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Electromigration in Molten-phase $Ge_2Sb_2Te_5$ and Effects of Doping on Atomic Migration Rate

Young-Chang Joo†, Tae-Youl Yang, Ju-Young Cho, and Yong-Jin Park

Department of Materials Science & Engineering, Seoul National University, Seoul 151-744, Korea

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ABSTRACT

Electromigration in molten $Ge_2Sb_2Te_5$ (GST) was characterized using pulsed DC stress to an isolated line structure. When an electrical pulse was applied to the GST, GST lines were melted by Joule heating, and Ge and Sb atoms migrate to the cathode, whereas Te atoms migrate to the anode. This elemental separation in the molten GST was caused by an electrostatic force-induced electromigration. The effects of O-, N-, and Bi-doping on the electromigration were also investigated, and atomic mobility changes by the doping were investigated by quantifying *DZ** values. The Bi -doping did not affect the *DZ** values of the constituent atoms in the molten GST, but the *DZ** values decreased by O-doping and N-doping.

Key words : ***$Ge_2Sb_2Te_5$, Electromigration, Doping, Free volume***

1. Introduction

$Ge_2Sb_2Te_5$(GST) is the most widely used phase change material in phase-change random access memory (PcRAM), and has been extensively researched with respect to its physical properties,[1-3] structural properties,[4,5] and bonding nature.[6] However, the stability of GST under the operating condition, which is closely related to the endurance failures in PcRAM, has not been studied intensively. Repetitive melting, solidification and high electric stress during the reset operation can induce cycling endurance failure such as *reset stuck* due to interfacial failures and *set stuck* due to compositional changes in phase change materials.[7,8)]

The compositional changes and void formation are caused by mass transport in the material. The phase change volume experiences very high current density (~10^7 A/cm^2) in the liquid phase during the reset operation. The liquid phase is vulnerable to mass transport because of the high atomic mobility (~10^5 cm^2/s). When a high electric field or current is applied to materials, electric-field-enhanced mass transport (electromigration) occurs,[9,10] and the compositional variation is induced by the flux differences of constituent elements. Therefore, the analysis for electromigration behavior in liquid GST is important to solve the endurance problems, but electromigration in multicomponent liquid-phase materials has not been studied intensively. In addition, because the driving forces for atomic transport are mixed in too tiny PcRAM cell structure, it is hard to observe and quantify electromigration in the device conditions thereby analyzing each driving force is also difficult. Therefore, we investigate the electromigration in GST by using a bridge-type cell structure.

The addition of an external dopant can be a solution to inhibit the electromigration, as well as to improve the electrical property or thermal stability of PcRAM.[11-14] Dopants are classified into interstitial-type, such as C, N, and O, and substitutional-type, such as Bi, Sn, and Se, according to the atomic site that dopants occupy. Because they induce different bonding characteristics, microstructures, and other physical properties, the effects to the electromigration are also different.[15,16]

In this article, we survey the electromigration characteristics of GST in the molten phase, and the effects of various dopants on the electromigration were also studied by comparing the atomic migration rate of doped GST with that of un-doped GST.

2. Experimental Procedure

Electromigration testing was conducted using a bridge-cell structure. The bridge structures were fabricated using an integrated circuit fabrication process as illustrated in our studies.[10,15,16] Fig. 1(a) shows the sample structure and test system used to test electromigration in this study. The test line of the phase change material, which were composed Mo. The test line of 20-μm-length, 2-μm-width, and 300-nm-thickness was isolated by molybdenum pads for electrical contact at both ends of the line. N- and O-doped GST films were deposited in the presence of nitrogen and oxygen, respectively, as reactive gases in the sputtering chamber at room temperature. Bi-doped GST was prepared by co-sputtering of $Ge_2Sb_2Te_5$ and $Ge_2Bi_2Te_5$, and powers for the targets were 80 W and 40 W, respectively.

