Ge₂Sb₂Te₅ Thin Film Doped with Silver

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(Ge₂Sb₂Te₅)_{100-x}Ag_x films (where $x = 0 \sim 3$ at.%) with 100 nm thickness were deposited on natural-oxidized silicon wafer and glass substrates by dc magnetron co-sputtering of Ge₂Sb₂Te₅ and Ag targets. The effects of Ag content on the optical properties of the (Ge₂Sb₂Te₅)_{100-x}Ag_x film were examined by X-ray diffraction, reflectivity and crystalline temperature analysis. It was found that the reflectivity and thermal properties of the Ge₂Sb₂Te₅ film could be improved by doping a small amount of Ag in the Ge₂Sb₂Te₅ film. The crystallization activity energy of the film decreased as the Ag content was increased. However, the crystalline temperature of the film increased with Ag content. The phase-transition temperature of the fcc to hcp phase increased to at least 450°C as $x > 0.3$. We found that the contrast of (Ge₂Sb₂Te₅)_{98.2}Ag_{1.8} film is suitable for blue laser wavelength recording. [DOI: 10.1143/JJAP.42.1026]

KEYWORDS: (Ge₂Sb₂Te₅)_{100-x}Ag_x film, optical properties, crystalline temperature, crystallization activity energy, phase-transition temperature

1. Introduction

Recently, compact disc systems (CDs) have come to be widely replaced by digital versatile disc systems (DVDs) because of the higher data recording density of DVDs. Based on the rapid crystalline-to-amorphous transition, the GeSbTe film has been investigated and applied widely in the phase-change recording media of DVD systems. However, the reflectivity and thermal properties have remained difficult problems in GeSbTe phase-change disks that should be resolved.¹⁻⁴⁾ In order to increase the reflectivity of the Ge₂Sb₂Te₅ film, Ag is being considered as a good candidate for addition to it.

In this work, we investigated the effects of Ag addition on the microstructure, reflectivity, crystalline temperature, and crystallization activation energy of the Ge₂Sb₂Te₅ film. We found that a small amount of Ag addition does increase the reflectivity, crystalline temperature, and fcc to hcp phase-transition temperature of the Ge₂Sb₂Te₅ film. However, the activity energy of amorphous to fcc phase decreased.

2. Experiment

(Ge₂Sb₂Te₅)_{100-x}Ag_x films (where $x = 0-3$ at.%) were co-sputtered on silicon wafer and glass substrates with Ge₂Sb₂Te₅ and Ag targets by dc magnetron sputtering at room temperature. ZnS-SiO₂ film was used as an upper protective layer. The thicknesses of the (Ge₂Sb₂Te₅)_{100-x}Ag_x film and protective layer were 100 nm and 30 nm, respectively. The base pressure of the sputtering chamber was 5×10^{-7} Torr, and the sputtering Ar gas pressure was maintained at 5 mTorr. After deposition, the films were annealed at various temperatures in vacuum for 10 min and then ice water quenched.

The crystallization temperature, T_c , and the activity energy of amorphous to fcc phase, E_a , were obtained from the reflective intensity change with temperature at various heating rates. The reflectivity was measured by means of a spectrophotometer in the wavelength range of 400–800 nm. The phases and structures of the films were examined by X-ray diffractometer (XRD) with Cu-K α radiation. Composition of the film was determined from the energy disperse

spectrum (EDS). The thickness of the film was measured by α -step.

3. Results and Discussion

Figure 1 shows the relationship between the reflectivity and temperature of the as-deposited Ge₂Sb₂Te₅ film. The heating rate is 60°C/min. We can see that the reflectivity increases rapidly to near 150°C which means that the phase transition of amorphous to fcc crystal phase occurred at about 150°C. This curve can be divided into three stages. The temperature range of the first stage is from room temperature to near T_c . In this stage, the arrangement of atoms is not obviously changed with temperature, and therefore, the reflectivity is not changed in this temperature range. The state of as-deposited film is amorphous and the arrangement of atoms is random, causing its low reflectivity. When the temperature is increased above T_c of the film, the atoms have sufficient energy to rearrange. The arrangement of atoms is ordered such that the film is transformed from amorphous state to crystal state and the reflectivity is rapidly increased; this is the second stage. When the temperature is above approximately 165°C, the reflectivity is increased slowly with increasing temperature. This is due to the grain growth of the film proceeding as the temperature is

Fig. 1. Relationship between reflectivity and temperature of the as-deposited Ge₂Sb₂Te₅ film.

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increased. This is the third stage, and we obtain high reflectivity in this stage. The T_c of pure $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film as estimated from Fig. 1 by the method given in ref. 5 is about 157°C .

