Characteristics of Phase Change Memory Devices based on Ge-doped SbTe and its derivative

Byung-ki Cheong*, Jeung-hyun Jeong, Suyoun Lee, In Ho Kim, Wu Zhe, Hyung Woo Ahn,
Seul Cham Kim, Hyun Seok Lee and Young Wook Park

Thin Film Materials Research Center, Korea Institute of Science and Technology,
39-1 Hawolgok-dong, Sungbuk-ku, Seoul 136-791, Korea
*e-mail: bkcheong@kist.re.kr

ABSTRACT

As a promising candidate for a phase change material of a highly fast and scalable non-volatile memory, Ge-doped SbTe with a certain range of Sb and Te content has interesting material properties such as a low melting temperature, fast crystallization with a high crystallization temperature, and a low electrical resistivity. Using test vehicles based on a cell structure with a contact pore of 100 to 200nm in size, Ge-doped SbTe of two different compositions (Sb/Te atomic ratio of 4.53 and 2.08) were examined and compared with $Ge_2Sb_2Te_5$ in term of important device characteristics such as SET speed, SET resistance as well as RESET current. Between the two compositions, Ge-doped SbTe of the higher Sb content was found superior by far in SET speed, which is considered to arise from fast growth-dominated crystallization characteristics of the material combined with the nature of a SET process within the device that does not necessarily require nucleation of crystallites in the presence of movable inter-phase boundaries. Ge-doped SbTe of the higher Sb content was also shown to provide a higher SET speed by more than two orders of magnitude and a lower SET resistance by about one tenth than $Ge_2Sb_2Te_5$. As for RESET current, the material was observed to require a higher current than $Ge_2Sb_2Te_5$ for a stable operation but there appears much room for improvement with a proper understanding of the apparently incomplete RESET at a much lower current level than the one for a stable RESET. Lastly, a derivative of Ge-doped SbTe of the higher Sb/Te content was formed by addition of nitrogen, which turned out to provide an effective means to reduction in RESET current without significantly decreasing SET speed.

Key words: Non-volatile memory, phase change memory material, Ge-doped SbTe, nitrogen

1. INTRODUCTION

Nonvolatile memory (NVM) devices using phase change materials (called PCRAM) are receiving the greatest attention among various NVM candidates [1-3]while the first commercial products are expected to be released this year. Presently, the PCRAM devices are using $Ge_2Sb_2Te_5$(GST)-based materials but it is uncertain whether the same materials may be appropriate for higher performance devices. For a high performance PCRAM, a high-speed SET to a low-resistance state is indispensable as well as a low RESET current, above all. However, the former device characteristics have been shown hard to obtain from the material properties tailored to satisfy the latter in the case of GST-based materials[4].

Ge-doped SbTe (Ge-ST) appears attractive in this regard. The material is known to crystallize at a higher temperature, yet increasingly fast with decreasing the size of a programmable volume and to have a significantly lower electrical resistivity than GST. It also has a melting temperature lower than GST by about a hundred degree. Despite its famous use in Blu-ray optical recording [5,6], there is found no report on the PCRAM using a Ge-ST except for a recent study on a memory device called phase change line memory[7] and the device characteristics are mostly unknown. Herein, a report is presented of our recent investigation on Ge-ST based materials with respect to important device characteristics such as SET speed, SET resistance and RESET current for potential use in a high performance phase change memory.

2. EXPERIMENTS

Shown in Fig. 1(a) is an optical plane view image as well as an SEM cross-section image of the memory cell device utilized in the present study. The device was made to have a conventional structure with a contact pore ranging from 100 to 200 nm by way of e-beam lithography. As memory materials, Ge-ST's of two different compositions were chosen to have Sb and Te contents belonging to the single δ phase field of Sb-Te binary phase diagram [8] as well as GST for comparison. Targets of these materials were sputtered respectively to produce the film compositions (in at.%) of $Ge_{5.5}Sb_{77.4}Te_{17.1}$ (Sb/Te atomic ratio 4.53; Ge-ST_h), $Ge_{5.3}Sb_{64.0}Te_{30.7}$ (Sb/Te atomic ratio 2.08), and $Ge_{23.2}Sb_{24.1}Te_{52.7}$ as measured by x-ray fluorescence analysis. Electrical characterization of the fabricated devices was conducted using the set-up shown in Fig. 1(b). RESET/SET programming pulses were applied to the cell device with a pulse generator (HP81110A) and the resulting pulse waveforms across the internal resistance (set to 50 Ω) of an oscilloscope (Tektronix TDS5104) were used to estimate the programming currents. A load resistor of 500 Ω was added in series with the cell device to suppress an excessive current flow in the circuit from threshold switching and the device resistance was measured by a source measure unit (Keithley SMU236) at 0.1V.

