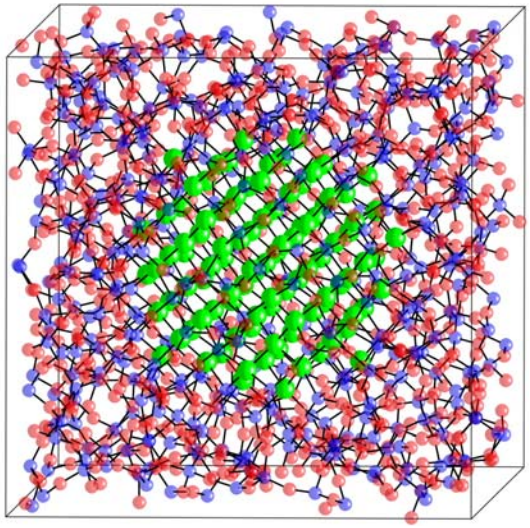
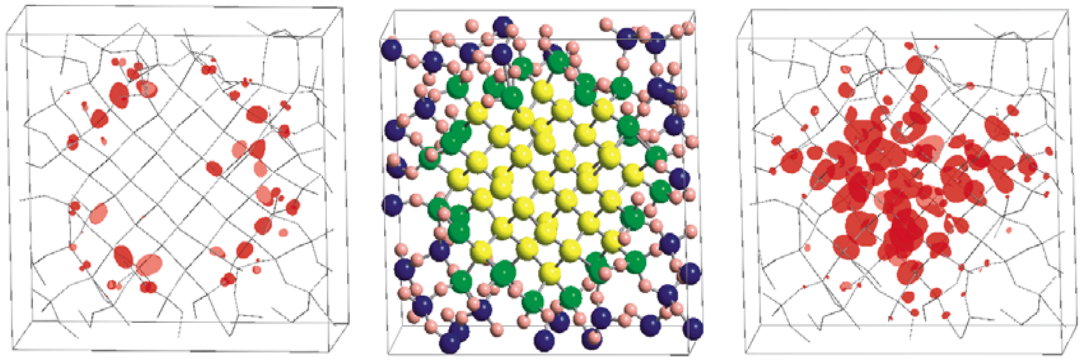


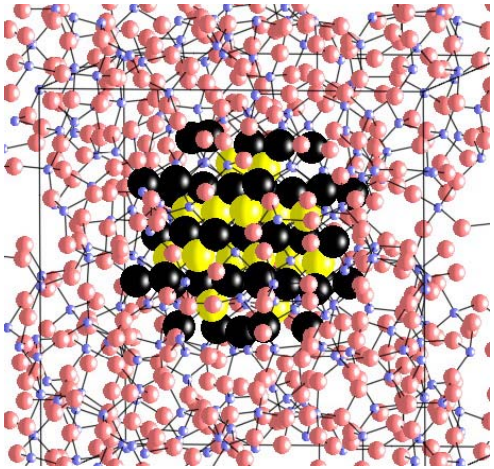
Si embedded in silica



"in-silico" computation of embedded nano-crystals

Peter Kroll
Chemistry & Biochemistry
UT Arlington, Texas, USA

Computer ressources:
FZ Jülich
TACC, UT Austin



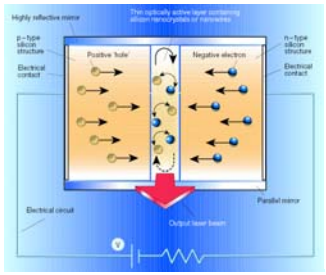
SiC embedded in silica

HiPCAT, Arlington, February 2008

nanocrystalline Si embedded in a-SiO_2

- growth of Si-clusters in Si-rich SiO_2

Nesbit, Appl. Phys. Lett. **1985**

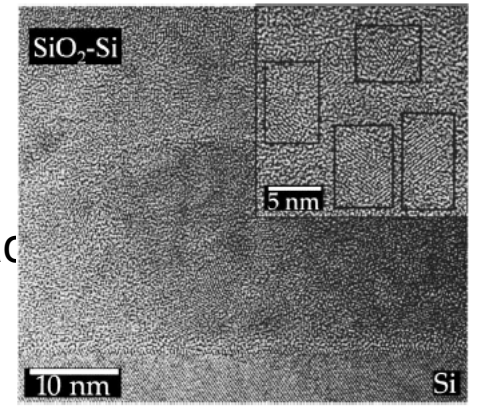


- silicon-based optoelectronics

Pavesi et al., Nature **2000**

Experiments:

- diameter of Si-clusters ≈ 2-5 nm
- much unknown about the Si/SiO_2 interfac
- trapped states (H, N, O) ?



