Atomic Reconfiguration of van der Waals Gaps as the Key to Switching in GeTe/Sb₂Te₃ Superlattices

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ABSTRACT: Nonvolatile memory, of which phase-change memory (PCM) is a leading technology, is currently a key element of various electronics and portable systems. An important step in the development of conceptually new devices is the class of van der Waals (vdW)-bonded GeTe/Sb₂Te₃ superlattices (SLs). With their order of magnitude faster switching rates and lower energy consumption compared to those of alloy-based devices, they are widely regarded as the next step in the implementation of PCM. In contrast to conventional PCM, where the SET and RESET states arise from the crystalline and amorphous phases, in SLs, both the SET and RESET states remain crystalline. In an earlier work, the superior performance of SLs was attributed to the reduction of entropic losses associated with the one-dimensional motion of interfacial Ge atoms located in the vicinity of Sb₂Te₃ quintuple layers. Subsequent experimental studies using transmission electron microscopy revealed that GeTe and Sb₂Te₃ blocks strongly intermix during the growth of the GeTe phase, challenging the original proposal but at the same time raising new fundamental issues. In this work, we propose a new approach to switching in SLs associated with the reconfiguration of vdW gaps accompanied by local deviation of stoichiometry from the GeTe/Sb₂Te₃ quasibinary alloys. The model resolves in a natural way the existing controversies, explains the large conductivity contrast between the SET and RESET states, and provides a new perspective for the industrial development of memory devices based on such SLs. The proposed concept of vdW gap reconfiguration may also be applicable to designing a broad variety of engineered two-dimensional vdW solids.

INTRODUCTION

Nonvolatile memory devices are currently key elements of a wide variety of electronics and portable systems (digital cameras, solid state disks, smartphones, computers, e-books, tablets, etc.), and their market has increased exponentially over the last decade. A leading nonvolatile technology, is currently a key element of various electronics and portable systems. An important step in the development of conceptually new devices is the class of van der Waals (vdW)-bonded GeTe/Sb₂Te₃ superlattices (SLs). With their order of magnitude faster switching rates and lower energy consumption compared to those of alloy-based devices, they are widely regarded as the next step in the implementation of PCM. In contrast to conventional PCM, where the SET and RESET states arise from the crystalline and amorphous phases, in SLs, both the SET and RESET states remain crystalline. In an earlier work, the superior performance of SLs was attributed to the reduction of entropic losses associated with the one-dimensional motion of interfacial Ge atoms located in the vicinity of Sb₂Te₃ quintuple layers. Subsequent experimental studies using transmission electron microscopy revealed that GeTe and Sb₂Te₃ blocks strongly intermix during the growth of the GeTe phase, challenging the original proposal but at the same time raising new fundamental issues. In this work, we propose a new approach to switching in SLs associated with the reconfiguration of vdW gaps accompanied by local deviation of stoichiometry from the GeTe/Sb₂Te₃ quasibinary alloys. The model resolves in a natural way the existing controversies, explains the large conductivity contrast between the SET and RESET states, and provides a new perspective for the industrial development of memory devices based on such SLs. The proposed concept of vdW gap reconfiguration may also be applicable to designing a broad variety of engineered two-dimensional vdW solids.
the possibility of fabricating GeTe/Sb$_2$Te$_3$ SLs even by methods such as sputtering.$^{14,15}$ Transmission electron microscopy (TEM) measurements on such samples demonstrated that they, indeed, possessed layered structures with vdW gaps separating covalently bonded blocks.$^{16}$ The improved performance of iPCM was attributed to the one-dimensional switching of interfacial Ge atoms during the phase-change process, which results in decreased entropic losses compared to a melt-quenched random 3D alloy material, resulting in significantly better cyclability, faster switching rates, and reduced power consumption.

