Structure and reconfiguration of epitaxial GeTe/Sb2Te3 superlattices

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Chapter 4**

Interface formation of 2D and 3D bonded materials in the case of GeTe-Sb$_2$Te$_3$ superlattices

The crystal structure of GeTe-Sb$_2$Te$_3$ superlattices is actually a van der Waals heterostructure of Sb$_2$Te$_3$ and trigonal GeSbTe.

Abstract

GeTe-Sb$_2$Te$_3$ superlattices are nanostructured phase-change materials which are under intense investigation for non-volatile memory applications. They show superior properties compared to their bulk counterparts and significant efforts exist to explain the atomistic nature of their functionality. The present work sheds new light on the interface formation between GeTe and Sb$_2$Te$_3$, contradicting previously proposed models in the literature. For this purpose epitaxial GeTe-Sb$_2$Te$_3$ superlattices were grown on passivated Si(111) at temperature ranging from 210°C to 230°C using molecular beam epitaxy and sputtering physical vapor deposition, and they have been characterized particularly with cross-sectional transmission electron microscopy. Contrary to the previously proposed models, it

is found that the ground state of the films actually consists of van der Waals bonded layers (i.e. a van der Waals heterostructure) of Sb$_2$Te$_3$ and trigonal GeSbTe. Moreover, it is shown by annealing the films at 400°C, which reconfigures the superlattice into bulk trigonal GeSbTe, that this van der Waals layer is thermodynamically favored. These results are explained in terms of the bonding anisotropy of GeTe and Sb$_2$Te$_3$ and the strong tendency of these materials to intermix. The findings thus debate the previously proposed switching mechanisms of superlattice phase-change materials and give new insights in their possible memory application.

4.1 Introduction

Phase-Change Materials (PCMs) based on Ge, Sb and Te (GeSbTe) are some of the most promising candidates for next-generation data-storage applications. Due to their unique combination of functional properties, they are currently under intense investigation for non-volatile random-access memory. Recently, a new concept of nanostructured PCMs has been developed based on GeTe-Sb$_2$Te$_3$ superlattices, referred to as Interfacial Phase-Change Material or Chalcogenide Superlattice (CSL). This type of material shows strongly improved switching properties compared to its bulk counterparts, as well as new possibilities for multi-level switchings and magnetic functionality. Initially it was proposed that the switching was due to the amorphous-crystalline phase-transition of the separate relatively thick superlattice sublayers, where the improved performance was attributed to the reduced thermal conductivity of the superlattice structure. However, it was demonstrated that the CSL kept functioning while the GeTe sublayer thickness was narrowed down to ≤ 1 nm, equivalent to two or three bilayers (BLs) GeTe, and that CSL had higher thermal conductivity compared with bulk GeSbTe. It was concluded that the phase-change occurred within the crystalline state, as was verified with transmission electron microscopy (TEM), not requiring the melt-quench cycle and thereby inherently acquiring improved properties and stability.

Despite these advances, the crystal structure and switching mechanism of CSL is currently not clearly understood. As both GeTe and Sb$_2$Te$_3$ are based on abc-
stacking of close-packed atomic planes, with repeating units (Ge-Te-)m and (Te-Sb-Te-Sb-Te-)n, CSL is being modeled for simplicity as (GeTe)2(Sb2Te3), with stacking sequences as shown in Figure 4.1 (a). The structure by Kooi et al. corresponds experimentally best to the stable phase of Ge2Sb2Te5 (trigonal Ge2Sb2Te5),9 the prototype conventional PCM, which is consistent with ab-initio calculations at zero temperature. However, at elevated temperatures of 180 °C and above these calculations suggest that the Kooi et al. phase becomes progressively unfavorable and therefore the other sequences dominate.8,10,11 Based on these results, two competing switching models were derived, which originate from the understanding of the Ge umbrella-flip mechanism in PCMs.12,13 Tominaga et al. propose that the two phases of CSL correspond to the Ferro low-resistance state and inv. Petrov high-resistance state with a single GeTe umbrella flip as shown in Figure 4.1 (b),8,10 while Ohyanagi et al. propose the Petrov low-resistance state and inv. Petrov high-resistance state with a double GeTe umbrella flip as shown in Figure 4.1 (c).14

There are several problems with these models that need to be addressed to progress the understanding of CSL operation. Bulk GeTe and Sb2Te3 are three-dimensionally (3D) and two-dimensionally (2D) bonded solids, respectively, where the Te-Te bond of the latter is predominantly of van der Waals (vdW) type.15,16 This implies that vdW-surfaces of “entire” quintuple layers (QLs) Sb2Te3, written schematically as (Te-Sb-Te-Sb-Te-vdW-), are passive and do not prefer to bind with dangling bonds of GeTe. In this respect the experimental structure by Kooi et al. best satisfies this condition, as the GeTe BLs are intercalated within the Sb2Te3 block where the bonding is 3D, while the other models do not properly match the GeTe and Sb2Te3 bonding types. Moreover, since it is known from experiments that stable Ge2Sb2Te5 contains mixed Ge/Sb atomic layers,17 lowering the free energy of the PCM at higher temperatures due to configurational entropy, it is debatable whether modelling CSL with pure Ge or Sb atomic planes as in Figure 4.1 is justified. Hence, it is not clear why the structures in Figure 4.1, other than the experimentally accepted one based on experiments by Kooi et al.9 and Matsunaga et al.17 would be thermodynamically stable, and why, therefore, the proposed switching mechanisms would be correct.
Figure 4.1: Models of GeTe-Sb$_2$Te$_3$ superlattices considered in the literature. (a) Simple CSL stacking sequences in case of (GeTe)$_2$(Sb$_2$Te$_3$); (b) CSL switching model proposed by Tominaga et al. considering a single Ge umbrella flip; (c) CSL switching model proposed by Ohyanagi et al. considering a double Ge umbrella flip. Note that in both cases of Figure 4.1 (b) and Figure 4.1 (c) the switching cannot be the result of only a vertical flip of Ge atoms (because this would disagree with the abc-type stacking).

