# Unstable Chalcogenide Glasses & Application of Crystal Nucleation: Phase-change Non-volatile Memory

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School on Glass-formers & Glasses: Bangalore (4-20 January 2010)

Or:

# A Replacement Memory Technology for Flash

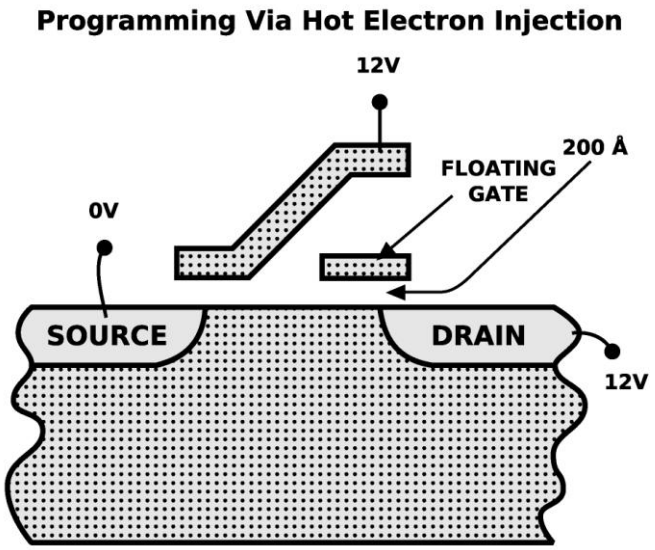
# Synopsis

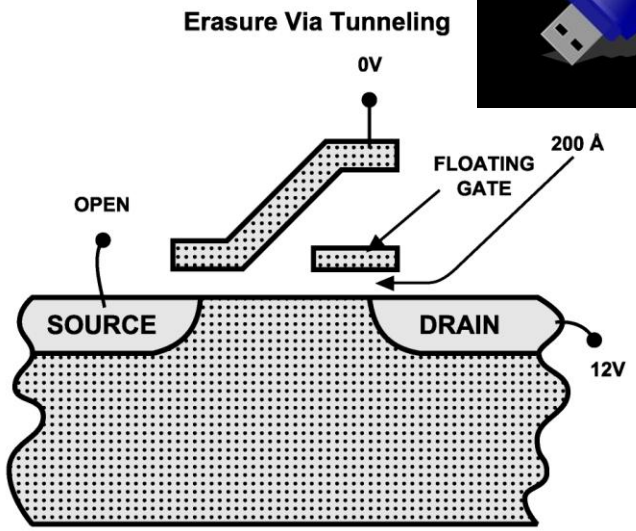
- Introduction - Flash memory
  - crystal nucleation/growth
- Molecular-dynamics (MD) simulation method
- Homogeneous nucleation & crystallization (Ge-Sb-Te) = GST*
- Heterogeneous nucleation & crystallization (GS,Sb) – ‘interface engineering’
- Structural analysis of amorphous GST-225, GS
- Summary

* Hegedus & SRE, Nature Materials, **7**, 399 (2008)

# Flash Memory : What is it?


- MOSFET with extra ‘floating’ gate (FG)




- electrons are stored (‘permanently’) in electrically isolated FG (**non-volatile** memory) → change threshold voltage controlling whether or not an inversion layer forms, allowing a source-drain current to flow (‘1’) or not (‘0’)
- NOR flash: slower, less memory → mobile phones
- NAND flash : faster, more memory → MP3, hard-drive replacement
- Market = $20 bn p.a. (2008)

# Flash Memory : The problem

- Flash (MOSFET) memory has been obeying *Moore's Law*:
  - memory capacity doubles every 2 years as feature size reduces

- Samsung and Toshiba announced, in October 2007,
  a 64Gb NAND flash memory
  - with **30nm** feature size

- But there is an ultimate limitation:
  - as the insulator thickness decreases below **7nm**, the electrons trapped in the floating gate (FG) will leak out → *volatility*
  - as the FG gets smaller → limit of 1 electron stored

→ FLASH technology will stop evolving in **~2012**

- What next?

# Phase-change Technology

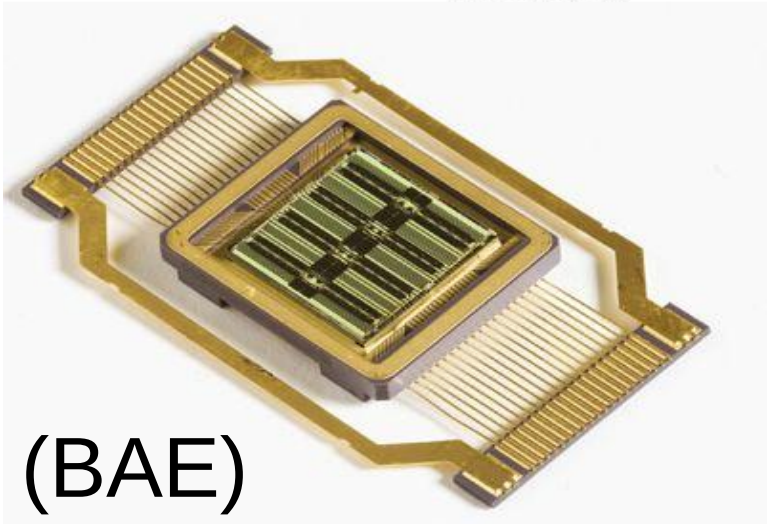
- Ge-Sb +Te alloys, eg $Ge_2Sb_2Te_5$ (GST-225), can be used for ***non-volatile*** memories

- based on ultrafast (~**10ns**) reversible, rewriteable (RW) phase change (PC) between amorphous & crystalline states

- property contrast between a- & c-states → (0,1) bit

**optical reflectivity** contrast
(DVD-RW, Blu-ray)

**electrical resistivity**
contrast (PC-RAM)





4 Mbit ‘rad-hard’ PC-RAM (BAE)

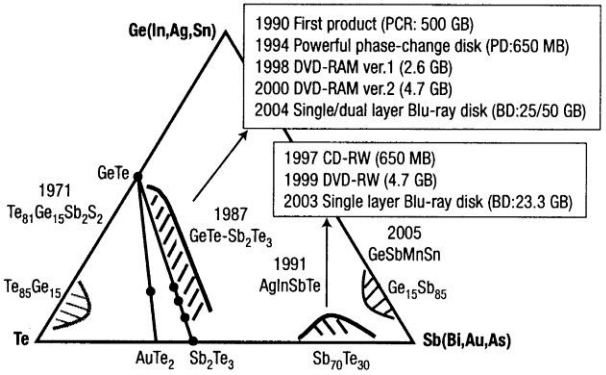
# New PCRAM technology

- Scalable
- Extremely fast
  - can rewrite data without erasure
    → 30x faster than Flash
- Fewer processing steps than NOR Flash

- Samsung mass-producing 512 MB PCRAM chips (see Nature online, Sept 25, 2009)

- → 1GB in late 2009?

# Materials for PC (optical) data storage



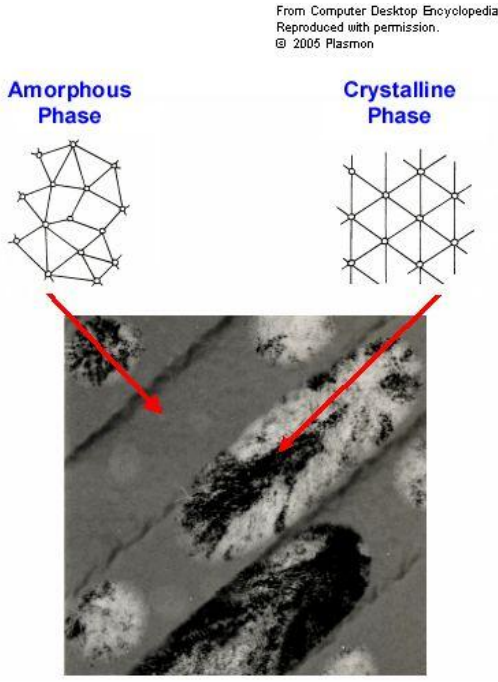

Main materials are:

- Ge-Sb-Te (GST), e.g. $Ge_2Sb_2Te_5$ (“225”)
- Ge-Sb (GS), AgInSbTe (AIST)

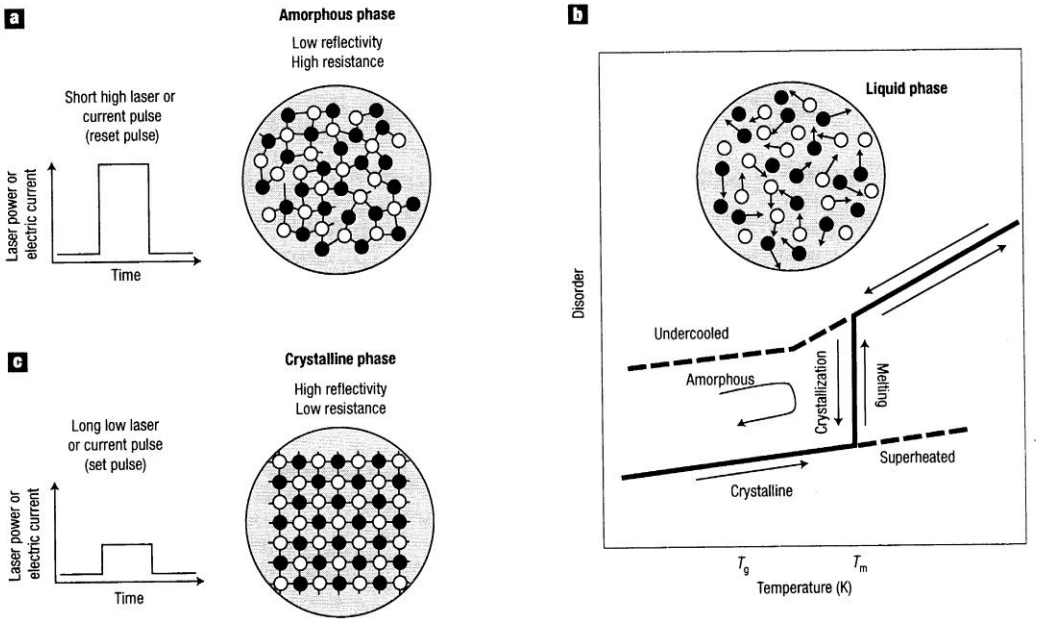
# How is the PC change caused?

