Synthesis and chemistry of elemental 2D materials

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Abstract | 2D materials have attracted considerable attention in the past decade for their superlative physical properties. These materials consist of atomically thin sheets exhibiting covalent in-plane bonding and weak interlayer and layer–substrate bonding. Following the example of graphene, most emerging 2D materials are derived from structures that can be isolated from bulk phases of layered materials, which form a limited library for new materials discovery. Entirely synthetic 2D materials provide access to a greater range of properties through the choice of constituent elements and substrates. Of particular interest are elemental 2D materials, because they provide the most chemically tractable case for synthetic exploration. In this Review, we explore the progress made in the synthesis and chemistry of synthetic elemental 2D materials, and offer perspectives and challenges for the future of this emerging field.

2D materials are atomically thin sheets that exhibit unique electronic, optical and mechanical properties with remarkable potential for technological applications and a plethora of unexplored fundamental science. For example, graphene is the prototypical 2D material, exhibiting high charge carrier mobilities, chemical inertness and high mechanical strength1,2. So far, most conventional 2D materials have been derived from a limited library of bulk solids consisting of stacked, weakly bound sheets (for example, graphite, MoS2, hexagonal boron nitride and black phosphorus). The relatively small number of bulk layered materials intrinsically limits the range of structures and properties accessible from 2D materials, reducing opportunities to realize materials by design. By contrast, the growth of entirely synthetic 2D materials4 — those without bulk analogues — expands the variety of materials with new, tailorable properties based on their composition and substrate.

Although many bulk materials exhibit layered structures with quasi-2D characteristics, 2D materials are defined here as those composed of one to several (generally, 10 or less) discrete, atomically thin layers that are weakly interacting, often through van der Waals forces. Unless specified otherwise, we will refer to monolayers, bilayers and so on based on the discrete number of well-differentiated, contiguous layer structures, rather than the number of atoms at a given height in the structure (although the latter is sometimes encountered in the literature). The superlative physical properties of 2D materials arise from the intrinsic chemical properties of their constituent elements, which are incorporated into covalently bonded structures of particular symmetry and low (that is, 2D) dimensionality. The chemically simplest cases exist in elemental 2D materials, of which two are known to also occur in bulk layered form: graphene and 2D black phosphorus. Graphene is composed of a honeycomb network of sp2-hybridized carbon atoms. The resulting electronic band structure exhibits a gapless, linear dispersion, causing the charge carriers to be effectively massless. Furthermore, the strong C–C bonds in pristine graphene result in its high mechanical strength, and the absence of dangling bonds in the basal plane results in chemical inertness. The numerous demonstrations of these superlative properties have been comprehensively reviewed in the literature4-6. The study of 2D black phosphorus (or phosphorene, in the monolayer case) is a more recent development and is discussed in further detail later. However, the limited number of elemental 2D materials in bulk form highlights the importance of moving beyond naturally occurring materials.

This Review focuses on synthetic elemental 2D materials (SE2DMs) discovered after graphene that are conceivably amenable to isolation from the growth substrate (including black phosphorus or phosphorene), which is not naturally occurring and was isolated in 2D form recently). Such isolation demonstrates that the in-plane bonding is stronger than the out-of-plane interactions, which is an essential aspect of SE2DMs. Furthermore, because SE2DMs have strong in-plane bonding, the range of possible constituent elements is narrowed to those with a propensity to form strong covalent bonds (that is, metalloids and non-metallic elements), as shown
in Fig. 1. As defined here, SE2DMs do not include atomically thin alkali films, transition metal films and surface reconstructions, which deserve separate consideration. When appropriate, this Review highlights concepts from the graphene literature that are relevant to the synthesis of SE2DMs.

SE2DMs have presented different challenges in synthesis, characterization and utilization compared with graphene. Atomically thin materials are synthesized by two broad methodologies: isolation from bulk solids or bottom-up synthesis (Box 1). The former is widely used through micromechanical cleavage. By contrast, bottom-up synthesis is not limited to materials derived from layered structures but requires pristine conditions and precise control over the resulting layer thickness. Several techniques satisfy these criteria, including physical vapour deposition (PVD), chemical vapour deposition (CVD), and surface decomposition and/or segregation (Box 1). The synthesis methods that have been demonstrated for each of the SE2DMs under consideration are summarized in Fig. 1.

Unlike graphene, the SE2DMs discussed in this Review are not derived from stable, naturally occurring bulk allotropes (with the exception of black phosphorus, which is not particularly stable nor naturally occurring). Thus, SE2DMs necessitate particularly comprehensive structural characterizations, which is challenging in the limit of substrate-supported monolayers. For example, structures such as surface alloys and subsurface precipitates are readily confused for 2D materials, especially when using probes that lack chemical specificity. Compounding this issue, SE2DMs are generally unstable in ambient atmosphere, which constrains the conditions for their synthesis, processing and characterization. This Review explores these constraints in detail, thus providing guidance for continuing efforts to grow and use SE2DMs in fundamental studies and applied technologies.

Following an overview of synthesis techniques, this Review covers predictions and experimental results for individual SE2DMs, organized by their periodic table group. For each material, we present the theoretical or computational predictions for its structure and properties, followed by a summary of its synthesis and characterization. We then discuss the ambient stability of the material and methods to modify its chemical properties, and conclude with an overview of the general outlook for the field, along with its challenges and opportunities.

Group III
Boron

Predicted structure and properties. Boron is among the most chemically complex elements owing to its trivalent electronic configuration. This prevents fulfillment of the octet rule, leading to anomalous 'electron poor' bonding configurations. As a result, electrons in boron and its compounds are often delocalized between three (or more) atoms. In a pure bulk phase, this complexity yields intrinsic geometric frustration between crystalline structures and results in between 5 and 16 different polymorphs, often with highly complex unit cells. This structural diversity is less evident at the atomic scale, in which boron atoms form small, quasi-planar clusters with an aromatic electronic structure analogous to hydrocarbons. The clusters are generally composed around a hexagonal B structural motif, which gains vacancies (that is, unoccupied sites at the centre of the B unit) and curvature with increasing size, eventually forming cage-like boron fullerenes.

