The New Skinny in Two-Dimensional Nanomaterials

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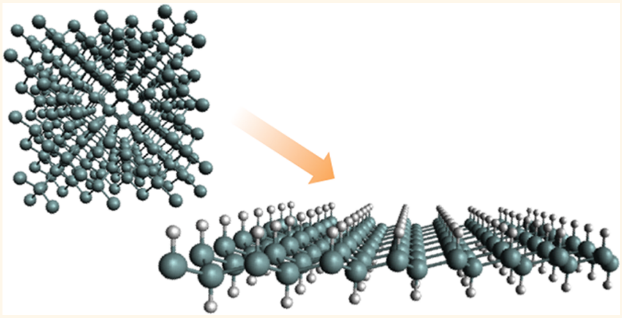

ABSTRACT While the advent of graphene has focused attention on the extraordinary properties of two-dimensional (2D) materials, graphene's lack of an intrinsic band gap and limited amenability to chemical modification has sparked increasing interest in its close relatives and in other 2D layered nanomaterials. In this issue of *ACS Nano*, Bianco *et al.* report on the production and characterization of one of these related materials: germanane, a one-atom-thick sheet of hydrogenated puckered germanium atoms structurally similar to graphane. It is a 2D nanomaterial generated *via* mechanical exfoliation from GeH. Germanane has been predicted to have technologically relevant properties such as a direct band gap and high electron mobility. Monolayer 2D materials like germanane, in general, have attracted enormous interest for their potential technological applications. We offer a perspective on the field of 2D layered nanomaterials and the exciting growth areas and discuss where the new development of germanane fits in, now and in the foreseeable future.

Ignited by immense technological promise, the field of two-dimensional (2D) layered nanomaterials has grown extensively over the past decade.[1,2] Two-dimensional nanomaterials are typically generated from bulk layered crystalline solids (Figure 1) such as graphite or dichalcogenides. These solids consist of successive layers of covalently bonded atomic layer planes ranging from one to multiple atoms thick, separated successively by van der Waals gaps. Single monolayers are generated *via* a variety of methods, primarily mechanical exfoliation, liquid exfoliation, or lithium-intercalation/deintercalation of these layered materials.

> In this issue of *ACS Nano*, Bianco *et al.* report the generation of stable, single-layered germanane.

Two-dimensional materials demonstrate a vast array of unique physical properties.[2] These include properties possessed by their bulk, layered counterparts[3] such as charge density waves, topological insulator behavior,[4] 2D electron gas physics, superconductivity, spontaneous magnetization, and anisotropic transport properties. Layered 2D materials find current applications in a wide array of capacities such as batteries, electrochromics, cosmetics, catalysts, and solid lubricants.[3]

With successive thinning of the layers to monolayer dimensions, the inherent properties of these bulk materials are altered. As research in this field has grown, many monolayer materials with unique physical, electronic, and structural properties have emerged. Exciting examples can be found in the numerous investigations of layered transition metal chalcogenides (MoS_2, WS_2, $TiSe_2$, Bi_2Se_3) approaching monolayer thicknesses.[2] These materials, in particular, demonstrate high mobilities and preserve a band gap approaching few-layer systems. An exceptional example is MoS_2, with a mobility of 200 $cm^2/(V\ s)$.[5] MoS_2 also undergoes a phase change from an indirect to direct band gap semiconductor with accompanying photoluminescence, drawing much interest as a possible 2D transistor material. Other metal chalcogenides, particularly Bi_2Se_3 (Figure 1), Sb_2Te_3, and Bi_2Te_3, demonstrate both thermoelectric and topological insulator properties, which have attracted significant interest for future applications.[4]

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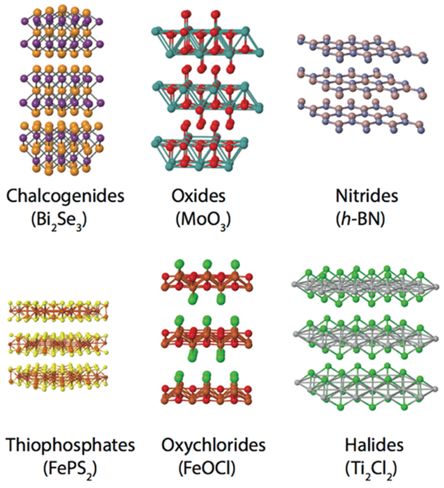

Figure 1. Examples of two-dimensional (2D) layered materials. An almost limitless array of layered materials exists from which 2D nanomaterials can be generated. The general structure of a 2D layered nanomaterial consists of a series of covalently bonded atomic layers bound together by van der Waals forces.

