

EXPLOSIVE CRYSTALLIZATION MECHANISM IN Sb-RICH EUTECTIC MATERIALS OF PHASE CHANGE OPTICAL MEMORY

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ABSTRACT

The excess Sb effect for the dynamics of rapid crystallization in eutectic amorphous films are discussed. This crystallization mechanism describe the propagation with high velocity in the interface separating the crystalline and amorphous phase for InSb, InSbTe and GaSb materials. From these analysis, it is clear that the crystallization is grown up in the boundary of crystalline-amorphous region of eutectic materials, which is different from the stoichiometric GeSbTe media.

Keywords: Crystallization mechanism, Sb rich recording layer, Explosive process, Phase change material

1. INTRODUCTION

For the materials of eutectic composition (AgInSbTe, InSbTe and GaSb) using as the phase change optical memory, Sb rich recording layer have been utilized in order to the rapid crystallization. But, the mechanism of excess Sb addition has not been clear, because a eutectic material is thought to cause the phase separation in its solidification process.

Recently, it was reported that a melt-quenched crystalline states of eutectic AgInSbTe and SbTe with excess Sb has a quasi-equilibrium state with single phase hexagonal structure based Sb(R3m) and some Sb atoms are randomly replaced with Te atoms.^{1,2)}

In this paper, we report the excess Sb effect for the dynamics of rapid crystallization in eutectic amorphous films. This crystallization mechanism describe the propagation with high velocity in the interface separating the crystalline and amorphous phase for AgInSbTe and Ge(Sb₇Te₃)+Sb materials.

From these analysis, it is clear that the crystallization is grown up in the boundary of amorphous-crystalline region of eutectic materials, which is different from the stoichiometric Ge₂Sb₂Te₅ media. Under favorable conditions, an explosive crystalline process results by laser irradiation. Then, once crystallization has been initiated in the amorphous-crystalline region, the entire amorphous films has been crystallized.

2. EXPLOSIVE CRYSTALLIZATION MECHANISM OF EUTECTIC MATERIALS

Crystallization of eutectic materials is reasonable for phase change optical disk, because it is well known that the smaller marks corresponds to the shorter the crystallization time. And, the rich Sb in AgInSbTe, InSbTe and GaSb recording materials were available for the improvement of crystallization velocity. These circumstance is shown in Table 1 and 2. For the recording materials of the low linear velocity (linear velocity 1.2 - 10m/s), the materials contained about 55-70% Sb content was used, but for high linear velocity (linear velocity 10 - 50 m/s), about 68 - 90% Sb content was used.

Main problem of this paper is to clear that, why so much Sb is necessary for the high speed optical disk. Then, we will discuss for the relation between the Sb contents and the erase ratio, the linear velocity of optical disk, as shown in Fig.1. One example of AgInSbTe composition is the Ag₅In₅Sb₆₀Te₃₀ material for the standard. In this case, it is clear that Sb/Te = 2. In Fig.1, if the Ag, and In contents are fixed at 5%, the Sb and Te contents are given at Sb_x and Te_{90-x}. Therefore, the ratio

of Sb and Te (Sb/Te) =2.8, 3.1, 4.6 and 5.4, respectively, in the disk materials of Fig.1. These high Sb/Te ratio of the high line velocity mean that the main material is Sb, and Ag, In and Te are the subsidiary materials.

Therefore, the crystallization mechanism of Sb element has been investigated mainly. It is well known that the Sb element and the some Sb compounds (GaSb, GaInSb) show the explosive cryatallization^{4,5)}. This explosive generation of crystallites caused by the highly exothermic transition and electron-hole contributed bond weakening .

The theoretical descriptions have been developed for the phase-boundary dynamics during crystallization of amorphous films by the pulsed laser beam. Depending on the background temperature, numerical solutions yield the runaway motion of the amorphous-crystalline (a-c) boundary. The minimum background temperature is necessary to obtain from the pulsed laser energy. Table 3 shows the thermal constants of Sb film for the latent heat, specific heat and crystallization temperature.