First-principles calculations have predicted structures for several nanoscale boron allotropes, including a diverse range of sheets and nanotubes. For the sake of simplicity, we refer to the general class of 2D boron sheets as borophene. The earliest studies considered relatively simple borophene structures, such as close-packed frameworks and graphene-like honeycombs. The inclusion of out-of-plane buckling further minimizes the energy of single- and bilayer borophene, bringing these more stabilized structures in closer agreement with the puckered structure of B, and other small clusters. Generally, these structures are predicted to be metallic or semi-metallic, with several exhibiting Dirac fermion charge carriers, similarly to graphene and silicene. Another promising structural model involves introducing ordered patterns of vacancies in a flat triangular lattice, with several exhibiting freestanding boron clusters tend to exhibit hexagonal vacancies. The proposed holey sheets are predicted to exhibit high thermal stability and metallic character, in contrast with the buckled triangular lattice. However, the formation of vacancies throughout the sheet lends itself to numerous nearly degenerate configurations, which increase the likelihood for structural complexity. These studies have considered borophene supported
on a range of substrates, leading to the conclusion that noble metals, such as copper, silver and gold, are most likely optimal for the growth of the hexagonal vacancy model. The stability of a 2D boron sheet suggests that boron nanotubes may also be constructed from borophene. These nanotubes are predicted to exhibit electrical conductivities that may exceed those of metallic carbon nanotubes, which could lead to improved transparent conductors or allow nanoscale interconnects to carry more current.

**Synthesis and characterization.** Despite the considerable interest in borophene and boron nanotubes, borophene synthesis has proven elusive. This is in part due to the tendency of boron to oxidize under ambient conditions, thus complicating chemical and structural analysis. Furthermore, boron forms carbides and intermetallic compounds in the presence of trace impurities. Early reports of the formation of single- and multiwall boron nanotubes by CVD demonstrated that these may feature a borophene-like atomic structure. However, the atomic-scale structure of boron nanotubes has not yet been determined, and their exposure to air leads to carbon and oxygen contamination. Recently, a new ultrathin boron phase was synthesized on copper foil by CVD from a solid precursor, exhibiting a structure derived from bulk γ-B. This phase exhibits an optical bandgap of ~2.25 eV, which is consistent with the phase being a direct bandgap semiconductor. However, this result contrasts with the predicted properties of the material, which point to the borophene being metallic in character. Moreover, the proposed structure is more consistent with the growth of an ultrathin bulk-like structure than with a distinct nanoscale allotrope. As a result of exposure to...

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**Box 1 | Synthesis methods and considerations**

2D materials are typically obtained by three different techniques — micromechanical cleavage, physical vapour deposition (PVD) and chemical vapour deposition (CVD) — as reported in the figure. Micromechanical cleavage (that is, the so-called Scotch tape method) involves exfoliation of single- and few-layer sheets from bulk crystals. This method affords crystalline samples that are ideal for micrometre-scale electronic and optical devices. Recent advances in exfoliation techniques have allowed researchers to selectively isolate, shape and stack sheets with controlled thickness and orientation. However, micromechanical cleavage is labour intensive and limited to materials with a layered, bulk allotrope (for example, graphite exfoliation into graphene). The scalability of this approach is dramatically enhanced through solution-based exfoliation techniques that generate large quantities of suspended 2D flakes at the expense of flake size.

PVD uses a heated atomic source to controllably deposit a material on a substrate. For the growth of synthetic elemental 2D materials (SE2DMs), PVD generally requires ultrahigh vacuum (UHV) conditions and well-calibrated, high-purity atomic sources. Samples prepared under UHV conditions can be studied in situ with surface sensitive techniques to preserve the pristine state of the material.

CVD utilizes the decomposition or reaction of gas, liquid or solid precursors under a controlled atmosphere to grow 2D materials. For CVD, catalytically active substrates are generally most effective, and synthesis can be performed at pressures ranging from atmospheric to UHV. The growth mechanism varies between substrates: those with low precursor insolubility may catalyse the self-limiting growth of atomically thin films, whereas other substrates dissolve significant amounts of the precursor that segregate to the surface upon cooling. Surface decomposition or segregation utilizes solid-state precursors incorporated on the growth substrate. Growth occurs when the substrate is heated enough to activate sublimation or diffusion processes, producing a surface layer enriched with the precursor element that then condenses as a 2D phase. The substrate choices are limited to those that contain the precursor element, such as the synthesis of epitaxial graphene on SiC. Additionally, it is possible to begin with a heterogeneous thin film (10–100 nm thickness) on a precursor substrate, the heating of which facilitates a diffusion-based segregation process.

Substrate interactions are vital to the growth of 2D materials and can tune the properties of the material through strain, symmetry and chemical interactions. Bottom-up synthesis is often highly dependent on the growth substrate, which must be carefully selected for compatibility with the desired 2D overlayer. When strong interactions exist between the substrate and the film, the lattice constants (and symmetry) of each must match, resulting in a crystallographically well-defined structural relationship. Weakly interacting substrates (that is, those without dangling bonds) support van der Waals epitaxy, which is nominally free from lattice matching and symmetry constraints.

Chemical compatibility between the overlayer and the substrate is further dictated by the synthesis methodology. Solubility is generally undesirable for some methodologies (such as PVD or self-limiting CVD). In most scenarios, compound formation between precursors and the substrate is detrimental to growth. These factors are complicated by the potential synthesis of metastable or non-equilibrium phases, which may be stabilized by interactions with specific substrates. Furthermore, the ultimate properties of the atomically thin film are often determined by its interaction with the substrate, which may necessitate removal from the substrate for applications or further characterization. Panels a and b are adapted from Ref. 182.
Ultrahigh vacuum
Pressures less than \( 10^{-9} \) mbar (that is, \( 10^{-9} \) mbar or \( 10^{-9} \) torr), at which the rate of atomic impingement is low enough to preserve atomically clean surfaces for highly reactive samples.

\( n \)-Fold symmetry
A term to denote the degree of rotational symmetry of a 2D material with respect to the normal direction of the substrate or material basal plane. The number of equivalent rotational configurations is denoted by \( n \) (for example, triangles, squares and hexagons have 3, 4 and 6-fold symmetry, respectively).

