



# Fundamental Aspects of Atomic Layer Deposition (ALD) and Molecular Layer Deposition (MLD)

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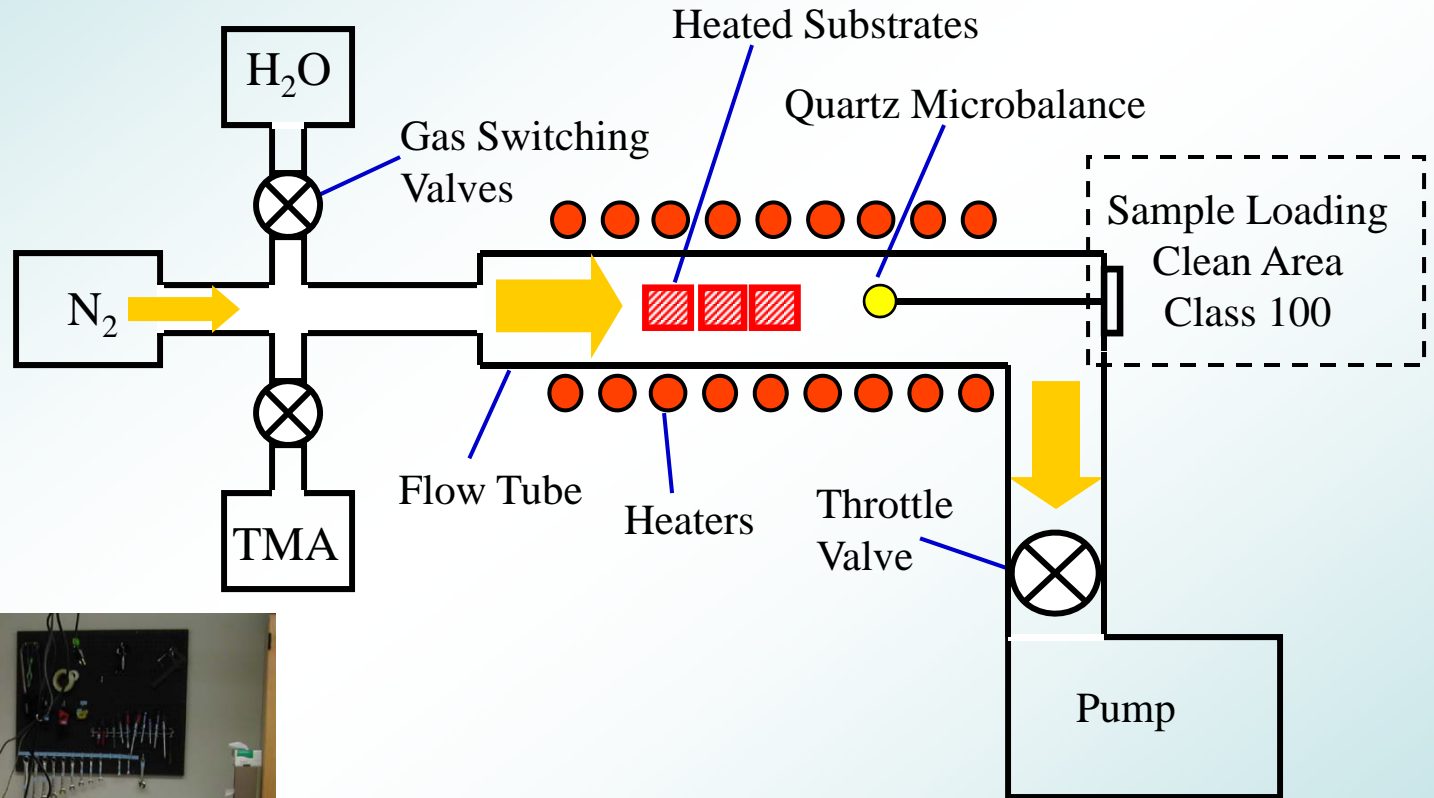
**DARPA/MTO Workshop**

***Materials and Technologies for 21st Century MEMS and NEMS***

**Miami, FL; January 8, 2008**

- **Atomic Layer Deposition**
  - **ALD for micro-scaled devices**
  - **ALD for nano-scaled devices**
  - **ALD for barrier coating**
- **Molecular Layer Deposition**
  - **Nylon 66**
- **Progress, Opportunities and Challenges**
- **Summary**

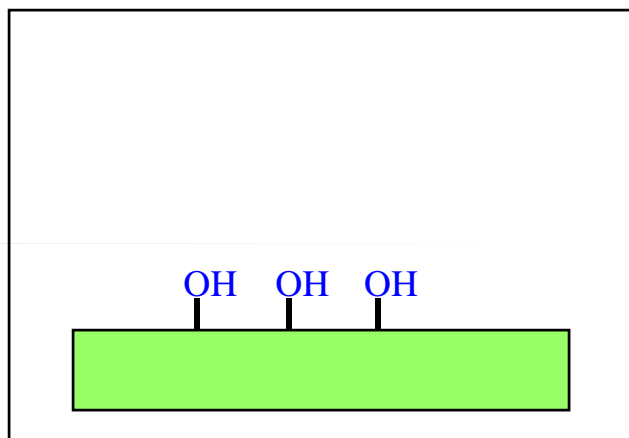
# Atomic Layer Deposition Viscous Flow Reactor



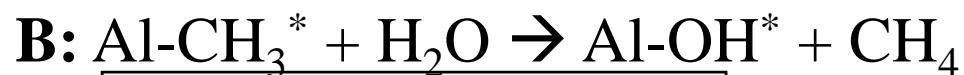
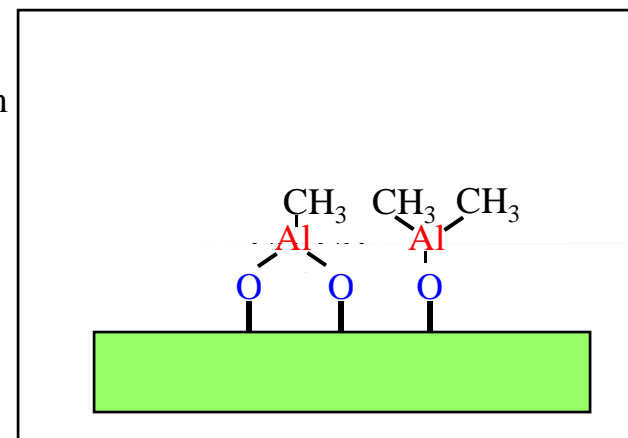
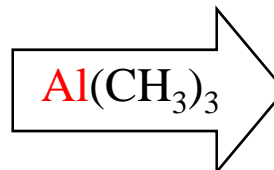
# ALD – Atomic Layer Deposition



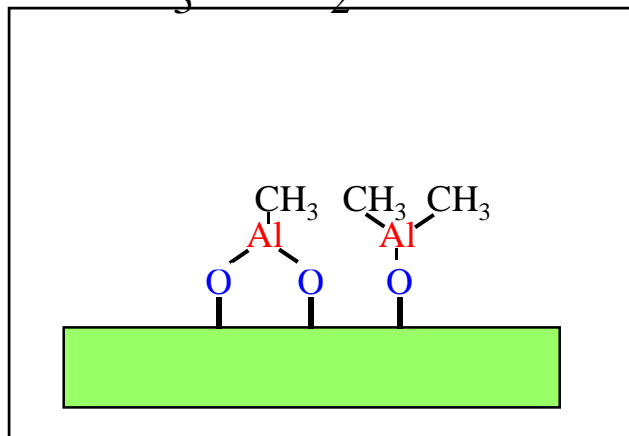
A)



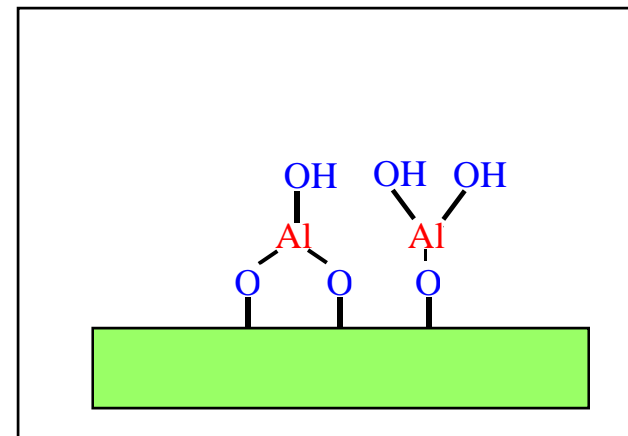
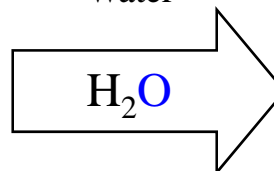
Trimethyl Aluminum  
(TMA)



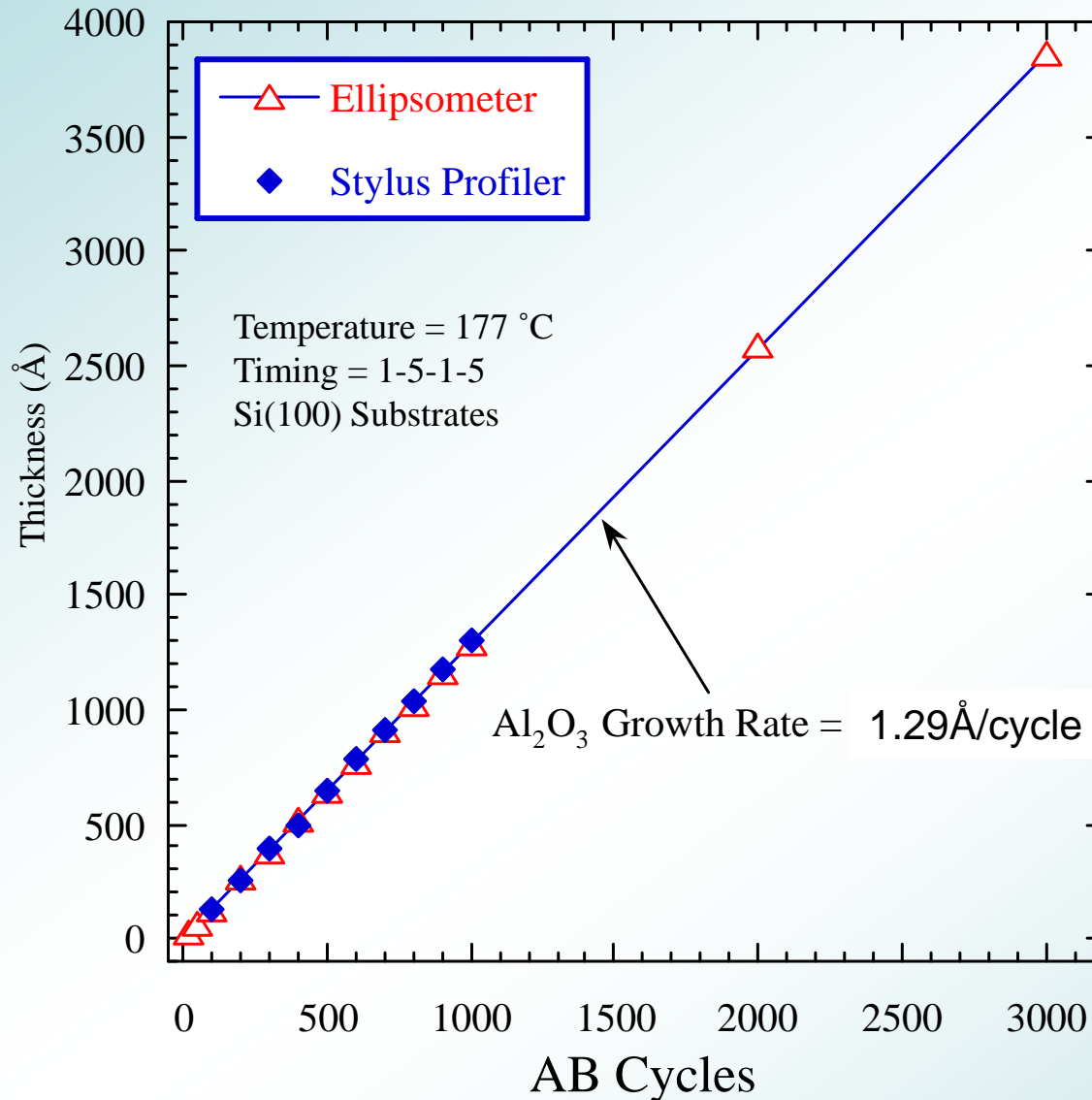
B)



