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Nanoscale

COMMUNICATION

Unconventional two-dimensional germanium dichalcogenides

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The recently discovered two-dimensional (2D) group IV chalcogenides attract much attention owing to their novel electronic and photonic properties. All reported materials of this class favor (distorted) octahedral coordination via sp² bonding; by contrast, in the dichalcogenides where the bonding tendency approaches sp³, no corresponding 2D phase has been realized so far. Here, by engineering the composition of a chalcogenide heterostructure, the hitherto elusive GeTe₂ is experimentally observed in a confined 2D environment. Density functional theory simulations predict the existence of a freestanding monolayer of octahedrally coordinated GeTe₂ under tensile strain, and the existence of GeSe₂ and GeS₂ in the same form at equilibrium conditions. These 2D germanium dichalcogenides are either metallic or narrow gap semiconducting, and may lead to new applications in nanoscale electronics.

Two-dimensional (2D) materials such as graphene¹,² and transition metal dichalcogenides³–⁴ provide a unique platform with extraordinary physical and chemical properties and a wide range of potential applications. Among them, the recently discovered 2D group IV chalcogenides (IV = Ge, Sn; chalcogen = S, Se, Te) have attracted significant attention owing to their earth-abundance, low cost, and environmental friendliness, as well as their tunable electronic structure. Hence, they are regarded as promising candidates for sustainable electronics and optoelectronics applications.⁵–⁶ Moreover, many interesting physical phenomena were found or predicted in this material class. Regarding the monochalcogenides, giant and robust in-plane ferroelectricity with high transition temperature was predicted in monolayer GeS, GeSe, SnS and SnSe,⁷–⁹ and was very recently demonstrated experimentally in one unit-cell thick SnTe at room temperature.¹⁰,¹¹ In addition, large ferroelasticity⁷–⁹ and piezoelectricity,¹² colossal optical second harmonic generation susceptibility,¹³ strong visible-light absorbance,¹⁴ high photosensitivity,¹⁵,¹⁶ and strong in-plane electronic anisotropy¹⁷ were theoretically predicted and partly confirmed experimentally in mono- or few-layer GeS, GeSe, SnS and SnSe, and phase change characteristics were shown in few-layer GeTe.¹⁸ Regarding the dichalcogenide compounds, monolayer and few-layer SnS₂ and SnSe₂ have been synthesized and incorporated into various devices, showing promising characteristics as field effect transistors,¹⁹–twenty one phototransistors,²² photodetectors,²³ and photoelectrochemical cells.²⁴

However, 2D phases of other group IV dichalcogenides remain to be explored. Regarding GeS₂ and GeSe₂, their bulk phase is a complex monoclinic structure with tetrahedral motifs (Figure 1 top right),²⁵ which differ from the local structure of most (transition-) metal chalcogenides, where (distorted) octahedral motifs are typically found. Although GeS₂/GeSe₂ nanostructures have been synthesized, it has been shown to be difficult to reach the 2D limit,²⁶,²⁷ possibly due to the presence of strong interlayer chemical bonds in addition to the weak van der Waals (vdW) forces. As far as GeTe₂ and SnTe₂ are concerned, their crystalline bulk phase is hitherto unknown.²⁸ There were some reports on crystalline GeTe₂ thin films,²⁹,³⁰ but a more recent work showed that GeTe₂ would easily decompose into Te and GeTe crystallites upon thermal annealing.³¹ This is due to the fact that the competing counterpart GeTe favors a peculiar bonding mechanism, termed as metavalent bonding.³²,³³ Very recently, we showed that the formation of this bonding mechanism in GeTe requires a critical thickness of four bilayers,³⁸ which points towards a scenario to explore the existence of unconventional germanium ditelluride at the 2D limit. Note that if a GeTe₂ crystal were to exist, it would conceptually lie at the boundary of the chemical realms of sp³ bonding and p bonding.³⁸
The stable bulk crystal structures of the existing germanium chalcogenides,\textsuperscript{24, 35, 36} reported in the 1930s already.\textsuperscript{25, 35} Layered compounds with vdW gaps are of particular interest as precursors for 2D materials.\textsuperscript{5, 6, 37} GeSbTe compounds along the GeTe-Sb\textsubscript{2}Te\textsubscript{3} pseudobinary are very well studied materials, which serve as the core of non-volatile phase change memory devices.\textsuperscript{38-40} The stable crystalline polymorphs of GeSbTe compounds, such as GeSb\textsubscript{2}Te\textsubscript{4}, GeSb\textsubscript{2}Te\textsubscript{3} and GeSb\textsubscript{2}Te\textsubscript{2} exhibit layered structures with alternating “cation” Ge/Sb, “anion” Te atomic layers and gaps arranged along the [0001] direction.\textsuperscript{41, 44} This leads to atomic building blocks of various size separated by gaps. For instance, GeSb\textsubscript{2}Te\textsubscript{4} consists of septuple-layer blocks with the stacking sequence \textasciitilde g-abcabc-g-bcacab-g-cabcac,\textsuperscript{2} where \textit{g} represents the gap, and we use the labels “\textit{a}”\textsuperscript{2} = (0, 0), “\textit{b}”\textsuperscript{2} = (2/3, 1/3) and “\textit{c}”\textsuperscript{2} = (1/3, 2/3) to indicate the in-plane positions of the atoms in each layer. The gaps between the building blocks are commonly referred to as “vdW gaps”, although the gap size (the spacing along the [0001] direction) is considerably smaller (~2.9 Å) than in other vdW crystals, such as Mo\textsubscript{3}S\textsubscript{2} (~4.2 Å), implying that additional chemical interactions stronger than pure vdW forces might be present.