- In optical discs, brief laser pulses cause melting & quenching to amorphous state/crystallization of amorphous spot

- In PC-RAM devices, electrical-current Joule-heating pulses cause amorphization/crystallization



# Write/erase steps in PC data storage



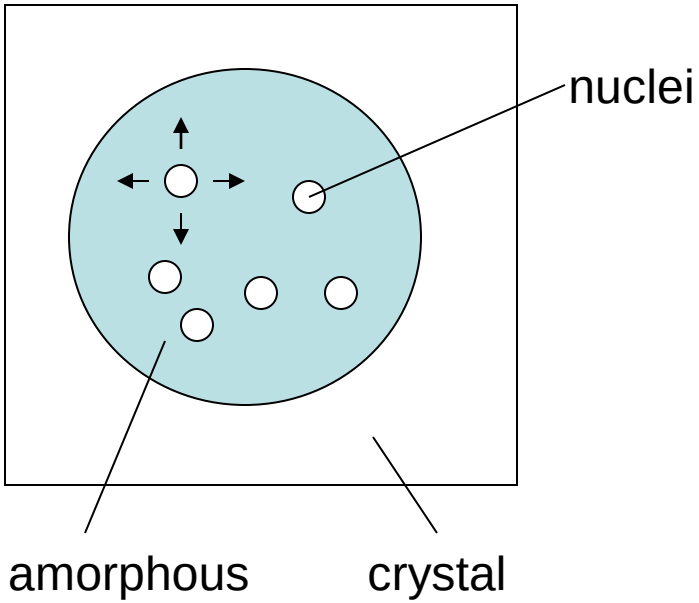

[Wuttig and Yamada
Nat. Mat., **6**,824 (2007)]

- Erased (optical) state is *crystal*
- written spot is *amorphous*

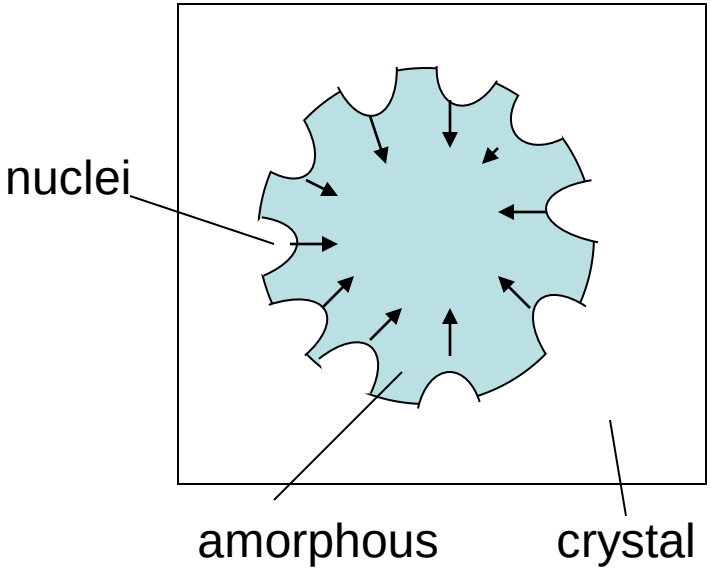
- Reset (electrical) state is *amorphous*
- set state is *crystal*

# Erasure Mechanism: Crystal Nucleation vs. Growth

- Homogeneous nucleation vs heterogeneous nucleation

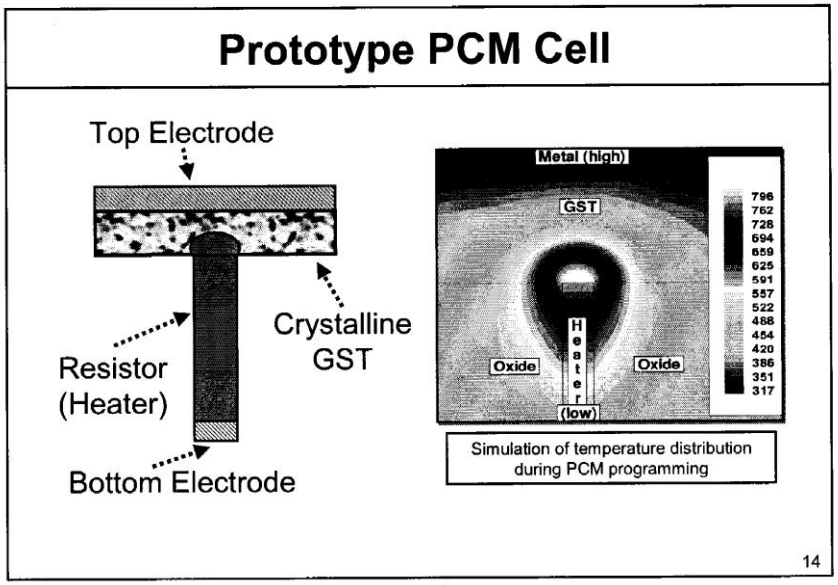


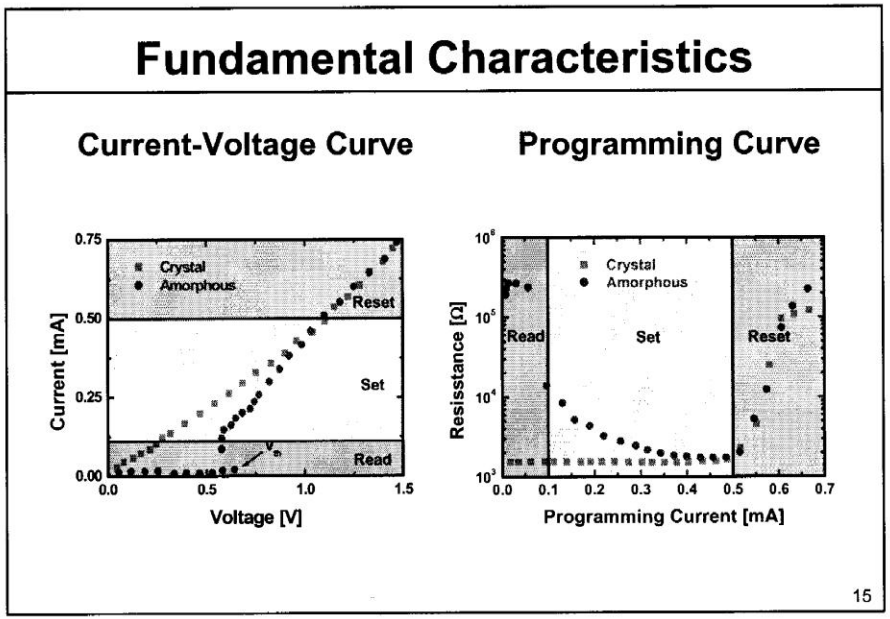

(GST-225, 124 etc.)




(AIST, GS)

# PC-RAM Memory devices

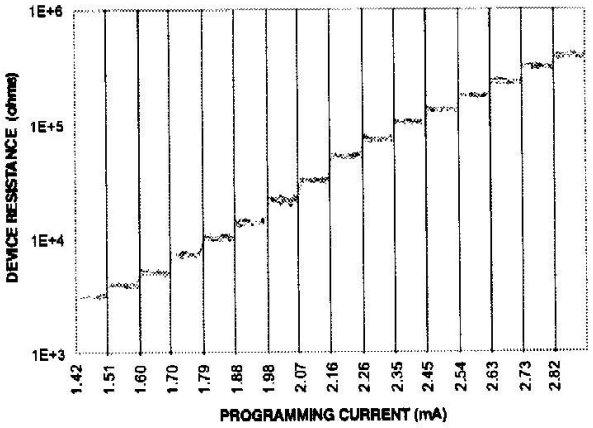



Attwood (Intel)

# PC-RAM memory devices

- Advantages:
  - scalability (IBM has demonstrated PC behaviour down to 2.5nm)
  - multi-level storage capability (>1 bit/cell)

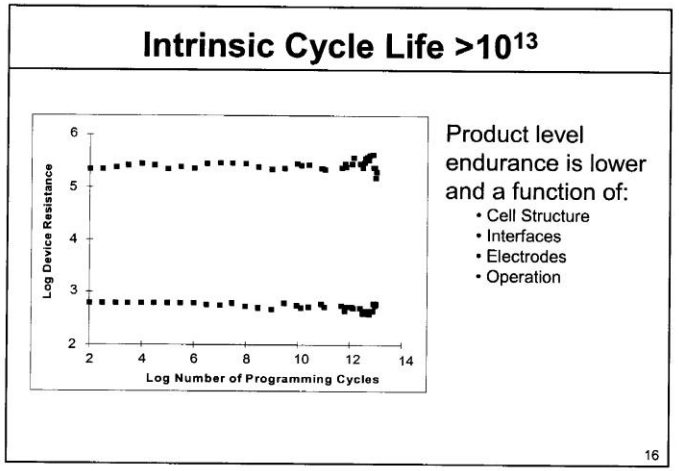



high/low resistance → 1 bit (0, 1)

$2^n$ intermediate resistance states → *n* bits

- very fast “set” speed (crystallization occurs in ~1-10 ns)

- very long cycle life




Attwood (Intel)

# Features of phase changes in GST materials: I

- Crystallization/amorphization is :

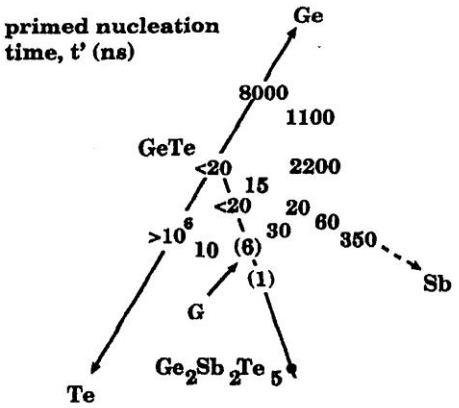
  -rapid (amorphous-crystal $t > 10$ns)
  (very ‘bad’ glass)

  -reversible

  WHY??

