News and Views

# 2014 symposium on phosphorene: An emerging 2D semiconductor

There is a new kid on the block among layered materials that can be exfoliated: phosphorene. In analogy to graphene, a monolayer of graphite, the name phosphorene has been adopted for a monolayer of black phosphorus. The interest in this system especially for electronic applications has been sky-rocketing since early 2014, exactly one hundred years after the discovery of black phosphorus by Percy W. Bridgman. For one, phosphorene can be exfoliated from bulk black phosphorus in the same way as graphene from bulk graphite. It is stable but, unlike graphene, displays a nonzero fundamental band gap. Early observations indicate that carrier mobility in phosphorene is rather high; even though it has not yet measured up to the semimetallic graphene, it appears to be superior to transition metal dichalcogenides such as MoS_2. To accommodate the interest of the scientific community in phosphorene, a 3-day workshop called the 2014 Informal Phosphorene Symposium (IPS14) has taken place on the campus of Michigan State University from August 4–6, 2014. While most of the 60 attendees had U.S. affiliations, a significant fraction came from Asia, Europe and Canada.

The general consensus reached in the five invited and eighteen contributed presentations was that phosphorene is definitely a system to watch out for. Many research groups have apparently already started working on it—high demand in bulk black phosphorus has caused a worldwide shortage of its supplies and the waitlist allegedly extends over many weeks.

The most common way to form single-layer and multilayer phosphorene is by mechanical exfoliation of black phosphorus, the most stable allotrope of this element. The process is similar to graphene, since the inter-layer interaction in both systems is rather weak. As an alternative, liquid exfoliation in isopropanol or benzonitrile, followed by ultra-centrifugation, has been found to produce sub-micron flakes of few-layer phosphorene. Most systems reported were more than one monolayer thick. It is expected that other techniques including chemical vapor deposition (CVD) may become methods of choice to produce larger phosphorene flakes, but no such progress has been reported yet.

All samples studied so far had the orthorhombic structure found in layered black phosphorus. Isomerism, illustrated in Figure 1, is an unusual property of phosphorene, as multiple layered structures are expected to be nearly equally stable. Even though blue phosphorene monolayers, which are believed to be as stable as black phosphorene, have not been observed yet, bulk samples of the related rhombohedral phase of A7 or blue phosphorus have been produced under high pressure. Since there are many ways to arrange sp^3-bonded P atoms in a monolayer, the number of equally stable allotropes is expected to be even higher. Since the electronic structure of each phase is different, this provides—at least in theory—extra flexibility in optimizing optical and electronic properties. On the other hand, synthesizing a particular pure phase rather than a mixture of different structural phases may turn out to be challenging.

Even though black phosphorus is the most stable elemental allotrope, it is still related to white and red phosphorus that are used in pyrotechnics and matches. Not surprisingly, much of the discussion at IPS14 has focused on ways to protect phosphorene from degradation in ambient conditions. Time evolution of the degradation process of phosphorene exposed to oxygen, water and light has been studied by scanning probe microscopy (STM, AFM and EFM), TEM, FTIR, XPS, EDAX, and Raman spectroscopy. Fastest degradation is observed in samples exposed to water vapor, oxygen and light. Dry oxygen causes much less physical damage and is believed not to affect the electronic properties to a large degree. In an attempt to isolate the most harmful conditions found in the ambient, oxygenated water seems to cause most damage to phosphorene. Presence of light accelerates the degradation in a photocatalytic process. In samples exposed to the ambient, evolution of small bumps and pits has been observed across the entire sample surface. Some reports indicated preferential degradation starting at the edges. In multi-layer phosphorene, degradation may have been assisted by intercalation from the exposed sides. The general consensus has been that the only permanent protection of phosphorene is by complete encapsulation. This can be achieved by depositing a thick layer of AlO_x using
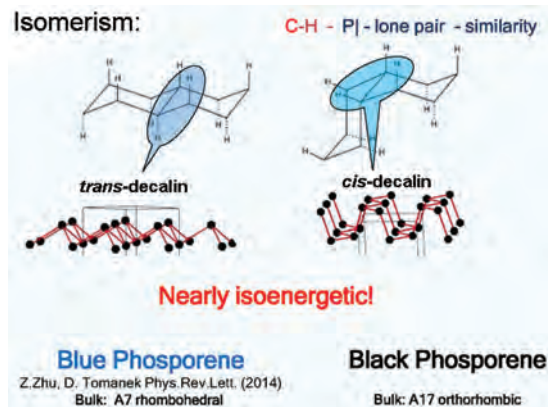
Fig. 1. Chemical origin of isomerism of phosphorus: structure of monolayers of orthorhombic (A17) and rhombohedral (A7) phosphorus in relation to the structures of trans- and cis-decalin, expressing the isoelectronicity of CH and P| (lone pair), Courtesy of Gotthard Seifert.

ALD, which encapsulates the sample and has the advantage of absorbing residual water during the deposition process. Also PMMA and parylene passivate and protect the samples over months. Passivation of the topmost layer has been achieved by deposition of graphene or hexagonal boron nitride, only the latter being a viable choice for electronic applications due to its wide band gap. This approach may be insufficient if the edges of multi-layer phosphorene are left exposed.

