Atomistic simulations of phase change materials for data storage

Marco Bernasconi

Department of Materials Science
University of Milano-Bicocca, Milano, Italy
Phase Change Materials for electronic and optical data storage

Optical data storage: DVD

Electronic non-volatile memory: Phase Change Memory Cell

Chalcogenides alloys \( \text{Ge}_2\text{Sb}_2\text{Te}_5 \) (GST), \( \text{GeTe} \)

fast and reversible change between crystalline and amorphous phases (50 ns)
Phase change Materials

Two states system $\rightarrow$ possibility of storing a “0” or “1” bit

Large difference in properties between the two phases
  (crystal - metallic  amorphous - semiconducting)

  Resistivity changes by 3 orders of magnitude $\rightarrow$ PCM

Reflectivity change 30 %: $\rightarrow$ optical storage (DVD)

Transition induced by heating (Joule or laser irradiation)
The Phase–Change memory cell

Schematic representation

SEM cross section

- Active region: a small drop within GST film undergoes the phase transition
- Phase–change by heating via Joule effect

Concept first proposed by Ovshinsky in 1968
**I(V) characteristic: threshold switching behavior**

- cell readout: performed at low bias ($V<V_{th}$)
- set/reset: bias higher than threshold ($V>V_{th}$)

- **RESET**:
  - higher current & shorter pulse
  - crystal $\rightarrow$ amorphous

- **SET**:
  - lower current & longer pulse:
  - amorphous $\rightarrow$ crystal

**Diagram:**
-RESET pulse
-SET pulse
-READ

**Graph:**
- Current [mA] vs. Voltage [V]
- Set points: ON, OFF, $V_{th}$
- Amorphous and Crystalline states
## PCM performances

<table>
<thead>
<tr>
<th></th>
<th>DRAM</th>
<th>NOR Flash</th>
<th>NAND Flash</th>
<th>PCM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell Area</td>
<td>$6F^2$</td>
<td>$10F^2$</td>
<td>$5F^2$</td>
<td>$16F^2$</td>
</tr>
<tr>
<td>Read Time</td>
<td>$&lt;10$ ns</td>
<td>10ns</td>
<td>50ns</td>
<td>60ns</td>
</tr>
<tr>
<td>Write/Erase Time</td>
<td>$&lt;10$ ns</td>
<td>1μs / 10 ms</td>
<td>1ms / 0.1 ms</td>
<td>50 ns / 120 ns</td>
</tr>
<tr>
<td>Retention Time</td>
<td>64 ms</td>
<td>$&gt; 10$ years</td>
<td>$&gt; 10$ years</td>
<td>$&gt; 10$ years</td>
</tr>
<tr>
<td>Write Cycles</td>
<td>$&gt; 10^{16}$</td>
<td>$10^5$</td>
<td>$10^5$</td>
<td>$10^9$</td>
</tr>
<tr>
<td>Write Operating Voltage</td>
<td>2.5V</td>
<td>12V</td>
<td>15V</td>
<td>3V</td>
</tr>
<tr>
<td>Read Operating Voltage</td>
<td>1.8V</td>
<td>2V</td>
<td>2V</td>
<td>$&lt; 3V$</td>
</tr>
<tr>
<td>Multiple-bit Operation</td>
<td>No</td>
<td>In production</td>
<td>In production</td>
<td>Research phase</td>
</tr>
</tbody>
</table>

PCM show higher speed and better scalability than Flash

**Goal:** Universal Memory
PCM faster and with better scalability than Flash

April 2010

Nunonyx (now bought by Micron) commercialized 90 nm PCM device
Research center based in Agrate Brianza (Milano-Italy)

July 2012

Micron: 45 nm devices in production (Agrate)

January 2013

Nokia Mobile phone Asha with Micron PCM inside
Neuromorphic Computing

PCM realization of spike-timing-dependent plasticity

Open issues

• Structure of the amorphous phase
• Origin of optical contrast amorphous vs crystal
• Origin of resistivity contrast
• Origin of electronic switch in the amorphous
• Mechanism of phase change

