Ultrabarriers by Atomic Layer Deposition

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Outline

1. Al_2O_3 ALD barriers on PEN & PET
2. Critical tensile strains for Al_2O_3 ALD films on PEN
3. Flexible alloy barriers using Al_2O_3 ALD & Alucone MLD
4. H_2O Corrosion & Al_2O_3 ALD multilayer barriers

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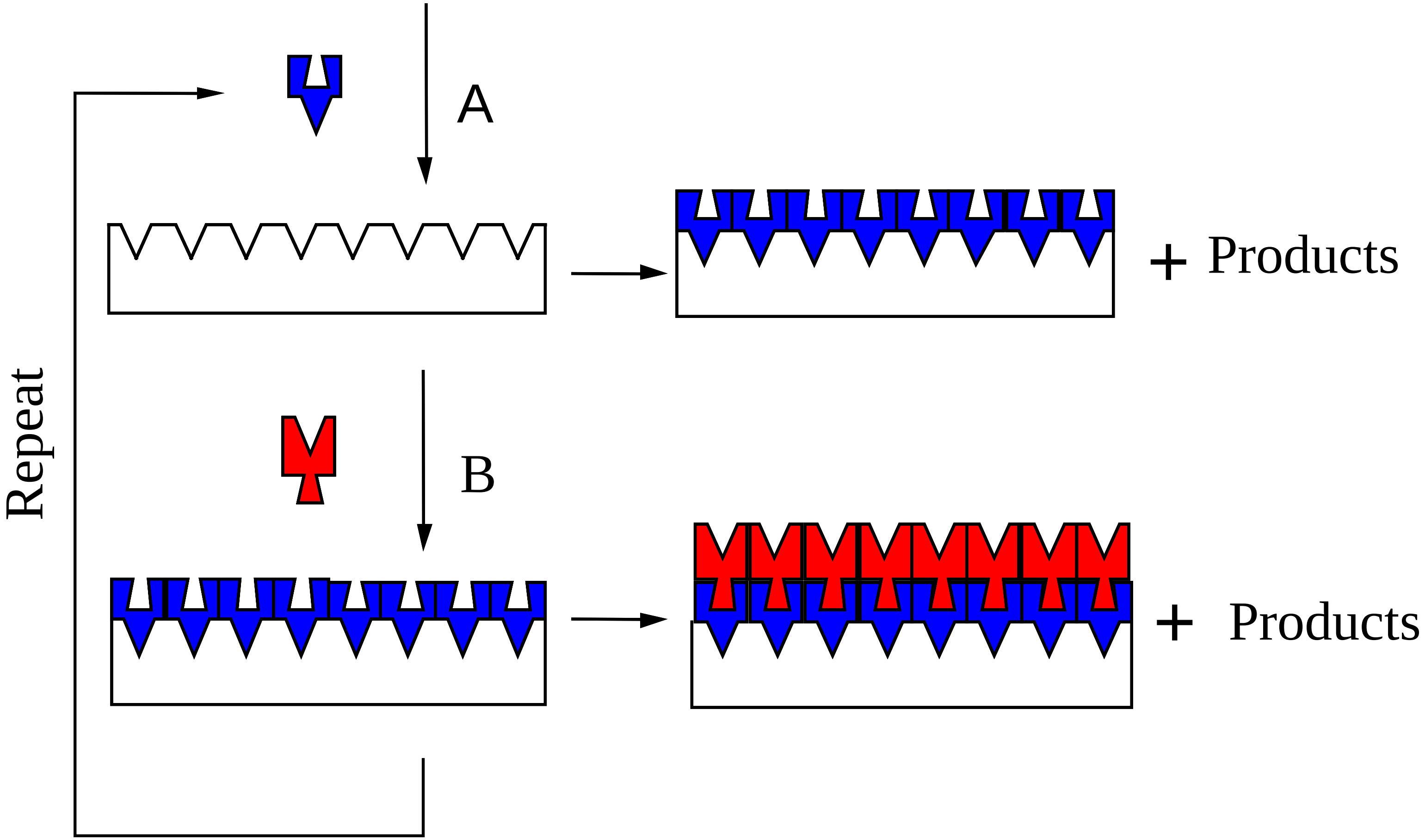
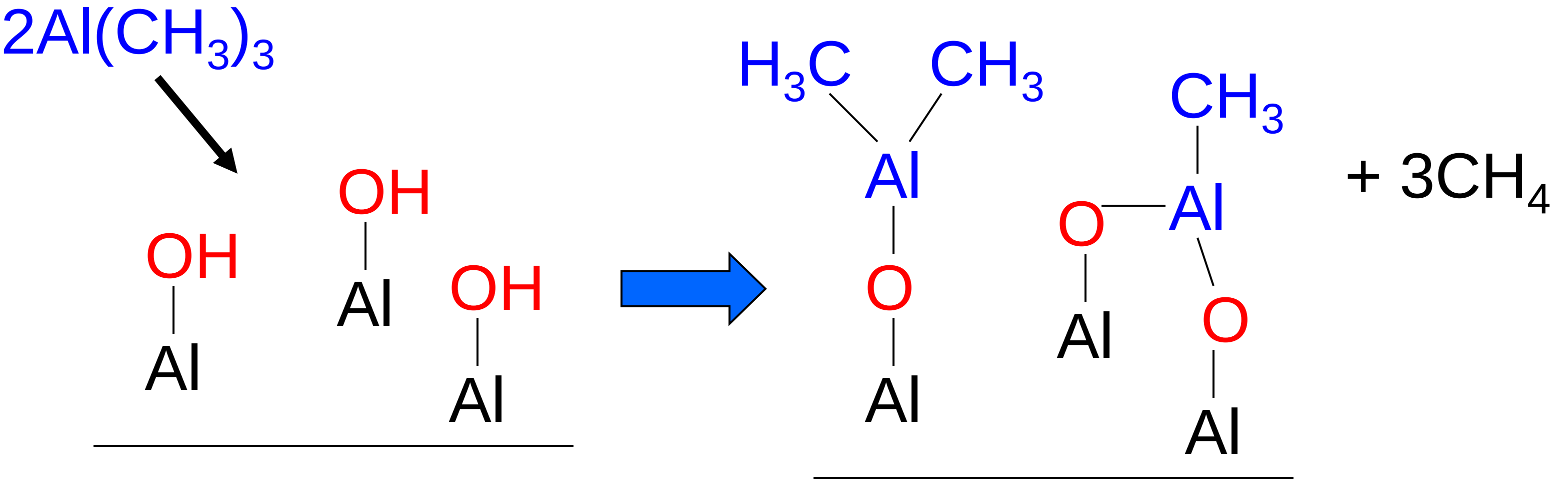
Atomic Layer Deposition Based on Sequential, Self-Limiting Surface Reactions



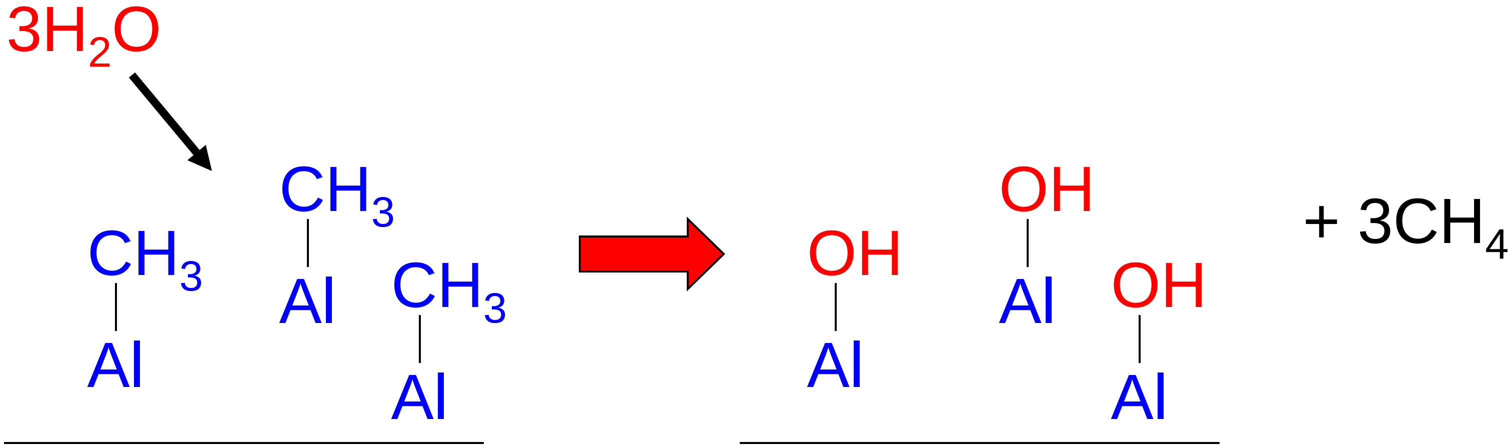
S.M. George, *Chem. Rev.* **110**, 111 (2010).

Al_2O_3 ALD Using TMA & H_2O

(A)

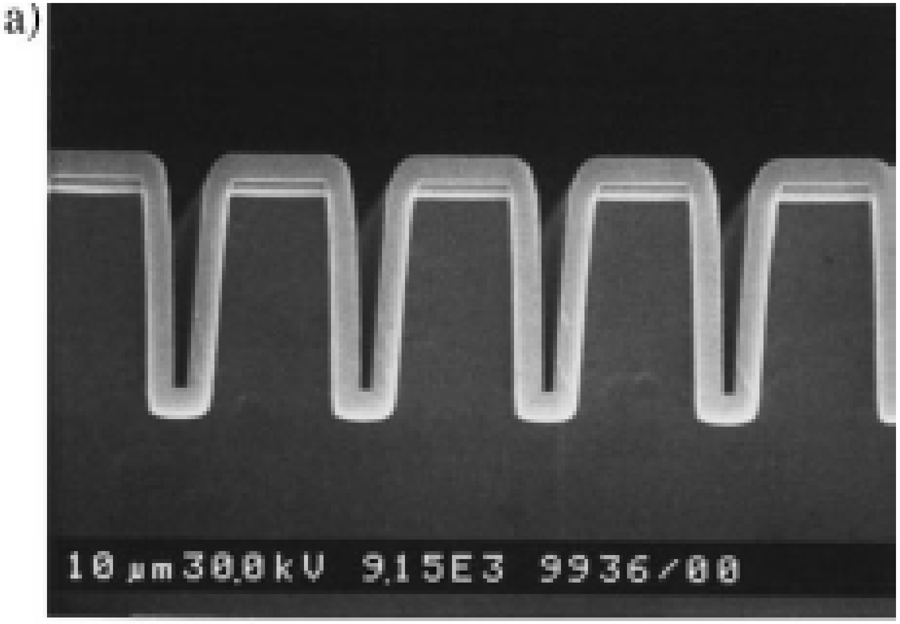


(B)



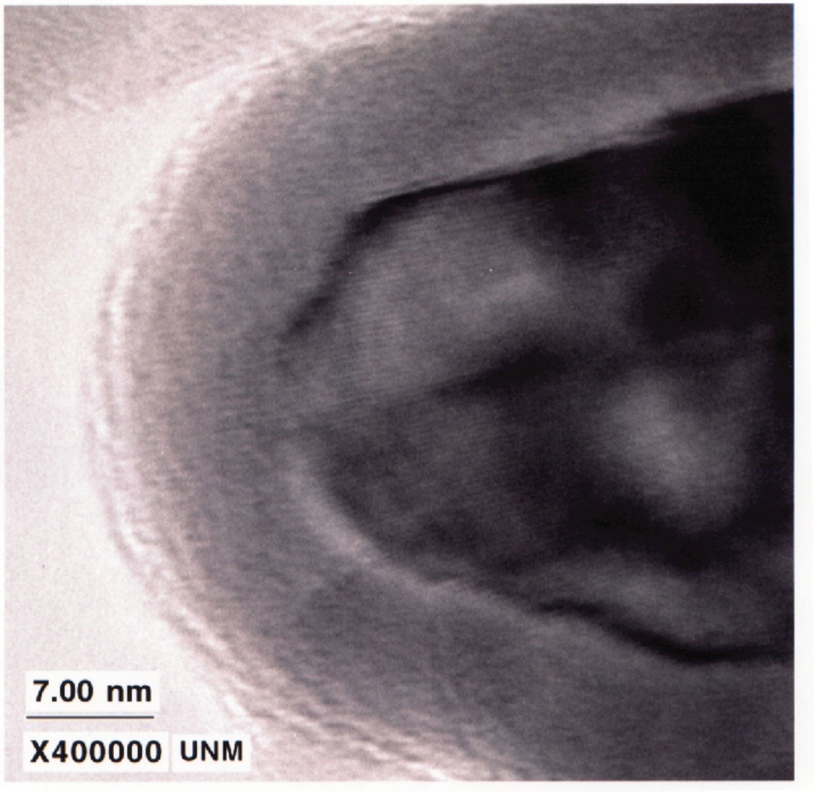
Conformality of Al_2O_3 ALD

Al_2O_3 ALD on Trenched Substrate



M. Ritala et al., *Chem. Vap. Deposition* **5**, 7 (1999).

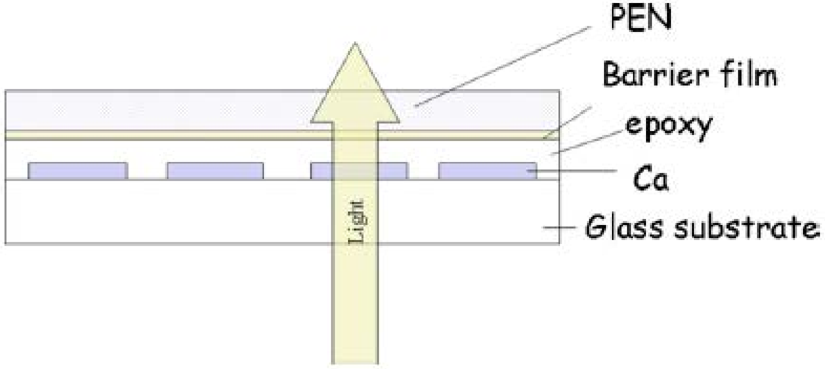
Al_2O_3 ALD on BN Nanoparticles



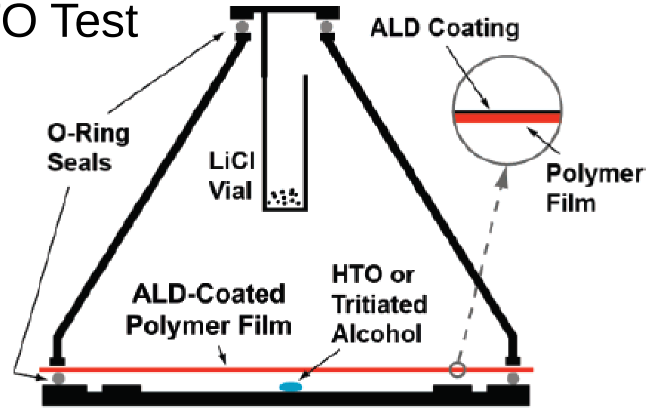
J.D. Ferguson, S.M.George et al., *Thin Solid Films* **371**, 95 (2000).