These problems are addressed in the present work, where the previously found switching models of CSL are challenged and an alternative ground state structure is presented. By using highly controlled Molecular Beam Epitaxy (MBE) and sputtering Physical Vapor Deposition (PVD) epitaxial GeTe-Sb$_2$Te$_3$ superlattices have been grown on passivated surfaces of Si(111) at substrate temperatures
between 210°C and 230°C. These methods have shown in our previous work to produce high-quality Sb₂Te₃ and GeTe thin films and GeSbTe memory devices.¹⁸ The crystal structure of the films is resolved using various characterization techniques, including High-Resolution Transmission Electron Microscopy (HRTEM), High-Angle Annular Dark Field Scanning TEM (HAADF-STEM), X-Ray Diffraction (XRD) and Energy Dispersive X-ray spectroscopy (EDX). Contrary to the previously proposed models, it is demonstrated that the structure of the films corresponds to van der Waals bonded layers (i.e. a van der Waals heterostructure)¹⁹ of Sb₂Te₃ and trigonal GeSbTe, in agreement with expectation based on models proposed by Kooi et al.⁹ and Matsunaga et al.¹⁷ Moreover, preliminary memory characterization shows that similar MBE grown films indeed display clear CSL memory behavior with for instance a reduction of the programming current by a factor three in comparison to the same devices containing bulk GeSbTe. The present results therefore indicate that the models for CLS switching as depicted in Figure 1 (b) and 1 (c) are unlikely and that a revision of the switching mechanism is required.

4.2 Results

4.2.1 MBE grown superlattices

The average XRD, XRR and EDX results in the Appendix demonstrate that [GeTe(1nm)-Sb₂Te₃(3nm)]₁₅ has been grown with a clear, well-defined and stoichiometrically consistent superlattice feature. The structure of this CSL is then studied with HAADF-STEM, of which an overview is shown in Figure 4.2 (a). The Si substrate at the bottom of the image appears darker than the film due to Z-contrast and the dark horizontal lines in the film correspond to the vdW type Te-Te bonds, referred to as vdW gaps. Since Sb₂Te₃ and GeTe have 2D and 3D bonding, respectively,¹⁵,¹⁶ the formation of vdW gaps is expected to be at least between adjacent QLs of Sb₂Te₃. The superlattice feature of the film can then be recognized in this image by (i) Z-contrast of Ge with respect to Sb and Te (having approximately equal Z) and (ii) the 2D bonded Sb₂Te₃ QLs, which are separated by vdW gaps. Hence, the periodicity of the alternating GeTe-Sb₂Te₃ block is indicated on the left in the figure, pointing each time roughly to the Sb₂Te₃ sublayers.
4. Interface formation of 2D and 3D bonded materials in the case of GeTe-Sb$_2$Te$_3$ superlattices

Two observations can be made from the overview image in Figure 4.2 (a). First, it is deduced by the number of vdW gaps that typically 1 or 2 instead of the expected 3 QLs Sb$_2$Te$_3$ are formed, where the vdW-layer thicknesses are 1 QL or larger. The reason is that the vdW-layers consist of entire QLs Sb$_2$Te$_3$, while for GeTe rather the formation of (GeTe)$_n$+Sb$_2$Te$_3$ or trigonal GeSbTe occurs. This is why almost exclusively vdW layers of odd number atomic planes are formed. Second, various stacking and layering faults are seen in the image, particularly double-plane defects in between the odd-numbered atomic plane vdW layers, which is a consequence of the fact that the film is not perfectly deposited plane by plane. However, the clear occurrence of vdW gaps and their special extension affirms the smoothness of growth achieved with MBE, reflecting its high-quality layer by layer growth. Also, twinning and twin-boundaries are observed as the
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crystal is viewed along Si\textit{<1-10>} or Sb\textsubscript{2}Te\textsubscript{3}\textit{<11-20>}, where the abc-stacking becomes apparent. From φ-scans around the Sb\textsubscript{2}Te\textsubscript{3}\textit{(220)}, shown in the Appendix, it is found that an approximately equal number of opposite twin-domains exist in the crystal. This is also seen in previous work on the growth of Sb\textsubscript{2}Te\textsubscript{3} and can be attributed to the weak bonding in between the vdW-layers.
planes, it is deduced that the stacking is of the form \((\text{Te-Sb-Te-Ge-Te-Ge-Te-Ge-Te-Sb-Te-})\). This linescan also demonstrates the atomic precision of the MBE growth by showing that almost pure Ge and Sb atomic planes have been formed during deposition with little intermixing of the Ge/Sb planes, as expected for the alloy.\(^{17}\) Hence, the deposition of 1 nm (or 3 BLs) of GeTe has resulted in the formation of a natural or trigonal \(\text{Ge}_3\text{Sb}_2\text{Te}_6\) layer and is labeled accordingly. There is an inherent asymmetry between the beginning and the end of the GeSbTe layer in the superlattice, which can be attributed to the growth direction and thus has a kinetic origin. The formation of the \((-\text{vdW-Te-Sb-Te-})\) stacking sequence is surprising in this respect, as \(\text{Sb}_2\text{Te}_3\) growth actually occurs in entire 1 nm QLs.\(^{15,23}\) This shows that during this layered \(\text{Sb}_2\text{Te}_3\) growth, after the flux transition from Sb to Ge, the film already has a strong tendency to reconfigure itself to form this type of surface and stacking sequence, rather than forming the proposed (inv.) Petrov or Ferro interfaces in Figure 4.1 (a).

