Chapter 5. Strain engineering of van der Waals heterostructures.

An unexpected long-range strain persists in 2D-bonded Bi$_2$Te$_3$-Sb$_2$Te$_3$ heterostructures.

5.1 Abstract

Modifying the strain state of solids allows control over a plethora of functional properties. The weak interlayer bonding in van der Waals (vdWaals) materials such as graphene, hBN, MoS$_2$, and Bi$_2$Te$_3$ might seem to exclude strain engineering, since strain would immediately relax at the vdWaals interfaces. Here we present direct observations of the contrary by showing growth of vdWaals heterostructures with persistent in-plane strains up to 5% and we show that strain relaxation follows a not yet reported process distinctly different from strain relaxation in three-dimensionally bonded (3D) materials. For this, 2D bonded Bi$_2$Te$_3$-Sb$_2$Te$_3$ and 2D/3D bonded Bi$_2$Te$_3$-GeTe multilayered films are grown using Pulsed Laser Deposition (PLD) and their structure is monitored in-situ using Reflective High Energy Electron Diffraction (RHEED) and post-situ analysis is performed using Transmission Electron Microscopy (TEM). Strain relaxation is modeled and found to solely depend on the layer being grown and its initial strain. This insight demonstrates that strain engineering of 2D bonded heterostructures obeys different rules than hold for epitaxial 3D materials and opens the door to precise tuning of the strain state of the individual layers to optimize functional performance of vdWaals heterostructures.¹

5.2 Introduction

Strain engineering has been used for several decades to tune and optimize a variety of material properties. The most renowned example is the engineering of Si-SiGe channels in semiconductor industry, improving conduction by an order of magnitude. Other successful implementations include optical band-gap tuning of InGaAs and high piezoelectric coefficient perovskites. Traditionally, strain engineering and studies of strain relaxation have focused on such three-dimensionally (3D)-bonded systems. Recent research has uncovered 2D bonded materials with fascinating and diverse behaviour. Notable examples are graphene, Transition Metal DiChalcogenides (TMDCs), Bi$_2$Te$_3$ and GeSbTe alloys, which offer novel physical/functional properties. It has already been shown, using calculations and deformable clamping substrates, that straining these 2D materials can significantly alter and augment their properties. Due to the exceptionally weak bonding nature in-between the layers of these 2D-systems however, individual layers were considered as unconstrained by the adjacent layers. Therefore, vdWaals heterostructures were thought to be strain–free. This concept of “vdWaals epitaxy” originally introduced by Koma was used by Geim and Grigorieva to propose designing “vdWaals heterostructures” where with carefully tailored stacking sequences one may obtain desired properties by combining multiple 2D materials. Recent reports indicate that significant interaction may take place between these 2D layers. This usually occurs when the lattice parameters and bond symmetry of adjacent layers is similar, which explains why this was not found in the original studies by Koma. This opens the way for strain engineering of vdWaals heterostructures. Sb$_2$Te$_3$ and Bi$_2$Te$_3$ have an identical unit cell symmetry (R-3m) consisting of |Te-(Sb/Bi)-Te-(Sb/Bi)-Te| Quintuple-Layers (QLs), and have an in-plane lattice mismatch of 3%. The QL blocks are weakly bonded by vdWaals forces between the outer Te planes, which makes this system quasi-2D bonded. GeTe has a distorted rocksalt structure (R3m) with no internal vdWaals gaps so it is in principle 3D-bonded, although with alternating strong and weakly bonded planes (normal to the [0001] axis). The in-plane lattice mismatch of GeTe with Bi$_2$Te$_3$ is 5%. Due to their shared tellurium content, similar sixfold symmetry with close packed planes stacked in a-b-c- fashion, and significant lattice mismatch they are ideal candidates to investigate vdWaals strain engineering. Several authors report straining these materials yields improved functional performance: lowered switching energies for memory devices, a stable Dirac point in the band gap, and improved thermoelectric figure of merit. We will present direct in- and ex-situ evidence that these vdWaals heterostructures can be grown epitaxially in a stable and controllable highly strained state. Using a model we will show that the strain relaxes in a predictable manner, allowing tuning of their functional properties through strain. Moreover, we will demonstrate that the strain relaxation occurs via a deterministic process that has to the best of our knowledge not been
reported before and that is thus distinctly different from the one(s) that hold(s) in case of epitaxy of 3D materials.