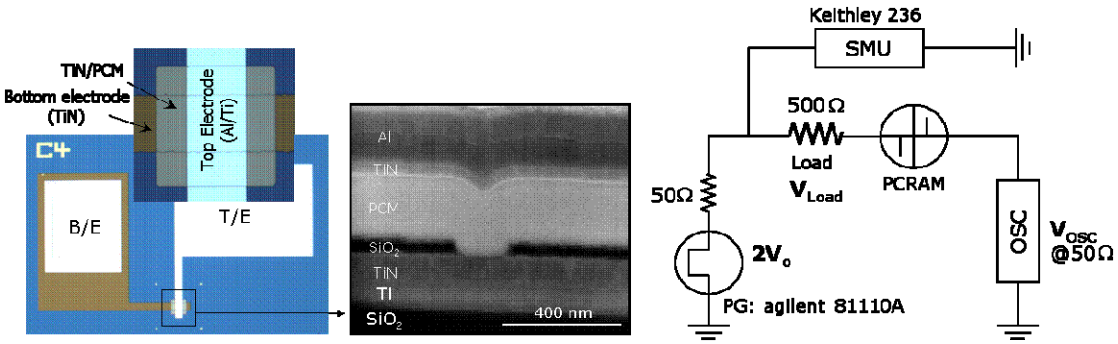

Figure 1. (a) Optical plane view image and an SEM cross section image of the memory cell device utilized to test the phase change materials (PCM) and (b) layout of an electrical measurement setup.

3. RESULTS & DISCUSSION

Effect of Sb/Te ratio on the SET characteristics of Ge-ST [9]

For Ge-ST's of the two different compositions as specified above, cell programming characteristics were examined with the device having a contact area of 200 x 200 (nm^2) and the results are shown in Fig. 2. From resistance(R)-current(I) curves of Fig. 2(a), it is found that Ge-ST_h requires less RESET and SET currents and is more favorable in respect of low power operation. There appears little difference in resistance ratio and SET resistance (R_{SET}) between the two, however. The two Ge-ST's bear the most striking differences in SET characteristics as illustrated in Fig. 2(b) and 2(c). To obtain the data, alternating RESET and SET operations were repeated using a RESET pulse of a fixed height (3V) and width (50ns) and SET pulses of a fixed height (0.9V) but of gradually increasing width from 50 ns to 1μs while low-field resistance was measured at the end of each operation. In each figure, a SET voltage waveform for the longest pulse (1μs) is superimposed as a fiducial aid to mark three different characteristic times in the manner of our previous work [10]; time to threshold switching (t_{th}), time to incubation (t_{inc}) and time to complete SET requiring crystal growth to percolation (t_{SET}). Notice that each of these characteristic times is much shorter in the case of Ge-ST_h hence much faster SET operation. Notice also that the shorter t_{SET} is mostly due to a great decrease in the duration of stage II and stage III, representing nucleation and growth stage of crystallization during a SET process. The observed trend did not vary with SET voltage.

