First-principles and empirical potential simulation study of intrinsic and carbon-related defects in silicon

F. Zirkelbach • **B. Stritzker**
Experimentalphysik IV, Universität Augsburg, 86135 Augsburg, Germany

K. Nordlund
Department of Physics, University of Helsinki, 00014 Helsinki, Finland

W. G. Schmidt • **E. Rauls** • **J. K. N. Lindner**
Department Physik, Universität Paderborn, 33095 Paderborn, Germany

E-MRS Spring Meeting, Strasbourg, 17.05.2012

Motivation & Outline

Ion beam synthesis (IBS) of epitaxial single crystalline 3C-SiC

- Implantation

  Stoichiometric dose | 180 keV | 500 °C

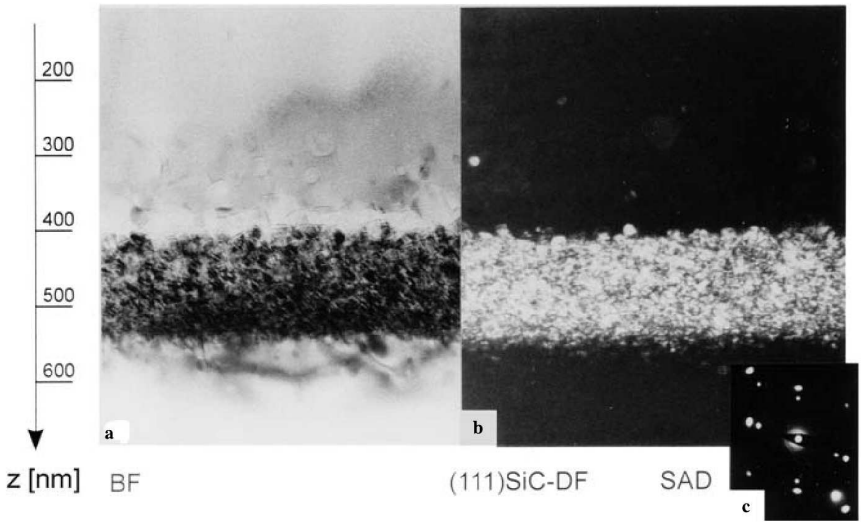
  ⇒ Epitaxial 3C-SiC layer & precipitates

- Annealing

  10 h at 1250 °C

  ⇒ Homogeneous 3C-SiC layer

3C-SiC precipitation
not yet fully understood



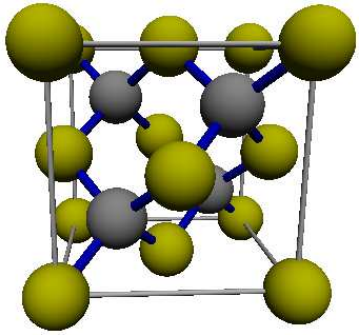
XTEM: single crystalline 3C-SiC in Si(1 0 0)

Outline

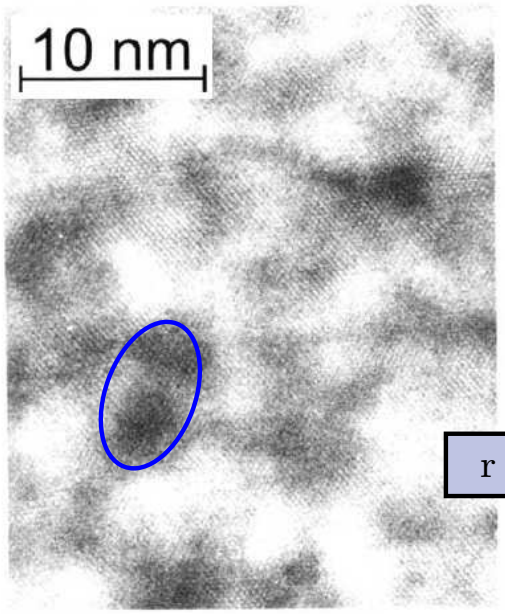
- Assumed SiC precipitation mechanisms / Controversy
- Utilized simulation techniques
- C and Si self-interstitial point defects in silicon
- Silicon carbide precipitation simulations

Supposed precipitation mechanism of SiC in Si

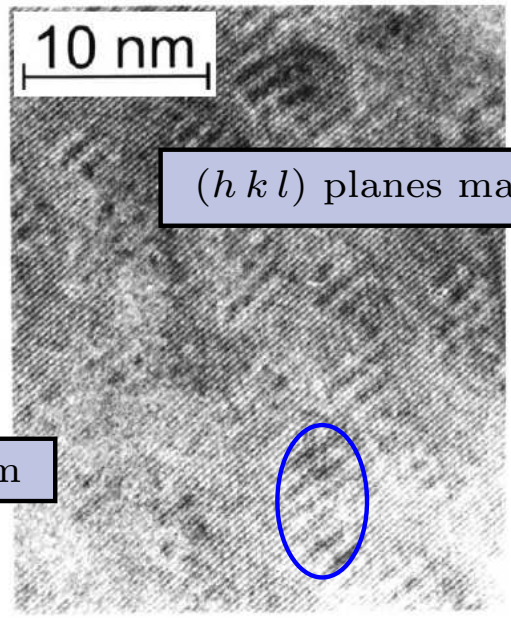
Si & SiC lattice structure



Silicon	Silicon carbide
• Si | • Si	• Si | • C
$a = 5.429$ A	$a = 4.359$ A
$\rho^*_{\mathrm{Si}} = 100\,\%$	$\rho^*_{\mathrm{Si}} = 97\,\%$

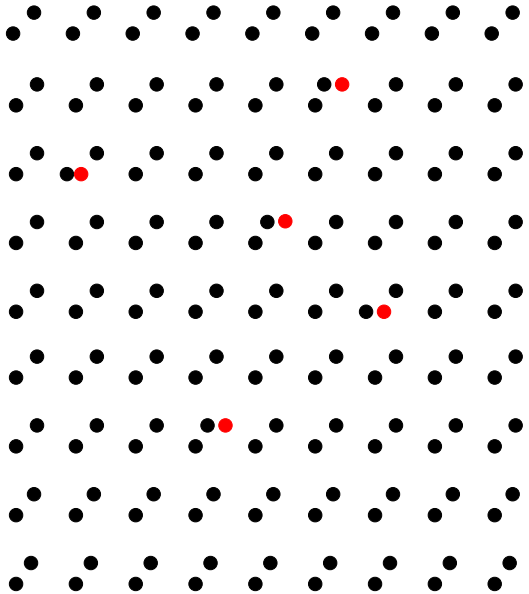


r = 2–4 nm

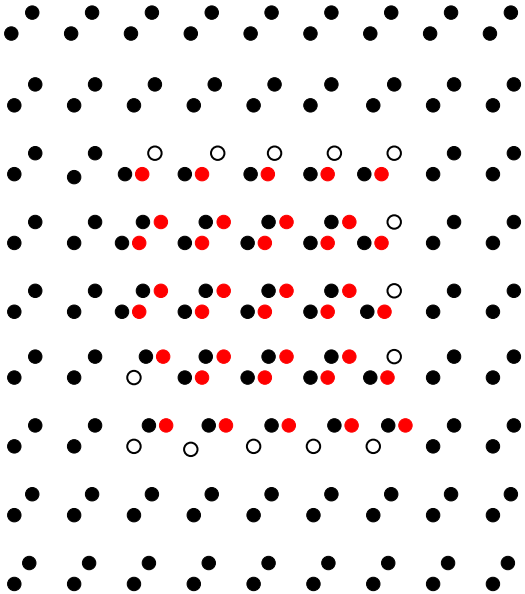


$(h\,k\,l)$ planes match

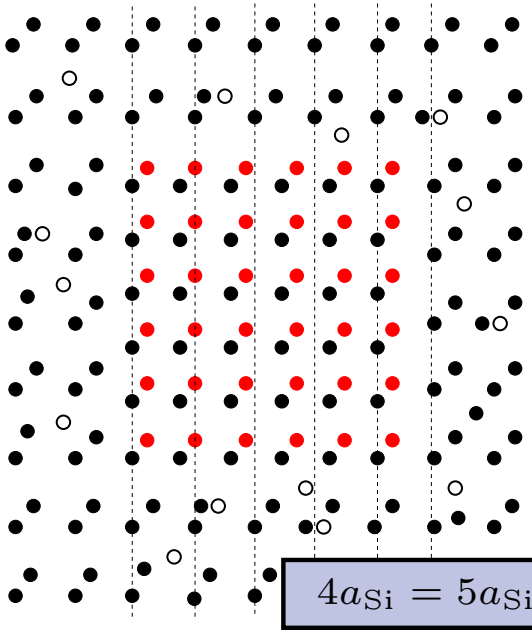
C-Si dimers (dumbbells)
on Si lattice sites



Agglomeration of C-Si dumbbells
⇒ dark contrasts



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



$4a_{\mathrm{Si}} = 5a_{\mathrm{SiC}}$

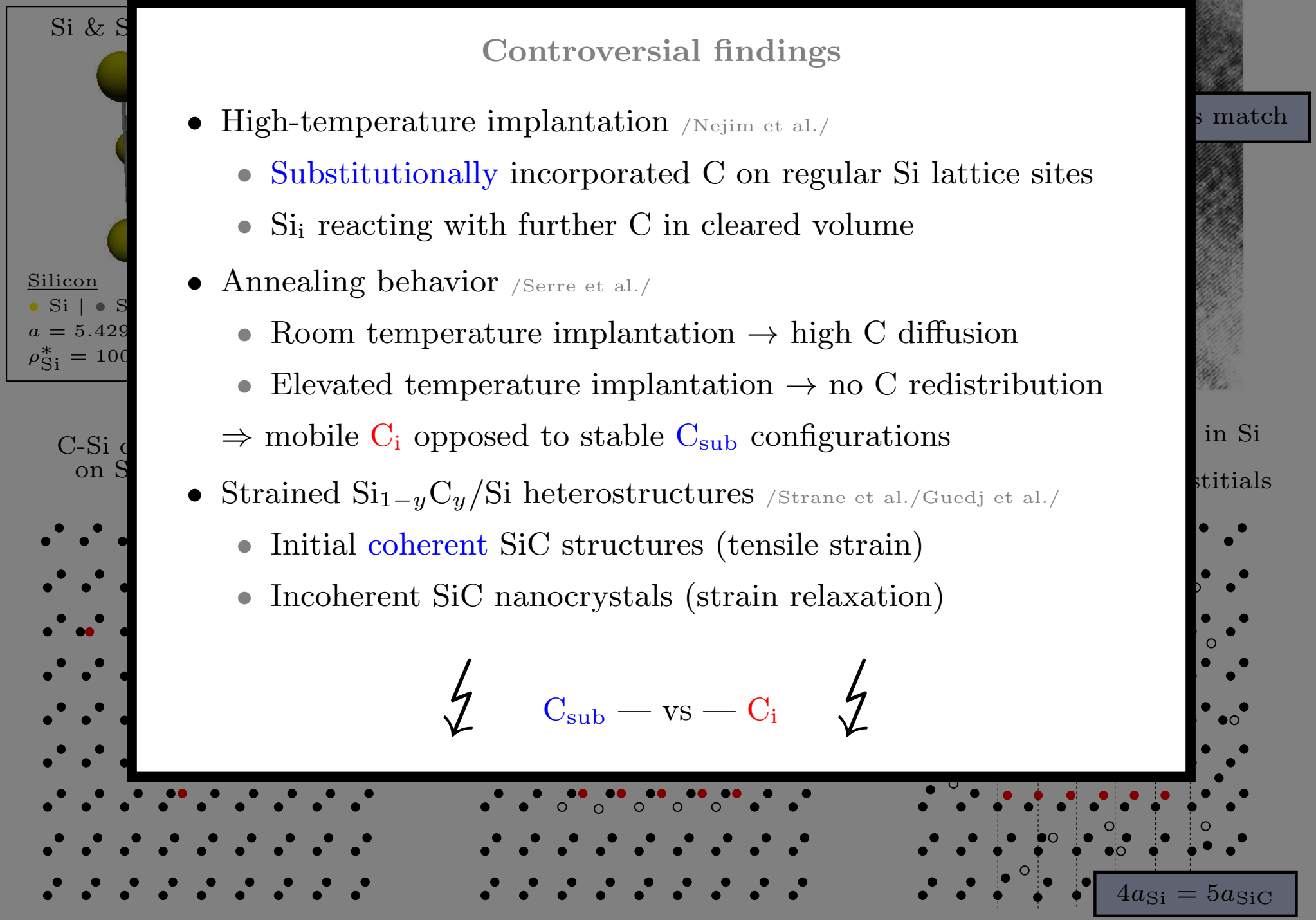
Supposed precipitation mechanism of SiC in Si

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 → high C diffusion
  - Elevated temperature implantation → no C redistribution

  ⇒ 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)

C_{sub} — vs — C_i



Utilized computational methods

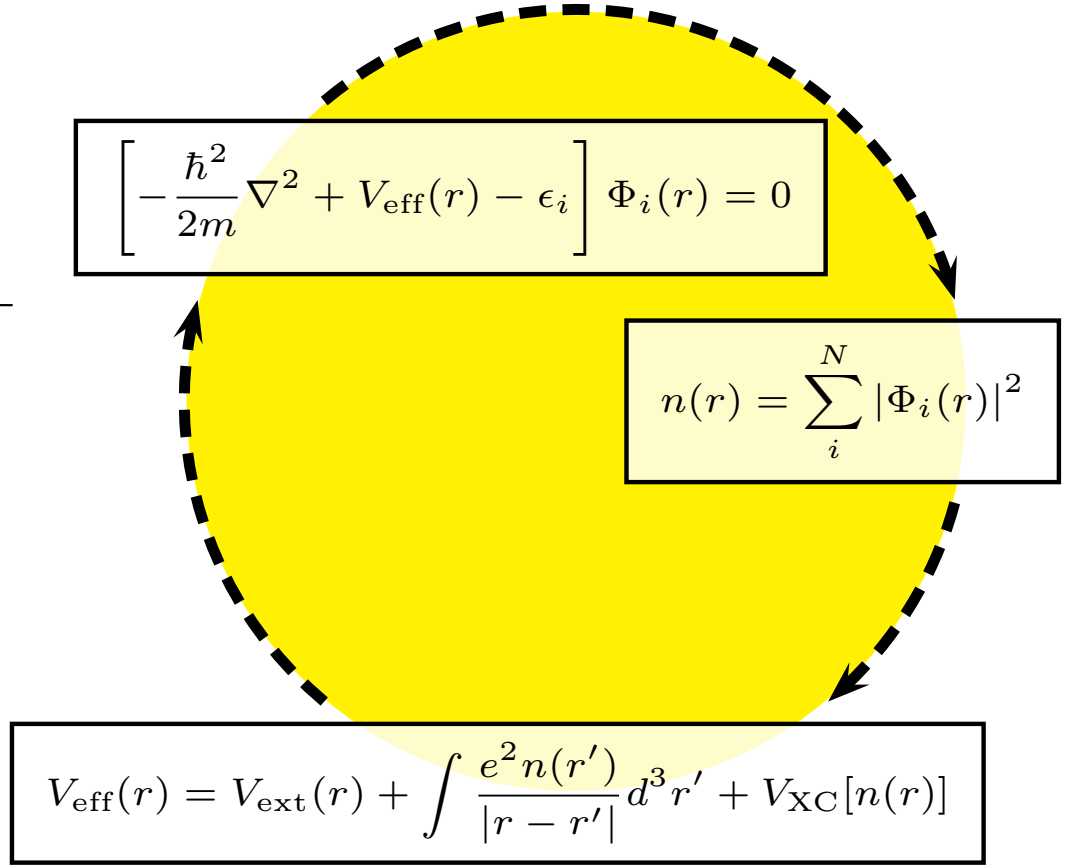
Molecular dynamics (MD)

