

Three Dimensional Crystallization Simulation and Recording Layer Thickness Effect in Phase Change Optical Recording

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The development of phase change optical recording requires better understanding of the crystallization kinetics of recording materials. Most of the existing simulation methods are based on two-dimensional crystallization models. In this work, we develop a new method to simulate the crystallization of phase change recording material in three dimensions. This method can be used to simulate the recording layer thickness effect on the crystallization. We first set up an isothermal model to explain the recording layer thickness effect. With this model, the 3-D crystallization simulation shows a similar trend as experimental data in the literature. We also discuss the parameter selection for the simulation. [DOI: 10.1143/JJAP.42.800]

KEYWORDS: phase change optical recording, GeSbTe, crystallization simulation, thickness effects, 3-D crystallization model

1. Introduction

The technique of phase change optical recording has developed very rapidly over the past several years. It is now being used in commercial products such as rewritable compact disk (CD) and digital video disk (DVD). Phase change optical recording is based on the reversible transformation of the crystalline and amorphous phases of the recording material by using pulsed laser heating. The writing process consists of amorphization of small regions of a crystalline matrix, while the erasing process consists of crystallization of these amorphous spots.

More complicated recording techniques are being studied to apply to the phase change recording. These techniques include multi-level recording and multi-layer recording.^{1–3)} They require precise control of laser power and pulse duration to obtain optimal disk performance (writing and erasing). Therefore a better understanding of the kinetics of the crystallization of the recording material is needed. Computer simulation has been extensively used in phase change optical recording research. Nishi *et al.* simulated the amorphous-crystalline boundary movement during crystallization;⁴⁾ Ewan *et al.* studied transient nucleation effects;⁵⁾ Shiela *et al.* modeled the jitter due to the statistical nature of the crystal nucleation and growth.⁶⁾ All of these simulations are based on a two-dimensional crystallization model. However, in order to understand some crystallization phenomena, such as the effects of recording layer thickness and the effects of dielectric layer interfaces, a three dimensional model of crystallization of thin film recording materials is needed. In this paper, we describe a method to simulate the crystallization in three dimensions. By using the 3-D crystallization simulation and an isothermal crystallization model, we successfully explain the recording layer thickness effects on the crystallization behavior of nucleation dominated recording materials (GeSbTe alloys).

2. 3-D Crystallization Simulation

Phase change optical recording is a complex process. It includes the propagation of a focused laser beam through a multi-layer disk structure, the absorption of laser power, thermal diffusion and the changing of material states (melting, crystallization and amorphization). Peng *et al.* studied the temperature distribution induced by laser heating

in a multiplayer structure.⁷⁾ In our simulation, we use a similar method to obtain a 3-D temperature profile. Here we use large grid size (50–100 nm) for temperature calculation. Since the recording material will change its state (from amorphous to crystalline or from crystalline to amorphous) during the laser heating, we need to check the state of the material at each calculation step. If the state of recording material is changed, the corresponding optical and thermal parameters are put into the program for the next step of calculation. The influence of latent heat (melting) and heat of formation (crystallization) are also taken into account.⁸⁾

We used the conventional nucleation and growth model⁹⁾ for the crystallization. The nucleation rate I can be expressed as:

$$I = \alpha_1 \exp\left(-\frac{E_{a1}}{RT}\right) \exp\left(\frac{-\Delta G^*}{RT}\right) \quad (2.1)$$

where, E_{a1} is the activation energy associated with the jump of an atom from the amorphous phase to the critical nucleus of the crystalline phase, α_1 is a frequency factor related to the atomic jumping frequency, critical nucleus size and atomic density, ΔG^* is the energy barrier to form a critical nucleus,

$$\Delta G^* = -\frac{16\pi}{3} \frac{\gamma^3}{\Delta G_v} f(\theta) \quad (2.2)$$

here γ is the amorphous-crystalline interface energy; ΔG_v is the difference in Gibbs free energy between amorphous and crystalline states; $f(\theta)$ is a function of contact angle θ . For homogeneous nucleation, $f(\theta)$ is equal to one.

The growth rate of a small crystallite is written as:

$$G = \alpha_2 \exp\left(-\frac{E_{a2}}{RT}\right) \left[1 - \exp\left(-\frac{\Delta G_v}{RT}\right)\right] \quad (2.3)$$

where, E_{a2} is the activation energy associated with the jump of an atom from the amorphous phase to the growing crystalline phase, α_2 is a constant related with atomic jumping distance and jumping frequency.