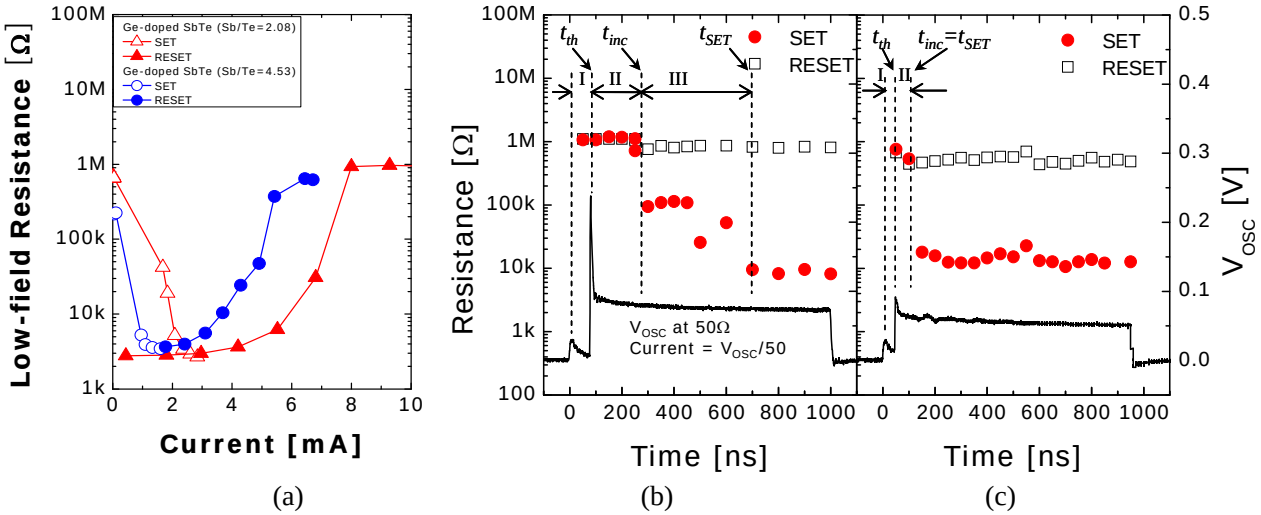

Figure 2. Comparison between Ge-doped SbTe of two different compositions (Sb/Te ratio; 2.08 and 4.53); (a) Resistance(R)-Current(I) curves, (b) SET characteristics (Sb/Te ratio; 2.08) and (c) SET characteristics (Sb/Te ratio; 4.53).

In order to find out the correlation of these findings with material characteristics, TEM microstructures were observed using the films sandwiched with thin protective layers of $ZnS.SiO_2$ on Cu grid, annealed at 300 ^oC for 5 min in a rapid thermal anneal (RTA) furnace; besides the preceding two compositions, films of a third composition (Sb/Te atomic ratio =3.06) and GST were also observed for comparison. It is apparent from Fig. 3 that crystalline grain size becomes dramatically reduced with decreasing Sb/Te ratio, and microstructures resemble closely those of GST in the case of Sb/Te ratio of 2.08. From these, it follows that nucleation becomes more difficult but growth becomes faster with increasing Sb/Te ratio. Indeed, our measurement of incubation time for nucleation and growth speed by way of laser-induced crystallization experiments [11,12] revealed longer incubation time as well as higher growth speed for Ge-ST_h. It is emphasized that these results are in no disagreement with those of the aforementioned device tests. Inside a memory cell, a RESET-programmed amorphous region is always surrounded by the crystalline background and therefore crystallization tends to be initiated by the motion of the interface boundary with no need of nucleation, especially in the case of a prominently growth-dominant material such as Ge-ST_h. This explains why stage II almost vanishes despite difficulty in nucleation, and t_{SET} is much shorter for Ge-ST_h in Fig. 2. Writing characteristics of a memory cell with Ge-ST_h is shown in Fig. 4. The SET operation can be completed within 20 ns including a leading edge (LE) and a trailing edge (TE) of 2 ns each and alternating RESET/SET operations using 20 ns pulses were able to be maintained stably at least up to 10^4 programming cycles. The speed of writing operation is indeed very impressive, especially considering that GST material turned out to have a SET time of the order of μs using the same test vehicle as discussed below.

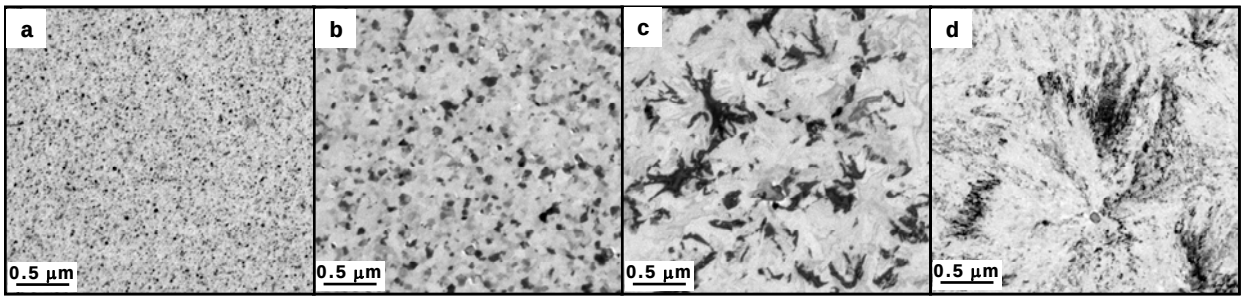

Figure 3. TEM bright field images of the annealed (at 300 ^oC for 5 min) films of; (a) $Ge_2Sb_2Te_5$, (b), (c) and (d) Ge-doped SbTe with the respective Sb/Te ratio of 2.08, 3.06, and 4.53.

