Effects of the Sb$_2$Te$_3$ crystallization-induced layer on crystallization behaviors and properties of phase change optical disk

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Abstract

The conventional phase-change optical disk is generally fabricated by the sputtering process, which has a drawback of requiring an initialization process to change the as-deposited recording layer in the disk from amorphous to crystalline phases before the disk can be used for reading or writing. In order to develop an initialization-free process, the Sb$_2$Te$_3$ alloy was used as an additional layer below or above the recording Ge$_2$Sb$_2$Te$_5$ layer to study its effect on crystallization behaviors of the recording layer. The layer structures were deposited on substrates of Si wafer, Cu-mesh to examine crystal structure (XRD), amorphous-to-crystal transformation (DSC) and microstructure (TEM). The complete disk specimens were prepared on PC board to measure their dynamic properties, such as reflectivity, jitter and modulation (dynamic tester); and to examine the effects of laser pulse duration time, position and thickness of Sb$_2$Te$_3$ layer on static reflectivity of the disk (static tester), where Avrami coefficient ‘q’ in J-M-A rate equation can be derived. The results show that effect of Sb$_2$Te$_3$ layer is essentially to induce crystallization of Ge$_2$Sb$_2$Te$_5$ recording layer from (110) plane of Sb$_2$Te$_3$ crystals. This is due to the fact that the crystallization temperature of Sb$_2$Te$_3$ crystal is 85 °C below that of Ge$_2$Sb$_2$Te$_5$ crystal, in addition to a lower lattice mismatch between two crystals. The is in agreement with the J-M-A kinetic analyses that the rate controlling step for amorphous-crystal transformation in disk specimens with Sb$_2$Te$_3$ layer over 15-nm thickness is mainly governed by nucleation with $q=2.53$–$2.79>2.5$ in J-M-A equation. Regarding the effects of Sb$_2$Te$_3$ layer on disk properties, the results show that under the 10 nm Ge$_2$Sb$_2$Te$_5$ layer thickness, the Sb$_2$Te$_3$-assisted disks with lower Sb$_2$Te$_3$ layer thickness between 13 and 20 nm show the best combination of reflectivity and modulation. The most important advantage of this process is that the Sb$_2$Te$_3$-assisted disks require no initialization process, because the as-deposited disks can be directly written and erased.

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Keywords: Phase-change optical disk; Initialization-free; Digital versatile disk; Ge$_2$Sb$_2$Te$_5$ recording layer

1. Introduction

Phase-change rewritable optical disks were widely applied in the data storage in the past few years. Phase-change disk (PD) is the first commercial product in the world and the rewritable compact disk (CD-RW) came to market in 1996 and became the main product of phase-change media until now. As the demand for storage capacity increased, the digital versatile disk-rewritable (DVD-rewritable) media were widely developed and commercialized within the past 5 years. The existing products have many kinds of formats including DVD-RAM, DVD-RW and DVD+RW. The recording material and layer design may be different between all kinds of re writable DVD products but the process of manufacturing is almost the same. The conventional phase-change optical disc is generally fabricated by the sputtering process, which has a drawback of requiring an initialization process to change the as-deposited recording layer in the disk from amorphous to crystalline phases. In order to minimize the cost, many researches have been carried out to skip this initialization process [1–3]. Miao et al. [1,2] proposed that Sb$_2$Te$_3$ film could be used as an additional layer to enhance the crystallization of recording layer during low temperature sputtering process, which is called ‘Initialization-free’ process. Tominaga et al. [3] reported that the additional Sb layer could also enhance the crystallization of AgVInSbTe recording material in the disk.

Although effect of enhanced crystallization with additional Sb$_2$Te$_3$ layer was reported in the literature, the exact kinetic mechanism has not been explored satisfac-
Table 1
Disk sample designations and their layer structures, including their thickness, reflectivity and modulation

