Barrier Technologies Workshop

Practical Principles for Ultrabarrier Films

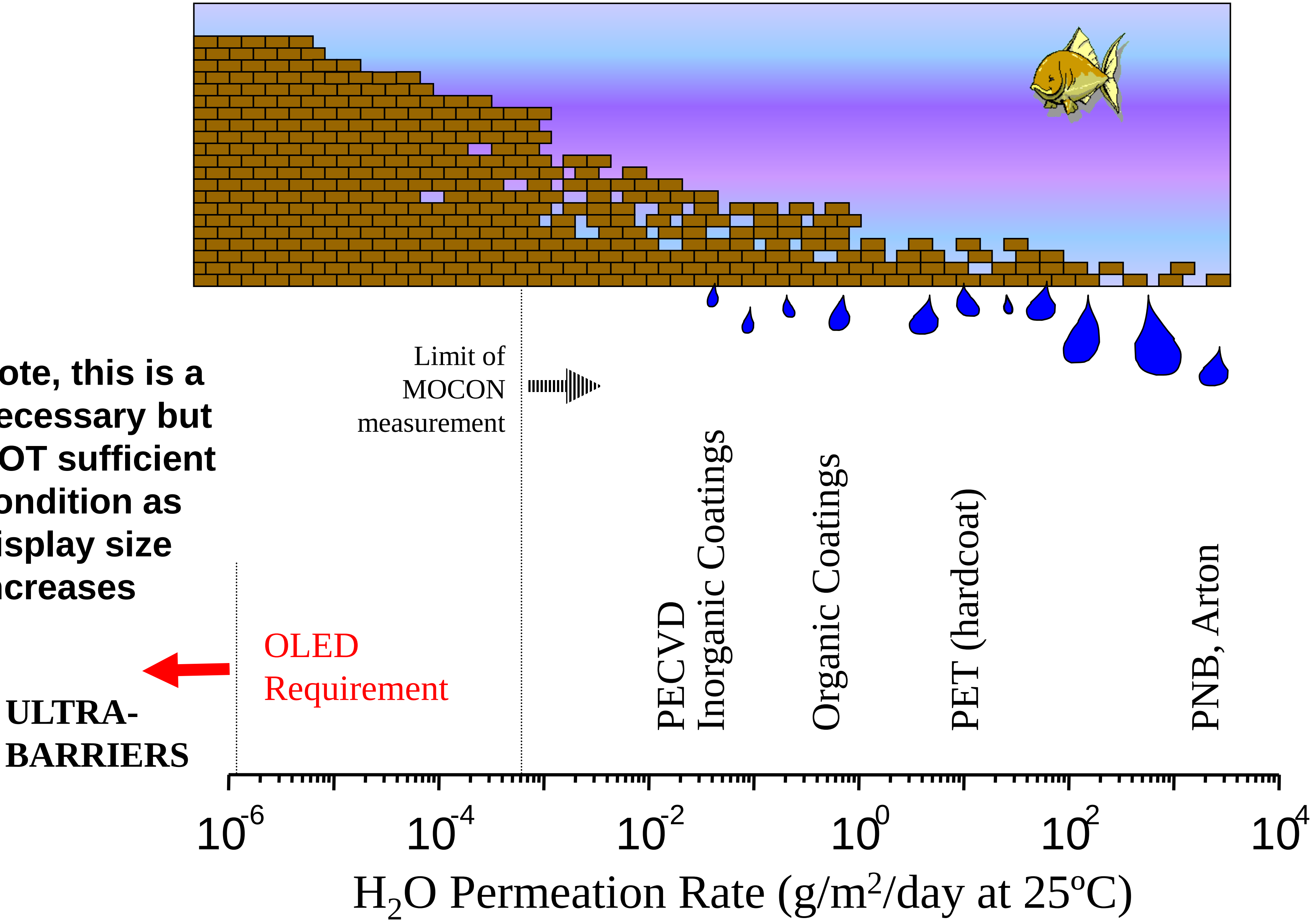
G.L. Graff, *M.E. Gross, P.E. Burrows, W.D. Bennett, C.C. Bonham, P.M. Martin, E.S. Mast, M.R. Zumhoff, M.G. Hall, D.W. Matson, L. Moro, N. M. Rutherford and R.E. Williford*

Pacific Northwest National Laboratory

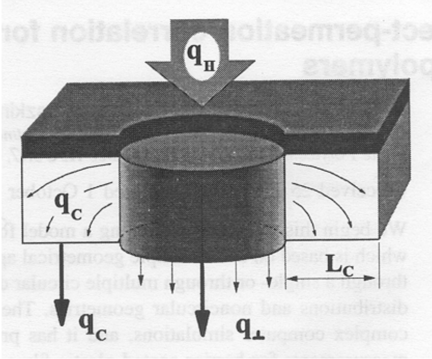
September 19, 2012

The Columbia River Near PNNL

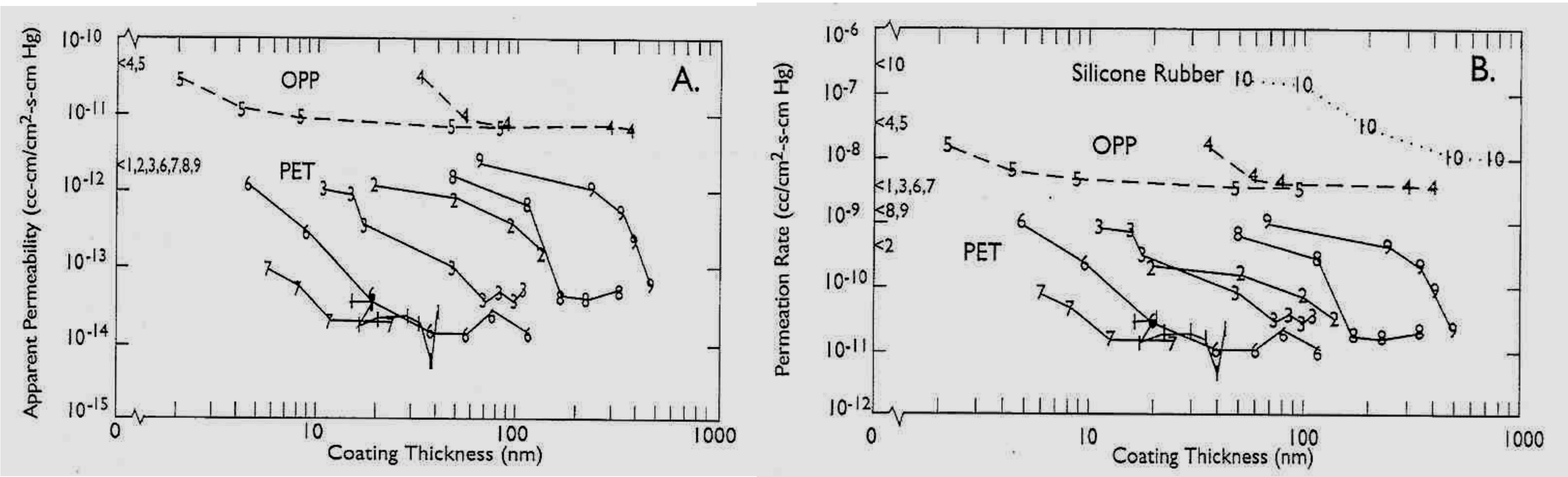
Note, this is a necessary but NOT sufficient condition as display size increases



Defects dominate gas permeation



da Silva Sobrinho, JVST A 18(1),2000

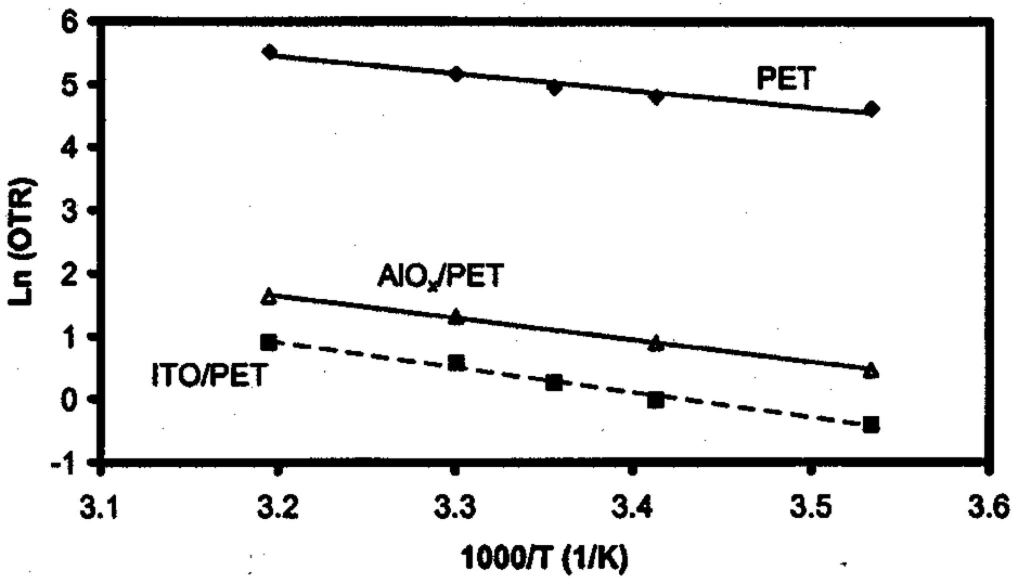


H. Chatham, Surfaces & Coatings Technology 78 (1996) 1-9

- ***permeation is defect controlled***
- ***permeation <u>not</u> following a solubility/diffusivity relation***

Defects dominate gas permeation

Activated rate theory $P = P_o exp^{(-E_A/RT)}$



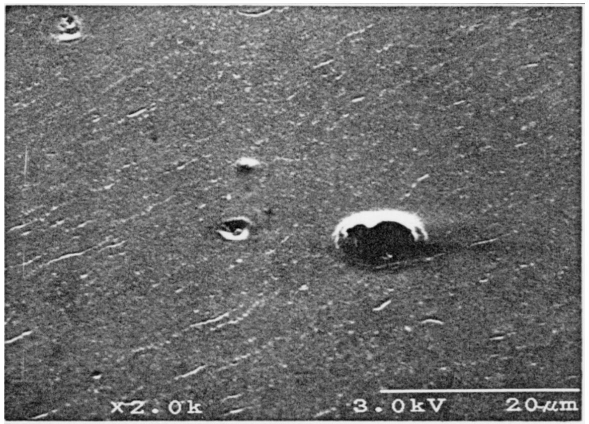
Film type	E_A (KJ/mol ± 3)
PET	27
PET/AlOx	33
PET/ITO	29

B.M. Henry et.al., Thin Solid Films 382 (2001) 194

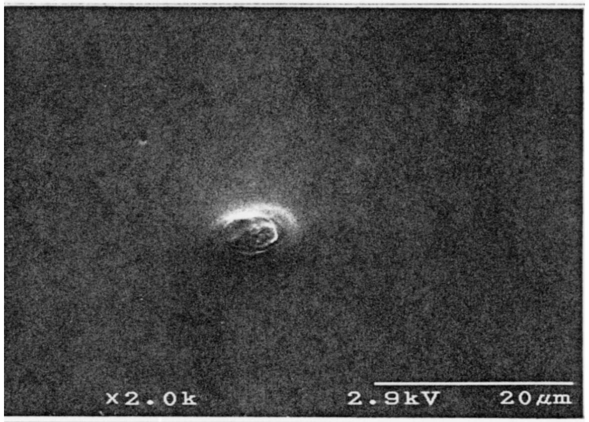
Rate controlling mechanism is diffusion of O_2 through PET

Thin-film coatings

Low temperature vacuum deposition leaves defects!

