NIST Diffusion Workshop

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Diffusion Barriers: Overview

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DIFFUSION BARRIERS

Objective: “Prevent” or at least minimize
diffusional intermixing between layers

Properties / Requirements

-Transport rate of A and B across X must be small
-The loss rate of A and B across X must be small
-X must be thermodynamically stable with A and B
-X must have strong adhesion to A and B
-X must be laterally uniform (thickness & structure)
-X must resist thermal/mechanical stress
-X must be thermally conducting (insulating)
-X must be electrically conducting (insulating)
-X must be compatible with materials processing

Conclusion: A “perfect” diffusion barrier does not exist.
It is often easier to specify what should not be done rather than what should be done.
M.a. Nicolet, Thin Solid Films, 52,415 (1978)

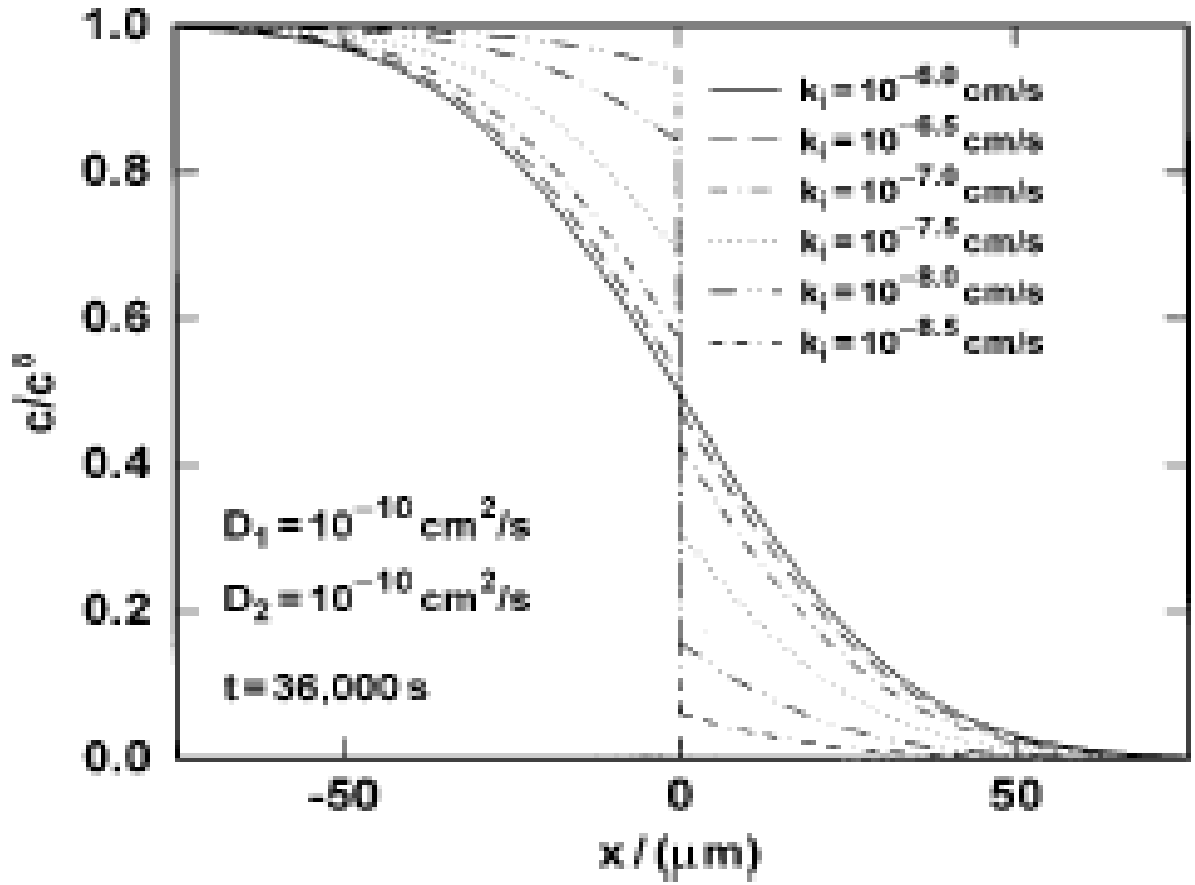
DIFFUSION BARRIERS

TYPES:

- -Immiscible layers
- -Single crystal layer
- -Amorphous layers
- -Compound layers
- -Reacted layers
- -Multilayers
- -Sacrificial layers
- -Stuffed barriers

Some Applications:

- Thin film metallizations
- Coatings
- Permeation barriers
  - Food packaging
  - Gas lines



L. Tian, et al, Jnl. Appl. Phys., 90, 3799(2001)

$$D_1\left(\partial c_1/\partial x\right)+k\left(c_2-c_1\right)=0$$

$$D_1\left(\partial c_1/\partial x\right)=D_2\left(\partial c_2/\partial x\right)$$

