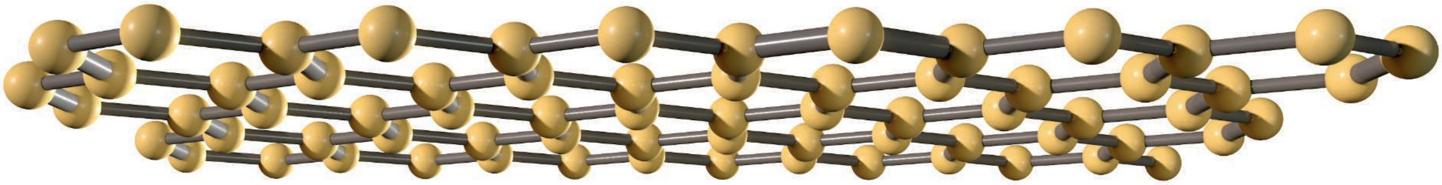
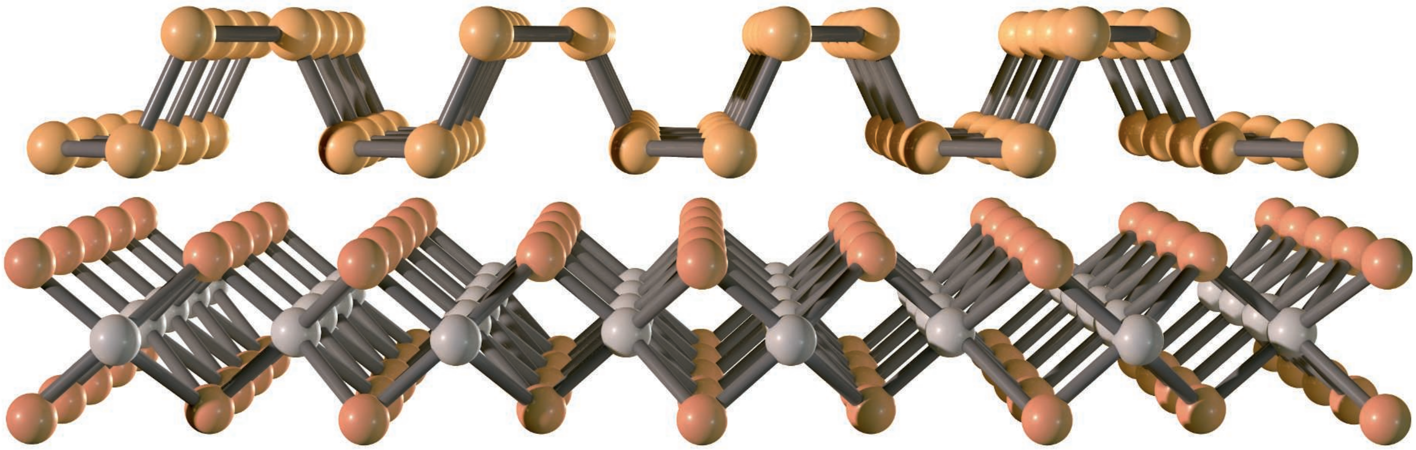
FEATURES



BEYOND GRAPHENE

The ultrathin form of carbon has inspired other atoms-thick materials that promise even bigger technological payoffs

By **Robert F. Service**, *in San Antonio, Texas*



Graphene (*top*) has spurred scientists to explore flat semiconductors such as phosphorene (*middle*) and molybdenum disulfide (*above*).

Sticky tape isn't normally thought of as the stuff of scientific breakthroughs. But when physicists Andre Geim and Konstantin Novoselov of the University of Manchester in the United Kingdom and colleagues reported in *Science* in 2004 that they had used clear tape to peel off single atomically thin sheets of carbon atoms from a chunk of graphite, it set off a revolution in materials science that is still unfolding.

Last year, researchers around the globe published more than 15,000 papers on single-layer graphite, called graphene, a number that has grown exponentially since the Manchester team's sticky innovation 11 years ago. And for good reason. Graphene is the thinnest material ever made. It's 100 times stronger than steel, a better electrical and heat conductor than copper, flexible, and largely transparent. Investigators envision a future for it in everything from the next generation of computer chips and flexible displays to batteries and fuel cells.