The naturally occurring stacking faults and layering disorder in the deposited superlattice seem inconsistent with the high quality that should be achievable with MBE, but this is another signature that the artificially grown CSL reconfigures into a lower energy state. Moreover, the stacking disorder is quite useful for characterization of different types of structures formed. In this way many different vdW layers can be observed, eliminating the necessity for many depositions and sample analyses. Figure 4.3 shows parts of the film where layers of different number of atomic planes are formed, namely 5-, 7-, 9-, 11- and 13-layered vdW systems. Starting from the 5-layered system in Figure 4.3 (a) and counting forward, it can be seen that the intensity lowering is particularly happening in the center of the vdW layer, confirming the results described above that pure Ge does not bind near the vdW gaps. The 5-layered system is just a QL \(\text{Sb}_2\text{Te}_3\) with equal intensity maxima, while the 7-layered system has a single Ge mixed plane with considerable amount of Sb at the center of the layer. The expected stacking sequences occur for 9-, 11- and 13 layers, where almost pure Ge atomic planes are formed, and already showing evidence for Ge intermixing in the Sb layer near the vdW gap. These findings thus confirm that the vdW gap is formed after the \(-\text{Te-Sb-Te}\) termination of the stack, such as in \(\text{Sb}_2\text{Te}_3\), and that the GeTe is thus intercalated within the
Sb$_2$Te$_3$ block, where the bonding is matched. Note that this is in contrast to phases richer in Sb than Sb$_2$Te$_3$ where Sb bilayers are intercalated within the vdW gaps of Sb$_2$Te$_3$.\textsuperscript{15,24} Hence, the present results lead to the conclusion that the structure of the as-deposited GeTe-Sb$_2$Te$_3$ superlattice is a vdW heterostructure of Sb$_2$Te$_3$ and trigonal GeSbTe.

![Figure 4.3](image)

**Figure 4.3:** Variety of vdW layers formed in the MBE grown as-deposited superlattice. The intensity linescans corresponding to the HAADF-STEM micrographs cover larger regions than shown in the representative images. (a) 5-layer; (b) 7-layer; (c) 9-layer; (d) 11-layer; (e) 13-layer; In the linescans the low intensity dips correspond to vdW gaps and the peaks to the Ge, Sb and Te atomic columns. Note that several atomic columns already show evidence of Ge/Sb intermixing.

To monitor the direction of chemical diffusion in the superlattice, another piece of the as-deposited sample has been annealed at 400°C for 30 min and has undergone the same characterization procedures. A drastic transformation can be observed by comparing XRD acquired on the sample before and after annealing. As shown Figure 4.4, after annealing, all the peaks attributed to Sb$_2$Te$_3$ at Qz = 2.4, 3.09, and 4.26 Å$^{-1}$ disappear and the CSL satellite peak at Qz = 3.46 Å$^{-1}$, characteristic for the superlattice structure, vanishes as well. The new spectrum displays peaks spaced by ~0.46 Å$^{-1}$ which corresponds in real space to the c lattice parameter of trigonal GeSb$_2$Te$_4$ when described with hexagonal axes. These results show that overall Sb$_2$Te$_3$ and GeTe intermix into an ordered GeSb$_2$Te$_4$ structure after annealing and the CSL structure is lost.
4. Interface formation of 2D and 3D bonded materials in the case of GeTe-Sb$_2$Te$_3$ superlattices

**Figure 4.4**: Symmetric 2θ-ω scan on [GeTe(1nm)-Sb$_2$Te$_3$(3nm)]$_{15}$ CSL before (blue line) and after (red line) annealing at 400°C for 30min.

The cross-sectional HAADF-micrograph in Figure 4.5 (a) shows an overview of the thermally reconfigured film's microstructure, which has retained its layered vdW structure and 2D nature, as is expected for natural GeSbTe.$^{9,17}$ Interestingly, it is observed that despite the large reconfiguration in the film, the Sb-monolayer terminating the Si substrate has seemingly remained intact, reflecting its stability and strong bonding. The Sb$_2$Te$_3$ QLs which were present in the superlattice stack have been dissolved, effectively destroying the superlattice structure, and the remaining film contains primarily 7- and 9-layered vdW systems with thickness of 1.36±0.02 nm and 1.73±0.02 nm, respectively.
4.2 Results

Figure 4.5: HAADF-STEM measurements on the MBE grown annealed superlattice. (a) Overview micrograph showing that the CSL has thermally reconfigured into trigonal GeSbTe, consisting of 7- and 9-layered vdW blocks; (b) Close-up of a region consisting of 7-layered vdW blocks; (c) Intensity linescan of a 7-layer shown in Figure 5 (b); (d) Close-up of a region consisting of 9-layered vdW blocks; (e) Intensity linescan of a 9-layer shown in Figure 4.5 (d); The asterisk in Figure 4.5 (c) and 4.5 (e) indicates that the Ge and Sb atomic planes are mixed.

