In-Plane Twinning Defects in Hexagonal GeSb$_2$Te$_4$

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Ge–Sb–Te (GST) alloys are an important family of phase-change materials employed in non-volatile memories and neuromorphic devices. Conventional memory cells based on GST rely on the switching between an amorphous state and a metastable, disordered rocksalt-like phase. Recently, however, it has been proposed that a special type of defect in layer-structured GST—the so-called “swapped bilayer” defect—is responsible for a novel phase-change mechanism observed in GST-based superlattices. Thus, disorder appears to play an important role in both types of switching mechanisms. Here, the observation of a new in-plane twinning defect in hexagonal GeSb$_2$Te$_4$ by direct atomic-scale imaging experiments is reported, which serves as the key ingredient to account for the abundance of inverted stacking faults in hexagonal GST and superlattices. Ab initio simulations reveal a low energy cost for these extended defects, and indicate that such defects can affect the electrical properties by inducing electron localization. This work provides additional insight into the nature and effects of structural disorder in GST phase-change materials.

1. Introduction

Phase-change materials (PCMs) undergo fast, reversible transitions between a crystalline and an amorphous state characterized by different optical and electronic properties.\([1–3]\) The resulting property contrast has been exploited in optical and nanophotonic devices\([4]\) and standalone electronic memories\([5–7]\) as well as embedded applications.\([8–10]\) Furthermore, the possibility to form intermediate partly amorphous, partly crystalline states makes PCMs promising materials for neuro-inspired computing applications.\([3,11–16]\) Ge-Sb-Te (GST) alloys along the GeTe-Sb$_2$Te$_3$ pseudo-binary line are the most widely used PCMs.\([17–19]\)

In particular, Ge$_x$Sb$_{2–x}$Te$_3$ and GeSb$_2$Te$_4$ are currently employed in phase-change memories.\([20,21]\) Upon fast crystallization or thermal annealing of thin amorphous samples, GST compounds form a rocksalt-like phase, in which Te atoms occupy the atomic sites of one sublattice, whereas Ge and Sb atoms and vacancies distribute themselves randomly in the second sublattice.\([22,23]\) The high level of disorder leads to insulating behavior at low temperatures due to Anderson localization\([24–26]\) of the electronic states near the Fermi level, which lies in the tail of the valence band owing to self-doping effects. The relevant wave functions are localized inside vacancy clusters,\([23,27]\) while states in the tail of the conduction band are typically localized along Sb chains or Te antisite defects.\([28]\) Thermal annealing at elevated temperatures leads to the formation of vacancy planes,\([29,30]\) thus inducing an insulator-metal transition, as well as a structural transition from cubic to hexagonal stacking.\([24]\) Analogous disorder-driven phenomena have been observed in other disordered binary and ternary chalcogenides, including Sb$_2$Te$_3$,\([31]\) PbSb$_2$Te$_4$, SnSb$_2$Te$_4$, and SnBi$_2$Te$_4$,\([32]\) and have been predicted to occur in a large number of homologous chalcogenides, so long as they can form a metastable rocksalt-like structure.\([31]\)

Recently, it has been claimed that a different type of switching involving two crystalline states occurs in chalcogenide heterostructures consisting of ultrathin layers of hexagonal GST and Sb$_2$Te$_3$—the so-called interfacial phase-change materials (iPCMs).\([34–38]\) Conventional thermal-based transitions were reported in superlattice devices.\([19,40]\) However, quasi-2D amorphization in the superlattice is unlikely due to the close melting temperature of GeTe and Sb$_2$Te$_3$ ($<100$ °C), which was corroborated by ab initio molecular dynamics simulations.\([43]\) Partial amorphization was instead achieved in TiTe$_2$/Sb$_2$Te$_3$ phase-change heterostructures,\([44–49]\) because of the large difference in melting temperature ($>500$ °C) between the two constituting alloys. Some models ascribe the switching in iPCMs to the presence of extended defects,\([46]\) namely, swapped bilayers connecting the edges of adjacent atomic stacks, which are consistently found in GST samples grown by deposition and epitaxy methods.\([47–52]\) Sb-Te intermixing in the bilayers...
was identified as the major ingredient to stabilize the swapped bilayer defects.\cite{52–54} These swapped bilayers are mobile upon thermal annealing\cite{46} or focused electron beam irradiation,\cite{47} and could serve as the forefronts to alter the stacking sequence of layered GST structures.\cite{55} However, it remains elusive whether this local structural rearrangement can account for the nanosecond switching in iPCM devices.