Then, we study a nonlinear heat conduction equation as shown in eq.(1)^{6,7)}.

$$\frac{\partial T(r,t)}{\partial t} = D \left[\frac{\partial^2 T(r,t)}{\partial r^2} + \frac{1}{r} \frac{\partial T(r,t)}{\partial r} \right] + \frac{J(r)}{cd} - \Gamma [T(r,t) - T_0] + qV(r,t) \delta(r - (r_0 - V(r,t)t)) \quad (1)$$

where, T(r,t) is the temperature at r and t, D is the thermal diffusivity, V(r,t) is the interface velocity or the growth rate, L is the latent heat of crystallization, c is the specific heat per unit volume,

d is the thickness of the sample layer, is the rate constant connected with heat loss to the substrate, J(r) is the power density provided by laser, and is the delta function. And, q=L/c, $\Gamma [T(r,t) - T_0]$ is the heat loss to the substrate at temperature T_0 .

Also, analyzed structure in thermal conduction is shown in Fig.2. We assume that the amorphous-crystalline (a-c) interface velocity (growth rate) is an explicit function only the a-c boundary temperature T_x and $V(r,t)=A(T(r,t)-T_x)^2$. In eq(1), the first term on the right hand side gives the heat conduction through the layer; the second term results from the transformation to the moving frame; the third one crudely describes the heat loss to the substrate at temperature T_0 . The fourth contribution is the thermal source term due to the latent heat at the a-c boundary.

3. RESULTS AND DISCUSSION

The relation between temperature distribution T(K) and radiation time t(ns) of laser is shown in Fig.3 at the condition of $A=10^{-4}$, $T_x = 400K$, $J=4.0 \times 10^{-9}J$ and $q = L/c = 800K$. As shown in Fig.3, it can be seen that during the forward motion of a-c boundary, a temperature pulse develops and propagates away from the edge($r=r_0$) to the center($r=0$) depending on the temperature profile due to the laser. These temperature distributions as shown in Fig.3 are investigated at the relation with the normalized latent heat $q=L/c$, the laser intensity J and the a-c boundary temperature T_x . Figure 4 shows the time dependence on the radius r and a-c interface velocity v. It is interesting that the interface velocity v increases from 5 m/s to 25 m/s at the inner part of the amorphous region.

Here, we discuss on the reason obtaining high normalized latent heat q. The effect of thermal history of an Sb melt abrupt transition from equilibrium crystallization to nonequilibrium-explosive crystallization was reported in Ref.8 . This paper showed a discontinuous dependence of the melt above the melting point , as shown in Fig.5.

Then, we studied the relation with the crystallization velocity v and q (=L/c: normalized latent heat). From the simulation of eq.(1), it is clear that the crystallization velocity v increases as q increases as shown in Fig.6.

Also, the relation between the crystallization velocity v and the crystallization time t with the parameters T_x are investigated, as shown in Fig.7. From these results, it is suggested that the lower a-c boundary temperature T_x corresponds to the higher crystallization velocity v.

Therefore, it is concluded that for Sb-rich eutectic materials, the ultra-rapid cooling structure is necessary to obtain the high line speed optical disk (30 ~ 100m/s).

4. CONCLUSION

Sb effect of crystallization has been investigated for the eutectic materials of phase change optical memory. In the eutectic materials (AgInSbTe, Ge(Sb₂Te₃)+Sb), it is necessary to analyze the relation between the propagation velocity of a-c interface and the latent heat liberated at the interface by Sb effect. In this paper, we can obtained that once crystallization has been initiated at the amorphous-crystalline region, the entire amorphous film has been crystallized and the interface velocity v increases from 5 m/s to 25 m/s at the inner part of the amorphous mark. From discussion on the effect of thermal history of Sb material, it is concluded that the materials having more large latent heat q and the disk with ultra-rapid cooling structure are necessary to obtain the high line speed optical disk.

From the discussion on the effect of thermal history of Sb materials, it is concluded that the materials having more larger latent heat q , more lower a-c boundary temperature T_x , and the disk with the ultra-rapid cooling structure are necessary to obtain the high line speed optical disk.

