

Doped Ge–Sb–Te phase-change materials for reversible phase-change optical recording

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Abstract

Differently doped Ge–Sb–Te phase-change recording films were prepared by the individual dc magnetron sputtering of $\text{Sn}_5\text{Ge}_3\text{Sb}_{72}\text{Te}_{20}$, $\text{In}_5\text{Ge}_3\text{Sb}_{72}\text{Te}_{20}$, $\text{Ga}_5\text{Ge}_3\text{Sb}_{72}\text{Te}_{20}$ and $\text{Bi}_5\text{Ge}_3\text{Sb}_{72}\text{Te}_{20}$ targets. A close relationship was observed between surface roughness and reflectivity. The Ge–Sb–Te films doped with Bi showed the highest surface roughness and reflectivity. The phase-change optical disks with Bi-doped Ge–Sb–Te recording films showed the best overwriting characteristics. Therefore, the reversible recording properties of the phase-change optical disk were dominated by the composition of the recording film.

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1. Introduction

In the recent years, the digital versatile disk (DVD) has been rapidly gaining acceptance for use in document, video, audio, personal and professional data storage. However, there are a limited number of phase-change materials that can be put into practical use [1]. Digital data in the phase-change optical disk exist in the form of amorphous marks in a crystal matrix, utilizing the reflectance difference between the two phases [2]. In a phase-change optical disk, the crystallization speed of the recording material determines the recording speed. The choice of the recording film material can lead to the difference of the recording characteristics [3].

It has been reported that the control of the crystallization speed of the material is easily accomplished by varying the recording film composition [4,5]. In this study, the doped Ge–Sb–Te phase-change recording films were prepared by dc magnetron sputtering of $\text{Sn}_5\text{Ge}_3\text{Sb}_{72}\text{Te}_{20}$, $\text{In}_5\text{Ge}_3\text{Sb}_{72}\text{Te}_{20}$, $\text{Ga}_5\text{Ge}_3\text{Sb}_{72}\text{Te}_{20}$ and $\text{Bi}_5\text{Ge}_3\text{Sb}_{72}\text{Te}_{20}$ targets, individually. The composition of recording films was varied by different dopants. The influence of doping Ge–Sb–Te films with Sn, In,

Ga and Bi on the recording properties of disks was investigated in this work.

2. Experimental procedures

Fig. 1 shows the structure of a phase-change optical disk. The disk had a six-layer stack with a structure ZnS-SiO_2 (60 nm)/ GeN_x (1.5 nm)/doped Ge–Sb–Te (16 nm)/ GeN_x (7 nm)/ ZnS-SiO_2 (0.5 nm)/Ag (150 nm), sputtered sequentially on a grooved polycarbonate (PC) substrate. The dielectric layers (ZnS-SiO_2) were deposited by rf magnetron sputtering in an atmosphere of Ar. The interface layers (GeN_x) were deposited by reactive rf magnetron sputtering in a mixed Ar– N_2 atmosphere. Two separate mass flow controllers (Hastings HFC-202) were applied to monitor the gas flow rates of argon and nitrogen. In Ar atmosphere, the doped Ge–Sb–Te phase-change recording films were prepared by the dc magnetron sputtering of $\text{Sn}_5\text{Ge}_3\text{Sb}_{72}\text{Te}_{20}$, $\text{In}_5\text{Ge}_3\text{Sb}_{72}\text{Te}_{20}$, $\text{Ga}_5\text{Ge}_3\text{Sb}_{72}\text{Te}_{20}$ and $\text{Bi}_5\text{Ge}_3\text{Sb}_{72}\text{Te}_{20}$ targets, individually. The targets are Sn–Ge–Sb–Te alloy (99.99% purity, 8 cm diameter, 0.6 cm thickness, MITSUBISHI) with a composition of 5:3:72:20 at.%, In–Ge–Sb–Te alloy (99.99% purity, 8 cm diameter, 0.6 cm thickness, MITSUBISHI) with a composition of 5:3:72:20 at.%, Ga–Ge–Sb–Te alloy (99.99% purity, 8 cm diameter, 0.6 cm thickness, MITSUBISHI) with a composition of 5:3:72:20 at.%, and Bi–Ge–Sb–Te alloy (99.99% purity,

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PC dummy substrate (0.6 mm)
UV-curing
Ag (150 nm)
ZnS-SiO ₂ (0.5 nm)
GeN _x (7 nm)
Doped Ge-Sb-Te (16 nm)
GeN _x (1.5 nm)
ZnS-SiO ₂ (60 nm)
PC substrate (0.6 mm)

Fig. 1. The structure of a phase-change optical disk.