Torrison et al., J. Appl. Phys. **2002**

What causes emission / absorption ? How to improve ?

Goal:

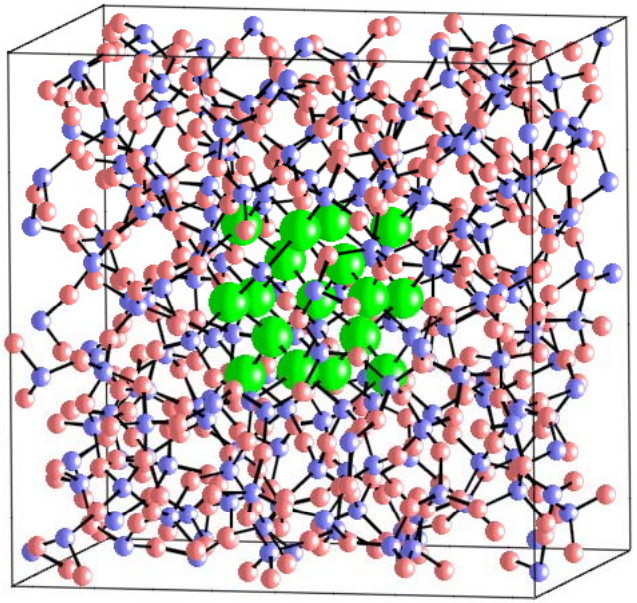
- create realistic models & calculate properties
- develop an understanding of the Si/SiO_2 interface & origin of absorption

computational approach

1. model generation

- 216 Si atoms (3x3x3 conventional unit cell)
  now out of 512 (4x4x4)
- define core atoms = nanocluster, radius r
- for all non-core Si: insert O into Si-Si bonds
  - Si in cristobalite SiO_2
- randomize the SiO_2 region, keep core intact

$\Rightarrow$ create a glass embedding the nc-Si

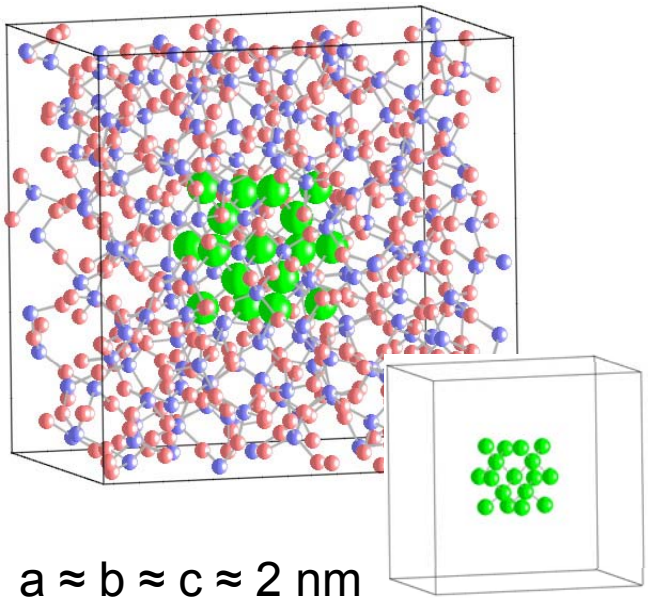


2. computation (VASP, LDA/GGA)

models with d ≈ 0.8 - 1.6 nm

- structure optimization (~300 cpu·h for 500 atoms, ~5000 cpu·h for 1500 atoms
- energy, density of states, optical properties

