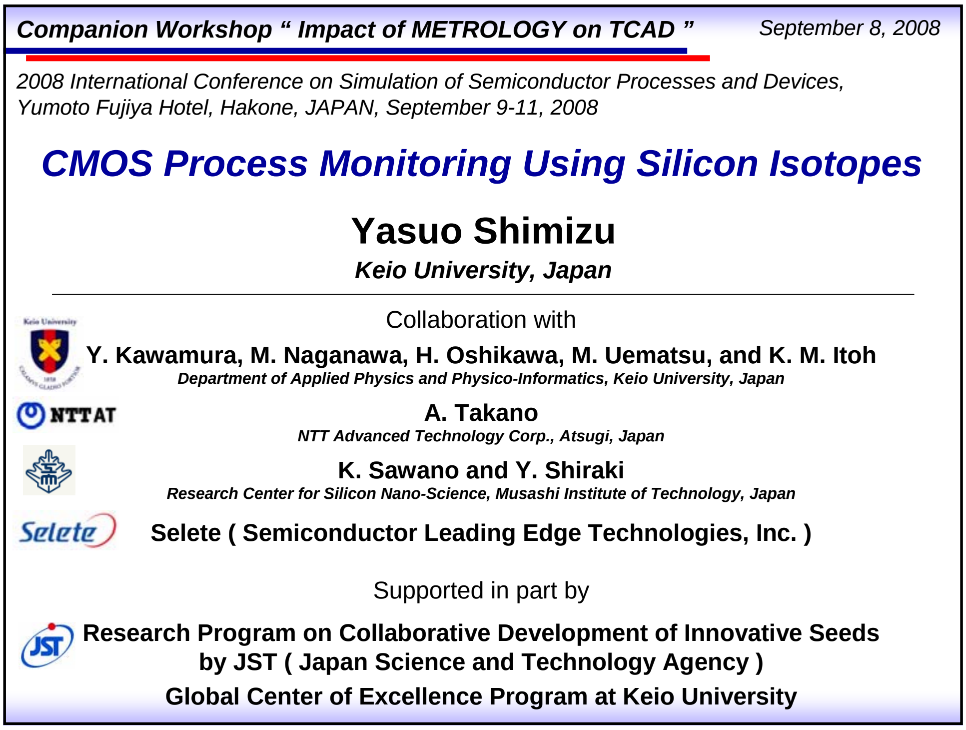


Companion Workshop " Impact of METROLOGY on TCAD " *September 8, 2008*

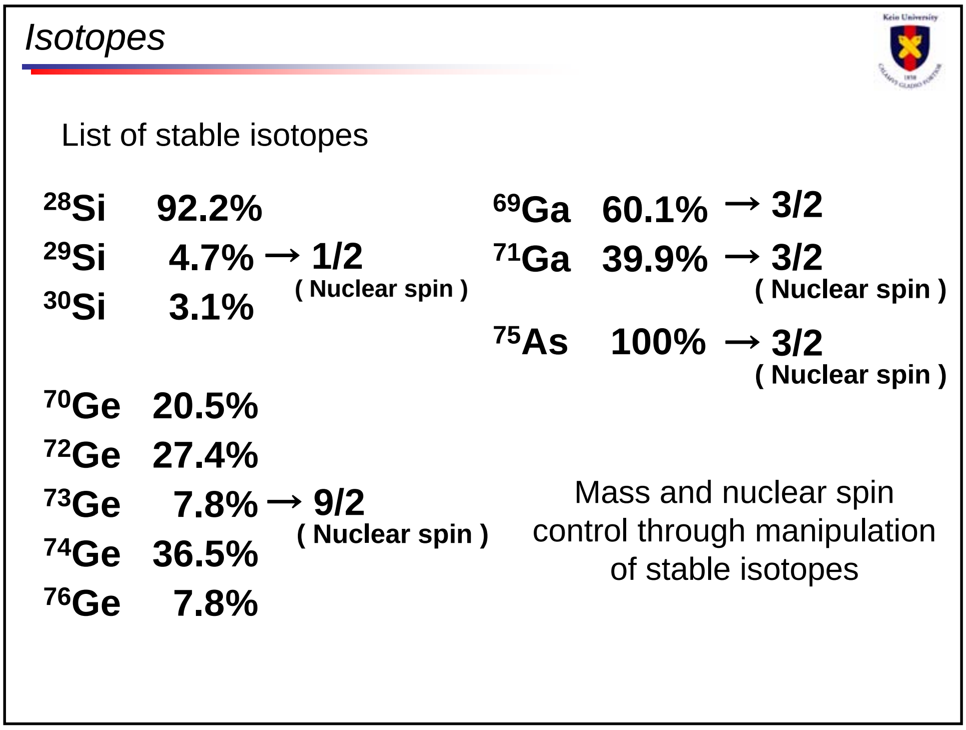
2008 International Conference on Simulation of Semiconductor Processes and Devices,
Yumoto Fujiya Hotel, Hakone, JAPAN, September 9-11, 2008

CMOS Process Monitoring Using Silicon Isotopes

Yasuo Shimizu
Keio University, Japan

Collaboration with
Y. Kawamura, M. Naganawa, H. Oshikawa, M. Uematsu, and K. M. Itoh
Department of Applied Physics and Physico-Informatics, Keio University, Japan
A. Takano
NTT Advanced Technology Corp., Atsugi, Japan
K. Sawano and Y. Shiraki
Research Center for Silicon Nano-Science, Musashi Institute of Technology, Japan
Selete (Semiconductor Leading Edge Technologies, Inc.)

Supported in part by
Research Program on Collaborative Development of Innovative Seeds
by JST (Japan Science and Technology Agency)
Global Center of Excellence Program at Keio University



Isotopes

List of stable isotopes

^{28}Si	**92.2%**	
^{29}Si	**4.7%**	**→ 1/2** (Nuclear spin)
^{30}Si	**3.1%**	

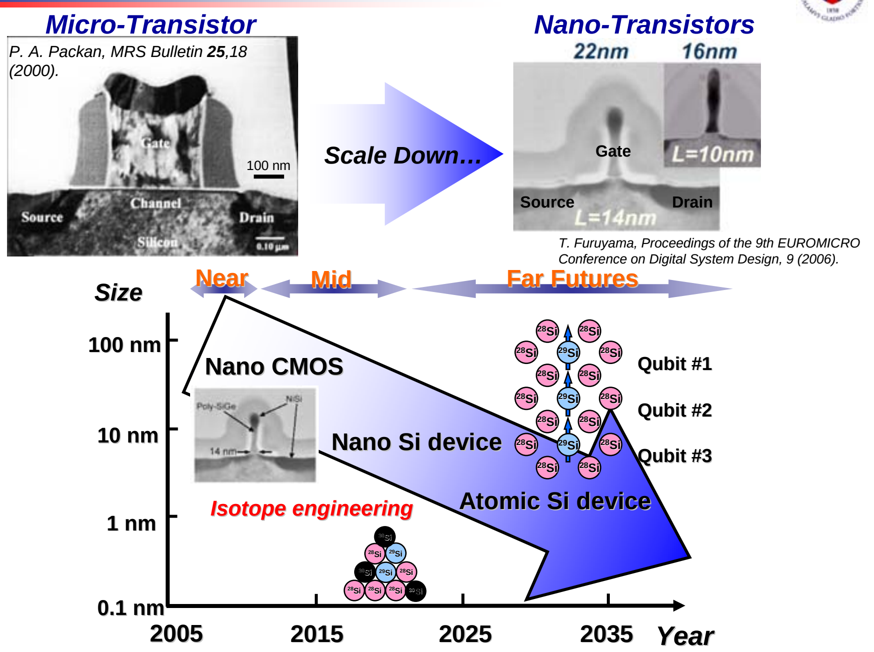
^{70}Ge	**20.5%**	
^{72}Ge	**27.4%**	
^{73}Ge	**7.8%**	**→ 9/2** (Nuclear spin)
^{74}Ge	**36.5%**	
^{76}Ge	**7.8%**	

^{69}Ga	**60.1%**	**→ 3/2**
^{71}Ga	**39.9%**	**→ 3/2** (Nuclear spin)

^{75}As	**100%**	**→ 3/2** (Nuclear spin)

Mass and nuclear spin
control through manipulation
of stable isotopes

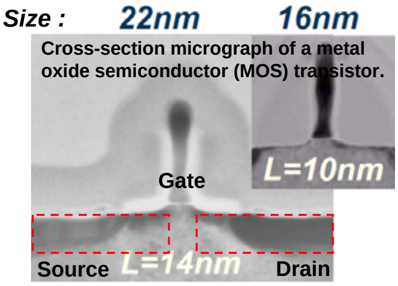
Device Size vs Year



P. A. Packan, MRS Bulletin ***25***,*18 (2000).*

T. Furuyama, Proceedings of the 9th EUROMICRO Conference on Digital System Design, 9 (2006).

Contents



Cross-section micrograph of a metal oxide semiconductor (MOS) transistor.

