# Graphene-like 2-D Materials Series

- **Black phosphorus**, phosphorene is one of three different crystal structures that pure phosphorus can adopt.
- <u>White phosphorus</u> is used in making fireworks.
- <u>Red phosphorus</u> is used to make the heads of matches.
- The bandgap is adjusted by varying the number of phosphorene layers stacking one atop another, significantly larger than the bulk value of 0.31- 0.36 eV.
- Much easier to engineer devices with the exact behavior desired.
- Mobility ~ 600
- Unstable in air.
- Passivated by Al<sub>2</sub>O<sub>3</sub> layer and teflon.
- Harnessing phosphorene's higher electron mobility for making electronic devices.



- Black phosphorus was synthesized under a constant pressure of 10 kbar by heating red phosphorus to 1,000 C.
- Then slowly cooling to 600 C at a cooling rate of 100 C per hour.



YB Zhang, Fudan Univ, NATURE NANOTECHNOLOGY | VOL 9 | MAY 2014 | , 372.



- Reliable transistor performance is achieved at room temperature in samples thinner than 7.5 nm. Channel length and width of the device are 1.6 mm and 4.8mm.
- Field-effect mobility (red open circles), and Hall mobility (filled squares, three different values of n) as a function of temperature on a logarithmic scale

$$\mu_{\rm FE} = \frac{L}{W} \frac{1}{C_{\rm g}} \frac{\mathrm{d}G}{\mathrm{d}(V_{\rm g} - V_{\rm th})} \qquad \qquad \mu_{\rm H} = \frac{L}{W} \frac{G}{ne}$$



- fabricating *p*-type FETs based on few-layer phosphorene.
- exhibit ambipolar behavior with drain current modulation up to 10<sup>5</sup>,
- a field-effect mobility to 1,000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at room temperature, and thickness dependent.

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Tomanek at Michigan State, and Peter Ye at Purdue reported phosphorene-based transistors, along with simple circuits. ACS Nano, 8 (4), 4033–4041, (2014).



Figure 1. Crystal structure and band structure of few-layer phosphorene. (a) Perspective side view of few-layer phosphorene. (b,c) Side and top views of few-layer phosphorene. (d) DFT-HSE06 band structure of a phosphorene monolayer. (e,f) DFT-HSE06 results for the dependence of the energy gap in few-layer phosphorene on (e) the number of layers and (f) the strain along the *x*- and *y*-direction within a monolayer. The observed band gap value in the bulk is marked by a cross in (e).

Phosphorene-based field effect transistors

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- Tomanek and Ye reported to have made phosphorene-based transistors, along with simple circuits. ACS Nano, 8 (4), 4033–4041, (2014).
- A few-layer phosphorene FET with 1.0 μm channel length displays a high on-current of 194 mA/mm, a high hole field-effect mobility of 286 cm<sup>2</sup>V<sup>-1</sup>·s<sup>-1</sup>, and an on/off ratio of up to 10<sup>4</sup>.
- Constructed a CMOS inverter by a phosphorene *p*-MOS transistor and a MoS<sub>2</sub> *n*-MOS transistor.

### **2-D Hetero-structures and applications**

- 2-D materials offer stacked like cards in a deck to create the different electronic layers as needed in functional electronic devices. Van der Waals bonding
- Because they do not form tight bonds with the layers above and below.
- Ye's group at Purdue reported to use both MoS<sub>2</sub> and phosphorene to make ultrathin photovoltaics (PVs).
- Geim et al reported in Nature Materials to have assembled multiple 2D materials to make efficient thin LEDs.
- □ Revolution in electronics and optics just began.
- Flexible, transparent, temperature stable, and cheap to manufacture

### Van der Waals heterostructures



#### Building van der Waals Heterostructures:

If one considers 2D crystals to be analogous to Lego blocks (right panel), the construction of a huge variety of layered structures becomes possible.

Conceptually, this atomic scale Lego resembles molecular beam epitaxy, but employs different 'construction' rules and a distinct set of materials.

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### **Current 2D library**

- Monolayers proved to be stable under room temperature in air are shaded **blue**;
- Those probably stable in air are shaded green;
- Those unstable in air but that may be stable in inert atmosphere are shaded **pink**.
- **Grey** shading indicates 3D compounds that have been successfully exfoliated down to monolayers.
- We note that, after intercalation and exfoliation, the oxides and hydroxides may exhibit stoichiometry different from their 3D parents.

