Electronics applications I

IMI
NFG

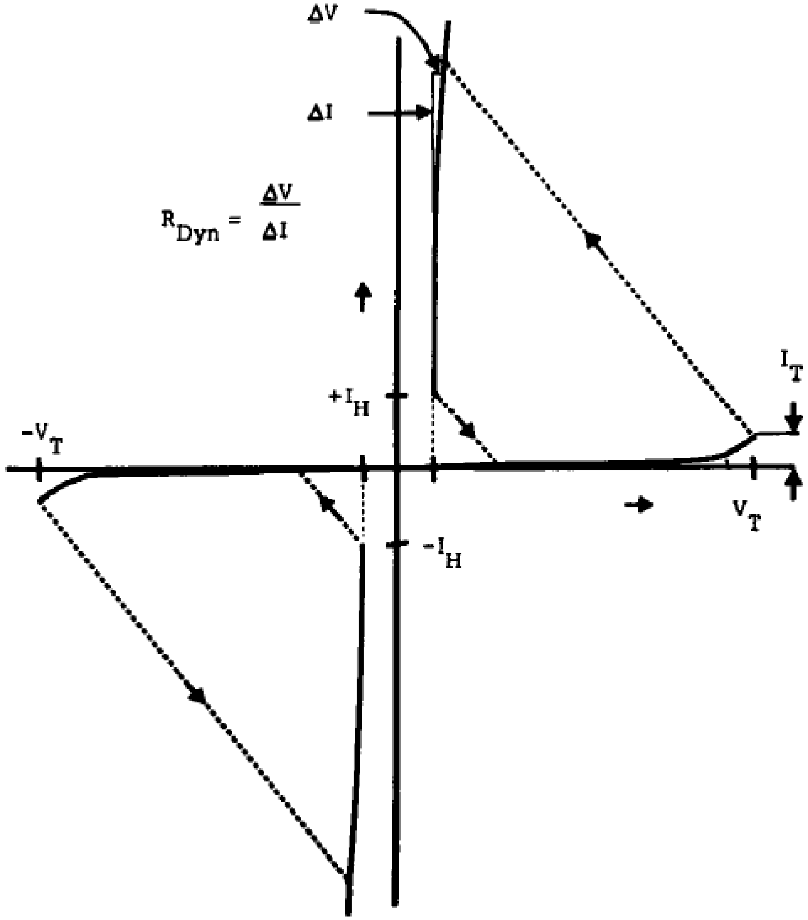
- ✓ Electrical switching in amorphous chalcogenides
  - ➢ Threshold switching and phase switching
- ✓ Phase change materials
  - ➢ Optical memory and electrical memory
- ✓ Scaling properties of phase change materials

LEHIGH
UNIVERSITY.

KOREA AEROSPACE
UNIVERSITY

- Important

Threshold switching



Phenomena

- ✓ For most MIM contacts, I-V chacteristics are essentially symmetric with respect to polarity.
- ✓ For fields below ~10^4 V/cm, conduction is ohmic with resistance of 10^5~10^7 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 1~10 Ω.
- ✓ If holding current is maintained, the material remains conducting. However, it returns to high-resistance state on removal of voltage.

Adler and Moss, J. Vac. Sci. Technol. 9 (1972) 1182.

- Important

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 nonboning 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.

Adler, Shur, Silver and Ovshinsky, J. Appl. Phys. 51 (1980) 3289.

- For information

Threshold switching

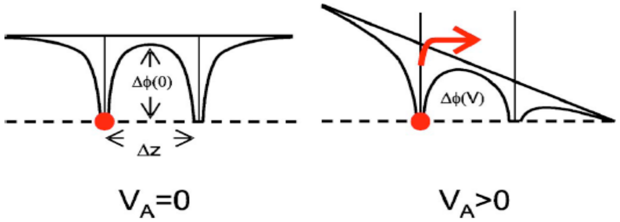
Proposed mechanisms

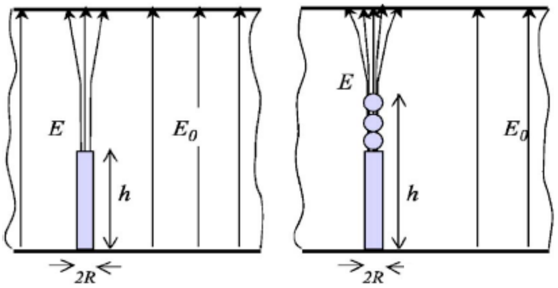
1) Thermal mechanisms

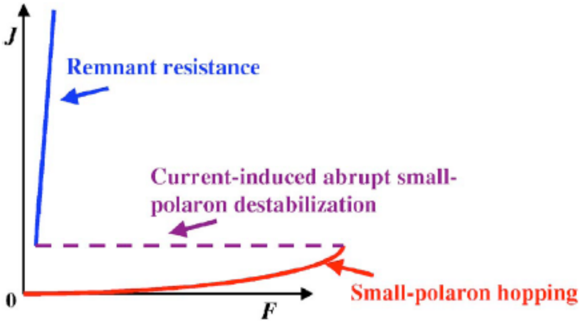
- ✓ Joule heating in conjunction with the exponential increase of conductivity with temperature.
- ✓ Electrons accelerated by the field emit phonons to return to equilibrium.
- ✓ It is generally believed that pure thermal model cannot account for threshold switching.
- ✓ Both electronic and thermal effects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



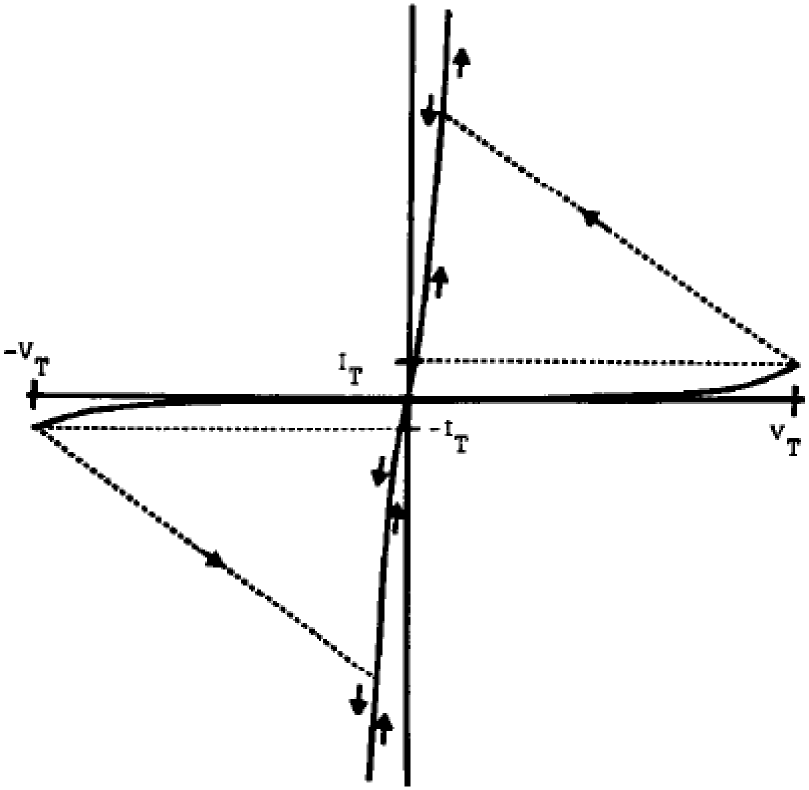




Adler and Moss, J. Vac. Sci. Technol. 9 (1972) 1182.
Adler, Henisch and Mott, Rev. Mod. Phys. 50 (1978) 209.
Raoux, Welnic and Ielmini, Chem. Rev. 110 (2010) 240.

- Important

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 ~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.