REFERENCES

1. T.Matsunaga, Y.Umetani and N.Yamada, Structural study of a $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$ quadruple compound utilized for phase-change optical disks, Phys. Rev. **B-64**, pp.184116-184122, 2001.
2. M.Horie, T.Ohno, K.Kiyono and M.Kubo, Material characterization of growth-dominant Ge(Sb₇₀Te₃₀)+Sb for phase-change optical recording media, Proc.PCOS'2001, pp.20-25.
3. T.Kikukawa, Recent research and development of Ag-In-Sb-Te alloy for phase-change disc material, Proc.PCOS'2001, pp.26-29.
4. O.Bostanjoglo and G.Schlotzhauer, Impulse stimulated crystallization of Sb films investigated by time resolved TEM, Phys.Stat.Sol.(a) **68**, pp.555-560, 1981.
5. C.E.Wickersham, G.Bajor and J.E.Greene, Impulse stimulated "explosive" crystallization of sputter deposited amorphous (In,Ga)Sb films, Solid State Commun., **27**, pp.17-20, 1978.
6. W.v.Saarloos and J.D.Weeks, Surface undulations in explosive crystallization: a thermal instability, Phys.Rev.Lett., **51**, 1046-1049, 1983.
7. D.A.Kurtze, W.v.Saarloos and J.D.Weeks, Front propagation in self-sustained and laser-driven explosive crystal growth: stability analysis and morphological aspects, Phys.Rev. **B-30**, pp.1398-1415, 1984.
8. V.D.Aleksandrow, Effect of the thermal history of an Sb melt on the abrupt transition from equilibrium crystallization to nonequilibrium-explosive crystallization, Inorganic Materials, **28**, pp.544-548, 1992.

Table 1. Composition for the eutectic materials of phase change memory

Component	Eutectic Composition	Sb quantity (%)
GaSb	$Ga_{11.6}Sb_{88.4}$	88.4
GeSb	$Ge_{17}Sb_{83}$	83.
GeInSbTe	$Ge_2In_7Sb_{80}Te_{11}$	80
InSbTe	$In_9Sb_{77.6}Te_{13.4}$	77.6
InSb	$In_{31.7}Sb_{68.3}$	68.3

Table 2. Recording speed of eutectic materials

Component	Eutectic Composition	Recording Speed (m/s)
AgInSbTe	$Ag_{55}In_{5}Sb_{60}Te_{30}$	25
GeInSbTe	$Ge_2In_7Sb_{80}Te_{11}$	35
InSbTe	$In_9Sb_{77.6}Te_{13.4}$	50
Sb	Sb	80

Table 3. Experimental values for various parameters in explosive crystallization

Element	L(cal/g)	C(cal/gK)	L/c(K)	T _x (K)
Sb	20	0.06	333	600
Ge	40	0.09	444	900

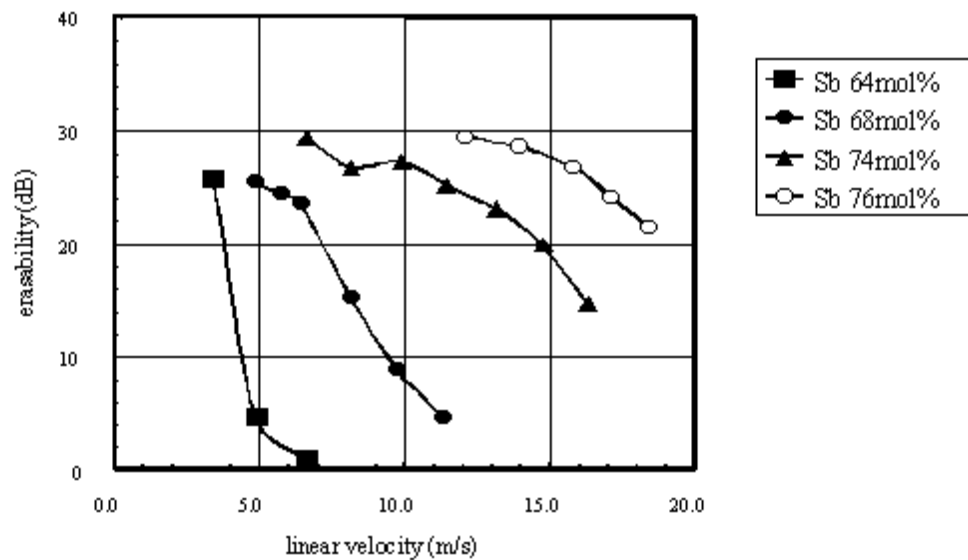


Figure 1. Erasability dependence on linear velocity with different Sb concentration AgInSbTe.

