Structure and reconfiguration of epitaxial GeTe/Sb2Te3 superlattices
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Chapter 1*

General Introduction

Abstract

The research presented in this thesis has been performed primarily in the context of phase-change materials and phase-change memory applications,† although it is certainly relevant for other fields such as thermoelectric materials and topological insulators. In this chapter GeSbTe alloys will be discussed as well as their crystallographic structures and bonding anisotropy, particularly on the GeTe-Sb₂Te₃ tie-line. Also, epitaxial phase-change materials will be discussed briefly. Finally, this chapter finishes with an outline of this thesis and a short introduction of the following chapters.

1.1 Phase-change materials

Human society has made incredible scientific and technological progress to get to the point of modern civilization where it is today. From controlling chemical reactions to produce heat and processing minerals and metals to industrialize the world, there appears to be no end in sight for this technological boom. One of the key drivers for this is realization of new and advanced materials, from steels which helped to construct buildings and bridges to semiconductors to develop transistors and modern-day electronics. Since Moore’s law is approaching its limits,¹ new concepts are required for the continuation of this development. Novel electronic materials are one of those developments, and they fuel applications such as electronic memories which encode information in the material’s phase² or


† The term “Phase-Change Materials” has also been used in another unrelated context of latent heat storage, which should not be confused with the memory application described here.
thermoelectric devices which manage heat and generate power from it. Ultimately, this scientific endeavor into matter has led to discoveries of new phases of materials, such as the existence of topological excitations and topological states. One of the founding works on the memory behavior using the phases of Te-based alloys was performed by Stanford R. Ovshinsky when he discovered the electrical switching phenomena in these alloys. In the late sixties he described in his seminal paper a rapid and reversible transition between highly resistive and conductive states of a $0.5 \mu m$ thick Ge$_{10}$Si$_{12}$As$_{30}$Te$_{48}$ film which was affected by an electric field. What happened was that the initially resistive amorphous semiconductor switched after the application of a sufficiently large voltage, the threshold voltage, to a conductive state. This state is then preserved above a sufficiently high current, the hold current, but it switches back to the resistive state as soon as the current falls below this hold value. Although at that time the switching mechanism was unclear, Ovshinsky described this behavior in terms of amorphous semiconductor theory. He postulated that the traps in the bandgap of the material would be occupied and ionized under the influence of the field, which would be followed by an increase of carrier concentration along a formed filament, explaining the change in resistivity. Interestingly, he mentions in the last paragraph of this paper that by decreasing the As content to 5% the conductive state would be preserved, even when the current would be completely removed. These basic phenomena and concepts were the first steps into what later evolved into what is nowadays referred to as the field of Phase-Change Memories and Phase-Change Materials (PCM).

The material described by Ovshinsky was actually switching between the resistive amorphous and conductive crystalline states. The described properties, including rapid and reversible switching, high conductivity contrast, as well as stability, are the trademarks of PCM for rewritable data storage. Nowadays, PCM are successfully implemented in rewritable optical disks such as CD, DVD and Blu-Ray and currently, after renewed interest, under intense investigation for electronic memories. Although the current memory market is particularly driven by slow and non-volatile Flash storage and fast and volatile DRAM, PCM could offer an intermediate solution in terms of a relatively fast non-volatile universal memory
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technology,\textsuperscript{10} with switching speed and scalability records up to 500 ps and down to 2 nm, respectively.\textsuperscript{11,12} Particularly materials lying on the ternary GeSbTe (GST) phase-diagram were found to be optimal for such applications, see Figure 1.1, where the alloys on the GeTe-Sb$_2$Te$_3$ tie-line are characterized as nucleation-dominated and Ge-doped Sb$_2$Te and Ge$_{0.15}$Sb$_{0.85}$ as growth-dominated crystallizers. More recently other PCM applications are emerging such as multilevel photonic memories\textsuperscript{13,14} and nanoscale display and data visualization.\textsuperscript{15,16} These developments pave way to new and futuristic technologies such as smart glasses, smart contact lenses and artificial retina devices.

