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Theoretical analysis of nanosecond crystallization kinetics of phase-change optical recording films*

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A theoretical investigation of nanosecond crystallization kinetics of the phase-change optical recording films is presented. An extended Kissinger equation for the square-root heating is derived, which properly describes the temperature evolution of the films by nanosecond laser heating. The extended Kissinger equation was used to explain our previous experimental results.

Keywords: phase-change, crystallization kinetics, activation energy
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1. Introduction

A commercial medium of high potential for rewritable data storage is based on the reversible transformation of micron sized bits, which can be switched between amorphous and crystalline states using a focused laser, resulting in changes of the optical properties of the phase-change (PC) material, usually a Te-rich chalcogenide alloy.[1,2] The increased information flow has stimulated an ever growing demand for mass data storage. Using short wavelength laser, multi-layer and multi-level recording, high storage densities can be attained.[3−5] Application of these techniques needs to control the reflectivity levels in PC media accurately. It is therefore of crucial importance to determine and understand the crystallization kinetics of the recording materials for optimizing the recording stacks, the shape of amorphous bits and writing/erasing strategies. Both isothermal and non-isothermal methods are used to investigate the crystallization kinetics. In the isothermal method,[6−10] the sample is brought quickly to a temperature slightly below the onset temperature of crystallization, T_c, and the heat evolution or optical reflectance during the crystallization process at a constant temperature is recorded as a function of time. The isothermal crystallization data are usually interpreted in terms of the Johnson–Mehl–Avrami (JMA) model. In contrast, in the non-isothermal methods,[11−14] the samples are heated at a fixed heating rate and the differential thermal analysis or differential scanning calorimetry peaks shift with heating rate. The well-known Kissinger analysis has derived a relationship between the peak shift and the effective activation energy of crystallization.[11]

It should be noted that all these methods are commonly performed at a fixed temperature or at a very low heating rate in a relatively low temperature regime in a furnace. However, in the process of PC optical recording, the heating and cooling rates may be as high as 10^9K/s, and crystallization is achieved at considerably higher temperature since the glass transition temperature and the crystallization temperature increase with heating rate.[15] In addition, the crystallization mechanism may be dependent on the sample temperature.[16] The mechanism of crystallization could be different for laser pulse heating and heating in a furnace. A method to study the crystallization kinetics for laser pulse heating is thus strongly desired.

Recently, we reported the experimental investigation of crystallization kinetics of amorphous $In_{44}Sb_{20}Te_{36}$ PC films on a nanosecond scale using a static tester.[17] The approach was based on Kissinger analysis and a square-root heating model, which prop-

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erly describes the temporal behaviour on short time scales. However, is Kissinger analysis of the linear heating valid for the square-root heating? Why can Kissinger's plots show good linear behaviour? Keeping these questions in mind, we report the theoretical investigation of the crystallization process induced by nanosecond laser heating in this work.

2. Theory

Let us consider the rate equation describing the crystallization process[11]

$$\frac{\mathrm{d}x}{\mathrm{d}t} = A(1-x)^n \mathrm{e}^{-\frac{E}{k_\mathrm{B}T}}, \tag{1}$$

where x is the crystallized volume fraction, $\mathrm{d}x/\mathrm{d}t$ is the crystallization rate, n is the empirical order of crystallization, T is the Kelvin temperature, k_B is the Boltzmann constant, E is the effective activation energy for crystallization. Using the method of separation of variables and integrating on both sides, we can rewrite Eq.(1),

$$X \equiv \int_0^{x_\mathrm{c}} \frac{1}{A(1-x)^n}\mathrm{d}x = \int_0^{t_\mathrm{c}} \mathrm{e}^{-\frac{E}{k_\mathrm{B}T}}\mathrm{d}t, \tag{2}$$

where X is a constant that stands for the effective crystallized volume fraction. In the process of crystallization, various heating models are used. If the temperature of the PC material keeps constant, it is isothermal crystallization; if $T(t) = T_0 + \beta t$, it is non-isothermal crystallization for the linear heating; if $T(t) = T_0 + \gamma\sqrt{t}$, it is non-isothermal crystallization for the square-root heating. Here T_0 is the room temperature, β is the linear heating rate and γ is the coefficient of the square-root heating. The first two heating models are commonly employed for annealing in a furnace, but the last one can be used to describe the annealing on short time scales.

