Matériaux chalcogénures pour le stockage des données

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Stockage des données

Demande croissante et variée :

- **densité d'information**
- **re-inscription**
- **stockage pérenne**

Contraintes différentes

Différentes voies de stockage possible

- **Optique (CD-ROM, CD-Rw,…)**
- **Electrique (mémoire flash)**
- **Magnétique (disque dur)**

Optical devices

CD-ROM (*Compact Disc- Read-Only Memory)* ➡ dye

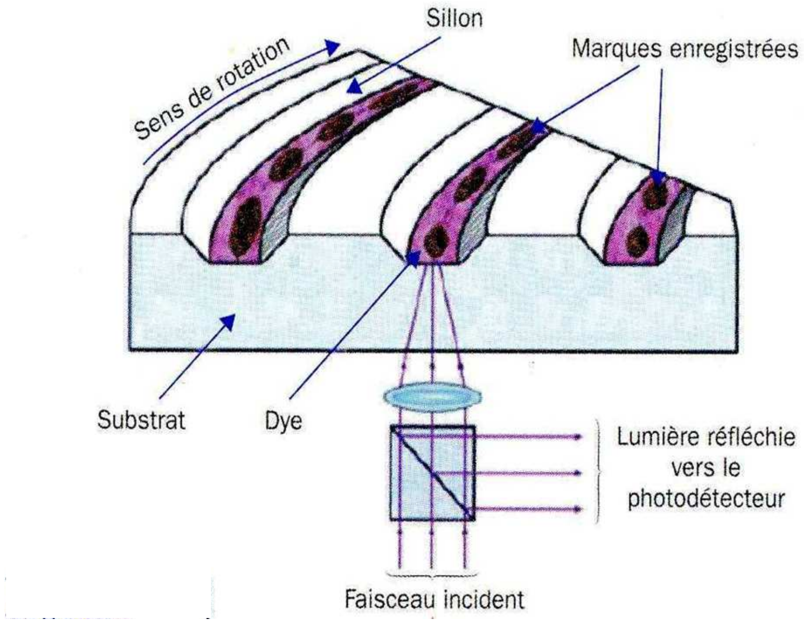
CD-RW *(Compact Disc-ReWritable)* ➡ ***Chalcogenide materials***

BD *(Blu-ray Disc)* ➡ ***Chalcogenide materials***

Mais aussi exploration de nouvelles voies

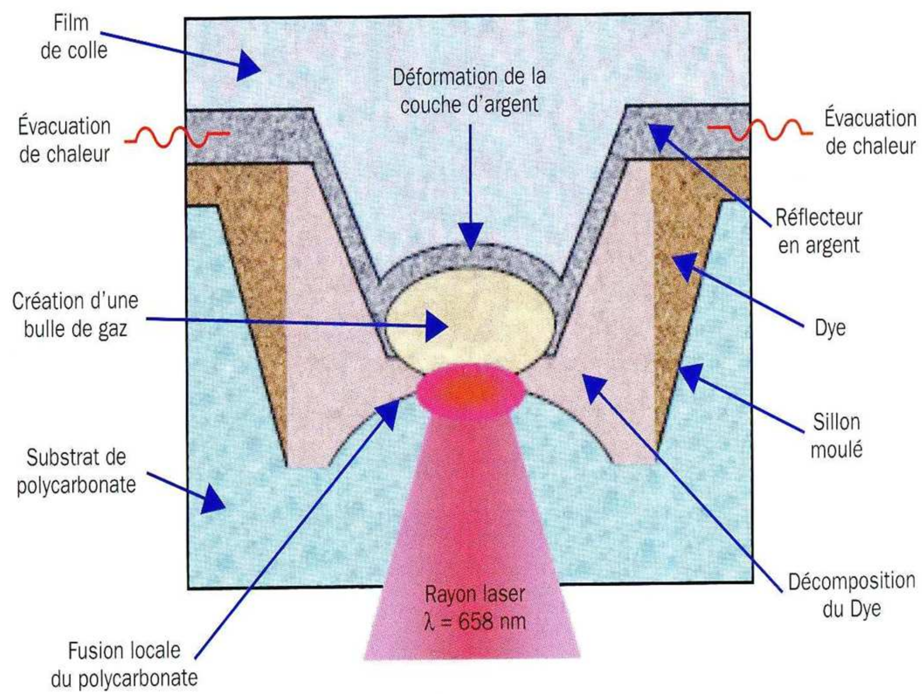
Cu/Si

CD-ROM (*Compact Disc- Read-Only Memory)*



Materiau actif:

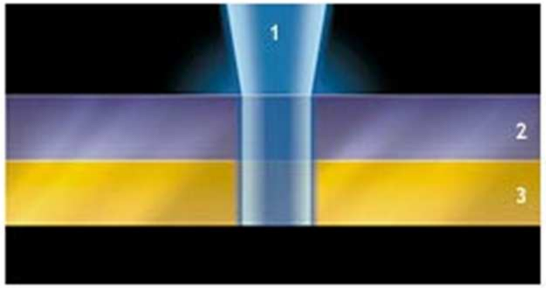
- ***colorant (phtalocyanine)***



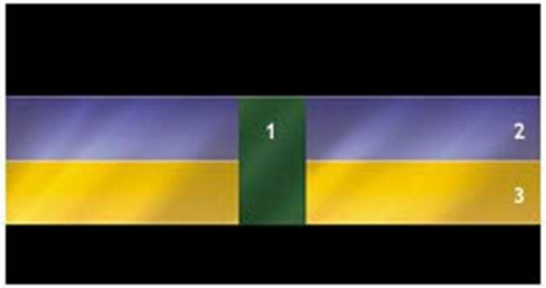
Longévité de l'information numérique,
Hourcade, Laloë, Spitz,
EDP Sciences 2010, p 84

BD *(Blu-ray Disc)*

Recording with TDK Blu–Ray Disc



1 Recording laser 2 Silicon coating
3 Copper alloy



1 Recorded mark 2 Silicon coating
3 Copper alloy

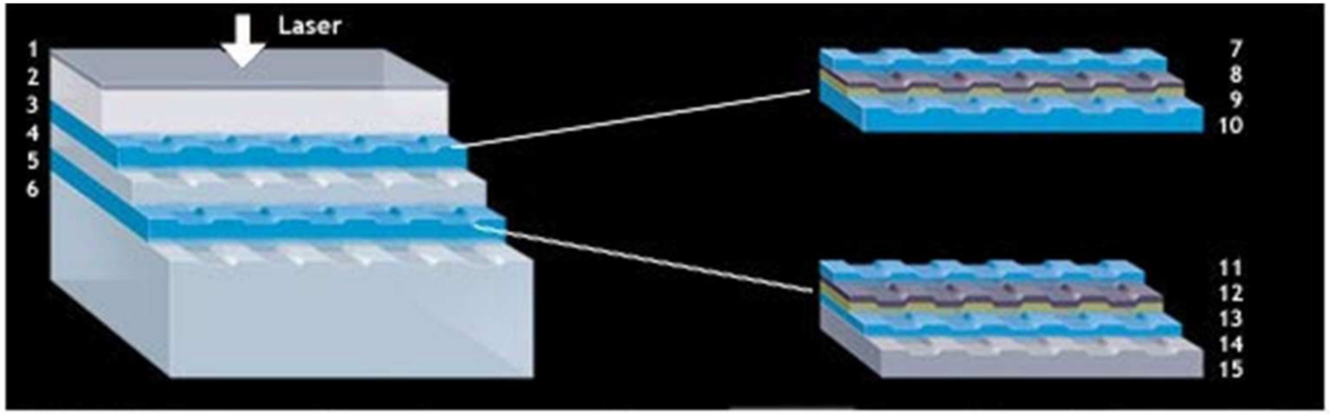
Materials:

- Cu/Si

Principle:

-Melting + alloying of Si and Cu alloy
-Creation of a metallic spot in a semiconductor medium

Blu–Ray Double Layers



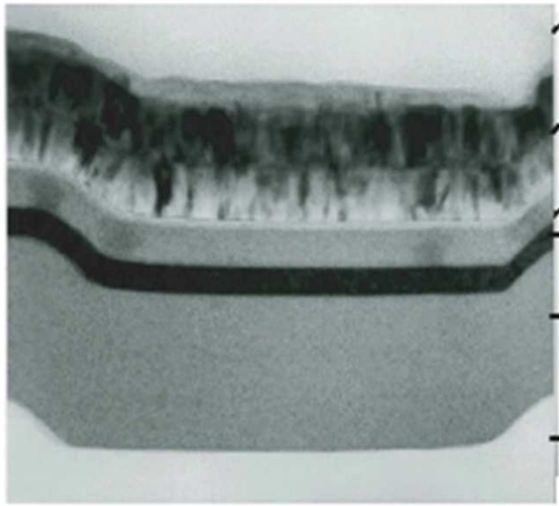
1 DURABIS2 layer 2 Cover layer 3 Layer 1 4 Spacer 5 Layer 0
6 Disc substrate 7 Dielectric layer 8 Silicon layer 9 Copper alloy
10 Dielectric layer 11 Dielectric layer 12 Silicon layer 13 Copper alloy
14 Dielectric layer 15 Reflective layer

Companies:

- TDK
- Philips

CD-RW *(Compact Disc-ReWritable)*

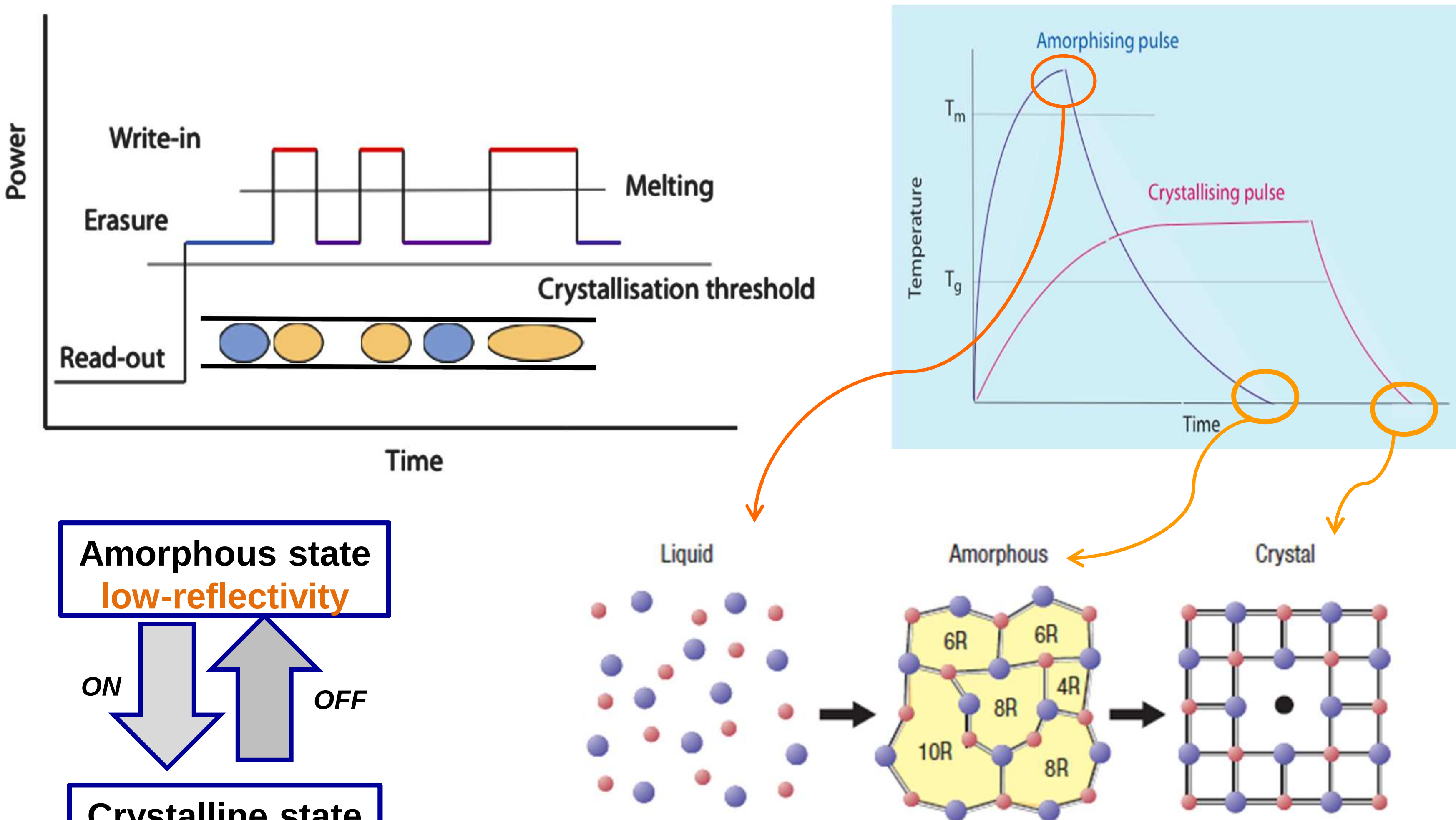
Active material : a phase change material i.e. a chalcogenide