Figure 1.1: The ternary phase-diagram of GST. The figure also indicates the rewritable optical disks applications. Adapted from Wuttig and Yamada.\textsuperscript{2}

To better understand the properties and resistance-switching mechanisms of GST PCM, particularly for materials on the GeTe-Sb$_2$Te$_3$ tie-line, it is necessary to study the crystalline structure and bonding anisotropy of the ternary as well as the separate binary compounds. Figure 1.2 (a)-(c) show the structural models of crystalline GeTe, Sb$_2$Te$_3$ and the stable phase of Ge$_2$Sb$_2$Te$_5$ (s-Ge$_2$Sb$_2$Te$_5$) according to Goldak et al.\textsuperscript{17}, Anderson et al.\textsuperscript{18} and Kooi et al.\textsuperscript{19}, respectively. As can be seen in the figures, all structures are based on consecutive $abc$-stacking of close-packed atomic planes. Within this simplified picture, GeTe is a three-dimensionally (3D) bonded solid which has approximately a rocksalt structure that is rhombohedrally and ferroelectrically distorted along one of the four $<111>$ directions ($c > a\sqrt{6}$ and $\text{z}$
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\[ c = a\sqrt{6} \] and \[ z = 0.250 \] for the rocksalt structure. Sb\(_2\)Te\(_3\) on the other hand has an additional feature of directly adjacent Te-Te planes stacked upon each other, which breaks the rocksalt symmetry by breaking the super-ABC stacking of the Te planes. This happens since Sb has (compared to Ge) one extra valence electron, and because of this the bonds on the outer Te planes are passivated and form two-dimensional (2D) van der Waals (vdW) bonds. This type of vdW bond, which also occurs in e.g. graphene-based materials and transition-metal di-chalcogenides, is referred to as vdW gap. Note that, although Sb\(_2\)Te\(_3\) has certainly a more 2D than 3D anisotropy, the Te-Te bond does not necessarily have to be of pure vdW type (e.g. the Te-Te interatomic distance is a bit smaller than what would be expected based on the vdW radius). Considering the above, the model for s-Ge\(_2\)Sb\(_2\)Te\(_5\) by Kooi et al. takes into account this 3D and 2D character of GeTe and Sb\(_2\)Te\(_3\), respectively, and fits best to experimental electron diffraction results when assuming pure atomic-plane models.

Figure 1.2: Structural models for crystalline phases of GeSbTe, displayed along hexagonal axes (a-axis horizontal and c-axis vertical). The unit cells are indicated with thin solid lines. (a) GeTe. (b) Sb\(_2\)Te\(_3\). (c) Stable phase of Ge\(_2\)Sb\(_2\)Te\(_5\) (s-Ge\(_2\)Sb\(_2\)Te\(_5\)). (d) Metastable phase of GeSbTe (m-GeSbTe) with comparison of vacancy layers and vdW gaps. (e) Switching models using single or double Ge umbrella flip. Note that the switch between the different structures cannot only result from a vertical motion, since this would disagree with the abc-stacking.

When GeSbTe crystalizes from the amorphous phase, it initially forms a metastable rocksalt structure (m-GeSbTe), where one sublattice is fully occupied with Te and the other sublattice is randomly occupied by Ge, Sb and a large amount
of stoichiometric vacancies (~20% for Ge₂Sb₂Te₅), see Figure 1.2 (d). To make the transition from m-GeSbTe to s-GeSbTe it has been suggested that the mechanism involves atomic diffusion of Ge and Sb in such a way that the vacancies order in layers and consequently collapse into vdW gaps. Note particularly the difference in stacking between vacancy layers and vdW gaps in Figure 1.2 (d). An appreciable amount of disorder on the Ge/Sb planes nevertheless remains after this transition: even though the structure of s-GeSbTe best fits the model of Kooi et al. with Sb-Te directly at the vdW gaps, it was found by Matsunaga et al. using Rietveld refinement on XRD spectra that the Ge-rich planes are mixed with Sb and Sb-rich planes with Ge. In later ab-initio studies relating to the ordering of vacancies it was indeed found that the pure atomic-plane model by Kooi et al. gives the lowest formation energy (at zero Kelvin), but that mixing only slightly increases this energy. Therefore, due to this low energy increase and the free energy decrease due to configurational entropy, which becomes increasingly relevant at higher temperatures, the stable phase of bulk GeSbTe is always found with some degree of mixing on the Ge/Sb atomic planes (at practical temperatures particularly dictated by production), but with the Sb-rich planes nearest to the vdW gaps.