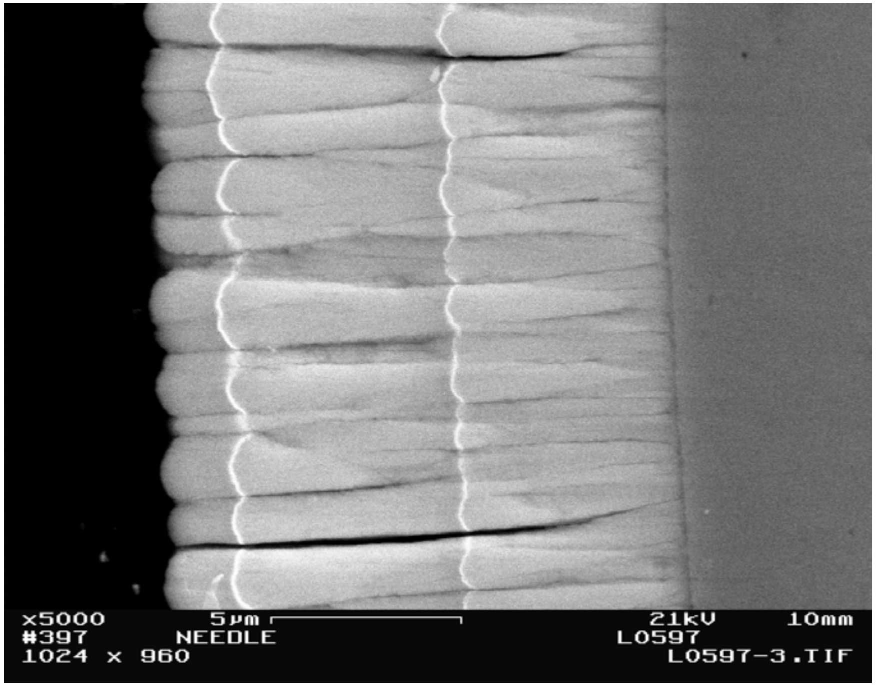


Metallized PP Film (control)



Metallized Acrylate Coated PP Film

Extrinsic

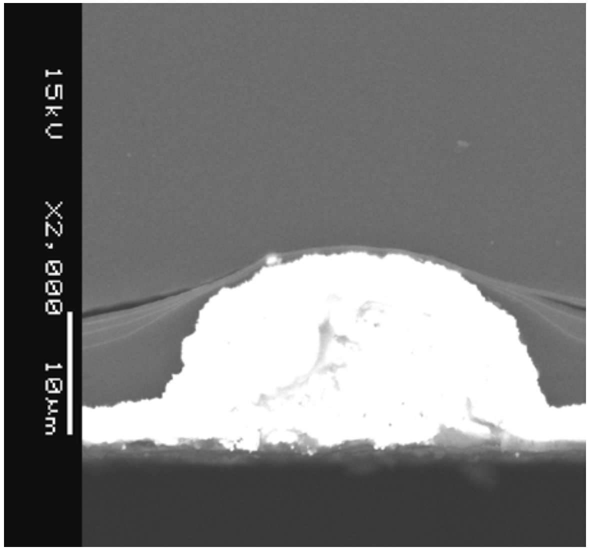


Intrinsic

Sources of Defects

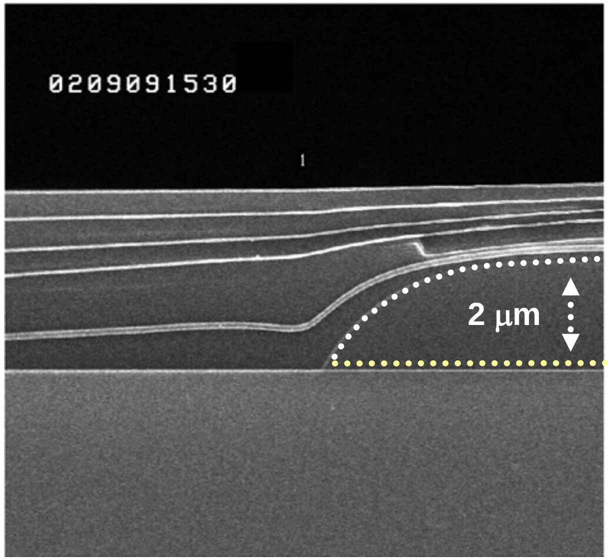
Intrinsic

- poor deposition (spitting)
- columnar growth
- stress cracking
- grain boundaries
- low density (porous) films

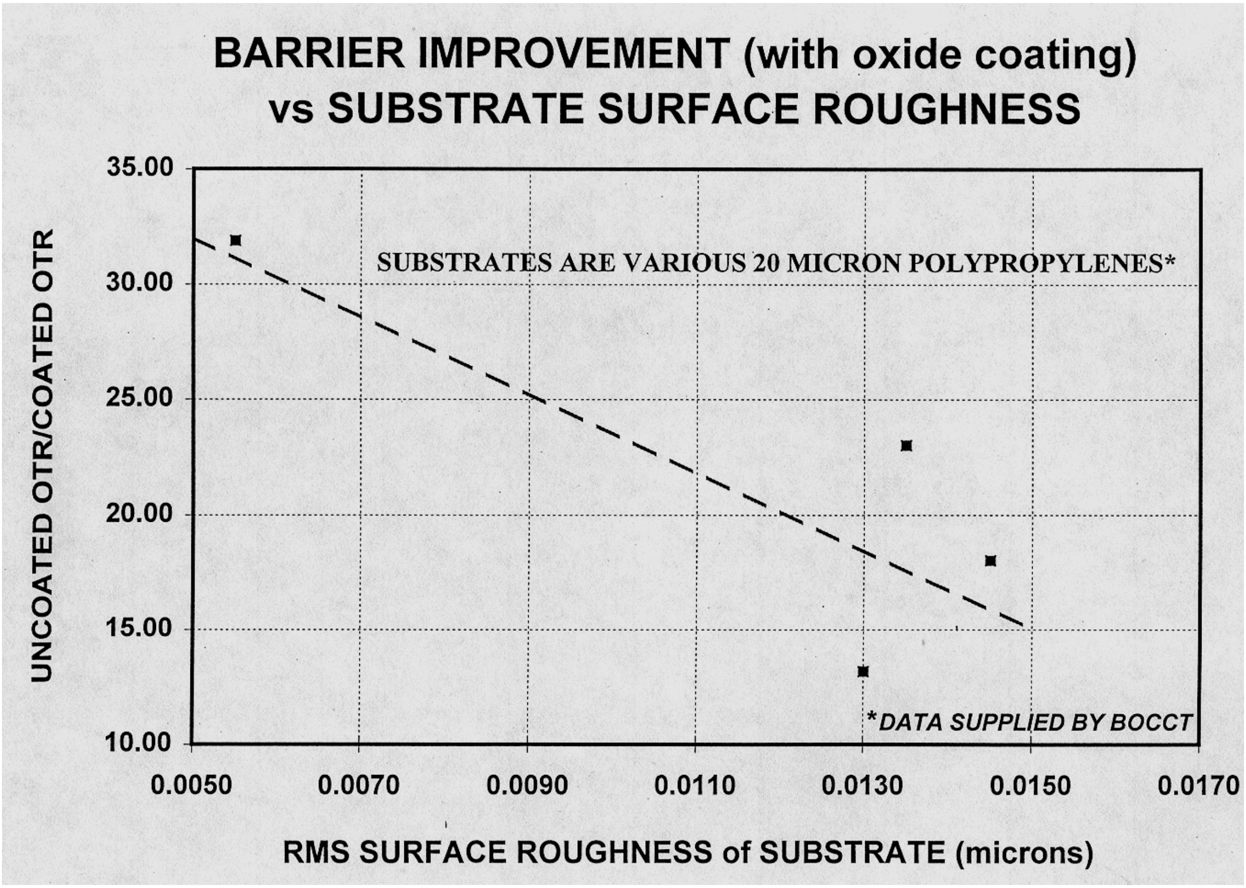


Extrinsic

- particles / debris
- surface roughness
- topography (step edges)



Key Requirements for Ultra-Barriers



Substrate surface roughness generates defects

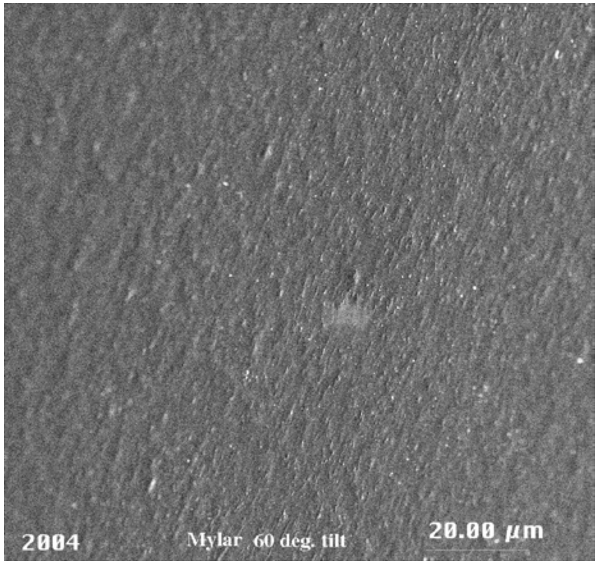
Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

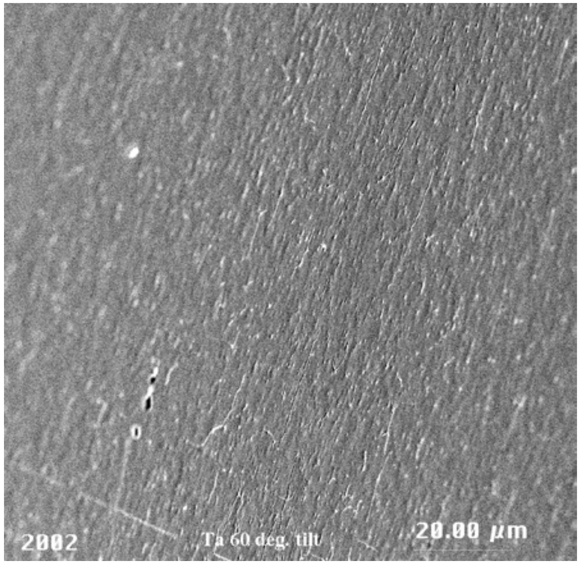
Key Requirements for Ultra-Barriers

- Surface roughness

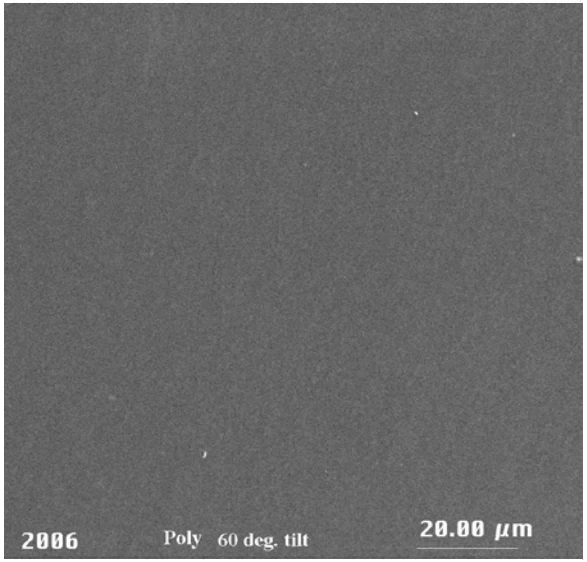
Native PET



Native PET + 25nm Ta



Native PET + 1.5µm poly



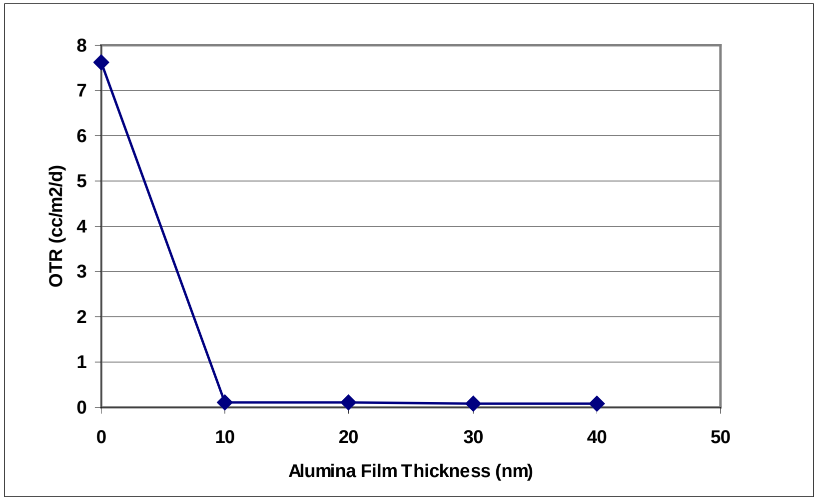
Affinito, et al., Thin Solid Films, 290-91, 63, 1996

<u>Conformal</u> *Vacuum PVD/CVD replicate surface features*

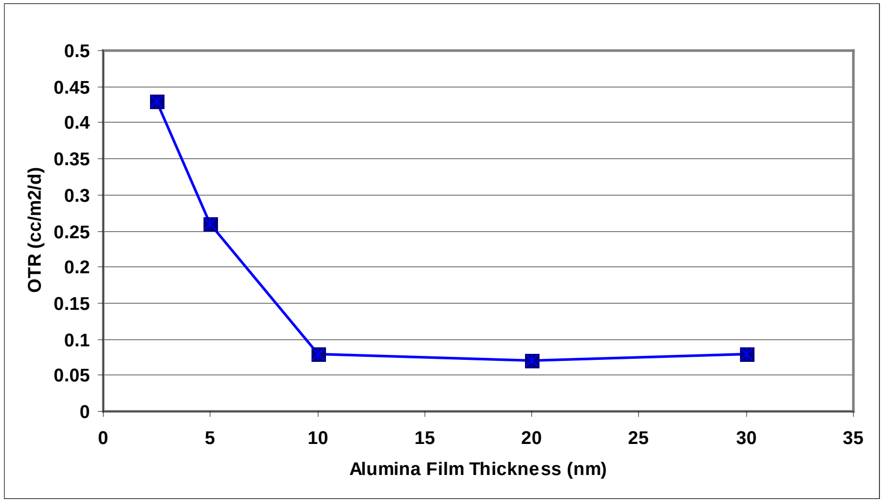
<u>Non-conformal</u> polymer deposition levels surface

Key Parameters for Ultra-Barrier Layers

- critical film thickness required (λ_c)



PNNL barrier on PET



Phillips, R., US# 5,792,550

- (λ_c) function of deposition process / substrate / barrier chemistry
  - (λ_c) for batch tool = 37.5 nm; for r2r = 52.5nm