At x=0

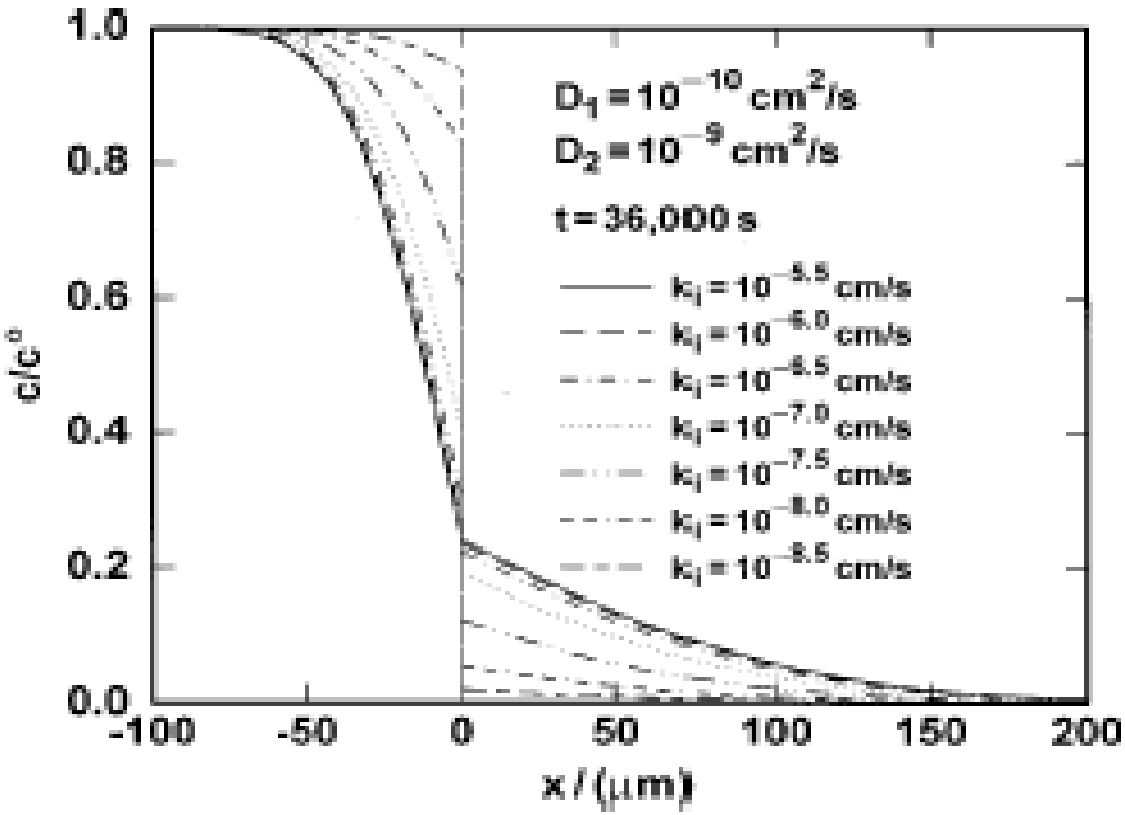
Interface Resistance

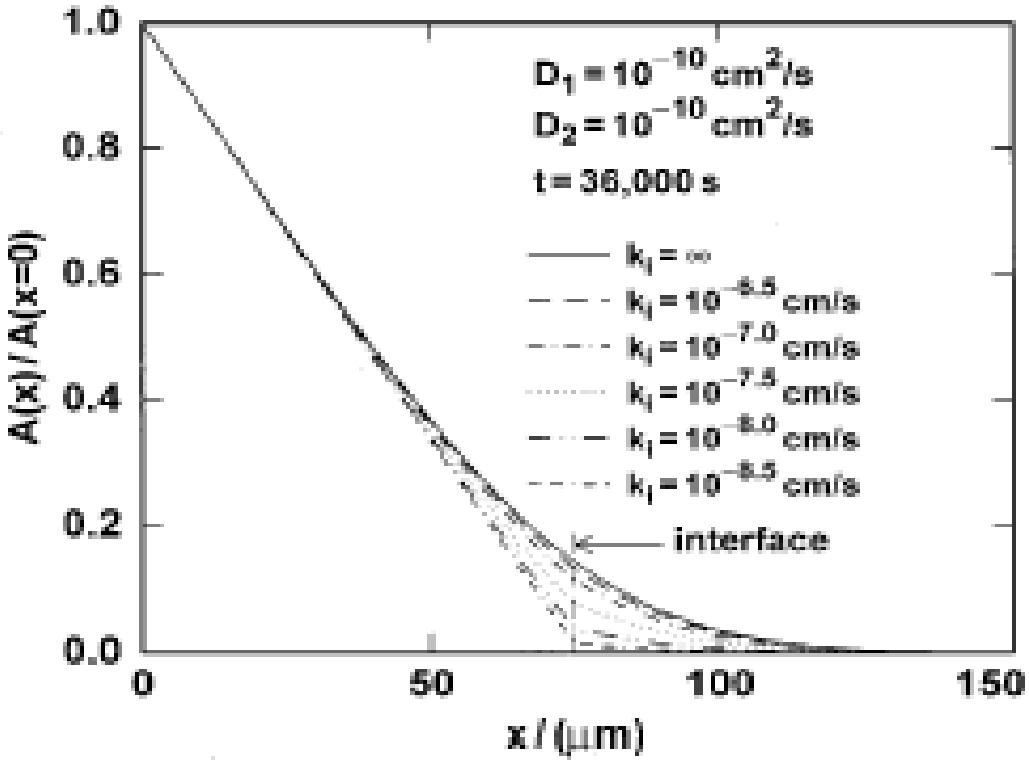
$$c_1 = \frac{c_0}{1+(D_2/D_1)^{1/2}}\left[1+\left(\frac{D_2}{D_1}\right)^{1/2}\left\{erf\,\frac{x}{2\sqrt{(D_1 t)}}+\exp\left(h_1 x+h_1^2 D_1 t\right)erfc\left(\frac{x}{2\sqrt{(D_1 t)}}+h_1\sqrt{(D_1 t)}\right)\right\}\right]$$

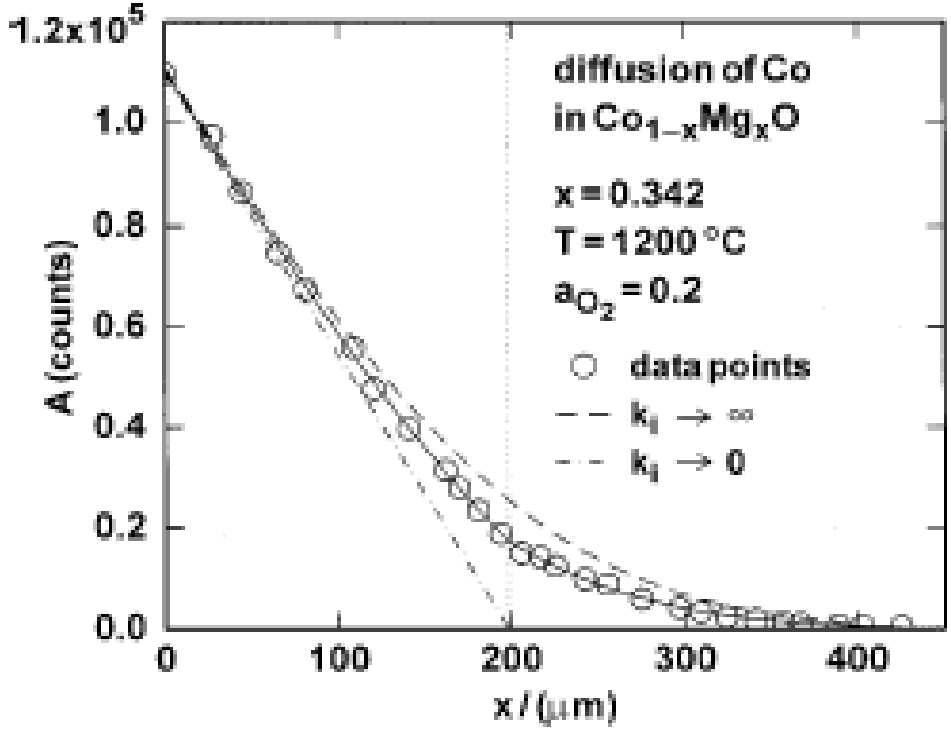
$$c_2 = \frac{c_0}{1+(D_2/D_1)^{1/2}}\left\{erfc\,\frac{x}{2\sqrt{(D_2 t)}}-\exp\left(h_2 x+h_2^2 D_2 t\right)erfc\left(\frac{x}{2\sqrt{(D_2 t)}}+h_2\sqrt{(D_2 t)}\right)\right\}$$

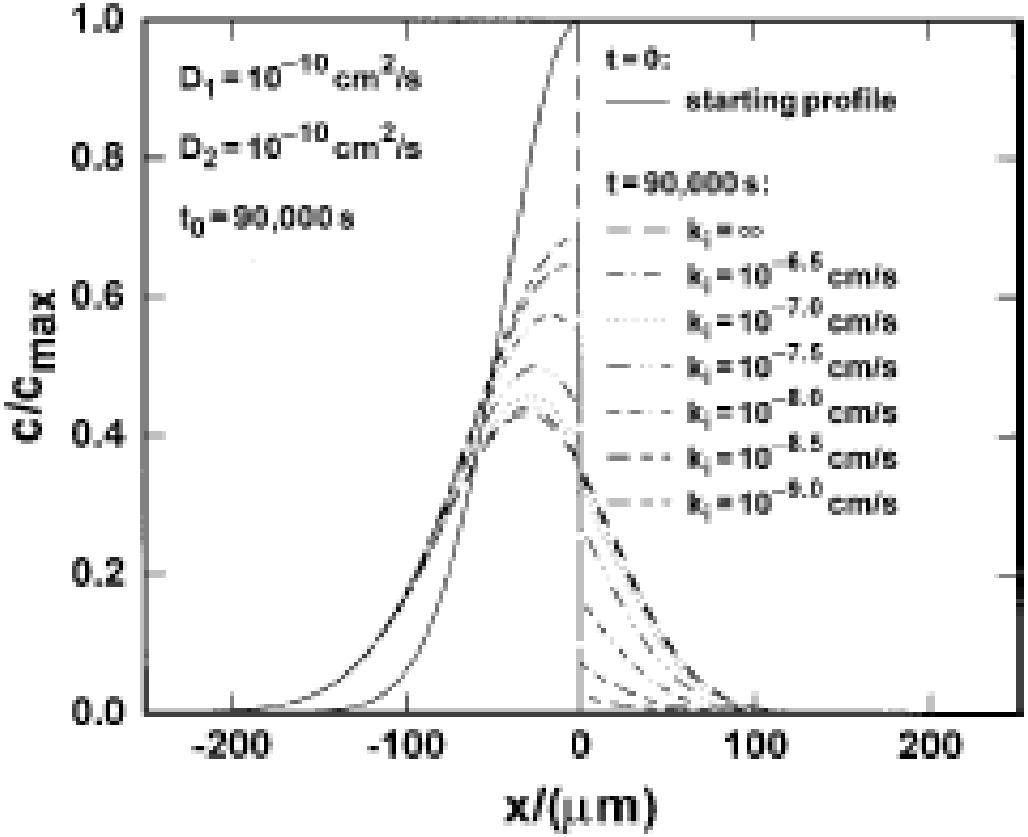
$$h_1 = \frac{k}{D_1}\left\{1+(D_1/D_2)^{1/2}\right\}$$

