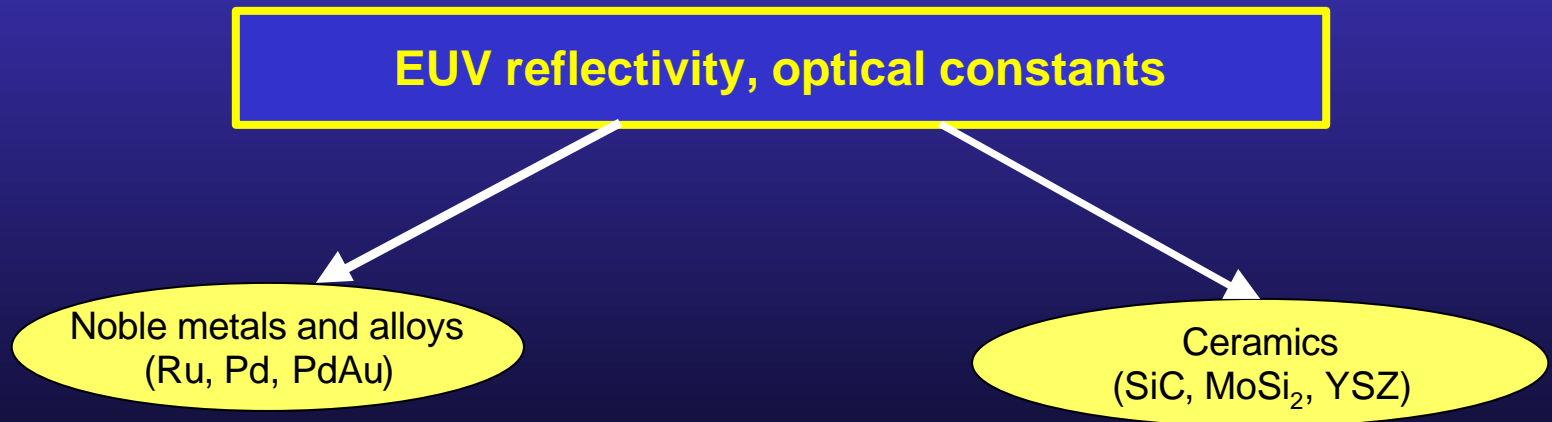


Multilayer Selection Criteria

Functional requirement:

Capping layer requirements:

- Long term stability EUV multilayers
- Impervious to diffusion of oxygen
- Limited thickness
- Complete coverage
- Chemically inert to the material underneath
- Thermally stable

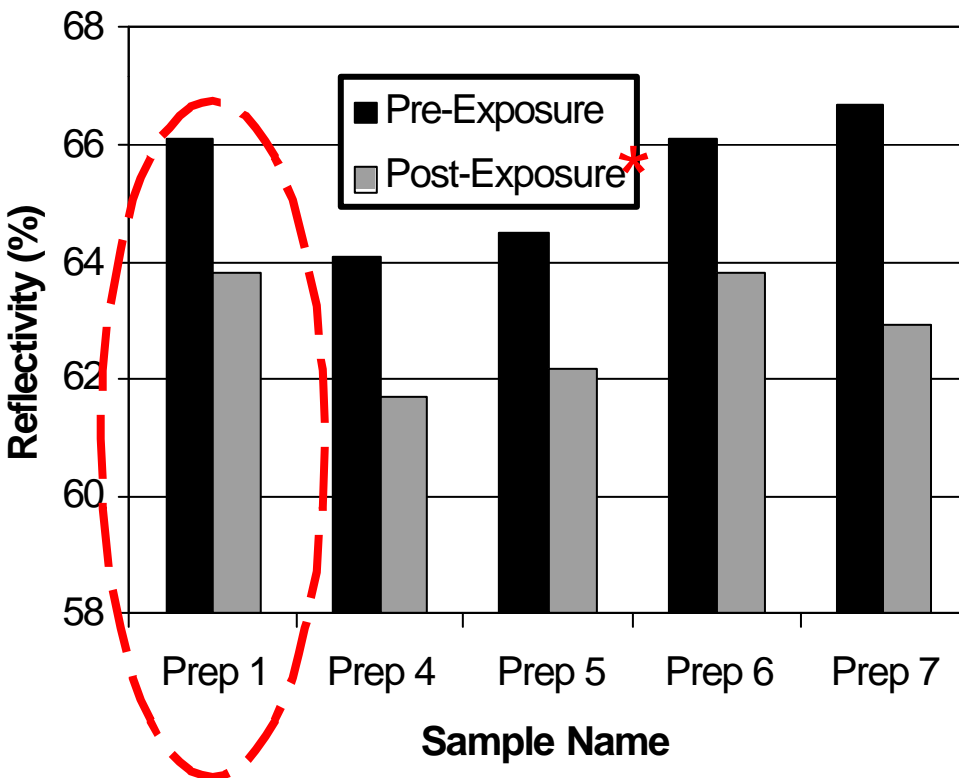


With the exception of Ru all these materials were only screened, not optimized for EUVL application