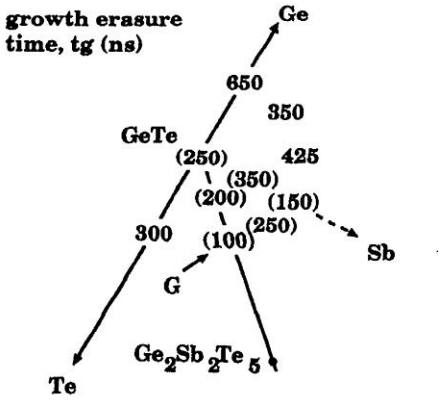
# GST nucleation and growth times

- Nucleation times, $t_{nuc}$




[Coombs *et al*, J. Appl. Phys. **78**, 4925 (1995)]

- Growth times, $t_{gr}$

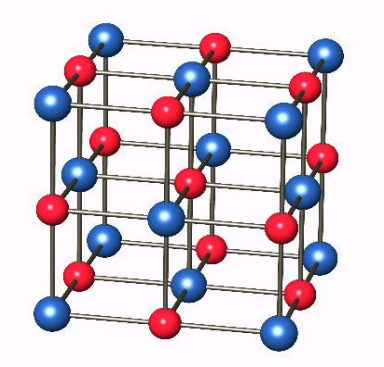



- $t_{nuc} < t_{gr}$ for 225 - GST (homogeneous nucleation dominant)
- $t_{nuc} > t_{gr}$ for GS (heterogeneous nucleation and growth dominant)

# Features of phase changes in GST materials: II

- Crystal structure of GST involved in PC transformation is the *metastable* rocksalt (NaCl) structure + atomic vacancies:

  NB: **4-rings, 90$^{o}$ bond angles**



- e.g. for 225-GST, 1 vacancy/formula unit distributed among the Ge/Sb sub-lattice
- (2 Ge+2 Sb+1 vacancy = 5 Te)
- how are vacancies distributed?

- What is the structure of the amorphous phase?

# Origin of *c*–*a* resistivity contrast

- *Crystal* octahedral coordination associated with **resonant** *p*-bonding

  → metallic behaviour

- *Amorphous* structure destroys long-range resonant bonding

  → semiconducting behaviour

(Wuttig 2009)

# What are the Problems?

- Why is crystallization so fast (~10ns)?
- How can it be made *even* faster?
- How to optimise property contrast between amorphous & crystalline phases of PC materials?

→ *ab initio* Molecular Dynamics (AIMD)

- ***in silico* rational materials design**

# Molecular-Dynamics (MD) Simulations

- Compute trajectories of an assembly of particles (‘atoms’), interacting via a given potential, according to Newton’s laws of motion

- Particles are in a simulation box with periodic boundary conditions (to eliminate surface effects)

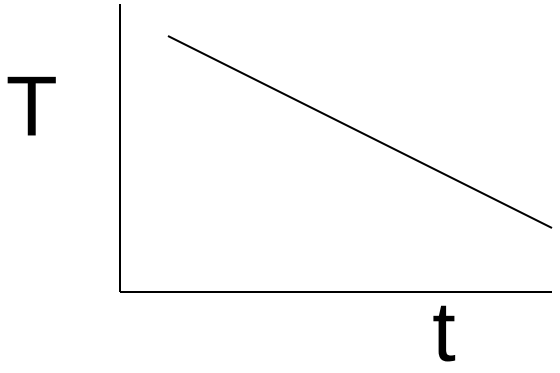
- Interatomic potential can be computed quantum-mechanically (*ab initio*), albeit with approximations (DFT-LDA, GGA)

# *Ab initio* MD of GS(T) phase changes

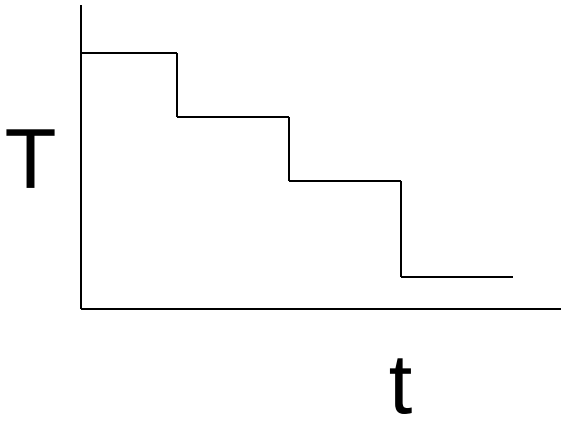
- VASP *ab initio* MD code
- 63-90 atom models for GST-225,124
- 150 atom models for GS, Sb
- Cubic cells + periodic-boundary conditions (+ crystal templates)
- Constant volume
- Quenching from melt + heating amorphous
- 6 month runs on 32 nodes of supercomputer

# Simulated cooling protocols

- Continuous ramp




- Discontinuous + isothermal

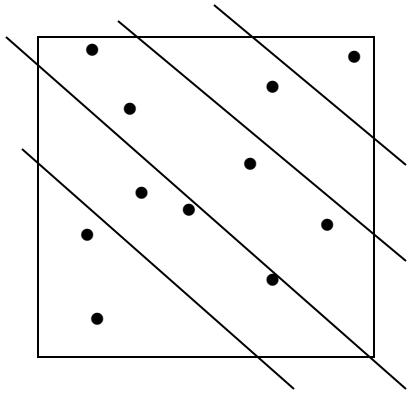


# Dynamic structural characterization of quenched/annealed models

**1. Long-range order**

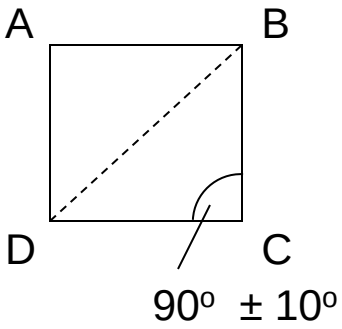
• Maximal 3D Fourier intensity

$I_{max} \rightarrow N$ if all atoms are on lattice sites/planes of a single crystal

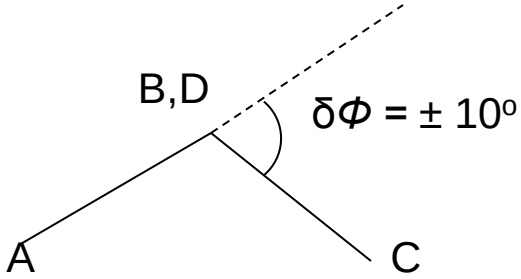


**2. Medium-range order**

• 4-rings (structural unit of rocksalt structure)



