

Thin film alloy mixtures for high speed phase change optical storage: A study on $(\text{Ge}_1\text{Sb}_2\text{Te}_4)_{1-x}(\text{Sn}_1\text{Bi}_2\text{Te}_4)_x$

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An approach is proposed to develop recording materials for high speed phase change optical data storage. It utilizes a thin film alloy mixture between a stoichiometric GeSbTe alloy and an additive ternary telluride alloy. Selection rules for an additive alloy are suggested. For a test, $(\text{Ge}_1\text{Sb}_2\text{Te}_4)_{1-x}(\text{Sn}_1\text{Bi}_2\text{Te}_4)_x$ thin films are deposited by co-sputtering and their structural and thermal properties are studied. $\text{Ge}_1\text{Sb}_2\text{Te}_4$ and $\text{Sn}_1\text{Bi}_2\text{Te}_4$ are found to form a completely soluble pseudo-binary system, whose crystalline lattice parameters obey Vegard's rule over the entire range of x ($0 < x < 1$). Furthermore, the alloy mixtures display an increasing tendency for crystallization with $\text{Sn}_1\text{Bi}_2\text{Te}_4$ content. Dynamic tests of disk samples are made to show the effectiveness of the approach for high speed erasure. © 2002 American Institute of Physics.
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In the area of optical data storage, gains in recording density and data transfer rate have been achieved primarily by reduction in laser spot size and/or increase in linear velocity of disk. Either of these approaches has been rendering a diminished beam dwell time. In phase change optical recording, therefore, faster crystallizing recording materials have been pursued continuously. As for widely used GeSbTe alloys, efforts have been made to enhance the crystallization kinetics by additive elements¹⁻³ and/or by use of crystallization promoting layers.⁴⁻⁶

Herein, we advance an approach that involves a deliberate use of an additive ternary telluride alloy which, on mixing with a stoichiometric GeSbTe alloy, forms a homogeneous pseudo-binary alloy mixture $(\text{Ge}_a\text{Sb}_b\text{Te}_c)_{1-x}(\text{A}_a\text{B}_b\text{Te}_c)_x$, where x is a mole fraction ($0 < x < 1$) and a , b , and c represent atomic mole ratios. The following selection rules are suggested for $\text{A}_a\text{B}_b\text{Te}_c$: First, $\text{A}_a\text{B}_b\text{Te}_c$ is a telluride compound with atomic mole ratios and a crystal structure essentially identical to the master stoichiometric $\text{Ge}_a\text{Sb}_b\text{Te}_c$ alloy. Second, A and B are elements belonging to the group IV and V, respectively, and at least one of them has a higher atomic number and thus a smaller elemental bond energy than its counterpart in the GeSbTe alloy. In light of the results of Coombs *et al.*,¹ $(\text{Ge}_a\text{Sb}_b\text{Te}_c)_{1-x}(\text{A}_a\text{B}_b\text{Te}_c)_x$ is expected to have enhanced crystallization kinetics compared to $\text{Ge}_a\text{Sb}_b\text{Te}_c$, and sulfide and selenide alloys may not be usable as an additive alloy. The following alloys may be taken as candidates for an additive alloy depending on the stoichiometry of a GeSbTe alloy:^{7,8} (1) $\text{Ge}_4\text{Sb}_1\text{Te}_5$ type: $\text{Pb}_4\text{Sb}_1\text{Te}_5$, $\text{Sn}_4\text{Bi}_1\text{Te}_5$, (2) $\text{Ge}_2\text{Sb}_2\text{Te}_5$ type: $\text{Pb}_2\text{Bi}_2\text{Te}_5$, (3) $\text{Ge}_1\text{Sb}_2\text{Te}_4$ type:

$\text{Ge}_1\text{Bi}_2\text{Te}_4$, $\text{Pb}_1\text{Bi}_2\text{Te}_4$, $\text{Sn}_1\text{Bi}_2\text{Te}_4$, $\text{Sn}_1\text{Sb}_2\text{Te}_4$, (4) $\text{Ge}_1\text{Sb}_4\text{Te}_7$ type: $\text{Ge}_1\text{Bi}_4\text{Te}_7$, $\text{Pb}_1\text{Bi}_4\text{Te}_7$, $\text{Sn}_1\text{Bi}_4\text{Te}_7$.

In this letter, we report our recent study on the co-sputtered thin film alloy mixtures $(\text{Ge}_1\text{Sb}_2\text{Te}_4)_{1-x}(\text{Sn}_1\text{Bi}_2\text{Te}_4)_x$ in order to find out if the proposed approach may be useful to develop GeSbTe-based recording materials for high speed phase change optical data storage.

