Bonding, structure, and mechanical stability of 2D materials: the predictive power of the periodic table

Peter Hess

This tutorial review describes the ongoing effort to convert main-group elements of the periodic table and their combinations into stable 2D materials, which is sometimes called modern ‘alchemy’. Theory is successfully approaching this goal, whereas experimental verification is lagging far behind in the synergistic interplay between theory and experiment. The data collected here gives a clear picture of the bonding, structure, and mechanical performance of the main-group elements and their binary compounds. This ranges from group II elements, with two valence electrons, to group VI elements with six valence electrons, which form not only 1D structures but also, owing to their variable oxidation states, low-symmetry 2D networks. Outside of these main groups reviewed here, predominantly ionic bonding may be observed, for example in group II–VII compounds. Besides high-symmetry graphene with its shortest and strongest bonds and outstanding mechanical properties, low-symmetry 2D structures such as various borophene and tellurene phases with intriguing properties are receiving increasing attention. The comprehensive discussion of data also includes bonding and structure of few-layer assemblies, because the electronic properties, e.g., the band gap, of these heterostructures vary with interlayer layer separation and interaction energy. The available data allows the identification of general relationships between bonding, structure, and mechanical stability. This enables the extraction of periodic trends and fundamental rules governing the 2D world, which help to clear up deviating results and to estimate unknown properties. For example, the observed change of the bond length by a factor of two alters the cohesive energy by a factor of four and the extremely sensitive Young’s modulus and ultimate strength by more than a factor of 60. Since the stiffness and strength decrease with increasing atom size on going down the columns of the periodic table, it is important to look for suitable allotropes of elements and binaries in the upper rows of the periodic table when mechanical stability and robustness are issues. On the other hand, the heavy compounds are of particular interest because of their low-symmetry structures with exotic electronic properties.

Introduction

The family of two-dimensional (2D) materials is growing rapidly by expanding to more elements of the periodic table and by their characterization being extended predominantly by theoretical studies. The preparation ranges from straightforward exfoliation of layered materials, such as graphene, with a huge reservoir of weakly bonded layered materials, to entirely synthetic methods, such synthetic 2D monolayers are borophene, silicene, bismuthene, and tellurene. Besides monolayers this includes bilayers, tri-layers, and few-layer assemblies up to about 10 layers, where a transition to bulk properties is observed. Strong covalent and ionic interatomic bonding in 2D materials and weaker interlayer interaction between monolayers are the focus of this review. Besides the quantum-mechanical concepts of electron sharing, electron transfer, and electron delocalization, phenomenological binding models describe the role played by the three fundamental types of interaction forces, termed covalent, ionic, and metallic bonding. Confining strong chemical bonding to one or a few layers, usually less than five, creates a huge flat molecule without dangling bonds at the surface. Mixing planar sp² hybridization with tetrahedral sp³ hybrids dramatically extends covalent bonding to quasi-two-dimensional corrugated phases, by introducing buckling and puckering but also chemical reactivity. Besides mechanical constraints, chemical stability under environmental conditions is a crucial requirement, made important by the extremely large surface area exposed to the environment.
**Ab initio** calculations are the first choice for computing the pristine structure as well as chemical and physical properties of 2D materials.\(^4\)\(^,\)\(^9\) It is important to note that first-principles calculations have not only predicted the existence of new 2D materials but also helped to find possible routes of synthesis and understand the growth process.\(^8\)\(^,\)\(^10\) Of the two main approaches, namely, the wave-function-based methods and density functional theory (DFT) calculations, the latter plays the major role. In the latter approach the many-body system of electrons is treated by considering non-interacting electrons moving in an effective potential. To take the exchange and correlation effects in the calculation of electron density into account, the local density approximation (LDA) uses Ceperley–Alder (CA) functionals or Troullier– Martins (TM) pseudopotentials. In most calculations the generalized gradient approximation (GGA) is employed with Perdew–Burke–Ernzerhof (PBE) functionals.\(^4\) Large differences may occur between the LDA and GGA approach, especially for few-layer systems, where, besides strong covalent in-plane interaction, weak interlayer forces such as van der Waals and electrostatic interactions must be considered.\(^4\) At present, most results are based on the numerical DFT-GGA-PBE approach, which plays a crucial role in our present understanding of 2D materials.

Molecular dynamics (MD) simulations complete the investigation of the atomic structure and mechanical behavior of monolayers because they can deal with system sizes of thousands or even millions of atoms, in comparison with about a hundred atoms usually manageable by DFT calculations. The simulation is based on classical Newtonian dynamics, where potential energy functions, which describe the interaction between atoms, play a critical role. These theoretical methods give access not only to the intrinsic structures of monolayers and few-layer systems but also provide valuable estimates of the thermal or thermodynamic stability of the 2D materials at temperatures above 0 K.\(^4\)

While the data presented for bonding, structure, and mechanical properties primarily is based on first-principles calculations, we also apply the tight-binding theory of solids that uses the linear combination of atomic orbitals (LCAO). The LCAO approach and hybridization concept can deliver analytical expressions for the coupling parameters and the electronic-state energies.\(^11\) Despite the fact that it is less exact than numerical first-principles computations, the simplified bonding model that follows chemical intuition often offers valuable insight and a deeper understanding of the nature of bonding and allows the recognition of chemical relationships within related groups of the periodic table.

Reliable mechanical performance of 2D materials from manufacture to final use is a key requirement for any application.\(^12\)\(^,\)\(^13\) While calculated intrinsic Young’s moduli and ultimate strengths are already available for various monolayers, toughness values that characterize the strength of large-area defective monolayers are available only for graphene. The following work concentrates primarily on calculated mechanical properties such as the intrinsic Young’s modulus, Poisson’s ratio, ultimate strength, and ultimate strain of both free-standing and surface-bonded monolayers. Most 2D materials exhibit a positive Poisson’s ratio between 0 and 0.5, where the material contracts in the transverse direction when stretched in the longitudinal direction. For some low-symmetry monolayers a negative Poisson’s ratio or auxetic behavior exists. This means, for example, that the material expands perpendicular to the plane when stretched in the in-plane direction.\(^14\) For a rigorous comparison of the 2D mechanical properties of monolayers, 2D units are needed, due to the thickness or volume dependence of the 3D properties.\(^15\) These 2D properties can be obtained by transforming 3D units (N m\(^{-2}\)) to 2D units (N m\(^{-1}\)) using the monolayer thickness or by direct measurement. Unfortunately, reliable measurements of the intrinsic stiffness and ultimate strength, e.g., by indentation, are available only for graphene, while the measurements for other monolayers such as graphene oxide, h-BN, and black P are still preliminary.\(^16\) The monolayer thickness can be defined for free-standing layers, whereas in few-layer assemblies the interlayer spacing changes with the strength of interlayer interaction.

Up to now, only a few 2D materials have been prepared in their free-standing form, for example by exfoliation, allowing a direct measurement of their intrinsic properties. It is possible to grow quasi freely suspended monolayers that retain their properties under ultrahigh vacuum (UHV) conditions by molecular beam epitaxy (MBE) on suitable substrates. A buffer layer may stabilize an otherwise unstable monolayer by weak interaction forces. However, often stronger electrostatic and covalent interaction forces dominate the interaction of a monolayer with the substrate and change the structure. Structural analysis is performed by scanning atomic force microscopy (AFM),\(^16\) scanning tunneling microscopy (STM), in situ microscopy techniques such as scanning electron microscopy (SEM), low energy electron diffraction (LEED), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), selected area electron diffraction (SAED), and high resolution transmission electron microscopy (HRTEM), supplemented by energy dispersive X-ray spectroscopy (EDX).\(^17\) Atomic steps in layered assemblies are used to give quasi freely suspended monolayers that retain their properties under ultrahigh vacuum (UHV) conditions by molecular beam epitaxy (MBE) on suitable substrates. A buffer layer may stabilize an otherwise unstable monolayer by weak interaction forces. However, often stronger electrostatic and covalent interaction forces dominate the interaction of a monolayer with the substrate and change the structure. Structural analysis is performed by scanning atomic force microscopy (AFM),\(^16\) scanning tunneling microscopy (STM), in situ microscopy techniques such as scanning electron microscopy (SEM), low energy electron diffraction (LEED), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), selected area electron diffraction (SAED), and high resolution transmission electron microscopy (HRTEM), supplemented by energy dispersive X-ray spectroscopy (EDX).\(^17\) Atomic steps in layered assemblies are used
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example, trivalent group III atoms cannot form a closed-shell electrons are missing or additional electrons are available. For monolayers changes if the octet rule is not fulfilled and valence electrons in the outer shell (see Fig. 2). It is well known that graphene with its four valence electrons per C atom forms the most stable covalent bonds in the plane, involving eight electrons in the closed outer shell. This is shown in Fig. 3. Boron is the lightest atom that can develop a boron motif of three shared boron atoms. 2. Electron configurations with eight atoms in the outer shell possess a lower energy and higher stability (‘octet rule’) due to the stable noble gas configuration. Group III atoms with three valence electrons cannot fulfill these conditions and therefore arrange as delocalized three-centered bonds or multi-centered bonds in σ and π frameworks, where electron pairs are shared at least among three or more atoms. This complex bonding behavior gives access to flexible chemistry with a wide variety of allotropes in 2D space. DFT calculations propose a series of dynamically stable 2D structures and a variety of 2D bonding types for borophene, aluminene, gallenene, and indiene, the single layers of boron, aluminium, gallium, and indium.

In the following, tight-binding theory is used to treat three-centered bonds by the LCAO ansatz, describing the formation of molecular orbitals, which are combined to produce covalent bonding of an extended 2D network. The electron configuration and the arrangement of orbitals for three-centered bonding is shown in Fig. 3. Boron is the lightest atom that can develop 2D extended metallic phases by sp2-type hybrids, described by delocalized three-center, two-electron bonds (3c-2e), involving a motif of three shared boron atoms.

Based on the LCAO method, the electron configuration with promoted electrons can be described by three equivalent atomic orbitals, which form the molecular orbitals of a triangular motif, where three atoms share one pair of electrons. In this triangular boron motif, the sp2-like hybrids overlap, yielding one bonding and two anti-bonding orbitals (see Fig. 4). These orbitals broaden into bands by adding more triangles with increasing orbital overlap. Two of the three electrons are in the in-plane bonding orbital, but one electron is in an in-plane antibonding orbital and not in the remaining empty 2p-bonding orbital. Therefore, a planar triangular hybrid prefers to hybridize with a high-energy electron to a σ-π mixture of in-plane and out-of-plane states to gain further stability in a buckled configuration. The fact that a

for the direct measurement of the interlayer spacing by AFM and STM.

The present review of main group elements provides a systematic discussion of covalently bonded elemental group-III monolayers and their isoelectronic group II–IV compounds, elemental and binary group-IV monolayers and their isoelectronic group III–V compounds, elemental and binary group-V monolayers and their isoelectronic group IV–VI compounds, and elemental group-VI monolayers (see Fig. 1). Extension to other groups, for instance to alkaline earth–halogen monolayers, may lead to strong ionic bonding due to the large difference in their electronegativities. Importantly, bonding by long-range Coulomb forces is less effective in 2D than in 3D materials. The relevant bonding information, structural data, and mechanical properties of the predominantly covalently bonded monolayers are presented in 13 tables. The explosive growth of studies on 2D compounds has allowed the identification of general relationships between bonding, structure, and mechanical stability and the extraction of basic rules governing the 2D world down the periodic table. These relationships are extracted for main group elements by plots of the cohesive energy, describing the bonding energy of an atom in the 2D solid, versus bond length. To elucidate the intrinsic linear and nonlinear mechanical behavior we plot the Young’s modulus and ultimate strength as a function of bond length.

**Group III elemental monolayers**

The bonding behavior of elements varies drastically with the main group of the periodic table. The reason for this is that group II elements have two, group III elements three, group IV elements four, group V elements five, and group VI elements six valence electrons in the outer shell (see Fig. 2). It is well known that graphene with its four valence electrons per C atom forms the most stable covalent bonds in the plane, involving eight electrons in the closed outer shell of a noble gas configuration (‘octet rule’). A fundamental question is how the behavior of monolayers changes if the octet rule is not fulfilled and valence electrons are missing or additional electrons are available. For example, trivalent group III atoms cannot form a closed-shell structure by conventional bonding.

Since group III atoms have three electrons in their outer valence shell, they can form extended covalent networks by sp2-type hybridization, however, only with electron-deficient bonds, because the 2p orbital is empty. According to the octet rule for efficient bonding, the missing electron reduces the bond energy and thus the energy of cohesion. The realized bonding type can be elucidated by comparison with the conventional two-center, two-electron bonds of carbon (2c-2e): 1. A single chemical bond is formed when each of two atoms provides an electron, and both share the formed electron pair. 2. Electron configurations with eight atoms in the outer shell possess a lower energy and higher stability (‘octet rule’) due to the stable noble gas configuration. Group III atoms with three valence electrons cannot fulfill these conditions and therefore arrange as delocalized three-centered bonds or multi-centered bonds in σ and π frameworks, where electron pairs are shared at least among three or more atoms. This complex bonding behavior gives access to flexible chemistry with a wide variety of allotropes in 2D space. DFT calculations propose a series of dynamically stable 2D structures and a variety of 2D bonding types for borophene, aluminene, gallene, and indiene, the single layers of boron, aluminium, gallium, and indium.

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Based on the LCAO method, the electron configuration with promoted electrons can be described by three equivalent atomic orbitals, which form the molecular orbitals of a triangular motif, where three atoms share one pair of electrons. In this triangular boron motif, the sp2-like hybrids overlap, yielding one bonding and two anti-bonding orbitals (see Fig. 4). These orbitals broaden into bands by adding more triangles with increasing orbital overlap. Two of the three electrons are in the in-plane bonding orbital, but one electron is in an in-plane antibonding orbital and not in the remaining empty 2p-bonding orbital. Therefore, a planar triangular hybrid prefers to hybridize with a high-energy electron to a σ-π mixture of in-plane and out-of-plane states to gain further stability in a buckled configuration. The fact that a
For corrugated monolayers, polymeric give in Table 1 and the structural data of the two phases that have already been synthesized (see Fig. 5(d)).

Furthermore, complex geometrical structures consisting of several covalently bonded sublayers exist. This includes a borophene phase with the space group $8-Pmmm$, consisting of four atomic sublayers (see Fig. 5(d)). This hard but flexible material has a large cohesive energy, which is in line with the high values of the other polymorphs. Contrary to the failure mechanism of triangular borophene, which shows elastic instability in the zigzag direction and phonon instability in the stronger armchair direction, the $8-Pmmm$ structure fails by elastic instability.

In the search for other defect-free polymorphs of borophene, a thermodynamically stable puckered phase with an asymmetric centered-washboard (acw) structure of orthorhombic symmetry has been discovered that, unlike other boron sheets, is a semiconductor (centered because there is another atom at the center of the hexagons). According to MD simulations, this semiconducting polymorph is dynamically and thermodynamically stable up to about 800 K. Interestingly, the application of uniaxial or biaxial tensile strain closes the gap and transforms the system back to the metallic state, and the positive Poisson ratio becomes negative.

For aluminene, besides the planar honeycomb structure of aluminium, a graphene-like buckled, triangular, and four-layer $8-Pmmm$ structure have been proposed (see Table 1). Note that some of these phases have not yet been fully characterized and confirmed by other authors and some allotrop modifications may only be stable if the phonon dynamics is stabilized by the strain exerted by monolayer–substrate interaction. For the dynamically and thermodynamically stable four-layer network of $8-Pmmm$ aluminene, covalent $sp^3$-type bonding seems to be stronger than $sp^2$ bonding, according to an analysis of the electron localization function (ELF).

In its bulk chemical behavior, $\pi$-Ga is known as the only elemental ‘molecular metal’ that favors both covalently bonded dimers and weaker metallic bonding in the plane perpendicular to the average alignment of the Ga–Ga dimers. Monolayers of gallium have been investigated by several authors. A tight-binding model based on the combination of LCAO and $ab$ initio calculations led to the proposal of the existence of a graphene-like planar $a_{100}$gallenene. This phase can be derived from bulk $\pi$-Ga by extracting a monolayer of Ga from the 100 surface ($a_{100}$-Ga) and allowing relaxation (see Fig. 6(a)). This slightly distorted honeycomb network needs stabilization, for example by strain engineering, due to dynamical instability in its free-standing form. A second phase studied by the tight-binding model is the $b_{100}$gallenene monolayer, which resembles a zigzag rhombohedral lattice. This phase can be derived from bulk $\pi$-Ga by extracting a monolayer of Ga from the 010 surface ($b_{100}$-Ga) and allowing relaxation (see Fig. 6(b)). The puckering effect originates from mixed hybridization of the in-plane orbitals with the $p_z$ orbitals. The Ga–Ga bonds in $a_{100}$gallenene are covalent in nature, whereas both metallic and covalent interaction is observed in $b_{100}$gallenene. It is important to note that the gallene structures exhibit imaginary frequencies, however,
they can be stabilized upon application of biaxial strain or by adsorption on a surface. In fact, few-layer assemblies of atomically thin 2D gallenene (\(-\sim 4\) nm) have been successfully exfoliated from the molten phase of \(\alpha\)-gallium (\(-\sim 30^\circ\) C) on a silicon substrate, where the substrate stabilizes the dynamically unstable quasi-free-standing layer.\(^{33}\)

The investigation of 2D phases of the heavier homologues In and, especially, TI is still in its infancy. First principles DFT-PBE calculations indicate the existence of two dynamically stable phases of indiene, namely a planar honeycomb phase that behaves like a metal and a buckled graphene-like allotrope, which is an indirect semiconductor that transforms to a metal under compressive and tensile strain.\(^{36}\) In addition, a dynamically unstable puckered structure with a comparable cohesive energy has been described by the authors.