Kapoor, et. al., SVC 505/856 2006

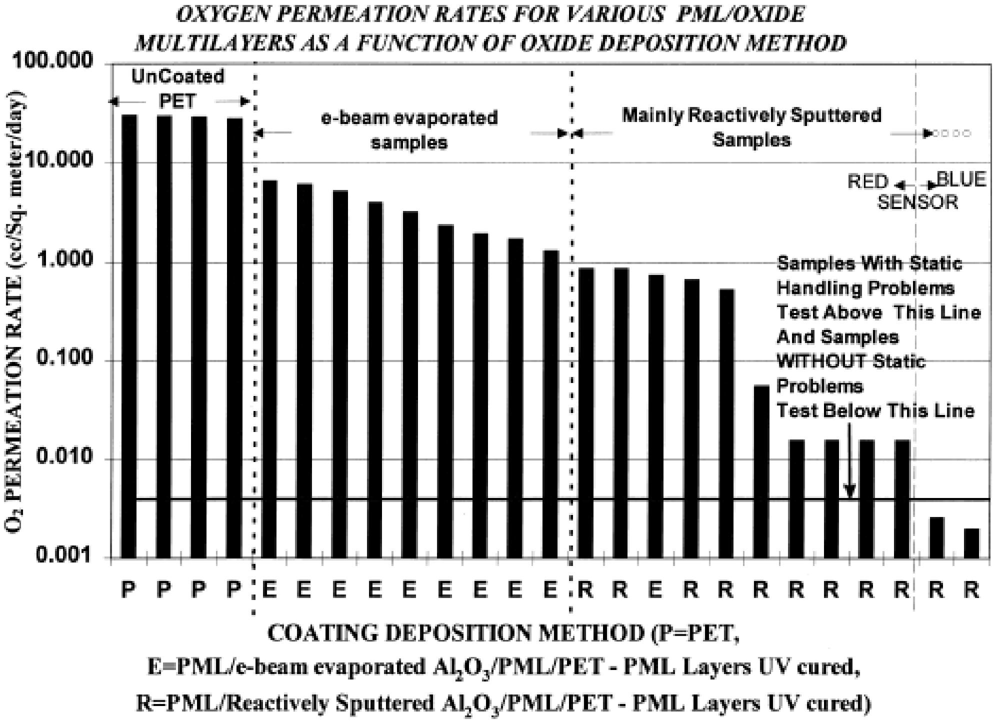
Key Requirements for Ultra-Barriers

Deposition process / conditions

Deposition Method	OTR (cc/m²/d)
EB-Evaporation	15-70
PE-CVD	4
Sputtering	0.5

Yamada et al., SVC Proc., 28, 1995

40-80 nm SiOx on PET

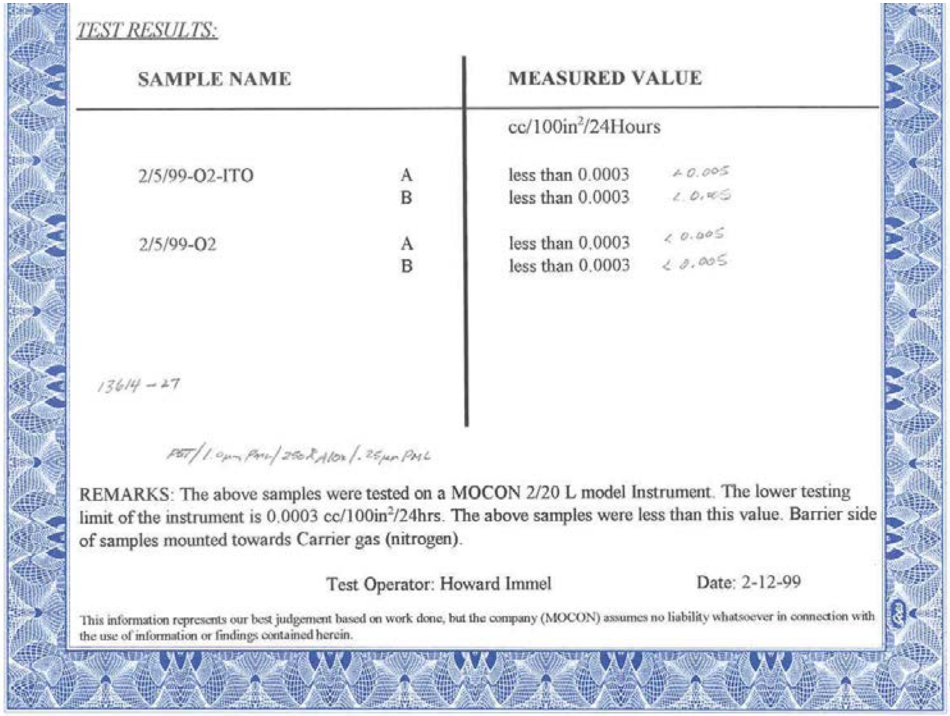


Affinito et al., Thin Sol. Films, 308, 1997

- quality of inorganic film is critical

Key Requirements for Ultra-Barriers

Single layer/dyad performance level



TEST RESULTS:

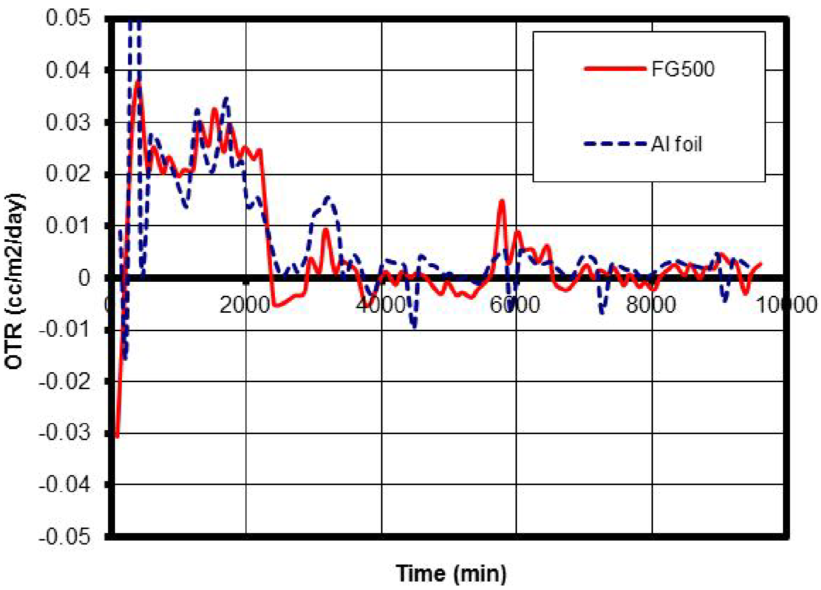
SAMPLE NAME		MEASURED VALUE	
		cc/100in²/24Hours	
2/5/99-O2-ITO	A	less than 0.0003	< 0.005
	B	less than 0.0003	< 0.005
2/5/99-O2	A	less than 0.0003	< 0.005
	B	less than 0.0003	< 0.005

13614 – 27

PET/1.0µm PML/250Å AlOx/.25µm PML

REMARKS: The above samples were tested on a MOCON 2/20 L model Instrument. The lower testing limit of the instrument is 0.0003 cc/100in²/24hrs. The above samples were less than this value. Barrier side of samples mounted towards Carrier gas (nitrogen).

Test Operator: Howard Immel Date: 2-12-99



Insert into multilayer design

Key Requirements - Summary

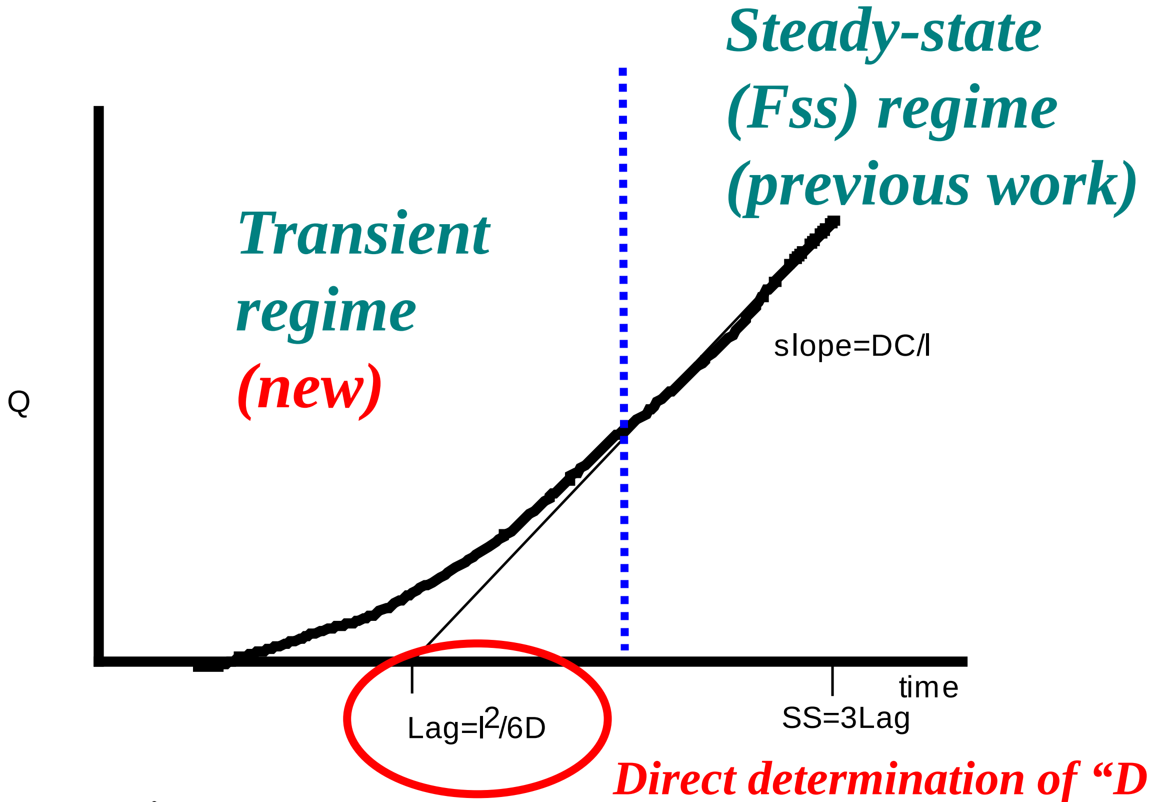
- Eliminate / minimize surface roughness
- Deposit highest quality inorganic layer(s) possible
- Determine critical thickness for inorganic layer(s)
- Minimize particulate / debris

- minimize sources of intrinsic and extrinsic defects!

Understanding Permeation Through Complex Barrier Structures

J. Applied Physics, 96, 4, 1840 (2004)
Flexible Flat Panel Displays, John Wiley & Sons,
Gregory P. Crawford (editor), 57-75 (2005)

Mechanisms Approach:



Direct determination of "D" from layer thickness and gas fluence

Single Layer equations

Lag time = $l^2/6D$ – *calculate diffusivity (D)*

S = Fss l / (DΔP) – *calculate solubility (S)*

J. Crank, The Mathematics of Diffusion, 1975

J. Crank, *The Mathematics of Diffusion*, Claredon University Press (1975)

- Single layer, concentration profile of vapor as a function of distance and time; *C(x,t)*.
- Non-condensable vapor is saturated in the carrier gas at a fixed concentration of C_1 on the "upstream" side of the layer and maintained at zero on the downstream side by a sweep gas, zero initial concentration in the layer.
- Fick's second law:

Diffusivity

$$C(x,t) = C_1\left(1 - \frac{x}{l}\right) - \frac{2C_1}{\pi}\sum_{n=1}^{\infty}\frac{1}{n}\sin\left(\frac{n\pi x}{l}\right)e^{-\frac{Dn^2\pi^2 t}{l^2}}$$

Layer thickness

- Obtain flux, F, by differentiation with respect to distance (Fick's first law).
- Integrate flux at the downstream surface ($x = l$) over time to give the total mass transmitted Q:

$$Q(t) = \int_{t'=0}^{t} F(x = l, t)\,dt' = \frac{DtC_1}{l} - \frac{lC_1}{6} - \frac{2lC_1}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}e^{-\frac{Dn^2\pi^2 t}{l^2}}$$

- As *t* becomes large:

$$Q(t\to\infty) = \frac{DC_1}{l}\left(t - \frac{l^2}{6D}\right) \quad : \quad Permeability = \frac{F_{SS}\,l}{\Delta P} = DS$$

steady state flux (F_{ss}) **Lag time (L)** **Solubility (S)**

Approach: Fickian models

Substitute measured D & S into multi-layer equations for…

$$F_{ss} = \frac{p_{H_2O}}{{}^{l_1}\!/_{D_1S_1} + {}^{l_2}\!/_{D_2S_2} + {}^{l_3}\!/_{D_3S_3} + \ldots. + {}^{l_n}\!/_{D_nS_n}}$$