Measurements of Water Vapor Transmission Rate (WVTR)

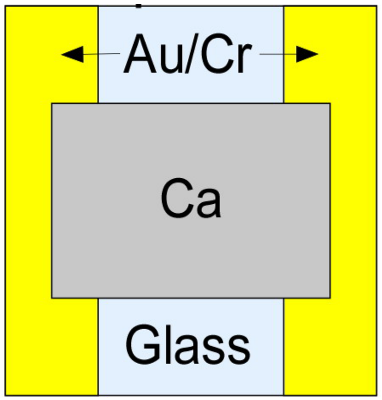
Optical Calcium Test



HTO Test



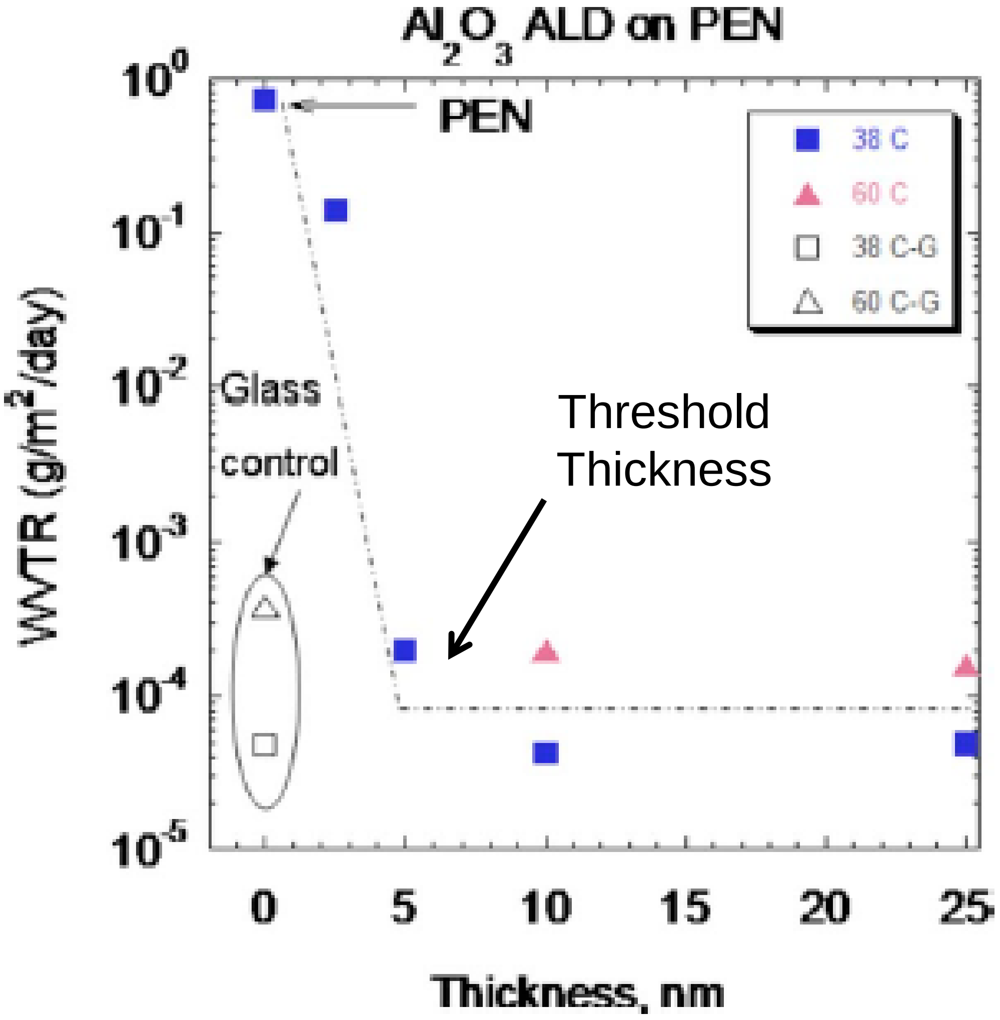
Electrical Calcium Test



MOCON Measurement

Coulometric AQUATRACE Sensor

WVTRs for Al_2O_3 ALD on PEN



Optical Ca Test

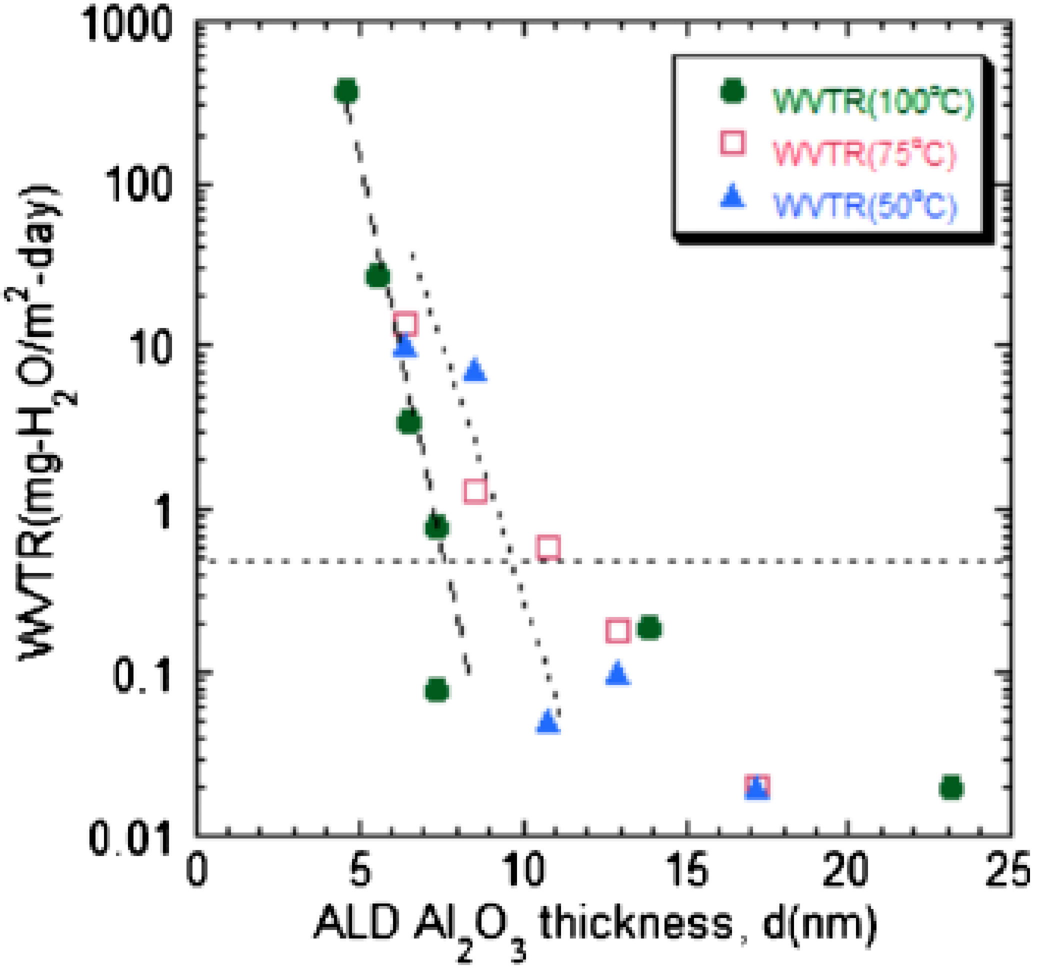
WVTR of ≤ 5 x 10^{-5} g/m^2/day at 38°C/85%RH

Threshold thickness ~5 nm

Equivalent to glass control

P.F. Carcia, S.M. George et al., *J. Appl. Phys.* **106**, 023533 (2009).

WVTRs for Al_2O_3 ALD on PET



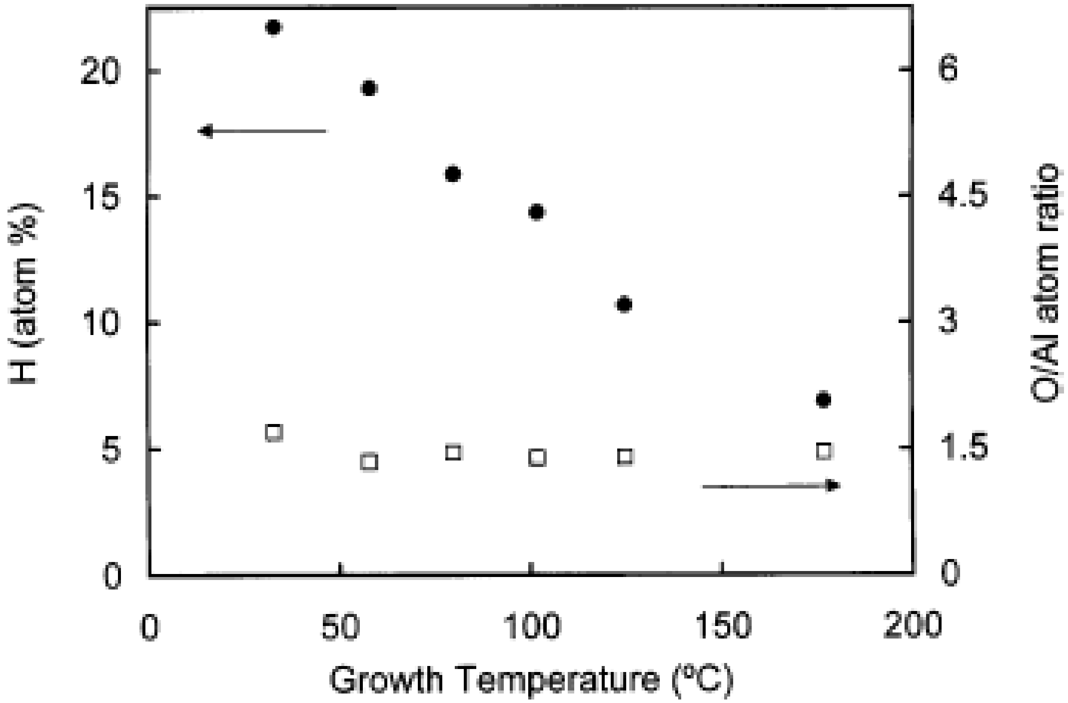
MOCON Measurement at 38°C/85%RH

Dependence of threshold thickness on Al_2O_3 ALD growth temperature

→ Postulate more AlOH species in Al_2O_3 ALD film at lower growth temperatures

P.F. Carcia et al., *Appl. Phys. Lett.* **97**, 221901 (2010).

Hydrogen Concentration in Al_2O_3 ALD Films vs. Growth Temperature



Forward Rutherford Scattering Measurements

More AlOH in Al_2O_3 ALD film at lower growth temperature

→ H_2O may percolate through AlOH regions in Al_2O_3 ALD film

M.D. Groner, S.M. George et al., *Chem. Mater.* **16**, 639 (2004).

