

Phase-Change Materials: Trends & Prospects

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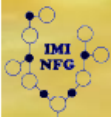
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Chalcogenide glasses

http://www.lehigh.edu/imi/WebCourse_ChalcogenideGlasses.html

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A *mini* Interactive Web Course on CHALCOGENIDE GLASSES

Instructors

Professor Yong Gyu Choi, IMI-NFG Sabbatical Faculty (currently on leave from Korea Aerospace University, South Korea)
Professor Himanshu Jain, Materials Science and Engineering, Lehigh University

Text

"Non-Crystalline Chalcogenides" by Mihai A. Popescu
Published by Kluwer Academic Publishers (ISBN: 1-4020-0359-5)
Useful but not necessary to purchase.

Dates and Time

Starts: January 17, 2011. Ends: March 9, 2011
Mondays and Wednesdays: 1.10-2.00 pm (Eastern Time)
Location for Lehigh University Students: Room 451 Whitaker Lab
Distance Learners: Web log-on information will be sent to all registered students prior to the first scheduled lecture.

Synopsis

This course will be taught during the Spring semester of 2011. It will provide a broad overview of chalcogenide glasses, which are a technologically important, high-tech sub-class of inorganic glasses that exhibit numerous unusual properties not found in common (oxide) glasses. The course will focus on distinctive characteristics (structure and properties) of chalcogenide glasses and how they lead to broad range of existing and potential applications in photonics, electronics, ionics, etc.

Navigation Links

Learning Library:

- Glass Education for Students, Teachers & General Public
- Technical Learning Library

Quick Links:

- Education Outreach

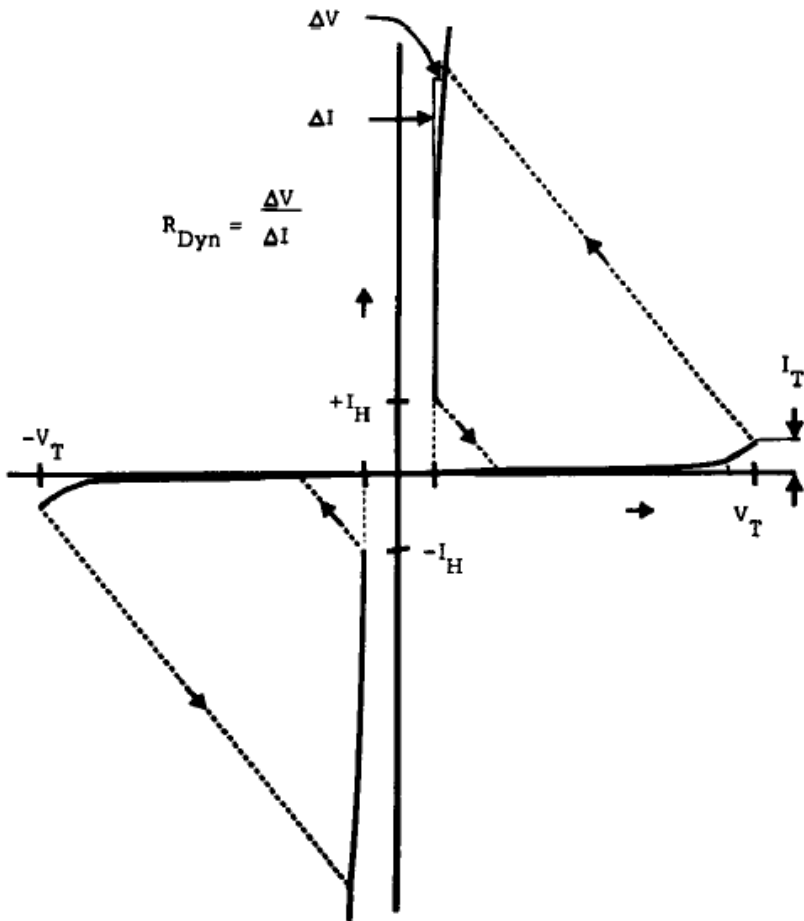
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Outline

- ✓ Electrical switching in amorphous chalcogenide
 - Threshold switching and phase switching
- ✓ Phase change materials
 - Optical memory and electrical memory
- ✓ Structure of phase change materials in general
 - Crystalline structure and related properties
- ✓ A specific case: $\text{Ge}_x\text{Te}_{1-x}$ film
 - Effects of local structures on the phase-change properties
- ✓ Prospects and opportunities from the material's viewpoint

Threshold switching



Phenomena

- ✓ For most MIM contacts, I-V characteristics are essentially symmetric with respect to polarity.
- ✓ For fields below $\sim 10^4$ V/cm, conduction is ohmic with resistance of $10^5 \sim 10^7$ Ohm at room temperature.
- ✓ With increasing voltage, non-ohmic conduction appears, which can be fitted by power laws initially but by an exponential function eventually.
- ✓ At threshold voltage, the device shows the negative-differential-resistance (NDR) behavior, switching very fast to a conducting state with the dynamic resistance of $1 \sim 10 \Omega$.
- ✓ If holding current is maintained, the material remains conducting. However, it returns to high-resistance state on removal of voltage.

Threshold switching

Why amorphous chalcogenide films?

- ✓ Threshold switching of amorphous chalcogenide films is quite unique with regard to **reproducibility and durability**.
- ✓ The cross-linking structures (for some ChGs) inhibits crystallization, resulting in relatively better stability of the amorphous structure.
- ✓ The fact that the valence electrons are nonbonding allows for the excitation of large free-carrier concentrations without any decrease in structural stability.

On the basis of (presence of) valence alternating pairs;

- ✓ The high resistivity of the OFF state resulting from the trap-limited mobility inhibits joule-heating effects, thus maintaining amorphous phase.
- ✓ The nearly equal densities of positively and negatively charged traps (i.e., Fermi level pinning) inhibit large ON-state bulk space-charge effects.
- ✓ The lone-pair electrons that are ordinarily nonbonding results in no net weakening of the amorphous matrix via VAP forming process.

Threshold switching

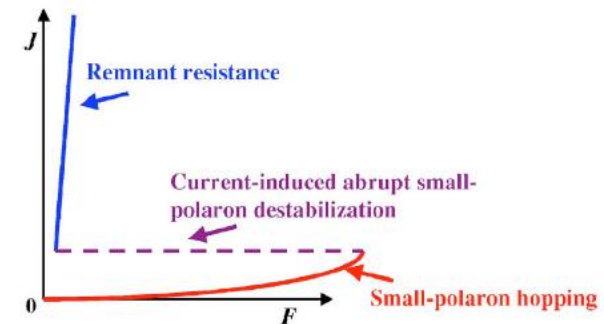
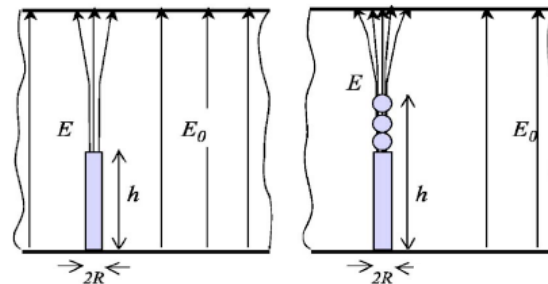
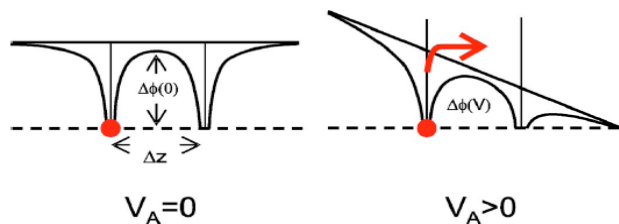
Proposed mechanisms

1) Thermal mechanisms

- ✓ Joule heating in conjunction with the exponential increase of conductivity with temperature.
- ✓ Electrons accelerated by the field emit phonons to return to equilibrium.
- ✓ It is generally believed that pure thermal model cannot account for threshold switching.
- ✓ Both electronic and thermal effects need to be considered; evolved into electrothermal model

2) Electronic mechanisms

- ✓ Models proposed before 1980; avalanche breakdown, Zener breakdown, sharp and non-equilibrium mobility increases, ferroelectric-like transition, double injection, thermal instabilities, impact ionization and recombination...
- ✓ Models proposed after 2000; polaron instabilities, nucleation of conductive phase, Poole-Frenkel transport under high electric fields

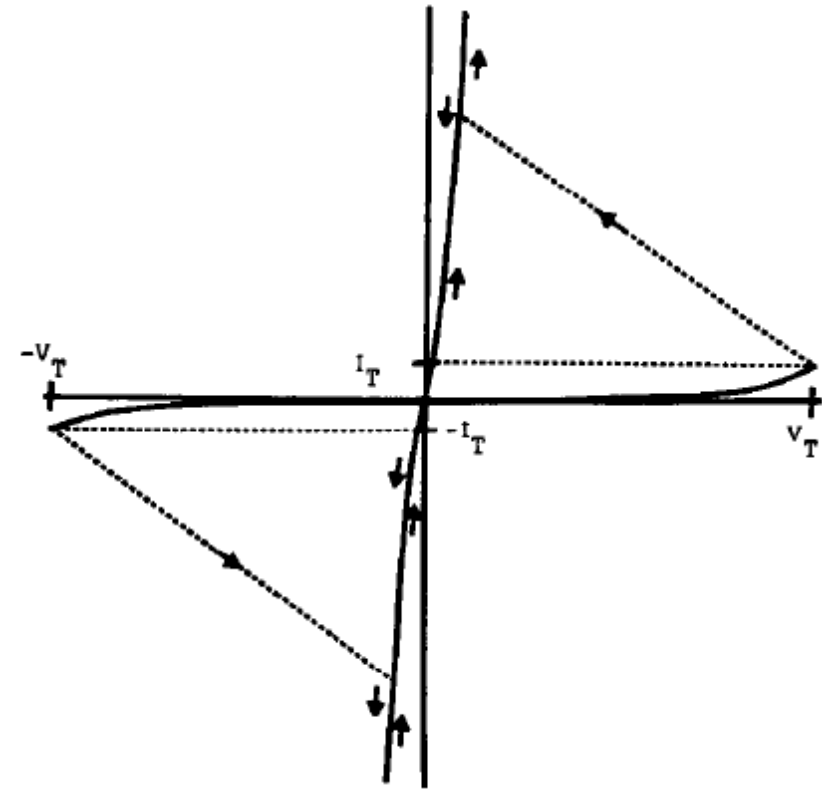


Adler and Moss, J. Vac. Sci. Technol. 9 (1972) 1182.
Adler, Henisch and Mott, Rev. Mod. Phys. 50 (1978) 209.
Raoux, Welnic and Ielmini, Chem. Rev. 110 (2010) 240.

Phase switching

Phenomena and mechanism

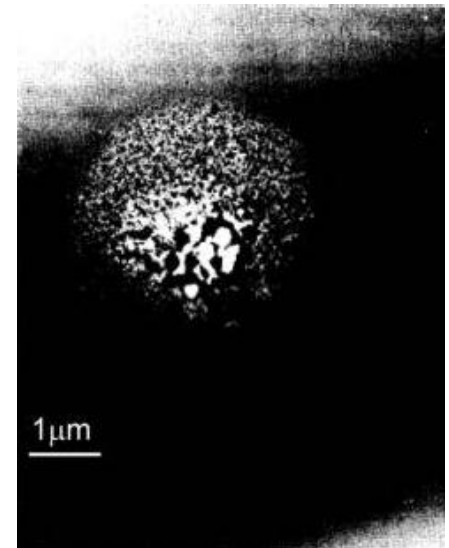
- ✓ Initially, a memory device behaves exactly like a threshold switch: it starts out in high-impedance state, exhibits non-ohmic conduction for fields in excess of $\sim 10^4$ V/cm, and switches to a low-impedance state above a threshold field of the order of 10^5 V/cm.
- ✓ If the field is maintained longer, the material remains in a low-impedance state even if the field is removed entirely, which is called ON or SET state.
- ✓ By application of a short intense current pulse with a rapid trailing edge, the ON state switches to OFF or RESET state.
- ✓ In memory switching, the conducting and nonconducting states represent crystalline and amorphous phases of the same material, respectively; *phase change material!*



History of phase change material

- ✓ Threshold switching (without memory switching) was described for As-Te-I in 1964 [1] and for As-Te-Se in 1966 [2].
- ✓ Ovshinsky recognized the potential technological implications for data storage and patented numerous possible device configurations for PCRAM in 1966 [3].
- ✓ Ovshinsky reported repeated threshold switching between a high resistive and a low resistive state using $48\text{Te}30\text{As}12\text{Si}10\text{Ge}$, and memory switching using other alloys with reduced As content [4].
- ✓ The first optical switching of phase change materials was reported in 1971 [5]. Laser-induced switching of a $81\text{Te}15\text{Ge}2\text{Sb}2\text{S}$ film was demonstrated on the microsecond time scale.

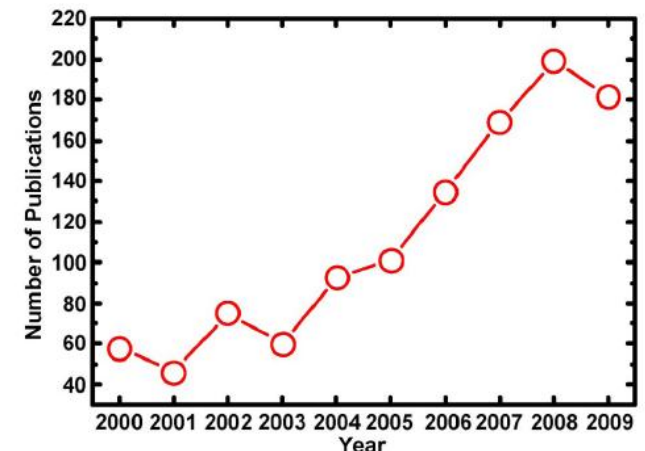
1. Northover and Pearson, U.S. Patent 3,117,013, 1964.
2. Dewald, Northover and Pearson, U.S. Patent 3,241,009. 1966.
3. Ovshinsky, U.S. Patent 3,271,591, 1966.
4. Ovshinsky, Phys. Rev. Lett. 22 (1968) 1450.
5. Feinleib et al, Appl. Phys. Lett. 18 (1971) 254.



History of phase change material

- ✓ In 1978, the prototype fabrication of a 1024-bit chip was demonstrated, but this was never commercialized [1]. The main reason for the delay in commercialization was the slow crystallization speed of these early alloys in the micro- to millisecond range and their limited cyclability.
- ✓ The discovery of fast switching alloys on the pseudobinary line between GeTe and Sb_2Te_3 was made by Yamada, et al. in 1987 [2] These alloys showed large optical contrast over a wide range of wavelengths and good cyclability in addition to their short crystallization times.
- ✓ These materials were used for the first optical storage product with 500 Mb capacity in 1990 and the following ones, rewritable DVD in 1998 and Blu-ray discs in 2003 [3].
- ✓ A second class of phase change materials, i.e., doped Sb_2Te or AIST, was found in 1991, and then used in rewritable CDs, DVDs and Blu-ray discs [3].
- ✓ This rapid and successful development in optical memory, and the scalability problems of the flash memory triggered renewed interest in PCRAM.

1. Shanks and Davis, ISSCC Digest of Technical Papers, 1978, p 112.
2. Yamada et al, Jpn. J. Appl. Phys. 26 (1987) (Suppl. 26-4), 61.
3. Wuttig and Yamada, Nat. Mater. 6 (2007) 824.



Towards better device performance

June 1999: Ovonyx joint venture is formed to commercialize PRAM technology

November 1999: Lockheed Martin works with Ovonyx on PRAM for space applications

August 2004: Samsung announces successful 64 Mbit PRAM array

September 2005: Samsung announces successful 256 Mbit PRAM array with 400 μA programming current

December 2005; Hitachi and Renesas announce 1.5 V PRAM with 100 μA programming current

July 2006: BAE Systems begins selling the first commercial PRAM, a radiation hardened C-RAM 512Kx8 chip

September 2006: Samsung announces 512 Mbit PRAM device

October 2006: Intel and STMicroelectronics show a 128 Mbit PRAM chip

December 2006: IBM Research Labs demonstrate a prototype 3 by 20 nanometers

April 2007: Intel's chief technology officer Justin Rattner is set to give the first public demonstration of the company's PRAM (phase-change RAM) technology

February 2008: Intel and STMicroelectronics announce four-state MLC PRAM and begin shipping samples to customers.

December 2008: Numonyx announces mass production 128 Mbit PRAM device to selected customer.

Towards better device performance

June 2009: Samsung's phase change RAM will go into mass production starting in June.

September 2009: Samsung announces mass production start of 512 Mbit PRAM device.

October 2009: Intel and Numonyx announce they have found a way to stack phase change memory arrays on one die.

December 2009: Numonyx announces 1 Gb 45 nm product.

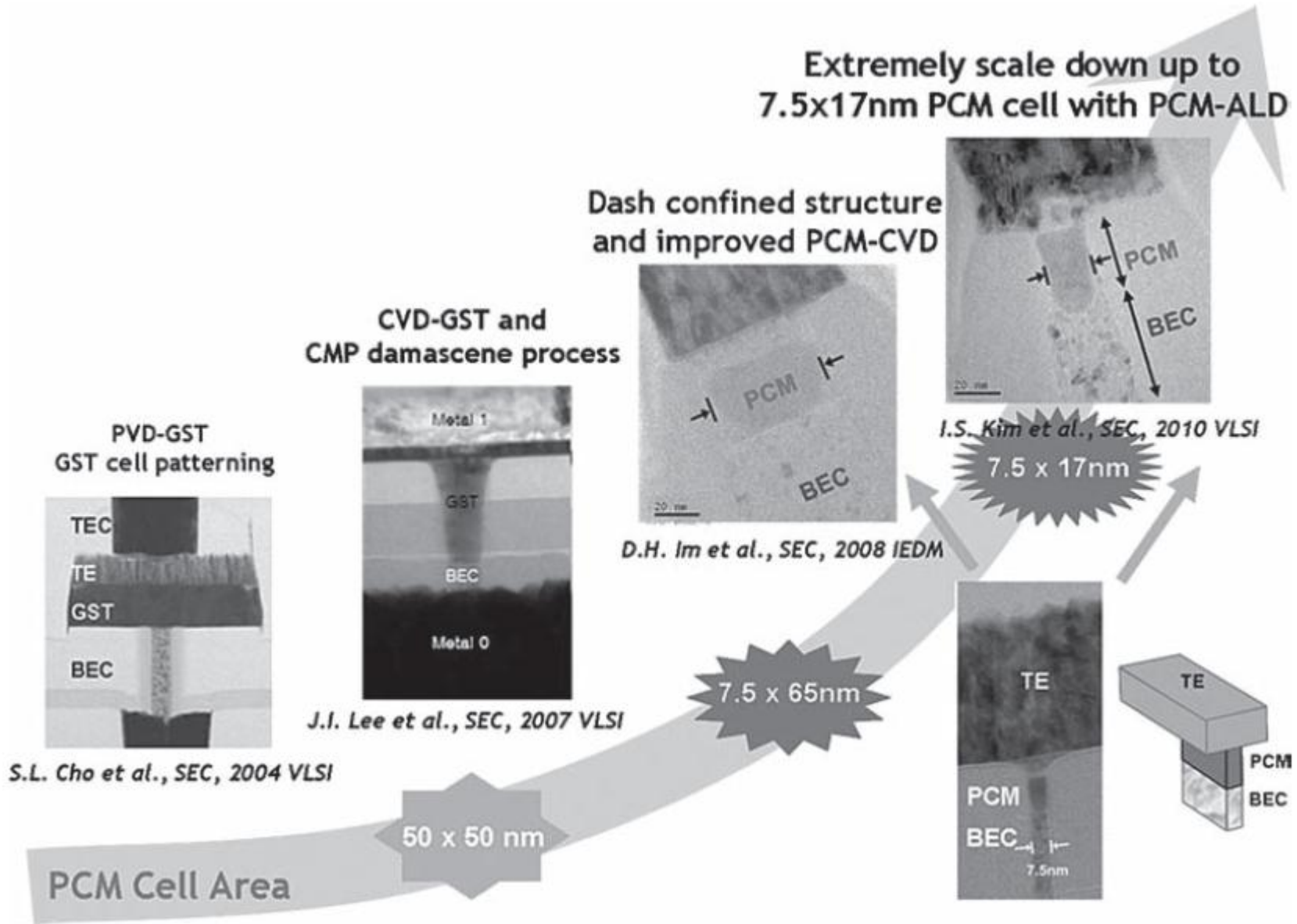
April 2010: Numonyx releases Omneo PRAM Series (P8P and P5Q), both in 90 nm.

