Crystallization phenomena in germanium antimony phase-change films
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Chapter 1

Introduction

Abstract. Phase-change materials have been intensively studied since the beginning of the 1960s and have seen many developments in the areas of scientific progress and industrial applications. These developments were strongly linked to the progress in (sub)micron and nanotechnology. The goal of this chapter is to provide insights into the achievements within the last 50 years. An overview will be given of the remarkable properties of phase-change materials, which made them very suitable as active media in rewritable optical disks, well-known from the CD, DVD and Blu-ray Disk formats, and makes them excellent candidates for replacing flash-memory in the near future. At the end of the chapter an outline of this thesis is given.

1.1 Phase-change materials

1.1.1 History

The first mentioning of a material with electrical phase-change properties is found in an article by Waterman in 1923. [1] While his work was focused on the thermionic emission of molybdenite (MoS$_2$), a large negative coefficient of resistivity was found during heating, as well as a threshold level for conduction when heated using an electric current; typical properties of currently used phase-change materials. As the digital computer had yet to be invented, no digital memory application was associated with these first findings. After the invention of the electronic computer in the 1939 by Atanasoff, the junction transistor in 1948 [2] and the integrated circuit in 1958 [3] the limit of memory devices was quickly reached and a faster, smaller and more reliable way of non-volatile computer memory was needed. Several new techniques were investigated. Chalcogenide materials, alloys with, in general, elements from group 16 from the periodic table (of which S, Se and Te are nowadays commonly used in phase-change materials), proved to be good candidates. The ability to switch was reported for AsTeI in 1962. [4]

In 1968 Ovshinsky published a paper demonstrating a reversible switching memory cells with a Te$_{48}$As$_{30}$Si$_{12}$Ge$_{10}$ composition. [5] Based on this alloy Shanefield built the first working memory device including a controlling circuit for reliable cell programming. [6] Promising memory devices were developed by several groups: a 16x16 array by Neale and Moore in
1970 [7] and a 1024-bit device in 1978 by Shanks and Davis. [8] However, due to the large phase-change cell sizes, the memories devices had a high power consumption compared to the competing techniques. This, combined with data reliability problems, resulted in a loss of interest in phase-change memories and halted the research for memory applications. It would take about 20 years before phase-change materials were found again in commercial memory devices.

In 1982 the Compact Disk-Read Only Memory (CD-ROM) was introduced. A memory where data is stored on a disk in a spiral track using reflective bumps and non-reflective holes. Using an infrared (780 nm) laser diode this difference in reflectivity is measured and zeros and ones are represented. The only-once recordable CD-R was introduced in 1988 and allowed to write marks in a photo-sensitive dye using a laser diode with a higher output power. Once the information has been written it could not be erased again. The development of rewritable CDs started shortly after the introduction of the CD-ROM [9, 10] but it took till 1997 before the CD-RW was commercially introduced. In the CD-RW a layer of phase-change material acts as the data layer. Initially in a crystalline state, amorphous marks, with a different reflectivity than the crystal phase, can be written in the data layer by locally melting the phase-change material with a short laser pulse. Rapid cooling causes this liquid state to be frozen, resulting in a melt-quenched amorphous mark. If the mark is heated again using a longer laser pulse, but with a lower laser power, the amorphous mark recrystallizes. Advancements in data capacity were mostly gained by moving to a shorter laser wavelength (650 nm for DVD and 405 nm for Blu-ray) and increasing the numerical aperture of the employed lens, resulting in smaller marks. By using double layered discs the capacity was further increased from ~780 MB to ~50 GB.

