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Crystallization of Ge:Sb:Te Thin Films for Phase Change Memory Application

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1. Introduction

Chalcogenide glasses are a chemical compound consisting of at least one chalcogen element, sulphur, selenium, or tellurium, in combination with other elements. These glasses obtained great attention after discovery between 1962 and 1969 by Kolomiets, Eaton, Ovshinsky and Pearson of the S-shape current-voltage characteristic in chalcogenide glasses and the switching phenomenon from high to low resistivity states (Popescu, 2005). In 1968 S. R. Ovshinsky demonstrated very short (about of $10^{-10}$ seconds) reversible electrical switching phenomena in $\text{Te}_{81}\text{Ge}_{15}\text{Sb}_{2}\text{S}_{2}$ thin films due to amorphous-crystalline phase transition (Ovshinsky, 1968). This work opened a new area of phase change technology, which now is one of the most important technologies for memory devices and applications in computers, CD, DVD, phase-change random access memories, etc.

The first electrical phase-change memory devices used various binary, ternary and quaternary Te-based films with compositions made up of Ge:Te, Si:As:Te, Ge:As:Si:Te, etc., systems (Stand, 2005). The early phase change materials used in optical storage comprised simple alloys based primarily on compositions in the vicinity of the tellurium-germanium eutectic. Antimony was primarily used, although other elements including selenium, arsenic and bismuth were all shown to have beneficial effects. Based on the results obtained from films with $\text{Ge}_{15}\text{Sb}_{4}\text{Te}_{81}$ composition (Ovshinsky, 1971) the first application of Ge:Sb:Te alloys was reported for phase change rewritable optical disks.

In the early 1990s, a second generation of high speed phase change materials based on Ge:Sb:Te alloys was reported by several optical memory research groups (Ohta et al 1989, Yamada et al, 1991, Gonzalez-Hernandez et al, 1992). These alloys have stoichiometric compositions along the $\text{GeTe}-\text{Sb}_{2}\text{Te}_{3}$ pseudobinary line of phase diagram such as $\text{Ge}_{2}\text{Sb}_{3}\text{Te}_{9}$, $\text{Ge}_{7}\text{Sb}_{2}\text{Te}_{4}$ and $\text{Ge}_{5}\text{Sb}_{4}\text{Te}_{7}$.

Ge:Sb:Te stoichiometric alloys have three phases: one amorphous and two crystal structures. The first crystalline phase is the rock salt NaCl-like and the second more stable phase is hexagonal. When the amorphous films are heated, the transition from amorphous to rock salt-like structure occurs at around 120-170°C; subsequent heating transforms this phase into a stable hexagonal structure at temperatures around 200-250°C. The exact transition temperature depends on the composition of the film. The hexagonal structure remains stable over a wide temperature range from 200-250°C to around the melting point (593-630 °C,
depending on composition) (Gonzalez-Hernandez et al, 1992). The principle of phase-change memory operation is based on a reversible phase-transformation from the amorphous (high resistance/low reflectivity state) to crystalline NaCl-type (low resistance/high reflectivity state) under short laser or electrical pulses. It is necessary to note that for phase-change memory applications only the amorphous-NaCl-type transition has been used, probably because the heating time produced by the laser or electrical pulse is too short to form the stable hexagonal structure (Yamada, 1991). This transformation is always accompanied by abrupt changes in reflection (about 20-30 %) and resistivity (about 3 orders of magnitude) in chalcogenide films. The reversible transformation from crystalline to the amorphous structurally disordered state can be obtained by increasing the local temperature of the Ge:Sb:Te layer above its melting point by short intense laser, or electrical pulses and the subsequent quenching with a cooling rate about $10^{10}$ deg/s (Yamada et al, 1991).

The phase transition between the amorphous and NaCl-type crystalline phase in stoichiometric materials is fast because atoms in the amorphous state do not need to travel long distances to take their position in the crystal lattice. On the other hand, non-stoichiometric compounds require long-range diffusion when they crystallize from an amorphous state (Yamada et al, 1991, Yamada 1996), which in general slows down the crystallization process. For example, 30 at. % of the deviation from Ge$_2$Sb$_2$Te$_5$ stoichiometric composition increased the crystallization time from 220 to 500 ns (Kyrsta et al., 2001).

For several years, Ge:Sb:Te alloys along the pseudobinary GeTe-Sb$_2$Te$_3$ line have been used as the main material for optical phase-change data storage devices and are currently being investigated for nonvolatile electronic storage purposes (which utilize the difference in the electrical resistance of the two phases) due to the high reflectivity and resistivity contrast between the amorphous and crystalline phases. Many investigations have been carried out on this type of phase-change materials with the purpose of improving their properties and to increase its storage capacity, stability, speed and versatility. These investigations have shown that the crystallization of the phase-change (or amorphous-NaCl-type transition) can be considered as a rate-limiting process to obtain a fast data transfer. That is why there are a considerable number of experimental and theoretical studies investigating the amorphous-to-crystalline NaCl-type phase transformation. In spite of the large number of publications, the activation energy for crystallization of Ge:Sb:Te materials reported in the literature shows a large discrepancy; the activation energy of crystallization for Ge$_2$Sb$_2$Te$_5$ reported in the literature varied between 0.8 and 2.9 eV, for example. Such dispersion in the kinetic parameters might depend on the differences in the deposition methods, type of substrate, dielectric cover layer, film thickness and/or parameters of deposition processes, which lead to differences in the crystallization temperature, activation energy, and the like. In addition, experimental data show relatively long incubation times for crystallization of Ge:Sb:Te films and a relatively large amount of crystallized material during this period of time (Morales-Sanchez et al 2010). Incubation time manifests itself as the time necessary to reach critical values of nucleus for the crystallization to occur (Senkader et al, 2004). The existence of a non-negligible amount of crystallite during the incubation time could also be responsible for the dispersion in the kinetic parameters reported in the literature.

