Deformation of particle-strengthened metal-oxide nanolaminates on polymer

Barbara Putza,b, Amit Sharmaa, Thomas Edwardsa, Daniel Többensc, Johann Michlera

a. Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland b. Department of Materials Science, Montanuniversität Leoben, Leoben, Austria c. Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany

Abstract: A unique deposition setup combining atomic layer (ALD), physical vapour (PVD, magnetron sputtering) and nanoparticle (NP) deposition was used to fabricate a series of thin film multilayer structures of particle-strengthened metal (Al, Au, PVD + W NPs) and oxide layers (Al₂O₃, ALD) on flexible polymer substrates without breaking vacuum. The multilayers were strained in uniaxial tension to investigate their deformation behavior. Film stresses in the metal layers, measured in situ with X-ray diffraction, in situ resistance measurements and post-mortem SEM analysis of the thin film surfaces reveal strengthening, and changes in the fragmentation behavior as a function of NP content, metal and oxide layer thickness.

Motivation

Deformation of flexible nanolaminates is dominated by the most brittle component. Cracks in the brittle layers cause ductile layers to fracture at low strains. Embrittlement depends on the modulation period $(t_{brittle} + t_{ductile})$ and ratio $(t_{brittle}/t_{ductile})$ [1].

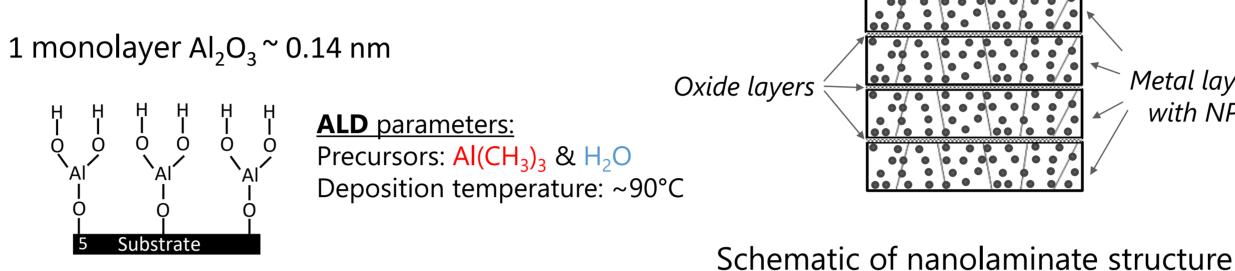
The ALD/PVD process with vacuum transfer opens up a wide range of otherwise unachievable modulation and thickness ratios for metal-oxide nanolaminates. Thickness control with precision down to 0.1nm can be achieved for Al₂O₃, well below the native oxide thickness of pure Al films. Incorporated NPs can enhance mechanical properties through strengthening or crack deflection.

- How does oxide failure influence deformation of the Al layers?
- Can we avoid through thickness cracking of Al by reduced oxide layer thicknesses?
- Can we control grain growth and stabilize nanostructures with monolayers of ALD?
- Can we strengthen laminates by reducing the metal layer thickness and incorporating NPs?

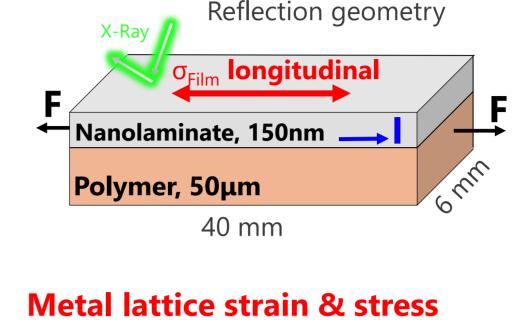
HR-TEM

Thin film deposition

1st half cycle Deposition chamber Film architectures Magnetron sputtering Schematic of combined metal and nanoparticle deposition



In situ² film stress measurements



(X-Ray Diffraction & sin²Ψ) Film resistance R/R₀

(4-Point-Probe)