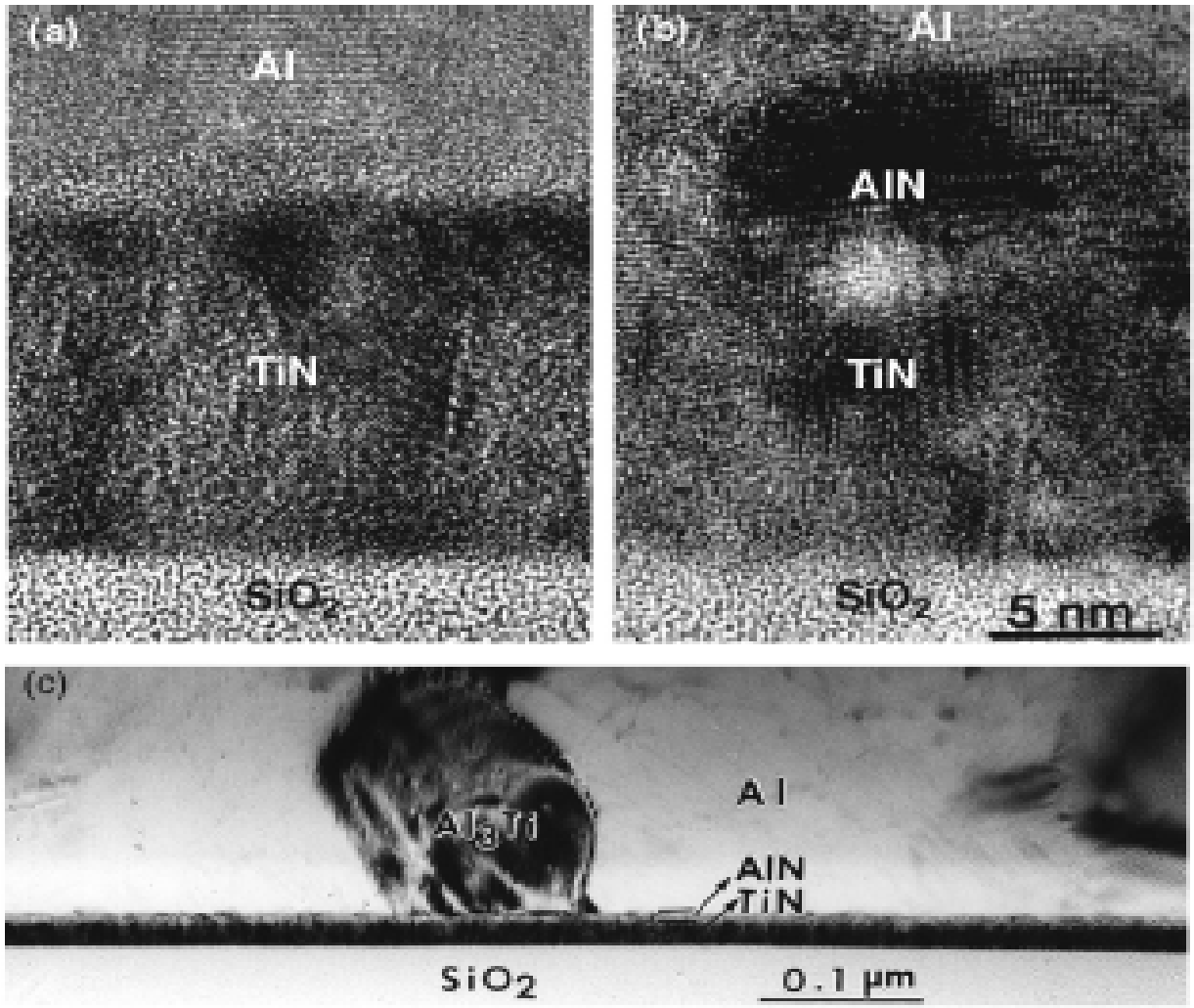
$$h_2 = \frac{k}{D_2}\left\{1+(D_2/D_1)^{1/2}\right\}$$


1.0
0.8
0.6
0.4
0.2
0.0
c/c°
-100
-50
0
50
100
150
200
x / (μm)
D1 = 10^-10 cm^2/s
D2 = 10^-9 cm^2/s
t = 36,000 s
k1 = 10^-5.5 cm/s
k1 = 10^-6.0 cm/s
k1 = 10^-6.5 cm/s
k1 = 10^-7.0 cm/s
k1 = 10^-7.5 cm/s
k1 = 10^-8.0 cm/s
k1 = 10^-8.5 cm/s

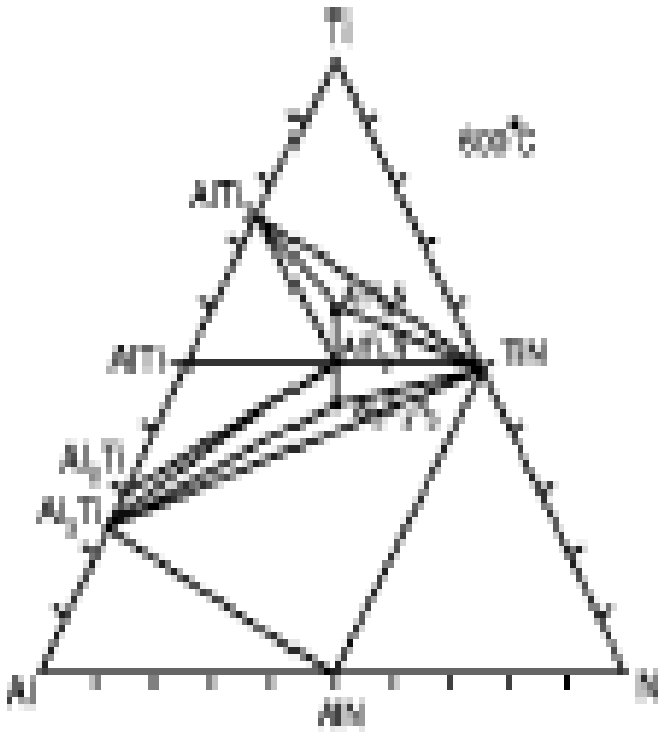

1.0
0.8
0.6
0.4
0.2
0.0
A(x) / A(x=0)
0
50
100
150
x / (μm)
D1 = 10−10 cm2/s
D2 = 10−10 cm2/s
t = 36,000 s
k1 = ∞
k1 = 10−5.5 cm/s
k1 = 10−7.0 cm/s
k1 = 10−7.5 cm/s
k1 = 10−8.0 cm/s
k1 = 10−8.5 cm/s
interface


1.2x10^5
1.0
0.8
0.6
0.4
0.2
0.0
A (counts)
0
100
200
300
400
x / (μm)
diffusion of Co
in Co1-xMgxO
x = 0.342
T = 1200 °C
aO2 = 0.2
data points
ki → ∞
ki → 0


1.0
0.8
0.6
0.4
0.2
0.0
c/c_max
-200
-100
0
100
200
x/(μm)
D1 = 10^-10 cm^2/s
D2 = 10^-10 cm^2/s
t0 = 90,000 s
t = 0:
starting profile
t = 90,000 s:
k1 = ∞
k1 = 10^-6.5 cm/s
k1 = 10^-7.0 cm/s
k1 = 10^-7.5 cm/s
k1 = 10^-8.0 cm/s
k1 = 10^-8.5 cm/s
k1 = 10^-9.0 cm/s