8 cm diameter, 0.6 cm thickness, MITSUBISHI) with a composition of 5:3:72:20 at.%. The reflective layer (Ag) was deposited by dc magnetron sputtering in an atmosphere of Ar. In the deposition of a six-layer stack deposition, the substrate was not heated. Table 1 lists all of the sputtering conditions of the six-layer stack in a phase-change optical disk. After sputtering, the disks were bonded with PC dummy substrates and initialized for the dynamic test.

Table 1
All of the sputtering conditions of the six-layer stack in a phase-change optical disk

Film	ZnS-SiO ₂	GeN _x	X-Ge-Sb-Te				GeN _x	ZnS-SiO ₂	Ag
			Sn	In	Ga	Bi			
Target	ZnS-SiO ₂	Ge	Sn ₅ Ge ₃ Sb ₇₂ Te ₂₀	In ₅ Ge ₃ Sb ₇₂ Te ₂₀	Ga ₅ Ge ₃ Sb ₇₂ Te ₂₀	Bi ₅ Ge ₃ Sb ₇₂ Te ₂₀	Ge	ZnS-SiO ₂	Ag
Sputter mode	rf	rf	dc	dc	dc	dc	rf	rf	dc
Power (kW)	4.5	2	0.5	0.5	0.5	0.5	2	0.5	4.5
Sputter gas and flow (sccm)	Ar, 12	Ar/N ₂ , 40/40	Ar, 60	Ar, 60	Ar, 60	Ar, 60	Ar/N ₂	Ar	Ar
Pressure (mTorr)	6	6	6	6	6	6	6	6	6
Film thickness (nm)	30	1.5	16	16	16	16	7	0.5	150

Table 2
The elemental composition of Sn-Ge-Sb-Te, In-Ge-Sb-Te, Ga-Ge-Sb-Te and Bi-Ge-Sb-Te recording films, as determined by XPS

Recording films	Ge content (at.%)	Sb content (at.%)	Te content (at.%)	Sn content (at.%)	In content (at.%)	Ga content (at.%)	Bi content (at.%)
Sn ₅ Ge ₃ Sb ₇₂ Te ₂₀	3.10	71.87	20.08	4.95			
In ₅ Ge ₃ Sb ₇₂ Te ₂₀	3.01	72.11	20.15		4.73		
Ga ₅ Ge ₃ Sb ₇₂ Te ₂₀	3.05	71.99	20.00			4.96	
Bi ₅ Ge ₃ Sb ₇₂ Te ₂₀	3.02	72.12	20.01				4.85

The dynamic test was carried out using a dynamic tester (Pulstec DVD TESTER ODU-1000) with a laser diode of 650 nm wavelength and a numerical aperture (NA) of 0.6. The film thickness was measured using a surface profiler (Alpha-Step 500, TENCOR) and the FE-SEM (XL-40FEG field emission scanning electron microscope). The elemental compositions were investigated by X-ray photoemission spectroscopy (XPS; VG. ESCA 210). The surface roughness was investigated by Atomic Force Microscopy (AFM; Digital Instruments Inc.). The reflectivity of the films was recorded using a spectrophotometer (ETA-ODT). The data of each analysis were obtained by measuring three samples for the same composition of the recording film.

3. Results and discussion

Table 2 shows the elemental composition of Sn-Ge-Sb-Te, In-Ge-Sb-Te, Ga-Ge-Sb-Te and Bi-Ge-Sb-Te recording films, as determined by XPS. The compositions of the films were similar to the compositions of the targets.

Fig. 2 shows the root-mean-square (RMS) roughness of different doped Ge-Sb-Te phase-change recording films. The surface roughness of Bi-Ge-Sb-Te film was relatively high. Generally, the composition of a film significantly affects its surface roughness [6]. Laukaitis et al. [7] observed that the roughness was strongly related to the morphology of a growing film, which fact probably explains why Bi-Ge-Sb-Te films were the roughest.