Figures 4.5 (b)-(c) and 4.5 (d)-(e) show the formation of 7- and 9-layered structures near the substrate with corresponding linescans, respectively. It is observed that the lowest intensity peaks of these structures, indicated by Ge* and Sb*, are again in the center of the vdW layers. Comparing this structure and the thickness of the vdW layers with literature, it shows that the superlattice created during growth by the alternating supply of Ge and Sb is reconfigured into bulk trigonal GeSbTe through the diffusion of Ge atoms. This result thus shows that the thermodynamically favored state of the system in this temperature range is trigonal GeSbTe, rather than the structures in Figure 4.1 (a) and suggests even stronger Ge intermixing in the superlattice for higher deposition or annealing temperatures. These findings are thus consistent with the previous results on the as-deposited superlattice, which already showed such driving force. However, due to limited time and temperature during deposition complete transformation to trigonal GeSbTe is not possible, but screening of GeTe by Te-Sb-Te was already achieved. Interestingly, as it is known from TEM-EDX measurements that the average composition, which has not changed after the reconfiguration, corresponds best to GeSb\textsubscript{2}Te\textsubscript{4}, the structure does not simply reconfigure to exclusively a 7-layered Kooi
et al. structure with pure atomic planes (Te-Sb-Te-Ge-Te-Sb-Te-vdW). In contrast, the formation of 9 layers supports the conclusion of intermixed Ge and Sb layers, as is observed in the HAADF intensities in Figure 4.5 (c) and Figure 4.5 (e). The present results are thus fully consistent with the structure proposed for the first time by Matsunaga et al. for stable Ge$_2$Sb$_2$Te$_5$ containing mixed Ge/Sb atomic layers. They also demonstrate that the models in Figure 4.1 (a) which only consider pure Ge and Sb planes cannot be used at elevated temperatures, because they neglect the importance of configurational entropy.

### 4.2.2 PVD grown superlattices

![Figure 4.6: HRTEM results of PVD grown [GeTe(4 nm)-Sb$_2$Te$_3$(3 nm)]$_{15}$ superlattice on Si(111)-H. (a) Overview image of the superlattice. (b) High-resolution image of the superlattice. The model for the structure that is formed is indicated on the right of the image.](image)

PVD is another technique for film-growth with the advantage that it is adopted much more easily in an industrial process than MBE. Beside this, most of the previous results in the literature have been achieved using PVD grown GeTe-Sb$_2$Te$_3$ films. Figure 4.6 shows (coherent) HRTEM micrographs of a [GeTe(4 nm)-Sb$_2$Te$_3$(3 nm)]$_{15}$ superlattice, produced at 210°C with PVD. The film is grown on H-passivated Si(111) which is the surface formed after an HF treatment of the substrate. Also in this case a strong substrate-film alignment occurs, as will be shown in more detail below. HRTEM has a different contrast mechanism than HAADF-STEM because the images are formed through coherent interference of electrons (phase contrast) and this makes interpretation typically more difficult and not directly Z-sensitive. However, due to the dimensionality difference of GeTe
and Sb$_2$Te$_3$ it is still possible to distinguish the QLs, and sometimes 7-layers, within the film as can be observed in Figure 4.6 (a).

Figure 4.6 (b) shows a close-up micrograph of the sublayers that are formed, which seem to disagree with the intended GeTe(4 nm)-Sb$_2$Te$_3$(3 nm) thicknesses. The GeTe sublayer appears to be 5 nm, while only 2 nm (2 QLs) of Sb$_2$Te$_3$ are observed. The bilayer thickness is also verified with EDX, which resulted on average in 29.2±0.5 at.% Ge, 15.3±0.7 at.% Sb and 55.5±0.9 at.% Te. This is equivalent to 61.6±0.9 at.% Ge$_{47}$Te$_{53}$ and 38.4±0.7 at.% Sb$_2$Te$_3$, where GeTe is a bit off-stoichiometric due to the inherent presence of ~10% vacancies on the Ge lattice.$^{25}$ Using these compositional results and the fact that the ~110 nm film is highly textured along the c-axis, which allows using the literature distances for GeTe (0.356 nm/bilayer), Sb$_2$Te$_3$, (0.1015 nm/QL) and trigonal GeSbTe, it is calculated that the film on average contains 4.3 nm GeTe and 2.7 nm Sb$_2$Te$_3$. So since 2 nm of Sb$_2$Te$_3$ have formed 5-layered vdW systems (QLs) the remaining amount of Sb is used in the termination of the GeTe sublayers, which is needed to form the vdW bond, as illustrated by the model in Figure 4.6 (b) on the right. Therefore, also these results of thicker GeTe-Sb$_2$Te$_3$ superlattices produced by sputtering clearly support the formation of trigonal GeSbTe with mixed Sb-rich planes next to the vdW gap.

The study of the thermal stability of the superlattices is also studied for PVD grown films, which is important because it is argued that there is a thermodynamic tendency to form isolated GeTe blocks within Sb$_2$Te$_3$ at elevated temperatures$^{8,10,11}$ and for industrial applications the material has to be able to withstand a certain amount of thermal processing. Beside this, growth at elevated temperatures above ~200°C is required for textured growth to occur.$^3$ As it was already shown above, that for growth around ~230°C the separate binary compounds intermix by terminating the GeTe blocks with Sb-Te vdW surfaces, it is interesting to know what the further development is at higher temperatures. In order to examine this a set of [GeTe(1 nm)-Sb$_2$Te$_3$(3 nm)]$_{15}$ superlattices were prepared on Si(111)-H with PVD at 210°C and capped with ZnS:SiO$_2$ (80:20) to prevent preferential evaporation of GeTe during annealing. Additionally a GeSb$_2$Te$_4$ film was grown from a stoichiometric target at 320°C on mica substrates for comparison of the
overall structure. Figure 4.7 (a) shows the θ-2θ XRD results of the as-deposited and 250°C, 300°C, 350°C and 400°C annealed films.