optimized $Si@SiO_2$ structures



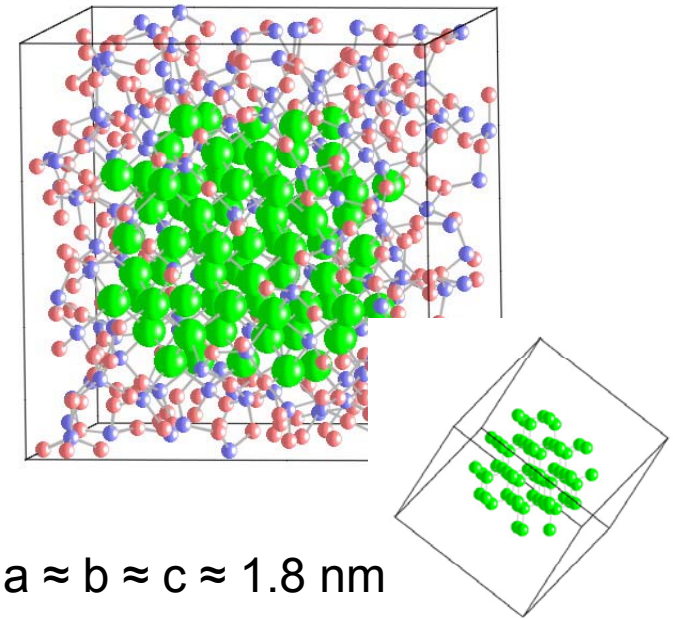
a ≈ b ≈ c ≈ 2 nm

d ≈ 0.8 nm

596 atoms

26 Si + 190 SiO_2

Core: 1+4+12 = 17 Si



a ≈ b ≈ c ≈ 1.8 nm

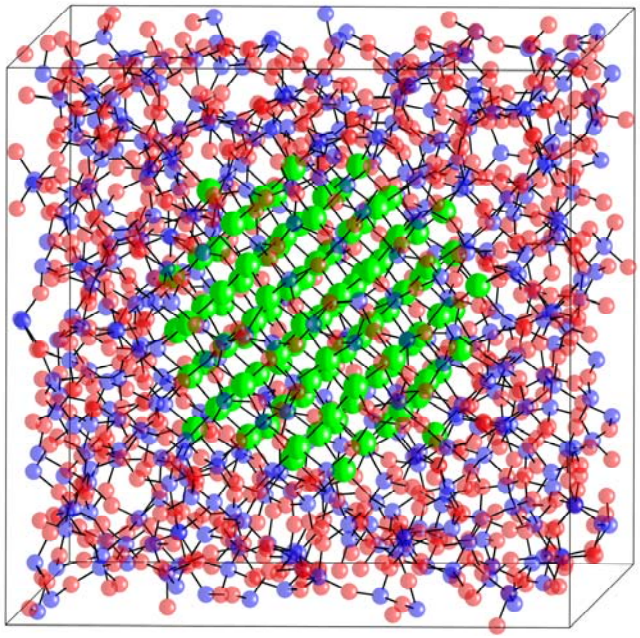
d ≈ 1.4 nm

464 atoms

92 Si + 124 SiO_2

Core: 1+4+12+12+6+12+24 = 71 Si

optimized $Si@SiO_2$ structures & quantum confi



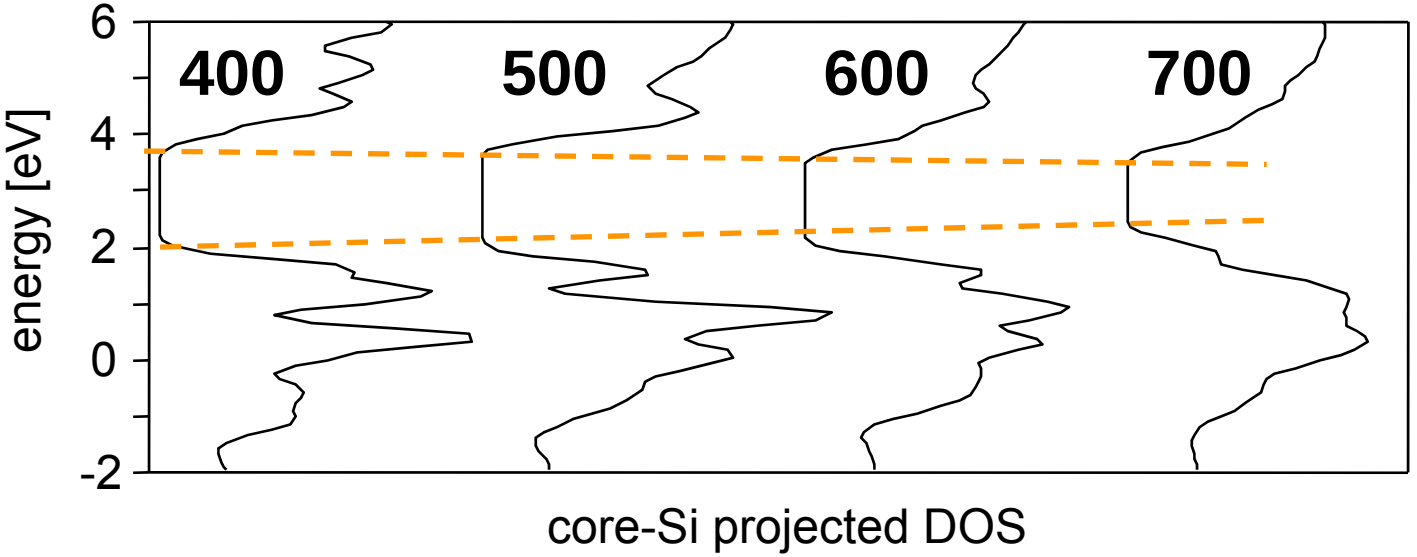
a ≈ b ≈ c ≈ 2.6 nm

d ≈ 1.6 nm

1288 atoms

124 Si + 388 SiO_2