April 2010: Samsung releases 512Mbit PRAM with 65 nm process, in Multi-Chip-Package.

February 2011: Samsung presented 58nm 1.8V 1Gb PRAM.

February 2012: Samsung presented 20nm 1.8V 8Gb PRAM.

July 2012: Micron announces availability of Phase-Change Memory for mobile devices - the first PRAM solution in volume production.



Useful resources

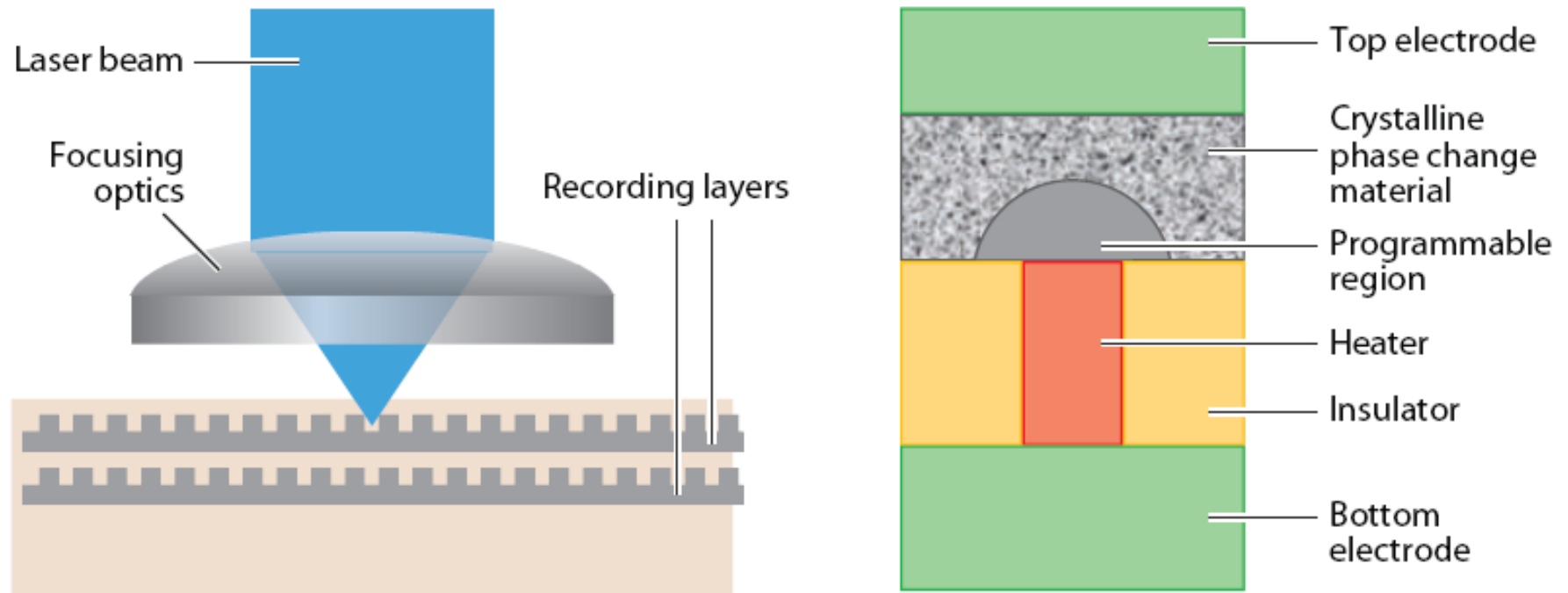
Reviews more focused on phase change materials

- ✓ Wuttig and Yamada, Phase-change materials for rewriteable data storage, *Nat. Mater.* 6 (2007) 824.
- ✓ Welnic et al, Phase change materials: From structures to kinetics, *J. Mater. Res.* 22 (2007) 2368.
- ✓ Welnic and Wuttig, Reversible switching in phase-change materials, *Mater. Today* 11 (2008) 20.
- ✓ Raoux, Phase change materials, *Annu. Rev. Mater. Res.* 39 (2009) 25.
- ✓ Raoux, Welnic, and Ielmini, Phase change materials and their application to nonvolatile memories, *Chem. Rev.* 110 (2010) 240.

Reviews more focused on phase change memory devices

- ✓ Kang et al, Phase Change Memory, in *Nonvolatile Memories: Materials, Devices and Applications*, Edited by Tseung-Yuen Tseng and Simon M. Sze, Vol. 2 (2012).
- ✓ Raoux et al, Phase-change random access memory: A scalable technology, *IBM J. Res. & Dev.* 52 (2008) 465.
- ✓ Wong et al, Phase change memory, *Proc. IEEE* 98 (2010) 2201.
- ✓ Burr et al, Phase change memory technology, *J. Vac. Sci. Technol. B* 28 (2010) 223.

Optical memory and electrical memory



- ✓ (Left) Schematic of a dual-layer Blu-ray recording disc. The recording is done in the groove to isolate adjacent tracks. Typical parameters are as follows: laser wavelength, 405 nm; minimum mark length, 149 nm; track pitch, 320 nm; and numerical aperture, 0.85.
- ✓ (Right) Schematic of a mushroom PCRAM cell. A typical electrode material is TiN with an insulator material SiO_2 , and a PCM consisting of a doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$.

Required properties of phase change materials

Table 1 Crucial properties of phase-change alloys

Required property of PC material	Specification
High-speed phase transition	Induced by nanosecond laser or voltage pulse
Long thermal stability of amorphous state	At least several decades at room temperature
Large optical change between the two states (for rewriteable optical storage)	Considerable difference in refractive index or absorption coefficient
Large resistance change between the states (for non-volatile electronic storage)	Natural consequence of the transformation from amorphous to crystalline state
Large cycle number of reversible transitions	More than 100,000 cycles with stable composition
High chemical stability	High water-resistivity

TABLE I. Some phase change material parameters and the device performance characteristics they influence.

Phase change material parameter	Influence on PCM device performance
Crystallization temperature and thermal stability of the amorphous phase	Data retention and archival lifetime
Melting temperature	Set power
Resistivity in amorphous and crystalline phases	Reset power
	On/off ratio
	Set and reset current
Threshold voltage	Set voltage and reading voltage
Thermal conductivity in both phases	Set and reset power
Crystallization speed	Set pulse duration (and thus power)
	Data rate
Melt-quenching speed	Reset pulse duration (and thus power)

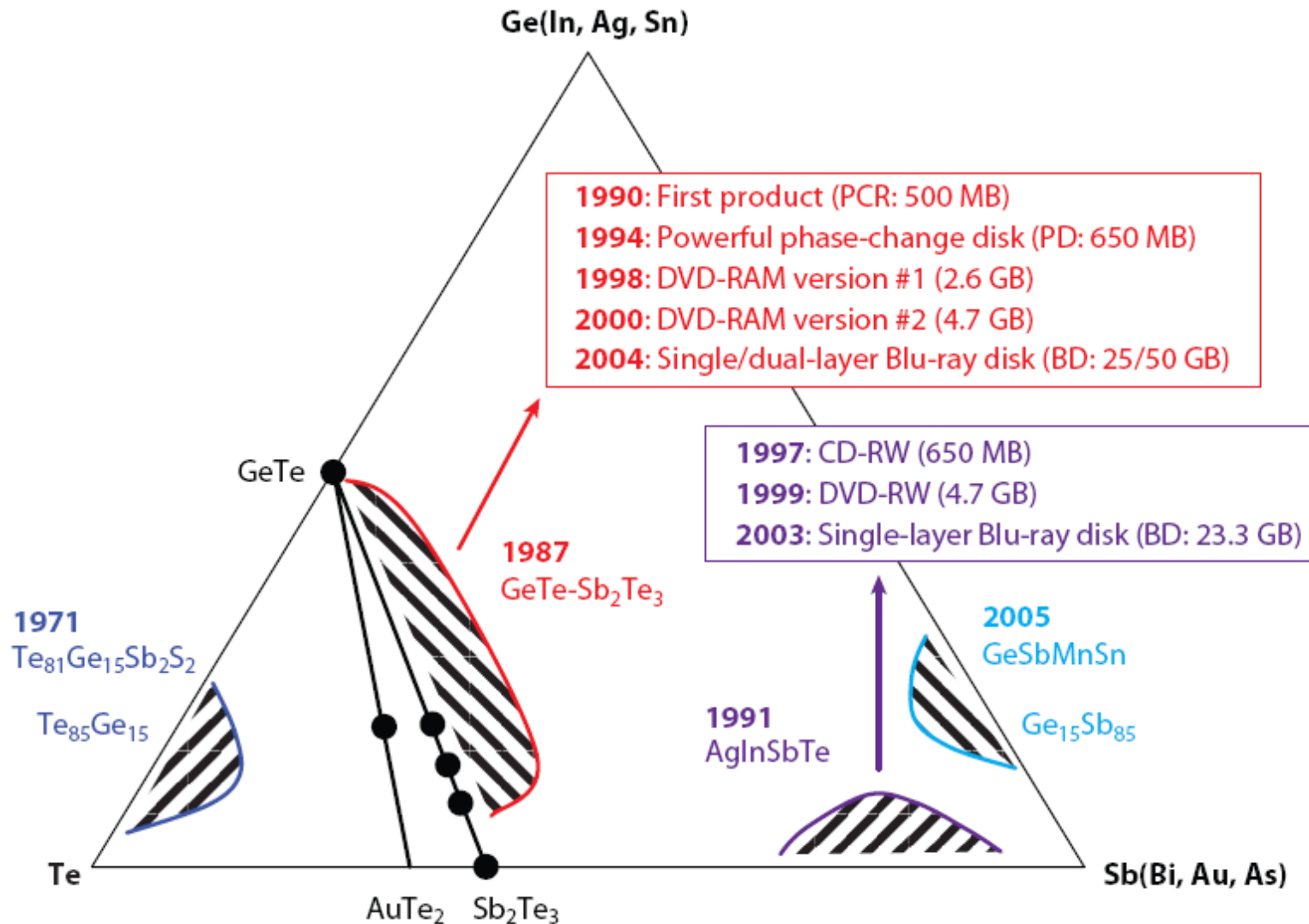
Wuttig and Yamada, Nat. Mater. 6 (2007) 824.

Burr et al, J. Vac. Sci. Technol. B 28 (2010) 223.

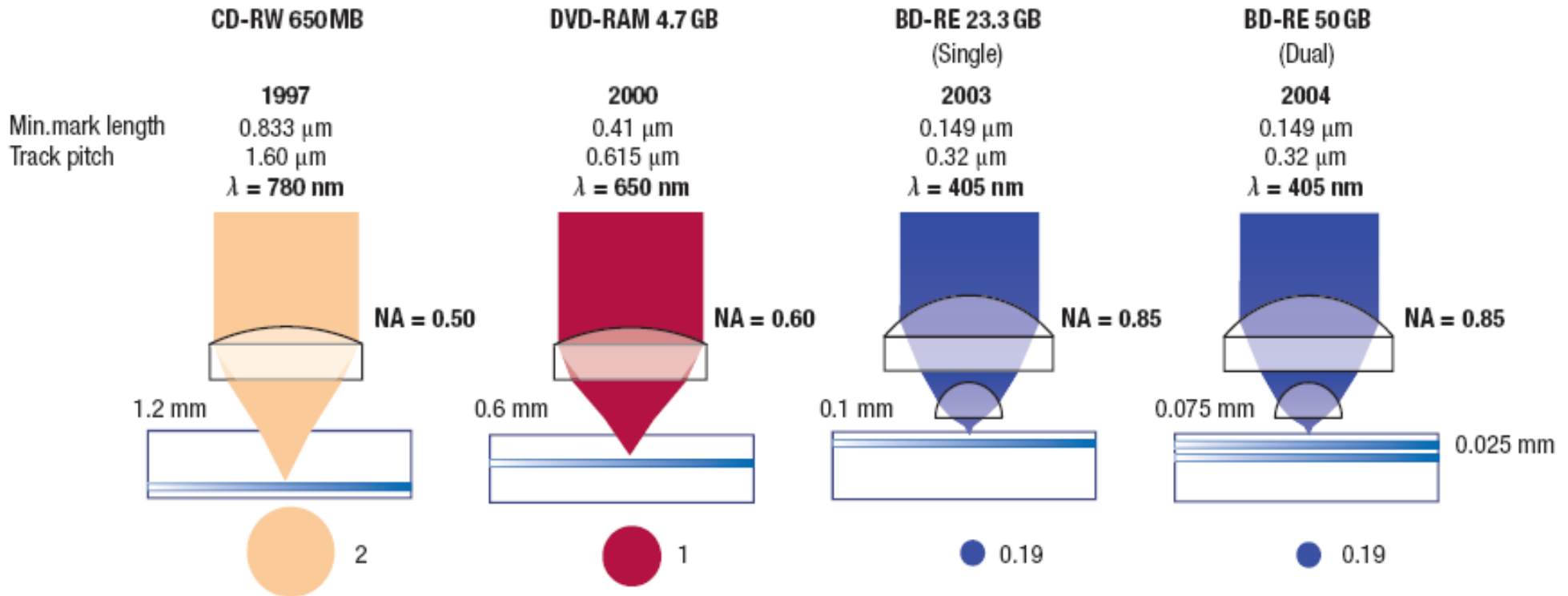
More specific requirements

- ✓ Phase transformation time (particularly the crystallization time) of an amorphous phase should be shorter than hundreds of nanoseconds. This is very critical to high-speed mobile applications such as a smart phone or a tablet personal computer (PC), and even shorter crystallization time of shorter than tens of nanoseconds is required for DRAM-like applications.
- ✓ Crystallization temperature should be high in the range of 150C to 200C, which is enough to keep an amorphous phase in the appropriate temperatures, while the melting temperature should be in the range of 500C to 1000C so that a phase change material can be melted with a Joule heat at a low voltage of 1.8 V or 3.3 V. The properties of surrounding dielectrics and electrode materials should not be affected by Joule heating for melting.
- ✓ Phase transformations between crystalline and amorphous phases should be reproducible over 10^5 cycles with no significant change in material's composition, which is a requirement for nonvolatile memory.

Representative phase change materials

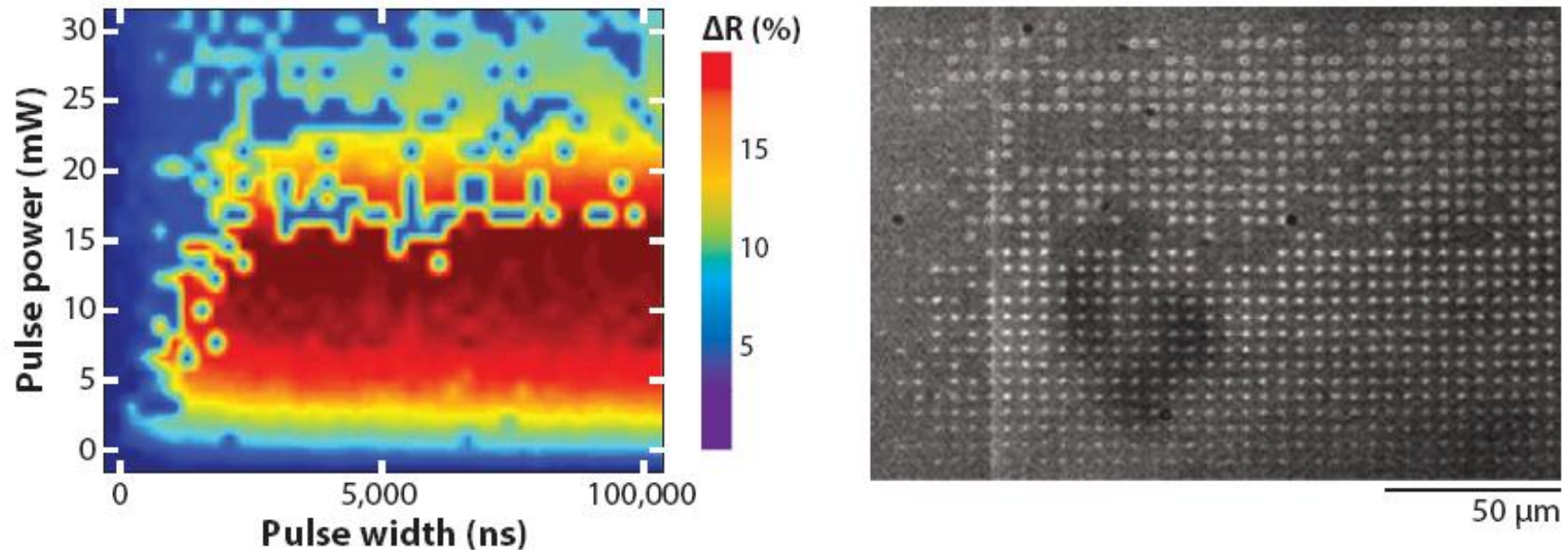


Increasing capacity of optical memory



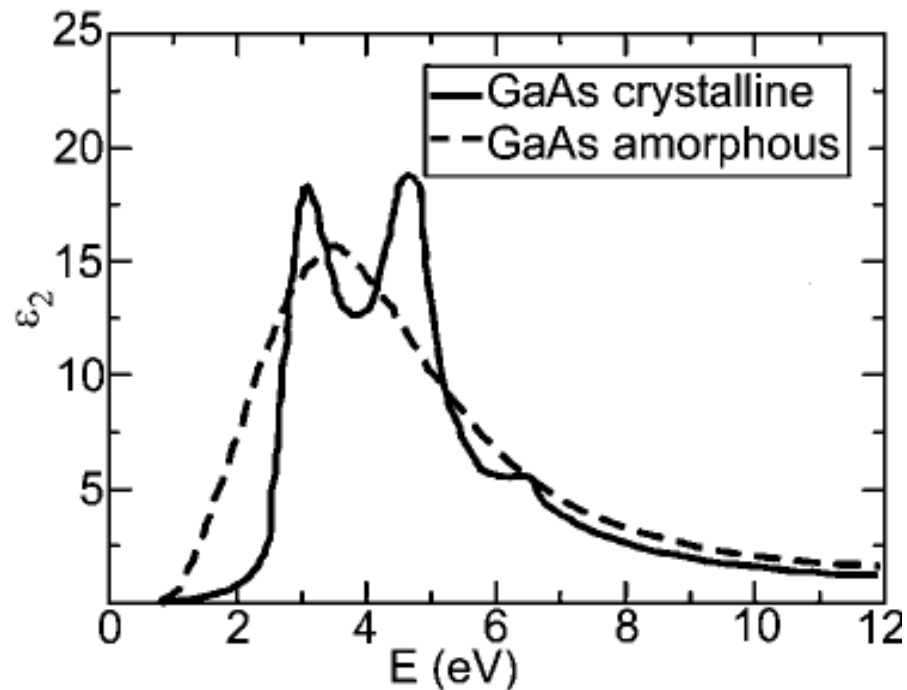
- ✓ Comparison of optics, recording densities, recording capacities and disk structures used for CD , DVD and BD. The change in beam cross-section is displayed at the bottom.
- ✓ From CD to DVD and DVD to BD, the effective laser beam cross-section has been reduced by a factor of 2 and 5, respectively. The recording density increased by a factor of 7 going from CD to DVD . Going from DVD to the dual-layer BD another increase by a factor of 11 has been accomplished.

