

Thickness-dependent crystallization behavior of fast-growth phase-change amorphous films

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Received 18 August 2007; received in revised form 5 September 2007; accepted 7 September 2007

Abstract

The crystallization behavior of amorphous films embedded in substrates with thickness of several nanometers is investigated based on a thermodynamic model. It is found that there is an optimum layer thickness where the crystallization speed of the films is maximized with the lowest energy barrier for crystallization. This is induced by an energetic change from glass/substrate interface energy to crystal/substrate interface energy as the crystal size is larger than the film thickness during the crystallization. Thus, the crystallization speed in thin films is affected by its thickness.

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Keywords: Amorphous alloy; Film; Thickness; Crystallization

1. Introduction

Re-writable optical-recording media are based on so-called phase-change materials where information is recorded in the form of amorphous marks in a polycrystalline background. The phase-change materials can be reversibly switched between crystalline and amorphous states. The crystallization rate of the phase-change materials determines the maximum achievable data-transfer rate (DTR) since the previously recorded data should be crystallized within the dwell time of the laser spot. Among known alloys, the alloy GeSbTe exhibits a high crystallization speed with a high DTR of amorphous marks in the recording layer [1–3]. Since the alloy usually is in thin-film shape and is sandwiched within dielectric substrates, it is found that the thickness of the amorphous film d affects the crystallization kinetics when the radius of the formed nucleus r in the film is larger than $d/2$ [4,5]. This is because, during the crystallization the nucleus has contacted not only the surrounding amorphous phase, but also the

substrate, which leads to a more rapid crystallization rate of the amorphous thin film due to the drop of crystallization resistance. The qualitative prediction of a theoretical model for the crystallization rates in thin fast-growth phase-change layers shows the presence of an optimum thickness where crystallization rate is maximized. This qualitative prediction is in accordance with experimental result [5].

In this contribution, through considering the Gibbs free energy difference between crystalline phase and amorphous phase of the film, interface energies of crystal/film and crystal/substrate based on several known thermodynamics models, the thickness-dependent crystallization rate of GeSbTe thin films sandwiched between substrates is determined quantitatively. It indicates a way to increase the DTR by film-thickness consideration.

2. Model

When a spherical crystal nucleus embedded in the middle plane of thin amorphous film sandwiched between dielectric substrates with a radius $r > d/2$ is formed, which is schematically indicated in Fig. 1, the nucleus has both the crystal/substrate and the crystal/film interfaces with the

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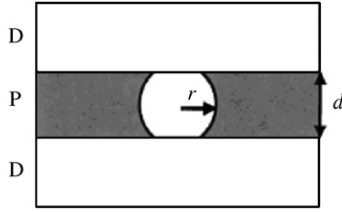


Fig. 1. Schematic diagram for nucleation process of a nucleus with radius r formed in an amorphous film (P) with thickness d sandwiched in two dielectric layers (D).

corresponding interface energies of γ_{cs} and γ_{cf} , respectively. Let the unit volume Gibbs free energy difference between the crystalline and the amorphous phase be $\Delta\mu$, then the total Gibbs free energy change during the crystallization $G(r, d, T)$ is given by [5]

$$G(r, d, T) = -\Delta\mu(T)V_c(r) + \gamma_{cf}S_{cf}(r) + \Delta\gamma S_{cs}(r), \quad (1)$$

where $V_c(r) = \pi d(r^2 - d^2/4) + \pi d^3/6$ is the crystal volume, $S_{cf}(r) = 2\pi r d$ and $S_{cs}(r) = 2\pi(r^2 - d^2/4)$ are the interface areas of the crystal/film interface and crystal/substrate interface, respectively, and

$$\Delta\gamma = \gamma_{fs} - \gamma_{cs}, \quad (2)$$

with γ_{fs} the film/substrate interface energy.

Because the amorphous phase can be considered as a supercooled liquid, γ_{cf} is approximately assumed to be the solid–liquid interface energy, which has been deduced by use of the Gibbs–Thomson equation and a model for the size-dependent melting temperature in the following form [6]:

$$\gamma_{cf} = 2hS_{vib}H_m/(3V_mR), \quad (3)$$

where h denotes the atomic diameter, R is the ideal-gas constant, H_m is the melting enthalpy of crystals, S_{vib} represents the vibrational part of the overall melting entropy S_m , S_{vib} is given by $S_{vib} = 3R \ln v_s/v_l$, where v_s and v_l are the characteristic vibration frequencies of the particles in the solid and in the liquid, respectively, [7]. For semiconductors, $S_m = R[1 + 3 \ln(\Theta_s/\Theta_l)]$, where Θ_s and Θ_l are the Debye temperatures of the solid and the liquid phases [8]. Since $\Theta_s/\Theta_l = v_s/v_l$,

$$S_{vib} = S_m - R. \quad (4)$$

A similar consideration can be utilized for the film/substrate interface. However, since the film and the substrate are different substances, as a first-order approximation,

$$\gamma_{fs} \approx 2\bar{h}\bar{S}_{vib}\bar{H}_m/(3\bar{V}_mR), \quad (5)$$

where \bar{h} , \bar{H}_m , \bar{S}_{vib} and \bar{V}_m are the mean values of corresponding substances consisting of interfaces.