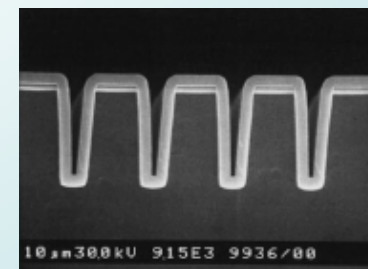
Water



# Al<sub>2</sub>O<sub>3</sub> ALD Film Thickness Measured Using Ellipsometer and Stylus Profiler

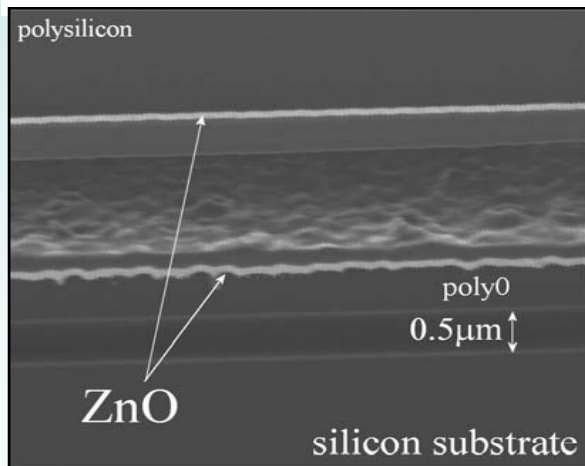
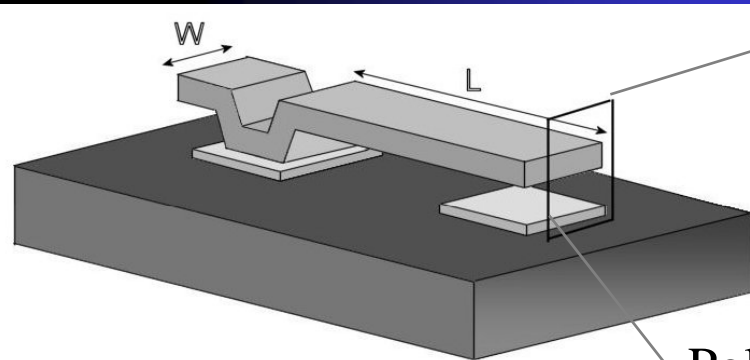


- Precise thickness control
- Excellent step coverage
- Conformal deposition on high aspect ratio structures
- Pinhole-free deposition
- Extendible to larger substrates
- No particle generation
- Low temperature process (< 150 or even 70 °C)
- Nano-scale multi-layer structures

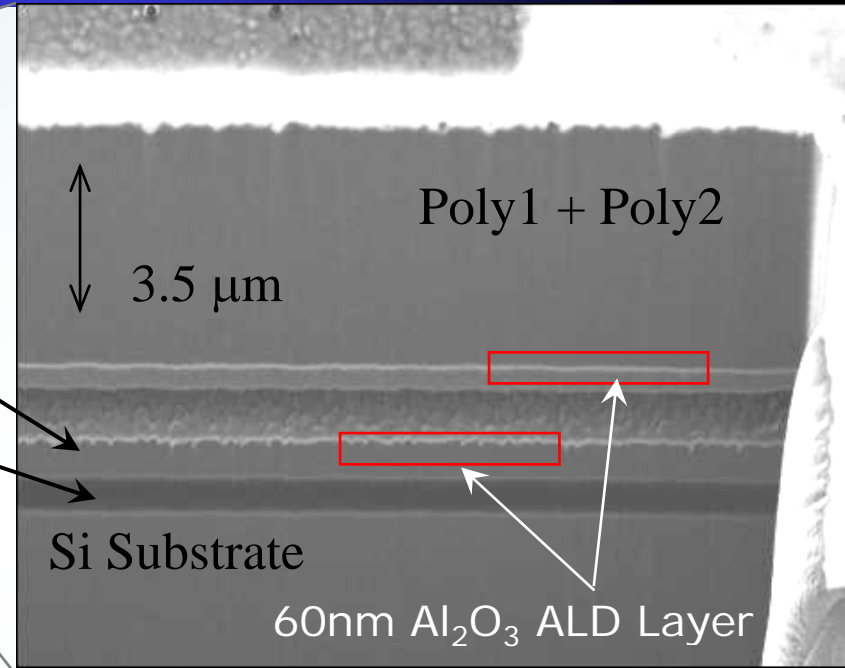


M. Ritala et al.,  
Chem. Vap.  
Depositions, 5, 7  
(1999).

# ALD on MEMS



100nm ZnO ALD Layer

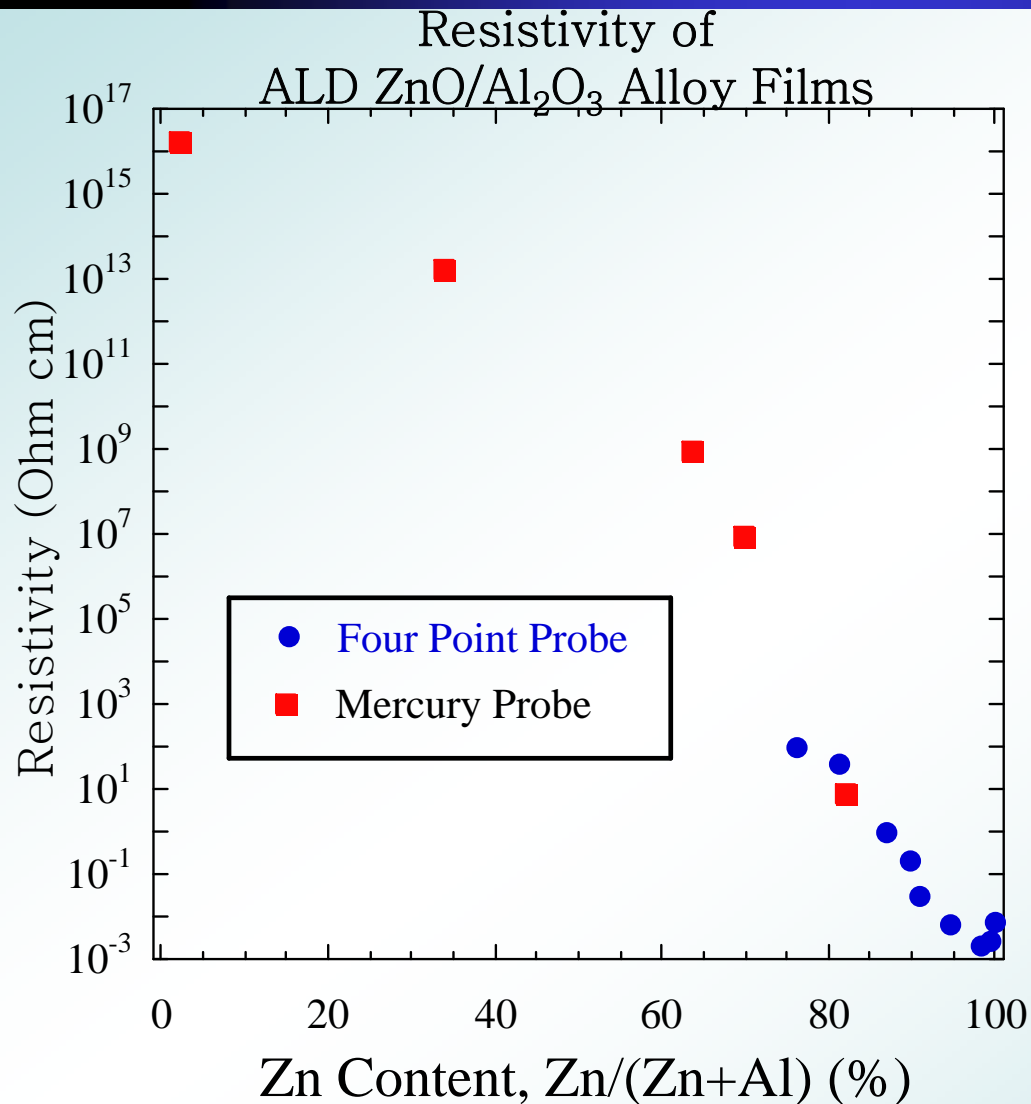


Note: Sample cut by FIB, re-deposition occurs under P1+P2 structure

**Excellent conformal interface and adhesive bond between the ALD deposited material and the polysilicon layers. The uniformity and thickness control of the ALD process is far superior to most common deposition processes.**

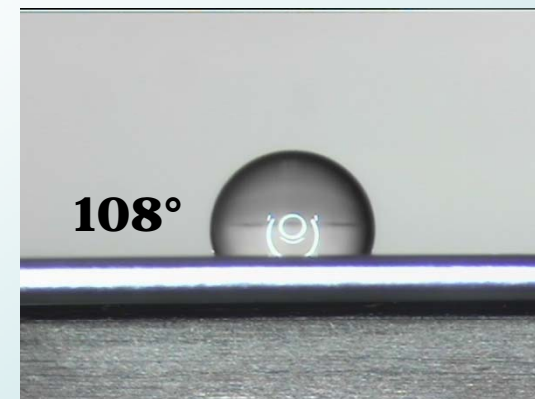
# ALD-Enabled MEMS?