By co-sputtering individual $\text{Ge}_1\text{Sb}_2\text{Te}_4$ and $\text{Sn}_1\text{Bi}_2\text{Te}_4$ targets with varying the sputtering power to the $\text{Ge}_1\text{Sb}_2\text{Te}_4$ target and at a fixed power to the $\text{Sn}_1\text{Bi}_2\text{Te}_4$ target, $(\text{Ge}_1\text{Sb}_2\text{Te}_4)_{1-x}(\text{Sn}_1\text{Bi}_2\text{Te}_4)_x$ thin films of various x were prepared in a radio frequency magnetron sputtering system. Mole fraction (x) was determined by Rutherford backscattering spectrometry (RBS) with 2 MeV He^{2+} ion beam using 100 nm films on Si (001) substrates. The films were annealed at 150 and 300 °C, respectively, in an Ar ambient vacuum furnace for 30 min, and x-ray diffractions were carried out with $\text{Cu } K\alpha$ radiation (M18XHF-SRA) for crystal structure analysis. Thermal analysis was carried out by differential scanning calorimetry (DSC, TA DSC 2010) with an Ar flow using a few μm $(\text{Ge}_1\text{Sb}_2\text{Te}_4)_{1-x}(\text{Sn}_1\text{Bi}_2\text{Te}_4)_x$ film deposits stripped off from glass substrates. Disk dynamic properties were also studied by use of disk samples with recording layers of a few selected compositions in four-layer stacks consisting of AlCr (100 nm)/ZnS-SiO₂ (20 nm)/recording layer (20 nm)/ZnS-SiO₂ (270 nm) on polycarbonate substrate (1.2 mm thickness, track pitch of 0.6 μm). An optical disk test bed⁹ was used, equipped with a laser diode of 650 nm in wavelength and an objective lens of a numerical aperture 0.6.

Shown in Fig. 1 is an example of RBS spectrum together with simulation curves. ⁵⁰Sn, ⁵¹Sb, and ⁵²Te are evidently indistinguishable because of their neighboring atomic numbers, but ³²Ge and ⁸³Bi yield clearly separable peaks from the

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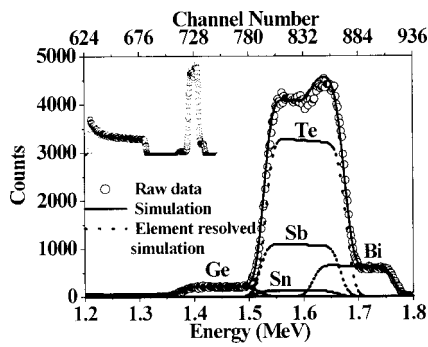


FIG. 1. A RBS spectrum with simulation curves for the sample $(\text{Ge}_1\text{Sb}_2\text{Te}_4)_{0.816}(\text{Sn}_1\text{Bi}_2\text{Te}_4)_{0.184}$. The inset is the spectrum in full energy range.

rest. From the intensities of Ge and Bi peaks, the film composition was estimated in terms of a mole fraction x on the assumption that the respective stoichiometry of $\text{Ge}_1\text{Sb}_2\text{Te}_4$ and $\text{Sn}_1\text{Bi}_2\text{Te}_4$ is preserved in the co-sputtered films. This led to $(\text{Ge}_1\text{Sb}_2\text{Te}_4)_{0.816}(\text{Sn}_1\text{Bi}_2\text{Te}_4)_{0.184}$ in the case shown. The $\text{Sn}_1\text{Bi}_2\text{Te}_4$ mole fraction accessible with the present co-sputtering method turned out to range from $x=0.125$ to $x=0.482$ including $x=0$ and 1.

In Fig. 2, DSC experiment results due to a heating rate of $35^\circ\text{C}/\text{min}$ are shown for the as-sputtered films of $x=0$, 0.125, 0.224, and 0.482. Two separate exothermic peaks are noticeable. According to a previous study,¹⁰ the first peak marked 1 results from an amorphous to face centered cubic (fcc) transformation and the second peak marked 2 from an fcc to hexagonal close packed (hcp) transformation. As will be shown later, the same interpretations hold for the peaks marked 3 and 4 in the case of $x=0.125$. From comparison with the $x=0$ case, a slight decrease can be noticed in the peak temperature of an amorphous to fcc transformation. The broad shoulders preceding the peaks 3 and 4 are presumed to have much to do with the presence of the embryonic crystalline states of a varying degree in the co-sputtered film, resulting from a prolonged sputtering of a few- μm -thick film as well as strain energy relaxation due to atomic reconfiguration. Unlike the above two cases, the films with higher mole fractions were found to display the absence of the first peak and a gradual vanishment of the second peak with increasing mole fraction, clearly signifying a progressive increase in crystallization tendency. The activation energy for an amorphous to fcc crystallization in each $x=0$ and $x=0.125$ case was derived via Kissinger's analysis¹¹ of DSC results due to three different heating rates of 15, 25, and