Figure 4.7: XRD results of thermal annealing experiments with PVD grown [GeTe(1 nm)-Sb2Te3(3 nm)]15. (a) θ-2θ scans of the superlattice at different temperatures in comparison with GeSb2Te4 which is directly deposited on Mica (top scan). The results clearly indicate that the superlattice structure thermally reconfigures into bulk GeSb2Te4 after 350°C. (b) Illustration of the structural models for the [GeTe(1 nm)-Sb2Te3(3 nm)] superlattice (CSL) (left) which reconfigures into the stable phase of bulk GeSb2Te4 (right).

The as-deposited film clearly shows superlattice peaks at Qz = 1.816 Å⁻¹ and Qz = 3.635 Å⁻¹, as well as the 250°C annealed film which hardly changed the as-deposited structure. However, new and distinct peaks of equally spaced Qz appear after annealing temperature of 350°C, which further develop at 400°C. Comparing the positions as well as the intensities of all peaks with the GeSb2Te4 film on mica, it becomes apparent that the superlattice has reconfigured into GeSb2Te4, as is
schematically illustrated in Figure 4.7 (b). This finding for the present PVD grown films is fully consistent and in line with the previously obtained results for the MBE grown ones. It implies that the intermixing of GeTe and Sb$_2$Te$_3$ to form trigonal GeSbTe is a thermodynamic tendency and that this becomes more pronounced at higher annealing or deposition temperatures such that the superlattice feature is lost after 30 min. annealing at 350 or 400°C. This outlines a delicate thermal balance which has to be achieved during growth: the temperature has to be high enough to favor texture of the superlattice material, but at the same time it has to be low enough to maintain sharp interfaces. Moreover, this shows that the superlattice materials have a limited thermal budget which they can handle, which has to be taken into account for potential industrial implementation. Overall, these findings thus disagree with the previously mentioned ab-initio results$^{25,28,29}$ and suggest that configurational entropy due to mixing, particularly of the Ge/Sb atomic planes, has to be taken into account for the modeling.

### 4.2.3 Surface preparation

![Figure 4.8](image)

**Figure 4.8:** Epitaxial matching between Si(111) and GeTe-Sb$_2$Te$_3$ superlattices. (a) XRD pole figure of the Si(111)-H PVD grown superlattice showing the {01-12} peak family (conducted at 2θ = 29.80° or |Q| = 2.098 Å$^{-1}$). The result shows that the superlattice not only has a good out-of-plane alignment, but it is also in-plane aligned with the Si substrate. Since the crystal structure of the superlattice is trigonal, the hexagonal pattern is the result of crystal twinning. (b) Schematic overlay of the nearest close-packed planes of the Si and Sb$_2$Te$_3$ lattices, illustrating the dominant epitaxial relationship according to (a).

An important prerequisite for the growth of GeTe-Sb$_2$Te$_3$ superlattices is the ability to achieve a film with large domains and a sharp texture due to a single [0001] out-
of-plane orientation of the trigonal structure, which typically occurs at deposition temperatures above ~200°C. Also here, several theories exist on what is the best way to achieve this based on the chemistry of the relevant materials. Since Sb$_2$Te$_3$ is a 2D bonded component of the film, preferring to organize itself in entire QLs, it becomes natural to exploit this property using vdW epitaxy. This approach has the additional advantage that the lattice-matching condition is much more relaxed than for 3D epitaxy, as the chemical bonding on the surface is much weaker. This is the reason why in the above experiments either Si(111)-Sb and Si(111)-H surfaces have been applied. Using these passive surfaces and the Sb$_2$Te$_3$ starting layer, it is possible to grow highly textured and substrate-oriented films. Figure 4.8 (a) shows an experimental XRD pole figure of the Si(111)-H PVD grown superlattice from Figure 4.6 along the {01-12} peak family (conducted at 2θ = 29.80° or |Q| = 2.098 Å$^{-1}$). From the figure it is clear that the superlattice not only has an excellent out-of-plane alignment, but it is also in-plane aligned with the Si substrate. Since the crystal structure of the superlattice is trigonal, the hexagonal pattern is the result of crystal twinning (60° or 180° rotation around the [0001] that is perpendicular to the interface). This epitaxy is schematically illustrated (by a simplified geometric model, excluding potential matching strains which will be small for this vdW-like epitaxy) in Fig 5 (b), where the last (111) plane of Si and the first Te plane of an Sb$_2$Te$_3$ quintuple relative to the interface are overlaid on top of each other.

Thus, a significant feature for lateral Sb$_2$Te$_3$ growth is that the starting surface is passive, but also smooth, which does not imply that the surface has to be crystalline. This is shown for PVD grown Sb$_2$Te$_3$ layers on the native oxide of the Si substrate. Figure 4.9 (a) shows a part of the film where the native oxide is relatively flat and therefore the quintuple structures of Sb$_2$Te$_3$ can properly organize. This happens during growth initiation to minimize dangling bond surfaces and maximize the passive vdW surface. However, if the surface is rough, tilted domains can form and are observed; see an example shown in Figure 4.9 (b). The tilt occurs because the initial QLs are formed with a tilt on the rough surface and this is a further seed for subsequent growth. Therefore, the surface roughness is of crucial importance for the growth of superlattices, consistent with the findings by Saito et
al.,\textsuperscript{27} who suggest a way to achieve it with ion-polishing (in order to produce an amorphous Si surface). Still, in the work of Saito et al. it is claimed that high quality lateral growth also requires materials at the surface that have preference to bond to Te and not Sb. In this respect silicon oxide would not be a suitable surface. However, the present work shows, as has also been pointed out by Ross et al.,\textsuperscript{28} that it is nevertheless possible to achieve lateral Sb\textsubscript{2}Te\textsubscript{3} growth on SiO\textsubscript{2} directly, indicating that it is rather the surface chemistry than bulk chemistry which is dominant for growth.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.9.png}
\caption{Sb\textsubscript{2}Te\textsubscript{3} films grown with PVD on the native oxide of Si(100). (a) Part of the film which shows good out-of-plane alignment due to the smooth SiO\textsubscript{2} starting surface. This can be seen since the vdW gaps of Sb\textsubscript{2}Te\textsubscript{3} are aligned parallel to the interface. (b) Part of the film which shows a tilted domain, recognized by the tilted vdW gaps of Sb\textsubscript{2}Te\textsubscript{3}, which has formed on a rough part of the substrate.}
\end{figure}
4.3 Discussion

