

The Crystallization Behavior of Ge-Sb-Te Materials as a Function of Composition for Phase-Change Memory

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ABSTRACT

The crystallization times, crystallization temperatures and crystallinity of $\text{Ge}_1\text{Sb}_x\text{Te}_1$ and $\text{Ge}_2\text{Sb}_{2+x}\text{Te}_5$ phase-change materials with various Sb concentrations were studied. $\text{Ge}_1\text{Sb}_x\text{Te}_1$ ($x>1$) materials exhibited fast crystallization speed with increasing Sb concentration, however, for $\text{Ge}_1\text{Sb}_x\text{Te}_1$ ($x<1$) slower crystallization speed was observed with increasing Sb concentration. It was found that doping Sb into $\text{Ge}_2\text{Sb}_2\text{Te}_5$ did not improve the crystallization speed. The Ge-Sb-Te phase-change material compositions must be carefully designed to produce the desired speed. $\text{Ge}_1\text{Sb}_6\text{Te}_1$ material is a promising candidate for storage-class memory (SCM) with fast speed.

Key words: Ge-Sb-Te, phase transitions, recrystallization time

1. INTRODUCTION

New memory technologies are drawing a lot of attention of computer manufacturers. Because the traditional hard disks and some new solid-state-drives (SSDs) cannot provide the high input/output (I/O) bandwidth required in advanced systems. New storage-class memory (SCM) is proposed to satisfy the system speed/power requirements [1, 2]. Phase-change memory (PCM) seems to be in the best position to serve as SCM due to its high speed and promising endurance performance.

Phase-change materials are at the core of PCM technology. Crystallization speed is one of the critically important parameters when designing a new phase-change material for PCM because it determines PCM's possible applications. Sb-based materials with a growth-dominated crystallization mechanism generally show high crystallization speed [3, 4]. They exhibit a different crystallization mechanism compared to $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST-225), which is a popular composition along the GeTe-Sb₂Te₃ pseudobinary tie line and the most commonly studied material. The drawback of Sb-based materials is the low thermal stability of the amorphous phase, however. The effects of various dopants in Sb₂Te such as Ga, Ge, In and Ag have been extensively studied [5, 6]. Doping extra Sb into GST-225 has also been proposed to improve the SET speed of GST-225 [3, 4, 7, -8]. However, the quantitative effect of Sb addition to GST-225 on the phase-change switching characteristics still needs to be clarified.

GeTe material also has been considered as an alternative phase-change material and has been demonstrated to be a fast phase-change material for PCM [9, 10]. Elemental Sb shows explosive crystallization and can be stabilized in the amorphous phase at room temperature only for very thin films. It is therefore an interesting dopant if crystallization speed needs to be increased. However, the phase-change characteristics of Sb doping into GeTe phase-change material has not been studied thoroughly yet. Previously, we investigated a special group of Sb-based $\text{Ge}_1\text{Sb}_x\text{Te}_1$ materials along an isoelectronic tie line with equal amounts of Ge and Te and with varying Sb concentration ($x>1$) [11]. These isoelectronic materials exhibit fast crystallization with increasing Sb concentration when $x>1$, but compositions with $x<1$ have not been studied yet.

In the first part of this study, we prepared and systematically evaluated $\text{Ge}_1\text{Sb}_x\text{Te}_1$ materials with equal amounts of Ge and Te but with varying Sb, especially for the compositions with $x < 1$. The quantitative effects of Sb addition to GeTe along the $\text{Ge}_1\text{Sb}_x\text{Te}_1$ tie line was carefully evaluated. In the second part of this study, Sb-rich GST-225 materials ($\text{Ge}_2\text{Sb}_{2+x}\text{Te}_5$, $x=0, 1, 2, 5$) were also systematically explored. The phase-change properties in terms of usefulness for PCM applications, including crystallization times (τ_x), crystallization temperatures (T_x), crystallinity

and resistivity (ρ) as functions of temperature (T) were evaluated for blanket thin films and also demonstrated in PCM devices.