Core: 1+4+12+12+6+12+24+16+12 = 99 Si



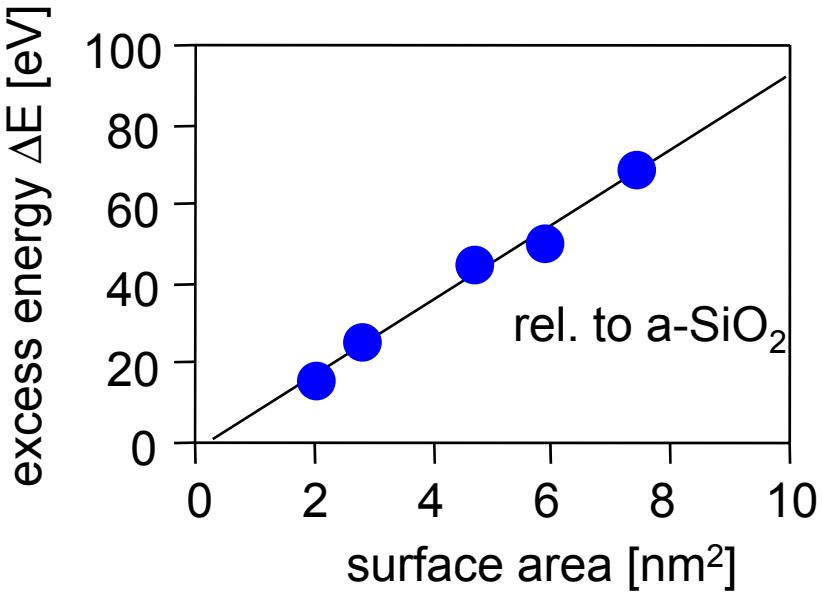
E_{gap} is significantly smaller than for bare or hydrogenated clusters

excess energy of $Si@SiO_2$-models / interface energy

- targeting interfacial energy/surface tension
- nucleation and growth of nano-crystals
- NO experimental results available for nc-Si

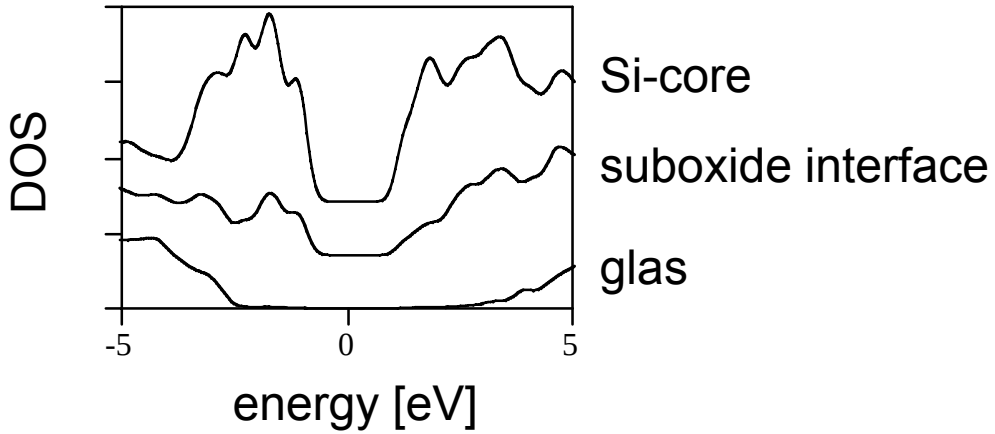
computed energy relative to crystalline Si and amorphous silica

