Ion Beam Mixing

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OUTLINE:

1) Introduction: Phenomenological Aspects of Ion Mixing

2) Ballistic Mixing

a) Recoil Mixing
b) Cascade Mixing

3) Thermodynamic Effects in Ion Mixing

4) Thermally-Assisted Ion Mixing

References:

- **Ion Beam Mixing in Metallic and Semiconductor Materials. M. Nastasi and J.W. Mayer, *Materials Science and Engineering*, R12, No. 1, May 1994**

- **Ion-Solid Interaction: Fundamentals and Applications, Nastasi *et al.,* (Cambridge University Press, 1996) Chapter 11**

OUTLINE:

1) **Introduction: Phenomenological Aspects of Ion Mixing**
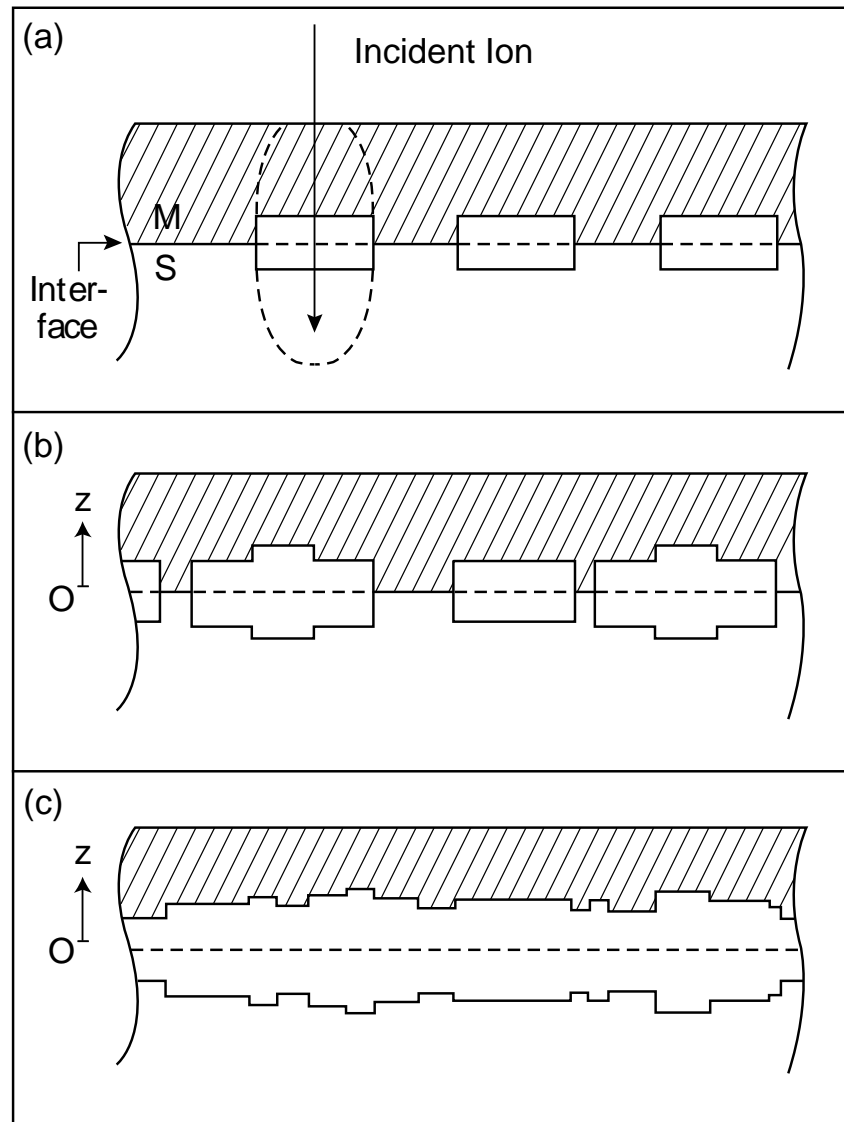
2) **Ballistic Mixing**

   a) **Recoil Mixing**
   b) **Cascade Mixing**

3) **Thermodynamic Effects in Ion Mixing**
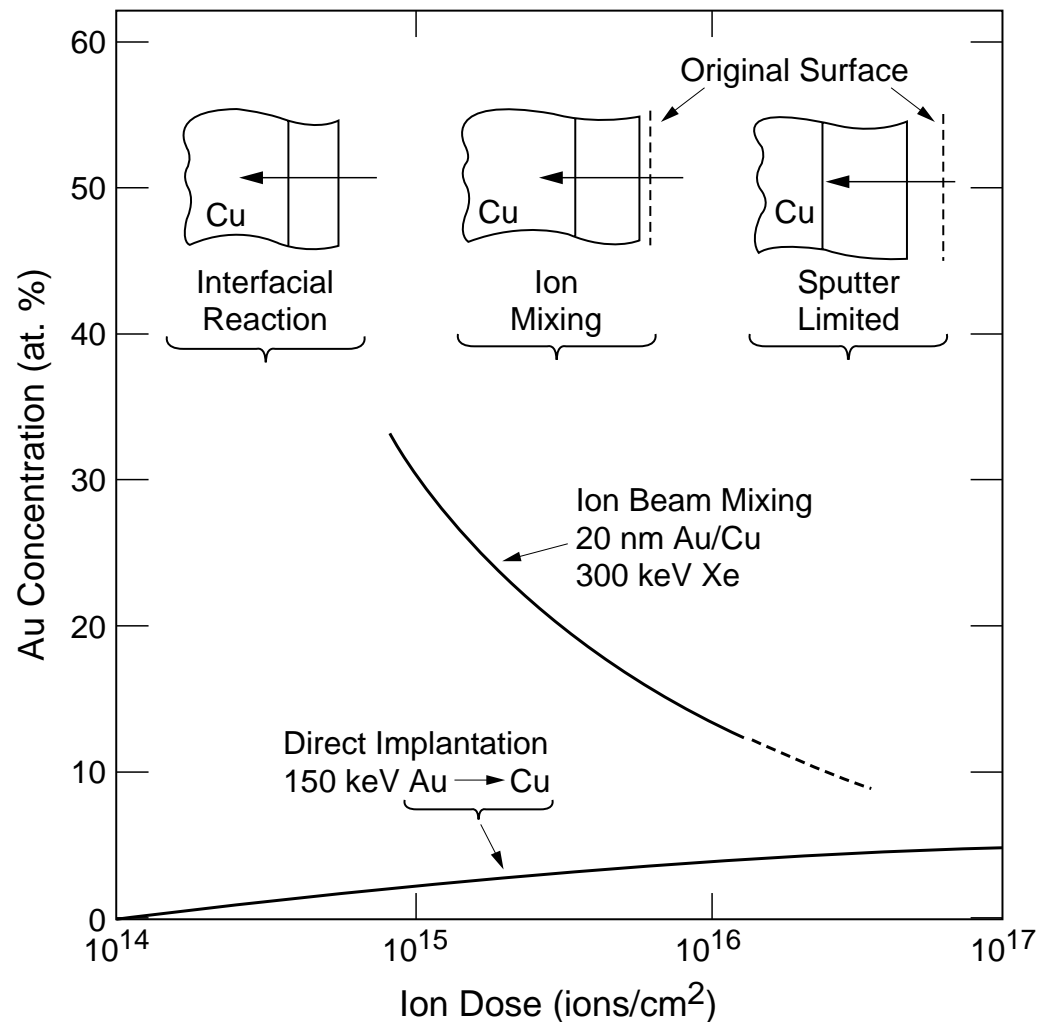
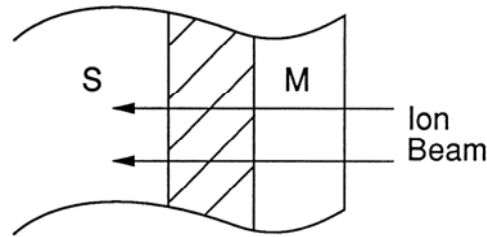4) **Thermally-Assisted Ion Mixing**

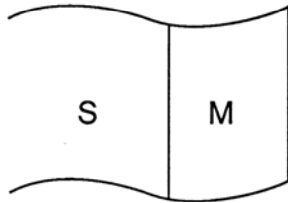# Ion Mixing: Phenomenological Aspects

M = surface layer
S = substrate

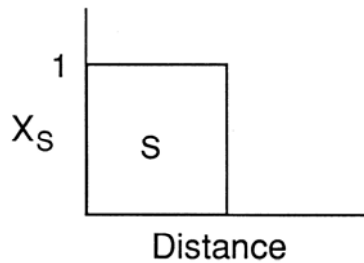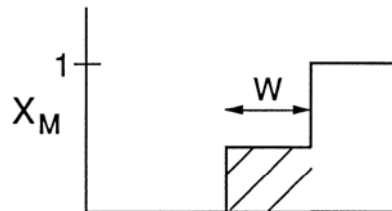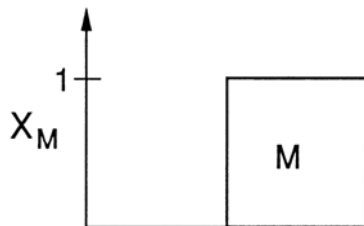# Why is Ion Beam Mixing Interesting?

Its ability to produce ion-modified materials with higher solute concentrations at lower irradiation doses than can be achieved with conventional high-dose implantation

Alloying During Ion Mixing

W = thickness of reacted layer

Q = amount of mixing

= number of S and M atoms in layer W

a) As-deposited
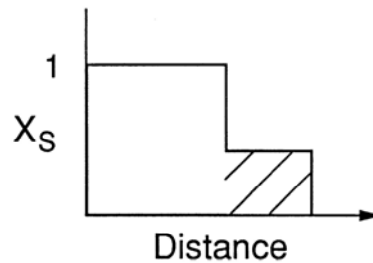
b) Ion beam mixing

Ion Mixing Trends

45 nm Pt/Si
300 keV, Xe, Kr or Ar
LN_2 temperature

Si, Pt

Xe   Kr   Ar

Q_{Si} (10^{17} atoms/cm^2)

(Dose)$^{1/2}$ (10^{15}/cm^2)$^{1/2}$
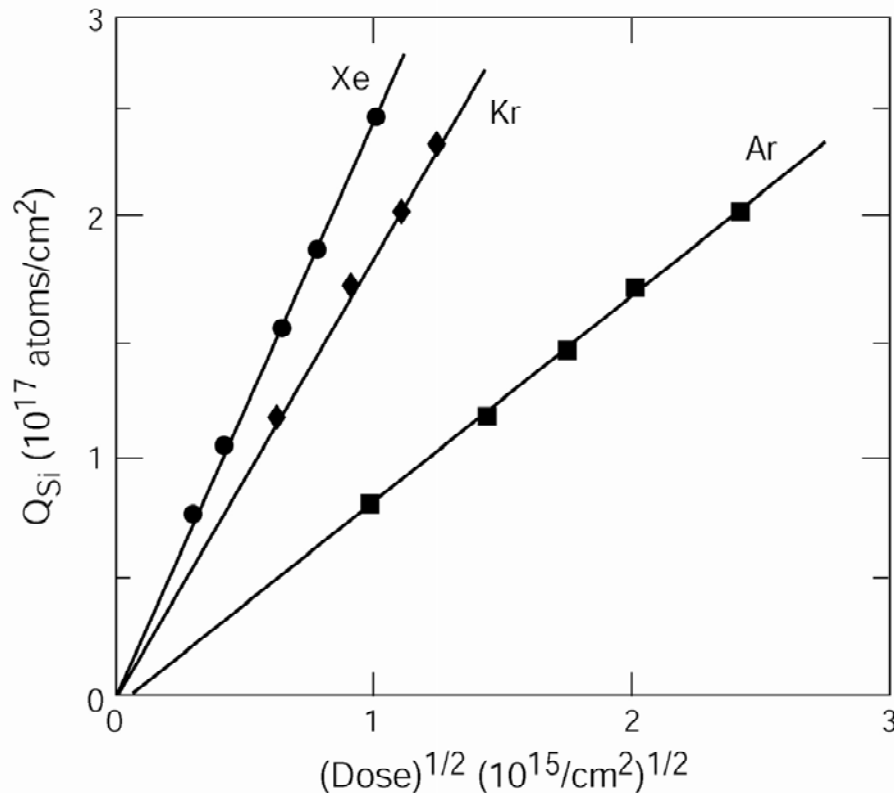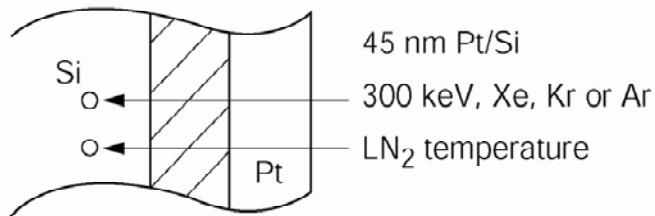
Q = amount of mixing
$Q \propto W$