Air, the phase described in this report was likely to be partially oxidized\(^4\), but, nevertheless, the large-area preparation represents an encouraging advance in the scalable synthesis of 2D boron structures.

From these early efforts, it is clear that the principal challenges associated with borophene synthesis are contamination, source purity and substrate compatibility. Recently, two independent studies addressed these issues, involving borophene synthesis by ultrahigh vacuum molecular beam epitaxy (UHV MBE) using a high-purity, solid boron-based atomic source on Ag(111) substrates\(^{44,45}\). The UHV environment minimized oxidation and adventitious carbon adsorption, while the Ag(111) substrate provided a flat, atomically clean and chemically inert surface for boron growth\(^4\). Mannix et al.\(^4\) observed two distinct borophene structures (Fig. 2a,b), which are identified as the striped and homogeneous phases. Both phases have highly anisotropic structures with \( n \)-fold symmetry (\( n = 2 \)). The striped phase (Fig. 2c) consists of regions with prominent stripe features that are structurally commensurate with areas of a rectangular lattice. The homogeneous phase (Fig. 2d) is composed of chain-like atomic-scale features that are buckled vertically out-of-phase with respect to their neighbours. Feng et al.\(^4\) observe similar phases, which they referred to as S1 and S2 phases. The S1 phase exhibits essentially the same periodicity and appearance as the rectangular lattice in the striped phase described before, while the S2 phase is identical to the homogeneous phase that Mannix et al.\(^4\) reported. These early works propose different structural models for borophene. Mannix et al.\(^4\) initially suggested that the rectangular lattice in the striped phase can be described by a buckled triangular lattice with slight distortions along the buckled rows. The other phases were proposed to arise from regular perturbations of the buckled triangular lattice, or a similar structure, occurring due to substrate interactions and phonon instabilities. By contrast, Feng et al.\(^4\) propose that the S1 and S2 structures correspond to the \( \beta_{12} \) and \( \chi \) structures\(^{29}\), respectively (Fig. 2e). These models are based on simulations that relax the flat triangular lattice with periodic vacancies on a substrate (that is, \( B_{12-x}x \)), where \( x \) denotes a vacancy and \( x \) is the fraction of sites that are vacant; when \( x = 1/6 \) and 1/5, the phases \( \beta_{12} \) and \( \chi \) are obtained, respectively\(^{33,36}\). Both proposed models give rise to simulated scanning tunnelling microscopy images in agreement with experimental data. In the freestanding case, the buckled triangular lattice\(^4\) is less energetically favourable than the structures featuring vacancies\(^2\). Further experiments are needed to disambiguate the structure models for these phases. For supported borophene, a recent computational and experimental study\(^4\)...

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**Figure 2 | Borophene.** a | Topography imaged by scanning tunnelling microscopy (STM) of mixed-phase borophene growth, where the white and blue arrows denote homogeneous and striped phase regions, respectively. b | closed-loop dI/dV (where I is current and V is voltage) map (or local density of states (LDOS) map) of the same mixed-phase borophene growth, with white and blue arrows denoting homogeneous and striped phase regions, respectively. c | Atomically resolved STM topography image of striped phase, in which prominent stripe features structurally commensurate with rectangular lattice regions (inset; where a and b represent the lattice vectors) are visible. d | Atomically resolved STM topography image of homogeneous phase. e | Atomic structure for proposed borophene models\(^{29}\). Here, \( \nu \) denotes a vacancy: when the fraction of sites that are vacant is 0 (\( \nu \)), a buckled triangular structure is obtained (left). If the fraction of vacant sites is 1/6 (\( \nu_1 \)) and 1/5 (\( \nu_2 \)), the phases \( \beta_{12} \) (centre) and \( \chi \) (right) are obtained, respectively. Panels a–d are adapted with permission from REF. 44, AAAS.
suggests that the undulating features in the striped phase are explained by the \( v_{\text{ss}} \) (or \( \beta_s \)) structure model, which reconstructs the underlying Ag(111) surface owing to a combination of anisotropic mechanical stress and chemical binding.

Most computational predictions agree that borophene should exhibit metallic or semi-metallic characteristics\(^{31–35}\), regardless of its exact atomic structure. To measure intrinsic borophene properties, the separation and transfer of the 2D material from the growth substrate, and/or the growth of the material on semiconductor or insulating substrates, is required. Two reports of borophene synthesis and STM characterization suggest the film has metallic characteristics\(^{34,41}\). Subsequent angularly resolved photoemission spectroscopy (ARPES) results\(^{43}\) confirm that the sheets are metallic in character, in line with the calculations. Furthermore, several studies predict that borophene is a relatively high temperature superconductor\(^{44–50}\), which is consistent with observations of superconductivity in the high-pressure, metallic phase of bulk boron\(^{51,52}\).

**Chemistry.** Because borophene synthesis was reported only very recently, its chemistry is still largely unexplored experimentally. Borophene has been found to rapidly degrade in air\(^{44,45}\), a reaction that can be slowed by depositing a thin (1–5 nm), amorphous silicon capping layer under UHV\(^{44}\). Furthermore, borophene reacts relatively slowly with oxygen under UHV conditions\(^{45}\), suggesting that the degradation is accelerated by water or other species in the air\(^{40}\). Chemically modified boron derivatives, such as 2D boron hydrides, are predicted to be stable and to host massless Dirac fermions\(^{53}\). It is also possible to dope borophene structures with a low concentration of metal atoms\(^{44}\), however, the effects of these modifications on the ambient stability of borophene are unknown.

**Group IV**

Because graphene is derived from the lightest of the group IV elements, it is natural to consider the possibility of heavier graphene analogues. However, the heavier group IV elements (that is, silicon, germanium, tin and lead) are not known to favour \( sp^2 \) hybridization as found in graphene\(^{50}\). As a result, the freestanding, post-carbon group IV elements are expected to adopt a buckled honeycomb structure\(^{56–58}\) with a mixed degree of \( sp^2–sp^3 \) character. Furthermore, these heavier elements are expected to exhibit topologically non-trivial electronic states due to their enhanced spin–orbit coupling\(^{59–61}\).