![Figure 1: Crystal structures of bulk germanium chalcogenides.](image)

We engineered the composition of the GeSbTe heterostructure by increasing the concentration of Te, relative to the ideal stoichiometric composition GeSb\textsubscript{2}Te\textsubscript{3}. Tellurium here is the essential element to create gaps: it has the highest number of valence electrons, and Te layers detach from each other to avoid Te-Te bonding, which is energetically unfavourable.\textsuperscript{46} If the excess Te content does not segregate, it has to be accommodated in Te-rich atomic blocks. Formally, there are two potential candidates for this: the well-known Sb\textsubscript{2}Te\textsubscript{3}, but also a hypothetical building block with the composition GeSb\textsubscript{2}Te\textsubscript{2}.

![Figure 2: Experimental data of conventional atomic blocks.](image)

To investigate the atomic structure of this Te-rich compound, state-of-the-art scanning transmission electron microscopy (STEM) experiments were performed (see ESI). Such imaging method has been shown to be powerful in identifying the atomic structure and defects in highly relevant chalcogenides.\textsuperscript{45-48} A representative high-angle annular dark-field (HAADF) image is shown in Figure 2a. The intensity peaks (bright spots) appear at the positions of atomic columns, and the intensity value of the spots is approximately proportional to the square of the averaged atomic number of each column along the view direction.\textsuperscript{49} Since Sb and Te have very close atomic numbers, 51 and 52 respectively, their corresponding intensities are very similar. In comparison with Sb and Te, Ge has a lower atomic number 32 and thus shows much lower image intensity. Intensity profiles of STEM image confirm the absence of Te elemental segregation, and show that septuple-layer blocks (as in ideal GeSb\textsubscript{2}Te\textsubscript{3}) are the major constituent of the samples. By evaluating the intensity of each atomic layer in these blocks in Figure 2b, a Ge-rich layer (center) can be clearly identified. According to the stoichiometry of GeSb\textsubscript{2}Te\textsubscript{3}, the other six layers can be considered as two Sb-rich layers and four Te layers. The parameters \textit{a}_{\text{surf}}\textsuperscript{2} and \textit{c}_{\text{surf}}\textsuperscript{2} of the GeSb\textsubscript{2}Te\textsubscript{3} septuple-layer blocks are estimated from the HAADF images as 4.23 Å and 41.3 Å, respectively (Figure S3), in good agreement with the values reported in previous work.\textsuperscript{43} Quintuple-layer blocks (Figure 2c) were also frequently observed in HAADF images. The image
intensity of all the atomic layers in these quintuple-layer blocks is high, suggesting the composition of Sb$_2$Te$_3$. The presence of Sb$_2$Te$_3$ blocks can be expected, as they are constituent blocks of some GeSbTe compounds, such as GeSb$_2$Te$_5$.

In addition, however, many triple-layer atomic stacks were also observed in our experiment, as shown in Figure 3. The thickness of these triple-layer blocks is 3.84 Å, which is comparable to the thickness of three atomic layers inside a GeSb$_2$Te$_5$ block. The triple-layer block is well separated from other blocks with a gap of 2.98 Å, similar to those found between GeSb$_2$Te$_5$ blocks (2.88 Å). The outer two atomic layers show the same image intensity as the Te layers, whereas the middle layer looks much darker, suggesting it to be either a Ge layer or a Sb layer with vacancies. EDS mapping experiments can now unambiguously distinguish the different elemental contributions at the atomic scale. As shown in Figure S4, EDS mapping rules out the possibility of Sb with vacancies, and therefore, the triple-layer structure must indeed be GeTe$_2$. Inside the triple-layer, the two Ge-Te spacings are equivalent, giving the building block inversion symmetry. The atoms occupy the same three special sites as in other blocks with the sequence $g$-abc-$g$-, and the bond angle derived is 86°. This gives a slightly distorted octahedral coordination for GeTe$_2$ (Figure 3d), similar to SnS$_2$/SnSe$_2$ and the 1T structure of MoS$_2$.5,6