Yet graphene may have its biggest impact not as a wonder material in its own right, but through its offspring. For all its dazzling promise, graphene has drawbacks, especially its inability to act as a semiconductor, the keystone of microelectronics. Now, chemists and materials scientists are striving to move beyond graphene. They're synthesizing other two-dimensional sheetlike materials that promise to combine flexibility and transparency with electronic properties graphene can't match. And they are already turning some of them into thin, flexible, speedy electronic and optical devices that they hope will form the backbone of industries of the future. "The field is wide open," says David Tomanek, a condensed matter physicist at Michigan State University in East Lansing. Keji Lai, a physicist at the University of Texas (UT), Austin, agrees, calling 2D materials "one of the hottest topics in physics."

IN ONE SENSE, 2D materials aren't new at all. Researchers have been growing atomically thin sheets of materials since the 1960s using tools called molecular beam epitaxy (MBE) machines. But MBE machines are typically used to deposit thin layers of materials like silicon and gallium arsenide: crystalline materials whose component atoms normally prefer to bond in three dimensions.

ILLUSTRATIONS: C. BICKEL (3)

Published by AAAS

In that respect, the layers made by MBE are like a slice of cheese, a 2D version of a 3D substance.

Graphene is different. It's more like the pages in a book, says Yi-Hsien Lee, a materials scientist at the National Tsing Hua University in Hsinchu, Taiwan. Its carbon atoms form strong, covalent links with other carbons in a single 2D plane, creating a hexagonal lattice that looks like miniature chicken wire. But separate planes of atoms are only loosely paired with weak bonds known as van der Waals interactions. As a result, the layers can slip past one another, which is why graphite is used to make the gray flaky "lead" in pencils.

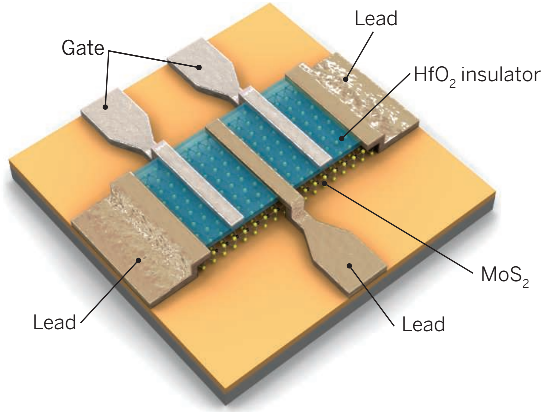
The big surprise was that when researchers began to study graphene closely, they discovered it had electronic and optical properties not found in bulk graphite. "The biggest lesson is that less is different," says Yuanbo Zhang, a condensed matter physicist at Fudan University in Shanghai, China. And with that lesson, Tomanek says, "graphene brought 2D materials into the limelight."

Yet when it comes to making high-tech devices, graphene's promise dims a bit. While the most prized materials of the electronics age are semiconductors, whose conductivity can be switched on and off to generate the digital currency of 1s and 0s, graphene is more like a conducting metal. "Graphene is an absolutely wonderful material," Tomanek says. "But it's irrelevant for electronics."

Researchers have spent years trying to convert graphene into a semiconductor by bonding oxygen to the graphene sheets or by cutting the sheets into ribbons just a few nanometers wide. Both changes do alter graphene's electronic structure, turning it into a semiconductor. But these "solutions" brought other problems. Graphene oxide's electronic properties are strongly affected by molecules that interact with it, a foible that undermines its reliability. And the nanoribbons' electronic properties depend so critically on a ribbon's precise structure that they are hard to control.

Yet graphene opened researchers' eyes to a new world of flatland electronics. They saw that similar materials might have novel optical and electrical properties. And because 2D sheets are so thin and mostly transparent, they offered the prospect of creating flexible and transparent electronics that could produce see-through displays of the sort dreamed up years ago by Hollywood. Since then, researchers have been surveying that landscape for richer treasures.

By looking for materials that naturally form 2D sheets and finding ways of stabilizing sheets of atoms that normally want to form a 3D architecture, materials scientists have already come up with dozens of new 2D materials, and many more are likely to follow. They've engineered single-layer silicon (known as silicene), single-layer germanium (germanene), and single-layer tin (stanene). They've created an insulator made from boron nitride, which has the same chicken-wire lattice structure as graphene. They've made single-layer metal oxides that may serve as highly active catalysts for controlling particular chemical reactions. And they've even trapped water molecules in thin sheets, although what this will be useful for isn't yet clear.



Researchers have made quick progress in turning 2D materials into devices, such as this simple circuit in which two transistors use MoS_2 to ferry charges between electrode leads.

ILLUSTRATION: ANDRAS KIS (EPFL)

But for now, most of the buzz among flatlanders surrounds just two materials: a compound called molybdenum disulfide (MoS_2) and a double layer of phosphorus atoms called phosphorene. Both have tantalizing electronic properties, and the competition between their acolytes is fierce.

