Chapter 7

Crystallization kinetics of GeTe nanoparticles

Abstract

Chalcogenide based phase change materials (PCMs) are of great interest as promising candidates for novel electrical nonvolatile memories and have been applied successfully in rewritable optical disks. Nano-structured PCMs are considered as the next generation building blocks for their low power consumption, high storage density and fast switching speed. Yet their crystallization kinetics at high temperature, the rate-limiting property upon switching, faces great challenges due to the short time and length scales involved. Here we present a facile method to synthesize highly controlled, ligand-free GeTe nanoparticles, an important PCM, with average diameter under 10 nm. Subsequent crystallization by slow and ultrafast rates allow unravelling of the crystallization kinetics, demonstrating the break-down of Arrhenius behavior of crystallization and a fragile-to-strong transition in the viscosity as well as the overall crystal growth rate for the as-deposited GeTe NPs. The obtained results pave the way for further development of phase-change memory based on GeTe at sub-lithographic sizes.

7.1 Introduction

Based on the rapid and reversible switching between the amorphous and crystalline phases that offers strong optical and electrical contrast between these two phases, phase-change materials (PCMs) have attracted attention in various fields, such as optical data storage and novel electrical nonvolatile memories. Very recently they were successfully utilized in emerging applications, like solid state displays, on-chip photonic circuitry and neuromorphic computing. The switching of the PCMs relies upon proper heating and cooling of the materials. Heating the amorphous PCMs with pulses (either electric or laser) at tens of ns triggers the crystallization, and melting followed with quenching them by ultrashort pulses induces the amorphization of the PCMs. Understanding the crystallization kinetics of PCMs thus lies at the heart of their switching. However, owing to the short time scale (tens of ns) and length scale (~tens of nm) involved, it has been highly challenging for a long time to investigate the crystallization kinetics by traditional measurements that allow only low heating rates (e.g. below 3 K s\(^{-1}\)). However, with the development of ultrafast differential scanning calorimetry (DSC), a powerful tool, that enables heating the specimen up to 40,000 K s\(^{-1}\), has become (commercially) available in recent years. Subsequently, the crystallization kinetics of (amorphous) Ge\(_2\)Sb\(_2\)Te\(_5\) and AgInSbTe, GeSb thin films and GeSbTe nanoparticles (NPs) have been investigated by ultrafast DSC. As a result, the crystallization behaviors at high heating rates were unraveled as well as the temperature dependency of viscosity and crystal growth rate. Apart from the ultrafast DSC, other techniques were developed to understand the crystallization kinetics of PCMs, such as laser-based time-resolved reflectivity measurements, isothermal technique monitoring the thickness change of amorphous PCMs and microthermal stage-based resistance measurements. Crystal growth rates over wide temperature ranges were unraveled for melt-quenched AgInSbTe and doped-Ge\(_2\)Sb\(_2\)Te\(_5\) PCMs.

GeTe, as a promising candidate for phase-change memory, has received considerable attention in particular regarding the understanding of its crystallization kinetics. Dynamic transmission electron microscope (DTEM) was adopted to study the crystal growth rate near the melting temperature. Very recently the crystallization kinetics of GeTe thin films was explored by crystalizing the specimen using ultrafast DSC with a large range of heating rates and subsequent modeling of the obtained results.

Another intriguing property of PCMs is their excellent scalability that is fundamental for future memory devices. Scaling PCMs provides huge advantages, such as high information storage density, fast switching speed and low power consumption per bit. Therefore many studies have been devoted to exploring the scaling of PCMs. Three dimensional down-scaling of GeTe PCMs into...
nanoparticles with diameters below 20 nm using chemical synthesis was successfully realized recently.\textsuperscript{19,20} In this case, size dependent polar ordering in crystalline GeTe NPs has been observed.\textsuperscript{21} In addition, a strong size dependence of the crystallization temperature has been observed for amorphous GeTe NPs, especially for NP diameters below 10 nm. For instance, the crystallization temperature reached 400 °C for GeTe NPs having a diameter of 1.8 nm,\textsuperscript{19} which is more than 220 °C higher in comparison with the crystallization temperature for the bulk GeTe, suggesting ultrahigh stability of the amorphous phase for these NPs. Despite the successful synthesis of the amorphous and crystalline GeTe nanoparticles (NPs), determining the crystallization kinetics of GeTe NPs is highly challenging owing to the short time scale involved in the crystallization at high temperature. On the other hand, inert gas condensation based on magnetron sputtering offers a one-step synthesis of ligand-free NPs in ultrahigh vacuum. The large yield of the deposition allows us to investigate the crystallization kinetics of the GeTe NPs by ultrafast DSC. In this work we present the synthesis of GeTe NPs with excellent size, crystallinity and composition control by inert gas condensation. Utilizing ultrafast heating (up to 20000 K s\textsuperscript{-1}) in conjunction with DSC and subsequent numerical modeling allowed us to assess the crystallization kinetics of as-deposited amorphous GeTe NPs in the (extrapolated) temperature range between the glass transition and melting temperatures.