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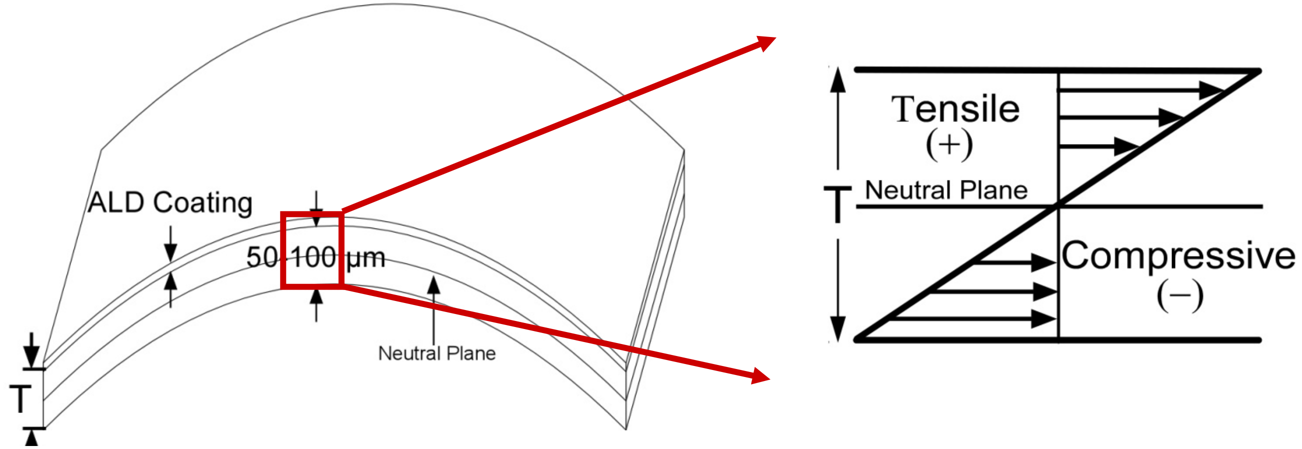
Flexible Gas Diffusion Barriers Required for OLEDs & Thin Film Solar

Need Flexible Films for:

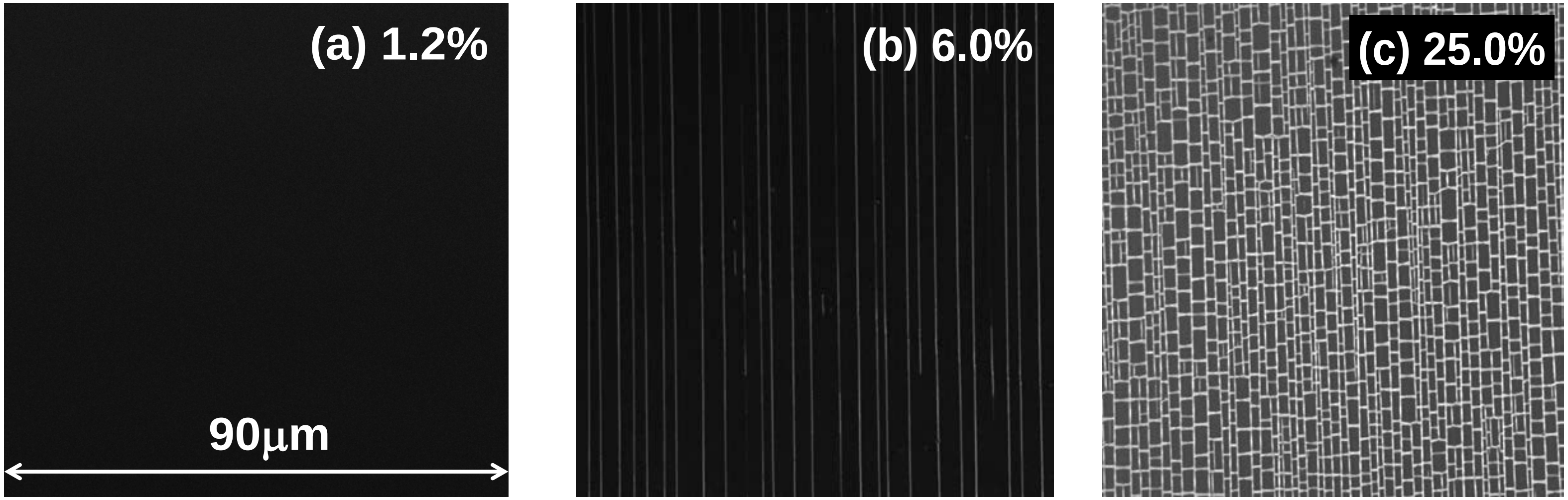
Bending

Thermal Expansion Mismatch



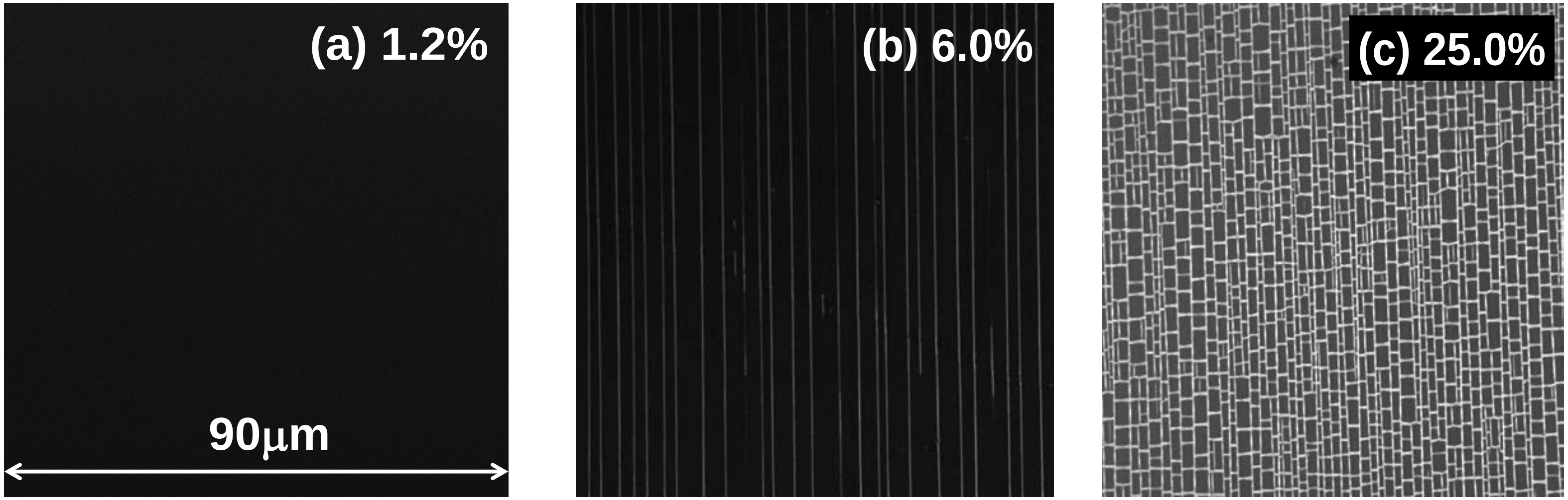
Cracking vs Tensile Strain on PEN

12.5 nm Film Thickness

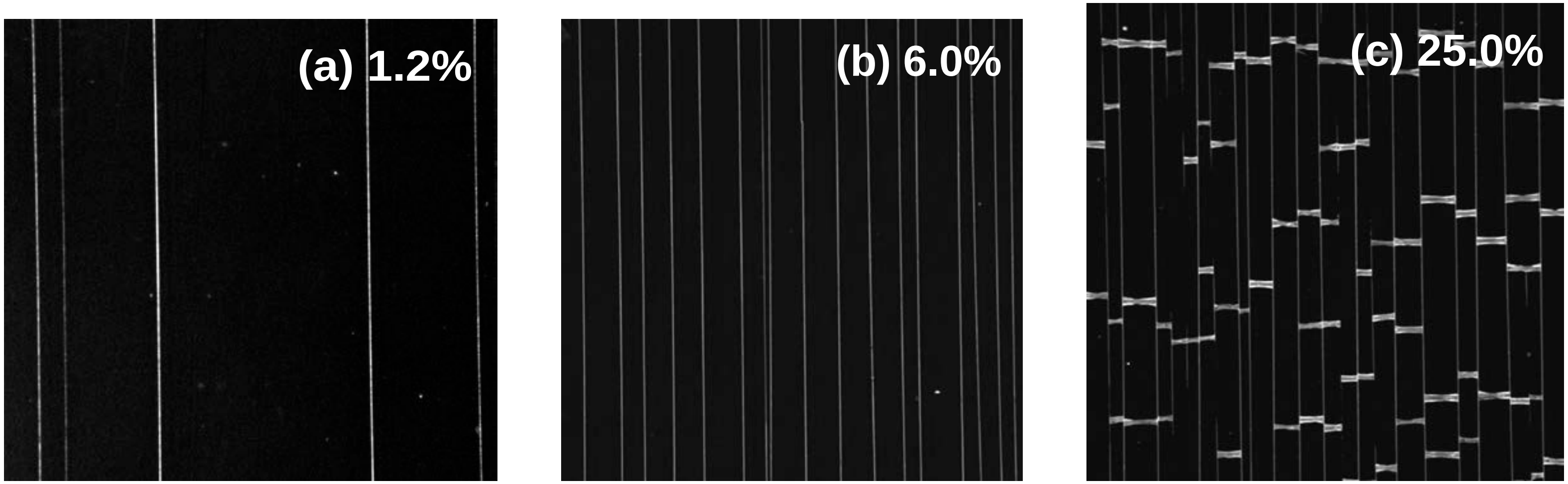


Cracking vs Tensile Strain on PEN

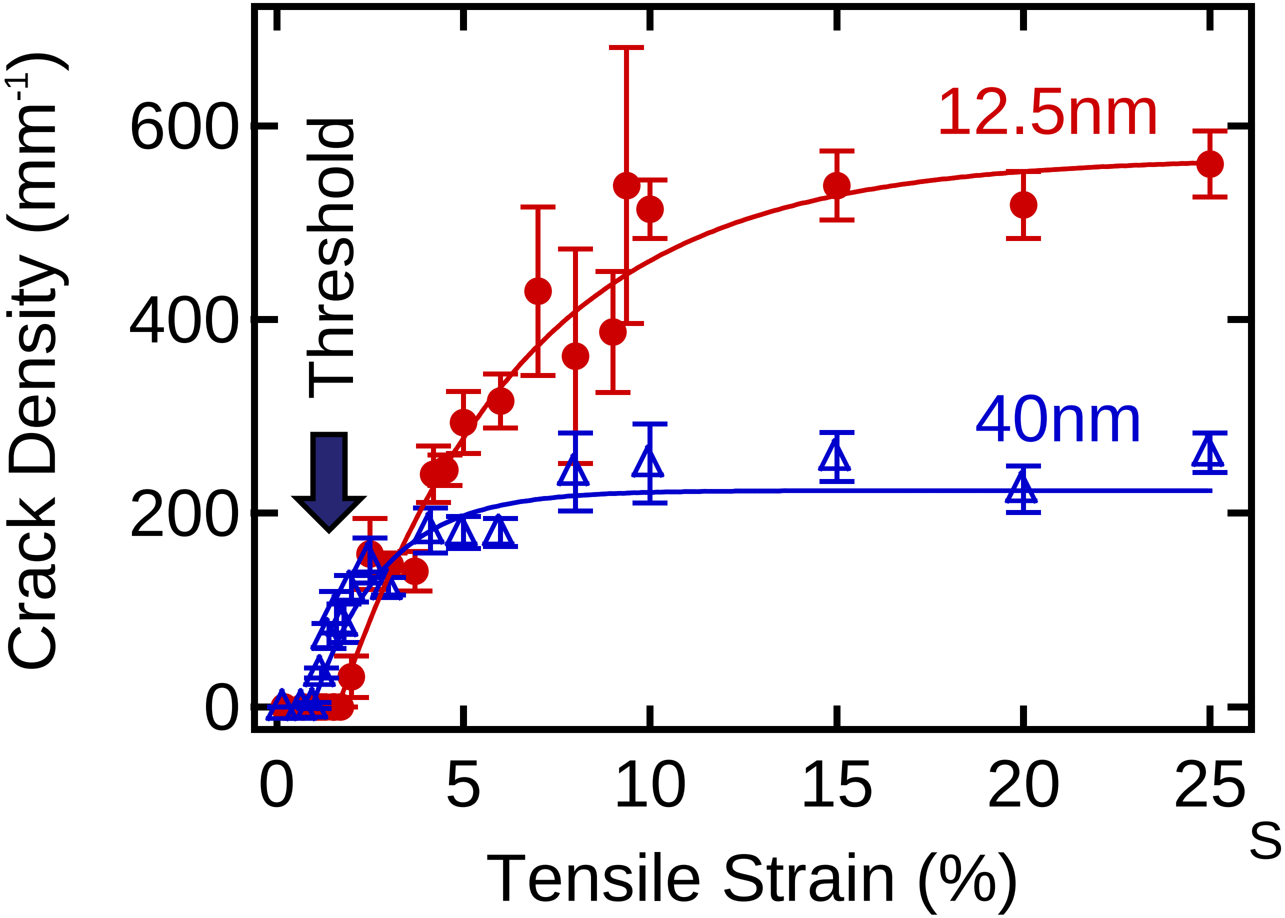
12.5 nm Film Thickness



40 nm Film Thickness



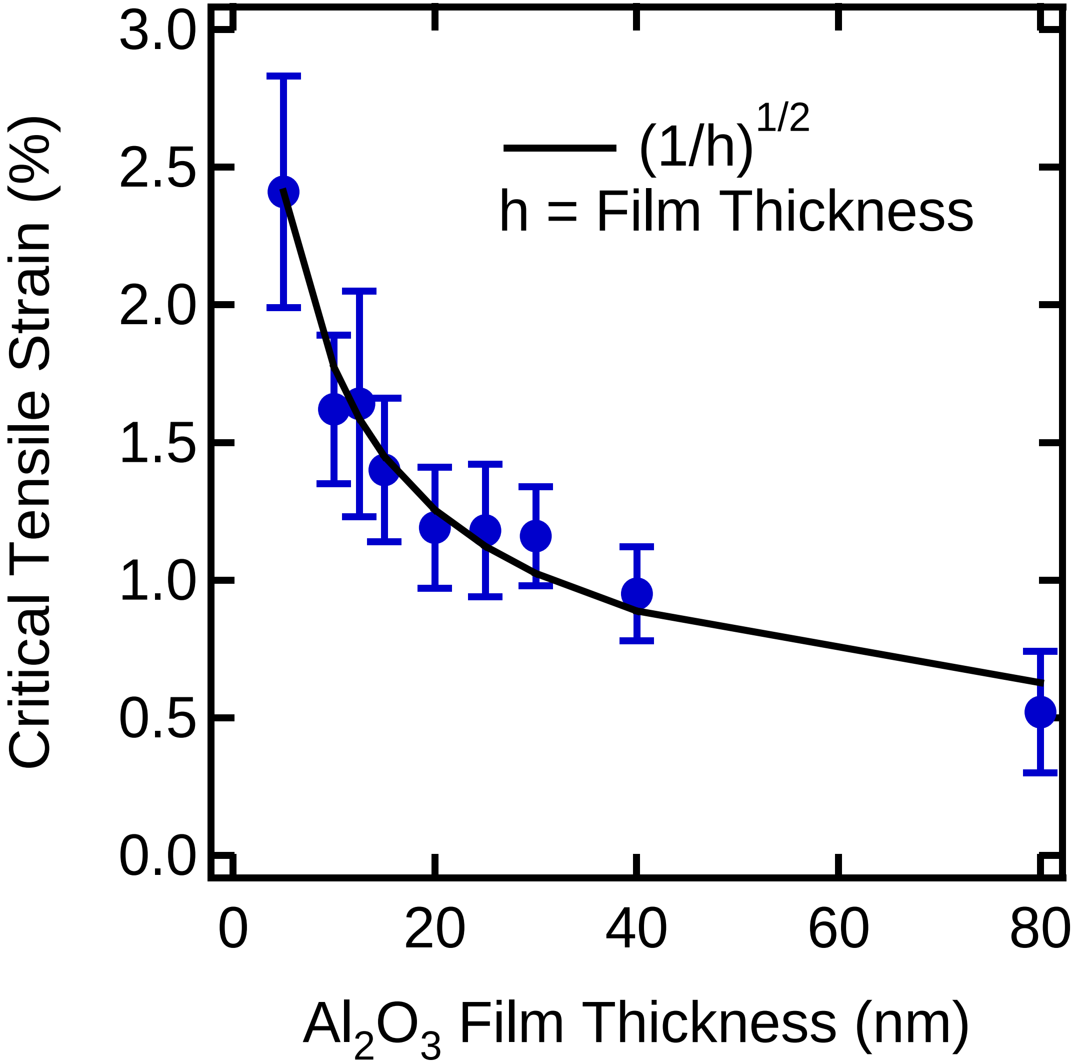
Crack Density vs. Tensile Strain for Al_2O_3 ALD Film on PEN



Higher threshold strains & saturation crack densities for thinner films

S.H. Jen, J.A. Bertrand & S.M. George, *J. Appl. Phys.* **109**, 084305 (2011).

Critical Tensile Strain for Cracking vs. Al_2O_3 ALD Film Thickness on PEN



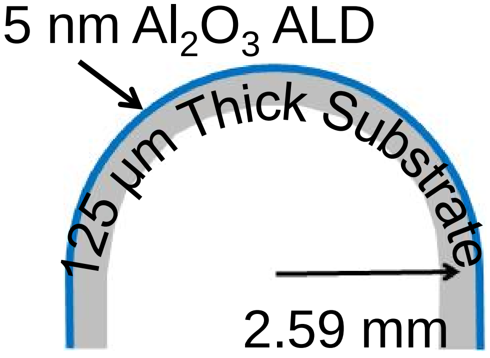
Higher critical tensile strains for cracking for thinner film thicknesses

S.H. Jen, J.A. Bertrand & S.M. George, *J. Appl. Phys.* **109**, 084305 (2011).

Threshold Bending Radius for Cracking from Threshold Strain

h, Al_2O_3 Thickness (nm)	**ε, Threshold Tensile Strain (%)**	**R, Threshold Bending Radius (mm)**
5	2.41 ± 0.42	2.59
10	1.62 ± 0.27	3.86
12.5	1.64 ± 0.41	3.81
15	1.40 ± 0.26	4.46
20	1.19 ± 0.22	5.25
25	1.18 ± 0.24	5.30
30	1.16 ± 0.18	5.39
40	0.95 ± 0.17	6.58
80	0.52 ± 0.22	12.02

Strain, ε = D/2R where D is substrate thickness



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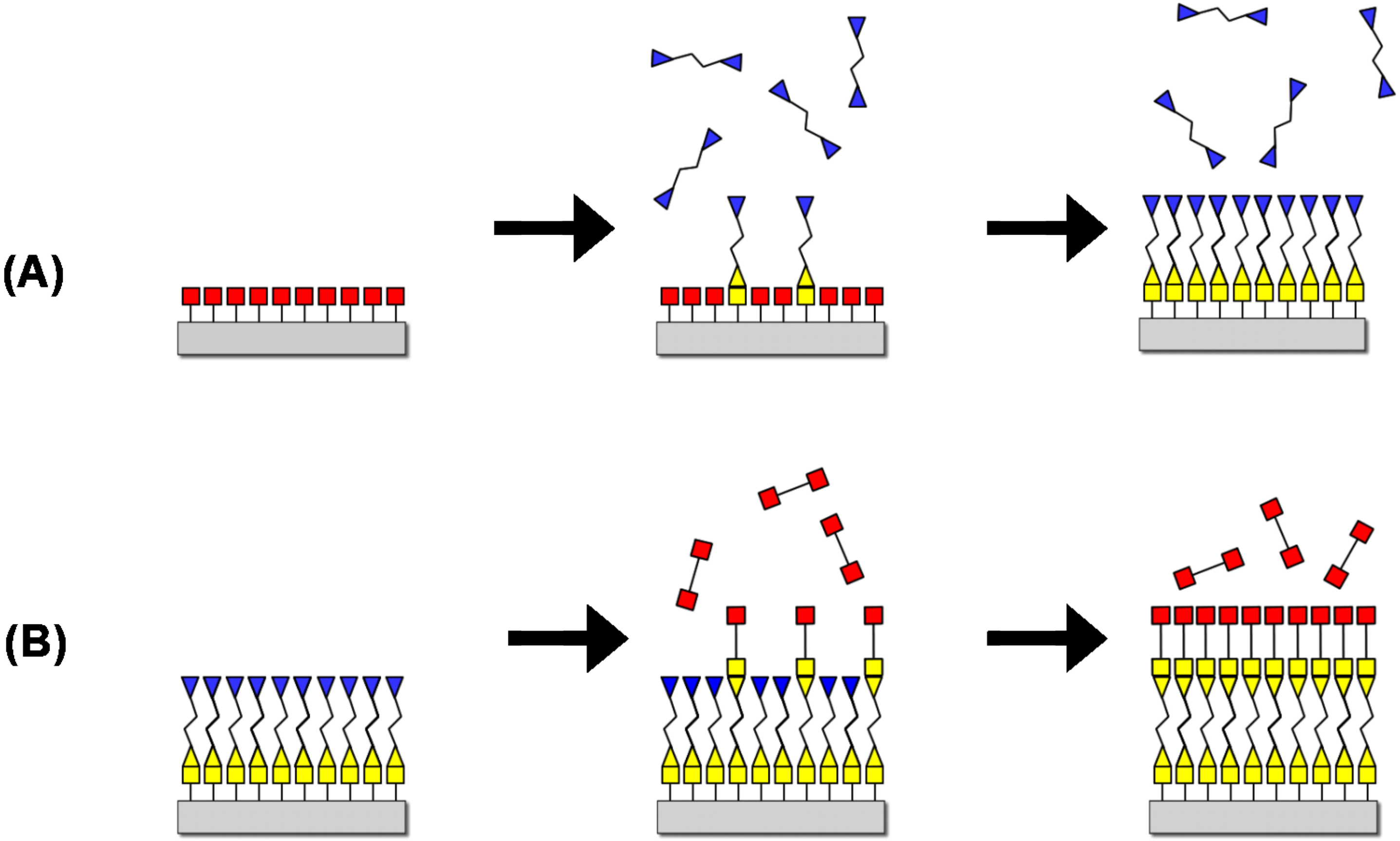
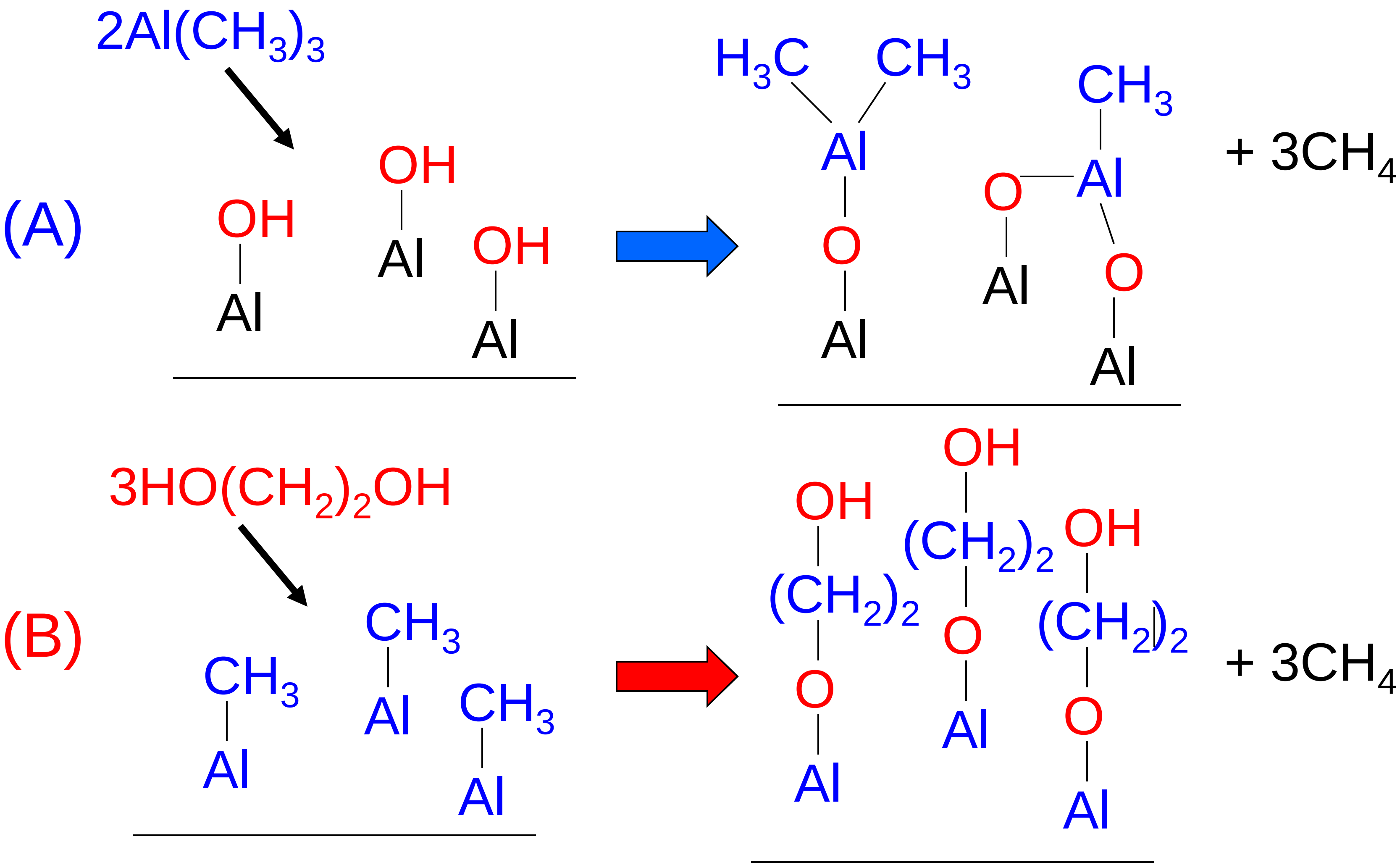
Molecular Layer Deposition (MLD): Molecular Fragments Deposited During Sequential Surface Reactions