T. Ohta, JOAM 2001

CD-RW *(Compact Disc-ReWritable)*

- **principle of a memory device based on phase change materials**



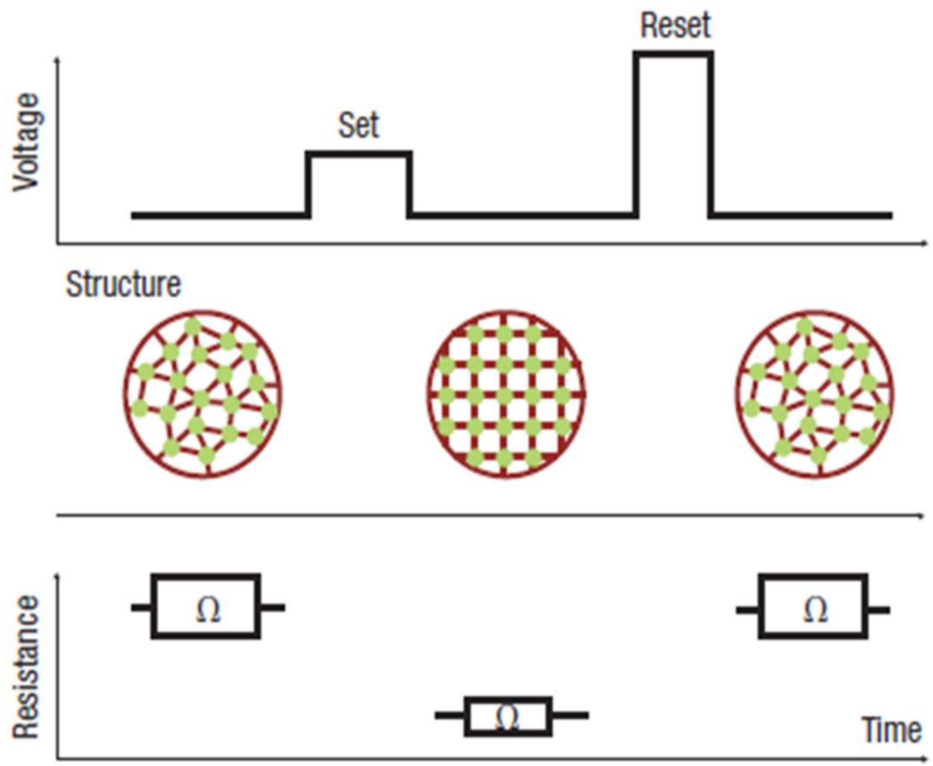
Amorphous state
low-reflectivity

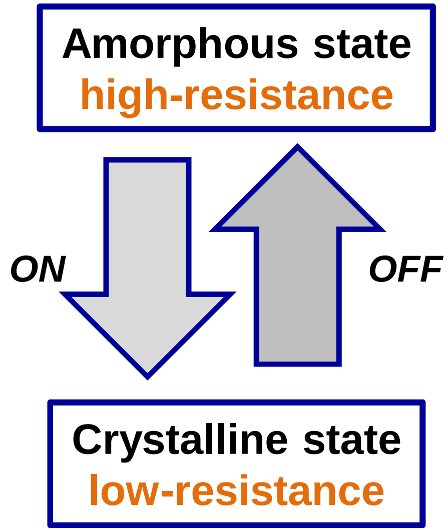
ON / *OFF*

Crystalline state
high-reflectivity

M. Wuttig and N. Yamada, Nature Materials 6 (2007) 824.

Electrical memory (PC-RAM)





M. Wuttig, Nature Materials 4 (2005) 265.

To be eligible a Phase Change Material (PCM) requires

- **Large optical and/or electrical contrasts between amorphous and crystalline phases**
- **Very fast crystallization**

Such a family of materials exists: it belongs to the **telluride family**

Ia	IIa	IIIb	IVb	Vb	VIb	VIIB	VIIIb			Ib	IIb	IIIa	IVa	Va	VIa	VIIa	0
1 **H**																	2 **He**
3 **Li**	4 **Be**											5 **B**	6 **C**	7 **N**	8 **O**	9 **F**	10 **Ne**
11 **Na**	12 **Mg**											13 **Al**	14 **Si**	15 **P**	16 **S**	17 **Cl**	18 **Ar**
19 **K**	20 **Ca**	21 **Sc**	22 **Ti**	23 **V**	24 **Cr**	25 **Mn**	26 **Fe**	27 **Co**	28 **Ni**	29 **Cu**	30 **Zn**	31 **Ga**	32 **Ge**	33 **As**	34 **Se**	35 **Br**	36 **Kr**
37 **Rb**	38 **Sr**	39 **Y**	40 **Zr**	41 **Nb**	42 **Mo**	43 **Tc**	44 **Ru**	45 **Rh**	46 **Pd**	47 **Ag**	48 **Cd**	49 **In**	50 **Sn**	51 **Sb**	52 **Te**	53 **I**	54 **Xe**
55 **Cs**	56 **Ba**	57 **La**	72 **Hf**	73 **Ta**	74 **W**	75 **Re**	76 **Os**	77 **Ir**	78 **Pt**	79 **Au**	80 **Hg**	81 **Tl**	82 **Pb**	83 **Bi**	84 **Po**	85 **At**	86 **Rn**
87 **Fr**	88 **Ra**	89 **Ac**	104 **Unq**	105 **Unp**	106 **Unh**	107 **Uns**											
				58 **Ce**	59 **Pr**	60 **Nd**	61 **Pm**	62 **Sm**	63 **Eu**	64 **Gd**	65 **Tb**	66 **Dy**	67 **Ho**	68 **Er**	69 **Tm**	70 **Yb**	71 **Lu**
				90 **Th**	91 **Pa**	92 **U**	93 **Np**	94 **Pu**	95 **Am**	96 **Cm**	97 **Bk**	98 **Cf**	99 **Es**	100 **Fm**	101 **Md**	102 **No**	103 **Lr**

Telluride materials: Phase Change Materials (PCM)

$Ge_2Sb_2Te_5$ (Hexagonal Stable phase)

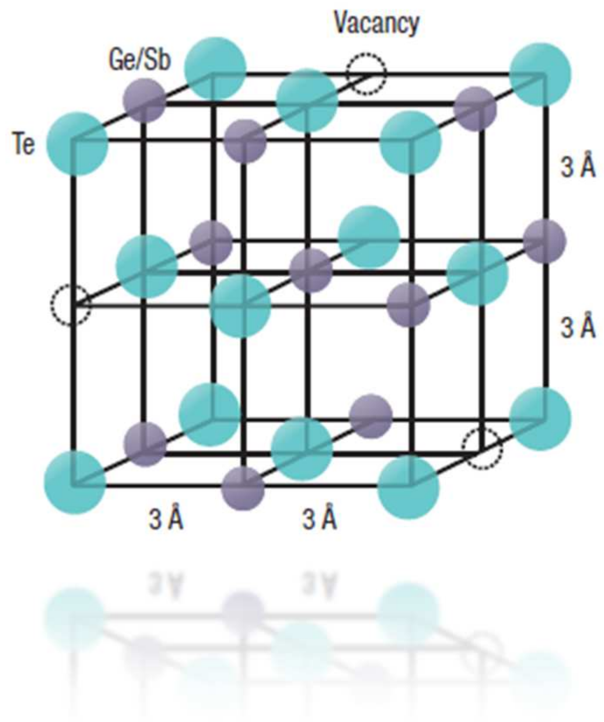
Cubic metastable phase

Rock-salt structure

OFF *ON*

Amorphous phase

Te atoms occupy one sublattice of the crystal, and Ge atoms, Sb atoms and vacancies randomly occupy the second sublattice.



