# Simulations of PCM crystallization and heterostructures with graphene

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# **Overview**

Phase-change materials (PCM):



VOUTO UNU OUT EEU









# **PCM diagram**

#### Chalcogenide alloys

- Three phases: amorphous, metastable and stable crystalline (with optical contrast and changes in resistivity)
- Ultra-fast phase transition (time scale 1-100 ns)
- Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> was invented 1987

   → DVD-RAM; Ag/In-doped Sb<sub>x</sub>Te (AIST) compounds are used for DVD±RW
- Emerging applications in nonvolatile computer memory, phase-change RAM (PRAM)





# Our previous work on PCMs: Structure

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 10

 2012
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J. Akola and R. O. Jones

From local structure to nanosecond recrystallization dynamics in AgInSbTe phase-change materials

Toshiyuki Matsunaga<sup>1,2</sup>, Jaakko Akola<sup>3,4,5</sup>, Shinji Kohara<sup>2,6</sup>, Tetsuo Honma<sup>6</sup>, Keisuke Kobayashi<sup>7</sup>, Eiji Ikenaga<sup>6</sup>, Robert O. Jones<sup>3,8</sup>, Noboru Yamada<sup>1,2</sup>\*, Masaki Takata<sup>2,6,9,20</sup> and Rie Kojima<sup>1</sup>

Phase-change optical memories are based on the autonishingly rapid nanoworond scale crystallization of nanosized anorphous 'marks' in a polytrystalline layer. Models of crystallization exist for the commarcially used phase-change alloy Ge, Sb, Te, (GST), but not for the opasity important class of Sb-Te-based alloys. We have combined X-ray diffraction, extended X-ray absorption fine structure and hard X-ray photoelectron spectroscopy experiments with density functional simulations to determine the crystallies and anorphous structures of Ag, alm, sSb, alloy, a Sb, allows mainly small rings and cavities. The local environment of Sb in both forms of AlST is a distorted 3 + 3 actabulan. These structures suggest a bond-interchange model, where a sequence of small displacements of Sb atoms accompanied by interchanges of short and long bonds is the origin of the rapid crystallization of a AIST. It differs performing these companies by interchanges of short and long bonds is the origin of the rapid crystallization of a AIST. It differs performing them or cytallization is a-GST.

T. Matsunaga, J. Akola, S. Kohara et al., Nature Materials **10**, 129 (2011). J. Akola and R.O. Jones, phys. stat. sol. (b) **249**, 1851 (2012).

#### Other crystallization simulations of GST-225 and GeTe:

• Loke *et al.*, Science **336**, 1566 (2012)

ARTICLES

• Sosso *et al.*, J. Phys. Chem. Lett. **4**, 4241 (2013)



nature

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## **Collected ideas**

# Image: state stat

AIST









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#### AIST (Group 2)

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GST (Group 1)



#### BUT: No atomic diffusion here!

T. Matsunaga, J. Akola, S. Kohara *et al.*, Nature Materials **10**, 129 (2011).

# **Simulation method**

- DFT and molecular dynamics (MD) → atomic and electronic structure, dynamics
- CPMD program package (<u>www.cpmd.org</u>)



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- Born-Oppenheimer MD driver, thermostat, predictor-corrector algorithm
- Scalar-relativistic TM91 pseudopotentials,<sup>1</sup> plane wave basis set
- **PBEsol**<sup>2</sup> for the exchange-correlation energy functional
- Amorphous structures from previous work;<sup>3,4</sup> melt-quench down to 300 K (460 atoms) and computer-aided deposition at 300 K (648 atoms)
- Crystallization simulations for systems of 460 and 648 atoms at 500, 600 and 700 K; individual process duration up to 8. ns.
- Massively-parallel simulations on IBM Blue Gene/Q (JUQUEEN) and Intel Xeon 5570 (JUROPA) supercomputers in FZ Jülich

<sup>1</sup>N.L. Troullier and J.L. Martins, PRB **43**, 1993 (1991). <sup>2</sup>J.P. Perdew et al., PRL **100**, 136406 (2008).

<sup>3</sup>J. Akola and R.O. Jones, PRB **83**, 094113 (2007)

<sup>3</sup>J. Akola and R.O. Jones, PRB **83**, 094113 (2007)



Y OF TECHNOLOGY <sup>4</sup>J. Akola, J. Larrucea, and R.O. Jones, PRB **76**, 235201 (2011).