Higher impurity concentration in extremely localized regions of S/D for low device resistance

- Low-temperature process to minimize the diffusion length.

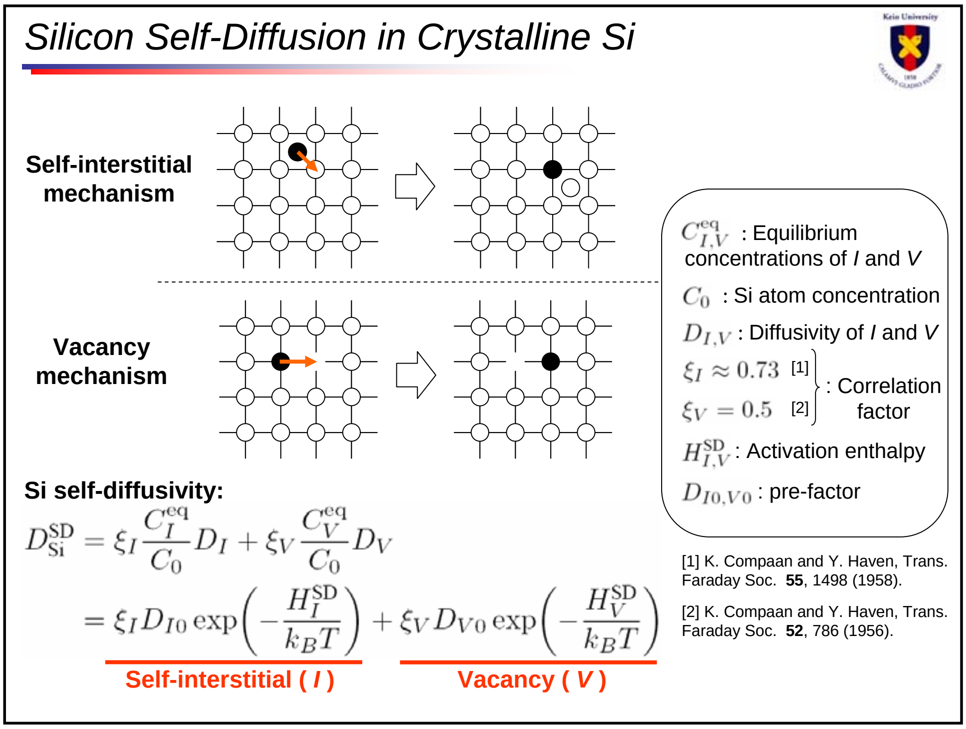
- Effect of interfaces becomes crucial.

1. Si self-diffusivity below 850 °C
This work: Si self-diffusivity determination down to ~ 700 °C

2. Dopant and Si atom interactions (nano-scale, near the surface)

(i) Si mixing and amorphization induced by implantation
This work: Si displacement including the critical value for amorphization

(ii) Dopant diffusion in Si during post-implantation annealing
This work: Simultaneous observation of self- and dopant diffusion in Si



Silicon Self-Diffusion in Crystalline Si

Self-interstitial mechanism

Vacancy mechanism

Si self-diffusivity:

$$D_{\mathrm{Si}}^{\mathrm{SD}} = \xi_I \frac{C_I^{\mathrm{eq}}}{C_0} D_I + \xi_V \frac{C_V^{\mathrm{eq}}}{C_0} D_V$$

$$= \underbrace{\xi_I D_{I0} \exp\left(-\frac{H_I^{\mathrm{SD}}}{k_B T}\right)}_{\text{Self-interstitial (} I \text{)}} + \underbrace{\xi_V D_{V0} \exp\left(-\frac{H_V^{\mathrm{SD}}}{k_B T}\right)}_{\text{Vacancy (} V \text{)}}$$

$C_{I,V}^{\mathrm{eq}}$: Equilibrium concentrations of *I* and *V*

C_0 : Si atom concentration

$D_{I,V}$: Diffusivity of *I* and *V*

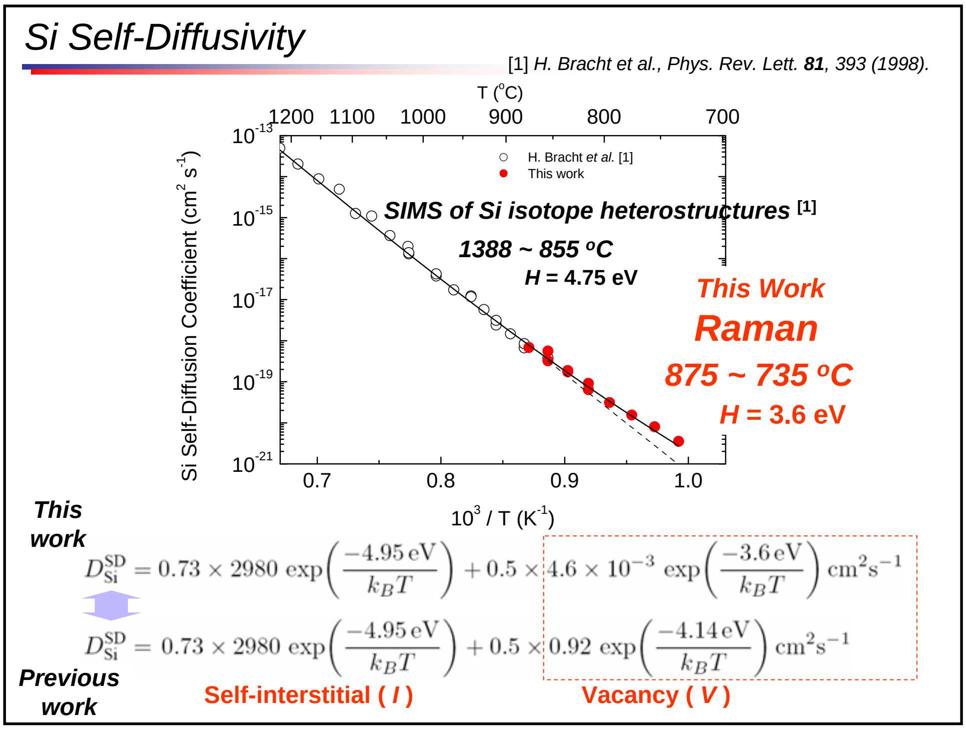
$\xi_I \approx 0.73$ [1], $\xi_V = 0.5$ [2] : Correlation factor

$H_{I,V}^{\mathrm{SD}}$: Activation enthalpy

$D_{I0,V0}$: pre-factor

[1] K. Compaan and Y. Haven, Trans. Faraday Soc. **55**, 1498 (1958).

[2] K. Compaan and Y. Haven, Trans. Faraday Soc. **52**, 786 (1956).



