Georgia Institute of Technology

*E*lectronics *M*anufacturing and *R*eliability *L*aboratory

Approaches to Barrier Coatings for the Prevention of Water Vapor Ingress

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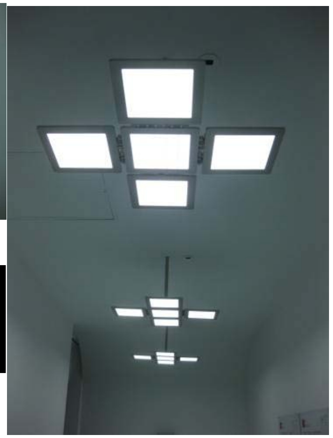
NSF MDITR

CIS:SEM
Center for Interface Science : Solar Electric Materials

COPE
Center for Organic Photonics and Electronics

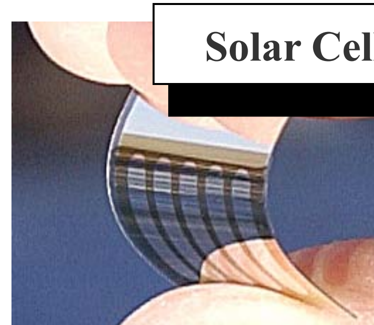
Motivation for Thin Film Barrier Development



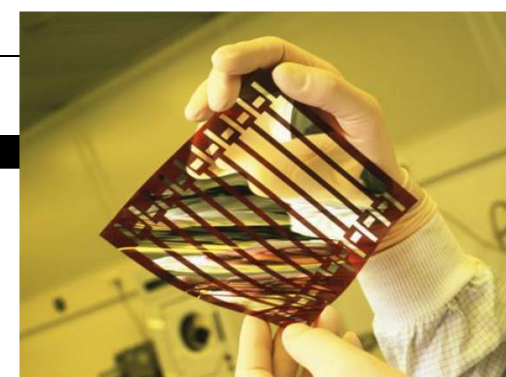
Solid State Lighting

Displays

Flexible Transistors



Solar Cells



Reliability issues: device encapsulation

Need for Barrier Layers

• Highly reactive electrodes and active layers are very sensitive to water vapor and oxygen.

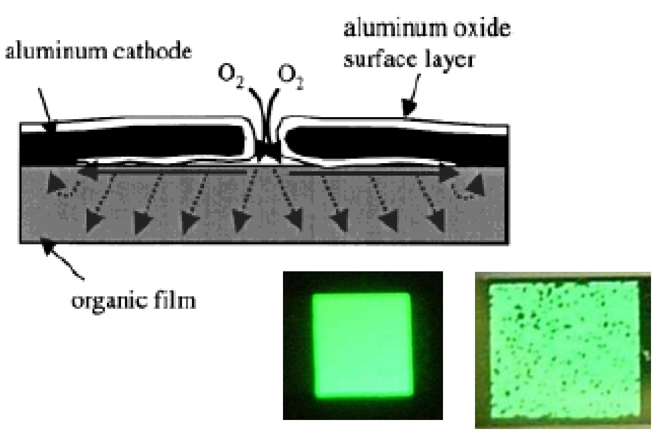
• Advancements in materials can reduce sensitivity, but not eliminate environmental degradation.

Must address:

⇒**Development of high barrier performance films.**

⇒**Process compatibility with device.**

⇒**Extending technology to large areas and devices with topography.**



Mechanical Concerns

• Inorganic layers found in encapsulation are generally very brittle and may crack during bending.

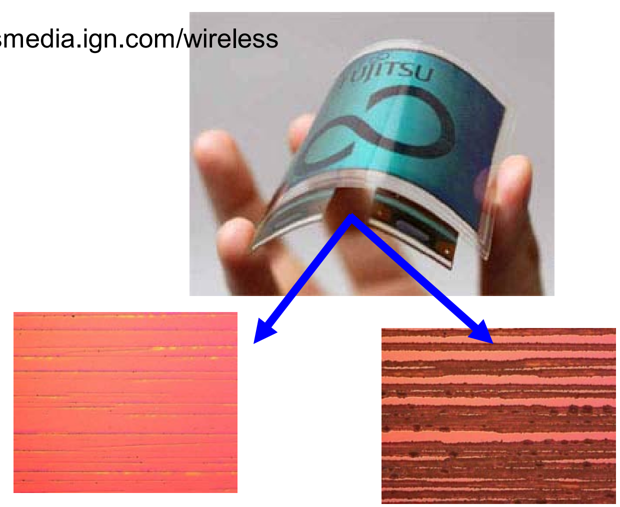
• Internal stresses from processing can impact the reliability of the encapsulation.

Must address:

⇒ **Mechanically robust barrier layers.**

⇒**Adhesion and stress management.**

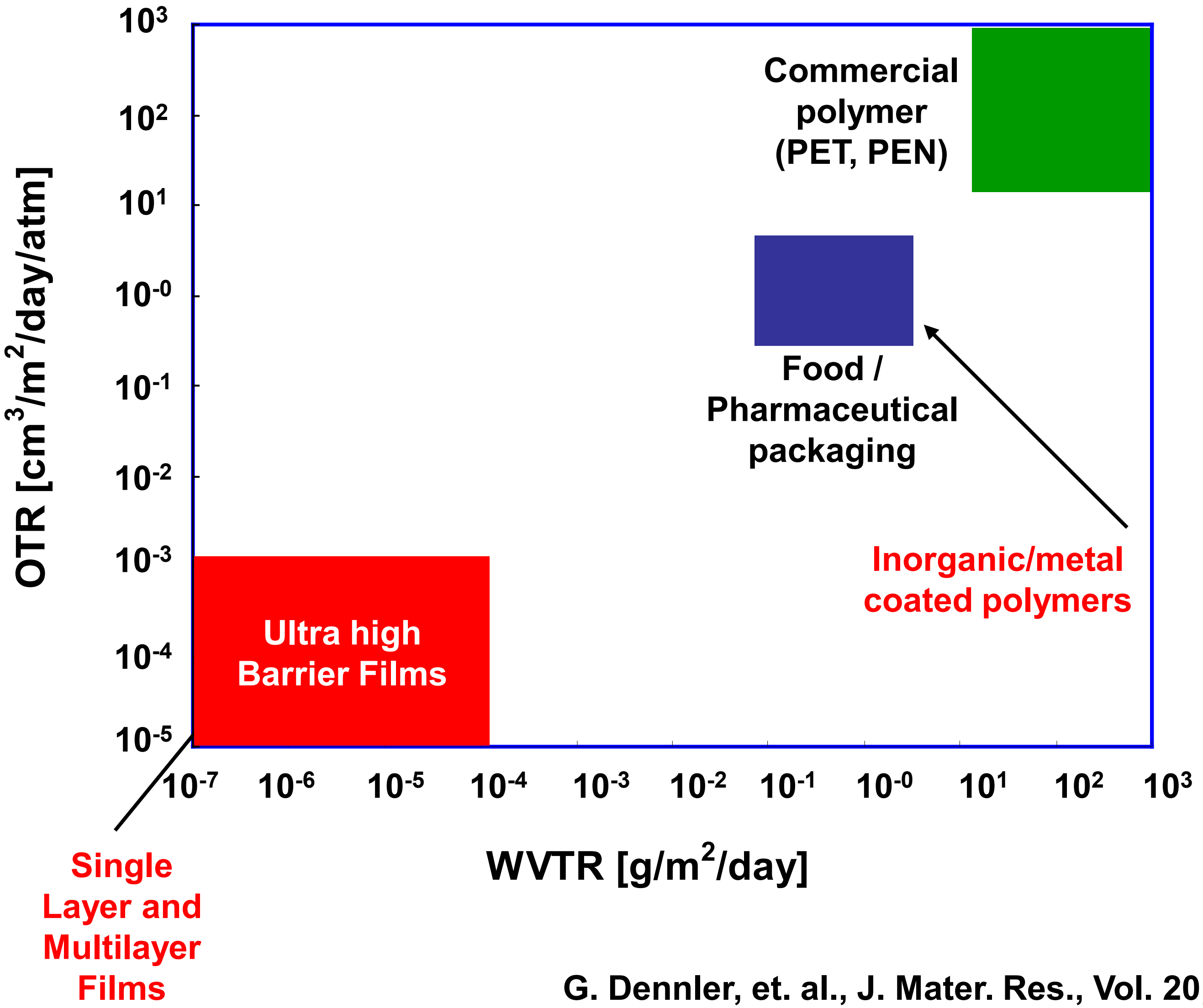
http://wirelessmedia.ign.com/wireless/image/article



