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2D OR NOT 2D

A wave of innovative flat materials is following in the wake of graphene — but the most exciting applications could come from stacking them into 3D devices.

BY ELIZABETH GIBNEY

Physicists have used almost every superlative they can think of to describe graphene. This gossamer, one-atom-thick sheet of carbon is flexible, transparent, stronger than steel, more conductive than copper and so thin that it is effectively two-dimensional (2D). No sooner was it isolated in 2004 than it became an obsession for researchers around the world.

But not for Andras Kis. As miraculous as graphene was, says Kis, “I felt there had to be more than carbon.” So in 2008, when he got the chance to start his own research group in nanoscale electronics at the Swiss Federal Institute of Technology in Lausanne (EPFL), Kis focused his efforts on a class of super-flat materials that had been languishing in graphene’s shadow.

These materials had an ungainly name — transition-metal dichalcogenides (TMDCs) — but a 2D form that was quite simple. A single sheet of transition-metal atoms such as molybdenum or tungsten was sandwiched between equally thin layers of chalcogens: elements, such as sulfur and selenium, that lie below oxygen in the periodic table. TMDCs were almost as thin, transparent and flexible as graphene,

says Kis, but “somehow they got a reputation as not that interesting. I thought they deserved a second chance.”

He was right. Work by his team and a handful of others soon showed that different combinations of the basic ingredients could produce TMDCs with a wide range of electronic and optical properties. Unlike graphene, for example, many TMDCs are semiconductors, meaning that they have the potential to be made into molecular-scale digital processors that are much more energy efficient than anything possible with silicon.

Within a few years, laboratories around the world had joined the 2D quest. “At first it was one, then two or three, and suddenly it became whole zoo of 2D materials,” says Kis. From a scattering of publications in 2008, 2D TMDCs alone now generate six publications each day. Physicists think that there may be around 500 2D materials, including not just graphene and TMDCs, but also single layers of metal oxides, and single-element materials such as silicene and phosphorene. “If you want a 2D material with a given set of properties,” says Jonathan Coleman, a physicist at Trinity College Dublin, “you will find one.”

Ironically, one of the most exciting frontiers in 2D materials is

Stacks of multiple kinds of flat materials can exploit the best properties of each.

materials, it should be possible to build entire digital circuits out of atomically thick components, creating previously unimagined devices. Applications are already being touted in fields from energy harvesting to quantum communications — even though physicists are just beginning to learn the materials' potential.

“Each one is like a Lego brick,” says Kis. “If you put them together, maybe you can build something completely new.”

ADVENTURES IN FLATLAND

A material that is just a few atoms thick can have very different fundamental properties from a material made of the same molecules in solid form. “Even if the bulk material is an old one, if you can get it into 2D form it opens up new opportunities,” says Yuanbo Zhang, an experimental condensed-matter physicist at Fudan University in Shanghai, China.

Carbon is the classic example, as physicists Andre Geim and Konstantin Novoselov found in 2004 when they first reported isolating graphene¹ in their laboratory at the University of Manchester, UK. Their technique was almost absurdly simple. The basic step is to press a strip of sticky tape onto a flake of graphite, then peel it off, bringing with it a few of the atom-thick layers that make up the bulk material. By repeating this process until they had single layers — which many theorists had said could not exist in isolation — Geim and Novoselov were able to start investigating graphene's remarkable properties. Their work won them the 2010 Nobel Prize in Physics.

Physicists were soon hurrying to exploit those properties for applications ranging from flexible screens to energy storage (see page 268). Unfortunately, graphene proved to be a poor fit for digital electronics. The ideal material for that application is a semiconductor — a material that does not conduct electricity unless its electrons are boosted with a certain amount of energy from heat, light or an external voltage. The amount of energy needed varies with the material, and is known as the band gap. Turning the material's conductivity on and off creates the 1s and 0s of the digital world. But graphene in its pure form does not have a band gap — it conducts all the time.

Still, Geim and Novoselov's success in making graphene spurred them, Kis and many others to start investigating alternative 2D materials that could have a band gap². They began with TMDCs, which had been studied in bulk form since the 1960s. By 2010, Kis's team had built its first single-layer transistor³ from the TMDC molybdenum disulfide (MoS₂; see ‘Flat-pack assembly’), speculating that such devices could one day offer flexible electronics whose small component size and low voltage requirements would mean that they consumed much less power than conventional silicon transistors. Being semiconducting was not their only advantage. Studies in 2010 showed that MoS₂ could both absorb and emit light^{4,5} efficiently, making it — and probably other TMDCs — attractive for use in solar cells and photodetectors.