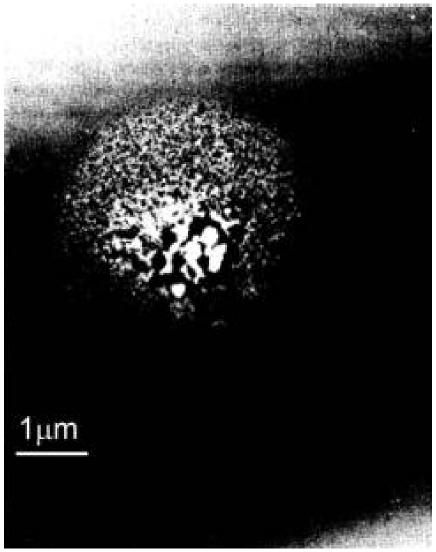
- ✓ In memory switching, the conducting and nonconducting states represent crystalline and amorphous phases of the same material, respectively; ***phase change material!***

Adler and Moss, J. Vac. Sci. Technol. 9 (1972) 1182.

- For information

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 48Te30As12Si10Ge, 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 81Te15Ge2Sb2S film was demonstrated on the microsecond time scale.

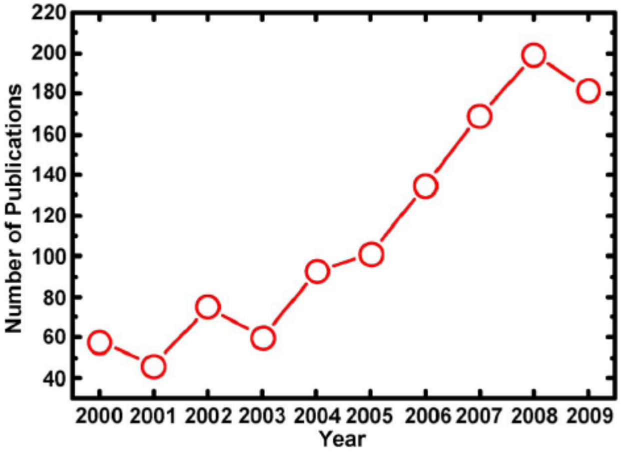


1. Northover and Pearson, U.S. Patent 3,117,013, 1964.
2. Dewald, Northover and Pearson, U.S. Patent 3,241,009. 1966.
3. Ovshinsky, U.S. Patent 3,271,591, 1966.
4. Ovshinsky, Phys. ReV. Lett. 22 (1968) 1450.
5. Feinleib et al, Appl. Phys. Lett. 18 (1971) 254.

- For information

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.

- For information

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

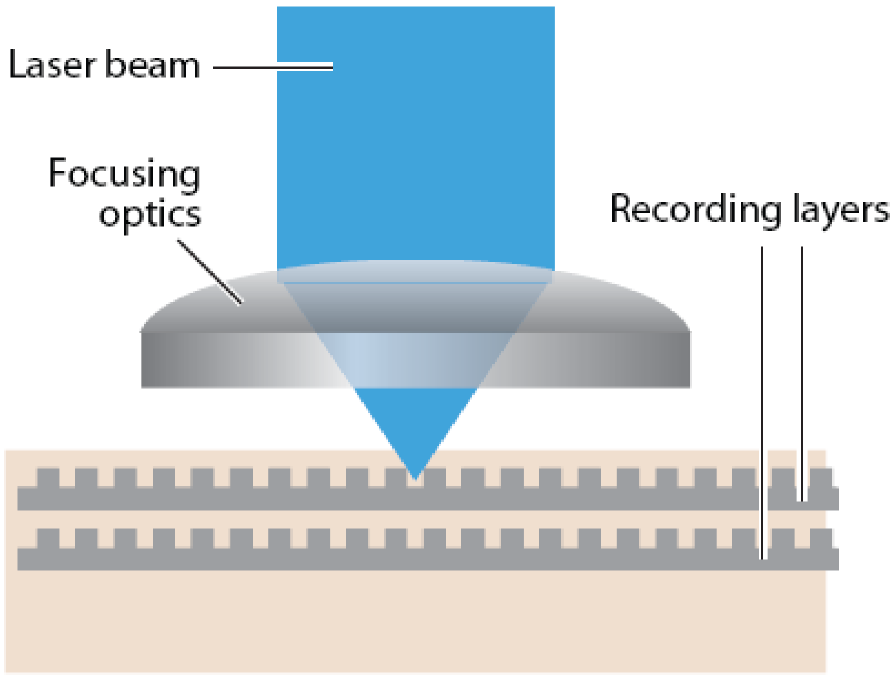
- ✓ Raoux et al, Phase-change random access memory: A scalable technology, IBM J. Res. & Dev. 52 (2008) 465.
- ✓ Wong et al, Phase change memory, Proc. IEEE 98 (2010) 2201.
- ✓ Burr et al, Phase change memory technology, J. Vac. Sci. Technol. B 28 (2010) 223.

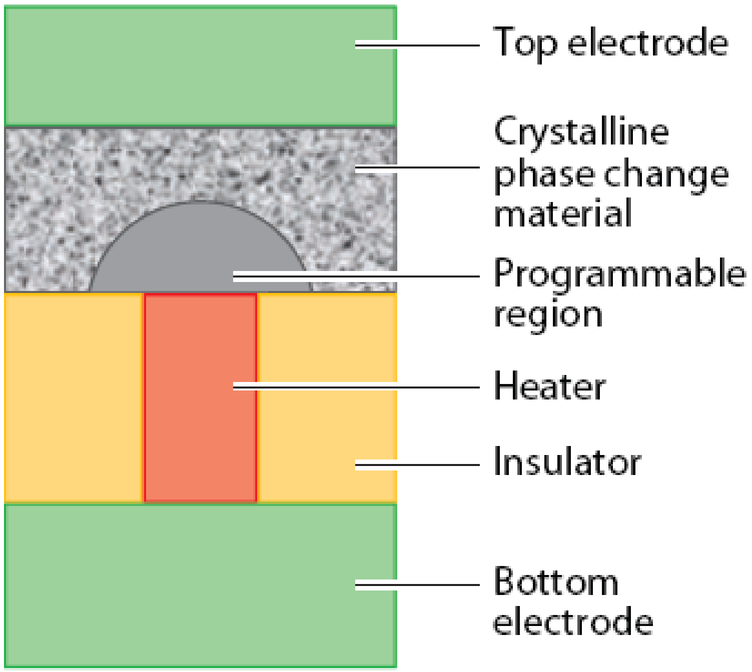
Reviews focused on ionics-based memories

- ✓ Waser and Aono, Nanoionics-based resistive switching memories, Nat. Mater. 6 (2007) 833.
- ✓ Waser et al, Redox-based resistive switching memories–Nanoionic mechanisms, prospects, and challenges, Adv. Mater. 21 (2009) 2632.

- For information

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 $Ge_2Sb_2Te_5$.