The key issues of the proposed model of phase-change in iPCM can be summarized as follows. Although the bulk phase of GeTe is ferroelectric, ultrathin layers of GeTe, in the few monolayer limit, may possess different structures determined by the overall symmetry of SLs and also by the need to minimize the surface dipole moment.$^{18,19}$ Four possible stacking sequences for the GeTe/Sb$_2$Te$_3$ SLs were proposed (Figure 1a), namely, the Petrov (P) [$\cdots$ Te-Ge-Te-Sb-Te-Ge-Te-Te-Ge-Te-Te-Sb-Te-$\cdots$] phase, the Kooi (K) [$\cdots$ Te-Sb-Te-Ge-Te-Ge-Te-Sb-Te-$\cdots$] phase (following the commonly used references to the different proposed structures for the bulk trigonal phases$^{20,21}$), the inverted Petrov (iP) [Ge-Te $\cdots$ Te-Sb-Te-Ge-Te-Te-Ge-Te-Te-Sb-Te-$\cdots$] phase (because the sequence of Ge and Te planes is inverted), and the ferro(electric) (F) phase [Te-Sb-Te-Sb-Te-$\cdots$ Te-Ge-Te-Ge], where the ferroelectric structure of bulk GeTe was preserved. In these notations the ‘’’ sign denotes covalent bonds, whereas the ‘‘’’ sign corresponds to weaker vdW interaction between chalcogen atoms. Through MD simulations, it was demonstrated that although at 0 K the K-phase is the most stable, at elevated temperatures the iP- and F-phases are energetically more favorable.$^{13}$ The conclusion about the reversal of the relative stabilities of the phases as a function of temperature was subsequently confirmed by a different group.$^{22}$

The structural transformations between these phases were considered to serve as the mechanism of the phase-change process in iPCM. It should be noted that following the original proposal of a Ge umbrella flip as the underlying mechanism for phase-change in composite Ge−Sb−Te alloys,$^{23}$ all proposed models centered around processes that involve Ge atoms, namely, transitions between F- and iP phases,$^{13}$ P and iP phases,$^{24}$ and a transition of Ge atoms between octahedral and tetrahedral sites$^{25}$ were proposed. In an earlier work$^{22}$ an additional layer sliding process was proposed in connection with the F- to iP structure transformation. In an earlier work,$^{26}$ it was noted that because the energy differences between different phases are rather small, real structures are likely to be mixtures of these phases and the phase transition may take place locally in places where the appropriate phases are formed. It was additionally argued that strain introduced due to the difference in the lattice constants of GeTe and Sb$_2$Te$_3$ may act to facilitate disordering of the GeTe phase.$^{27}$

Subsequently, TEM studies of GeTe/Sb$_2$Te$_3$ SLs grown by MBE revealed that GeTe blocks were not located between Sb$_2$Te$_3$ blocks as intuitively expected but were instead incorporated into the Sb$_2$Te$_3$ blocks.$^{17,28,29}$ Furthermore, it was found that Ge atoms were located toward the core of the covalently bonded blocks with Sb atoms located closer to surfaces suggesting strong Ge/Sb intermixing during the
growth (Figure 1b). An additional finding was that the grown structures locally possessed different stoichiometries. Thus, a nominal Ge$_2$Sb$_2$Te$_5$ (GST225) composition, which is expected to be built of 9-layer blocks, possessed blocks with the number of layers varying from 5 to 13, identified as local stoichiometries ranging from Sb$_2$Te$_3$ to Ge$_4$Sb$_2$Te$_7$ (GST427).\textsuperscript{28} In other words, vdW-gap-separated covalent blocks containing a varying number of GeTe bilayers and capped by SbTe, that is, all located along the quasibinary GeTe/Sb$_2$Te$_3$ tie line, were identified (Figure 1c). These findings strongly challenged the structures and switching mechanism of the GeTe/Sb$_2$Te$_3$ superlattices proposed earlier but at the same time raised new questions that are very difficult to answer within the proposed Ge/Sb interdiffusion interpretation of the results.