Based on such antecedents, we aimed in this chapter at investigating the crystallization kinetics of thin films on a glass substrate obtained by the same deposition process (DC sputtering), with the same thickness (around 200 nm), and composition along the GeTe–
Sb₂Te₃ pseudobinary line (Ge₄Sb₁Te₅, Ge₁Sb₂Te₄, and Ge₁Sb₄Te₇) including GeTe and Sb₂Te₃ (which lie at the end of GeTe-Sb₂Te₃ pseudobinary line), taking into account the processes during the incubation time. It is necessary to note that GeTe and Sb₂Te₃, as well as Ge:Sb:Te, can be used in phase-change data storage. Additionally, the crystallization kinetics of Ge₄Sb₁Te₅ films will be present in this chapter. The structure of this alloy is unclear. In contrast to other Ge:Sb:Te ternary compounds, it does not belong to the GeTe – Sb₂Te₃ homologous series, although it lies on (or very close to) the GeTe-Sb₂Te₃ pseudobinary line in the Ge:Sb:Te phase diagram between GeTe and Ge₂Sb₂Te₅. It is suggested (Coombs et al., 1995) that this alloy is a solid solution between GeTe and a compound with a composition close to Ge₄Sb₁Te₅. This material, in contrast to stoichiometric alloys, demonstrates only one amorphous-NaCl-type phase transition, but it has the largest optical (Kato et al., 1999) and electrical (Morales-Sanchez et al., 2005) contrast between the crystalline and amorphous states, compared with other Ge:Sb:Te ternary alloys.

Necessary to note that as-prepared and melt-quenched Ge:Sb:Te amorphous materials show different crystallization kinetics (Nobukuni et al., 1999, Park et al., 1999, Khulbe et al., 2000, Wei et al., 2003, Kalb et al., 2004, Raoux et al., 2008). It has been proposed in the literature that for melt-quenched amorphous materials may exist: embryos following the condensation and evaporation of embryos to form crystalline clusters (Khulbe et al., 2000), preexisting clusters (Park et al., 1999), crystal nuclei (Wei et al., 2003), sinks and voids after repeated overwriting (Nobukuni et al., 1999), locally ordered regions with structure similar to that of crystalline Sb (Naito et al., 2004) or a crystalline amorphous border (Raoux et al., 2008). In spite of different models, crystallization in the melt-quenched amorphous material can start from these nucleation centers, which decrease incubation time and increase crystallization speed. But in this chapter only crystallization of as-prepared materials will be discussed.

Studies of crystallization kinetics of phase change materials are mostly analyzed using the Johnson–Mehl–Avrami-Kolmogorov (JMAK) model for isothermal annealing (see for example: (Weidenhof et al., 2001, Ruitenberg et al., 2002, Trappe et al., 2000, Morales-Sanchez et al., 2010)), which permitted to determine the activation energy for the crystallization process. This method will be used for investigation of the crystallization kinetics in the compositions mentioned above.

Figure 1 shows in-situ optical reflection (using a laser diode emitting at 650 nm) as a function of temperature with a heating rate of 5°C/min for all investigated films with composition indicated on the graph. An abrupt change in reflection is associated with the onset of phase crystallization. Stoichiometric Ge₄Sb₁Te₅, Ge₁Sb₂Te₄ and Ge₁Sb₄Te₇ materials demonstrate two changes: the first corresponds to amorphous-NaCl-type transition and the second to NaCl-type-hexagonal transformation. In contrast, GeTe, Ge₁Sb₂Te₅ and Sb₂Te₃ show only one amorphous-crystalline transition. The highest crystallization temperature (T_c) has been observed in GeTe, the lowest in Sb₂Te₃. The crystallization kinetics of the GeTe-Sb₂Te₃ pseudobinary line will be analyzed according to this Figure from the highest to the lowest crystallization temperature.

2. Deposition of phase change films

An important aspect to develop thin films of phase change materials is the deposition method. It is well known from the literature that deposition technology strongly affects
the microstructure and as a result the optical, electrical and crystallization (especially the crystallization temperature) properties of phase-change materials. For example, the crystallization temperature of the films with the same composition but obtained by different deposition methods can differ for more than 20°C, and no suitable explanation has yet been proposed (Morales-Sanchez et al., 2005). That is why, to compare crystallization properties all studied films have to be obtained with the same deposition process (DC sputtering), with the same thickness (around 200 nm), and composition along the GeTe–Sb₂Te₃ pseudobinary line. This method has been chosen because sputtering can produce films with the desired stoichiometry. Compared, for example, with thermal evaporation, in sputtering the thickness and chemical composition of thin films are easier to control.

Fig. 1. Dependencies of optical reflection on temperature for films with compositions indicated on the graph.

Fig. 2. Surface topography of as-prepare amorphous (a) and crystalline (b) Ge₂Sb₂Te₅ films.
The thin films have been prepared on glass and Si substrates by DC magnetron sputtering from one composite target. The deposition conditions were: $4.5 \times 10^{-6}$ mbar base pressure, $2.0 \times 10^{-5}$ mbar work pressure, $180$ cm$^3$/min Ar gas input flow, $0.49$ W/cm$^2$ DC power density, and $10$ min deposition time. Before films sputtering, the targets were cleaned for $10$ minutes by sputtering to remove the oxide from the surface. According to XRD measurements all films were obtained in amorphous state. Energy dispersive spectroscopy has shown that deviations of films compositions from the targets were approximately $2\%$.

Figure 2a shows typical surface topography obtained from AFM measurements of as-prepared amorphous thin films. All amorphous films demonstrated vary smooth surface with the surface roughness between 1 and 3 nm. In contrast, in the crystalline films (annealed to the temperature of $200^\circ$C) the topography image shows grains with average size between 20-120 nm (Fig. 2b). The dimensions of grains are dependent on the films composition.

3. Crystallization of GeTe

GeTe is a promising candidate for the application of in phase-change technology due to its higher crystallization temperature (onset of crystallization temperature at about $184^\circ$C) when compared to other alloys, since it offers a significant improvement in data-retention at high temperature (Perniola et al., 2010, Fantini et al., 2010). Amorphous films, in contrast to Ge:Sb:Te ternary alloys, crystallize in the rhombohedral phase. This phase can be viewed as a rock salt structure distorted along the [111]-direction (Caravati et al., 2010). Additionally, the central atom is displaced along the [111]-direction from the center of the rhombohedron. Upon crystallization, in a rhombohedral (distorted rock salt) structure appeared about $10\%$ of vacancies occurring on Ge sites (Kolobov 2004). GeTe is a classical ferroelectric material that shows displacive type ferroelectric-paraelectric transition from a rhombohedral ferroelectric phase to a rock salt type structure with paraelectric properties. Two sublattices form this rock salt structure: Ge atoms compose one of the lattices and tellurium atoms the other (Rabe et al., 1987).

The NaCl type crystalline structure of GeTe is an unstable phase. This crystalline structure exists for temperatures above $300^\circ$C. The ferroelectric-paraelectric transition occurs in the interval of $327$-$427^\circ$C depending on various factors, such as exact composition, carrier density, etc. For example, changes in Te composition from 50 to 50.7 at. $\%$ shift the transition temperature from $427^\circ$C to $356^\circ$C (Okura, 1992).