1 min

1 hr

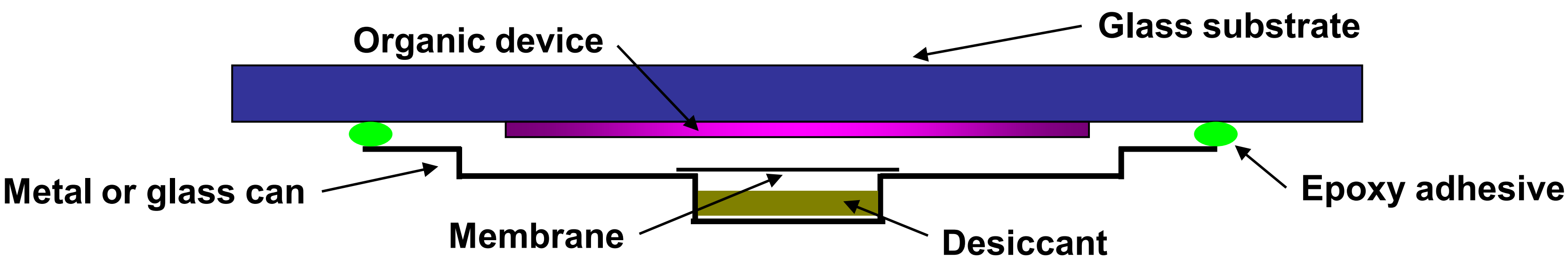
Encapsulation Performance Needs

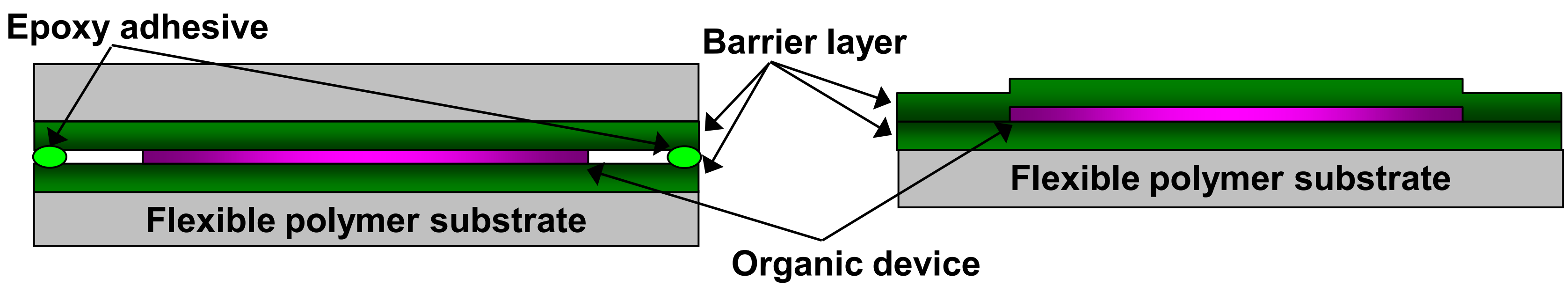


G. Dennler, et. al., J. Mater. Res., Vol. 20, No. 12, Dec 2005. Vol.20, 3224

Encapsulation Structures

heavy, thick, rigid,
side permeation through epoxy





+ : flexible, light

- : need to fabricate barrier layer on both substrates, side permeation

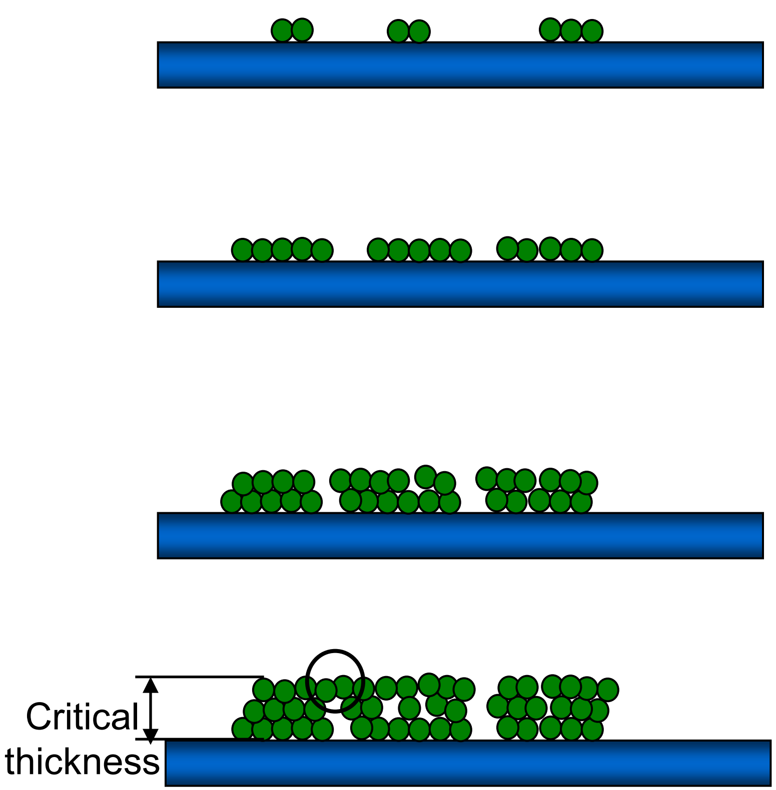
+ : thin, very flexible, light, no side permeation

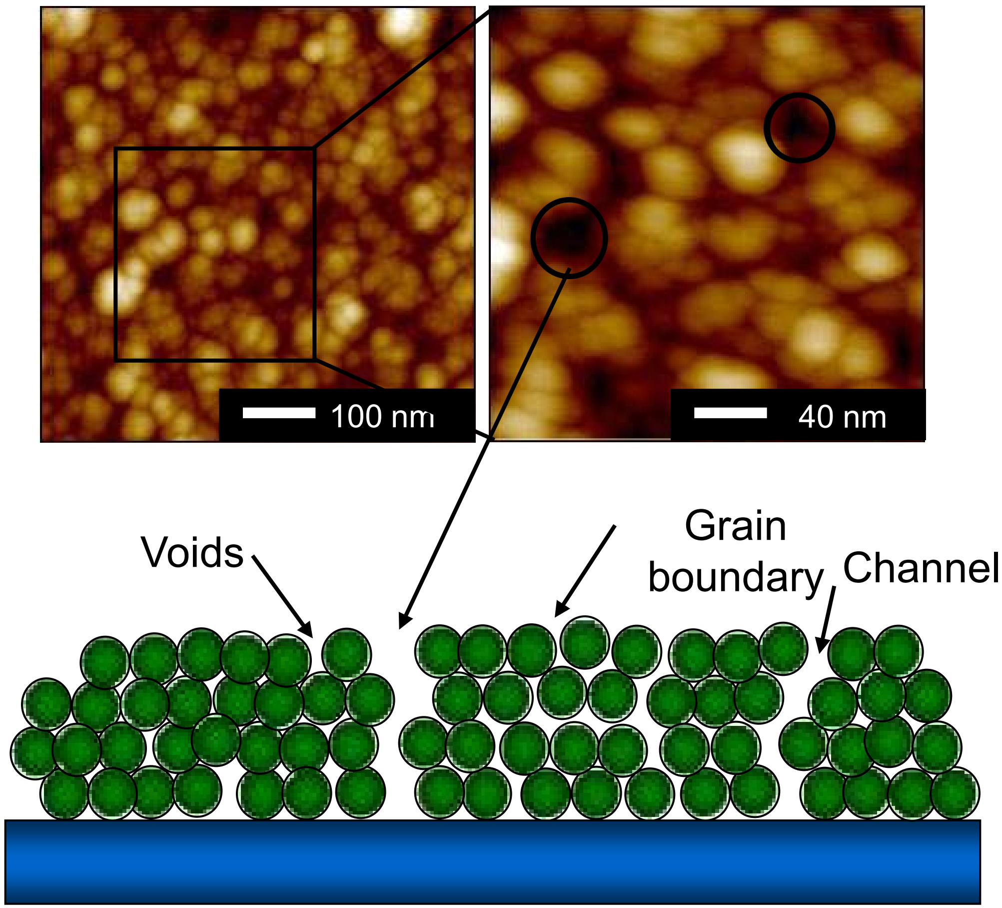
- : need to fabricate barrier layer

J. S. Lewis, et. al., *IEEE Journal of Selected Topics in Quantum Electronics* 2004, *10*, 45-57

Defects in Barrier Films

Single Layer Thin Films



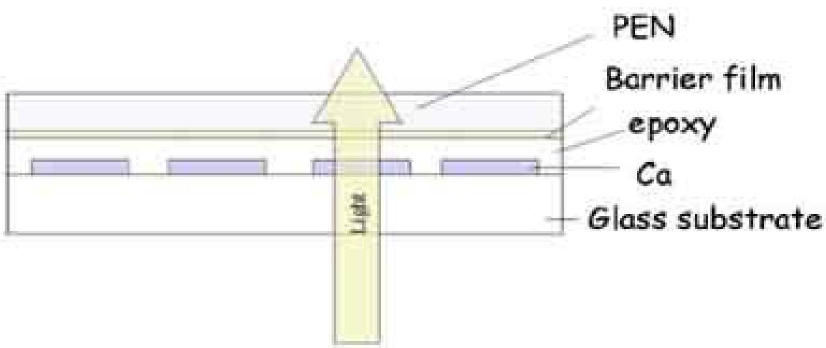


Thin Film Encapsulation Methods

High Quality Single Layer Encapsulation: Al_2O_3

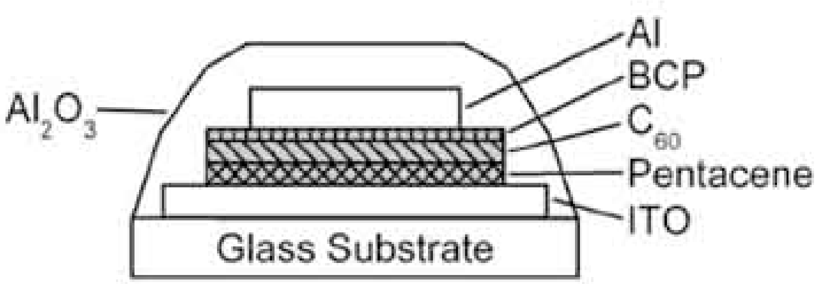
High density, pinhole free, conformal deposition

Permeation governed by nanoscale defects vs macrodefects.

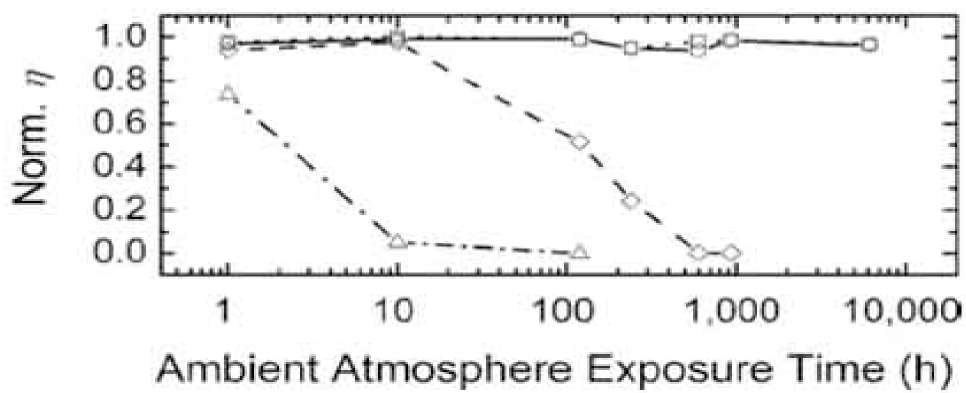


Structure	PEN/ Al_2O_3
Deposition	ALD
WVTR [g/m^2/day]	$1.7x10^{-5}$
Test condition	38°C and 85% R.H.

P. F. Carcia, R. S. McLean, M. H. Reilly, M. D. Groner, S. M. George, *Applied Physics Letters* **2006**, *89*, 031915.



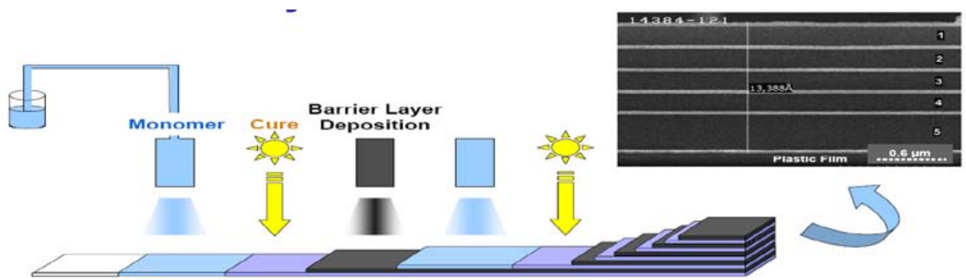
200 nm Al_2O_3 by ALD



W. J. Potscavage, S. Yoo, B. Domercq, B. Kippelen, *Applied Physics Letters* **2007**, *90*, 253511

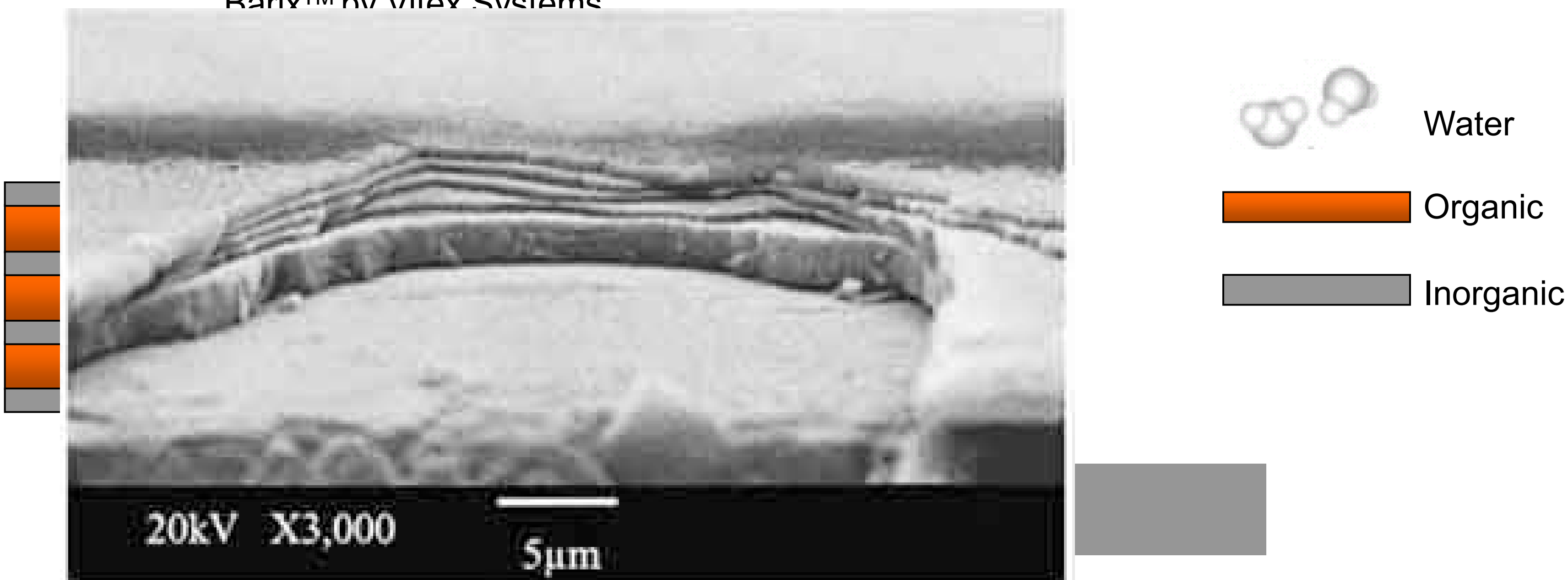
Thin Film Encapsulation Methods

Multilayer Encapsulation



Barix^{TM} by Vitex Systems

Structure	Al_2O_3/ Polyacrylate
Deposition	DC Sputtering, Evaporation/ UV curing
WVTR [$g/m^2/day$]	Maximum: $2.1x10^{-6}$
Test condition	20°C, 50% R.H.

