Tailoring the epitaxy of Sb$_2$Te$_3$ and GeTe thin films using surface passivation†

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Chalcogenide thin films are exciting candidates for electronic applications such as spintronic devices, non-volatile memories and thermoelectric materials. To achieve such applications the understanding of their thin film growth is of paramount importance. In this work the epitaxy of exemplary chalcogenides Sb$_2$Te$_3$ and GeTe on different surfaces of Si(111) with atomically sharp interfaces is presented and compared using plan-view transmission electron microscopy and electron diffraction. It is shown that depending on the monolayer surface termination the resulting films present drastic differences in terms of film morphology and crystallinity. In particular, a profound difference is found between the films grown on H-passivated and Sb-passivated surfaces. In both cases, the out-of-plane texture is strongly c-axis oriented, but the case of Si(111)–H shows the frequent occurrence of random in-plane twist for both films, while for Si(111)–Sb this is strongly suppressed. The role of the substrate-film interface for the epitaxy is discussed and the consequences for the properties of the films are highlighted. In general, the insights of these results shed light on chalcogenide thin film growth for topological insulator, ferroelectric, thermoelectric and phase-change materials research.

Introduction

The growth of highly ordered chalcogenide thin films is of significant importance for the development of new applications in topological insulators,$^{1,2}$ Rashba-type materials,$^3$ thermoelectric materials$^4$ and interfacial phase-change memories.$^5$ In this respect Sb$_2$Te$_3$ and GeTe are exemplary chalcogenides. The Sb$_2$Te$_3$ system has for instance been studied for its protected surface states using the weak anti-localization effect$^6,7$ and scanning tunneling spectroscopy$^8,9$ and GeTe is shown to have a spin-split surface and bulk bands using angle-resolved photoemission spectroscopy (ARPES)$^{10,11}$ Both materials are also long known for their usage in phase-change memories.$^{12}$ For heteroepitaxial growth of such films typically substrates with smallest lattice mismatch are chosen. However, it is argued that by passivating the dangling bonds on reactive surfaces using properly chosen surface terminations, van der Waals epitaxy can be achieved where the lattice matching condition can be significantly relaxed.$^{13}$ In this way, by each time initiating growth on passive surfaces, many artificial vdW heterostructures could be grown with a wide range of new physical phenomena.$^{14–16}$

Here the focus is particularly on crystalline substrates, while the growth of these materials on amorphous substrates is discussed elsewhere.$^{17–19}$ The chalcogenides Sb$_2$Te$_3$ and GeTe are epitaxially grown on differently prepared Si(111) surfaces with molecular beam epitaxy (MBE) and studied with plan-view transmission electron microscopy (TEM) and selected area electron diffraction (SAED). Previous cross-sectional TEM analyses, as also shown in the micrographs in Fig. 1, have demonstrated the high quality of the films and the atomically sharp interfaces between substrate and films.$^{20–22}$ However, these analyses lack sufficient overview to assess the more global quality of the epitaxy. In addition it will be argued that care should be taken when interpreting large volume averaging techniques like X-ray diffraction (XRD) due to experimental limitations. For instance, the films studied here could be misunderstood to be single crystalline due to the occurrence of single φ-scan peaks, but plan-view TEM images show that these films actually contain nano-sized low-angle twist domains.

The surfaces analyzed in the present work are the 1 × 1 H-terminated (after HF treatment), 7 × 7 bare (after annealing at 720 °C) or $(\sqrt{3} \times \sqrt{3})R30^\circ$ Sb-terminated (after Sb treatment), which are referred to as Si(111)–H, Si(111) and Si(111)–Sb, respectively.$^{23–26}$ On all the surfaces the rhombohedral chalcogenides, when described with hexagonal axes,
grow exclusively with the [00.1] axis perpendicular to the surfaces (‘out-of-plane’). However, for the ‘in-plane’ directions the epitaxy proceeds remarkably different for Si(111)–H compared with Si(111)–Sb, even though the films have atomically sharp interfaces and single preferred orientation from XRD φ-scans.20,22,27 While for films on Si(111)–H randomly twisted domains occur, these are strongly suppressed towards single-crystalline character for Si(111)–Sb, implying that the substrate surface termination plays a dominant role for the quality of such chalcogenide films. In general, these results illustrate how the surface chemistry can affect the epitaxy of chalcogenides, which are of general interest for films used in many disciplines of materials science and physics.