7.2 Experimental methods

7.2.1 Sample preparation

The GeTe phase-change nanoparticles (NPs) were synthesized by magnetron sputtering inert gas condensation using a home-modified nanoparticle deposition system (Nanogen 50). The sample chamber was evacuated to 10\textsuperscript{-8} mbar before NPs deposition. Amorphous GeTe NPs were directly synthesized by sputtering the GeTe target (purity of 99.99\%), employing a low current (0.15 A) to avoid the formation of crystalline NPs. The Ar gas flow (purity 99.9999\%) used to sputter the target is 35 sccm. A small amount of methane was used to promote the formation of the nascent GeTe clusters in the plasma.\textsuperscript{22} Analogous to chapter 5, the NPs were deposited directly on a pre-cleaned glass substrate and transmission electron microscope (TEM) holey carbon grids taped outside the periphery of the NPs beam for subsequent characterization of crystallization.

7.2.2 Morphology and slow crystallization

Analogous to chapter 4, the morphology, composition and slow crystallization of the as-deposited GeTe NPs were characterized by TEM (JEOL 2010) at 200 kV after deposition. The slow crystallization process for the GeTe NPs was monitored by in-situ heating in TEM. The detailed
methodology is described in chapter 2 and 4. The temperature interval used here is 3 °C after the appearance of observable diffraction spots on the SAED patterns. The heating rate above 200 °C is estimated as 0.03 K s\(^{-1}\). At each temperature step (3 °C), a time interval of 60 seconds was taken for the sake of stabilization of the TEM membrane to avoid the influence of drifting caused by thermal expansion. The diameter of the selected area aperture for the SAED patterns is 2.5 μm. The NP density is assessed as ~ 6000 μm\(^{-2}\), however the total number of NPs selected in the SAED patterns cannot be estimated accurately because of the irregularly distributed holes in the carbon support film.

### 7.2.3 Fast crystallization and modelling

Similar to chapter 5, the phase transitions of the samples were subsequently measured by ultrafast differential scanning calorimetry (DSC, Mettler-Toledo Flash DSC 1), with the sensor chips (USF-1) each containing the actual sensor and reference area. The details of measurements can be found in chapter 5. The approximate size of the individual flakes measured is roughly 20×20 μm\(^2\). The heating rates (Φ) adopted in this work varied from 100 to 20000 K s\(^{-1}\). The thermal lag has no significant influence on the kinetics, as discussed in the Appendix of this chapter. Analogous to chapters 3 and 5, numerical modeling was performed to understand the crystallization kinetics of the GeTe NPs, with the details of the method shown in the Appendix of chapter 3. In the numerical modeling, the generalized MYEGA model was used to describe the temperature dependency of viscosity of the as-deposited amorphous GeTe NPs.\(^{23}\) The nucleation process was simplified by a constant nuclei density (site saturation) and the crystallization process is thus largely governed by the temperature dependence of the growth, as used in chapters 3 and 5. In the fitting process, a data point derived from the in-situ heating in TEM was also adopted, with the Φ assessed as 0.03 K s\(^{-1}\).

### 7.3 Results and discussion

#### 7.3.1 Low heating rate crystallization

The composition, morphology and the crystallinity of the as-deposited GeTe nanoparticles (NPs) were characterized by transmission electron microscopy (TEM). The composition of the GeTe NPs was scrutinized by energy dispersive X-ray spectrometry (EDS), showing the atomic ratio of Ge:Te=45:55 (±1); see Figure 7.5 of the Appendix. The slight deficiency (~ 2-3 at%) of Ge element is consistent with the results obtained earlier for the GeSbTe and GeTe NPs synthesized by inert gas condensation. The most probable explanation is that the effective sputtering rate of Ge is slightly lower in comparison to Sb and Te. Figure 7.1a shows the morphology of the as-deposited GeTe NPs, indicating that no coalescence of the NPs but only aggregation takes place during deposition.
The average diameter of the NPs was then determined as 9.4±1.6 nm, as demonstrated in Figure 7.6 of the Appendix, indicating a relatively narrow size distribution of the GeTe NPs. The selected area electron diffraction (SAED) patterns, as shown in Figure 7.1b, demonstrate the amorphous nature of the as-deposited GeTe NPs due to the lack of sharp diffraction rings associated with crystal planes.

