정보저장시스템학회논문집, 제 1 권 제 1 호, pp.93-98

Influence of Sn/Bi doping on the phase change characteristics of $Ge_2Sb_2Te_5$

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ABSTRACT

Rewritable optical disk is one of the essential data storage media in these days, which takes advantage of the different optical properties in the amorphous and crystalline states of phase change materials. As well known, data transfer rate is one of the most important parameter of the phase change optical disks, which is mostly limited by the crystallization speed of recording media. Therefore, we doped Sn/Bi to Ge2Sb2Te5 alloy in order to improve the crystallization speed and investigated the dependence of phase change characteristics on Sn/Bi doping concentration. The Sn/Bi doped Ge2Sb2Te5 thin film was deposited by RF magnetron co-sputtering system and phase change characteristics were investigated by X-ray diffraction (XRD), static tester, UV-visible spectrophotometer, electron probe microanalysis (EPMA), inductively coupled plasma mass spectrometer (ICP-MS) and atomic force microscopy (AFM). Optimum doping concentration of Bi and Sn were 5~6 at.% and the minimum time for crystallization was below than 20 ns. This improvement is correlated with the simple crystalline structure of Sn/Bi doped Ge2Sb2Te5 and the reduced activation barrier arising from Sn/Bi doping. The results indicate that Sn/Bi might play an important role in the transformation kinetics of phase change materials..

Key Words: optical recording, phase change, chalcogenide, thin film, optical properties

1.INTRODUCTION

Phase change materials, namely chalcogenides, plays an important role in rewritable optical disks such as DVD-RAM and DVD±RW. Information is written and erased in phase change materials by changing the irradiation condition of laser. Melting and rapid quenching of the phase change materials with intensive-power laser leads to amorphous state, and the amorphous state turns to the crystalline state by heating the phase change materials above crystallization temperature using moderate-power laser. Between crystalline and amorphous state, there are optical contrast exist due to the different reflectivity upon its state. Thus, written information can be read by detecting the optical contrast.

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(논문접수일 : 2005 년 4 월 3 일)

Recently, the optimum recording materials in terms of data transfer rate, archival life and optical contrast were found to be $Ge_2Sb_2Te_5$ (used in DVD-RAM) and AgInSbTe (used in CD-RW and DVD+RW).[1-2] The elements Bi, Sn and In are considered as dopants to tailor the crystallization speed of GST. [3-8] We doped Sn/Bi to $Ge_2Sb_2Te_5$ alloy in order to improve the crystallization speed and investigated the dependence of phase change characteristics on Sn/Bi doping concentration.

2. EXPERIMENTAL DETAILS

The Bi and Sn doped $Ge_2Sb_2Te_5$ film was deposited by Radio-Frequency magnetron sputtering system (SNTek, Korea) on to Si (100) wafers and slide glass. Bi/Sn target (99.99%, R&D Korea, Korea) and $Ge_2Sb_2Te_5$ target (4N, High purity chemicals, Japan) were sputtered by co-sputtering method. Base pressure was 1×10^{-7} torr and working pressure was adjusted to 1 mtorr by flowing Ar (6N, Seoul gas, Korea) through MFC (mass flow controller). Targets were pre-sputtered for 5 mim in order to remove oxidized

Table 1 The film composition with different Bi/Sn gun power.

Sample (Gun power)	Bi content (at%)	Sample (Gun power)	Sn content (at%)
GB3 (Bi 3W)	3.8	GS10 (Sn 10W)	5.5
GB5 (Bi 5W)	4.4	GS20 (Sn 20W)	11.0
GB7 (Bi 7W)	5.9	GS30 (Sn 30W)	17.7
GB10 (Bi 10W)	9.8	GS40 (Sn 40W)	22.0
GB20 (Bi 20W)	19.6	GS50 (Sn 50W)	27.5

surface and contaminations. For homogenized composition and thickness, substrate holder was rotated with 10 RPM and deposition rate was controlled by applying different RF power to each target. Except for deposition rate measurement, RF power of $Ge_2Sb_2Te_5$ gun was fixed to 100W and that of Bi/Sn gun was varied to control the doping concentration.