The change in Gibbs free energy for crystallization ΔG_v in eqs. (2.2) and (2.3) is normally temperature dependent. When the temperature T is higher than crystallization temperature, we can approximate this change through the latent heat ΔH_v and melting temperature T_m :

$$\Delta G_v = \Delta H_v \frac{T_m - T}{T_m} \quad (2.4)$$

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For the purpose of crystallization simulation, the large grids of the phase change layer will be further divided into small grids. These small grids have the size of 1 nm × 1 nm × 1 nm. Hence there are two sets of grids for the phase change layer: one is large grid for temperature calculation; the other is small grid for crystallization simulation. Hereafter we will call these two sets of grids thermal grid and PC grid respectively. The thermal and optical properties of the thermal grid are the combination of those of the PC grid inside. We choose these dimensions of grids to obtain both high resolution of the crystallization simulation process and reasonable simulation time. During the simulation, the probability of one PC grid becoming a crystalline nucleus during the time interval Δt is given by $P = I(T) \times \Delta t \times \Delta V$, where ΔV is the volume of the PC grid. If this PC grid is transformed into a crystalline nucleus, information about its position and time t is stored and a crystalline grain will grow from this nucleus. Instead of simulating grain growth by calculating the crystallization probability of grain growth,⁷⁾ we directly calculate the grain radius from the growth rate. Since the strain energy between the crystalline state and the amorphous state is small, the growth rate should be nearly isotropic, and the shape of a growing grain is spherical. At time t , the grain radius can be calculated as $r(t) = \sum_{t=\tau}^t G(T) \times \Delta t$, where $G(T)$, the growth rate, is a function of temperature and changes for each time step. The temperature for calculating the growth rate should be the temperature at the amorphous-crystalline interface of the growing grain. However in our simulation, the grain size (10–50 nm) is smaller than the thermal grid size (50–100 nm) for calculating the temperature. Therefore we can use the temperature at the nucleus site to calculate the growth rate. By using this approximation, we reduce the simulation time significantly.

3. Application of 3-D Crystallization Simulation

3.1 Effects of recording layer thickness and Isothermal model

Zhou *et al.* studied the effects of recording layer thickness on the crystallization of phase change recording media.¹⁰⁾ They found the complete erase time (CET) of Ge–Sb–Te recording materials decreases with increasing of the recording layer thickness, where the CET is defined as the minimum duration of the erasure pulse for complete crystallization of a written amorphous mark. Furthermore, when a SiC layer is introduced between the recording layer and the dielectric layer, the CET is reduced to about 20 ns and varies only slightly with the recording layer thickness. The mechanism of these effects of recording layer thickness is not discussed in their paper.

The Johnson-Mehl-Avrami (JMA) equation is often used to describe the kinetics of phase transformations under isothermal conditions. It shows how the volume fraction of phase transformation changes with time. The volume fraction of transformed phase can be written in terms of the “extended” volume fractions:¹¹⁾

$$X = 1 - \exp(-X_x) \tag{3.1}$$

where X is the volume fraction of the crystallization, X_x is the extended volume fraction, i.e. the volume fraction of crystallization without accounting for impingement. The

extended volume fraction $X_x(t)$ can be calculated as following,

$$X_x = \int_0^t V(t - \tau) I d\tau \tag{3.2}$$

where $V(t - \tau)$ is the volume of one growing grain at time t , τ is time when this crystal nucleated, I is the nucleation rate. It is called “extended” volume fraction because it ignores intersections of particles with each other. Equation (3.1) takes these intersections into account.

If grain impingement is the only limit for grain growth, the JMA equation predicts the same transformation behavior regardless of the thickness difference. However if the thickness of the recording layer is smaller than the grain size, the grain growth along the direction of the thickness will be stopped by the interfaces of recording layer. From transmission electron microscopy (TEM) studies, it was shown the crystalline grain size in an erased mark is in the range of 10–50 nm.⁶⁾ This is greater than or comparable to the thickness of the recording layer. Therefore the thickness is another limit to the grain growth. We should add this effect into the JMA equation.

For simplicity, we assume a constant nucleation rate I and a constant uniform growth rate G for crystalline grains. We also assumed the nucleation occurs at the middle plane of the recording layer. At the early stage of crystallization, the crystal can grow in three dimensions, so its volume can be written as:

$$V(t - \tau) = \frac{4\pi}{3} G^3 (t - \tau)^3 \tag{3.3}$$

If we assume the recording layer has a thickness of h , when $t - \tau$ is greater than $h/2G$, this crystalline grain touches both the top and the bottom interfaces of the recording layer. The growth along the direction of the thickness is stopped, so the growth changes to two-dimensional. For 2-D growth,

$$V(t - \tau) = \pi h G^2 (t - \tau)^2 - \frac{\pi}{6} h^3 \tag{3.4}$$

We use discrete time summation instead of the continuous integration to calculate the crystallization volume fraction change with time. The results are shown in Fig. 1. The

