Progress, Challenges, and Opportunities in Two-Dimensional Materials Beyond Graphene


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ABSTRACT Graphene’s success has shown that it is possible to create stable, single and few-atom-thick layers of van der Waals materials, and also that these materials can exhibit fascinating and technologically useful properties. Here we review the state-of-the-art of 2D materials beyond graphene. Initially, we will outline the different chemical classes of 2D materials and discuss the various strategies to prepare single-layer, few-layer, and multilayer assembly materials in solution, on substrates, and on the wafer scale. Additionally, we present an experimental guide for identifying and characterizing single-layer-thick materials, as well as outlining emerging techniques that yield both local and global information. We describe the differences that occur in the electronic structure between the bulk and the single layer and discuss various methods of tuning their electronic properties by manipulating the surface. Finally, we highlight the properties and advantages of single-, few-, and many-layer 2D materials in field-effect transistors, spin- and valley-tronics, thermoelectrics, and topological insulators, among many other applications.

KEYWORDS: two-dimensional materials · graphene · nanosheets · graphane · van der Waals epitaxy · van der Waals solid

Two-dimensional (2D) materials have historically been one of the most extensively studied classes of materials due to the wealth of unusual physical phenomena that occur when charge and heat transport is confined to a plane. Many materials with properties dominated by their two-dimensional structural units such as the layered metal dichalcogenides (LMDCs), copper oxides, and iron pnictides exhibit correlated electronic phenomena such as charge density waves and high-temperature superconductivity.1–3 The (re)discovery4,5 of single-layer graphene in 2004 by Novoselov and Geim has shown that it is not only possible to exfoliate stable, single-atom or single-polyhedral-thick 2D materials from van der Waals solids, but that these materials can exhibit unique and fascinating physical properties. In single-layer graphene’s band structure, the linear dispersion at the K point gives rise to novel phenomena, such as the anomalous room-temperature quantum Hall effect, and has opened up a new category of “Fermi-Dirac” physics. Even at one-atom-thick, graphene is a fantastic electronic and thermal conductor, and graphene-based materials have been proposed for a host of...
applications ranging from transparent conductors to thermal interface materials to barristor transistor-like devices.\textsuperscript{6–8} Furthermore, as single-layer graphene is entirely surface area, its properties and reactivity profoundly depend on the substrate, its local electronic environment, and mechanical deformations.

Still, there exists an entire periodic table of crystalline solid-state materials each having different electronic, mechanical, and transport properties, and the possibility to create single-atom or few-atom polyhedral thick 2D layers from any material remains. It was shown decades ago by Frindt \textit{et al.} that layered van der Waals materials, such as layered metal dichalcogenides, could be mechanically and chemically exfoliated into few and single layers.\textsuperscript{9,10} This early work focused on attempts to obtain and characterize these thin layers.\textsuperscript{9–13} Experiments probing transport\textsuperscript{11} only scratched the surface of the unique properties these 2D materials exhibit. It was not until the recent surge of intense research on graphene that the general potential of 2D materials became apparent. Additionally, the past 8 years of graphene research has yielded many methods for synthesizing, transferring, detecting, characterizing, and manipulating the properties of layered van der Waals materials. Furthermore, novel synthetic methods including topotactic, solution-based, solvothermal, and UHV surface epitaxial approaches have unleashed the potential to create new van der Waals solids and single-layer-thick materials. These established methods have enabled the field of 2D materials beyond graphene to mature very quickly.

Many novel materials that had been initially considered to exist only in the realm of theory have been synthesized. These include groups IV and II–VI semiconductor analogues of graphene/graphane (the sp\textsuperscript{2}/H-terminated sp\textsuperscript{2} derivatives) such as silicene,\textsuperscript{14–17} and germanane.\textsuperscript{18} Similar to graphene, the properties at the single layer are also distinct from the bulk. Furthermore, these 2D materials are useful building blocks that can be restacked and integrated into composites for a wide range of applications.

Herein, we present a forward-looking review article that discusses the state-of-the-art of 2D materials beyond graphene. Initially, we will outline the different chemical classes of 2D materials and discuss the various strategies to prepare single-layer and multi-layer assemblies in solution, on substrates, and on the wafer scale. Additionally, we present an experimental how-to-guide for identifying and characterizing single-layer-thick materials, as well as outline emerging techniques that yield both local and global information. We describe the differences that occur in the electronic structure between the bulk and the single layer and discuss various methods of tuning the properties by manipulating the surface. Finally, we highlight the properties and advantages of single-, few-, and many-layer 2D materials in field-effect transistors, spin- and valleytronics, thermoelectrics, and topological insulators, among many other applications.

**Vocabulary:**

- **two-dimensional material** - a material in which the atomic organization and bond strength along two-dimensions are similar and much stronger than along a third dimension.
- **van der Waals solid** - a material whose crystal structure features neutral, single-atom-thick or polyhedral-thick layers of atoms with covalent or ionic bonding along two dimensions and van der Waals bonding along the third.
- **graphane** - a single layer of a two-dimensional hexagonal network of sp\textsuperscript{2}-bonded carbon atoms in which every carbon is bonded to a terminal hydrogen, alternatingly above and below the layer.
- **van der Waals epitaxy** - the growth of a thin layer on the surface of a substrate in which the material–substrate are held together by weak van der Waals forces.

**Structure and Synthesis of Two-Dimensional Materials.** The reliable synthesis of single- and few-layer 2D materials is an essential first step for characterizing the layer-dependent changes in their properties, as well as providing pathways for their integration into a multitude of applications. In general, there are three main classes of materials that can be prepared as a single-atom or single-polyhedral-thick layer.

**Classes of Single- and Few-Layer Two-Dimensional Materials.** Layered van der Waals Solids. The most common class of crystalline structures that can be exfoliated as stable single layers are the layered van der Waals solids. These crystal structures feature neutral, single-atom-thick or polyhedral-thick layers of atoms that are covalently or ionically connected with their neighbors within each layer, whereas the layers are held together via van der Waals bonding along the third axis. The weak interlayer van der Waals energies (∼40–70 meV) enable the facile exfoliation of these layers. The most common approaches for obtaining single- and few-layer-thick 2D materials from many of these solids include mechanical exfoliation of large crystals using “Scotch tape”, chemical exfoliation by dispersing in a solvent having the appropriate surface tension, and molecule/atom intercalation in order to exfoliate these layers and enable their dispersion in polar solvents. This mechanical exfoliation process has been used to prepare and study the properties of few-layer van der Waals materials, such as MoS\textsubscript{2} and NbSe\textsubscript{2}, since the 1960s.\textsuperscript{9,11,19} The isolation of individual and few layers using mechanical exfoliation remains the most powerful approach for studying their properties since it is considerably less destructive than the other methods and has successfully been used to create large, 10 \textmu m single-layer flakes on a variety of substrates.

One of the most well-studied families of van der Waals solids is the layered metal chalcogenides (LMDCs), the most common being MoS\textsubscript{2}. Early transition metal
dichalcogenides with stoichiometry MX₂ (M = Ti, Zr, Hf, V, Nb, Ta, Re; X = S, Se, Te) crystallize into layered 2D structures in which hexagonally packed MX₆ octahedra (for d⁰, d¹, and some d² metals) or trigonal prisms (for d¹ and d² metals) share edges with their six nearest MX₆ neighbors within each layer (Figure 1a).¹ There are over 30 different LMDCs which have many technologically interesting properties, and an emerging body of experimental work investigating the structure and properties of single- and few-layer-thick derivatives has evolved for many of these compounds (MoS₂, WS₂, and TiS₂).²⁻²² Other families of van der Waals solids that have been exfoliated into single layers include hexagonal boron nitride,²³ vanadium oxide derivatives, and other chalcogenides including Bi₂Te₃, Sb₂Te₃, and β-FeSe.²⁴,²⁵ Many novel van der Waals compounds can be created via the topotactic deintercalation of precursor solids. For example, the layered CaSe₂ and CaS₂ Zintl phases can be topochemically deintercalated in aqueous HCl to produce layered hydrogen-terminated or half-hydrogen-terminated/half-hydroxy-terminated GeH and SiH₆(OH)₆, respectively (Figure 1b).¹⁸,²⁶⁻²⁸ These group IV graphane analogues²⁹⁻⁻³² are a particularly intriguing class of systems due to the possibility of utilizing covalent chemistry to modulate and tune the properties. As another example, recently, the exfoliation of metal carbides such as Ti₃AlC₂ using HF to produce neutral layers of Ti₃C₂(OH)₂ has been demonstrated.³³ New layered van der Waals solids are constantly being discovered by the solid-state community. In 2012, ReN₂ was synthesized for the first time using high-pressure techniques and was found to have the MoS₂ crystal structure type.³⁴

Neutral, dimensionally reduced hybrid organic/inorganic van der Waals derivatives of nonlayered solids have also recently been discovered. Dimensional reduction refers to the creation of novel crystal structures of metal-anion (M-X) frameworks by the addition of a reagent that disrupts the polyhedral connectivity along one or more dimensions while retaining a degree of the metal coordination geometry and general polyhedral connectivity.³⁵ In these hybrid van der Waals solids, stoichiometric equivalents of neutral organic ligands bind to the metal and disrupt the M-X-M framework without changing the electron count and relative metal-anion radii. For example, it has been shown that almost every II–VI semiconductor that typically crystallizes into the three-dimensional sphalerite or wurtzite lattices, such as ZnS, ZnSe, and ZnTe, can be converted into atomically thin 2D crystalline frameworks when synthesized via solution-phase solvothermal techniques in the presence of alkylamine ligands.³⁶⁻⁻⁴⁰ The bulk sphalerite or wurtzite structure consists of a corner-sharing metal-anion tetrahedral.

