

# Thermal phase change and activation energy of crystallization of Ge-Sb-Te-Sn thin films

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To improve the optical storage performance, Sn was doped into Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> phase change thin films. The optical and thermal properties of Sn-doped Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> film were investigated. The crystal structures of the as-sputtered and the annealed films were identified by the X-ray diffraction (XRD) method. The differential scanning calorimeter (DSC) method is used to get the crystallization temperature and crystallization energy ( $E_a$ ). It was found that proper Sn-doping could highly improve storage performance of the Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> media.

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Recently, the demand of high-speed and high-density optical recording media is very high. Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> alloy is one of the most widely used recording materials for phase-change optical media. The working principle is that phase-change film is the reflectivity difference between the amorphous phase and the crystalline phase of the films<sup>[1]</sup>.

To get higher density storage, we can increase the numerical aperture (NA) of the objective lens and use shorter laser wavelength. But when the laser wavelength becomes shorter, the reflectivity of the recording films will become lower. In addition, we need materials of high crystallization rates to achieve high speed recording. So, the manipulation of the chemical composition of Ge-Sb-Te based chalcogenide has been attempted by doping small amount of other elements into the phase-change recording films to improve their optical recording performance<sup>[2,3]</sup>.

In this paper, we investigated the optical and thermal properties of the Sn-doped Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> films to develop new recording media for short wavelength high density and high-speed optical storage.

The approximate thickness films of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> with or without Sn doping were deposited on glass substrates using direct current (DC) sputtering method. The sputtering power used in experiments was 150 W, and the background pressure was  $6.0 \times 10^{-4}$  Pa. The Sn content of the films can be controlled by changing the number of Sn chips which put on the Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> target. The composition of the films was analyzed by using the inductively coupled plasma atomic emission-spectrometry (ICP-AES). Thermal annealing of the as-deposited films was carried out under protection of argon in a chamber. The samples were heated to 275°C at a heating rate of 10°C/min and kept at the temperature for 30 minutes.

A reflectivity of amorphous and crystalline films was measured by using a UV/VIS/NIR spectrometer (Perkin Elmer, Lambda 900). The structures of the films before and after annealing were examined by using a Rigaku D/MAX 2550V X-ray diffraction (XRD).

The differential scanning calorimeter (DSC; TA Instruments 2910) was used to analyze the thermal behavior of the sputtered materials. Different heating rates (5, 10,

15 K·min<sup>-1</sup>) were adopted to study the dependence of crystallization temperatures on heating-rate.

It is clear from Fig. 1(a) that the Sn-doped films have higher reflectivity than the undoped film in both amorphous and crystalline states. The addition of Sn at 2.1 at.-% considerably increases the reflectivity of the crystalline state and from 2.1 at.-% up to 5.8 at.-% the reflectivity keeps almost constant, while that of the amorphous state shows a slight increase with increasing Sn content. Especially, the reflectivity of the Sn-doped thin films is as high as 70% at 405 nm and 60% at 300 nm.

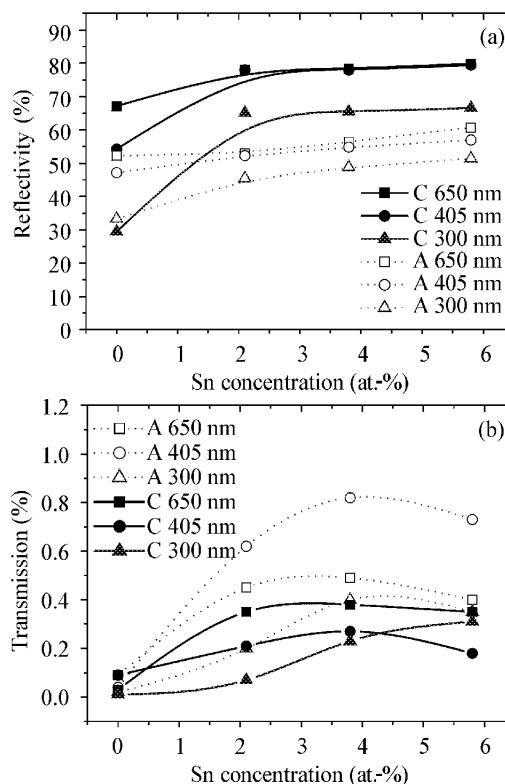


Fig. 1. Reflection (a) and transmission (b) spectra of the Sn-doped Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> films at amorphous (A) and crystalline (C) states as a function of Sn content at wavelengths of 650 nm, 405 nm and 300 nm, respectively.

Figure 1(b) shows the transmission spectra of the films less than 1%. It can be seen that all the films have a very low transmission.

For practical applications, a rewritable material should possess a high signal-to-noise ratio. This can be translated into a high reflectivity contrast ( $C$ ), which is defined as<sup>[4]</sup>

$$C = 2 \times \left| \frac{R_c - R_a}{R_c + R_a} \right| \times 100\%, \quad (1)$$

where  $R_c$  and  $R_a$  are the reflectivities at crystalline and amorphous states, respectively. Since no protecting or reflecting layers were used,  $C$  is the only contribution to the phase change recording film.