Testing Parameters: Continuous uniaxial tensile test

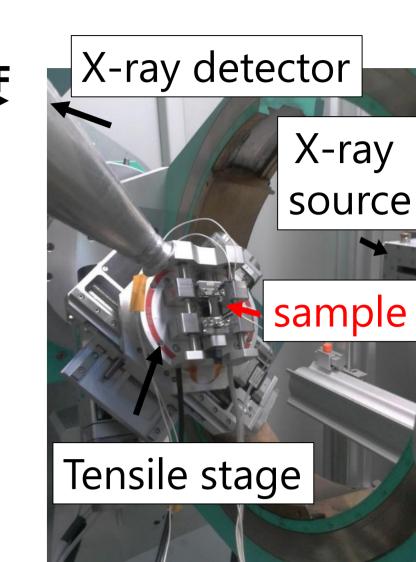
 $\varepsilon_{\text{max}} = 12\%$ Gauge length: 20 mm Displacement rate: 0.1 mm/min Strain rate: $\sim 5 \times 10^{-5}/s$

50-2.4

10 12

150 nm Al

Anton Paar TS 600



X-Ray Parameters: Spot Size: 300 µm diameter Beam energy: 8 keV Sin²Ψ analysis: 5 angles (0°-45°)

ductile

Schematic of ALD cycle for Al₂O₃ layers

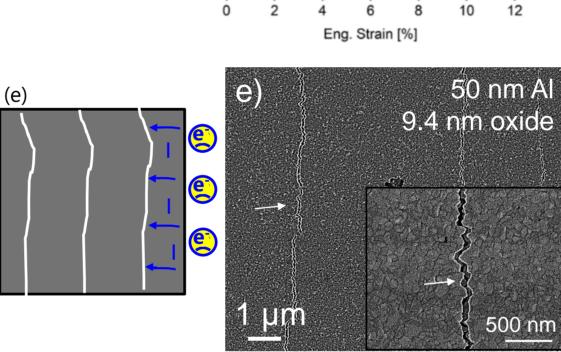
HR-TEM

2nd half cycle

Substrate

I) 150 nm Al/Al₂O₃ nanolaminates - Variation of Oxide Layer Thickness





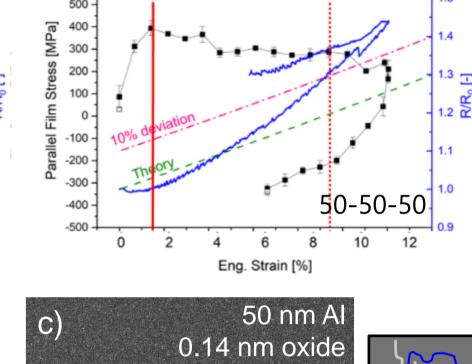
Electro - Mechanical Behavior ductile-like

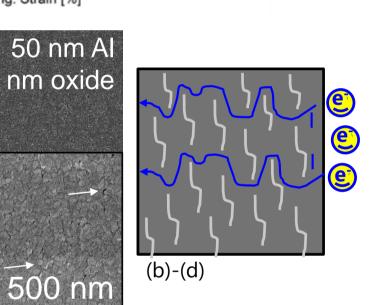
Eng. Strain [%]