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) $E = \frac{1}{2}\sum_{i \neq j} \mathcal{V}_{ij}, \quad \mathcal{V}_{ij} = f_C(r_{ij})\,[f_R(r_{ij}) + b_{ij}\, f_A(r_{ij})]$
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 \| $E_{\text{cut}} = 300\,\text{eV}$
- Ultrasoft pseudopotential
- Exchange & correlation: GGA
- Brillouin zone sampling: Γ-point
- Supercell: $N = 216 \pm 2$



Point defects & defect migration

Defect structure

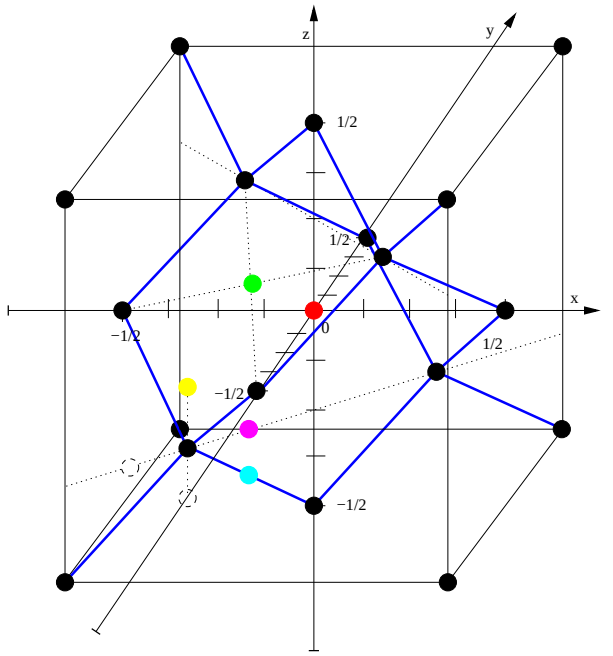
- Creation of c-Si simulation volume
- Periodic boundary conditions
- $T = 0$ K, $p = 0$ bar

↓

Insertion of interstitial C/Si atoms

↓

Relaxation / structural energy minimization



- Tetrahedral
- Hexagonal
- ⟨1 0 0⟩ DB
- ⟨1 1 0⟩ DB
- Bond-centered
- Vac. / Sub.

Defect formation energy

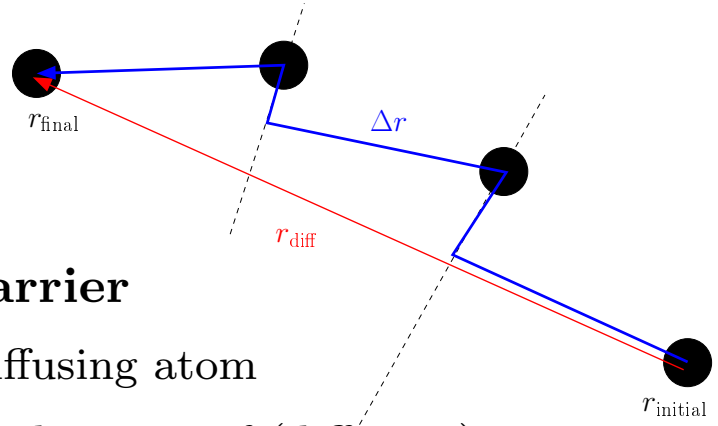
$$E_\mathrm{f} = E - \sum_i N_i \mu_i$$

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

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



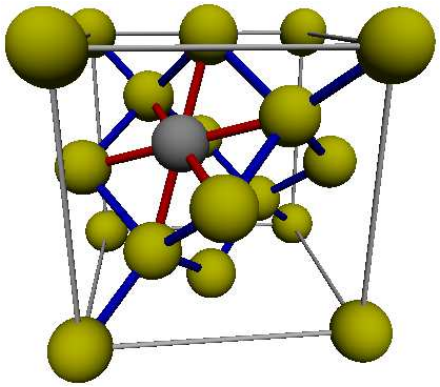
Migration barrier

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

C interstitial point defects in silicon

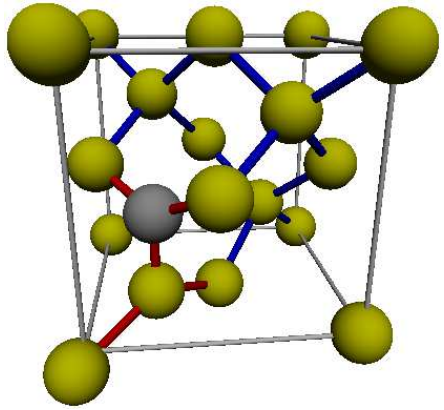
E_f [eV]	T	H	⟨1 0 0⟩ DB	⟨1 1 0⟩ DB	S	B	C_{sub} & Si_i
VASP	unstable	unstable	3.72	4.16	1.95	4.66	4.17
Erhart/Albe	6.09	9.05*	3.88	5.18	0.75	5.59*	4.43

Hexagonal ▷
$E_f^* = 9.05$ eV

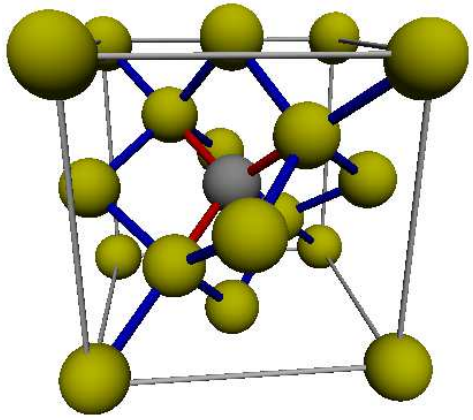


⇒

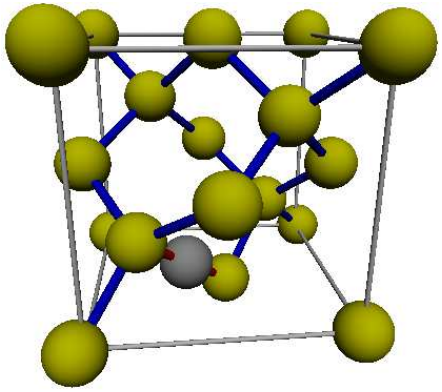
⟨1 0 0⟩
$E_f = 3.88$ eV



Tetrahedral

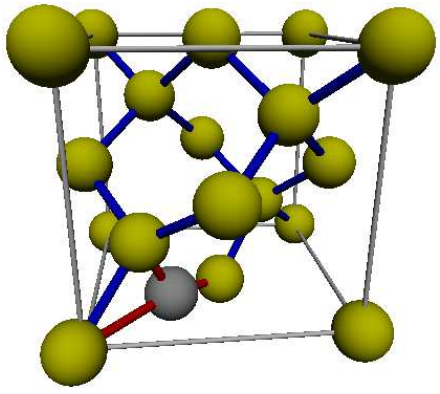


Bond-centered
$E_f^* = 5.59$ eV

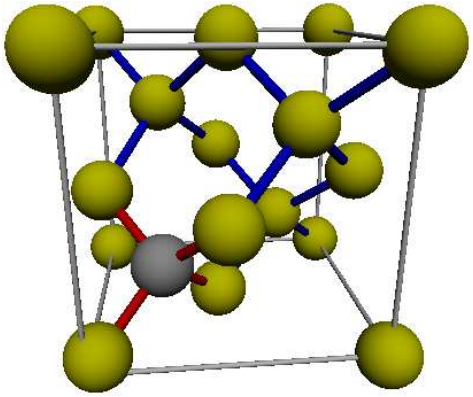


⇒

⟨1 1 0⟩ dumbbell
$E_f = 5.18$ eV

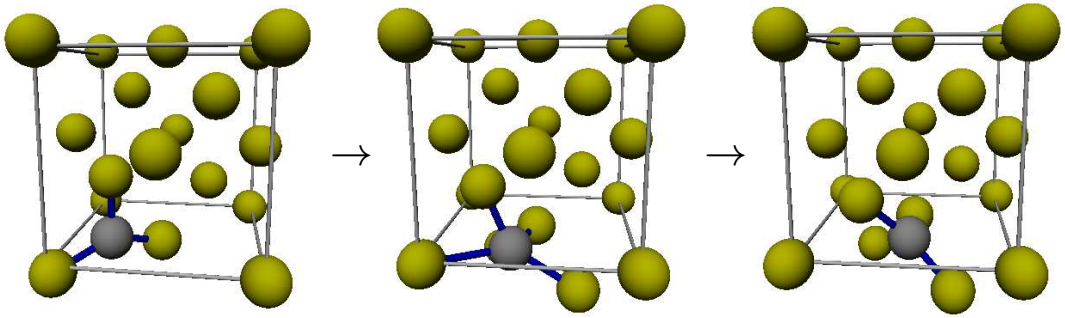


Substitutional



C interstitial migration

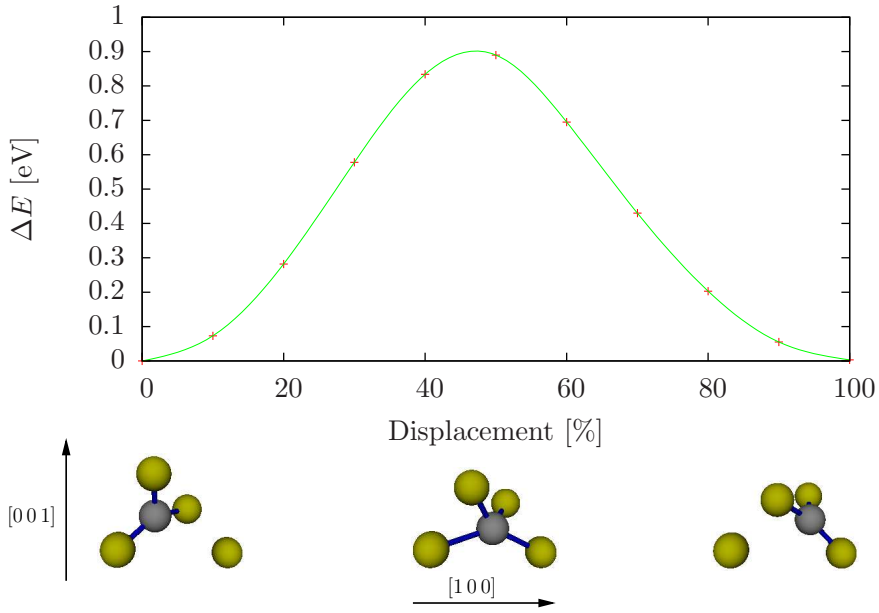
First-principles $[0\,0\,\bar{1}] \rightarrow [0\,\bar{1}\,0]$



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

$\Rightarrow$ Migration mechanism identified!

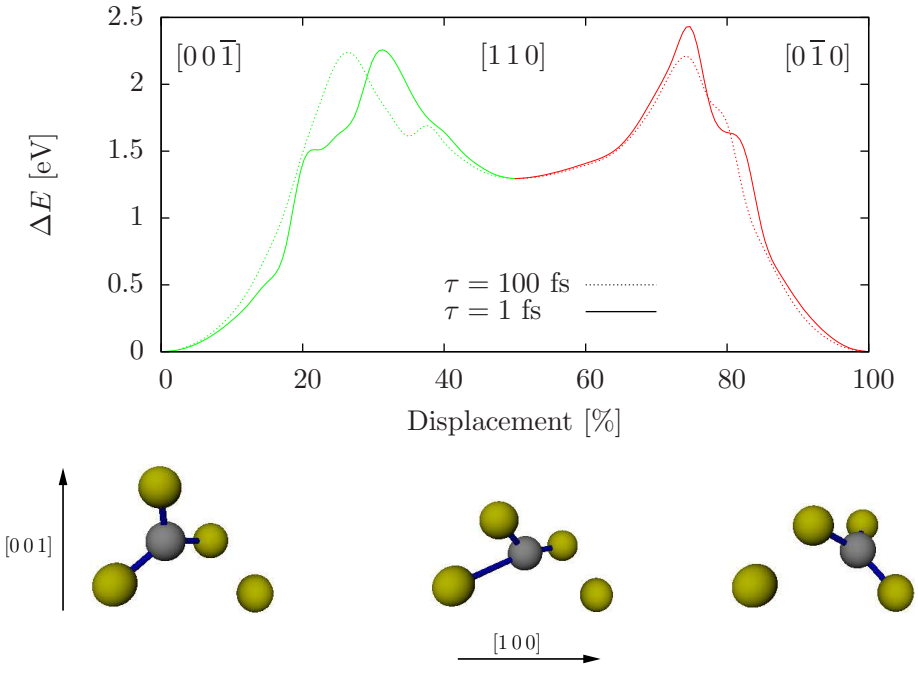
Note: Change in orientation



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

- Transition involving [1 1 0] DB (instability of BC configuration)
- $\Delta E \approx 2.2\,\text{eV}$ & $0.9\,\text{eV}$
- 2.4 – 3.4 times higher than ab initio result
- After all: Change of the DB orientation