One of the bottlenecks for PCM technology is the large programming currents required to switch the material from the crystalline to the amorphous phase. Several mechanisms have been proposed to reduce the programming current including engineering the dimensions of the crystals using e.g. nanowires, nanogaps and nanoparticles, defect engineering and straining the crystal to a higher energy state. The latter idea is probably realized in the recently proposed nanostructured PCM using GeTe-Sb₂Te₃ multi-layers or superlattices. This new type of memory not only showed improved programming currents, but also better performance in terms of switching speed and durability, as well as new magnetic functionalities. For GeTe-Sb₂Te₃ superlattices the separate binary compounds are deposited alternatingly, which hypothetically could produce pure atomic planes. In addition, since Sb₂Te₃ grows in entire 1 nm quintuple layer (QL) terraces, preferring to form layers with passive vdW surfaces, it was speculated that isolated ultra-thin GeTe layers could grow between the vdW surfaces of Sb₂Te₃. In combination with the research on superlattices and understanding of the role of
Ge atoms in PCM phase-transitions, it was proposed that the superlattice resistance-switching is entirely within the crystalline state. Two alternative mechanisms were derived by competing groups based on the Ge-umbrella-flip models, illustrated in Figure 1.2 (e). Tominaga et al. proposed a single Ge atomic-plane flip between the so-called Ferro and inv. Petrov states, while Ohyanagi et al. proposed a double Ge atomic-plane flip between the so-called Petrov and inv. Petrov states. In later ab-initio simulations, Yu and Robertson showed that such a transition could not result from exclusive vertical motion of Ge atoms and suggested detailed pathways for the transition to occur. In this thesis, particularly Chapters 4 and 5, the structure of GeTe-Sb2Te3 superlattices will be scrutinized also to examine whether it is possible to grow pure atomic planes and to trap GeTe layers between the vdW surfaces of Sb2Te3 and also to test whether the switching mechanisms of Tominaga et al. or Ohyanagi et al. can hold.

**Figure 1.3:** HAADF-STEM results of MBE grown [GeTe(1 nm)-Sb2Te3(3 nm)]15 superlattice on Si(111)-Sb. Above the intensity scans it is indicated whether the atomic plane is Ge-, Sb- or Te-rich with circles, triangles and squares, respectively. (a) Overview image of the superlattice. (b) 5-layers corresponding to Sb2Te3. (c) 7-layer. (d) 11-layer. (e) 13-layer.

The development of superlattice PCM are an inspiration for the research presented in this thesis. Together with the development of epitaxial PCM, the thesis describes the growth and characterization of nanostructured GeTe-Sb2Te3 superlattices, using particularly Molecular Beam Epitaxy (MBE), sputtering Physical Vapor Deposition (PVD) and Transmission Electron Microscopy (TEM). Figure 1.3 (a) shows an example of such a heterostructure which has been grown epitaxially on Si substrates and Figure 1.3 (b)-(e) shows examples of the detailed
One of the surprising findings in this thesis are that these heterostructures are best described as van der Waals heterostructures of Sb$_2$Te$_3$ and GST and that the van der Waals gaps trapped in these superlattices are mobile and can migrate upon thermal annealing. These findings will be discussed in Chapters 4 and 5.

1.2 Outline of this thesis

The topic of this thesis is thus the growth and characterization of MBE and PVD grown GeTe and Sb$_2$Te$_3$ thin films and GeTe-Sb$_2$Te$_3$ superlattices. All of the studied samples were grown on Si substrates with different surfaces due to its ease of use and quality of epitaxial films. Chapter 2 discusses elaborately the experimental methods and techniques employed for this thesis and gives specific TEM specimen preparation recipes. The following chapters can be read independently, where Chapter 3 shows the first TEM analysis results of the initial epitaxial samples grown on Si(111). It shows that highly textured GeTe-Sb$_2$Te$_3$ superlattices can be successfully grown and characterized. Although these samples have relatively thick GeTe and Sb$_2$Te$_3$ sublayer thicknesses, between 3 nm and 12 nm, they were an important step for the continued development of superlattice PCM. Chapter 4 then shows that thin sublayer GeTe-Sb$_2$Te$_3$ superlattice are successfully grown with MBE and PVD. Using TEM characterization it is unambiguously resolved that the (at that time) prevailing structural models in the literature were incorrect and a new structure for the films was proposed. Chapter 5 discusses then the dynamics of the reconfiguration of GeTe-Sb$_2$Te$_3$ films during annealing. It is shown that the van der Waals gaps trapped in the structure due to deposition kinetics are actually mobile and reconfigure themselves throughout the film. Finally, Chapter 6 analyzes the growth of GeTe and Sb$_2$Te$_3$ films on Si(111) and discusses the importance of the substrate-film interfacial structure and bonding for epitaxy.

1.3 References

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