Simulations of phase change materials: Order-disorder phase transitions in nanoseconds

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Order-disorder phase transitions in nanoseconds

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“Modern” personal computer: Long wait after switching on. Why?

Random access memory (RAM) is “volatile” [contents vanish if no power]

Non-volatile memory? Yes, USB sticks (Si/SiO\textsubscript{2} arrays), DVD-RAM (Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} alloy)

Battle between Blu-ray Disc (BD) and HD-DVD decided 2008:

“Phase change (PC) memories”
Phase change memories

“Reversible electrical switching phenomena in disordered structures”

Rapid and reversible transition between resistive and conducting state in semiconductor films (caused by electric field).

Current view: Transition between crystalline (conducting) and amorphous (resistive) states. Can use laser pulses to cause reversible transitions in nanosized “bits” in a film

“Melt-quench” stage (∼ 1 ns), “crystallization” stage (20 − 100 ns)
Which semiconductors? Many Ge/Sb/Te alloys


Technical progress:

H. F. Hamann et al. (IBM, 2006) 500 GB cm$^{-2}$!!
Two main families with different crystallization mechanisms:
Ge/Sb/Te (GST) and doped Sb/Te (near eutectic) alloys

**GST:** nucleation from inside bit

**AIST:** growth from crystalline surroundings
Simulation of structural phase transitions:

**Geometric structure:** is a central problem in condensed matter physics, chemistry, biology

“If you want to study function, study structure”


Need a method to calculate energy surfaces $E(R_I)$: $R_I$: ionic positions

- without adjustable parameters (if possible) and for many atoms (100’s to 1000’s), time scales $O(1 \text{ ns})$

**Density functional calculations** of ground state properties (here $E(R_I)$)

**Combination of DF calculations with molecular dynamics** (R. Car and M. Parrinello)

Follow trajectories of ions moving under forces calculated using DF method

**Present limitations of DF calculations:** few hundred atoms, some hundreds of picoseconds
Phase change materials (Ge$_2$Sb$_2$Te$_5$ is prototype): Why is crystallization so rapid?


Model structure for Ge$_1$Sb$_2$Te$_4$: **Wełnic et al.** (2006)
**Ge$_2$Sb$_2$Te$_5$: new experiments (SPring-8):**


JUBL. IBM Blue Gene/L (installed January 2006)
JUGENE. IBM Blue Gene/P (installed 2008, expanded May 2009)

MD/DF possible on PC materials (e.g. Ge$_2$Sb$_2$Te$_5$) with “large” samples over “long” times:
\textbf{Ge}_2\textbf{Sb}_2\textbf{Te}_5: \text{ (material of DVD-RAM)}


- 10\% vacancies
- liquid $\rightarrow$ amorphous transition also metal $\rightarrow$ semiconductor transition
- order-disorder transition (time scale?). Why is it so rapid?

\textbf{Strategy:}

- Simulation of 460 atoms (102 Ge, 102 Sb, 256 Te), 52 vacancies initially in NaCl structure (Na: Te, Cl: random Ge, Sb, vacancies)
- Melt (3000 K), cool to MP (900 K, 42 ps) data collection 21 ps
- Cool to 300 K (139 ps), data collection 21 ps
- Quench using simulated annealing to 100 K (74 ps)

\text{Car-Parrinello method, Pseudopotential: Troullier-Martins,}
\[ E_{xc} : \text{Perdew, Burke, Ernzerhoff (1996), plane wave basis cutoff 20 Ry.)} \]

All components “heavy” elements, relatively compact PW basis,
\textbf{Born-Oppenheimer dynamics} with long time steps (use of predictor-corrector algorithm).

RDF of $\alpha$–GST and $\ell$–GST at 300 K:

Figure 1: Partial RDF of $\alpha$– (thick black) and $\ell$-GST (red). Blue curve and bars are for $\epsilon$-GST at 300 K (with different scale).

