Discussion on the Mechanism of Reversible Phase Change Optical Recording

Masahiro Okuda, Hiroyoshi Naito and Tatsuhiko Matsushita[1]

University of Osaka Prefecture, Mozu, Sakai, Osaka
[1]*Osaka Sangyo University, Nakagaito, Daito, Osaka*

In stoichiometric GeTe-Sb$_2$Te$_3$ films, reversible phase change optical recording materials, Sb addition is used widely in order to improve the crystallization speed, the data retention time and the stability of cyclic operation, but its mechanism is not clear. V-VI compounds (GeTe, SnTe) are well known as compounds in which the ferroelectric structural phase transition occurs. The dielectric constant ε_0 changes largely due to a change in the short-range order of weakly bound nearest neighbors in the crystal to more strongly bound nearest neighbors in the amorphous phase. Therefore, it is necessary to discuss the effect of Sb addition in the stoichiometric GeTe-Sb$_2$Te$_3$ composition upon the thermal stabilities, the dynamic properties of crystallization and the dielectric constant change $\Delta\varepsilon_0$ based on the amorphous-to-crystalline phase transition.

KEYWORDS: optical memory, ferroelectric phase change, amorphous-crystalline phase change

§1. Introduction

A great variety of reversible phase change optical recording materials have been extensively investigated. These alloy films are mainly composed of the IV-VI group (GeTe, SnTe) and V group (Sb, Bi) in the periodic table. At present, it is considered that reversible phase change optical storage is based on amorphous-crystalline structural change. As for IV-VI compounds (GeTe, SnTe), it is well known that the ferroelectric structural phase transition from the rhombohedral phase to a cubic rock salt structure occurs as the temperature increases. Therefore, it seems that both phase changes from the amorphous to crystalline phase and the ferroelectric phase change from a rhombohedral to a cubic rock salt structure contribute to the mechanisms of reversible phase change optical recording.

One type of beam overwrite phase change optical disk requires materials that crystallize rapidly. Terao *et al.*,[1] Chen *et al.*[2] and Ohta *et al.*[3] reported on desirable materials and their characteristics. The alloys for optical disks should have the characteristics of a short crystallization time and a long data retention time. For obtaining a high crystallization speed, stoichiometric compounds such as GeTe,[2] Sb$_2$Te$_3$[4] and Sb$_2$Se$_3$[5] were proposed.

The Sb$_x$Te$_{1-x}$ film shows a short crystallization time of about 1 μs at $x=0.4$ in the stoichiometric composition. Also, at this composition, the crystallization activation energy has the maximum value of 3.1 eV and the retention time may be long. The Ge$_x$Te$_{1-x}$ film at $x=0.5$ shows a higher crystallization speed (about 30 ns) than that of Sb$_2$Te$_3$ films.

For achieving fast crystallization and stable cyclic operation, a binary alloy system of GeTe-Sb$_2$Te$_3$ has been investigated.[6] Also, it is well known that for achieving a long data retention time, compounds with high transition temperature are necessary, and the excess Sb component of pseudoternary alloy of GeTe-Sb$_2$Te$_3$-Sb can improve both data retention time and crystallization

speed, as shown in the experimental results.[7] Figure 1 shows the pseudoternary alloy system of GeTe-Sb$_2$Te$_3$-Sb, where the Sb-rich region is useful for the optical disk.

In this paper, we discuss why the excess Sb component in the GeTe-Sb$_2$Te$_3$ alloy system is necessary for achieving a high crystallization speed, long data retention time and stability of cyclic read-write operation. As mentioned above, it is important to investigate the relation between the ferroelectric phase change and the amorphous-to-crystalline phase transition in order to discuss the mechanism of crystallization in Sb-rich phase change optical disks.

§2. Ferroelectric Phase Transition of GeTe

The structural phase transition from a rhombohedral phase to a cubic rock salt structure occurring in GeTe has been extensively studied.[8] The phase transition is characterized by the softening of a zone-center transverse optical-mode phonon propagating in the (111) direction, and by the freezing-in of a relative displacement of the crystal sublattices.

