

A model for the phase-change process in GeSbTe thin films used for optical and electrical data storage

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ABSTRACT

We have developed a model to simulate the phase-change behavior of GeSbTe thin film alloys. Based on classical nucleation theory we described formation of crystalline clusters using chemical rate equations. Assuming that the phase-change proceeds by interactions of single GeSbTe molecules with growing or decaying crystalline clusters we used a set of differential equations to account for the population density changes of clusters. We defined reaction rates encountered in model equations by considering possible molecular processes during the phase-change process. To validate the model we simulated experiments on crystallization of GeSbTe during isothermal and ramped thermal treatments. We showed that the model can simulate experiments taken from the literature. It can predict the kinetics of crystallization well, describe transient effects correctly, and consider influences of substrates on crystallization successfully.

Keywords: GeSbTe, phase-change, crystallization.

1. INTRODUCTION

Both optical and electrical data storage based on chalcogenide materials, like GeSbTe or AgInSbTe, rely on reversible phase-change between amorphous and (poly)crystalline states^{1,2}. On optical disks data is recorded by forming an amorphous dot on a crystalline film by melting with a focused laser beam. In contrast, erasing of data is achieved by heating the amorphous dot to temperatures sufficiently high to allow the amorphous dot to crystallize. During writing or erasing the rate limiting step is crystallization. It is much slower than amorphization and needs to be optimized to satisfy two opposing prerequisites: it must be slow to allow a successful amorphization, and it must proceed fast for a rapid erasure of amorphous dots. As the laser power increases and the pulse length decreases to achieve faster and denser data storage the minimum time for crystallization becomes a major obstacle. Because the physical properties of a material are inextricably linked to its microstructure an ability to predict and control the microstructural development during phase-change is desirable to reach faster and denser data storage capabilities.

In the early stages of the phase transformation the small regions of the new phase are generally far apart allowing the total volume transformed to be computed by simply summing the transformed volumes associated with each region. As transformed regions continue to grow, however, they eventually impinge upon one another, slowing the rate of transformation. Typically this impingement is analysed following the approach suggested Kolmogorov, Johnson and Mehl, and Avrami (JMAK analysis). It is important to recognise that JMAK analysis is valid only for isothermal transformations with time-independent crystallization rate. Moreover, nucleation of crystalline clusters should be random and uniform everywhere. Crystallization of GeSbTe does not satisfy these conditions: nucleation and growth of crystalline clusters are neither random nor uniform³ nor time-independent^{4,5}. Therefore JMAK formalism is not suitable for modelling the crystallization process in GeSbTe films.

Another approach to model the phase transformation in GeSbTe is to use expressions for nucleation rate based on classical nucleation theory^{6,7}. This formalism relies on the assumption that steady-state conditions are maintained during crystallization of GeSbTe. For situations involving metastable phase formation, however, where the material is heated or cooled rapidly on the time scale required for atomic rearrangements, the steady-state is not maintained. The relaxation of the cluster distribution underlying nucleation then results in a time dependent nucleation rate⁸.

In order to develop a physically-realistic phase-transition model to describe the time dependent nucleation and growth we have used an approach based on the kinetic description of the phase-change process. Nucleation, growth and dissolution of crystalline phase in an amorphous medium have been described using rate equations. It is assumed that a crystalline cluster can grow or shrink by addition or loss of a single molecule. According to this scheme one can write a differential equation for each cluster size to describe time dependent density changes. Once all possible cluster sizes are considered then the complete description of the phase-change process is attainable in terms of reaction rates between clusters of different sizes. It is therefore of utmost importance to relate these rates to underlying physical processes. A major drawback of this modelling approach, however, is heavy computational requirements because of the large number of coupled differential equations.

2. THEORY

Amorphization of GeSbTe is its reluctance to undergo crystallization although the crystalline phase is energetically more stable; it is a competition between crystallization and cooling. In contrast, overall crystallization is a complex process involving nucleation and growth of separate crystalline clusters. Crystallization starts with the formation of small, unstable clusters of new phase. Eventually some clusters reach to a critical size beyond which they are stable such that they can grow rather than dissolve. Homogeneous nucleation occurs at a random position in the original phase while heterogeneous nucleation takes place at preferential sites like surfaces, interfaces, impurities. Formation of a crystalline cluster with n molecules in an amorphous background changes total energy of system. The energy change written in terms of Gibbs free energy ΔG can be expressed as

$$\Delta G = 4 \pi r^2 \sigma - n \Delta g \quad (1)$$

where σ is the interfacial energy density between amorphous and crystalline phases and r is the cluster radius. The first term on the right hand side of Eq. (1) describes changes related to formation of a new interface between crystalline and amorphous phases while second term is volume energy (Fig. 1). Here it has been assumed that clusters are of spherical shape such that the relation between cluster radius and number of GeSbTe molecules in the cluster is