Si Self-Diffusivity

[1] *H. Bracht et al., Phys. Rev. Lett.* ***81****, 393 (1998).*

SIMS of Si isotope heterostructures [1]

1388 ~ 855 ºC

***H* = 4.75 eV**

This Work

Raman

875 ~ 735 ºC

***H* = 3.6 eV**

This work

$$D_{\mathrm{Si}}^{\mathrm{SD}} = 0.73 \times 2980 \exp\left(\frac{-4.95\,\mathrm{eV}}{k_B T}\right) + 0.5 \times \boxed{4.6 \times 10^{-3} \exp\left(\frac{-3.6\,\mathrm{eV}}{k_B T}\right) \mathrm{cm}^2\mathrm{s}^{-1}}$$

$$D_{\mathrm{Si}}^{\mathrm{SD}} = 0.73 \times 2980 \exp\left(\frac{-4.95\,\mathrm{eV}}{k_B T}\right) + 0.5 \times \boxed{0.92 \exp\left(\frac{-4.14\,\mathrm{eV}}{k_B T}\right) \mathrm{cm}^2\mathrm{s}^{-1}}$$

Previous work

Self-interstitial (*I*) **Vacancy (*V*)**

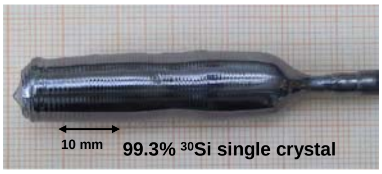
Silicon Isotope Superlattices (SLs)

T. Kojima et al., Appl. Phys. Lett. ***83****, 2318 (2003).*
Y. Shimizu and K. M. Itoh, Thin Solid Films ***508****, 160 (2006), etc.*

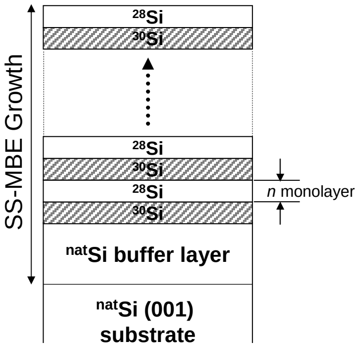
Isotopes in natural silicon

Isotopes	Abundances (at.%)
^{28}Si	92.23
^{29}Si	4.67
^{30}Si	3.10

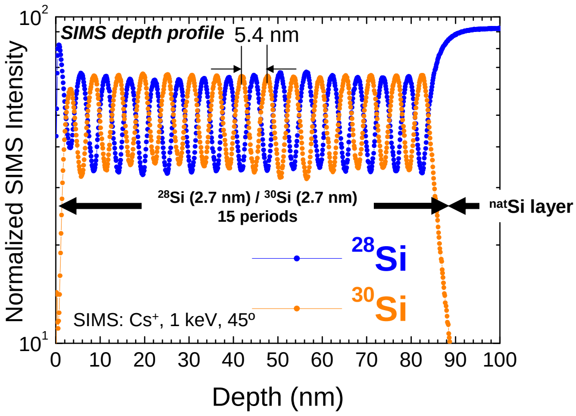
99.92% ^{28}Si single crystal



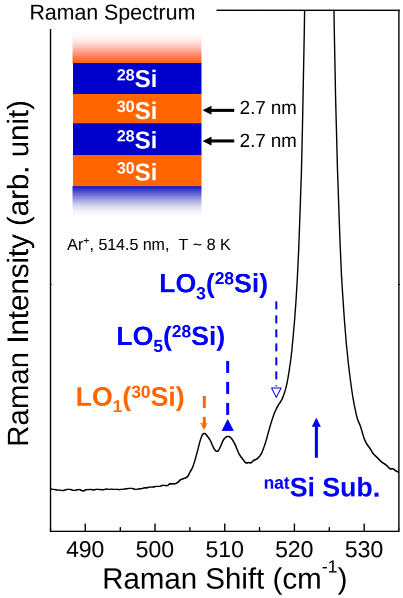
99.3% ^{30}Si single crystal



^{28}Si$_n$ / ^{30}Si$_n$ isotope superlattices

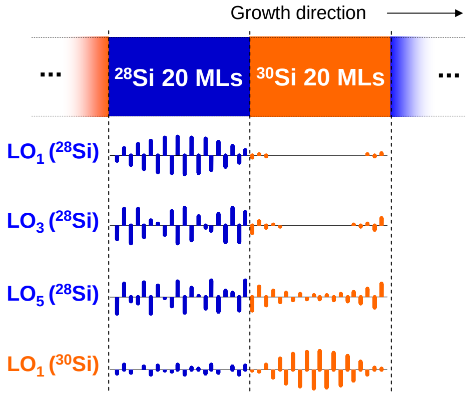


Raman Scattering in Si Isotope SL



LO : Longitudinal Optical

Local vibration modes in as-grown ^{28}Si$_{20}$/^{30}Si$_{20}$



Modes position depends on

1. ***Periodicity*** ← ***Isotope mass***
2. ***Sharpness at the interface*** ← ***Self-diffusion***

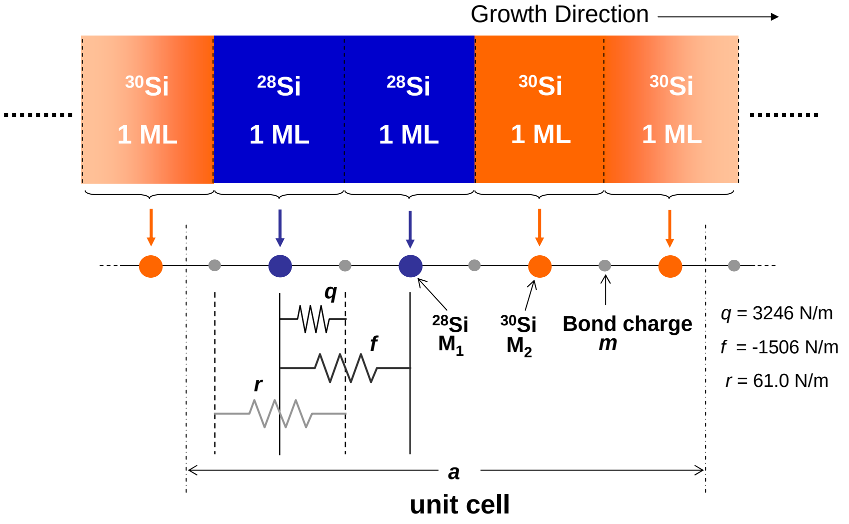
Ge self-diffusion: E. Silveira et al., Phys. Rev. B ***56****, 2062 (1997).*

Phonon Frequency Calculation

P. Molinàs-Mata and M. Cardona, Phys. Rev. B ***43****, 9799 (1991).*

Planar bond-charge model

(ML: Monolayer)



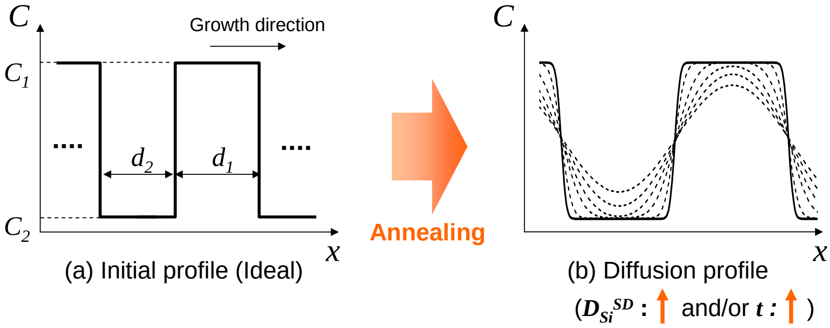
q = 3246 N/m

f = -1506 N/m

r = 61.0 N/m

Application to Self-Diffusion Study

Y. Shimizu et al., Phys. Rev. Lett. ***98****, 095901 (2007).*



(a) Initial profile (Ideal)

(b) Diffusion profile

$$C(x,t) = C_2 + \frac{C_1 - C_2}{2}\sum_{k=1}^{m}\left[\mathrm{erf}\left(\frac{x-\{(k-1)d_1+kd_2\}}{2(l+\sqrt{\boxed{D_{\mathrm{Si}}^{\mathrm{SD}}}t})}\right) - \mathrm{erf}\left(\frac{x-(kd_1+kd_2)}{2(l+\sqrt{\boxed{D_{\mathrm{Si}}^{\mathrm{SD}}}t})}\right)\right]$$

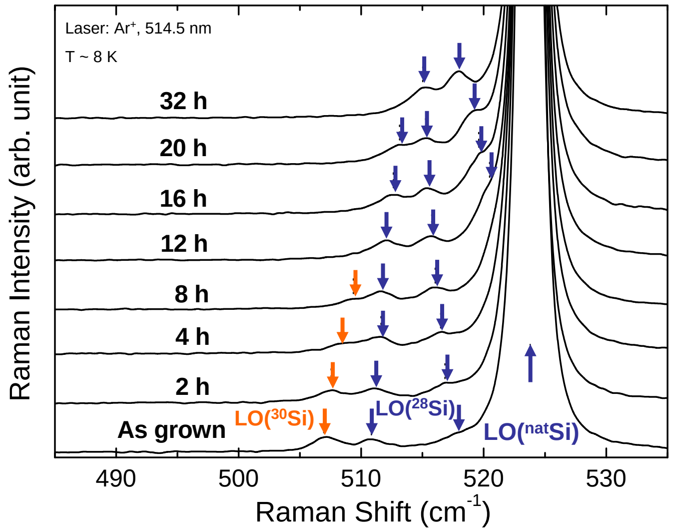
$C_{1,2}$: Concentration, x : Growth direction, $d_{1,2}$: Thickness of $C_{1,2}$

m : Number of period, l : mixing parameter, D_{Si}^{SD} : Si self-diffusivity, t :Time

Experimental peak position is as a function of Si self-diffusivity.

