Atomistic simulation study on the silicon carbide precipitation in silicon

F. Zirkelbach

Yet another seminar talk

Augsburg, 26. Mai 2011
PROPERTIES

- wide band gap
- high electric breakdown field
- good electron mobility
- high electron saturation drift velocity
- high thermal conductivity
- hard and mechanically stable
- chemically inert
- radiation hardness

APPLICATIONS

- high-temperature, high power and high-frequency electronic and optoelectronic devices
- material suitable for extreme conditions
- microelectromechanical systems
- abrasives, cutting tools, heating elements
- first wall reactor material, detectors and electronic devices for space
### Polytypes of SiC

<table>
<thead>
<tr>
<th></th>
<th>3C-SiC</th>
<th>4H-SiC</th>
<th>6H-SiC</th>
<th>Si</th>
<th>GaN</th>
<th>Diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness [Mohs]</td>
<td></td>
<td>9.6</td>
<td></td>
<td>6.5</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>Band gap [eV]</td>
<td>2.36</td>
<td>3.23</td>
<td>3.03</td>
<td>1.12</td>
<td>3.39</td>
<td>5.5</td>
</tr>
<tr>
<td>Break down field [10^6 V/cm]</td>
<td>4</td>
<td>3</td>
<td>3.2</td>
<td>0.6</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Saturation drift velocity [10^7 cm/s]</td>
<td>2.5</td>
<td>2.0</td>
<td>2.0</td>
<td>1</td>
<td>2.7</td>
<td>2.7</td>
</tr>
<tr>
<td>Electron mobility [cm²/Vs]</td>
<td>800</td>
<td>900</td>
<td>400</td>
<td>1100</td>
<td>900</td>
<td>2200</td>
</tr>
<tr>
<td>Hole mobility [cm²/Vs]</td>
<td>320</td>
<td>120</td>
<td>90</td>
<td>420</td>
<td>150</td>
<td>1600</td>
</tr>
<tr>
<td>Thermal conductivity [W/cmK]</td>
<td>5.0</td>
<td>4.9</td>
<td>4.9</td>
<td>1.5</td>
<td>1.3</td>
<td>22</td>
</tr>
</tbody>
</table>

Values for $T = 300$ K
Fabrication of silicon carbide

SiC - *Born from the stars, perfected on earth.*

Conventional thin film SiC growth:

- **Sublimation growth using the modified Lely method**
  - SiC single-crystalline seed at $T = 1800^\circ C$
  - Surrounded by polycrystalline SiC in a graphite crucible at $T = 2100 - 2400^\circ C$
  - Deposition of supersaturated vapor on cooler seed crystal

- **Homoepitaxial growth using CVD**
  - Step-controlled epitaxy on off-oriented 6H-SiC substrates
  - $C_3H_8/SiH_4/H_2$ at $1100 - 1500^\circ C$
  - Angle, temperature $\rightarrow$ 3C/6H/4H-SiC

- **Heteroepitaxial growth of 3C-SiC on Si using CVD/MBE**
  - Two steps: carbonization and growth
  - $T = 650 - 1050^\circ C$
  - SiC/Si lattice mismatch $\approx$ 20 %
  - Quality and size not yet sufficient

+ Hex: micropipes along c-axis
+ 3C-SiC fabrication less advanced
Fabrication of silicon carbide

Alternative approach: Ion beam synthesis (IBS) of buried 3C-SiC layers in Si(1 0 0)

1. **Implantation step 1**
   - 180 keV C⁺, \( D = 7.9 \times 10^{17} \text{ cm}^{-2} \), \( T_i = 500 \degree \text{C} \)
   - ⇒ box-like distribution of equally sized and epitactically oriented SiC precipitates

2. **Implantation step 2**
   - 180 keV C⁺, \( D = 0.6 \times 10^{17} \text{ cm}^{-2} \), \( T_i = 250 \degree \text{C} \)
   - ⇒ destruction of SiC nanocrystals in growing amorphous interface layers

3. **Annealing**
   - \( T = 1250 \degree \text{C}, t = 10 \text{ h} \)
   - ⇒ homogeneous, stoichiometric SiC layer with sharp interfaces

Precipitation mechanism not yet fully understood!

