Effect of Ag or Cu Doping on Erasable Phase-Change Sb-Te Thin Films

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Abstract — The crystallization process of the Ag or Cu doped Sb_2Te_3 amorphous film was investigated by isothermal treatment for one hour at 100 ℃, 200 ℃ and 300 ℃ respectively. The crystallization temperatures of $Ag_{8.3}Sb_{34.9}Te_{56.8}$ and $Cu_{8.4}Sb_{35.1}Te_{56.5}$ films determined by DSC analysis were more than 125 ℃ and 120 ℃ respectively, while that of the undoped Sb_2Te_3 film was 97 ℃. It indicates that doping Ag or Cu can improve the room temperature stability of Sb_2Te_3 amorphous films. For pure and some Ag, Cu doped Sb_2Te_3 films, phase transformations from lower temperature metastable phases to higher temperature thermodynamic stable phases were found. This kind of phase transformation would cause the appearance of ambiguous exothermic peak in DSC curve. When the Ag content is increased to about 6.6 at%, the melting temperature of the film is enhanced from 415 ℃ for undoped film to higher than 450 ℃. For the Cu doped film, same tendency can be achieved as Cu content is increased to 8.4 at%. The contrast ratios between as-deposited and 300 ℃ annealed films of $Ag_{3.2}Sb_{35.8}Te_{61.0}$ and $Cu_{4.1}Sb_{37.4}Te_{58.5}$ films were more than 42% and 37% respectively.

I. Introduction

Reversible phase-change of amorphous-crystalline transformation for optical data storage has been developed mainly in Te-based alloys[1]. It is known that pure Te can be easily quenched into amorphous phase, but it will crystallize rapidly at about 10 ℃[2]. In order to stabilize the amorphous phase of Te-based films at room temperature, numbers of early studies had concentrated on stability improvements of these films by adding some elements such as As, Ge, Sn, Sb, Se and O[3-6].

In 1988, Fujimori et al.[7] developed Sb_2Te_3 alloy films as a phase-change recording material. It showed favorable characteristics were considered to originate in the wide composition margin for forming a single phase Sb_2Te_3 in the film. Jiang et al.[8] investigated theoretically the crystallization kinetics of the films, to which small amount of foreign elements such as Cu, Co, Ag, Pb, and Sb were added. They found that the erasure speed and film's stability can be improved if the adding elements have lower Tg/Tm and higher Tg, where Tg and Tm are glass transformation temperature and melting temperature, respectively. Recently, AgInSbTe was considered to be a promising recording material[9], in addition to GeSbTe systems.

Although many studies adopted Ag, Cu as adding elements of optical recording medium, few of them showed the detail effects of these doping elements on the film structure, thermal stability and optical property. In this study, we investigated the crystallization processes of the amorphous Ag or Cu doped Sb_2Te_3 films, their structure changes, thermal stability, and optical properties.

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II. Experiment

Different amounts of high purity Ag (0, 15.0, 25.0, 35.0, 45.0 at%) and Cu (0, 15.0, 25.0, 35.0, 45.0 at%) with Sb, Te powers were placed in a fused quartz tube, evacuated to 10^{-6} Torr and sealed. The atomic ratio of Sb and Te is 2/3. The powders in tube were violently mixed together then placed in a furnace. The furnace temperature was increased to 1000 ℃ to melt the mixed powders. The ingot was then homogenized at 300 ℃ for 12 hours. Ag or Cu doped Sb_2Te_3 films that contain different amounts of Ag (0, 3.2, 6.6, 8.3, 11.4 at%) or Cu (0, 2.5, 4.1, 6.4, 8.4 at%) were prepared by evaporating the ingots. After deposition, these films were isothermally treated for one hour at 100 ℃, 200 ℃ and 300 ℃, respectively . Thickness of the films was 1500Å.

Compositions of the films were confirmed by EDAX and EPMA. We use the average value of these two measurements as the film composition. The deviation is about 1 at.%. Structure of the film was examined by X-ray diffraction analysis. Crystallization temperatures and melting temperatures were measured by DSC in argon atmosphere with heating rates of 5 ℃/min. Reflectivity of the film was measured by spectrophotometer with laser wavelength among 400 and 850nm.