A Series of Raman Spectra (815 °C)

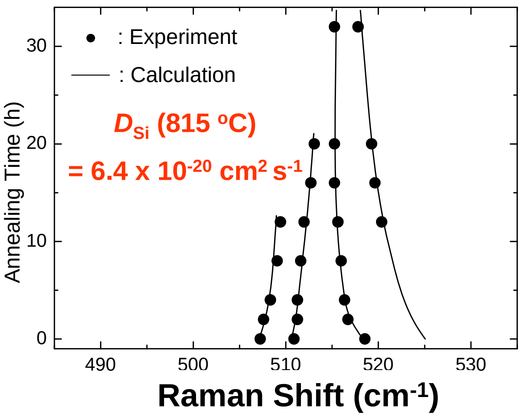
Silicon Self-Diffusion



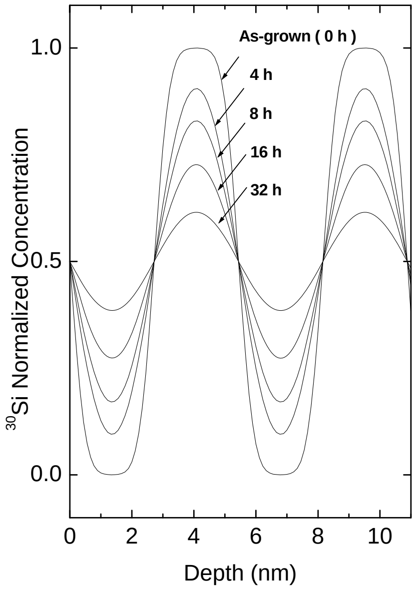
$^{28}Si_{20}/^{30}Si_{20}$ isotope SL annealed at 815 °C

Y. Shimizu et al., Phys. Rev. Lett. ***98****, 095901 (2007).*

Time Dependence of Raman Shift (815 °C)

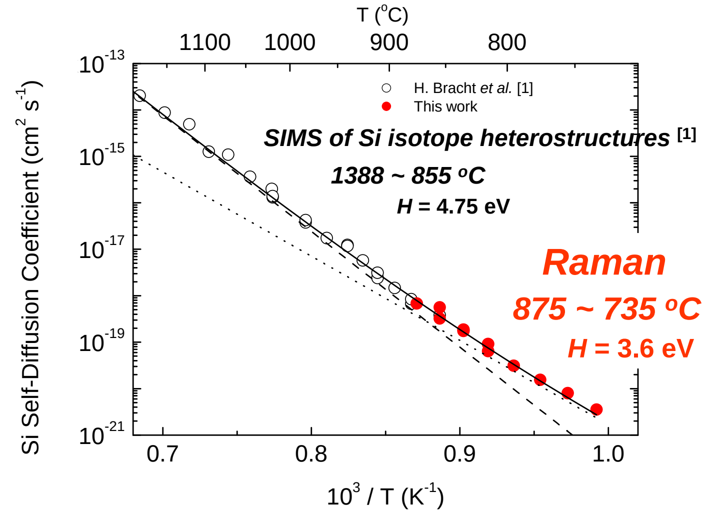


>>> Si self-diffusivity is obtained for a given temperature.



Si Self-Diffusivity

[1] *H. Bracht et al., Phys. Rev. Lett.* ***81****, 393 (1998).*



SIMS of Si isotope heterostructures **[1]**

1388 ~ 855 °C

***H* = 4.75 eV**

Raman

875 ~ 735 °C

***H* = 3.6 eV**

$$D_{\mathrm{Si}}^{\mathrm{SD}} = \underbrace{0.73 \times 2980 \exp\left(\frac{-4.95\,\mathrm{eV}}{k_B T}\right)}_{\textbf{Self-interstitial (}\textit{I}\textbf{)}} + \underbrace{0.5 \times 4.6 \times 10^{-3} \exp\left(\frac{-3.6\,\mathrm{eV}}{k_B T}\right)}_{\textbf{Vacancy (}\textit{V}\textbf{)}} \mathrm{cm^2 s^{-1}}$$

Self-Interstitials and Vacancies Contribution

Previous work : 855 ~ 1400 °C [H. Bracht *et al.*, Phys. Rev. Lett. **81**, 393 (1998).]

$$D_{\mathrm{Si}}^{\mathrm{SD}} = 0.73 \times 2980 \exp\left(\frac{-4.95\,\mathrm{eV}}{k_B T}\right) + 0.5 \times 0.92 \exp\left(\frac{-4.14\,\mathrm{eV}}{k_B T}\right) \mathrm{cm^2 s^{-1}}$$

This work : 735 ~ 875 °C

$$D_{\mathrm{Si}}^{\mathrm{SD}} = 0.73 \times 2980 \exp\left(\frac{-4.95\,\mathrm{eV}}{k_B T}\right) + 0.5 \times 4.6 \times 10^{-3} \exp\left(\frac{-3.6\,\mathrm{eV}}{k_B T}\right) \mathrm{cm^2 s^{-1}}$$

Vacancy Activation Enthalpy (This work) : $3.6^{+0.3}_{-0.1}$ eV

Other previous work

$$H_V^{\mathrm{SD}} = H_V^f + H_V^m = \underline{3.17} + \underline{0.4} = \underline{3.57\ \mathrm{eV}}$$

***Ab initio* calculation**

M. I. J. Probert and M. C. Payne, Phys. Rev. B **67**, 075204 (2003).

Electron Paramagnetic Resonance Study

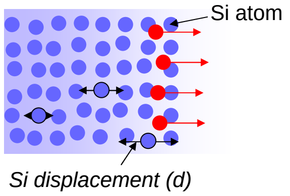
G. D. Watkins, Mater. Res. Soc. Symp. Proc. **469**, 139 (1997).

