ECE 538: 2D Material Electronics and Photonics

Chapter 3: Black phosphorus

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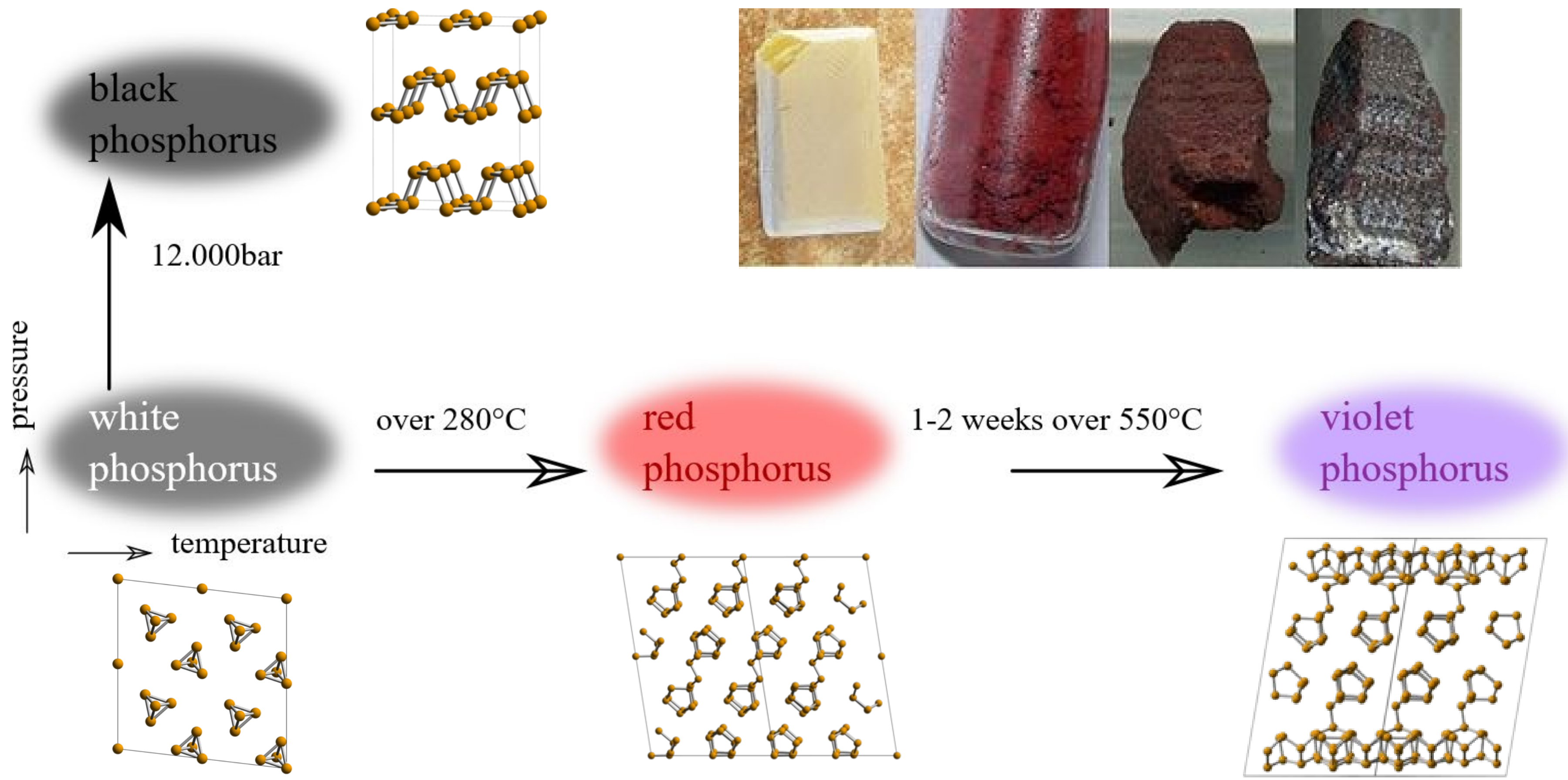
Outline

- **Introduction of black phosphorus**
- **Synthesis of black phosphorus**
- **Thermal stability of black phosphorus**
- **Electronic properties and electronic devices**
- **Optical properties and photonic devices**

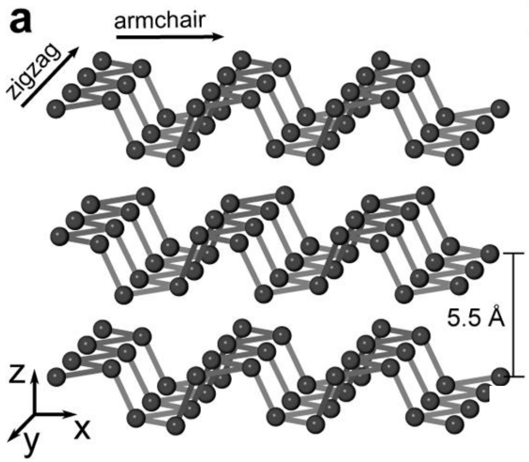
Allotrope of phosphorus



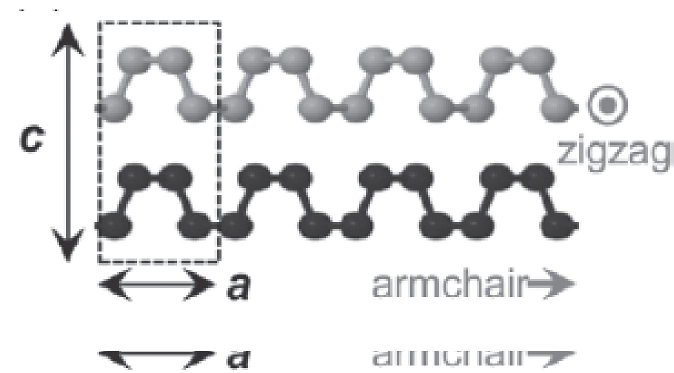
- **Elemental phosphorus can exist in several allotropes, the most common of which are white, red, violet and black allotropes.**

Crystal structure and Brillouin zone of BP

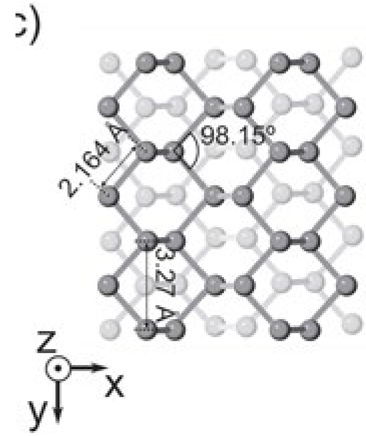
Perspective view



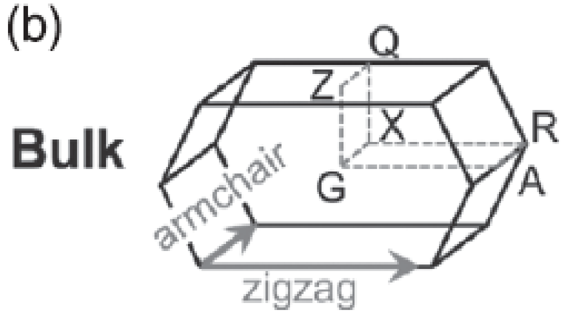
Side view

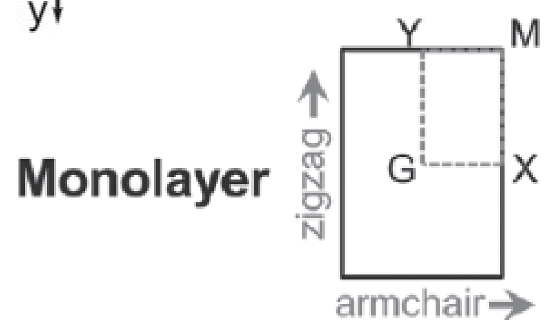


Top view



First Brillouin zone

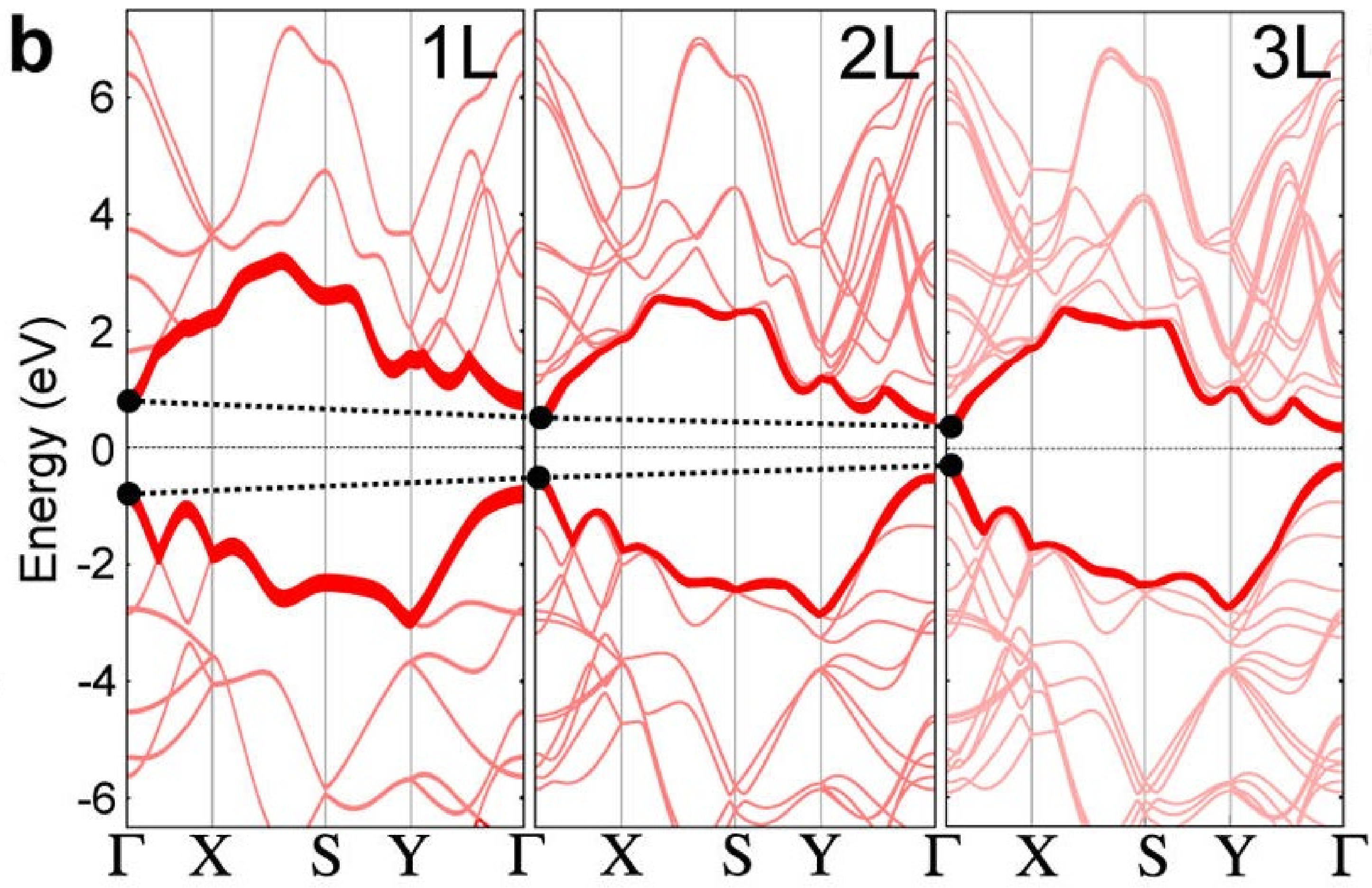


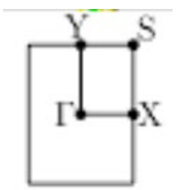


- **The atomic rings in BP layers exhibit a puckered structure, resulting in the opening of a bandgap and yielding strongly anisotropic in-plane properties.**
- **Bulk and monolayer BP have a base-centered orthorhombic and simple orthorhombic crystal structure**

Ph. Avouris, et al., “2D Materials : Properties and Devices”, Chapter 21, Cambridge University Press, 2017

Band structure of BP

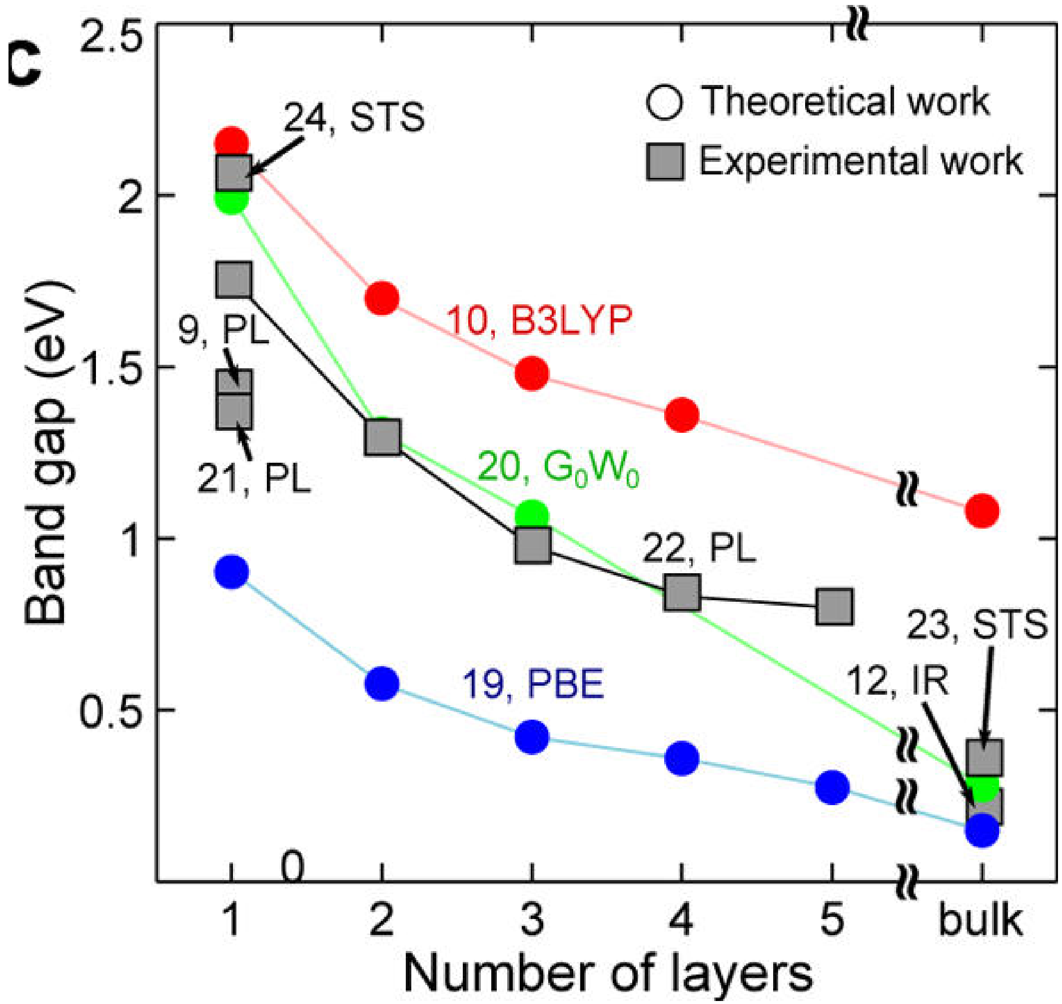




- **The band structure for any number of BP layers exhibits a direct gap around the Γ point of the first Brillouin zone.**

J.O. Island, Semiconductors and Semimetals, 95, 2016, 279-303

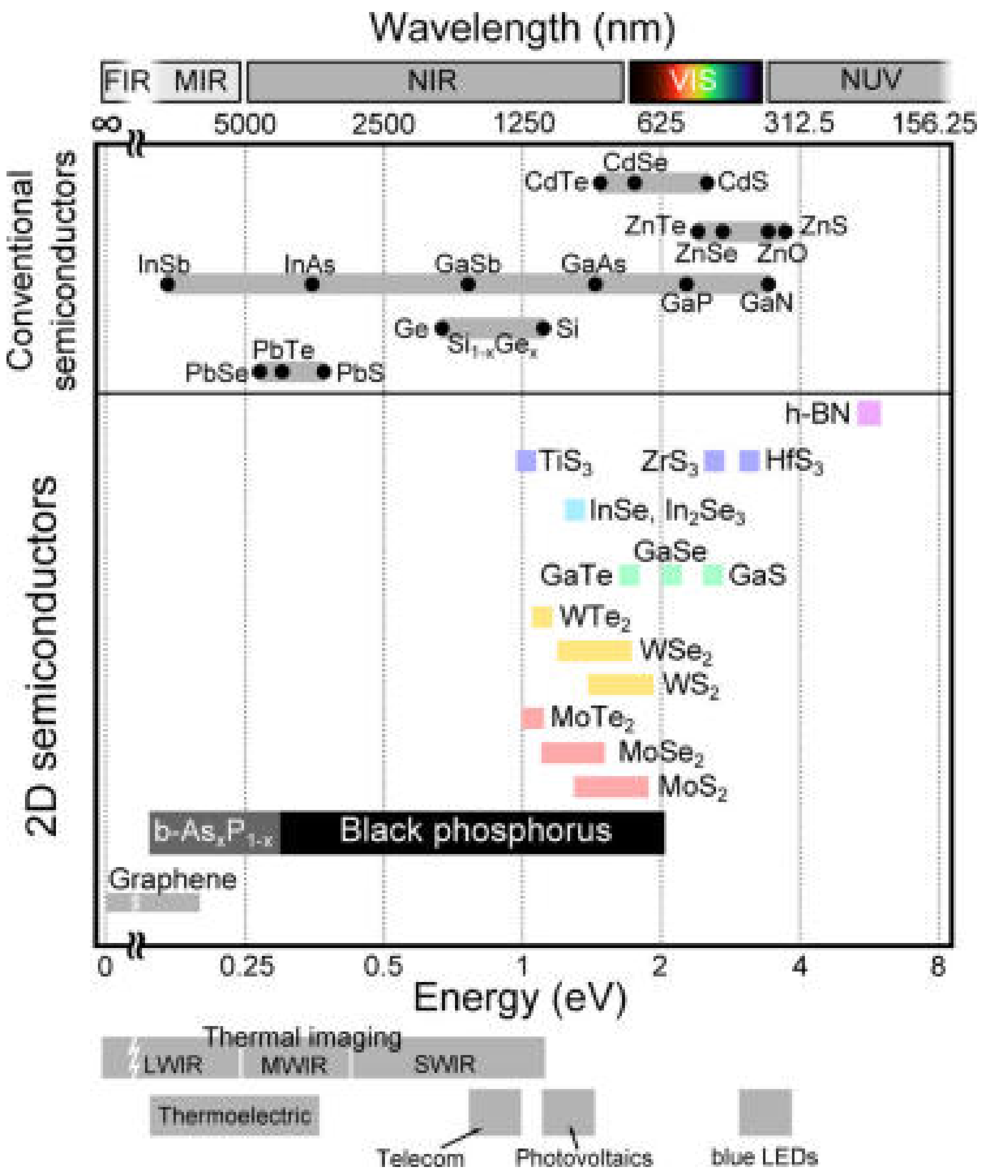
Thickness dependence of the band gap



- **The band gap of BP decreases with the number of layers.**

Andres Castellanos-Gomez, J. Phys. Chem. Lett. 6, 4280, 2015

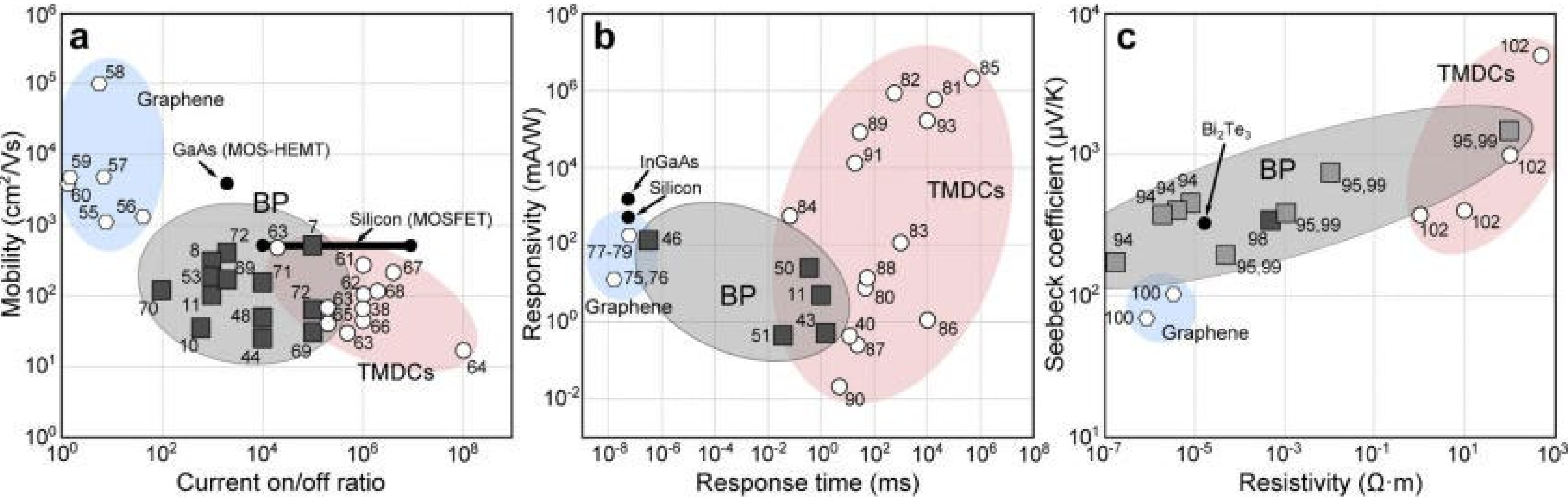
Band gap of BP



- **Black phosphorus bridges the gap between graphene and transition metal dichalcogenides**

Andres Castellanos-Gomez, J. Phys. Chem. Lett. 6, 4280,2015

Overview of BP devices



- The performance of black phosphorus FETs, photodetectors and thermoelectric devices also bridges the gap between graphene and transition metal dichalcogenides.

Andres Castellanos-Gomez, J. Phys. Chem. Lett. 6, 4280,2015

Stacking of BP layers

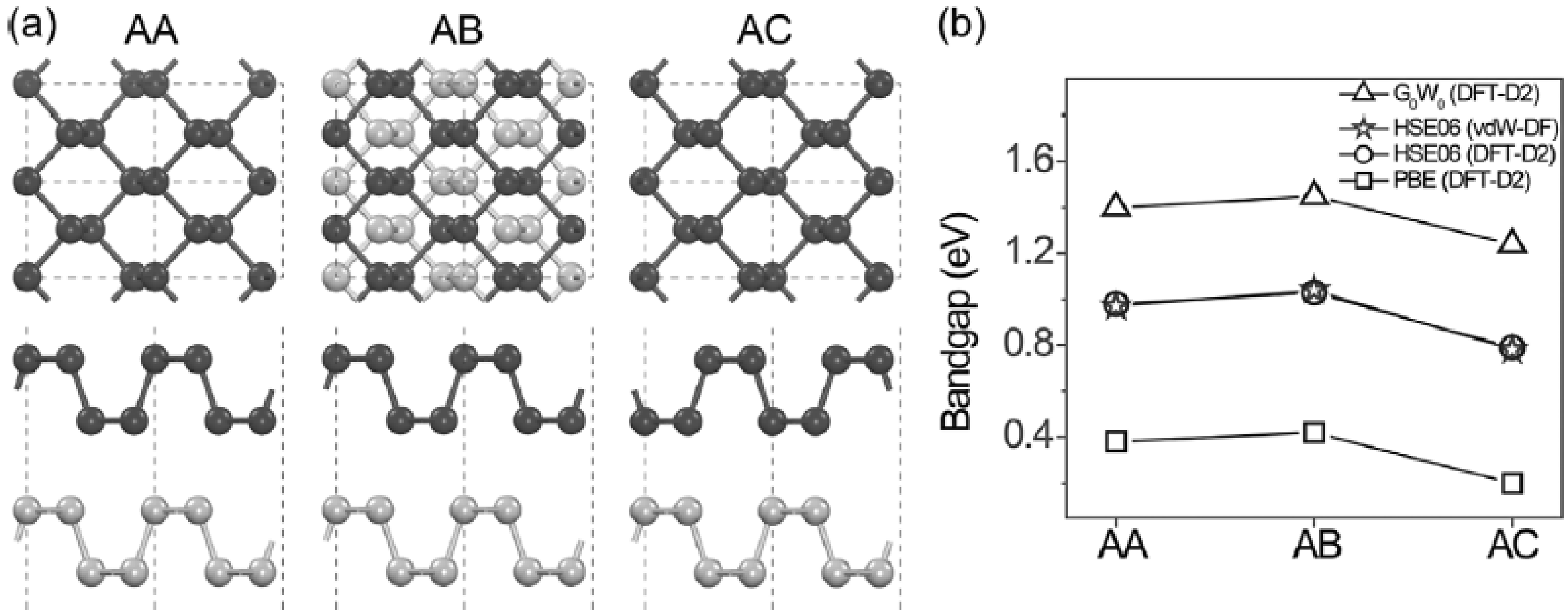


Fig. 21.7 Atomic configuration and predicted band gap of three stacking orders for bilayer BP. (a) Top and side views of the AA-, AB-, and AC-stacked bilayer BP. (b) Band gaps of different stacking orders calculated with the PBE [21] and HSE06 functionals [21, 27], as well as with GW approximation [21].

- **There are at least three types of stacking orders, namely AA, AB, and AC. The AB-stacked BP has the lowest energy among the three.**

Ph. Avouris, et al., “2D Materials : Properties and Devices”, Chapter 21, Cambridge University Press, 2017

Anisotropic effective mass and mobility

Table 2 | Predicted carrier mobility.

Carrier type	N_L	m_x^*/m_0 G-X	m_y^*/m_0 G-Y	μ_{x_2D}	μ_{y_2D}
				(10^3 cm^2 V^{-1} s^{-1})	
e	1	0.17	1.12	1.10–1.14	~0.08
	2	0.18	1.13	~0.60	0.14–0.16
	3	0.16	1.15	0.76–0.80	0.20–0.22
	4	0.16	1.16	0.96–1.08	0.26–0.30
	5	0.15	1.18	1.36–1.58	0.36–0.40
h	1	0.15	6.35	0.64–0.70	10–26
	2	0.15	1.81	2.6–2.8	1.3–2.2
	3	0.15	1.12	4.4–5.2	2.2–3.2
	4	0.14	0.97	4.4–5.2	2.6–3.2
	5	0.14	0.89	4.8–6.4	3.0–4.6

- **Both hole and electron effective masses along the Γ-X direction in the k space (associated to the armchair or x direction in real-space) are roughly ten times smaller than those along the Γ-Y direction (i.e. zigzag or y direction in real space).**
- **As a result, the carrier mobility along the armchair direction is higher than that along zigzag direction.**

J. Qiao, et al. Nature Communications, 5, 4475 (2014).

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- Optical properties and photonic devices

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  - High pressure synthesis
  - Catalyst-based synthesis
  - PLD
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Discovery of BP

TWO NEW MODIFICATIONS OF PHOSPHORUS.

By P. W. Bridgman.

Received May 4, 1914.

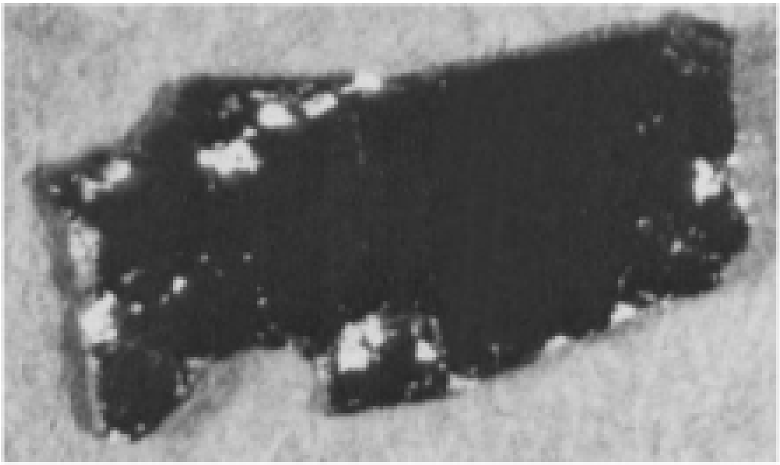
Black Phosphorus.

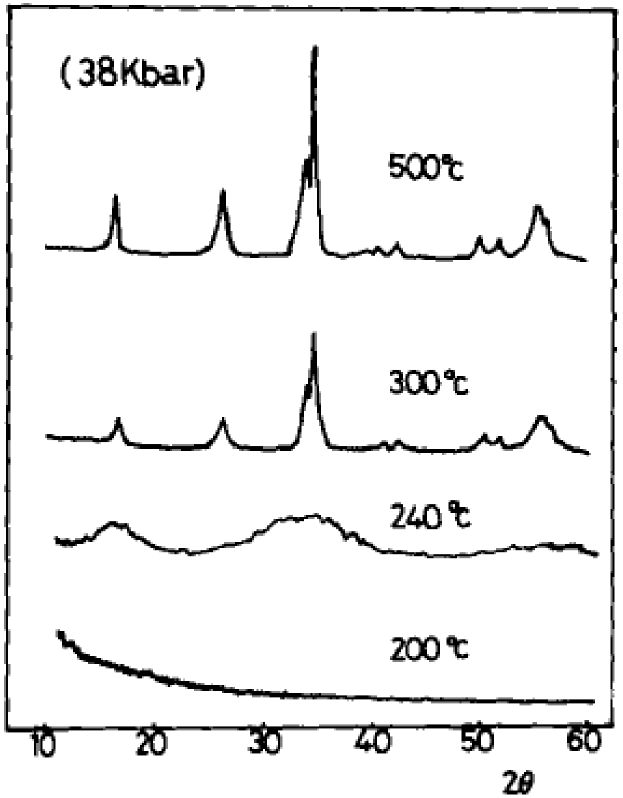
Black phosphorus was discovered during an attempt to force ordinary white phosphorus to change into red phosphorus by the application of high hydrostatic pressure, at a temperature below that at which the the transformation runs with appreciable velocity at atmospheric pressure.

- **Bridgman first reported that white phosphorus can be converted into BP under hydrostatic pressure of 1.2 GPa at 200 ºC within 5 to 30 minutes. With a further step of high pressure at 3.4 GPa, BP can also be prepared at room temperature from white phosphorus.**

P. W. Bridgman, J. Am. Chem. Soc., 36, 1344, 1914

Synthesis of single crystal BP



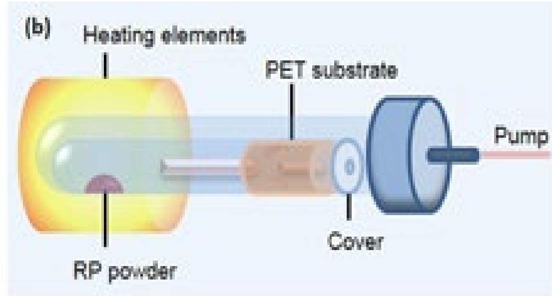


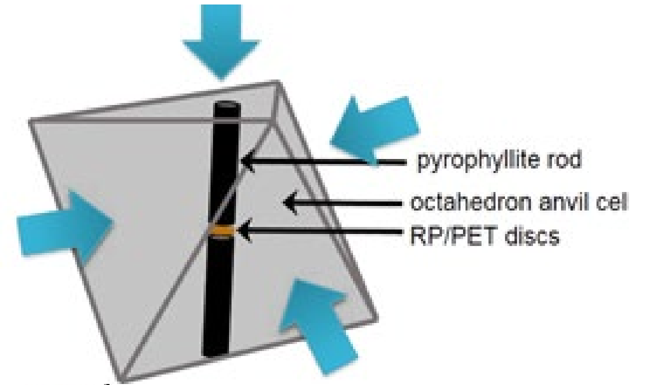
3.8GPa

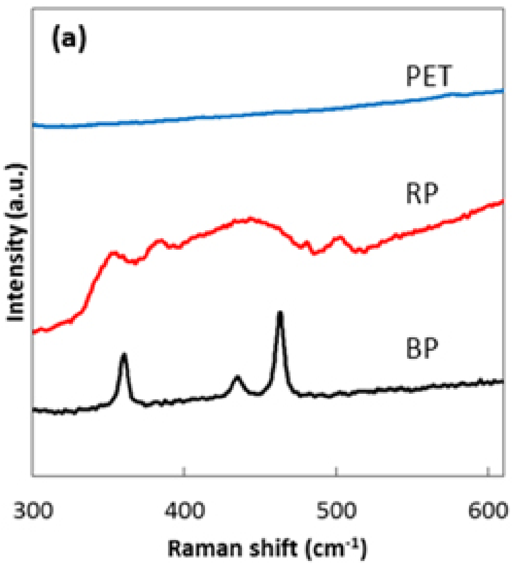
- Large single crystals of BP were successfully synthesized from red phosphorus melted at high temperatures under high pressure using a wedge-type cubic high-pressure apparatus.
- Samples grown under 3.8 GPa at temperature higher than 270 ºC were crystalized into a single crystal.