The method used to characterize electromigration in phase change materials was wafer-level electrical pulse stressing. Fig. 1(b) shows the electromigration test system using pulse

†Corresponding author : Young-Chang Joo
E-mail : ycjoo@snu.ac.kr
Tel : +82-2-880-8986 Fax : +82-2-883-8197

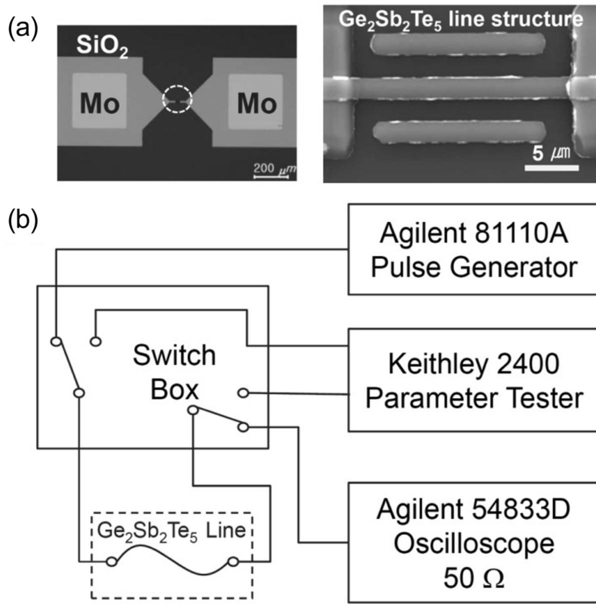

Fig. 1. (a) Optical microscope image and magnified SEM image of the large, symmetric, and line-shaped cell, (b) Schematic diagram of the electromigration test setup.[10]

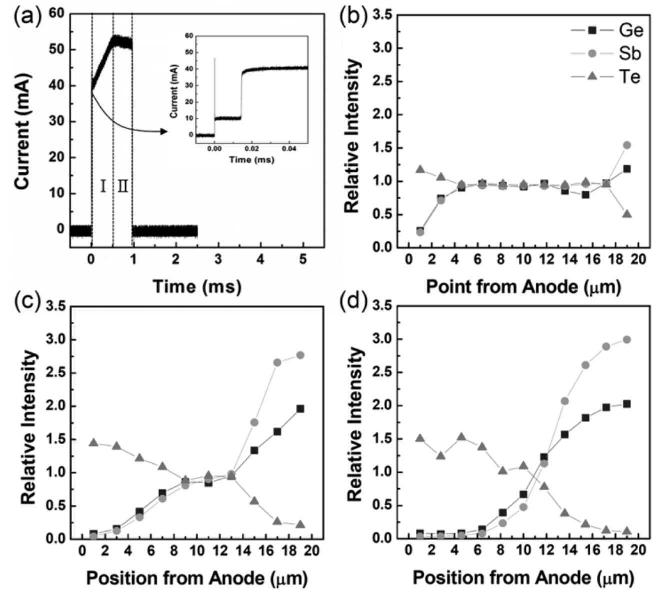

Fig. 2. (a) The change in current under an electrical stress of 12 V for 5 ms in the undoped GST. (b)-(d) Composition profiles of Ge, Sb, and Te in undoped GST with pulse duration during the electromigration.[15]

stressing. A DC current pulse was applied to the test sample by a pulse generator (Agilent 81110A) under ambient air, and the current pulse was identified from the voltage measured by an oscilloscope (Agilent 54833D) with a 50 Ω input impedance. A electrical pulse of 12 V was applied to the device with a duration on the order of millisecond enough for the melting of GST, and current was monitored using an oscilloscope. The compositional analysis was performed after the stressing along the longitudinal direction by wavelength-dispersive X-ray spectroscopy (WDS).