2. EXPERIMENTS

The $\text{Ge}_1\text{Sb}_x\text{Te}_1$ films were prepared by co-sputtering from compound $\text{Ge}_{50}\text{Te}_{50}$ and elemental Sb targets and the film composition was varied by controlling the relative power for these two sputtering sources. The film compositions were determined by Rutherford Backscattering Spectrometry (RBS) and Particle-induced X-ray Emission (PIXE) with an error of ± 0.5 at. % for Ge and ± 5.0 at. % for Sb and Te. The substrates were Si wafers covered with a 30 nm SiO_2 thermal barrier layer for crystallization time measurements and a $1\mu\text{m}$ thick SiO_2 films for ρ vs. T measurements. Deposition was performed at room temperature and films were amorphous as deposited. Crystallization times were measured using a custom-made static laser tester. ρ vs. T was measured using a custom-made setup in van der Pauw geometry in nitrogen at a heating rate of $5^\circ\text{C}/\text{min}$ and during subsequent cool down.

The laser tester uses a 160mW diode laser with a peak wavelength of 658 nm. It provides pulses with varying amplitude and duration to affect heating of the phase-change sample. A separate highly attenuated HeNe continuous wave laser at a wavelength of 633 nm is used to monitor the sample's optical reflectance. Crystallization was indicated by a sudden increase in reflectivity that persisted after the end of the high power laser pulse. The phase transformation behavior can be deduced by plotting the change in reflectivity r (defined as $\Delta r/r = (r_{\text{after}} - r_{\text{before}})/r_{\text{before}}$ where r_{before} and r_{after} are the reflectivity before and after the single laser pulse, respectively) as a function of laser power and duration. To measure the re-crystallization times of melt-quenched, amorphous samples first the pulsed laser was rastered over the sample at suitable power in such a way that the overlapping heating pulses produced overlapping crystalline spots on the sample creating a square fully crystalline area. Second, a laser pulse with fixed duration and power was applied to produce melt-quenched spots in this crystalline area. Third, a second pulse with variable power and duration at the same location was used to induce re-crystallization of the melt-quenched spots.

Time-resolved x-ray diffraction (XRD) was used to study the crystallization behavior of these materials. Beam line X20C at the National Synchrotron Light Source has a sample chamber which contains a boron nitride heater to anneal samples in a purified helium atmosphere. The beam line is equipped with a high-throughput synthetic multilayer monochromator delivering a photon flux of about 10^{13} photons/s, and the X-ray wavelength was 1.797 \AA .

3. RESULTS & DISCUSSION

Figure 1 shows ρ vs. T as a function of composition for $\text{Ge}_1\text{Sb}_x\text{Te}_1$ for $x < 1$ and $x > 1$, respectively. T_x is indicated by the first sudden drop in ρ . For the $\text{Ge}_1\text{Sb}_x\text{Te}_1$ compositions with $x < 1$, both T_x and ρ in the crystalline state increase with Sb incorporation that allow lower RESET current and better thermal stability. However, for $\text{Ge}_1\text{Sb}_x\text{Te}_1$ films with $x > 1$, both T_x and ρ in the crystalline state decrease with increasing Sb concentration. Figure 2 shows the recrystallization times of various $\text{Ge}_1\text{Sb}_x\text{Te}_1$ phase-change materials measured using the custom-made static laser tester. It was found that the recrystallization time of $\text{Ge}_1\text{Sb}_x\text{Te}_1$ ($x < 1$) in Fig. 2(a) monotonously increased with increasing x .