Results and discussion

Fig. 1(a) illustrates the schematic cross-sectional structures of the studied GeTe and Sb₂Te₃ samples, while Fig. 1(b) and (c) show the corresponding experimental TEM micrographs, respectively. Atomic force microscopy (AFM) scans of the films are included in the ESI† The indicated axes are hexagonal, where a-axis or [10.0] is aligned in-plane to Si [1–10] and c-axis or [00.1] is aligned out-of-plane to Si[111], which is the predominant orientation relation of such films as evidenced by XRD.20,22,27,28 The Si surface before growth is either Si(111)–H, Si(111) or Si(111)–Sb. This termination is not shown in these figures, however, since it is not clear at this stage if it remains stable after growth. Nevertheless, previous investigations indicate that the 7 × 7 bare surface as well as the Sb-termination remain stable after deposition.16,20 From Fig. 1(b) and (c) it is observed that these films are fully crystalline with atomically sharp interfaces when grown on Si(111)–Sb, illustrating the high-quality epitaxial growth achieved for these samples. This is also evident from previous studies with GeTe grown on Si(111)–H.72 Although this conclusion is tempting from these experimental cross-section TEM results, in the following discussion with plan-view TEM it is shown that the quality of the films is highly sensitive to the single-atomic layer surface termination of the substrate.

The plan-view schematics of the studied samples are illustrated in Fig. 2, where Fig. 2(a) illustrates the real-space view of Si(111)–Sb₂Te₃. When viewing the samples in SAED along Si [111] or chalcogenide [00.1] the relevant reflections are schematically indicated in Fig. 2(b) on the left. The black spots correspond to the substrate’s cubic (2–20) (note that (1–10) spots are forbidden) and the blue and red to the film’s hexagonal (10.0) and (11.0), respectively. The film’s (10.0) reflections are also forbidden for the expected Sb₂Te₃ and GeTe structures,29,30 but they are reported to occur for Bi₂Se₃ and Bi₂Te₃, which are isostructural to Sb₂Te₃ and are possibly related to defects in the bulk or at the surfaces.31 Fig. 2(b) on the right shows the convoluted double-diffraction pattern of the substrate (2–20) and film (11.0), which occurs due to multiple electron scattering if the electron beam passes through both crystals. This is shown for the experimental 140 nm SAED of a Si(111)–Sb₂Te₃ sample in Fig. 2(c), grown on Si(111)–Sb. As described, the double diffraction pattern of substrate and film is clearly observed and the substrate (1–10) and film (10.0) spots are not detected. The moiré interference lattice, which is schematized as in real-space in Fig. 2(a) and experimentally observed in reciprocal space in Fig. 2(c), is then given by the inner set of reflections in Fig. 2(b).

