Vol 11 No 3, March 2002
1009-1963/2002/11(03)/0293-05

Chinese Physics

© 2002 Chin. Phys. Soc.
and IOP Publishing Ltd

Crystallization of $Ge_2Sb_2Te_5$ phase-change optical disk media*

Liu Bo(刘 波)†, Ruan Hao(阮 昊), and Gan Fu-Xi(干福熹)

Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, *China*

(Received 12 September 2001; revised manuscript received 4 October 2001)

In this paper, the crystallization behaviour of amorphous $Ge_2Sb_2Te_5$ thin films is investigated using differential scanning calorimetry), x-ray diffraction and optical transmissivity measurements. It is indicated that only the amorphous phase to face-centred-cubic phase transformation occurs during laser annealing of the normal phase-change structure, which is a benefit for raising the phase-change optical disk's carrier-to-noise ratio (CNR). For amorphous $Ge_2Sb_2Te_5$ thin films, the crystallization temperature is about 200°C and the melting temperature is 546.87°C. The activation energy for the crystallization, E_a, is 2.25eV. The crystallization dynamics for $Ge_2Sb_2Te_5$ thin films obeys the law of nucleation and growth reaction. The sputtered $Ge_2Sb_2Te_5$ films were initialized by an initializer unit. The initialization conditions have a great effect on the reflectivity contrast of the $Ge_2Sb_2Te_5$ phase-change optical disk.

Keywords: $Ge_2Sb_2Te_5$, phase-change, initialization, face-centred-cubic
PACC: 7820D, 8130H, 0570, 4280T

1. Introduction

In rewritable phase-change optical recording, a bit of information is written by applying a short pulse of a focused laser beam to a crystallized area of the disk. This pulse increases the local temperature of the storage layer above its melting point. When the pulse ends, the molten spot cools at rates approaching 10^9–10^{10} °C/s, and subsequently amorphizes. The mark can later be identified by using the same focused laser beam at a much lower incident power to measure the reflection (or transmission) of the spot relative to its crystalline surroundings. Erasure is achieved by exposing the film to intermediate levels of laser power, raising the local temperature of the storage layer above its crystallization but below the melting temperature. The amorphous mark thus recrystallizes while the surrounding crystalline matrix remains largely unaffected, and the optical contrast is removed. The amorphization and crystallization behaviour of the storage layer is therefore of fundamental importance to phase-change recording.

The GeSbTe amorphous thin film is extensively used as optical memory material in the recording layer of phase-change optical disk media such as compact disk rewritable (CD-RW) and rewritable digital versatile disk-random access memories (DVD-RAMs). Extensive experimental studies using different methods, including atomic force microscopy (AFM),[1] transmission electron microscopy (TEM),[2] differential scanning calorimetry (DSC), x-ray diffraction (XRD),[3–6] Raman spectroscopy[7] and coherent phonon spectroscopy,[8] have been conducted to understand the crystallization phenomenon of GeSbTe phase-change material. But most of these use the thermal-induced method to crystallize GeSbTe phase-change material. Thermal-induced crystallization shows a very low crystallization rate, which is very different from laser-induced crystallization. In this work, we used XRD, DSC and optical transmissivity measurements to examine the crystallization behaviour of the $Ge_2Sb_2Te_5$ phase-change media. The crystallization has been carried out using an initializer subjected to various initialization laser powers and velocities. We have also measured the reflectivity contrast of the disks.

2. Experiments

2.1. Disk preparation

Figure 1 shows a typical quadrilayer phase-change

*Project supported by the Shanghai Applied Physics Centre and the National Natural Science Foundation of China (Grant No. 59832060).

†Corresponding author: Fax 86-021-59528812; Tel. 86-021-59534890–552; E-mail, lb73sd@sina.com.cn.

optical disk stack deposited on a 1.2mm thick polycarbonate substrate. The stack consists of a 110nm thick lower dielectric layer (ZnS–SiO_2), an X nm thick $Ge_2Sb_2Te_5$ layer (here X=20 nm for reflection contrast measurements and X=100 nm for XRD measurements), a 25nm thick upper dielectric layer (ZnS–SiO_2), and a 70nm thick aluminium reflective layer.