Figure 2 shows the relationship between the T_c and Ag contents of various as-deposited $(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{100-x}\text{Ag}_x$ films. We can see that T_c of each film increases with Ag content. The T_c of pure $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film is about 157°C which increases to 177°C as the Ag content is increased to about 3 at.%. Figure 3 shows the relationship between E_a and Ag contents of the as-deposited $(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{100-x}\text{Ag}_x$ film. E_a is estimated from the Kissinger plot.⁶⁾ It is found that E_a decreases as the Ag content is increased. The crystallization of the film is associated with two processes, nucleation and grain growth. E_a changes with Ag content, indicating that Ag plays an important role in the process of nucleation or grain growth. From an inhomogeneous nucleation point of view, the new crystal will nucleate at Ag atom that improves nucleation and reduces the E_a of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film as it is added. However, Ag is a high melting temperature metal and will thus increase the T_c of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film. The reduction of E_a is believed to increase the crystalline rate of the film and thus is expected to increase the erasing speed of the disk.

Figure 4 shows the XRD patterns of various annealed $(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{100-x}\text{Ag}_x$ films. The annealing temperature is 450°C . This indicates that the annealed pure $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film

Fig. 2. Relationship between crystallization temperature and Ag content of the as-deposited $(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{100-x}\text{Ag}_x$ film.

Fig. 3. Relationship between E_a and Ag content of various as-deposited $(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{100-x}\text{Ag}_x$ films.

Fig. 4. X-ray diffraction patterns of various annealed $(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{100-x}\text{Ag}_x$ films. These films are annealed at 450°C .

($x = 0$) has been transformed from fcc to hcp phase at this temperature but the annealed $(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{100-x}\text{Ag}_x$ film is still in fcc phase when $x \geq 0.3$. The fcc to hcp phase-transition temperature of the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film increases as a small amount of Ag is added. This means that the fcc phase of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film is more stable after Ag is added. This may be because the doped Ag atoms substitute for the Ge, Sb, Te atoms or vacancies in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film, or form compounds with the Ge, Sb, or Te atoms. The above three reasons all will form a more stable fcc phase and increase the phase-transition temperature of the fcc to hcp phase. Enhancing the fcc to hcp phase-transition temperature will increase the existing temperature range of the fcc phase. In the overwrite process of a phase-change optical disk, the tolerance to laser power increases as the temperature range of the fcc phase is increased. The recording mark stability can also be improved as Ag is added, because the thermal stability of fcc phase is increased.

Figure 5 shows the relationship between reflectivity and Ag content for various as-deposited and annealed $(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{100-x}\text{Ag}_x$ films, the annealing temperature is 200°C and the laser beam wavelengths are 650 and 430 nm, respectively. We can see that the reflectivities of the as-deposited and annealed films are increased with Ag content as $x < 1.8$, then decreased as $x > 1.8$; the maximum reflectivity occurs at $x \sim 1.8$. From images obtained by means of transition electron microscopy (TEM), we infer that the change of reflectivity with Ag content is associated with the variation of the microstructure of the film. The as-deposited pure $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film is amorphous, but the film becomes nano-crystalline as a small amount of Ag is added.⁷⁾ The average grain size of the as-deposited $(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{98.2}\text{Ag}_{1.8}$ film is about 9.5 nm. From the TEM selected electron diffraction patterns, it is evident that the crystalline phases are AgTe and AgSbTe₂.⁷⁾ The increase of reflectivity with the Ag content of the as-deposited film as

Fig. 5. Relationship between reflectivity and Ag content of as-deposited and annealed $(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{100-x}\text{Ag}_x$ films.

$x < 1.8$ is due to the slight crystallization of the film. However, the decrease of reflectivity with increasing Ag content, as $x > 1.8$, is still not understood. The reflectivity of annealed film is higher than that of as-deposited film because of the better crystallization and grain growth of the annealed film.

Figure 6 shows the reflectivity spectrum and contrast of the as-deposited and annealed $(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{98.2}\text{Ag}_{1.8}$ film. The contrast, C , was defined as $C(\%) = 100\% \times (R_c - R_a)/R_c$, where R_c is the reflectivity of the crystal state and R_a is the reflectivity of the amorphous state. We can see that the contrast between 400 nm and 800 nm is larger than 15%, and the contrast increases from 15.5% to 32% as the laser wavelength is decreased from 650 nm to 400 nm. Therefore, this film is suitable for blue laser wavelength recording.

4. Conclusion

We have shown that the crystalline temperature, reflectivity, phase-transition temperature of fcc to hcp phase, and

Fig. 6. Reflectivity spectra and contrast of as-deposited and annealed $(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{98.2}\text{Ag}_{1.8}$ films, annealing temperature is 200 °C.

the activity energy of amorphous to fcc phase can be improved by doping a small amount of Ag into the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ film. In addition, the $(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{98.2}\text{Ag}_{1.8}$ film is suitable for blue laser application.

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