The electronic structure of phosphorene is special, since the fundamental band gap is rather large and may be further modified by applying in-layer strain or by changing the number of layers. Whereas the 0.3 eV fundamental band gap of bulk black phosphorus is small, it increases monotonically with decreasing number of layers to reach 2.0 eV in the monolayer. Band gap widening is also observed when layers become decoupled by relative twisting or upon intercalation of a foreign substance. The band gap of black phosphorene is direct—an important factor for optoelectronics applications. The band gap in monolayers of other postulated phosphorene allotropes spans the range from 0.5 eV to about 3.0 eV and may be either direct or indirect. A significant exciton binding energy of 0.7–0.8 eV has been predicted for a free-standing monolayer. This value gets reduced to about 0.5 eV on a dielectric substrate such as SiO_2, which explains the observed photoluminescence peak of supported black phosphorene near 1.5 eV. Black phosphorene is an ambipolar semiconductor, but in most situations appears to be p-type. Doping with Te may change its character to n-type.

It appears that the most attractive application of phosphorene is in a field-effect transistor in 2D electronics. An early device and its performance are shown in Figure 2. An on/off ratio of up to 10^5 has been achieved in vacuum or N_2 atmosphere, an important prerequisite for semiconductor applications.

Apart from the desirable sample passivation even at the early cleaving stage, which was discussed above, important aspects of fabricating a high-performance device include forming low-resistance Ohmic contacts and protecting the phosphorene channel material from the ambient and the substrate. Several groups reported room temperature Ohmic contacts on hole-doped samples using Au/Cr or Au/Ti contacts, but good electrical contacts to electron-doped samples are yet to be realized. Even though Schottky or tunneling barriers could not be avoided, the contact transparency is generally superior to those in MoS_2 and related systems, where the saturated chalcogen layer typically forms a significant tunneling barrier. Encapsulation of the channel has been reported to significantly improve transport properties and reduce hysteresis caused by mobile trapped charges. Due to the ridged structure shown in Figure 1, transport in black phosphorene is anisotropic. The mobility in most current samples is limited by the substrate, presence of adsorbates at the surface and sample quality. Still, most participants seem to agree on the typical room temperature value of the hole mobility at around 200 cm^2 V^{-1} s^{-1}. The electron mobility is lower, but is of the same order of magnitude.

Combination of high electrical conductivity with a poor thermal conductivity raised the intriguing possibility to use layered black phosphorus as a thermoelectric.
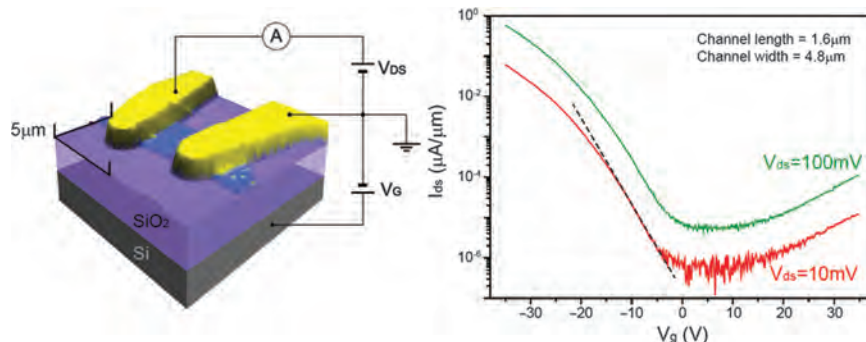
Fig. 2. Structural setup and I–V characteristic of a few-layer phosphorene field effect transistor on SiO$_2$/Si, as described in Likai Li et al., *Nature Nanotechnology* 9, 372 (**2014**), Courtesy of Yuanbo Zhang.

Other applications that were discussed besides the above-mentioned 2D electronics include optoelectronics, in particular optical detectors. Infrared black phosphorus photo-detectors were able to generate diffraction-limited images exposed to $\lambda = 1.55$ μm light in a confocal microscope setup. Anisotropy in the conductivity for $\lambda \approx 4$ μm may allow the construction of a plasmonic polarizer.

The interest of participants in this material became most obvious during extensive discussion and brainstorming sessions that filled a significant part of the workshop. Ideas and topics were captured on the whiteboard and transcribed to a file that is linked to the web site of the IPS14 symposium at http://nanotube.msu.edu/IPS14. With overwhelming majority, participants agreed to join a follow-up workshop in early August 2015. Since the anticipated number of participants is expected to triple, the format of IPS15 will likely become less informal, changing the meaning of the acronym IPS15 to the "2015 International Phosphorene Symposium."

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David Tománek studied Physics in Switzerland and received his Ph.D. from the Free University in Berlin. While holding a position as Assistant Professor of Physics in Berlin, he got engaged in theoretical research in Nanostructures at the AT&T Bell Laboratories and the University of California at Berkeley. He established the field of Computational Nanotechnology at Michigan State University, where he holds a position as Full Professor of Physics. His scientific expertise lies in the development and application of numerical techniques for structural, electronic and optical properties of surfaces, low-dimensional systems and nanostructures. Since he was working on his Ph.D. Thesis, he promoted the use of computer simulations to understand atomic-level processes at surfaces and in atomic clusters. Witnessed in several hundred publications and invited talks are his results on the electronic structure, mechanical, thermal, and optical properties, as well as quantum conductance of nanostructures. His contributions to Computational Nanotechnology, in particular in the field of fullerenes and nanotubes, have been rewarded by a Fellowship of the American Physical Society, the Alexander-von-Humboldt Foundation Distinguished Senior Scientist Award and the Japan Carbon Award for Life-Time Achievement.

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