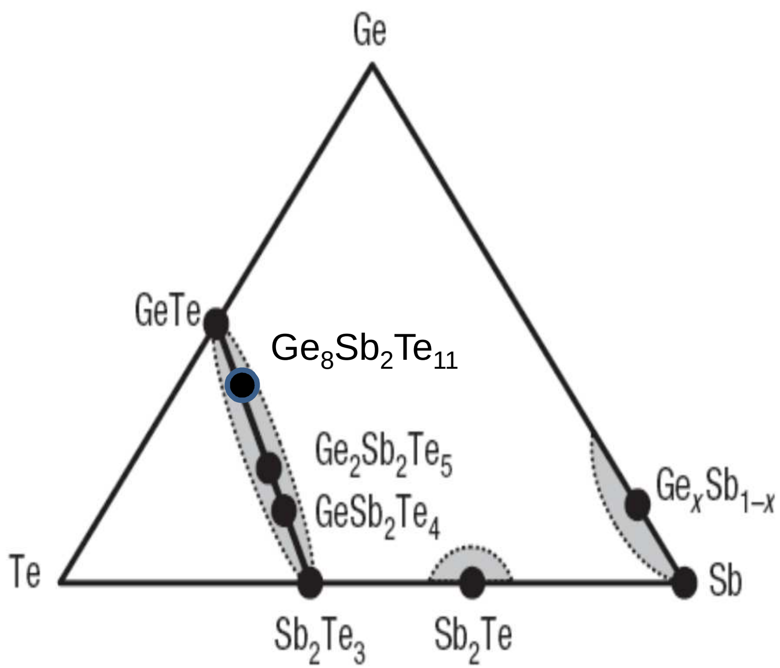
The amorphous phase not so well known:
Presence of Ge in Td environment
.

M. Wuttig and N. Yamada, Nature Materials 6 (2007) 824.

Telluride materials: Phase Change Materials (PCM)

Different classes of phase-change materials were empirically discovered:

- **the tie line between GeTe and Sb_2Te_3**
- **the region around Sb2Te**
- **the area around Sb**

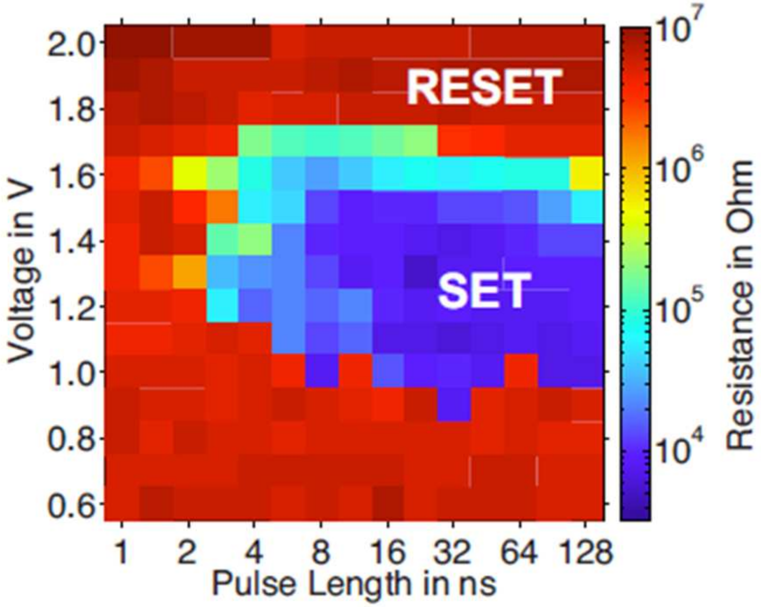


All of these alloys crystallize in a metastable rock-salt structure, where Te atoms occupy one lattice site (anion site) and Ge and Sb atoms as well as vacancies occupy the second lattice site (cation site).

Lencer *et al.* Nature Mater.7 (2008), 972

Telluride materials: Phase Change Materials (PCM)

Very fast crystallization



Cell resistance after application of set pulses with different amplitude and length, each starting from the amorphous reset state.

The color of each data point represents the cell resistance after the test pulse.

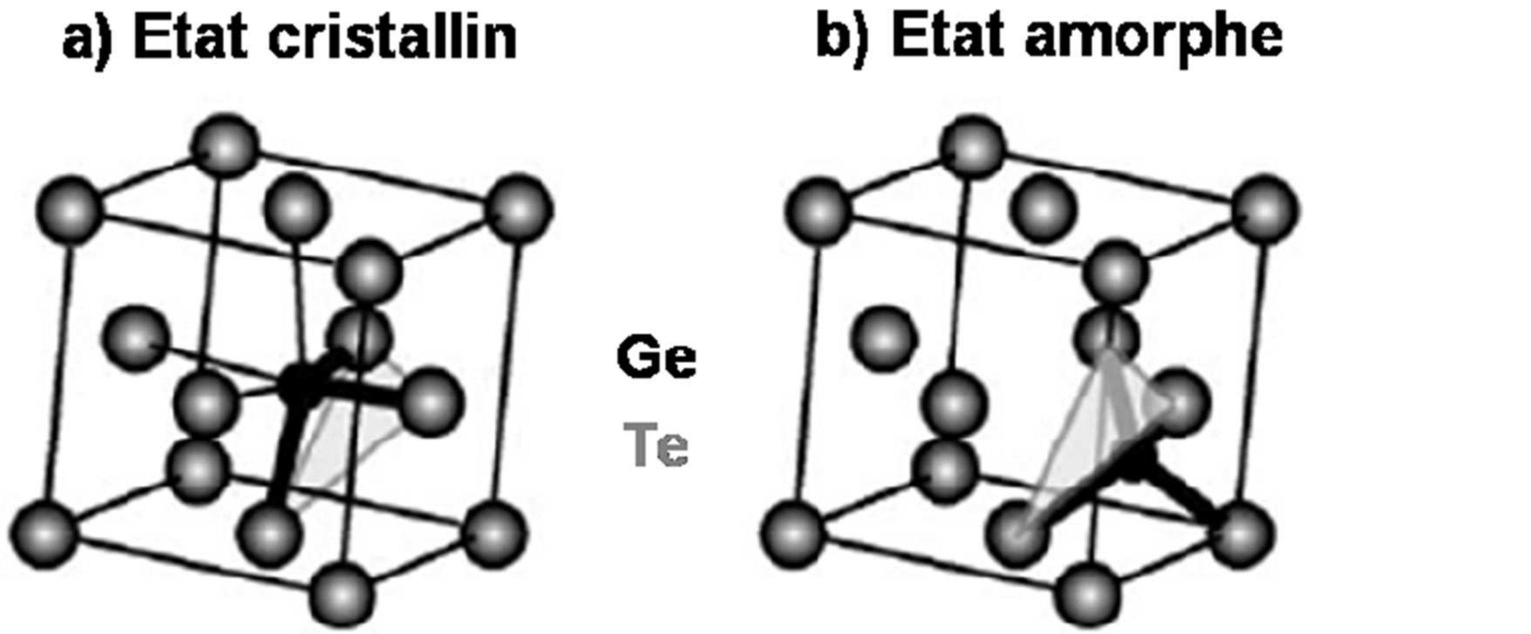
For pulses longer than 4 ns a broad crystallization window opens between 1.0 and 1.5 V.