3. Resultsand Discussion

A single voltage pulse with a duration on the order of milliseconds and high amplitude was applied to the GST cell. In this study, the amplitude of the voltage was 12 V for the electromigration testing. Fig. 2(a) shows the current evolution under electrical stressing in undoped GST. The voltage drop over 5 ms electrical stressing was monitored using an oscilloscope with a 50 Ω impedance, which was connected to the lines in series. The voltage can be related to the current of a test circuit that includes the test sample. As shown in Fig. 2(a), the current abruptly increased 15 μs after stressing, which is shown in the inset. This current jump was caused by the melting of the GST by self Joule heating. Because the resistivity of liquid GST is lower than that of the crystalline phase, current flow in the circuit increases under a certain voltage. Following melting, the current linearly increased with time until 0.5 ms. The increase in current was due to the resistivity change in the phase change material caused by a compositional change. The period during which the current was increasing was designated as stage I. The current level subsequently decreased after 0.5 ms: this period was designated stage II. The change in slope of the current versus time indicates a change in the electromigration behavior. From the compositional change and morphological analysis we notice that electromigration-induced compositional change was completed in stage I, and only void evolution occurred in stage II. Finally, the test sample catastrophically failed at 1.3 ms, after which current ceased to flow. This failure was induced by void formation in the GST line at the anode contact.[15]

Compositional analysis was conducted by varying the duration of the applied electrical stress. Fig. 2(b)-(d) presents a compositional plot, the relative X-ray intensity from WDS along the longitudinal direction for each element, when current stressing was interrupted at (b) 0.1, (c) 0.3, and (d) 0.5 ms. These profiles were acquired from the different samples. Electrical pulse stressing caused complete compositional demixing to GeSb and Te. Ge and Sb atoms migrated to the cathode and were, thus completely depleted at the anode. Te atoms migrated toward the anode. Pure Te phase was detected along the anode direction. The compositional redistribution of GST to GeSb and Te phases was explained by electrostatic-force-induced electromigration. The direction of electromigration can be determined by the valence difference of each atom in the molten state. The electronegativities of Ge, Sb, and Te are 4.6, 4.85, and 5.49 eV, respectively.[17] Therefore, the anionic Te ions diffuse to the anode, and the cationic Ge ions and Sb ions diffuse to the cathode due to electrostatic forces.

Fig. 3 shows the current evolution under electrical stress in the (a) Bi (6.6 at.%)-doped, (b), O (5.3 at. %)-doped, and (c) N (4.3 at. %)-doped GST lines. The doped lines showed current

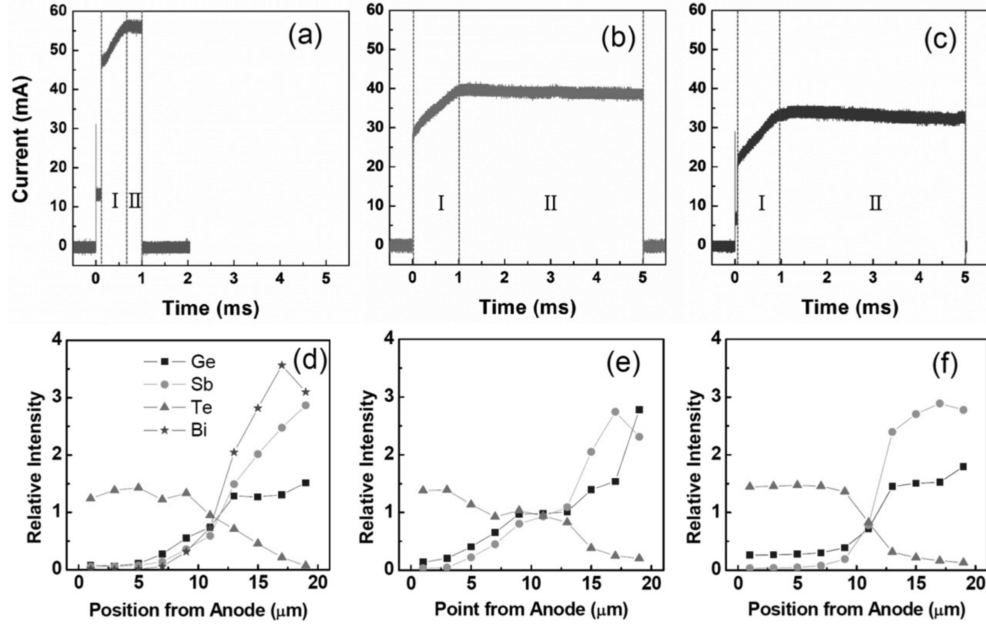

Fig. 3. (a)-(c) The change in current and (b)-(d) the composition profiles during the duration of 5 ms in (a), (d) Bi-doped, (b), (e) O-doped, (c), (f) N-doped GST with pulse duration during the electromigration.[16)]

