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Te-based chalcogenide films with high thermal stability for phase change memory

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This study reports on the synthesis of tellurium-based chalcogenide films that have high thermal stability for phase change memory application. Several Te-based chalcogenide alloys of In-Bi-Te, Ag-Bi-Te, In-Sb-Te, Sn-Sb-Te, Zn-Ge-Te, and Ga-Ge-Te are reported. Their thermal, optical, and electrical properties are investigated. The results show that Bi-Te-based films have a higher crystallization temperature and greater activation energy compared with the other Sb-Te-based and Ge-Te-based films. Especially, $\text{In}_{2.8}\text{Bi}_{36.6}\text{Te}_{60.6}$ film exhibits high crystallization temperature (252 °C) and great activation energy (5.16 eV), showing much improved amorphous thermal stability. A relatively wider optical band gap (0.674 eV) of thermal annealed $\text{In}_{2.8}\text{Bi}_{36.6}\text{Te}_{60.6}$ film is obtained. In addition, it also has a higher amorphous/crystalline resistance ratio of about 10^5 , implying that current consumption could be low in the phase-change memory operation. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4711069>]

I. INTRODUCTION

Phase-change random access memory (PRAM) has been regarded as the promising candidate for the next-generation nonvolatile memory due to its excellent characteristics such as fast write/read speed, good endurance, low power consumption, and good compatibility with complementary metal-oxide semiconductor (CMOS) technologies.^{1,2} The research and development of PRAM technology have obtained great progress during the last decade. One of the dominating phase-change memory materials is represented by $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) thin films which offer amazing changes of optical and electrical properties occurring on reversible crystallization from the amorphous to the metastable fcc phase and vice versa.^{3–5} However, several critical problems still remain to be improved and resolved, such as a relatively large RESET current, a relatively short data retention life in high-temperature environment, and a lack of comprehensive understanding of device failure mechanisms.^{6,7} The former two problems are closely related to the phase-change material properties, thus the optimization of phase-change material is very important. Most of studies are underway in two ways: one is to improve $\text{Ge}_2\text{Sb}_2\text{Te}_5$ material by doping other elements and another one is to develop novel phase-change materials.

Previous reports^{8–15} have shown that doping GST with N, O, Si, Al, Sn, and In increases the crystallization temperature and improves PRAM amorphous stability. To develop novel phase-change materials, several authors^{16–20} have investigated the effect of the impurities, like Se, Ag, Sb, Ga or Co, on the performance of Te-based chalcogenide films. Matsunaga *et al.*²¹ reported that replacement of a proportion

of Sb atoms in the pseudo-binary system- $\text{GeTe-Sb}_2\text{Te}_3$ -with Bi could result in faster crystallization, because the Bi, which lies in the same group as Sb, has larger atomic radius ($r_{\text{Bi}} = 0.163 \text{ nm}$, $r_{\text{Sb}} = 0.153 \text{ nm}$).

Therefore, in this paper, Bi-Te-based films are first investigated for phase-change memory application and other Sb(Ge)-Te-based films are also prepared for comparison. Here, our purpose aims to explore new compositions which could overcome the problems, such as a relatively large RESET current and a relatively short data retention life in high-temperature environment. We are expected to find phase-change materials, which possess higher crystallization temperature, wider optical band gap, and higher resistance of the crystalline state, for PRAM application.

II. EXPERIMENTAL

The bulk targets were prepared using a conventional melt-quenching technique. The five N constituent elements were sealed at given atomic-weight percentage ratios in evacuated quartz ampoules with a diameter of 10 mm. Then the quartz ampoules containing the raw materials were heated at 870 °C for 20 h in rocking furnaces to ensure the homogenization of mixtures. Then, the ampoules were quenched in water, swiftly moved to a preheated furnace to anneal at 10 °C below T_g for 4 h to minimize inner tension induced by a quenching step. Bulk samples were obtained by breaking the ampoules.

Thin films were deposited on glass substrates, which were subjected to cleaning with soap solution, ultrasonically cleaning by trichloroethylene, acetone followed by methyl alcohol. Then, the substrate was washed by double-distilled water and dried in an oven. Then thin films were prepared by thermal evaporation technique at $\sim 3.6 \times 10^{-4} \text{ Pa}$ pressure in a

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vacuum coating system (JGP-450 model). Rate of evaporation was kept low ($\sim 2 \text{ \AA s}^{-1}$). The film thickness (d) was controlled at about 200 nm with a fluctuation of $\pm 5 \text{ nm}$ using a thickness monitor equipped in the chamber and further confirmed by Veeco Dektak 150 surface profile-meter. The as-prepared films were annealed at different temperatures for 1 h in the same vacuum chamber at pressure of $\sim 5 \times 10^{-4} \text{ Pa}$.