**Silicon**

**Predicted structure and properties.** Despite the commonalities between group IV elements, the properties of silicon depart strikingly from those of carbon\(^{62,63}\). In bulk form, silicon features \( sp^3 \)-hybridized, tetrahedrally bonded atoms\(^{63}\) instead of the \( sp^2 \)-hybridized atoms in graphite\(^1\). Similarly, atomic-scale silicon clusters\(^{64}\) form non-planar assemblies of primarily tetrahedral silicon.

The importance of silicon in the microelectronic industry has motivated considerable interest in a silicon analogue to graphene — silicene. First-principles calculations indicate that monolayer silicon with a honeycomb crystal structure is stable in a non-planar buckled configuration\(^{66,67,68,69}\) (FIG. 5a). Predicted phonon dispersions and molecular dynamics simulations indicate that minor two-stage, out-of-plane buckling (<1 Å) persists at temperatures of up to 1,000 K (REF. 57). Further calculations have revealed that several, more complex buckling arrangements can also exist in the freestanding material\(^{66}\). Fewer calculations have incorporated the influence of the supporting substrate; however, initial reports suggest that the non-planar bonding configuration holds for substrate-supported silicene as well\(^{67}\). These substrate interactions are likely to influence the structure and properties of silicene.

Silicene is predicted to exhibit semi-metallic characteristics, with graphene-like Dirac fermions\(^{65}\). However, these properties deviate slightly from graphene for two main reasons: silicene features a lower symmetry, buckled honeycomb structure and exhibits enhanced spin–orbit coupling effects. These differences with respect to graphene theoretically imply that silicene could host topologically non-trivial electronic states\(^{69,70,71}\), spin-polarized edge states\(^{72,73}\) and a gate-tunable bandgap\(^{74,75}\). These properties would have important technological implications, allowing silicene-based devices to preserve quantum information, support spin-based computer logic, or enable tunable transistors or photodetectors.

**Synthesis and characterization.** Atomically thin silicon was first reported\(^{75,76}\) in the growth of 1D nanoribbon configurations on Ag(110), where it forms a honeycomb lattice consistent with predictions for silicene\(^{57}\). However, the 1D structures exhibit Raman modes inconsistent with freestanding silicene\(^{76}\), possibly indicating strong interactions with the substrate.

The first synthesis of a SE2DM was by Vogt et al.\(^1\), who observed silicene growth on Ag(111). Several later studies disclosed the coexistence of multiple phases (FIG. 3b), which exhibit distinct superstructures depending on the relationship between the silicon and the underlying silver\(^{60,61,62}\). The resulting phase is strongly dependent on both the silicon flux and the substrate temperature. Furthermore, the growth typically results in multiple phases unless performed at higher temperatures\(^{60,61,62}\).

Additional studies have reported the growth of silicene on Ir(111)\(^8\), MoS\(_2\) (REF. 84) and ZrB\(_2\)(0001)\(^8\) crystals under UHV. The growth of silicene on ZrB\(_2\)(0001)\(^8\) involves a distinct surface segregation mechanism using an epitaxial ZrB\(_2\)(0001) layer grown on Si(111). Upon heating under UHV, silicon diffuses to the ZrB\(_2\)(0001) surface and forms a honeycomb monolayer. Unlike Ag(111), these substrates do not appear to produce multiple phases.

The properties of silicene have been most thoroughly investigated on Ag(111) surfaces. In situ scanning tunnelling spectroscopy (STS) suggests that the monolayer phases are metallic or semi-metallic\(^8\). The 4 × 4 buckled phase was initially proposed to host Dirac fermions\(^1\), but this observation has subsequently been explained by states arising from Si–Ag hybridization\(^8\). Despite the growing literature in this area, the physical
and electronic properties of the resulting material are still under debate\(^9\)\(^{29-34}\). In particular, the \(\sqrt{3} \times \sqrt{3}\) phase\(^9\) was initially believed to be multilayer silicene and was reported to show properties consistent with the presence of Dirac fermions\(^9\)\(^{35,36}\). Later work concluded that the sheets consist of bulk silicon\(^9\) terminated by a silver-induced reconstruction\(^9\)\(^{10}\). As recently asserted in the work of De Padova et al.\(^9\), multilayer silicene can only be grown at lower substrate temperatures (~200 °C). Other studies suggested miscibility between silicon and silver\(^11\), structural instabilities upon annealing\(^37\), and silicon dissolution into the silver crystal\(^38\), further complicating the interpretation of this SE2DM. The isolation and subsequent study of encapsulated silicene films without the growth substrate was recently achieved, and the measurement of their electronic transport found graphene-like electronic properties (that is, Dirac-like ambipolar charge transport)\(^39\). This study did not address the structure of the isolated monolayers, but it nevertheless represents a crucial step towards the unambiguous characterization of freestanding silicene. However, future efforts will probably have to address the limited stability of the transferred sheets, as discussed below.

**Chemistry.** Owing to the reactivity of silicon, monolayer silicene is not stable under ambient conditions\(^40\). Preparations that yield materials with ambient stability will prove essential for silicene integration into devices, because the only silicene devices to date have lifespans on the order of tens of seconds in air\(^9\). Initial efforts towards the chemical modification of 2D silicon sheets have pursued atomic covalent modification under UHV conditions\(^40\). Recent attempts have involved the reaction of monolayer, lower temperature silicene phases with hydrogen\(^9\)\(^{36,38}\), oxygen\(^40\) and chlorine\(^40\). Atomic-scale STM has been the primary characterization tool for