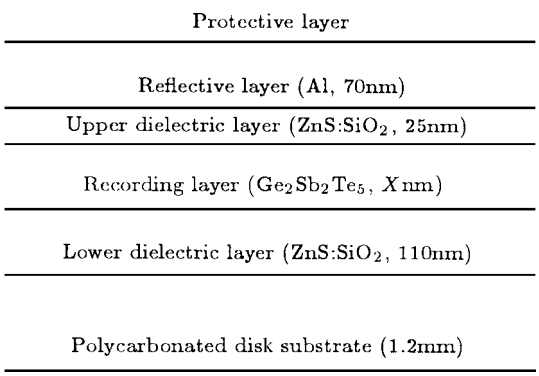


Fig.1. Structure of the phase-change optical disk.

2.2. Disk initialization

Disk initialization was performed in a POP120-5F type initializer which was made by Hitachi Computer Peripherals Co. Ltd, Japan. The wavelength of the laser was 810 nm and the laser beam spot size was 1μm×192μm (full width at half maximum (FWHM) 1800mW). The initialization mode is CLV mode. The laser spot feed per rotation (radius) is 96μm. The disk was initialized either at various laser powers (P_i=1000, 1150, 1300, 1450 and 1600mW) with a fixed initialization velocity (V_i=4.2m/s) or with various initialization velocities (V_i=2.4, 3.0, 3.6, 4.2 and 4.8m/s) at a fixed laser power (P_i=1300mW).

2.3. DSC and XRD studies

To prepare the XRD samples, the disk was first cut into small pieces using a pair of scissors. A 3M scotch tape was applied to the disk to peel off the upper dielectric and Al reflection layers. The residual part can be directly used for XRD measurements (as shown in Fig.2). For XRD experiments, Cu $K\alpha$ (λ=0.15418 nm) radiation was used. The XRD pattern of every sample was taken at room temperature using a Rigaku D/MAX 2550V diffractometer.

The 200 nm thick $Ge_2Sb_2Te_5$ film was deposited on a glass wafer by direct current magnetron sputtering at 0.6 Pa of Ar pressure. A differential scanning calorimeter (Rheometric Scientific DSC-SP) was employed to measure the crystallization and melting temperatures of the amorphous films at heating rates of 10, 30 and 50°C/min.

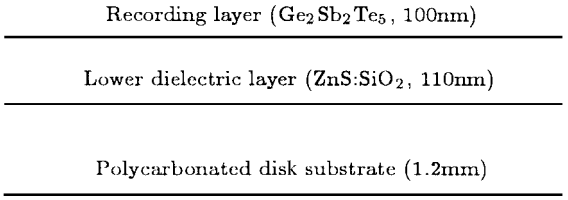


Fig.2. Structure of the XRD samples of $Ge_2Sb_2Te_5$ film.

The reflectance of the disk before and after initialization was measured using the UV/Vis/NIR spectrometer (model: Perkin Elmer, Lambda 900).

3. Results and discussion

3.1. The crystallization behaviours of the $Ge_2Sb_2Te_5$ film

3.1.1. Phase change of the GeSbTe system in a disk sample

Figure 3 shows the XRD patterns for (a) the 180 nm thick ZnS-SiO_2 film, (b) the as-deposited $Ge_2Sb_2Te_5$ film, and (c) the laser-crystallized $Ge_2Sb_2Te_5$ film (the initialization conditions: power of 1300mW and velocity of 4.2m/s). In patterns (a) and (b), no peak is observed and therefore the ZnS–SiO_2 and the as-deposited films are in an amorphous state. What should be pointed out is that the broad peak at about 17°(2θ) in all the patterns is caused by the PC substrate just under the ZnS–SiO_2 and the $Ge_2Sb_2Te_5$ films.