Multilayer 1 Sample Set Details



ML1 EUV Reflectivity



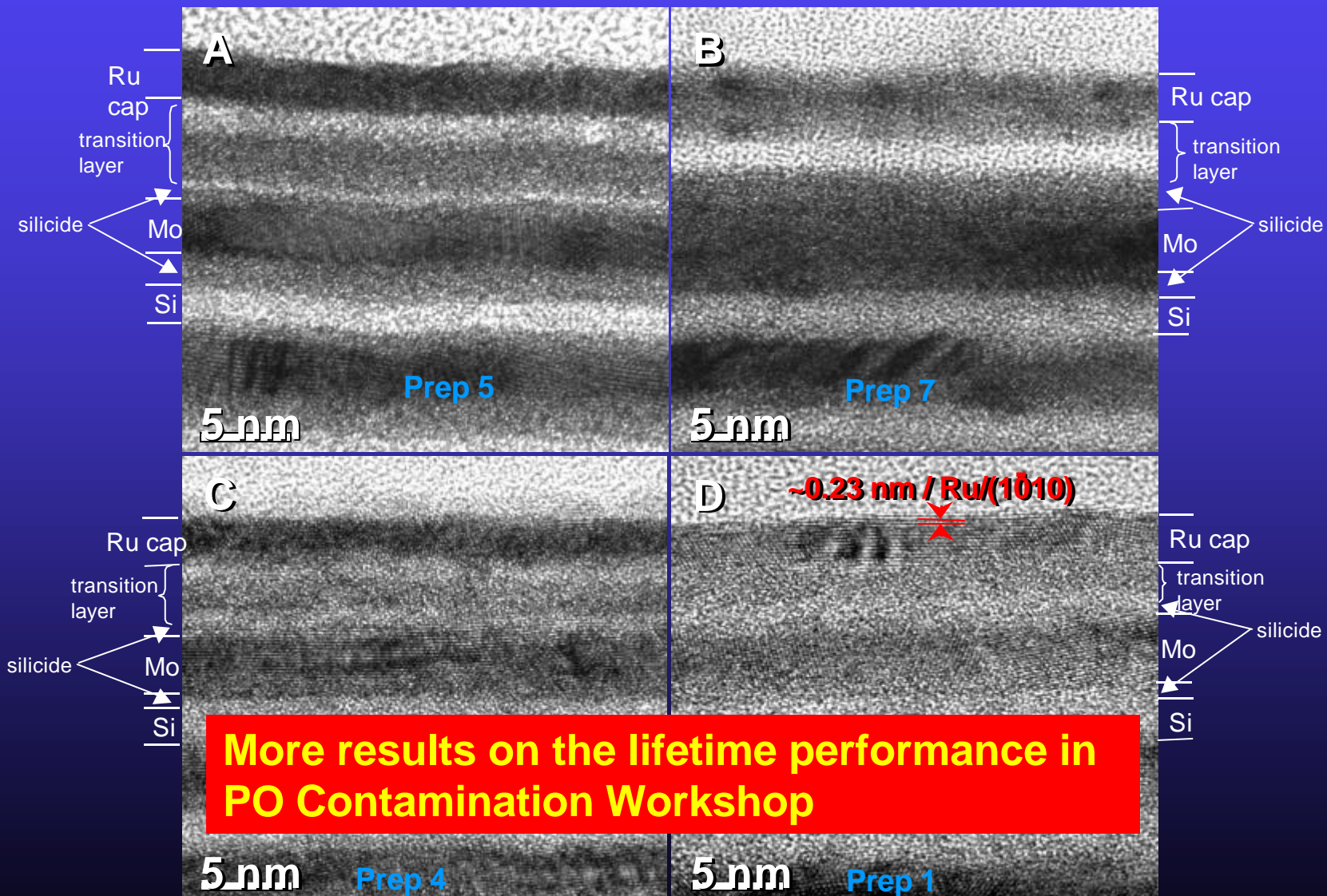
- Candidate for accelerated life-testing protocol development needed
- ML1 was a large set of candidate samples
- Deposition parameters strongly influenced EUV reflectivity & lifetime response
- Sample with best combination of reflectivity, thermal stability, and e-beam lifetime chosen

Preparation 1 (power change)
Preparation 4, 5 and 6 (gas mixture variation)
Preparation 7 (material variation)

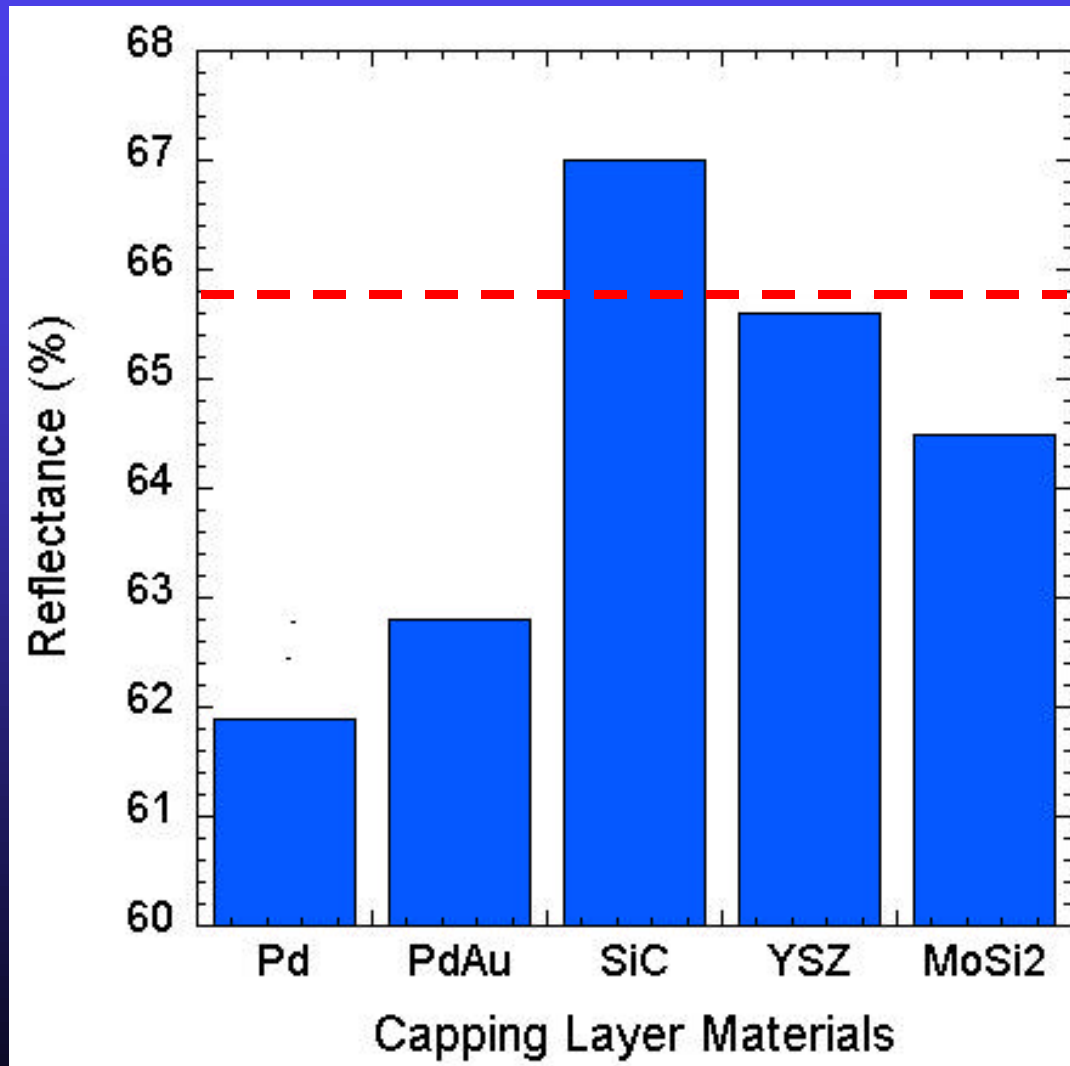
*

Exposure = electron beam exposure; 1 KeV;
5mA/ mm²; 5 x 10⁻⁷ Torr water; Time = 40 hours

High lifetime of ML1 (Prep 1) is associated with a dense, crystalline capping layer



