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Optical properties and structure of Sb-rich AgInSbTe phase change thin films*

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A new composition content quaternary-alloy-based phase change thin film, Sb-rich AgInSbTe, has been prepared by DC-magnetron sputtering on a K9 glass substrate. After the film has been subsequently annealed at 200°C for 30min, it becomes a crystalline thin film. The diffraction peak of antimony (Sb) are observed by shallow (0.5 degree) x-ray diffraction in the quaternary alloy thin film. The analyses of the measurement from differential scanning calorimetry (DSC) show that the crystallization temperature of the phase change thin film is about 190°C and increases with the heating rate. By Kissinger plot, the activation energy for crystallization is determined to be 3.05eV. The reflectivity, refractive index and extinction coefficient of the crystalline and amorphous phase change thin films are presented. The optical absorption coefficient of the phase change thin films as a function of photon energy is obtained from the extinction coefficient. The optical band gaps of the amorphous and crystallization phase change thin films are 0.265eV and 1.127eV, respectively.

Keywords: thin films, phase change, Sb-rich AgInSbTe
PACC: 7865K, 9160H, 4280T

1. Introduction

Optical data storage plays a key role for future multimedia applications. Phase change recording is a particularly promising technique for future optical data storage for it is conceptionally compatible with present compact disc-recordable (CD-R) and compact disc-rewritable (CD-RW) formats.[1,2] The principle behind phase change recording is the reversible transformation of small areas (bits) of the active layer between the stable crystalline and the metastable amorphous phases. Amorphization is achieved by locally melting the film using a focused, intensive laser beam. After the laser pulse ends, the melt cools rapidly with a rate of 10^9 to 10^{10}K/s and quenches into the amorphous state. Heating the amorphous area up to a moderate temperature below the melting point T_m but above the glass transition temperature T_g leads to fast recrystallization. The amorphous and crystalline phases have very different optical properties. Therefore the data can be read by monitoring the local changes in the reflection of the media. Erasure is achieved by laser heating the medium to intermediate temperatures, which enables the fast recrystallization of the amorphous bits. This reversible transformation allows rewritable data storage.[3]

$Ge_2Sb_2Te_5$ is one of typical recording materials in the sense of its reflectivity change between the amorphous and crystalline states, its cyclability for recording and erasing, and also its duration at room temperature.[4–6] But in the case of Ge–Sb–Te, two main problems are faced: one is material flow and the other is diffusion of sulfur from the protective layer ($ZnS–SiO_2$) to the recording layer (Ge–Sb–Te).[7] AgInSbTe alloy has been used as the recording layer in compact disc rewritable (CD-RW) and digital versatile disc rewritable (DVD-RW) media and other promising commercial phase change optical discs. Compared with GeSbTe, AgInSbTe alloy are typically used for groove-only formats, where the lower radial density must be compensated by a higher linear density to achieve same overall data capacity on the discs. In AgInSbTe materials, the erase process of the amorphous marks proceeds via the growth of the surround-

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ing crystalline edge to the centre of the mark, rather than by nucleation and subsequent growth. Consequently, the marks written in AgInSbTe-based media have a well-defined shape and sharp edges, leading to intrinsically lower jitter values. As jitter is the limiting factor in increasing the linear density, AgInSbTe materials enable having higher linear density. Moreover, recrystallization is faster in AgInSbTe, as it does not involve a nucleation process.[8,9]

In current optical storage technologies, great attention has been devoted to the AgInSbTe phase change thin films. Sb-rich AgInSbTe phase change thin films obtained by increasing Sb content (>65at.%) and by decreasing Ag and In contents is a new composition content quaternary AgInSbTe alloy. The structure and optical properties of Sb-rich AgInSbTe thin film are studied in this paper. These thin films may be a potential material in terms of applicability for phase change optical recording media in CD-RW and DVD-RW.

2. Experiments

Sb-rich AgInSbTe thin films (Sb>65at%) with a thickness of 60nm were deposited on K9 glass by DC-magnetron sputtering using an alloy target with a diameter of 180mm. The target is bonded to a water cooled copper plate. The base pressure in the deposition chamber is typically 1.8×10^{-3}Pa. Sputtering is performed using Ar ions at a pressure of 1Pa. After the deposited film had been annealed at 200°C for 30min in vacuum, it became a crystalline film.

