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Phase change behaviors of Zn-doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films

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Zn-doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ phase-change materials have been investigated for phase change memory applications. $\text{Zn}_{15.16}(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{84.84}$ phase change film exhibits a higher crystallization temperature ($\sim 258^\circ\text{C}$), wider band gap ($\sim 0.78\text{ eV}$), better data retention of 10 years at 167.5°C , higher crystalline resistance, and faster crystallization speed compared with the conventional $\text{Ge}_2\text{Sb}_2\text{Te}_5$. The proper Zn atom added into $\text{Ge}_2\text{Sb}_2\text{Te}_5$ serves as a center for suppression of the face-centered-cubic (fcc) phase to hexagonal close-packed (hcp) phase transition, and fcc phase has high thermal stability partially due to the bond recombination among Zn, Sb, and Te atoms.

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One of the most promising candidates for non-volatile memories (NVM) is phase change memory (PCM) based on the reversible switching of phase change material accompanying with a large change in resistance between its amorphous (reset) and crystalline state (set).¹ Among various phase change materials available, $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) is one of the most popular chalcogenide phase change materials used as storage media in PCM due to its excellent electrical and structural properties that combines the advantage of good thermal stability of GeTe and fast phase change ability of Sb_2Te_3 material together.² However, when GST is switched from crystalline state to the amorphous state, high melting temperature (620°C) and low crystalline resistance will cause a high RESET current in PCM devices, leading to higher power consumption.³ Another drawback of GST for PCM application is its low crystallization temperature ($\sim 160^\circ\text{C}$), which could lead to the instability with a data retention capability of 10 years at a maximum temperature of $85\text{--}110^\circ\text{C}$ (Refs. 4 and 5) that is not ideal for the applications at high temperatures.

During the past few years, great efforts have been made by doping a small amounts of the elements such as Ag,⁶ Ti,⁷ N,⁸ Al,⁹ and O (Ref. 10) into the conventional GST in order to explore phase change materials for PCM applications. It has been reported that a relatively weak bonding strength can cause a significant increase of the crystallization speed in phase change materials.^{11–13} For example, Ge-Te has a bond energy of 397 kJ/mol that is larger than Sn-Te bond (359 kJ/mol). Therefore replacement of Ge-Te by Sn-Te with weak bonding energy will increase the crystallization speed. In fact, this has been confirmed by the fact that Sn-doped GST exhibits a faster crystallization speed as well as slightly higher crystallization temperature and lower melting point compared with pure GST.¹¹ Naturally, it is also very interesting to see how the structure and physical properties of GST

can be modified if an element is doped into GST with much weaker connection to Te. Therefore, in this letter, we deposited Zn-doped GST thin films by magnetron co-sputtering and investigated the structural, thermal, optical, and electrical properties, since bonding energy of Zn-Te (155.2 kJ/mol)¹⁴ is lower than that of Ge-Te or Sn-Te. We aim at developing Zn-doped GST materials that possess the characteristics of better thermal stability and faster crystallization speed or even show better phase-change properties than any others.

Zn-doped GST films with a thickness of 200 nm were deposited on quartz substrates and SiO_2/Si (100) by magnetron co-sputtering method using separate Zn and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ alloy targets. In each run of the experiment, the chamber was evacuated to $1.6 \times 10^{-4}\text{ Pa}$, and then Ar gas was introduced to 0.3 Pa for the film deposition. A GST film with the same thickness was also prepared for comparison. The concentration of Zn dopant in the Zn-doped GST films, measured by using energy dispersive spectroscopy (EDS), was identified to be 6.37 at.%, 8.13 at.%, 15.16 at.%, 19.78 at.%, and 21.21 at.%, respectively. The sheet resistances of as-deposited films as a function of elevated temperature (non-isothermal) and as a function of 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 GST and Zn-doped GST thin films was examined by x-ray diffraction (XRD), Raman scattering, and x-ray photoelectron spectroscopy (XPS). The optical band gap of the films was measured using UV-VIS-NIR spectrophotometer.

