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Improved phase-change characteristics of Zn-doped amorphous Sb$_7$Te$_3$ films for high-speed and low-power phase change memory

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The superior performance of Zn-doped Sb$_7$Te$_3$ films might be favorable for the application in phase change memory. It was found that Zn dopants were able to suppress phase separation and form single stable Sb$_2$Te crystal grain, diminish the grain size, and enhance the amorphous thermal stability of Sb$_7$Te$_3$ film. Especially, Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ film has higher crystallization temperature ($\sim$258°C), larger crystallization activation energy ($\sim$4.15 eV), better data retention ($\sim$170.6°C for 10 yr), wider band gap ($\sim$0.73 eV), and higher crystalline resistance. The minimum times for crystallization of Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ were revealed to be as short as $\sim$10 ns at a given proper laser power of 70 mW. © 2013 AIP Publishing LLC [http://dx.doi.org/10.1063/1.4816062]

The ability to explore advanced phase-change material has become increasingly important in phase change memory (PCM) technology. Accurate research on phase-change material is critical for further technology development and Ge$_2$Sb$_2$Te$_5$ (GST) has also recently gained special interest in material is critical for further technology development and phase-change material applications. Recently, Zn could be a preferential dopant candidate.

It was found that doping Ge$_3$In$_{10}$ and Ag (Ref. 11) into Sb$_7$Te$_3$ could increase crystallization temperature, and Ag, In, Ge doped Sb$_7$Te$_3$ alloys have been frequently used in the rewritable optical record media such as DVD-RW and DVD+RW. However, these pseudo-ternary phase change materials are not good in all aspects. For instance, Ag-doped Sb$_7$Te$_3$ always faces the problem of phase separation during the crystallization process, which will lead to poor endurance for phase-change material applications. Recently, Zn element has been reported to be an effective chemical modifier in Zn-doped films. Zn was able to form chemical bonds with Sb or Te in the films, and the increase of the Zn content could improve the uniform distribution of the grains, enhance the thermal stability of the amorphous phase, and increase the phase change speed. Here, we further explored structural, thermal, optical, and electrical properties of Zn-doped Sb$_7$Te$_3$ films that have never been reported before. Comprehensive evaluation on the trade-off between thermal stability, crystallization speed, and other properties opens up the avenue of the applications for the Zn-doped Sb$_7$Te$_3$ films as PCM active layers.

Zn-doped Sb$_7$Te$_3$ films with a thickness of 150 nm were deposited on quartz and SiO$_2$/Si (100) substrates by magnetron co-sputtering method using individual Zn and Sb$_7$Te$_3$ alloy targets. In each run of the experiment, the chamber was evacuated to $2.2 \times 10^{-4}$ Pa and then Ar gas was introduced to 0.3 Pa for the film deposition. Pure Sb$_7$Te$_3$ and GST films with the same thickness were also prepared for comparison. The concentration of Zn dopant in the Zn-added Sb$_7$Te$_3$ films, measured by using energy dispersive spectroscopy (EDS), was identified to be 6.18at. %, 18.52at. %, 27.26at. %, and 30.19at. %, respectively. The sheet resistances of as-deposited films as functions of elevated temperature (non-isothermal)
and time at specific temperatures (Isothermal) were in situ measured using a four-point probe in a homemade vacuum chamber. The structure of as-deposited and annealed Sb$_7$Te$_3$ and Zn-doped Sb$_7$Te$_3$ thin films was examined by X-ray diffraction (XRD) and Raman spectra. The optical band gap of the films was measured using UV-VIS-Near Infra-red (NIR) spectrophotometer. The crystallization behavior on a nanosecond scale was observed using a static tester (PST-1, NANOStorage Co. Ltd., KOREA).

Fig. 1(a) shows the in situ temperature-dependence sheet resistance (R-T) of GST, undoped and Zn-doped Sb$_7$Te$_3$ films. The sheet resistance of the films falls with temperature until a sudden drop occurs at respective crystallization temperature ($T_c$), which is determined by the minimum of the derivative of in situ R-T curve. The obtained $T_c$ values are $\sim 142$, $\sim 184$, $\sim 210$, $\sim 237$, and $\sim 258$ °C for Sb$_7$Te$_3$, Zn$_{6.18}$(Sb$_7$Te$_3$)$_{93.82}$, Zn$_{18.52}$(Sb$_7$Te$_3$)$_{81.48}$, Zn$_{27.26}$(Sb$_7$Te$_3$)$_{72.74}$, and Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$, respectively. Higher $T_c$ is helpful to improve the amorphous thermal stability. On the other hand, it is found that only Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ film has the similar amorphous electrical resistance value at room temperature as the GST film, while the crystalline resistance of Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ is larger than that of GST film, which is helpful to reduce RESET current. The amorphous/crystalline resistance ratio of Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ film is more than $10^5$ during the crystallization process, indicating a large ON/OFF ratio for reading in PCM applications. Moreover, the change of the sheet resistance across the crystallization temperatures in both Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ and GST is sharp when the films transform from the amorphous into crystalline state, indicating that the Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ film has a similar faster crystallization speed as the GST film.