Atomic-scale structural characterization experiments via transmission electron microscopy revealed the presence of various defects in hexagonal GST and related superlattices, in addition to swapped bilayer defects. For instance, although perfect hexagonal GeSb$_2$Te$_4$ (h-GST) consists of periodically stacked seven-layer atomic blocks, five-, nine-, and 11-layer blocks were also found in post-annealed thin films, corresponding to the stoichiometry of Sb$_2$Te$_3$, Ge$_2$Sb$_2$Te$_4$, and Ge$_3$Sb$_2$Te$_5$, respectively.\cite{52} In Te-richer GST thin film or grains, even triple-layer atomic blocks were observed and were shown to be strain-stabilized, octahedrally bonded GeTe$_2$ nanostructures.\cite{56} Another major stacking fault consists of atomic blocks with the same stoichiometry but inverse stacking sequence of the atomic layers. In this work, we provide a thorough understanding of the genesis of these inverted blocks via the identification of an in-plane twinning structure by sub-angstrom transmission electron microscopy. We also thoroughly investigate the structural and electronic properties of models of h-GST containing such defects by ab initio simulations based on density functional theory (DFT).

2. Results and Discussion

We deposited GeSb$_2$Te$_4$ thin films via magnetron sputtering and annealed the samples at 300 °C for half an hour. X-ray diffraction (XRD) measurements confirmed that the hexagonal phase formed in the thin films (Figure S1, Supporting Information). The films were then used to prepare the specimen for transmission electron microscopy experiments. The technical details can be found in Experimental Section. As shown in Figure 1a, the unit cell of the perfect h-GST phase consists of three septuple-layer structure blocks, and the compositional order inside an ideal septuple-layer block is –Te-Sb-Te-Ge-Te-Sb-Te–, as indicated by the yellow, green, and red spheres. We use “a,” “b,” and “c” to denote the atomic layers with in-plane atomic positions (0, 0), (2/3, 1/3), and (1/3, 2/3) of the hexagonal cell, respectively (see the side view in Figure 1a and the top view in Figure S2, Supporting Information). The complete stacking sequence of the unit cell is –g-acbacga-bcacab-g-cabcabc–, where g represents a pseudo van der Waals (vdW) gap between the structural blocks. As displayed in Figure 1b, the inverse stacking corresponds to the sequence –g-acbacga-g-bcacab-g-bcacabc–. These two models are equivalent when periodically repeated.

The investigations of the h-GST thin film specimen by means of spherical aberration corrected (Cs-corrected) scanning transmission electron microscopy (STEM) showed a mixture of the two stacking sequences at the nanometer scale. Figure 1c,d shows two images of the h-GST film recorded using high angle annular dark field (HAADF) imaging technique along the [1120] direction. For the HAADF STEM image, the intensity peaks (bright spots) appear at the positions of the atomic columns and the image intensity is approximately proportional to the square of the averaged atomic number Z of each column along the view direction. The Ge-rich columns show lower image intensity than the Sb-rich and Te columns due to the relatively low Z value (Z = 32, 51, and 52 for Ge, Sb, and Te atom, respectively). In the images, the stacking sequences “abc” and “acb” are indicated by the blue and red arrows, respectively. Apparently, the size of the inverse blocks varies largely and these blocks are distributed randomly. From the image, the boundaries between the inverse blocks are flat and exhibit darker contrast (deep black lines) than the gaps between the regular stacking planes. We also found the boundaries where the blocks with inverse stacking sequence meet in-plane, as marked by orange boxes. The switching of the stacking sequence along the horizontal direction looks smooth, without any obvious cracks or strong lattice distortion. These

![Figure 1](https://www.advancedsciencenews.com/content/22000214/fig/1)

Figure 1. a) The typical atomic structure of hexagonal GeSb$_2$Te$_4$. The stacking sequence is –g-acbacga-g-bcacab-g-cabcabc–. The Ge, Sb, and Te atoms are shown as red, yellow, and blue spheres. b) The atomic structure with inverted stacking. The stacking sequence is –g-acbacga-g-bcacab-g-bcacabc–. c,d) Large scale HAADF images of GeSb$_2$Te$_4$ with out-of-plane twin-like structures and in-plane twins. The blocks with normal and inverted stacking are indicated by the blue and red arrows, respectively. The in-plane twins are marked by the dashed orange boxes. A swapped bilayer defect is marked by the white box at the top right corner. The enlarged view of this defect is shown as inset at the bottom right corner.
in-plane twinning boundary structures can span over a single atomic block or a few blocks with swapped bilayers. A typical swapped bilayer defect is marked by the white box at the top right corner in Figure 1d. The zoom-in view of this defect is shown in the inset.