Figures 1(a)–1(d) show x-ray diffraction patterns of the as-deposited films with different Zn-doping concentration and subsequently annealed at 200 , 250 , and 350°C for 3 min, respectively. No diffraction peaks are observed in Fig. 1(a), indicating that all the as-deposited samples are amorphous in nature. On the other hand, the diffraction peaks corresponding to face-centered-cubic (fcc) phase peaks (200) and (220) orientations appear in the GST, $\text{Zn}_{6.37}(\text{GST})_{93.63}$, and

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FIG. 1. XRD patterns of GST and Zn-doped GST films (a) as-deposited, (b) 200 °C, (c) 250 °C, and (d) 350 °C, respectively.

$\text{Zn}_{8.13}(\text{GST})_{91.87}$ films annealed at 200 °C as shown in Fig. 1(b), indicating that the heating treatment at 200 °C induces a transformation from amorphous to fcc phase. Nevertheless, these fcc-(200) and (220) diffraction peaks can not be observed in $\text{Zn}_{15.16}(\text{GST})_{84.84}$ and $\text{Zn}_{19.78}(\text{GST})_{80.22}$ films annealed at 200 °C. However, with increasing annealing temperature to 250 °C, the diffraction peaks corresponding to the fcc phase appear in the $\text{Zn}_{15.16}(\text{GST})_{84.84}$ and $\text{Zn}_{19.78}(\text{GST})_{80.22}$ films as shown in Fig. 1(c). This implies that the onset transition temperatures from amorphous phase to fcc phase in GST increase gradually with increasing Zn-doping concentration. It is also interesting to see that the phase transition from fcc to hexagonal close-packed (hcp) phase occurs in $\text{Zn}_{6.37}(\text{GST})_{93.63}$ and $\text{Zn}_{8.13}(\text{GST})_{91.87}$ films with further increasing annealing temperature to 350 °C, while the structure of the $\text{Zn}_{15.16}(\text{GST})_{84.84}$ and $\text{Zn}_{19.78}(\text{GST})_{80.22}$ films are still kept at fcc phase as shown in Fig. 1(d). All these results indicate that GST film with high Zn-doping concentration has a higher crystallization temperature and the fcc phase has high thermal stability owing to the Zn dopants. This also suggests that high concentration of Zn atoms that are incorporated into the GST film serve as a center for suppression of the fcc-to-hcp phase transition, leading to a one-step crystallization process (i.e., amorphous $\rightarrow$ fcc).

Figure 2(a) displays the variation of resistance as a function of temperature for all films at a heating rate of 40 K/min. One can observe a continuous decrease of the resistance

for all the films with increasing temperature up to their respective crystallization temperature (T_c) where a drop of the sheet resistance indicates phase transition from amorphous to fcc-crystalline phase. One also can find a second drop of the resistance in the GST, $\text{Zn}_{6.37}(\text{GST})_{93.63}$, and $\text{Zn}_{8.13}(\text{GST})_{91.87}$ films, respectively, corresponding to the transformation from fcc to hcp phase. These results are in excellent agreement with the XRD patterns in Figs. 1(a)–1(d).

On the other hand, it is found that both T_c and the resistance of Zn-doped GST films increase with increasing Zn-doping concentration as shown in Fig. 2(a). The amorphous/crystalline resistance ratio of Zn-doped GST films is more than 10^5 during the crystallization process, indicating a large signal to noise ratio for reading in PCM applications. In addition, higher crystalline resistance will increase the joule heat generated by identical electrical current; thus, the programming energy can be delivered more effectively and less power is required for RESET operation.¹⁵ Therefore, Zn-doped GST films have an advantage in low power operation for high-density PCM compared to the GST film.