The structure, space group, cohesive energy, lattice constants, bond length, corrugation effect, and monolayer thickness of group III monolayers are presented in Table 1 for the known triangular, planar, \(8\text{-Pmmn}\), and puckered allotropes. To elucidate the nature of the bonding, we plot the cohesive energies as a function of the accurately known bond lengths (see Fig. 7(a)). The cohesive energy describes the interaction of an atom with its surrounding atoms of the 2D network and controls the mechanical stability of the whole network. In the case of corrugated monolayers, usually the largest bond length is employed, designating the bond with lowest critical fracture strength, and for the large differences of some puckered phases the mean value is used. For comparison, graphene is included, which has the largest cohesive energy and shortest bond of any uniform single-atom layer.\(^{37,38}\)

The boron allotropes assemble in a region of short bonds and consequently strong bonding. Note the striking similarity of cohesive energies for the diverse phases. To explain the unusual stability of planar and quasi-planar 2D boron
structures, the bonding concepts of aromaticity and anti-aromaticity have been invoked. The three heavier group III monolayers cluster in a region with significantly longer bonds and thus much lower cohesive energies. Surprisingly, the atom size, approximated by the van der Waals diameter of B (0.384 nm), Al (0.368 nm), Ga (0.374 nm), and In (0.386 nm), does not increase and the corrugation effects are comparable. It is the drastic extension of bond length observed from borophenes (0.16–0.19 nm) to aluminene phases (0.26–0.29 nm) that strongly reduces orbital overlap and leads to the large decrease of bond energy of the homologues of boron. The missing fourth valence electron seems to have a much stronger effect on the stability of the higher homologues than on borophenes.

The structure, Young’s modulus, Poisson’s ratio, ultimate strength, and ultimate strain of the studied phases of borophene, aluminene, gallenene, and indiene are collected in Table 2. The plot of the Young’s moduli and ultimate strengths as a function of the bond lengths offers an overview of the mechanical behavior of elemental group III monolayers (see Fig. 7(b)). Note the different scales of the left and right ordinates, which differ by a factor of ten and therefore give direct insight into the applicability of Griffith’s rule $\sigma = E/10$, where $\sigma$ is the ultimate strength and $E$ is the Young’s modulus. This rule connects the elastic stiffness with the about ten times smaller critical stress or ultimate strength. The intrinsic or ultimate strength is the maximum stress a perfect crystal can withstand at zero temperature, and thus is a measure of the strength of bonding at the ultimate strain. To illustrate the mechanical performance of group III monolayers, we included the outstanding mechanical properties of graphene with the highest Young’s modulus of 340 N m$^{-1}$, confirmed by experiment and theory, and the theoretical mean strength of 37 N m$^{-1}$ for uniaxial tension, in good agreement with 34 N m$^{-1}$ measured by biaxial indentation using AFM.

Note that in the armchair direction the Young’s modulus of triangular borophene is larger than the stiffness of graphene due to extreme directional bonding. In the zigzag direction, however, a significantly smaller stiffness is calculated and the whole structure becomes dynamically unstable. Altogether, the phases of borophene cover a huge range of stiffnesses and fracture strengths originating from the diversity of accessible 2D structures, which, however, possess comparable cohesive energies. The latter describes the mean reaction energy of the homologues of boron. The missing fourth valence electron seems to have a much stronger effect on the stability of the higher homologues than on borophenes.

Table 2 Structure, Young’s modulus, Poisson’s ratio, ultimate strength, and ultimate strain of group III monolayers

<table>
<thead>
<tr>
<th>Monolayer</th>
<th>Structure, space group</th>
<th>Young’s modulus (N m$^{-1}$) $E_{xx}$ $E_{yy}$</th>
<th>Poisson’s ratio $\nu_{xx}$ $\nu_{yy}$</th>
<th>Ultimate strength (N m$^{-1}$) $\sigma_{xx}$ $\sigma_{yy}$</th>
<th>Ultimate strain, $\epsilon_{xx}$ $\epsilon_{yy}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borophene</td>
<td>Triangular, $\delta_b$</td>
<td>382, 163</td>
<td>$-0.07^{25}$</td>
<td>22.8, 14.0</td>
<td>$0.11, 0.15^{25}$</td>
</tr>
<tr>
<td>Borophene</td>
<td>Planar, $h_{12}$</td>
<td>399, 163</td>
<td>$-0.23, 0.19^{19}$</td>
<td>20.9, 12.2</td>
<td>$0.087, 0.14^{19}$</td>
</tr>
<tr>
<td>Borophene</td>
<td>Planar, $\delta_3$</td>
<td>208, 205</td>
<td>$0.15, 0.17^{19}$</td>
<td>16.4, 15.4</td>
<td>$0.12, 0.11^{19}$</td>
</tr>
<tr>
<td>Borophene</td>
<td>Planar, $\delta_5$</td>
<td>253, 208</td>
<td>$0.11, 0.12^{19}$</td>
<td>19.9, 20.2</td>
<td>$0.21, 0.16^{19}$</td>
</tr>
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<td>253, 208</td>
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<td>Aluminene</td>
<td>Triangular</td>
<td>31</td>
<td>0.54</td>
<td>21.6, 27.8</td>
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</tr>
<tr>
<td>Gallenene</td>
<td>Triangular</td>
<td>37</td>
<td>0.49</td>
<td>11</td>
<td>$0.30^{14}$</td>
</tr>
<tr>
<td>Indiene</td>
<td>Planar</td>
<td>28</td>
<td>0.085</td>
<td>0.30</td>
<td>$0.30^{14}$</td>
</tr>
<tr>
<td>Indiene</td>
<td>Triangular</td>
<td>25</td>
<td>0.37</td>
<td>0.28, 0.38</td>
<td>$0.30^{14}$</td>
</tr>
</tbody>
</table>

![Fig. 6](image-url) (a) Honeycomb graphene-like lattice of gallenene obtained by cleaving bulk $\alpha$-Ga along the (100) direction after relaxation (a$_{100}$-Ga). (b) Distorted rhombic lattice of gallenene obtained by cleaving bulk $\alpha$-Ga along the (010) direction after relaxation (b$_{010}$-Ga). The dashed rectangle and square show the unit cells.
cohesive energy by a factor of about three, the stiffness and strength of all phases decrease drastically by a factor of about ten. This illustrates the severe deterioration of mechanical performance within group III elements, in line with an increase of bond length by a factor of approximately two (see Fig. 7(b)). Thus, besides the higher reactivity, problems with the mechanical in-plane rigidity and strength may appear for the heavier homologues. Amazingly, the strongly anisotropic triangular phase has a negative Poisson ratio (see Table 2). Instead of shrinking along the out-of-plane direction, the ridge-to-ridge distance increases upon application of in-plane strain, due to a much smaller in-plane modulus across the ridges than along the ridges.39 Delocalized multi-center bonding enables structural fluxionality that causes structural phase transitions under tension, for example by inducing atomic rearrangements by bond rotation at small strains. As can be seen in Table 2, the ultimate strains increase substantially, namely by a factor of about three, from borophene to indiene. Surprisingly, \( \beta_{12} \) borophene exhibits a strain-induced phase transition by atomic rearrangement via bond rotation at a strain of \(~0.12\), and then resists loading up to a strain of 0.36.39 A high mechanical toughness with ultimate strains in the range of the latter value is reported for indiene.42

The mechanical properties of few-layer systems (1–4 layers) of metallic triangular borophenes without holes have been studied theoretically.43 The interlayer separations of 0.31 nm (AA stacking) and 0.34 nm (AB stacking) are much smaller than the estimated layer thickness of buckled borophene, taking the corrugation effect into account.43 This points to strong interlayer interaction between the metallic layers. Calculations of the metallic bilayer structure of planar hexagonal aluminene yielded an interlayer separation of 0.270 nm, which is also much smaller than the van der Waals diameter. The small spacing allows interlayer electron transfer, as confirmed by a huge interlayer interaction energy of \(-519\) meV per atom.44 Therefore, aluminene has been recommended as a promising material for electric charge storage and as a nanocapacitor.

In 3D structures the metalloid boron shows neither metallic nor non-metallic behavior, whereas metallic properties are found in its 2D structures. Despite the energetic and dynamic stability suggested by DFT calculations for several allotropes of group-III monolayers, the thermodynamic stability of metallic monolayers remains a fundamental problem. Owing to the absence of electrons occupying \( \pi \) bonds, the stability is significantly reduced. However, close-packed triangular and planar polymorphs with different vacancy patterns have been grown on Ag[111] substrates and identified by STM.22,26 A recent progress report covers the experimental synthesis of metallic and also semiconducting borophene sheets, e.g., on metal substrates by CVD and MBE, and discusses relevant stability issues, which are a prerequisite for practical applications in nanoelectronics and optoelectronics.45

**Group II–IV and III–IV monolayers**

The distinctive nature of bonding of several group II–IV and III–IV monolayers has been studied theoretically, while experimental verification is still missing. Remarkably, these monolayers show the rule-breaking phenomenon of quasi-planar hypercoordinate chemistry. This is of enormous significance for the development of 2D materials due to the enforced restriction of covalent bonding to two dimensions. Contrary to conventional 3D tetrahedral and planar tricoordinate \( sp^3 \) bonding of carbon, binary monolayers with Be, Mg, Ca, B, and Al atoms exhibit quasi-planar tetracoordinate (ptc), quasi-planar pentacoordinate (ppC), and quasi-planar hexacoordinate (phC) moieties, deviating from carbon’s established tetrahedral bonding and its maximum coordination number of four.46 Reasons for this unusual coordination in the plane are delocalization of electrons of the carbon \( 2p_z \) orbitals by efficient \( \pi \)-acceptors and the donation of \( \sigma \) electrons to electron-deficient bonding. Moreover, electron transfer is promoted in these compounds by different electronegativities, leading to ionic contributions. The increase of electron density at the C (Si) moiety enforces planarity of the \( \sigma \) bonds. In isolated molecular species besides electronic

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**Fig. 7** (a) Plot of cohesive energy versus bond length for group III elemental monolayers. (b) Plot of Young’s modulus and ultimate strength versus bond length of group III elemental monolayers.
stabilization of planar hypercoordination mechanical effects such as steric constraints have been studied intensively by theory and by experiments. 47

The peculiar molecular motifs with unconventional bonding may serve as building blocks for an extension to infinite monolayers (see Fig. 8). To incorporate these generally unstable entities in a monolayer, mechanical interconnects such as non-hexagonal rings can be used to stabilize hypercoordinate bonding in 2D space. This additional structural degree of freedom opens the door to novel although complex structures with unforeseen physico-chemical properties, as well as promising applications. It is well known that elements with multicenter bonding such as boron allow a variety of strong bonding types and various configurations with delocalized charge distribution. The nature of interlinks combining the individual hypercoordinate motifs plays a fundamental role in the stabilization of infinite layers and in the realization of distinct monolayer properties.

The necessary information on charge distribution and type of bonding in the extended systems is mainly based on two methods. The interpretation of charge distributions in terms of electron lone pairs, two-center and multicenter bonding are usually examined by the solid state adaptive natural density partitioning (SSadNDP) method. 48 The second method delivering insight into the electron distribution and nature of bonding is ELF. 49 The key ELF values of approximately 0, 0.5, and 1 refer to extremely low electron density, fully delocalized electrons, and extremely high density of electrons, respectively.

The theoretical strategies employed to find stable hypercoordinated 2D arrangements of atoms are bottom-up approaches, maintaining the number of valence electrons by isoelectronic substitution, and direct global minimum search. Clearly, 2D materials with the lowest energy configuration of the global minimum on the potential energy surface (PES) have a high chance to be realized experimentally. Quite often, however, additional configurations with a local minimum and quite similar cohesive energies exist. If these monolayers are thermodynamically and dynamically stable, experimental synthesis may be possible, especially if further stabilization takes place by adsorption on a suitable surface.

Global structure search resulted in a minimum energy monolayer of BeC with a complicated structure, containing rings with three, six, and eight atoms. 50 In this planar low symmetry structure with ptC moieties the carbon atoms bind four Be atoms. The perfect planarity has been explained by the small-ring mechanical strain and π electron delocalization. Table 3 presents the structure, cohesive energy, lattice constants, bond lengths, Poisson’s ratios, and in-plane mechanical moduli of all hypercoordinated compounds considered here. Furthermore, the table gives the sum of the van der Waals radii (d_v) of the two constituents and in case of corrugation the van der Waals diameter plus buckling effect (d_v+C) as an estimate of the layer thickness. 45,46 Besides BeC, based on DFT calculations and particle swarm optimization (PSO), global minimum search resulted in quasi-planar phC moieties incorporated in a weakly buckled monolayer of Be_2C. 51,52 Each C atom binds to six Be atoms, while each Be atom is connected to three C atoms and three Be atoms (see Fig. 9(a)). Symmetric buckling of two adjacent Be atoms of 0.046 nm out of the central C atom plane reduces repulsion between neighboring cations. 52 The thermodynamic, dynamic, and thermal stability up to 1500 K have been confirmed for Be_2C.

The computationally designed Be_2C monolayer contains quasi-planar pentacoordinate carbon motifs (quasi-ppC) in a global minimum structure. 53 Remarkably, the Be_2C monolayer contains no classical lone pairs or localized conventional 2c-2e bonds, but only three-, four, and six-center bonds. 46 The large buckling effect of 0.214 nm reduces the repulsive interaction between Be atoms. The negative cohesive energy reveals thermodynamic stability, the positive phonon modes dynamic stability, and the high melting point of >1500 K thermal stability. The unit cell contains eight Be_2C units with 72 electrons. The Be_2C monolayer is a gapless semiconductor with a Dirac-like point in the band structure.

DFT calculations, including electronic structure calculations, revealed that Mg_2C monolayers with quasi-planar hexacoordinate C (phC) and hexacoordinate Mg represent a global minimum structure. 54,55 The corrugation of the puckered hinge structure is 0.179 nm. 54 Owing to the larger Mg atom the bond lengths increase and the cohesive energy decreases to −3.43 eV per atom. 54 The monolayer is thermodynamically, dynamically, and, as MD simulations indicate, thermally stable up to 900 K. The strain-tunable band can be tuned from its metallic equilibrium state to a gapless semimetal and narrow semiconductor by modest biaxial tensile strain. 54 The monolayers possess the rare intrinsic in-plane negative Poisson’s ratio, where responsive strain is observed in the armchair direction if strain is applied in the zigzag direction.

A structure with quasi-planar hexacoordinate C (phC), as already described for Be_2C and Mg_2C, is also formed by Ca_2C, however, with a larger corrugation of 0.234 nm. 56 This monolayer is dynamically, mechanically, and thermally stable up to 700 K. 56 According to the long Ca–Ca bonds of 0.326 nm the low cohesive energy and in-plane stiffness is expected. The 2D network shows only small deviations from isotropic mechanical behavior and belongs to the family of MXenes that has received enormous attention for potential use in supercapacitors and batteries. 56

Inspired by the bonding of the molecular species CaSi_2 with a ppSi center as building block, following the 18-electron rule, a CaSi monolayer has been designed by DFT computations (see Fig. 9(b)). 57 Stabilization occurs by delocalization of Si 3p, 3d, 4s orbitals and π bonding.
AMM and thermally stable up to about 2000 K.59 Another proposed metal network forms by strong bonds and dynamically, and thermally stable up to about 1200 K.57

For Be2C first-principles lattice dynamics and electron-phonon coupling calculations predicted a monolayer consisting of a mosaic of hexagons and rhombuses with quasi-ptC moieties, ensuring a preferred 18 valence electron count (see Fig. 9(c)).58 The C layer and B layer are separated by only 0.0032 nm (∼0.0085 nm).58 Global minimum search on 2D boron-carbon compounds revealed that this thermodynamically and dynamically stable structure has not the lowest-energy configuration, however, a comparable stability.59,60 The possibly metallic network is formed by strong bonds and is dynamically and thermally stable up to about 2000 K.59 Another proposed boron carbide is the B4C3 monolayer derived from quasi-planar hexacoordinated B4C3 clusters61 with tetracoordinate carbon (quasi-ptC).62 This global minimum structure was obtained by DFT computations and swarm-intelligence structure-searching methods. Since the central B atom of each B4C3 motif is situated about 0.03 nm above the hexagonal B4C3 ring, the monolayer is slightly buckled. The strongly bonded thermodynamically stable monolayer is dynamically and thermally stable up to 1600 K.

The Al2C monolayer can be derived from the planar molecular species C3Al2− and follows the already described structure of B2C with tetracoordinate carbon (ptC) and tricoordinate Al atoms with a global minimum structure.63 Better σ-donation due to the larger electronegativity difference between C and Al (∼1.0) than between C and B (∼0.5) completely avoids buckling by delocalized electrons. Note that the size of Al atoms implies much larger bond lengths, resulting in a moderate cohesive energy.64 This semiconducting monolayer is thermodynamically and dynamically stable, and maintains its structural integrity up to 1500 K.