● Q increase with ion mass
($dE/dx|_n$ scales with ion mass)
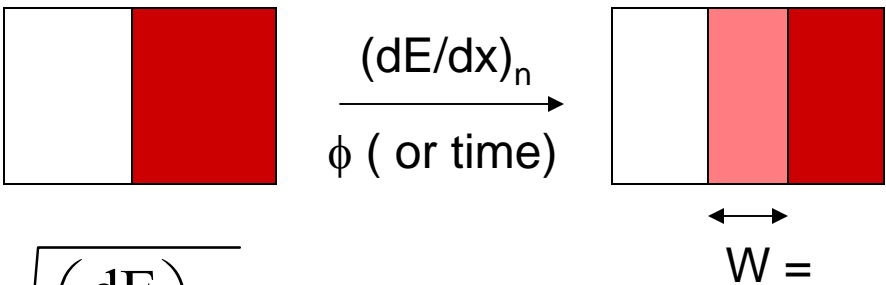
● $Q \propto$ (dose)$^{1/2} \propto$ (time)$^{1/2}$
(for constant dose rate)

$$Q \propto \sqrt{\phi \left(\frac{dE}{dx} \right)_n}$$

ϕ = ion dose (ions/cm^2)
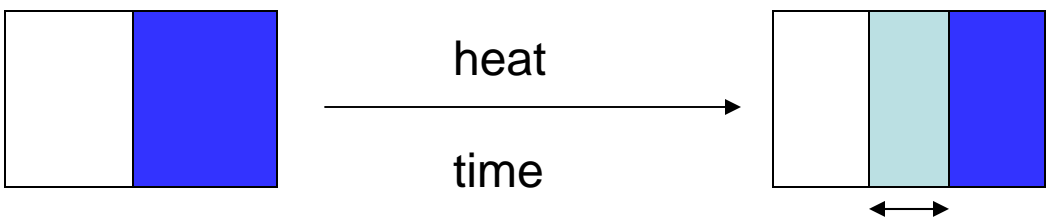
Similarities between Ion Mixing and Diffusion

Amount of mixing: $W \propto \sqrt{\left(\dfrac{dE}{dx}\right)_n \phi}$

for constant dose rate $\phi \propto t \Rightarrow$ $W \propto \sqrt{\left(\dfrac{dE}{dx}\right)_n t}$

$\xrightarrow[\phi \text{ (or time)}]{(dE/dx)_n}$

W = reacted layer

Interdiffusion:

$\xrightarrow[\text{time}]{\text{heat}}$

W = reacted layer

Amount of interdiffusion: $\boxed{W \propto \sqrt{\widetilde{D}\, t}}$ $\widetilde{D}$ = interdiffusion coefficient

Because of these similarities many ion mixing models are based on diffusion and interdiffusion analogs with mixing described in terms of an effective "Dt"

Effect of Temperature on Ion Mixing
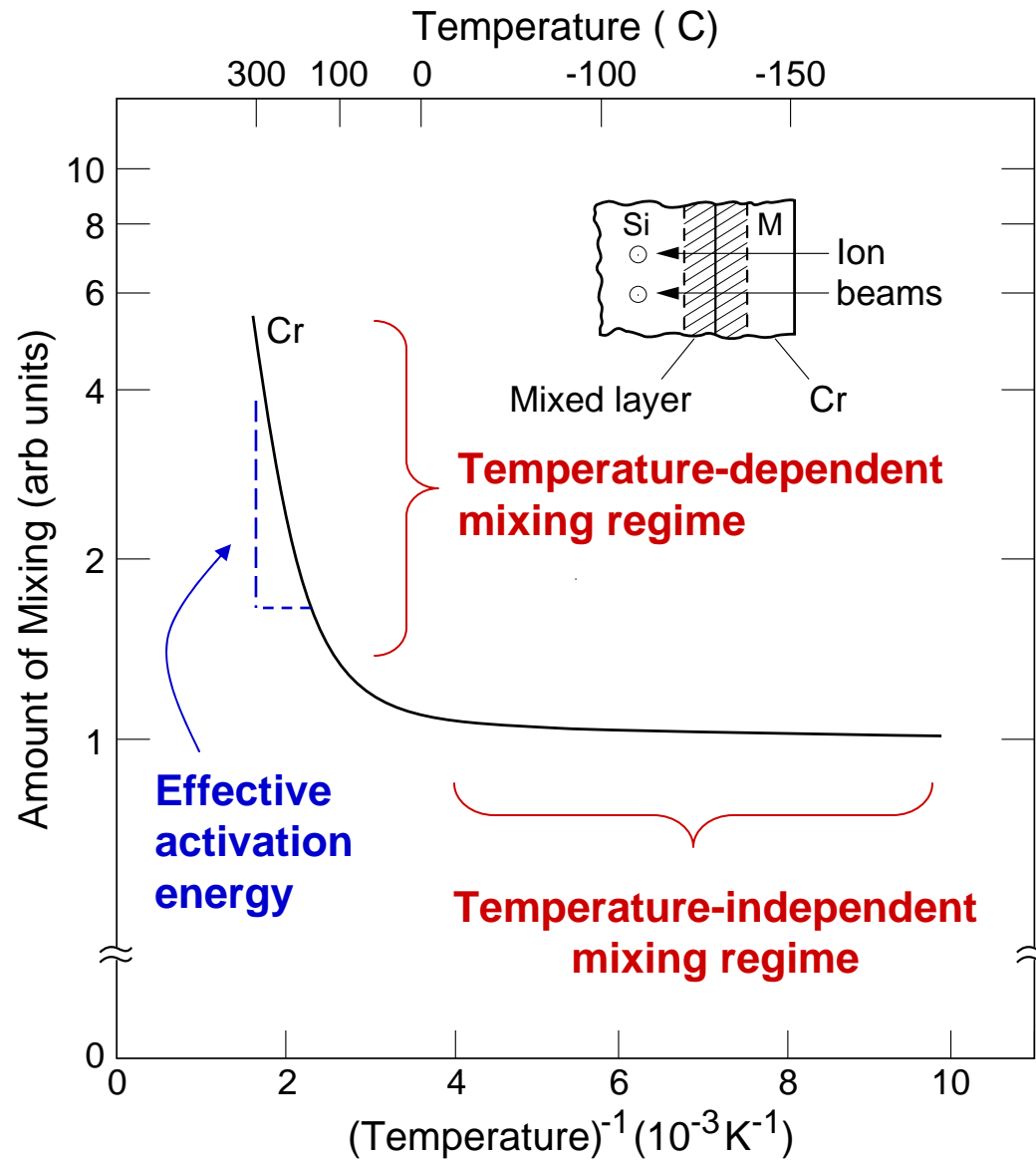
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Ballistic Mixing: Basic Concepts

Ballistic mixing is an atomic collision derived process

- As an ion penetrates a solid, it slows down by depositing energy to both the atoms and the electrons of the solid.

- During the nuclear collision portion of the slowing process, target atoms can be permanently displaced from their lattice sites and relocated several lattice sites away.

- When this process takes place at the boundary separating two different materials, interface mixing results.

The displacement mechanism of atomic rearrangement is the fundamental principle governing ballistic mixing.

An Example of a Ballistic Process

+ ≡ Displaced Atom

□ ≡ Vacant Site

Primary Recoil Atom

Incident Particle

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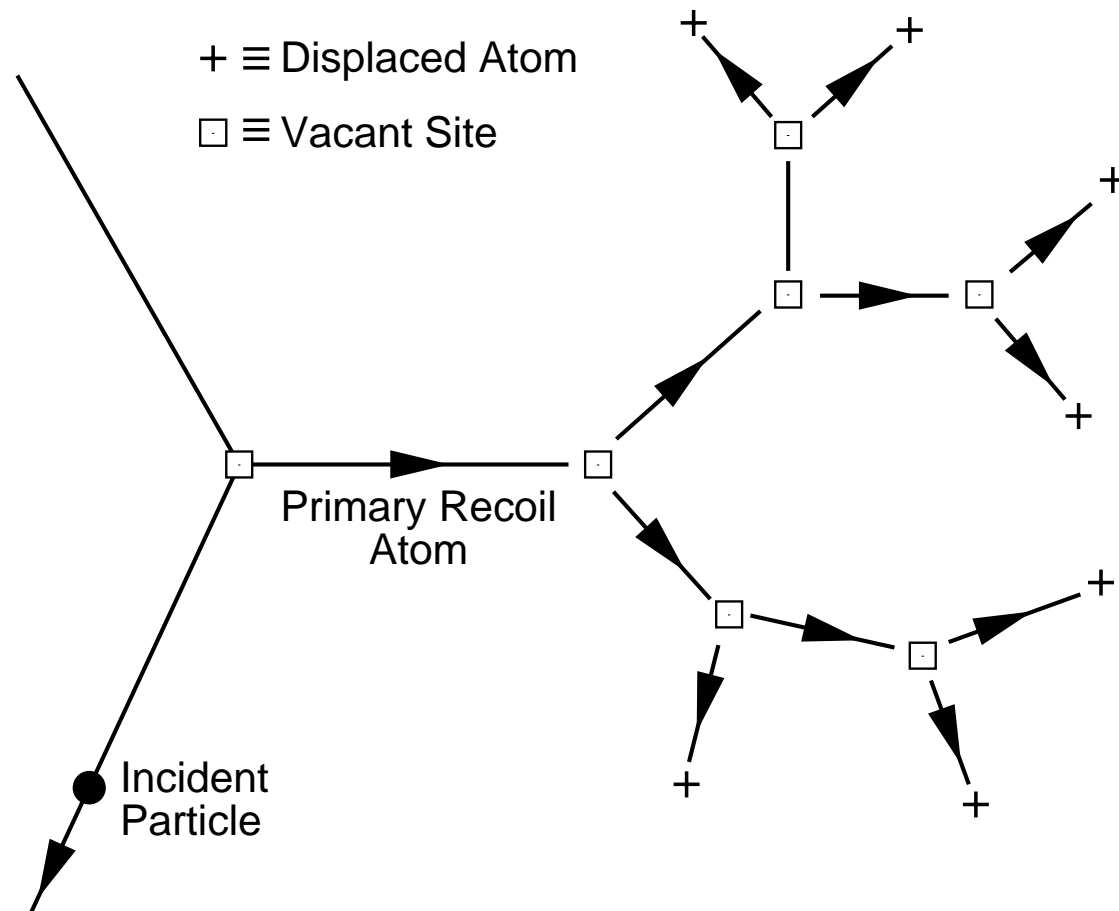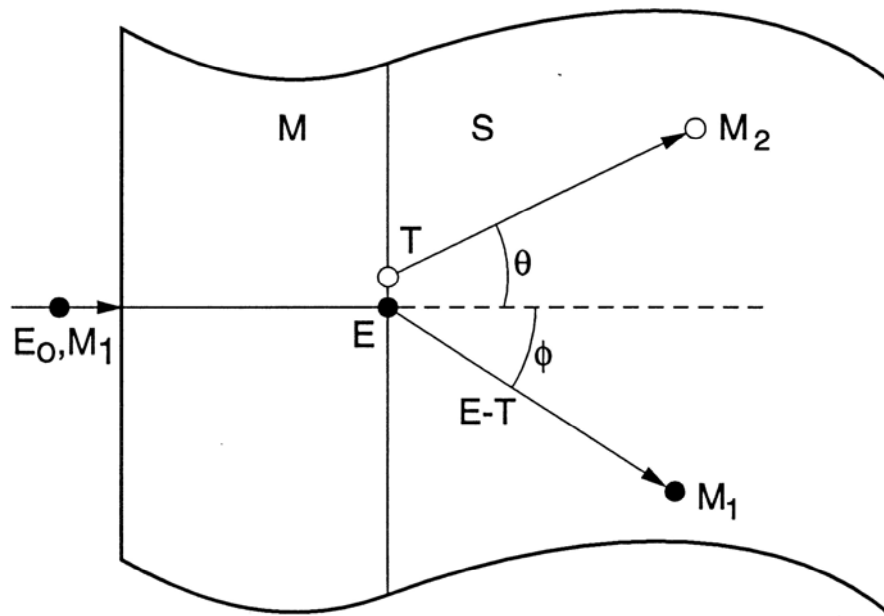
4) Thermally-Assisted Ion Mixing