It is well known that a liquid may be regarded as a solid with such a high concentration of dislocation cores that they are in contact everywhere [9]. Based on this theory, the solid–solid interface energy can be considered to be approximately twice the solid–liquid interface energy [6]. If a solid–solid interface as concerned above consists of

different substances, as a first-order approximation, their mean value is taken. Based on this consideration and in terms of Eq. (3)

$$\gamma_{cs} \approx 4\bar{h}\bar{S}_{vib}\bar{H}_m/(3\bar{V}_mR). \quad (6)$$

In Eq. (1), $\Delta\mu(T) = g_m(T)/V_m$, where $g(T)$ is the temperature-dependent molar Gibbs free energy difference between liquid and crystal, V_m is the molar volume. For semiconductors [6]

$$g_m(T) = H_m T(T_m - T)/T_m^2, \quad (7)$$

where T_m is the melting temperature.

Since the considered temperature is room temperature while liquid cannot exist below the ideal glass transition temperature, or Kauzmann temperature T_k , $T = T_k$ is taken in Eq. (7) [as $T < T_k$, the function remains constant because the liquid is now a glass which has a similar specific heat as a crystal and leads to $g_m(T < T_k) \approx g_m(T_k)$]. At T_k , $g_m(T)$ reaches its maximum or $dg_m(T)/dT = 0$ [10], which results in $T_k = T_m/2$, or

$$g_m(T_k) = H_m/4. \quad (8)$$

When the crystallization speed is the largest, the maximum of $dG(r, d, T_k)/dr$ function should take its minimum at a certain d value. For $dG(r, d, T_k)/dr = 0$, the corresponding critical radius for nucleation $r_{crit}(T_k)$ is represented by

$$r_{crit}(T_k) = \frac{\gamma_{nf}d}{\Delta\mu(T_k)d - \Delta\gamma}. \quad (9)$$

Substituting Eq. (9) and related functions into Eq. (1), this equation becomes

$$G_{max}(d, T_k) = -\Delta\mu(T_k)V_c(r_{crit}) + \gamma_{cf}S_{nf}(r_{crit}) + \Delta\gamma S_{cs}(r_{crit}). \quad (10)$$

Eq. (10) gives the crystallization energy barrier as a function of d where the first term of Eq. (10) is the driving

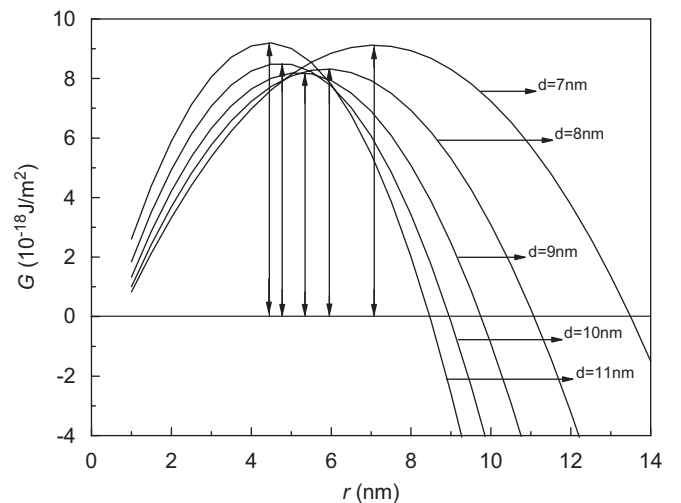


Fig. 2. $G(r, d, T_k)$ functions of GeSbTe thin films sandwiched in two dielectric layers in terms of Eq. (1). The related parameters are cited from Table 1.

Table 1
Thermodynamic parameters for ZnS and Ge₂Sb₂Te₅

	Ge ₂ Sb ₂ Te ₅	ZnS
h (nm)	0.601 ^a [11]	0.234 [12]
M (g/mol)	1026.7	97.44
ρ (g/cm ³)	6.13 [11]	4.10 [13]
V_m (cm ³ /g-atom)	167.5	11.9
H_m (KJ/g-atom)	18.33 ^a	22.0 [15]
S_m (J/g-atom-K)	22 [14]	10.46 [15]
S_{vib} (J/g-atom-K)	13.69	2.15
$\Delta\gamma$ (J/m ²)	0.059	
γ_{ca} (J/m ²)	0.027×10^9	
$\Delta\mu$ (J/m ³)	0.072	

$V_m = M/\rho$ with M and ρ being the molecular weight per mole of atoms and the density.

^a h of Ge₂Sb₂Te₅ is taken as the lattice constant value of Ge₂Sb₂Te₅ because Ge₂Sb₂Te₅ has the NaCl structure [11]. H_m of Ge₂Sb₂Te₅ is $H_m = S_m T_m$ ($T_m = 833$ K [11]).