Change in optical properties



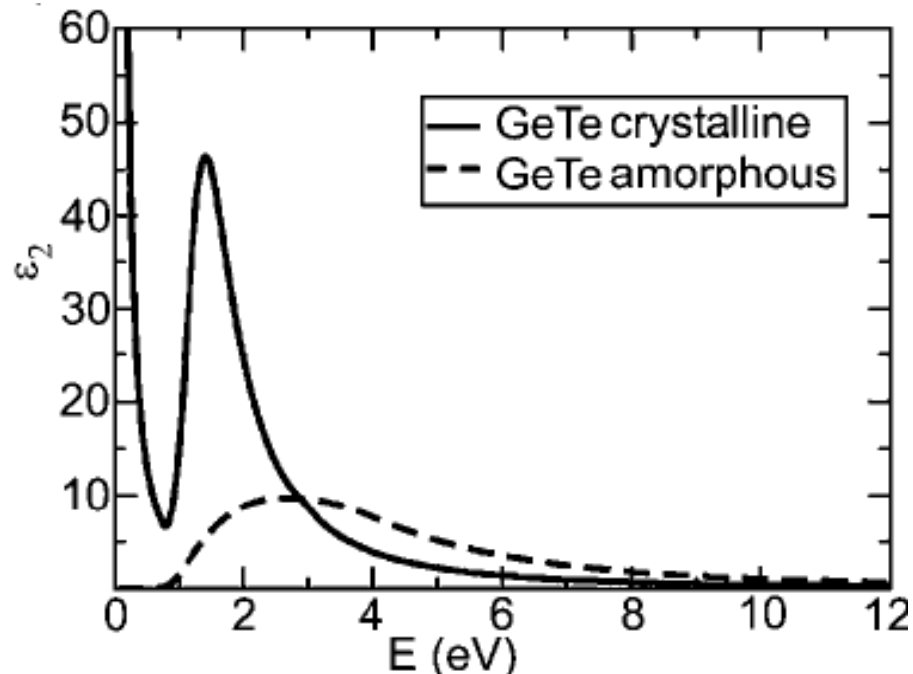
- ✓ (Left) Reflectivity change in amorphous, as-deposited 50-nm $\text{Ag}_7\text{In}_{11}\text{Sb}_{48}\text{Te}_{34}$ on 30-nm Al_2O_3 on Si due to a laser pulse of variable power and duration. The reflectivity is increased if the laser power and duration are sufficient to crystallize the film. The contour plot is the change in reflectivity after the sample has been exposed to laser pulses of variable pulse length (1 ns~10 μs , increasing on the horizontal axis) and variable power (1~30 mW, increasing on the vertical axis).
- ✓ (Right) Contrast-enhanced optical microscope image of the same sample. Bright spots are crystalline.

Change in optical properties



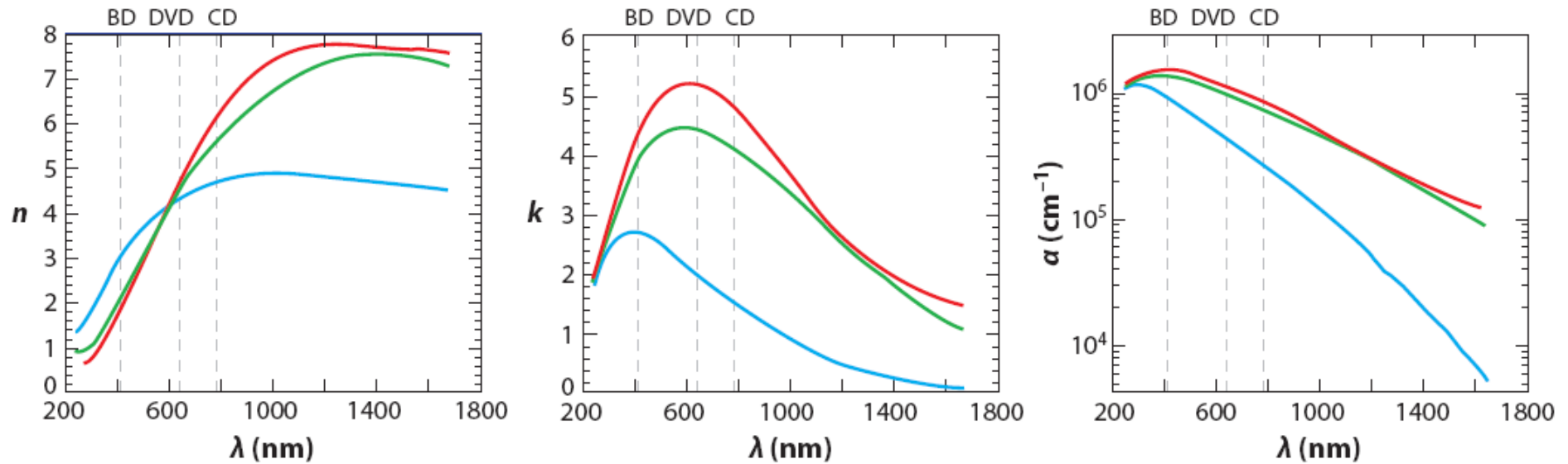
- ✓ Experimental optical absorption of GaAs in the crystalline and amorphous phase.
- ✓ No valence-four alloy such as GaAs or Si has been reported to be suitable for phase-change applications.
- ✓ These differences are explained by a smearing of the electronic density of states resulting from the loss of long range order and the formation of defect states in the optical gap of the amorphous state.

Change in optical properties



- ✓ Experimental optical absorption of GeTe in the crystalline and amorphous phase. Compared to the changes in GaAs, the differences between the two spectra in GeTe are huge.
- ✓ Three major differences observed: a Drude peak present in the crystalline phase but absent in the amorphous one, a blue shift of the amorphous curve, and a strong decrease of the peak intensity in the amorphous phase.
- ✓ This decrease of intensity is of particular importance for the application in optical data storage, as it ensures two different read-out signals for the two phases

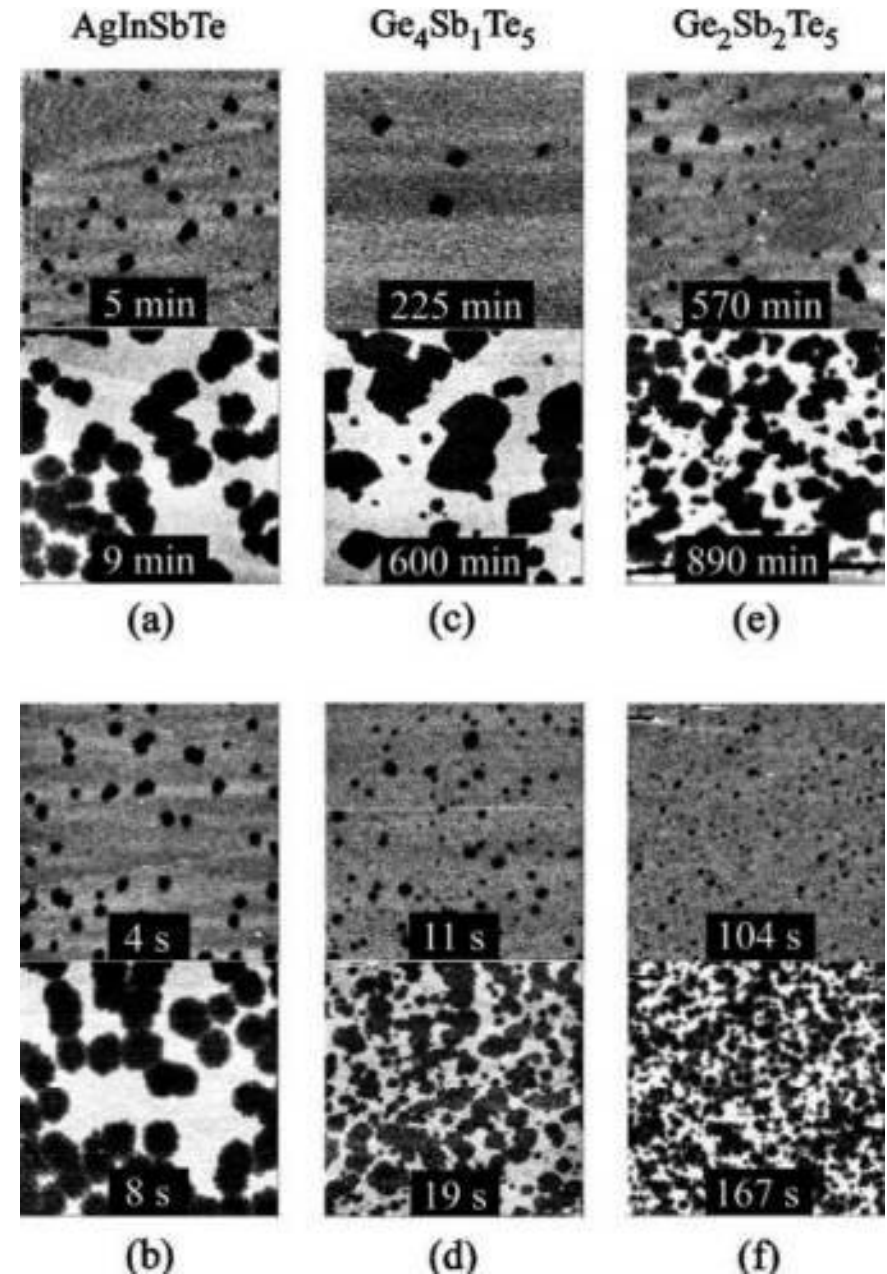
Change in optical properties



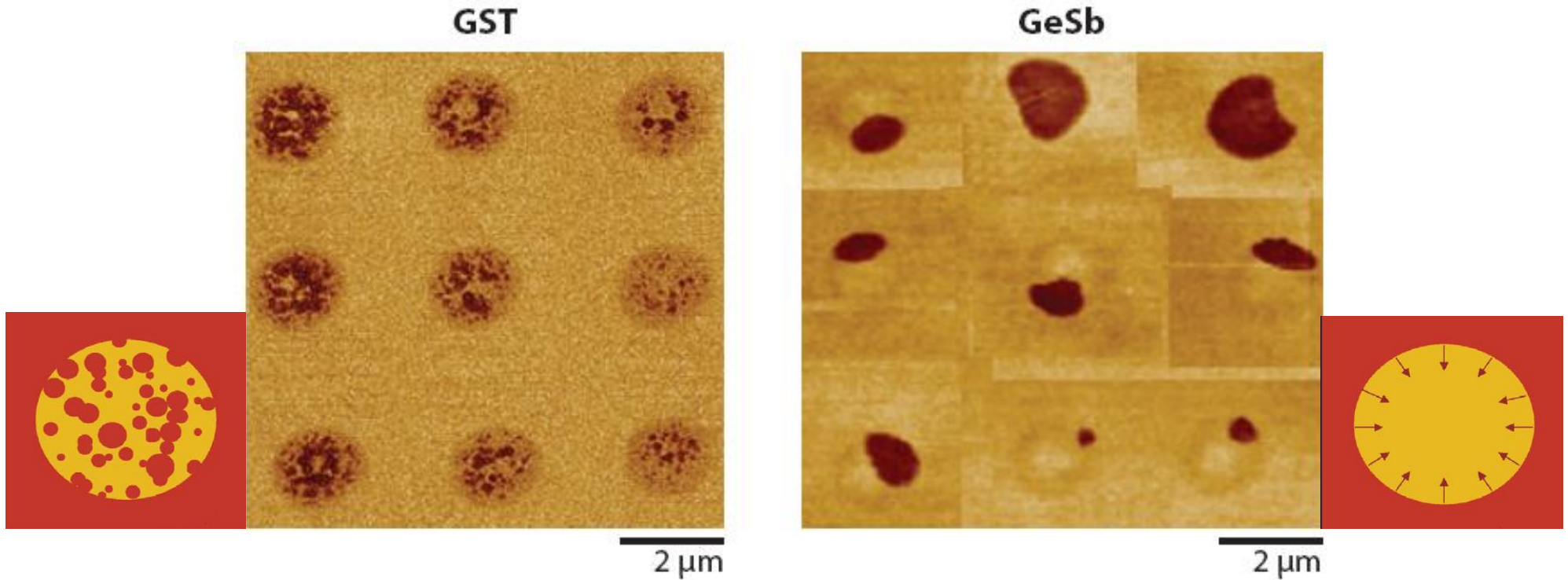
- ✓ Optical constants of the amorphous, rocksalt, and hexagonal phases of GST-225.
- ✓ Relatively large differences between the amorphous and the rock-salt phases and much smaller differences between the two crystalline phases.
- ✓ At shorter wavelengths, the optical contrast is reduced. That is why Blu-ray discs apply compositions other than GST-225.
- ✓ Another important optical parameter is the optical band gap, which is ~ 0.7 eV for amorphous phase and ~ 0.5 eV for crystalline phase.
- ✓ Large differences in structures of both phases and in addition presence of 'resonant bonding' in the crystalline phase. This bonding appears to be an inherent feature of fast-switching PCMs and is related to their large optical contrast.

Difference in crystallization

- ✓ **PCMs are categorized into nucleation-dominated and growth-dominated materials.**
- ✓ AFM scans (field of view $3\ \mu\text{m} \times 3\ \mu\text{m}$) of various phase change materials after various heating times (total times including preceding anneals). The dark areas are crystalline (high mass density), the bright areas amorphous (low mass density).
- ✓ (a) AIST $160\ ^\circ\text{C}$; (b) AIST $180\ ^\circ\text{C}$; (c) GST-415 $140\ ^\circ\text{C}$; (d) GST-415 $180\ ^\circ\text{C}$; (e) GST-225 $115\ ^\circ\text{C}$; (f) GST-225 $145\ ^\circ\text{C}$.
- ✓ Nucleation-dominated materials have relatively short incubation times, high nucleation rates, but slow growth velocities while growth-dominated materials have relatively long incubation times, low nucleation rates, and high growth velocities.

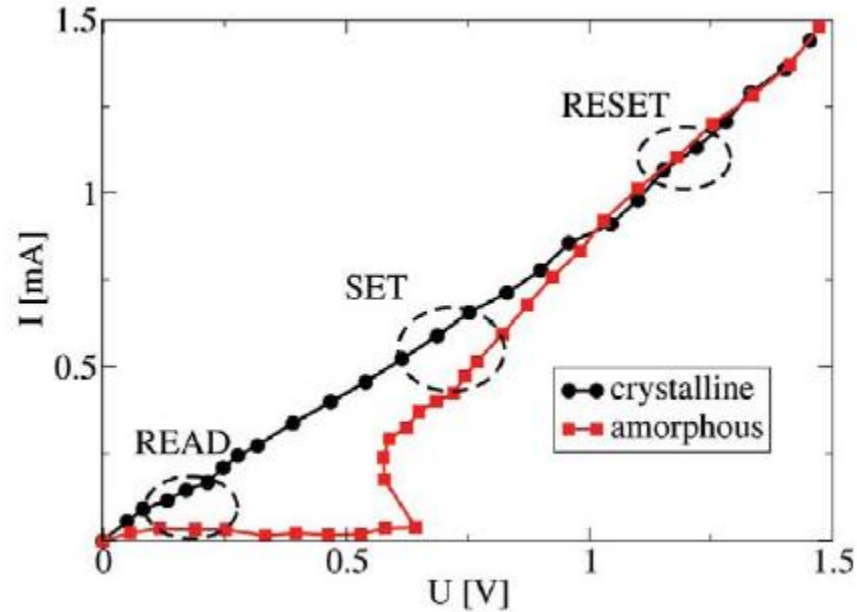
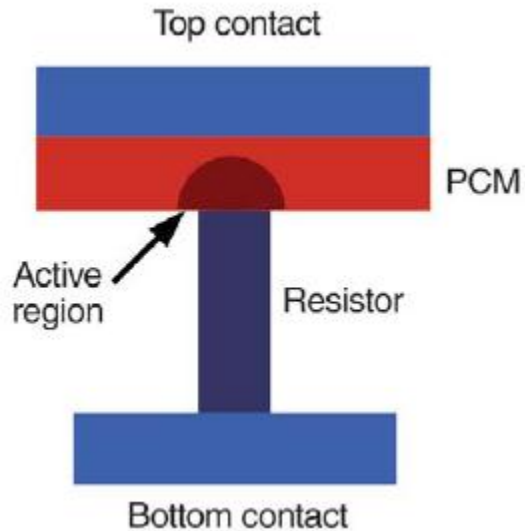


Difference in crystallization



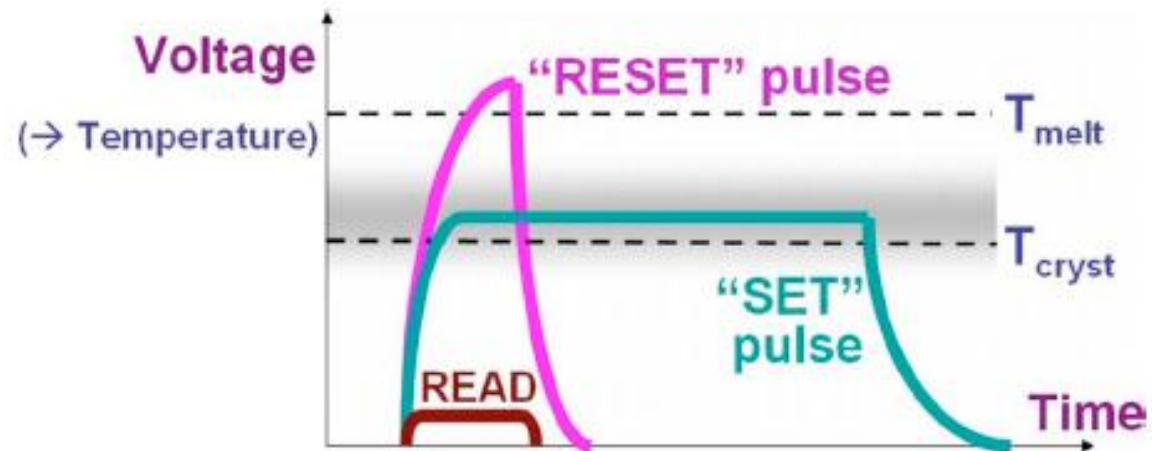
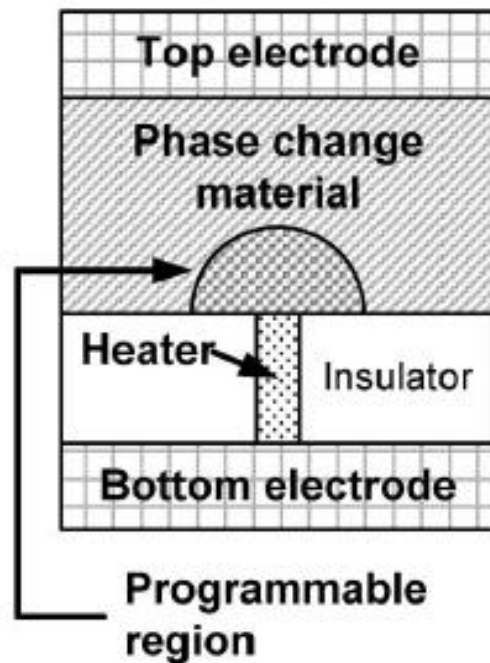
- ✓ AFM images of GST-225 (nucleation-dominated) and 15Ge85Sb (growth-dominated) thin films exposed to a laser pulse that had a power and duration that led to partial crystallization of the films.
- ✓ The dark areas of the images are crystalline regions that have a higher mass density. The GST film was 30nm thick, deposited on 40-nm alumina on Si. The GeSb film was 30 nm thick, deposited on 30-nm alumina on Si.