<table>
<thead>
<tr>
<th>Layer Sample design</th>
<th>ZnS–SiO₂ a (nm)</th>
<th>Sb₂Te₃ b (nm)</th>
<th>Ge₂Sb₂Te₅ c (nm)</th>
<th>Sb₂Te₅ d (nm)</th>
<th>ZnS–SiO₂ e (nm)</th>
<th>Al–Ti f (nm)</th>
<th>R g (%)</th>
<th>M h (%)</th>
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<tr>
<td>DK1</td>
<td>95</td>
<td>7</td>
<td>10</td>
<td>3</td>
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<td>7</td>
<td>10</td>
<td>7</td>
<td>15</td>
<td>100</td>
<td>10.12</td>
<td>43</td>
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<td>10</td>
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<td>100</td>
<td>16.29</td>
<td>46</td>
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<tr>
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<td>15</td>
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<td>15</td>
<td>15</td>
<td>100</td>
<td>19.24</td>
<td>18</td>
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<tr>
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<td>15</td>
<td>15</td>
<td>100</td>
<td>100</td>
<td>1</td>
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<td>100</td>
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<td>1</td>
<td>1</td>
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<td>0</td>
<td>15</td>
<td>100</td>
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<td>0</td>
<td>15</td>
<td>100</td>
<td>14.41</td>
<td>45</td>
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<tr>
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<td>20</td>
<td>10</td>
<td>0</td>
<td>15</td>
<td>100</td>
<td>17.21</td>
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<td>DK11</td>
<td>95</td>
<td>25</td>
<td>10</td>
<td>0</td>
<td>15</td>
<td>100</td>
<td>15.0</td>
<td>1</td>
</tr>
</tbody>
</table>

Lower dielectric layer.
Lower Sb₂Te₃ layer.
Recording layer.
Upper nucleation assisting layer.
Upper dielectric layer.
Reflective layer.
Reflectivity.
Modulation = (I₉max − I₉min) / I₉max × 100%.
They are too low to be measured.

Fig. 1. Layer structure of disk samples.

Fig. 2. Overwriting cycle dependence of jitter for samples DK3 and DK9.

In this study, the effect of additional Sb₂Te₃ layer on crystallization behaviors of Ge₂Sb₂Te₅ layer and its kinetic mechanisms were examined. An initialization-free process for commercial applications will be proposed.

2. Experimental

The disk samples with various layer structures were prepared on the 2.6 GB DVD-RAM polycarbonate substrates of 0.6-mm thickness by a sputtering machine with six DC magnetron and RF sputtering guns (Helix). After layer structure depositions, a bonding process is carried out to cover with another plane polycarbonate substrate to become a complete disk sample. The deposition conditions are shown in Table 1, and the layer structures are depicted in Fig. 1. In these samples, a Sb₂Te₃ additional layer was deposited on one side or both sides of the Ge₂Sb₂Te₅ recording layer with various thickness to examine their effects on disk reflectivity and modulation. A dynamic tester (Pulstec DDU-1000) was used to determine the reflectivity, modulation and jitter of the disk samples. Where the jitter as a function of overwriting cycle for Samples DK3 and DK9 is shown in Fig. 2.

The three different samples on Si wafer were prepared for XRD examination to determine the degree of amorphous-crystal transformation after sputtering or sputtering + annealing processes: (1) the as-deposited
Fig. 3. XRD patterns of the as-deposited Sb$_2$Te$_3$/Si and Sb$_2$Te$_3$/Ge$_2$Sb$_2$Te$_5$/Sb$_2$Te$_3$/Si stacks, the annealed Ge$_2$Sb$_2$Te$_5$/Si stack.

Sb$_2$Te$_3$(40 nm)/Si and (2) Sb$_2$Te$_3$ (7 nm)/Ge$_2$Sb$_2$Te$_5$ (10 nm)/Sb$_2$Te$_3$ (15 nm)/Si, (3) the annealed Ge$_2$Sb$_2$Te$_5$ (50 nm)/Si at 200 °C for 30 min.

The reflectivity vs. laser pulse duration time for disk samples DK7–DK9 was measured by a two-laser static tester (Tueoptics) to study J-M-A kinetic equation for amorphous-crystal transformation. Here, the 659 and 633 nm lasers were used to write and erase mark and to monitor the reflectivity change of mark, respectively. The reflectivity of completely amorphous state ($R_a$) of the disk could be obtained by using the writing power of 11 mW for 70 ns duration. The reflectivity ($R_i$) for different laser pulse duration time was determined by using the erasing power of 6 mW. When the reflectivity approaches a constant value as the pulse time increases, the value is called the reflectivity ($R_c$) of complete crystalline state.

The sample for TEM examination was prepared by sputtering the multi-layer Ge$_2$Sb$_2$Te$_5$ (10 nm)/Sb$_2$Te$_3$ (10 nm) on Cu-mesh to study the interface structure of the layers. The sample for Auger analysis was prepared by sputtering the Sb$_2$Te$_3$ (10 nm)/Ge$_2$Sb$_2$Te$_5$ (10 nm)/Sb$_2$Te$_3$ (15 nm) on Si wafer to examine the possible diffusion among three layers and Si wafer.