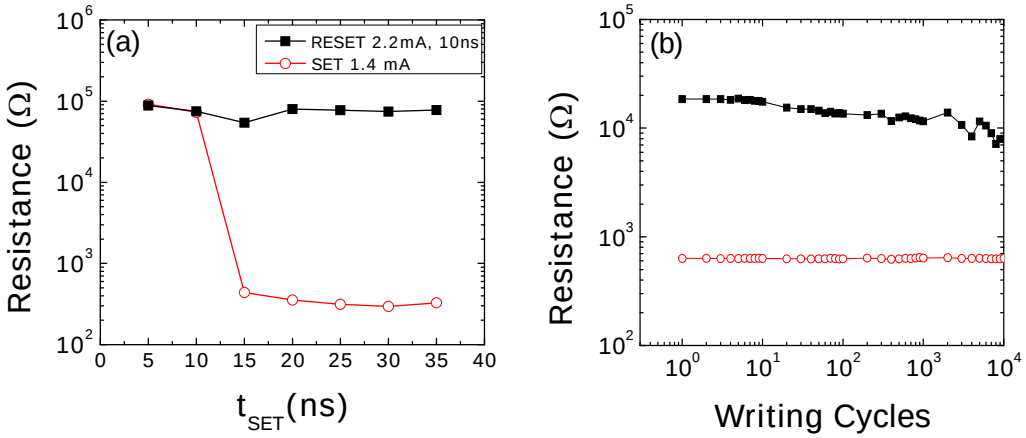

Figure 4. Writing characteristics of a device having Ge-doped SbTe with the Sb/Te ratio of 4.53 to show (a) very fast SET speed and (b) stable cyclic operation.

Comparison of the device characteristics between Ge-ST$_h$ and GST

Between Ge-ST$_h$ and GST, important device characteristics such as R_{SET}, t_{SET} and I_{RESET} were compared. Shown in Fig. 5(a) are a pair of R-I curves, obtained from the respective sequence of RESET and SET programming operations using a memory cell with Ge-ST$_h$ and a contact area of 100x100 (nm^2). Similar curves are also shown for GST in Fig. 5(b). In each figure, RESET/SET pulse patterns were somewhat optimized so as to form the programmed states of a reasonable resistance ratio with a low R_{SET} for most of the tested cells; RESET/SET pulses for Ge-ST$_h$ were made to have the pulse width (PW) of 30ns/60 ns with LE and TE of 2 ns/5 ns for each whereas the ones for GST were made to consist of 2(LE)+50(PW)+2(TE) (ns) for RESET programming and 1(LE)+2(PW)+2(TE) (μs) for SET programming. It should be emphasized that the SET pulse pattern for the GST case was designed to produce melting followed by slow cooling[13], thereby to yield R_{SET} as small as possible. This is because a PW as long as 20 μs was required for the SET operation with a conventional SET pulse pattern having a short trailing edge.

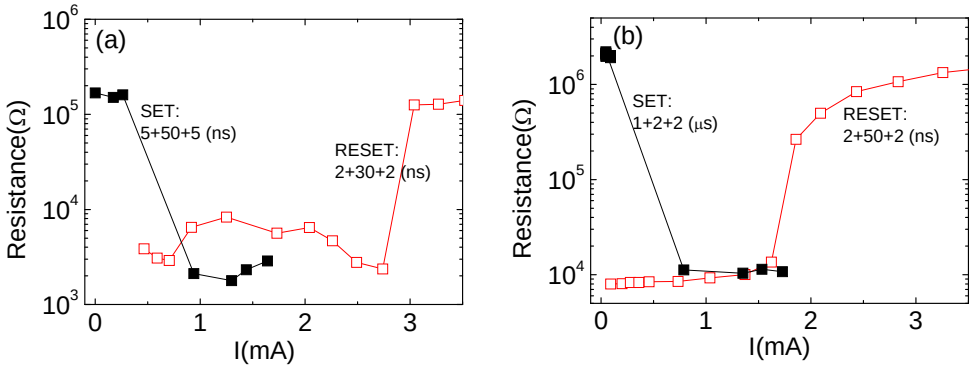

Figure 5. Resistance(R)-Current(I) curves of a memory cell having; (a) Ge-doped SbTe with the Sb/Te ratio of 4.53 and (b) $Ge_2Sb_2Te_5$.