With the enhancements in lithography, especially the reduction in minimum feature size, electrical phase-change memory (PCM) became of interest again in the early 2000s. Based on phase-change compositions used for DVD±RW (mainly Ag$_5$In$_5$Sb$_{60}$Te$_{30}$), [11] new alloys were developed suitable for fast electric cells. The first commercial available memories arrived in 2008 [12] and are now used, although still on a small scale, in mobile phones. [13] Additionally, germanium-doped antimony based alloys are becoming more popular and look like good candidates for future devices. [14, 15]

1.1.2 Remarkable properties

Phase-change materials based on (doped) germanium, tellurium and antimony alloys show some truly remarkable properties suitable for memory purposes. The large change in optical contrast between the amorphous and crystalline phase can be easily detected, which is why they are widely employed for the application in rewriteable optical media, like CD-RW, DVD±RW
1.1. Phase-change materials

and Blu-ray RE. For electrical memories the large difference (several orders of magnitude) in electrical conductivity between the amorphous and crystalline phase is exploited to store information.

The usability of phase-change materials in a memory device originates from several favorable properties. The first is the low energy needed to switch between the amorphous and crystalline phase. Heating to a temperature above the glass transition temperature, $\sim 150^\circ C$ [16] for the commonly used phase-change material Ge$_2$Sb$_2$Te$_5$, is enough for fast crystallization. Switching to the amorphous phase needs heating to above the melting temperature, which is relatively low for Ge$_2$Sb$_2$Te$_5$ ($\sim 600^\circ C$). In optical discs the heating is provided by a laser pulse, a (semi-transparent) heat-absorption layer is present to provide enough cooling for freezing the liquid phase into a solid amorphous phase (melt-quenching). In electric memory devices the phase-change cells are heated by exploiting Joule heating: the current flowing through the cell when a voltage is applied over the cell will heat the phase-change material to the desired temperature. When the cell is in the crystalline phase, and thus in the low resistance state of typically several k$\Omega$s, a short voltage pulse is already enough to melt the cell and quench it in the amorphous phase afterwards. For a typical line-cell it has been shown that a pulse with a 30 ns pulse width and an amplitude of 1.4 V will amorphize the phase-change cell. [17] To crystallize the amorphous cell a lower temperature is needed, between the glass transition temperature and melting temperature. However, due to the high resistance state of the cell, typically $\sim 100$ k$\Omega$–10 M$\Omega$, a much higher voltage, with respect to the crystalline cell, would be needed to generate a current that is high enough. The reason phase-change materials remain useable is due to the threshold switching behavior they exhibit. When a sufficient large electric field is applied over the amorphous cell the electrical resistance will drop significantly, allowing a large enough current to flow that will heat the cell above the glass transition temperature. [18, 19] A pulse width of 30 ns with an amplitude of $\sim 1.1$ V is enough to crystallize a typical line-cell. [17] It has already been shown that phase-materials are able to switch to the crystalline state with even shorter pulses of 1–30 ns. [20] These short electrical pulses are sufficient, because of the extreme crystallization speeds of more than a few meters per second that are possible in phase-change materials. Amorphization can be done even faster, and it has been shown that femtosecond pulses are able to amorphize a crystalline Ge$_2$Sb$_2$Te$_5$-film. [21]

The second property, making phase-change materials suitable for memory applications, is the capability to switch at a short time scale between the two phases, while at the same time both phases are stable for a long time at operational temperatures. The short pulses used for switching are in strong contrast with the retention time of the amorphous phase at operational temperatures (maximum 80 $^\circ C$ for consumer products). Current materials are stable for more than 10 years (more than 15 orders of magnitude higher than the switching time!) at these
temperatures before losing their information due to unwanted crystallization. Apart from being stable at elevated temperatures, it is also important that the phase-change cells are able to switch often, while remaining reliable. For optical applications, like CD-RW and DVD±RW, the phase-change materials can be switched up to 1000 times. Electrical phase change memories have already been switched up to $10^{11}$ times. [22] The PCM cells fail when they get stuck in either one of the two states and are unable to switch back under normal writing conditions. Set-stuck, when the cell stays crystalline, is typically caused by compositional (stoichiometric) changes. Reset-stuck, the cell stays amorphous, is typically caused by void formation. The high electric field needed to switch a phase-change cells induces electric field- or current-induced atomic transport and electromigration which in turn cause compositional changes and void formation. [23] The compositions of the phase-change materials are crucial for their functionality. Changing the composition with only several percent will already change the crystallization properties significantly. This will also be shown in chapter 3.