$$n = \frac{4}{3} \pi \frac{r^3}{v_m} \quad (2)$$

where v_m is the volume of a molecule (or monomer), which can be estimated from the density and the molar weight of the material ($v_m=2.9 \times 10^{-22} \text{ cm}^3$). Δg in Eq. (1) is the bulk free energy difference per molecule between two phases. It has been approximated as

$$\frac{\Delta g}{v_m} = \Delta H_f \frac{T_m - T}{T_m} \left[\frac{7 T}{T_m + 6 T} \right] \quad (3)$$

where T is the absolute temperature and T_m is the melting temperature of GeSbTe (=900 K), ΔH_f is the enthalpy of fusion at melting point (=620 J/cm³).

The free energy given by Eq. (1) increases with n up to a maximum critical value n^* given by

$$n^* = \frac{32 \pi v_m^2 \sigma^3}{3 \Delta g^3} \quad (4)$$

The critical value of ΔG , which can be defined as energy barrier to nucleation, is

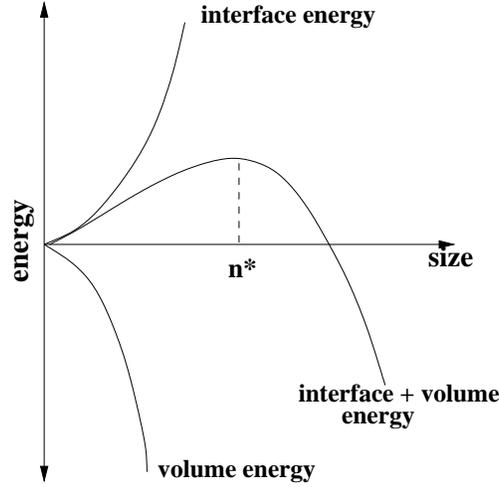


Figure 1. Schematic depiction of energy changes associated with formation of a crystalline cluster as a function of cluster size n .

$$\Delta G^* = \frac{16 \pi v_m^2 \sigma^3}{3 \Delta g^2} \quad (5)$$

Clusters larger than critical size n^* are called supercritical clusters. On average they have larger probabilities for growth while clusters smaller than critical size, called subcritical clusters, will dissolve. During nucleation in a real system there will be not only clusters of critical size but a distribution of clusters of different sizes. These clusters will interact with each other and this interaction will determine the progress of the crystallization process. Therefore instead of considering only clusters of critical size we should take into account both subcritical and supercritical clusters to establish the size distribution. Considering that smallest possible cluster size is two GeSbTe molecules, and assuming the interactions among different sizes to be through single molecules at a given time, a cluster can gain or lose a GeSbTe molecule to grow or dissolve, respectively. One can easily envisage four possible reactions for a cluster of (n) molecules interacting with clusters of size $(n-1)$ and $(n+1)$ such that



In view of these reactions we can write a kinetic rate equation, which describes the development of the density of the clusters of size (n) , $f(n,t)$:

$$\frac{\partial f(n,t)}{\partial t} = g(n-1,t)f(n-1,t) - d(n,t)f(n,t) - g(n,t)f(n,t) + d(n+1,t)f(n+1,t) \quad (7)$$

where $g(n,t)$ and $d(n,t)$ are reaction rate coefficients describing growth and dissolution of size (n) , respectively. Since one must consider all possible size of clusters Eq. (7) needs to be applied for $n \geq 2$. For single molecules ($n=1$) the requirement of the conservation of matter in a given volume requires that

$$f(1,t) = f(1,0) - \sum_{n=2}^{n_{\max}} n \cdot f(n,t) \quad (2)$$

where $f(1,t)$ is the concentration of single molecules at a given time, $f(1,0)$ is the initial concentration of GeSbTe molecules, i.e., for $t=0$. Here a summation over all possible cluster sizes, starting from smallest possible cluster size ($n=2$) to the largest possible one ($n=n_{\max}$), is carried out. It is possible for a large cluster to contain millions of molecules. For example, an easy calculation would show that a crystalline cluster of about few 10 nm of radius contains several millions of molecules of GeSbTe. This fact indicates that one needs to consider several millions of coupled rate equations for a successful simulation of crystallization.

To solve the set of rate equations it is necessary to know the growth and dissolution rates, $g(n)$ and $d(n)$, respectively. We modeled these rates by considering the atomic processes accompanying the phase-change. Following the theory of reaction rates⁹ we assumed that the growth rate of a crystalline cluster of (n) molecules is governed by

(i) The number of clustering monomers at amorphous-crystalline interface; it is assumed to be proportional to GeSbTe concentration determined by the density of material and the size of the cluster.