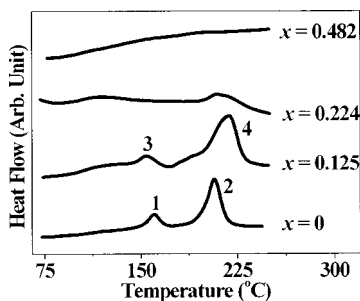


FIG. 2. DSC experiment results due to a heating rate $35^\circ\text{C}/\text{min}$ for the as-sputtered $(\text{Ge}_1\text{Sb}_2\text{Te}_4)_{1-x}(\text{Sn}_1\text{Bi}_2\text{Te}_4)_x$ films of various mole fractions (x).

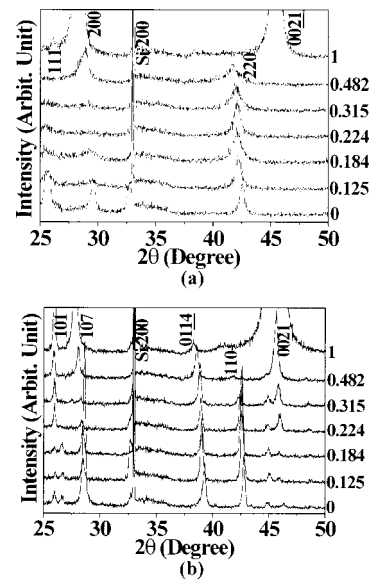


FIG. 3. X-ray diffraction spectra of the $(\text{Ge}_1\text{Sb}_2\text{Te}_4)_{1-x}(\text{Sn}_1\text{Bi}_2\text{Te}_4)_x$ films annealed at (a) 150°C and (b) 300°C . The numbers on the right of each figure indicate mole fractions (x).

$35^\circ\text{C}/\text{min}$. The analysis led to 1.83 and 1.60 eV, respectively, hence a decrease in activation energy by 0.23 eV due to additive mixing of the $\text{Sn}_1\text{Bi}_2\text{Te}_4$ alloy by $x=0.125$.

X-ray diffraction spectra are shown in Figs. 3(a) and 3(b) for the co-sputtered films with various mole fractions of $\text{Sn}_1\text{Bi}_2\text{Te}_4$ annealed at 150 and 300°C , respectively. Diffraction spectra in Fig. 3(a) can be indexed unambiguously as a single fcc phase except for the $x=1$ ($\text{Sn}_1\text{Bi}_2\text{Te}_4$) case, for which indexing accorded with a two phase mixture of an fcc and an hcp phase. As for the films annealed at 300°C , every diffraction spectra can be indexed according essentially to a single hcp phase, which is in agreement with the DSC results. One should notice striking features particularly from Fig. 3(a). With increasing mole fraction, each fcc peak, for instance (220) peak, undergoes a gradual negative shift in 2θ angle without peak splitting and it is accompanied by growth in peak width. Both of these results suggest a homogeneous mixing of the two alloys occurred on the atomic scale, attended by lattice distortion due to accommodation of atoms of different sizes: without mixing, (220) peak would have appeared split with 2θ angle separation of more than 2° between $\text{Ge}_1\text{Sb}_2\text{Te}_4$ ($a_{\text{fcc}}=6.01\text{ \AA}$) and $\text{Sn}_1\text{Bi}_2\text{Te}_4$ ($a_{\text{fcc}}=6.33\text{ \AA}$). The dependence of lattice parameters (a_{fcc} and c_{hcp}) on the mole fraction is shown in Fig. 4 that was derived from Fig. 3 via a least square method. It vividly illustrates

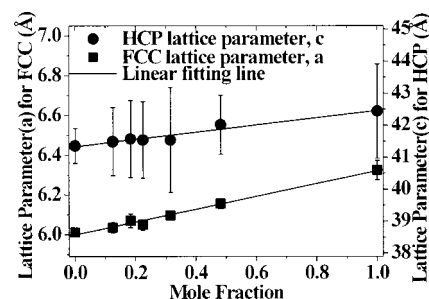


FIG. 4. Variation of lattice parameters (a_{fcc} and c_{hcp}) with mole fraction; notice linear relationships; called Vegard's rule.