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

- For information

Required properties of phase change materials

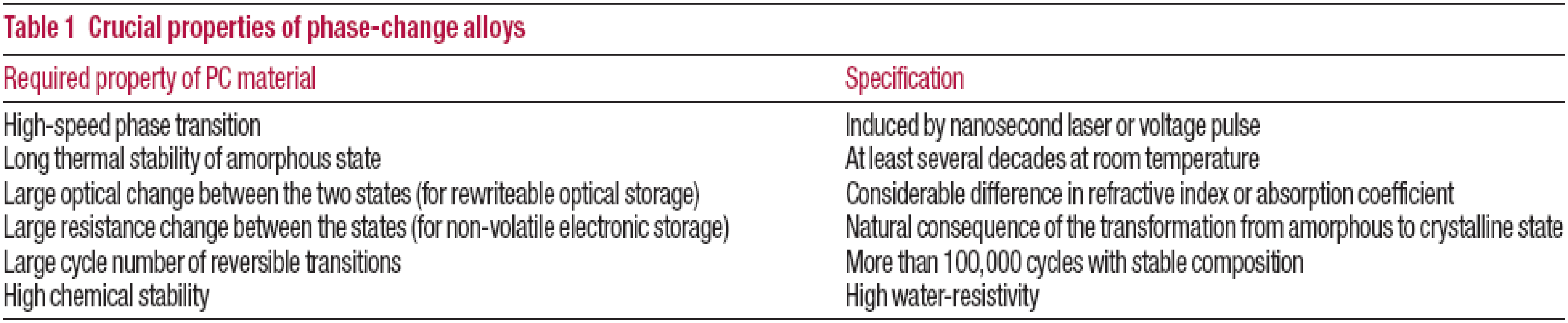


Table 1 Crucial properties of phase-change alloys

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

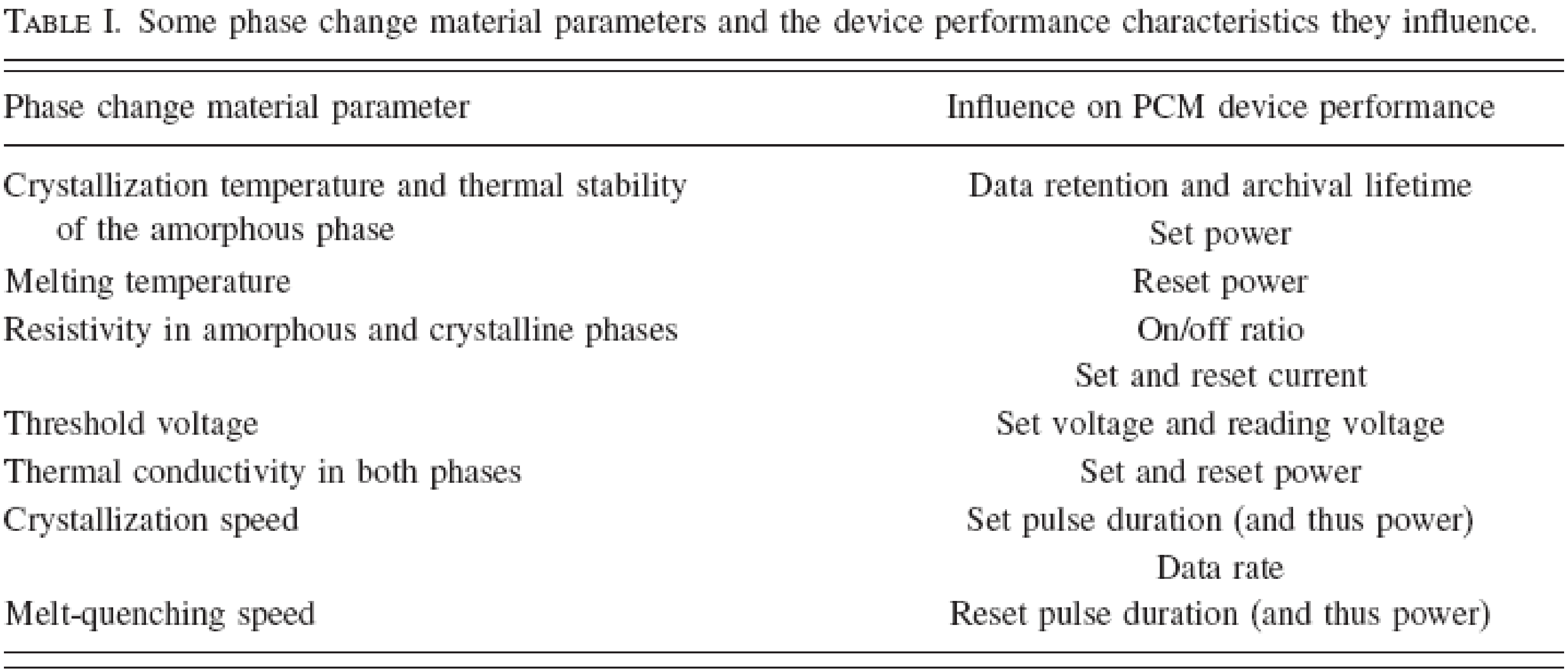


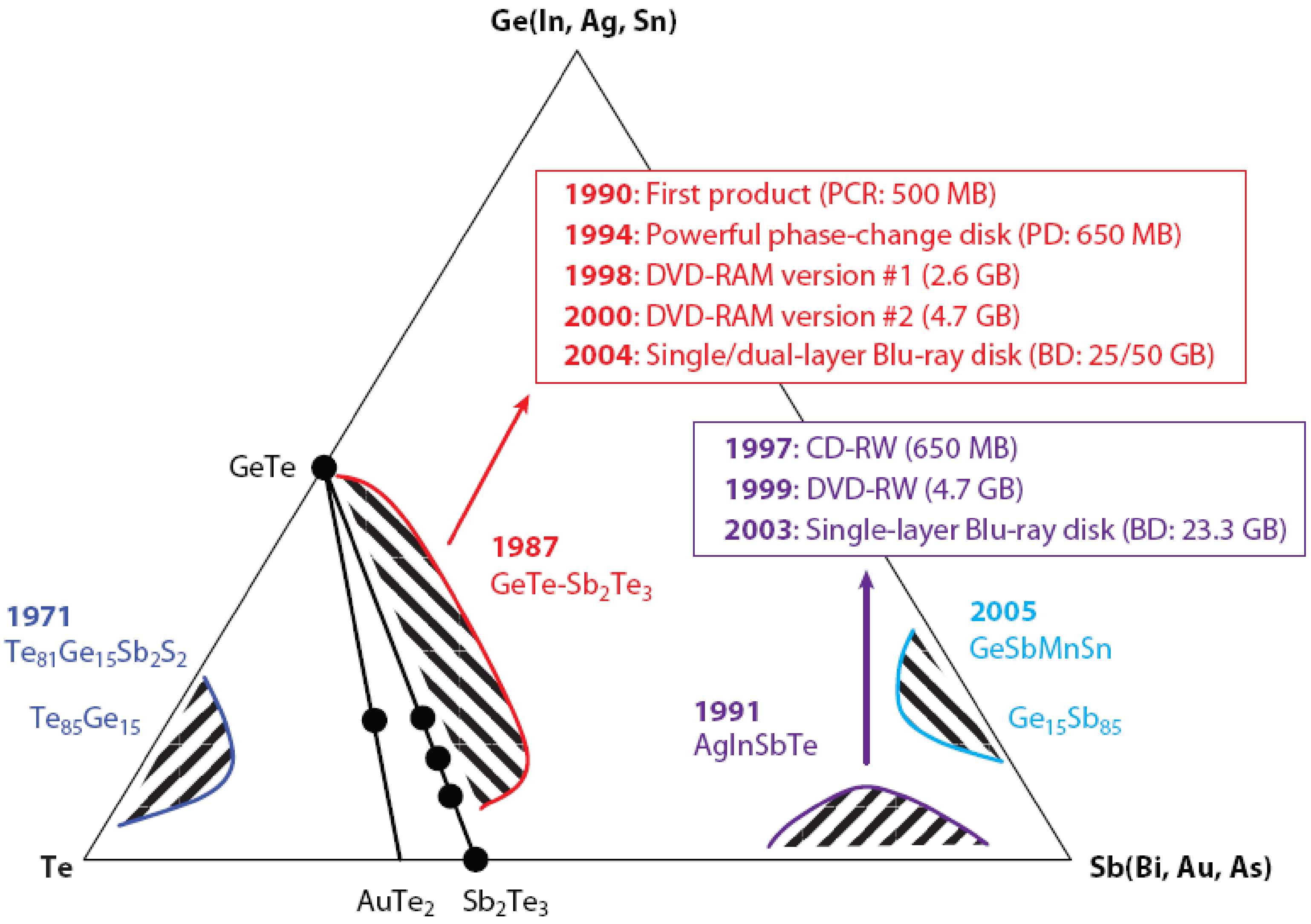
TABLE I. Some phase change material parameters and the device performance characteristics they influence.

Phase change material parameter	Influence on PCM device performance
Crystallization temperature and thermal stability of the amorphous phase	Data retention and archival lifetime Set power
Melting temperature	Reset power
Resistivity in amorphous and crystalline phases	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.