In the following, we will first derive the Kissinger equation on the basis of Eq.(2) for the linear heating, and then extend Kissinger analysis to the square-root heating.

2.1. Kissinger equation

In the case of linear heating, $T(t) = T_0 + \beta t$. With the variable substitution $\mathrm{d}T = \beta \mathrm{d}t$ Eq.(2) can be transformed to

$$X = \int_{T_0}^{T_\mathrm{c}} \frac{1}{\beta}\mathrm{e}^{-\frac{E}{k_\mathrm{B}T}}\mathrm{d}T \approx \int_0^{T_\mathrm{c}} \frac{1}{\beta}\mathrm{e}^{-\frac{E}{k_\mathrm{B}T}}\mathrm{d}T, \tag{3}$$

where $T_\mathrm{c} = T_0 + \beta t_\mathrm{c}$. On the right-hand side of Eq.(3) we have made the reasonable assumption that no crystallization occurs for $T < T_0$, and thus one can set the lower integration limit to T=0. Setting $y = T_\mathrm{c}/T$ and with the help of an integral relation

$$\int_1^\infty \frac{1}{y^2}\mathrm{e}^{-zy}\mathrm{d}y = \frac{\mathrm{e}^{-z}}{z}\left(1 - \frac{2}{z} + \frac{6}{z^2} - \cdots\right), \tag{4}$$

Eq.(3) can be rewritten as

$$\begin{aligned} X =& \frac{T_\mathrm{c}}{\beta}\int_1^\infty \frac{1}{y^2}\mathrm{e}^{-zy}\mathrm{d}y \\ =& \frac{T_\mathrm{c}\mathrm{e}^{-z}}{\beta z}\left(1 - \frac{2}{z} + \frac{6}{z^2} - \cdots\right), \end{aligned} \tag{5}$$

where $z = E/(k_\mathrm{B}T_\mathrm{c})$.

Now, under the condition of $z \gg 1$, neglecting small quantities, Eq.(5) simplifies to

$$X = \frac{T_\mathrm{c}e^{-z}}{\beta z}. \tag{6}$$

Substituting $z = E/(k_\mathrm{B}T_\mathrm{c})$ into Eq.(6), taking the logarithm on both sides and rearranging, we get the standard Kissinger equation[11]

$$\ln\left(\frac{\beta}{T_\mathrm{c}^2}\right) = C - \frac{E}{k_\mathrm{B}T_\mathrm{c}}, \tag{7}$$

where C is a constant. Kissinger equation provides a simple method to determine the effective activation energy E by measuring the crystallization temperatures at a number of linear heating rates.

2.2. Extended Kissinger equation

In the case of square-root heating, $T = T_0 + \gamma\sqrt{t}$, we write Eq.(2) on the integral of temperature

$$\begin{aligned} X \equiv& \int_{T_0}^{T_\mathrm{c}} \frac{2(T-T_0)}{\gamma^2}\mathrm{e}^{-\frac{E}{k_\mathrm{B}T}}\mathrm{d}T \\ \approx& \int_0^{T_\mathrm{c}} \frac{2(T-T_0)}{\gamma^2}\mathrm{e}^{-\frac{E}{k_\mathrm{B}T}}\mathrm{d}T, \end{aligned} \tag{8}$$

where $T_\mathrm{c} = T_0 + \gamma\sqrt{t_\mathrm{c}}$. Using the same treatment as in Section 2.1, from Eq.(8), we can deduce an analytical form of the effective crystallized volume, namely,

$$\begin{aligned} X =& \int_1^\infty \frac{2T_\mathrm{c}(T_\mathrm{c} - T_0 y)}{\gamma^2 y^3}\mathrm{e}^{-zy}\mathrm{d}y \\ =& \frac{2T_\mathrm{c}}{\gamma^2}\frac{\mathrm{e}^{-z}}{z}\left[T_\mathrm{c}\left(1 - \frac{3}{z} + \frac{12}{z^2} - \cdots\right)\right. \\ & \left. - T_0\left(1 - \frac{2}{z} + \frac{6}{z^2} - \cdots\right)\right]. \end{aligned} \tag{9}$$