These dimensionally reduced structures can be envisioned as a single (1–10) plane of corner-sharing metal-anion tetrahedra where every metal is bonded to three anions and capped with a short-chain alkylamine and every anion is bonded to three different metals (Figure 1c). The exfoliation into single-layer-thick derivatives of these hybrid materials, such as ZnSe, has been recently demonstrated.³¹

Layered Ionic Solids. The second class of materials that can be prepared as single or few layers features bulk crystal structures with charged 2D polyhedral layers that are typically held together with strongly electro-positive cations or strongly electonegative anions such as halides, or OH⁻. To enable their dispersion as single layers in solution, these cations/anions are typically exchanged with bulky organic cations/anions, such as tetrabutylammonium/dodecylsulfate. These materials can then be easily dispersed onto substrates, with the majority of materials depositing as single to few layers. There are numerous examples of oxide materials that have been prepared this way including (1) cation-exchanged layers from Ruddlesden–Popper perovskite-type structures, such as KLn₂TiO₇, KLnNb₂O₇, RbLnTa₂O₇, and KCa₂Nb₂O₇.
(Figure 1d)42–47 (Ln = lanthanide ion); (2) cation-exchanged layered metal oxides such as LiCoO2 and Na2Ti3O7;48,49 (3) halide- or hydroxide-exchanged layers derived from metal hydroxides, such as Ni(OH)2−x or Eu(OH)2.5Cl0.5.50,51 Additionally, many neutral layered transition metal oxides such as MnO2 can undergo changes in oxidation state and become protonated in aqueous acidic solutions.52 This proton can then be substituted for bulky organic cations. The observed thicknesses from atomic force microscopy (AFM) for these classes of materials are typically larger than their expected values due to the presence of hydration layers or intercalating ions, which results in a surface—sheet interface with a thickness between 0.5 and 1.0 nm. The lateral sizes of exfoliated layers from ionic materials typically depend on the size of the starting crystalline material, and single-layer flakes in the range of tens of micrometers have been observed.48

Surface Growth of Nonlayered Materials. The deposition of materials on substrates offers the potential to grow and study the properties of single- to few-atom-thick materials beyond those existing as layered bulk crystals. For example, recently, it was demonstrated that monolayers of silicon deposited on Ag(111) or ZrB2 organize into a puckered hexagonal graphene-like lattice with sp2 bonding configuration.17,53 This silicene material shares a similar band structure to graphene; however, the interactions with the substrate induce a band gap opening at the K point. Additionally, ultrathin insulators such as Cu3N5.54,55 Al2O356 NaCl57 MgO58 TiO259 and metal adlayers have been prepared in this fashion on metal substrates. Unlike exfoliation, the choice of substrate has been typically limited to metals due to the prevalence of STM as a characterization tool.

Solution-Phase Growth. Solution-phase methods such as solvothermal or colloidal growth reactions offer a facile production method to synthesize gram scale quantities of 2D materials with precise thicknesses and basal-plane sizes.60–64 Recently, general colloidal synthetic methods have been developed to prepare LMDCs such as TiS2, V2S, ZrS2, HfS2, NbS2, TaS2, TiSe2, VSe2, and NbSe2 via the reaction of metal halides and carbon sulfide or elemental selenium in the presence of primary amines.65 The colloidal materials typically range in lateral dimensions from 10 to 100 nm and have thicknesses from single sheets to tens of nanometers. As an example, TiS2 nanosheets that have lateral lengths of 500 by 500 nm with thicknesses on the order of 5 nm have been created (Figure 2). These methods use abundant low-cost precursors and mild colloidal growth conditions.66 However, strategies for controlling the thicknesses and lateral dimensions have yet to be established.

One of the key steps in using solution-phase methods to grow transition LMDCs is the generation of chalcogenide anions in the appropriate oxidation state (S2−, Se2−, and Te2−). To grow sulfides, primary amines and sulfur are typical reactants because they form sulfur-containing alkylammonium polythioamine,67 polythiobisamine,68,69 and alkylammonium polysulfide70 complexes. These sulfur-containing species, in turn, exhibit favorable decomposition kinetics and produce H2S when heated, which reacts with the metal precursor.

Vapor Deposition. Vapor deposition stands as an appealing, versatile synthetic strategy. However, the development of a controlled synthetic method of 2D materials such as 2D chalcogenides by vapor deposition requires a better understanding of the fundamentals involved. While vapor deposition has been extensively used for the growth of thin films and nanomaterials such as nanowires,71 nanotubes,72 and graphene,74 knowledge obtained from these materials may not simply apply to 2D materials. Unlike typical nanomaterials whose growth is primarily governed by a catalyst, the vapor deposition growth of 2D chalcogenides is often noncatalytic.24,74,75 Without the dominance of catalysts, the growth of 2D nanosheets is subject to strong influences of many experimental parameters that may play only a negligible role in catalyzed growths. For example, the diffusion of source material vapor through the gas flow boundary layer strongly controls the vapor deposition growth of GeS nanosheets (Figure 3).74

The growth of single-layer substrate-wide 2D materials is essential for commercialization and would also benefit fundamental studies of single-layer phenomena. The key to the preparation of substrate-wide single-layer van der Waals 2D materials and their heterojunctions is monolayer (ML) epitaxy. van der Waals forces have associated energies of 40–70 meV, which
are much smaller than covalent bonding energies of 200–6000 meV. We infer that epitaxy of crystalline 2D materials on crystalline substrates is defined by strong bonding at the reactive edges of the single-crystal domains of the material and weak interlayer forces between the sheets. This van der Waals epitaxy occurs between 2D sheets of the same material (homoepitaxy) as well as 2D sheets of different materials (heteroepitaxy). Because of the weak interlayer forces, epitaxy is possible even if there is significant lattice mismatch between the materials. The resulting heterojunctions do not suffer from the interfacial defects that are generated during 3D heteroepitaxy due to the large stresses generated by bent or broken interlayer bonds. van der Waals heteroepitaxy has also been shown to be possible with 3D substrates that have been suitably passivated. Table 1 shows a listing of crystalline 2D heterojunctions that have been produced using van der Waals epitaxy.

Large-Area CVD Growth of Graphene and Hexagonal Boron Nitride. It is worthwhile to re-evaluate the successful vapor deposition growth of single-layer graphene in order to understand the extent to which we can transfer these methods to the substrate-wide growth of other van der Waals sytems. Thin carbon films were originally grown on single-crystal transition metals such as platinum by exposing the metal surface to a hydrocarbon at high temperature in ultrahigh vacuum (UHV) conditions. LEED patterns observed by the Somorjai group were assigned in 1969 to being from single- and few-layer graphene (SLG and FLG, respectively). The formation of these graphene layers was later explained by the dissociation of the hydrocarbon on the metal surface, carbon diffusion into the bulk of the metal, and its segregation during cooling or by carbon supersaturation. There is an interest in synthetic approaches for the formation of large-area graphene, for basic research as well as a variety of applications, and this has driven the re-evaluation of FLG growth on transition metals by the diffusion—segregation technique. The growth of FLG on Ru, Ir, Co, Ni, Pt, and Pd by chemical vapor deposition (CVD) has been reported. Control of the quality and number of layers grown has proven challenging, and often inhomogeneous films are obtained. FLG was also achieved by the sublimation of silicon in SiC crystals.

