

# Transportation Vehicle Light-Weighting with Polymeric Glazing and Mouldings

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## Organosilicate Films and Coatings

Scott Isaacson, Joe Burg, [Siming Dong](#), [Michael Hovish](#), [Florien Hilt](#)

## Polymers and Hybrid Nanomaterials

Jeff Yang, Marta Giachino, Qiran Xiao, [Linying Cui](#), [Zhenlin Zhao](#), Yichuan Ding

## Membranes for Fuel Cells and Batteries

Daisy Yuen

## Complex Multi-Junction Device Structures

Ryan Brock

## Photovoltaic and Flexible Electronic Materials

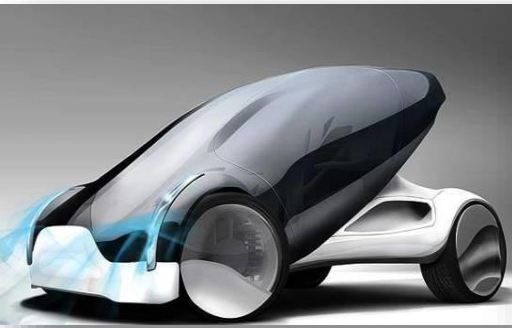
Fernando Novoa, Chris Bruner, Stephanie Dupont, Nick Rolston, Warren Cui, Brian Watson

## Biological Hybrids

Krysta Biniek, Jacob Bow, Chris Berkey, David Kanno

DOE-BES and AFOSR programs on hybrid materials, BA PV Consortium, Stanford-GCEP program on lightweighting.

# Processing and Thermomechanical Reliability of Hybrid Films



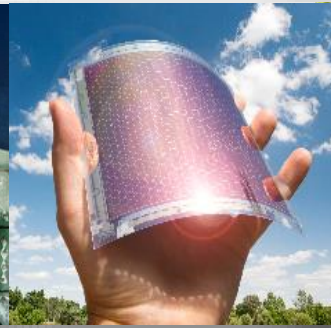
light-weight vehicle



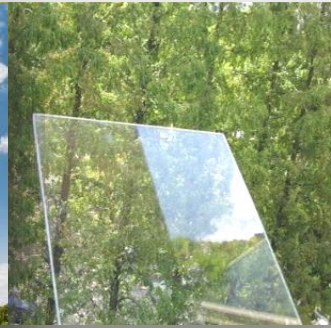
touch display



wearable



sensors and PV

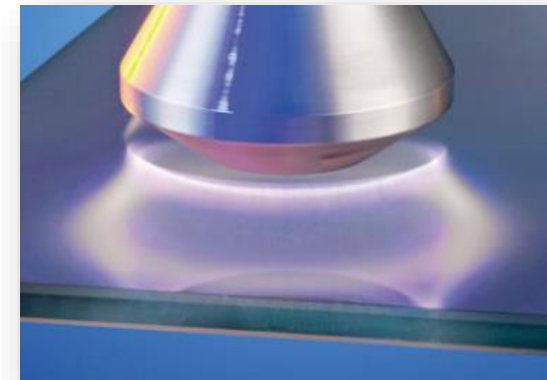


AR coatings

...current polymeric glazings do not meet durability/performance requirements for near-term implementation

*Coatings and deposition methods need improvement*

- Vacuum-based techniques: high cost and inconvenient
- Solution-based techniques: multiple steps, coating low crosslinking density, solvents pollution



atmospheric plasma

# Outline

- Coating Reliability and Lifetimes
  - coating characterization techniques for reliability
  - accelerated testing and lifetime prediction
- Protective and Transparent Coating Systems
  - controlling organosilicate molecular structure
  - bi-layers with optimized adhesion and hardness
  - strategies for incorporating UV protection
- Anti-Reflection Coating Systems
  - single and graded layer strategies
- Transparent and Conducting Films
  - applications for sensor and display technologies

# Coating Reliability and Evolution of Defects

damage propagates if mechanical stresses are large enough so that

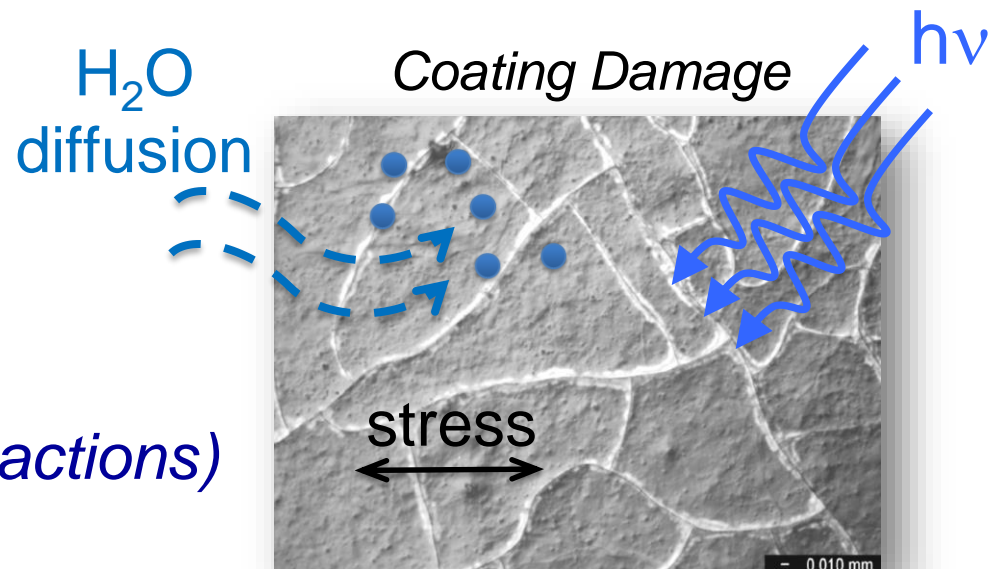
$$\text{mechanical "driving force"} \quad G \geq G_c \left[ J / m^2 \right] \quad \text{cohesion or adhesion}$$

presence of chemical species and photons, damage propagates even if

$$G < G_c \left[ J / m^2 \right] \quad \text{environment and stress accelerates defect evolution}$$

Role of coupled "stress" parameters in coating reliability and lifetimes:

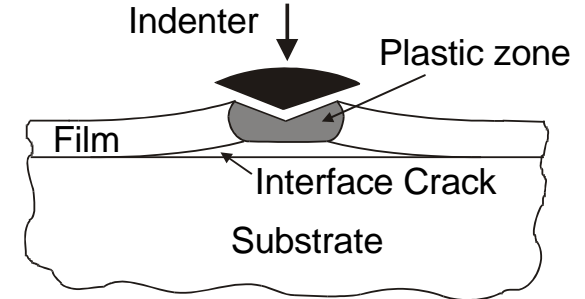
- *mechanical stress*
- *temperature*
- *environmental species*
- *photons (photochemical reactions)*



# Limitations of Thin-Film Adhesion Tests

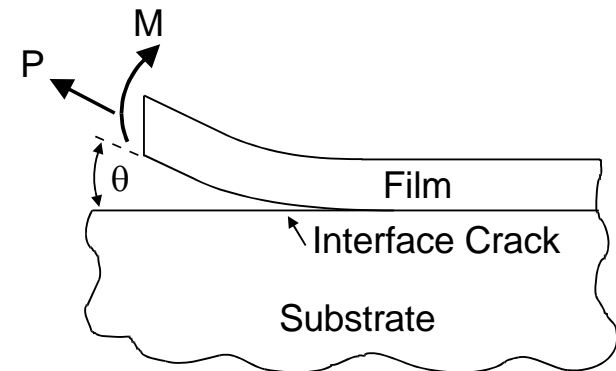
- Indentation/Scratch Test

- complex stress and deformation fields
- principally qualitative results
- (nano) scratch test even less quantitative



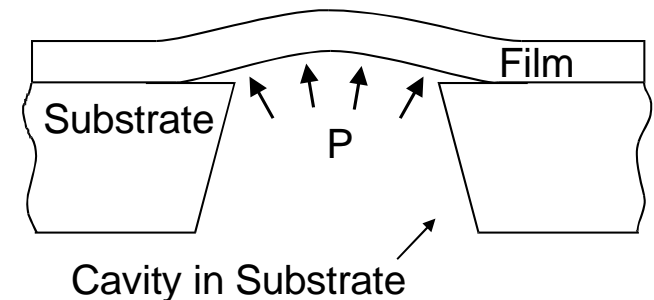
- Peel/m-ELT Test

- difficult to apply loads
- plastic deformation of film
- temperature complications in m-ELT



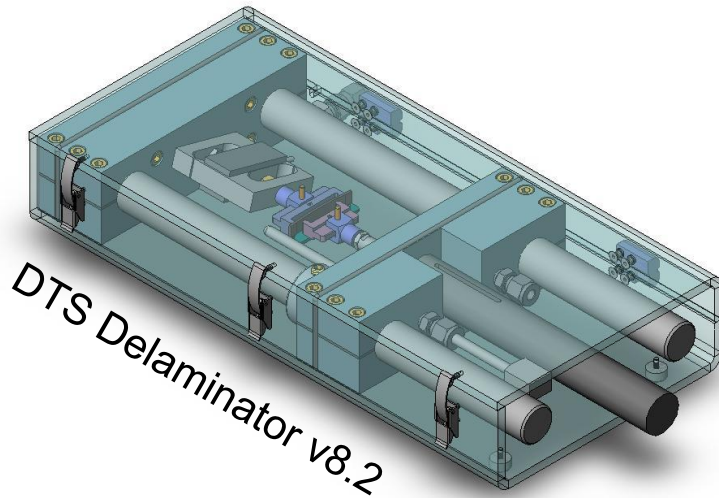
- Blister Test

- compliant loading system
- environmental effects
- etching/machining of cavity difficult

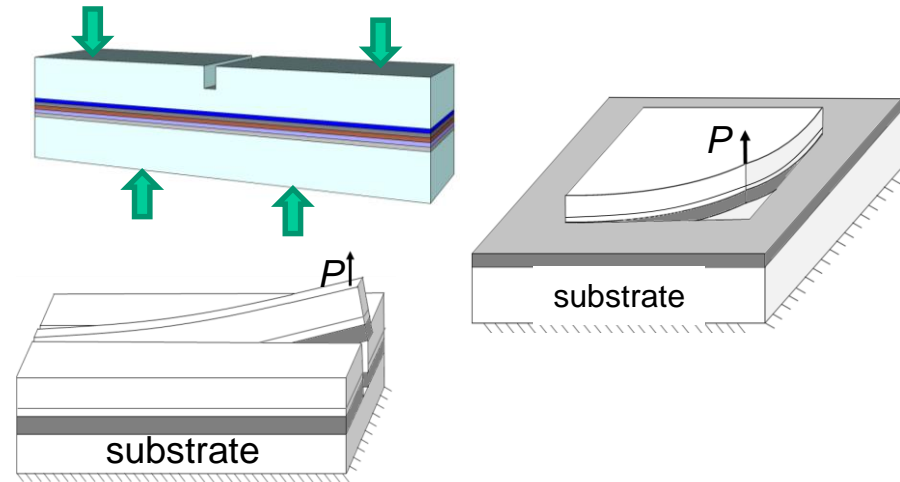


Major limitations: need detailed film properties, film stress relaxation and film plasticity  
⇒ principally qualitative results for all above methods!

