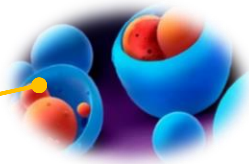
Amorphous materials for electronic devices

Amorphous solid

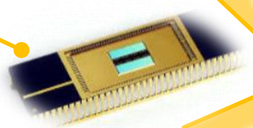
Devices

- **Low temperature process**
  - no need of crystallization *Polymeric glass*
- **Flexible & Transparent applications**

- **High thermodynamic solubility**
  - no crystalline lattice to break *Polymeric glass*
- **Bio-applications**



- **Electrical/optical contrast with crystalline** *Chalcogenide glass*
- **Phase change memory (PcRAM), Optical storage**



- **Large area uniformity** *Oxide glass / Ionic glass*
  - no grain boundary
- **Large-area applications**

Amorphous semiconductor for electronics

Large-area Electronics

- Low temperature process and large-area uniformity (no GB)

- Displays
- Solar cells

Amorphous Si, Amorphous In-Ga-Zn-O (α-IGZO)…

Storage Devices

- Contrast of resistance between amorphous and crystalline

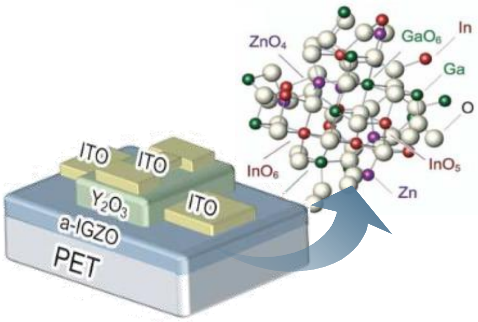
- Phase-change Random Access Memories (PcRAM)

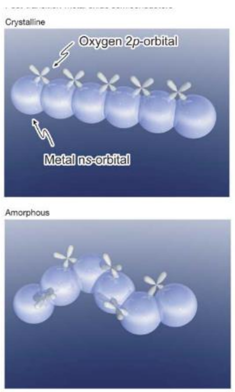
Amorphous Ge-Sb-Te (α-GST)…

Issues: Reliability of amorphous electronic devices due to structural instability of amorphous semiconductors.

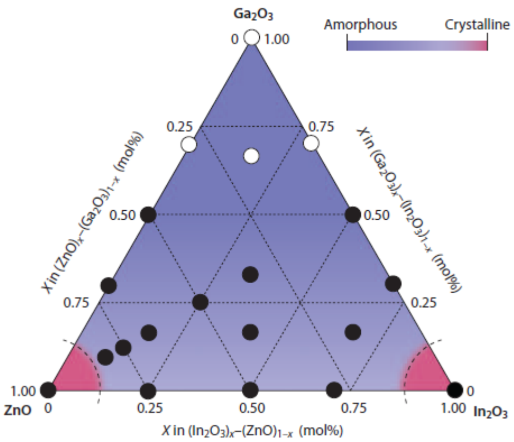
Amorphous In-Ga-Zn-O (a-IGZO) TFT

- ✓ High carrier mobility (5 ~ 50 $cm^2/V \cdot s$)
- ✓ Transparency (wide bandgap)
- ✓ Low temperature process

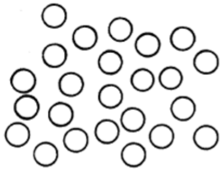




❖ High structural stability of a-IGZO



- ✓ A-IGZO: Ionic bonding system



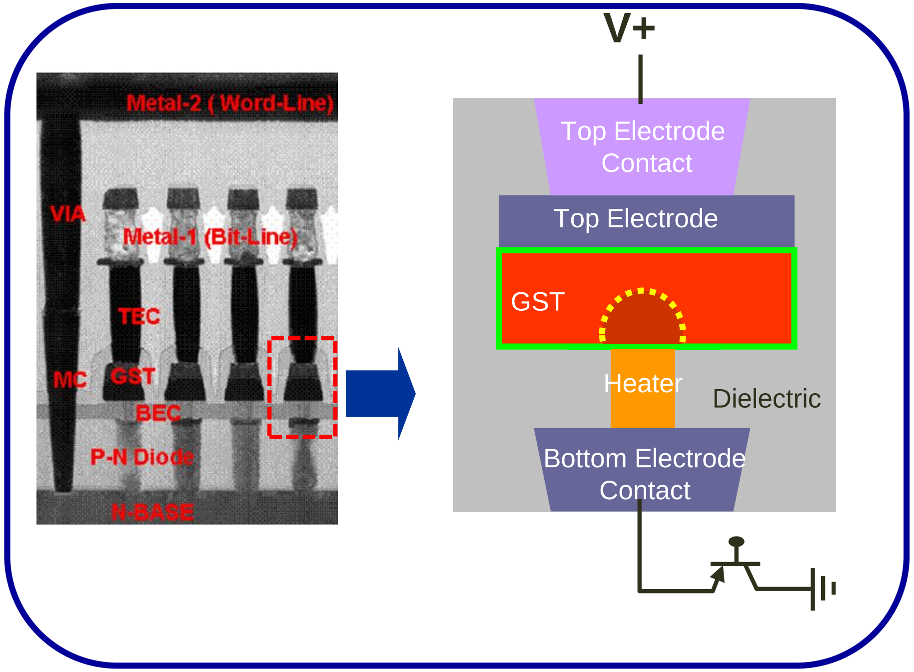
H. Hosono, Handbook of Transparent Conductors (2010)