Understanding the SiC precipitation

⇒ significant technological progress in SiC thin film formation

⇒ perspectives for processes relying upon prevention of SiC precipitation
Outline

• Supposed precipitation mechanism of SiC in Si
• Utilized simulation techniques
  • Molecular dynamics (MD) simulations
  • Density functional theory (DFT) calculations
• C and Si self-interstitial point defects in silicon
• Silicon carbide precipitation simulations
• Summary / Conclusion / Outlook
Supposed precipitation mechanism of SiC in Si

Si & SiC lattice structure

C-Si dimers (dumbbells) on Si interstitial sites

Agglomeration of C-Si dumbbells ⇒ dark contrasts

Precipitation of 3C-SiC in Si ⇒ Moiré fringes & release of Si self-interstitials

\[ 4a_{\text{Si}} = 5a_{\text{SiC}} \]

(h k l) planes match

\[ r = 2 - 4 \text{ nm} \]
Supposed precipitation mechanism of SiC in Si

Si & SiC lattice structure

C-Si dimers (dumbbells) on Si interstitial sites

Agglomeration of C-Si dumbbells ⇒ dark contrasts

Precipitation of 3C-SiC in Si ⇒ Moiré fringes & release of Si self-interstitials

\[ 4a_{\text{Si}} = 5a_{\text{SiC}} \]

Controversial views

- Implantations at high T (Nejim et al.)
  - Topotactic transformation based on \( C_{\text{sub}} \)
  - Si\(_i\) as supply reacting with further C in cleared volume

- Annealing behavior (Serre et al.)
  - Room temperature implants → highly mobile C
  - Elevated T implants → no/low C redistribution/migration
    (indicate stable \( C_{\text{sub}} \) configurations)

- Strained silicon & Si/SiC heterostructures
  - Coherent SiC precipitates (tensile strain)
  - Incoherent SiC (strain relaxation)
Molecular dynamics (MD) simulations

MD basics:

- Microscopic description of N particle system
- Analytical interaction potential
- Numerical integration using Newtons equation of motion as a propagation rule in 6N-dimensional phase space
- Observables obtained by time and/or ensemble averages

Details of the simulation:

- Integration: Velocity Verlet, timestep: 1 fs
- Ensemble: NpT (isothermal-isobaric)
  - Berendsen thermostat: $\tau_T = 100$ fs
  - Berendsen barostat:
    $\tau_P = 100$ fs, $\beta^{-1} = 100$ GPa
- Erhart/Albe potential: Tersoff-like bond order potential

\[
E = \frac{1}{2} \sum_{i \neq j} \mathcal{V}_{ij}, \quad \mathcal{V}_{ij} = f_C(r_{ij}) \left[ f_R(r_{ij}) + b_{ij} f_A(r_{ij}) \right]
\]
Density functional theory (DFT) calculations

Basic ingredients necessary for DFT

- **Hohenberg-Kohn theorem** - ground state density $n_0(r)$...
  - ... uniquely determines the ground state potential / wavefunctions
  - ... minimizes the systems total energy

- **Born-Oppenheimer** - $N$ moving electrons in an external potential of static nuclei

  $$
  H \Psi = \left[ - \sum_i \frac{\hbar^2}{2m} \nabla_i^2 + \sum_i V_{\text{ext}}(r_i) + \sum_{i<j} V_{\text{e-e}}(r_i, r_j) \right] \Psi = E \Psi
  $$

- **Effective potential** - averaged electrostatic potential & exchange and correlation

  $$
  V_{\text{eff}}(r) = V_{\text{ext}}(r) + \int \frac{e^2 n(r')}{|r - r'|} d^3 r' + V_{\text{XC}}[n(r)]
  $$

- **Kohn-Sham system** - Schrödinger equation of $N$ non-interacting particles

  $$
  \left[ - \frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(r) \right] \Phi_i(r) = \epsilon_i \Phi_i(r) \Rightarrow n(r) = \sum_i |\Phi_i(r)|^2
  $$

- **Self-consistent solution**
  $n(r)$ depends on $\Phi_i$, which depend on $V_{\text{eff}}$, which in turn depends on $n(r)$

- **Variational principle** - minimize total energy with respect to $n(r)$
Density functional theory (DFT) calculations