EUV reflectivity is one of the selection criteria for capping layer candidates

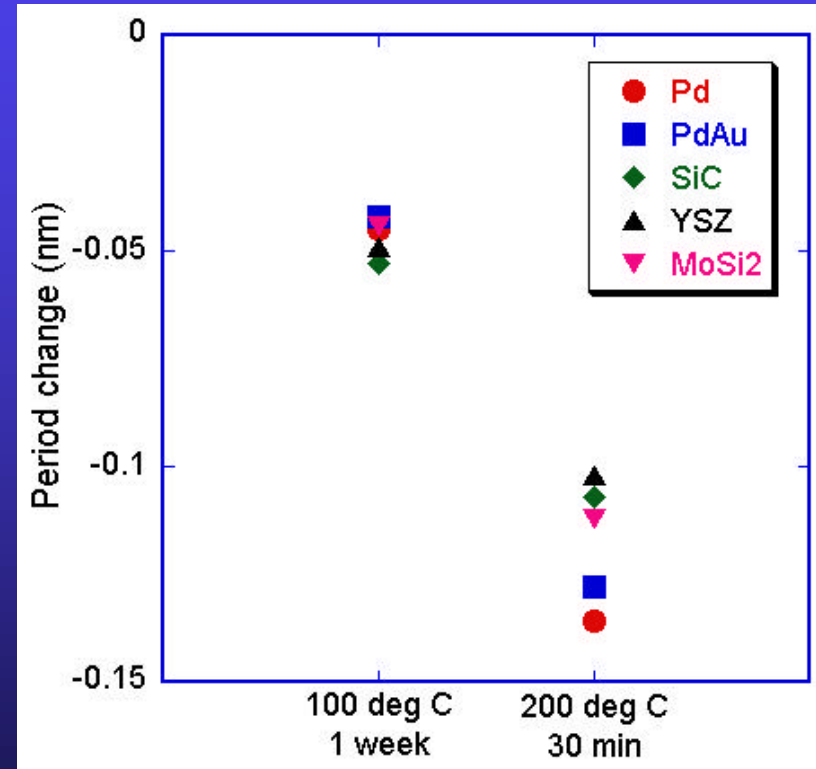
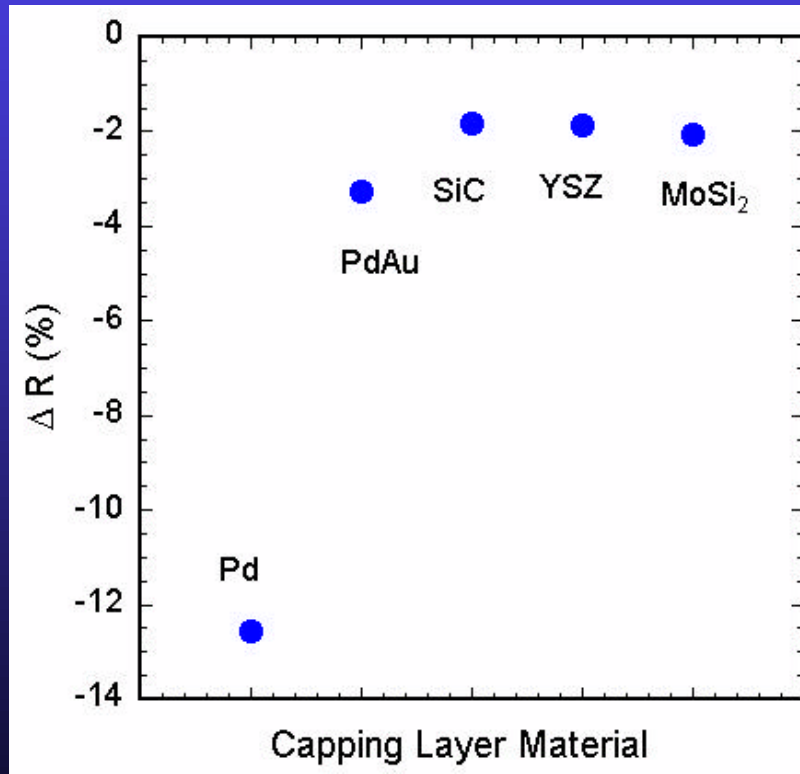


Ru benchmark

Annealed Pd-capped MLs show high reflectivity loss with notable period change



Multilayers exposed to 200°C for 30 minutes



Pd- and PdAu-capped MLs show significantly larger period change than other multilayers although all of them consists of the same Mo/Si stack with 50 bilayers.



Thermal annealing considerably increased surface roughness of Pd- and PdAu-capped MLs

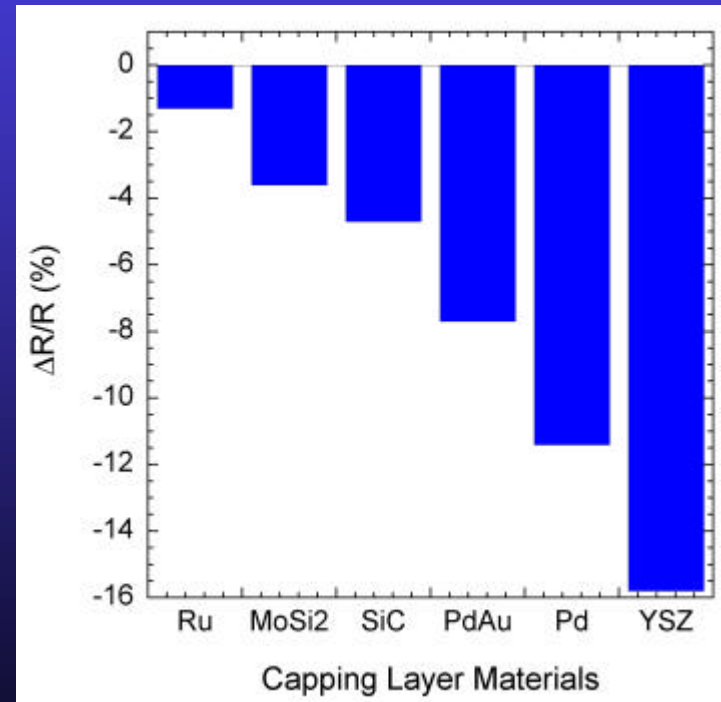
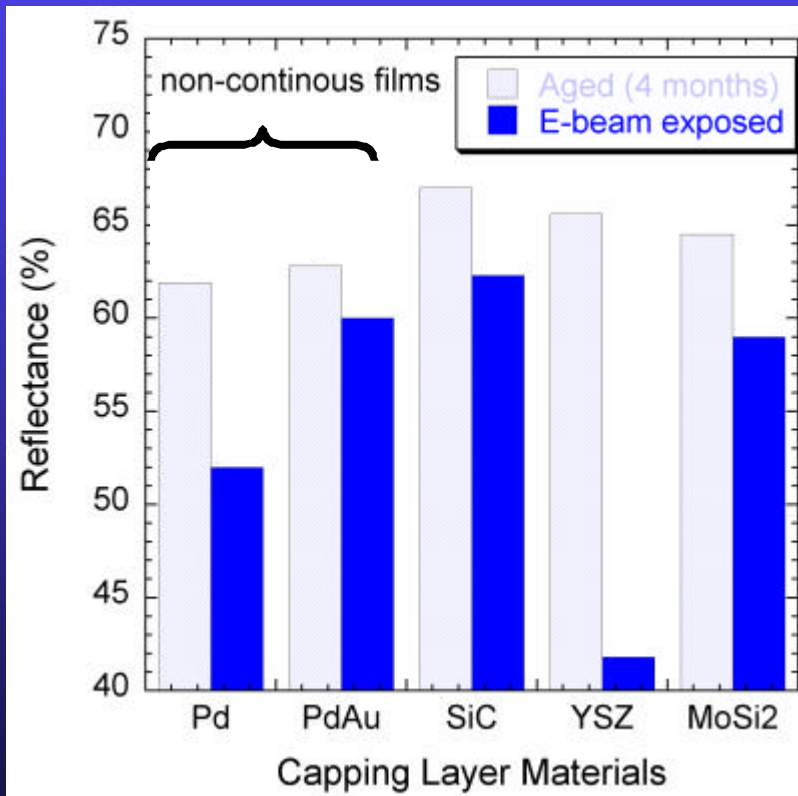
Material	As-deposited HSFR (nm)	After 200°C for 30 min HSFR (nm)
Pd	0.22	0.70
PdAu	0.39	0.57
SiC	0.17	0.17
YSZ	0.22	0.20
MoSi ₂	0.21	0.26