In summary of the above results, the formation of this unconventional GeTe$_2$ phase can be considered as the result of excess Te in the sample, in comparison with the stoichiometry of GeSb$_2$Te$_5$. The extra Te leads to the formation of GeTe$_2$ and Sb$_2$Te$_3$ in addition to GeSb$_2$Te$_5$ compensating the Te-rich stoichiometry GeSb$_2$Te$_{5-x}$. We note that the formation of GeTe$_2$ is not expected to occur only in GeSb$_2$Te$_5$, but could also be obtained with other GeSbTe compositions, such as Ge$_2$Sb$_2$Te$_5$, as long as excess Te is integrated into the layered structures. In fact, a similar triple-layer structure has been observed in a slightly Te-rich composition with respect to Ge$_2$Sb$_2$Te$_5$.51 Although the chemical composition of the structural fragment was not determined, it could still be taken as the indication of GeTe$_2$.

Next, we determine whether the observed GeTe$_2$ units can be stable in the freestanding case. Since our samples are polycrystalline, we cannot directly apply exfoliation methods to obtain freestanding GeTe$_2$. Instead, DFT simulations are performed to shed light on this question (see ESI). Idealized monolayer GeTe$_2$ is modeled in a hexagonal cell with a large vacuum slab (20 Å) along the vertical direction (Figure 4a). Upon atomic and cell relaxation, GeTe$_2$ keeps the octahedral geometry with a lattice parameter of 3.86 Å, six equivalent Ge-Te bonds with length 2.81 Å, and a slightly distorted Te-Ge-Te bond angle of 86.4°. Upon relaxation, GeTe$_2$ displays metallic behaviour. The corresponding electronic density of states (DOS) and band structure are presented in Figure 4b-c. To determine whether a system is stable or not, it is important to assess both its chemical and dynamical stability, which can be done by performing the quantum chemical Crystal Orbital Hamiltonian Population (COHP) bonding analysis$^{52-54}$ and phonon dispersion calculations,$^{55}$ respectively. The COHP dissects the electronic band structure into bonding (stabilizing) and antibonding (destabilizing) interactions between neighbouring atoms, and has been applied to GeSbTe materials with success before.$^{56}$ In monolayer GeTe$_2$, a finite antibonding interaction (red arrow) is found at the Fermi level (Figure 4b), indicating chemical instability. In addition, small but non-negligible imaginary phonon frequencies near the Γ point are found, implying that the model is not fully dynamically stable.

It is important to note that the computationally optimized lattice parameter of freestanding GeTe$_2$ (3.85 Å) is much smaller than that obtained from STEM experiments (4.23 Å), suggesting that the GeTe$_2$ units are under in-plane tensile strain inside the GeSbTe heterostructure. Similar situation occurs in another type of GeSbTe heterostructures, where GeTe and Sb$_2$Te$_3$/Sb$_2$Te slabs with various thickness are grown repeatedly. Tensile strain on GeTe slabs across gaps was observed and the origin was attributed to the lattice mismatch between GeTe and Sb$_2$Te$_3$/Sb$_2$Te$^{57-59}$. In our case, the mismatch is even stronger. If 2D GeTe$_2$ would adopt the calculated lattice parameter with the presence of GeSb$_2$Te$_5$ surrounding, a large amount of unfavorable Te-Te covalent bonds would form (Figure 55), resulting in very high energy penalties.$^{54}$ This indicates that the gap between GeTe$_2$ and GeSbTe is not a pure vdW gap, and there exists covalent interaction across the gap.

To mimic the experimental conditions, we applied in-plane tensile strain to monolayer GeTe$_2$, and found that tensile strain indeed stabilizes the dynamical properties of the lattice. For instance, at 4% tensile strain, the imaginary phonon frequencies are all removed (see Figure 4d and a zoomed-in version in Figure S6). Our combined theoretical and experimental results, therefore, point to a potential recipe to produce monolayer or even few-layer GeTe$_2$ based on the application of an in-plane tensile strain of a few percent.