Details of applied DFT calculations in this work

- **Exchange correlation functional** - approximations for the inhomogeneous electron gas
  - LDA: \( E_{\text{XC}}^{\text{LDA}}[n] = \int \epsilon_{\text{XC}}(n)n(r)d^3r \)
  - GGA: \( E_{\text{XC}}^{\text{GGA}}[n] = \int \epsilon_{\text{XC}}(n, \nabla n)n(r)d^3r \)

- **Plane wave basis set** - approximation of the wavefunction \( \Phi_i \) by plane waves \( \varphi_j \)

\[
\rightarrow \text{Fourier series: } \Phi_i = \sum_{|G+k|<G_{\text{cut}}} c^i_j \varphi_j(r), \quad E_{\text{cut}} = \frac{\hbar^2}{2m} G_{\text{cut}}^2 \quad (300 \text{ eV})
\]

- **Brillouin zone sampling** - \( \Gamma \)-point only calculations
- **Pseudo potential** - consider only the valence electrons
- **Code** - VASP 4.6

MD and structural optimization

- **MD integration**: Gear predictor corrector algorithm
- **Pressure control**: Parrinello-Rahman pressure control
- **Structural optimization**: Conjugate gradient method
C and Si self-interstitial point defects in silicon

Procedure:

- Creation of c-Si simulation volume
- Periodic boundary conditions
- \( T = 0 \) K, \( p = 0 \) bar

Insertion of interstitial C/Si atoms

Relaxation / structural energy minimization

<table>
<thead>
<tr>
<th>size [unit cells]</th>
<th># atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>VASP 3 × 3 × 3</td>
<td>216 ± 1</td>
</tr>
<tr>
<td>Erhart/Albe 9 × 9 × 9</td>
<td>5832 ± 1</td>
</tr>
</tbody>
</table>

- Tetrahedral
- Hexagonal
- \( \langle 100 \rangle \) dumbbell
- \( \langle 110 \rangle \) dumbbell
- Bond-centered
- Vacancy / Substitutional
Si self-interstitial point defects in silicon

<table>
<thead>
<tr>
<th></th>
<th>〈110〉 DB</th>
<th>H</th>
<th>T</th>
<th>〈100〉 DB</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>VASP</td>
<td>3.39</td>
<td>3.42</td>
<td>3.77</td>
<td>4.41</td>
<td>3.63</td>
</tr>
<tr>
<td>Erhart/Albe</td>
<td>4.39</td>
<td>4.48*</td>
<td>3.40</td>
<td>5.42</td>
<td>3.13</td>
</tr>
</tbody>
</table>

Hexagonal

$E_f^* = 4.48 \, \text{eV}$

$E_f = 3.96 \, \text{eV}$

Vacancy

〈100〉 dumbbell
C interstitial point defects in silicon

<table>
<thead>
<tr>
<th>$E_f$</th>
<th>T</th>
<th>H</th>
<th>⟨100⟩ DB</th>
<th>⟨110⟩ DB</th>
<th>S</th>
<th>B</th>
<th>$C_{\text{sub}} &amp; \text{Si}_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VASP</td>
<td>unstable</td>
<td>unstable</td>
<td>3.72</td>
<td>4.16</td>
<td>1.95</td>
<td>4.66</td>
<td>4.17</td>
</tr>
<tr>
<td>Erhart/Albe MD</td>
<td>6.09</td>
<td>9.05*</td>
<td>3.88</td>
<td>5.18</td>
<td>0.75</td>
<td>5.59*</td>
<td>4.43</td>
</tr>
</tbody>
</table>