Electrical memory: operation



- ✓ The cell is essentially a nonlinear resistor and the readout is performed at low bias (READ region), where the low-field resistance changes by orders of magnitude depending on whether the material in the active region of the device is crystalline or amorphous.
- ✓ To reach the switching regions (SET and RESET), the bias is raised above the switching voltage (threshold voltage) so that enough current can flow through the cell, heating up the active region, and resulting in the crystalline-amorphous phase change.

Electrical memory: operation



- ✓ Programming of a PCM device involves application of electrical power through applied voltage, leading to internal temperature changes that either melt and then rapidly quench a volume of amorphous material (RESET), or which hold this volume at a slightly lower temperature for sufficient time for re-crystallization (SET).
- ✓ A low voltage is used to sense the device resistance (READ) so that the device state is not perturbed.

Phase change memory: device characteristics

Device Characteristics of DRAM, Flash, and PCM

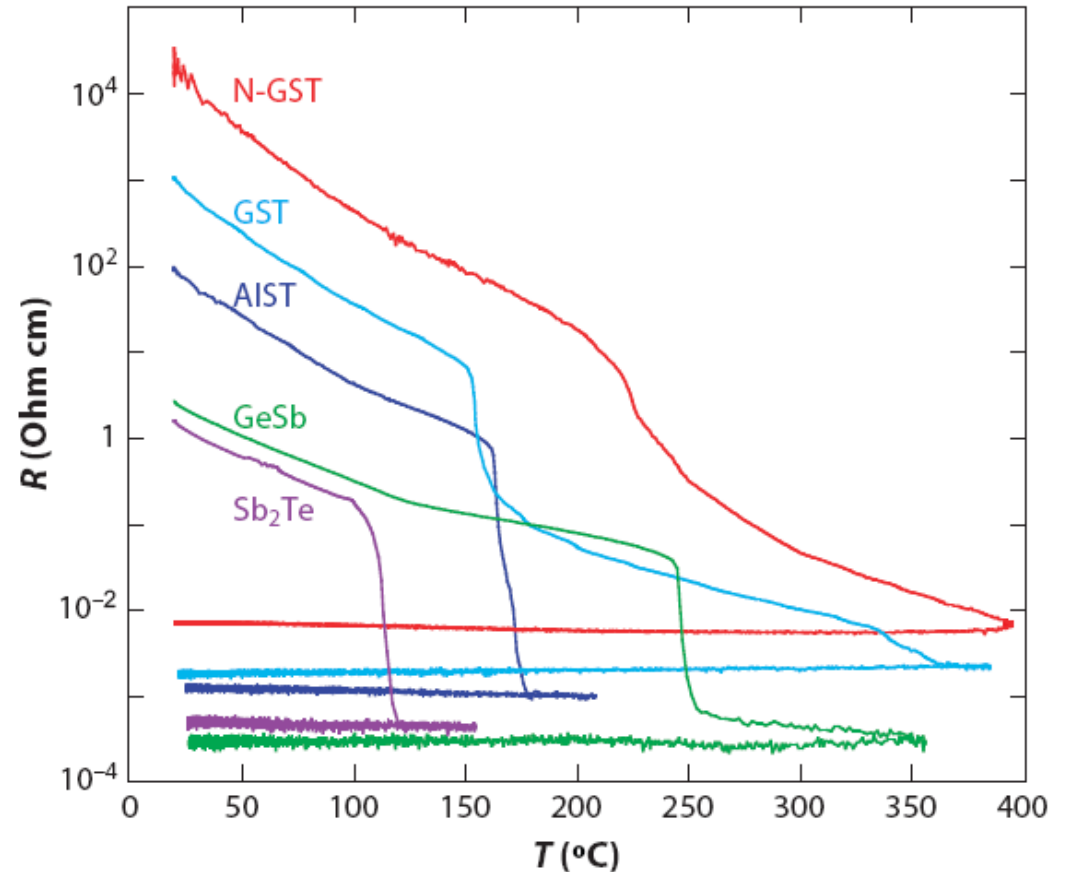
	DRAM	NOR Flash	NAND Flash	PCM
Cell Area	6F ²	10F ²	5F ²	16F ²
Read Time	<10 ns	10ns	50ns	60ns
Write/Erase Time	<10ns	1μs / 10 ms	1ms / 0.1 ms	50 ns / 120 ns
Retention Time	64 ms	> 10 years	> 10 years	> 10 years
Write Cycles	> 10 ¹⁶	10 ⁵	10 ⁵	10 ⁹
Write Operating Voltage	2.5V	12V	15V	3V
Read Operating Voltage	1.8V	2V	2V	< 3V
Multiple-bit Operation	No	In production	In production	Research phase

✓ Drawbacks

- Temperature sensitivity and high RESET currents

Phase change materials for electrical memory

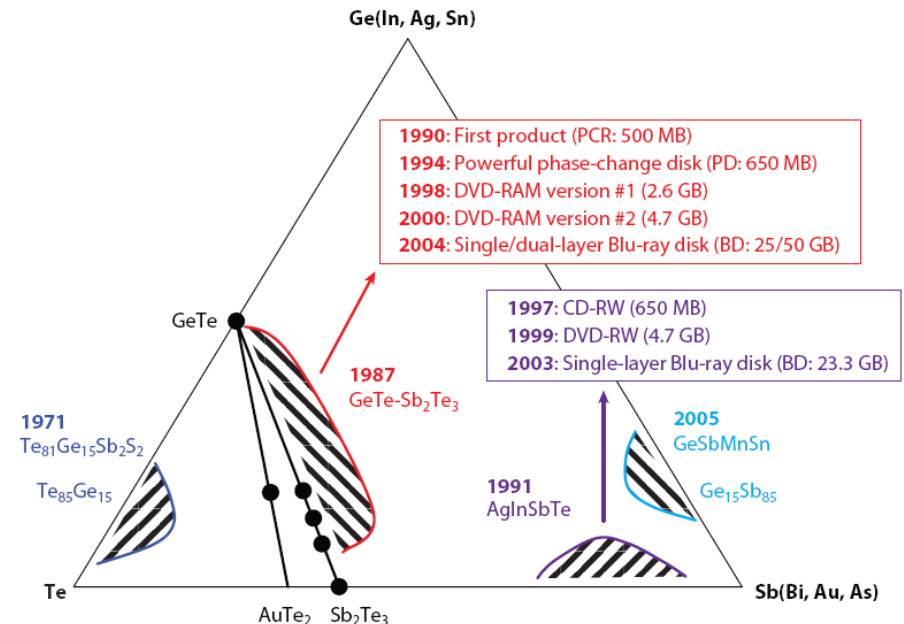
Binary	Ternary	Quaternary
Ga Sb	Ge₂Sb₂Te₅	Ag In Sb Te
In Sb	In Sb Te	(Ge Sn)Sb Te
In Se	Ga Se Te	Ge Sb (Se Te)
Sb ₂ Te ₃	Sn Sb ₂ Te ₄	Te ₈₁ Ge ₁₅ Sb ₂ S ₂
Ge Te	In Sb Ge	Ge ₂ Sb ₂ Te ₅ :O
Ge Sb	Ga Sb Te	Ge₂Sb₂Te₅:N



- ✓ Numerous compositions are being tested basically by trial and error.
- ✓ Structural information, especially on the amorphous phases, is available only for limited compositions.

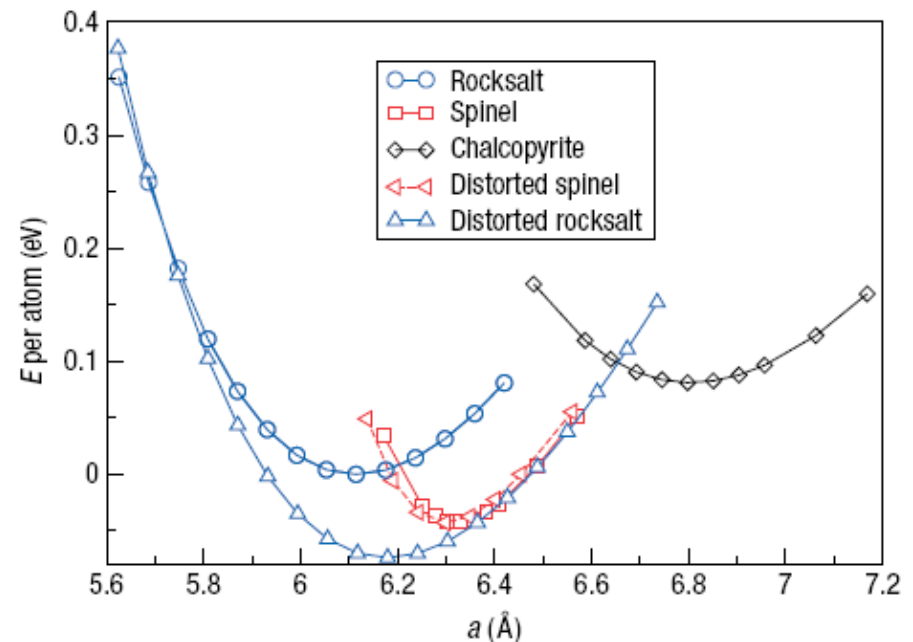
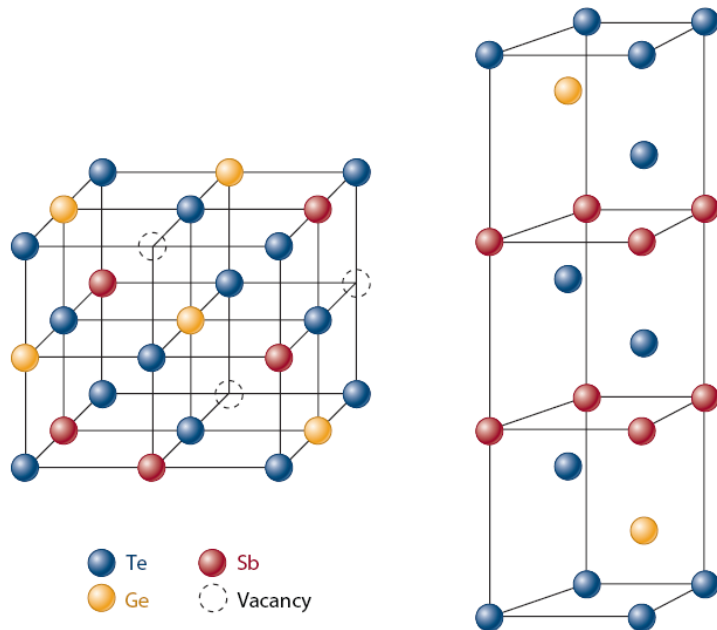
Phase change materials; structural aspects

- ✓ The crystalline side of the phase change material is being revealed rapidly.
 - Only a certain family of crystalline structures seem to be suitable.
 - Only specific chemical bonds, thus atomic combinations, seem to be allowed.
 - Very high dielectric constant and disorder-driven (Anderson-type) MIT
- ✓ The amorphous side of the phase change material is relatively not known.
 - Lack of good experimental probes for structural analysis
 - Diverse structural parameters, sometimes contradictory each other



Crystal structure of GST

- ✓ In general, the most successful (fastest-switching) PCMs show a simple cubic or a (distorted) rocksalt structure, often with random occupation of the lattice sites by the atoms composing the alloy.
- ✓ Crystalline GST-225 is formed at $\sim 140^\circ\text{C}$, depending on the heating rate.
- ✓ Te atoms occupy one FCC sublattice, while Ge, Sb, and a relatively large amount of vacancies ($\sim 20\%$) randomly occupy the other sublattice.
- ✓ At $\sim 310^\circ\text{C}$, more stable hexagonal phase is formed.

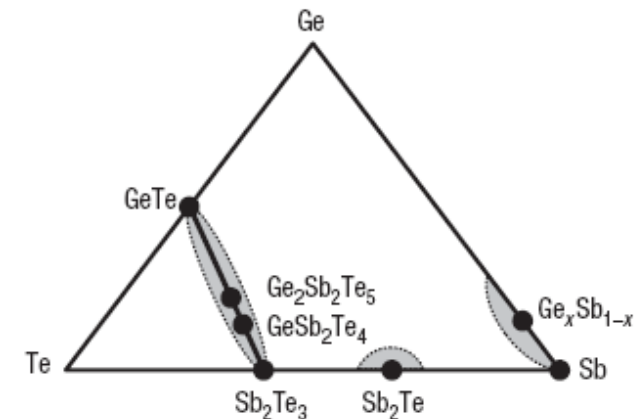


Welnic et al, Nat. Mater. 5 (2006) 56.

Raoux, Annu. Rev. Mater. Res. 39 (2009) 25.

Crystal structure of PCMs

Material	Structure	Average number of valence electrons
Successful samples*		
GeTe	Rocksalt	5
Ge ₁ Sb ₂ Te ₄	Rocksalt (metastable)	4.75
Ge ₂ Sb ₂ Te ₅	Rocksalt (metastable)	4.8
Ge ₄ Sb ₁ Te ₅	Rocksalt	5.1
In ₃ SbTe ₂	Rocksalt	4.33
AgSbTe ₂	Rocksalt	4.5
AuSbTe ₂	Rocksalt	4.5
Au ₂₅ Ge ₄ Sn ₁₁ Te ₆₀	Cubic	4.45
Ag ₃ In ₄ Sb ₇₆ Te ₁₇	Cubic	4.93
Ag _{5.5} In _{6.5} Sb ₅₉ Te ₂₉	Cubic-like/hexagonal	4.94
Unsuccessful samples		
AgInTe ₂	Chalcopyrite	4
AuInTe ₂	Chalcopyrite	4



*Success is defined as the existence of a significant difference in the dielectric function of the amorphous and crystalline state ensuring optical contrast. Note that Ge₁Sb₂Te₄ and Ge₂Sb₂Te₅ each have one vacancy per unit cell in the cubic structure.

Resonant bonding of crystalline PCMs

- ✓ The crystal structures of PCMs are all based on distorted cubic structures and all possess resonant bonding which is the cause of their higher optical dielectric constants.
- ✓ Resonant bonding requires a longer-range order than the conventional electron pair bond of the 8-*N* rule. In the amorphous state, the structure seems to revert to a simple 8-*N* rule structure.

Table 1 Optical dielectric constants and energy gaps. This table comprises the measured optical dielectric constants ϵ_∞ of amorphous and crystalline phases of phase-change materials without Drude contribution, and Se, Te (refs 24,25). In addition, on the right-hand side the optical gaps E_g are listed. The third column is a measure of resonance bonding in the crystalline state. AIST: $\text{Ag}_5\text{In}_6\text{Sb}_{59}\text{Te}_{30}$.

	ϵ_∞			E_g		
	Amorphous	Crystalline	% increase	Amorphous	Crystalline	% decrease
$\text{Ge}_1\text{Sb}_2\text{Te}_4$	16.6 ± 0.3	36.2 ± 0.9	118	0.76	0.39	49
$\text{Ge}_1\text{Sb}_1\text{Te}_2$	14.8 ± 0.4	47.7 ± 0.8	222	0.77	0.20	74
GeTe	13.2 ± 0.2	33.2 ± 0.8	152	0.78	0.55	35
$\text{Ge}_2\text{Sb}_2\text{Te}_5$	16.0 ± 0.4	33.3 ± 0.8	108	0.77	0.48	29
$\text{Ge}_{15}\text{Sb}_{85}$	26.9 ± 0.7	—	—	0.41	—	—
$\text{Ge}_2\text{Sb}_1\text{Te}_4$	14.5 ± 0.3	29.8 ± 1.6	106	0.80	0.61	24
$\text{Ge}_3\text{Sb}_4\text{Te}_8$	15.6 ± 0.2	43.4 ± 1.2	178	0.79	0.24	70
AIST	19.6 ± 0.5	52.8 ± 1.5	169	0.63	0.18	71
Te	11	33.4	204			
Se	5.7	9.79	72			

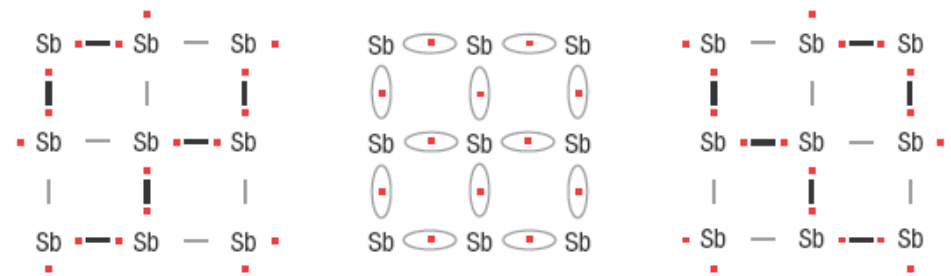
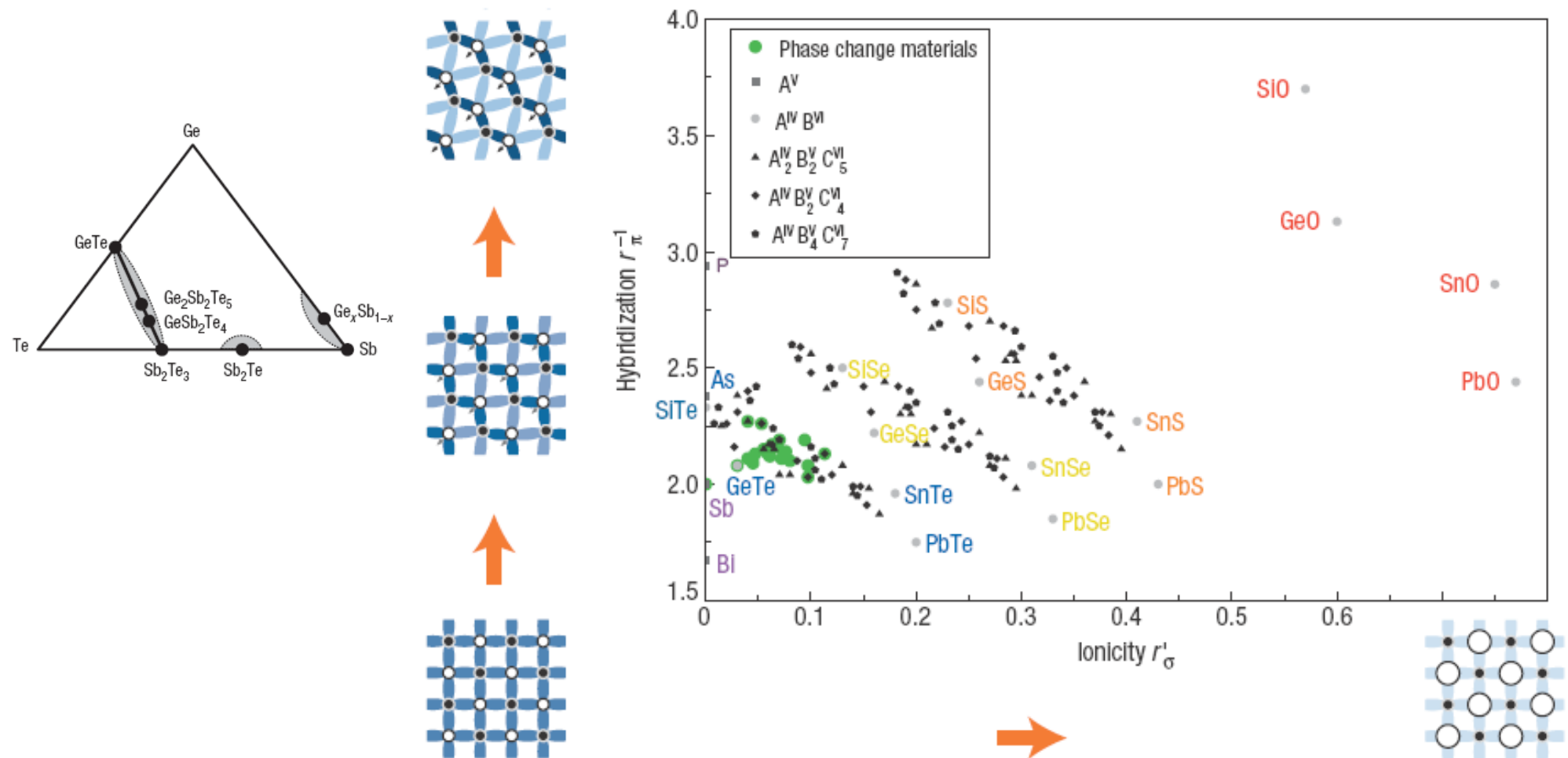


Figure 5 Schematic diagram demonstrating the origin of resonance bonding for Sb. On the left-hand side, one limiting case for bonding in an undistorted Sb phase is shown. A second limiting case is shown on the right-hand side. The solid can minimize its energy by forming a hybrid wavefunction, which is shown in the middle of this figure. This bonding is described as resonance bonding. The pronounced electron delocalization gives rise to an increased electronic polarizability.

