



**9TH LETI MEMORY WORKSHOP**  
**Grenoble June 27<sup>th</sup>**

**AN INSIGHT INTO THE HIGH TEMPERATURE RELIABILITY OF  
N-DOPED AND Ge-RICH GeSbTe PHASE CHANGE MEMORIES**

V. Sousa<sup>1</sup>, G. Navarro<sup>1</sup>, N. Castellani<sup>1</sup>, J. Kluge<sup>1,2</sup>, O. Cueto<sup>1</sup>, C. Sabbione<sup>1</sup>, A. Roule<sup>1</sup>, V. Delaye<sup>1</sup>, N. Bernier<sup>1</sup>,  
F. Fillot<sup>1</sup>, P. Noé<sup>1</sup>, L. Perniola<sup>1</sup>, S. Blonkowski<sup>2</sup>, M. Borghi<sup>2</sup>, E. Palumbo<sup>2</sup>, P. Zuliani<sup>2</sup>, R. Annunziata<sup>2</sup>

<sup>1</sup> CEA-LETI-MINATEC Campus  
<sup>2</sup> STMicroelectronics



## OUTLINE

- 1** Background and Objectives
- 2** Thin Film Characterization
- 3** Device Characterization
- 4** Analysis of the Programmed States
  - Morphological Characterization
  - Simulation of the Programming Operations
- 5** Conclusions



## OUTLINE

### **1** Background and Objectives

**2** Thin Film Characterization

**3** Device Characterization

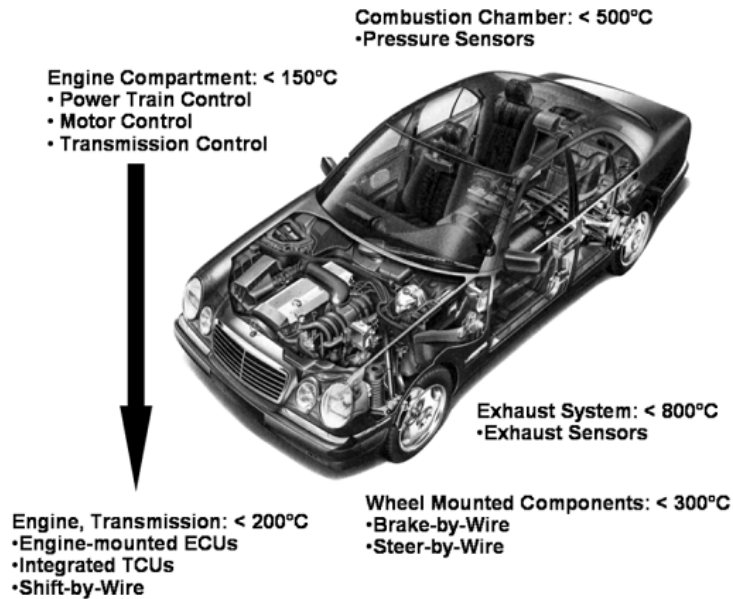
**4** Analysis of the Programmed States

- Morphological Characterization
- Simulation of the Programming Operations

**5** Conclusions

# WHY A HIGH THERMAL STABILITY FOR eNVM ?

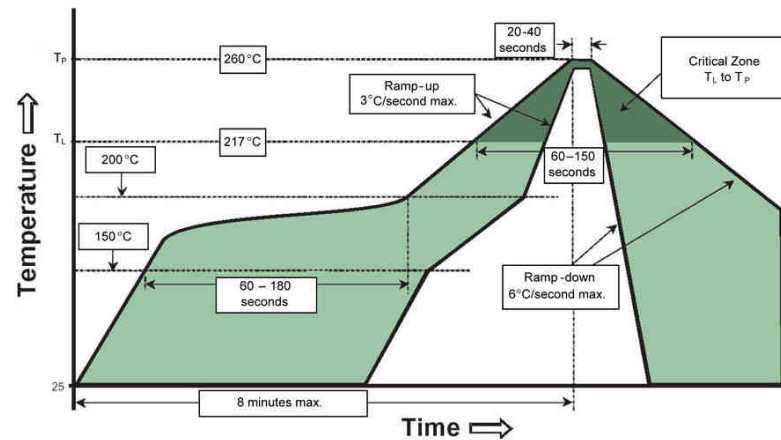
- Automotive applications challenge electronics at above 125 °C.



R. Wayne Johnson et al. *TEPM* (2004)

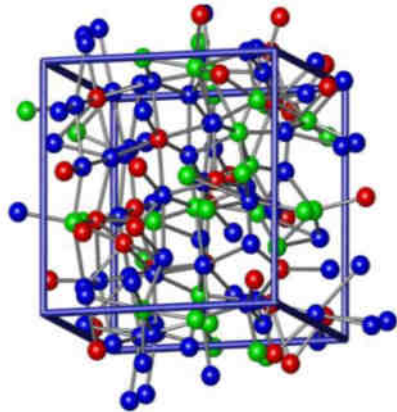
- Solder Reflow temperature profile → peak @ 260°C

Profile Classification per IPC/JEDEC J-STD-020C Pb-Free Small Body Assembly  
**Typical Pb-Free Solder Reflow profile for Surface Mount Components**

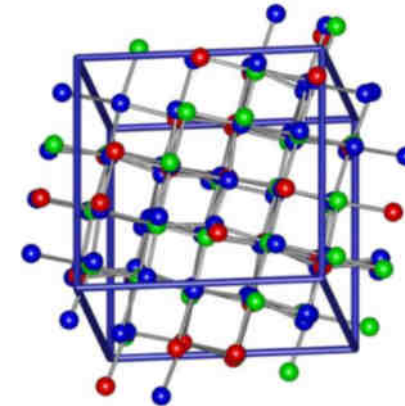
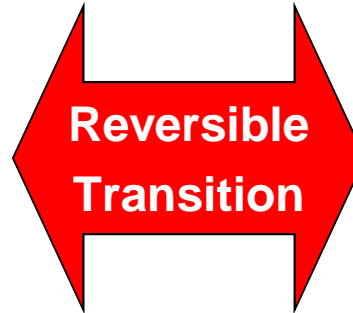


Profile Classification per IPC/JEDEC J-STD-020C Pb-Free Small Body Assembly

## PHASE-CHANGE MATERIALS

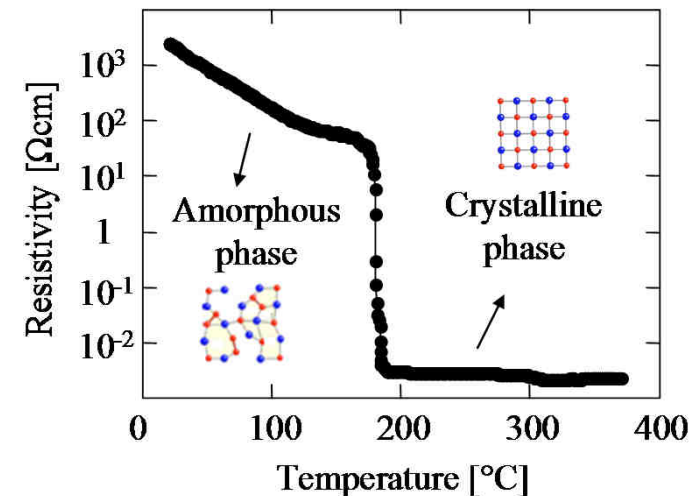


AMORPHOUS PHASE

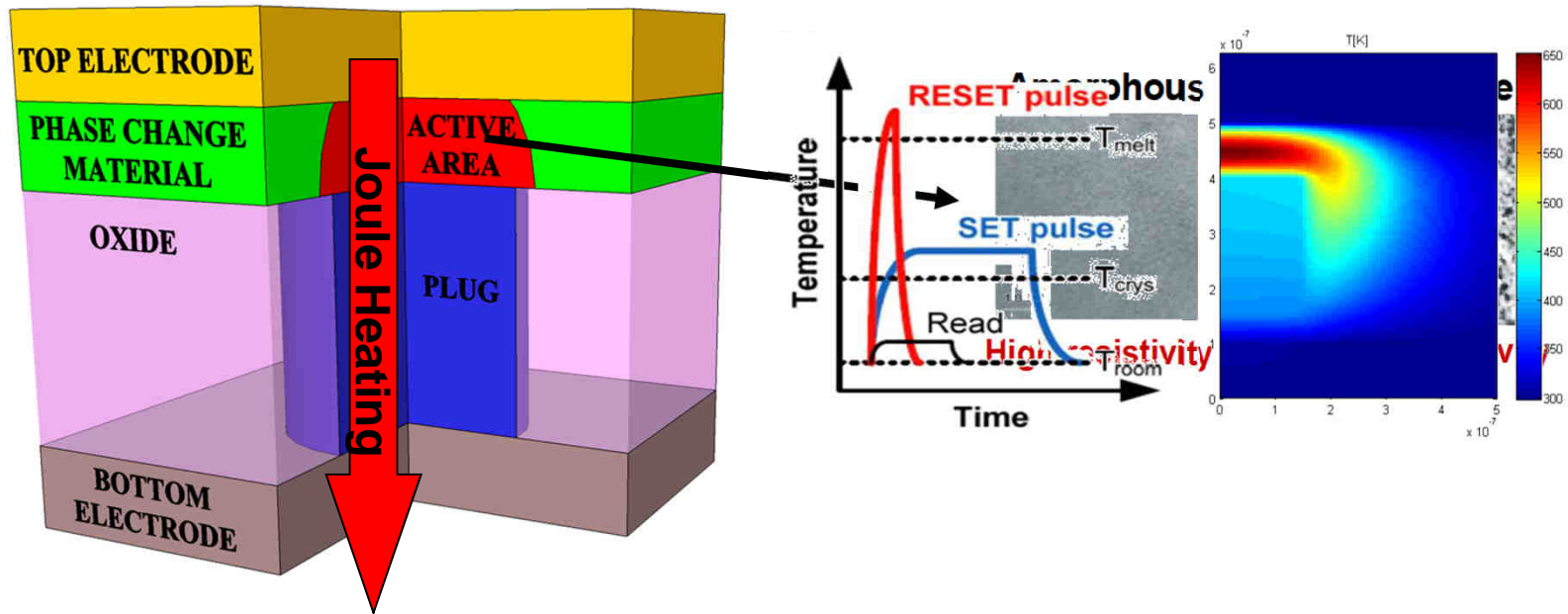


CRYSTALLINE PHASE

- Chalcogenide materials are alloys based on VI group elements
- Exhibit reversible transition (Phase-Change) e.g.  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  (GST) or GeTe
- High contrast between resistivity of amorphous and crystalline phase



# THE PCM CELL CONCEPT



- Information stored in the resistance of the chalcogenide alloy (Crystalline / Amorphous).
- Phase transition of chalcogenide alloy obtained by current-induced Joule heating.



