Atomistic simulation study on silicon carbide precipitation in silicon

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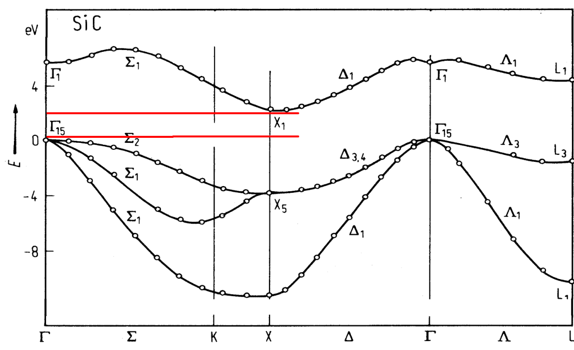
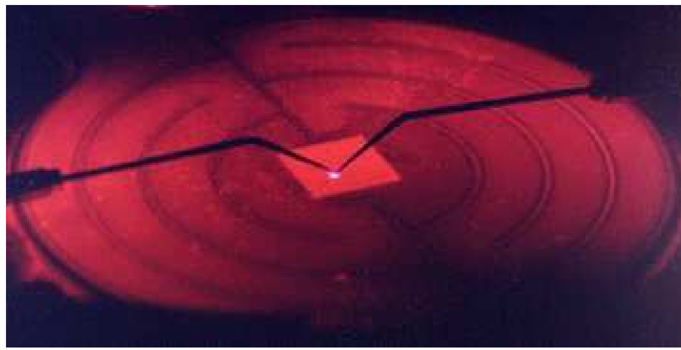
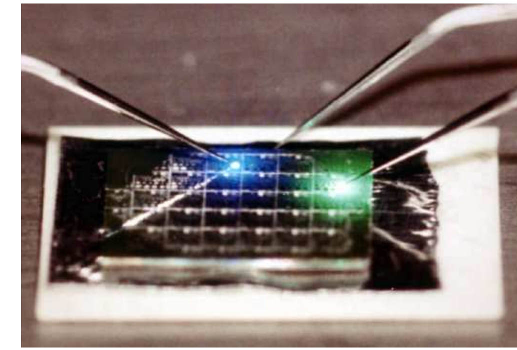
Defense of doctor's thesis

Augsburg, 10.01.2012







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

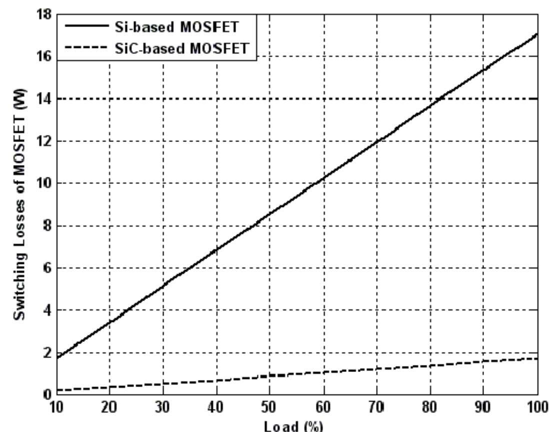
radiation hardness

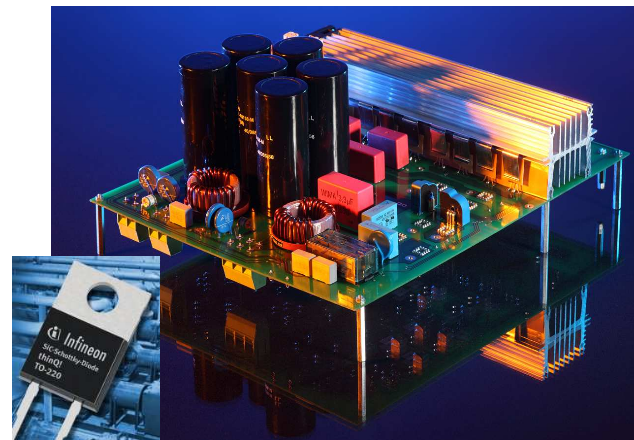
APPLICATIONS

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





IBS of epitaxial single crystalline 3C-SiC

- Implantation step 1

  Almost stoichiometric dose | 180 keV | 500 °C

  ⇒ Epitaxial 3C-SiC layer & precipitates

- Implantation step 2

  Low remaining amount of dose | 180 keV | 250 °C

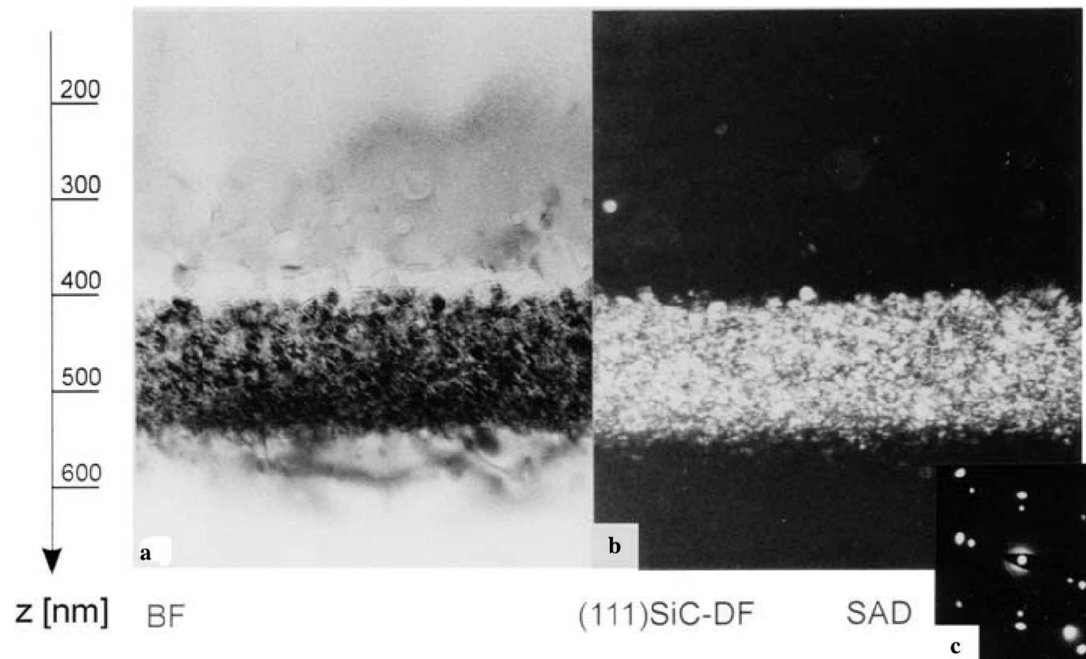
  ⇒ Destruction/Amorphization of precipitates at layer interface

- Annealing

  10 h at 1250 °C

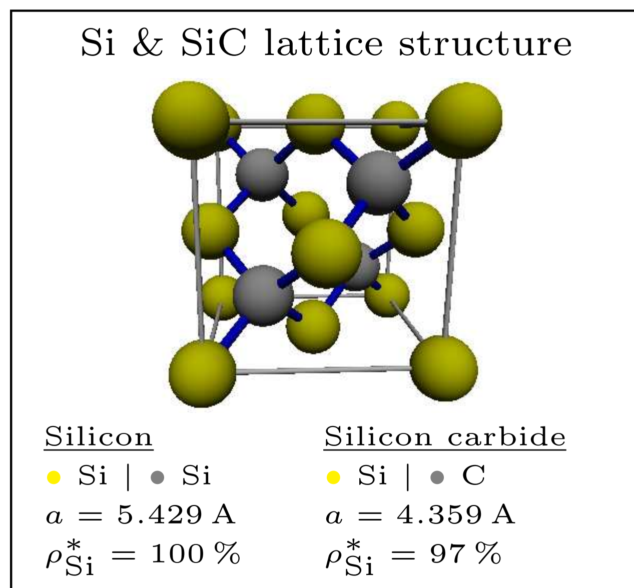
  ⇒ Homogeneous 3C-SiC layer with sharp interfaces

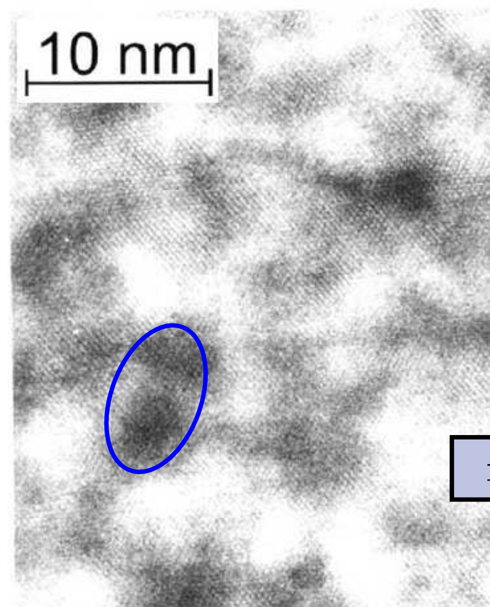
3C-SiC precipitation
not yet fully understood



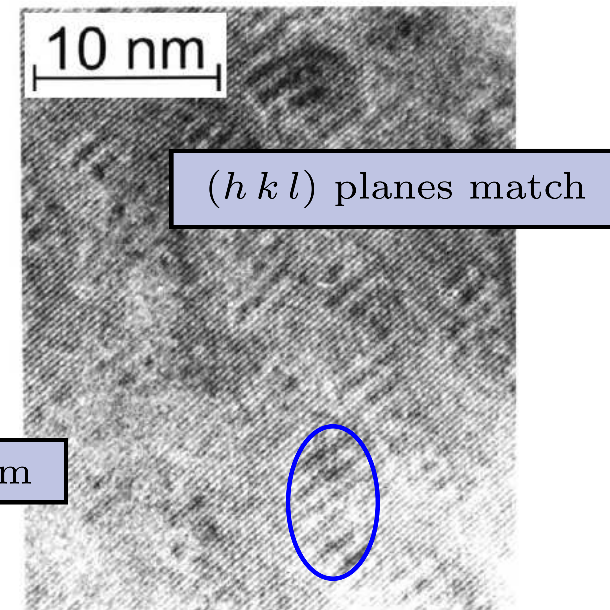
XTEM: single crystalline 3C-SiC in Si(1 0 0)