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**Figure 3 | Silicene, germanene and stanene.** **a** | Top and side views of the buckled honeycomb structure predicted for freestanding silicene, germanene and stanene. **b** | Scanning tunnelling microscopy (STM) topography images showing the progression in monolayer silicon-derived phases on Ag(111) as a function of growth temperature. The nomenclature N \(\times\) N denotes shorthand for Wood’s notation, which is used to describe the periodicity of the structure with respect to the Ag(111) substrate (for example, the 4 \(\times\) 4 silicene structure has a unit cell that is larger than Ag(111) by a factor of 4). The 4 \(\times\) 4 structure was the first to be reported and grows at the lowest temperatures. The disordered regions adjacent to the 4 \(\times\) 4 phase are always present to some extent during growth. The \(\sqrt{13} \times \sqrt{13}\) phase is shown in two adjacent domains with different Moiré patterns (highlighted in black for the lower domain). The \(\sqrt{7} \times \sqrt{7}\) phase exhibits honeycomb-like features but is too large to be the intrinsic silicene honeycomb. Similarly, the \(\sqrt{3} \times \sqrt{3}\) lattice has a honeycomb appearance but actually corresponds to a bulk-like silicon phase with a gold-induced surface reconstruction. **c** | STM topography images of germanene phases grown on Pt(111) (left), Au(111) (centre) and Al(111) (right). The atomic structure of germanene on each metal substrate is highlighted in the magnified insets. **d** | STM topography image of monolayer stanene grown on Bi\(_2\)Te\(_3\). The image shows only the high-buckled stanene atoms, which demonstrate different apparent brightness because of buckling within the sheet. Panel **b** is adapted with permission from REF 9, American Chemical Society. Panel **c** is adapted with permission from REF 106, Wiley-VCH; REF 107, Institute of Physics; and REF 108, American Chemical Society. Panel **d** is adapted with permission from REF 117, Macmillan Publishers Limited.
these early studies, demonstrating both atomic-scale and weakly ordered large-scale chemical modification\textsuperscript{9,10}. Preliminary STS measurements suggest electronic modifications to the silicene layers upon either hydrogenation or oxidation\textsuperscript{9,10}. In the latter case, if the oxidation of multilayer silicon structures is controlled, the product has electronic characteristics similar to that of quasi-freestanding silicene\textsuperscript{10}. However, further characterization is required to fully understand the effects of these functionalizations on the electronic properties. Chemical functionalization may also stabilize silicene in air; for example, both hydrogen and deuterium are effective in passivating silicon surfaces\textsuperscript{103} and monolayer germanium\textsuperscript{104}, which suggests that these chemistries may be promising avenues for producing air-stable silicene monolayers.

**Germanium**

Germanium, like silicon, is predicted to form 2D sheets termed germanane, which has a buckled honeycomb structure\textsuperscript{11} (FIG. 3a). Germanane sheets are expected to have similar properties to silicene and are thus discussed briefly. The primary difference concerns the larger atomic number of germanium. This causes an enhanced spin–orbit coupling that results in stronger topological insulator characteristics compared with silicene\textsuperscript{105,27,28}. This effect may be further enhanced by halogenation, resulting in more pronounced topological insulator properties\textsuperscript{105}.

Like silicene, germanane has been synthesized on metal surfaces using UHV MBE. Highly buckled phases have been observed on Pt(111)\textsuperscript{106}, Au(111)\textsuperscript{107} and Al(111)\textsuperscript{108}, as illustrated in FIG. 3c. Unreconstructed germanane with a buckled honeycomb structure has also been grown on Ge\textsubscript{2}Pt\textsubscript{109} (REF. 109) and Mo\textsubscript{2}S\textsubscript{3} (REF. 110). Successful growth on semiconducting substrates, such as Mo\textsubscript{2}Se\textsubscript{3}, decreases the overlap between the electronic density of states of the substrate and germanane. This is especially significant because the decreased overlap improves the effectiveness of \textit{in situ} analytical methods, including STS, in accurately measuring the intrinsic electronic properties. However, much like silicene, germanane phases will require more comprehensive characterization to establish their structure and properties. For example, some studies propose that the formation of silicene or germanane on Pt(111) is not possible because of the formation of surface alloys\textsuperscript{111}. This work again underscores the importance of using multiple, orthogonal characterization techniques in the study of a newly synthesized SE2DMs.

Chemically modified germanane derivatives\textsuperscript{104,112} provide enhanced stability and tunable properties. These have been synthesized and isolated through chemically enhanced exfoliation techniques that utilize bulk precursors with a layered crystal structure (BOX 2), resulting in hydrogen-terminated germanane (that is, germanane) and methyl-terminated germanane. These materials show semiconducting properties, with methyl termination inducing a thickness-independent, direct electronic bandgap that may prove useful in optoelectronic applications\textsuperscript{112}.

**Tin**

Predicted structure and properties. Structural predictions for freestanding monolayers of tin (that is, stanene) have converged on a buckled honeycomb lattice\textsuperscript{113,114} (FIG. 3a). As with silicon and germanium, the two-level buckling causes some overlap of \(\sigma\) and \(\pi\) orbitals, stabilizing the relatively weak \(\pi–\pi\) bonding within the atomic plane\textsuperscript{113,114}. The heavier atomic mass of the tin atoms causes enhanced spin–orbit coupling compared with carbon, silicon and germanium. Including the spin–orbit coupling effects into band structure calculations causes a divergence from the Dirac fermion behaviour typical of graphene, leading to an opening of a \(\sim\)0.1 eV bandgap bridged by a topologically non-trivial state at the material edges\textsuperscript{58}. This state hosts spin-polarized, low resistance conduction that may be useful for applications in spintronics or to preserve quantum information for quantum computing applications. It is noteworthy that the crystal structure of buckled stanene is identical to a bilayer and thin films of \(\alpha\)-Sn(111). The latter have been studied on a range of substrates\textsuperscript{115,116}; the key difference between the epitaxy of \(\alpha\)-Sn(111) and stanene is the exposed \(p\) orbitals in the monolayer material. These orbitals account for the low-energy band structure of the material and are the source of the topologically non-trivial edge state. These subtle differences underpin the importance of thoroughly understanding the physical and chemical structure of novel SE2DMs.