## PCM PERFORMANCE VS MATERIAL PROPERTIES

PERFORMANCE  MATERIAL PROPERTIES

Speed

Crystallization Speed

Programming Power

Material thermal &  
electrical conductivity,  
geometry

Data Retention

Amorphous phase  
thermal stability

Endurance  
& Life Time

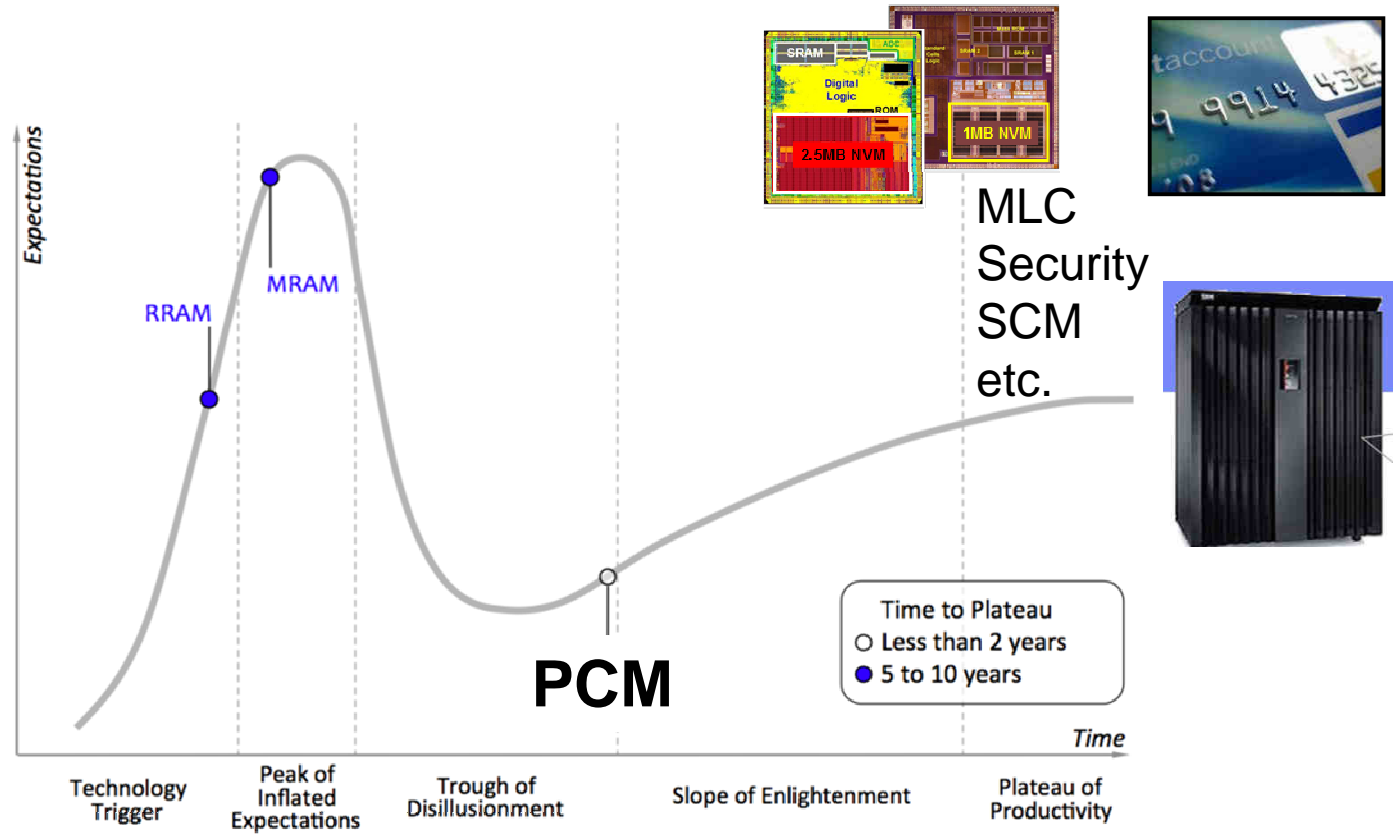
Material composition stability

### Phase-Change Memory

- Non-volatile memory technology
- Compatible with CMOS Back-End-Of-Line
- Fast access time (~10ns)
- Fast write/erase (~100ns)
- Low voltage operation (< 3V)
- Large Roff/Ron (~1000)
- High endurance (up to  $10^{12}$ )
- Good scalability



# PCM HYPE CYCLE



C.H. Lam, IEDM 2014

Phase-Change Memory: a flexible technology for a memory market in constant diversification.

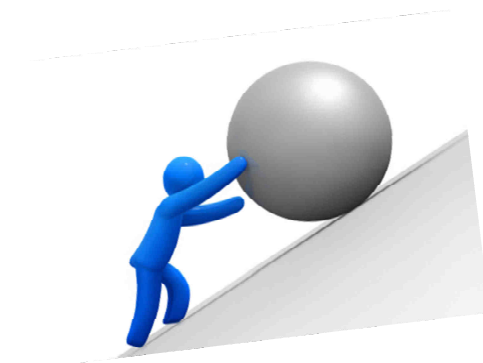
### Phase-Change Memory

- Non-volatile memory technology
- Compatible with CMOS Back-End-Of-Line
- Fast access time (~10ns)
- Fast write/erase (~100ns)
- Low voltage operation (< 3V)
- Large Roff/Ron (~1000)
- High endurance (up to  $10^{12}$ )
- Good scalability

## PCM CHALLENGES

### Phase-Change Memory

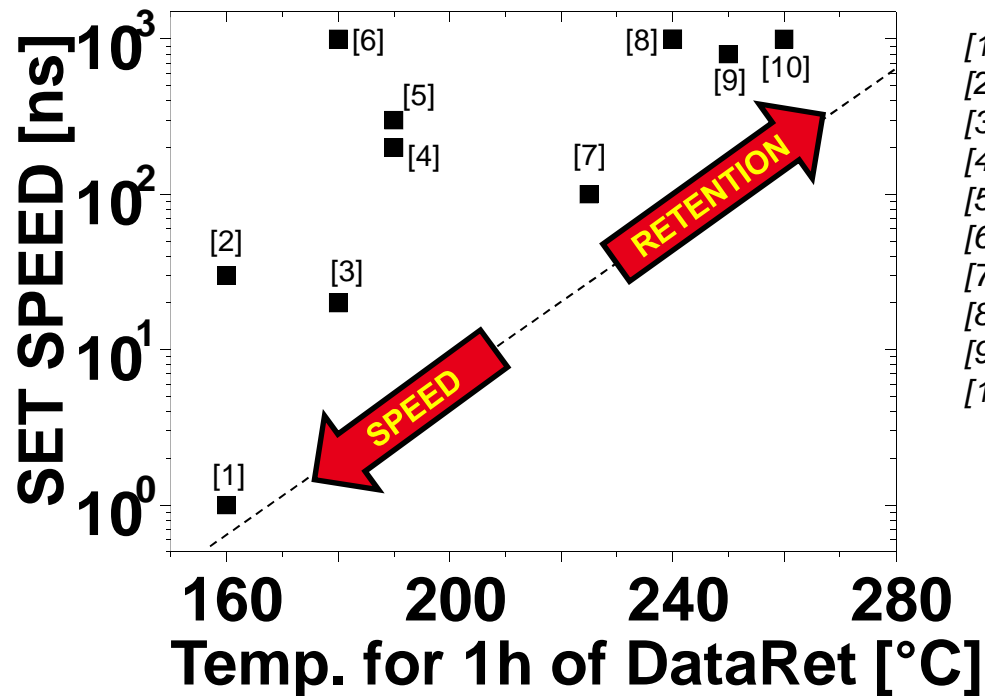
- Non-volatile memory technology
- Compatible with CMOS Back-End-Of-Line
- Fast access time (~10ns)
- Fast write/erase (~100ns)
- Low voltage operation (< 3V)
- Large Roff/Ron (~1000)
- High endurance (up to  $10^{12}$ )
- Good scalability



## CHALLENGES

- ✓ Improve the Thermal Stability of the programmed states

## PCM SPEED VS RETENTION: A MATTER OF COMPROMISE

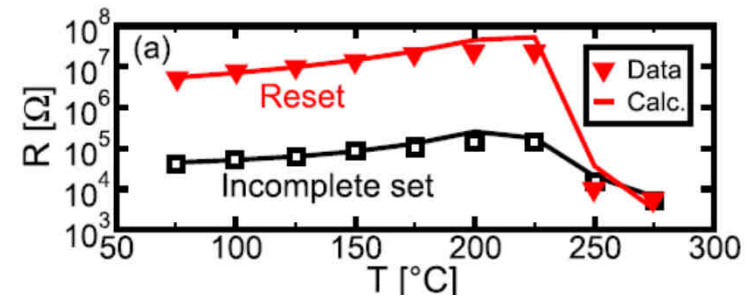
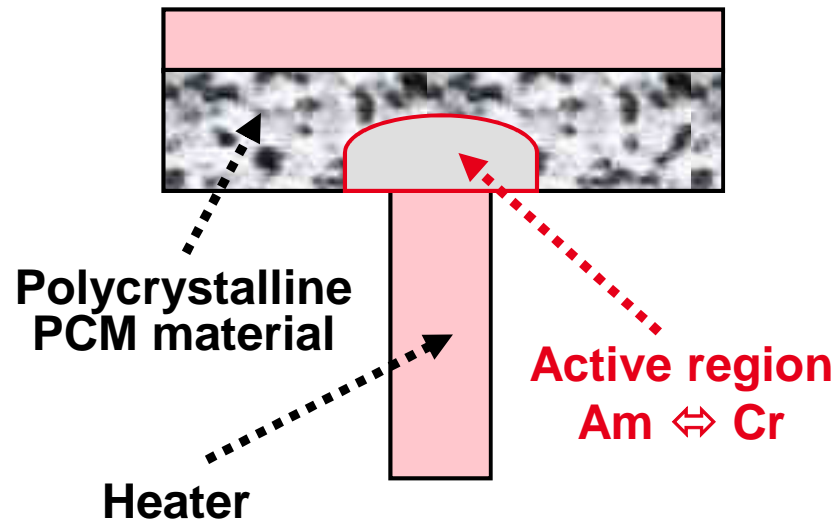


- [1] Cheng Peng et al., *J. Appl. Phys.* 2013
- [2] F. Pellizzer et al., *VLSI* 2004
- [3] G. Navarro et al., *IRPS* 2013
- [4] H. Y. Cheng et al., *IEDM* 2011
- [5] H. Y. Cheng et al., *IEDM* 2012
- [6] G.B. Beneventi et al., *IMW* 2010
- [7] A. Fantini et al., *IEDM* 2010
- [8] P. Zuliani et al., *TED* 2013
- [9] S.H. Lee et al., *IEDM* 2011
- [10] G. Navarro et al., *IEDM* 2013

- Phase-Change Material Engineering can boost PCM performance
- Trade-off to be found between SET Speed and Data Retention

# THERMAL STABILITY ISSUES WITH PCM DEVICES

- The thermal stability of the programmed states can be compromised by:
  - **The crystallization**       $\Rightarrow$  Resistance decay  $\searrow$        $\Rightarrow$  RESET failure



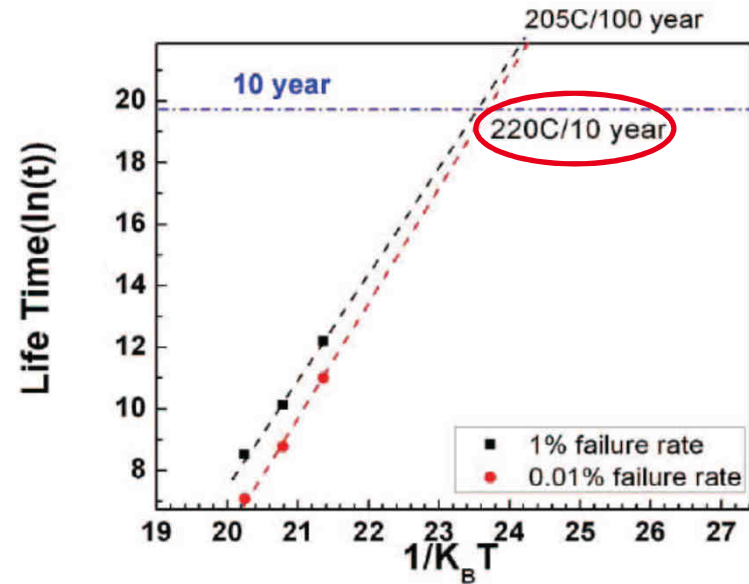
Ciocchini et al. TED (2014)

# PCM MATERIALS WITH HIGH TEMPERATURE RELIABILITY

- **GaSb-Ge materials (10ys @ 220 °C)** validated in a 128Mbit test vehicle

Pass the soldering criteria

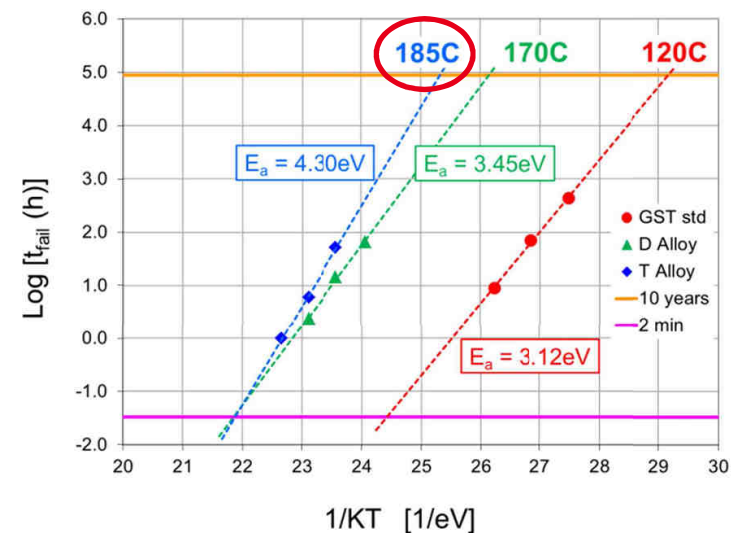
*H. Y. Cheng et al., IEDM 2015.*



- **Ge-rich GST materials (10ys @ 185 °C)** validated in a 12Mbit test vehicle.

