GeCu Thin Films for Inorganic Write-Once Media

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The $Ge_{100-x}Cu_x$ thin films ($x = 50$ at.%–69 at.%) were deposited on nature oxidized Si (100) wafer by dc co-sputtering of Ge and Cu targets. Microstructures was analyzed by X-ray diffractometer. The optical and thermal properties were measured from static test. It was found that the as-deposited phase was single supersaturated ε-Cu_3Ge phase and it was transformed to Ge and ε-Cu_3Ge coexisting phases after annealing at 400°C. The reflectivity of as-deposited film was higher than that of annealed film.

***Index Terms*—GeCu, inorganic optical recording media, write-once.**

I. Introduction

FOR WRITE-ONCE blue-ray disc with organic recording material, the low absorption and physical defects during spin-coating process were unavoidable. From the view of ecological point, environmentally friendly inorganic material is considered for the write-once media recently. [1] In 1994, M. Haritani *et al.* [2] used Ge/Au bi-layers as the recording materials for write-once media. Under the condition of laser power 10 mW and wavelength $\lambda = 830$ nm, they found its CNR value was 53 dB. In 2003, H. Inoue *et al.* [3] used semiconductor material Si and metal Cu to form Si/Cu bi-layers films in 25 GB write-once optical disk. They found that the jitter value was lower than 8% under writing power of 5 mW. In this study, we add a fast crystallized metal, Cu, in the semiconductor Ge, for write-once recording film application. The optical properties were measured in static way and the crystal structures were analyzed below and above phase transition temperature. We found that GeCu thin film has better optical contrast for blue laser than that of red laser. This means that GeCu film has potential to be a recording layer of write-once Blu-ray discs.

II. Experiments

The $Ge_{100-x}Cu_x$ thin films ($x = 50$ at.%–69 at.%) were deposited on nature oxidized Si (100) wafer by dc co-sputtering of Ge and Cu targets. The background vacuum pressure was 5×10^{-7} torr. The thickness of the $Ge_{100-x}Cu_x$ film is 500 Å, and it was sandwiched with 20 Å ZnS-SiO_2 protective layers. After deposition, the films were annealed at various temperatures in vacuum for 5 min then quenched into ice water. Crystalline structure of the film was identified by X-ray diffractionmeter with Cu-K α radiation. Composition of the film was determined by energy dispersive spectrometer. The phase transition temperature Tx was obtained from the reflective intensity versus temperature curve.

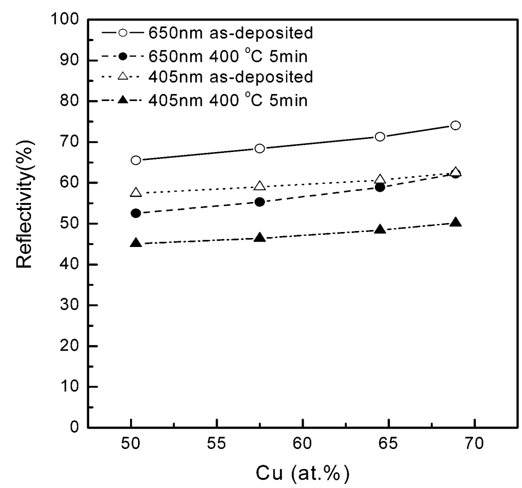

Fig. 1. Relationship between reflectivity and Cu content of the $Ge_{100-x}Cu_x$ films under laser wavelengths of 650 and 405 nm.

III. Results and Discussion

Fig. 1 shows the relationship between reflectivity and Cu concentration of the as-deposited and annealed GeCu films under red laser (650 nm) and blue laser (405 nm). The annealing condition is 400 °C, 5 min. In both wavelengths, the reflectivity of the as-deposited film is higher than that of the annealed film. We can see that the contrast of $Ge_{100-x}Cu_x$ film at $\lambda = 405$ nm is higher than that at 650 nm for $x = 50$ at.%–69 at.%. This indicates that the GeCu film is suitable for blue laser recording.

