Research on Phase-Change of Disc Recording Media GaSbBi

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Abstract: A new phase-change recording materials, Bi-doped eutectic composition GaSb, was researched experimentally. The films were prepared by vacuum evaporation. The crystallization temperature decreases as the Bi concentration increases. The crystallization activation energy, calculated by Kissinger method, is more than 2.0eV and meets the requirement of the films stability. The crystallization rate enhances with the increase of the Bi concentration. The Ga₁₂Sb₁₂₉₂Bi₈₈ satisfies the demand of optical property by means of spectrophotometer. The absorption of the Ga₁₂Sb₁₂₉₂Bi₈₈ crystalline films is more than that of the Ga₁₂Sb₁₂₉₂Bi₈₈ amorphous films, which can reduce the change when reads information. The least reflectivity of Ga₁₂Sb₁₂₉₂Bi₈₈ is 28.78%, corresponding with the reflection demand.

1. Introduction

An important aspect of all information transmission is the storage and detection of encoded information [1]. Compact disc (CD) storage technology is a high and new technology, and initiated in the early 1970s. In comparison with other recording media, it combines excellent properties, such as higher density packing, large capacity, random access available, long lifetime of information storage. To date phase-change disc is the most important compact disc-rewritable (CD-RW). Three systems of phase-change disc recording media materials, containing binary, ternary, and quaternary, have been researching (as shown in Table 1) through decades of development [2].

| Binary | Ternary       | Quaternary            |
|--------|--------------|-----------------------|
| GaSb   | Ge₂Sb₂Te₅    | AgInSbTe              |
| InSb   | InSbTe       | (Ge,Sn)SbTe           |
| InSe   | GaSeTe       | GeSb(SeTe)            |
| Sb₂Te₃ | SnSbTe₄      | Te₈₁Ge₁₂Sb₂S₂         |
| GeTe   | InSbGe       |                       |

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Although Ge–Sb–Te alloys has been widely researched [3,4], non-tellurium (Te)-based phase-change disc materials have been mostly studied nowadays, for Sb-Te alloys have the disadvantage, such as amorphous state stability and bigger noise. Non-Te based phase-change disc materials have a very high stibium (Sb) content, for instance, germanium stibium (GeSb) and gallium stibium (GaSb), GaSb was first used for amorphous state and crystal condition transformation in 1987 [5]. These non-Te-based materials have the advantage of thermal stability of amorphous recording point and fast crystalline growth rate. Crystalline growth velocity of Ga₁₂Sb₈₈ in GaSb series can reach 23.3m/s, besides a good thermal stability. However, the melting point of Ga₁₂Sb₈₈ is high. The melting point of bismuth (Bi) is lower than that of Ga₁₂Sb₈₈. Moreover, Sb and Bi belong to a same family. Based on the reasons above, this article attempts to gain a new phase-change disc recording materials GaSbBi by Bi-doped eutectic composition GaSb. The following research indicates optical property of new GaSbBi is consistent with that of phase-change disc materials.

2. Experimental procedure
Ingredients of GaSbBi targets prepared according as literature [6] were shown in Table 2. The films were prepared by vacuum evaporation. The substrate was quartz glass with dimensions of 25.4mm×76.2mm×1.0mm. The degree of vacuum was 5×10⁻⁵ Torr. The annealing temperature of films was 350°C, maintained for 90 minute in the quartz tube by argon shielding. The amorphous powders were got by lightly scraping the films on the substrate without heat treatment. Differential scanning calorimeter (DSC: STA 449C) was used to analyze the crystallization temperature dynamics of the films. The optical property of the films was analyzed using spectrophotometer (UV-22101 and UV-22100).

| Sample ID | Recipe of targets | Sample ID | Recipe of targets |
|-----------|-------------------|-----------|-------------------|
| 1#        | Ga₁₂Sb₈₈          | 4#        | Ga₁₂Sb₈₁.₄Bi₆.₆ |
| 2#        | Ga₁₂Sb₈₅.₈Bi₂.₂  | 5#        | Ga₁₂Sb₇₉.₂Bi₈.₈ |
| 3#        | Ga₁₂Sb₈₃.₆Bi₄.₄  |           |                   |

3. Results and discussion
3.1. Thermodynamic properties of amorphous powders
Write and stability of the disc are closely related to thermodynamic properties of phase-change materials. Phase-change materials have to be with suitable melting and phase-change temperature because the write of recording layer corresponded with formation of amorphous state. Generally, the crystallization temperature of amorphous state exceeds 150°C, and the crystallization activation energy was over 2.0eV [7].

