Novel Fast-switching and High-data Retention Phase-change Memory Based on New Ga-Sb-Ge Material

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IBM/Macronix PCRAM Joint Project

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Abstract

Attempts to improve the retention so far must sacrifice switching speed. This work explores new phase change material based on pseudobinary GaSb-Ge system. The resulting new phase-change material has demonstrated fast switching speed of 80 ns, long endurance of 1G cycles and excellent data retention that survives 250 °C-300 hrs. The 10 years-220 °C data retention is the best ever reported. It is also the fastest material that can pass the solder bonding criteria for embedded automotive applications.

Introduction

Extensive material and device research continues to improve the phase-change material properties and device performance, however all run into conflicting requirements. Materials based on Ge-Sb-Te (GST) system inherited from optical disk memory always suffer from conflicts between speed and data retention [1]. And high endurance or good data retention by doping usually slows down the speed [2-3]. The performance trade-offs for different applications not only prevented phase-change memory (PCM) from becoming a universal memory but also impeded its wider acceptance in the industry.

Table I compares the performance of published GST materials with the Ga-Sb-Ge material in this study, especially on SET speed, data retention and solder bonding thermal budget test. High temperature data retention materials largely suffer from switching speed degradation [3-5]. No GST based material can meet all data retention, solder bonding thermal budget and fast speed requirements. Thus the fundamental conflict between switching speed and data retention is very difficult to solve without exploring new materials beyond GST based systems.

Ga-Sb based alloys have been studied as possible phase change materials for PCM and they have been demonstrated to have high crystallization temperatures, which implies good thermal stability of the amorphous phase, and fast switching [6-7]. This opens up a new path for materials engineering with expectation of preserving fast speed and high data retention. In this work we further improve the stoichiometric GaSb material by incorporation of Ge and by adding another doping. The performance of this new material along the pseudobinary GaSb-Ge system was verified in 128 Mb PCM test chips. We demonstrated fast SET speed (~80 ns), ~1G cycling endurance, ~100 % yield in a 128 Mb test chip after 250 °C-300 hrs baking, with projected 10-year retention at 220 °C. This is the highest temperature data retention reported and also passes solder bonding criteria. This breakthrough in PCM material is very promising for future automotive and embedded applications.

Phase-Change Material Characterization

Figure 1 shows the Tx as a function of composition in the Ga-Sb-Ge ternary phase diagram. The pseudobinary GaSb-Ge system resembles to a simple eutectic system [8]. The crystallization temperature of the stoichiometric GaSb (measured films: $Ga_{46}Sb_{54}$) can be greatly increased by Ge incorporation along the GaSb-Ge tieline and is further enhanced by additional doping. All studied materials based on Ga-Sb-Ge system have much higher Tx at >365 °C, compared to GST-225 (~ 150 °C), indicating excellent thermal stability. **Figure 2** compares the resistivity vs. temperature curves of GST-225, $Ga_{46}Sb_{54}$, $Ga_1Sb_1Ge_1$ and lightly doped GaSbGe. Although, the thermal stability of $Ga_1Sb_1Ge_1$ is strong enough to allow it to pass the solder bonding criteria, lightly doping is necessary for further enhance material properties and resulted in a film with extremely high Tx of 450 °C. Doped GaSbGe material shows the inverse optical contrast where the crystalline phase has lower reflectance than amorphous phase as shown in **Fig. 3**. It is similar to stoichiometric GaSb material, where it also shows a decrease in mass density upon crystallization (~ -5%) [9]. The re-crystallization time is very fast (~100 ns) as shown in **Fig. 3(a),** comparable to GST-225 (~50 ns). This is in sharp contrast to GST system where Ge-enriched GST materials always show very slow speed [3]. Time-resolved XRD (**Fig. 4**) shows a single GaSb zincblende structure with slightly different lattice constant when the annealing temperature is lower than 490 °C. This forecasts that this new material would stay in amorphous phase with no mass density change and void formation caused by the phase-transition after the normal back-end of line (BEOL) process. This also helps making the subsequent etching more uniform and less damaging. The new material exhibits very dense and uniform morphology (**Fig. 5**) compared to huge and non-uniform grains typical for GST-225 after BEOL process. Whether the special tetrahedrally bonded zincblende type crystal structure of this new material is responsible for its unusual optical behavior, fast switching speed and excellent thermal stability needs to be confirmed by further studies.