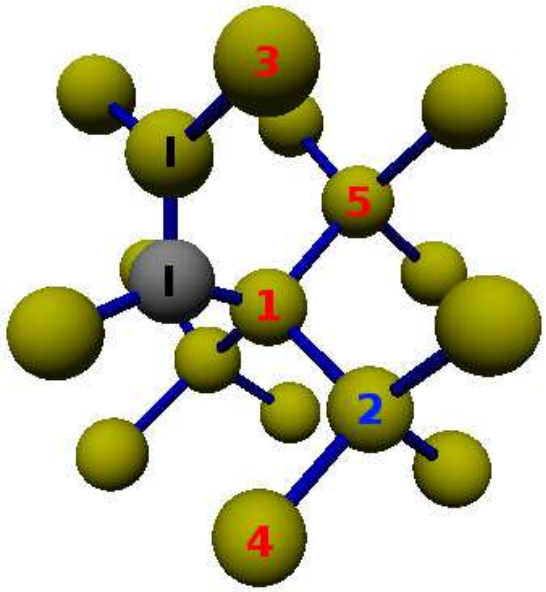
Drastically overestimated diffusion barrier



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

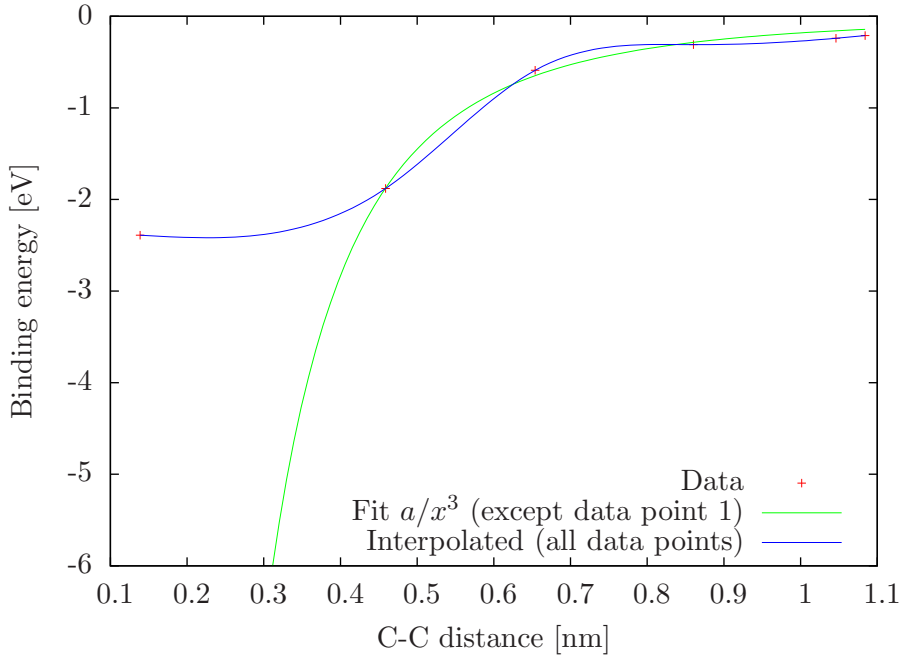


Combinations of ⟨1 0 0⟩-type interstitials

- C_i agglomeration energetically favorable
- Reduction of strain
- Capture radius exceeding 1 nm
- Disappearance of attractive forces between two lowest separations.

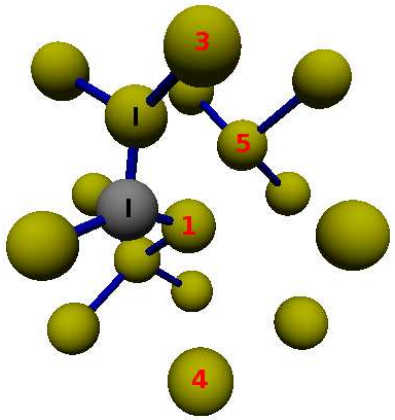
C_i agglomeration / no C clustering

Interaction along [1 1 0]

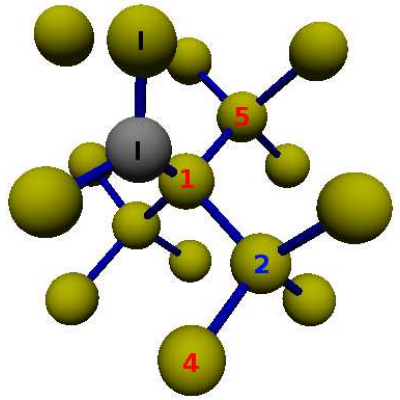


Defect combinations of C-Si dimers and vacancies

V at 2: $E_b = -0.59$ eV



V at 3, $E_b = -3.14$ eV



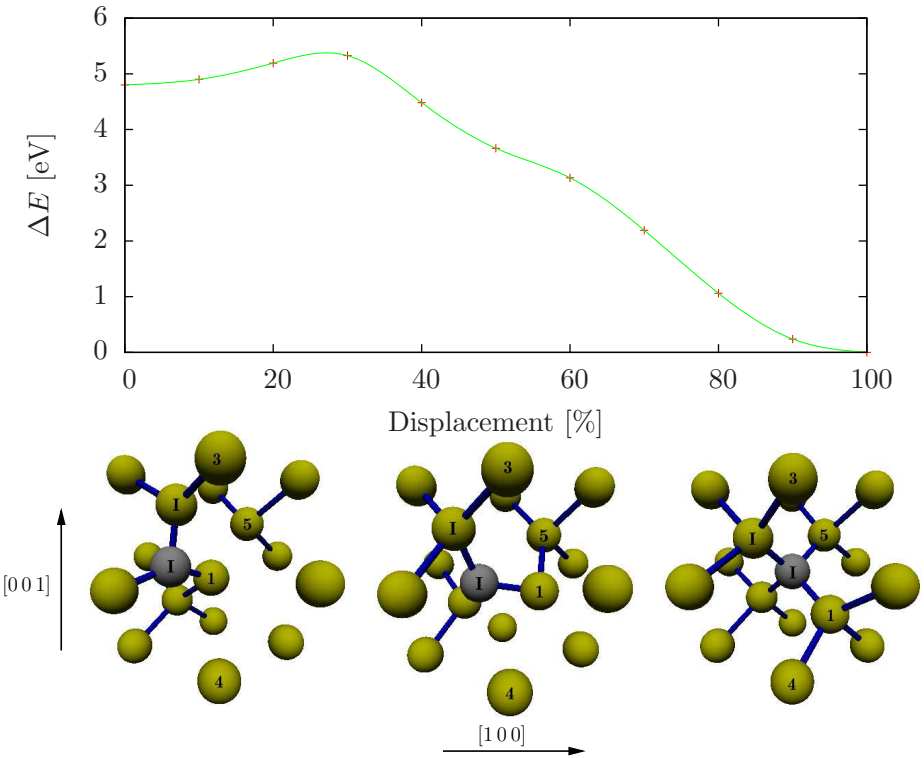
IBS: Impinging C creates V & far away Si_i

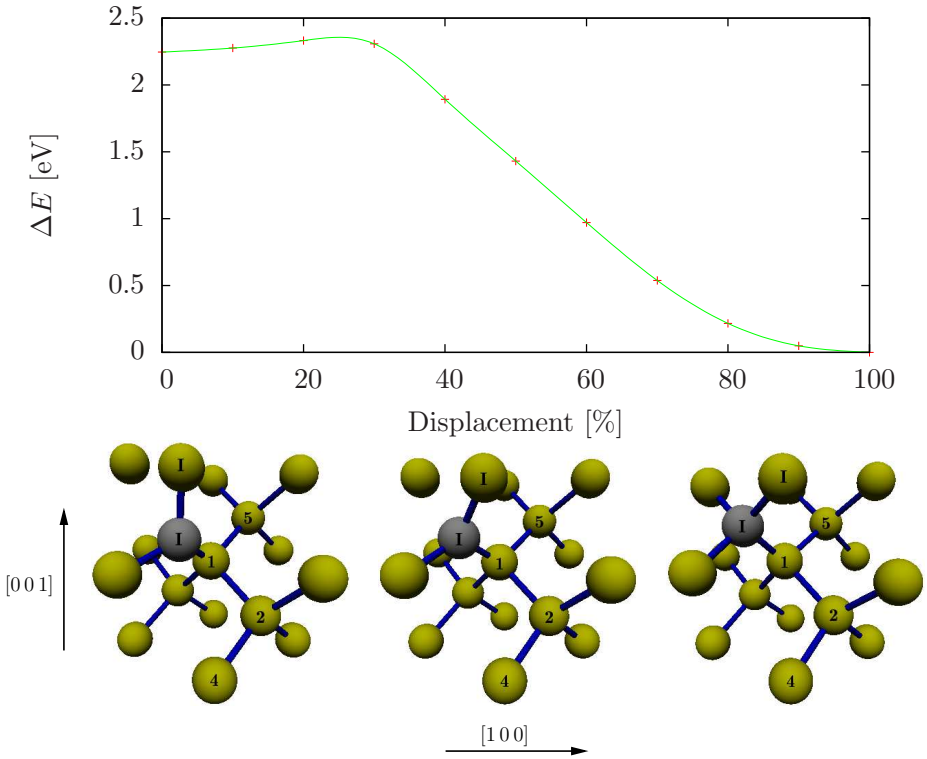
Low migration barrier towards C_{sub}

&

High barrier for reverse process

High probability of stable C_{sub} configuration

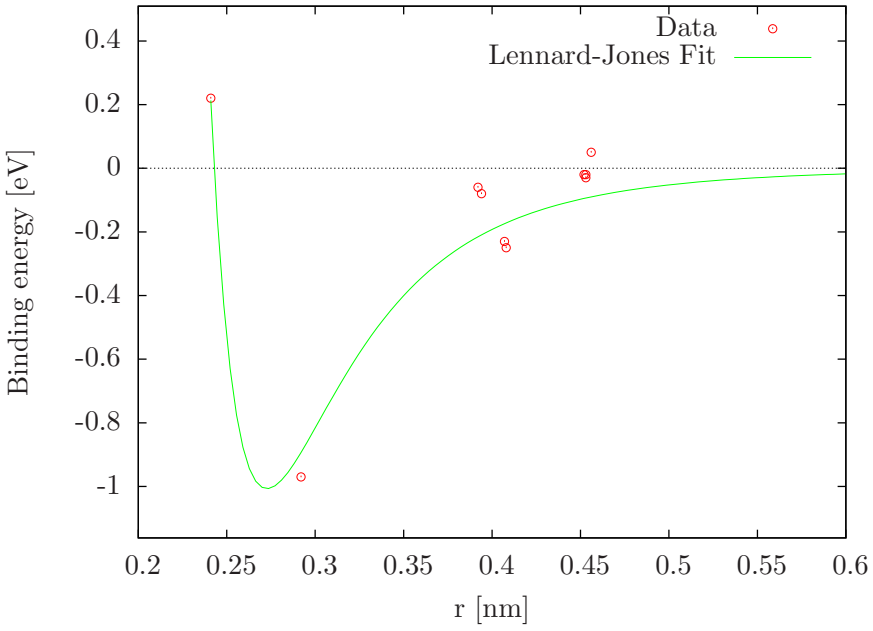




Combinations of substitutional C and Si self-interstitials

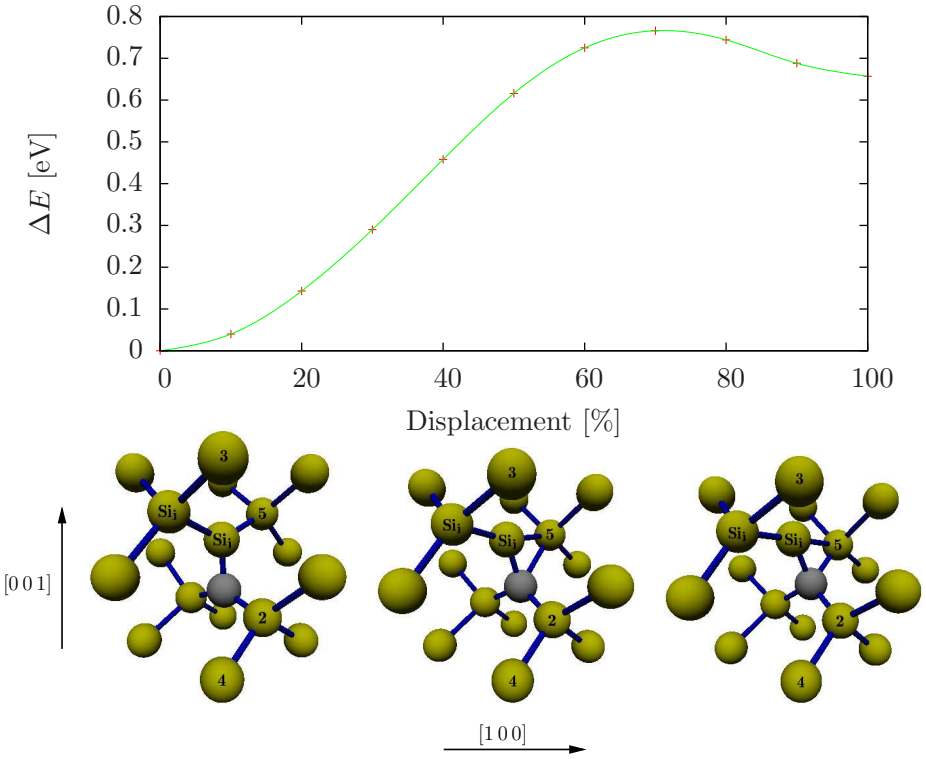
C_{sub} - Si_i $\langle 1\,1\,0\rangle$ interaction

- 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

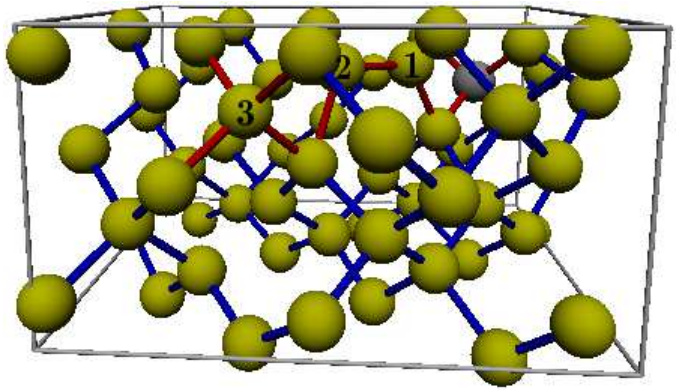
C_{sub} - Si_i $\langle 1\,1\,0\rangle$ interaction

