

1. *Title of the project*

Ultrafast crystallization of phase-change material thin films and nanoparticles

2. *Abstract*

In the research proposed here, the focus is on phase-change materials (PCMs) in thin films and nanoparticles. PCMs are highly relevant for memory applications due to their excellent switching properties between the amorphous and crystalline states. They are therefore used as active medium in rewritable optical disks (CD, DVD and Blu-Ray Disks) and have a bright future in non-volatile solid state memories (used in e.g. laptops, smartphones tablets, etc.). The novelty and the power of the proposed approach is the use and combination of new techniques, based on recently developed ultrafast heating and cooling rates in Differential Scanning Calorimetry (DSC) and in dedicated sample holders for Scanning and Transmission Electron Microscopy (SEM and TEM), making it possible to extract both macroscopic and microscopic information in great detail, respectively. In addition, a static laser tester will be used to determine the ultimate crystallization speeds that can be achieved in the PCMs. A standard DSC and a high accuracy TEM heating holder will be employed to particularly study very low crystal growth rates which are crucial for knowing and understanding the archive stability of memories based on PCMs. An additional novelty of the proposed approach is that a particular focus will be held on the so-called fast-growth type PCMs, which have hardly been studied, and on gas-phase synthesized PCM nanoparticles, allowing the study of (up to now unexplored) size dependent crystallization rates. Overall the presented research thus allows innovative quantitative studies of the crystallization kinetics of PCMs from the slowest to the fastest rates, including detailed macroscopic and microscopic information.

3. *Applicant(s)*

J. Momand and prof.dr.ir. B.J. Kooi

4. *Key publications of the applicants*

- P.A. Vermeulen, J. Momand, and B.J. Kooi
Reversible amorphous-crystalline phase changes in a wide range of $Se_{1-x}Te_x$ alloys studied using ultrafast differential scanning calorimetry
The Journal of Chemical Physics **141**, 024502 (2014)
- G. Eising, B.J. Niebuur, A. Pauza, and B.J. Kooi
Competing Crystal Growth in Ge-Sb Phase-Change Films
Advanced Functional Materials **24**, 1687 (2014)
- G. Krishnan, M.A. Verheijen, G.H. ten Brink, a G. Palasantzasa, and B.J. Kooi
Tuning structural motifs and alloying of bulk immiscible Mo-Cu bimetallic nanoparticles by gas-phase synthesis
Nanoscale **5**, 5375 (2013)
- G. Torricelli, P.J. van Zwol, O. Shpak, G. Palasantzas, V.B. Svetovoy, C. Binns, B.J. Kooi, P. Jost and M. Wuttig
Casimir Force Contrast Between Amorphous and Crystalline Phases of AIST
Advanced Functional Materials **22**, 3729 (2012)
- B.J. Kooi, W.M.G. Groot, and J.Th.M. De Hosson
In situ transmission electron microscopy study of the crystallization of $Ge_2Sb_2Te_5$
Journal of Applied Physics **95**, 924 (2004)

5. *FOM research group*
N/A

6. *Institute*
Nanostructured Materials and Interfaces group (NMI)
Zernike Institute for Advanced Materials
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7. *Duration of the project*
4 years PhD project starting from September 2014

8. *Personnel*

8.1 - *Senior scientists*

Prof.dr.ir. B.J. Kooi will supervise and spend 15% of his time on this project

8.2 - *Junior scientists and technicians*

PhD student J. Momand will spend 100% of his time on this project

Ing. G.H. ten Brink will assist various phases of this project as research technician

9. *Cost estimates*

9.1 - *Personnel positions*

One PhD student for standard period of 4 years (k€ 204)

9.2 - *Running budget*

Standard expenses for experimental position (4 years x k€ 15)

9.3 - *Equipment*

All the necessary equipment for the proposed research is directly available within the Zernike Institute for Advanced Materials.