5.3 Experimental

Thin (multilayer) films of Bi$_2$Te$_3$, Sb$_2$Te$_3$, and GeTe have been grown using a Pulsed Laser Deposition (PLD) system. The film growth is monitored using RHEED. All films are grown on SiO$_2$ substrates, which are sonicated in isopropanol and rinsed using ethanol before being glued on the deposition stage. During deposition the chamber is kept under argon gas pressure at 0.12 mBar with a 1 sccm flow. The background pressure was below 10$^{-7}$ mBar. A fluence of 1 J/cm$^2$ (spot size 1.3 mm$^2$) was used with a target-substrate distance of 6 cm. The achieved growth rate was approximately 1 nm per 50 pulses. Using a 2-step growth method, flat, textured, stoichiometric films can be grown. First a thin (3 nm) ‘seed’ layer of the desired 2D film material (e.g. Bi$_2$Te$_3$) was grown at room temperature, and heated with 5 K/min to 210 °C. Growth is immediately continued at 210 °C to prevent excessive evaporation.

5.4 Results

RHEED Analysis

A typical RHEED pattern of a bilayer Sb$_2$Te$_3$-Bi$_2$Te$_3$ deposition is shown Figure 1. Well-defined streaks typical for these quintuple-layered materials are visible. Streaks corresponding to 30° in-plane rotational domains (<01-10> and <11-20> zone axes, cf. Figure S1a) are visible, showing that the film is polycrystalline but strongly c-axis oriented out of plane and thus with only in-plane rotated domains. The spacing of the streaks is proportional to the in-plane lattice parameter of the layer, and is calibrated internally. By using a fitting algorithm to extract the precise peak locations, sub-pixel (± 0.01 Å) resolution can be achieved. Several trends are observed when the lattice parameter is plotted versus the film thickness. Most notably, when Sb$_2$Te$_3$ deposition is stopped (at a layer thickness of 37 nm) and Bi$_2$Te$_3$ deposition is started, the lattice parameter of the top layer starts gradually increasing towards the one of bulk Bi$_2$Te$_3$. The bulk value is approached with a decaying exponential trend, and does not reach the bulk value in the first 30 nm: this is a direct observation of strain. We also note that the lattice parameter of the initial Sb$_2$Te$_3$ layer reduces at the start of the growth, during the first ~10 nm. This is expected since it was grown in the amorphous phase: upon heating the film crystallizes, which is normally associated with a volume reduction. Since the film is confined by the substrate however, it cannot immediately relax this strain. The strain relaxes when subsequent quintuple layers are added. This relaxed value is chosen as the calibration point, where the spacing is assumed to match the bulk value. This calibration related to Sb$_2$Te$_3$ appears correct, because the lattice
parameter of the subsequently growing Bi$_2$Te$_3$ film relaxes towards the expected bulk lattice parameter of Bi$_2$Te$_3$. We also note that the reduction in RHEED intensity during the first part of the Bi$_2$Te$_3$ deposition, which we speculate is due to slight roughening of the surface during the initial deposition phase, is partially restored during the second part of the Bi$_2$Te$_3$ deposition.

**Figure 1.** The post-deposition RHEED image (a) shows sharp streaks indicative of atomically flat films. Two sets of streaks corresponding to <11-20> (blue arrows) and <01-10> (white arrows) zone axes (cf. Appendix figure 1a) indicate that 30° rotational domains are present. The peak spacing is inversely related to the lattice parameter and is measured throughout the deposition, with an accuracy of ±0.01 Å. A bilayer Sb$_2$Te$_3$-Bi$_2$Te$_3$ film deposition is shown (b). The measured lattice spacing (c) as well as the bulk values (dashed lines) are plotted as a function of film thickness. When Bi$_2$Te$_3$ deposition starts, denoted by the vertical dotted line, the film clearly does not relax immediately to the bulk value, which proves the film is grown initially in a strained state.
Structural Analysis

Surface and structural characterization using AFM and TEM is shown in Figure 2. The Bi$_2$Te$_3$ - Sb$_2$Te$_3$ films where both sublayers are 40 nm thick, show exceptionally low roughness below 1 nm. The GeTe films grew rougher as thicknesses increased, in this scan 2.3 nm rms for a GeTe layer thickness of 30 nm on 40nm Bi$_2$Te$_3$ (Figure 2a-e). It is speculated this is due the rhombohedral distortion in GeTe, which forces the formation of domains with slightly misoriented crystal faces. In figure 2 c-g the vdWaals gaps are clearly visible and are spaced 1 nm apart in the QL-forming materials, which shows that the expected crystal structures are formed. We observe a well-defined sharp interface between the Sb$_2$Te$_3$ and Bi$_2$Te$_3$ components of the bilayer. The fact that intermixing is negligible is proven using the layer thickness obtained from cross-section images (e.g. Figure 2b-f) and the composition analysis using Electron Dispersive Spectroscopy (EDS) (see Appendix section 2). The cross-sectional and selected area electron diffraction (SAED) images corroborate the RHEED observation, showing a perfect out-of-plane texture. The SAED images also show a blurring of the rings, which is due to strain broadening. Summarizing, Figure 2 shows the layers are of high quality, comparable to those grown in other works and with other techniques.
Chapter 5. Strain engineering of van der Waals heterostructures.