- 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
- I

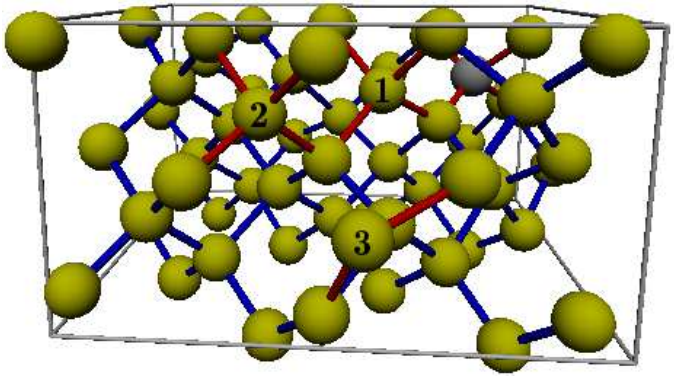
Transition from the ground state

- Low transition barrier
- Barrier smaller than C_i migration barrier

Ab initio MD at 900 °C

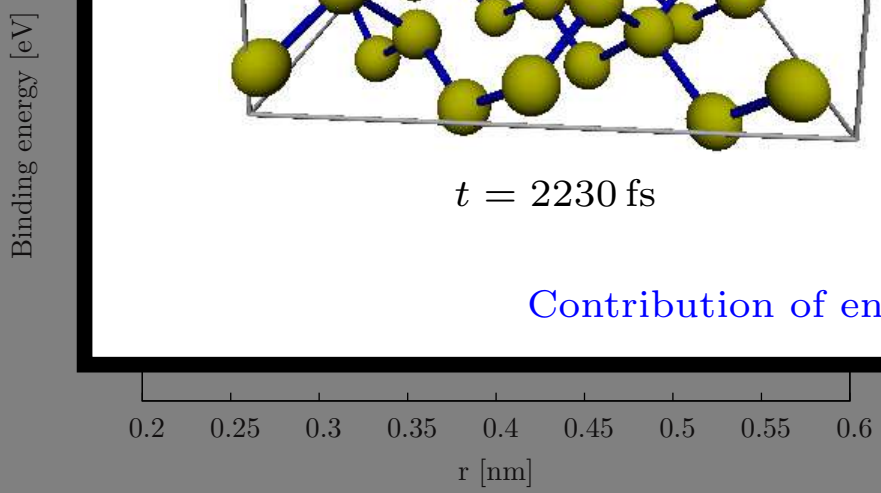


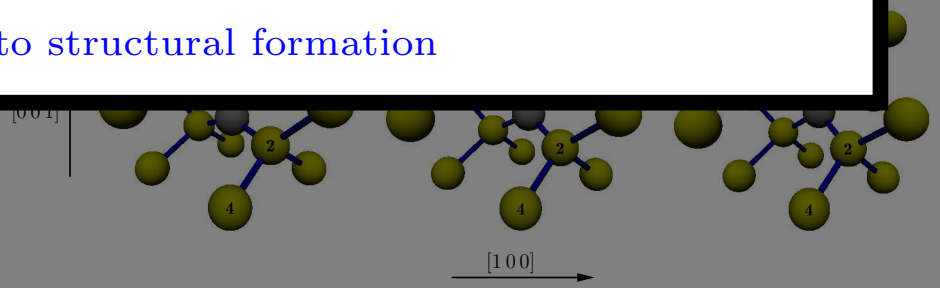
$t = 2230$ fs



$t = 2900$ fs

Contribution of entropy to structural formation





C_{sub} & Si_i instead of thermodynamic ground state

IBS — process far from equilibrium

Silicon carbide precipitation simulations

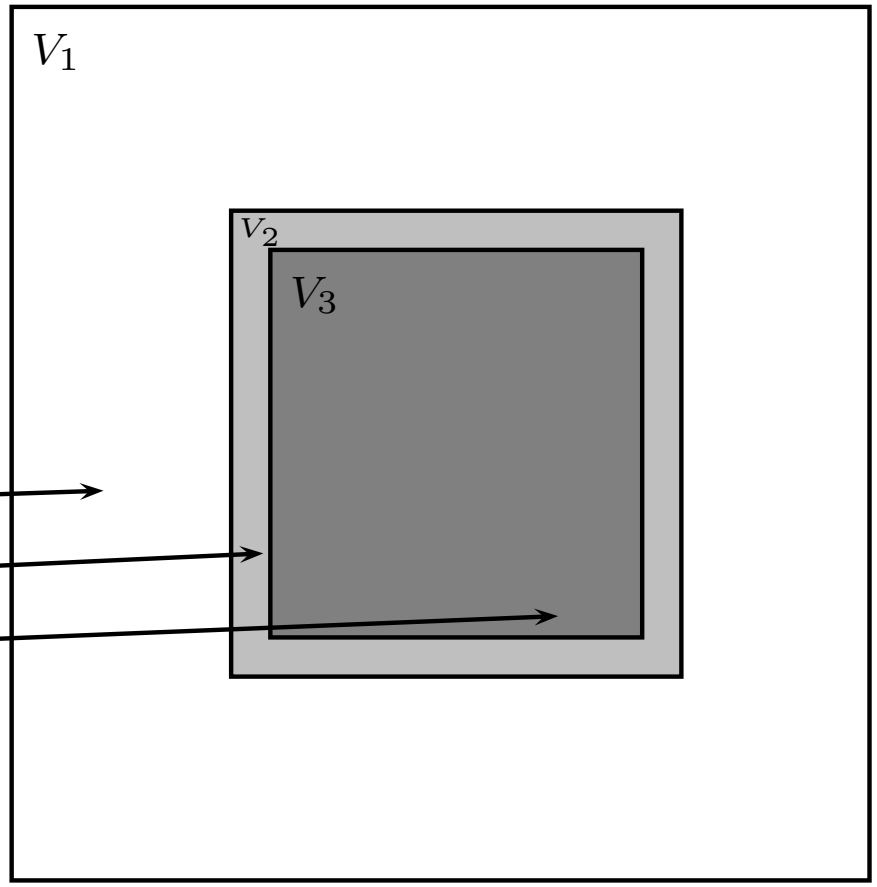
Procedure

- 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

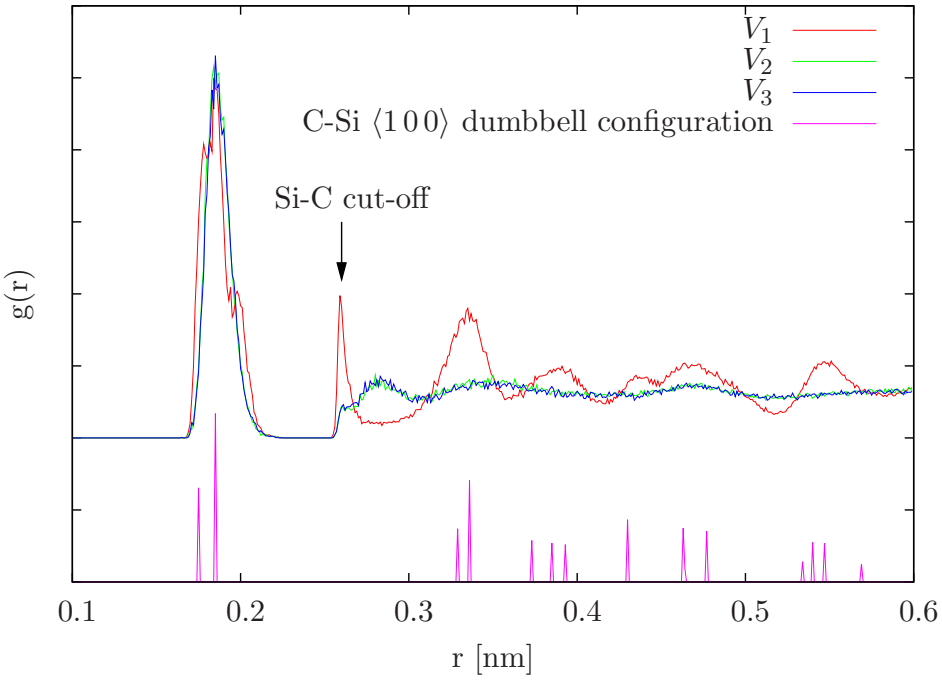


Note

- Amount of C atoms: 6000
  ($r_{\mathrm{prec}} \approx 3.1$ 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



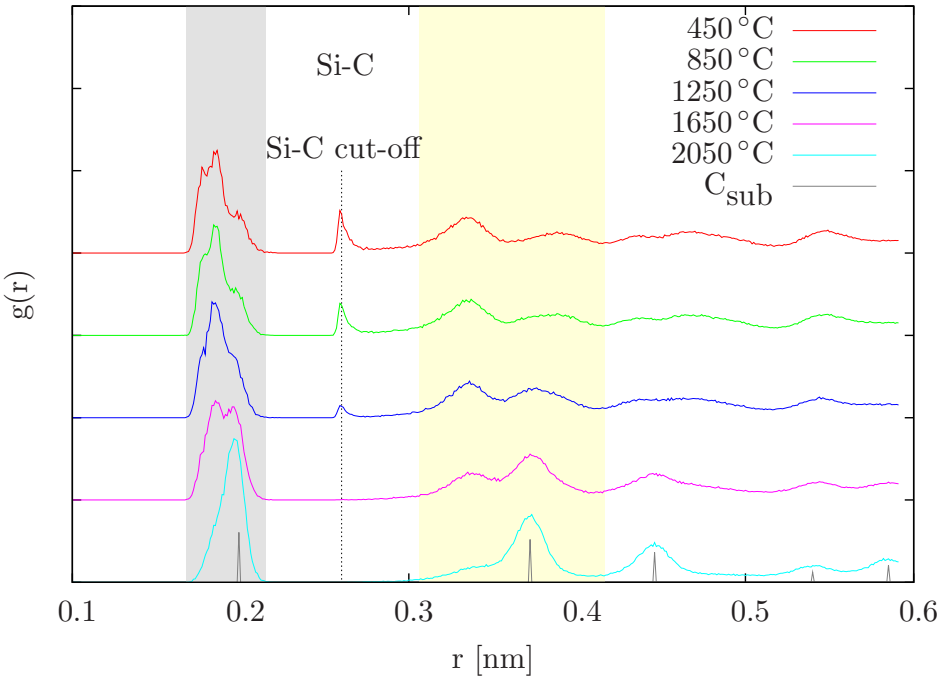
Temperature as used in IBS (450 °C)

C_i ⟨1 0 0⟩ dumbbell dominated structure

Formation of C_i DBs
No agllomeration / precipitation

Limitations:

- Time scale problem of MD
  ⇒ slow phase space propagation
- Short range potential
  ⇒ overestimated diffusion barrier



Increased temperatures

C_{sub} dominated structure

Si-C_{sub}-Si along ⟨1 1 0⟩
C_{sub}-Si-C_{sub} & nearby Si_i

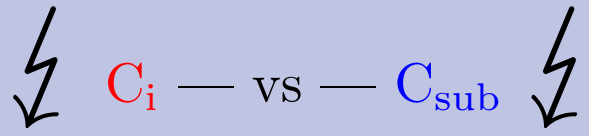
Conclusions:

- Stretched coherent SiC structures
  ⇒ C_{sub} involved in precipitation mechanism
- Reduction in strain by Si_i

Summary and Conclusions

Summary

- First-principles investigation of defect combinations and mobilities in Si
- Empirical potential MD simulations on SiC precipitation in Si

Conclusions on SiC precipitation  C_i — vs — C_{sub}

- C_{sub} involved in the precipitation mechanism
- Role of the Si_i
  - 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

Further conclusions

- High T $\leftrightarrow$ IBS conditions far from equilibrium

Acknowledgements

Thanks to ...

Augsburg

- Prof. B. Stritzker

Helsinki

- Prof. K. Nordlund

Munich

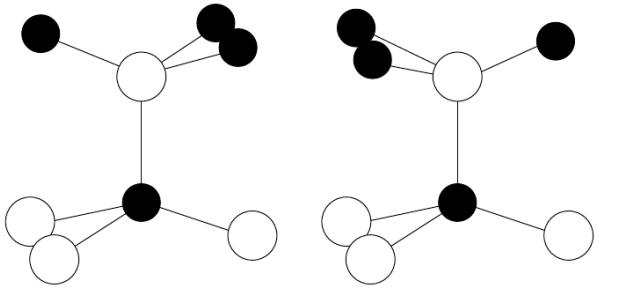
- Bayerische Forschungsstiftung

Paderborn

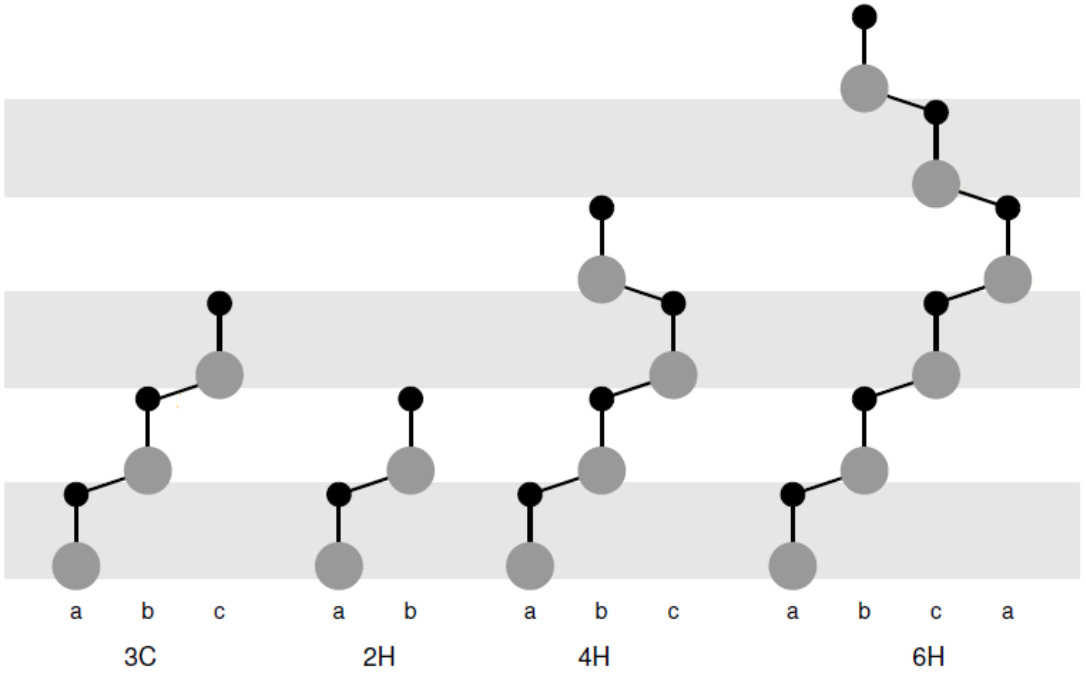
- Prof. J. Lindner
- Prof. G. Schmidt
- Dr. E. Rauls

Thank you for your attention!