The crystallization behaviour shows that the phase transition can be operated within a few nano seconds.

G. Bruns *et al.*, Applied Phys. Lett. 95 (2009) 043108

Telluride materials: Phase Change Materials (PCM)

- Fast switching: « Umbrella flip »

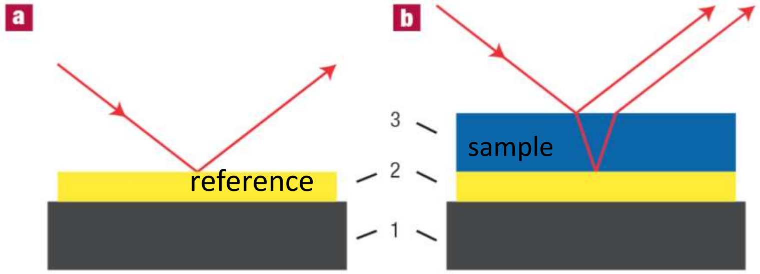


Kolobov et al., Nature Mater. 3 (2004) 703

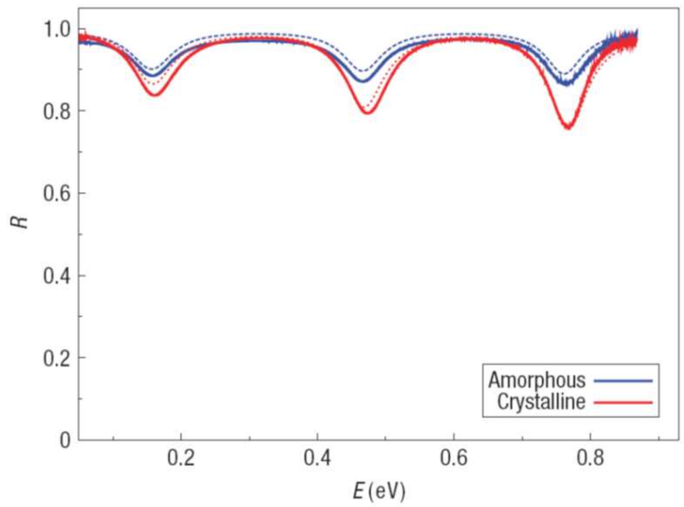
- Tellurides are very bad glass formers (Tg ~ Tcryst.)

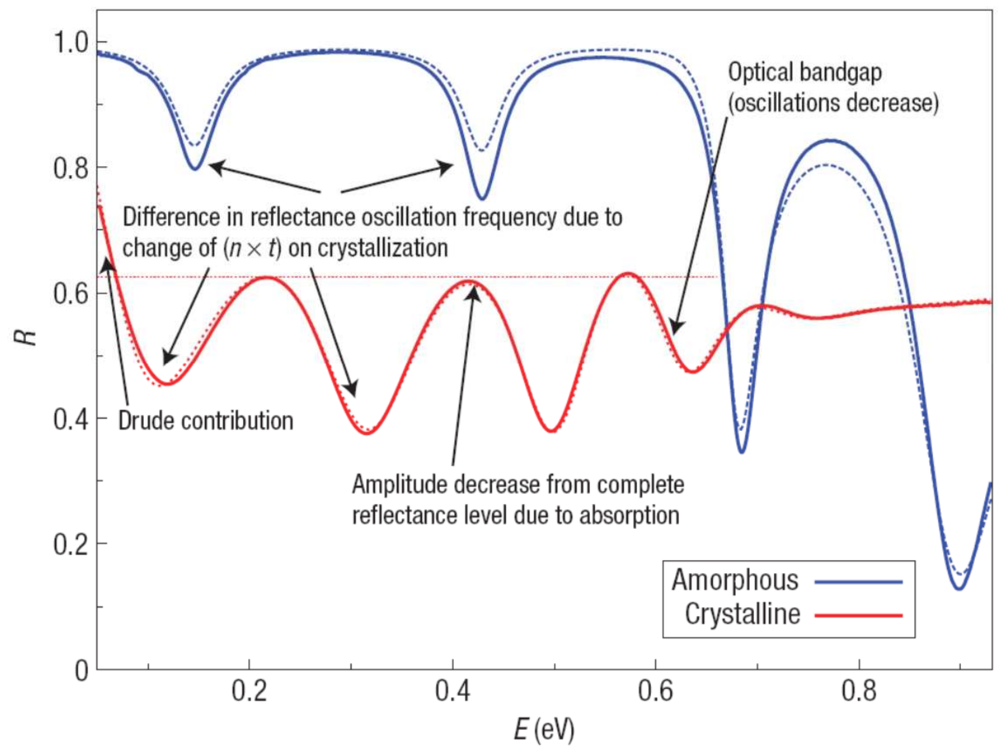
Telluride materials: Phase Change Materials (PCM)

Large optical contrast between amorphous and crystalline phases



Infrared reflectance spectra of a PCM film





Infrared reflectance spectra of an $AgInTe_2$ film (no PCM material)

K. Shportko, S. Kremers, M. Woda, D. Lencer, J. Robertson, M. Wuttig, Nature Mater. 7 (2008) 653.

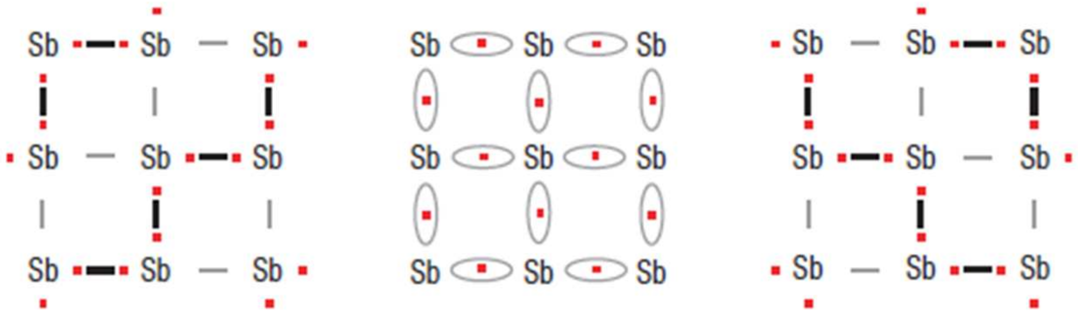
Telluride materials: Phase Change Materials (PCM)

- Amorphous phase behaves in a conventional way (expected polarisability for covalent semiconductor)
- The crystalline phase has a much larger polarisability. Its refractive index is larger than that of the homologous amorphous phase by 50%

Resonance bonding

In phase-change materials, an average of three *p-electrons per atom is present while the environment is octahedral* → *less than 2 electrons per bond*