Recoil Mixing or Recoil Ion Implantation
(atom relocation by single-collision events)

T is the energy transferred to the target atom M_1 by incident ion M_2 at the interface between the M and S layer

$$T = \frac{(4\, M_1\, M_2)}{(M_1 + M_2)^2}\, E\, \cos^2\theta$$

$T = T_{max}$ for $\theta = 0$ (head-on collision)

Example: Consider a bilayer sample composed of a Pt layer on a Si substrate. An Ar ion ($M_1 = 40$ amu) with E = 100 keV collides with a Pt atom ($M_2 = 195$ amu) at the Pt/Si interface. The maximum energy transferred, T_{max}, will be

$$T_{max} = \frac{4M_1M_2}{(M_1 + M_2)^2}\, E = \frac{4 \times (40 \times 195) \times 100}{(40 + 195)^2} = 56\ \text{keV} \quad \Rightarrow T/E = 0.56$$

The projected range of 56 keV Pt in Si is 31 nm

Recoil Mixing Details
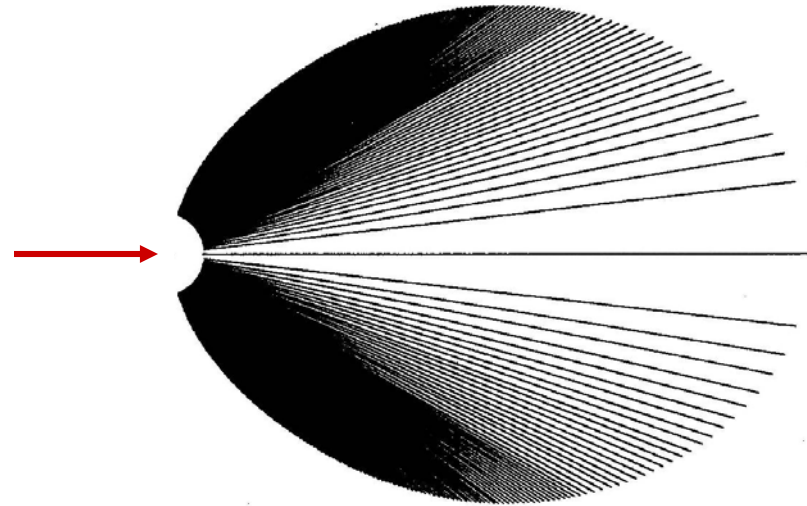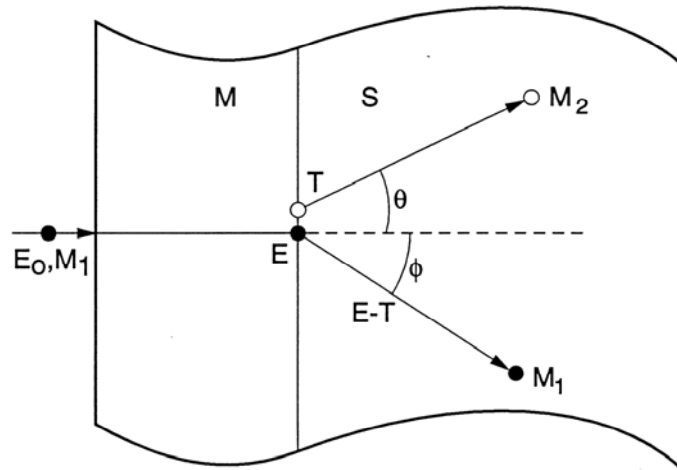
TABLE 1. 100 keV Ar on Pt

θ (°)	T (keV)	$d\sigma/dT$ ($\times 10^{19}$ cm^2 keV^{-1})	$R_p(T)$ for Pt in Si[a] (nm)
0	56.50	0.27	32
20	49.89	0.32	29
40	33.15	0.59	23
60	14.12	2.13	14
70	6.61	6.67	10
80	1.70	50.96	5.6
85	0.43	403.00	3.4
89	0.02	5.02×10^4	1.2

[a]R_p from TRIM[10].

The most probable collisions are at large angles (*soft collisions*)

Recoil Mixing and Ion Dose
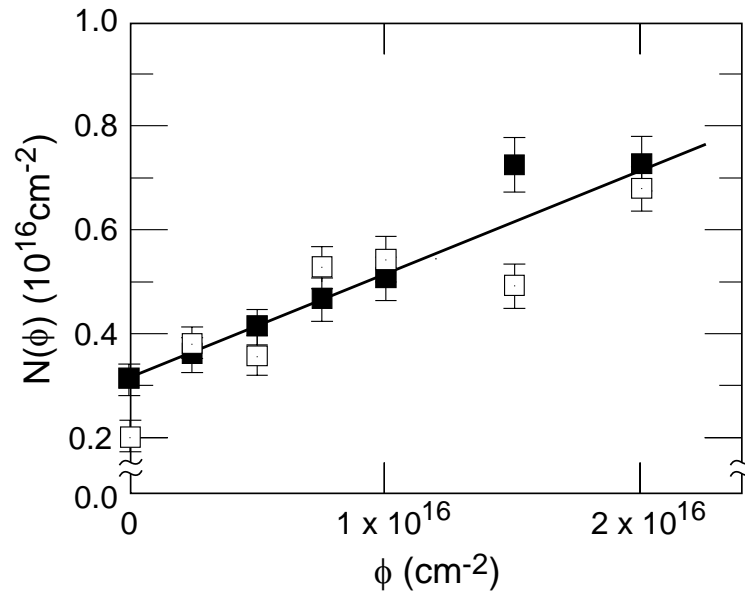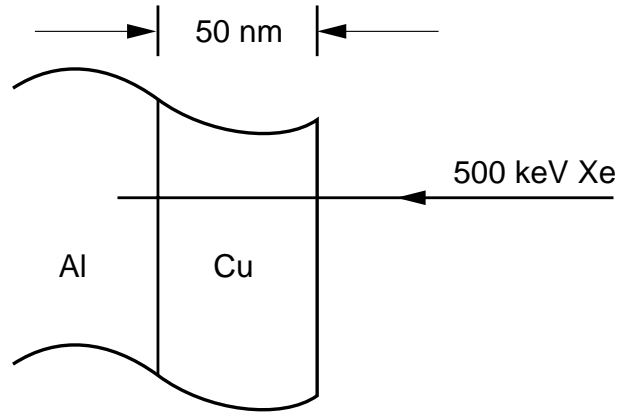
These data show that the number, of Cu atoms, $N(\phi)$, that undergo recoil implantation into the Al substrate varies linearly with ion dose, ϕ.

Ion Mixing Marker Studies
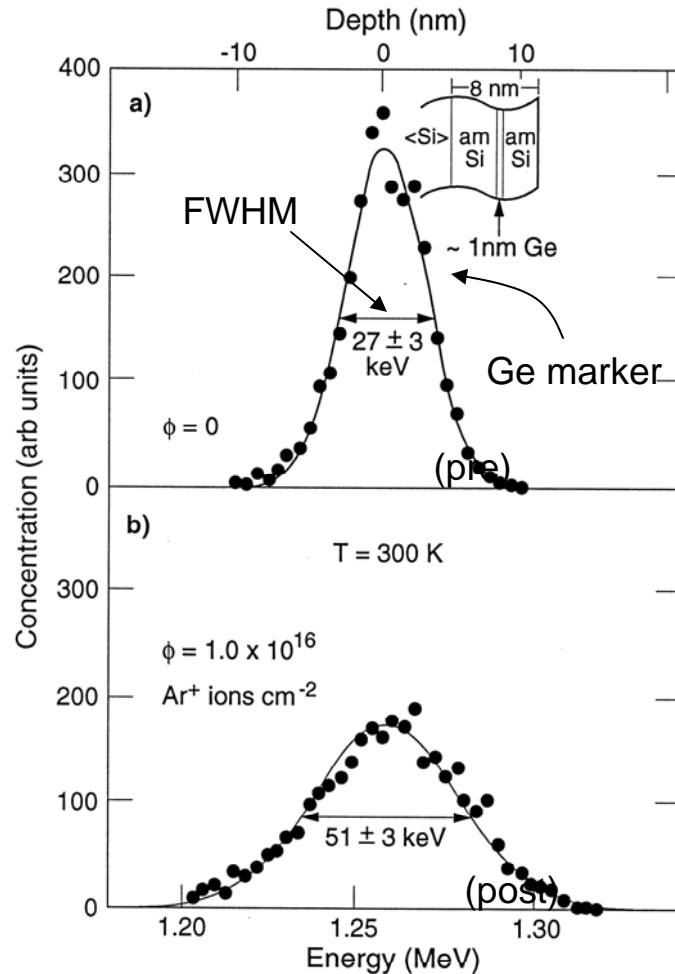
The symmetric spreading during ion mixing indicates the occurrence of an isotropic displacement process, much like a random walk diffusion process.