3. Results and discussion

3.1. Effect of the SbTe layer position and thickness

The reflectivity is an index to indicate the degree of amorphous–crystalline transformation of the Ge$_2$Sb$_2$Te$_5$ recording layer in the disk. The modulation is defined in Table 1, where $I_{1.4\text{max}}$ and $I_{1.4\text{min}}$ represent the maximum and minimum intensities of the disk with 14T laser pulse duration time, respectively ($T = 34.2$ ns). It is an index to indicate the ability of signal to be detected. Table 1 shows that the upper Sb$_2$Te$_3$ layer has no significant effect on reflectivity of the as-deposited disk samples, where the upper layer is the layer deposited after deposition of Ge$_2$Sb$_2$Te$_5$ recording layer. In contrast, dependence of the reflectivity and modulation of the disk on thickness of lower Sb$_2$Te$_3$ layer is shown in Fig. 6. It indicates that the maximum values of reflectivity and modulation of the disks are around a thickness of 20 nm and 13 nm, respectively. In other words, under the 10 nm Ge$_2$Sb$_2$Te$_5$ layer thickness, the Sb$_2$Te$_3$-assisted disk with lower Sb$_2$Te$_3$ layer thickness between 13 and 20 nm shows the best combination of reflectivity and modulation. When the thickness of lower Sb$_2$Te$_3$ layer is too low, the layer will become the isolated islands instead of continuous film. If the thickness is too thick, the transmittance of the films will decay drastically and the modulation of signal will become undetectable. Where the lower Sb$_2$Te$_3$ layer is deposited before Ge$_2$Sb$_2$Te$_5$ recording layer. In other words, the lower Sb$_2$Te$_3$ layer can enhance the crystallization of the Ge$_2$Sb$_2$Te$_5$ recording layer during its deposition. This is due to the fact that the crystallization temperature of the Sb$_2$Te$_3$ alloy is 85 °C below that of Ge$_2$Sb$_2$Te$_5$ alloy. Where the crystallization temperature was analyzed by differential scanning calorimetry (DSC). In other words, the lower Sb$_2$Te$_3$ layer can be much easier to become crystalline state after deposition, and then acts as the nucleation site to enhance crystallization of the Ge$_2$Sb$_2$Te$_5$ layer. It is known that the lattice mismatch between the Sb$_2$Te$_3$ and Ge$_2$Sb$_2$Te$_5$ crystals is low, which favors nucleation of crystal on the matching crystallographic plane. On the contrary, when the Ge$_2$Sb$_2$Te$_5$ layer is solidified after its deposition, the additional upper Sb$_2$Te$_3$ layer will have no significant effect on crystallization of the Ge$_2$Sb$_2$Te$_5$ recording layer. Therefore, it is concluded that the position and thickness of the additional Sb$_2$Te$_3$ layer are two important factors to affect the crystallization behavior of recording layer.
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Fig. 5. Auger depth profile of the as-deposited Sb₂Te₅/Ge₂Sb₂Te₅/Sb₂Te₅/Si stack.

3.2. XRD analysis

The XRD patterns are shown in Fig. 3 for the as-deposited Sb₂Te₅ (40 nm)/Si and Sb₂Te₅ (7 nm)/Ge₂Sb₂Te₅ (10 nm)/Sb₂Te₅ (15 nm)/Si, the annealed Ge₂Sb₂Te₅ (50 nm)/Si stacks, respectively. It indicates same diffraction angle near 42.4 degree for the annealed Ge₂Sb₂Te₅/Si and as-deposited Sb₂Te₅/Si stacks. The same but lower intensity diffraction peak of 42.4° can also be detected for the as-deposited Sb₂Te₅/Ge₂Sb₂Te₅/Sb₂Te₅/Si stack. This signifies that the Ge₂Sb₂Te₅ layer can partly become a crystalline state after deposition due to the presence of lower Sb₂Te₅ stack. The lattice matching plane between Sb₂Te₅ and Ge₂Sb₂Te₅ crystals must be (110) plane of the Sb₂Te₅ crystal. In other words, the self-crystallization of Ge₂Sb₂Te₅ layer during deposition is possible by applying an optimum thickness of the lower Sb₂Te₅ layer.