Polytypes of SiC



cubic (twist) hexagonal (no twist)



	3C-SiC	4H-SiC	6H-SiC	Si	GaN	Diamond
Hardness [Mohs]		—— 9.6 ——		6.5	-	10
Band gap [eV]	2.36	3.23	3.03	1.12	3.39	5.5
Break down field [10^6 V/cm]	4	3	3.2	0.6	5	10
Saturation drift velocity [10^7 cm/s]	2.5	2.0	2.0	1	2.7	2.7
Electron mobility [cm^2/Vs]	800	900	400	1100	900	2200
Hole mobility [cm^2/Vs]	320	120	90	420	150	1600
Thermal conductivity [W/cmK]	5.0	4.9	4.9	1.5	1.3	22

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

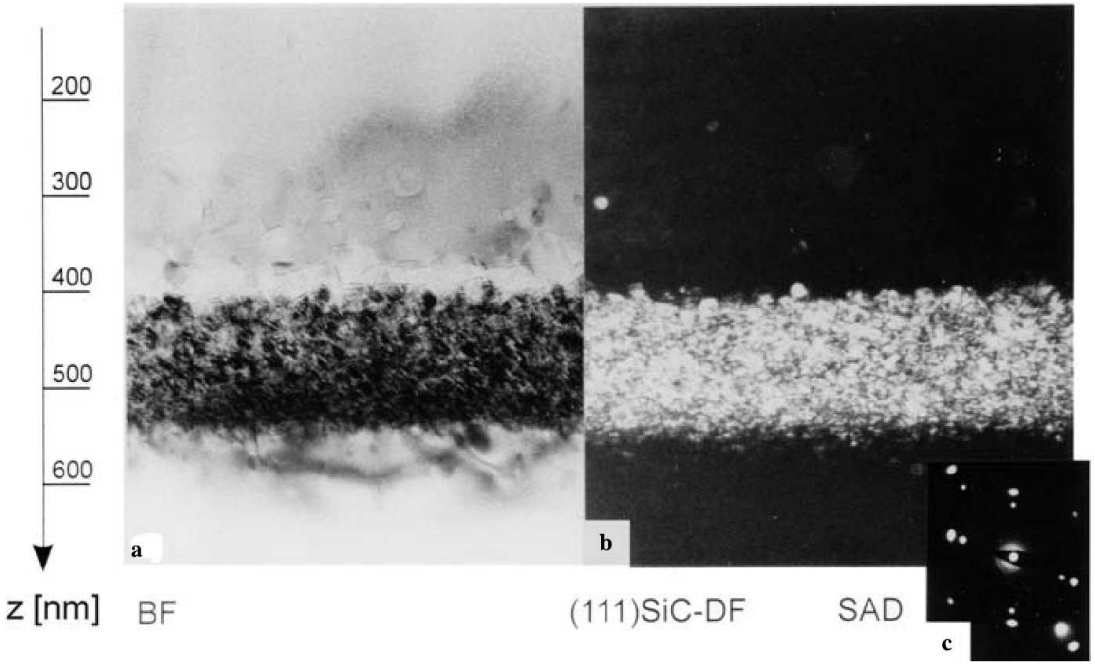
  Low remaining amount of dose | 180 keV | 250 °C

  ⇒ Destruction/Amorphization of precipitates at layer interface

- Annealing

  10 h at 1250 °C

  ⇒ Homogeneous 3C-SiC layer with sharp interfaces



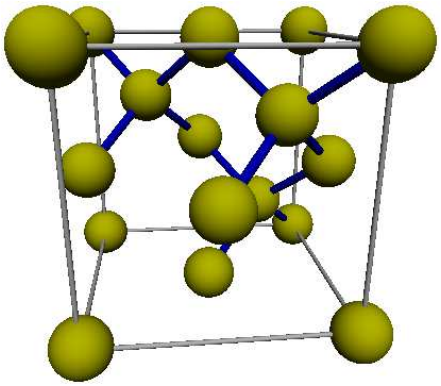
3C-SiC precipitation
not yet fully understood

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

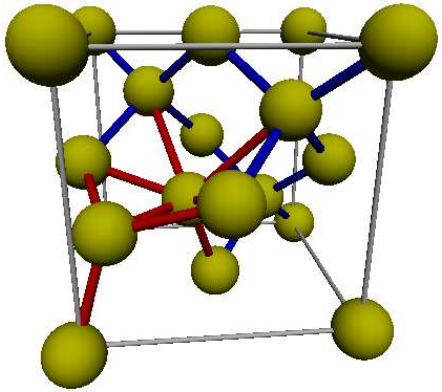
Si self-interstitial point defects in silicon

E_f [eV]	$\langle 1\,1\,0\rangle$ DB	H	T	$\langle 1\,0\,0\rangle$ DB	V
VASP	3.39	3.42	3.77	4.41	3.63
Erhart/Albe	4.39	4.48*	3.40	5.42	3.13

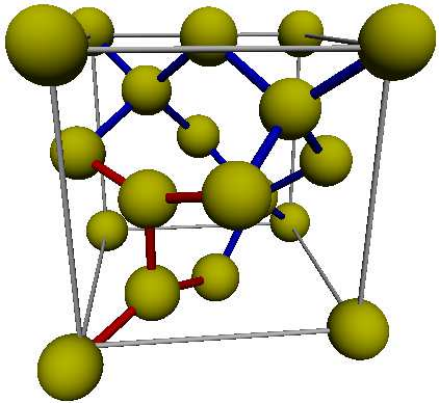
Vacancy



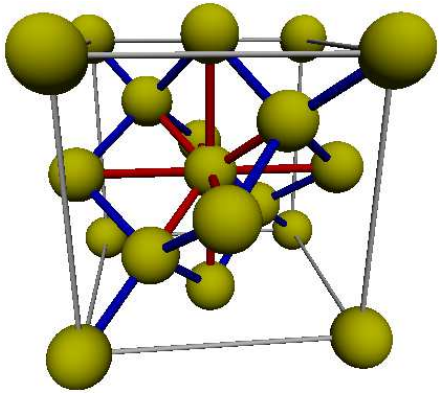
$\langle 1\,1\,0\rangle$ DB



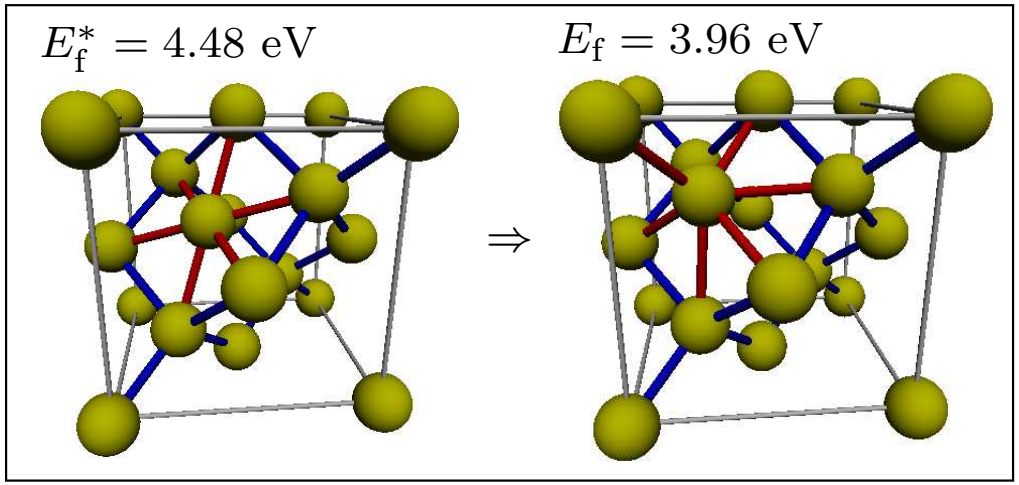
$\langle 1\,0\,0\rangle$ DB

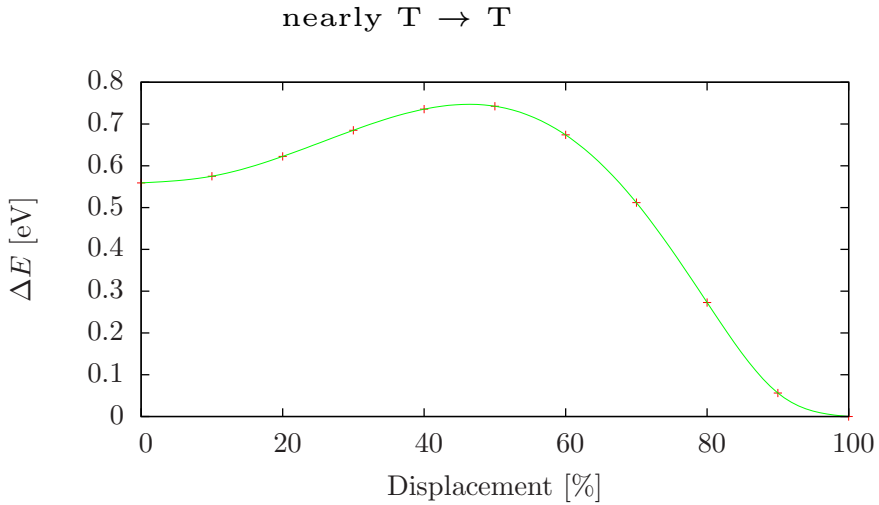


Tetrahedral



Hexagonal ▷

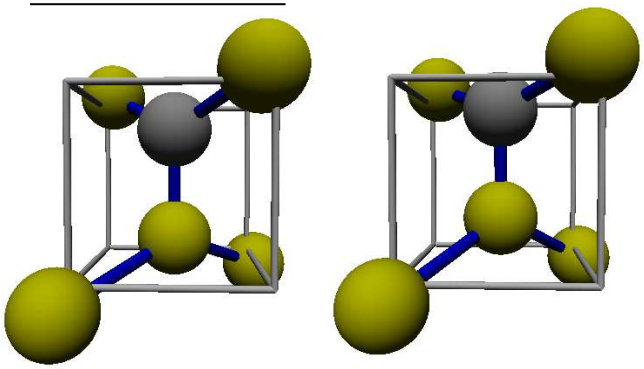




C-Si dimer & bond-centered interstitial configuration

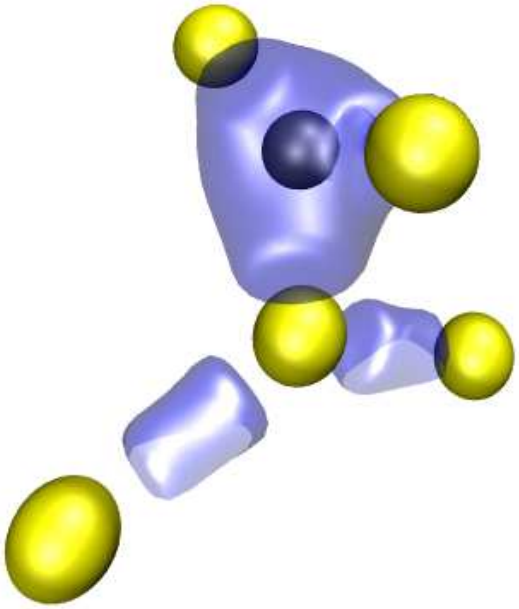
C ⟨1 0 0⟩ DB interstitial

Erhart/Albe VASP



Si-C-Si bond angle → 180 °
⇒ *sp* hybridization

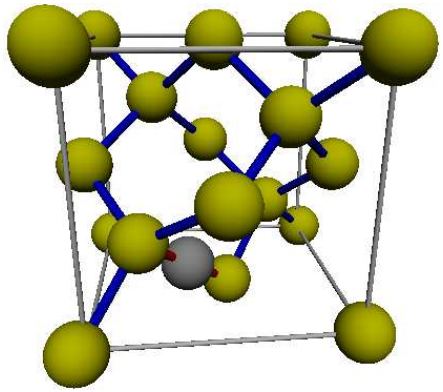
Si-Si-Si bond angle → 120 °
⇒ sp^2 hybridization

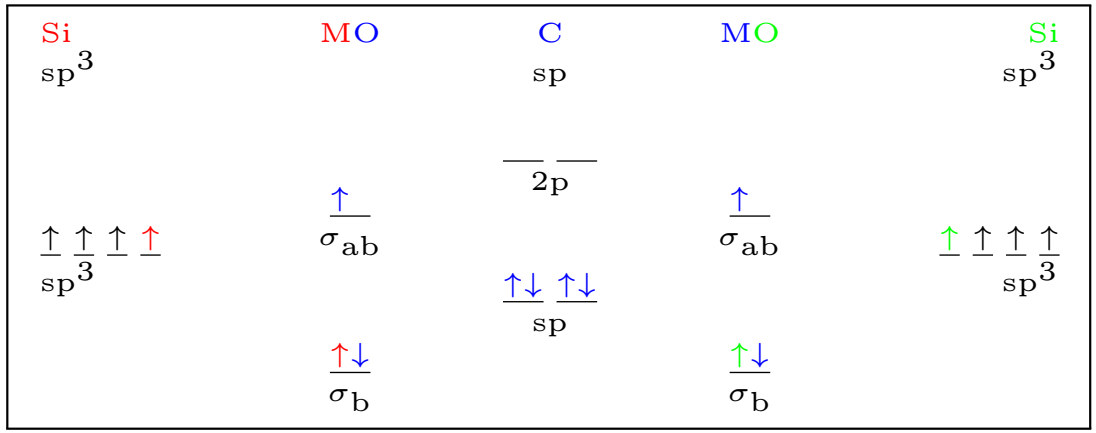


Charge density isosurface

Bond-centered interstitial

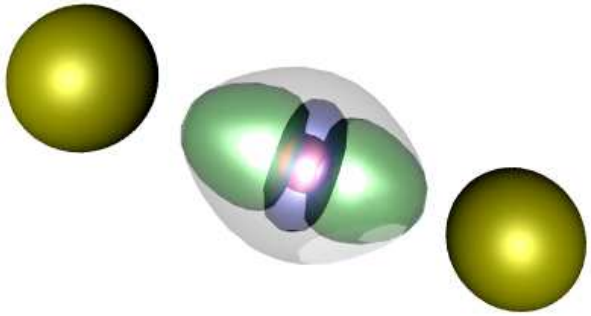
- Linear Si-C-Si bond
- Si: one C & 3 Si neighbours
- Spin polarized calculations
- No saddle point!
  Real local minimum!