Resonant bonding of crystalline PCMs

- ✓ PCMs are located at relatively well-defined narrow region that is an inherent characteristic of PCMs.



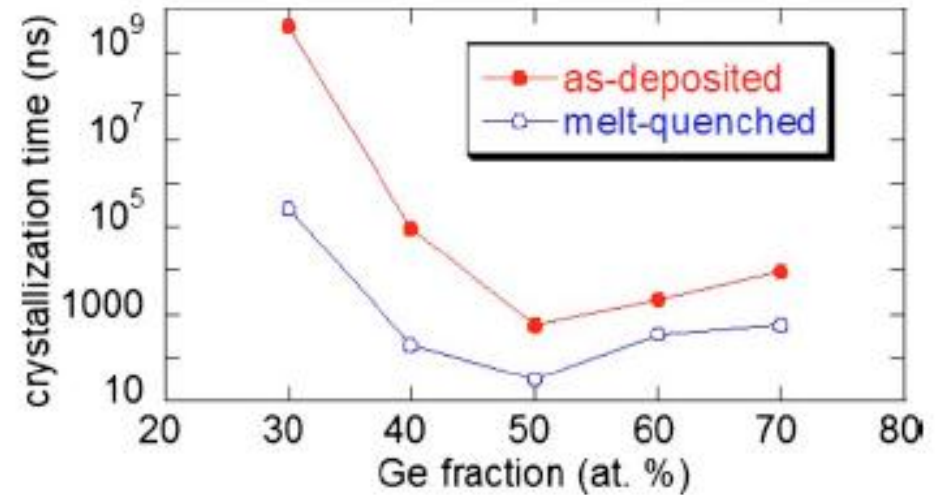
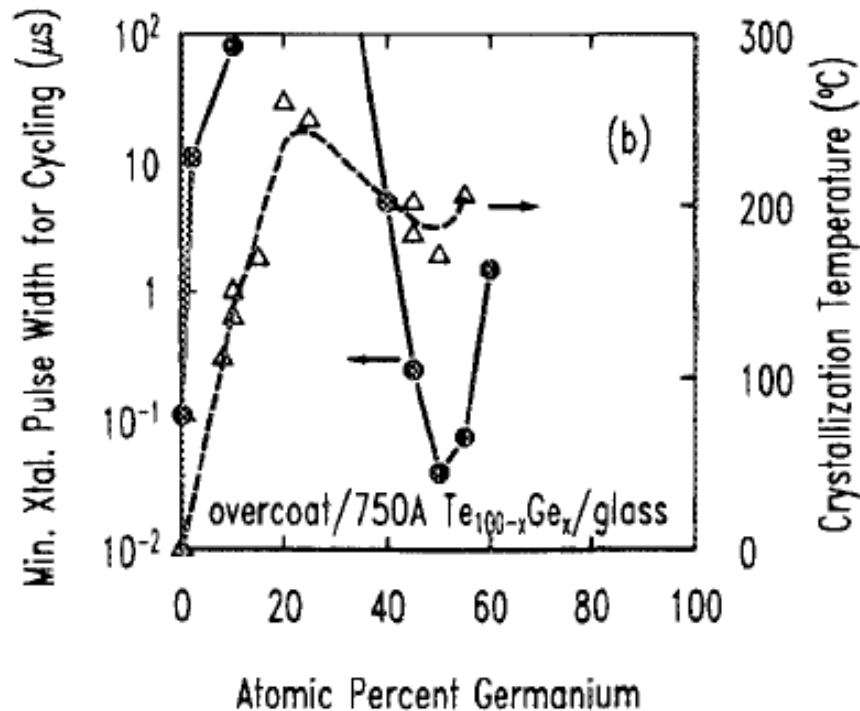
EXAFS Spectroscopic Analysis of $\text{Ge}_x\text{Te}_{1-x}$ Thin Films

Why GeTe film for phase change memory?

- ✓ Higher crystallization temperature with reasonably fast crystallization time
 - Crystallization occurs at higher temperature but more slowly than $\text{Ge}_2\text{Sb}_2\text{Te}_5$.
 - Increasing demand on phase change memory devices operating at high temperatures, e.g., automobile applications
- ✓ Binary system simpler in compositions than GST or AIST
 - Possibly more economical in terms of cost and time for processing
 - A good model system for a detailed structural analysis

Phase change properties of GeTe films

- ✓ Crystallization temperature and time of the $\text{Ge}_{50}\text{Te}_{50}$ composition
 - Crystallization temperature ranging from $\sim 170^\circ\text{C}$ for $\text{Ge}_{50}\text{Te}_{50}$ composition to $\sim 350^\circ\text{C}$ for Ge-rich composition
 - Crystallization time ranging from a few tens ns for $\text{Ge}_{50}\text{Te}_{50}$ composition to a few seconds for Te-rich composition

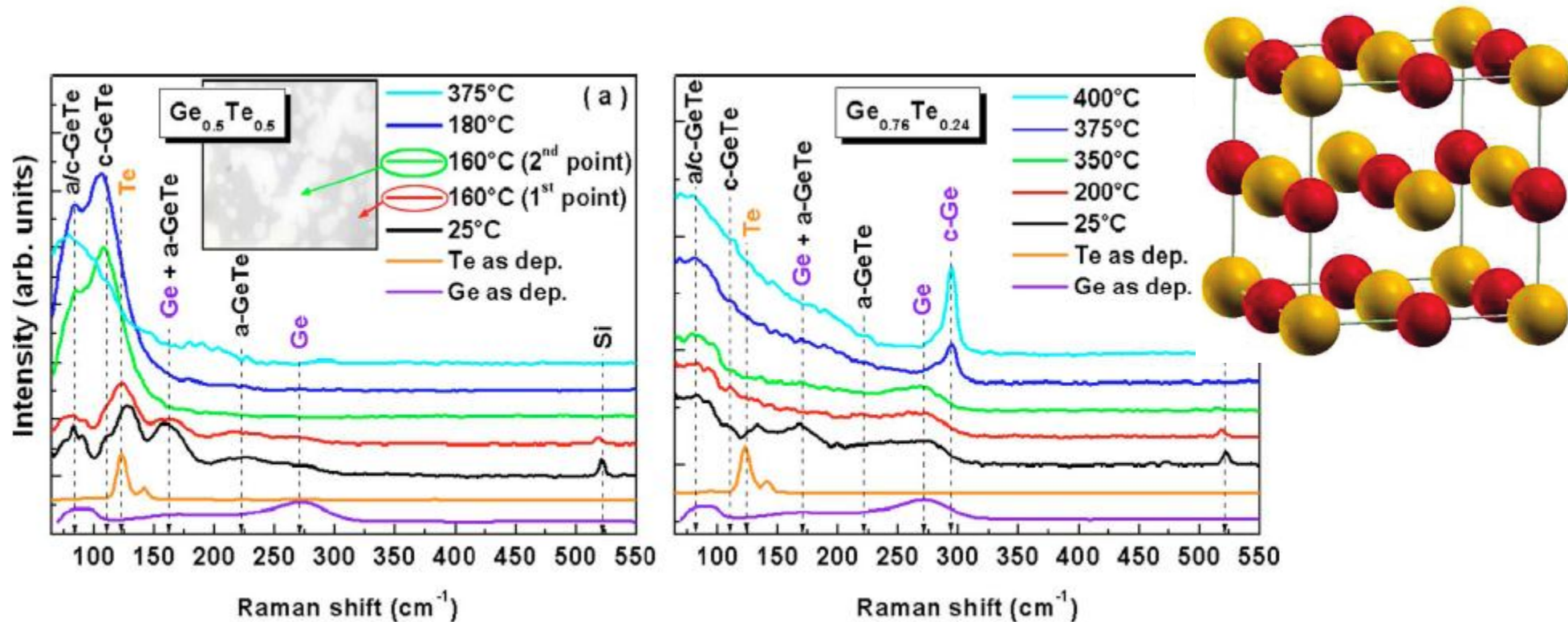


* M. Chen, K. A. Rubin, R. W. Barton, Appl. Phys. Lett. 49 (1986) 502

** S. Raoux, H.-Y. Cheng, M. A. Caldwell, H.-S. P. Wong, Appl. Phys. Lett. 95 (2009) 071910

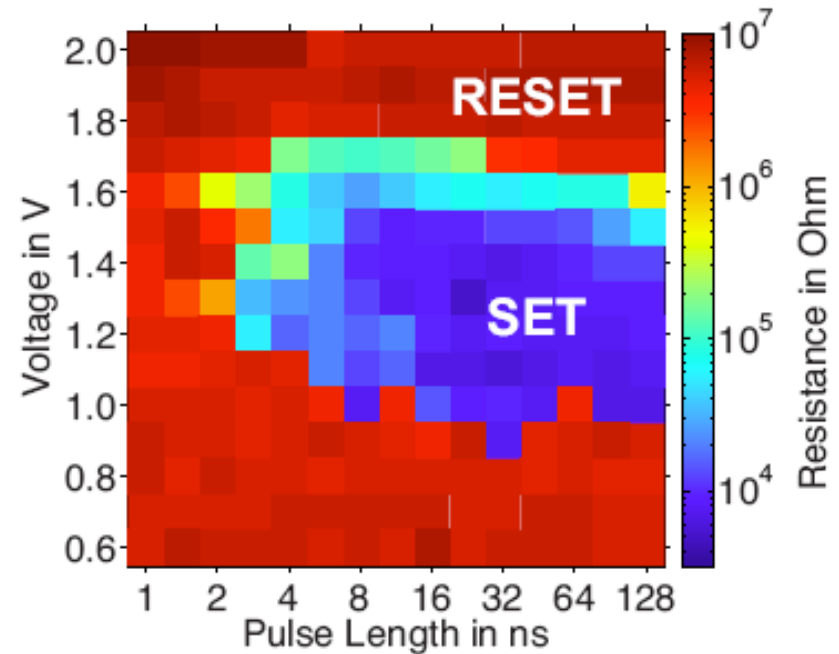
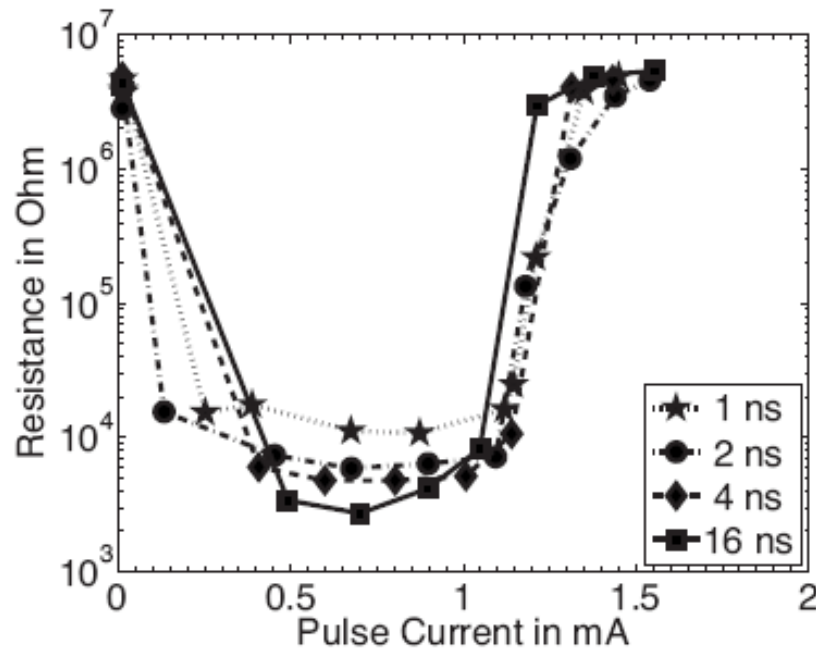
Phase change properties of GeTe films

- ✓ Crystalline phases formed upon heating
 - Crystallized phase with the rhombohedral α -GeTe (distorted rock-salt) structure
 - For Ge-rich compositions, precipitation of Ge crystals with cubic phase



Phase change properties of GeTe films

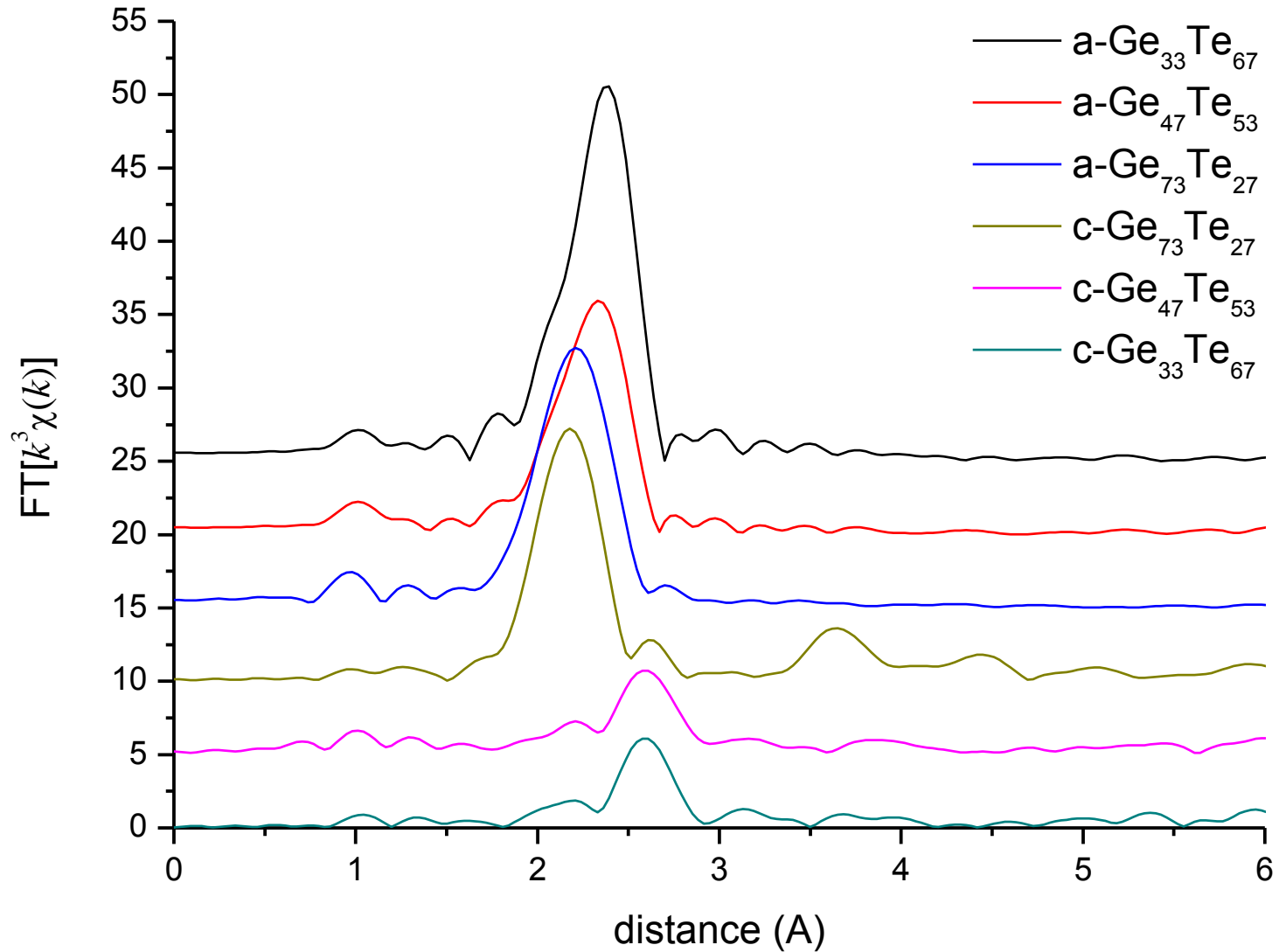
- ✓ Fast switching in GeTe phase change memory cells
 - SET pulses shorter than 16 ns even down to 1 ns
 - The increasing impact of crystal growth upon decreasing switchable volume
 - “Nonvolatile phase change memories with DRAM-like switching speeds”