T_c values of $\text{Zn}_{6.37}(\text{GST})_{93.63}$, $\text{Zn}_{8.13}(\text{GST})_{91.87}$, $\text{Zn}_{15.16}(\text{GST})_{84.84}$, and $\text{Zn}_{19.78}(\text{GST})_{80.22}$ films are estimated from Figure 2(a) to be ~ 188 °C, ~ 196 °C, ~ 258 °C, and ~ 272 °C, respectively, much higher than that of conventional GST (~ 168 °C). The material with higher T_c is favored since the thermal stability of the film can be improved. However, higher T_c means lower crystallization speed. The crystallization speed is also one of the most

FIG. 2. (a) Sheet resistance as a function of temperature for undoped and Zn-doped GST films. (b) The Arrhenius extrapolation at 10-year of data retention for undoped and Zn-doped GST films.

important parameters for phase-change materials, because it strongly influences the overall operating speed of a PCM device. According to Ref. 16, the crystallization speed is usually estimated from the slope of sheet resistance vs. temperature in Fig. 2(a). Noteworthy is that there is an abrupt change in sheet resistance across the crystallization temperatures for Zn_{15.16}(GST)_{84.84} and Zn_{19.78}(GST)_{80.22} films, in contrast to the gradual change in sheet resistance for Zn_{6.37}(GST)_{93.63} and Zn_{8.13}(GST)_{91.87} films. This indicates that the crystallization speed in GST films with high Zn-doping concentration is much faster than that with low Zn-doping concentration, which is believed to come from the improvement in both the nucleation and growth processes.⁹

Fig. 2(b) presents the data retention characteristics for Zn-doped GST films. The maximum temperature for 10-years' data retention can be extrapolated by fitting the data in Fig. 2(b) with the Arrhenius equation:¹⁷ $t = \tau \exp(E_a/k_B T)$, where τ is a proportional time constant and E_a is crystalline activation energy. The failure time (t) is defined as the time when the sheet resistance reaches half of its initial magnitude at a specific isothermal temperature (T). The data retention temperatures for 10 years of the amorphous Zn_{6.37}(GST)_{93.63}, Zn_{8.13}(GST)_{91.87}, Zn_{15.16}(GST)_{84.84}, and Zn_{19.78}(GST)_{80.22} films are thus determined to be 109.4°C, 120.2°C, 167.5°C, and 175.5°C with the activation energy

E_a of 3.55 eV, 3.66 eV, 3.71 eV, and 3.72 eV, respectively. These results are much higher than those of conventional GST (88.9°C, 2.98 eV). Higher activation energy implies better thermal stability for applications as phase-change material. Therefore, PCM based on GST films with high Zn-doping concentration can store the information far long time than any others.

Based on the results above, it appears that GST films with high Zn-doping concentration are ideal with better amorphous stability, faster crystallization speed, larger crystallization activation energy, and better data retention of 10 years for PCM applications. Here, in the rest part of the paper, we will concentrate on GST film with high Zn-doping concentration, saying Zn_{15.16}(GST)_{84.84}.

Similar to that of GST films,¹⁸ the conductivity of Zn_{15.16}(GST)_{84.84} film is confirmed to be p-type using Hall effect measurements. The carrier density and mobility as a function of temperature are shown in Figure 3(a). We can see that the carrier density grows rapidly about two to three orders of magnitude from $4.646 \times 10^{18} \text{ cm}^{-3}$ at 220°C to $3.832 \times 10^{20} \text{ cm}^{-3}$ at 250°C near T_c . However, Hall mobility only increases from 0.121 cm²/Vs at 220°C to 0.134 cm²/Vs at 250°C. In connection to the five orders of magnitude drop in resistance at T_c in Fig. 2(a), it is concluded that the sharp increase of carrier density plays a major contribution to the

FIG. 3. (a) Carrier density and Hall mobility of Zn_{15.16}(GST)_{84.84} film as a function of temperature. (b) Plots of $(\alpha h\nu)^{1/2}$ vs $h\nu$ for Zn_{15.16}(GST)_{84.84} films; up-left inset figure is Vis-IR transmission spectra corresponding.

quick drop of film resistance (fast speed for PCM use) since the change of the mobility is relatively small. The rapid increase in carrier concentration also corresponds to the structural change from amorphous to a crystalline state at T_c . As the annealing temperature increases, the grain size becomes bigger from 20 to 40 nm estimated from the line-width of XRD patterns in Figure 1 using Scherer equation, which helps to reduce the grain-boundary scattering on carrier and leads to the increase in mobility.