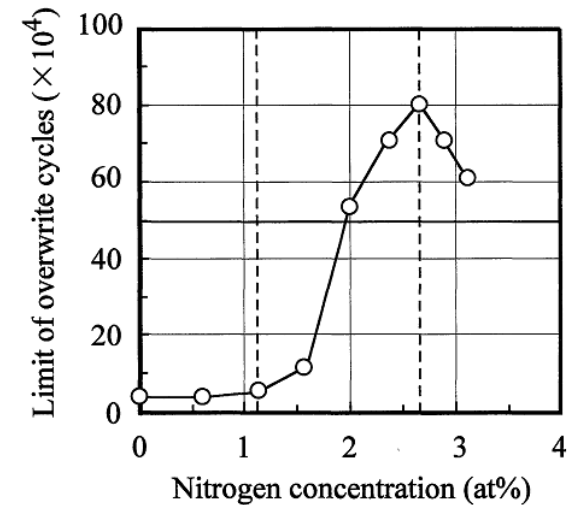
Pass the soldering criteria

*P. Zuliani et al., IEEE Trans. Electron Devices, 2013.*

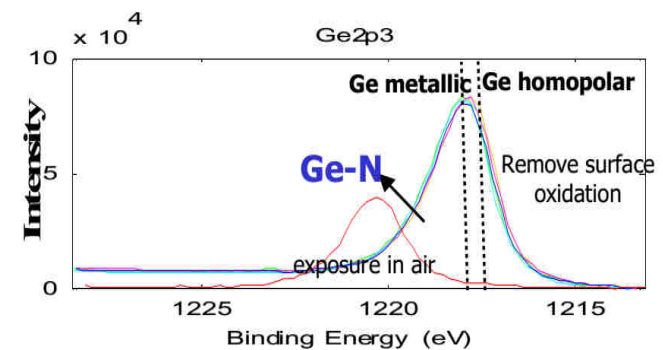


## N-DOPING IN PCM COMPOUNDS

- N doping in Ge-Sb-Te recording layer (Optical Disks) improves their recording sensitivity, erasability and overwrite cycles.
- N doping in  $GexSbyTez$  compounds suppresses the elemental segregation indicating a better endurance performance.



Rie Kojima et al.,  
*Jpn. J. Appl. Phys.* 37 2098 (1998).



H. Y. Cheng et al., *IEDM 2012*.

## Ge-RICH GST MATERIALS FOR ePCM

- **High reliability performances of Ge-rich GST devices**
  - High thermal stability of the RESET state wrt crystallization
  - Low drift of the SET state wrt structural relaxation



### OBJECTIVES OF THE STUDY

- Highlight the benefits of N-doping in Ge-rich GST
- Provide an insight into the operation fundamentals of N-doped and Ge-rich GST storage elements



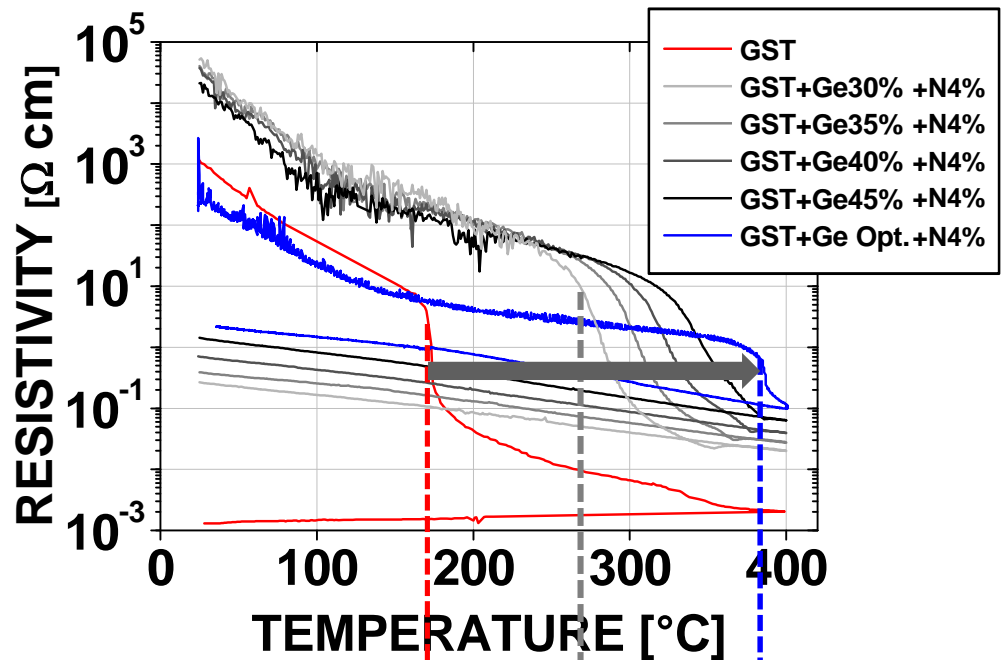


## OUTLINE

- 1 Background and Objectives
- 2 Thin Film Characterization**
- 3 Device Characterization
- 4 Analysis of the Programmed States
  - Morphological Characterization
  - Simulation of the Programming Operations
- 5 Conclusions

# THIN FILM CHARACTERIZATION

## ELECTRICAL RESISTIVITY VERSUS T → CRYSTALLIZATION TEMPERATURE $T_c$



« GST + Ge x% + N4% »

Co-sputtering  
from  $Ge_2Sb_2Te_5 + Ge$

GST  
 $T_c \sim 170^\circ C$

GST+Ge30%+N4%  
 $T_c \sim 260^\circ C$

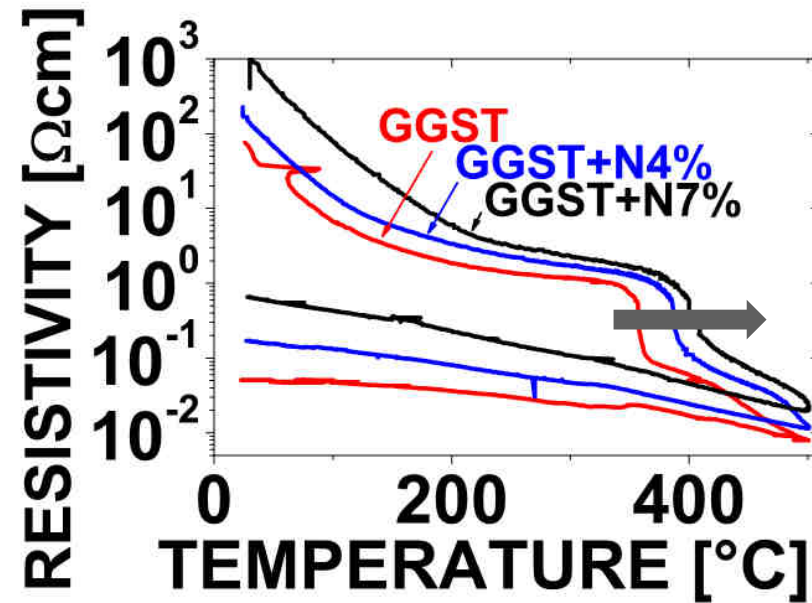
GST+Ge opt.+N4%  
 $T_c \sim 380^\circ C$

Increase of Ge at. % → Increase of  $T_c$

## THIN FILM CHARACTERIZATION

### ELECTRICAL RESISTIVITY VERSUS T → CRYSTALLIZATION TEMPERATURE $T_c$

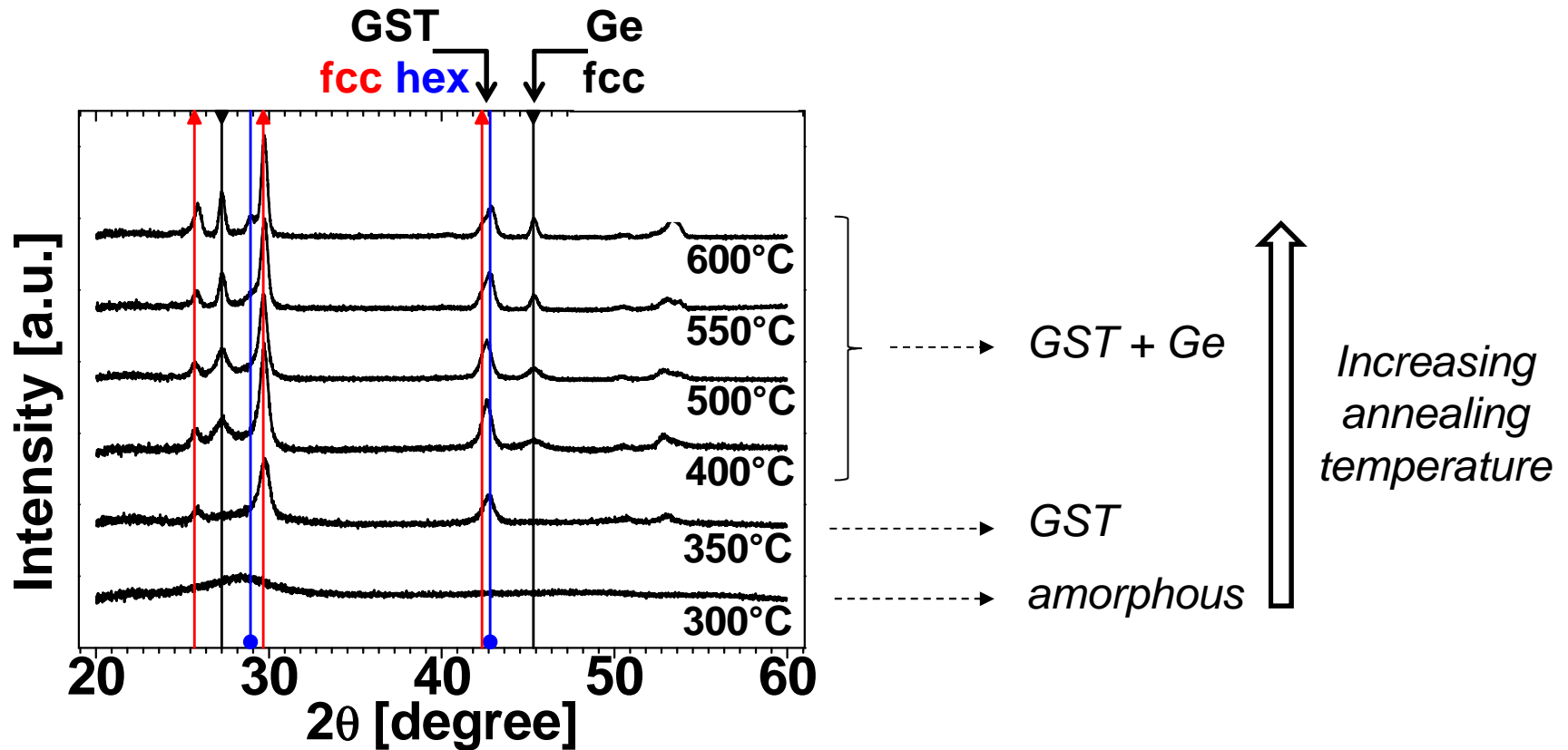
Effect of N additions in GST+Ge opt.



N-doping in Ge-rich GST → Increase of  $T_c$

# THIN FILM CHARACTERIZATION

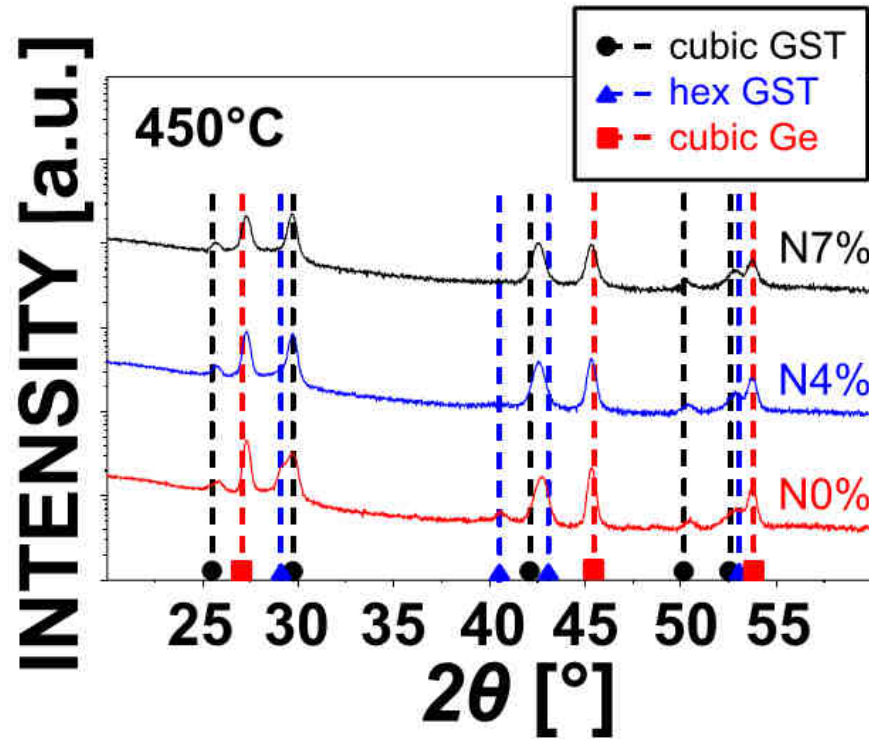
## X-RAY DIFFRACTION → CRYSTALLINE STRUCTURE



Ge-rich GST crystallization → Phase separation GST + Ge.