Activation energy of amorphous to rhombohedral phase crystallization reported in the literature demonstrates large dispersion: $1.7$ eV (Libera et al., 1993), $1.77$ eV (Lu et al., 1995), $1.96$ eV (Fantini et al., 2010), $2.5$ eV (Fan et al., 2004), $3.9$ eV (Matsushita et al., 1989). Such dispersion can be dependent on the differences in the deposition methods, type of substrate, method of results interpretation, etc. According to the literature and to our measurements (Fig. 1), GeTe has the highest crystallization temperature for materials on the GeTe-Sb$_2$Te$_3$ pseudobinary line and must demonstrate the highest activation energy of crystallization.

Figure 3 shows X-ray patterns of GeTe film measured at the temperature indicated on the graph. At temperatures below $180^\circ$C, the material shows only wide bands, which are characteristic of amorphous materials. At higher temperatures, a rhombohedral GeTe phase appears. At a temperature of $350^\circ$C two phases have been observed: rhombohedral and
NaCl-type, and at higher temperatures the material transforms into a NaCl-type phase. This phase exists only at temperatures above 400°C and in the process of cooling, again transforms into the stable rhombohedral phase.

Crystallization kinetics in GeTe, as in other materials, has been investigated using optical reflection during isothermal measurements. Reflection measurements were made with a 650 nm wavelength laser diode and a PIN diode as detector. In the reflectance measurements, the generally employed assumption has been used; the reflection signals are linearly related to the total transformed crystalline volume fractions $x$ (Weidenhof et al., 2001):

$$x = \left[ \frac{R(t) - Ra}{Rc - Ra} \right], \quad (1)$$

where $R(t)$, the experimental measurement value of reflectance, $Ra$ and $Rc$ are reflectance of amorphous and fully crystalline phases, respectively.

Figure 3. XRD patterns of GeTe film measured at the temperature indicated on the graph. Blue patterns correspond to rhombohedral phase. Red patterns correspond to NaCl-type phase.

Figure 4 shows the evolution of the total crystalline volume fraction $x$, for GeTe samples, calculated from reflection measurements for films isothermally annealed at the temperatures indicated on the graph.

In this chapter, crystallization kinetics will be analyzed using the Johnson–Mehl–Avrami-Kolmogorov (JMAK) model for isothermal annealing. According to the classical JMAK model, the transformed volume fraction $x$ can be determined by the following expression:

$$x(t) = 1 - \exp(-Kt^n), \quad (2)$$

where $K = \gamma \exp(-E/kT)$, $\gamma$ is the frequency factor, $E$ is the effective activation energy, $t$ is the annealing time, and $n$ the Avrami exponent, which provides information about the mechanisms of crystallization. The value of $n$ can be evaluated from the slope of the $\ln[-\ln(1 - x)]$ versus $\ln(t)$ plot, which in materials with random nucleation and isotropic growth should be linear. The JMAK model is based on several assumptions such as:
homogeneity of the system, random and uniform nucleation, and nucleation rate taking place at the very beginning of the transformation is time independent and applied for isotropic growth at a constant rate.

Fig. 4. Dependencies of the volume fraction $x$ versus time obtained for GeTe samples from reflection measurements at the temperature indicated on the graph.

The value of activation energy for GeTe obtained using Equation (2) was very high: close to 12 eV. Such high value of activation energy has been obtained because GeTe, as other Ge:Sb:Te materials, shows long incubation times $\tau$ for crystallization, namely, the annealing time required to reach a critical nuclei size or to observe an abrupt increase in the crystalline volume fraction. In this case, the nucleation rate cannot be considered to be time independent for the entire crystallization process as is considered in classical JMAK models (Senkader et al., 2004).

In the case of GeTe, the volume fraction of crystalline phase approximately equals zero during all the incubation time (see Fig. 4). In such cases than the volume fraction of crystalline phase does not demonstrate a substantial increase during the incubation time it is possible to define the beginning of the transformation after the incubation time (Weidenhof et al., 2001). The JMAK equation can now be expressed as:

$$x(t) = 1 - \exp[-K(t-\tau)^n],$$  \hspace{1cm} (3)

where $\tau$ is the incubation time. According to Equation (3) the plot $\ln[-\ln(1-x)]$ versus $\ln(t-\tau)$ must be a straight line with slope $n$. Figure 5 shows such modification of an Avrami plot for GeTe. The insert shows the rate constant as a function of the reciprocal temperature.

The calculated activation energy for GeTe as determined from the modification of the Avrami Equation (3) using the Arrhenius type relation for $K$ was $3.98\pm0.12$ eV. The value of the Avrami exponent was about 1.6, which corresponds to diffusion controlled growth from small dimension grains with decreasing nucleation rate (Christian, 1975).
In addition, X-ray measurements have shown that during isothermal annealing from amorphous phase only one rhombohedral phase appeared. As time increases, the volume fraction of amorphous phase decreases (Figure 6); in the same time, the volume fraction of crystalline phase increases. No shift in the position of diffraction peaks was observed. This observation will be important in the analysis of crystallization processes of Ge$_2$Sb$_2$Te$_5$ and Ge$_2$Sb$_2$Te$_4$ materials.

Fig. 5. Avrami plot of $\ln[-\ln(1-x)]$ vs $\ln(t-\tau)$ for GeTe. Points – experiment, lines – result of fitting using JMAK equation (3). The insert shows the rate constant $K$ as function of the reciprocal temperature.

Fig. 6. X-ray diffraction spectra for a GeTe film obtained in the process of isothermal annealing at a temperature of 164°C during the time indicated on the plot. The upper pattern corresponds to film annealing at 200°C.
4. Crystallization of Ge₄Sb₁Te₅

As mentioned above, the structure of Ge₄Sb₁Te₅ is not known. It lies on or is close to the GeTe-Sb₂Te₃ pseudobinary line in the Ge:Sb:Te phase diagram between GeTe and Ge₄Sb₂Te₅. Because of such position, the onset of crystallization temperature is about 160°C, less than in GeTe but higher than in another Ge:Sb:Te ternary alloys. This alloy crystallizes in NaCl-type structure (Gonzalez-Hernandez et al., 1992, Wamwangi et al., 2002, Ruiz Santos et al., 2010). For Ge₄Sb₁Te₅ films the reported values of the activation energy varied in a wide range: 1.13 eV (Kato et al., 1999), 3.09 eV (Morales-Sanchez et al., 2005), 3.48 eV (Wamwangi et al., 2002).

