A Map for Phase-Change Materials

Invited talk at the IEEE Nano Symposium on "Emerging Non-volatile Memory Technologies" in Santa Clara, CA, USA

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Why are people interested in phase change materials?

Application in memory devices

Unique physics
- (meta-)stable in amorphous and crystalline state
- very fast phase transitions
- strong property contrast between both states
- unusual electronic behavior
Switching principle of phase change materials

Power

Resistivity

Temperature

Time

Crystallization

Amorphization

Regime of fast crystallization

Tm

T1

T2
Relevant scientific questions

Why is there such a strong property contrast between amorphous and crystalline phase?
⇒ physics of bonding

How do switching times depend on structure size and pulse parameters?
⇒ crystallization kinetics

How does the electronic excitation of the material work?
⇒ electronic properties

The ultimate question:
How does all this change upon a variation of composition?

How is the amorphous phase stabilized against crystallization at moderate temperatures?
⇒ physics of glass formation
Overview

Introduction

Part 1: Crystallization kinetics
- Viscosity and glass formation
- Crystallization speed
- Distinction between nucleation and growth

Part 2: Physics of bonding

Part 3: Compositional trends

Part 4: Electronic behavior
What drives crystallization?

- System minimizes Gibbs free enthalpy in equilibrium
- Crystallization is not favorable above $T_m$
- Crystalline state is favored below $T_m$
- $\Delta G_V$ is driving force

However, the system is hindered from following the thermodynamic driving force by a limited atomic mobility. (Locally there must be an activation barrier, otherwise it would just crystallize immediately)
Connection between crystallization speed and viscosity

How is a glass formed?

How does this influence crystallization?

\[ \text{temperature} \uparrow = \text{viscosity} \downarrow = \text{atomic mobility} \uparrow = \text{crystallization rate} \uparrow \]
Crystallization – a kinetic process

Temperature $T / \text{K}$

<table>
<thead>
<tr>
<th>$10^9$</th>
<th>$10^8$</th>
<th>$10^7$</th>
<th>$10^6$</th>
<th>$10^5$</th>
<th>$10^4$</th>
<th>$10^3$</th>
<th>$10^2$</th>
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<td>1000</td>
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Time $t / \text{s}$

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Liquid

Crystalline

Amorphous

300
400
500
600
700
800
900
1000

Temperature $T / \text{K}$

Time $t / \text{s}$

10% crystalline

90% crystalline

10 yrs.

Liquid

Crystalline

Amorphous

Atomic mobility

Driving force

Liquid

Crystalline

Amorphous

10% crystalline

90% crystalline

10 yrs.

Temperature $T / \text{K}$

Time $t / \text{s}$

10% crystalline

90% crystalline

10 yrs.

Temperature $T / \text{K}$

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Temperature $T / \text{K}$

Time $t / \text{s}$

10% crystalline

90% crystalline

10 yrs.
Connection between crystallization speed and viscosity

How is a glass formed?

viscosity $\eta$ drops at glass transition

How does this influence crystallization?

$\log_{10}(\eta)$ in 1/Poise

$1/(k_B T)$ in 1/eV

Definition of fragility: steepness of temperature dependence of viscosity at glass transition temperature

$$m = \frac{\partial \log_{10} \eta(T)}{\partial \left( \frac{T_g}{T} \right)}$$

$T = T_g$
Using ultra-fast calorimetry, Greer et al. found a strong deviation from Arrhenius behavior in Ge$_2$Sb$_2$Te$_5$ at high temperatures:

High fragility => pronounced increase of crystallization speed above glass transition temperature.
Measuring fast crystallization by laser heating

Reflectivity change upon recrystallization of a melt-quenched amorphous mark:

Transmission Electron Microscopy on Ge$_{15}$Sb$_{85}$: evidence for formation of multiple crystallites in one laser spot
Formation of critical nuclei

Consider interfacial energy!

$$\Delta G_{cluster}(r) = \frac{4}{3} \pi r^3 \Delta G_V + 4\pi r^2 \sigma$$

$$r_c = -\frac{2\sigma}{\Delta G_V}$$

$$\Delta G_c = \frac{16\pi}{3} \frac{\sigma^3}{(\Delta G_V)^2}$$
Nucleation and growth: AgInSbTe

Dimensions: 3 µm by 3 µm. Anneal temperature: 160°C (DSC furnace). Film thickness: 30 nm.

AFM scans on AgIn-Sb2Te: Crystals (dark) are visible in amorphous surrounding (bright).

Direct measurement of growth velocity and nucleation rate at a certain temperature
Why is it important to be aware of nucleation and growth?

How long does it take to crystallize a certain volume?
How does it crystallize?

=> It depends on the material.

Often materials with high nucleation rates were chosen for faster crystallization.
Why is it important to be aware of nucleation and growth?

How long does it take to crystallize a certain volume?

How does it crystallize?

The smaller the volume the more growth dominated it will crystallize.

=> It depends on the size.

For electronic memory: materials with low nucleation rates can be good candidates, since crystal growth velocities become crucial for switching speeds.

