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Dynamic reconfiguration of van der Waals gaps within GeTe–Sb₂Te₃ based superlattices†

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Phase-change materials based on GeSbTe show unique switchable optoelectronic properties and are an important contender for next-generation non-volatile memories. Moreover, they recently received considerable scientific interest, because it is found that a vacancy ordering process is responsible for both an electronic metal–insulator transition and a structural cubic-to-trigonal transition. GeTe–Sb₂Te₃ based superlattices, or specifically their interfaces, provide an interesting platform for the study of GeSbTe alloys. In this work such superlattices have been grown with molecular beam epitaxy and they have been characterized extensively with transmission electron microscopy and X-ray diffraction. It is shown that the van der Waals gaps in these superlattices, which result from vacancy ordering, are mobile and reconfigure through the film using bi-layer defects and Ge diffusion upon annealing. Moreover, it is shown that for an average composition that is close to GeSb₂Te₄ a large portion of 9-layered van der Waals systems is formed, suggesting that still a substantial amount of random vacancies must be present within the trigonal GeSbTe layers. Overall these results illuminate the structural organization of van der Waals gaps commonly encountered in GeSbTe alloys, which are intimately related to their electronic properties and the metal–insulator transition.

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Introduction

Phase-Change Materials (PCM) are multifunctional materials with extraordinary properties, including large differences in optical reflectivity and electrical resistivity between the amorphous and crystalline phases and ultrafast switching kinetics, making them excellently suited for memory and switchable optoelectronic applications.^{1–4} In most PCM, such as the prototypical GeSbTe (GST) or specifically Ge₂Sb₂Te₅ (GST225), switching occurs between the amorphous and metastable crystalline phases. The metastable phase is characterized by a rocksalt structure, where (referring to NaCl) the anion sublattice is fully occupied by Te and the cation sublattice is randomly occupied by Ge/Sb and a significant amount (up to ~33%) of vacancies.^{5,6} Although there is several orders of magnitude difference in resistance between the amorphous and rocksalt phases, this latter state is typically semiconducting

and a Metal–Insulator Transition (MIT) is found to occur parallel with the transition to a stable trigonal structure.^{7–15} This trigonal structure is based on a stacking of close-packed planes in *abc* (*i.e.* rhombohedral) fashion with the most distinct feature of having directly adjacent Te close-packed planes, where the mutual bonding is predominantly of van der Waals (vdW) type.^{16–18} It has been observed that the transition from the rocksalt to the trigonal structure occurs by gradual ordering of vacancies on cation close-packed planes that subsequently can collapse into vdW gaps, which distinctly differ in their *abc*-stacking from the preceding vacancy layers.^{19–25} In parallel it has been argued that although the rocksalt to trigonal transition and MIT are driven by the same mechanism of vacancy ordering, they are of different nature and independent from each other.^{26,27} Hence, the behavior of ordered and disordered vacancies in GST remains of crucial importance for understanding both the structural transition as well as the Anderson-type MIT.

The nano-structuring of PCM in the form of GeTe–Sb₂Te₃ based SuperLattices (SL), referred to as GeTe–Sb₂Te₃ SL in the remainder of the text, has aroused large interest in the field, because it enables, compared to conventional GST memories, switching with a substantially lower power.²⁸ This was attributed to a solid-state switching mechanism, which therefore does not rely on the energy intensive step *via* the liquid phase that occurs normally in melt-quenched amorphous PCM. In

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our previous work it was demonstrated that high-quality GeTe-Sb₂Te₃ SL, which are grown at elevated temperatures with Molecular Beam Epitaxy (MBE), actually form SL of Sb₂Te₃ and GST vdW layers, where the vdW bonds are pinned along the film's growth direction due to deposition kinetics.^{29,30} Moreover, it was shown that trigonal GST is the thermodynamically stable phase below the melting temperature, because it formed upon annealing the as grown GeTe-Sb₂Te₃ SL. Hence, it was demonstrated that GeTe-Sb₂Te₃ SL, and particularly their interfaces, provide a valuable and useful platform to study the solid-state chemistry for PCM at the GeTe-Sb₂Te₃ tie line.