# **Order parameter**



#### How to define "crystalline" atoms?

Order parameter by Steinhardt *et al.* uses **spherical harmonics** to calculate the relative angles of bonds.

$$\bar{Q}_{l}(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |\bar{Q}_{lm}(i)|^{2}}, \qquad \bar{Q}_{lm}(i) = \frac{1}{N_{b}(i)} \sum_{k=0}^{N_{b}(i)} Q_{lm}(k),$$
$$Q_{lm}(i) = \frac{1}{N(i)} \sum_{j=1}^{N(i)} Y_{lm}(\vec{r}_{ij}),$$

 $Y_{lm}$  is spherical harmonics function of the unit vector from atom *i* towards atom *j*.  $N_b(i)$  is the number of atoms neighboring atom *i* plus one and the *k* sum runs over atom *i* and its neighbors while the *j* sum runs over the neighbors only.

The order parameter effectively takes into account the local environment up to the second coordination shell.

P.J. Steinhardt, D.R. Nelson and M. Ronchetti, PRB 28, 784 (1983).



# Crystallization of $Ge_2Sb_2Te_5$ with a cubic seed of 58 atoms, T=600 K





# Energetics, local order, rings

- Clear correlation between energy, order parameter and ABAB ring growth
- Crystallization: 600 and 700 K (460 atoms)
- Some sudden jumps caused by changing cell size
- 460-atom 500 K and 648-atom 600 K simulations show early signs of crystallization







600 K: 100 ps



600 K: 200 ps



600 K: 300 ps



600 K: 400 ps



600 K: 500 ps

## **Electronic density of states (DOS)**



# **Crystallization** without "seed"

- Amorphous starting structure, memory-effect (dissolved seed)
- 460 atoms
- T = 600 K, "*run0*"
- Simulation time: 1.25 ns





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# **Cavities and percolation**

Amorphous starting structure, *memory-effect* due to dissolved seed  $\rightarrow$  crystallization occurs in 1.25 ns







Crystallization starts immediately  $\rightarrow$  memory!

Percolation continuous in all directions after 750 ps (~40% of atoms)

Cavities "transform" to vacancies



# Wrong bonds



T = 600 K, no seed



- Final structure comprises few wrong bonds
- Tetrahedral Ge atoms in marginal role (only few)
  - Vacancies randomly distributed
- Relative fraction of
   Te sites surrounded
   by N vacancies
   → experiments





Ν	0	1	2	3	4
NMR (%)	26.2	39.3	24.6	8.2	1.5
DF/MD (%)	24.2	38.7	25.8	10.9	0.4

S. Sen et al., Phys. Rev. Lett. 108, 195506 (2012).

# Three other runs: stochastic nature



run2: Nucleus of ~200 atoms





run1

run2

run3

#### run3: 1.25 ns and 2.94 ns



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## **Three other runs: nuclei sizes**



Note: Same initial structure and temperature, different initial velocities!

- Crystal growth directions differ from the unit cell axes
- Two nuclei clash in *run1* → temporary blocking of each other
- run2 proceeds fast once percolation sets in + no clash

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• Subcritical nuclei (before 1.5 ns) and three largest cluster sizes

• Interface between the two largest clusters fluctuates  $\rightarrow$  merging ON/OFF

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## **Three other runs: Wrapping up...**





Individual processes and end products, grain boundaries, crystallization velocity,...

# **PCM-graphene heterostructures**

- Graphene has interesting properties (zero-gap semiconductor, Dirac cone) but poor performance in optical devices
- Heterostructures with graphene display improved properties<sup>1</sup> → 2D materials engineering ("hot topic")
- Layered chalcogenides display "similar" electronic properties, e.g. Bi<sub>2</sub>Te<sub>3</sub> and Sb<sub>2</sub>Te<sub>3</sub> (Dirac cone, topological insulators)
- Graphene used as an electrode interface material in PC-RAM benchmarks<sup>2</sup> → reduced heat loss, low set/reset currents, reduced degradation at the PCM-heater (TiN) interface
- Idea 1: Ferroelectric RAM built from GST materials ← lattice constants of GeTe or GST-225 rocksalt (111) surface and √3 × √3 overlayer on graphene are almost the same (commensurate)
- Idea 2: Can one combine the remarkable ultra-fast phase transition of PCMs with the 2D properties of graphene?

<sup>1</sup>H. Qiao et al. ACS Nano 9, 1886 (2015). <sup>2</sup>C. Ahn, Nano Lett. 15, 6809 (2015).