The transition temperature, T_c, of ferroelectric phase change is given as follows,[9,10]
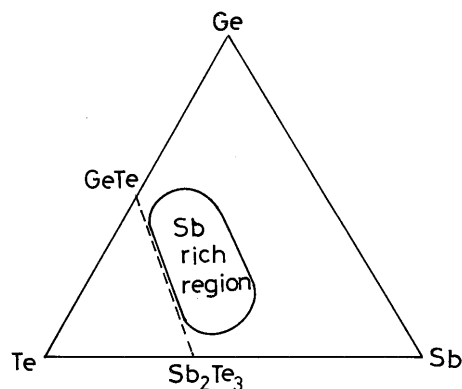

Fig. 1. Ge-Sb-Te composition region suitable for overwriting.

$$kT_c = 0.914 v_{as}(1 - a_2/\Delta a_2), \qquad (1)$$

where v_{as} is the antisymmetric pseudopotential form factor, and a_2 and Δa_2 are the harmonic coefficients of the optical phonon amplitudes. v_{as}, a_2 and Δa_2 are listed in Table I, for GeTe and SnTe. Applying eq. (1) to GeTe and SnTe using the values of the parameters given in Table I, we find (experimental results in brackets) $T_c = 1700$ K in GeTe (700 K) and $T_c = 300$ K in SnTe (145 K).

The dependence of the phase transition temperature T_c on the carrier density, p, (here, p is governed by the laser beam irradiation intensity) is shown in Fig. 2.[11] It is evident from Fig. 2 that the carrier density dependence of T_c in GeTe is smaller than that in SnTe. This result suggests that the laser-induced phase transition of GeTe is stable for the variation of laser intensity. This result is very useful for the phase change optical disk materials.

There is another interesting property of GeTe for the

Table I. Pseudopotential parameter v_{as} and harmonic coefficients of the optical phonon amplitude, Δa_2 and a_2.[9]

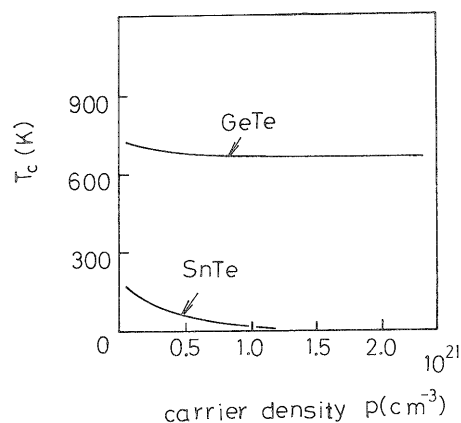|	v_{as}	Δa_2	a_2
GeTe	0.02	51.93	20.75
SnTe	0.041	22.73	21.56

Fig. 2. Carrier density dependence of the phase change temperature T_c for GeTe and SnTe.[11]
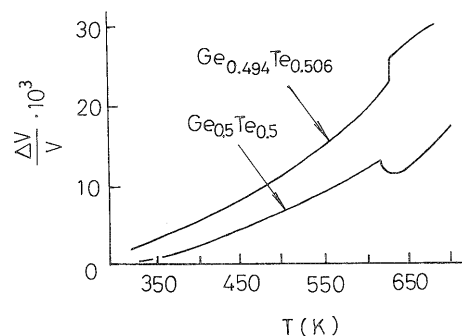

Fig. 3. Temperature dependence of the relative change in volume of GeTe.[12]

Table II. Composition dependence of volume change ΔV and phase transition temperature T_c.[13]

Te (at.%)	T_c(K)	ΔV(%)	Crystal system
50.0	700	−0.02	Rhombohedral
50.1	680	−0.01	Rhombohedral
50.3	670	−0.01	Rhombohedral
50.4	629	−0.01	Rhombohedral
50.5	626	+0.25	Orthorhomic
50.6	627	+0.52	Orthorhomic
50.7	629	+0.15	Orthorhomic

optical disk application. It is reported that the thermal expansion (volume change) coefficient of $Ge_{1-x}Te_{1+x}$ ($x < 0.08$) changes from negative to positive as the composition x increases.[12] This experimental result is shown in Fig. 3, and the details are listed in Table II.[13] It is known that migration of recording film materials occurs in rotating disks, and the migration direction depends on the disk structure or the composition of Ge–Sb–Te materials. We speculate that the compositional dependence of the thermal expansion coefficient in $Ge_{1-x}Te_{1+x}$ governs the migration of recording materials.