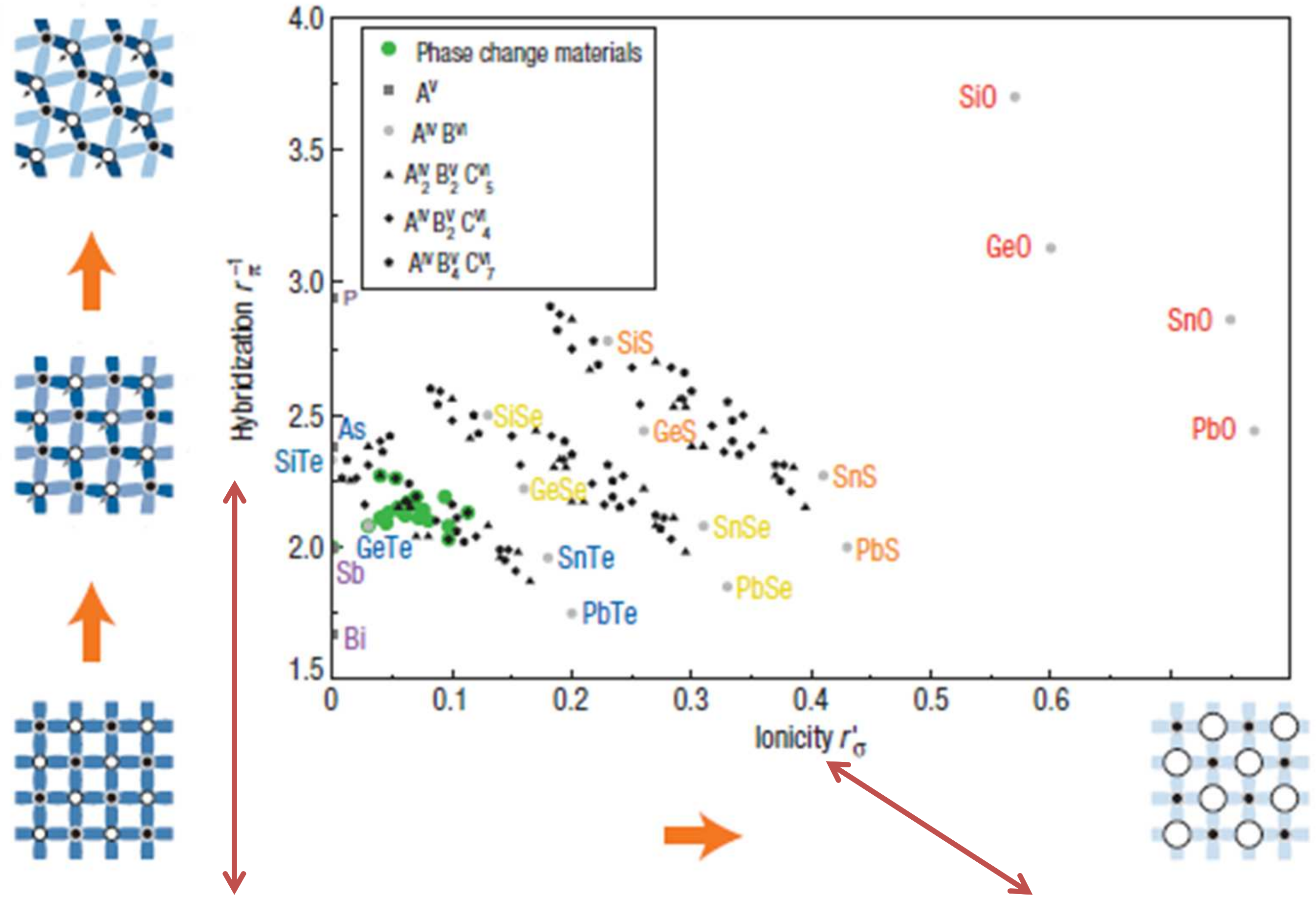
Schematic diagram demonstrating the origin of resonance bonding for Sb



K. Shportko, S. Kremers, M. Woda, D. Lencer, J. Robertson, M. Wuttig, Nature Mater. 7 (2008) 653.

Telluride materials: Phase Change Materials (PCM)

A map for phase-change materials: Resonance bonding



Energetic splitting of s- and p-states

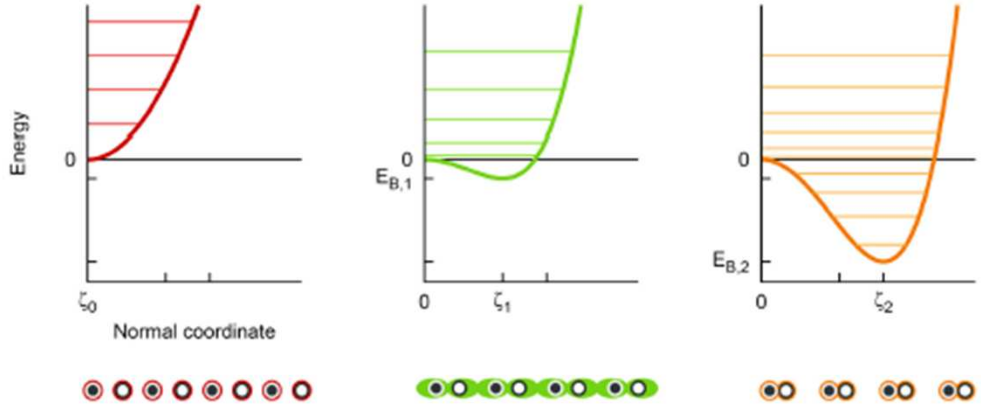
Difference in valence radii
of p- orbitals of anions and cations

Lencer *et al.* Nature Mater.7 (2008), 972

Telluride materials: Phase Change Materials (PCM)