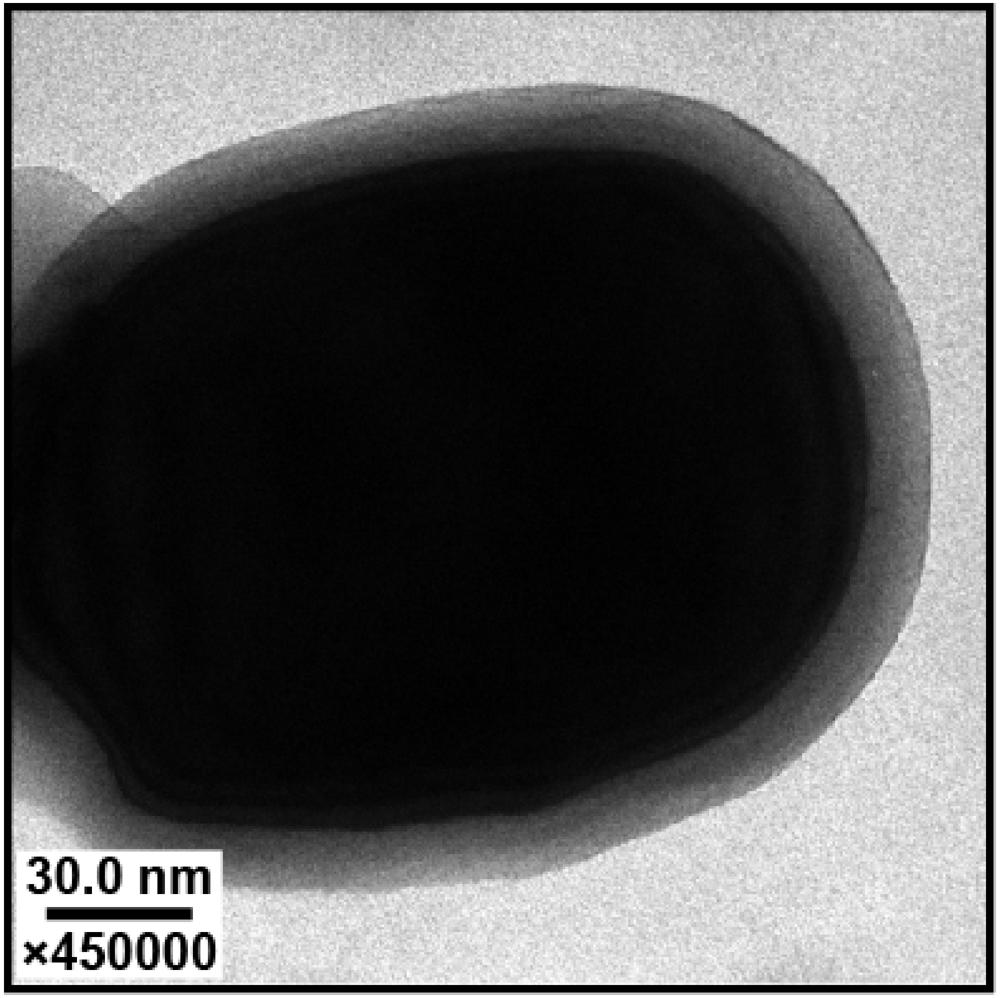


S.M. George et al., *Acc. Chem. Res.* **42**, 498 (2009).

Alucone MLD Using TMA & EG



Conformal Alucone MLD Film on $BaTiO_3$ Nanoparticles



40 Cycles Al_2O_3 ALD

50 Cycles Alucone MLD

~1.6 Å/Cycle for Alucone MLD at 135°C

A.A. Dameron, S.M. George et al., *Chem. Mater.* **20**, 3315 (2008).

Alloy Growth Using Metal Oxide ALD & Metalcone MLD

Growth Sequence:

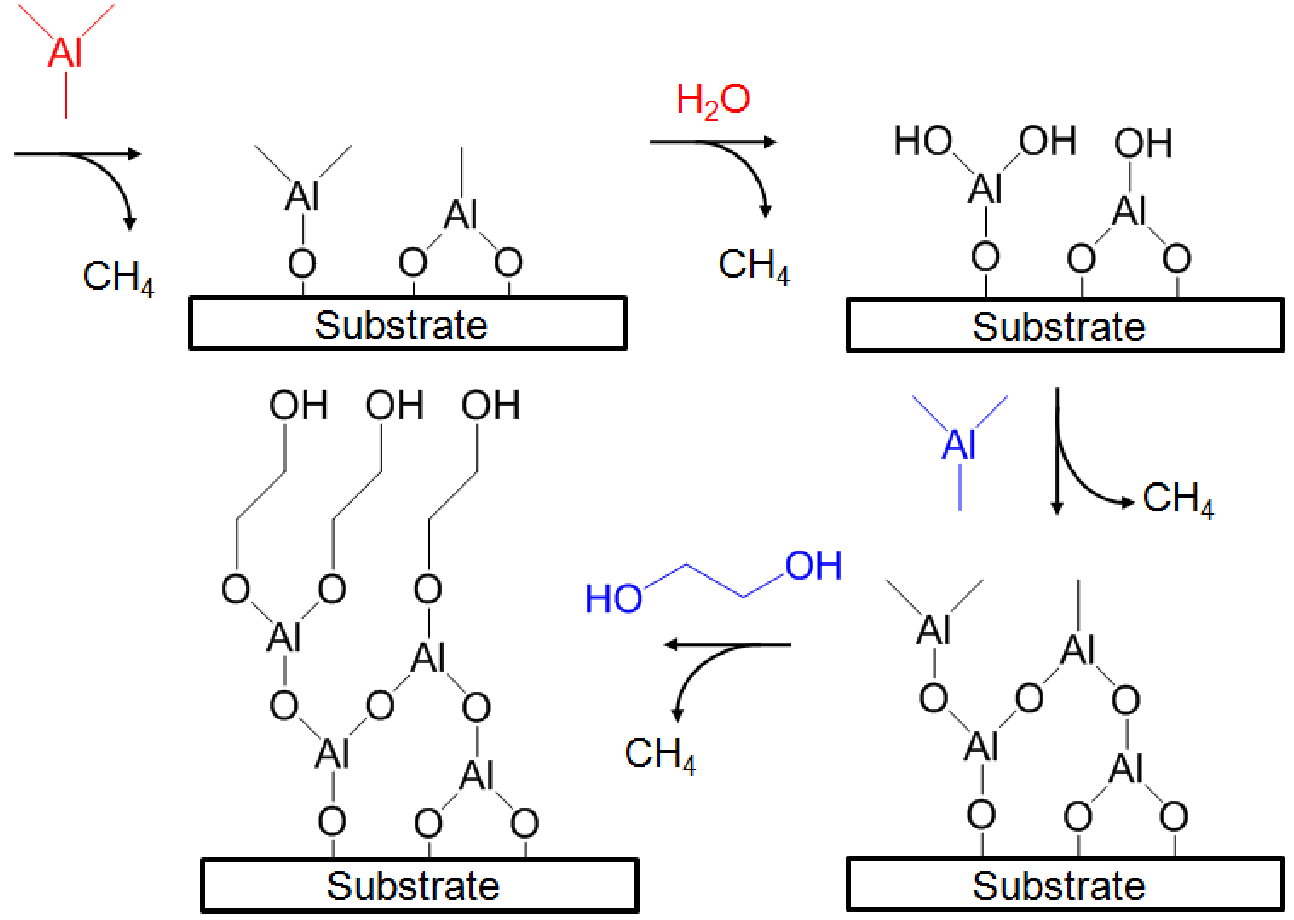
M Cycles of Metal Oxide ALD

N Cycles of Metalcone MLD

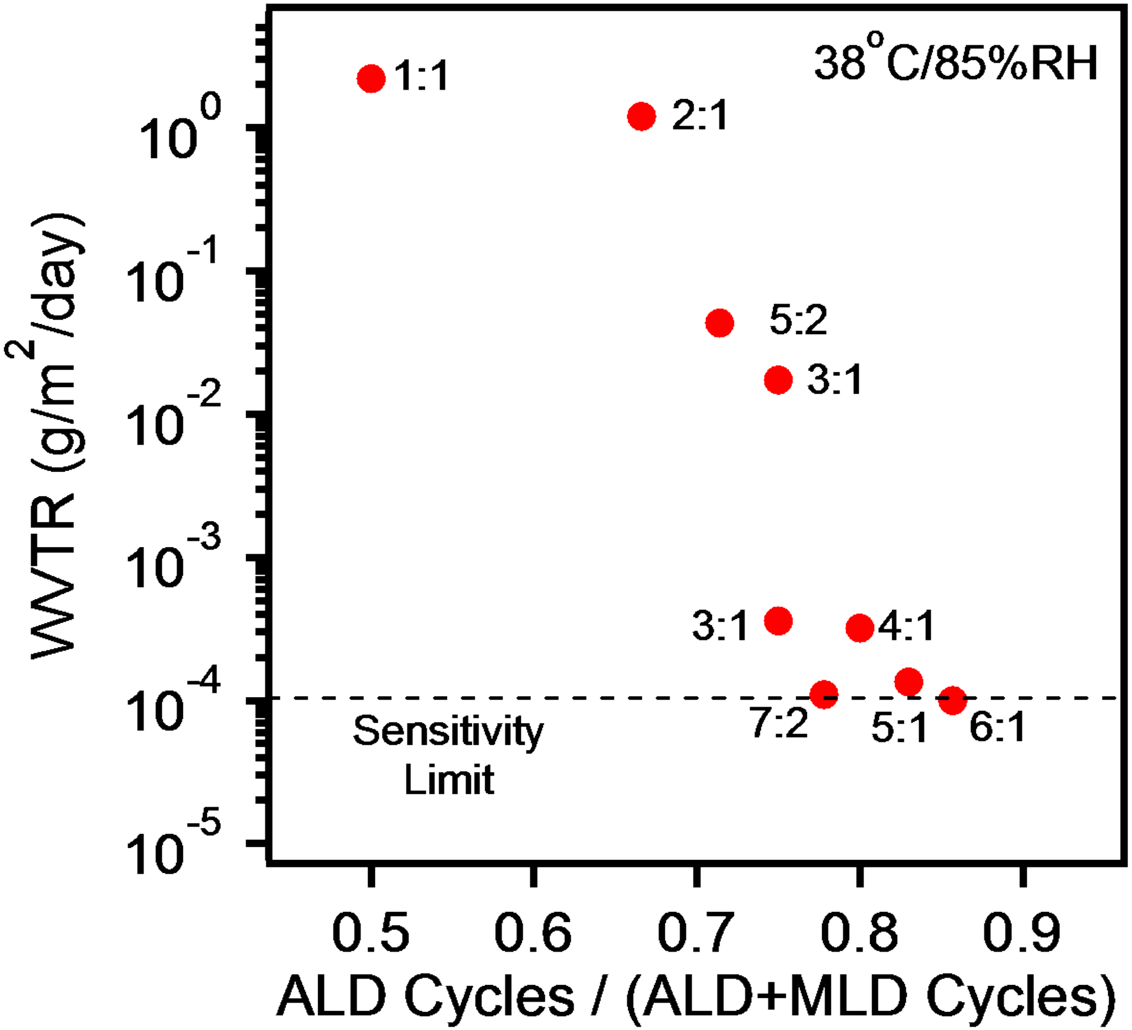
Repeat MNMN…

→ **M:N ALD:MLD Alloy**

1:1 Al_2O_3 ALD:Alucone MLD Alloy



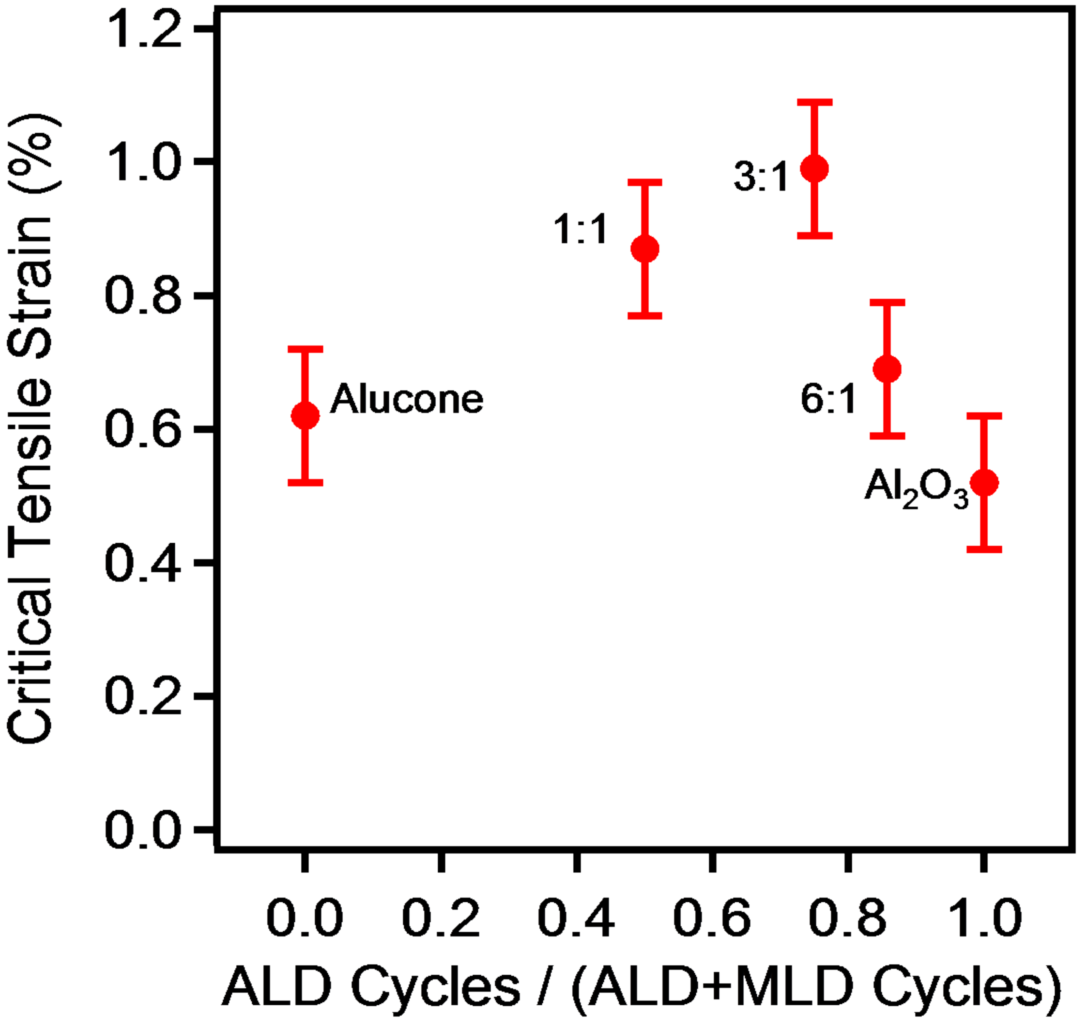
Water Vapor Transmission Rate (WVTR) vs Fraction of ALD Cycles