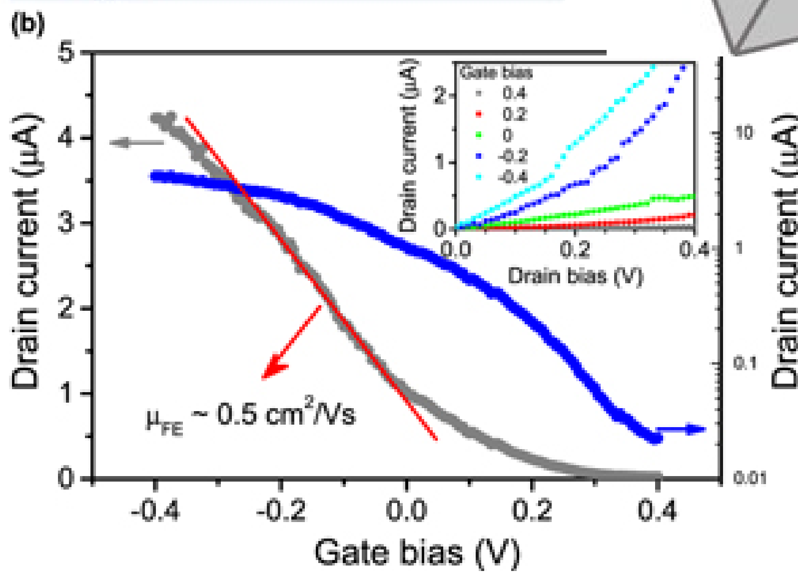
I. Shirotani, Molecular Crystals and Liquid Crystals, 86, 203,1982

Synthesis of BP on flexible substrates









- Red phosphorus thin-film was deposited on a flexible polyester substrate, followed by its conversion to BP in a high-pressure multi-anvil cell at room temperature. Raman spectroscopy confirm the formation of a nano-crystalline BP thin-film. Thin-film BP transistors exhibit a field-effect mobility of around 0.5 cm^2/V-s.

Xuesong Li, Fengnian Xia. 2D Material, 2 031002, 2015

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  - **Catalyst-based CVT synthesis**
  - **PLD synthesis**
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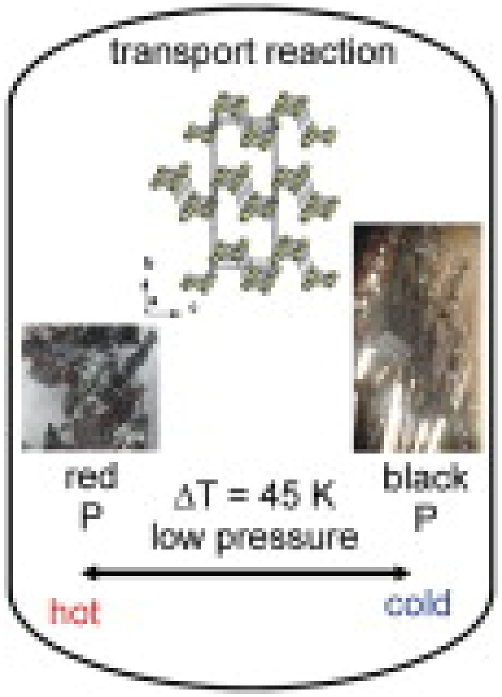
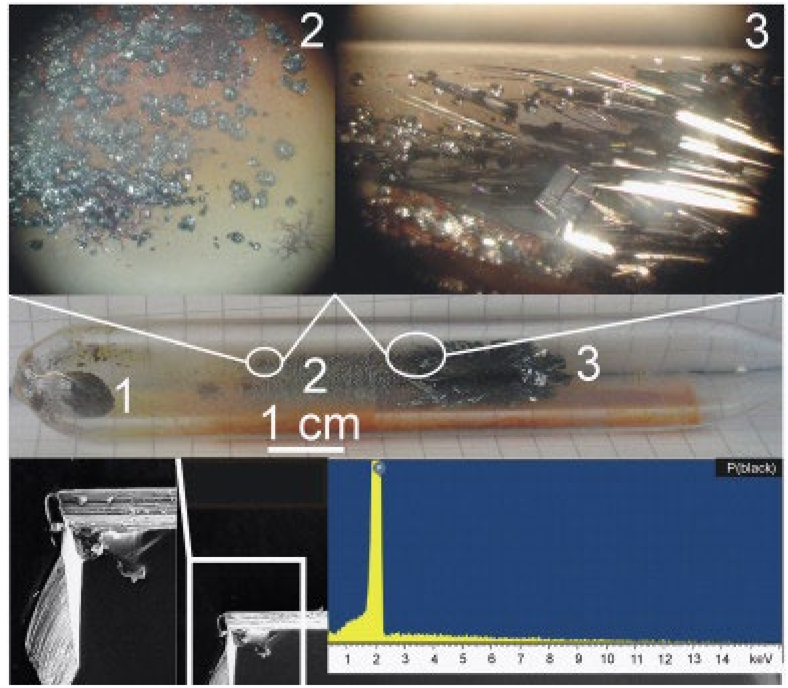
Catalyst-based synthesis of BP





- **A low-pressure method to produce high-quality BP using a mineralizer as a reaction promoter under non-toxic conditions. BP was prepared by the reaction of AuSn, red phosphorus, and SnI_4 in evacuated silica ampoules. The starting materials were heated to 823, 873, or 923 K and kept at this temperature for 5–10 days.**

Tom Nilges, Thorben Pfeifer, Journal of Solid State Chemistry, 181, 1707, 2008

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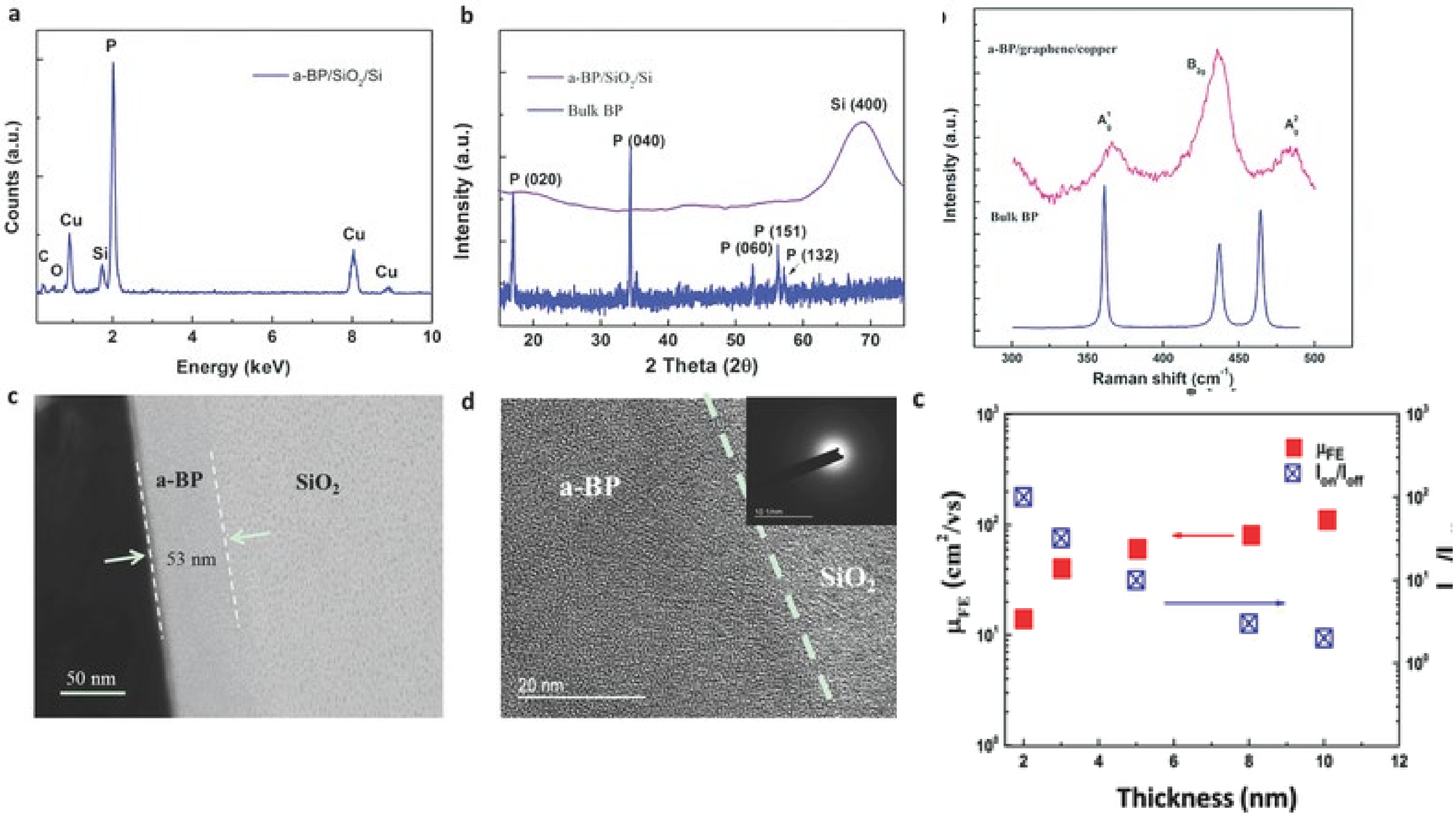
Synthesis of BP by PLD



- **Amorphous black phosphorus (a-BP) ultrathin films are deposited by pulsed laser deposition (PLD). Amorphous BP field-effect transistors exhibit high carrier mobility.**

Zhibin Yang, Shu Ping Lau, Advanced Materials, 27, 3748, 2015

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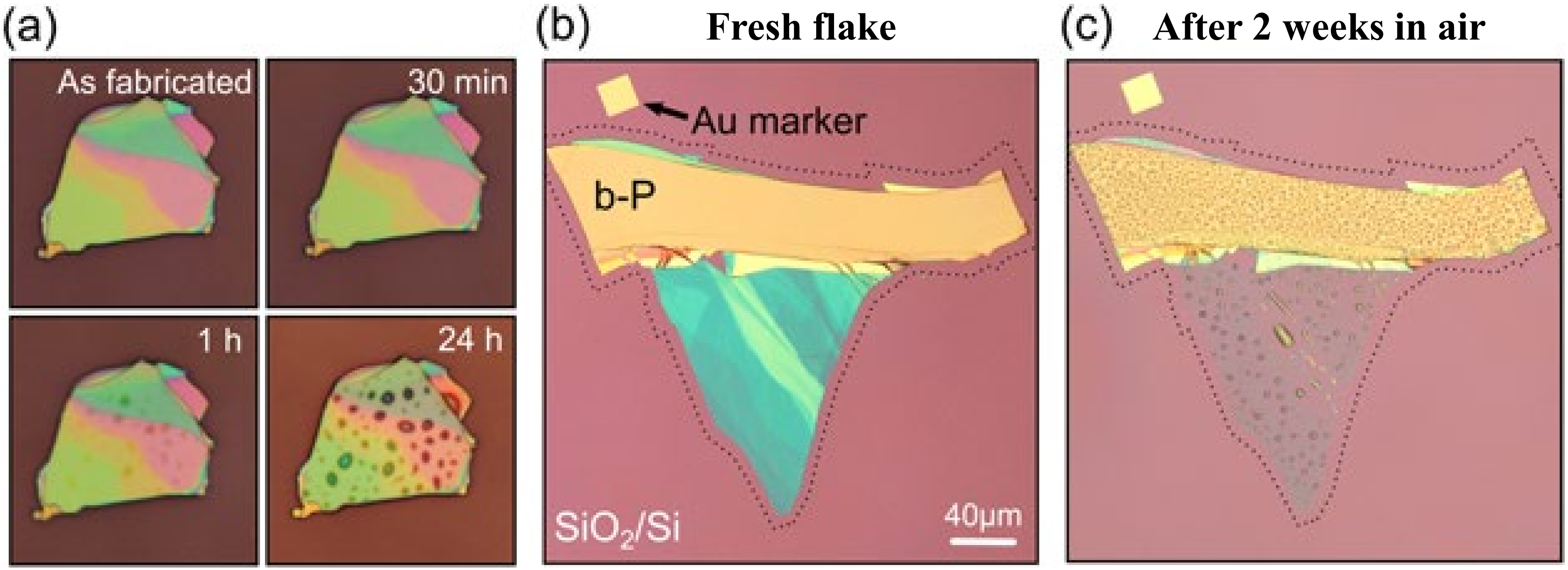
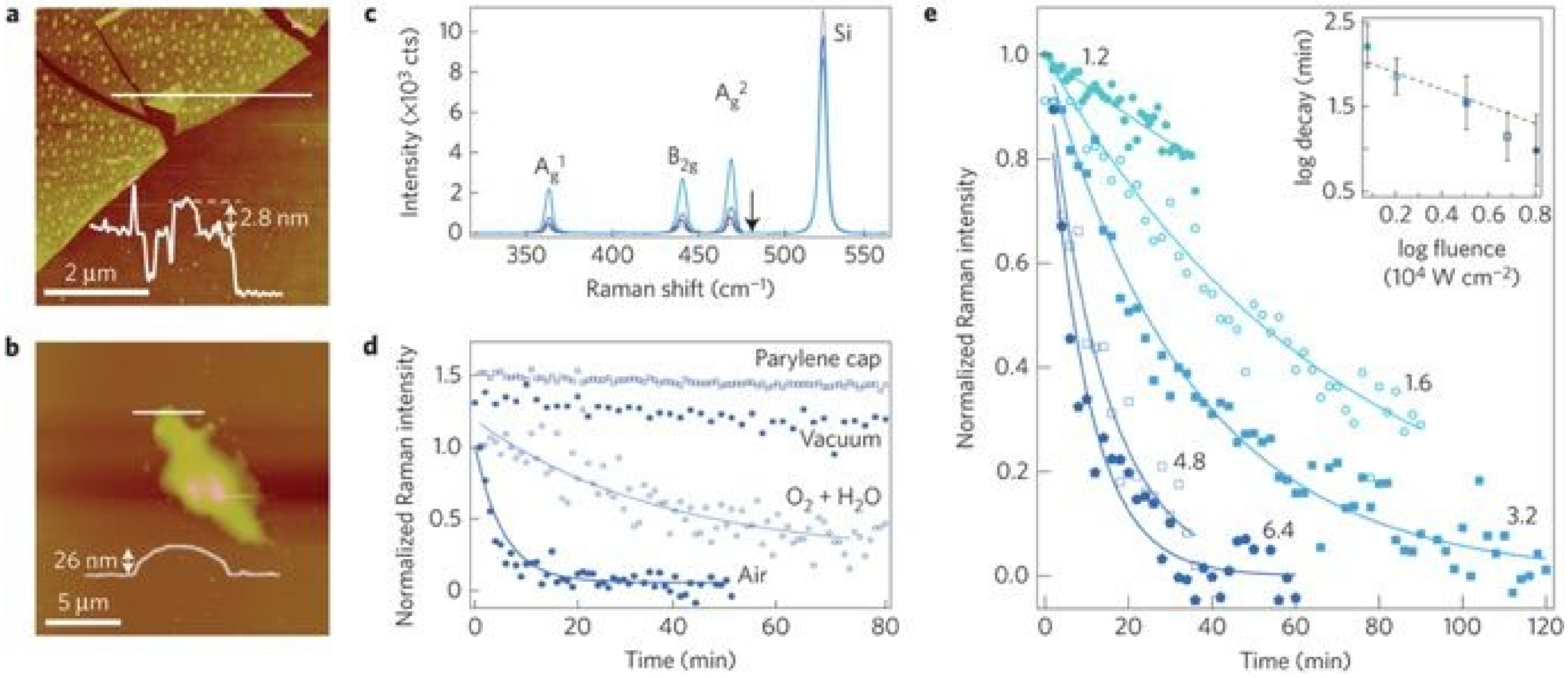
Aging of black phosphorus flakes



- After storing in air, droplets become visible on the surface of BP due to moisture adsorption. After storing the sample in a vacuum chamber for a few hours these droplets disappear.
- A long exposure to air (more than one week) deteriorates the black phosphorus etching away the thinner parts of the flakes.

Andres Castellanos-Gomez, J V Alvarez, 2D Materials, 1, 025001, 2014

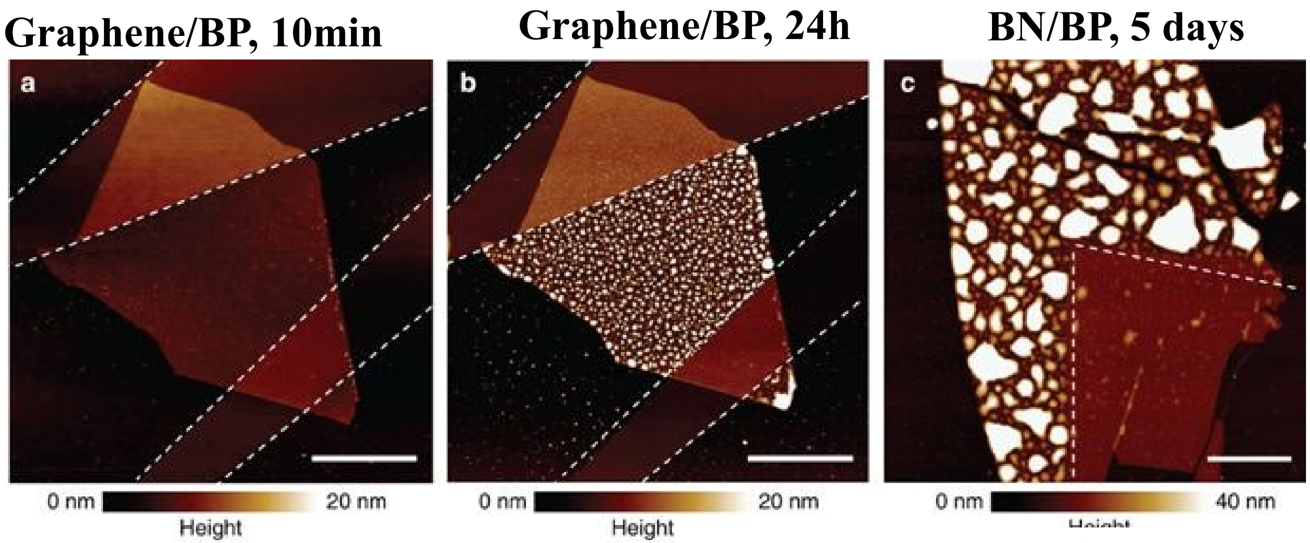
Photo-oxidation of BP

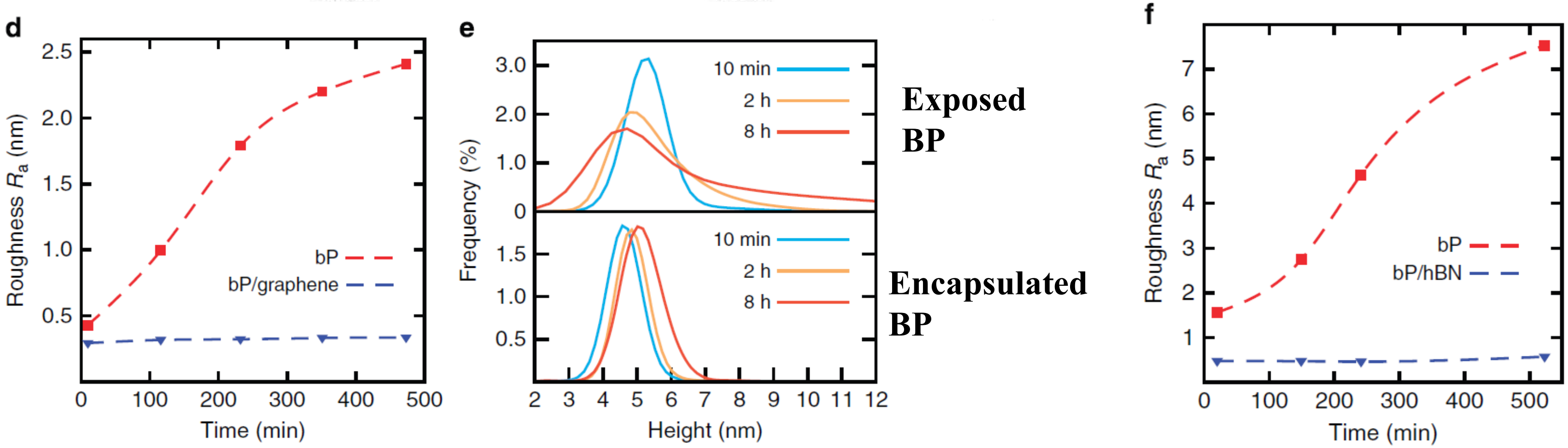


- **In situ Raman and transmission electron spectroscopies show that BP degradation is a thickness-dependent photoassisted oxidation reaction with oxygen dissolved in adsorbed water.**
- **Three major environmental parameters are simultaneously required for degradation: water, oxygen and visible light.**

Alexandre Favron, Richard Martel, Nature Materials, 14, 826, 2015

Passivation of BP using graphene or BN

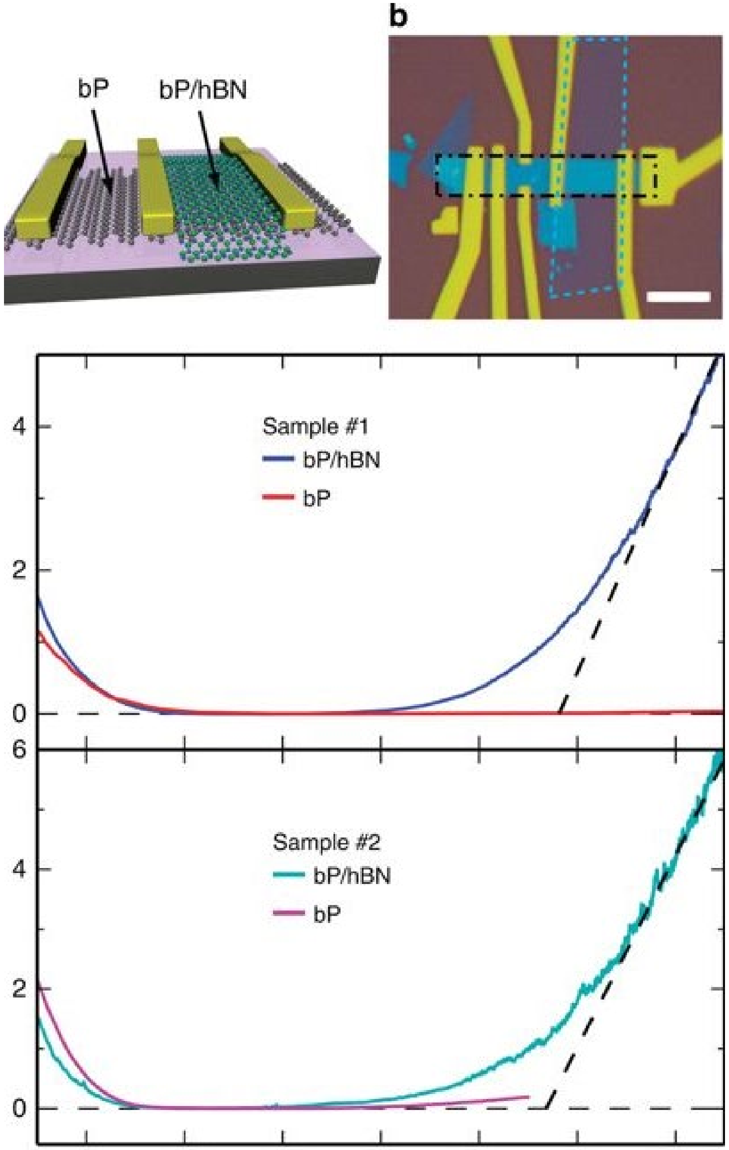




- **Atomically thin graphene and hexagonal boron nitride can be used for passivation of ultrathin black phosphorus.**

Rostislav A. Doganov, Barbaros Özyilmaz, Nature Communications, 6, 6647, 2015

Passivation of BP on current transport



- **Few-layer pristine black phosphorus channels passivated in an inert gas environment, without any prior exposure to air, exhibit greatly improved n-type charge transport resulting in symmetric electron and hole transconductance characteristics.**

Rostislav A. Doganov, Barbaros Özyilmaz, Nature Communications, 6, 6647, 2015

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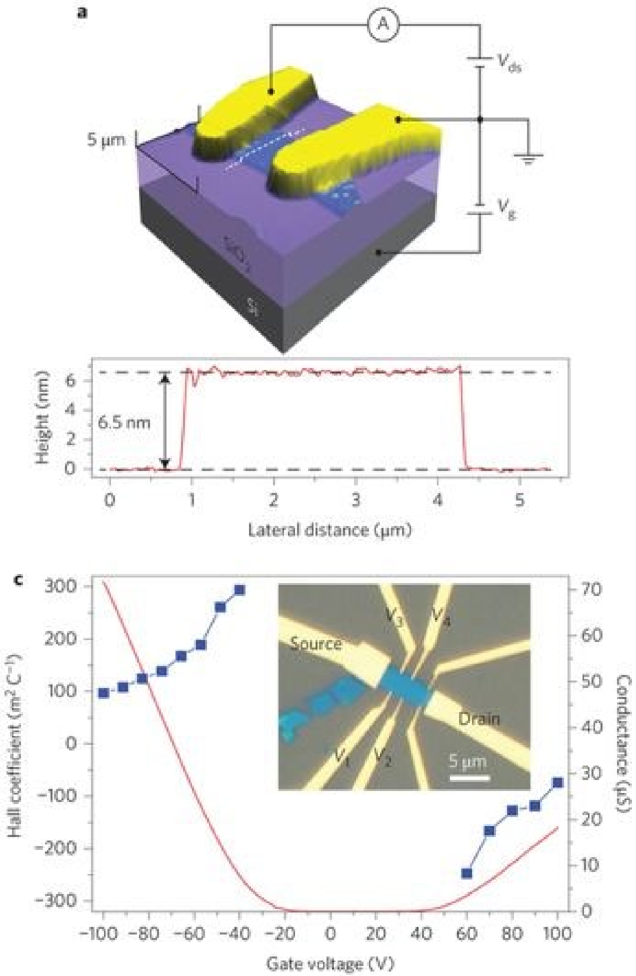
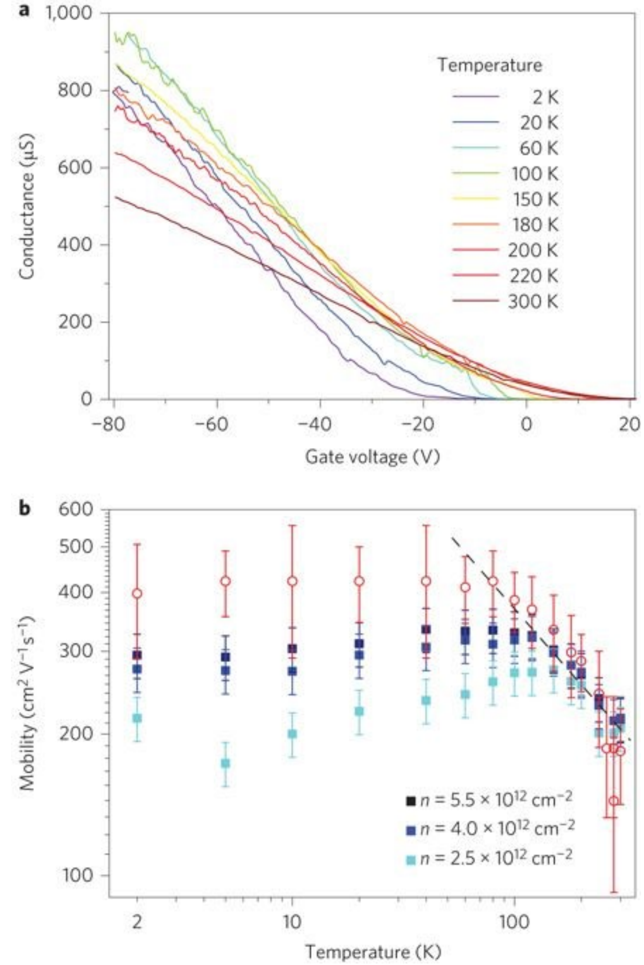
BP transistor

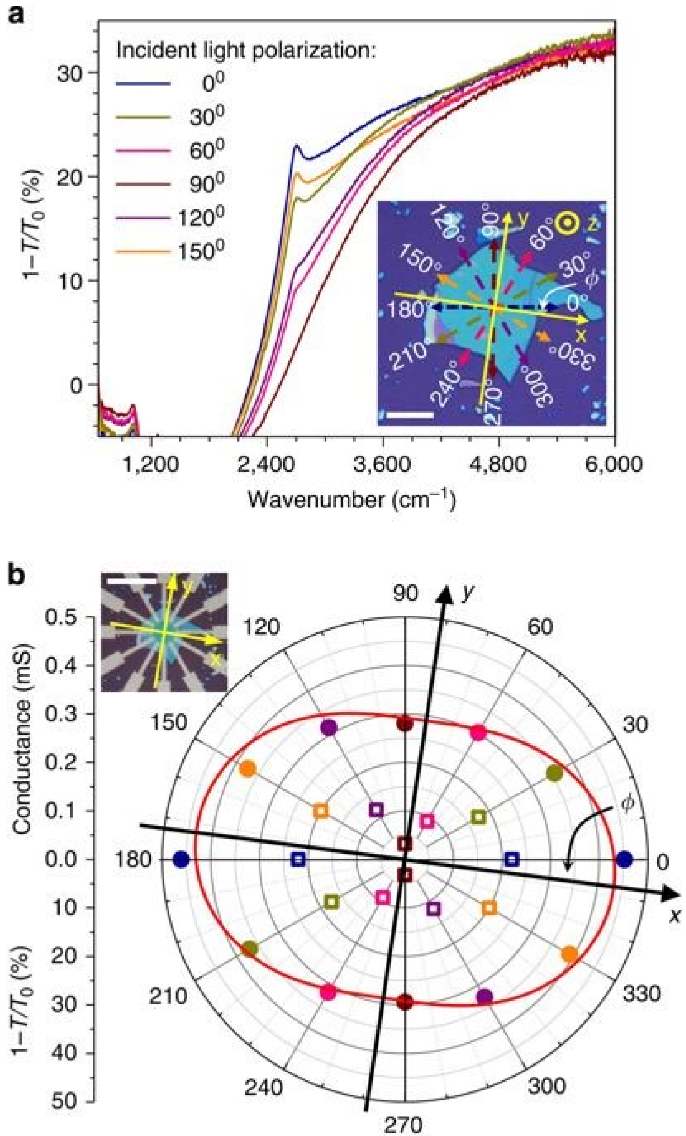


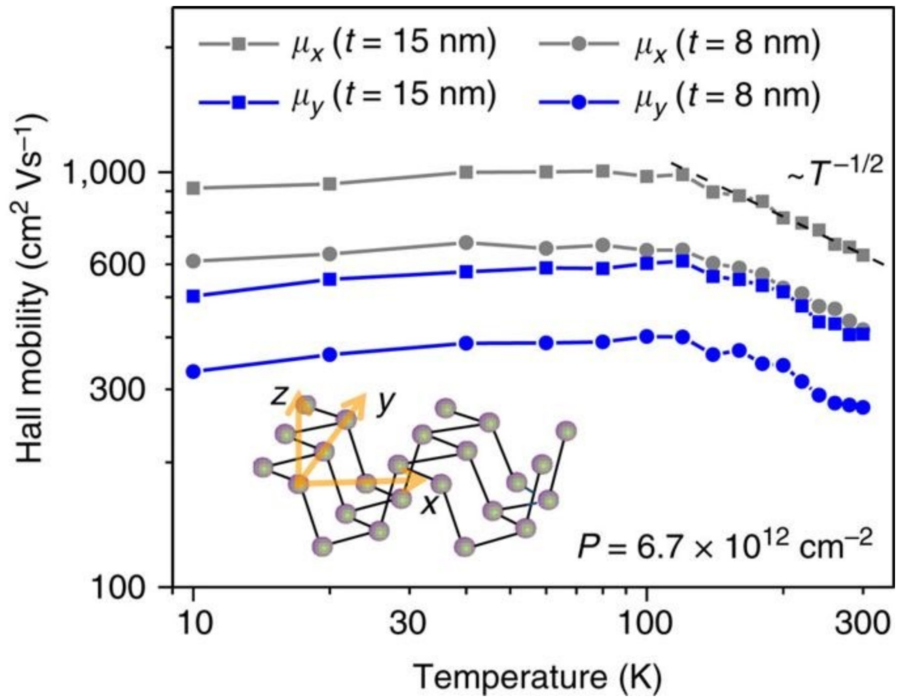


- **The charge-carrier mobility is found to be thickness-dependent, with the highest values up to ~1,000 cm^2 V^{-1} s^{-1}obtained for a thickness of ~10 nm.**