Large change

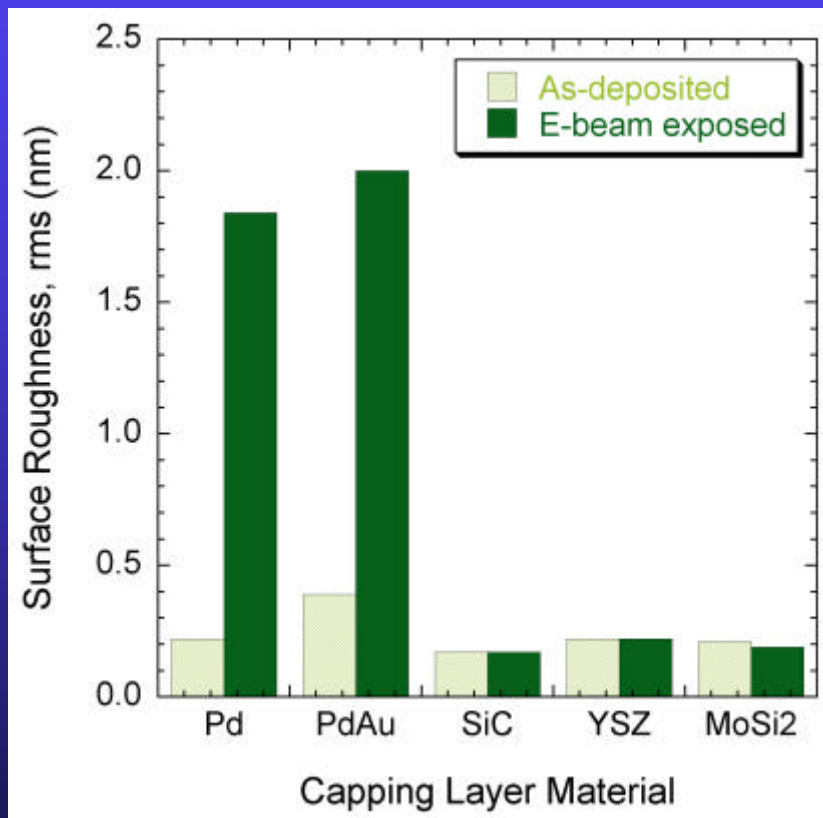
No change

What is the cause of the reflectance drop in these materials?

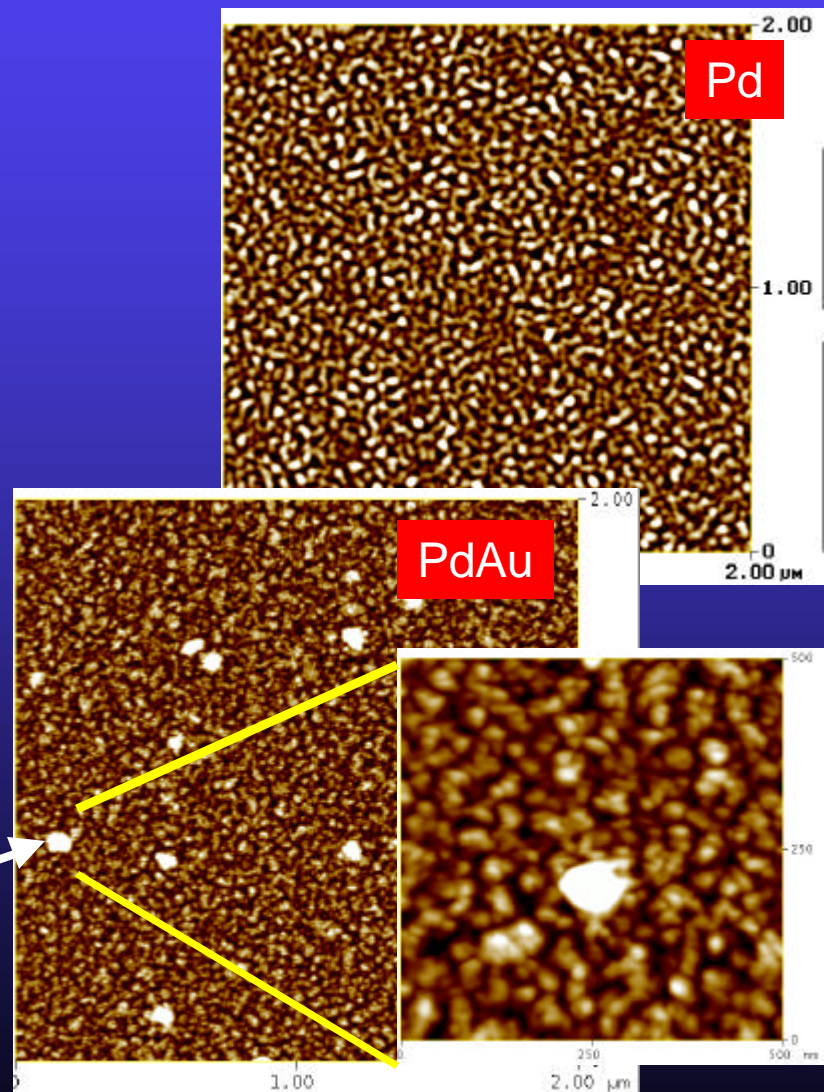
Large variation in reflectance drop for different capping layer materials suggests different degradation mechanisms