Composition and abbreviation of the film are presented in table1. The thickness of the film was measured by surface profiler (AS500, KLA-Tencor, U.S.A.), and surface roughness was observed by AFM (AutoProbe CP-R scanning probe microscope, Digital instrument, U.S.A). As-deposited films were annealed at 100, 150, 200, 300 and 400 ℃ in Ar atmosphere for 10 min and heating rate was 5 K/min. The optical reflectivity was measured by UV-VIS-NIR spectrophotometer (V-570, Jasco, Japan) and the structure of the film was analyzed by X-ray reflectivity using synchrotron radiation at X-ray diffraction beamline BL3C2 of the Pohang Light Source in Korea. The crystallization behavior in nano second scale was observed by using static tester (Media test-I, Toptica photonics, Germany).

3.RESULTS AND DISCUSSIONS

3.1 Film deposition and morphology

Thickness variation of the film according to deposition time and RF power are shown in Fig.1 Thickness of the film is linearly proportional according to deposition time and RF power. Deposition rate of the film was 0.45 nm/s when the RF power of $Ge_2Sb_2Te_5$ gun was 100 W. Fig. 2 present the surface profile of $Ge_2Sb_2Te_5$, Sn doped $Ge_2Sb_2Te_5$ and Bi doped $Ge_2Sb_2Te_5$ film.

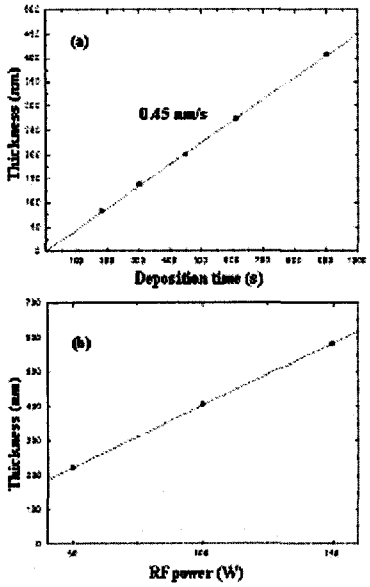

Fig. 1 Thickness of $Ge_2Sb_2Te_5$ film as a function of (a) deposition time (RF power = 100W) and (b) RF power (deposition time=10 min)

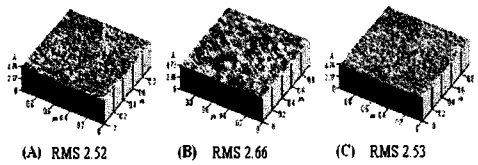

Fig. 2 AFM image (a)$Ge_2Sb_2Te_5$(B)GS(C)GB

Root-mean-square (RMS) roughness is very important in phase change optical disk, since protective layer and reflective layer are deposited on the phase change media. RMS roughness of all films were in the range from 2.5 to 2.7 Å. Considering that the RMS roughness of bare Si wafer is 2.0 Å, RF magnetron co-sputtered film has very smooth surface which is favorable for optical disk.

3.2 Structural analysis

Fig.3 present the XRD patterns of as deposited $Ge_2Sb_2Te_5$ film and films annealed at different temperature. As deposited $Ge_2Sb_2Te_5$ film is amorphous due to the high quenching rate at the substrate during deposition, and it crystallize to metastable structure between 100 and 150 ℃. The second phase transformation to stable structure is occurred between 300 and 400 ℃.[9]

An analysis of the peak positions identifies the

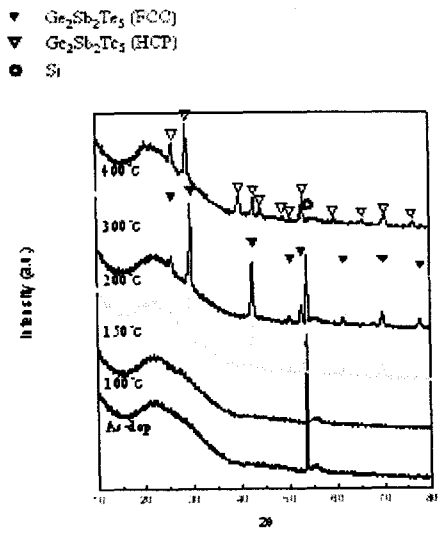

Fig. 3 XRD Patterns of as-deposited $Ge_2Sb_2Te_5$ film and films annealed at different temperatures.

