Ge-Sb-Te based phase-change nanoparticles
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Chapter 5

Crystallization Kinetics of GeSbTe Nanoparticles

Abstract

Although nanostructured phase-change materials (PCMs) are considered as the building blocks of next generation phase-change memory and other emerging optoelectronic applications, the kinetics of the crystallization, the central property in switching, remains ambiguous in the high temperature regime. Therefore, we present here an innovative exploration of the crystallization kinetics of Ge$_2$Sb$_2$Te$_5$ (GST) nanoparticles (NPs) exploiting differential scanning calorimetry with ultrafast heating up to 40 000 K s$^{-1}$. Our results demonstrate that the non-Arrhenius thermal dependence of viscosity at high temperature becomes an Arrhenius-like behavior when the glass transition is approached, indicating a fragile-to-strong (FS) crossover in the as-deposited amorphous GST NPs. The overall crystal growth rate of the GST NPs is unraveled as well. This unique feature of the FS crossover is favorable for memory applications as it is correlated to improved data retention. Furthermore, we show that methane incorporation during NP production enhances the stability of the amorphous NP phase (and thereby data retention), while a comparable maximum crystal growth rate is still observed. These results offer deep insight in the crystallization kinetics of nanostructured GST, paving the way for designing non-volatile memories with PCM dimensions below 20 nm.

5.1 Introduction

Ge$_2$Sb$_2$Te$_5$ (GST), one of the prototypical phase-change materials (PCMs), enables rapid and reversible switching between its amorphous and crystalline phases, which is accompanied by large optical and electrical contrast. This unique feature makes GST attractive for data-storage applications$^{1-3}$ and a strong contender for emerging applications, such as solid-state displays,$^4$ optical modulators,$^5$ neuromorphic computing,$^6,7$ on-chip photonic circuitry,$^8$ and plasmonic-based circuits.$^9$ Crystallization lies at the heart of the switching in phase-change technology, thus a solid understanding of the crystallization kinetics entails a crucial aspect of designing phase-change memory.

Conventional measurements are only able to investigate crystallization kinetics within a relatively low temperature range (near the glass transition temperature).$^{10-13}$ However, in actual applications, crystallization generally takes place at higher temperatures. Despite its scientific and technologic relevance, the analysis of the crystallization kinetics at these high temperatures has remained for a long time highly challenging due to the ultrashort time and length scales (ns and nm) involved. This situation persisted until very recently, where ultrafast differential scanning calorimetry (DSC) was utilized to explore the crystallization process of GST films with heating rates up to 40 000 K s$^{-1}$.\textsuperscript{14} Using subsequent extensive modeling, growth rates ranging from the glass transition temperature to the melting temperature were derived for the film structures, showing a remarkable breakdown of Arrhenius behavior in the viscosity at heating rates beyond \~500 K s$^{-1}$. Non-Arrhenius thermal dependence of the viscosity at high temperatures has lately been widely observed in both nucleation-dominated and growth-dominated PCMs. For instance, for GST confined in memory cells it was demonstrated that non-Arrhenius thermal dependence of crystallization at high temperatures crosses over to a wide temperature range at lower temperatures where still Arrhenius behavior prevails.$^{15-17}$ In recent years, also for other PCMs, such as GeTe films,\textsuperscript{18} supercooled and melt-quenched AgInSbTe films\textsuperscript{19-21} and GeSb films,$^{22,23}$ the crystallization kinetics have been determined based on non-conventional techniques with measurements spanning relatively wide temperature ranges. All these works confirm the breakdown of Arrhenius dependence for amorphous PCMs at high temperatures. However, a question that remains is whether this breakdown can be described on the basis of a model for viscosity with a single value for the fragility.

In parallel, down-scaling the GST into (sub-lithographic) nanostructures generates tremendous advantages for PCM-based memory including ultrafast switching, low switching power and ultra-high density. Therefore, many efforts have been devoted to enter this promising field.$^{24,25}$ In this
context, the fabrication of monodisperse GST nanoparticles (NPs) with good size- and composition-control has been a great challenge for a long time. We achieved a breakthrough by exploiting a technique based on gas-phase condensation and magnetron sputtering, which is capable to meet the requirements of GST NPs fabrication. Size dependent crystallization was observed through in-situ heating in a transmission electron microscope. Yet this previous work mainly focused on the crystallization at relatively low temperatures because of the limitation inherent to the in-situ TEM heating method. Therefore, the crystallization kinetics of GST NPs remains unknown for the high temperature regime. In this manuscript we present a facile method to synthesize size- and composition-controlled Ge₂Sb₂Te₅ nanoparticles via gas-phase condensation, followed by the unprecedented exploration of crystallization kinetics of GST NPs via ultrafast DSC. By varying the heating rate more than three orders of magnitude, the temperature dependent viscosity and growth rate of the crystallization have been unraveled, providing evidence for a fragile-to-strong crossover in as-deposited amorphous GST NPs. Moreover, it is shown that methane addition during NP production is advantageous for application of NPs in PCMs based devices due to the fact that it increases the amorphous phase stability near the glass transition temperature, whereas the maximum switching speed at high temperature is not reduced.