In addition, similarly to GeTe, bulk material and thin Ge₄Sb₁Te₅ films demonstrate at a temperature of approximately 327°C ferroelectric-paraelectric transition (Bahgat et al., 2004, Ruiz Santos et al., 2010). But in contrast to GeTe, in which ferroelectric-paraelectric transition relates to a transformation from a rhombohedral phase to a rock salt type structure, in Ge₄Sb₁Te₅ the ferroelectric-paraelectric transition relates to a transformation between two different rock salt type structures.

Figure 7 shows DSC measurements on a crystalline Ge₄Sb₁Te₅ bulk alloy and on the amorphous material obtained by removing the as-deposited films from the glass substrates. In the bulk alloys, a nonsymmetrical endothermic peak at a temperature of 327°C has been observed. In contrast, DSC measurements on amorphous material showed an exothermic peak at 176°C, which is associated with the crystallization of the sample and a broad endothermic peak, with a maximum at approximately 327°C, and that corresponds to the same temperature as in the bulk alloy. The observed endothermic peak can be associated with the ferroelectric-paraelectric transition.

Fig. 7. DSC measurements on a bulk crystalline alloy and on the amorphous material, obtained by removing the as-deposited films from the glass substrates.
Additional confirmation of ferroelectric-paraelectric transition in Ge$_4$Sb$_1$Te$_5$ films has been obtained by temperature capacitance measurements (Ruiz Santos et al., 2010). In this work, it has been shown that the reciprocal capacitances (which are proportional to the reciprocal dielectric constant) as a function of temperature show a typical Curie-Weiss behavior for temperatures above 327°C.

Specific data of crystallization process and ferroelectric-paraelectric transition in Ge$_4$Sb$_1$Te$_5$ films can be obtained by in situ XRD measurements at different temperatures. Figure 8 shows that below the crystallization temperature the film is in an amorphous state (pattern at 140°C). As the temperature is increased, the material crystallizes in the NaCl type structure. As the temperature continues increasing, the position of all Ge$_4$Sb$_1$Te$_5$ peaks shift to lower 2θ values, reaching saturation at a temperature of approximately 327°C at positions close to the NaCl type of GeTe structure (ICSD cart #602124), which demonstrate paraelectric properties. The position of the NaCl type of GeTe is marked on the graph with the horizontal line. This shift can be clearly seen on the insert of Figure 8, which shows the temperature dependence of the (200) diffraction peak in Ge$_4$Sb$_1$Te$_5$. The horizontal line on the insert indicates the position of the (200) peak in crystalline GeTe.

Figure 9 shows the evolution of the total crystalline volume fraction $x$, for Ge$_4$Sb$_1$Te$_5$ samples, calculated from reflection measurements for films isothermally annealed at temperatures indicated on the graph. As in the case of GeTe, the volume fraction of crystalline phase of Ge$_4$Sb$_1$Te$_5$ is approximately equal to zero during all the incubation time. The same as for GeTe, kinetics parameters for Ge$_4$Sb$_1$Te$_5$ can be calculated using Eq. (3).

Figure 10 shows the modification of an Avrami plot for Ge$_4$Sb$_1$Te$_5$. The insert shows the rate constant as a function of the reciprocal temperature. The effective activation energy, determined from the Avrami plot for different temperatures using the Arrhenius type
relation for \( K \), was 3.46±0.22 eV (insert in Fig. 10). This value is in good agreement with other values reported in the literature (3.48 eV±0.12 eV) obtained using the Kissinger analysis (Wamwangi et al., 2002). The Avrami exponent for Ge\(_4\)Sb\(_1\)Te\(_5\) was close to 1.8, which corresponds to a diffusion controlled growth from small dimension grains with decreasing nucleation rate, an exponent similar to that of GeTe (Christian 1975).

Additional X-ray measurements have shown that during isothermal annealing from amorphous phase only one NaCl-type phase appeared.

![Fig. 9. Dependencies of the volume fraction \( x \) versus time obtained for Ge\(_4\)Sb\(_1\)Te\(_5\) samples from reflection measurements at the temperature indicated on the graph.](image)

![Fig. 10. Avrami plot of \( \ln[-\ln(1-x)] \) vs \( \ln(t-\tau) \) for Ge\(_4\)Sb\(_1\)Te\(_5\) films. Points – experiment, lines – results of fitting using JMAK equation (3). The insert shows the rate constant \( K \) as function of the reciprocal temperature.](image)
5. Crystallization of Ge$_2$Sb$_2$Te$_5$

Ge$_2$Sb$_2$Te$_5$ thin films are the most commonly employed materials for phase-change memory technology application due to its high crystallization speed and relatively high crystallization temperature (but less than in GeTe and Ge$_4$Sb$_1$Te$_5$), which lead to high thermal stability. Because of this, many extensive experimental and theoretical studies have been conducted to understand the structure and crystallization phenomena in this material (see for example (Yamada et al., 1991, Weidenhof et al., 2001, Matsunaga et al., 2004, Matsunaga et al., 2006, Paesler et al., 2007, Im et al., 2008, Claudio et al., 2006)).

As mentioned above, Ge$_2$Sb$_2$Te$_5$ material demonstrates two phase changes: first at a temperature close to 145°C there is an amorphous-NaCl-type transition and second (at about 240°C) a NaCl-type-hexagonal transformation.

Under heating, the amorphous Ge$_2$Sb$_2$Te$_5$ films crystallize at around 130-170°C, depending on the preparation method and heating rate, into a phase with a NaCl-type structure ($Fm\bar{3}m$). In this structure, the 4(a) site is fully occupied by Te atoms, whereas the 4(b) site is randomly occupied by Ge and Sb atoms and vacancies. The composition of Ge:Sb:Te ternary system, which lie on the GeTe-Sb$_2$Te$_3$ pseudobinary line, can be described as (GeTe)$_x$+(Sb$_2$Te$_3$)$_{1-x}$ ($0<x<1$). In such case the site occupancy of the vacancy varies continuously according to $(1-x)/(3-2x)$ (Matsunaga et al., 2004, Matsunaga et al., 2006). But Ge and Sb atoms deviate from the ideal rock-salt positions in Ge$_2$Sb$_2$Te$_5$ not in a random way but in a strongly correlated manner with respect to the neighboring Te atoms (Kolobov et al., 2004, Kolobov et al., 2006). The off-center location of Ge atoms means that there is a net dipole moment and suggests that a NaCl-type phase of the Ge$_2$Sb$_2$Te$_5$ is a ferroelectric material (Tominaga et al., 2004). The ferroelectric properties in Ge$_2$Sb$_2$Te$_5$NaCl-type phase have been observed using capacitance-temperature measurements. The temperature dependence of the capacitance shows an abrupt change with a maximum at the temperature that corresponds to the end from a NaCl-type to a hexagonal transition. In addition, the reciprocal capacitance for temperatures above this transition shows the Curie-Weiss dependence, which is typical of ferroelectric materials (Gervacio Arciniega et al., 2010).

