Available online at www.sciencedirect.com

SCIENCE DIRECT®

Surface and Coatings Technology 177–178 (2004) 795–799

SURFACE & COATINGS TECHNOLOGY

www.elsevier.com/locate/surfcoat

Effects of the Sb_2Te_3 crystallization-induced layer on crystallization behaviors and properties of phase change optical disk

Wei Hsiang Wang, Li Chun Chung, Cheng Tzu Kuo*

Department of Materials Science and Engineering, National Chiao Tung University, 1001 Ta-Hsueh Road, Hsinchu 300, ROC Taiwan

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_2Te_3 alloy was used as an additional layer below or above the recording $Ge_2Sb_2Te_5$ 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_2Te_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_2Te_3 layer is essentially to induce crystallization of $Ge_2Sb_2Te_5$ recording layer from (110) plane of Sb_2Te_3 crystals. This is due to the fact that the crystallization temperature of Sb_2Te_3 crystal is 85 °C below that of $Ge_2Sb_2Te_5$ 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_2Te_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_2Te_3 layer on disk properties, the results show that under the 10 nm $Ge_2Sb_2Te_5$ layer thickness, the Sb_2Te_3-assisted disks with lower Sb_2Te_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_2Te_3-assisted disks require no initialization process, because the as-deposited disks can be directly written and erased.

Keywords: Phase-change optical disk; Initialization-free; Digital versatile disk; $Ge_2Sb_2Te_5$ 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 rewritable 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_2Te_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_2Te_3 layer was reported in the literature, the exact kinetic mechanism has not been explored satisfac-

---

*Corresponding author. Tel.: +886-3-5731-949; fax: +886-3-5721-065.

E-mail address: ctkuo@mail.nctu.edu.tw (C.T. Kuo).

0257-8972/04/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2003.06.016

Table 1
Disk sample designations and their layer structures, including their thickness, reflectivity and modulation

Layer Sample design	$ZnS–SiO_2$[a] (nm)	Sb_2Te_3[b] (nm)	$Ge_2Sb_2Te_5$[c] (nm)	Sb_2Te_3[d] (nm)	$ZnS–SiO_2$[e] (nm)	Al–Ti[f] (nm)	R[g] (%)	M[h] (%)
DK1	95	7	10	3	15	100	9.45	24
DK2	95	7	10	7	15	100	10.12	43
DK3	95	10	10	10	15	100	16.29	46
DK4	95	15	10	15	15	100	19.24	18
DK5	95	0	10	10	15	100	[i]	[i]
DK6	95	0	10	15	15	100	[i]	[i]
DK7	95	5	10	0	15	100	9.4	24
DK8	95	10	10	0	15	100	10.41	42
DK9	95	15	10	0	15	100	14.41	45
DK10	95	20	10	0	15	100	17.21	43
DK11	95	25	10	0	15	100	15.0	[i]

[a] Lower dielectric layer.
[b] Lower Sb_2Te_3 layer.
[c] Recording layer.
[d] Upper nucleation assisting layer.
[e] Upper dielectric layer.
[f] Reflective layer.
[g] R = reflectivity.
[h] m = modulation = $(I_{14\max} - I_{14\min})/I_{14\max} \times 100\%$.
[i] They are too low to be measured.

torily. Therefore, it has not been accepted commercially. In this study, the effect of additional Sb_2Te_3 layer on crystallization behaviors of $Ge_2Sb_2Te_5$ 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 cove 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, the Sb_2Te_3 additional layer was deposited on one side or both sides of the $Ge_2Sb_2Te_5$ 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

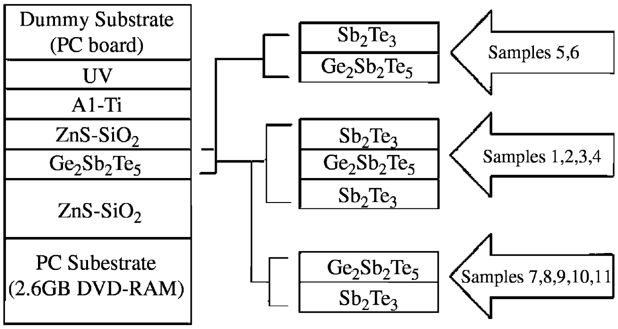

Fig. 1. Layer structure of disk samples.