To rule out the effects of other defects, we focus on the in-plane twinning boundary structure that occurs within one atomic block. Figure 2a shows an enlargement of the in-plane twin boundary area in Figure 1d. At the core area inside the orange box, the shape and intensity of some image spots become less regular, due to the overlap of two stacking sequence structures and local distortions. As discussed later, the presence of extra image spots and atomic distortions can be attributed to the local shifts of atoms and the presence of compositional Ge/Sb disorder in the cation-like layers, which also affect the nearest bonding neighbors in the anion-like Te layers. Figure 2b,c shows a symmetrical boundary model that was proposed according to the local stacking sequence, representing the basic structural unit of the in-plane twin defects.

We carried out DFT calculations on defective h-GST models with orthorhombic supercells using the projector-augmented wave (PAW) pseudo-potentials[58] the Perdew–Burke–Ernzerhof (PBE) functional,[59] and the Grimme’s D3 correction for the van der Waals forces[60] with the VASP code.[61] More technical details can be found in Experimental Section. The defective model contained two standard septuple-layer (SL) GeSb2Te4 blocks and one defective SL block (in total, 36 Ge, 72 Sb, and 144 Te atoms). Both the atomic positions and the vibrational density value below 1 in-plane twinning defect per 9.1 nm² versus 1 bilayer per 75 nm². As discussed later, when the defect density of in-plane twinning is reduced by 50%, the energy cost is decreased to ≈1.18 eV nm⁻¹ (=6.9 meV per atom) with much reduced lattice expansion. In experiments, the planar density of in-plane twinning defects is also much lower than that of bilayer defects (1 bilayer per 75 nm²). The statistical HAADF scans showed an estimated density value below 1 in-plane twinning defect per ≈150 nm².

For an SL block in pristine h-GST, both Ge and Sb atoms are in sixfold octahedral coordination. Regarding Te, the coordination number (CN) of the middle two Te atoms is six, but is reduced to three at the two edges. The center Ge atom forms six equivalent bonds with the neighboring Te atoms (≈3.00 Å), while the two outer Sb atoms both form three short bonds with edge Te atoms (≈3.01 Å) and three long bonds with middle Te atoms (≈3.15 Å). The atoms forming these bonds are sixfold coordinated but have one non-octahedral bond. Regarding the middle Ge atom, it moves upward to form four short bonds with the upper four Te atoms (≈3.00 Å), and two long bonds with the two lower Te atoms (≈3.33 Å), resulting in six non-octahedral bonds with its Te neighbors. At the top edge, the under-coordinated Te atoms form two short Sb–Te bonds (≈2.89 Å), while at the bottom edge, the over-coordinated Te atoms form four.

Figure 2. a) Zoomed-in HAADF image of an in-plane twin. b–c) The defective model that contains in-plane twin defects in the middle QL block, viewed along the b) x-axis and c) the y-axis.
This bonding mechanism is a peculiar type of \( p \)-bonding characterized by pronounced electron delocalization. In the parent compound GeTe, the average number of \( p \) electrons per site is three; in h-GST, MVB still requests three \( p \) electrons per site on average, counting the vacant sites in the pseudo vdW gaps. These special sites in the pseudo gaps play an important role when a vacancy disordering process is triggered in h-GST via strong knock-on effects induced by extensive electron or ion beam irradiation.\(^{[71-73]}\) Hence, the threefold \( \text{Te} \) atoms at the edge of the atomic septuple blocks are regarded as normal motifs, while under- or over-coordinated \( \text{Te} \) atoms are regarded as defects. Since the \( \text{Te} \) (CN = 4) atom forms four \( \text{Sb–Te} \) bonds, it shows a DOS at low energy, while the \( p \) electrons of the \( \text{Te} \) (CN = 2) atom creating an energetically less favorable trap state at about \(-0.5\) eV (Figure 3).