The first such question is what is the driving force for the Ge/Sb plane reversal? The total energies of the Petrov and Kooi phases (i.e., phases where Ge atoms are located toward the surfaces and toward the core of the covalently bonded blocks) are very similar\textsuperscript{22,30} and thus should not drive the intermixing. What then? In addition, the activation energies for atomic diffusion are rather large\textsuperscript{31} and the process should be kinetically limited. Although we most certainly do not deny the important role of (Ge/Sb inter)mixing in the growth process, we argue that intermixing alone cannot possibly provide an explanation for the observed reversal of Ge and Sb planes (see, e.g., Figure 2d of ref 28 where the outer BLs almost exclusively contain Sb atoms, whereas Ge atoms are concentrated toward the core).

The second question relates to the experimentally observed blocks with differing numbers of layers. MBE is the most accurate method to grow solids with well-defined compositions. How can it produce structures with the local stoichiometry varying so much? In the original publication, the following statement was provided. “The naturally occurring stacking faults and layering disorder in the deposited superlattice seem inconsistent with the high quality that should be achievable with MBE, but this is another signature that the artificially grown SL figures into a lower energy state”.\textsuperscript{17} How does the SL reconfigure? What happens if the growth process is terminated at, say, the moment indicated by a dashed line in Figure 1c? Would the uppermost layer just below the dashed line still have three GeTe BLs? If the answer is yes, then what is the source of these extra Ge and Te atoms? If the answer is no and to achieve the ‘lower energy state’ one has to grow the complete structure shown in Figure 1c, then a different question arises. Once the uppermost Ge–Sb–Te block is formed, how does one GeTe BL migrate downward from there? Does it tunnel through two Sb$_2$Te$_3$ blocks (leaving alone SbTe capping layers) as a whole? This does not seem possible. Do Ge atoms diffuse through the Sb$_2$Te$_3$ phase without any
intermixing? For the case of a strong tendency to intermix, (i) some of the Ge atoms should remain inside the Sb$_2$Te$_3$ blocks and (ii) such a strong interdi ffusion would almost certainly destroy the SL nature of the sample. Furthermore, such a long-distance diffusion in a solid phase is bound to be kinetically limited. Consequently, although it has rather convincingly been demonstrated that the earlier theoretical models of phase change in GeTe/Sb$_2$Te$_3$ SLs, such as a transition between the Petrov and inverted Pertov phases, were oversimplif ied and possibly incorrect, the recent experimental results have raised new fundamental questions that cannot be answered within simple intermixing arguments. In this work, on the basis of density-functional theory simulations and TEM imaging (see Methods for details), we propose an alternative model for the growth of GeTe/Sb$_2$Te$_3$ SLs that provides a natural answer to these questions (and which is fundamentally different from the proposed intermixing idea). We further propose a conceptually novel mechanism of switching in SLs that is associated with the inversion of SbTe BLs and the subsequent reconf iguration of the vdW gaps leading to local deviations in stoichiometry from the quasibinary tie line. Finally, we demonstrate that Ge/Sb intermixing, to the extent that it may occur, should not have a noticeable effect on SL switching performance.

**RESULTS AND DISCUSSION**

To address the issue of the SL growth, we start by noting that the crucial experimental requirement for the growth of SLs with good layer orientation using sputtering is the formation of a few nm thick Sb$_2$Te$_3$ seed layer and it is believed that the layered nature of Sb$_2$Te$_3$ determines the orientation of subsequently grown GeTe blocks. With this in mind, we initially simulated the energies (and enthalpies over an extended temperature range) for a single GeTe BL atop Sb$_2$Te$_3$. The relaxed structures and the comparison of their enthalpies are shown in Figure 2a. The structure with the Ge plane facing Sb$_2$Te$_3$ has a significantly lower energy than that of the alternative configuration, indicating that the first layer of GeTe grows with the Te plane terminating the surface, which is also in perfect agreement with the conclusion of a previous work. We note that this structure corresponds to the Petrov termination of a covalent block of trigonal GST. It should also be noted that the Ge−Te interatomic distances for the Te-terminated sample are very close to the longer Ge−Te distance in the bulk GeTe phase, suggesting covalent interaction between the Sb$_2$Te$_3$ “substrate” and the GeTe overlayer. The Te−Te distance, on the other hand, is significantly larger and is closer to the interatomic separation across the vdW gap.