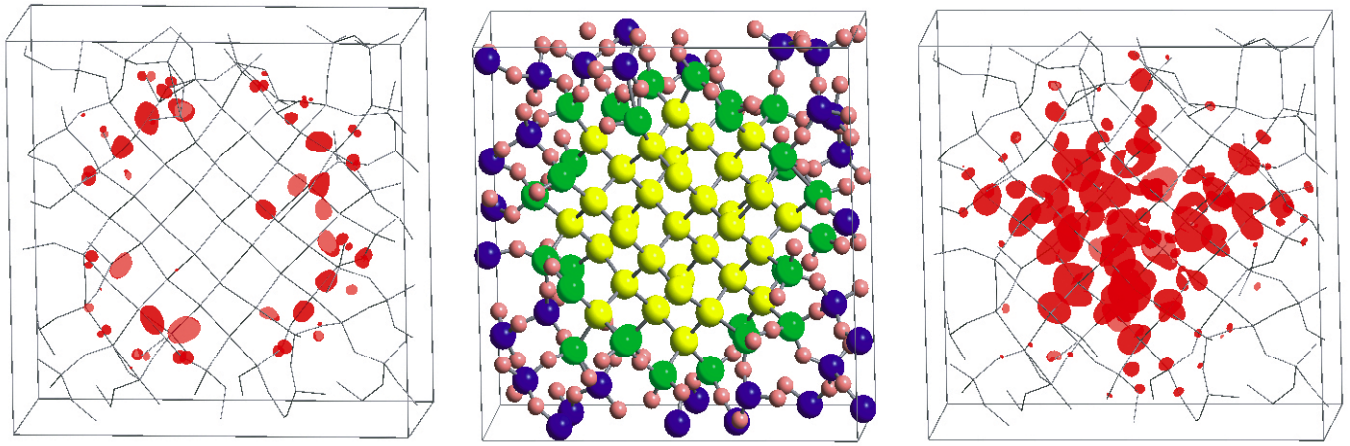
$$\Delta E^{am} = E(Si@SiO_2) - [\, E(c\text{-}Si) + E(a\text{-}SiO_2)]$$