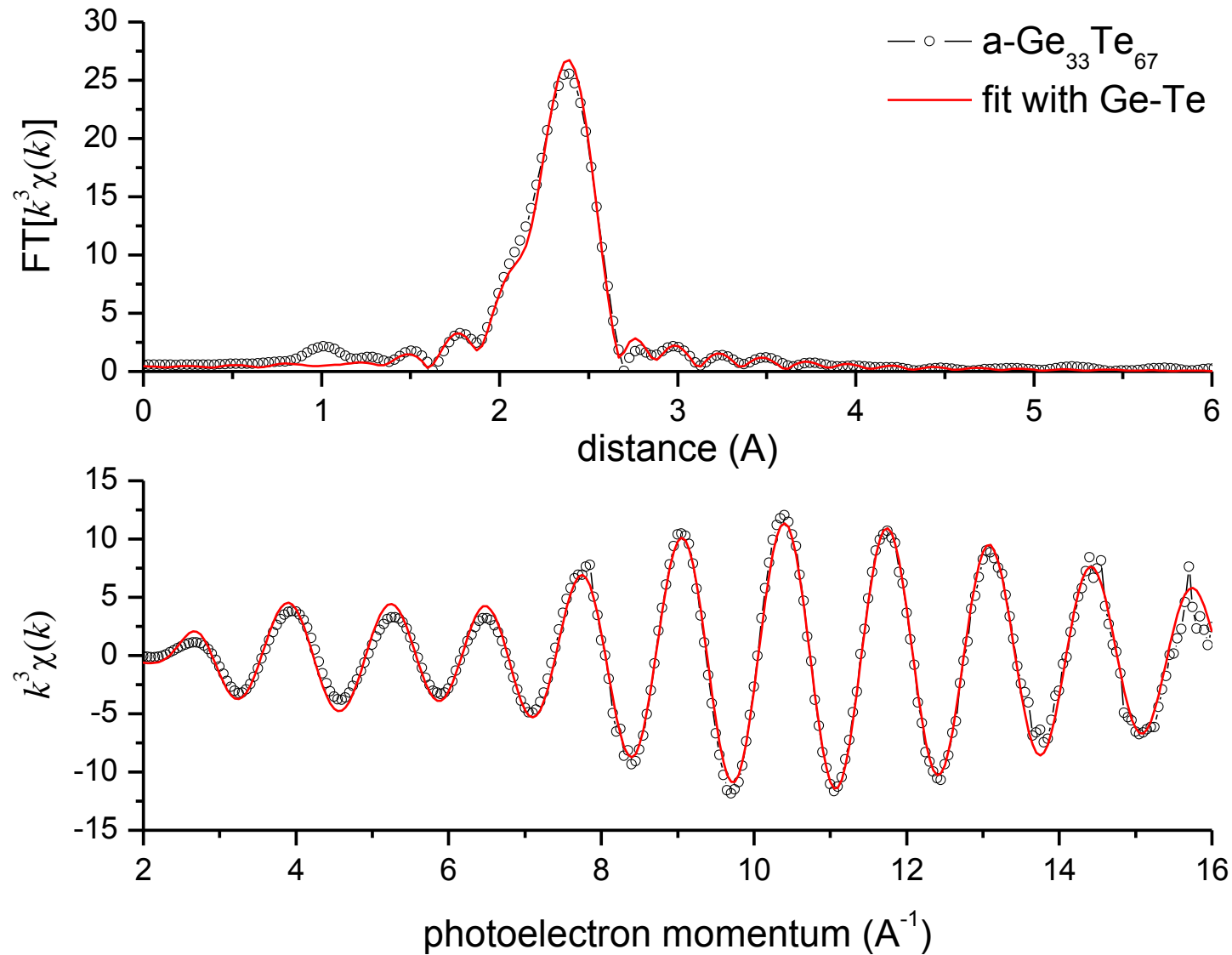
Experiments

- ✓ Prepared amorphous and crystallized film samples;
 - Deposited $\text{Ge}_x\text{Te}_{1-x}$ layer of $\sim 1 \mu\text{m}$ thick via co-evaporation
 - Fused silica substrate with a 5-nm-thick $\text{ZnS}\cdot\text{SiO}_2$ layer for better adhesion
 - Compositions confirmed to be $\text{Ge}_{33}\text{Te}_{67}$, $\text{Ge}_{47}\text{Te}_{53}$ and $\text{Ge}_{73}\text{Te}_{27}$ (at.%)
 - Heat treated at 350°C ($\text{Ge}_{33}\text{Te}_{67}$ and $\text{Ge}_{47}\text{Te}_{53}$) and 400°C ($\text{Ge}_{73}\text{Te}_{27}$) for 10 min
- ✓ Measured X-ray absorption at Ge K-edge and Te K-edge;
 - The X-18B beamline of NSLS, Brookhaven National Laboratory
 - Fluorescence mode using a Si detector at room temperature
- ✓ Analyzed EXAFS spectra
 - The IFEFFIT software package
 - The FEFF6 and FEFF8 codes

Ge K-edge EXAFS spectra

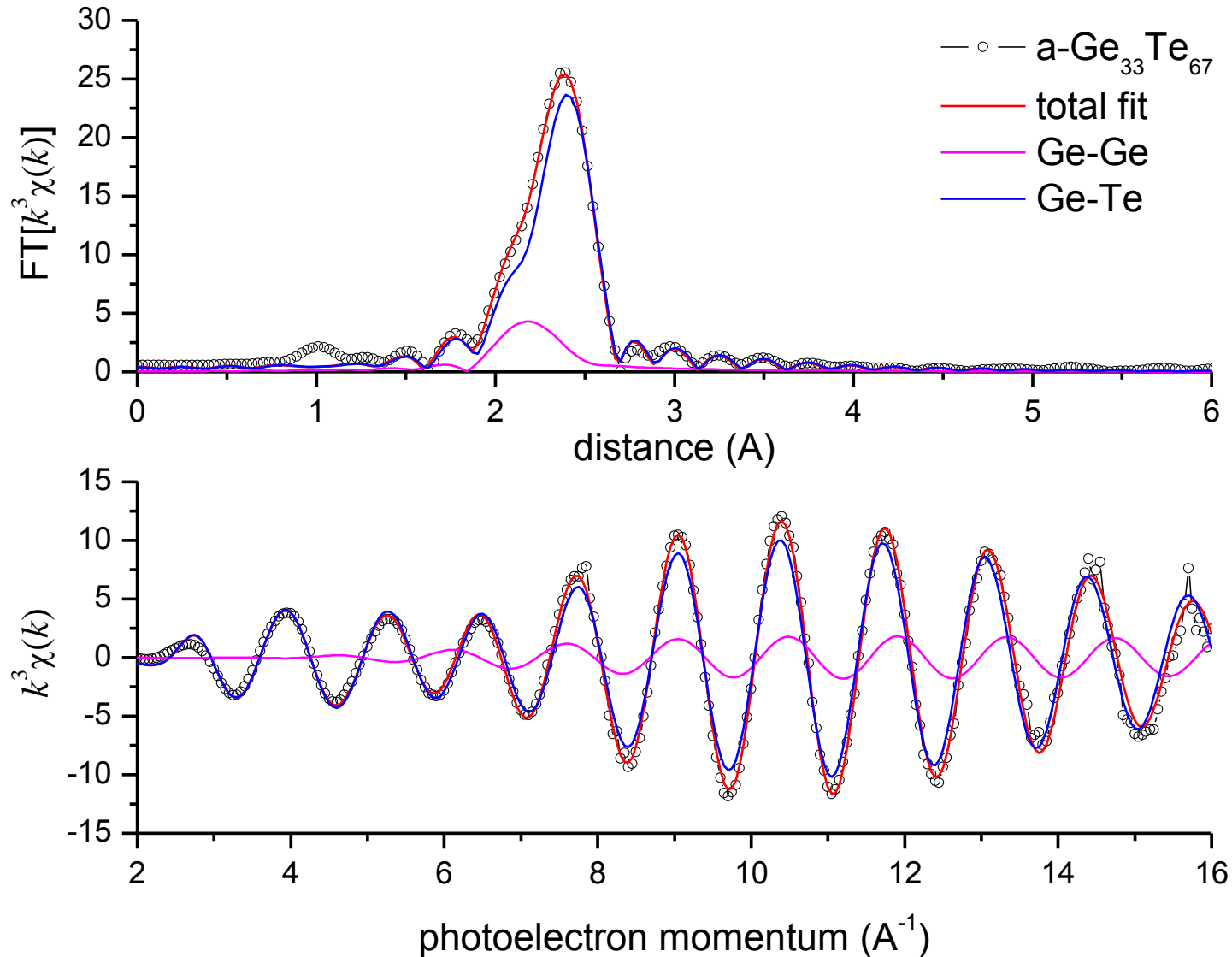


Ge in amorphous Te-rich composition



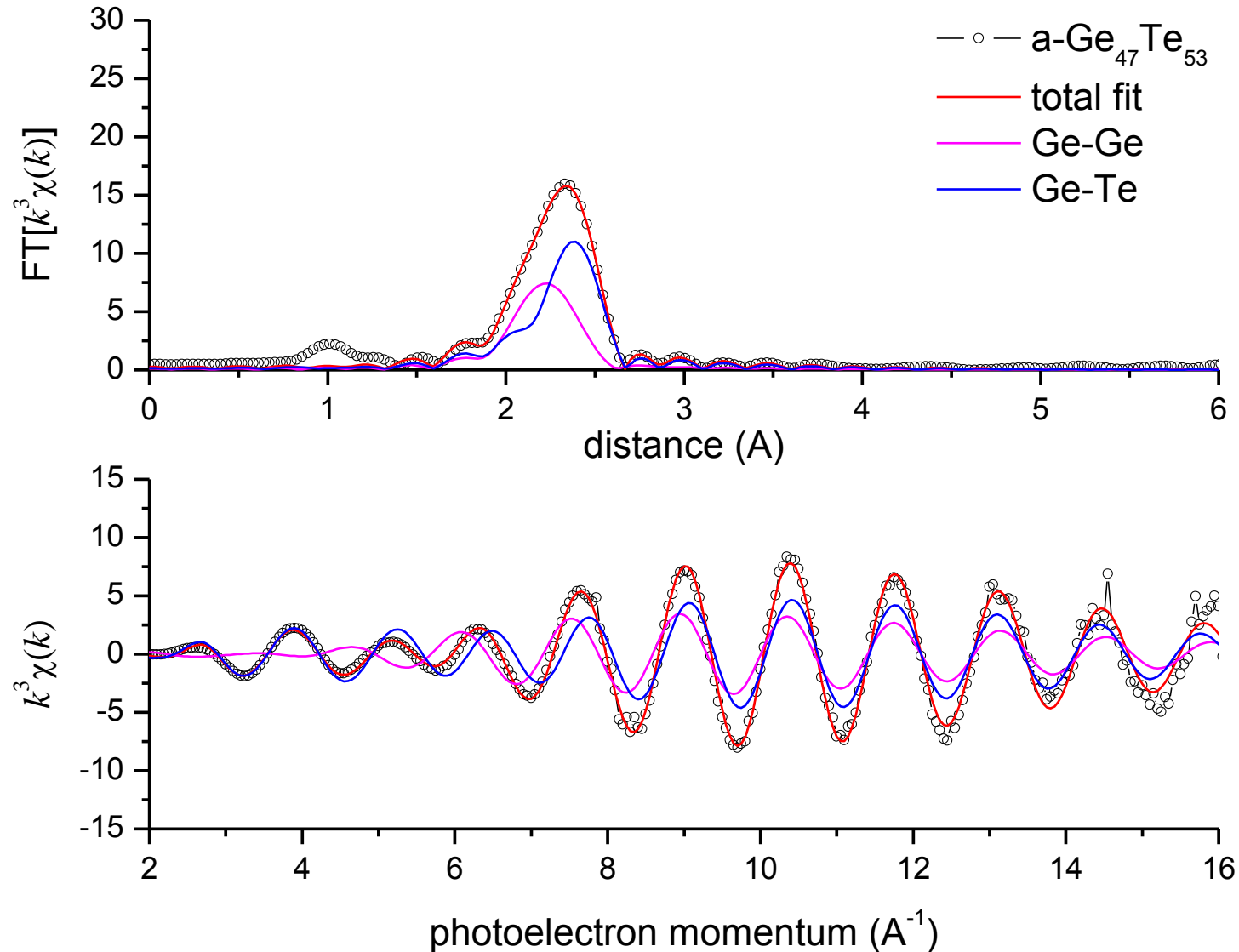
Ge in amorphous Te-rich composition

- ✓ Presence of homopolar Ge-Ge bonds in addition to heteropolar Ge-Te bonds!

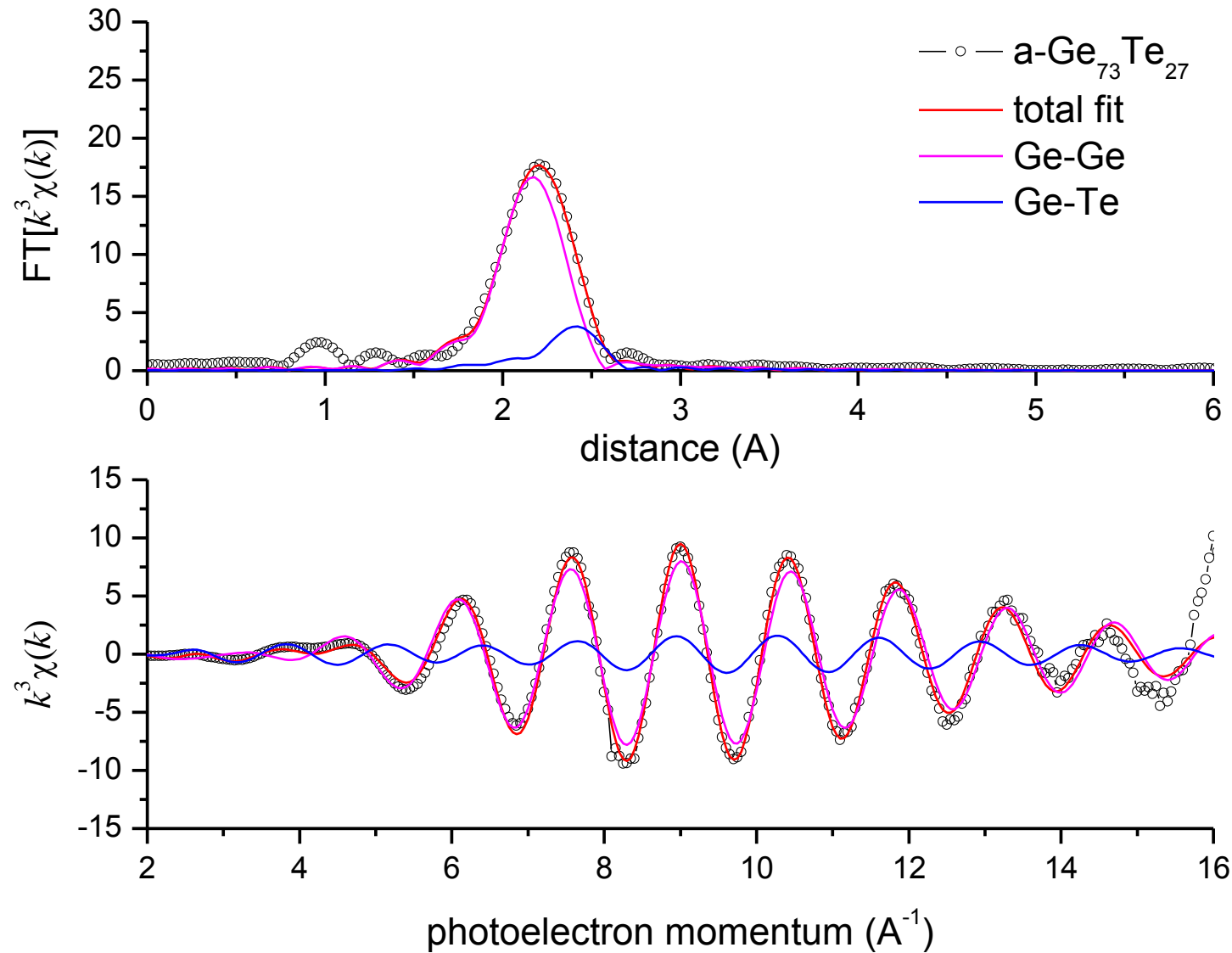


Ge in amorphous stoichiometric composition

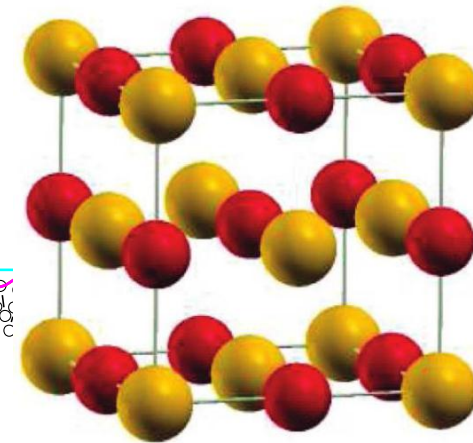
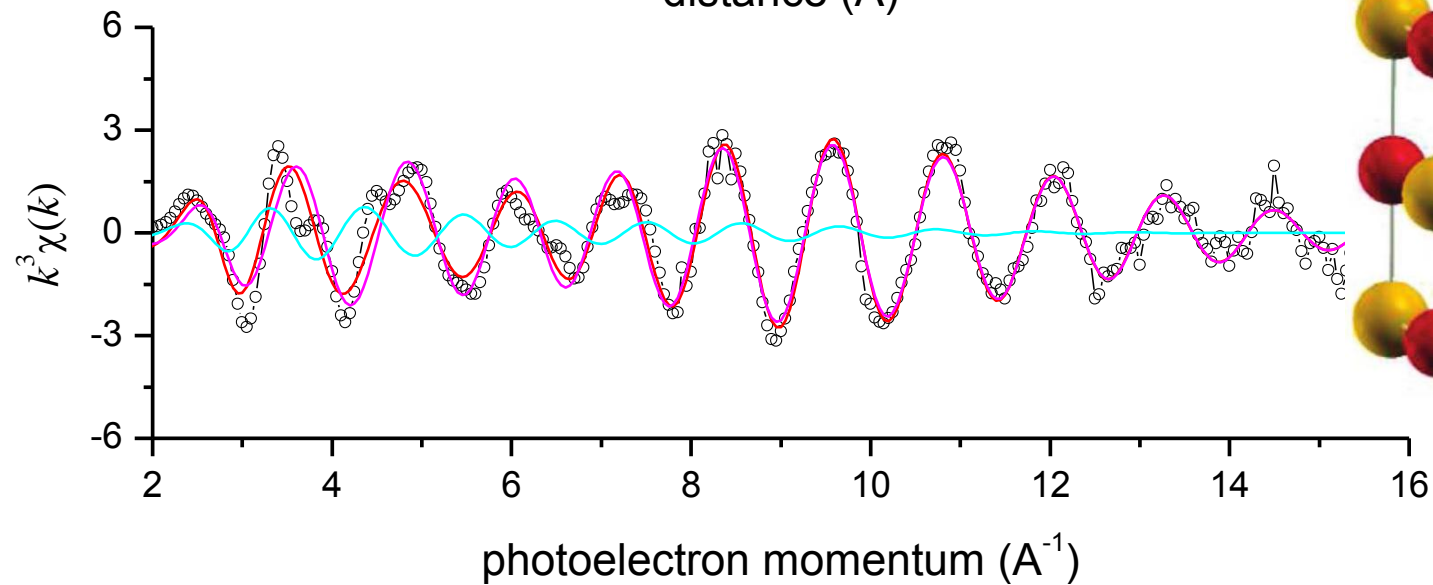
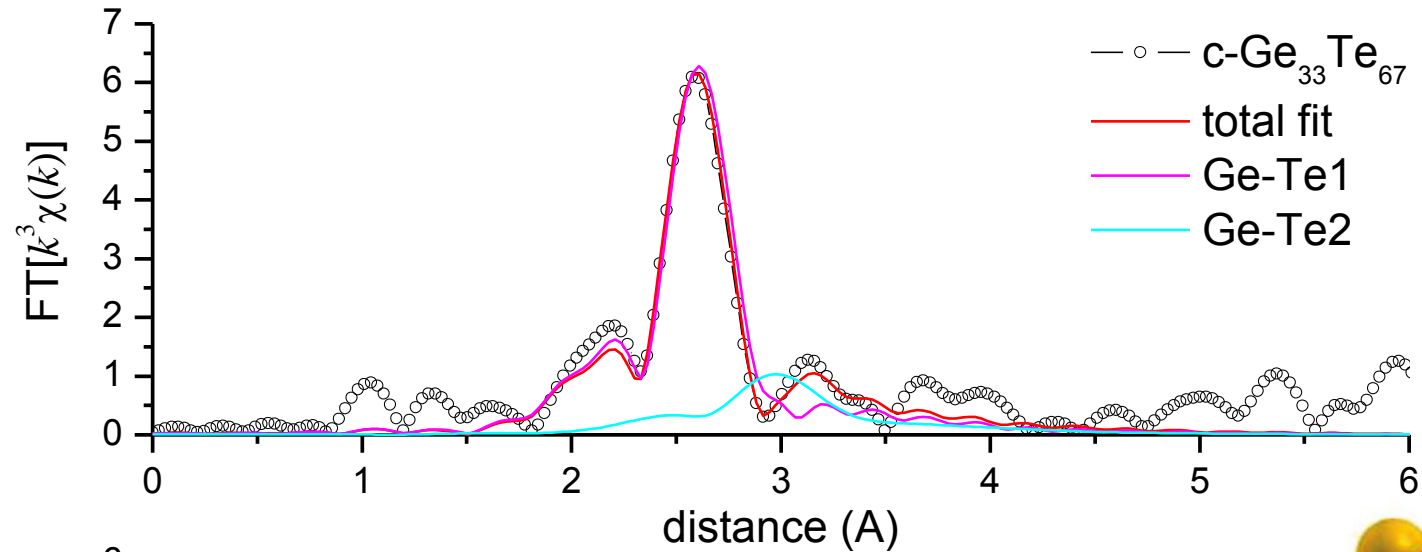
- ✓ CN of Ge is lowest among the amorphous samples, less than 4!