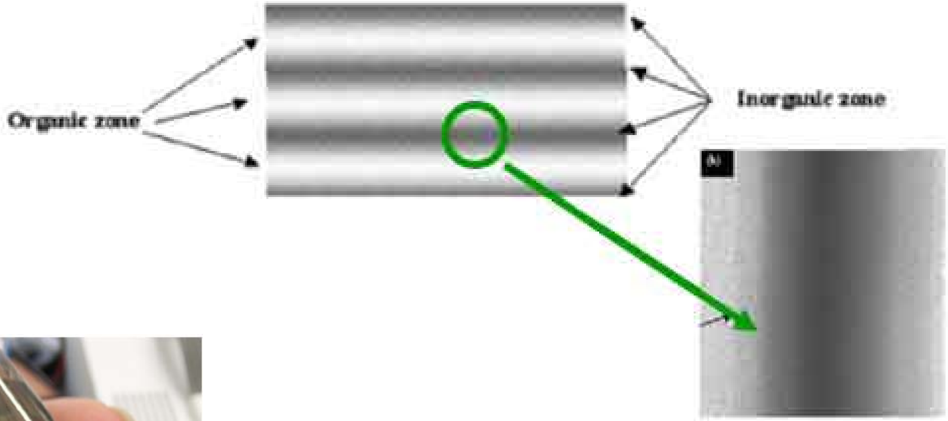


M. S. Weaver, L. A. Michalski, K. Rajan, M. A. Rothman, J. A. Silvernail, J. J. Brown, P. E. Burrows, G. L. Graff, M. E. Gross, P. M. Martin, M. Hall, E. Mast, C. Bonham, W. Bennett, M. Zumhoff, *Applied Physics Letters* **2002**, *81*, 2929.

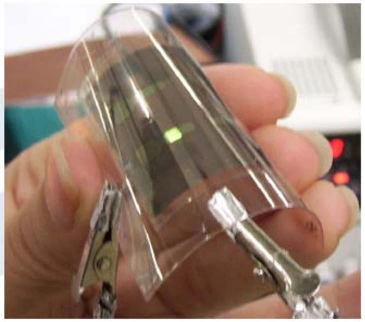
G. Nisato, *Prod. Soc. Info. Display Symp., Digest Tech, Papers* **2003**, *34*, 550.

Thin Film Encapsulation Methods

Graded organic and inorganic layer (GE, Shaepkens, et al., JVST 2004)

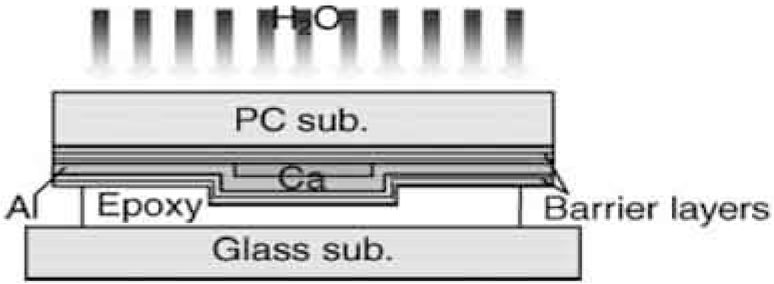


Structure	SiOxNy/ SiOxCy
Deposition	PECVD
WVTR [g/m²/day]	$5x10^{-5}$ ~ $5x10^{-6}$
Test condition	23°C, 50% R.H. for 20 days



IMRE, Singapore

Multi layer Plus Bonding (Chen, et al., Plasma Process and Polymers 2007)



Structure	3 pairs SiOx/SiNx/ + Parylene + 3 pairs SiOx/ SiNx
Deposition	PECVD, PVD
WVTR [g/m²/day]	Maximum: $2.5x10^{-7}$
Test condition	23°C and 40% R.H. for 75 day

Processing of Barrier Films

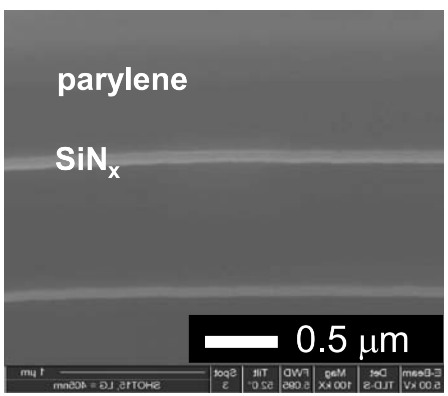
Materials Used

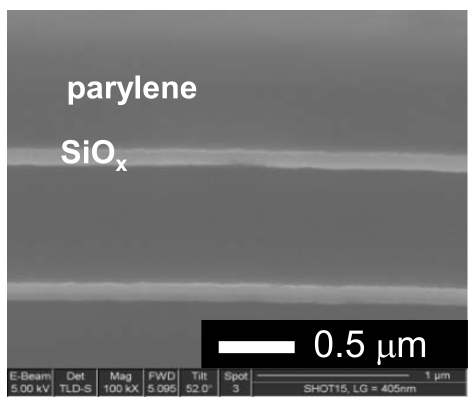
PECVD: SiOx, SiNx

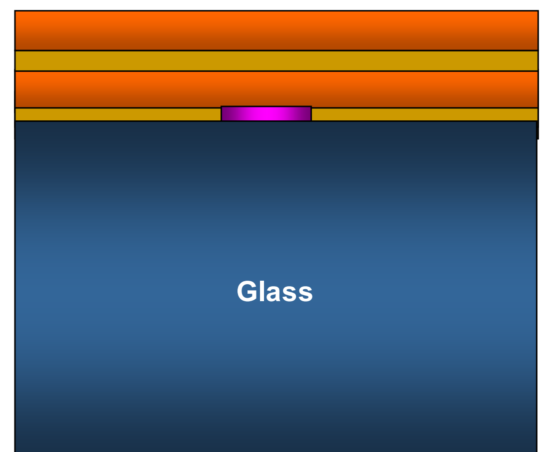
PVD: Parylene

ALD: Al_2O_3

Environmental Chamber

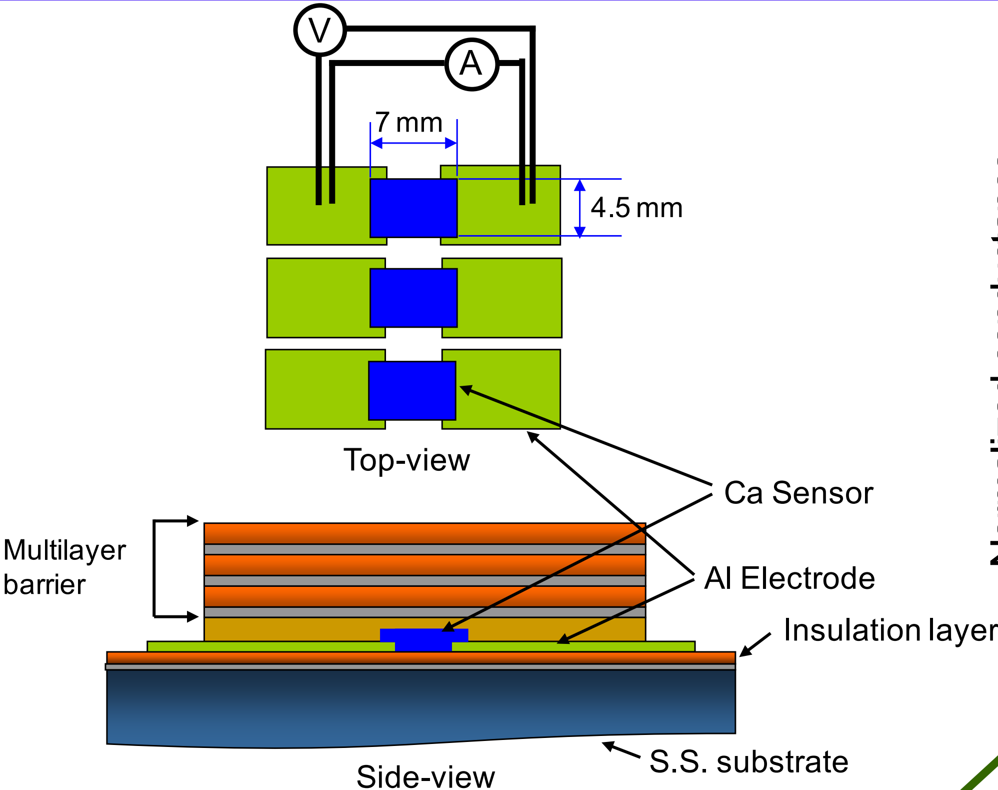


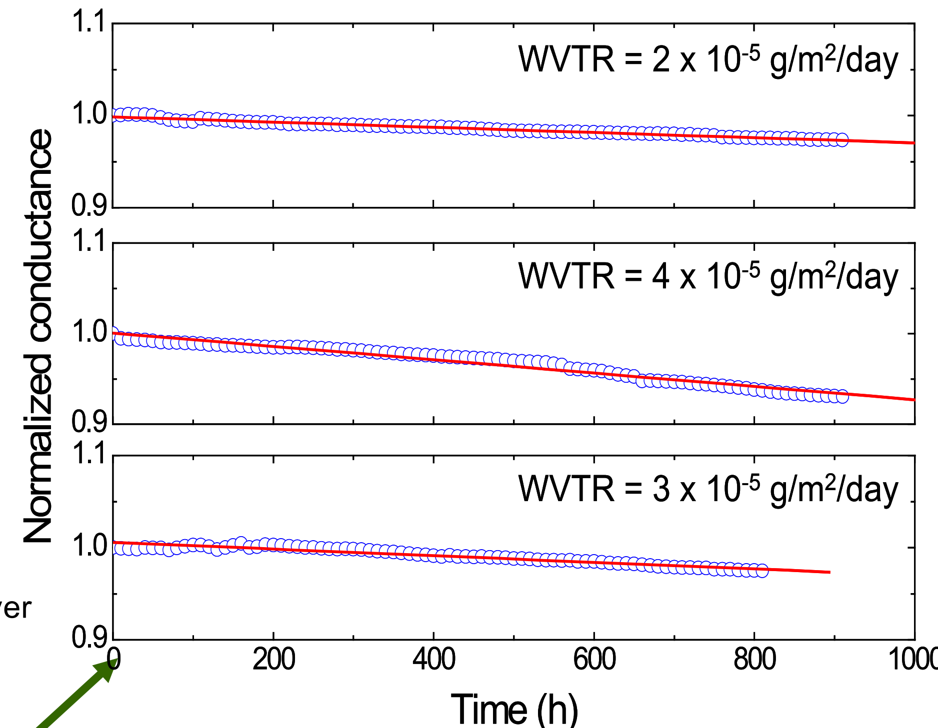




Measured by Ca Corrosion Method at 50 % R.H. and 20 °C

Ca Corrosion Tests





$$WVTR[g/m^2/day] = 2\delta_{Ca} \times \rho_{Ca} \times \frac{dG_S}{dt} \times \frac{M(H_2O)}{M(Ca)} \times \frac{Ca\_Area}{Window\_Area}$$