Wuttig and Yamada, Nat. Mat. 6, 824 (2007)
GST crystalline phase: Rocksalt

- NaCl-type

$\text{Ge}_2\text{Sb}_2\text{Te}_5$

- One sublattice fully occupied by Te
- The other randomly occupied by Ge, Sb and 20% vacancies
- Octahedral environment each atom 6-fold coordinated

Metastable phase: transition to hexagonal structure at ~250 °C
Ab-initio models of amorphous GST

Model of amorphous GST generated by quenching from the melt in ab-initio molecular dynamics

• Caravati, Bernasconi, Kühne, Krack, and Parrinello, Appl. Phys. Lett. 91, 171906 (2007)

• Akola and Jones, Phys. Rev. B 76, 235201 (2007)


Phase Change Materials from First Principles

- First principles molecular dynamics simulations
- Density Functional Theory (GGA-PBE + pseudopotentials)
- Code Quickstep, open source CP2K project [www.cp2k.org](http://www.cp2k.org)
  Basis sets: Gaussian (wavefunctions) + plane waves (elec. density)

  Second generation Car-Parrinello method
  Factor 25 speed up with respect to conventional BO-MD CP2K
  (Kühne, Krack, Mohamed, Parrinello, PRL 2007)

  270-500 atoms, quenching from the melt in 80-100 ps
Coexistence of octahedra and tetrahedra in amorphous PCM

(defective) octahedral Ge, Sb and Te

4–coor Ge

3–coor Te

tetrahedral
4–coor Ge, 25 %
agreement with EXAFS
Kolobov et al, Nat. Mat 2004

3+1 coordination

→ p-bonding
dative bond by lone pair of Te

4–coor Sb

sp³ bonding
s + p valence states

Caravati, Bernasconi, Kuhne, Krack, Parrinello, APL 2007
Dative bonds

p-like bonding

Dative bonds from lone pairs of Te to Ge atoms in pyramids and defective octahedra
Tetrahedral Ge: vibrational fingerprint

Amorphous GeTe: Raman spectrum (Bond Polarizability Model)


Mazzarello, Caravati, Angioletti, Bernasconi, Parrinello
Electronic properties

Electronic Density of States very similar in amorphous and crystalline phases

Theory

Exp. Photoemission
J-J. Kim et al, PRB 07

Optical Tauc gap:

- c-GST → 0.5 eV
- a-GST → 0.7 eV
GST stoichiometric crystal is semiconducting

Electronic properties: cubic crystal

Ge/Sb deficiency: → holes in VB
Ge/Sb excess: → electrons in CB

HSE hybrid functional

Degenerate p-type semiconductor due to Sb/Ge deficiency
Electronic Properties
Non-stoichiometric GST: amorphous phase

Crystal can be doped
Amorphous can not

This explains electronic contrast (PCM)

Ge excess, Sb deficiency  →  \( E_f \) at midgap

Pinning of $E_F$ at midgap in amorphous

Huang and Robertson
PRB 85, 125305 (2012)

negative U states, e.g. valence alternation pairs as in $\text{As}_2\text{Se}_3$?
Optical contrast between amorphous and crystal

**GaAs**

**Ge$_2$Sb$_2$Te$_5$**
Optical contrast in PCM due to change in optical matrix elements

\[ \varepsilon_2(\omega) = \frac{8\pi^2}{3V_o N_k \omega^2} \sum_{v,c,k} |\langle c, k | p | v, k \rangle|^2 \delta(\omega - E_{c,k} + E_{v,k}) \]

Joint Density of States (valence-conduction) weighted by optical matrix elements

Shportko, et al., Nat. Mat. 2008
Huang and Robertson, PRB 2010
Welnic, Botti, Reining, Wuttig, PRL 2007
Optical contrast in PCM

\[ \epsilon_2(\omega) \text{ dielectric function in RPA with hybrid functional HSE} \]