The plot in Fig. 10(a) displays the cohesive binding energies versus the range of bond lengths found in the nonuniform monolayer structures of BeC50 Be2C51,52 Be5C2,53 Mg2C54,55

<table>
<thead>
<tr>
<th>Monolayer</th>
<th>Planar structure, space group</th>
<th>Cohesive energy, E\text{c}(eV per atom)</th>
<th>Lattice constants a, b (nm)</th>
<th>Bond lengths d_{C,X,Si,X}(nm)</th>
<th>d_{B,Al,Y,Z}(nm)</th>
<th>Buckling distance Δz (nm)</th>
<th>van der Waals diameter d_{vW}(nm)</th>
<th>Poisson’s ratio ν_{ac,ab}</th>
<th>Young’s modulus E_{ac,ab}(N m\text{−1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeC</td>
<td>ptC, AMM250</td>
<td>−6.6550</td>
<td>a = b = 0.43550</td>
<td>0.138, 0.16650</td>
<td>0\text{−}50</td>
<td>0.32125</td>
<td>0.32324 0.415</td>
<td>14650</td>
<td></td>
</tr>
<tr>
<td>Be2C</td>
<td>phC, P3m1351</td>
<td>−4.8652</td>
<td>a = b = 0.29952</td>
<td>0.173, 0.19852</td>
<td>0.09252</td>
<td>0.32324 0.537</td>
<td>−0.041, −0.1653</td>
<td>32.7, 13053</td>
<td></td>
</tr>
<tr>
<td>Be4C6</td>
<td>ppC</td>
<td>−4.5853</td>
<td>0.892, 0.92153</td>
<td>0.170, 0.23953</td>
<td>0.21453</td>
<td>0.34325 0.522</td>
<td>0.03, −0.02535</td>
<td>59.6, 56855</td>
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<tr>
<td>Mg2C</td>
<td>phC, P3m1355</td>
<td>−3.4354</td>
<td>0.354, 0.33555</td>
<td>0.223, 0.27155</td>
<td>0.17954</td>
<td>0.40125 0.635</td>
<td>0.448, 0.44856</td>
<td>72.9, 32.56</td>
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</tr>
<tr>
<td>CaC</td>
<td>phC, P3m11</td>
<td>−3.0056</td>
<td>0.394, 0.3656</td>
<td>0.256, 0.3256</td>
<td>0.23456</td>
<td>0.44125 0.517</td>
<td>−0.15, −0.1657</td>
<td>21.8, 24.657</td>
<td></td>
</tr>
<tr>
<td>CaSi</td>
<td>ppsi</td>
<td>−3.0756</td>
<td>0.933, 0.68657</td>
<td>0.297, 0.39857</td>
<td>0.07657</td>
<td>0.36225 0.371</td>
<td>0.148, 0.12359</td>
<td>237, 19759</td>
<td></td>
</tr>
<tr>
<td>B2C</td>
<td>ptC, Pmma70</td>
<td>−6.4759</td>
<td>0.256, 0.34559</td>
<td>0.156, 0.16959</td>
<td>∼0.008559</td>
<td>0.384, 0.414</td>
<td>0.35425 0.114, 0.10464</td>
<td>252, 28762</td>
<td></td>
</tr>
</tbody>
</table>
| Al2C      | ptC                           | −4.4963                                | 0.304, 0.5061               | 0.196, 0.26063             | 0\text{−}63     | 0.35425 0.114, 0.10464 | 252, 28762       |}

Fig. 9 (a) Top and side view of the Be2C monolayer. The black hexagon shows the quasi-phC motif and the red dashed rhombus displays the unit cell. Braun and yellow balls represent C and Be atoms, respectively, a and b are the lattice vectors, and Δ z is the buckling effect. (b) Top and side view of the CaSi monolayer, containing the quasi-ppSi motif as indicated by the black circle. The yellow and blue balls present the Si and Ca atoms, respectively. The red dashed lines label the unit cell. (c) Top and side view of the B2C monolayer with quasi-ptC motif. Braun and yellow balls are the C and B atoms, respectively. The black rectangular box shows the quasi-ptC motif.
The distinctive inverse dependence of the cohesive energies on the range of calculated bond lengths is consistent with the prediction of tight-binding theory. Due to the nonuniform structure the cohesive energy represents a mean value of individual bond energies, which is plotted versus the resulting spread of bond lengths. Notably, the mean values exhibit a characteristic inverse behavior comparable to that of the mean values of bond lengths realized in group II–IV and III–IV monolayers. For comparison, the values of planar binary and buckled elemental group–IV monolayers are displayed. Moreover, the Young’s moduli of honeycomb graphene and BC₃ monolayers are displayed.

The plot, however, demonstrates surprisingly strong bonding of quasi-planar hypercoordinate structures with their unconventional bonding types. A comparison of planar tetracoordinated structures with the strong 3D tetragonal structure of diamond with a cohesive energy of −7.71 eV per atom (exp. −7.54 eV per atom) and bond length of 0.154 nm supports the statement. Obviously, not only stabilization of the molecular moieties achieved by delocalization of lone-pair electrons combined with σ-accepting and σ-donating substituents is efficient but also the whole 2D arrangement by inter-motif bonding.

The introduction of boron atoms in BC₃ monolayers generates B–C bonds of 0.156 nm length, whereas the C–C bonds of the carbon hexagons are still ~0.142 nm. The cohesive energy of graphene of ~7.86 eV per atom (exp. 7.54 eV per atom) decreases to ~6.86 eV per atom in BC₃. The reasons for the decay are the missing valence electrons and the larger atom size of boron. Increasing the boron content, e.g., in hypercoordinated B₃C₄ and B₄C₃ monolayers, reduces the cohesive energy only slightly to ~6.56 and ~6.47 eV per atom, respectively. While B₃C contains two different B–C bonds (0.153 nm and 0.159 nm) and one B–B bond (0.169 nm), B₄C has one B–C bond (0.156 nm) and one B–B bond (0.169 nm). These observations imply efficient covalent bonding not only within the planar moieties.

To benchmark the bonding–structure relationships of hypercoordinated monolayers with those of the planar sp²-bonded binary group IV carbides SiC, GeC, and SnC, as well as the weakly buckled hexagonal group–IV elements Si, Ge, Sn, and Pb, Fig. 10(a) gives a direct comparison that provides

Fig. 10 (a) Plot of cohesive energies versus the range of bond lengths realized in group II–IV and III–IV monolayers. For comparison, the dependence of planar binary and buckled elemental group–IV monolayers are displayed. Furthermore, the binding energy and bond lengths of honeycomb graphene and BC₃ monolayers are included. (b) Plot of in-plane stiffness of group II–IV and III–IV monolayers versus bond lengths. For comparison, the values of planar binary and buckled elemental group–IV monolayers are displayed. Moreover, the Young’s moduli of honeycomb graphene and BC₃ monolayers are displayed.
additional insight into the characteristics of hypercoordination. It is well known that the group-IV compounds follow the established octet rule. The used cohesive energy of SiC (−5.97 eV per atom) has been calculated, while those of GeC (−5.57 eV per atom) and SnC (−4.54 eV per atom) are based on the correlation with other group-IV and binary group IV data, because for the two latter compounds much larger and lower values can be found in the literature, as discussed below. As visible in Fig. 10(a), the planar sp²-bonded carbides and weakly buckled group-IV elements show a related inverse behavior, as observed for the mean bond lengths of the hypercoordinated compounds. Only the heaviest elements Sn and Pb show a tendency to lower cohesive energies. Obviously, quasi-planar hypercoordinated motifs can be effectively incorporated into monolayer structures by efficiently coordinating patterns between the motifs. This conclusion is supported by a comparison of hexagonal siligaphene SiC2 with a binding energy of −6.46 eV per atom⁶⁸ and silaphene SiC₂ with tetracoordinate silicon (pSi) motifs at −6.04 eV per atom, containing rings with four and six atoms.⁶⁹ Of course, when the interconnects do not reflect the steric requirements of the motifs with their specified shapes, the overall stability of the whole network will decrease.

The dependence of the Young's moduli or in-plane stiffnesses on bond lengths is plotted in Fig. 10(b) for the quasi-planar hypercoordinated monolayers (see Table 3). For comparison, the stiffnesses of the hexagonal monolayers of graphene, BC₃, binary group IV, and elemental group-IV monolayers are included. By excepting the BeC monolayer, all hypercoordinated monolayers follow roughly the inverse dependence of the stiffness of group-IV monolayers if the range of bond lengths found for each compound is considered. The in-plane stiffness of 146 N m⁻¹ presented for BeC seems not to be consistent with the much lower values, which can be derived from the given elastic constants, nor with the short chemical bonds presented in the publication.⁷⁴ In any case, the established correlation suggests a much larger in-plane stiffness.

It is important to note the enormous sensitivity of in-plane stiffness on bond length. The stiffness decreases drastically by a factor of about ten for a change of the mean bond length by less than a factor of two. One of the main reasons for this drastic decay is the reduction of orbital overlap by the increasing size of atoms that leads to the loss of planarity in group-IV monolayers and the hypercoordinated compounds. The existence of longer interconnecting bonds between the motifs in the nonuniform 2D networks has an additional influence on the in-plane moduli. In many cases the weaker interconnects reduce the overall mechanical performance to some extent, however, not drastically for the linear in-plane stiffness.

Unfortunately, information on nonlinear mechanical properties such as fracture strength and ultimate strain of monolayers with hypercoordinated motifs is widely missing. This is a fundamental issue, since nonuniform networks with short and long bonds are prone to easier bond rupture. While the linear mechanical behavior of hypercoordinated compounds seems to follow broadly that of regular bonded monolayers, nonlinear properties, such as the ultimate strength, may respond sensitively on the nonuniformity. Since local bond rupture affects the strength of the whole network, the strongest bonds with their weaker bond energy will control the overall stability.

### Group IV monolayers

**Elemental monolayers.** Carbon atoms have the ground-state electronic configuration (1s²2s²2pₓ²2pᵧ²2pₛ²) with four electrons in their outer valence shell. In the promoted state they can not only form four σ bonds by sp³ hybridization but also three planar...
σ bonds by sp^3 hybridization and an out-of-plane π bond by interaction of the remaining 2p_z orbitals. The tetragonal sp^3 hybrids create ideal bonding strength in 3D space (diamond), while the sp^2 hybrids allow the strongest bonding in the plane. The planar hexagonal structure, formed by overlap of the three 2sp_z orbitals and the 2p_z orbital with those of three neighbors, consists of three strong σ bonds and one π bond and is called graphene. In this configuration, all in-plane bonding states are full and the antibonding states above the Fermi level are empty. Fig. 11 presents two schemes, one with the electron configuration and one with the sp^2 and π orbitals of the C–C double bond. This double bond has the shortest bond length and largest bond energy with the highest density of bonding electrons between the two nuclei in a hexagonal network. It is noteworthy that the honeycomb structure used by bees is the optimum way to divide a surface into equal areas with the smallest total perimeter. Interestingly, graphene is labeled as a zero-gap semiconductor (‘semimetal’), because its π valence and π* conduction bands contact at the Dirac points at the Fermi level.70,71 To open a band gap, the in-plane lattice symmetry must be broken. Mechanical deformation is an appealing means to manipulate the electronic structure by strain. However, the strain necessary for opening a sizable band gap in graphene is still controversial.71

Since Si, Ge, Sn, and Pb belong to the same group as carbon, they have four valence electrons with the electron configuration (ns^2 np^2). However, as known from chemical experience, these elements prefer sp^3 hybridization with tetrahedrally bonded atoms. According to DFT calculations, only buckled monolayers are dynamically stable, because buckling allows in this case better interaction of p_z–p_z orbitals.72 The main reason for buckling is the increasing atom size, which destabilizes π-bonding and stabilizes σ-backbonds. Fig. 12(a) displays the top and side views and Fig. 12(b) a perspective view of a buckled network. For example, the standard van der Waals diameter increases substantially from d_w = 0.34 nm to 0.420 nm from carbon to silicon.24 Due to the larger distance between Si atoms, interaction of the p_z orbitals is diminished and their mixing with s orbitals creates partial sp^3 character, which enhances overlap and thus stability. The smaller difference between 3s and 3p sublevels in comparison to graphene favors this mixing process. Note that in stable low-buckled silicene, σ–π orbital mixing is closer to sp^2 than to sp^3 hybridization with a small buckling effect of 0.041 nm.73

For the larger Ge atoms, π bonding is further weakened and the contribution of sp^3 orbitals and thus buckling increases. This change in the bonding character is clearly visible in the bond angle, which decreases from 120° in graphene to 116.9° in silicene, 112.6° in germanene, and 110.4° in stanene, which is near the bond angle of sp^3 hybridization of 109.5°.73 With the further increasing atom size of Sn and Pb, interaction between π orbitals is further reduced and leads to dominant sp^3 hybridization in the mixed sp^2–sp^3 hybrids of plumbene.74 Larger buckling allows a better overlap between σ and π orbitals and stabilizes the network, whereas s–p mixing reduces with increasing atomic number, since in higher homologues s orbitals lower their energy with respect to p orbitals.

The relevant structural data of graphene,74,75–79 silicene,74,75,79,80–82 germanene,73,75,83–85 stanene,73,75,85,84,86,87 and plumbene74,88–90 are presented in Table 4. In Fig. 13(a) we characterize the bonding behavior of the elemental group IV monolayers by plotting the cohesive energy as a function of the bond length. Graphene is the champion, with the shortest bond and the largest cohesive energy (larger than diamond) and largest dissociation energy of a single C–C bond. A comparison of the bond lengths of graphene (0.142 nm) and diamond (0.154 nm) underlines the high stability of planar sp^2 hybridization. However, due to the much longer bonds of the elemental 2D networks of Si, Ge, Sn, and Pb, the cohesive energy decreases dramatically. Note that bonding power is now no longer completely confined to the plane. Remarkably, the bond length of mixed hybridization of silicene, at 0.228 nm, is much larger than that of graphene but still slightly smaller than the bond length of the 3D Si diamond structure (0.235 nm). Continuing down the group, the further increasing influence of sp^3 hybrids causes the bond length of germanene to increase to 0.244 nm, agreeing with that of bulk
germanium of 0.245 nm. The large increase of bond length from graphene to silicene causes a drastic reduction of the cohesive energy from $-7.85$ to $-3.91$ eV per atom.\(^7\) This effect slows down for the heavier elements, which show an asymptotic inverse dependence of cohesive energy with modest changes of binding energy at longer bond lengths, similar to the Young's modulus and strength (see Fig. 13(b)).

The energy level scheme presented in Fig. 14 illustrates the transition of atomic s and p orbitals to atomic hybrids and bonding orbitals that are responsible for the formation of bands and eventually a band gap in an extended covalently bonded 2D network. Of interest is the bonding–antibonding splitting 2B that results from the energetic stabilization by the bonding orbitals and determines the binding energy.\(^1\) In nonpolar materials such as elemental monolayers, splitting B is identical with the strength of orbital overlap $V$, which varies strongly with the bond length as $V \sim 1/d^2$. Consequently, the energy of covalent bonding declines strongly with the inversely related bond length. In Fig. 13(a) this widely unknown dependence is shown for the cohesive energy of the elemental and binary group IV monolayers.

The mechanical properties of graphene,\(^3\) silicene,\(^9\) germanene,\(^8\) stanene,\(^0\) and plumbene\(^7\) are displayed in Table 5. The plot of the Young's moduli and ultimate strengths as a function of bond length offers insight into the linear and nonlinear mechanical behavior of the elemental group IV monolayers (see Fig. 13(b)). This plot reveals a drastic change of mechanical performance from graphene to silicene. The enormous loss of bonding energy from C to Si causes a large decrease of both intrinsic stiffness and ultimate strength, which controls failure. The heavier homologues of Si with their minor increase of atom size experience a much smaller weakening of stiffness and strength, mostly following Griffith's rule. While graphene is the stiffest 2D material, surviving the largest critical stress, these properties weaken enormously down the group, for instance by a factor of about five for buckled silicene. Since mechanical performance declines further from silicene to plumbene, mechanical stability becomes a crucial issue for the heaviest compounds. For example, low stiffness values give rise to rippling and wrinkling of the monolayer structure, with detrimental influence on the electronic properties, and permits easy incorporation of impurities.

Graphene is the building block for forming bilayers and few-layer assemblies with new properties up to about ten layers, where the electronic structure approaches the 3D limit of graphite.\(^9\) The interlayer interaction energy (sometimes called exfoliation energy) and the stacking order are crucial quantities controlling the stability and the chemical and physical properties of multilayers. The reported interlayer binding energies vary in a large range between $-22$ and $-85$ meV per atom for graphite\(^9\) and between $-18$ and $-70$ meV per atom for AB-stacked bilayers of graphene.\(^0\) This large range of values is due to the approximations used in the theoretical treatment of soft layered materials with weak interlayer and strong in-plane forces. Several recent publications have confirmed the early results of a low interlayer interaction energy of about $-25$ meV per atom\(^0\) and interlayer spacing of 0.335 nm\(^7\) for graphene.
Table 5  Structure, Young’s modulus, Poisson’s ratio, ultimate strength, ultimate strain, and method employed to study elemental and binary group IV monolayers

<table>
<thead>
<tr>
<th>Monolayer</th>
<th>Structure</th>
<th>Young’s modulus $E_{ac}, E_{zz}$ (N m$^{-1}$)</th>
<th>Poisson’s ratio $\nu_{ac}, \nu_{zz}$</th>
<th>Ultimate strength $\sigma_{ac}, \sigma_{zz}$ (N m$^{-2}$)</th>
<th>Ultimate strain $\varepsilon_{ac}, \varepsilon_{zz}$</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>Planar</td>
<td>333$^{97}$</td>
<td>0.14-0.24$^{91}$</td>
<td>40, 37$^{92}$</td>
<td>0.31$^{93}$</td>
<td>Ab initio</td>
</tr>
<tr>
<td>SiGe</td>
<td>Buckled</td>
<td>144$^{179}$</td>
<td>0.28-0.49$^{179}$</td>
<td>12.7, 12.8$^{118}$</td>
<td>0.17, 0.21$^{118}$</td>
<td>DFT-PBE</td>
</tr>
<tr>
<td>SnC</td>
<td>Planar</td>
<td>160$^{114}$</td>
<td>0.31$^{114}$</td>
<td>16.5, 16.7$^{114}$</td>
<td>0.20, 0.25$^{114}$</td>
<td>DFT-PBE</td>
</tr>
<tr>
<td>SiGe</td>
<td>Buckled</td>
<td>40, 52$^{128}$</td>
<td>0.37, 0.35$^{128}$</td>
<td>12.6, 12.8$^{118}$</td>
<td>0.17, 0.21$^{118}$</td>
<td>DFT-PBE</td>
</tr>
<tr>
<td>SnGe</td>
<td>Buckled</td>
<td>35, 51$^{128}$</td>
<td>0.38, 0.36$^{128}$</td>
<td>12.6, 12.8$^{118}$</td>
<td>0.17, 0.21$^{118}$</td>
<td>DFT-PBE</td>
</tr>
</tbody>
</table>

In silicene partial sp$^3$-type bonding intensifies the interlayer interaction between bilayers and multilayers and thus reduces the interlayer separation. The calculated interlayer spacings of bilayers with AA and AB stacking are 0.246 nm and 0.253 nm, respectively (see Fig. 15).$^{83}$ For free-standing few-layer sheets, interlayer spacings of 0.34 nm were measured by HRTEM and SAED in layered silicene sheets.$^{82}$ Calculations of interlayer separations point to configurations where the spacing of multilayers decreases, because the still existing weak in-plane π bonds are replaced by covalent-type interlayer bonds to further minimize the total energy.$^{102}$ Similarly, it could be shown theoretically that under external pressure the interlayer spacing of buckled silicene, germanene, and stanene bilayers approaches the intra-layer bond length with a flat honeycomb network.$^{83}$ Interestingly, the dynamically stable and chemically inert flat phases of bilayer germanene and stanene are topologically nontrivial.$^{83}$

In germanene an even larger contribution of sp$^3$ orbitals to bonding intensifies the interlayer interaction in bi- and multi-layers.

