Van der Waals heterostructures

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Research on graphene and other two-dimensional atomic crystals is intense and is likely to remain one of the leading topics in condensed matter physics and materials science for many years. Looking beyond this field, isolated atomic planes can also be reassembled into designer heterostructures made layer by layer in a precisely chosen sequence. The first, already remarkably complex, such heterostructures (often referred to as ‘van der Waals’) have recently been fabricated and investigated, revealing unusual properties and new phenomena. Here we review this emerging research area and identify possible future directions. With steady improvement in fabrication techniques and using graphene’s springboard, van der Waals heterostructures should develop into a large field of their own.

Graphene research has evolved into a vast field with approximately ten thousand papers now being published every year on a wide range of graphene-related topics. Each topic is covered by many reviews. It is probably fair to say that research on ‘simple graphene’ has already passed its zenith. Indeed, the focus has shifted from studying graphene itself to the use of the material in applications1 and as a versatile platform for investigation of various phenomena. Nonetheless, the fundamental science of graphene remains far from being exhausted (especially in terms of many-body physics) and, as the quality of graphene devices continues to improve2–4, more breakthroughs are expected, although at a slower pace.

Because most of the ‘low-hanging graphene fruits’ have already been harvested, researchers have now started paying more attention to other two-dimensional (2D) atomic crystals5 such as isolated monolayers and few-layer crystals of hexagonal boron nitride (hBN), molybdenum disulphide (MoS2), other dichalcogenides and layered oxides. During the first five years of the graphene boom, there appeared only a few experimental papers on 2D crystals other than graphene, whereas the last two years have already seen many reviews (for example, refs 7–11). This research promises to reach the same intensity as that on graphene, especially if the electronic quality of 2D crystals such as MoS2 (refs 12, 13) can be improved by a factor of ten to a hundred.

In parallel with the efforts on graphene-like materials, another research field has recently emerged and has been gaining strength over the past two years. It deals with heterostructures and devices made by stacking different 2D crystals on top of each other. The basic principle is simple: take, for example, a monolayer, put it on top of another monolayer or few-layer crystal, add another 2D crystal and so on. The resulting stack represents an artificial material assembled in a chosen sequence—as in building with Lego—with blocks defined with one-atomic-plane precision (Fig. 1). Strong covalent bonds provide in-plane stability of 2D crystals, whereas relatively weak, van-der-Waals-like forces are sufficient to keep the stack together. The possibility of making multilayer van der Waals heterostructures has been demonstrated experimentally only

Figure 1 | Building van der Waals heterostructures. If one considers 2D crystals to be analogous to Lego blocks (right panel), the construction of a huge variety of layered structures becomes possible. Conceptually, this atomic-scale Lego resembles molecular beam epitaxy but employs different ‘construction’ rules and a distinct set of materials.
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search for new layered superconductors. Indeed, intercalated graphite Moreover, graphene seems to be a natural choice of 2D component in the conductors depends on many materials parameters, including the CuO...7–11. In contrast, van...T...when the mechanism of high-C...C superconductivity in doped graphene has been widely checking grand ideas against contemporary reality. Having said that, it is equally important not to get lost on the way by...are monolayers of hBN were used as gate dielectrics 14,39 and tunnel barriers (2D hBN) are expected to survive isolation from its parent substrate or exposure to air. Another important consideration is interfacial contamination. Adsorbs such as water, hydrocarbons, and so on cover every surface, unless it is prepared under extreme surface-science conditions. Graphene is densely covered with hydrocarbons, even after annealing in the high vacuum of a transmission electron microscope. It takes considerable effort to find clean patches several nanometres in size 46. (Note that this contamination is highly mobile and usually remains unnoticeable for scanning probe microscopy.) If isolated 2D crystals are stacked together, the surface contamination becomes trapped in between layers. Therefore, van der Waals heterostructures should generally be expected to become ‘layer cakes’ glued by contamination rather than the neat crystals imagined in Fig. 1. This scenario would remove much of the appeal from van der Waals heterostructures because it is difficult to control the manufacture and reproducibility of ‘layer cakes’. Fortunately, it turns out that contamination can clean itself off the interfaces 16,19,35, as further discussed below.