Steady state flux (Fss)

$$Lag = \left[\sum_{i=1}^{n}\left[\frac{l_i}{D_i}\prod_{j=1}^{i-1}K_j\right]\right]^{-1}\left[\begin{array}{l}\displaystyle\sum_{i=1}^{n}\left\{\frac{l_i^2}{2D_i}\sum_{m=1}^{n}\left[\frac{l_m}{D_m}\prod_{j=1}^{m-1}K_j\right]-\frac{l_i^3}{3D_i^2}\prod_{j=1}^{i-1}K_j\right\} \\ \displaystyle+\sum_{i=1}^{n}\left\{\frac{l_i}{D_i}\prod_{j=1}^{i-1}K_j\sum_{\beta=i+1}^{n}\left[\frac{l_\beta}{\prod_{j=1}^{\beta-1}K_j}\sum_{m=\beta}^{n}\left[\frac{l_m}{D_m}\prod_{j=1}^{m-1}K_j\right]-\frac{l_\beta^2}{2D_\beta}\right]\right\}\end{array}\right]$$

Lag time (L)

Ash Barrer & Palmer, Brit. J. Appl. Phys, 16, 884, 1965

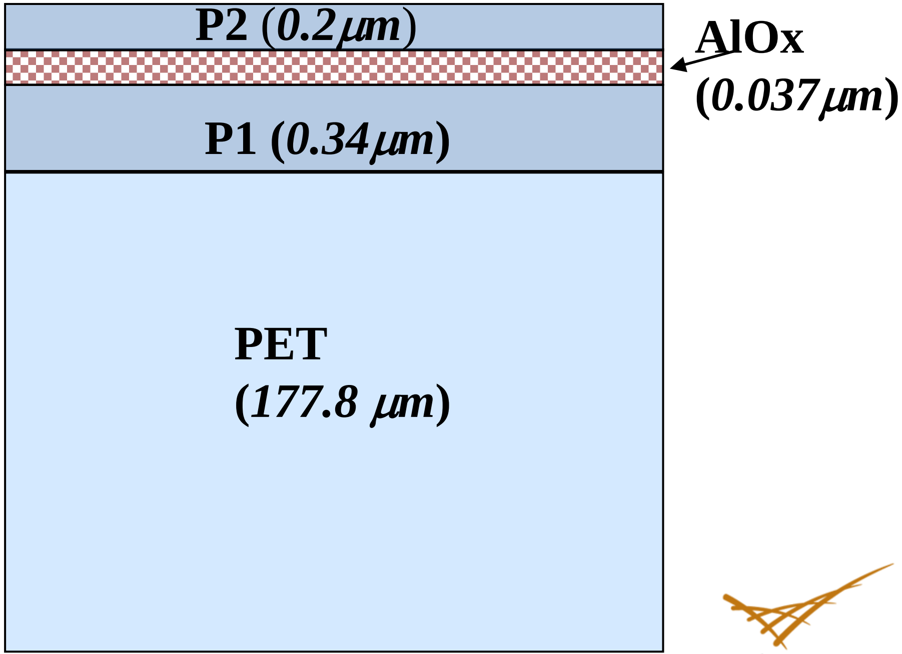
Our Test Structures:

combine Mocon measurements with Fickian diffusion models

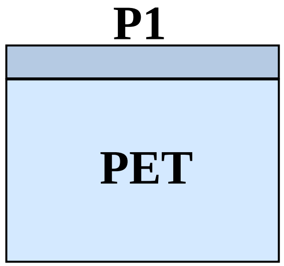
Permeability = Diffusivity x Solubility (P=DS)

Need to determine D & S

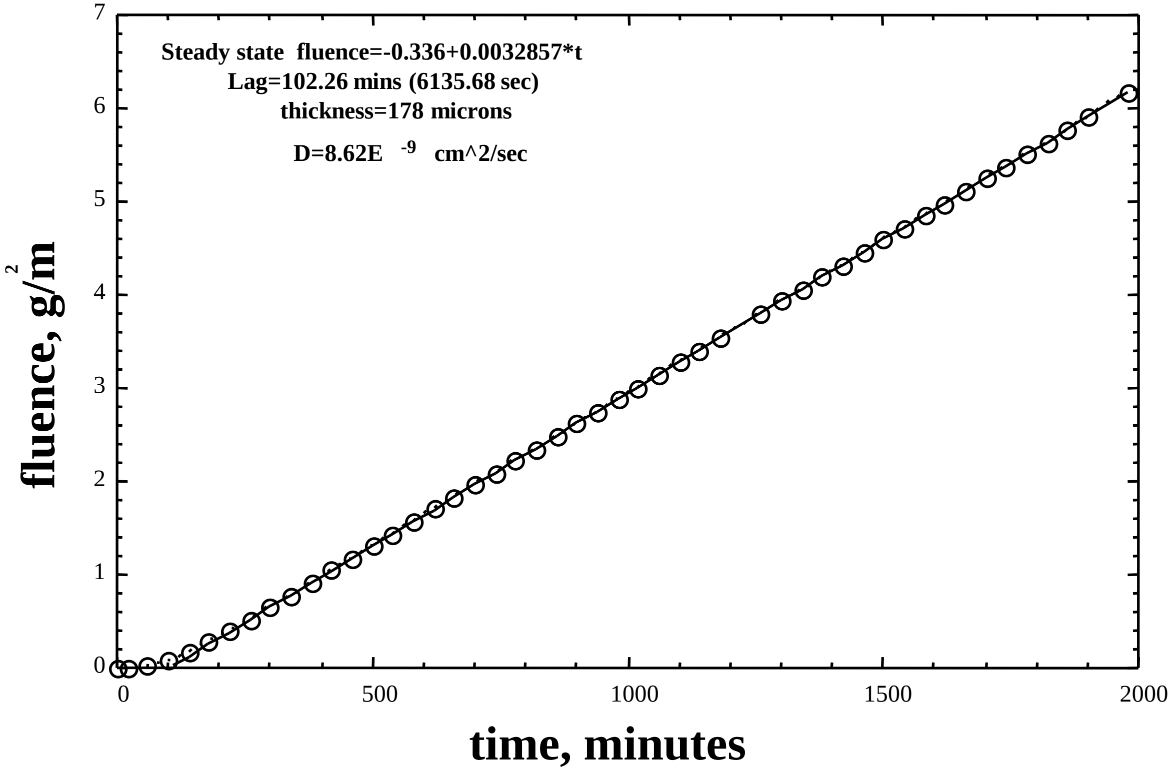
- *use simple structures with known thickness*
  - *PET/P1*
  - *PET/P1/AlOx/P2*
- *degas substrate/barrier film*
- *measure fluence as a function of time (Mocon)*



Barrier Mechanisms

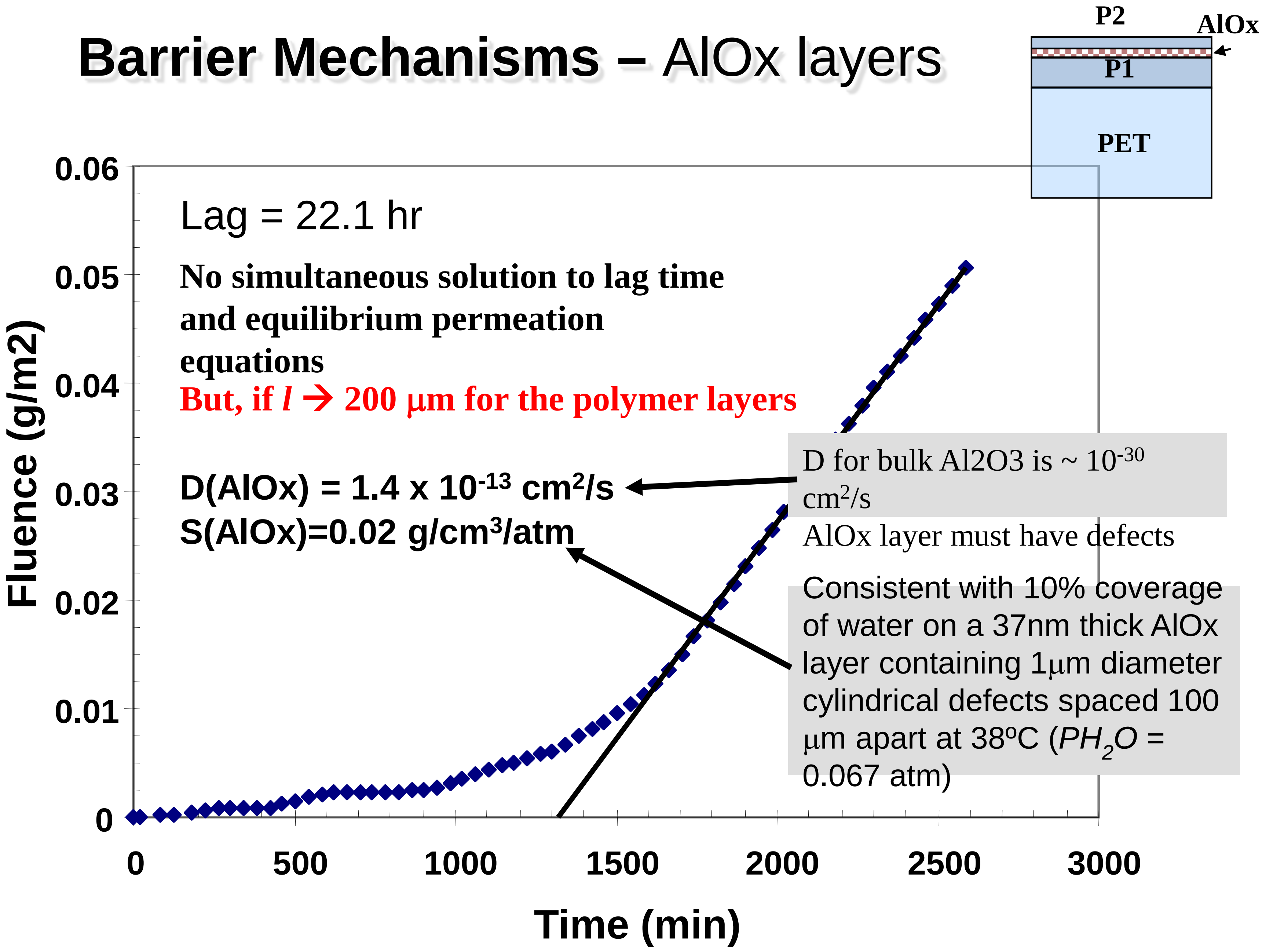


Polymer layers (PET/P1)


Steady state fluence=-0.336+0.0032857*t
Lag=102.26 mins (6135.68 sec)
thickness=178 microns
D=8.62E $^{-9}$ cm^2/sec

$D = 8.5\text{x}10^{-9}\ \text{cm}^2/\text{s}$ $S = 0.17\ \text{g/cm}^3/\text{atm}$

Barrier Mechanisms – AlOx layers



Lag = 22.1 hr

No simultaneous solution to lag time and equilibrium permeation equations

But, if *l* → 200 µm for the polymer layers

D(AlOx) = 1.4 x 10^{-13} cm^2/s

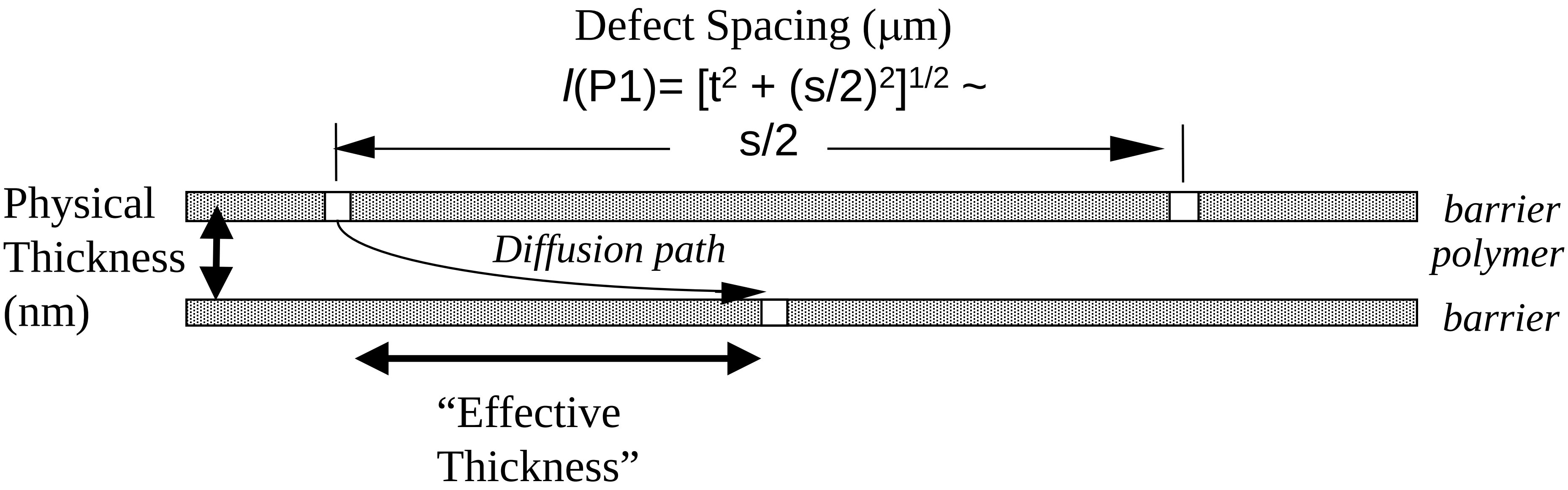
S(AlOx)=0.02 $g/cm^3/atm$

D for bulk Al2O3 is ~ 10^{-30} cm^2/s

AlOx layer must have defects

Consistent with 10% coverage of water on a 37nm thick AlOx layer containing 1µm diameter cylindrical defects spaced 100 µm apart at 38°C (PH_2O = 0.067 atm)

