Dopant and Self-Diffusion in Semiconductors:
A Tutorial

Eugene Haller and Hughes Silvestri
MS&E, UCB and LBNL
FLCC Tutorial
1/26/04
Outline

• Motivation

• Background
  – Fick’s Laws
  – Diffusion Mechanisms

• Experimental Techniques for Solid State Diffusion

• Diffusion with Stable Isotope Structures

• Conclusions
Motivation

• Why diffusion is important for feature level control of device processing
  
  – Nanometer size feature control: - any extraneous diffusion of dopant atoms may result in device performance degradation
    • Source/drain extensions

  – Accurate models of diffusion are required for dimensional control on the nanometer scale
Semiconductor Technology Roadmap

(International Technology Roadmap for Semiconductors, 2001)

**Difficult Challenges of the International Technology Working Groups**

*Modeling and Simulation*

<table>
<thead>
<tr>
<th>Difficult Challenges ≥ 65 nm, Through 2007</th>
<th>Summary Of Issues</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modeling of Ultra Shallow Dopant Distributions, Junctions, and Silicidation</td>
<td>Dopant models and parameters (damage, high-concentration, activation, metastable effects, diffusion, interface and silicide effects). Characterization tools for these ultra shallow geometries and dopant levels.</td>
</tr>
</tbody>
</table>

**Thermal & Thin-film, Doping and Etching Technology Requirements, Near-Term**

<table>
<thead>
<tr>
<th></th>
<th>2001</th>
<th>2002</th>
<th>2003</th>
<th>2004</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drain extension $X_j$ (nm) [G]</td>
<td>27.45</td>
<td>22.36</td>
<td>19.31</td>
<td>15.25</td>
<td>13.22</td>
<td>12.19</td>
<td>10.17</td>
</tr>
<tr>
<td>Maximum drain extension sheet resistance (PMOS) ($\Omega$/sq) [H]</td>
<td>400.0</td>
<td>460.0</td>
<td>550.0</td>
<td>660.0</td>
<td>770.0</td>
<td>830.0</td>
<td>760.0</td>
</tr>
<tr>
<td>Extension lateral abruptness (nm/decade) [I]</td>
<td>7.2</td>
<td>5.8</td>
<td>5.0</td>
<td>4.1</td>
<td>3.5</td>
<td>3.1</td>
<td>2.8</td>
</tr>
</tbody>
</table>

*White—Manufacturable Solutions Exist and Are Being Optimized*
*Yellow—Manufacturable Solutions are Known*
*Red—Manufacturable Solutions are NOT Known*
Fick’s Laws (1855)

Fick’s 1st Law: Flux of atoms
\[ J = -D \frac{\partial C_S}{\partial x} \]

Diffusion equation does not take into account interactions with defects!

2nd Law
\[ \frac{\partial C_S}{\partial t} = \frac{\partial}{\partial x} \left( D_S \frac{\partial C_S}{\partial x} \right) \]

only valid for pure interstitial diffusion

Example: Vacancy Mechanism \( A_s + V \Leftrightarrow AV \)
\[ G_{AV} = k_f[A_s][V] \quad R_{AV} = k_r[AV] \]
\[ \frac{\partial C_{AV}}{\partial t} = \frac{\partial}{\partial x} \left( D_{AV} \frac{\partial C_{AV}}{\partial x} \right) - k_r[AV] + k_f[A_s][V] \]
Analytical Solutions to Fick’s Equations

\[ D = \text{constant} \quad \frac{\partial C_s}{\partial t} = \frac{\partial}{\partial x} \left( D_s \frac{\partial C_s}{\partial x} \right) = D_s \frac{\partial^2 C_s}{\partial x^2} \]

- Finite source of diffusing species:
  Solution:
  Gaussian - \( C(x,t) = \frac{S}{\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}} \)

- Infinite source of diffusing species:
  Solution:
  Complementary error function -
  \[ C(x,t) = C_o \left( 1 - \frac{2}{\pi} \int_0^y e^{-z^2} dz \right), \quad y = \frac{x}{2\sqrt{Dt}} \]
Solutions to Fick’s Equations (cont.)

\[ D = f(C) \] Diffusion coefficient as a function of concentration

Concentration dependence can generate various profile shapes and penetration depths
Solid-State Diffusion Profiles