Two-dimensional family values

At the time of writing, we can be certain of the existence of more than a dozen different 2D crystals under ambient conditions. First of all, these are monolayers of graphite, hBN and MoS2, which have been studied extensively. It is probably not coincidental that these materials are widely used as solid lubricants, which requires high thermal and chemical stability. There are also 2D tungsten disulphide (WS2), tungsten diselenide (WSe2) and molybdenum diselenide (MoSe2), which are chemically, structurally and electronically similar to MoS2. Despite little research having been done so far on the latter monolayers, it is safe to add them to the 2D library, too (Fig. 2).

Among the above 2D crystals, graphene is an unequivocal champion, exhibiting the highest mechanical strength and crystal and electronic quality. It is likely to be the most common component in future van der Waals heterostructures and devices. Latest developments on graphene include micrometre-scale ballistic transport at room temperature (refs 3, 36) and low-temperature carrier mobilities of \( \mu \approx 10^6 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \). The runner-up is 2D hBN, or ‘white graphene’. Its rise started when bulk hBN crystals 37,38 were shown to be an exceptional substrate for graphene, allowing a tenfold increase in its electronic quality 4. This advance attracted immediate attention and, shortly after, few-layer crystals and monolayers of hBN were used as gate dielectrics 15,43 and tunnel barriers (2D hBN can sustain biases up to about 0.8 V nm\(^{-1}\)) and be free from pinholes 40,41. Monolayers of MoS2 were studied earlier 42, including the demonstration of the electric field effect, but they received little attention until devices with switching on/off ratios of >10\(^8\) and room-temperature \( \mu \approx 100 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \) were reported 42. Although these mobilities are much lower than in graphene, they are still remarkably high compared with thin-film semiconductors. The large on/off ratios are due to a sizeable bandgap in MoS2. It is direct in a monolayer (about 1.8 eV), whereas bilayer and few-layer MoS2 are indirect bandgap semiconductors 43,44.
Semiconductors with a direct gap are of special interest for use in optics and optoelectronics. Further interest in monolayer MoS\(_2\) is due to the broken centrosymmetry that allows efficient spin and valley polarization by optical pumping\(^{45,46}\). This research is stimulated by the availability of large molybdenite crystals from several mining sources. The absence of such supply is probably the reason why 2D WS\(_2\), WSe\(_2\) and MoSe\(_2\) attract relatively little attention despite the fact that Raman and transport studies have revealed their electronic structures and quality to be similar to that of MoS\(_2\) (refs 47–49). The differences between these dichalcogenides worth noting are the stronger spin–orbit coupling in the W compounds and the lower stability of the Se compounds.

There have been reports on exfoliation of many other layered chalcogenides down to a monolayer (Fig. 2). However, we have chosen only to ‘pencil’ them into the 2D library because little is known about their stability, let alone their optical and transport properties. In some cases, it is even unclear whether the observed flakes and suspensions are indeed considered for designing van der Waals heterostructures. Nonetheless, we note that hydroge-nerated graphene or other derivatives can sometimes be more stable than 2D crystals themselves\(^{41}\). Finally, let us mention graphene oxide\(^{42}\) and monolayers of boron carbon nitride\(^{43–45}\), which although non-stoichiometric, can also be considered for designing van der Waals heterostructures.

**Rules of survival**

As interest in graphene-like crystals rapidly grows\(^{7–11}\), the search for new 2D candidates is expected to intensify, too. In this regard, the following rule of thumb can be helpful. First, 3D materials with melting temperature over 1,000 °C have the best chances of having 2D counterparts stable at room temperature. Second, 3D parents must be chemically inert and exhibit no decomposed surface layer in air or an alternative environment where exfoliation takes place. Third, insulating and semiconducting 2D crystals are more likely to be stable than metallic ones, owing to the generally higher reactivity of metals. In all cases, visual evaluation and Raman spectroscopy are helpful to provide a rapid test for the absence of corrosion and the presence of essential signatures indicating a similarity to the parent crystal. However, the ultimate proof lies with electrical measurements of either in-plane transport for conducting 2D crystals or out-of-plane tunnelling through insulating ones that check for their homogeneity and the absence of pinholes.

As a further step towards expanding the 2D library, one can perform isolation and encapsulation in an inert atmosphere. Many metallic 2D dichalcogenides may then remain stable at room temperature, as their stability in solvents seems to indicate\(^{55,56}\). This approach can also lead to higher electronic quality for present favourites such as graphene and 2D MoS\(_2\). Exfoliation-encapsulation at low temperature (such as in liquid nitrogen) is in principle possible but for the moment too difficult to contemplate for practical use. Lastly, monolayers may exist without a layered 3D parent (examples are silicene and monolayers of Y\(_2\)O\(_3\) and ZnO\(^{57,58}\)). If the monolayers are sufficiently stable, the substrate can be etched away, as demonstrated for graphene grown on metal foils\(^{59–61}\). This can provide access to 2D crystals without 3D layered analogues in nature.