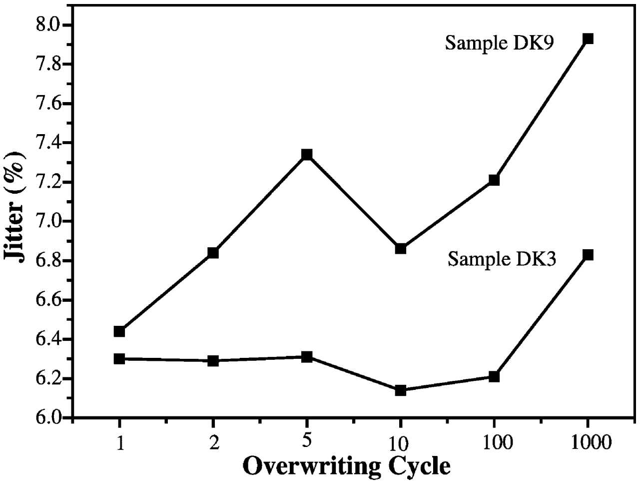

Fig. 2. Overwriting cycle dependence of jitter for samples DK3 and DK9.

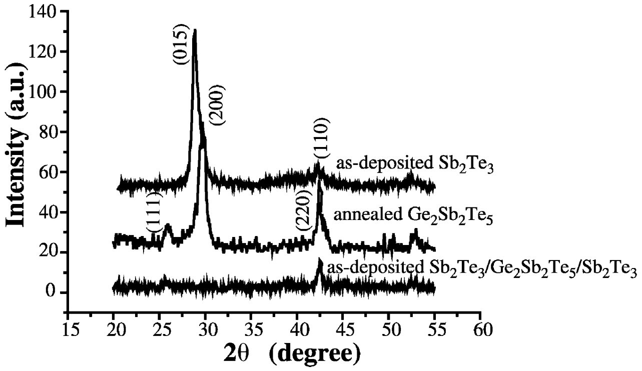

Fig. 3. XRD patterns of the as-deposited Sb_2Te_3/Si and $Sb_2Te_3/Ge_2Sb_2Te_5/Sb_2Te_3$/Si stacks, the annealed $Ge_2Sb_2Te_5$/Si stack.

Sb_2Te_3(40 nm)/Si and (2) Sb_2Te_3 (7 nm)/$Ge_2Sb_2Te_5$ (10 nm)/Sb_2Te_3 (15 nm)/Si, (3) the annealed $Ge_2Sb_2Te_5$ (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_t) 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 $Ge_2Sb_2Te_5$ (10 nm)/Sb_2Te_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_2Te_3 (10 nm)/$Ge_2Sb_2Te_5$ (10 nm)/Sb_2Te_3 (15 nm) on Si wafer to examine the possible diffusion among three layers and Si wafer.

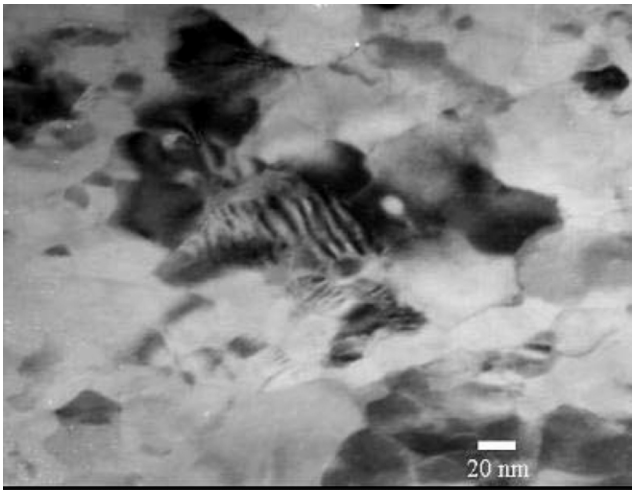

Fig. 4. TEM micrograph of $Ge_2Sb_2Te_5/Sb_2Te_3$ stack on Cu-mesh.