***Ab initio* calculation**

F. El-Mellouhi *et al.*, Phys. Rev. B **70**, 205202 (2004).

Dopant and Si Atom Interactions

TOPIC 1 : *Quantitative determination of Si displacement (d)*



Large *d* ⟶ Amorphous
Small *d* ⟶ Single-crystalline

< d_c (Si) ~ 0.5 nm

TOPIC 2 : *TED of Si during post ion-implantation annealing*

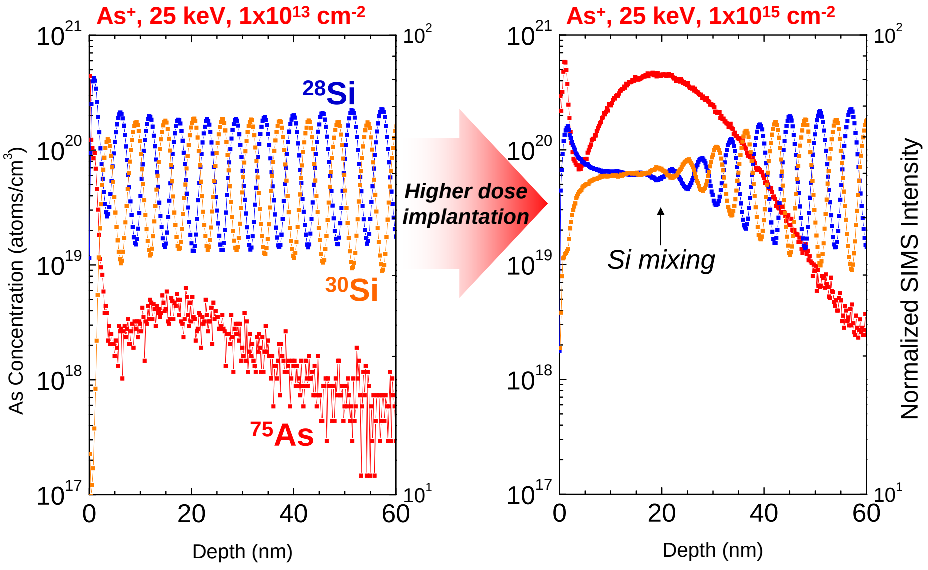
Contribution of self-interstitials

Si implantation ⟶ Contribution of I^0

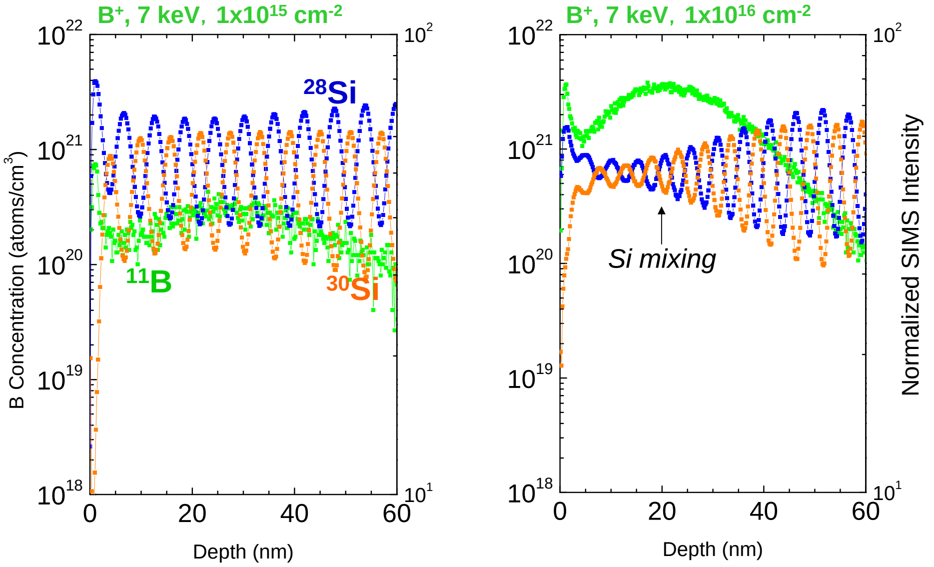
B implantation ⟶ Contribution of I^{2+} (Fermi-level effect)

Quantitative Determination of Si Displacement

Y. Shimizu et al., Appl. Phys. Express ***1****, 021401 (2008).*

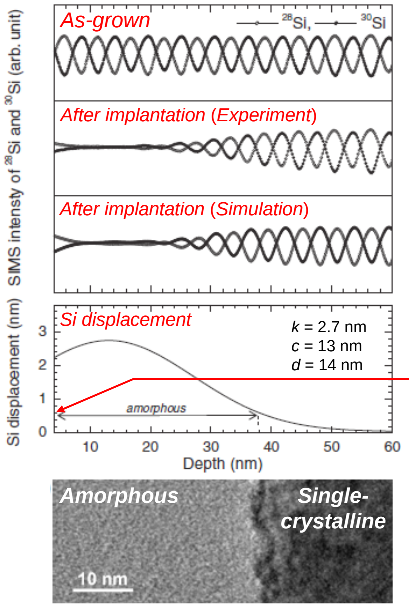


Quantitative Determination of Si Displacement



Si Displacement / Condition for Amorphization

Y. Shimizu et al., Appl. Phys. Express **1**, 021401 (2008).



$$C_{\text{aft}-\text{imp}}(x) = \int C_{\text{bef}-\text{imp}}(x')\, g(x - x')\, dx'$$

$C_{\text{aft-imp}}(x)$: *The concentration after implantation*

$C_{\text{bef-imp}}(x)$: *The concentration before implantation*

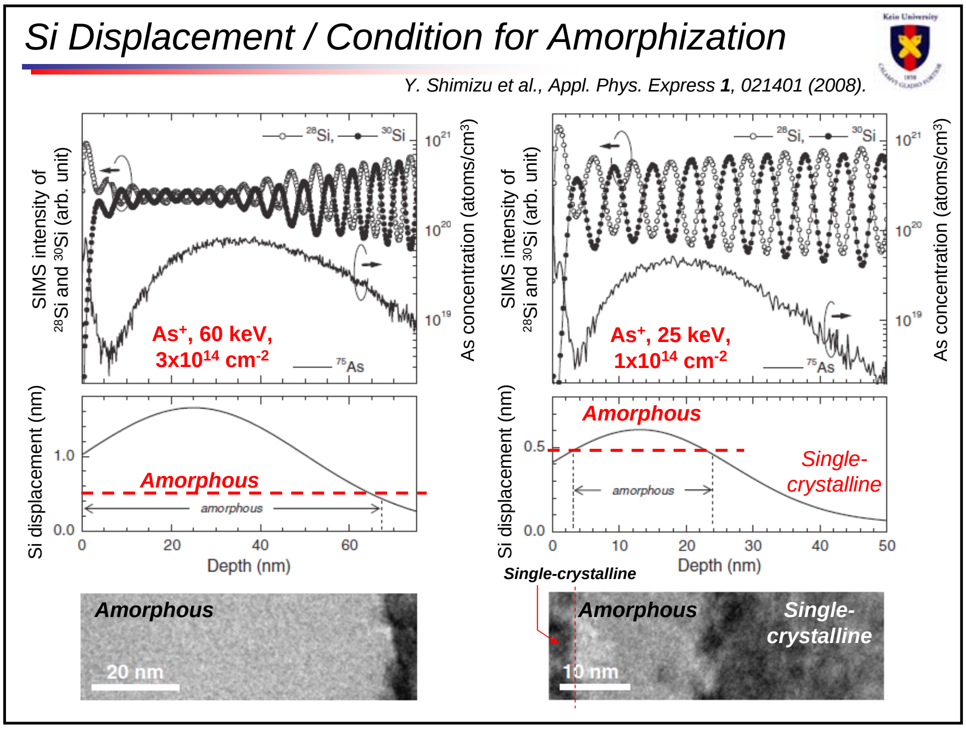
$$\sigma(x) = k \exp\left[-\frac{(x-c)^2}{2d^2}\right]$$

k : *peak amplitude* c : *peak position*

c : *peak width*

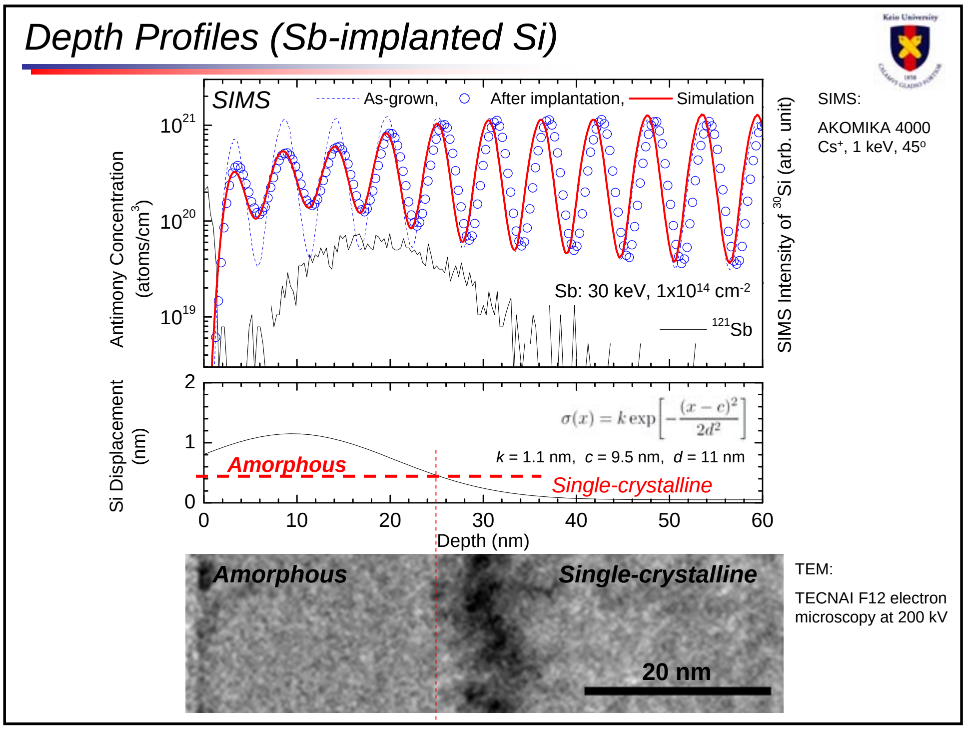
Critical displacement : ~ 0.5 nm

(Amorphous / Crystalline)