# **Model structures**



- Crystalline and amorphous films of GeTe and Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> with graphene (432 and 475 atoms in total, 216 carbon atoms)
- Optimized with PBE+vdW (DFT, CP2K program)
- Crystalline films laterally commensurate with graphene, asymmetric in perpendicular direction → polarization



# **Electronic band structure**



- Crystalline film of GeTe + graphene
- Dirac cone relocated from K to Γ due to supercell
- Band gap opens!
- Test: Shirley method for k-point interpolation (black) → greatly reduced computational cost for band structure calculations of large systems

D. Prendergast and S. G. Louie, Phys. Rev. B 80, 235126 (2009).

(b)





- Band structure around Dirac cones computed with the method of Shirley (interpolation)
- Flat bands due to PCM, splitting due to graphene undulation
- Crystalline films open up a gap, sensitive to pressure
- Amorphous films shift the Fermi energy to the valence band



S. Kulju, J. Akola, D. Prendergast, and R.O. Jones, PRB **93**, 195443 (2016).

# **Polarization and local DOS**



# Crystalline films induce a strong asymmetry across the sample





# **2D** heterostructures with PCMs

#### **Collected findings and ideas:**

- Graphene is sensitive to the state (amorphous/crystal) of the neighboring PCM layer (Dirac cone)
- Crystalline PCM layer renders graphene semiconducting  $\rightarrow$ piezoelectric
- Amorphous PCM layer tunes graphene more conductive (?)
- **Note:** We have used ideal compositions (50:50 for GeTe, 2/2/5 for GST)

2D heterostructure where individual graphene sheets display different electronic properties depending on the neighboring PCM layers

#### $\rightarrow$ (opto)electronic applications?

S. Kulju, J. Akola, D. Prendergast, and R.O. Jones, PRB 93, 195443 (2016).





# Ag chalcogenides: Simulations of ionic memory

#### **Experimentally constrained:**

- Starting structure by RMC
- Annealing at 500-600 K with CPMD, gradual cooling (>100 ps)
- Data collection 30-40 ps at 300 K

#### Systems:

- 500+ atoms
- AsS<sub>2</sub> and Ag-AsS<sub>2</sub>
- Ge<sub>41</sub>S<sub>59</sub> and Ag<sub>20</sub>(Ge<sub>41</sub>S<sub>59</sub>)<sub>80</sub>,
   "Ge-rich"

#### → Simulations of Ag dynamics and diffusion at finite T

JA, P. Jovari, I. Kaban et al., PRB **89**, 064202 (2014). JA, B. Beuneu, R.O.Jones et al., JPCM **27**, 485304 (2015).



# Cavities = trapping sites



Ag-Ge-S, 500 K / 600 K: Diffusion constant



#### Trapping / jumps

# Conclusions





• Crystallization of  $Ge_2Sb_2Te_5$ : Occurs in nanoseconds at 600 K depending on the sample preparation (1 – 10 ns). The stochastic nature of the process is evident, and the forming crystallites do not necessarily grow in the unit cell axis directions  $\rightarrow$  grain boundaries

Percolation of the crystalline domain is important. The initial anisotropic percolation occurs before the onset of rapid crystallization.

Significant deviation from the picture of *classical nucleation theory*

 PCM-graphene heterostructure: Chemical interaction between PCM and graphene is weak, but (asymmetric) crystalline layers induce polarization and opening of the Dirac cone

- Contrast due to crystalline and amorphous PCM films, crystalline layers commensurate with graphene
- The band gap varies upon compression → piezoelectricity

Band structure calculations (with k-point sampling) for large samples challenging → Shirley method



# Acknowledgements



- Janne Kalikka, Tampere University of Technology, FI
- Sampo Kulju, Tampere University of Technology, FI
- David Prendergast, Lawrence Berkeley National Laboratory, U.S.A.
- R.O. Jones, Forschungszentrum Jülich, DE



# **Spare slide**





Cavities (voids) are regions of empty space, analogous to vacancies

Cavity domain (red area I) determined by inserting spherical test particles (R>2.8 Å, dashed circle) in real space mesh (spacing 0.08 Å)

Cavity volume (yellow area II) determined via Voronoi construction (Wigner-Seitz cell) with respect to cavity domain (not center alone)



J. Akola and R.O. Jones, PRB **76**, 235201 (2007). J. Akola and R.O. Jones, PRL **100**, 205502 (2008).