The Role of Defects in Permeation



Defect Spacing (μm)

$l(\mathrm{P1}) = [t^2 + (s/2)^2]^{1/2} \sim s/2$

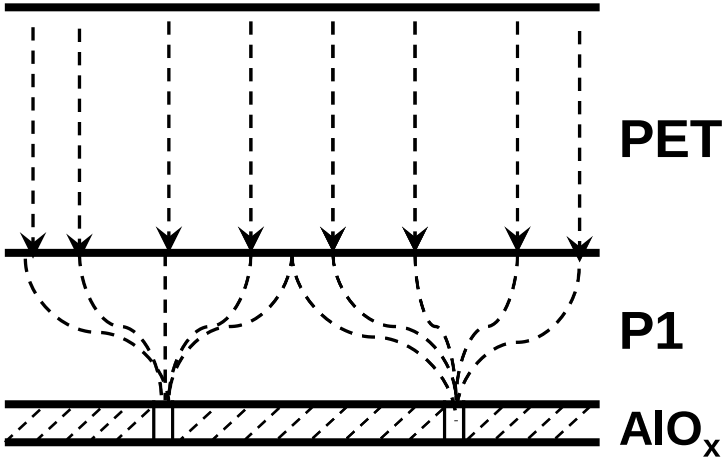
Physical Thickness (nm)

Diffusion path

“Effective Thickness”

-diffusion of gas in x-y plane dominates

-results in extremely long “effective” diffusion path



Barrier Mechanism

Summary of calculated layer properties

- ***D(PET)=D(P1)=D(P2) = 8.5x10^{-9} cm^2/s***
  - ***Handbook values: PET = Acrylic = 4 x 10^{-9} cm^2/s***

- ***S(PET)=S(P1)=S(P2) = 0.17 g/cm^3/atm***
  - ***Handbook values: PET = 0.17, Acrylic = 0.19***

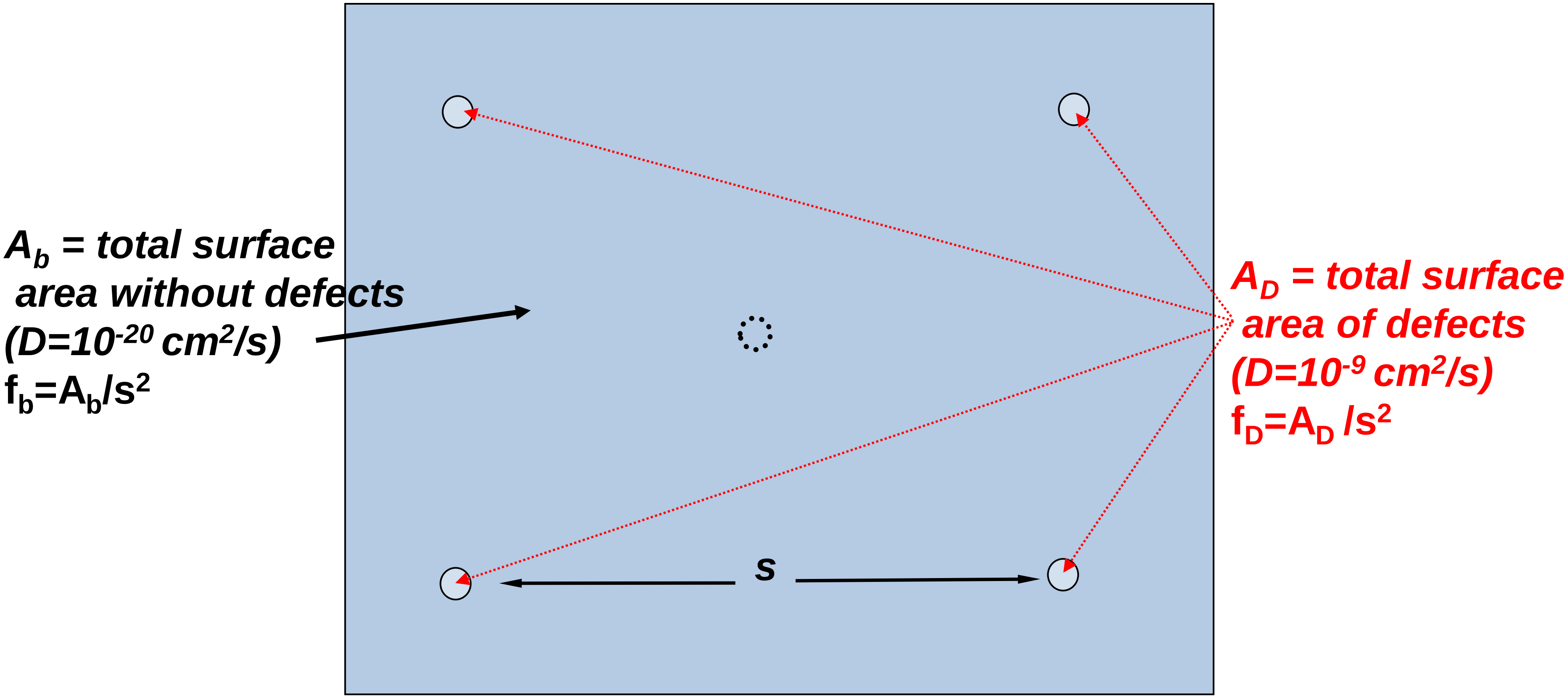
-***D_{eff}(AlOx) = 1.4x10^{-13} cm^2/s*** *(sapphire ~10^{-30} cm^2/s)*

-***S(AlOx) = 0.029 g/cm^3/atm*** *(equates to ~10% surface coverage)*

- ***l(P2) = ½ defect spacing in AlOx layers (not physical thickness)***

Barrier Mechanisms – Defect model

$$D(AlOx)=D_b f_b + D_D f_D$$



A_b = total surface area without defects
($D=10^{-20}$ cm^2/s)
$f_b=A_b/s^2$

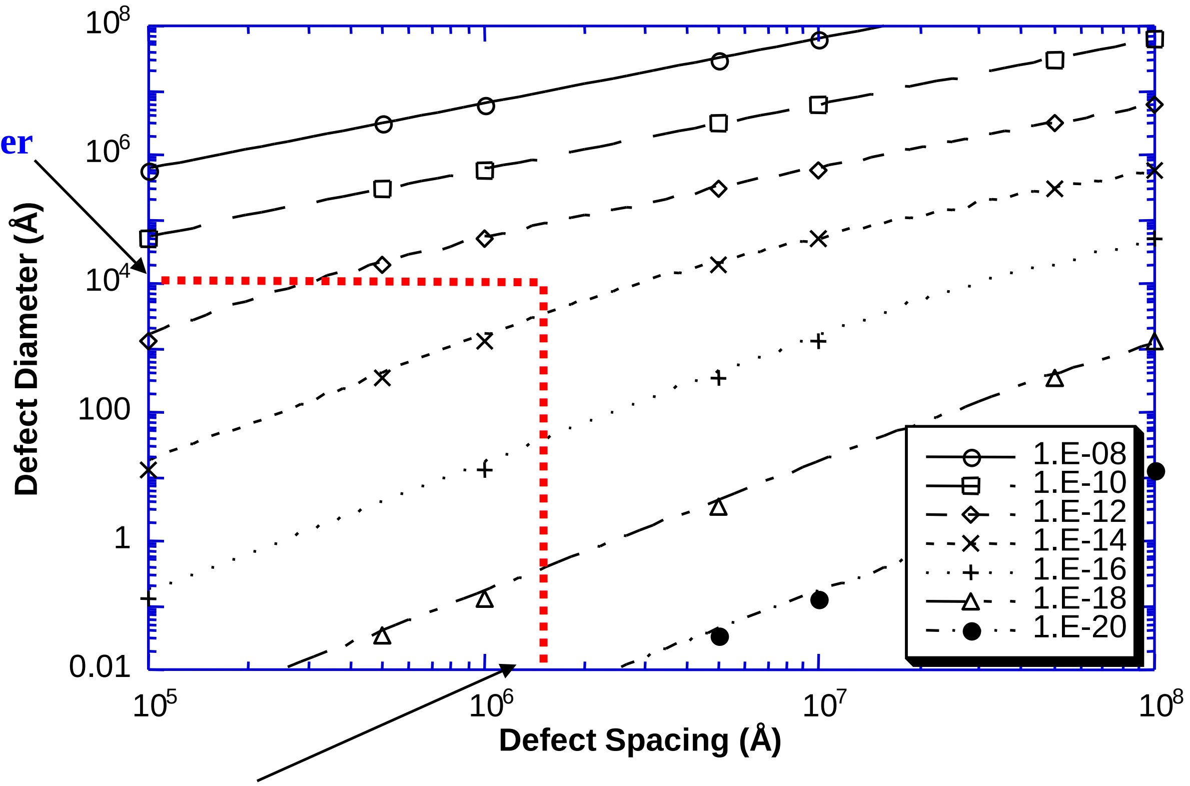
A_D = total surface area of defects
($D=10^{-9}$ cm^2/s)
$f_D=A_D/s^2$

- ***for $D_{eff}=1.4\text{x}10^{-13}$ cm^2/s, A_D:A_b ~ 1:10,000, Flux$_D$:Flux$_b$ ~ $5\text{x}10^8$:1***
- ***essentially <u>all</u> the gas flux is through the defects***

23

Barrier Mechanisms – Defect model

$$D(AlOx)=D_b f_b + D_D f_D$$



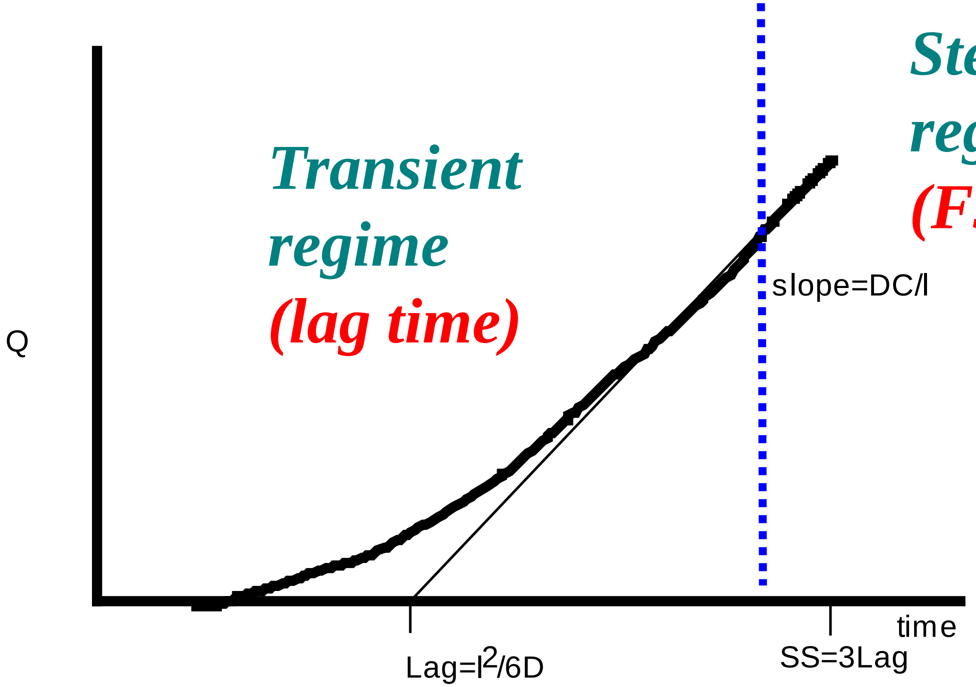
1µm diameter

Increasing film quality

~200µm spacing between defects @ $D_{eff} = 10^{-13}$cm^2/s

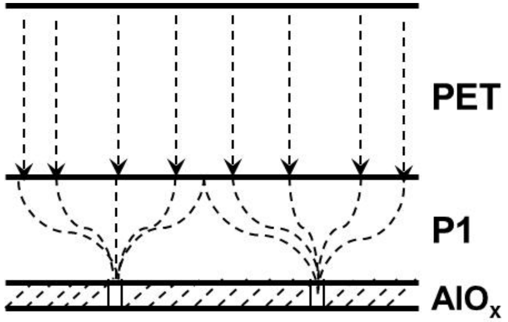
What do the models teach us?