5.2 Experimental methods

5.2.1 GeSbTe nanoparticles synthesis

The Ge₂Sb₂Te₅ (GST) nanoparticles (NPs) were directly deposited on a pre-cleaned glass substrate without capping layer. The deposition system is demonstrated in detail in chapter 2. The substrate was put close to the aperture of the aggregation chamber in order to synthesize a large amount of NPs. The main chamber (to collect the NPs) is evacuated to a pressure of 10⁻⁸ mbar. Amorphous GST NPs were directly synthesized by sputtering the GST target (purity of 99.99%), employing a low current (0.105 A) to avoid the formation of crystalline NPs. The Ar gas flow (purity of 99.9999%) used for the two types of samples analyzed in the present work is 35 sccm, with H₂/CH₄ (purity of 99.99%) as extra gas to facilitate the development of nascent clusters in the plasma. In this chapter, we show the ability of preparing nanoparticles with a large yield that is enough to perform ultrafast heating in DSC. The morphology and stoichiometry were characterized by transmission electron microscope (JEOL 2010) at 200 kV.

5.2.2 Ultrafast differential scanning calorimetry measurement

The phase transitions of the samples were measured by ultrafast DSC. Instead of the loose powder/multi-flakes we used for Ge-Sb PCMs, a single planar flake consisting of GST NPs parallel
to the sensor surface was adopted here to run the measurements. The approximate area that was subjected to ultrafast heating is roughly $60 \times 60 \, \mu m^2$ and $20 \times 20 \, \mu m^2$ for NPs (H$_2$) and NPs (CH$_4$), respectively. This methodology remarkably increases the thermal contact between the materials and the chip sensor. Actually, our results show that all previously published ultrafast DSC work employing loose powder or multi-flakes (of PCMs) can contain erroneous results for the higher heating rate (and thus temperature) regime. The heating rates ($\Phi$) adopted in this manuscript vary from 10 to 40 000 K s$^{-1}$. The thermal lag of the measurement was evaluated in the Appendix B of this chapter.

5.2.3 Numerical modeling

As described in chapter 2, numerical modeling was adopted to interpret the data obtained by ultrafast DSC. The viscosity model (MYEGA model) we employed successfully for the Ge-Sb alloy turned out inadequate to explain the Arrhenius behavior persisting for such a large temperature range in the Kissinger plot (Figure 5.3) presented in this chapter. Therefore, the generalized MYEGA model was adopted for the fitting.$^{27}$ Note that in all the fittings performed in this manuscript, the fractional Stokes-Einstein relation between viscosity and growth rate has been used, with $\xi=0.65$ suggested by previous work.$^{14}$ The details of JMAK modeling can be found in chapter 2. For this JMAK model, descriptions of nucleation and growth are required. For the description of nucleation it is assumed that it is independent of time and temperature, i.e. we assume a constant nuclei density (site saturation), analogous to what was adopted for the modeling of GST films.$^{14}$ However, in Figure 5.8 of the Appendix A of this chapter, we show that the results hardly change when we adopt a more intricate steady-state nucleation model. The details of the fitting process in the Kissinger plot can be found in Appendix of chapter 3.

Apart from the ultrafast DSC data presented in the Kissinger plot also two relevant data points, one for GST NPs (H$_2$) and one for GST NPs (CH$_4$), were added for very low heating rates $\Phi (0.03 \, K \, s^{-1})$ based on our previous in-situ TEM work.$^{26}$ The data point for GST NPs (H$_2$) is reliable, but it is not precise for GST NPs (CH$_4$). The reason is that it is hard to accurately control for different sample batches the amount of methane incorporated in the gas phase during the NPs sample production. Therefore, this single data point for GST NPs (CH$_4$) in the Kissinger plot is not used when fitting the JMAK based model to the experimental data.
5.3 Results and Discussion

5.3.1 Morphology and size distribution

Size-dependent crystallization has been observed for Ge$_2$Sb$_2$Te$_5$ (GST) nanoparticles (NPs),\textsuperscript{26} where the size, morphology, structure and crystallization temperature of the as-deposited NPs have been characterized by transmission electron microscopy (TEM). As shown in Figure 5.1, relatively mono-disperse GST NPs have been synthesized, with average diameters 16.0±1.3 and 16.8±1.7 nm for NPs synthesized with either H$_2$ or CH$_4$ added to the base Ar gas, hereafter named NPs (H$_2$) and NPs (CH$_4$). Detailed size distributions of these two samples can be found in Figure 5.6 of the Appendix A. The similar sizes and narrow size distribution of the two GST NPs (CH$_4$) and (H$_2$) samples exclude size effects on the crystallization observed in the present work. Although the NPs were produced with a relatively high coverage, they are not coalesced but only aggregated, as can be seen clearly in Figure 5.1.

![Figure 5.1 Morphology of Ge$_2$Sb$_2$Te$_5$ (GST) nanoparticles (NPs). (a), (b) Bright field image of the GST NPs produced with H$_2$ (NPs (H$_2$)) and CH$_4$ (NPs (CH$_4$)), respectively. The average diameters of the NPs in these two samples are 16.0±1.3 and 16.8±1.7 nm, respectively. Insets show the selected area electron diffraction patterns of the corresponding NPs, clearly demonstrating the amorphous nature of the as-deposited NPs.](image)

The spherical morphology is an indication of the amorphous nature of the NPs, which is further confirmed by selected area electron diffraction (SAED). As manifested by the insets of Figure 5.1, the SAED patterns demonstrate that the NPs are amorphous due to the lack of sharp crystalline
rings. The composition of these NPs is Ge:Sb:Te = 19:24:57 (±1) at.%, as determined by energy dispersive X-ray spectrometry. Note that the TEM grids were located at the periphery of the NP cluster beam during production, retaining a lower coverage in comparison to the center part. High yield synthesis of GST NPs has been achieved by gas-phase condensation in order to obtain a good signal to noise ratio when performing differential scanning calorimetry (DSC) with ultrafast heating. Moreover, we have demonstrated that the NPs do not coalesce during thermal heating in a transmission electron microscope. Therefore, the above factors enable and ensure the thermal analysis of well-characterized NPs via ultrafast DSC.