The reflectivity of the phase change thin films was measured by a Perkin–Elmer Lambda (900UV/VIS/NIR) spectrophotometer in a visible wavelength range of 400–800nm. A variable angle spectroscopic ellipsometer (RAP-1, Fudan University and DG Instruments) was used to measure the refractive index in the wavelength range 400–800nm. The measurement was carried out at atmospheric pressure and room temperature for the incident angles of 70°. The structure of the annealed thin films was examined by shallow (0.5degree) x-ray diffractometry (D/max2550V). Crystallization temperature was measured by differential-scanning calorimetry (DSC, DSC 2119) at various heating rates. Activation energy of crystallization was obtained by Kissinger's method.

3. Results and discussions

3.1. Structure analyses

X-ray patterns were obtained at a shallow (0.5 degree) x-ray incident angle on the exposed recording layer surface, from which the XRD information only from a thin film on a substrate surface can be obtained.

The diffractograms for the Sb-rich AgInSbTe phase change thin films before being annealed show no peak. The absence of the signatures of the crystallization confirms the amorphous nature of as-deposited thin films, whereas the Sb-rich AgInSbTe phase change thin films annealed for 0.5h are found to be crystalline, as shown in Fig.1. The peak observed may be attributed to the phase change from amorphous to crystalline (a to c). The peak assignment of Sb-rich AgInSbTe thin films is similar to that of the hexagonal structure of pure Sb (from PDF original data, 35-0732>antimony Sb), which indicates that the annealed Sb has a crystalline structure. Mongia and Bhatnagar[10] also observed Sb crystalline peak during heat-treatment at 200°C. Liu Huiyong[11] pointed out that AgInSbTe thin film with high Sb content was easy to separate out Sb crystalline state firstly when heat-treatment was carried out at low temperature. The reason for the formation of Sb crystalline state may be the introduction of other nucleation sites into the network of alloy. Jiang and Okuda[12] suggested that a high critical cooling rate of Sb compared with many other metals, which also suggested easy formation of Sb clusters or crystal grains could result in a high nucleation probability. In the Sb-rich AgInSbTe thin films, the contents of Sb are high, and its high cooling rate leads to the forming of crystalline Sb prior to other phases, such as $AgSbTe_2$.

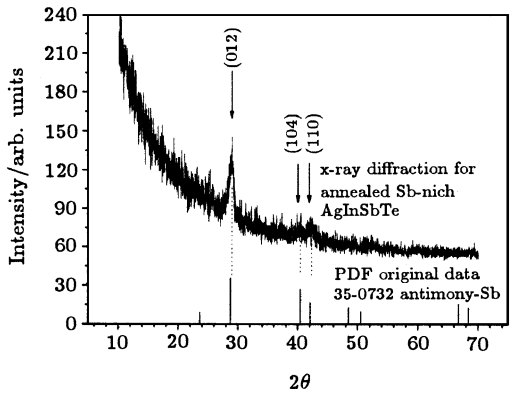


Fig.1. X-ray diffraction pattern for annealed Sb-rich AgInSbTe phase change film.

3.2. Thermal analyses

Thermal analyses by DSC on an as-deposited

Sb-rich AgInSbTe amorphous thin film show major exothermic (crystallization) peak.

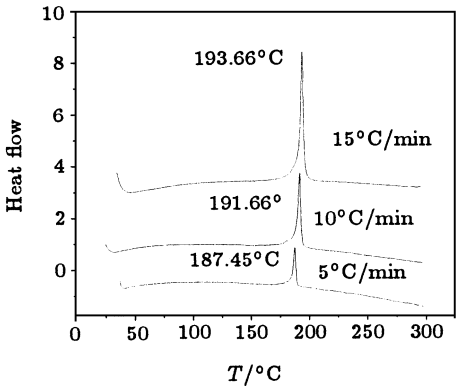


Fig.2. DSC curves of Sb-rich AgInSbTe phase change films at different heating rates.