§3. Effect of Sb Addition in Stoichiometric GeTe–Sb₂Te₃ Films

3.1 Thermal properties of Sb added to GeTe–Sb₂Te₃ films

The melting temperature, T_m, of GeTe is 725°C and the T_m of Sb_2Te_3 is 622°C. On the other hand, the crystallization temperature T_x of GeTe is 200°C and the T_x of Sb_2Te_3 is 120°C. As GeTe concentration increases in the GeTe–Sb₂Te₃ films, the crystallization temperature also increases. Further, as the excess Sb in the pseudoternary alloy of GeTe–Sb₂Te₃–Sb increases, T_x increases from 172°C to 180°C.

The melting temperature T_m of Ge Sb-Te is shown in Fig. 4.[14] It is shown that Sb addition does not influence T_m of the stoichiometric GeTe–Sb₂Te₃ compound. Therefore, GeTe–Sb₂Te₃–Sb is as stable as GeTe–Sb₂Te₃ for cyclic operation of melt and crystallization.

3.2 Discussion in terms of T-T-T curves

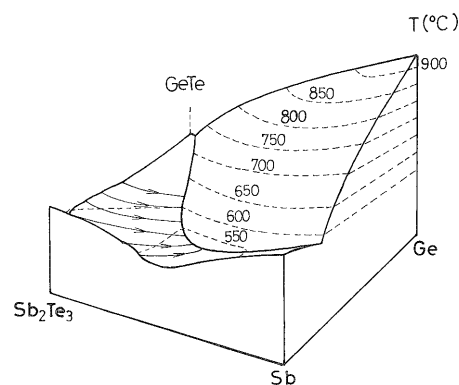The mechanism of amorphous-to-crystalline phase

Fig. 4. Perspective of the liquidus surface in composition-temperature coordinates.[14]

change is discussed in terms of the Avrami equation and its dynamic transition is investigated from T–T–T (time-temperature-transition) curves.[15] Figure 5 shows the T–T–T curves.[16] By using the values of T_m, T_n (temperature at the nose of T–T–T curves) and t_n (time at the nose of T–T–T curves), the critical cooling rates of these elements are calculated by the equation of $R_c = (T_m - T_n)/t_n$. The values T_n, t_n and $\log R_c$ are given in Table III. From Table III, we know that $\log R_c$ values of these elements are in the order of Sb > Ag > Cu > Co > Pb. Referring to the data of Te and Ge, we find that the value of critical cooling rate, $\log R_c$, increases with decreasing reduced temperature T_g / T_m. A plot of $\log R_c$ against T_g / T_m is shown in Fig. 6. Thus, the values of $\log R_c$ of other elements can also be easily estimated by their T_g / T_m.

On the basis of the above discussion and the data shown in Fig. 6, we can conclude that the elements having low values of T_g / T_m are favorable for improving the erasure speed of reversible phase change optical recording films.

Sb, having a low T_g / T_m value, is introduced in the stoichiometric GeTe–Sb$_2$Te$_3$ composition. This low

Fig. 6. The variation of crystal cooling rate for glass formation R_c with reduced temperature T_g / T_m for some elements.

T_g / T_m element may exist in combination with other elements, and they may also exist as clusters or small crystal grain in the films. These crystal grains of Sb are so small that they may be melted when the corresponding erased spot is irradiated by a laser beam with a suitable writing power and pulse duration. When the spot is next irradiated by a laser beam with an erasing power, the low T_g / T_m atoms of Sb again crystallize. The small crystal grains of the low T_g / T_m Sb atoms may be dominant in corresponding erased spots at the initial stage of crystallization, because the critical cooling rates of such Sb elements are faster than those of the related compounds. Therefore, we can use these elements to control the erasing speed of the erasable phase change optical recording materials.