Experimentally determined profiles can be much more complicated
- no analytical solution

B implant and anneal in Si with and without Ge implant

Direct Diffusion Mechanisms in Crystalline Solids

(no native defects required)

Elements in Si: Li, H, 3d transition metals

No experimental evidence
High activation energy
Vacancy-assisted Diffusion Mechanisms
(native defects required)

Vacancy mechanism

\[ A_s + V \rightleftharpoons AV \]

(Sb in Si)

Dissociative mechanism

\[ A_s \rightleftharpoons A_i + V \]

(Cu in Ge)
Interstitial-assisted Diffusion Mechanisms
(native defects required)

Interstitialcy mechanism

$$A_s + I \iff AI$$ (P in Si)

Kick-out mechanism

$$A_s + I \overset{11}{\iff} A_i$$ (B in Si)
Why are Diffusion Mechanisms Important?

- Device processing can create non-equilibrium native defect concentrations
  - Implantation: *excess interstitials*
  - Oxidation: *excess interstitials*
  - Nitridation: *excess vacancies*
  - High doping: *Fermi level shift*
Oxidation Effects on Diffusion

Oxidation during device processing can lead to non-equilibrium diffusion

- Oxidation of Si surface causes injection of interstitials into Si bulk
- Increase in interstitial concentration causes enhanced diffusion of B, As, but retarded Sb diffusion
- Nitridation (vacancy injection) causes retarded B, P diffusion, enhanced Sb diffusion

(Fahey, et al., Rev. Mod. Phys. 61 289 (1989).)
Implantation Effects on Diffusion

- Transient Enhanced Diffusion (TED) - Eaglesham, et al.

- Implantation damage generates excess interstitials
  - Enhance the diffusion of dopants diffusing via interstitially-assisted mechanisms
  - Transient effect - defect concentrations return to equilibrium values

- TED can be reduced by implantation into an amorphous layer or by carbon incorporation into Si surface layer
  - Substitutional carbon acts as an interstitial sink


Doping Effects on Diffusion

Heavily doped semiconductors - extrinsic at diffusion temperatures
- Fermi level moves from mid-gap to near conduction (n-type) or valence (p-type) band.

<table>
<thead>
<tr>
<th></th>
<th>Dopant charge state</th>
<th>Native defect charge state</th>
</tr>
</thead>
<tbody>
<tr>
<td>extrinsic n-type</td>
<td>( A_s^+ )</td>
<td>( \Gamma, V^- )</td>
</tr>
<tr>
<td>extrinsic p-type</td>
<td>( A_s^- )</td>
<td>( \Gamma^+, V^+ )</td>
</tr>
</tbody>
</table>

- Fermi level shift changes the formation enthalpy, \( H_F \), of the charged native defect

\[
C_{V,I}^{\text{eq}} = C_{Si}^o \exp \left( \frac{S_{V,I}}{k_B} \right) \exp \left( - \frac{H_{F}^V}{k_B T} \right), \quad H_{F}^V = H_{F}^o - \left( E_F - E_{V^-} \right)
\]

- Increase of \( C_{I,V} \) affects Si self-diffusion and dopant diffusion

V states (review by Watkins, 1986)
Doping Effects on Diffusion

Fermi level shift lowers the formation enthalpy, $H_F$, of the charged native defect

- Increase of $C_{I,V}$ affects Si self-diffusion and dopant diffusion

$$C_{V,I}^{eq} = C_{Si}^o \exp\left(\frac{S_{V,I}^F}{k_B}\right) \exp\left(-\frac{H_{V,I}^F}{k_B T}\right), \quad H_{V}^{F} = H_{V}^{F^o} - (E_F - E_{V^-})$$

**Numerical example:** If $E_F$ moves up by 100 meV at 1000 °C, the change in the native defect concentration is:

$$\frac{C_{ext}^{eq}}{C_{int}^{eq}} = e^{\left(\frac{H_{int}^F - H_{ext}^F}{k_B T}\right)} \sim 3$$

Native defect concentration is 3 times larger for a Fermi level shift of only 100 meV.
Doping Effects on Diffusion

The change in native defect concentration with Fermi level position causes an increase in the self- and dopant diffusion coefficients.
Experimental Techniques for Diffusion

Creation of the Source
- Diffusion from surface
- Ion implantation
- Sputter deposition
- Buried layer (grown by MBE)