Device and Test Chip Characterization

Our new doped GaSbGe material was evaluated using PCM devices with TiN ring bottom electrode of 20~40 nm diameter [10]. Before device characterizations, the wafer was given a 525 ^{o}C/2 mins RTA process to make sure phase-change material is crystallized due to its high Tx. **Figure 6** shows the TEM images and EDX elemental maps for doped GaSbGe material after high temperature annealing and switching cycling. Although, the Ge/Sb elemental segregations were observed around active region after 1E5 cycling, the overall material compositions are the same and it can survive until 1E9 cycling. (This is consistent with XRD observation (**Fig. 4**) where Ge segregation was detected at 540 ^{o}C.)

One decade programming window is achieved as fast as 80 ns in a 128 Mb PCM chip as shown in the Shmoo plot in **Fig. 7**. **Figure 8** shows the SET and RESET state resistance distributions are well separated for doped GaSbGe PCM cell in the 128 Mb test chip. Both SET and RESET resistance are one order of magnitude lower than GST based materials [5]. Lower resistance is also a good benefit for read speed. However, this new material requires relatively high SET current.

Figure 9 shows that this new material passes the solder bonding reflow test easily. A long 480 ns SET pulse was used to program the cell to get a tight SET distribution for the 128Mb chip before the reflow test. The SET resistance distribution went up only slightly. The RESET resistance distribution went up by more than one order of magnitude, which is similar to high Tx Ge-enriched GST material, compared in **Fig. 9 (c)** [11]. The RESET state drift up in a desirable way was previously explained by structural relaxation (SR) of the non-equilibrium amorphous state where defects annihilation by annealing leads to an increase of the barrier height for Poole-Frenkel hopping and results in resistance drift [11]. It is not surprising that such high Tx material of doped GaSbGe shows similar behavior. Conversely, for poor data retention material, such as GST-225, it already crystallized at as low temperature as to 150 ^{o}C. **Figure 10** shows the SET and RESET state resistance distributions before/after baking at 250 ^{o}C/300 hrs for the 128 Mb test chip; nearly 100% switching yield is achieved. Some cells showed the decrease of RESET resistance due to their crystallization after baking at 270 ^{o}C/7 days (**Fig. 11**). After 300 ^{o}C/1 day baking (**Fig. 12**), the RESET resistance drops to close to SET state indicating full crystallization.

The failure rates of doped GaSbGe in 128 Mb chips after three different baking temperatures are shown in **Fig. 13**. The lifetime in **Fig. 14** was defined at 0.01 % failure rate from three different baking temperatures. From the Arrhenius plot, the activation energy is Ea=3.3 eV. Thus the new material can satisfy 220 ^{o}C, 10 years retention, which is the highest record for PCM. **Figure 15** summarizes the performance of doped GaSbGe compared with GST based materials. Doped GaSbGe exhibits excellent data retention, passes the solder bonding criteria but yet preserves the fast switching speed, thus fulfills all the requirements for PCM.

Conclusion

We have developed a material that can provide fast SET speed (~80 ns); excellent data retention (220 ^{o}C-10 years) and passing solder bonding criteria. The desired properties are due to two factors: (1) high Tx that delays recrystallization until after > 270 ^{o}C/1day of heating, and (2) structure relaxation that decreases Poole-Frenkel hopping thus increases the RESET resistance which widens the memory window instead of narrowing the window. Further studies are still needed to understand its unusual optical contrast and fast speed. Already this unique new material opens up the possibility of PCM serving new markets such as for automotive applications.

References

[1] I. S. Kim, S. L. Cho, D. H. Im, E. H. Cho, D. H. Kim, G. H. Oh, H. Ahn, S. O. Park, S. W. Nam, J. T. Moon and C. H. Chung, Symp. on VLSI Tech. Dig., 203 (2010).

[2] C. F. Chen A. Schrott, M. H. Lee, S. Raoux, Y. H. Shih, M. Breitwisch, F. H. Baumann, E. K. Lai, T. M. Shaw, P. Flaitz, R. Cheek, E. A. Joseph, S. H. Chen, B. Rajendran, H. L. Lung and C. H. Lam, IEEE International Memory Workshop, IMW Tech. Dig. 64 (2009).

