Strain engineering of van der Waals heterostructures†

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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, MoS2, and Bi2Te3 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 Bi2Te3–Sb2Te3 and 2D/3D bonded Bi2Te3–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 in 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.

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 the 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), Bi2Te3 and GeSbTe alloys, which offer novel physical/functional properties. It has already been shown, using calculations and deformable clamping substrates, that strain engineering of 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. Sb2Te3 and Bi2Te3 have an identical unit cell symmetry (R3m) 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 Bi2Te3 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.

**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 Reflective High-Energy Electron Diffraction (RHEED). This enables *in situ* analysis of the structure of the top (∼1 nm) layer of the film. All films are grown on SiO$_2$ substrates, which are sonicated in isopropanol and rinsed using ethanol before being glued on the deposition stage. The alloy targets are commercially obtained from KTECH and have a purity of 99.999%. 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 4 cm. The achieved growth rate was approximately 1 nm per 50 pulses. Transmission Electron Microscopy (TEM) samples were prepared by mechanical grinding, dimpling and argon ion milling using a Gatan PIPS TEM analysis was performed using JEOL 2010 and 2010F, of which the images were analyzed using (Gatan) GMS3. Atomic Force Microscopy (AFM) was performed on a Bruker MultiMode 8 and analysed using the Gwyddion software package. Using a 2-step growth method, flat, textured, stoichiometric films can be grown (see ESI section 1†). 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$^{-1}$ to 210 °C, which induces self-organized growth with c-axis out of plane even on an amorphous substrate (thermally grown SiO$_2$). Due to vdWals epitaxy, subsequent layers adopt the texture of the seed layer. Growth is immediately continued at 210 °C to prevent excessive evaporation.

**Results**

A typical RHEED pattern of a bilayer Sb$_2$Te$_3$-Bi$_2$Te$_3$ deposition is shown Fig. 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. Fig. S2a†) 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 (see ESI section 2†) 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.

Surface and structural characterization using AFM and TEM is shown in Fig. 2. The Bi$_2$Te$_3$–Sb$_2$Te$_3$ films where both sub-layers 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 40 nm Bi$_2$Te$_3$ (Fig. 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 Fig. 2c–g the vdWals 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. Fig. 2b–f) and the composition analysis using Electron Dispersive Spectroscopy (EDS) (see ESI section 3†). 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, Fig. 2 shows the layers are of high quality, comparable to those grown in other works and with other techniques.30,33–37

The evolution of the lattice parameter during deposition is shown in Fig. 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 Bi₂Te₃ 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.38–40 This is consistent with the notion
of weak vdWaals bonds between layers. Fig. 3b shows a depo-
sition of a Bi₂Te₃–Sb₂Te₃–Bi₂Te₃ trilayer, now with growth
being interrupted (vertical lines) at one-third of the thickness
needed for nearly complete relaxation (cf. Fig. 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 Fig. 3a). Therefore, multi-
layers of two component materials (Bi₂Te₃ + Sb₂Te₃ and Bi₂Te₃
+ GeTe) are grown, where both components strain each other.
The lattice parameters (Fig. 3c) are observed to oscillate using
the decaying behavior between both bulk lattice parameters,
ever 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’ Bi₂Te₃–Sb₂Te₃ trilayers in Fig. 3a, where strain relax-
ation always occurs at the same rate too. Although both multi-
layer depositions are performed on a base layer of 40 nm
Bi₂Te₃, 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.11 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.

Model

The results presented in Fig. 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 dis-
locations are generated. When this critical thickness is
exceeded, threading dislocations travel down from the
(growth) surface to the substrate–film interface.38,40 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,42,43
grain boundaries in-between islands (domains) can readily
introduce dislocations.44 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 (predo-
minantly) covalent bonds (see ESI section 4†). This immedi-
ate strain relaxation prevents the build-up of sufficient strain
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
therefore can be regarded as a separate system, where the dis-
location 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 inter-
face, 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 ε in a
growing (quintuple) layer as an overdamped harmonic oscilla-
tor.

\[
\frac{d^2 \varepsilon}{dh^2} = C \varepsilon - \beta \frac{d \varepsilon}{dh} \tag{1}
\]

The rate of change of strain (left-hand side of eqn (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 \( C_{ijkl} \).46,47 This
stress is the restoring force (first RHS term) of the oscillator. A
damping term is added to eqn (1) to account for the relaxation
retardation force due to inter-layer vdWaals bonding and forma-
tion 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 \( h \):
\( \frac{de}{dh} \). 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 neces-
sary 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
\( \beta \). Eqn (1) can be solved for strain as a function of thickness:

\[
\varepsilon(h) = A e^{-\beta h} \tag{2}
\]

where \( A \) is just a normalization constant, and \( b \) gives the rate
of strain relaxation.

Our phenomenological model allows for quantitative com-
parison of strain relaxation in the presented multilayer
systems. Strain relaxation is fitted (ESI section 5†) using eqn
(2); where strain values are calculated with respect to their
fitted bulk lattice parameter value. Fig. 4 shows fits of the relaxation curves presented in Fig. 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. \( \text{Bi}_2\text{Te}_3 \) and \( \text{Sb}_2\text{Te}_3 \) can be stacked interchangeably; strain relaxation fits identically on compressive and tensile epitaxy of these QL-structures. The tensile strain relaxes slightly faster in \( \text{GeTe} \) than in \( \text{Sb}_2\text{Te}_3 \) (when grown on \( \text{Bi}_2\text{Te}_3 \)), and relaxation of \( \text{Bi}_2\text{Te}_3 \) on \( \text{GeTe} \) occurs even more rapidly. Due to the naturally occurring domain formation in \( \text{GeTe} \), it is expected that its rougher surface increases nucleation density, reduces domain size (as shown in Fig. S5†), and thereby increases the probability of (reduces the energy barrier for) strain relaxation. The relaxation curves of Fig. 3c, obtained for comparatively thin-layered multilayers were fitted as well and are also shown in Fig. 4. They are in good agreement with the values found for the thicker layered structures in Fig. 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 Fig. 4. Therefore, this exponentially decaying function can be used as a predictor for strain values.

Discussion

The RHEED measurements shown in Fig. 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 vdWaals 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 ESI section 7†). Accordingly, the diffraction patterns (Fig. 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 (Fig. 2). Assuming full relaxation of a layer of \( \text{Sb}_2\text{Te}_3 \) on \( \text{Bi}_2\text{Te}_3 \), it is easily calculated that the distance between neighboring dislocations in the array should be about 34 nm (see ESI section 6†). 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 ESI section 6†). This is a relatively low density of dislocations, and confirming this number using atomic-resolution TEM, or indeed any other technique, will be a non-trivial task (and their observation is therefore beyond the scope of the present work).

Several publications mention the promises of straining these functional materials.25–28,48–52 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 non-uniform 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.10,25,33,51,53,54

Conclusions

We have demonstrated engineering control over the strain state of vdWaals heterostructures of \( \text{Bi}_2\text{Te}_3 \), \( \text{Sb}_2\text{Te}_3 \), and \( \text{GeTe} \) 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 vdWaal’s 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.

Conflicts of interest

There are no conflicts of interest to declare.

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