By analogy with the theory describing the diffusion of a thin planar source into a semi-infinite solid, the effective diffusion coefficient during ion mixing can be obtained from the spreading of a Gaussian profile using the expression

$$V_{irr}^2 = 2Dt$$

V is the marker variance in units of *distance*

Ω = variance in the energy distribution of the Ge marker measure by RBS

$$FWHM = 2.355\Omega, \quad \Omega_{irr}^2 = \Omega_{post}^2 - \Omega_{pre}^2$$

$$V = \frac{\Omega}{[S]_a^B} \qquad [S]_a^B = \text{RBS energy loss conversion factor for a marker a in a matrix B}$$

Collision Factors in Ion Beam Mixing

(a) Irradiation: 220 keV Kr, LN$_2$ Temp

Marker
▲ Ge
● Sb
■ Pt

Dt (10^{-13} cm^2)

ϕ (ions cm^{-2})

~1 nm marker

xl Si | am Si | am Si

20 nm

(b)

$\dfrac{Dt}{\phi}$ (10^{-29} cm^4)

F_D (eV/nm)

Xe
Kr
Ar
Ne
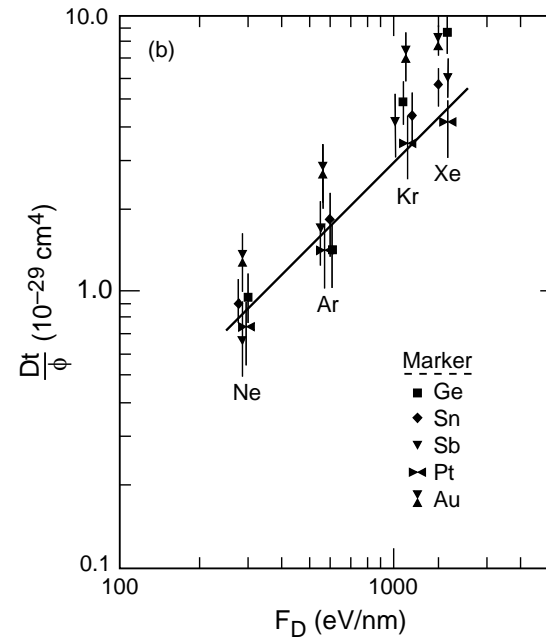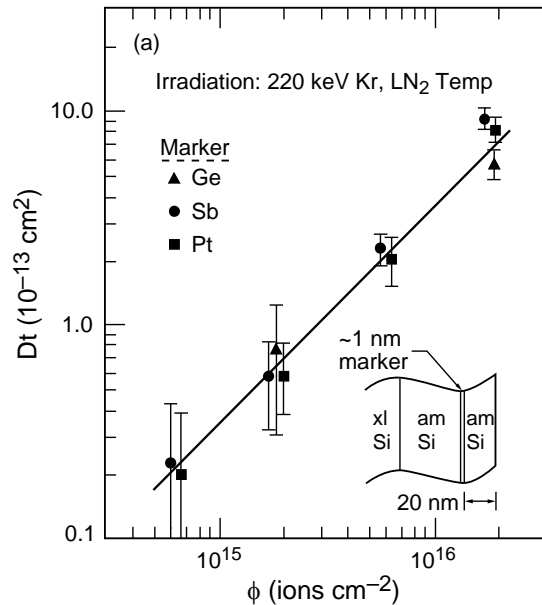
Marker
■ Ge
◆ Sn
▼ Sb
⊢⊣ Pt
⊻ Au

Dt = the *effective diffusion coefficient* observed during marker ion mixing

Dt/ϕ = *effective mixing parameter*

F_D = *damage energy* = the total kinetic energy of the incident ion deposited into nuclear collisions per unit length

$$\textbf{Dt} \propto \boldsymbol{\phi} \qquad \textbf{Dt/}\boldsymbol{\phi} \propto \textbf{F}_\textbf{D}$$
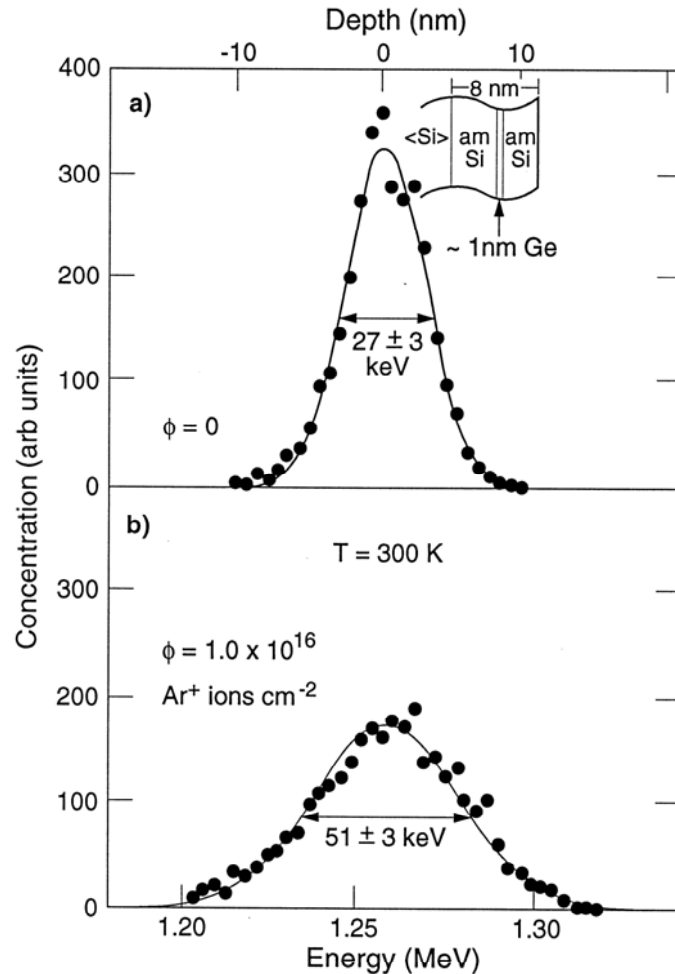
The isotropic broadening observed in thin markers, strongly suggest that a series of single-event, forward-momentum recoils is not the dominant mixing mechanism.

Instead, marker broadening appears to be related to a process dominated by an isotropic displacement mechanism.

=> Cascade Effects??

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Cascade Mixing

Sputtering

Solid

Displacement

Recoil

Implantation

Cascade

○ Normal atom
● Interstitial atom
◉ Incident ion
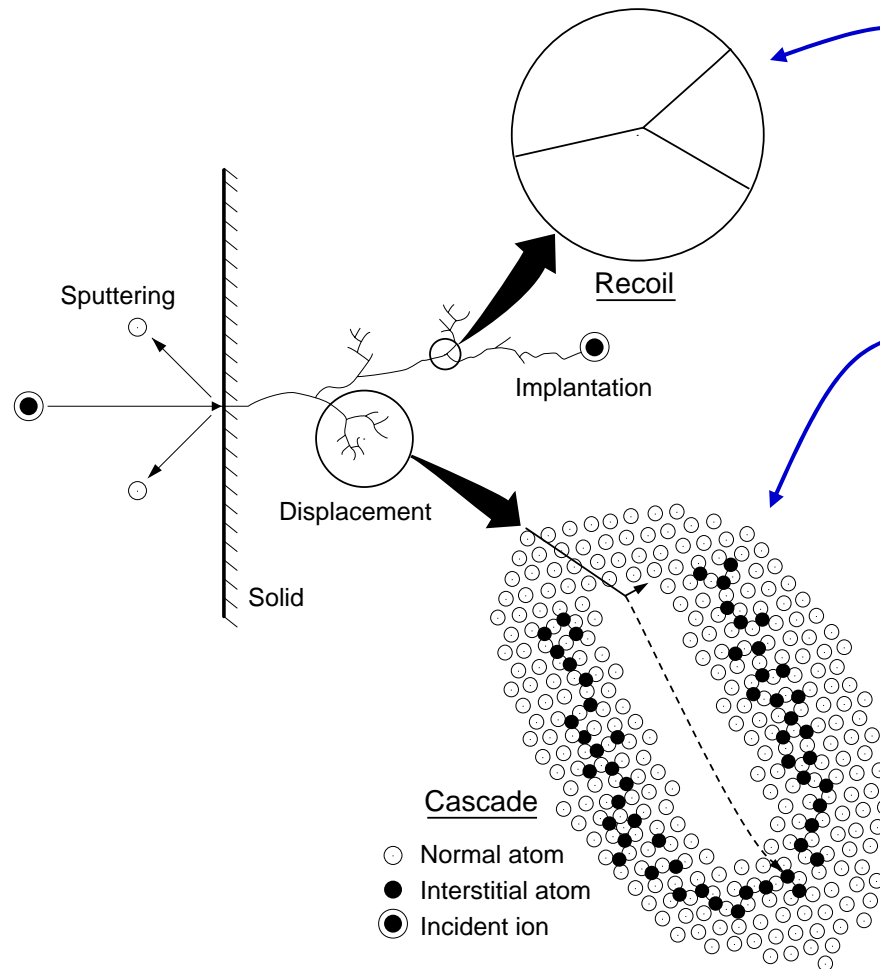
Recoil mixing: A highly directed process, in which one atom receives a large amount of kinetic energy in a single displacement,

Collision cascade: Atoms in a collision cascade undergo many multiple uncorrelated low-energy displacement and relocation events.

Atomic mixing resulting from a series of uncorrelated low-energy atomic displacements is referred to as ***cascade mixing***

Cascade Mixing

Cascade
○ Normal atom
● Interstitial atom

The isotropic motion of atoms in the cascade gives rise to a *random-walk* like atomic redistribution
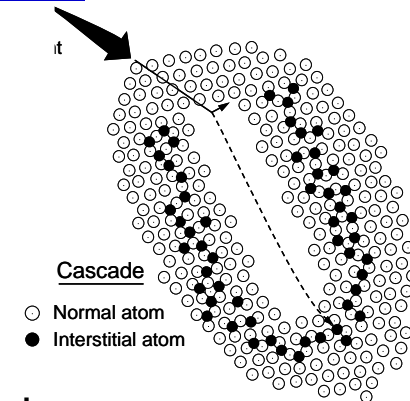
For thermally activated diffusion, the diffusivity, D, for a random walk process is defined as:

$$Dt = \frac{n\alpha^2}{6}$$

n = number jumps the diffusing atom makes
α = jump distance

The effective diffusivity, D_{cas}, for a collision-cascade-induced random-walk process is expressed in the diffusion equation as:

$$D_{cas}\, t = \frac{dpa(x) <r^2>}{6}$$

dpa = number of displacements per atom
<r²> = the mean squared range of the displaced target atom

Cascade Mixing

$$D_{cas}\, t = \frac{dpa(x) < r^2 >}{6}$$

dpa = number of displacements per atom
<r²> = the mean squared range of the displaced target atom

The dpa resulting from a given dose of ions can be expresses as:

$$dpa = \frac{0.4\, F_D\, \phi}{E_d\, N}$$

F$_D$ = deposited damage energy per unit length
ϕ = ion dose
N = atomic density

Combining the 2 equation, we obtain the effective diffusion coefficient due to ballistic cascade mixing as:

$$D_{cas}\, t = 0.067 \frac{F_D < r^2 >}{N\, E_d} \phi$$

$$D_{cas}\, t \propto \phi \quad \text{or} \quad x_{cas} \propto \sqrt{D_{cas}\, t} \propto \sqrt{\phi}$$

Cascade Mixing

$$D_{cas}t = 0.067 \frac{F_D <r^2>}{N E_d} \phi$$

What is the average range of the displaced target atom during cascade mixing?