[3] P. Zuliani, E. Varesi, E. Palumbo, M. Borghi, I. Tortorelli, D. Erbettam G. D. Libera, N. Pessina, A. Gandolfo, C. Prelini, L. Ravazzi and R. Annunziata, IEEE Trans. Electro. Dev. **60**, 4020 (2013).

[4] G. Navarro, M. Coué, A. Kiouseloglou, P. Noé, F. Fillot, V. Delaye, A. Persico, A. Roule,M. Bernard, C. Sabbione, D. Blachier, V. Sousa, L. Perniola, S. Maitrejean, A. Cabrini, G. Torelli, P. Zuliani, R. Annunziata, E. Palumbo, M. Borghi, G. Reimbold, B. De Salvo, Tech. Dig.- Int. Electron Devices Meet., **21.5** (2013).

[5] H. Y. Cheng, J. Y. Wu, R. Cheek, S. Raoux, M. BrightSky, D. Garbin, S. Kim, T. H. Hsu, Y. Zhu, E. K. Lai, E. Joseph, A. Schrott, S. C. Lai, A. Ray, H. L. Lung and C. Lam, Tech. Dig.- Int. Electron Devices Meet., **31.1** (2012).

[6] Y. Lu, S. Song, Z. Song, and B. Liu, J. Appl. Phys. **109**, 064503 (2011).

[7] H. Y. Cheng, S. Raoux, K. V. Nguyen, R. S. Shenoy, and M. BrightSky, ECS J. Solid State Sci. Technol. **3**, 263 (2014).

[8] S. I. Shah, K. C. Cadien and J. E. Greene, J. Electron. Mater. **11**, 53 (1982).

[9] M. Putero, M.-V. Coulet, T. Ouled-Khachroum, C. Muller, C. Baehtz, and S. Raoux, APL Mater. **1**, 062101 (2013).

[10] H. Y. Cheng, M. BrightSky, S. Raoux, C. F. Chen, P. Y. Du, J. Y. Wu, Y. Y. Lin, T. H. Hsu, Y. Zhu, S. Kim, C. M. Lin, A. Ray, H. L. Lung and C. H. Lam, Tech. Dig.- Int. Electron Devices Meet., **30.6** (2013).

[11] N. Ciocchini, E. Palumbo, M. Borghi, P. Zuliani, R. Annunziata and D. Ielmini, Tech. Dig.- Int. Electron Devices Meet., **22.1** (2013).

[12] H. Y. Cheng, T. H. Hsu, S. Raoux, J.Y. Wu, P. Y. Du, M. BrightSky, Y. Zhu, E. K. Lai, E. Joseph, S. Mittal, R. Cheek, A. Schrott, S. C. Lai, H. L. Lung and C. H. Lam, Tech. Dig.- Int. Electron Devices Meet., **3.4** (2011).

Table I Different phase-change materials comparison. SET speed, data retention and solder boding thermal budget test results are included.

Materials	SET Speed	Retention	Pass Solder bonding Criteria
GST-Ge45%-N4% [4]	800 ns (with R-SET procedure)	210 °C-10 years	V
T-alloy Ge-rich GST [3]	1.5 us	185 °C-10 years	V
N-GexSbyTez [5]	160~240 ns	120 °C-10 years	X
Doped GaSbGe (This work)	80 ns (480 ns for 128 Mb)	220 °C-10 years	V