From comparison between the two materials, R_{SET} and t_{SET} values are clearly much smaller for Ge-ST$_h$; R_{SET} is smaller by nearly an order of magnitude despite use of a slow quenching method for GST and t_{SET} is shorter by about two orders of magnitude. As for I_{RESET} for stable RESET operation, it is about 50% higher in the case of Ge-ST$_h$, however. One may be tempted to conclude that this result might be due to lower electrical and thermal resistivity of Ge-ST$_h$ than GST, whereby a greater loss in I_{RESET} from reduced Joule heating as well as enhanced heat dissipation is made to overrule a gain from lower melting temperature. A completely different view in favor of Ge-ST$_h$ may be

advanced, however, when certain features of Fig 5(a), namely, a take-off of resistance in the SET curve at a current above ~1.2 mA as well as the presence of a resistance bump in the RESET curve below I_{RESET} are construed as related possibly to melting and subsequent formation of an amorphous region within the pore. These features are considered as signatures of what may be called the first (incomplete) RESET in contrast with the second RESET for stable operation. In fact, we were able to observe the first and the second RESET from R-I curves of almost all of the tested cells with Ge-ST_h and their origins are under careful investigation presently. We tend to believe that the appearance of dual RESETs has a root in the pore-type structure of the tested cells and the onset current, for instance, for the first RESET may be used as a more proper index to evaluate the Ge-ST_h's inherent capability of I_{RESET} reduction when compared with that of GST.

A closer examination of the SET characteristics was made between Ge-ST_h and GST. As stated above, it is hard to SET the device with GST using a conventional pulsing scheme that would induce solid state crystallization of the material and therefore a pulsing scheme that can cause melting followed by slow cooling was employed instead. For varying PW and TE as major variables in the respective SET pulse patterns for Ge-ST_h and GST, device resistance was measured similarly as in Fig. 2(b) and 2(c) and the results are shown in Fig. 6. From Fig. 6(a), notice that t_{SET} can be reduced down to 60 ns in total (50 ns in PW). Considering that t_{SET} of the device with a contact area of 150 x150 (nm^2) was 20 ns in total (see Fig. 4(a)), the present device yields t_{SET} longer than what could be estimated from scaling of the resistance with decreasing contact area. A close look of the SET voltage waveform shows that a time delay to threshold switching amounts to about 40 ns, constituting a greater portion of the measured t_{SET}. This may be ascribed to a relatively larger contribution of parasitic capacitance in the present device. As for the device with GST, SET programming time was roughly 100+200+500 (ns); with PW at 150 ns, SET programming was not possible regardless of TE in the range of 100 ns to 1.5 μs and PW was set to 200 ns, accordingly. Despite use of a slow quenching method, t_{SET} for GST is still incomparably long and R_{SET} is higher by an order of magnitude. The voltage waveform reveals a long delay to threshold switching (~150ns) but it comprises a less portion of the total t_{SET} as compared with the case of Ge-ST_h. This suggests that nucleation of crystallites and their growth to a crystalline state of a reasonably low electrical resistivity are much more difficult in the device with GST for some reasons yet to be illuminated.