Steady State (Single Layer) Regime



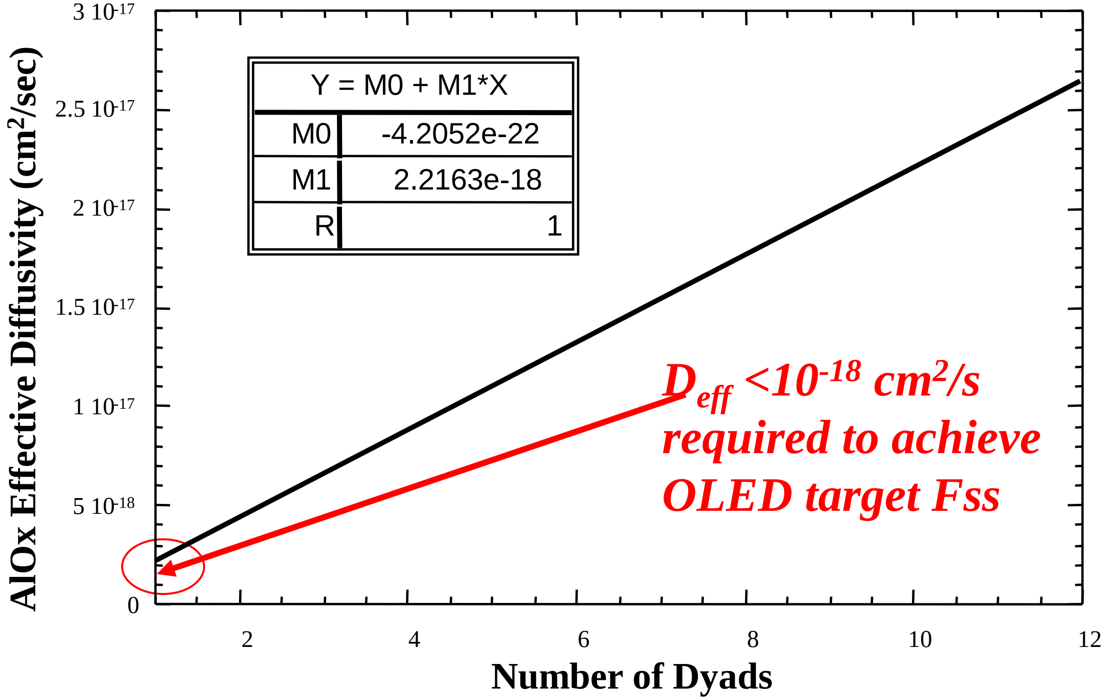
Transient regime
(lag time)

Steady-state regime
(Fss)



Why not use <u>One</u> Inorganic Layer?

Number of dyads required to achieve $F_{SS} = 10^{-6}$ g/m^2/d



$D_{eff} < 10^{-18}$ cm^2/s required to achieve OLED target Fss

Very difficult to manufacture using PVD or CVD methods

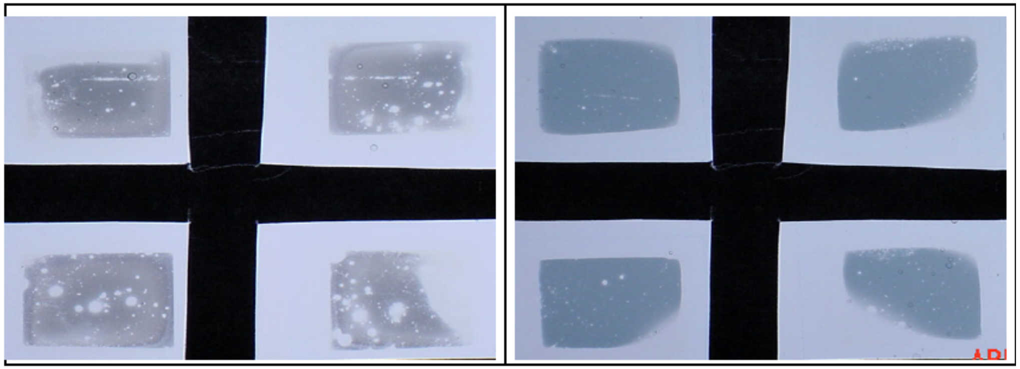
- *equivalent to 1nm defects @ 1000μm spacing*
- *or 10nm defects @ 10,000 μm spacing*

Why not use One Inorganic Layer?

Symmorphix – Magnetron sputtered $Al_2O_3:SiO_2$

Pakbaz, H., OSC04 Europe (9/27/2004)

- **Ca test of pre-cleaned vs. non cleaned PEN after 569Hrs in 60C/90%RH**



As received substrate followed by barrier deposition

Cleaned substrate before barrier dep

Measured WVTR of 1-5 x 10^{-4} g/m^2/d

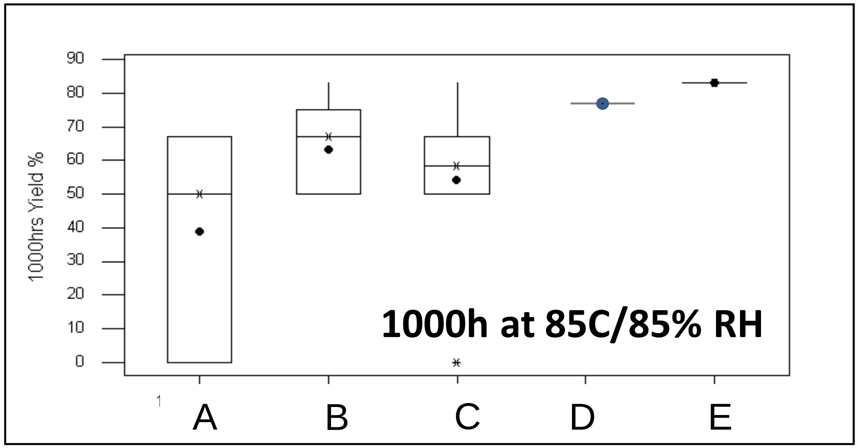
25 nm Al_2O_3 deposited by ALD: WVTR of <1 x 10^{-5} g/m^2/d

(Zhang, Thin Solid Films 517, 2009)

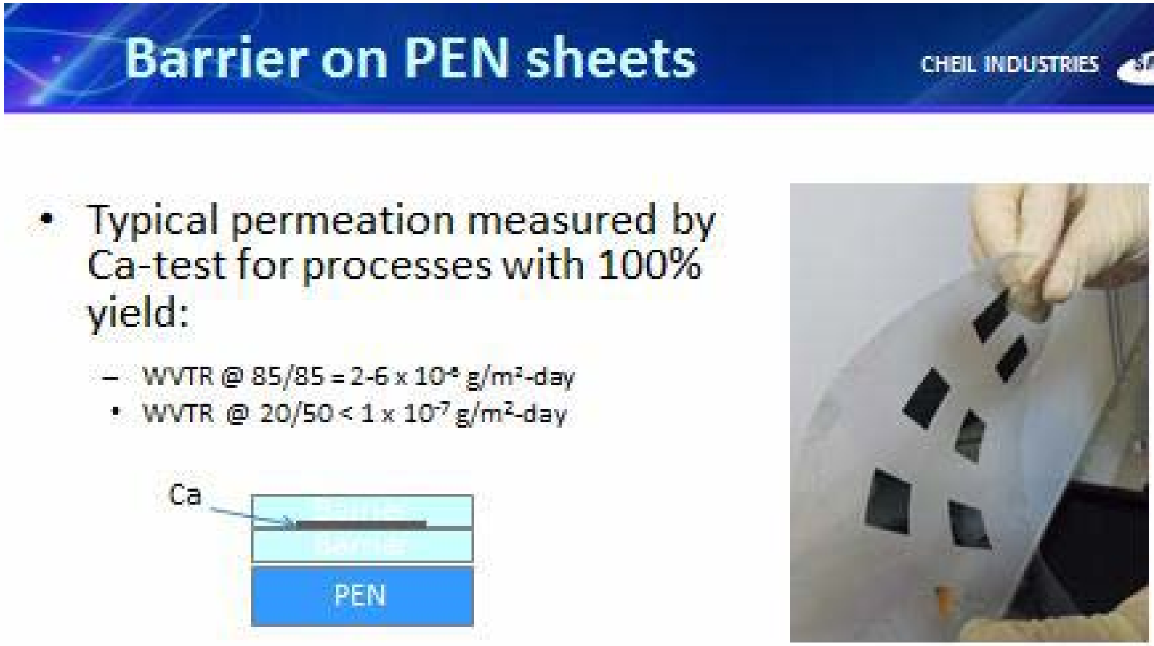
Single dyad barrier on glass

WVTR<10^{-6} g/m²/day

CHEIL INDUSTRIES SAMSUNG



Condition	Average of 1000hrs WVTR 20/50
A	3.09E-07
B	3.91E-07
C	4.06E-07
E	3.53E-07

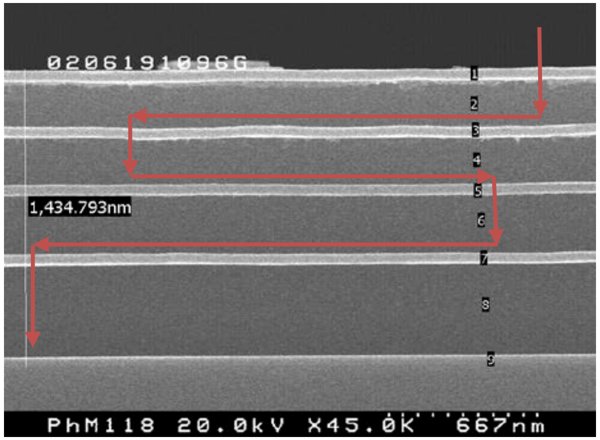


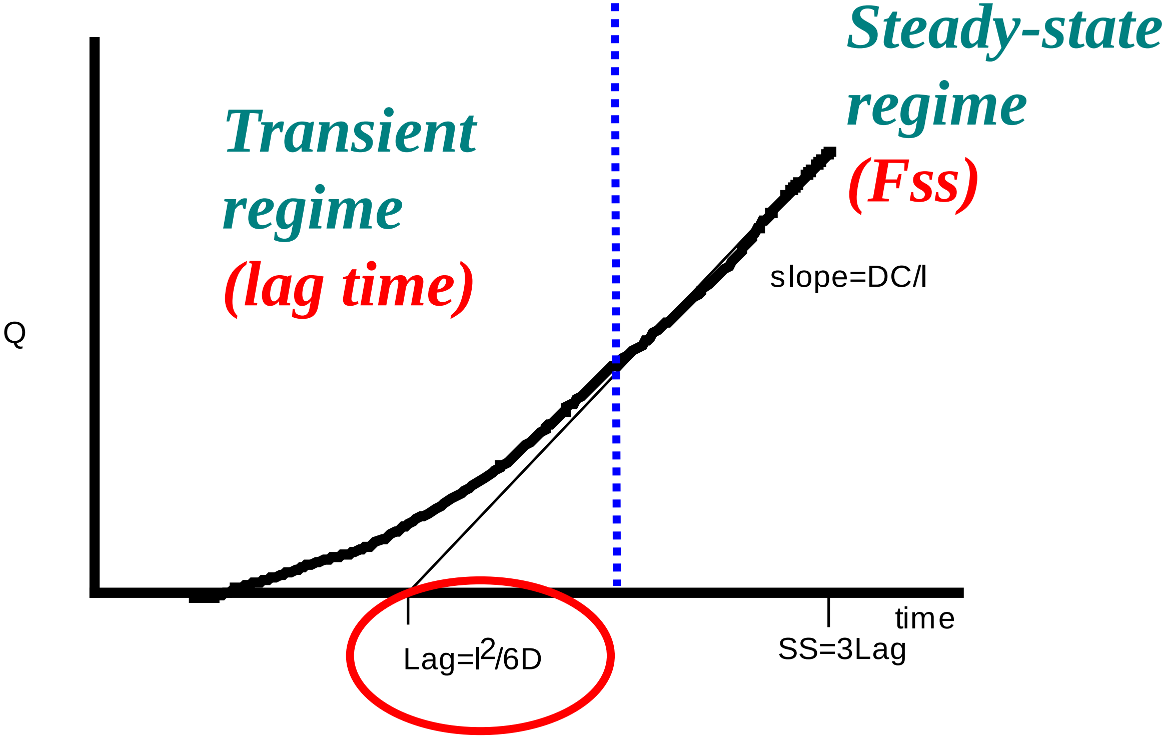
Barrier on PEN sheets

- Typical permeation measured by Ca-test for processes with 100% yield:
  - WVTR @ 85/85 = 2-6 x 10^{-6} g/m²-day
    - WVTR @ 20/50 < 1 x 10^{-7} g/m²-day