**Figure 3.** Possible pathways of SL growth. (a) The formation of an Sb$_2$Te$_3$ QL and (b) initial termination of GeTe by an inverted SbTe BL with subsequent Sb$_2$Te$_3$ growth. Simulated relative energies of the two structures with different sequences of Te and Sb atomic planes are compared on the right.

**Figure 4.** Schematics of the growth of GeTe/Sb$_2$Te$_3$ SLs. Even if the supply of Ge, Sb, and Te species has been adjusted to grow spatially separated GeTe and Sb$_2$Te$_3$ blocks (a), in reality, because of the inversion of the initial SbTe BL, a Kooi-like phase is formed (b).
The formation of a quintuple layer (as was assumed in the original work\textsuperscript{13} and indicated in Figure 3 as path “a”), the situation is actually more complex. As mentioned above, GeTe is not a proper 2D material. In other words, the Te-terminated surface of 3D GeTe is not passive and as such is not suitable for the growth of a 2D layer across a vdW gap. Although Sb\textsubscript{2}Te\textsubscript{3} has a tendency to form full quintuples, literature data\textsuperscript{35–37} suggest that the layer-by-layer growth mode is equally possible; hence, our simplified approach seems reasonable. The obtained results show that the former process, that is, the formation of an inverted SbTe cap layer is energetically more favorable (by ca. 0.2 eV per formula unit) during the layer-by-layer growth. Consequently, even though the fluxes may be optimized to supply the number of atoms required to sequentially grow two bilayers of GeTe followed by one quintuple layer of Sb\textsubscript{2}Te\textsubscript{3} (Figure 4a), the situation is actually more distributed between the two GeTe layers, Figure 5b). We note a certain analogy between the formation of reversed SbTe bilayers and the stacking faults, discussed, for example in ref\textsuperscript{31} and ref\textsuperscript{39}, respectively.

To determine which of the processes are more likely to take place, we compared the total energies of SbTe-terminated GeTe and a TeSb bilayer (as a seed for a QL) grown on GeTe across a vdW gap. Although Sb\textsubscript{2}Te\textsubscript{3} has a tendency to form full quintuples, literature data\textsuperscript{35–37} suggest that the layer-by-layer growth mode is equally possible; hence, our simplified approach seems reasonable. The obtained results show that the former process, that is, the formation of an inverted SbTe cap layer is energetically more favorable (by ca. 0.2 eV per formula unit) during the layer-by-layer growth. Consequently, even though the fluxes may be optimized to supply the number of atoms required to sequentially grow two bilayers of GeTe followed by one quintuple layer of Sb\textsubscript{2}Te\textsubscript{3} (Figure 4a), in reality the Kooi phase is formed instead (Figure 4b). The crucial point in the conversion of a GeTe/Sb\textsubscript{2}Te\textsubscript{3} SL into a Kooi-like phase is the fact that the Te-terminated surface of 3D GeTe is not passive and as such is not suitable for the growth of a 2D layer using vdW epitaxy, as was intuitively assumed in the earlier work considering the quasilayered structure of bulk GeTe.

We note that this process is substantially different from the Ge in-diffusion proposed earlier\textsuperscript{17} to account for the formation of the Kooi-like phase in lieu of a GeTe/Sb\textsubscript{2}Te\textsubscript{3} SL. We further note that the process proposed in this work is not in disagreement with the published TEM results\textsuperscript{28,29}. Indeed, the formation of an SbTe cap on top of two GeTe BLs grown on an Sb\textsubscript{2}Te\textsubscript{3} QL results in an 11-layer block, exactly as was reported in the literature\textsuperscript{28}. In addition, the fact that the upper layer is Sb-rich (consists of almost exclusively Sb species, as evidenced by the near identical peak heights for the outermost Te plane and the adjacent plane) is also in perfect agreement with the result shown in Figure 2d of ref\textsuperscript{28} and in disagreement with the intermixing idea that cannot explain the observed nearly complete reversal of Ge and Sb planes. One may argue that in the cited work\textsuperscript{28} an SL with nominally three (as opposed to two) GeTe BLs was studied and hence the eleven-layer block is inconsistent with our model. Although this argument cannot be outright dismissed, we note that during the nominal growth of three GeTe BLs, there were multiple occurrences where blocks with the number of GeTe BLs within covalent blocks varied from zero to four\textsuperscript{28} and hence the composition of each grown block cannot be accurately predicted.