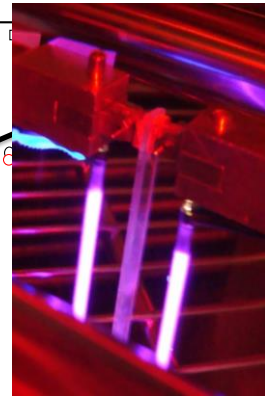
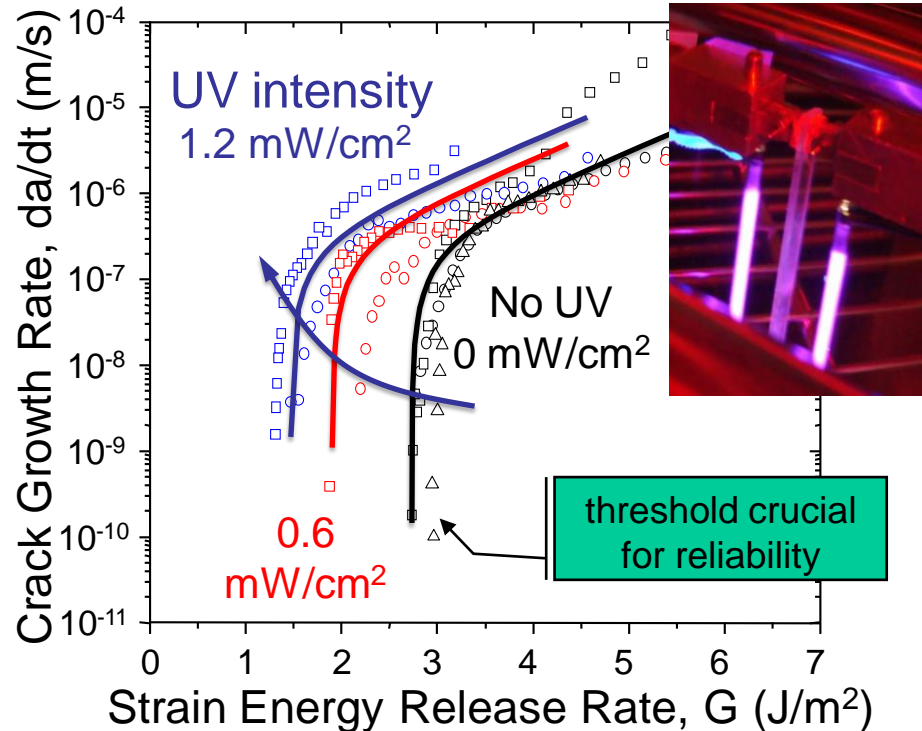
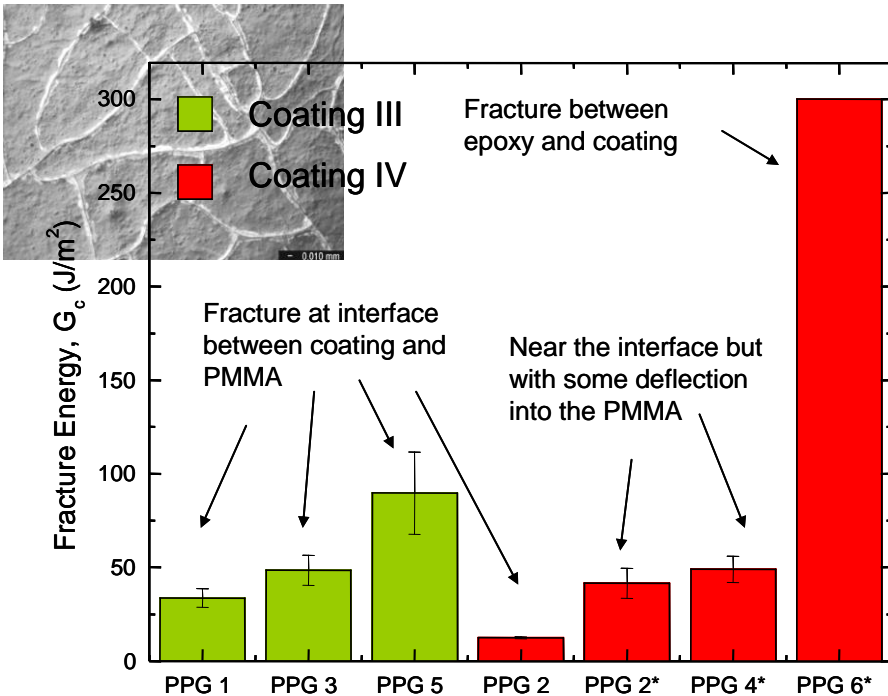
# Quantitative Adhesion/Cohesion and Debond Kinetics



Adhesion/Cohesion



Degradation Kinetics  
(temp/environment /UV effects)

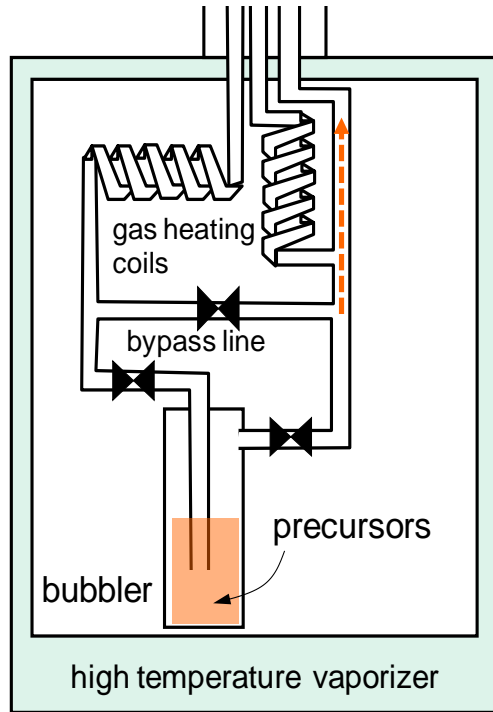


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# Atmospheric Plasma Deposition of Hybrid Films

## Innovation in Precursor Delivery



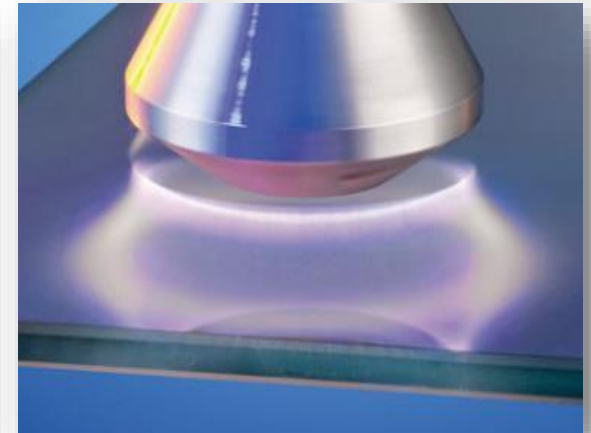
- higher molecular weight precursors
- higher boiling point
- larger range of material choices

## Capacitively Coupled Plasma

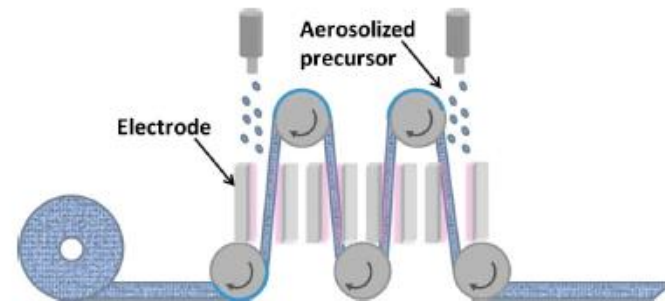
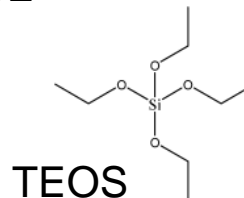
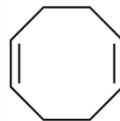
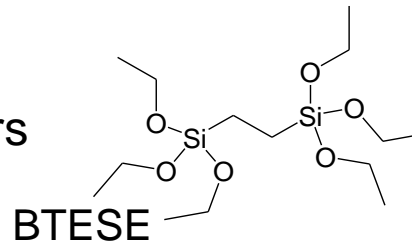