Likai Li, Yuanbo Zhang, Nature Nanotechnology, 9, 372, 2014

Anisotropic carrier mobility

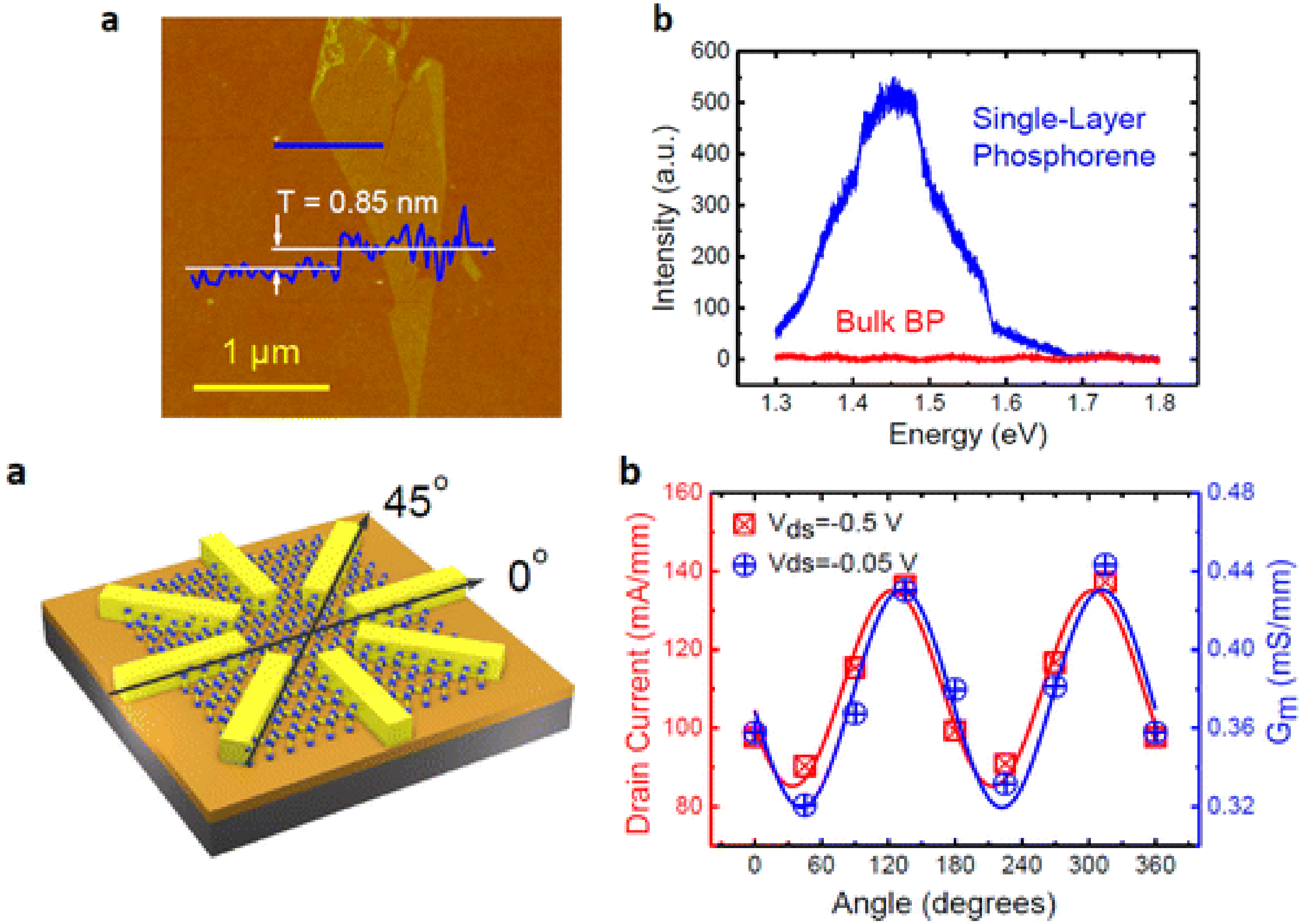




- **For 15-nm-thick BP, we measure a Hall mobility of 1,000 and 600 cm²/V-s for holes along the light (x) and heavy (y) effective mass directions at 120 K. BP thin films also exhibit large and anisotropic in-plane optical conductivity.**

Fengnian Xia, Yichen Jia, Nature Communications, 5, 4458, 2014

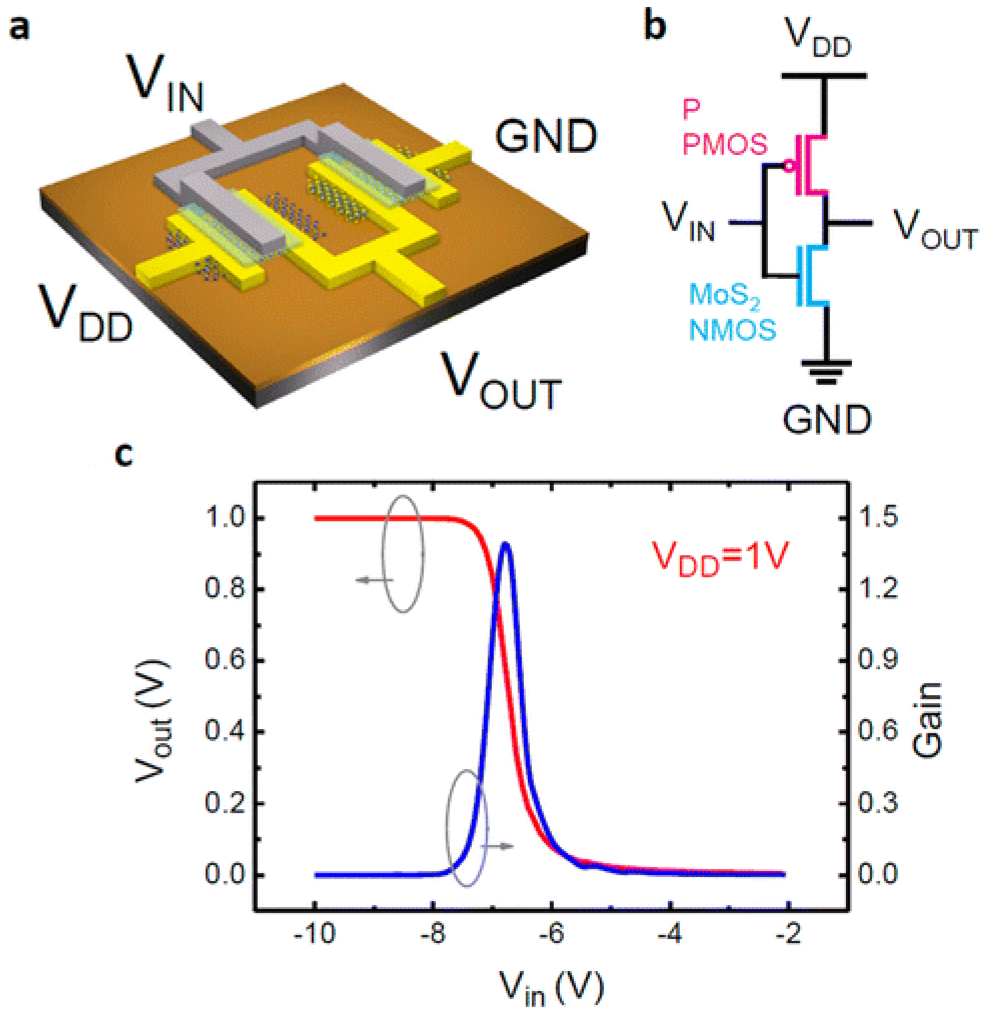
Anisotropy of electric conductance



- **Single layer BP was obtained by exfoliation.**
- **experimental results demonstrate the angle-dependent transport behavior of BP. The anisotropic behavior of the maximum drain current is roughly sinusoidal.**

Han Liu, Peide Ye, ACS Nano, 8, 4033, 2014

Inverter based on BP



- **An invertor based on integration of phosphorene PMOS and MoS_2 NMOS transistors is demonstrated.**

Han Liu, Peide Ye, ACS Nano, 8, 4033, 2014

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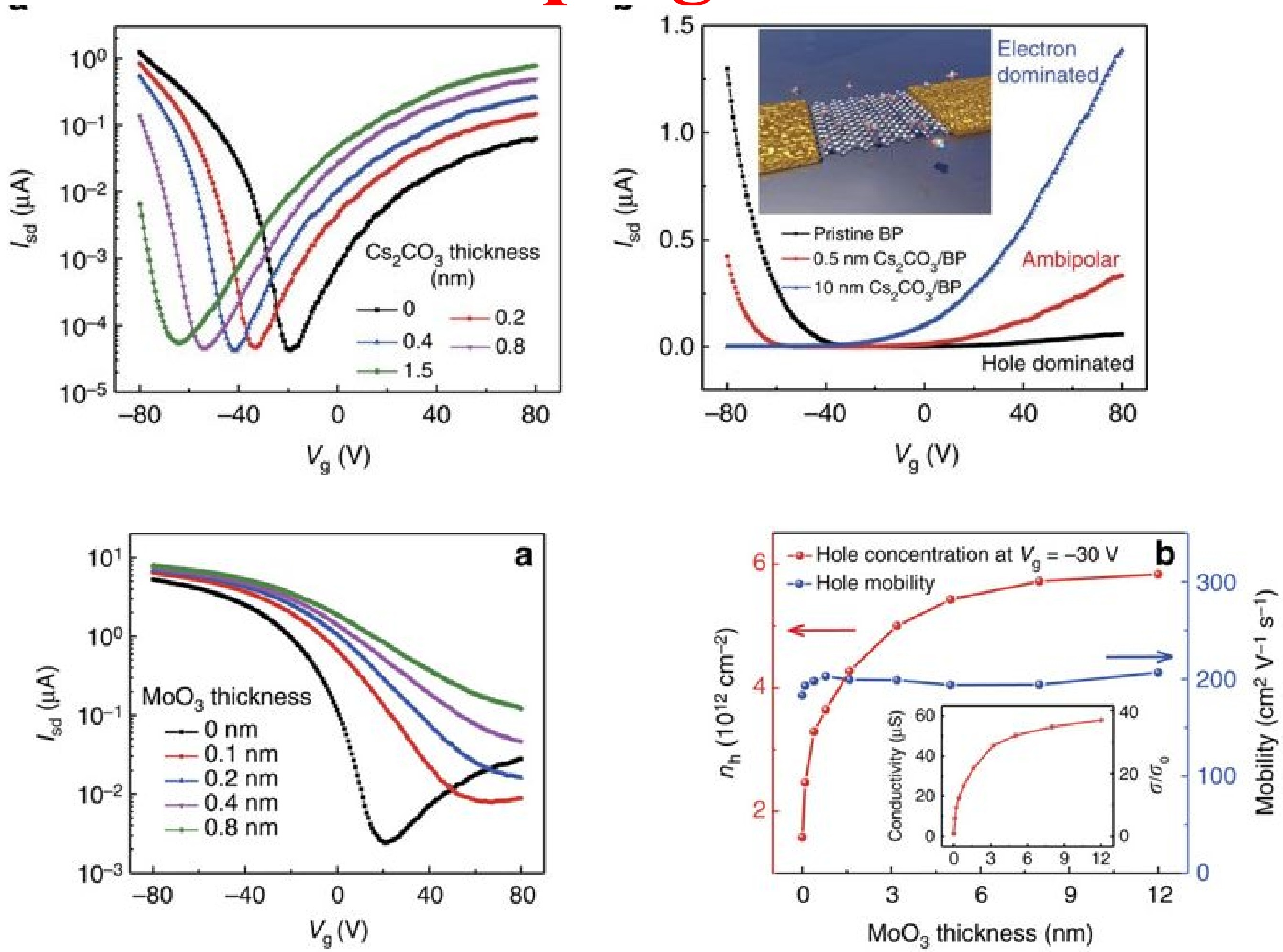
Doping in BP



- In situ surface functionalization with caesium carbonate (Cs_2CO_3) can strongly electron dope BP, while molybdenum trioxide (MoO_3) decoration demonstrates a giant hole-doping effect.

Du Xiang, Wei Chen, Nature Communications, 6, 6485, 2015

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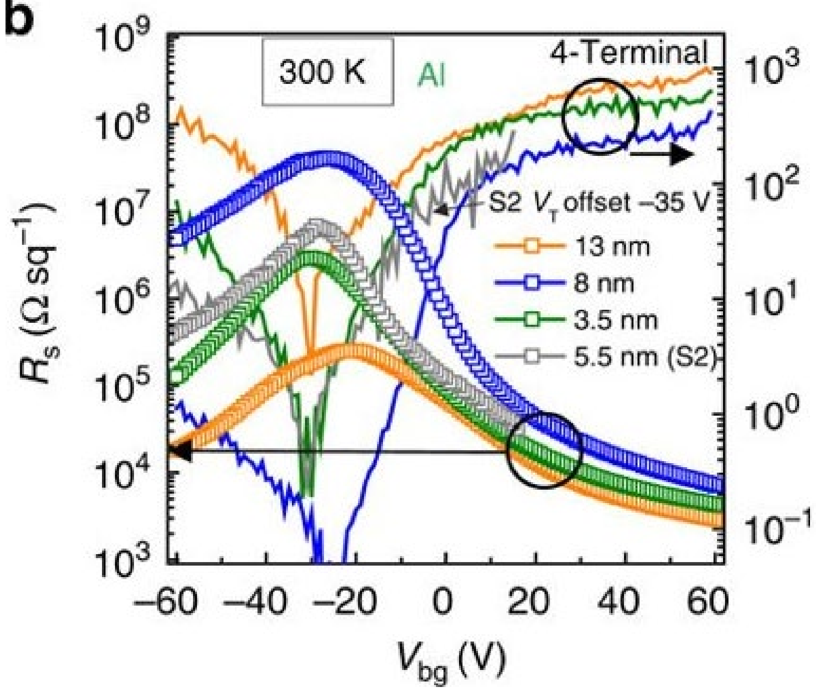
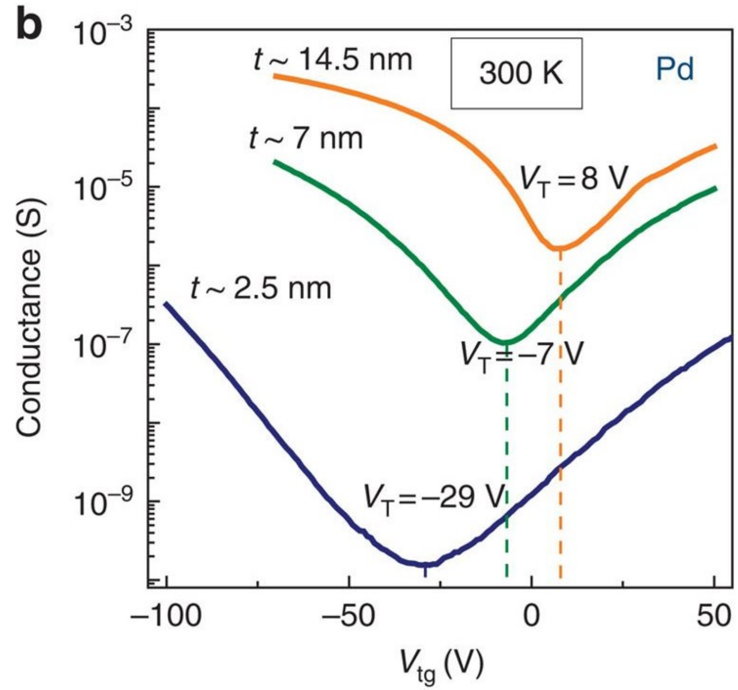
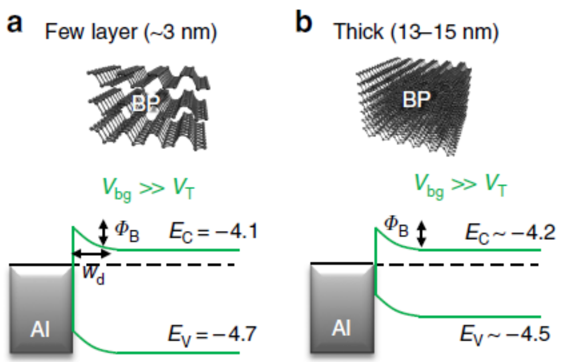
Impact of contact metal on BP transistor type

Aluminum contact



Palladium contact

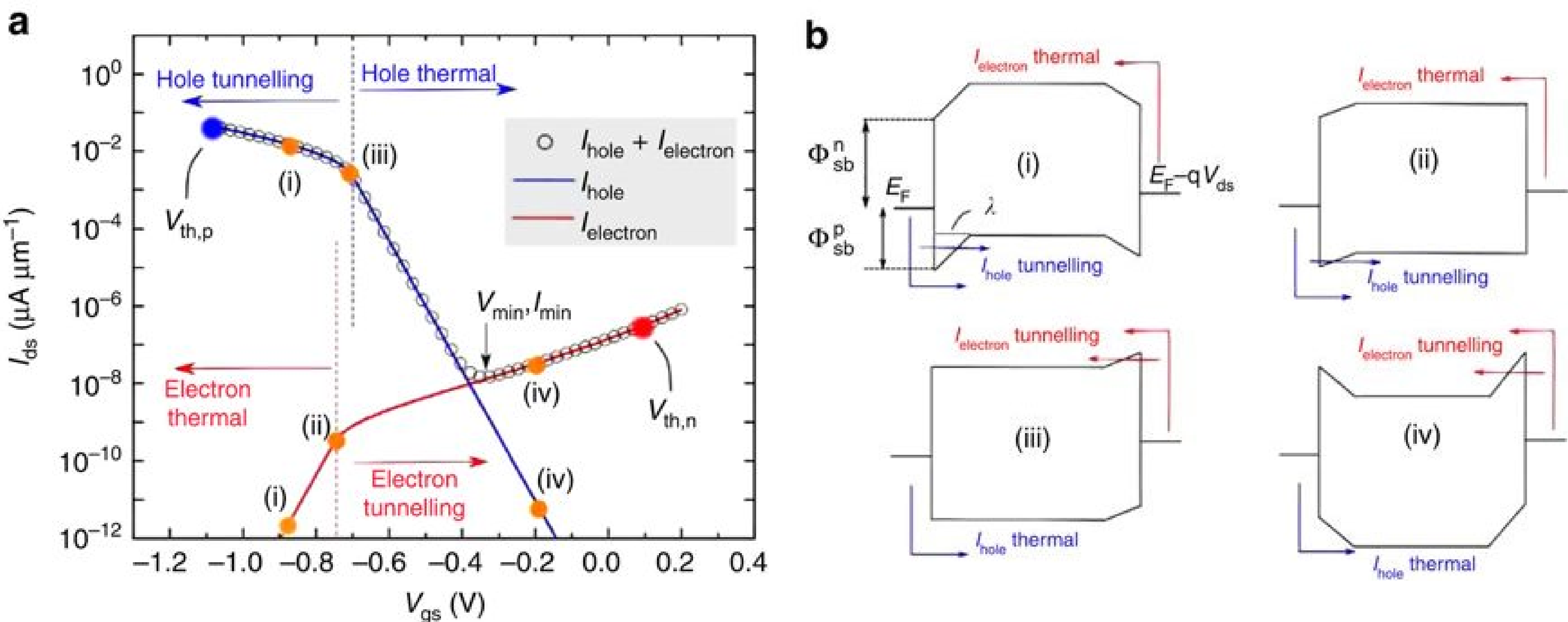




- **With aluminum contacts to black phosphorus, a unipolar n-type to ambipolar transition occurs as flake thickness increases from 3 to 13 nm.**
- **For palladium contacts, p-type behavior dominates in thick flakes, while 2.5–7 nm flakes have symmetric ambipolar transport.**

David J. Perello, Young Hee Lee, Nature Communications, 6, 7809, 2015

Metal/BP barrier height extraction



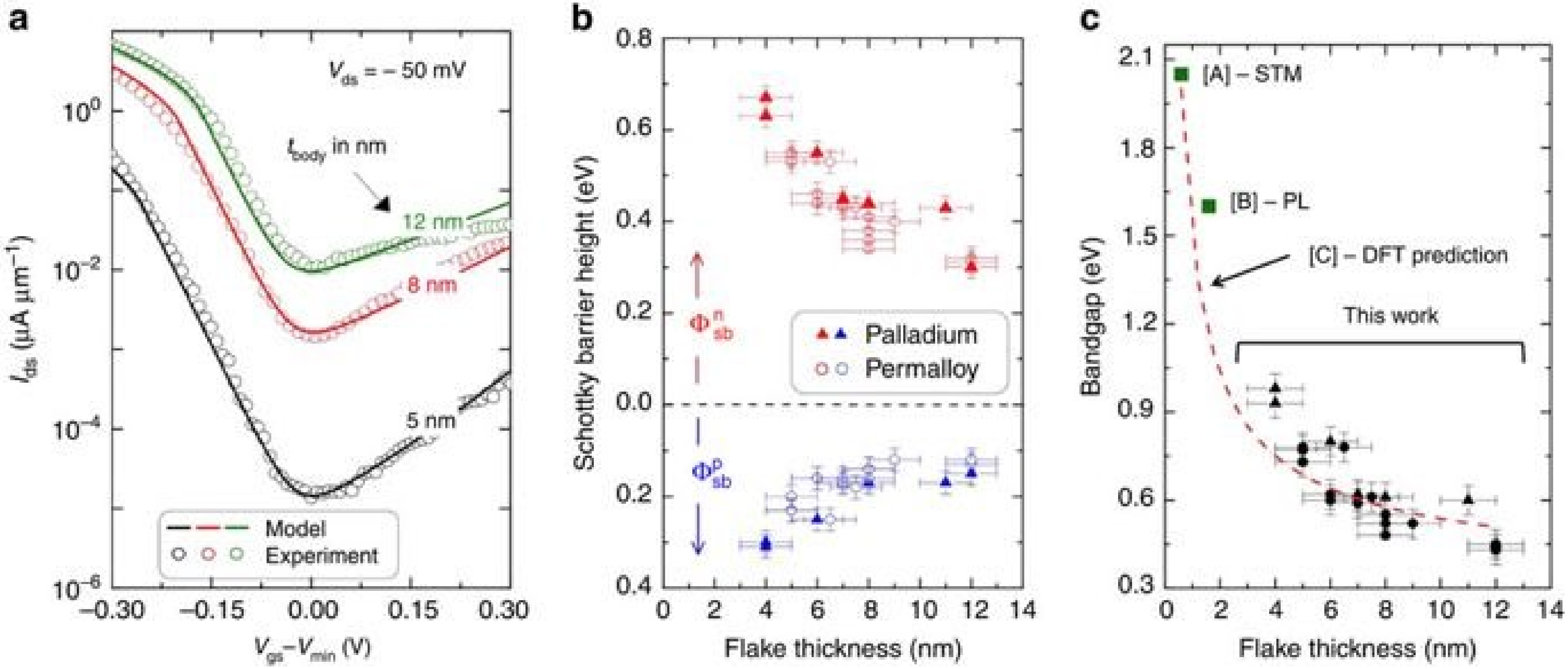
Thermionic emission current: $I_{thermal} = q\int_{\Phi_{SB}}^{\infty} M(E)f(E)\,dE$

Tunneling current: $I_{tunnel} = q\int_{0}^{\Phi_{SB}} M(E)T(E)f(E)\,dE$

where $M(E) = (2/h^2)\sqrt{2m_{eff}E}$, and $T(E)$ is the tunneling probability, $f(E)$ is Fermi–Dirac function

Ashish V. Penumatcha, Joerg Appenzeller,Nature Communications, 6, 8948, 2015

BP band gap extraction



- **Using the model to fit experimental results, the authors extracted Schottky barrier heights for electrons and holes in black phosphorus devices and calculated bandgap for a large range of body thicknesses.**

Ashish V. Penumatcha, Joerg Appenzeller,Nature Communications, 6, 8948, 2015

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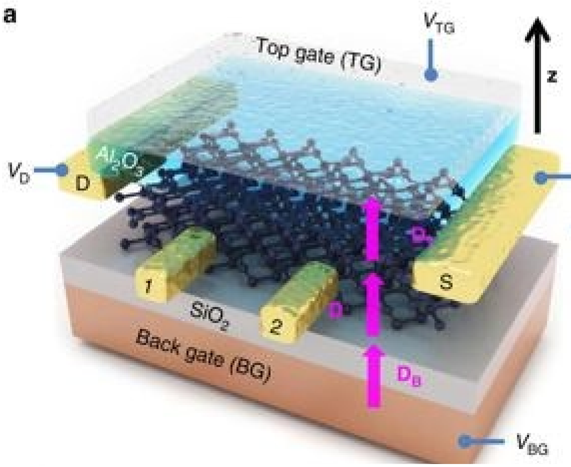
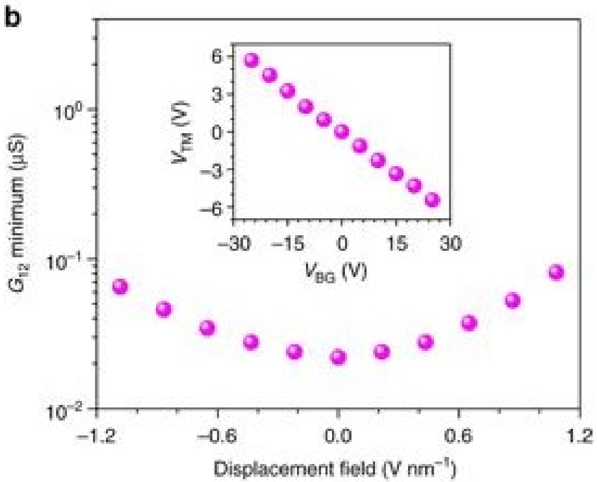
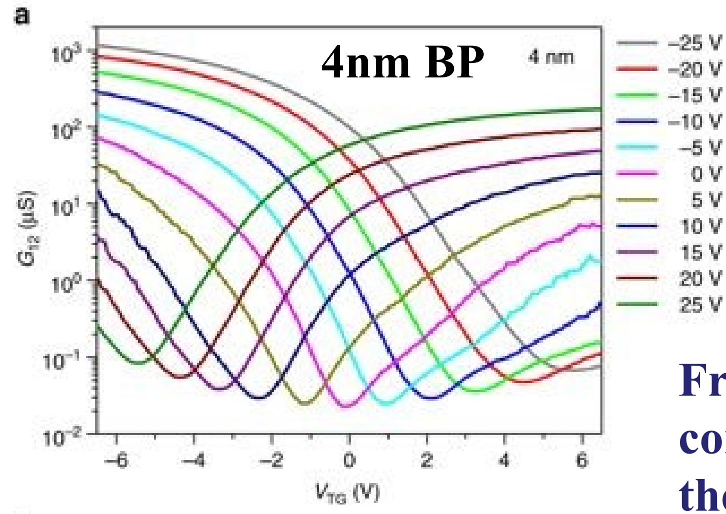
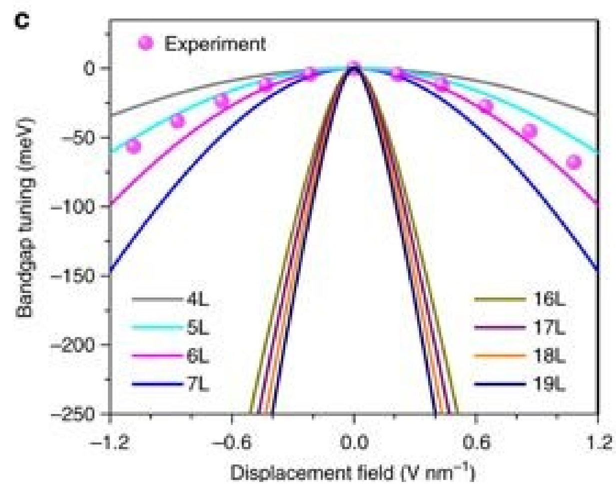
Band gap tuning









From the minimum conductivity variation, the bandgap reduction can be estimated, as the intrinsic carrier concentration:

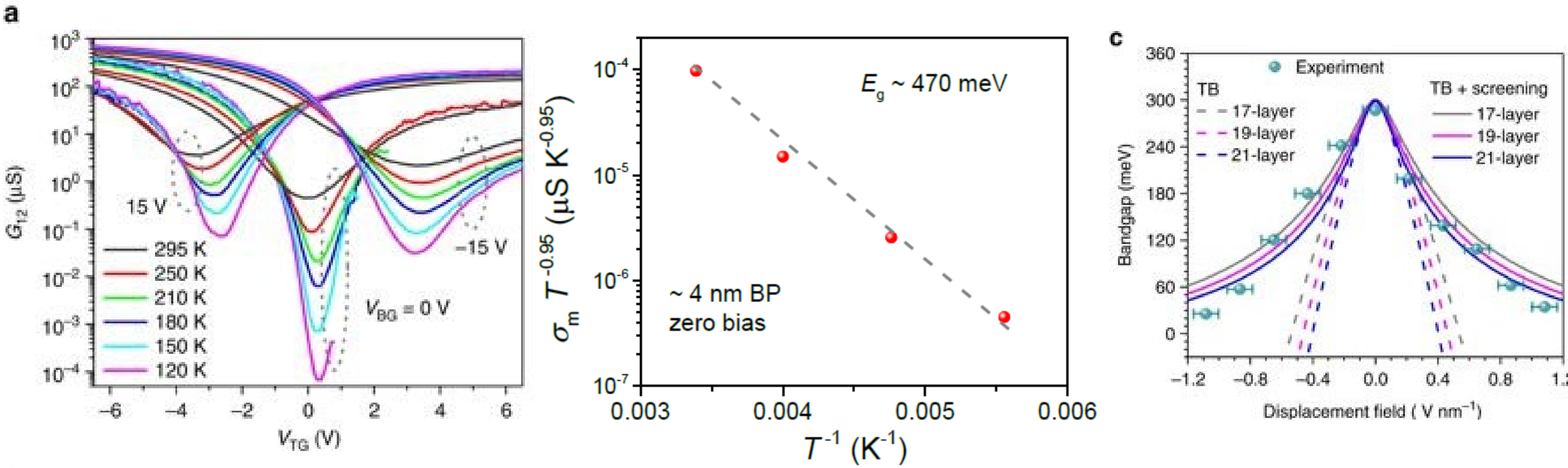
$$n_i \propto exp(-E_g/2k_BT)$$

- **The bandgap of BP can be tuned by vertical electric field.**

Bingchen Deng, Fengnian Xia, Nature Communications, 8, 14474,2017

Band gap extraction from temperature dependence of IVs

10nm BP



Carrier density $n_i \propto T^{1.5} exp(-E_g/2k_BT)$

Carrier mobility has a temperature dependence of $T^{-\gamma}$, where γ varies from 0.5 to 1

Minimum conductance $\sigma_m = qn_i(\mu_e + \mu_h)$

⇨ **The bandgap can be extracted from the temperature dependence of σ_m**

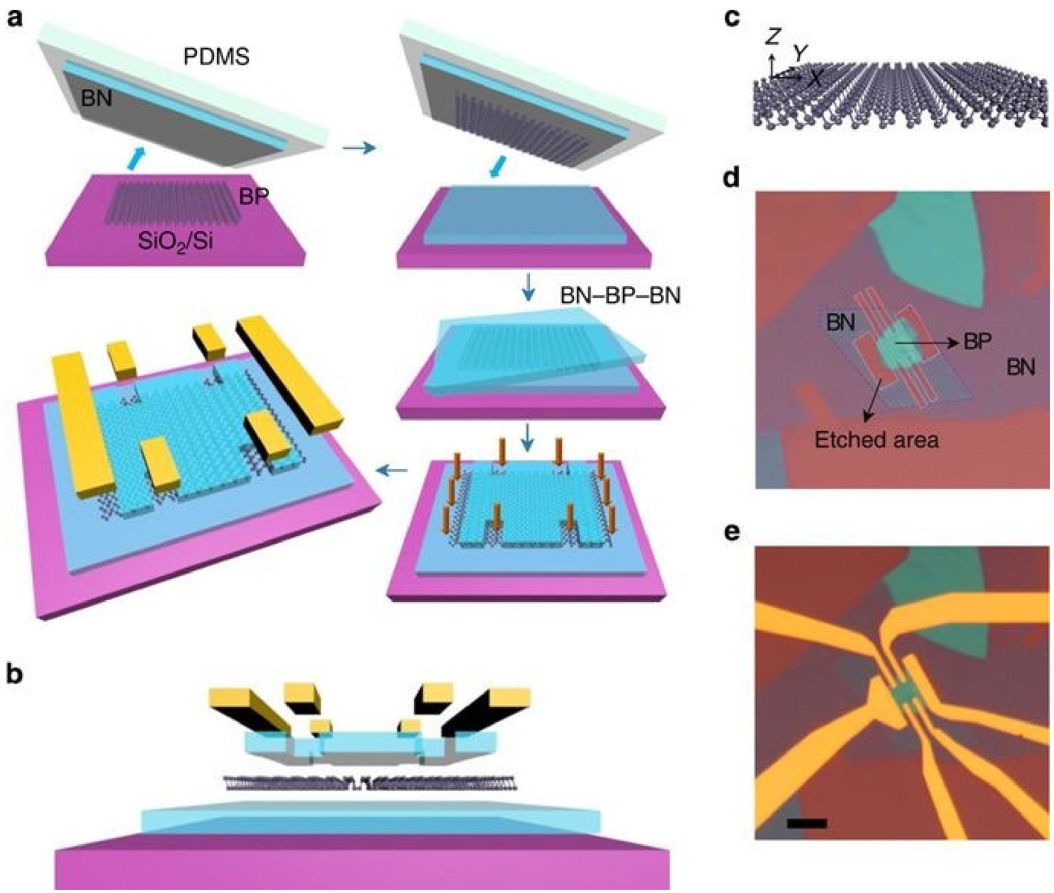
- **The bandgap of a 10 nm-thick BP can be continuously tuned from 300meV to below 50meV.**