- For information

Representative phase change materials



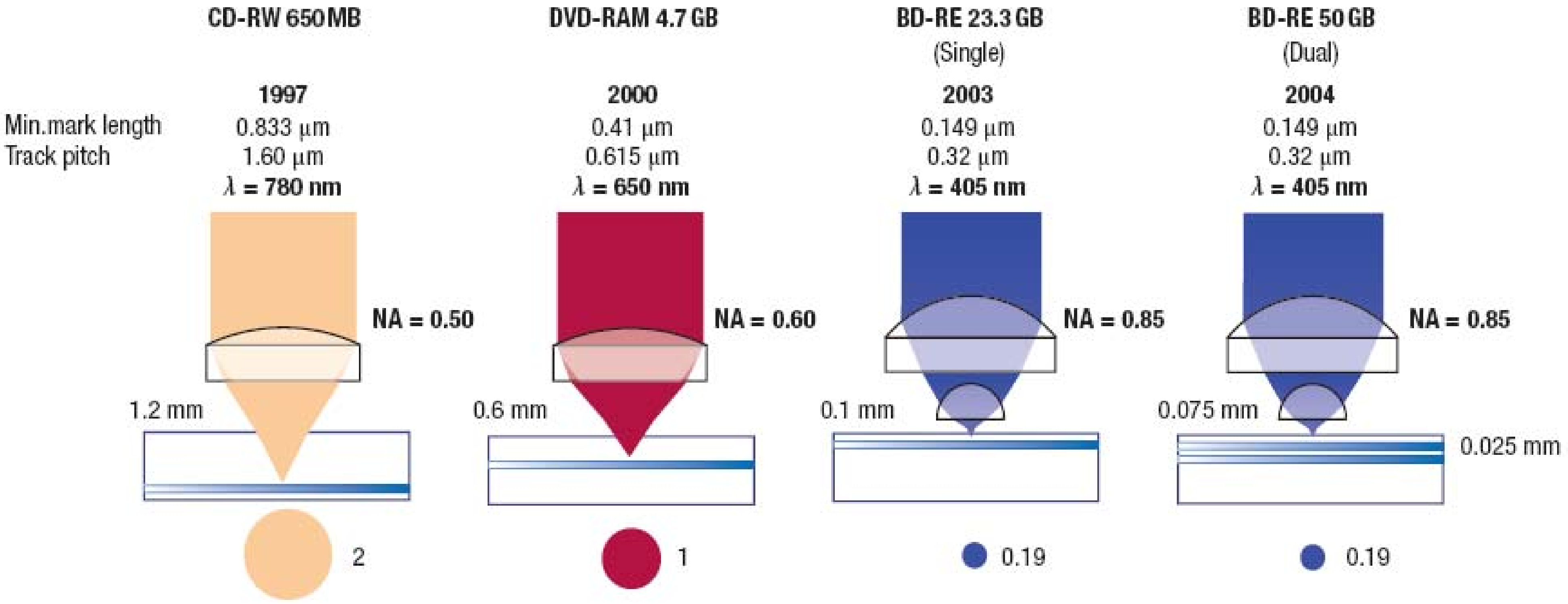
1990: First product (PCR: 500 MB)
1994: Powerful phase-change disk (PD: 650 MB)
1998: DVD-RAM version #1 (2.6 GB)
2000: DVD-RAM version #2 (4.7 GB)
2004: Single/dual-layer Blu-ray disk (BD: 25/50 GB)

1997: CD-RW (650 MB)
1999: DVD-RW (4.7 GB)
2003: Single-layer Blu-ray disk (BD: 23.3 GB)

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

- For information

Increasing capacity of optical memory

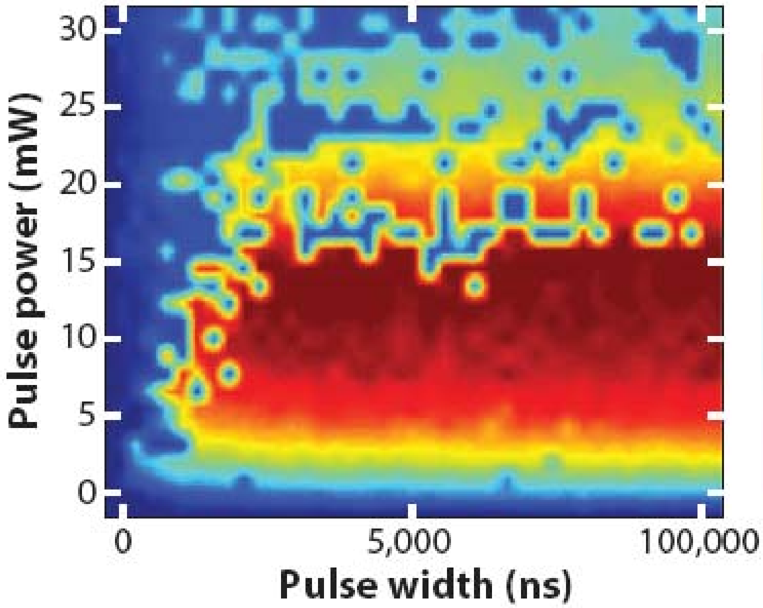


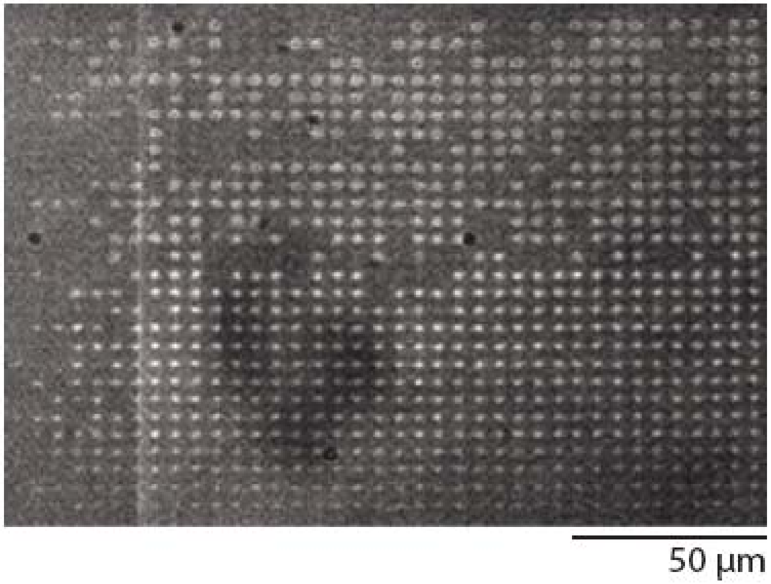
- ✓ Comparison of optics, recording densities, recording capacities and disk structures used for CD , DVD and BD. The change in beam cross-section is displayed at the bottom.
- ✓ From CD to DVD and DVD to BD, the effective laser beam cross-section has been reduced by a factor of 2 and 5, respectively. 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.

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

- For information

Change in optical properties



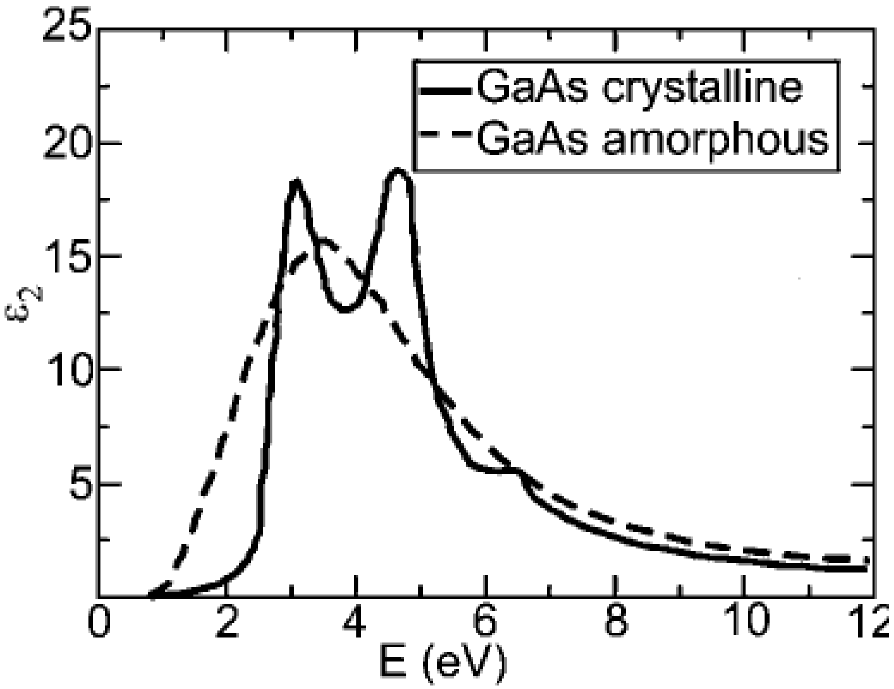


- ✓ (Left) Reflectivity change in amorphous, as-deposited 50-nm 71Ag11In48Sb34Te on 30-nm Al_2O_3 on Si due to a laser pulse of variable power and duration. The reflectivity is increased if the laser power and duration are sufficient to crystallize the film. The contour plot is the change in reflectivity 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.