## High Quality Coatings with Precise Surface Properties



High quality coatings  
achieved easily:

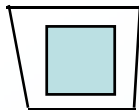
- ALD for Electrical Insulation
- ALD for Dielectric Contact
- ALD for Anti-Stiction
- ALD for Charge Dissipation
- ALD for Optical Reflectivity
- ALD for Wear-Resistance
- ALD for Creep-Resistance
- ALD for Corrosion-Resistance
- ALD for Crack-Resistance



Reference: J.W. Elam, D. Routkevitch and S.M. George, "Properties of ZnO/Al<sub>2</sub>O<sub>3</sub> Alloy Films Grown Using Atomic Layer Deposition Techniques", *J. Electrochem. Soc.* **150**, G339-G347 (2003).

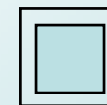
# ALD-Enabled NEMS? Yes!

**CVD or other  
Coatings on MEMS**



**Coating variations on  
NEMS unacceptable!**

**ALD on MEMS**



**25 to 100 nm  
ALD Coating**

**ALD on NEMS**

- **Atomic Layer Deposition**
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  - ALD for barrier coating
- **Molecular Layer Deposition**
  - Nylon 66
- **Progress, Opportunities and Challenges**
- **Summary**

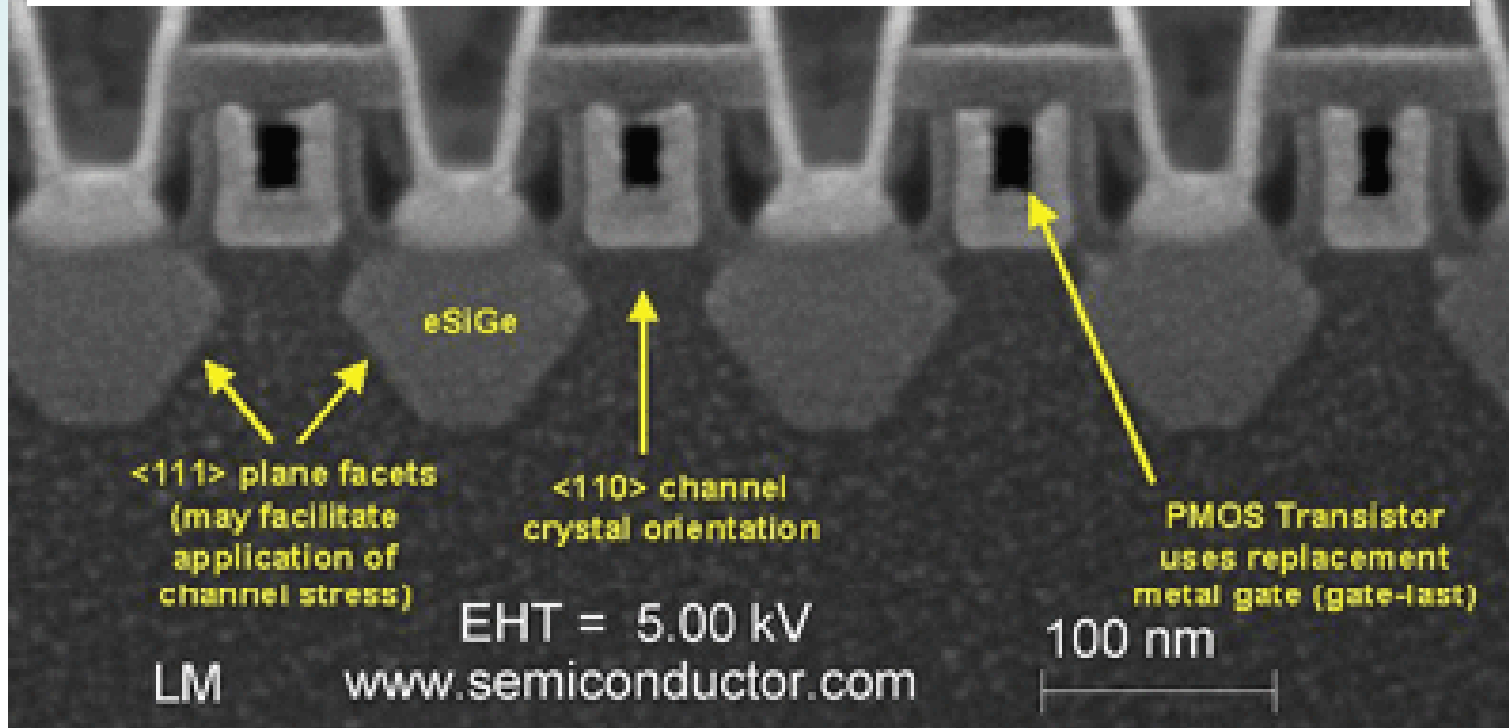
# ALD HfO<sub>2</sub> for 45-nm Microprocessors

SI-18979

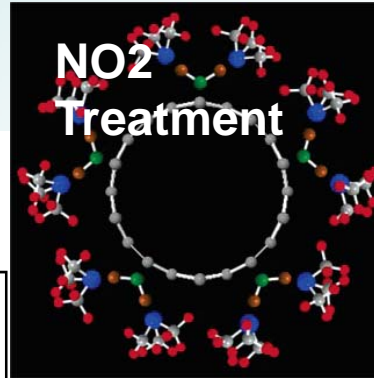
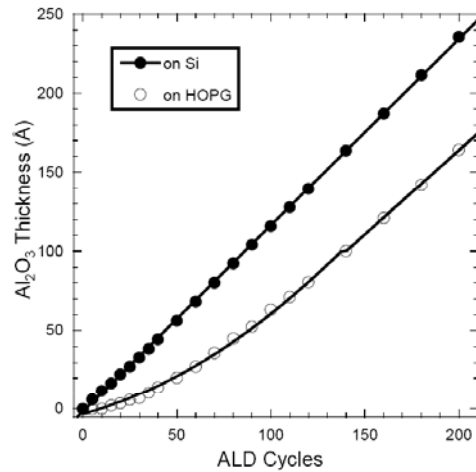
Date :9 Nov 2007

4328187

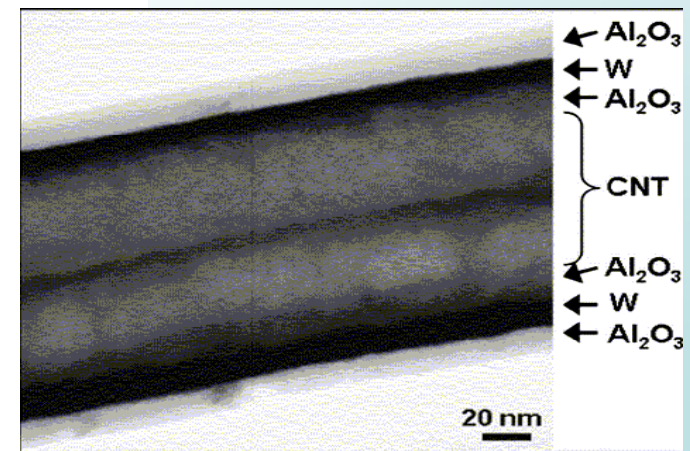
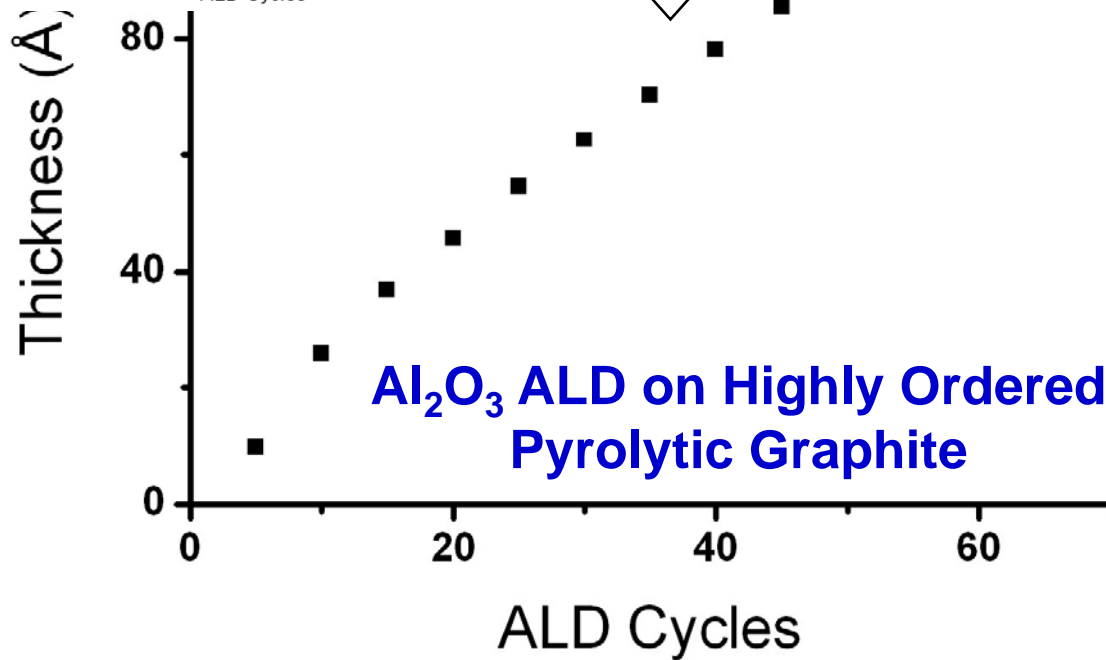
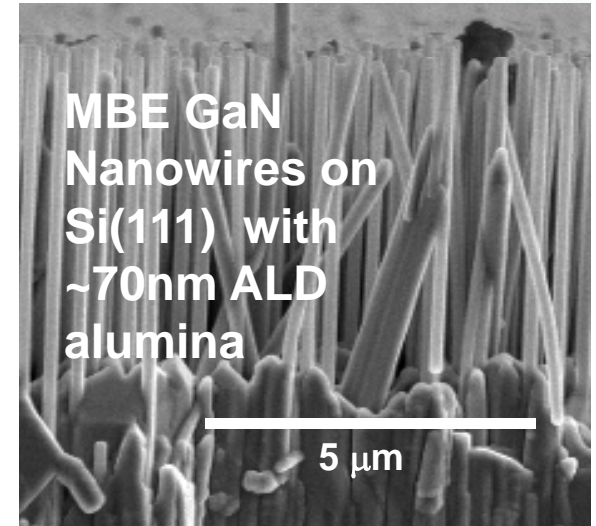
On Nov. 12, 2007, Intel shipped the first 45-nanometer microprocessors using high-k metal-gate technology. Gordon Moore describes the innovations as "the biggest change in transistor technology since the introduction of polysilicon-gate MOS transistors in the late 1960s."



