



**Informal Phosphorene Symposium** East Lansing, Michigan, USA August 4-6, 2014

> Symposium organizer: David Tománek Michigan State University

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Department of Physics and Astronomy, MSU



Center of Research Excellence in Complex Materials (CORE-CM), MSU

### **Conference secretary:** Cathy Cords

# **IPS14** Program

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### Introduction: What is so special about phosphorene?

There is rising interest in phosphorene, a 2D monolayer of black phosphorus, for electronic applications in the post-graphene era. Phosphorene can be exfoliated from bulk black phosphorus in the same way as graphene from bulk graphite. Phosphorene is stable and, unlike graphene, displays a nonzero fundamental band gap. Early observations indicate that carrier mobility in phosphorene is rather high; even though it does not measure up to the semimetallic graphene, it appears to be superior to transition metal dichalcogenides such as  $MoS_2$ .

The IPS14 symposium has been conceived in March 2014 as a response to the rapidly increasing number of studies dedicated to phosphorene, as a way to facilitate communication and promote progress in the field.

To help with discussions, this abstract booklet contains – besides the abstracts – also a *Little Wiki of Phosphorene* with structural parameters and electronic as well as phonon band structure. With the help of my graduate students Zhen Zhu and Jie Guan, I put together the abstracts and bibliographic information of studies dedicated to few-layer black phosphorus/phosphorene in the Section called *Bibliography of black phosphorus*. Referring to publications by number may turn out to be useful at IPS14.

David Tománek

### Little wiki of Phosphorene

Definition

Phosphorene<sup>[1]</sup> is a 2-dimensional, crystalline allotrope of phosphorus, which can be mechanically exfoliated from bulk black phosphorus.



Intrinsic band gap: 0.9 eV (DFT-PBE)<sup>[1]</sup> 2.0 eV (GW)<sup>[2]</sup> Optical gap: 1.4 eV (GW-BSE)<sup>[2]</sup> 1.45 eV (experiment)<sup>[1]</sup>

### Reference

[1] H. Liu, A. T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tomanek, and P. D. Ye, ACS Nano 8, 4033 (2014).

[2] V. Tran, R. Soklaski, Y. Liang, and L. Yang. Phys. Rev. B 89, 235319 (2014).

[3] Z. Zhu and D. Tomanek, Phys. Rev. Lett. **112**, 176802 (2014).

## Invited talks

### Few-layer Phosphorene Field-effect Transistors

### Yuanbo Zhang

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We investigate the electric property of black phosphors thin flakes with thickness down to a few atomic layers. High conductance modulations up to  $10^5$  and field effect mobility up to  $1000 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  at room temperature are achieved in a field effect transistor configuration. We further uncover the mechanism that limits the mobility in black phosphorus thin flakes through temperature-dependent electronic transport measurements. Our results provide some basic understanding of the electronic properties of few-layer black phosphorus thin flakes.

### Shining light on phosphorus

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Phosphorus shows a great variety of structures in the solid state, the most common forms being or- thorhombic black, cubic white, monoclinic violet (Hittorff's), fibrous red and amorphous red phosphorus. The structures of the crystalline allotropes are generally well known, and there have been numerous structural investigations of amorphous phosphorus. Also the relationship between the structures of phosphorus clusters and amorphous phosphorus has been investigated theoretically. Furthermore, the stability of cagelike (fullerenic) phosphorus based structures was studied, and the existence of tubular phosphorus forms were discussed. Recently much attention has been paid to the layered forms of phosphorus. Therefore, the electronic structure of black phosphorus and of the semimetallic arsenic-type structure as well as the interconversion of these allotropes will be discussed. Finally, the similarities in the polymorphism of phosphorus and the heavier elements of the group V in the PSE (As, Sb, Bi) will also be discussed briefly.

### A Carbon Nanomaterial Perspective on the Emerging Field of Phosphorene

### Mark C Hersam

### Northwestern University

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The National Science Foundation recently completed and published a global study of the first decade of the National Nanotechnology Initiative and a projection for this field through the year 2020 [1,2]. Among its many conclusions, this study highlights the following two concepts that differentiate nanomaterials from bulk materials: (1) Nanomaterials possess exceptionally high surface area to volume ratio, which implies that surface functionalization and interfacial control are critical to achieving optimized and reproducible performance, especially in fully integrated devices; (2) Nanomaterials possess size-dependent properties, which necessitates the development of processing schemes that yield geometrically homogeneous samples with atomically precise tolerances. My laboratory has spent the past decade addressing both of these issues for carbon nanomaterials (e.g., carbon nanotubes and graphene), leading to the development of a variety of carbon-based device applications [3]. This talk will comment on the likely opportunities and challenges for phosphorene based on our experiences transitioning carbon nanomaterials from a nascent research laboratory curiosity to a successfully commercialized technology.

[1] M. C. Roco, C. A. Mirkin, and M. C. Hersam, "Nanotechnology research directions for societal needs in 2020: Summary of international study," J. Nanopart. Res., **13**, 897 (2011).

[2] Nanotechnology Research Directions for Societal Needs in 2020, M. C. Roco, C. A. Mirkin, and M. C. Hersam, eds., Springer, 2011, ISBN: 978-94-007-1167-9.

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### Strain-induced gap modification in black phosphorus

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The band structure of single-layer black phosphorus and the effect of strain are predicted using density functional theory and tight-binding models. Having determined the localized orbital composition of the individual bands from firstprinciples, we use the system symmetry to write down the effective low-energy Hamiltonian at the  $\Gamma$  point. From numerical calculations and arguments based on the crystal structure of the material, we show that the deformation in the direction normal to the plane can be use to change the gap size and induce a semiconductor-metal transition.

### Phosphorene: A Layered 2D Material with Different Structure and Properties

Mildred S Dresselhaus

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We review studies on the group theory of phosphorene, as well as spectroscopy studies and possible interesting thermoelectric properties, emphasizing similarities and differences with other layered materials, and looking to the future.

## Contributions

### Photoresponse of Black Phosphorus

 $\label{eq:michael Engel 1} \underbrace{\mbox{Michael Engel}^1,\,\mbox{Mathias Steiner}^2,\,\mbox{Damon B Farmer}^1,}_{\mbox{Phaedon Avouris}^1}$ 

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Black phosphorus (BP) is a re-emerging elemental semiconductor. In its bulk form it has a small energy band gap of 0.3 eV. Moreover, black phosphorus has a layered atomic structure which enables the preparation of thin layers analogous to graphene through its mechanical exfoliation. Its small energy band gap makes it a potentially promising candidate for broad-band photodetection. Here we report on the photoresponse of few-layer BP in a field-effect transistor configuration. We will present results on the responsitivity and time response of our BP-photodectectors as a function of the light wavelength and the applied electric fields. Based on our findings we will comment on the implications and future directions of black phosphorus photodetectors.

### Rediscovering Black Phosphorus: An Anisotropic Layered Material for Optoelectronics and Electronics

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Graphene and transition metal dichalcogenides (TMDC) are the two major types of layered materials currently under intensive investigations. However, the zero bandgap nature of graphene and the relatively low mobility in TMDCs limit their applications in electronics and optoelectronics. Here, we reintroduce black phosphorous (BP), the most stable allotrope of phosphorus with strong intrinsic in-plane anisotropy, to the layered material family. We reveal its anisotropic nature using polarization-resolved Raman scattering and infrared spectroscopy, and angle-resolved transport studies. For 15 nm thick BP, we measure a Hall mobility of 1000 and 600  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  for holes along the light (x) and heavy (y) effective mass directions at 120 K. BP thin films also exhibit large and anisotropic in-plane optical conductivity in the 2 to 5  $\mu$ m spectrum range. Field effect transistors using 5 nm BP along x-direction exhibit an on-off current ratio exceeding  $10^5$ , a field-effect mobility of  $205 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ , and good current saturation characteristics at room temperature. Black phosphorus not only shows great potentials for thin film electronics and infrared optoelectronics, but may also lead to conceptually novel devices in which anisotropic properties are desirable.

### Photostability of thin exfoliated black phosphorus

<u>Alexandre Favron</u><sup>1</sup>, Étienne Gaufrès <sup>1</sup>, Frédéric Fossard <sup>2</sup>, Pierre L Lévesque <sup>1</sup>, Anne-Laurence Phaneuf <sup>3</sup>, Andreas Dietrich <sup>1</sup>, Annick Loiseau <sup>2</sup>, Richard Leonelli <sup>4</sup>, Sébastien Francoeur <sup>3</sup>, Richard Martel <sup>1</sup>

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In its bulk form, black phosphorus has a direct gap of about 0.3 eV. Because of its lamellar structure, similar to that of graphite, black phosphorus can be exfoliated down to a single monolayer. The interesting properties is the possible tuning of the energy gap in the Near-IR using control of the layer thickness, which is of great interesting to develop sensors and other Near-IR optoelectronic devices.

Preliminary studies on thin exfoliated layers revealed a fast photo-induced oxidation of black phosphorus, in room condition with an excitation higher than 1.8 eV. Using Raman spectroscopy as a probe of the quality and integrity of exfoliated layers, we present in this talk the results of a dynamical study of the photo-oxidation process at room temperature in a controlled atmosphere with the presence of the oxygen-water redox couple. A photo-induced charge transfer from black phosphorus to the redox couple is found to be responsible of the fast deterioration of the structure. Finally, we present Raman and Photoluminescence results on un-oxidized thin-layers measured at low temperature using different passivation schemes.