9.4 - *Other support*

N/A

9.5 - *Budget summary*

A brief summary of the budget requested from FOM is given below (in k€):

	2013	2014	2015	2016	2017	2018	TOTAL
PhD students	0	17	51	51	51	34	204
postdocs	0	0	0	0	0	0	0
technicians	0	0	0	0	0	0	0
guests	0	0	0	0	0	0	0
personnel	0	17	51	51	51	34	204
running budget	0	5	15	15	15	10	60
equipment	0	0	0	0	0	0	0
TOTAL	0	22	66	66	66	44	k€ 264

10. Research programme

10.1 – Research plan and motivation

For this research it is proposed to exploit recent developments with unsurpassed heating and cooling rates that have become available in Differential Scanning Calorimetry (DSC) and in dedicated sample holders (Aduro™ System in combination with E-Chips™) for Scanning and Transmission Electron Microscopy (SEM and TEM). Although both developments by themselves offer strong innovations to experimental research, particularly the uniquely combined approach proposed here will enable major breakthroughs in the analysis of many substances and materials for which high heating and cooling rates largely alter their structure and properties. Many materials like polymers, alloys, polymorphic substances and composites develop a variety of structures, generally with a metastable nature, which depend on the cooling conditions during their production. During heating, reorganization processes such as (re)crystallization, phase separation and melting may occur. Although the potential application range is huge, in the present work the focus is on phase-change materials (PCMs), which include chalcogenides typically on the ternary phase diagram of Ge, Sb and Te (GST), and particularly on crystallization processes in amorphous thin films and nanoparticles.

PCMs are currently investigated intensively, mainly to replace in the near future the popular Flash and DRAM types of memory, which are used in e.g. laptops, smartphones, tablets, etc. PCMs already have been applied successfully in optical recording, well-known from the rewritable CD, DVD and Blu-Ray Disk formats. Phase-change memories can be switched reversibly billions of times between amorphous and crystalline phases and they exploit the large differences in optical reflectivity or electrical resistance of the two states. A fast high energy pulse transforms the crystalline cell into an amorphous phase by melt-quenching, where the liquid gets ‘trapped’ in the amorphous solid due to application of high cooling rates. The crystalline state can be re-obtained via a longer lower energy pulse that heats the cell optimally below the melting temperature, where the mobility of the atoms becomes high, allowing crystallization. This can also be done fast (<100 ns), but not as fast as melt-quenching, which is possible in picoseconds. Particularly, the combination of ultra-fast crystallization kinetics with large electrical/optical property changes is a unique feature of PCMs.¹⁻⁴

The power of ultrafast DSC in PCM research has been demonstrated recently, showing that for the important $\text{Ge}_2\text{Sb}_2\text{Te}_5$ material the kinetic coefficient for crystal growth (which is the limiting growth velocity when the thermodynamic factor is one) has a non-Arrhenius temperature dependence, indicating a high kinetic fragility of the liquid ($m \approx 90$).⁵ Furthermore, there was evidence for substantial decoupling of crystal growth from viscous flow on cooling towards the glass transition temperature T_g : the growth rate extrapolated to T_g was found to be 10^5 times faster than would be calculated from the viscosity of 10^{12} Pa·s at the glass transition. In a subsequent paper also the effect of sandwich layers around the PCM films has been studied.⁶ At heating rates up to 1000 K/s, the sandwich layers retard crystallization, an effect attributed to crystallization induced stress. At greater heating rates (≥ 5000 K/s), and consequently higher crystallization temperatures, the stress is relaxed, and sandwich layers catalyze crystallization. Although this work is of excellent quality, an important element that is missing is that only the overall crystallization rate is assessed using the ultrafast DSC measurements, but not the microscopic information needed to distinguish between nucleation and growth rates and to determine growth morphologies (crystal shapes and orientations). In the approach proposed here it is planned to subject identical (and other) sample types to the same ultrafast heating rates in both the ultrafast DSC and in the ultrafast heating TEM holder. Using the latter also the required microscopic information of the crystallization process can be obtained. Moreover, as will be explained in more detail below, the plan is to study different types of PCMs not studied before.