Bingchen Deng, Fengnian Xia, Nature Communications, 8, 14474, 2017

Outline

- Introduction of black phosphorus
- Synthesis of black phosphorus
- Thermal stability of black phosphorus
- Electronic properties and electronic devices
  - Electronic properties
    - Anisotropic conductance and mobility
    - Ambipolar and unipolar transport
    - Bandgap tuning and bandgap extraction
    - Quantum Hall effect and Shubnikov–de Haas (SdH) oscillation
  - Electronic devices based on BP
- Optical properties and photonic devices

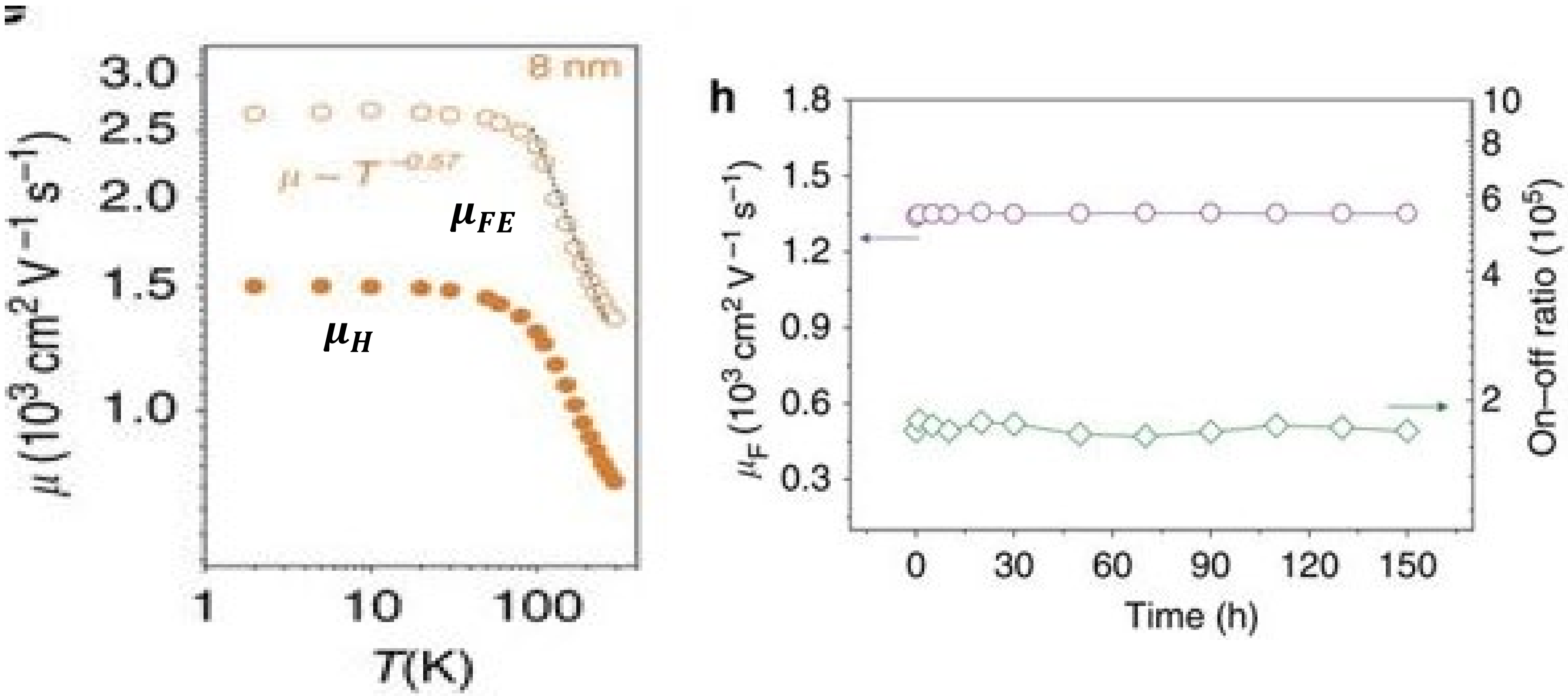
Encapsulating BP with hBN



- **Stable sandwiched heterostructures were fabricated by encapsulating atomically thin black phosphorus between hexagonal boron nitride (hBN) layers to realize ultra-clean interfaces.**

Xiaolong Chen, Ning Wang, Nature Communications, 6, 7315, 2015

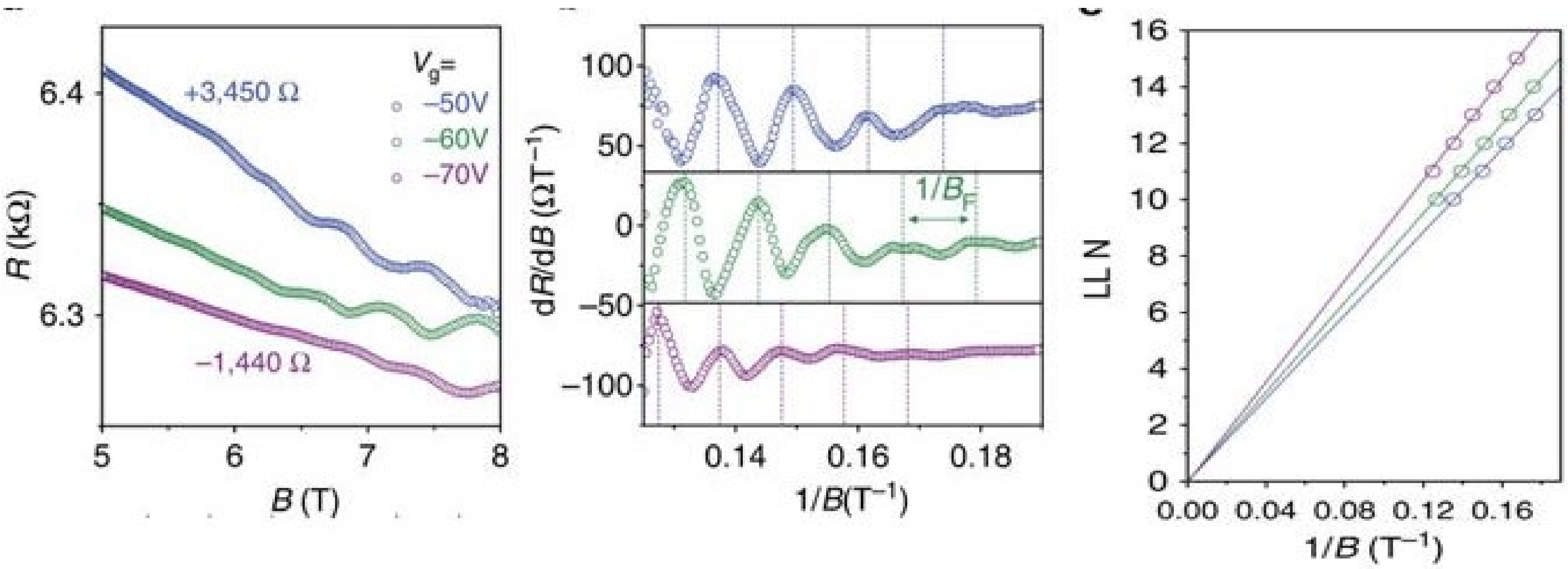
High carrier mobility in encapsulated BP



- These encapsulated BP with clean interface allows a high field-effect mobility of ~1,350 cm^2/V-s at room temperature and ~2,700 cm^2/V-s at low temperatures.
- The mobility is stable even after several weeks of exposure to air.

Xiaolong Chen, Ning Wang, Nature Communications, 6, 7315, 2015

Quantum oscillation in BP



Oscillation period: $\Delta(1/B_F) = \dfrac{2e}{nh}$ **Where n is carrier density**

- **At low temperatures, quantum oscillations in black phosphorus two-dimensional hole gas are observed at low magnetic fields.**

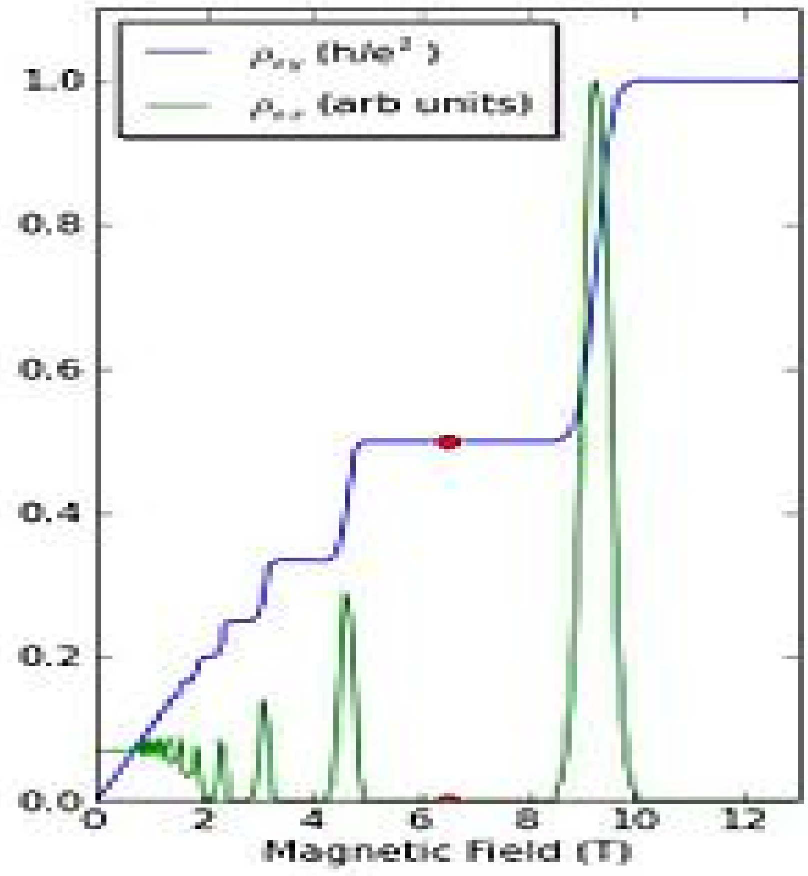
Xiaolong Chen, Ning Wang, Nature Communications, 6, 7315, 2015: (hBN/BP/hBN)

Likai Li, Yuanbo Zhang, Nature Nanotechnology, 10, 608, 2015: (BP/hBN)

V. Tayari, T. Szkopek, Nature Communications, 6, 8702, 2015: (BP/PMMA)

Shubnikov–de Haas Oscillation

- **Shubnikov–de Haas (Sdh) Oscillation: An oscillation in the conductivity of a material that occurs at low temperatures in the presence of intense magnetic fields**



SdH oscillation period

The magnetic field causing all the states in an energy range $\hbar\omega_c$ to be concentrated into a single Landau level. Since the 2D density of states is $m/\pi\hbar^2$, we can expect that the number of states (or degeneracy) in each Landau levels is

$$N_o = \hbar\omega_c \times \frac{m}{\pi\hbar^2} = 2\mathrm{eB/h}$$

The total electron density in the sample is:

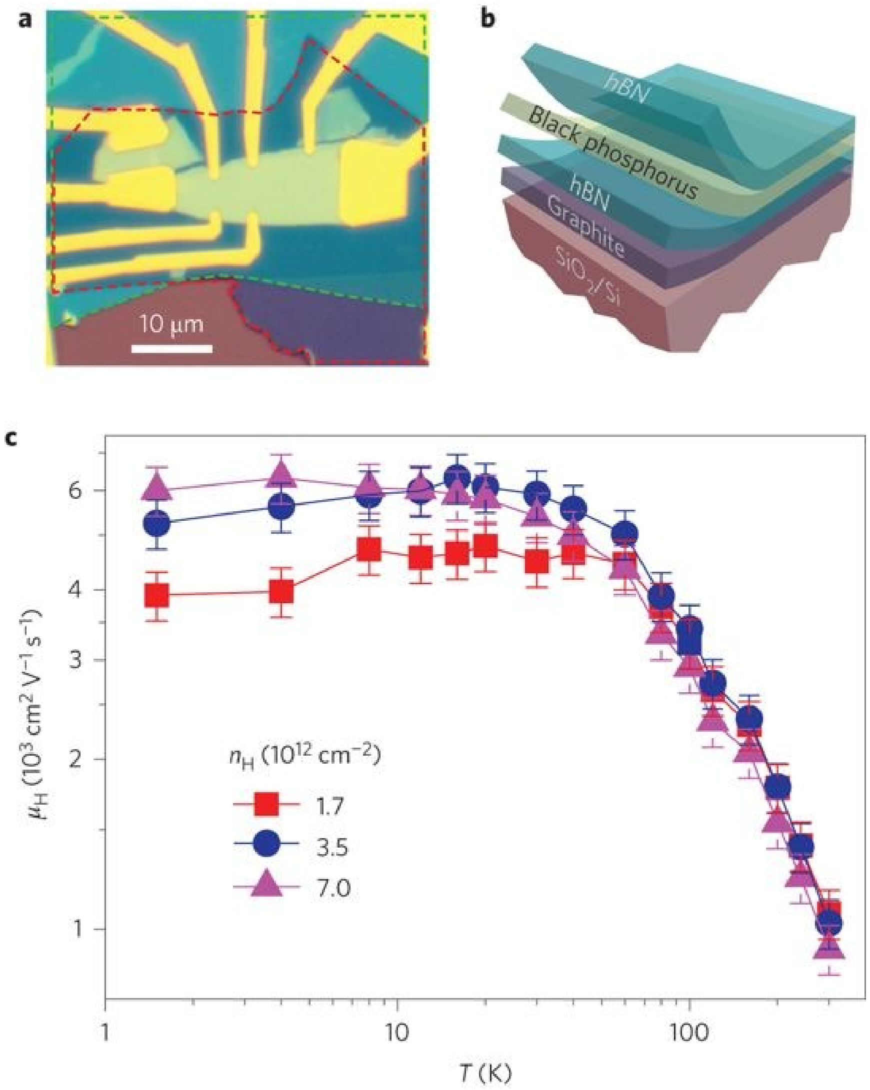
$$n_e = N_o \times \mathrm{i} = 2\mathrm{i}\frac{eB}{h}$$

Where i is the number of Landau levels below Fermi level

⇨ **The magnetic field corresponding to i Landau levels** $B_i = \dfrac{n_e h}{2ei}$

Oscillation period: $\Delta\left(\frac{1}{B}\right) = \frac{1}{B_{i+1}} - \frac{1}{B_i} = \frac{2e}{n_e h}$

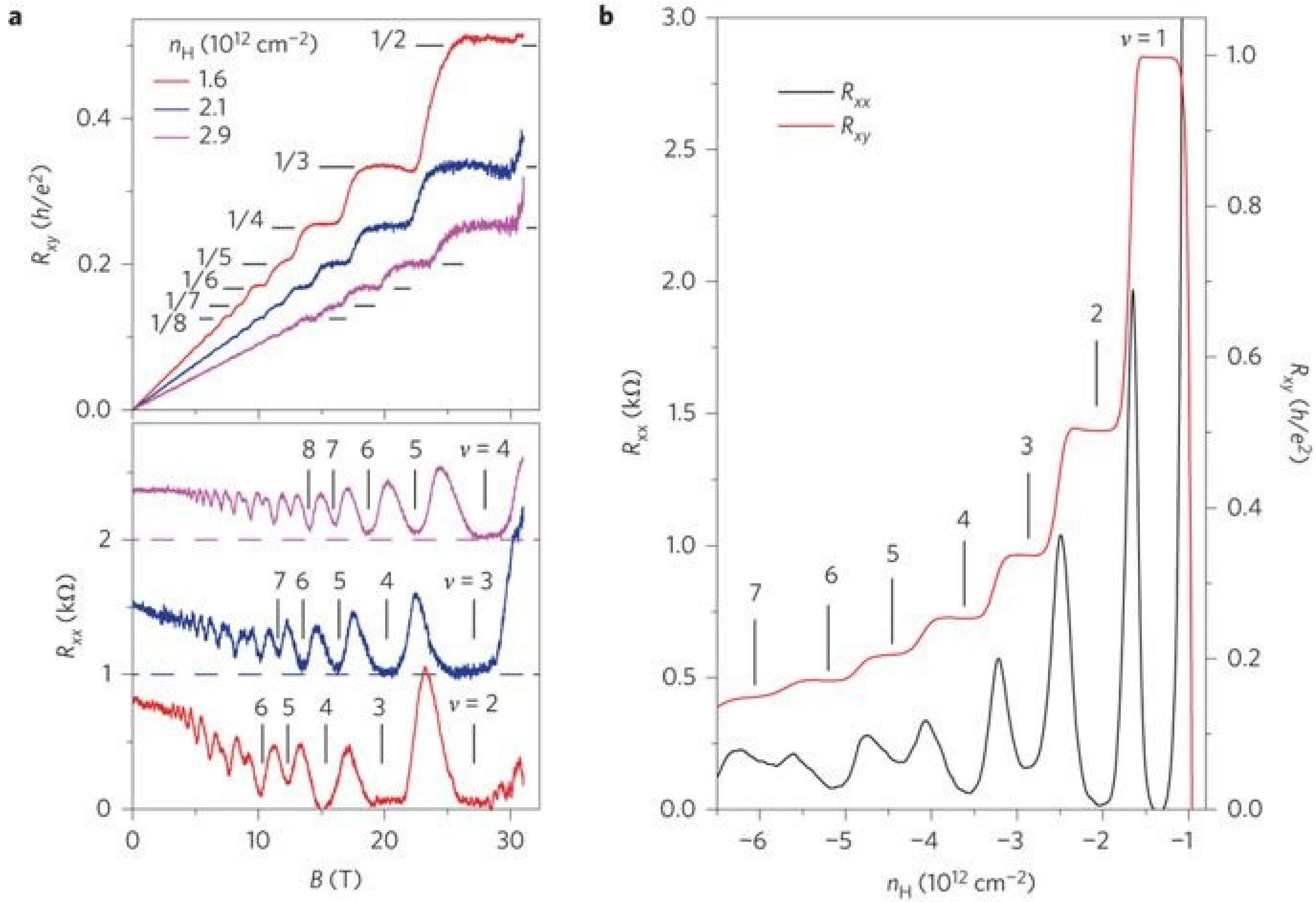
Quantum Hall Effect in BP



- **The high quality BP devices was made by embedding the black phosphorus 2DES in a van der Waals heterostructure close to a graphite back gate. The carrier Hall mobility reach 6,000 cm^2/V-s.**

Likai Li, Yuanbo Zhang, Nature Nanotechnology, 11,593, 2016

Quantum Hall Effect in BP



- **The exceptional mobility in the embedded BP enabled the authors to observe the quantum Hall effect.**

Likai Li, Yuanbo Zhang, Nature Nanotechnology, 11,593, 2016

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- **Introduction of black phosphorus**
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  - **Electronic properties**
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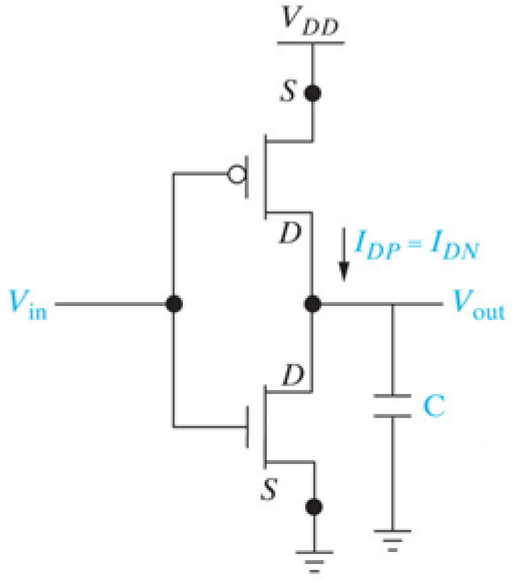
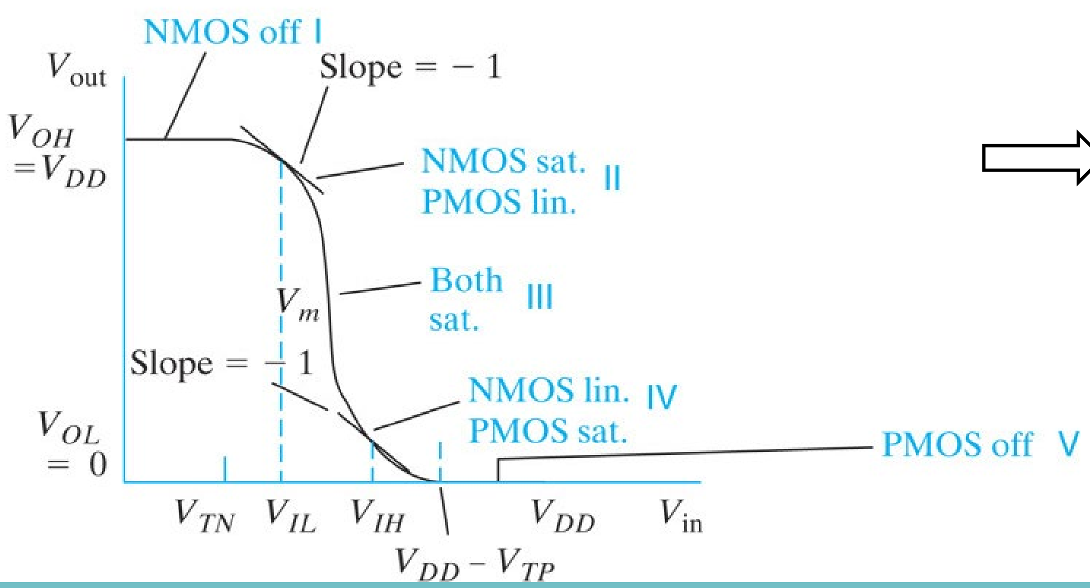
    - **Logic devices and circuits**
    - **Analog devices**
    - **Memory devices**
    - **Esaki diodes**
- **Optical properties and photonic devices**

Review: Si CMOS inverter

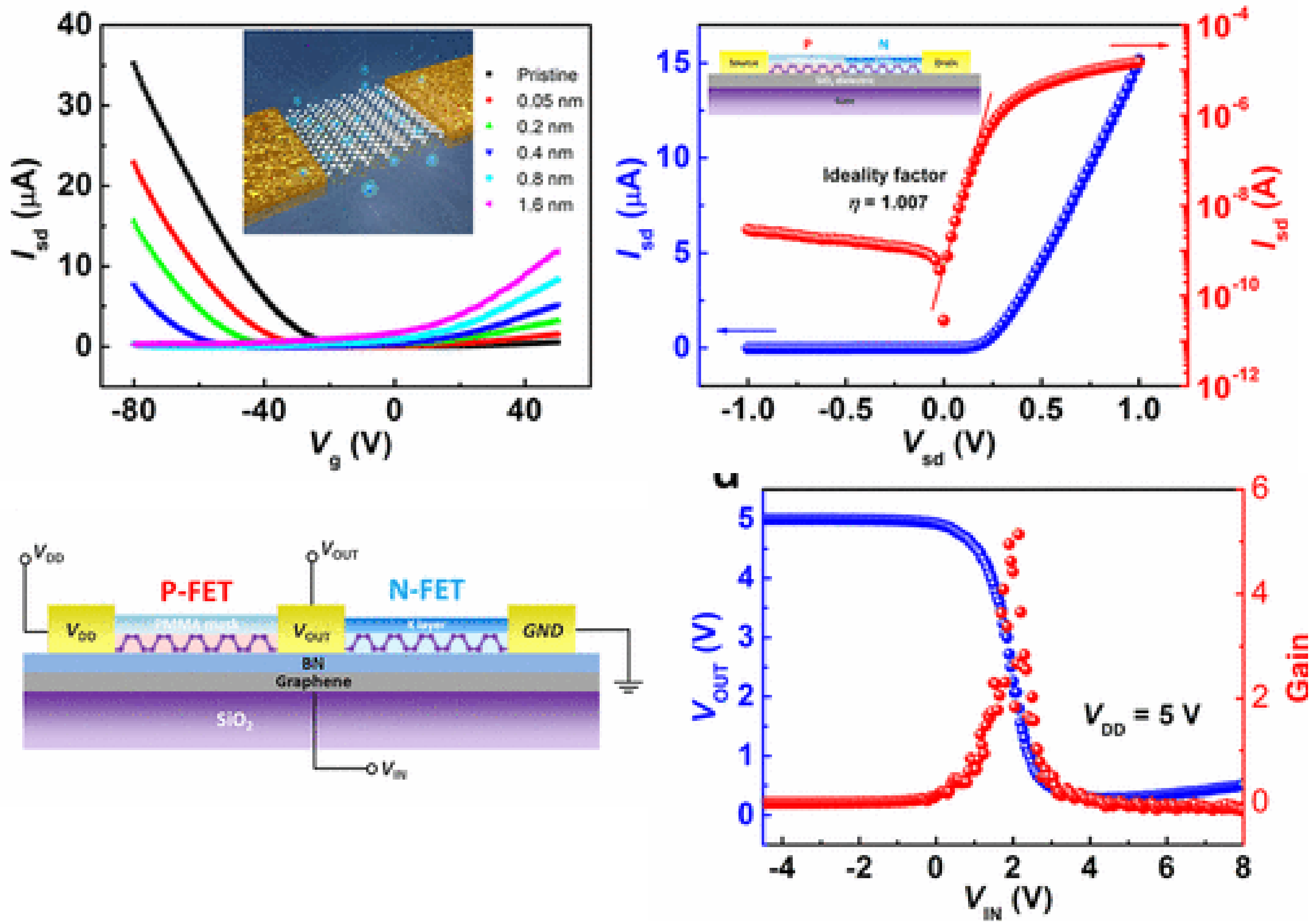


- When V_{in} is low, NMOS is off, PMOS is on →V_{out} is high
- When V_{in} is high, NMOS is on, PMOS is off →V_{out} is low

⇨ **Inverter**



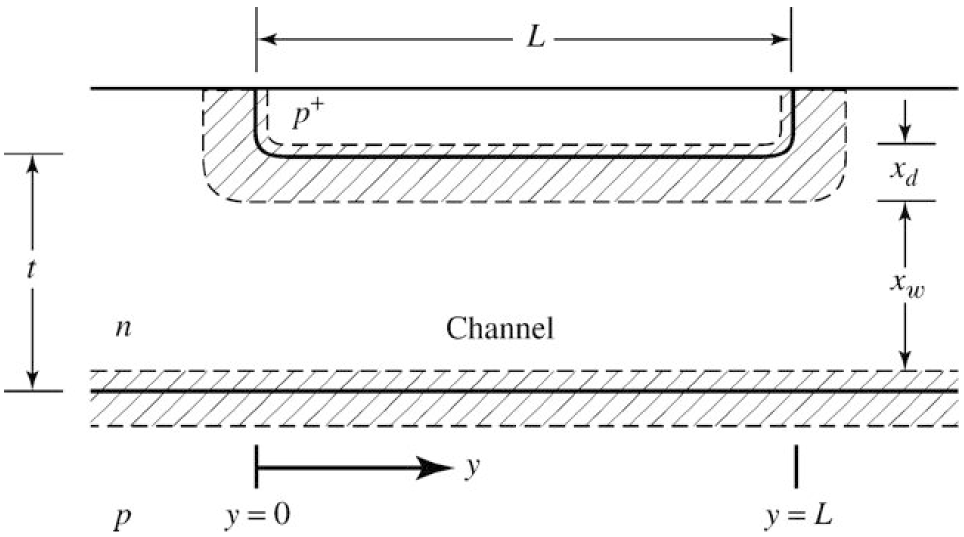
Invertor based on BP

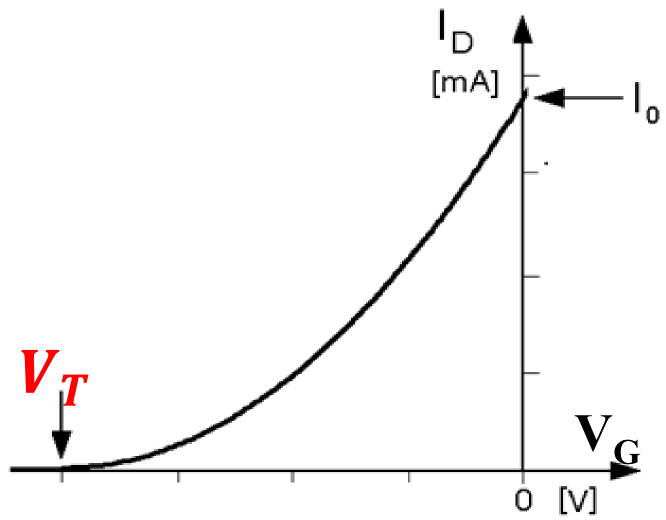


- **Potassium induces an electron doping effect on BP along with a bandgap reduction. The electron mobility is enhanced to 262 cm^2/V-s after potassium modification.**
- **A logic inverter with a highest gain of ~5 was made using this doping scheme.**

Cheng Han, Wei Chen, Nano Letters, 17, 4122, 2017

Review: Silicon Junction Field-Effect Transistors (JFET)

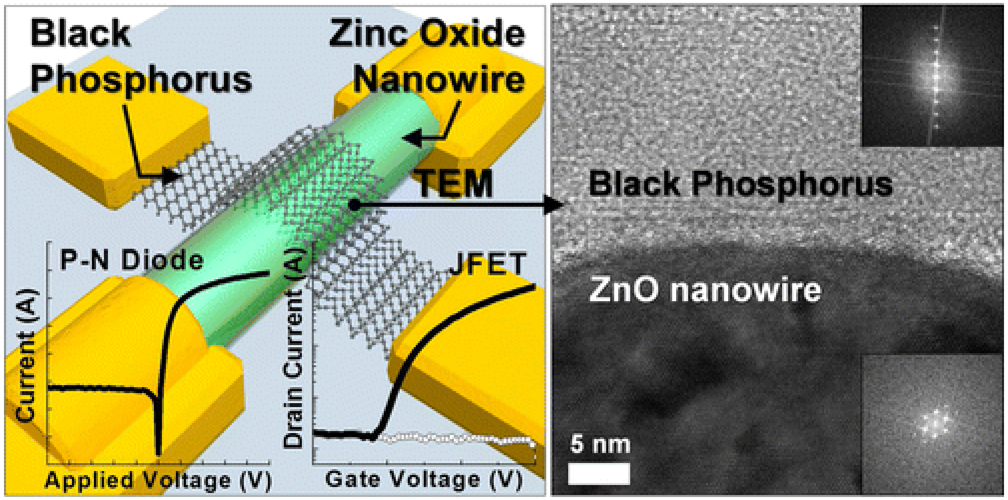


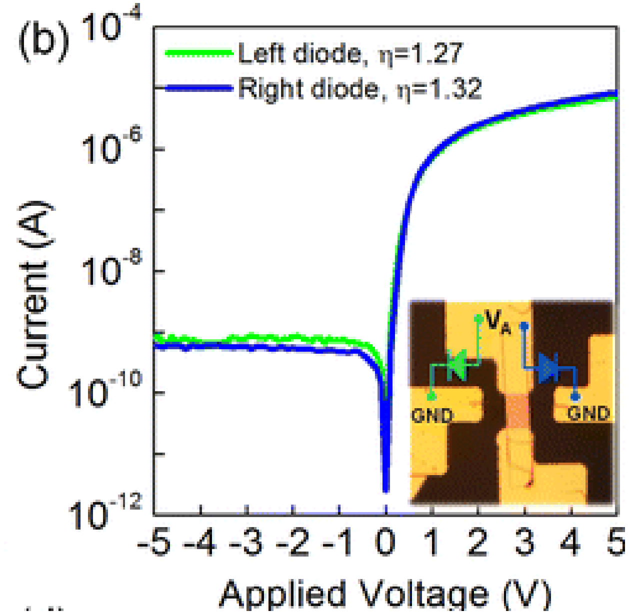


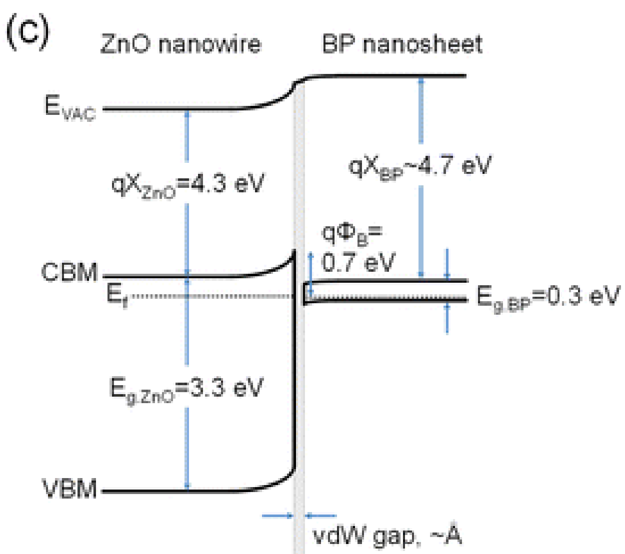
Operating principle:

- **If we ground the source and apply a positive voltage on the drain and a negative voltage to the p$^+$ gate, the depletion region of the pn junction widens and the channel narrows. Therefore, the channel resistance increases and less current flow from source to drain.**
- **A voltage applied to the gate controls the current flowing through the channel.**

PN junction based on BP/ZnO heterostructure



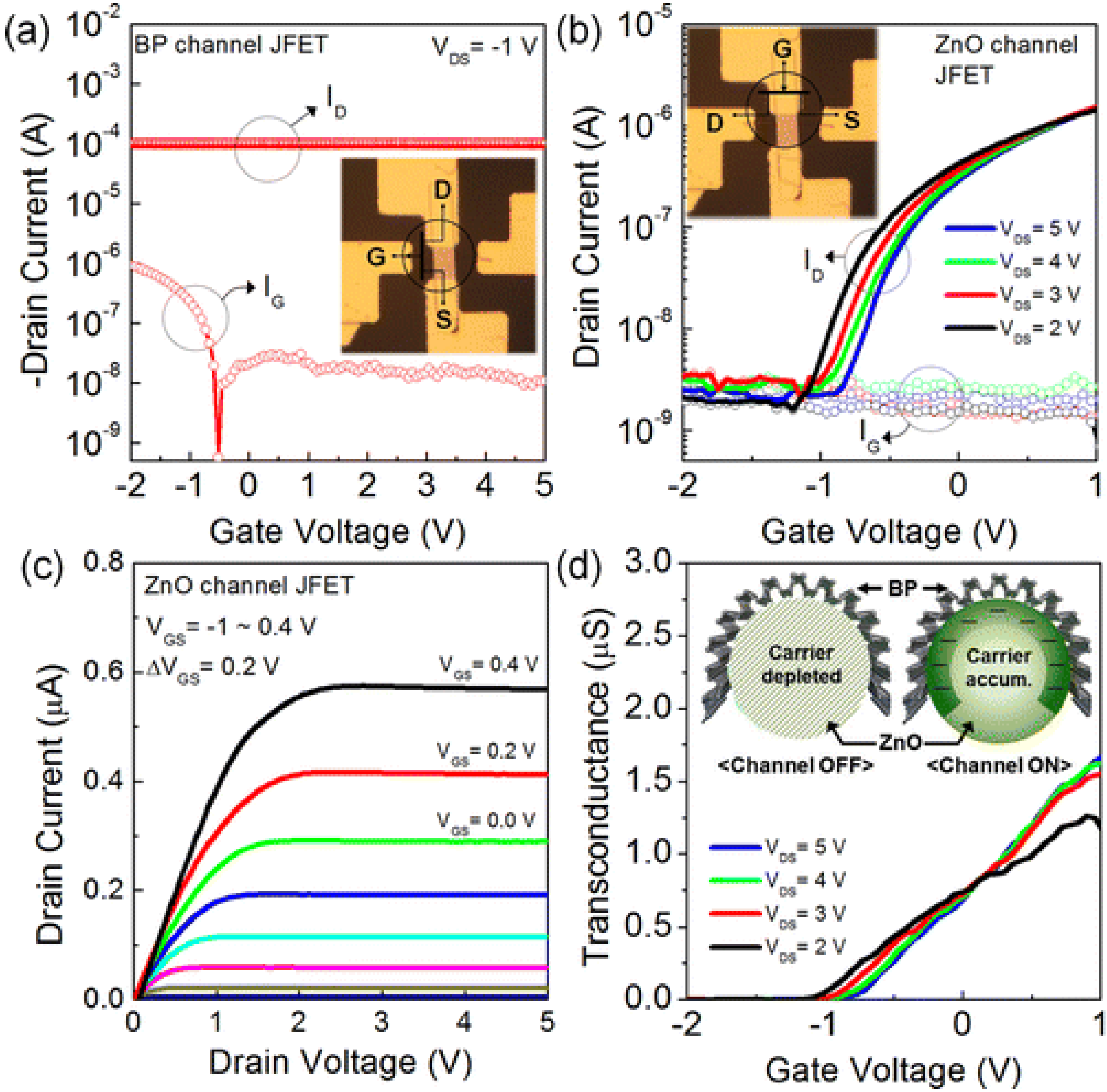




- BP nanosheet–ZnO nanowire 2D–1D heterojunction was made, where BP is p-type and ZnO is n-type. As a result, the BP–ZnO heterostructures forms a p–n diode displays a high ON/OFF ratio of ~10^4 in static rectification

Pyo Jin Jeon, and Seongil Im, Nano Letters, 16, 1293, 2016

Junction field effect transistor (JFET) based on BP

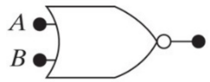


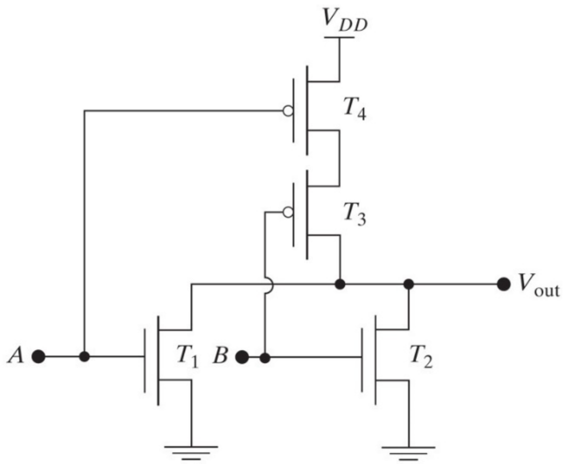
- **JFET with ZnO nanowire channel and BP gate shows switching in both electrostatics and kilohertz dynamics.**

Pyo Jin Jeon, and Seongil Im, Nano Letters, 16, 1293, 2016

Review: Silicon NOR and NAND gate

NOR gate

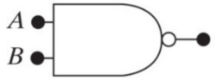


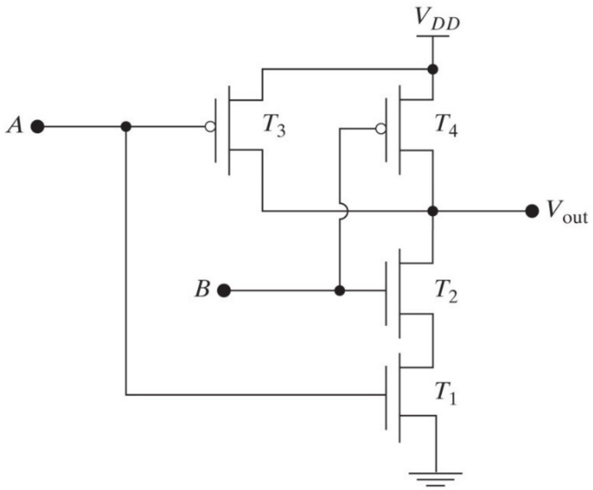


(a)

Input		Output Y	
A	B	OR	NOR
0	0	0	1
0	1	1	0
1	0	1	0
1	1	1	0

NAND gate

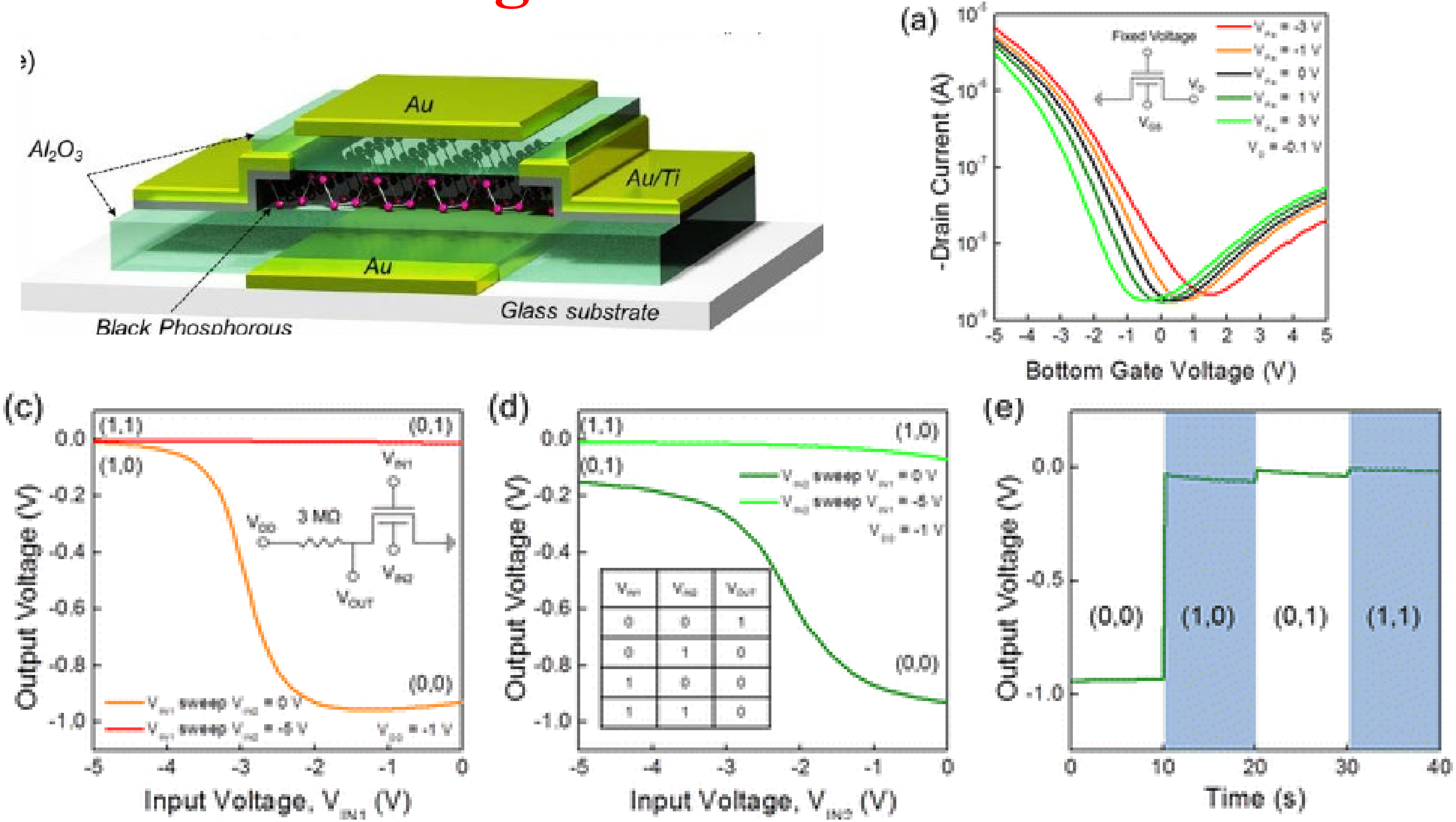




(b)

Input		Output Y	
A	B	AND	NAND
0	0	0	1
0	1	0	1
1	0	0	1
1	1	1	0

NOR gate based on BP



- **Dual gate BP transistor with Al_2O_3 gate dielectric show NOR logic function by separately using top and bottom-input.**

Jin Sung Kim,Seongil Im, Nano Letters, 15, 5778, 2015

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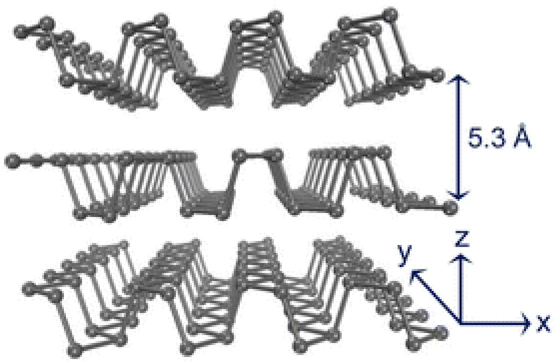
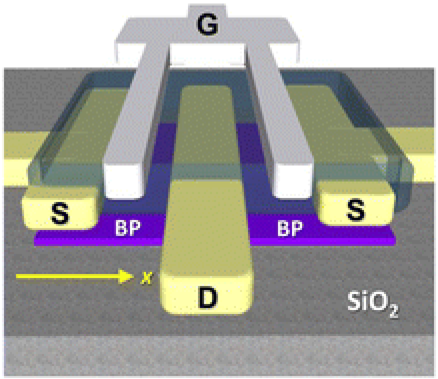
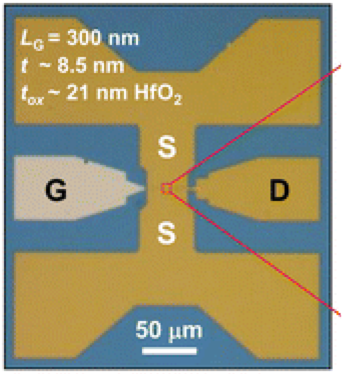
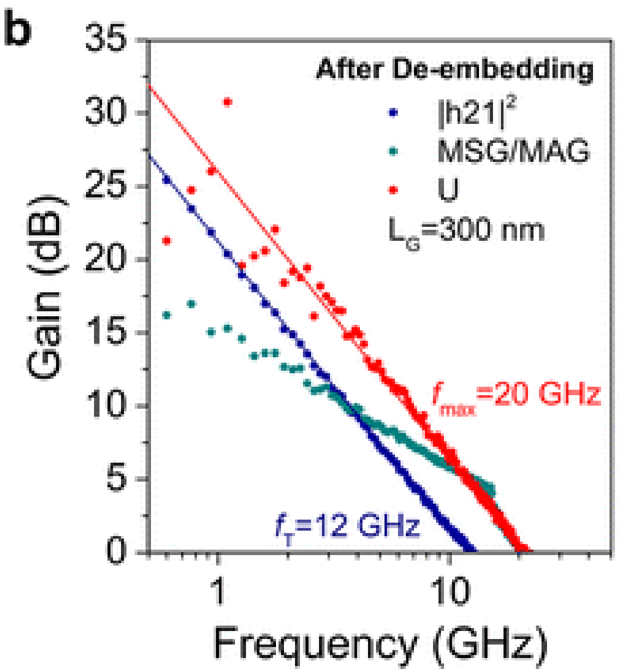
BP RF devices





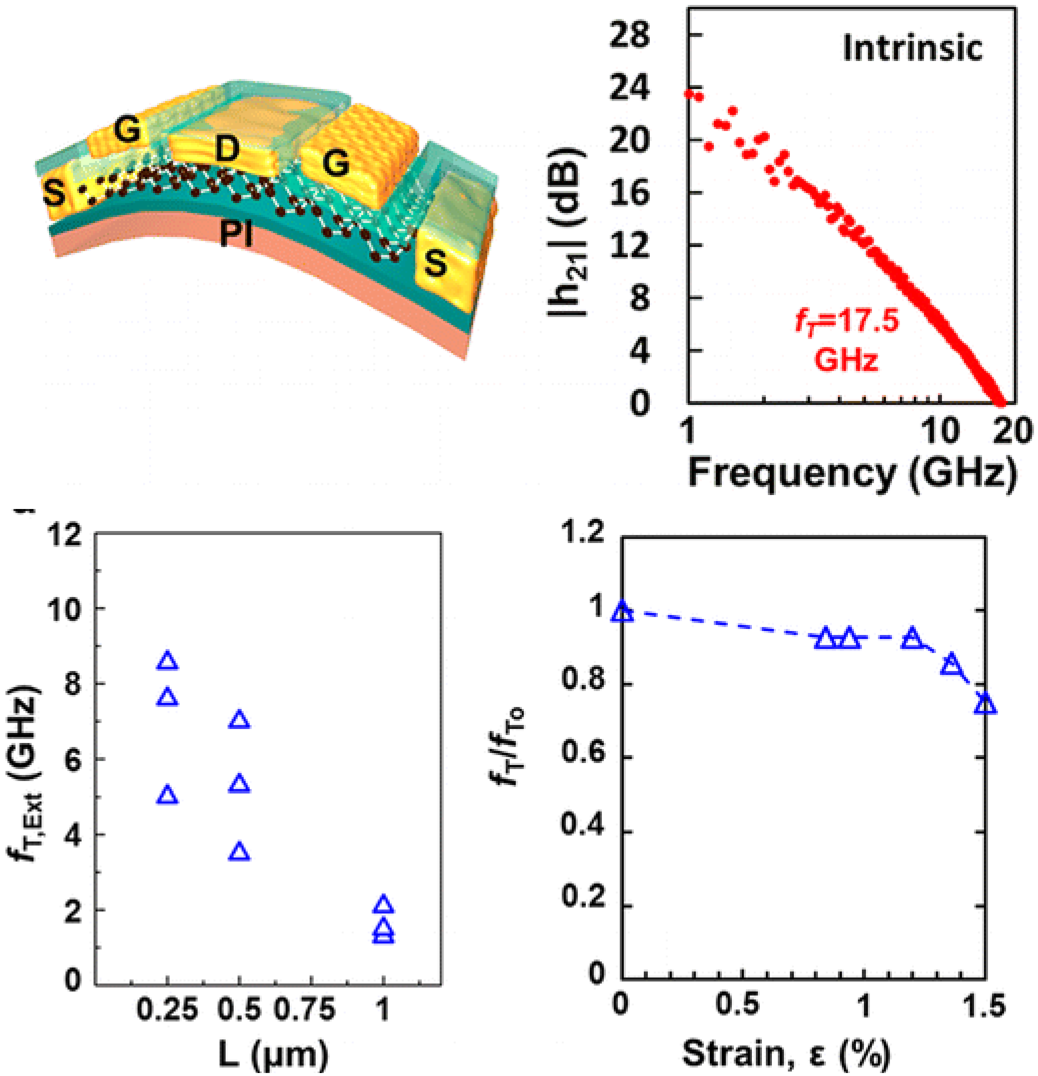




- BP RF device with HfO_2 top gate dielectrics shows a short-circuit current-gain cutoff frequency f_T of 12 GHz and a maximum oscillation frequency f_{max} of 20 GHz in 300 nm channel length devices.

Han Wang, Shu-jen Han, Nano Letters, 14, 6424, 2014

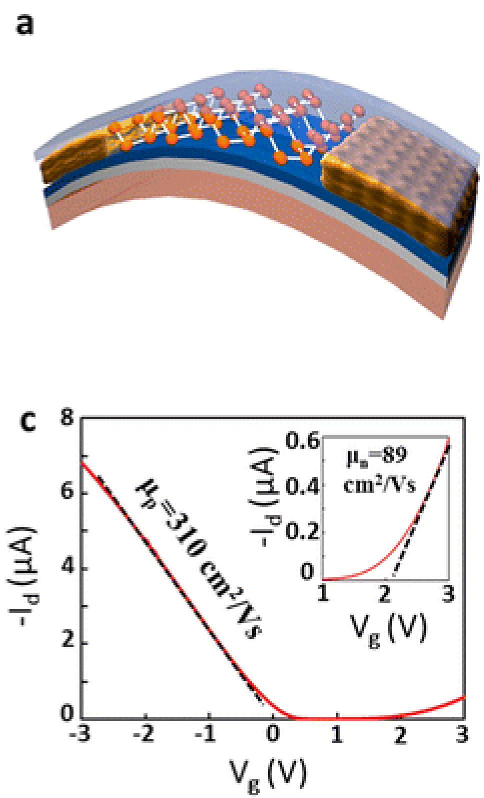
Flexible RF device based on BP



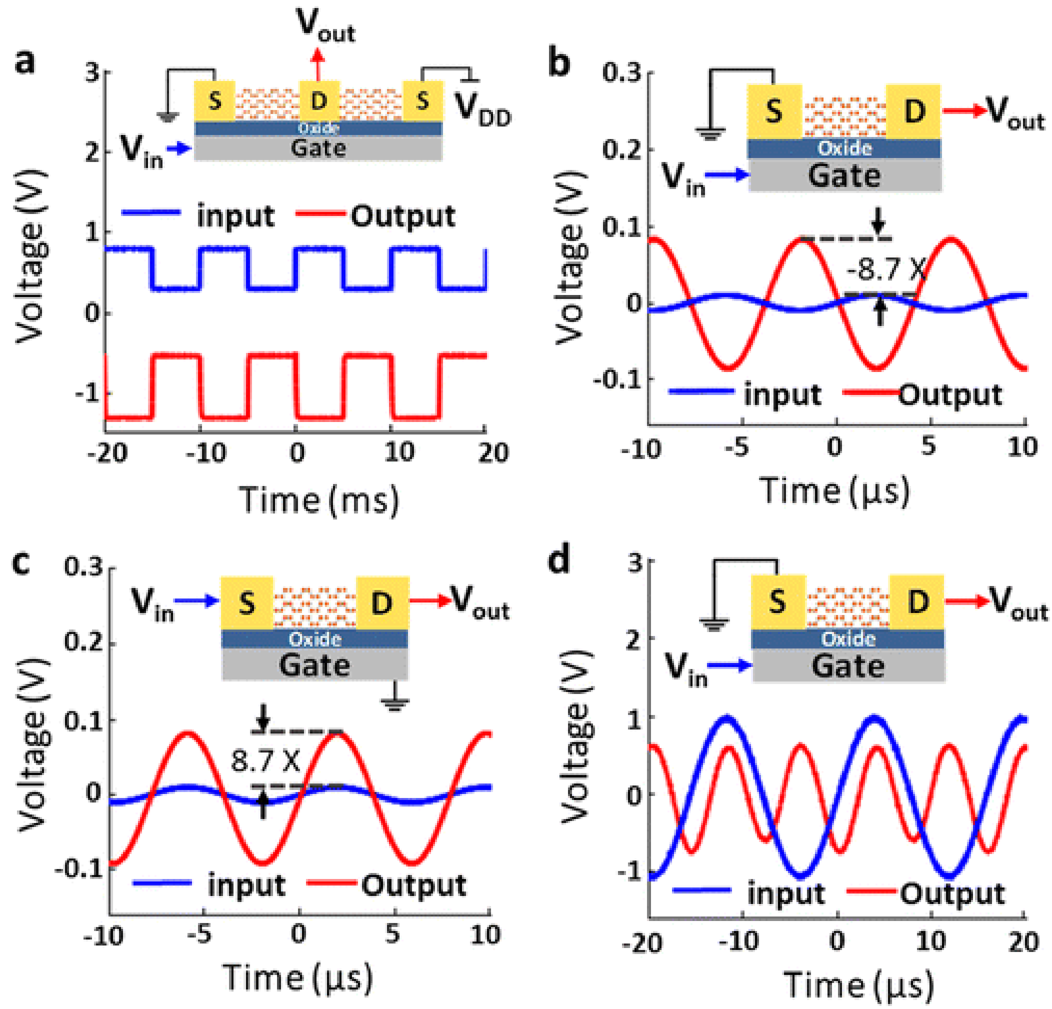
- Radio frequency (RF) flexible top-gated BP thin-film transistors on highly bendable polyimide substrate was fabricated.
- Carrier mobility ~233 $cm^2/V \cdot s$ were obtained.
- Flexible BP RF transistors show intrinsic maximum oscillation frequency f_{MAX} ~ 14.5 GHz and unity current gain cutoff frequency f_T ~ 17.5 GHz at a channel length of 0.5 μm.

Weinan Zhu, and Deji Akinwande, Nano Letters, Nano Letters, 16, 2301, 2016

Amplifier and frequency doubler



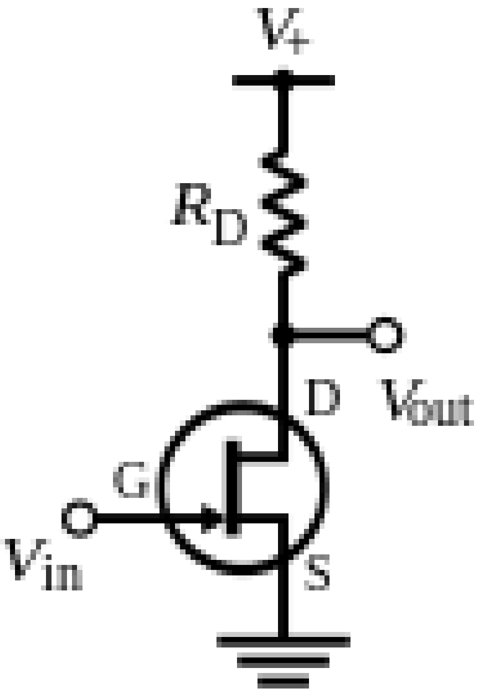
Weinan Zhu, Deji Akinwande,Nano Letters, 15, 1883, 2015



- The device ambipolar functionality and high-mobility were employed to realize essential circuits of electronic systems for flexible technology including ambipolar digital inverter, frequency doubler, and analog amplifiers

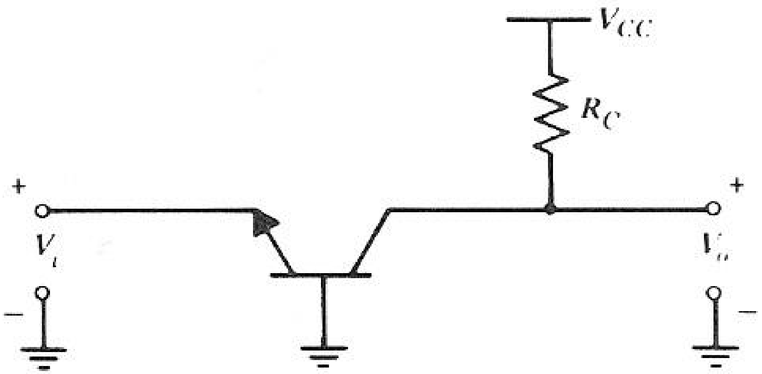
Review: silicon transistor amplifier

Common-source amplifier



- The signal is applied on the gate (base) of the transistor, and the output is taken from the drain (collector). The source (emitter) is tied to the ac ground.

Common-gate amplifier



- The signal is applied the source (emitter) of the transistor, and the output is taken from the drain (collector). The gate (base) is tied to the ac ground.

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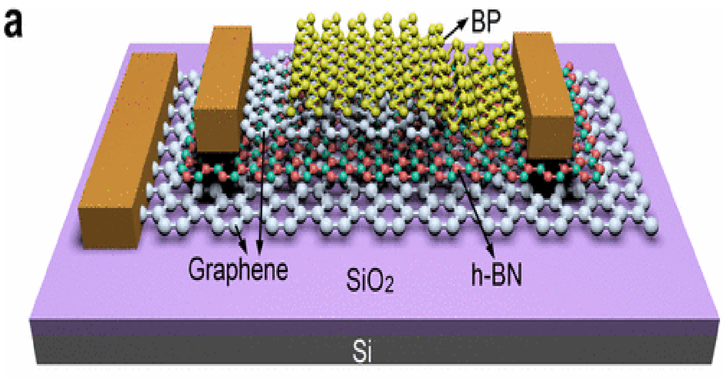
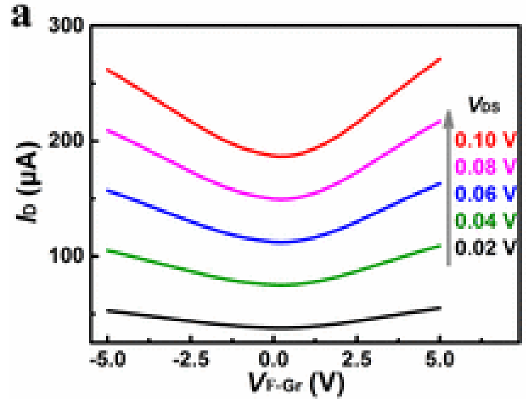
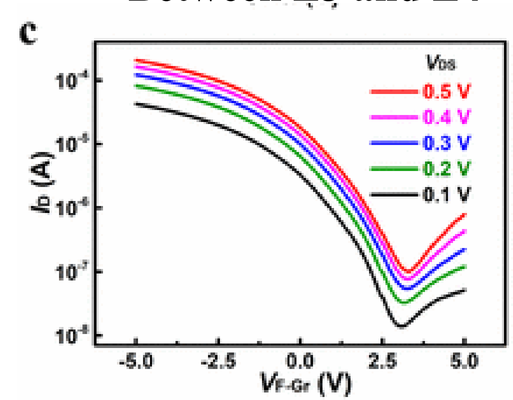
BP/graphene diode

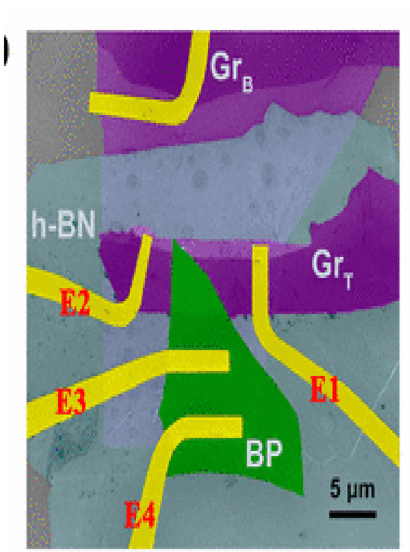


Graphene transistor
Between E1 and E2

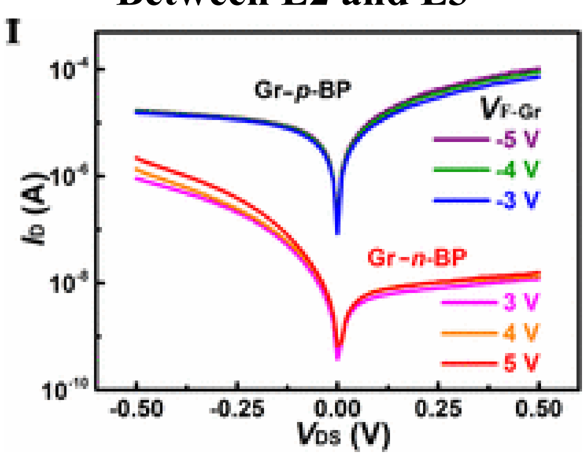


BP transistor
Between E3 and E4





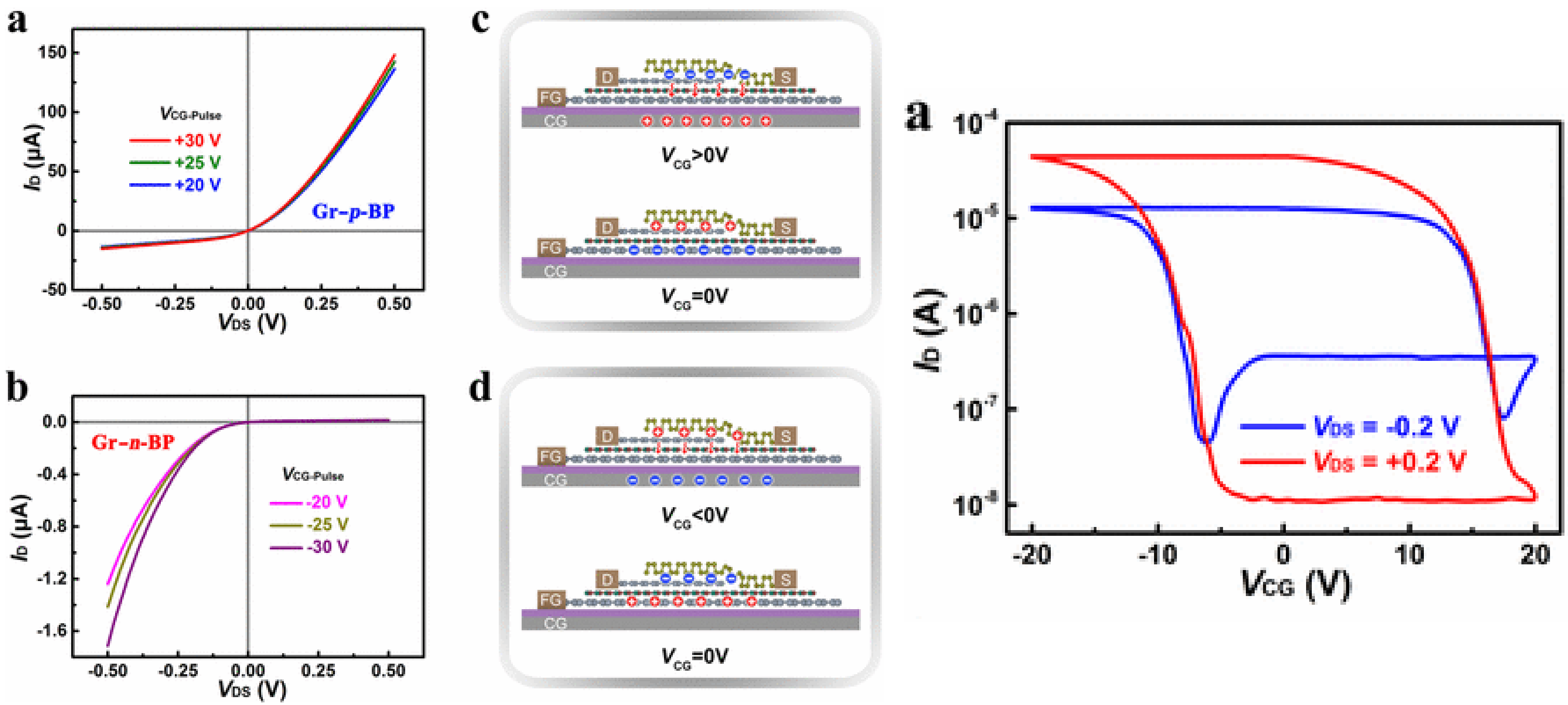
Graphene/BP diode
Between E2 and E3



- **BP/graphene diode shows ambipolar characteristics, depending on the voltage of the gate voltage on the bottom graphene layer.**

Dong Li, and Zengxing Zhang, Nano Letters, 17, 6353, 2017

Nonvolatile Ambipolar Schottky Junction Memories



- By applying voltage on the Si back gate (control gate), carrier are injected from the BP channel to the bottom graphene layer, which serves as a floating gate and tune the BP layer from p-type to n-type.
- This ambipolar Schottky junction device shows clear hysteresis and can serve as a nonvolatile memory device.

