Atomistic simulations of point defect diffusion in Si and SiGe

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Context and outline

Diffusion in the microelectronic material

Ge & PD diffusion
Strain
Charge state
Dopant

The need of multi-scale for diffusion simulations!

• Some insight of Ge diffusion in SiGe

• The case of Si vacancy diffusion

• Summary and outlooks
The multi-scale method for diffusion studies

**DFT** (CPMD, SIESTA): 216 atoms simulation box, Γ or 2x2x2, only some typical configurations; **NEB driver** for saddle point calculation

**Coupling** through **models** that reproduce the DFT energies for all possible configurations

**BKL-type KLMC simulations** (resident time)
Diffusion in Si$_{y}$-Ge$_{1-y}$ alloys (DFT step only)

**Vacancy and interstitial diffusion**

* Vacancy diffusion for $y < 0.70$ and $T < \sim 1000$ °C

* Dual diffusion for lower concentration

DFT study of Ge diffusion in Si

[Strohm et al. 2002]

[Ge@Si]

[Fahey et al. 1989]
The vacancy mechanisms

Only one Ge in the Si box

Formation energy $E_f = 3.6 \text{ eV}$

Migration path with a ring mechanism

$\langle E_m \rangle = 0.37 \text{ eV}$

The interstitial formation

Mixed dumbbell $d_{\langle 110 \rangle}$ 3.16 eV

Hexagonal Si$^H$ 3.33 eV

Hexagonal Ge$^H$ 3.45 eV

The migration mechanism of the $<110>$ dumbbell

Second neighbor diffusion

Through hexagonal interstitial

The interstitial migration mechanism

Direct migration of $\text{Ge}^H$: $\langle E_m \rangle \approx 0.10 \text{ eV}$

Back movement $\text{Ge}^H \rightarrow d_{\langle 110 \rangle}$: $E_m = 0.15 \text{ eV}$

Kick-off scheme diffusion

but with a dumbbell to hexagonal ratio is not $<< 1$!

$\langle E_m \rangle = 0.44 \text{ eV}$

The FFCD mechanism: an intrinsic mechanism

Low formation energy:

\[ E_f = 2.62 \text{ eV} \]

High migration energy:

\[ E_m = 1.63 \text{ eV} \]

Ge diffusion in Si (comparison with experiments)

Direct use of ab initio value:  

For FFCD \( E_a = 4.2 \text{ eV} \) Saddle point unknown

For interstitials \( E_a = 3.7 \text{ eV} \) \( E_a = E_f + \langle E_m \rangle \) unknown

For vacancies \( E_a = 4.0 \text{ eV} \) \( E_a = E_f + \langle E_m \rangle \) 4.18 eV [Strohm et al. 2002]

All mediators might contribute to diffusion as observed in experiments but the Ge diffusion activation energy is \( \sim 5 \text{ eV} \) ?!

For complex diffusion mechanism, effective activation energies could be higher than the direct sum of individual one?

Need of Monte Carlo step for correct physical average!

The case of Si vacancy

An old but controversial story for migration energy ...

<table>
<thead>
<tr>
<th></th>
<th>( E_m ) (eV)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Watkins</td>
<td>0.45</td>
<td>[MSS. Proc. 3, 227-235 (2000)]</td>
</tr>
<tr>
<td>Bracht et al.</td>
<td>1.8</td>
<td>[PRL 91, 245502 (2003)]</td>
</tr>
<tr>
<td>Ranki et al.</td>
<td>1.2</td>
<td>[PRL 93, 255502 (2004)]</td>
</tr>
</tbody>
</table>

Can we explain these scattered data from effective phenomena?
DFT step: vacancy formation energy

**3.52 eV** (216-1k) **3.6 eV** (Dannefaer 1986)

In Si, DFT fit well with exp

[D. Caliste PhD (2005); see also Wright (2006)]

Only neutral vacancy!

**Jahn-Teller effect** [G. Watkins 1992]
DFT step: vacancy migration energy

- 0.30 eV
  - Exp: 0.45 eV
  - [Watkins '79]

- 1.19 eV
  - Exp: 1.3 eV
  - [Watkins '65]
Coupling step: migration landscape


E-MRS – Strasbourg 2010
Monte Carlo step

2 vacancies and 0.1 to 18 M silicon atoms

\[ T = 1200 \text{ K} \]

Einstein formula

\[ \langle r^2(t) \rangle = 2 dD t \]

Average on 20 trajectories

\[ \rightarrow D \text{ as function of } T \text{ and } C_v \]
Non-Arrhenius diffusion is predicted!