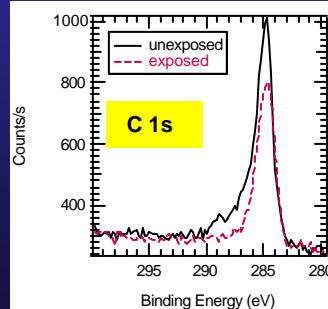
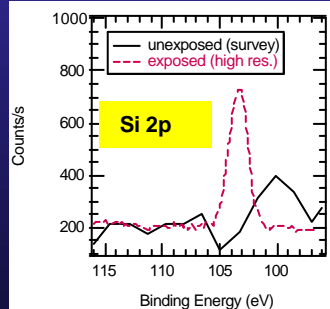
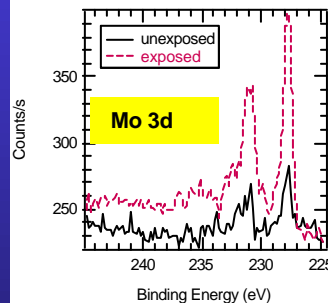
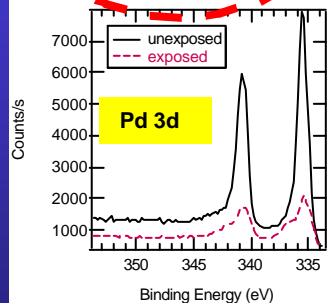
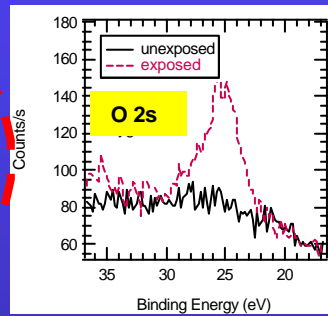
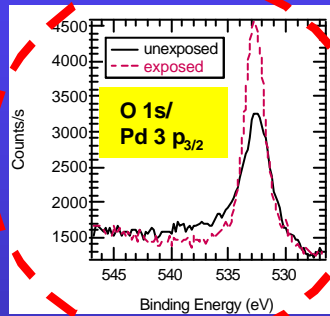
Surface roughness in e-beam exposed areas of Pd- and PdAu-capped MLs increased dramatically



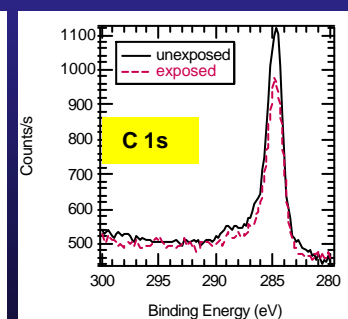
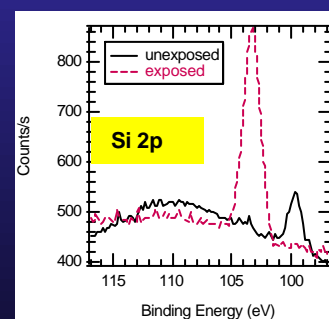
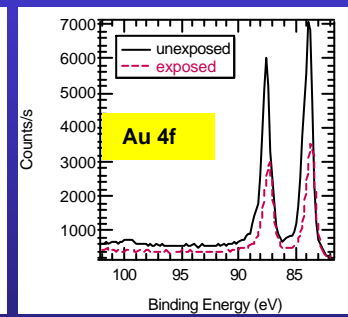
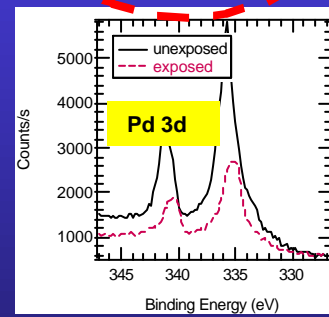
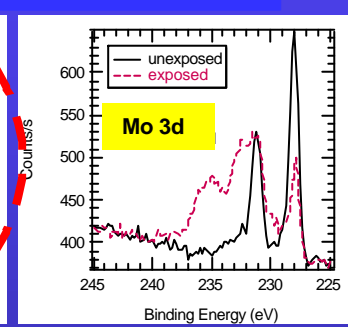
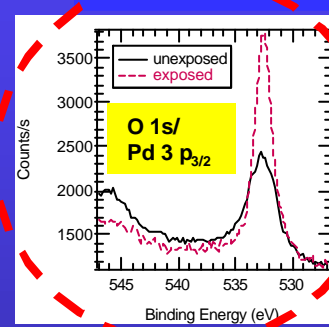
These bright spots are ~14 nm tall and their chemical composition could not be determined



Exposed areas in Pd and PdAu-capped MLs show increase in oxygen peak



Pd-capped multilayer



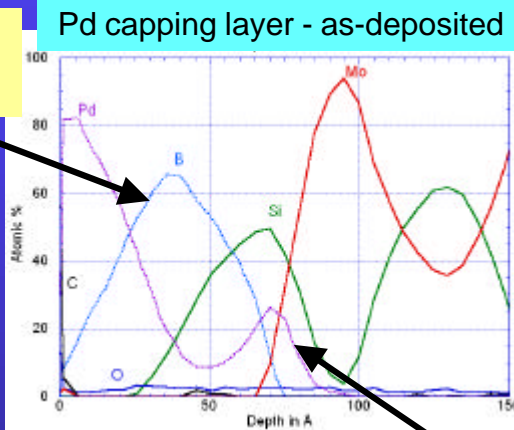
PdAu-capped multilayer

Depth Auger profiles reveal diffusion barrier breakdown in the e-beam exposed areas

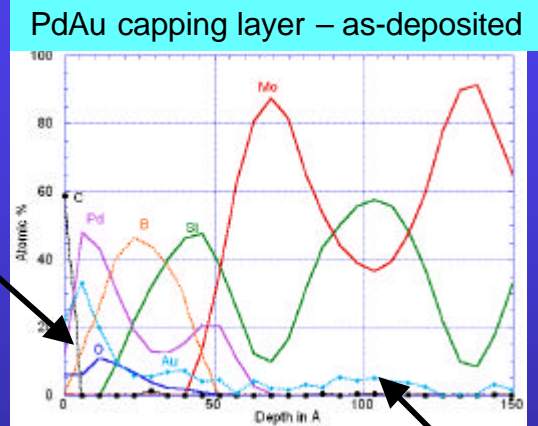


Boron carbide diffusion barrier

Where is carbon?



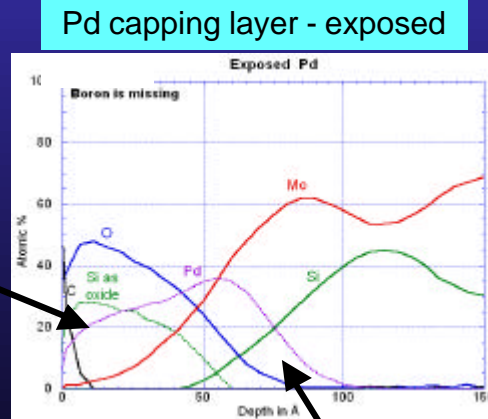
Partly oxidized Pd even in as-deposited state