In this work extensive microscopic analysis is presented of MBE grown GeTe-Sb₂Te₃ SL with particular focus on the reconfiguration of vdW gaps, analyzed using High-Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM), X-Ray Diffraction (XRD) and Transmission Electron Microscopy Energy Dispersive X-ray spectroscopy (TEM-EDX). A quantitative analysis of HAADF-STEM images is presented that provides statistical information on the vdW layer distributions in the films. It is inferred from the results that the initially formed vdW gaps are mobile and can redistribute themselves within the film upon annealing. This process illustrates how the evolution of the initial broad distribution of the vdW layer systems in the SL due to deposition kinetics reconfigures into a narrow distribution corresponding to the film's average stoichiometry. The findings imply that the stable trigonal phase of GST must be more sparse, *i.e.* must contain random vacancies, than previously assumed to provide such mobility and that the crystal phases for stable GST can stoichiometrically deviate from the model of homologous (GeTe)_m-(Sb₂Te₃)_n layers. Overall the results shed light on previously unreported mechanisms of vacancy ordering which are related to the complex bonding interplay and disorder in GST.

Results and discussion

Table 1 shows the description of SL used in this study, both grown on Sb-terminated Si(111) using a substrate temperature of 230 °C. SL2 has been prepared with a new slow-growth method where deliberate growth interruptions were introduced when switching the deposition from GeTe to Sb₂Te₃, and *vice versa*, to improve the sharpness of the interfaces (see Methods). Results of SL2 are compared against SL1 which has been grown without interruptions and this type of film has also been presented in our previous work,^{29,30} but not with the quantitative and statistical analysis that is performed here. Fig. 1(a) shows an overview HAADF-STEM micrograph of SL2. Similar as for SL1, also here almost exclusively odd-numbered

atomic-plane GST and Sb₂Te₃ vdW blocks are formed because GeTe and Sb₂Te₃ intermix.³¹ Due to the Z-contrast between Ge and Sb/Te (see also the ESI section 1† for more details)^{22,32,33} and the presence of vdW gaps in Sb₂Te₃, the individual sublayers can be recognized and are roughly indicated by the black arrows, pointing each time to Sb₂Te₃. To better visualize the occurrence of and to allow quantitative analysis of the distances between vdW gaps in the films Geometric Phase Analysis^{34,35} (GPA) is applied. When for example GPA is applied to Fig. 1(a), the resulting ϵ_{zz} phase map is shown in Fig. 1(b) (see the ESI section 2† for details). Although the GPA algorithm was originally developed as a tool for strain mapping, in this case it is used to map relative displacements of the atomic planes which relate to the bonding in the film's stacking sequence. In this way the relative displacement "strain" ϵ_{zz} helps to visualize short distance Ge/Sb-Te in the negative ϵ_{zz} range (blue/green) and long distance vdW gaps in the positive ϵ_{zz} range (red).

The vdW layer distribution of several micrographs has then been quantified in the histogram in Fig. 1(c) (see ESI section 2† for details). Both SL films show a large fraction of 5-layers, corresponding to Sb₂Te₃, and a small peak around the 11-layer, corresponding to GST326 which formed due to mixing of 1 nm (3 bi-layers) GeTe with 1 nm (1 quintuple) Sb₂Te₃. Although SL2 has a slightly higher concentration of Sb₂Te₃, the main difference is that the 11-layered peak appears sharper for SL2 than for SL1. It is also observed that even though more Sb₂Te₃ quintuples are present, the formation of 7-layers is not drastically changed, supporting the previously found conclusion that mixing of GeTe/Sb₂Te₃ is a thermodynamic tendency. To complement such localized STEM measurements both SL films have also been characterized with XRD, of which the ω -2 θ scans are shown in Fig. 1(d) (see also the extended scans in ESI section 5†). The reflections at $Q_z = 3.63 \text{ \AA}^{-1}$ (SL1) and $Q_z = 3.66 \text{ \AA}^{-1}$ (SL2) correspond to the film's average out-of-plane Te(222) spacing, the $Q_z = 3.47 \text{ \AA}^{-1}$ (SL1) and $Q_z = 3.53 \text{ \AA}^{-1}$ (SL2) to the SL satellite peaks and the $Q_z = 3.1 \text{ \AA}^{-1}$ till $Q_z = 3.3 \text{ \AA}^{-1}$ to the 5-, 7-, 9 and 11-layer vdW layer peaks, which arises due to the formation of these respective vdW blocks.¹⁴ Comparing the spectra, the two Te(222) reflections are shifted with respect to each other. This is because there is more Sb₂Te₃ in SL2 and therefore more low-distance vdW gap Te-Te bonds, shifting this peak to higher Q_z . Also, the satellite peak of SL2 is at a different positions and is sharper than that of SL1, indicating larger as well as better defined GeTe/Sb₂Te₃ repeating unit even though SL2 has fewer repetitions (10 vs. 15). The vdW layer peak for the 9-layers can be recognized in the lower relative intensity at $Q_z = 3.27 \text{ \AA}^{-1}$, indicating that the vdW layer distribution is sharper and narrower for SL2 compared with SL1, corroborating the histogram in Fig. 1(c).