To conclude this section, we argue that during the nominal growth of a GeTe/Sb\textsubscript{2}Te\textsubscript{3} superlattice, a Kooi-like phase is obtained instead due to the 3D nature of GeTe. This result is obtained not because of Ge/Sb interdiffusion in the solid phase but due to inversion of the Sb and Te planes during the growth of the first SbTe bilayer. Because this inversion takes place during the formation of the first SbTe BL and both Sb and Te species are simultaneously present in the flux, this process does not require any interatomic diffusion within the solid phase and consequently is not kinetically limited.

We further studied the stability of GeTe/Sb\textsubscript{2}Te\textsubscript{3} SLs assuming that one way or another, an SL with the F-phase can be formed. We concentrate on the F-phase because this phase has been consistently predicted\textsuperscript{13,22} to be energetically most favorable at elevated temperatures and also because only this phase allows for a reconstruction into a Kooi-like phase without inversion of Ge/Te BLs. To this end, we started with the F-phase (Figure 5a), and allowed the Sb\textsubscript{2}Te\textsubscript{3} layer to melt, whereas the GeTe layers were fixed in the crystalline phase to act as a crystallization template (Sb and Te atoms are randomly distributed between the two GeTe layers, Figure 5b). We note that although there is no experimental evidence that this is what happens in real structures, the higher melting point of GeTe (998 K) compared with that of Sb\textsubscript{2}Te\textsubscript{3} (893 K) justifies this approach. Although there may seem to be a contradiction between this assumption and the results reported in the literature\textsuperscript{58}, where GeTe was demonstrated to amorphize, whereas Sb\textsubscript{2}Te\textsubscript{3} remained crystalline, this is not the case. In the cited work, significantly thicker Sb\textsubscript{2}Te\textsubscript{3} blocks were used.
inducing non-negligible tensile strain in GeTe, which was argued to be the driving force for easier amorphization.

On the basis of the previous results, we were expecting that upon recrystallization, the quintuple layer will break down to terminate the 3D GeTe slab transforming the F-phase into a Kooi-like phase. Rather unexpectedly, the quintuple layer was re-established upon recrystallization (perfect Sb and Te layer ordering can be clearly seen in Figure 5c,d), demonstrating that the Ferro phase is actually more stable than the Kooi phase at temperatures close to the melting point. We attribute this result to the remarkable stability of Sb2Te3 QLs. To make sure that the obtained result was not an artifact of the fixed unit cell size, we repeated the simulation, fixing the cell size to that of the K-phase and obtained the same result: a restoration of the F-phase upon cooling.

The high stability of the F-phase suggests that the K- and F-phases may coexist in proportions determined by the sample prehistory and a schematic illustration and an experimental indication of this are shown in Figure 6a,b. One can clearly see a step in the vdW gap position. With some imagination, one can see a reversal of Sb and Te planes across the step in the high-angle annular dark-field (HAADF) image (Figure 6b).

Far more interestingly, the vdW gaps can be reconfigured by external stimuli, as illustrated in Figure 6c,d. Figure 6c shows an HAADF image of an as-deposited SL. One can see that in this structure there are blocks with two and five layers separated by the red arrows. After STEM mapping of the region marked by a red quadrangle (Figure 6d), the $2 + 5 + 2$ layer blocks merge and form a nine-layer block, as shown in the right panel. The blue arrows in the right panel indicate the vdW gaps that survived being outside of the mapped region. Presently, we cannot differentiate unambiguously whether the presence of charge from the electrons in the beam or the heating effect of the beam caused the vdW gap motion. The main point we want to make here is that the vdW gaps in an SL structure are reconfigurable. Furthermore, the provided images are not meant to serve as a proof of the proposed concept; they only demonstrate that the existing experimental evidence is in line with it.