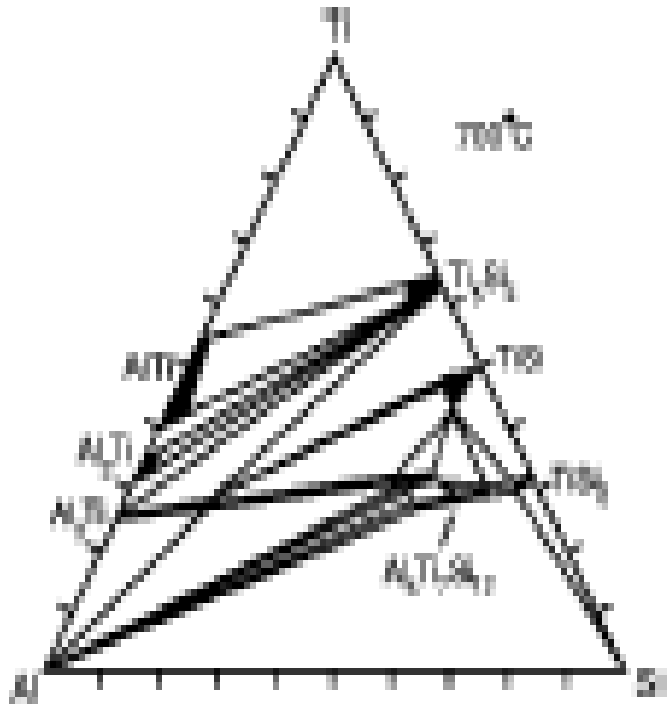


H-J. Lee, et al, Jnl. Appl. Phys.,86, 3097(1999)



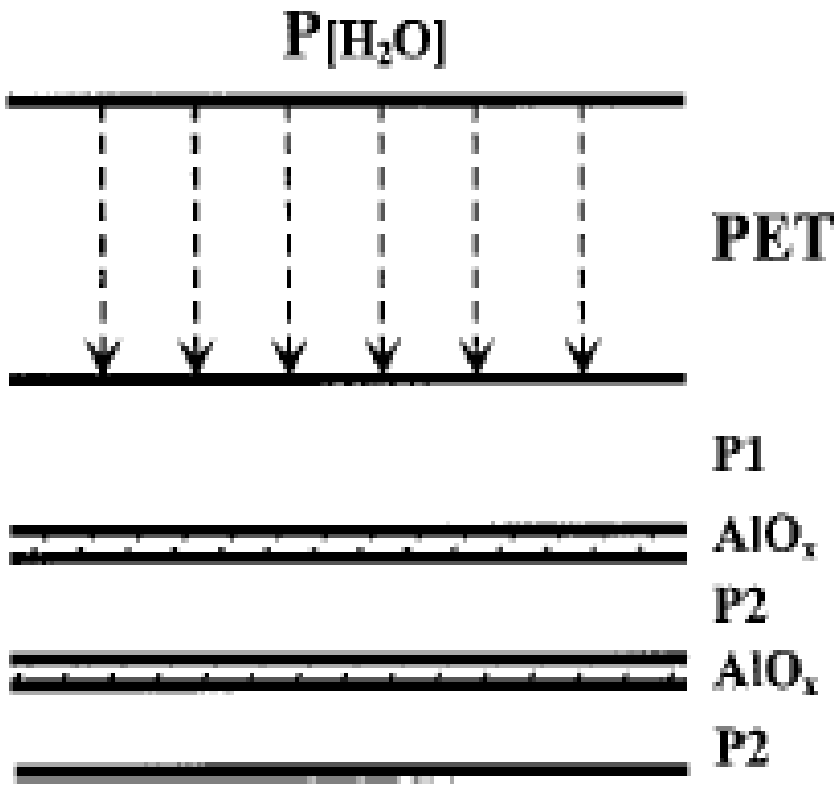
Al - Ti - N

(A.S. Murakami, PhD Thesis, Stanford, 1987)

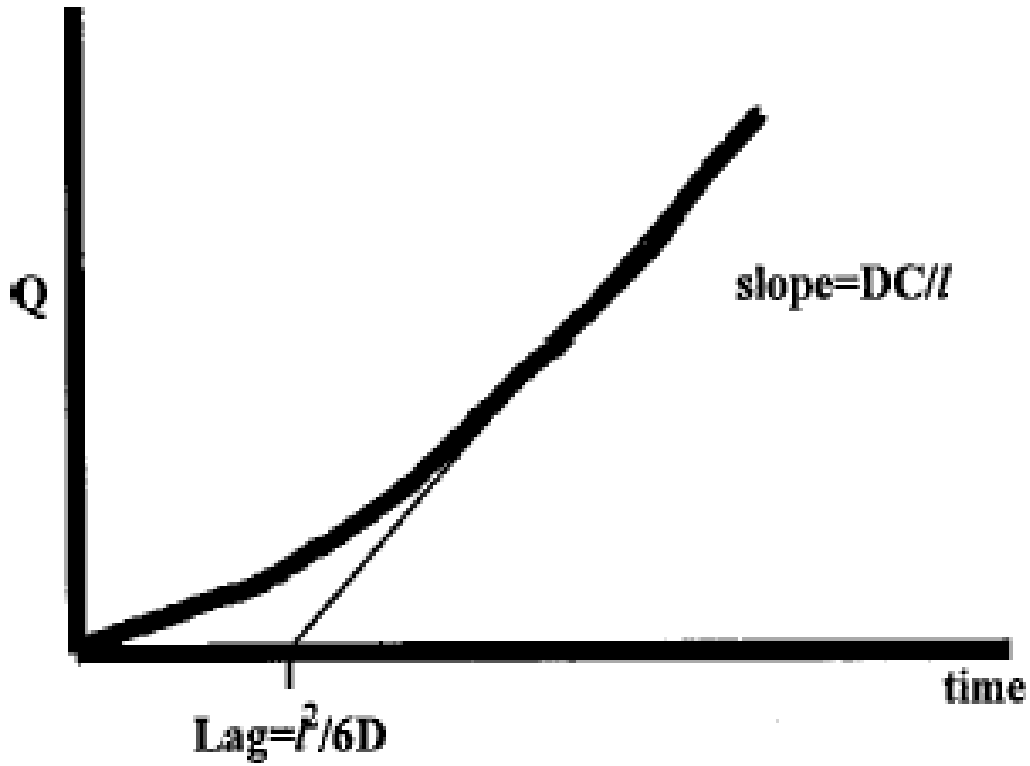


Al - Ti - Si

(redrawn after A Ramos et. al., Z. Metallkde. 74, 44, 1983)



G.L. Graff, et. al.,Jnl. Appl. Phys. 96, 1840(2004)


Q
slope=DC/l
time
Lag=l²/6D

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

$$Q(t) = \int_0^t J(x=l,t)dt = \frac{DtC_l}{l} - \frac{lC_l}{6}$$

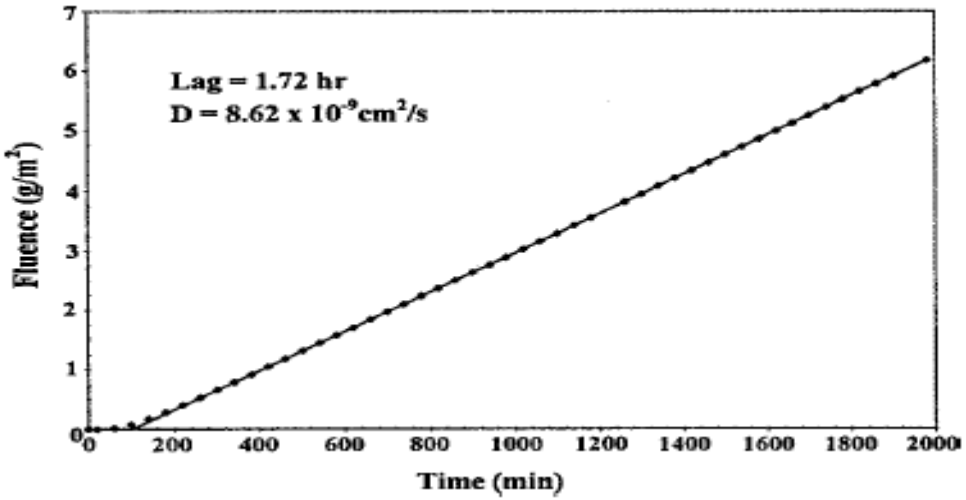
$$-\frac{2lC_l}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left(-Dn^2\pi^2 t/l^2\right)$$

