GeCu Thin Films for Inorganic Write-Once Media

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The Ge₁₀₀₋ₓCuₓ thin films (x = 50 at.%, 60 at.%) were deposited on nature oxidized Si (100) wafer by dc co-sputtering of Ge and Cu targets. Microstructures were 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-Cu₂Ge phase and it was transformed to Ge and ε-Cu₅Ge 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 λ = 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 Ge₁₀₀₋ₓCuₓ thin films (x = 50 at.%, 60 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 Ge₁₀₀₋ₓCuₓ film was 500 Å, and it was sandwiched with 20 Å ZnS-SiO₂ 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 diffraction meter with Cu-Kα 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.

III. RESULTS AND DISCUSSION

Fig. 1 shows the relationship between reflectivity and Cu concentration of the Ge₁₀₀₋ₓCuₓ films under laser wavelengths of 650 and 405 nm.

Fig. 2 shows the variation of reflectivity with temperature of various Ge₁₀₀₋ₓCuₓ films. The heating rate is 50°C/min. The reflectivity changes quickly around the phase transformation temperature Tx. It can be seen that the Tx of Ge₁₀₀₋ₓCuₓ 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
is decreased as Cu content is increased when the Cu content is lower than eutectic point (Ge$_{36}$Cu$_{64}$), [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 liquidus 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 $\varepsilon$-Cu$_3$Ge (002), (020) and (111) are found in those films, this reveals that the as-deposited films have $\varepsilon$-Cu$_3$Ge supersaturated crystalline structure.

Fig. 4 shows the X-ray diffraction patterns of these films after annealing at 400 $^\circ$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 $\varepsilon$-Cu$_3$Ge phase during sputtering, and form a supersaturated $\varepsilon$-Cu$_3$Ge single phase in the as-deposited film. After annealing at 400 $^\circ$C, those supersaturated Ge atoms got enough energy to overcome the activation energy then diffuse out the $\varepsilon$-Cu$_3$Ge phase and segregated. Therefore, the annealed film has two phases structure including Ge and $\varepsilon$-Cu$_3$Ge.

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

$$\ln \frac{\phi}{T_x^2} = \frac{E_a}{K_b T_x} + \text{const},$$

where $\phi$ 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 $\times$ 10$^{-5}$ eV/K). We can obtain the activation energy $E_a$ 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 $^\circ$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 $\varepsilon$-Cu$_3$Ge phase. The Ge atoms...
will diffuse out of the $\varepsilon$-Cu$_3$Ge grain to form pure Ge phase after annealing at temperature higher than $T_x$, and the film is a mixture of Ge and $\varepsilon$-Cu$_3$Ge phases. The reflectivity of annealed film is lower than the supersaturated as-deposited film ($\varepsilon$-Cu$_3$Ge 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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