1.1.3 Memory applications

The next step for phase-change memory is the commercial application in electric solid state memory devices. Compared to traditional hard disk drives (HDDs), which employ a thin ferromagnetic film for data storage, PCM memories are faster due a reduced access time and higher data throughput, and provide true random access. Additionally, a HDD uses mechanical parts, for spinning the magnetic disks and moving the read and writing heads, which can cause mechanical wear. For mass storage a HDD is still preferable as the price per GB is still favorable due to the lower production costs per GB.

Flash memories (in particular NOR flash) will be most likely replaced sooner than HDDs by PCM. Both Flash and PCM technologies provide a solid state memory solution. However, PCM has some significant benefits. Flash memory derives its name from the writing method it employs: it “flashes” whole blocks when erasing data as it cannot write and erase a single cell at a time. PCM does not have this drawback and provides much faster bit-wise programming and reading. Additionally, PCM has lower latency and higher writing and erasing speeds; [24] and also provides better downscaling of the phase-change cell size than the flash cells. Where for flash memory the programming of the cell becomes more difficult with decreasing sizes and reaches fundamental limits soon, [25, 26] it has been shown for PCM that the cells remain switchable and that, additionally, the programming currents also go down. [27] However, flash memory can write many bits parallel due to its low power consumption. If PCM wants to be really competitive to flash memory the power requirements of PCM need to be reduced.

Next to replacing non-volatile memories, it might be possible to replace the volatile dy-
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Dynamic random-access memory (DRAM) with PCM. Currently, PCM already has a similar latency and write speeds as DRAM. [24] Moreover, DRAM is reaching its limits in scalability at a feature size of \( \sim 30 \text{ nm} \) while PCM remains scalable below \( \sim 10 \text{ nm} \) and is capable of having a smaller feature size when using diode switches. [28] Additionally, PCM is a more energy efficient technology than DRAM which, inherent to its reading and writing procedures, requires relatively much energy. [19] It has been demonstrated for single cells that the endurance of PCM (the amount of times a cell can switch between the crystalline and amorphous phase) can match that of DRAM. [29] Large scale PCM devices currently reach \( \sim 10^8 \) cycles, which will result in an estimated lifetime of the PCM devices of 5 to 6 years, [30] whereas DRAM has a practical infinite lifetime.

In conclusion, the scalability and fast switching times makes phase-change memories an excellent replacement for current hard disks and solid state drives solutions. If the endurance and reliability can be further improved it can also replace DRAM in the future to form a universal memory. This would additionally require new software architectures and memory concepts as the traditional boundary between RAM and data storage will fade.

1.1.4 Germanium-doped antimony alloys

The research presented in this thesis was started with the aim to investigate (the presence of) so-called explosive crystallization (EC) phenomena in phase-change films. Upon crystallization of the amorphous phase, induced by an external energy source, the entropy decreases as the system goes from the randomly ordered amorphous phase (high in configurational entropy) to the highly ordered crystalline phase (lower in configurational entropy). The latent heat released during crystallization can be used to create a self-sustaining crystallization process under certain conditions. This process is known as explosive crystallization (EC). The first report (from 1869) of explosive crystallization can be found for antimony layers with a thickness of “at least half a sixpence up to half an inch” (0.5 – 12.7 mm). [31] It was found that if these layers are “struck gently or rubbed” an explosion occurs with a flash of light and significant heat production. Later experiments showed the presence of explosive crystallization in films of other pure elements as silicon and germanium [32, 33] and (In,Ga)Sb alloys [34] where extremely fast crystal growth rates have been reported (>10 m s\(^{-1}\)). However, literature does not provide systematic experimental studies on EC in phase-change material alloys.