Interestingly, under structural optimization the buckled phase converts into the most stable flat bilayer arrangement, with AA stacking, a larger lattice constant, and the same in-plane bond length and interlayer spacing (0.254 nm and 0.255 nm, respectively$^{83,103}$). This small interlayer spacing is consistent with the large interlayer interaction energy of ~300 meV per atom.$^{103}$ In the flat configuration of bilayer germanene the topological trivial state can be tuned into a 2D topological insulator (TI) by external tensile strain of 6% (Si: > 8%).$^{83}$ Such a strong interlayer interaction with sp$^3$-like inter-layer bonding has also been reported for plumbene.$^{104}$

In general, the synthesis of 2D materials with the desired perfect structure, domain size, scalability, growth rate, and versatile substrate material is the main challenge in fabricating 2D materials for future applications. The controlled growth of high-quality monolayers and few-layer assemblies of graphene is an active field. An up-to-date overview describes the progress made in the synthesis of graphene and graphene-based materials and specifically covers the practical aspects of this topic.$^{105}$ A recent report reveals the enormous progress made in growing large-area (> cm$^2$) adlayer-free homogeneous graphene monolayers by using as-received Cu substrates and common chemical vapor deposition (CVD) methods to achieve controlled layer-by-layer growth.$^{106}$

The preparation of monolayers inevitably leads to defects. Various types of defects have been extensively studied for graphene and are generally categorized as corrugations such as ripples, topological effects such as dislocations or grain boundaries, vacancies, adatoms, and sp$^3$-defects.$^{98}$ An introduction of disorder such as dislocation alters the bond length and causes re-hybridization of σ and π orbitals and thus may change electronic properties such as the band structure. Point defects such as vacancies function as scattering center for electron waves and reduce the conductivity. While a single vacancy has a negligible effect on the elastic modulus, it may decrease substantially with increasing density of vacancies.
The ultimate strength is extremely sensitive to vacancies especially if their separation is small. In polycrystalline graphene the decrease of the grain size from ~10 nm to ~2.5 nm leads to a reduction of both Young’s modulus and strength, whereas a high density of sp²-defects seems to cause only a minor degradation of the elastic performance.⁹⁸

The interest in silicene and the heavier elemental group IV monolayers termed Xenes (silicene, germanene, stanene, and plumbene) originates from unique solid-state properties. With increasing sp³ contribution in mixed sp²–sp³ hybridization of heavier Xenes a topologically nontrivial electronic structure develops, originating from larger spin–orbit coupling (SOC). This results in the quantum spin Hall (QSH) effect that is a 2D TI state.⁸³,¹⁰⁷ The QSH systems have gapless edge or surface states on the boundary that are topologically protected and immune to geometric perturbations, whereas the bulk is insulating. Since no layered bulk materials exist in nature for silicene (‘silicite’) and its heavier homologues, it is necessary to synthesize these compounds either by exfoliation using a suitable synthetic compound or by CVD or MBE.¹⁰⁷ The synthesis of nanosheets of few-layer silicene has been achieved by liquid oxidation and exfoliation of CaSi₂.⁸² A problem originating from mixed sp²–sp³ hybridization states is their reactivity and low environmental stability. Consequently, in practical applications silicene and homologues may require passivation by functionalization or encapsulation.

The synthesis of germanene is possible either chemically (CVD) or by epitaxial growth (MBE) on suitable supporting substrates. As for silicene, the existence of an isolated sheet of germanene has not yet been confirmed. A significant step forward in the direction of 2D topological materials with nontrivial features, including quantum spin/anomalous Hall behavior of elemental and binary group IV monolayers, despite the two constituents. The assumption of similar bonding influences of the two constituents are different. The van der Waals diameter increases from 0.340 nm to 0.420, 0.422, and 0.434 nm, and the electronegativity changes from 2.55 to 1.9, 2.01, and 1.96 for carbon, silicon, germanium, and tin, respectively. Thus, charge transfer from the higher homologues to the C atom with the highest electronegativity leads to an asymmetric distribution of charge density.¹¹² The resulting polarization has a marginal influence on covalent bonding. Evidently, introduction of larger atoms into a 2D network stretches the bonds and decreases the bond energy.

Without an element of the second period of the periodic table, the three mixed compounds SiGe, SnSi, and SnGe considered here possess buckled phases. Owing to the increased atom size, the s, pₓ, and pᵧ orbitals combine to a variable extent with the pᵧ orbital to form mixed sp²–sp³ orbitals. Three of these orbitals form strong σ bonds with nearest neighbors and the fourth, upward directed orbital can form a weaker bond with neighbors or with an adjacent orbital of another layer. The three compounds exhibit weak polarity, since the electronegativity changes only slightly between Si, Ge, and Sn. According to theory the free-standing monolayers of all three sheets are thermodynamically and dynamically stable.

Table 4 provides the cohesive energies and structural data of the planar group IV carbides SiC, GeC, and SnC¹¹²–¹¹⁷ and SnC¹¹⁵,¹₂¹,¹₂² and the buckled monolayers SiGe¹¹⁵,¹₂₃,¹₂₄,¹₂₈ SnSi¹¹₅,¹₂₁,¹₂₅,¹₂₆ and SnGe¹¹₅,¹₂₂,¹₂₅,¹₂₆. The dependence of the cohesive energy on bond length of these binary compounds is displayed in Fig. 13(a). One reason for the strong decay of the cohesive energy of the carbides compared with graphene is the increasing size of Si, Ge, and Sn and, which gradually reduces efficient π–π bonding. The large scatter of the published cohesive energies, which deviate by more than a factor of two, predicts different inverse behaviors. Bonding energies of binaries consistent with those of elemental monolayers, as observed for SiC, would point to cohesive energies that are roughly the mean of the extreme values presented in Fig. 13(a), resulting in the mean values ~5.7 eV per atom for GeC and ~4.6 eV per atom for SnC. A similar situation is encountered for the cohesive energies of buckled SiGe, SnSi, and SnGe monolayers. Once again, much larger and smaller cohesive energies were reported than estimated from the cohesion of the two constituents. The assumption of similar bonding behavior of elemental and binary group IV monolayers, despite ionic contributions in the binary compounds, is strongly supported by the similarities of their mechanical properties, as discussed in more detail below.

To explain this finding, we apply the tight-binding model to describe the formation of bonding orbitals in 2D heteronuclear group IV compounds. In polar networks with elements of different electronegativity, the hybrids of the atomic orbitals of atom M and atom X, with an energy difference ΔA, hybridize to form the bonding state E (MX) and the antibonding state E* (MX) (see Fig. 16). As mentioned before, the bonding–antibonding splitting 2B delivers the binding energy resulting from the stabilization of the bonding orbitals and the destabilization of the antibonding orbitals. Now, the energy of orbital overlap V
depends also on the hybrid polar energy $A$ according to $V = (B^2 - A^2)^{1/2}$. If the polar energy $A$ increases, the covalent energy $V$ decreases, or in other words, with increasing difference of the electronegativities the contribution of covalent orbital overlap diminishes. Consequently, in the polar binary group IV compounds bonding depends on both covalency and ionicity. However, the data points to comparable cohesive energies in elemental and binary monolayers and thus to modest ionic contribution.

Table 5 displays the corresponding mechanical properties of the carbides SiC, $\text{GeC}^{114,118,127}$, $\text{GeN}^{118,119}$, and $\text{SnC}^{115}$ and the binary monolayers $\text{SiGe}^{115,118,128}$, $\text{SnSi}^{115,128}$ and $\text{SnGe}^{115,128}$. The plot of Young’s moduli and ultimate strengths of the planar carbides and buckled compounds versus bond length in Fig. 13(b) shows a joint inverse dependence of elementary and binary compounds and reasonable agreement of the few available critical strength values with Griffith's rule. The inverse decay coinciding for homo- and heteronuclear monolayers owing to related bond lengths supports the assumption of quite similar covalent bonding energies in both cases. The enormous deterioration of mechanical performance from the planar carbides to the buckled elemental and binary monolayers is related to the rising loss of in-plane bonding power.

While the effect of stacking order is relatively small for bilayers of elemental monolayers, the band gap of heteronuclear compounds may change considerably with interlayer separation. For fundamental stacking sequences of SiC, contradictory results can be found in the literature. The strongest interaction of bilayers was found for AA stacking, where Si atoms are located over C atoms and vice versa. In this configuration, minimization of the forces reduced the interlayer separation to 0.232 nm, and the planar layers started to buckle. Therefore, the authors concluded that no van der Waals bonded layered structure of SiC can exist because it is unstable against interlayer linking similar as in silicene multilayers. It seems that the large charge transfer from Si to C and the preference of Si for sp$^3$ hybridization makes bilayers reactive. Calculations concentrating on charge transfer properties and stability predict larger interlayer spacings and interaction energies of 0.324 nm and −156 meV per atom for AB stacking and 0.338 nm and −154 meV per atom for AA stacking. For AA' stacking the bond length increases to 0.184 nm and the interlayer separation reduces to 0.221 nm, in agreement with the results described above.

The increasing focus of attention on silagrapheene (SiC) originates from a wide spectrum of optoelectronic properties and highly anisotropic transport properties. Therefore, SiC layers are of particular interest for commercial applications as light-emitting diodes (LEDs) and in photovoltaic devices. Owing to its unusual band structure it is suitable for strain engineering, for instance in highly sensitive sensors. While the preparation of free-standing honeycomb SiC monolayers has not been confirmed, few-layer assemblies have been prepared by nano-cleavage exfoliation of nanoflakes in polar solutions and characterized by TEM, XRD, and XPS. The authors concluded from the measured step heights, which varied between 0.5 and 1.5 nm for the exfoliated flakes, that some monolayer sheets had been realized.

The optical properties resulting from the capability of direct-to-indirect band gap transitions under in-plane strain make the wide-band-gap material GeC suitable for blue and ultraviolet LEDs, anti-reflection and protection coatings, energy engineering, and applications in photovoltaics. Unfortunately, experimental results on the preparation of semiconducting GeC and SnC monolayers and their few-layer assemblies seem not yet to be available.

**Group III–V monolayers**

The group of III–V monolayers MX ($M = B, Al, Ga, In, Tl; X = N, P, As, Sb, Bi$) with 25 compounds contains many well-studied monolayers, and some of them have already found applications in electronics and optoelectronics. A recent comprehensive publication presents the structural data and linear elastic properties of these compounds and discusses correlations between related compounds (see Table 6). This data agrees well with a previous compilation, where only the Bi and Tl compounds are missing. The results are also consistent with former studies, for example on the Ga-compounds GaN, GaP, GaAs, and GaSb and the As-compounds BAs, GaAs, and InAs.

From the planar binary monolayers containing either a boron or nitrogen atom, boron nitride, also called boronitrene, is the best-studied monolayer of the III–V compounds. Carbon and BN are isoelectronic because boron and nitrogen are left and right neighbors of carbon in the periodic table. The electronic structure of group III atoms is (ns$^2$np$^3$), with three valence electrons, and that of group V atoms is (ns$^2$np$^5$), with five valence electrons. In the planar hexagonal lattice, the sp$^3$ orbitals form a backbone of three σ bonds in a structure like graphene. This leaves an unoccupied p$_z$ orbital in the group III atom and a lone pair of electrons in the group V atom. Owing to the difference in electronegativity between boron and nitrogen, π electrons tend to localize around the nitrogen atoms. The mixed ionic–covalent bonding of planar group III nitrides is characterized by a significant difference of the electronegativities: 3.0 (N), 2.0 (B), 1.5 (Al), 1.8 (Ga), and 1.7 (In).
In the large number of III-V monolayers without a second-period element, the buckled configuration is the most stable phase, maintaining the hexagonal symmetry, as discussed for silicene and its heavier homologues.

The main reason for the astonishing similarity of the bonding behavior of III–V monolayers with those of group IV compounds is the identical number of valence electrons. This becomes obvious by the striking relationship between group IV carbides and group III nitrides. Within the errors involved in such calculations, both groups reveal quite a similar dependence of the cohesive energy on bond length. Owing to the small size of carbon and nitrogen atoms, these compounds realize strong planar sp\(^2\) hybrids with minor deviations from planarity only for the heaviest compound TlN, as can be seen in Table 6. The monolayer of TlN has a bond angle of 119.9° and a tiny buckling effect of Δz = 0.006 nm. Furthermore, most boron compounds are almost planar, with corrugations of Δz = 0.0005, 0.0012, 0.0033, and 0.048 nm for h-BP, h-BAs, h-BSb, and h-BBi, respectively. Consequently, these compounds have shorter bonds and larger cohesive energies than the heavier buckled compounds.

Table 6 contains the cohesive energies and structural data of the groups of related monolayers BX\(_2\), AlX\(_2\), GaX, InX\(_3\), and TIX\(_3\), with X = N, P, As, Sb, and Bi. As revealed in Fig. 17(a), which displays the cohesive energy as a function of bond length, the planar and buckled group III–V monolayers can be divided into five distinct groups of chemically related compounds, each containing one group III element. The group with the strongest bonding is that with the boron compounds BN, BP, BAs, BSb, and BBi, with almost planar monolayers. While the cohesion-bond length plot of the boron group shows the largest decay of bond energy and a pronounced inverse behavior, the dependence changes to a nearly linear modest decay of the thallium group with lowest cohesive energies. For example, the cohesive energy of the planar boron group changes from −6.7 to −2.8 eV per atom, whereas in the buckled thallium group the binding energy varies from −2.2 to −1.7 eV per atom. The pronounced inverse decay follows the prediction of the tight-binding model. This has enormous consequences for mechanical stability and performance.

The mechanical properties of the BX\(_2\), AlX\(_2\), GaX, InX\(_3\), and TIX\(_3\) groups, with X = N, P, As, Sb, and Bi, are compiled in Table 7. In a plot of the Young’s modulus and ultimate strength versus bond length, especially the Young’s moduli of the BX monolayers, but also the stiffness of other related groups, display a characteristic inverse dependence as a function of bond length (see Fig. 17(b)). Notably, the Young’s modulus of graphene can be considered as the upper limit of stiffness. The same is true for the few available strength values, which roughly follow Griffith’s rule. The relations revealed by the plot allow a first estimate of largely unknown critical strengths. It is important to note that the characteristic dependence observed for related groups demonstrates a systematic decay of the Young’s moduli and ultimate strengths with increasing row number of the incorporated group III element. This is in accordance with the behavior of the cohesive energies discussed above, however, with a huge decrease of stiffness by a factor of 34 from 276 N m\(^{-1}\) for h-BN to 8.1 N m\(^{-1}\) for TIBi. In comparison,
the total decrease of the cohesive energy from h-BN to TlBi is only a factor of four. This demonstrates the ultra-sensitivity of mechanical behavior on the cohesive binding energy. Note the enormous alteration of the mechanical properties compared to the modest change of binding energy by a factor of two. The increasing Poisson’s ratios indicate less stiffness and more plasticity with increasing row number (see Table 7).