TABLE 1. Layered Crystal Structures That Have Been or May Potentially Be Mechanically Exfoliated

Group IV	**Dichalcogenides**	**Trichalcogenides**	**Oxides**	**Halides**	**Potential 2D**
Graphene C	VSe_2, $NbSe_2$,	Bi_2Se3, Bi_2Te_3,	MoO_3, V_2O_5,	$FeCl_3$,	**Zintl Hosts**
Graphane CH	TiS_2, ZrS_2, HfS_2,	Sb_2Te3, Bi_2S_3,	WO_3, ...	$FeBr_3$,	$CaSi_2$, $CaGe_2$,
Fluorographene CF	ReS_2, PtS_2,	In_2Se3, As_2S_3,		$CrCl_3$,	$Ca(Si_{1-x}Ge_x)_2$
Silicene Si	$TiSe_2$, $ZrSe_2$,	As_2Se_3, $NbSe_3$,	**Nitrides**	$CrBr_3$,	$Ba_3Sn_4As_6$
Germanane GeH	$HfSe_2$, $ReSe_2$,	TiS_3, ZrS_3, $ZrSe_3$,	BN	$MoCl_3$,	$CaMg_2N_2$
	$PtSe_2$, $SnSe_2$,	$ZrTe_3$, HfS_3,		$MoBr_3$,	$CaIn_2$
	$TiTe_2$, $ZrTe_2$,	$HfSe_3$, $HfTe_3$,	**Oxychlorides**	$TiCl_2$,	$CaNi_2P_2$
MXenes	VTe_2,$NbTe_2$,	NbS_3, TaS_3,	BiOCl, FeOCl,	$TiBr_3$,	*CaAuGa*, ...
Ti_3C2,Ti_2C, Ta_4C_3,	$TaTe_2$, $MoTe_2$,	$TaSe_3$, ...	HoOCl, ErOCl,	$InBr_3$,	
$Ti_3(Co._5No.5)2$, ...	WTe_2, $CoTe_2$,		ErOCl, TmOCl,	PbI_2,	
	$RhTe_2$, $IrTe_2$,	**Mono-Chalcogenides**	YbOCl, LnOCl, ...	$A1C1_33$,	
	$NiTe_2$, $PdTe_2$,	GeSe, GeTe,	**Layered Silicate**	$InBr_33$,	
	$PtTe_2$, $SiTe_2$,	GaSe, GaS	**Minerals**	$CrBr_33$,	
	NbS_2, TaS_2,		Egyptian Blue, ...	$FeCl_2$,	
	MoS_2, WS_2,	**Thiophosphates**		$MgCl_2$,	
	$TaSe_2$, $MoSe_2$,	FePS3, MnPS3,		$CoCl_2$,	
	WSe_2, $MoTe_2$,	NiPS3, ...		$VC1_2$,	
	$SnSe_2$, SnS_2, ...			VBr_2, VI_2	
				$CdCl_2$,	
				CdI_2, ...	

Other unique chemical approaches to develop new 2D materials have also arisen. Treating ternary carbides, nitrides, and carbonitrides with hydrogen fluoride (HF) gives rise to layered metal carbide and nitride systems. Materials, dubbed MXenes, such as Ti_3C_2, Ti_2C, Ta_4C_3, and $Ti_3(C_{0.5}N_{0.5})_2$, have been generated.[6] An extensive list of bulk layered compounds that have been or can be mechanically exfoliated is found in Table 1.

The 2D nanomaterial field was fueled by the discovery of graphene in 2004, a single atomic layer of graphite with sp^2 hybridized carbon.[1] Graphene attracted tremendous interest due to its unique properties such as thinness, high electrical and thermal conductivity, high mechanical strength, and high mobility, yielding strong potential for future electronics. Graphene is particularly interesting because the electronic band structure has a Dirac cone, the consequence of linear dispersion in its electronic band diagram, which makes graphene a high-mobility conductor and produces a veritable playground for theoretical physicists. But graphene does not have an intrinsic bandgap, and attempts to engineer a bandgap often reduce its mobility drastically. There has been much drive to develop graphene variants from similar carbon-based materials and other 2D layered materials such as layered nitrides, silicon, and transition metal dichalcogenides. This has led to enormous developments of 2D monolayer materials.