3.3 Discussion on electronic dielectric constants ε_0

The dramatic changes in the electronic dielectric constant ε_0 between the crystalline and amorphous forms of average valence V materials (GeTe and Sb) have been investigated by a straightforward application of the extension of Phillips's theory.[17,18] The success of these applications shows the usefulness of Phillips's underlying concept of the importance of the short-range bonding in determining the dielectric properties of solids.

Amorphous GeTe has a dielectric constant, ε_0, 55 to 70% smaller than that of crystalline GeTe. As we will show, the large decrease in ε_0 results from a change in the short-range order from weakly bound nearest neighbors ($d = 2.99$ Å) in the crystal to more strongly bound nearest neighbors ($d = 2.65$ Å) in the amorphous phase, where d is the nearest-neighbor distance of GeTe. It is considered that the large change of nearest-neighbor distance, d, is due to the ferroelectric phase change of GeTe, from the rhombohedral to the cubic structure. Here, the weakly bound nearest-neighbor distance, $d = 2.99$ Å, corresponds to the cluster of rhombohedral structure, which is stable at room temperature. On the other hand, the
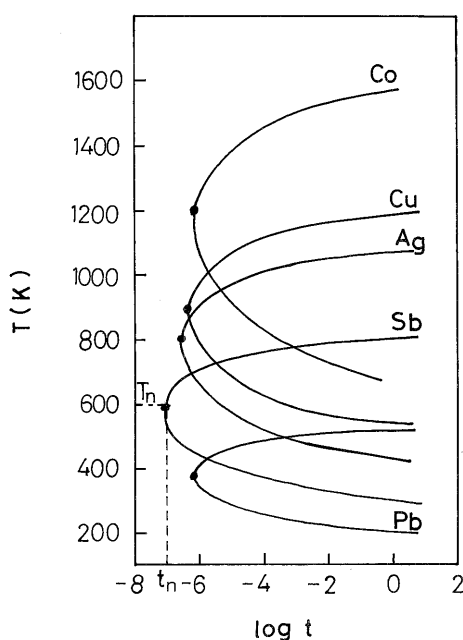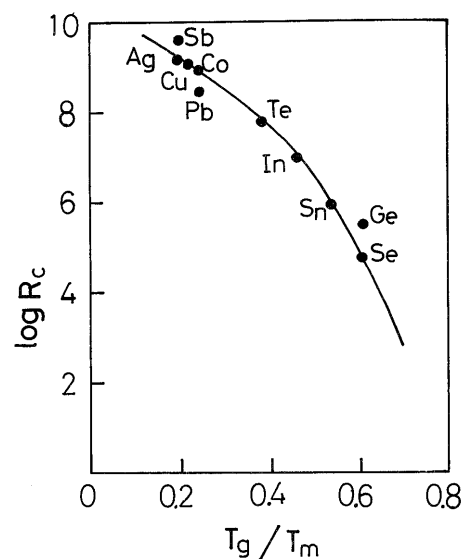

Fig. 5. Time-temperature-transformation curves for Co, Cu, Ag, Sb and Pb corresponding to a volume fraction crystallized of 10^{-6}.

Table III. Estimated values of T_g, T_g / T_m and calculated values of T_n, t_n, $\log R_c$ of some elements.

Element	T_g(K)	T_g / T_m	T_n(K)	t_n(s)	$\log R_c$(K/s)
Sb	182	0.20	600	7.41×10^{-8}	9.61
Ag	250	0.20	800	2.98×10^{-7}	9.16
Cu	298	0.22	900	3.38×10^{-7}	9.13
Co	445	0.25	1200	$6.54 \times 10-7$	8.94
Pb	152	0.25	375	7.07×10^{-7}	8.50
Te	285	0.39	500	5.75×10^{-6}	7.59
Ge	750	0.62	945	8.96×10^{-4}	5.47

strongly bound nearest-neighbor distance, $d = 2.65$ Å, corresponds to the cluster of cubic structure.

It is estimated that, when the write pulse is applied to the film, the recording medium is melt-quenched and then the medium has the cluster of cubic structure (the so-called amorphous state), while, when the erase pulse is applied, the medium changes from the cubic to the rhombohedral structure (crystalline state).