Next to employing these ultrafast heating rates in DSC and TEM (with rates up to 40000 K/s), also laser pulses with pulse durations down to about 5 ns will be used. Then the reversible switching between amorphous and crystalline phases can be studied as a function pulse power and pulse duration. Using nanosecond pulses the ultimate speed in crystallization of PCMs can be studied. Note that a memory that can switch with speeds of 20 ns is still very competitive, because SRAM and DRAM, which are currently used as the fastest memories, have comparable access times.⁴ Using ordinary DSC and a high accuracy TEM heating holder for isothermal and isochronal crystallization studies with low heating rates, also the amorphous phase stability can be scrutinized. This is very relevant for determining the data retention, i.e. archive stability of PCM-based memories, which typically has to be 10 years at 90 °C (and thus longer at lower temperatures). The group of the applicants has extensive experience in performing in situ heating crystallization studies in a TEM.^{7,8} A few example images are shown in Fig. 1.

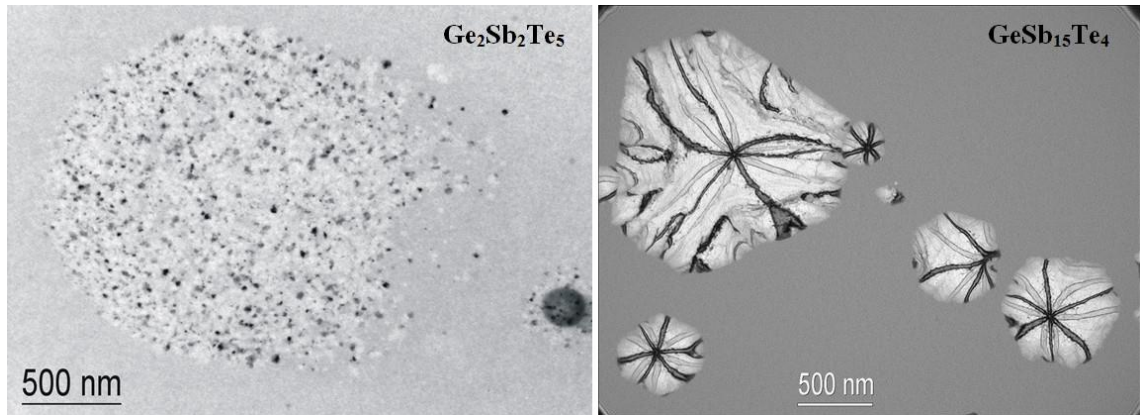


Fig. 1: TEM images of nucleation-dominant material (left) and fast-growth material (right) obtained by in-situ heating in the TEM, allowing the imaging of crystal nucleation and growth down to atomic resolution.⁷

Focus of the present work will be on thin films and nanoparticles. The sensor chips employed in ultrafast DSC are consumables, i.e. the material to be investigated is directly deposited on the sample area on these chips, which therefore should only be used once. A logical starting point when investigating thin films, is to deposit these films directly on the sensor chips. However, this approach was also initially followed in the seminal work where PCMs were studied for the first time using ultrafast DSC.^{5,6} It turned out that this approach does not work for the reason that during the extreme heating rates the difference in thermal expansion between the chip and the PCM film results in fracture and delamination such that proper contact between the sensor sample is lost. An alternative method is scraping an as-deposited thin film off glass substrates and placing a small amount (50-100 ng) of the flaky powder onto the sample area of the sensor chip.^{5,6} With such samples, there is inevitably some variation in the quality of the thermal contact with the instrument sensor. At a given heating rate there is a spread in peak temperature corresponding to crystallization. In fitting the data, most weight should be given to the lowest peak temperature, reflecting the best thermal contact. This can provide a reliable basis for applying the Kissinger analysis to the data.