Figure 2 shows the crystallization temperatures corresponding to the peak of the differential signal from the differential scanning calorimetry. They are 187.45°C at 5°C/min, 191.66°C at 10°C/min, and 193.66°C at 15°C/min, respectively. Three different crystallization temperatures at different heat rates were plugged into the Kissinger plot to calculate the activation energy for the crystallization. For a constant heating rate, $\alpha = \mathrm{d}T/\mathrm{d}t$, the Kissinger equation[13] is

$$\ln(T_\mathrm{p}^2/\alpha) = c + (E_\mathrm{a}/k_\mathrm{B})T_\mathrm{p}^{-1}, \qquad (1)$$

where T_p is the crystallization temperature, c a constant, E_a the activation energy, and K_B the Boltzmann constant. A plot of $\ln(T_\mathrm{p}^2 \cdot \alpha^{-1})$ against $1/T_\mathrm{p}$ yields a straight line, as shown in Fig.3. The activation energy for the crystallization, E_a, was calculated from its slope and turned out to be 3.05eV.

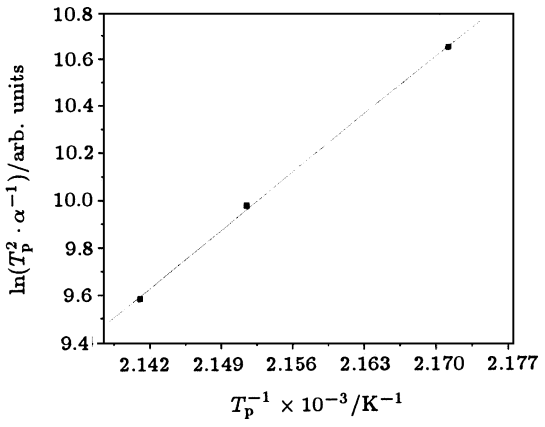


Fig.3. Plot of $\ln(T_\mathrm{p}^2 \cdot \alpha^{-1})$ vs T_p^{-1} of Sb-rich AgInSbTe phase change films.

3.3. Reflectivity spectra and optical constants

Figure 4 gives the reflectivity spectra of the studied thin films in the wavelength region of 400–800nm. It is found that the amorphous and crystalline Sb-rich AgInSbTe thin films have different maxima of reflectivity, and their variation in reflectivity increases with the wavelength in the measured range. For amorphous phase change thin films, the reflectivity changes from 51.44% to 59.65%, and for crystalline thin films the reflectivity increases from 61.09% up to 65.94%. Figure 5 shows the reflectivity contrast between the amorphous and crystalline thin films in the wavelength range 400–800nm. The reflectivity contrast, C, is defined as

$$C = 100\% \times 2 \times (R_\mathrm{c} - R_\mathrm{a})/(R_\mathrm{c} + R_\mathrm{a}). \qquad (2)$$

The reflectivity contrast increases from about 17% at 400nm to 21.12% at 503nm, and then decreases to 10% at 800nm. The maximum of the reflectivity contrast appears at 503nm, so Sb-rich AgInSbTe phase change thin films may be a promising material for short-wavelength recording.

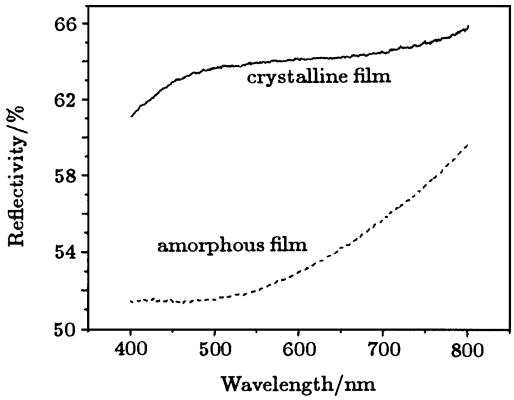


Fig.4. Reflectivity of Sb-rich AgInSbTe phase change film.