(a) and (e) AFM images showing the surface morphology of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ layers.

(b) and (f) STEM images of Bi$_2$Te$_3$, Sb$_2$Te$_3$, and GeTe layers with SiO$_2$ as the substrate.

(c) and (g) High-resolution STEM images at 5 nm scale showing the layered structure of Bi$_2$Te$_3$ and Sb$_2$Te$_3$.

(d) and (h) X-ray diffraction patterns indicating the crystal structure of Bi$_2$Te$_3$ and GeTe.
Figure 2. a, b, c, d) and e, f, g, h) show results of Sb$_2$Te$_3$-Bi$_2$Te$_3$ and Bi$_2$Te$_3$-GeTe films, respectively. a) and e) show AFM tapping mode images. A higher roughness is found for multilayers containing GeTe. b, c) and f, g) show cross-section HRTEM images indicating sharp interfaces. Individual Te planes, as well as the vdWaals gaps (in the QL materials) are resolved. d) and h) show the respective SAED patterns taken of a circular area of 2.5 µm diameter. These rings correspond directly to the streaks observed using RHEED (SI section 2), proving the film is epitaxially grown with random in-plane and fully textured out-of-plane orientation. With TEM we are now sensitive to the whole thickness of the film. Distinct ring broadening is observed, indicating that the film layers are strained.

Multilayers

The evolution of the lattice parameter during deposition is shown in Figure 3a for Bi$_2$Te$_3$-Sb$_2$Te$_3$-Bi$_2$Te$_3$, Sb$_2$Te$_3$-Bi$_2$Te$_3$-Sb$_2$Te$_3$ and Bi$_2$Te$_3$-GeTe-Bi$_2$Te$_3$ trilayers. For the Bi$_2$Te$_3$-Sb$_2$Te$_3$ systems we observe an identical and mirrored behavior: no difference between initial compressive or tensile strain states is observed. Growth of GeTe on Bi$_2$Te$_3$ induces a slightly more rapid strain relaxation, while the strain relaxation during the growth of Bi$_2$Te$_3$ on GeTe is the fastest. All the observed final lattice parameters differ slightly from their literature bulk values, which might be due to the initial calibration being slightly off, and/or a drift in the electronics of the RHEED system. The layers grow in an initially matched state with the layer below, but start relaxing the internal strain immediately; no ‘critical thickness’ characteristic of 3D-bonded systems is observed in any system. This is consistent with the notion of weak vdWaals bonds between layers. Figure 3b shows a deposition of a Bi$_2$Te$_3$-Sb$_2$Te$_3$-Bi$_2$Te$_3$ trilayer, now with growth being interrupted (vertical lines) at one-third of the layer thickness needed for nearly complete relaxation (cf. Figure 3a). After deposition is interrupted, strain relaxation immediately stops, and continues as if uninterrupted when deposition is resumed. These observations all indicate that the relaxation mechanism is identical for tensile and compressive strain, and that the film layers are in relative equilibrium during growth: no transient (time dependent) changes are observed after growth.