Analogous to our previous study on GeSbTe NPs (chapter 4), the crystallization of the GeTe NPs at low heating rate was characterized by in-situ heating in TEM. The GeTe NPs were annealed within the TEM, with the corresponding SAED patterns recorded at each temperature step. Figure 7.1c illustrates the SAED patterns at 270 °C, with diffraction rings distinctly detectable. Figure 7.1d demonstrates the azimuthal integral of the SAED patterns, showing that the crystalline peak appears at a temperature of ~230 °C and saturates at ~260 °C. It is noticeable that the GeTe NPs coalesce during crystallization. This can be distinguished by comparing bright field images of the same area before and after the in-situ heating, as shown in Figure 7.7 of the Appendix. The interplanar spacing derived from the SAED patterns are: $d_{202}=0.297$ nm and $d_{024/220}=0.210$ nm, showing excellent agreement with the value for GeTe NPs obtained earlier. The peaks for \{024\} and \{220\} planes cannot be resolved for such small NPs. Another work has found that the two peaks merged into one in synchrotron X-ray diffraction for GeTe NPs smaller than 17 nm. Through recording and normalizing the evolution of the diffraction intensity for \{024\}/\{220\} peak as a function of temperature, the crystallinity as a function of temperature can be obtained, as shown in Figure 7.1f. After fitting the data with the Boltzmann function, the crystallization temperature, defined as the temperature where the maximum 1st order derivative occurs, is then derived as 238.3±0.3 °C that is 60 °C higher than that of the bulk GeTe (~175 °C). The fitting was excellent, as assessed by the adjusted $R^2=0.997$. Figure 7.1f compares the size dependency of crystallization temperature for GeTe and GeSbTe NPs. Opposite trends for the size dependency can be detected for these two kinds of NPs, where the crystallization temperature drastically rises for GeTe while a slight decrease is found for GeSbTe NPs when the size of the NPs decrease. Despite the different methods to grow NPs, the data derived for the GeTe NPs in this work agree excellently with the size dependency determined for previous NPs prepared by chemical synthesis. Note that the crystallization temperature of GeTe NPs in this work is slightly higher compared to the previous GeTe NPs due to the small amount of methane incorporation to facilitate the formation of nascent NPs during NPs deposition. We have observed in previous work that the methane addition can enhance the stability of the amorphous phase of GeSbTe NPs therefore a similar effect is expected for GeTe NPs.
Figure 7.1 The morphology, crystallinity and slow crystallization of GeTe NPs. (a) Bright field TEM image showing the morphology of the as-deposited GeTe NPs. Selected area electron diffraction (SAED) patterns of the GeTe NPs recorded at room temperature (b) and 270 °C (c) show the amorphous to crystalline transition. (d) Azimuthal integral of the SAED patterns recorded at different temperatures. The crystallization fraction as a function of temperature is shown in (e), and the size-dependent crystallization temperatures of GeTe and GeSbTe NPs are shown in (f).

7.3.2 Ultrafast crystallization

The fast crystallization was accomplished by heating single GeTe flakes, that are scraped off from the glass substrate, at various heating rates ranging from 100 to 20000 K s⁻¹ by ultrafast differential scanning calorimetry (DSC). The obtained DSC traces are shown in Figure 7.2a, where the exothermic crystallization peaks are distinctly observed, as shown by the arrows in Figure 7.2a. The crystallization peak temperature ($T_p$) shifts from ~280 °C at 100 K s⁻¹ to 365 °C at 20000 K s⁻¹. Note that for the GeTe NPs, the crystallization peak was not observed above 20000 K s⁻¹ due to the limit of the maximum temperature that the ultrafast DSC can reach (450 °C). The shift of $T_p$ is expected according to Kissinger:²⁵