3 diffusion regimes!
Step-like trajectory in intermediate temperature?

\[ T = 1200 \text{ K} \]

Dissociated

Associated

<table>
<thead>
<tr>
<th>Mean square displacement</th>
<th>time (s)</th>
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<tr>
<td>5e+07</td>
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<tr>
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<tr>
<td>0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

\[ 2 \times 1V \]

\[ \frac{1}{2} \times V \]

\[ \frac{1}{2} \times V \]

\[ 2 \times 1V \]

Coordinate of reaction
Three temperature regime rationalization

Concurrent diffusion in 1V or 2V

\[ \tilde{D}(T, C_v^*) = f_\tau(T, C_v^*) \times D_{1V}(T) + [1 - f_\tau(T, C_v^*)] \times D_{2V}(T) \]

2V dissociation

1V migration (fast)

2V migration (slow)

Analytical derivative gives a model for effective migration energy

\[ \tilde{E}_m(T, C_v^*) = f_\alpha E_{1V}^m + f_\beta (2E_{1V}^f - E_{2V}^f) + (1 - f_\alpha)E_{2V}^m \]

With \( f_\alpha \) and \( f_\beta \) being [0-1] bounded

Model vs MC simulations (high $T$)

$$\tilde{E}_m(T, C_\nu^*) = f_\alpha E_{1\nu}^m$$

$0.45 \text{ eV}$

> high $T$ or low $C_\nu$

region I

$E_{1\nu}^m$

labelling for $T < 200 K$

$\sim$ equilibrium

$650-900 K$

Highly doped

$E_{1\nu}^m = 1.3 \text{ eV}$

$1050-1150 K$

$e^{-}\text{irradiation}$

$E_{1\nu}^m = 1.8 \pm 0.5 \text{ eV}$

Watkins '79

Ranki '04

Bracht '03


low $C_\nu$  <--  medium $C_\nu$  <--  high $C_\nu$

Laboratoire de Simulation atomistique
http://inac.cea.fr/sp2m/L_Sim
\[ \tilde{E}^m(T, C^*_v) = (1 - f_{\alpha})E^m_{2\nu} \]

- \( E^m_{2\nu} \) is the effective migration energy.
- For \( T < 850 \text{ K} \) and \( C^*_v = 10^{-7} \text{ at}^{-1} \):
  - Region III: 1.25 eV

D. Caliste and P. Pochet, PRL 97, 135901 (2006)
\[
\tilde{E}^m(T, C_v) = f_\alpha E_{1v}^m + f_\beta (2E_{1v}^f - E_{2v}^f)
\]

\[E_{1v}^m = 0.45 \text{ eV}\]

\[E_{1v}^m = 1.3 \text{ eV}\]

\[E_{1v}^m = 1.8 \pm 0.5 \text{ eV}\]

850-1300 K for \(C_v = 10^{-7} \text{ at}^{-1}\)

2.1 eV

\[E_{1v}^m + (2E_{1v}^f - E_{2v}^f)\]

T < 200 K
~ équilibium
$E_m = 0.45$ eV

1050-1150 K
e$^-$ irradiation
$E_m = 1.8 \pm 0.5$ eV

650-900 K
Highly doped
$E_m = 1.3$ eV

$E_m = 0.45$ eV

$E_m = 1.25$ eV

$E_m = 2.1$ eV

[ Watkins '79 ]

[ Bracht '03 ]

[ Ranki '04 ]

3 temperature regimes already observed in Si!

**Evolution of the He cavity radius as function of implantation T**

[M. L. David *et al*  JAP 93 1438 (2003)]

*Fast diffusion allows effusion*; slow diffusion allows cavity formation. The slower the diffusion the bigger the mean cavity radius.

Summary

In complex diffusion mechanism effective activation energies might be higher than the direct sum of individual one!

Multi-scale simulation is a powerful tool for diffusion studies

DFT step is not enough when concurrent mechanisms are involved.
Coupling between DFT and KLMC is a good solution
Effective mechanisms might explain simulation/experiment discrepancy

Drawbacks:

On lattice simulations
Pre-calculated events database
Outlooks

Strain effect:

Work in progress to go above our first analysis

[K. Z. Rushchanskii, et al. APL 92, 152110 (2008)]

Charge effect:

Work in progress to develop an accurate \textit{ab initio} scheme

Growth on Ge QD on Si using \textit{ab initio} and off-lattice \textit{on-the-fly} KMC

MUSCADE project founded 2010-2012

Study of possible mechanisms of LID in SOG silicon (cf 4.3)
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References:
K. Z. Rushchanskii, P. Pochet and F. Lançon APL 92, 152110 (2008)