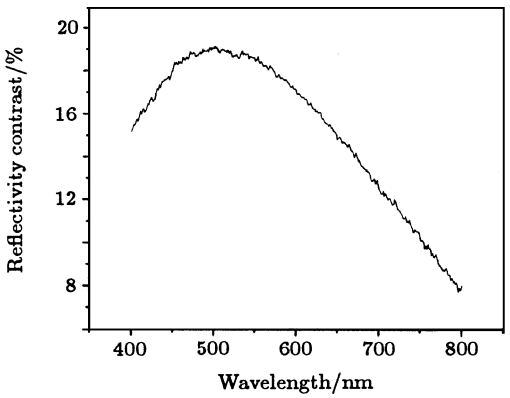


Fig.5. Reflectivity contrast between amorphous and crystalline Sb-rich AgInSbTe phase change film.

The wavelength-dependent optical constants of Sb-rich AgInSbTe thin films in the amorphous and crystalline state are compared in Fig.6. All the optical constants gradually increase with wavelength in the range 400–800nm except the k_a value of amorphous Sb-rich AgInSbTe thin films. In Fig.6, the k_a value of the extinction coefficient decreases with the wavelength increasing from 400nm to 800nm. The refractive index of the annealed Sb-rich AgInSbTe thin film (n_c) is lower than that of amorphous thin films (n_a) in the whole measurement range but for the wavelength close to 800nm. Different from the relationship between n_a and n_c, the extinction coefficient of the annealed Sb-rich AgInSbTe thin film (k_c) is higher than that of amorphous thin films (k_a). In a longer wavelength region, k_c value is obviously higher than that of k_a, however, in a shorter wavelength region, both of them are close to each other.

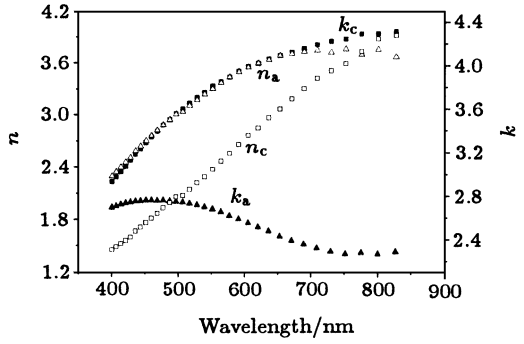


Fig.6. The comparison between refractive indices and between extinction coefficients for Sb-rich AgInSbTe phase change film at amorphous and crystalline states (k_a, k_c and n_a, n_c are extinction coefficients and refractive indices of the films in the amorphous and crystalline states respectively.)

3.4. Optical band gaps

Optical energy gaps of Sb-rich AgInSbTe thin films were investigated. The optical absorption coefficient α_{abs} of the investigated thin films as a function of photon energy has been obtained from the spectrally dependent extinction coefficient k according to the relation $\alpha_{abs}=4\pi k/\lambda$, as shown in Fig.7. Three distinct regions have been generally recognized in absorption edge spectrum of an amorphous semiconductor. They are[14] (1) the weak-absorption tail (α_{abs} <1cm^{-1}) which originates from defects and impurities; (2) the exponential-edge region (1< α_{abs} < 10^4cm^{-1}) which is strongly related to the randomness of structure; and (3) the high-absorption region ($\alpha_{abs} > 10^4$cm^{-1}) which determines the optical energy gap. Figure 7 shows the characteristics of the high absorption ($10^5 < \alpha_{abs} < 10^6$cm^{-1}); the absorption for the Sb-rich AgInSbTe thin films is in the visible region. In the high absorption region, the expression relating the absorption coefficient to optical energy gap E_g as described in Ref.[15] is adopted as follows:

$$\alpha_{abs} h\upsilon = B(h\upsilon - E_g)^n, \qquad (3)$$

where B is the quality factor depending on the transition probability, $h\upsilon$ is the photon energy, and the power term n is an index which characterizes the optical absorption process: n =1/2 for a direct allowed transition, n =3/2 for a direct forbidden transition, n=2 for an indirect allowed transition, and n=3 for an indirect forbidden transition.

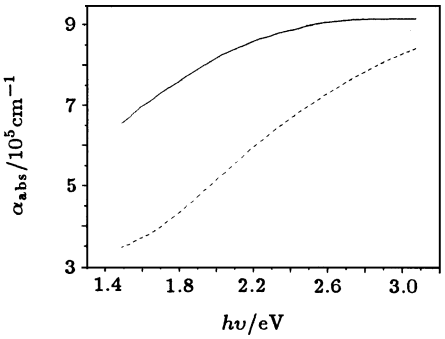


Fig.7. The absorption coefficient plotted as a function of photon energy $h\upsilon$ for amorphous (dashed) and crystalline (solid) Sb-rich AgInSbTe phase change film.