<http://www.eetimes.eu/203101162Don Scansen EE Times 11/14/2007>

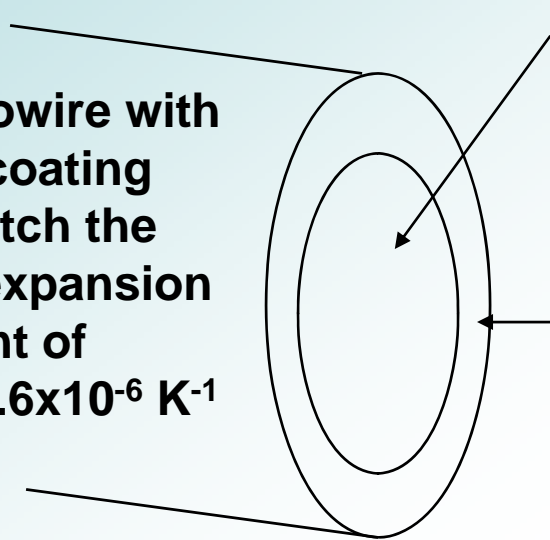


D.B. Farmer and R.G. Gordon, Nano Lett., **6**, 699 (2006).



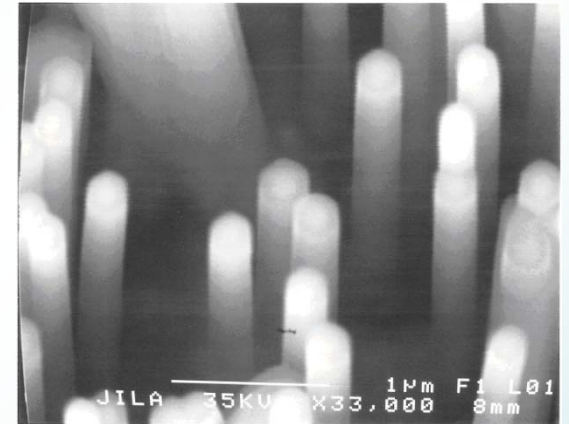
# ALD-Enabled Nanotube/Nanowire/Graphene Devices

GaN nanowire with BN ALD coating could match the thermal expansion coefficient of silicon,  $2.6 \times 10^{-6} \text{ K}^{-1}$

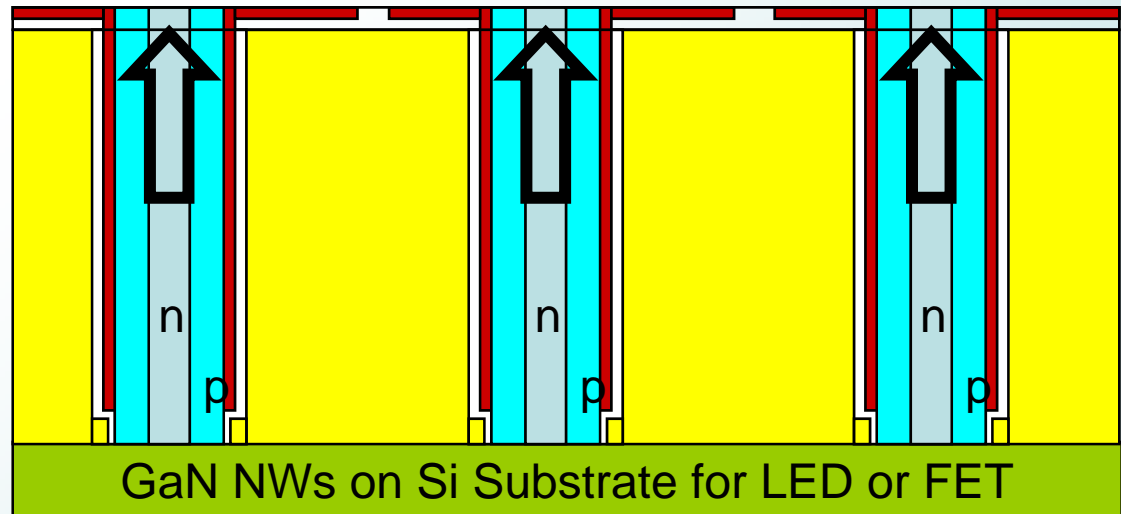
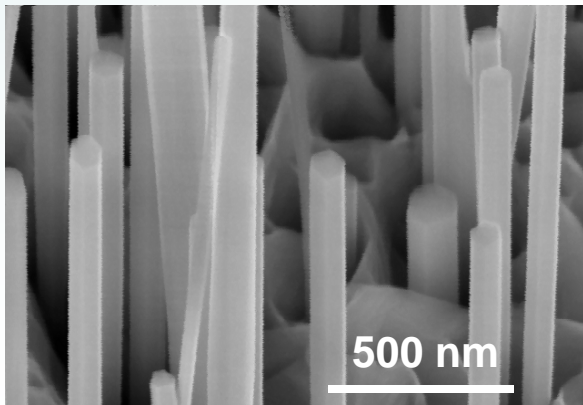


GaN:  
 $E_{\text{GaN}} = 330 \text{ GPa}$   
 $\alpha_{\text{GaN}} = 3.2 \times 10^{-6} \text{ K}^{-1}$

BN:  
 $E_{\text{BN}} = 700 \text{ GPa}$   
 $\alpha_{\text{BN}} = 1.2 \times 10^{-6} \text{ K}^{-1}$

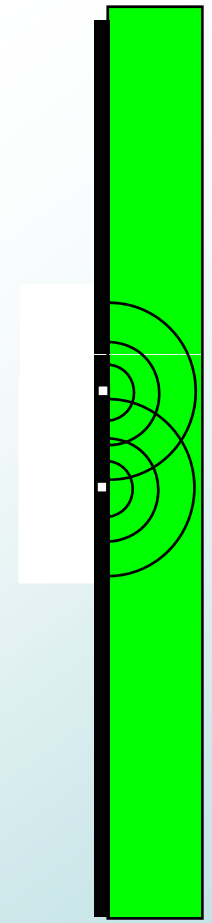
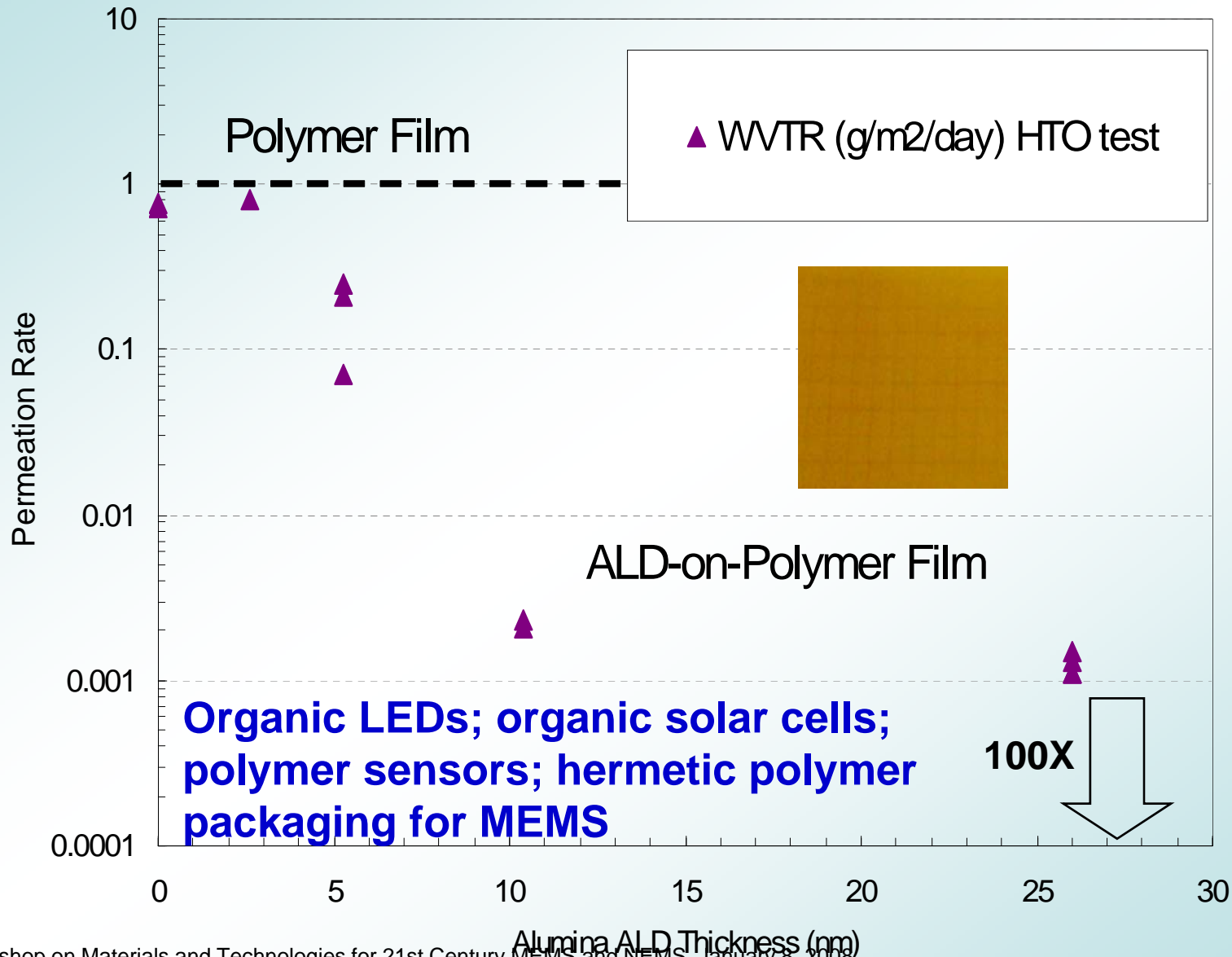


Electrical, thermal and mechanical interfaces



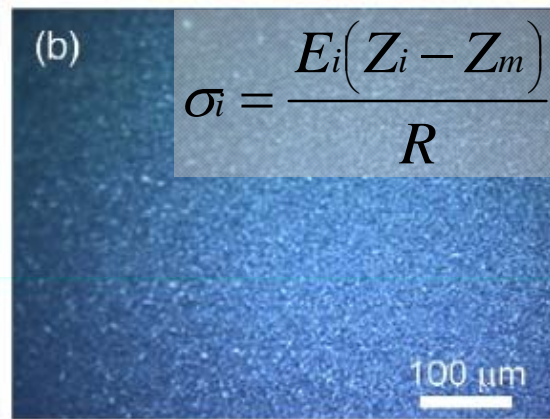
- **Atomic Layer Deposition**
  - ALD for micro-scaled devices
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# ALD-Based Barrier Coating (Moisture and Oxygen Permeation)