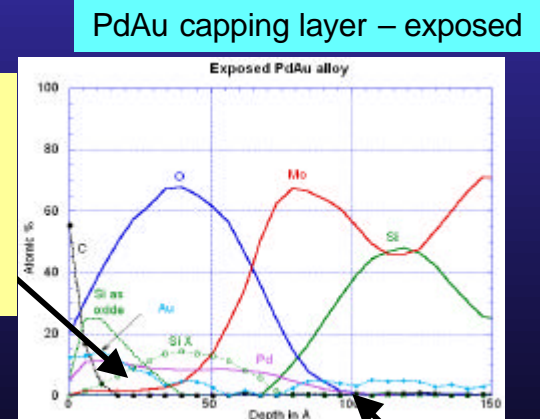
Pd peak increase below diffusion barrier

Presence of Au deeper in the ML

No boron - Boron possibly reacted with hydrogen to form gaseous species



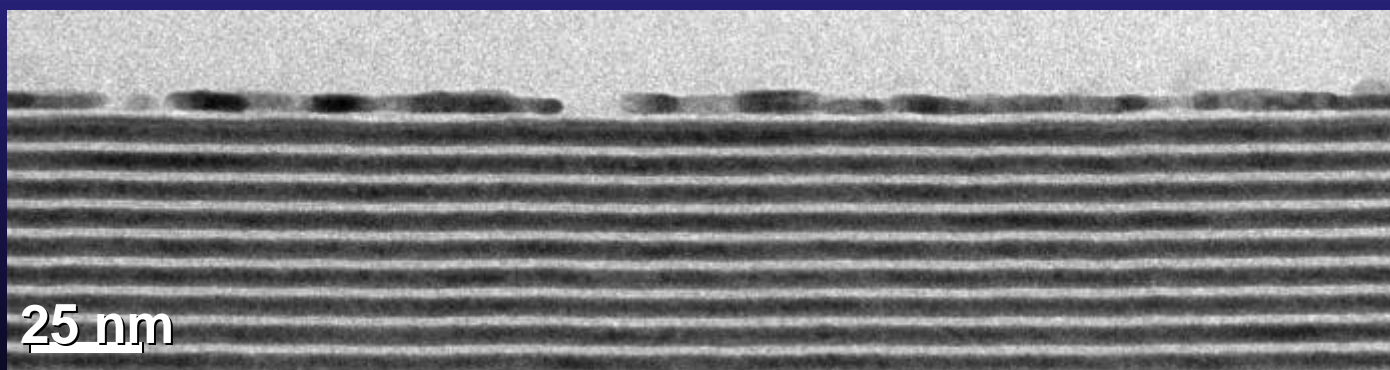
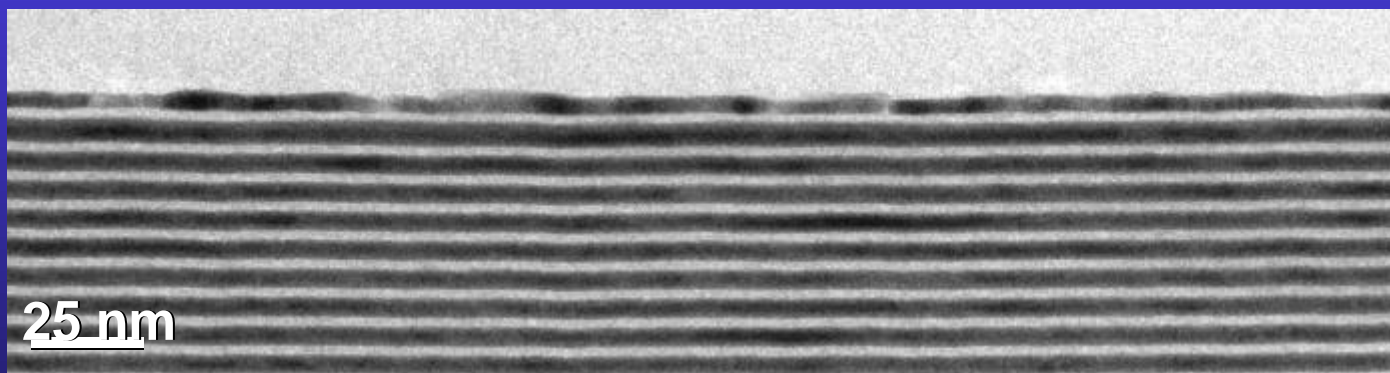
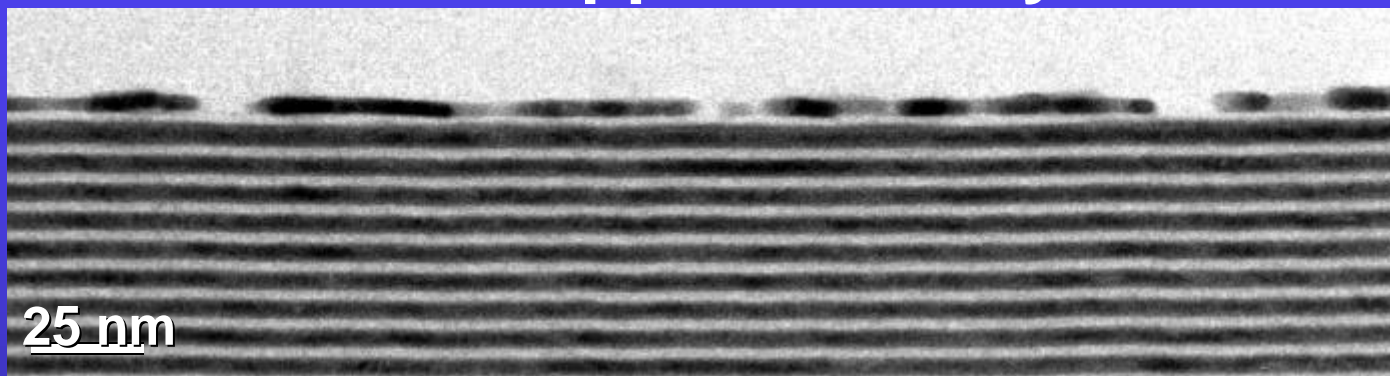
Highly oxidized surface – Some silicon formed an unidentified alloy