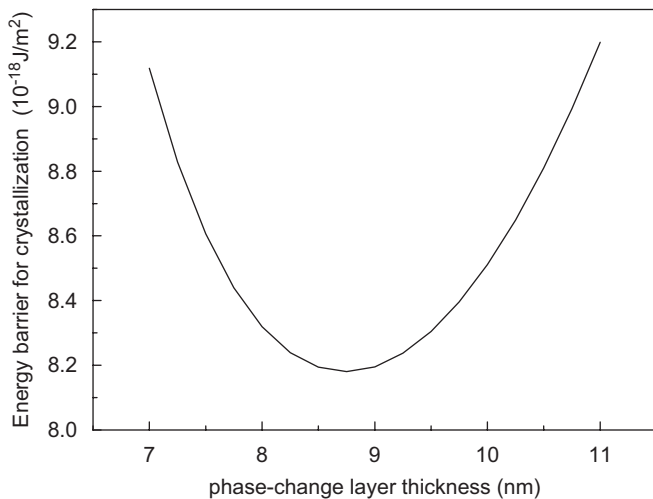


Fig. 3. $dG(r,d,T_k)/dr$ curve as a function of d for GeSbTe thin films sandwiched in two dielectric layers.

force of the phase transformation, while the second and third terms of Eq. (10) are phase-transition barriers.

3. Results and discussion

Fig. 2 illustrates $G(r,d,T_k)$ functions of amorphous GeSbTe thin film sandwiched within ZnS dielectric substrate in terms of Eq. (1). The necessary thermodynamic parameters of Eq. (1) are shown in Table 1. For $d = 8.7$ nm, the barrier height for crystallization reaches its minimum where the crystallization rate is the fastest.

Substituting r_{crit} determined by Eq. (9) into Eq. (1), the calculated barrier heights for crystallization as a function of d are presented in Fig. 3. As d decreases, the energy

barriers for crystallization are minimum with the fastest crystallization rate at $d = 8-9$ nm due to the contribution of $\Delta\gamma S_{cs}(r)$ to the $G(r)$ function. Both the driving force $\Delta\mu$ and the barrier $\Delta\gamma$ for crystallization increase with increasing d . When the increase of the former is larger than that of the latter, the crystallization rate increases; when the tendency is reverse, the crystallization rate decreases. Between them, there is a critical thickness where the crystallization rate is the fastest.

4. Summary

In summary, the investigation of the crystallization rates in thin fast-growth phase-change layers shows the presence of an optimum thickness where the crystallization rate is maximized. The barrier-height for crystallization as derived from a Gibbs free-energy equation, including the phase-change-dielectric interface-energy contribution, is in agreement with the experimental results. It implies that optimization of the phase-change-dielectric interfaces is required to limit the barrier for crystallization and to obtain optimum thickness where the crystallization rate is maximized.

Acknowledgements

The financial support from National Key Basic Research and Development Program (Grant no. 20004CB619301), National Natural Science Foundation of China (Grant no. 50571040) and “985 Project” of Jilin University are acknowledged.

References

- [1] E.R. Meinders, H.J. Borg, M.H.R. Lankhorst, J. Hellmig, A.V. Mijiritskii, J. Appl. Phys. 95 (2004) 8130.
- [2] Z.H. Fan, D.E. Laughlin, Jpn. J. Appl. Phys. 42 (2003) 800.
- [3] A.V. Mijiritskii, J. Hellmig, H. Borg, E. Meinders, Jpn. J. Appl. Phys. 41 (2002) 1668.
- [4] G.F. Zhou, Mater. Sci. Eng. A 304 (2001) 73.
- [5] H.C.F. Martens, R. Vlutters, J.C. Prangma, J. Appl. Phys. 95 (2004) 3977.
- [6] Q. Jiang, H.X. Shi, M. Zhao, J. Chem. Phys. 111 (1999) 2176.
- [7] N.F. Mott, Proc. Roy. Soc. A 146 (1934) 465.
- [8] L. Battezzati, A.L. Greer, Acta Metall. 37 (1989) 1791.
- [9] A. Kotzél, D. Kuhlmann-Wilsdorf, Appl. Phys. Lett. 9 (1966) 96.
- [10] C.V. Thompson, F. Spaepen, Acta Metall. 27 (1979) 1855.
- [11] T. Nonaka, G. Ohbayashi, Y. Toriumi, Y. Mori, H. Hashimoto, Thin Solid Films 370 (2000) 258.
- [12] Y.R. Wang, C.B. Duke, Phys. Rev. B 36 (1987) 2763.
- [13] R.C. Weast, D.R. Lide, CRC Handbook of Chemistry and Physics, CRC Press Inc., Florida, 1989, pp. B145–B227.
- [14] E.R. Meinders, H.J. Borg, M.H.R. Lankhorst, J. Hellmig, A.V. Mijiritskii, J. Appl. Phys. 93 (2003) 9794.
- [15] A.R. Regel, V.M. Glazov, Semiconductors 29 (1995) 405.