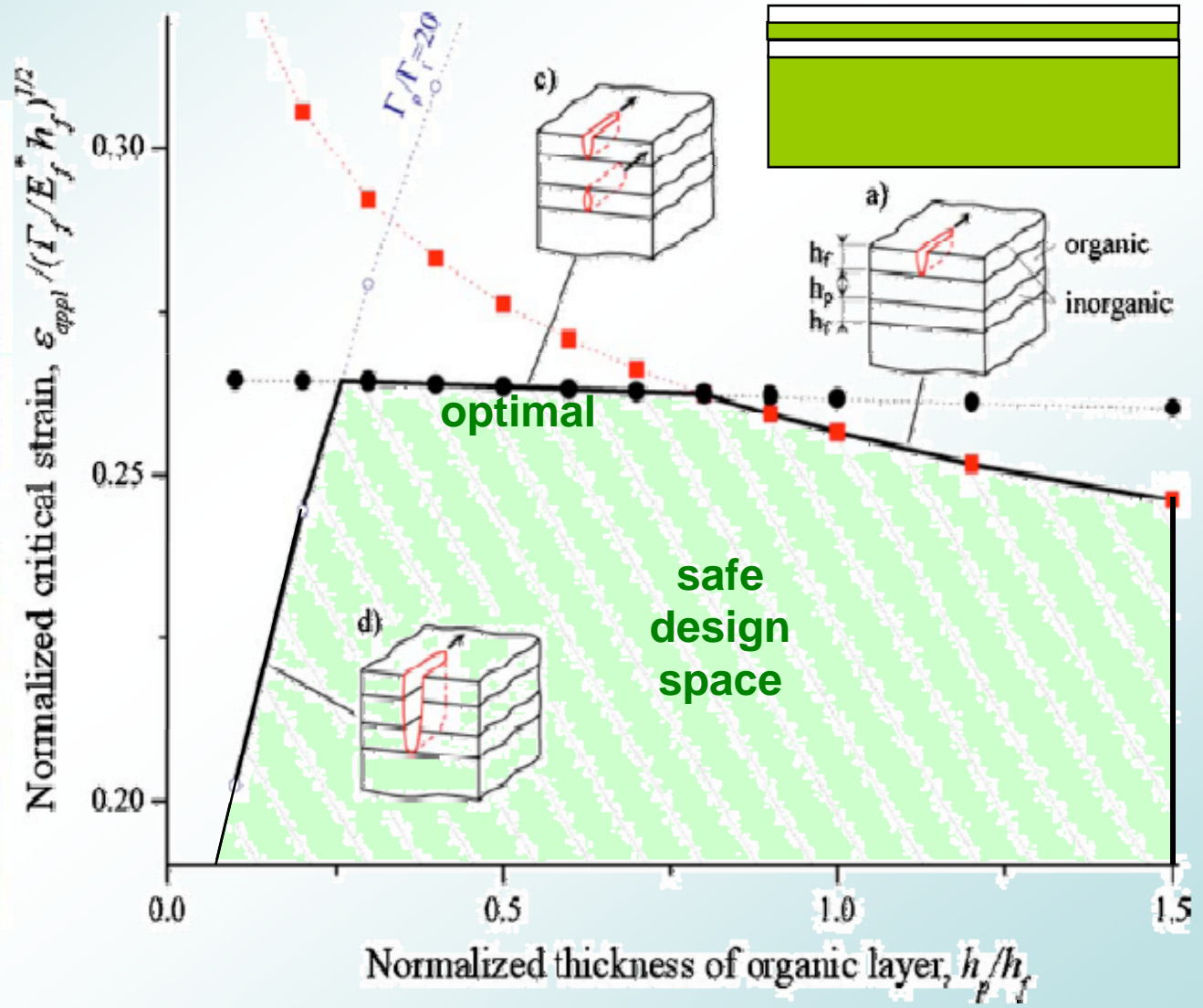
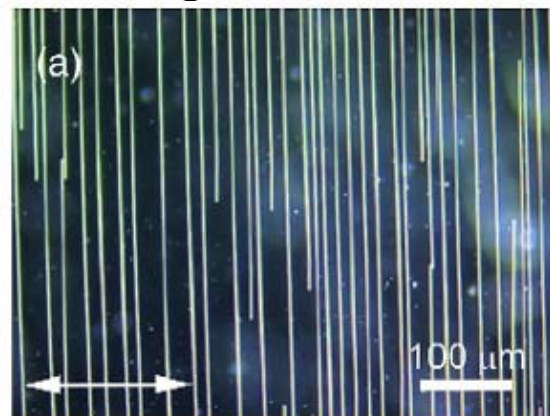
# Cracking of $\text{SiO}_x\text{N}_y$ and Organic/Inorganic Barrier Films on Polymer Substrates

Bending Radius = 0 mm



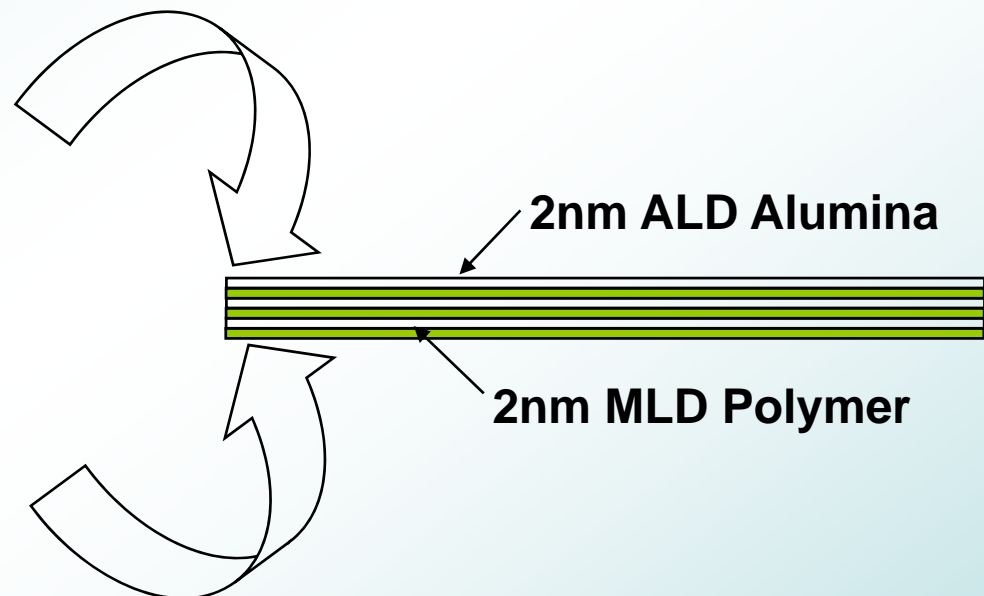
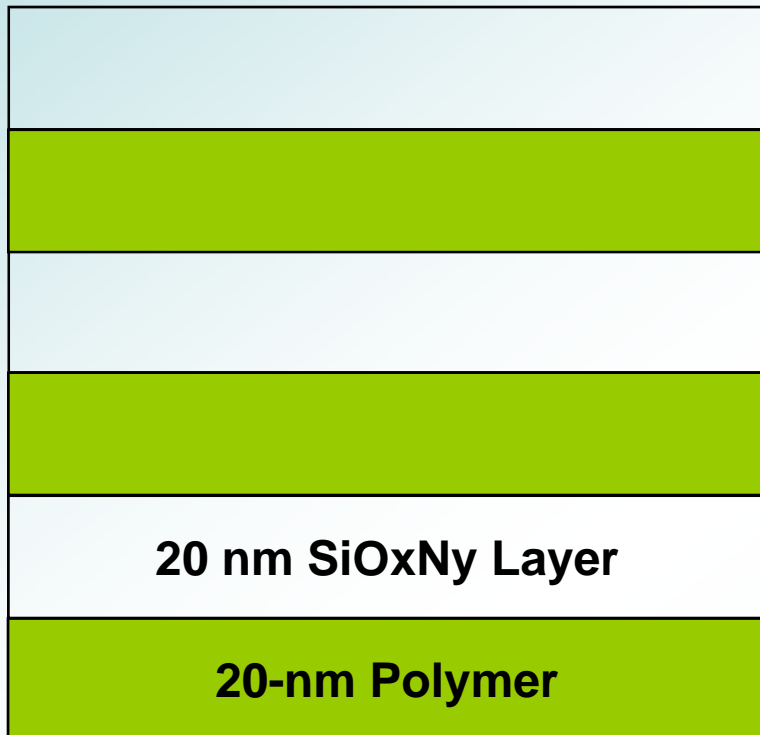
$$\sigma_i = \frac{E_i(Z_i - Z_m)}{R}$$

Bending Radius = 5 mm



Grego, et al., 2007, *Thin Solid Films*, Vol. 515, pp. 4745-4752; Cordero, N., Yoon, J., and Suo, Z., 2007, *Applied Physics Letters*, Vol. 90, 111910.