Supposed precipitation mechanism of SiC in Si





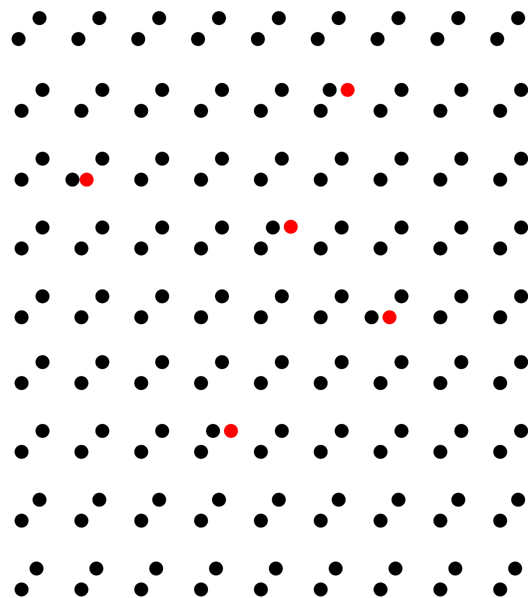
r = 2–4 nm

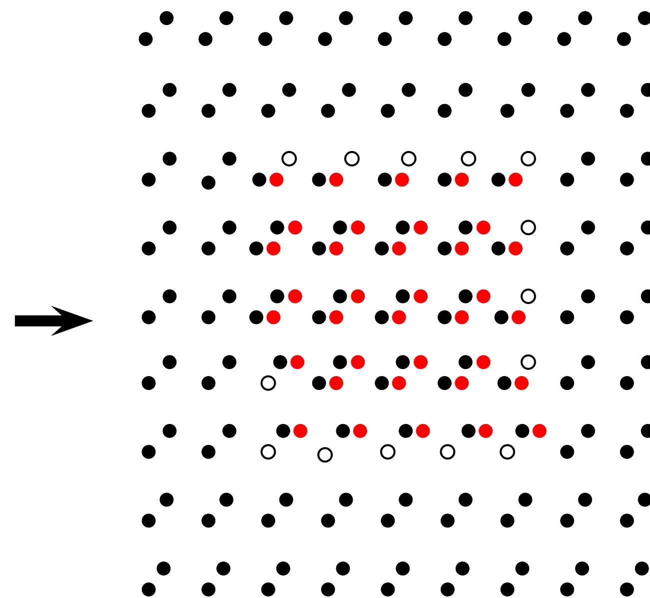


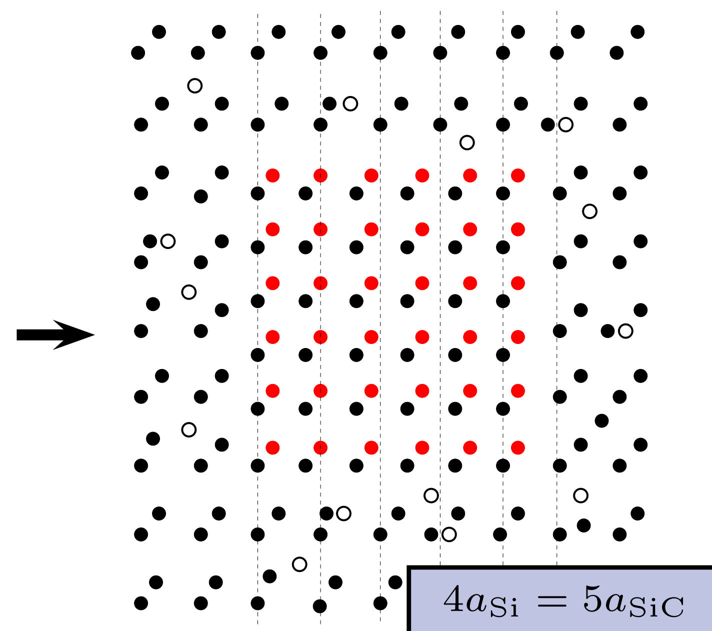
C-Si dimers (dumbbells) on Si lattice sites

Agglomeration of C-Si dumbbells
⇒ dark contrasts

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





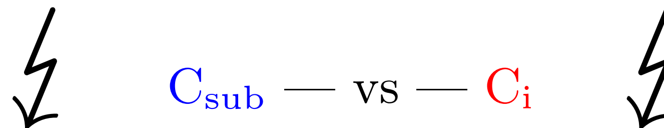


Supposed precipitation mechanism of SiC in Si

Controversial findings

- High-temperature implantation /Nejim et al./
  - Substitutionally incorporated C on regular Si lattice sites
  - Si_i reacting with further C in cleared volume
- Annealing behavior /Serre et al./
  - Room temperature implantation $\rightarrow$ high C diffusion
  - Elevated temperature implantation $\rightarrow$ no C redistribution

  $\Rightarrow$ mobile C_i opposed to stable C_{sub} configurations
- Strained $Si_{1-y}C_y$/Si heterostructures /Strane et al./Guedj et al./
  - Initial coherent SiC structures (tensile strain)
  - Incoherent SiC nanocrystals (strain relaxation)



Outline

- Introduction / Motivation
- Assumed SiC precipitation mechanisms / Controversy
- Utilized simulation techniques
  - Molecular dynamics (MD) simulations
  - Density functional theory (DFT) calculations
- Simulation results
  - C and Si self-interstitial point defects in silicon
  - Silicon carbide precipitation simulations
- Summary / Conclusion

Utilized computational methods

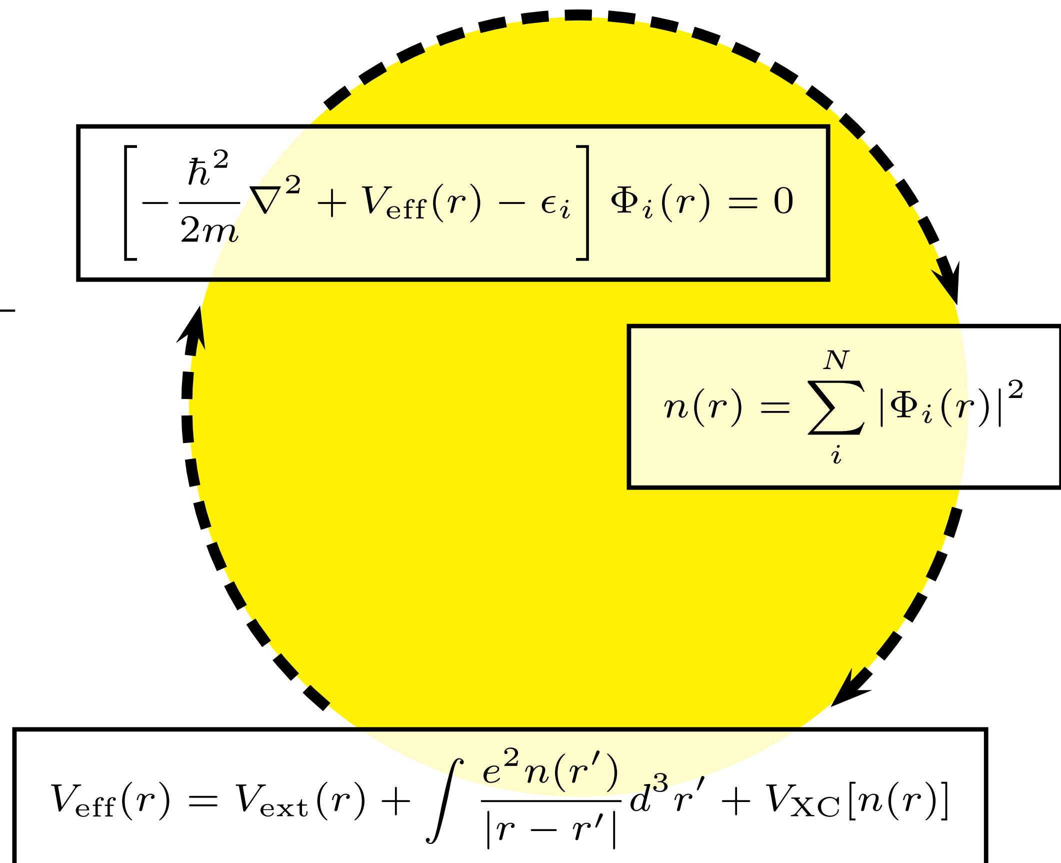
Molecular dynamics (MD)

System of N particles	$N = 5832 \pm 1$ (Defects), $N = 238328 + 6000$ (Precipitation)
Phase space propagation	Velocity Verlet | timestep: 1 fs
Analytical interaction potential	Tersoff-like short-range, bond order potential (Erhart/Albe) $E = \frac{1}{2}\sum_{i \neq j} \mathcal{V}_{ij}, \quad \mathcal{V}_{ij} = f_C(r_{ij})\left[f_R(r_{ij}) + b_{ij} f_A(r_{ij})\right]$
Observables: time/ensemble averages	NpT (isothermal-isobaric) | Berendsen thermostat/barostat

Density functional theory (DFT)

- Hohenberg-Kohn theorem:
  $\Psi_0(r_1, r_2, \ldots, r_N) = \Psi[n_0(r)]$, $E_0 = E[n_0]$
- Kohn-Sham approach:
  Single-particle effective theory

- Code: VASP
- Plane wave basis set | $E_{\mathrm{cut}} = 300\,\mathrm{eV}$
- Ultrasoft pseudopotential
- Exchange & correlation: GGA
- Brillouin zone sampling: Γ-point
- Supercell: $N = 216 \pm 2$



Point defects & defect migration

Defect structure

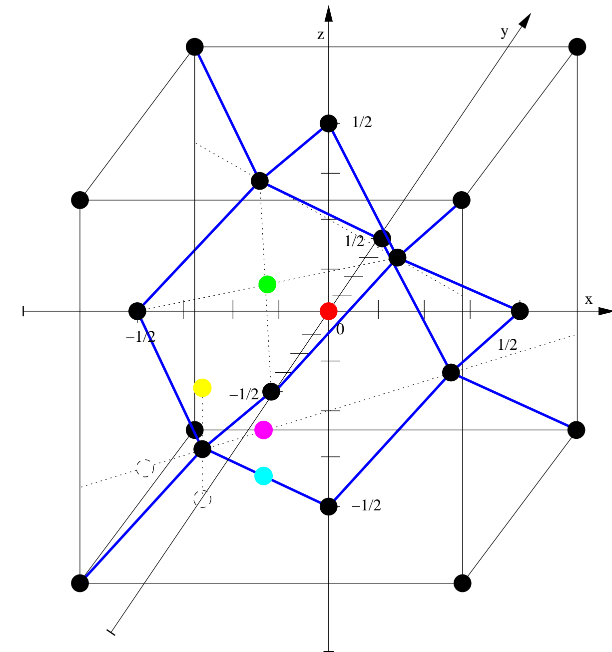
- Creation of c-Si simulation volume
- Periodic boundary conditions
- $T = 0$ K, $p = 0$ bar

↓

Insertion of interstitial C/Si atoms

↓

Relaxation / structural energy minimization



- Tetrahedral
- Hexagonal
- $\langle 1\,0\,0 \rangle$ DB
- $\langle 1\,1\,0 \rangle$ DB
- Bond-centered
- Vac. / Sub.