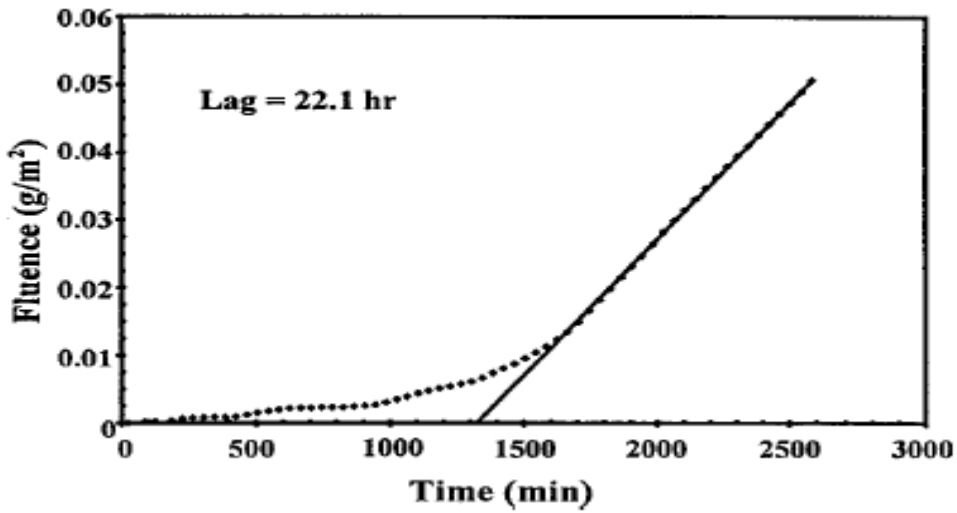
$$Q(t\to\infty) = \frac{DC_l}{l}\left(t-\frac{l^2}{6D}\right)$$