# THIN FILM CHARACTERIZATION

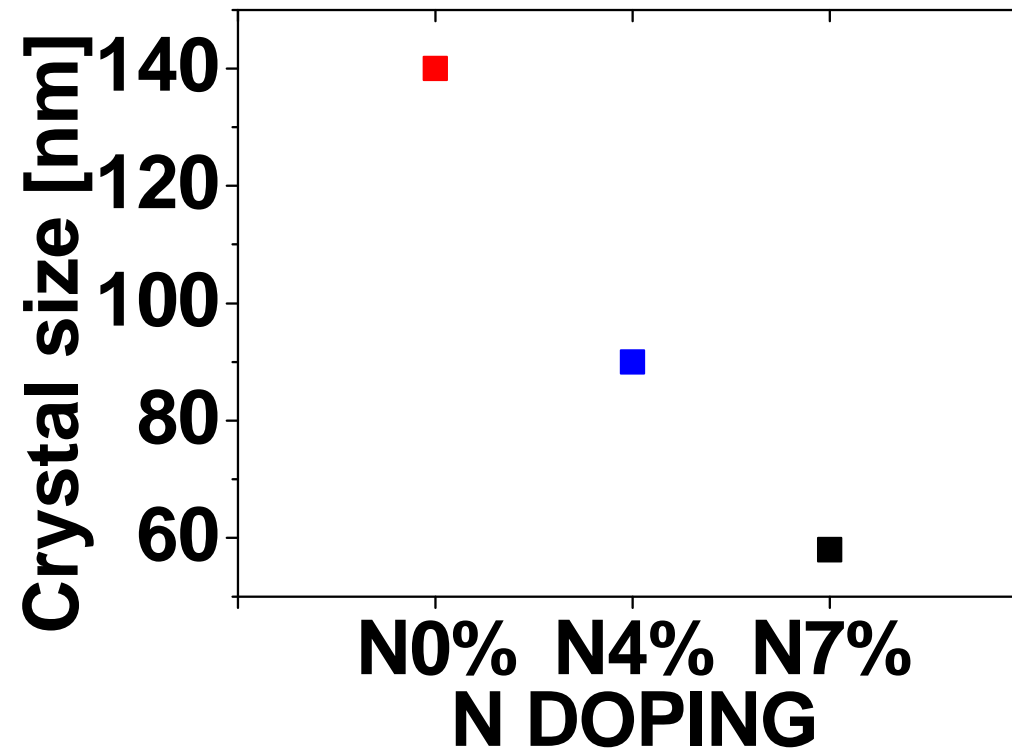
## X-RAY DIFFRACTION → CRYSTALLINE STRUCTURE



Ge-rich GST, w/o or with N-doping → Phase separation GST + Ge

## THIN FILM CHARACTERIZATION

### X-RAY DIFFRACTION → GRAIN SIZE

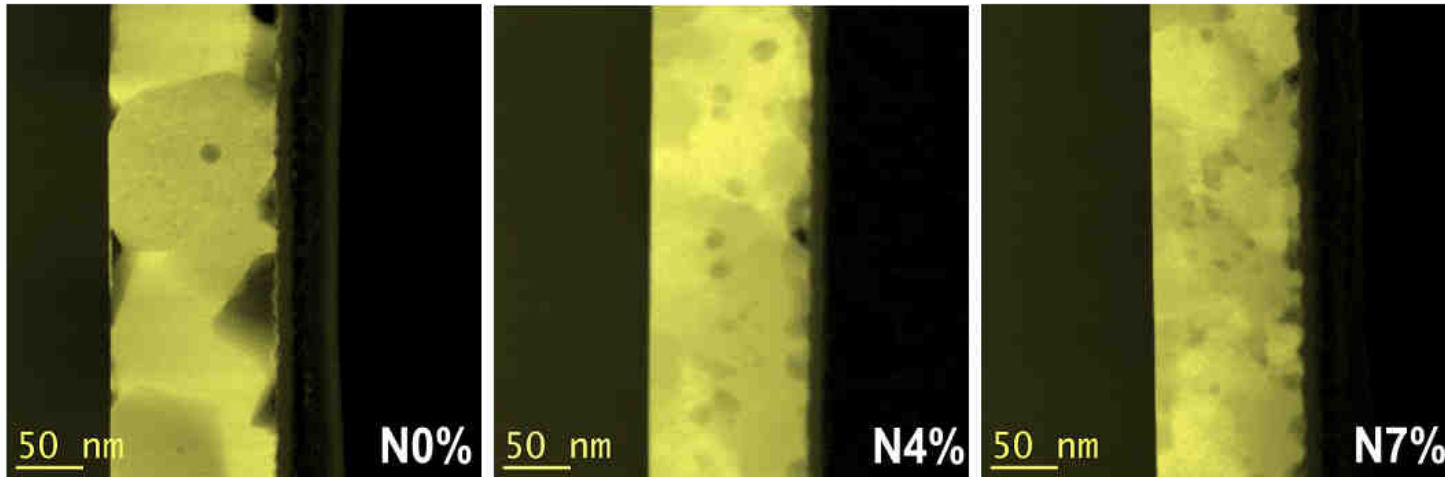


Ge-rich GST, with increasing N-doping → Smaller grain size

# THIN FILM CHARACTERIZATION

## HAADF/STEM IMAGING

450 °C annealing

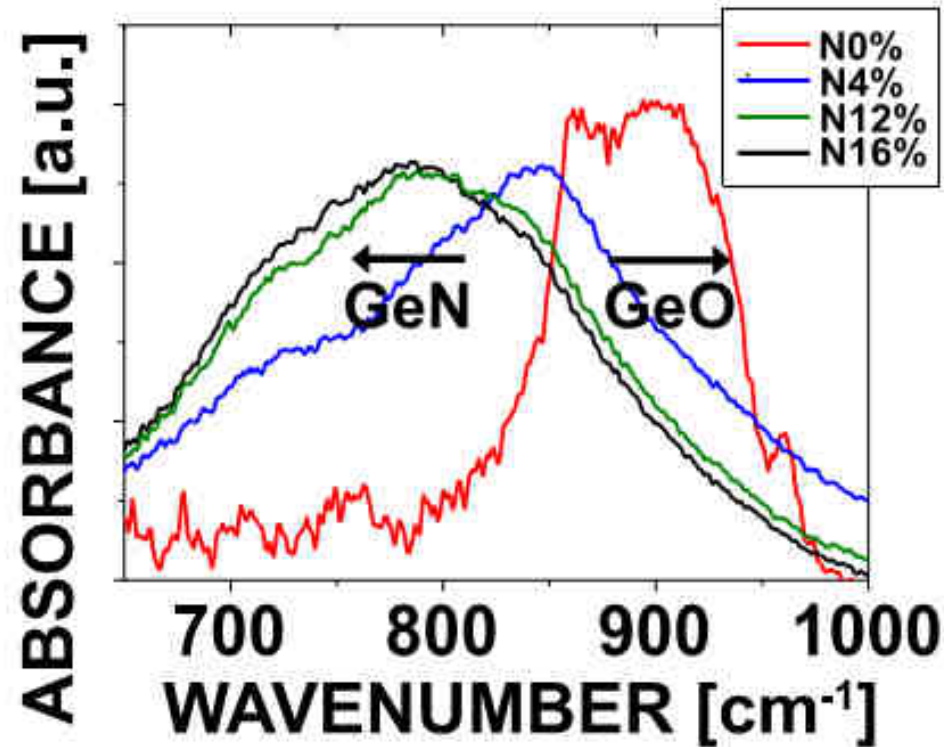


w/o N doping  
↓  
Large grain size  
↓  
Local density lowering

with N-doping  
↓  
Small grain size

# THIN FILM CHARACTERIZATION

## FTIR ANALYSIS



Ge-rich GST with N-doping → Lower Ge-O peak intensity

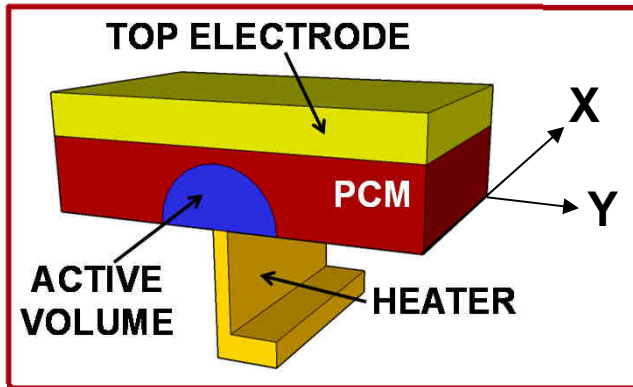




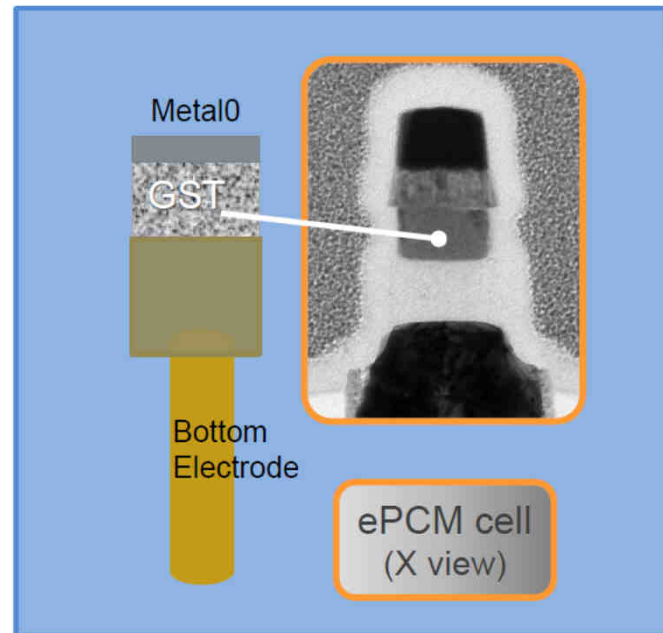
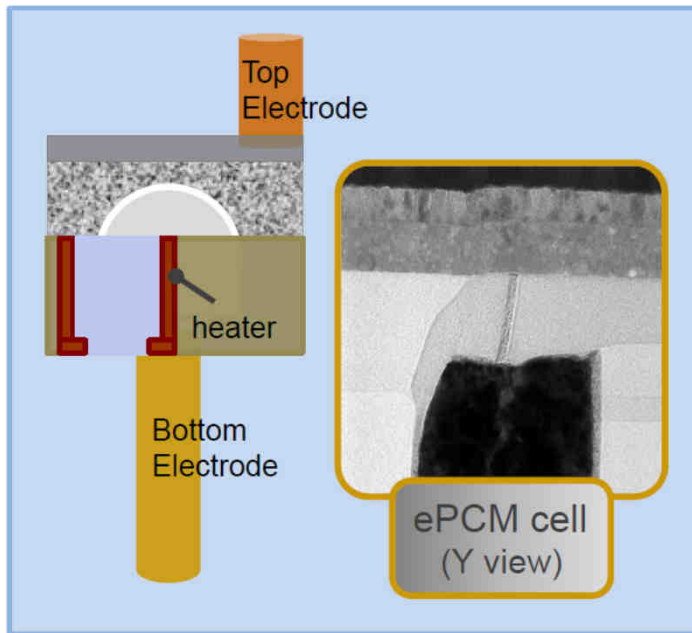
## OUTLINE

- 1 Background and Objectives
- 2 Thin Film Characterization
- 3 Device Characterization**
- 4 Analysis of the Programmed States
  - Morphological Characterization
  - Simulation of the Programming Operations
- 5 Conclusions