All the measurements reported were taken at room temperature. The compositions of the as-prepared films were measured by using energy dispersive spectroscopy (EDS), and the results were listed in the Table I. The structure of as-prepared thin films was examined by the x-ray diffraction technique (Bruker D2 PHASER Diffractometer) using $\text{CuK}\alpha$ source and the change in the sheet resistance was measured as a function of the annealing temperature using a four-point probe. Crystallization temperature (T_x) was measured by Differential Scanning Calorimetry (DSC) in argon atmosphere with heating rates of 5, 10, 15 $^\circ\text{C/min}$. The activation energy (E_a) can be obtained by the Kissinger's equation: $\ln(T_x^2/\alpha) = \ln(E/R) - \ln v + E_a/RT_x$.²² The transmission spectra of the thin films in the spectral range 800–2500 nm was obtained using Perkin-Elmer Lambda 950 UV-VIS-NIR spectrophotometer. The absorption coefficient was calculated using the relation $\alpha = -(1/d)\ln(T/A)$ (Ref. 23) and the optical band gap was also evaluated using the absorption properties, which were expressed as $\alpha(h\nu) \cdot h\nu = B(h\nu - E_{opt})^2$.²⁴

III. RESULTS AND DISCUSSION

Thermal stability in amorphous state is a dominated parameter in determining the performance of data retention in PRAM devices. To understand the thermal behaviors of the materials, we prepared three groups of the films Sb-Te-based, Ge-Te-based, and Bi-Te based films and measured their physical properties. The results are shown in Table I. For comparison, the physical parameters for some similar compositions in the literatures are also listed in Table I. Let

TABLE I. The parameters of the as-deposited and annealed Te-based chalcogenide films. For comparison, the results from the literatures are also listed.

Compositions	T_x ($^\circ\text{C}$) ^a	E_{opt} (eV)	E_a (eV)	V (min^{-1})
$\text{In}_{1.4}\text{Bi}_{37.5}\text{Te}_{61.1}$	210	0.522	4.36	4.24×10^{42}
200 $^\circ\text{C}$ -annealed		0.620		
$\text{In}_{2.8}\text{Bi}_{36.6}\text{Te}_{60.6}$	252	0.569	5.16	4.49×10^{46}
200 $^\circ\text{C}$ -annealed		0.674		
$\text{Ag}_{5.4}\text{Bi}_{61.2}\text{Te}_{33.4}$	202	0.474	3.45	4.96×10^{33}
$\text{In}_{2.5}\text{Sb}_{70}\text{Te}_{27.5}$	156	0.566	2.44	4.28×10^{25}
$\text{Sn}_{2.9}\text{Sb}_{36.7}\text{Te}_{60.4}$	124	0.530	2.04	7.76×10^{22}
$\text{Ag}_{8.3}\text{Sb}_{34.9}\text{Te}_{56.8}$ ^b	126	—	—	—
$\text{Cu}_{8.4}\text{Sb}_{35.1}\text{Te}_{56.5}$ ^b	121	—	—	—
$\text{Zn}_{5.3}\text{Ge}_{22.5}\text{Te}_{72.2}$	150	0.509	3.24	4.52×10^{35}
$\text{Ga}_{2.2}\text{Ge}_{11.4}\text{Te}_{86.4}$	200	0.609	3.47	9.45×10^{33}
$(\text{InTe})_{0.1}(\text{GeTe})$ ^c	220	0.530	—	—
$\text{Ge}_2\text{Sb}_2\text{Te}_5$ ^d	160	0.5	2.98	6.95×10^{34}

^aMeasured at a heating rate of 10 $^\circ\text{C/min}$.

^bReference 25.

^cReference 26.

^dReference 3.

us start from the Sb-Te-based films. Previous works^{25,26} have shown the thermal stability of the binary Sb-Te phase change material could be improved by adding specific foreign elements, such as Ag, Cu, etc. In this paper, the crystallization temperatures (T_x) for as-deposited $\text{In}_{2.5}\text{Sb}_{70}\text{Te}_{27.5}$ film is the highest at 156 $^\circ\text{C}$, compared with other films doped with Sn, Ag, or Cu as shown in Table I. This crystallization temperature of 156 $^\circ\text{C}$ is also higher than the reported T_x of 97 $^\circ\text{C}$ for $\text{Sb}_{38.6}\text{Te}_{61.4}$, of 121 $^\circ\text{C}$ for $\text{Cu}_{8.4}\text{Sb}_{35.1}\text{Te}_{56.5}$, and of 126 $^\circ\text{C}$ for $\text{Ag}_{8.3}\text{Sb}_{34.9}\text{Te}_{56.8}$ films,²⁵ indicating that In doping is best option to improve thermal stability in Sb-Te-based films.