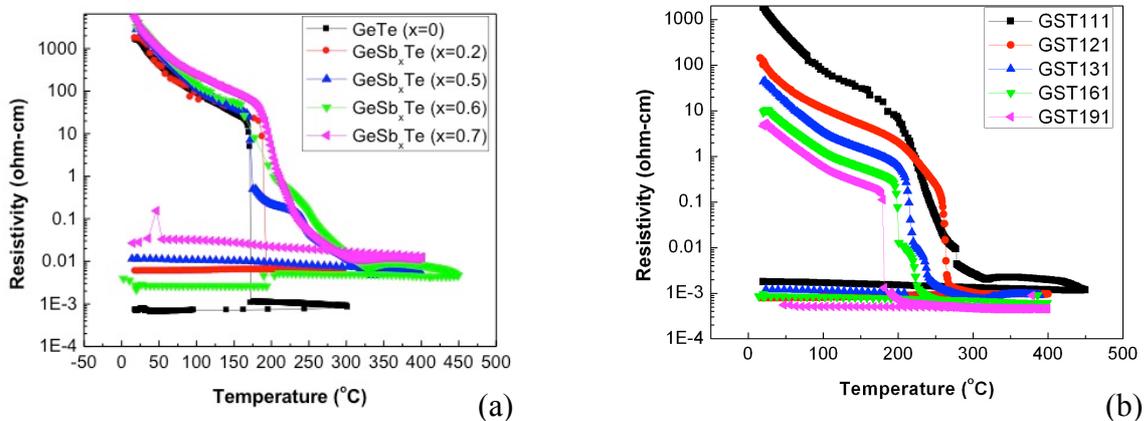


Fig. 1 Resistivity as a function of temperature for $\text{Ge}_1\text{Sb}_x\text{Te}_1$ films for (a) $x < 1$ and (b) $x > 1$, respectively, during a heating ramp to $300 \sim 450^\circ\text{C}$ at $5^\circ\text{C}/\text{min}$ and subsequent cooling back to room temperature.

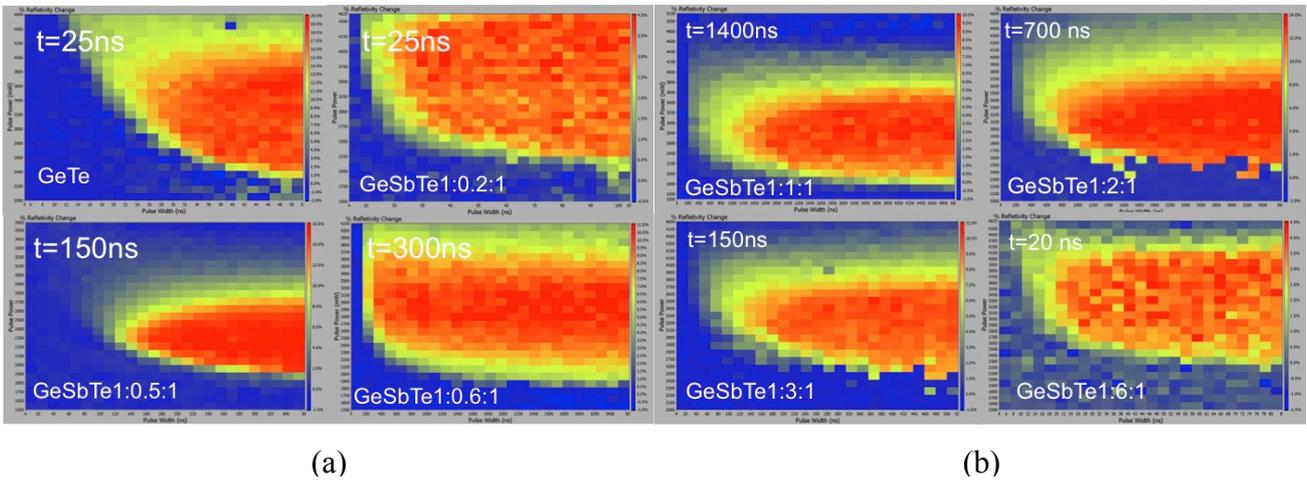


Fig. 2 Relative change in reflectivity as a function of pulse power and pulse duration for melt-quenched, amorphous $\text{Ge}_1\text{Sb}_x\text{Te}_1$ films with (a) $x < 1$ and (b) $x > 1$, respectively.

The results differ from literature where it is generally reported that doping Sb into Ge-Sb-Te phase-change materials increases the crystallization speed. $\text{Ge}_1\text{Sb}_x\text{Te}_1$ ($x > 1$) materials exhibited a different crystallization behavior with increased Sb content as shown in Fig. 2(b). $\text{Ge}_1\text{Sb}_1\text{Te}_1$ had the longest recrystallization time and the recrystallization time was monotonously reduced with increasing Sb content when $x > 1$. Figure 3 summarizes the recrystallization time of $\text{Ge}_1\text{Sb}_x\text{Te}_1$ materials along the isoelectronic tie line. Crystallization times were reduced in both directions from $\text{Ge}_1\text{Sb}_1\text{Te}_1$; either highly Sb doped alloys such as $\text{Ge}_1\text{Sb}_6\text{Te}_1$ or alloys with very little or no Sb doping, such as pure GeTe or $\text{Ge}_1\text{Sb}_{0.2}\text{Te}_1$, exhibited the fastest speed. The isoelectronic materials exhibit fast crystallization with very high or very low Sb doping but also suffer from conflicting requirements between speed and thermal stability of the amorphous phase. The trade-off needs to be made when choosing optimal x value for a specific memory application. In addition, fast crystallizing materials on the $\text{Ge}_1\text{Sb}_x\text{Te}_1$ tie line have lower resistivity in the crystalline state which is correlated to undesirable higher RESET currents.

