# A Map for Phase-Change Materials

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

> April, 6th 2012 Martin Salinga



# Why are people interested in phase change materials?

# Application in memory devices





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# **Unique physics**

- (meta-)stable in amorphous <u>and</u> crystalline state
- very fast phase transitions
- strong property contrast between both states
- unusual electronic behavior



# Switching principle of phase change materials



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# **Relevant scientific questions**

Why is there such a strong property contrast between amorphous and crystalline phase?

 $\Rightarrow$  physics of bonding

How does the electronic excitation of the material work?

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⇒ electronic properties >



# **Overview**

Introduction

# Part 1: Crystallization kinetics

- Viscosity and glass formation
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- Distinction between nucleation and growth

Part 2: Physics of bonding

Part 3: Compositional trends

Part 4: Electronic behavior





- System minimizes Gibbs free enthalpy in equilibrium
- Crystallization is not favorable above T<sub>m</sub>
- Crystalline state is favored below T<sub>m</sub>
- $\Delta G_{\rm V}$  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)



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### How is a glass formed?



How does this influence crystallization?

temperature $\uparrow$  = viscosity $\downarrow$  = atomic mobility $\uparrow$  = crystallization rate6/IV/2012M. SalingaIEEE Nano Symposium 20127

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# **Crystallization – a kinetic process**



# **Connection between crystallization speed and viscosity**



#### M. Wuttig and M. Salinga, Nature Materials 11, 270–271 (2012); M. Salinga, PhD thesis RWTH Aachen (2008)

# Fragility

Using ultra-fast calorimetry Greer et al. found a strong deviation from Arrhenius behavior in  $Ge_2Sb_2Te_5$  at high temperatures:





High fragility => pronounced increase of crystallization speed above glass transition temperature

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# Measuring fast crystallization by laser heating

M. Salinga PhD Thesis, RWTH Aachen (2008)

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Transmission Electron Microscopy on Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>: evidence for formation of multiple crystallites in one laser spot

# Consider interfacial energy!



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# Nucleation and growth: AgInSbTe

#### J. Kalb, PhD Thesis, RWTH Aachen (2006)



5 min

7 min

9 min

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

Dimensions: 3  $\mu$ m by 3  $\mu$ m. Anneal temperature: 160°C (DSC furnace). Film thickness: 30 nm.

# **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.

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# Why is it important to be aware of nucleation and growth?



#### $2.3 \pm 0.7 \text{ M}\Omega$ $4.2 \pm 0.5 \text{ M}\Omega$ $5.2 \pm 0.7 \text{ M}\Omega$ $6.2 \pm 1.0 \text{ M}\Omega$ 10<sup>7</sup> 0.1 D Crurent in mA 8.0 C 0.4 O 10<sup>6</sup> Ц **Reduction of** switching time by .⊆ 0 reduction of Resistance 2.2 10<sup>5</sup> Voltage in V 0.1 0.1 0 0 0 amorphous volume ...as expected for growth dominated **10<sup>4</sup>** crystallization 0.6 16 64 16 64 4 64 6 64 4 16 4 4 Top electrode Pulse Length in ns current $\mathbf{0}$ Extremely fast switching speeds! In the range of DRAM, SiO<sub>2</sub> but non-volatile! voltage Bottom electrode

**Crystallization kinetics in electronic memory** 

G. Bruns et al., Applied Physics Letters 95, 043108 (2009)

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# **Reduction of energy per switching event**

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



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### **Measurement of FTIR reflectance**

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### **Modeling dielectric function**



# 'Resonance bonding' in the crystalline phase

K. Shportko et al., Nature Materials 7, 653-658 (Aug. 2008)

- with  $N_{sp} \sim 5$  resp.  $N_p \sim 3$
- octahedral coordination ~ 6 bonds
- covalent bonding,

but unsaturated bonds

- prototype: GeTe

- Strong coupling between phonons and electronic states
- $\rightarrow$  Large Born effetive charges  $Z_{T}$
- $\rightarrow$  Large value of dielectric constant  $\varepsilon_{\!\scriptscriptstyle\infty}$

resonant bonding relies on long-range order, only feasible for crystalline phase  $\rightarrow$  contrast

# **Resonance bonding (delocalized bonds)**

- = groundstate  $\psi$  (unsaturated bonds) is superposition
- of saturated bond-configurations  $\Phi_{x}$

groundstate  $\psi$ 



# mixing coefficient $\alpha$

Pauling, Nature of Chemical Bond (Cornell Univ. Press, NY, 1939) Lucovsky and White, Phys. Rev. B, Vol. 8, Nr. 2 (1973)
Littlewood and Heine, J. Phys. C.: Solid State Phys. Vol. 12 (1979) Littlewood, J. Phys. C.: Solid State Phys. Vol. 12 (1979) Robertson et al, Thin Solid Films 515, 7538–7541 (2007).

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# Impact of local distortions

# Static local distortion (Peierls)



=> reduced resonance bonding effects







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?

Matsunaga and Yamada, JJAP 43, 4704-4712 (2004)

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# **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)



Figure 1. St John-Bloch plot for the IV–VI compounds and group V elements, using the bond orbital coordinates  $r'_{\sigma}$  and  $r_{\pi}^{-1}$  (equations (1.3) and (1.5)), calculated from the orbital radii of Chelikowsky and Phillips (1978). Increasing ionicity is measured by  $r'_{\sigma}$ , and increasing covalency by  $r_{\pi}^{-1}$ .

Littlewood, J. Phys. C.: Solid St. Phys. 13 (1980) Littlewood, CRC Critical Reviews in Solid State and Material Sciences Vol. 11, 3 (1985)

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D. Lencer, M. Salinga, et al., Nature Materials 7, 972-977 (Dec. 2008)

Littlewood:

$$r_{\sigma}' = r_p^{\mathrm{A}} - r_p^{\mathrm{B}},$$
$$r_{\pi}^{-1} = \left[ \left( r_p^{\mathrm{A}} - r_s^{\mathrm{A}} \right) + \left( r_p^{\mathrm{B}} - r_s^{\mathrm{B}} \right) \right]^{-1}$$

Generalization for non-binaries:



two coordinates:

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

ionicity ~ size difference hybridization ~ s-p-splitting

treat materials as effective binaries

average cations	=	Α
<sup></sup> average anion	=	В

St. John and Bloch, PRL Vol. 33 Nr. 18 (1974) Littlewood, J. Phys. C.: Solid St. Phys. 13 (1980) Phillips, Solid. State. Communications Vol. 22 (1977) Chelikowsky and Phillips, Phys. Rev. B Vol. 17 Nr. 6 (1978)

# Map for phase change materials

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# Map for phase change materials (zoomed in)

D. Lencer, M. Salinga, et al., Nature Materials 7, 972-977 (Dec. 2008)



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# Voltage-time-dilemma

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Driving force

0.25

 $\Delta G / H_{f}$ 



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0.50

RHEINISCH-WESTFÄLISCHE TECHNISCHE HOCHSCHULE AACHEN I. PHYSIKALISCHES INSTITUT (IA) : PHYSIK NEUER MATERIALIEN



# **Threshold switching: field dependent**

D. Krebs et al., Applied Physics Letters 95, 082101 (2009)



# 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

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# Thank you for your attention!

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