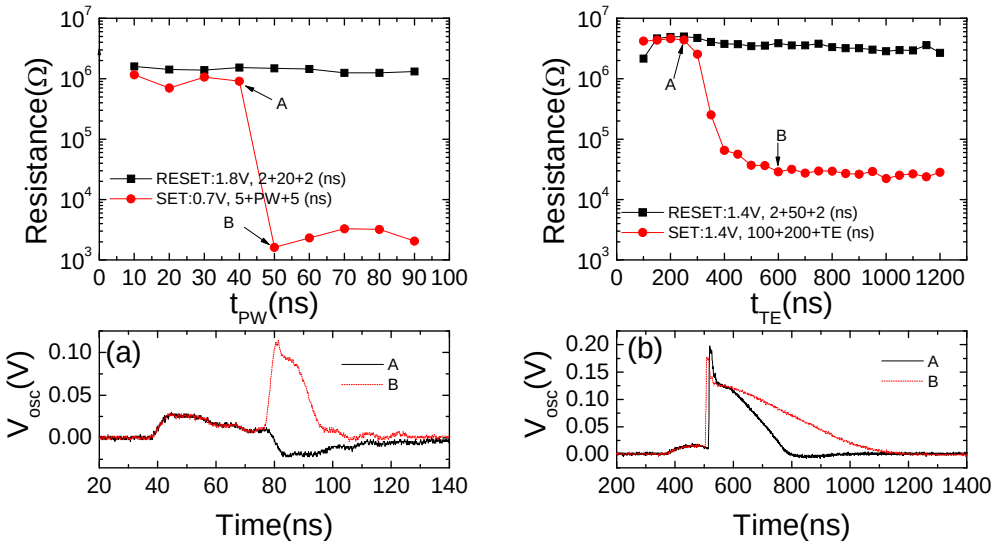

Figure 6. SET characteristics of (a) Ge-doped SbTe with the Sb/Te ratio of 4.53 and (b) $Ge_2Sb_2Te_5$. Shown in upper and lower panels are respectively dependence of SET resistance on primary variables in SET pulse patterns (pulse width for the case (a) and trailing edge for the case (b)) and pulse waveforms at the selected SET conditions.

Effect of nitrogen addition in Ge-ST$_h$ [14]

Aside from the question as to whether Ge-ST$_h$ has indeed the inherent capability of yielding lower I_{RESET} relative to GST, one can always make a supporting approach by taking advantage of a large room for increase in R_{SET} inherited from crystalline Ge-ST$_h$'s low electrical resistivity. Nitrogen was added to Ge-ST$_h$ to find if the approach may serve to reduce I_{RESET} as in the case of GST [15]. With nitrogen content increasing, the resulting Ge-ST$_h$ tends to have higher sheet resistances in both the amorphous and crystalline states and to crystallize at increasingly higher temperature as shown in Fig. 7(a). Both of these changes in material properties are surely desirable for a high density memory device in respect of enhanced Joule heating and improved stability against thermal crosstalk, respectively. For the crystallized states, the increase of sheet resistance with increasing nitrogen addition was found to result from decrease in Hall mobility as shown in Fig. 7(b). TEM images of Fig. 7(c) taken from the crystallized states, respectively with no nitrogen and 13 at% nitrogen reveal that nitrogen addition produces very fine-grained microstructures with a large density of faults, which would clearly promote electron and phonon scattering, hence reduced Hall mobility and possibly reduced thermal conductivity as well. Ge-ST$_h$ of varying nitrogen content was examined in terms of programming characteristics using the devices with a contact area of 150 x 150 (nm^2). Shown in Fig. 8(a) is a summary of RESET characteristics; for these, SET pulse of 300ns and RESET pulse of 50 ns were used. Complying with the aforementioned material characteristics, a gradual decrease in I_{RESET} as well as the increasing tendency of R_{SET} is noticed with increasing nitrogen content. Notice also from Fig. 8(b) that these characteristics were obtained with an essentially fixed resistance ratio and at little sacrifice of t_{SET} with nitrogen addition.