**Synthesis and characterization.** The first report of stanene appeared from Zhu \textit{et al.}\textsuperscript{117} in 2015. The researchers synthesized monolayer stanene on the surface of a Bi\textsubscript{2}Te\textsubscript{3}(111) crystal under UHV conditions by evaporating tin onto the surface at room temperature\textsuperscript{117}. STM images (FIG. 3d) revealed the close-packed crystalline structure of only the buckled sublattice. Band structure calculations based on density functional theory agree well with ARPES measurements\textsuperscript{117} near the \(\Gamma\) point in reciprocal space, but the predicted topological band structure near the \(K\) point (that is, a Dirac cone) was not observed experimentally. The authors ascribe the absence of these topological bands to the presence of adsorbates (for example, hydrogen), which modify the chemical structure of the unbonded \(p\) orbitals responsible for those bands\textsuperscript{117}. In any case, the absence of these topological states should be addressed to enable fundamental and technological applications of stanene. To this end, further experiments are needed to remove the adsorbates and to understand the nature of the interaction between stanene and its substrate. The former may be addressed through non-reactive encapsulation (that is, to exclude hydrogen), whereas the latter may be accomplished through more advanced characterization (that is, cross sectional microscopy, X-ray diffraction and spectroscopy, or Raman spectroscopy) and/or growth on additional substrates. Moreover, it may be possible to restore the missing topological states, or enhance the topological properties of stanene, through chemical functionalization, as discussed below.
**Dopants**

Atomic or molecular species added to a material to controllably tune its properties. These may include species that modify the carrier concentration, magnetic properties, or chemical reactivity.

**Chemistry.** Although experimental work into 2D tin is relatively new, theoretical investigations into chemically modified allotropes abound. These studies have focused on the chemical saturation of the $p_z$ orbitals, which leads to stronger topological insulator characteristics by enhancing the magnitude of the bandgap induced by spin–orbit coupling. The stability of stanene when exposed to air has not been studied explicitly, but the high reactivity of these $p_z$ orbitals implies that stanene would not survive unaltered in ambient conditions without encapsulation. Several groups included substrates in their calculations, effectively concluding that chemical interactions between the stanene and substrate may resemble those between the stanene and chemical functionalizations in passivated monolayers.

A particular case of functionalization arises from the addition of magnetic dopants, which would support dissipationless electronic transport that may enable robust quantum computing. These examples demonstrate how stanene may serve as a platform on which topological states can be chemically engineered and patterned through spatially selective functionalization. Such patterning may be possible through scanning probe techniques such as STM, which have already been applied in the initial characterization of stanene. This, in turn, would enable dissipationless (that is, low power) electronic circuitry.

**Group V**

Besides nitrogen, all group V elements (that is, phosphorus, arsenic, antimony and bismuth) are known to form bulk solids with layered structures, although black phosphorus is the only example among these to be readily cleavable towards the monolayer limit.

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**Box 2 | Solution-based exfoliation for air-unstable materials**

Chemically enhanced ‘wet’ exfoliation processes provide a scalable route to isolate atomically thin sheets with controlled thicknesses. However, synthetic elemental 2D materials (SE2DMs) often require special preparation methods because of their instability in air. Derivatives of materials that lack bulk analogues, such as germanane, can be isolated from bulk crystals with an appropriate structure, such as CaGe2, (panel a, centre), which consist of covalently bonded layers inserted between layers of metal cations. Treating CaGe2 in HCl (panel a, left) yields hydrogenated germanane (that is, germanane), which is stable in ambient conditions. More stable layers are generated by treating CaGe2 with CH3I, which results in methylated germanane (panel a, right). These functionalizations increase the stability of the layers and, in the methylated case, enhance their light-emitting properties.

Aqueous exfoliation processes are generally the most scalable; however, materials such as black phosphorus are sensitive to H2O exposure. Although it is possible to exfoliate black phosphorus in organic solvents, methods using deoxygenated water (panel b) were recently demonstrated to yield high-quality flakes, while maintaining the structure and properties of pristine black phosphorus, as shown in the transmission electron microscopy large-scale bright field and atomic-scale images of black phosphorus flakes in panel c. Panel a (left and centre) is adapted with permission from American Chemical Society. Panel a (right) is adapted with permission from Macmillan Publishers Limited. Panels b and c are adapted with permission from National Academy of Sciences.
Strikingly, all post-nitrogen group V elements are expected to form buckled honeycomb allotropes. This similarity suggests that alloying between these SE2DMs may be possible\(^{123,124}\), providing a great degree of tunability in their properties (particularly their electronic characteristics). Despite the fact that these bulk structures bode well for the formation of atomically thin SE2DMs, the direct synthesis of group V monolayers is complicated by the significant toxicity of phosphorus, arsenic and antimony. Experimental evidence exists for atomically thin phosphorus and bismuth, and there has been a very recent report of antimony-based 2D materials (antimonene)\(^{125}\). Only phosphorus and bismuth are discussed in the following sections.

**Phosphorus**

*Predicted structure and properties.* Phosphorus exhibits multiple bulk allotropes\(^{126}\), including highly reactive white phosphorus, red phosphorus and purple phosphorus, and the relatively inert black phosphorus. 2D phosphorus, or phosphorene\(^{121,122}\), is among the few SE2DMs isolated directly from a bulk solid, specifically from black phosphorus. Black phosphorus exhibits an orthorhombic crystal structure composed of stacked, weakly bound layers. However, these layers are buckled out of the plane to form corrugated rows (FIG. 4a), resulting in significant anisotropy in mechanical strength, electrical and thermal conductivity, and optical properties\(^{123}\). As a point of nomenclature, it is worth noting that current literature often addresses isolated 2D phosphorus as black phosphorus because the samples consist of >5 layers of the black phosphorus structure (and often many more). Several other distinct 2D allotropes have been predicted for phosphorus. These include a semiconducting buckled honeycomb monolayer (structurally similar to FIG. 5a), termed blue phosphorus\(^{127}\), and more complex structural variants based on various buckling schemes\(^{128}\).

*Synthesis and characterization.* At present, exfoliation of bulk black phosphorus is the most common route towards phosphorene. In bulk form, black phosphorus is synthesized primarily by the chemical vapour transport technique, which displays some similarity to CVD but produces bulk crystals\(^{129-131}\). 2D sheets are isolated from the bulk by micromechanical exfoliation\(^{131,132}\) or solution-based exfoliation processes\(^{132-134}\). Micromechanical processes are labour intensive and rely on effectively stochastic methods to locate and process flakes of a desired thickness, which is complicated by the relatively rapid ambient degradation of black phosphorus\(^{133,134}\). Several groups have made progress in the CVD growth of black phosphorus and phosphorene. Black phosphorus thin films were grown directly on Si/SiO\(_2\) wafers\(^{135}\) and flexible polymers\(^{137}\), although high-pressure processing was required to form black phosphorus thin films. More recently, a monolayer derivative of blue phosphorus (FIG. 4b,c) was grown by UHV MBE on Au(111) substrates\(^{138}\). This phase is buckled in a 4 × 4 reconstruction with respect to the freestanding predictions for blue phosphorus and exhibits a 1.1 eV bandgap. Although the detailed properties of this phase have not yet been established, this synthesis technique shows promise for the direct growth of phosphorene phases.