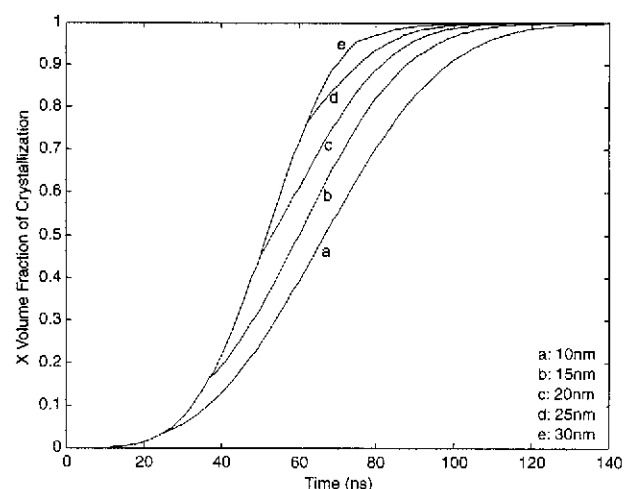


Fig. 1. Crystallization Volume fraction vs. time for thin film thickness of 10 nm, 15 nm, 20 nm, 25 nm, 30 nm, 35 nm.

calculated results show clearly the crystallization behavior change with the recording layer thickness that have been experimentally observed. That is, thinner films take a longer time to fully crystallize. The drastic change in the slopes of the curves occurs at the time when the 3-D growth of the crystalline grains changes to 2-D growth.

3.2 Parameter selection

The thickness effects (in the range of 15–35 nm thickness) occur only in some certain combinations of nucleation rate and growth rate, because the grain size needs to be comparable to the thickness. The isothermal model results can help us choose proper parameters for numerical simulation. At the same time, we also need to correlate the parameter values to experimental data. Otherwise the simulation results will not be realistic.

The activation energy measured from Kissinger analysis is in the range of 2.2–3 eV.¹²⁾ This activation energy is actually an apparent activation energy, including both the nucleation and growth activation energy. By relating the Kissinger analysis to the JMA equation,¹³⁾ we can obtain $nE_a = E_{a1} + \Delta G^* + (n-1)E_{a2}$, where n is the time exponential in JMA equation. At low temperature (100–200°C), ΔG^* is small in comparison with other terms, so $nE_a = E_{a1} + (n-1)E_{a2}$. If we assume the activation energy for an atom to jump from the amorphous phase to the critical nucleus of the crystalline phase is equal to the activation energy for an atom to jump from the amorphous phase to the growing crystalline phase (i.e. $E_{a1} = E_{a2}$), we obtain $E_a = E_{a1} = E_{a2}$. This means the value of the activation energy for the crystallization obtained from Kissinger analysis is equal to E_{a1} and E_{a2} . We use the average 2.6 eV as the activation energy.

It is difficult to obtain amorphous-crystalline interface free energy from experiments. Its value is of the order of $1 \times 10^{-5} \text{ J/cm}^2$.¹⁴⁾ From ref. 12, we calculated the volume latent heat ΔH_v to be 782 J/cm^3 . All these parameter values are fixed; other parameter values such as α_1 and α_2 are varied during the simulation to fit the experimental data. Table I lists all the crystallization parameters used in our simulation.

3.3 Simulation details and results

The disk structure used for simulation is shown in Fig. 2. The simulation procedure follows the experiments described in reference.¹⁰⁾ First, we calculate the laser power (P_{melt}) required to melt the recording material for each different recording layer thickness. Then we use laser power of $1.2 \times P_{\text{melt}}$ to simulate the mark formation on the disk. The written amorphous marks have approximately the same area. In the

Table I. Parameter values in crystallization simulation.

Parameter	Value
α_1	$1.5 \times 10^{41} \text{ cm}^{-3} \cdot \text{s}^{-1}$
α_2	$1.8 \times 10^8 \text{ cm} \cdot \text{s}^{-1}$
E_{a1}	2.6 eV
E_{a2}	2.6 eV
ΔH_v	782 J/cm^3
γ	$1 \times 10^{-5} \text{ J/cm}^2$

simulation, we also assumed 0.02% crystalline embryos existing in the amorphous mark. This is because the cooling rate in the writing process is not high enough to suppress all crystallization. After that, we input lower laser powers to simulate the crystallization of the amorphous mark. The time when the crystallized volume fraction reaches 99% is chosen as the complete erasure time (CET). The simulation results are plotted in Fig. 3. Each point on the curve is the shortest CET for that recording layer thickness and is the average result of one hundred simulation-runs. The simulated results show the same trend of recording layer thickness effects as the experimental data.¹⁰⁾ The CET decreases as the recording layer thickness increases.