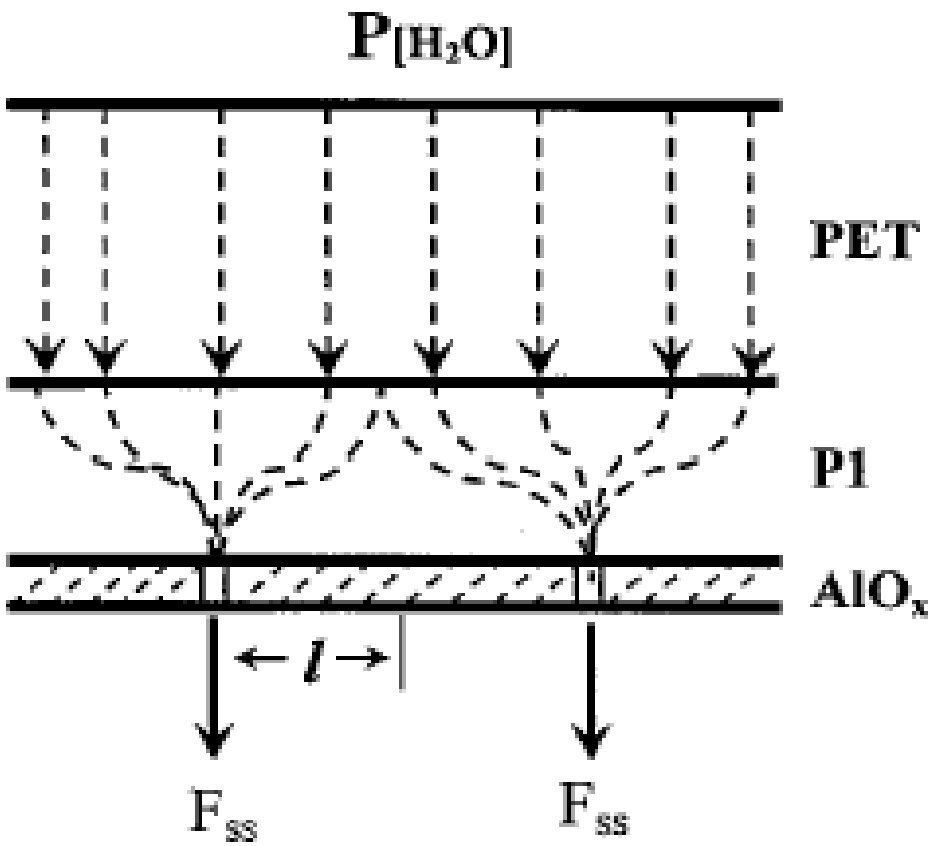
$$P_e = {J_{ss}l}\big/{\Delta P} = DS$$

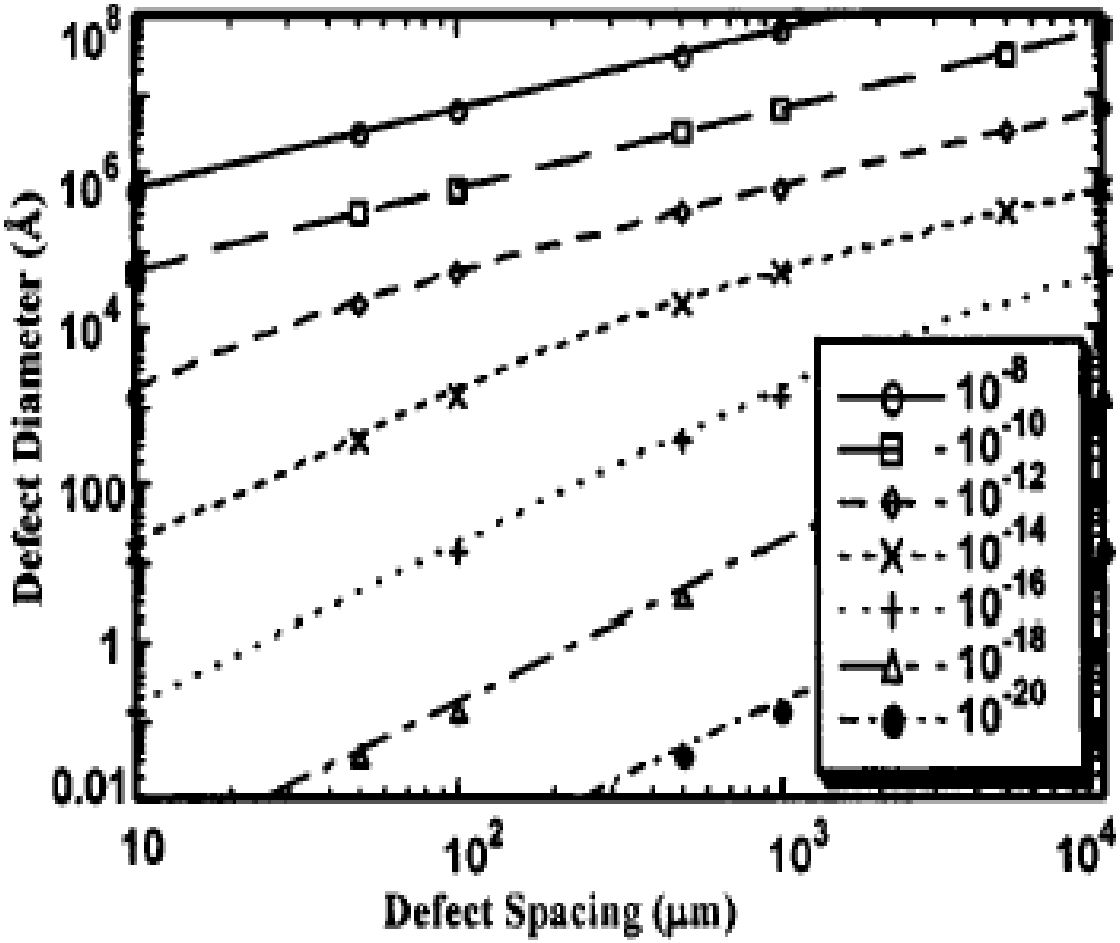
$$S = J_{ss}l/D\Delta P$$

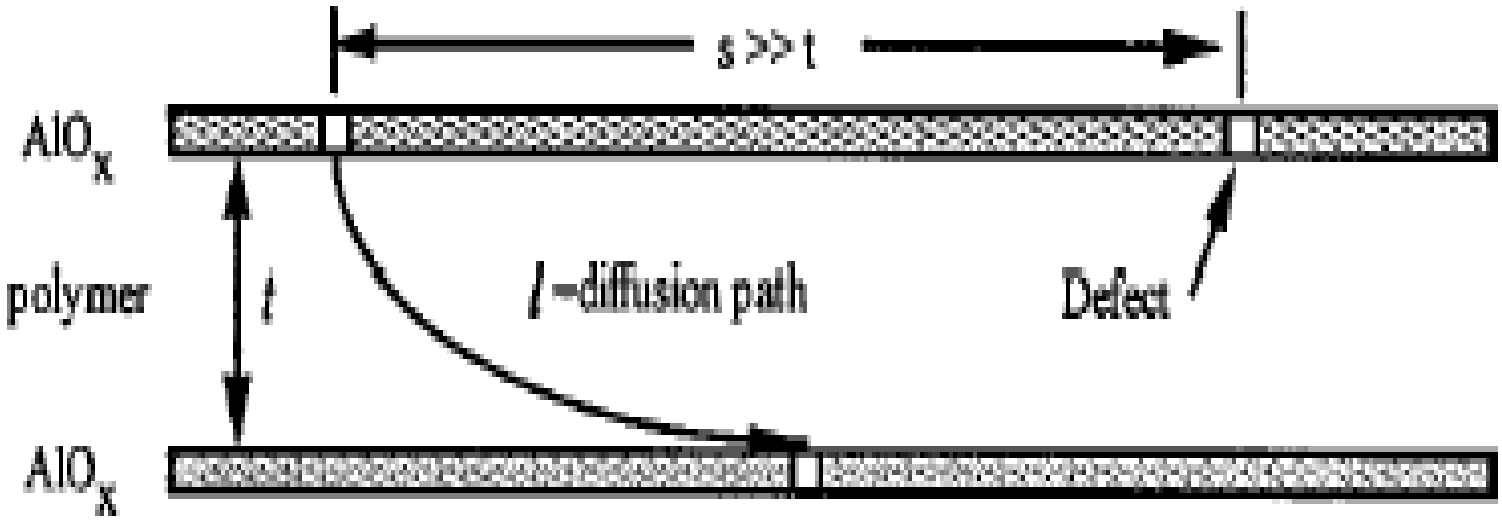
$$Jss = \frac{P}{\frac{l_1}{D_1S_1}+\frac{l_2}{D_2S_2}+.....+\frac{l_n}{D_nS_n}}$$

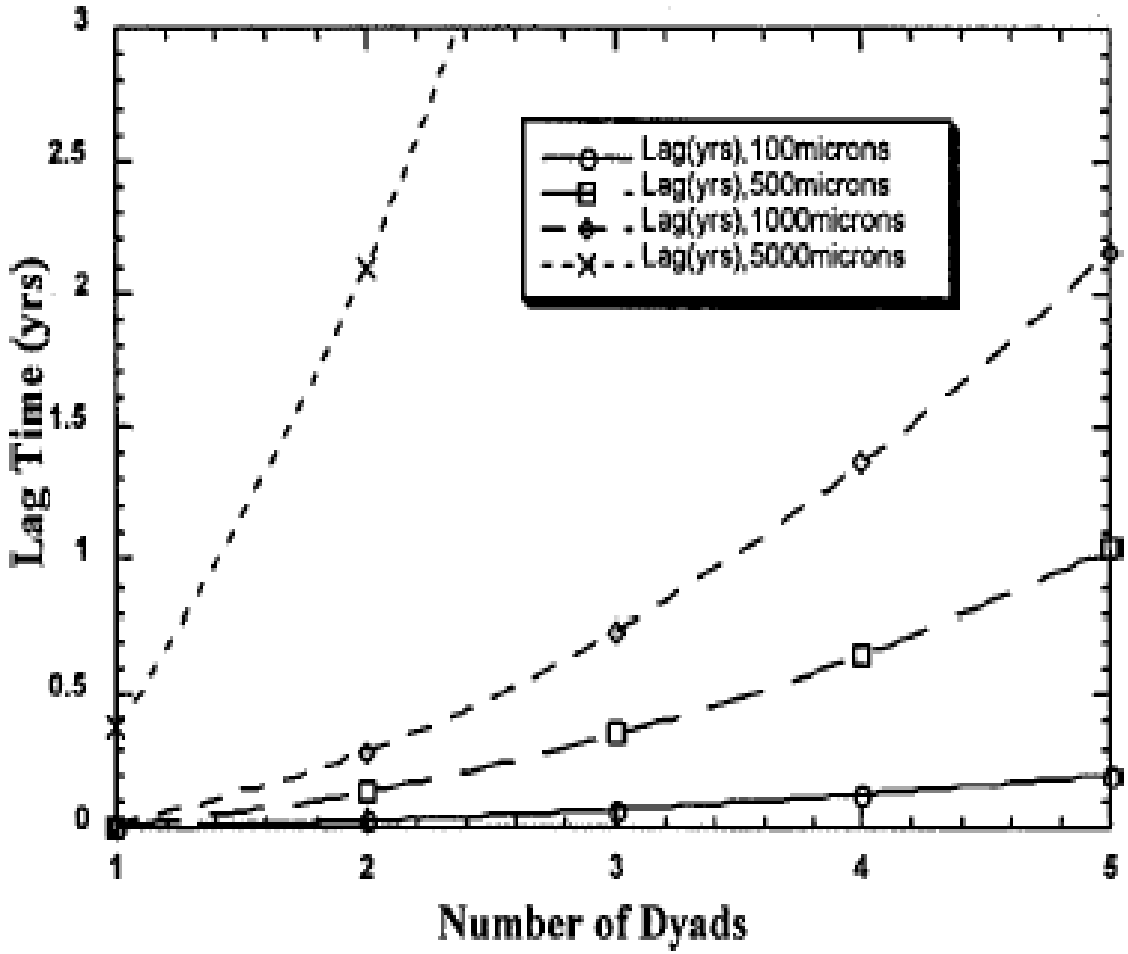

Lag = 1.72 hr
D = 8.62 x 10^{-9}cm^2/s
Fluence (g/m^2)
Time (min)
0
1
2
3
4
5
6
7
0
200
400
600
800
1000
1200
1400
1600
1800
2000