Si Displacement / Condition for Amorphization

Y. Shimizu et al., Appl. Phys. Express **1**, 021401 (2008).



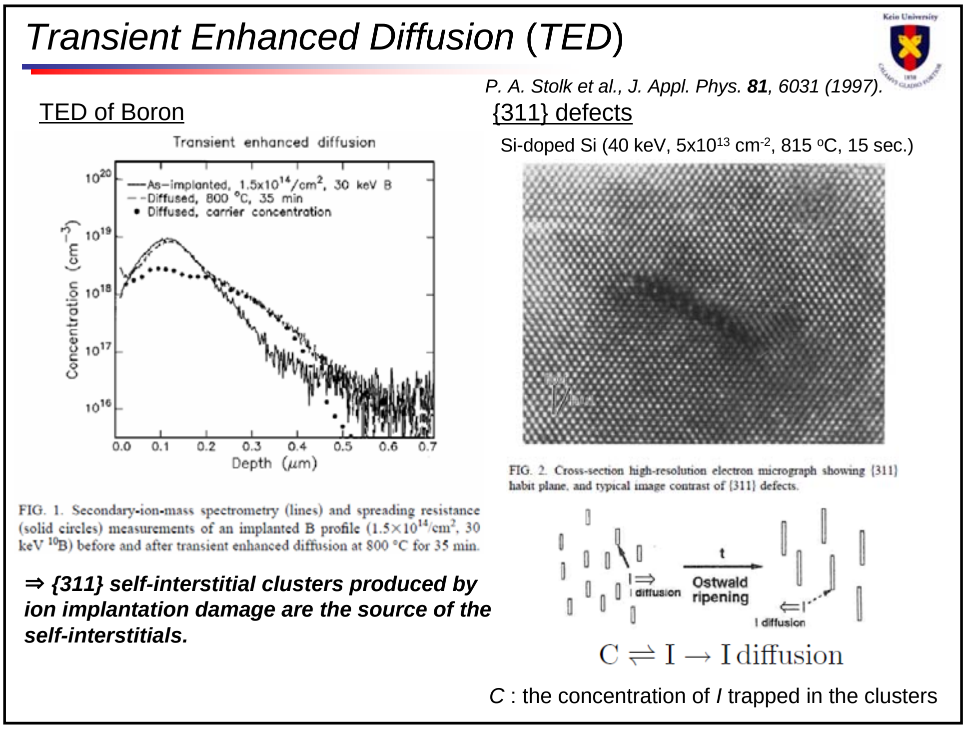
Depth Profiles (Sb-implanted Si)

SIMS:

AKOMIKA 4000
Cs$^+$, 1 keV, 45°

TEM:

TECNAI F12 electron microscopy at 200 kV



Transient Enhanced Diffusion (TED)

P. A. Stolk et al., J. Appl. Phys. ***81****, 6031 (1997).*

TED of Boron

FIG. 1. Secondary-ion-mass spectrometry (lines) and spreading resistance (solid circles) measurements of an implanted B profile (1.5×10^{14}/cm², 30 keV ^{10}B) before and after transient enhanced diffusion at 800 °C for 35 min.

⇒ {311} self-interstitial clusters produced by ion implantation damage are the source of the self-interstitials.

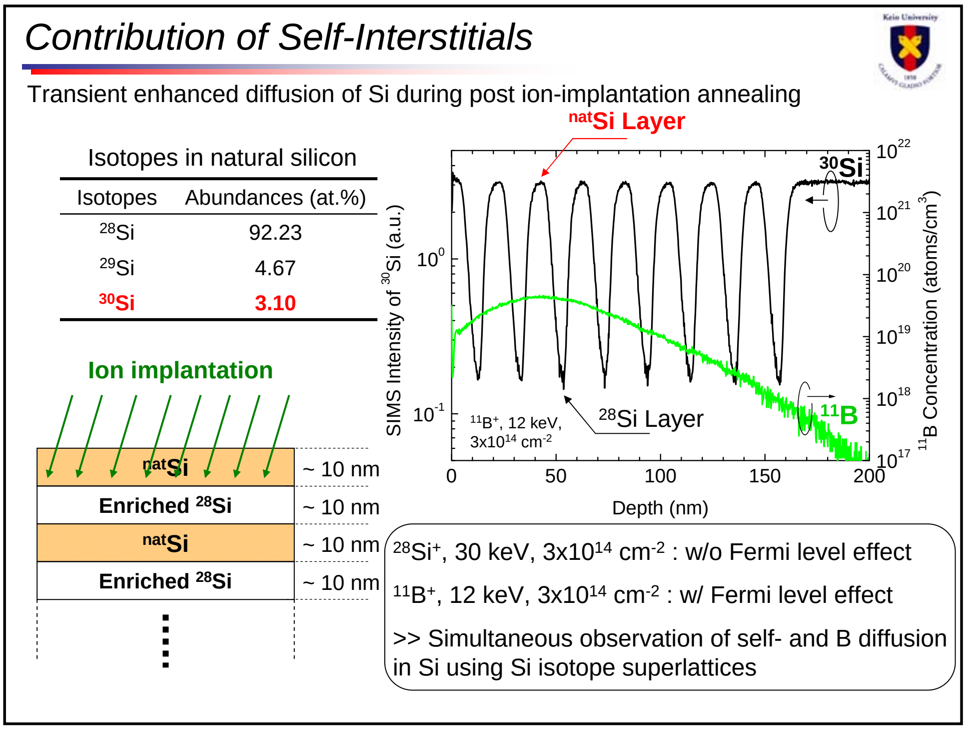
{311} defects

Si-doped Si (40 keV, 5x10^{13} cm^{-2}, 815 ^{o}C, 15 sec.)

FIG. 2. Cross-section high-resolution electron micrograph showing {311} habit plane, and typical image contrast of {311} defects.

$$\mathrm{C} \rightleftharpoons \mathrm{I} \rightarrow \mathrm{I\,diffusion}$$

C : the concentration of *I* trapped in the clusters



Contribution of Self-Interstitials

Transient enhanced diffusion of Si during post ion-implantation annealing

Isotopes in natural silicon

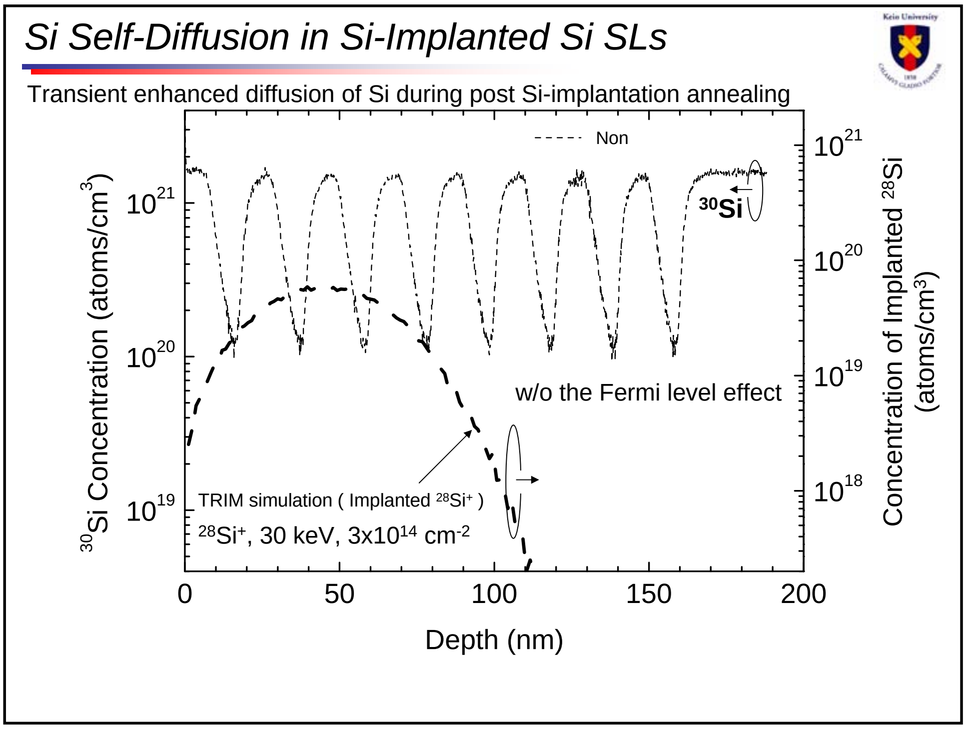
Isotopes	Abundances (at.%)
^{28}Si	92.23
^{29}Si	4.67
^{30}Si	**3.10**