Dong Li, and Zengxing Zhang, Nano Letters, 17, 6353, 2017

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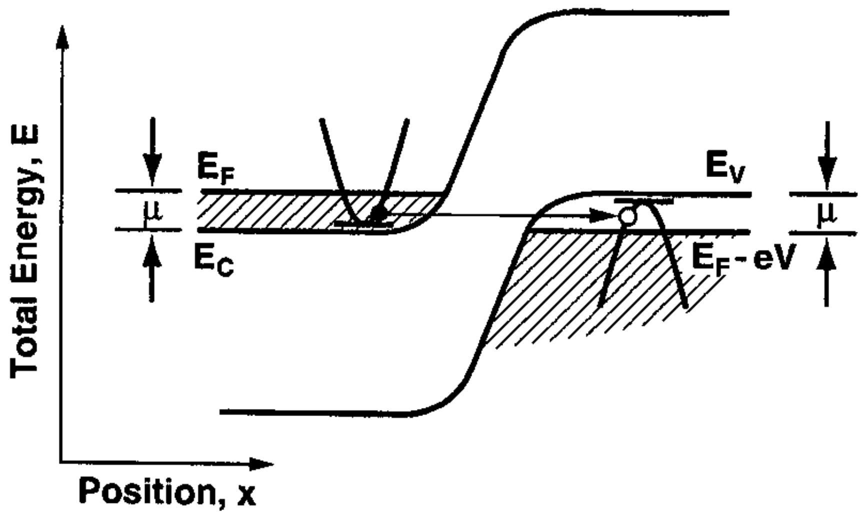
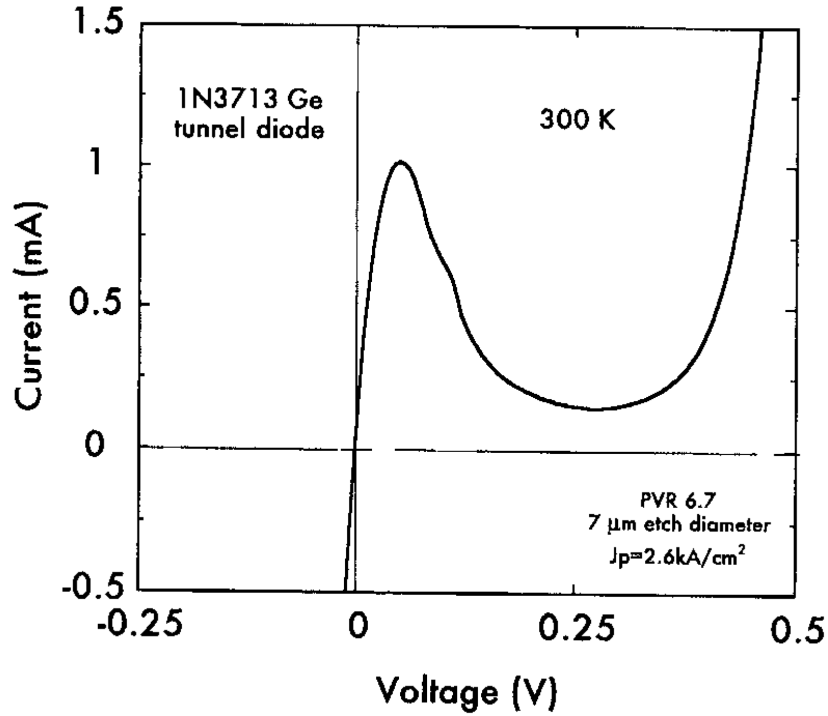
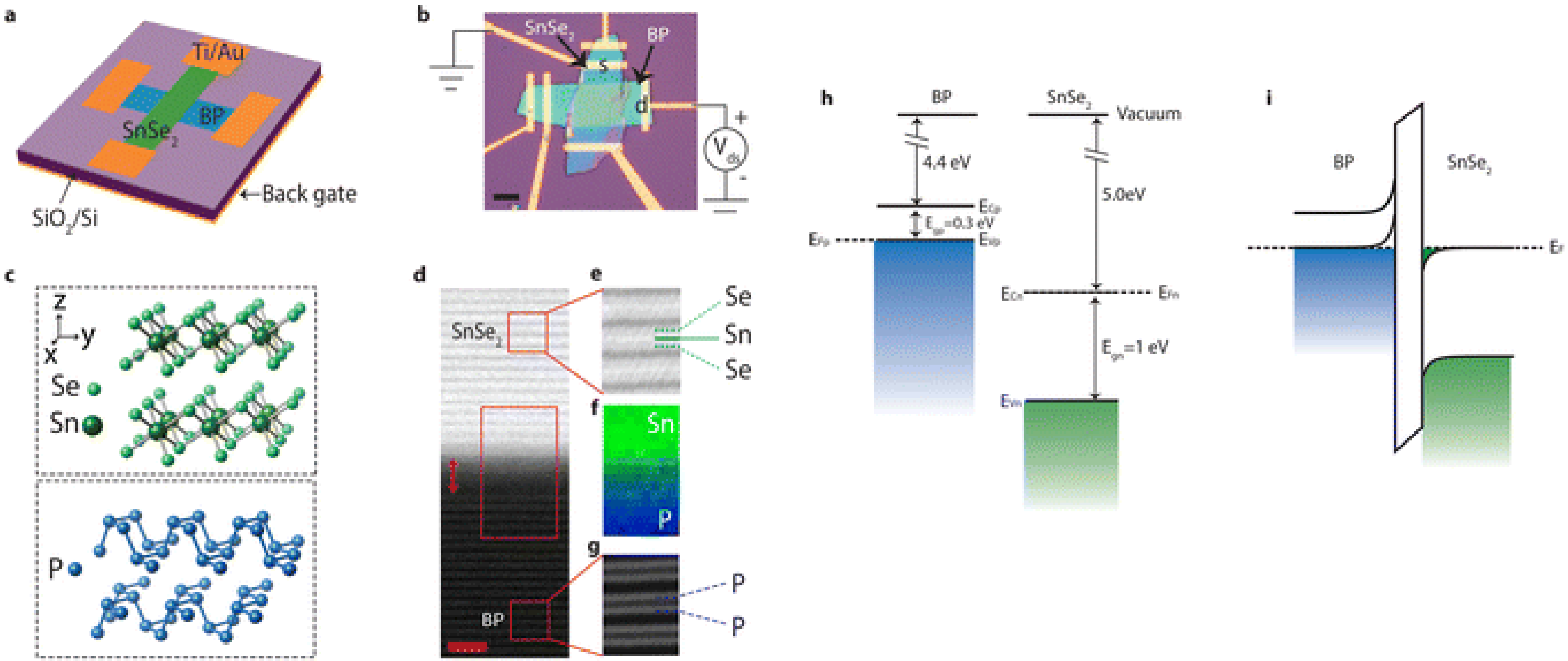
Review: Esaki diode





- **Esaki Diode is the p-n junction device that exhibits negative resistance.**
- **As bias is applied, electrons flow from the filled emitter states in the conduction band on the left to empty states in the valence band on the right.**
- **As bias is increased, the conduction band of the emitter is eventually raised above the valence band of the collector, electrons can no longer tunnel into a valence-band state in the collector and the current is reduced to a minimum value.**

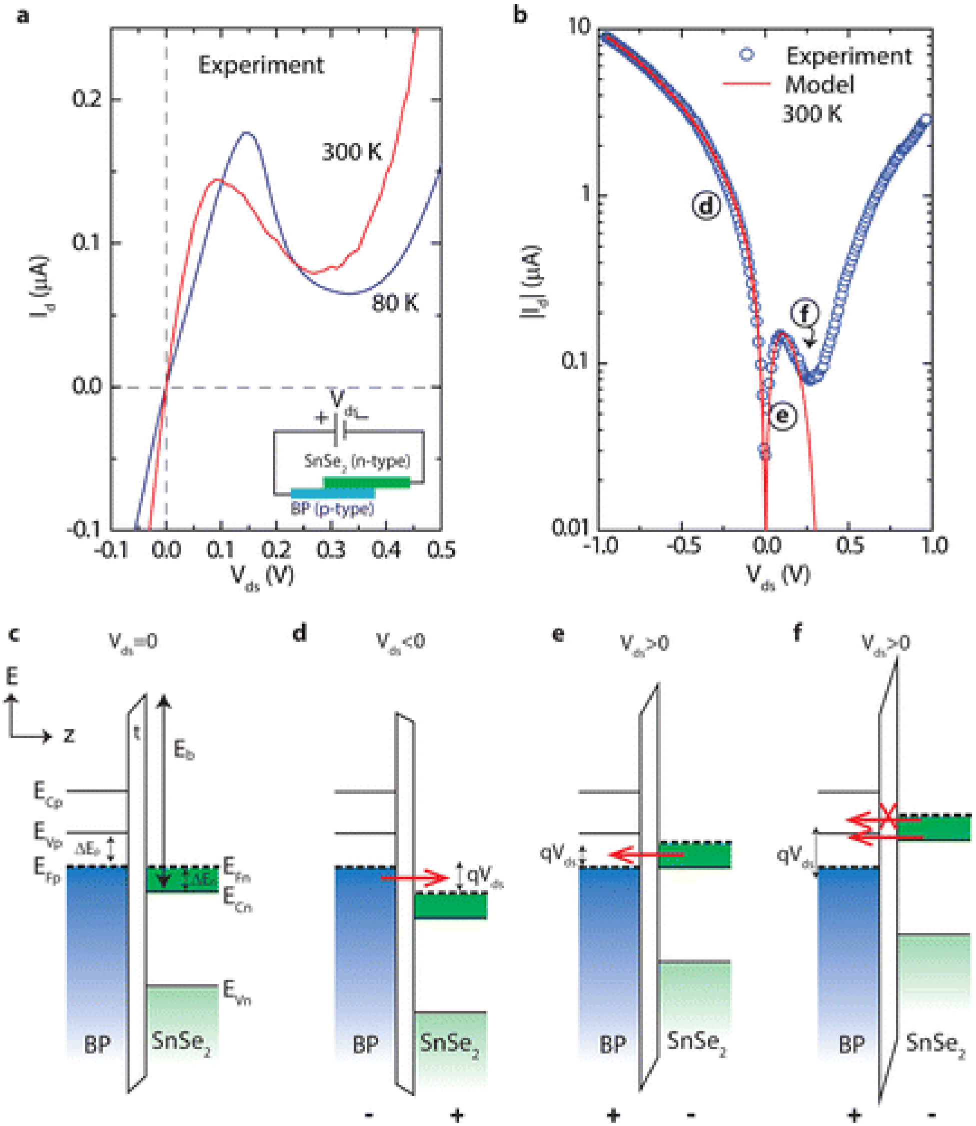
BP/$SnSe_2$ heterostructure



- **The Esaki diodes were realized in vdW heterostructures made of black phosphorus (BP) and tin diselenide ($SnSe_2$), two layered semiconductors that possess a broken-gap energy band offset.**

Rusen Yan, and Huili Grace Xing, Nano Letters, 15, 5791,2015

Esaki diode based on BP/$SnSe_2$



- The presence of a thin insulating barrier between BP and $SnSe_2$ enabled the observation of a prominent negative differential resistance (NDR) region in the forward-bias current–voltage characteristics, with a peak to valley ratio of 1.8 at 300 K and 2.8 at 80 K.

Rusen Yan, and Huili Grace Xing, Nano Letters, 15, 5791,2015

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- Photonic devices based on black phosphorus
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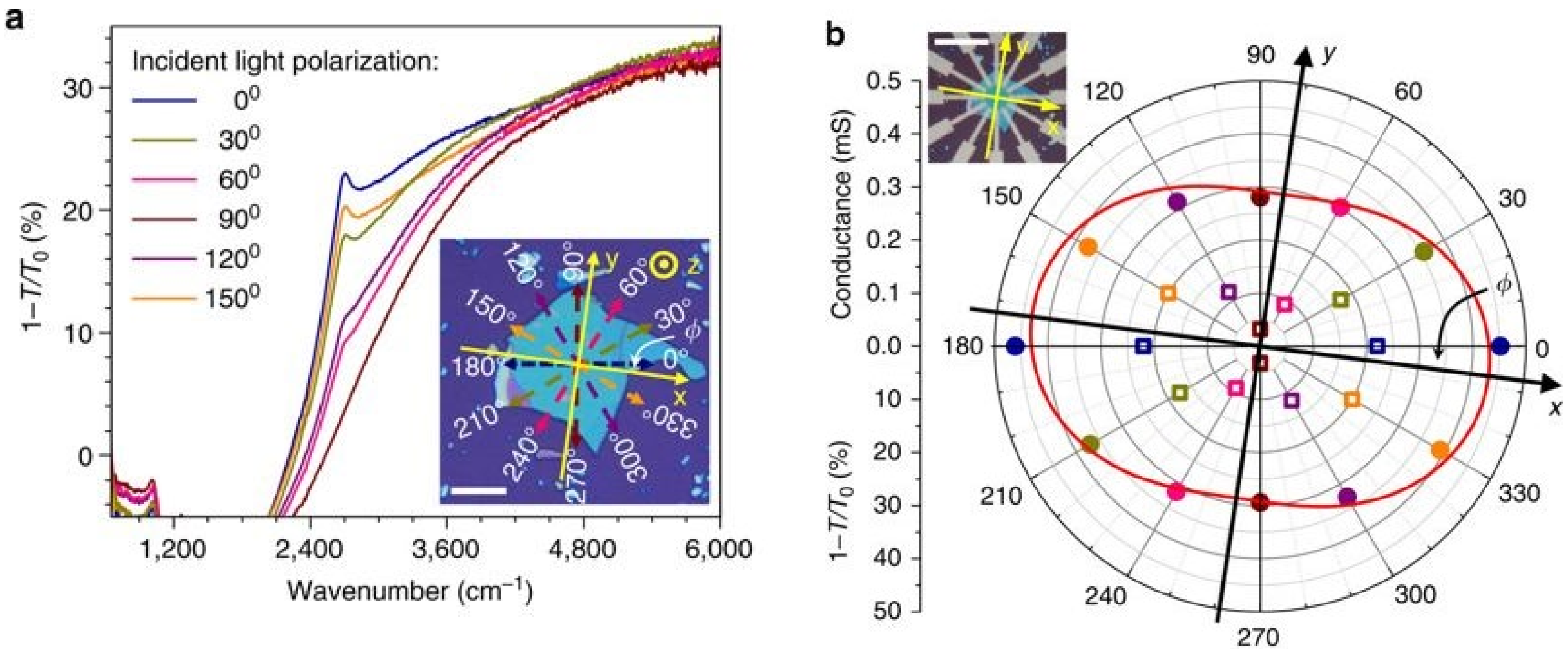
    - Optical absorption
    - Excitons in BP
  - Photonic devices

Anisotropic optical absorption

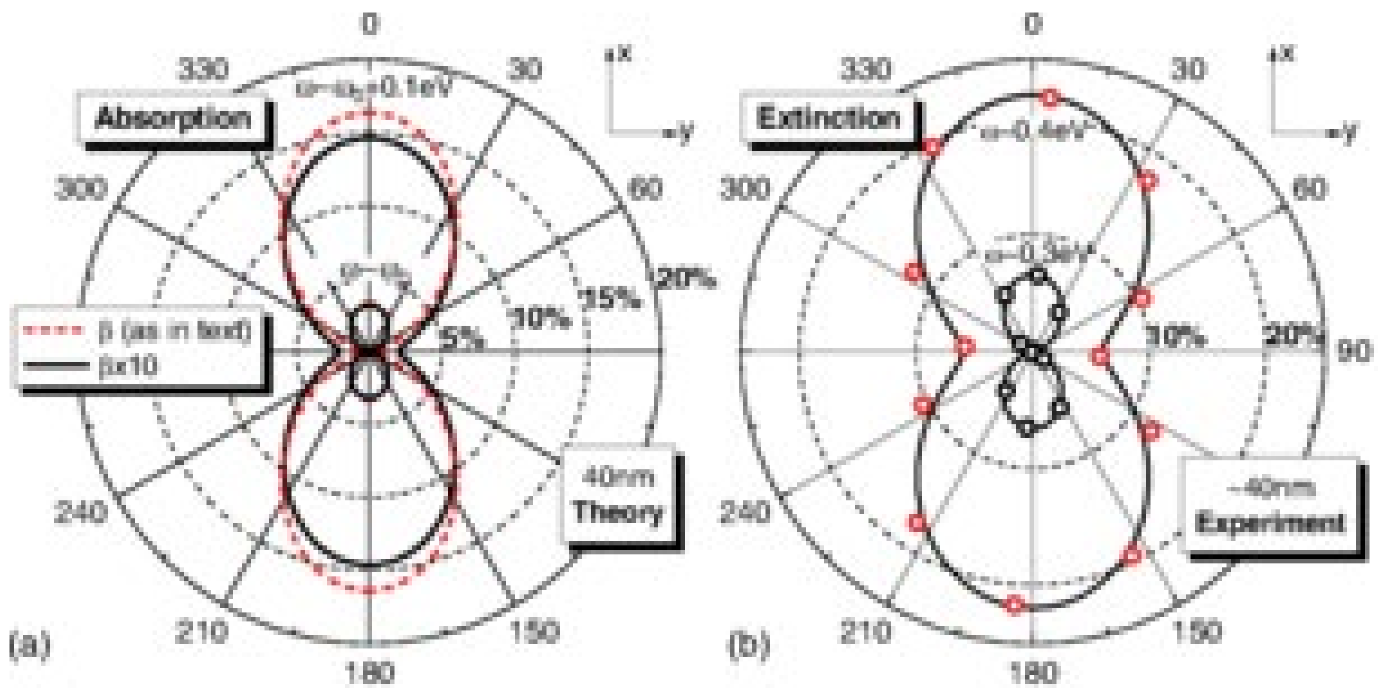


Extinction: $Z = 1 - T/T_0$, where T and T_0 are the transmission with and without BP.

- BP thin films also exhibit large and anisotropic in-plane optical conductivity.

Fengnian Xia, Yichen Jia, Nature Communications, 5, 4458, 2014

Anisotropy of optical absorption in BP: modeling



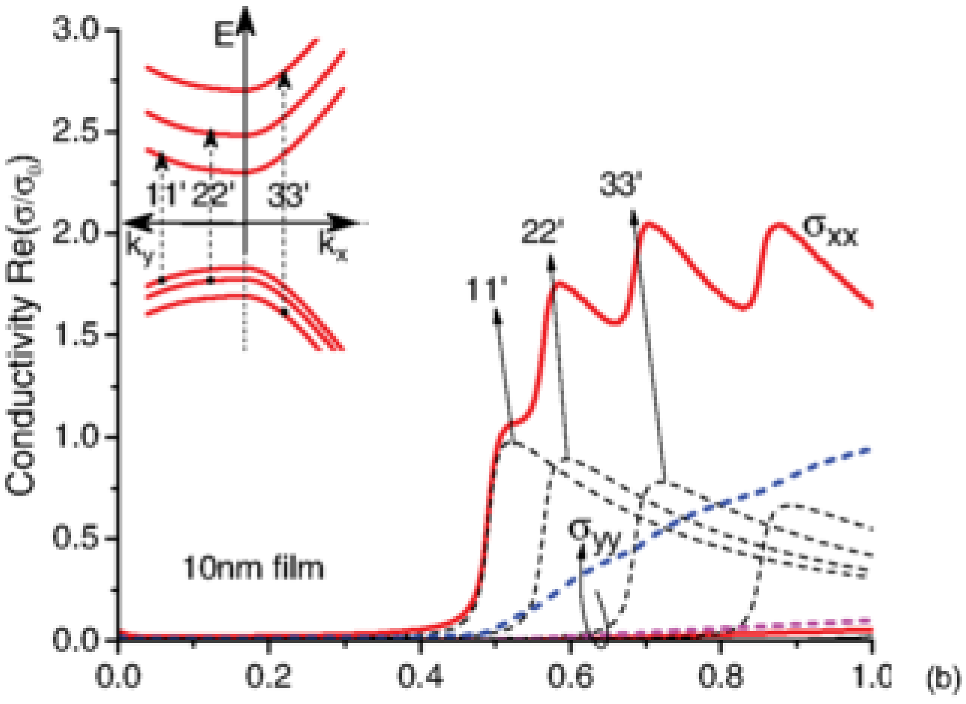
For normal incidence, the reflectivity $r = -\dfrac{\epsilon_0 c(\sqrt{\epsilon_2} - \sqrt{\epsilon_1}) + \sigma_{xx}cos^2\alpha + \sigma_{yy}sin^2\alpha}{\epsilon_0 c(\sqrt{\epsilon_2} + \sqrt{\epsilon_1}) + \sigma_{xx}cos^2\alpha + \sigma_{yy}sin^2\alpha}$

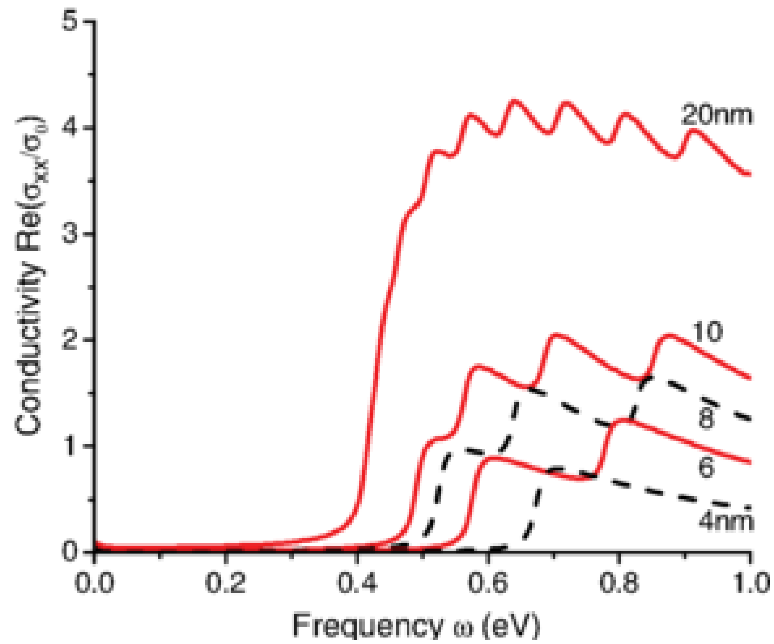
The reflection probability $\mathrm{R} \approx |r|^2$ and transmission probability $\mathrm{T} \approx |1 + r|^2\sqrt{\epsilon_2/\epsilon_1}$

The absorption coefficient $\mathrm{A} = 1 - R - T.$

Tony Low, A. H. Castro Neto, et.al., Physical Review B, 90, 075434 (2014)

Thickness dependence of optical absorption





- **As the thickness increases, the band edge reflected in the absorption spectra moves towards lower energies and eventually reaches 0.3 eV (for bulk BP).**
- **The thicker the sample, the more peaks in the spectra. These peaks are ascribed to the intersubbands transition.**

Tony Low, A. H. Castro Neto, et.al., Physical Review B, 90, 075434 (2014)

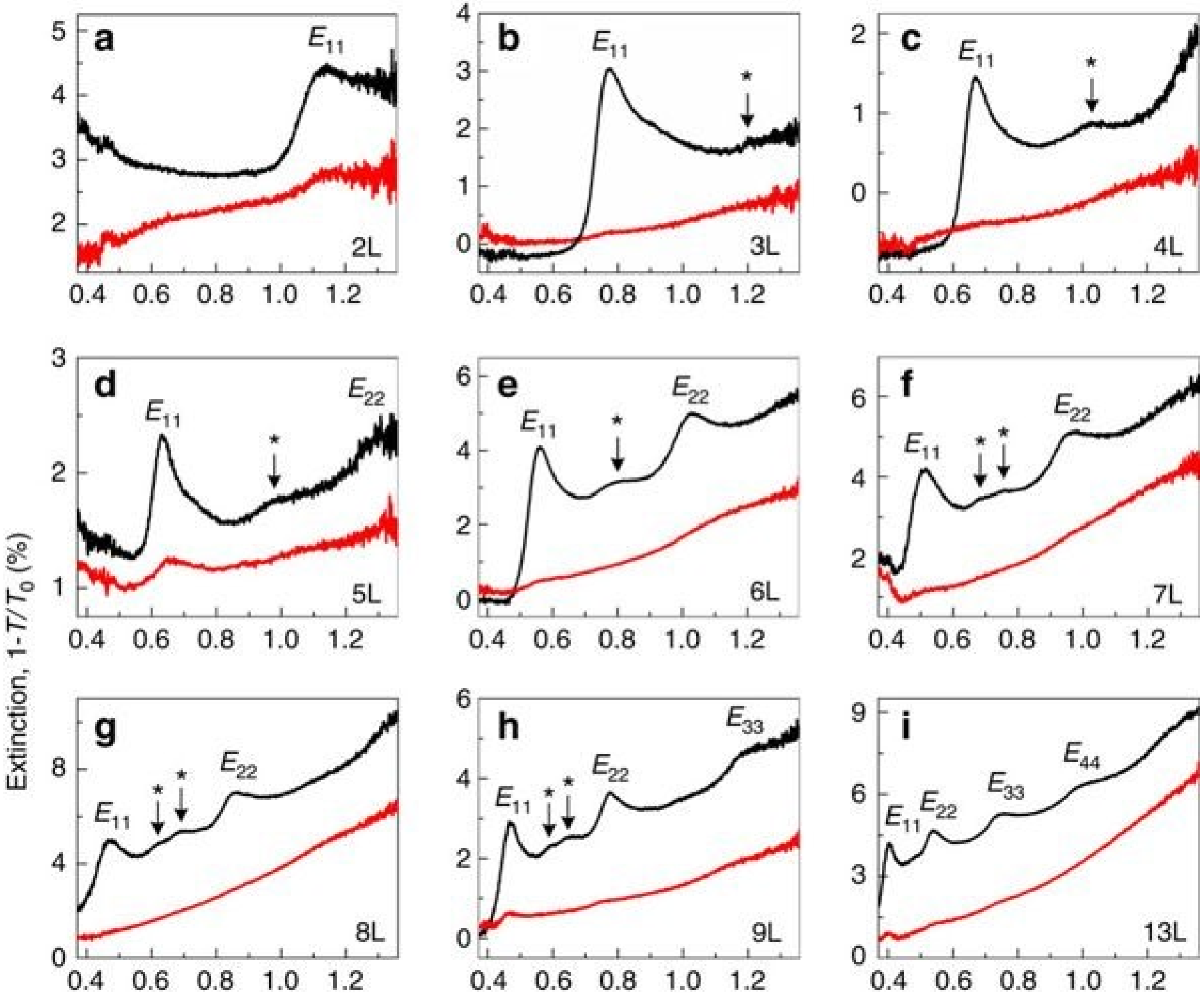
Optical conductivity

- **Optical conductivity is a material property, which links the current density to the electric field for general frequencies.**
- **Electrical conductivity is usually considered in the static limit, i.e., for a time-independent (or sufficiently slowly varying) electric field.**

- **The electric current density (a three-dimensional vector), the scalar optical conductivity and the electric field vector are linked by the equation:**

$$\overrightarrow{\boldsymbol{J}(\boldsymbol{\omega})} = \boldsymbol{\sigma}(\boldsymbol{\omega})\overrightarrow{\boldsymbol{E}(\boldsymbol{\omega})}$$

Infrared fingerprints of BP

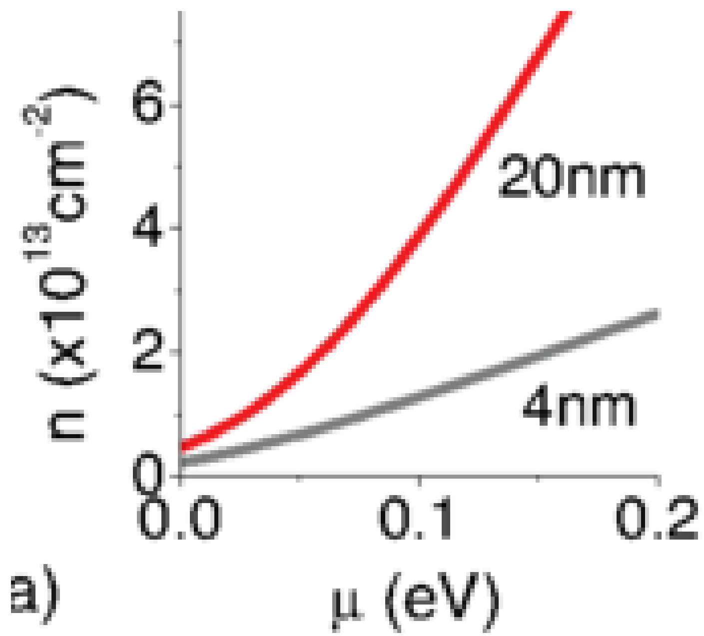


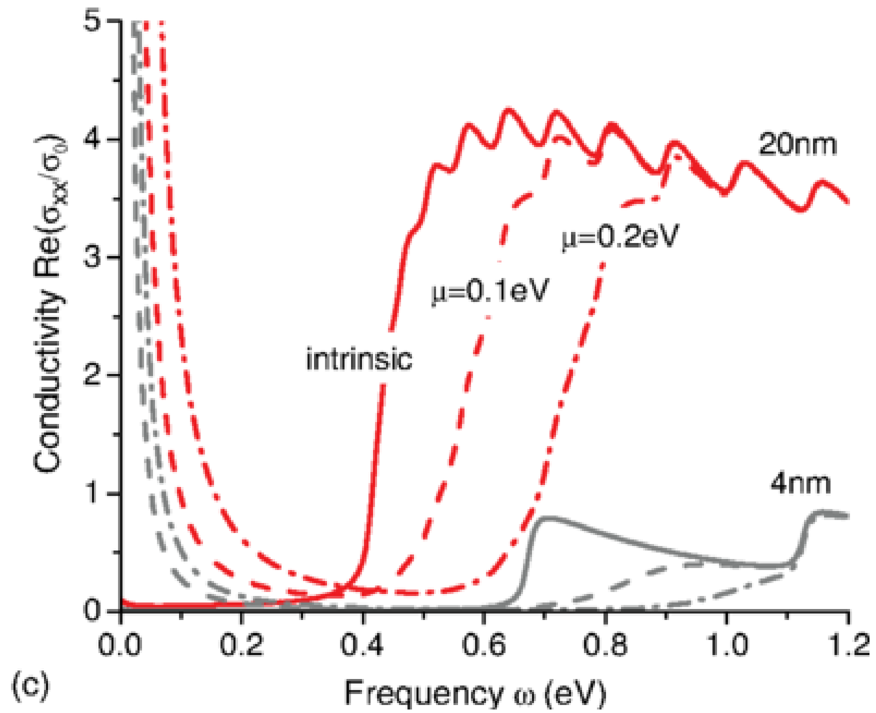
Black curve: armchair
Red curve: zigzag

- **Black phosphorus exhibits a thickness-dependent unique infrared spectrum with a series of absorption resonances, which serves as its infrared fingerprints**