ρ_{Ca} 1.55 g/cm^3

δ_{Ca} 3.4*10^{-6} cm Ω

$G_s = 1/R_s = (W/L)*(1/R)$

L : Length of Ca

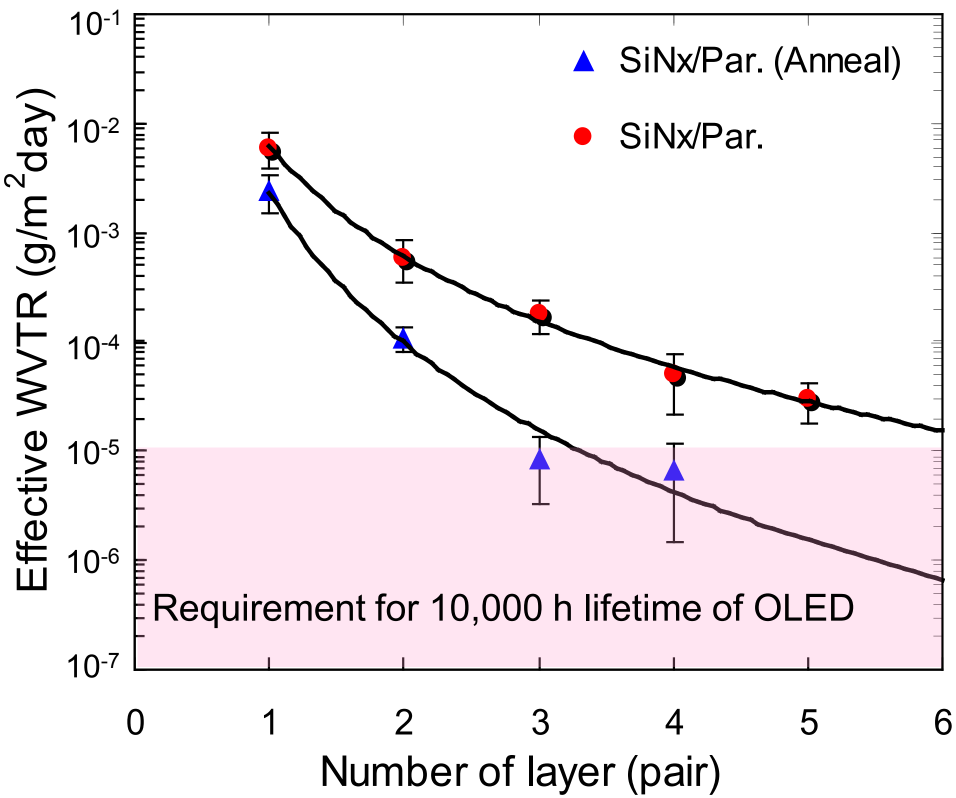
W : Width of Ca

$M(H_2O)$ 18 amu

M(Ca) 40.1 amu

R. Paetzold, et. Al., Rev. of Sci. Inst., 2003, 74, 5147

Multilayer Results



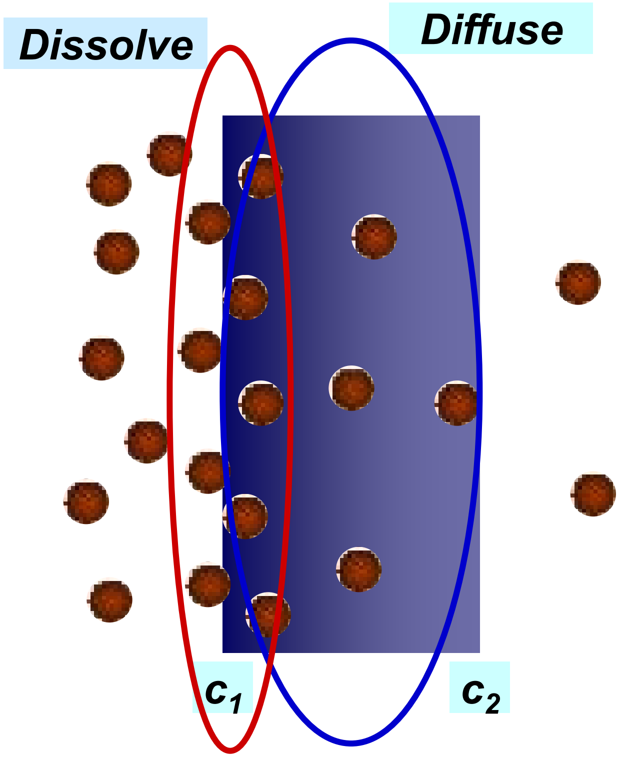
No. of Layers [pairs]	WVTR [g/m²/day] Before annealing	WVTR [g/m²/day] After annealing	Decrease in WVTR [%]
1	4.3×10^{-3}	2.4×10^{-3}	**44**
2	4.4×10^{-4}	1.3×10^{-4}	**70**
3	1.3×10^{-4}	7.3×10^{-6}	**94**
4	4.4×10^{-5}	6.6×10^{-6}	**85**

SiOx/ Parylene (3 pairs)

8.4×10^{-4} ► 6.6×10^{-5} (g/m²/day), (85 %↓)

Mass Transport in Barrier Films

Principles of permeation



$$P = DS$$

P : Permeation coefficient (permeability)

D : Diffusion coefficient, determines how **fast** the permeant can **move** in the media

S : Solubility coefficient, determines how **much** of the permeant can **be dissolved in in the film**

Driving force

$$J = -D(\frac{\partial c}{\partial x})$$ *Fick's first Law*

$$\rightarrow c = Sp$$ *Henry's Law*

$$J = DS\frac{\Delta p}{l}$$

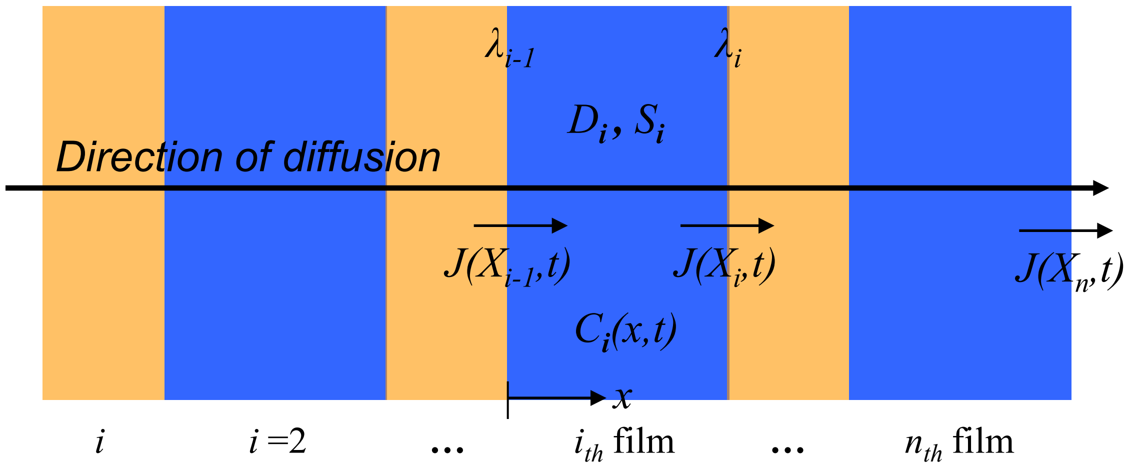
J : Flux of permeant

$\partial c / \partial x$: concentration gradient

p : Partial pressure of permeant

Mass Transport in Barrier Films

Diffusion in multilayer structure



D_i (diffusivity),
S_i (Solubility),
L_i (thickness)-fixed
Defect spacing

WVTR, Lag time

WVTR calculation

$$WVTR \Leftrightarrow \frac{P_{total}\cdot \Delta p}{L_{total}}$$

Δp : pressure drop
L_{total} : thickness

For inorganic layers, use effective permeability

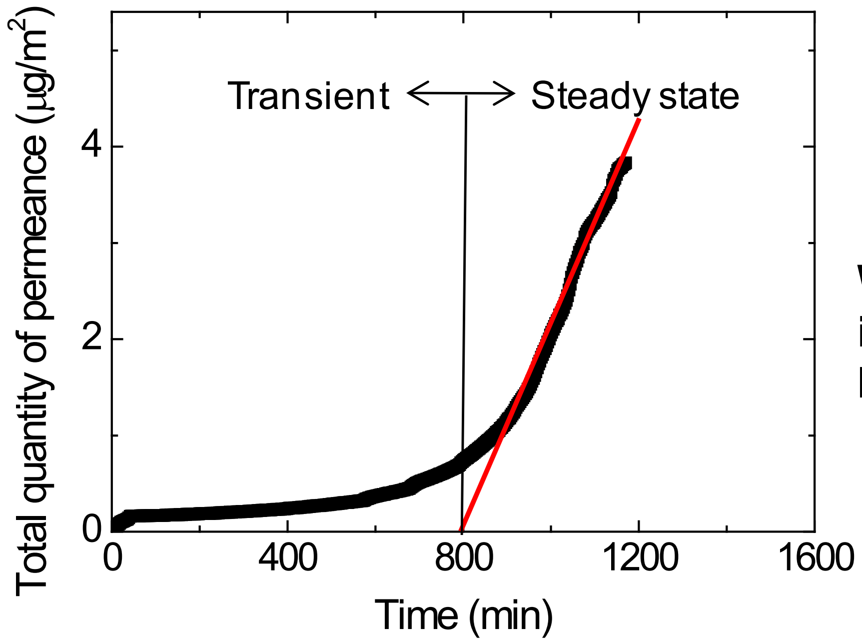
$$\frac{L_{total}}{P_{total}} = \frac{1}{\frac{L_1}{P_1}+\frac{L_2}{P_2}+\frac{L_3}{P_3}+\ \cdots\ +\frac{L_n}{P_n}}$$

Lag time calculation

$$L = \left(\sum_{i=1}^{n}\frac{L_i}{D_i}\prod_{j=1}^{i-1}k_j\right)^{-1}\sum_{i=1}^{n}\left\{\frac{L_i^2}{2D_i}\sum_{i=1}^{n}\left[\frac{L_m^2}{D_m}\prod_{j=1}^{i-1}k_j\right]-\frac{L_i^3}{3D_i^2}\prod_{j=1}^{i-1}k_j\right\}+\sum_{i=1}^{n}\left\{\frac{L_I}{D_I}\prod_{j=1}^{i-1}k_j\sum_{\beta=i+1}^{n}\left[\frac{L_\beta}{\prod_{j=1}^{\beta-1}k_j}\sum_{m=\beta}^{n}\left(\frac{L_m}{D_m}\prod_{j=1}^{m-1}k_j\right)-\frac{L_\beta^2}{2D_\beta}\right]\right\}$$

$$\text{where, } k_j = \frac{k_j}{k_{j+1}}$$

Mass Transport in Barrier Films



We have seen lag times greater than 1000 hours in our films.
Impacts the WVTR measured.