While moving to Ge-Te-based films in Table I, we found that the $\text{Zn}_{5.3}\text{Ge}_{22.5}\text{Te}_{72.2}$ and $\text{Ga}_{2.2}\text{Ge}_{11.4}\text{Te}_{86.4}$ films we prepared as well as $\text{Ge}_2\text{Sb}_2\text{Te}_5$ in Ref. 3 exhibit low T_x values compared with the $(\text{InTe})_{0.1}(\text{GeTe})$ (220 $^\circ\text{C}$) film reported by Song.²⁶ Again, the results confirm that Ge-Te based films containing indium have better thermal stability. Furthermore, the similar behavior can be observed in the Bi-Te-based films. Two ternary Bi-Te-based films in Table I, $\text{In}_{1.4}\text{Bi}_{37.5}\text{Te}_{61.1}$ and $\text{In}_{2.8}\text{Bi}_{36.6}\text{Te}_{60.6}$, show higher T_x compared with $\text{Ag}_{5.4}\text{Bi}_{61.2}\text{Te}_{33.4}$. All these results confirm that the addition of indium into various films leads to the increase of the crystallization temperature.

We note that the Bi-Te-based films we deposited in the paper have a similar Bi/Te ratio but different In concentrations; the present results appear to confirm that the increase of In concentration would further raise the crystallization temperature as a result of the strong ionic bond between indium and tellurium, since $\text{In}_{2.8}\text{Bi}_{36.6}\text{Te}_{60.6}$ exhibits a higher crystallization temperature than $\text{In}_{1.4}\text{Bi}_{37.5}\text{Te}_{61.1}$. However, it is noteworthy that the crystallization temperature of an as-deposited film could be affected not only by the addition of foreign elements but also by the value of Bi/Te ratio.²⁷ Therefore changing Bi/Te ratio in the films could be another way to tune the thermal stability.

The activation energy for crystallization is another parameter to evaluate the amorphous stability of the phase change material. The Kissinger's plots for the investigated films are shown in Fig. 1. The obtained activation energies of $\text{In}_{1.4}\text{Bi}_{37.5}\text{Te}_{61.1}$, $\text{In}_{2.8}\text{Bi}_{36.6}\text{Te}_{60.6}$, $\text{Ag}_{5.4}\text{Bi}_{61.2}\text{Te}_{33.4}$, $\text{In}_{2.5}\text{Sb}_{70}\text{Te}_{27.5}$, $\text{Sn}_{2.9}\text{Sb}_{36.7}\text{Te}_{60.4}$, $\text{Zn}_{5.3}\text{Ge}_{22.5}\text{Te}_{72.2}$, and

FIG. 1. Kissinger's plots for the as-deposited Te-based films.

$\text{Ga}_{2.2}\text{Ge}_{11.4}\text{Te}_{86.4}$ are 4.36 eV, 5.16 eV, 3.45 eV, 2.44 eV, 2.04 eV, 3.24 eV, and 3.47 eV, respectively. Among them, only $\text{In}_{1.4}\text{Bi}_{37.5}\text{Te}_{61.1}$, $\text{In}_{2.8}\text{Bi}_{36.6}\text{Te}_{60.6}$, and $\text{Zn}_{5.3}\text{Ge}_{22.5}\text{Te}_{72.2}$ films have both higher activation energy and frequency factor than $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (2.98 eV, $6.95 \times 10^{34} \text{ min}^{-1}$),³ but the crystallization temperature of $\text{Zn}_{5.3}\text{Ge}_{22.5}\text{Te}_{72.2}$ is lower than that of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, because Zn-Te (155.2 kJ/mol) has a weaker bonding strength compared with the Ge-Te bond (379 kJ/mol).²⁸ Similar conclusion can be drawn that high indium concentration can increase the activation energy of the Bi-Te-based film. Therefore, in terms of two important criteria judging the thermal stability, both crystallization temperature and activation energy can be effectively improved by adding indium, which is important for data retention in PRAM applications.