In order to obtain Eq.(9), one has to apply two integral relations, Eqs.(4) and (10),

$$\int_1^\infty \frac{1}{y^3}\mathrm{e}^{-zy}\mathrm{d}y = \frac{\mathrm{e}^{-z}}{z}\left(1 - \frac{3}{z} + \frac{12}{z^2} - \cdots\right). \tag{10}$$

Again, under the condition of $z \gg 1$, neglecting small quantities, Eq.(9) can be simplified as

$$X = \frac{2T_c}{\gamma^2}\frac{e^{-z}}{z}\left[T_c - T_0\right]. \tag{11}$$

Taking the logarithm on both sides of Eq.(11) leads to the extended Kissinger equation

$$2\ln\left(\frac{T_c}{\gamma}\right) + \ln(T_c - T_0) = C + \frac{E}{k_B T_c}, \tag{12}$$

where C is a constant. A plot of $2\ln\left(\frac{T_c}{\gamma}\right)+\ln(T_c-T_0)$ against $\frac{1}{T_c}$ will yield a straight line with a slope E/k_B. It is interesting to note that the standard Kissinger equation and the extended one are similar and the two equations are derived under the same approximate conditions.

3. Application and discussion

3.1. Extract the activation energy from the Power–Time–Effect diagram

Now, we apply the extended Kissinger equation to extract the activation energy of crystallization from our previous experimental results.[17] In the experiments the Power–Time–Effect (PTE) diagram of the amorphous InSbTe film was recorded using a static tester. From the PTE diagram the pulse condition in terms of laser power and pulse width required for the onset of crystallization was established as[17]

$$P = P_0 t_P^{-\alpha}, \tag{13}$$

where $P_0 = (77.5 \pm 1.0)\text{mW}\cdot\text{ns}^{0.68}$, $\alpha = 0.68 \pm 0.01$, the unit of t_P is ns and that of P is mW.

The temperature at the centre of the focus beam, T, can be approximated by a square-root heating model,[18,19] namely,

$$T = T_0 + AA_0P\sqrt{t}, \quad 0 \le t \le t_P, \tag{14}$$

where A is a constant determined by the thermal properties of the film and the beam radius, and A_0 is the fraction of the power absorbed by the film, which is constant for the same state of the film if nonlinear optical absorption is negligible. By the end of the pulse, the temperature rises up to the maximum T_c given by

$$T_c = T_0 + AA_0P\sqrt{t_P}. \tag{15}$$

For the pulse limited by Eq.(13), T_c is the onset temperature of crystallization. All those pulses will produce the same crystalline fraction. According to Eq.(15), the coefficient of the square-root heating is $\gamma = AA_0P$. Substituting γ into the extended Kissinger Eq.(12) and considering that AA_0 is constant, we can rewrite the extended-Kissinger-equation dependent P as

$$2\ln\left(\frac{T_c}{P}\right) + \ln(T_c - T_0) = C + \frac{E}{k_B T_c}. \tag{12'}$$

So far, the laser power P and crystallization temperature T_c can be calculated using Eqs.(13) and (15), respectively. The activation energy for crystallization is then extracted from the extended Kissinger plot of $2\ln(T_c/P) + \ln(T_c - T_0)$ against $1/T_c$, as shown in Fig.1. For the three different values of T_1 (500, 700 and $900(\text{K}\cdot\text{ns})^{0.18}$), defined by $T_1 = AA_0P_0$, the activation energies are determined to be 0.58, 0.56 and 0.57eV. These values are exactly the same as those of our previous report.[17] The good linear behaviour of all the three plots in Fig.1 provides experimental support to the validity of the extended Kissinger equation.