Annealing

Analysis of the Profile
- Radioactivity (sectioning)
- SIMS
- Neutron Activation Analysis
- Spreading resistance
- Electro-Chemical C/Voltage

Modeling of the Profile
- Analytical fit
- Coupled differential eq.
Primary Experimental Approaches

• Radiotracer Diffusion
  – Implantation or diffusion from surface
  – Mechanical sectioning
  – Radioactivity analysis

• Stable Isotope Multilayers
  – Diffusion from buried enriched isotope layer
  – Secondary Ion Mass Spectrometry (SIMS)
  – Dopant and self-diffusion
Radiotracer diffusion

- Diffusion using radiotracers was first technique available to measure self-diffusion
  - Limited by existence of radioactive isotope
  - Limited by isotope half-life (e.g. $^{31}$Si: $t_{1/2} = 2.6$ h)
  - Limited by sensitivity
    - Radioactivity measurement
    - Width of sections

Application of radioisotopes to surface → annealing → Mechanical/Chemical sectioning → Measure radioactivity of each section → Generate depth profile
Diffusion Prior to Stable Isotopes

What was known about Si, B, P, and As diffusion in Si

Si: self-diffusion: interstitials + vacancies
   known: interstitialcy + vacancy mechanism, \( Q^{SD} \sim 4.7 \) eV
   unknown: contributions of native defect charge states

B: interstitial mediated: from oxidation experiments
   known: diffusion coefficient
   unknown: interstitialcy or kick-out mechanism

P: interstitial mediated: from oxidation experiments
   known: diffusion coefficient
   unknown: mechanism for vacancy contribution

As: interstitial + vacancy mediated: from oxidation + nitridation experiments
   known: diffusion coefficient
   unknown: native defect charge states and mechanisms
Stable Isotope Multilayers

- Diffusion using stable isotope structures allows for *simultaneous* measurements of *self- and dopant diffusion*
  - No half-life issues
  - Ion beam sputtering rather than mechanical sectioning
  - Mass spectrometry rather than radioactivity measurement

![Diagram of stable isotope multilayers](image-url)

- a-Si cap
- nat. Si
- $^{28}\text{Si}$ enriched
- FZ Si substrate

![Graph showing concentration vs. depth](image-url)
Stable Isotope Multilayers

Simultaneous dopant and self-diffusion analysis allows for determination of native defect contributions to diffusion.

Multilayers of enriched and natural Si enable measurement of dopant diffusion from cap and self-diffusion between layers simultaneously.

Secondary Ion Mass Spectrometry (SIMS) yields concentration profiles of Si and dopant.
Secondary Ion Mass Spectrometry

- Incident ion beam sputters sample surface - Cs⁺, O⁺
  - Beam energy: ~1 kV
- Secondary ions ejected from surface (~10 eV) are mass analyzed using mass spectrometer
  - Detection limit: ~10^{12} - 10^{16} cm^{-3}
- Depth profile - ion detector counts vs. time
  - Depth resolution: 2 - 30 nm
Diffusion Parameters found via Stable Isotope Heterostructures

- Charge states of dopant and native defects involved in diffusion
- Contributions of native defects to self-diffusion
- Enhancement of dopant and self-diffusion under extrinsic conditions
- Mechanisms of diffusion which mediate self- and dopant diffusion
Si Self-Diffusion

- Enriched layer of $^{28}\text{Si}$ epitaxially grown on natural $\text{Si}$
- Diffusion of $^{30}\text{Si}$ monitored via SIMS from the natural substrate into the enriched cap (depleted of $^{30}\text{Si}$)
- $855 \degree C < T < 1388 \degree C$
  - Previous work limited to short times and high $T$ due to radiotracers
- Accurate value of self-diffusion coefficient over wide temperature range:

\[
D_{\text{Si}} = \left(560^{+240}_{-170}\right)\exp\left[-\frac{(4.76 \pm 0.04)eV}{k_B T}\right]
\]

(Bracht, et al., PRL 81 1998)
Si and Dopant Diffusion

Arsenic doped sample annealed 950 °C for 122 hrs

\[ (AsV)^o \leftrightarrow As_s^+ + V^- \]

Vacancy mechanism

\[ (AsI)^o \leftrightarrow As_s^+ + I^o + e^- \]

Interstitialcy mechanism
Si and Dopant Diffusion

![Graph showing concentration vs. depth for an arsenic-doped sample annealed at 950 °C for 122 hours.]