For the phase change material, a large optical band-gap is required in order to reduce the threshold current.¹⁹ We measured UV-VIS-NIR spectra of the amorphous and crystalline $\text{Zn}_{15.16}(\text{GST})_{84.84}$ films in order to determine their optical band gaps, and the results are shown in Fig. 3(b). The optical band gap of amorphous $\text{Zn}_{15.16}(\text{GST})_{84.84}$ film (~ 0.78 eV) is slightly larger than that of GST (~ 0.70 eV). When the $\text{Zn}_{15.16}(\text{GST})_{84.84}$ film crystallizes from an amorphous to a NaCl-type fcc structure, its band gap is decreased to 0.43 eV. The decrease in optical band gap corresponds directly to a decrease in activation energy for electrical conduction and better conductivity.²⁰

Figure 4(a) shows that Raman spectra of GST and $\text{Zn}_{15.16}(\text{GST})_{84.84}$ films annealed at 250 °C and 350 °C. As for GST film, Raman modes located at 105 cm^{-1} can be associated with A_1 mode of GeTe_4 corner-sharing tetrahedral and a broad band at 155 cm^{-1} is ascribed to Sb-Te vibrations in SbTe_3 units.²¹ When the annealing temperature increases up to 350 °C, the band at 155 cm^{-1} seems to be significantly influenced by the crystallization process, which is in well agreement with general consensus about changed local arrangement of atoms around Sb on crystallization.²¹ In other words, Sb_2Te_3 component of GST alloys is mainly responsible for the phase transformation from fcc to hcp. Once Zn is introduced into GST film, two major changes in the

Raman spectra can be detected: a peak appears at 130 cm^{-1} (A_1 mode of $\text{GeTe}_{4-n}\text{Ge}_n$ ($n=1,2$) corner-sharing tetrahedral) and the Raman shift occurs at 155 cm^{-1} is restrained. Therefore, it reveals that a significant change in local bonding arrangement around Sb atoms has occurred in a GST film but this can be restrained by the Zn addition due to the suppression of phase transformation from fcc to hcp.²¹ All these could be further testified by XPS analysis.

Figures 4(b)–4(d) show XPS Zn 2p, Sb 3d, and Te 3d spectra, respectively. The binding energy of Zn 2p_{3/2} for $\text{Zn}_{15.16}(\text{GST})_{84.84}$ is 1021.7 eV that is 0.7 eV higher than metal Zn-Zn binding energies.²² This implies that Zn is bonding with other elements. In the case of Sb 3d and Te 3d spectra, it is obvious that the both peak positions shift to lower binding energy after Zn doping. It is well known that the negative shift of the binding energy increases with the decrease of neighboring atom electro-negativity from Te(2.1) to Sb(2.05), and Zn(1.6).²³ Therefore the decrease of the binding energy of Sb 3d and Te 3d is due to the fact that part of the Sb and Te atoms in Sb-Te bonds are replaced by Zn atoms, forming Zn-Sb and Zn-Te bonds. The bonding recombination among Zn, Sb, and Te atoms can also account for the suppression of the phase transformation from fcc to hcp as shown in Figure 1(d).

In conclusion, Zn-doped GST films are promising to improve phase-change characteristics for the PCM devices based on the present results. A hexagonal structure can be suppressed with high concentration of Zn addition. Especially, the $\text{Zn}_{15.16}(\text{GST})_{84.84}$ film exhibits high crystallization temperature, large crystallization activation energy, and high crystalline resistance. All these advantages assure that the phase change devices based on the films possess fast phase-change switching speed, low power consumptions, and good data retention capability. Therefore, $\text{Zn}_{15.16}(\text{GST})_{84.84}$ films

FIG. 4. (a) Raman spectra of GST and $\text{Zn}_{15.16}(\text{GST})_{84.84}$ films annealed at 250 °C and 350 °C. XPS spectra for 350 °C-annealed GST and $\text{Zn}_{15.16}(\text{GST})_{84.84}$ films: (b) Zn 2p, (c) Sb (3d), and Te (3d).

show great potentials as one of phase change materials in the future PCM applications.

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