Hexagonal

$E_f^* = 9.05$ eV

$\langle 100 \rangle$

$E_f = 3.88$ eV

⇒

Tetrahedral

Bond-centered

$E_f^* = 5.59$ eV

$\langle 110 \rangle$ dumbbell

$E_f = 5.18$ eV

⇒

Substitutional
C $<100>$ dumbbell interstitial configuration

<table>
<thead>
<tr>
<th>Distances [nm]</th>
<th>$r(1C)$</th>
<th>$r(2C)$</th>
<th>$r(3C)$</th>
<th>$r(12)$</th>
<th>$r(13)$</th>
<th>$r(34)$</th>
<th>$r(23)$</th>
<th>$r(25)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Erhart/Albe</td>
<td>0.175</td>
<td>0.329</td>
<td>0.186</td>
<td>0.226</td>
<td>0.300</td>
<td>0.343</td>
<td>0.423</td>
<td>0.425</td>
</tr>
<tr>
<td>VASP</td>
<td>0.174</td>
<td>0.341</td>
<td>0.182</td>
<td>0.229</td>
<td>0.286</td>
<td>0.347</td>
<td>0.422</td>
<td>0.417</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Angles [$^\circ$]</th>
<th>$\theta_1$</th>
<th>$\theta_2$</th>
<th>$\theta_3$</th>
<th>$\theta_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Erhart/Albe</td>
<td>140.2</td>
<td>109.9</td>
<td>134.4</td>
<td>112.8</td>
</tr>
<tr>
<td>VASP</td>
<td>130.7</td>
<td>114.4</td>
<td>146.0</td>
<td>107.0</td>
</tr>
</tbody>
</table>

| Displacements [nm] | $a$     | $b$     | $|a| + |b|$ |
|--------------------|--------|--------|--------|
| Erhart/Albe        | 0.084  | -0.091 | 0.175  |
| VASP               | 0.109  | -0.065 | 0.174  |
Bond-centered interstitial configuration

- Linear Si-C-Si bond
- Si: one C & 3 Si neighbours
- Spin polarized calculations
- No saddle point!
  Real local minimum!

Spin up / down

435 / 433 (Delta: 2)
Migration of the C $\langle 100 \rangle$ dumbbell interstitial

Investigated pathways

$\langle 00\bar{1} \rangle \rightarrow \langle 001 \rangle$

$\langle 00\bar{1} \rangle \rightarrow \langle 0\bar{1}0 \rangle$

$\langle 00\bar{1} \rangle \rightarrow \langle 0\bar{1}0 \rangle$ (in place)

Constrained relaxation technique (CRT) method

- Constrain diffusing atom
- Static constraints

Modifications

- Constrain all atoms
- Update individual constraints
Migration of the C ⟨100⟩ dumbbell interstitial

VASP results

- Energetically most favorable path
  - Path 2
  - Activation energy: ≈ 0.9 eV
  - Experimental values: 0.73 ... 0.87 eV
  ⇒ Diffusion path identified!

- Reorientation (path 3)
  - More likely composed of two consecutive steps of type 2
  - Experimental values: 0.77 ... 0.88 eV
  ⇒ Reorientation transition identified!
Migration of the C ⟨1 0 0⟩ dumbbell interstitial

Erhart/Albe results
- Lowest activation energy: ≈ 2.2 eV
- 2.4 times higher than VASP
- Different pathway

Transition involving Cᵢ ⟨1 1 0⟩
- Bond-centered configuration unstable
  → Cᵢ ⟨1 1 0⟩ dumbbell
- Transition minima of path 2 & 3
  → Cᵢ ⟨1 1 0⟩ dumbbell
- Activation energy: ≈ 2.2 eV & 0.9 eV
- 2.4 - 3.4 times higher than VASP
- Rotation of dumbbell orientation

Overestimated diffusion barrier
Combinations with a C-Si $⟨100⟩$-type interstitial

Binding energy: $E_b = E_{\text{defect combination}} - E_{\text{dumbbell}}^C - E_{\text{2nd defect}}$

<table>
<thead>
<tr>
<th>$E_b$ [eV]</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>$⟨00\bar{1}⟩$</td>
<td>-0.08</td>
<td>-1.15</td>
<td>-0.08</td>
<td>0.04</td>
<td>-1.66</td>
<td>-0.19</td>
</tr>
<tr>
<td>$⟨001⟩$</td>
<td>0.34</td>
<td>0.004</td>
<td>-2.05</td>
<td>0.26</td>
<td>-1.53</td>
<td>-0.19</td>
</tr>
<tr>
<td>$⟨0\bar{1}0⟩$</td>
<td>-2.39</td>
<td>-0.17</td>
<td>-0.10</td>
<td>-0.27</td>
<td>-1.88</td>
<td>-0.05</td>
</tr>
<tr>
<td>$⟨010⟩$</td>
<td>-2.25</td>
<td>-1.90</td>
<td>-2.25</td>
<td>-0.12</td>
<td>-1.38</td>
<td>-0.06</td>
</tr>
<tr>
<td>$⟨\bar{1}00⟩$</td>
<td>-2.39</td>
<td>-0.36</td>
<td>-2.25</td>
<td>-0.12</td>
<td>-1.88</td>
<td>-0.05</td>
</tr>
<tr>
<td>$⟨100⟩$</td>
<td>-2.25</td>
<td>-2.16</td>
<td>-0.10</td>
<td>-0.27</td>
<td>-1.38</td>
<td>-0.06</td>
</tr>
</tbody>
</table>