Exp. (Welnic 2007; Shportko 2008)

Exp. (Welnic 2007; Orava 2008)

Caravati, Bernasconi, Parrinello
Angular disorder in p-bonds in amorphous phases decrease of the optical matrix elements optical contrast

This explains why DVDs work

(Huang and Robertson PRB 2010)
Open issues

- Structure of the amorphous phase
- Origin of resistivity contrast
- Origin of optical contrast

Origin of high crystallization speed

large simulations cells and long simulations time needed!
Large scale atomistic simulations of PCM

DFT results as database to develop interatomic potentials based on Neural Network to simulate $10^4$ atoms for 10 ns

(Behler and Parrinello PRL 2007)

already applied to elemental carbon, silicon, sodium, copper, ZnO
Neural Networks - Symmetry Functions

Total energy as sum of atomic energies \( E = \sum_i E_i \)

\[
E_i = F(\{G(\vec{r})\})
\]

Symmetry functions \( \{G\} \): information on local atomic environment up to a certain cutoff radius

\( F \) is EXTREMELY complicated, but analytic!

Input numbers: functions of atomic positions (symmetry functions)
Some manipulations: linear and non-linear combinations of input numbers
Output number: energy of the input configuration
Neural Networks - The algorithm

A (VERY) simple example:

\[ E_{\text{atom}} = f_1^2 \left( b_1^2 + \sum_{j=1}^{3} a_{j1} \cdot f_j^1 \left( b_j + \sum_{i=1}^{2} G_i \cdot a_{ij}^0 \right) \right) \]

\( a_{ij}, b_{ij} = \) fitting parameters
\( G_i = \) Symmetry Functions
\( f_{ij} = \) Activation Functions

\[ \sum \rightarrow \text{Total energy!} \]
Neural Network: liquid GeTe

pair correlation functions

NN: 4096-atom cell

Sosso, MB, et al. PRB 2012

Diffusion coefficient

D= 4.29 $10^{-5}$ cm$^2$/s

(DFT 4.29 $10^{-5}$ cm$^2$/s)

NN potential depends on 8000 parameters fitted on DFT energies of 30000 models (64-, 128-atoms)
Crystallization of supercooled liquid GeTe

Radius of a crystalline nucleus as a function of time
4096-atom cell of GeTe with NN potential

Speed of crystal growth

\[ u = u_{\text{kin}} \left(1 - e^{-\frac{\Delta \mu}{kT}}\right) \]

\[ \Delta \mu(T) = \frac{\Delta H(T_m - T)}{T_m} \frac{2T}{(T_m + T)} \]

\[ \Delta H = 0.188 \text{ eV/atom} \]

\[ E_a = 0.26 \text{ eV (0.30 eV from D self-diffusion coeff.)} \]
Crystal growth velocity

\[ u = u_{\text{kin}}(1 - e^{-\frac{\Delta \mu}{kT}}) \quad u_{\text{kin}} = \gamma \frac{4D}{\lambda} \]

\[ \lambda \sim 3 \, \text{Å} \quad \Rightarrow \quad \gamma = 0.9 \pm 0.2 \]

Consistent with classical nucleation theory

structural (Ge-Ge bonds) and dynamical heterogeneity \( \rightarrow \)
breakdown of Stokes-Einstein relation / liquid fragility \( \rightarrow \)
high mobility at high supercooling \( \rightarrow \)
large crystal growth velocity

Ultrafast DSC (10^4 K/s)

Orava, Greer et al., Nat. Mat. 11, 279 (2012)

Ge_2Sb_2Te_5
Coworkers


PSI-Villigen: M. Krack

Aachen University: R. Mazzarello

Bochum University: J. Behler

Mainz University: T. Kühne

ETH, Zurich: J. Colombo, E. Del Gado, M. Parrinello

Experimental colleagues at Micron (Agrate-Brianza)