GST coordination numbers: Ge: 4.2, Sb: 3.7, Te: 2.9 (cf. “8-N rule”: 4, 3, 2)

Medium- to long-range order of Te atoms in a “disordered” material !!!
Ring configurations in a-GST and a-GeTe at 300 K:

Figure 2: Statistics of irreducible $n$-fold ring configurations of a-GST and a-GeTe at 300 K. Black: corresponding alternating AB configurations ($A$: Ge/Sb, $B$: Te).

Ge$_2$Sb$_2$Te$_5$ simulations:

Evaluate pair correlation functions, structure factors $S(Q)$, diffusion constants, order parameters, ...
Electronic DOS in α-GST (and c-GST):

Figure 3: (a) XPS valence band spectrum of c- (thick black) and α-GST (red lines) [J.-J. Kim et al., Phys. Rev. B 76, 115124 (2007)], upper panel) and the calculated electronic DOS (lower panel). (b) Theoretical DOS of α-GST projected onto atom-centered s-, p-, and d-components and atomic types. (c) DOS difference (α-GST – c-GST, from panel (a)). (d) Electronic DOS of ℓ-GST. The vertical dashed lines mark the Fermi energy.
Problem in DFT/MD simulation

Agreement with diffraction data is insufficient
Problem in RMC simulation

RMC model exhibits a metallic DOS
RMC refined model exhibits very broad bond angle distribution, because RMC produces the most disordered structure consistent with given diffraction data.
New RMC refined model

Agreement with diffraction data is excellent!
We succeeded to constrain the peak width of bond angle distribution in the RMC refinement.

BAC: Bond angle constraints
DOS of new RMC refined model

New RMC refined model has a band gap!

Panasonic BD-RE (2010-11) Ge$_x$Sb$_y$Te$_z$: 100 GB φ 120 mm

Fig. 2 Compositional dependence of phase-change properties along GeTe-Sb$_2$Te$_3$ tie line

Fig. 3 Compositional dependence of crystal-crystal phase-transition temperature, Tc, on the increased Sb$_2$Te$_3$ concentration, 1/(1+x). (the original figure is from the reference[4].)

Liquid $\text{Ag}_{3.5}\text{In}_{3.8}\text{Sb}_{75.0}\text{Te}_{17.7}$ (AIST) simulations: (DVD-RW)

Left: (Ag: silver, In: magenta, Sb: blue, Te: yellow)

- medium-range order present
- Ag and In prefer to be near Te rather than Sb
- Ag atoms are the most mobile, have the shortest bonds and highest coordination number, and are anionic,
- In bonds to Sb and Te are longer and more flexible than those with Ag

Two main families with different crystallization mechanisms: Ge/Sb/Te (GST) and doped Sb/Te (near eutectic) alloys

**GST:** nucleation from inside bit

**AIST:** growth from crystalline surroundings
AIST Simulations: 640 atoms, ca. 200 ps

Experimental: XRD, EXAFS, XPS (SPring-8)

T. Matsunaga et al. *Nature Materials* DOI: 10.1038/NMAT2931 (online 9 January 2011)
Proposed crystallization mechanism in AIST:

**Bond exchange model:** exchange of short Sb-Sb bonds with longer Sb-Sb bonds
Differences between crystallization in GST and AIST familes:
Progress:

- Identification of basic structural unit in GST, GeTe, .. (“ABAB squares”)
- Order (medium- to long-range) in “disordered” materials (Te, cavities)
- Vibrational and electronic structure
- Eutectic structure ($\text{Ge}_{15}\text{Te}_{85}$): Corner and edge-sharing $\text{GeTe}_4$ units
- Role of cavities
- $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ Blu-ray Disc (BD) [630 atoms], remarkable similarities to $\text{Ge}_2\text{Sb}_2\text{Te}_5$
- Need “large” simulations (identify “order”, role of cavities, .. )
- Need “long” simulations (increasing order, decreasing number of “wrong bonds”, AIST (DVD-RW) [640 atoms, liquid, amorphous] “Bond exchange” model
- Comparison of “as-deposited” and “melt-quenched” structures [Phys. Rev. B (2011, accepted)]

Other systems:

- Te (with several functionals) [343 atoms]
- Role of different functionals: PBE, PBEsol, TPSS, ...