Chapter 1

General introduction

1.1 History of phase-change materials

The first observation of phase-change characteristics dates back to the 1920s, when Waterman observed a large negative coefficient of resistivity as a function of temperature in MoS₂.¹ Further exploration led him to the discovery of the breakdown of the resistivity coefficient when MoS₂ is heated above a critical voltage by an electrical current, where a permanent increase in electrical conductivity was obtained by applying a voltage higher than the threshold values. It was pointed out that two different phases existed in the material with respect to temperature. However, this discovery attracted little attention due to the lack of a practical application. After the invention and development of the computer drive, the search for a non-volatile random access memory to replace the non-volatile magnetic core memory in the 1950s resulted in more intense studies of chalcogenide based materials. In 1962, the reversible switching between stable high and low conductivity states was observed by applying a proper electrical pulse to As-Te-I glass by Pearson et al., but no explanation of the switching mechanism nor applications was mentioned.² The threshold switching that is important in phase-change memory application was detected by Ovshinsky in chalcogenide glasses in 1968.³ Ge₁₀Si₁₂As₃₀Te₄₈ alloy showed the reversible switching over period of several months, yielding it as a potential memory. This breakthrough triggered the practical interest of using chalcogenides in memory technology. Many patents came out disclosing the operations and appropriate compositions in 1960s, with the first phase-change memory device built by Shanefield.⁴ In the early 1970s, a 256-bit array consisting of phase-change memory was built by Neale and Nelson.⁵ However, due to the enormous power consumption needed to program the phase-change memory in comparison to the conventional metal oxide semiconductor memory, phase-change memory went into hibernation for 2 decades without commercial interest.⁶

The other interest in phase-change materials (PCMs) relates to optical recording media due to the high difference in optical reflectivity between the two phases. After the first demonstration of laser-induced reversible phase-change by Feinleib in 1971, Yamada found superior properties in pseudo-binary alloy, GeTe-Sb₂Te₃, which could be crystalized within 50 nanoseconds in 1987.⁷ This
extremely fast crystallization triggered commercial interest rapidly. In 1990 Panasonic introduced the first product: R/W phase-change optical disc drive (500 MB). After the development of GeSbTe alloy, Ag and In doped SbTe and Ge doped Sb alloys were also developed as storage medium in optical discs.

The application in optical storage facilitated the rebirth of PCMs as the active element in non-volatile random access memory. In early 2000s, the emerging photolithography technology enabled the scaling of components as small as 180 nm. The large decrement in dimensions could efficiently lower the power needed for programming, making phase-change memory again promising. After the formation of Ovonyx by Lowrey and Parkinson in 1999, BAE Systems granted the phase-change memory technology for space applications. In 2006 BAE introduced the first commercial phase-change memory that is 3.3 V, 4 Mb memory device. Ovonyx reached an agreement with Intel in 2000, after which Intel and Ovonyx re-introduced the phase-change memory to the industry in 2001. Hence, the interest from industry and academy grew dramatically, leading to the exponential increase of the US patents and publications on PCMs. Many prototypes of phase-change memory were then developed by various companies, such as 46.7 nm cell (512 Mb) by Samsung in 2004, 90 nm device (256 Mb) by Intel in 2008 and the recent 3D Xpoint based on chalcogenides that is claimed 1000 times faster than NAND and 10 times denser than DRAM. In 2017 Intel released their first SSD (solid state drive) based on 3D Xpoint memory (375 GB).

Nowadays the most widely used and studied PCMs can be categorized in three groups: alloys lying on (or very close to) the GeTe-Sb2Te3 tie line, such as GeTe, Ge1Sb2Te4 and Ge2Sb2Te5; Ag, In and Ge doped Sb2Te, such as Ag5In5Sb60Te30 and the more recently discovered Ge doped Sb.