Fig. 3 shows the reflectivity of differently doped Ge-Sb-Te phase-change recording films at a wavelength of 650 nm. The Bi-Ge-Sb-Te film exhibited relatively high reflectivity, probably because the surface roughness was quite high, promoting the scattering of light [6,8,9]. This result was consistent with those in Fig. 2.

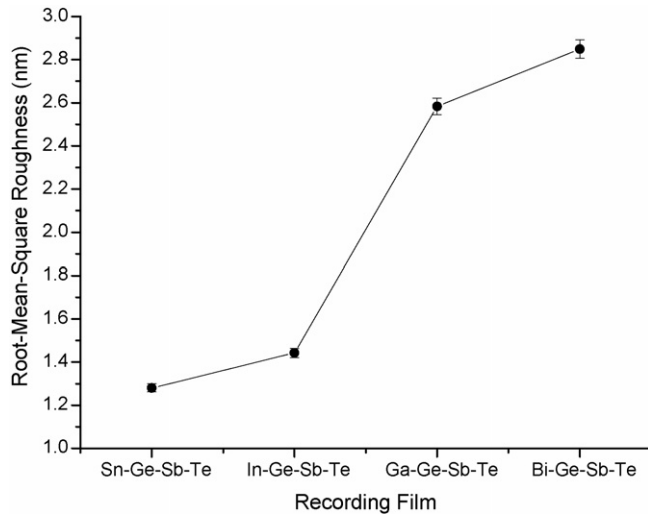


Fig. 2. The root-mean-square (RMS) roughness of different doped Ge–Sb–Te phase-change recording films.

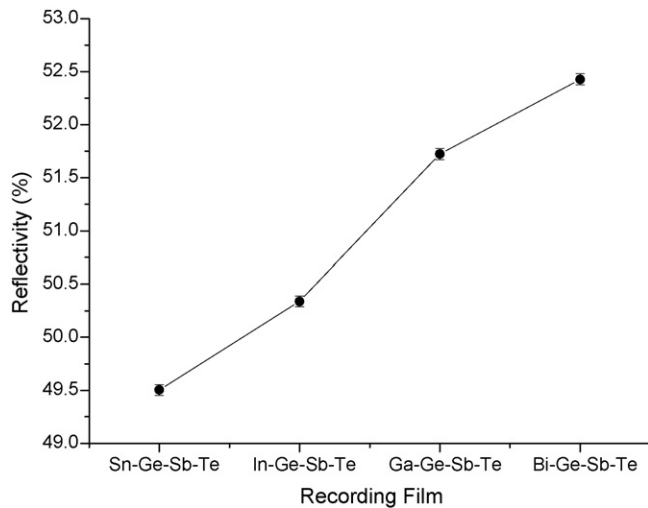


Fig. 3. The reflectivity of differently doped Ge–Sb–Te phase-change recording films at a wavelength of 650 nm.

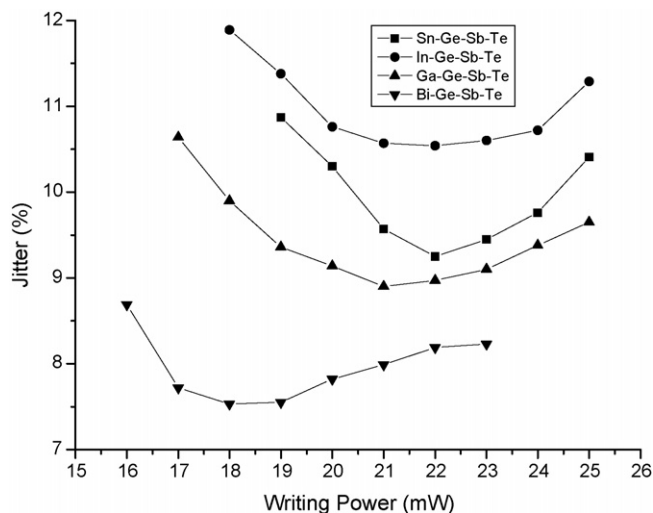


Fig. 4. The jitter vs. the writing power for disks with different recording films.