Defect formation energy

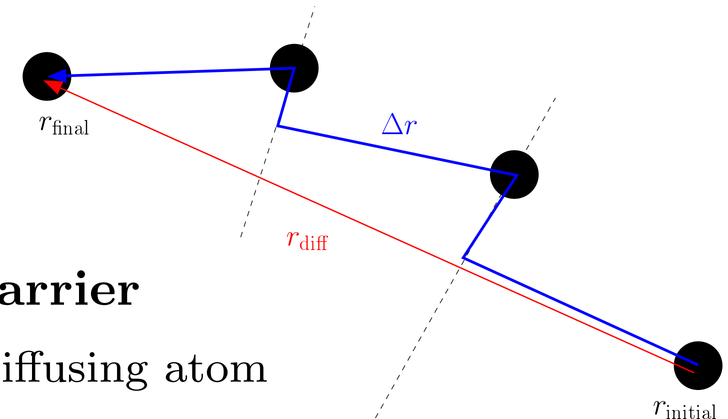
$$E_{\mathrm{f}} = E - \sum_i N_i \mu_i$$

Binding energy

$$E_{\mathrm{b}} = E_{\mathrm{f}}^{\mathrm{comb}} - E_{\mathrm{f}}^{1^{\mathrm{st}}} - E_{\mathrm{f}}^{2^{\mathrm{nd}}}$$

$E_{\mathrm{b}} < 0$: energetically favorable configuration

$E_{\mathrm{b}} \rightarrow 0$: non-interacting, isolated defects

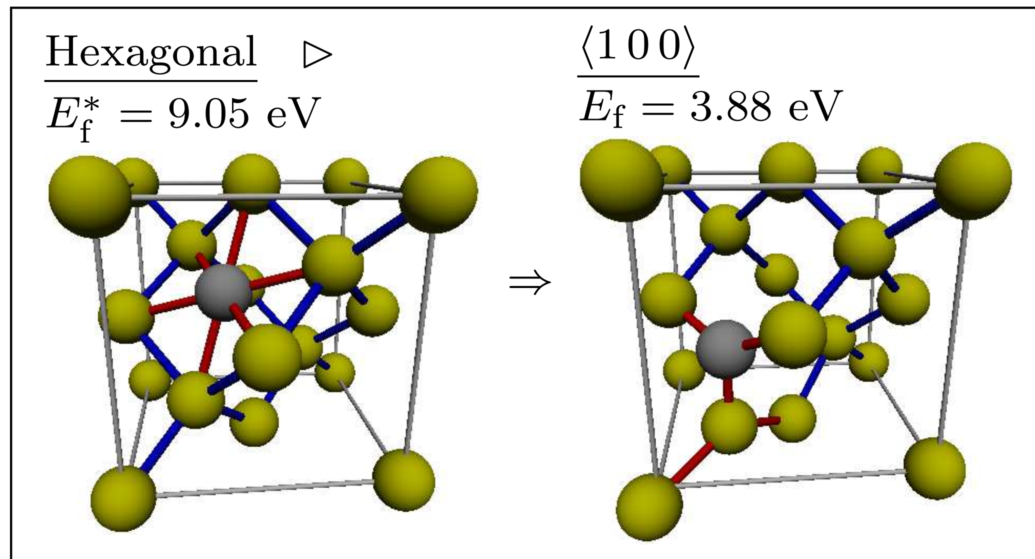


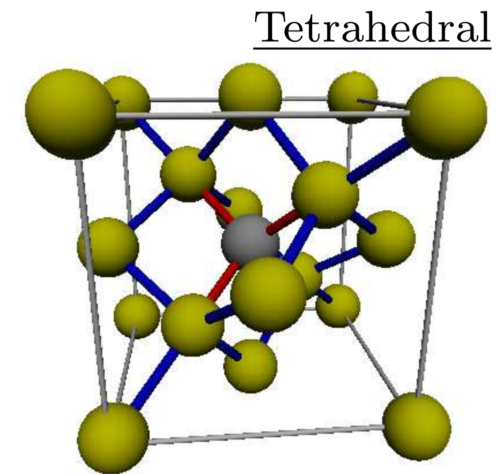
Migration barrier

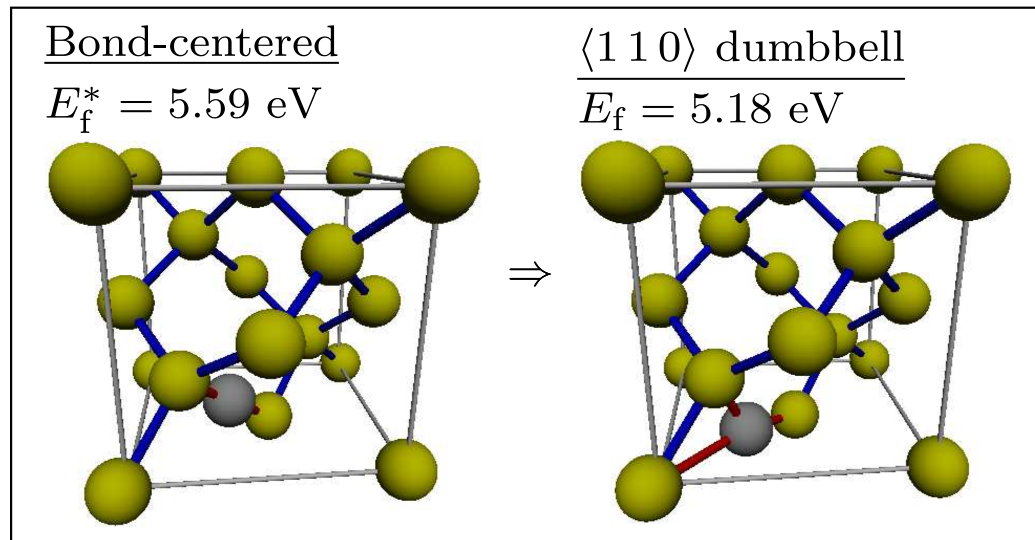
- Displace diffusing atom
- Constrain relaxation of (diffusing) atoms
- Record configurational energy

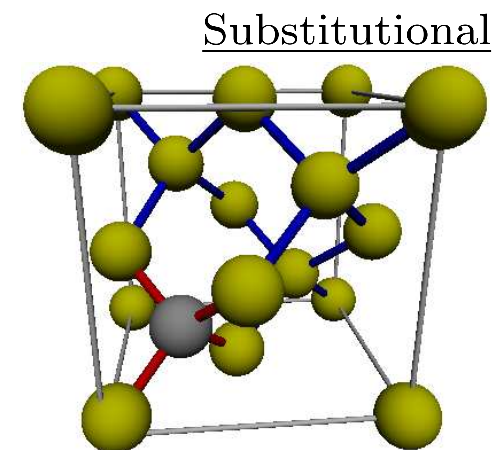
C interstitial point defects in silicon

E_f [eV]	T	H	⟨1 0 0⟩ DB	⟨1 1 0⟩ DB	S	B	C_{sub} & Si_i
VASP	unstable	unstable	3.72	4.16	1.95	4.66	4.17
Erhart/Albe	6.09	9.05*	3.88	5.18	0.75	5.59*	4.43