1.2 Properties

Standard PCMs contain two types of structures, i.e., amorphous and crystalline phases. Due to the absence of long-range order in the amorphous phase, it is complicated to obtain the structural properties. Two crystalline phases exist in the GeSbTe alloy when the PCMs are annealed above their crystallization temperature. At low temperature it is present in the rock-salt structure (space group \( Fm\tilde{3}m \)) that consists of two face-centered cubic sublattices shifted by half the lattice parameter in each direction (1/2,1/2,1/2), where one sublattice is occupied by tellurium atoms and the other is statistically occupied by germanium, antimony and vacancies. When the alloy is annealed at high temperature (350-400 °C), the rock-salt structure then changes to an ordered stacking structure with a rhombohedral structure (in general space group \( \bar{R}\tilde{3}m \)). The amorphous phase can be obtained again by melting the materials (usually around 600-650 °C) and quenching them with extremely
high cooling rate ($>10^9$ K/s). Another switching mechanism, bipolar switching, has been proposed in a special case, where the drift of the Ge and Sb atoms induced by the polar electric field leads to the resistance switching of the mushroom-like GST dome.\textsuperscript{10–13}

In order to be used in optical storage or phase-change memory, the materials have to meet several requirements: large optical/electrical contrasts between the amorphous and crystalline states; high speed crystallization for fast memory switching; low threshold voltage switching the materials for PCRAM (phase-change random access memory); long thermal stability of amorphous phase (at least up to 80 °C) and excellent endurance (high cyclability).\textsuperscript{14}

The electrical conductivity of the crystalline phase is up to 5 orders of magnitude higher than the one of the amorphous phase.\textsuperscript{15} The dielectric function also varies significantly upon crystallization, from $5.0+i1.3$ to $6.5+i3.5$ for Ge$_2$Sb$_2$Ge$_5$ for a wavelength of 830 nm, providing up to 30\% difference in reflectivity.\textsuperscript{16} The optical and electrical contrasts between these two phases enable the PCMs to encode information.

The amorphous state of the PCM can be obtained by a short and large electrical or laser pulse (RESET) which can melt the PCM and where the subsequently high quenching rate makes the PCM amorphous. The amorphous phase can be crystallized (SET) by a longer and lower pulse that enables the heating of the PCM above its crystallization temperature. Typical PCMs crystallize in a time scale of 1-100 ns,\textsuperscript{17} while amorphization takes place much faster than crystallization. The crystallization speed of 500 picoseconds has been achieved for Ge$_2$Sb$_2$Te$_5$ cells by pre-ordering the structure with a low voltage pulse before the SET pulse.\textsuperscript{18} For PCRAM technology, the threshold switching is of key importance without which the PCRAM would not be feasible. Above the threshold voltage the amorphous phase (high resistivity state) starts to become conductive and only then starts to dissipate sufficient heat to allow crystallizing by which the resistivity drops. By applying a higher voltage the RESET process to the amorphous can be achieved. A doped-SbTe phase-change cell (with the dimension of $200 \times 20 \times 20 \text{ nm}^3$) switched from high to low resistivity states at 1.0 V with 30 ns pulses while the RESET could be performed by 1.4 V voltage with 30 ns pulses.\textsuperscript{19} Similar transitions can also be observed for GeTe and GeSbTe phase-change cells. For example, a threshold voltage of 0.65 V was obtained for a 60 nm thick Ge$_2$Sb$_2$Te$_5$ film.\textsuperscript{20} The PCMs present excellent endurance for switching. A PCRAM cell using nitrogen-doped GeSbTe thin films can be switched $10^8$ times.\textsuperscript{21,22} Another cell based on phase-change memory reached $10^{12}$ SET/RESET cycles.\textsuperscript{23} The thermal stability of the amorphous phase is also outstanding. For a 60 nm wide Ge$_2$Sb$_2$Te$_5$ nanowire the data retention time can be as long as 25 years at 80 °C via isothermal characterization at different temperatures.\textsuperscript{24} Although down-scaling the nanowires
decreases the data retention time, the amorphous phase of a 30 nm wide nanowire is still stable for \(\sim5\) years at 80 °C.\textsuperscript{24} Furthermore, doping the PCMs with proper elements, such as Cu,\textsuperscript{25} Sn,\textsuperscript{26} Al,\textsuperscript{27} C,\textsuperscript{28,29} and N,\textsuperscript{30} increases the activation energy for crystallization and increases the thermal stability. For instance 2.7% of Al doping increased the activation energy of GeTe thin film from 3.14 to 5.56 eV. The crystallization temperature then also increased from 179 °C for GeTe to 277 °C for 3.6% Al-doped GeTe film.\textsuperscript{27}