The successful synthesis of SLG with high homogeneity and reproducibility was achieved in 2009 by low-pressure CVD on copper foils with methane as the carbon source. Aspects of the growth kinetics and mechanisms were elucidated using an isotope-labeling technique in which the Cu is exposed sequentially to $^{13}$CH$_4$ and then normal methane. 13C-labeled graphene can be readily distinguished from normal graphene by Raman spectroscopy and mapping (Figure 4a). A comparison of the growth of monolayer graphene and FLG on Cu versus Ni showed that the graphene growth on Cu is surface-mediated; that is, dissociation of the hydrocarbon followed by carbon species diffusion on the surface leads to nucleation, island growth, and finally completion of a monolayer. This is rationalized by the extremely low carbon solubility in Cu even at the growth temperature of about 1040 °C that inhibits the diffusion of C into the bulk Cu, making Cu foil an excellent substrate for growth of large-area SLG. Kinetic studies on the growth of graphene led to the conclusion that the graphene grain size could be increased by raising the growth temperature and

Table 1. Two-dimensional Heterojunctions Produced by van der Waals Epitaxy

<table>
<thead>
<tr>
<th>layer</th>
<th>substrate</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphene</td>
<td>sapphire</td>
<td>322</td>
</tr>
<tr>
<td>C$_{60}$</td>
<td>MoS$_2$</td>
<td>323</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>graphene</td>
<td>75</td>
</tr>
<tr>
<td>GaS</td>
<td>GaSe, Si(111)</td>
<td>324</td>
</tr>
<tr>
<td>GeS</td>
<td>SiO$_2$/Si</td>
<td>74</td>
</tr>
<tr>
<td>Ta$_2$O$_5$</td>
<td>mica</td>
<td>325</td>
</tr>
<tr>
<td>WS$_2$</td>
<td>graphite</td>
<td>326,327</td>
</tr>
<tr>
<td>HfS$_2$</td>
<td>WSe$_2$</td>
<td>328</td>
</tr>
<tr>
<td>GaS</td>
<td>InSe/H-Si(111)</td>
<td>329</td>
</tr>
<tr>
<td>Si$_2$S$_2$</td>
<td>WSe$_2$, MoS$_2$, MoTe$_2$, GaSe, WSe$_2$</td>
<td>330,331</td>
</tr>
<tr>
<td>Si$_2$Se$_2$</td>
<td>Si$_2$Se$_2$, MoS$_2$, MoTe$_2$, GaSe</td>
<td>330,331</td>
</tr>
<tr>
<td>Bi$_2$Se$_3$</td>
<td>graphene/SiC, Si(111)</td>
<td>238,332</td>
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<td>h-BN</td>
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<td>ZnSe</td>
<td>InSe, GaSe</td>
<td>334</td>
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<td>MoS$_2$</td>
<td>Si$_2$S$_2$, MoS$_2$, GaAs(111)</td>
<td>335</td>
</tr>
<tr>
<td>GaSe</td>
<td>GaAs(111), Si(111)</td>
<td>336,337</td>
</tr>
<tr>
<td>NbSe$_2$</td>
<td>mica, GaAs(111)</td>
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<td>MoS$_2$, WSe$_2$</td>
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<tr>
<td>PbTe</td>
<td>Si(111)</td>
<td>340</td>
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Figure 3. (a) Schematic illustration of experimental setup for synthesis by a noncatalytic vapor deposition process. The precursor vapor can be introduced from outside or generated inside the tube furnace. (b) TEM image of a typical GaS nanosheet. Inset is an electron diffraction pattern of the nanosheet.
reducing the partial pressure of the hydrocarbon, and grain size was thereby increased, at first, from a few micrometers to tens of micrometers. The domain size of SLG has since been increased to several hundred micrometers and even millimeters (Figure 4c). One measure of graphene “quality” is the magnitude of the carrier mobility, and larger grain size has been correlated with higher carrier mobility values. “Good” conditions to grow SLG include (1) hydrocarbon dissociation (catalytic or thermal); (2) a catalyst favoring growth of graphene; and (3) nucleation, growth, and completion of the monolayer film by having all reactions occurring on the surface of the substrate. Indeed, SLG was shown to grow in UHV conditions on single-crystal metals with high carbon solubility and more recently by low-pressure CVD on Ni films by controlling the kinetic factors during the growth and, in particular, having the reaction occur only on the metal substrate surface. Other relevant parameters are the sticking coefficient of the carbon species on the metal surface and these species’ ability to diffuse on the surface.

In contrast to graphene, other layered systems are composed of two or more elements, making the synthesis more complex. Hexagonal boron nitride (h-BN) might be the most studied layered material after graphene, although reports on the CVD synthesis of MoS2 are emerging. The synthesis of single- and few-layer h-BN was achieved first in UHV CVD systems on single-crystal metals. Recently, the synthesis of single-layer h-BN and few-layer h-BN was reported in CVD systems using solid and gaseous precursors. Submonolayer domains on Cu foils were achieved using very low partial pressure of ammonia borane (Figure 4d), while control over the number of layers was achieved using diborane and ammonia on Ni foils as...
depicted in Figure 4e. Despite such achievements, the growth mechanism for h-BN remains unclear. The growth of SLG was significantly improved in only a few years by understanding some of the key parameters for growth. Can we apply similar methodologies to the growth of single or multiple layers of other layered materials? It calls for further nucleation and growth studies as well as an adequate set of characterization tools comparable to those used to characterize graphene.

**Multilayer Assemblies.** As will be discussed later, there are numerous applications for multilayer assemblies and hybrid composites from single- to many-layer (thickness < 1 μm) 2D materials, which we will define as nanosheets. The most common methods for assembly rely on solution processing. Colloidal dispersions of nanosheets can be self-assembled into useful constructions like porous solids, nanostructured thin films, hybrid polymer— inorganic nanocomposites, superlattices, and other hierarchical structures.

Effective wet-processing assembly techniques are electrostatic layer-by-layer assembly,102–105 Langmuir–Blodgett (LB),106–108 flocculation,12,109 and electrostatic self-assembly deposition (ESD).110,111 In these methods, the nanosheets are colloidal dispersions and then either deposited directly onto a substrate (layer-by-layer, LB) or aggregated into a nanocomposite in solution (flocculation, ESD). Other techniques to create single- and few-layer nanosheet assemblies during the gas-phase growth such as “chemical blowing” are emerging.112,113

The layer-by-layer method is one of the most precise approaches for constructing multilayered films with controlled architecture, composition, and thickness. This method employs polyelectrolytes absorbed onto the sheets and substrates to enhance the absorption of charged nanosheets.102,109,114 Nanosheet multilayer assemblies are formed by alternately dipping substrates in colloidal suspensions of charged nanosheets and in aqueous solutions of polyelectrolytes having the opposite charge.103 This technique has successfully been used to prepare interstratified composite materials with two separate nanosheet materials (superlattices) by sequential absorption of each layer.109

Electrostatic interactions between cations and nanosheets at the air/water interface can allow nanosheets to float, thus enabling use of conventional LB procedures.63,115,116 In this technique, a floating monolayer of nanosheets is formed in a Langmuir trough on a fluid surface, which is then horizontally compressed and then transferred onto a substrate by vertical dipping. The LB techniques can be used to deposit nearly perfect monolayer and multilayer films that are atomically smooth, high density, and without pinholes. For example, the LB method has been employed to produce single- and several-nanometer-thick titanio niobate and titantate layers that have a clean interface with the substrate.117,118

Recent work has demonstrated a new method to create millimeter-scale stacks of nanosheet assemblies with aligned layers. The method involves the sol–gel creation of 2D amorphous flakes, followed by pressurization-induced alignment of the flakes, electric-field-induced kinetic demixing, and finally calcination into stacks of single-crystalline sheets (Figure 5d).119 The kinetic demixing is the critical component to forming millimeter-length nanosheets: the kinetic demixing locally concentrates the mobile cations, which then diffuse laterally outward during calcination, forming the nanosheet stacks. For example, this method has produced Na₄CoO₂ nanosheet nanocomposites containing tens of thousands of self-assembled ~20 nm thick nanosheets that display interesting properties, such as extreme ductility, and can be bent up to 180° (Figure 5a–c) despite being composed from a ceramic.119 In the nanocomposites, the individual nanosheets are oriented to each other with turbostratic axial alignment. After exfoliation, the nanosheet lateral lengths can measure 350 μm. This procedure should be applicable to other ternary layered metal oxides.

**Characterization of Two-Dimensional Materials.** Probing the molecular and vibrational structure of 2D materials is inherently challenging due to the small sample size. However, numerous methods have been developed to enable their identification and characterization. In this section, we will provide a standard how-to guide for studying single-layer-thick materials. Furthermore, we will highlight emerging, less commonly used techniques that have the potential to simultaneously merge
structural or spectroscopic information with properties at the local scale.

The first challenge in single-layer characterization is single-layer preparation and detection. Mechanical exfoliation from bulk crystals is typically the simplest method for transferring 2D sheets of layered van der Waals solids such as graphene,5,20,120,121 metal chalcogenides,122 and GeH18 to any substrate. Exfoliation typically produces 10 μm sized flakes ranging in thickness from single to few layers. Optical microscopy is initially the most powerful high-throughput method for initially identifying single- and multiple-layer flakes.20,58,122,123 Dielectric-coated SiO2/Si substrates are the most common substrates used to visualize and locate single and few layers (Figure 6a,e,f). The color of the dielectric-coated wafer depends on an interference effect from reflection off of the two surfaces of the dielectric. Single- and few-layer flakes on the surface of the dielectric modify the interference and create a color contrast between the flake and the substrate.122 For optimal contrast, the thickness of the dielectric coating needs to be within 5 nm of the ideal value. However, since the index of refraction of many novel materials is unknown, it is often necessary to first experimentally exfoliate onto a range of substrates having different dielectric thicknesses to initially determine the optimal thickness.