As shown in Fig.8, a linear relation of $\alpha_{abs} h\upsilon$ vs $h\upsilon$ is found for an amorphous Sb-rich AgInSbTe thin films, and n has a value of 0.5, obtained from the slope ($1/n$); however, for annealed thin films a linear relation is obtained when the n value is 3/2. The transition mechanism is not yet fully understood. Judged from the n value, the optical absorption of amorphous Sb-rich AgInSbTe thin films is a direct allowed transition, and E_g=0.265eV, whereas the optical absorption of annealed Sb-rich AgInSbTe thin films is a direct forbidden transition, E_g=1.127eV. The different n value may be related to the changes in structure of Sb-rich AgInSbTe thin films before and after being annealed. The mechanism is unclear as yet.

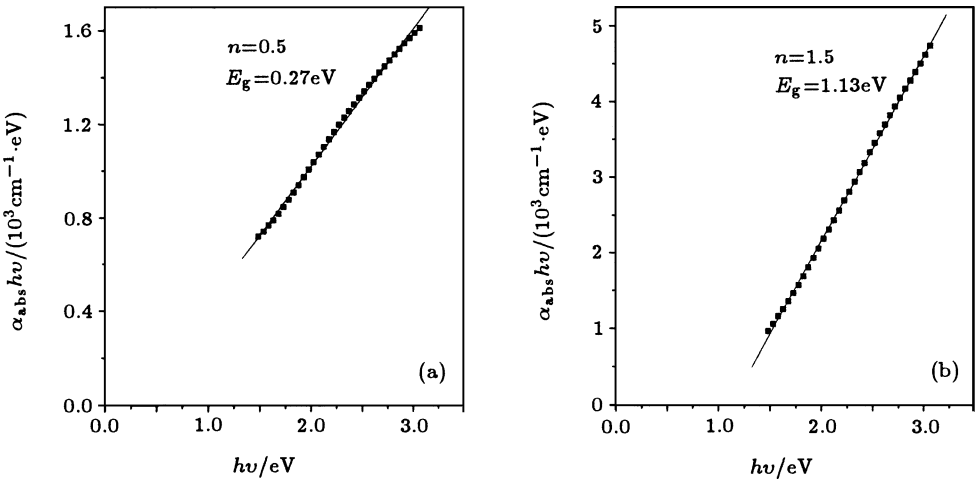


Fig.8. The linear dependence of $\alpha_{abs}h\upsilon$ vs $h\upsilon$ plots for (a) as-deposited and (b) annealed (200°) Sb-rich AgInSbTe phase change film.

4. Conclusions

By increasing Sb content (up to higher than 65 at%) and decreasing Ag and In contents, a new composition content AgInSbTe phase change thin film, Sb-rich AgInSbTe, has been obtained. A shallow (0.5 degree) x-ray pattern indicates that the amorphous thin films can change to the crystalline state after being annealed at 200°C for 30min. The crystallization temperatures determined in the experiments are 187.45°C, 191.66°C, and 193.66°C at the heating rates of 5°C/min, 10°C/min and 15°C/min, respectively. The activation energy for crystallization of the Sb-rich AgInSbTe thin films is calculated from the Kissinger equation to be 3.05eV. The reflectivity of the crystallization the phase change thin films is higher than that of the amorphous one in the whole measured wavelength range, and the maximum of the reflectivity contrast for the phase change thin films appears around 503nm. In the range 400–800nm, all the optical constants (n_a, n_c and k_c) gradually increase with wavelength except the k_a value of the amorphous Sb-rich AgInSbTe thin film. Both the amorphous Sb-rich AgInSbTe thin film and the crystalline one show the high-absorption characteristics, and their optical band gaps are 0.265eV and 1.127eV for the amorphous and crystallization phase change thin films, respectively. The Sb-rich AgInSbTe thin films may be one of the promising materials in optical recording such as for short-wavelength read-write and multi-wavelength recording, or a special mask-layer material for super-resolution.

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