### 1.3 Applications of phase-change materials

The remarkable properties of PCMs shown above enable their applications in many fields. The most successful application that PCMs achieved is data storage. Rewritable optical data storage has been commercially used and is based on the difference in reflectivity between the amorphous and crystalline phases of the PCMs. The phase-change thin films (GeSbTe ternary alloy or AgInSbTe) are usually sandwiched between two dielectric layers, ZnS-SiO\textsubscript{2}. A laser beam is used to read, write and erase the data. Three generations of rewritable optical data storage have been developed. Rewritable compact discs (CDs) using a 780 nm laser were firstly released in early 1990s, containing a capacity of 500 MB. Then the digital versatile discs (DVDs) increase the storage ability to 4.7 GB using a 650 nm laser and smaller feature size. The third generation is the Blu-ray discs with single (25 GB) and dual layer (50 GB) using a 405 nm laser.\textsuperscript{8}

Another promising application of PCMs is PCRAM that is based on the resistivity difference between amorphous and crystalline phases. The amorphous phase has a resistivity usually 3-4 orders of magnitude higher than the crystalline state. The pulse used to read the memory state is low enough to avoid the phase transition of the materials. The phase-change memory has long been considered as the most promising candidate to replace the popular Flash memory, but this recently changed towards application as storage-class memory. Comparing to the long write/erase time (in the scale of \(\mu\)s/ms) of Flash, the PCMs require much less time (in the time scale of tens of ns).\textsuperscript{31} This time can be even reduced into a few ns by either decreasing the cell size or pre-annealing the PCMs.\textsuperscript{18,32} Another advantage of PCRAM is that it has better endurance, i.e., more write/erase cycles compared to Flash memory (\(10^9\) vs \(10^5\)).\textsuperscript{31} Moreover, the voltage needed for the write operation for PCMs is lower than the one of Flash memory (3 vs 12 V). There are also some other contenders for the storage-class memory, such as ferroelectric RAM, magnetic RAM, resistive RAM etc. Scalability and cost will mainly decide which technology will dominate the storage-class memory area, but the strong scalability of the PCRAM make it a strong candidate.\textsuperscript{33} The phase-change memory is also used in neuromorphic computing, where nanoscale phase-change memory was used.\textsuperscript{34} Recently GeSbTe PCMs were used for display and data visualization purposes.\textsuperscript{35}
1.4 Down-scaling ability of phase-change materials

The ability to store information develops along with the human development. From the hieroglyphs in ancient Egypt and oracle in China to the movable type printing in eleven century in China, the search for faster information storage drives the improvement of data storage along the history. The amount of created information did not explode until the invention of the computer and the internet. The generated data doubles almost every two years.36 The gap between the data generation and storage supply is becoming wider with time. Down-scaling the storing unit provides a promising way to increase the storage capacity.37 Moreover, it offers more intriguing properties for applications such as, high speed switching and low power consumption per bit.38 Before the usage of the PCMs in down scaled devices, it is necessary to understand the behaviors of the PCMs shrunk to the feature size of the devices. Therefore many efforts have been devoted to studying the down-scaling of the PCMs.