Visualizing single layers on other substrates without the need for interference methods has also been explored. Some metal dichalcogenides (MoS2, WS2) have direct band gaps only as single layers, enabling their direct visualization by fluorescence microscopy.125 However, as the number of layers increases, these materials’ band gaps become indirect, significantly reducing their fluorescence.

Fluorescence Quenching Microscopy (FQM) uses an organic fluorophore whose fluorescence is quenched in the presence of single- or few-layer sheets (Figure 6f). Many 2D materials feature either low enough band gaps or the appropriate band alignment to quench nearby fluorophores via a FRET mechanism or charge transfer mechanism. One can locate single layers of 2D materials on a substrate by monitoring the reduction in fluorescence intensity of a thin fluorophore layer that was spun-coat on top.126

AFM is a powerful technique to determine layer thickness (Figure 6b,d) with a precision of 5%.114,118,129 However, discrepancies arise from differences in the interactions of the tip with the sample and substrate.130 For example, the thickness of a single layer can be better determined by measuring the height of a second layer on a first layer, rather than the height between a single layer and the substrate because in the former the tip–layer interactions are constant. To control these differences and obtain the most accurate height profile of a single layer, one must first optimize the tip–surface distance to exclude any hysteretic artifacts.130

Raman Spectroscopy is a useful method for fingerprinting a material and layer-dependent changes of the vibrational structure (Figure 6c). It is necessary to
use low power (e.g., 16 kW/cm² for Bi₂Te₃¹³¹ or 40 kW/cm² for GeH) when obtaining Raman spectra of single layers to prevent sample decomposition. The Stokes/anti-Stokes peak ratio can be used to determine the local temperature.¹³² Raman spectra can also detect vibrational modes that are active due to symmetry breaking in single-layer films and enhanced vibrations in out-of-plane modes when the single layer is suspended.¹³¹ When varying the layer number between bulk, few, and single layers, the Raman spectra differ in spectral width and intensity due to differing interlayer interactions.¹²²,¹²⁶ Substrates that have vibrational modes that overlap with those in the material of interest should be avoided. Vibrational spectroscopy, in general, and Raman spectroscopy, in particular, could be used to detect isotopic-enriched 2D materials to study the growth mechanism as demonstrated and thus be used to study the growth mechanism.⁸⁹

Transmission Electron Microscopy (TEM) can provide detailed information on the nature of crystallinity, layer sizes, interlayer stacking relationships, and elemental composition (Figure 7a,b).⁶³,¹¹⁴,¹¹⁹,¹²²,¹³³–¹³⁵ In the case of graphene, selected area electron diffraction can distinguish between monolayer and multilayer graphene when the intensity ratio of the (100) to (110) diffraction spots is larger or smaller than 1, respectively. This deviation in diffraction intensity can also distinguish between single- and multilayer flakes of other 2D materials when there is a change in interlayer registration. Recent advances have shown that dark-field microscopy can quantitatively determine the layer number and stacking order of multilayer graphene.¹³⁶ Scanning transmission electron microscopy (STEM), using high-angle annular dark-field detector coupled with electron energy loss spectroscopy can be used to visualize individual atoms in an isolated layer. Here a sub-angstrom electron beam is rastered across a sample and is scattered when it hits a particular atom. Figure 7c shows a STEM image of carbon and oxygen substitutions in a single layer of boron nitride. Low accelerating voltages (<60 keV) are often necessary to minimize beam damage.

Scanning Tunneling Microscopy (STM) is a probe-based technique that can measure the electronic and topographic structure of single-atom-thick materials and can manipulate single atoms at specific points in order to build and characterize nanostructures that are well isolated from the substrate (Figure 7d). Examples include STM studies of the unusual cyclotron quantization in graphene,¹³⁷,¹³⁸ as well as characterization of MoS₂ nanosheets and BN.¹⁴⁰ Recent focus has shifted toward studies of adsorbates and defects, including metal adatoms on graphene¹⁴¹,¹⁴² and h-BN¹⁴³,¹⁴⁴ and molecules on MoS₂.¹⁴⁵ Due to the challenge of aligning a particular region of the substrate with the remote STM tip, the most commonly studied samples are epitaxially grown. Near-field tip-enhanced Raman spectroscopy (TERS), in which an AFM or STM tip is coated with Au or Ag to enhance the local Raman spectra, has proven to be a powerful combined spectroscopic and imaging technique and, for example, has been used to identify defects and grain boundaries.⁴,⁵

X-ray Diffraction (XRD)—both small-angle X-ray scattering (SAXS) and wide-angle XRD—can supply information about the unit cell structure and constituents, the sheet thickness and lateral dimensions, and the arrangement of restacked nanosheets. SAXS provides information about inter-nanosheet stacking since these peaks occur at lower angles.⁶³ By simulating the SAXS pattern, the stacking direction, sheet thickness, and distance between the sheets (from ligands or absorbed molecules) can be determined. For instance, patterns of wet colloidal aggregates of nanosheets and dried aggregates of nanosheets will display different XRD patterns: layer-to-layer registry can be disturbed for wet colloidal aggregates, while in-plane lattice planes are maintained, suggesting isolated nanosheets (Figure 8).¹¹¹,¹¹⁶ For dried
The layered metal dichalcogenides (LMDCs) constitute one of the most studied families of van der Waals solids beyond graphite. These materials display remarkably diverse electronic properties, ranging from metals to semiconductors to insulators. They also exhibit interesting strongly correlated electron phenomena, such as charge density waves and superconductivity. Among them, molybdenum disulfide (MoS₂; semiconductor), has attracted particular attention. Several distinctive properties, related both to its optical and transport characteristics, have been demonstrated in MoS₂ at the mono- and few-layer level. Examples of these properties include the existence of a direct gap, unlike the bulk material, with strong excitonic effects and the possibility of strong excitonic effects and the possibility of...
full control of the valley and spin occupation by optical pumping with circularly polarized light. MoS$_2$ has also been shown to yield field-effect transistors with very high current on-off ratios at monolayer thickness and to function within a vertical graphene-MoS$_2$-graphene tunneling transistor structure. These properties, in combination with the promise of synthesis of large-area high-quality samples (notably by recently developed CVD methods), suggest interesting possibilities for applications of this and related materials in electronics and optoelectronics. Here we summarize some of the recent progress in understanding the electronic properties of ultrathin MoS$_2$ layers.

The overall physical structure of the MoS$_2$ monolayer is similar to that of the graphene honeycomb lattice. For MoS$_2$, however, the A and B sublattices, rather than both being occupied by C atoms, are occupied either by Mo atoms or by a pair of S atoms (Figure 12c), with the entire MoS$_2$ monolayer structure forming a triple layer of atoms. The difference between the A and B sublattices lifts the degeneracy in the electronic structure at the K (K') point in the Brillouin zone. This degeneracy is responsible for the distinctive Dirac cone dispersion relation in graphene. In contrast, in monolayer MoS$_2$, a substantial energy gap is present.

The bulk MoS$_2$ crystal, consisting of MoS$_2$ monolayers arranged with Bernal stacking, is known to be an indirect gap semiconductor, with a band gap of 1.29 eV. The calculated band structure for bulk MoS$_2$ shows that the valence and conduction band extrema occur away from the K (K') point (Figure 9a). Through characterization by absorption, photoluminescence (PL), and photoconductivity spectroscopy (Figure 9c–e) as a function of thickness, Mak and co-workers have traced the effect of quantum confinement on the electronic structure of MoS$_2$ layers. With decreasing thickness, the indirect band gap, which lies below the direct gap in the bulk material, shifts upward in energy by more than 0.6 eV. This leads to a crossover to a direct gap material in the limit of monolayer thickness since the electronic states near the K point are more localized within the layer and shift up in energy only modestly with decreasing layer thickness (Figure 9a,b). The result of this crossover in the band structure is the emergence of bright photoluminescence, which is absent for thicker films, in the monolayer material (Figure 9c). The direct gap character of monolayer MoS$_2$ has also been confirmed by ab initio calculations.

The ability to control the material's electronic structure through the sample thickness is not unique to MoS$_2$. 