**Lego on atomic scale**

It is no longer adventurous to imagine the automated, roll-to-roll assembly\(^{62}\) of van der Waals heterostructures using sheets of epitaxially grown 2D crystal\(^{59–63}\). However, concerted efforts towards such assembly are expected only when a particular heterostructure proves to be worthy of attention, as happened in the case of graphene on hBN\(^{64}\). For scouting which area to focus on, manual assembly is likely to remain the favourite approach. It offers high throughput and relatively easy changes in layer sequences. Likewise, individual 2D compounds will continue to be obtained by the Scotch-tape technique, which has so far provided crystallites of unmatched quality. Nevertheless, we expect the increasingly frequent use of epitaxially grown graphene, 2D hBN, 2D MoS\(_2\), and so on for making proof-of-concept van der Waals heterostructures.

At the time of writing, only a few groups have reported van der Waals heterostructures made from more than two atomically thin crystals, and only graphene and few-layer hBN, MoS\(_2\) and WS\(_2\) were used for this
A typical stacking procedure starts by isolating micrometre-sized 2D crystals on top of a thin transparent film (for example, polymer). The resulting 2D crystal provides one brick for the Lego wall in Fig. 1 and can now be put face down onto a chosen target. The supporting film is then removed or dissolved. More 2D crystals are produced, and the transfer is repeated again and again, until a desired stack is assembled. Conceptually, this is simple and requires only basic facilities such as a good optical microscope. In practice, the fabrication technique takes months to master. In addition to the standard cleanroom procedures (cleaning, dissolving, resist spinning and so on), it is necessary to position different 2D crystals over each other with micrometre accuracy. This is done under the microscope by using micromanipulators. The crystals must be put in soft contact without rubbing and, ideally no liquid or polymer should be allowed in contact with cleaved surfaces to minimize contamination. Thermal annealing in an inert atmosphere can often be helpful after adding each new layer. For transport measurements, 2D crystals are plasma etched into, for example, Hall bars with contacts evaporated as the final step.

Despite the dozens of steps involved, sophisticated multilayer structures can now be produced within a matter of days. Figure 3 shows two such examples. One is a van der Waals superlattice made from six alternating bilayers of graphene and hBN. This is the largest number of 2D crystals in a van der Waals heterostructure reported so far. The most challenging design has probably been double-layer graphene devices such as those shown in Fig. 3b, c. We emphasize that interfaces in these heterostructures are found to be clean and atomically sharp, without the contaminating ‘goo’ that always covers 2D crystals even in high vacuum (see the ‘Layered reality check’ section). The reason for the clean interfaces is the van der Waals forces that attract adjacent crystals and effectively squeeze out trapped contaminants or force them into micrometre-sized ‘bubbles’. This allows 10-μm-scale devices that are effectively free from contamination. We also note that atomically sharp interfaces are in practice impossible to achieve by other techniques, including molecular beam epitaxy, because of island growth.

**Little evolutionary steps**

Although the availability of various isolated 2D crystals had been recognized, practical steps towards their van der Waals assembly were taken only after 2010. An important stimulus was the demonstration that hBN could serve as a high-quality substrate for graphene (many other substrates, including pyrolytic hBN, were unsuccessfully tried before). This led to rapid development of transfer procedures. The next logical step was encapsulation, where thin hBN crystals served not only as the substrate but also as a protective cover for graphene. Encapsulation has proved its worth by enabling devices with consistently high quality that do not deteriorate under ambient conditions. The most commonly achieved mobility for graphene on hBN is $\mu = 100,000$ cm$^2$ V$^{-1}$ s$^{-1}$ but up to 500,000 cm$^2$ V$^{-1}$ s$^{-1}$ can be reached at low temperature. Such high quality (as indicated by high mobility) can be witnessed directly as negative bend resistance and magnetic focusing (Fig. 4a). These ballistic effects persist up to room temperature. The encapsulation also results in high spatial uniformity so that capacitors over 100 μm$^2$ in size exhibit quantum oscillations in magnetic fields as low as 0.2 T (ref. 68).