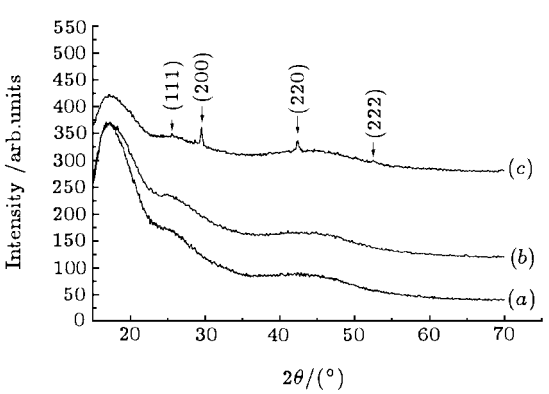


Fig.3. Diffraction patterns of the (*a*) ZnS–SiO_2 film, (*b*) as-deposited $Ge_2Sb_2Te_5$ film, and (*c*) laser-crystallized $Ge_2Sb_2Te_5$ film.

The crystal structure of the $Ge_2Sb_2Te_5$ thin film after initialization was identified as face-centred-cubic

(fcc) NaCl type structure with a lattice parameter a of 0.602 nm. The corresponding indices are shown in Table 1. It was indicated that the 4a site contains Ge atom, Sb atom and vacancy, and the 4b site is fully occupied by Te atom. The amount of vacancy is 20% of all the 4a sites.[9] It should be pointed out that the laser-induced crystallization of the $Ge_2Sb_2Te_5$ film is very different from the thermal-induced one. When the $Ge_2Sb_2Te_5$ film is annealed from room temperature to 400°C, the amorphousness to fcc crystalline and the fcc crystalline to hexagonal close-packed (hcp) crystalline transformations occur.[10,11] It was also indicated that the fcc structure was the metastable phase and the hcp structure was the stable phase. But only the amorphous phase to fcc phase transformation occurs during laser annealing of the normal phase-change structure because the phase transforming from fcc to hcp will be forbidden after the heating rate exceeds the laser writing rate.[11] This phenomenon may explain the high carrier-to-noise ratio of the fcc structure obtained by laser annealing.

Table 1. Index results of x-ray diffraction pattern of $Ge_2Sb_2Te_5$ crystalline.

$\{hkl\}$	111	200	220	222
$2\theta/(°)$	25.65	29.62	42.56	52.62
d/nm	0.347	0.302	0.212	0.174
a/nm	0.601	0.604	0.600	0.603

3.1.2. The crystallization thermodynamics of $Ge_2Sb_2Te_5$ film

Figure 4 shows the crystallization and melting temperatures corresponding to the peak of the differential signal in the DSC. The values of crystallization temperature increase as the heating rate increases: 197.16°C at 10°C/min; 206.61°C at 30°C/min; and 212.00°C at 50°C/min. The melting temperature is about 546.87°C. 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, φ=dT/dt, the Kissinger equation is

$$\ln(v/T^2) = -E_a/(kT) + A \qquad (1)$$

where v is the heating rate, T is the crystallization temperature, E_a is the activation energy, k is the Boltzmann constant, and A is a constant. A plot of $\ln(v/T^2)$ against $1/T$ yields a straight line (see Fig.5). The activation energy for the crystallization, E_a, was calculated from its slope and turned out to be 2.25eV.

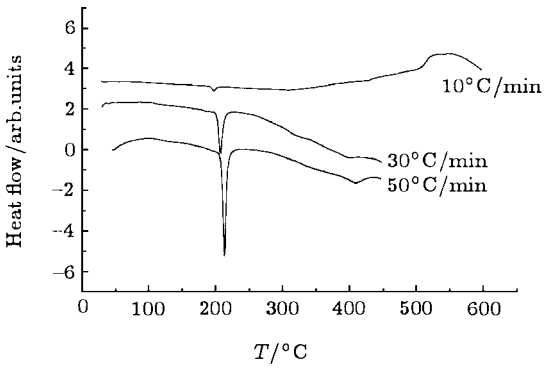


Fig.4. DSC curves for $Ge_2Sb_2Te_5$ thin films at three different heating rates.