In addition, the average composition of both films is analyzed with large-scale TEM-EDX giving stoichiometries approximately GST124 and GST139 for SL1 and SL2, respectively (see ESI sections 3 and 4† for details). This allows both the quantification of the separate average sublayer thicknesses as well as

Table 1 Presented SL sample results

SL1	[Sb ₂ Te ₃ (3 nm)/GeTe (1 nm)] ₁₅ -Si ₃ N ₄ (10 nm)
SL2	[Sb ₂ Te ₃ (3 nm)/GeTe (1 nm)] ₉ -Sb ₂ Te ₃ (3 nm)

Fig. 1 HAADF-STEM and XRD of SL films after growth. (a) Overview micrograph of SL2. The black numbered arrows indicate the positions of Sb₂Te₃ sublayers. Scale bar: 10 nm; (b) GPA image of micrograph (a) visualizing vdW gaps through ϵ_{zz} relative displacements. The blue/green regions indicate shorter Ge/Sb–Te and the red regions indicate longer Te–Te inter-planar distances; (c) distributions of 5-, ..., 17-layered vdW systems for SL1 and SL2, derived from the analysis of HAADF-STEM images; (d) XRD symmetric ω - 2θ scans of SL1 and SL2. The Q_z positions for 5-, ..., 11-layer ordering is indicated by vertical lines.

finding the degree of vacancy ordering. SL1 has 1.0 nm GeTe and 2.8 nm Sb₂Te₃, while SL2 has 1.2 nm GeTe and 3.7 nm Sb₂Te₃, consistent with the intended sublayers in Table 1. Regarding the vacancy ordering it is found that SL2 has a stoichiometry which is closer to decomposable stoichiometries of epitaxial GeTe and Sb₂Te₃ than SL1, meaning that SL2 is more ordered as would be expected for the slower growth method. Therefore, the results on the films in Table 1 show that SL have been grown with well-defined and stoichiometrically consistent SL features as seen from both micro- and macro-scale (HAADF-STEM and XRD/TEM-EDX). The present quantitative

results are then fully consistent with previously obtained qualitative ones and further quantify the characteristics of the films. The main conclusion from the present comparison of SL1 and SL2 is thus that the growth interrupts can slightly improve the quality of the SLs, but they cannot prevent (the thermodynamic driving force) that GeTe is passivated by Sb₂Te₃ such that GeTe is intercalated in GST vdW layers. This reconfiguration dynamics, limited by the kinetics during growth at the deposition temperature, is therefore responsible for the relative broad distribution of the vdW layer systems in the SL as observed in Fig. 1(c).

SL1 is then further studied using the same procedures after annealing at different temperatures above the deposition temperature. Fig. 2(a) shows an overview HAADF-STEM micrograph of the film which was annealed for 30 min at 300 °C, while the 30 min 400 °C annealed film was presented previously.²⁹ It is observed, as will also be shown in the histogram below, that a significant reconfiguration has occurred, narrowing down the distribution of vdW layers. Also, many additional bi-layer defects at the edges of stacking disorder are seen in the film, where some examples are indicated by the orange arrows. This suggest that these bi-layer defects play a signifi-

cant role in the reconfiguration of the film's stacking and are probably moving through the film in a sliding fashion along (0001) vdW planes while doing so. Performing vertical line-scans along such bi-layer defects, as shown in Fig. 2(b), nevertheless indicates that mainly Sb rather than Ge is present near the vdW gap (see the ESI section 1† for more details). Note that, since within such vdW layers Te is alternated with Ge/Sb, the atomic species along such a defect have to switch their stacking sequence. As it is always Te followed by Sb-rich planes which are directly adjacent to the vdW gaps due to valence requirements,¹⁷ the Sb and Te planes must flip their position.

Fig. 2 HAADF-STEM and XRD of SL1 after annealing. (a) Overview micrograph of SL1 after 300 °C annealing. The orange arrows indicate the occurrence of bi-layer layer defects. Scale bar: 5 nm; (b) close-up and intensity line-scans of the bi-layer layer defects. The scans show that, directly after Te, Sb is most prevalent near the defects. Scale bar: 2 nm; (c) distributions of 5-, ..., 17-layered vdW systems for SL1 after different annealing temperatures, derived from the analysis of HAADF-STEM images; (d) XRD symmetric ω -2 θ scans of SL1 after different annealing temperatures. The Q_z positions for 5-, ..., 11-layer ordering is indicated by vertical lines.