The main reason for the striking similarity of the interlayer separation of multilayers of boronitrene and graphene was suggested to be that van der Waals forces, rather than electrostatic interaction, are the dominant interaction forces at the interlayer equilibrium distance, while ionic interactions preferentially control the stacking order and interlayer sliding corrugation.\(^5\) The experimentally observed AA stacking mode (e.g., Al over N and N over Al), is the most stable stacking order not only for BN, with bilayer interaction energies between \(-26.0\) and \(-38.1\) meV per atom\(^1\),\(^3\),\(^8\),\(^16\) but also with interlayer interaction energies of \(-125\) meV per atom\(^1\) for bilayers of AlN, and \(-142\) meV per atom for GaN.\(^1\) The low interlayer separations, which vary in the range

Table 7  Space group, Young’s modulus, Poisson’s ratio, ultimate strength, and ultimate strain of group III–V monolayers

<table>
<thead>
<tr>
<th>Monolayer</th>
<th>Structure space group</th>
<th>Young’s modulus (E) (N m(^{-1}))</th>
<th>Poisson’s ratio (\nu)</th>
<th>Ultimate strength (\sigma_{\text{acc}}, \sigma_{\text{zz}}) (N m(^{-1}))</th>
<th>Ultimate strain (\varepsilon_{\text{acc}}, \varepsilon_{\text{zz}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>h-BN</td>
<td>(P6m2) (^{149})</td>
<td>276,(^{131}) 270,(^{150}) 276,(^{118}) 279,(^{151})</td>
<td>0.23(^{131})</td>
<td>23.6, 26.3(^{151})</td>
<td>0.18, 0.26(^{151})</td>
</tr>
<tr>
<td>h-BP</td>
<td>139,(^{131}) 135,(^{115})</td>
<td>116,(^{131}) 119,(^{115})</td>
<td>0.28,(^{131}) 0.28,(^{115})</td>
<td>26, (^{118})</td>
<td>0.18, 0.29(^{152})</td>
</tr>
<tr>
<td>h-BAs</td>
<td>84,(^{131}) 91,(^{115})</td>
<td>61,(^{131})</td>
<td>0.33,(^{131}) 0.34,(^{115})</td>
<td>125 meV per atom (\times 10^{-19})</td>
<td>118</td>
</tr>
<tr>
<td>h-BBi</td>
<td>61,(^{131})</td>
<td>0.30,(^{131})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>h-AlN</td>
<td>(P6/mmc) (^{143})</td>
<td>113,(^{131}) 136,(^{153}) 138,(^{127})</td>
<td>0.46,(^{131}) 0.37,(^{153})</td>
<td>16.2, 15.9(^{153}) 13, 15(^{127})</td>
<td>0.22, 0.27(^{153}) 0.18, 0.23(^{127})</td>
</tr>
<tr>
<td>h-AlP</td>
<td>64,(^{131}) 58,(^{154})</td>
<td>47,(^{131}) 46,(^{154})</td>
<td>0.34,(^{131}) 0.36,(^{154})</td>
<td>32,(^{131}) 37,(^{115})</td>
<td>0.32, 0.37(^{115})</td>
</tr>
<tr>
<td>h-AlAs</td>
<td>33,(^{131}) 35,(^{115})</td>
<td>27,(^{131})</td>
<td>0.37,(^{131})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>h-AlBi</td>
<td>106,(^{131}) 110,(^{115})</td>
<td>83,(^{131}) 82,(^{127})</td>
<td>0.45,(^{131}) 0.48,(^{115})</td>
<td>11.9, 12.1(^{155}) 10,11(^{127})</td>
<td>0.18, 0.22(^{155}) 0.17, 0.19(^{127})</td>
</tr>
<tr>
<td>h-GaP</td>
<td>59,(^{131}) 55,(^{154})</td>
<td>44,(^{131}) 44,(^{154})</td>
<td>0.31,(^{131}) 0.34,(^{154})</td>
<td>33,(^{131}) 34,(^{154})</td>
<td>0.33, 0.34(^{154})</td>
</tr>
<tr>
<td>h-GaAs</td>
<td>28,(^{131}) 32,(^{154})</td>
<td>62,(^{131}) 62,(^{157})</td>
<td>0.39,(^{131}) 0.35,(^{154})</td>
<td>38,(^{131}) 59,(^{157})</td>
<td>0.38, 0.59(^{157})</td>
</tr>
<tr>
<td>h-InN</td>
<td>(P-6m2) (^{156})</td>
<td>88,(^{131}) 90,(^{127})</td>
<td>0.45,(^{131}) 0.48,(^{115})</td>
<td>11.9, 12.1(^{155}) 10,11(^{127})</td>
<td>0.18, 0.22(^{155}) 0.17, 0.19(^{127})</td>
</tr>
<tr>
<td>h-InP</td>
<td>40,(^{131}) 35,(^{154})</td>
<td>31,(^{131}) 36,(^{154})</td>
<td>0.38,(^{131}) 0.42,(^{154})</td>
<td>39,(^{131}) 42,(^{154})</td>
<td>0.39, 0.42(^{154})</td>
</tr>
<tr>
<td>h-InAs</td>
<td>25,(^{131}) 22,(^{154})</td>
<td>20,(^{131})</td>
<td>0.32,(^{131}) 0.44,(^{154})</td>
<td>41,(^{131})</td>
<td>0.41(^{131})</td>
</tr>
<tr>
<td>h-InBi</td>
<td>14,(^{131})</td>
<td>17,(^{131})</td>
<td>0.69,(^{131})</td>
<td>5.8, 3.7(^{159})</td>
<td>3.8(^{145})</td>
</tr>
<tr>
<td>h-TIP</td>
<td>14,(^{131})</td>
<td>17,(^{131})</td>
<td>0.79,(^{131})</td>
<td>5.8, 3.7(^{159})</td>
<td>3.8(^{145})</td>
</tr>
<tr>
<td>h-TIP</td>
<td>14,(^{131})</td>
<td>17,(^{131})</td>
<td>0.79,(^{131})</td>
<td>5.8, 3.7(^{159})</td>
<td>3.8(^{145})</td>
</tr>
<tr>
<td>h-TiAs</td>
<td>17,(^{131})</td>
<td>0.58,(^{131})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>h-Tlsb</td>
<td>8,(^{131})</td>
<td>0.73,(^{131})</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 17  (a) Cohesive energy versus bond length of group III–V monolayers in comparison to graphene. (b) Young’s modulus and ultimate strength versus bond length of group III–V monolayers in comparison to graphene.
of 0.21–0.25 nm for AlN, GaN, InN, and TIN, indicate effective electrostatic anion–cation interaction between the layers as the major contribution to strong interlayer interaction (see Table 6). For bilayer honeycomb TI compounds a p–p band inversion type QSH effect was predicted that is independent of SOP.\textsuperscript{148}

Planar h-BN, with its strong bonding and large band gap, seems to be the best insulator and is particularly attractive as the ultimately thin insulator, barrier, or encapsulant. It is chemically inert and resistant to oxidation up to elevated temperatures and to corrosion. Owing to its high thermal conductivity, it is a useful material for electronic devices and will find use as an ultraviolet (UV) light emitter in optoelectronics. It is useful for far-ultraviolet (FUV) device applications and is of interest as a transparent and flexible material in electronics.\textsuperscript{135,137,139} Current electronic and photonic device concepts still rely primarily on h-BN exfoliated from small bulk crystallites. In an effort to achieve reproducible and tunable growth of mono- and few-layer systems, different approaches have been investigated, such as CVD on Cu\textsuperscript{162} or high-temperature plasma-assisted MBE on highly oriented pyrolytic graphite (HOPG) substrates.\textsuperscript{163} In a recent breakthrough, epitaxial growth of 100 cm\textsuperscript{2} single crystals of h-BN was accomplished on copper, demonstrating unidirectional alignment and seamless stitching on an annealed industrial copper foil.\textsuperscript{164} In the meantime, single-crystal h-BN, without undesirable grain boundaries, has been grown on a single-crystal Cu(111) film across a two-inch c-plane sapphire wafer and successfully detached and transferred to a wafer.\textsuperscript{165}

Monolayers of h-AlN show a distinct single absorption peak at \(\sim 6\) eV, and therefore they are transparent in the visible region and have promising applications in the UV spectral range. A theoretical analysis revealed that the energetically favored hexagonal phase of up to about 10 monolayers has an indirect band gap.\textsuperscript{166} Similarly to the onset of interband absorption, the band gaps vary from 2.9 eV for monolayers to \(\sim 3.5\) eV for few-layer assemblies, with a transition from an indirect gap to a direct gap of the bulk.\textsuperscript{166,167} Layered h-AlN bulk assemblies do not exist in nature and single layers of h-AlN are difficult to isolate owing to the strong interlayer interaction. Since the absorption intensity increases with the number of layers, few-layer assemblies are of great interest. Synthesis of the hexagonal form of AlN has been achieved by plasma-assisted MBE on Ag(111) substrates from submonolayer to 12 layers.\textsuperscript{168} A review covering the applications of single-layer and few-layer sheets on different substrates is available.\textsuperscript{169}

The indirect band gap of monolayer h-GaN turns into a direct gap in few-layer h-GaN.\textsuperscript{170} Furthermore, this wide-bandgap material is a candidate for the fabrication of energy-efficient deep-UV LEDs and it is suitable for biomedical applications and photovoltaics.\textsuperscript{155} The fundamental band gap of vertical structures varies with the stacking sequence and the number of sheets in the stack.\textsuperscript{171} Chemical tailoring, on the other hand, shifts the optical activity to the UV region and simultaneously eliminates its instability and generates a direct band gap.\textsuperscript{172} It is necessary to synthesize monolayers and few-layer assemblies on substrates since layered bulk h-GaN does not exist in nature. The growth of h-GaN sheets on Si(100) substrates and – preferably – on Si(111) substrates with a better crystalline structure, has been achieved by high-temperature pulsed laser deposition (PLD) with intermittent control of the crystalline structure by TEM and SEM.\textsuperscript{173}

Despite many desirable properties of InN the synthesis of mono- or few-layers is still in its infancy. It seems that the formation of 3D structures with strong covalent bonding impedes layer-by-layer growth of 2D structures. Based on the narrow band gap, small effective mass, and high electron mobility of InN compared to the lighter group-III nitrides, interest concentrates on potential applications as a field effect transistor, in lasers, solar cells, photodetectors, and in thermoelectric devices.\textsuperscript{146} The deposition conditions and structural properties of InN films have been studied by the growth of self-standing films using low-temperature electron cyclotron resonance plasma-enhanced metal organic CVD (ECR-MOCVD).\textsuperscript{174}

**Group V monolayers**

**Elemental monolayers.** The search for stable 2D phases of phosphorus, arsenic, antimony, and bismuth resulted in the discovery of four main 2D allotropes: a weakly buckled honeycomb structure hb-X (\(\beta\)-X), \(X = \text{P, As, Sb, and Bi}\); a symmetric puckered or washboard structure sw-X (\(\gamma\)-X) (see Fig. 18(a)); an asymmetric puckered or washboard structure aw-X (\(\gamma\text{-}z\)-X) (see Fig. 18(b and c)); and finally a square-octagon structure so-X. Table 8 presents the structural data of the two most-stable 2D phases of phosphorene and arsenene (hb and sw), as well as those of antimonene and bismuthene (hb, aw), taken from the most comprehensive data collection available for elemental pnictogenes.\textsuperscript{175} A recent review covers besides the elemental monolayers also the binary V–V compounds.\textsuperscript{176} While the structural data agrees well with former studies, the reported cohesive energies may deviate by more than a factor of two for application of the DFT-GGA-PBE approach, while for other approaches deviations may be even larger (see Table 8). Current interest in these 2D materials comes from potential applications in electronics, for example as TIs, in spintronics, as a photodetector and a solar cell in optoelectronics, in catalysis, and in thermoelectrics.\textsuperscript{177,178}

The pnictogen atoms P, As, Sb, and Bi have an electron configuration (\(ns^2np^3\)) with five valence electrons in the outer shell and therefore need three extra electrons to reach octet stability. Most calculations assume that the s and p orbitals deliver a reasonable description of bonding and that the influence of d orbitals is negligible even for the heavy Bi atom. A planar structure of sp\(^2\) hybrids is not stable as a free-standing layer. Thus, sp\(^2\)-like hybridization of s and p orbitals stabilizes a buckled or puckered configuration, because corrugation allows better overlap of p\(_x\)-p\(_x\) orbitals. Fig. 19 shows the electron configuration and atomic orbitals after promotion and hybridization. Accordingly, the monolayer consists of sp\(^2\)-like hybrids (intermediate between sp\(^3\) and sp\(^2\)) forming three \(\sigma\) backbonds with nearest atoms, which build a pyramid of
covalent bonds that provides the rigidity. The lone pair of valence electrons in a p$_z$-like orbital (not pure p state) primarily interacts with neighboring layers. In the stabilized monolayer structure, the distance between the repulsive lone electron pairs is maximized. Note that threefold-coordinated layered structures can be topologically mapped onto a honeycomb lattice. While the unit cell of the buckled rhombohedral structure contains two atoms, there are four atoms in the unit cell of the puckered orthorhombic structure.

The strongly folded accordion-like ridged or puckered structure is responsible for the anisotropy, with strongly varying properties parallel to the grooves along the zigzag direction (b direction or y-axis) compared to perpendicular to the grooves in the armchair direction (a direction, x-axis), as visible in Fig. 18(c). Calculations of the cohesive energy indicate that sw-P, sw-As, aw-Sb, and aw-Bi are the energetically most stable puckered phases, together with the cohesive energy indicates that sw-P, sw-As, aw-Sb, and aw-Bi are puckered phases. The buckled phase of pnictogen structural resemblance of their stability and higher homologues, with a buckling effect that increases with row number.

The data collection in Table 8 includes cohesive energies, lattice constants, bond angles, bond lengths, layer thicknesses, and few-layer separations for the elemental monolayers P$\text{P1}$, As$\text{P1}$, Sb$\text{P1}$, Bi$\text{P1}$, and the binary V–V compounds PN$\text{P1}$, AsN$\text{P1}$, SbN$\text{P1}$, BiN$\text{P1}$, AsSb$\text{P1}$, SbP$\text{P1}$, AsP$\text{P1}$, SbP$\text{P1}$, and SbN$\text{P1}$ in Fig. 18(a) we present a scheme of the symmetric puckered or washboard structure sw-X. The red dashed lines label the rectangular unit cell with four atoms. The upper dependence in Fig. 20(a) with the large cohesive energies of binary V–V compounds is not consistent with the much lower values reported for the corresponding elemental monolayers, and therefore these large binding values have not been included in Table 8. On the other hand, for each of the two elemental groups, there are four atoms in the unit cell of the puckered orthorhombic structure.

The mechanical properties reported for the elemental monolayers belong to two lower almost parallel inverse dependences, one with medium and the other one with much lower energies of cohesion. Note that the included results are based on DFT calculations, treating the exchange–correlation functional by the PBE form of GGA. Unfortunately, a detailed description of the specific approximations used is lacking and the authors do not discuss reasons for the deviations of their results from already existing literature values. A difference stated is that the major study of the small cohesive energies took the SOC effect into account.$^\text{176}$ To what extent this explains the observed differences is not clear.

The upper dependence in Fig. 20(a) with the large cohesive energies of binary V–V compounds is not consistent with the much lower values reported for the corresponding elemental monolayers, and therefore these large binding values have not been included in Table 8. On the other hand, for each of the two elemental groups, there are four atoms in the unit cell of the puckered orthorhombic structure.

The strongly folded accordion-like ridged or puckered structure is responsible for the anisotropy, with strongly varying properties parallel to the grooves along the zigzag direction (b direction or y-axis) compared to perpendicular to the grooves in the armchair direction (a direction, x-axis), as visible in Fig. 18(c). Calculations of the cohesive energy indicate that sw-P, sw-As, aw-Sb, and aw-Bi are the energetically most stable puckered phases, together with the cohesive energy indicates that sw-P, sw-As, aw-Sb, and aw-Bi are puckered phases. The buckled phase of pnictogen structural resemblance of their stability and higher homologues, with a buckling effect that increases with row number.
ultimate strengths (right) of the group V elements are shown in Table 9. In Fig. 20(b) the available Young's moduli (left) and stiffness in the armchair direction is that tension unfolds for the heavier elements. The reason for the extremely low action energy of \( \text{Waals diameter plus corrugation effect} \). The interlayer interaction forces is the main reason for studying the layered systems. This includes indirect-to-direct transitions and the width of the band gap. Usually, the gap increases with decreasing number of layers due to confinement effects. For AB stacking in sw-As, the spacing is \( 0.554 \) nm and the interlayer interaction of \( 53 \) meV per atom, a comparable value for AA stacking.\(^{183}\) A comparable behavior is observed for AA stacking of hb-As, with an interlayer action energy of \( 68 \) meV per atom, which agrees with the van der Waals diameter plus corrugation effect. The interlayer interaction energy of \( -20 \) meV per atom equals the van der Waals interaction of bilayer graphene.\(^{179}\) This is also the case for hb-P with \( d_s = 0.446 \) nm and interlayer interaction of \( -12.5 \) meV per atom for AB stacking and comparable values for AA stacking.\(^{183}\) For AB stacking in sw-As, the spacing is \( 0.554 \) nm and the interaction increases to \( -53 \) meV per atom.\(^{185}\) A comparable behavior is observed for AA stacking of hb-As, with an interaction energy of \( -30 \) meV per atom and layer spacing of \( 0.492 \) nm.\(^{185}\) While for AB stacking in aw-Sb the layer separation of \( 0.616 \) nm is consistent with the interaction of \( -68 \) meV per atom, and minor chirality of the ultimate strength and strain is observed only when the hexagonal symmetry is broken by uniaxial strains in the nonlinear part of the stress–strain relationship. The intrinsic strength measures the overall stability of chemical bonding of the 2D network and the values available for phosphorene, arsenene, and antimonene follow Griffith’s rule well. Thus, a reasonable first estimate of the ultimate strength for buckled bismuthene of \( \sim 2.5 \) N m\(^{-1}\) can be extracted from this correlation.

