High-Speed Reversible Phase-Change Optical Recording in GeSb – Based Alloys

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ABSTRACT

GeSb based thin films doped with Sn and In are prepared and crystallization temperatures, crystalline microstructure and phases are determined. The dynamic writing/erasing characteristics of GeSbSnIn and GeSbIn phase change optical disks with simple four layers stack design are measured using blue laser tester. Good optical contrast and erasability are obtained at linear velocities of 14 m/s and 12.5 m/s on 400 nm and 250 nm marks respectively. The influence of the ratio of erasing and writing powers on the recording performance of disks is highlighted.

Keywords: phase-change recording, antimony based alloys, blue-violet laser, rewritable disk, dynamic testing, high-speed writing/erasing.

1. INTRODUCTION

One of the main aims of phase-change optical recording is to increase the writing/erasing speed[1]. The recrystallization velocity of phase-change material optimization (i.e. increasing of the velocity) is most important for the achievement of high data rate performance. Crystallization should be fast at elevated temperatures (below the melting point of the phase-change layer) to allow for high erasure speeds in the direct overwrite mode, while it should be low at room temperature to prevent amorphous marks from spontaneous crystallization during storage and operation conditions[2]. Furthermore, the optical and thermal properties of the phase-change material and disk multilayer stack should be such that a good optical contrast between the amorphous and crystalline state and sensitivity to laser beam irradiation phase transformations can be obtained. Current phase-change materials meeting these criteria are doped eutectic Sb–Te compositions as AgInSbTe and SbTeGe. However, high-speed disks made with these materials show low amorphous phase stability and high media noise, which makes applicability for recording speeds over 28 m/s unlikely [3]. Recently there is an increasing interest on non-tellurium based materials for phase-change recording. Usually these are alloys with high antimony content as GeSb[4] and GaSb[5] with some dopants. GeSb and GaSb with compositions around eutectics are Sb-based phase change materials characterized by both fast crystallization and high thermal stability of their amorphous recorded mark. These materials have hexagonal structure, which is the same as that of Sb as identified[6] by XRD analyses. Crystallization temperatures of these materials are higher than that of Sb. In this paper we report on the studies of a new In and Sn doped GeSb materials for high-speed phase-change optical recording.

2. EXPERIMENTAL DETAILS

Optical transmittance and reflectance of the as –deposited and crystallized phase-change layers were measured in 400 – 1200 nm spectral range at normal light incidence by Cary 5E spectrophotometer. Optical constants (refractive index, n and absorption coefficient, k) were determined by three-step algorithm[7]. It includes application of the so-called (TR_fR_m) algebraic inversion method[8], followed by (TR_f) and (TR_m) methods and finally a selection of the most accurate solution of each of the above methods. T and R_f are transmittance and reflectance of samples deposited on transparent substrates

BK-7 and R_m is reflectance of the corresponding films deposited on Si-substrates. Application of (TR_fR_m) method allows simultaneously determination of *n*, *k* and *d* (film thickness). Then, the value of the film thickness obtained is used for recalculating of *n* and *k* by the more accurate (TR_f) and (TR_m) methods using Newton-Raphson iterative algorithm[9]. The combination of the most accurate solutions from each of the applied methods is accepted as final dispersion curves for *n* and *k*. For reflection measurements as a function of temperature, sandwich stacks (phase-change recording film between two ZnS-SiO_2 layers) were sputtered on silicon substrates. X-ray diffraction (XRD) spectra of the crystalline (crystallized by annealing to 250 °C) thin films (thickness, 150 nm) on glass substrates were measured on a grazing-angle incidence diffractometer using Cu K_α radiation. Data were collected in the diffraction angle range of $2\theta = 20^\circ$ to 80°, at the scanning rate of 2°/min and with the step of 0.02°. Transmission electron microscopy (TEM) was performed using a Philips CM12ST TEM, operated at 120 kV. Optical disks with conventional four layers stack structure consisting on a phase-change layer sandwiched between two ZnS-SiO_2 layers and an Ag layer acting as a mirror and heat sink were studied. All layers were deposited by sputtering onto a 120 mm polycarbonate substrate with 0.74 μm track pitch. No additional layers for crystallization enhancement or absorption control were applied. CNR and erasability were measured using a Pulstec DDU 1000 dynamic tester with λ = 405 nm and NA = 0.65.