Fig. 2 shows the variation of reflectivity with temperature of various $Ge_{100-x}Cu_x$ films. The heating rate is 50 °C/min. The reflectivity changes rapidly around the phase transformation temperature Tx. It can be seen that the Tx of $Ge_{100-x}Cu_x$ films with $x = 50, 57, 64$, and 68 are about 311 °C, 308 °C, 304 °C, and 320 °C, respectively. This indicates that the Tx

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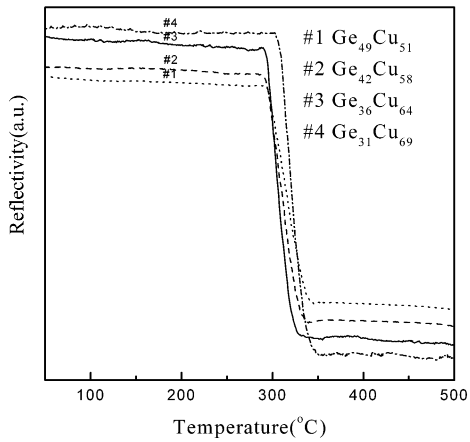

Fig. 2. Relationship between reflectivity and temperature of various GeCu films.

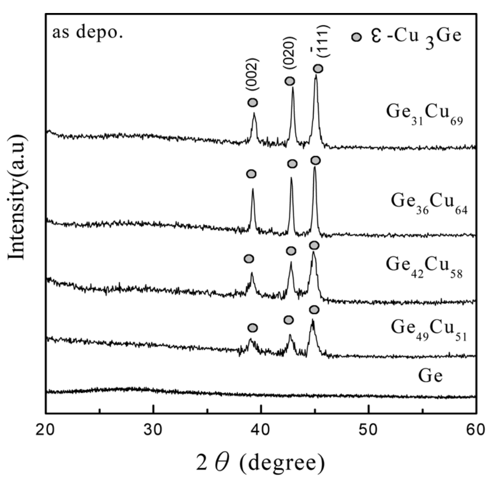

Fig. 3. X-ray diffraction patterns of various as-deposited $Ge_{100-x}Cu_x$ films.

is decreased as Cu content is increased when the Cu content is lower than eutectic point ($Ge_{36.5}Cu_{63.5}$), [4] and Tx is increased when the Cu content is higher than the eutectic point. Comparing with the Ge-Cu phase diagram,[4] this decrease and increase of Tx curve near the eutectic point agrees with the V shape of the liguidus line near the eutectic point in the phase diagram.

Fig. 3 shows the X-ray diffraction patterns of the as-deposited $Ge_{100-x}Cu_x$ films with $x = 51, 58, 64$, and 69. The diffraction peaks of ε-Cu_3Ge (002), (020) and $(\bar{1}11)$ are found in those films, this reveals that the as-deposited films have ε-Cu_3Ge supersaturated crystalline structure.

Fig. 4 shows the X-ray diffraction patterns of these films after annealing at 400 °C which is higher than the Tx of these films (see Fig. 2). The (111) and (311) peaks of Ge phase appeared after annealing. This is due to that the Ge atoms are forced into ε-Cu_3Ge phase during sputtering, and form a supersaturated ε-Cu_3Ge single phase in the as-deposited film. After annealing at 400 °C, those supersaturated Ge atoms got enough energy to overcome the activation energy then diffuse out the ε-Cu_3 Ge phase and segregated. Therefore, the annealed film has two phases structure including Ge and ε-Cu_3Ge.

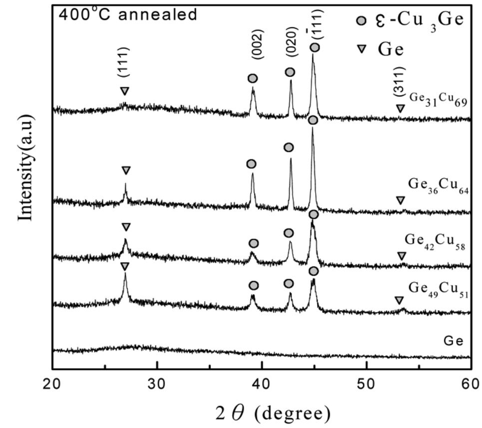

Fig. 4. X-ray diffraction patterns of various annealed $Ge_{100-x}Cu_x$ films.

