Ge-Sb-Te based phase-change nanoparticles
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Chapter 2

Methods

Abstract

This chapter describes the general methods utilized to prepare samples and the subsequent methods employed for sample characterization and data analysis. Two different routes were pursued to study the crystallization behavior of the phase-change materials: (1) slow crystallization by in-situ heating in a transmission electron microscope and (2) fast crystallization by ultrafast heating in differential scanning calorimetry. The analytical methods adopted and described here are the basis for the analyses performed and presented in the next chapters. Specific deviations of these general methods will be mentioned in the chapters separately.

2.1 Sample preparation

In this thesis, Ge$_7$Sb$_{93}$ thin films and Ge$_2$Sb$_2$Te$_5$ (GST) nanoparticles were studied. Amorphous Ge$_7$Sb$_{93}$ films with thickness of 200 nm were deposited on glass substrates using co-sputtering with a Unaxis Sputter coater. The deposition rate was 2.5 nm s$^{-1}$. The films were, without breaking the vacuum, directly capped with a (5 nm) layer of ZnS-SiO$_2$ to avoid oxidation of the films.

The phase-change nanoparticles (NPs) were produced by magnetron sputtering with inert gas condensation in a home-modified nanoparticle system Nanosys50 from Mantis Deposition Ltd. (http://www.mantisdeposition.com). The setup is shown in Figure 2.1. This system consists of two chambers, i.e., the main chamber (indicated by the left dashed square in Figure 2.1a) and the aggregation chamber (marked by the right dashed rectangle in Figure 2.1a).

The main chamber is used to collect the produced NPs. The substrate for the sample is placed in the holder that locates in the main chamber. Up to 10 samples can be put into the sample holder (in 5 arrays), enabling the production of NPs at five different settings without opening the system. Two Leybold turbo molecular pumps with a capacity of 300 lt/s are present to evacuate the two chambers and they are both backed by one scroll pump (Varian LTH10). The vacuum can reach $1 \times 10^{-8}$ mbar in the main chamber and $1 \times 10^{-6}$ mbar in the aggregation chamber. The settings and vacuum are controlled and monitored by the Mantis controller, as shown in Figure 2.1b.
Figure 2.1 The cluster source for producing nanoparticles (a) and the corresponding controller (b). The schematic of the aggregation chamber is shown in (c).

The aggregation chamber is the core of the system, which is schematically illustrated in Figure 2.1c. It consists of several parts: (1) a water cooled magnetron head, (2) a double gas inlet system controlled by 2 MKS mass flow meters, (3) pressure readings inside the aggregation chamber and the main chamber and (4) water cooling for both the magnetron head and aggregation chamber wall. A target (2 inches in diameter and with tunable thickness) is placed on top of the magnet head. On
Methods

The mechanism of magnetron sputtering can be summarized as follows. When a deposition starts, a noble gas (usually Ar in this thesis) is flown into the aggregation zone. Due to the applied potential between the target and the anode, the inert gas is ionized above the magnetron head to create a plasma. Then the positive ions in the plasma (Ar\(^+\)) are accelerated by the DC potential and impacts on the target, thereby breaking off particles which together compose the desired target material vapor. The magnetron under the target can increase the efficiency of the sputtering process by making the ions travel in a helical path through the plasma, leading to the longer effective path therefore higher chance of colliding with the target. The target material vapor is then swept to the aggregation volume that is just above the plasma. The relatively high pressure caused by the inert gas and the cooling limit the vapors mean free path, resulting in the supersaturation in which nucleation and growing of the cluster can take place.

After their growth the NPs are swept to the main chamber through the small nozzle because of the much higher pressure in the aggregation chamber in comparison to the main chamber. Hydrogen or methane was used to facilitate the formation of nascent clusters during the deposition process.\(^1\) Note that the amount of hydrogen or methane used, supplied using a needle valve, could only be specified qualitatively, because a gauge measuring the gas flow precisely was lacking. The NPs then land on the substrates located in the sample holder in the main chamber. The deposition rate can be monitored by a home-built quartz crystal microbalance (QCM) placed slightly off-center of the conical NPs beam.