Fig. 1(b) shows the data retention characteristics for these investigated films. The maximum temperature for 10-years' data retention can be extrapolated by fitting the data with the Arrhenius equation: $t = \tau \exp(-E_a/k_BT)$, where $\tau$ is a proportional time constant, $E_a$ is crystalline activation energy and $k_B$ is Boltzmann’s constant, respectively. The failure time ($t_f$) is defined as the time when the film resistance reaches half of its initial value at a specific isothermal temperature $T$. The data retention temperatures for 10 yr of the amorphous Sb$_7$Te$_3$, Zn$_{6.18}$(Sb$_7$Te$_3$)$_{93.82}$, Zn$_{18.52}$(Sb$_7$Te$_3$)$_{81.48}$, Zn$_{27.26}$(Sb$_7$Te$_3$)$_{72.74}$, and Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ films are thus determined to be $\sim 30.6$, $\sim 104.9$, $\sim 131.5$, $\sim 152.6$, and $\sim 170.6$ °C with the activation energy $E_a$ of $\sim 1.58$, $\sim 3.29$, $\sim 3.67$, $\sim 3.70$, and $\sim 4.15$ eV, respectively. The values for Zn-doped Sb$_7$Te$_3$ films are much higher than those of conventional GST ($\sim 88.9$ °C, $\sim 2.98$ eV). Especially, while most automotive electronics applications require a data retention temperature of at least 120 °C for 10 yr, it appears that the superior performance in the Zn-doped Sb$_7$Te$_3$ films, especially in those with high Zn doping concentration, can meet the challenges. Apparently, PCM based on Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ film can store the information longer time than that based on anyone else.

Structural changes related to a phase transition were investigated by XRD. Figs. 2(a)–2(e) show XRD patterns of undoped and Zn-doped Sb$_7$Te$_3$ films, respectively. As evident in Fig. 2(a), no crystallization peaks can be observed, indicating an amorphous nature of the as-deposited Sb$_7$Te$_3$ film. However, a crystallized rhombohedral Sb phase can be found in the film annealed at 150 °C and 200 °C, and another new crystalline phase of Sb$_2$Te$_3$ appears in the film annealed at 250 °C. XRD peaks corresponding to the crystallized Sb and Sb$_2$Te$_3$ phases become sharper with increasing annealing temperature to 300 °C. Finally, further increasing annealing temperature leads to the disappearance of the metastable rhombohedral Sb phase, and stable rhombohedral Sb$_2$Te$_3$ phase becomes dominated in the film annealed at 350 °C. A similar structural evolution has been reported in Ref. 11 as well.

In the case of Zn-doped Sb$_7$Te$_3$ films, the XRD patterns shown in Figs. 2(b)–2(e) indicate that all the as-deposited films are amorphous. The crystallization peaks begin to appear at 200 °C for Zn$_{6.18}$(Sb$_7$Te$_3$)$_{93.82}$ films and at 250 °C for Zn$_{18.52}$(Sb$_7$Te$_3$)$_{81.48}$, Zn$_{27.26}$(Sb$_7$Te$_3$)$_{72.74}$, and Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$, respectively. Together with the fact that the first crystallized peak appears in the undoped Sb$_7$Te$_3$ film annealed at 150 °C, the crystallization temperature apparently increases with the increase of Zn-doping concentration, which is in good agreement with the results shown in Fig. 1(a). On the other hand, only crystallized XRD peaks corresponding to single Sb$_7$Te$_3$ hexagonal phase can be found in all Zn-doped Sb$_7$Te$_3$ films even annealed at 350 °C. This is in sharp contrast with that observed in Sb$_7$Te$_3$ films, where the separated Sb and Sb$_2$Te$_3$ crystalline phases can be formed at a certain annealing temperature. Moreover, the crystallization peaks are suppressed gradually with increasing Zn content. Particularly, the Sb$_2$Te$_3$ (103) peak in the annealed Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ film appears to be broader and weaker compared with that in any other Zn-doped Sb$_7$Te$_3$ films, suggesting that increasing Zn content in the film could restrain crystal grain growth. Our previous X-ray photoelectron spectra (XPS) measurements have revealed that Zn,
Sb, and Te can be bonded each other in Zn-Sb-Te systems, but no crystalline Zn-Sb and Zn-Te phases can be observed in the XRD patterns and TEM images of the annealed films, suggesting that the Zn-Sb and Zn-Te bonds may exist in the amorphous part of the film. Consequently, it can be concluded that the formation of amorphous Zn-Sb and Zn-Te phase plies up at the Sb$_2$Te grain boundaries hindering the crystallization process and help to improve the overall thermal stability of the Sb$_7$Te$_3$ material.