The values of ε_0 of a-GeTe and c-GeTe are given in Table IV.[18] Electron diffraction studies of the structure of c-GeSb$_2$Te$_4$ and c-Ge$_2$Sb$_2$Te$_5$ have been reported.[19] GeSb$_2$Te$_4$ and Ge$_2$Sb$_2$Te$_5$ were found to possess a hexagonal cell, with lattice constants of $a = 4.21$ Å, $c = 40.6$ Å and $a = 4.20$ Å, $c = 16.97$ Å, respectively. According to Agaev and Talybov,[19] the volume of the unit cell for three "molecules" of GeTe is equal to 160 Å^3 and that for three "molecules" of Sb$_2$Te$_3$ is equal to 463 Å^3, where Sb$_2$Te$_3$ has a hexagonal lattice. The experimental volume of the GeSb$_2$Te$_4$ unit cell for three "molecules" is 623 Å^3, which is equal to the sum of the volumes of the unit cells for three "molecules" of both GeTe and Sb$_2$Te$_3$. Therefore, GeSb$_2$Te$_4$ can be assumed to be composed of GeTe and Sb$_2$Te$_3$.

The crystal spaces of one molecule of Ge$_2$Sb$_2$Te$_5$, two molecules of GeTe and one molecule of Sb$_2$Te$_3$ are 255.1, 106.1 and 153.1 Å^3, respectively. That is, the crystal space of one molecule of Ge$_2$Sb$_2$Te$_5$ is equal to the sum of the crystal spaces of two molecules of GeTe and one molecule of Sb$_2$Te$_3$.

The dielectric constants ε_0 of the crystalline and amorphous states of GeSb$_2$Te$_4$ and Ge$_2$Sb$_2$Te$_5$ are calculated using Phillips's theory and the above structure discussions. These results are given in Table V.[20]

It is necessary to investigate the effect of Sb addition in the stoichiometric GeTe–Sb$_2$Te$_3$ composition on the dielectric constant ε_0. The dielectric constant ε_0 of crystalline Sb film is given as 108 from the experimental result,[21] and the ε_0 of an amorphous Sb film is estimated as 80 by Stiles.[17] The refractive index n $(= \sqrt{\varepsilon_0})$ is calculated from the experimental result of reflectivity as $n = 4.3$ ($\varepsilon_0 = 18.5$) at the wavelength $\lambda = 830$ nm for a crystalline Sb film. On the other hand, the refractive index n for an amorphous Sb film is estimated as $\varepsilon_0 = 13.7$
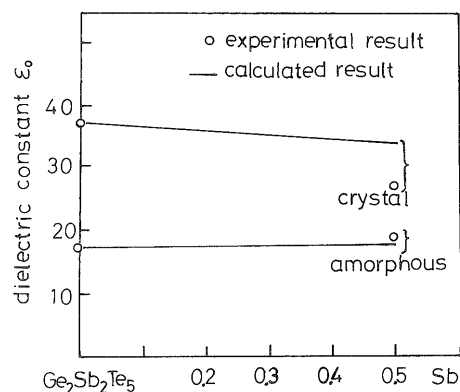

Fig. 7. Dependence of dielectric constant ε_0 on Sb addition in Ge$_2$Sb$_2$Te$_5$.

($n = 3.7$) at $\lambda = 830$ nm.

From the above data, the dielectric constants of Ge$_2$Sb$_2$Te$_5$–Sb composition for crystalline and amorphous states are calculated by using the volume fraction of Ge$_2$Sb$_2$Te$_5$ and Sb. The results are given in Fig. 7. For the composition of Ge$_2$Sb$_2$Te$_5$–0.5Sb film, the dielectric constant is given by Ohta et al.[6] as 25.6 ($0.8n^2$) for the crystalline state and 19.2 ($0.8n^2$) for the amorphous state a $\lambda = 830$ nm. These results coincide with the calculated results in tendency.