To truly strain-engineer a multilayer the functional layer cannot be allowed to fully relax its strain (as we allowed to reveal the full relaxation curves in Figure 3a). Therefore, multilayers of two component materials (Bi$_2$Te$_3$+Sb$_2$Te$_3$ and Bi$_2$Te$_3$+GeTe) are grown, where both components strain each other. The lattice parameters (Figure 3c) are observed to oscillate using the decaying behavior between both bulk lattice parameters, never reaching a relaxed state in the 10 nm thick layers. The relaxation behavior has a highly repeatable character and does not depend on the thickness of the previous layer(s), but is solely based on the type of layer growing and the initial strain when its growth starts. This can also be seen from the ‘inverted’ Bi$_2$Te$_3$-Sb$_2$Te$_3$ trilayers in Figure 3a, where strain relaxation always occurs at the same rate too. Although both multilayer depositions are
performed on a base layer of 40 nm Bi$_2$Te$_3$, the average lattice parameter of the multilayers is quickly brought to the average of the bulk lattice parameter of the separate components, reminiscent of Vegard’s law. This gives a design rule on strain engineering of multilayers or superlattices (SLs), where for a large number of SL repetitions the individual layer thicknesses directly determine their strain state.
Figure 3. a) The in-plane lattice parameter of the top layer of the films is continuously measured as shown in Figure 1. Relaxation of Bi$_2$Te$_3$-Sb$_2$Te$_3$-Bi$_2$Te$_3$, Sb$_2$Te$_3$-Bi$_2$Te$_3$-Sb$_2$Te$_3$ and Bi$_2$Te$_3$-GeTe-Bi$_2$Te$_3$ trilayers is shown. The initial lattice parameter is seen to relax to lower value regardless of material, indicating initial tensile strain within the seed layer. When the deposition switches to another material, the lattice parameter increases/decreases to relax strain in the top layer, approaching the new materials bulk value at a decaying rate. Strain relaxation is faster in systems containing GeTe. b) A similar Bi$_2$Te$_3$-Sb$_2$Te$_3$-Bi$_2$Te$_3$ trilayer deposition as in a, but with growth interrupts (vertical lines) at 1/3 layer thickness required for approaching full relaxation. The lattice parameter remains constant, demonstrating that no further strain relaxation occurs without deposition. c) Lattice parameter evolutions during growth of multilayers of Bi$_2$Te$_3$-Sb$_2$Te$_3$ and Bi$_2$Te$_3$-GeTe are compared. Highly similar behavior is observed for both systems. Due to the alternating material depositions, an oscillation around their average lattice parameter is observed. The oscillations for GeTe have a larger amplitude than for Sb$_2$Te$_3$ due to the larger difference in lattice parameter with Bi$_2$Te$_3$. 

5.4 Results
5.5 Model

The results presented in figure 3 clearly demonstrate that the current type of strain relaxation differs completely from the classical mechanisms in 3D materials. In these classical systems there is a critical thickness below which the film is lattice matched to the substrate and above which misfit dislocations are generated. When this critical thickness is exceeded, threading dislocations travel down from the (growth) surface to the substrate-film interface. In the present case however there is no critical thickness: relaxation starts immediately. Since the deposited materials grow in a mixed layer-islanded (Stranski-Krastanov) growth mode, grain boundaries in-between islands (domains) can readily introduce dislocations. Mutual slip of weakly (vdWaals) bonded telluride planes is energetically favourable compared to dislocation movement through the quintuple layer in the vertical direction, which requires breaking of stronger (predominantly) covalent bonds (see Appendix section 3). This immediate strain relaxation prevents the build-up of sufficient strain energy to allow dislocation movement with a component parallel to the c-axis (e.g. threading dislocation downward to the more highly strained interface). Each (quintuple layer) island can therefore be regarded as a separate system, where the dislocation energy is balanced against the island’s strain energy. Once a QL reaches full coverage on the surface and the layer is closed, introduction or slip of additional dislocations will be unfavourable due to the need for interface compatibility. Misfit dislocations will therefore not be localized at the interface, but instead distributed over the thickness of the film on the vdWaals gaps.

To the best of our knowledge no model describing strain relaxation of 2D materials exists in literature yet. We propose a model for predictive control of the strain state of a quasi-2D bonded vdWaals multilayer, where we describe a strain $\varepsilon$ in a growing (quintuple) layer as an overdamped harmonic oscillator.

$$\frac{d^2\varepsilon}{dh^2} = C \varepsilon - \beta \frac{d\varepsilon}{dh}$$

(5.1)

The rate of change of strain (left-hand side of eq. 1) is equal to the sum of all forces/stresses acting on the growing layer, described by the right-hand side (RHS). The driving force for strain relaxation can be described according to Hooke’s law $\sigma_{ij} = C_{ijkl} \varepsilon_{kl}$, where stress and strain are linearly related through the general stiffness tensor $C_{ijkl}$. This stress is the restoring force (first RHS term) of the oscillator. A damping term is added to eq. 1 to account for the relaxation retardation force due to inter-layer vdWaals bonding and formation energy of dislocations. These effects are dependent on the lattice mismatch between consecutive (quintuple) layers, which is equivalent to the change in strain over height $h$: $d\varepsilon/dh$. Since lattice mismatch increases the length of the Te-Te vdWaals bonds beyond equilibrium, this increases the energy of the system.
Furthermore, the number of dislocations necessary to accommodate this mismatch is also linearly dependent on the lattice mismatch. Both damping terms are therefore combined in the second RHS term with an unknown prefactor $\beta$. Eq.1 can be solved for strain as a function of thickness:

$$\varepsilon(h) = Ae^{-bh}$$  \hspace{1cm} (5.2)

Where $A$ is just a normalization constant, and $b$ gives the rate of strain relaxation.