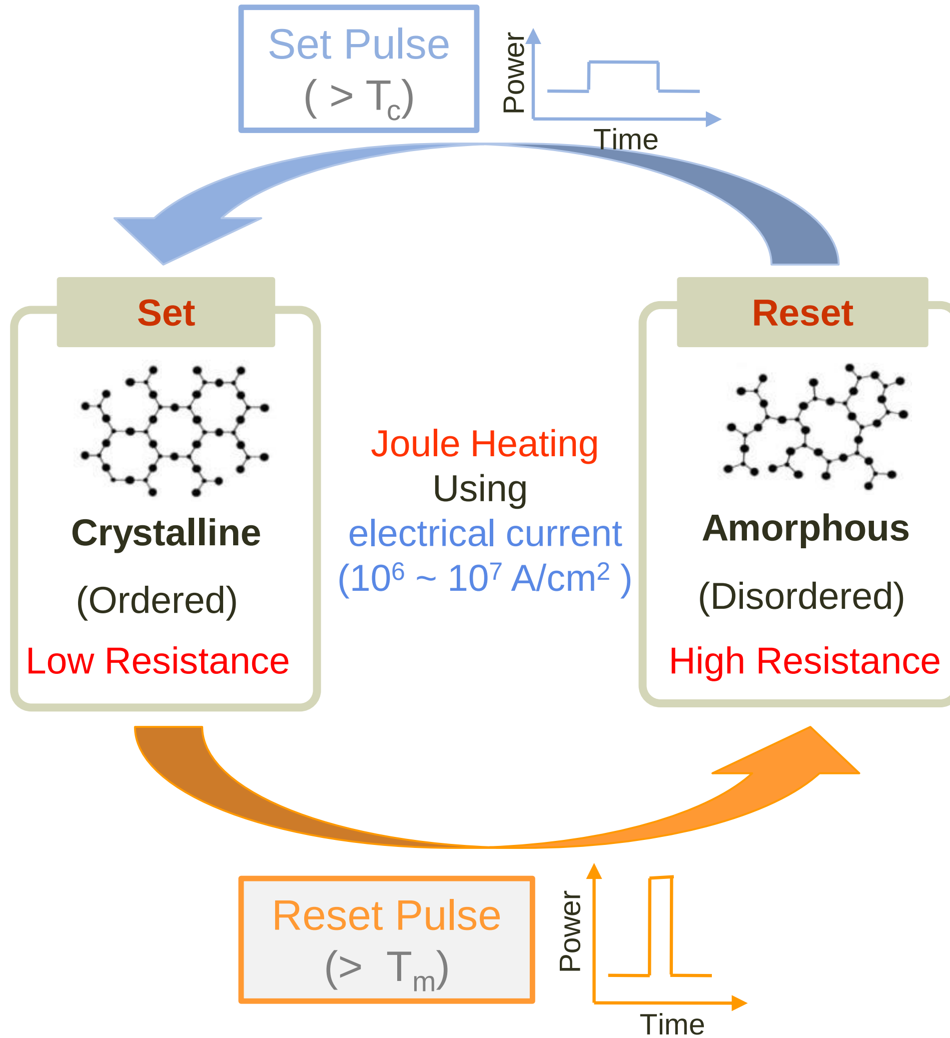
- ✓ Large size and charge mismatch between the ions leads to <u>inherent high structural stability of amorphous materials</u>.

T. Kamiya et al., NPG Asia Mater. (2010)

Operation Principle of PcRAM

❖ Phase-Change Random Access Memory



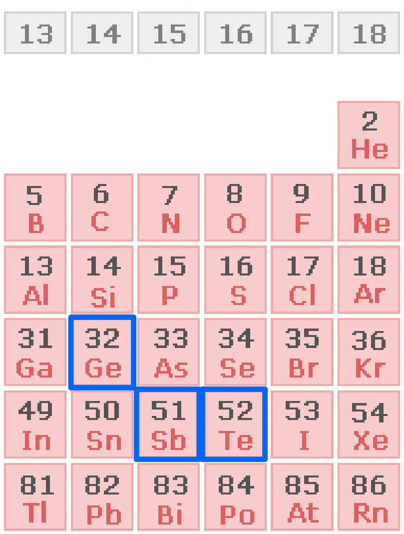


- Resistance difference between crystalline and amorphous phase
- Phase change by joule heating.

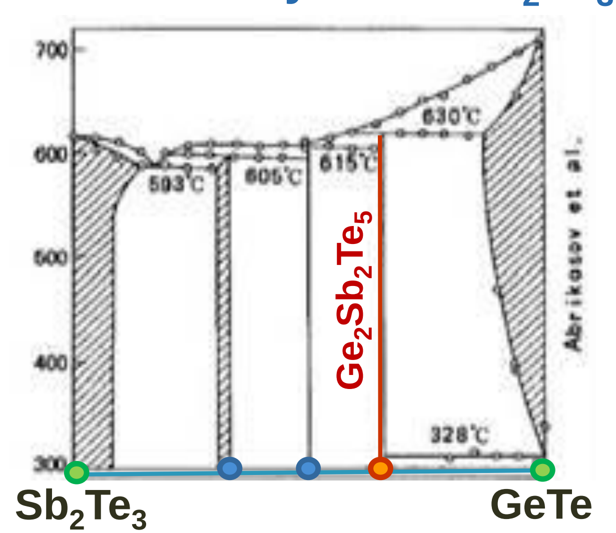
Chalcogenide Materials

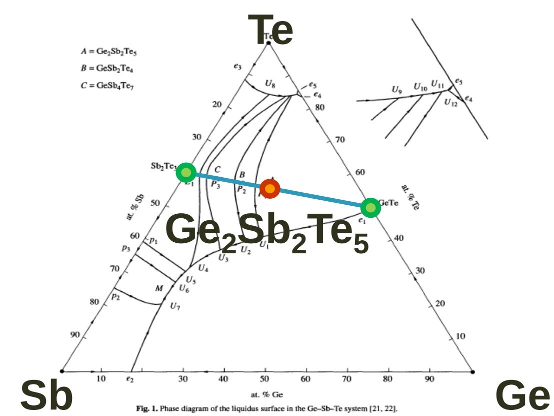
- **Chalcogenides: alloys with at least one Group VI element**
  - PcRAM uses a Ge-Sb-Te alloy as phase change material.
  - Can exist in either of two stable states.
  - **$Ge_2Sb_2Te_5$** is most widely used due to its nature of phase stability and rapid crystallization.
  - Also used in CD-RW and DVD-RW applications .