# DEVICE PRESENTATION

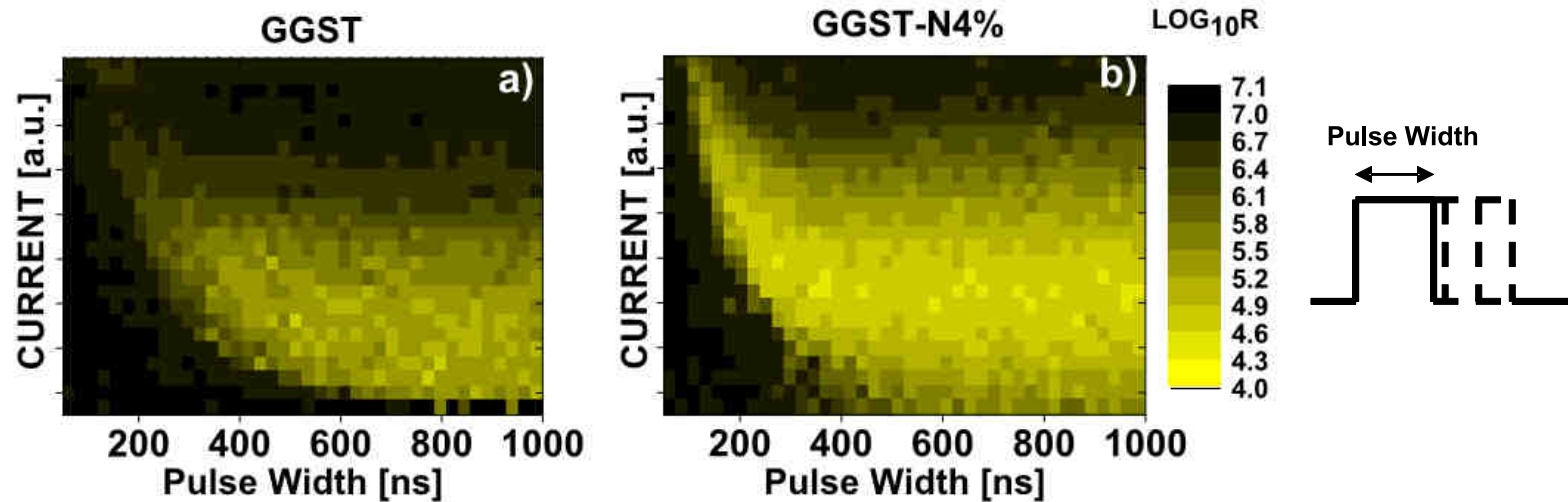


Wall storage element  
Aggressive 90nm technology node



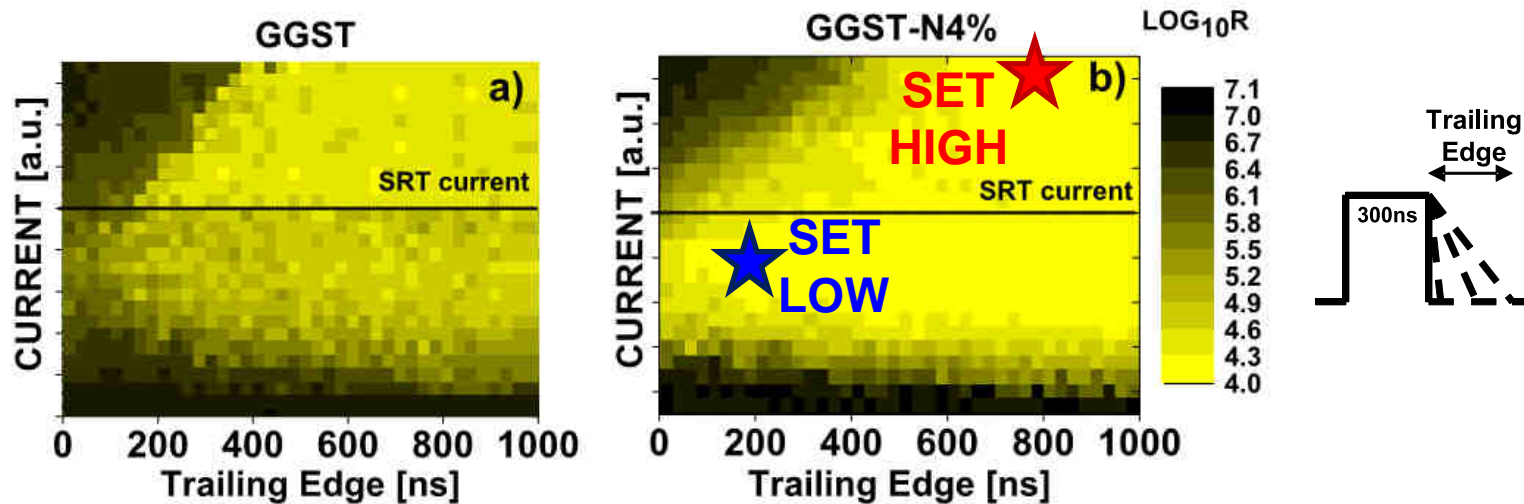
Source: P. Zuliani, presented at the « eNVM workshop » Gardanne, Sept 2013

## CRYSTALLIZATION CARTOGRAPHERIES SET SPEED ANALYSIS



Ge-rich GST with N-doping  $\rightarrow$  A lower resistance state is achievable

## CRYSTALLIZATION CARTOGRAPHERIES SET SPEED ANALYSIS

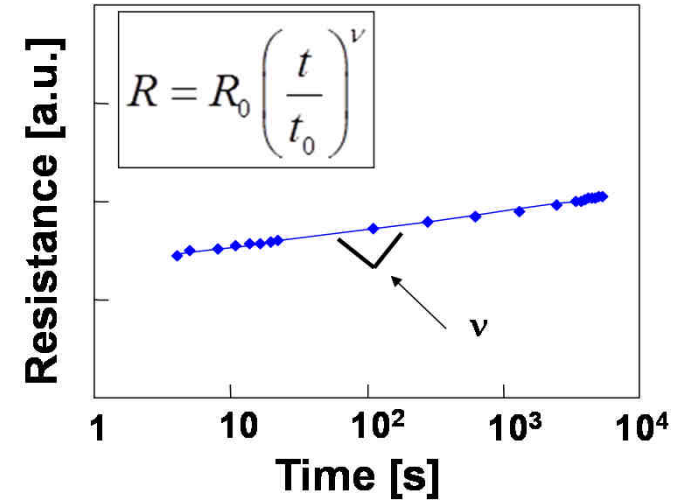
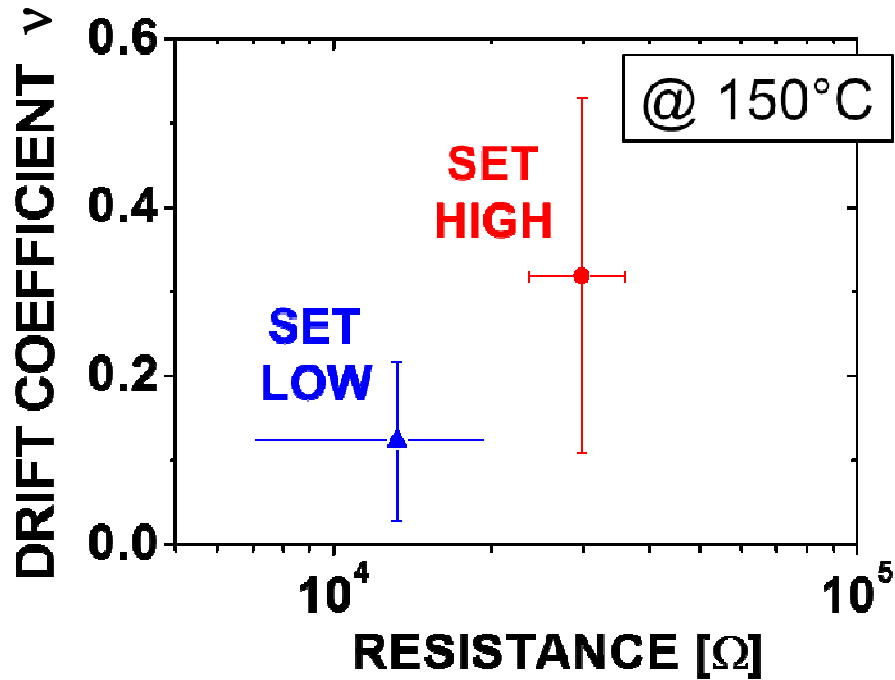


Ge-rich GST with N-doping → SET programming is more efficient

Two different programming conditions for SET:  
SET\_low & SET\_high

# DEVICE CHARACTERIZATION

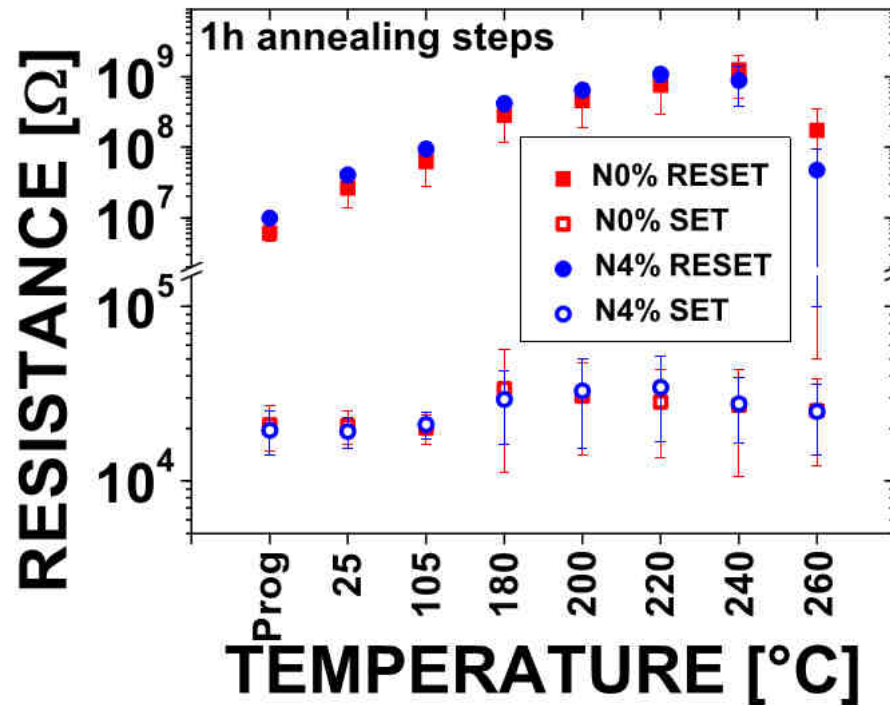
## SET STATE DRIFT



SET at LOW current → low resistance & low drift

# DEVICE CHARACTERIZATION

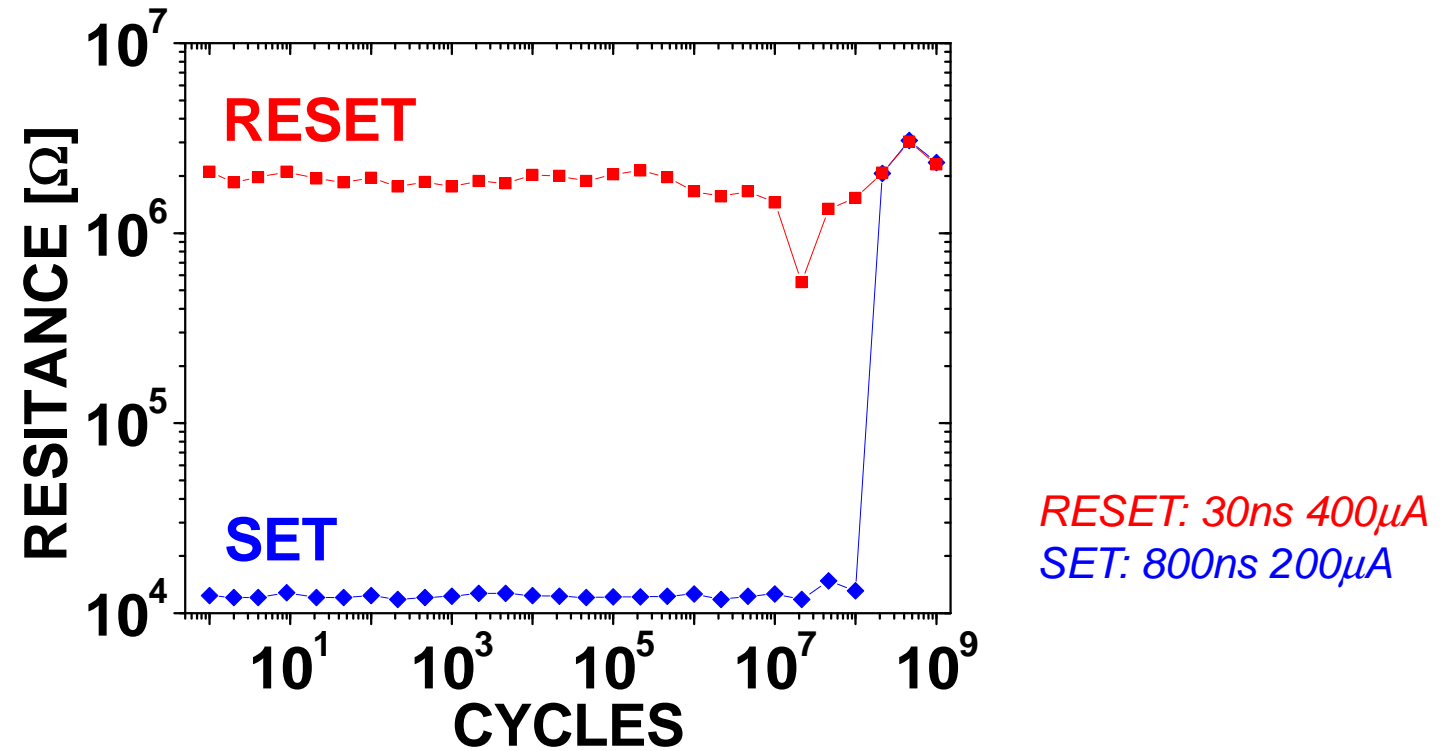
## THERMAL STABILITY OF THE PROGRAMMED STATES



Ge-rich GST, w/o or with N-doping  
 → RESET state retention is granted up to 240 °C.