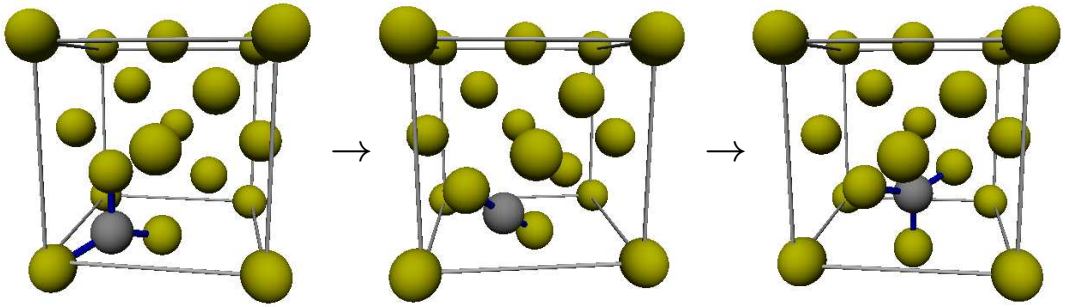
Charge density

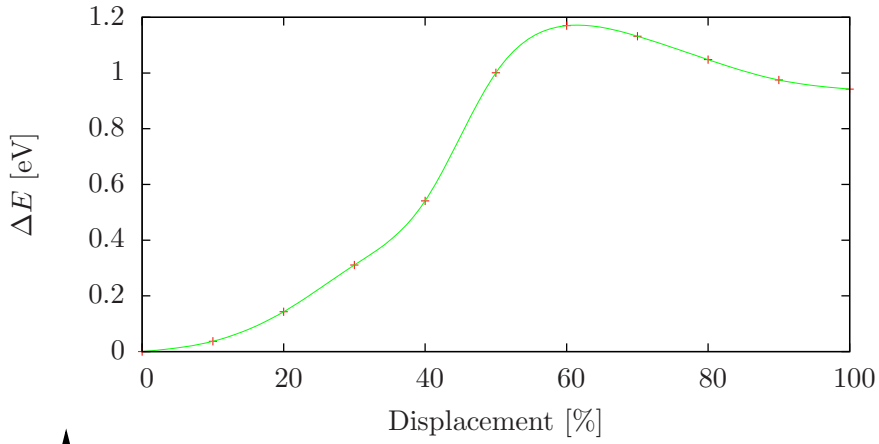
- Spin up
- Spin down
- Resulting spin up
- Si atoms
- C atom

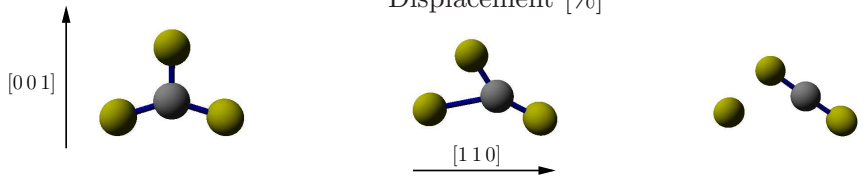


C interstitial migration — ab initio

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





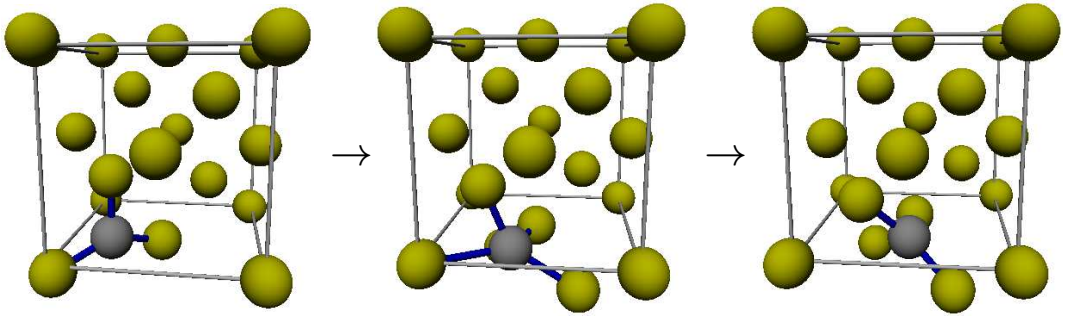


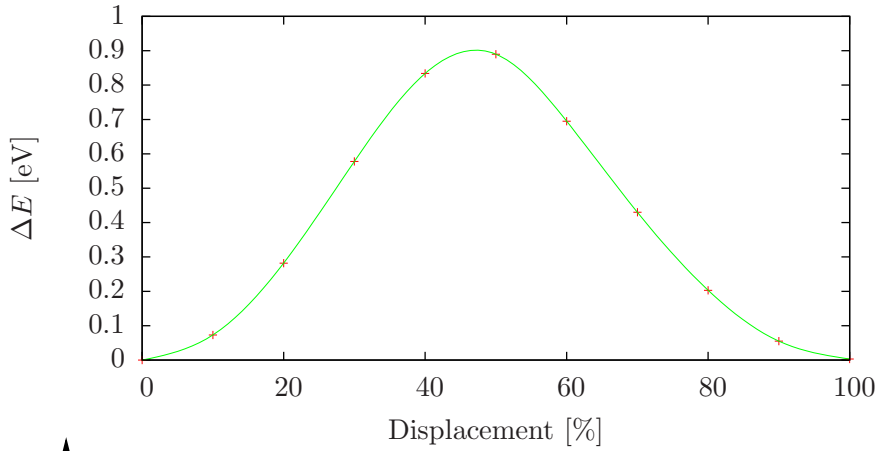
Symmetry:

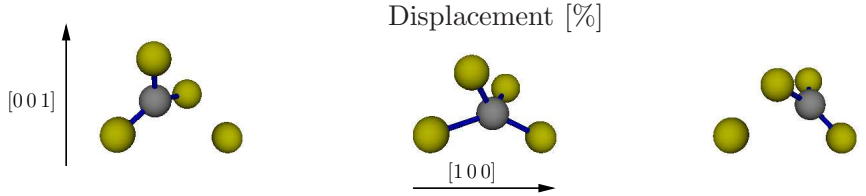
⇒ Sufficient to consider $[0\,0\,\bar{1}]$ to BC transition

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

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







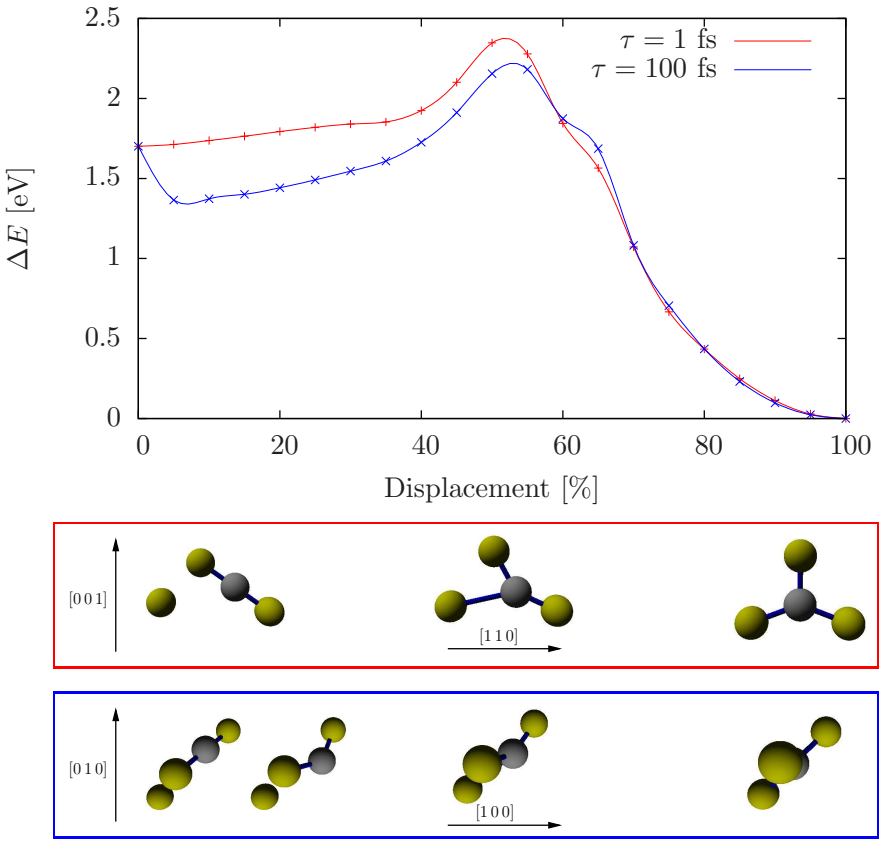
$\Delta E = 0.9\,\text{eV}$ | Experimental values: 0.70–0.87 eV

⇒ Migration mechanism identified!

Note: Change in orientation

C interstitial migration — analytical potential

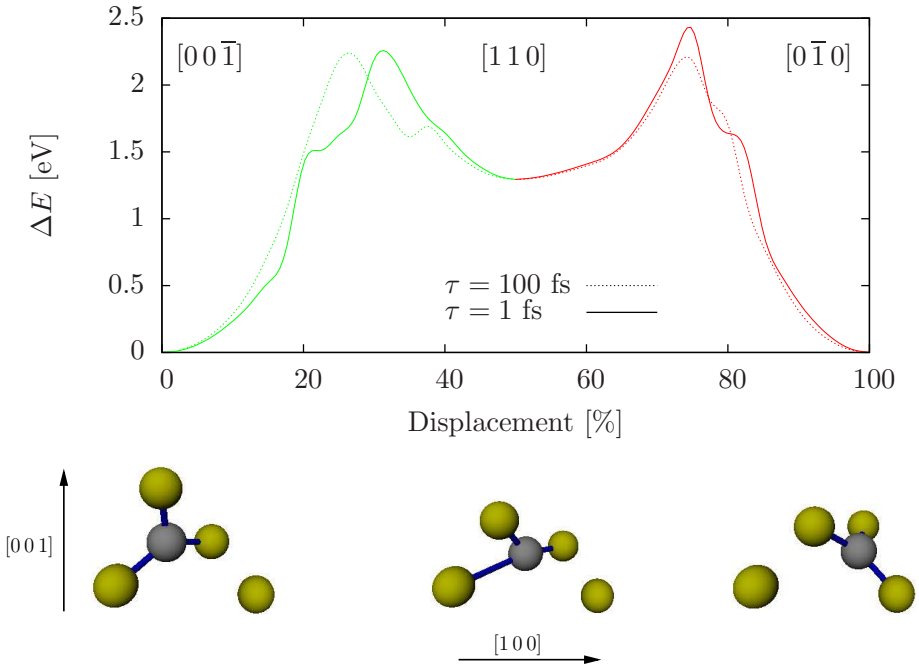
BC to $[0\,0\,\bar{1}]$ transition



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

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

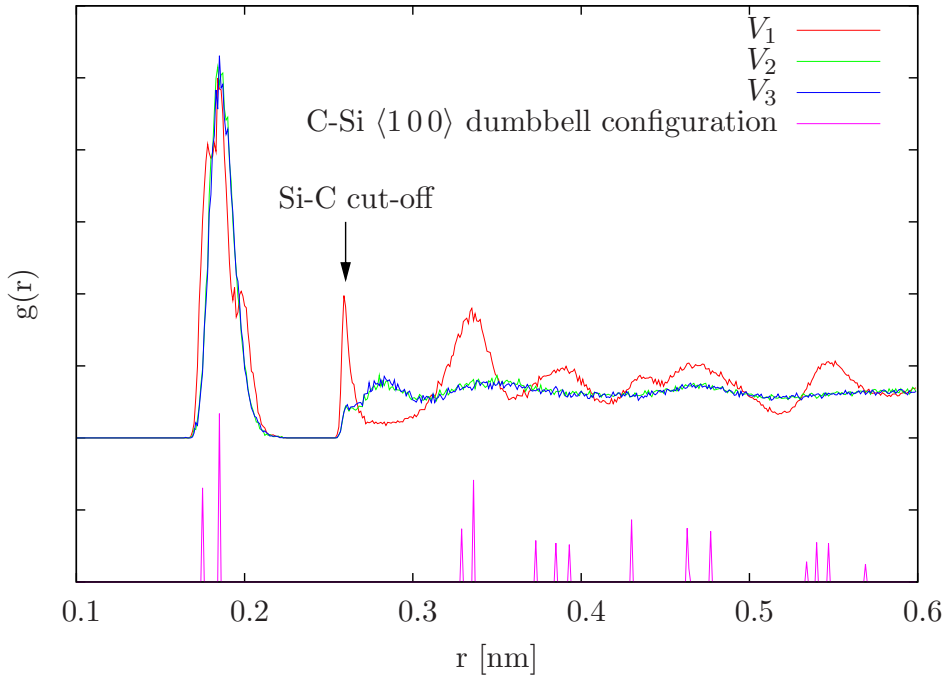
- Bond-centered configuration unstable
  $\rightarrow$ C_i $\langle 1\,1\,0 \rangle$ dumbbell
- Minimum of the $[0\,0\,\bar{1}]$ to $[0\,\bar{1}\,0]$ transition
  $\rightarrow$ C_i $\langle 1\,1\,0 \rangle$ DB