Periodic Table



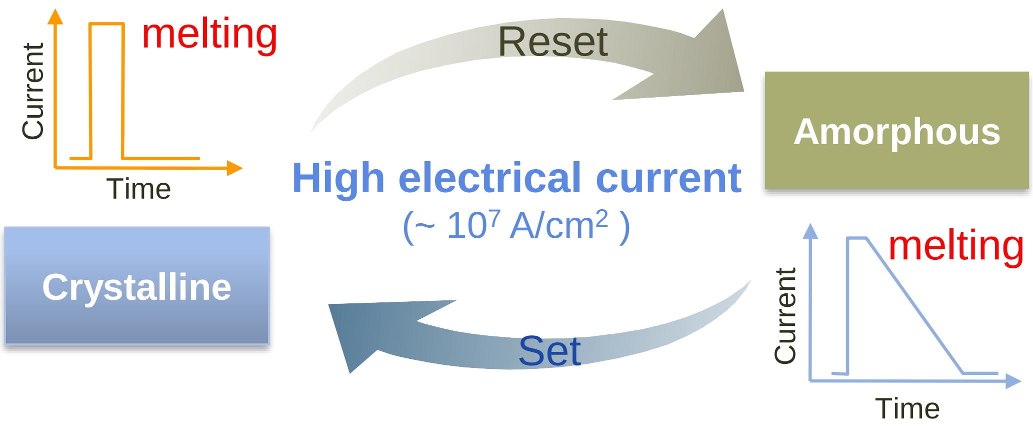
Pseudo Binary GeTe-Sb_2Te_3

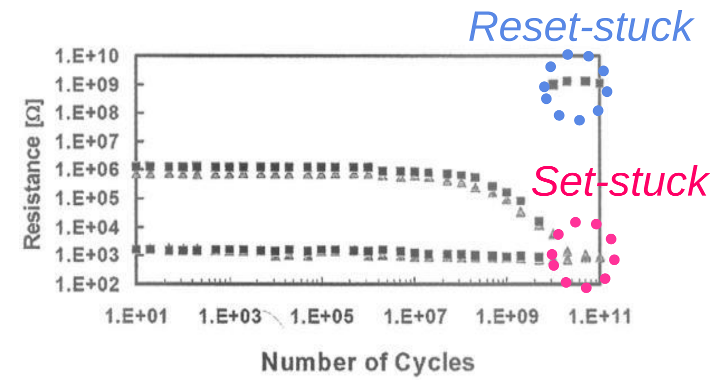




Abrikosov et al.

Endurance issues in PRAM





Kim *et al*., *IRPS* (2005)

***Set-Stuck*: fixed at low R**

Compositional change of phase change material during operations

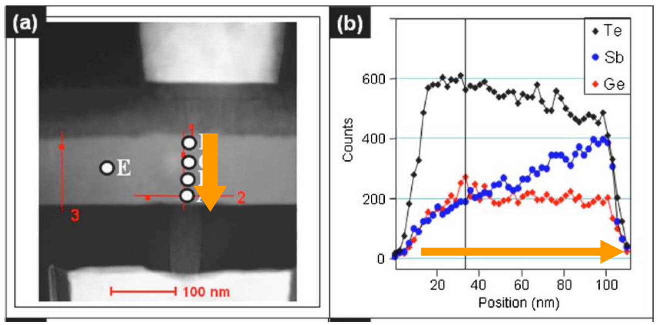
***Reset-Stuck*: fixed at high R**

- **Void formation at the BEC interface**
- **Interfacial Delamination**

Material degradation in **phase change volume** → Operational failure

Composition change in PcRAM during operation

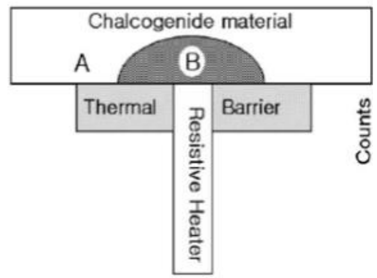
Sb-rich / Te-deficient



- Nonstoichiometric phase in the active regions
- Thermal interdiffusion of Sb and Te
- Sb-rich / Te-deficient composition

J. B. Park *et al.* (Samsung)
J. Electrochem. Soc., (2007)

Sb-excess

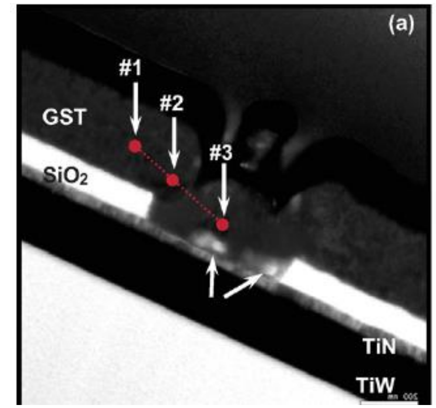


Element	active region is **amorphous** phase		active region is **crystalline** phase	
	A	B	A	B*
Ge(K)	22.4	16.8	22.3	15.3
Sb(K)	22. 3	43.5	21.6	46.9
Te(K)	55.3	39.7	56.1	37.8