C substitutional (Cs) | 0.26 | -0.51 | -0.93 | -0.15 | 0.49 | -0.05 |
Vacancy | -5.39 (→ Cs) | -0.59 | -3.14 | -0.54 | -0.50 | -0.31 |

<table>
<thead>
<tr>
<th><strong>$⟨100⟩$ at position 1</strong></th>
<th><strong>$⟨0\bar{1}0⟩$ at position 1</strong></th>
</tr>
</thead>
</table>

- $E_b = 0 ⇔$ non-interacting defects
- $E_b \to 0$ for increasing distance (R)
- Stress compensation / increase
- Unfavored: antiparallel orientations
- Indication of energetically favored agglomeration
- Most favorable: C clustering
- However: High barrier ($> 4$ eV)
- $4 \times -2.25$ versus $2 \times -2.39$ (Entropy)
Combinations of C-Si ⟨1 0 0⟩-type interstitials

Energetically most favorable combinations along ⟨1 1 0⟩

<table>
<thead>
<tr>
<th>Type</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eb [eV]</td>
<td>-2.39</td>
<td>-1.88</td>
<td>-0.59</td>
<td>-0.31</td>
<td>-0.24</td>
<td>-0.21</td>
</tr>
<tr>
<td>C-C distance [Å]</td>
<td>1.4</td>
<td>4.6</td>
<td>6.5</td>
<td>8.6</td>
<td>10.5</td>
<td>10.8</td>
</tr>
</tbody>
</table>

- Interaction proportional to reciprocal cube of C-C distance
- Saturation in the immediate vicinity
  ⇒ Agglomeration of $C_i$ expected
  ⇒ Absence of C clustering

Consistent with initial precipitation model
Combinations of substitutional C and $\langle 110 \rangle$ Si self-interstitials

- IBS: C may displace Si
  $\Rightarrow C_{sub} + \langle 110 \rangle$ Si self-interstitial
- Assumption:
  $\langle 110 \rangle$-type $\Rightarrow$ favored combination
  $\Rightarrow$ Most favorable: $C_{sub}$ along $\langle 110 \rangle$ chain Si$_i$
  $\Rightarrow$ Less favorable than C-Si $\langle 100 \rangle$ dumbbell
  $\Rightarrow$ Interaction drops quickly to zero
    $\rightarrow$ low capture radius

IBS process far from equilibrium
$C_{sub}$ & Si$_i$ instead of thermodynamic ground state

**Ab initio MD at 900°C**

$t = 2230$ fs

$t = 2900$ fs

Contribution of entropy to structural formation
Migration in C-Si $\langle 1\,0\,0 \rangle$ and vacancy combinations

Pos 2, $E_b = -0.59$ eV

Low activation energies
High activation energies for reverse processes
\[ \downarrow \]
$C_{\text{sub}}$ very stable

Without nearby $\langle 1\,1\,0 \rangle$ Si self-interstitial (IBS)
\[ \downarrow \]
Formation of SiC by successive substitution by C

Pos 3, $E_b = -3.14$ eV
Conclusion of defect / migration / combined defect simulations

Defect structures

- Accurately described by quantum-mechanical simulations
- Less accurate description by classical potential simulations
- Underestimated formation energy of $C_{\text{sub}}$ by classical approach
- Both methods predict same ground state: $C_i \langle 100 \rangle$ dumbbell

Migration

- C migration pathway in Si identified
- Consistent with reorientation and diffusion experiments
- Different path and ...
- Overestimated barrier by classical potential calculations