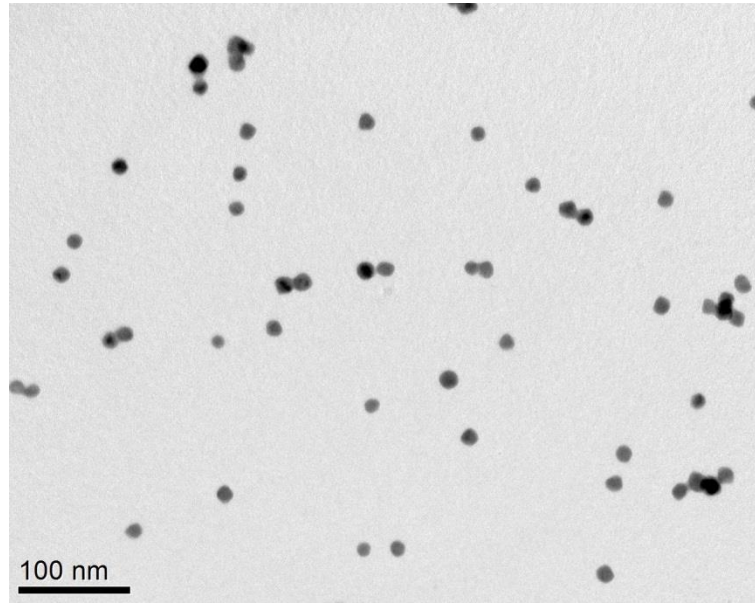


Fig. 2: TEM image of as deposited crystalline nanoparticles grown from a $\text{Ge}_2\text{Sb}_2\text{Te}_5$ target, deposited for initial tests of the project. These particles have a relatively monodisperse size distribution as produced with the dedicated nanocluster source. It can be shown that the particles are crystalline by electron diffraction. Also, the different contrast between the particles is due to different crystallographic orientations.

In this work the same approach for thin films will be used and additionally, a more powerful approach, to directly deposit PCM nanoparticles with a good size control on the sensor area, will be applied. The group of the applicants has extensive experience in producing nanoparticles with a dedicated nanocluster source based on magnetron sputtering and cluster formation and growth in an aggregation volume, before they are deposited. Such a source allows, under favorable conditions, an excellent size control of the nanoparticles produced, i.e. the particles have a relatively monodisperse size distribution. Initial tests for PCM nanoparticle production have succeeded, giving monodisperse coverage, shown in Fig. 2, and both amorphous and crystalline particles, shown in Fig.3, made from a $\text{Ge}_2\text{Sb}_2\text{Te}_5$ source target. These initial tests were meant as proof of concept for the project, indicating that it is feasible to produce amorphous nanoparticles for the proposed experiments.