III. Results and Discussion

Table I is the results of X-ray analysis of the as-deposited and the isothermally treated the pure and various Ag doped Sb_2Te_3 films. Most of the as-deposited films showed amorphous-like diffraction peaks except the $Sb_{38.6}Te_{61.4}$ and $Ag_{3.2}Sb_{35.8}Te_{61.0}$ films having small broaden peaks that were identified to be Te. It means that Te particles would disperse in the as-deposited $Sb_{38.6}Te_{61.4}$ and $Ag_{3.2}Sb_{35.8}Te_{61.0}$ films. After heat treatment, we found that the main crystalline phase is gradually transferred from Te to Sb_2Te_3 as temperature is increased to 300 ℃. This indicates that Sb_2Te_3 is more thermodynamically stable than Te at higher temperature. As Ag contents are 3.2 and 6.6 at%, Ag_5Te_3 compound will crystallize with Te at 100 ℃, and it

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also gradually disappears at higher temperature treatment. When Ag content is increased to 8.3 at%, Ag_5Te_3 can still exist even at higher annealing temperature. In the meantime, we found that Sb can precipitate at lower temperature. As Ag content is increased to 11.4 at%, a lot of different Ag-Te binary compounds are crystallized at about 100 ℃, and they can still exist when annealing temperature is raised to 300 ℃.

It is found that Ag can only combine with Te but not with Sb. When the Ag content is lower than 6.6 at%, it plays a role as the nuclei, because it can precipitate with Te at temperature lower than the precipitating temperature of Sb_2Te_3. Once Sb_2Te_3 starts to precipitate at higher temperature, it takes Te atoms back from Ag-Te compounds and Ag-Te dis-appears after annealed at 300 ℃. When the Ag content is 8.3 at%, Ag will combine with more Te atoms than that of 6.6 at% Ag so that the amount of Sb_2Te_3 is reduced, and we can even find the precipitation of Sb.

Table II is the result of X-ray diffraction analysis of various Cu doped Sb_2Te_3 films. In this CuSbTe system, Te also precipitates below 100 ℃ when Cu content is less than 2.5 at%, and it is gradually transferred to Sb_2Te_3 at higher annealed temperature as the AgSbTe film does. As Cu content is increased to 8.4 at%, the difference between two systems is that Cu_7Te_4 compound becomes the main phase after annealed at 300 ℃.

TABLE I

The crystalline phases in the Ag doped Sb_2Te_3 films analyzed by X-ray diffraction.(★ means the main crystalline phase)

compositions	as-deposited	100 ℃	200 ℃	300 ℃
$Sb_{38.6}Te_{61.4}$	Te ★	Te ★ Sb_2Te_3 ★	Te Sb_2Te_3 ★	Sb_2Te_3 ★
$Ag_{3.2}Sb_{35.8}Te_{61.0}$	Te ★	Te ★ Ag_5Te_3 ★	Te ★ Sb_2Te_3 ★ Ag_5Te_3	Sb_2Te_3 ★
$Ag_{6.6}Sb_{35.7}Te_{57.7}$		Te ★ Ag_5Te_3 ★	Te Sb_2Te_3 ★ Sb	Sb_2Te_3 ★
$Ag_{8.3}Sb_{34.9}Te_{56.8}$		Sb ★ Sb_2Te_3 ★ Ag_5Te_3 ★	Sb Sb_2Te_3 ★ Ag_5Te_3	Te Sb_2Te_3 ★ Ag_5Te_3
$Ag_{11.4}Sb_{34.5}Te_{54.1}$		Ag_2Te ★	Sb ★ Sb_2Te_3 ★ AgTe ★ Ag_2Te ★ Ag_7Te_4 ★	Sb ★ Sb_2Te_3 ★ AgTe ★ Ag_2Te ★ Ag_7Te_4 ★

TABLE II

The crystalline phases in the Cu doped Sb_2Te_3 films analyzed by X-ray diffraction.(★ means the main crystalline phase)

compositions	as-deposited	100 ℃	200 ℃	300 ℃
$Sb_{38.6}Te_{61.4}$	Te ★	Te ★ Sb_2Te_3 ★	Te Sb_2Te_3 ★	Sb_2Te_3 ★
$Cu_{2.5}Sb_{37.2}Te_{60.3}$	Te ★ CuTe ★	Sb_2Te_3 ★ CuTe	Sb_2Te_3 ★	Sb_2Te_3 ★
$Cu_{4.1}Sb_{37.4}Te_{58.5}$		Te ★ Sb_2Te_3 ★ CuTe ★	Te Sb_2Te_3 ★ CuTe	Sb_2Te_3 ★ Cu_7Te_4
$Cu_{6.4}Sb_{36.0}Te_{57.6}$		Sb_2Te_3 Cu_7Te_4 ★	Sb_2Te_3 ★	Sb_2Te_3 ★
$Cu_{8.4}Sb_{35.1}Te_{56.5}$			Sb_2Te_3 ★ Cu_7Te_4 ★ Sb	Sb_2Te_3 ★ Cu_7Te_4 ★