$$\frac{Q}{R} = -\frac{d \ln(\Phi/T_p^2)}{d(1/T_p)} \quad (7.1)$$
with $Q$ the activation energy for crystallization, $R$ the gas constant, and $\Phi$ the heating rate. Then the data obtained by DSC are depicted in a Kissinger plot, as shown in Figure 7.2b. As shown in the Kissinger plot, the crystallization follows Arrhenius behavior (i.e. a linear dependence in the Kissinger plot) for heating rates $\Phi$ below $2500 \text{ K s}^{-1}$ and it breaks down for $\Phi$ above $2500 \text{ K s}^{-1}$. The linear fit in the Kissinger plot below $2500 \text{ K s}^{-1}$ provides the activation energy for crystallization, $E_a=4.09\pm0.29 \text{ eV}$. The activation energy is higher compared to the one of the GeSbTe NPs ($\sim2.2 \text{ eV}$).\(^9\) Above $2500 \text{ K s}^{-1}$, the Arrhenius behavior in the Kissinger plot breaks down, generating a strong curvature in the Kissinger plot. Hence, the activation energy of crystallization becomes temperature dependent where it decreases with the increase of temperature.

To understand the break down in the Arrhenius behavior as well as the overall crystallization kinetics, the Johnson-Mehl-Avrami-Kolmogrov (JMAK) theory was adopted to numerically model the crystallization peak temperature at various $\Phi$. In the JMAK modeling, the crystal growth rate is the key factor that dominates the crystallization process. Analogous to our previous work,\(^8,^9\) the crystal growth rate between the glass transition and melting temperature is described as:

$$U(T) = \frac{4r_{\text{atom}}k_BT}{3\pi\lambda^2R_{\text{hyd}}\eta(T)}[1-\exp(-\frac{\Delta G(T)}{k_BT})]$$ \hspace{1cm} (7.2)$$

with $U(T)$ the growth rate, $r_{\text{atom}}$ the atomic radius ($\sim1.5 \text{ Å}$), $\lambda$ the diffusional jump distance (here $\sim2.99 \text{ Å}$),\(^{26}\) $R_{\text{hyd}}$ the hydrodynamic radius ($R_{\text{hyd}} = r_{\text{atom}}$), $k_B$ the Boltzmann constant, $\eta(T)$ the temperature dependent viscosity, $\xi$ the decoupling parameter of Stokes-Einstein equation ($\xi = 0.65$ as used for the GeSbTe NPs\(^9\)) and $\Delta G(T)$ the change of Gibbs free energy, which can be described, according to Thomson and Spaepen, as:\(^{27}\)

$$\Delta G(T) = \frac{\Delta H_m(T_m - T)}{T_m}\left(\frac{2T}{T_m + T}\right)$$ \hspace{1cm} (7.3)$$

where $\Delta H_m$ is the latent heat of melting, approximately $0.186 \text{ eV at}^{-1}$, and $T_m$ is set to $1000 \text{ K.}\(^{26}\) In Equation 7.2, the viscosity description is of vital importance in the modeling. As demonstrated by our previous work,\(^9\) the generalized MYEGA model\(^{23}\) that was originally proposed to describe the viscosity of metallic glass forming liquids outperformed the single fragility MYEGA model to describe the viscosity of as-deposited GeSbTe NPs, because of the relatively clear presence of Arrhenius behavior up to a certain heating rate and only a breakdown of this behavior above this
heating rate. Since this is also observed in the present work for a heating rate of 2500 K s\(^{-1}\), it is obvious to adopt the generalized MYEGA model here as well:

\[
\log_{10} \eta(T) = \log_{10} \eta(\infty) + \frac{1}{T} \left[ W_1 \exp\left(-\frac{C_1}{T}\right) + W_2 \exp\left(-\frac{C_2}{T}\right) \right]
\]  

(7.4)

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. After the optimization, the modeled \(T_p\) at various \(\Phi\) were depicted as red dotted curve in the Kissinger plot, showing an excellent fitting with the adjusted \(R^2=0.990\). The fitting parameters in Equation 7.4 were determined as: \(W_1=6184.98\), \(C_1=9061.17\), \(W_2=4.42 \times 10^{-4}\), \(C_2=609.17\). One can evidently observe that the generalized MYEGA model can nicely fit both the linear (Arrhenius behavior) and the curved (non-Arrhenius behavior) parts in the Kissinger plot.

**Figure 7.2** DSC traces for heating rates ranging from 100 to 20000 K s\(^{-1}\) (a) and the corresponding Kissinger plot (b). The unit for the heating rate in (a) is K s\(^{-1}\). The inset of (b) demonstrates the zoomed-in Kissinger plot below 2500 K s\(^{-1}\), with the linear fit indicating the activation energy of crystallization. The extrapolation of the linear fit is close to the TEM data point.