MOCON
Measurement

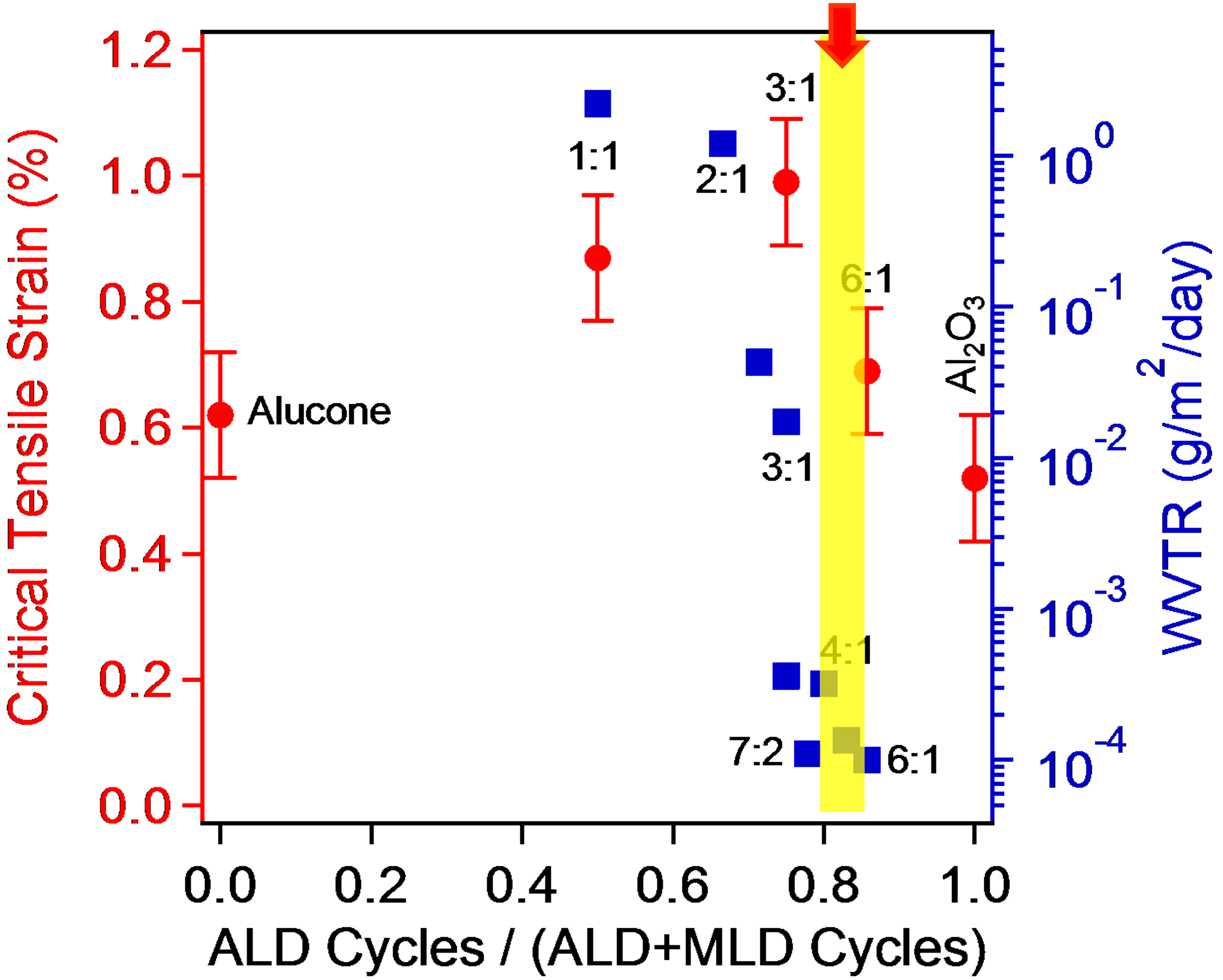
Reach sensitivity limit at ~5:1 ALD:MLD alloy

Critical Tensile Strain vs Fraction of ALD Cycles for 100 nm Films



Maximum critical tensile strain of ~1.0% for 3:1 ALD:MLD alloy

Comparison of WVTR and Critical Tensile Strains



ALD:MLD alloys can have higher critical tensile strain & equivalent WVTR compared with Al_2O_3 ALD

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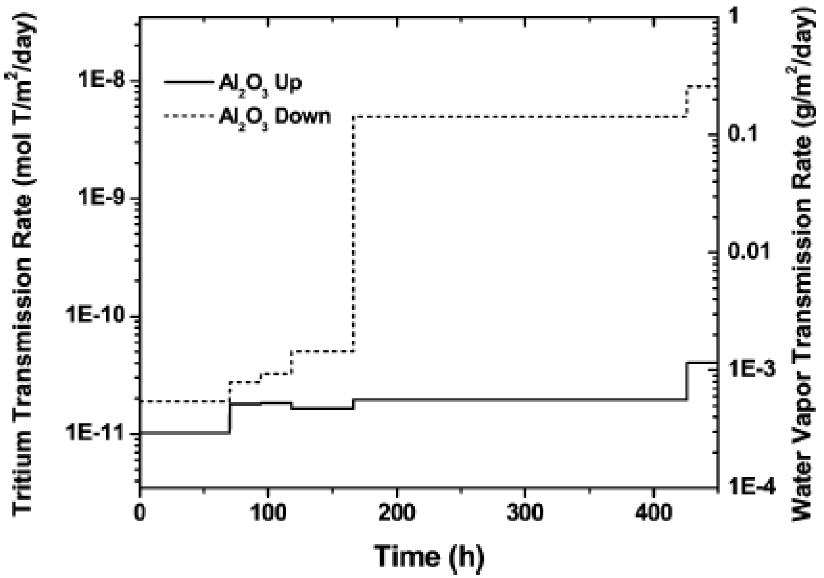
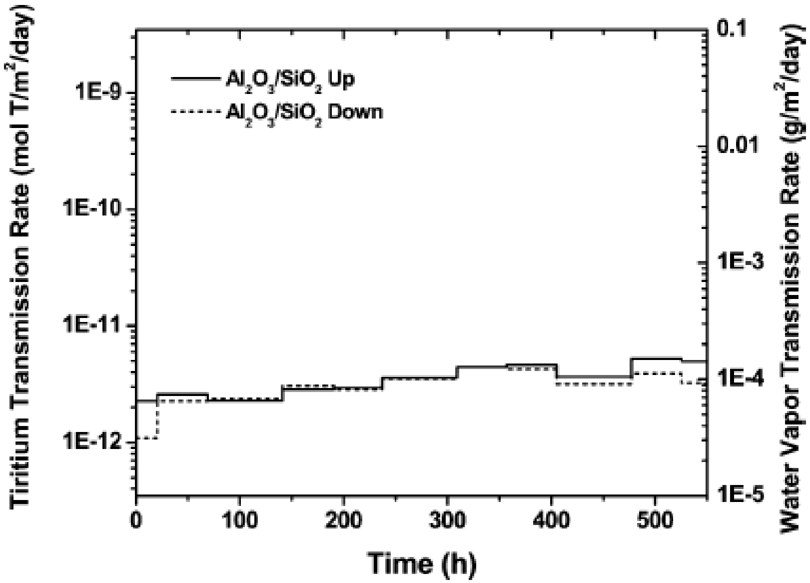
WVTR of Al_2O_3 & Al_2O_3/SiO_2 on Kapton

HTO Test, RT/100%RH

Direct H_2O exposure leads to barrier failure



SiO₂ ALD on Al₂O₃ ALD prevents failure



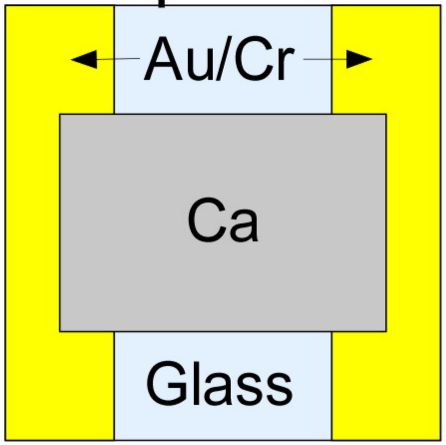
→ Al_2O_3 ALD film susceptible to H_2O corrosion

A.A. Dameron, S.M. George et al., *J. Phys. Chem. C* **112**,4573 (2008).

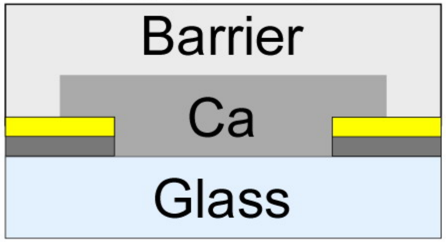
Al_2O_3 ALD Barrier Deposited Directly on Ca Film

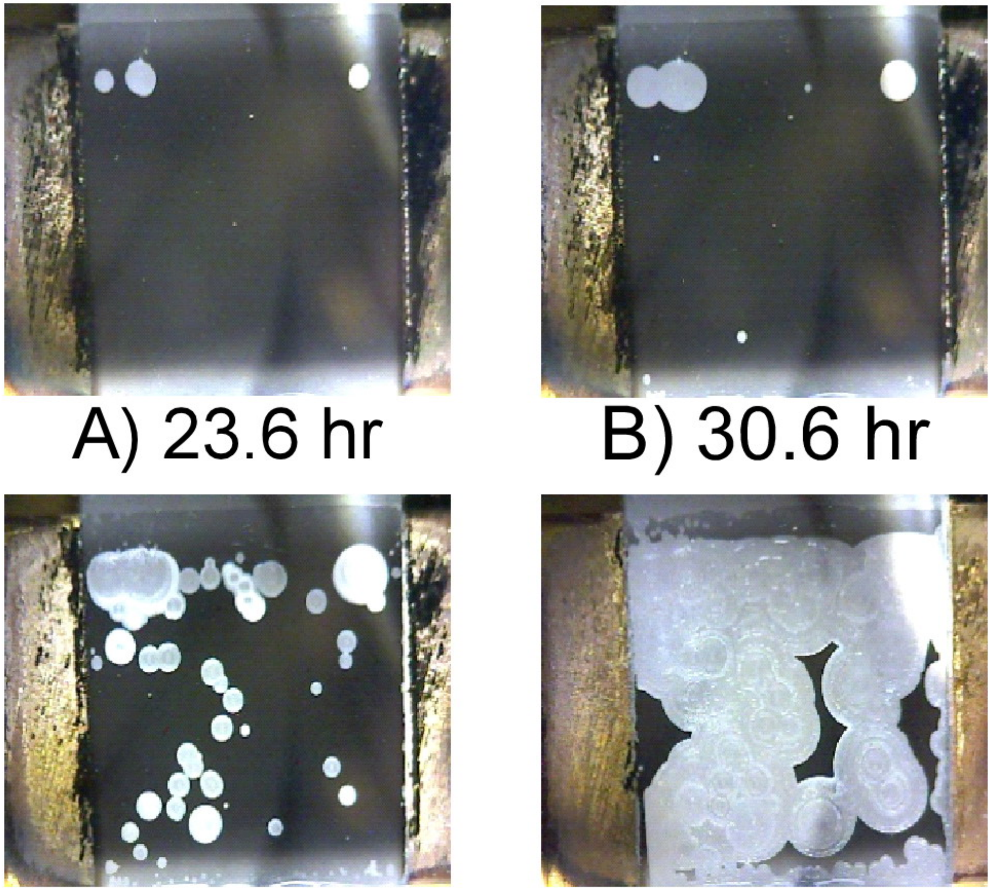
18.7 nm Al_2O_3 ALD film, 70°C/28%RH

Top View



Side View




A) 23.6 hr

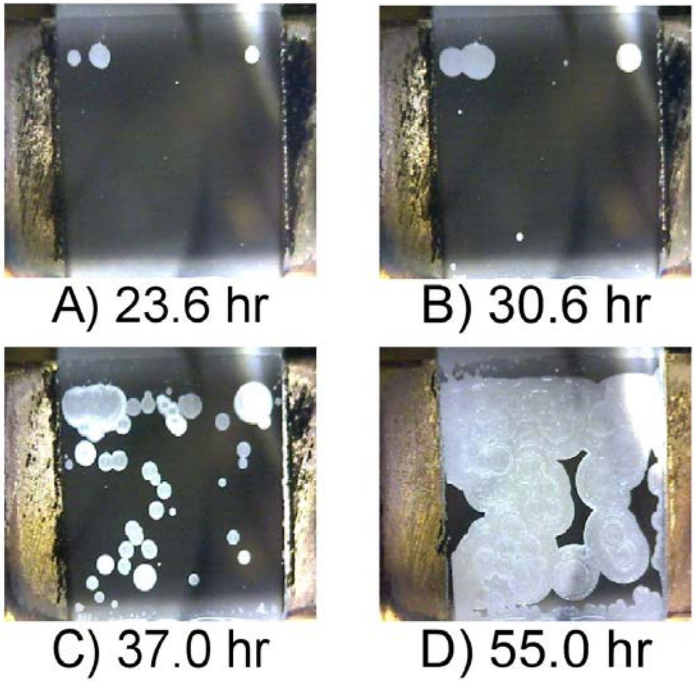
B) 30.6 hr

C) 37.0 hr

D) 55.0 hr

Sudden “Blooming” of Circular Spots at Threshold Time

H_2O vapor in direct contact with Al_2O_3 ALD film.