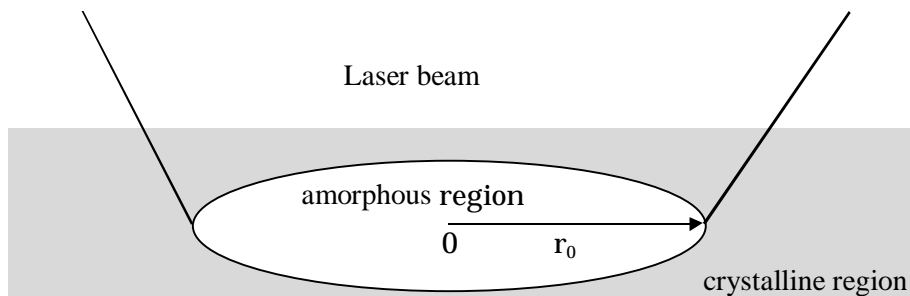


Figure 2. Crystallization model by laser illumination

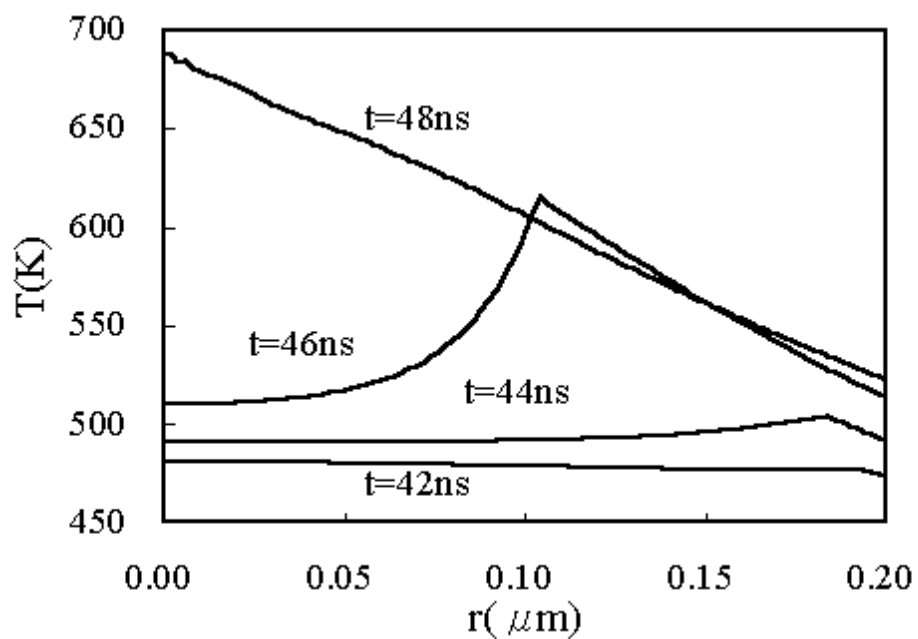


Figure 3. Temperature distribution in crystalline region

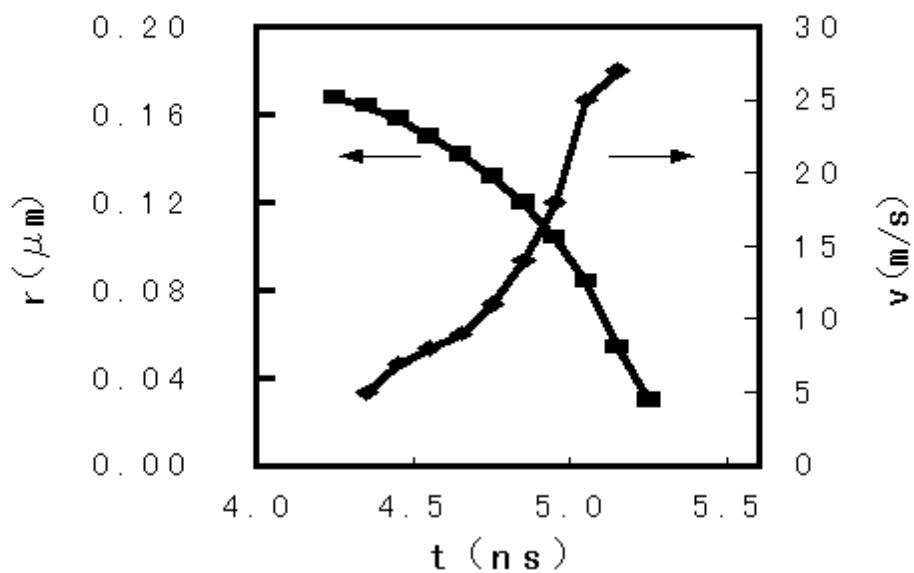