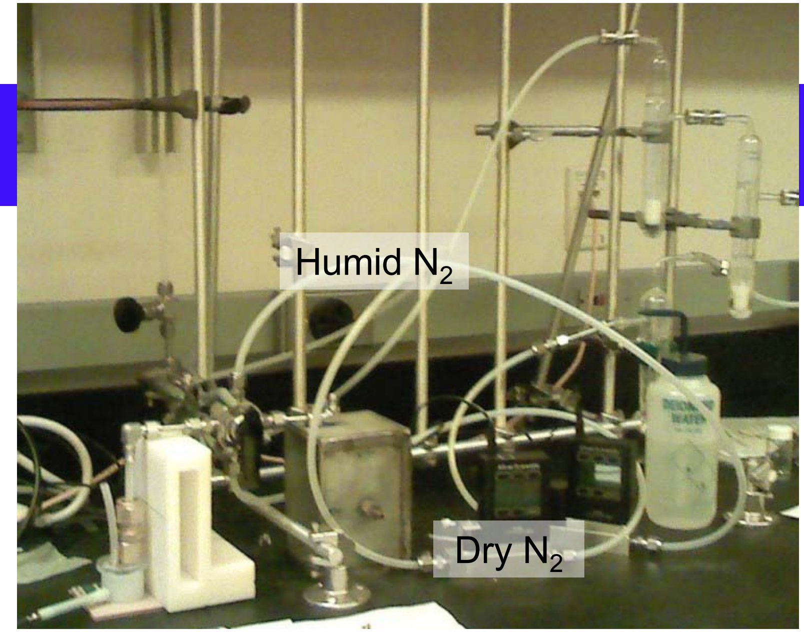
Lag Time: 1300 hours

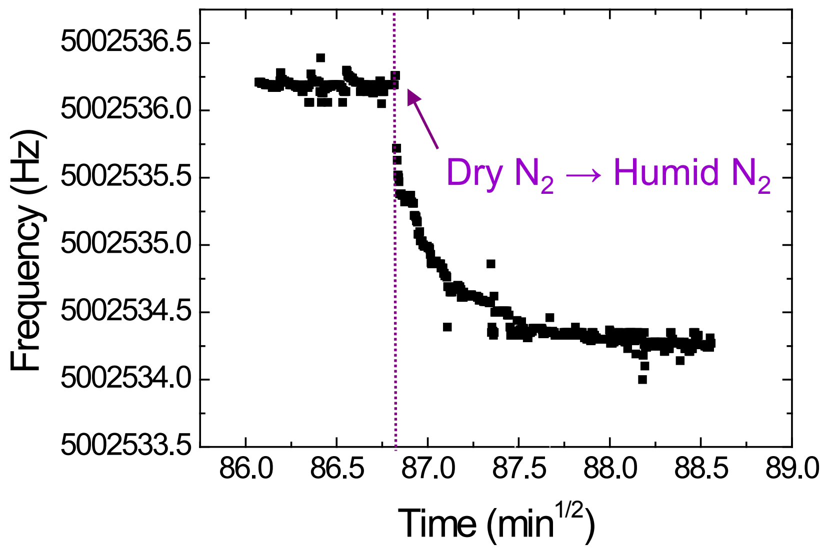
Transient WVTR: $8x10^{-6}$ g/m²/day

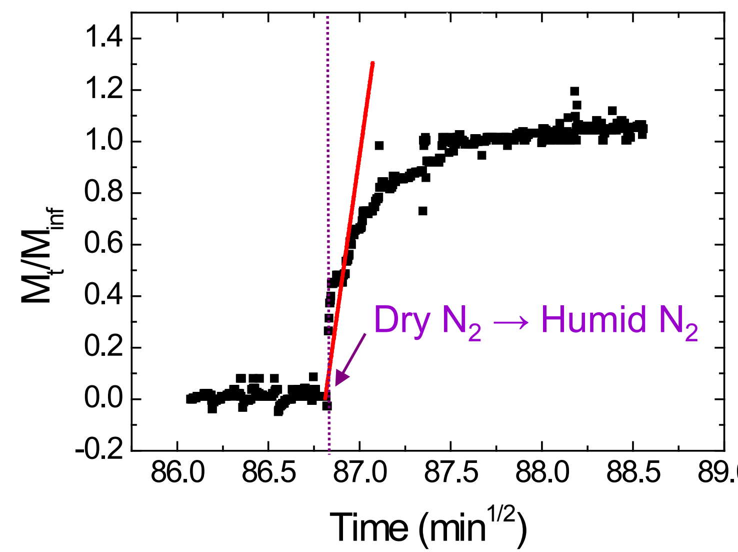
Steady State: 2 x 10^{-3} g/m²/day

(Data not obtained from graph on left)

QCM







$$\frac{M_t}{M_\infty} = \frac{2}{L}\left(\frac{Dt}{\pi}\right)^{1/2}$$

M : Mass uptake

D : Diffusion coefficient

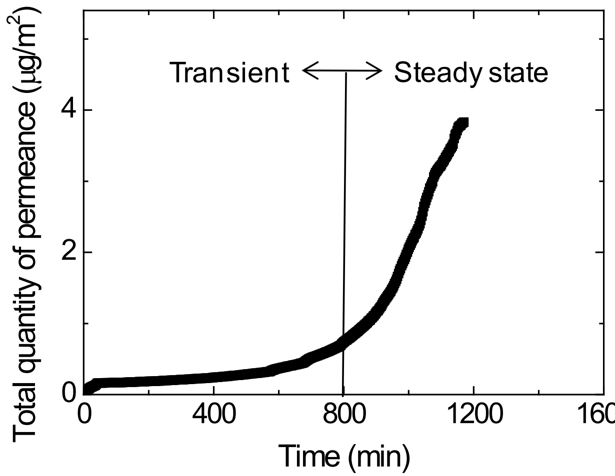
L: Thickness of film

Solution to Fick's 2nd law for short times (Valid only $M_t/M_\infty < 0.6$)

Diffusion Coefficient and Solubility

Diffusion Coefficient (cm²/s)

Test #	Before Anneal	After Anneal for 10 min
Average	3.27×10^{-9}	2.06×10^{-9}
STDV	4.29×10^{-9}	1.01×10^{-10}



Solubility coefficient measurement

$$S = \frac{M_\infty}{M_0}\frac{\rho_{polymer}}{MW_{penetrant}} \times \frac{22,414}{p}$$

M_∞ : Equilibrium mass uptake
M_0 : Mass of the water –free polymer
$MW_{penetrant}$ molecular weight (g/mole)
p : Vapor pressure [atm]
22,241 : Conversion from moles to cm³(STP)

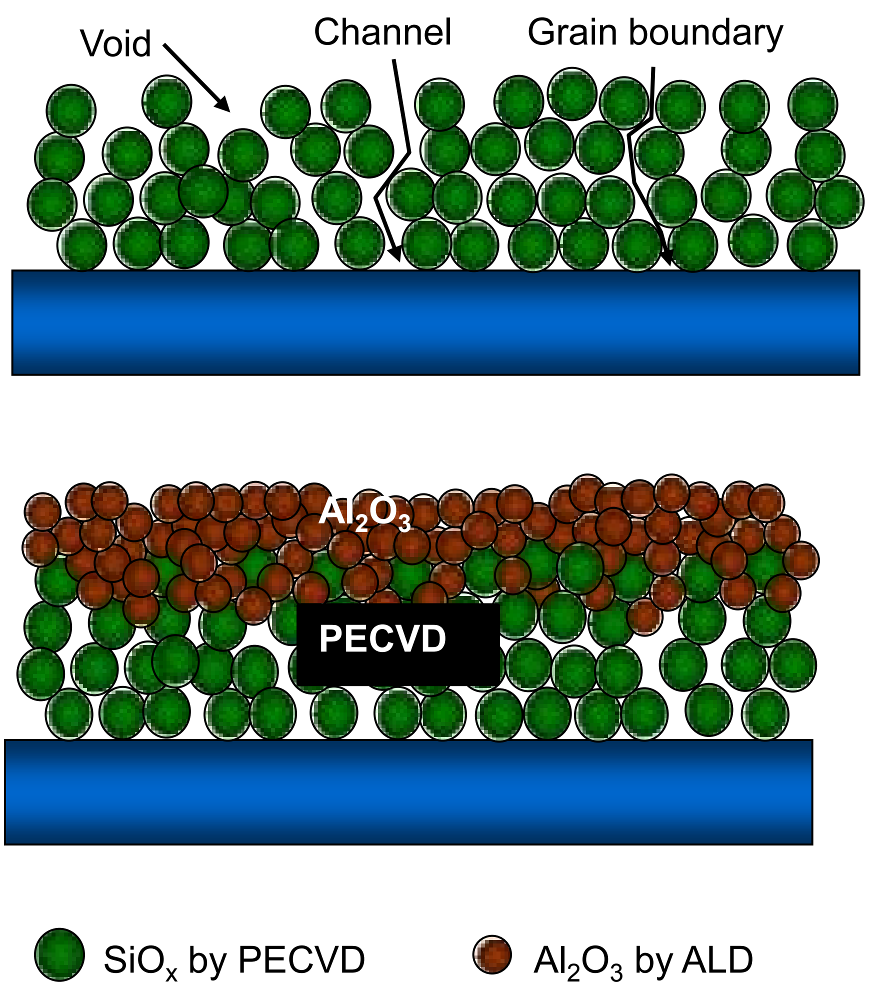
Solubility (g/cm³atm)

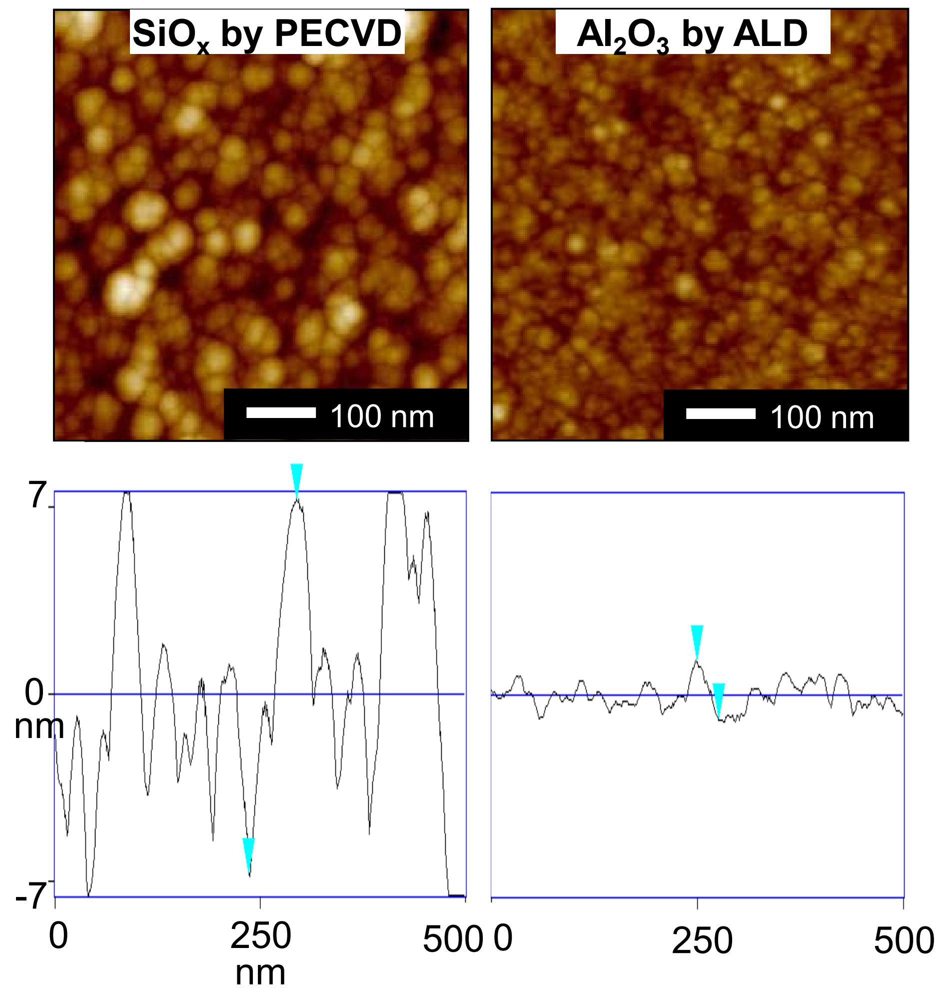
Test #	Before Anneal	After Anneal for 10 min
Average	0.286	0.140
STDV	0.054	0.044

Initial water content in sample impacts the lag time and WVTR observed unless measured for a long time.