5.3.2 Crystallization by ultrafast DSC

The obtained ultrafast DSC traces for the two GST NPs (H2) and NPs (CH4) samples are shown in Figure 5.2a-b. The heating rates (Φ) used to obtain the data of the present work vary more than three orders of magnitude, from 10 to 40 000 K s⁻¹. Note that a detectable signal of crystallization only appears for Φ beyond 50 K s⁻¹ for the NPs (CH4). The temperatures for the amorphous to rock-salt transition (T_p1) drastically increase when higher Φ are applied to both samples; e.g., T_p1 of NPs (H2) shifts from 440 K at 10 K s⁻¹ to 542 K at 40 000 K s⁻¹. Figure 5.2 also shows that NPs (CH4) have an (expected) higher T_p1 than NPs (H2), particularly at low Φ. For example, T_p1 for NPs (CH4) is ~20 K higher than that of NPs (H2) at 50 K s⁻¹. In a previous work, we have revealed by in-situ heating in a TEM that methane addition during GST NPs production remarkably increase the T_p1 at relatively low heating rates. Nevertheless, here we observe that this gap of T_p1 gradually decreases when Φ becomes higher, and finally vanishes when Φ reaches 40 000 K s⁻¹. Surprisingly, at high Φ we observe a big divergence in T_p1 for GST NPs (H2) compared to GST films as reported in earlier work. While the T_p1's are very similar at 50 K s⁻¹, the T_p1 of GST films becomes ~90 K higher than that of the NPs (H2) at 40 000 K s⁻¹. This gap can (at least partly) stem from two origins: 1) the thermal lag between the thin film and the ultrafast chip sensor, as is discussed in detail in chapter 3. 2) It is still very well likely that the kinetics of NPs differs from that of thin films. We did not have the appropriate thin film samples to verify this and these tests are beyond the scope of the present work, but they are of interest for future research. Furthermore, the rock-salt to trigonal structural transition is also unambiguously observed for the NPs (H2) in the ultrafast DSC traces when Φ is above 250 K s⁻¹. The signal of this transition is unexpected but intriguing as it was not detected for GST films via ultrafast DSC measurement in
Figure 5.2 Ultrafast DSC traces for GST NPs. (a), (b) Ultrafast DSC traces for GST NPs (H_2) and NPs (CH_4), respectively, for heating rates (\( \Phi \)) ranging from 10 to 40 000 K s\(^{-1}\). Insets of (a) and (b) show the close-up of the crystallization peaks at lower \( \Phi \). (c) Zoomed-in ultrafast DSC traces of rock-salt to rhombohedral structural transition in NPs (H_2) at \( \Phi \) ranging from 250 to 20 000 K s\(^{-1}\). (d) Evolution of the structural relaxation temperatures with \( \Phi \) for NPs (H_2) and NPs (CH_4). The blue and red curves in the figures hold for NPs (H_2) and NPs (CH_4), respectively.

previous work.\(^{14}\) This transition temperature (denoted hereafter as \( T_{p2} \)) displays a clear dependence on \( \Phi \) as well, where it increases when \( \Phi \) rises, even with a more drastic increment compared to \( T_{p1} \). Locating at around 553 K at 250 K s\(^{-1}\), \( T_{p2} \) moves to 633 K at 20 000 K s\(^{-1}\), as depicted in Figure 5.2c. It is noticeable that \( T_{p2} \) is invisible in the DSC signal at the lowest \( \Phi \), because of the small heat release involved compared to the amorphous to rock-salt transition. Interestingly, the
rock-salt to trigonal structural transition is unobservable in NPs (CH$_4$) in the present work (as shown in Figure 5.2b). Several explanations could correlate to this feature: i) the addition of methane alters $T_{p2}$ to too high temperature which is beyond the upper limit of ultrafast DSC (450 °C); ii) the incorporation of methane suppresses this structural transition completely; iii) with methane the transition can still occur but with reduced latent heat (or spread over a larger temperature range) such that it is not detected by the ultrafast DSC. More systematic research is necessary before drawing conclusions on this second transition and this is out of the scope of the present work. However, the appearance of this specific transition also indicates good thermal contact between the chip sensor and the NPs flake, as the heat release involved in this transition is much smaller than that of the amorphous to rock-salt transition. The obtained $T_{p2}$ for GST NPs is much lower than that of the GST films due to the expected strong size-dependence of $T_{p2}$, where it has been observed to reduce sharply with decreasing thickness of GST films.$^{28}$

In the ultrafast DSC traces, a heat release prior to the amorphous to rock-salt transition is also observed, indicated as $T_i$ in Figure 5.2d. This exothermic heat flow was ascribed to structural relaxation of the amorphous phase by previous researchers,$^{29}$ as the temperature is too low for crystallization. For instance, for GST NPs (H$_2$) at a heating rate of 100 K s$^{-1}$ the temperature $T_i$ is 120 °C compared to the crystallization temperature $T_{p1}$ of ~180 °C. At this $T_i$ temperature, crystallization only occurs after very long times. For example, for GST nanowires with a width of 60 nm, the amorphous phase can remain present for ~10$^6$ seconds.$^{24}$ Therefore, with high heating rate (100 K/s), the heating process from 25 to 125 °C takes only 1 second that is way below the time required to start crystallization at 120 °C. Therefore no signal for crystallization should be observed at these temperatures indicated by the arrows in Figure 5.2d. This structural relaxation has been found in other amorphous materials, such as silicon and germanium, and it is attributed to the presence of a spectrum of activation energies for the sites where relaxation takes place.$^{30,31}$ For both the GST NPs (CH$_4$) and NPs (H$_2$) samples, $T_i$ moves towards the onset of the amorphous to rock-salt transition as $\Phi$ rises.