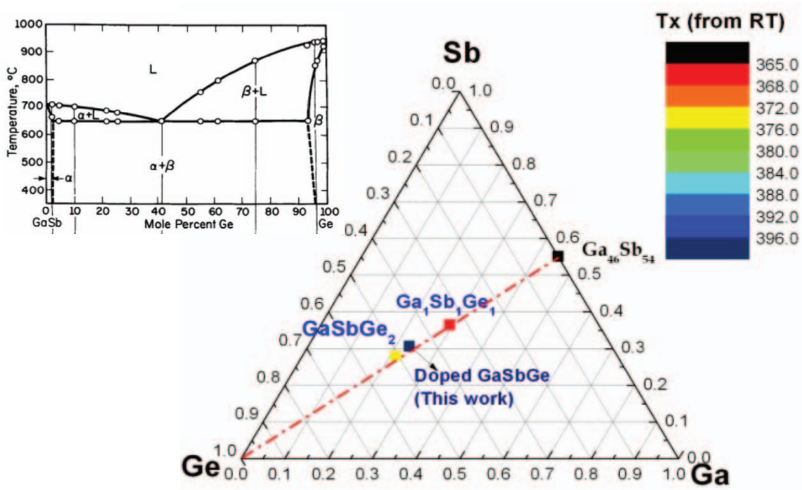


Fig. 1 Crystallization temperature Tx as a function of compositions in the Ga-Sb-Ge ternary phase diagram. Tx is increased by Ge and dopants incorporation along Ge/GaSb tieline. Insert is the GaSb-Ge pseudobinary phase diagram from ref. [8].

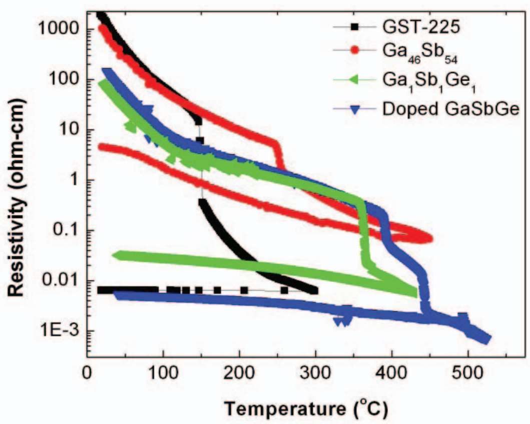


Fig. 2 Resistivity as a function of temperature for GST-225, $Ga_{46}Sb_{54}$, $Ga_1Sb_1Ge_1$ and doped GaSbGe during a heating ramp to 300~525 °C at 0.1 °C/s and subsequent cooling back to room temperature.

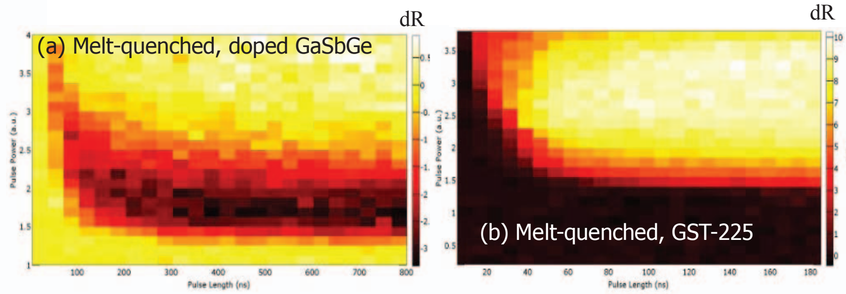


Fig. 3 Relative change in reflectivity in crystallization for (a) Melt-quenched, doped GaSbGe and (b) Melt-quenched, GST-225. Amorphous spots were created by laser pulses 150 ns/7W and 150 ns/5W for doped GaSbGe and GST-225, respectively. Doped GaSbGe material exhibited unusual inverse optical contrast where the crystalline phase has lower reflectance than amorphous phase compared to GST-225. 100 ns re-crystallization time was achieved for doped GaSbGe material, comparable to GST-225.

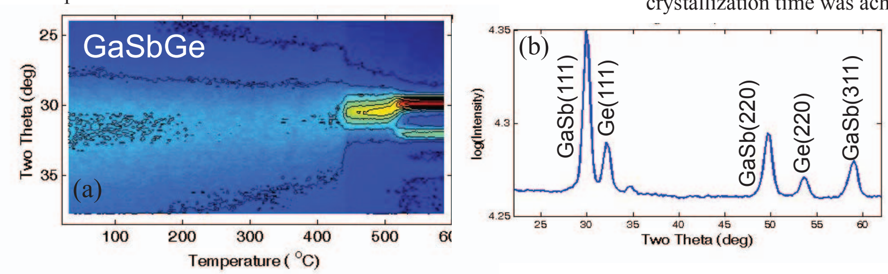


Fig. 4 (a) XRD peak intensity as a function of temperature for GaSbGe during heating at 3 °C/s to 600 °C and (b) x-ray diffraction scans after ramping to 600 °C. A single phase was confirmed after annealing at 490 °C, however, Ge phase-segregation was unfortunately detected after 600 °C annealing.