3. RESULTS AND DISCUSSION

The wavelength dependence of optical constants (refractive index n and extinction coefficient k) of the amorphous and crystalline phases of GeSb and GaSb phase-change alloy films is given in Fig. 1. The refractive index n of the as-deposited (amorphous) state and crystalline (annealed) state monotonically decreases towards the shorter wavelengths in both alloy films. After 650 nm downwards n of the amorphous phase of GeSb was higher than the crystalline one. On the other hand, k of the as-deposited state increases from 800 nm up to 450 nm then and remain nearly constant to the shortest measured wavelength of 400 nm. The behavior of k in crystalline state was continuous increasing from 400 nm up to 600 nm and slight decrease afterward to 800 nm. The optical constants change at wavelength of 405 nm, which is of current technological interest seems to be appropriate to obtain the necessary optical contrast. The optical constants of GaSb alloy film however especially the refractive index almost not changed between the amorphous and crystalline states. Moreover the extinction coefficient and refractive index at 405 nm are nearly the same for as-deposited and annealed GaSb films. It could be suggested that the optical contrast of the disks with GaSb phase-change layer will be not high enough. Nevertheless Ga and GaSb are of interest for us as doping components to GeSb based phase-change alloys for high- speed recording[10].

To determine the crystallization temperature, the phase change layer is sandwiched between dielectrics (as in an actual recording stack) and heated in an oven at a constant heating rate while monitoring the reflection of the sample. Fig. 2 shows typical reflection measurements for $Ge_{10}Sb_{90}$ doped with different single dopants during heating at 50°C/min. For the $Ge_{10}Sb_{90}$ composition, the amorphous-to-crystalline phase transition occurs abruptly at 174 °C. In such kind of transition, it is believed that nucleation occurs (if any) only sporadically, but once some nuclei have been formed, the high growth speed results in rapid crystallization of the sample. It was observed that GeSb alloys are growth-dominated type materials[11]. Qualitatively the same are phase transitions in doped phase-change layers although in some cases the amorphous-to-crystalline transition proceeds rather more smoothly. According to the crystallization temperature dopants may be divided in three groups: dopants which leads to crystallization temperature increasing – Ge, dopants which cause almost no change in Tx as Sn[12] and dopants which decrease the crystallization temperature of basic $Ge_{10}Sb_{90}$ composition – Ag, Bi, Sb. The crystallization temperatures of GeSbIn and GeSbInSn alloys are 190 °C and 179 °C respectively. Generally, the crystallization temperature (Tx) of a phase change material is used as a first indication of its archival life stability[13]. A more accurate prediction of archival life stability can be obtained by determining the (low temperature) activation energy for crystallization, and by using this value to estimate the lifetime of the recorded marks at ambient temperatures. Very good archival stability was estimated for GeSb based phase-change media[4].

Thin films of doped GeSb based phase-change material crystallize in a hexagonal structure. The hexagonal structure is similar to the Sb structure, with a small change in the lattice parameters due to dissolution of the dopant atoms. Most of the peaks detected in crystallized GeSbIn and GeSbSnIn films were of Sb. Cubic InSb crystals or SbSn crystals are not easily to be detected (if exist) because of XRD peak overlapping. The grain size estimated from the Sb (012) peaks is indicated on Fig. 3. Addition of In and Sn to the main GeSb composition leads to the grain size refinement. The average grain size was 52 nm in $Ge_{10}Sb_{90}$, and only 20 nm in GeSbInSn. TEM measurement (Fig. 4) confirms the size estimated by x-ray diffraction. Additional experiments are underway to clarify the possible existence of InSb and SbSn phases.