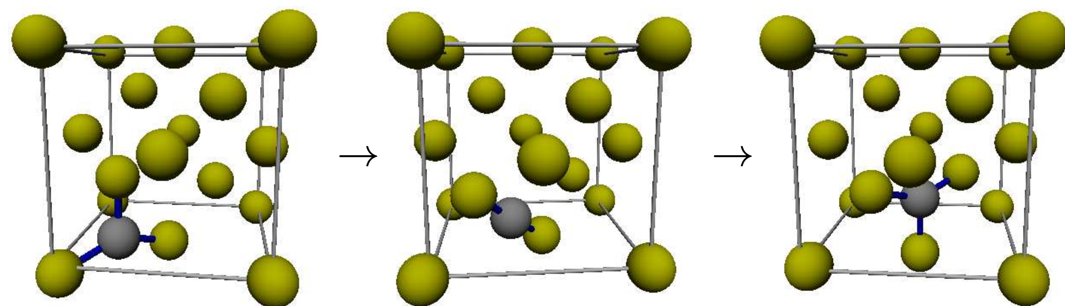


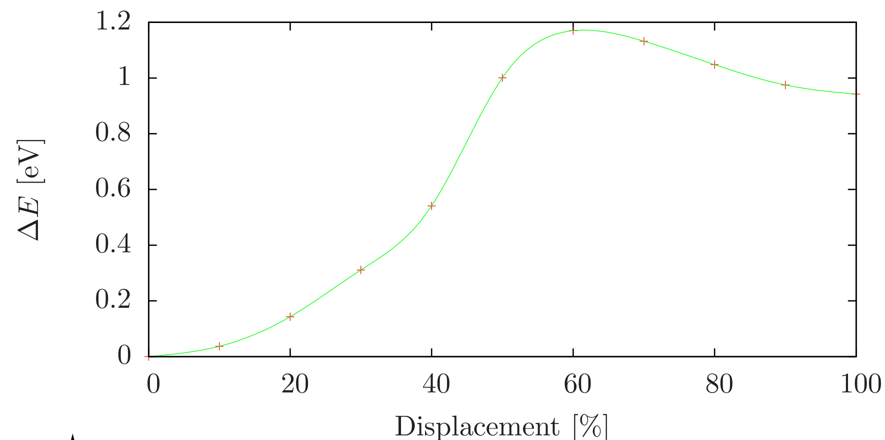


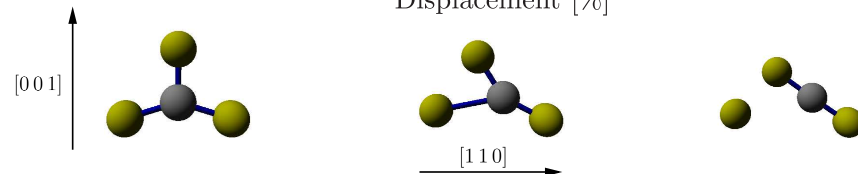


C interstitial migration — ab initio

$[0\,0\,\bar{1}] \rightarrow [0\,0\,1]$





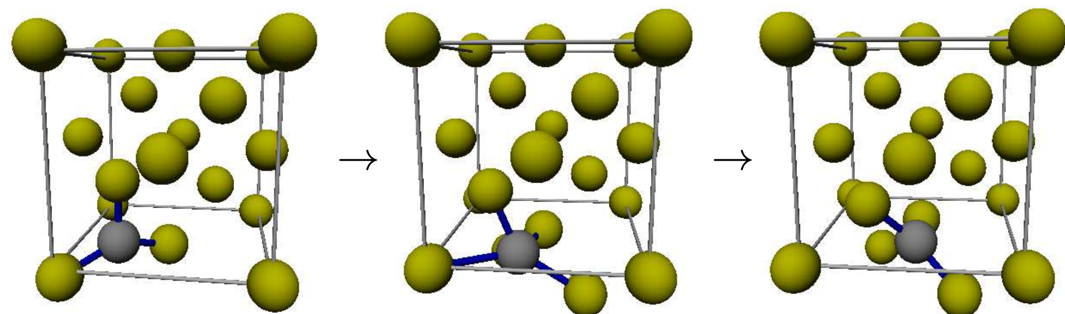


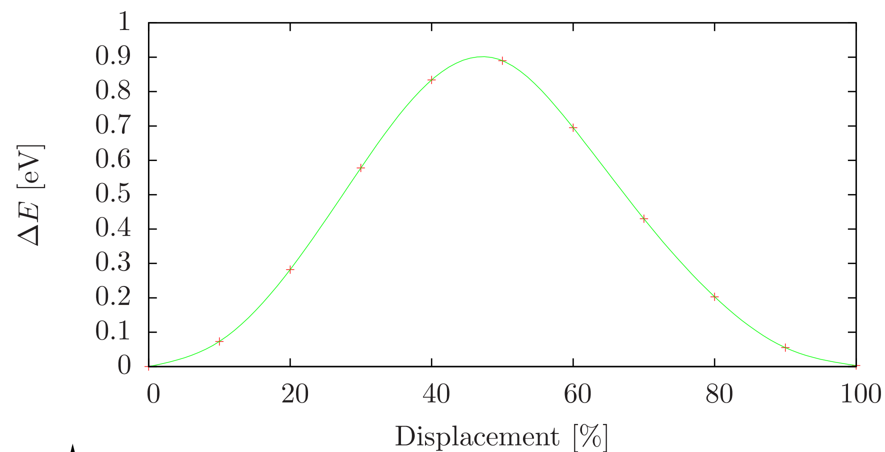
Symmetry:

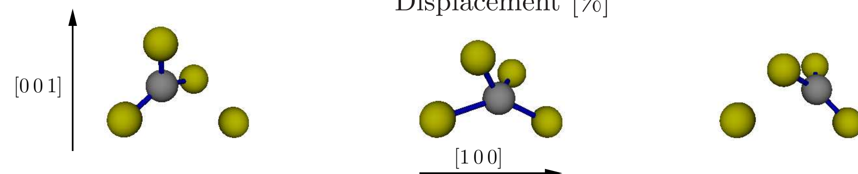
$\Rightarrow$ Sufficient to consider $[0\,0\,\bar{1}]$ to BC transition

$\Rightarrow$ Migration barrier to reach BC | $\Delta E = 1.2\,\text{eV}$

$[0\,0\,\bar{1}] \rightarrow [0\,\bar{1}\,0]$







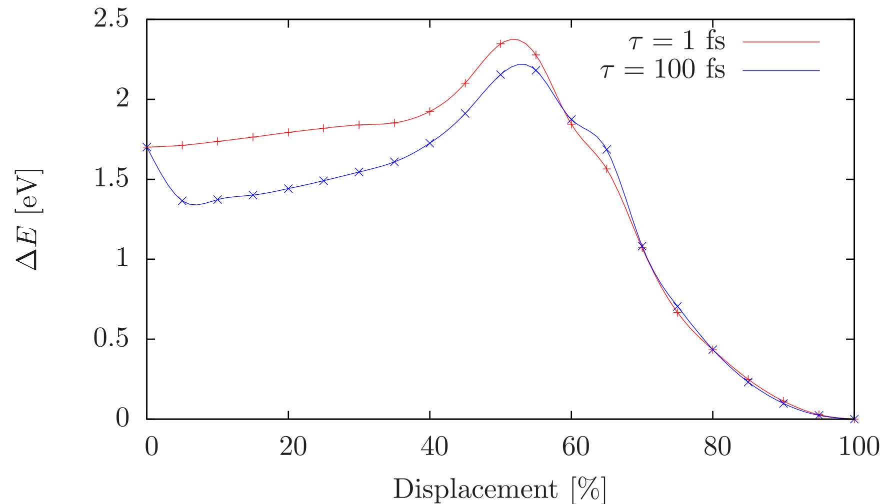
$\Delta E = 0.9\,\text{eV}$ | Experimental values: 0.70–$0.87\,\text{eV}$

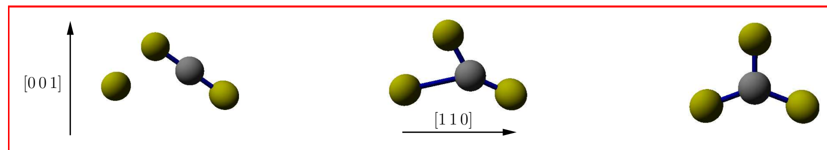
$\Rightarrow$ Migration mechanism identified!

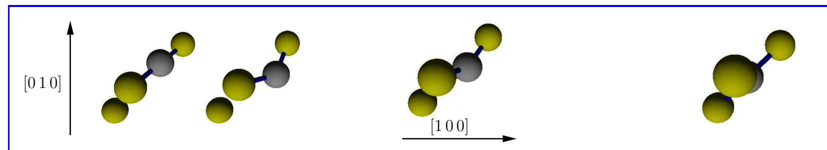
Note: Change in orientation

C interstitial migration — analytical potential

BC to $[0\,0\,\bar{1}]$ transition



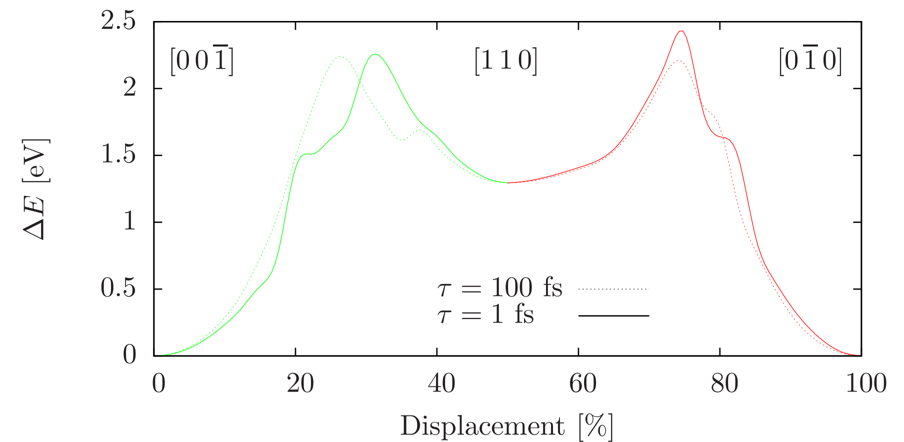


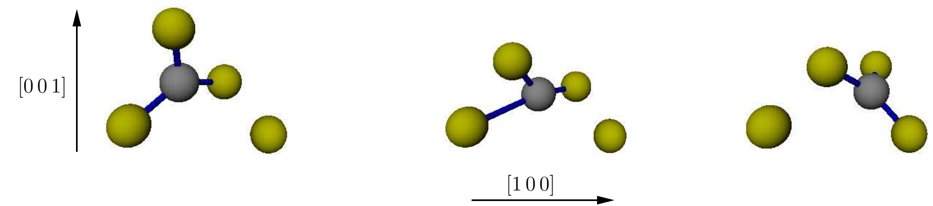


- Lowermost migration barrier
- $\Delta E \approx 2.2\,\text{eV}$
- 2.4 times higher than ab initio result
- Different pathway

Transition involving a $\langle 1\,1\,0 \rangle$ configuration

- Bond-centered configuration unstable
  $\rightarrow$ C_i $\langle 1\,1\,0 \rangle$ dumbbell
- Minimum of the $[0\,0\,\bar{1}]$ to $[0\,\bar{1}\,0]$ transition
  $\rightarrow$ C_i $\langle 1\,1\,0 \rangle$ DB





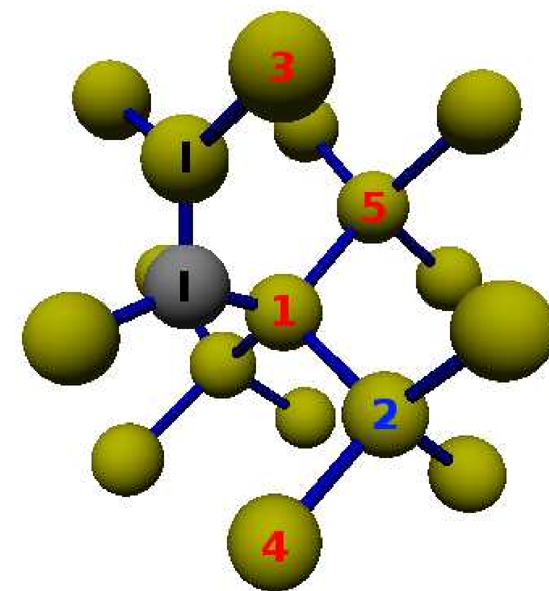
- $\Delta E \approx 2.2\,\text{eV}$ & $0.9\,\text{eV}$
- 2.4 – 3.4 times higher than ab initio result
- After all: Change of the DB orientation