### 7.3.3 Viscosity and fragility

After fitting the data in the Kissinger plot, the viscosity of the as-deposited GeTe NPs is then obtained from Equation 7.4. Figure 7.3 depicts the temperature dependency of the viscosity of the as-deposited amorphous GeTe NPs. Note that in the generalized MYEGA model, the glass
transition temperature \( T_g \) is not directly provided. The \( T_g \) is set as the temperature where the viscosity is \( 10^{12} \) Pa s, which results in \( T_g = 467 \) K for the GeTe NPs. This value for \( T_g \) is higher than the one for GeTe film because of the higher crystallization temperature of the NPs.\(^{26}\) The fragility, defined as:

\[
m = \frac{d(\log_{10} \eta(T))}{d(T_g/T)} \bigg|_{T=T_g}
\]

was then derived as 78 for the amorphous GeTe NPs from Figure 7.3. The value for the fragility is lower than that determined for the GeTe thin films \( (m=132) \) owing to the different viscosity models adopted during numerical modeling.\(^{15}\) However the fragility of GeTe NPs is higher in comparison with GeSbTe NPs, which is reasonable since GeTe NPs show a higher activation energy for crystallization than GeSbTe NPs \( (4.09 \text{ vs } 2.43 \text{ eV}) \). For comparison, the viscosity for GeSbTe NPs is also depicted in the Figure 7.3. The viscosity exhibits a strong (Arrhenius) behavior approaching \( T_g \) and becomes fragile (non-Arrhenius) at temperatures above \( \sim 1.2 T_g \). The extrapolated viscosity fits very well with the value at melting temperature \( (\eta = 10^{-3.05} \text{ Pa s}) \) determined by molecular dynamics simulation.\(^{26}\)

**Figure 7.3** Temperature dependent viscosity of the GeTe NPs. The high activation energy for the crystallization supports the high fragility. The viscosity at melting temperature, \( 10^{-3.05} \text{ Pa s} \),\(^{26}\) is also depicted as red open square for comparison. The thick red marked region indicates the temperature regime accessed by ultrafast DSC.
7.3.4 Crystal growth rate

The overall crystal growth rate is one of the most relevant properties of PCMs as it indicates the stability of amorphous phase at relatively low temperatures and the crystallization speed at high temperatures and is thus of key technological importance for applications such as phase-change memory. As illustrated by the solid red curve in Figure 7.4, the crystal growth rate between glass transition and melting temperatures is determined by Equation 7.2 for the as-deposited amorphous GeTe NPs. In contrast, crystal growth rates at low temperatures for GeTe thin films are shown in Figure 7.4. The maximum growth rate ($U_m$) of GeTe NPs is 1.9 m s$^{-1}$, occurring at ~720 K ($\sim 0.72 \ T_m$), slightly higher than GeSbTe NPs ($\sim 0.70 \ T_m$) and lower in comparison to GeTe film ($\sim 0.79 \ T_m$). The $U_m$ of GeTe NPs is comparable to that of the GeTe thin films ($U_m = 3.5 \ m\ s^{-1}$). However, the GeTe NPs show 2-3 orders of magnitude lower crystal growth rate at temperature approaching $T_g$ in comparison with the GeTe thin film and the GeSbTe NPs, indicating a higher stability of the amorphous phase of the GeTe NPs. Due to the comparable $U_m$ between the GeTe and GeSbTe PCMs, the GeTe NPs are the most favorable for memory applications among the PCMs shown in Figure 7.4. However the concern is the melting temperature of the GeTe NPs, which is not accessible by ultrafast DSC. Due to the large increase in the crystallization temperature of the GeTe NPs and well-known decreasing trend in melting temperature during down scaling, the

![Figure 7.4](image)

**Figure 7.4** Temperature dependency of crystal growth rate of GeTe NPs. The growth rates for GeTe thin films and GeSbTe NPs are depicted for comparison.
operation window for crystallizing GeTe NPs can become very small, limiting the applicability of GeTe NPs. For instance the melting temperature of GeTe thin film with a thickness of 2 nm is about 600 °C, 120 °C lower than the bulk value. So further measurements on the size dependence of the melting temperature are required before GeTe NPs can be considered for applications.