Ge in amorphous Te-deficient composition

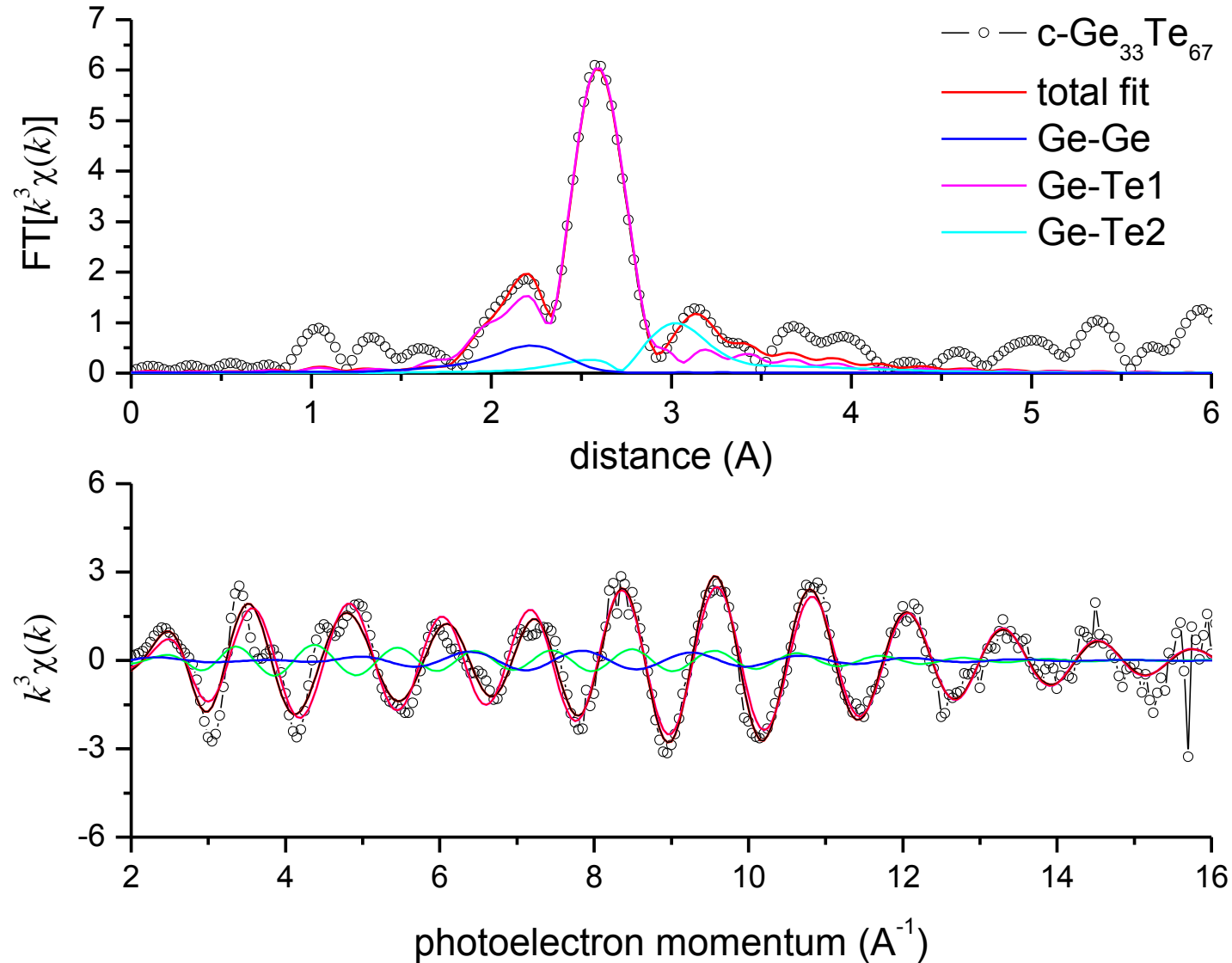


Ge in crystallized Te-rich composition



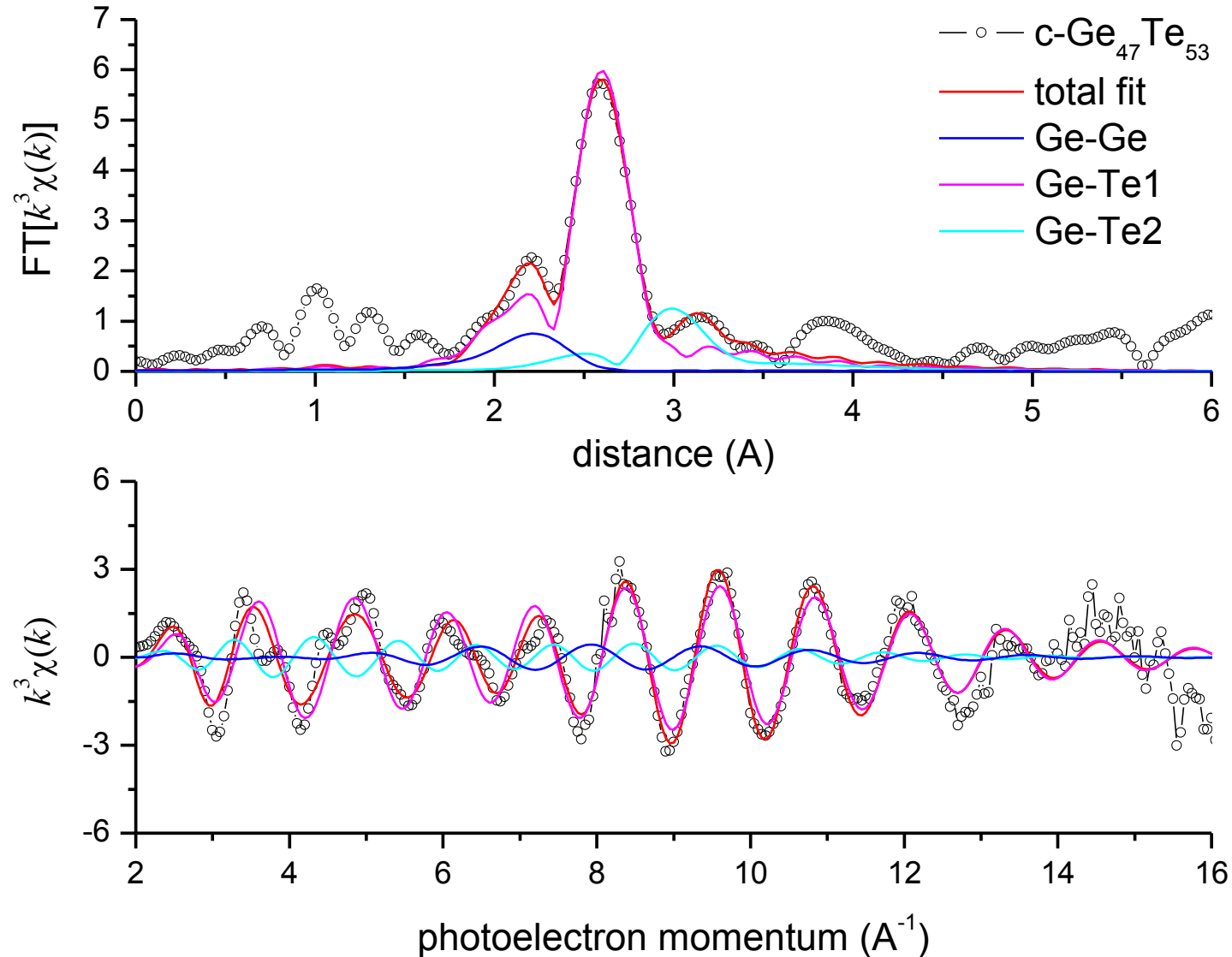
Ge in crystallized Te-rich composition

- ✓ Presence of homopolar Ge-Ge bonds in addition to the GeTe crystalline phase!



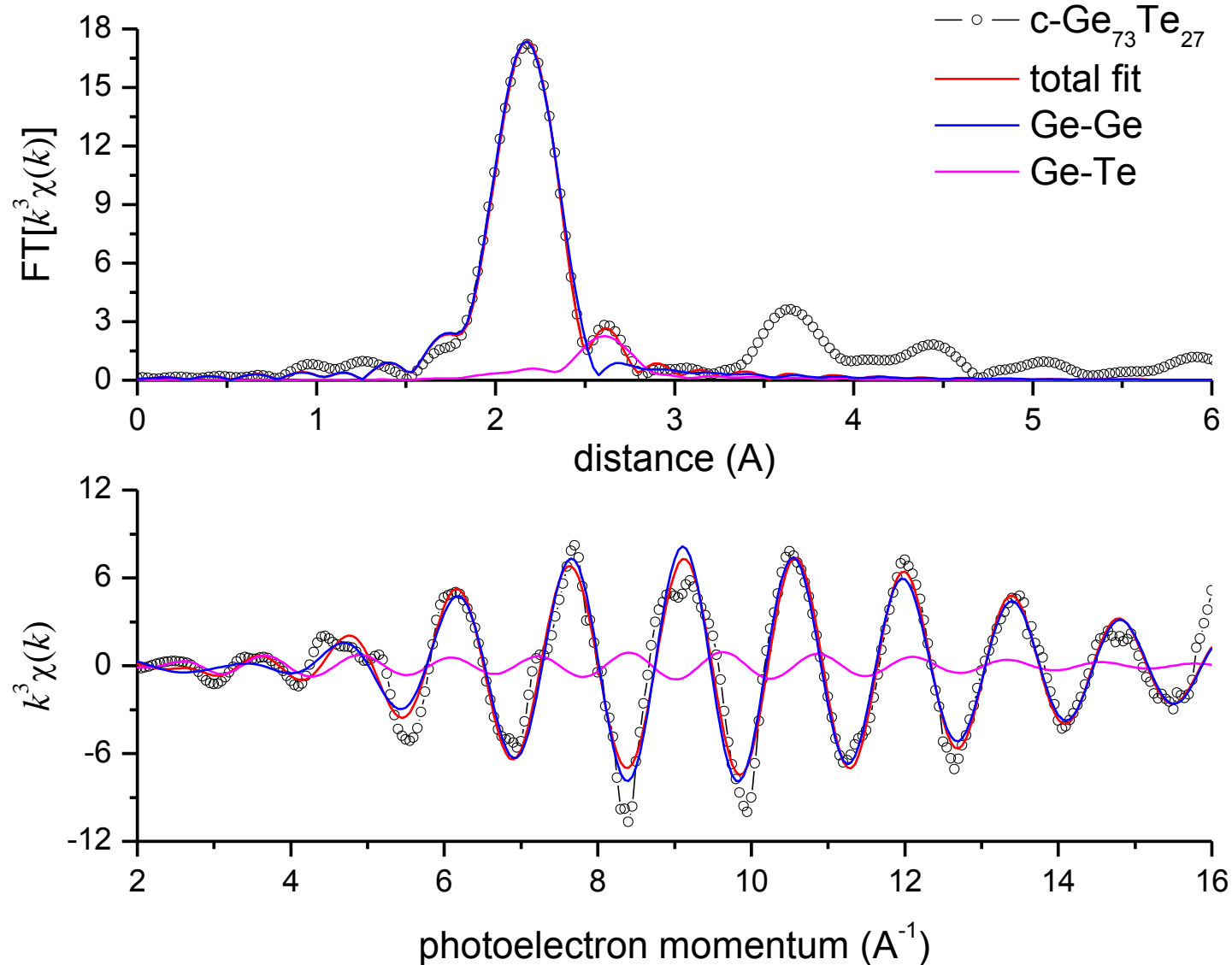
Ge in crystallized stoichiometric composition

- ✓ Presence of homopolar Ge-Ge bonds in addition to the GeTe crystalline phase!

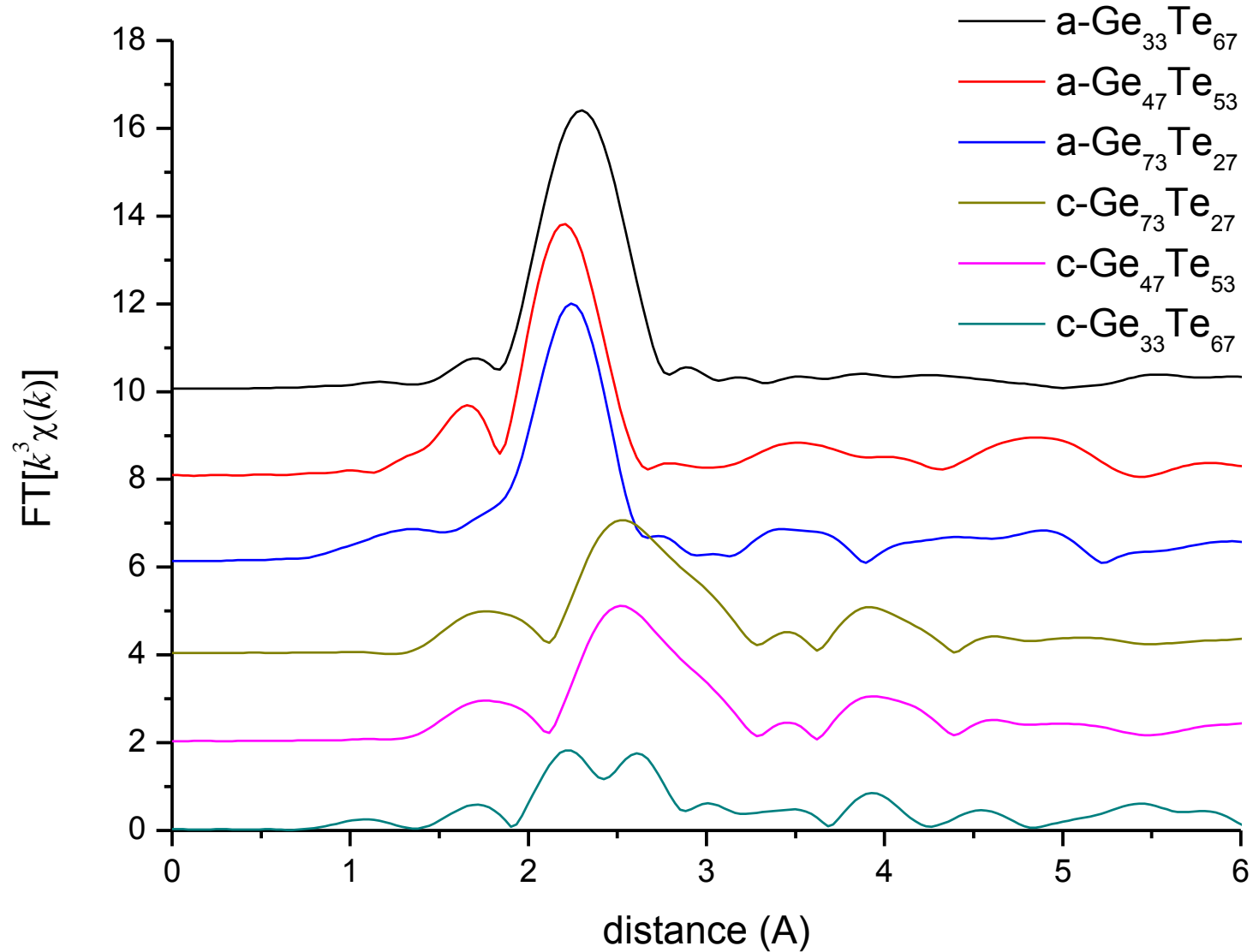


Ge in crystallized Te-deficient composition

- ✓ Presence of Ge crystalline phase and the GeTe crystalline phase



Te K-edge EXAFS spectra



Structure and phase-change properties

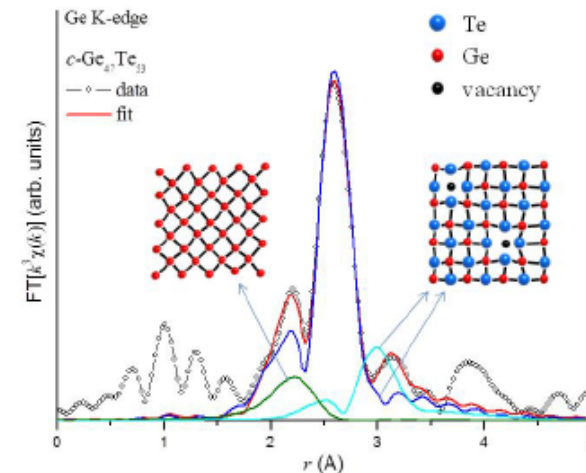
- Why lowest crystallization temperature at around $\text{Ge}_{50}\text{Te}_{50}$?
 - ✓ Across the compositional variations, Ge and Te atoms turn out to satisfy the 8- N rule in the amorphous state, but at the stoichiometric composition CN of Ge is less than 4, while CN of Te is close to 2, which may be related in terms of activation energy to its lowest crystallization temperature.
- Why crystallization of $\text{Ge}_{50}\text{Te}_{50}$ is slower than GST:225?
 - ✓ Coexistence of Ge clusters (or crystals with poor crystallinity) in the crystallized stoichiometric composition is responsible for its slower crystallization time than that of GST system.

Structure and phase-change properties

- Why fastest crystallization at around $\text{Ge}_{50}\text{Te}_{50}$ composition?
 - ✓ In the amorphous Te-rich and stoichiometric films, homopolar Ge-Ge bonds are present, which are also observed after crystallization.
 - ✓ The GeTe crystals have non-negligible amount of Ge-site vacancy which is believed to play an important role in the phase change properties.
 - ✓ The α -GeTe crystalline phase dominates only at the stoichiometric composition, and other phases (Ge and/or Te crystals) seems to delay the overall crystallization speed.