Next, we focus on the localization of the electronic states, which could have an impact on the transport properties. We considered larger models and employed the CP2K code\(^ {74} \) to optimize the geometry and compute the electronic properties. We took the relaxed defective orthorhombic supercell presented in Figure 2c and expanded the model along the \( x \) direction by three times, which allowed to assess the impact of compositional \( \text{Ge/Sb} \) disorder. The cell edges of the supercell model are \( 12.87 \times 44.84 \times 40.81 \) Å (containing 756 atoms). In the disordered models, 50\% Ge and 50\% Sb atoms occupy the center cation-like layer, whereas 25\% Ge and 75\% Sb occupy the two outer cation-like layers. The models with and without compositional disorder were relaxed further, prior to the electronic structure calculations. To determine the degree of localization of the Kohn–Sham states \( \alpha \), we employed the inverse participation ratio (IPR). This quantity is defined as:

\[
\text{IPR} = \sum_{\alpha, i} |\Psi_{\alpha i}|^4 \left( \sum_{\alpha, i} |\Psi_{\alpha i}|^2 \right)^{-\frac{1}{2}}
\]

As shown in Figure 3, we computed the total density of states (TDOS) for the pristine and the in-plane twin model and the local density of states (LDOS) for defective atoms in the in-plane twin model. The LDOS for \( \text{Sb} \) and \( \text{Te} \) atoms with standard chemical environment are also shown for comparison.

![Figure 3](image)

**Figure 3.** Total density of states (TDOS) for the pristine and the in-plane twin model and local density of states (LDOS) for defective atoms in the in-plane twin model. The LDOS for \( \text{Sb} \) and \( \text{Te} \) atoms with standard chemical environment are also shown for comparison.

long Sb–Te bonds (≈3.18 Å). None of these \( \text{Sb–Te} \) bonds are octahedral bonds. Due to the periodic boundary conditions, our defective model contains an inverse in-plane twin located at the left boundary in Figure 2c.

As shown in Figure 3, we computed the total density of states (TDOS) for the pristine and the in-plane twin model and the local density of states (LDOS) for defective atoms in the in-plane twin model. The pristine model has larger TDOS near the conduction band minimum (CBM). However, there is a very small region (indicated by the red arrow) where the in-plane twin model has a larger TDOS. This region corresponds to the peak in the LDOS of the \( \text{Sb} \) atom forming the homopolar bond. There is also a shoulder at slightly higher energies corresponding to a small peak in the LDOS of under-coordinated \( \text{Te} \) atoms (CN = 2). Furthermore, \( \text{Te} \) atoms with wrong coordination number (CN = 2/4) have larger LDOS near the valence band maximum (indicated by the blue arrow) as compared with standard threefold coordinated \( \text{Te} \) atoms (CN = 3). In particular, the LDOS of \( \text{Te} \) (CN = 2) has a large peak at about \(-0.5\) eV. Note that the \( \text{Te} \) atoms with CN = 2/4 are regarded as defects in h-GST; despite that, in pure \( \text{Te} \) crystal, each \( \text{Te} \) atom has only two neighbors. In h-GST and other related PCMs, a special bonding mechanism is dominant, known as metavalent bonding (MVB). This bonding
Te atoms, as shown in Figure 4d. We stress again that these states are, in fact, 1D, since they are strongly localized along the y- and z-axis but are extended along the x-axis, as shown in the top view of the structures in Figure 4c,d. Thus, they differ from exponentially localized states in disordered systems, such as the ones observed at the tail of valence band in rocksalt GST due to vacancy clusters.[25] Apparently, compositional Ge/Sb disorder in the cation-like layers does not alter the extended nature of the state along the x-axis. Regarding the conduction band, there are a few states with large IPR values of ≈0.01 in the energy range of 0.3–0.4 eV. An example of such states is plotted in Figure 4e. The state is localized around the Sb–Sb homopolar bond, in agreement with our previous DOS analysis. The presence of compositional Ge/Sb disorder affects these states significantly, turning the wave functions into a more complex shape. As shown in Figure 4f, the charge density is localized not only around the homopolar Sb–Sb bonds but also along Sb–Te chains.[29] We also doubled the size of the orthorhombic model along the y-axis by adding regions with perfect stacking (resulting in large models that contain 1512 atoms), which reduces the defect density by 50%. The localization features remain the same (Figure S3, Supporting Information). Hence, we can conclude that in-plane twins lead to the formation of 1D electronic states along the x direction that are strongly localized along the perpendicular directions.