Pd oxidized and diffused further into the ML

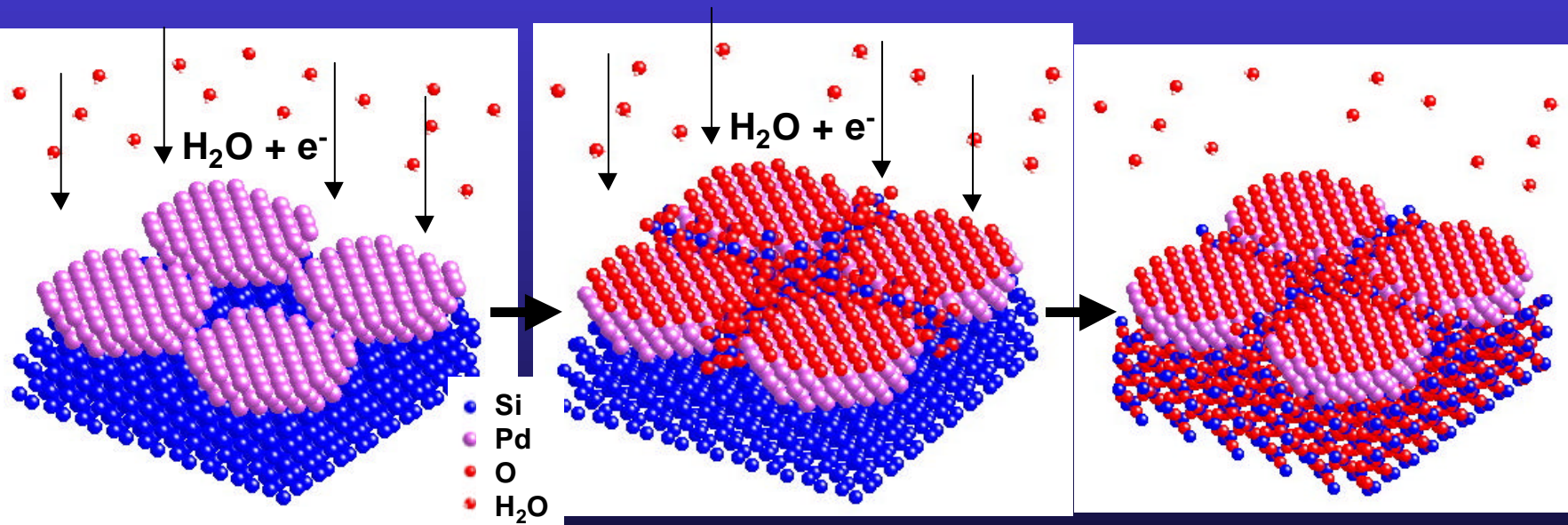
Both Pd and Au diffused into the ML

Cross section TEM image clearly shows coverage problems on PdAu-capped multilayer



Oxidation mechanism in Pd-capped multilayers

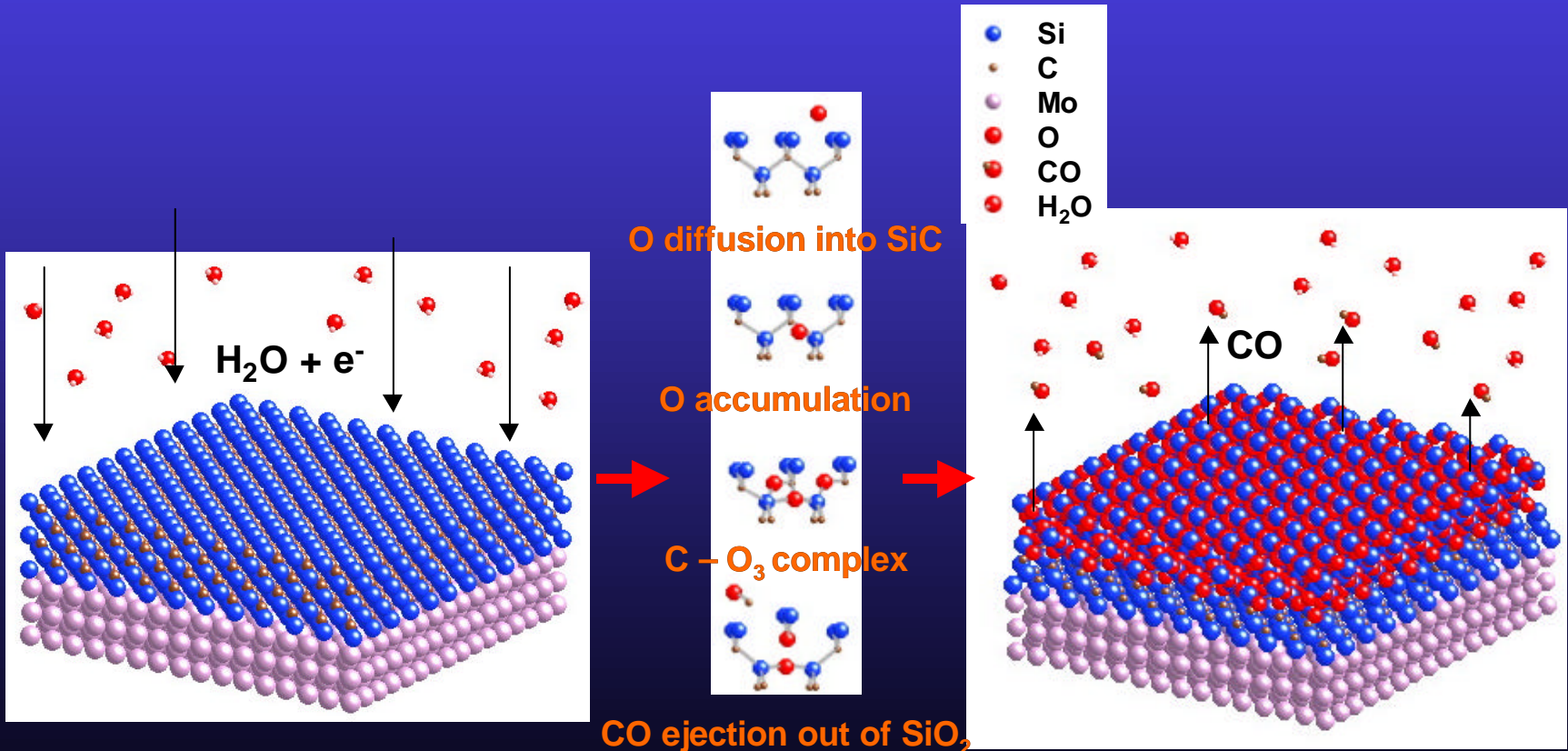
- Pd island growth
- Pd oxidation
- Expansion of SiO_2 into spaces between islands
- Oxidation of Si and Mo layers underneath