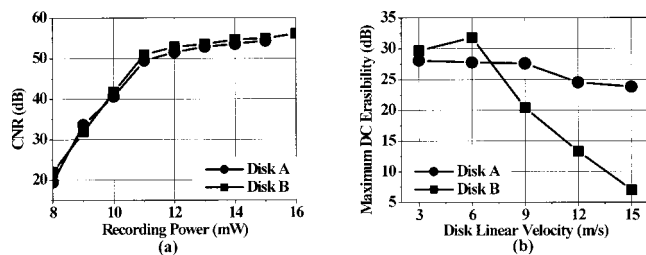


FIG. 5. Comparison of disk dynamic characteristics between the two disks using recording layers of $(\text{Ge}_1\text{Sb}_2\text{Te}_4)_{0.85}(\text{Sn}_1\text{Bi}_2\text{Te}_4)_{0.15}$ (disk A) and $\text{Ge}_1\text{Sb}_2\text{Te}_4$ (disk B). (a) Dependence of carrier to noise ratio (CNR) on recording power, (b) dependence of maximum dc erasibility on disk linear velocity.

linear relationships, so-called Vegard's rule, over the entire range of mixing, and therefore confirms that $\text{Ge}_1\text{Sb}_2\text{Te}_4$ and $\text{Sn}_1\text{Bi}_2\text{Te}_4$ constitute a completely soluble pseudo-binary system.

Dynamic properties of disk samples with recording layers of $(\text{Ge}_1\text{Sb}_2\text{Te}_4)_{0.85}(\text{Sn}_1\text{Bi}_2\text{Te}_4)_{0.15}$ (disk A) and $\text{Ge}_1\text{Sb}_2\text{Te}_4$ (disk B) were studied. Reflectivity values of the as-prepared amorphous (R_a) and of the initialized crystalline states (R_c) were, respectively, 3% and 11% for disk A and 3.5% and 10% for disk B. Writing of amorphous marks was carried out at the disk linear velocity of 9 m/s by use of a recording pattern of $3T_w$ ($T_w = 23.3$ ns) duration at a recording power level followed by $7T_w$ duration at a readout power level (1 mW). Carrier to noise ratio (CNR) values at the readout frequency of 4.29 MHz are shown in Fig. 5(a) as a function of recording power. One can notice that CNR values are remarkably similar between the two disks, yielding only 1–2 dB difference regardless of a recording power. Since the difference in contrast ratio $(R_c - R_a)/(R_c + R_a)$ of the two disks (0.48 for disk A and 0.57 for disk B) accounts for 1.5 dB CNR difference, it follows that recording characteristics and underlying material characteristics thereof are quite similar.

By contrast, a striking difference in erasing or crystallization characteristics was observed between the two disks. For erasing experiments, amorphous marks were formed first at 15 mW recording power with the same conditions as above and subsequently dc erased with varying erasing power at a disk linear velocity ranging from 3 to 15 m/s. The results are shown in Fig. 5(b), tracing out maximum dc erasibility as a function of linear velocity. As for disk B, erasibility decreases very rapidly with increasing linear velocity, reaching below 20 dB near 9 m/s. On the contrary, disk A is found to maintain a high erasibility around 25 dB even at the

velocity of 15 m/s, consistent with the DSC experiment results.

In summary, thin film alloy mixtures were proposed as promising recording materials for high speed phase change optical data storage. $\text{Ge}_1\text{Sb}_2\text{Te}_4$ with an additive $\text{Sn}_1\text{Bi}_2\text{Te}_4$ alloy were tested and found to form a homogeneous single phase mixture with enhanced crystallization kinetics. The results are understandable in view of the selection rules set out in the beginning. First, the equilibrium phases of $\text{Ge}_1\text{Sb}_2\text{Te}_4$ and $\text{Sn}_1\text{Bi}_2\text{Te}_4$ have the same space group symmetry ($R\bar{3}m$), a small lattice parameter misfit (4.8% in a and 2.2% in c),^{12,13} and the same valencies of the constituent elements. All these together warrant the formation of a stoichiometric pseudo-binary solid solution with a complete solubility between the two alloys. Second, the bond energies of Sn–Sn, Bi–Bi, Sn–Te, and Bi–Te are smaller than those of Ge–Ge, Sb–Sb, Ge–Te, and Sb–Te, respectively.¹⁴ These reduced bond energies would benefit promoted nucleation in particular during amorphous to crystalline transformation of the mixed alloy.

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