Ge2Sb2Te5 thin films with thickness ranging from 30 to 5 nm were deposited and capped by or sandwiched between ZnS-SiO2 films using magnetron sputtering.39 The crystallization temperature was then characterized by resistivity measurements. A clear thickness dependence in crystallization temperature was observed, where it increased from 138 to 157 °C for a heating rate of 0.5 °C/min when the thickness reduced from 30 to 5 nm.39 In another work, similar trends were detected for other PCMs, like GST, N-doped GST, Sb2Te and GeSb thin films sandwiched between SiO2 and Al2O3 layers.40 This work also showed that at the ultimate thickness of 1.5 nm crystallization did not take place anymore. However, for GST thin films sandwiched between SiO2 and SiN layers the crystallization temperature was found independent of the thickness when the thickness decreased from 87 to 11 nm.41 Still, the rock-salt to rhombohedral structure transition temperature was significantly decreased with the reduction of film thickness. The capping layers play an important role in crystallization, especially when the films become thinner as for instance the boundary induced heterogeneous nucleation and the stress field induced by the capping layer become more important. It has been observed that the SiN layer can facilitate the nucleation process for GST thin films while SiO2 layer retards it.42 Also it was found that at the metal/PCMs interfaces, like W/GeSb and Al/GeSb, the crystallization process is facilitated, especially when the film thickness is below 5 nm.43 The crystallization time as a function of film thickness has been investigated as well. An increase of crystallization time was found with the decreasing of film thickness for nucleation-dominated PCMs (GST), while the opposite trend was detected for growth-dominated PCMs (AIST).32,44
Two dimensional down scaling of PCMs has been achieved by the VLS (vapour-liquid-solid) process.\textsuperscript{24,45} The GST nanowires with widths shrinking from 200 to 30 nm were synthesized. Strong size dependency of the activation energy for crystallization was detected, where it decreased from 2.34 eV for a 200 nm nanowire to 1.9 eV for a 20 nm nanowire. The surface-induced heterogeneous nucleation was proposed to be responsible for the size dependency.\textsuperscript{45} The writing current and power consumption decrease from 1.4 mA (100 ns) and 2.8 mW for 200 nm width nanowire to 0.16 mA and 0.7 mW for a 30 nm width nanowire.\textsuperscript{24} Similar effects have also been observed for GeTe nanowires.\textsuperscript{46}

When the phase-change memory is further scaled down in three dimensions, the active area of PCMs is like a (semi) nanoparticle. Thus, size dependent properties become crucial before using PCMs in phase-change devices. The first success was achieved using GeTe nanoparticles. By chemical synthesis, both amorphous and crystalline GeTe nanoparticles with average diameter down to 1.8 nm were produced. These nanoparticles showed a strong size dependence of the crystallization temperature,\textsuperscript{47,48} where the crystallization temperature reaches \( \sim 400 \) °C for nanoparticles with a diameter of 1.8 nm, a huge increase in comparison to the bulk GeTe (\( \sim 175 \) °C). Size-dependent polar ordering was also observed in the rhombohedral phase of these nanoparticles.\textsuperscript{49} Ge\textsubscript{15}Sb\textsubscript{85} nanodots with average diameter around 18.5 nm were produced by self-assembled polymer lithography. These NPs showed a crystallization temperature close to the one for bulk GeSb. Yet, growing smaller NPs is not feasible because of the limitations of optical lithography. Due to its complex stoichiometry, preparation of GST nanoparticles with narrow size distribution, composition and crystallinity control has been for a long time a huge challenge. Pulsed laser ablation was utilized to prepare GST nanoparticles, but the limitation of this method is that the size of the obtained nanoparticles showed a large variation (5-50 nm).\textsuperscript{50} An anomalous sequence of phase transitions was detected, in which the amorphous nanoparticle first changed to the rhombohedral structure and then to the rock-salt structure. Another group used magnetron sputtering to grow GST nanoparticles.\textsuperscript{51} Another nanoscaled phase-change memory was achieved by depositing the PCMs in the nanogap between two carbon nanotubes electrodes.\textsuperscript{38} The nanogaps were generated by electrical breakdown, in the size ranging from 20 to 300 nm. In this configuration programming currents of 0.5 and 5 \( \mu \)A for SET and RESET were achieved, respectively. The programming voltage and energy were highly scalable and could be below 1 V and 1 fJ per bit.\textsuperscript{38} Variations in either composition or sizes can be found for all the GST nanoparticles described above. So, GST nanoparticles with better tunable size, crystallinity and composition control are necessary to obtain a sound understanding of the crystallization behavior of the nanoparticles.
1.5 Motivation