- Sb-excess GST

S. O. Ryu *et al.* (ETRI)
J. Electrochem. Soc., (2006)

Sb-rich / Ge-deficient

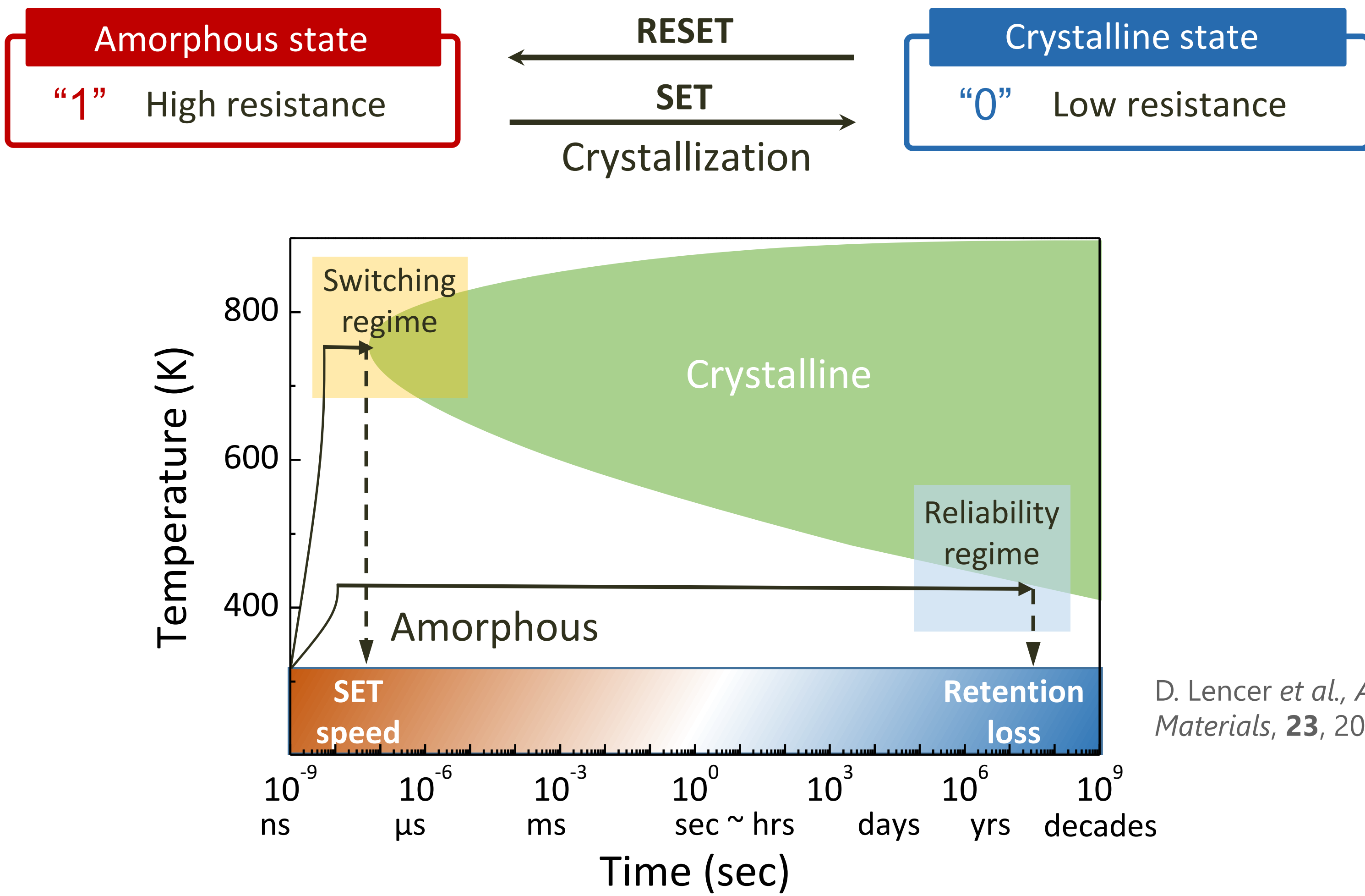


- Ge segregated to the boundary region where it then was oxidized
- Sb-rich / Ge-deficient GST in the active region

S. M. Yoon *et al.* (ETRI)
Appl. Surf. Sci., (2007)

Stoichiometric change of multi-element alloy is induced by **flux difference in electromigration**