γ^{am} = 1.5 +/- 0.3 J/m^2

electronic density of states & spatial distribution of ρ

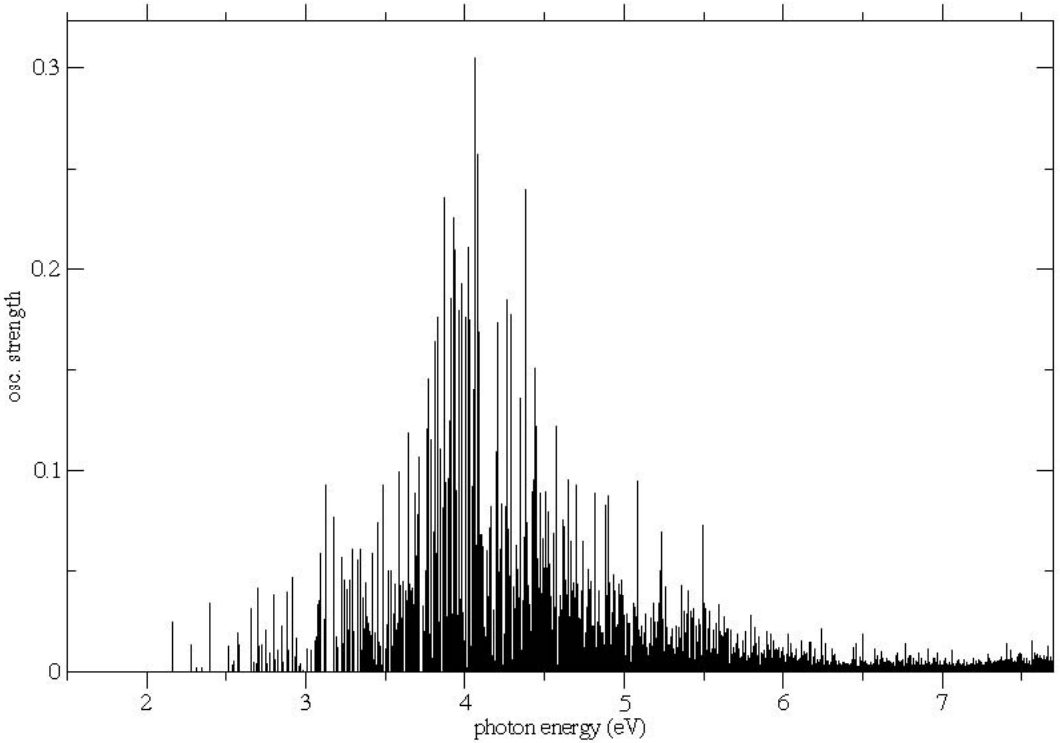




top of valence band (HOMO) *structure* bottom of conduction band (LUMO)

- significant differences to free and hydrogenated nc-Si clusters

oszillator strengths of optical excitations



GW-calculations, treating excited states (L. Ramos, F. Bechstedt, U Jena)

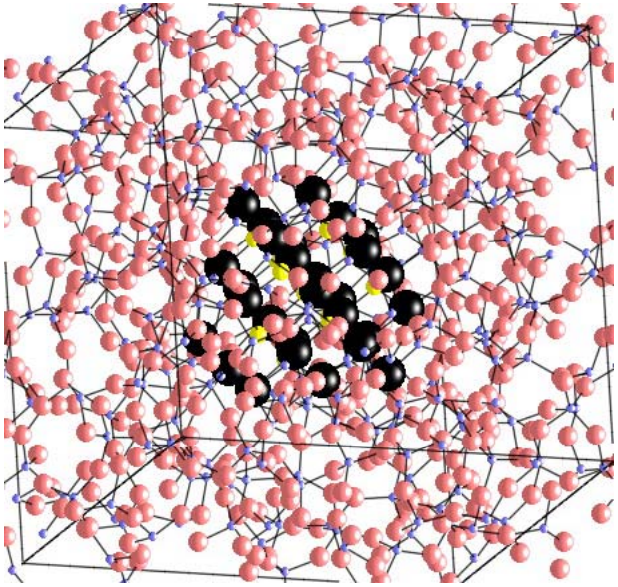
- maximum of absorption at 4 eV (UV-light)

Can this be tailored to visible light ?