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

- Important

Change in optical properties

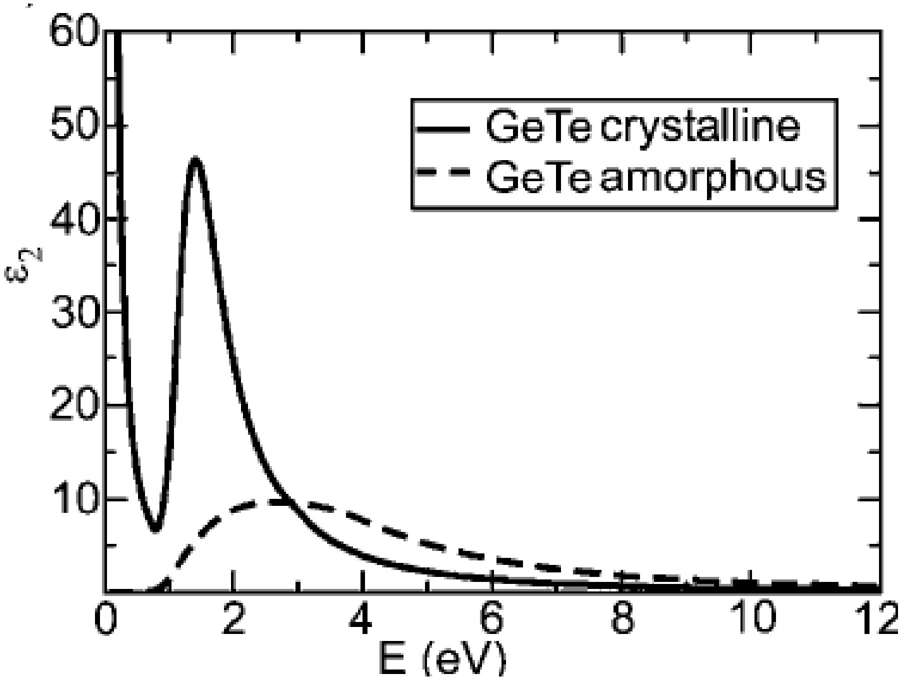


- ✓ Experimental optical absorption of GaAs in the crystalline and amorphous phase.
- ✓ No valence-four alloy such as GaAs or Si has been reported to be suitable for phase-change applications.
- ✓ These differences are explained by a smearing of the electronic density of states resulting from the loss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

Raoux, Welnic, and Ielmini, Chem. Rev. 110 (2010) 240.

- Important

Change in optical properties

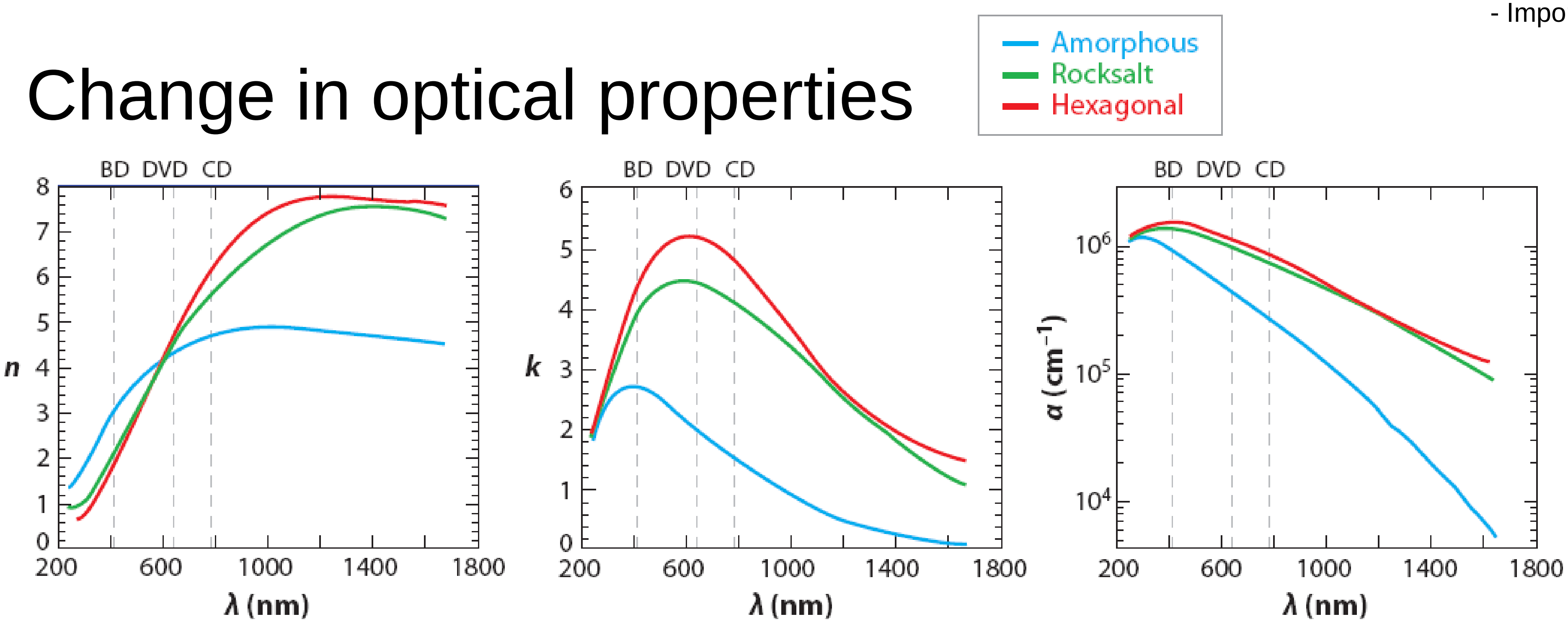


- ✓ Experimental optical absorption of GeTe in the crystalline and amorphous phase. Compared to the changes in GaAs, the differences between the two spectra in GeTe are huge.
- ✓ Three major differences observed: a Drude peak present in the crystalline phase but absent in the amorphous one, a blue shift 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

Raoux, Welnic, and Ielmini, Chem. Rev. 110 (2010) 240.

- Important

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.

Shportko et al, Nat. Mater. 7 (2008) 653.