Two kinds of dynamic testing experiments are used. In the first one CNR and DC erasability of GeSbInSn disks were measured at 4X DVD-RW speed (14 m/s). In the second one measurements of CNR and DC erasability of small mark size (3T – 250 nm) were performed at disk rotation speed of 12.5 m/s (5.7 X HD-DVD). GeSbIn disks were used and for both experiments 3T marks were recorded on grooves. The write power dependence of the carrier-to-noise ratio (CNR) and erasability of the disks with a GeSbSnIn phase-change recording layer, with different compositions of the recording layer P are shown in Fig. 5. The recording layer thickness and the I_2 dielectric layer thickness were 12 and 15 nm respectively. The disks stacks therefore have so called rapid cooling structures. More than 50 dB CNR was measured at linear velocity of 14m/s. The writing power needed to achieve over 47-dB CNR was approximately 8 mW. Over 25 dB erasabilities using erase powers Pe of 3 mW or higher are measured on GeSbSnIn disks. An important factor for obtaining an appropriate erasability is the erasing power ratio ε, which is simply the ratio between the erasing power and the writing power. Erasability depends strongly on ε, however CNR usually is changed gradually in rather larger interval of ratios as shown in Fig. 5. Both CNR and erasability were in the practical range using wide ε interval from 0.33 to 0.50. Using GeSbIn disks writing/erasing experiments were performed at 5.7X HD-DVD linear speed (12.5 m/s, CLV) and the results are shown in Fig. 6. Writing powers necessary to obtain more than 47 dB in these disks were between 7 and 8 mW depending on Pe/Pw ratio at fixed recording layer composition and disk stack structure. The erasing powers between 2.9 mW and 4.3 mW depending on ε were used to obtain 25 dB or more eras ability. Pe/Pw ratios between 0.36 and 0.48 are suitable for achievement of adequate writing/erasing parameters as shown in Figure 6. Since the maximum available channel clock frequency in our tester is 149.13 MHz, it is not possible to record 3T marks with length of 250 nm at higher disc rotation speeds. The dynamic testing results seems promising but still many aspects of the recording/ erasing process must be optimized and tuned, which is the object of our ongoing research.

4. CONCLUSIONS

We have investigated GeSbSnIn and GeSbIn based phase change materials. Good CNR and erasability are obtained at 4X DVD-RW and 5.7X HD-DVD disks linear velocities. Strong dependence of CNR and erasability on Pe/Pw ratio was found. Writing/ erasing characteristics of these doped GeSb based materials can be tuned further by adjusting the phase-change composition, disk structure and writing strategy. These materials are promising for application in a phase-change media for high data rate optical recording.

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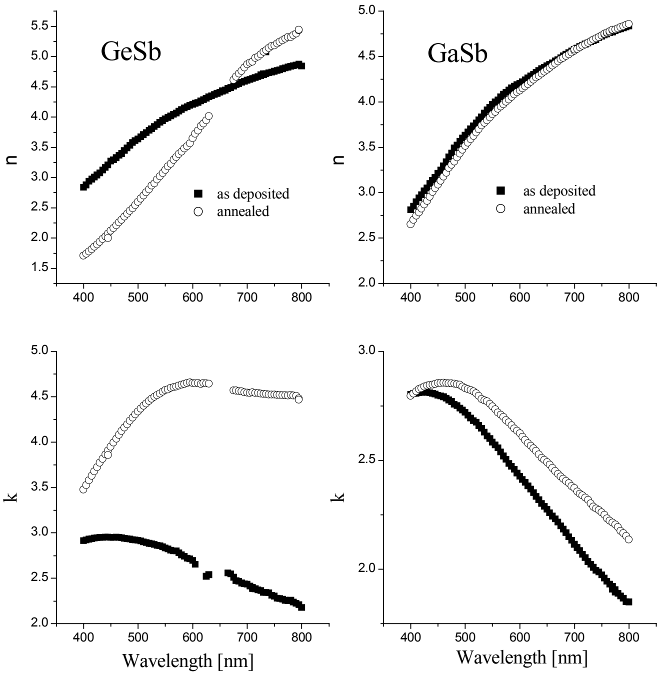