Fig. 3(a)–(c) show the plan-view TEM and Fig. 3(d)–(f) the 2.5 µm SAED results of Sb₂Te₃ crystals epitaxially grown on Si(111)–H, Si(111) and Si(111)–Sb, respectively. AFM scans of the films are included in the ESI† Even though these films
have atomically sharp interfaces and are highly textured and oriented to the Si(111) substrate, of which the films on Si(111)–H and Si(111)–Sb show single peaks in XRD 2θ-scans,20 the poly-crystal morphology and domain boundaries are clearly resolved. The film grown on Si(111)–H in Fig. 3(a) contains voids, as seen by the bright spots highlighted by white circles. This is not observed for films grown on Si(111) and Si(111)–Sb, which indicates that these surfaces have stronger interaction with the film than Si(111)–H. An estimate of the domain sizes by counting boundaries along line scans gives ∼70 nm, ∼50 nm and ∼120 nm for Si(111)–H, Si(111) and Si(111)–Sb, respectively, indicating that the bare Si(111) surface is more reactive providing a higher nucleation density than Si(111)–H. This can be attributed to the higher density of dangling bonds on the surface. The SAED pattern in Fig. 3(d) for the film on Si(111)–H shows diffraction rings on which the intensity is highest along the Si (2–20), meaning that many in-plane randomly oriented domains have formed besides the predominant (2–20)〈11.0〉 in-plane orientation. For films grown on bare Si(111) and Si(111)–Sb these randomly oriented domains are strongly suppressed, although they do occur occasionally for the latter substrate. This is consistent with the previous statement that bare Si(111) and Si(111)–Sb have stronger interaction with the substrate than Si(111)–H. Thus the epitaxial Sb2Te3 growth, and that of similar vdW materials, can drastically be altered by the single atomic layer surface termination. The findings imply that the surface termination plays a dominant role in the epitaxy of such chalcogenides and that vdW epitaxy is not always preferable. As shown by the results of films grown on Si(111)–H, poor interaction limits domain orientation preference as well as nucleation.

Surprisingly, a similar effect of improved epitaxy was found for the growth of GeTe for different surface terminations of the Si(111) substrate.22,27,28 Contrary to Sb2Te3, GeTe can rather be considered a 3D bonded material, which lacks vdW gaps due to its electronic valence and has a strong tendency to form rhombohedral twin structures.22,33 Also here, Fig. 4(a) and (b) show the plan-view TEM and Fig. 4 (c) and (d) the Ø 2.5 μm SAED results of GeTe crystals epitaxially grown on Si(111)–H and Si(111)–Sb, respectively. The TEM of Fig. 4(a) and (b) show that the films completely cover the substrate, but that the morphology of the films is less homogeneous than for the case of Sb2Te3, which results possibly from the different {111} twin orientations of the crystal.27,33 A remarkable crystallographic difference of the films is observed in the SAED patterns in Fig. 4(c) and (d). While the film grown on Si(111)–H has randomly oriented twist domains (in-plane), the domains for films on Si(111)–Sb rigorously orient with the Si(111) substrate. Thus, also in the case of GeTe the single atomic layer termination drastically changes the epitaxial quality of the films. It is for this reason such high-quality GeTe films could be used for ARPES measurements, revealing the Rashba spin-splitting in GeTe.10,11

Fig. 5(a) and (b) show extracted polar plots from the (11.0) SAED reflections of Fig. 3(d)–(f) and 4(c) and (d), respectively, where the Si(2–20) spots are positioned at 30° + 60° × n. Note that the figures have to be read with caution, as additional peaks could result from double diffraction. Fig. 3(a) shows that Sb2Te3 aligns itself with the Si(111) substrate with (2–20)〈11.0〉, but that other twist reflections occur for the Si(111)–H and Si(111)–Sb passivated substrates. The results for bare Si(111) and Si(111)–Sb appear to be similar at this

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**Fig. 2** (a) Plan-view schematics of the studied samples. (b) Left: SAED spots of Si (black, cubic axes) and Sb2Te3 or GeTe (red and blue, hexagonal axes) when viewed along [00.1], where (10.0) reflections are forbidden for Sb2Te3 and GeTe.29,30 Right: Double-diffraction pattern due to multiple scattering from substrate and film. (c) Experimental Ø 140 nm SAED of Si and Sb2Te3 along [00.1] showing the double-diffraction pattern.
scale, but XRD scans over mm-sized areas show that significant amounts of ±16° and ±6.7 twists are present in case of Si(111) (and not in case of Si(111)-Sb). Also, the inset of Fig. 5(a) shows the extracted polar plots from the $\langle 10.0 \rangle$ SAED reflections of Fig. 3(d)–(f), which should be forbidden for the Sb$_2$Te$_3$ structure. While these spots are clearly observed for the film on bare Si(111), they become progressively weaker for Si(111)-H and Si(111)-Sb. So, as these spots are possibly associated with defects, the results in Fig. 5(a) show that the films on Si(111)-Sb have the highest quality from the twist orientation and defect point of view. Fig. 5(b) shows that also GeTe aligns itself with the Si(111) substrate with $\langle 2-20 \rangle || \langle 11.0 \rangle$, although it appears relatively weak for the film on Si(111)-H. Nevertheless this is the predominant orientation relation as is evidenced by previous XRD results. Thus, in both cases of Sb$_2$Te$_3$ and GeTe the single Sb atomic layer drastically improves the epitaxial quality of the films.