Figure 4. The absolute strain in a thin layer as a function of layer thickness. Equation 2 is fitted to the strain profiles of Figure 3. Thin lines are fitted to the shown raw data of trilayers of Figure 3a, dashed lines are extrapolated, thick lines are fits of the multilayer data of Figure 3c, showing that the relaxation in multilayers is the same as in trilayers. The inset values show the thickness needed to obtain half the initial strain value. The Bi$_2$Te$_3$-Sb$_2$Te$_3$ systems are the slowest to relax strain.

Our phenomenological model allows for quantitative comparison of strain relaxation in the presented multilayer systems. Strain relaxation is fitted (Appendix section 4) using equation 2; where strain values are calculated with respect to their fitted bulk lattice parameter value. Figure 4 shows fits of the relaxation curves presented in Figure 3. The fits are extrapolated and offset to coincide at a strain of 0.06 to show the difference in relaxation rate $b$ between various multilayers. This rate is also a direct measure for the thicknesses needed to obtain half the original strain. Bi$_2$Te$_3$ and Sb$_2$Te$_3$ can be stacked interchangeably; strain relaxation fits identically on compressive and tensile epitaxy of these QL-structures. The tensile strain relaxes slightly faster in GeTe than in Sb$_2$Te$_3$ (when grown on Bi$_2$Te$_3$), and
relaxation of Bi$_2$Te$_3$ on GeTe occurs even more rapidly. Due to the naturally occurring domain formation in GeTe, it is expected that its rougher surface increases nucleation density, reduces domain size (as shown in Figure S5), and thereby increases the probability of strain relaxation. The relaxation curves of Figure 3c, obtained for comparatively thin-layered multilayers were fitted as well and are also shown in Figure 4. They are in good agreement with the values found for the thicker layered structures in Figure 3a. This is an important result, since it shows again that the strain relaxation is only dependent on the lattice parameter of the previous (quintuple) layer, and is not dependent on the previous layer thickness. All strain relaxation for a given set of layer materials falls on the ‘master curve’ shown in Figure 4. Therefore, this exponentially decaying function can be used as a predictor for strain values.

5.6 Discussion

The RHEED measurements shown in Figure 3 clearly prove that these materials are grown in a strained fashion, even during classic vdWals epitaxial growth. However, RHEED is only sensitive to the topmost layer, and cannot probe the lattice parameter at greater depth. As we have shown in the previous section, strain relaxation can be modeled and predicted well using a simple model. The basic premise of the model is that a newly growing layer is only sensitive to the lattice parameter of the current surface layer on which it grows. The newly grown layer will therefore introduce a number of dislocations on this new vdWals interface based on the current mismatch. It therefore does not alter the strains state of the previously grown layer. The post-growth strain gradient is therefore considered identical to the RHEED observations, and no further strain relaxation occurs. This is corroborated by TEM investigations in both plan-view and cross section. In plan-view, an epitaxial bilayer with two well-defined lattice parameters would yield regular moiré interference fringes. We only observe alternatingly areas with no contrast and highly irregular moiré patches (see Appendix section 7). Accordingly, the diffraction patterns (Figure 2) show ring broadening indicative of non-constant lattice parameters. For strain-relaxed 3D bonded materials, a dislocation array should be visible at the bilayer interface in a cross-section (Figure 2). Assuming full relaxation of a layer of Sb$_2$Te$_3$ on Bi$_2$Te$_3$, it is easily calculated that the distance between neighboring dislocations in the array should be about 34 nm (see Appendix section 5). This is clearly not observed. It can be easily shown that if dislocations are assumed to be distributed across the film according to the observed strain gradient, their density at the interface drops by an order of magnitude (see Appendix section 5). This is a relatively low density of dislocations, and confirming this number using atomic-resolution TEM, or indeed any other technique, will be a nontrivial task (and their observation is therefore beyond the scope of the present work).
5.7 **Outlook**

Several publications mention the promises of straining these functional materials. We have demonstrated engineering control over the strain state of single- and multilayered telluride systems. Using this control, we envision tuning the strain state of the various multilayer components to maximize their performance for a given application. It is important to note that this strain is nonuniform, and has a gradient throughout the layer, and this needs to be taken into account when predicting functional properties. Of course, the effect of nonuniform strain in sublayers will be less pronounced for thinner layers. In fact several authors have either unknowingly or with a less direct method of characterizing the strain state already taken steps on this path. Many reports exist on thickness-tuning and improved performance of thin-film multilayers which we now know to be strained. Shortly after the initial publication of this article, a publication by Wang and Lange et al. showed similar strain relaxation in the GST-Sb₂Te₃ system, and also posed a rather different model of the relaxation behaviour in these systems. Further investigations will reveal whether their or our description are closer to the actual mechanism.