(ii) The probability that a GeSbTe molecule overcomes the energy barrier at the amorphous-crystalline interface; it is written using Boltzmann statistics and is related to Gibbs free energy changes of phase-change process[Eq. (1)].

(iii) The trial-frequency of molecules to overcome the energy barrier; it is estimated from data on viscosity of the material.

It is a well known fact that the crystallization behavior of thin film GeSbTe is strongly dependent on the substrate material on which GeSbTe is deposited³. This fact indicates that the nucleation of crystalline clusters takes place preferentially at the GeSbTe-substrate interface so that the phase-change process is not homogenous, where the nucleation may proceed randomly anywhere with equal probability, but heterogeneous, where energetically favorable places are preferential nucleation sites. In order to take into account the heterogeneous effects we modified the model by using the so-called “the spherical-cap” approach⁹. Based on largely geometrical considerations the spherical-cap model considers the nucleation to proceed at the substrate-GeSbTe interface by assuming the shape of nucleus to be a truncated sphere instead of a full sphere. The volume and the surface area of a nucleus are then determined not only by the radius but also by the angle between the nucleus surface and the substrate.

3. RESULTS AND DISCUSSION

We solved model equations numerically by considering appropriate initial and boundary conditions. For all calculation results presented here initial state of the GeSbTe was always amorphous, i.e., there were no crystalline clusters and only GeSbTe molecules were present. The number of rate equations n_{\max} was chosen sufficiently large so that the calculation results were not dependent on it. It was found out that depending on the thermal treatment 10^4 to 10^7 rate equations were needed to simulate a given experiment.

For crystallization studies the change of optical properties of the material is measured and this information is then related to the amount of material crystallized. During isothermal treatments the changes in reflectivity can be measured in real-time if low temperature treatments are used. Figure 2 shows experimental⁵ and calculated results of crystallization of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ as a function of annealing time. Simulations carried out to mimic these experiments could predict both crystallization onset and total crystallization time successfully. The model was capable to take into account minute temperature differences as seen in figure 2. It is interesting to see how sensitive crystallization to temperature changes is: crystallization time changes more than four-fold with a change of temperature of 8°C. It is therefore critical to consider the influence of any temperature ramp preceding the isothermal step.

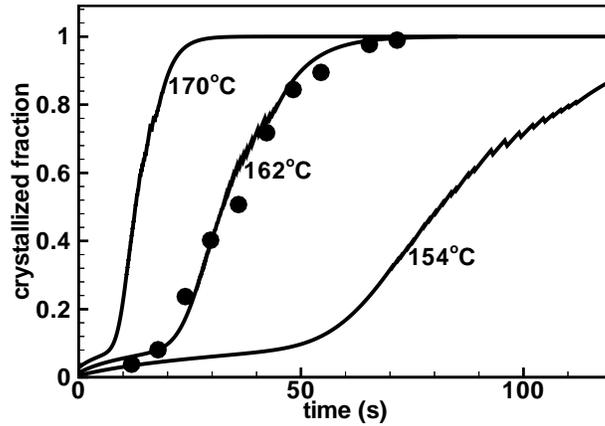


Figure 2. Experimental⁵ (symbols) and simulated (lines) results of crystallized fraction of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ as a function of annealing time during isothermal treatments.

The effect of a temperature ramp before the annealing can be illustrated by the evolution of size distribution function, i.e., cluster density as a function of cluster size, during thermal treatments. Fig. 3 shows the size distribution function during and after the annealing at 162 °C, presented in Fig. 2. These experiments were carried out with a temperature ramp of 5 °C/s before annealing at 162 °C. Although the temperature ramp did not induce any measurable crystallization, which, according to simulations, was less than 2 %, it led to formation of very small crystalline clusters in high densities. As seen in Fig. 3, after the ramp crystalline clusters containing less than 10 molecules were formed so that before the onset of isothermal treatment a partial nucleation had already taken place. This behavior is similar to priming of phase-change media or to the influence of quenching after an amorphizing laser pulse: material is amorphous but contains minute crystalline clusters which act as precursors of crystallization for subsequent thermal treatments.