(a) Irradiation: 220 keV Kr, LN$_2$ Temp

Marker
▲ Ge
● Sb
■ Pt

~1 nm marker

xl Si | am Si | am Si

20 nm

Dt (10^{-13} cm^2)
ϕ (ions cm^{-2})

$Dt/\phi \sim 3.5 \times 10^{-29}$ cm^4
~ 0.4 nm^4

(b)

Xe

Kr

Ar

Ne

Marker
■ Ge
◆ Sn
▼ Sb
◄► Pt
Ⅰ Au
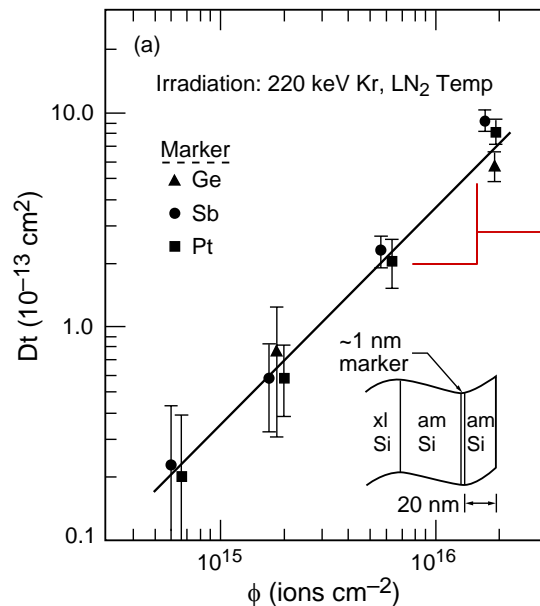
$\frac{Dt}{\phi}$ (10^{-29} cm^4)
F_D (eV/nm)

$N_{Si} = 50$ atoms/nm^3
$E_d \sim 13$ eV
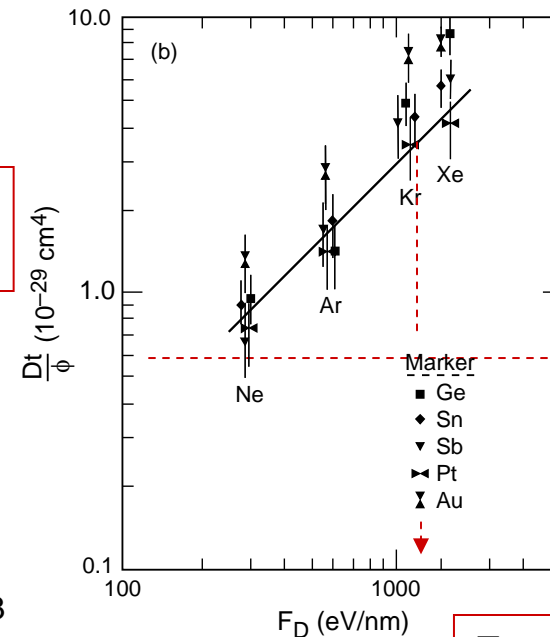
$F_D \sim 1500$ eV/nm

$$\sqrt{\frac{D_{cas}t}{\phi} \frac{N E_d}{0.067 F_D}} = \sqrt{<r^2>} \sim 1.6 \text{ nm}$$

=> average energy of recoils is ~ 200 - 300 eV

The Breakdown of the Cascade Mixing Model

$$D_{cas} t = 0.067 \frac{F_D <r^2>}{N E_d} \phi$$

If F_D, N, E_d and ϕ are all approximately the same, $D_{cas}T$ should also be the same.

TEST: Compare ion mixing of Au/Cu and W/Cu bilayer systems

Element	N at/nm^3	$E_{d(min)}$ eV	System	$(dE/dx)_n$ eV/nm
Cu	85	19	Cu/W	32
W	63	38	Cu/Au	31
Au	59	36		

(dE/dx values for 300 keV Kr ions)

Cu/W and Cu/Au should experience similar amounts of intermixing

The Breakdown of the Cascade Mixing Model
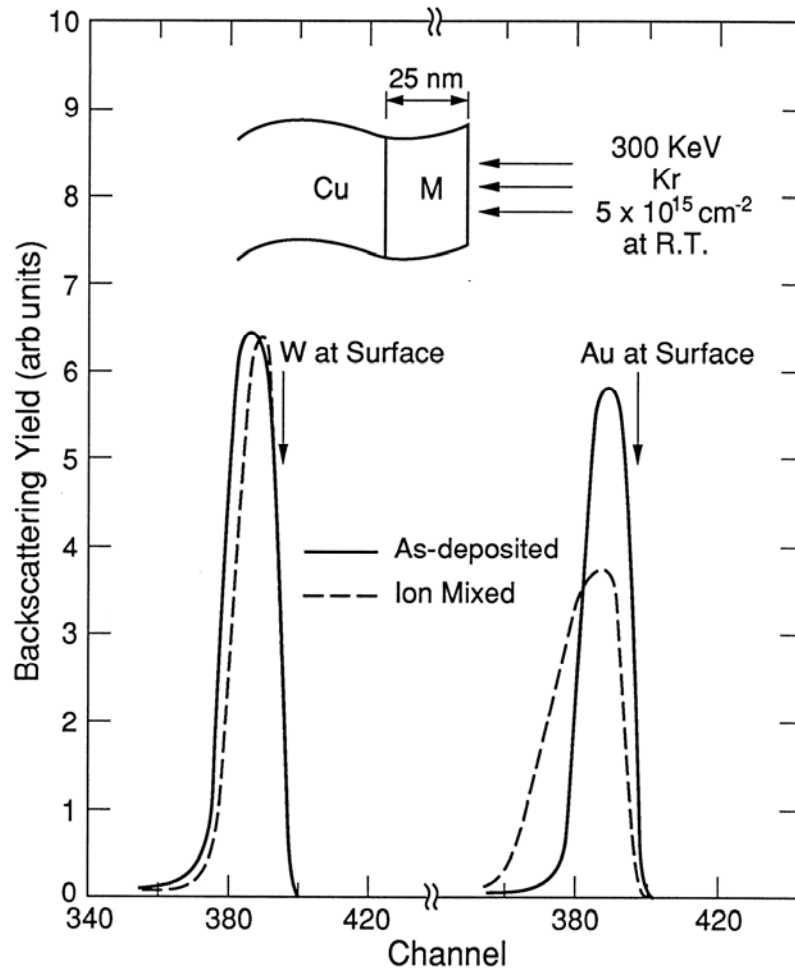
Virtually no mixing between Cu & W

Good intermixing between Cu and Au

WHY?
Cu/W is an immiscible system
ΔH_{mix} = + 36 kJ/(mole of atoms)

Cu/Au is an alloy former
$\Delta H mix$ = -9 kJ/(mole of atoms)

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Thermodynamic Effects

●The enthalpy difference, ΔH_{mix}, results from the chemical joining of A and B atoms and the formation of A-B bonds during alloying.

●The more negative the heat of mixing, the greater the tendency to form an A-B alloy.

In the regular solution model, the heat of mixing for elements A and B is defined as:

$\Delta H_{mix} = X_A X_B \Omega_{H,}$ where X_i = the mole fraction of element I, and

$$\Omega_H \cong Z_c N_a [H_{AB} - 1/2(H_{AA} + H_{BB})]$$

Z_c = coordination number (the number of nearest neighbors)
N_a = Avogadro's number
H_{ij} = mean potential between atom pairs (bonding enthalpies) in a close-packed array ($\propto$ heat of sublimation).

If there is an attractive interaction between unlike atoms, the A-B pair enthalpy will be more negative than the A-A pair enthalpy or the B-B pair enthalpy, yielding a negative value for both Ω and ΔH_{mix}.

Heat of Mixing

For dilute systems X_B is very small and $\Delta H_{mix} = X_A X_B \Omega_H$ will also be small => minimal thermo effects in marker expts

Enthalpy as s function of concentration for an alloy system with Ω negative

H (enthalpy)

0

ΔH_{mix}

B

A

0
A

25

50

75

100
B

% B
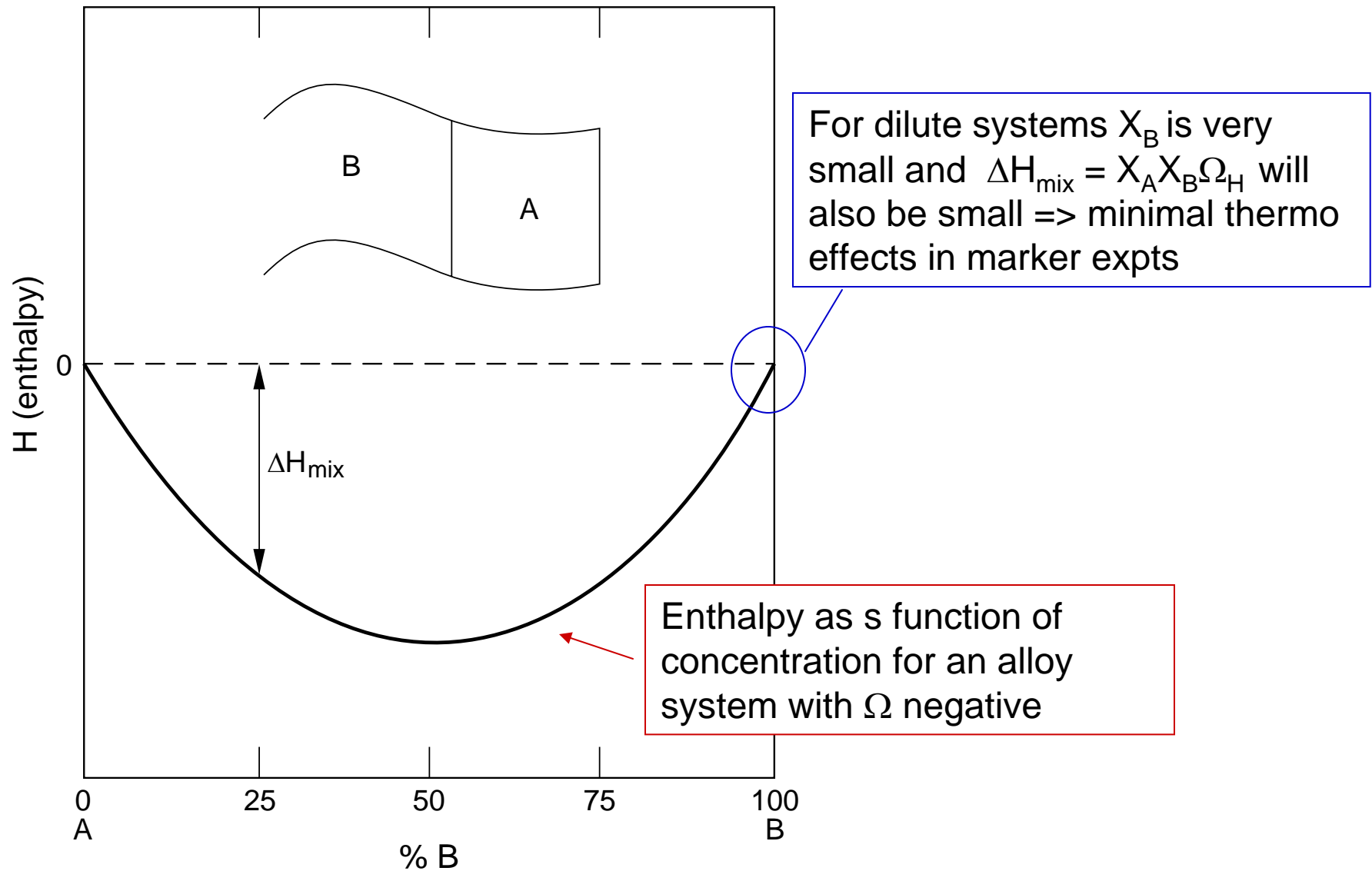
Thermodynamics in Interdiffusion
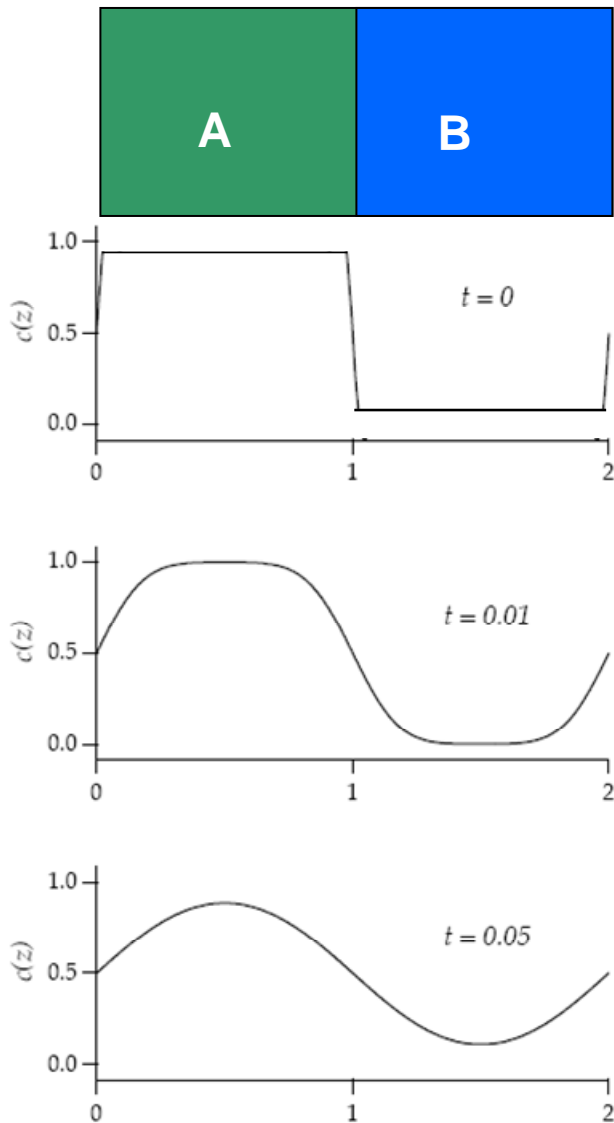
The interdiffusion coefficient In the presence of a chemical driving force is given by (Darken analysis):

$$\tilde{D} = \tilde{D}_o \left(1 - \frac{2\,\Delta H_{mix}}{k_B T} \right)$$

Where

$$\tilde{D}_o = [D_1^* X_1 + D_2^* X_2]$$

Where X_i, and D_i are respectively the mole fraction and tracer diffusivity of element i.