Concerning the precipitation mechanism

- Agglomeration of C-Si dumbbells energetically favorable (stress compensation)
- C-Si indeed favored compared to $C_{\text{sub}} \& \langle 110 \rangle$ Si self-interstitial
- Possible low interaction capture radius of $C_{\text{sub}} \& \langle 110 \rangle$ Si self-interstitial
- Low barrier for $C_i \langle 100 \rangle \rightarrow C_{\text{sub}} \& Si_i \langle 110 \rangle$
- In absence of nearby $\langle 110 \rangle$ Si self-interstitial: C-Si $\langle 100 \rangle +$ Vacancy $\rightarrow C_{\text{sub}} (\text{SiC})$

Results suggest increased participation of $C_{\text{sub}}$
Silicon carbide precipitation simulations

- Create c-Si volume
- Period boundary conditions
- Set requested $T$ and $p = 0$ bar
- Equilibration of $E_{\text{kin}}$ and $E_{\text{pot}}$

Insertion of C atoms at constant $T$
- total simulation volume
- volume of minimal SiC precipitate
- volume consisting of Si atoms to form a minimal precipitate

Run for 100 ps followed by cooling down to 20$^\circ$C

- Restricted to classical potential simulations
- $V_2$ and $V_3$ considered due to low diffusion
- Amount of C atoms: 6000 ($r_{\text{prec}} \approx 3.1$ nm, IBS: 2 ... 4 nm)
- Simulation volume: $31 \times 31 \times 31$ unit cells (238328 Si atoms)
Silicon carbide precipitation simulations at 450 °C as in IBS

Low C concentration ($V_1$)

\langle 100 \rangle C-Si dumbbell dominated structure

- Si-C bumps around 0.19 nm
- C-C peak at 0.31 nm (as expected in 3C-SiC): concatenated dumbbells of various orientation
- Si-Si NN distance stretched to 0.3 nm

⇒ C atoms in proper 3C-SiC distance first

High C concentration ($V_2$, $V_3$)

High amount of strongly bound C-C bonds

Defect density ↑ ⇒ considerable amount of damage

Only short range order observable

⇒ amorphous SiC-like phase
Silicon carbide precipitation simulations at 450 °C as in IBS

3C-SiC formation fails to appear
- Low C concentration simulations
  - Formation of C\textsubscript{i} indeed occurs
  - Agglomeration not observed
- High C concentration simulations
  - Amorphous SiC-like structure
    (not expected at prevailing temperatures)
  - Rearrangement and transition into 3C-SiC structure missing

- Si-Si NN distance stretched to 0.3 nm
  ⇒ C atoms in proper 3C-SiC distance first
- High C concentration (V\textsubscript{2}, V\textsubscript{3})
  - High amount of strongly bound C-C bonds
  - Rearrangement and transition into 3C-SiC structure missing

⇒ amorphous SiC-like phase
Limitations of molecular dynamics and short range potentials

Time scale problem of MD

Minimize integration error
⇒ discretization considerably smaller than reciprocal of fastest vibrational mode

Order of fastest vibrational mode: $10^{13} - 10^{14}$ Hz
⇒ suitable choice of time step: $\tau = 1$ fs = $10^{-15}$ s
⇒ slow phase space propagation

Several local minima in energy surface separated by large energy barriers
⇒ transition event corresponds to a multiple of vibrational periods
⇒ phase transition made up of many infrequent transition events

Accelerated methods: Temperature accelerated MD (TAD), self-guided MD . . .

Limitations related to the short range potential

Cut-off function pushing forces and energies to zero between 1st and 2nd next neighbours
⇒ overestimated unphysical high forces of next neighbours

Potential enhanced problem of slow phase space propagation

Approach to the (twofold) problem

Increased temperature simulations without TAD corrections
(accelerated methods or higher time scales exclusively not sufficient)

IBS
- 3C-SiC also observed for higher T
- higher T inside sample
- structural evolution vs. equilibrium properties

retain proper thermodynamic sampling
Increased temperature simulations at low C concentration

Si-C bonds:
- Vanishing cut-off artifact (above 1650 °C)
- Structural change: C-Si $\langle 1\ 0\ 0 \rangle \rightarrow C_{\text{sub}}$

Si-Si bonds: Si-C$_{\text{sub}}$-Si along $\langle 1\ 1\ 0 \rangle$ ($\rightarrow 0.325$ nm)