Drastically overestimated diffusion barrier

Defect combinations — ab inito

Summary of combinations

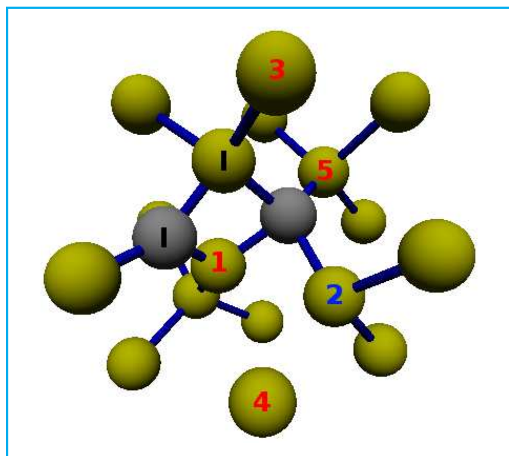
E_b [eV]	1	2	3	4	5	R
$[0\,0\,\bar{1}]$	-0.08	-1.15	-0.08	0.04	-1.66	-0.19
$[0\,0\,1]$	0.34	0.004	-2.05	0.26	-1.53	-0.19
$[0\,\bar{1}\,0]$	-2.39	-0.17	-0.10	-0.27	-1.88	-0.05
$[0\,1\,0]$	-2.25	-1.90	-2.25	-0.12	-1.38	-0.06
$[\bar{1}\,0\,0]$	-2.39	-0.36	-2.25	-0.12	-1.88	-0.05
$[1\,0\,0]$	-2.25	-2.16	-0.10	-0.27	-1.38	-0.06
C_{sub}	0.26	-0.51	-0.93	-0.15	0.49	-0.05
Vacancy	-5.39 ($\rightarrow C_{sub}$)	-0.59	-3.14	-0.54	-0.50	-0.31



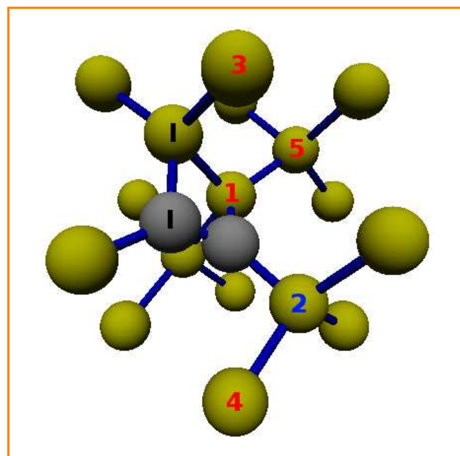
E_b explainable by stress compensation / increase

Combinations of $\langle 1\,0\,0 \rangle$-type interstitials

$[1\,0\,0]$ at position 1



$[0\,\bar{1}\,0]$ at position 1



- C_i agglomeration energetically favorable
- Most favorable: strong C-C bond
  However ...
  ...high migration barrier ($> 4\,$eV)
  ...entropy: $4 \times [-2.25]$ versus $2 \times [-2.39]$

C_i agglomeration / no C clustering

Defect combinations — ab inito

Summary of combinations

E_b [eV]	1	2	3	4	5	R
[0 0 $\bar{1}$]						
[0 0 1]						
[0 $\bar{1}$ 0]						
[0 1 0]						
[$\bar{1}$ 0 0]						
[1 0 0]						
C_{sub}						
Vacancy	-5.39					

E_b expl

Interaction along [1 1 0]

Binding energy [eV]

C-C distance [nm]

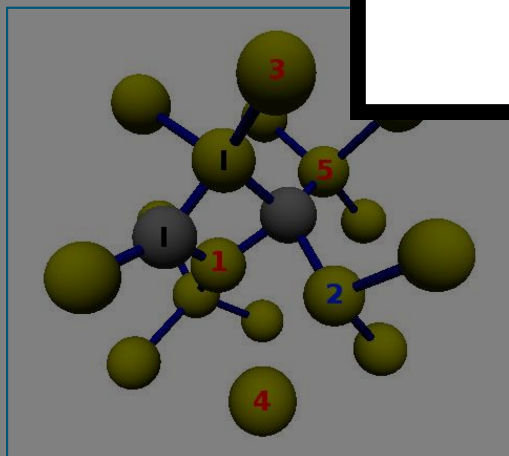
Data

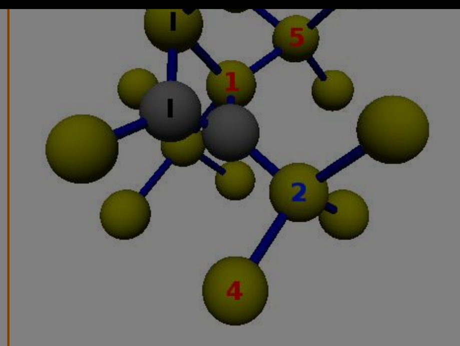
Fit a/x^3 (except data point 1)

Interpolated (all data points)

Combinations

[1 0 0] at position





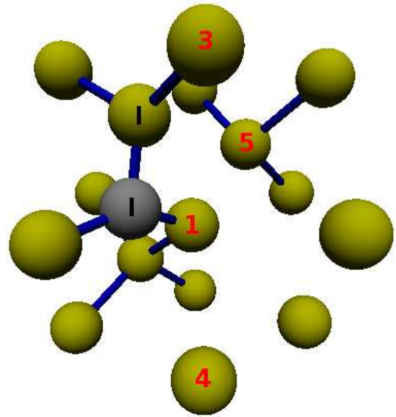
ly favorable

- Most favorable: C clustering
  However . . .
  . . . high migration barrier (> 4 eV)
  . . . entropy: 4 × [−2.25] versus 2 × [−2.39]

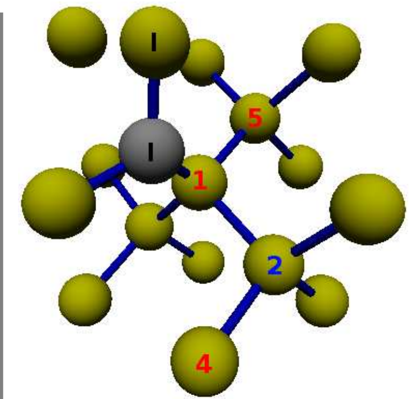
C_i agglomeration / no C clustering

Defect combinations of C-Si dimers and vacancies

V at 2: $E_b = -0.59$ eV



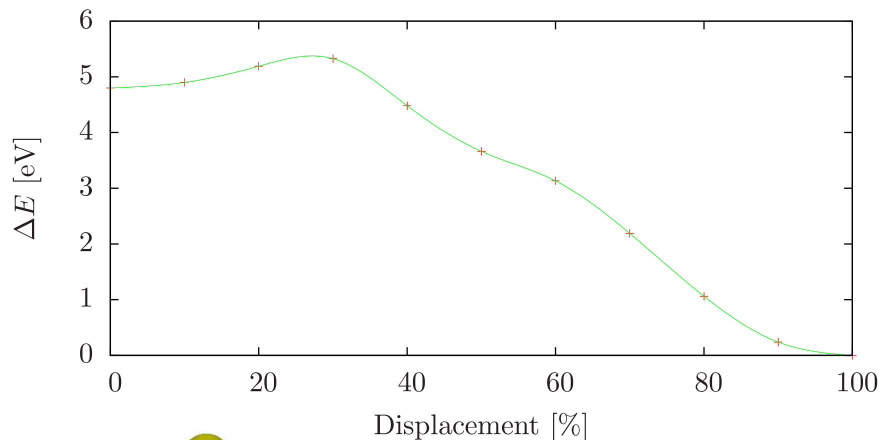
V at 3, $E_b = -3.14$ eV

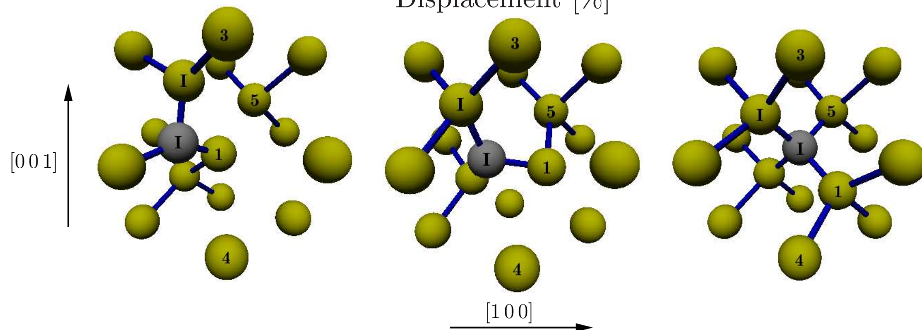


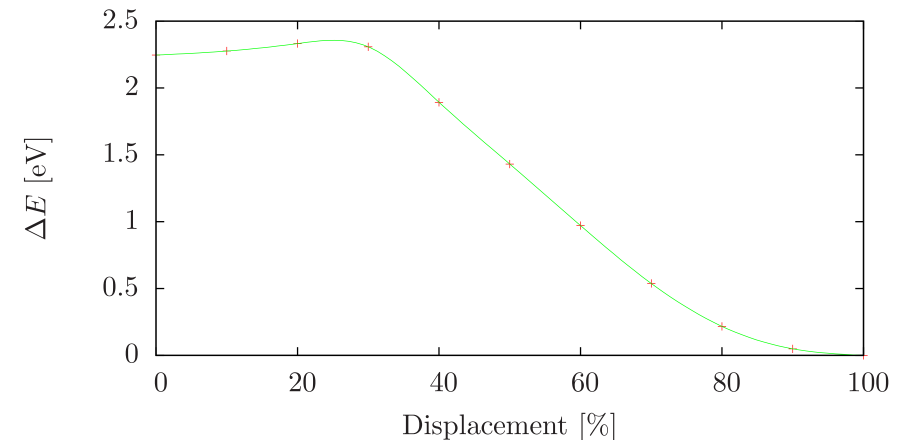
IBS: Impinging C creates V & far away Si_i

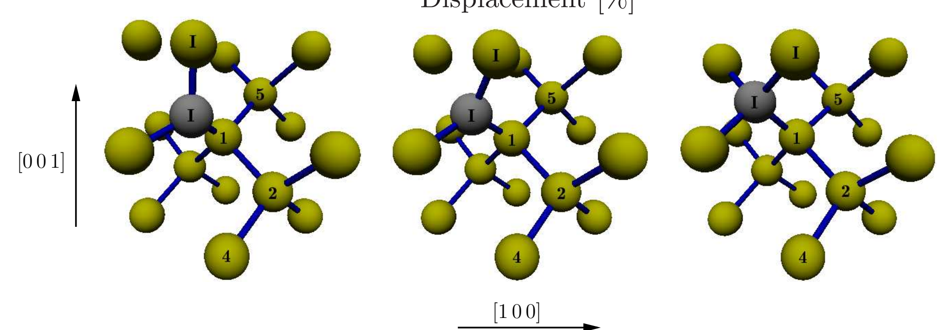
Low migration barrier towards C_{sub}
&
High barrier for reverse process