### 7.4 Conclusions

Amorphous GeTe nanoparticles with size, crystallinity and composition control has been successfully synthesized by inert gas condensation. In-situ heating in a transmission electron microscope reveals that the crystallization temperature of the GeTe NPs at relatively low heating rate is 60 °C higher than the one for the bulk GeTe. Ultrafast heating by differential scanning calorimetry is then utilized to unravel the crystallization kinetics of the crystallization at higher temperatures. The breakdown of Arrhenius behavior in crystallization is distinctly observed at heating rate above 2500 K s⁻¹. Numerical modeling with proper description for viscosity reveals the temperature dependency of the viscosity and crystal growth rate of the GeTe NPs. The high maximum crystal growth rate at high temperature in combination with the low crystal growth rate when the glass transition temperature is approached implies a promising application perspective of GeTe NPs in memories, but the strongly reducing temperature window between the crystallization temperature and the melting temperature when the NP size reduces can be an obstacle.
Appendix

Thermal lag

The theory to estimate thermal lag has been detailed in 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 (0.23 W m$^{-1}$ K$^{-1}$ at 20 °C) for GeTe thin films, the Boit number is then derived in the range 0.004 to 0.04 according to Equation 3.8, indicating that the assumption of a uniform temperature distribution within the sample is reasonable.

Taking the heat capacity per unit volume of GeTe thin films as $7.4 \times 10^5$ J m$^{-3}$ K$^{-1}$, the thermal lag caused by the heat transfer between the chip sensor and the sample is determined in the range 0.2 to 1.2 K at the maximum heating rate 20000 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 2500 K s$^{-1}$.

![Figure 7.5](image.png) The composition of the GeTe NPs, giving a ratio Ge:Te=45:55 (±1) at%. The carbon and copper are from the membrane (holey carbon grids).
Figure 7.6 The size distribution of the as-deposited GeTe NPs, showing an average diameter of 9.4±1.6 nm.

Figure 7.7 Bright field images of GeTe NPs before (a) and after (b) annealing. Coalescence of NPs can be clearly observed after annealing.
References

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Phase-change materials (PCMs) have been successfully used in optical storage and are among the most promising candidates for next generation memory technology. The application is based on the rapid and reversible switching between the amorphous and crystalline phases of the materials that provides high optical/electrical contrast between these two phases. Although a lot of attentions have been dedicated to the exploration of the phase transition in PCMs for more than two decades, the crystallization kinetics of the transition at relatively high temperatures remained for a long time highly challenging due to the short time and length scales involved. However, the crystallization kinetics at high temperature is essential for applications as the switching mostly takes place within the temperature interval 400-500 °C.

In this thesis we investigated the crystallization kinetics of PCMs. In chapter 3 we applied ultrafast heating to Ge$_7$Sb$_{93}$ thin films with various heating rates by ultrafast differential scanning calorimetry (DSC). A breakdown of Arrhenius behavior was observed for crystallization at high heating rates. With numerical modeling using Johnson-Mehl-Avrami-Kolmogorov theory in combination with two different models for crystal growth rate we studied the crystallization kinetics in the temperature range in-between the glass transition and the melting temperatures. By comparing the modeled crystal growth rates with the experimentally obtained direct growth data for Ge$_7$Sb$_{93}$ films, we derived a proper model to describe the viscosity and growth rate for PCMs, paving the way for later research on the kinetics of phase-change nanoparticles.

The search for a next generation, potentially universal, memory drives the exploration of non-volatile memory with larger storage capability and faster switching speed. Down-scaling PCMs provides a promising solutions to reach these goals. Inert gas condensation based on magnetron sputtering offers us a facile way to deposit ligand-free nanoparticles at room temperature. Using this method, we synthesized Ge$_2$Sb$_2$Te$_5$ nanoparticles, one of the most widely used PCMs, in diameters below 20 nm with excellent composition, crystallinity and size control (Chapter 4). Subsequent characterization by transmission electron microscopy revealed the size dependence of crystallization of these nanoparticles, where the crystallization temperature slightly decreases with the reduction of size. A small amount of methane, added during deposition, efficiently increases the crystallization temperature of the nanoparticles, resulting in an enhanced stability of the amorphous phase of the nanoparticles. To understand the crystallization kinetics of these nanoparticles at high temperature, ultrafast crystallization was employed (Chapter 5). The crystallization follows
Arrhenius behavior for a quite long heating rate range, while it breaks down at heating rates above \( \sim 10000 \) K/s. We interpreted this phenomenon by adopting a viscosity model with a strong-to-fragile transition within the supercooled liquid, a phenomenon ubiquitously existing in metallic glasses. Adopting the model established for the Ge\(_7\)Sb\(_{93}\) thin films, we unraveled the viscosity as well as the crystal growth rate in-between the glass transition and the melting temperatures for the as-deposited amorphous Ge\(_2\)Sb\(_2\)Te\(_5\) nanoparticles. The methane incorporation did not influence the maximum crystal growth rate in the nanoparticles, but improves the low temperature retention and therefore provides an effective way to improve the overall performance of the PCM. This improvement by methane was observed for the GeTe nanoparticles as well (Chapter 7).