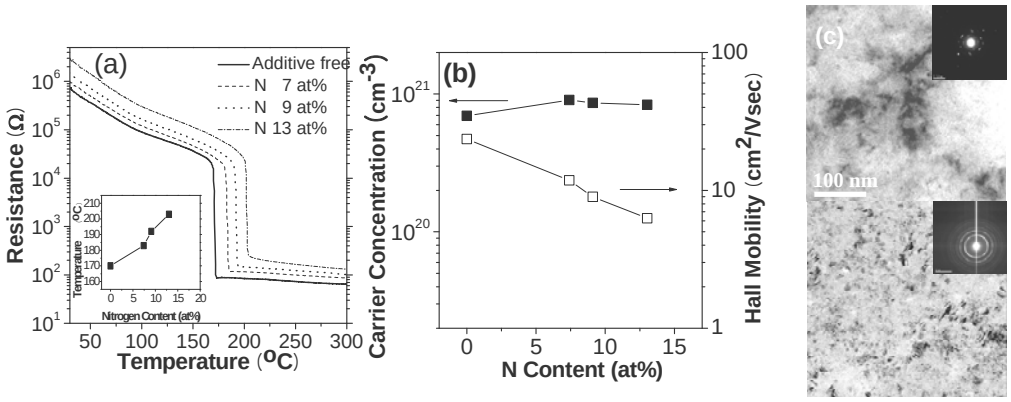

Figure 7. Effects of nitrogen addition on the material properties of Ge-doped SbTe with the Sb/Te ratio of 4.53; (a) variation of sheet resistance with temperature for varying nitrogen content, (b) variation of carrier concentration and Hall mobility of the crystallized films with increasing nitrogen content, and (c) TEM microstructures of the crystallized films without nitrogen and with 13 at% nitrogen.

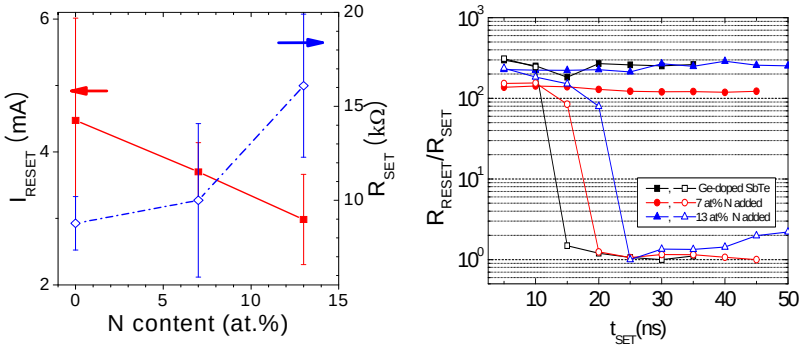

Figure 8. Effects of nitrogen addition on the device chracteristics of Ge-doped SbTe with the Sb/Te ratio of 4.53; (a) variation of RESET current and SET resistance with increasing nitrogen content and (b) dependence of normalized resistance (resistance ratio) on SET time for varying nitrogen content.

4. CONCLUSION

In the present study, we addressed the question; “whether GST materials presently used in PCRAM prototypes are appropriate for a high-speed and high-density memory of the future?”. The answer does not seem positive in light of the mounting cost of increase in R_{SET} and t_{SET} to further the reduction of I_{RESET}. We note that Ge-ST materials have quite a few promising properties that may offer a solution to the problem. Using test vehicles with a pore-type cell structure, we demonstrated that the Ge-ST_h and its derivative with nitrogen addition could provide device characteristics essentially required for a high performance memory, *i.e*. a lower R_{SET}, a shorter t_{SET} and potentially a lower I_{RESET} than GST. As for I_{RESET}, potentially beneficial material properties have not been substantiated by stable device characteristics in the present work and some improvements need to be made based on a proper understanding of the problem.

ACKNOWLEDGEMENTS

This work was supported by the National Research Program for 0.1 Terabit Non-volatile Memory Devices sponsored by the Korean Ministry of Commerce, Industry, and Energy. Authors would like to acknowledge Dr. K. Suu and his colleagues of Ulvac Inc. in Japan for their help in composition analysis of various phase change materials utilized in the present study and also to Professor K. H. Oh, Mr. H. S. Chung and Mr. S. H. Lee of Seoul National University for allowing us to utilize their FIB analysis technique to improve the devices.