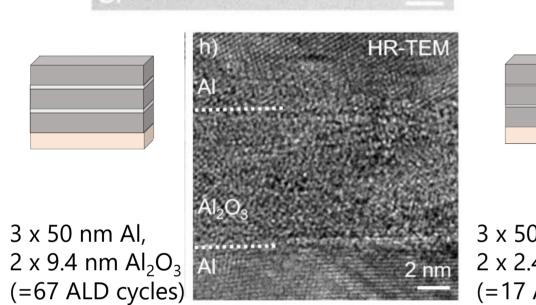
Ductile reference

Metal layers

with NPs



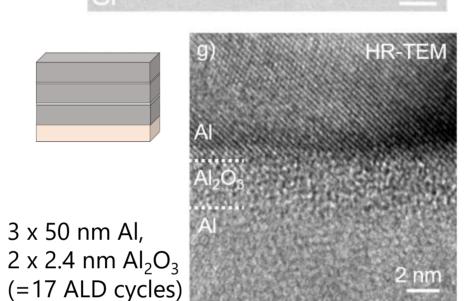




Al₂O₃

Al₂O₃

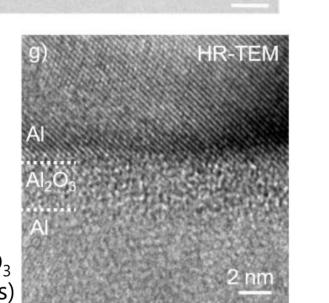
67 ALD cycles

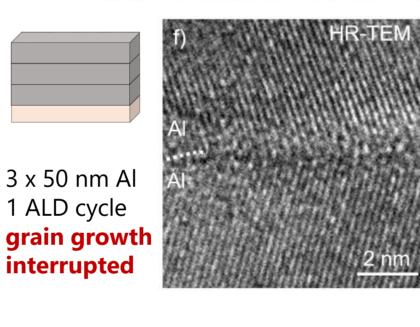