L. Moro, et. al.,
Flextech Workshop
Sep. 14, 2011
(with permission)

Transient (Multilayer) Regime



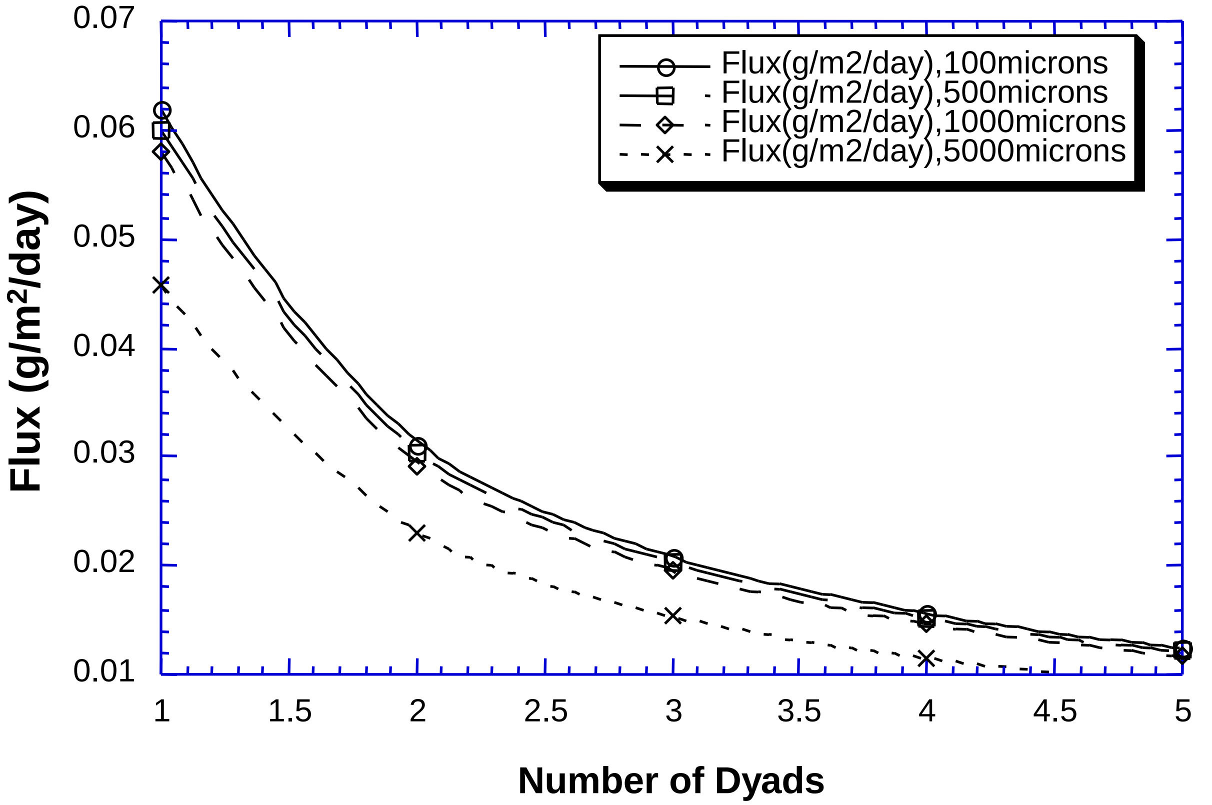


Transient regime ***(lag time)***

Steady-state regime ***(Fss)***

Application of models to multilayer systems

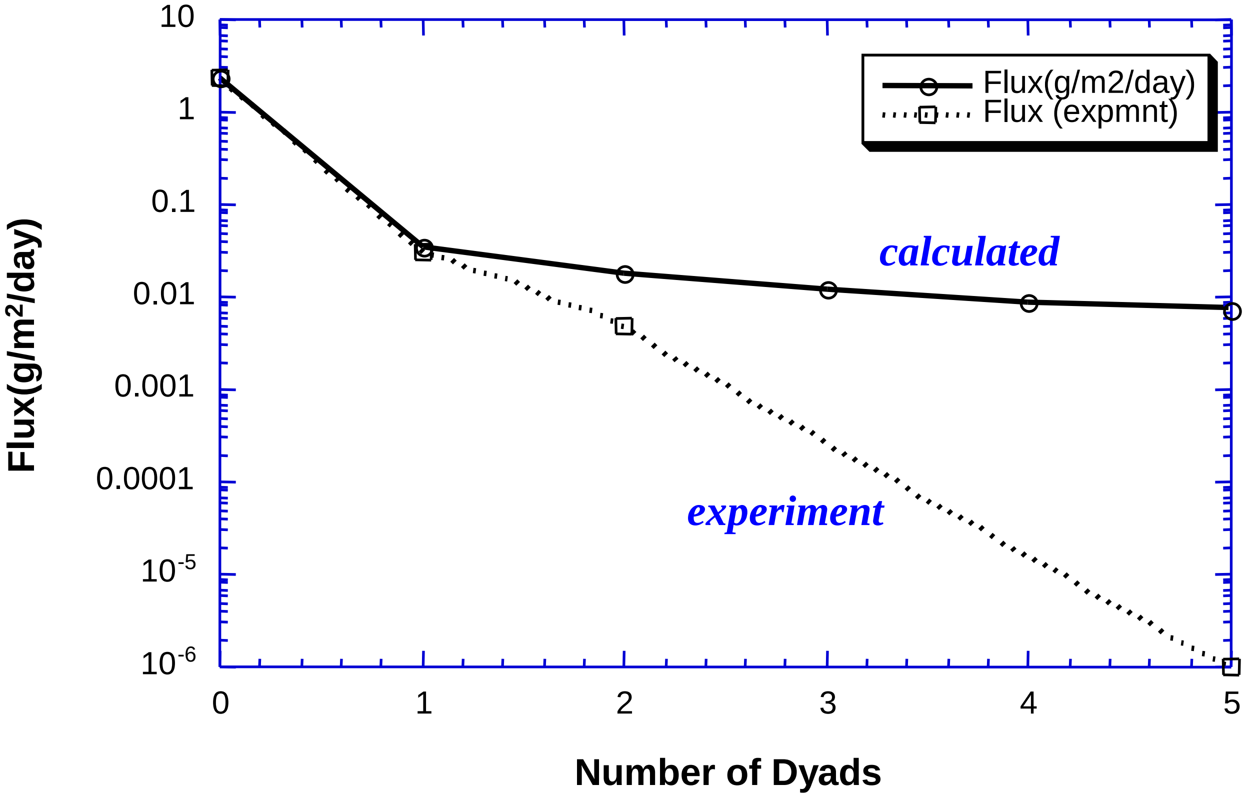
Steady state flux (Fss) calculations with varying D(AlOx)