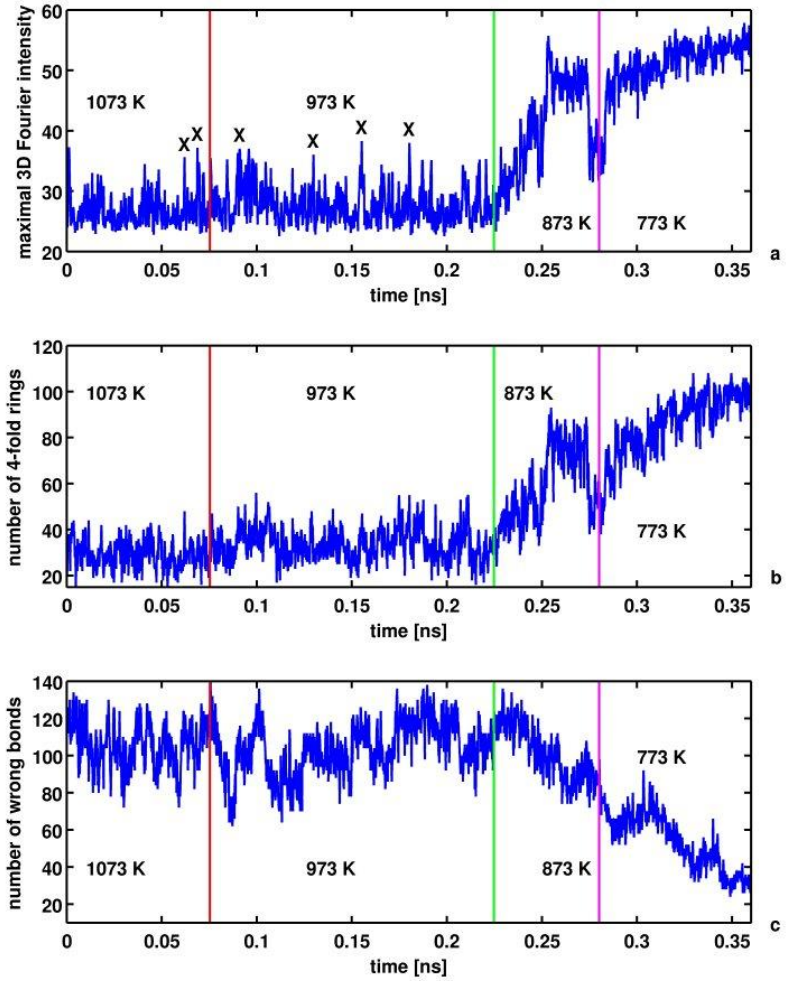

4-rings are included with some variations in bond/flex angles




**3. Short-range order**

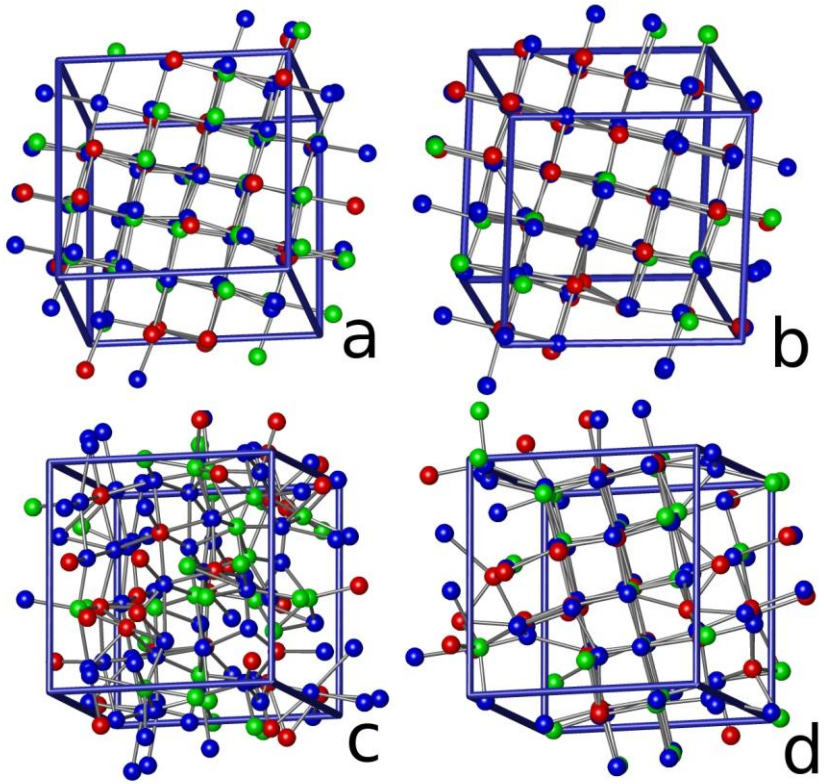
• Wrong bonds (Ge-Ge, Sb-Sb, Te-Te, Ge-Sb in GST)

# Liquid quench: GST 225



# Simulated Crystallization

a) GST-225
(slow liquid-quenched)




b) GST-124
(slow liquid-quenched)

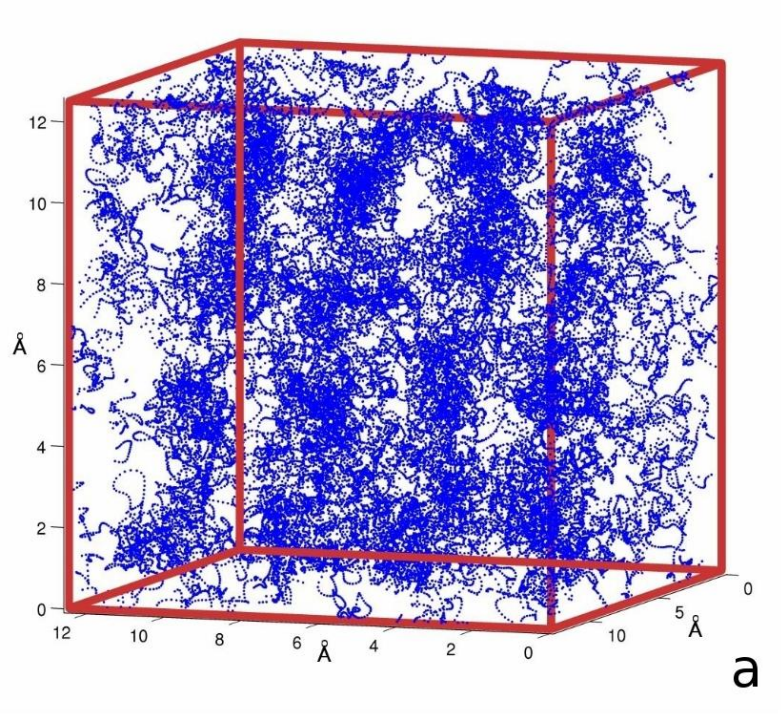
c) a-GST-225
(fast liquid-quenched)

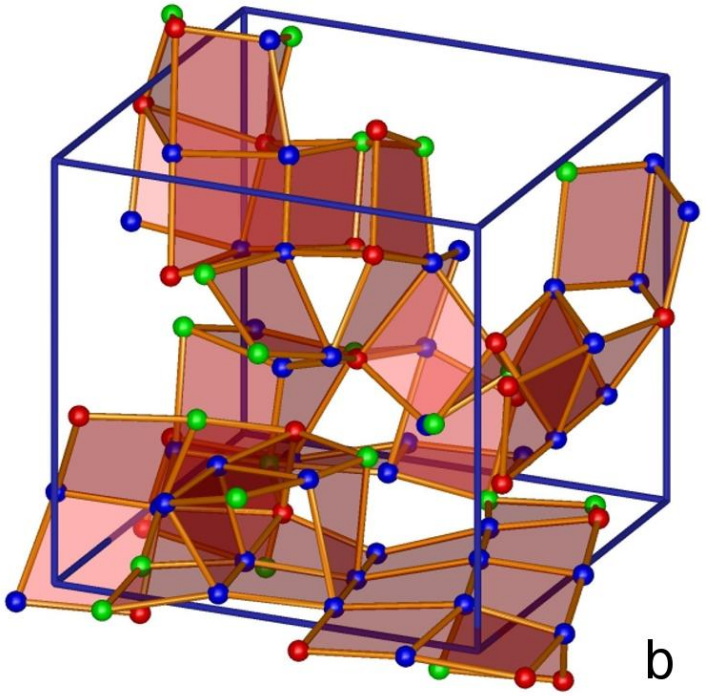
d) GST-225
(amorphous-annealed)

Ge= green; Sb= red; Te= blue

Hegedus & SRE, Nature Materials, **7**, 399 (2008)