**Chemistry.** Phosphorene is reactive\(^{139}\) and quickly oxidizes in ambient conditions\(^{123,135,140}\), which provides a small window where samples can be processed outside of a controlled environment. The degradation mechanism\(^{140}\) involves exposure to oxygen dissolved in adsorbed water and is accelerated by light exposure. As a result, black phosphorus can be processed in deoxygenated aqueous solution\(^{133}\), yielding a scalable route towards phosphorene (BOX 1). However, to achieve technological relevance, black phosphorus and phosphorene will require robust passivation schemes. Methods of physical encapsulation under polymer\(^{141}\) or hexagonal boron nitride layers\(^{142}\) have proven effective, but neither shows concurrent scalability and stability. By contrast, encapsulation with thin aluminium oxide layers by atomic layer deposition\(^{143}\) has proven effective for long-term stability (FIG. 4d). Furthermore, technological applications will also require methods for tuning the carrier type and concentration in phosphorene and black phosphorus. Non-covalent, inorganic functionalization can induce n-type and p-type doping through surface charge transfer, as demonstrated by the deposition of Cs\(_2\)CO\(_3\) and MoO\(_3\), respectively\(^{144}\). Alternatively, covalent functionalization using diazonium salts forms a stable passivation layer on black phosphorus\(^{145}\) that results in p-type doping (FIG. 4e) and enhances ambient stability.

**Bismuth**

*Predicted structure and properties.* Bismuth is the heaviest of the group V elements and crystallizes into a layered, rhombohedral lattice with the space group R3m (REFS 15,145). In 2D form, bismuth is predicted to form buckled honeycomb structures similar to silicone or blue phosphorus\(^{146,147}\) (FIG. 5a). As a point of nomenclature, this structure is sometimes referred to as a bilayer because the atoms reside at two distinct heights in the buckled honeycomb configuration.

The heavy atomic mass and concomitantly large spin-orbit coupling of bismuth make it a common component in technologically non-trivial systems. Indeed, 2D bismuth monolayers have been predicted to be a 2D topological insulator\(^{148,149}\). However, the topological characteristics of buckled honeycomb bismuth layers are still under debate, with conflicting experimental reports\(^{146}\) suggesting strong substrate influence on the properties of the overlying bismuth layers. In light of this conflicting evidence, electrical transport measurements on isolated buckled honeycomb layers are vital to understanding the electronic properties in this system.

*Synthesis and characterization.* Despite being one of the first SE2DMs isolated, 2D bismuth has been relatively understudied in the 2D materials community. Early experiments towards 2D bismuth have focused on thin films grown on various substrates using MBE, resulting in two distinct atomically flat phases: a buckled honeycomb allotrope that resembles the (111) plane of bulk bismuth\(^{148,150}\) (FIG. 5a,b), and a black-phosphorus-like sheet that resembles the distorted Bi(110) plane\(^{151}\) (FIG. 5c,d).
The weak interlayer bonding in 2D bismuth makes it possible to grow atomically flat, planar layers\textsuperscript{152,153}. To realize buckled honeycomb or (111) oriented layers, researchers commonly use surfaces with three-fold or six-fold symmetry (for example, Si(111) or Bi\textsubscript{2}Te\textsubscript{3})\textsuperscript{151,154}, albeit not exclusively (for example, Si(001) or W(110), which have four-fold symmetry)\textsuperscript{155,156}. In both cases, the presence of either surfactant layers or van der Waals interfaces between the substrate and the 2D bismuth mediate the formation of electronically independent bismuth layers. Initial experiments with few-layer buckled honeycomb films thoroughly characterized the growth modes and crystalline symmetry of the resulting overlayers\textsuperscript{154}, while preliminary experimental electronic characterization confirmed that the layers do retain the electronic signature of freestanding films predicted by density functional theory calculations\textsuperscript{157,158}. These results are encouraging in light of accurate electronic transport measurements that establish the topological properties of 2D bismuth. Such transfer may be facilitated by the weak mechanical adhesion of buckled honeycomb films on Si(111)\textsuperscript{158,159}.

The black-phosphorus-like structure has been demonstrated on both reconstructed silicon surfaces\textsuperscript{151,160} and highly oriented pyrolytic graphite (HOPG)\textsuperscript{153,161}. Here, the (110) crystal plane of the bismuth film is oriented parallel to the growth surface and is characterized by the so-called pseudo-cubic surface symmetry\textsuperscript{152}. During growth, the resulting allotrope is thickness dependent; for example, on Si(111), the first ~4 monolayers of deposition result in the black-phosphorus-like phase, whereas subsequent deposition results in the buckled honeycomb phase.

Buckled honeycomb and black-phosphorus-like allotropes show similar weak interlayer bonding and in-plane atomic corrugation\textsuperscript{152}. Local measurements of the electronic structure have shown varying results that have been attributed to local strain and doping effects from the supporting substrates\textsuperscript{162}. Again, the verdict is unclear on the topological nature of the 2D atomic layers, although initial measurements suggest non-trivial edge states in the black-phosphorus-like allotrope on HOPG\textsuperscript{163,164}.

**Chemistry.** Bismuth oxidizes in air to give a brilliant, iridescent thin film of oxide on the surface. This suggests that atomically thin bismuth films will be susceptible to oxidation. However, the chemistry of nanoscale bismuth allotropes remains largely unexplored. Incidental reports suggest buckled honeycomb bismuth displays a relative insensitivity to adventitious adsorbate contamination under UHV conditions\textsuperscript{165}. Theoretical investigations of the methyl terminated buckled honeycomb allotrope suggest that the freestanding layer should retain a buckled honeycomb structure with extremely robust topological states (that is, increasing the energy gap by an order of magnitude to nearly 1 eV)\textsuperscript{164}. Therefore, chemical functionalization holds promise as a means to realize 2D bismuth layers with increased stability under ambient conditions and enhanced topological electronic properties.