- *low temperature*
- *He and N<sub>2</sub> plasma gas*

## Dielectric Barrier Discharge Plasma



- *medium temperature*
- *N<sub>2</sub>, O<sub>2</sub>, air plasma gas*



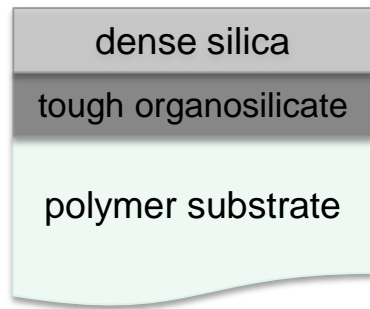




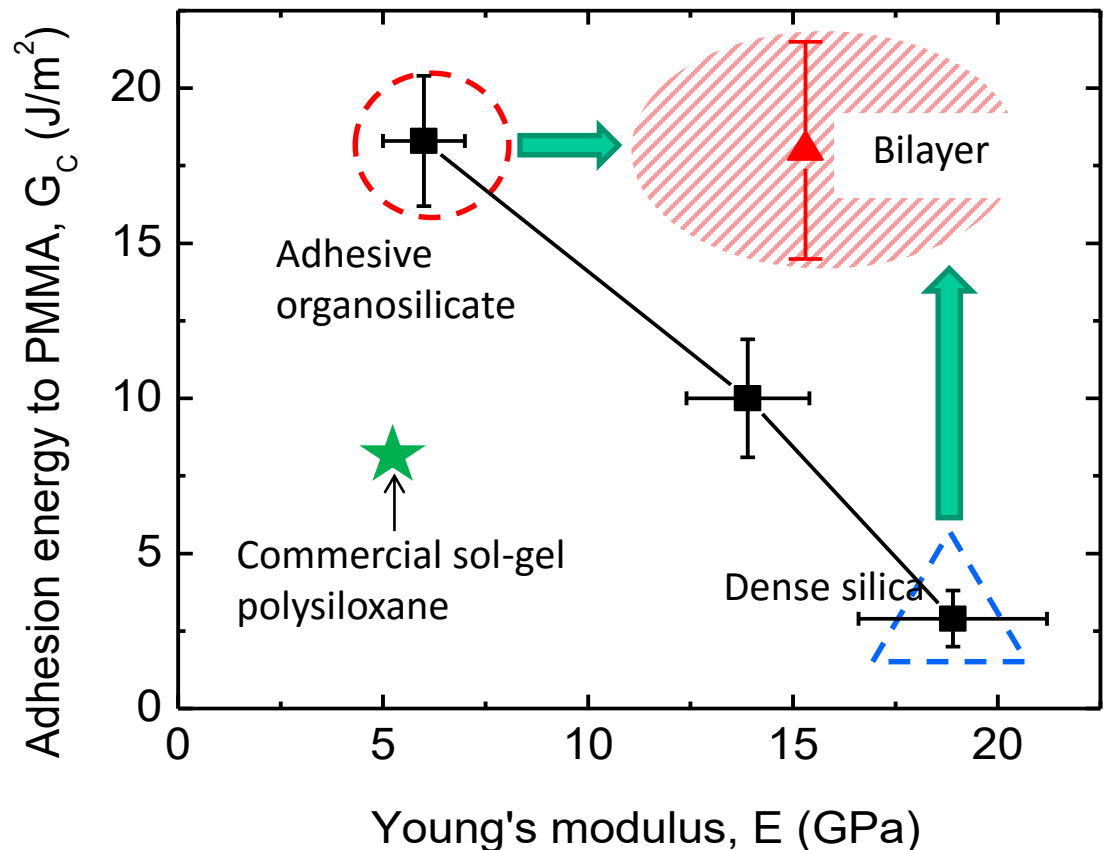
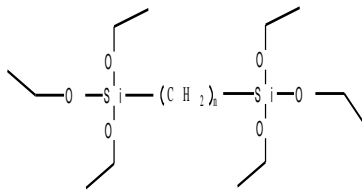
# Single Precursor Method - Hard and Adhesive Bilayer

Integrate layers deposited under different conditions

- carbon-bridged organosilicate bottom layer exhibits excellent adhesion to PMMA
- dense silica top layer exhibits high hardness and scratch resistance



Carbon  
bridged  
precursors



# Strategies for Highly Adhesive Multilayer Deposition

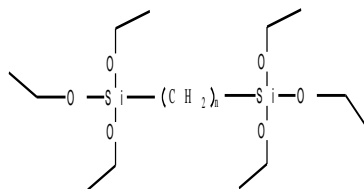
Integrate multi-layers layers deposited under different conditions

- high toughness carbon-bridged organosilicate bottom layer
- dense silica top layer with high hardness and scratch resistance
- ~100% visible transparency