§4. Conclusions

The effects of Sb addition to stoichiometric GeTe–Sb$_2$Te$_3$ films upon the thermal properties, the dynamic crystallization transition and the dielectric constant change caused by an amorphous-to-crystalline phase change have been discussed. We concluded that (1) for the thermal properties, Sb addition yields stability for crystalline and amorphous cyclic operation, (2) the small crystal grains of low T_g / T_m Sb atoms may be dominant at the initial stage of crystallization because the critical cooling rates of such Sb elements are faster than those of related compounds, (3) the large change of dielectric constant, ε_0 between the amorphous and crystalline states of GeTe is due to the ferro-electric phase change, and is enhanced by the addition of Sb element.

Table IV. The dielectric constants of amorphous and crystalline GeTe.[18]

	meas.	calc.
c-GeTe	36	36
a-GeTe	11	11.6

Table V. The eielectric constants of amorphous and crystalline GeSb$_2$Te$_4$ and Ge$_2$Sb$_2$Te$_5$.[20]

	meas.	calc.
c-GeSb$_2$Te$_4$	38.1	37.7
a-GeSb$_2$Te$_4$	17.6	17.7
c-Ge$_2$Sb$_2$Te$_5$	38.1	37.5
a-Ge$_2$Sb$_2$Te$_5$	17.6	17.7

References

1) M. Terao, T. Nishida, Y. Miyauchi, S. Horigome, T. Kaku and N. Ohta: SPIE Proc. **695** (1986) p. 105.

2) M. Chen, K. A. Rubin and R. W. Barton: Appl. Phys. Lett. **49** (1986) 502.

3) T. Ohta, M. Uchida, K. Yoshida, K. Inoue, T. Akiyama, S. Furukawa, K. Kotera and S. Nakamura: SPIE Proc. **1078** (1989) p. 27.

4) S. Fujimori, S. Yagi, H. Yamazaki and N. Funakoshi: J. Appl. Phys. **64** (1988) 1000.

5) A. L. Jung, H. Situ, Y. W. Lu, Z. T. Wang and Z. G. He: J. Non-Cryst. Solids **114** (1989) 55.

6) T. Ohta, K. Inoue, M. Uchida, K. Yoshida, T. Akiyama, S. Furukawa, K. Nagata and S. Nakamura: *Proc. Int. Symp. on Optical Memory, Kobe, 1989*, Jpn. J. Appl. Phys. **28** (1989) Suppl. 28-3, p. 123.

7) K. Nishimura, M. Suzuki, I. Morimoto and K. Mori: *Proc. Int. Symp. on Optical Memory, Kobe, 1989*, Jpn. J. Appl. Phys. **28** (1989) Suppl. 28-3, p. 135.

8) P. B. Littlewood: J. Phys. C-**13** (1980) 4855.
9) P. B. Littlewood: J. Phys. C-**13** (1980) 4875.
10) P. B. Littlewood: J. Phys. C-**12** (1979) 4459.
11) M. A. Korzhuev, L. I. Petrova, G. K. Demenskii and O. A. Teplov: Sov. Phys. Solid State **23** (1981) 1966.
12) S. I. Novikova, L. E. Shelimova, N. Kh. Abrikosov and B. A. Evseev: Sov. Phys. Solid State **13** (1972) 2310.
13) S. I. Nobikova, N. Kh. Abrikosov, L. E. Shelimova and O. G. Karpinskii: Sov. Phys. Solid State **19** (1977) 683.
14) S. Bordas, M. T. Clavaguera, B. Legendre and C. Hancheng: Thermochimica Acta **107** (1986) 239.
15) H. A. Davies: Phys. & Chemi. Glasses **17** (1976) 159.
16) F. Jiang and M. Okuda: Jpn. J. Appl. Phys. **30** (1991) 97.
17) P. J. Stiles: Solid State Commun. **11** (1972) 1063.
18) M. H. Brodsky and P. J. Stiles: Phys. Rev. Lett. **25** (1970) 798.
19) K. A. Agaev and A. G. Talybov: Sov. Phys. Cryst. **13** (1968) 339.
20) R. Yokota: Jpn. J. Appl. Phys. **28** (1989) 1407.
21) M. Cardona and D. L. Greenaway: Phy. Rev. **133** (1964) A1685.