C-C bonds:
- C-C next neighbour pairs reduced (mandatory)
- Peak at 0.3 nm slightly shifted
  - C-Si $\langle 1\ 0\ 0 \rangle$ combinations (dashed arrows)
  - C-Si $\langle 1\ 0\ 0 \rangle$ & C$_{\text{sub}}$ combinations ($\downarrow$)
- Range $[\sim]$: C$_{\text{sub}}$ & C$_{\text{sub}}$ with nearby Si$_I$
Increased temperature simulations at low C concentration

**Stretched SiC in c-Si**

- Consistent to precipitation model involving $C_{\text{sub}}$
- Explains annealing behavior of high/low T C implants
  - Low T: highly mobile $C_i$
  - High T: stable configurations of $C_{\text{sub}}$

⇒ High T ↔ IBS conditions far from equilibrium
⇒ Precipitation mechanism involving $C_{\text{sub}}$

**Si-Si bonds:** $\text{Si-}C_{\text{sub}}\text{-Si}$ along $\langle 110 \rangle$ ($\rightarrow 0.325 \text{ nm}$)

**C-C bonds:**
- C-C next neighbour pairs reduced (mandatory)
- Peak at 0.3 nm slightly shifted
  - C-Si $\langle 100 \rangle$ combinations (dashed arrows)
    $\rightarrow C\text{-Si }\langle 100 \rangle \& C_{\text{sub}}$ combinations ($\downarrow$)
    $\rightarrow$ pure $C_{\text{sub}}$ combinations ($\downarrow$)
- Range $[\leftarrow\downarrow]$: $C_{\text{sub}} \& C_{\text{sub}}$ with nearby $\text{Si}_I$
Increased temperature simulations at high C concentration

0.186 nm: Si-C pairs ↑
(as expected in 3C-SiC)

0.282 nm: Si-C-C

≈0.35 nm: C-Si-Si

- Decreasing cut-off artifact
- **Amorphous** SiC-like phase remains
- High amount of damage & alignment to c-Si host matrix lost
- Slightly sharper peaks ⇒ indicate slight acceleration of dynamics due to temperature

0.15 nm: C-C pairs ↑
(as expected in graphite/diamond)

0.252 nm: C-C-C (2nd NN for diamond)

0.31 nm: shifted towards 0.317 nm → C-Si-C

High C & small V & short t ⇒ Slow restructuring due to strong C-C bonds ⇐ High C & low T implants
Summary and Conclusions

Precipitation simulations

- High C concentration → amorphous SiC like phase
- Problem of potential enhanced slow phase space propagation
- Low T → C-Si ⟨1 0 0⟩ dumbbell dominated structure
- High T → C_{sub} dominated structure
- High T necessary to simulate IBS conditions (far from equilibrium)
- Precipitation by successive agglomeration of C_{sub}(epitaxy)
- Si_{i}: vehicle to form C_{sub} & supply of Si & stress compensation (stretched SiC, interface)

Defects

- DFT / EA
  - Point defects excellently / fairly well described by DFT / EA
  - C_{sub} drastically underestimated by EA
  - EA predicts correct ground state: C_{sub} & Si_{i} > C_{i}
  - Identified migration path explaining diffusion and reorientation experiments by DFT
  - EA fails to describe C_{i} migration: Wrong path & overestimated barrier
- Combinations of defects
  - Agglomeration of point defects energetically favorable by compensation of stress
  - Formation of C-C unlikely
  - C_{sub} favored conditions (conceivable in IBS)
  - C_{i} ⟨1 0 0⟩ ↔ C_{sub} & Si_{i} ⟨1 1 0⟩
    - Low barrier (0.77 eV) & low capture radius
Acknowledgements

Thanks to …

Augsburg
- Prof. B. Stritzker (accomodation at EP IV)
- Ralf Utermann (EDV)

Helsinki
- Prof. K. Nordlund (MD)

Munich
- Bayerische Forschungsstiftung (financial support)

Paderborn
- Prof. J. Lindner (SiC)
- Prof. G. Schmidt (DFT + financial support)
- Dr. E. Rauls (DFT + SiC)
- Dr. S. Sanna (VASP)

Thank you for your attention!