In spite of the large number of publications about crystallization phenomena in Ge$_2$Sb$_2$Te$_5$, the activation energy of crystallization reported in the literature shows a large discrepancy in the range between 0.8 and 2.9 eV and between 1.2 and 4.4 for the Avrami exponent (Morales-Sanchez et al., 2010, Liu et al., 2009). Such parameter dispersion can be related not only to the difference in the preparation methods but to the specific crystallization process.

Experimental data in Ge$_2$Sb$_2$Te$_5$ films, as in all materials along the pseudobinary GeTe-Sb$_2$Te$_3$ line, show relatively long incubation times during isothermal crystallization (Weidenhof et al., 2001, Laine et al., 2004, Zhang et al., 2008, Morales-Sanchez et al., 2010). But in GeTe and Ge$_4$Sb$_1$Te$_5$ the amount of crystallized material is close to zero during the incubation. In contrast, in Ge$_2$Sb$_2$Te$_5$ films large amount of crystallized material has been observed during this period of time (ranging from 50% in Ref. (Zhang et al., 2008), 10% in Ref. (Sian et al., 2008), 9% in Ref. (Laine et al., 2004) and 8% in Ref. (Weidenhof et al., 2001)). It is necessary to note that the amount of crystalline phase material during incubation time depends on the annealing temperature. The existence of a non-negligible amount of
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crystallite during the incubation time, as will be shown below, is the most important factor responsible for the dispersion in the kinetic parameters reported in the literature.

Figure 11 shows the evolution of the total crystalline volume fraction \( x \), for Ge\(_2\)Sb\(_2\)Te\(_5\) samples, calculated from reflection measurements for films isothermally annealed at the temperatures indicated on the graph. In contrast to GeTe and Ge\(_2\)Sb\(_1\)Te\(_5\), the volume fraction of crystalline phase of Ge\(_2\)Sb\(_2\)Te\(_5\) does not equal zero during incubation time.

![Fig. 11. Dependencies of the volume fraction \( x \) versus time obtained for Ge\(_2\)Sb\(_2\)Te\(_5\) samples from reflection measurements at the temperature indicated on the graph. Black curves results from fittings using equation (7).](image)

A typical JMAK plot for Ge\(_2\)Sb\(_2\)Te\(_5\) films is shown in Figure 12. If we evaluate the slope only on a linear behavior, which is observed after incubation time \( \tau \), using a classical equation (2), the effective activation energy and the Avrami exponent will be equal to 5.61 eV and 3.3, respectively. The evaluation using a modification of a JMAK equation (3), which takes into account the incubation time, renders values for effective activation energy and an Avrami exponent equal to 2.07 eV and 1.5, respectively. This value of activation energy correlates well with what is reported in the literature (2.0 eV) and is obtained from the same interpretation of the reflection measurements (Weidenhof et al., 2001). Thus what comes into question is the pertinence of using these two approximations.

As has been mentioned above, the JMAK model is based on the following assumptions: the system is homogeneous, nucleation is random and uniform, the nucleation rate is time independent and takes place at the very beginning of the transformation, the isotropic growth maintains a constant rate, etc. (Henderson, 1979). However, nucleation in Ge\(_2\)Sb\(_2\)Te\(_5\) films is not random nor uniform (Senkader et al., 2004) and due to partial crystallization during incubation time the nucleation rate cannot be considered to be time independent for the entire crystallization process as is considered in the classical model (equation 2). To overcome this limitation it has been proposed to avoid using a modification of the JMAK model (equation 3); after incubation time the rate constant can be considered as independent in time (Weidenhof et al., 2001). But in the case of Ge\(_2\)Sb\(_2\)Te\(_5\) a large amount of crystallized
material has been observed during incubation time. Moreover, experimental investigation has shown that nuclei, which appeared in Ge$_2$Sb$_2$Te$_5$ films during incubation time, have a composition corresponding to Ge$_2$Sb$_4$Te$_7$ which differs from the nominal value for the amorphous matrix (Laine et al., 2004, Claudio et al., 2006). Figure 13 shows X-ray diffraction patterns for Ge$_2$Sb$_2$Te$_5$ film isothermal annealing at the temperature 118$^\circ$C and times indicated on the graph. The patterns of samples annealed during 50, 100, and 200 minutes show weak peaks, with positions corresponding to Ge$_2$Sb$_4$Te$_7$ NaCl-type phase. After annealing for more than 200 min, the positions of the peaks begin to change to those

Fig. 12. Avrami plot of $\ln(-\ln(1-x))$ vs $\ln(t)$ for Ge$_2$Sb$_2$Te$_5$ films. Points – experiment, black line – results of fitting using equation (7).

Fig. 13. X-ray diffraction spectra for a Ge$_2$Sb$_2$Te$_5$ film obtained in the process of isothermal annealing at a temperature of 118$^\circ$C during the time indicated in the plot. Upper patterns correspond to Ge$_2$Sb$_4$Te$_7$ (red curve) and Ge$_2$Sb$_2$Te$_5$ (blue curve) taken at 180$^\circ$C. The positions of the Ge$_2$Sb$_4$Te$_7$ peaks are indicated with the vertical lines.
corresponding to the NaCl-type phase of Ge$_2$Sb$_2$Te$_5$ composition. In this figure the blue pattern corresponds to material annealed at 180°C; the upper pattern corresponds to Ge$_2$Sb$_2$Te$_5$ film annealed at 180°C. Thus, in Ge$_2$Sb$_2$Te$_5$ films the formation of a stable rock salt type crystalline phase is preceded by the formation of a metastable Ge$_2$Sb$_2$Te$_5$ phase.

On the basis of these results, the crystallization of Ge$_2$Sb$_2$Te$_5$ material during isothermal annealing can be considered as a process which takes place in two stages: in the first stage nuclei of a metastable Ge$_1$Sb$_4$Te$_7$ phase appear; in the second stage, the nuclei transform into the equilibrium NaCl-type stoichiometric Ge$_2$Sb$_2$Te$_5$ structures.