Single precursor method

- graded or multi-layers

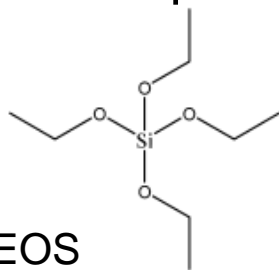
BTSE



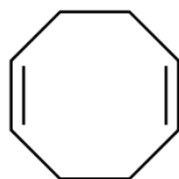
Multi-precursor method

- graded or multi-layers
- fast deposition

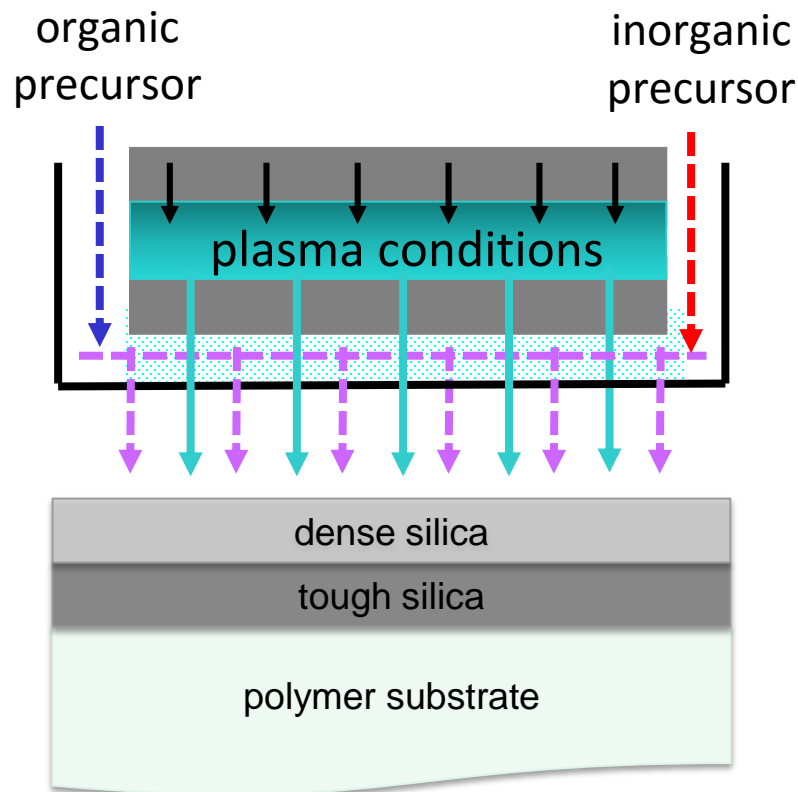
TEOS  
widely used, cheap



1,5-cyclooctadiene  
easy ring opening and  
network former



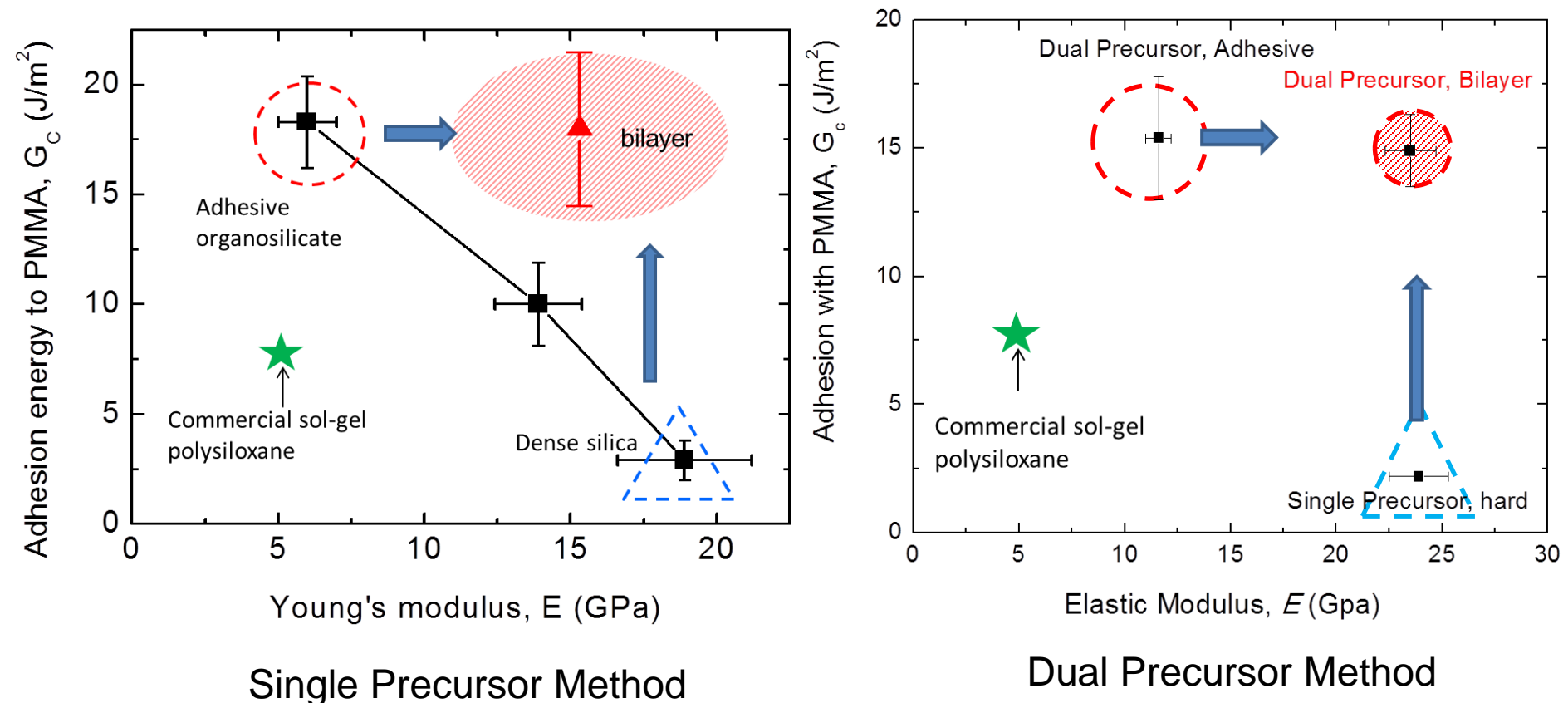
## Processing Parameters



# Strategies for Highly Adhesive Multilayer Deposition

Integrate bilayer deposition under single/dual precursors choice

- high adhesion organosilicate bottom layer and dense silica top layer
- ~100% visible transparency



Cui, Dauskardt, et. al., ACS Nano, 2014.

Dong, Zhao, Dauskardt, ACS Appl. Mater. Interfaces, 2015.

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# Atmospheric Plasma and Anti-Reflection Coatings (ARC)

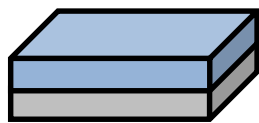
## Applications

- transportation windows
- sensor technologies
- ophthalmic lenses



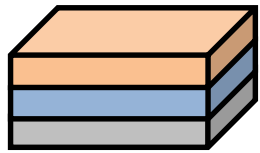
## Architecture

Single Layer



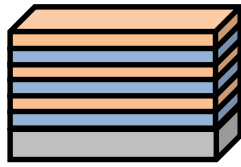
$$n_{slarc} = \sqrt{n_{sub} * n_{air}}$$