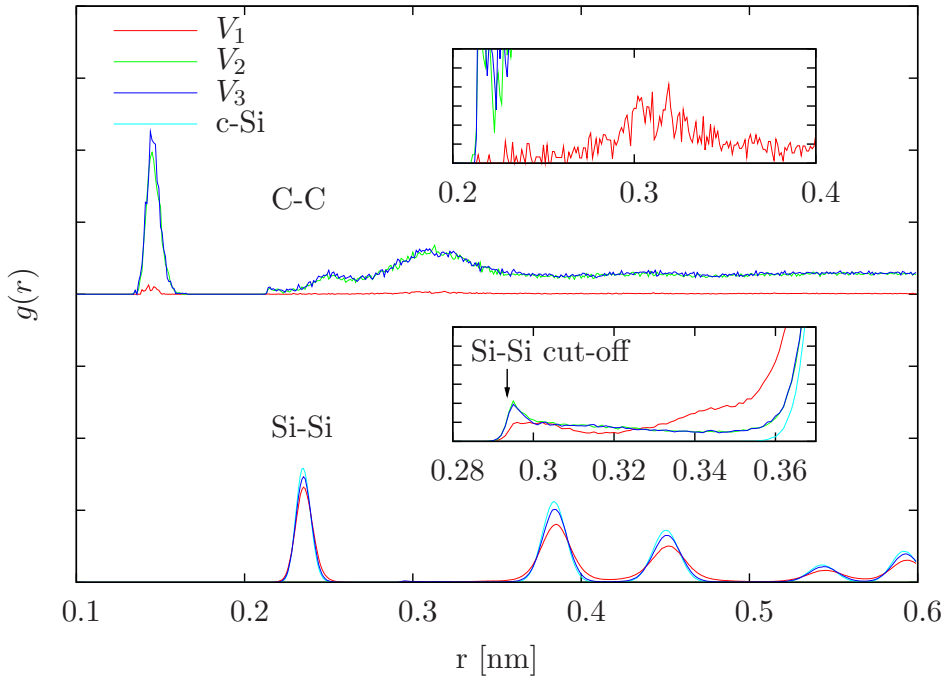


- $\Delta E \approx 2.2\,\mathrm{eV}$ & $0.9\,\mathrm{eV}$
- 2.4 – 3.4 times higher than ab initio result
- After all: Change of the DB orientation

Drastically overestimated diffusion barrier

Silicon carbide precipitation simulations at 450 °C as in IBS





Low C concentration — V_1

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

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

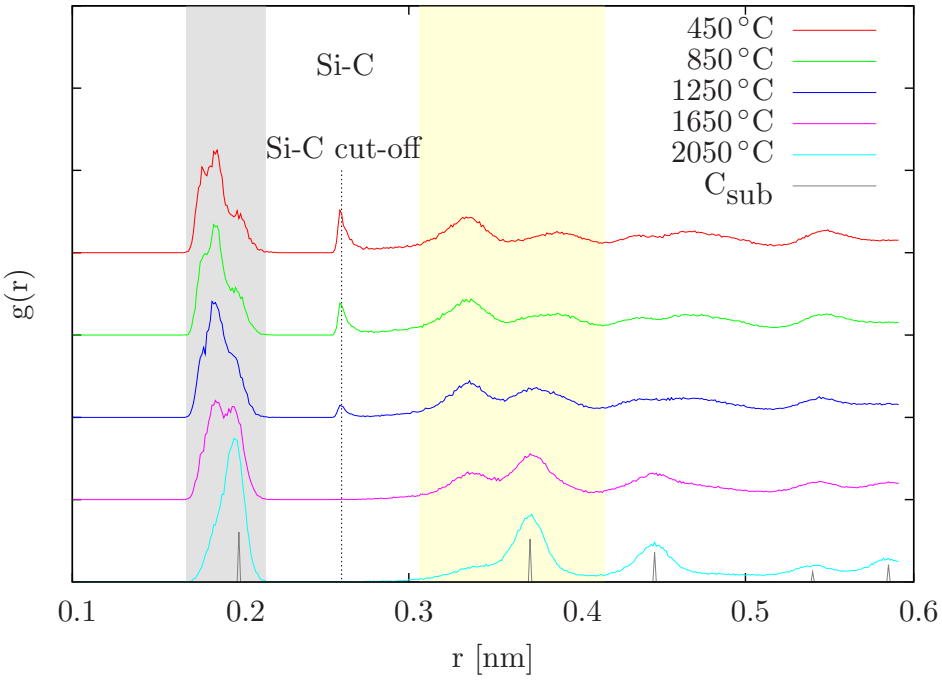
Amorphous SiC-like phase

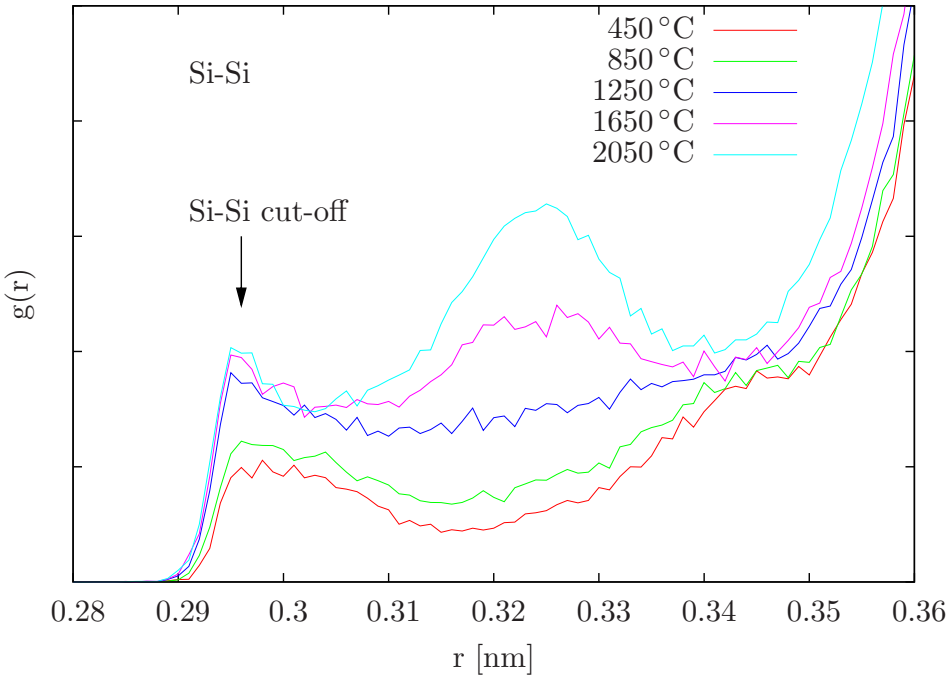
Formation of 3C-SiC fails to appear

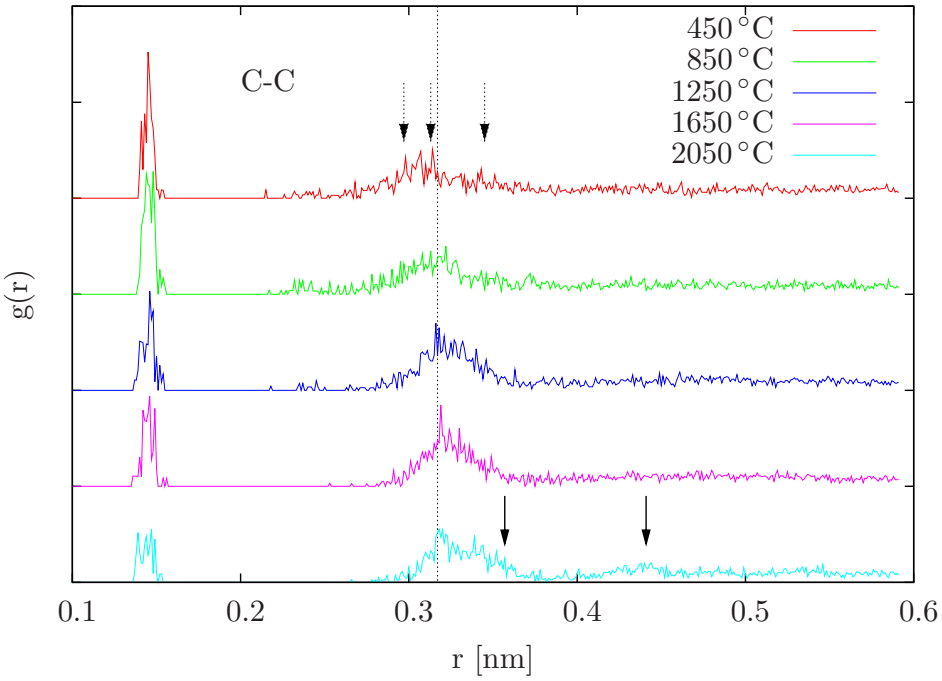
V_1: Formation of C_i indeed occurs
Agglomeration not observed

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

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)

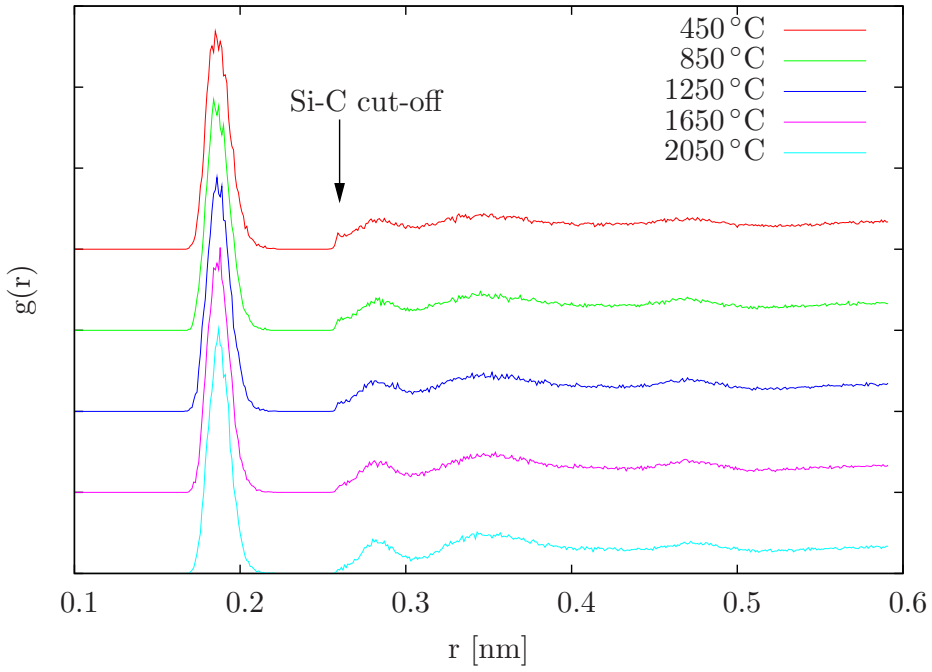
C-C bonds:

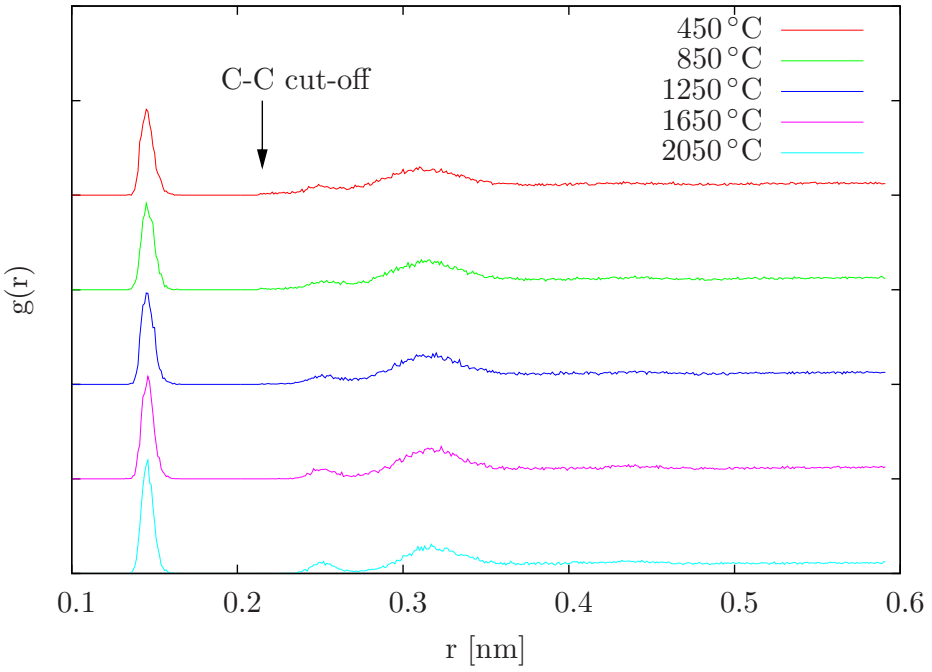
- C-C next neighbour pairs reduced (mandatory)
- Peak at 0.3 nm slightly shifted

  ↘ 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 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

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

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

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

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

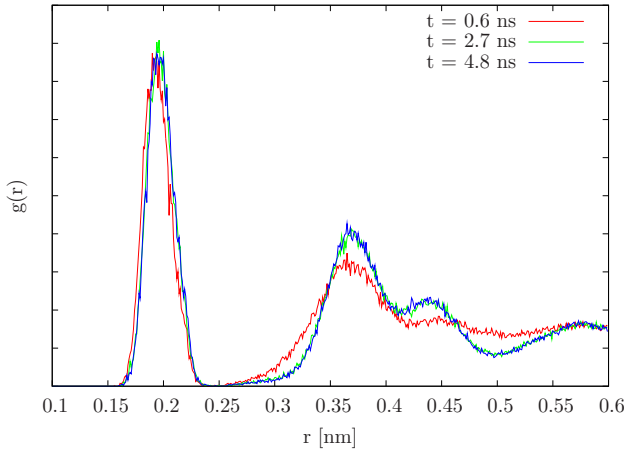
High C & small V & short t ⇒ Slow structural evolution due to strong C-C bonds ⇐ High C & low T implants

Long time scale simulations at maximum temperature

Differences

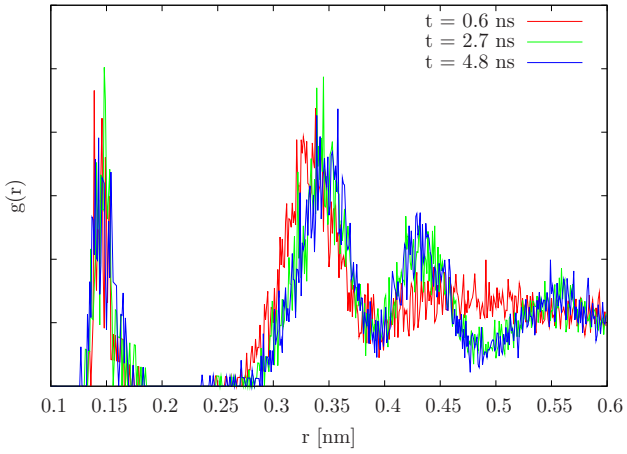
- Temperature set to $0.95 \cdot T_{\mathrm{m}}$
- Cubic insertion volume $\Rightarrow$ spherical insertion volume
- Amount of C atoms: $6000 \rightarrow 5500 \Leftrightarrow r_{\mathrm{prec}} = 0.3$ nm
- Simulation volume: 21 unit cells of c-Si in each direction

Low C concentration, Si-C



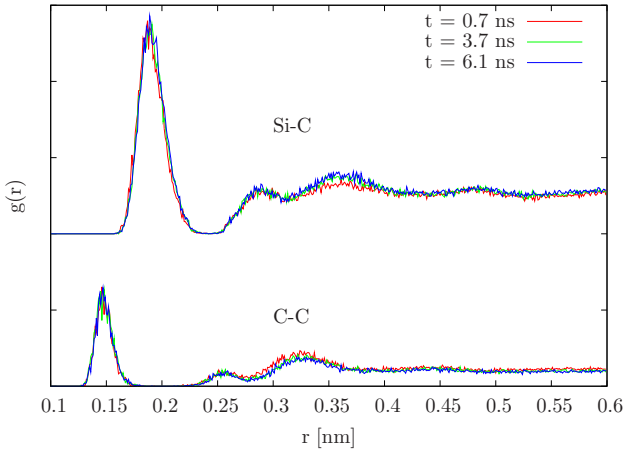
Sharper peaks!