As can be deduced from the above literature review, research on phase-change nanoparticles with sizes smaller than achievable with (optical) lithography is highly relevant. Concerning the most important phase-change material Ge$_2$Sb$_2$Te$_5$, hardly any relevant research on nanoparticles appears present. Nanoparticles with relatively monodisperse size distribution have only been demonstrated in Ref. 51, although the finally obtained composition of these nanoparticles showed a relatively large deviation from the stoichiometric 2:2:5 composition. The crystallization temperature of these NPs was assessed from synchrotron X-ray diffraction, but the influence of the NP size on the crystallization temperature was not determined. In the present thesis it is shown that Ge$_2$Sb$_2$Te$_5$ NPs with better tunable size (in the range between 8 and 20 nm), crystallinity and composition control could be synthesized. Detailed structure, morphology and composition analysis was performed using transmission electron microscopy (TEM) based techniques. The crystallization temperature of the NPs based on very low heating rate was determined using in-situ heating TEM as well as the influence of the NP size on the crystallization temperature. In order to obtain a more complete understanding of the crystallization kinetics, ultrafast differential scanning calorimetry has been employed to crystallize single flake of NPs with controlled heating rates in the range from 10 K/s to 40000 K/s. The present thesis thus covers a large existing gap in literature on this highly relevant topic of phase-change nanoparticles.

1.6 Thesis outline

In the next chapter 2, the general methods applied throughout the thesis are described. The main emphasis is on: (1) the synthesis of phase-change nanoparticles based on magnetron sputtering and gas-phase aggregation, (2) the characterization of the NPs using TEM and in-situ heating in the TEM, (3) ultrafast DSC employing controlled heating rates up to 40000 K/s and finally on the models used to interpret the DSC data. In this thesis there are some repetitions on the introduction and equations for different chapters. These parts are kept so that one can directly read individual chapters as a whole story.

Chapter 3 focuses on the crystallization kinetics of Ge$_7$Sb$_{93}$ thin films as obtained by Ultrafast DSC. Modeling the experimentally obtained DSC data allowed extraction of the crystal growth rate extrapolated over a large temperature range in-between the glass temperature and the melting temperature. By comparing the modeled crystal growth rate to directly measured experimental growth rates, we verified the validity of two different models, where one showed to be adequate and
the other not. This work turned out very instrumental for selecting the more suitable model to further analyze the crystallization kinetics of GeSbTe nanoparticles.

Chapter 4 describes the preparation of GeSbTe NPs and subsequent characterization using transmission electron microscopy. The size dependence of crystallization temperature for the GeSbTe NPs was revealed by in-situ heating in TEM. Also observed is that the addition of minor amounts of CH$_4$ to the argon sputtering gas during the NPs production plays an important role in increasing the crystallization temperature of the NPs and thus in improving the stability of the amorphous phase.

Chapter 5 demonstrates the crystallization kinetics of the GeSbTe NPs produced by magnetron sputtering and gas aggregation. The kinetics was studied by ultrafast heating over a large range of heating rates in differential scanning calorimetry (DSC). By analyzing the data with numerical modelling the temperature dependent viscosity and crystal growth rate of the amorphous nanoparticles were unraveled and extrapolated over a large temperature range from the glass temperature to the melting temperature. CH$_4$ incorporation was found as an excellent method to improve the performance of the nanoparticles.

Chapter 6 shows the interaction of the GeSbTe nanoparticles with graphene as support film, studied by state-of-the-art aberration corrected scanning transmission electron microscopy. A large difference in coverage of the NPs has been observed between suspended graphene and graphene supported by an amorphous carbon film, showing the different attachment dynamics of the nanoparticles on graphene and graphene/carbon supports. After aging the nanoparticles, the oxidation dynamics of the nanoparticles was studied as well.

Finally, in chapter 7 the synthesis of GeTe NPs, their crystallization temperature as determined by (low rate) in-situ heating in TEM and their crystallization kinetics as determined by ultrafast DSC are presented also allowing the comparison in behavior of GeTe NPs with the one of GeSbTe NPs as presented in chapters 4 and 5.
References

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