# Structural order in *liquid* GST-225

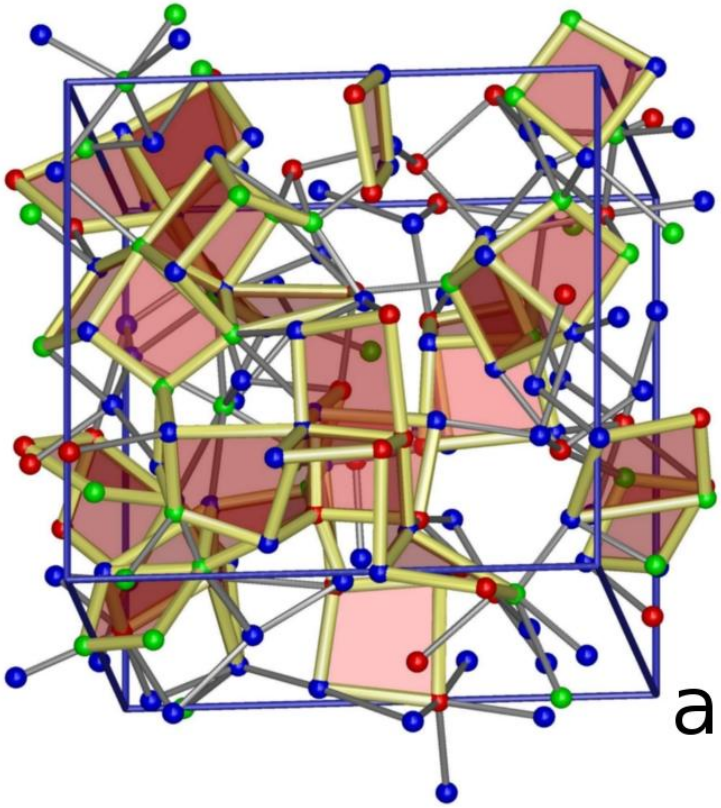


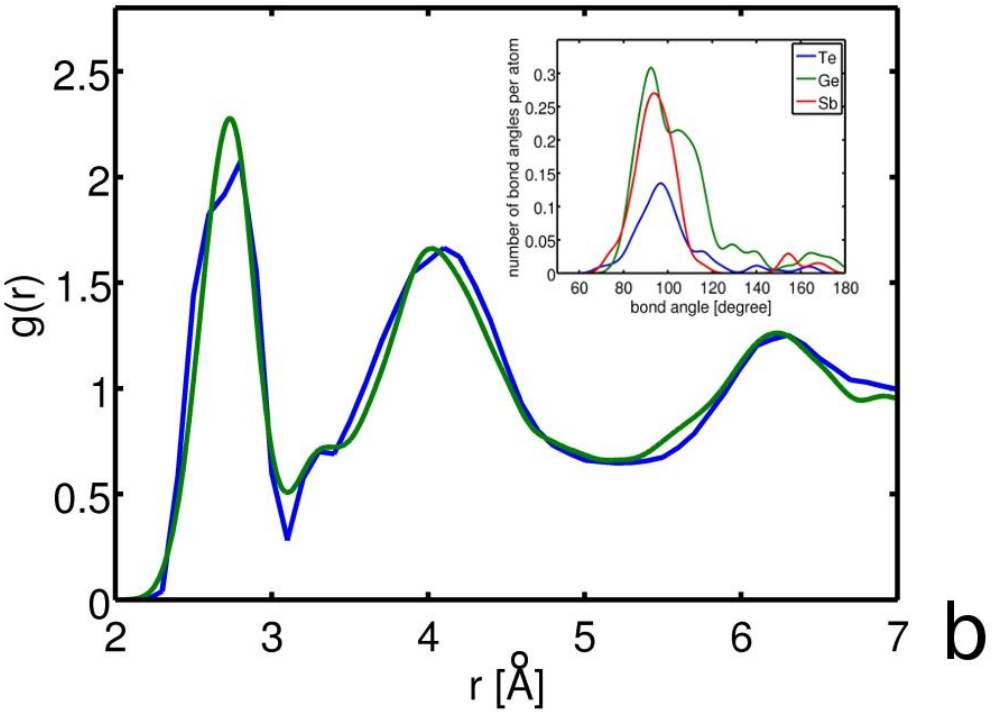

a) Cumulative trajectories of all 63 atoms for 20ps at 973K

b) Highly-ordered transient cluster of 4-rings at 1073K

# Structure of *amorphous* GST-225



a

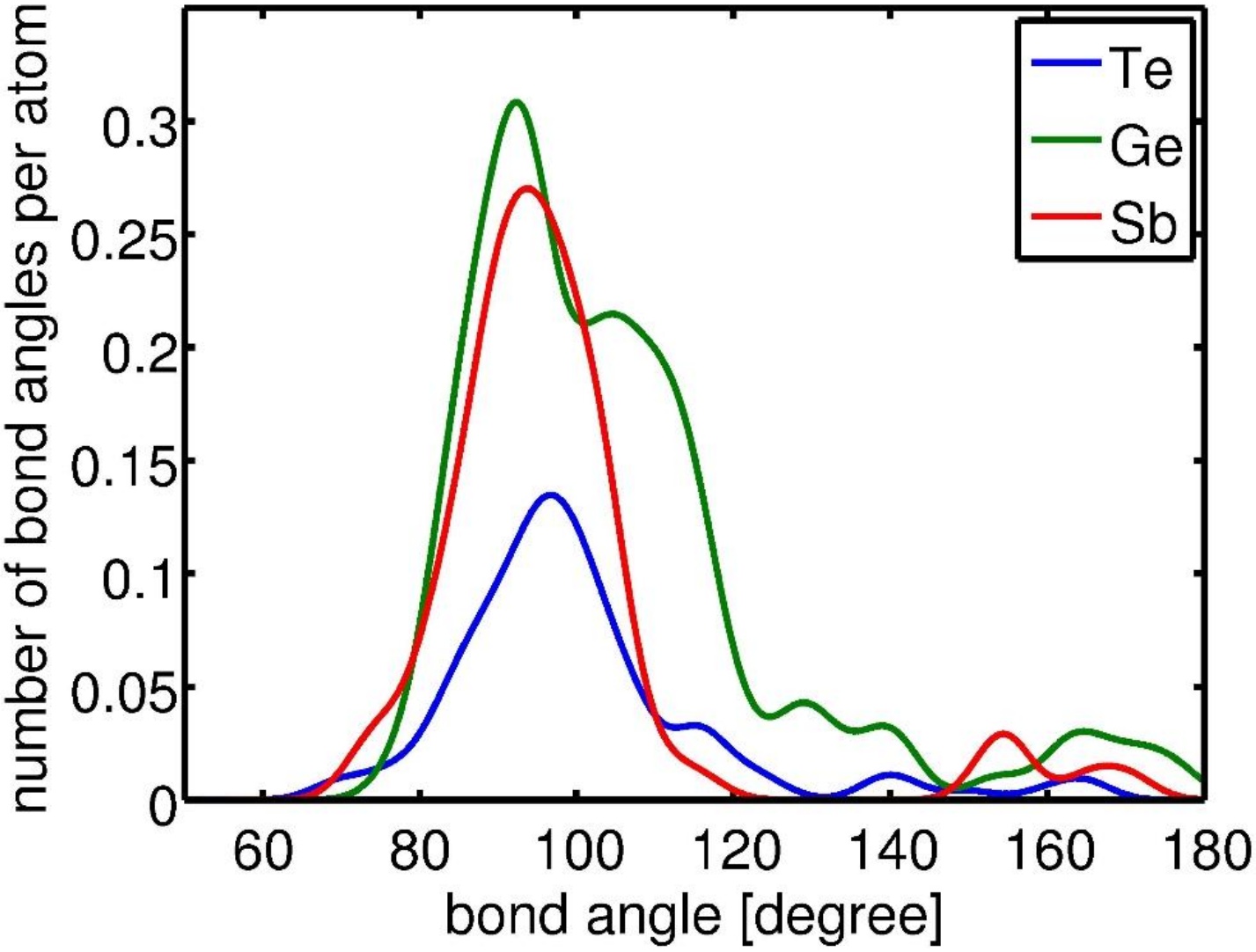



b

Nb square 4-rings

Pair distribution function

# Bond-angle distributions for amorphous GST-225



# Structure of amorphous GST

- Ge coordination is mainly 4 – but mostly **defective octahedral**, *not* tetrahedral
- Ge bond-angle distribution (BAD) peaks mostly at ~90$^{o}$ (octahedral)
- Subsidiary Ge BAD peak at ~109$^{o}$ (tetrahedral)
- Sb coordination is mainly 3 – but also 4 - BAD peak at ~ 90$^{o}$
- Te coordination is mainly 2 – but also 3 - BAD peak at ~ 90$^{o}$

# Structure of amorphous/glassy GST

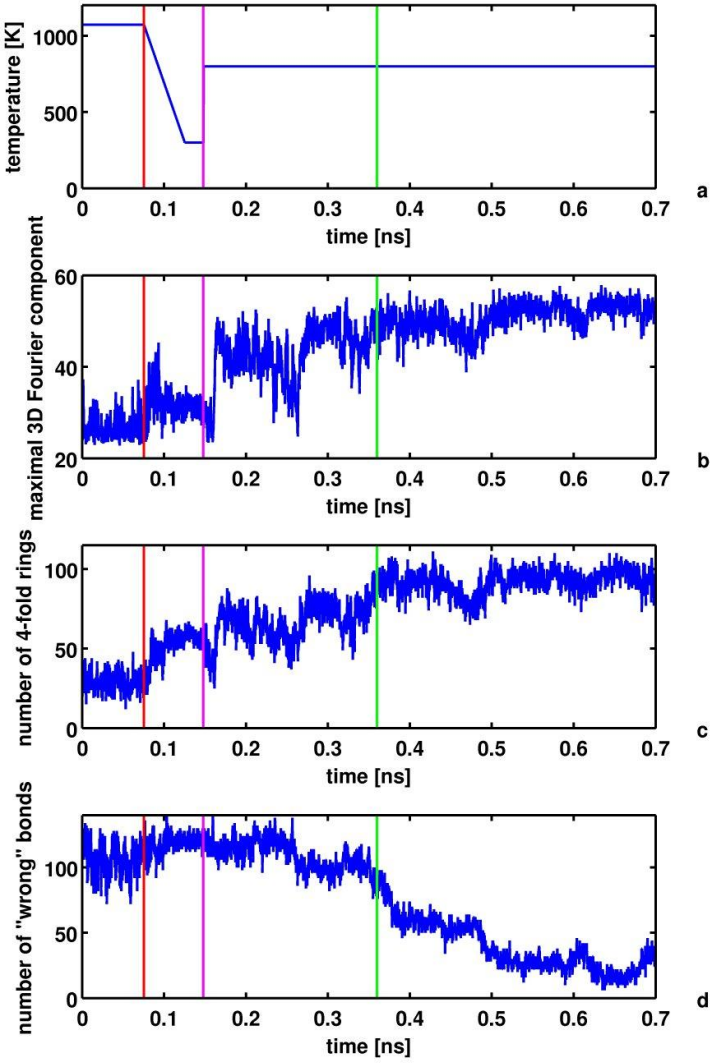
- Structure of as-deposited (sputtered) a-GST is ***NOT*** the same as device-quenched glass
  - (EXAFS, XANES)

- More *tetrahedral* Ge in as-deposited material

- XANES spectra calculated from AIMD model are in good agreement with experimental data for device-quenched material

(Kolobov, SRE 2010)

# GST-225: amorphization on rapid quenching, and crystallization on annealing



# Why is crystallization so rapid?

- Crystal-nuclei seeds (fragments of octahedral rocksalt structure, e.g. 4-rings) *already* present in the liquid & amorphous states