Explosive crystallization is not present in optical discs, as the heat absorption control layer present in these discs, needed to write the amorphous marks, is expected to prevent the occurrence of EC. Moreover, optical discs are in the crystalline phase before first usage, and therefore, EC would not reach neighboring amorphous marks. The initialization of an as-deposited
amorphous disc to the crystalline phase could possibly benefit from EC as it only would need a single energy pulse. In PCM applications each data bit is an individual cell embedded in SiO$_2$ and therefore explosive crystallization could be exploited to speed up the relatively slow crystallization process. Additionally, the energy requirements for crystallization can be lowered as only an initial energy pulse is needed to start the process, instead of continuously heating the cell until it has been crystallized. PCM cells are often embedded in poorly heat-conducting silicon oxide which may allow explosive crystallization to take place. To study these phenomena we choose to use Ge-doped and Ga-doped Sb-rich phase-change compositions. These alloys were selected as they are directly of interest in PCM applications and the pure elements all show explosive crystallization. Antimony already shows EC at room temperature and is stabilized by germanium or gallium doping. A condition for explosive crystallization is that enough latent heat has to be locally released upon crystallization. Data found in literature often uses thick films (>1 µm) where enough latent heat is released for explosive crystallization. However, for application in PCM cells the phase-change films/cells have to be downscaled to the nanometer regime. Below a critical thickness explosive crystallization does not occur anymore. Therefore, we tested a range of film thicknesses (50 nm – 2000 nm) on the presence of EC. To initiate EC any energy pulse can be used. Reports have shown EC after a mechanical, electrical, electron beam or laser impulses. The latter was used for our study. However, no explosive crystallization was found in both alloys for different film thicknesses and different compositions. However, the Ge-doped Sb alloys did exhibit many interesting crystallization and material properties, which we studied in more detail.

One of the initial experiments was the observation of the crystallization process in Ge$_7$Sb$_{93}$ films with a thickness of 200 nm on a polycarbonate substrate. From previously obtained results we expected to find near isotropic crystal growth in the amorphous film. However, star-shaped crystals with an increased crystal growth rate of the tips were observed (∼5 times faster than expected from isothermal growth), see Fig. 1.1. Additionally, the amorphous surfaces show buckling parallel to the crystal tips. In the crystalline areas buckling perpendicular to the growth direction is observed. By further investigating the crystallization properties, as is done in chapters 3 and 5, we will be able to explain many details regarding the observed crystallization process in Ge-doped Sb films.

## 1.2 Thesis outline

This thesis can be divided into two parts. The first part, chapters 2 to 6, is concerned with the research on different crystallization properties and material properties of the used GeSb films with various thicknesses and compositions. A description of the measurement setup and
Figure 1.1 | Frames from an optical recording of crystallization in 200 nm thick Ge$_7$Sb$_{93}$ phase-change films on a polycarbonate substrate at 180 °C. After initially isotropic growth, star shaped crystals form. The recording was taken at 60 frames per second. The time between the frames displayed here is 4.8 s.

Techniques used for sample preparation and analysis is given in chapter 2. Chapter 3 focusses on the crystal growth during isothermal measurements. The effects of small changes in the phase-change composition on the growth rate, but also the crystal structure, are shown. Interestingly, for some compositions competing, i.e., simultaneously occurring growth modes have been observed. Using additional laser heating the crystal growth is studied at temperatures not available in isothermal experiments and the results are shown in chapter 4. Mechanical stresses play an important role in the small confined PCM cells. The effects of in-plane stresses on the crystal growth in thin films are investigated in chapter 5. The differences in surface potential between the crystalline and amorphous phase and the presence of a Schottky barrier on the crystalline-amorphous interface are scrutinized in chapter 6. Nucleation plays an important role in the phase-change process from amorphous to crystalline. In the second part, chapter 7, the growth and decay of the nuclei is studied within a two dimensional Ising model. Using Monte Carlo simulations and numerical enumerations of so-called lattice animals the critical nuclei needed for growth on square and triangular lattices are determined, compared and evaluated.
References