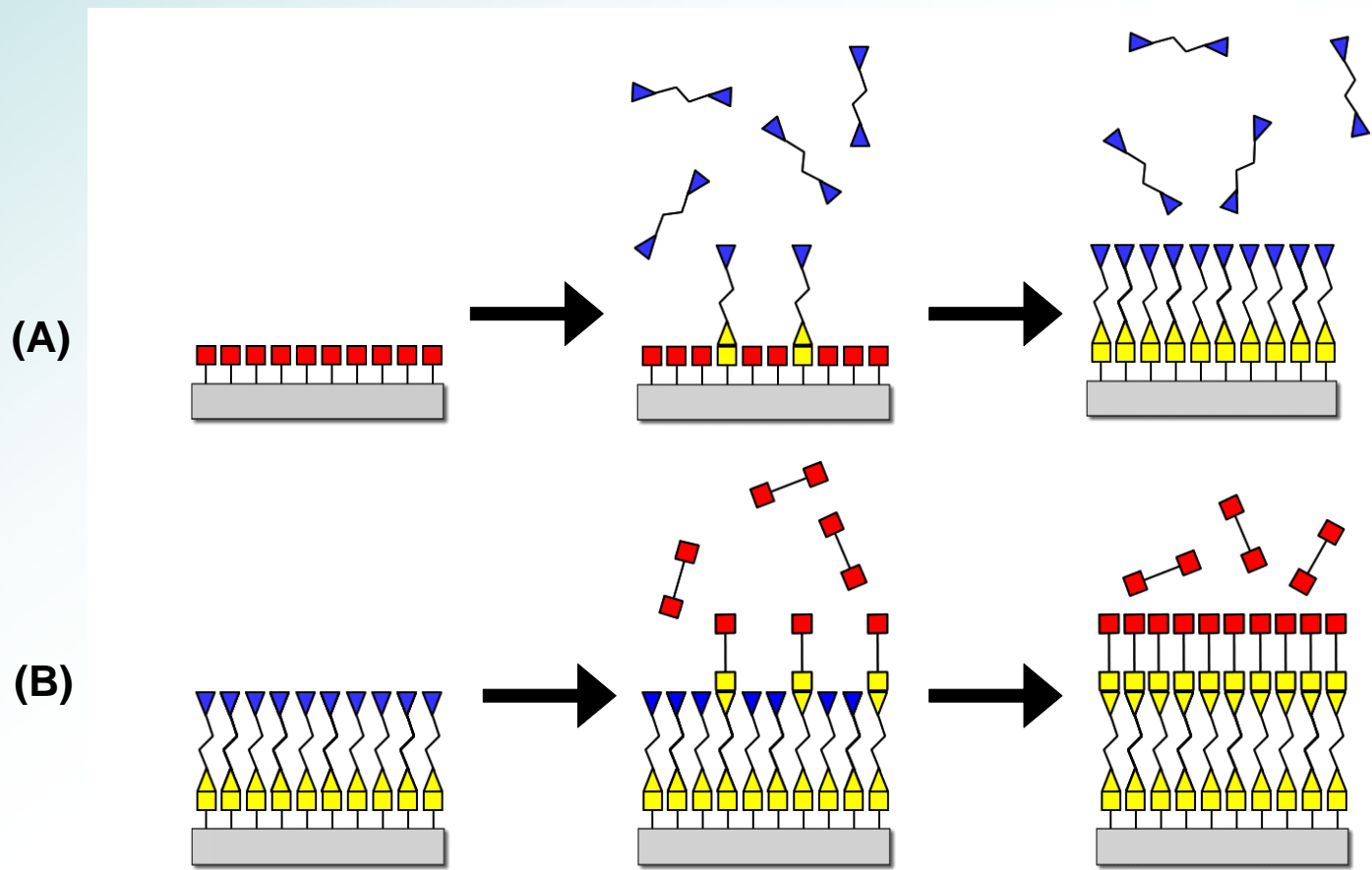
# Molecular Layer Deposition (MLD) for Multilayer Barrier



**3X mechanically improved toughness**  
**?X chemically improved toughness**  
**due to covalent bonds between**  
**polymer and alumina layers**

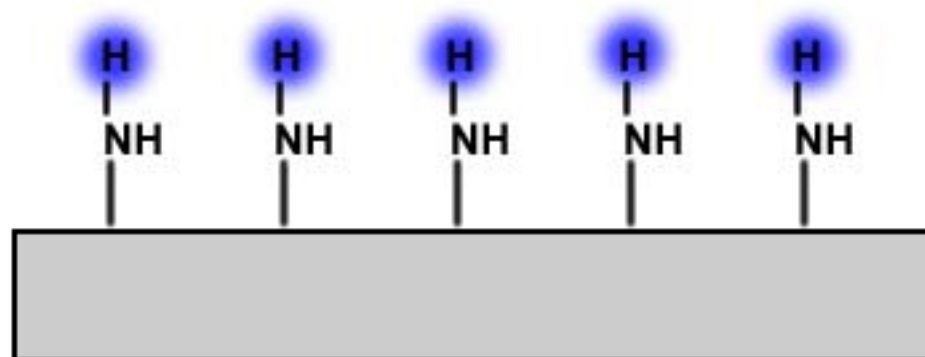
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# Polymer Molecular Layer Deposition