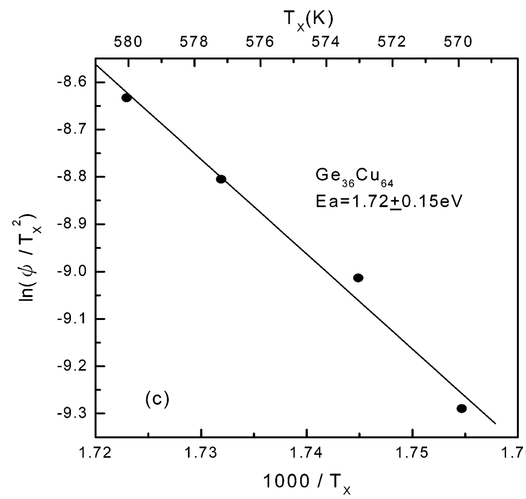

Fig. 5. Kissinger's plots of $Ge_{36}Cu_{64}$ films and the corresponding activation energy Ea.

The equation for Kissinger's method [5], [6] is

$$\ln \frac{\phi}{T_x^2} = \frac{E_a}{K_b} X \frac{1}{T_x} + \text{const.} \tag{1}$$

where ϕ is the heating speed in the unite of temperature degree per minute (K/min.); Tx is the phase change temperature; and K_b is the Boltzmann constant (8.6×10^{-5} eV/K). We can obtain the activation energy Ea from the slope of the $\ln(\phi/T_x^2)$ versus $(1/T_x)$ curve. The $\ln(\phi/T_x^2)$ versus $(1/T_x)$ curve of the $Ge_{36}Cu_{64}$ film with 4 different heating speeds of 20, 30, 50, 60 °C/min is shown in Fig. 5. We can obtain the activation energies of various $Ge_{100-x}Cu_x$ films as shown in Fig. 6. The activation energy of the $Ge_{100-x}Cu_x$ film decreases from 3.54 eV to 1.01 eV as the Cu content is increased from 51 at% to 69 at%. This means that more Cu atoms added into semiconductor Ge will lower the Ea.

IV. Conclusion

In summary, we have prepared new inorganic write-once $Ge_{100-x}Cu_x$ films by dc co-sputtering of Ge and Cu targets. The co-sputtering process made the as-deposited $Ge_{100-x}Cu_x$ film to be a supersaturated ε-Cu_3Ge phase. The Ge atoms

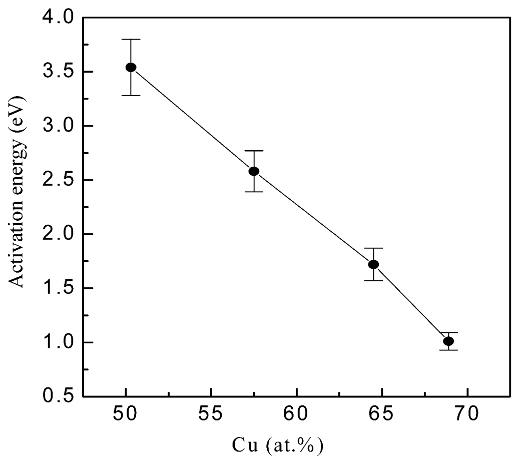

Fig. 6. Relationship between activation energy and Cu content.

will diffuse out of the ε-Cu_3Ge grain to form pure Ge phase after annealing at temperature higher than Tx, and the film is a mixture of Ge and ε-Cu_3Ge phases. The reflectivity of annealed film is lower than the supersaturated as-deposited film (ε-Cu_3Ge single phase film). Furthermore, by Kissinger's method, we found that increased Cu content from 51 at% to 69 at% will lower the activation energy of the GeCu films from 3.54 eV to 1.01 eV.

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