At higher resolutions additional structural information from the films can be extracted. Fig. 6(a) shows an example of the domain structure of GeTe grown on Si(111)-Sb, where moiré interference is seen due to transmission through two crystals with different lattice constants. Using then the lattice distances $d_1$ and $d_2$, corresponding to the distances of the substrate’s (2-20) and film’s (11.0) spacing (see Fig. 2(b)), the expression for the moiré spacing $d_M$ is given by eqn (1). From this, the twist between substrate and film can be extracted and is indicated in the figure. It is seen, as the diffraction pattern in Fig. 4(d) also indicates, that most of the domains have a small-angle twist. Such small-angle twist in between domains has the consequence that the boundaries have threading patterns due to formation of dislocations, which could locally change the band structure due to strain. Note that even though Fig. 6(a) is an example with GeTe, the moiré interference can be observed for all films. This implies that when the twist angles are small, the boundaries can locally change the band structure for both Sb$_2$Te$_3$ and GeTe. Fig. 6(b) shows an additional phenomenon of transrotational domains, observed in the GeTe film grown on Si(111)-H. Such domains typically occur when the film’s onset of growth is in the amorphous phase and later crystallizes, which is consistent with previous observations. These transrotational domains are absent for GeTe grown on Si(111)-Sb because the film directly grows in the crystalline phase.

$$d_M = \frac{d_1d_2}{\sqrt{d_1^2 + d_2^2 - 2d_1d_2\cos\theta_i}}$$ (1)
implications, contrary to the current prevailing opinion in the field, is that passive, *i.e.* non-reactive, surfaces are poor candidates to achieve chalcogenide thin film growth, because they have been argued best for the case of vdW epitaxy.13–15 This is even more so illustrated for Sb$_2$Te$_3$ growth on different kinds of graphene substrates, which are more inert than the current surfaces, where the films show even a wider distribution of crystallites in the AFM micrographs.35 Thus the counterpart of the relaxed lattice matching condition due to weaker bonding, as argued by Koma,13 is that it impedes nucleation and orientation of the resulting film. This becomes particularly important if highly-oriented crystalline films are required for *e.g.* angle-resolved photo-emission spectroscopy,10,11 high-mobility films27 or micrometer sized devices.36

The results also show that, while the Sb$_2$Te$_3$ and GeTe films grown on both Si(111)–H and Si(111)–Sb show single peaks in laboratory XRD φ-scans,20,22,27 which have been considered indicative for the films’ single crystalline character, the films have in-plane twisted polycrystalline structures and they differ largely as seen in plan-view TEM and SAED. This illustrates that XRD data obtained from such type of films should always be interpreted with caution because the micro-structural details are averaged out. The small-angle twist domains, which occur for both Sb$_2$Te$_3$ and GeTe on Si(111)–Sb, have the consequence that dislocation lines are formed in the c-direction to accommodate the mismatch, see Fig. 6(a).

Such dislocations induce strain fields in the film which can act as scattering points on the surface and change the local band structure, as has been shown for the case of Bi$_2$Se$_3$.34 This is another intrinsic subtlety of such films which has to be accounted for.