5.3.3 Kissinger analysis

To further understand the crystallization kinetics of the NPs, Kissinger analysis is employed. For crystallization, the activation energy can be obtained using the following equation proposed by Kissinger.$^{32}$
Crystallization kinetics of GeSbTe nanoparticles

\[ \frac{Q}{R} = -\frac{d \ln(\Phi/T_p^2)}{d(1/T_p)} \]  

(5.1)

with \( Q \) the activation energy for crystallization, \( R \) the gas constant, \( \Phi \) the heating rate, and \( T_p \) the peak temperature in the DSC signal. For a crystallization process complying with Arrhenius behavior, the (constant) activation energy can be derived straightforwardly. Figure 5.3a shows the crystallization data for GST NPs obtained by ultrafast DSC at different \( \Phi \), with the blue and red solid circles signifying \( T_{p1} \) data for NPs (H\(_2\)) and NPs (CH\(_4\)), respectively. The single flake methodology (instead of an ensemble of loose flakes) utilized in running the ultrafast heating here effectively improves the thermal contact between the chip sensor and the NPs flake, inducing clearly less scatter in \( T_{p1} \) in comparison with the employment of loose powder or multi-flakes. At low \( \Phi \), the Arrhenius behavior is maintained, as indicated by the Kissinger plot (Figure 5.3). Surprisingly, the Arrhenius behavior for the NPs persists for a considerably larger \( \Phi \) range (up to 10 000 K s\(^{-1}\)) in contrast to GST films previously studied where Arrhenius behavior was reported to break down already at ~500 K s\(^{-1}\),\(^{14}\) as shown in Figure 5.3a by the black stars. It is also observable that NPs (CH\(_4\)) have a higher activation energy for crystallization than NPs (H\(_2\)) within the Arrhenius behavior range. The Kissinger plot at lower \( \Phi \) has been zoomed in and linearly fitted (Figure 5.3b), with an activation energy for crystallization determined as 2.22 and 2.43 eV at\(^{-1}\) for NPs (H\(_2\)) and NPs (CH\(_4\)), respectively. These values coincide well with the reported values for GST films, in a range between 2 and 3 eV by conventional DSC or electrical resistance measurements.\(^{10,33–36}\) The increase of activation energy induced by CH\(_4\) incorporation is similar to the enhanced activation energy by carbon doping of GST films.\(^{37}\)

Nevertheless, further increase in \( \Phi \) (beyond 10 000 K s\(^{-1}\)) prompts the breakdown of the Arrhenius behavior, generating a curvature in the Kissinger plot. As a result, the activation energy for crystallization diminishes with the increment of temperature and vanishes at higher temperatures. In order to appropriately interpret these data, Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory has been adopted to fit the Kissinger plot, analogous to our previous work on GeSb alloy.\(^{23}\) The growth rate of crystallization is vital to utilize the JMAK theory, which can be written as:\(^{19}\)

\[ U(T) = \frac{4r_{\text{atom}}^2k_BT}{3\pi\kappa R_{\text{hyd}}\ell(T)^2} \left[ 1 - \exp\left( -\frac{\Delta G(T)}{k_BT} \right) \right] \]  

(5.2)
with \( U(T) \) the growth rate, \( r_{\text{atom}} \) the atomic radius (~1.5 Å), \( \lambda \) the diffusional jump distance (~2.99 Å), \( R_{\text{hyd}} \) the hydrodynamic radius (\( R_{\text{hyd}} = r_{\text{atom}} \)), \( k_B \) the Boltzmann constant, \( \eta(T) \) the temperature dependent viscosity, \( \zeta \) the decoupling parameter of Stokes-Einstein equation (\( \zeta \leq 1 \)) and \( \Delta G(T) \) the change of Gibbs free energy, which can be described, according to Thomson and Spaepen, as:38

\[
\Delta G(T) = \frac{\Delta H_m(T_m-T)}{T_m} \left( \frac{2T}{T_m + T} \right) \quad (5.3)
\]

where \( \Delta H_m \) is the latent heat of melting, approximately 0.152 eV at\(^1\),\(^39\) and \( T_m \) is set to 890 K.\(^16\)

Note that fractional Stokes-Einstein equation (\( U \propto \eta^{\zeta} \)) with \( \zeta \leq 1 \)) is intrinsically included in Equation (5.2), as the breakdown of Stokes-Einstein relation has been observed in a large number of supercooled glass forming liquids and in particular PCMs and it is attributed to dynamical heterogeneities.\(^14,40\) For the GST NPs we set \( \zeta = 0.65 \), a value similar to GST films.\(^14\)

An appropriate viscosity model is required to determine the growth rate in Equation (2). Although the model proposed by Mauro et al.\(^41\) (MYEGA model hereinafter) provides, as we proved,\(^23\) a much better description of the viscosity of Ge-Sb phase-change materials as compared to the one from Cohen & Grest,\(^42\) it yields inferior fits to the present data for GST NPs owning to its inability to afford Arrhenius behavior in a large temperature range. If the The MYEGA model (with a single fragility value) is adopted, it provides very high values of fragility for the NPs (\( H_2 \), \( m = 203 \), which is higher than the theoretical value for kinetic fragility for glass forming liquids (\( m = 176 \)).\(^43\)