### Laser polarization dependence of the Raman spectra of black phosphorus

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As the most stable allotrope of phosphorus, black phosphorus (BP) has the layered structure similar as graphite. Few-layer or single layer BP can be mechanically exfoliated from the bulk BP. Due to the intrinsic bandgap of BP, it is predicted to have promising application in near and mid-infrared photodetector. In addition, BP has unique orthorhombic crystal structure  $(D_{2h}^{18})$  with puckered honeycomb lattice, which makes it anisotropic in many properties. To relate the properties with the crystalline directions, it is necessary to develop a quick and nondestructive tool to identify the crystalline direction of BP. In this work, we investigate the incident laser polarization dependence of the Raman spectra of BP, including the three vibrational modes,  $A_g^1$ ,  $B_{2g}$  and  $A_g^2$ . It can be used to identify the crystalline direction of the BP.

## Raman spectroscopy of atomically thin black phosphorus

<u>Anne-Laurence Phaneuf-L'Heureux</u><sup>1</sup>, Alexandre Favron<sup>2</sup>, Étienne Gaufrès<sup>2</sup>, Richard Martel<sup>2</sup>, Sébastien Francoeur<sup>1</sup>

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Black phosphorus is a lamellar direct-gap semiconductor offering relatively high mobilities and a thickness-controlled band gap tunability possibly ranging from 0.3 to 2 eV. After presenting a group-theoretical analysis of vibrational modes in few-monolayer samples, we show a study of Raman modes as a function of thickness, temperature, and polarisation. As sample thickness decreases to that of the bilayer, all three bulk vibrational modes broaden, slight frequency shifts are observed, and a new bulk-forbidden Raman mode appears. Frequency shifts are attributed to variations in interlayer interactions and broadening is explained from symmetry arguments: 1) Davydov splitting of bulk modes and 2) new modes originating from Raman-allowed out-of-phase combinations of IR modes.

### High quality ambipolar transport in ultrathin black phosphorus encapsulated with two-dimensional atomic crystals

 $\frac{\text{Steven P Koenig}}{\text{H Castro Neto}^2, \text{ Borbaros Oezyilmaz}^2, \text{ Eoin C O'Farrell}^2, \text{ Antonio}}{\text{H Castro Neto}^2, \text{ Barbaros Oezyilmaz}^2}$ 

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Ultrathin black phosphorus, or phosphorene, is the second known elementary two-dimensional crystal. Unlike graphene it is a semiconductor with a sizeable band gap and its excellent electronic properties make it attractive for applications in transistor, logic, and optoelectronic devices. However due to its sensitivity to ambient air a passivation method is required for further progress in phosphorene research. Here we show that graphene and hexagonal boron nitride can be used for encapsulation of ultrathin black phosphorus. We demonstrate that pristine black phosphorus channels passivated in an inert gas environment, without any prior exposure to air, show greatly improved electron mobility and symmetric electron and hole trans-conductance characteristics.

### Synthesis and characterization of phosphorene

<u>Scott C Warren,</u> Adam H Woomer, Tyler W Farnsworth, Rebekah A Wells, Jun Hu

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We present a general strategy for isolating significant quantities of black phosphorus monolayers, bilayers, and few-layer flakes.

### Spontaneous origami in multi-phase 2D phosphorus

Zhen Zhu, Jie Guan, David Tomanek

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Similar to graphitic carbon, phosphorus monolayers, dubbed phosphorene [1], can be exfoliated from layered black phosphorus. Phosphorene is a p-type semiconductor with a significant band gap. It is stable, flexible, and displays a high carrier mobility [1], suggesting its potential use in 2D electronics. Most interesting, based on *ab initio* density functional calculations, we found that phosphorus can form four different 2D structural phases [2,3] that are almost equally stable and may be inter-connected. Connection of two planar phases resembles a sharp origami-style fold. This fold occurs naturally in this multiphase system, whereas in single-phase systems like graphene it requires the presence of defect lines or lines of adsorbed atoms. We also find the possibility of moving this fold by structural transformation from one allotrope to another, with an unusually low activation barrier of < 0.5 eV per bond. Since the electronic properties of multi-phase phosphorene may also be tuned by inlayer strain, including a semiconductor-to-metal transition, we postulate that origami-style folded phosphorene should display an unprecedented richness in its electronic behavior.

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[2] Zhen Zhu and David Tománek, Semiconducting layered blue phosphorus: A computational study, Phys. Rev. Lett. **112**, 176802 (2014).

[3] Jie Guan, Zhen Zhu, and David Tománek, Phase coexistence and metalinsulator transition in few-layer phosphorene: A computational study, Phys. Rev. Lett. **113**, 046804 (2014).

### High stability of faceted nanotubes and fullerenes of multi-phase layered phosphorus: A computational study

Jie Guan, Zhen Zhu, David Tomanek

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Similar to graphite, black phosphorus is a layered structure that can be exfoliated to monolayers dubbed phosphorene[1]. Similar to carbon nanotubes, which are related to few-layer graphene, we propose the existence of phosphorus nanotubes formed of phosphorene, Different from graphite, besides the black allotrope, layered phosphorus has three stable structural phases, called blue-P [2],  $\gamma$ -P and  $\delta$ -P [3], which can be connected naturally. The fact that connected structures do not lie in a plane allows us to design nanotubes by connecting laterally nanoribbons of different phases. Unlike single-phase nanotubes consisting of a layer rolled up to a cylinder, multi-phase phosphorene nanotubes will have a polygonal cross-section. Both single-wall and multi-wall phosphorene nanotubes may be constructed in this way. The availability of more than one structural phase offers much larger structural richness than the carbon counterpart with one single phase. Consequently, we find that the electronic properties of phosphorene nanotubes depend not only on the chiral vector that defines the edge structure, but also the presence of the individual phosphorene phases. In analogy to the successful synthesis of carbon nanotubes by ball milling of graphite, we believe that phosphorene nanotubes may be formed in the same way in an inert atmosphere.

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[2] Zhen Zhu and David Tománek, Semiconducting layered blue phosphorus: A computational study, Phys. Rev. Lett. **112**, 176802 (2014).

[3] Jie Guan, Zhen Zhu, and David Tománek, Phase coexistence and metalinsulator transition in few-layer phosphorene: A computational study, Phys. Rev. Lett. **113**, 046804 (2014).

### Stability and Flexibility Study of Few-layer Black Phosphorene

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Stability and flexibility are among the biggest topics concerning few-layer black phosphorene, 2D atomic sheets with buckled structure. The air-stability issue is investigated with AFM, elemental EDAX, and microwave impedance microscopy (MIM), with comparison between bare and dielectric capped few-layer flakes (<20nm). Flexible phosphorene FET on PI is first demonstrated with 1.8% compressive strain applied. Both mobility and  $I_{on}$  after bending are within 5% of initial values.

### Quasiparticle Band Gap and Anisotropic Optical Response in Few-layer Black Phosphorus

### Li Yang

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We report the quasiparticle band gap, excitons, and highly anisotropic optical responses of few-layer black phosphorous (phosphorene). It is shown that these new materials exhibit unique many-electron effects; the electronic structures are dispersive essentially along one dimension, leading to particularly enhanced self-energy corrections and excitonic effects. Additionally, within a wide energy range, including infrared light and part of visible light, few-layer black phosphorous absorbs light polarized along the structure's armchair direction and is transparent to light polarized along the zigzag direction, making them viable linear polarizers for applications. Finally, the number of phosphorene layers included in the stack controls the material's band gap, optical absorption spectrum, and anisotropic polarization energy-window across a wide range. If time allows, I will also introduce our recent works on tuning the anisotropic conductance of phosphorene and energy applications.

### Quantum Monte Carlo Studies of Bulk and Few-/Single-Layer Allotropes of Phosphorus

<u>Luke Shulenburger</u> <sup>1</sup>, Andrew Baczewski <sup>1</sup>, Zhen Zhu <sup>2</sup>, Jie Guan <sup>2</sup>, David Tomanek <sup>2</sup>

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The optical properties of phosphorus depend strongly on the structural properties of the material. For example, the band gap of few-layer black phosphorus can be tuned by changing the number of layers or straining the material in plane [1]. Given the limited experimental information on the structure of phosphorene, it is natural to turn to electronic structure calculations to provide this information. Unfortunately, given phosphorus' propensity to form layered structures bound by van der Waals interactions, the standard density functional theory (DFT) methods provide results of uncertain accuracy [2]. Recently, it has been demonstrated that Quantum Monte Carlo (QMC) methods achieve high accuracy when applied to solids in which van der Waals forces play a significant role [3]. I will present results from our recent calculations on black and blue phosphorus, including exciton binding energies, exfoliation energies and structural properties.

\*Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

[1] V. Tran, R. Soklaski, Y. Liang, and L. Yang. Tunable Band Gap and Anisotropic Optical Response in Few-layer Black Phosphorus. arXiv:1402.4192 (2014).

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Contribution C.13

### On the structural stability and the electronic properties of hexagonal-close-packed bilayers of tin and lead

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So-called high-buckled phases of heavy column-IV elements tin and lead have the structure of hexagonal-close-packed bilayers. The structural stability and the electronic properties of these two-dimensional materials will be discussed.

### **Phosphorene Nanoribbons**

<u>Alexandra Carvalho</u> <sup>1</sup>, Aleksandr Rodin <sup>2</sup>, Antonio H Castro Neto <sup>2</sup>

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Edges and boundaries, unavoidable in real-life nanostructures, can be used as an additional means to engineer the electronic and optical properties of these materials. In this talk, edge-induced gap states in finite phosphorene layers are examined based on the results of density functional theory and analytical models. It is found that the nature of such gap states depends on the direction of the cut. Further, we examine how edge states are removed by passivation.