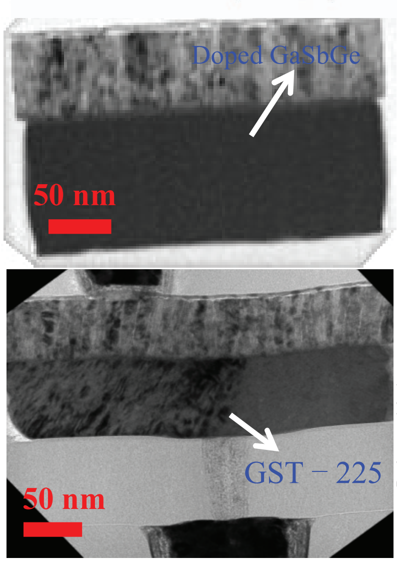
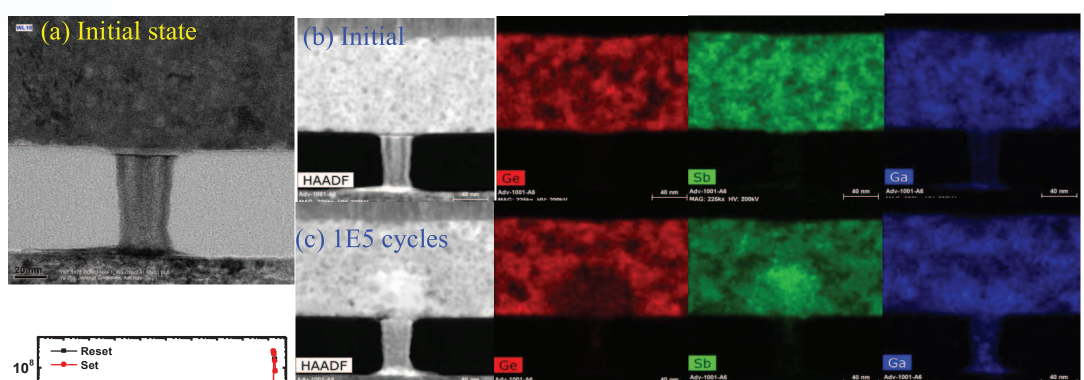
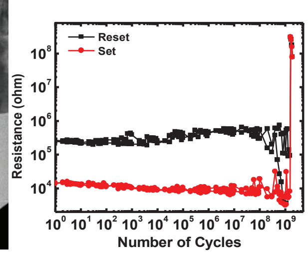


Fig. 5 Cross sectional TEM micrograph of doped GaSbGe and undoped GST PCM cells. After BEOL process, the doped GaSbGe material is still amorphous and dense.





(d) Endurance

Fig. 6 (a) TEM micrograph and (b) HAADF-TEM micrograph and the EDX elemental map of doped GaSbGe material after 525 °C/2 mins RTA. (c) HAADF-TEM micrograph and the EDX elemental map of doped GaSbGe material after 1E5 cycles. Ge and Sb phase segregation were observed around the active region. But, the average compositions are not changed (d) Endurance characteristics for doped GaSbGe. Even though elemental phase-segregations were observed, 1E9 cycling endurance was achieved.

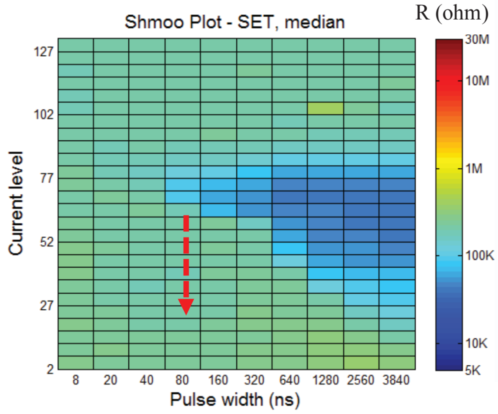


Fig. 7 Shmoo plot for doped GaSbGe PCM cells in a 128 Mb test chip using a ring bottom electrode. 10x resistance ratio can be achieved at 80 ns. Doped GaSbGe with high Tx still can preserve fast speed.