When $\Delta H_{mix} = 0 \qquad \tilde{D} = \tilde{D}_o$

When $\Delta H_{mix} < 0 \qquad \tilde{D} > \tilde{D}_o$

When $\Delta H_{mix} > 0 \qquad \tilde{D} < \tilde{D}_o$

Ion Mixing analogy to Interdiffusion

$$\frac{4\widetilde{D}t}{\phi} \approx \frac{4\widetilde{D}_{cas}t}{\phi}\left(1 - \frac{2\,\Delta H_{mix}}{k_B T}\right)$$

Where

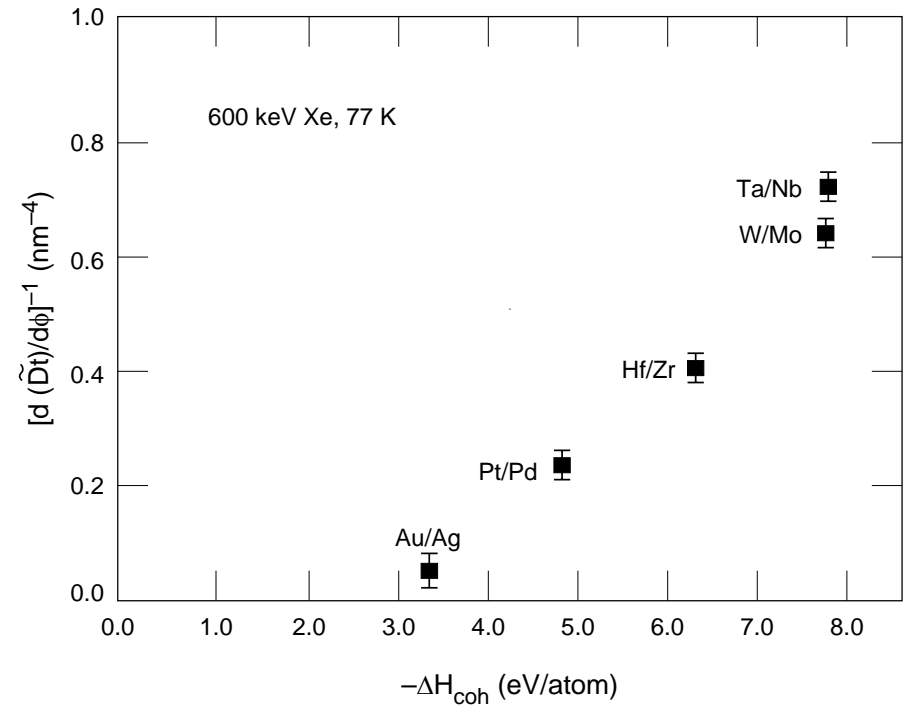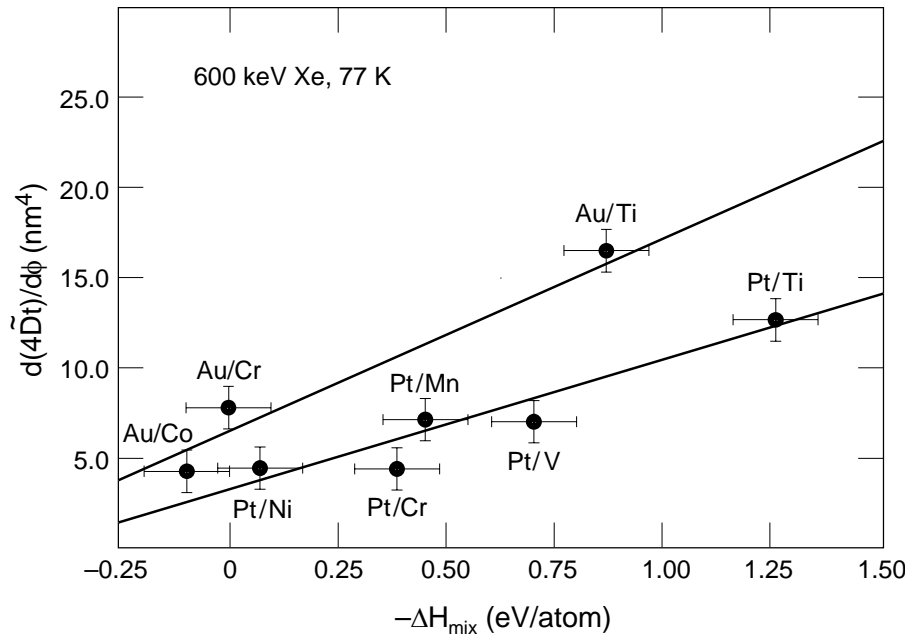$$\frac{D_{cas}\,t}{\phi} = 0.067\,\frac{F_D <r^2>}{N\,E_d}$$

When $\Delta H_{mix} < 0$ $\dfrac{\widetilde{D}t}{\phi} > \dfrac{\widetilde{D}_{cas}t}{\phi}$

When $\Delta H_{mix} > 0$ $\dfrac{\widetilde{D}t}{\phi} < \dfrac{\widetilde{D}_{cas}t}{\phi}$

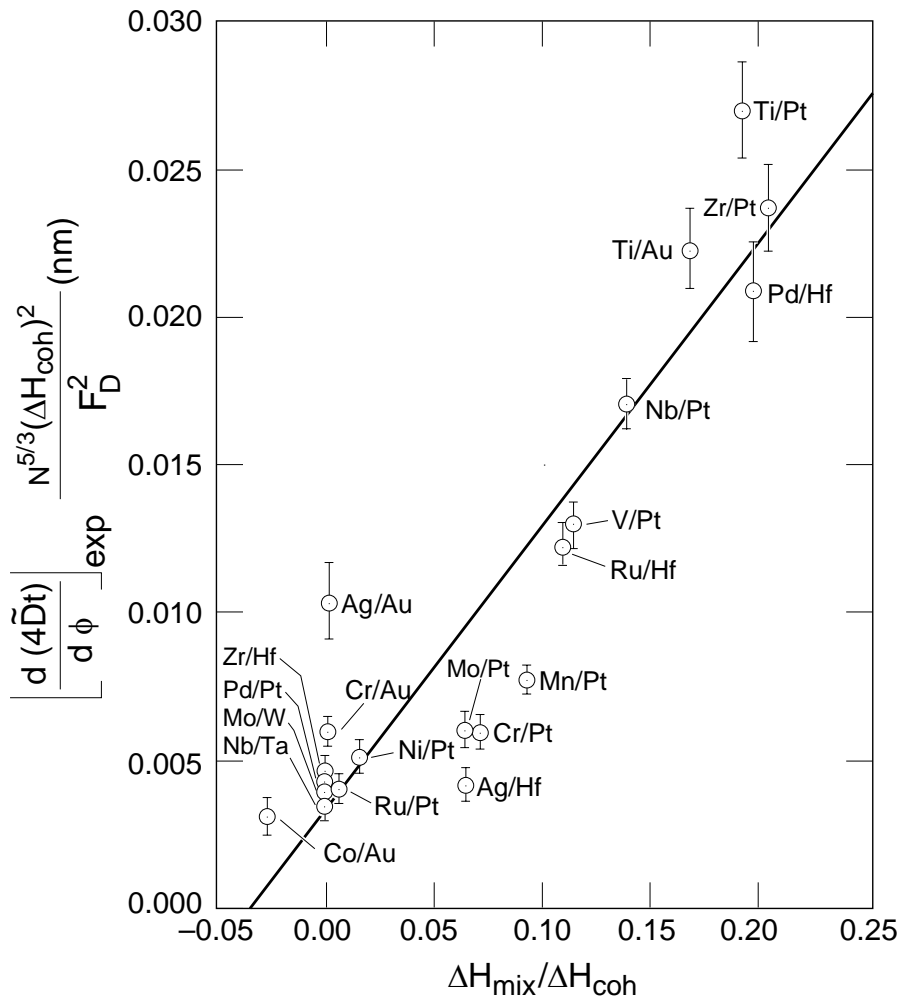# Thermodynamic Effects in Ion Mixing

(Johnson and Cheng Model of Ion Mixing)

$$\frac{d4\tilde{D}t}{d\phi} = \frac{K_1 F_D^2}{N_o^{5/3} (\Delta H_{coh})^2} (1 + K_2 \frac{\Delta H_{mix}}{\Delta H_{coh}})$$

F_D is the damage energy per unit length, N_o is the average atomic density, and K_1 and K_2 are fitting parameters.

Thermodynamic Effects in Ion Mixing

(Johnson and Cheng Model of Ion Mixing)

$$\frac{d4\widetilde{D}t}{d\phi} = \frac{K_1\, F_D^2}{N_o^{5/3}\, (\Delta H_{coh})^2}\,(1 + K_2\,\frac{\Delta H_{mix}}{\Delta H_{coh}})$$

$$\Downarrow$$

$$\frac{\Delta H_{mix}}{\Delta H_{coh}} \propto \frac{d(4\widetilde{D}t)}{d\phi}\,\frac{N_o^{5/3}\,(\Delta H_{coh})^2}{F_D^2}$$

Data taken from heavy ion irradiation at low temperatures
=> strong cascade effects