This thesis demonstrates extensive investigations on the crystallization of phase-change nanoparticles. Ge\(_2\)Sb\(_2\)Te\(_5\) nanoparticles incorporated with methane present promising properties for applications in memory. However, to use these nanoparticles in memories, knowledge of the conductivities of the amorphous and crystalline nanoparticles is essential. However, the small size of the nanoparticles makes the connection of the nanoparticles to electrodes highly challenging. One of the options is conductive atomic force microscope which can readily probe the nanoparticles with sizes around ten nanometers and is able to measure the current through the nanoparticle at certain applied voltages. This approach opens a door to study the scalability of the threshold voltage as well as power consumption of crystallization which is key to phase-change memory.

The interaction of the phase-change nanoparticles with the underlying substrate is also relevant for the potential usage of the nanoparticle-based systems. So we investigated the sticking dynamics of the Ge\(_2\)Sb\(_2\)Te\(_5\) nanoparticles on graphene (Chapter 6). The areal density of nanoparticles landed on suspended graphene is \( \sim 3 \) times higher than the one on graphene supported by a thin amorphous carbon film, which we attribute to the difference in surface energy of both types of graphene. Exposure to air for 8 weeks leads to significant oxidation of the Ge atoms while Sb and Te did not show obvious oxidation, where oxidation was more severe for the nanoparticles on the suspended graphene than on the supported graphene.

An intriguing example of the applications of the phase-change nanoparticles is the ability to modify the surface wettability. Amorphous phase-change nanoparticles deposited on highly oriented pyrolytic graphite increased the hydrophobicity of the surface. By annealing the system (to a moderate temperature of \( 120 \) °C), the hydrophobic surface switched to hydrophilic. This interesting phenomenon indicates a novel approach to control the surface wettability by phase-change nanoparticles.
**Samenvatting**

*Phase-Change* Materialen (PCMs) zijn succesvol geïmplementeerd in optische dataopslag, en behoren tot de meest veelbelovende kandidaten voor een volgende generatie geheugen-technologie. Deze toepassing is gebaseerd op snel en reversibel wisselen tussen de amorfe en kristallijne fasen van een materiaal, dat een groot optisch of elektrisch contrast heeft tussen deze beide fasen. Hoewel de afgelopen twee decennia veel inspanningen gewijd zijn aan het onderzoek naar de faseovergang op relatief hoge temperaturen, bleef het ontrafelen van de kristallisatie-kinetiek tot voor kort een grote uitdaging vanwege de korte tijd- en lengteschalen waarop deze processen plaatsvinden. Toch is kennis van deze kinetiek essentieel, omdat het schakelen van de geheugentoestanden merendeels plaatsvindt in het temperatuurregime tussen de 400 en 500 °C. In deze thesis hebben we de kristallisatie-kinetiek van PCMs onderzocht. In hoofdstuk 3 beschrijven we onderzoek waarbij met behulp van ultrasnelle *differential scanning calorimetry* (DSC) dunne Ge7Sb93 films ultrasnel verhit zijn. We vonden een afwijking van Arrhenius-gedrag voor kristallisatie bij snelle verhitting. Door middel van numeriek modelleren met behulp van de Johnson-Mehl-Avrami-Kolmogorov theorie, in combinatie met twee verschillende modellen voor de kristalgroeisnelheid, hebben we de kristallisatiekinetiek in het temperatuurbereik van glastransitie tot smelttemperatuur bestudeerd. Door de gemodelleerde kristalgroei te vergelijken met direct verkregen experimentele kristalgroeidata van Ge7Sb93, hebben we een model afgeleid om de viscositeit en groeisnelheid van PCMs te beschrijven. Dit heeft de weg vrijgemaakt voor verder onderzoek naar de kinetiek van *phase-change* nanodeeltjes.