Furthermore, this model leads to very high crystallization temperatures at low heating rates, resulting in a large mismatch to the data obtained by in-situ heating in TEM, as shown in Figure 5.7 of the Appendix A. Furthermore, for NPs (\( CH_4 \)), it only fits well at low heating rates range. In contrast, the generalized MYEGA model can avoid all the above problems. Note that the quality of the fits using either the MYEGA model or the Cohen & Grest model remains poor even using more sophisticated models for nucleation instead of the simple constant nuclei density (site saturation) adopted initially. Therefore we tested a generalized MYEGA model, since it enabled a successful description of the complex viscosity in metallic glass forming liquids:\(^27\)

\[
\log_{10} \eta(T) = \log_{10} \eta(\infty) + \frac{1}{T} \left[ W_1 \exp\left(-\frac{C_1}{T}\right) + W_2 \exp\left(-\frac{C_2}{T}\right) \right] \quad (5.4)
\]
Figure 5.3 Kissinger plot with optimized model fits to the data. (a) Kissinger plot for NPs (H₂) and NPs (CH₄). Blue solid circles and blue open circles denote the amorphous to rock-salt transition temperatures ($T_{p1}$) and rock-salt to rhombohedral transition temperatures ($T_{p2}$) of NPs (H₂). The red solid circles represent $T_{p1}$ of NPs (CH₄). Dotted lines show the corresponding fits to these data. The black stars show earlier reported $T_{p1}$ of GST films by ultrafast DSC.¹⁴ The blue and red triangles correspond to the $T_{p1}$ of NPs (H₂) and NPs (CH₄), respectively, as obtained using in-situ heating in the TEM.²⁶ (b) Linear fit to the Kissinger plot at lower $\Phi$ (up to 10 000 K s⁻¹), leading to crystallization activation energy 2.22 and 2.43 eV at¹ for NPs (H₂) and NPs (CH₄), respectively.
with \( \eta(\infty) \) viscosity at infinite temperature (here it is taken as \( 10^{-3} \) Pa s), \( T \) the temperature and \( W_1, C_1, W_2, C_2 \) the fitting parameters. This model illustrates that two intrinsic terms of viscosity subsist in the liquid, and these two terms can transfer to each other upon cooling or heating. The blue and red dotted curves in Figure 5.3a denote the modeled Kissinger plots utilizing the generalized MYEGA model (Equation (5.4)), showing excellent fits to the corresponding experimental data, with fitting quality evaluated by adjusted \( R^2 \) (0.973 and 0.984, respectively). The derived fitting parameters are: \( W_1=6921.8, C_1=7490.2, W_2=6.63 \times 10^{-4}, C_2=517.2 \) for NPs (H\(_2\)) and \( W_1=8259.3, C_1=8091.9, W_2=5.27 \times 10^{-4}, C_2=510.2 \) for NPs (CH\(_4\)). Note that the data become more scattered when \( \Phi \) becomes high, particularly for \( \Phi \) above 10 000 K s\(^{-1}\). Therefore, only three data points at the most right side for \( \Phi \) beyond 10 000 K s\(^{-1}\) are weighted to be the most representative data, as they exemplify the best thermal contact between the chip sensor and the NPs flake.

Moreover, the evolution of \( T_{p2} \) with \( \Phi \) is also depicted in Figure 5.3a. A non-Arrhenius behavior is evidently revealed in this figure, inferring a temperature dependent activation energy for this structural transition. Without a proper growth rate model for this transition, it is currently not possible to model the Kissinger curve via JMAK theory.

### 5.3.4 Viscosity and fragility of Ge\(_2\)Sb\(_2\)Te\(_5\) nanoparticles

Viscosity is of fundamental and practical relevance for glass forming liquids as it is directly associated with the glass transition and relaxation process, indicating the mobility of the atoms and therefore it is coupled to the growth rate of crystallization. As the unknown parameters in Equation (5.4) have been determined through fitting, the viscosity of the as-deposited amorphous NPs as a function of temperature can be derived straightforwardly; see the red and blue solid curves in the Angell plot of Figure 5.4, where the temperature dependent viscosity of GST films reported previously by Orava et al. is also depicted in comparison (black dotted curve in Figure 5.4).\(^{14}\) Unlike the MYEGA model, Equation (5.4) does not directly provide the value of glass transition temperature (\( T_g \)) and fragility. Here we set \( T_g \) as the temperature at which the viscosity equals \( 10^{12} \) Pa s, then \( T_g \) are determined as 373 K and 403 K for NPs (H\(_2\)) and NPs (CH\(_4\)), respectively. This value for the NPs (H\(_2\)) is close to the reported values for the GST films (373~383 K).\(^{14,44}\) As indicated in a previous work,\(^{26}\) the crystallization temperature for NPs (H\(_2\)) is slightly lower than that of GST films (~10 K), therefore the akin \( T_g \) is plausible as the glass transition usually takes
place ~10 K lower than $T_{p1}$ at a $\Phi$ of 40 K min$^{-1}$ for GST films.\textsuperscript{29} The increase of $T_g$ caused by the CH$_4$ incorporation is ~30 K, which agrees excellently with the rise of $T_{p1}$, as shown here by the ultrafast DSC measurements and by the \textit{in-situ} TEM characterization of our earlier work.\textsuperscript{26} The fragility, defined as $m = \left. \frac{d(\log_{10} \eta(T))}{d(T_g/T)} \right|_{T=T_g}$, is determined from the Angell plot for these NPs as well. The fragility of NPs (H$_2$) is 57, consistent with the value from a previous work ($m=47$ for non-doped GST films).\textsuperscript{45} Methane addition slightly increases the fragility to a value of 62. These values for fragility are considerably lower compared to the value obtained earlier for GST films ($m=90$).\textsuperscript{14}