Double Layer

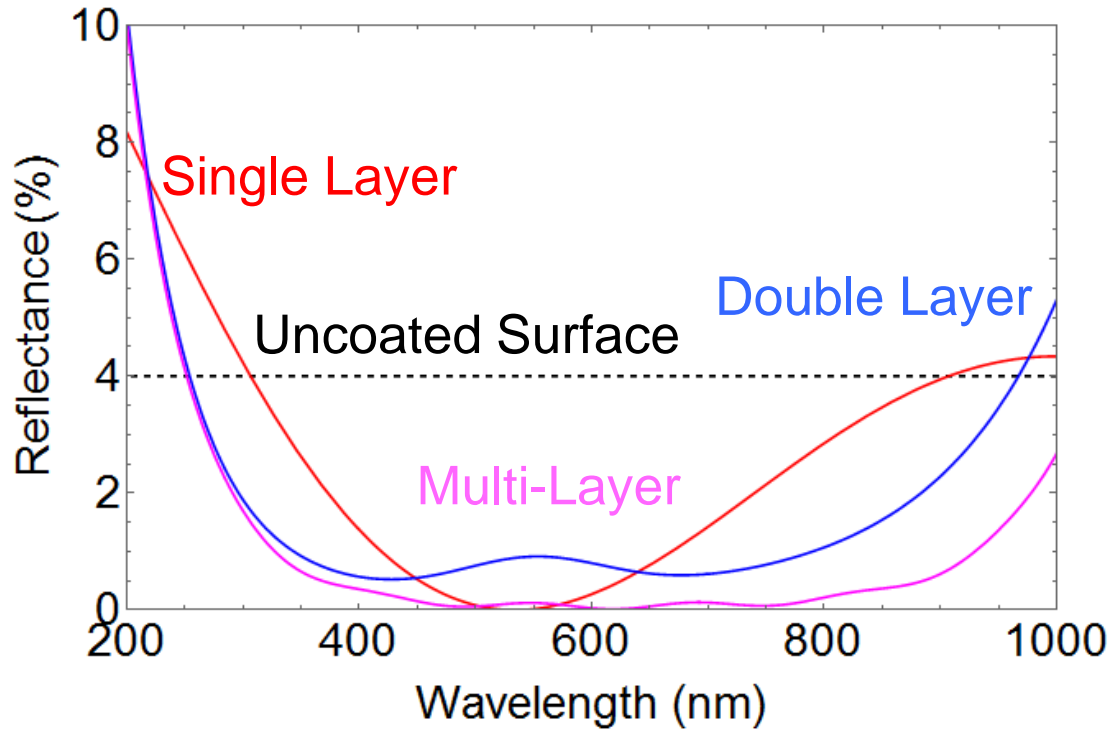


$$\frac{n_{air}}{n_{substrate}} = \frac{n_1^2}{n_2^2}$$

Multi-Layer

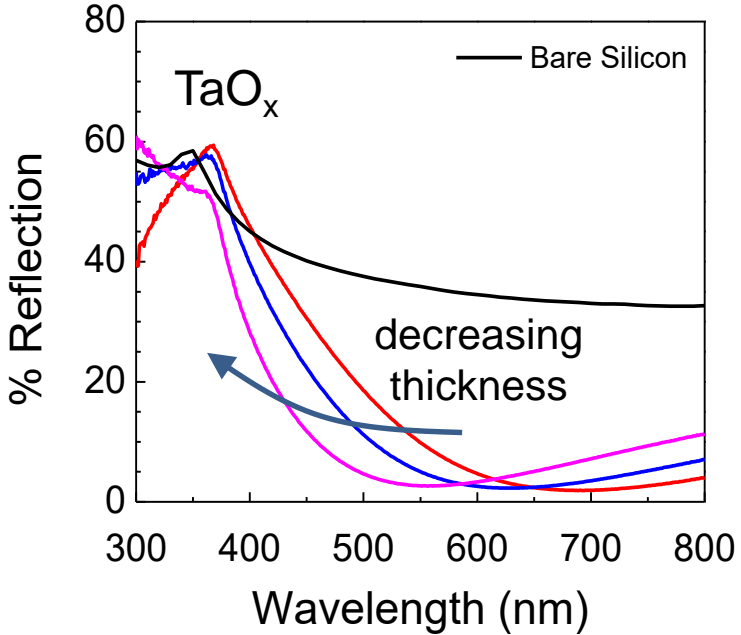
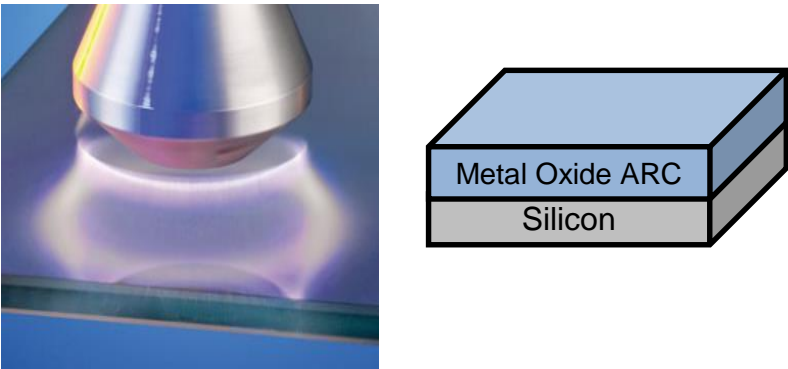