Guowei Zhang, Hugen Yan, Nature Communications, 8, 14071, 2017

Impact of doping on optical absorption





- Charge doping, regarded as a shift in chemical potential $\mu = E_F - E_{c1}$, can be realized by either electrically gating or chemically introducing charge donor or acceptor impurities.
- Extra electrons shift the band edge in the absorption spectra towards higher energies, because of the Pauli blocking by the extra charges of the direct optical transition

Tony Low, A. H. Castro Neto, et.al., Physical Review B, 90, 075434 (2014)

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- Introduction of black phosphorus
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- Photonic devices based on black phosphorus
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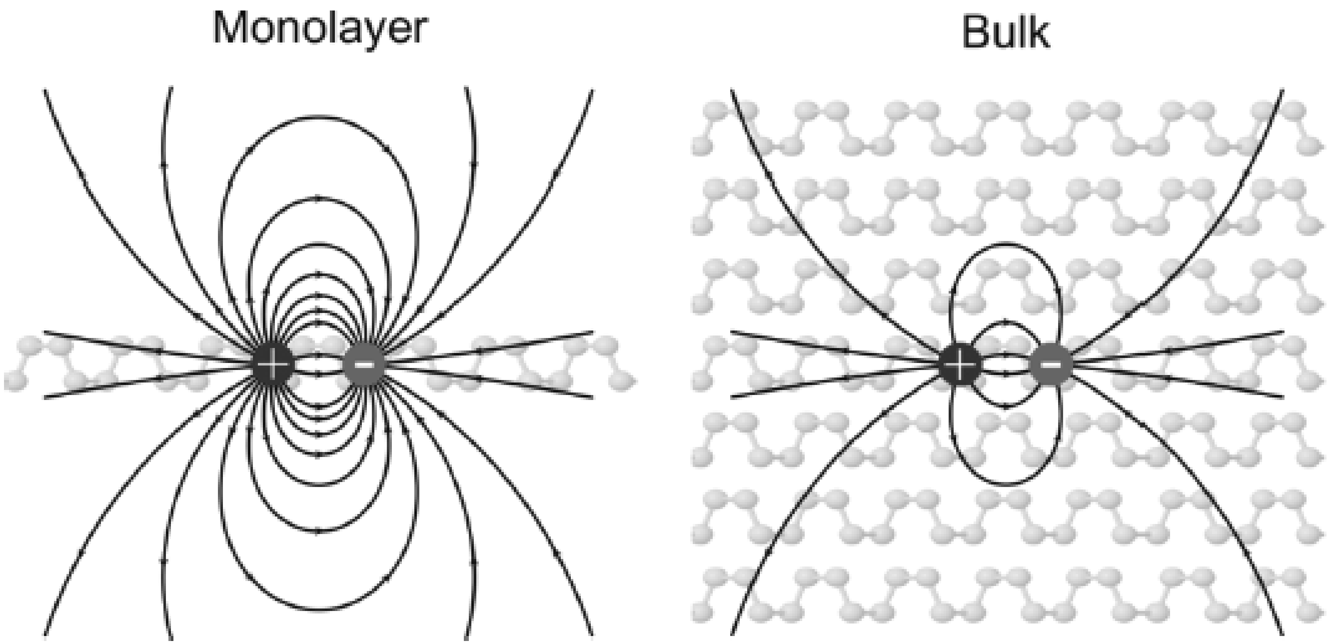
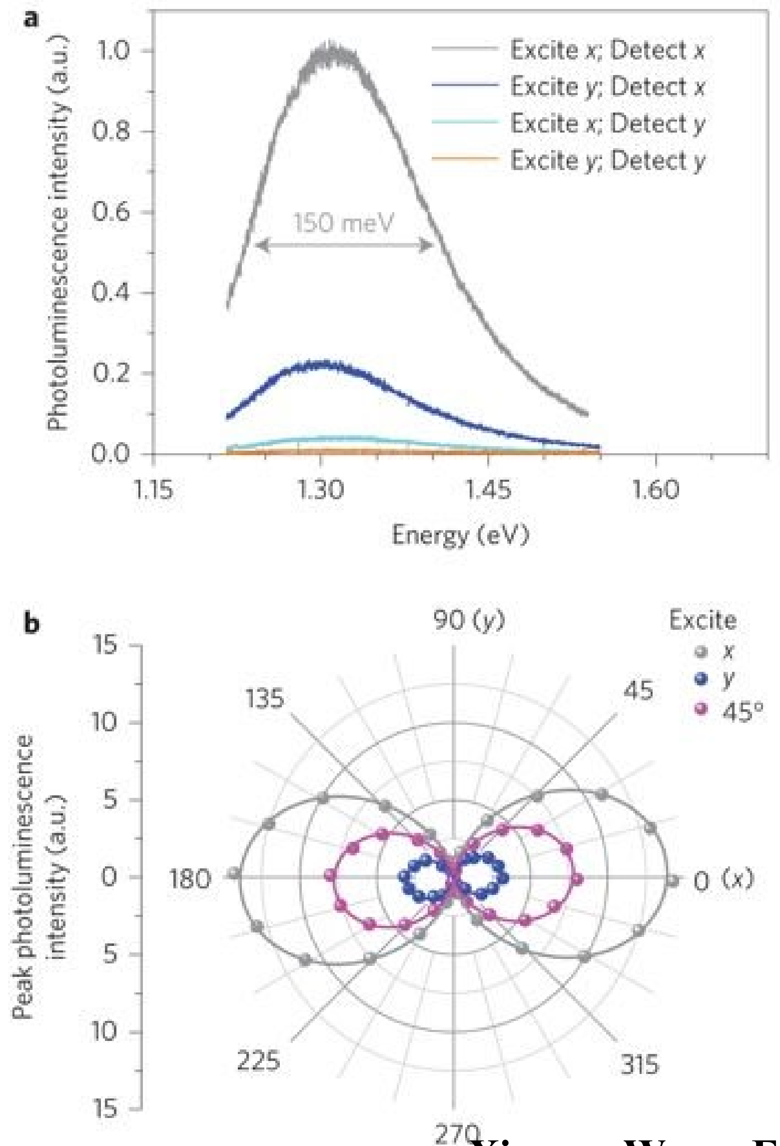
    - Optical absorption
    - Excitons in BP
  - Photonic devices

Exciton in BP



- Similar to TMDs, BP also has high electron–hole (exciton) binding energies due to electron–hole Coulomb interaction in these materials undergoes a much lower screening by the vacuum surrounding the sample,

Anisotropic excitons in BP

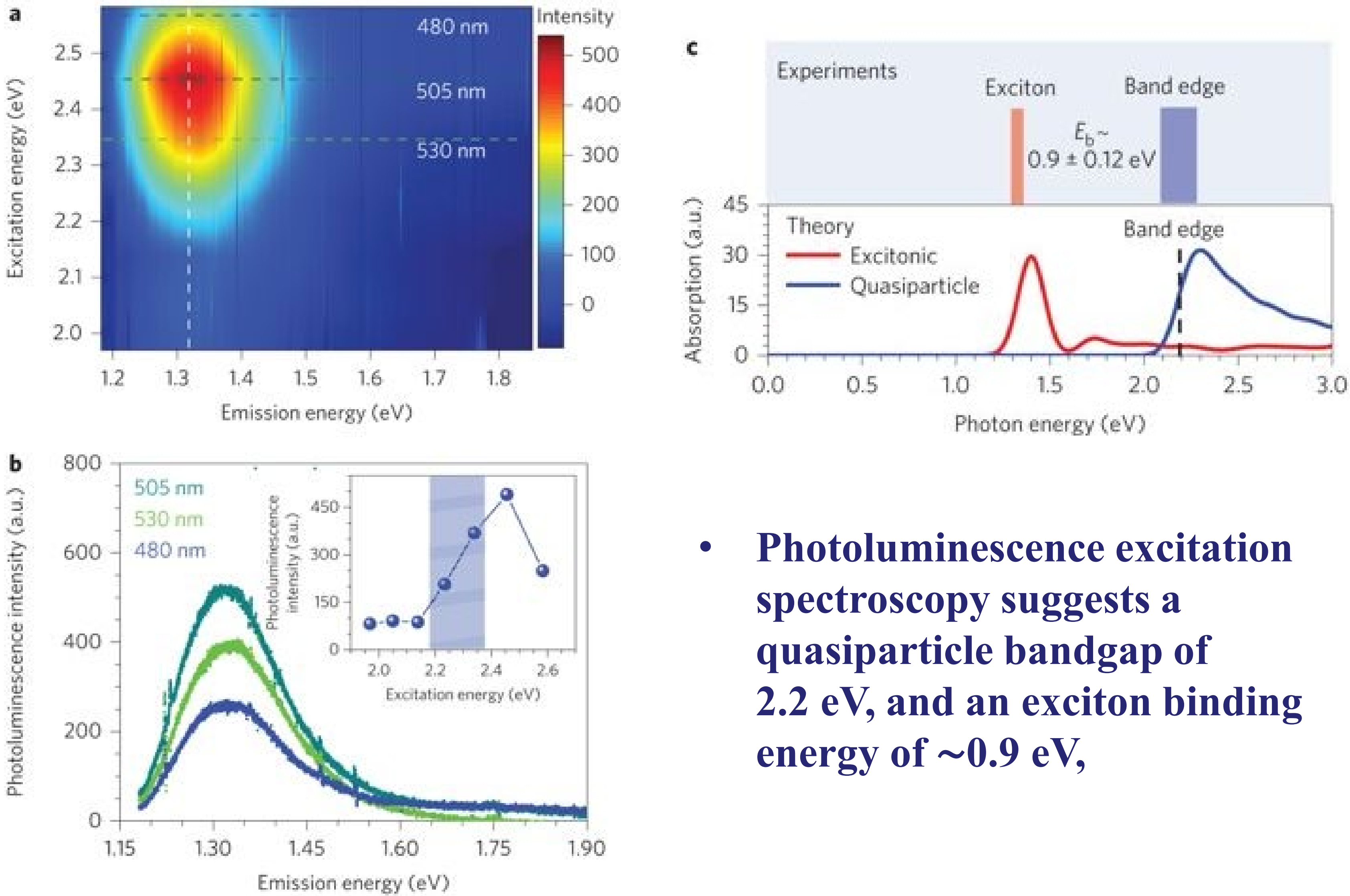


Highly anisotropic and strongly bound excitons in monolayer black phosphorus was observed using polarization-resolved photoluminescence measurements at room temperature.

Regardless of the excitation laser polarization, the emitted light from the monolayer is linearly polarized along the light effective mass direction and centers around 1.3 eV, a clear signature of emission from highly anisotropic bright excitons.

Xiaomu Wang, Fengnian Xia, Nature Nanotechnology, 10, 517, 2015

Exciton binding energy in BP



- **Photoluminescence excitation spectroscopy suggests a quasiparticle bandgap of 2.2 eV, and an exciton binding energy of ~0.9 eV,**

Xiaomu Wang, Fengnian Xia, Nature Nanotechnology, 10, 517, 2015

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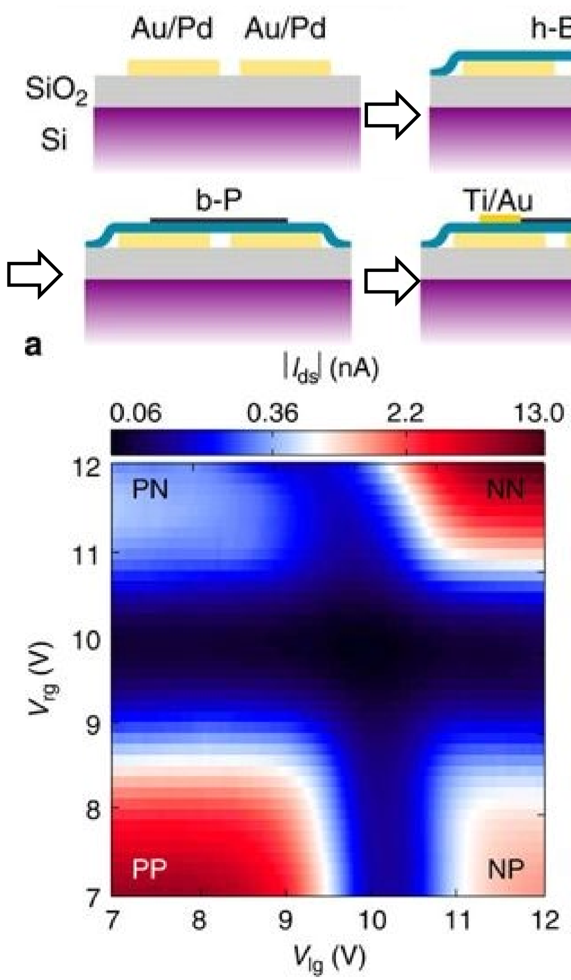
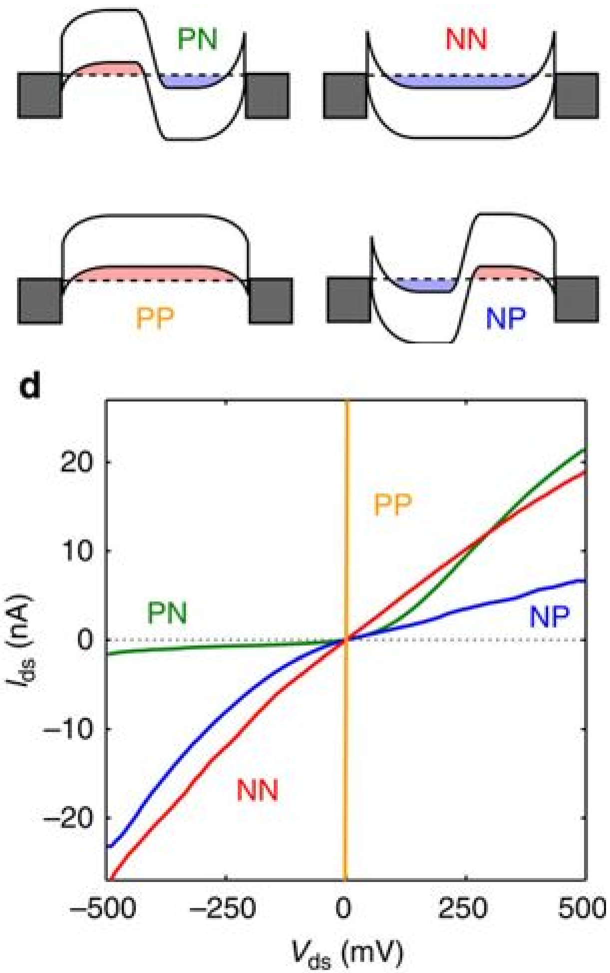
    - Plasmonic device
    - Electro-optical modulators

PN junctions controlled by the local split gates

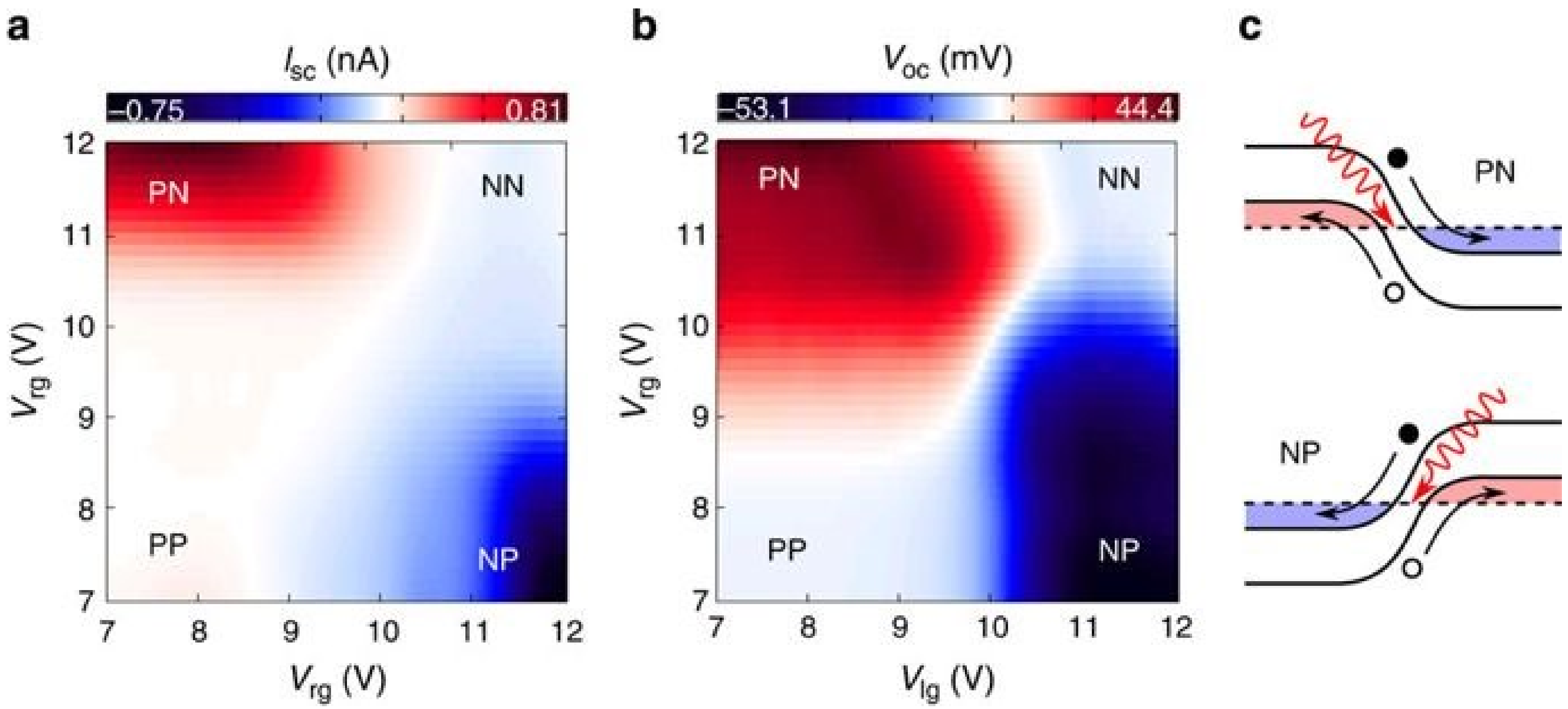




- **BP field-effect transistors with split gates shows electrostatic control of the local charge carrier type and density in the device.**

Michele Buscema1, Andres Castellanos-Gomez, Nature Communications, 5, 4651, 2014

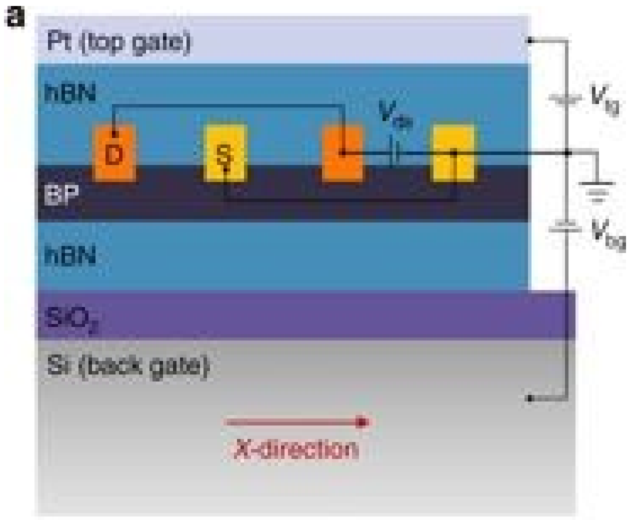
Photovoltaic effect in BP pn junctions

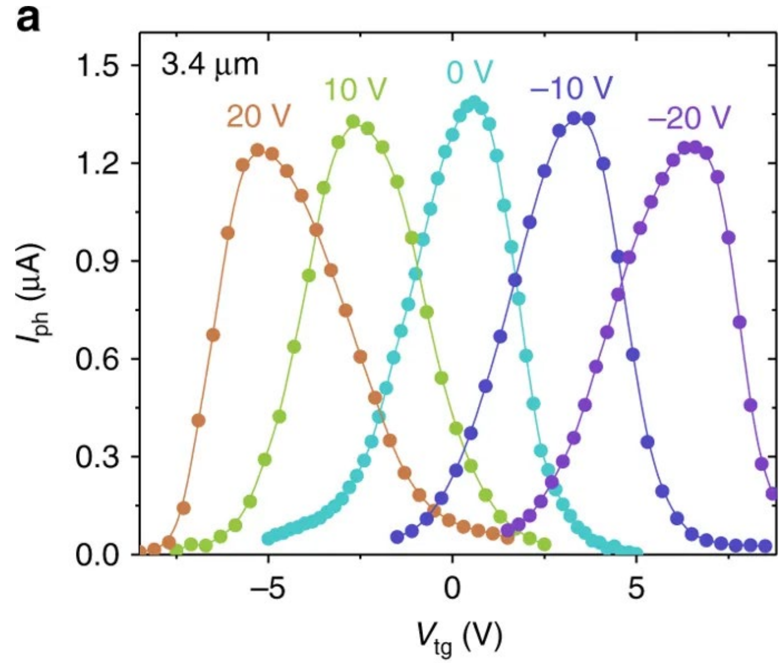


- **Illuminating the BP transistor with split gates, zero-bias photocurrents and significant open-circuit voltages due to the photovoltaic effect was observed when the transistor are bias into pn or np junctions.**

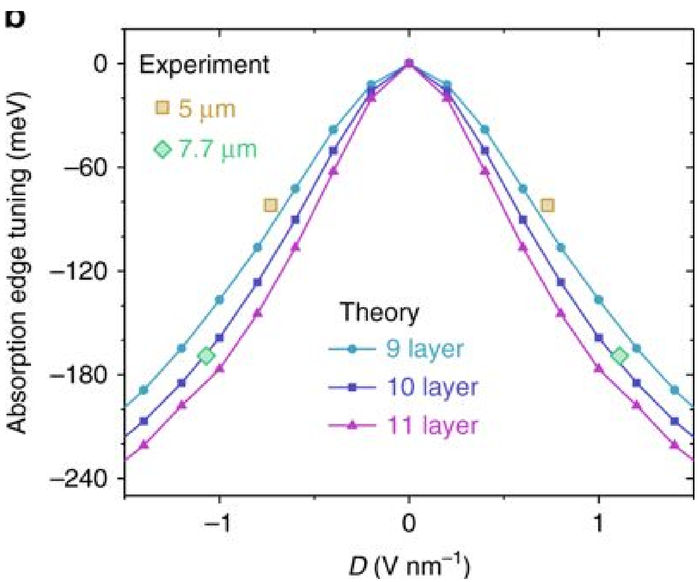
Michele Buscema1, Andres Castellanos-Gomez, Nature Communications, 5, 4651, 2014

Tunable photodetectors





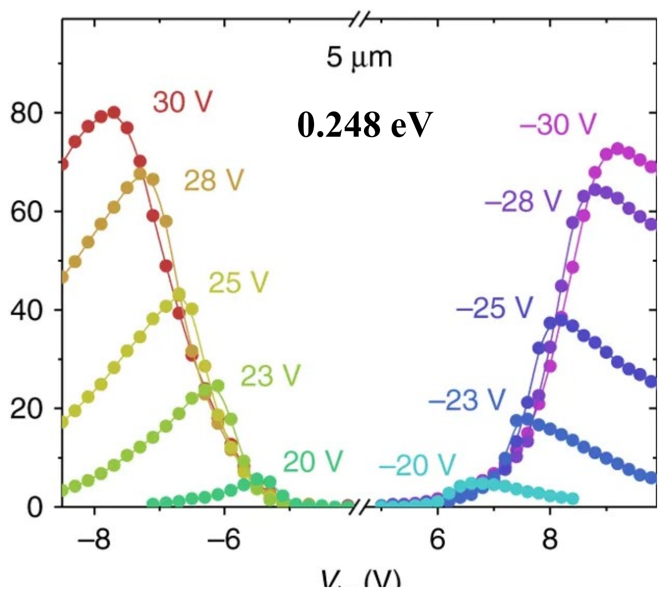
0.36 eV

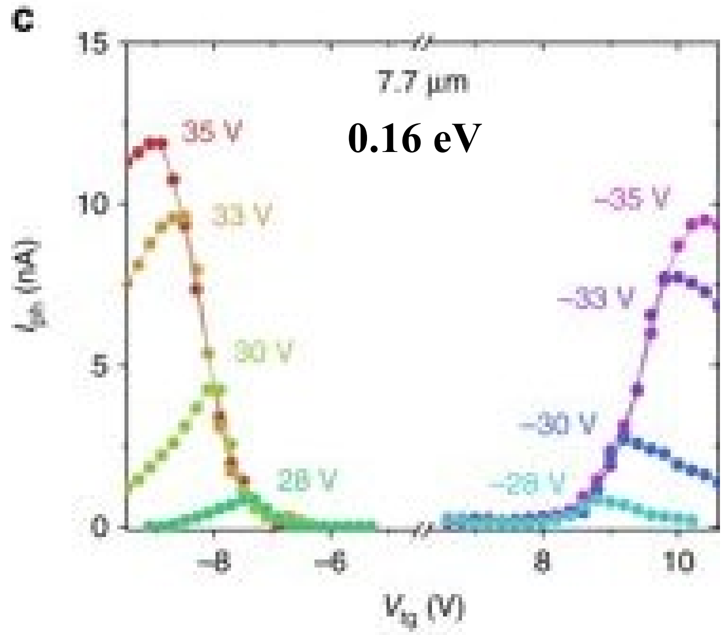


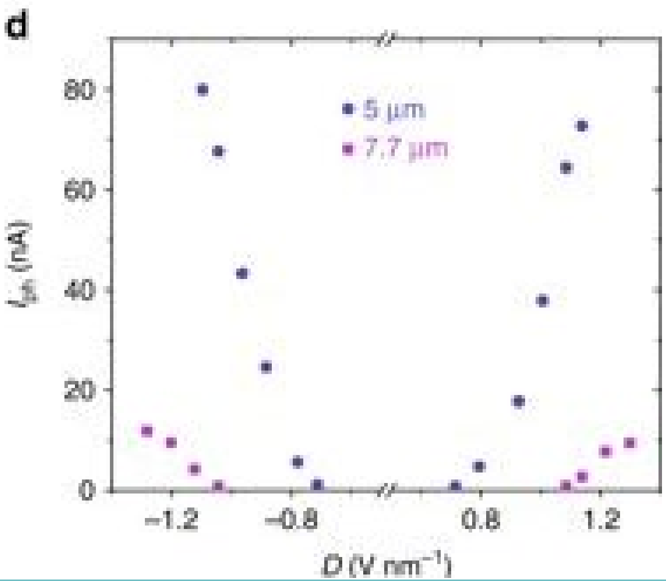
Photocurrent reach maximum at charge neutrality point, due to higher photo-carrier scattering rate when the carrier density increases. This is the key signature of the photoconductive effect.

Xiaolong Chen, Fengnian Xia, Nature Communications, 8, 1672, 2017

Tunable photodetectors

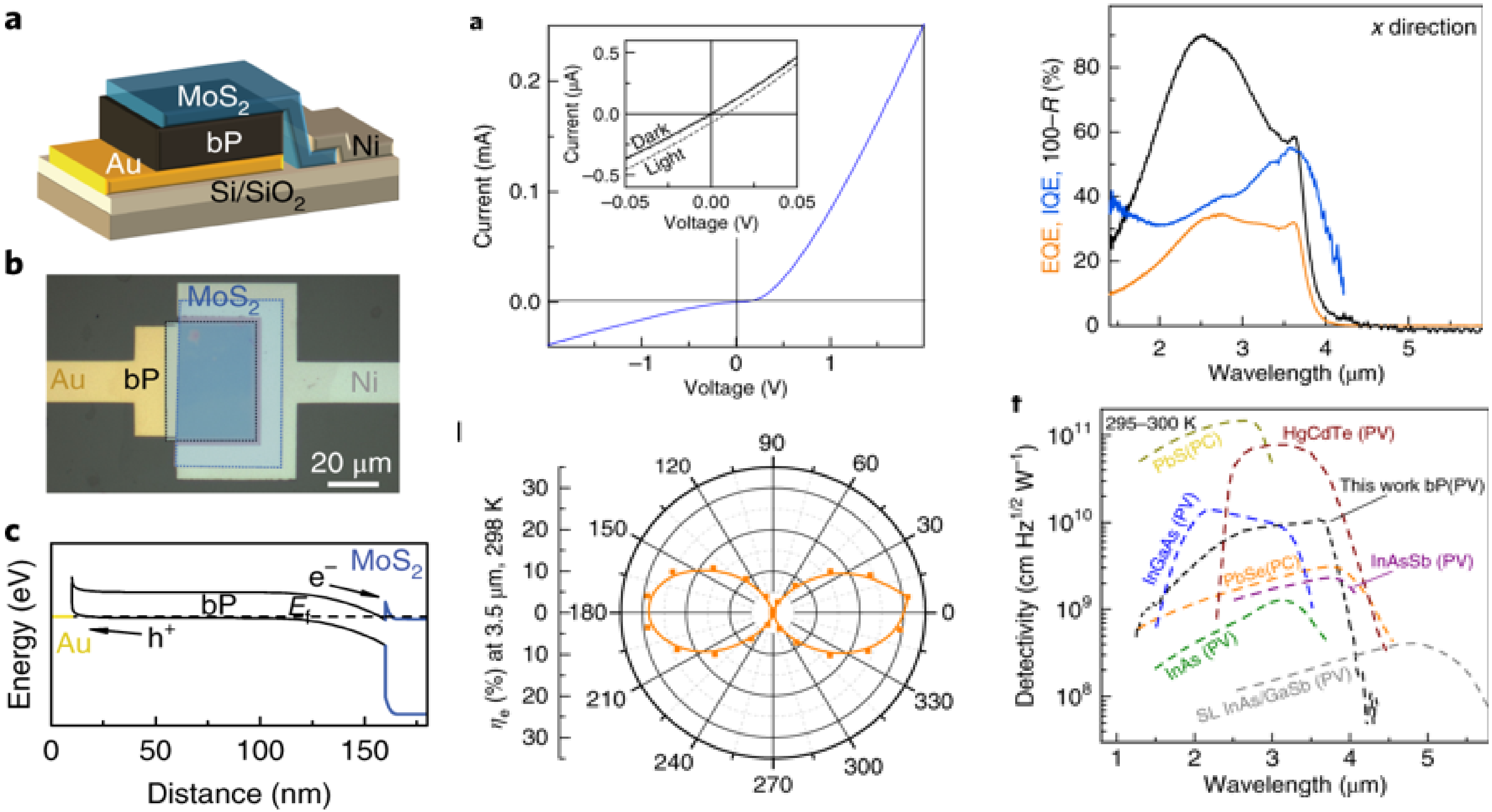






- **A vertical electric field can dynamically extend the photoresponse in a 5 nm-thick BP photodetector from 3.7 to beyond 7.7 µm.**

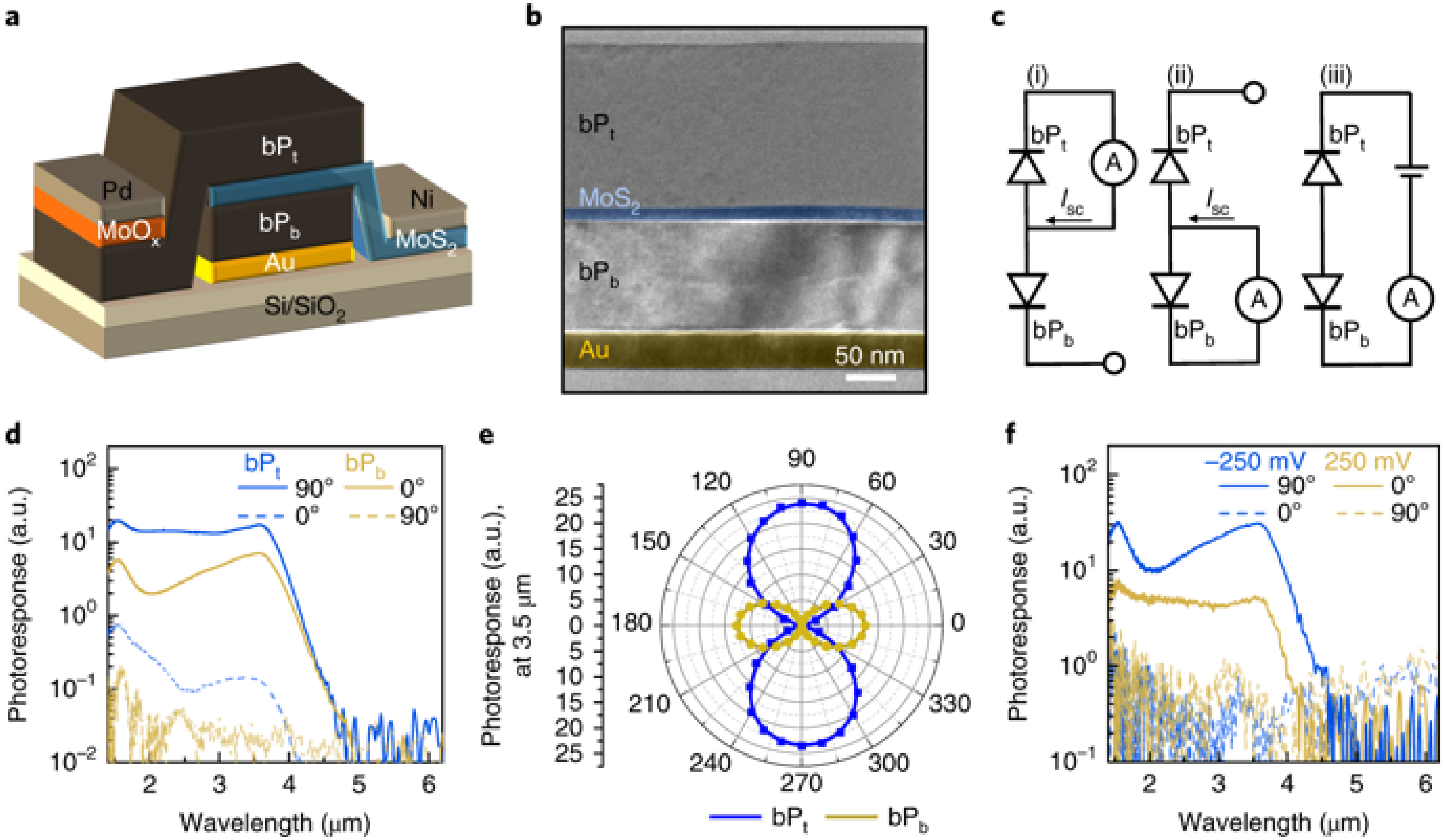
Photodetector based on BP/MoS_2



- By using BP/MoS_2 heterostructure, the room-temperature external quantum efficiencies reach 35% and specific detectivities (D*) is as high as 1.1×10^{10} cm $Hz^{1/2}$ W^{-1} in the mid-wave infrared region.