High probability of stable C_{sub} configuration





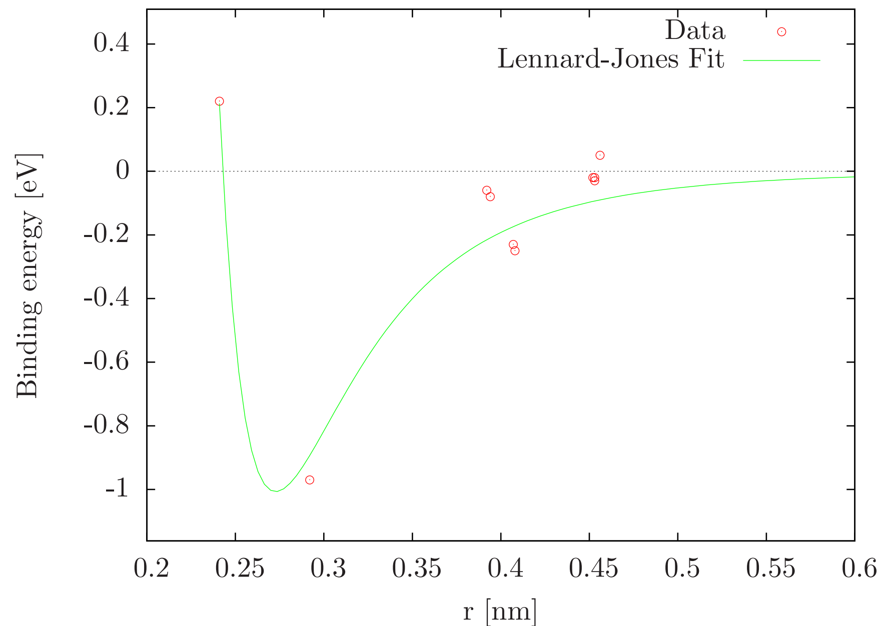




Combinations of substitutional C and Si self-interstitials

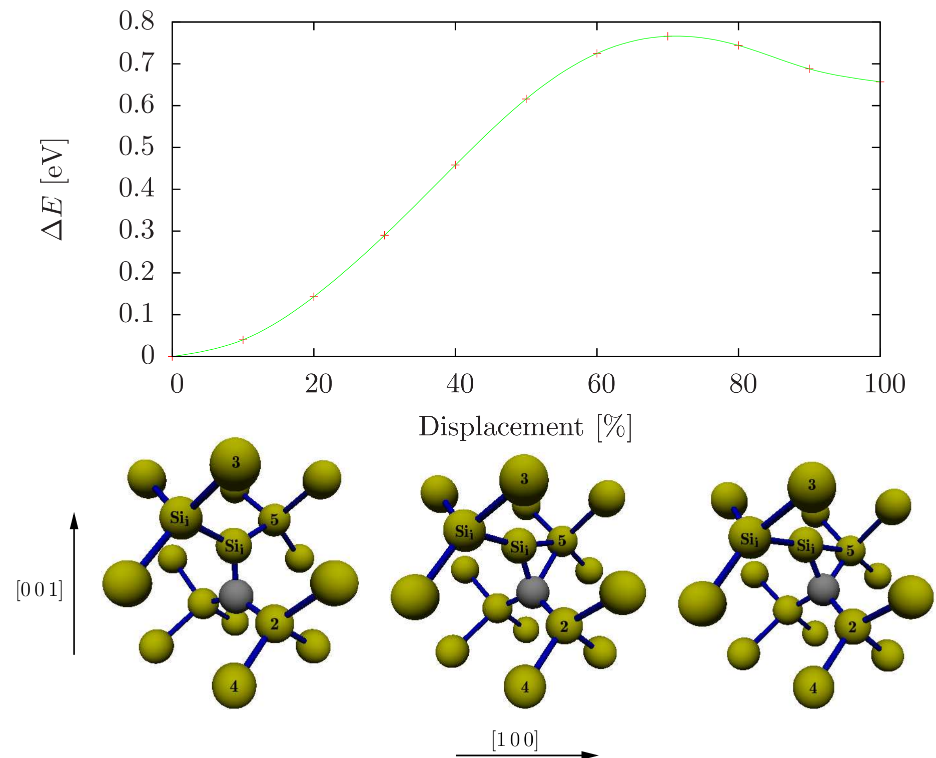
C_{sub} - Si_i $\langle 1\,1\,0\rangle$ interaction

- Most favorable: C_{sub} along $\langle 1\,1\,0\rangle$ chain of Si_i
- Less favorable than ground-state C_i $\langle 1\,0\,0\rangle$ DB
- Interaction drops quickly to zero
  $\rightarrow$ low capture radius



Transition from the ground state

- Low transition barrier
- Barrier smaller than C_i migration barrier
- Low Si_i migration barrier (0.67 eV)
  $\rightarrow$ Separation of C_{sub} & Si_i most probable



C_{sub} & Si_i instead of thermodynamic ground state

IBS — process far from equilibrium

Combinations of substitutional C and Si self-interstitials

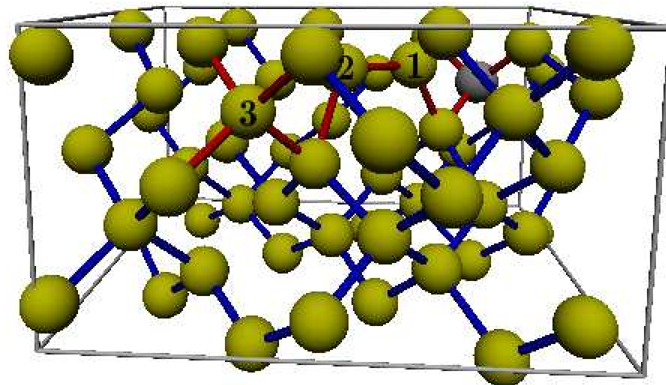
C_{sub} - Si_i $\langle 1\,1\,0 \rangle$ interaction

- Most favorable: C_{sub} along $\langle 1\,1\,0 \rangle$ chain of Si_i
- Less favorable than ground-state C_i $\langle 1\,0\,0 \rangle$ DB

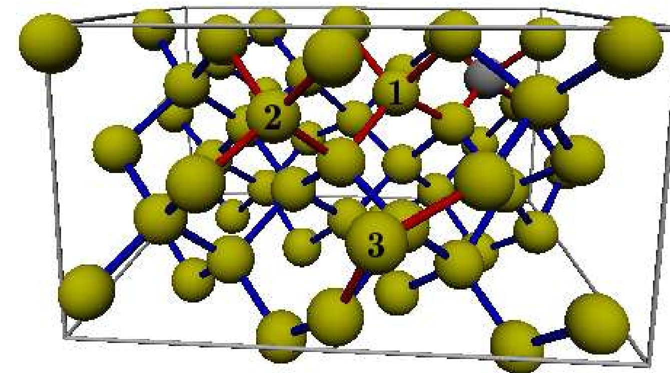
Transition from the ground state

- Low transition barrier
- Barrier smaller than C_i migration barrier

Ab initio MD at 900 °C



$t = 2230\,$fs



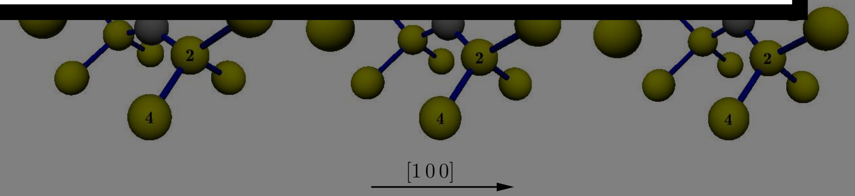
$t = 2900\,$fs

Contribution of entropy to structural formation

Binding energy [eV]

0.2 0.25 0.3 0.35 0.4 0.45 0.5 0.55 0.6

r [nm]



C_{sub} & Si_i instead of thermodynamic ground state

IBS — process far from equilibrium

Silicon carbide precipitation simulations

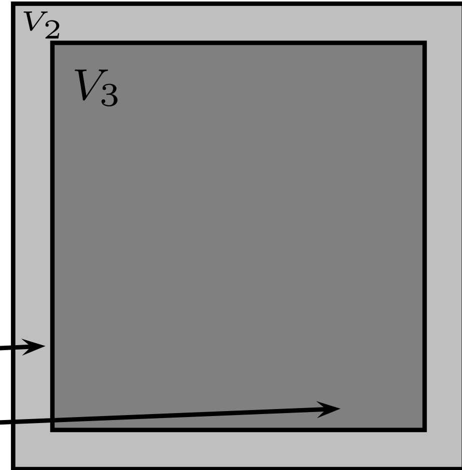
Procedure

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

Insertion of C atoms at constant T

- total simulation volume
- volume of minimal SiC precipitate size
- volume containing Si atoms to form a minimal precipitate