The tunability of electronic properties of few-layer assemblies by changing the interlayer interaction via stacking order and interlayer interaction forces is the main reason for studying the layered systems. This includes indirect-to-direct transitions and the width of the band gap. Usually, the gap increases with decreasing number of layers due to confinement effects. For AB stacking of sw-P bilayers, for example, the layer spacing is around \( 0.53 \) nm, which agrees with the van der Waals diameter plus corrugation effect. The interlayer interaction energy of \( -20 \) meV per atom equals the van der Waals interaction of bilayer graphene.\(^{179}\) This is also the case for hb-P with \( d_s = 0.446 \) nm and interlayer interaction of \( -12.5 \) meV per atom for AB stacking and comparable values for AA stacking.\(^{183}\) For AB stacking in sw-As, the spacing is \( 0.554 \) nm and the interaction increases to \( -53 \) meV per atom.\(^{185}\) A comparable behavior is observed for AA stacking of hb-As, with an interaction energy of \( -30 \) meV per atom and layer spacing of \( 0.492 \) nm.\(^{185}\) While for AB stacking in aw-Sb the layer separation of \( 0.616 \) nm is consistent with the interaction of \( -68 \) meV per atom, and minor chirality of the ultimate strength and strain is observed only when the hexagonal symmetry is broken by uniaxial strains in the nonlinear part of the stress–strain relationship. The intrinsic strength measures the overall stability of chemical bonding of the 2D network and the values available for phosphorene, arsenene, and antimonene follow Griffith’s rule well. Thus, a reasonable first estimate of the ultimate strength for buckled bismuthene of \( \sim 2.5 \) N m\(^{-1}\) can be extracted from this correlation.
for AA stacking of hb-Sb multilayers the large interaction energy of \(-124\) meV per atom reduces the layer spacing to 0.365 nm. Various theoretically predicted monolayer properties of pnictogens, such as large band gap, band gap tuning by strain, thermolectric and optoelectronic properties, topological phases, high electron mobility, superconductivity, and QSH effect, have aroused the interest of experimentalists. According to theory, both hb-P and sw-P form energetically and dynamically stable free-standing sheets. Epitaxial growth of single monolayers of phosphorene on an Au(111) surface leads to a structure identical with hb-P, as verified by STM and LEED analysis. While the sw and hb phases are equally stable, the latter seems to be the preferred phase that grows on a substrate with hexagonal symmetry. A recent review describes in detail the progress made with top-down methods (mechanical, liquid, and electrochemical exfoliation) and bottom-up methods (CVD, MBE) in the fabrication of group V monolayers. The quick oxidative degradation of reactive phosphorene, induced by oxygen dissolved in adsorbed water and light exposure, requires effective passivation schemes for synthesis, characterization, and processing.

Exfoliation of layered bulk grey arsenic, existing in nature, allows the isolation of buckled arsenene monolayers. While the production of few-layer systems of hb-As has been achieved by several methods, such as exfoliation with adhesive tape or ultrasonication, the realization of monolayers is much more demanding. Using LEED, STM, and angle-resolved photo-emission spectroscopy (ARPES) in combination with DFT calculations for characterization, the formation of a quasi-free-standing buckled honeycomb layer of arsenene on Ag(111) has been confirmed. The physicochemical properties of antimonene allotropes resemble those of arsenene. The growth of buckled

**Table 9**  Phase, space group, Young’s modulus, Poisson’s ratio, ultimate strength, and ultimate strain of elemental and binary group V monolayers

<table>
<thead>
<tr>
<th>Monolayer</th>
<th>Phase</th>
<th>Space group</th>
<th>Young’s modulus $E_{ac}$ $E_{zz}$ (N m$^{-1}$)</th>
<th>Poisson’s ratio $\nu_{ac}$ $\nu_{zz}$ $\nu_{xy}$ $\nu_{yx}$</th>
<th>Ultimate strength $\sigma_{ac}$ $\sigma_{zz}$ (N m$^{-1}$)</th>
<th>Ultimate strain $\varepsilon_{ac}$ $\varepsilon_{zz}$</th>
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<tbody>
<tr>
<td>Phosphorene</td>
<td>sw</td>
<td>$Pmna$</td>
<td>25, 93$^{182}$</td>
<td>0.17, 0.62$^{182}$</td>
<td>4.4, 10$^{182}$</td>
<td>0.30, 0.27$^{182}$</td>
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<tr>
<td></td>
<td>hb</td>
<td>$P3m1$</td>
<td>22, 36$^{182}$</td>
<td>0.18, 0.70$^{182}$</td>
<td>2.2, 4.5$^{208}$</td>
<td>0.30, 0.16$^{184}$</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>75, 175$^{181}$</td>
<td>0.11$^{175}$</td>
<td>7.1, 6.7$^{182}$</td>
<td>0.16, 0.21$^{182}$</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>20, 55$^{184}$</td>
<td>0.33, 0.91$^{184}$</td>
<td>5.2, 4.7$^{182}$</td>
<td>0.17, 0.20$^{182}$</td>
</tr>
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<td></td>
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<td></td>
<td>58, 184$^{181}$</td>
<td>0.21$^{184}$</td>
<td>3.6, 1.20$^{175}$</td>
<td>0.18, 0.32$^{182}$</td>
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<td></td>
<td></td>
<td></td>
<td>12, 29$^{175}$</td>
<td>0.21$^{188}$</td>
<td>2.3, 5.8$^{182}$</td>
<td>0.20, 0.21$^{182}$</td>
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<td></td>
<td>41, 33$^{181}$</td>
<td>0.33$^{181}$</td>
<td>3.8, 3.1$^{182}$</td>
<td>6.4, 5.8$^{189}$</td>
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<td></td>
<td></td>
<td></td>
<td>10, 26$^{191}$</td>
<td>0.11, 0.54$^{198}$</td>
<td>4.7$^{207}$ (100 K)</td>
<td>0.24, 0.27$^{207}$</td>
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<td></td>
<td></td>
<td></td>
<td>24, 30$^{175}$</td>
<td>0.13$^{198}$</td>
<td>0.12, 0.91$^{198}$</td>
<td>0.22$^{198}$</td>
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<td>39, 199$^{198}$</td>
<td>0.11, 0.54$^{198}$</td>
<td>0.06, 0.82$^{198}$</td>
<td>0.21$^{198}$</td>
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<td>149$^{198}$</td>
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<td></td>
<td>18, 133$^{198}$</td>
<td>0.12, 0.91$^{198}$</td>
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<td>7.2, 97$^{198}$</td>
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<td>53$^{198}$</td>
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<td>0.28$^{198}$</td>
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<td></td>
<td></td>
<td>62, 194$^{208}$</td>
<td>0.15, 0.44$^{208}$</td>
<td>0.13, 0.44$^{208}$</td>
<td>0.20, 0.44$^{208}$</td>
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<td></td>
<td></td>
<td></td>
<td>42$^{194}$</td>
<td>0.13, 0.44$^{208}$</td>
<td>0.13, 0.44$^{208}$</td>
<td>0.20, 0.44$^{208}$</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>39$^{194}$</td>
<td>0.13, 0.44$^{208}$</td>
<td>0.13, 0.44$^{208}$</td>
<td>0.20, 0.44$^{208}$</td>
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</tbody>
</table>
monolayers of antimonene has been achieved on a 2D layered 
PdTe2 substrate by MBE.215 The analysis confirmed a weak 
interaction with the substrate and a high chemical stability in air.
Large-area antimonene has been grown on c-plane sapphire by 
MBE and characterized by XRD and Raman spectra.216 Van der 
Waals heteroepitaxial deposition allowed the growth of high-quality 
Sb monolayers with the puckered honeycomb structure.217 A 
progress report reviews the approaches employed the obtain 
antimonene and the main characterization techniques used to 
study this material.218

Interest in monolayers of heavy Bi is based on its strong SOC 
and the inverted gap. The deposition of supported bismuthene 
with the MBE method using a SiC(0001) substrate yielded a 
honeycomb $\sqrt{3} \times \sqrt{3} \ R30^\circ$ superstructure of Bi in a planar 
configuration, owing to the strain effect of the SiC substrate.219

The large band gaps of hexagonal bismuthene, antimonene, 
and arsenene may offer the possibility of room temperature 
QHS applications.220 A detailed investigation of the oxidation 
mechanism and structural stability of 2D pnictogens under 
oxogen and water exposure comes to the conclusion that the 
higher stability of antimonene and bismuthene originates from 
an acceptor role of water, which impedes the formation of acids 
by the interaction of water molecules and oxygen species.221

**Binary group V monolayers.** Binary group V monolayers 
consist of multivalent atoms with nonmetallic (N and P), 
semi-metallic (As), and metallic (Sb and Bi) elements with 
versatile hybridization (sp2 versus sp3) and variable bonding 
type (covalent versus ionic). Just as in elemental monolayers, 
bonding is governed by the five valence electrons (ns2np5).

First-principles calculations treating the electron-electron 
interaction by the DFT-GGA-PBE approach and the interaction 
between valence and core electrons by the projector augmented 
wave (PAW) method reveal that P atoms favor the formation of 
sp3 hybrids and N atoms sp2 hybrids.192 As for elemental group 
V monolayers, the specific binding configuration, for instance 
between the tetrahedrally coordinated phosphorus atom and 
three nitrogen atoms, consists of three non-planar $\sigma$ bonds 
with either buckled or puckered corrugation. Furthermore, 
owing to different electronegativities of the constituents, charge 
transfer induces ionic contributions. Usually, the electro-
negativity of group elements decreases going down the periodic 
system, here from P to Bi. Noteworthy, this change is relatively 
small for the heavier elements. Explicitly, the electronegativity of 
nitrogen is 3.04 (N) and that of other group V atoms varies only 
slightly between 2.19 (P) and 2.02 (Bi). Charge transfer in ionic 
bonds occurs from lower to higher electronegativity.

Of the large number of phases described in the literature, 
the buckled (hb or $\beta$) and asymmetric washboard structures 
(aw or $\alpha$) are the most extensively investigated monolayers due 
to their stability (see Fig. 18d). Owing to different atom sizes, 
the binary compounds become asymmetric. This reduces the 
symmetry of the network, which is no longer centrosymmetric.

The compounds discussed here are energetically stable, with a 
negative cohesive energy, and their free-standing monolayers are 
dynamically stable, with no soft or imaginary phonon modes. 
Eventually, MD simulations verified the thermal stability at finite 
temperatures. Theoretical calculations of structural data such as 
the bond length are in good agreement, while large deviations 
exist for the cohesive energies.

Besides the bonding behavior of elemental monolayers, 
Fig. 20(a) presents the published small, medium, and large 
cohesive energies of binaries as a function of the longer bond 
for the most stable sw and aw phases. Generally, we may 
assume that the stiffness of a particular binary phase lies 
between those of the two constituents. Some values presented 
for the cohesive energies of the nitrides PN, AsN, SbN, and AsP 
are much larger than those of their constituents.193 Of course, 
the strongest bonding is anticipated for the nitrides, where 
besides efficient overlap of orbitals owing to the small size of 
nitrogen atoms, ionic interaction makes the largest contribution 
to in-plane ionic–covalent bonding. However, we would expect 
the cohesive energy and bond length of AsP to be located 
 somewhere between the corresponding values of its constituents, 
As and P. Similarly, the cohesive energies of SbP and SbAs seem to 
be too large. It is difficult to rationalize why the bonding strength 
of the AsP monolayer should be much stronger than that of 
phosphorene with a similar bond length. The same is true for 
the large cohesive energies of SbP and SbAs. The principle that 
binary compounds have cohesive energies that correlate with those of the 
corresponding elemental compounds is clearly followed by the 
dependences with medium186,187 and small cohesion.176 Like 
the elements, the binary group IV and binary group V monolayers 
with medium cohesive energies possess comparable cohesive 
energies and bond lengths, and thus a similar structural stability.

Besides the mechanical properties of elemental compounds, 
Fig. 20(b) shows a plot of the available Young's moduli versus 
the bond lengths of binary group V compounds. Noteworthy is the 
large anisotropy of the Young's moduli between the armchair 
and the zigzag directions of the puckered nitrides, which again 
decreases abruptly for the heavier compounds. As can be seen in 
Fig. 20(b), the strong mechanical performance of binary 
group V monolayers in the zigzag direction follows the periodic 
trend of the elements, where graphene defines the upper limit of 
stiffness. The observed dependences clearly demonstrate 
correlated cohesive energies of homonuclear and heteronuclear 
monolayers, despite ionic interaction in the latter case. Unfortunately, calculations of the ultimate strengths and 
strains are still largely lacking for binary group V sheets.

The fact that the P–N bond is stronger than the P–P bond 
follows from the better orbital overlap yielding a larger cohesive 
energy. Therefore, the higher dynamic stability and better 
oxidation resistance of PN is not surprising.192 PN is a 
semiconductor with a wide band gap suitable for application 
as a high-speed transistor, in power electronics, and as an 
efficient LED. The piezoelectric coefficients, which control 
mechanical-to-electrical energy conversion, have high values 
in binary group V monolayers such as PN, owing to their 
flexible structure and low symmetry.94 The realization of PN 
monolayers may be possible either as a free-standing sheet or 
as a monolayer on a suitable substrate. There is evidence 
from theory that the two configurations considered here are 
dynamically stable and authors propose potential growth of
aw-PN and hb-PN on Ag substrates by CVD with cyclic phospha-zene, which contains a 1:1 mole ratio of P and N, to overcome difficulties with the strong nitrogen triple bond.\textsuperscript{192} A large separation between PN and the Ag substrate is expected and theoretical STM images suggest a non-planar periodic structure of the adsorbed monolayer. The other binary mono-layers are not as well studied as PN.

**Group IV–VI monolayers**

The elements of 2D group IV–VI compounds or group IV monochalcogenide monolayers are, as direct neighbors of group V elements, their isoelectronic counterparts, with ten valence electrons in total. For example, SnS, with the electronic configurations Sn(4d\textsuperscript{10}5s\textsuperscript{2}5p\textsuperscript{6}) and S(3s\textsuperscript{2}3p\textsuperscript{4}), is isoelectronic to group V elements with the electronic configuration (ns\textsuperscript{2}np\textsuperscript{0}). Of particular interest are stereochemically active cations with the formal electronic configuration (ns\textsuperscript{2}np\textsuperscript{4}), based on an electron lone pair (ns\textsuperscript{2}), as studied already in detail for bulk crystals of SnX (X = O, S, Se, and Te).\textsuperscript{222} In the classical picture of ionic bonding in SnS, the Sn (5s\textsuperscript{2}) subshell electrons of the cation Sn\textsuperscript{2+} with oxidation state two form a chemically inert orbital of lone-pair electrons projecting out on one side of the plane after hybridization. The Sn\textsuperscript{2+} ion interacts with three S\textsuperscript{2-} ions and, together with the lone-pair electrons of Sn (5s\textsuperscript{3}), sp\textsuperscript{3}-like hybridization with a higher chemical reactivity is achieved. This reactivity causes a stronger interlayer coupling between adjacent layers. DFT calculations delivered evidence that the Sn (5s) and (5p) states may be too far apart for direct coupling and therefore hybridization of Sn (5s) via anion X p states of suitable energy has been postulated, allowing a sterically active asymmetric electron density distribution with nominally filled ns and nominally empty np states of the cation.\textsuperscript{222} Alternatively, it has been assumed that if the energy gained by s–p hybridization is larger than the energy cost of moving the cation electron from its s to its p state, symmetry will be broken and an asymmetric electron distribution can be generated by the response of the cation’s ns and nominally empty np orbitals.\textsuperscript{223}

In any case, the structural distortions caused by the lone pair electrons are responsible for the generation of the characteristic orthorhombic structure of the monolayer with strong interlayer interaction and enhanced chemical reactivity. The lone pair of each atom pushes the three covalently bonded atoms towards a tetrahedral coordination. Notwithstanding that a complete molecular understanding is still lacking, the stereo-chemically active lone pair is the source of the structural changes leading to the distinctive elastic, piezoelectric, and optoelectronic properties, and to the anisotropy of thermal expansion.\textsuperscript{223} Owing to the difference in electronegativity, the bonds of these compounds are polar, with considerable ionic contributions to bonding. Charge transfer occurs from group IV to group VI atoms, with C-containing compounds as an exception. As a result of the different electronegativity and atom size of the constituents, the single-layer structures lack centrosymmetry, and therefore SOC is allowed.

From the geometrical monolayer configurations studied, we consider here the two most stable 2D structures, namely the puckered and buckled phases. In cases where the binding energies of these two phases are comparable, they may even coexist. The aw-phase of the four compounds GeS, GeSe, SnS, and SnSe, with band gaps covering part of the infrared and visible spectrum, has attracted enormous attention.\textsuperscript{224} These monolayers entail six-membered rings in the so-called chair conformation, with four sublayers (see Fig. 18[d]). The properties of interest are the high flexibility, high carrier mobility, low lattice thermal conductivity, and strong absorbance of visible light, which offer potential applications in optoelectronics, thermoelectrics, piezoelectricity, as photodetectors, and as sensors. Remarkable phenomena related to in-plane strain are giant piezoelectricity and multiferroicity, combining ferroelastic and ferroelectric behavior. Finally, strong SOC opens the door to spintronics. Interestingly, Ge and Sn as well as S and Se have similar electronegativities and comparable, weak bond energies responsible for their surprisingly low stiffness. The unique properties are linked with weak chemical bonding of the puckered structure, which is the minimum energy configuration, except for SiS and SiSe.\textsuperscript{225}

The structural data of group IV–VI monolayers MX, with M = C, Si, Ge, Sn and X = S, Se, Te, has been determined in a comprehensive study by first-principles calculations.\textsuperscript{225} Table 10 contains the cohesive energies and structural data of C\textsubscript{2}\textsuperscript{225–227} Si\textsubscript{2},\textsuperscript{225} Si\textsubscript{2}–Si\textsubscript{0},\textsuperscript{225} Ge\textsubscript{2},\textsuperscript{224,225,228} Sn\textsubscript{2},\textsuperscript{224,225,229} C\textsubscript{Se},\textsuperscript{225,226,230,231} Si\textsubscript{Se},\textsuperscript{225–227} Ge\textsubscript{Se},\textsuperscript{224,225,232} Sn\textsubscript{Se},\textsuperscript{224,225,232} C\textsubscript{Te},\textsuperscript{225,226} Si\textsubscript{Te},\textsuperscript{225,226,234} and Sn\textsubscript{Te}.\textsuperscript{225,234} In a plot of cohesive energies versus the bond lengths of IV–VI monolayers, we group together chemically related compounds, obtained by combining one group IV element with all other group VI elements (see Fig. 21[a]). As can be seen in Table 10, the in-plane bond lengths and those between the sublayers of the puckered structure deviate to some extent. Since longer bonds, with weaker dissociation energy, determine the stability of the network, they are taken in the plot. Based on the results discussed before for other C-containing binaries the planar structure of the carbon group should have the highest energetic stability. According to DFT calculations, however, the puckered and buckled phases have larger cohesive energies than the planar phase, as observed for the other groups.\textsuperscript{225} Note that the carbon group is clearly separated by shorter bonds from the Si, Ge, and Sn groups, which partially coincide. The puckered structure of the group IV–VI monolayers has the highest energetic stability, closely followed by the buckled phase. Besides the three carbon monochalcogenides (C group) with shorter bonds but only slightly larger cohesion, the other three related groups show a similar bonding behavior in a narrow range of cohesive energies between −3 and −4 eV per atom.