Figure 9. Calculated band structures of (a) bulk and (b) monolayer MoS$_2$. The solid arrows indicate the lowest-energy transitions. (c) PL spectra for mono- and bilayer MoS$_2$ samples. Inset: PL quantum yield of thin layers of MoS$_2$ for number of layers $N = 1$–6 in log scale. (d) Absorption spectra (left axis) normalized by the layer number $N$ in the photon energy range from 1.3 to 2.4 eV for mono- and bilayer MoS$_2$. The corresponding PL spectra (right axis, normalized by the intensity of the peak A) are included for comparison. The spectra are displaced along the vertical axis for clarity. (e) Band gap energy of thin layers of MoS$_2$ for $N = 1$–6. The band gap values were inferred from the energy of the indirect gap PL feature I for $N = 2$–6 and from the energy of the PL peak A for $N = 1$. As a reference, the (indirect) band gap energy of bulk MoS$_2$ is shown as a dashed line.
Similar changes in the electronic band structure as a function of sample thickness have been predicted for other semiconducting LMDCs compounds MX$_2$ (M = Mo, W and X = S, Se, Te).\textsuperscript{182} Furthermore, recent calculations have shown that the electronic and optical properties of monolayer and few-layer MoS$_2$ can be controlled through strain engineering.\textsuperscript{183}

Another important aspect of the properties of 2D semiconducting LMDCs such as MoS$_2$ is the important role of many-body electronic interactions. In particular, the optical properties are dominated by excitonic transitions. The enhanced Coulomb interactions existing in these materials can be attributed to reduced dielectric screening in these atomically thin systems. The absorption spectrum of the undoped MoS$_2$ monolayer (Figure 9d) shows pronounced absorption peaks from excitonic transitions, rather than the steps that would be expected for absorption arising from band-to-band transitions in a 2D system with a direct gap. The two features, known as the A ($\sim$1.9 eV) and B ($\sim$2.1 eV) excitons,\textsuperscript{125,149,187} arise from transitions from the two highest-lying spin-split valence bands to the lowest conduction bands.

The influence of doping on the optical properties of monolayer MoS$_2$ has been studied recently by Mak \textit{et al.} using FET structures\textsuperscript{156} for electrostatic control of the doping level. By analyzing the absorption and emission line shapes at low temperature, Mak \textit{et al.} have identified, in addition to the presence of the usual neutral excitons, negative trions, quasi-particles composed of two electrons and a hole. The trion binding energy has been determined to be $\sim$20 meV, which far exceeds that observed in conventional 2D semiconductor quantum wells and renders trions significant even at room temperature. Similar phenomena have also recently been observed in MoSe$_2$ FETs by Ross \textit{et al.}.\textsuperscript{157}

Because of symmetry, crystals frequently have independent, degenerate valleys in the conduction or valence band. Access to this so-called “valley” degree of freedom has attracted interest both from the point of view of fundamental physics and a possible new control variable for new classes of electronic devices, commonly called “valley-trionics” and discussed in more detail below. To date, however, it has proven difficult to selectively populate a given valley to produce valley polarization. MoS$_2$ monolayers with a direct energy gap at the K and K’ points in the Brillouin zone have recently been predicted to be suitable for the \textit{control of valley population} using optical pumping with circularly polarized light.\textsuperscript{154,188} Because of the broken inversion symmetry, strong spin–orbit interactions split the spin-degenerate valence bands by $\sim$160 meV in MoS$_2$ monolayers. This broken spin degeneracy, in combination with time-reversal symmetry, implies that the valley and spin of the valence bands are inherently coupled. When optical transitions between the upper valence band and the conduction band (corresponding to the A exciton) are induced by circularly polarized photons, excitation occurs only at either the K or K’ valley, depending on the helicity of the light. This excitation process, because of the coupled valley and spin degree of freedom, also gives rise to photogenerated particles of a well-defined spin state. These theoretical predictions have been recently verified by several experimental groups\textsuperscript{153–155,158} through a demonstration of the retention of the circular polarization state of light emission induced by resonant excitation with circularly polarized light. The important role of inversion symmetry in establishing valley polarization was further confirmed by a comparison of the behavior of MoS$_2$ bilayers in which inversion symmetry, unlike for the case of the monolayer, is present. More general discussion of 2D materials for spin- and valley-tronics is provided in later sections of this review.

\textbf{Edge Effects on the Electronic Structure.} As we discuss in the previous section, LMDCs exhibit novel physicochemical properties when the bulk (3D) form is reduced to a monolayer (2D). The most notorious change is related to the electronic band structure, which can change from an indirect band gap in 3D to a direct band gap in a 2D monolayer.\textsuperscript{135,149} If the monolayer has finite lateral dimensions, contributions from the edges might become important and new phenomena are expected.\textsuperscript{135,159} Although a monolayer of LMDCs is actually composed of three atomic layers in which each layer of metal atoms is sandwiched between two layers of chalcogen atoms (X-M-X), the projection in the plane exhibits a hexagonal or honeycomb-like crystal structure similar to graphene; hence the edge terminations can be zigzag, armchair, chiral, or a mixture of these types.

Both the structural and chemical terminations of the edge are crucial to determine the local physicochemical properties of these systems. First principles calculations have predicted that diverse edge passivation in metal dichalcogenides could produce different spins states that modify the edge electronic and magnetic properties.\textsuperscript{135,158} In addition, high spin density could be localized surrounding metal vacancies.\textsuperscript{191} The experimental exploration of edges in inorganic 2D materials is still at an early stage. From the experimental point of view, triangular clusters of MoS$_2$ on Au substrates have been studied by STM,\textsuperscript{138,192} revealing metallic electronic states localized close to the edges. For perfect continuous edges, those metallic states can be viewed as one-dimensional conducting wires.\textsuperscript{192} The same group studied the size dependence of the cluster morphology and electronic structure and consistently found sulfur-terminated edges in single-layer clusters.\textsuperscript{139} Enhanced catalytic activity has also been correlated with the density of edge sites in MoS$_2$ 2D clusters.\textsuperscript{194}

To date, MoS$_2$ has been the testing ground for many experiments in monolayers of metal
dichalcogenides. However, other compounds of this family are also good candidates to study new and exciting properties. Recently, the optical behavior of WS$_2$ triangular monolayers was investigated by Raman spectroscopy and micro-PL. Monolayers of WS$_2$ exhibited a single PL peak between 1.9 and 2.0 eV, corresponding to a 2D exciton associated with the direct band gap transition. A remarkable enhancement of the PL intensity was observed in regions close to the edges of the 2D triangular clusters (Figure 10a). PL mappings of the WS$_2$ triangular island (Figure 10b) showing the peak position and absolute maximum intensity, respectively, are shown in Figure 10c.e. In general, the spectrum closer to the edge shows both a significantly stronger PL signal when compared to the central region, as well as a red shift of the PL peak. TEM analysis revealed that the triangular islands possess mainly zigzag edges, and the synthesis conditions provided a sulfur-rich environment. Determining the exact mechanism for PL enhancement demands a one-to-one correlation between the chemical structure of the edge and its optical response. The main challenge consists of implementing experiments that reveal the exciton dynamics, such as temperature-dependent PL, and/or time-resolved PL, with spatial resolution of the order of tens of nanometers.

**Surface Tuning of Band Structure.** The need to tune the optical and electronic properties of graphene for applications has created a large number of proposed methods to engineer its band structure by introducing defects and/or dopants. Both p-doping and n-doping of graphene have been reported, the latter by doping with nitrogen species and the former by functionalization of graphene with hydrogen, oxygen, hydroxyl groups, or carboxylic groups. However, adsorbed molecules have been found to have an extremely high mobility and low adhesion in ambient atmosphere, which makes reliable device fabrication challenging. Chemisorbed molecules change the band structure dramatically from a near-zero gap semimetal to a wide gap semiconductor, turning graphene into a highly effective insulator. The carrier mobility has also been shown to be decreased by more than 3 orders of magnitude to ~10 cm$^2$/V·s. Overall, tuning the electronic and carrier properties of graphene in a useful range has been a very challenging task, stimulating the search for alternative 2D semiconductors with better tunability.

Even though the graphene-like band structure of silicene and germanane and the explanation for puckered versus flat 2D sheets was reported many years ago, much less effort has been spent in examining the tunability of these alternative elemental 2D materials, which have been successfully synthesized recently. Traditional density functional theory (DFT) suggests that a 2.75 eV direct band gap is formed after complete hydrogenation of silicene, whereas other types of functional groups (F, Cl, Br, and I) lead to different band gap values. H-terminated Ge graphane analogues have been calculated to also have a direct band gap of 1.7 eV. Here we summarize recent theoretical results that explain how to controllably manipulate the relative band energies and local extrema of a covalently modifiable group IV silicon graphane analogue by termination with different organic substituents.