versus time behavior similar to that of the GST line, though the stage I and II durations in N-doped and O-dopedGST were longer than the corresponding durations for the undoped GST line. The duration of stage I for the N-doped and O-doped GST was about 1.0 ms, which is twice as long as that for undoped GST. Current evolution in stage I was shown to correspond to atomic diffusion due to electromigration. Therefore, the extension of stage I suggests that the time required for complete elemental separation was increased by the dopants. In other words, the electromigration rate decreased with N and O doping. Stage II is determined by the void formation in the line sample. In O-doped and N-doped GST, catastrophic failure were not observed during the 5 ms of pulse stressing. However, in Bi-doped GST, the duration time of stage I was about 0.5 ms, which is similar to that of the undoped GST sample, as shown in Fig. 3(a). This result indicates that the electromigration rate in Bi-doped GST is also similar to that in undoped GST. However, stage II in Bi-doped GST decreased compared with that in the undoped GST. The decrease in the duration of stage II indicates fast void growth, which induces failure.

Compositional demixing was also generated in doped GST samples by electromigration after applying the voltage pulse with the duration time corresponding to stage I, as shown in Fig. 3(d)-(f). The overall atomic migration behaviors in the doped GST lines were very similar to those in the undoped GST line. Ge and Sb migrated to the cathode, and Te migrated to the anode by the electrostatic force. The migration behavior of Bi-dopant toward the cathode was also detected by WDS analysis. Bi migrated toward the same direction as the Sb atoms, which were replaced by Bi upon doping. The electronegativity of Bi is 4.69 eV, which is similar to that of Ge. Therefore, Bi atoms showed cationic behavior in the molten phase of GST. O-dopant and N-dopant did not affect the ionization tendency of the constituent elements. However, Ge was completely depleted at the anode in the O-doped and N-doped GST. The Ge residue is related to the formation of germanium oxideand nitride phase.[18,19)] The oxide and nitride bonds were not broken during melting, and the Ge atoms in the oxide and nitride phase were not affected by the electrical field, thereby exhibiting the immobile during electromigration in the molten phase.

The quantification of the electromigration rate is important in addition to the driving force to predict the electromigration behavior in real PcRAM devices and to estimate the life time of devices. The electromigration rate determines how many atoms migrate through a certain area over a unit time, which is the definition of the atomic flux. The atomic flux of element i by electromigration can be written as

$$J_i^{EM} = \frac{C_i D_i}{RT} Z_i^* e E \qquad (1)$$

where C_i is the number concentration, $D_i$is the atomic diffusion coefficient, Z_i is the effective charge number of $i$atom, kT is the thermal energy, e is the charge of electron, and E is the electric field. The temperature T and electric field E are determined by operating conditions. The gas constant R and electron charge e are constant, and the initial concentration C_i is also fixed. Therefore, the atomic flux of i is determined by the product of the effective charge number Z_i* and diffusion coefficient D_i. The DZ* value of each constituent element is the standard to compare the atomic mobility during elec-