In materials in which phase transformation starts with the formation of metastable phases the isothermal crystallization process cannot be simply described by JMAK theory and the plots of $\ln(-\ln(1-x))$ versus $\ln(t)$ are not linear, which implies that the Avrami exponent $n$ does not remain constant during the crystallization process.

In ref. (Claudio et al., 2006) an analytical model that can describe the isothermal crystallization process of materials is proposed. In this process, the stable crystalline phase is preceded by the formation of a metastable phase. The model assumes that the volume fraction of metastable phase $f_m$ grows up to a maximum value $f_{\text{max}}$ and then stops growing when the stable phase that has nucleated into it overpasses the metastable grain boundaries. The kinetics of the metastable fraction can be represented by a JMAK-type equation subtracting the fraction of stable phase $f_{\text{sm}}$ which grows inside the metastable phase:

$$f_m(t) = f_{\text{max}}(1 - \exp(-K_m t^n_m)) - f_{\text{sm}}(t),$$

where $K_m$ is the crystallization rate constant and $n_m$ the Avrami exponent.

The kinetic behavior of the stable phase into a metastable phase can be represented by the modification of classical JMAK formula, which takes into account the incubation time $t_{\text{sm}}$ of the stable phase into the metastable phase:

$$f_{\text{sm}}(t) = f_{\text{max}}(1 - \exp(-K_{\text{sm}}(t - t_{\text{sm}})^n_{\text{sm}})) \quad \text{for } t \geq t_{\text{sm}}$$

$$f_{\text{sm}}(t) = 0 \quad \text{for } t < t_{\text{sm}}$$

where $K_{\text{sm}}$ and $n_{\text{sm}}$ are the crystallization rate constant and the Avrami exponent, respectively, which represent the kinetic parameters of the transformation from stable phase into metastable phase.

Furthermore, it is possible to propose that the stable phase can grow into the amorphous phase. The stable phase transformation kinetics in amorphous phase can be described by JMAK-type equation with its specific parameters:

$$f_{\text{sa}}(t) = (1 - f_{\text{max}})(1 - \exp(-K_{\text{sa}}(t - t_{\text{sa}})^n_{\text{sa}})) \quad \text{for } t \geq t_{\text{sa}}$$

$$f_{\text{sa}}(t) = 0 \quad \text{for } t < t_{\text{sa}}$$

where $f_{\text{sa}}$ is the fraction of the stable phase in amorphous phase (from 0 to $1-f_{\text{max}}$), $K_{\text{sa}}$ and $n_{\text{sa}}$ are the JMAK parameters and $t_{\text{sa}}$ is the incubation time of stable phase in amorphous phase.

The total fraction of transformed material is given by the equation:
\[ f_{\text{total}}(t) = f_m(t) + f_{\text{sm}}(t) + f_{\text{st}}(t) \] (7)

This model allows fitting the experimental transformation data obtained in Ge\(_2\)Sb\(_2\)Te\(_5\) films using a genetic algorithm. The continuous lines on Fig. 11 show the evolution on time of the volume fractions of metastable Ge\(_2\)Sb\(_2\)Te\(_5\) and stable Ge\(_2\)Sb\(_2\)Te\(_5\) phase obtained from fitting using Equation (7). Results of simulations have shown that the volume fraction of metastable Ge\(_2\)Sb\(_2\)Te\(_5\) phase grows up to a maximum value and then decreases and disappears. After some incubation time, the Ge\(_2\)Sb\(_2\)Te\(_5\) phase began to grow and all material is transformed into a stable crystalline phase.

In addition, the model is capable of predicting the three slopes clearly shown in the JMAK plot (Fig. 12) corresponding to three distinguishable stages in the crystallization process observed at dependencies obtained at low annealing temperature: the first one related to the metastable transformation, the second one (low value) with the step between metastable and stable transformation, and the last one with the stable phase nucleation and growth. It is quite evident from these simulated results that the first slope of the JMAK plot can be related to the kinetic behavior of the metastable phase.

The results of the investigation have shown that during the isothermal process of amorphous to crystalline phase transformation in Ge\(_2\)Sb\(_2\)Te\(_5\) film a metastable phase with composition Ge\(_2\)Sb\(_2\)Te\(_7\) and a stable NaCl-type Ge\(_2\)Sb\(_2\)Te\(_5\) phase coexist within a certain time range. The appearance of nuclei of the Ge\(_2\)Sb\(_2\)Te\(_7\) composition could be related to the local fluctuation in the film composition and to the fact that the crystallization temperature of Ge\(_2\)Sb\(_2\)Te\(_5\) is lower than in Ge\(_2\)Sb\(_2\)Te\(_5\) material.

6. Crystallization of Ge\(_2\)Sb\(_2\)Te\(_4\)

Ge\(_2\)Sb\(_2\)Te\(_4\), as with Ge\(_2\)Sb\(_2\)Te\(_5\) film, during annealing crystallize at a temperature of approximately 133°C (lower than the crystallization temperature of Ge\(_2\)Sb\(_2\)Te\(_5\)) into a NaCl-type structure (\(\text{Fm} \bar{3} \text{m}\)) (Matsunaga et al., 2004) and at a higher temperature (about 235°C) into a hexagonal phase. Because of the lower crystallization temperature, if compared with Ge\(_2\)Sb\(_2\)Te\(_5\) this material may possess a low programming current in random access memory.