Figure 4. Relation between the radius of amorphous region, the crystallization velocity and the crystallization time.

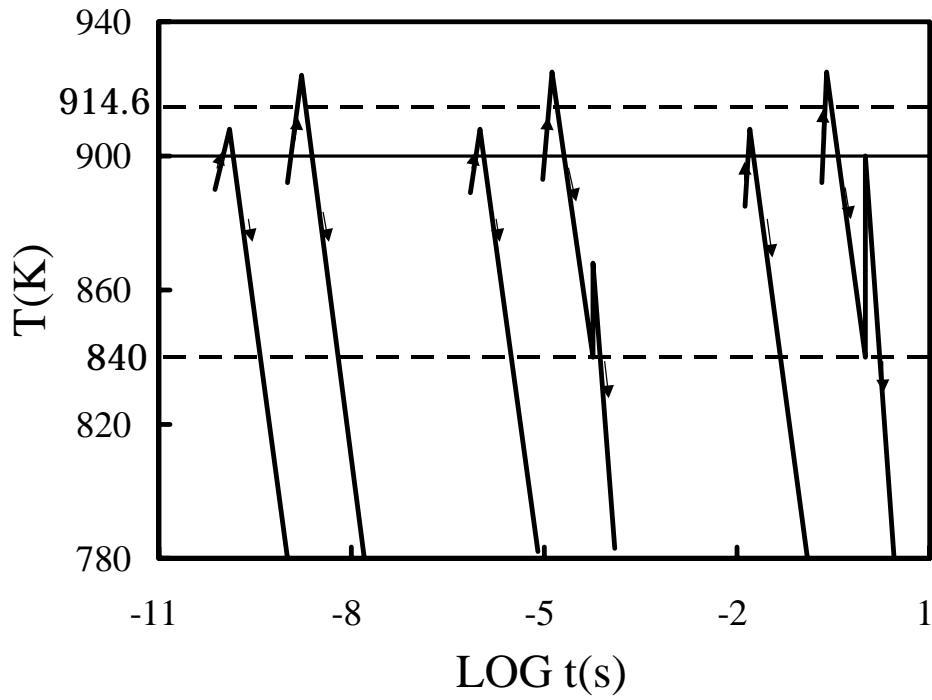


Figure 5. Effect of the thermal history of an Sb melt abrupt transition from equilibrium crystallization to nonequilibrium-explosive crystallization.