Alternate  $n_1, n_2$  from DLARC

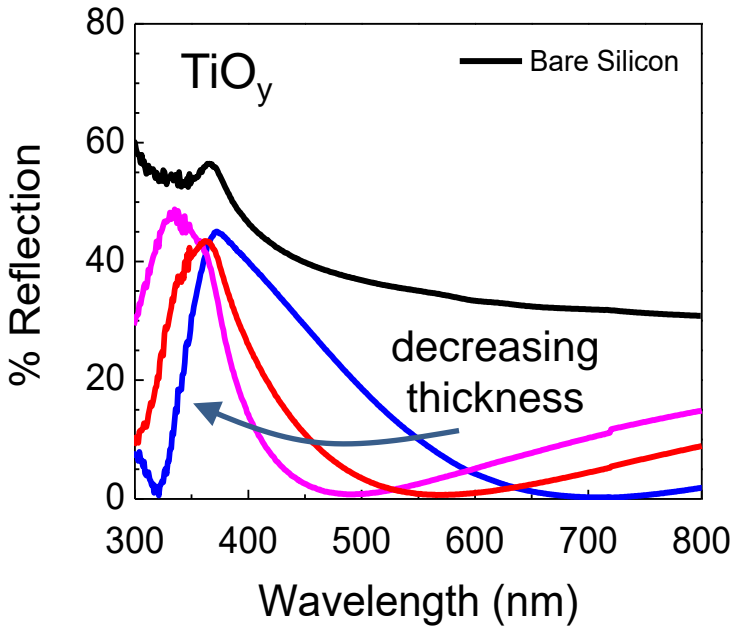


# Atmospheric Plasma and Anti-Reflection Coatings (ARC)

Single Layer ARC



Significant AR reduction in both systems



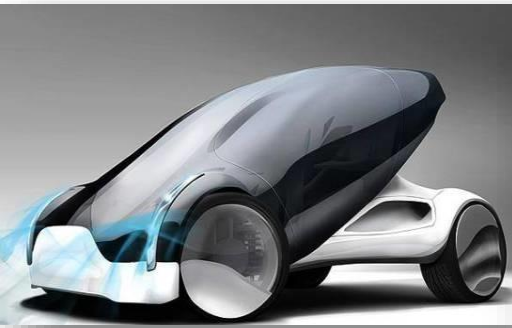
SLARC	Average Reflectance	Absolute Reflection Minimum
Silicon	42%	38%
TaO <sub>x</sub>	<7%	1.90%
TiO <sub>y</sub>	<5%	0.3%

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# Deposition of Transparent Conducting ZnO Thin Films



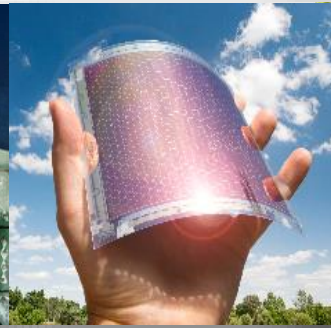
light-weight vehicle



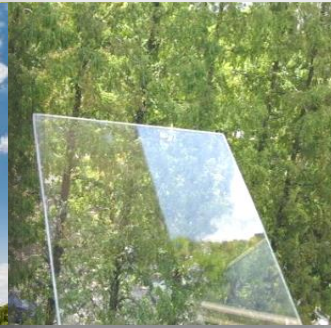
touch display



wearable



sensors and PV



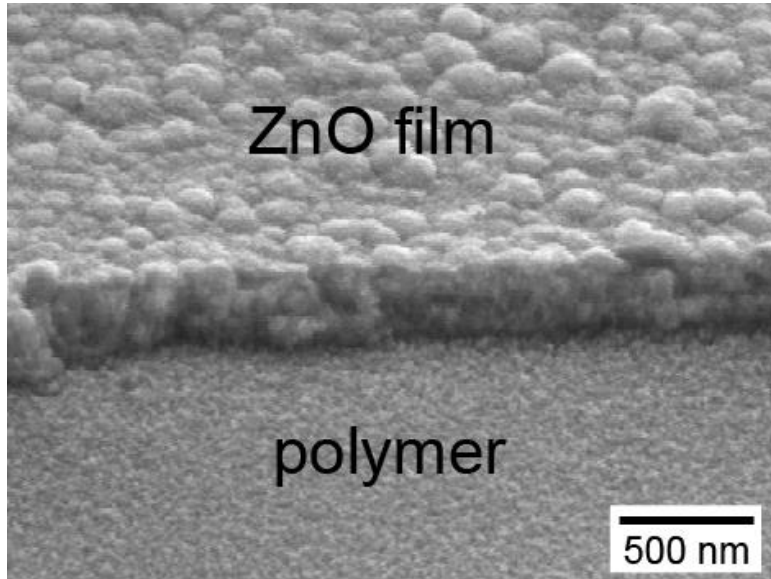
AR coatings

## Characteristic features of ZnO:

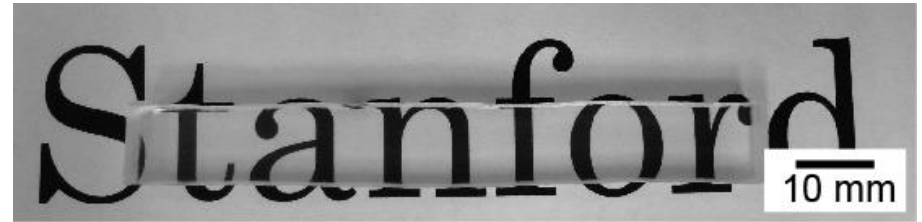
- wide bandgap semiconducting material
- high electric conductivity
- high visible transmittance
- abundant resource
- replacement for Indium Tin Oxide (ITO)

...atmospheric plasma deposition of ZnO films in ambient air at low temperature on plastics.