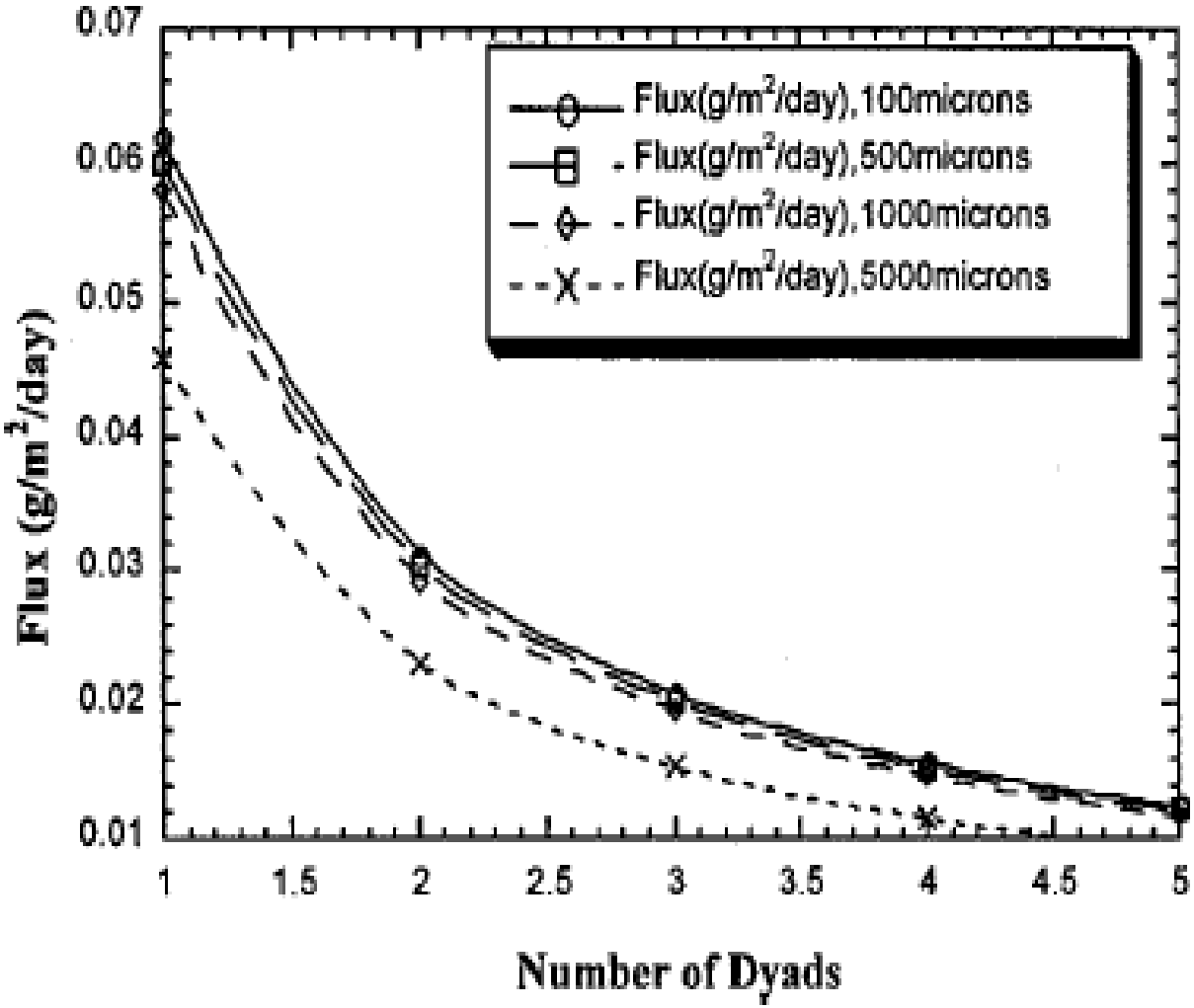

Lag = 22.1 hr
Fluence (g/m^2)
Time (min)
0
0.01
0.02
0.03
0.04
0.05
0.06
0
500
1000
1500
2000
2500
3000