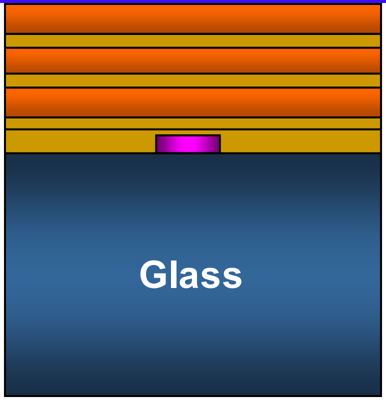
New Approach: Hybrid Architecture

Combine rapid low temperature deposition by PECVD with high quality atomic layer deposition to simplify barrier architecture.

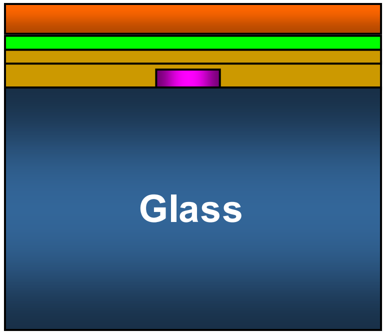




Comparison of Results



Multilayer Film	**WVTR** (g/m²/day)
3 dyads of SiOx/Parylene	6± $2x10^{-5}$
3 dyads of SiNx/Parylene	7 ± $2x10^{-6}$



Hybrid Architecture	**WVTR** (g/m²/day)*
SiOx/Al_2O_3/Parylene	2 ± $1x10^{-5}$
SiNx/Al_2O_3/Parylene	3 ± $2x10^{-5}$

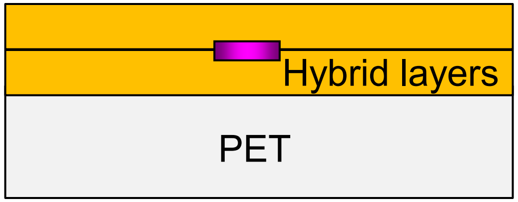
***Films contain 50 nm of Al_2O_3**

****Al_2O_3 layer   3 x 10^{-4} g/m²/day**

Reducing ALD thickness: minimal impact!!!

Al_2O_3 thickness : 10 nm

SiO_x/Al_2O_3 /Parylene :   **4 ± 0.5 x 10^{-5} g/m²/day**



Coated PET Substrate

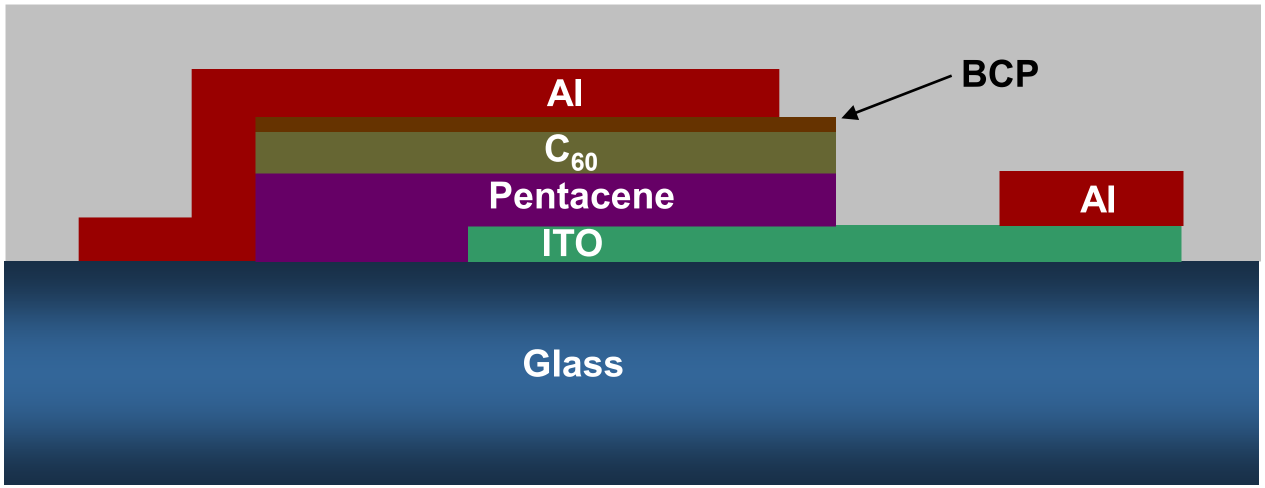
Al_2O_3 thickness : 50 nm

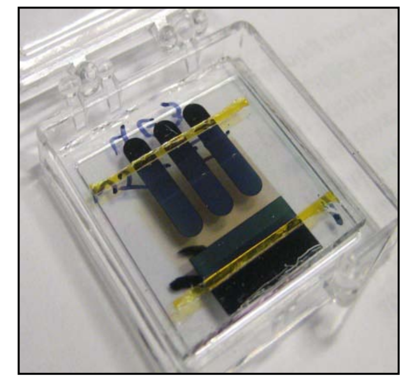
SiO_x/Al_2O_3 /Parylene :   **2.5 ± 1.5 x 10^{-5} g/m²/day**

Integration with OPVs

Device fabrication and encapsulation

Encapsulation (1~4 pairs of SiNx/ Parylene)





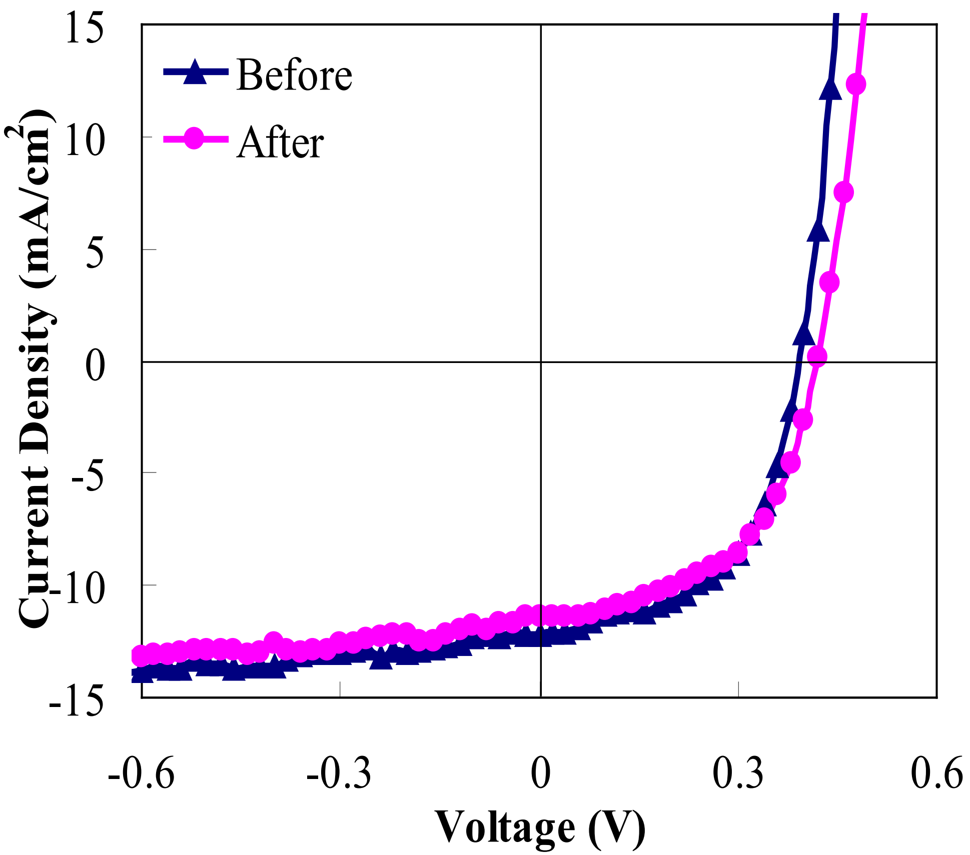
ITO/ Pentacene (50 nm)/ C_{60} (45nm)/ BCP (8 nm)/ Al

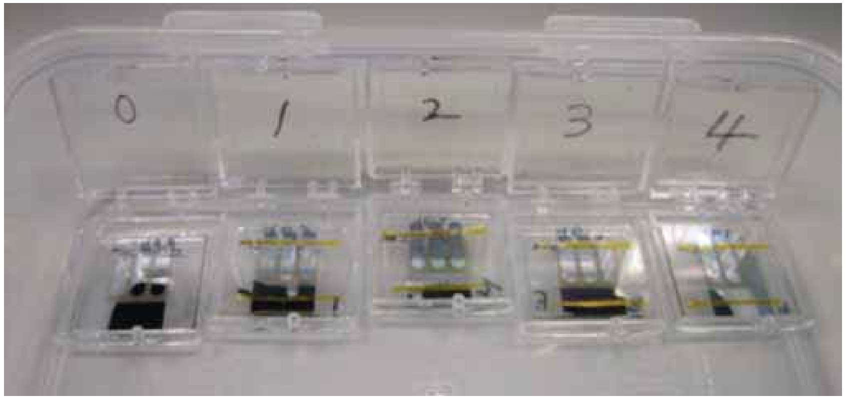
S. Yoo, et., Al., Appl. Phy. Lett., 2004, 85, 5427

Measurement procedure

Performance measurement → OPVs encapsulation → Performance measurement ⇄ Keep in environmental chamber