Crystalline Phase

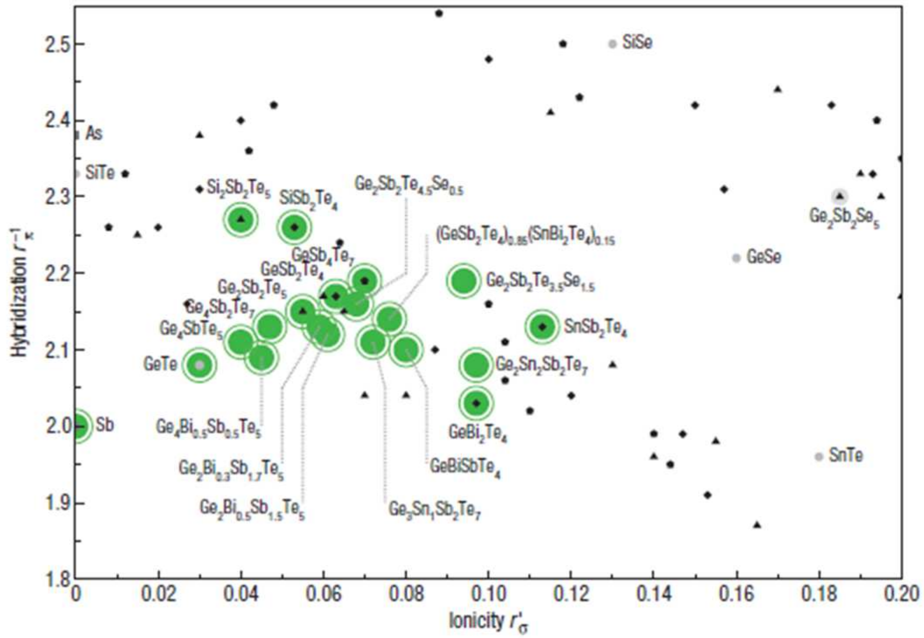
Potentials for atomic displacements



Undistorted structure

Slightly distorted structure

Strongly distorted structure



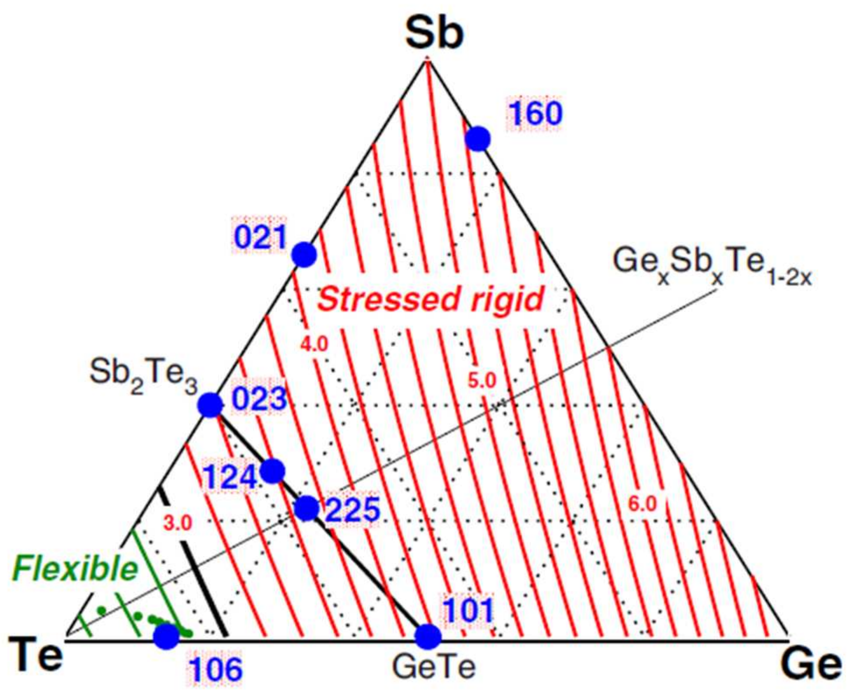
Hybridization vs. Ionicity

Telluride materials: Phase Change Materials (PCM)

- **Application of rigidity theory (Maxwell constraint) to Ge-Sb-Te system**

Fully relaxed region: tie line $GeTe_4$-$SbTe_4$

Amorphous Phase



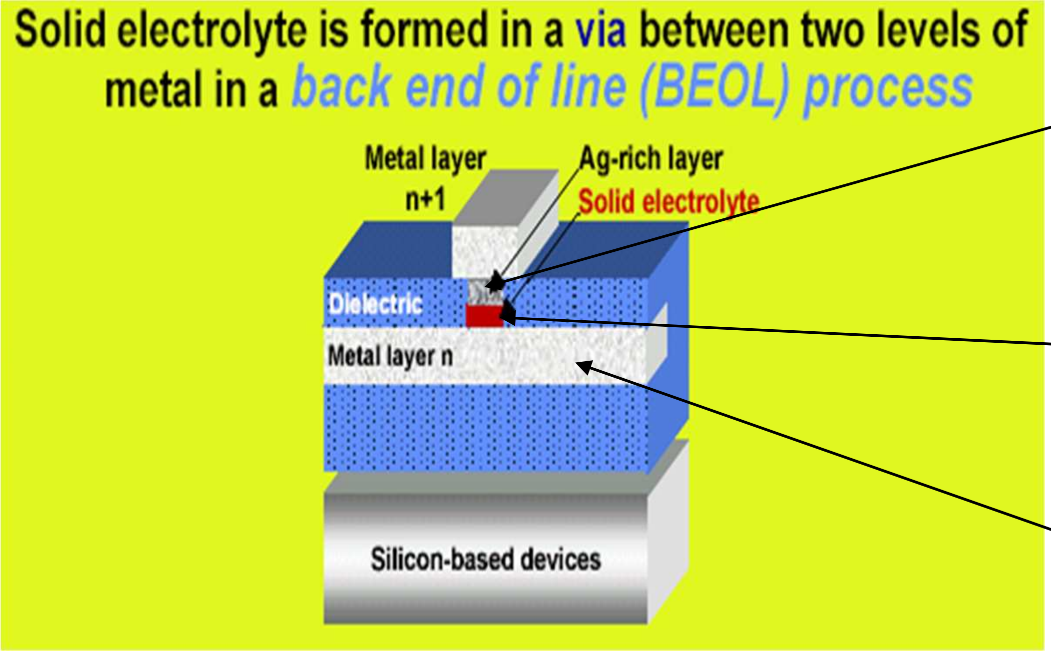
Constraint contour plot in the Ge-Sb-Te triangle defining a flexible (green) phase and a stressed rigid phase (red).

Micoulaut *et al., Phys. Rev. B 2009*

Increased stability in time for the “fully relaxed” glasses? No expected ageing

Ag-Ge-Se(S) systems: Electrical memory (CB-RAM)

Conductive Bridging RAM (CB-RAM)



N. Kozicki, M. Mitkova, M. Park, M. Balakrishnan, C. Gopalan, Superlattices and Microstructures 34 (2003) 459.

Anode: **Ag or Ag-containing material**

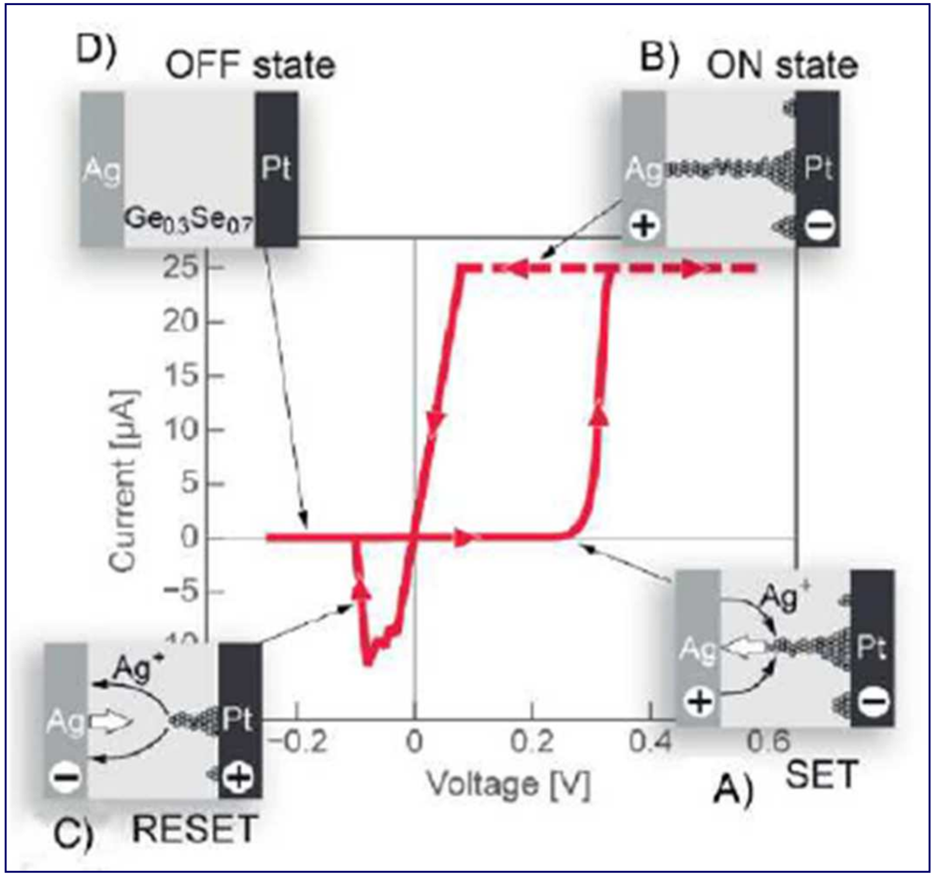
Solid electrolyte: **Ag photo-dissolution in $GeSe(S)_y$ (~ 30-50nm)**