Ion implantation

^{28}Si^{+}, 30 keV, 3x10^{14} cm^{-2} : w/o Fermi level effect

^{11}B^{+}, 12 keV, 3x10^{14} cm^{-2} : w/ Fermi level effect

>> Simultaneous observation of self- and B diffusion in Si using Si isotope superlattices



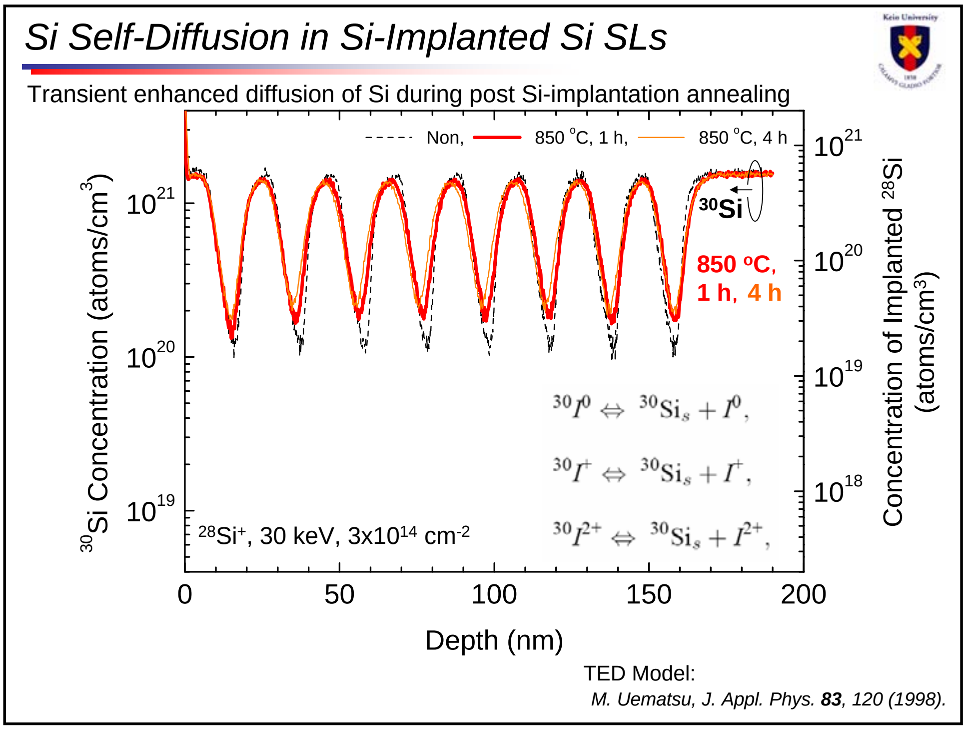
Si Self-Diffusion in Si-Implanted Si SLs

Transient enhanced diffusion of Si during post Si-implantation annealing

w/o the Fermi level effect

TRIM simulation (Implanted $^{28}Si^+$)

$^{28}Si^+$, 30 keV, 3x10^{14} cm^{-2}



Si Self-Diffusion in Si-Implanted Si SLs

Transient enhanced diffusion of Si during post Si-implantation annealing

850 °C, 1 h, 4 h

$$^{30}I^0 \Leftrightarrow {}^{30}\mathrm{Si}_s + I^0,$$

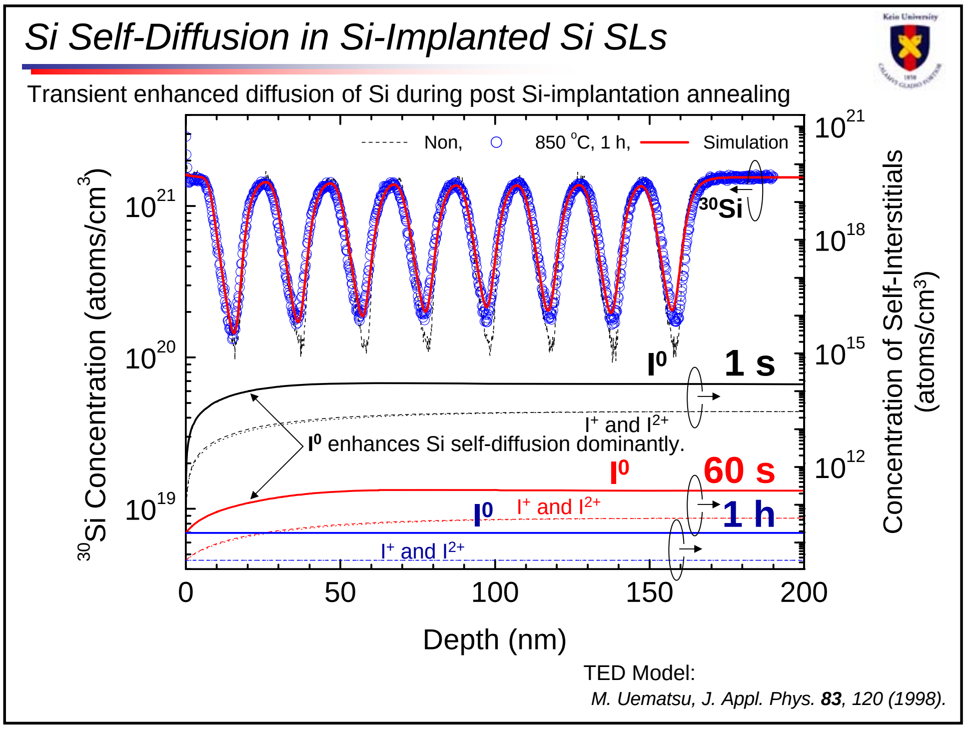
$$^{30}I^+ \Leftrightarrow {}^{30}\mathrm{Si}_s + I^+,$$

$$^{30}I^{2+} \Leftrightarrow {}^{30}\mathrm{Si}_s + I^{2+},$$

$^{28}Si^+$, 30 keV, 3x10^{14} cm^{-2}

TED Model:

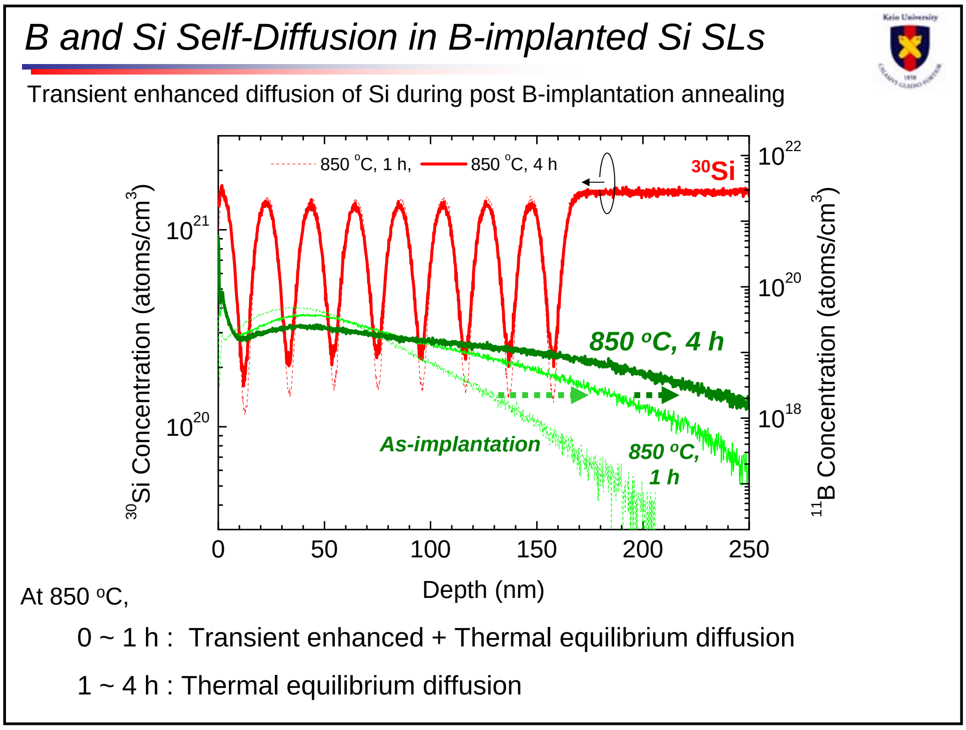
M. Uematsu, J. Appl. Phys. ***83****, 120 (1998).*



Si Self-Diffusion in Si-Implanted Si SLs

Transient enhanced diffusion of Si during post Si-implantation annealing

TED Model:
M. Uematsu, J. Appl. Phys. ***83****, 120 (1998).*



B and Si Self-Diffusion in B-implanted Si SLs

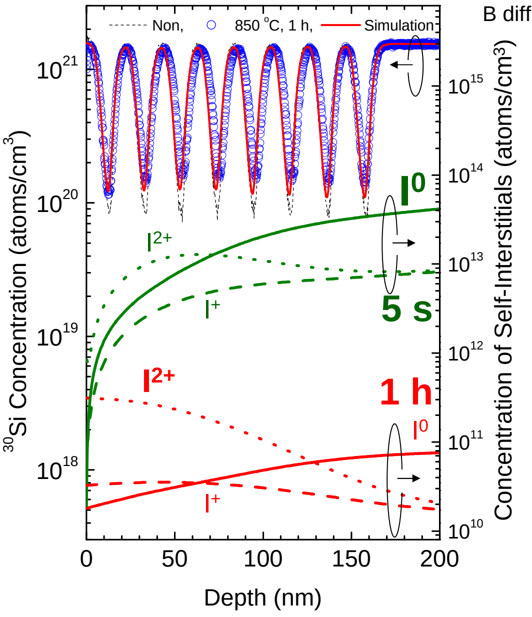
Transient enhanced diffusion of Si during post B-implantation annealing

At 850 °C,

0 ~ 1 h : Transient enhanced + Thermal equilibrium diffusion

1 ~ 4 h : Thermal equilibrium diffusion

Time Evolution of Self-Interstitials



B diffusion in Si : *kick-out mechanism*

$$B_i^0 \rightleftharpoons B_s^- + I^0 + h$$

$$B_i^0 \rightleftharpoons B_s^- + I^+$$

$$h + B_i^0 \rightleftharpoons B_s^- + I^{2+}$$

and TED and BI clusters.

M. Uematsu, J. Appl. Phys. ***83****, 120 (1998).*

M. Uematsu, J. Appl. Phys. ***84****, 4781 (1998).*

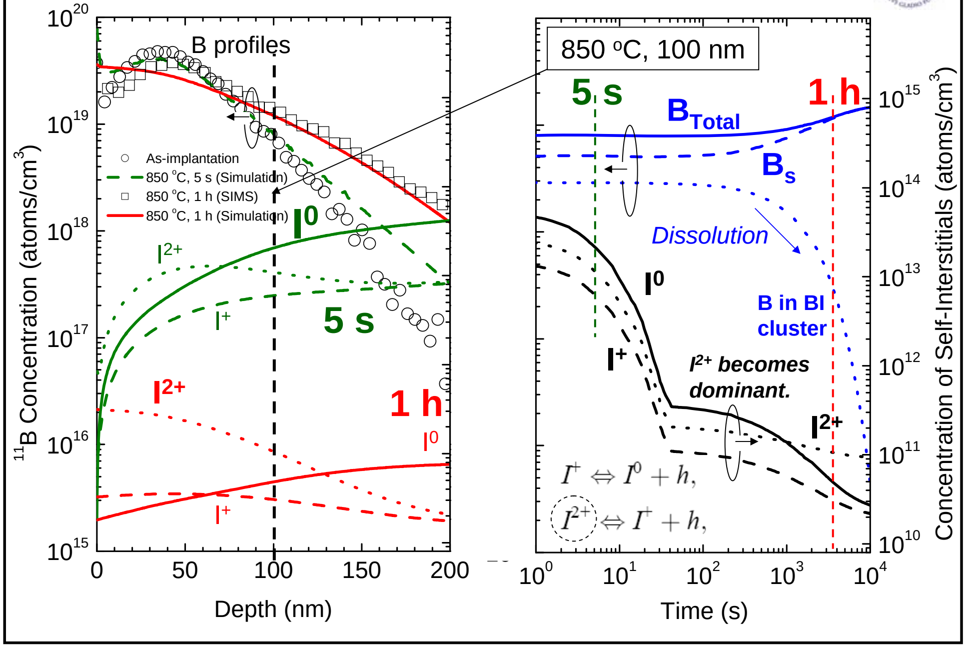
Short Time Annealing : << 1 h

I^0 enhances Si self-diffusion dominantly.

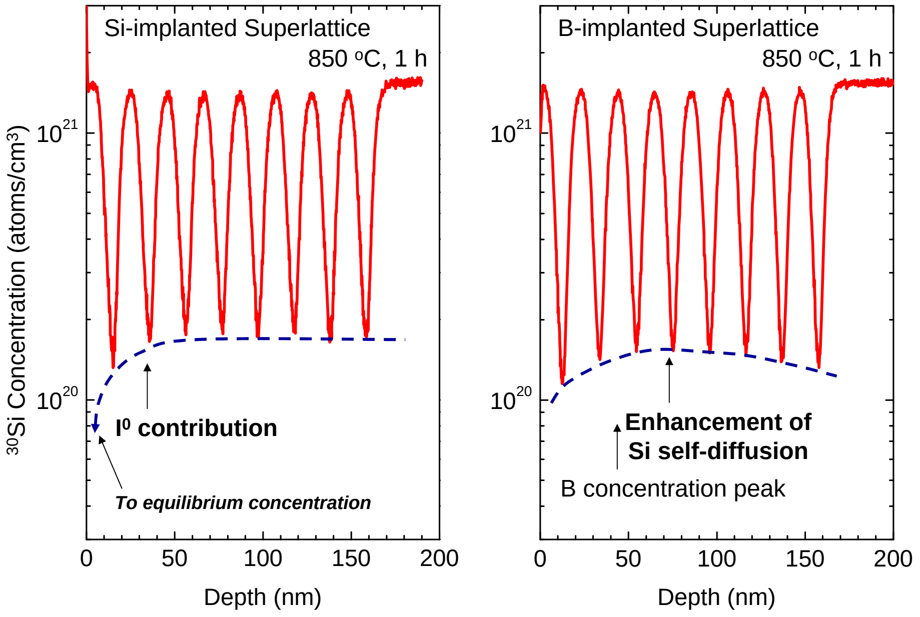
Long Time Annealing : > 1 h

I^{2+} enhances Si self-diffusion in the shallower region. Fermi-level effect, etc.

Time Evolution of Self-Interstitials



Post Ion-Implantation Annealing (Si and B)



Summary

- Diffusion studies using Si isotopes to identify what types of kinetics and reactions are relevant to nano-CMOS processing
- Non-equilibrium (transient) behaviors of defect interactions

1. Si self-diffusion in Si at low temperatures ($T < 850$ °C)
2. Dopant and (host) Si atom interactions
   (i) Si displacement induced by ion implantation
   (ii) Simultaneous observation of self- and dopant diffusion in Si

"Nano is completely different from Micro."