### Atom-based geometrical fingerprinting of conformal two-dimensional materials

<u>Mehrshad Mehboudi</u><sup>1</sup>, Kainen Utt<sup>1</sup>, Pablo Rivero<sup>1</sup>, Alejandro Pacheco Sanjuan<sup>2</sup>, Edmund Harriss<sup>1</sup>, Salvador Barraza-Lopez<sup>1</sup>

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The chemical, electronic, optical, thermal, and mechanical behavior of twodimensional materials will be dictated by their shape. We introduce a novel mathematical framework [1] to describe the shape of 2D materials without any continuum fitting. We can tell shape from atoms for conformal graphene and hexagonal Boron Nitride [2,3], and we have generalized the mathematical framework to inform of shape for other 2D materials such as: 2D AlP and monolayer black phosphorus; low-buckled silicene, germanene, newly predicted III-V buckled 2D compounds, and blue phosphorus monolayers; conformal "thicker" layered materials such as "single-layer" transition metal dichalcogenides ( $MX_2$ 's), and a single-quintuple-layer of the topological insulator Bi<sub>2</sub>Se<sub>3</sub>. The framework is particularly useful when the structural distortion is beyond linear continuum mechanics, a regime that leads to considerable change in materials properties.

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# Local curvature and stability of two-dimensional systems

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We propose a fast method to determine the local curvature in two-dimensional (2D) systems with arbitrary shape. The curvature information, combined with elastic constants obtained for a planar system, provides an accurate estimate of the local stability in the framework of continuum elasticity theory. Relative stabilities of graphitic structures including fullerenes, nanotubes and schwarzites, as well as phosphorene nanotubes, calculated using this approach, agree closely with *ab initio* density functional calculations. The continuum elasticity approach can be applied to all 2D structures and is particularly attractive in complex systems, where the quality of parameterized force fields has not been established.

### Understanding the Surface Reactivity of 2-D Black Phosphorus

 $\underline{\mbox{Tyler W Farnsworth}},$ Rebekah A Wells, Adam H Woomer, Jun Hu, Carrie Donley, Scott C Warren

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We present an experimental study of the stability of black phosphorus in bulk and near the two-dimensional limit.

### **Optoelectronic Properties of Black Phosphorus**

<u>Adam H Woomer,</u> Tyler W Farnsworth, Rebekah A Wells, Jun Hu, Scott C Warren

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Here we present the optoelectronic properties of thin-layer black phosphorus as synthesized from novel fabrication methods.

# Bibliography of black phosphorus

The number of publications dedicated to few-layer phosphorus has been increasing rapidly especially since early 2014. We have searched the *Web of Science* and *arXiv* for "black phosphorus" in the title or abstract. The results of the search follow. Please feel welcome to refer to these documents during the symposium also by the sequence number.

1. Phase coexistence and metal-insulator transition in few-layer phosphorene: A computational study

Jie Guan, Zhen Zhu, David Tomanek arXiv:1407.1894 and Phys. Rev. Lett. 113, 046804 (2014) http://www.pa.msu.edu/cmp/csc/eprint/DT232.pdf Abstract:

Based on *ab initio* density functional calculations, we propose  $\gamma$ -P and  $\delta$ -P as two additional stable structural phases of layered phosphorus besides the layered  $\alpha$ -P (black) and  $\beta$ -P (blue) phosphorus allotropes. Monolayers of some of these allotropes have a wide band gap, whereas others, including  $\gamma$ -P, show a metal-insulator transition caused by in-layer strain or changing the number of layers. An unforeseen benefit is the possibility to connect different structural phases at no energy cost. This becomes particularly valuable in assembling heterostructures with well-defined metallic and semiconducting regions in one contiguous layer.

#### 2. Black Phosphorus Monolayer<br/> $\mathbf{MoS}_2$ van der Waals Heterojunction p-n Diode

Yexin Deng, Zhe Luo, Nathan J. Conrad, Han Liu, Yongji Gong, Sina Najmaei, Pulickel M. Ajayan, Jun Lou, Xianfan Xu, Peide D. Ye ACS Nano ASAP (2014) http://pubs.acs.org/doi/abs/10.1021/nn5027388

Abstract:

Phosphorene, a elemental 2D material, which is the monolayer of black phosphorus, has been mechanically exfoliated recently. In its bulk form, black phosphorus shows high carrier mobility (10000 cm<sup>2</sup>/Vs) and a 0.3 eV direct band gap. Well-behaved p-type field-effect transistors with mobilities of up to 1000 cm<sup>2</sup>/Vs, as well as phototransistors, have been demonstrated on few-layer black phosphorus, showing its promise for electronics and optoelectronics applications due to its high hole mobility and thickness-dependent direct band gap. However, p-n junctions, the basic building blocks of modern electronic and optoelectronic devices, have not yet been realized based on black phosphorus. In this paper, we demonstrate a gate-tunable pn diode based on a p-type black phosphorus/n-type monolayer MoS<sub>2</sub> van der Waals pn heterojunction. Upon

illumination, these ultrathin p-n diodes show a maximum photodetection responsivity of 418 mA/W at the wavelength of 633 nm and photovoltaic energy conversion with an external quantum efficiency of 0.3%. These p-n diodes show promise for broad-band photodetection and solar energy harvesting.

#### 3. Excitons in anisotropic 2D semiconducting crystals

A. S. Rodin, A. Carvalho, A. H. Castro Neto arXiv:1407.0807 http://arxiv.org/abs/1407.0807 Abstract:

The excitonic behavior of anisotropic two-dimensional crystals is investigated using numerical methods. We employ a screened potential arising due to the system polarizability to solve the central-potential problem using the Numerov approach. The dependence of the exciton energies on the interaction strength and mass anisotropy is demonstrated. We use our results to obtain the exciton binding energy in phosphorene as a function of the substrate dielectric constant.

#### 4. Lattice Vibrational Modes and Raman Scattering Spectra of Strained Phosphorene

Ruixiang Fei, Li Yang arXiv:1407.0736 http://arxiv.org/abs/1407.0736 Abstract:

Strain is prominent in fabricated samples of two-dimensional semiconductors and it also serves as an exploitable tool for engineering their properties. However, quantifying strain and characterizing its spatially inhomogeneous distribution across a material are challenging tasks. Here, we report the lattice vibrational modes and corresponding Raman spectra of strained monolayer black phosphorus (phosphorene) by first-principles simulations. We show that frequencies of vibrational modes of phosphorene and their Raman scattering peaks exhibit substantial and distinct shifts according to the types and size of strain. Therefore, combined with high spatial-resolution Raman scattering measurements, our calculated results can quantify strain distributions in phosphorene. This information is essential for understanding structures of future large-scale fabrication and strain engineering of phosphorene.

5. Extraordinary Photoluminescence and Strong Temperature/Angledependent Raman Responses in Few-layer Phosphorene Shuang Zhang, Jiong Yang, Renjing Xu, Fan Wang, Weifeng Li, Muhammad Ghufran, Yong-wei Zhang, Zongfu Yu, Gang Zhang, Qinghua Qin, Yuerui Lu arXiv:1407.0502 http://arxiv.org/abs/1407.0502 *Abstract:* 

Phosphorene is a new family member of two-dimensional materials. We observed strong and highly layer-dependent photoluminescence in few-layer phosphorene (2 to 5 layers). The results confirmed the theoretical prediction that few-layer phosphorene has a direct and layer-sensitive band gap. We also demonstrated that few-layer phosphorene is more sensitive to temperature modulation than graphene and  $MoS_2$  in Raman scattering. The anisotropic Raman response in few-layer phosphorene has enabled us to use an optical method to quickly determine the crystalline orientation without tunneling electron microscope (TEM) or scanning tunneling microscope (STM). Our results provide much needed experimental information about the band structures and exciton nature in few-layer phosphorene, paving the way for various optoelctronic and electronic applications.

#### 6. Structure and electron bands of phosphorus allotropes

L.A. Falkovsky arXiv:1406.7616 http://arxiv.org/abs/1406.7616 Abstract:

The small difference between the rhombohedral phosphorus lattice (A-7 phase) and the simple cubic phase as well as between phosphorene and the cubic structure is used in order to construct their quasiparticle band dispersion. We exploit the Peierls idea of the Brillouin zone doubling, which has been previously employed in consideration of semimetals of the V period and IV–VI semiconductors. In the common framework, individual properties of phosphorus allotropes are revealed.

#### 7. Access and in situ Growth of Phosphorene-Precursor Black Phosphorus

Marianne Köpf, Nadine Eckstein, Daniela Pfister, Carolin Grotz, Ilona Krüger, Magnus Greiwe, Thomas Hansen, Holger Kohlmann, Tom Nilges arXiv:1406.7275

http://arxiv.org/abs/1406.7275

Abstract:

Single crystals of orthorhombic black phosphorus can be grown by a short way transport reaction from red phosphorus and  $Sn/SnI_4$  as mineralization additive. Sizes of several millimeters can be realized with high crystal quality and purity, making a large area preparation of single or multilayer phosphorene possible. An in situ neutron diffraction study has been performed addressing the formation of black phosphorus. Black phosphorus is formed directly via gas phase without the occurrence of any other intermediate phase. Crystal growth was initiated after cooling the starting materials down from elevated temperatures at  $500^{\circ}$ C.

#### 8. Enhanced thermoelectric performance of phosphorene by straininduced band convergence

*H. Y. Lv, W. J. Lu, D. F. Shao, Y. P. Sun* arXiv:1406.5272 http://arxiv.org/abs/1406.5272 *Abstract:* 

The newly emerging monolayer phosphorene was recently predicted to be a promising thermoelectric material. In this work, we propose to further enhance the thermoelectric performance of phosphorene by the strain-induced band convergence. The effect of the uniaxial strain on the thermoelectric properties of phosphorene was investigated by using the first-principles calculations combined with the semi-classical Boltzmann theory. When the zigzag-direction strain is applied, the Seebeck coefficient and electrical conductivity in zigzag direction can be greatly enhanced simultaneously at the critical strain of 5% where the band convergence is achieved. The largest ZT value of 1.65 at 300 K is then achieved conservatively estimated by using the bulk lattice thermal conductivity. When the armchair-direction strain of 8% is applied, the room-temperature ZT value can reach 2.12 in the armchair direction of phosphorene. Our results indicate that strain induced band convergence could be an effective method to enhance the thermoelectric performance of phosphorene.