There are some parameters that can affect the size and crystallinity of the as-deposited NPs. (1) The length of the aggregation volume can influence the size of the NPs. A longer length provides a longer time and length for the NPs to grow. (2) The addition of He gas (to the Ar) tends to decrease the size of the NPs. Due to the higher thermal conductivity of He compared to Ar, He can cool down the supersaturated vapor faster leading to reduced NPs growth. (3) The discharge current can influence the phase of the as-deposited phase-change NPs. High discharge current (0.3-0.35 A) results in crystalline NPs while amorphous NPs are produced at low current. (4) A backing plate (usually copper) underneath the target reduces the size of the NPs significantly. The thicker the
backing plate is, the smaller the NPs become. Adjusting the above parameters, we have been able to tune the size and crystallinity of the as-deposited phase-change NPs.

2.2 Morphology characterization

The morphology, crystallographic structure and the stoichiometry of the NPs were characterized by transmission electron microscope (TEM) at 200 kV. The phase-change NPs were directly deposited on the TEM grids (holey/continuous carbon or silicon nitride membranes). The composition of the NPs was characterized by energy disperse X-ray spectrometry (EDS) attached to the TEMs (Thermo Instruments on the JEOL 2010 and Bruker Quantax on the JEOL 2010F). The crystal structure of the crystalline phase-change NPs were investigated by high resolution TEM (JEOL 2010F).

2.3 Crystallization

In this thesis, two kinds of crystallization were performed to the phase-change NPs, i.e., slow crystallization and ultrafast crystallization. The slow crystallization were performed to study the size dependence of crystallization temperature for the phase-change NPs, while the ultrafast heating was conducted to study the crystallization kinetics of the phase-change NPs at high temperature.

2.3.1 Slow crystallization

The slow crystallization of the phase-change nanoparticles was studied by in-situ heating in TEM. A single tilt heating holder (Gatan Model 628) with the temperature controlled by a SmartSet Hot Stage controller (Gatan Model 901, with temperature accuracy of 0.1 °C) was used for in-situ heating. The selected area electron diffraction patterns probing at the same area were recorded at different temperatures; an example for GST NPs is shown in Figure 2.2. The specific heating procedure applied to the various samples are detailed in chapter 4. Then the azimuthal integration procedure was applied to the diffraction patterns recorded at different temperatures. This integration procedure derives in a straightforward manner the intensities for different diffraction rings as function of the distance in reciprocal space to the diffraction centre point, as shown in Figure 2.2c. This integration was performed by the PASAD plug-in (http://www.univie.ac.at/-pasad/) in Digital Micrograph software in order to derive the evolution of the diffraction intensity with temperature. Since the diffraction intensity is directly related to the crystallinity of the NPs, we can obtain the crystallization fraction as a function of temperature by taking peak intensity of certain reflection (220 in Figure 2.2d) at various temperatures, as demonstrated in Figure 2.2d. Fitting this plot with the Boltzmann function, as shown in the red dashed curve in Figure 2.2d, the crystallization
temperature of this sample was then derived. The crystallization temperature was defined as the temperature at which the maximum 1st order derivative takes place in the fitting curve, as indicated by the red arrow in Figure 2.2d.

![Image](image.png)

Figure 2.2 Selected area electron diffraction pattern at 25 °C (a) and 180 °C (b). (c) showing the diffraction intensities of different crystal planes at corresponding temperatures and (d) demonstrating the crystallization fraction as a function of temperature. The unit for temperature in (c) is °C.