3.3. TEM analysis

In order to examine the coherency of the interface between the Ge₂Sb₂Te₅ and Sb₂Te₅ crystal, the multi-layer Ge₂Sb₂Te₅ (10 nm)/Sb₂Te₅ (10 nm) films were prepared on Cu-mesh by sputtering. The corresponding TEM micrograph of the as-deposited films is shown in Fig. 4. The surface is mainly the Ge₂Sb₂Te₅ phase. It is obvious that there are some Moire fringes at certain positions. It may signify a slight mismatch between two layers. This is in agreement with the XRD results.

3.4. Auger analysis

The as-deposited Sb₂Te₅ (10 nm)/Ge₂Sb₂Te₅ (10 nm)/Sb₂Te₅ (15 nm) stacks on Si wafer were examined by Auger depth profile analysis, as depicted in Fig. 5. It is obvious that three distinct layers can be observed. There is no significant inter-diffusion between layers after sputtering deposition, though the layer thicknesses are in nanometer ranges.

3.5. J-M-A kinetic analysis

By assuming a linear relation between the reflectance and the crystallized fraction [4], it leads to Eq. (1):

\[ \chi(t) = \frac{(R_c - R_a)}{(R_s - R_a)} \]

where \( \chi(t) \) is the crystallized fraction of specimen collected by static tester, \( R_c \) and \( R_a \) denote the reflectance of completely crystalline and completely amorphous films, respectively, and \( R_s \) is the reflectance of the sample at laser pulse time ‘t’. According to the J-

\[ \ln(y) = \ln(x(t)) - \exp(y(kt)) \]

where \( q \) is called Avrami coefficient [5,6], and \( k \) is Boltzmann’s constant. By plotting \( \ln(-\ln(1-\chi(t))) \) against \( \ln(t) \), it results in a straight line with slope \( q \). Fig. 7 shows dependence of \( q \) value on thickness of lower Sb₂Te₅ layer in the disk. It indicates that \( q \) value increases as the thickness increases. Generally speaking, \( q \) value determines the rate controlling mechanism of crystallization. When \( q \) value is less than 1.5, the crystallization process is dominated by grain growth. When \( q \) value lies between 1.5 and 2.5, the rate controlling processes are both of grain growth and nucleation. As the \( q \) value is greater than 2.5, the nucleation is the dominant rate controlling process [5,6]. In other words, it shows that the process is governed by nucleation as the thickness of lower Sb₂Te₅ layer > 15 nm (\( q = 2.53 \pm 2.79 \)). This is in agreement with the previous conclusion that the lower Sb₂Te₅ layer with

Fig. 6. Thickness dependence of reflectivity and modulation of lower Sb₂Te₅ nucleation assisting layer (samples DK7–DK11).
optimum thickness can effectively act as nucleation sites to enhance crystallization of Ge$_2$Sb$_2$Te$_5$ layer.

3.6. Jitter analysis

Jitter is an index to indicate the S.D. of the signal mark after writing-erasing cycles. Fig. 2 shows the jitter dependence on two different disk designs: one disk with an additional lower Sb$_2$Te$_3$ layer (sample DK9), another disk with both upper and lower Sb$_2$Te$_3$ layers (sample DK3). It implies that both disks are within commercially acceptable jitter values (jitter < 8.5%) [7]. The jitter values are better for sample DK3 than for DK9. In other words, the upper Sb$_2$Te$_3$ layer has no significant effect on crystallization of the recording layer during deposition, but it is beneficial in terms of jitter value.

4. Conclusions

The Sb$_2$Te$_3$ additional layer was deposited on the one side or both sides of the recording Ge$_2$Sb$_2$Te$_5$ layer of the commercial 2.6 GB DVD-RAM disk to examine their effects on disk properties and crystallization behaviors. From the experimental results, the following conclusions can be drawn: (1) The lower Sb$_2$Te$_3$ layer at an optimum thickness (approx. 13–20 nm) can effectively act as the nucleation sites for crystallization of the Ge$_2$Sb$_2$Te$_5$ recording layer during deposition, i.e. the initialization-free disk can be obtained. (2) The upper Sb$_2$Te$_3$ layer has no significant effect on crystallization of recording layer, but it is beneficial to jitter improvement. (3) The lower Sb$_2$Te$_3$ layer can assist nucleation of the recording layer and was proved by J-M-A kinetic analysis, where Avrami coefficient $q$ is greater than 2.5.

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References