We now want to draw the readers’ attention to the fact that switching between the structures shown in Figure 6a (which can also be viewed as the formation or movement of a stacking fault considered in the literature) changes the thickness of the covalent blocks by two atomic layers. This may be significant because in experimentally grown SLs, thicknesses of individual blocks vary (from 5 to 138) with an increment of two atomic layers, which was attributed to a local change in stoichiometry in terms of the number of GeTe BLs. At the same time, MBE is known to be a very accurate growth method and it is very difficult to believe that layers of GeTe containing tens of atoms (for the images shown in the literature) can easily migrate from inside one covalently bonded block and inside a neighboring covalently bonded block penetrating through multiple SbTe layers. Even if variable layer thicknesses may be thermodynamically favorable, such motion of GeTe layers is bound to be limited kinetically. On the other hand, the inversion of an Sb2Te3 QL (stacking fault motion) is much more realistic and we propose that it is this process and not the variation in the number of GeTe BLs that causes the different thicknesses of the covalent blocks observed experimentally.

At this point, we would like to propose a mechanism for phase change in SLs associated with the reconfiguration of vdW gaps (similar to the formation and motion of stacking faults described above). Indeed, in the ideal Kooi-like phase, with the composition corresponding to the GeTe--Sb2Te3 quasibinary tie line, the number of valence electrons and the number of bonds are such that saturated covalent bonds with two electrons per bond are formed, resulting in the material being a semiconductor. In the cubic phase of Ge−Sb−Te, the coexistence of Ge and Sb necessitates the formation of intrinsic...
vacancies, as discussed for example in the literature. In SLs, on the other hand, the overall structure is fixed and there are no vacancies inside the covalently bonded blocks (they are pushed out to form vDW gaps). This limitation for the formation of vacancies has an important consequence.

When an SbTe BL inverts (Figure 7a), one of the blocks becomes Sb-rich and the other one becomes Ge-rich, as compared with the quasibinary Kooi phase (with the appropriate electron count). Because Ge atoms possess four valence electrons and Sb atoms possess five (Figure 7b), the electron balance necessary to form saturated covalent bonds is disturbed. (Using an analogy with semiconductor doping one might say that one of the blocks becomes n-doped, whereas the other one becomes p-doped. The doping is very heavy because one out of nine atoms is replaced by a "dopant" for a Ge$_2$Sb$_2$Te$_5$ (GST225) average composition.) Such "heavily doped" blocks are likely to possess significantly higher conductivity than that of the "intrinsic" quasibinary Kooi phase. We propose that this reconfiguration of vDW gaps may be the origin of the pronounced conductivity contrast between the two phases that remain crystalline in both states. The net result of which is a translation of a terminating SbTe bilayer from one covalently bonded block to the neighboring one. The bilayer translation is intrinsically linked with inversion of the Sb and Te planes.

To substantiate this proposal, we calculated the density of states of the quasibinary Kooi phase and of a phase with inverted SbTe BLs, as shown in Figure 7. Our results demonstrate that although the quasibinary Kooi phase (GST225) essentially possesses a gap (GGA is known to underestimate the band gap), the phase with the reconfigured gap and local stoichiometries different from the quasibinary (2GST225 ⇒ GST214 + GST236) clearly possesses a finite density of states at the Fermi level (Figure 7c), providing a perfect explanation for the large resistivity contrast between the two phases despite them both being in a crystalline state. We do not associate the SET and RESET states directly with pure 2GST225 and (GST214 + GST236) phases. The only claim made here is that the proposed gap reconfiguration may lead to dramatic changes in electronic properties.