The variable contribution of ionicity plays an important role in reducing orbital overlap and thus the bonding strength of group IV–VI monolayers. Since the electronegativities of C (2.55), S (2.58), and Se (2.5) are comparable, a significant charge transfer occurs in the C group only from the Te (2.10) to the C atom. In the other groups, an opposite charge transfer
The available linear and nonlinear mechanical properties studied for the compounds CSe, SiS, SiSe, SiTe, GeS, GeSe, GeTe, SnS, SnSe, SnTe and SnTe are summarized in Table 11. The plot of Young’s modulus and strength versus bond length in Fig. 21(b) illustrates the enormous difference to the outstanding mechanical performance of covalently bonded planar graphene, carbides, and nitrides. The calculated Young’s moduli and intrinsic strengths disclose a low stiffness and fracture strength of both the puckered and buckled phases. The substantial contribution of far-reaching electrostatic forces reduces orbital overlap and thus the strength of localized covalent bonding. Certainly, the mechanical performance can be a critical problem for any practical application of these compounds. Interestingly, the stiffness and strength of Ge and Sn sulfides and selenides reveal takes place to the chalcogenide atoms, owing to the smaller electronegativities of Si (1.90), Ge (2.01), and Sn (1.96). Since the difference of the electronegativities decreases within each group, electrostatic interactions become less important with increasing atomic number. This may contribute to the characteristic inverse bonding dependence observed for these groups, where the decay of the cohesive energy decreases asymptotically with increasing bond length. The relatively small changes of atom size and electronegativity in the Si, Ge, and Sn groups explain their striking similarity in bonding energy and in their mechanical behavior.

Table 10: Space group, cohesive energy, lattice constants, bond lengths, corrugation effect, and van der Waals diameter of group IV–VI monolayers

<table>
<thead>
<tr>
<th>Monolayer</th>
<th>Space group</th>
<th>Cohesive energy, ( E_c ) (eV per atom)</th>
<th>Lattice constants ( a, b ) (nm)</th>
<th>Bond lengths ( d_1, d_2 ) (nm)</th>
<th>Pucker, buckle ( \Delta z ) (nm)</th>
<th>van der Waals diameter ( d_{w+}, d_{w-}\Delta z ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS</td>
<td>( Pmn_2 )</td>
<td>-4.37245</td>
<td>0.280, 0.43225</td>
<td>0.176, 0.183225</td>
<td>-3.91225</td>
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<td>SiS</td>
<td>( Pmn_2 )</td>
<td>-4.08225</td>
<td>0.335, 0.477225</td>
<td>0.230, 0.234225</td>
<td>-3.92225</td>
<td>0.330225, 0.232225, 0.133227</td>
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<tr>
<td>GeS</td>
<td>( Pmn_2 )</td>
<td>-3.66224</td>
<td>0.364, 0.446225</td>
<td>0.248, 0.242224</td>
<td>-3.64223</td>
<td>0.243223</td>
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<tr>
<td>SnS</td>
<td>( Pmn_2 )</td>
<td>-3.35524</td>
<td>0.405, 0.435225</td>
<td>0.273, 0.260225</td>
<td>-3.37524</td>
<td>0.262225, 0.146224</td>
</tr>
<tr>
<td>CTe</td>
<td>( Pmn_2 )</td>
<td>-3.84225</td>
<td>0.303, 0.430225</td>
<td>0.196, 0.204225</td>
<td>-3.895231</td>
<td>0.306225</td>
</tr>
<tr>
<td>SiSe</td>
<td>( Pmn_2 )</td>
<td>-3.55225</td>
<td>0.374, 0.440225</td>
<td>0.252, 0.245225</td>
<td>-3.60224</td>
<td>0.293225, 0.297225</td>
</tr>
<tr>
<td>GeSe</td>
<td>( Pmn_2 )</td>
<td>-3.37223</td>
<td>0.397, 0.430225</td>
<td>0.266, 0.254225</td>
<td>-3.38524</td>
<td>0.257225</td>
</tr>
<tr>
<td>SnSe</td>
<td>( Pmn_2 )</td>
<td>-3.28225</td>
<td>0.426, 0.445225</td>
<td>0.289, 0.273225</td>
<td>-3.57224</td>
<td>0.295225</td>
</tr>
<tr>
<td>CTe</td>
<td>( Pmn_2 )</td>
<td>-3.68225</td>
<td>0.339, 0.389225</td>
<td>0.216, 0.218225</td>
<td>-3.70224</td>
<td>0.335225</td>
</tr>
<tr>
<td>SiTe</td>
<td>( Pmn_2 )</td>
<td>-3.43225</td>
<td>0.323, 0.360225</td>
<td>0.264, 0.272225</td>
<td>-3.45224</td>
<td>0.318225</td>
</tr>
<tr>
<td>GeTe</td>
<td>( Pmn_2 )</td>
<td>-3.30225</td>
<td>0.384225</td>
<td>0.269225, 0.153223</td>
<td>-3.32724</td>
<td>0.274225</td>
</tr>
<tr>
<td>SnTe</td>
<td>( Pmn_2 )</td>
<td>-3.09225</td>
<td>0.424, 0.438225</td>
<td>0.274, 0.288225</td>
<td>-3.10924</td>
<td>0.277225</td>
</tr>
<tr>
<td>SnTe</td>
<td>( Pmn_2 )</td>
<td>-3.06225</td>
<td>0.394225</td>
<td>0.291, 0.316225</td>
<td>-3.07224</td>
<td>0.295225</td>
</tr>
<tr>
<td>SnTe</td>
<td>( Pmn_2 )</td>
<td>-2.99225</td>
<td>0.454, 0.458225</td>
<td>0.390, 0.477225</td>
<td>-3.00224</td>
<td>0.423224</td>
</tr>
</tbody>
</table>

Fig. 21: (a) Cohesive energy versus bond lengths of binary group IV–VI monolayers. (b) Young’s moduli and ultimate strengths versus bond length of binary group IV–VI monolayers.
good agreement with Griffith’s rule for the armchair direction of the puckered phase, but not for the stronger zigzag direction, where the calculated strengths are much larger than expected.

One reason for the exceptionally small stiffness and strength of these compounds is the contribution of electrostatic forces, which reduces the strength of local covalent bonding. An important consequence of this fact is the superior flexibility of GeS, SnS, and SnSe. Note that this ultrahigh flexibility occurs in the armchair direction, which is the direction with a negative out-of-plane Poisson’s ratio under uniaxial strain, as discussed below. Based on their high stretchability, these 2D materials can reversibly withstand extreme structural deformations. Under small mechanical strain, several of these semiconductors undergo an indirect-to-direct gap transition. Owing to the small elastic stiffness, a large polarization is induced by stress, which leads to piezoelectric coefficients enhanced by one-to-two orders of magnitude.

Interestingly, the three monolayers aw-GeS, aw-SnS, and aw-SnSe exhibit a negative Poisson’s ratio between the armchair (x) direction and the perpendicular out-of-plane (z) direction, whereas for aw-GeSe the auxetic effect appears between the zigzag (y) and the z direction. The different auxetic behavior of aw-GeSe is attributed to a change in the position of M and X atoms in the four sublayers of the puckered structure and the smaller bending stiffness of the M–X–M bond angle. Recent reviews give a comprehensive description of the enormous progress made by both theory and experiment in understanding this phenomenon.

Optical and electronic properties of 2D materials can be tuned by alloying compounds with little variation of the lattice parameters or by forming few-layer assemblies with variable interaction forces. The most stable AA and AB stacking orders of group IV–VI bilayers exhibit covalent-like interaction beyond van der Waals interlayer forces (see Fig. 22). A shortest distance between adjacent layers of \( d_{\text{int}} = 0.279 \) nm and an interlayer interaction energy of \(-98 \) meV per atom were obtained. For aw-GeSe also lower interlayer interaction energies of \(-52.3 \) meV per atom and \(-48.1 \) meV per atom have been reported for AA and AB stacking, with \( d_{\text{int}} = 0.303 \) nm and \( d_{\text{int}} = 0.312 \) nm, respectively. Bilayers of aw-SnS with AB stacking sequence have a shortest distance of adjacent layers of \( d_{\text{int}} = 0.291 \) nm and an interlayer interaction energy of \(-164 \) meV per atom. The interaction energy increases further for bilayers of aw-SnSe to \(-185 \) meV per atom with \( d_{\text{int}} = 0.302 \) nm for AB stacking. These results point to the preferred generation of few-layer assemblies, explaining the difficulties faced in isolating single layers by mechanical exfoliation.

The present status of preparation methods available for the synthesis of selected group IV monochalcogenides, such as mechanical exfoliation, solution-based methods, CVD, atomic layer deposition, and post-etching methods has been reviewed extensively. Even in the case of the best developed mechanical exfoliation techniques, it is difficult to control the yield, number of layers, and size of the uniform area of the fabricated nanosheets and nanoflakes. While micrometer-sized GeS sheets have been synthesized by solution-based methods, most studies used CVD techniques, for example for the synthesis of single-crystalline nanoribbons. The separation of the already-grown bilayers is difficult owing to the large exfoliation

### Table 11 Structure, Young’s modulus, Poisson’s ratio, ultimate strength, and ultimate strain of group IV–VI monolayers

<table>
<thead>
<tr>
<th>Monolayer</th>
<th>Structure</th>
<th>Young’s modulus ( E_{ac}, E_{zz} ) (N m(^{-1}))</th>
<th>Poisson’s ratio ( \nu_{ac}, \nu_{zz} )</th>
<th>Intrinsic strength ( \sigma_{ac}, \sigma_{zz} ) (N m(^{-1}))</th>
<th>Ultimate strain ( \varepsilon_{ac}, \varepsilon_{zz} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSe</td>
<td>hb</td>
<td>( 86.1, 83.3^{206} )</td>
<td>( 0.14, 0.16^{206} )</td>
<td>( 5.6, 5.9^{206} )</td>
<td>( 0.10, 0.14^{206} )</td>
</tr>
<tr>
<td>SiS</td>
<td>hb</td>
<td>( 51.3^{202} )</td>
<td>( 0.13^{202} )</td>
<td>( 0.17^{202} )</td>
<td></td>
</tr>
<tr>
<td>SiSe</td>
<td>hb</td>
<td>( 41.5^{202} )</td>
<td>( 0.17^{202} )</td>
<td>( 0.21, 0.41^{14} )</td>
<td>( 1.4, 5.2^{211} )</td>
</tr>
<tr>
<td>SiTe</td>
<td>aw</td>
<td>( 20.8–62.9^{208} )</td>
<td>( 24.4^{202,208} )</td>
<td>( 0.58, 0.43^{14} )</td>
<td>( 1.4, 5.0^{211} )</td>
</tr>
<tr>
<td>GeS</td>
<td>aw</td>
<td>( 15.5, 33.3^{209} )</td>
<td>( 13.4, 33.3^{210} )</td>
<td>( 12.5, 30.6^{209} )</td>
<td>( 12.1, 28.4^{210} )</td>
</tr>
<tr>
<td>GeSe</td>
<td>aw</td>
<td>( 12.0, 21.1^{209} )</td>
<td>( 14.2, 26.9^{209} )</td>
<td>( 14.1, 26.1^{210} )</td>
<td>( 11.0, 24.9^{206} )</td>
</tr>
<tr>
<td>GeTe</td>
<td>aw</td>
<td>( 12.0, 21.1^{209} )</td>
<td>( 14.2, 26.9^{209} )</td>
<td>( 14.1, 26.1^{210} )</td>
<td>( 11.0, 24.9^{206} )</td>
</tr>
<tr>
<td>SnS</td>
<td>aw</td>
<td>( 14.2, 26.9^{209} )</td>
<td>( 14.1, 26.1^{210} )</td>
<td>( 11.0, 24.9^{206} )</td>
<td>( 11.4, 4.2^{211} )</td>
</tr>
<tr>
<td>SnSe</td>
<td>aw</td>
<td>( 12.5, 24.8^{210} )</td>
<td>( 12.5, 24.8^{210} )</td>
<td>( 12.5, 24.8^{210} )</td>
<td>( 12.5, 24.8^{210} )</td>
</tr>
<tr>
<td>SnTe</td>
<td>aw</td>
<td>( 5.6, 12.9^{209} )</td>
<td>( 5.6, 12.9^{209} )</td>
<td>( 5.6, 12.9^{209} )</td>
<td>( 5.6, 12.9^{209} )</td>
</tr>
</tbody>
</table>

Fig. 22 The stacking orders AA and AB of bilayers of binary symmetric puckered monolayers.
energy.242 By sonication-assisted liquid phase exfoliation of bulk GeSe powders, 4–10 layer stacks of GeSe with lateral sizes >200 nm were obtained in different solvents, as characterized by SAED, HRTEM, and XPS analysis.243 While tape exfoliation and crystal growth lead to few-layer systems, the liquid-phase exfoliation method allowed the production of bilayer SnS nanosheets through size-selective centrifugation.244 The deposition of wafer-scale vertically standing SnS layers of high quality has been realized by sulfur reduction from sputtered deposition of wafer-scale vertically standing SnS layers of high valence electrons 4p4 (5p4) form two covalent bonds with their are not directly involved in covalent binding. Thus, the four 4p (5p) states, the s electrons are treated as core states, which these elements form stable 1D-like chain structures with two extra electrons are needed to reach octet stability. Accordingly, the characteristic bonding of bulk Se and Te is displayed in Fig. 24. Thehelical chains are arranged along the c-axis in a hexagonal pattern of chains and exhibit equilateral triangles in the plane perpendicular to the c-axis. The arrangement of the chains is controlled by the interaction of the lone-pair electrons and interchain van der Waals interaction. Several stable monolayers and few-layer systems can be formally derived by cuts through low index planes, e.g., (0001) and (10–10), by cleaving the bulk either perpendicular or parallel to the chain direction, respectively.

One of the most stable (2D) phases is the helical-chain or trigonal phase, which may be considered as a dimension-reduced bulk phase (see Fig. 25(a)). Another stable configuration is the tetragonal phase with mirror-plane and rectangular unit cell that originates from a helix-to-layer transformation process of the trigonal monolayer. It is composed of deformed four-membered and deformed six-membered rings with the coordination number 4 for the central and 3 for the outer atoms, as illustrated in Fig. 25(b). The rhombic phase with 1T-MoS2-like structure is a three-layer structure with coordination number 6 of the central atom and 3 for the atoms in the lower and upper layers, as displayed in Fig. 25(c). Finally, the low-symmetry monoclinic phase forms a chair-like buckled structure as silicene, however, with a square unit cell instead of a hexagonal one (see Fig. 25(d)).

Unfortunately, the currently used nomenclature using Greek letters is not standardized and introduces confusion. Therefore, symmetry elements and space groups are employed here to unambiguously classify individual phases. Note that the rhombic phase, for example, is named χ-phase, γ-phase, and T-phase in the literature.246–248 In the following, the thickness direction is defined as the z-direction, and the chain direction is defined as the y-direction for the chain-like and tetragonal phases, whereas for the rhombic phase the y-direction extends

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**Group VI monolayers**

**Elemental monolayers.** The most-stable bulk structures of the chalcogens selenium and tellurium consist of quasi-1D helical chains of covalently bonded atoms with strong directional bonding, held together by weaker van der Waals and covalent-like forces in a hexagonal array.246 With just two bonds these atoms are not qualified to play an important role in 2D materials science. However, owing to variable oxidation states (−2 and +6), chemical bonding is not restricted to low-dimensional chains. Based on the multivalent nature of these elements with metallic and nonmetallic character, several stable and metastable 2D phases have been discovered that differ from honeycomb or buckled honeycomb structures and have unique symmetry and characteristics. However, controversial discussions are still going on concerning the existence, dynamics, and thermal stability of various phases derived by global structural searching combined with first-principles calculations.246

The two chalcogenide atoms Se and Te have an electron configuration with six valence electrons in the outer shell, explicitly Se (4s24p4) and Te (5s25p4), and therefore only two extra electrons are needed to reach octet stability. Accordingly, these elements form stable 1D-like chain structures with two covalent bonds. Based on the large separation of the 4s (5s) and 4p (5p) states, the s electrons are treated as core states, which are not directly involved in covalent binding. Thus, the four valence electrons 4p1 (5p1) form two covalent bonds with their direct neighbors arranged in a chain and a lone pair of the remaining p electrons. Since this configuration is threefold degenerate, helical chains with a helical turn of 120° are formed (see Fig. 23). Based on the transition from the nonmetal S to metal Po in group VI, of the two metalloid elements selenium and tellurium the latter is more metallic in nature. This fact is responsible for a stronger delocalization of electrons in the interchain region of tellurene, with an interaction that is sometimes called ‘covalent-like,’ because it is stronger than van der Waals interaction in selenene.