- Vacancy mechanism: $(AsV)^o \leftrightarrow As_s^+ + V$
- Interstitialcy mechanism: $(AsI)^o \leftrightarrow As_s^+ + I^o + e^-$
Si and Dopant Diffusion

Arsenic doped sample annealed 950 °C for 122 hrs

Vacancy mechanism

\[(AsV)^o \leftrightarrow As^+_s + V^-\]

Interstitialcy mechanism

\[(AsI)^o \leftrightarrow As^+_s + I^- + e^-\]
Native Defect Contributions to Si Diffusion

Diffusion coefficients of individual components add up accurately:

\[ D_{Si}(n_i)_{tot} = f_{I^0} C_{I^0} D_{I^0} + f_{I^+} C_{I^+} D_{I^+} + f_{V^-} C_{V^-} D_{V^-} = D_{Si}(n_i) \]

(As diffusion)  (B diffusion)  (As diffusion)

(Bracht, et al., 1998)
GaSb Self-Diffusion using Stable Isotopes

“as-grown structure”
GaSb Self-Diffusion using Stable Isotopes

Annealed 650 °C for 7 hours

Isotope Concentrations (cm$^{-3}$) vs. Depth (microns)
GaSb Self-Diffusion using Stable Isotopes

Simultaneous isotope diffusion experiments revealed that Ga and Sb self-diffusion coefficients in GaSb differ by 3 orders of magnitude.
GaAs Self-Diffusion using Stable Isotopes

Temperature dependence of Ga self-diffusion in GaAs under intrinsic (x), p-type Be doping (○), and n-type Si doping (■).

Ga self-diffusion is retarded under p-type doping and enhanced under n-type doping due to Fermi level effect on Ga self-interstitials.

Diffusion in AlGaAs/GaAs Isotope Structure

Ga self-diffusion coefficient in AlGaAs found to decrease with increasing Al content.

Activation energy for Ga self-diffusion - 3.6 ± 0.1 eV

Diffusion in Ge Stable Isotope Structure

Ge self-diffusion coefficient determined from $^{74}\text{Ge}/^{70}\text{Ge}$ isotope structure

$$D_{\text{Ge}} = \left(1.2 \times 10^{-3}\, \text{cm}^2\,\text{s}^{-1}\right) \exp\left[-\frac{(3.0 \pm 0.05)\,\text{eV}}{k_B T}\right]$$

Annealed 586 °C for 55.55 hours

Diffusion in GaP Stable Isotope Structure

Ga self-diffusion coefficient in GaP determined from $^{69}$GaP/$^{71}$GaP isotope structure

Annealed 1111 °C for 231 min

\[ D_{Ga} = \left(2.0 \text{cm}^2 \text{s}^{-1}\right) \exp \left[-\frac{4.5\text{eV}}{k_B T}\right] \]

Diffusion in $\text{Si}_{1-x}\text{Ge}_x$

- SiGe will be used as “next generation” material for electronic devices
  - Will face same device diffusion issues as Si
  - Currently, limited knowledge of diffusion properties

SiGe HBTs with cut-off frequency of 350 GHz
Previous Results on Diffusion in Si_{1-x}Ge_{x}

Strohm, et al., (2001)  
$^{71}$Ge diffusion in SiGe alloys

McVay and DuCharme (1975)  
$^{71}$Ge diffusion in poly-SiGe alloys
Stable Isotope Diffusion in Si_{1-x}Ge_x

- Use isotope heterostructure technique to study Si and Ge self-diffusion in relaxed Si_{1-x}Ge_x alloys. (0.05 \leq x \leq 0.85)
  - No reported measurements of simultaneous Si and Ge diffusion in Si_{1-x}Ge_x alloys

Fitting of SIMS diffusion profile to simulation result of simultaneous Si and Ge self-diffusion will yield self-diffusion coefficients of Si and Ge

Simulation result of simultaneous Si and Ge self-diffusion
Conclusions

• Diffusion in semiconductors is increasingly important to device design as feature level size decreases.

• Device processing can lead to non-equilibrium conditions which affect diffusion.

• Diffusion using *stable isotopes* yields important diffusion parameters which previously could not be determined experimentally.