5.8 **Conclusions**

We have demonstrated engineering control over the strain state of vdWaals heterostructures of Bi₂Te₃, Sb₂Te₃ and GeTe layers, by directly monitoring the lattice parameter during growth using RHEED. We have presented evidence showing that strain relaxation in 2D bonded materials differs from 3D bonded materials. Maximum strains up to 5% relaxed over a thickness of about 40 nm, and a strain gradient persists after deposition. Using a predictive model, multilayer strain was found to depend solely on the initial lattice mismatch. We find an exponentially decaying strain in all studied material systems, where the addition of GeTe increases relaxation rate, which we speculate is due to increased roughening and smaller domain size. The direct observations and predictions of strain and relaxation imply that this newly reported behavior occurs in many heterostructures grown using the principle of vdWaals epitaxy, which has so far not been recognized in the literature. We demonstrate that strain engineering control in these weakly interacting layer systems can be achieved, and the proposed model allows ample freedom to engineer 2D bonded material systems to optimize functional properties.


5.9 Literature

5.9 Literature


5.10 Appendix

Observed Reflections in RHEED and TEM Diffraction

The RHEED images were analyzed by obtaining an intensity line profile across the RHEED streaks. The intensity peak locations were determined by fitting a Gaussian function, and the peak separation of all detected peaks was fitted to a linear profile using a least squares fit. From this fit the streak spacing (in pixels) was extracted. The camera pixel spacing was calibrated using the literature bulk value of the relevant material and under the assumption that only the planes shown in figure S1 were in a reflection condition. The spacing of the first material layer, just before switching to a different material was taken for calibration, since this is the layer which is closest to bulk equilibrium.

Figure S1. The red atoms indicate the positions of the atoms in the outermost surface layer in Bi$_2$Te$_3$ and Sb$_2$Te$_3$ when grown with c-axis-up texture, the blue atoms the subsurface layer positions. Since the RHEED beam penetrates ~1nm, the shorter-scale symmetry is not probed, and the red $\{01\overline{1}0\}$ and purple $\{11\overline{2}0\}$ plane spacings are observed as streaks on the phosphor screen. The peaks are also marked accordingly in figure 1 of the main paper. In TEM diffraction, the beam penetrates through the whole sample, and the smaller scale symmetry is probed. The $\{01\overline{1}0\}$ reflection then becomes forbidden due to the intermediate planes at 1/3 spacing (blue) and the prevailing reflection becomes $\{03\overline{3}0\}$. The $\{11\overline{2}0\}$ spacing is unaffected. Due to the trigonal symmetry of the structure, this means the ratio between both allowed reflections stays $\sqrt{3}$. 
**Cross-section TEM versus Plan-View EDS.**

By measuring individual layer thicknesses from cross-section TEM images, one can calculate the overall elemental composition of the film when assuming stoichiometric Bi$_2$Te$_3$, GeTe and Sb$_2$Te$_3$ films. These values are compared to those obtained using Electron Dispersive Spectroscopy EDS scans of large (few micron) sized areas. The results are shown in table S1. The two types of measurements are considered to be in good agreement, which means no significant intermixing has occurred during growth. This is in agreement with the reports by Lanius et al. $^{34}$

<table>
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<th>Bi$_2$Te$_3$/GeTe</th>
<th>Cross (at.%)</th>
<th>EDS (at.%)</th>
<th>Sb$_2$Te$_3$/Bi$_2$Te$_3$</th>
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*Table S1. Elemental composition from cross-section thickness measurement is indicated by “Cross.” Composition from EDS scans is denoted by “EDS”. The composition is shown per constituent element. The independent measurements agree within a reasonable error of 2 at.%.*
Dislocation Movement

As discussed in the main text, a likely mechanism for strain relaxation is dislocation movement. In (isotropic) 3D Materials, it is energetically favourable for dislocations to glide to the interface, where strain is highest. The amount of broken bonds at the dislocation core remains the same. For 2D materials however, a dislocation core will generally be situated at the vdWaals gap. Glide to the strained interface involves severing covalent bonds within the quintuple layer. This is energetically unfavourable, so the dislocation is blocked and can only slide parallel to the strained interface. This mechanism could (partly) explain the persistence of a strain gradient in 2D materials.