Fig.1 Optical constants of amorphous and crystalline GeSb and GaSb thin films

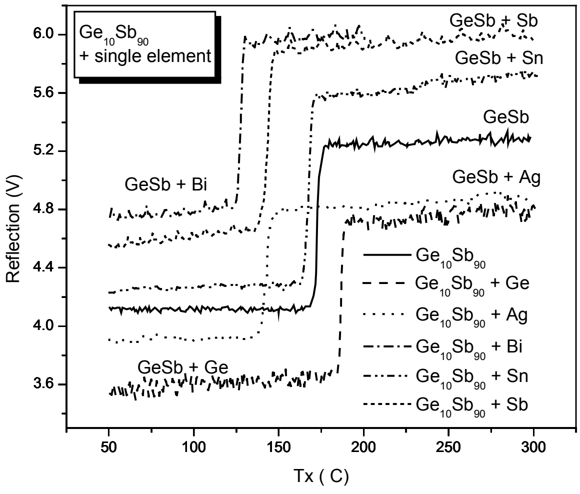

Fig.2. Reflection changes during constant rate heating for crystallization temperature measurements of GeSb films with different doping elements

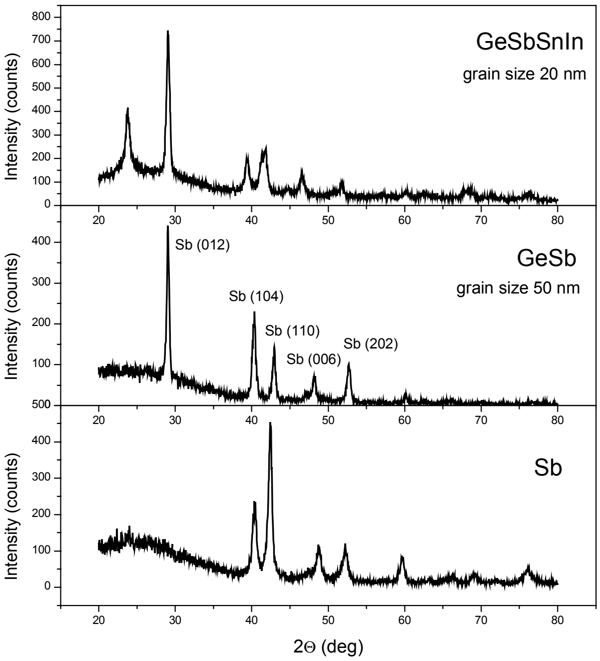

Fig.3 XRD patterns of Sb, GeSb and GeSbSnIn films

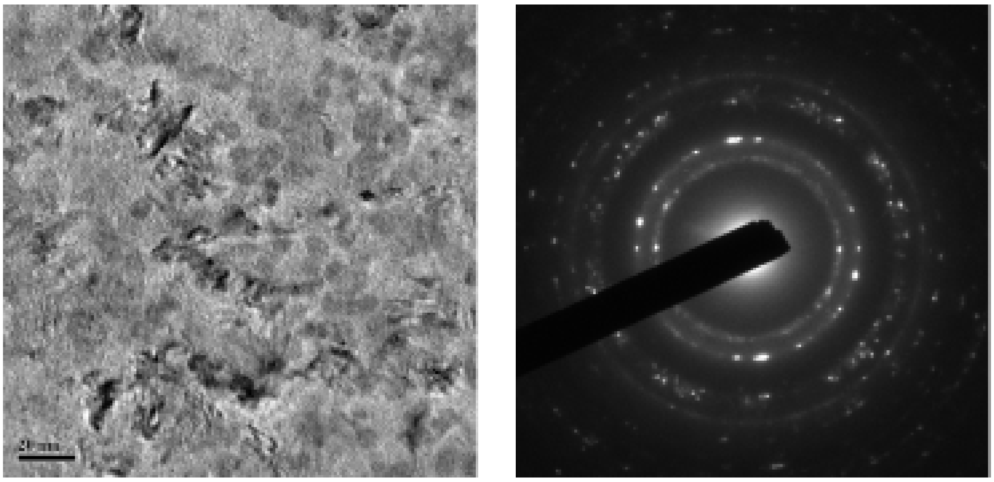