d)50-2.4

Al2O3

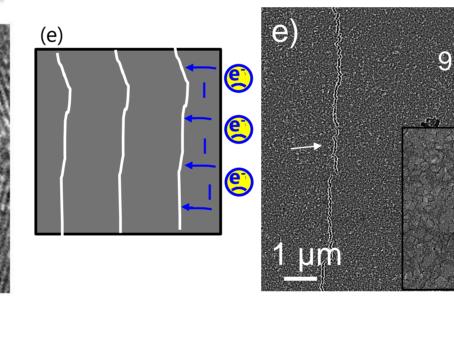
Al₂O₃ 17 ALD cycles



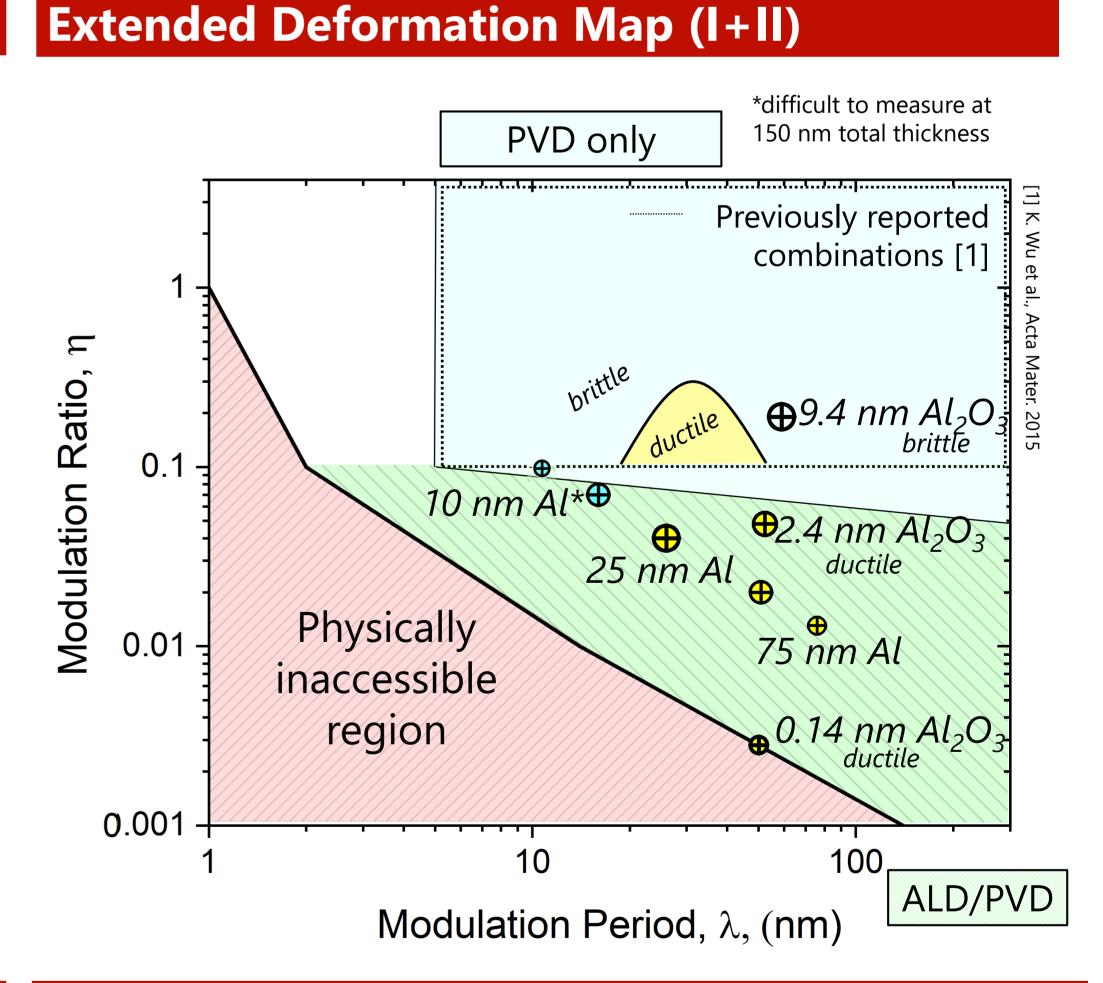


Al₂O₃

1 ALD cycle

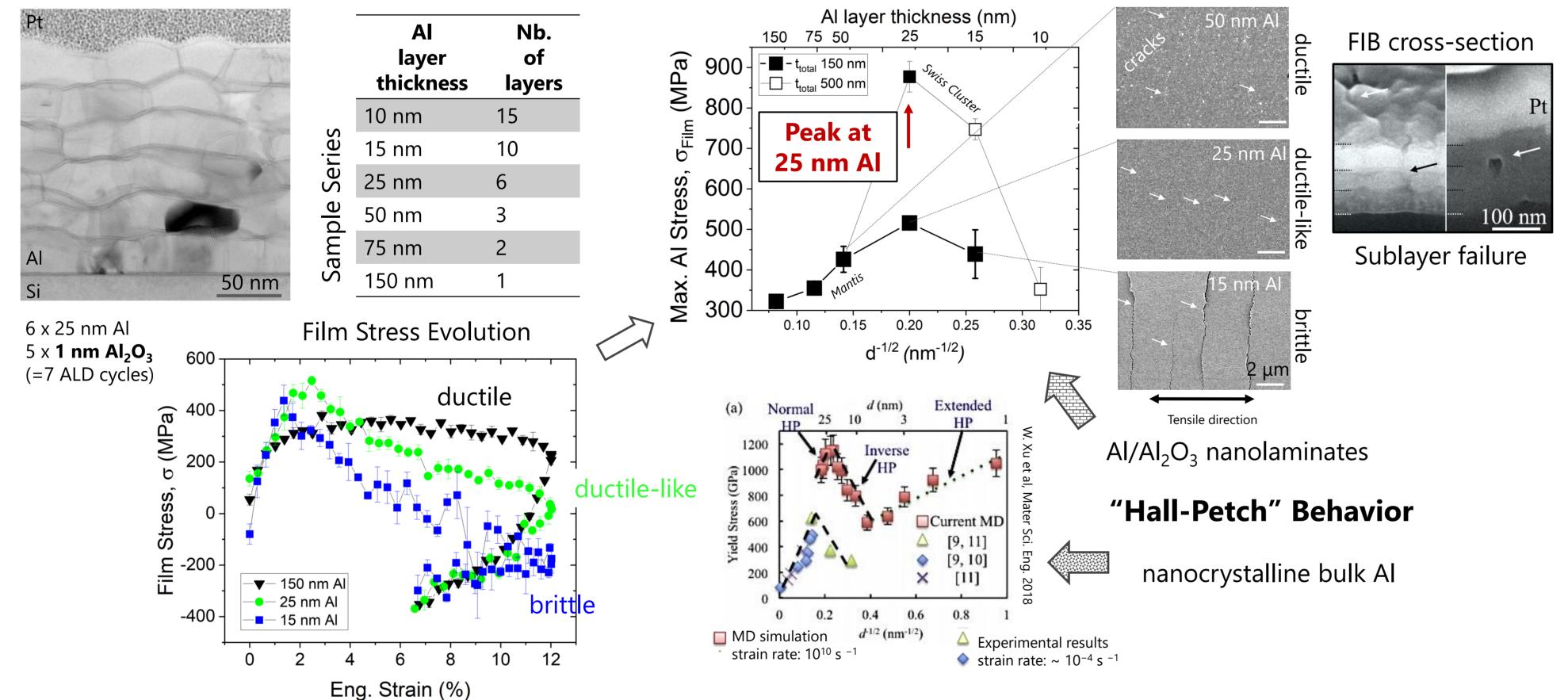


Eng. Strain [%]