We do not go into details of the possible atomic scale mechanism of vDW gap reconfiguration, but one possibility for it may be an umbrella flip of Sb atoms. We would also like to note that a similar process of SbTe bilayer reversal (albeit from a solely structural perspective without any reference to the SL

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**Figure 7.** (a) Quasibinary Kooi phase (left) and a phase with inverted SbTe BLs (right). The upper part shows a single in-plane unit cell and the bottom panel shows a schematic 3D image of the two phases around the reconfigured vDW gap; (b) schematics of Ge, Sb, and Te p orbitals, valence p electrons are shown as arrows; and (c) simulated density of states around the Fermi level for the quasibinary Kooi (GST225) phase and the phase with inverted SbTe BLs (GST214 + GST236).
properties) was considered earlier as stacking fault formation and motion.\textsuperscript{31} In this work, various microscopic processes within SbTe BLs resulting in SbTe reversal were considered and we believe that similar processes may take place during the phase-change process. We also note that the energy cost of such SbTe BL inversion translation is relatively low.\textsuperscript{31}

The proposed phase-change mechanism is substantially different from earlier models in that previously only Ge motion was considered, whereas the motion of Sb atoms was entirely, and undeservedly, neglected. Even if this Ge motion could lead to a similar gap reconfiguration (e.g., a transition between the P- and F-phases may be considered as a transfer of a GeTe bilayer from one GST225 block to another, that is, 2GST225 ⇒ GST124 + GST326), this would change the local stoichiometry of blocks but would not cause a deviation from the quasibinary condition, a condition necessary to ensure the formation of saturated covalent bonds, consequently causing no change in the electronic properties. For the density of states at the Fermi level to change, a local deviation from the quasibinary compositions of covalently bonded blocks, achieved due to SbTe BLs inversion, is crucial. At the same time, it should be stressed that the proposed model is similar to the initial key idea\textsuperscript{13} in that the phase change in SLs is due to one-dimensional motion of cation atoms located in the vicinity of vdW gaps.

We further note that Ge/Sb intermixing does not compromise the proposed model, provided there is a sufficient number of Sb atoms in inverting BLs. Experimental evidence demonstrates that, fortunately, this is generally the case.\textsuperscript{17,28,29}

The main findings of this work can be summarized as follows.

Contrary to the previously proposed models of Ge/Sb intermixing based on Ge in-diffusion into Sb\textsubscript{2}Te\textsubscript{3} QLs with concomitant Sb atoms’ out-diffusion, our results suggest that the reversal of the expected Ge and Sb planes occurs as a result of an SbTe BL for the subsequent vdW growth to proceed. The proposed model does not require atomic diffusion within a solid phase and hence is energetically significantly more favorable.

We propose that covalently bonded blocks with different thicknesses form in SLs not as a result of GeTe plane redistribution between different covalently bonded blocks, which requires significant atomic diffusion, but are caused by detachment/reattachment of SbTe BLs, analogous to the motion of stacking faults, a process that requires significantly less diffusion.

We demonstrate that at temperatures close to the melting point, an Sb\textsubscript{2}Te\textsubscript{3} QL in the vicinity of GeTe is very stable and re-forms after melting, whereas at low temperatures (0 K in our simulation), the formation of a Kooi-like phase is energetically more favorable. We propose that this reversal of the phase stability plays an important role in the phase-change process in SLs.

More specifically, we associate the phase-change mechanism in SLs with the reconfiguration of vdW gaps through the inversion of SbTe BLs between neighboring blocks. We showed that the quasibinary (Kooi) structure is a gapped phase, whereas a structure built of blocks with inverted SbTe BLs possesses a finite density of states at the Fermi level and we argue that this transition, accompanied by a local deviation in stoichiometry from quasibinary compositions, is the origin of phase-change in GeTe/Sb\textsubscript{2}Te\textsubscript{3} SLs. A very important feature of the proposed model is that it is not compromised by Ge/Sb intermixing. We also note that the proposed model does not affect the original explanation of the superior efficiency of SL-based memories offered in terms of one-dimensional motion of cation atoms.

The reported results represent significant progress in understanding the structure and switching mechanism in GeTe/Sb\textsubscript{2}Te\textsubscript{3} SLs and open a new avenue for the industrial development of GeTe/Sb\textsubscript{2}Te\textsubscript{3} SL-based memory devices based on insightful engineering of van der Waals gaps. Furthermore, we believe that the proposed concept of vdW gap reconfiguration as a means to control the properties of vdW-bonded layered materials may be more general and applicable to the broad class of vdW solids beyond iPCM.