Process Impact on OPVs



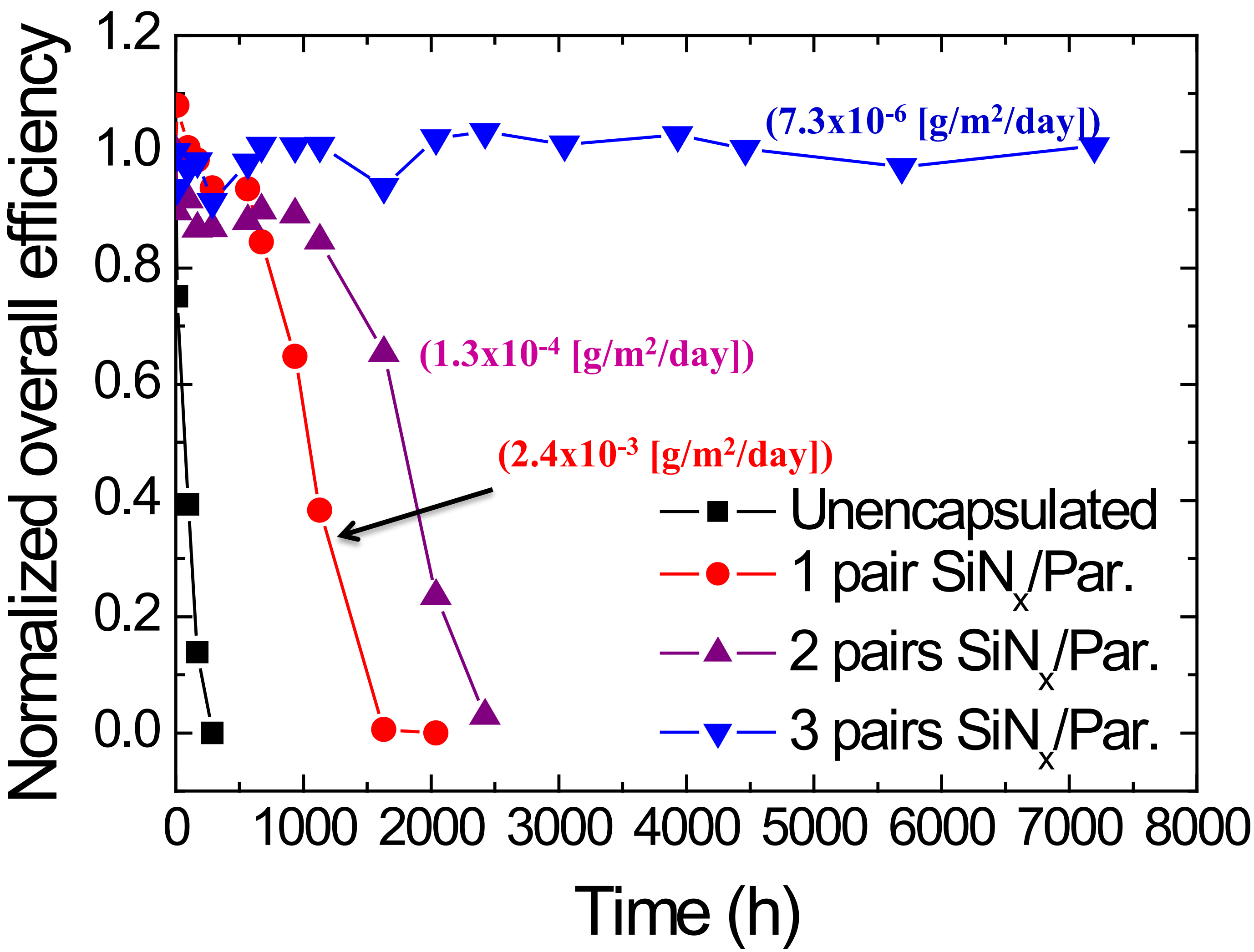


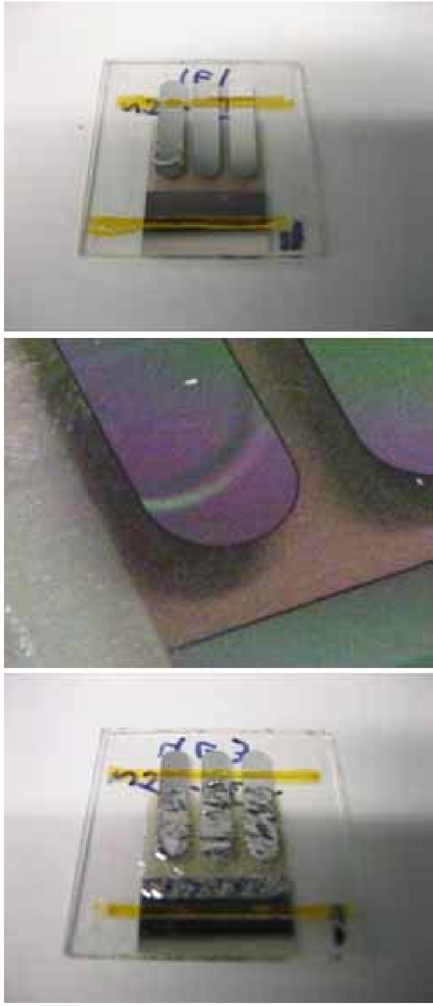
	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)	Average (%)
Before	0.39	-12.19	0.54	3.3	3.4
After	0.41	-11.40	0.54	3.3	3.3

- Average is based on 12 devices
- Light source : 175W Xenon Lamp

Device Performance Vs. Time

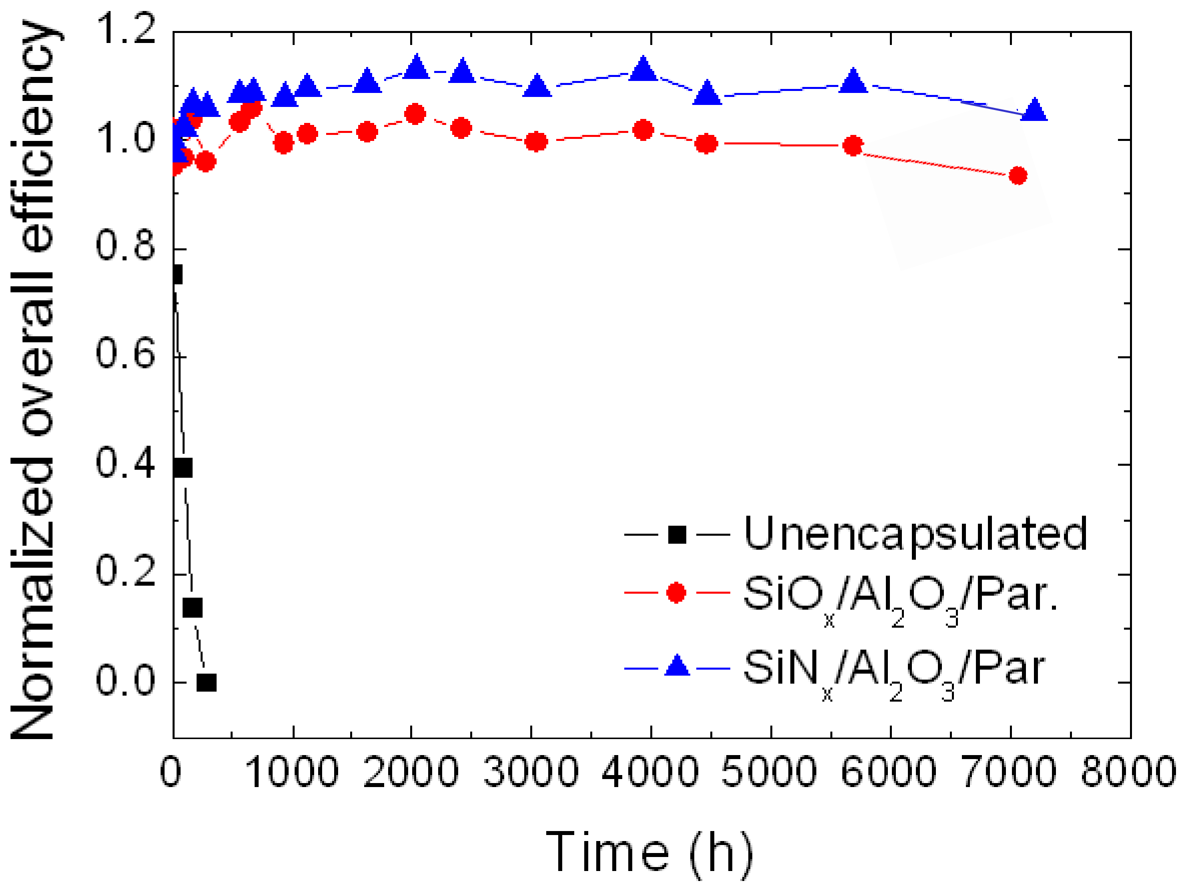
Overall device efficiency (Oriel 91160, AM 1.5G)





Hybrid Encapsulation Architecture

Overall device efficiency (Oriel 91160, AM 1.5G)



Excellent performance for simple architecture. (WVTR~10^{-5}).

Reduction in deposition time by a factor of 5.

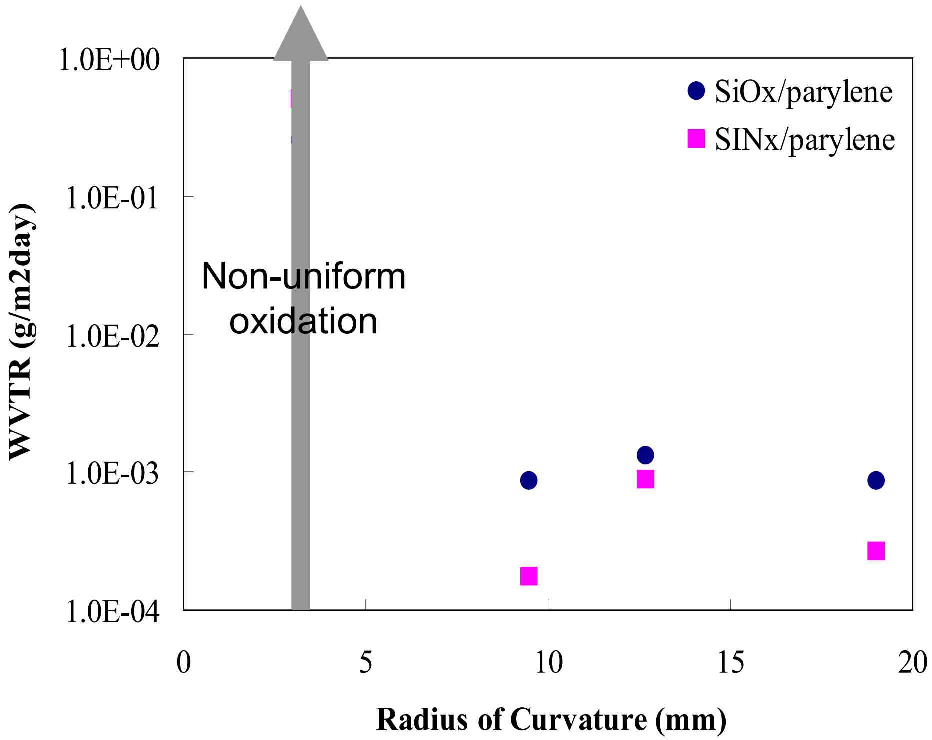
Delamination and buckling were eliminated

Additional work on reducing processing time by an order of magnitude are underway.

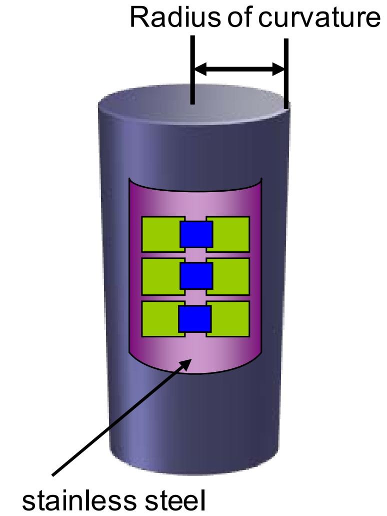
(N. Kim, et al., Applied Physics Letters, 2009)