OF THE TWO MATERIALS, MoS_2 had the head start. Originally synthesized in 2008, MoS_2 is a member of a broader family of materials called transition metal dichalcogenides (TMDs). The name is just a fancy term for their makeup: one transition metal atom (in this case molybdenum) and a pair of atoms from column 16 of the periodic table (a family known as the chalcogens), which contains sulfur and selenium, among others. Much to the delight of electronics makers, all TMDs are semiconductors. They aren't quite as thin as graphene (in MoS_2, twin sheets of sulfur atoms sandwich a middle layer of molybdenum atoms), but they offer other advantages. In the case of MoS_2, one is the speed at which electrons travel through the flat sheets—a property called electron mobility. MoS_2's mobility is a decent 100 or so centimeters squared per volt second (cm^2/vs). That's well below the 1400 cm^2/vs mobility of crystalline silicon, but it's better than the number for amorphous silicon and many other ultrathin semiconductors being tested for use in futuristic applications such as roll-up displays and other flexible, stretchable electronics.

MoS_2 also turns out to be fairly easy to make, even in large sheets. And that has helped engineers move quickly to testing it in devices. In 2011, for example, researchers led by Andras Kis of the Swiss Federal Institute of Technology in Lausanne reported in *Nature Nanotechnology* that they had made the first transistors using a single layer of MoS_2 just 0.65 nanometers thick. Those devices and their successors turned out to have other exceptional properties that rival those of far more developed silicon-based technology. They can switch on and off billions of times per second. They also boast a large on/off ratio, which makes it easy to differentiate between digital 1s and 0s—a property prized by circuit designers. Since 2011, Kis's group and others have engineered a host of MoS_2-based electronic devices including logic circuits and always-on flash memory devices, both of which are widely used in today's computers.

Beyond that, MoS_2 has another desirable property known as a direct bandgap, which enables the material to convert electrons into photons of light—and vice versa. That makes MoS_2 a good candidate for use in optical devices, such as light emitters, lasers, photodetectors, and even solar cells. Lee, an expert in growing large-area MoS_2 films, notes the material is also abundant, cheap, and nontoxic. "It has a bright future," he says.

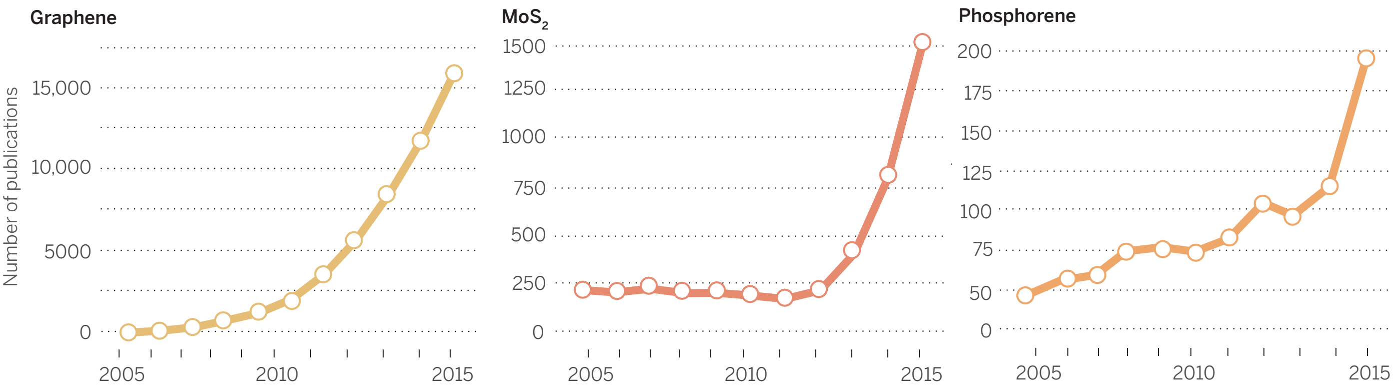
Tomanek, however, is among MoS_2's detractors, saying "it has been oversold." In particular, Tomanek says he isn't convinced that MoS_2's electron mobility will ever be high enough to compete in the crowded electronics marketplace. The reason, he says, lies in the material's very makeup. Electrons traveling through it ricochet off large metal atoms in its structure and slow down.

That stumbling block will prove temporary, Lee says. Researchers are already learning to navigate around it by growing slightly thicker multilayers of MoS_2 that offer zipping electrons alternative routes to bypass roadblocks. "The mobility issue of MoS_2 will be solved," Lee says.