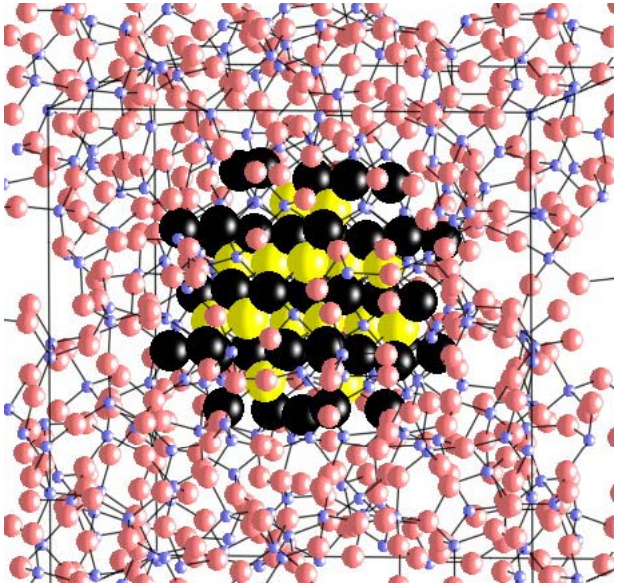
embedding nc-SiC in a-SiO_2

- model generation analogous to nc-Si @ SiO_2

β-SiC @ a-SiO_2: Si-termination of SiC-cluster



diameter ≈ 1 nm

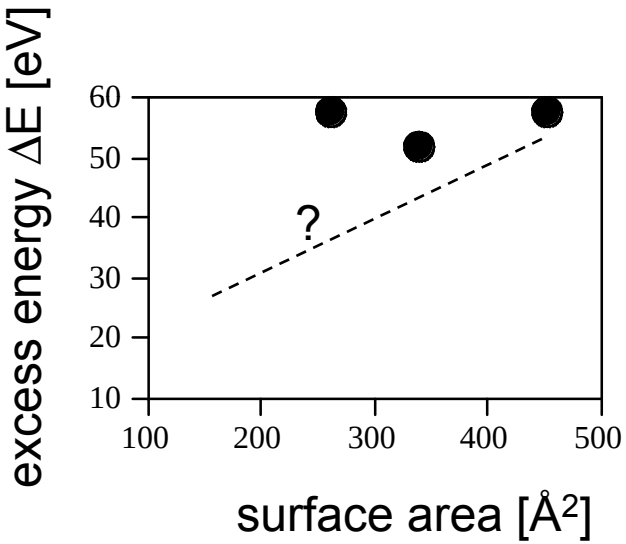


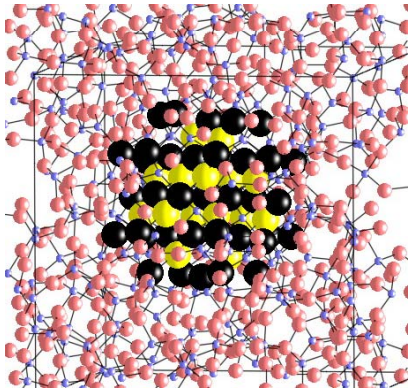
diameter ≈ 1.5 nm

interfacial energy of β-SiC @ a-SiO_2

- targeting nucleation and growth, NO experimental results available

- reference: a-SiO_2 and β-SiC



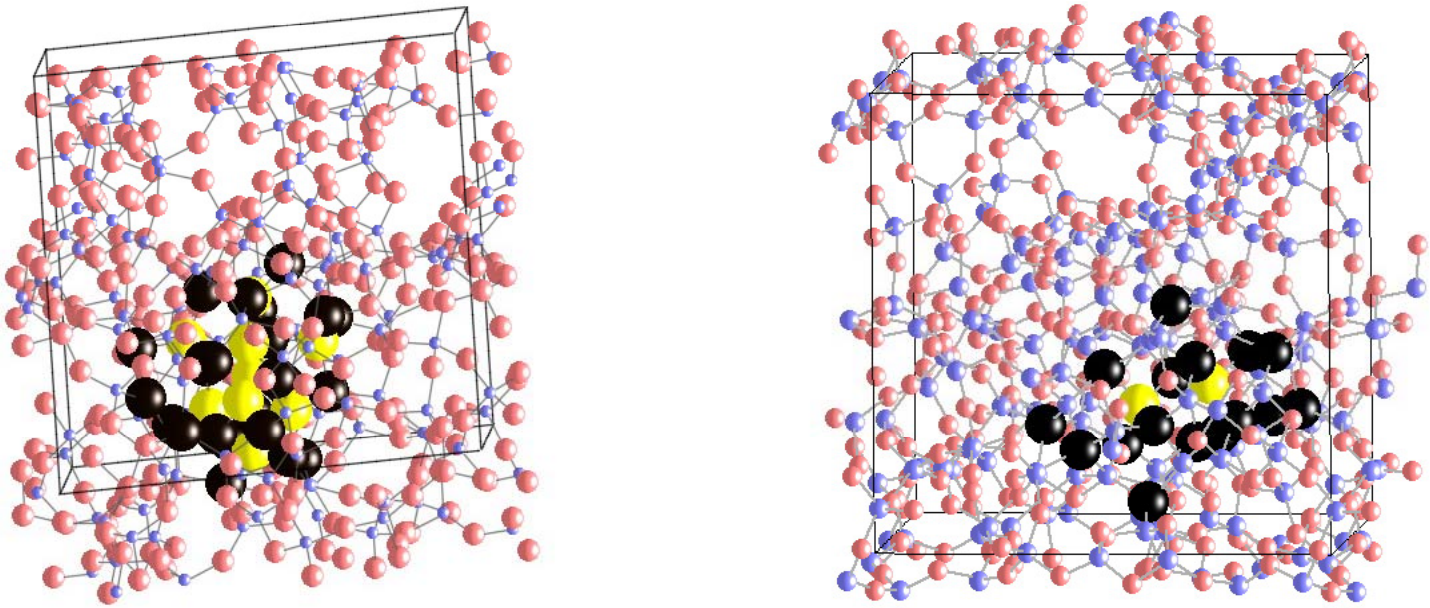


a bit odd !?
not the expected linear relation

segregated SiC in SiO_2

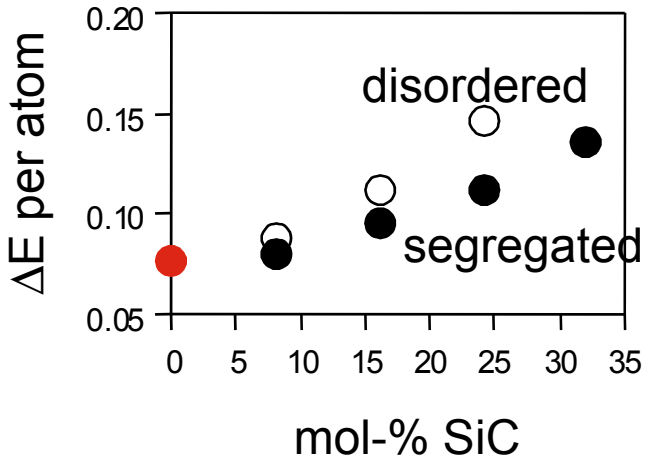
- modelled from random SiCO networks
- through <u>biased</u> construction by increasing the fraction of **Si**C_4 and **Si**O_4-tetrahedr

$\Rightarrow$ separation of an a-SiC cluster from the ternary phase



this SiC is closer to being 'amorphous'

energetics of random and segregated a-SiCO

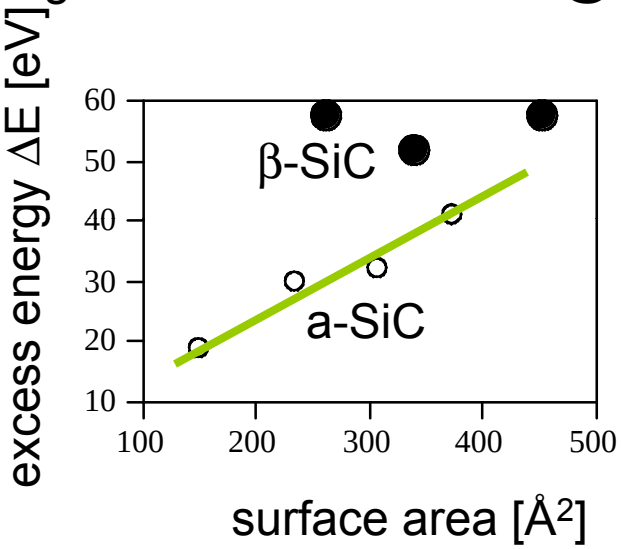


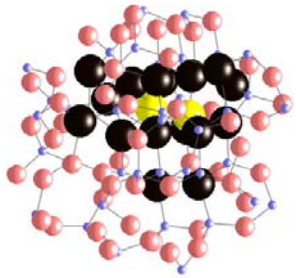
$-T \cdot \Delta S \approx 2\text{-}4\%$ of ΔE

- ΔE of a-SiO_2 well reproduced
- starting with 25 mol-% SiC, segregation of SiC clearly favored