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**Fig. 23** Scheme of degenerate electron configurations of group VI elements with six valence electrons.

**Fig. 24** Bulk structure of Se and Te with helical chains oriented in the z-direction assembled in a hexagonal arrangement. Two low-index crystal planes are indicated to illustrate possible cuts.
along the armchair direction, due to the loss of the original chain structure by reconstruction.247

The space group, cohesive energy, lattice constants, bond length, corrugation, and layer thickness of the trigonal,246,248–250 tetragonal,246,251,252 rhombic,245,248,252–254 and monoclinic224,249 structures of selenene are presented in Table 12, along with the bonding information and structural properties of the trigonal,247,250,255,256 tetragonal,247,255 rhombic,252–255 and monoclinic249 structures of tellurene. This data makes possible a discussion of bonding–structure–performance relationships for these recently discovered 2D materials with novel structures deviating from previous hexagonal 2D materials. In Fig. 26(a) the cohesive energies of the four allotropes of selenene and tellurene are plotted versus bond length, including the short and the longer interchain bond lengths of the trigonal bulk phases. Surprisingly, quite different atomic arrangements of selenene and tellurene have comparable cohesive energies in the narrow range of \(-2.5\) to \(-2.8\) eV per atom. Despite the longer covalent bonds of the tellurenes, the cohesive energies of the polymorphs are only slightly smaller. The anisotropic structure of bulk and few-layer assemblies of helical-chain selenene and tellurene is characterized by two strongly deviating atom spacings. For the trigonal Se bulk structure, the length of covalent intrachain bonds is 0.243 nm and for interchain interaction between neighboring chains it is 0.334 nm with a cohesive energy of \(-2.88\) eV per atom.250 In the case of the trigonal Te bulk structure, the difference of the two bond lengths of 0.290 nm and 0.342 nm is much smaller and the cohesive energy is \(-2.71\) eV per atom.250 For a single layer of the trigonal Te phase, the theoretical bond lengths are 0.278 nm and 0.304 nm.256 In the layered covalently bonded tetragonal and square phases, these large differences in the bond lengths are reduced, and in

<table>
<thead>
<tr>
<th>Table 12</th>
<th>Space group, cohesive energy, lattice constants, bond lengths, corrugation, and van der Waals diameter of group VI monolayers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolayer, structure</td>
<td>Space group</td>
</tr>
<tr>
<td>Selenene Trigonal chain-like</td>
<td>(P2_1)</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>(Pm1)</td>
</tr>
<tr>
<td>Rhombic</td>
<td>(Cm)</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>(Cm)</td>
</tr>
<tr>
<td>Tellurene Trigonal chain-like</td>
<td>(P2_1)</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>(Pm1)</td>
</tr>
<tr>
<td>Rhombic</td>
<td>(Pm1)</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>(Cm)</td>
</tr>
</tbody>
</table>
the layered rhombic phase, the difference reduces to zero, leaving just a single bond length.

The observation of quasi the same cohesive energy for monolayer and bulk phases with widely varying bonding types seems to be a unique performance of the two chalcogenides Se and Te. The increasing metallic character and delocalized interchain interaction of electron lone pairs may be the reason for a comparable cohesion of the Se and Te phases with 1D-like helical chains. In the 2D networks of trigonal, tetragonal, rhombic, and monoclinic monolayers, multivalency of the two elements plays an important role and allows the realization of distinct structures with nearly the same cohesive energy (‘multiple structures with similar cohesion’). This is achieved by varying a pair of bond lengths in the low-symmetry structures in such a way that their mean bond energy approaches that of the single bond of the corresponding high symmetry structure. Of course, this does not imply a similar ultimate strength. However, the comparable cohesive energies make transformation between these phases possible even by thermal energy and by adsorption at surfaces. It seems that the activation barrier of the transition from helix to layer phases can be easily overcome. Thus, several stable allotropes may co-exist, especially at higher temperatures. Moreover, helix-to-layer transformations from 1D trigonal to 2D tetragonal phases can be induced by mechanical strain.

The currently available mechanical properties, which are limited to tetragonal and rhombic selenene and tellurene as well as trigonal, tetragonal, and rhombic tellurene, are shown in Table 13. The dependence of the Young’s moduli and ultimate strengths on the bond lengths of the tetragonal and rhombic structures of selenene and tellurene is presented in Fig. 26(b). These are two strong layered phases with covalent bonding in both in-plane directions. The Young’s moduli of rhombic selenene of 59 N m⁻¹ and rhombic tellurene of 44.5 N m⁻¹ exhibit the largest stiffness. The intrinsic strengths of the rhombic phases mostly follow Griffith’s rule. With its smaller stiffness and larger Poisson’s ratio, rhombic tellurene is softer and more flexible than rhombic selenene (see Table 13). The maximum stiffnesses of anisotropic tetragonal selenene and tellurene are 31 N m⁻¹ and 20.4 N m⁻¹ respectively. While for the rhombic phase the ultimate strengths agree with the E/10 rule, this is not the case for tetragonal tellurene. Due to weak interchain forces the stiffness of the trigonal phases is much smaller; for example, for tellurene the stiffness of the monolayer extrapolated from the calculated few-layer values is <10 N m⁻¹.

It is worth noting that rhombic selenene with its 1T-MoS₂-like structure is about a factor of three softer than the well-studied MoS₂ monolayer, with a measured stiffness of 166 N m⁻¹ for biaxial tension and a calculated mean stiffness of 131 N m⁻¹ for uniaxial tension. Interestingly, the elastic moduli of the two rhombic phases reach the mechanical performance of their group V neighbors in the periodic table, arsenene and antimonene, which possess a graphene-like network. The reason for the higher modulus of the rhombic phase is that in this 2D network any in-plane strain causes an extension of chemical bonds, while the buckled structure of the tetragonal phase allows stretching in the armchair direction without extending covalent bonds but flattens the structure under low strain conditions. As discussed above, the stiffness decreases further for the chain-like-phases.

Table 13  Structure, Young’s modulus, Poisson’s ratio, ultimate strength, and ultimate strain of group VI monolayers

<table>
<thead>
<tr>
<th>Monolayer, structure</th>
<th>Young’s modulus Eₜₜₑₜ (N m⁻¹)</th>
<th>Poisson’s ratio νₑₜₑₜ</th>
<th>Intrinsic strength σₑₜₑₜ (N m⁻³)</th>
<th>Ultimate strain εₑₜₑₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selenene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetragonal</td>
<td>5.4, 31²⁵¹</td>
<td>-</td>
<td>0.27, 0.25²⁵²</td>
<td>4.6, 6.6²⁵⁴</td>
</tr>
<tr>
<td>Rhombic</td>
<td>59.²⁵², 55.¹⁵³</td>
<td>0.27, 0.25²⁵²</td>
<td>4.6, 6.6²⁵⁴</td>
<td></td>
</tr>
<tr>
<td>Tellurene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetragonal</td>
<td>11.6, 20.4²⁵⁹</td>
<td>0.29, 0.49²⁵⁹</td>
<td>4.6, 6.6²⁵⁴</td>
<td></td>
</tr>
<tr>
<td>Rhombic</td>
<td>44.5,²⁵², 44.5²⁵⁹</td>
<td>0.29, 0.28²⁵⁸</td>
<td>4.6, 6.6²⁵⁴</td>
<td>5.2, 5.5²⁵⁸, 0.26, 0.3⁰²⁵⁸</td>
</tr>
</tbody>
</table>
Despite a crop of interesting first results, up to now the study of few-layer systems has not attracted much attention. For example, 2D ferroelectricity in elemental tellurium multilayers is expected to occur by spontaneous in-plane polarization due to interlayer interaction between the lone pairs of electrons that can be preserved for bilayers above room temperature.\textsuperscript{260} It is worth mentioning that not only group IV and group V Xenes with honeycomb structure but also group VI selenene and tellurene with square structure are promising topological insulators, hosting nontrivial QSH states. Meanwhile the growth of monolayer tellurene has been achieved by an anisotropic ultrasonication process and evidence of topological insulator behavior has been observed using scanning tunneling spectroscopy (STS) by detecting the insulating interior and the metallic edge states.\textsuperscript{261}

Current interest in selenene and tellurene is based on their favorable properties, such as strong optical absorption, high carrier mobilities, excellent thermoelectric performance, piezoelectricity, high stretchability, and good environmental stability.\textsuperscript{262,263} While to date detailed studies on interlayer bonding and structure of few-layer assemblies are lacking, such sheets have been attained experimentally. By liquid-phase exfoliation (LPE) 2D Se sheets of the trigonal bulk chain-like structure with 40–120 nm lateral dimension and 3–6 nm thickness could be exfoliated by sonication.\textsuperscript{264} Physical vapor deposition (PVD) has been employed to grow high-quality Se nanosheets with large size, a minimum thickness of 5 nm, and strong in-plane anisotropy.\textsuperscript{265} Few-layer assemblies derived from the α-Se and α-Te bulk phase are stable, whereas the trigonal monolayers transform to the tetragonal phase.\textsuperscript{263}

Diverse methods such as LPE and PVD have been applied to deposit tellurene but free-standing single layers have not been realized. Monolayer and few-layer tellurene have been grown by MBE on graphene/SiC substrates\textsuperscript{266} and HOPG,\textsuperscript{267} which were analyzed by STM/STS. For ultrathin layers, the cell size was consistent with the predicted rectangular surface cells of the tetragonal phase, whereas for thicker films the detected structure agreed better with the (10–10) surface of the trigonal bulk crystal (α-Te),\textsuperscript{267} as theoretically predicted.\textsuperscript{255} For 2D nanoflakes of tellurene a comprehensive review exists, which covers the superior physical properties, synthesis techniques, practical applications, and fabrication of nanodevices.\textsuperscript{268} A comprehensive review treats the preparation methods, electrical properties, and device applications of group VI materials.\textsuperscript{269}

### Summary

The extensive data presented above for chemically related groups of monolayers gives a clear picture of bonding, structure, and resulting mechanical stability of the main group II–VI elements and their binary compounds. As summary, Fig. 27(a) offers an overview of the bonding behavior of the considered columns of the periodic table. This plot shows graphene as a monolayer with limiting properties, such as the largest cohesive energy and the shortest bond. Besides graphene, the strongest compounds belong to the planar structures with a steep decay of cohesive energies versus bond length. These are the homonuclear and heteronuclear compounds with a small atom from the second row of the periodic table (B, C, N). The dependence of the other monolayers with a buckled or puckered structure is characterized by a much faster increase of bond length and an asymptotically decreasing cohesive energy. The plot supports the marked inverse dependence of the bonding energy on the bond length for 2D materials, as predicted by tight-binding theory. A coinciding decay of cohesive energies is postulated for elemental and low polarity binary monolayers of group IV and group V elements. Conversely, the elemental monolayers of group IV and group V have larger cohesive energies and bond energies than their isoelectronic counterparts. Generally, an increase of the bond length by a factor of two causes a decrease of the bonding energy by a factor of about four, owing to the strong reduction of orbital overlap. The revealed

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**Fig. 27** (a) Overview of cohesive energies of group II–VI elemental and binary monolayers as a function of bond length. (b) Overview of the Young's moduli of group II–VI elemental and binary monolayers as a function of bond length.
relationships offer useful guidance for future theoretical and experimental studies.

Additionally, Fig. 27(b) displays the Young’s moduli of the studied monolayers, as a function of their bond lengths. Interestingly, the stiffness of all related groups follows the same characteristic inverse behavior, at least in the stiffest direction. Note the extremely small Young’s moduli of the strongly anisotropic puckered group V compounds in the armchair direction. Only the plane borophene phases and the rhombic configuration of selene and tellurene deviate slightly from the general dependence. Remarkable is the extreme variation of the Young’s modulus from 340 N m\(^{-1}\) to values below 10 N m\(^{-1}\). This demonstrates the enormous sensitivity of stiffness on bond energy that varies by less than a factor of four. Owing to the quite limited data reported for the ultimate strength, this information has not been included in Fig. 27(b) but is given only in the individual plots. At least for some directions the ultimate strength follows Griffith’s rule and thus correlates with the stiffness.

### Outlook

The extensive results presented here provide an up-to-date picture of calculated intrinsic bonding and mechanical properties of stable elemental and binary 2D materials of main group elements with fully occupied or blocked d orbitals, where only s and p electrons contribute to bonding. The large variation of the configuration of valence electrons dictates the possible types and strengths of bonding. In principle, in-plane bonding forces consist of normally predominant covalent and ionic interaction, where the latter long-range forces are not favorable for binding 2D structures.\(^{276}\) For specific groups conflicting results could be easily recognized and existing gaps were closed using the revealed relationships. Cohesive energies deviating be a factor of two or more have been excluded primarily based on their mechanical behavior. For the heaviest elemental monolayers of strontium, thallium, lead, and bismuth and their binary compounds not only experimental but also theoretical data on mechanical performance is missing. First reasonable estimates can be obtained by extrapolating the presented dependencies of mechanical properties on bond length. Note that for these compounds the low mechanical stability may be a crucial issue.

Experimental verification of the extensive theoretical findings is still widely missing. It seems that it is possible to measure intrinsic properties of 2D materials, however, this has been achieved only in a few selected cases. Measurements of the inherent stiffness and ultimate strength, e.g., by AFM nanoindentation, are available for quasi freely suspended graphene, while the results for most other monolayers such as graphene oxide, h-BN, black P, transition metal-dichalcogenides such as MoS\(_2\) and WSe\(_2\), and MXenes are still preliminary.\(^{16,271,272}\) Besides the problem of preparing a perfect suspended monolayer uncertainties are due to the interpretation of the experimental data by simple mechanical models. Furthermore, it has been shown that ripples on suspended monolayers may have profound effects on the measured in-plane modulus. Notably, the calculated intrinsic properties can serve as a criterion to judge the quality of real defective samples studied experimentally.

An important issue that has not yet found the necessary attention is the change of mechanical properties induced by the ubiquitous interaction of monolayers with substrates during preparation, manipulation, and service. While van der Waals forces may preserve the intrinsic monolayer properties stronger covalent-like and ionic interactions can change the bond length and bonding energy and therefore may modify the fundamental mechanical and electronic properties. Here quantitative data is urgently needed.

Large area samples inevitably contain defects and the effects of prevailing defects have been studied theoretically only for selected 2D materials. While the ultimate strength, already studied in detail, is defined as the maximum stress a material can sustain in the absence of defects, the behavior of defective samples is described by the fracture toughness. Toughness values, which describe the ability of a material containing a crack to resist failure, are rare and seem to be restricted to graphene. Since graphene is brittle, its toughness is not an outstanding property as stiffness and strength.\(^{277,273}\) Its estimated toughness is largely independent of small nanometer defect sizes, whereas for larger defect sizes the experimental values increase as expected for non-ideal micrometer-sized crack paths.\(^{37}\) It is important to note that by intentionally introducing toughening mechanisms, for example, by proper manipulation of grain boundaries or effective use of interacting microdefects fracture resistance could be significantly improved.\(^{273}\)

Besides the homonuclear, heteronuclear, and isoelectronic binary compounds considered here, all elements can be mixed in new combinations and stoichiometries, which represents an additional chemical parameter. Already known structures can be used to predict new ones by the method of ‘atomic transmutation’ by changing an element in the periodic table into its neighboring elements while keeping the total number of valence electrons constant. Furthermore, binary structures, consisting of other combination of main group elements such as II–VI, III–VI, IV–V, or V–VI, with stable MX and M\(_2\)X\(_3\) phases, have been studied, thorough characterization, however, often is still missing.\(^{274,275}\) For example, only first results on the structure of three energetically stable phases are available for group III–VII compounds, which are isoelectronic to group V semiconductors.\(^{276}\) Besides different stoichiometries, chemistry allows the grouping of more than two elements to realize a plethora of chemical bonding types and structural arrangements, e.g., in ternary or quaternary 2D materials.\(^{277}\)

Besides compounds of main group elements\(^{278}\) transition metal-dichalcogenides (TMDs), with partially empty d orbitals, such as the semiconductors MoS\(_2\) and WS\(_2\), have already attracted enormous attention.\(^{277}\) Furthermore, layered transition metal oxides (LTMO), layered halide perovskites, and layered double hydroxides (LDHs) belong to emerging 2D materials.\(^{280}\) Analogous to SiC and SiN with excellent mechanical and optical
properties the family of MXenes, consisting of 2D transition metal carbides and nitrides, has found increasing interest. Mostly, MXenes contain functional groups such as fluorine, hydroxyl, and O2 and are endowed with beneficial electronic, magnetic, and optical properties. The extension of this large family to borides is under way. Besides monolayers the development of multilayer assemblies with hybrid/hierarchical structures opens innovative avenues to realize presently unknown 2D materials with novel tailored properties. Unfortunately, present approaches employed to treat the crucial properties such as the interlayer interaction energy show large deviations due to difficulties of theory treating the simultaneous action of quite different forces such as weak van der Waals interaction and strong covalent bonding. Since interlayer binding forces strongly influence not only the interlayer separation but also the electronic properties of multilayers and heterostructures this is a crucial point. Importantly, the observed deviations of literature values are often larger than a factor of about two found for the calculation of the cohesive binding energy of monolayers. Since the sources of these discrepancies are not understood improved approaches must be developed. Thorough understanding of interlayer interaction will be the key for using heterostructures as building blocks with the perspective of engineering functional materials with high performance, e.g., transistors, sensors, and photocatalysts.

Conflicts of interest

There are no conflicts to declare.

References


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