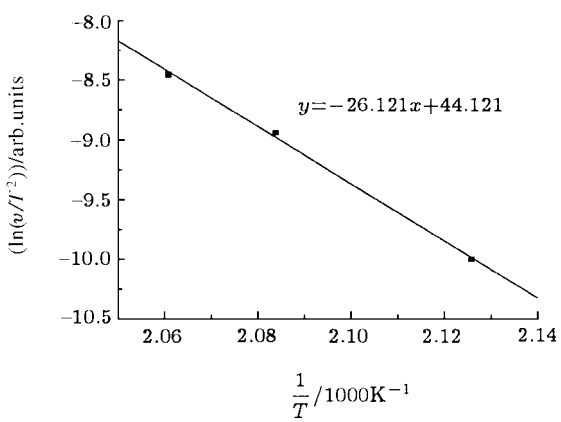


Fig.5. Kissinger plots for the $Ge_2Sb_2Te_5$ thin film.

3.1.3. The crystallization dynamics of the $Ge_2Sb_2Te_5$ film

Figure 6 shows the temperature transmissivity cure at a heating rate of 10°C/min for the 20nm thick single-layer film covered by a 50nm thick ZnS–SiO_2 film. The wavelength used for transmissivity measurements is 650nm. The transmissivity of the $Ge_2Sb_2Te_5$ film begins to decrease at about 150°C, which indicates that the crystallization has begun before the temperature approaches the crystallization temperature. When the temperature is higher than 200°C, the crystallization has completed because the transmissivity is almost constant. The curve exhibits an abrupt transmissivity change in a narrow temperature range. This phenomenon should correspond to the melting process of the $Ge_2Sb_2Te_5$ film. When the temperature is in the 570–610°C range, the transmissivity again remains constant and the melting is over. Finally, the transmissivity increases greatly due to the evaporation of the $Ge_2Sb_2Te_5$ film.

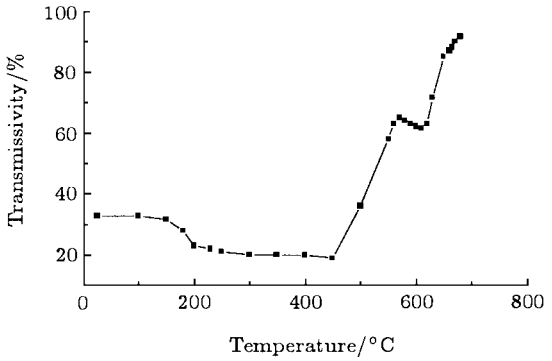


Fig.6. Transmissivity versus temperature cure for the single $Ge_2Sb_2Te_5$ film.

Figure 7 shows the "low"-temperature (180°C) crystallization behaviour of $Ge_2Sb_2Te_5$. The sample is the same as that used in Fig.6. The wavelength used for the transmissivity measurement is also 650nm. The pattern is classified into two categories. In the first stage, the transmissivity decreases slowly and this transmissivity change may corresponds to the nucleation. After the $Ge_2Sb_2Te_5$ film has been heated for about 340 seconds, the curve exhibits an abrupt transmissivity change in a very narrow time range, and this indicates that the grain growth occurs in the second stage.

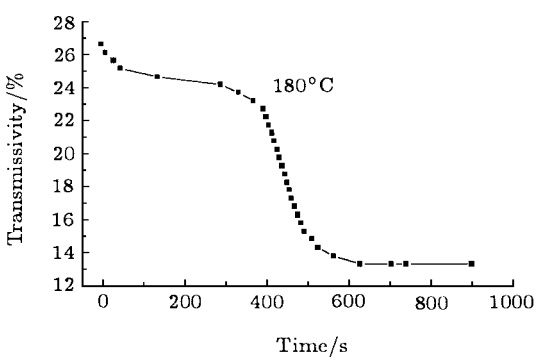


Fig.7. Transmissivity versus time cure for the single $Ge_2Sb_2Te_5$ film.