surface energy in SiC @ SiO_2

- cluster models are β-SiC @ SiO_2
- reference to a-SiO_2 and β-SiC
- segregated models are a-SiC @ SiO_2





$\gamma^{am} \approx 1.6$ +/- 0.3 J/m^2

- trend: "amorphous"-SiC @ a-SiO_2 for small clusters < 3 nm
- γ^{am} comparable to that of nc-Si@SiO_2

one model β-SiC @ SiO_2 explicitely a) randomized and b) segregated again
⇒ new optimized structure is lower in energy than initial β-SiC @ SiO_2 !!

summary

- "real-size" models of nc-Si and nc-SiC —— *in-silico* computation
- embedded clusters can be **very different** in comparison to free clusters

- interfacial energy of nc-Si @ SiO_2
- charge distribution & “spatial” band gap structure

- segregation of SiC in a-SiCO comprehensible
- "amorphous"-SiC @ a-SiO_2 favored for small cluster size <≈ 3 nm

Outlook

- Fe, Co, Ni @ SiO_2
- semi-conducting particles embedded in glass SiC, GaN, GaAs

- model problem limits: cluster of ~2 nm @ ~2.5 (3) nm of matrix
  ⇒ **larger models**
- defects and interface chemistry (N,H)
  ⇒ **a manifold of sligthly different models**