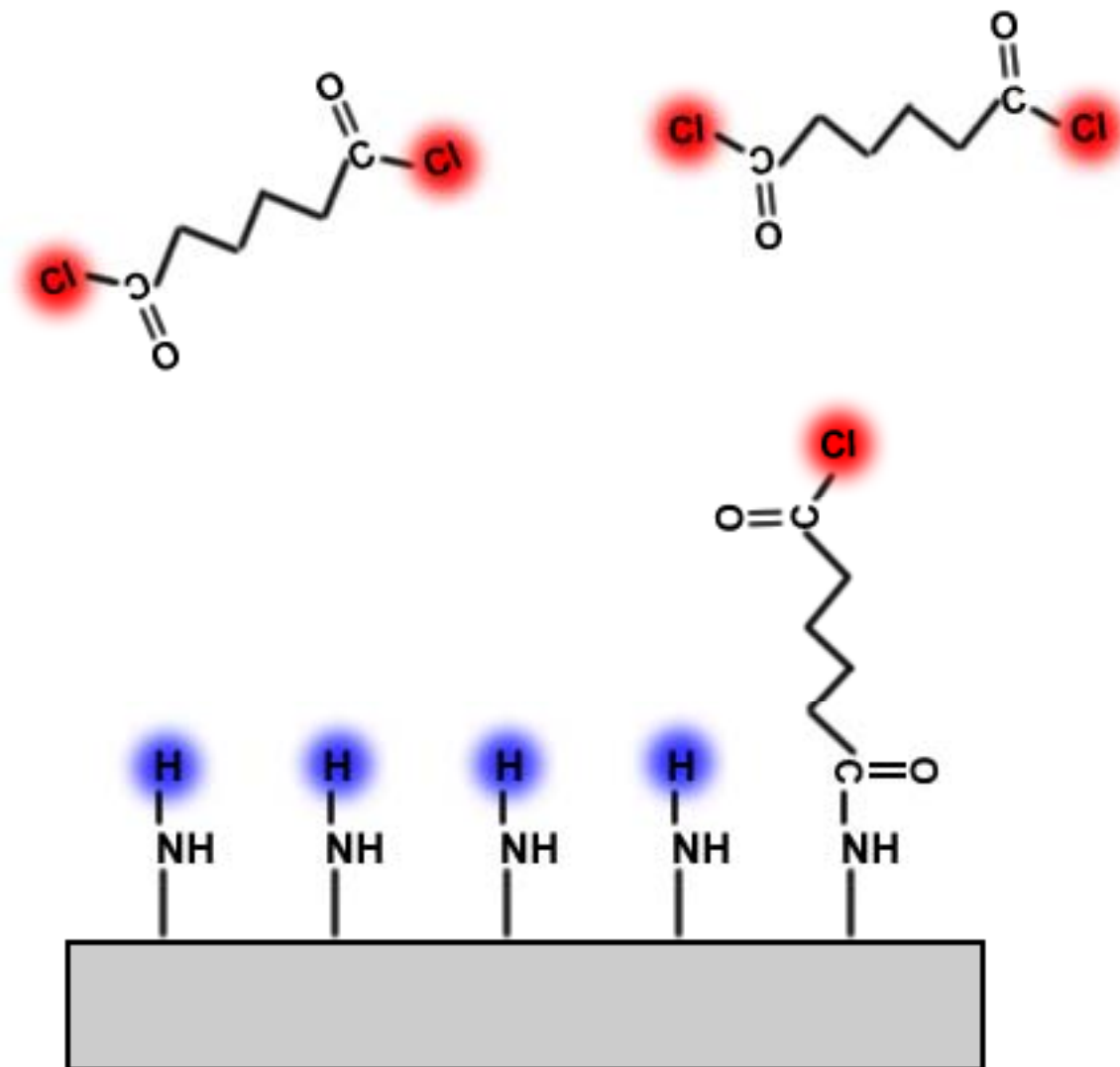




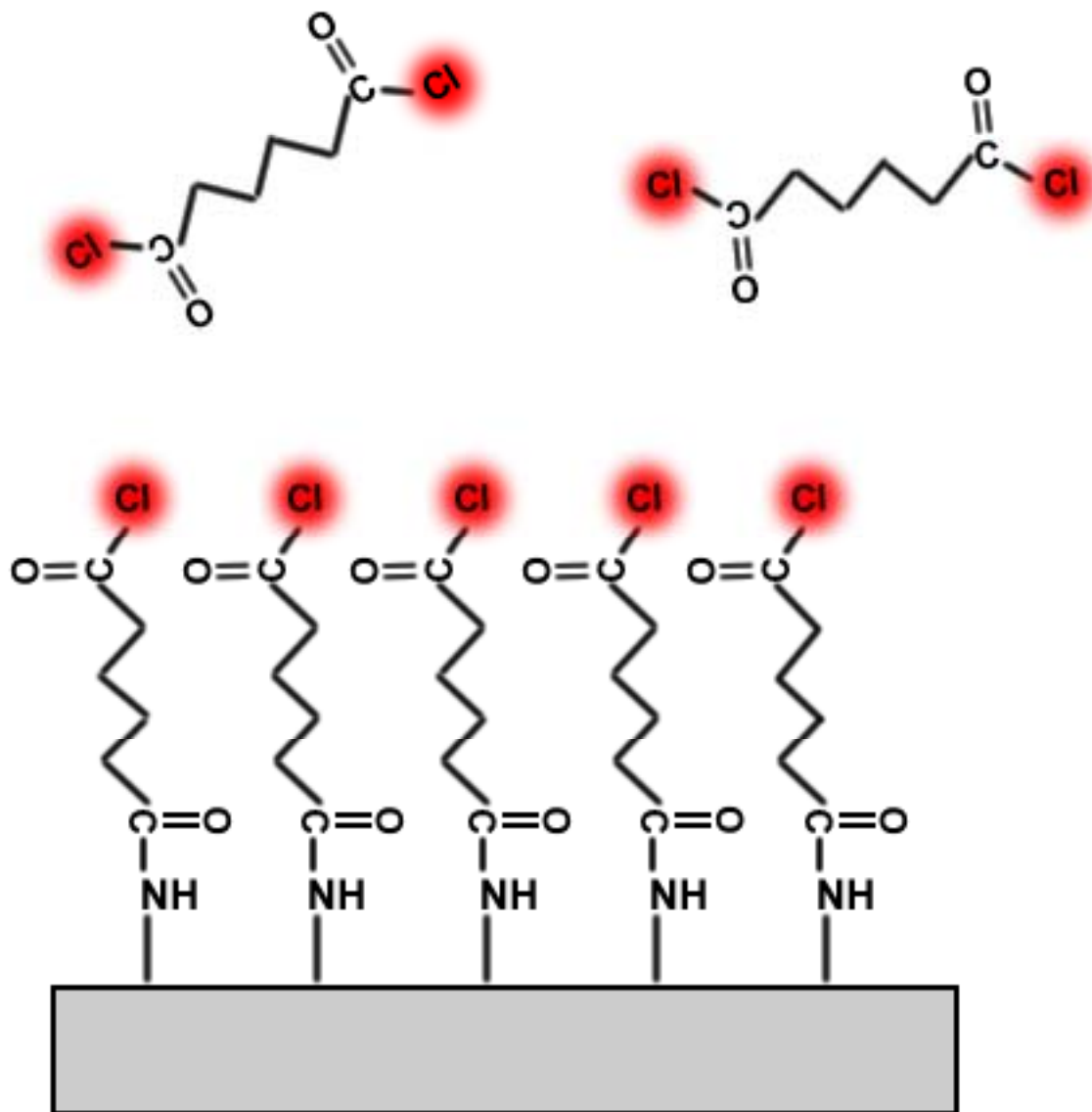
# Nylon Molecular Layer Deposition



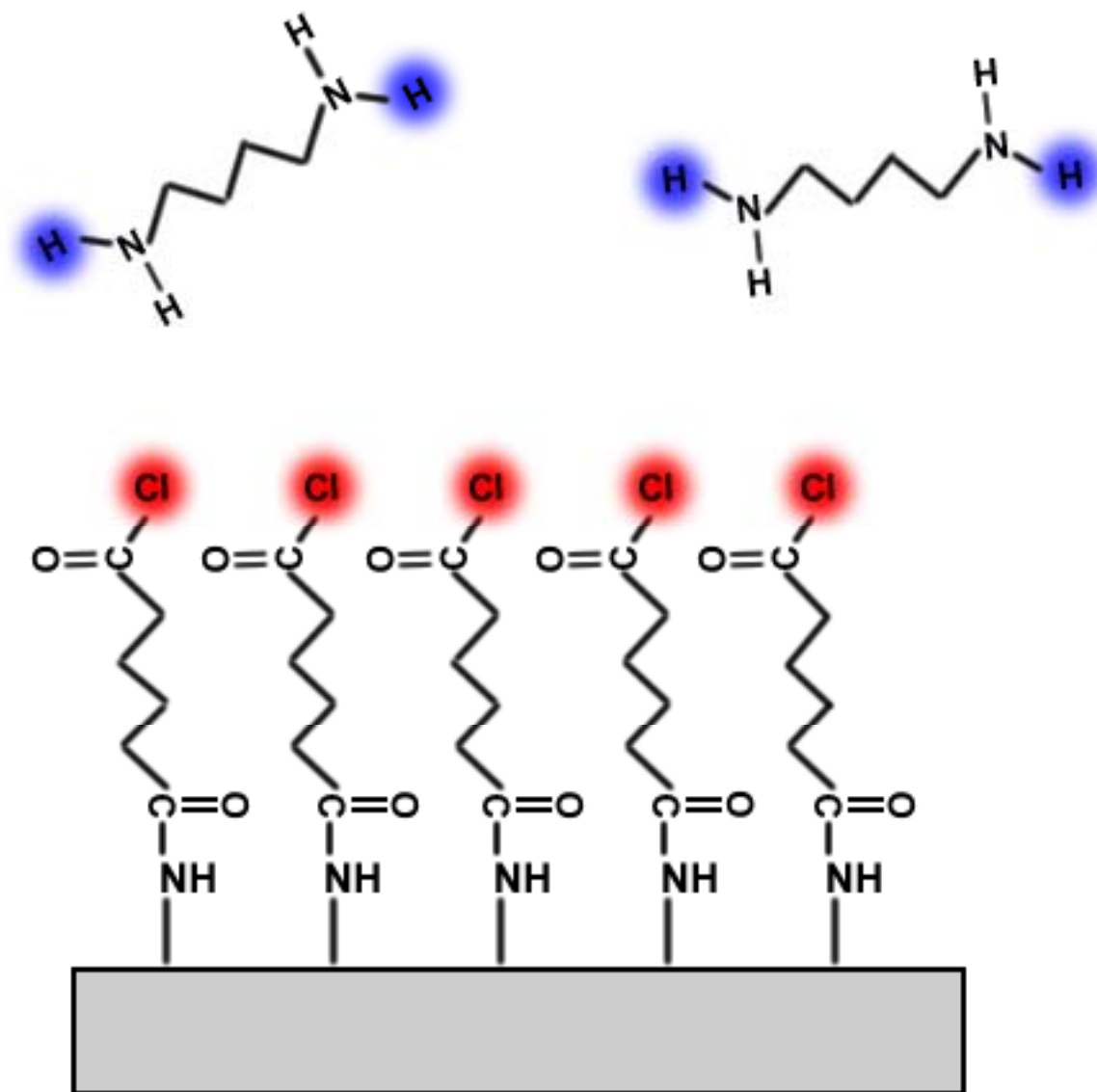
# Nylon Molecular Layer Deposition



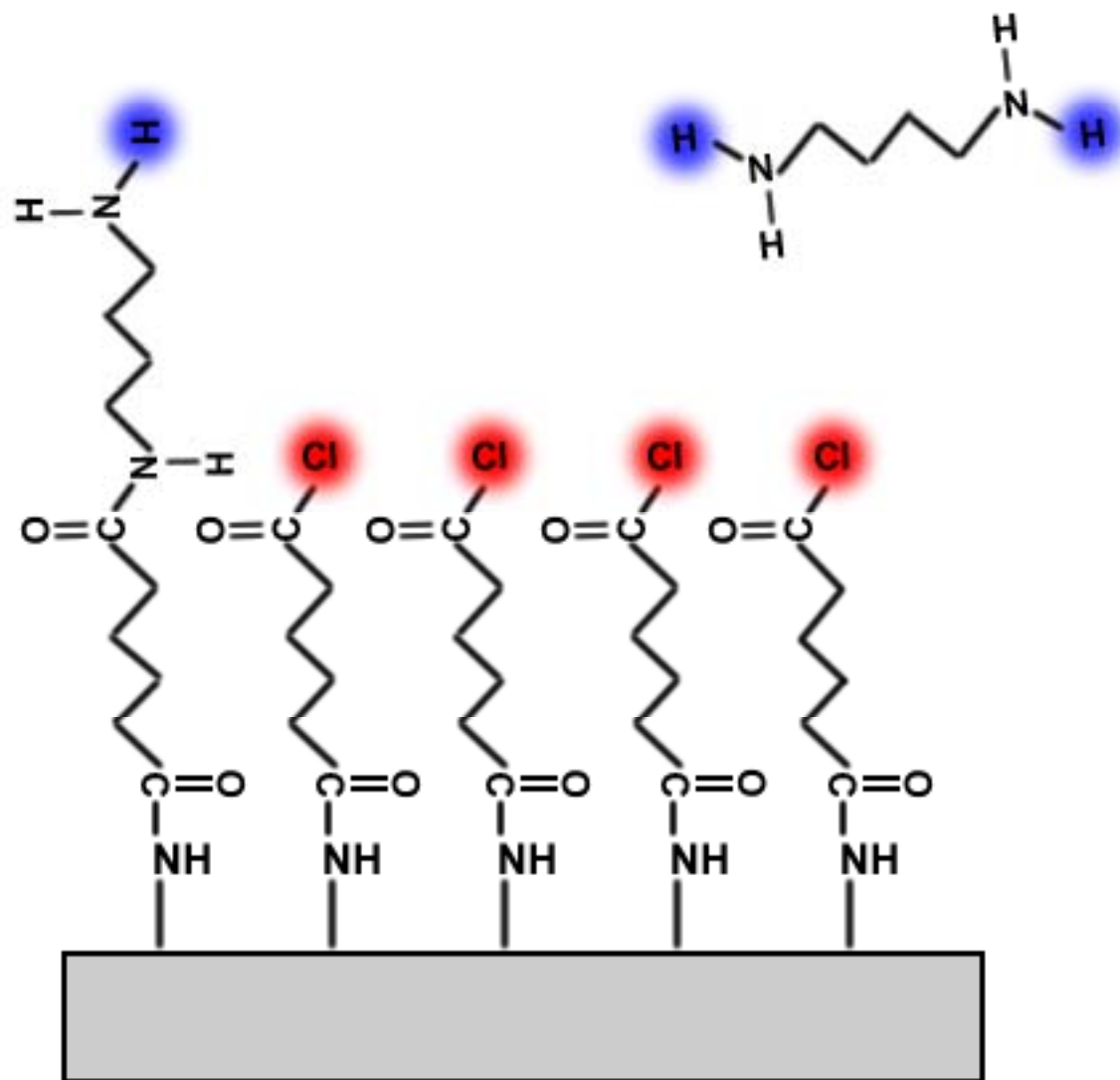
# Nylon Molecular Layer Deposition



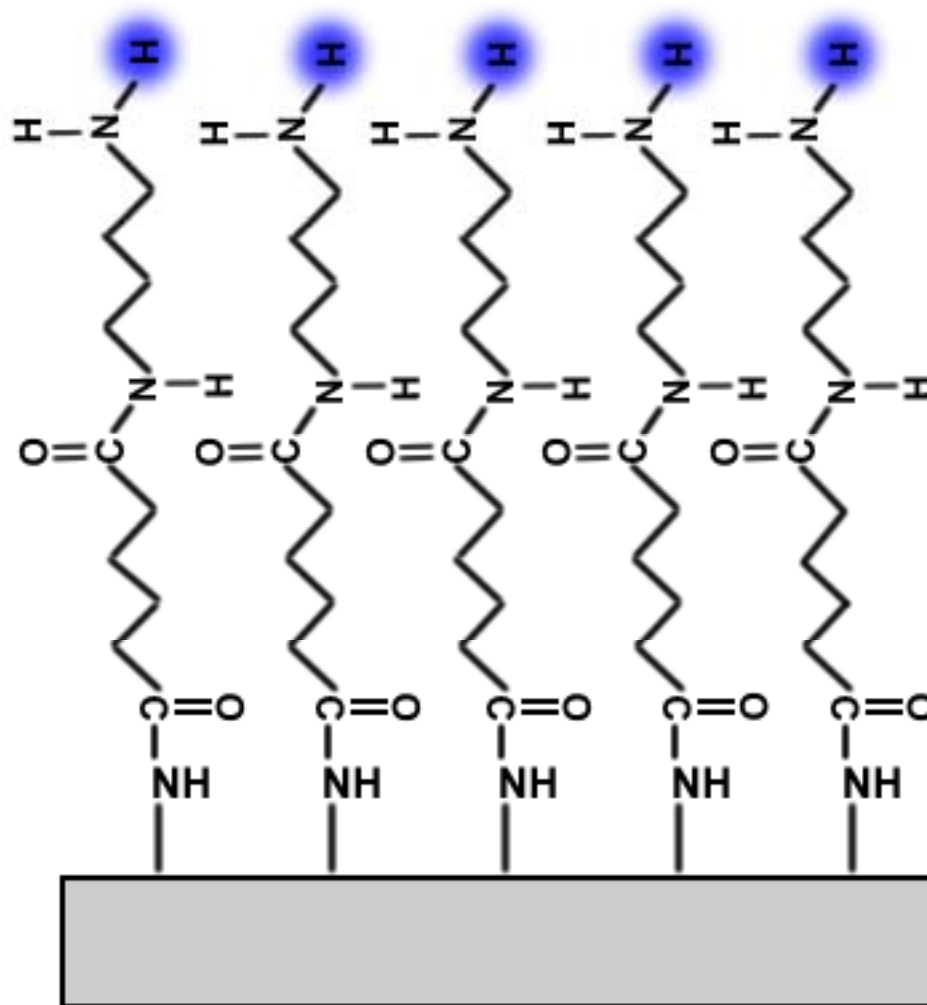
# Nylon Molecular Layer Deposition



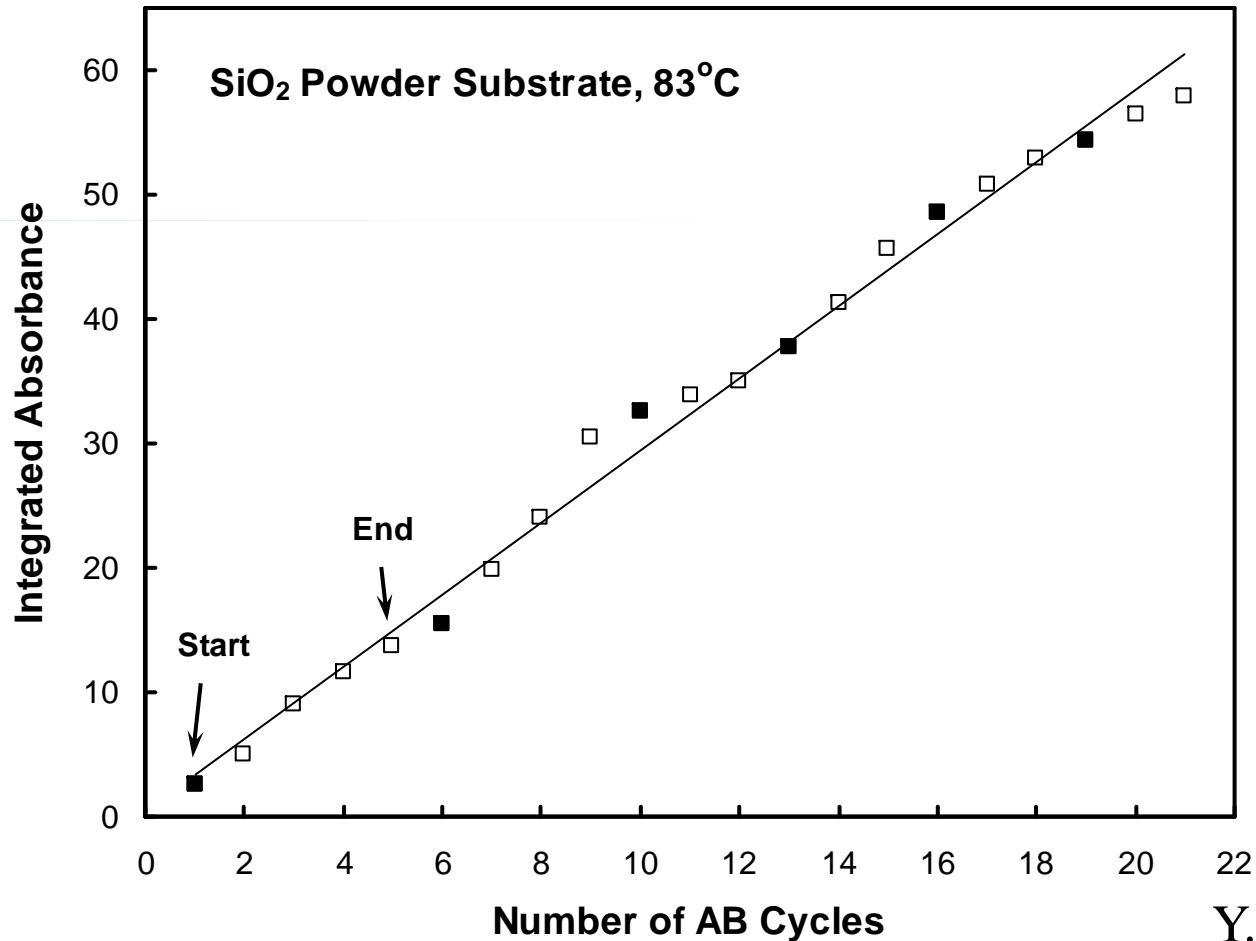
# Nylon Molecular Layer Deposition



# Nylon Molecular Layer Deposition



# Integrated Absorbance Increase versus Number of AB Cycles at 83°C



Combined  
Absorbance of Amide  
I and II Bands is  
Linear with Number  
of AB Cycles

Y. Du & S.M. George, *J. Phys. Chem. C* 111, 8509 (2007).<sup>26</sup>

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# Atomic Layer Deposition: Progress, Opportunities and Challenges

## ALD at CU-Boulder (George Research Group)

- Alumina ( $\text{Al}_2\text{O}_3$ )
- Tungsten (W)
- Ruthenium (Ru)
- Aluminum Nitride (AlN)
- Tantalum Nitride (TaN)
- Tin Oxide ( $\text{SnO}_2$ )
- Silicon Dioxide ( $\text{SiO}_2$ )
- Hafnium Oxide ( $\text{HfO}_2$ )
- Zinc Oxide (ZnO)
- Titanium Oxide ( $\text{TiO}_2$ )
- Magnesium Oxide (MgO)
- Manganese Oxide ( $\text{MnO}_2$ )
- Hydrophobic Layers

- ALD processes are well developed. CVD with binary reactions  $\rightarrow$  ALD possible.
- ALD for MEMS
  - high quality coatings
  - manufacturable now
  - quality (yield/defect)?
  - reliability?
- ALD for NEMS
  - enabling technologies for devices and interfaces
  - improved processes for novel applications, NT/NW/graphene.

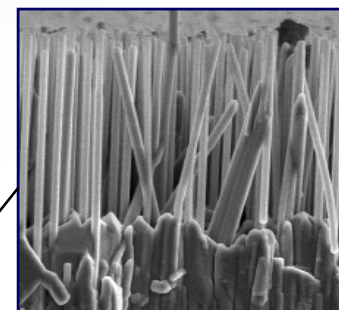
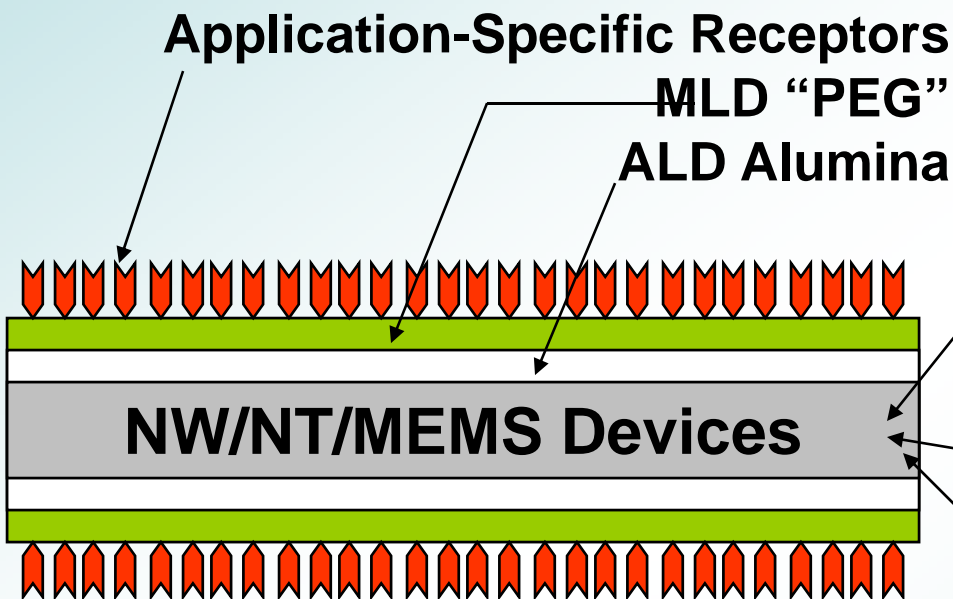
- **Nylon 66 MLD** – First report by CU in Summer 2006, Others: NC State and Helsinki Institute of Technology
- **Poly(p-Phenylene Terephthalamide) [PPTA]** “Kevlar” MLD – Demonstrated by CU in Spring 2007. Higher Thermal Stability Polyamide Polymer