![Dislocation Movement Diagram](image)

Figure S2. Comparison of Dislocation mobility in 3D materials (left) and 2D materials (Right). In 3D materials, dislocations are expected to glide to the interface and form a regularly spaced array, relieving strain in the film. In 2D materials, dislocations are expected to be confined to the height where they originally were introduced: only the layers are relaxed.

Model for Strain Relaxation

We propose a model for predictive control of the strain state of a quasi-2D bonded vdWaals multilayer, where we describe a strain $\varepsilon$ in a growing (quintuple) layer as an overdamped harmonic oscillator.

$$\frac{d^2 \varepsilon}{dh^2} = C\varepsilon - \beta \frac{d\varepsilon}{dh}$$  \hspace{1cm} (5A.1)

The rate of change of strain (LHS of eq. 1) is obtained by adding all forces/stresses acting on the growing layer, which are described on the RHS. The driving force for strain relaxation is given using Hooke’s law $\sigma_{ij} = C_{ijkl}\varepsilon_{kl}$, which describes stress as linearly related to the strain through the general stiffness tensor $C_{ijkl}$.\textsuperscript{47,48} This stress is the restoring force (first RHS term) of the oscillator. A damping term is added to eq.1 to account for the relaxation retardation force due to inter-layer vdWaals bonding and formation energy of dislocations. These effects are dependent on the lattice mismatch between consecutive (quintuple) layers, which is equivalent to the change in strain over height $h$: $d\varepsilon / dh$. Since lattice mismatch
Chapter 5. Strain engineering of van der Waals heterostructures.

increases the length of the Te-Te vdWaals bonds beyond equilibrium, this increases the energy of the system. Furthermore, the number of dislocations necessary to accommodate this mismatch is also linearly dependent on the lattice mismatch. Both damping terms are therefore combined in the second RHS term with an unknown prefactor $\beta$. Eq.1 can be solved for strain as a function of thickness:

$$\epsilon(h) = Ae^{-bh}$$  \hspace{1cm} (5A.2)

Where $A$ is just a normalization constant, and $b$ gives the rate of strain relaxation. The solutions of the harmonic oscillator contain a solution for an overdamped system, where the system returns with exponential decay to the equilibrium position:

$$\epsilon = e^{bh} \text{ with } b = \frac{1}{2} (-\beta \pm \sqrt{\beta^2 - 4C})$$

Which is overdamped (valid) for $\beta^2 - 4C > 0$.  \hspace{1cm} (5A.3)

Equation 2 can be fitted to the experimentally obtained lattice parameters, which will yield a value for $b$. The observed lattice parameters $\alpha$ at layer thickness $h$ were fitted to an equation of the form:

$$\alpha = \alpha_f + \alpha_i e^{-bh}$$  \hspace{1cm} (5A.4)

Where absolute strain $\epsilon$ can be obtained by normalizing to the final lattice parameter $\alpha_f = \epsilon(h = \infty)$

$$\epsilon = \left| \frac{\alpha_i}{\alpha_f} \right| e^{-bh} = e^{-bh + \ln \left( \frac{\alpha_i}{\alpha_f} \right)}$$  \hspace{1cm} (5A.5)

Since the prefactor $A = \alpha_i / \alpha_f$ is purely a scaling parameter which determines the strain at $h = 0$, it can be arbitrarily set to the desired strain value. The strain curves can be described from any hypothetical strained starting point. The defining parameter is the strain relaxation rate $b$.

The thickness for half strain $h_f$ can be obtained:

$$e^{-bh_f} = \frac{1}{2} e^{-bh_i}, \text{ with } h_i = 0, \text{ yields } h_f = \frac{\ln(2)}{b}$$  \hspace{1cm} (5A.6)

Formula 3 can be rewritten to obtain $\beta = \frac{-b^2 - C}{b}$ Plugging in $C = 50$ GPa \(^{57}\) (in-plane Youngs modulus) yields $\beta = 500$ GPa (b=0.1). This should be interpreted as the combination of pressures preventing relaxation, e.g. the interlayer vdWaals force and the dislocation formation potential.
**Dislocation Density Calculation**

Using the strain relaxation described by equation 2 of the main text, we can readily derive the dislocation density as a function of layer thickness. We note that this explicit model and formula is not strictly needed, and a numerical result can be obtained directly from the data. Since for 2D materials dislocations are not concentrated at the (strained) interface, two steps are added to calculate the dislocation density at arbitrary film height – which is then irrespective of actual film thickness. The dislocations considered here are always of edge-type with Burgers vector and line direction oriented in a plane parallel to the interface. Such edge dislocations are the most efficient in relaxing strain. A single array of dislocations can only relax the strain in one dimension however. Since the strain is bidirectional (in a plane parallel to the interface) a network of dislocations is required. Due to hexagonal symmetry of the individual telluride planes (parallel to interface) which are stacked in a-b-c fashion (perpendicular to the interface), it is expected that a triangular network of dislocation lines is present in planes parallel to the interface. The Burgers vectors have a size equal to the a lattice parameter (and are of 1/3<11-20> type).\(^{58}\) For the present analysis it is sufficient to only consider a single plane spanned by the a-lattice vector parallel to the interface and the c-vector perpendicular to the interface, where the strain is relaxed in one dimension.