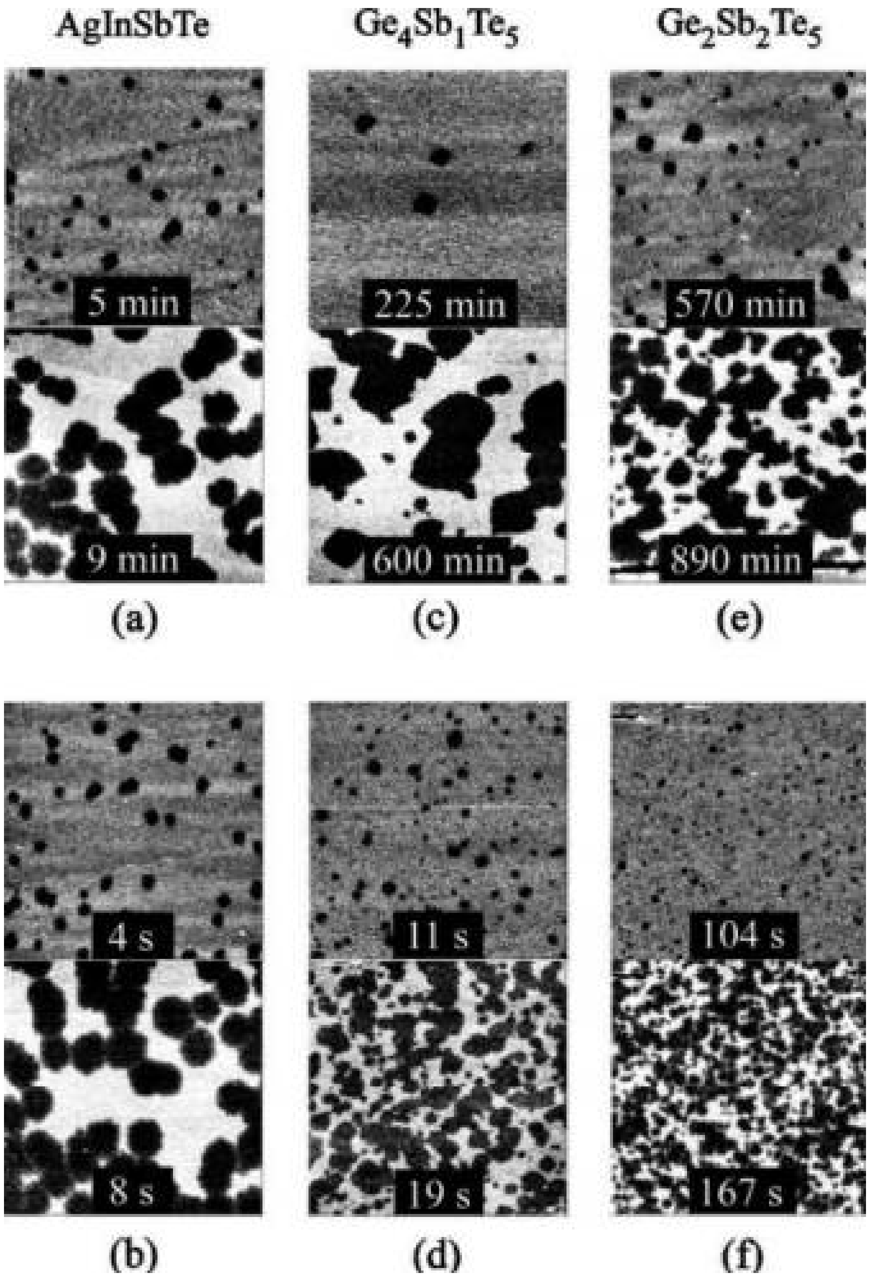
- Important

Difference in crystallization

- ✓ **PCMs are categorized into nucleation-dominated and growth-dominated materials.**

- ✓ AFM scans (field of view 3 μm × 3 μm) 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 °C; (b) AIST 180 °C; (c) GST-415 140 °C; (d) GST-415 180 °C; (e) GST-225 115 °C; (f) GST-225 145 °C.

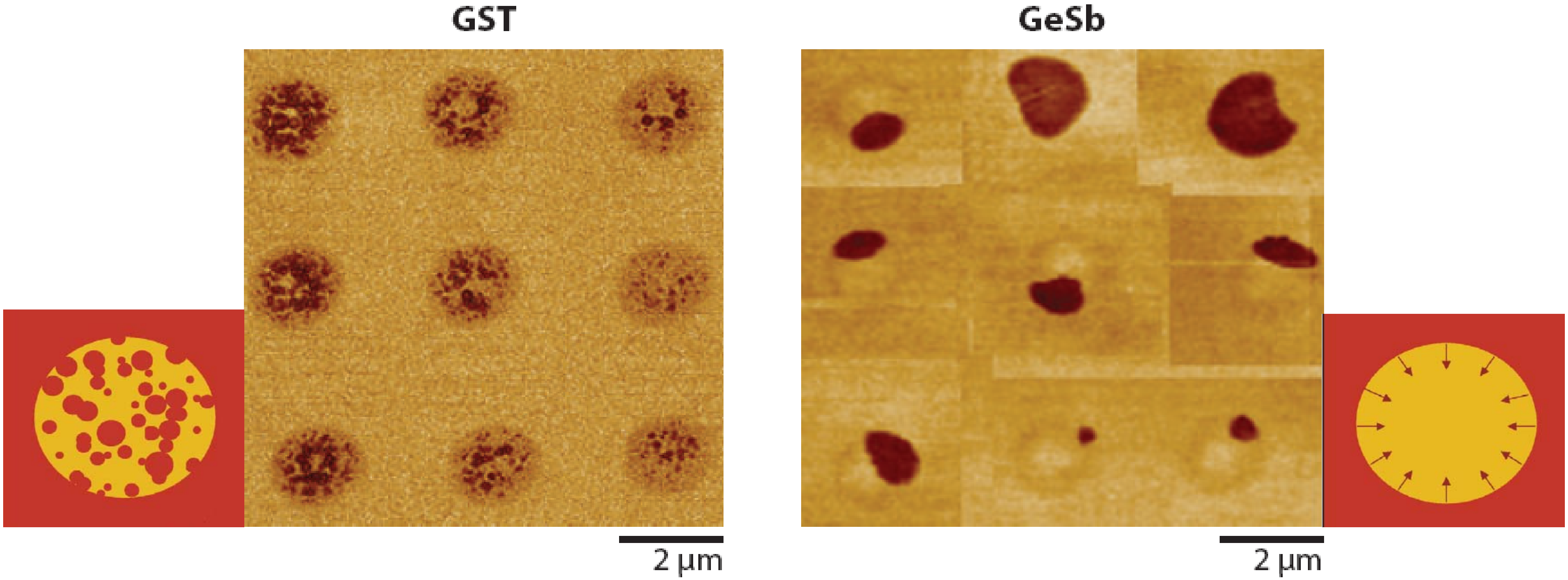
- ✓ Nucleation-dominated materials have relatively short incubation times, high nucleation rates, but slow growth velocities while growth-dominated materials have relatively long incubation times, low nucleation rates, and high growth velocities.



Kalb et al, J. Appl. Phys. 84 (2004) 5240.

- For information

Difference in crystallization

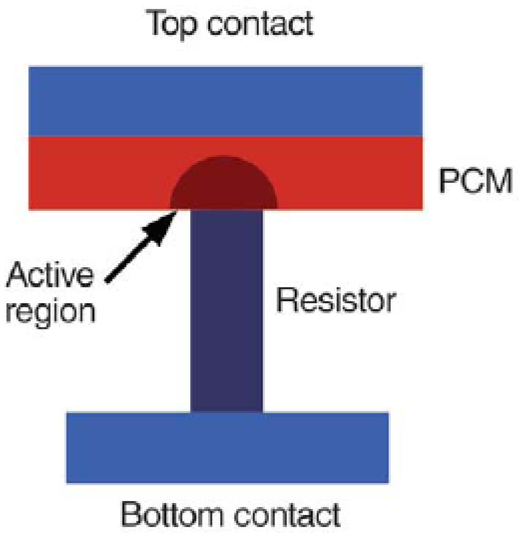


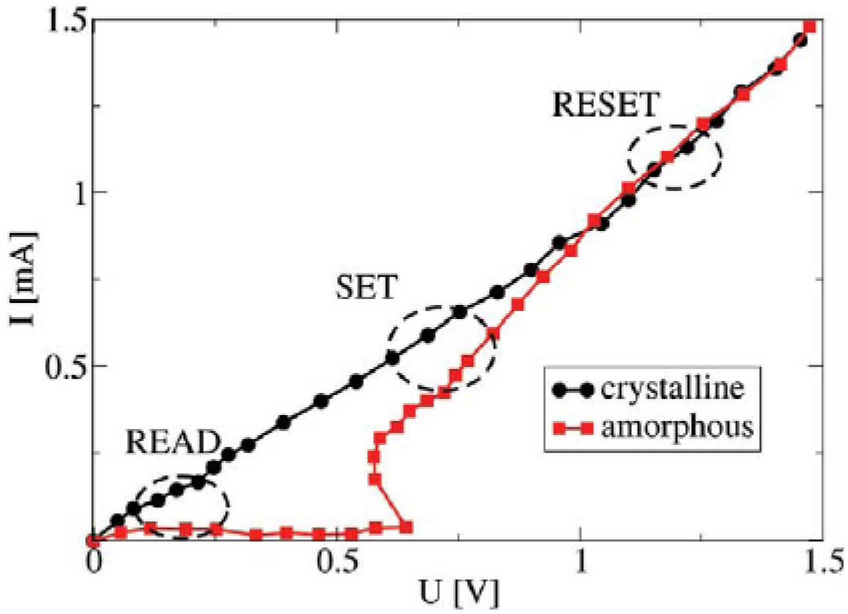
- ✓ AFM images of GST-225 (nucleation-dominated) and 15Ge85Sb (growth-dominated) thin films exposed to a laser pulse that had a power and duration that led to partial crystallization of the films.
- ✓ The dark areas of the images are crystalline regions that have a higher mass density. The GST film was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

Chen et al, Int. Electron. Devices Meet. Tech. Dig., San Francisco (2006) pp. 777–80.