Raman spectra also provide important information relative to phase transformation which is in well agreement with XRD data. Figs. 3(a) and 3(b) show Raman spectra of Zn$_{27.26}$(Sb$_7$Te$_3$)$_{72.74}$ and Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ films annealed the different temperatures. As-deposited, 150°C- and 200°C-annealed films show a broad peak A in the range from 120 to 180 cm$^{-1}$ which is related to the vibration of amorphous Sb-Te bonds. Differently, the peak A locates at $\sim$147 cm$^{-1}$ in Raman spectra of Zn$_{27.26}$(Sb$_7$Te$_3$)$_{72.74}$ film, while the Raman spectra of the Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ film features a broader peak A at $\sim$152 cm$^{-1}$, suggesting that adding more Zn leads to a higher degree of disorder in the amorphous phase of the material. Obviously, with the increase of the annealing temperature to 250°C, the broad band is divided into two different sharp peaks, which is marked as B&C in Figs. 3(a) and 3(b). The peak B is located at $\sim$151 cm$^{-1}$ and kept almost unchanged with the increase of the annealing temperature to 350°C, while peak C downshifts from 120 to $\sim$113 cm$^{-1}$ in Zn$_{27.26}$(Sb$_7$Te$_3$)$_{72.74}$ film and from 128 to $\sim$117 cm$^{-1}$ in Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ film, implying that the local bonding arrangement around Sb atoms has been influenced by the crystallization process. During crystallization process, the dangling bonds and defects in the amorphous films are gradually annealed out, and a great fraction of saturated bonds are produced with the formation of Zn-Sb bonds. More
importantly, the intensity of peak C is suppressed in Zn$_{30.19}$ (Sb$_7$Te$_3$)$_{69.81}$ film compared with that in Zn$_{27.26}$ (Sb$_7$Te$_3$)$_{72.74}$ film. It implies that the disorder level of the crystalline films is increased with high Zn content. The results also correspond to the results of XRD, since the XRD peak intensities are decreased with more Zn-doping concentration.

A large optical band-gap is essential for the phase change material in order to reduce the threshold current.\textsuperscript{16} The optical band gap values were obtained based on the Tauc’ plot of the absorption spectra of the amorphous undoped and Zn-doped Sb$_7$Te$_3$ films, and the results were shown in Fig. 3(c). We can find that the optical band gap increases from ~0.28 to ~0.73 eV with the addition of Zn increasing. Especially, the optical band gap of amorphous Zn$_{30.19}$ (Sb$_7$Te$_3$)$_{69.81}$ film is ~0.73 eV, which is slightly larger than that of GST (~0.70 eV). Thus, the average threshold current of Zn$_{30.19}$ (Sb$_7$Te$_3$)$_{69.81}$ is expected to be smaller than that of GST. This could be also explained by the following reasons. It is well known that, the element Zn has a melting temperature at 419.5°C which is lower than that of any other elements in Zn-Sb-Te system. Therefore, the overall melting temperature in Zn-doped Sb$_7$Te$_3$ films will be reduced with the presence of Zn, and the required energy or heating temperature will be lower. Accordingly, the increase of the temperature caused by Joule heating in the Zn$_{30.19}$ (Sb$_7$Te$_3$)$_{69.81}$ film will be smaller than that of the Ge$_2$Sb$_2$Te$_5$ film. Both a lower required temperature and a higher resistance (see Fig. 1(a)) could contribute to lower current and thus a lower energy consumption in a memory device based on the Zn$_{30.19}$ (Sb$_7$Te$_3$)$_{69.81}$ film. On the other hand, the size of the Sb$_2$Te grains was found to be about 10 nm estimated from the linewidth of the XRD peaks using Scherrer equation,\textsuperscript{17} and our previous TEM observation has indicated that these grains can be homogeneously dispersed among amorphous contents of Zn-Sb and Zn-Te.\textsuperscript{14} While amorphous-crystalline phase is localized at such a small area around ten-nanometer scale, the speed of the phase change is obviously faster compared with that happened in the larger grain size. Thus, Zn$_{30.19}$ (Sb$_7$Te$_3$)$_{69.81}$ could be potential for PCM applications in terms of energy consumption and phase change speed.