Typical DSC curve of the $Sb_{38.6}Te_{61.4}$ film is shown in Fig.1. For $Sb_{38.6}Te_{61.4}$ and some Ag or Cu doped Sb_2Te_3 films, their DSC curves show one sharp exothermic peak and one ambiguous exothermic peak as Fig.1 shows. However, the other films show only one sharp exothermic peak. The first sharp peak always appears at temperature lower than that of the second ambiguous peak. First sharp peak means one crystalline phase precipitates from amorphous matrix. So the peak position defines crystallization temperature T_c. The second ambiguous peak means the occurrence of exothermic chemical reaction. It indicates that some metastable phases are transferred to the final thermodynamic stable phases. In table I, when Ag content is lower than 8.3 at% and the annealed temperature is raised to 300 ℃, low temperature metastable phases Te and Ag_5Te_3 are transferred to high temperature thermodynamic stable phases Sb_2Te_3. They all have the second exothermic peak in their DSC curves. When Ag contents of the films are increased to 8.3 and 11.4 at%, they do not have this kind of transformation and their DSC curves do not have the second exothermic peak.

In CuSbTe system, the disappearance of second exothermic peak is also dependent on the increasing of Cu content, as shown in Table II. When Cu contents are 2.5, 4.1 and 6.4 at%, they all have this phase transformation as annealed temperature is higher than 200 ℃, and their DSC curves all have the second exothermic peak. However, the film with 8.4 at% Cu has no this kind of phase transformation and it also has no second exothermic peak.

Table III is the results of DSC measurement from 25 ℃ to 450 ℃. From this table, we found that as the Ag content is increased from 0 to 11.4 at%, the crystallization temperature T_{c1} is increased from 97.4 ℃ to 125.7, and the melting temperature T_m also increases from 415.6 ℃ to more than 450 ℃. For Cu doped films, T_{c1} is increased from

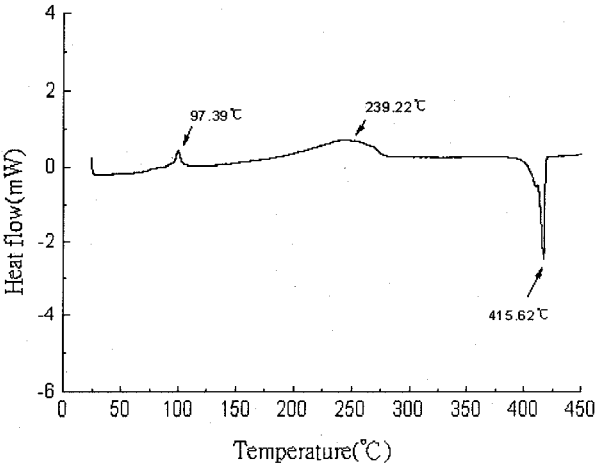

Fig.1 The DSC curve of $Sb_{38.6}Te_{61.4}$ film with heating rate of 5 ℃/min.

TABLE III
The result of DSC measurement, where Tc_1 is the crystallization temperature, Tc_2 is the temperature of the second exothermic peak, and Tm is the melting temperature.

compositions	Tc_1(℃)	Tc_2(℃)	Tm(℃)
$Sb_{38.6}Te_{61.4}$	97.4	239.2	415.6
$Ag_{3.2}Sb_{35.8}Te_{61.0}$	114.5	232.4	411.3
$Ag_{6.6}Sb_{35.7}Te_{57.7}$	120.3	241.5	>450
$Ag_{8.3}Sb_{34.9}Te_{56.8}$	126.0	No	>450
$Ag_{11.4}Sb_{34.5}Te_{54.1}$	125.7	No	>450
$Cu_{2.5}Sb_{37.2}Te_{60.3}$	97.8	237.5	328.1
$Cu_{4.1}Sb_{37.4}Te_{58.5}$	107.7	235.6	418.5
$Cu_{6.4}Sb_{36.0}Te_{57.6}$	118.6	211.7	333.4
$Cu_{8.4}Sb_{35.1}Te_{56.5}$	120.8	No	>450

97.4 ℃ to 120.8 ℃ as Cu content increases from 0 to 8.4 at%. When Cu content is increased to 8.4 at%, T_m is over 450 ℃. This shows that doping Ag or Cu in the Sb_2Te_3 film can improve the thermal stability of amorphous state.