James Bullock, Ali Javey, Nature Photonics, 12, 601, 2018

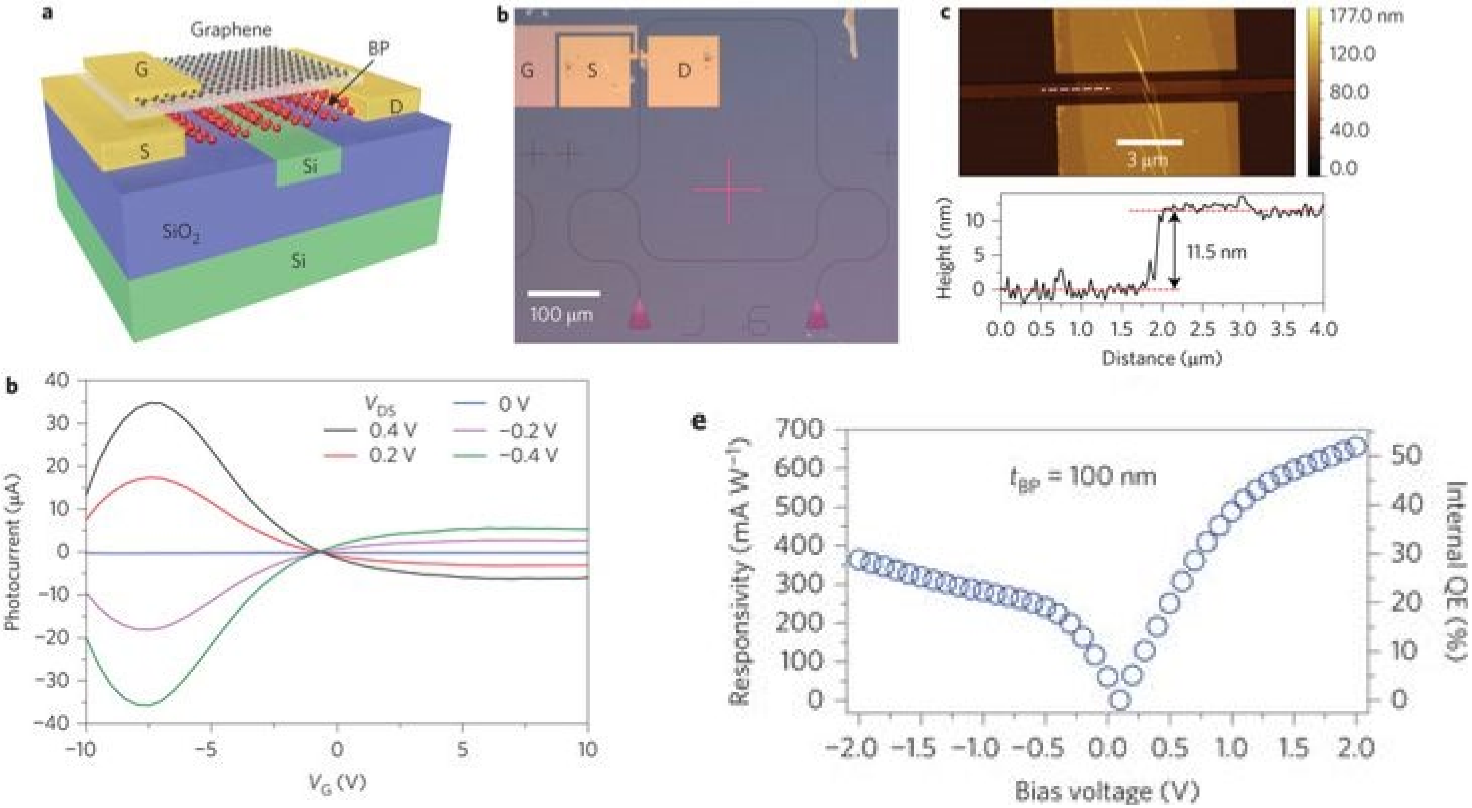
Polarization-resolved photodetector



- The device consists of two vertically stacked BP layers arranged so that their crystal orientations are perpendicular to one another.
- In configuration iii, the device exclusively collect only 0° or 90° linearly polarized light, under negative or positive biasing, i.e. this detector's polarization can be controlled electrically.

James Bullock, Ali Javey, Nature Photonics, 12, 601, 2018

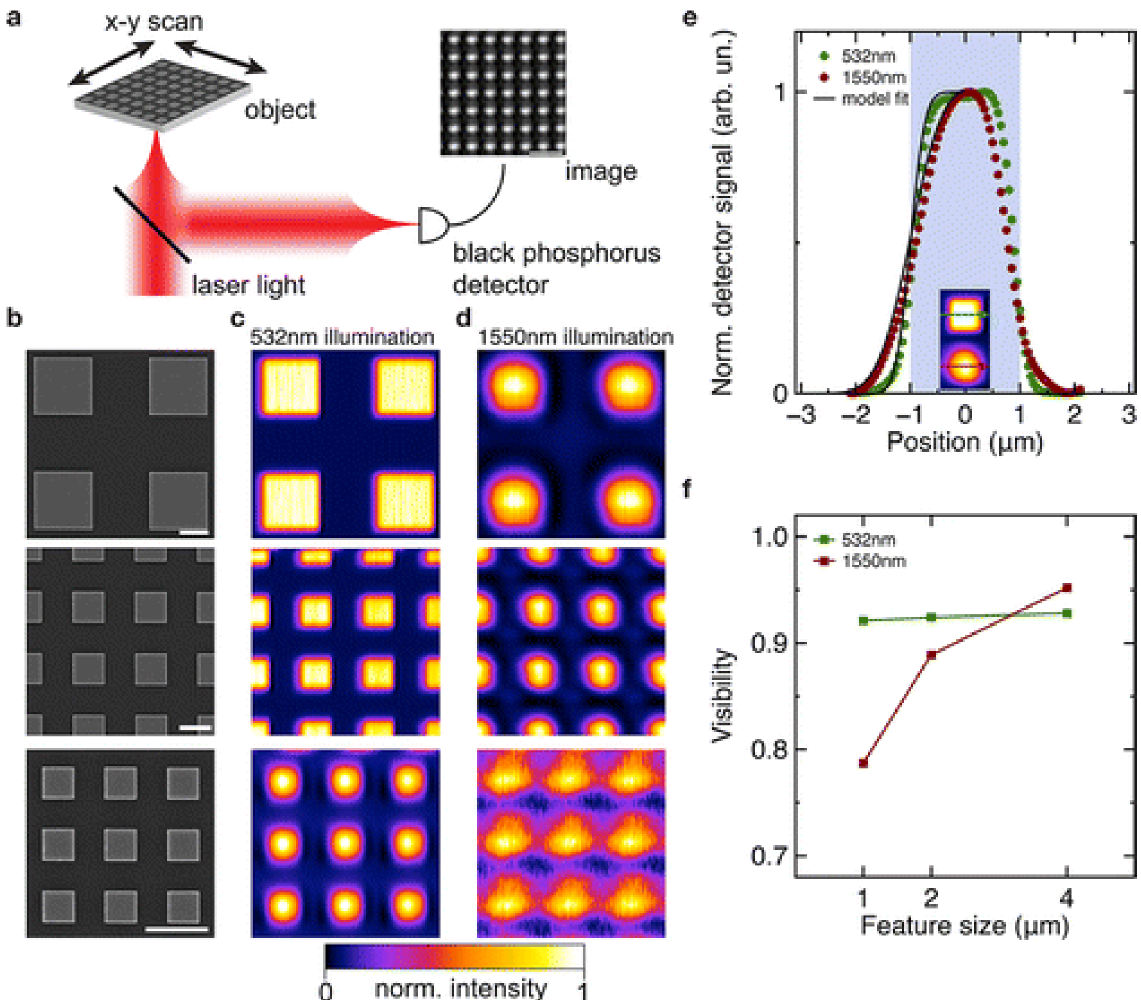
Waveguide-integrated BP photodetector



- **BP photodetector was integrated with silicon photonic waveguide so that the optical interaction length is not bound by the thickness of the materials. These devices show an intrinsic responsivity up to 657 mA/W and internal quantum efficiency of ~50%.**
- **As compared to graphene devices, black phosphorus photodetectors have the advantages of low dark current.**

Nathan Youngblood, Mo Li, Nature Photonics, 9, 247, 2015

BP photodetector for imaging

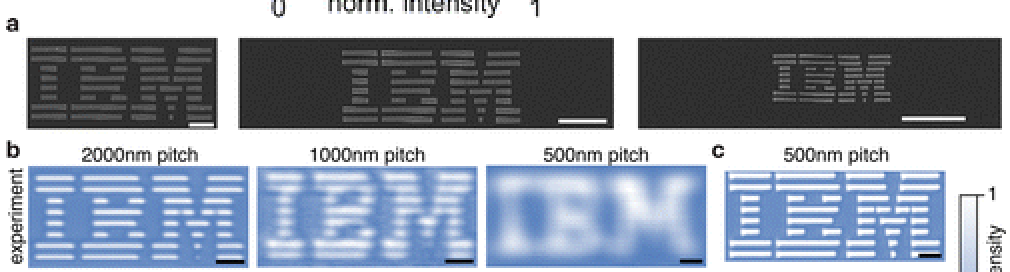


4µm

2µm

1µm

By deploying the black phosphorus device as a point-like detector in a confocal microsope setup, the authors acquire diffraction-limited optical images with submicron resolution.



λ_{IR} = 1550 nm λ_{vis} = 532 nm

Michael Engel, Phaedon Avouris, Nano Letters, 14, 6414, 2014

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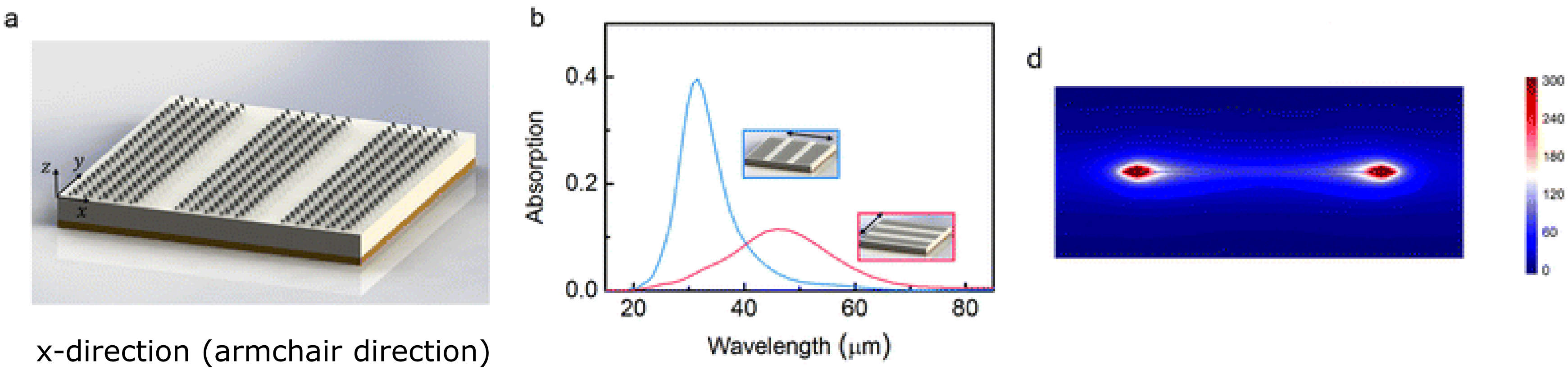
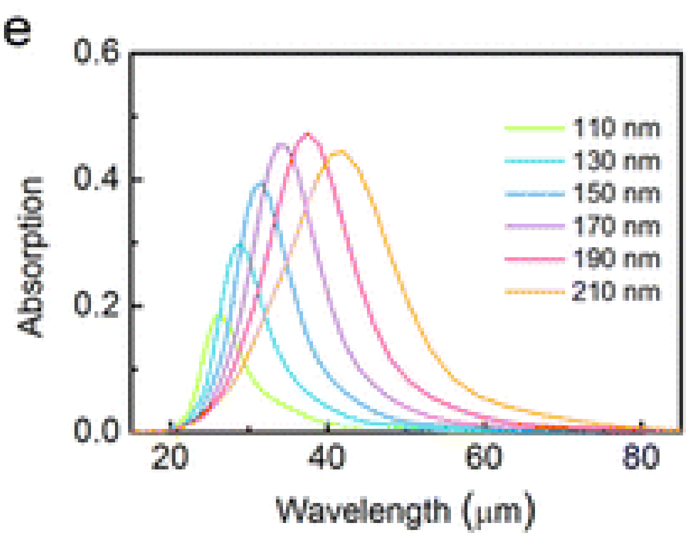
    - Modulators

Polarization dependent plasmonic structures



x-direction (armchair direction)



- **Localized surface plasmon resonances (LSPR) in a monolayer, nanostructured black phosphorus (BP) were calculated theoretically.**
- **Because of strong anisotropic in-plane properties of black phosphorus, BP nanostructures provide polarization dependent, anisotropic plasmonic response.**

Drude weight $D_j = \dfrac{\pi e^2 n}{m_j}$

j denotes the x or y direction

Plasmon resonant frequency $\omega_p = \sqrt{\dfrac{3D_j}{8\varepsilon_m \varepsilon_0 d}}$

Zizhuo Liu, Koray Aydin, Nano Letters, 16, 3457, 2016

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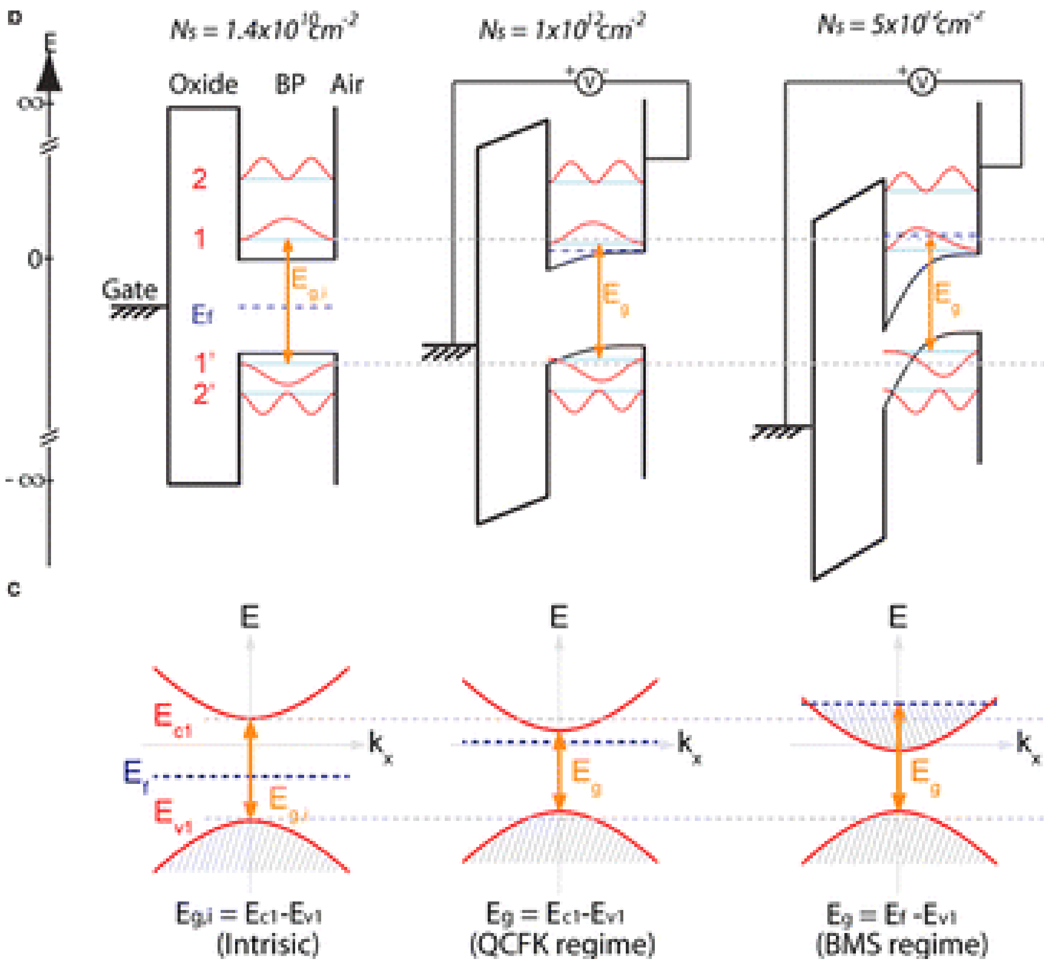
Electro-optic properties of BP



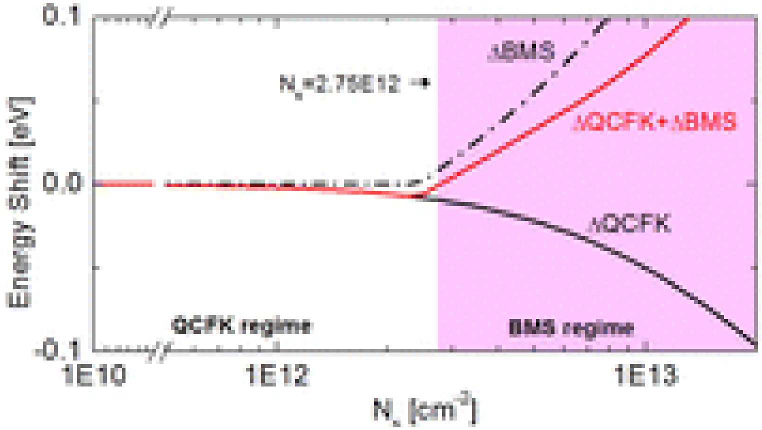
- **Quantum-confined Franz-Keldysh (QCFK) effect: With the application of a positive external gate bias, the out-of-plane electric field leads to band-bending across the quantum well, bringing the electron and hole subbands closer in energy, hence effectively reducing E_g.**

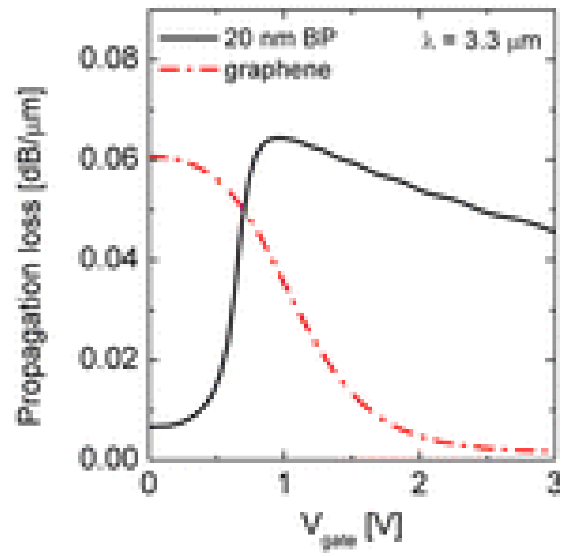
- **Pauli-blocked Burstein−Moss shift (BMS) : As the electron gas becomes more degenerate, Pauli blocking of the optical transitions lead to broadening of E_g.**

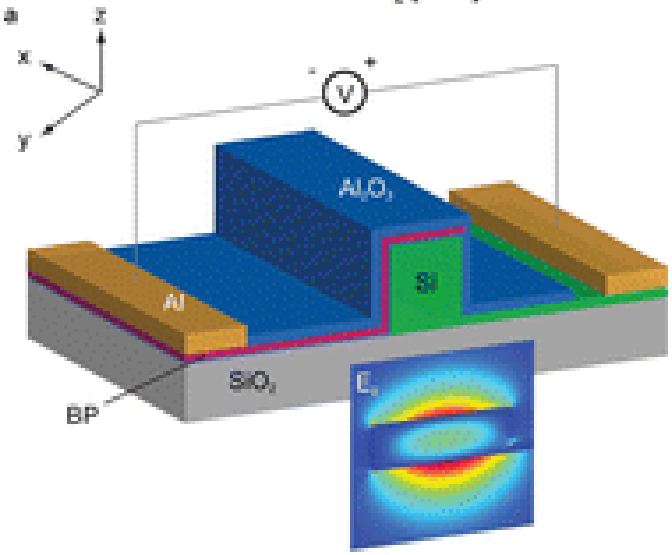
An applied out-of-plane electric field may lead to red-, blue-, or bidirectional shift in BP's absorption edge.

Charles Lin, Amr S. Helmy, Nano Letters, 16, 1683, 2016

Modulator based on BP







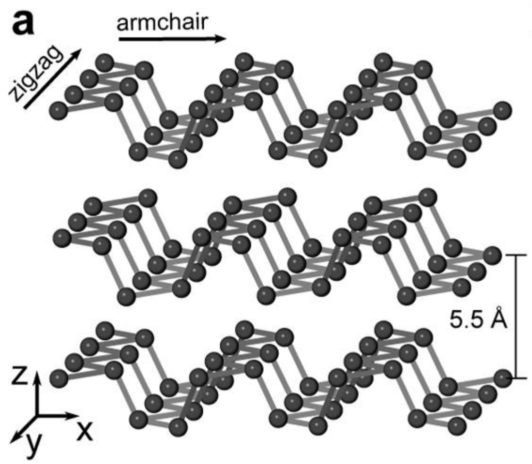
- The change in waveguide loss is more rapid in the QCFK regime, since the modulation is via an effective change in transition energy gap, below which there are no available electronic density of states for the optical transition. Conversely, BMS relies on Pauli blocking, where the optical transition edge is smeared in energy by kT.

- Electro-optical modulator configuration with BP overlaid over a silicon nanowire shows strong gate response.

Charles Lin, Amr S. Helmy, Nano Letters, 16, 1683, 2016

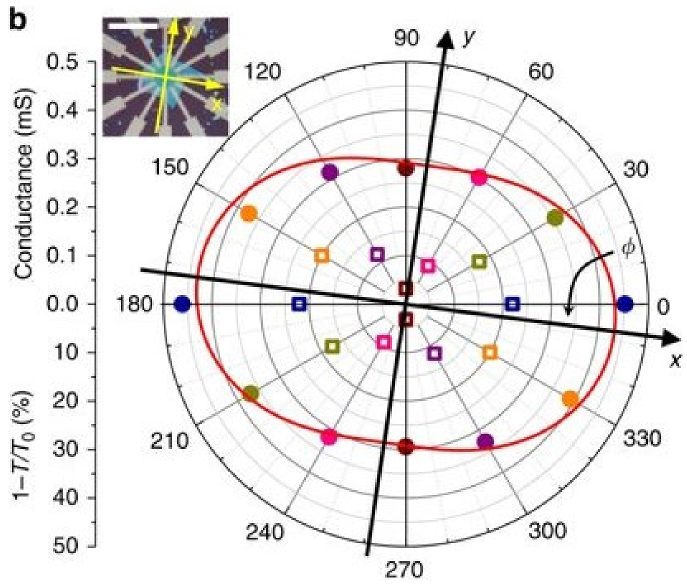
Summary (1)

Crystal structure



Puckered honeycomb structure

Anisotropic electric and optical conductivity

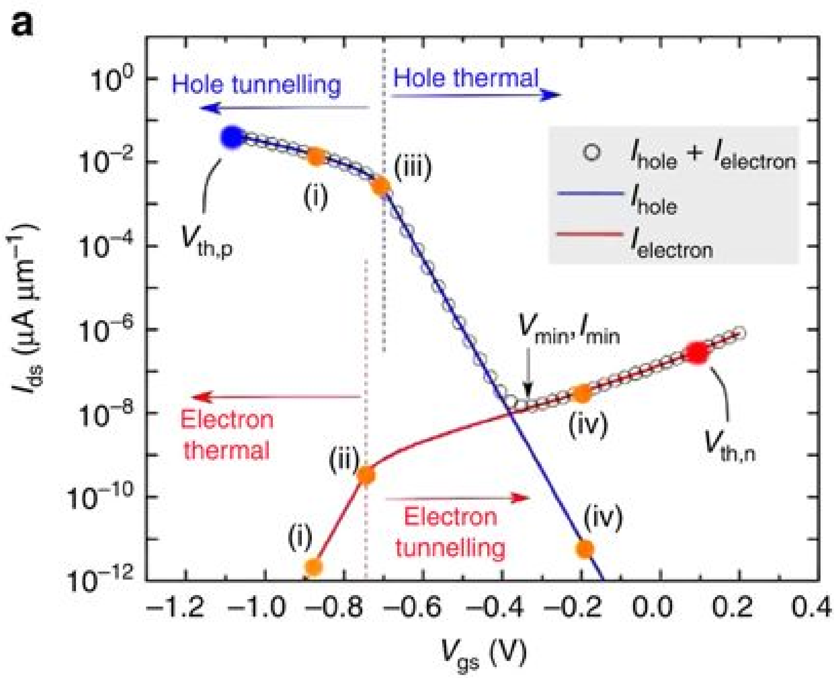


Thermal stability

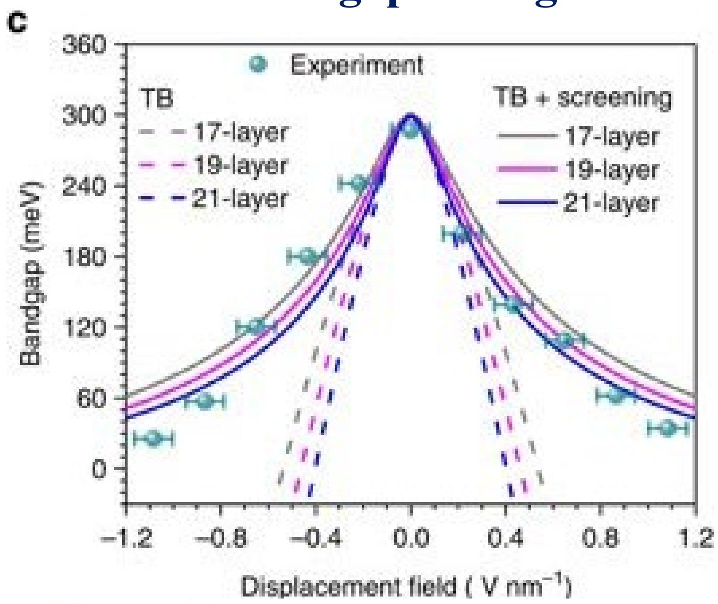
- **Effective masses along the armchair direction are roughly ten times smaller than that in the zigzag direction.**
- **The carrier mobility in armchair direction is much higher than that in the zigzag direction.**

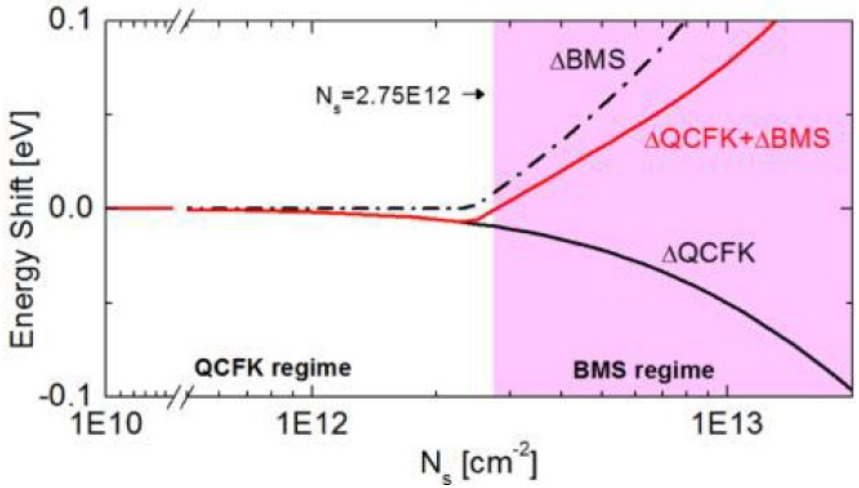
Summary (2)

Ambipolar transport



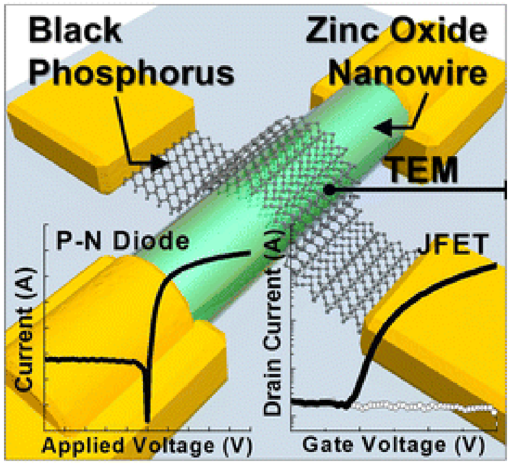
Bandgap tuning



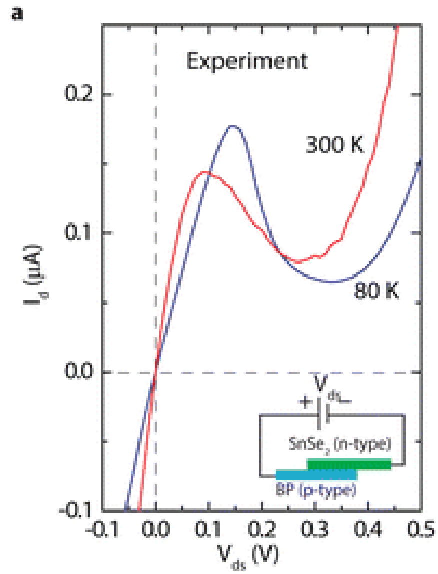


Summary (3)

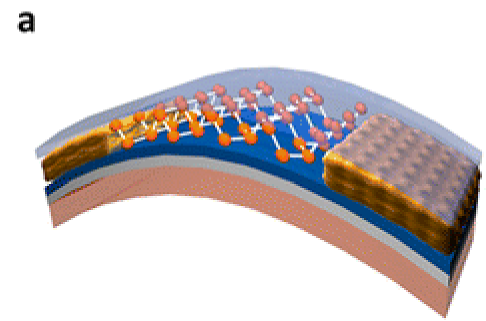
JFET



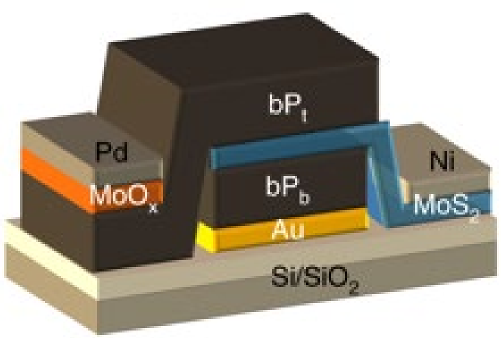
Esaki diode



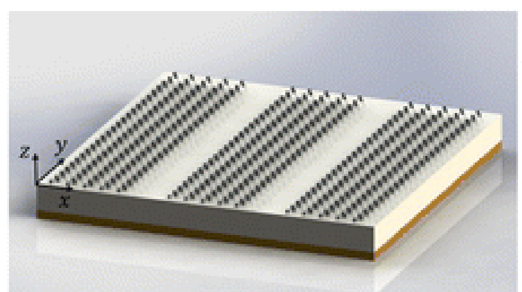
Amplifier and frequency doubler



Polarization-resolved photodetector



Plasmonic device



Electro-optical modulator