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Thermally-Assisted Ion Mixing
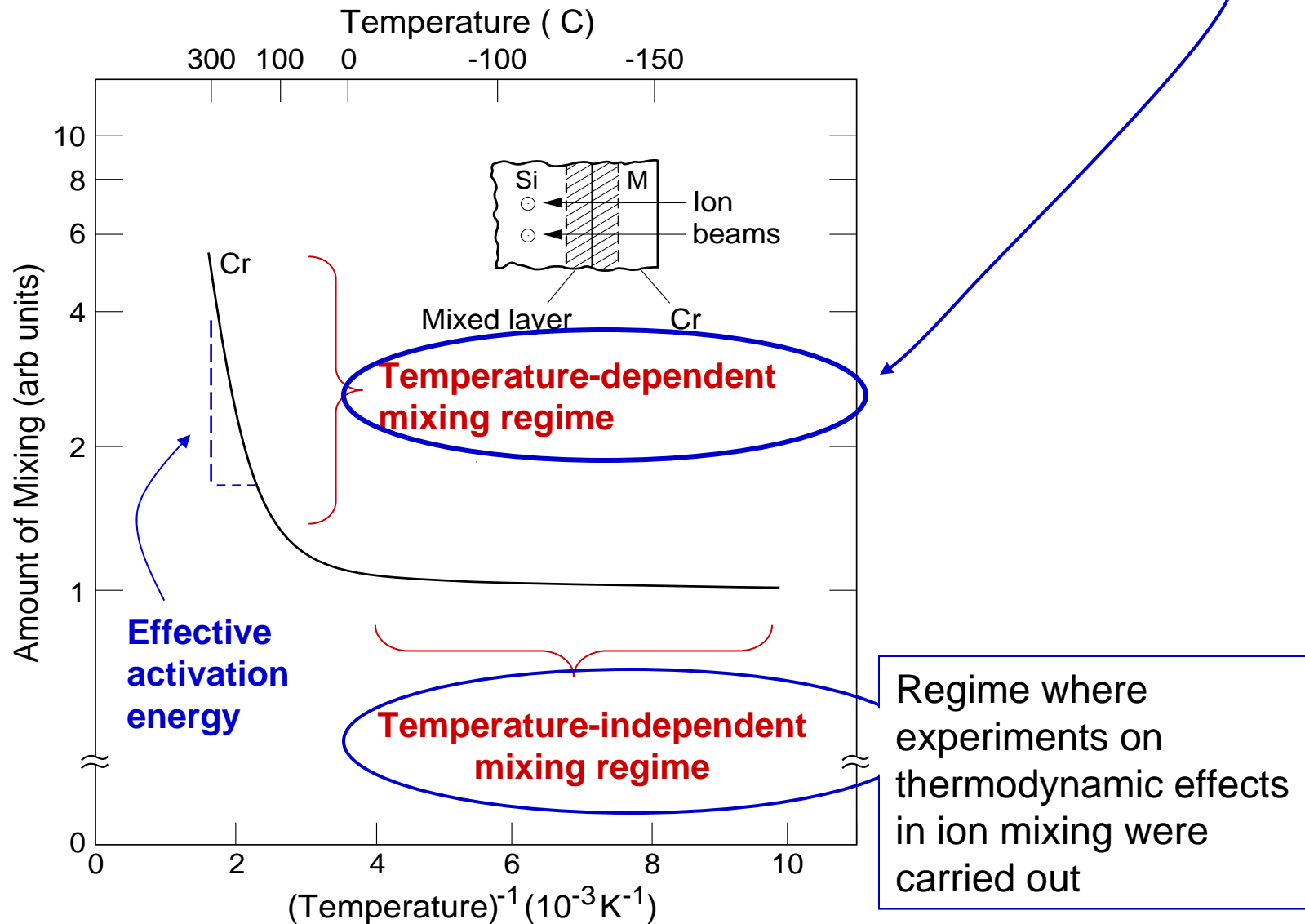
Thermally-Assisted Ion Mixing
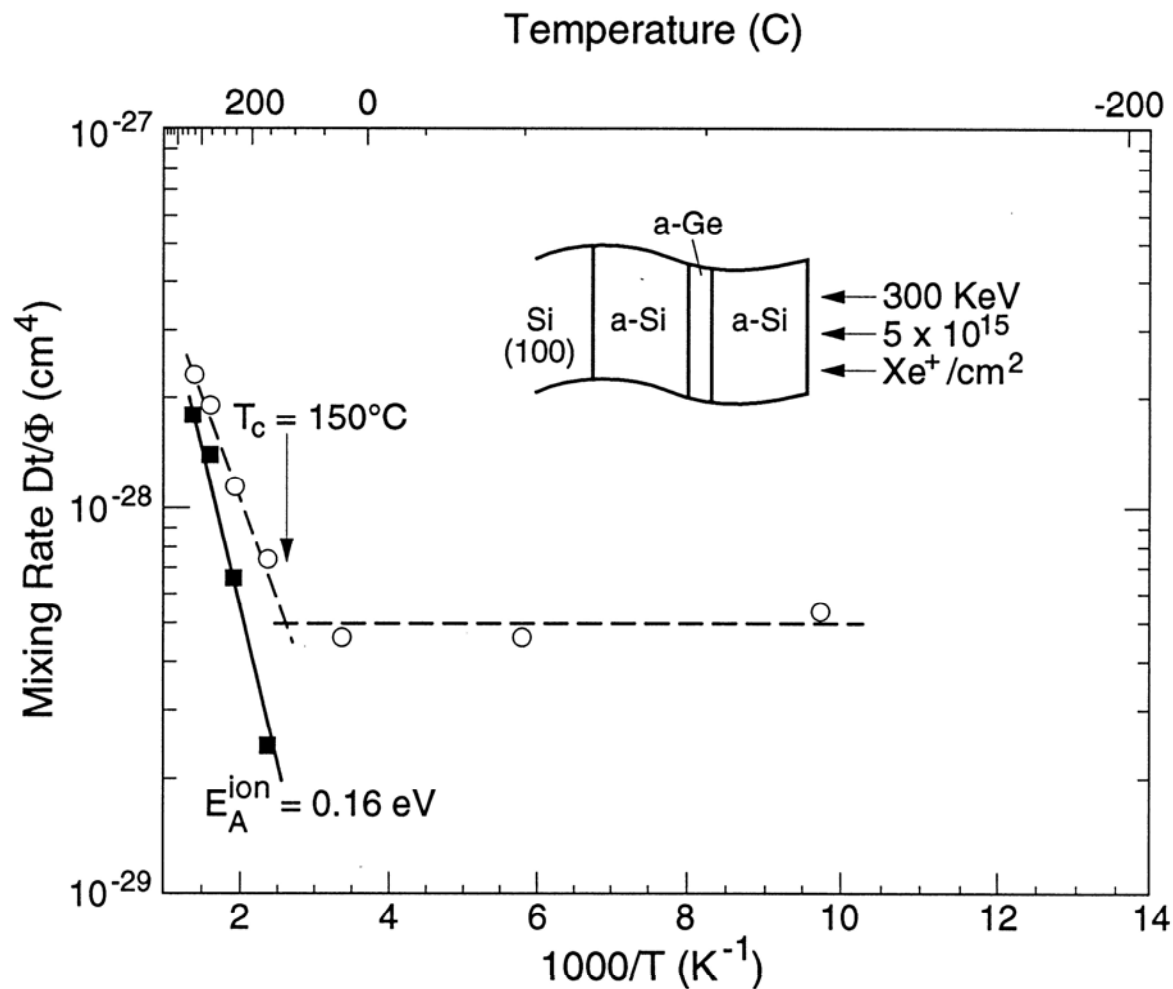
A characteristic of the thermally-assisted ion mixing regime is that the *ion mixing activation energy*, E_A^{ion}, for most mixing experiments is approximately in the range of 0.1 to 0.3 eV

Activation Energies

TABLE 6. Activation energy for thermally assisted ion mixing

System (top–bottom)	E_A^{ion} (eV atom^{-1})	T_0 (K)	Ion	Ion energy (keV)	Interface depth (nm)	$(dE/dx)_n$ (eV nm^{-1})
Au–Zr	0.06	330–550	Kr	1000	70	22.5
Zr–Fe	0.07	320–430	Kr	1000	80	17.5
Ni–Si	0.09	255–450	Ar	250	55	9.0
Pt–Si	0.11	305–525	Xe	300	–	25.0
U–Ti	0.12	400–470	Ar	400	160	5.5
Si–Si$_5$Ge$_5$–Si	0.15	425–650	Xe	300	30/4	25.0
Cr–Si	0.20	415–570	Xe	300	30	35.0
U–Al	0.25	350–470	Xe	400	300	37.0
Nb–Si	0.25	380–700	Xe	500	75	10.0
Cu–Al	0.27	300–400	Xe	500	50	40.0
Mo–Si	0.03	390–630	As	200	40	18.0
	0.30	630–790				
Co–Si	0.33	320–525	Xe	300	53	5.0
U–Si	0.34	400–470	Ar	400	600	6.0
Zr–Ni	0.40	350–500	Kr	1000	80	19.0
U–Al	0.57	350–470	Ar	400	300	5.5
Nb–Si	0.90	530–640	Si	275	144	5.0

TABLE 7. Diffusion activation energies for elemental f.c.c. metals [64]

| Element	E (eV atom^{-1})	E_v^F (eV atom^{-1})	E_v^M (eV atom^{-1})
Al	1.28	0.67	0.62
Ag	1.76	1.13	0.66
Au	1.76	0.95	0.83
Cu	2.07	1.28	0.71
Ni	2.88	1.58	1.27
Pb	1.13	0.54	0.54
Pt	2.96	1.51	1.45

- In many cases the E_v^M values from elemental metals are larger by a factor of 4 to 10 than the activation energies obtained in ion mixing

- The extremely low values of suggest that the motion of atoms during ion beam mixing occurs by a non-activated process.

$\Rightarrow$ **Liquid Diffusion??**

Cascade temperatures and Cascade Diffusivities

MD calculated temperature and self-diffusion data from a 3 keV displacement cascade in Cu (Hsieh et al PRB 40 (1989) 9986)
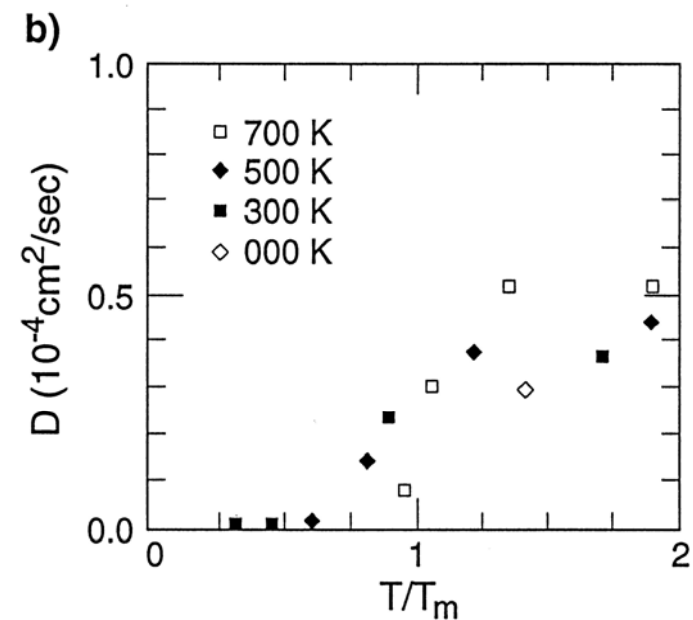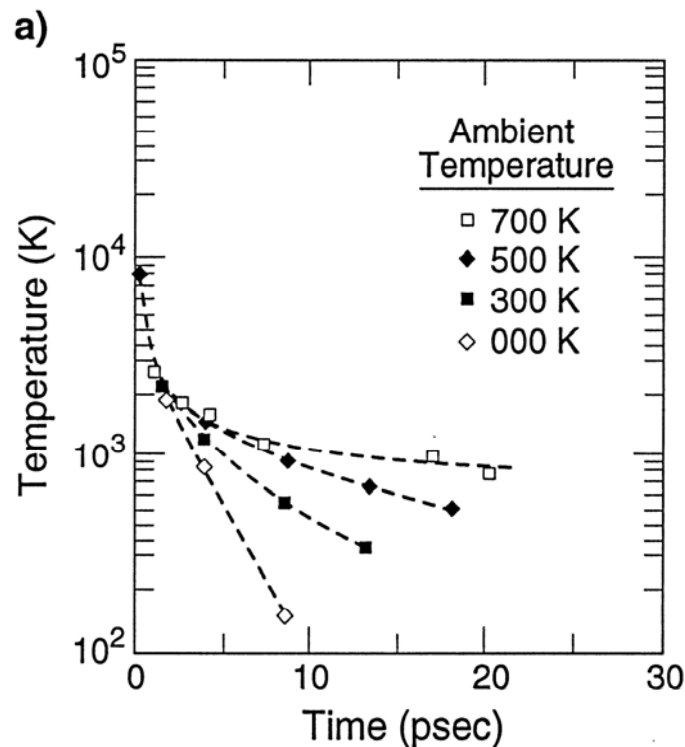
The cascade temperature and the diffusivity in the cascade increases with increasing ambient temperature. Cascade diffusivity values are *liquid-like*
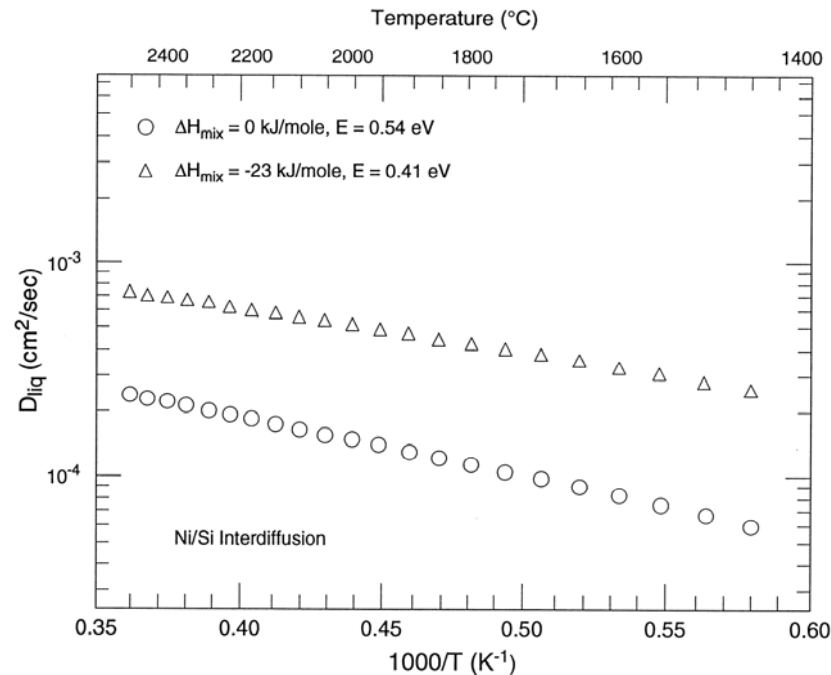
Liquid State Diffusion