PcRAM characteristics: SET speed vs. Retention

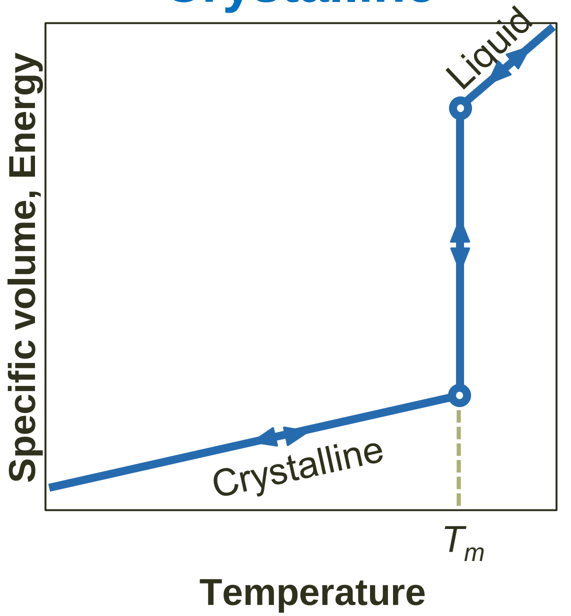


D. Lencer *et al.*, *Advanced Materials*, **23**, 2030 (2011).

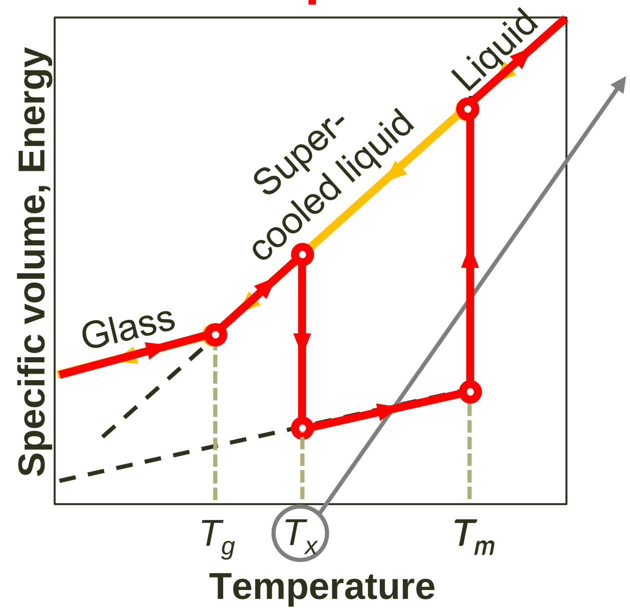
- ***Issues*** - Prediction of behaviors in a wide range of time (10^{-9} to 10^{9} sec.).
  - Contradictory requirement for crystallization kinetics.