Figure 2 shows the reflectivity contrast of the Sn-doped  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  thin films at the selected wavelengths, 300, 405 and 650 nm, respectively. A significant increase in  $C$  is noticed when minor amount of Sn is doped into the  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  thin films. The reflectivity contrasts of the film containing 2.1 at.-% Sn are as high as 38% at 405 nm and 36% at 300 nm, indicating that proper Sn-doping can considerably improve the recording performance of the  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  thin films at short blue wavelength. It is worth mentioning here that there is no data of the reflectivity contrast for the film where Sn-doping at 300 nm in Fig. 2. This is because the reflectivity of the crystalline state is lower than that of the amorphous state as shown in Fig. 1(a). So the reflectivity contrast is minus value. In this case we can also conclude that the optimum content of Sn is still 2.1 at.-% in terms of maximum reflectivity contrast at 300 nm.

The XRD measurements presented in Fig. 3 show the amorphous structure for the as-sputtered and the crystallization structure for the annealed thin films. After the heat treatment, the main crystalline phases in the  $b, c$ , and  $d$  samples are the pseudobinary  $\text{GeTe-Sb}_2\text{Te}_3$  and  $\text{SnTe}$ , while a sample only has  $\text{GeTe-Sb}_2\text{Te}_3$ . The phase of  $\text{GeTe-Sb}_2\text{Te}_3$  has a face centered cubic (fcc) lattice and the  $\text{SnTe}$  has a cubic lattice. From the above we can see that the Sn doping in the  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  films promotes the formation of  $\text{SnTe}$  phase. The reason may be related to some of the Ge replaced by Sn and forming the  $\text{SnTe}$  phase.

Elements having low values of  $T_g/T_m$  ( $T_g$  is the glass

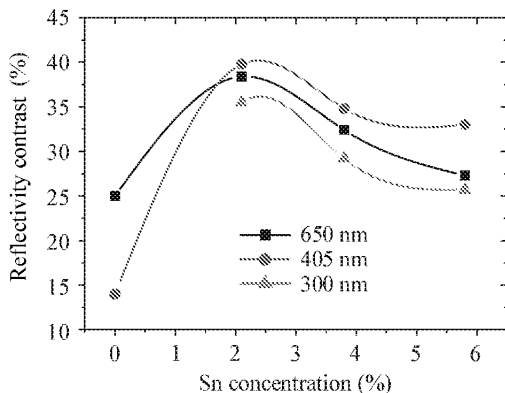


Fig. 2. Reflectivity contrast as a function of Sn content at different wavelengths.

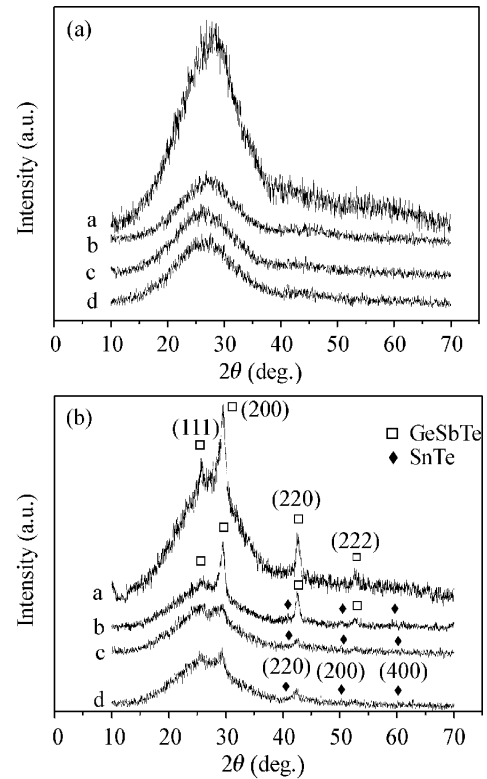


Fig. 3. XRD patterns for the as-sputtered (a) and annealed (b) samples.

Table 1.  $T_g$  and  $T_g/T_m$  of Some Elements

Elements	Sb	Te	Ge	Sn
$T_g$ (K)	180	285	750	286
$T_g/T_m$	0.2	0.39	0.62	0.56

transition temperature,  $T_m$  is the melting temperature) are favorable to improve the crystallization speed of reversible phase-change optical recording films<sup>[5]</sup>. From Table 1 we can see the  $T_g/T_m$  of Sn is lower than Ge, so the Sn-doping increases the crystallization rates.

Figure 4 shows the crystallization peaks in the DSC profiles of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  thin films with different Sn content. The thickness of all the film samples used for DSC measurements is approximately 20 nm. The crystallization temperature decreases with the increase of Sn content in the films.

It is well known that the chalcogenide alloy involves a thermal activation process and the behavior can be described by the Johnson-Mehl-Avrami (J-M-A) equation<sup>[6]</sup>

$$\ln(T_p^2/\alpha) = \ln(E_a/R) - \ln \nu + \frac{E_a}{R} \frac{1}{T_p}, \quad (2)$$

where  $\nu$  and  $E_a$  are the frequency factors and the activation energy for the overall transformation process, respectively,  $R$  is the Boltzmann's constant,  $T_p$  is the crystallization temperature and  $\alpha$  is the heating rate.