# 9. Phosphorene as a superior gas sensor: Selective adsorption and distinct I-V response

Liangzhi Kou, Thomas Frauenheim, Changfeng Chen arXiv:1406.2670 http://arxiv.org/abs/1406.2670 Abstract:

Recent reports on the fabrication of phosphorene, i.e., mono- or few-layer black phosphorus, have raised exciting prospects of an outstanding two-dimensional (2D) material that exhibits excellent properties for nanodevice applications. Here we study by first-principles calculations the adsorption of CO,  $CO_2$ ,  $NH_3$ , NO and  $NO_2$  gas molecules on a mono-layer phosphorene. Our results predict superior sensing performance of phosphorene that rivals or even surpasses other 2D materials such as graphene and  $MoS_2$ . We determine the optimal adsorption positions of these molecules on the phosphorene and identify molecular doping, i.e., charge transfer between the molecules and phosphorene, as the driving mechanism for the high adsorption strength. We further calculated the current-voltage (I-V) relation using a non-equilibrium Greens function (NEGF) formalism. The transport features show large (one to two orders of magnitude) anisotropy along different (armchair or zigzag) directions, which is consistent with the anisotropic electronic band structure of phosphorene. Remarkably, the I-V relation exhibits distinct responses with a marked change of the I-V relation along either the armchair or the zigzag directions depending on the type of molecules. Such selectivity and sensitivity to adsorption makes phosphorene a superior gas sensor that promises wide-ranging applications.

#### 10. A theoretical study of blue phosphorene nanoribbons based on first-principles calculations

Jiefeng Xie, M. S. Si, D. Z. Yang, Z. Y. Zhang, D. S. Xue arXiv:1405.4407 http://arxiv.org/abs/1405.4407 Abstract:

Based on first-principles calculations, we present a quantum confinement mechanism for the band gaps of blue phosphorene nanoribbons (BPNRs) as a function of their widths. The BPNRs considered have either armchair or zigzag shaped edges on both sides with hydrogen saturation. Both the two types of nanoribbons are shown to be indirect semiconductors. An enhanced energy gap of around 1 eV can be realized when the width decreases to about 10 Å. The underlying physics is ascribed to the quantum confinement. More importantly, the quantum confinement parameters are obtained by fitting the calculated gaps with respect to their widths. The results show that the quantum confinement in armchair nanoribbons is stronger than that in zigzag ones. This study provides an efficient approach to tune the energy gap in BPNRs.

11. Phosphorene nanoribbon as a promising candidate for thermoelectric applications

J. Zhang, H.J. Liu, L. Cheng, J. Wei, J.H. Liang, D.D. Fan, J. Shi, X.F. Tang, Q. J. Zhang arXiv:1405.3348 http://arxiv.org/abs/1405.3348 Abstract:

In this work, the electronic properties of phosphorene nanoribbons with different width and edge configurations are studied by using density functional theory. It is found that the armchair phosphorene nanoribbons are semiconducting while the zigzag nanoribbons are metallic. The band gaps of armchair nanoribbons decrease monotonically with increasing ribbon width. By passivating the edge phosphorus atoms with hydrogen, the zigzag series also become semiconducting, while the armchair series exhibit a larger band gap than their pristine counterpart. The electronic transport properties of these phosphorene nanoribbons are then investigated using Boltzmann theory and relaxation time approximation. We find that all the semiconducting nanoribbons exhibit very large values of Seebeck coefficient and can be further enhanced by hydrogen passivation at the edge. Taking armchair nanoribbon with width N=7 as an example, we calculate the lattice thermal conductivity with the help of phonon Boltzmann transport equation. Due to significantly enhanced Seebeck coefficient and decreased thermal conductivity, the phosphorene nanoribbon exhibit a very high figure of merit (ZT value) of 4.0 at room temperature, which suggests its appealing thermoelectric applications.

#### 12. Band Gaps and Giant Stark Effect in Nonchiral Phosphorene Nanoribbons

Qingyun Wu, Lei Shen, Ming Yang, Zhigao Huang, Yuan Ping Feng arXiv:1405.3077 http://arxiv.org/abs/1405.3077 Abstract:

From the first demonstration of carbon nanotube field-effect-transistors (FETs) in 1998 to graphene nanoribbon FETs in 2008 and MoS<sub>2</sub> nanoribbon FETs in 2012, various 1D nanotube or nanoribbon FETs are proposed. However, the chiral behaviour (armchair and zigzag), the structural symmetry, and screening of electric fields of these 1D materials seriously hampers the development of their applications in FETs. In this work, we find very unique electronic structures of monolayer black phosphorus (phosphorene) nanoribbons, i.e., nonchirality and no symmetry-dependent edge states, in contrast to all known 1D nanomaterials. It is because the s-p hybridization of central phosphorus atoms contributes to the valence band (hole) and conduction band (electron) based on our band structure calculations. The most importance is that such band gaps can have a strong response to the transverse electric field, i.e., a giant Stark effect. We give a clear physics explanation on the giant Stark effect. Finally, our transport calculations show that PNR-FETs, utilizing such giant Stark effect, can have high on/off ratio which is the key feature of logic operation in transistors.

### 13. The Effect of Dielectric Capping on Few-Layer Phosphorene Transistors: Tuning the Schottky Barrier Heights Han Liu, Adam T. Neal, Mengwei Si, Yuchen Du, Peide D. Ye arXiv:1405.3010 http://arxiv.org/abs/1405.3010 Abstract: Phosphorene is a unique single elemental semiconductor with two-dimensional

layered structures. In this letter, we study the transistor behavior on mechanically exfoliated few-layer phosphorene with the top-gate. We achieve a high on-current of 144 mA/mm and hole mobility of 95.6 cm<sup>2</sup>/Vs. We deposit Al<sub>2</sub>O<sub>3</sub> by atomic layer deposition (ALD) and study the effects of dielectric capping. We observe that the polarity of the transistors alternated from p-type to ambipolar with Al<sub>2</sub>O<sub>3</sub> grown on the top. We attribute this transition to the changes for the effective Schottky barrier heights for both electrons and holes at the metal contact edges, which is originated from fixed charges in the ALD dielectric.

#### 14. Enhanced Thermoelectric Efficiency via Orthogonal Electrical and Thermal Conductances in Phosphorene

Ruixiang Fei, Alireza Faghaninia, Ryan Soklaski, Jia-An Yan, Cynthia Lo, Li Yang arXiv:1405.2836 http://arxiv.org/abs/1405.2836 Abstract:

Thermoelectric devices that utilize the Seebeck effect convert heat flow into electrical energy and are highly desirable for the development of portable, solid state, passively-powered electronic systems. The conversion efficiencies of such devices are quantified by the dimensionless thermoelectric figure of merit (ZT). which is proportional to the ratio of a device's electrical conductance to its thermal conductance. High ZT (> 2) has been achieved in materials via all-scale hierarchical architecturing. This efficiency holds at high temperatures (700K-900K) but quickly diminishes at lower temperatures. In this paper, a recentlyfabricated two-dimensional (2D) semiconductor called phosphorene (monolayer black phosphorus) is assessed for its thermoelectric capabilities. First-principles and model calculations reveal that phosphorene possesses spatially-anisotropic electrical and thermal conductances. The prominent electrical and thermal conducting directions are orthogonal to one another, enhancing the ratio of these conductances. As a result, ZT can reach 2.5 (the criterion for commercial deployment) along the armchair direction of phosphorene at T=500K and is greater than 1 even at room temperature given moderate doping (  $2 \times 10^{16} m^{-2}$ ). Ultimately, phosphorene stands out as an environmentally sound thermoelectric material with unprecedented qualities: intrinsically, it is a mechanically flexible material that converts heat energy with high efficiency at low temperatures (300K) - one whose performance does not require any sophisticated engineering techniques.

# 15. Chemical scissors cut phosphorene nanostructures and their novel electronic properties

Xihong Peng, Qun Wei

arXiv:1405.0801 http://arxiv.org/abs/1405.0801 *Abstract:* 

Phosphorene, a recently fabricated two dimensional puckered honeycomb structure of phosphorus, showed promising properties for applications of nano-electronics. In this work, we report our findings of chemical scissors effects on phosphorene, using first principles density functional theory methods. It was found that several chemical species, such as H, F, Cl and OH group, can act effectively as scissors to cut phosphorene. Phosphorus chains and nanoribbons can be obtained using different surface coverage of the chemical species. The scissor effects of these species are resulted from their strong chemical bonds with the P atoms. Species such as O, S and Se were not able to cut phosphorene nanostructures due to their lack of strong binding with P. The electronic structure calculations of the produced P-chains reveal that the saturated chain is an insulator while the pristine chain demonstrates a Dirac point at X with a Fermi velocity of  $8 \times 10^5$  m/s. The obtained zigzag phosphorene nanoribbons show either metallic or semiconducting behaviors, depending on the treatment of the edge P atoms.

16. Electron-doped phosphorene: A potential monolayer superconductor

D. F. Shao, W. J. Lu, H. Y. Lv, Y. P. Sun arXiv:1405.0092 http://arxiv.org/abs/1405.0092 *Abstract:* 

We predict by first-principles calculations that the electron-doped phosphorene is a potential BCS-like superconductor. The stretching modes at the Brillouinzone center are remarkably softened by the electron-doping, which results in the strong electron-phonon coupling. The superconductivity can be introduced by a doped electron density (n2D) above  $1.3 \times 10^{14}$  cm<sup>2</sup>, and may exist over the liquid helium temperature when  $n_{2D}>2.6 \times 10^{14}$  cm<sup>2</sup>. The maximum critical temperature is predicted to be higher than 10 K. The superconductivity of phosphorene will significantly broaden the applications of this novel material.