A single layer of TMDCs can capture more than 10% of incoming photons, an incredible figure for a material three atoms thick, says Bernhard Urbaszek, a physicist at the Physics and Chemistry of Nano-Objects Laboratory in Toulouse, France. This also helps them in another task: converting light into electricity. When an incoming photon hits the three-layer crystal, it boosts an electron past the band gap, allowing it to move through an external circuit. Each freed electron leaves behind a kind of empty space in the crystal — a positively charged ‘hole’ where an electron ought to be. Apply a voltage, and these holes and electrons circulate in opposite directions to produce a net flow of electric current.

This process can also be reversed to turn electricity into light. If electrons and holes are injected into the TMDC from an outside circuit;

stacking them into structures that are still very thin, but definitely 3D. By taking advantage of the vastly different properties of various super-flat

when they meet, they recombine and give up their energy as photons.

This ability to convert light to electricity and vice versa makes TMDCs promising candidates for applications that involve transmitting information using light, as well as for use in tiny, low-power light sources and even lasers. This year, four different teams demonstrated the ultimate control over light emission, showing that the TMDC tungsten diselenide (WSe₂) could absorb and release individual photons^{6–9}. Quantum cryptography and communications, which encode information in one photon at a time, need emitters like this, where you “press a button and get a photon now”, says Urbaszek. Existing single-photon emitters are often made of bulk semiconductors, but 2D materials could prove smaller and easier to integrate with other devices. Their emitters are necessarily on the surface, which could also make them more efficient and easier to control.

Even as researchers were getting to grips with TMDCs, theorists were seeking other materials that could be engineered in two dimensions. One obvious candidate was silicon, which sits right below carbon in the periodic table, forms chemical bonds in a similar way, has a natural band gap and is already widely used in the electronics industry. Calculations suggested that, unlike graphene, a sheet of atomically thick silicon would have a ridged structure that could be squashed and stretched to create a tunable band gap. But like graphene, this ‘silicene’ would be a much faster conductor of electrons than most TMDCs.

Unfortunately, theory also suggested that a 2D sheet of silicene would be highly reactive and completely unstable in air. Nor could it be ripped from a crystal like other 2D materials: natural silicon exists only in a 3D form analogous to a diamond crystal, with nothing resembling the layered sheets of carbon found in graphite.

“People said it was insane and would never work,” says Guy Le Lay, a physicist at Aix-Marseille University in France. But Le Lay, who had been growing metals on silicon surfaces for years, saw a way to make silicene by doing the reverse — growing atomically thin sheets of silicon on metal. And in 2012 he reported success¹⁰: he had grown layers of silicene on silver, which has an atomic structure that matches the 2D material perfectly (see *Nature* **495**, 152–153; 2013).

Buoyed by that effort, Le Lay and others have since moved down the carbon column of the periodic table. Last year, he demonstrated a similar technique to grow a 2D mesh of germanium atoms — germanene — on a substrate of gold¹¹. His next target is stanene: a 2D lattice of tin atoms. Stanene should have a band gap larger than either silicene and germanene, which would allow its devices to work at higher temperatures and voltages. And it is predicted to carry charges only on its outside edges, so

it should conduct with super efficiency. But Le Lay has competition. Although no one has yet reported growing stanene successfully, research groups in China are rumoured to be close.

ELEMENTAL SHIFT

Others are exploring different parts of the periodic table. Zhang's team and another led by Peide Ye at Purdue University in West Lafayette, Indiana, last year described^{12,13} stripping 2D layers of phosphorene from black phosphorus, a bulk form of the element that has been studied for a century. Like graphene, phosphorene conducts electrons swiftly. But unlike graphene, it has a natural band gap — and it is more stable than silicene.

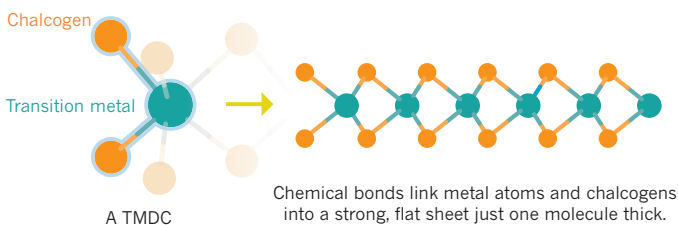
Phosphorene has enjoyed a meteoric rise. At the 2013 meeting of the American Physical Society, it was the subject of a single talk by members of Zhang's group; by 2015, the meeting had three entire sessions devoted to it. But like its fellow pure-element 2D materials, phosphorene reacts very strongly with oxygen and water. If it is to last longer than a few hours, it needs to be sandwiched between layers of other materials. This natural instability makes fabricating devices with the ‘enes’ difficult; Le Lay estimates that around 80% of the papers about them are still theoretical.

Nonetheless, both Zhang and Ye succeeded in making phosphorene transistors. This year, the first transistor from silicene emerged¹⁴,

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FLAT-PACK ASSEMBLY

Transition-metal dichalcogenide (TMDC) crystals contain one transition-metal atom (green) for every two chalcogen atoms (orange). Some 40 such TMDCs — mostly those made with the metals highlighted in dark green in the periodic table — can be split into 2D layers that are flexible, transparent and excellent conductors of electricity. Some are also semiconductors.