- Therefore minimal atomic diffusion is required for crystal nucleation & growth

# GS - why change from GST?

- No Te in CMOS fab. line  (IBM)
- GS crystallizes faster

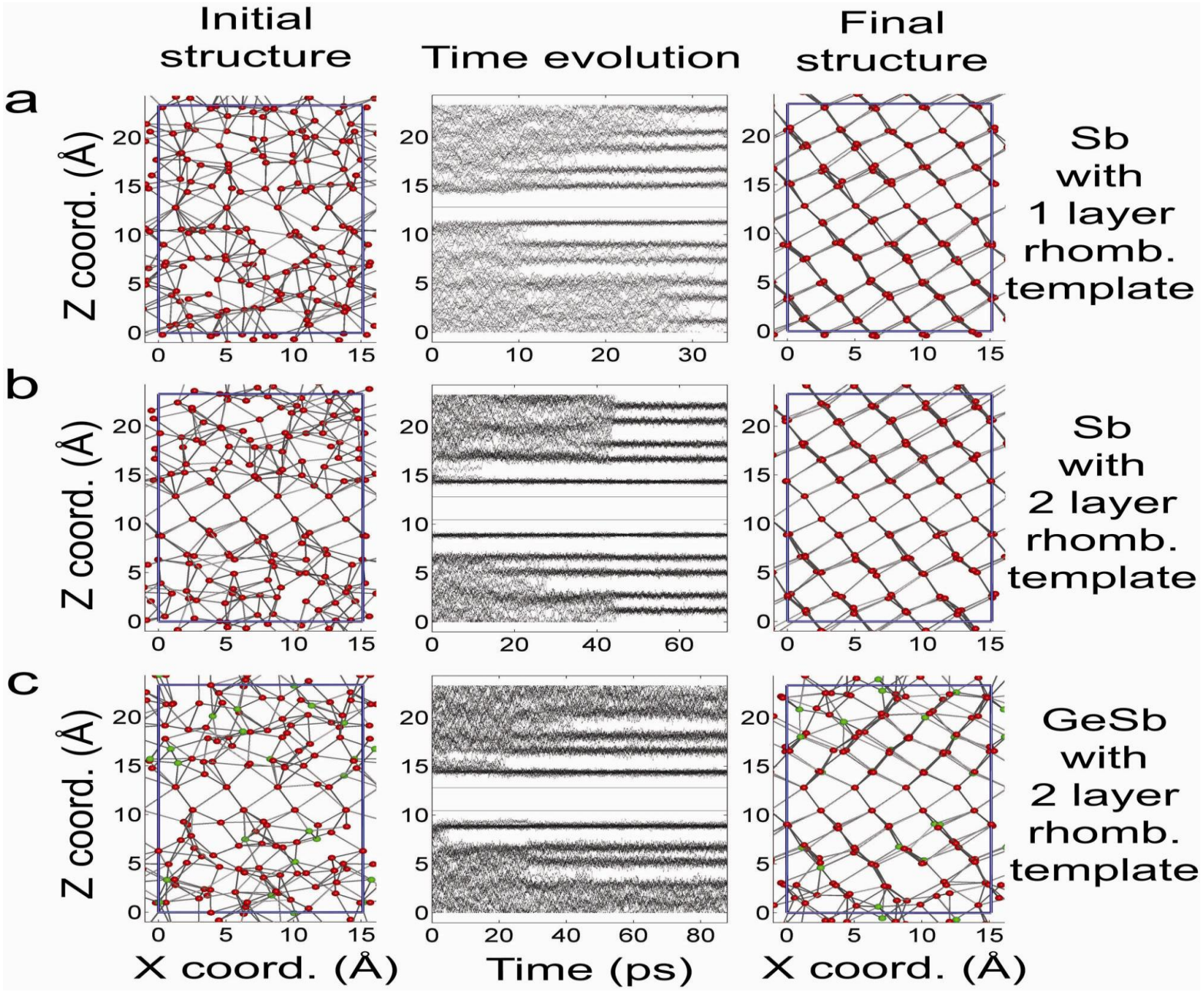
- But crystallization is growth-limited
- And crystal phase is rhombohedral (A7) Sb
- But material phase-separates on cycling (Sb, Ge)

# Simulation of heterogeneous nucleation: I

- Simulate *growth-limited* crystallization in GS,Sb
- Isothermal MD runs at 600K
- Introduce crystal template into simulation box

  -rhombohedral (A7) template of Sb

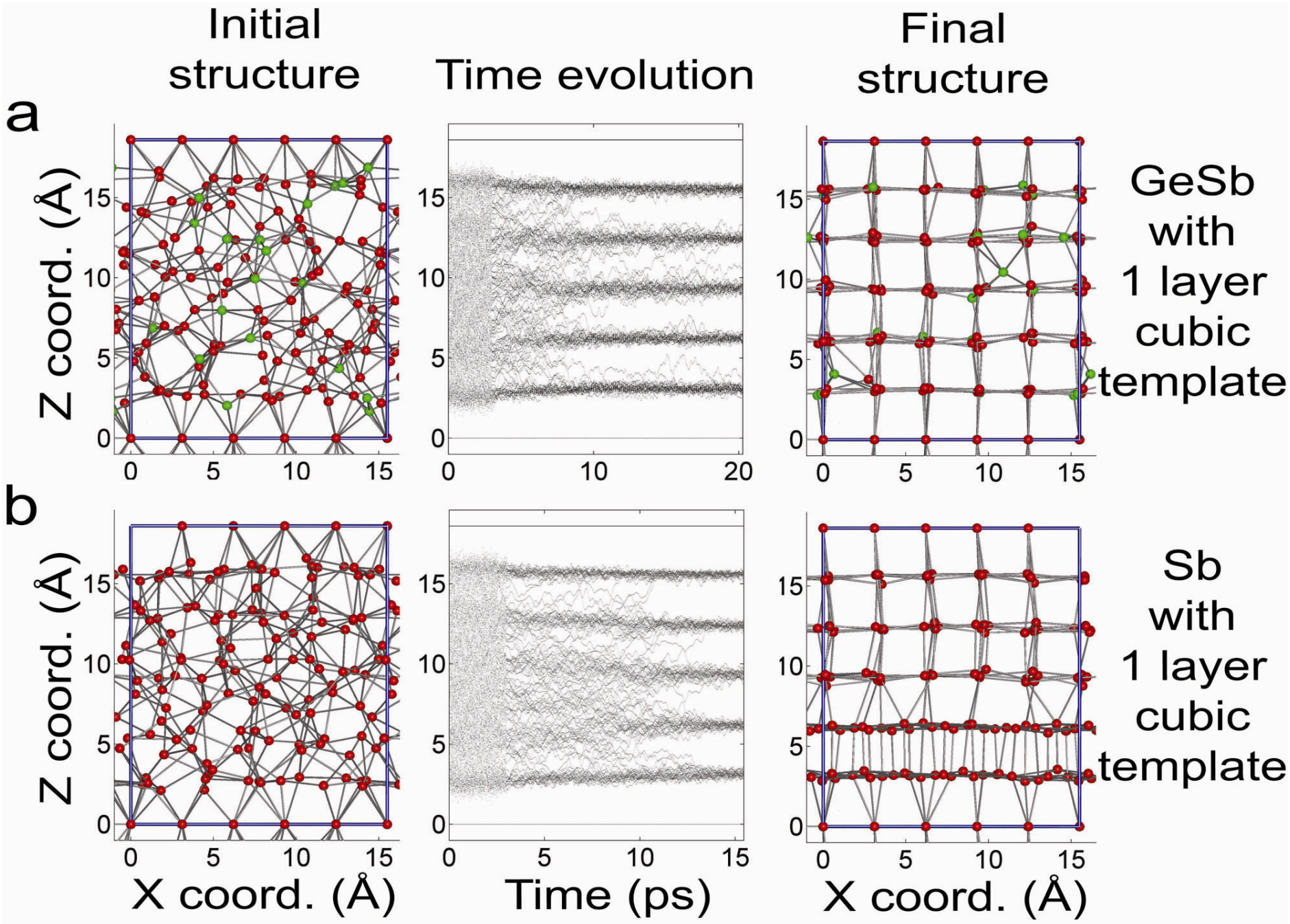
  Nb **NO** *untemplated* crystallization in >100ps


Initial structure
Time evolution
Final structure
a
b
c
Z coord. (Å)
X coord. (Å)
Time (ps)
Sb with 1 layer rhomb. template
Sb with 2 layer rhomb. template
GeSb with 2 layer rhomb. template

# Simulation of heterogeneous nucleation: II

- Design *new* materials by choice of appropriate templates

- Choose **cubic** template to try to force GS, Sb materials to crystallize into cubic crystal structure  (like GST)


Initial structure
Time evolution
Final structure
a
b
Z coord. (Å)
X coord. (Å)
Time (ps)
GeSb with 1 layer cubic template
Sb with 1 layer cubic template