To develop the relationship between the band structure and the terminating functional group on silicene, Restrepo et al. used DFT calculations with spin–orbit coupling and a hybrid HSE06 exchange-correlation functional, which features exact exchange not included in previous calculations. Silicane (H-terminated silicene) is found to have an indirect band gap of 2.94 eV with the conduction band minimum at the M point and a direct gap of 3.14 eV at the $\Gamma$ point (Figure 11). The local conduction band minimum at $\Gamma$ originates from the Si–H $\sigma^*$-bonds, whereas the global minimum at M corresponds to the Si–Si $\sigma^*$-bonds. These two conduction band minima react differently to manipulation of the silicane atomic structure. Strain that increases the Si–Si bond lengths lowers the minimum at $\Gamma$ while having a nearly negligible effect on the minimum at M. This leads to a change from indirect to direct band gap when the ground-state Si–Si bond length of 2.36 Å is increased to 2.40 Å. This change also causes the effective mass at the conduction band minimum to decrease from 0.18 to 0.087 $m_0$ (48%). Changes in the Si–H bond length also mostly affect the $\Gamma$ and not the M point states but are smaller than those induced by varying the Si–Si bond length. This high sensitivity of the $\Gamma$ point minimum to changes in the bond between the Si atoms
and the terminating hydrogen atom suggests that it is possible to tune the band gap using different terminating substituents. Small organic moieties such as methyl or ethynyl groups have also been calculated to decrease the conduction band energies and result in direct band gaps or equal conduction band minimum energies at M and Γ (Figure 11), with varying effective masses. These results show that in contrast to graphene, where functionalization leads to drastic changes in the semimetallic band structure, silicene functionalization should allow for a wide continuous tunability in band and conduction properties and offer exciting prospects for the engineering of new electronic materials.

**Figure 11. DFT results calculated with HSE06 hybrid potentials for silicene functionalized with (a) H, (b) half H and half hydroxyl (OH), (c) methane CH₃, and (d) acetylene C₂H.**

Two-Dimensional Materials for Spin- and Valleytronics. Expanding charge-based microelectronics to take advantage of the spin and “valley” degrees of freedom is expected to increase computing power, reduce energy consumption, and enable the development of entirely novel devices. Graphene is an attractive material for spintronic applications because of its tunable carrier concentration and intrinsically low spin–orbit interaction and hyperfine couplings, which are expected to lead to long spin lifetimes. Here, graphene serves as an important test case for the expansion of spintronics to other 2D materials beyond graphene.

Many benchmarks toward spin functional graphene devices have already been met, the most important of which is the demonstration of room-temperature gate-tunable spin transport, as shown in Figure 12a. These experiments used lateral spin valves (Figure 12a, inset), which have ferromagnetic electrodes to preferentially inject spin-up or spin-down electrons. The spin diffuses from the injection site and can be detected nonlocally by an electrode outside of the current path. Record spin lifetimes in graphene of 6.2 ns at 20 K have been observed (Figure 12b). Essential to this achievement was overcoming the so-called conductance mismatch problem at the injection interface with the incorporation of a high-quality, half-monolayer tunnel barrier of MgO. Despite these successes, measured spin lifetimes in graphene are orders of magnitude lower than those expected from *ab initio* calculations. A central challenge in graphene spin-transport studies is to find the source of this additional spin scattering. Recent measurements of spin transport in bilayer graphene spin valves as well as those in single-layer graphene spin valves doped with adatoms indicate that local inhomogeneities in the electronic environment are primarily responsible for the low measured spin lifetimes. If true, then while unfortunate for applications requiring robust spin coherence this extreme sensitivity of spin transport to adsorbates and screening might be intentionally exploited for novel functionality.

The spin properties of graphene provide a framework for the exploration of spin functionality in other 2D materials. MoS₂ is a specific example of how that functionality can be expanded. MoS₂ exhibits strong spin–orbit coupling, which can significantly suppress spin scattering for a certain spin direction (Figure 12c). Though similar to graphene in other ways, the strong spin coupling in MoS₂ makes this material insensitive to spin scattering where graphene is sensitive. Achieving tunable spin scattering through creative combination of graphene and MoS₂ could provide a spectrum of new
spin functionality. Even more, MoS$_2$ has the potential to link spin and orbital degrees of freedom, combining two of the most exciting new ideas for novel approaches to electronics: spintronics and valley-tronics.

Valley-tronics, as described above, is the manipulation of the population of degenerate low-energy valleys that are exhibited in the band structure of some materials, including graphene and MoS$_2$. Of particular relevance for electronic transport, these valleys are separated widely enough in momentum space that intervalley scattering is strongly suppressed.$^{231,232}$ The potential for computing with valley-tronics was first

Figure 12. (a) Nonlocal magnetoresistance scans of single-layer graphene spin valves measured at room temperature. The black (red) curve shows the nonlocal resistance as the in-plane magnetic field is swept up (down). The nonlocal MR ($\Delta R_{NL}$) of 130 $\Omega$ is indicated by the arrow. Inset: Nonlocal spin transport measurement on this device with a spacing of $L = 2.1 \mu m$ and SLG width of $W = 2.2 \mu m$.\footnote{229} (b) Hanle magnetoresistance measurement (with field applied out-of-plane) of a bilayer graphene spin valve at the charge neutrality point gate voltage measured at a temperature of 20 K (inset at 300 K). The spin lifetime ($\tau_s = 6.2$ ns) and diffusion constant ($D = 0.0047$ m$^2$/s) are determined by a fit to the Hanle curve.\footnote{228} (c) (Left, top) Representation of the trigonal prismatic structure of monolayer MoS$_2$ where each layer is a honeycomb lattice structure with each sublattice occupied by a Mo and two S atoms. (Left, bottom) The lowest-energy conduction bands and the highest-energy valence bands labeled by the z-component of their total angular momentum near the $K$ and $K'$ point of the Brillouin zone. The spin degeneracy at the valence band edges is lifted by spin–orbit interactions. The valley and spin degrees of freedom are coupled. Under left-circularly polarized excitation, only the $K$-valley is populated, whereas under right-circularly polarized excitation, only the $K'$-valley is populated.\footnote{156} (Right) Illustration of polarized spins (blue arrows) excited by right-circularly polarized light (red beam) populating the $K$-valley in an MoS$_2$ sample. (d) Band lines near the Fermi level of BN/graphene heterobilayers with specific stacking patterns (shown on the right), calculated using local density approximation functional. The interlayer distances are $x = 5, 3.3, 3, 2.7$, and 2.4 Å and the Fermi level is set to 0.\footnote{240} Panel d reprinted with permission from ref 233. Copyright 2011 American Institute of Physics.
discussed for 2D electron gas devices, like AlAs and Si,\textsuperscript{233} but may be better realized with 2D materials with appropriate band structures. Because inversion symmetry is broken in MoS\textsubscript{2}, the valley and spin degrees of freedom are coupled and new optical selection rules enable excitation of specific spin carriers into a specific valley, as illustrated in Figure 12c.\textsuperscript{156,231} This spin-valley coupling forbids independent spin or valley flipping, ensuring robust indices useful for spintronic and valleytronic applications. There is likely a lot of functionality yet to be discovered in 2D materials beyond graphene. Not only in MoS\textsubscript{2} just one of many transition metal dichalcogenides,\textsuperscript{248} but similar phenomena may also be exploited in non-MX\textsubscript{2} materials such as silicene or germanane.

Finally, mechanically assembled heterostructures of van der Waals bonded 2D materials might be expected to show combined functionality of the individual layers.\textsuperscript{234} The unique properties of the independent layers, which could include spin or charge density waves, superconductivity, and carefully chosen band structures, coupled with an anticipated high rate of electron tunneling between layers could lead to emergent properties.\textsuperscript{235} Not being limited by epitaxy, like traditional thin film heterostructures, a nearly infinite number of 2D material heterostructures with various properties can be imagined. Historically, heterostructures such as semiconductor superlattices have led to the development of novel technologies such as dielectric mirrors,\textsuperscript{236} microwave metamaterials,\textsuperscript{237} and negative refraction index materials.\textsuperscript{238}

Emergent functionality in 2D material heterostructures is anticipated theoretically. Density functional theory calculations predicted a band gap in graphene/BN bilayers.\textsuperscript{239} More recently, first principles calculations show that the band gap and effective electron mass in graphene/BN heterostructures might be tuned by the interlayer spacing and stacking arrangement of the individual layers, as shown in Figure 12d.\textsuperscript{240} Experimentally, graphene/BN heterostructures have proved important for achieving high electron mobility in graphene since the underlying BN lattice creates a better dielectric environment and reducing sensitivity to charged point defects in the underlying SiO\textsubscript{2}.\textsuperscript{241,242} These heterostructures have also led to an understanding of the observed “minimal conductivity” in graphene,\textsuperscript{243} which results from charge puddles created by the nearby SiO\textsubscript{2} substrate.\textsuperscript{244,245} Additionally, tunneling field-effect transistors made from graphene/BN or graphene/MoS\textsubscript{2} heterostructures have been demonstrated to have high on/off ratios (up to 10,000).\textsuperscript{171} While these heterostructures do not yet show emergent phenomena, they represent important technological advances.