The XRD patterns of the as-deposited and annealed In-doped Bi-Te-based thin films are shown in Fig. 2. For comparison, XRD result for as-deposited Bi_2Te_3 film is also displayed in Fig. 2. It is surprising that Bi_2Te_3 film exhibits a number of XRD peaks among which the (101) peak is relatively sharp and very intense as shown in Fig. 2(a). This is in sharp contrast with the XRD patterns of as-deposited In-doped Bi-Te-based films as shown in Figs. 2(b) and 2(c) where the amorphous nature of the films is evident. In Figs. 2(b) and 2(c), the broad peak in the XRD pattern of the as-

FIG. 2. XRD pattern of the 200-nm-thick (a) Bi_2Te_3 , (b) $\text{In}_{1.4}\text{Bi}_{37.5}\text{Te}_{61.1}$, and (c) $\text{In}_{2.8}\text{Bi}_{36.6}\text{Te}_{60.6}$ films as a function of the annealing temperature.

deposited film corresponds to the amorphous phase or the uncompleted crystallization. The amorphous structure is maintained well even though the films were annealing at 150 °C. However, with further increasing the annealing temperature, the $\text{In}_{1.4}\text{Bi}_{37.5}\text{Te}_{61.1}$ film becomes crystallized into a hexagonal close-packed (hcp) P312 structure at 200 °C, while the $\text{In}_{2.8}\text{Bi}_{36.6}\text{Te}_{60.6}$ film is only crystallized at 250 °C, which is close to its crystallization temperature ($T_x = 252$ °C). No peaks assigned to other structure can be observed in the In-Bi-Te films, even annealed at 300 °C. On the other hand, the crystallized peaks of the $\text{In}_{2.8}\text{Bi}_{36.6}\text{Te}_{60.6}$ film appears to be broader in width and lower in intensity compared to the $\text{In}_{1.4}\text{Bi}_{37.5}\text{Te}_{61.1}$ film annealed at 250 °C, which reveals that the increasing In atom could restrain crystal grain growth in Bi-Te-based films.

It is well known that dangling bonds are formed during the deposition of amorphous films and they will lead to the formation of the defects which produce localized states in amorphous solids.²⁹ In order to understand the effect of various doping as well as thermal annealing process on the optical band gap of the films, the optical transmission spectra of the films were measured as shown in the up-left insets of Figs. 3 and 4, and $(\alpha(h\nu))^{1/2}$ as a function of $h\nu$ (being photo energy in an unit of eV) were plotted in the main panel of Figs. 3 and 4. By extrapolating the linear portion of the curves to zero absorption, the optical band gaps (E_{opt}) are determined and listed in Table I. E_{opt} of $\text{In}_{1.4}\text{Bi}_{37.5}\text{Te}_{61.1}$, $\text{In}_{2.8}\text{Bi}_{36.6}\text{Te}_{60.6}$, $\text{Ag}_{5.4}\text{Bi}_{61.2}\text{Te}_{33.4}$, $\text{In}_{2.5}\text{Sb}_{70}\text{Te}_{27.5}$, $\text{Sn}_{2.9}\text{Sb}_{36.7}\text{Te}_{60.4}$, $\text{Zn}_{5.3}\text{Ge}_{22.5}\text{Te}_{72.2}$, and $\text{Ga}_{2.2}\text{Ge}_{11.4}\text{Te}_{86.4}$ films were determined to be 0.522 eV, 0.569 eV, 0.474 eV, 0.566 eV, 0.535 eV, 0.509 eV, and 0.609 eV, respectively. All of them have higher E_{opt} than $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (0.5 eV) film,³ except the $\text{Ag}_{5.4}\text{Bi}_{61.2}\text{Te}_{33.4}$ (0.474 eV) film. Moreover, three films including $\text{In}_{2.8}\text{Bi}_{36.6}\text{Te}_{60.6}$, $\text{In}_{2.5}\text{Sb}_{70}\text{Te}_{27.5}$, and $\text{Ga}_{2.2}\text{Ge}_{11.4}\text{Te}_{86.4}$ were found to have higher optical band gaps in comparison with $(\text{InTe})_{0.1}(\text{GeTe})_1$ (0.530 eV) film, which has been claimed to be a good candidate for PRAM application reported by Song.²⁶ The higher optical band gap illustrates that the band tail of the valence band induced by the localized Te lone pairs or the structural defects along the Te-Te chains in amorphous phase are supposed to be

FIG. 3. Plots of $(\alpha h\nu)^{1/2}$ vs $h\nu$ for some Te-based films; up-left inset figure is Vis-IR transmission spectra.