H																				He
Li	Be									B	C	N	O	F	Ne					
Na	Mg									Al	Si	P	S	Cl	Ar					
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr			
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe			
Cs	Ba	Ln	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn			
Fr	Ra	An	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg										
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			

although it survived for only a few minutes. Still, Le Lay is optimistic that these issues are not insurmountable. Just two years ago, he points out, Geim and other physicists were saying that a silicene transistor could not be made with current technology. “So it’s always dangerous to predict the future,” laughs Le Lay.

THE NEXT DIMENSION

Even as some physicists search for new 2D materials and try to understand their properties, others are already sandwiching them together. “Instead of trying to pick one and say this is the best, maybe the best thing to do is to combine them in such a way that all their different advantages are properly utilized,” says Kis.

This could mean stacking components made of different 2D materials to make tiny, dense 3D circuits. Materials could also be layered inside components — something that chip designers already do when they grow layers of different semiconductors on top of one another to make devices such as the lasers inside DVD players. In standard devices, this is tricky: each layer has to chemically bond with the next, and only certain combinations can be matched. Otherwise, the strain between the different crystal lattices in each layer makes bonding impossible. With 2D materials, that problem goes away: the atoms in each layer bond only very weakly to the neighbouring sheets, so the strain is minimal. Many layers of semiconductors, insulators and conductors can be stacked to form complex devices known generically as van der Waals heterostructures, after the weak bonds that bind the layers.

Already, for example, graphene has been used alongside MoS₂ and WSe₂ to create the junctions at the heart of solar cells¹⁵ and photodetectors¹⁶, exploiting the semiconductor’s abilities to absorb photons and graphene’s swift ability to carry the freed electrons away. In February this year, Novoselov and his team reversed the solar-cell concept to make a light-emitting diode¹⁷ from MoS₂ and other TMDCs between graphene electrodes. By selecting different TMDCs, the team could choose the wavelength of the photons released.

Better still, sandwiching together different 2D layers can allow physicists to fine-tune their devices. Although the bonds between layers are

weak, the close proximity of their atoms means that they can affect each other’s properties in subtle ways, says Wang Yao, a physicist at the University of Hong Kong. Stacking order, spacing and orientation all control device behaviour. “Modelling this gives theorists like me a headache, but the new physical properties are definitely there,” says Yao.

Even graphene can get a leg up from other 2D materials, says Marco Polini, a physicist at the National Enterprise for Nanoscience and Nanotechnology (NEST) in Pisa, Italy. His team has been working on devices in which graphene is sandwiched between 2D layers of the insulator boron nitride¹⁸. When laser light is focused on the device, it gets compressed and channelled through the graphene layer, much more than in devices that sandwich graphene between bulk materials. In principle, this could provide a way for information to be carried between chips using photons rather than electricity. That, says Polini, could mean faster and more efficient communications within the chips.

PRACTICAL PREDICTIONS

The current buzz around 2D materials is reminiscent of the excitement about graphene in 2005, says physicist Jari Kinaret of Chalmers University of Technology in Gothenburg, Sweden, who heads the European Union’s Graphene Flagship — a programme that also studies other 2D materials. But Kinaret cautions that it could take two decades to really assess the potential of these materials. “The initial studies on 2D materials are focusing a lot on their electronic properties, because these are close to physicists’ hearts,” says Kinaret. “But I think that the applications, if and when they come, are likely to be in a completely unpredicted area.”

Materials that look good in the lab are not always those that make it out into the real world. One major issue facing all 2D materials is how to produce uniform, defect-free layers cheaply. The sticky-tape method works well for TMDCs and phosphorene, but is too time-consuming to scale up. It is also expensive to make bulk black phosphorus, because it involves subjecting naturally occurring white phosphorus to extreme pressure. No one has yet perfected the process of growing single sheets of 2D materials from scratch, let alone the layered structures that physicists find so promising. “It took a long time to make our heterostructures,” says Xiaodong Xu, a physicist at the University of Washington in Seattle. “How can we speed that up or make it automatic? There is a lot of work to do.”

Such practical considerations could prevent 2D materials from living up to their early promise. “There have been many rushes like this, and some have turned out to be fads,” says Kis. “But I think the sheer number of materials and different properties should make sure something comes out of this.” Meanwhile, the zoo is expanding, says Coleman. Arsenene, a heavier cousin to phosphorene, is already on researcher’s minds.

“As people start to branch out, they are discovering new materials that have these wonderful properties,” says Coleman. “The most exciting 2D material is probably one that hasn’t been made yet.” ■ [SEE BOOKS & ARTS P.284](#)

Elizabeth Gibney is a reporter for Nature in London.

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