**Topological Insulators.** On the surface of bulk materials, either dangling bonds or band bending by an electrostatic potential can result in the appearance of 2D electronic states. Topological insulators (TIs) have unusual bulk properties that allow them to accommodate 2D electronic states on their surface.\textsuperscript{246} In TIs, strong spin−orbit effects create metallic electronic states on the materials' surfaces, while the bulk of the material remains insulating. Furthermore, the surface bands of TIs have an interesting electronic property in which the spin of a surface electron is always perpendicular to its momentum.\textsuperscript{247} This extraordinary spin property does not allow electrons to be backscattered by impurities,\textsuperscript{248} suggesting electronic channels of high mobility.

Following the first observation of this surface band from a Bi−Sb alloy,\textsuperscript{249} many materials, especially layered van der Waals materials, have been reported to be topological insulators. Layered binary chalcogenides, such as Bi\textsubscript{2}Se\textsubscript{3}, Bi\textsubscript{2}Te\textsubscript{3}, and Sb\textsubscript{2}Te\textsubscript{3}, are particularly interesting candidates for applications\textsuperscript{250} due to their relatively large bulk band gap (\textasciitilde 0.2 eV) and simple band structure, which is similar to the Dirac band of graphene (Figure 13a,b). The existence of surface states in this family of materials is confirmed experimentally\textsuperscript{251−254} (Figure 13c). However, the surface electron transport is not yet straightforward to observe mainly due to the large contribution of bulk electrons. Imperfections in the bulk crystal structure create vast amounts of additional electrons, overwhelming the surface electron transport.\textsuperscript{253,254} Therefore, the TIs need to be engineered to reduce the bulk contribution in order to achieve transport dominated by surface electrons.

Lowering the dimensionality of these TIs might provide a route to study their surface state. Reducing sample size can suppress bulk carriers by increasing a surface-to-volume ratio.\textsuperscript{254} Also, low-dimensional TIs will allow the electron chemical potential to be modulated by an electric field, which can also reduce bulk carriers. TI nanodevices can be prepared from CVD-grown nanostructures\textsuperscript{254−256} (Figure 13d,e) and via the mechanical exfoliation of single crystals (Figure 13f).\textsuperscript{257} Field-effect measurements have successfully demonstrated the modulation of the carrier types by gate voltage, showing a potential for electronic applications.\textsuperscript{255−257} To control bulk electrons in TIs, compensational doping\textsuperscript{253,255,256} and proper surface encapsulation\textsuperscript{256} are crucial.

The unusual properties of the TI surface states suggest many applications not feasible in conventional materials. The intrinsic spin properties of TIs are attractive for spintronics applications.\textsuperscript{258} Also, superconducting TIs are expected to generate exotic quantum modes, potentially useful for quantum computation.\textsuperscript{258,259} Additionally the surface states can play a role in energy science by enhancing thermoelectric effects in Bi\textsubscript{2}Te\textsubscript{3} and Bi\textsubscript{2}Se\textsubscript{3}, which are well-known thermoelectric materials.\textsuperscript{260} Finally, this newly discovered electronic state, often called “graphene with a
spin texture\textsuperscript{a}, is a platform for a number of interesting studies and applications.

**Thermal and Thermoelectric Properties.** Recent advances in the synthesis and isolation of graphene and other atomic layered materials have enabled fundamental studies of unique thermal and thermoelectric transport properties of 2D systems, as well as the potential applications of these 2D materials for thermal management and thermoelectric energy conversion. Because of the absence of interlayer phonon scattering, the thermal conductivity of an ideal 2D system, such as suspended SLG or h-BN, is expected to be higher than the basal-plane values of their three-dimensional stacks, namely, graphite and bulk h-BN. Although the results from several micro-Raman measurements\textsuperscript{261,262} of suspended SLG are in agreement with these theoretical predictions, other Raman measurements\textsuperscript{263,264} of suspended SLG samples have yielded values comparable to or lower than the basal-plane values of graphite, as shown in Figure 14. In addition, further experiments are needed to verify recent theoretical predictions that flexural phonons (out-of-plane modes) make a large contribution to the thermal conductivity in suspended few-layer graphene and h-BN.\textsuperscript{265,266}

In addition, both theoretical and experimental studies have found considerable reduction of the basal-plane thermal conductivity in graphene or h-BN supported on or encased in an amorphous material\textsuperscript{267} or contaminated by polymer residue,\textsuperscript{270} as shown in Figure 14. In particular, the interface interaction with an amorphous material has been found to decrease the basal-plane thermal conductivity with decreasing layer thickness of FLG\textsuperscript{268,271} or suspended few-layer h-BN with polymer residue.\textsuperscript{272} This trend is opposite to that suggested for suspended FLG or h-BN.\textsuperscript{261,265,266} These findings indicate that the basal-plane values for high-quality graphite and h-BN bulk crystals present a practical limit in the thermal conductivity of few-layer graphene and h-BN when these 2D layered materials are used as heat spreaders in contact with a heat source and a heat sink or as nanofillers to increase the effective thermal conductivity of a composite. However, even supported SLG can possess a basal-plane thermal conductivity higher than that of copper.\textsuperscript{267} Moreover, further theoretical and experimental research may potentially find new approaches to increasing the basal-plane thermal conductivity of supported graphene and h-BN by choosing the right support material or tuning

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**Figure 13.** (a) Electronic structure of Bi\textsubscript{2}Se\textsubscript{3} reconstructed by angle-resolved photoemission spectroscopy (ARPES), showing bulk conduction band (upper pocket), bulk valence band (lower pocket), and surface-state band (linear band).\textsuperscript{251} Reprinted with permission from ref 251. Copyright 2009 Nature Publishing Group. (b) Crystal structure of Bi\textsubscript{2}Se\textsubscript{3} (layered structure). Each quintuple layer is made of five atomic layers of bismuth (Bi) and selenium (Se).\textsuperscript{254} (c) Magnetoresistance of a Bi\textsubscript{2}Se\textsubscript{3} nanoribbon in parallel magnetic field, showing periodic oscillations from the Aharonov–Bohm interference of the surface electrons.\textsuperscript{254} (d) Optical microscopy image of topological insulator (Bi\textsubscript{x}Sb\textsubscript{2}Te\textsubscript{3}) nanoplates (5–10 nm thickness) on SiO\textsubscript{2} substrate.\textsuperscript{255} The scale bar indicates 5 μm. (e) Scanning electron microscopy image of topological insulator (Bi\textsubscript{2}Se\textsubscript{3}) nanowires and nanoribbons (50–200 nm thickness).\textsuperscript{266} The scale bar indicates 10 μm. (f) Optical microscopy image of a topological insulator (Bi\textsubscript{2}Se\textsubscript{3}) flake on SiO\textsubscript{2} substrate from mechanical exfoliation of a bulk crystal.\textsuperscript{257} The scale bar indicates 2 μm. Reprinted with permission from ref 257. Copyright 2011 Nature Publishing Group.
rather conformal to the surface roughness. In addition, graphene is an insulator, which can be advantageous for its applications as a heat spreader in direct contact with high-power density semiconductor nanodevices. Moreover, other 2D layered materials such as MoS$_2$ and germanane provide different band gap values suitable for various functional devices. In these functional devices made of 2D layered materials, local heating can become an important issue similar to the challenge faced by silicon nanoelectronic devices, especially if the in-plane thermal conductivity of these 2D materials is suppressed by phonon scattering by interface disorder or interactions with another material. However, little is currently known about the thermal transport properties of these 2D materials and heterostructure devices made of multiple 2D materials.

The possibly suppressed thermal conductivity ($\kappa$) of 2D layered materials with surface disorder or perturbation is desirable for thermoelectric materials. During the past two decades, nanostructures have been actively investigated for suppressing the phonon contribution to the thermal conductivity of thermoelectric materials. In such efforts, it is critical to control the interface charge states and scattering in the nanostructured materials, so that these effects do not result in a considerable reduction of the charge mobility, power factor, $S^2\alpha$, and figure of merit, $Z = S^2\alpha/\kappa$, where $S$ is the Seebeck coefficient and $\alpha$ is the electrical conductivity. Moreover, research along this direction was initially stimulated by theoretical predictions of power factor enhancement in 2D and one-dimensional quantum structures. Recent theoretical studies have further suggested that the power factor can be enhanced by the coupling of the two topological surface states in few quintuple layers of Bi$_2$Te$_3$ and Bi$_2$Se$_3$. A careful control of the surface quality and surface band bending will be required for these effects due to quantum confinement and topological surface states to be verified in experiments. These challenges suggest abundant opportunities for research in thermal and thermoelectric properties of 2D materials beyond graphene.

Applications to Transistor Scalability. Progress in the semiconductor industry has been driven by a continuous reduction of the transistor geometry. Current silicon-based field-effect transistors (FETs) feature 22 nm gate lengths, and further size reductions motivate the need to search for alternative device concepts and materials. A conventional FET consists of a semiconducting channel that is connected to source and drain electrodes and can be switched on and off by the application of a field via a gate electrode that is separated by a dielectric material (Figure 15a). Desirable features of switching transistors include high on/off current ratios, low power consumption, and fast switching times.