Amorphous materials vs. device characteristics

Crystalline



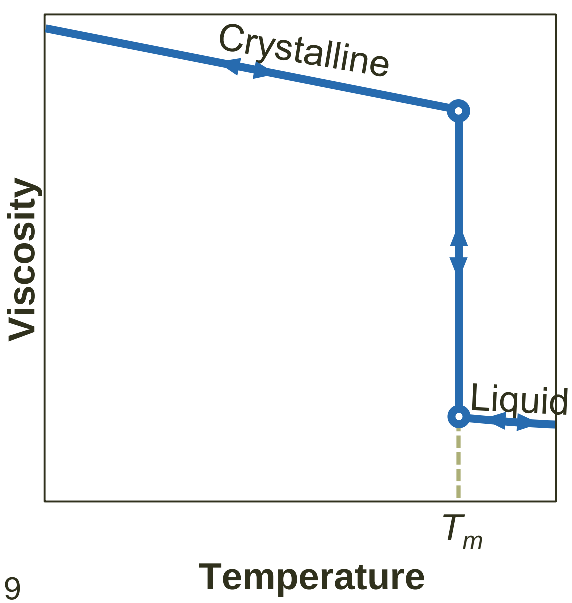
Amorphous

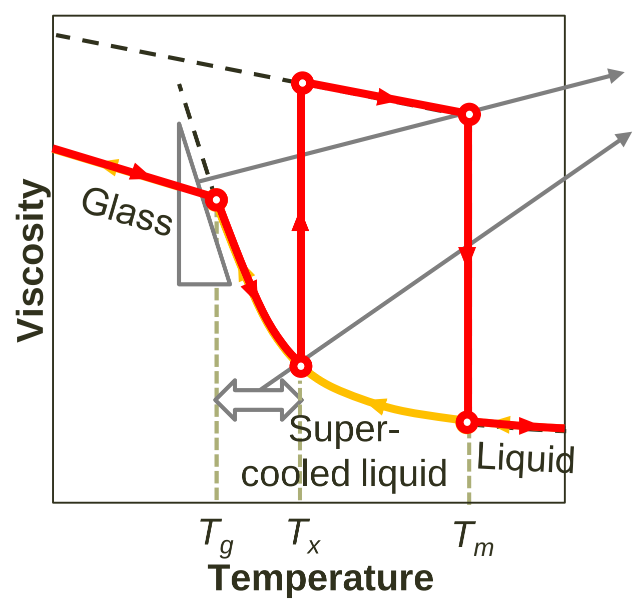


- **Crystallization temperature (T_x)**

  Amorphous phase stability at low temperature

  → **Retention**



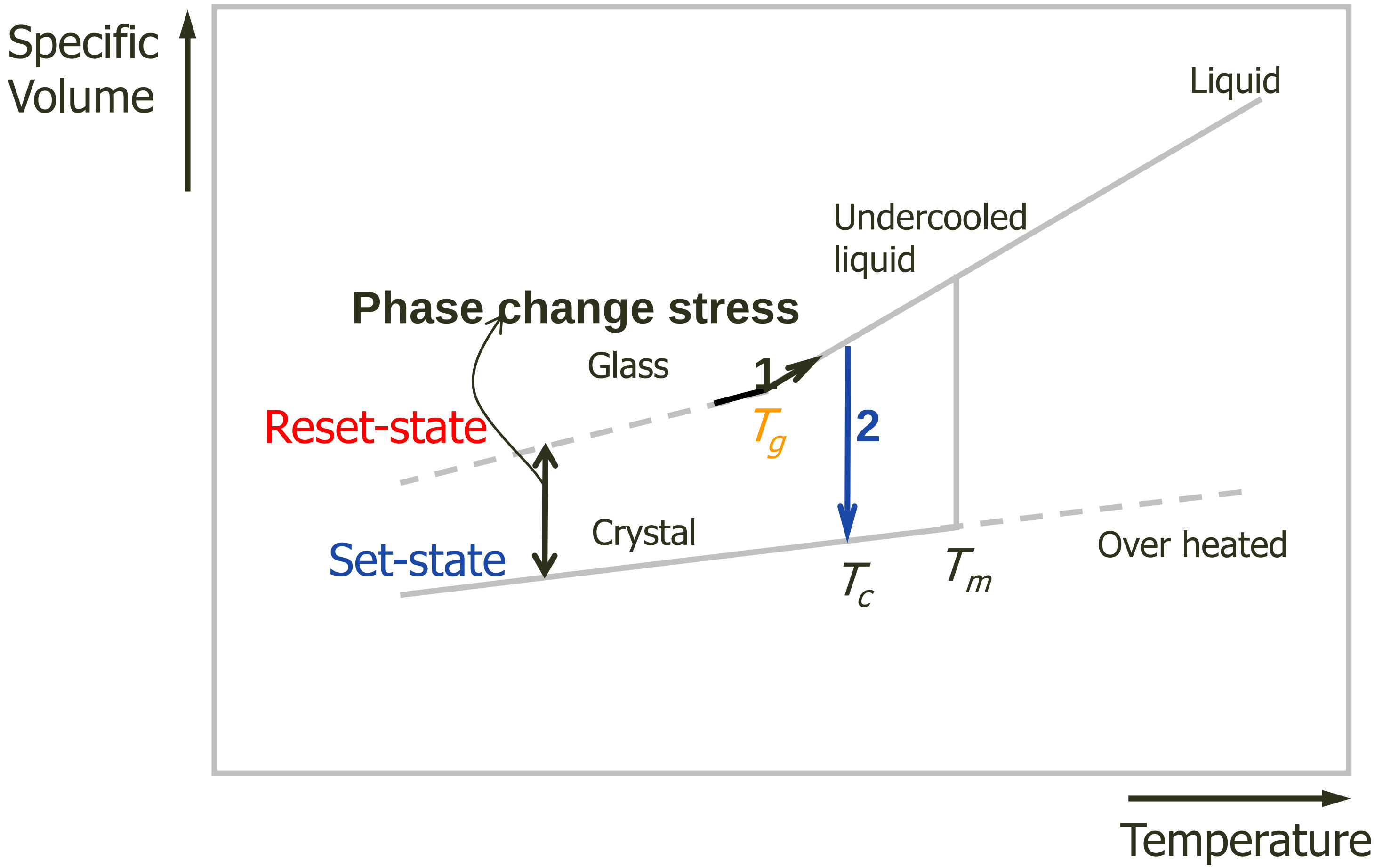


- **Fragility (*m*)**
- **Super-cooled liquid region (T_x - T_g)**

  Low viscosity at high temperature

  → **SET speed**

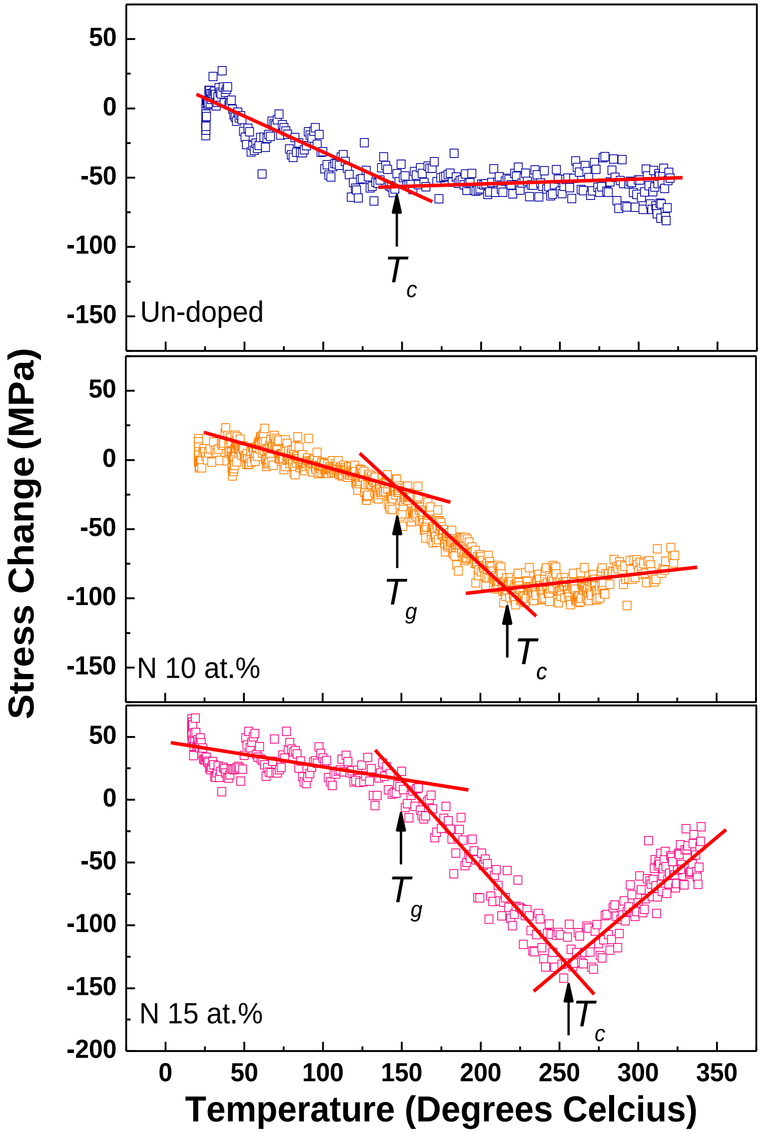
Volume Change during the Heating



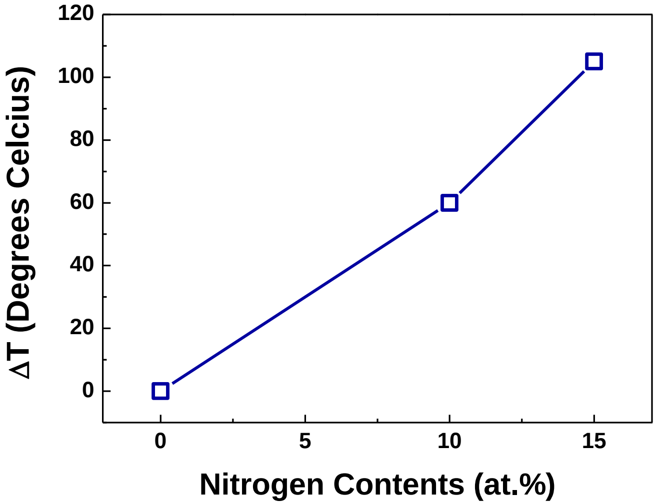
1. Glass transition: Volume expansion (Compressive stress side)