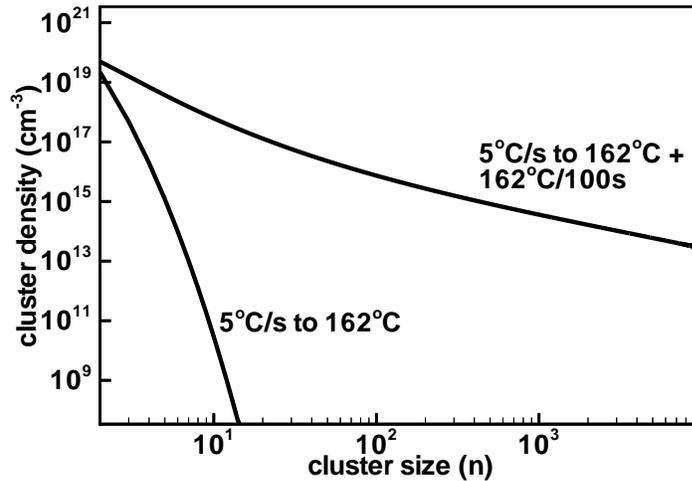


Figure 3. Size distribution function of crystalline clusters after the temperature ramp of 5°C/s and the isothermal annealing following this temperature ramp.

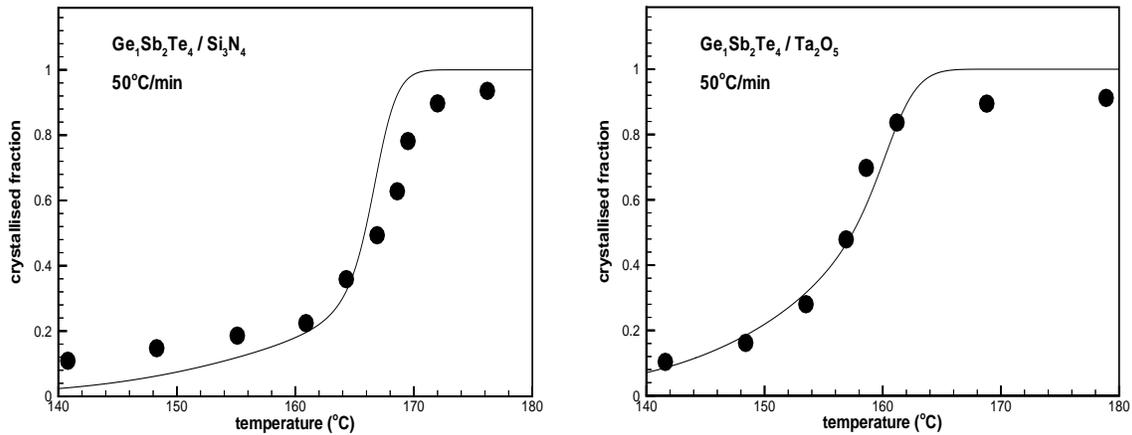


Figure 4. Experimental³ (symbols) and simulated (lines) results of ramped-temperature treatments. The effect of the substrate on crystallization is shown here for SiN (left) and TaO (right).

Non-isothermal treatments, during which the temperature increases with a constant rate, are common in the literature to study phase-change behavior of GeSbTe thin films. Depending on the rate of temperature the onset of crystallization shifts: the higher the rate, the higher the onset-temperature. In Fig. 4 one can see two different experiments³ and corresponding simulations, where the ramp rate is 50 °C/min.

As previously mentioned the substrate, on which the GeSbTe layer is deposited, has a profound effect on crystallization. Minute changes in surface conditions cause large effects in crystallization kinetics. The onset of crystallization and crystallization time depend on substrate type and preparation. We could simulate such effects successfully as seen in Fig 4. Since we could explain all heterogeneous effects with a simple “spherical cap” model based on geometrical considerations it is justifiable to argue that the main effect of a substrate on crystallization kinetics is the change of energetics of the phase-change process. Instead of formation of a nucleus in the shape of a whole sphere, for example, the GeSbTe-substrate interface offers preferential nucleation sites where a nucleus can form in the shape of a truncated sphere. Thus, the change of Gibbs free energy for nuclei formation, i.e., the driving force for crystallization, is considerably increased. The differences among different substrates attest to the different surface activity of these substrates.

4. CONCLUSIONS

We have developed a comprehensive model for the phase-change process of GeSbTe. The model, based on the classical nucleation theory, accounts for the kinetics of phase-change by using rate equations. In the model formation of crystalline clusters has been described by a set of rate equations. Rate coefficients for these equations have then been modeled by considering the molecular processes taking place during phase-change process.

This model has been then used in a calculation program to simulate crystallization behavior of GeSbTe. In particular we simulated successfully experiments involving isothermal and non-isothermal treatments. It has been shown that the model is capable of explaining the effects of minute temperature changes, influences of different substrates on which GeSbTe was deposited, and the role of transient nucleation and growth.

5. ACKNOWLEDGMENT

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