um

II) 150 nm Al/Al₂O₃ nanolaminates – Variation of Metal Layer Thickness



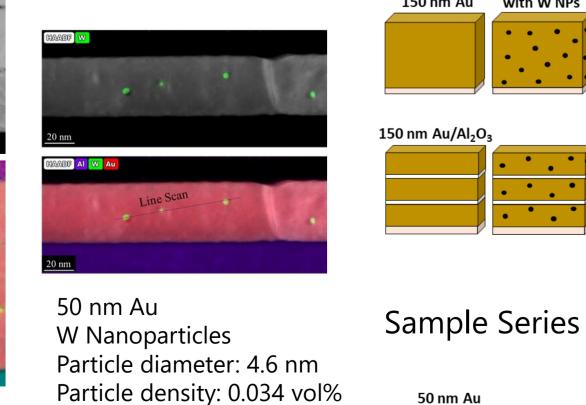
III) 150 nm Au/Al₂O₃ nanolaminates with W nanoparticles

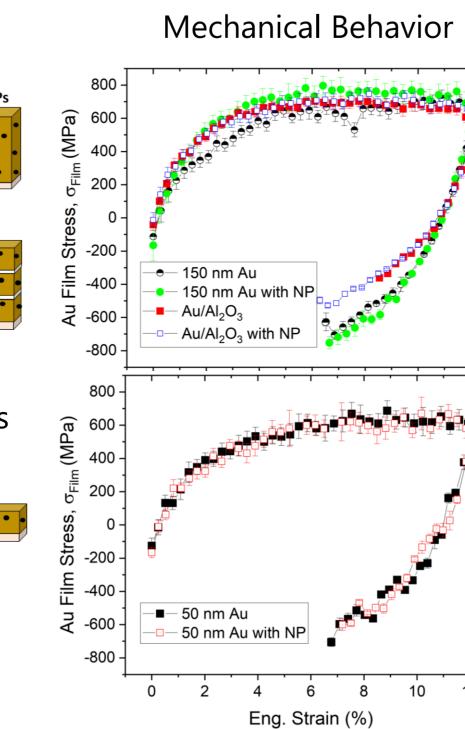
3 x 50 nm Au

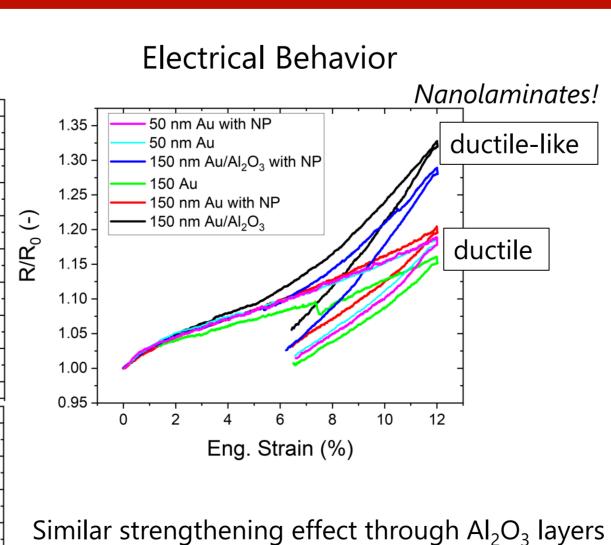
 $2 \times 1 \text{ nm Al}_2 O_3$

(=7 ALD cycles)

W Nanoparticles







and W NPs for 150 nm Au film

No effect of NPs on 50 nm Au layers!

Conclusions (I-III)

- Al grain size can be controlled by 1 cycle of ALD
- Improved lateral and through thickness damage tolerance with decreasing oxide layer thickness
- No embrittlement for $Al_2O_3 \le 2.4$ nm
- Maximum strength achieved with 25 nm Al layer thickness
- At 25 nm Al thickness ductile-like failure is maintained
- Nanoparticles and Al₂O₃ layers yield similar strength increase for 150 nm Au films
- No effect of nanoparticles observed in thinner, 50 nm Au films











192-08532ST, 202-09765ST

Barbara Putz Swiss Federal Laboratories for Materials Science and Technology Feuerwerkerstrasse 39 3602 Thun Switzerland barbara.putz@empa.ch +41 58 765 62 54