- Important

Electrical memory: operation



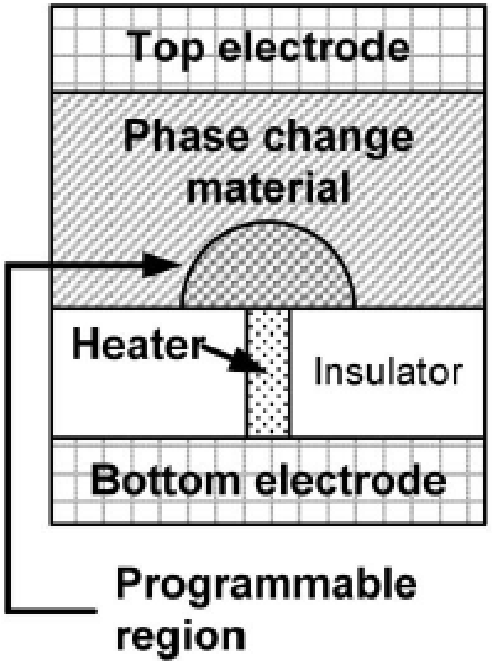


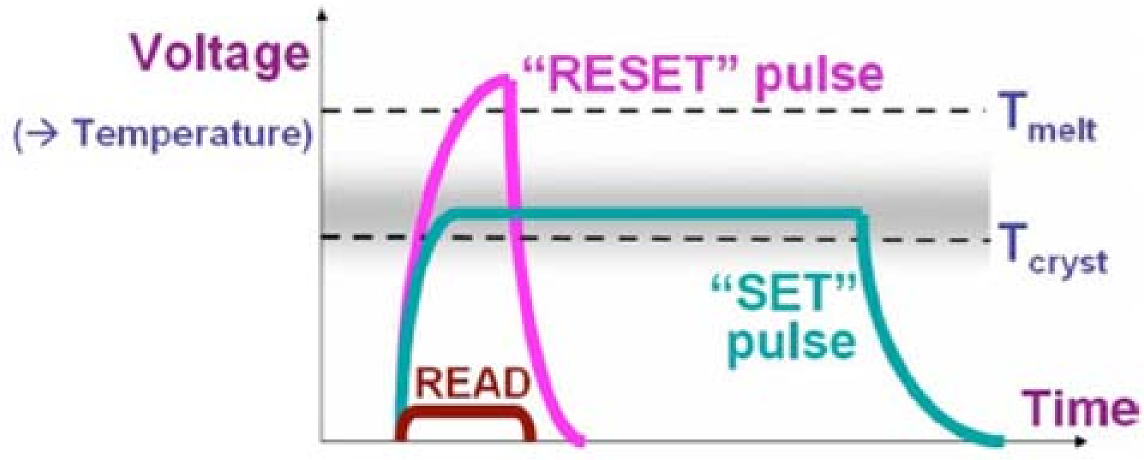
- ✓ The cell is essentially a nonlinear resistor and the readout is performed at low bias (READ region), where the low-field resistance changes by orders of magnitude depending on whether the material in the active region of the device is crystalline or amorphous.
- ✓ To reach the switching regions (SET 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.

Pirovano et al, IEEE Trans. Electron Devices 51 (2004) 714.

- Important

Electrical memory: operation





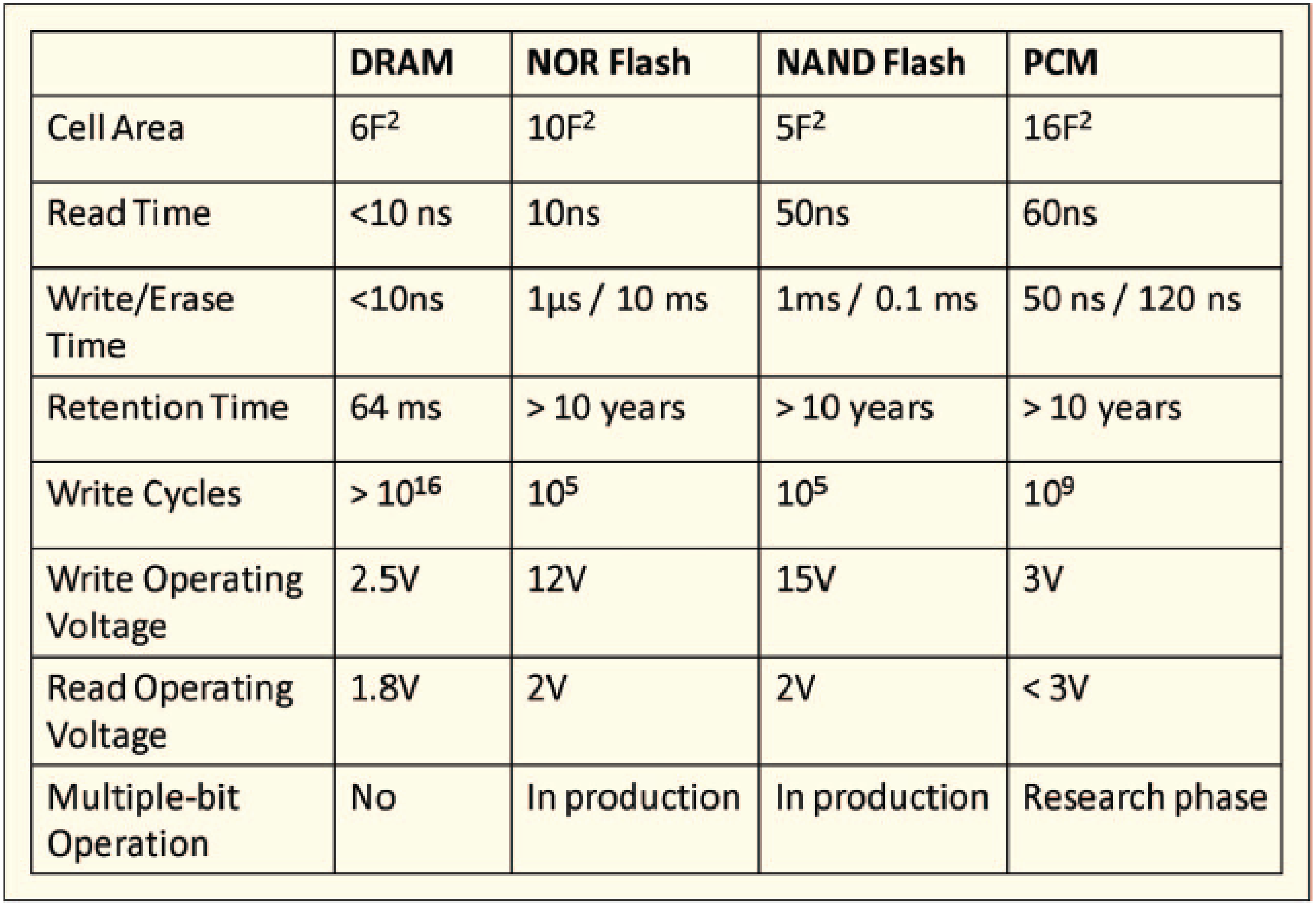
- ✓ Programming of a PCM device involves application of electrical power through applied voltage, leading to internal temperature changes that either melt and then rapidly quench a volume of amorphous material (RESET), or which hold this volume at a slightly lower temperature for sufficient time for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