# Crystal templating

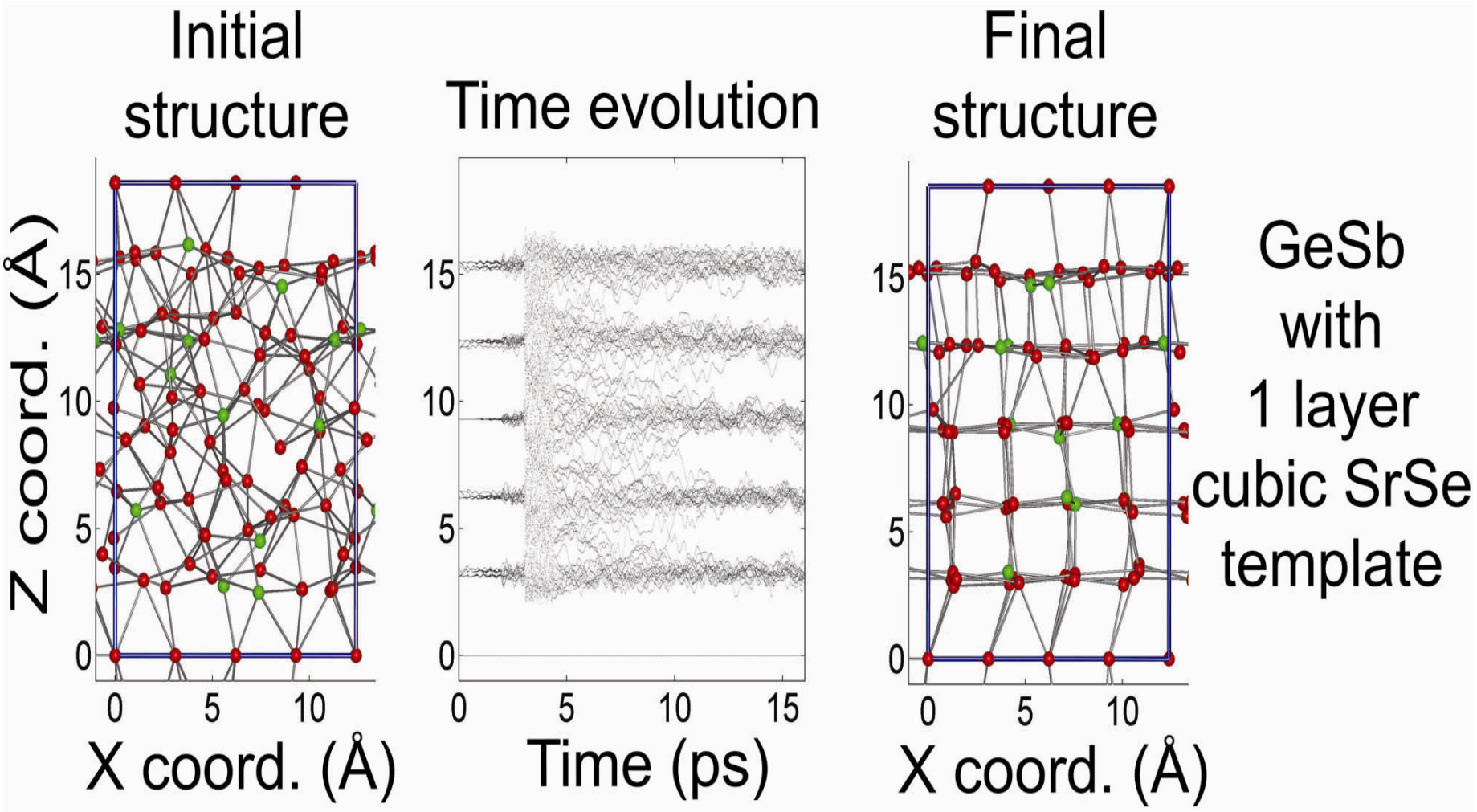
- Unfeasible to use cubic Sb/GS template in real PCRAM cells because rhombohedral phase is stable (and would melt during reset operation)

- Use different, refractory cubic material for template layer with matched lattice constant:

  -eg rocksalt SrS (*a*=6.024A; MP=2000$^{o}$C), or
  SrSe (*a*=6.236A; MP=1600$^{o}$C)

  -cf cubic Sb (*a*=3.1A); MP(eutectic GS)=600$^{o}$C

# Designing new PCRAM materials using templates

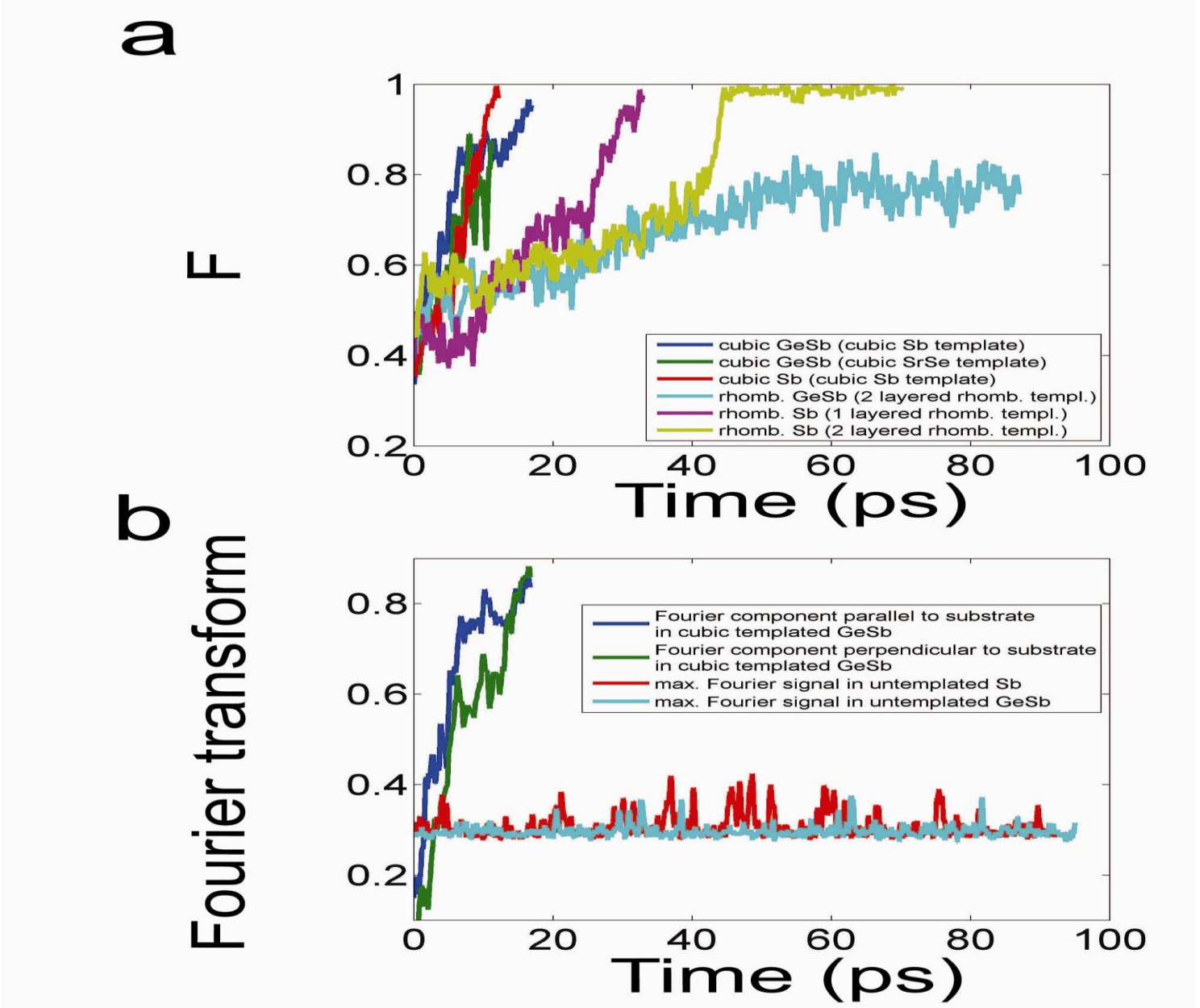


# Time dependence of crystallization

- a) Calculate time-dependent fraction, ***f(t)***, of atoms lying closer to crystal plane than a chosen value

- b) Calculate time-dependent 3D Fourier transform

# Time Dependence of Crystallization



# Templated crystallization speeds

- Cubic templated GS in simulation box of width ~20A

  -crystallizes to cubic phase in ~ 20ps

- Extrapolated to **25-nm** wide PCRAM cell,
  cubic crystallization is predicted to occur in ~ **0.25ns**