De zoektocht naar een volgende generatie, potentieel meer universeel, geheugen is een stimulans voor het onderzoek naar niet-volatiele geheugen met grotere opslagcapaciteit en snellere schakelsnelheid. Het verkleinen van PCMs kan hierbij een beloftevolle oplossing bieden. Inerte gas condensatie gebaseerd op magnetron-sputteren is een geschikte methode om ligand-vrije nanodeeltjes bij kamertemperatuur te deponeren. Met deze methode hebben we Ge2Sb2Te5-nanodeeltjes, een van de meest gebruikte PCMs, gesynthetiseerd met diameters beneden 20 nm, met excellente compositie, kristalliniteit, en grootte-controle. Tijdens daarop volgende karakterisatie in een transmissie-elektronen microscoop bleek dat de kristallisatietemperatuur van de nanodeeltjes licht afnam naarmate de deeltjes kleiner werden. Kleine hoeveelheden methaan, toegevoegd tijdens het depositieproces, bleek effectief in het verhogen van de kristallisatietemperatuur van de nanodeeltjes, wat resulteerde in een toegenomen stabilitéit van de amorfe fase van de nanodeeltjes. Om de kristallisatiekinetiek van de nanodeeltjes op hoge temperatuur te begrijpen, is ultrasnelle
DSC gebruikt. De kristallisatie bleek Arrhenius-gedrag te vertonen over een grote range van verhittingssnelheden, maar bleek hiervan af te wijken voor snelheden boven 10 000 K/s. We hebben dit fenomeen geïnterpreteerd door middel van een viscositeitsmodel met een *fragile-to-strong* transitie in de supergekoelde vloeistof, een fenomeen alomtegenwoordig in metallische glazen. Met het eerder vastgestelde model voor de dunne Ge$_7$Sb$_{93}$ films, hebben we vervolgens de viscositeit en de kristalgroesnelheid bepaald tussen de glastransitie en de smelttemperatuur voor de als-gedeponeerd amorf Ge$_2$Sb$_2$Te$_5$ nanodeeltjes. De methaan-opname had geen invloed op de maximale groesnelheid van de nanodeeltjes bij hoge temperatuur, maar bleek dus wel de stabiliteit van de amorf fase bij lage temperatuur te verbeteren en is daarom een effectieve manier om de algehele prestaties van de nanodeeltjes te verbeteren. Deze verbetering door methaan hebben wij ook bij GeTe-nanodeeltjes waargenomen.

Deze thesis toont dus uitgebreid onderzoek aan de kristallisatie van *phase-change*-nanodeeltjes. Ge$_2$Sb$_2$Te$_5$ nanodeeltjes met toegevoegd methaan laten veelbelovende eigenschappen voor toepassingen in geheugen zien. Om deze nanodeeltjes in geheugen te gebruiken is kennis van de elektrische geleiding van de amorf en kristallijne nanodeeltjes essentieel. De kleine omvang van de nanodeeltjes maakt het een grote uitdaging om de nanodeeltjes te verbinden met elektroden. Een van de opties is het gebruik van een *conductive atomic force microscope*, die nanodeeltjes met een grootte rond 10 nm kan detecteren, en de elektrische stroom door een nanodeeltje kan meten voor een gegeven aangebracht voltage. Deze aanpak opent de deur voor het bestuderen van de schaalbaarheid van het drempel-voltage en energieverbruik van kristallisatie, wat essentieel is voor *phase-change*-geheugen.

De interactie van nanoparticles met het onderliggende substraat is ook relevant voor het potentiele gebruik van nanodeeltjes gebaseerde systemen. We hebben de stictie-dynamica van Ge$_2$Sb$_2$Te$_5$ nanodeeltjes op grafeen onderzocht. De dichtheid van nanodeeltjes die landden op vrijhangend grafeen was ~3 keer hoger dan de dichtheid op grafeen ondersteund door een dunne amorf carbonfilm, wat we toeschrijven aan het verschil in oppervlakte-energie van beide typen oppervlakken. Blootstelling aan lucht gedurende 8 weken leidt tot sterk preferente oxidatie van de Ge atomen terwijl Sb en Te niet duidelijk oxideerden, waarbij de oxidatie van de deeltjes op vrijhangend grafeen weer sterker is dan op ondersteund grafeen. Een bijzonder voorbeeld van de toepassing van PCM nanodeeltjes is het modificeren van de oppervlakte-wetting. De PCM-nanodeeltjes werden gedeponeerd op sterk georienteerd pyrolytisch grafiet, en verhoogden hierdoor de hydrofobiciteit van het oppervlak. Door het systeem te gloeien (bij een relatief lage temperatuur van 120 °C), veranderde het hydrofobe oppervlak naar hydrofiel. Dit interessante fenomeen geeft
een nieuwe aanpak om de oppervlaktewetting te modificeren en wellicht te kunnen schakelen met behulp van *phase-change* nanodeeltjes.