In the current work the films grown on Si(111)–Sb show the best quality in terms of in-plane twist orientation. However, it remains unclear what the exact role of Sb is in the epitaxy of these materials and further study may be necessary. It is interesting to note that for the case of GeTe this epitaxy has been carefully analyzed using RHEED.21 In this previous work it is found that the ordered Peierls distortion of GeTe is prevented at growth onset and that the in-plane lattice constant is initially larger than that for the bulk value. One of the hypotheses in that work is that Sb actually mixes to form a GST phase, as described in another work,37 and thereby coordinates the epitaxy of the crystallites. This scenario has to be further analyzed to resolve the role of Sb on the epitaxy of such chalcogenides.

**Conclusions**

This work shows plan-view TEM and SAED results of epitaxial Sb$_2$Te$_3$ and GeTe films grown with MBE on different surfaces of Si(111). The results reveal that for both cases the epitaxy is drastically affected in terms of film morphology and crystallinity depending on the single atomic
layer surface termination of the substrate. While for growth of these materials on Si(111) the primary crystalline orientation is $\langle 2-20 \rangle \parallel \langle 11.0 \rangle$, it is shown that randomly twisted domains occur with highest frequency in the order of Si$_{IJ}$111)-H + Sb$_2$Te$_3$ > Si$_{IJ}$111)-Sb + Sb$_2$Te$_3$ for Sb$_2$Te$_3$ and Si$_{IJ}$111)-H + GeTe > Si$_{IJ}$111)-Sb + GeTe for GeTe. This implies that Sb functionalization of the substrates significantly improves epitaxy for these and similar materials and that a passive surface, as in the case of H passivation, is not always preferred for highly oriented film growth. Also, since the random twist domain frequency Si$_{IJ}$111)-Sb + Sb$_2$Te$_3$ > Si$_{IJ}$111)-Sb + GeTe, these results suggests that for the epitaxial growth of GeTe/Sb$_2$Te$_3$ superlattices on Si$_{IJ}$111)-Sb it may be preferable, contrary to current practice, to start the growth with GeTe. In the present work, it has not become clear what the exact role of Sb is on the Si surface to explain the improved quality of films and further research for this is necessary. Additionally, it is discussed that large scale XRD results should be interpreted with caution, as they could lack resolution or could average out microstructural details. In general this work highlights the effect of the surface preparation on thin film epitaxy of chalcogenides, which is an important step in realizing application of these novel electronic materials.

**Experimental section**

The Si(111) substrate preparation and MBE growth of Sb$_2$Te$_3$ and GeTe are detailed in previous publications. In short for Sb$_2$Te$_3$ a deposition temperature of 227 °C was used. Furthermore, the bulk (hot lip) temperature of the Sb effusion cell was kept at 425.5 °C (602.5 °C) during the deposition and the bulk (hot lip) temperature of the Te effusion cell was kept at 340 °C (476 °C). The deposition time was 2 hours. From XRD estimates (cross-section TEM) the Sb$_2$Te$_3$ film thicknesses on Si(111), Si(111)-Sb and Si(111)-H were determined to be 45 nm (42 ± 3 nm), 51 nm (49 ± 3 nm) and 42 nm (44 ± 2 nm), respectively. For GeTe a deposition temperature of 260 °C was used and the bulk (hot lip) temperatures of the Ge and Te effusion cells were 1120 °C (1140 °C) and 340 °C (476 °C). The deposition time was 2 hours. From XRD estimates (cross-section TEM) the GeTe film thicknesses on Si(111)-Sb/Si(111)-H were determined to be 58 nm (51 ± 4 nm) and 20 nm (22 ± 2 nm), respectively. The plan-view TEM specimens are prepared by mechanical grinding and Ar-polishing using a Gatan PIPS II (Gatan Inc., Pleasanton, California).
The TEM and SAED results in this work are obtained using a JEOL 2010 (JEOL Ltd., Tokyo, Japan) and the crystal structures are illustrated using the VESTA software package.18

Conflicts of interest

There are no conflicts to declare.

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