Time-resolved XRD revealed the crystallization behavior of these films as a function of x in $\text{Ge}_1\text{Sb}_x\text{Te}_1$ as shown in Fig. 4. It confirmed that all as deposited films were amorphous. The intensity of diffracted X-rays was recorded over a 2θ range of 15° using the diode-array detector centered at 31° during a heating ramp at 1°C/s to $450^\circ\text{C} \sim 550^\circ\text{C}$. XRD peaks indicative of crystallization appeared around $T_x = 278^\circ\text{C}$ for $\text{Ge}_1\text{Sb}_1\text{Te}_1$ and at lower T_x with increasing Sb content with the lowest $T_x = 198^\circ\text{C}$ for $\text{Ge}_1\text{Sb}_9\text{Te}_1$ films on $\text{Ge}_1\text{Sb}_x\text{Te}_1$ ($x > 1$) tie line. Due to the similar peak positions of GST-225 and GeTe and the low energy resolution of beam line X20C it is difficult to determine whether the $\text{Ge}_1\text{Sb}_1\text{Te}_1$ material crystallized in a combination of Sb and GeTe crystal phases or in a combination of Sb and cubic GST-225 crystal phases. θ - 2θ scans acquired at room temperature after the ramps showed superposition of either rocksalt-like GST-225 plus rhombohedral Sb or a superposition of rhombohedral GeTe with rhombohedral Sb in Fig. 4(b). In addition, the crystalline structure of Ge-Sb-Te materials around $\text{Ge}_1\text{Sb}_1\text{Te}_1$ is very sensitivity to the compositions. Just 5 at. % difference in compositions resulted in a different crystalline structure where it crystallized in a pure Sb crystallized structure [11]. For the Sb-rich $\text{Ge}_1\text{Sb}_x\text{Te}_1$ ($x > 1$) films, only strong (003) and (006) peaks were exhibited indicating the formation of the rhombohedral Sb crystal structure with high texture as shown in Fig. 4(c).

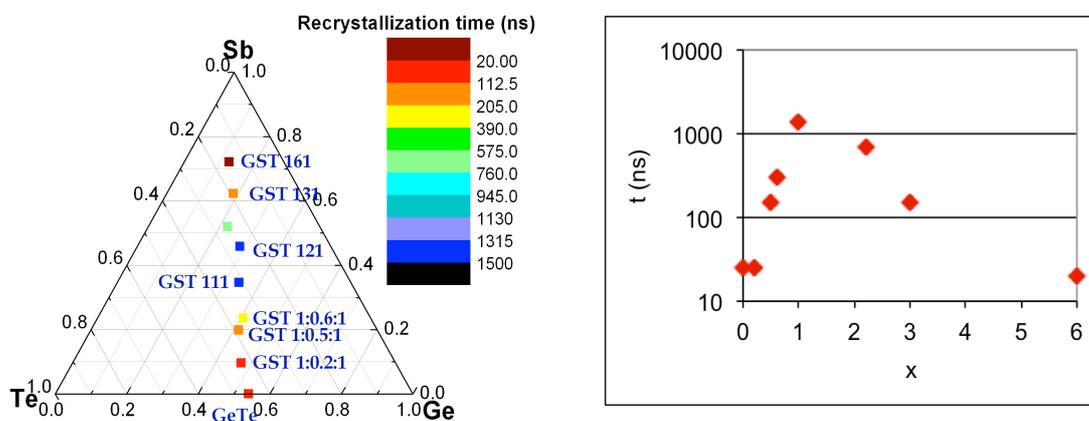


Fig. 3 Re-crystallization times of $\text{Ge}_1\text{Sb}_x\text{Te}_1$ materials along isoelectronic tie line in the Ge-Sb-Te ternary diagram. Plotted is the re-crystallization time of melt-quenched-amorphous samples needed to complete 90 % of the phase transformation (90 % reflectivity change) as a function of x .