Run for 100 ps followed by cooling down to 20 °C

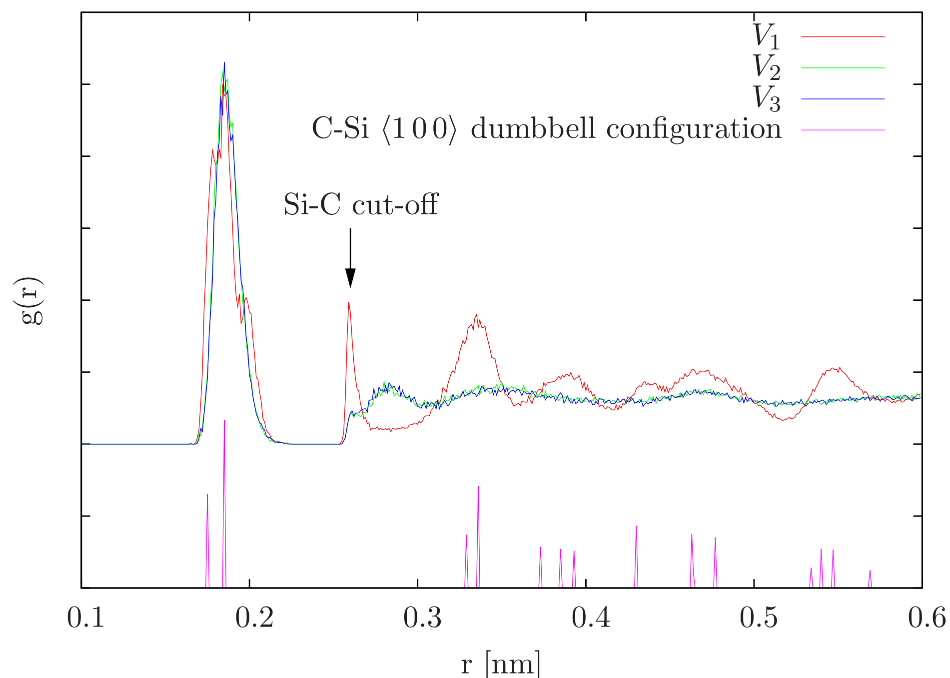


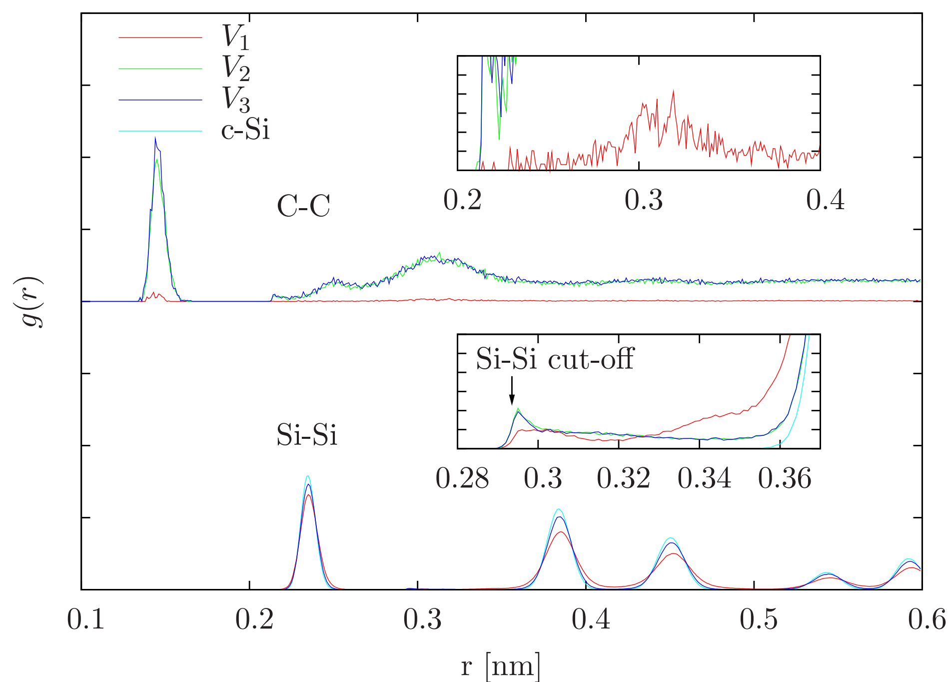
Note

- Amount of C atoms: 6000 ($r_{\text{prec}} \approx 3.1$ nm, IBS: 2–4 nm)
- Simulation volume: 31^3 Si unit cells (238328 Si atoms)

Restricted to classical potential caclulations
→ Low C diffusion / overestimated barrier
→ Consider V_2 and V_3

Silicon carbide precipitation simulations at 450 °C as in IBS





<u>Low C concentration — V_1</u>

C_i ⟨1 0 0⟩ dumbbell dominated structure

- Si-C bumbs around 0.19 nm
- C-C peak at 0.31 nm (expected in 3C-SiC): concatenated differently oriented C_i DBs
- Si-Si NN distance stretched to 0.3 nm

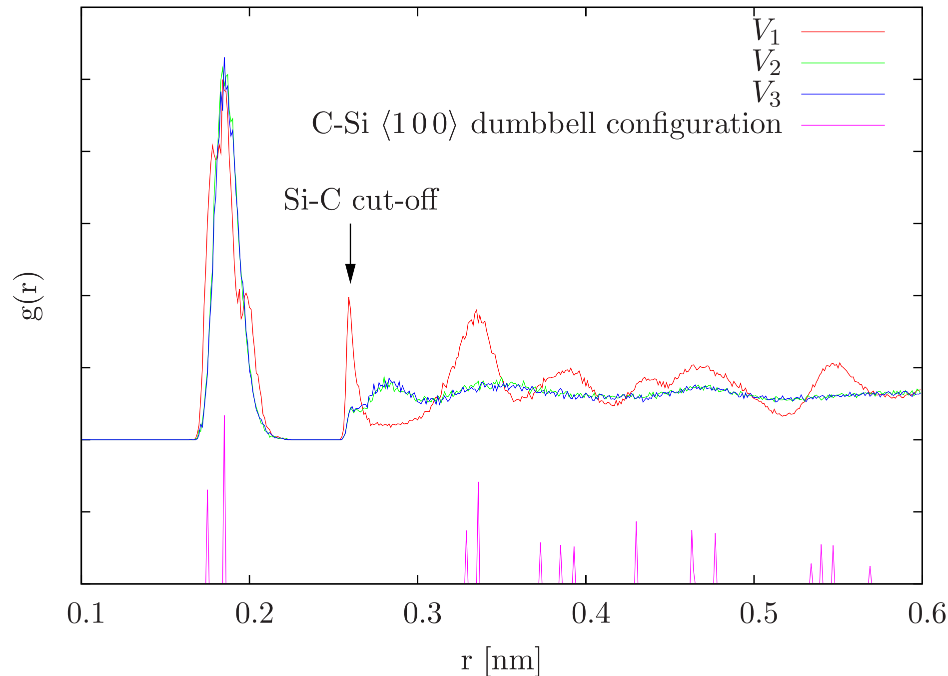
Formation of C_i dumbbells
C atoms separated as expected in 3C-SiC

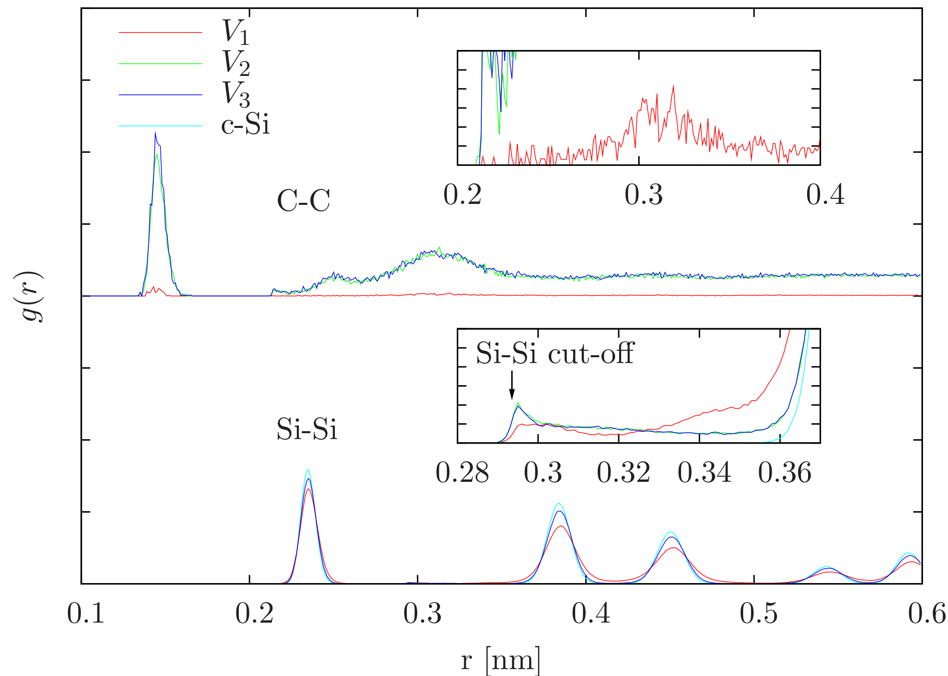
<u>High C concentration — V_2/V_3</u>

- High amount of strongly bound C-C bonds
- Increased defect & damage density
  → Arrangements hard to categorize and trace
- Only short range order observable

Amorphous SiC-like phase

Silicon carbide precipitation simulations at 450 °C as in IBS





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High C concentration — V_2/V_3

- High amount of strongly bound C-C bonds
- Increased defect & damage density
  → Arrangements hard to categorize and trace
- Only short range order observable

Amorphous SiC-like phase

Formation of 3C-SiC fails to appear

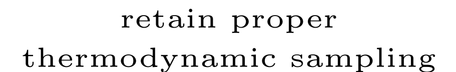
V_1: Formation of C_i indeed occurs
Agglomeration not observed

$V_{2,3}$: Amorphous SiC-like structure
(not expected at 450 °C)
No rearrangement/transition into 3C-SiC

Limitations of MD and short range potentials

Time scale problem of MD

Minimize integration error & precise thermodynamic sampling
$\Rightarrow \Delta t \ll (\max \omega)^{-1}$, ω: vibrational mode
$\Rightarrow$ Slow phase space propagation



Several local minima separated by large energy barriers
$\Rightarrow$ Transition event corresponds to a multiple of vibrational periods
$\Rightarrow$ Phase transition consists of many infrequent transition events

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

Limitations related to the short range potential

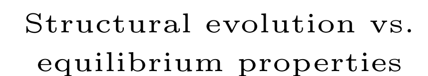
Cut-off function limits interaction to next neighbours
$\Rightarrow$ Overestimated diffusion barrier (factor: 2.4–3.4)