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

- For information

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

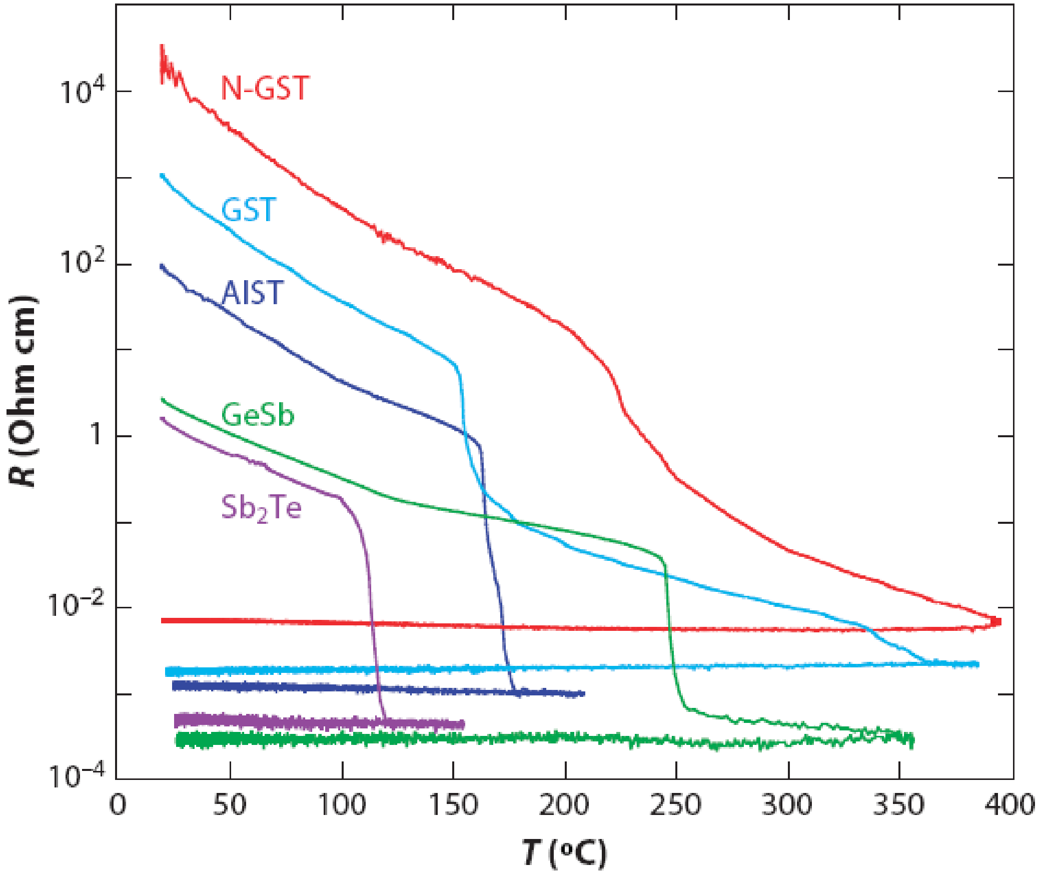
- ✓ Drawbacks
  - ➢ Temperature sensitivity and high RESET currents

Wong et al, Proc. IEEE 98 (2010) 2201.

- For information

Phase change materials for electrical memory

Binary	**Ternary**	**Quaternary**
Ga Sb	$Ge_2Sb_2Te_5$	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	$Te_{81}Ge_{15}Sb_2S_2$
Ge Te	In Sb Ge	$Ge_2Sb_2Te_5$:O
Ge Sb	Ga Sb Te	$Ge_2Sb_2Te_5$:N



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

Raoux et al, J. Appl. Phys. 102 (2007) 94305.

- For information

Scaling properties of phase change materials

- ✓ The crystallization time
  - ➢ Vary as a function of substrate and capping layer, and this influence becomes stronger as film thickness is reduced because the interfaces play a more and more important role.
  - ➢ Heterogeneous nucleation typically dominates the nucleation process, and with reduced film thickness, this becomes even more pronounced.
  - ➢ From a memory device perspective, the scaling behavior is favorable because switching times are reduced.

- ✓ The amorphization time
  - ➢ Determined by the time to heat the material above its melting temperature, which in turn is determined by the melting temperature, the available power, and the thermal environment.
  - ➢ Fast optical heating is easier to achieve than fast Joule heating caused by electrical current pulses because inherent capacitances limit pulse rise times to hundreds of picoseconds.
  - ➢ The fastest reported re-amorphization of a memory cell was 400 ps.

Raoux, Welnic, and Ielmini, Chem. Rev. 110 (2010) 240.

- For information

Scaling properties of phase change materials

✓ The melting temperature

- ➢ As a function of size, melting temperature has been studied for thin films, nanowires, and nanoparticles. In all cases a reduction of melting temperature appeared as dimensions are reduced.
- ➢ Reduced melting temperatures are technologically favorable, since they lead to reduced power requirements for switching.

✓ The thermal stability of the amorphous phase

- ➢ For test purpose, phase change memory devices fabricated with 180 and 90 nm lithography technologies. Cells were reset into the amorphous state, and time to failure (drop in resistance) was measured at elevated temperature.
- ➢ The devices fabricated with 90 nm technology failed at slightly shorter times than the larger devices, indicating a reduced stability of the amorphous phase at smaller dimensions.
- ➢ This scaling behavior needs to be of concern because it leads to reduced data retention. One practical way to solve this problem is to use phase change materials with higher crystallization temperature, which is correlated to higher activation energy.

Raoux, Welnic, and Ielmini, Chem. Rev. 110 (2010) 240.

- For information

Scaling properties of phase change materials

- ✓ The crystallization temperature
  - ➢ Crystallization temperatures were measured as a function of film thickness using the drop in resistivity connected with the phase change or time-resolved XRD during heating.
  - ➢ It was found that crystallization temperatures increase for films thinner than 10-15 nm.
  - ➢ Increased crystallization temperatures are technologically favorable because they lead to better data retention.
  - ➢ The increase in required switching power is not a drawback because the melt-quench (reset) operation needs the highest power, not the crystallization (set) operation.

- ✓ The optical constants
  - ➢ Optical constants *n* and *k* between 400 and 800 nm for GST-124 were found increased for thinner films, in particular at smaller wavelengths.
  - ➢ Stronger light absorption, in particular at smaller wavelength is favorable because for very thin films the optical contrast is reduced, since the films are almost transparent.

Raoux, Welnic, and Ielmini, Chem. Rev. 110 (2010) 240.

- For information

Scaling properties of phase change materials

- ✓ The thermal conductivity
  - ➢ Measured as a function of film thickness using nanosecond laser heating and thermal reflectance measurements on Ge-Sb-Te films with thicknesses between 60 and 350 nm.
  - ➢ A substantial decrease in thermal conductivity for both the amorphous and crystalline phases as film thickness was reduced. Reduced thermal conductivity is desirable to reduce heat losses in memory devices.

- ✓ The resistivity
  - ➢ The resistivity as a function of film thickness does not change very much.
  - ➢ Observed a small increase in the resistivity of the amorphous phase for the thinnest GST-225 films between 3.5 and 10 nm.
  - ➢ This hardly influences the on/off ratio of several orders of magnitude between the amorphous and crystalline phases.

Raoux, Welnic, and Ielmini, Chem. Rev. 110 (2010) 240.

- For information

Scaling properties of phase change materials

- ✓ The threshold voltage
  - ➢ Threshold fields have been reported for doped SbTe (8~14 V/μm) and 15Ge85Sb (9 V/μm).
  - ➢ In today's phase change memory devices, typical threshold voltages are in the 1 V range because a typical switching volume is about 50-100 nm thick along the dimension of the applied voltage. Typical reading voltages are around 50 mV.
  - ➢ There is a certain operating window for which the reading voltage is well below the threshold voltage that depends on the resistance of both phases and the threshold field of a given material. This window shifts with device dimensions and depends on the material.

- ✓ The smallest size at which phase change occurs
  - ➢ Under optimized film thickness, capping layer, and substrate conditions, stable amorphous marks in a crystalline film or crystalline marks in an amorphous film with diameters in the range of 10-30 nm can be written by an electrical probe.

Raoux, Welnic, and Ielmini, Chem. Rev. 110 (2010) 240.