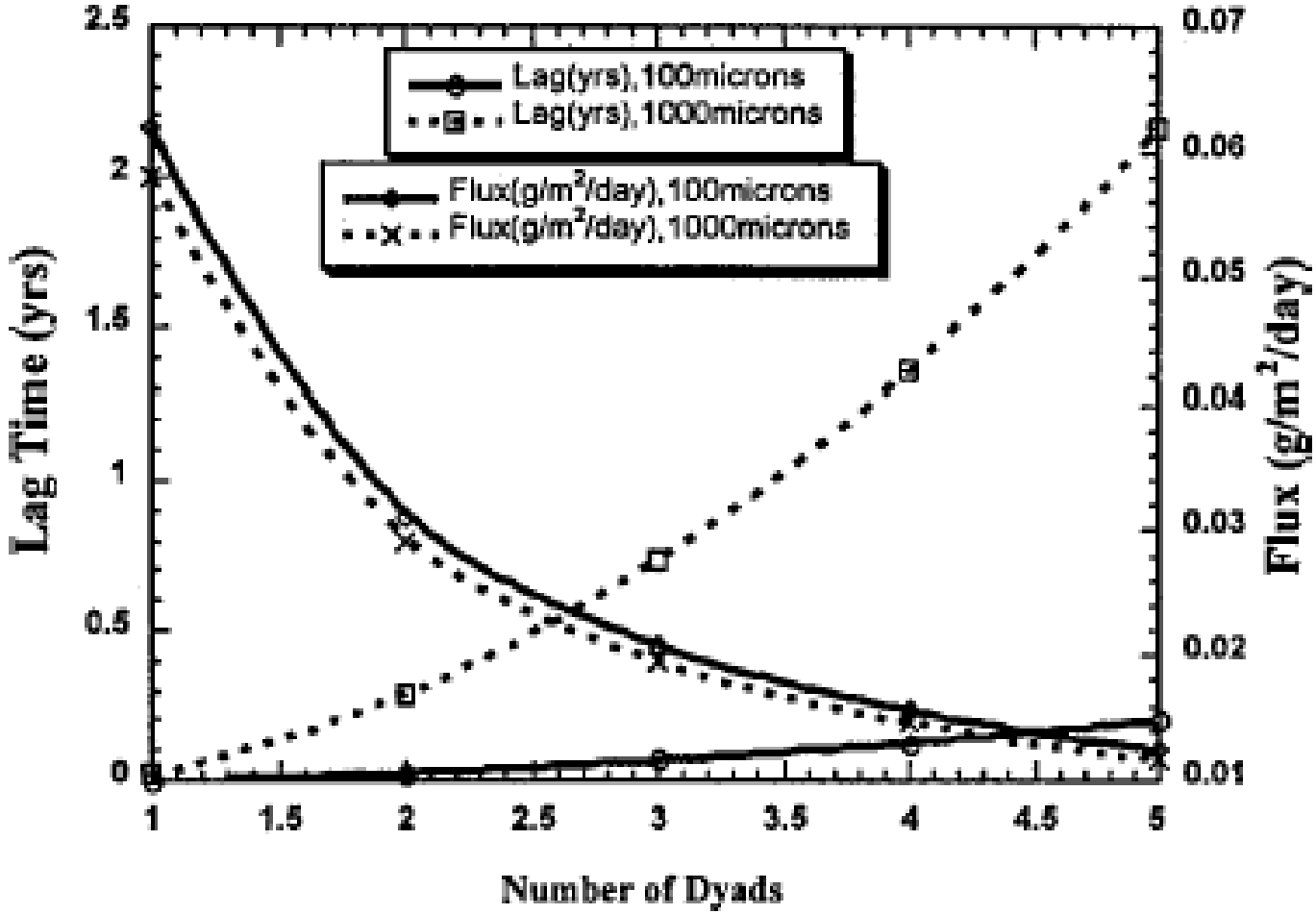

P[H2O]
PET
P1
AlOx
l
Fss
Fss

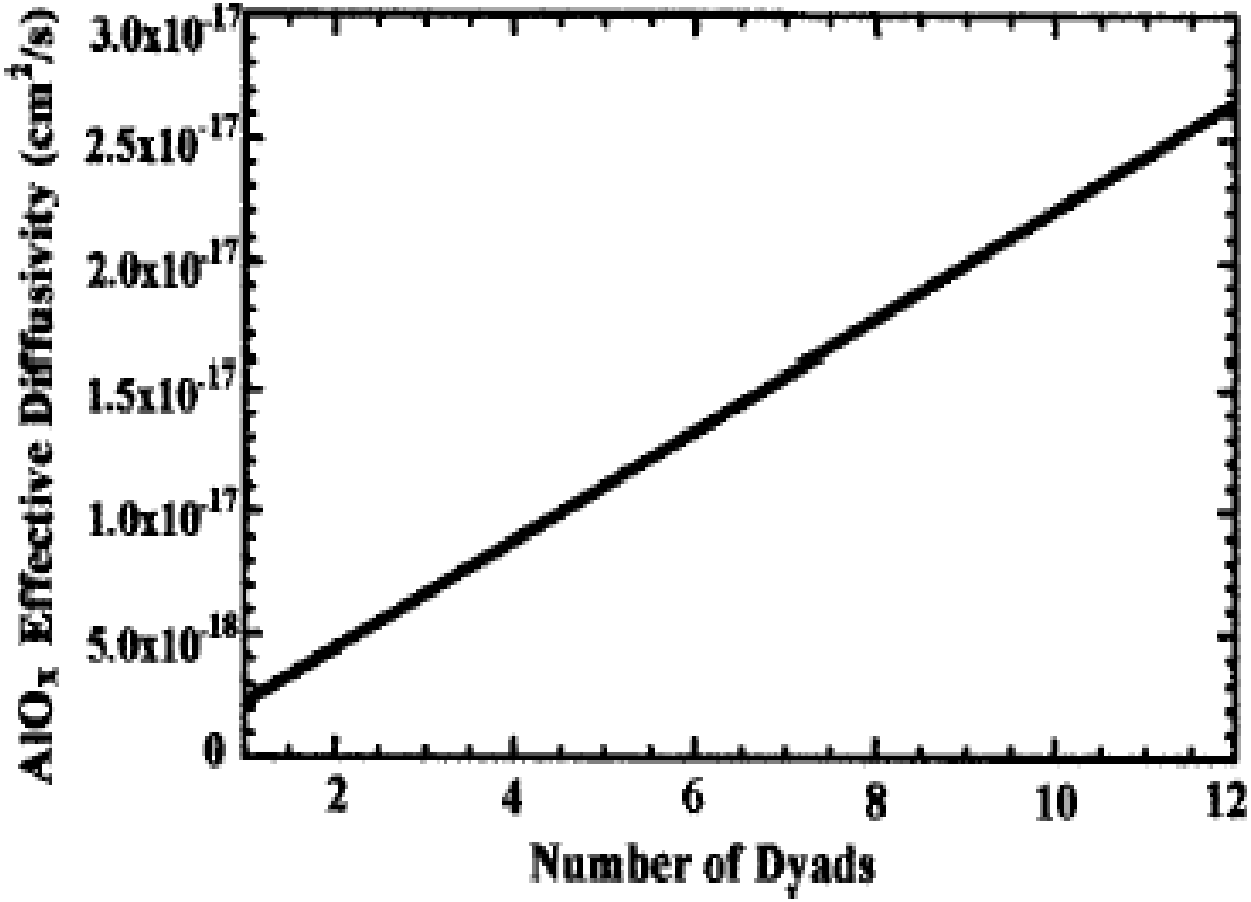
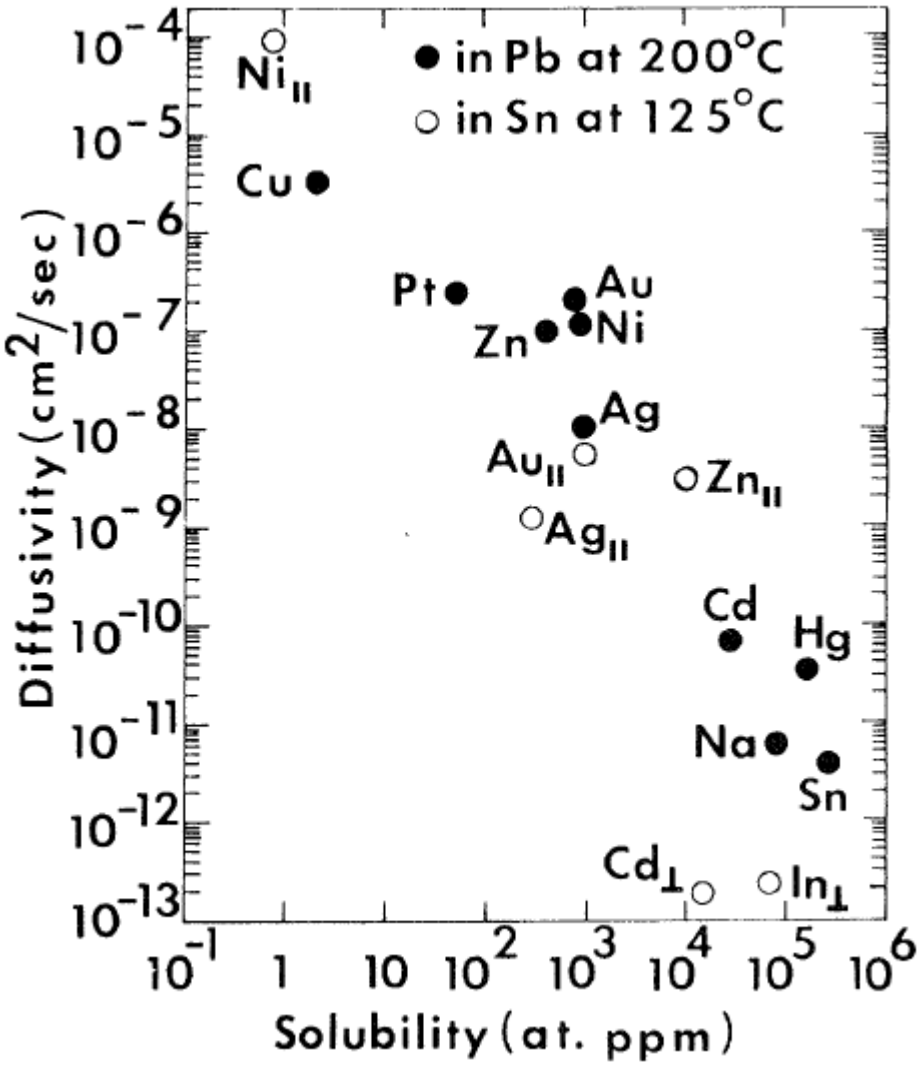

Defect Diameter (Å)
10^8
10^6
10^4
100
1
0.01
10
10^2
10^3
10^4
Defect Spacing (μm)
10^{-8}
10^{-10}
10^{-12}
10^{-14}
10^{-16}
10^{-18}
10^{-20}


s >> t
AlO$_x$
polymer
t
l =diffusion path
Defect
AlO$_x$


Lag Time (yrs)
Number of Dyads
Lag(yrs),100microns
Lag(yrs),500microns
Lag(yrs),1000microns
Lag(yrs),5000microns
0
0.5
1
1.5
2
2.5
3
1
2
3
4
5


Flux(g/m²/day),100microns
Flux(g/m²/day),500microns
Flux(g/m²/day),1000microns
Flux(g/m²/day),5000microns
Flux (g/m²/day)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
1
1.5
2
2.5
3
3.5
4
4.5
5
Number of Dyads


Lag(yrs),100microns
Lag(yrs),1000microns
Flux(g/m²/day),100microns
Flux(g/m²/day),1000microns
Lag Time (yrs)
Flux (g/m²/day)
Number of Dyads
2.5
2
1.5
1
0.5
0
0.07
0.06
0.05
0.04
0.03
0.02
0.01
1
1.5
2
2.5
3
3.5
4
4.5
5


AlOx Effective Diffusivity (cm2/s)
3.0x10-17
2.5x10-17
2.0x10-17
1.5x10-17
1.0x10-17
5.0x10-18
0
2
4
6
8
10
12
Number of Dyads

Yeh & Huntington