meta stable structure as a face-centered cubic (FCC) structure, and determines the lattice constant to $a = 6.006 \pm 0.013$ Å, and the stable structure as a hexagonal close-packed (HCP) structure and determines the lattice constant to $a = 4.256 \pm 0.043$ Å, $c = 16.887 \pm 0.175$ Å. The corresponding Miller indices and the calculated peak position for the patterns shown in Fig.3 are listed in Table 2. These values are similar to the result of other studies conducted by DC magnetron sputter and molecular beam epitaxy[10-11],which means that the $Ge_2Sb_2Te_5$ film deposited with RF magnetron sputter also has similar properties with $Ge_2Sb_2Te_5$ film deposited by other methods.

XRD patterns of Bi doped $Ge_2Sb_2Te_5$ film with different doping concentration and annealing temperatures are shown in Fig.4 (a-c). The results indicate that increasing the Bi doping concentration facilitates the FCC to HCP transformation. When the 20 at.% of Bi was doped to $Ge_2Sb_2Te_5$ film.

FCC structure was not formed and as-deposited $Ge_2Sb_2Te_5$ film directly crystallized to HCP structure.

Fig.5 (a-c) present the XRD patterns of Sn doped $Ge_2Sb_2Te_5$ film with different doping concentration and annealing temperatures. In case of 5.5 at.% Sn doped $Ge_2Sb_2Te_5$ film shows a similar crystallization behavior with undoped $Ge_2Sb_2Te_5$ film. However, more than 10 at.% Sn

Table 2 The Observed and calculated *d*-spacing for the XRD spectra shown in Fig.3

GST film annealed at 200 ℃								
h	*k*	*l*	d_{obs}	d_{cal}	Δd	$2\Theta_{obs}$	$2\Theta_{cal}$	$\Delta 2\Theta$
1	1	1	3.4515	3.4676	−0.016	25.662	25.670	0.121
2	0	0	3.0479	3.003	0.0449	29.15	29.726	−0.448
2	2	0	2.1194	2.1234	−0.004	42.5	42.540	0.084
3	1	1	1.8092	1.8109	−0.0017	50.279	50.349	0.051
2	2	2	1.731	1.7338	−0.0028	52.727	52.756	0.09
4	0	0	1.5028	1.5015	0.0013	61.556	61.730	−0.06
4	2	0	1.3413	1.343	−0.0017	69.992	70.000	0.101
4	2	2	1.2271	1.226	0.0012	77.66	77.852	−0.089
a = 6.006 ± 0.013 α = 90°								
b = 6.006 ± 0.013 β = 90°								
c = 6.006 ± 0.013 γ = 90°								
Cell−Volume: 216.649 Å^3								
GST film annealed at 400 ℃								
h	*k*	*l*	d_{obs}	d_{cal}	Δd	$2\Theta_{obs}$	$2\Theta_{cal}$	$\Delta 2\Theta$
1	0	2	3.3571	3.377	−0.0199	25.82	26.371	0.159
1	0	3	3.0259	3.0819	−0.0561	28.79	28.948	0.548
1	0	6	2.2256	2.2344	−0.0088	39.81	40.332	0.166
1	1	1	2.0778	2.1112	−0.0335	42.84	42.798	0.724
1	0	8	1.8314	1.8293	0.002	49.08	49.806	−0.059
2	0	3	1.7791	1.7511	0.028	50.65	52.194	−0.88
2	0	4	1.7016	1.6885	0.0131	53.175	54.284	−0.453
0	0	11	1.5307	1.5325	−0.0018	59.79	60.350	0.077
1	0	11	1.4093	1.4151	−0.0058	65.65	65.962	0.306
2	0	9	1.3262	1.3137	0.0125	70.42	71.801	−0.78
2	1	6	1.238	1.2481	−0.0101	76.38	76.221	0.738
a = 4.256 ± 0.043 α = 90°								
b = 4.256 ± 0.043 β = 90°								
c = 16.857 ± 0.175 γ = 120°								
Cell−Volume: 264.436 Å^3								

doping also facilitate the structural transformation from FCC to HCP. There were no phase separation even if Bi or Sn were doped more than 20 %. Therefore, doped Bi/Sn might randomly occupied the vacancy of $Ge_2Sb_2Te_5$ or be segregated at grain boundaries. The result suggest that the Bi/Sn doping lowers the activation barrier between FCC and HCP structure.