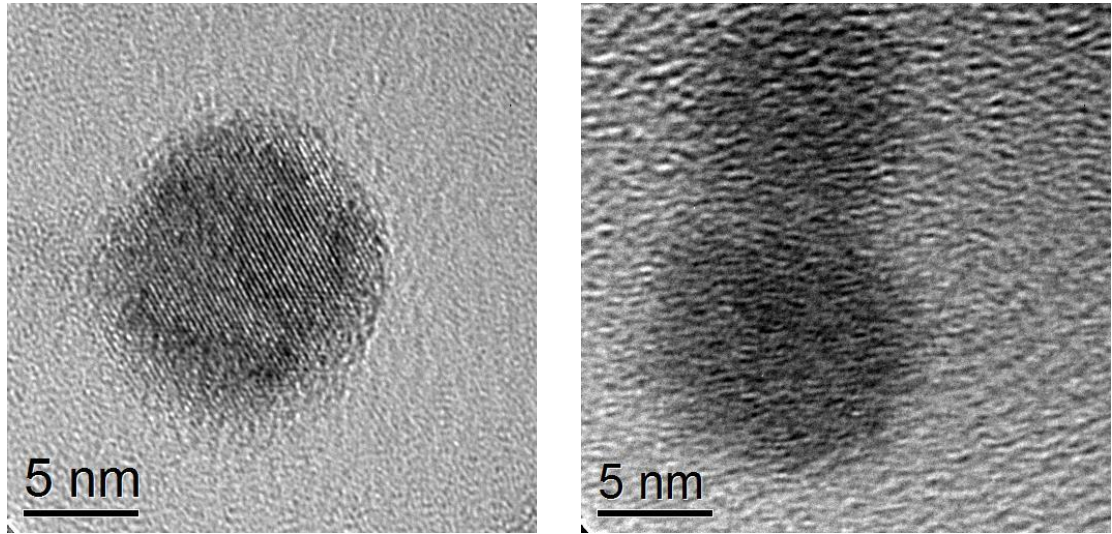


Fig. 3: Atomic resolution TEM images of crystalline (left) and amorphous (right) nanoparticles, prepared using different conditions from a $\text{Ge}_2\text{Sb}_2\text{Te}_5$ target as proof of concept for the project. The crystallinity of the particles can be easily detected by electron diffraction in the TEM and therefore the particle on the left shows modulations of the atomic layers. The particles on the right do not have this property and thus contrast due to a crystalline atomic structure cannot be resolved indicating the amorphous nature of the particles.

For the present work the plan is to also deposit Sb-based nanoparticles, where the starting point is pure Sb. Such pure Sb thin films do not allow controlled crystallization studies because they demonstrate explosive crystallization at room temperature, even for film thicknesses of tens of nanometers and it is therefore hardly possible to analyze these films in the amorphous state. If after thin film deposition Sb is still amorphous, it will show spontaneous crystallization (at room temperature) shortly after. Therefore, to stabilize the amorphous phase, Sb requires 'doping' for instance with Ge. However, there are good reasons to expect that pure Sb nanoparticles have a (meta)stable amorphous phase at room temperature and thus allow controlled crystallization studies during heating. If these particles also show crystallization at room temperature, then the same type of doping, e.g. with Ge, as needed for thin films will also be applied to the nanoparticles. Study of Ge-doped Sb nanoparticles is anyhow planned for allowing a close comparison with the results of thin films with the same composition.

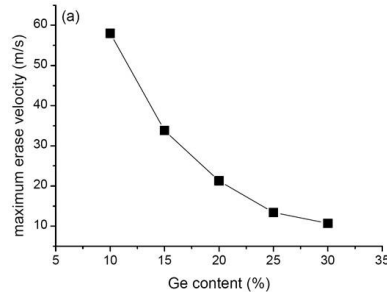


Fig. 4: Maximum erase velocity of Sb-rich alloys as function of Ge doping. This trend indicates that the crystallization speed of such alloys can exceed 60 m/s.

The interest for Sb comes from the fact that it is probably impossible to find a material with higher crystallization speed. Fig. 4 shows results reported by Philips for the maximum crystallization speed of Sb as a function of Ge doping.^{9,10} Decreasing the Ge concentration from 15 to 10 at. % increases the crystallization speed from 34 to 58 m/s. Simple linear extrapolation thus indicates that pure Sb should have a maximum speed of ~100 m/s. These doped Sb alloys are thus extremely interesting from point of view of crystallization rates and will be studied in detail in the present work. With doping, also the data retention can be tuned to reach good specifications. The major problems of these alloys for applications is their cyclability (high temperature stability), because they have a strong driving force for decomposition. Decomposed alloys cannot be switched to the amorphous state anymore and result in memory failure. Such problems will be tackled in the proposed research.