#### 17. Edge effects on the electronic properties of phosphorene nanoribbons

Xihong Peng, Qun Wei, Andrew Copple arXiv:1404.5995 http://arxiv.org/abs/1404.5995 Abstract: Two dimensional few-layer black phosphorus crystal structures have recently fabricated and demonstrated great potential in applications of electronics. In this work, we employed first principles density functional theory calculations to study the edge effects and quantum confinement on the electronic properties of the phosphorene nanoribbons (PNR). Different edge functionalization groups, such as H, F, Cl, OH, O, S, and Se in addition to a pristine case, were studied for a series width of the ribbon up to 3.5 nm. It was found that the armchair-PNRs (APNRs) are semiconductors for all edge groups considered in this work. However, the zigzag-PNRs (ZPNRs) show either semiconductor or metallic behavior in dependence on their edge chemical groups. Family I edges (H, F, Cl, OH) form saturated bonds with P atoms and the edge states keep far away from the band gap. However, Family II edges (pristine, O, S, Se) form weak unsaturated bonds with the pz orbital of P atoms and bring edge states within the band gap. These edge states of Family II ribbons present around the Fermi level within the band gap, which close up the band gap of the ZPNRs. For the APNRs, these edge states are at the bottom of the conduction band and result in a reduced band gap.

#### 18. Electrically Tunable Quasi-Flat Bands, Conductance and Field Effect Transistor in Phosphorene

Motohiko Ezawa arXiv:1404.5788 http://arxiv.org/abs/1404.5788 Abstract:

Phosphorene, a honeycomb structure of black phosphorus, was isolated recently. We investigate electric properties of phosphorene nanoribbons based on the tight-binding model. A prominent feature is the presence of quasi-flat edge bands entirely detached from the bulk band. We explore the mechanism of the emergence of the quasi-flat bands analytically and numerically from the flat bands well known in graphene by a continuous deformation of a honeycomb lattice. The quasi-flat bands can be controlled by applying in-plane electric field perpendicular to the ribbon direction. The conductance is switched off above a critical electric field, which acts as a field-effect transistor. The critical electric field is anti-proportional to the width of a nanoribbon. This results will pave a way toward nanoelectronics based on phosphorene.

19. Large thermoelectric power factors in black phosphorus and phosphorene

*H. Y. Lv, W. J. Lu, D. F. Shao, Y. P. Sun* arXiv:1404.5171 http://arxiv.org/abs/1404.5171 *Abstract:*  The electronic properties of the layered black phosphorus (black-P) and its monolayer counterpart phosphorene are investigated by using the first-principles calculations based on the density functional theory (DFT). The room-temperature electronic transport coefficients are evaluated within the semi-classical Boltzmann theory. The electrical conductivity exhibits anisotropic behavior while the Seebeck coefficient is almost isotropic. At the optimal doping level and room temperature, bulk black-P and phosphorene are found to have large thermoelectric power factors of 118.4 and 138.9  $\mu$ Wcm<sup>-1</sup>K<sup>-2</sup>, respectively. The maximum dimensionless figure of merit (ZT value) of 0.22 can be achieved in bulk black-P by appropriate n-type doping, primarily limited by the reducible lattice thermal conductivity. For the phosphorene, the ZT value can reach 0.30 conservatively estimated by using the bulk lattice thermal conductivity. Our results suggest that both bulk black-P and phosphorene are potentially promising thermoelectric materials.

#### 20. Phosphorene nanoribbons

A. Carvalho, A. S. Rodin, A. H. Castro Neto arXiv:1404.5115 http://arxiv.org/abs/1404.5115 Abstract:

Edge-induced gap states in finite phosphorene layers are examined using analytical models and density functional theory. The nature of such gap states depends on the direction of the cut. Armchair nanoribbons are insulating, whereas nanoribbons cut in the perpendicular direction (with zigzag and clifftype edges) are metallic, unless they undergo a reconstruction or distortion with cell doubling, which opens a gap. All stable nanoribbons with unsaturated edges have gap states that can be removed by hydrogen passivation. Armchair nanoribbon edge states decay exponentially with the distance to the edge and can be described by a nearly-free electron model.

#### 21. Peierls transition and edge reconstruction in phosphorene nanoribbons

Ajanta Maity, Akansha Singh, Prasenjit Sen arXiv:1404.2469 http://arxiv.org/abs/1404.2469 Abstract:

Atomic and electronic structures of phosphorene nanoribbons are studied within density functional theory. These novel materials present different physical phenomena expected in two very different physical systems: one dimensional metallic chains and semiconductor surfaces. While 'rugged' nanoribbons are semiconducting in their layer-terminnated structures, pure 'linear' and 'zigzag' nanoribbons are metallic due to metallic edge states. Linear nanoribbons undergo edge reconstruction and zigzag nanoribbons beyond a certain width undergo Peierls transition leading to opening of a band gap in the electronic structure and lowering of total energy. Mixed nanoribbons with linear and zigzag edges on the two sides turn out to be a curious case that display both edge reconstruction and Peierls transition simultaneously. Most phosphoeren nanoribbons turn out to be semiconductors having important implications for their application.

#### 22. Unusual Scaling Laws of the Band Gap and Optical Absorption of Phosphorene Nanoribbons

Vy Tran, Li Yang arXiv:1404.2247 and Phys. Rev. B 89, 245407 (2014) http://arxiv.org/abs/1404.2247 Abstract:

We report the electronic structure and optical absorption spectra of monolayer black phosphorus (phosphorene) nanoribbons (PNRs) via first-principles simulations. The band gap of PNRs is strongly enhanced by quantum confinement. However, differently orientated PNRs exhibit distinct scaling laws for the band gap vs the ribbon width w. The band gaps of armchair PNRs scale as  $1/w^2$ , while zigzag PNRs exhibit a 1/w behavior. These distinct scaling laws reflect a significant implication of the band dispersion of phosphorene: electrons and holes behave as nonrelativistic particles along the zigzag direction but resemble relativistic particles along the armchair direction. This unexpected merging of nonrelativistic and relativistic properties in a single material may produce novel electrical and magnetotransport properties of few-layer black phosphorus and its ribbon structures. Finally, the respective PNRs host electrons and holes with markedly different effective masses and optical absorption spectra, which are suitable for a wide range of applications.

# 23. Plasma-assisted fabrication of monolayer phosphorene and its Raman characterization

Wanglin Lu, Haiyan Nan, Jinhua Hong, Yuming Chen, Chen Zhu, Zheng Liang, Xiangyang Ma, Zhenhua Ni, Chuanhong Jin, Ze Zhang arXiv:1404.0742 http://arxiv.org/abs/1404.0742 Abstract:

There have been continuous efforts to seek for novel functional two-dimensional semiconductors with high performance for future applications in nanoelectronics and optoelectronics. In this work, we introduce a successful experimental approach to fabricate monolayer phosphorene by mechanical cleavage and the following Ar+ plasma thinning process. The thickness of phosphorene is unambiguously determined by optical contrast combined with atomic force microscope (AFM). Raman spectroscopy is used to characterize the pristine and plasma-treated samples. The Raman frequency of  $A_g^2$  mode stiffens, and the intensity ratio of  $A_g^2$  to  $A_g^1$  modes shows monotonic discrete increase with the decrease of phosphorene thickness down to monolayer. All those phenomena can be used to identify the thickness of this novel two-dimensional semiconductor efficiently. This work for monolayer phosphorene fabrication and thickness determination will facilitates the research of phosphorene.

# 24. Superior mechanical flexibility of phosphorene and few-layer black phosphorus

Qun Wei, Xihong Peng arXiv:1403.7882 and Appl. Phys. Lett. 104, 251915 (2014) http://arxiv.org/abs/1403.7882 Abstract:

Recently, fabricated two dimensional (2D) phosphorene crystal structures have demonstrated great potential in applications of electronics. Mechanical strain was demonstrated to be able to significantly modify the electronic properties of phosphorene and few-layer black phosphorus. In this work, we employed first principles density functional theory calculations to explore the mechanical properties of phosphorene, including ideal tensile strength and critical strain. It was found that a monolayer phosphorene can sustain tensile strain up to 27%and 30% in the zigzag and armchair directions, respectively. This enormous strain limit of phosphorene results from its unique puckered crystal structure. We found that the tensile strain applied in the armchair direction stretches the pucker of phosphorene, rather than significantly extending the P-P bond lengths. The compromised dihedral angles dramatically reduce the required strain energy. Compared to other 2D materials, such as graphene, phosphorene demonstrates superior flexibility with an order of magnitude smaller Young's modulus. This is especially useful in practical large-magnitude-strain engineering. Furthermore, the anisotropic nature of phosphorene was also explored. We derived a general model to calculate the Young's modulus along different directions for a 2D system.

#### 25. Phosphorene nanoribbons, nanotubes and van der Waals multilayers

Hongyan Guo, Ning Lu, Jun Dai, Xiaojun Wu, Xiao Cheng Zeng arXiv:1403.6209 and The Journal of Physical Chemistry C 2014 118 (25), 14051-14059 http://arxiv.org/abs/1403.6209 Abstract:

We perform a comprehensive first-principles study of the electronic properties of phosphorene nanoribbons, phosphorus nanotubes, multilayer phosphorene sheets, and heterobilayers of phosphorene and two-dimensional (2D) transitionmetal dichalcogenide (TMDC) monolayer. The tensile strain and electric-field effects on electronic properties of low-dimensional phosphorene nanostructures are also investigated. Our calculations show that the bare zigzag phosphorene nanoribbons (z-PNRs) are metals regardless of the ribbon width, whereas the bare armchair phosphorene nanoribbons (a-PNRs) are semiconductors with indirect bandgaps and the bandgaps decrease with increasing ribbon width. We find that compressive (or tensile) strains can reduce (or enlarge) the bandgap of the bare a-PNRs while an in-plane electric field can significantly reduce the bandgap of the bare a-PNRs, leading to the semiconductor-to-metal transition beyond certain electric field. For edge-passivated PNR by hydrogen, z-PNRs become semiconductor with nearly direct bandgaps and a-PNRs are still semiconductor but with direct bandgaps. The response to tensile strain and electric field for the edge-passivated PNRs is similar to that for the edge-unpassivated (bare) a-PNRs. For single-walled phosphorus nanotubes, both armchair and zigzag nanotubes are semiconductors with direct bandgaps. With either tensile strains or transverse electric field, behavior of bandgap modulation similar to that for a-PNRs can arise. It is known that multilayer phosphorene sheets are semiconductors whose bandgaps decrease with an increase in the number of multilayers. In the presence of a vertical electric field, the bandgaps of multilayer phosphorene sheets decrease with increasing electric field and the bandgap modulation is more significant with more layers. Lastly, heterobilayers of phosphorene (p-type) with an n-type TMDC ( $MoS_2$  or  $WS_2$ ) monolayer are still semiconductors while their bandgaps can be reduced by applying a vertical electric field as well. We also show that the combined phosphorene/ $MoS_2$  heterolayers can be an effective solar cell material. Our estimated power conversion efficiency for the phosphorene/MoS2 heterobilayer has a theoretical maximum value of 17.5%.