In this study, the crystallization temperatures of amorphous powders are got through DSC curves at different heating rate. The crystallization activation energy $E_a$ and frequency factor $K_0$ are acquired with Kissinger method [8] (as shown in formula 1). The integral constant $n$ which is associated with crystal mechanism was obtained by Ozawa method [9] (as indicated in formula 2).

$$\ln\left(\frac{\alpha}{T_p^2}\right) = \ln A + \ln\left(\frac{K_0R}{E_a}\right) - \frac{E_a}{RT_p} \approx \ln\left(\frac{K_0R}{E_a}\right) - \frac{E_a}{RT_p} \quad (1)$$

$$-n = \frac{d\{\ln\ln[1/(1-\chi)]\}}{d\ln \alpha} \quad (2)$$

Where $R$ is Avogadro constant, $\alpha$ is rate of temperature rise, $E_a$ is crystallization activation energy, $A$ is constant, $T_p$ is crystallization temperature.

Where $\chi$ is nucleation, $\alpha$ is rate of temperature rise.
The thermodynamics coefficients calculated in the experiment are shown in Table 5. The results indicated that the ratio of $T_p / T_m$ is about 0.46. Moreover, the value of the ratio increased with the increase of Bi content. Thus the increase of Bi content is in favor of the amorphization. The crystallization activation energy depends on the mobility of the atoms in the order-disorder transition [10]. The weak bond easily makes the phase-change occurred, as a result the crystallization temperature is declined. The $E_a$ from Table 3 are all over 2.0eV, these values of the $E_a$ can be content the requirement of the stability comes up with by Zhong Chao’an [7]. The mode of the crystal growth is bi-dimensional growth when $n$ fall in between two and three, while the mode is one-dimensional growth when $n$ fall in between one and two, according to nucleus theory presented by Avrami [11]. The $n$ calculated in this study fall in between one and two, thus crystal growth of the GaSbBi is reckoned as one-dimensional growth.

Table3. The thermodynamics coefficients of GaSbBi

| Sample ID | $T_m$ (℃) | $T_p$ (℃) | $E_a$(eV) | $K_o$(min$^{-1}$) | n       |
|-----------|-----------|-----------|-----------|-------------------|---------|
| 1#        | 601       | 267.436   | 2.807     | 1.57E+26          | 1.04295 |
| 3#        | 587       | 266.01    | 2.229     | 5.12E+20          | 1.01762 |
| 5#        | 573.4     | 264.484   | 2.1046    | 4.14E+19          | 1.00534 |

3.2. Heat treatment of films

Sample 1# and sample 2# have more diffraction maximum, compared with other three different samples before annealing, according to Figure 1. It is indicated that Bi is good for the amorphization of the films. In contrast with the as-deposited films, the crystallization of the annealed sample 3#, 4# and 5# has obviously occurred.

![Fig 1. X-ray diffraction patterns of films](image)

3.3. Optical properties of films

The optical maser wavelength used in the DVD disc is 650 nm nowadays, while blue-ray disc have a good developing potential. So 450nm and 650nm is used for comparison in this experiment. We only investigate optical properties of sample 1#, 3#, and 5# according to their other good properties. The reflectance, transmittance, reflectivity and absorption of films with sample 1#, 3#, and 5# are followed in Figure 2. The results indicate that the light stability of eutectic composition GaSb is minimally affected by Bi-doped. It is reported that reflectivity of the films have to be over 20% [12]. As far as the reflectivity, both sample 1# and sample 5# are over 20%, which could corresponded with the reflection demand, and the least reflectivity of sample 5# (Ga12Sb79.2Bi8.8) is 28.78%. While sample 3# is not up to the reflection demand. The high value of sample 3# is caused by the experimental error.
The absorption of sample 5# crystalline films is more than that of amorphous films, which could reduce the change when reading information, particularly. When a disc is designed, design practice demands for a higher monolithic reflectivity of the disc. In comparison with sample 1# and 5#, sample 3# has the highest reflectivity. It comes to the conclusion that not only crystalline films but also amorphous films have the same variation trend caused by Bi-doped.

![Graphs showing optical properties](image)

(a) Wavelength of 650nm

(b) Wavelength of 450nm

Fig 2. Optical properties of films (The solid symbols represent the annealed state, the open ones correspond to the as-deposited state)

The energy gap of films was calculated by Tauc equation [13] (as indicated in formula 3). The results of sample 1#, 3# and 5# are shown in Figure 3. The values of energy gap raised by Bi-doped have marginal discrepancies. So it is reasonable to consider that a handful of Bi contents have little effect of the energy gap.

\[ \alpha h \nu = A(h \nu - E_g)^2 \]  

(3)

Where \( \alpha \) is absorption coefficient, \( h \nu \) is photon energy, \( E_g \) is energy gap, \( A \) is constant.
4. Conclusion
1. The crystallization temperature decreases as the Bi concentration increases;
2. The crystallization activation energy is more than 2.0 eV, which meets the requirement of the films stability;
3. The crystallization rate enhances with the increase of the Bi concentration;
4. The least reflectivity of Ga$_{12}$Sb$_{79.2}$Bi$_{8.8}$ is 28.78%, which corresponds with the reflection demand.

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