A static tester using pulsed laser irradiation was employed to investigate the phase transition behavior in the scale of nanoseconds. The phase change induced by laser irradiation via tuning the laser power and pulse width,\textsuperscript{18} can lead to a change in the optical reflectance.\textsuperscript{19} Figs. 4(a) and

![FIG. 4. PTE diagrams of (a) GST and (b) Zn$_{30.19}$ (Sb$_7$Te$_3$)$_{69.81}$.](image-url)

![FIG. 5. Relative crystallization of GST and Zn$_{30.19}$ (Sb$_7$Te$_3$)$_{69.81}$ by laser power and pulse width: (a) Laser power at 10 mW, (b) laser power at 30 mW, (c) laser power at 50 mW, and (d) laser power at 70 mW.](image-url)
4(b) show the changes in the reflectance of GST and Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ as functions of the laser power and pulse width, e.g., so-called Power-Time Effect (PTE). In such PTE diagrams, optical contrast values were obtained with a varying power and pulse width of the focused laser pulse, and they were calculated by the following equation: $\Delta R = (R_{\text{after}} - R_{\text{before}})/R_{\text{before}}$, where $R_{\text{after}}$ and $R_{\text{before}}$ were the reflectivity before and after irradiation, respectively.

It is clear that there is no change in reflectivity in the initial region I in Figs. 4(a) and 4(b), since the laser power and/or the pulse width is insufficient to induce the crystallization of the films. The threshold conditions to induce the crystallization can be traced approximately in the boundary of the region of I, where the films start to crystallize exhibiting increasing $\Delta R^{20,21}$ With further increasing laser power and/or pulse width, $\Delta R$ increases before it becomes saturated at region II which may correspond to a full crystallization of the film. However, after full crystallization (maximum $\Delta R$, $\Delta R_{\text{max}}$), an extremely long pulse width and high power can decrease $\Delta R$ as shown in Fig. 4(a) III for GST film since phase change material experiences a laser ablation process. This is in contrast with that for Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ film where the region III cannot be found in Fig. 4(b), indicating that Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ film possesses a better stability against laser irradiation.

The GST and Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ have different $\Delta R_{\text{max}}$ due to their own reflectivity and crystallinity after crystallization. According to Ref. 22, the optical reflectivity showed perfect linear dependence upon crystallinity. Therefore, we deduced the relative crystallization during the crystallization process by using the ratio of $R$ to $\Delta R_{\text{max}}$ and plotted this against laser power and pulse width in Fig. 5. The laser-induced phase transition time of Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ film at low laser power of 10 mW is longer than that of GST as shown in Fig. 5(a), which is in excellent agreement with the results in Fig. 4 (see blue color region). With increasing laser power to 30 mW, there is an abrupt increase of the relative crystallization for Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ as shown in Fig. 5(b). In contrast, the relative crystallization in the GST film increases slightly in the initial stage, and then increases rapidly before achieving full crystallization. With further increasing laser power to 50 mW and 70 mW, crystallization time becomes fast and a full crystallization can be achieved in the Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ film, while the crystallization time almost has no change and relative crystallization even decreases due to the ablation in GST films with high laser power of 70 mW and long pulse width of $\sim$280 ns. From Fig. 5, we can also see that the Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ film generally shows relatively faster crystallization during the whole crystallization process using the same laser power compared with the GST film. The minimum times for crystallization of Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ films are determined to be $\sim$40 ns, $\sim$20 ns, and $\sim$10 ns at a given proper laser power of 30 mW, 50 mW, and 70 mW, respectively, sufficient for the application in high data recording.

In summary, Zn-doped Sb$_7$Te$_3$ films have been investigated for the applications in PCM. Compared to GST, Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ film shows higher $T_c$ ($\sim$258 °C) and larger $E_c$ ($\sim$4.15 eV), which results in a better data retention maintaining for 10 yr at $\sim$170.6 °C. Higher crystalline resistance will be helpful to reduce RESET current. Meanwhile, it retains the stable phase of Sb$_7$Te and exhibits rapid crystallization; thus the minimum time for crystallization is as short as $\sim$10 ns at a given laser power of 70 mW. Owning good thermal stability, rapid phase transition, high crystalline resistance, and stable phase, Zn$_{30.19}$(Sb$_7$Te$_3$)$_{69.81}$ film can be applied to high-speed and low-power phase change memory.

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