Fig.4 TEM and SAD micrograps of polycrystalline GeSbSnIn film

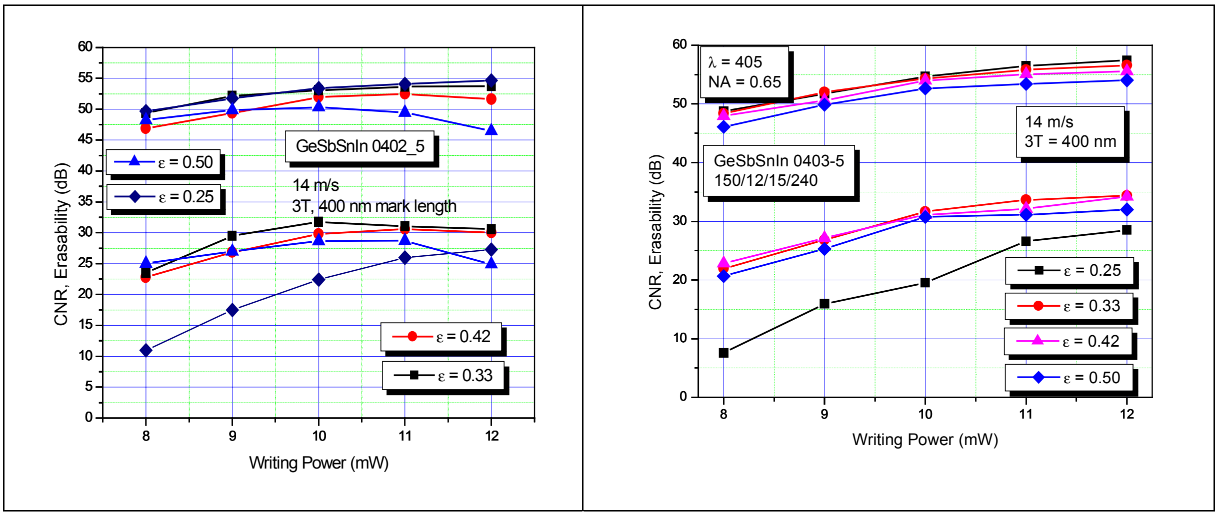

Fig.5 CNR and DC erasability dependence of writing power and Pe/Pw ratio for GeSbSnIn disks with two different compositions

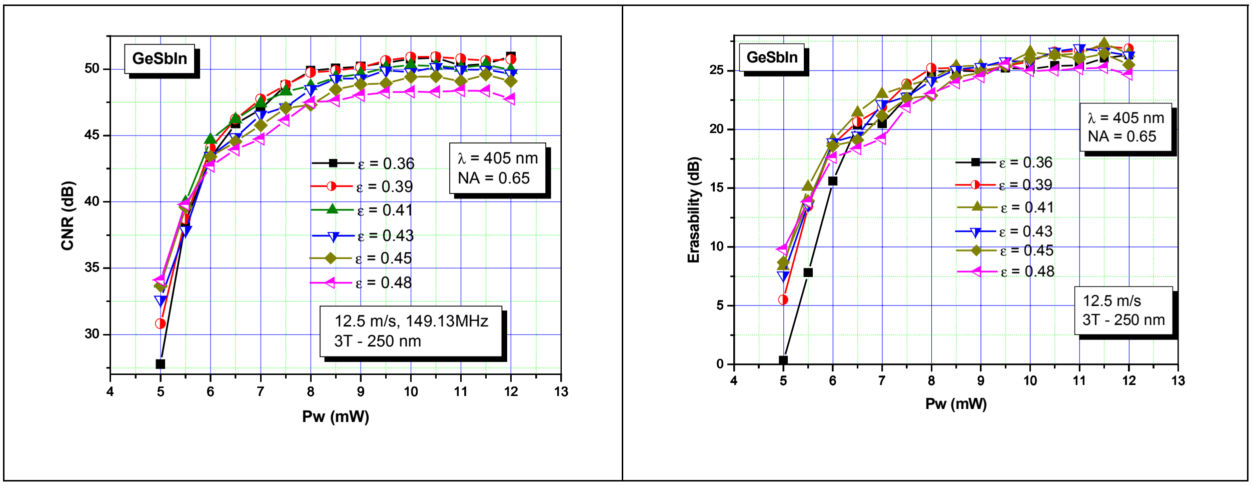

Fig.6 CNR and DC erasability dependence of writing power and Pe/Pw ratio for GeSbIn disks