Also, the bi-layer defects at the edges of the reconfiguration planes appear to be well defined when looking along the [11–20] zone axis of the film, but due to different orientation possibilities of this direction some defects seem to stretch out over large parts of the film due to one specific projection. These bi-layer defects are not only limited to multilayer systems, but are also frequently observed in bulk GST,²⁰ where they may act as a possible source of electronic scattering, reducing the mobility compared with ideally ordered layers. It is worthwhile to note that after 400 °C annealing the film has totally mixed into stable GST and most of the bi-layer defects have disappeared. Therefore, these observations seem to indicate, as also supported by the XRD results discussed below, that at 400 °C bulk diffusion saturates (also because the initial three quintuples acting as seed layers for the growth of the SL completely dissolve), whereas at 300 °C the reconfiguration is in process, as the occurrence of the bi-layer defects is observed in the process of the (thermodynamic) reconfiguration of the SL film.

Quantifying the vdW layer distributions with the analogous procedure used to obtain the ones depicted in Fig. 1(c), gives the histogram shown in Fig. 2(c). It demonstrates that the Sb₂Te₃ quintuples, which have formed in the as-deposited SL due to deposition kinetics, dissolve and disappear after annealing. Since the average composition of this film is GST₁₂₄, it is then expected that more 7-layers will develop in accordance with the homologous GeTe–Sb₂Te₃ structural model of GST. This indeed is the case, but surprisingly, also the 9-layered system (seemingly GST₂₂₅) is growing upon annealing. These findings are further corroborated on a larger scale by XRD in Fig. 2(d), where the overall distribution can also be observed in the relative intensity of the XRD features indicated by vertical lines. The persistence of the satellite peak even after annealing at 300 °C shows that mixing is limited to the interfaces. At 400 °C however this peak disappears, signaling that the nominal SL structure is lost to the complete mixing of the SL. The shift in the Te(222) peak can also be explained by the collapse of vacancy layers into tighter vdW gaps, reducing the Te–Te distance locally between the vdW blocks, and dragging down the average Te–Te distance as measured by XRD.

These results thus clearly and quantitatively illustrate the mixing of GeTe/Sb₂Te₃ encountered in epitaxial SL films. The vdW layer distribution extracted from different HAADF-STEM micrographs shows that a wide range of vdW blocks is formed during such depositions, which is also evidenced by the wide range of vdW layer reflections in XRD. So a good agreement is achieved between small-scale STEM and large-scale XRD and TEM-EDX measurements. The results of SL₂, grown by a modified slow-growth method, show that the film indeed has a better SL structure and is more ordered compared to SL₁, but that this is insufficient to suppress the strong tendency to mix GeTe and Sb₂Te₃. Still, a large fraction of the Sb₂Te₃ 5-layers have reconfigured into 7-layers, almost similarly for SL₁ and SL₂ as seen from XRD. To identify the driving force for this mixing, it is interesting to note that *ab initio* studies by Da Silva *et al.* indicate positive formation energies for GST formation out of separate GeTe and Sb₂Te₃, implying that the tri-

gonal GST phases are less stable than the separate binary compounds.¹⁶ Similarly Zhang *et al.* have calculated that the pure atomic-plane model by Kooi *et al.* are lower in energy than when small amount of mixing is introduced in the cation layers.²⁶ Therefore the driving force for mixing in GST must be strongly driven by configurational entropy S , while the bonding is dominated by formation energies E (and the actual overall driving force is the Helmholtz free energy $F = E - TS$). This illustrates the thermal balance which has to be maintained during SL growth in the epitaxial regime and it is questionable whether it is possible to sufficiently isolate GeTe from Sb₂Te₃ 5-layers.

The effect of entropy is even more so demonstrated by the annealing experiments on SL₁, where two additional phenomena are observed:

First, the vdW gaps formed during SL deposition are not fixed at a specific height in the SL, but can redistribute themselves within the film, implying that they are mobile. This process is correlated with the (out-of-plane) Ge diffusion, where the vdW gaps including Sb-rich planes reconfigure through bi-layer defects in-between the different vdW stacks. The overarching (thermodynamic) driving force for these processes is the reconfiguration of the initial SL into GST (with perfect *c*-axis alignment out-of-plane). Then, the vdW gap reconfiguration is inferred to happen due to Ge mobility³⁶ and due to the valence requirement of –Te–Sb–Te next to the vdW gap,¹⁷ since Sb has one extra valence electron compared to Ge which is used in the formation of the vdW bond. As the temperature was insufficiently high to randomize the ordered vacancies, the mechanism of the bi-layer defects movement at the edges of the reconfiguration planes could be as suggested by Yu *et al.*^{37,38} These sliding line-defects, which are probably oriented along the [11–20] close-packed directions and slide on (0001) vdW gaps, require a substantial amount of vacancies in the lattice. However, more research is needed to find out their exact structure and mechanism of movement and whether it is “over-head” or “snake-like”.^{37,38} Still, by the sliding of these line-defects parallel to the (0001) planes the vdW gaps move along the *z*-direction and can thus in a collective process not only reposition the vdW gap, but also reposition the Sb-rich planes which are both required to allow the correlated process of Ge diffusion.