For the $\text{Ge}_1\text{Sb}_x\text{Te}_1$ ($x < 1$) materials, pure GeTe crystallized in a rhombohedral structure. Slightly Sb doped GeTe, such as composition of $\text{Ge}_1\text{Sb}_x\text{Te}_1$ with $x=0.2\sim 0.5$, still crystallized in a rhombohedral structure, similar to pure GeTe. However, with more Sb doping the crystal structure becomes more complex. For $\text{Ge}_1\text{Sb}_x\text{Te}_1$ ($x=0.6$) material, we cannot distinguish whether it crystallizes in a rocksalt-like GST-225 or GeTe rhombohedral structures. The T_x of $\text{Ge}_1\text{Sb}_x\text{Te}_1$ determined by XRD is very consistent with that from ρ vs. T measurements. It was found that doping Sb into GeSbTe does not guarantee fast speed. The crystalline structures of phase-change materials have to be considered as well. Highly Sb doped $\text{Ge}_1\text{Sb}_x\text{Te}_1$ materials ($\text{Ge}_1\text{Sb}_6\text{Te}_1$) form the Sb rhombohedral structure and pure or very slightly Sb doped GeTe crystallizes in a rhombohedral structure as well. Rhombohedral structures often allow fast crystallization.

Figure 5 shows the relative change in reflectivity as a function of pulse power and pulse duration of melt-quenched, amorphous Sb-rich $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films and the summarized recrystallization times (with 90% recrystallization fraction) as a function of compositions in the Ge-Sb-Te ternary diagram. We find that Sb doping into GST-225 degrades crystallization speed performance instead of improving it which is contradictory to some of the literature [3, 8]. However, based on Yoon's data [7], the SET time of PCM memory devices increased when the Sb composition increased from 22 to 39 at. %, and inversely decreased when the Sb composition approached 47 at. % along $\text{Ge}_2\text{Sb}_2\text{Te}_5$ -Sb tie line, which means GST-225 is still the fastest material along this tie line. This is consistent with our results where Sb doping into GST-225 does not improve the speed, but it differs with results reported in [3] and [8]. In addition, we also have confirmed our blanket film results using similar alloys in PCM devices with a thermally confined bottom electrode [13]. We found that Sb-rich GST-225 materials such as GST-235 and GST-245 have slower SET speed than GST-225 as shown in Fig. 6, consistent with the laser tester results. GST-235 and GST-245 materials crystallized in a rocksalt-like structure and then formed a hexagonal structure at higher temperature, similar to GST-225. However, highly Sb-rich GST-275 material crystallized in a rhombohedral structure, similar to Sb_2Te_3 . Although GST characteristics often strongly depend on detailed processing conditions and are not simple functions of composition, the Sb-rich GST materials in our experiment exhibit slower speed with increasing Sb content both in the thin films and device performances.

4. CONCLUSIONS

This study carefully explores the $\text{Ge}_1\text{Sb}_x\text{Te}_1$ phase-change materials along the isoelectronic tie line in terms of usefulness for PCM applications. It is found that doping Sb into GeSbTe phase-change materials does not guarantee fast speed.