### 2.3.2 Ultrafast crystallization

The ultrafast crystallization of the phase-change NPs has been performed by ultrafast differential scanning calorimetry (DSC, Mettler-Toledo Flash DSC 1), as demonstrated in Figure 2.3a. A special chip sensor (USF-1, see Figure 2.3b), containing the active area for heating the sample and the reference area, is used for the ultrafast heating. Figure 2.3c shows a zoomed-in image of an active area of the chip sensor, with a single-flake specimen transferred onto the area. The active area of the chip sensor is only at the central square, in dimension 250×250 μm². Unlike traditional
DSC that can only heat and cool the materials up to ~200 K/min, the ultrafast DSC is able to heat the sample with a maximum rate of 40 000 K/s and cool it with a maximum rate of ~10 000 K/s. This ultrafast heating rate thus enables us to investigate the crystallization kinetics of phase-change materials at high heating rate.

Figure 2.3 The Mettler Toledo ultrafast differential scanning calorimeter used for the present thesis work (a) and the accompanying chip sensor used for the heating (b). (c) shows a zoomed-in image of the active area of a chip sensor on which a small sample (flake containing NPs) is present.

The amorphous phase-change materials that were deposited on pre-cleaned substrates (an example shown in Figure 2.4a) were scraped off into small pieces. Note that a silicon nitride membrane (dedicated TEM grid) was fixed relatively far off-center with respect to the NPs beam hitting the substrate (see Figure 2.4a), in order to reduce the NPs coverage for the aim of characterizing the morphology of the as-deposited individual NPs. Then the materials from the high coverage area in the center of the NPs beam were transferred onto the active area of the chip sensor by a hair, as shown in Figure 2.3c. The materials were then crystallized at different heating rates. Note that in this thesis only crystallization of the phase-change materials can be conducted, because the amorphization of the crystalline phase-change materials requires extremely high cooling rate that is beyond the maximum cooling rate of the system. So the crystallized sample has to be removed from the chip sensor after each heating run in order to analyze a next sample. To minimize the oxidation of the materials during heating, a steady N₂ gas flow is introduced.

Heating rates varying from 10 to 40 000 K/s were used for the phase-change materials. At each heating rate, measurements were repeated at least 3 times for low heating rates and 5-10 times for high heating rates, as the crystallization temperatures become more scattered at high heating rates.
Figure 2.4b demonstrates an example of the DSC traces for GST NPs at 250 K/s and 5 000 K/s. In the DSC traces at 250 K/s, an exothermic peak can be obviously observed around 190 °C ($T_{p1}$). This peak corresponds to the amorphous to rock-salt structural transition according to previous (conventional) DSC measurements. When the heating rate is increased, for instance to 5 000 K/s, the $T_{p1}$ shifts to 215 °C. The crystallization kinetics (such as activation energy, crystal growth rate, viscosity) can be then obtained by investigating the $T_{p1}$ at various heating rates ranging from 10 to 40 000 K/s in combination with proper modeling. In Figure 2.4b, a second exothermic peak that relates to the rock-salt to rhombohedral structural transition can be detected in the trace at 5 000 K/s.

![Figure 2.4](image)

Figure 2.4 The as-deposited GST NPs on a glass substrate (a) for the ultrafast DSC measurements and the corresponding DSC traces at different heating rates (b).

### 2.4 Numerical modeling

In order to understand the crystallization kinetics of the phase-change materials from the data obtained by ultrafast heating, numerical modeling relying on Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory and growth rate models was performed to simulate the DSC traces for different heating rates. Then the modeled crystallization temperatures at different heating rates are fitted to the experimental data by adjusting the parameters in the model. After the fitting, the temperature dependent viscosity and crystal growth rate are derived from the fitted models.

Due to the constant heating rate applied, the heating was for the modeling segmented into a series of small isothermal steps (here we took 0.05 K as step size). At each isothermal step the crystals grew...
at a given growth rate with a certain shape (i.e. spheres for 3-dimensional growth or flat cylinders for 2-dimensional growth in the thin film flakes). At the end of each temperature, the extended transformed volume can be calculated and therefore the real transformed volume can be obtained, according to JMAK theory. In order to calculate the extended volume descriptions of both nucleation and growth are required.