Second, it is shown that SL₁ forms a substantial amount of 9-layers, seemingly GST₂₂₅, while it is known from TEM-EDX that the actual composition is GST₁₂₄. This is another indication that random vacancies form in the GST layers and are also adding entropy (an estimated 3% vacancies on the cation sublattice, in this case from the fact that the composition is GST₁₂₄ and ~2/3 of 7-layers and ~1/3 of 9-layers are observed in Fig. 2(c)). Although the present results are a strong indication (but not a proof) of these effects, it is known from previous work by Jung *et al.* on the isoelectronic GeBiTe (GBT) that vdW gaps can completely dissolve if either the Bi concentration is too dilute or the annealing temperature is sufficiently high.³⁹ *E.g.* the trigonal Ge₃Bi₂Te₆ phase is shown to reconfigure again to the (more disordered) rocksalt phase at 400 °C.

Due to the formation of random vacancies in GST and GBT, this implies that the homologous $(\text{GeTe})_m-(\text{Sb}_2\text{Te}_3)_n$ structural models are not always accurate as they omit the contribution of random vacancies. This is why GST in practical conditions is always found with disorder on the cation lattice and in vdW layer distribution.^{7,9–12,19–23,33}

Conclusions

In conclusion, quantitative analysis of HAADF-STEM images shows that initial as-deposited $\text{GeTe-Sb}_2\text{Te}_3$ SL are actually composed of Sb_2Te_3 and GST layers, in this case varying from 5-layers with a peak at 11-layers up to rare occasions of vdW stacks with 17-layers. Upon annealing the as-deposited films up to 400 °C it is shown that this vdW stack distribution gradually narrows down to a combination of 7 layer stacks (seemingly GST124) and a substantial fraction of 9 layer stacks (seemingly GST225), although the average composition is close to GST124. The results thus illustrate the interplay of bonding and disorder encountered in the development of $\text{GeTe-Sb}_2\text{Te}_3$ SL, but also tuning the structural and thereby electronic properties in GST itself. They show that due to practical conditions GST is always found in a mixed state with disorder on the cation sublattice and in the vdW layer distribution. In addition, it is argued that random vacancies must be playing an important role relating to entropy at higher temperatures, which has the consequence that the homologous $(\text{GeTe})_m-(\text{Sb}_2\text{Te}_3)_n$ structural models can deviate from the actual structure. These finding thus helps to better understand the nature and driving forces in PCM during the vacancy ordering and disordering processes.

Methods

The experimental details of MBE growth, annealing, TEM specimen preparation, HAADF-STEM, EDX, XRD and XRR are detailed in previous publications.²⁹ To prevent preferential evaporation during annealing SL1 is capped with ~10 nm Si_3N_4 by sputtering it at room temperature in the load-lock of the MBE system. EDX measurements verified that the annealing experiments did not significantly alter the overall composition (see ESI section 4†). SL2 was grown using a modified method where growth interruptions were applied to improve the interface sharpness between sub-layers. After the deposition of each nominal GeTe or Sb_2Te_3 sublayer, the sample is kept at the deposition temperature of 227.5 °C and exposed to the nominal flux of pure Te for 5 min. After each interruption, the deposition of the next sublayer is resumed as in the normal uninterrupted growth.

HAADF-STEM image analysis was in all cases carried out on raw data and the linescans in Fig. 2(b) were normalized to the background by dividing them with a spline through the Te peaks in the vdW layer. The quantification of the vdW layer distribution is done with the aid of GPA³⁴ and manually by

analyzing $6.8 \times 10^3 \text{ nm}^2$, $12.5 \times 10^3 \text{ nm}^2$ and $2.5 \times 10^3 \text{ nm}^2$ HAADF-STEM area for SL1 as-deposited, 300 °C and 400 °C annealed specimen and $4.2 \times 10^3 \text{ nm}^2$ area for SL2 as-deposited specimen, respectively. For better visibility, HAADF-STEM micrographs shown in Fig. 2 were filtered with the Average Background Subtraction Filter.⁴⁰

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