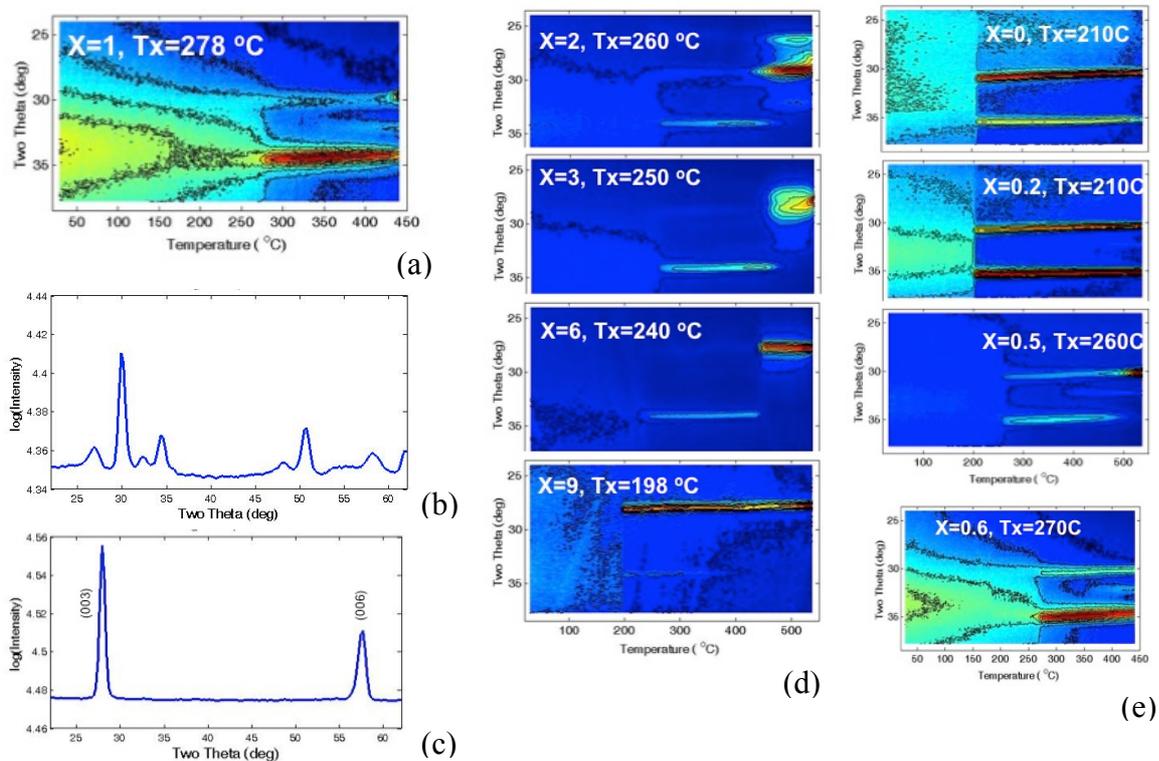


Fig. 4 (a) XRD peak intensity as a function of temperature T during heating at 1 °C/s to 450 °C of a $\text{Ge}_1\text{Sb}_1\text{Te}_1$ film. (b) θ - 2θ scan acquired at room temperature after the ramp for $\text{Ge}_1\text{Sb}_1\text{Te}_1$. (c) θ - 2θ scan acquired at room temperature after the ramp for $\text{Ge}_1\text{Sb}_3\text{Te}_1$. (d) and (e) XRD peaks intensity during heating at 1 °C/s to 450 °C of $\text{Ge}_1\text{Sb}_x\text{Te}_1$ films with ($x > 1$) and ($x < 1$), respectively.

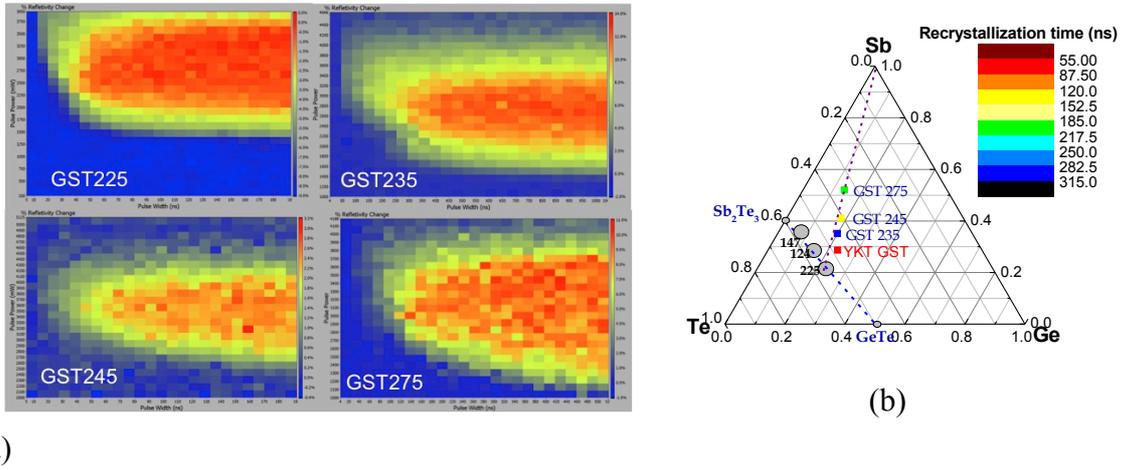


Fig. 5 (a) Relative change in reflectivity as a function of pulse power and pulse duration of melt-quenched, amorphous $\text{Ge}_2\text{Sb}_{2+x}\text{Te}_5$ films with $x=1\sim 5$. (b) Recrystallization time as a function of Sb concentration along the Sb-GST-225 tie line in the Ge-Sb-Te ternary diagram.