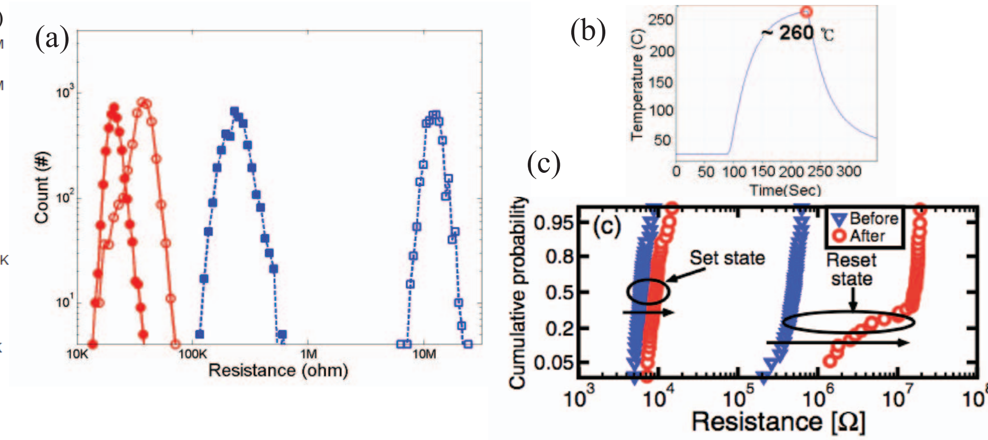


Fig. 9 (a) SET and RESET resistance distributions before and after solder bonding reflow thermal budget. (b) The temperature/time curve for the 260℃ baking that emulates the soldering reflow process. The profile is cross checked by a commercial soldering tool. (c) Cumulative probability of SET/RESET resistance for Ge-enriched GST material before/after solder bonding reflow test from reference [11].

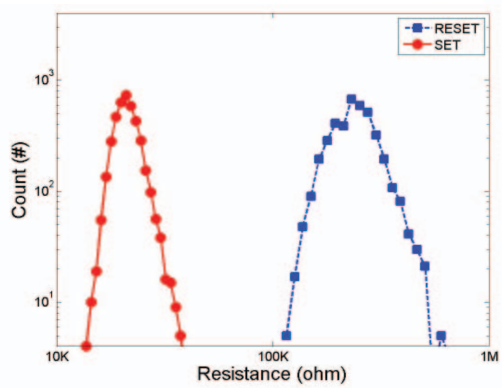


Fig. 8 SET and RESET resistance distributions of doped GaSbGe PCM cells for 4K cells in a 128 Mb test chip. SET and RESET state resistance distributions are well separated and show ~10x operation window.

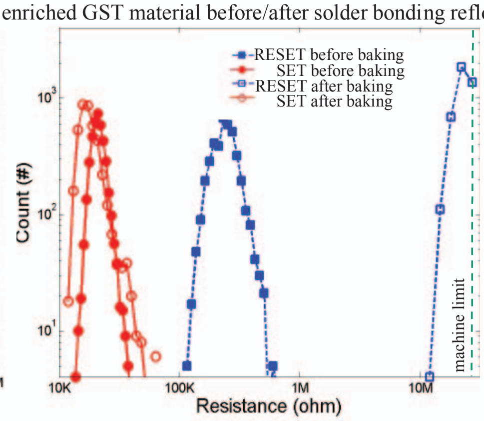


Fig. 10 SET and RESET resistance distributions of doped GaSbGe material for 4K cells in a 128 Mb PCM chip before and after baking at 250 °C for 300 hrs, ~100% yield was demonstrated.

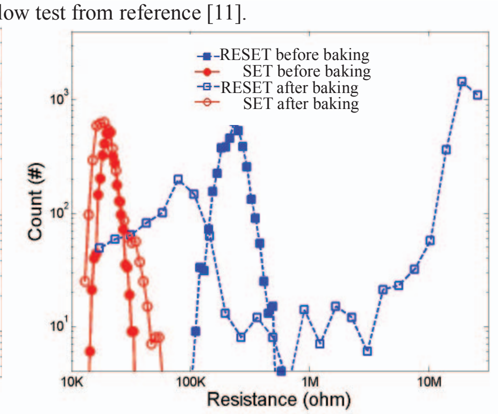


Fig. 11 SET and RESET resistance distributions of doped GaSbGe material of 4K cells in a 128 Mb PCM chip before and after baking at 270 °C for 7 days. RESET resistance decreased seriously. Baking for 1 day, however, results in a RESET distribution similar to that in Fig. 10. Thus this new material does not recrystallize until after > 1 day at 270C.