The reflectivity versus laser wavelength curves for as-deposited and various annealed $Ag_{3.2}Sb_{35.8}Te_{61.0}$ films are shown in Fig.2. The reflectivity measurements show that when Ag contents are 3.2, 6.6 and 8.3 at%, the reflectivity ofthe film is enhanced from 35% ~ 50% for the amorphous state to 63%~68% for the crystalline state which after annealing at 300 ℃. From Fig.2, we can see that the contrast ratio between as-deposited and 300 ℃ annealed $Ag_{3.2}Sb_{35.8}Te_{61.0}$ films is about 42%.

Fig.3 shows the reflectivity versus laser wavelength curves for as-deposited and various annealed $Cu_{4.1}Sb_{37.4}Te_{58.5}$ films. We can see that the reflectivity of the film can be changed from 41% for amorphous state to 65% for crystalline state which after annealing at 300 ℃. The contrast ratio between as-deposited and 300 ℃ annealed $Cu_{4.1}Sb_{37.4}Te_{58.5}$ films is about 37% within laser wavelength among 680 and 830nm.

IV. Conclusion

The crystallization process of the Ag or Cu doped Sb_2Te_3 amorphous film was investigated by isothermal treatment. For pure and some Ag or Cu doped Sb_2Te_3 films, phase transformations from lower temperature metastable phases to higher temperature thermodynamic stable phases were found. This kind of phase transformation would cause the appearance of ambiguous exothermic peak in DSC curve. Doping 11.4 at% Ag or 8.4 at% Cu in Sb_2Te_3 can enhance crystallization temperature of the film from 97.4 ℃ to 125.7 ℃ and 120.8 ℃, respectively. This indicates that doping Ag or Cu in the Sb_2Te_3 film can improve the thermal stability of amorphous state. Melting temperature can also be increased to more than 450 ℃ as Ag content is higher than 3.2 at% or Cu content is higher than 6.4 at%. Contrast ratio of the 3.2 at% Ag doped film is about 42%, and it is about 37% for the 4.1 at% Cu doped film at laser wavelength among 680 and 830nm.

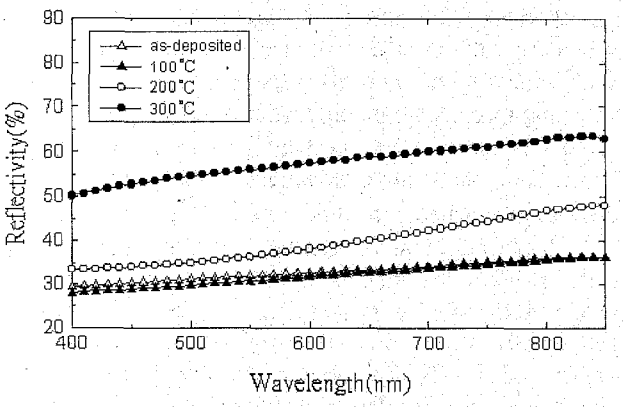

Fig.2 The relation between reflectivity and laser wavelength at 400 ~ 850nm for as-deposited and various annealed $Ag_{3.2}Sb_{35.8}Te_{61.0}$ film.

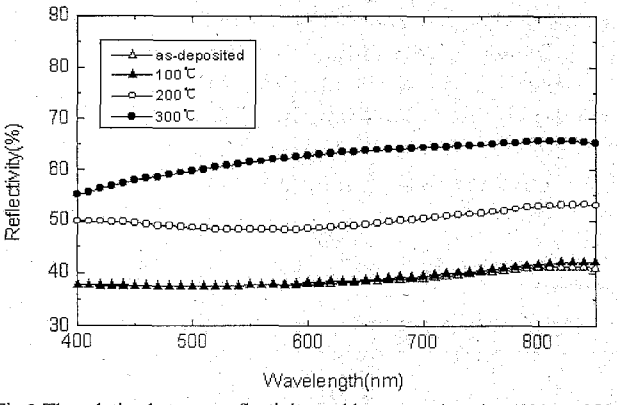

Fig.3 The relation between reflectivity and laser wavelength at 400 ~ 850nm for as-deposited and various annealed $Cu_{4.1}Sb_{37.4}Te_{58.5}$ film.

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