Low C concentration, C-C



Sharper peaks!
No C agglomeration!

High C concentration



No significant changes
iC-Si-Si ↑
C-Si-C ↓

Long time scales and high temperatures most probably not sufficient enough!

Investigation of a silicon carbide precipitate in silicon

$$\frac{8}{a_{\mathrm{Si}}^3}(\underbrace{21^3 a_{\mathrm{Si}}^3}_{=V} - \frac{4}{3}\pi x^3) + \underbrace{\frac{4}{y^3}\frac{4}{3}\pi x^3}_{\stackrel{!}{=}5500} = 21^3 \cdot 8$$

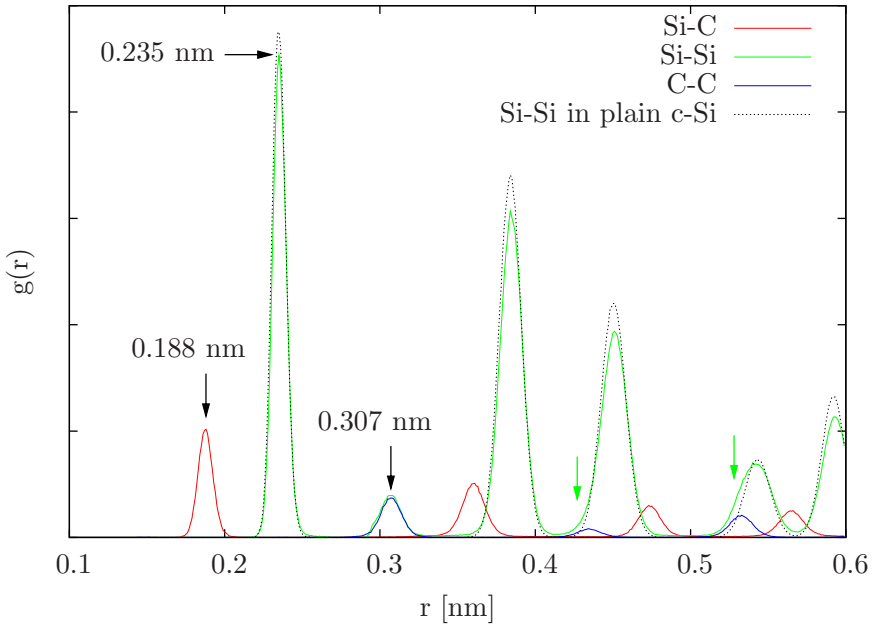
$$\Downarrow$$

$$\frac{8}{a_{\mathrm{Si}}^3}\frac{4}{3}\pi x^3 = 5500 \Rightarrow x = \left(\frac{5500 \cdot 3}{32\pi}\right)^{1/3} a_{\mathrm{Si}}$$

$$y = \left(\frac{1}{2}\right)^{1/3} a_{\mathrm{Si}}$$

<u>Construction</u>

- Simulation volume: 21^3 unit cells of c-Si
- Spherical topotactically aligned precipitate $r = 3.0$ nm $\Leftrightarrow \approx 5500$ C atoms
- Create c-Si but skipped inside sphere of radius x
- Create 3C-SiC inside sphere of radius x and lattice constant y
- Strong coupling to heat bath ($T = 20\,^{\circ}\mathrm{C}$)



<u>Results</u>

- Slight increase of c-Si lattice constant!
- C-C peaks
  (imply same distanced Si-Si peaks)
  - New peak at 0.307 nm: 2^{nd} NN in 3C-SiC
  - Bumps (↓): 4^{th} and 6^{th} NN
- 3C-SiC lattice constant: 4.34 Å(bulk: 4.36 Å)
  $\rightarrow$ compressed precipitate
- Interface tension:
  20.15 eV/nm^2 or 3.23×10^{-4} J/cm^2
  (literature: $2 - 8 \times 10^{-4}$ J/cm^2)

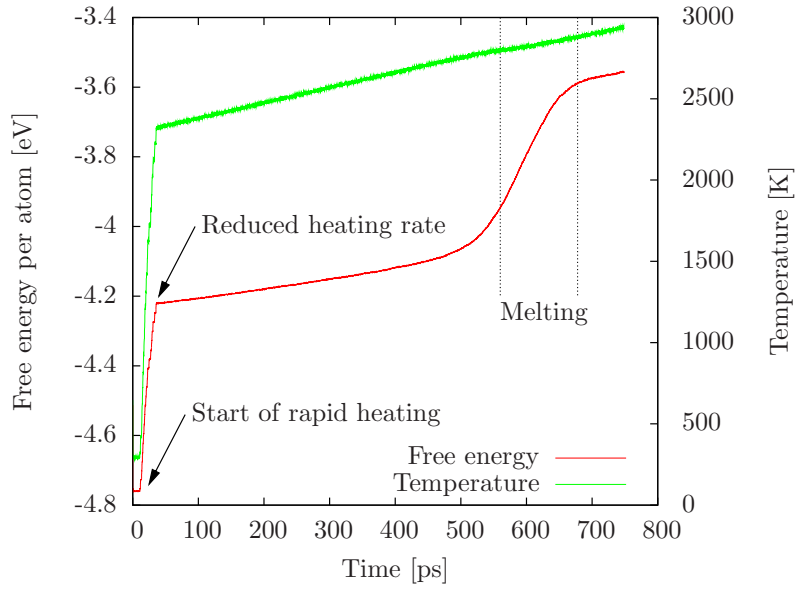
Investigation of a silicon carbide precipitate in silicon

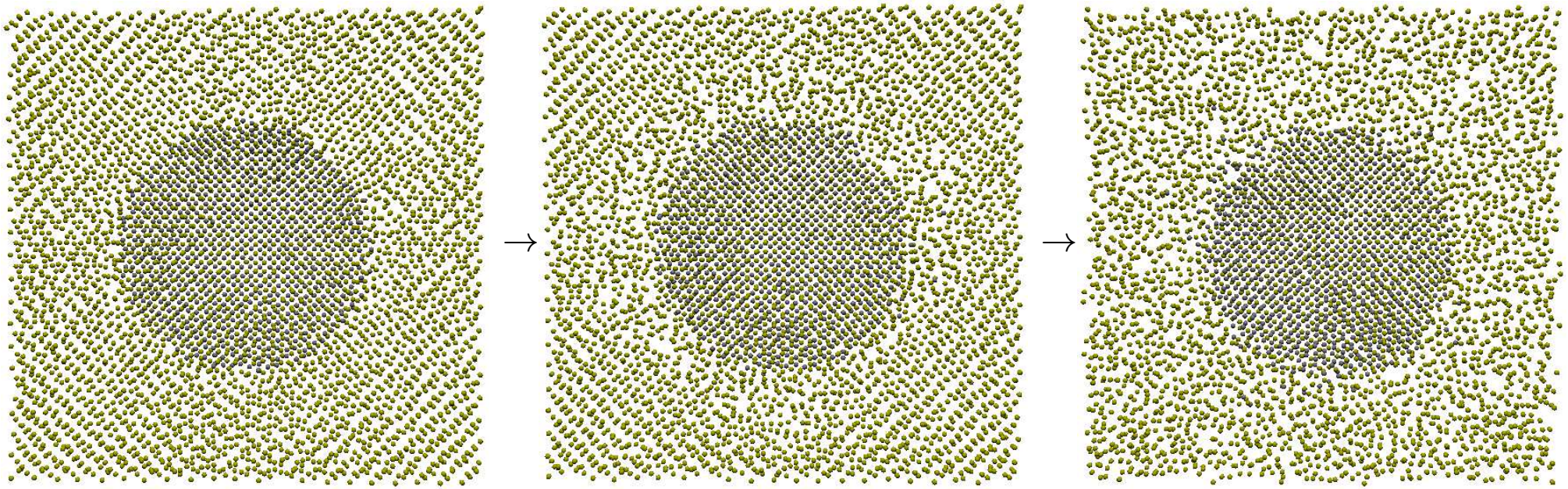
Appended annealing steps

- artificially constructed interface
  → allow for rearrangement of interface atoms
- check SiC stability

Temperature schedule

- rapidly heat up structure up to 2050 °C
  (75 K/ps)
- slow heating up to $1.2 \cdot T_\mathrm{m} = 2940$ K by 1 K/ps
  → melting at around 2840 K (▷)
- cooling down structure at 100 % T_m (1 K/ps)
  → no energetically more favorable struture





DFT parameters

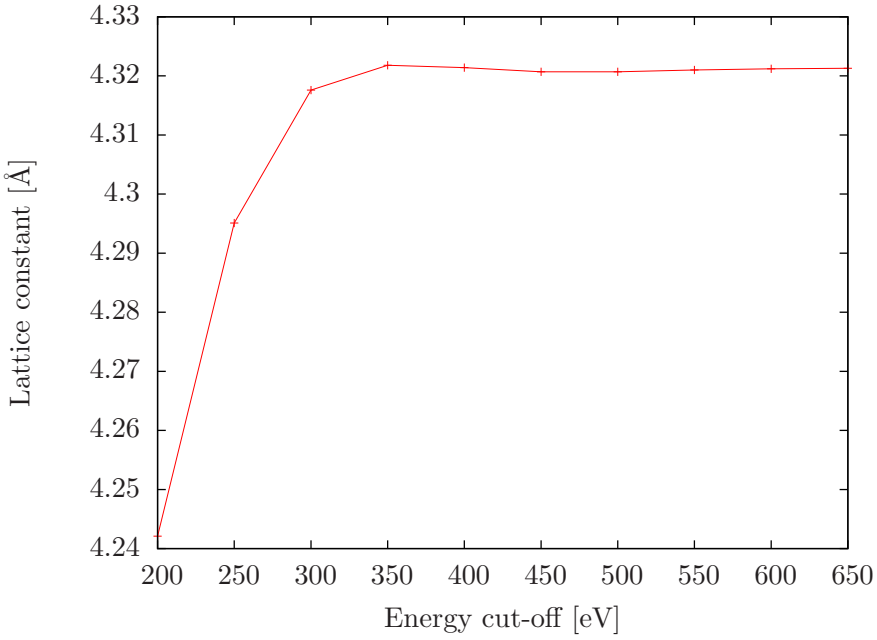
Equilibrium lattice constants and cohesive energies

		USPP, LDA	USPP, GGA	PAW, LDA	PAW, GGA	Exp.
Si (dia)	a [Å]	5.389	5.455	-	-	5.429
	Δ_a [%]	0.7 %	0.5 %	-	-	-
	E_{coh} [eV]	-5.277	-4.591	-	-	-4.63
	Δ_E [%]	14.0 %	0.8 %	-	-	-
C (dia)	a [Å]	3.527	3.567	-	-	3.567
	Δ_a [%]	1.1 %	0.01 %	-	-	-
	E_{coh} [eV]	-8.812	-7.703	-	-	-7.374
	Δ_E [%]	19.5 %	4.5 %	-	-	-
3C-SiC	a [Å]	4.319	4.370	4.330	4.379	4.359
	Δ_a [%]	0.9 %	0.3 %	0.7 %	0.5 %	-
	E_{coh} [eV]	-7.318	-6.426	-7.371	-6.491	-6.340
	Δ_E [%]	15.4 %	1.4 %	16.3 %	2.4 %	-

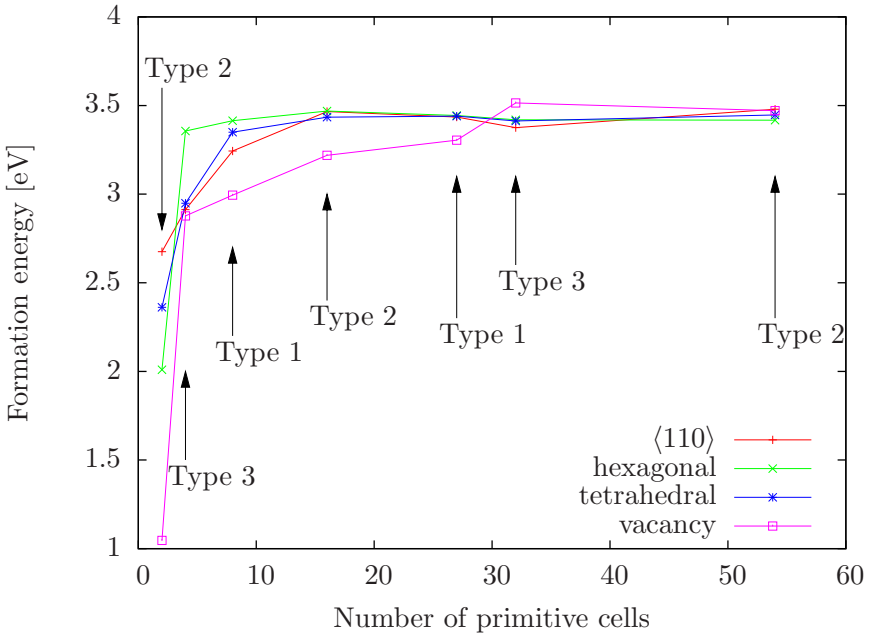
	Si (dia)	C (dia)	3C-SiC
a [Å]	5.458	3.562	4.365
Δ_a [%]	0.5	0.1	0.1
E_{coh} [eV]	-4.577	-7.695	-6.419
Δ_E [%]	1.1	4.4	1.2

← entire parameter set

DFT parameters



Lattice constants with respect to the PW cut-off energy



Defect formation energy with respect to the size of the supercell