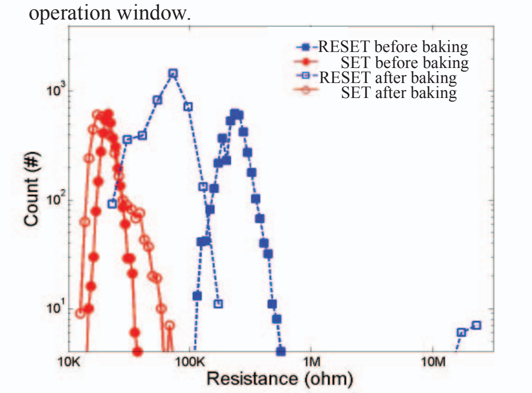


Fig. 12 SET and RESET resistance distributions of the doped GaSbGe material for a 4K cells block in a 128 Mb PCM chip before and after baking at 300 °C for 1 day. RESET resistance decreased to close to SET state.

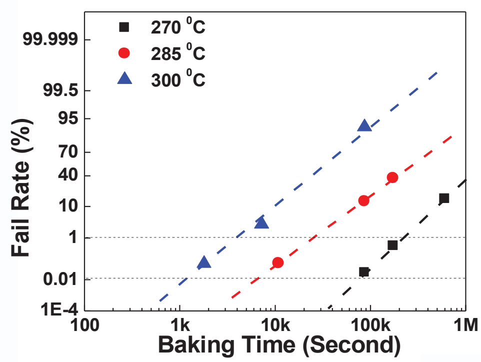


Fig. 13 The failure rate of doped GaSbGe in 128 Mb test chips after baking at 270, 285 and 300 °C temperatures.

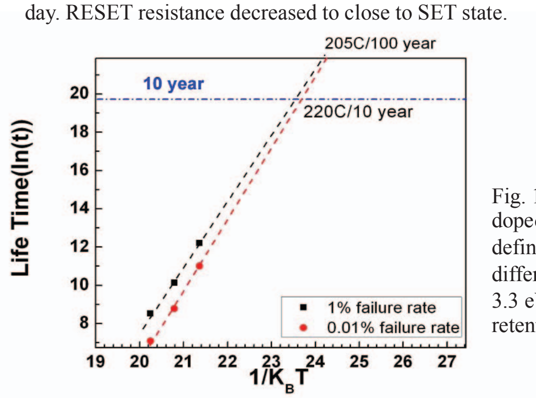


Fig. 14 Data retention characteristics of doped GaSbGe. The liftetime was defined at 0.01 % failure rate from three different baking temperatures. The Ea is 3.3 eV and with projected 10-year retention at 220 °C.

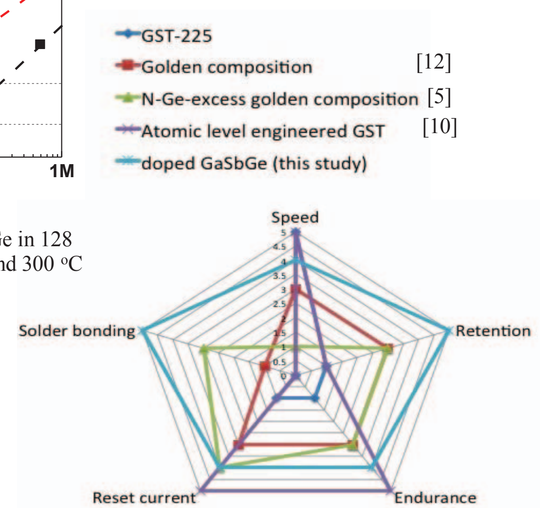


Fig. 15 Summary of performance of doped GaSbGe compared to Ge-Sb-Te based materials. Doped GaSbGe exhibits the desired pentagon shape that fulfills all requirements for PCM