10.2 – Time management

Prof.dr.ir. B.J. Kooi will assume responsibility on daily basis for:

- i) Administrative, technical, and financial project execution with the associated reporting duties
- ii) Efficient planning to ensure accomplishment of each task objectives, as described below.
- iii) Proper supervision and monitoring adjustments of the work plan as a consequence of results obtained in order to achieve the project goals.
- iv) Assessment of the quality of the outputs from each task, including the dissemination and exploitation of the results through publications, congress participation, and joint progress meetings where relevant industrial partners (through M2i and Micron) will be involved.

The time planning for the 4 year PhD project is given in the table below:

	2014-2015				2015-2016				2016-2017				2017-2018			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 1																
Task 2																
Task 3																
Task 4																
Task 5																
Task 6																
Task 7																
Task 8																

Task 1: Extensive literature review.

Task 2: Ultrafast DSC on readily available PCM thin films from previous research ($\text{Ge}_x\text{Sb}_{1-x}$ and doped $\text{Sb}_{3.3}\text{Te}$). During this task the student will learn how to use the Flash DSC and perform ultrafast DSC experiments independently (required for experiments with nanoparticles).

Task 3: PCM nanoparticle production employing an available dedicated Mantis Nanocluster Source. Training for the deposition source will be given by ing. G.H. ten Brink, who will also assist in the modification of the deposition chamber for direct deposition on UFS1 and E-chip sensors. Additional training on PCM thin film growth will be given through a two months exchange between the RUG and RWTH Aachen under supervision of prof.dr. M. Wuttig.

Task 4: Learning to work with TEM and with dedicated TEM heating holder. The TEM is useful in this stage to be able to characterize nanoparticle growth and perform ultrafast heating experiments on PCM thin films ($\text{Ge}_x\text{Sb}_{1-x}$ and doped $\text{Sb}_{3.3}\text{Te}$ or newly acquired samples from RWTH) for direct comparison with ultrafast DSC results.

Task 5: Ultrafast DSC on the PCM nanoparticles produced, allowing determination of size dependent crystallization kinetics of PCMs. During this task period also standard DSC (with low heating rates) will be performed, because this has also not been studied before for size-controlled nanoparticles and is important for understanding data retention.

Task 6: TEM analysis including in-situ slow and ultrafast heating of the PCM nanoparticles produced, allowing direct comparison with slow and ultrafast heating DSC results on nanoparticles.

Task 7: Laser and high-speed camera characterization of PCM thin films, nanoparticles and nanoparticle based films. Laser pulses with various powers and durations (down to 5 ns) will be employed, particularly for determining the ultimate crystallization speeds of the thin films and nanoparticles also studied with ultrafast DSC and TEM. The crystallization results in as-deposited and in melt-quenched structures will be compared.

Task 8: Writing the PhD thesis.

10.3 – Background information

Phase-change materials (PCMs), such as the materials presented in the proposed research, exhibit a unique and unconventional set of properties:^{1-4,11-13}

1. Large electrical/optical contrast between the amorphous and crystalline phases.
2. High thermal stability of amorphous marks at low temperature, corresponding to data retention of say 10 years at 100 °C (and longer at lower temperatures).
3. High crystallization rates, i.e. allowing erasure of amorphous marks within 100 ns at elevated temperatures, e.g. 450-500 °C.
4. Excellent cyclability between the amorphous and crystalline phases, e.g. 10^9 times.
5. Low melting points (typically 600 °C), enabling easy amorphization by melt-quenching.

Apart from the first point, crucial and largely unanswered fundamental questions are related to how PCMs can combine this set of complementary properties.