\section{METHODS}

First-principles calculations were carried out using the pseudopotential plane-wave density-functional theory formalism using the Vienna ab initio simulation package (VASP) code.\textsuperscript{30} Projector-augmented wave (PAW) pseudopotentials that included the electron configurations 3d\textsuperscript{4}s\textsuperscript{4}p, 5s\textsuperscript{5}p, and 5s\textsuperscript{5}p as valence states for Ge, Sb, and Te, respectively, were used. The PBE exchange-correlation functional\textsuperscript{43} was used with a plane-wave basis, with a cutoff energy of 500 eV. A 6 × 6 × 2 gamma-centered Monkhorst-Pack grid was used to sample the Brillouin zone of the conventional cell.\textsuperscript{42} The PAW projections were conducted in a reciprocal space, and nonspherical contributions to the gradient corrections within the PAW spheres were included. Calculations were carried out in the scalar relativistic approximation and spin–orbit coupling was not included. Van der Waals forces were accounted for by using the DFT-D2 dispersion correction of Grimme.\textsuperscript{45} To simulate surface properties, a 15 Å vacuum gap was introduced between periodic replicas along the growth direction.

Lattice dynamics calculations were carried out using a combination of Phonopy\textsuperscript{46} and VASP using density-functional perturbation theory (DFPT). The conventional cell was relaxed using a tolerance of 10\textsuperscript{−8} eV for the electronic minimization and both ion positions and the lattice were relaxed until the forces were less than 3 × 10\textsuperscript{−4} eV/Å. The DFPT calculations were carried out using 2 × 2 × 1 supercells to account for extended forces, and the resulting phonon density of states were sampled using a 128 × 128 × 128 gamma-centered \textbf{q} grid with respect to the reciprocal space form of the conventional cell to derive the partition function used for the calculation of the enthalpy. The enthalpy was calculated in terms of the energy per formula unit.

Molecular dynamics simulations of the Ferro phase were performed for an NVT ensemble of 36 atoms, with lattice constants corresponding to the relaxed Ferro and Kooi phases at 0 K corrected for higher temperatures using the experimental values of the thermal expansion of trigonal Ge\textsubscript{5}Sb\textsubscript{4}Te\textsubscript{6}\textsuperscript{46} GeTe bilayers were fixed at the top and bottom of the cell, as described in the text. A Nosé–Hoover chain thermostat was employed and a gamma-centered 2 × 2 × 1 Monkhorst–Pack grid was used for \textbf{k}-space sampling, with an energy cutoff of 250 eV. The molten phase was obtained by maintaining a temperature of 1700 K for 200 ps ensuring the equilibrium molten state was reached. The temperature of the structure was subsequently decreased to 1300 K in 100 ps, and the temperature was maintained at 1300 K for another 200 ps. The onset of subsequent recrystallization at 1300 K (plane ordering) was noted at 46 ps, which continued to 200 ps. The DFT-D2 dispersion correction was applied throughout.
The GeTe/Sb2Te3 superlattices used in this work were fabricated using helicon sputtering. The films were grown on Si single crystal wafers, where the native oxide of the substrate was preliminarily removed by Ar reverse sputtering. A 3 nm thick Sb2Te3 seed layer was grown first at room temperature, followed by heating up the substrate to 230 °C. The superlattices were fabricated by depositing GeTe and Sb2Te3 layers alternately. The growth rates used were 5.5 nm/min (GeTe) and 4.6 nm/min (Sb2Te3).

TEM specimens were prepared by mechanical polishing, followed by Ar-ion beam milling (Dual Mill 600; Gatan, Inc.). The cross-sectional microstructures were observed by STEM (JEM-ARM200F, JEOL Co. Ltd.). The acceleration voltage was 200 kV. The probe size was 2 Å, and the probe current was 60 pA. The total acquisition time for energy-dispersive system mapping was about 20 min, with a dwell time of 15 μs.

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**Notes**
The authors declare no competing financial interest.

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NOTE ADDED IN PROOF

After the submission of this manuscript, two papers that support the ideas developed in this work were published.46,47