#### 26. Bilayer Phosphorene: Effect of Stacking Order on Bandgap and its Potential Applications in Thin-Film Solar Cells

Jun Dai, Xiao Cheng Zeng

arXiv:1403.6189 and The Journal of Physical Chemistry Letters 2014 5 (7), 1289-1293 http://arxiv.org/abs/1403.6189 *Abstract:* 

Phosphorene, a monolayer of black phosphorus, is promising for nanoelectronic applications not only because it is a natural p-type semiconductor but also because it possesses a layer-number-dependent direct bandgap (in the range of 0.3

to 1.5 eV). On basis of the density functional theory calculations, we investigate electronic properties of the bilayer phosphorene with different stacking orders. We find that the direct bandgap of the bilayers can vary from 0.78 to 1.04 eV with three different stacking orders. In addition, a vertical electric field can further reduce the bandgap to 0.56 eV (at the field strength 0.5 V/Å). More importantly, we find that when a monolayer of MoS<sub>2</sub> is superimposed with the p-type AA- or AB-stacked bilayer phosphorene, the combined trilayer can be an effective solar-cell material with type-II heterojunction alignment. The power conversion efficiency is predicted to be 18 or 16% with AA- or AB-stacked bilayer phosphorene, higher than reported efficiencies of the state-of-the-art trilayer graphene/transition metal dichalcogenide solar cells.

## 27. Strain engineered direct-indirect band gap transition and its mechanism in 2D phosphorene

Xihong Peng, Andrew Copple, Qun Wei arXiv:1403.3771 http://arxiv.org/abs/1403.3771 Abstract:

Recently fabricated two dimensional (2D) phosphorene crystal structures have demonstrated great potential in applications of electronics. In this work, strain effect on the electronic band structure of phosphorene was studied using first principles methods. It was found that phosphorene can withstand a surface tension and tensile strain up to 10 N/m and 30%, respectively. The band gap of phosphorene experiences a direct-indirect-direct transition when axial strain is applied. A moderate -2% compression in the zigzag direction can trigger this gap transition. With sufficient expansion (+11.3%) or compression (-10.2%)strains), the gap can be tuned from indirect to direct again. Five strain zones with distinct electronic band structure were identified and the critical strains for the zone boundaries were determined. The origin of the gap transition was revealed and a general mechanism was developed to explain energy shifts with strain according to the bond nature of near-band-edge electronic orbitals. Effective masses of carriers in the armchair direction are an order of magnitude smaller than that of the zigzag axis indicating the armchair direction is favored for carrier transport. In addition, the effective masses can be dramatically tuned by strain, in which its sharp jump/drop occurs at the zone boundaries of the direct-indirect gap transition.

#### 28. Strain-Engineering Anisotropic Electrical Conductance of Phosphorene and Few-Layer Black Phosphorus

*Ruixiang Fei, Li Yang* arXiv:1403.1003 and Nano Lett. 14, 2884 (2014)

#### http://arxiv.org/abs/1403.1003 Abstract:

Newly fabricated few-layer black phosphorus and its monolayer structure, phosphorene, are expected to be promising for electronic and optical applications because of their finite direct band gaps and sizable but anisotropic electronic mobility. By first-principles simulations, we show that this unique anisotropic free-carrier mobility can be controlled by using simple strain conditions. With the appropriate biaxial or uniaxial strain (4-6%), we can rotate the preferred conducting direction by 90 degrees. This will be useful for exploring unusual quantum Hall effects and exotic electronic and mechanical applications based on phosphorene.

#### 29. Tunable Band Gap and Anisotropic Optical Response in Fewlayer Black Phosphorus

Vy Tran, Ryan Soklaski, Yufeng Liang, Li Yang arXiv:1402.4192 and Phys. Rev. B 89, 235319 (2014) http://arxiv.org/abs/1402.4192 Abstract:

We report the quasiparticle band gap, excitons, and highly anisotropic optical responses of few-layer black phosphorous (phosphorene). It is shown that these materials exhibit unique many-electron effects; the electronic structures are dispersive essentially along one dimension, leading to particularly enhanced self-energy corrections and excitonic effects. Additionally, within a wide energy range, including infrared light and part of visible light, few-layer black phosphorous absorbs light polarized along the structures' armchair direction and is transparent to light polarized along the zigzag direction, making them potentially viable linear polarizers for applications. Finally, the number of phosphorene layers included in the stack controls the material's band gap, optical absorption spectrum, and anisotropic polarization energy window across a wide range.

#### 30. Phosphorene: A New 2D Material with High Carrier Mobility

Han Liu, Adam T. Neal, Zhen Zhu, Zhe Luo, Xianfan Xu, David Tománek, and Peide D. Ye arXiv:1401.4133 and ACS Nano, 8, 4033-4041 (2014) http://arxiv.org/abs/1401.4133 Abstract:

We introduce the 2D counterpart of layered black phosphorus, which we call phosphorene, as an unexplored p-type semiconducting material. Same as graphene and  $MoS_2$ , single-layer phosphorene is flexible and can be mechanically exfoliated. We find phosphorene to be stable and, unlike graphene, to have an

inherent, direct, and appreciable band gap. Our ab initio calculations indicate that the band gap is direct, depends on the number of layers and the in-layer strain, and is significantly larger than the bulk value of 0.31-0.36 eV. The observed photoluminescence peak of single-layer phosphorene in the visible optical range confirms that the band gap is larger than that of the bulk system. Our transport studies indicate a hole mobility that reflects the structural anisotropy of phosphorene and complements n-type MoS<sub>2</sub>. At room temperature, our few-layer phosphorene field-effect transistors with 1.0  $\mu$ m channel length display a high on-current of 194 mA/mm, a high hole field-effect mobility of 286 cm<sup>2</sup>/Vs, and an on/off ratio of up to 104. We demonstrate the possibility of phosphorene PMOS and MoS<sub>2</sub> NMOS transistors.

# 31. A black phosphorus photo-detector for multispectral, high-resolution imaging

Michael Engel, Mathias Steiner, Phaedon Avouris arXiv:1407.2534 http://arxiv.org/abs/1407.2534 Abstract:

Among the different 2-dimensional inorganic materials with their unique electronic and optical properties, the layered semiconductor black phosphorus is currently intensely researched for its potential applications in electronics and optoelectronics. The band gap energy of the bulk is 0.3 eV, however, it increases with decreasing layer number; to 1.5 eV for a single layer. Therefore, a multi-layer black phosphorus device should, in principle, allow photo-detection over a broad spectral range with sufficient sensitivity for practical imaging applications. Here, we map the active area of a multi-layer black phosphorus photo-detector and we characterize responsivity and gain of the device in the visible ( $\lambda_{VIS}$ =532nm) as well as the near-infrared ( $\lambda_{IR}$ =1550nm) spectral domain. By using the same device as a point-like detector at the two test wavelengths, we acquire diffraction-limited images of structures that exhibit sub-micron feature sizes. The results demonstrate the usefulness of two-dimensional, layered semiconductors for practical imaging applications where a broad spectral range is needed.

32. Engineering Schottky Barrier in Black Phosphorus field effect devices for spintronic applications

M. Venkata Kamalakar, B. N Madhushankar, André Dankert, Saroj P. Dash arXiv:1406.4476 http://arxiv.org/abs/1406.4476 Abstract:

Black phosphorous (BP) is is recently unveiled as a promising two-dimensional direct bandgap semiconducting material. Here, we report the ambipolar field effect transistor behavior of multilayers of BP with ferromagnetic tunnel contacts. We observe a reduced of Schottky barrier < 50 meV by using TiO<sub>2</sub>/Co contacts, which could be further tuned by gate voltages. Eminently a good transistor performance is achieved in BP devices, with drain current modulation on the order of four to six orders of magnitude. The charge carrier mobility is found to be 155 and 0.18 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for holes and electrons respectively at room temperature. Furthermore, magnetoresistance calculations reveal that the resistances of the BP device with applied gate voltages are in the appropriate range for injection and detection of spin polarized holes. Our results demonstrate the prospect of engineering BP nanolayered devices for efficient nanoelectronic and spintronic applications.