$$D_{liq} = D_{kin}\left(1 - \frac{2\Delta H^{L}_{mix}}{k_{B}T}\right)$$
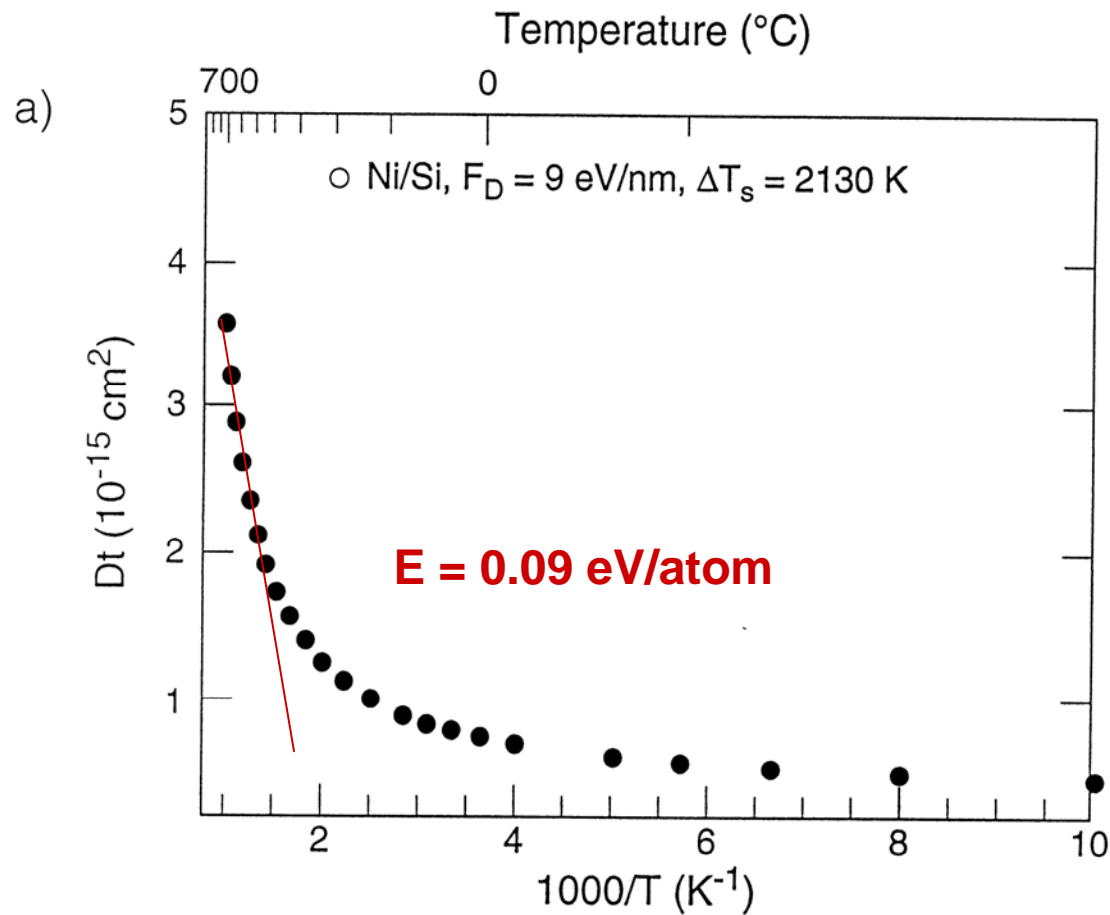
D_{kin} = MD corrected Enskog kinetic diffusion coefficient

$\Delta H_{mix}{}^{L}$ = compositional-dependent liquid heat of mixing.

$(1 - \Delta H_{mix}{}^{L}/kBT)$ is the thermodynamic factor and accounts for the nonideality of the solution (Darken equation)

Temperature (°C)

ΔH_{mix} = 0 kJ/mole, E = 0.54 eV

ΔH_{mix} = -23 kJ/mole, E = 0.41 eV

Ni/Si Interdiffusion
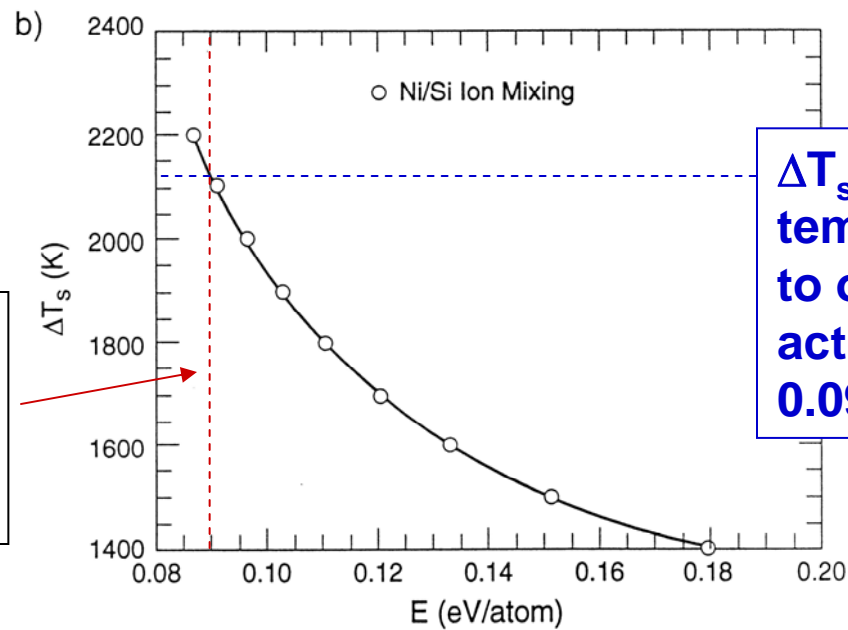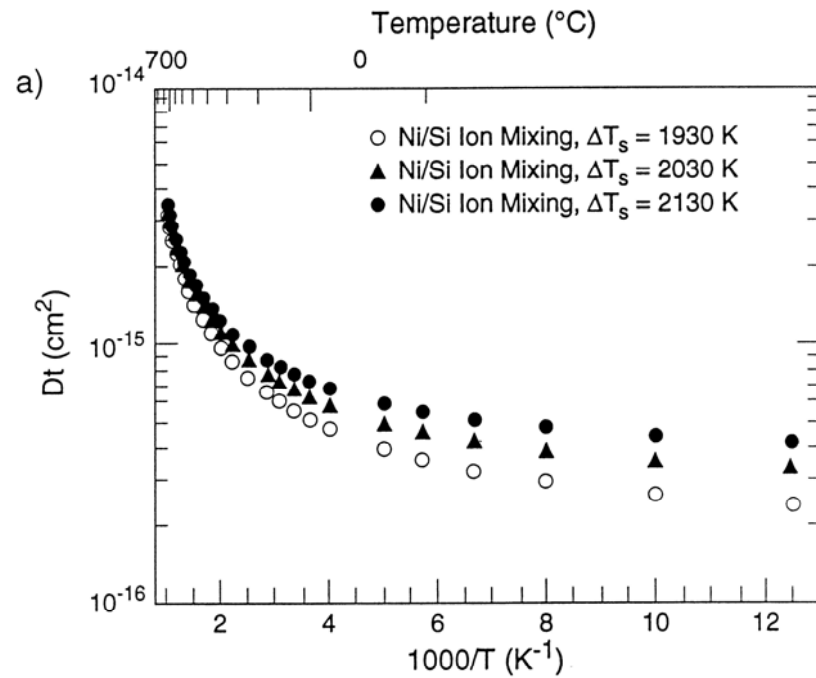
D_{liq} (cm²/sec)

1000/T (K⁻¹)

Nastasi & Mayer, *Radiation Effects and Defects in Solids*, 130-131 (1994) pp. 367-385.

Liquid Diffusion Model of the Cascade

ΔT_s = assumed spike temperature

a) Ni/Si Ion Mixing, ΔT_s = 1930 K
Ni/Si Ion Mixing, ΔT_s = 2030 K
Ni/Si Ion Mixing, ΔT_s = 2130 K

Temperature (°C)

Dt (cm^2)

$1000/T$ (K^{-1})

b) Ni/Si Ion Mixing

ΔT_s (K)

E (eV/atom)

Experimentally observed activation energy for Ni/Si 0.09 eV/atom

ΔT_s = 2130 K = spike temperature needed to obtain an activation energy of 0.09 eV/atom

Spike Temperatures During Temperature Dependent Ion Mixing

TABLE 10. Activation energies and spike temperatures from the cylindrical spike model. T_{melt} is the melting temperature of the lowest melting compound, eutectic or element

System	E_A^{ion} (eV atom^{-1})	ΔH_{mix}^{liq} (kJ mol^{-1})	ΔT_s (K)	T_{melt} (K)
Au–Zr	0.06	−74	3800	1473
Zr–Fe	0.07	−25	2940	1247
Ni–Si	0.09	−23	2130	1239
Pt–Si	0.11	−36	1480	1103
U–Ti	0.12	−18	2180	1405(U)
Si–Ge	0.16	0	1860	1210(Ge)
Cr–Si	0.20	−20	1750	1578
U–Al	0.25	−62	1075	913
Nb–Si	0.25	−39	2250	1648
Cu–Al	0.27	−8	975	821
Mo–Si	0.30	−18	2300	1673
Co–Si	0.33	−21	1200	1468
U–Si	0.34	−99	1140	1258
Zr–Ni	0.40	−49	1730	1233
U–Al	0.57	−62	720	913
Nb–Si	0.90	−39	1900	1648