At last, we also built models with misaligned twinning defects to account for the extra image spots observed in Figure 2a. Starting with the orthorhombic model shown in Figure 4c, we broke the alignment of the in-plane twinning defects in the three slices along the x direction, separating them consecutively by one lattice unit, 7.47 Å (= 1/6 × 44.84 Å) along the y direction, as shown in Figure 5a. Note that, owing to the periodic boundary condition in the x direction, the model we built has extremely large density of "kinks" (i.e., shifts) between adjacent in-plane twinning defects. This model turns out to be rather energetically unfavorable with a large energy
penalty of $\approx 122$ meV per atom as compared to the model with aligned twinning defects (shown in Figure 4). Moreover, after atomic relaxation, the atoms in the kink region move away from the initial atomic sites (Figure 5a), which is inconsistent with the HAADF image in Figure 2a. The large energy penalty and serious atomic distortions indicate that the actual in-plane twinning defect structures should be highly aligned with only a small number of kinks, as sketched in Figure 5b. To describe such structures, one should thus consider huge models, which constitute a challenge for ab initio methods. However, the marginal presence of kinks is not expected to have strong influence on the overall electronic structure as yielded by our models with aligned twinning defects.

3. Conclusion

We reported a thorough atomic scale characterization of the in-plane twinning defects with inverted stacking sequence inside a single atomic block. The DFT calculations indicate the relatively low energy cost of ideal defects without kinks. Local distortion, homopolar bonds, and under- and over-coordinated Te atoms were observed in these models. Regarding the electronic structure, the homopolar bonds and wrong coordinated Te atoms inside the twinning defect lead to the formation of 1D electronic states near the valence band maximum and the conduction band minimum. These states are extended along the direction parallel to the defect but strongly localized along the other two directions. The presence of kinks (which are needed to explain the extra spots in the HAADF images) is expected not to affect significantly the electronic structure, as long as their concentration is low. We note that extended defects, such as bilayer and stacking faults, can be manipulated through heat treatment,[16] synthesis methods, and chemical composition.[75] This property could in principle be exploited for tuning the density of these in-plane twinning defects, thus tailoring the electrical transport properties of layer-structured phase-change chalcogenides.
In summary, our investigation of the structural and electronic properties of in-plane twinning defects enhances the understanding of structural disorder in GeSb2Te4 materials at atomic scale.

4. Experimental Section

Sample Preparation: GeSb2Te4 thin films with thickness of ~450 nm were deposited with the magnetron sputtering technique on a Si (111) substrate. The films were annealed by a regular tube furnace with a 3 cm diameter quartz tube. The annealing started from room temperature with heating rate of 5 K min⁻¹, holding time of 30 min, followed by a cooling process to room temperature in argon atmosphere (flow rate of 200 sccm). The structure of annealed GeSb2Te4 films was analyzed by XRD using a Philips X’pert Materials Research Diffractometer.

TEM Measurement: Cross-section TEM specimens were prepared by a Helios NanoLab 400S focused ion beam system with a Ga ion beam at 30 keV beam energy and polished at 5 keV. The cleaning process were carried out in a Fischione Nanomill with an Ar beam at 30 keV beam energy and polished at 5 keV. The thinning and cleaning were performed on a Fischione Nanomill with an Ar ion beam at 900 eV for thinning and 500 eV for cleaning. The atomic-resolution high-angle annular dark field (HAADF) experiments were performed on a FEI Titan 80–300 instrument with probe aberration correctors, operated at 200 keV.

DFT Simulations: We carried out DFT calculations for models in orthorhombic supercells (containing 252 atoms) by using VASP package[29] PBE functional[30] and PAW pseudopotentials[31] were used with the energy cutoff value set as 500 eV. The 10 × 1 × 1 k-point mesh was used for the pristine and defective models. Both the atomic positions and lattice parameters were fully relaxed. CP2K package[32] was employed for electronic structure calculations of larger models (containing 756 and 1512 atoms). Goedecker pseudopotentials[76] and the PBE functional were used, and the Brillouin zone was sampled at (containing 756 and 1512 atoms).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

chalcogenides, electron localization, non-volatile memories, phase-change materials

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