#### 33. Strain enhanced anisotropic thermoelectric performance of Black Phosphorus

Guangzhao Qin, Zhenzhen Qin, Sheng-Ying Yue, Hui-Juan Cui, Qing-Rong Zheng, Qing-Bo Yan, Gang Su arXiv:1406.0261 http://arxiv.org/abs/1406.0261 Abstract:

The anisotropic geometric, electronic, and thermoelectric (TE) properties of bulk black phosphorus (BP) with strain applied along three lattice directions have been systematically investigated using first-principles calculations combined with semi-classical Boltzmann transport theory. The lattice constant b always increase whatever compressive or tensile strain is applied along z direction, showing an unusual mechanical response with a transition between positive and negative Poisson's ratio, which may due to the hinge-like structure of BP. The electronic properties are sensitive to strain that there exist transitions of band gap among direct, indirect and zero with strain varying from compressive to tensile. For the TE performance of BP, when there is no strain applied, the ZT value is found to be maximal along x direction as 0.722 at 800K with an electron (n-type) doping concentration of  $6.005 \times 10^{19} \text{ cm}^3$ , while being smaller for hole (p-type) doping or along other directions, indicating a distinctly anisotropic TE performance. Furthermore, the greatest enhanced ZT values could be obtained for electron (n-type) doped BP as 0.866 at 800K with a tensile strain of 7% applied along y direction.

#### 34. Electronic Structures of Black Phosphorus Studied by Angleresolved Photoemission Spectroscopy

C. Q. Han, M. Y. Yao, X. X. Bai, Lin Miao, Fengfeng Zhu, D. D. Guan, Shun Wang, C. L. Gao, Canhua Liu, Dong Qian, Y. Liu, Jin-feng Jia arXiv:1405.7431
http://arxiv.org/abs/1405.7431
Abstract:
Electronic structures of single crystalline black phosphorus were studied by state-of-art angleresolved photoemission spectroscopy. Through high resolution photon energy dependence measurements, the band dispersions along out-ofplane and in-plane directions are experimentally determined. The electrons were found to be more localized in the ab-plane than that is predicted in cal-

culations. Beside the  $k_z$ -dispersive bulk bands, resonant surface state is also observed in the momentum space. Our finds strongly suggest that more details need to be considered to fully understand the electronic properties of black phosphorus theoretically.

# 35. Electrical contacts to monolayer black Phosphorus: a first principles investigation

Kui Gong, Lei Zhang, Wei Ji, Hong Guo arXiv:1404.7207 http://arxiv.org/abs/1404.7207 Abstract:

We report first principles theoretical investigations of possible metal contacts to monolayer black phosphorus (BP). By analyzing lattice geometry, five metal surfaces are found to have minimal lattice mismatch with BP: Cu(111), Zn(0001), In(110), Ta(110) and Nb(110). Further studies indicate Ta and Nb bond strongly with monolayer BP causing substantial bond distortions, but the combined Ta-BP and Nb-BP form good metal surfaces to contact a second layer BP. By analyzing the geometry, bonding, electronic structure, charge transfer, potential and band bending, it is concluded that Cu(111) is the best candidate to form excellent Ohmic contact to monolayer BP. Other four metal surfaces or combined surfaces also provide viable structures to form metal/BP contacts, but they have Schottky character.

#### 36. Plasmons and screening in monolayer and multilayer black phosphorus

Tony Low, Rafael Roldn, Han Wang, Fengnian Xia, Phaedon Avouris, Luis Martn Moreno, Francisco Guinea arXiv:1404.4035 http://arxiv.org/abs/1404.4035 Abstract: Black phosphorus exhibits a high degree of band anisotropy. However, we found that its in-plane static screening remains relatively isotropic for momenta relevant to elastic long-range scattering processes. On the other hand, the collective electronic excitations in the system exhibit a strong anisotropy. Band non-parabolicity leads to a plasmon frequency which scales as  $n^{\beta}$ , where n is the carrier concentration, and  $\beta < 12$ . Screening and charge distribution in the out-of-plane direction are also studied using a non-linear Thomas-Fermi model.

#### 37. Tunable optical properties of multilayers black phosphorus

Tony Low, A. S. Rodin, A. Carvalho, Yongjin Jiang, Han Wang, Fengnian Xia, A. H. Castro Neto arXiv:1404.4030 http://arxiv.org/abs/1404.4030 Abstract:

We calculated the optical conductivity tensor of multilayers black phosphorus using the Kubo formula within an effective low-energy Hamiltonian. The optical absorption spectra of multilayers black phosphorus are shown to vary sensitively with thickness, doping, and light polarization. In conjunction with experimental spectra obtained from infrared absorption spectroscopy, we discuss the role of interband coupling and disorder on the observed anisotropic absorption spectra. Multilayers black phosphorus might offer attractive alternatives to narrow gap compound semiconductors for optoelectronics across midto near-infrared frequencies.

#### 38. Quasiparticle band structure and tight-binding model for singleand bilayer black phosphorus

Alexander N. Rudenko, Mikhail I. Katsnelson arXiv:1404.0618 and Phys. Rev. B 89, 201408(R) http://arxiv.org/abs/1404.0618 Abstract:

By performing ab initio calculations for one- to four-layer black phosphorus within the GW approximation, we obtain a significant difference in the band gap ( $\sim 1.5 \text{ eV}$ ), which is in line with recent experimental data. The results are analyzed in terms of the constructed four-band tight-binding model, which gives accurate descriptions of the mono- and bilayer band structure near the band gap, and reveal an important role of the interlayer hoppings, which are largely responsible for the obtained gap difference.

#### 39. Young's Modulus of Single-Layer Black Phosphorus Jin-Wu Jiang, Harold S. Park arXiv:1404.0232 http://arxiv.org/abs/1404.0232

#### Abstract:

The mechanical properties of single-layer black phosphrous under uniaxial deformation are investigated using first-principles calculations. Both Young's modulus and the ultimate strain are found to be highly anisotropic and nonlinear as a result of its quasi-two-dimensional puckered structure. Specifically, the in-plane Young's modulus is 44.0 GPa in the direction perpendicular to the pucker, and 92.7 GPa in the parallel direction. The ultimate strain is 0.48 and 0.20 in the perpendicular and parallel directions, respectively.

#### 40. Negative Poisson's Ratio in Single-Layer Black Phosphorus

Jin-Wu Jiang, Harold S. Park arXiv:1403.4326 http://arxiv.org/abs/1403.4326 Abstract:

The Poisson's ratio is a fundamental mechanical property that relates the resulting lateral strain to applied axial strain. While this value can theoretically be negative, it is positive for nearly all materials, though negative values have been observed in so-called auxetic structures. However, nearly all auxetic materials are bulk materials whose microstructure has been specifically engineered to generate a negative Poisson's ratio. In the present work, we report using first principles calculations the existence of a negative Poisson's ratio in a singlelayer, two-dimensional material, black phosphorus. In contrast to engineered bulk auxetics, this behavior is intrinsic for single layer black phosphorus, and originates from its unique, puckered structure, where the pucker can be regarded as a re-entrant structure that is comprised of two coupled orthogonal hinges. As a result of this atomic structure, a negative Poisson's ratio is observed in the out-of-plane direction under uniaxial deformation in the direction parallel to the pucker, with the Poisson's ratio becoming increasingly negative with both increased tension and compression. The puckered structure also results in highly anisotropic in-plane Poisson's ratios, which are found to be 0.4in the direction perpendicular and 1.28 in the direction parallel to the pucker.

#### 41. Semiconducting layered blue phosphorus: A computational study Zhen Zhu, David Tománek

arXiv:1403.1300 and Phys. Rev. Lett. 112, 176802 (2014) http://arxiv.org/abs/1403.1300 Abstract:

We investigate a previously unknown phase of phosphorus that shares its layered structure and high stability with the black phosphorus allotrope. We find the in-plane hexagonal structure and bulk layer stacking of this structure, which we call 'blue phosphorus', to be related to graphite. Unlike graphite and black phosphorus, blue phosphorus displays a wide fundamental band gap and should exfoliate easily to form quasi-2D structures suitable for electronic applications. We study a likely transformation pathway from black to blue phosphorus and discuss possible ways to synthesize the new structure.

#### 42. Fast and broadband photoresponse of few-layer black phosphorus field-effect transistors

Michele Buscema, Dirk J. Groenendijk, Sofya I. Blanter, Gary A. Steele, Herre S.J. van der Zant, Andres Castellanos-Gomez arXiv:1403.0565 and Nano Letters 2014 14 (6), 3347-3352 http://arxiv.org/abs/1403.0565 Abstract:

Few-layer black phosphorus, a new elemental two-dimensional (2D) material recently isolated by mechanical exfoliation, is a high-mobility layered semiconductor with a direct bandgap that is predicted to strongly depend on the number of layers, from 0.35 eV (bulk) to 2.0 eV (single layer). Therefore, black phosphorus is an appealing candidate for tunable photodetection from the visible to the infrared part of the spectrum. We study the photoresponse of field-effect transistors (FETs) made of few-layer black phosphorus (38 nm thick), as a function of excitation wavelength, power, and frequency. In the dark state, the black phosphorus FETs can be tuned both in hole and electron doping regimes allowing for ambipolar operation. We measure mobilities in the order of 100  $\text{cm}^2/\text{V}$  s and a current ON/OFF ratio larger than 10<sup>3</sup>. Upon illumination, the black phosphorus transistors show a response to excitation wavelengths from the visible region up to 940 nm and a rise time of about 1 ms, demonstrating broadband and fast detection. The responsivity reaches 4.8 mA/W, and it could be drastically enhanced by engineering a detector based on a PN junction. The ambipolar behavior coupled to the fast and broadband photodetection make few-layer black phosphorus a promising 2D material for photodetection across the visible and near-infrared part of the electromagnetic spectrum.