The results show that for both MBE and PVD grown GeTe-Sb$_2$Te$_3$ superlattices the crystal structure is actually a vdW heterostructure of Sb$_2$Te$_3$ and trigonal GeSbTe, consistent with the provided reasons in the introduction. The -Te-Sb-Te vdW layer termination plays an important role in the pinning of vdW gaps, as is also expected and found in related compounds such as GeBiTe.$^{29}$ This is in striking contradiction with the models proposed in the literature,$^{8,10,14}$ for which the necessary (inv.) Petrov and Ferro structures do not seem to occur in experiments. In addition, these models can hardly be compatible with actual experimental conditions to grow superlattices such as substrate temperature control and surface roughness. It is known from previous work on bulk GeSbTe that GeTe molecules evaporate from the films between 200°C and 250°C during growth,$^{30}$ narrowing the window of deposition. This is not taken into account in previous experiments$^{14}$ and could play an important role for CSL growth by determining the average GeSbTe layer thickness. Concerning the roughness, all CSL memories reported in the literature have been grown with 1 nm GeTe thickness.$^{3,7,8,14}$ These sublayers are always modelled with 2 GeTe BLs, but this is in fact incorrect, because 1 nm corresponds closely to 3 BLs and it is not clear how the structures and mechanisms generalize with such an increased sublayer thickness. When actual memories would rely very sensitively on having either 2 or 3 GeTe BLs, the whole technology becomes hardly realizable in practice. Furthermore, the experimental evidence provided for the different states of Figure 4.1 (b) and 4.1 (c), based, as in this work, on HAADF-STEM images,$^{7,8}$ does not include (and even shows inconsistencies with) the Z-contrast in these images. Moreover, these images focused on particularly small regions, making it difficult to analyze and compare the overall film structure. The TEM results in the original work by Simpson et al. on CSL memory switching$^3$ indeed show a crystalline feature of the memory in the high-resistance state. However, since it is known that GeSbTe can have the amorphous-crystalline transition in films down to 2 nm$^{31}$ and the images were captured using coherent TEM, which suffers from electron delocalization, it is not clear whether this film is partly or entirely crystalline. The present findings thus disagree with the proposed
4.3 Discussion

switching mechanisms of CSL and debate whether it is proven that CSL switching is a fully crystalline-crystalline transition.

On the other hand, the currently proposed ground state structure suggests that CSL switching may possibly be a limiting case of the amorphous-crystalline transition of very thin GeSbTe sublayers sandwiched between Sb$_2$Te$_3$ QLs. However, the thermal conductivity of CSL was measured to be lower than for bulk GeSbTe in the work by Simpson et al.,$^3$ dismissing the explanation by Chong et al.$^{4,5}$ Hence, another mechanism for the reduced programming current should be responsible for the transition. A possible solution to resolve this issue can still be related to the pronounced interfacial and strain energy effects present in CSL. For instance, it has been established that that amorphous-crystalline interfaces may be of lower energy than crystalline-crystalline interfaces under certain energetic considerations,$^{32}$ which thus would reduce the switching energy for thin GeSbTe sublayers sandwiched between crystalline spacer layers than for bulk GeSbTe. Furthermore, the effect of strain can also play a significant role as can be deduced from the a-lattice parameters of the relevant compounds, $a_{\text{GeTe}} = 0.417$ nm,$^{16,33-34}$ $a_{\text{Sb}_2\text{Te}_3} = 0.426^{9,15}$ and $a_{\text{Ge}_2\text{Sb}_2\text{Te}_5} = 0.422$ nm,$^{17,35}$ which indicate that the thicker the trigonal GeSbTe vdW sublayer becomes, the more it changes its constant from $a_{\text{Sb}_2\text{Te}_3}$ to $a_{\text{GeTe}}$. Thus, the GeSbTe vdW layer can mismatch to a maximum of ~2% with the Sb$_2$Te$_3$ matrix, depending on its thickness, adding the strain energy to the overall crystalline layer.$^{36}$ Therefore, straining the trigonal GeSbTe layer could lower its amorphization energy and the enhanced growth speed can be explained by template growth within the crystalline Sb$_2$Te$_3$ matrix,$^{37}$ consistent with the crystalline feature of TEM observations.$^3$ If this would be correct, a scheme would emerge to design optimal CSL stacks by introducing thin spacer layers that tailor interfacial energy and introduce sufficiently strained GeSbTe layers to lower the amorphization energy (e.g. by adjusting the GeSbTe layer thickness with proper Sb$_2$Te$_3$/GeSbTe ratio), but not too strained as to facilitate sufficiently fast regrowth. Recently, it was also found that Ge$_x$Te$_{1-x}$ with $x << 0.5$ in the superlattice, which thus has Ge vacancies and therefore contains more strain of the crystal, reduced the switching energy compared with its stoichiometric Ge$_x$Te$_{1-x}$ with $x = 0.5$ counterpart,$^{38}$ consistent with the proposed hypothesis.
4.4 Conclusions