2.4.1 JMAK theory

In classical JMAK theory, the extended transformed space $X_e$ can be described as:\(^{5,6,8,9}\)

$$X_e = f \int_0^t I(\tau) \left[ \int_0^\tau u(t) \, dt \right]^n \, d\tau$$  \hspace{1cm} (2.1)

in which $I(\tau)$ is the time-dependent nucleation rate (per unit of untransformed space) and $u(t)$ is the time-dependent growth rate of the crystals. $f$ and $n$ are shape factors related to the growth shape; i.e. for circular growth in 2 dimensions $f$ and $n$ are $\pi$ and 2, respectively, and for spherical growth in 3 dimensions $f$ and $n$ are $4\pi/3$ and 3, respectively. The nucleation for the Ge$_2$Sb$_2$Te$_5$ thin film (which is a nucleation dominant phase-change material) can be treated using a constant density of pre-existing nuclei (site saturation).\(^{10}\) In this dissertation, we also adopted this assumption to simplify the modeling. The justification of this simplification will demonstrate in chapter 3 and 5 for Ge-Sb thin film and GeSbTe nanoparticles. We can simplify $X_e$ as:

$$X_e = fN \left[ \int_0^\tau u(t) \, dt \right]^n$$ \hspace{1cm} (2.2)

with $N$ the density of pre-existing nuclei (per unit of untransformed space).

The real transformed space ($X(t)$) can then, according to the JMAK formulism, be directly related to the extended transformed space:

$$X(t) = 1 - \exp \left[ -X_e(t) \right]$$ \hspace{1cm} (2.3)

If we assume that the changing rate of enthalpy ($dH/dt$) scales linearly with the changing rate of the real transformed space, then the DSC signal can be written as:\(^{11}\)

$$\text{DSC signal: } \propto \frac{X(T + \delta t) - X(T)}{\delta t}$$ \hspace{1cm} (2.4)

with $X(T)$ the real transformed volume at temperature $T$, $\delta t$ the time consumed for each isothermal step. In this case, $\delta t$ is inversely proportional to heating rate ($\delta t = \delta T/\Phi$). Therefore the DSC traces
can be modeled based on the above JMAK theory. It is also noticeable that higher heating rates lead to increments of the (area under) exothermic peaks in the DSC traces at higher temperatures.

2.4.2 Crystal growth models

Two models were used in this dissertation to describe the kinetics of the phase-change materials. One is from the work of Orava et al.,\textsuperscript{10} which is based an expression by Cohen and Grest (CG model) for the viscosity of glass-forming liquids.\textsuperscript{12} The other one is based on the work of Salinga et al.\textsuperscript{13} who used the MYEGA model for the description of the viscosity of supercooled liquids.\textsuperscript{14} The details of these models will be provided in chapter 3. The validity of these two models were verified by comparing the measured crystal growth rate for GeSb thin films with the modeled data from both the models. Note that these above two viscosity models only predict a continuous decrease in slope of the viscosity versus temperature for increasing temperature above the glass temperature. Therefore, these models, although accounting for differences in strong to fragile liquid behavior, can only describe relatively basic viscosity behaviour. For the data obtained by ultrafast heating of GeSbTe NPs this basic behavior turned out insufficient and then a generalized MYEGA model for viscosity, whose details are provided in chapter 5, was utilized to model the DSC traces and fit to the experimental data.
References

(1) Krishnan, G.; Graaf, S. de; Brink, G. H. ten; Persson, P. O. Å.; Kooi, B. J.; Palasantzas, G. 
2849–2856.
279–283.
(13) Salinga, M.; Carria, E.; Kaldenbach, A.; Bornhöft, M.; Benke, J.; Mayer, J.; Wuttig, M. Nat. 
Commun. 2013, 4.
106 (47), 19780–19784.