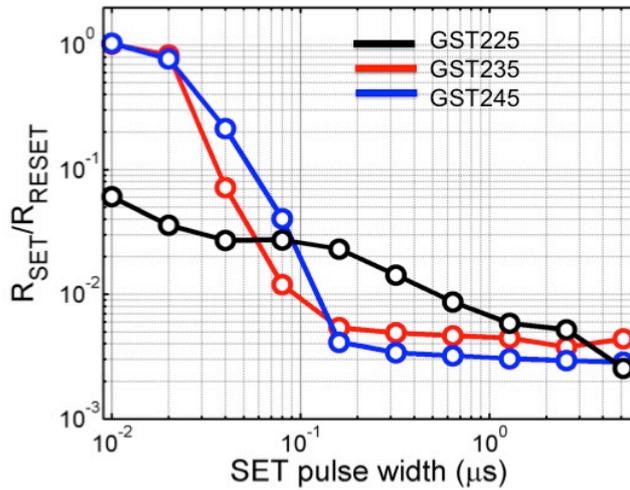


Fig. 6 (a) $R_{\text{SET}}/R_{\text{RESET}}$ ratio as a function of SET pulse width for GST-225, GST-235 and GST-245 phase-change materials.

Either highly doping Sb into GeTe, such as $\text{Ge}_1\text{Sb}_6\text{Te}_1$ or pure GeTe without Sb doping showed the fastest crystallization speed among the films we studied in this isoelectronic tie line. The complicated crystalline structure for the compositions close to $\text{Ge}_1\text{Sb}_1\text{Te}_1$ implies a possible reason for slower speed. Unfortunately, $\text{Ge}_1\text{Sb}_x\text{Te}_1$ materials still suffer from conflicting requirements between speed, thermal stability of the amorphous phase, and lower RESET current. The trade-off needs to be made when choosing the optimum composition for a given application. The very fast crystallization speed of $\text{Ge}_1\text{Sb}_6\text{Te}_1$ is encouraging and suggests this material for SCM application. In addition, it is also shown that doping Sb into GST-225 does not necessarily improves speed, either. The results are confirmed both by laser testing and electrical testing in PCM devices.

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REFERENCES

1. R. F. Freitas et al., IBM J. Res. & DEV., 52, 439 (2008).
2. A. Bivens et al., IMW Tech. Dig. (2010).
3. M. Boniardi, D. Ielmini, I. Tortorelli, A. Redaelli, A. Pirovano, M. Allegra, M. Magistretti, C. Bresolin, D. Erbetta, A. Modelli, E. Varesi, F. Pellizzer, A. L. Lacita and R. Bez, Solid-State Electron., 58, 11 (2011).
4. I. S. Kim, S. L. Cho, D. H. Im, E. H. Cho, D. H. Kim, G. H. Oh, D. H. Ahn, S. O. Park, S. W. Nam, J. T. Moon and C. H. Chung, VLSI Tech. Dig., 203 (2010).
5. H. Y. Cheng, S. Raoux and J. L. Jordan-Sweet, Appl. Phys. Lett. 98, 121911 (2011).
6. H. Y. Cheng, K. F. Kao, C. M. Lee, and T. S. Chin, IEEE Trans. Magn. 43, 927 (2007).
7. S. M. Yoon, K. J. Choi, N. Y. Lee, S. Y. Lee, Y. S. Park and B. G. Yu, Jpn. J. Appl. Phys., 46, 7225 (2007).
8. S. O. Ryu, J. Electron. Mater., 37, 535 (2008).
9. S. Raoux, H.-Y. Cheng, M. A. Caldwell, and H.-S. P. Wong, Appl. Phys. Lett., 95, 071910 (2009).
10. G. Bruns, P. Merkelbach, C. Schlockermann, M. Salinga, M. Wuttig, T. D. Happ, J. B. Philipp and M. Kund, Appl. Phys. Lett., 95, 043108 (2009).
11. H. Y. Cheng, S. Raoux, M. Wuttig, B. Munoz, and J. L. Jordan-Sweet, "The Crystallization Behavior of $\text{Ge}_1\text{Sb}_x\text{Te}_1$ Phase-Change Materials", Mater. Res. Soc. Spring Meet., San Francisco, April, H 6.5 (2010).
12. H. Y. Cheng, S. Raoux and Y.-C. Chen, J. Appl. Phys., 107, 074308 (2010).
13. J. Y. Wu, M. BrightSky, S. Kim, T. H. Hsu, R. Cheek, P. Y. Du, J. Li, E. K. Lai, Y. Zhu, T. Y. Wang, H. Y. Cheng, A. Schrott, E. A. Joseph, R. Dasaka, S. Raoux, M. H. Lee, H. L. Lung, and C. Lam, IEDM Tech. Dig. 32.1. (2011).

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