#### 43. Isolation and characterization of few-layer black phosphorus

Andres Castellanos-Gomez, Leonardo Vicarelli, Elsa Prada, Joshua O. Island, K. L. Narasimha-Acharya, Sofya I. Blanter, Dirk J. Groenendijk, Michele Buscema, Gary A. Steele, J. V. Alvarez, Henny W. Zandbergen, J. J. Palacios, Herre S.J. van der Zant arXiv:1403.0499 http://arxiv.org/abs/1403.0499 Abstract:

Isolation and characterization of mechanically exfoliated black phosphorus flakes with a thickness down to two single-layers is presented. A modification of the mechanical exfoliation method, which provides higher yield of atomically thin flakes than conventional mechanical exfoliation, has been developed. We present general guidelines to determine the number of layers using optical microscopy, Raman spectroscopy and transmission electron microscopy in a fast and reliable way. Moreover, we demonstrate that the exfoliated flakes are highly crystalline and that they are stable even in free-standing form through Raman spectroscopy and transmission electron microscopy measurements. A strong thickness dependence of the band structure is found by density functional theory calculations. The exciton binding energy, within an effective mass approximation, is also calculated for different number of layers. Our computational results for the optical gap are consistent with preliminary photoluminescence results on thin flakes. Finally, we study the environmental stability of black phosphorus flakes finding that the flakes are very hydrophilic and that long term exposure to air moisture etches black phosphorus away. Nonetheless, we demonstrate that the aging of the flakes is slow enough to allow fabrication of field-effect transistors with strong ambipolar behavior. Density functional theory calculations also give us insight into the water-induced changes of the structural and electronic properties of black phosphorus.

#### 44. Electric field effect in ultrathin black phosphorus

Steven P. Koenig, Rostislav A. Doganov, Hennrik Schmidt, A. H. Castro Neto, Barbaros Oezyilmaz arXiv:1402.5718 and Appl. Phys. Lett. 104, 103106 (2014) http://arxiv.org/abs/1402.5718 Abstract:

Black phosphorus exhibits a layered structure similar to graphene, allowing mechanical exfoliation of ultrathin single crystals. Here, we demonstrate fewlayer black phosphorus field effect devices on Si/SiO<sub>2</sub> and measure charge carrier mobility in a four-probe configuration as well as drain current modulation in a two-point configuration. We find room-temperature mobilities of up to 300 cm<sup>2</sup>/Vs and drain current modulation of over  $10^3$ . At low temperatures, the onoff ratio exceeds  $10^5$ , and the device exhibits both electron and hole conduction. Using atomic force microscopy, we observe significant surface roughening of thin black phosphorus crystals over the course of 1 h after exfoliation.

#### 45. Rediscovering Black Phosphorus: A Unique Anisotropic 2D Material for Optoelectronics and Electronics

Fengnian Xia, Han Wang, Yichen Jia arXiv:1402.0270 and Nature Communications 5, 4458 (2014) http://arxiv.org/abs/1402.0270 Abstract: Anisotropy refers to the property of a material exhibiting directionally dependent features. In this paper, we introduce black phosphorous (BP), the most stable allotrope of phosphorus in layered orthorhombic structure with a bandgap of 0.3 eV in bulk, as a unique 2D material in which electrons, phonons and their interactions with photons behave in a highly anisotropic manner within the plane of the layers. The unique anisotropic nature of BP thin films is revealed using angle-resolved Raman and infrared spectroscopies, together with angle-resolved transport study. For 15 nm thick BP, we measure Hall mobility of 1000 and 600  $\text{cm}^2/\text{Vs}$  for holes along the light (x) and heavy (y) effective mass directions, respectively, at 120 K. These BP thin films also exhibit large and anisotropic in-plane optical conductivity from 2 to 5 micrometer wavelength. Field effect transistors using 4 to 30 layers of BP (2 to 15 nm) as channel material exhibit an on-off current ratio exceeding  $10^5$ , a field-effect mobility of 205 cm<sup>2</sup>/Vs, and good saturation properties all at room temperature, suggesting its promising future in high performance thin film electronics. By introducing narrow bandgap BP into the 2D material family, we fill the space between semi-metallic graphene and large bandgap TMDCs, where great potentials for infrared optoelectronics lie. Most importantly, the unique anisotropic nature of this intriguing material creates unprecedented possibilities for the realization of conceptually new optoelectronic and electronic devices in which angle-dependent physical properties are highly desirable.

#### 46. High-mobility transport anisotropy and linear dichroism in fewlayer black phosphorus

Jingsi Qiao, Xianghua Kong, Zhi-Xin Hu, Feng Yang, Wei Ji arXiv:1401.5045 and Nature Communications 5, 4475 (2014) http://arxiv.org/abs/1401.5045 Abstract:

Two-dimensional crystals are emerging materials for nanoelectronics. Development of the field requires candidate systems with both a high carrier mobility and, in contrast to graphene, a sufficiently large electronic bandgap. Here we present a detailed theoretical investigation of the atomic and electronic structure of few-layer black phosphorus (BP) in order to predict its electrical and optical properties. This system has a direct bandgap, tunable from 1.51 eV for a monolayer to 0.59 eV for a 5-layer sample. We predict that the mobilities are hole-dominated, rather high and highly anisotropic. The monolayer is exceptional in having an extremely high hole-mobility (of order 10000 cm<sup>2</sup> V1s1) and anomalous elastic properties which reverse the anisotropy. Light absorption spectra indicate linear dichroism between perpendicular in-plane directions, which allows optical determination of the crystalline orientation and optical activation of the anisotropic transport properties. These results make few-layer BP a promising candidate for future electronics.

#### 47. Black phosphorus field-effect transistors

Likai Li, Yijun Yu, Guo Jun Ye, Qingqin Ge, Xuedong Ou, Hua Wu, Donglai Feng, Xian Hui Chen, Yuanbo Zhang arXiv:1401.4117 and Nature Nanotechnology 9, 372–377 (2014) http://arxiv.org/abs/1401.4117 Abstract:

Two-dimensional crystals have emerged as a class of materials that may impact future electronic technologies. Experimentally identifying and characterizing new functional two-dimensional materials is challenging, but also potentially rewarding. Here, we fabricate field-effect transistors based on few-layer black phosphorus crystals with thickness down to a few nanometres. Reliable transistor performance is achieved at room temperature in samples thinner than 7.5 nm, with drain current modulation on the order of  $10^5$  and well-developed current saturation in the IV characteristics. The charge-carrier mobility is found to be thickness-dependent, with the highest values up to ~1,000 cm<sup>2</sup> V<sup>1</sup> s<sup>1</sup> obtained for a thickness of ~10 nm. Our results demonstrate the potential of black phosphorus thin crystals as a new two-dimensional material for applications in nanoelectronic devices.

#### 48. Strain-induced gap modification in black phosphorus

A. S. Rodin, A. Carvalho, A. H. Castro Neto arXiv:1401.1801 and Phys. Rev. Lett. 112, 176801 (2014) http://arxiv.org/abs/1401.1801 Abstract:

The band structure of single-layer black phosphorus and the effect of strain are predicted using density functional theory and tight-binding models. Having determined the localized orbital composition of the individual bands from first-principles, we use the system symmetry to write down the effective low-energy Hamiltonian at the  $\Gamma$  point. From numerical calculations and arguments based on the crystal structure of the material, we show that the deformation in the direction normal to the plane can be use to change the gap size and induce a semiconductor-metal transition.

#### 49. Effect of van der Waals interactions on the structural and elastic properties of black phosphorus

S. Appalakondaiah, G. Vaitheeswaran, S. Lebegue, N. E. Christensen, A. Svane

arXiv:1211.3512 and Physical Review B 86, 035105 (2012)

http://arxiv.org/abs/1211.3512 Abstract:

The structural and elastic properties of orthorhombic black phosphorus have been investigated using first-principles calculations based on density functional theory. The structural parameters have been calculated using the local density approximation (LDA), the generalized gradient approximation (GGA), and with several dispersion corrections to include van der Waals interactions. It is found that the dispersion corrections improve the lattice parameters over LDA and GGA in comparison with experimental results. The calculations reproduce well the experimental trends under pressure and show that van der Waals interactions are most important for the crystallographic b axis in the sense that they have the largest effect on the bonding between the phosphorus layers. The elastic constants are calculated and are found to be in good agreement with experimental values. The calculated  $C_{22}$  elastic constant is significantly larger than the  $C_{11}$  and  $C_{33}$  parameters, implying that black phosphorus is stiffer against strain along the a axis than along the b and c axes. From the calculated elastic constants, the mechanical properties, such as bulk modulus, shear modulus, Young's modulus, and Poisson's ratio are obtained. The calculated Raman active optical phonon frequencies and their pressure variations are in excellent agreement with available experimental results.

#### 50. Effect of van der Waals interaction on the structural and cohesive properties of black phosphorus

Hanchul Kim

Journal of The Korean Physical Society 64, 4, 547-553 (2014) http://dx.doi.org/10.3938/jkps.64.547 *Abstract:* 

We investigated the structural and the binding properties of black phosphorus (black-P) by employing density functional theory (DFT) calculations in combination with various implementations of the van der Waals (vdW) interaction. Both the binding energy curve of the two isolated puckered layers and the equation of states of the bulk black-P suggest that the conventional generalized gradient approximation (GGA) functional is incapable of describing the interlayer vdW interaction. From the comparison of the seven different vdW implementations, the appropriate vdW schemes in describing layer-structured black-P are found to be either the Grimmes dispersion correction (DFT-D2) or the optB86b vdW denisty-functional approach.

51. Polarization- and Gate-Dependent Scanning Photocurrent Measurements of Black Phosphorus Field-Effect Transistors

Tu Hong, Bhim Chamlagain, Hsuen-Jen Chuang, Minghu Pan, Zhixian

Zhou, and Ya-Qiong Xu Nanoscale, 2014,6, 8978-8983 http://dx.doi.org/10.1039/C4NR02164A Abstract:

We investigate electrical transport and optoelectronic properties of field effect transistors (FETs) made from few-layer black phosphorus (BP) crystals down to a few nanometers. In particular, we explore the anisotropic nature and photocurrent generation mechanisms in BP FETs through spatial-, polarization-, gate-, and bias-dependent photocurrent measurements. Our results reveal that the photocurrent signals at BP-electrode junctions are mainly attributed to the photovoltaic effect in the off-state and photothermoelectric effect in the on-state, and their anisotropic feature primarily results from the directionaldependent absorption of BP crystals.

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