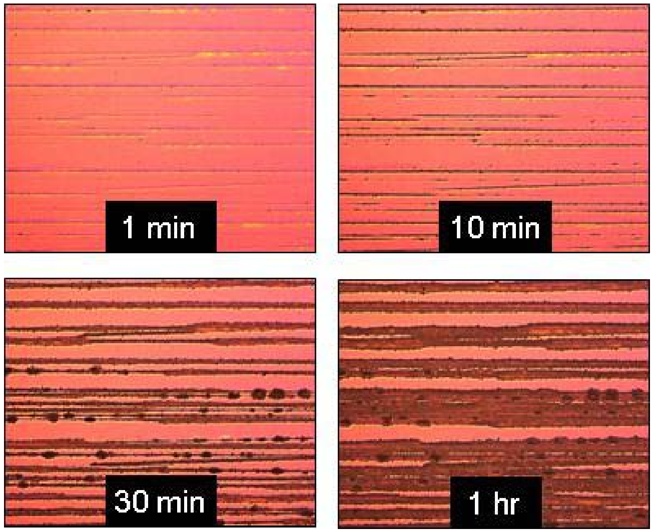
Barrier Performance under Bending

Results



WVTR as the function of the radius of curvature



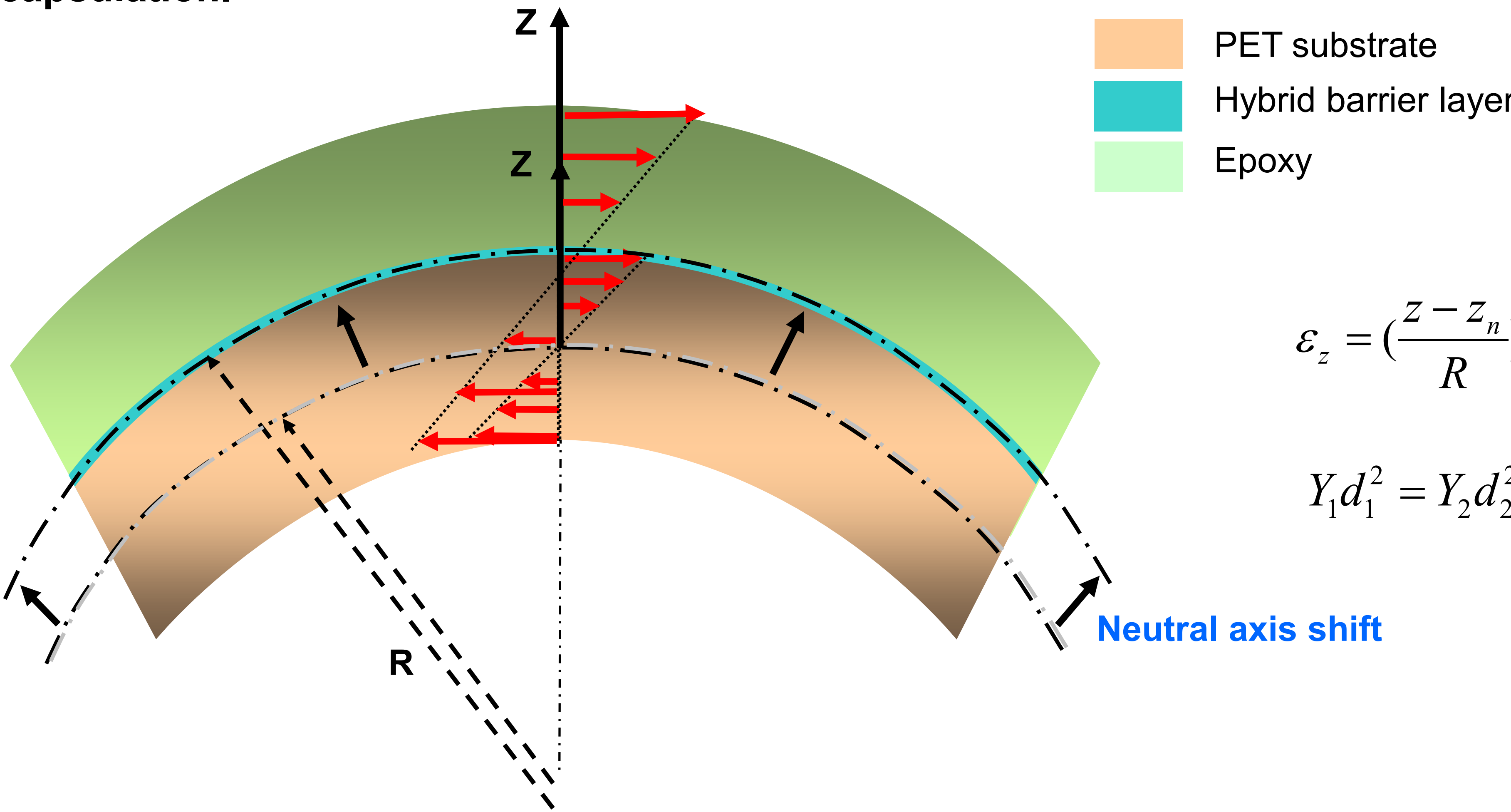


Oxidation through cracks in inorganic layer

Improving Flexibility

Flexibility is limited by the failure strain of the inorganic layer (0.5-2%).

Must improve failure strain without reducing WVTR or reduce strain on the encapsulation.



$$\varepsilon_z = \left(\frac{z - z_n}{R}\right)$$

$$Y_1 d_1^2 = Y_2 d_2^2$$

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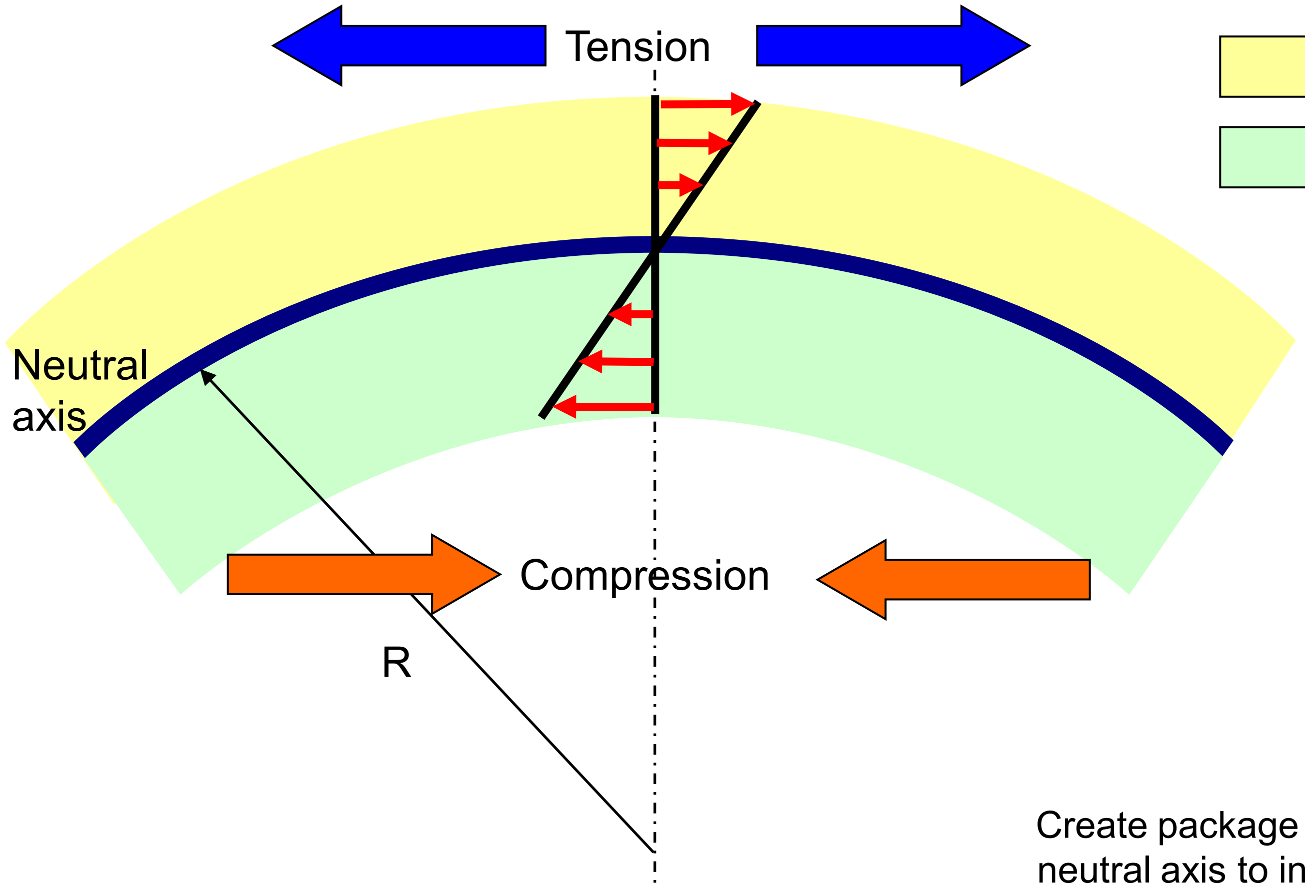
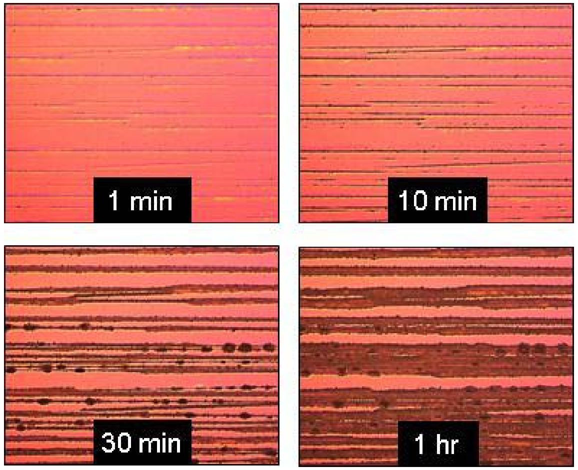


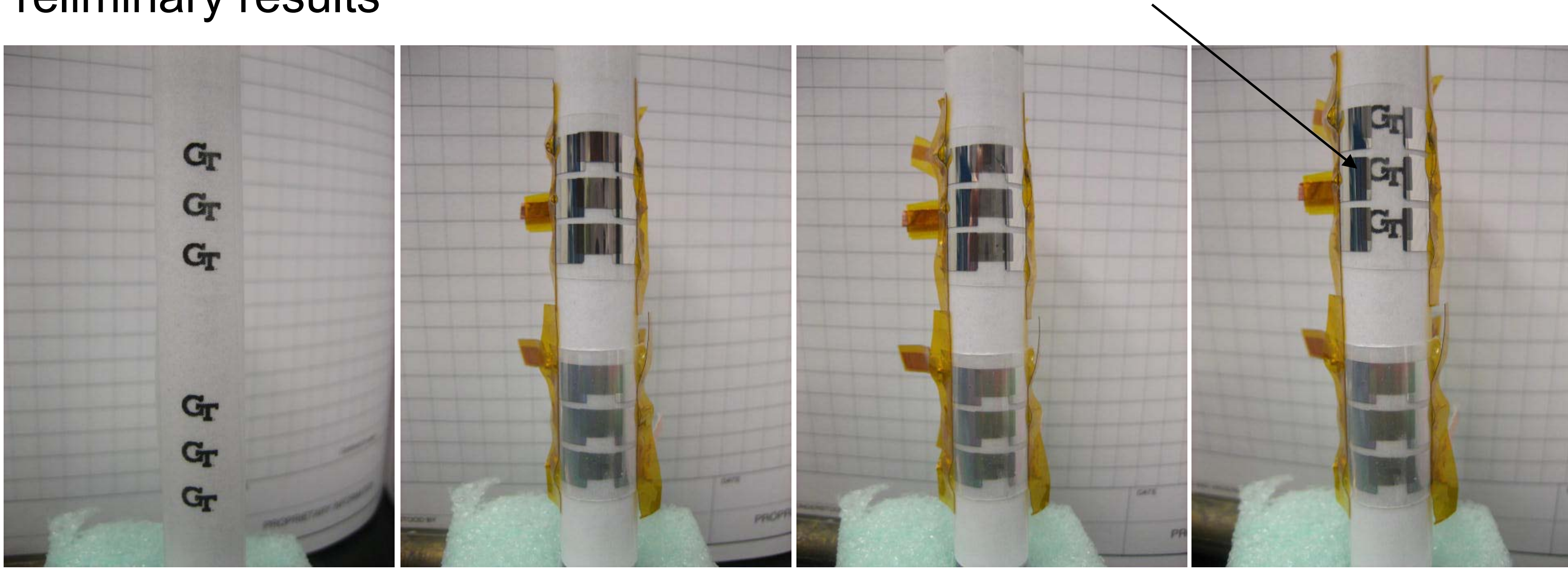


Create package which places the device on the neutral axis to increase durability under flexural deformation.

Improving Flexibility

Preliminary results

Oxidation



Bending

10 min

6 -100 hr

GT logo was used for visual qualitative comparison and not WVTR measurement.

Summary

■ Multilayer Encapsulation

- Defect structure and solubility of polymer layer control laminate performance

- Reporting WVTR and lag time may be necessary for understanding barrier performance.

■ Hybrid Encapsulation

- Simplified Architecture provides ultralow barrier performance

- Promising opportunities exist for further reductions in processing time.

■ Device Integration

- Successful direct encapsulation of OPVs by hybrid thin films

■ Future Efforts

- Development of Edge Seals important for the packaging toolbox.

- Accelerated testing under harsh environments including light soaking!

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Q & A