FIG. 4. Plots of $(\alpha hv)^{1/2}$ vs hv for the as-deposited and the 200 °C-annealed (a) $\text{In}_{1.4}\text{Bi}_{37.5}\text{Te}_{61.1}$, (b) $\text{In}_{2.8}\text{Bi}_{36.6}\text{Te}_{60.6}$ films; up-left inset figure is Vis-IR transmission spectra.

suppressed or reduced due to the defect saturation effect, which is favorable to decrease the threshold current of PRAM.^{30,31}

Thermal annealing can also modify the band gap of the films as evident in Figs. 4(a) and 4(b). For $\text{In}_{1.4}\text{Bi}_{37.5}\text{Te}_{61.1}$ and $\text{In}_{2.8}\text{Bi}_{36.6}\text{Te}_{60.6}$ films, thermal annealing at 200 °C can upshift the optical band gap with approximately 0.098 eV and 0.105 eV more, respectively, compared with that in as-deposited films. A larger upshift of the optical band gap could improve the signal-to-noise ratio in optically operating DVD-RAM. The upshift of the optical band gap in the annealing films could be due to the fact that the defects are gradually annealed out, and a great number of saturated bonds are produced during thermal annealing.²¹ It appears that the saturated bonds would reduce the number of defects and decrease the density of localized states in the band structure, leading to an increasing band gap.

We also investigated temperature-dependent sheet resistance (R_s) using the four-probe method. The results are shown in Fig. 5, where the decrease of R_s with increasing annealing temperature corresponds to an amorphous-to-crystalline transition in the films. The sheet resistance (R_s) of the as-deposited $\text{In}_{1.4}\text{Bi}_{37.5}\text{Te}_{61.1}$, $\text{In}_{2.8}\text{Bi}_{36.6}\text{Te}_{60.6}$, $\text{Ag}_{5.4}\text{Bi}_{61.2}\text{Te}_{33.4}$, $\text{In}_{2.5}\text{Sb}_{70}\text{Te}_{27.5}$, and $\text{Sn}_{2.9}\text{Sb}_{36.7}\text{Te}_{60.4}$ films is approximately $2.24 \times 10^6 \Omega/\square$, $2.54 \times 10^6 \Omega/\square$, $1.44 \times 10^6 \Omega/\square$, 3.56×10^5

FIG. 5. Temperature-dependent sheet resistance (R_s) for the 200-nm-thick Te-based films; all of the points represent the average values of three measurements.

$\Omega/\square$, and $3.22 \times 10^5 \Omega/\square$, which correspond to the resistivity of 44.8 Ωcm , 50.8 Ωcm , 28.8 Ωcm , 7.12 Ωcm , and 5.81 Ωcm , respectively. After annealed at various crystallization temperatures, R_s is drastically reduced to $\sim 10^1 \Omega/\square$. Among all these films, the $\text{In}_{2.8}\text{Bi}_{36.6}\text{Te}_{60.6}$ film exhibits a higher amorphous/crystalline resistance ratio of about 10^5 . Moreover, it also exhibits a higher sheet resistance (R_s) in the crystalline state compared with $\text{In}_{1.4}\text{Bi}_{37.5}\text{Te}_{61.1}$, $\text{Ag}_{5.4}\text{Bi}_{61.2}\text{Te}_{33.4}$, $\text{In}_{2.5}\text{Sb}_{70}\text{Te}_{27.5}$, $\text{Sn}_{2.9}\text{Sb}_{36.7}\text{Te}_{60.4}$, and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (Ref. 3) films, which means that it could lead to a low current consumption in the PRAM operation.

IV. CONCLUSIONS

We have prepared several Sb-Te-based, Ge-Te-based film, and Bi-Te-based chalcogenide films doped with various elements and measured their structural and physical properties using various diagnosis tools. DSC results indicate that Bi-Te-based films have higher thermal stability in terms of crystallization temperature and activation energy compared with Sb-Te- and Ge-Te-based films, and this could be further improved with indium doping. XRD measurements show that there is an amorphous-to-crystalline phase transition in the films annealed at certain temperatures, and a stable hexagonal close-packed (hcp) P312 structure in the annealed films can be significantly suppressed by increasing the indium doping. The optical band gap can be modified by thermal annealing and various doping, and the maximum band gap of 0.674 eV can be found in thermal annealed $\text{In}_{2.8}\text{Bi}_{36.6}\text{Te}_{60.6}$ film. Moreover, $\text{In}_{2.8}\text{Bi}_{36.6}\text{Te}_{60.6}$ film exhibits a higher crystalline resistance, which means that the RESET current can be reduced when the film is used in the PRAM device. These outstanding properties will make the $\text{In}_{2.8}\text{Bi}_{36.6}\text{Te}_{60.6}$ film promising for the PRAM application.

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