Two-dimensional materials have an innate advantage over bulk materials, like Si, for device scalability because of their favorable electrostatic properties. In particular, due to their dimensionality, these materials can approach the ideal effective screening length $\lambda$, and can be operated beyond the quantum capacitance...
limit (QCL). To reduce the channel length in today’s typical silicon-on-insulator transistor, the semiconductor thickness must also be reduced to ensure that 2D electrostatic screening effects are minimized.\textsuperscript{284} Electrostatic potential variations along the channel are screened out within a material-dependent $\lambda$.\textsuperscript{285,286} To prevent the electric field of the drain from being totally screened in a small channel, like those of ultrascaled MOSFETs, it is desirable for $\lambda$ to be as small as possible. While the exact form of $\lambda$ depends on the details of the device structure, for single and double gate geometries, it can be approximated by\textsuperscript{285}

$$\lambda = \sqrt{\frac{\varepsilon_s d_s d_{ox}}{\varepsilon_{ox}}} \quad (1)$$

Here, $\varepsilon_s$ and $d_s$ denote the dielectric constant and thickness of the semiconductor, respectively, and $\varepsilon_{ox}$ and $d_{ox}$ are the respective quantities for the dielectric oxide. In either case, minimizing $d_s$ will minimize $\lambda$. Thus, single-layer-thick 2D materials represent the best possible scenario that nature has to offer.

A second advantage of 2D material-based transistors is their ability to operate beyond the QCL, the limit at which the oxide capacitance is equal to the quantum capacitance, the capacitance due to gate-voltage-induced free charges in the channel.\textsuperscript{287,288} In the QCL regime, the intrinsic gate delay is reduced ($\tau$), and the $P\cdot\tau$ (where $P$ is the dynamic power) now decreases linearly with channel length in the QCL regime.\textsuperscript{289,290} Thus the energy consumption required for switching is minimized in the QCL. In addition, many 2D materials from the dichalcogenide family, and even silicane and germanane, possess a larger band gap than bulk Si. This property could result in a much lower direct source-to-drain leakage current, which is especially important for ultrascaled transistors.\textsuperscript{291}

Recognizing the potential impact of 2D materials for transistor applications, a significant amount of work has been devoted to making these transistors in the past few years.\textsuperscript{163,167,292–295} Recently, the performance of MoS$_2$ transistors has been theoretically examined\textsuperscript{164} using real space, self-consistent, and fully parallel non-equilibrium Green’s function transport simulation within a $k\cdot p$ approach and band structure fitted to first principles calculations. Figure 15b shows the drain current ($I_D$) versus gate voltage ($V_G$) characteristic for a simulated MoS$_2$ transistor. The maximum ON current can be as high as 2 mA/$\mu$m, and the OFF current could be as small as 10 fA/$\mu$m, thereby giving an incredibly large ON/OFF ratio (~$10^{10}$). Figure 15c shows the subthreshold swing as a function of gate oxide thickness. These simulation results show fantastic immunity to short channel effects. Note that almost an ideal subthreshold swing (60 mV/decade) is achievable with a reasonably large gate oxide thickness of around 5 nm even for a 30 nm channel length device. This result can be attributed to the fact that the screening length $\lambda$ is very small as expected for a 2D material. Figure 15d

Figure 15. (a) Schematic illustration of cross section of MoS$_2$ FET.\textsuperscript{163} Reprinted with permission from ref 163. Copyright 2011 Nature Publishing Group. (b) Transfer characteristic of a monolayer MoS$_2$ transistor in both log and linear scales. (c) Subthreshold swing as a function of gate oxide thickness for two different gate lengths. (d) Capacitance vs voltage characteristics. Inset shows the change in surface potential $\psi_s$ with gate voltage $V_G$.\textsuperscript{164}
shows the capacitance–voltage characteristic. Note that the total capacitance (shown in blue) is much smaller than the oxide capacitance (black dashed line) and closer to the quantum capacitance (shown in solid red). This means that the device is working close to the QCL. These simulations confirm the fantastic electrostatic control, QCL operation, and low leakage current for a 2D material.

**Multilayer Assemblies and Their Applications.** Nanosheets (Figure 5), referring to “restacked” or assembled 2D materials, provide new opportunities and advantages for devices. For many applications, these nanosheets and their composites have inherent and predicted advantages: they can be solution processed, they can display new behavior due to their extremely high surface area, and as free-standing multilayer assemblies, they are flexible and can be manipulated either mechanically or by deposition on templates. Mixing of nanosheets with other materials, including metal nanoparticles, polymers, and small molecules, can be a route to interesting solution-phase nanocomposite hybrids, such as superlattice-like assemblies.99,119,297

Reassembly of nanosheets into multilayer films can lead to improved properties in the areas of supercapacitors,300 pseudocapacitors,301 photoconductive materials,302,303 and heterojunction photodiodes304 as new magnetic materials305 and as magneto-optical components.306,307 Additional applications include the following:

**Batteries:** The morphological and size advantages of nanosheets have shown improved performance as battery electrodes. For example, reassembled octatitanate nanosheets have better reversible capacities than electrodes made from bulk octatitanate, presumably due to the ability of these nanosheets to better withstand damage caused by lithium insertion and extraction.300,308

**Magnetic Properties:** Ferromagnetic nanosheets can display unique properties such as anisotropic magnetization and stronger influences from surface atoms.309 For instance, gigantic magneto-optical effects have been observed in Ti$_{0.8}$Co$_{0.2}$O$_2$ nanosheets. Because these nanosheets are composed entirely of surface atoms, surface cobalt spins and their local ferromagnetic couplings are much stronger than those that occur in dilute magnetic semiconductors and bulk magnets.309

**Photoconductors:** Restacked nanosheets have higher surface area than their bulk precursors, and this aspect, coupled with the finite thickness effects on electronic activity in solar energy conversion111 and in capacitance,301 has been recently demonstrated that a vertically oriented 2D organic/inorganic lamellar photodetector architecture can have better detectivities than sensitized nanoparticle thin films.310 This is because the excellent 2D conduction channel allows for reduced majority carrier transit times, and the atomic-scale thickness of the 2D material enables a high sensitization ratio.

**High Dielectric Constant Materials:** As high-k dielectrics, nanosheets can be used where thin films from vapor deposition cannot. Metal oxide thin films grown by conventional vapor deposition techniques often show decreasing dielectric constants with decreasing film thickness.118,310,311,312 One reason for the degradation in dielectric properties is the high temperatures that complex vapor processing requires, often above 600 °C, which reduces the polarizability due to nonstoichiometry.312 Free-standing and stacks of nanosheets, however, have been shown to have low leakage current densities and high dielectric constants for thicknesses down to 10 nm (Figure 16a).117,118,312 Reassembled nanosheets also have the advantage of electronic isolation of each nanosheet in these multilayer assemblies.309

**Liquid Crystals:** Inorganic magnetic nanoparticles of magnetite have been mixed with niobate nanosheets and placed in a magnetic field to guide the nanoparticles’ orientation.111,313 Light scattering shows orientational dependence on the magnetic field (Figure 16b). Potassium niobate nanosheets have been successfully functionalized with silane and dispersed in organic solvents to create liquid crystals.314 The nanosheet colloids were dispersed in chloroform and exhibited birefringence characteristics of a nematic phase.111,314 Liquid-crystal properties of nanosheets have also been reported for nanosheets made of niobates315 and KCa$_2$Nb$_2$O$_{10}$ among others. The lateral dimensions, aspect ratio, and colloid concentration of the nanosheets strongly dictate the liquid-crystal properties.315

**OPPORTUNITIES AND OUTLOOK**

In this nascent field of 2D materials, the salient differences between bulk and few or single layers are just starting to be understood. New fundamental studies can address single-layer scale differences in many-body interactions; phonon transport, such as flexural phonon modes; interfacial electron–electron, electron–phonon, electron–magnon, etc. coupling; excitonic and other quasiparticle properties; the nature of...
and impact of defects and the substrate; the influence of high doping, strain effects, and electric fields; mechanical properties; quantum size effects; and edge effects in transport. At the single-layer scale, interactions with the surroundings often dominate experimental observations, and consequently, there are a multitude of unexpected experimental challenges in isolating the intrinsic material properties. There are numerous exciting opportunities in developing the growth of high-quality large-area materials with controllable layer thicknesses. Such systems would not only expand our understanding of the underlying physics but potentially lead to the discovery of unanticipated phenomena and applications. Already, new understanding of the 2D materials has contributed to entirely new scientific frontiers such as spin- and valley-ronics. The ability to harness such unique properties and phenomena will surely lead to exciting technological advances. Conflict of Interest: The authors declare no competing financial interest.

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REFERENCES AND NOTES