Since GeTe$_2$ might be difficult to obtain without strain, one may wonder whether its lighter homologues, Ge$_2$S and GeSe$_2$, can be produced in a freestanding configuration. As shown in Figure 1 (top right), the bulk isomorphous crystal structures of Ge$_2$S and GeSe$_2$ are rather complex, and it remains unclear whether such a phase can be synthesized in 2D form. Here, instead we consider 2D GeSe$_2$ and GeS$_2$ in the simpler octahedral coordination. The atomic structures and the corresponding DFT data are shown in Figure 4e-h and 4i-l. Similar to their telluride analogue, 2D GeSe$_2$ and GeS$_2$ retain the octahedral coordination environments upon relaxation, but with smaller equilibrium lattice parameters (3.62 Å, 3.44 Å) and...
bond lengths (2.58 Å, 2.43 Å). Both models are dynamically stable, as no imaginary frequency is present in the phonon dispersion curves, and they are chemically stable, as the antibonding interaction at the Fermi level is either marginal or completely absent (black arrow). 2D GeSe₂ displays metallic behaviour at equilibrium and undergoes a metal–semiconductor transition under in-plane tensile strain. A narrow and indirect band gap (~0.12 eV) appears at 4% tensile strain (Figure 4g and Figure S7). 2D GeS₂ is instead predicted to be a narrow gap semiconductor with an indirect gap of 0.73 eV. The band gap widens to 0.86 eV at 4% tensile strain. In all semiconducting states, the minimum of the conduction band is located at the M point of the Brillouin zone, while the top of the valence band is found along the Γ→M path. Since freestanding GeSe₂ and GeS₂ are predicted to be stable from DFT simulations, it should be possible to produce them following the same strategy as for GeTe₂: first produce GeSe₂/GeS₂ triple-layers inside Se/S-rich gapped heterostructures, then apply mechanical exfoliation or other methods to obtain freestanding GeSe₂/GeS₂.

In conclusion, we have explored the existence of crystalline GeTe₂, a compound unknown in the bulk that is located at the interface of sp³ and p bonded main-group chalcogenides. We started with the stable GeSb₂Te₄ compound and engineered its composition to be Te-rich. We confirmed that a moderate excess of Te does not lead to phase segregation, but instead drives the formation of Te-rich atomic blocks. Upon sputtering and subsequent thermal annealing, we successfully obtained 2D crystalline GeTe₂ confined within a gapped GeSbTe heterostructure. The central Ge atom is octahedrally coordinated, and the chemical identity was clearly established using EDS mapping, which, to our knowledge, together represent the first proof of such structural feature in the germanium dichalcogenide family. Clear gaps between the GeTe₂ triple layers and the adjacent 2D GeSb₂Te₄/Sb₂Te₄ building blocks were found, which suggests the possibility to isolate this material experimentally: first growing a single crystal of Te-rich GeSbTe heterostructure, e.g. through epitaxial methods;⁴⁵, ⁴⁷ then, applying exfoliation techniques to produce monolayer GeTe₂. In such case, in-plane tensile strain may be needed to stabilize this material. It is also known that distortions induced by hydrogenation can stabilize 2D metal dichalcogenides,⁶⁰, ⁶¹ which could be an alternative approach to stabilizing monolayer GeTe₂ as well. We note that the synthesis strategy proposed in this work could be used to form other unconventional 2D materials, such as octahedrally bonded 2D GeSe₂ and GeS₂, where strain engineering is no longer required. These newly proposed 2D germanium dichalcogenides show metallic or narrow-gap semiconducting band structures at equilibrium, and tunable electronic behaviour under tensile strain. Contrary to most 2D group IV chalcogenides having band gaps larger than silicon, 2D germanium dichalcogenides have narrow gaps below 1 eV, which may lead to new applications in nanoscale and flexible electronic devices. It is worth mentioning that another unconventional 2D phase of group IV monochalcogenides in the X-IV-IV-X form with interesting electronic and topological properties has been predicted through DFT calculations⁶², ⁶³ and partially realized in experiments.⁶⁴ Our work on unconventional germanium dichalcogenides further enriches the 2D IV-VI material family and shall stimulate further investigations in this exciting direction.
Conflicts of interest

There are no conflicts to declare.

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Author contribution

JW performed sample preparation and TEM experiments with the help of LL and analyzed the data with TL, HD, CJ, MW and WZ. DFT calculations were carried out by ID, LZ and BZ. The paper was written by WZ, VLD, QX and RM with the help and through contributions from all co-authors. The project was initiated and conceptualized by WZ.

Notes and references

A novel 2D phase of germanium dichalcogenides (GeTe$_2$) is achieved by engineering the composition of a GeSbTe heterostructure.