A step by step derivation is given below.

Strain is approximated using a decaying exponential:

\[ \varepsilon(h) = A e^{-bh} \] \hspace{1cm} (5A.7)

The number fraction of dislocations \(N\) in an area defined by the unit cell width \(a\) (parallel to interface) and between height zero and final height \(h\) (perpendicular to interface), is directly proportional to the strain, with \(\varepsilon_0\) the strain at height zero (\(\varepsilon(0)\)):

\[ N = \varepsilon_0 - \varepsilon = \varepsilon_0 - A e^{-bh} \] \hspace{1cm} (5A.7)

The total dislocation density \(\delta_T\) (number of dislocations per unit of area \(A\)) is then given by:

\[ \delta_T = \frac{N}{A} = \frac{-A e^{-bh} + \varepsilon_0}{a} \] \hspace{1cm} (5A.8)

For 2D materials dislocations will not move to the interface, and an additional step is required to calculate the dislocation density at arbitrary distance from the interface, for a given layer thickness.

To calculate the number of dislocations at arbitrary distance from the interface, for a given strain profile, we take the derivative of \(N\), which gives the dislocation number at a given thickness.

\[ n(h) = \frac{dN}{dh} = Ab e^{-bh} \] \hspace{1cm} (5A.9)

The dislocation number can again be normalized to a density:

\[ \delta_{2D} = \frac{Ab e^{-bh}}{a} \] \hspace{1cm} (5A.10)
The relevant spacings between equidistantly spaced dislocations can trivially be obtained by $d = 1/\delta$

Figure S3. Dislocation densities per unit area in a cross section are plotted, assuming Sb$_2$Te$_3$ growth on Bi$_2$Te$_3$. A=0.127, b=0.0929, $a = 4.26$ nm. Top Left: Total dislocation density in the film (#/nm$^2$) versus film thickness (nm). Top Right: Distance (nm) in between equidistantly spaced dislocations versus film thickness when it is assumed that the total dislocation density in the top left image translates to a single array of misfit dislocations at the interface, resembling the case of 3D materials where misfit is relaxed at the interface. Such a single array is rather hypothetical because it is inconsistent with the assumed exponentially decaying strain profile. Bottom Left: Dislocation density (#/nm$^2$) versus distance from the interface (nm) for 2D materials where dislocations are not localized at the interface. Bottom Right: Distance (nm) in between equidistantly spaced dislocations versus distance from the interface (nm). The dislocation concentration is still highest at the interface, but decaying for increasing height within the film. In contrast to the hypothetical top right image, this bottom right image displays an actual physical picture consistent with the exponential strain relaxation observed, which could be verified in for instance cross-sectional TEM images.
Plan-view TEM imaging

TEM analysis of plan-view samples has been performed on bilayers of Sb$_2$Te$_3$ on Bi$_2$Te$_3$ (Figure S6ab) and GeTe on Bi$_2$Te$_3$ (Figure S6cd). The real-space images show that no regular moiré fringes appear, which would be the signature of a stacked system with 2 distinct lattice parameters. This indicates the strain gradient observed through RHEED still persists even in a TEM foil. The domain sizes of Sb$_2$Te$_3$ and GeTe are difficult to estimate, but it is clear the domain size in GeTe is significantly smaller, which can be seen from both the real-space image, and the diffraction rings, where for Sb$_2$Te$_3$ distinct spots belonging to a specific domain can be observed.

Figure S4. ab and cd show bilayers of Sb$_2$Te$_3$ on Bi$_2$Te$_3$ and GeTe on Bi$_2$Te$_3$ respectively. The layers were sufficiently thick to allow a full relaxation curve to be recorded with RHEED. ac show plan-view TEM, revealing some regions with disordered moiré, and small domains in GeTe compared to Sb$_2$Te$_3$. bd Shows the diffraction patterns of ac, revealing broadened rings, with distinct spots visible for Sb$_2$Te$_3$ due to its larger domain size compared to the one for GeTe.