Crystallization kinetics, the same as in Ge\(_2\)Sb\(_2\)Te\(_5\) material, is sufficiently complicated. Figure 14 shows the dependence of the total crystalline volume fraction \(x\) versus time for Ge\(_2\)Sb\(_2\)Te\(_4\) samples calculated from reflection measurements for films isothermally annealed at the temperatures indicated on the graph and Figure 15 shows a typical JMAK plot. If we evaluate the slope only on a linear behavior, which is observed after incubation time \(\tau\), using classical equation (2), the effective activation energy will be equal to 5.45 eV. The evaluation using modification of JMAK equation (3), which takes into account incubation time, renders values of effective activation energy equal to 1.77 eV. But in Ge\(_2\)Sb\(_2\)Te\(_4\) the same as in Ge\(_2\)Sb\(_2\)Te\(_5\) films, a large amount of crystallized material has been observed during the incubation time. Moreover, XRD measurements (Figure 16) have shown that nuclei, which appeared in Ge\(_2\)Sb\(_2\)Te\(_4\) films during the incubation period, have a composition corresponding to the Ge\(_2\)Sb\(_2\)Te\(_7\) structure. The upper XRD pattern in this Figure corresponds to a fully crystallized film with the Ge\(_2\)Sb\(_2\)Te\(_7\) composition; the peak positions of this phase are marked with the vertical lines. The pattern mark as Ge\(_2\)Sb\(_2\)Te\(_4\) shows diffraction lines of Ge\(_2\)Sb\(_2\)Te\(_4\) film annealing to 180°C.
The results obtained have shown that in Ge$_1$Sb$_2$Te$_4$, the same as in Ge$_2$Sb$_2$Te$_5$ film, during the isothermal process of amorphous to crystalline phase transformation, a metastable phase appeared with composition of Ge$_1$Sb$_2$Te$_7$. Thus, for the interpretation of the crystallization process in Ge$_1$Sb$_2$Te$_4$ an analytical model can be used in which the formation during crystallization of metastable phase is taken into account (Equation 7).

Fig. 14. Dependencies of the volume fraction $x$ versus time obtained for Ge$_1$Sb$_2$Te$_4$ samples from reflection measurements at the temperature indicated on the graph. Black curves – results from fittings using equation (7).

Fig. 15. Avrami plot of $\ln(-\ln(1-x))$ vs $\ln(t)$ for Ge$_1$Sb$_2$Te$_4$ films. Points – experiment, black curve – results from fitting using equation (7).
Continuous black curves on Fig. 14 show the calculated volume fractions of metastable Ge$_1$Sb$_4$Te$_7$ and stable Ge$_1$Sb$_2$Te$_4$ phase obtained from fittings using Equation (7). Results of simulation have shown that the same as in Ge$_2$Sb$_2$Te$_5$, the volume fraction of metastable Ge$_1$Sb$_4$Te$_7$ phase grows up to a maximum value and then decreases and disappears. After some incubation time, Ge$_1$Sb$_2$Te$_4$ phase began to growth and all material was transformed into a stable crystalline phase.

Additionally, the model is capable to simulate the JMAK plot of Fig. 15, in which the first slope of the JMAK plot can be related to the kinetic behavior of the metastable Ge$_1$Sb$_4$Te$_7$ phase.

Fig. 16. X-ray diffraction spectra for a Ge$_1$Sb$_4$Te$_7$ film obtained in the process of isothermal annealing at a temperature of 120°C during the time indicated on the plot. Upper patterns correspond to Ge$_1$Sb$_4$Te$_7$ (red curve) and Ge$_1$Sb$_2$Te$_4$ (blue curve) taken at 180°C. The position of the Ge$_1$Sb$_4$Te$_7$ peaks is indicated with the vertical lines.

7. Crystallization of Ge$_1$Sb$_4$Te$_7$

Similarly, as with Ge$_2$Sb$_2$Te$_5$ and Ge$_1$Sb$_2$Te$_4$, Ge$_1$Sb$_4$Te$_7$ demonstrates a two phase transition: amorphous to the rock salt-like structure at a temperature of approximately 110°C and a second transition to the hexagonal phase at the temperature close to 168°C. This material demonstrates the fastest phase transformation among Ge:Sb:Te ternary alloys and phase-reversible transformations can be observed in the femtoseconds range (Huang et al., 2006). But because of the low crystallization temperature, Ge$_1$Sb$_4$Te$_7$ has lower thermal stability when compared with other ternary alloys (Miao et al., 2006).

Crystallization transformation from amorphous to NaCl-type structure in Ge$_1$Sb$_4$Te$_7$ differs from the transformations observed in Ge$_2$Sb$_2$Te$_5$ and Ge$_1$Sb$_2$Te$_4$ films. In contrast with Ge$_2$Sb$_2$Te$_5$ and Ge$_1$Sb$_2$Te$_4$, in-situ X-ray diffraction measurements show that amorphous films with the Ge$_1$Sb$_4$Te$_7$ composition crystallize in the NaCl-type phase with the same composition as at the beginning of the transformation (Figure 17). Moreover, isothermal reflection measurements (Figure 18) have shown practically zero value of crystalline phase during the much shorter incubation time compared with Ge$_2$Sb$_2$Te$_5$ films (Figure 11). In this
case, as is for GeTe and Ge$_2$Sb$_2$Te$_5$, it is also possible to neglect the amount of crystallized material during $\tau$, and describe the transformation using the modified JMAK equation (3).

Figure 19 shows a plot of $\ln[-\ln(1-x)]$ versus $\ln(t-\tau)$ for a Ge$_1$Sb$_4$Te$_7$ film, which demonstrates a linear dependence. This means that the crystallization process in Ge$_1$Sb$_4$Te$_7$ material displays random nucleation and isotropic growth with effective activation energy of 1.7±0.27 eV and an Avrami exponent $n$ close to 1.94. According to (Christian, 1975), the values of $n$ in the range $1.5 < n < 2.5$ correspond to a crystallization process dominated by all shapes growing from small dimensions with decreasing nucleation rate.

Fig. 17. X-ray diffraction spectra for a Ge$_1$Sb$_4$Te$_7$ film obtained in the process of isothermal annealing at a temperature of 90°C during the time indicated on the plot.

Fig. 18. Dependencies of the volume fraction $x$ versus time obtained for Ge$_1$Sb$_4$Te$_7$ samples from reflection measurements at the temperature indicated on the graph.
8. Crystallization of Sb$_2$Te$_3$

Sb$_2$Te$_3$ lies at the end of the GeTe-Sb$_2$Te$_3$ pseudobinary line and has the lowest crystallization temperature but the highest crystallization speed. This material is an attractive candidate for phase change random access memory due to its rapid crystallization speed, but the crystallization temperature of Sb$_2$Te$_3$ (about 94°C in material investigated in this chapter and between 90-100°C reported in the literature (Yin et al., 2007, Kim et al., 2010)) is too low for it to be of practical use.

Upon annealing, amorphous Sb$_2$Te$_3$ films crystallize in rhombohedral Sb$_2$Te$_3$ (Kim et al., 2008, Lv et al., 2010) or fcc structure, which at a temperature above 200°C transforms into an hexagonal phase (Yin et al., 2007, Zhu et al., 2011). In the investigated Sb$_2$Te$_3$ films within the temperature range comprised between 95-200°C, only the rhombohedral phase (JCPDS data #15-0874) has been observed.