# Atmospheric Plasma Deposition of Transparent Conducting ZnO Thin Films



$T_v = 98\%$



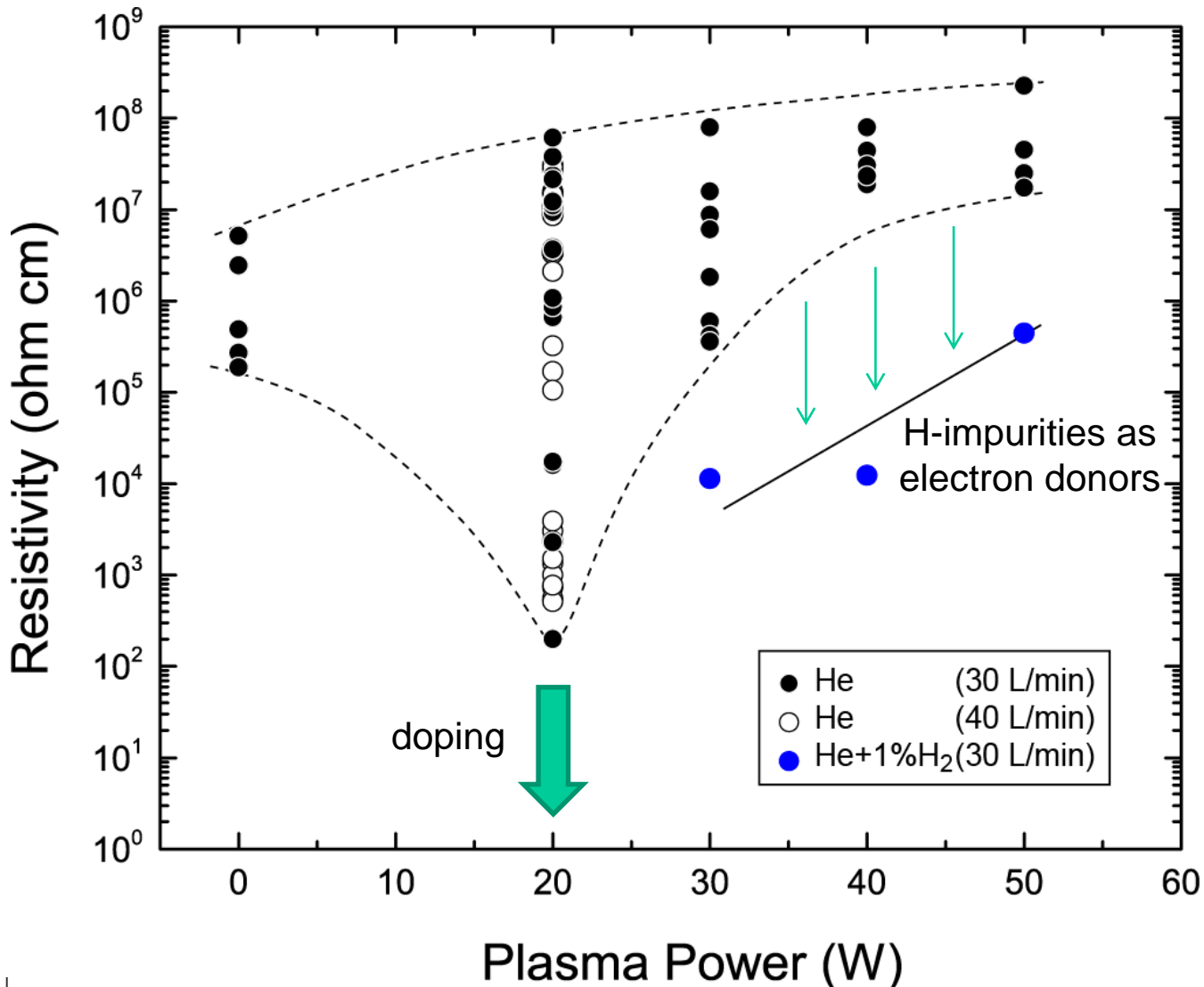
$T_v = 84\%$



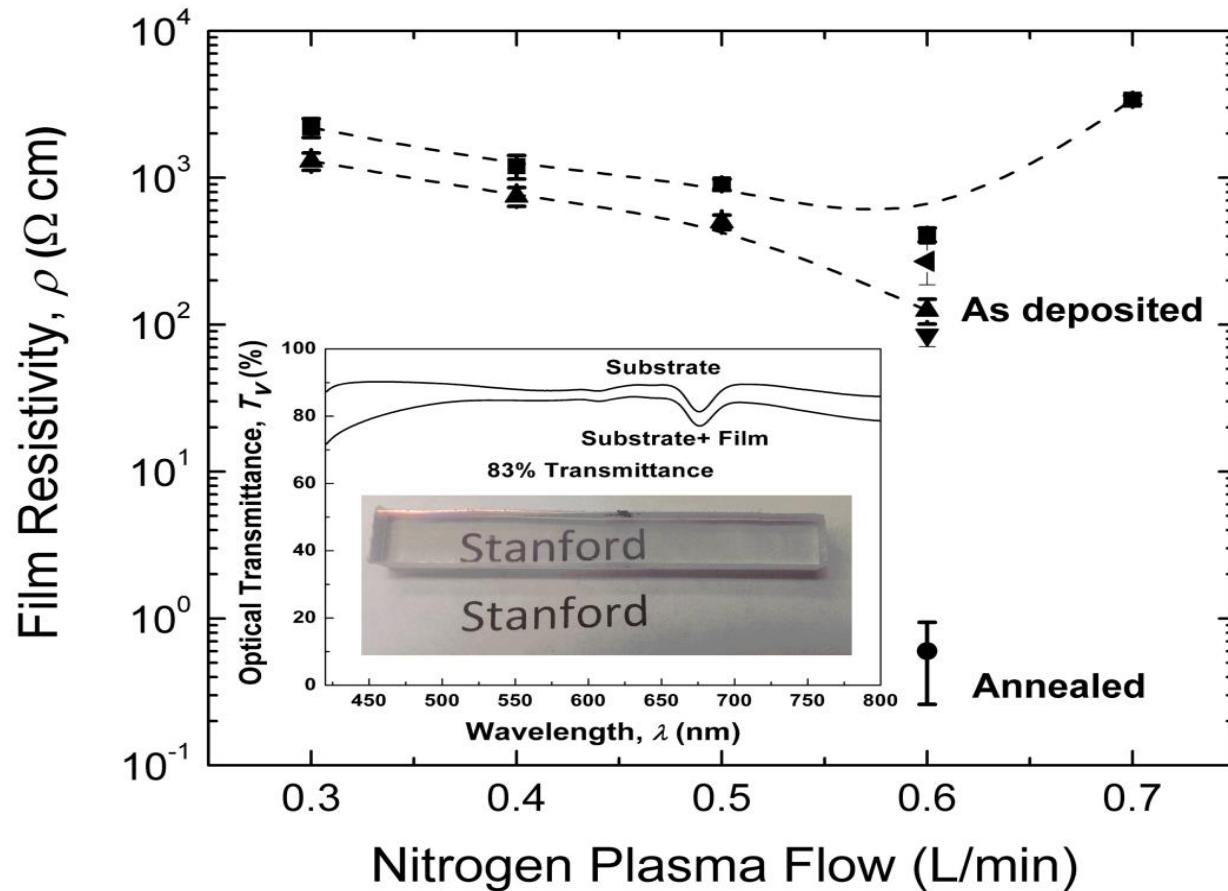
ZnO films with a transmittance above 98% successfully obtained in ambient air at 25 °C by atmospheric plasma deposition.

- Precursor: Diethylzinc ( $\text{Zn}(\text{C}_2\text{H}_5)_2$ )
- Substrate: PMMA, PET, PC

# Atmospheric Plasma Deposition of Transparent Conducting ZnO Thin Films



# Atmospheric Plasma Deposition of Transparent Conducting $\text{TiN}_x/\text{TiO}_2$ Hybrid Films



Visible transmittance  $\sim 80\%$  and resistivity as low as  $10^{-1}$  ohm cm successfully obtained in ambient air

Precursor: titanium ethoxide on PC substrate

# Summary

- Coating Reliability and Lifetimes
  - coating characterization techniques
  - accelerated testing and lifetime prediction
- Protective and Transparent Coating Systems
  - current polymeric glazings/windows do not meet durability/performance requirements
  - hybrid coatings with optimized adhesion and hardness
- Anti-Reflection Coating Systems
  - single and graded layer strategies
- Transparent and Conducting Films
  - sensor and display technologies