The present work shows that the ground state of GeTe-Sb$_2$Te$_3$ superlattices is actually a vdW heterostructure of Sb$_2$Te$_3$ and trigonal GeSbTe, which is in striking contradiction with the previously proposed models in the literature. These GeSbTe layers are formed due to the bonding dimensionality of the superlattice sublayers, as GeTe prefers to be 3D bonded within the Sb$_2$Te$_3$ block and not adjacent to a vdW gap. Such considerations are not taken into account when modeling superlattice PCM, which explains why the model structures are not observed experimentally. Additionally, the ab-initio modeled structures do not address the experimentally established atomic intermixing in Ge/Sb layers, omitting the configurational entropy effects on the free energy. More generally, these results shed light on the bonding types in PCMs lying on the GeTe-Sb$_2$Te$_3$ tie-line, illustrating e.g. why metastable rock-salt GeSbTe structure reconfigures into the stable trigonal GeSbTe structure with Te-Te vdW bonds. This is thermodynamically favorable, which is thus also the driving force behind this crystalline order-disorder transition that changes the overall bonding from 3D to 2D. Also, the degree of vdW bonding in trigonal GeSbTe probably depends on the degree of Ge/Sb intermixing adjacent to the Te atomic layer at the vdW gap. An increasing mixing of this layer with Ge will then change the Te-Te bond from a passive vdW gap to an actual vacancy layer with dangling bonds, changing the coupling between adjacent GeSbTe layers and thereby probably affecting thermal and electrical conductivities. Overall the present results thus have important implications for understanding the structures and properties of GeTe-Sb$_2$Te$_3$ based CSLs, which are shown to be technologically relevant vdW heterostructures.

4.5 Methods

**MBE growth and annealing:** The cleaning of the Si substrate, its introduction into the MBE system, and the preparation of the Si(111)-$(\sqrt{3}\times\sqrt{3})$R30°-Sb surface are detailed in a previous publication$^{16}$. The substrate and cells are brought to the deposition temperature of 227.5 °C for the substrate, T(Ge)base=1120 °C and T(Ge)tip=1140 °C for the Ge cell, T(Sb)base=450 °C and T(Sb)tip=600 °C for the
Methods

Sb cell, T(Te)base=340 °C and T(Te)tip=476 °C for the Te cell. According to previous flux calibration by XRR measurements on amorphous Ge, Sb, and Te films grown at room temperature, these cell temperatures correspond to a Ge flux of 0.16 nm/min, a Sb flux of 0.15 nm/min, and a Te flux of 0.45 nm/min, for a Ge/Sb/Te flux ratio of ~2/2/5. During growth, the shutter of the Te cell remained open, while the shutters of the Ge and Sb cells are alternatively opened and closed depending on the desired sublayer. The deposition time for each GeTe sublayer of 1 nm is 200 s, and 400 s for Sb₂Te₃ sublayers of 3 nm. After the deposition of the 15 repetitions, the sample is cooled down to room temperature, and prior to removal from the MBE chamber, the surface is capped with ~10 nm of Si₃N₄ by sputtering in the load-lock to prevent oxidation of the last GeTe sublayer. For the annealing experiment, a rapid thermal annealing (RTA) furnace was used. The annealing was performed on different pieces of the same sample, in less than 1 bar of nitrogen atmosphere. The temperature of 400 °C was reached from RT with a ramp of 10 °C/s.

TEM characterization:

Cross-sectional TEM specimen were prepared along the Si(111)<1-10> substrate crystallographic directions by mechanical polishing, dimple grinding and low-voltage Ar⁺ ion-milling for final thinning using a Gatan PIPS II. Average EDX measurements were performed on 4 different cross-sectional specimen of the [GeTe-Sb₂Te₃]₁₅ superlattice using a JEOL 2010 equipped with a LN₂-cooled SiLi detector. The spectra were fitted (< 1.4% error) with the Cliff-Lorimer (MBTS) correction method w/o absorbance as implemented in the NSS 2.3 software package from Thermo Scientific. HAADF-STEM measurements were carried out using a JEOL ARM200F with sub-Å point resolution settings, where the accelerating voltage was 200 kV, the semi-convergence angle was 22 mrad and ADF collecting angles were 68-280 mrad. Calibration of images is typically performed on the basis of the Si(111) interplanar distance (0.3135 nm). Image analysis was in all cases carried out on raw data using GMS 2.30 software and all linescans in this paper were normalized to the background by dividing them with a highest order unique polynomial through the Te peaks in the vdW layer + 2 neighboring Te peaks outside this layer. For better visibility, micrographs in Figure
4. Interface formation of 2D and 3D bonded materials in the case of GeTe-Sb$_2$Te$_3$ superlattices

4.3 and Figure 4.5 (a) were filtered with the Average Background Subtraction Filter (ABSF) filter$^{32}$, freely available at www.dmscripting.com/hrtem_filter.html.

**XRD and XRR characterization:** XRD and XRR characterizations were performed using a PANalytical X’PertTM triple-axis diffractometer with Cu(Kα-1) radiation (λ=1.540598Å) and Ge(220) hybrid monochromator. The XRR fits were carried out with the specular interface model of the X’Pert reflectivity fitting software.