Most experimental and theoretical work on PCMs is focused on so-called Nucleation-Dominant Materials (NDMs), with typical $\text{Ge}_2\text{Sb}_2\text{Te}_5$ composition. These materials show ultra-fast crystal nucleation leading to nano-sized crystals, as shown in Fig. 1. Another class of PCMs is the one of so-called Fast-Growth Materials (FGMs), with typical $\text{GeSb}_{15}\text{Te}_4$, also in Fig. 1 or $\text{Ge}_{15}\text{Sb}_{85}$ composition. They show low nucleation

rates, but ultra-fast growth leading to micron-sized crystals; see earlier work (Kooi et al.), demonstrating clearly this difference between NDM and FGM.⁷ In many publications the results for NDMs are considered representative for all PCMs, but they neglect the large differences between NDMs and FGMs. Fast crystal nucleation is not required for PCMs, because in actual applications the amorphous mark is generally surrounded by crystalline material that can provide re-growth into the amorphous mark. Particularly with the continuous down-scaling of memory sizes, all PCMs increasingly shift towards FG behaviour.¹⁵ The present work will also particularly focus on FGMs, because they are much less investigated than NDMs and thus leave more room at the bottom for new exciting findings. Moreover, FGMs have not been studied at all with ultrafast DSC.

The high crystallization rates of PCMs, with velocities up to 60 m/s,^{9,10} can only be explained in case of short-range atomic movements. These rates require that at least every picosecond an atom has to jump effectively across each nm² interfacial area from the amorphous to the crystalline phase. With a vibration frequency of atoms of 10¹³ Hz this means that an extreme large fraction of jump attempts must be successful or more likely that a collective (phonon) process is operational. In a seminal publication, Kolobov et al.¹⁶ presented the first explanation for both the large differences in optical/electrical and kinetic properties of PCMs and attributed these to a so-called umbrella flip of Ge atoms in alloys like GeSb₂Te₄, Ge₂Sb₂Te₅. Extended X-ray Absorption Fine-Structure (EXAFS) experiments showed that the Ge atoms are tetrahedrally coordinated in the amorphous phase and octahedrally in the crystalline phase. This coordination switch can be explained by a kind of umbrella flip of the Ge atoms. Such a flip can be expected to occur ultra-fast and thus explains the high crystallization rates. However, several problems are associated with this explanation. First, it (over)simplifies the difference in structure between the amorphous and crystalline phases to only the Ge atom positions, neglecting the significant repositioning/ordering of Sb and Te atoms. Second, density-functional theory calculations showed that 4-fold coordinated Ge atoms would relax without energy barrier to octahedral positions of the crystalline phase.¹⁷ Third, it only holds for PCMs having a significant concentration of Ge atoms and many PCMs exist, particularly of FG-type, that do not contain any group IV element, like AgInSbTe, GaSb or GaSbTe.^{1-3,9,10,18} Therefore, the umbrella flip cannot be a generic explanation for the fast crystallization kinetics of PCMs. Moreover, the main issue is not the high crystallization rates itself, but the combination of these high rates at elevated temperatures like 500 °C with the very low rates at low temperatures like 100 °C.

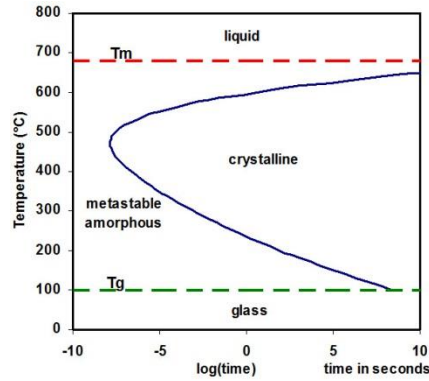


Fig. 5: Time-Temperature-Transformation diagram showing schematically the time required to crystallize an amorphous bit in a typical PCM as function of temperature. PCMs can show extreme variation in times; more than 30 years to crystallize at 90 °C and ~14 ns at 470 °C (at the 'nose' of the blue line).