A) 23.6 hr

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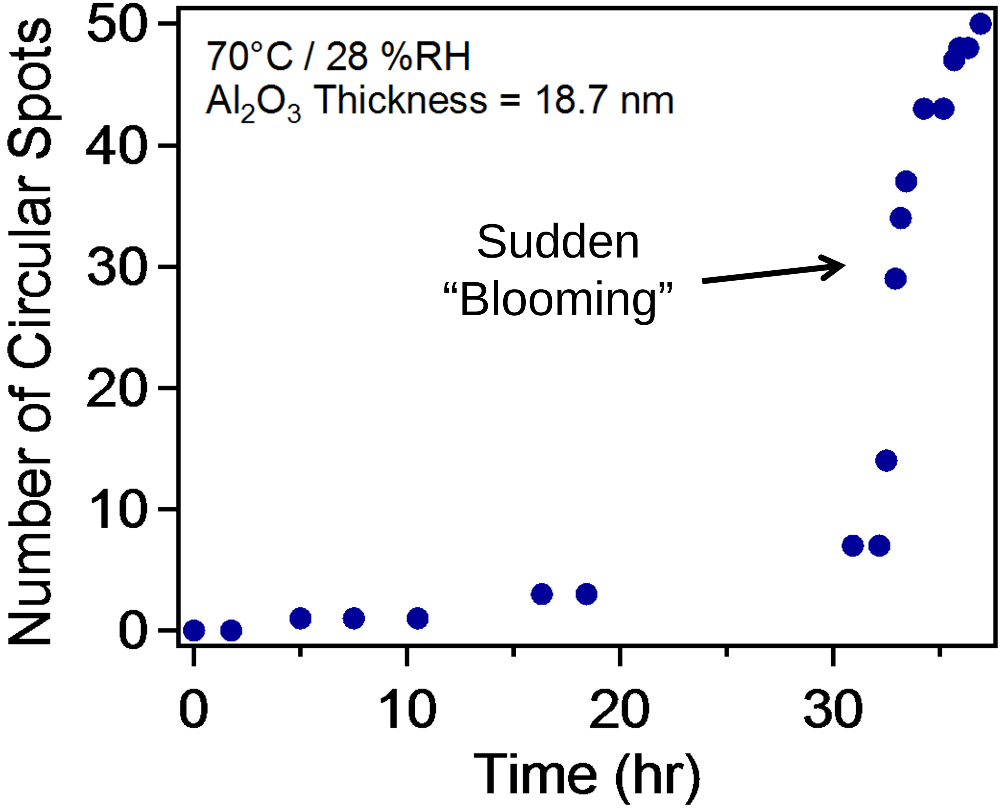
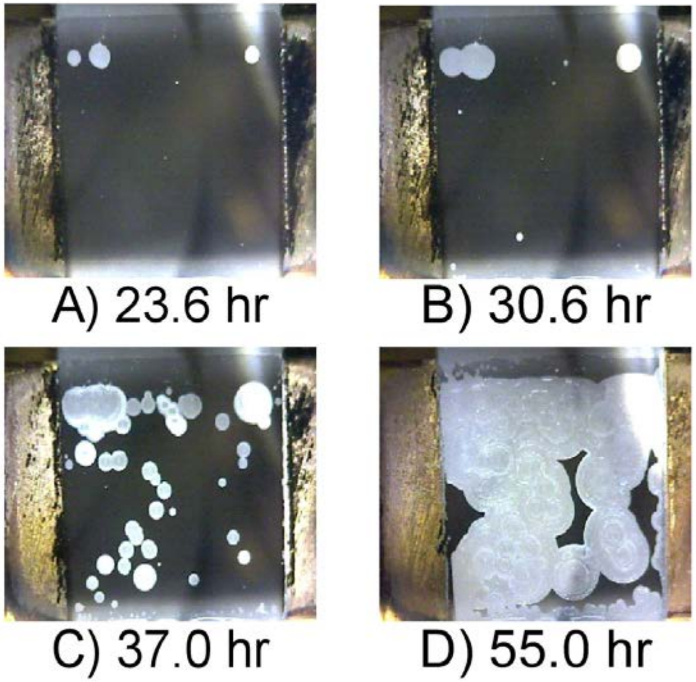


→ “Blooming” could indicate the sudden failure of Al_2O_3 ALD film resulting from H_2O corrosion.

Ca Conductance Displays Little Change until Close to “Blooming”



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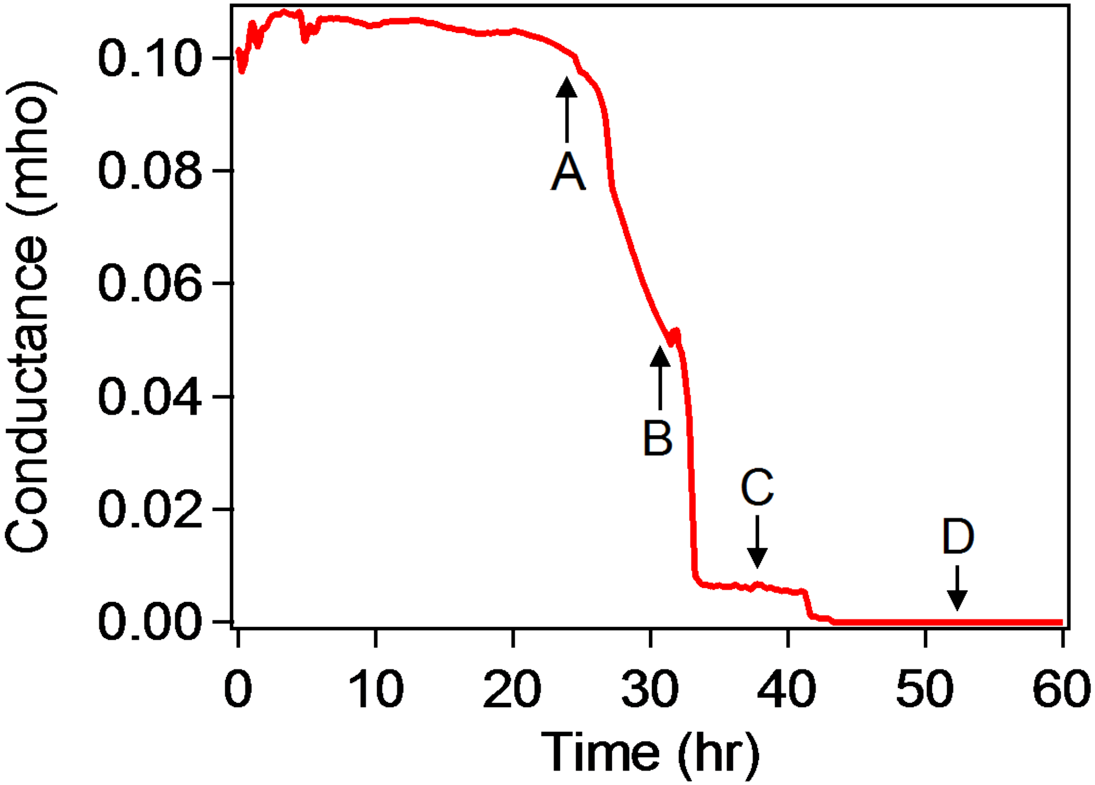
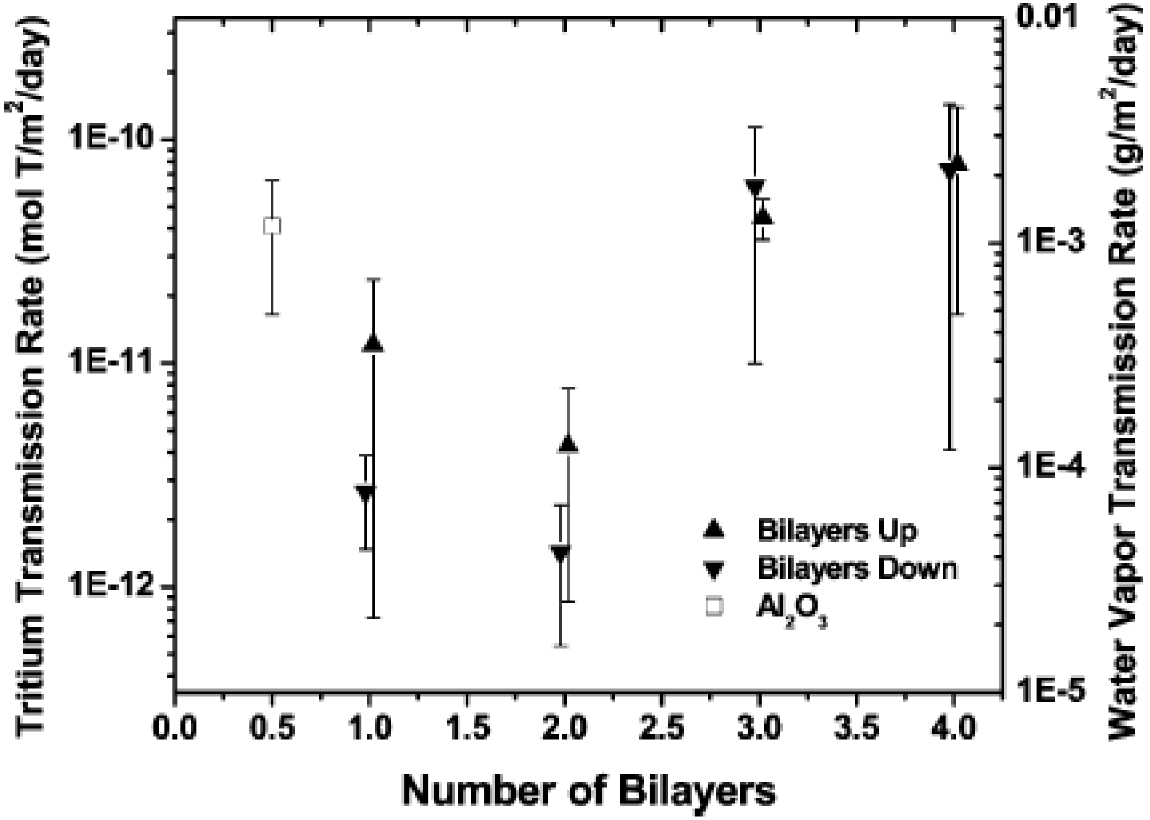


WVTR vs. Number of Al_2O_3/SiO_2 Bilayers on Kapton

HTO Test, RT/100%RH



Each Bilayer: 26 nm Al_2O_3 & ~60 nm SiO_2

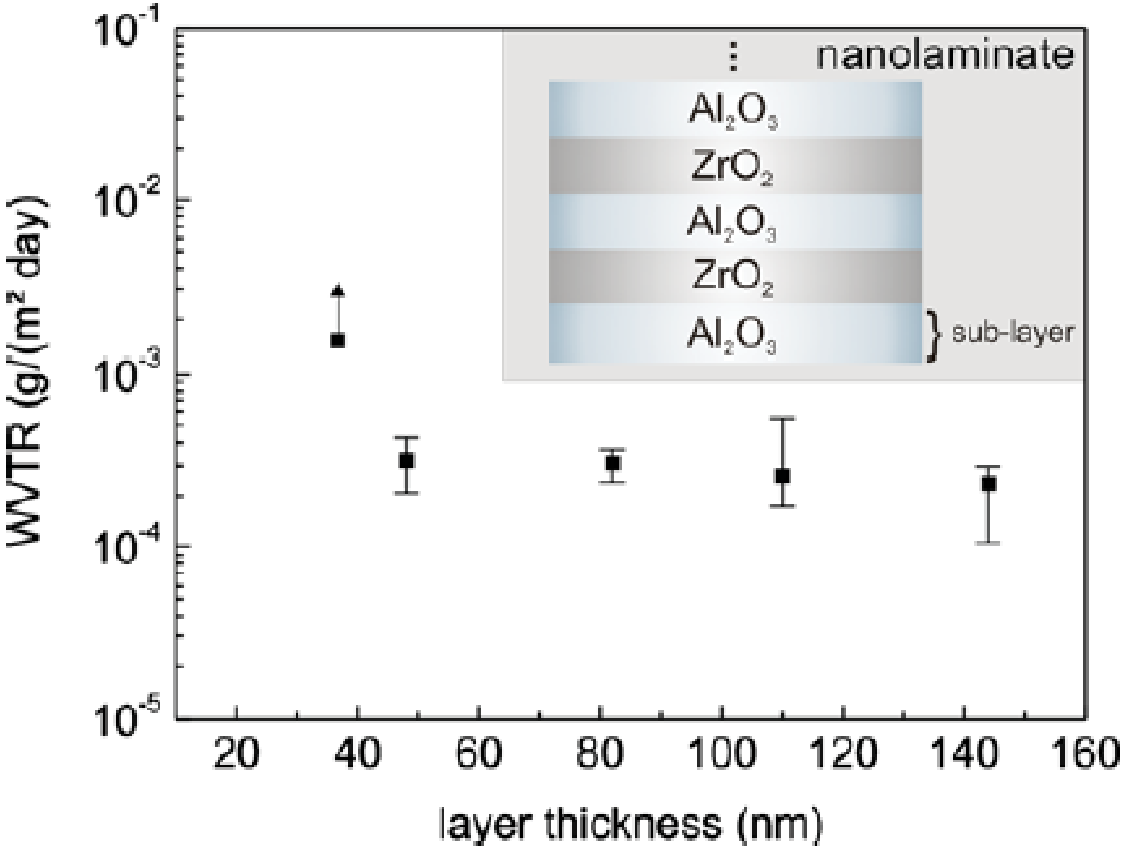
Additional Al_2O_3/SiO_2 bilayer lowers WVTR

Cracking may affect thicker films

A.A. Dameron, S.M. George et al., *J. Phys. Chem. C* **112**,4573 (2008).