Hydrogenation of graphene brought about graphane (Figure 2).[7] Graphane is a fully saturated 2D hydrocarbon of chemical formula CH with sp^3 hybridized bonds that opens up a gap of 5.4 eV.[8] Graphane retains the flexibility, the 2D flatness, and much of the strength of graphene, but it is an insulator. Graphane lacks the Dirac cone of graphene. Both graphene and graphane, however, lack a direct band gap thus making these materials not useful for most optoelectronic applications (Table 2).

Specific progress in graphene and graphane has driven even greater interest in the semiconducting silicon and germanium counterparts, silicene and germanene. Both of these materials are predicted to have mixed sp^2—sp^3 hybridization, which results in puckering (Table 2) of the silicon and germanium atoms but retains the semiconducting characteristics of the bulk material. Of these, silicene has been demonstrated experimentally *via* vapor growth on a silver substrate.[9] It has interesting physical and electronic properties. Silicene shows high mobility, a characteristic Dirac cone, and a band gap that opens with, and is proportional to, an applied electric field.[10] Silicene, however, requires a supporting layer such as silver, zirconium diboride, or iridium, all of which conduct electricity, thereby eliminating the overall usefulness of silicene's properties.[9]

Consequently, these germanene and silicene graphene analogues have driven focus toward hydrogenated silicenes and germanenes. In this issue of *ACS Nano*, Bianco *et al.*

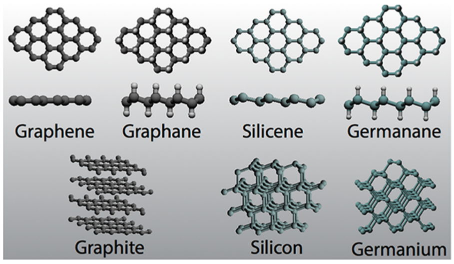

Figure 2. The growing family of Group IV monolayers. Generating group IV layered compounds has garnered significant interest for potential technological value in the semiconducting industry. The latest of these new materials is germanane, developed recently by Biano *et al.*

TABLE 2. Electronic Properties of Group IV (C, Si, Ge) Two-Dimensional Nanomaterials

	Band Gap [eV]	atomic puckering	mobility [$cm^2/(V\ s)$]	classification
Graphene	0 eV	0.00 Å	~200,000	Semimetal[19]
Graphane	3.6–5.4 eV	0.46 Å	-	Insulator[8]
Silicene	0.0 eV	0.44–0.72 Å	$\sim 10^5$	Semimetal[8]
Germanane	1.53–2.4 eV	0.63–0.73 Å	18,195	Direct-Gap Semiconductor[11]

report the generation of stable, single-layered germanane, which is a hydrogenated single layer of germanium, a 2D graphane analogue material with a direct band gap.[11] Germanane is a graphane analogue that has been predicted to show better theoretical use in electronics applications because hydrogenation destroys the Dirac cone and opens up a finite band gap. Bulk-hydrogen-saturated silicon and germanium sheets have been synthesized as layered polysilanes or polygermynes.[8,12,13] Investigations on those bulk layered materials have shown a direct band gap of 1.7 eV for polygermyne as well as strong optical photoluminescence at 1.35 eV.[14]

All of these 2D materials, and particularly Ge- or Si-based 2D materials with their nonzero band gaps, offer significant promise in technological areas such as thinner transistors, solar cells, photodetector materials, and thermoelectrics. These materials are unique in exhibiting new combinations of fundamental physical behavior such as photoluminescence, a Dirac cone, and exceptional transport properties. Approaching 2D, the fundamental material physical properties appear distinct from those of the bulk materials. New properties tied with thin material dimensionality offer much promise in a limitless array of technological applications ranging from thermoelectrics, transparent electrodes, batteries, ultra-thin solar cells, and high mobility electronic transition devices, to new opto-electronic devices. The emerging 2D layered semiconducting graphene and graphane material analogues, such as germane, silicene, germanane, and silicane offer much exciting promise for future electronic materials.