# DEVICE CHARACTERIZATION

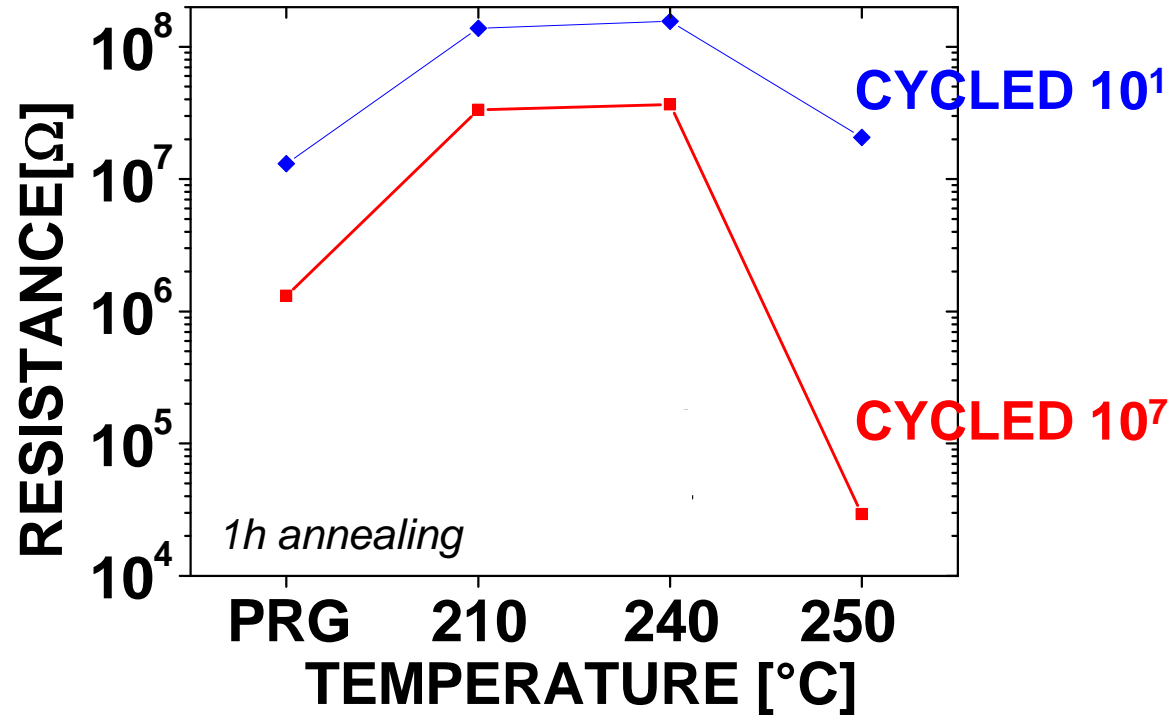
## ENDURANCE



Stability of the reading window up to at least  $10^7$  cycles.

## DEVICE CHARACTERIZATION

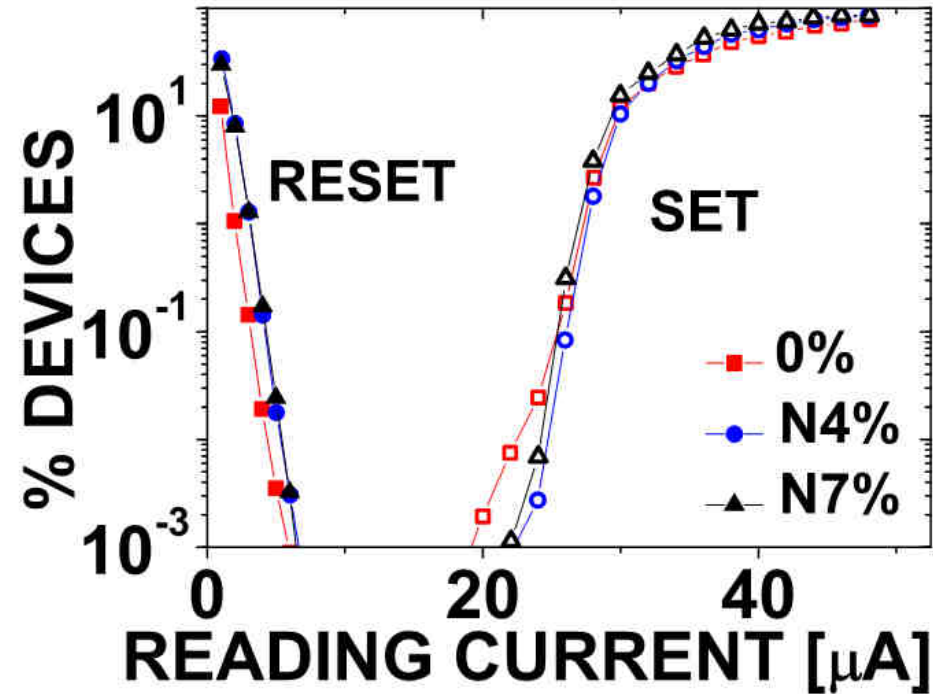
### THERMAL STABILITY AFTER CYCLING



After 10<sup>7</sup> SET/RESET cycles,  
the fail temperature is lowered by only 10°C at maximum.



## SET/RESET RESISTANCE DISTRIBUTIONS



Ge-rich GST, w/o or with N-doping → Reliable reading window for the intrinsic parts of the distributions (> 0.001%).

## N-DOPED AND Ge-RICH GST DEVICE PERFORMANCES

### SUMMARY

- Optimized SET operation at low current  
→ low resistance & low drift
- Stability of the SET & RESET states for 1h at 240°C



### MORPHOLOGICAL CHARACTERIZATION OF THE PROGRAMMED STATES

Representative alloy: GST+Ge45%+N4%

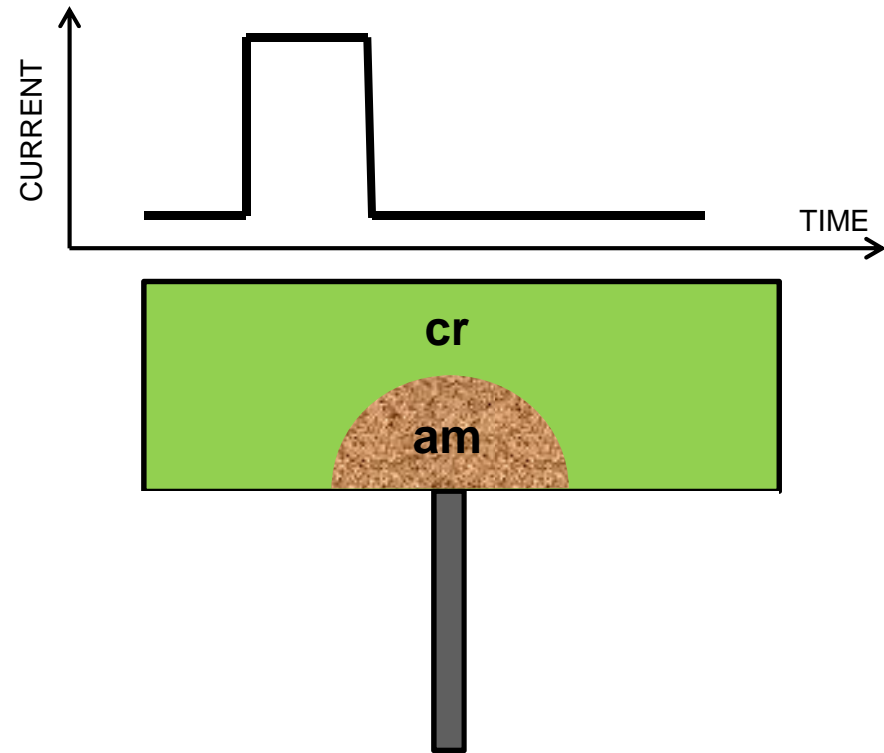
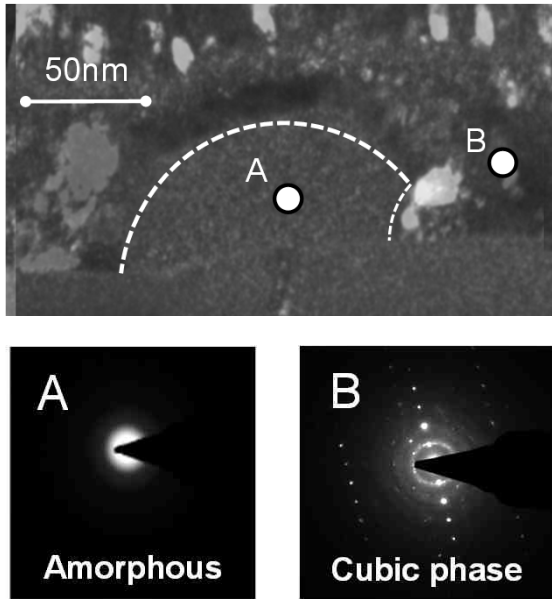


## OUTLINE

- 1 Background and Objectives
- 2 Thin Film Characterization
- 3 Device Characterization
- 4 **Analysis of the Programmed States**
  - Morphological Characterization
  - Simulation of the Programming Operations
- 5 Conclusions

# DEVICE CHARACTERIZATION

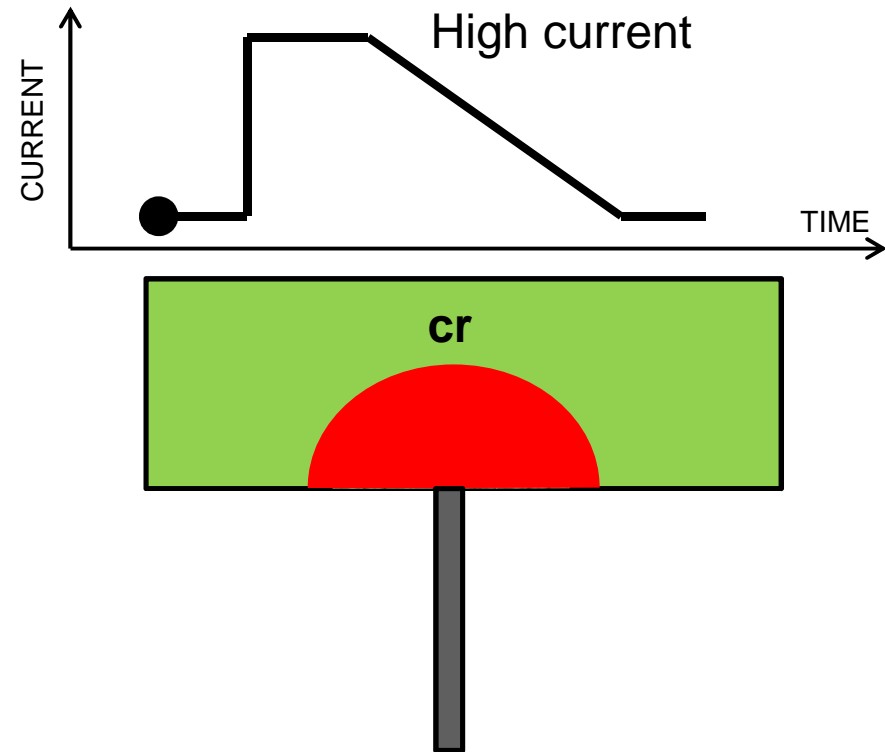
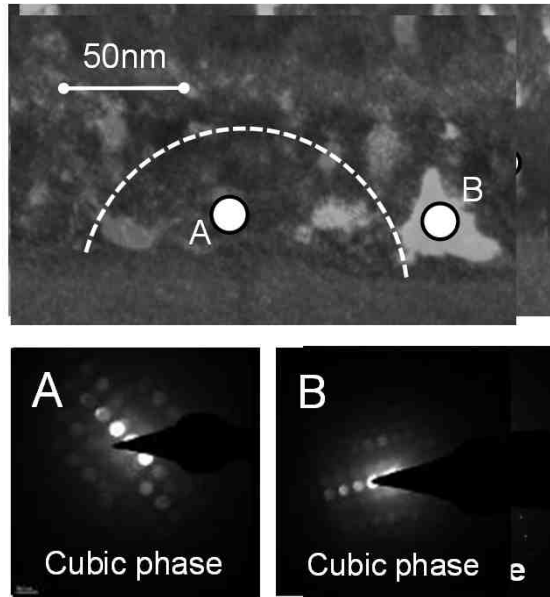
## THE RESET STATE



- Amorphous dome within a polycrystalline PCM layer.