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 $Ge_2Sb_2Te_5$ recording layer in the disk. The modulation is defined in Table 1, where $I_{14\max}$ and $I_{14\min}$ 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_2Te_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 $Ge_2Sb_2Te_5$ recording layer. In contrast, dependence of the reflectivity and modulation of the disk on thickness of lower Sb_2Te_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 $Ge_2Sb_2Te_5$ layer thickness, the Sb_2Te_3-assisted disk with lower Sb_2Te_3 layer thickness between 13 and 20 nm shows the best combination of reflectivity and modulation. When the thickness of lower Sb_2Te_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_2Te_3 layer is deposited before $Ge_2Sb_2Te_5$ recording layer. In other words, the lower Sb_2Te_3 layer can enhance the crystallization of the $Ge_2Sb_2Te_5$ recording layer during its deposition. This is due to the fact that the crystallization temperature of the Sb_2Te_3 alloy is 85 °C below that of $Ge_2Sb_2Te_5$ alloy. Where the crystallization temperature was analyzed by differential scanning calorimetry (DSC). In other words, the lower Sb_2Te_3 layer can be much easier to become crystalline state after deposition, and then acts as the nucleation site to enhance crystallization of the $Ge_2Sb_2Te_5$ layer. It is known that the lattice mismatch between the Sb_2Te_3 and $Ge_2Sb_2Te_5$ crystals is low, which favors nucleation of crystal on the matching crystallographic plane. On the contrary, when the $Ge_2Sb_2Te_5$ layer is solidified after its deposition, the additional upper Sb_2Te_3 layer will have no significant effect on crystallization of the $Ge_2Sb_2Te_5$ recording layer. Therefore, it is concluded that the position and thickness of the additional Sb_2Te_3 layer are two important factors to affect the crystallization behavior of recording layer.

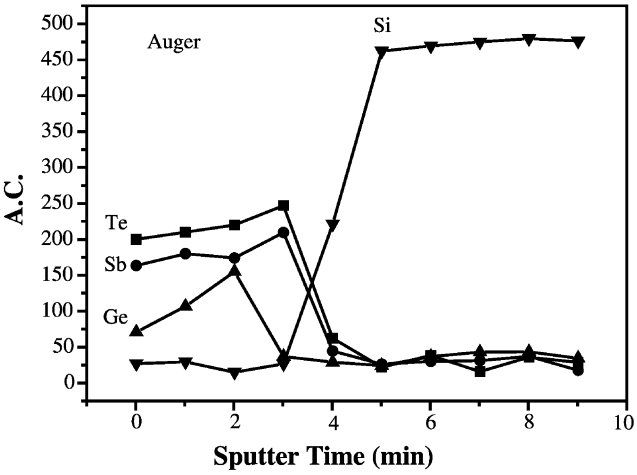

Fig. 5. Auger depth profile of the as-deposited $Sb_2Te_3/Ge_2Sb_2Te_5/Sb_2Te_3/Si$ stack.

3.2. XRD analysis

The XRD patterns are shown in Fig. 3 for the as-deposited Sb_2Te_3 (40 nm)/Si and Sb_2Te_3 (7 nm)/ $Ge_2Sb_2Te_5$ (10 nm)/Sb_2Te_3 (15 nm)/Si, the annealed $Ge_2Sb_2Te_5$ (50 nm)/Si stacks, respectively. It indicates same diffraction angle near 42.4 degree for the annealed $Ge_2Sb_2Te_5$/Si and as-deposited Sb_2Te_3/Si stacks. The same but lower intensity diffraction peak of 42.4° can also be detected for the as-deposited $Sb_2Te_3/Ge_2Sb_2Te_5/Sb_2Te_3$/Si stack. This signifies that the $Ge_2Sb_2Te_5$ layer can partly become a crystalline state after deposition due to the presence of lower Sb_2Te_3 stack. The lattice matching plane between Sb_2Te_3 and $Ge_2Sb_2Te_5$ crystals must be (110) plane of the Sb_2Te_3 crystal. In other words, the self-crystallization of $Ge_2Sb_2Te_5$ layer during deposition is possible by applying an optimum thickness of the lower Sb_2Te_3 layer.