**Outlook and conclusions**

Expanding beyond naturally occurring materials, the synthesis and characterization of entirely synthetic, elemental 2D materials has emerged as an exciting frontier of 2D materials research. In particular, SE2DMs present the opportunity to develop synthetic low-dimensional materials with increased structural flexibility and hence more diverse properties than those in extant bulk layered materials. This tailorable is achieved through careful modulation of the substrate properties and growth conditions, resulting in an expansive phase space even for pure mono-elemental systems. As such, extensive collaboration with computational materials scientists is crucial to realizing the full potential of these materials in an efficient manner. The initial advances in SE2DM synthesis have provided motivation for the
buckled honeycomb allotrope

Black-phosphorus-like allotrope

**Figure 5** | **Bismuth.** a | Side view (left) and top view (right) of the atomic structure models of the bismuth buckled honeycomb allotrope. b | 3 × 3 nm² scanning tunnelling microscopy (STM) topography image for the buckled honeycomb allotrope, where the unit structure is highlighted in red. c | Side view (left) and top view (right) of the atomic structure models of the bismuth black-phosphorous-like allotrope. d | 3 × 3 nm² STM topography image for the black-phosphorus-like allotrope of bismuth, where the unit structure is highlighted in red. Panels b and d are adapted with permission from REF. 181, Physical Society of Japan.

renewed examination of the periodic table, with a focus on accelerating the discovery of materials that complement the properties of bulk van der Waals solids. This synergy between computational modelling (for example, predictive modelling of stable structures and understanding the quantum states of matter that emerge in the 2D limit) and experimental efforts (for example, synthesis, characterization and processing) encapsulates the fundamental purpose underlying the ambitious Materials Genome Initiative, which will prove critical for advancing SE2DMs.

The early progress in the synthesis of SE2DMs highlights several promising opportunities concerning new materials systems and their future use in a range of applications. It is notable that many SE2DMs (that is, those based on silicon, germanium, tin, arsenic, antimony or bismuth) exhibit great potential for topologically non-trivial properties owing to their high atomic number. Topological insulators and related electronic phases hold great potential as new electronic states of matter with dissipationless, spin-polarized conduction channels suitable for high-speed electronic spintronic and quantum computing applications. The intersection between these fields will probably generate numerous technological and fundamental advances in the years to come. Furthermore, the collective opportunities for these materials are enhanced by the potential to incorporate them into vertical and lateral heterostructures that impart new properties based on the interlayer coupling between these atomically thin sheets.

Additionally, there are many areas of opportunity available for individual materials. Borophene is likely to exhibit highly directional metallic conduction and anisotropic optical properties that may find use in transparent conductors. Furthermore, these properties may provide an avenue to study metallicity (and potentially superconductivity) at the atomically thin limit. 2D group-IV materials, including silicon, germanane and stanene, exhibit graphene-like electronic characteristics in a platform that is more amenable to chemical modification and topologically non-trivial electronic properties. In terms of applications, phosphorene is perhaps the most mature SE2DM, because it has already shown great promise as a 2D semiconductor with a thickness-tunable bandgap, high carrier mobility, and anisotropic electronic and optical properties. However, there is currently no high-throughput CVD or PVD method to synthesize large-area, thickness-controlled phosphorene. Arsenic and antimony are predicted to have bulk layered structures resembling highly buckled honeycomb sheets similar to that of blue phosphorus, with relatively strong interlayer coupling, and the propensity to form 2D allotropes (that is, arsenene and antimonene). The synthesis of antimonene has only recently been reported, and arsenene has yet to be prepared. As a consequence, there are many opportunities to study the properties of these materials. Finally, 2D bismuth exhibits topologically non-trivial electronic states that are likely to be amenable to fundamental and technological exploration in device platforms, although the precise characteristics of the black-phosphorus-like allotrope remain undetermined.

However, despite substantial progress in this field, many challenges remain unaddressed. SE2DMs encounter significant challenges in their synthesis, characterization and utilization, often constrained by the need for pristine conditions and well-controlled growth techniques, as well as the selection of elements with covalent bonding tendencies and substrates exhibiting weak interactions. Furthermore, SE2DMs typically lack a bulk layered allotrope and display some degree of air sensitivity, which compound the difficulties associated with the characterization of atomically thin materials. With that said, the semiconductor industry has been built on the success of air-sensitive materials, such as silicon and Si,Ge, suggesting the possibility for the widespread use of these materials. Moreover, clever chemical processing techniques, such as those applied in phosphorene and germanane synthesis, obviate the need for complex passivation measures.

Moving forward, computational efforts could provide considerable guidance by evaluating the degree of chemical interaction between the overlayer and substrate, which may reduce the likelihood of experimental efforts encountering the formation of surface alloys and reconstructed bulk materials. Similarly, the long-term viability of the field depends on thorough characterization using multiple independent techniques to establish the structure, 2D character and properties of the materials. Many studies so far have relied solely on in situ UHV synthesis and characterization. However, this limited characterization is not always sufficient to provide a complete picture of the structure and properties of the resulting material. At a bare minimum, orthogonal techniques should be used to determine the structure with minimal artefacts and misinterpretation (for example, scanning tunnelling
microscopy and cross-sectional transmission electron microscopy). Additionally, the separation of SE2DMs from their growth substrates should be an important research priority. In particular, borophene, germanene, stanene and 2D bismuth have not been isolated from their growth substrates for independent characterization. To enhance the efficacy of these experiments, generalizable, robust methods are needed to preserve the intrinsic SE2DM structures and properties for ex situ characterization and device fabrication. Promising candidates include non-covalent but fully encapsulating layers deposited in situ (for example, silicon or AlO₃) or potentially an organic or atomic molecular passivation layer that provides inert, conformal protection and the potential for reversible desorption. Nevertheless, the rapid growth of this field suggests that there is great potential to develop materials with unprecedented properties that cannot be realized in naturally occurring materials.


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Competing interests statement
The authors declare no competing interests.