![Fig. 19. Avrami plot of ln[-ln(1-x)] vs ln(t-τ) for Ge$_4$Sb$_4$Te$_7$ films. Points – experiment, lines – results from fittings using JMAK equation (3). Insert shows the rate constant $K$ as a function of the reciprocal temperature.](image1)

Isothermal reflection measurements (Figure 20) have shown the same as for Ge$_4$Sb$_4$Te$_7$: practically zero value of crystalline phase during the incubation time. In this case, the same as for GeTe, Ge$_4$Sb$_4$Te$_7$ and Ge$_4$Sb$_4$Te$_7$, it is possible to neglect the amount of crystallized material during $\tau$, and describe the transformation using the modified JMAK equation (3).

Figure 21 shows a plot of $\ln[-\ln(1-x)]$ versus $\ln(t-\tau)$ for a Sb$_2$Te$_3$ film, which demonstrates a linear dependence. This means that the crystallization process in Sb$_2$Te$_3$ films, the same as in Ge$_4$Sb$_4$Te$_7$ material, display random nucleation and isotropic growth with an effective activation energy of 1.54±0.15 eV and an Avrami exponent $n$ close to 1.1, which according to ref. (Christian, 1975), corresponds to a crystallization growth of particles of appreciable initial volume. It is necessary to note that the values obtained for crystallization activation energy is in good agreement with values reported in the literature (1.51 eV) obtained using...
the Kissinger analysis in the films deposited on the glass substrates by the same DC magnetron sputtering (Zhai et al., 2009).

![Graph](image)

**Fig. 20.** Dependencies of the volume fraction $x$ versus time obtained for Sb$_2$Te$_3$ samples from reflection measurements at the temperatures indicated on the graph.

![Graph](image)

**Fig. 21.** Avrami plot of $\ln(-\ln(1-x))$ vs $\ln(t-\tau)$ for Sb$_2$Te$_3$ films. Points – experiment, lines – results from fittings using JMAK equation (3). Insert shows the rate constant $K$ as function of the reciprocal temperature.

### 9. Conclusions

This chapter presents some of the results concerning the crystallization properties of the most commonly employed materials on the GeTe–Sb$_2$Te$_3$ pseudo-binary line for phase...
change memory application. Despite the fact that these alloys have found application in already commercialized optical disc and workable electrical phase change memory devices, their properties are not well known so far. This leads to many contradictory and controversial results in the literature.

As has been shown in this chapter, the crystallization properties of GeTe, Ge$_2$Sb$_2$Te$_5$, Ge$_4$Sb$_4$Te$_7$, and Sb$_2$Te$_3$ cannot be analyzed using the classical Johnson–Mehl–Avrami-Kolmogorov model for isothermal annealing due to the long incubation times. This limitation can be avoided by using a modification of the JMAK model, which takes into account that after incubation time the rate constant of crystallization can be considered as independent from time. Such model gave reasonable values of crystallization energy, which proved compatible with crystallization energy obtained by other methods. The difference in interpretation of isothermal measurements, in addition to the difference in preparation methods, can be responsible for the dispersion of crystallization parameters reported in the literature. But this modified model can be applied if during incubation time non-negligible amounts of crystalline phase material are observed. In the case of Ge$_2$Sb$_2$Te$_5$ and Ge$_4$Sb$_4$Te$_7$ films during incubation times, the nuclei fraction is of about 10% and has a composition corresponding to Ge$_2$Sb$_3$Te$_7$, which is different from the nominal value for the amorphous matrix. That is why the crystallization in Ge$_2$Sb$_2$Te$_5$ and Ge$_4$Sb$_4$Te$_7$ materials during isothermal annealing can be considered as a process that takes place in two stages: in the first stage, nuclei of a metastable Ge$_2$Sb$_3$Te$_7$ phase appear; in the second stage, the nuclei transforms into the equilibrium NaCl-type stoichiometric structures correspondent to the material composition. Such crystallization process can be described by a model in which the stable crystalline phase is preceded by the formation of a metastable phase. The most questionable issue is to explain these crystallization properties.

It is necessary to note that crystallization with phase separation has been observed in materials close to the GeTe-Sb$_2$Te$_3$ pseudo-binary line with excess of Ge (Ge$_{2+x}$Sb$_2$Te$_5$, $x=0.5$ (Privitera et al., 2003) and Sb (Ge$_{2-x}$Sb$_x$Te$_5$, $0<x<1$, (Yamada et al., 2000), and Ge$_2$Sb$_{2.3}$Te$_5$ (Yao et al., 2003)). In all of these materials, separation occurs during the crystallization phase, with segregation of small amounts of the excess elements, which remain in the amorphous state at the grain boundaries. By increasing the annealing temperature, the residual amorphous material can convert into another polycrystalline NaCl-type structure with a slightly lower lattice parameter. As a result, after the formation of the first phase, the crystallization rate is strongly reduced and a further conversion of the film into another crystalline structure that crystallizes at higher temperatures can occur (Privitera et al., 2003).

Furthermore, Ge$_2$Sb$_2$Te$_5$, Ge$_4$Sb$_4$Te$_7$ and Ge$_4$Sb$_4$Te$_7$ materials crystallize into the same NaCl-type ($Fm \bar{3}m$) structure (Matsunaga et al., 2004, Matsunaga et al., 2006) with lattice constants of 6.001, 6.044 and 6.0876 Å respectively (Morales-Sanchez et al., 2005). In materials with excess Sb, as the content of Sb increases, the lattice constant also increases (Yamada et al., 2000). Thus, during crystallization, atoms in the amorphous state must travel less distance to take their position in the Ge$_4$Sb$_4$Te$_7$ crystal lattice than in any other ternary alloys. This effect is responsible for the highest crystallization speed of Ge$_4$Sb$_4$Te$_7$ when compared with Ge$_2$Sb$_2$Te$_5$ and Ge$_4$Sb$_2$Te$_3$ materials. Also, Ge$_4$Sb$_4$Te$_7$ has the lowest crystallization
temperature. All these factors and the possible existence of a local composition fluctuation can be responsible for the appearance of Ge$_{1}\text{Sb}_{4}\text{Te}_{7}$ nuclei in the process of crystallization in Ge$_2\text{Sb}_2\text{Te}_5$ and Ge$_5\text{Sb}_2\text{Te}_6$ materials.

The clarification of crystallization mechanisms in alloys that lie on the GeTe–Sb$_2$Te$_3$ pseudo-binary line will allow the production of phase-change materials with better recording properties.

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