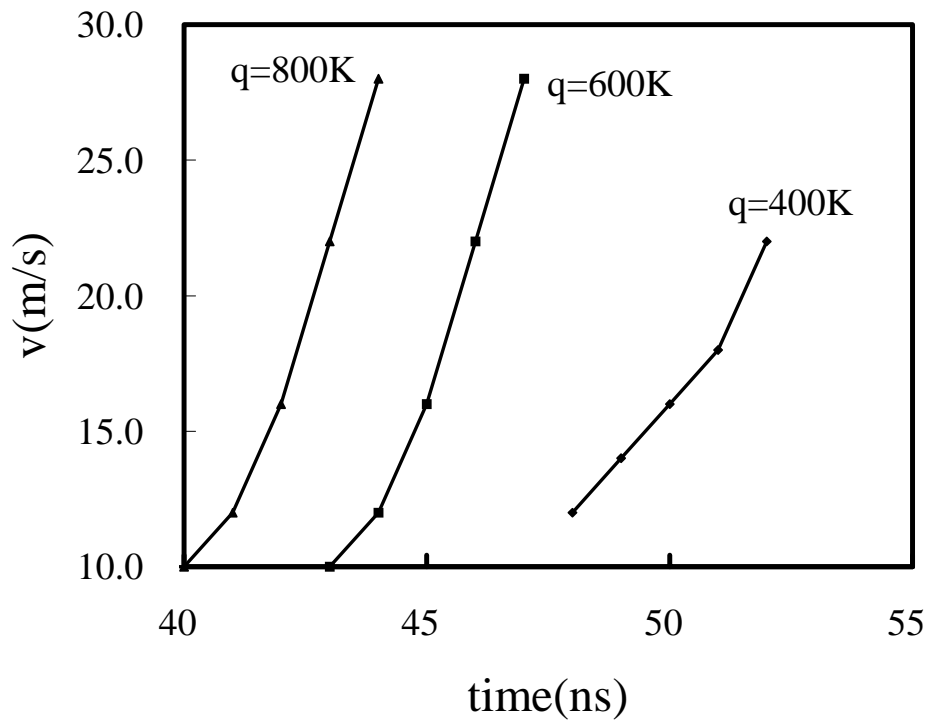


Figure 6. Relation between the crystallization velocity v and the crystallization time t with the parameters q .

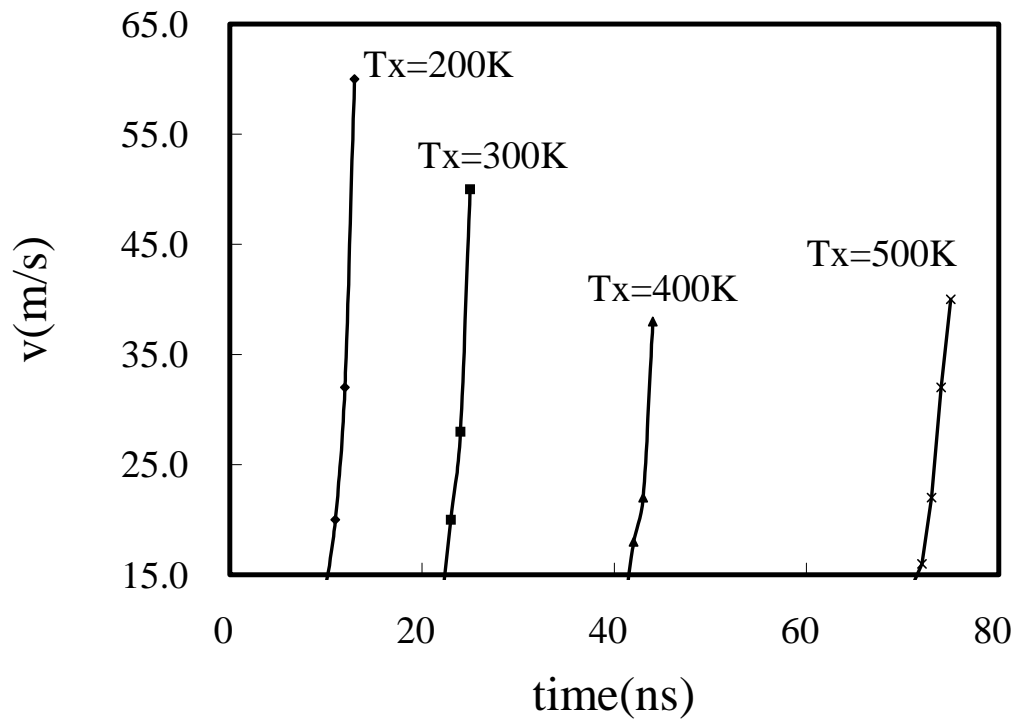


Figure 7. Relation between the crystallization velocity v and the crystallization time t with the parameters T_x .