\textbf{Figure 5.4} Angell plot for viscosity. The blue and red solid curves represent the modeled viscosity for NPs (H$_2$) and NPs (CH$_4$), respectively. The black open circles are the viscosity data for SiO$_2$ in order to show a strong (undercooled) liquid.\textsuperscript{46} The black open triangles and the corresponding fitting curve are the experimental data\textsuperscript{47,48} and fitting curve utilizing Equation (5.4) for Ge$_{15}$Te$_{85}$. The blue stars are the viscosity data for nitrogen doped GST films,\textsuperscript{16} with corresponding fitting curves adopting Equation (5.4). Black dotted curve shows the viscosity for GST films explored by ultrafast DSC.\textsuperscript{14}

\textbf{5.3.5 Fragile-to-strong crossover}

In the Angell plot, an Arrhenius behavior resulting in a fragility approaching ~15, such as holds for SiO$_2$,\textsuperscript{46} is categorized as a strong (supercooled) liquid (cf. Figure 5.4). Larger values of fragility lead
to non-Arrhenius behavior, classified as fragile, such as has been presented for the GST films.\textsuperscript{14} However, in some (undercooled) liquids a single fragility model is not able to describe the temperature dependence of viscosity. Then, the coexistence of Arrhenius behavior at low temperature and non-Arrhenius behavior at high temperature has been successfully explained by a fragile-to-strong (FS) crossover,\textsuperscript{27} which is a ubiquitous feature in glass formers. First discovered in water,\textsuperscript{49} this phenomenon has thereafter been observed in glass forming liquids,\textsuperscript{27} chalcogenides\textsuperscript{50,51} and Ag-In-Sb-Te PCMs.\textsuperscript{20} For instance, Figure 5.4 portrays the experimental viscosity data for Ge\textsubscript{15}Te\textsubscript{85} (black open triangles) at temperatures near $T_g$\textsuperscript{48} and melting temperature ($T_m$),\textsuperscript{47} fitted with the corresponding dash curve utilizing Equation (4), where a distinct FS crossover is illustrated. The FS crossover in Ge\textsubscript{15}Te\textsubscript{85} is confirmed by another work employing the Adam-Gibbs equation to fit the viscosity.\textsuperscript{51} For GST NPs, the FS crossover is likewise discerned, demonstrated by the red and blue solid curves in Figure 5.4. With the strong segment near $T_g$, the viscosity drops exponentially with the increment of temperature with an intermediate fragility (strong), whereas a further increase in temperature yields a non-exponential decline of viscosity (fragile). The FS crossover in GST NPs is weaker than that of Ge\textsubscript{15}Te\textsubscript{85}, where the two segments of viscosity are clearly distinguished. Still, as we explain in the next paragraph, there are strong arguments that the FS crossover actually occurs in GST NPs and that it is not a misinterpretation of a (more ordinary) glass transition.

A similar temperature dependence of the growth rate as in the present work was also observed for AgInSbTe PCMs, where the Arrhenius dependence of viscosity was found at lower temperatures, while the MYEGA model (non-Arrhenius dependence) was obtained at higher temperatures.\textsuperscript{19,21} At that time it was proposed that the Arrhenius behavior correlates to the glassy state whereas the non-Arrhenius behavior is associated with the supercooled liquid state. In this scenario, this divergence in temperature dependence of viscosity appears at the junction between glass and supercooled liquid. If our observed (FS transition) behavior is explained as a glass transition, that would lead to a $T_g$ of ~438 K for GST NPs (H2). Taking this value for $T_g$, we then obtain a viscosity at $T_g$ of $10^3$ Pa s. It is obvious that this viscosity is in conflict with the definition of glass transition temperature (where the viscosity is $10^{12}$ Pa s). Moreover, we also observed crystallization at a temperature about 20 K lower than this supposed $T_g$ of ~438 K,\textsuperscript{26} which is also inconsistent with the notation that crystallization is only possible above $T_g$. Clearly, with the fragile-to-strong crossover model, these
conflicts are avoided. Therefore, the FS crossover is a more plausible explanation of our observations than the (supercooled liquid to) glass transition.

The present results therefore show the presence of the FS crossover, which already was signified by the large Arrhenius region shown in Figure 5.3b. It occurs for both samples approximately at 0.85 $T_g / T$, a $T_g$-scaled temperature lower than that of Ge$_{15}$Te$_{85}$ and AgInSbTe. The CH$_4$ addition has negligible influence on this crossover. For GST films reported by Orava et al., however, the FS crossover was not observed and a viscosity model with a single fragility value (Cohen&Grest model) was adopted to fit the Kissinger plot obtained through ultrafast DSC, denoted as the black dotted curve in Figure 5.4. The high fragility of GST films results in a sharp reduction of viscosity at temperatures just above $T_g$. Yet, the lower fragility for GST NPs, caused by the FS crossover, yields a less acute decline in viscosity. Consequently, the GST NPs exhibit a higher viscosity at lower temperature in comparison to the GST films, as distinguished at $\sim 0.9-1$ $T_g / T$ in Figure 5.4. These results thus suggest that NPs are advantageous in phase-change memory as higher viscosity correlates to lower atomic diffusivity therefore longer data retention time.