Similar mechanism expected in PdAu-capped multilayers

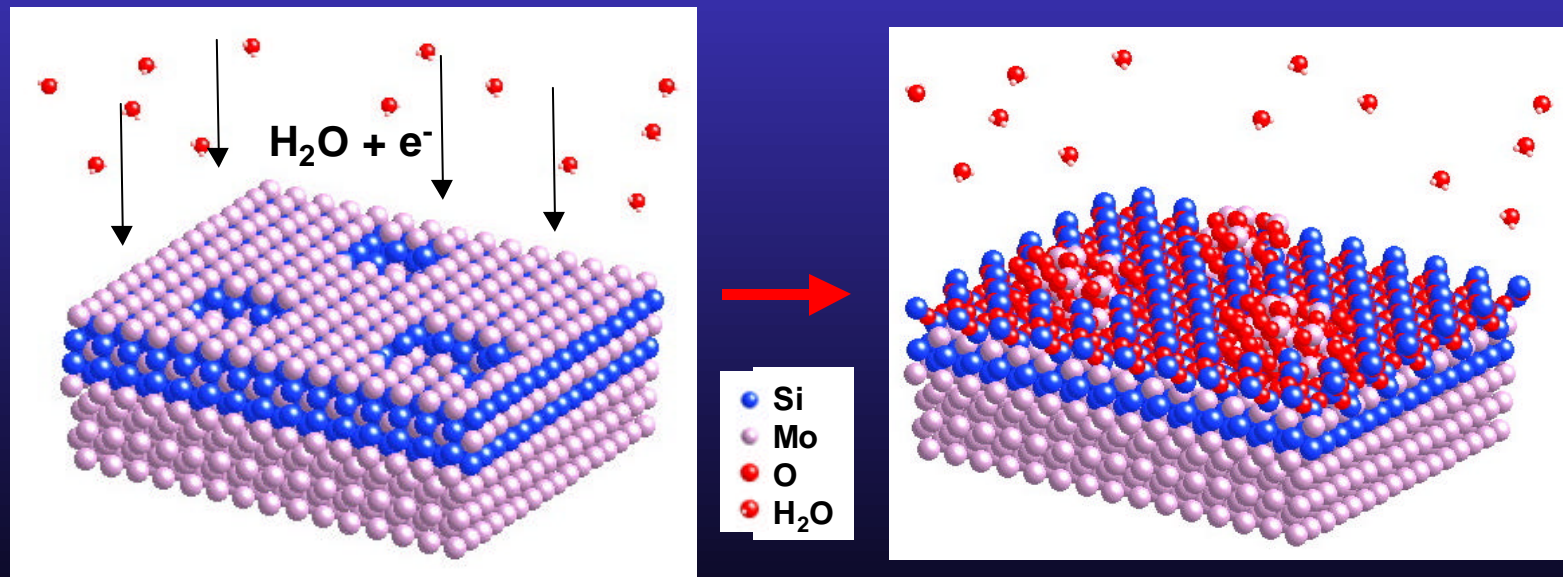
Oxidation mechanism in SiC-capped multilayers

- SiC converts to $\text{SiO}_2 + \text{C} + \text{CO(g)}$
- O diffuses into SiC, CO gas escapes through SiO_2 , C left at interface
- M. Di Ventura and S. T. Pantelides, Phys. Rev. Lett. **83**, 1624 (1999).



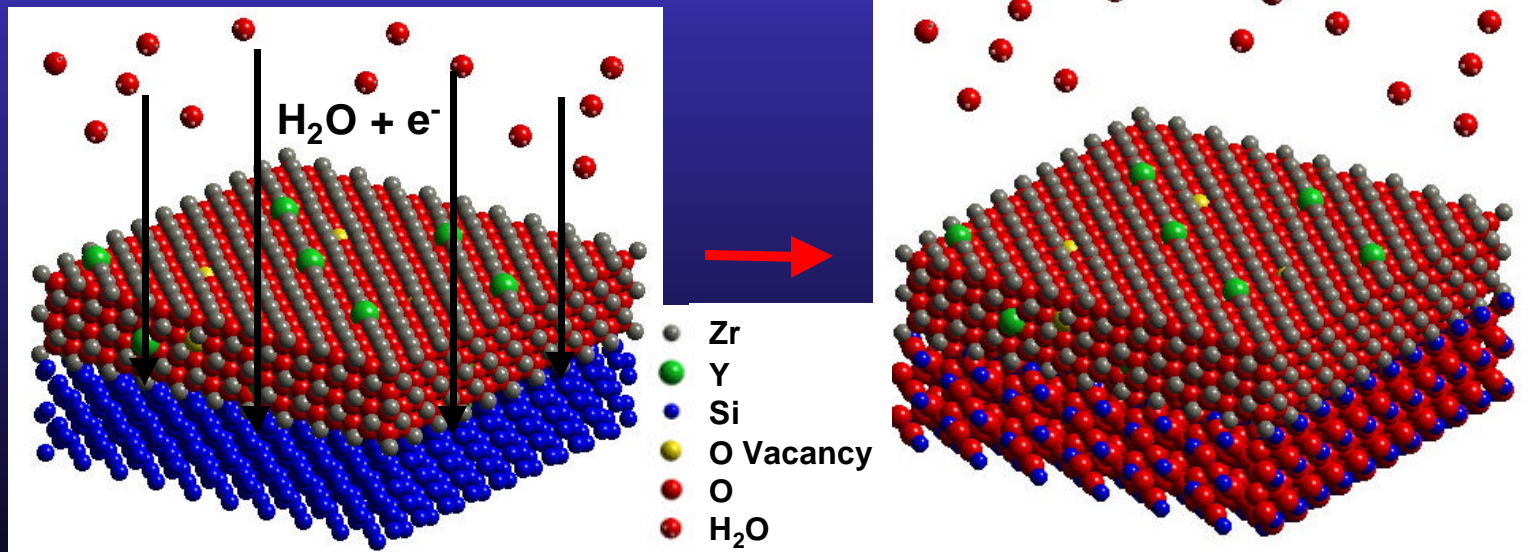
Oxidation mechanism in MoSi₂-capped multilayers

- Oxidation accelerated by non-stoichiometry, defects
- Protective SiO₂ formation on smooth stoichiometric surface, no MoO₃
- MoO₃ and SiO₂ formation starts at defects (pores, cracks)
- Volume increase at defects -> peeling



Oxidation mechanism in YSZ-capped multilayers

- Yttria-stabilized Zirconia (YSZ) unchanged
- Y stabilizes fluorite structure and introduces vacancies
 - 3% Y doping makes 0.75% of O sites vacant
- Mobile vacancies -> Enhanced oxygen diffusion in YSZ
- Oxidation of Si and Mo layers underneath



XPS and depth Auger results summary



Non-destructive XPS technique was used to obtain local chemical environment analyzing up to 5 nm into the multilayer

	E-beam exposed samples	
Capping layer	Capping layer XPS results	Underlying multilayer XPS results
Pd	Partial Pd oxidation, Pd diffusion into bulk	Si layer fully oxidized to SiO ₂ , Mo layer partially oxidized
Au _{0.5} Pd _{0.5}	Partial Pd oxidation, Au & Pd diffusion into bulk	Si layer fully oxidized to SiO ₂ , Mo layer partially oxidized to MoO ₃
SiC	SiC converts to SiO ₂ + C + CO	Si layer fully oxidized to SiO ₂ , Mo layer unchanged
YSZ	YSZ unchanged	Si layer partially oxidized to SiO ₂ , Mo layer partially oxidized to MoO ₃
MoSi ₂	Si oxidized to SiO ₂ , Mo removal or diffusion into bulk	Si layer fully oxidized to SiO ₂ , Mo layer partially oxidized



Summary

- Fabricated and pre-screened ML1 and ML2 samples. No capping layer development efforts were funded.
- Oxidation/EUV reflectivity degradation mechanisms determined for selection of novel capping layer materials for EUV multilayer mirrors.
- Ruthenium capping layer still a leading candidate for oxidation protection. Further improvements are required, however, need fundamental understanding of Ru surface science.
- The differences in the mechanisms demonstrate that test protocols will have materials dependence that cannot be ignored.