WVTR for Al_2O_3/ZrO_2 Nanolaminates

Conductance Ca test, 80°C/80%RH



Each bilayer: 2.1 nm Al_2O_3; 3.1 nm ZrO_2

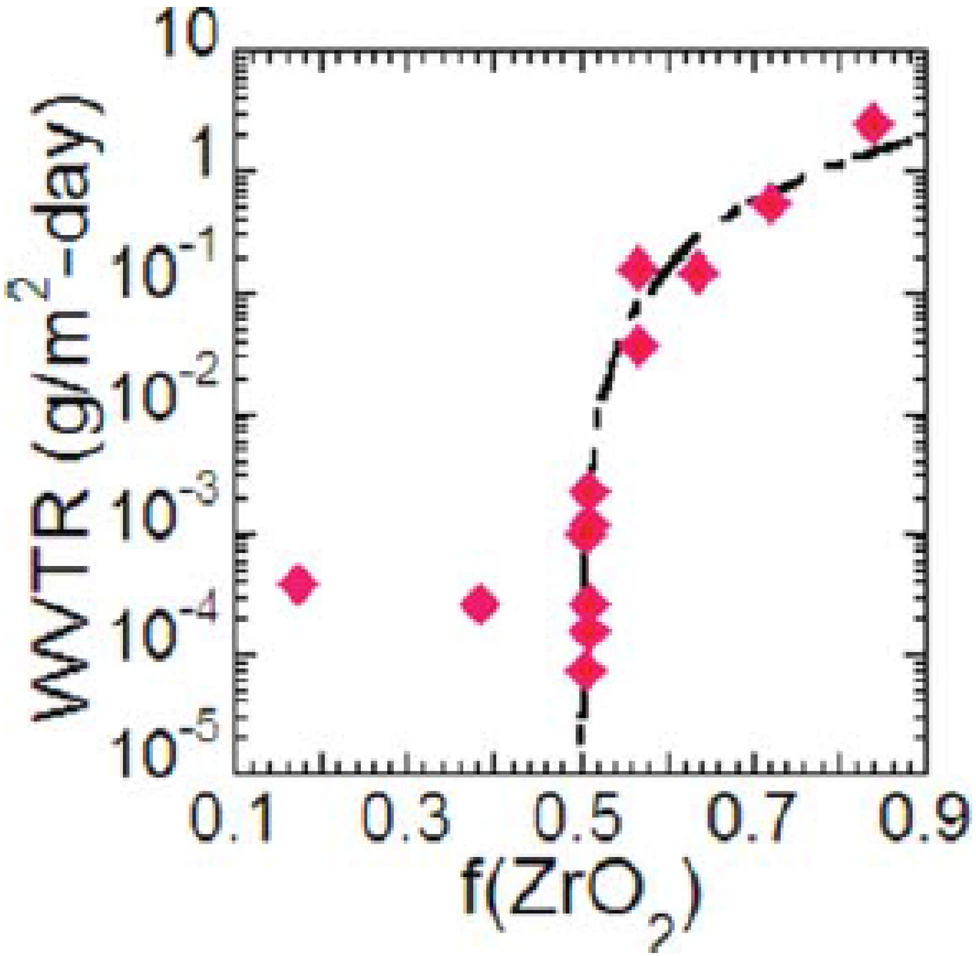
Threshold thickness of ~40 nm

Postulate zirconium aluminate phase that improves H_2O corrosion resistance

J. Meyer et al., *Appl. Phys. Lett.* **96**, 243308 (2010).

WVTR for Al_2O_3/ZrO_2 Nanolaminate vs. ZrO_2 Fraction

MOCON Measurement, 38°C/85%RH



Total film thickness ~10 nm

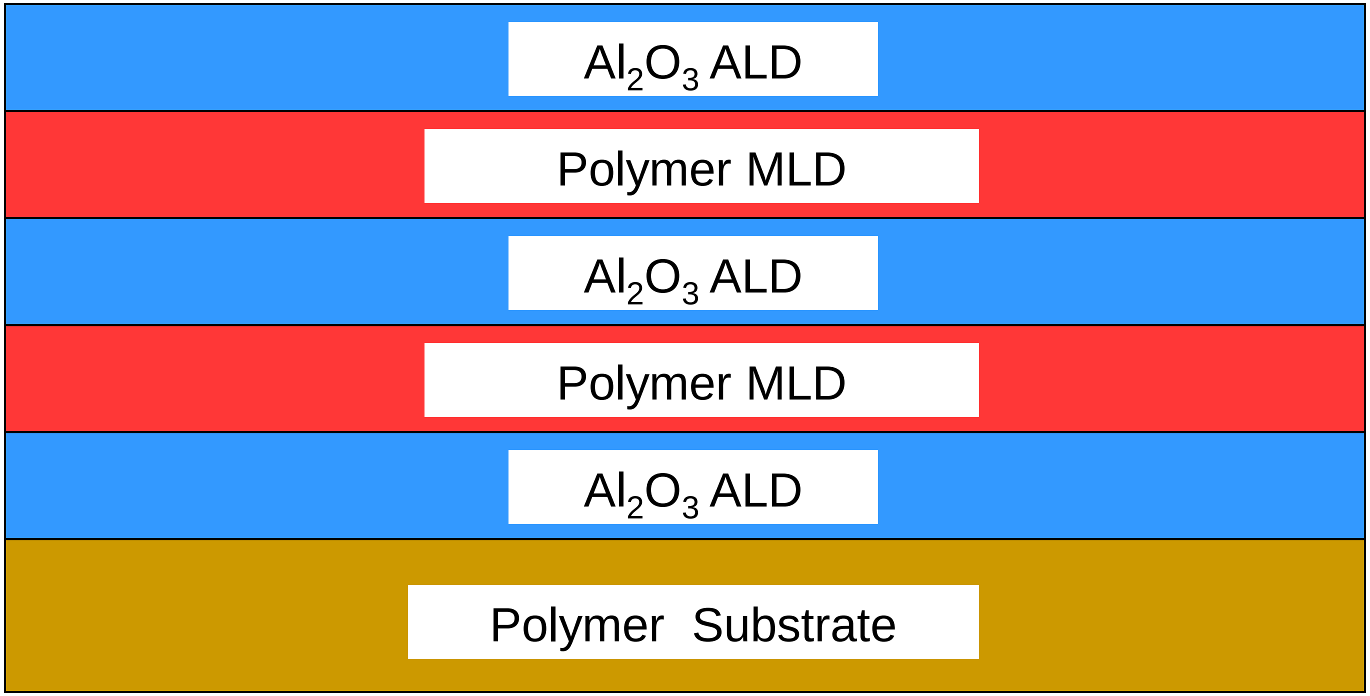
Al_2O_3 ALD/ZrO_2 ALD cycle ratios from 5:1 to 1:5

Importance of ZrO_2 volume fraction

WVTR at sensitivity limit for f(ZrO_2) < 0.5

P.F. Carcia et al., *J. Vac. Sci. Technol. A* **30**, 041515 (2012).

Flexible ALD-MLD Inorganic-Organic Multilayer Barriers



Al_2O_3 ALD

Polymer MLD

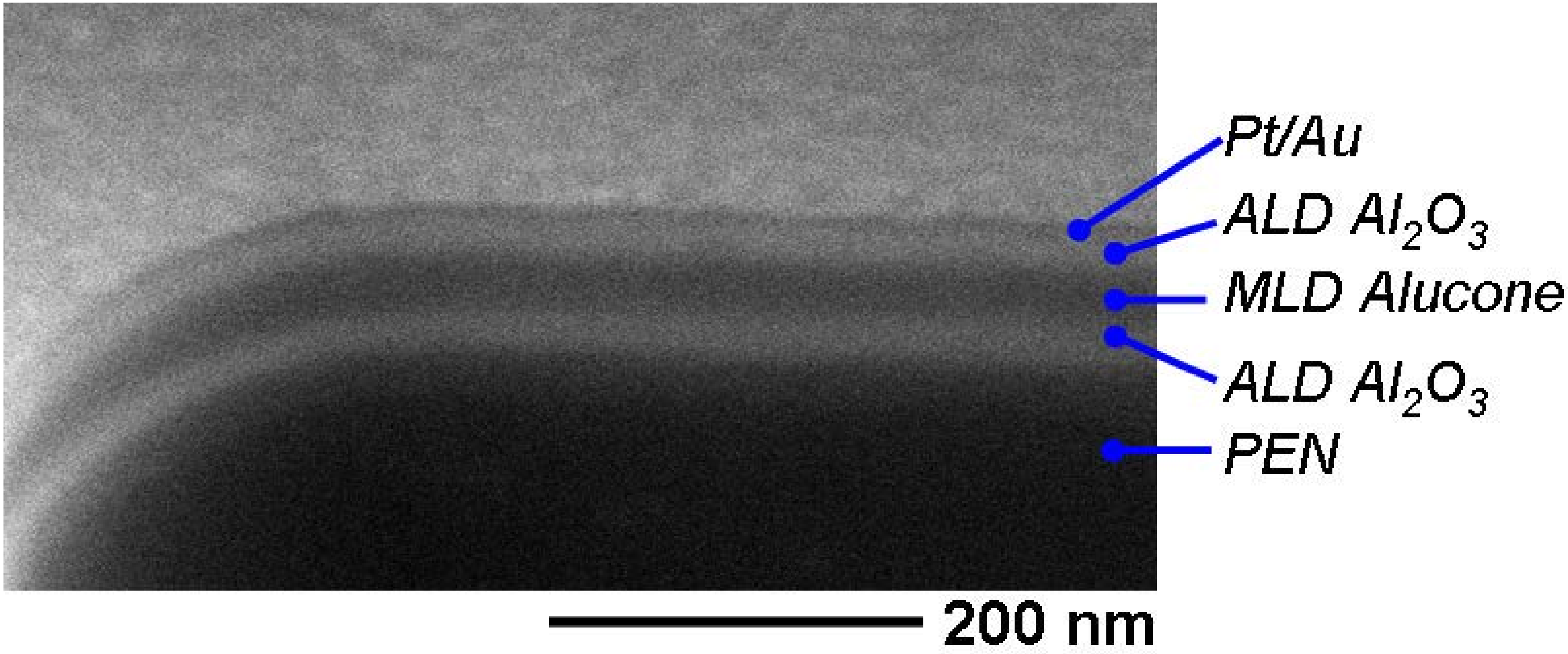
Al_2O_3 ALD

Polymer MLD

Al_2O_3 ALD

Polymer Substrate

SEM of Al_2O_3 ALD/AB Alucone MLD/Al_2O_3 ALD Trilayer on PEN



D.R. Miller, S.M. George et al., *J. Appl. Phys.* **105**, 093527 (2009)

Conclusions

1. Al_2O_3 ALD film is excellent gas diffusion barrier. WVTR $\leq 5 \times 10^{-5}$ g/(m^2 day). Properties depend on deposition temperature.

2. Al_2O_3 ALD with thicknesses ≥ 80 nm crack at tensile strains ≤ 0.5%. Thinner films can achieve ≥ 2.0% at ≤ 5 nm.

3. Al_2O_3 ALD/Alucone MLD alloys can obtain higher critical tensile strains than Al_2O_3 ALD with comparable WVTR.

4. Nanolaminates obtain lower WVTR values. Explanation may include protection from H_2O corrosion.

Acknowledgements

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Jacob Bertrand, Daniel Higgs

Senior Collaborators:

Peter Carcia & Scott McLean (DuPont), Martin Dunn (CU)