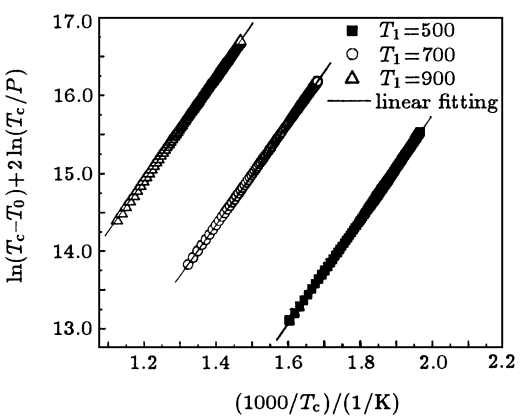


Fig.1. Extended Kissinger plots for T_1=500 (squares), 700 (circles), $900(\text{K}\cdot\text{ns})^{0.18}$ (triangles) and the corresponding linear fits (solid lines).

Almost the same value of the activation energy determined from Fig.1 shows that the activation energy is insensitive to the parameter T_1. It implies that our method is independent of the thermal parameters of the film and the beam radius. This can be verified theoretically based on the extended Kissinger equation.

Let us consider the influence of the T_1 parameter on the extended Kissinger equation. Solving Eqs.(13) and (15) gives the laser power P as

$$\ln P = \frac{2\alpha}{2\alpha - 1}\ln\left(\frac{T_c - T_0}{AA_0}\right) - \frac{1}{2\alpha - 1}\ln P_0. \tag{16}$$

Substituting Eq.(16) into Eq.(12′), the left-hand side of the extended Kissinger equation can be written as

$$\begin{aligned}&\ln(T_c - T_0) + 2\ln(T_c/P)\\ =&2\ln T_c - \frac{2\alpha+1}{2\alpha-1}\ln(T_c - T_0)\\ &+ \frac{4\alpha}{2\alpha-1}\ln(AA_0) + \frac{2}{2\alpha-1}\ln P_0. \end{aligned} \quad (17)$$

The third and forth terms on the right-hand side of Eq.(17) are independent of the crystallization temperature T_c. This means that the parameter T_1 (notice that $T_1 = AA_0P_0$) only changes the intercept of the extended Kissinger plot, as shown in Fig.1. However, the activation energy is determined by the slope of this plot. Hence, for the determination of activation energy, we do not need to know the thermal parameters of the film, the size of the beam radius as well as the fraction of the power absorbed by the film with precision. This is very important since the thermal properties of the film are difficult to determine experimentally.

3.2. Equivalence of the standard and the extended Kissinger equations

Now we turn our attention to the proving of the equivalence of the standard and the extended Kissinger equations. For the square-root heating, if we define an effective linear heating rate as

$$\beta = \frac{T_c - T_0}{t_P}, \quad (18)$$

the square-root heating can be treated as the linear heating. Substituting $T_c = T_0 + \gamma\sqrt{t_P}$ in Eq.(18) leads to a relation between the linear heating rate and the coefficient of the square-root heating as

$$\beta = \frac{\gamma^2}{T_c - T_0}. \quad (19)$$

Now substituting Eq.(19) into Eq.(7), one can easily derive the extended Kissinger equation. So, the standard and the extended Kissinger equations are equivalent. It shows that we may use the square-root heating to study crystallization kinetics instead of the linear heating.

4. Conclusion

We investigated theoretically the nanosecond crystallization kinetics of the phase-change optical recording films. From the rate equation describing the crystallization process, we derived an extended Kissinger equation for the square-root heating. The same value of the effective activation energy for crystallization in the InSbTe films was extracted from the PTE diagram with the extended and standard Kissinger equations. It showed theoretically and experimentally that the extended Kissinger equation and the standard one are equivalent if we treat the square-root heating as the linear heating by introducing an effective linear heating rate. Applying the extended Kissinger equation, we have proved theoretically that the method to determine effective activation energy from the PTE diagram is independent of the thermal parameters of the film and the beam radius.

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