“growth dominated”

“nucleation dominated”
Crystallization kinetics in electronic memory


- Reduction of switching time by reduction of amorphous volume
- ...as expected for growth dominated crystallization

**Extremely fast switching speeds!**

**In the range of DRAM, but non-volatile!**
Reduction of energy per switching event

Electrical pulses shorter and with lower amplitude => lower energy consumption

less material to be heated up = less power necessary

scaling down device size => reduction of power consumption
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Measurement of FTIR reflectance

layer stack:
1. substrate
2. gold layer
3. material under investigation

Analysis: model dielectric function

$$\varepsilon(\omega) = \varepsilon_{\text{const}} + \varepsilon_{\text{Drude}}(\omega) + \varepsilon_{\text{Tauc-Lorentz}}(\omega)$$
Modeling dielectric function

What is the origin of this polarizability enhancement?
‘Resonance bonding’ in the crystalline phase

- with $N_{sp} \sim 5$ resp. $N_p \sim 3$
- octahedral coordination $\sim 6$ bonds
- covalent bonding, but unsaturated bonds
- prototype: GeTe

Strong coupling between phonons and electronic states
→ Large Born effective charges $Z_T$
→ Large value of dielectric constant $\varepsilon_{\infty}$

resonant bonding relies on long-range order, only feasible for crystalline phase
→ contrast

Resonance bonding (delocalized bonds) = groundstate $\psi$ (unsaturated bonds)
is superposition of saturated bond-configurations $\Phi_x$

$\psi = \frac{1}{(1 + \alpha^2)^{1/2}} (\Phi_I + \alpha \Phi_{II})$

mixing coefficient $\alpha$

Pauling, Nature of Chemical Bond (Cornell Univ. Press, NY, 1939)
Lucovsky and White, Phys. Rev. B, Vol. 8, Nr. 2 (1973)
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Impact of local distortions

Static local distortion (Peierls)

Model potential:
\[ V(x) = a x^2 + b x^4 \]

None or strong distortions:
~ harmonic behaviour

Slight distortions:
pronounced anharmonicity
flat, 'box-like' potential
large atomic fluctuations
(~ Debye-Waller factor)
possibly enabling fast kinetics

What materials have such slightly distorted structures?


Classification of structures based on valence radii

**FIG. 2.** Electronegativity difference versus average hybridization for the $A^N B^{8-N}$ binary compounds.

- Simons and Bloch, Phys. Rev. B Vol. 7 Nr. 6 (1973)
- St. John and Bloch, PRL Vol. 33 Nr. 18 (1974)

Introduce coordinates for a map for PCMs

Littlewood:

\[
\begin{align*}
    r'_{\sigma} &= r^A_p - r^B_p, \\
r_{\pi}^{-1} &= \left[ \left( r^A_p - r^A_s \right) + \left( r^B_p - r^B_s \right) \right]^{-1}.
\end{align*}
\]

Generalization for non-binaries:

\[
\begin{align*}
    r'_{\sigma} &= \left( \frac{\sum_i n_i r_{p,i}}{\sum_i n_i} \right) - \left( \frac{\sum_j n_j r_{p,j}}{\sum_j n_j} \right), \\
r^{-1}_{\pi} &= \left[ \left( \frac{\sum_i n_i (r_{p,i} - r_{s,i})}{\sum_i n_i} \right) + \left( \frac{\sum_j n_j (r_{p,j} - r_{s,j})}{\sum_j n_j} \right) \right]^{-1}.
\end{align*}
\]

two coordinates:

based on valence radii of s- and p-orbitals derived from pseudopotential calculations

ionicity ~ size difference
hybridization ~ s-p-splitting

treat materials as effective binaries

average cations = A
average anion = B

St. John and Bloch, PRL Vol. 33 Nr. 18 (1974)
3.4 A Map for Phase-Change Materials

Figure 1:

Shown is the empiric map for materials with about three p-electrons per lattice site and approximately even numbers of anions and cations. The axes that span the map are the tendency towards hybridization, $r_{\pi}^{-1}$, and the ionicity, $r'_{\sigma}$, both defined in the text.

The coordinates of a large number of materials have been calculated (see Chapter C for a table of materials that for clarity cannot be labeled here). Phase-change materials (indicated by green circles) are located within a small region of the map that is prone to the occurrence of resonant bonding. The graphs on the outside illustrate the weakening of resonance effects as one leaves this region due to the formation of less, more saturated covalent bonds via distortions or due to charge localization at the ions due to increasing ionicity.
Map for phase change materials (zoomed in)

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Crystallization kinetics is already extremely sensitive to temperature

But in phase-change materials an additional strong non-linearity is active …
Threshold switching: field dependent

Linear dependence $\Rightarrow$ existence of a threshold field

Offset $\Rightarrow$ interface effect with electrode material

<table>
<thead>
<tr>
<th>Material</th>
<th>Threshold Field (V/µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge$<em>{15}$Sb$</em>{85}$</td>
<td>8.1 ± 0.2</td>
</tr>
<tr>
<td>AIST</td>
<td>19 ± 1</td>
</tr>
<tr>
<td>doped Ge$<em>{15}$Sb$</em>{85}$</td>
<td>20 ± 2</td>
</tr>
<tr>
<td>Ge$<em>{15}$Te$</em>{85}$</td>
<td>38 ± 3</td>
</tr>
<tr>
<td>Ge$_2$Sb$_2$Te$_5$</td>
<td>56 ± 2</td>
</tr>
<tr>
<td>4 nm thick Sb</td>
<td>94 ± 9</td>
</tr>
</tbody>
</table>
Conclusion on voltage-time-dilemma in phase change materials

Crystallization kinetics strongly thermally activated

Heating strongly dependent on electrical threshold switching

Extreme non-linearity of voltage and time
Thank you for your attention!

Jülich Aachen Research Alliance – Fundamentals of Future Information Technologies

Questions?
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