Atomic Arrangements in Germanium Telluride Influence Phase Change Memory

- Phase change memory (PCM) stores information using a special glass that can morph between crystalline and amorphous states. PCM is one of the newest memory technologies under development. Like flash memory, PCM retains stored information even when not powered. But PCM is faster.
- An international collaboration of scientists has investigated the structural basis of phase-change speed using germanium telluride as the model system. They determined the local atomic arrangements of each constituent element before and after the phase-change event. Their results indicate how the phase-switching speed and crystallization temperature strongly depend on the composition.
- Using EXAFS at NSLS beamline X18B, the team characterized thermally deposited germanium-telluride films, systematically covering a much wider range of Ge-Te formulations than previously attempted. The comprehensive, quantitative structural information has given deeper insight of the phase-change process.
- These findings will help fine-tune the compositional window and the film-processing conditions for improved PCM performance in more demanding applications.



Ge K-edge (innermost electron shell) EXAFS analysis of crystallized $\text{Ge}_{47}\text{Te}_{53}$ film, which shows presence of Ge quasi-crystals and GeTe crystals with non-negligible amount of Ge-site vacancies

Y.G. Choi et al., "Role of local structure in the phase change of Ge-Te films," *Chemical Physics Letters*, 534 (2012) 58-61

Prospects and opportunities

- ✓ Optical memory based on phase change driven by laser irradiation?
- ✓ Electrical memory based on phase change driven by electrical field
 - Replacement of Flash memory
 - A nonvolatile DRAM
- ✓ Switch array (logic) based on phase switching
- ✓ Cognitive computing based on phase switching
- ✓ Switch fabric based on threshold switching

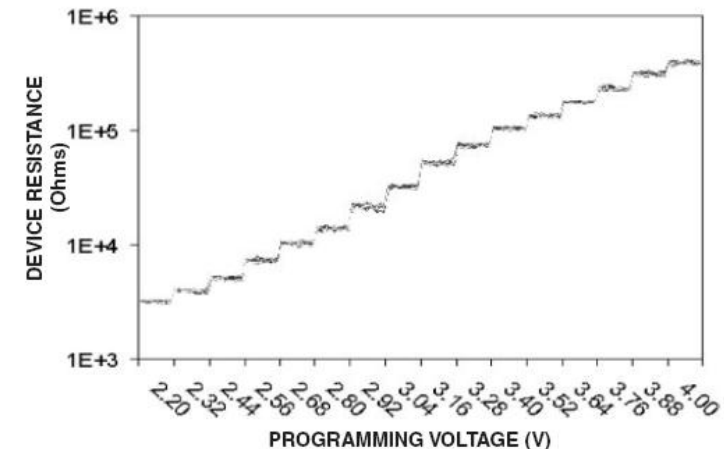
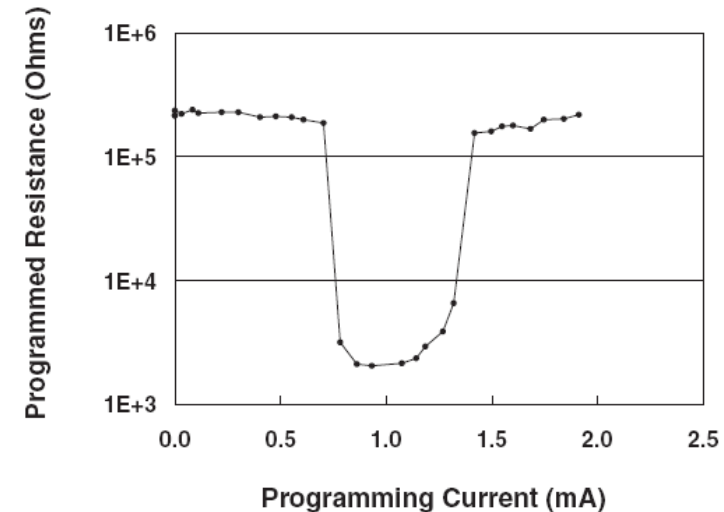
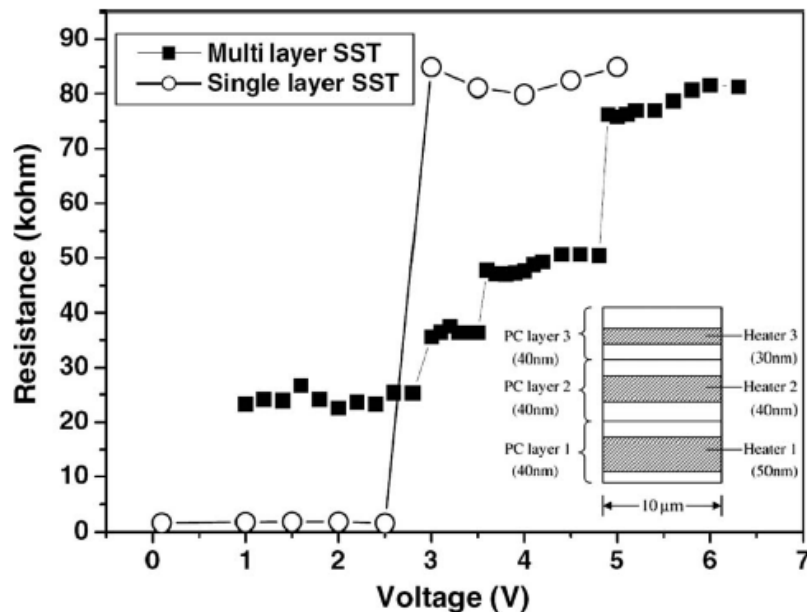


Figure in the left: Zhang et al, Phys. Stat. Sol., Rapid Res. Lett. 1 (2007) R28.

Figures in the right: Ovshinsky, Jap. J. Appl. Phys. 43 (2004) 4695.

Concluding remarks

- ✓ What are the **key scientific challenges** related to the topic of your presentation?

For device production;

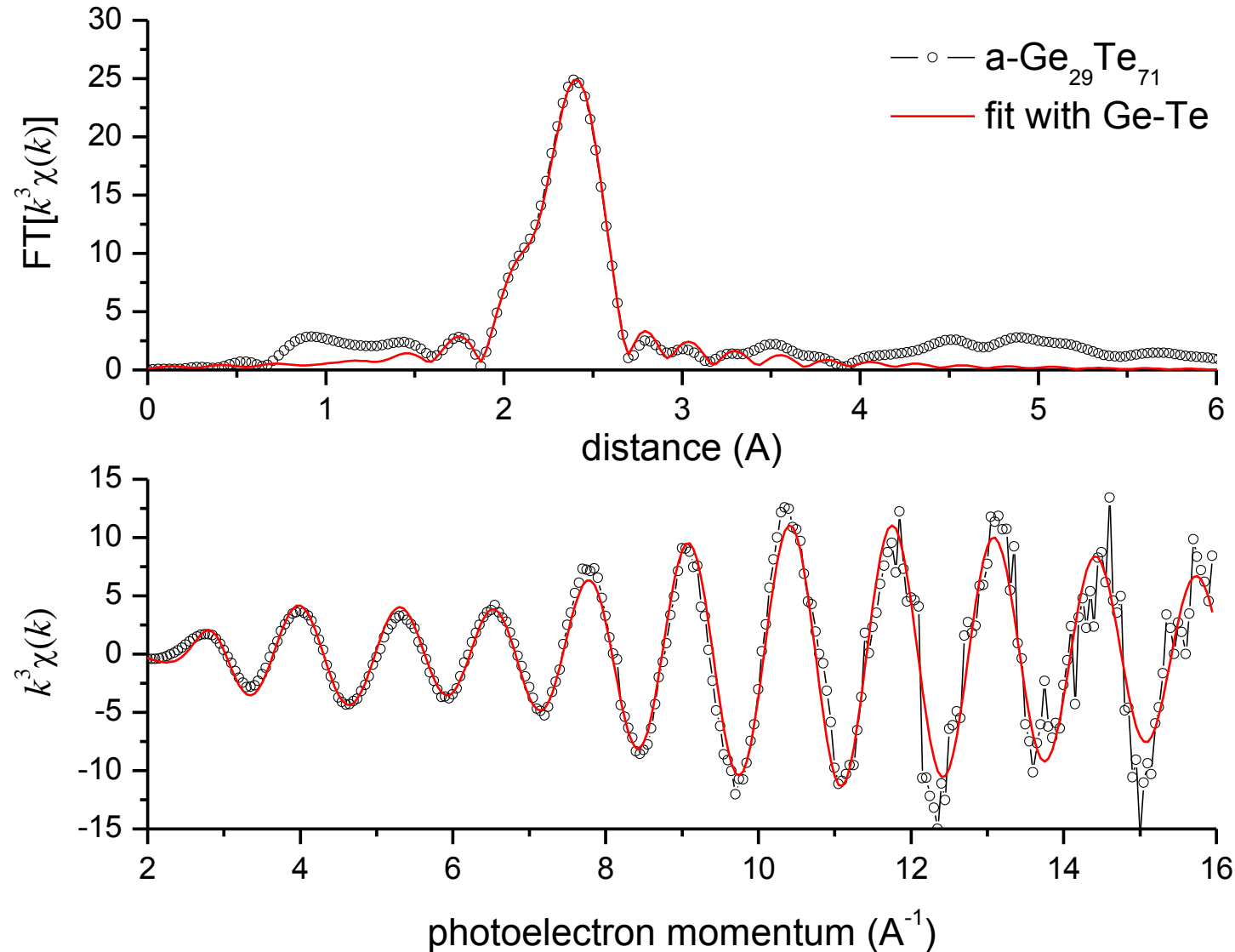
- The requirement of high programming current density ($>10^7$ A/cm², compared to 10^5 - 10^6 A/cm² for a typical transistor or diode) in the active volume.
- The contact between the hot phase-change region and the adjacent dielectric.
- A fundamental tradeoff of unintended vs. intended phase-change.
- Long-term resistance and threshold voltage drift.

A more precise understanding of the electrical switching phenomena, the threshold switching in particular.

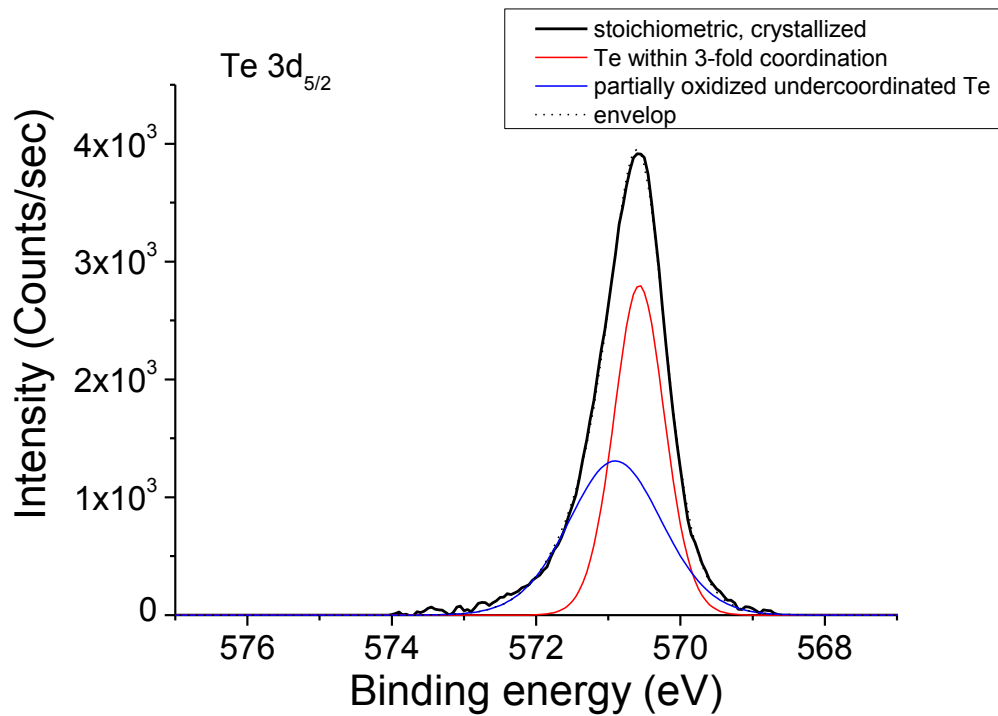
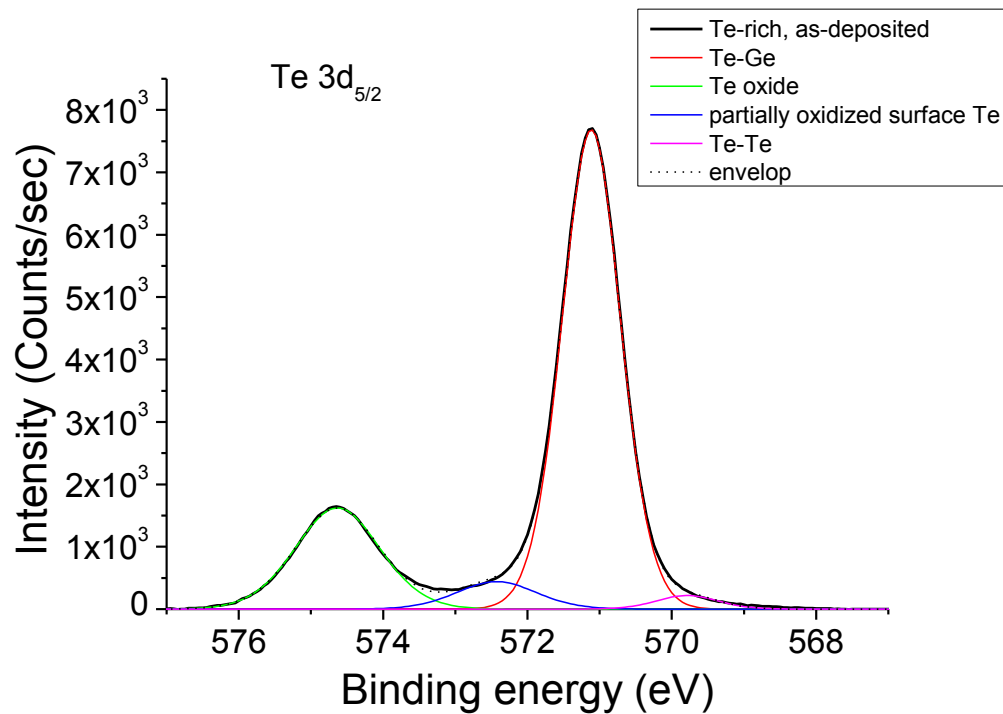
Designing and processing of phase-change films that are capable of the multi-level cell performance.

Ge in amorphous Te-super rich composition

- ✓ Absence of homopolar Ge-Ge bonds for further increased Te amount



High-resolution XPS spectra



Ge K-edge EXAFS analysis

	<i>a</i> -Ge ₃₃ Te ₆₇	<i>c</i> -Ge ₃₃ Te ₆₇	<i>a</i> -Ge ₄₇ Te ₅₃	<i>c</i> -Ge ₄₇ Te ₅₃	<i>a</i> -Ge ₇₃ Te ₂₇	<i>c</i> -Ge ₇₃ Te ₂₇
<i>R</i> -factor * (10 ⁻⁵)	0.7	61	0.3	75	1.8	32
fitting range						
ΔR (Å)	1.6 ~ 3.2	1.8 ~ 3.5	1.6 ~ 3.2	1.8 ~ 3.5	1.6 ~ 3.2	1.6 ~ 3.0
ΔK (Å ⁻¹)	2.0 ~ 15.5	2.0 ~ 15.5	2.0 ~ 15.5	2.0 ~ 15.5	2.0 ~ 15.5	2.0 ~ 15.5
<i>N</i> [Ge-Ge1]	0.28 ± 0.05	0.25 ± 0.05	1.20 ± 0.05	0.25 ± 0.05	3.0 ± 0.1	2.7 ± 0.1
<i>R</i> [Ge-Ge1] (Å)	2.46 ± 0.01	2.46 ± 0.01	2.50 ± 0.01	2.46 ± 0.01	2.47 ± 0.01	2.46 ± 0.01
σ^2 [Ge-Ge1] (10 ⁻⁴ Å ²)	25 ± 10	107 ± 90	40 ± 11	88 ± 80	47 ± 11	41 ± 4
<i>N</i> [Ge-Te1]	3.5 ± 0.1		2.1 ± 0.1		0.85 ± 0.1	
<i>R</i> [Ge-Te1] (Å)	2.60 ± 0.01		2.59 ± 0.01		2.61 ± 0.02	
σ^2 [Ge-Te1] (10 ⁻⁴ Å ²)	39 ± 8		51 ± 5		59 ± 31	
<i>N</i> [Ge-Te2]		2.4 ± 0.1		2.6 ± 0.1		0.9 ± 0.1
<i>R</i> [Ge-Te2] (Å)		2.80 ± 0.01		2.80 ± 0.01		2.79 ± 0.01
σ^2 [Ge-Te2] (10 ⁻⁴ Å ²)		79 ± 9		84 ± 15		79 ± 28
<i>N</i> [Ge-Te3]		1.2 ± 0.2		1.7 ± 0.2		
<i>R</i> [Ge-Te3] (Å)		3.16 ± 0.04		3.15 ± 0.04		
σ^2 [Ge-Te3] (10 ⁻⁴ Å ²)		127 ± 53		136 ± 64		

Te K-edge EXAFS analysis

	<i>a</i> -Ge ₃₃ Te ₆₇	<i>c</i> -Ge ₃₃ Te ₆₇	<i>a</i> -Ge ₄₇ Te ₅₃	<i>c</i> -Ge ₄₇ Te ₅₃	<i>a</i> -Ge ₇₃ Te ₂₇	<i>c</i> -Ge ₇₃ Te ₂₇
<i>R</i> -factor *	0.00094	0.0026	0.0078	0.0015	0.0044	0.0018
fitting range						
ΔR (Å)	1.4 ~ 3.0	1.8 ~ 3.2	1.8 ~ 3.0	2.0 ~ 3.2	1.6 ~ 3.0	1.6 ~ 3.4
ΔK (Å ⁻¹)	2.0 ~ 14.0	2.0 ~ 14.0	2.0 ~ 14.0	2.0 ~ 13.0	2.0 ~ 14.0	2.0 ~ 14.0
<i>N</i> [Te-Ge1]	1.56 ± 0.3		1.87 ± 0.28		2.1 ± 0.3	
<i>R</i> [Te-Ge1] (Å)	2.60 ± 0.01		2.61 ± 0.01		2.60 ± 0.01	
σ^2 [Te-Ge1] (10 ⁻⁴ Å ²)	42 ± 15		55 ± 12		57 ± 8	
<i>N</i> [Te-Te1]	0.38 ± 0.07	1.37 ± 0.1				
<i>R</i> [Te-Te1] (Å)	2.77 ± 0.02	2.81 ± 0.01				
σ^2 [Te-Te1] (10 ⁻⁴ Å ²)	29 ± 17	66 ± 86				
<i>N</i> [Te-Ge2]		0.68 ± 0.40		1.7 ± 0.1		2.21 ± 1.40
<i>R</i> [Te-Ge2] (Å)		2.86 ± 0.01		2.84 ± 0.01		2.84 ± 0.02
σ^2 [Te-Ge2] (10 ⁻⁴ Å ²)		77 ± 39		74 ± 15		95 ± 28
<i>N</i> [Te-Ge3]				1.23 ± 0.20		1.79 ± 0.25
<i>R</i> [Te-Ge3] (Å)				3.21 ± 0.02		3.19 ± 0.02
σ^2 [Te-Ge3] (10 ⁻⁴ Å ²)				79 ± 34		94 ± 35