2. Crystallization: Volume shrinkage (Tensile stress side)

Supercooled Liquid Region

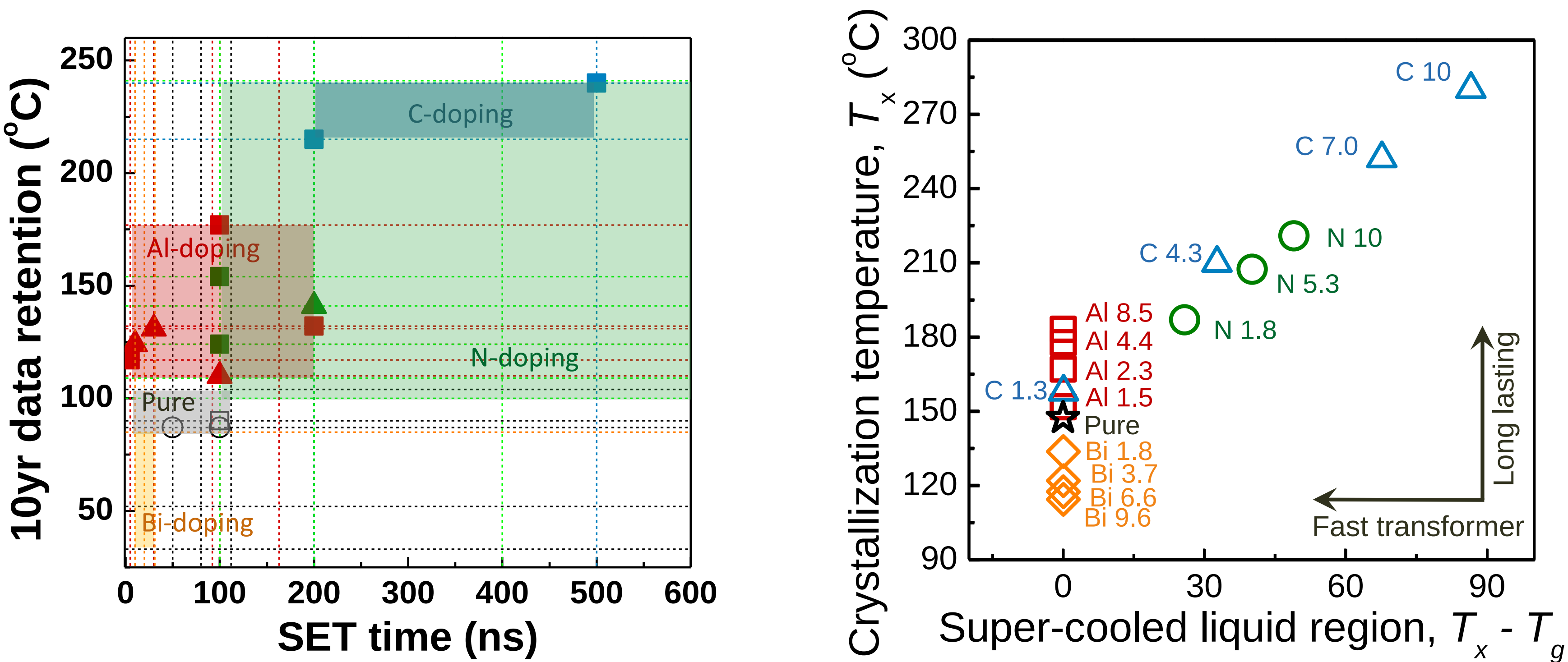


Difference between T_g and T_c:
Supercooled liquid region (ΔT)



N-doping increase supercooled region
=> N-doped GST has superior **glass-forming ability (GFA)**

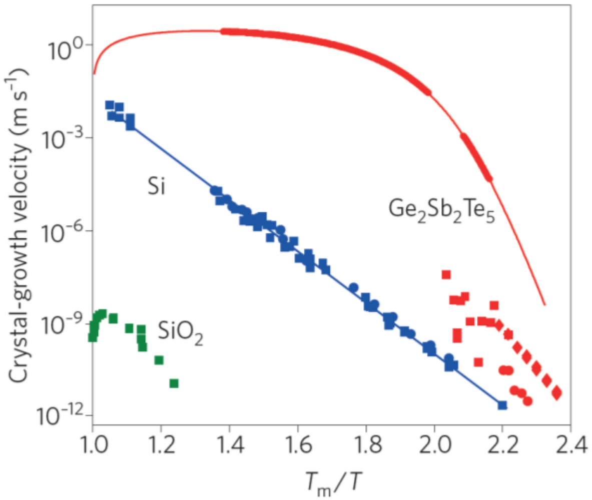
Structure-properties map for PcRAM characteristics



- **SET speed – Super-cooled liquid region (T_x - T_g)**
- **Data retention - Crystallization temperature (T_x)**

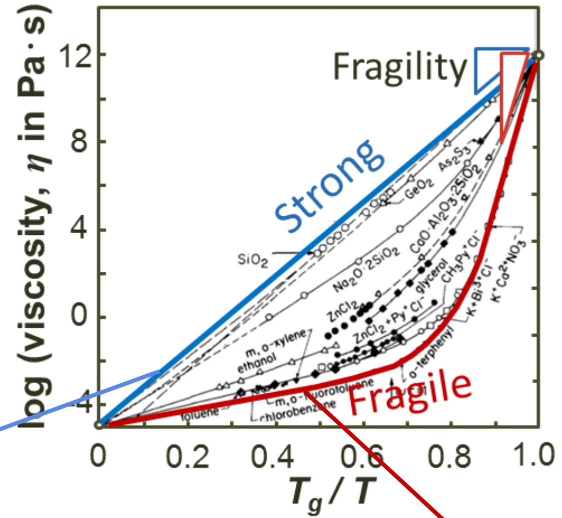
Acta Materialia (2015)

Origin of fast crystallization of *a*-$Ge_2Sb_2Te_5$



M. Wuttig *et al., Nat. Mater.,* **11** (2012)
J. Orava *et al., Nat. Mater.,* **11** (2012)

Fragile nature (m ~ 90) of *a*-$Ge_2Sb_2Te_5$ leads to *"fast transforming"* characteristics.