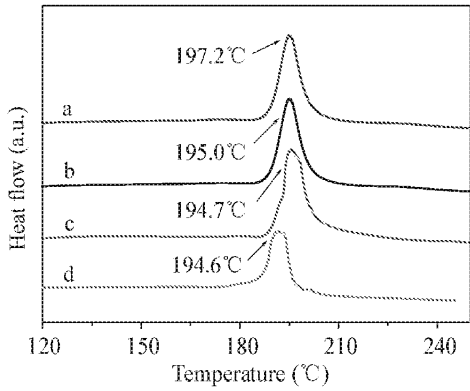


Fig. 4. DSC curves of the Sn doped  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  films at heating rate of  $10^\circ\text{C}/\text{min}$ .

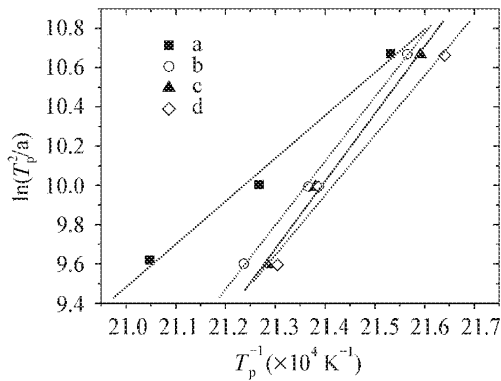


Fig. 5. Kissinger plots of the Sn-doped Ge-Sb-Te films.

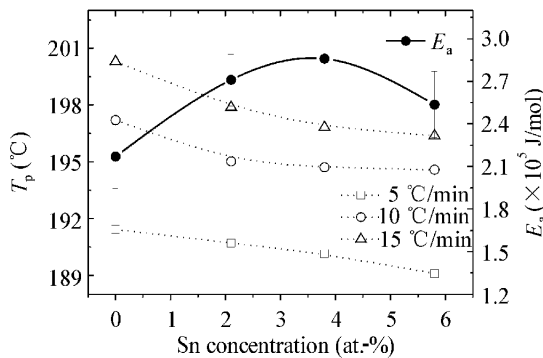


Fig. 6. Crystallization temperature ( $T_p$ ) and activation energy ( $E_a$ ) as a function of Sn content.

To calculate the activation energy of crystallization, we plugged three different crystallization temperatures at different heating rates into Kissinger plots.

Figure 5 shows the Kissinger of Sn-doped  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  samples. According to the J-M-A equation, from the slopes of the curves in Fig. 5 we can calculate the activation energy of crystallization ( $E_a$ ).

Figure 6 shows the crystallization temperature and activation energy of Sn-doped  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  thin films as a function of Sn content. The crystallization temperature decreases with the Sn content and increases as the heating rates increase. It was found that activation energy of crystallization of the Sn-doped Ge-Sb-Te films increases with increasing Sn content up to 3.8 at.-%, and then decreases as the Sn content increases to 5.8 at.-%. The activation energy has a highest value ( $E_a = 2.86 \times 10^5 \text{ J/mol}$ ) at 3.8 at.-% Sn-doping. According to the thermodynamic theory, the greater the  $E_a$  value, the easier the crystallization process<sup>[7]</sup>, so the Ge-Sb-Te-Sn film possesses a higher crystallization rate than the undoped Ge-Sb-Te film ( $E_a = 2.17 \times 10^5 \text{ J/mol}$ ).

In conclusion, the reflectivity contrasts of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  films increase due to Sn-doping. The  $C$  value of the film with 2.1 at.-% Sn-doping is as great as 38% at 405 nm (blue light), and 36% at 300 nm (UV light). The crystallization activation energy is as high as  $2.86 \times 10^5 \text{ J/mol}$  at 3.8 at.-% Sn doping. This means that the proper Sn-doping not only improves the reflectivity contrasts but also increases the crystallization rates. Thus the Ge-Sb-Te-Sn films can be used for high speed and high density optical storage as the recording media.

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References

1. T. H. Jeong, M. R. Kim, and H. Seo, *J. Appl. Phys.* **89**79, 774 (1999).
2. M. R. Kim, H. Seo, and T. H. Jung, *Proc. SPIE* **3401**, 259 (1998).
3. C.-M. Lee, T.-S. Chin, and Y.-Y. Huang, *Jpn. J. Appl. Phys.* **39**, 6369 (2000).
4. F. X. Gan, L. S. Hou, and G. B. Wang, *Mat. Sci. and Eng. B* **76**, 63 (2000).
5. F. S. Jiang and M. Okuda, *Jpn. J. Appl. Phys.* **30**, 97 (1991).
6. H. F. Hu, F. Y. Lin, and Y. B. Yuan, *J. Non-Cryst. Solids* **112**, 306 (1989).
7. H. Yinnon and D. R. Uhlmann, *J. Non-Cryst. Solids* **54**, 253 (1983).