**Visuals:** The visuals in Figure 4.1 were created using the freely available VESTA software package$^{33}$.

### 4.6 References


4. Interface formation of 2D and 3D bonded materials in the case of GeTe-Sb$_2$Te$_3$ superlattices


38. Takaura, N. *et al.* 55-μA Ge$_x$Te$_{1-x}$/Sb$_2$Te$_3$ superlattice topological-switching random access memory (TRAM) and study of atomic arrangement in Ge-Te and Sb-Te structures. in *Electron Devices Meeting (IEDM), 2014 IEEE International* 29.2.1-29.2.4 (2014).
4.7 Appendix

4.7.1 Average Structural Characterization

The epitaxial relationship between the chalcogenide super-lattice (CSL) and the silicon substrate is investigated using a symmetric $\omega-2\theta$ XRD-scan in Figure 4.10.

![Symmetric $\omega-2\theta$ XRD scan on nominal [GeTe(1nm)-Sb$_2$Te$_3$(3nm)]$_{15}$ CSL.](image)

The sharpest peaks at $Q_z = 2.00$, and $4.01 \text{ Å}^{-1}$ are reflections from the Si(111) substrate, while the Bragg reflections at $Q_z = 1.816$, and $3.63 \text{ Å}^{-1}$ correspond to a set of planes spaced by $3.452 \text{ Å}$ in real-space and are ascribed to the average periodicity of the Te sublattice that is shared throughout the whole CSL structure. These reflections are therefore named CSL 1st order and 2nd order. The peak at $Q_z = 3.465 \text{ Å}^{-1}$ is at a distance of $0.165 \text{ Å}^{-1}$ from the main CSL 2nd order peak, which corresponds to a periodicity of $3.77 \text{ nm}$ in real-space. This is in good agreement with the nominal thickness of $4 \text{ nm}$ for one superlattice repeating unit in the observed sample (1 nm GeTe + 3 nm Sb$_2$Te$_3$). This peak is therefore assigned as a superlattice satellite (sat.) peak. The reflections at $Q_z = 2.44$, $3.09$, and $4.26 \text{ Å}^{-1}$ can be attributed to the Sb$_2$Te$_3$(00.12), (00.15), and (00.21) reflections. The additional broad peak at $Q_z = \sim 3.25 \text{ Å}^{-1}$ is attributed to a convolution of peaks that occur at $1/4^{th}$, $1/5^{th}$, and $1/6^{th}$ of the distance between CSL 1st order and 2nd order. In real
4. Interface formation of 2D and 3D bonded materials in the case of GeTe-Sb₂Te₃ superlattices

space, these peaks correspond to structures of the same size as the c lattice parameters of rhombohedral GeₓSb₂Te₄, GeₓSb₂Te₅, and GeₓSb₂Te₆ when described with hexagonal axes.

![Graph](image)

**Figure 4.11**: High-resolution $2\theta$-$\omega$ scan around CSL 1st order peak.

Interference (int.) fringes around the 1st order peak in Figure 4.11, are also used to evaluate a total CSL thickness. The value is about 51.2 nm, which is not in good agreement with the nominal thickness of 60 nm. XRR spectra are complementary to XRD and help in better assessing the total thickness. Best results of the fit, shown in Figure 4.12, provide for the total thickness a value of 56.4 nm, closer to the nominal one. Because the densities of GeTe and Sb₂Te₃ are very similar, the XRR fitting is not sensitive to the thickness of each individual sublayer.
The composition of the superlattice has also been verified with cross-sectional TEM-EDX resulting in 15.1±1.7 at.% Ge, 27.9±0.9 at.% Sb and 57.0±1.5 at.% Te, which is stoichiometrically equivalent to 30±3 at.% GeTe and 70±2 at.% Sb₂Te₃. Using these results and the fact that the 57±1 nm film is highly textured along the c-axis, which allows using literature distances for GeTe (0.356 nm/BL), Sb₂Te₃ (1.015 nm/QL) and GST⁹,¹⁷, it is calculated that the film contains on average 15 sublayers of 1.05 nm GeTe (3.0 BLs) and 2.75 nm Sb₂Te₃ (2.7 QLs). These results are in excellent agreement with XRD and XRR analysis as summarized in Table 4.1.

Table 4.1: Summary of XRD, XRR and TEM-EDX results

<table>
<thead>
<tr>
<th></th>
<th>XRD int.</th>
<th>XRD sat.</th>
<th>XRR</th>
<th>TEM-EDX</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Film thickness (nm)</strong></td>
<td>51.2</td>
<td>56.6</td>
<td>56.4</td>
<td>57.0</td>
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<tr>
<td><strong>Bilayer thickness (nm)</strong></td>
<td>3.41</td>
<td>3.77</td>
<td>3.76</td>
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<tr>
<td><strong>GeTe sublayer thickness (nm)</strong></td>
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<td></td>
<td></td>
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<tr>
<td><strong>Sb₂Te₃ sublayer thickness (nm)</strong></td>
<td></td>
<td></td>
<td></td>
<td>2.75</td>
</tr>
</tbody>
</table>
4.7.2. φ-scans on Sb$_2$Te$_3$(220)

![Image of φ-scan on Sb$_2$Te$_3$(220) reflection]

*Figure 4.13: φ-scan of the CLS on the Sb$_2$Te$_3$(220) reflection.*

From the φ-scan around Sb$_2$Te$_3$(220), shown in Figure 4.13, it is found that an approximately equal number of opposite twin-domains exist in the as-deposited superlattice. This is not to be confused with a hexagonal structure, as the abc-stacking in Sb$_2$Te$_3$ has trigonal symmetry.