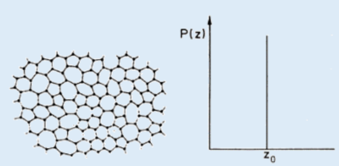
C.A. Angell, *J. Non-Cryst. Solids* (1988)

Strong Glass
Arrhenius behavior

$$\eta(T) = \eta_0 \exp\left(\frac{E}{RT}\right)$$

- α-SiO_2, α -InGaZnO etc.
- Stability against crystallization
- **Fragility, *m* ~ 16**

in covalent bonds



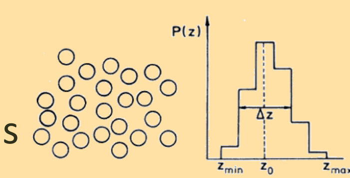
Fragile Glass
Non-Arrhenius behavior

$$\eta(T) = \eta_0 \exp\left(\frac{D \cdot T_0}{T - T_0}\right)$$

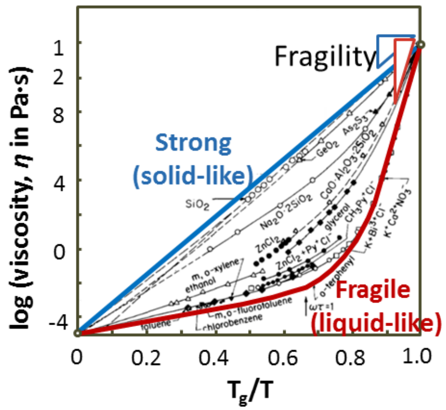
Vogel-Fulcher-Tammann

- Polymer, **<u>$Ge_2Sb_2Te_5$</u>** etc.
- Extremely rapid crystallization
- **Fragility, *m* » 16**

in organic, ionic bonds



Doping Effects on Fragility



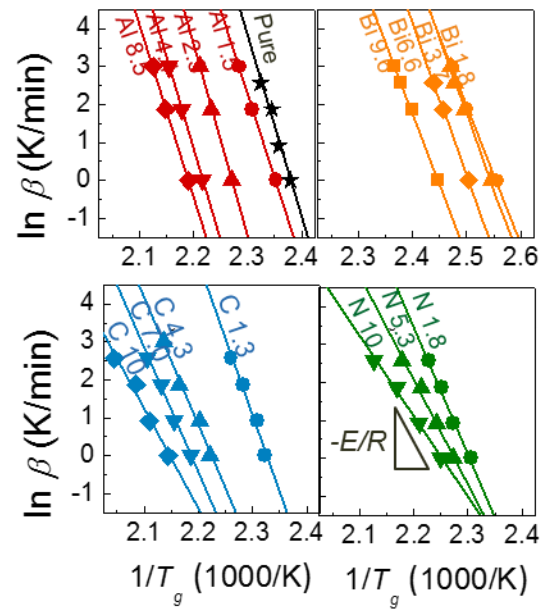
C.A. Angell, *J. Non-Cryst. Solids* (1988)

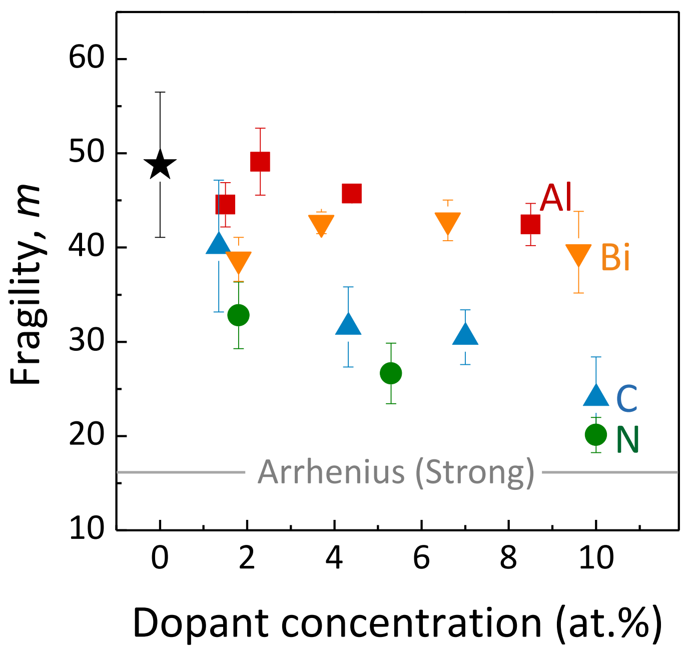
- **Fragility (*m*)**

$$m = \left.\frac{d\log\eta}{d(T_g/T)}\right|_{T_g} = \frac{E}{\ln 10 R T_g}$$

$$\ln\beta = -\frac{E}{RT_g} + C$$

→ Heating rate variation
: 1.0 - 20 °C/min





- **Substitutional doping (Al, Bi)**
  : *Fragile* to *Strong* transition

- **Interstitial doping (C, N)**
  : maintained as *Fragile*

→ Consistent results with changes in T_x - T_g