- **Alucone MLD**: Novel Hybrid Organic/Inorganic Polymer. Published by CU and University of Oslo in Summer 2007. New Nanocomposite Flexible Polymer.
- **MLD of “ABC” Polymers**. Novel Hybrid Organic/Inorganic Polymer based on ABC Reaction Sequence. Demonstrated by CU in Fall 2007. Enlarges Material Set for Nanocomposite Films.
- ALD/MLD processes are new and good for a large number of inorganic/organic combinations.
- ALD/MLD for MEMS
  - > 10X in quality and reliability
  - new surface properties resulting from polymer layers.
- ALD/MLD for NEMS
  - exciting enabling technologies for devices and interfaces
  - organic molecules essential to NEMS; multiple inorganic/organic layers with molecular precision.
- applications, science and technology?



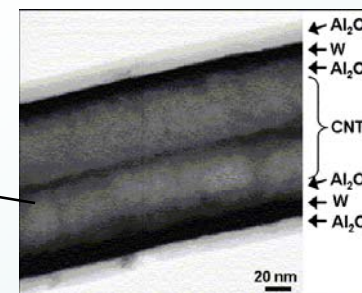
# Opportunity: ALD/MLD-Enabled Highly Selective, Stable and Manufacturable Biosensors

Wei Tan, Xiohua Du, Steven M. George and Y. C. Lee

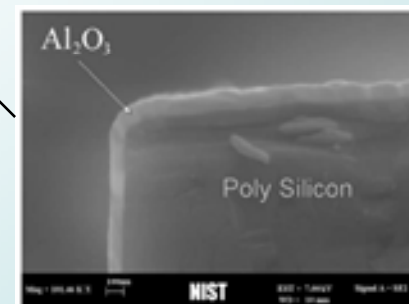
## Universal Functionalization Platform



ALD Alumina-on-NW



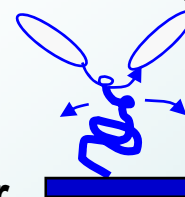
ALD Alumina-on-NT



ALD Alumina-on-MEMS

PEG for anti-fouling to reduce false alarms:

- Single layer PEG coating? density?
- Multi-layer PEG coating? Conformation?
- MLD "PEG" can give us a precise number



of high-quality anti-fouling layers for a quantitative understanding leading to highly selective, stable and manufacturable biosensors.

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- **Progress, Opportunities and Challenges**
  - **ALD for MEMS: manufacturing, quality and reliability**
  - **ALD for NEMS: enabling technologies for devices and interfaces for system integration**
  - **ALD/MLD for MEMS: >10X improvement over ALD in quality and reliability**
  - **ALD/MLD for NEMS: Exciting inorganic/organic multilayers for repeatable, predictable and reliable NEMS.**