calculated values are orders of magnitude higher than the empirical data

Application of models to multilayer systems

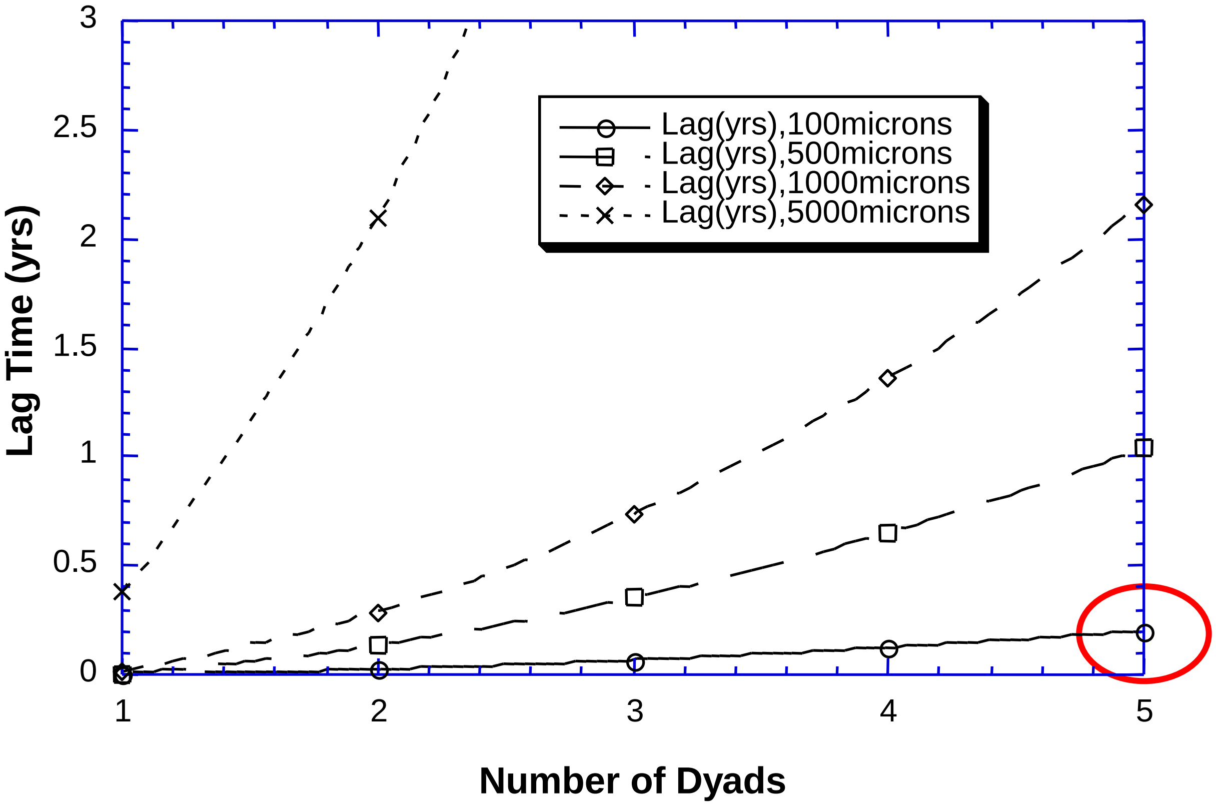
Steady state flux (Fss) calculations



- ***poor fit of models to empirical data***

Application of models to multilayer systems

Lag time (L) calculations

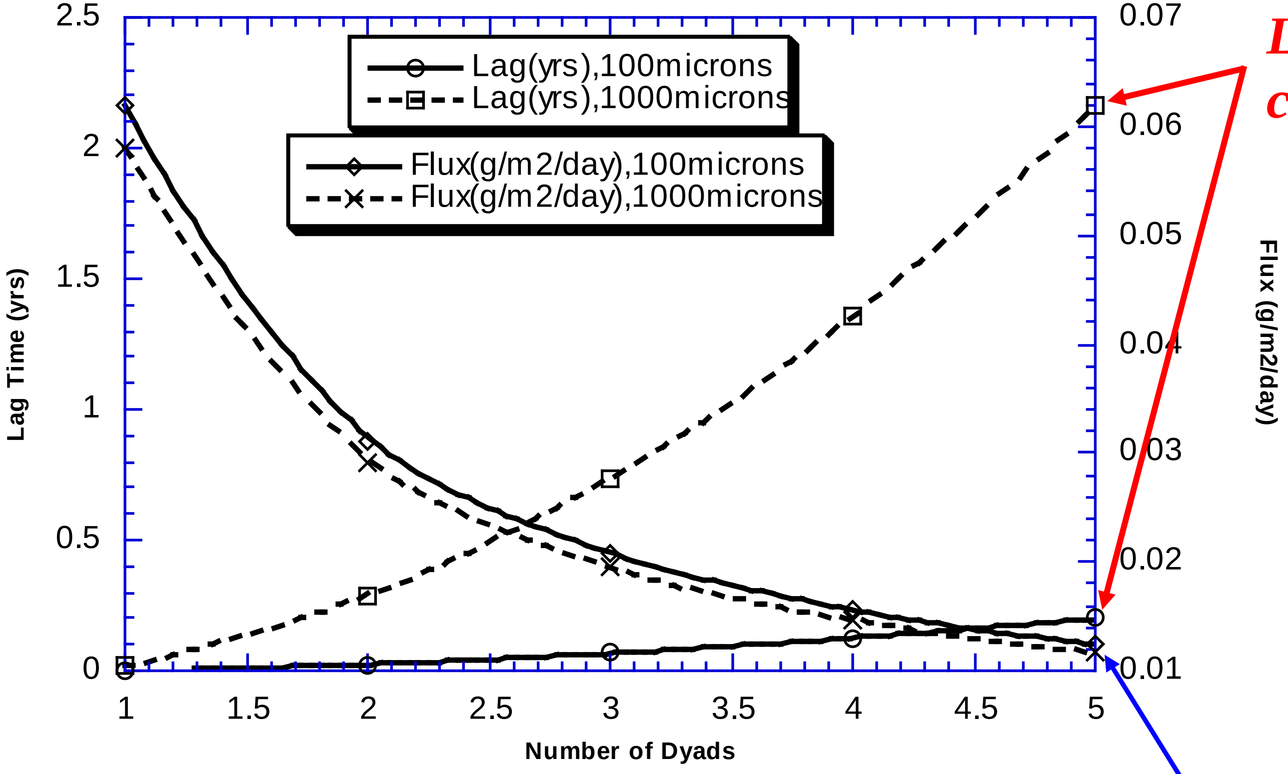


Lag time is >2000 hours

- *lag times are substantial (years)!*

Application of models to multilayer systems

Relative importance of 10x change in defect spacing on Fss versus L



Lag time change

Fss change

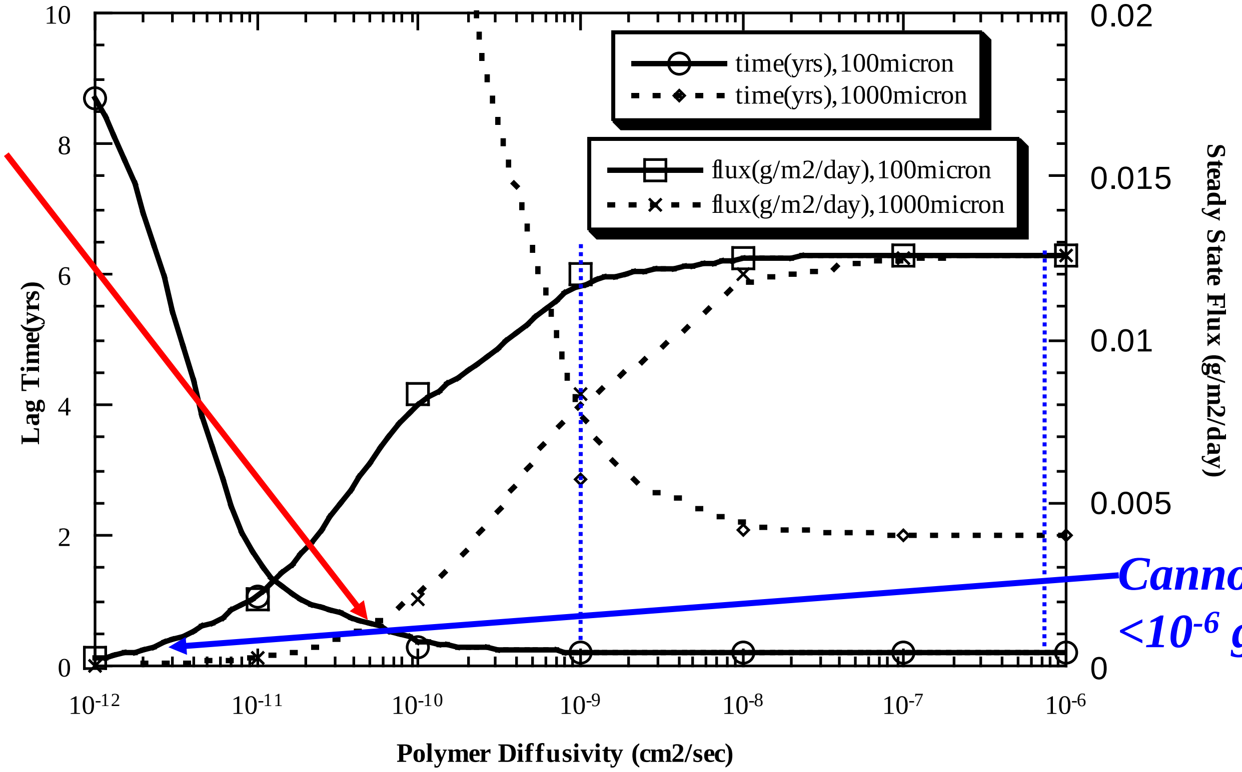
- ***Fss decreases by <0.005 g/m^2/d***
- ***L increases by >10x***

Pacific Northwest
NATIONAL LABORATORY

Polymer effects in multilayer systems

Polymer "D" effects – 5dyad stack

D <10^{-10} required to improve Lag time

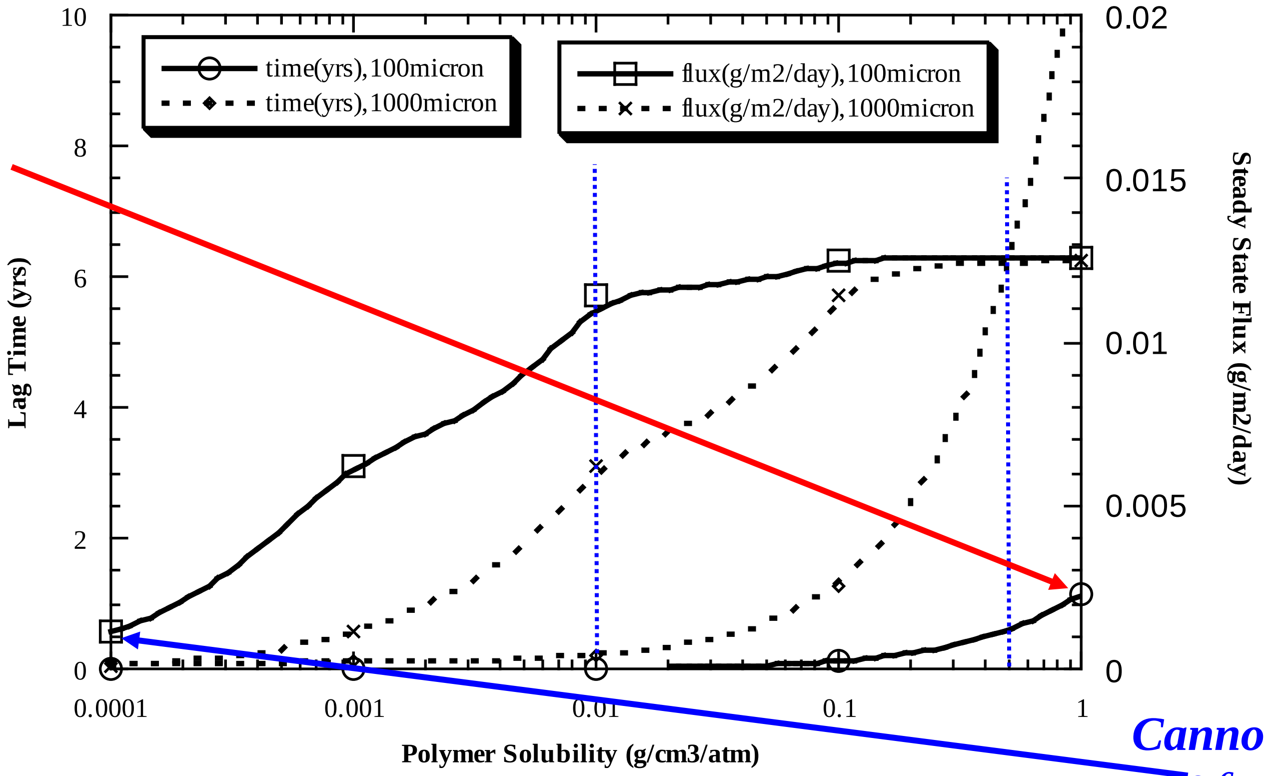


Cannot attain Fss <10^{-6} g/m^2/d

Practical range for polymers: D = 10^{-9} to 10^{-6} cm^2/s

Polymer effects in multilayer systems

Polymer "S" effects – 5dyad stack



S >1.0 required to improve Lag time

Cannot attain Fss $<10^{-6}$ g/m^2/d

Practical range for polymers: S = 0.01 to 0.5

Reported Defect Sizes and Spacings in Thin Films

Defect diameter (μm)	Defect density (mm^{-2})	Defect Spacing (μm)	Coating material	Deposition Method	Substrate	Ref.
1.2	11-1100	30 -300	SiO_2	PECVD	PET	i
1.2	5-1000	32 - 450	Si_3N_4	PECVD	PET	i
2.0	25-400	50 - 200	Al	evap	PET	ii
2.0	100-300	58 - 100	Al	evap	PET	iii
4-6	200	71	Al	sputtering	PET	iv
1.0-2.8	600	41	AlO_xN_y	sputtering	PET	v
0.8	100-1000	32 - 100	Al	evap	BOPP	vi
1.0	700	38	AlO_xN_y	sputtering	PET	vii

Construct hypothetical 5-dyad stacks using measured defect distributions

i. S. da Silva Sobrinho, G. Czeremuszkin, M. Latrache and M. R. Wertheimer, J. Vac. Sci. Technol. A, **18,** 1, 149 (2000).

ii. E. H. H. Jamieson and A. H. Windle, J. Mater. Sci., **18,** 64 (1983)

iii. H. Chatham, Surfaces and Coatings Technology, **78,** 1 (1996)

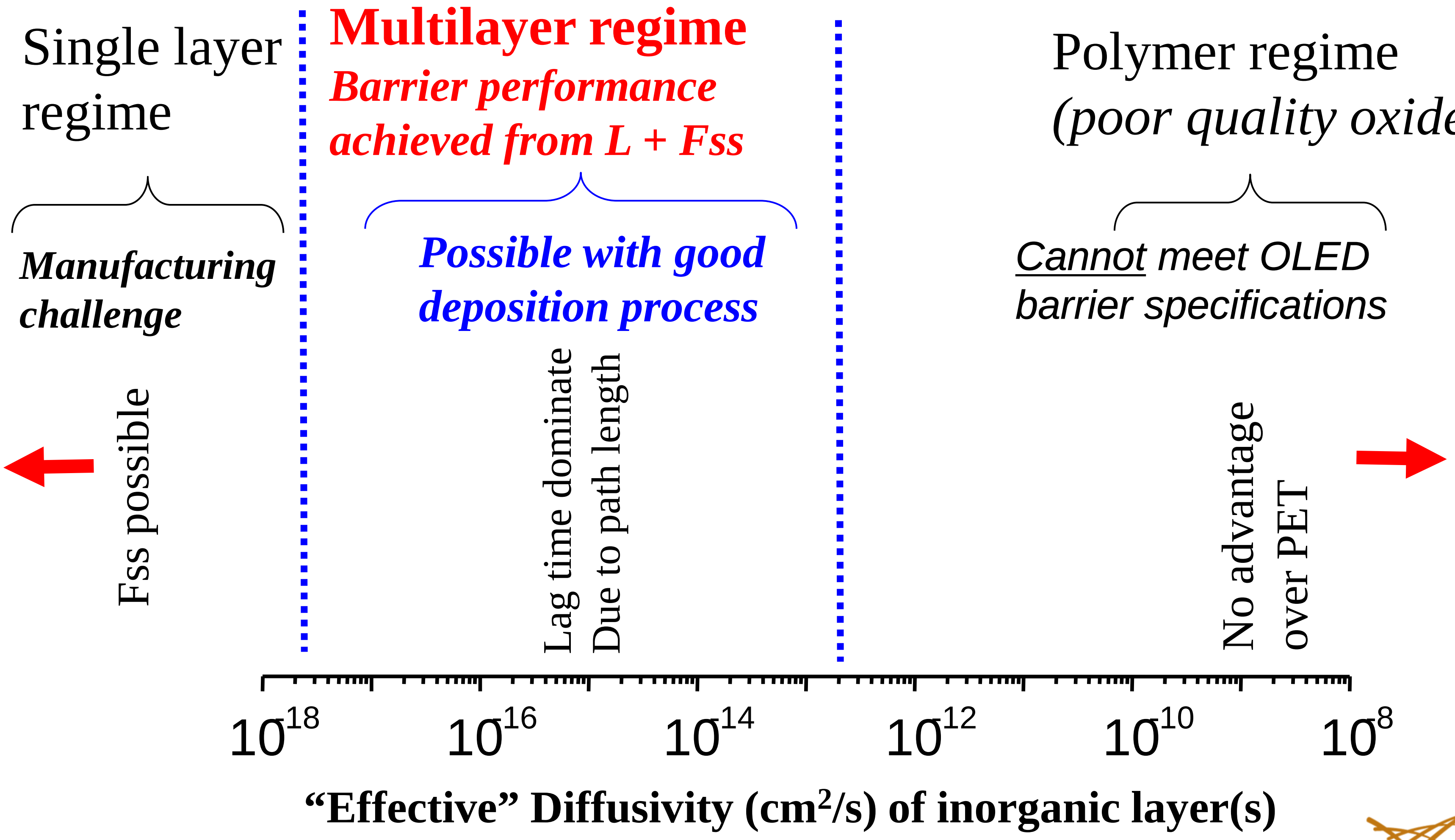
iv. H. Hanika, H.-C. Langowski and U. Moosheimer, 45th Annual Tech. Conf. Preceedings, Soc. Vac. Coat., 519-24 (2002)

v. A. G. Erlat et.al., Thin Solid Films, **388,** 78-86 (2001)

vi. H. Hanika, H.-C. Langowski and W. Peukert, 46th Annual Tech. Conf. Preceedings. Soc. Vac. Coat., 592-599 (2003)

vii. A. G. Erlat, B. M. Henry, C. R. M. Grovenor, A. G. D. Briggs, R. J. Chater and Y. Tsukahara, J. Phys. Chem. B, **108,** 883-890 (2004)

Thin-film Barrier "Regimes"



Single layer regime

Manufacturing challenge

Fss possible

Multilayer regime

Barrier performance achieved from L + Fss

Possible with good deposition process

Lag time dominate
Due to path length

Polymer regime
(poor quality oxide)

<u>Cannot</u> meet OLED barrier specifications

No advantage
over PET

Conclusions

- **High quality inorganic films *coupled* with a multilayer architecture are necessary to achieve OLED barrier requirements**
- **Lag time (transient diffusion), not steady-state flux, has a significant effect on gas permeation in these multilayer thin-film systems**
- **Consideration of steady state flux, alone, is not sufficient to describe (and predict) the performance of multilayer barrier films – must consider the transient regime**

Implications for Manufacturing

- Greatest gains come from improving inorganic layers (minimize defects, increase defect spacing and lower D_{eff} of AlOx layers)
- Lowering the P (D&S) of the polymer (crosslinking, surface treatments, composite gradients) will improve the barrier performance
- Once the lag time is exceeded, the steady state flux for the multilayer systems should exceed the permeation requirement (F_{SS}) for OLED devices
- Multiple polymer/inorganic layering allows use of “high-quality, manufacturable” thin-films – and does not require “near-perfect” inorganic layers
- Poor quality (high defect density) inorganic films cannot be used for OLED applications – even if assembled in multilayer structures
- Measurement of steady-state diffusion (F_{SS}) may require testing >2000hrs

Future Needs

- High rate, low cost, scalable "ultrabarrier quality" thin-film deposition techniques
- More accurate predictive models – preferably ones that can use single layer/dyad validated data and predict permeation in more complex assemblies
- Standardized permeability measurement techniques for ultrabarriers (WVTR of 10^{-8} to 10^{-4} g/m^2/d)
- Failure mechanisms (WVTR tolerance) of sensitive electronic devices (such as thin-film PV or OPV)