## DEVICE CHARACTERIZATION

### THE SET\_HIGH STATE

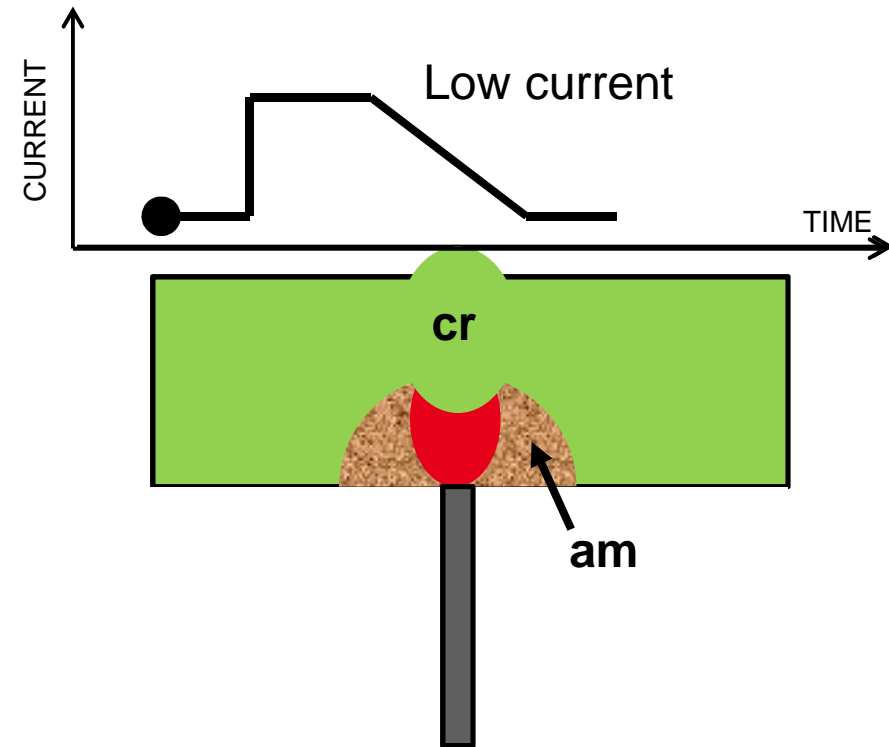
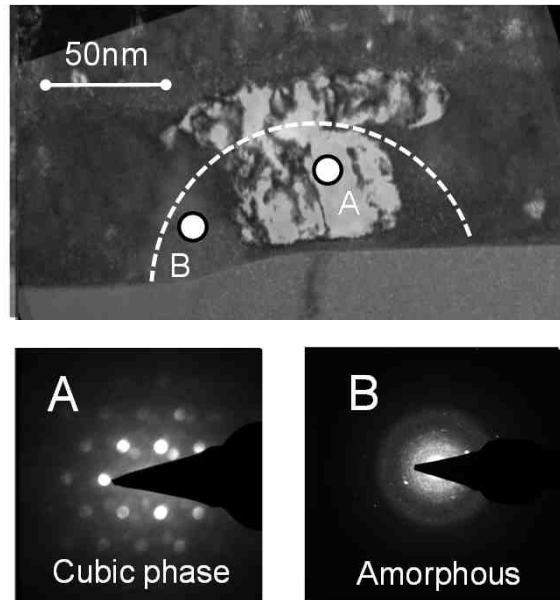


- Fully polycrystalline PCM layer with randomly oriented grains.
- High number of GBs → high SET state drift\*.

\* N. Ciocchini et al., TED 2014.

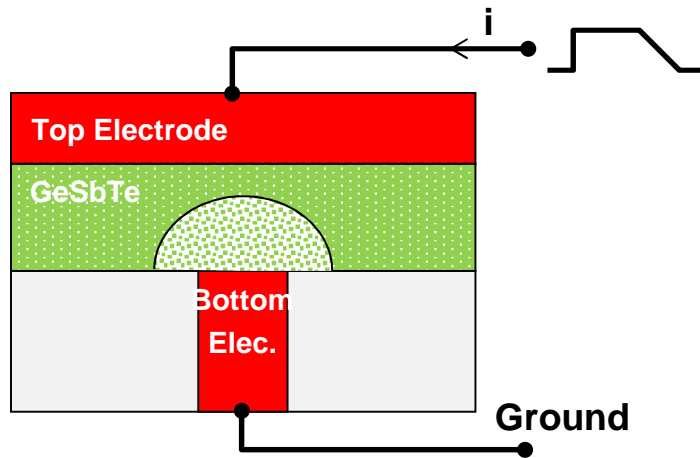
## DEVICE CHARACTERIZATION

### THE SET\_LOW STATE



- Partially crystalline PCM layer.
- Single crystalline orientation along the conductive path.
- Low number of GBs → Lower drift wrt SET HIGH

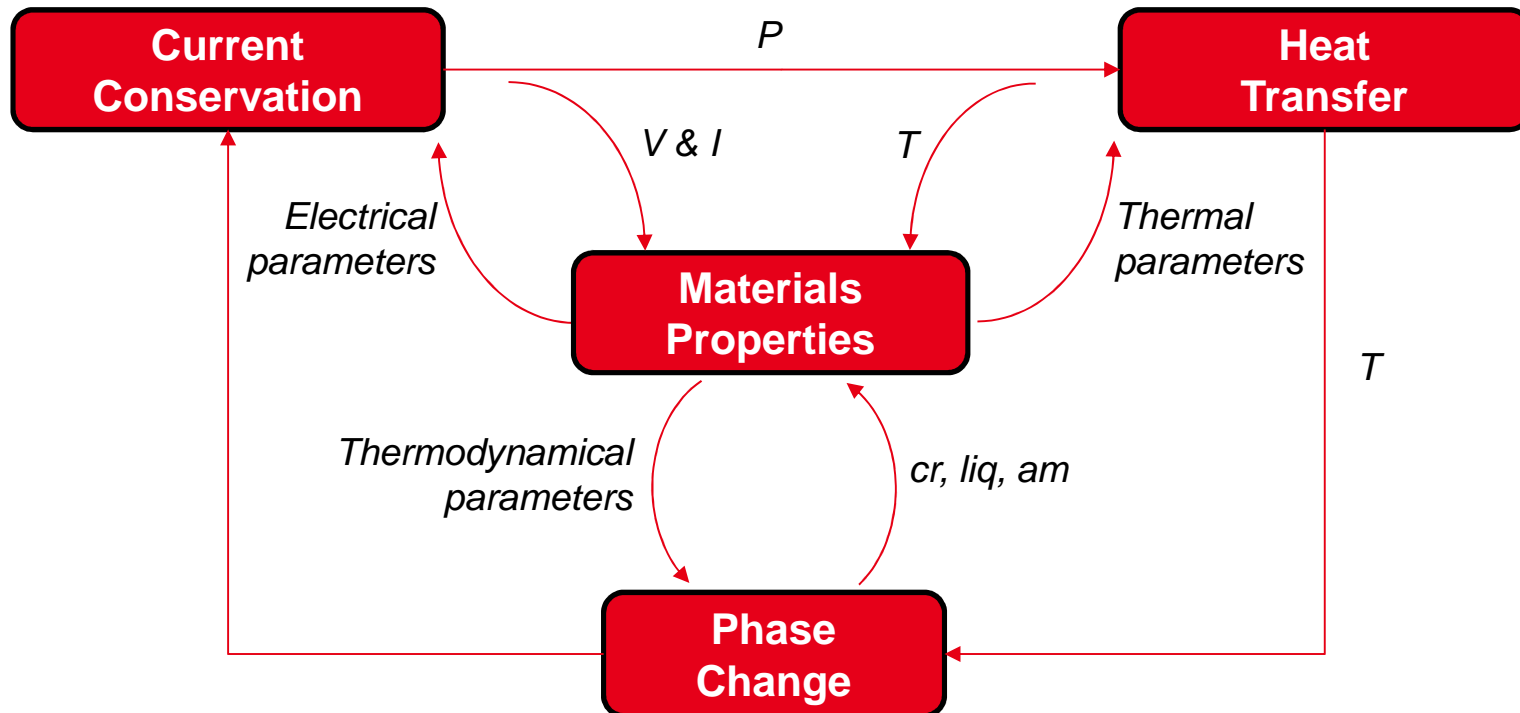
# MULTIPHYSICAL SIMULATIONS



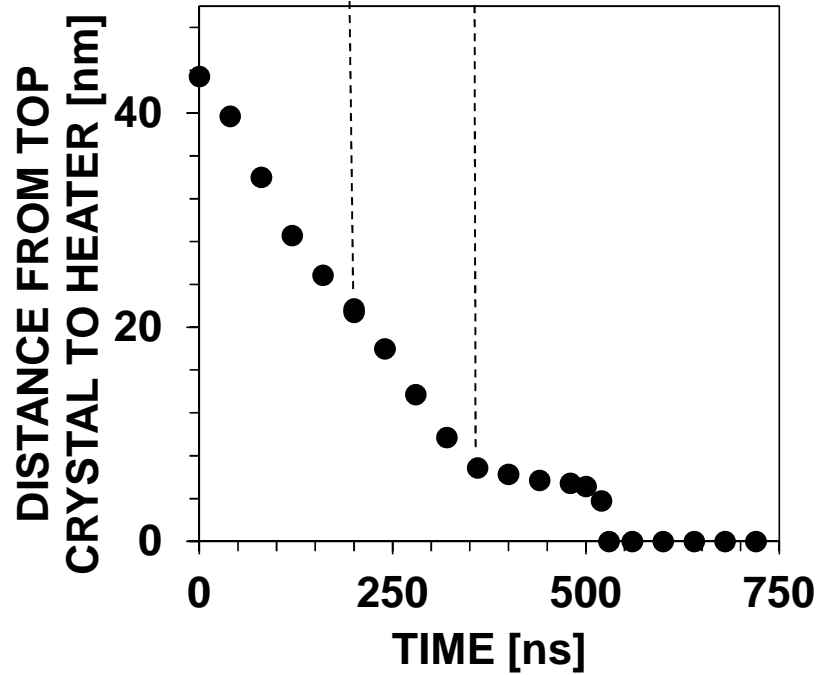
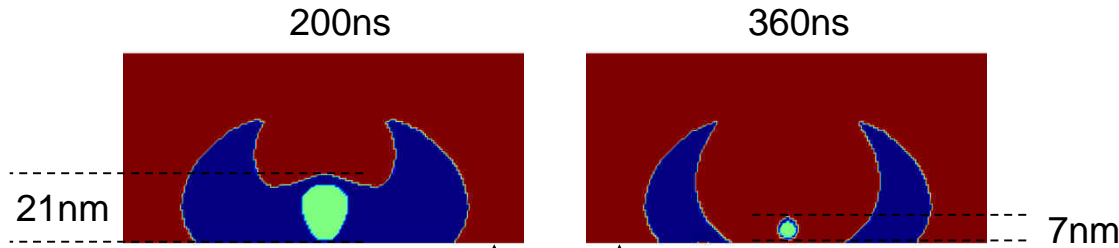
A. Glière et al., *IEEE Conf. SISPAD (2011)*