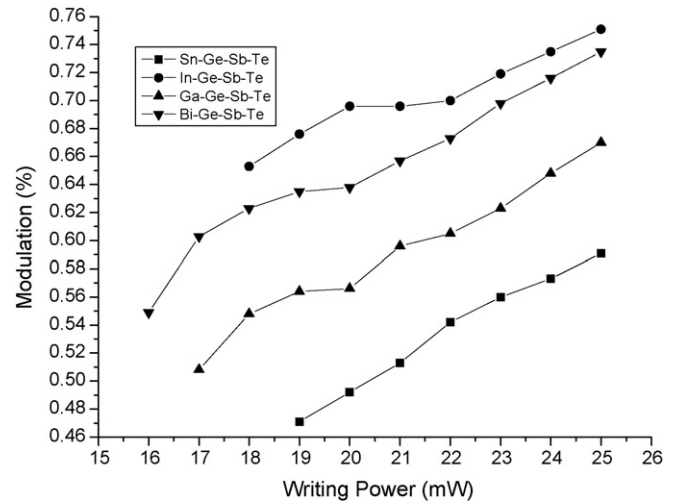


Fig. 5. The modulation vs. the writing power for disks with different recording films.

In this study, a dynamic test was used to investigate the recording properties of phase-change optical disks with different recording films. During testing, the rate of rotation of disk was 13.96 m/s (4×) for recording and 3.49 m/s (1×) for reading. Fig. 4 shows the jitter versus the writing power for disks with different recording films. The disks were directly overwritten (DOW) 10 times with different writing powers. The jitter value of the Bi-Ge-Sb-Te disk was relatively low, and the effective writing power of the Bi-Ge-Sb-Te disk was low.

Fig. 5 shows the modulation versus the writing power for disks with different recording films. After 10 DOW cycles, the modulation value increased with the writing power for all disks. The Sn-Ge-Sb-Te disk had showed lower modulation values at various writing powers. A high writing power improved the modulation value of the disk.

Fig. 6 shows the DOW performance of the different phase-change optical disks (4× DVD + RW) at a writing power of 22 mW.

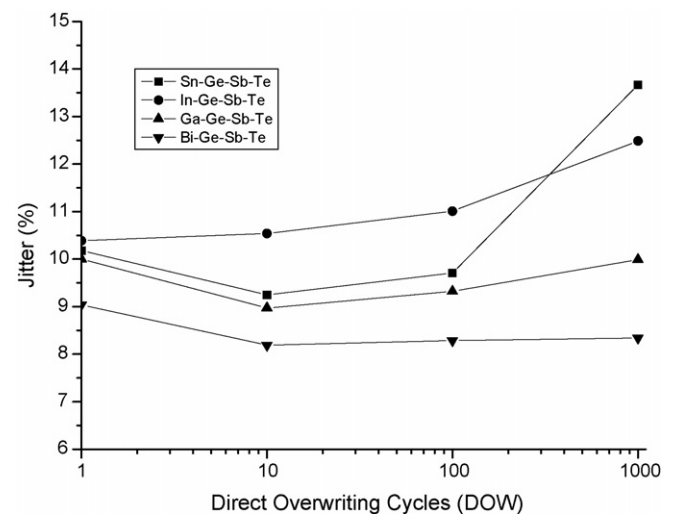


Fig. 6. The DOW performance of the different phase-change optical disks (4× DVD + RW) at writing power of 22 mW.

22 mW. The jitter value of the Bi–Ge–Sb–Te disk remained below 9% for up to 1000 DOW cycles, suggesting that the transfer rate between amorphous and crystalline states was higher for a Bi–Ge–Sb–Te recording film at a recording speed of 13.96 m/s. However, the jitter value of the Sn–Ge–Sb–Te disk clearly increased after 1000 DOW cycles. Adding Sn distorted the crystallites of the Ge–Sb–Te film, causing in structural instability. The structure of the Sn–Ge–Sb–Te film was collapsed for up to 1000 direct overwriting cycles, significantly increasing the jitter value of disk [1,4,10,11].

4. Conclusions

Recording films were obtained by doping Ge–Sb–Te films with Sn, In, Ga and Bi. The composition of the recording films varied by doping. Ge–Sb–Te films doped with different dopants showed different values of surface roughness and reflectivity. The Bi–Ge–Sb–Te film had a relatively high reflectivity, probably because the surface roughness was quite high, promoting the scattering of light. The Bi–Ge–Sb–Te disk exhibited good overwriting characteristics probably because doping Ge–Sb–Te films with Bi strongly reduced the crystallization temperature, indicating that the phase-change optical disks with Bi-doped Ge–Sb–Te recording films had the best reversible recording properties.

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