We also examine the grain growth in the direction of thin film thickness. Figure 4 shows the cross-sectional view of the recording layer at different volume fraction of crystal-

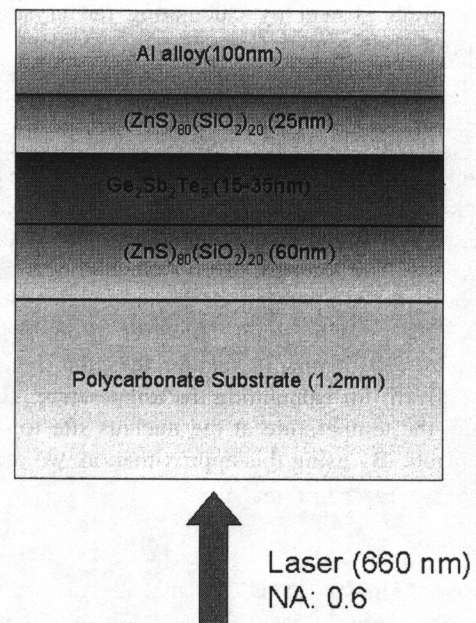


Fig. 2. Phase change recording disk structure used in numerical simulation.

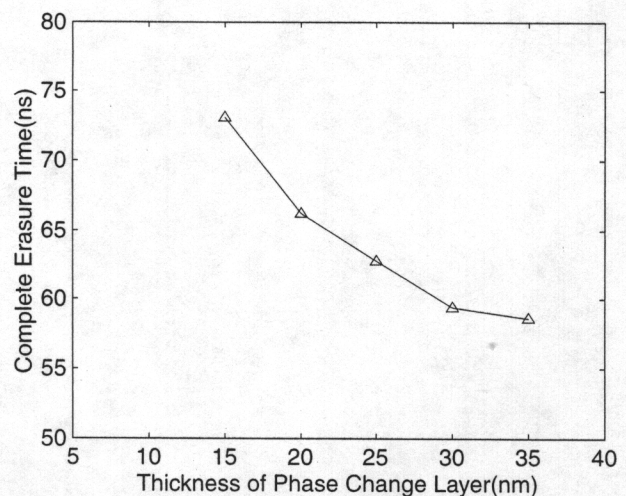


Fig. 3. Calculated complete erasure time (CET) for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ recording material for different thickness: 15 nm, 20 nm, 25 nm, 30 nm, 35 nm.

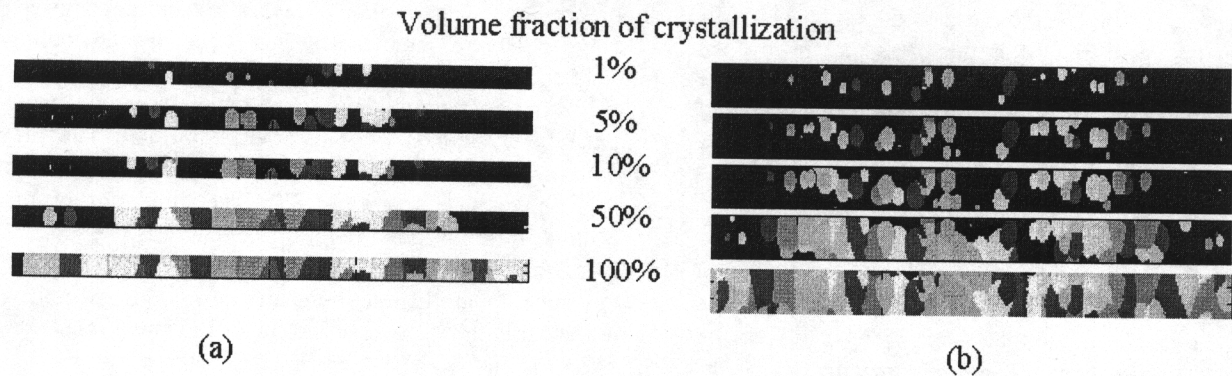


Fig. 4. Sideview of simulated crystallization process of phase change recording layer, (a) thickness is 15 nm, (b) thickness is 30 nm.

lization. The crystallization process (the nucleation and growth of crystalline grains) of two samples are compared here: (a) with the recording layer thickness of 15 nm, (b) with the recording layer thickness of 30 nm. As predicted, the effect of thickness on the growth is clearly shown in Fig. 4: 2-D growth for thin layer, 3-D growth for thick layer.

4. Conclusion

In conclusion, we have developed a method to simulate the crystallization of the film using a 3-D model. This 3-D crystallization simulation helps us to understand the recording layer thickness effects on the crystallization. In particular, we examined how the recording layer thickness influences the grain growth. By choosing appropriate crystallization parameters, we simulated the recording layer thickness effects. The 3-D simulation results match well with the experimental results in the literature. In future work, we will set up in-situ experiments to study the crystallization of the phase change recording materials.

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