3.3 Optical properties

The difference in reflectance between the amorphous and crystalline states, defined as the optical contrast, is of great importance for phase-change optical recording. The higher optical contrast the larger is the signal modulation during reading. The optical contrast (C) is defined as equation (1).

$$C = (R_c - R_a) / R_c \quad (1)$$

Where, R_c and R_a of the reflectance at crystalline and amorphous states, respectively. Optical contrast of Sn/Bi doped $Ge_2Sb_2Te_5$ films at 650 nm are presented in fig.6 Wavelength

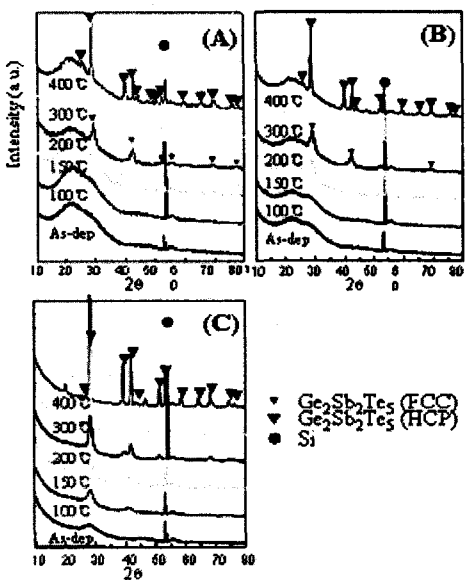

Fig. 4 XRD Patterns of (a) GB5, (b) GB10 and (c) GB20 films annealed at different temperatures

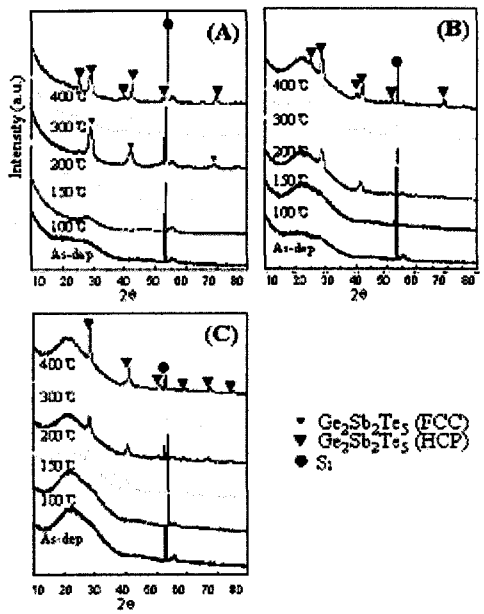

Fig. 5 XRD Patterns of (a) GS10, (b) GS20 and (c) GS40 films annealed at different temperatures

of 650 nm is that of laser used for DVD.

In case of Bi doping less than 10 at.%, optical contrast is similar to that of Ge2Sb2Te5 film. Doping Sn , however, decrease the optical contrast

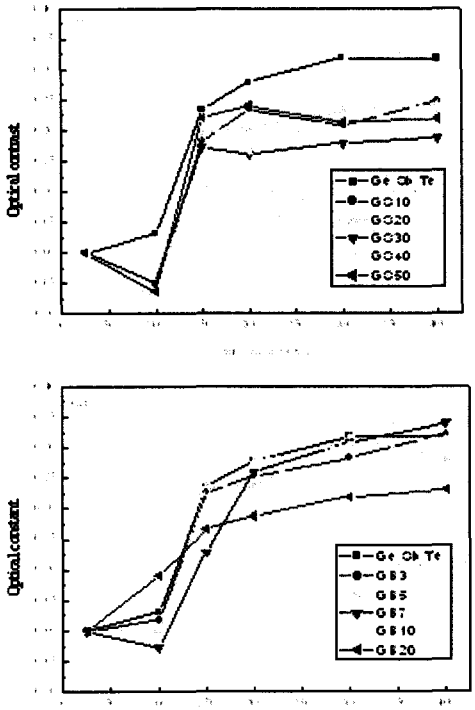

Fig. 6 Optical contrast of (a) GB and (b) GS series films annealed at different temperatures

of the film. Thus doping concentration of Sn should be limited up to 10 at.%.