In a previous work, the growth rate of nitrogen doped GST (N-GST) in memory cells was directly measured in a large temperature regime (from $\sim 420$ to $\sim 530$ K), where the overall growth rate of the N-GST deviates in temperature dependence: Arrhenius behavior at low temperature and non-Arrhenius behavior at high temperature. The experimental data for growth rate were transposed to viscosity using Equation (5.2), with decoupling parameter $\xi=0.72$ and other parameters (viz. $\tau_m$, $r_{\text{atom}}$, $\lambda$, and $R_{\text{hyd}}$ in Equation (5.2)) from this article. $\xi$ is adjusted to make $\eta(T_g)\approx 10^{12}$ Pa s, and this value of $\xi$ is close to that for GST films reported previously. The transposed viscosity is presented as blue stars in Figure 5.4. The MYEGA model for viscosity with one fragility cannot fit these data when specifying $\eta(T_m)$ as $1.2\times 10^3$ Pa s. In contrast, the generalized MYEGA model (Equation (5.4)) yields a good fit to the viscosity of N-GST, providing a strong indication that the FS crossover also occurs in these N-doped GST films employed in memory cells. In another work, a similar temperature dependence in the growth rate of GST is observed, and two terms of temperature dependence were utilized to fit the Kissinger plot for GST confined in a memory cell. Yet, the FS crossover was not proposed to explain the observed behavior, but in the light of the present work it has thus been generally observed for GST in memory cells.
It has been suggested that FS crossover exists only in growth-dominated PCMs, but not in nucleation-dominated PCMs. Melt-quenched GST PCMs confined in a cell are considered (by their nanoscale volume) as growth-dominated PCMs. While GST films are considered as nucleation-dominated PCMs, GST NPs, on the other hand also possess growth-dominated crystallization ascribed to the extremely small volume for crystallization caused by down-scaling. For instance, in our previous work we found by high resolution TEM only single crystalline NPs. Nevertheless, small crystal domains are generally expected for surface-induced heterogeneous nucleation dominated crystallization of GST PCMs. However, the NPs in the present work are apparently that small that they still form single crystals. Therefore, it might be possible that presence of the FS crossover in GST NPs compared to its absence in GST films can be attributed to the down-scaling induced change in crystallization mechanism from nucleation dominant to growth dominant.

5.3.6 Overall growth rate of Ge$_2$Sb$_2$Te$_5$ nanoparticles

The overall growth rate of the crystallization for the GST NPs is of technological relevance, e.g. for PC memories, as it is associated with data retention at the lower temperatures and the switching speed at higher temperatures. The blue and red solid curves in Figure 5.5 show the overall growth rate, as derived using Equation 5.2, ranging from $T_g$ to $T_m$ for both NPs (H$_2$) and NPs (CH$_4$), respectively. In comparison, the growth rate of GST films obtained by Orava et al. is also depicted as black dash curve in Figure 5.5. The maximum growth rate ($U_m$) for these 2 types of NPs is very similar, 1.7 and 1.6 m s$^{-1}$, with $U_m$ taking place at approximately 0.7 $T/T_m$. These values for NPs are reasonably close to $U_m$ of GST films, as can be observed in Figure 5.5 by comparing the blue and red solid curves for the GST NPs with the black dash curve holding for GST films. In a previous work, the growth rate of Ge-Sb alloy reaches maximum value at ~0.9 $T/T_m$, which is plausible, because the $U_m$ of growth-dominated PCMs is considered to occur at a higher $T/T_m$ compared to nucleation-dominated PCMs.

Although the NPs (CH$_4$) possess a lower growth rate at lower temperature range (below 520 K), it coincides with the one for NPs (H$_2$) when the temperature is beyond 590 K. The lower growth rate for NPs (CH$_4$) at low temperature is similar to the retardation induced by carbon doping in GST films, as carbon (a byproduct decomposed from methane in plasmas) is expected to be incorporated into the NPs. When the temperature becomes higher, the FS crossover appears and
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then the fragile regime of viscosity is accessed. As a consequence, the viscosity strongly drops to equivalent values generating final convergence of the growth rates. This trend is also indicated by the viscosity in Figure 5.4, where the difference is less apparent, because Figure 5.4 is normalized with respect to $T_g$. This makes the NPs (CH$_4$) preferable for PC memory application as lower growth rates at low temperatures associated with a higher activation energy indicates a longer data retention time, meanwhile the still comparable growth rates at higher temperature enable sufficient rapid switching (to the crystalline SET state); see Figure 5.9.

The growth rate undergoes an Arrhenius-like behavior at temperatures just above $T_g$, and non-Arrhenius behavior emerges with a further increase of temperature, demonstrating a temperature dependent activation energy ($E_g$, derived from the gradient of this curve) for crystal growth during crystallization. With similar slopes to the independent data near $T_g$, the $E_g$ is determined as $\sim$2.8 and $\sim$3.2 eV at$^{-1}$ for the NPs(H$_2$) and NPs (CH$_4$). For Ge$_2$Sb$_2$Te$_5$ films it is well-established that the activation energy for crystallization and for growth near $T_g$ is in the range 2.2 – 3.0 eV at$^{-1}$. In comparison, the growth rate of GST films derived in Ref. 14 presents a considerably higher activation energy, $\sim$5.0 eV at$^{-1}$ near $T_g$, which appears unrealistic. Although a high fragility of the GST thin film can lead to a high activation energy, this fragility was obtained fully through modelling and fitting and not based on any directly measured data, inferring that the high fragility for the thin film could be erroneous.