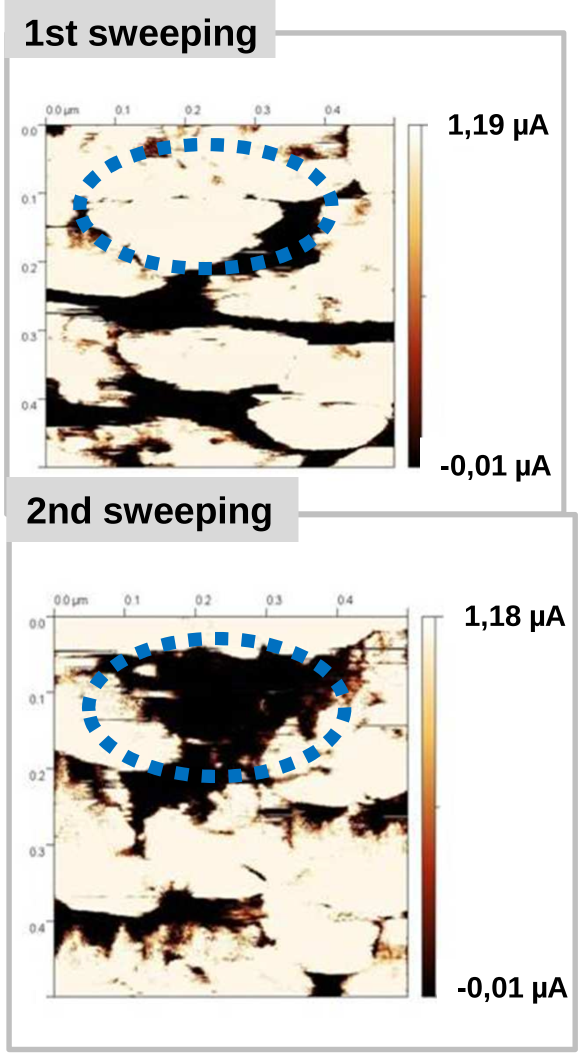
Cathode: **inert metal (Cr, Ni..)**

- **Bipolar resistive switching:** write-in and erasure occur under different polarities.

PC-RAM

Operation principle of an electrical memory



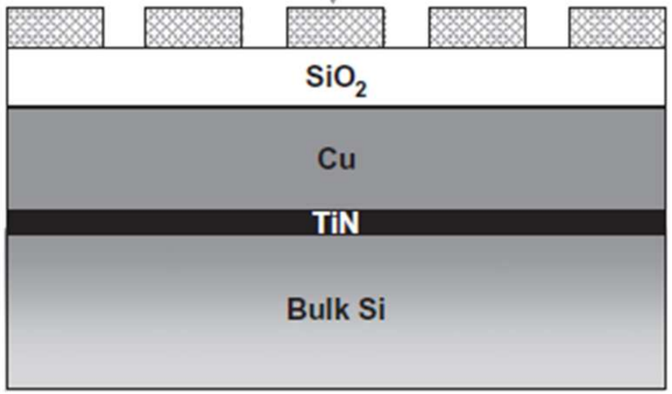


Conductive spots do not occur at the same place

Waser *et al.*, Adv. Mater. 21 (2009) 2632

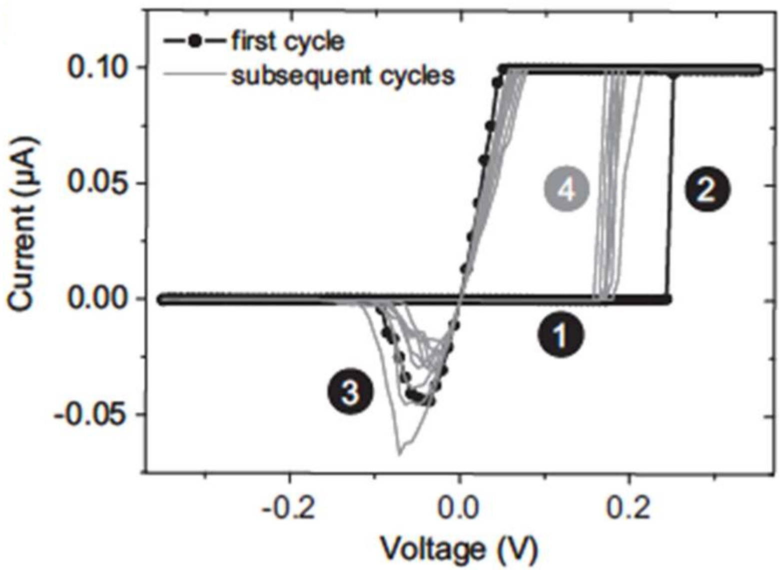
N. Frolet, PhD Thesis 2009
U. Montpellier

Recently…. Cu/SiO_2 studied as CB-RAM memory



- ✓ Bipolar resistive switching
- ✓ Similar operation principle to Ag/GeSe(S) memories

The couple Cu/SiO_2 is a good choice in order to make CB-RAM integration easier with fabrication processes that are already in use



Y. Bernard *et al.*, Microelectronic Engineering 88 (2011) 814.

Conclusion

Tellurures

Matériaux à changement de phase cristallisée-amorphe
Étudiés surtout pour la réalisation de **mémoires re-inscriptibles** et/ou à forte densité de stockage

Réflectivité très différente entre amorphe et cristallisé car nature très différente des liaisons chimiques (liaison résonante dans le cas du cristallisé)

Vieillissement

Cristallisé → rôle de lacunes, distorsion, nano-separation de phase

Amorphe → modèle de rigidité de Maxwell (pas de vieillissement pour la « phase intermédiaire »)

Sulfures, séléniures

Mémoire à pont conducteur
Propriété exploitée: très grande mobilité de l'argent dans les chalcogénures