REFERENCES

[1] S. Lai, *IEDM Tech. Dig*., 2004, pp.255-258
[2] S. J. Ahn, Y. J. Song, C. W. Jeong, J. M. Shin, Y. Fai, Y. N. Hwang, S. H. Lee, K. C. Ryoo, S. Y. Lee, J. H. Park, H. Horii, Y. H. Ha, J. H. Yi, B. J. Kuh, G. H. Koh, G. T. Jeong, H. S. Jeong, Kinam Kim, and B. I. Ryu, *IEDM Tech. Dig*., 2004, pp. 907-910
[3] F. Pellizzer, A. Pirovano, F. Ottogalli, M. Magistretti, M. Scaravaggi, P. Zuliani, M. Tosi, A. Benvenuti, P. Besana, S. Cadeo, T. Marangon, R. Morandi, R. Piva, A. Spandre, R. Zonca, A. Modelli, E. Varesi, T. Lowrey, A. Lacaita, G. Casagrande, P. Cappelletti, and R. Bez, Symp. *VLSI Tech*., 2004, pp. 18.
[4] Kinam Kim and Gitae Jeong, *Microsyst. Technol*., 13, 145 (2007)
[5] H.J. Borg, M. Schijndel, J.C.N. Rijpers, M.H.R. Lankhorst, G. Zhou, M.J. Dekker, I.P.D. Ubbens, and M. Kuijper, *Jpn J. Appl. Phys*., 40, part I, 1592 (2001)
[6] M. H. R. Lankhorst, L. Pieterson, M. Schijndel, B.A.J. Jacobs, and J.C.N. Rijpers, *Jpn J. Appl. Phys.*, 42, part I, 863 (2003)
[7] M. H. R. Lankhorst, B.W.S.M.M. Ketelaars, and R. A. M. Wolters, *Nature Materials*, 4, 347 (2005)
[8] T. D. Massalski, *Binary Alloy Phase Diagrams*, 2nd ed., vol. 3, p. 3310, ASM International (1990).
[9] J.-h. Jeong, S.Y. Lee, Wu Zhe, T. S. Lee, W. M. Kim, B. Cheong, H.-S. Chung, and K. H. Oh, MRS Spring Meeting, 2007, I11.3,.
[10] D. -H. Kang, B. Cheong, J. -H. Jeong, T. S. Lee, I. H. Kim, W. M. Kim, J. Y. Huh, *Appl. Phys. Lett*. 87, 253504-1 (2005)
[11] J. H. Coombs, A.P.J.M. Jongenelis, W. van Es-Spiekman, and B.A. Jacobs, *J. Appl. Phys*., 78, 4906 (1995).
[12] P. K. Khulbe, T. Hurst, M. Horie, and M. Mansuripur, *Appl. Opt.*, 41, 6220 (2002).
[13] D.-S. Suh, K.H.P. Kim, J.-S. Noh, W.-C. Shin, Y.-S. Kang, C. Kim, Y. Khang, I.K. Yoo, *IEDM Tech. Dig*., 2006, 30.2
[14] Wu Zhe, S. Y. Lee, J.-h. Jeong, I. H. Kim, S. C. Kim, K. H. Oh and B. Cheong, MRS Spring Meeting, 2007, I10.1.
[15] H. Horii, J. H. Yi, J. H. Park, Y. H. Ha, I. G. Baek, S. O. Park, Y. N. Hwang, S. H. Lee, Y. T. Kim, K. H. Lee, U-In Chung, J. T. Moon, in Symp. *VLSI Tech. Dig.*,2003, pp.177-178

Biographies of major authors

“Byung-ki Cheong”, Ph.D. has been a senior/principal researcher at KIST since 1994. His major area of research has been chalcogenide thin film materials for phase change optical recording, super-resolution optical storage and non-volatile phase change electrical memory. He received a B.E and a M.E. degree in Metallurgy from Seoul National

University, Seoul, Korea and a Ph.D. degree in Materials Science and Engineering with a thesis on phase transformation in solids from Carnegie Mellon University, Pittsburgh, U.S.A. He spent two years as a postdoctoral research associate in Data Storage Systems Center (DSSC) of Carnegie Mellon University, doing research on thin film materials for magnetic and magneto-optical information storage until joining KIST in 1994.

“Jeung-hyun Jeong”, Ph.D. has been a senior researcher at KIST since 2004. His current major area of research includes phase change memory, MEMS sensors specifically employing diamond and PZT films, and mechanical characterization of thin films. He received a B.E., a M.E., and a Ph.D degree in Material Science and Engineering from Seoul National University, Seoul, Korea. He spent two years as a postdoctoral research associate in Department of Mechanical Engineering of Massachusetts Institute of Technology, Massachusetts, U.S.A., doing research on the mechanical assembly of carbon nanotubes and the development of micro energy harvesting device.

“Suyoun Lee”, Ph.D. is a senior researcher at KIST. His major area of research has been chalcogenide thin film materials for phase change non-volatile memories, threshold switching devices, and spintronic devices. He received a B.S. degree in Nuclear Engineering and M. S. degree and Ph. D. in School of Physics from Seoul National University, Korea. He spent three and a half years as a senior researcher for developing a phase change random access memory and magnetic random access memory in Samsung Electronics. He has joined KIST in 2006 and has been working in the field of phase change memory.