ITS RIVAL, phosphorene, has sparked even more excitement. Also known as black phosphorus, phosphorene is one of three

The rise of the flattest materials

The number of papers on graphene has grown exponentially since the material was isolated in 2004. Publications about molybdenum disulfide (MoS_2) and phosphorene are now repeating the pattern.



DATA SOURCE: WEB OF SCIENCE

different crystal structures—or allotropes—that pure phosphorus can adopt. The others are white phosphorus, which is used in making fireworks, and red phosphorus, used to make the heads of matches. Phosphorene, which consists of a corrugated pattern of phosphorus atoms that lie in two different planes, was first synthesized only last year. But its properties have already made it a materials-science darling. It has an electron mobility of 600, which some researchers hope to increase even further, and its bandgap—the voltage needed to drive a current through it—is tunable. Electrical engineers can adjust the bandgap simply by varying the number of phosphorene layers they stack one atop another, making it easier to engineer devices with the exact behavior desired. "All this makes black phosphorus a superior material," Tomanek says.

Researchers have made rapid progress toward incorporating it into devices. On 2 March 2014, Zhang and his colleagues at Fudan University reported online in *Nature Nanotechnology* that they had made phosphorene-based field effect transistors, devices that serve as the heart of computer logic circuitry. Two weeks later, Tomanek and colleagues at Michigan State, together with researchers led by Peter Ye, an electrical engineer at Purdue University in West Lafayette, Indiana, reported online in *ACS Nano* that they, too, had made phosphorene-based transistors, along with simple circuits.

Unfortunately, phosphorene is unstable in air. "We see bubbles cover the surface after 24 hours and total device failure in days," says Joon-Seok Kim, a phosphorene device maker at UT Austin. The culprit, Lee says, is water vapor, which reacts with the phosphorus, eroding it by converting it to phosphoric acid. Even so, Kim's group at Texas and others are making progress in protecting it. Kim reported at the March meeting of the American Physical Society (APS) in San Antonio, Texas, for example, that he and his colleagues were able to stabilize phosphorene-based transistors for 3 months and counting by encapsulating them in a protective layer of aluminum oxide and Teflon. At the same meeting, researchers from Northwestern University in Evanston, Illinois, reported that a similar strategy gave them stable devices out to 5 months and counting.

But Lee, for one, is not convinced the fixes will lead to long-term stability. "You can put a capping layer on top, but it just reduces the degradation rate," Lee says. Phosphorene, he argues, is gaining attention because it's easy for researchers to get their hands on: It can simply be peeled off a chunk of black phosphorus with sticky tape, like graphene. "It's a kind of fashion," Lee says. "But that doesn't mean it will have a future."

IN THE END, there may be plenty of room for both materials. "We're still just at the beginning," says Luis Balicas, a physicist at Florida State University and the National High Magnetic Field Laboratory in Tallahassee. He suggests that over time engineers may wind up favoring MoS_2's strong interactions with light to make solar cells, light emitters, and other optical devices, while harnessing phosphorene's higher electron mobility for making electronic devices.

Two-dimensional materials also offer another tantalizing option: They can be stacked like cards in a deck to create the different electronic layers needed in functional electronic devices.

In devices made using conventional 3D materials, neighboring crystalline layers usually bind tightly to one another. But if the atomic lattice of adjacent layers differs by more than 15% or so, the strain at the interface causes one or both layers to crack, a potential device killer. That means electrical engineers must either severely limit their selection of neighboring materials so that the layers can join without strain, or resort to complex workarounds, such as adding "buffer" layers at each interface. With stacked 2D materials, "we don't need to worry about this," Lee says, because they don't form tight bonds with the layers above and below.

That advantage has prompted scientists to build such devices, called van der Waals heterostructures after the weak bonds between adjacent layers. The first ones are already emerging. Last year, Ye's group at Purdue reported that they had used both MoS_2 and phosphorene to make ultrathin photovoltaics (PVs). At the APS meeting, Balicas's group reported similar PVs made by combining layers of TMDs, boron nitride, and graphene. And in February, Geim and colleagues reported online in *Nature Materials* that they had assembled multiple 2D materials to make efficient, thin light-emitting diodes.

Such progress has the community of device makers salivating over what may soon be possible. "In principal, we can build an electronic system fully based on 2D materials," says Xiaomu Wang, an electrical engineer at Yale University. Such devices would be flexible, transparent, temperature stable, and cheap to manufacture, Wang says. Contemplating prospects like that, Tomanek thinks the latest revolution in electronics and optics is just getting started: "2D materials are here to stay." ■