Fig. 5 is instrumental for better understanding the extreme kinetic properties of PCMs. It is a Time-Temperature-Transformation diagram depicting the time required to crystallize an amorphous mark (a memory bit) as a function of temperature. At 90 °C crystallization takes more than 30 years. However, at the 'nose' temperature of ~470 °C it takes only about 14 ns to crystallize the mark. This huge decrease in crystallization times by an increase of ~400 °C is only possible when the activation energy for crystallization is very high, i.e. of the order of 3 eV.⁸ It can be attributed largely to increased atomic mobilities with increasing temperature. However, at the same time the driving force for crystallization (Gibbs-free energy difference between the amorphous and crystalline phases) decreases, because the undercooling with respect to the melting temperature decreases. These two competing effects result in a minimum crystallization time at the 'nose' temperature. So, the main question to be answered for PCMs is how the atomic mobilities, more accurately the effective jump rate of atoms from the amorphous to the crystalline phase, can be so extremely different at say 100 °C and at the nose temperature. The planned experiments for the present research project should provide new important knowledge and understanding of the crystallization kinetics of PCMs across this entire range from say 100 °C up to the nose temperature and in specific cases also up to the melting temperature of the PCMs.

11. Infrastructure

The following infrastructure and equipment are directly available to perform the presented research:

- Electron microscopy instruments: JEOL 2010 TEM/STEM-LaB₆+EDX (200 kV, point resolution 0.23 nm), JEOL 2010F TEM-FEG+GIF+EDX (200 kV, information limit 0.11 nm), Dedicated heating holders for JEOL 2010 and 2010F, Tescan Lyra FIB-SEM-FEG, Philips ESEM-FEG+EDX
- Veeco PicoForce AFM (combined Atomic Force Measurements and surface analysis, such as topography and electric/magnetic characterization).

- Vacuum system has been developed for pumping the PicoForce AFM under high vacuum conditions.
- Mettler-Toledo Flash DSC 1 (ultrafast Differential Scanning Calorimeter).
- Perkin Elmer DSC 7 (standard Differential Scanning Calorimeter).
- Photron high speed camera (10^5 frames/sec).
- Static laser tester inducing and measuring reversible phase transformations using variable power and duration laser pulses (wavelength 630 nm, minimum spot size 0.8 μm , shortest pulses 5 ns, maximum power 150 mW).
- An UHV nanoparticle deposition system (Nanogen 50 / Mantis deposition System), which is equipped a quadrupole mass filter and with additional magnetron sputters (2 sputter sources) for thin film deposition.
- Additional sputter and optical characterization facilities for PCM films at RWTH Aachen.

12. *Application perspective in industry, other disciplines or society*

With respect to technology, the proposed research has direct relevance to non-volatile electronic solid-state memories, as e.g. used in laptops, smartphones, tablets, etc. Already companies such as Micron and Samsung have started shipping such devices into the market.^{1-4,19,20} The group of the applicants has good connections with Micron and NXP who are interested in the gained knowledge of PCMs and the types of materials necessary for use in such memories. These companies typically already have the facilities to manufacture PCM memory chips, so that transfer of knowledge could be implemented without much modification. The reason that so much attention is paid to find an alternative to Flash and DRAM types of memory is because it is expected that further improvement of such technology would become unfeasible, e.g. NAND Flash memory will reach optimum conditions in 2024.²⁰

Additionally, memories based on PCMs obviously have the properties of fast switching in combination with high thermal stability of the amorphous phase (non-volatility). These memories thus can function for both storage and processing (working memory). Such universal²¹ memory devices could then not only improve the performance of modern day electronic technology, but on a more fundamental level give possibilities of new computer architectures, e.g. computers based on PCM memories would boot instantly. While technology is marching forward along the trend of Moore's law, it is good to realize that no memory application has thus far reached the performance, particularly in terms of operating power of the human brain. PCM architectures also have been proposed and tested to perform (non von-Neumann) cognitive computing and to function as neurons and synapses creating artificial brain function with simplified schemes than possible with CMOS based transistors.²² This illustrates how much room there is at the bottom and the necessity for the search of new phenomena advanced materials.

13. *FOM subfield classification*

NANO

14. *References*

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