The next evolutionary step has been ‘vertical’ devices in which few-layer-thick crystals of hBN, MoS$_2$ or WS$_2$ are used as tunnel barriers with graphene serving as one or both electrodes. These devices require three to four transfers, but no plasma etching, to define their geometry. Although sensitive to charge inhomogeneity, vertical devices usually do not pose critical demands on $\mu$. The tunnelling heterostructures allow the demonstration of a new kind of electronic device: field-effect tunnelling transistors. In these, the tunnel current is controlled by changes in the electrode’s Fermi energy, which can be varied by gate voltage by as much as about 0.5 eV owing to the low density of states in monolayer graphene. An increase in the Fermi energy effectively lowers the tunnel barrier, even if no bias is applied. This is in contrast to the standard Fowler–Nordheim mechanism, which is based on tilting the top of the tunnel barrier by applied bias. The van der Waals tunnelling devices exhibit an on/off switching ratio of over 10$^6$ at room temperature.

A higher level of complexity is presented by the graphene–hBN superlattice shown in Fig. 3a. It proves the concept that thin films of new 3D materials consisting of dozens of atomic layers are in principle possible by reassembly, as discussed in the ‘Dreamscape’ section. In the case of Fig. 3a, hBN bilayers serve as spacers whereas bilayer graphene (rather than its monolayer) was chosen to facilitate intercalation to reach a high density of states. Further efforts in making and investigating such multilayer structures are expected, given the interest generated by a large amount of literature on possible collective phenomena in graphene-based systems.

The double-layer devices in Fig. 3 represent the state of the art for van der Waals heterostructures. They were designed to probe in-plane transport in the regime of the strongest possible electron–electron interaction between electrically isolated 2D systems. The separation of the graphene layers can be as small as three hBN layers (about 1 nm) but this still provides a sufficiently high potential barrier to suppress electron tunnelling. The layers continue to ‘feel’ each other strongly through Coulomb interactions. The 1-nm separation is much smaller than the in-plane distance between charge carriers in graphene, which is typically around 10 nm and nominally diverges near the neutrality point. This makes the interlayer separation the smallest spatial parameter in the problem. Therefore, the two electronic liquids in double-layer graphene effectively nest within the same plane, but can still be tuned and measured separately.
Many other types of van der Waals structure and device are expected to be demonstrated soon, initially using only a small number of 2D crystals. Among obvious objectives are various proximity effects. To this end, 2D crystals can be put on top of atomically flat crystals exhibiting magnetism, ferroelectricity, spin–orbit coupling and so on. For example, graphene encapsulated in WS₂ is likely to exhibit an induced spin–orbit interaction that should affect transport properties.

**Handicraft on industrial scale**

The growing interest in van der Waals heterostructures is not limited to new physics and materials science. There is also a massive potential for applications. Here we avoid early speculations because interest in van der Waals heterostructures is already justified if one considers them as a way of accelerating the development of the myriad applications offered by graphene itself. The recently demonstrated new graphene-based device architectures²⁵,⁷⁴ provide straightforward examples.

Any industrial application will require a scalable approach to van der Waals assembly. To this end, significant efforts have been reported to grow graphene, 2D hBN and 2D MoS₂ epitaxially on top of each other. However, it is a daunting task to find the right conditions for so-called van der Waals epitaxy because the weak interlayer interaction generally favours island growth rather than that of continuous monolayers.

Another scalable approach is layer-by-layer deposition from 2D-crystal suspensions by using Langmuir–Blodgett or similar techniques. One can also mix suspensions of different 2D crystals and then make layer-by-layer laminates, relying on self-organizational assembly (flocculation). Unfortunately, micrometre-sized crystallites in suspensions cannot provide large continuous layers, and this would limit possible applications.

At the time of writing, the most feasible approach to industrial-scale production of van der Waals heterostructures seems to involve growing...
After many years of intensive effort, graphene research should logically reach a mature stage. However, the possibility of combining graphene with other 2D crystals has expanded this field dramatically, well beyond simple graphene or 2D MoS$_2$. The interest in van der Waals heterostructures is growing as quickly as interest in graphene did a few years ago. As the technology of making van der Waals heterostructures moves from its humble beginnings, increasingly sophisticated devices and materials should become available to more and more research groups. This is likely to cause a snowball effect because, with so many 2D crystals, sequences and parameters to consider, the choice of possible van der Waals structures is limited only by our imagination. Even with the 2D components that have been shown to be stable, it will take time and effort to explore the huge parameter space. The decades of research on semiconductor heterostructures and devices may serve as a guide to judge the probable longevity of research on van der Waals materials, beyond simple graphene.

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