However, it is still evident that the growth rates for the NPs (H$_2$) observed in the present work exhibit a large gap ($\sim$2 orders of magnitude) with the directly measured data obtained for GST films (open black data points in Figure 5.5). This discrepancy can have several origins, e.g.: 1) The NPs (H$_2$) crystallize at lower temperature than films, leading to a faster growth rate at the same temperature. The NPs (CH$_4$) represent an evidently lower growth rate at the same temperature compared to NPs (H$_2$) due to the increase of $T_p$. Similarly, the nitrogen doped GST films (confined in memory cells) even show smaller growth rate than GST films, as demonstrated by the blue stars in Figure 5.5; 2) The constant nuclei density hypothesis that was adopted in JMAK modeling is oversimplified and may result in an erroneous fitting of the data in the Kissinger plot and therefore may cause a considerable shift to higher growth rates at the lower temperatures. However, several clearly more advanced models for nucleation were also tested and these models did not significantly reduce the gap between the growth rates derived for the NPs (H$_2$) (blue solid line in Figure 5.5) and
the directly measured data obtained for GST films (black open data points in Figure 5); for more details see Figure 5.8 of the Appendix A.

**Figure 5.5** The growth rates of GST NPs between $T_g$ and $T_m$. Blue and red curves represent the data for GST ($H_2$) and GST ($CH_4$), respectively. The black dash curve is the growth rate for GST films, while the black data points are from direct measurements via transmission electron microscope and atomic force microscopy. The directly measured growth rate for nitrogen doped GST films is also shown in this figure; see the blue stars in this figure. The light yellow shaded area denotes the actual measurement regime accessed by ultrafast DSC.

**5.4 Conclusions**

Ultrafast differential scanning calorimetry has been employed to investigate the crystallization kinetics of Ge$_2$Sb$_2$Te$_5$ phase-change nanoparticles (NPs) synthesized by gas-phase condensation. The NPs show a relatively narrow size distribution around an average diameter of ~16 nm. Varying the heating rate during the DSC measurements with three orders of magnitude, it is observed that: (1) the crystallization rate complies with Arrhenius behavior within an (unexpectedly) large temperature range directly above $T_g$ (for $T_g/T$ values from 0.85-1), and (2) a non-Arrhenius fragile behavior occurs at higher temperatures (for $T_g/T$ values lower than 0.85). This unique feature can be explained well (only) by utilizing a fragile-to-strong crossover model for the viscosity, from
which the overall viscosity and growth rate of the NPs have been derived. This crossover is clearly observed here for the Ge$_2$Sb$_2$Te$_5$ NPs, while it was not observed earlier for GST films. This enables NPs to have both longer data retention times at low temperatures and high switching speed at high temperatures, entailing the NPs to be an advantageous contender in phase-change materials based devices. Moreover, it is demonstrated that CH$_4$ incorporation during the NPs production reduces the crystal growth rate by about two orders of magnitude at lower temperatures, and thus improves the data retention, whereas the maximum growth rate remains unchanged. This positive “doping” effect makes Ge$_2$Sb$_2$Te$_5$ NPs even more suitable candidates for phase-change memory applications.
Appendix A

**Figure 5.6** The size distribution of the Ge\_2Sb\_2Te\_5 (GST) nanoparticles (NPs) synthesized with H\_2 (black) and CH\_4 (red) as derived from TEM images. The average diameters of these two samples are 16.0±1.3 and 16.8±1.7 nm, respectively. The NPs size distribution is relatively mono-disperse.

**Figure 5.7** Fit of Kissinger plot utilizing the MYEGA model. Red and blue solid curves denote the inferior fits to the data via MYEGA model for viscosity for NPs (H\_2) and NPs (CH\_4), respectively. In contrast, the generalized MYEGA model shows much better fits for the whole temperature range.
Figure 5.8 Overall growth rate of GST NPs (H₂) as a function of temperature using two models for nucleation. In the present work as in the previous work on GST films a very simple model for nucleation is adopted: constant nuclei density (independent of time and temperature). In order to test whether the results are sensitive to changing the nucleation model also a more intricate model has been tested including time- and temperature-dependent nucleation. The result shown by the blue dotted curve yields a similar growth rate at lower temperature side to the one with constant nucleation density (blue solid curve). Therefore, the present results show that the gap between the measured \(^{11-13,16}\) and the modelled data is not caused by the model that is adopted for the nucleation.

Figure 5.9 Modeled isothermal crystallization curve as a function of time at 110 °C. It can be nicely observed that the incubation time for crystallization becomes several orders of magnitude longer in case of GST NPs (CH₄) than in case of GST NPs (H₂).
Appendix B

Thermal lag

The theory to estimate thermal lag has been detailed in the Appendix of chapter 3. Taking the values for heat transfer coefficient (5 to 20 kW m\(^{-2}\) K\(^{-1}\)), sample thickness (200 to 500 nm) and thermal conductivity (0.19 W m\(^{-1}\) K\(^{-1}\) at 20 °C\(^{56}\)) for Ge\(_2\)Sb\(_2\)Te\(_5\) thin films, the Boit number is then derived in the range 0.005 to 0.05 according to Equation 3.8, indicating that the assumption of a uniform temperature distribution within the sample is reasonable.

Taking the heat capacity of Ge\(_2\)Sb\(_2\)Te\(_5\) thin films as \(1.4 \times 10^6\) J m\(^{-3}\) K\(^{-1}\),\(^{39}\) the thermal lag caused by the heat transfer between the chip sensor and the sample is determined in the range 0.5 to 6 K at the maximum heating rate 40 000 K s\(^{-1}\) according to Equation 3.9. This thermal lag will not affect the breakdown of the Arrhenius behavior, since the breakdown starts at 10 000 K s\(^{-1}\).
References


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