Germanane. Bianco *et al.* report a unique method for generation of stable, single-layered germanane, the newest of the novel 2D nanomaterials (Figure 2).[11] Using topotactic deintercalation, the authors converted β-$CaGe_2$, a Zintl phase material, into a layered GeH by placing a large synthesized crystal into aqueous HCl at −40 °C. Zintl phase materials consist of an alkali or alkaline metal (group 1,2) and a metal or metalloid (group 13,14,15,16). In the $CaGe_2$ Zintl phase materials, the crystal structure resembles that of an intercalation layered compound. β-$CaGe_2$ has alternating planes of covalently bonded germanium atom layers separated by ionically bonded interstitial calcium.

Topotactic deintercalation extracts the calcium ion to form a hydride:[12]

$$(CaGe_2)_n + 2nHCl \rightarrow (GeH)_2n + nCaCl_2$$

The host $CaGe_2$ matrix undergoes a structural change to a crystalline covalently bonded solid of GeH, a layered hydrogenated germanium hydride. The bonding type appears to have mixed sp^2 and sp^3 hybridization.[8,11] Layered GeH can be made in fairly substantial quantities. Bianco *et al.* proceeded to use mechanical exfoliation to generate single layers of these atomically thin hydrogenated germaniums, dubbed germanane. These materials have remarkable resistance to oxidative degradation over a substantial period of five months. It was found that in layers of germanane, only the top layer would be oxidized, thus potentially protecting the unique features of subsequent stacked germanane layers.

Germanane is silver-black. Unlike silicene, it does not require a substrate to be stable. GeH has a van der Waals gap of 5.9 Å—much larger than similar layered structures such as MoO_3 and large enough to serve as a host for the possible intercalation of many different species.[3,16] The atomic structure of germanane is puckered rather than flat like graphane or graphene (Figure 2). Calculations do not show the existence of a Dirac cone but germanane still has surprising high mobility—much higher than that of its bulk material. Calculations by Bianco *et al.* show a mobility of 18 200 $cm^2/(V\ s)$, which is almost a 5-fold increase over that of bulk Ge (3900 $cm^2/(V\ s)$). By comparison, the mobility of suspended graphene is ~200 000 $cm^2/(V\ s)$, while on a substrate the value drops to 15 000 $cm^2/(V\ s)$.[14] It will be exciting to see future measurements of the electronic conductivity of germanane to confirm this high mobility.

Theoretical calculations and absorption measurements show that germanane has a theoretical direct band gap of 1.53 eV, potentially making it a viable material for solar cells. This value was roughly

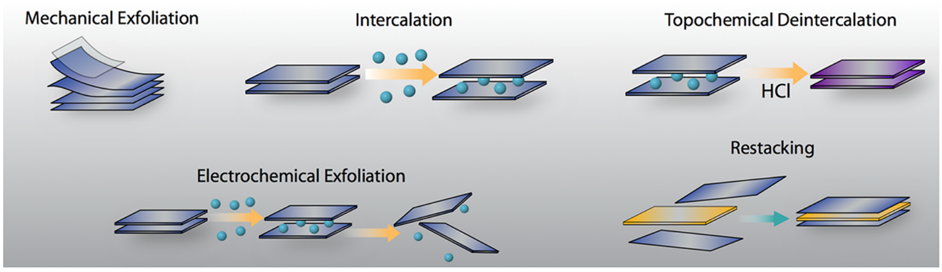

Figure 3. Developing chemistries of two-dimensional (2D) layered materials. Beyond various crystal growth methods, chemistry techniques specific to generating or altering 2D layered nanomaterials have arisen. These include mechanical exfoliation, new intercalation techniques, electrochemical exfoliation, heterostructure restructuring, and, now, topochemical deintercalation followed by mechanical exfoliation.

confirmed with absorption measurements, although it is understood that future angle-resolved photoelectron spectroscopy measurements will be needed to characterize the band structure fully. Band calculations of germanane do not show a Dirac cone similar to that of graphene or graphane. Despite the optical bandgap, no photoluminescence was observed, possibly due to the presence of trace amounts of impurity Ge–Cl. This is quite surprising since polygermanes (GeH) have previously shown strong optical photoluminescence.[15] Further investigations may ultimately reveal strong photoluminescence in this material.

The greatest drawback to this new material, germanane, is its behavior with increased temperature. Whereas in graphane annealing allows the hydrogen to disperse, thus reverting graphane to graphene,[7] in germanane this is not the case. Instead, it becomes amorphous with dehydrogenation above 75 °C. Thus, there remains some question of how well germanane could work in electronic materials. Many transistors can operate up to hundreds of degrees Celsius, temperatures that would lead to destruction of germanane-based electronics. Germanane-based electronics may require cooling or may be limited to low-power applications.