Figure 8 is the degree of crystallization versus time cure for the single $Ge_2Sb_2Te_5$ film that deviates from Fig.7. The relationship between T and the degree of crystallization χ of a sample is assumed to be linear

$$\chi(T) = \left|\frac{T_a - T}{T_a - T_c}\right|, \qquad (2)$$

where T_a, T_c and T are the transmissivities for the amorphous state, crystallization state and the state at time t, respectively. The crystallization dynamics shown in Fig.8 obeys the laws of a homogeneous reaction without any delay at t=0. This is expected for a nucleation and growth reaction.

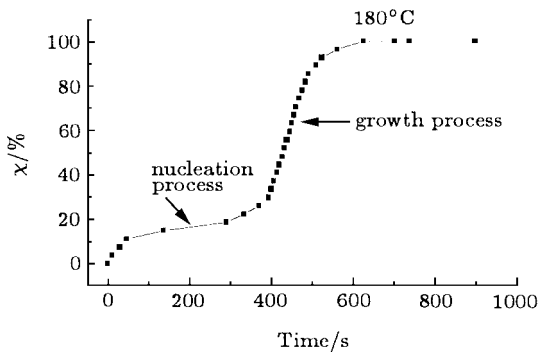


Fig.8. Degree of crystallization versus time cure for the single $Ge_2Sb_2Te_5$ film.

3.2. Reflectivity contrast

Figure 9 gives the reflectivity contrast of the $Ge_2Sb_2Te_5$ phase-change optical disk at wavelengths of 780, 650 and 430 nm, which correspond to the wavelengths of CD, DVD and the forthcoming HD DVD, respectively. The reflectivity (optical) contrast is defined as[1,12]

$$\Delta R(\%) = [(R_c - R_a)/R_c] \times 100\%, \qquad (3)$$

where R_c and R_a are the reflectivities of the crystalline state and the as-deposited amorphous film, respectively. It was found that the reflectivity contrast changes greatly at different wavelengths and initialization conditions. The reflectivity contrast ranges from about 30% at 430 nm to about 67% at 650 nm and to about 50% at 780 nm. On the whole, the reflectivity contrast decreases as the initialization velocity increases at a fixed initialization power. When the initialization velocity is constant, the reflectivity contrast increases as the initialization power increases at a lower velocity. In contrast, it decreases as the initialization power increases at a higher velocity. This phenomenon arises from the degree of crystallization at different initialization conditions. Different crystallization fractions give different reflectivity contrasts. From Fig.9 it can be seen that the maximum modulation $(R_c\text{-}R_a)/R_c$ could be achieved if the initialization condition is carefully chosen.