Potential enhanced slow phase space propagation

IBS

3C-SiC also observed for higher T

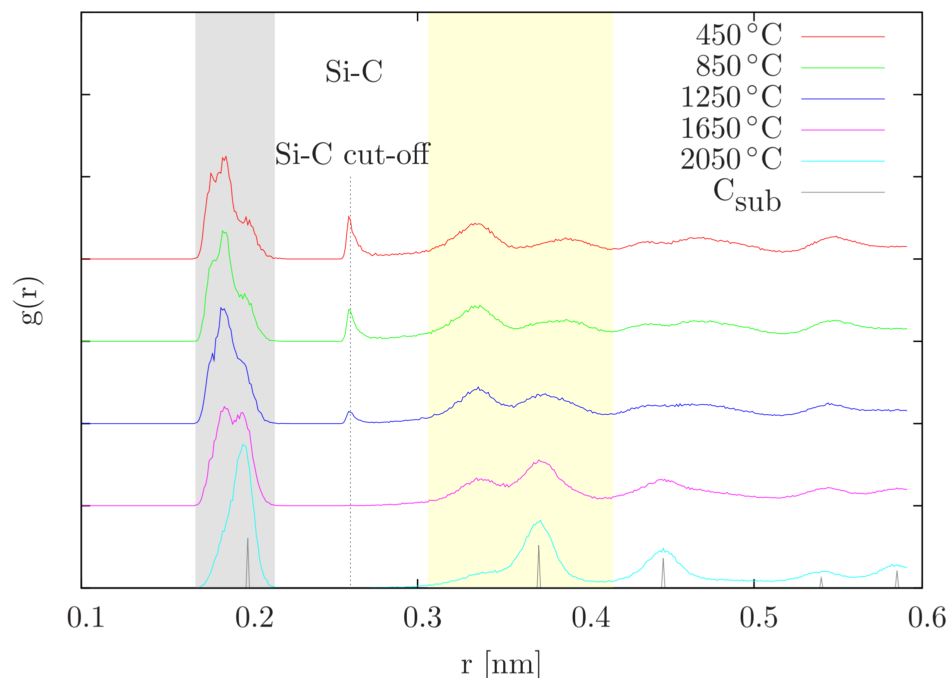
Higher T inside sample

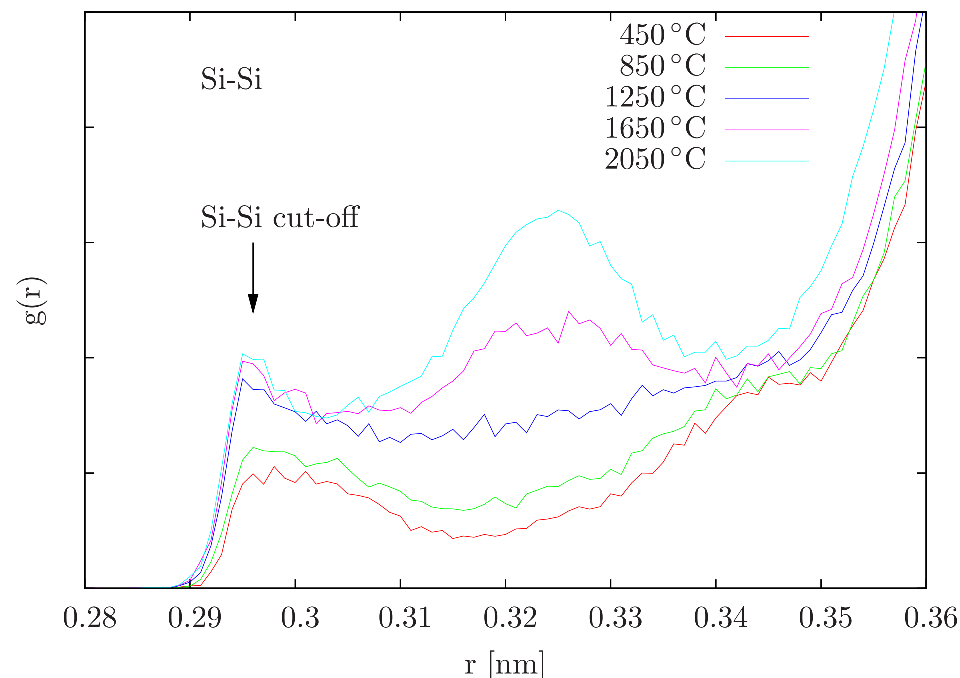


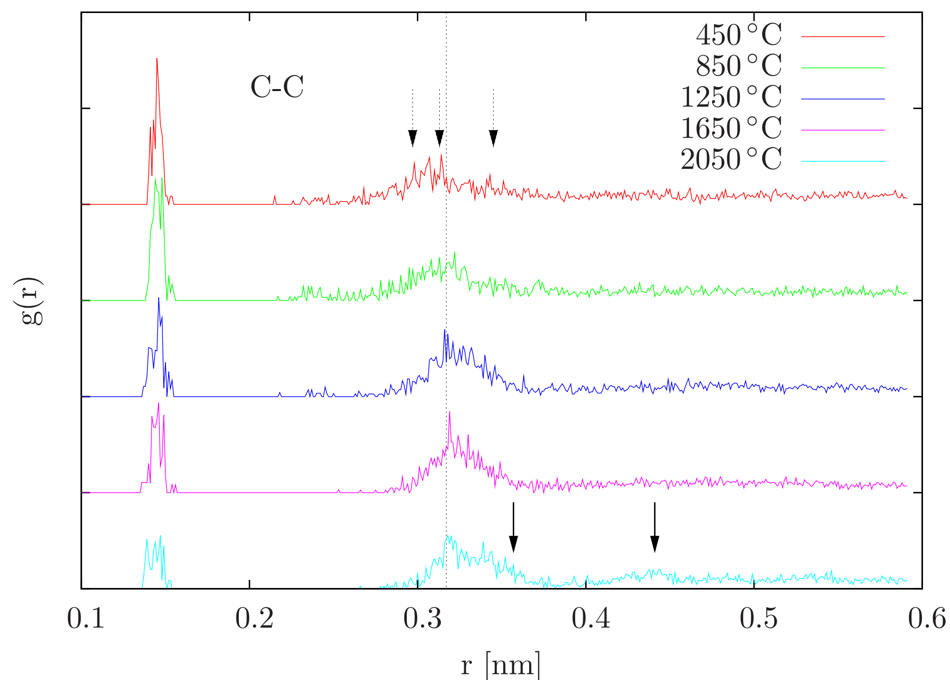
Approach to the (twofold) problem

Increased temperature simulations without TAD corrections
Accelerated methods or higher time scales exclusively not sufficient!

Increased temperature simulations — V_1







Si-C bonds:

- Vanishing cut-off artifact (above 1650 °C)
- Structural change: C_i ⟨1 0 0⟩ DB → C_{sub}

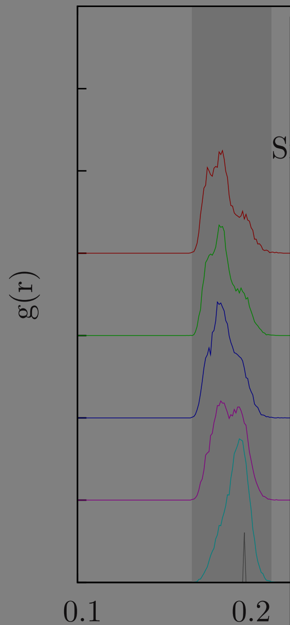
Si-Si bonds: Si-C_{sub}-Si along ⟨1 1 0⟩ (→ 0.325 nm)

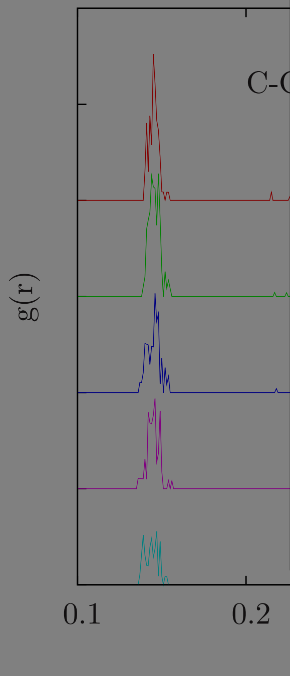
C-C bonds:

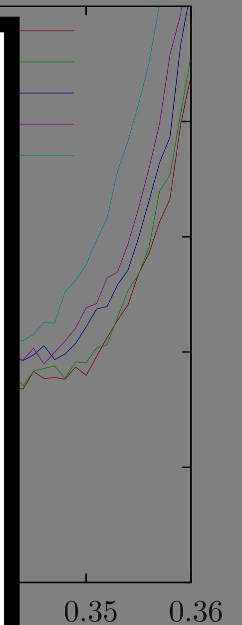
- C-C next neighbour pairs reduced (mandatory)
- Peak at 0.3 nm slightly shifted

  ↘ C_i combinations (dashed arrows)
  ↗ C_i ⟨1 0 0⟩ & C_{sub} combinations (|)
  ↗ C_i pure C_{sub} combinations (↓)
  Range [|-↓]: C_{sub} & C_{sub} with nearby Si_i

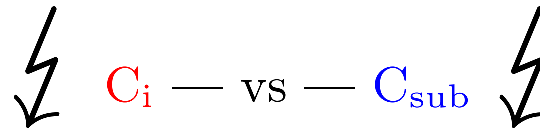
Increased temperature simulations — V_1







Conclusions on SiC precipitation



- Stretched coherent SiC structures directly observed

  C_{sub} involved in the precipitation mechanism

- Emission of Si_i serves several needs:
  - Vehicle to rearrange C_{sub}— [C_{sub} & $Si_i \leftrightarrow C_i$]
  - Building block for surrounding Si host & further SiC
  - Strain compensation …

    … Si/SiC interface

    … within stretched coherent SiC structure

- Explains annealing behavior of high/low T C implantations
  - Low T: highly mobile C_i
  - High T: stable configurations of C_{sub}

  High T $\leftrightarrow$ IBS conditions far from equilibrium

50 °C)

C_{sub}

0.325 nm)

mandatory)

C_i pure C_{sub} combinations (↓)

Range [|-↓]: C_{sub} & C_{sub} with nearby Si_i

Summary and Conclusions

Defects

- DFT / EA
  - Point defects excellently / fairly well described by DFT / EA
  - Identified C_i migration path
  - EA drastically overestimates the diffusion barrier
- Combinations of defects (DFT)
  - Agglomeration of point defects energetically favorable
  - C_{sub} favored conditions (conceivable in IBS)
  - C_i $\langle 1\,0\,0 \rangle \leftrightarrow C_{sub}$ & Si_i $\langle 1\,1\,0 \rangle$
    Low barrier (0.77 eV) & low capture radius

Pecipitation simulations

- Problem of potential enhanced slow phase space propagation
- High T necessary to simulate IBS conditions (far from equilibrium)
- Low T $\rightarrow$ C-Si $\langle 1\,0\,0 \rangle$ dumbbell dominated structure
- High T $\rightarrow$ C_{sub} dominated structure / Structures of stretched SiC
  $\Rightarrow$ C_{sub} involved in the precipitation process at elevated temperatures
- Si_i: vehicle to form C_{sub} & supply of Si & stress compensation (stretched SiC, interface)

IBS: 3C-SiC precipitation occurs by successive agglomeration of C_{sub}

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