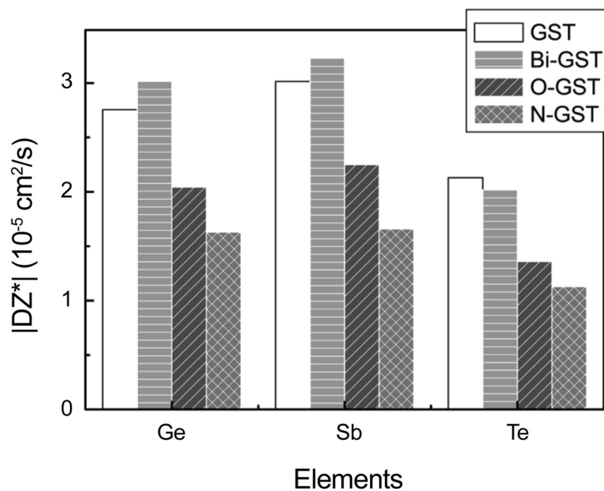

Fig. 4. Value of *DZ** in undoped, Bi-doped, O-doped, and N-doped GST.*DZ** decreased in the doped GST compared with undoped GST; the largest decrease of *DZ** is observed in N-doped GST.[16]

tromigration.

We calculated the *DZ** value from quantifying the number of migrating atoms as increasing the duration of pulse.[10,15) Fig. 4 shows the calculated *DZ** values of Ge, Sb, and Te in undoped, Bi-doped, O-doped, and N-doped GST.*DZ** values in Bi-doped GST was not affected by doping. Bi doping does not retard electromigration in molten GST. However, The *DZ** values of all of the elements in the O-doped and N-doped GST samples were smaller than those in the undoped GST. The decrease in *DZ** values suggests that the dopants retarded the diffusion of Ge, Sb, and Te. Hence, O-doping and N-doping suppressed the electromigration of all elements in the molten phase of GST. The ratio of the reduction in the *DZ** values revealed a similar value. The ratio of *DZ** values of O-doped GST to those of undoped GST is about 0.71. In the N-doped GST, the ratio of the reduction is about 0.56. Although the doping concentration of oxygen is higher than the concentration of nitrogen, the effect of electromigration retardation is more dominant in N-doped GST than in O-doped GST.

The decrease in *DZ** may be caused by the densification of GST due to the difference in atomic size between the dopants and the constituent elements. The atomic radii of N (r = 0.092 nm) and O (r = 0.065 nm) are smaller than those of Ge (r = 0.137 nm), Sb (r = 0.159 nm), and Te (r = 0.142). The difference in atomic radius between the solvent and solute leads to an efficient packing of atoms in the liquid phase, resulting in the decrease in free volume. Because the atomic diffusion rate in the liquid phase is inversely proportion to the viscosity, if the free volume decreases, the diffusion coefficient exponentially increases. The formation of secondary phases such as Ge nitride and Ge oxide[20-22] in doped GST can also explain the decrease in *DZ**. As mentioned above, the nitride and oxide were not melted by electrical stressing and did not migrate by electromigration. The immobile secondary phase induces scattering with the moving ions; therefore, this phase reduces the migration rate of diffusing ions. Moreover, nitrogen can form three bonds, whereas oxygen is bivalent.[18] Therefore, nitrogen can be more effective in forming covalent bonds, which may induce more scattering than oxygen, resulting in a large decrease in the electromigration rate. However, substitutional-type dopant, bismuth, cannot reduce the free volume by occupying interatomic positions, but rather increases the free volume because of its large atomic radius. Therefore, the atomic mobility in liquid phase is not altered by Bi doping.

4. Conclusions

In this study, we showed the electromigration behaviour of GST in the molten phase by using a voltage pulse stressing. Based on our study, the endurance failure by compositional change of GST can be explained by the electrostatic-force-induced electromigration in the molten state. In addition, we will investigate the effect of O-doping, N-doping, and Bi-doping on the electromigration in the molten phase. Interstitial-type dopants, oxygen and nitrogen, decreased the atomic mobility during electromigration by reducing free volume in liquid GST. They were expected to retard the endurance failures. However, substitutional-type dopant, bismuth, could not affect the atomic mobility. These results indicate that interstitial type dopants are effective to improve the PcRAM reliability, but substitutional type dopant has no effect to improve the reliability. This study on electromigration of GST and effects of doping provide useful information to improve the endurance characteristics of PcRAM by selecting an appropriate dopant.

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