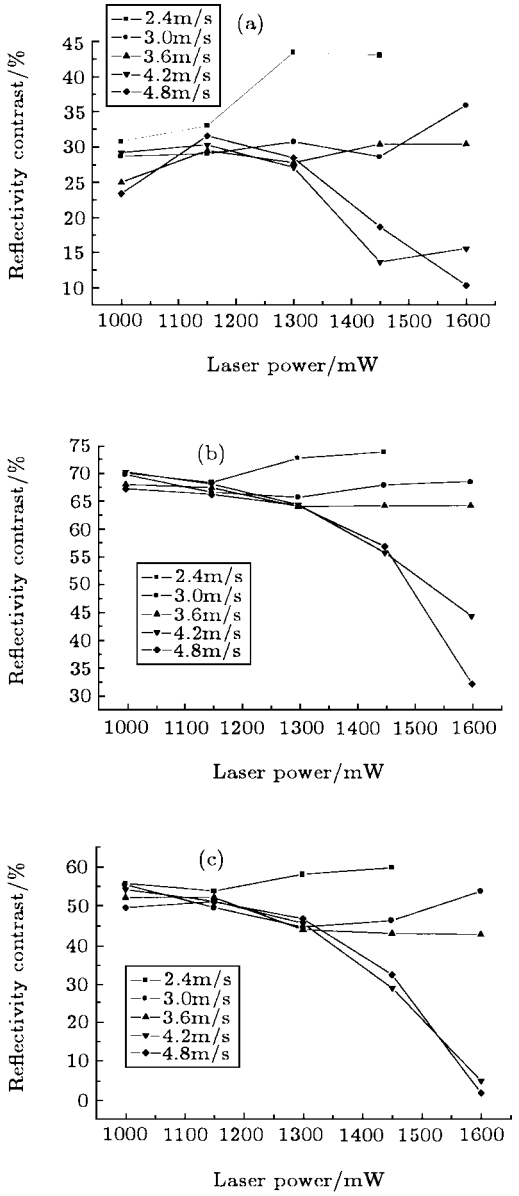


Fig.9. Relationship between initialization power/velocity and reflectivity contrast of the $Ge_2Sb_2Te_5$ phase-change optical disks at (a) 430, (b) 650 and (c) 780nm.

4. Conclusion

We have investigated the crystallization behaviours of the $Ge_2Sb_2Te_5$ phase-change film. It is indicated that only the amorphous phase to fcc phase transformation occurs during laser annealing of the normal phase-change structure, which is beneficial for raising the CNR of the phase-change optical disk. The phase transformation from fcc to hcp does not occur in laser heating, but occurs during the heat-induced phase-change process. For the amorphous $Ge_2Sb_2Te_5$ thin film, the crystallization temperature is about 200°C with an activation energy for the crystallization, E_a, being 2.25eV and the melting temperature is 546.87°C. The crystallization dynamics for the $Ge_2Sb_2Te_5$ thin film obeys the law of nucleation and growth reaction. The initialization conditions have a great effect on the reflectivity contrast of the $Ge_2Sb_2Te_5$ phase-change optical disk. It is indicated that with a low velocity the reflectivity contrast increases as the initialization power increases, while it decreases with a high velocity. It also decreases as the initialization velocity increases. Also the reflectivity contrast is very different when the measurement wavelength ranges from 400 to 900nm. There are many factors affecting the reflectivity contrast, including the crystallinity, the crystalline phase, the disk structure, and so on.

Acknowledgment

We would like to express our appreciation to Hitachi Computer Peripherals Co. Ltd for their free offer of the POP120-5F type initializer.

References

[1] Weidenhof V, Friedrich I, Ziegler S *et al* 1999 *J. Appl. Phys.* **86** 5879
[2] Chen H W, Hsieh T E, Liu J R *et al* 1999 *Japan. J. Appl. Phys.* **38** 1691
[3] Jeong Tae H, Kim Myong R, Hun Seo *et al* 1999 *J. Appl. Phys.* **86** 774
[4] Noboru Y and Toshiyuki M 2000 *J. Appl. Phys.* **88** 7020
[5] Norikazu O 1996 *J. Appl. Phys.* **79** 8357
[6] Khulbe Pramod K, Wright Ewan M and Mansuripur M 2000 *J. Appl. Phys.* **88** 3926
[7] Junji T and Nobufumi A 1999 *Japan. J. Appl. Phys.* **38** L322
[8] Forst M, Dekorsy T, Trappe C *et al* 2000 *Appl. Phys. Lett.* **77** 1964
[9] Toshihisa N, Gentaro O, Yoshiharu T *et al* 2000 *Thin Solid Films* **370** 258
[10] Chiang D, Jeng T R, Huang D R *et al* 1999 *Japan. J. Appl. Phys.* **38** 1649
[11] Noboru Y, Eiji O, Kenichi N *et al* 1991 *J. Appl. Phys.* **69** 2849
[12] Lee C M, Chin T S, Huang Y Y *et al* 1999 *Japan. J. Appl. Phys.* **38** 6369