3.4 Static tester

Fig.7 indicates the nano second scale crystallization behavior of $Ge_2Sb_2Te_5$ film and Bi/Sn doped $Ge_2Sb_2Te_5$ film. $\triangle R$ is defined as the reflectivity difference between before and after the laser pulse irradiation. The film begins to crystallize as a laser pulse width increases, and minimum time for crystallization which corresponds to incubation time decreases as the laser power increases. The minimum time for crystallization is related to nucleation and shortening of incubation time with Bi/Sn doping. It can be presumably explained by the decrease of the average bond energy between elements. If the elements, Ge or Sb are replaced by Bi or Sn of the same group, then substitution of the stronger Ge-Te (456 kJ/mol) and Sb-Te (277.4 kJ/mol) bonds by the weaker Sn-Te (359.8 kJ/mol) or Bi-Te (232.3 kJ/mol) bonds can take place[12]. The decrease of the average bonding energy leads to decrease of activation energy barrier for crystallization. Thus Bi doping is more effective to reduce the incubation time than Sn doping.

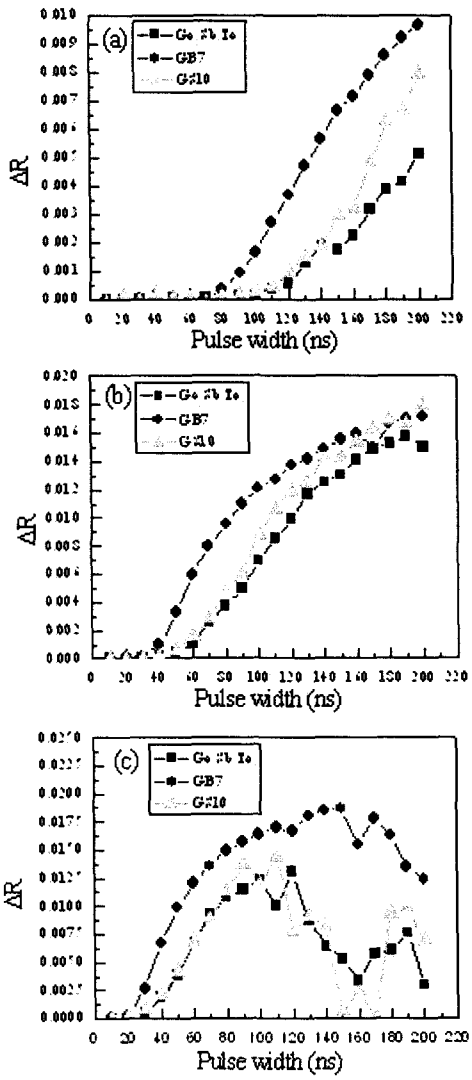

Fig. 7 Reflectivity difference as a function of laser pulse width according to different laser power. (a) 5 mW, (b) 10 mW and (c) 15 mW.

4.CONCLUSION

Bi/Sn doping to $Ge_2Sb_2Te_5$ facilitate the formation of HCP structure, which is correlated with lowering the activation barrier between FCC and HCP structure. Doped Bi/Sn atom might randomly occupied the vacancy of Ge2Sb2Te5 or be segregated at grain boundaries since phase separation did not take place regardless of Bi/Sn doping concentration up to 20 at. % or more. Minimum time for crystallization nearly 20 ns are observed when 6 at. % of Bi was doped to Ge2Sb2Te5. These results indicate that Bi/Sn doping might play an important role in the transformation kinetics of phase change materials.

5. ACKNOWLEDGEMENT

This work was supported by Korea Engineering and Science Foundation through the Center of Information Storage Device (CISD) in Yonsei University. Experiments at PLS were supported in part by MOST and POSTECH. The author would like to thank H. Horii of Samsung electronic for the static tester measurement.

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