Future Outlook. Despite drawbacks, the future of germanane itself may be limitless. Germanane is an exciting new 2D functionalized material with much promise, especially with the possibility of using covalent chemistry to alter its optoelectronic or material properties. Hydrogen termination means the chemical surface can be further modified to adjust the band gap, temperature dependent stability, or other properties of the material. For example, hydrogen groups could be replaced by OH groups to form single-layered germoxanene.[12,15] It may be possible to use various ligands to influence the luminescence properties and band gap position. A similar example exists in bulk-layered polysiloxene, which shows photoluminescence shifts with varying ligands.[12] Functionalization may also be able to make this material more stable with temperature.

> Despite drawbacks, the future of germanane itself may be limitless.

Because germanane derives from a layered host structure, established techniques on layered materials could be utilized for further adjustment of structural and behavioral properties. (The growing list of novel chemistries on 2D layered nanomaterials can be seen in Figure 3.) Germanane can be restacked with other materials. As a layered material, new and old intercalation techniques[3] may offer remarkable promise for further enhancement or molecular optimization of the electronic and optical properties. Electrochemical intercalation can be used to insert alkali metals such as Li^+ between few layers. Organic intercalation, or the similar zero-valent metal intercalation, may also be worth investigating.[16]

With germanane's structural anisotropy, it will be interesting to see the layer dependence on the vibrational, optical, and electronic properties. The anisotropic properties of germanane could be very appealing, potentially because of electron-hole localization in one dimension. Bianco *et al.* demonstrate a 2D semiconducting material with a strong direct band gap, offering promise for a world of electronics requiring thinner devices. In terms of specific applications, this material could be used in solar cells, transistor devices, or even like graphene, as a cooling layer.

From a synthetic standpoint, the topotactic deintercalation technique used to make germanane, coupled with mechanical or chemical exfoliation, may offer an exciting new pathway toward many novel 2D materials. Topotactic deintercalation of only a minor number of Zintl phase compounds has been performed. This technique has been used to make polygermananes, polysilanes, layered siloxenes, and layered spinel materials. Many of these layered products were sensitive to oxidation. For example, the silicon-based Zintl phase material, $CaSi_2$, quickly leads to siloxene, an oxidated silicon-based layered structure rather than a hydrogenated silicon host structure. A wide variety of Zintl phase materials exist for which topochemical transformation has never been performed (Table 1 suggests several). Potentially, this could give rise to a whole host of novel layered materials, which could be directly exploited to make new 2D monolayers with unique electronic, physical, and structural properties. There are many examples of Zintl phase alloy materials such as CaGaSi, $CaZn_2Sb_2$, and $Ca_{11}GaSb_9$.[17,18] Using a method similar to Bianco *et al.*, combining topochemical deintercalation with mechanical exfoliation, it might be possible to generate a host of 2D hydrogenated/oxygenated semiconductors with precisely tuned electronic properties. Two-dimensional nanomaterials provide opportunities for the creation of complex multilayers, while preserving a dominant surface-to-volume ratio. New 2D materials could be coupled into heterostructured stacks of alternating physical characteristics using restacking methodologies. This may provide a new way to engineer three-dimensional (3D) electronic device architectures from 2D layers.

Future of 2D Layered Nanomaterials. The development of the graphane analogue germanane offers a whole new avenue of worthwhile investigations in the 2D layered materials field. As more 2D materials are generated and new relevant materials chemistry techniques, ranging from intercalation to atomic manipulation, arise (Figure 3), the future will likely see expanded growth in the 2D layered nanomaterial field where the electronic properties of a material can be altered by molecular-scale materials chemistry. It may someday be possible to alter chemically, atom by atom or substitutional group by substitutional group, the crystal where alternating atomic scale $p-n$ junctions exist per each atomic set, therefore, generating a flat material with an exceptionally high mobility and electronic functionality on the molecular scale. Similarly, this may be achieved using 2D layers to develop new 3D transistor architectures. The materials themselves exhibit unique and novel fundamental physical properties that are all worth investigating, ranging from massless electrons to novel transport behavior. Ultimately, these materials may find applications in touch screens, capacitors, batteries, fuel cells, sensors, high frequency circuits, and flexible electronics.

Conflict of Interest: The authors declare no competing financial interest.

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