3.3. TEM analysis

In order to examine the coherency of the interface between the $Ge_2Sb_2Te_5$ and Sb_2Te_3 crystal, the multi-layer $Ge_2Sb_2Te_5$ (10 nm)/Sb_2Te_3 (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 $Ge_2Sb_2Te_5$ 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 Sb_2Te_3 (10 nm)/$Ge_2Sb_2Te_5$ (10 nm)/Sb_2Te_3 (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):

$$\chi(t)=(R_t-R_a)/(R_c-R_a) \tag{1}$$

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_t is the reflectance of the sample at laser pulse time 't'. According to the J-M-A model, the crystallized fraction, $\chi(t)$, can be expressed by:

$$\chi(t)=1-\exp[-(kt)^q] \tag{2}$$

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 Sb_2Te_3 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 Sb_2Te_3 layer >15 nm ($q=2.53$–2.79). This is in agreement with the previous conclusion that the lower Sb_2Te_3 layer with

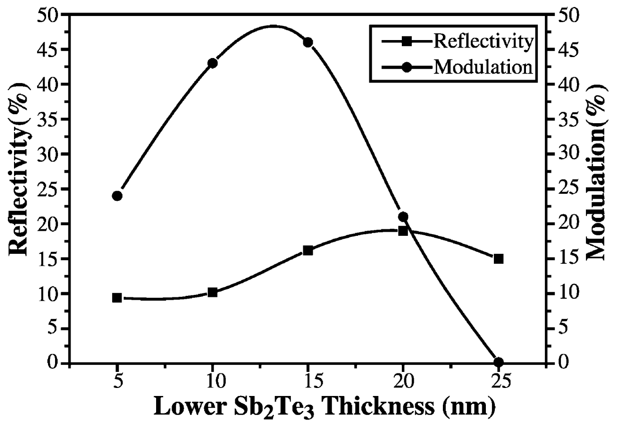

Fig. 6. Thickness dependence of reflectivity and modulation of lower Sb_2Te_3 nucleation assisting layer (samples DK7–DK11).

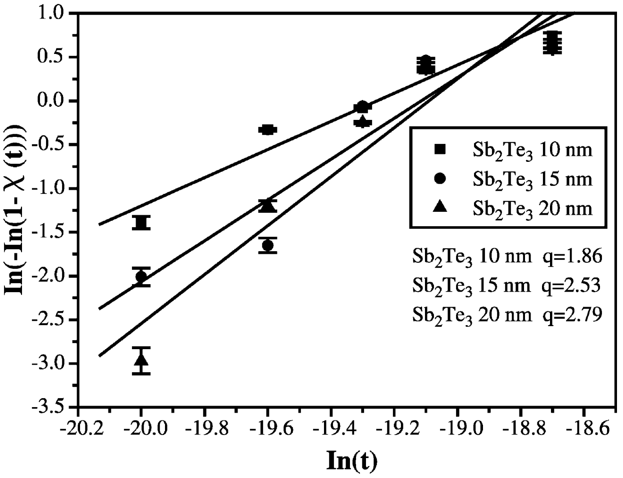

Fig. 7. The $\ln[-\ln(1-\chi(t))]$ versus $\ln(t)$ curves at three different thicknesses of the lower Sb_2Te_3 layer, which are used to derive Avrami coefficient (q) (slope of the curves) for samples DK8, DK9 and DK10.

optimum thickness can effectively act as nucleation sites to enhance crystallization of $Ge_2Sb_2Te_5$ 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_2Te_3 layer (sample DK9), another disk with both upper and lower Sb_2Te_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_2Te_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_2Te_3 additional layer was deposited on the one side or both sides of the recording $Ge_2Sb_2Te_5$ 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_2Te_3 layer at an optimum thickness (approx. 13–20 nm) can effectively act as the nucleation sites for crystallization of the $Ge_2Sb_2Te_5$ recording layer during deposition, i.e. the initialization-free disk can be obtained. (2) The upper Sb_2Te_3 layer has no significant effect on crystallization of recording layer, but it is beneficial to jitter improvement. (3) The lower Sb_2Te_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.

Acknowledgments

The authors would like to thank the support of the National Science Council of Taiwan under Contract No.: NSC91-2216-E-009-025 and -028.

References

[1] X.S. Miao, Jpn. J. Appl. Phys. 39 (2000) 729.
[2] X.S. Miao, Jpn. J. Appl. Phys. 41 (2002) 1679.
[3] J. Tominaga, T. Nakano, N. Atoda, Appl. Phys. Lett. 73 (1998) 2078.
[4] V. Weidenhof, I. Friedrich, S. Ziegler, M. Wutting, J. Appl. Phys. 89 (2001) 3168.
[5] W.A. Johnson, R.F. Mehl, Trans. AIME 135 (1939) 416.
[6] N. Ohshima, J. Appl. Phys. 79 (11) (1996) 8357.
[7] DVD Specification for Rewritable Disc (DVD-RAM), DVD-FORUM, Version 1.0, 1997, p. 54.