O. Cueto al., *IEEE Conf. SISPAD (2012)*

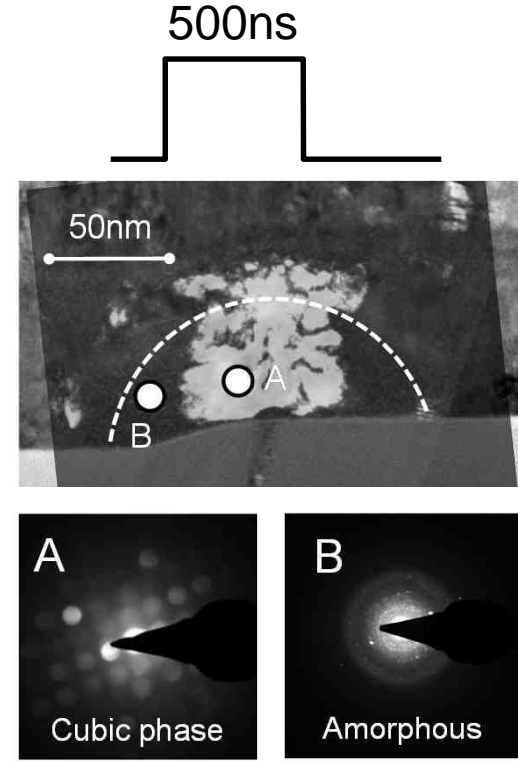
O. Cueto al., *IEEE Conf. SISPAD (2015)*



# SIMULATION: THE SET\_LOW OPERATION



**SET\_LOW**  
w/o trailing edge

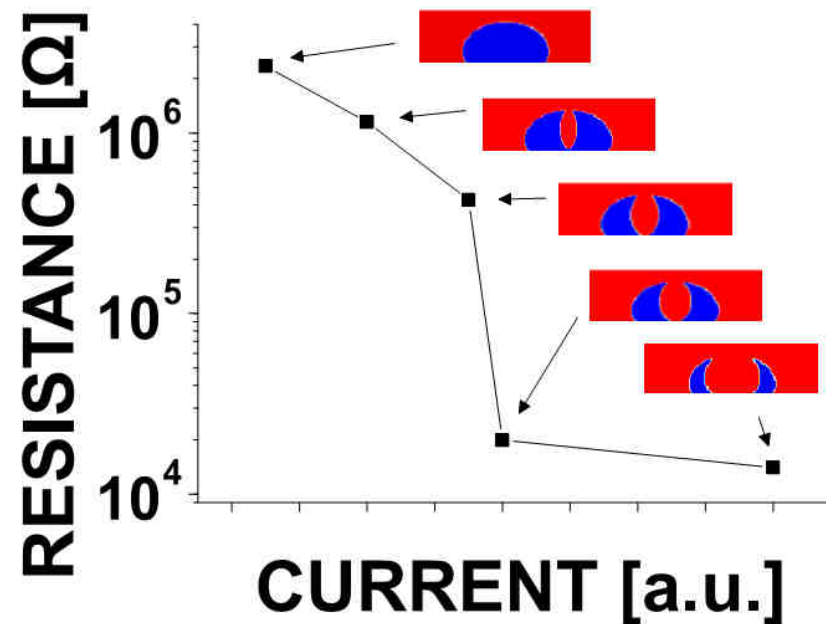


Good agreement between simulations, electrical results & TEM



## ELECTROTHERMAL SIMULATIONS

### PROGRAMMING CHARACTERISTICS R(I)

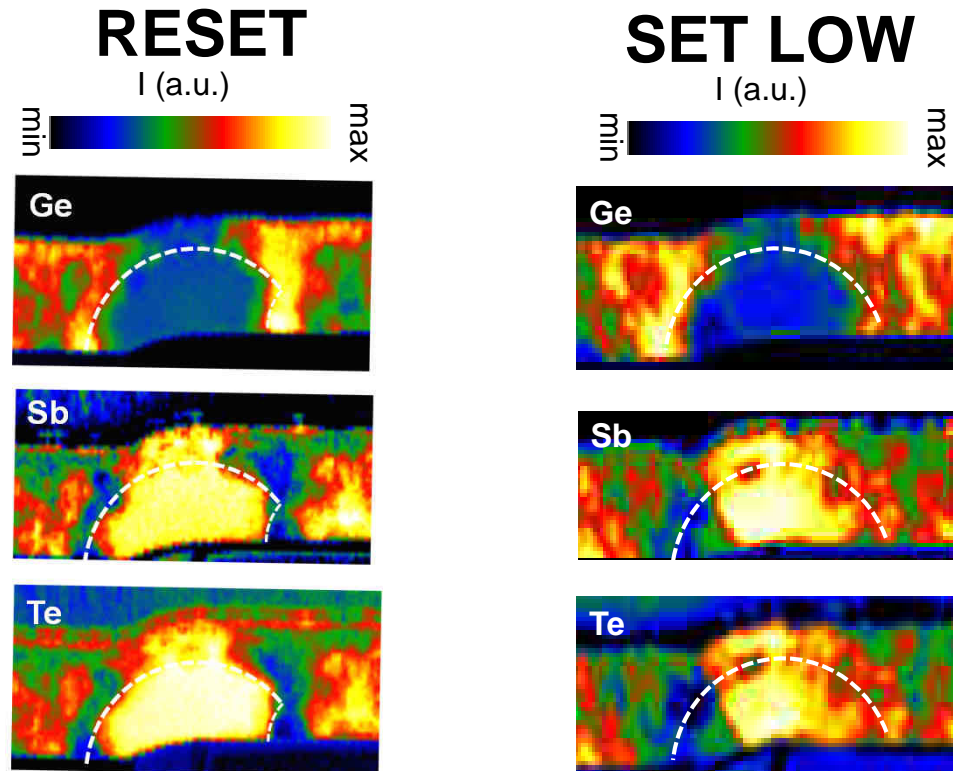


- Demonstration of the SET operation at performed at low current
- N-doping → No large Ge grains that can cross the conductive path made of GST grains → Reliable SET operation.

## DEVICE CHARACTERIZATION

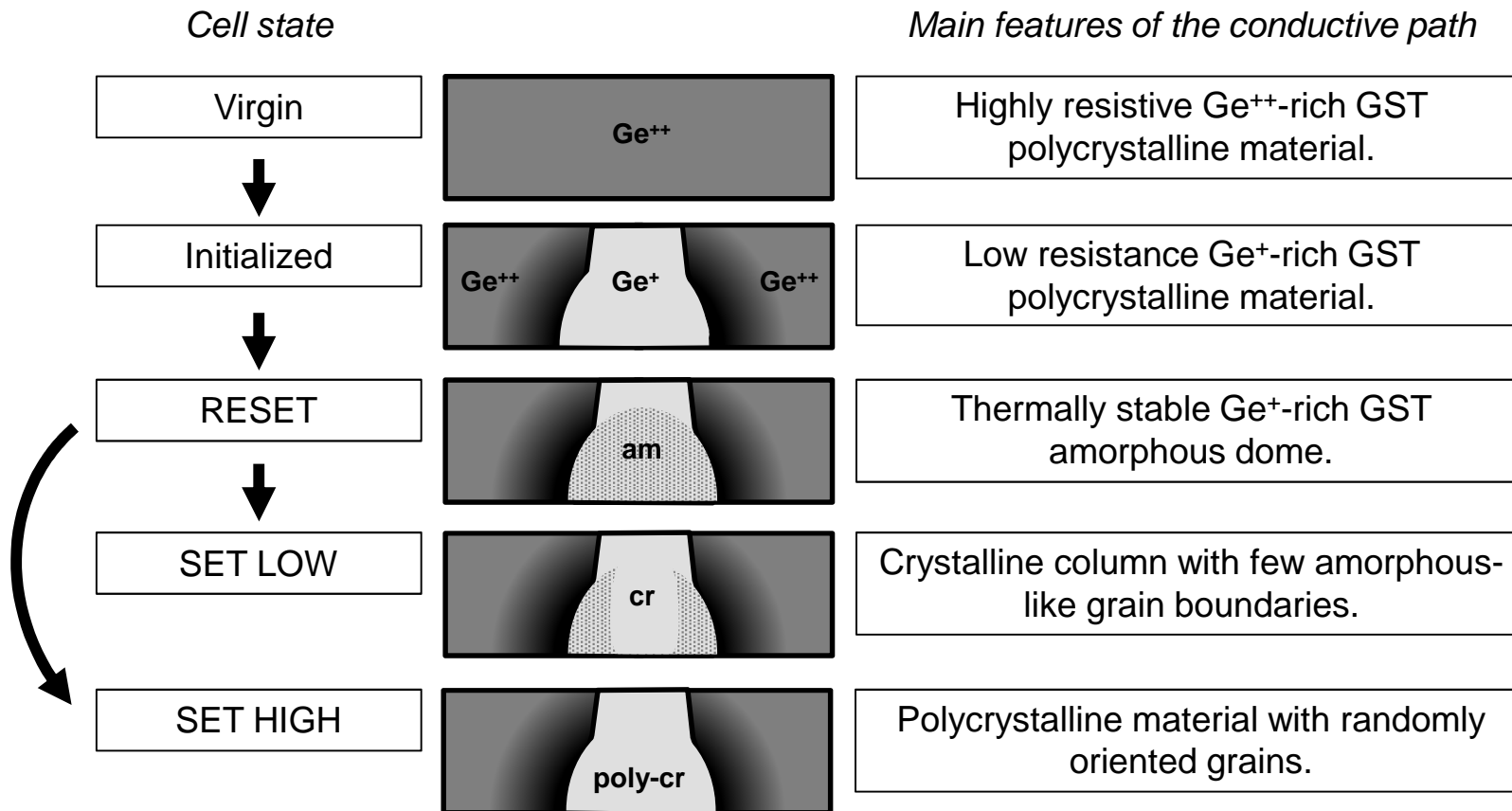
### STEM/EELS ANALYSIS → ELEMENTAL DISTRIBUTION

Core composition  
 ~ GST+Ge25%  
 →  $T_c \sim 250^\circ\text{C}$



- Ge-depletion from the heater up to the top electrode.
- Lateral Ge-rich zones are crystalline
- Segregation effect likely to result from the initial seasoning.

# UNDERSTANDING THE HIGH THERMAL STABILITY OF N-DOPED AND Ge-RICH GST BASED PCM DEVICES





## OUTLINE

- 1** Background and Objectives
- 2** Thin Film Characterization
- 3** Device Characterization
- 4** Analysis of the Programmed States
  - Morphological Characterization
  - Simulation of the Programming Operations
- 5** Conclusions

# AN INSIGHT INTO THE HIGH THERMAL STABILITY OF N-DOPED AND Ge-RICH GeSbTe BASED PCM DEVICES

## CONCLUSIONS

Ge segregation at the  
periphery of the active area  
+  
Very high initial Ge content



Ge-rich alloy wrt GST  
at the core of the cell



**High stability of the RESET state**  
wrt crystallization

Peculiar crystallization mechanism  
of the SET\_LOW operation



Only few amorphous-like grain  
boundaries along the conduction path



**Low drift of the SET\_LOW state**

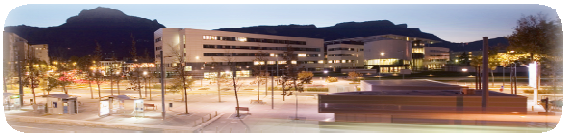
# AN INSIGHT INTO THE HIGH THERMAL STABILITY OF N-DOPED AND Ge-RICH GeSbTe BASED PCM DEVICES

## CONCLUSIONS

- N-doping can guarantee a finer crystallization structure of the phase-change material layer after BEOL.
- SET operation reliability is granted in N-doped GGST devices at low current, enabling faster and energy saving programming.
- Integration of Ge-rich and N-doped GST PCM materials was validated in a 12Mbit test vehicle.
- The good thermal stability of N-GGST devices was proved by HTDR of 1 hour till 240 °C.
- We confirm the PCM potential for embedded applications.

# 9TH LETI MEMORY WORKSHOP

Grenoble June 27<sup>th</sup>



*“ If you want to make it faster, you scale it...  
if you want to make it more dense, you scale it...  
if you want to make it less consuming, you scale it...  
if to scale becomes impossible...*

*you Phase-Change it...”*

## THANK YOU

## ANY Q&A?



Leti, technology research institute  
Commissariat à l'énergie atomique et aux énergies alternatives  
Minatec Campus | 17 rue des Martyrs | 38054 Grenoble Cedex | France  
[www.leti.fr](http://www.leti.fr)