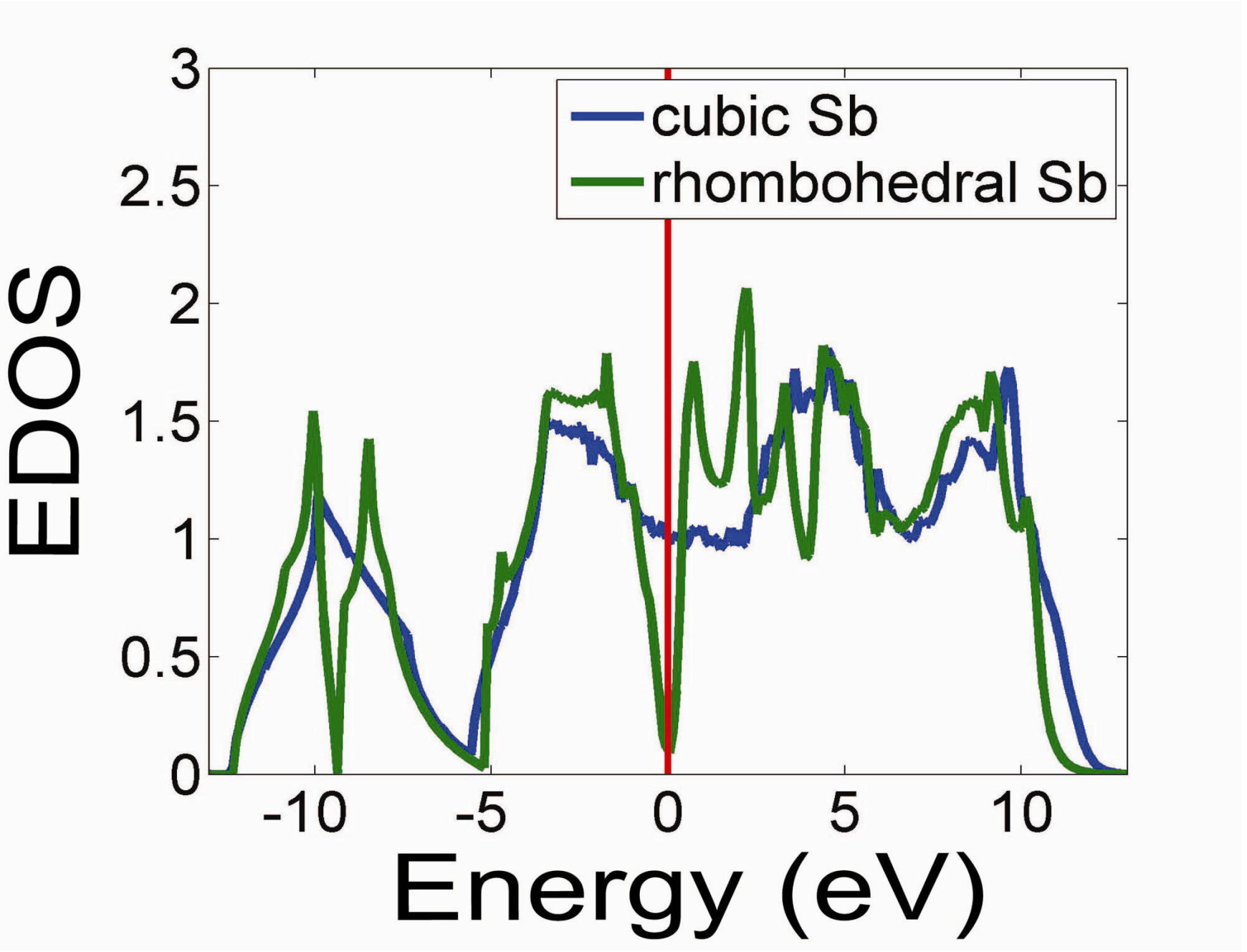
- **PCRAM using cubic-templated Sb/GS may be suitable for non-volatile DRAM replacement ( *t* < 1.5ns) ?**

# Electronic Properties of cubic Sb

- Electronic density of states (EDOS)

  (how many electron states at a given energy)

  – cubic vs rhombohedral

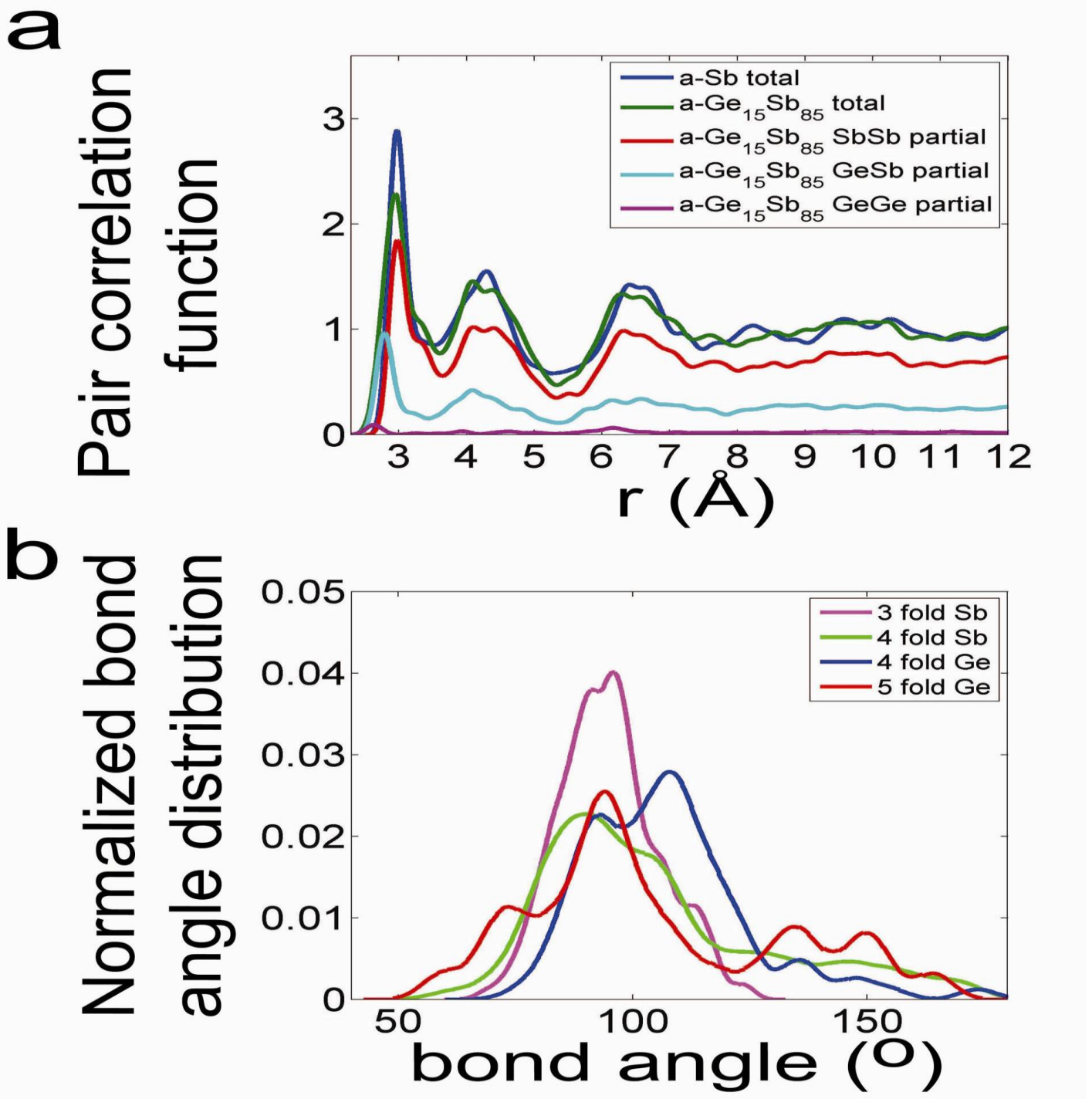

cubic Sb
rhombohedral Sb
EDOS
Energy (eV)
3
2.5
2
1.5
1
0.5
0
-10
-5
0
5
10

# Electronic properties of cubic GS/Sb

- DOS at Fermi energy ($E_F$) is much greater for *cubic (cb)* than for rhombohedral (rh) phase
- Electrical resistivity contrast is predicted to be greater for {cb/am} than for {rh/am}
- **Thus, cb-Sb/GS is predicted to be more suitable for multilevel memory operation**

# Structure of amorphous Sb, GS

- Atom-Atom Pair Correlation Function
- Bond-Angle Distribution


a
Pair correlation function
a-Sb total
a-Ge15Sb85 total
a-Ge15Sb85 SbSb partial
a-Ge15Sb85 GeSb partial
a-Ge15Sb85 GeGe partial
0
1
2
3
3 4 5 6 7 8 9 10 11 12
r (Å)
b
Normalized bond angle distribution
3 fold Sb
4 fold Sb
4 fold Ge
5 fold Ge
0
0.01
0.02
0.03
0.04
0.05
50 100 150
bond angle (°)

# Structural features of a- Sb, GS

- Average bond angle in a-Sb is ~90$^{o}$
- → p-bonded, locally defective octahedral, configuration
- <3>,<4> Sb and <4>,<5> Ge in a-GS have ‘octahedral’ configurations
- <4> Sb and <4> Ge in a-GS *also* have tetrahedral configurations (average bond angle ~109$^{o}$)

**‘octahedral’ Ge → reduced phase separation in cb-GS?**

# Summary: AIMD

- First(?) example of AIMD simulations matching experiment in time and size

# Summary: homogeneous nucleation

- *Ab initio* MD simulations of Ge-Sb-Te PC materials show crystallization, on *slow* cooling (~ 1ns) from the melt, of 225, 124, 101, 023, but NOT 160 (Ge-Sb, GS)

- Results can be interpreted in terms of *homogeneous* crystal nucleation

- Crystal seeds in liquid state are (connected) 4-rings, characteristic of octahedral rocksalt structure

  - 4-rings → fast crystallization on annealing

# Summary: amorphous state

- Amorphous GST-225, obtained by *rapid* quenching, contains:

- ‘octahedral’ + tetrahedral <4> Ge configurations
  - 〈3〉coordinated Sb, 〈2〉coordinated Te

- <3> Sb in a-Sb, and <3> Sb and <5> Ge in a-GS have ‘octahedral’ configurations

- <4> Sb and <4> Ge in a-GS also have tetrahedral configurations (average bond angle ~109$^{o}$)

# Summary: heterogeneous nucleation

- Eutectic GS and Sb do *not* nucleate homogeneously
- Heterogeneous nucleation and crystal growth can be simulated by templating in simulation box
- Crystallization to the experimental rhombohedral phase can be simulated using rh-Sb template
- Crystallization to metastable *cubic* phase occurs with cubic templates – eg Sb, or SrS, SrSe
- Cubic crystallization is much faster than rhombohedral - 0.25ns for a 25nm PCRAM cell
- Cubic phase has much higher EDOS at $E_F$ than for rhomb.
- Cubic-templated GS etc might be suitable for **DRAM**?

  → *in silico* rational design of new PCRAM materials

# Acknowledgements


- J. Hegedus & T-H. Lee
- EU Marie-Curie Fellowship (JH)
- UK EPSRC (THL)
- Cambridge High-Performance Computer Facility
- Cambridge Enterprise