Graphene family	Graphene	hBi 'white gra		BCN	Fluorograph	ene	Graphene oxide	
2D chalcogenides	Mag. WG	Semiconducting dichalcogenides:			$\begin{array}{l} \mbox{Metallic dichalcogenides:} \\ \mbox{NbSe}_2, \mbox{NbS}_2, \mbox{TaS}_2, \mbox{TiS}_2, \mbox{NiSe}_2 \mbox{ and so on} \end{array}$			
	MOS <sub>2</sub> , WS <sub>2</sub> , MOSe <sub>2</sub> , WSe <sub>2</sub>		MoTe <sub>2</sub> , WTe <sub>2</sub> , ZrS <sub>2</sub> , ZrSe <sub>2</sub> and so on		Layered semiconductors: GaSe, GaTe, InSe, Bi <sub>2</sub> Se <sub>3</sub> and so on			
2D oxides	Micas, BSCCO	MoO <sub>3</sub> , WO <sub>3</sub>		Perovskite-type: LaNb <sub>2</sub> O <sub>7</sub> , (Ca,Sr) <sub>2</sub> Nb <sub>2</sub> Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub> , Ca <sub>2</sub> Ta <sub>2</sub> TiO <sub>10</sub> ar		pe: Ni(OF		Hydroxides: H) <sub>2</sub> , Eu(OH) <sub>2</sub> and so on
	Layered Cu oxides	$TiO_2$ , $MnO_2$ , $V_2O_5$ , $TaO_3$ , $RuO_2$ and so on				$D_{10}$ and so on	Others	







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# State-of-the-art van der Waals structures and devices

**a, Graphene–hBN superlattice** consisting of six stacked bilayers. On the right its crosssection and intensity profile as seen by scanning transmission electron microscopy are shown; on the left is a schematic view of the layer sequence. The topmost **hBN** bilayer is not visible, being merged with the metallic contact.

#### b, c, Double-layer graphene

**heterostructures**. An optical image of a working device (b), and its schematics in matching colors (c). Two graphene Hall bars are accurately aligned, separated by a trilayer hBN crystal and encapsulated between relatively thick hBN crystals (hBN is shown in c as semitransparent slabs). The entire heterostructure is placed on top of an oxidized Si wafer (SiO<sub>2</sub> is in turquoise). The colors in b indicate the top (blue) and bottom(orange) Hall bars and their overlapping region (violet). The graphene areas are invisible in the final device image because of the top Au gate outlined by dashes. The scale is given by the width of the Hall bars, 1.5 µm.

### Heterostructure devices with SQW and MQWs by band structure engineering



- **a**. Schematic of the SQW heterostructure:  $hBN/Gr_B/2hBN/WS_2/2hBN/Gr_T/hBN$ .
- b. Cross-sectional bright-field STEM image of the type of heterostructure presented in a.
  Scale bar, 5 nm.
- c.d. Schematic and STEM image of the MQW heterostructure : hBN/Gr<sub>B</sub>/2hBN/MoS<sub>2</sub>/2hBN/MoS<sub>2</sub>/2hBN/MoS<sub>2</sub>/2hBN/MoS<sub>2</sub>/2hBN/Gr<sub>T</sub>/hBN. The number of hBN layers between MoS<sub>2</sub> QWs in d varies. Scale bar, 5 nm.
- **g**. Schematic of the heterostructure  $Si/SiO_2/hBN/Gr_B/3hBN/MoS_2/3hBN/Gr_T/hBN$ .
- h–j. Band diagrams for (h) the case of zero applied bias; (i) intermediate applied bias; and (j) high bias for the heterostructure presented in g.

## Silicene, Germanene, and Stanene

- To investigate the growth and characterizations for novel graphene-derived 2D materials, such as *silicene, germanene, stanene, and borophene*.
- Stanene is recently predicted to be quantum spin Hall (QSH) insulator with a large bulk gap ~0.3 eV.
- Their QSH states can be effectively tuned by chemical functionalization and external strain, viable for low-power-consumption electronics.

### Another emerging wonder material : Silicene

- Graphene-like 2-D silicon
- A finite band gap < 0.1V, more compatible with existing silicon-based electronics
- Potential application as a high-performance field effect transistor



To grow Silicene, Germanine, and even stanene on insulating or semiconducting substrate.





Nature, Scientific Reports 2, # 853, 2012

Superconductivity predicted in alkaline or alkaline earth elements doped silicene (CaC<sub>6</sub>  $T_c = 13K$ ; CaSi<sub>6</sub>  $T_c = ?$ )





- Via deposition of Si on Ag (111) at 450K -500K.
- B. Lalmi, APL (2010), and more.
- A buckled structure with a small gap of ~ 1.5 mV



### (2√3 x 2√3)R30°



### Si/Ag(111)

### **Electronic properties (HRPES)**

#### (4x4) superstructure



FIG. 2 (color). (a) Filled-states STM image of the 2D Si layer on Ag(111)-(1 × 1) ( $U_{\text{bias}} = -1.3$  V, I = 0.35 nA). Clearly visible is the honeycomblike structure. (b) Line profile along is dashed white line indicated in (a). The dark centers in the STM micrograph are separated by 1.14 nm, corresponding to united the Ag(111) lattice constant, in agreement with the (4 × 4) symmetry. (c) High-resolution STM topograph (3 × 3 nm  $U_{\text{bias}} = -1.3$  V, I = 0.35 nA) of the Si adlayer.



FIG. 3 (color). (a) ARPES intensity map for the claim Ag surface (left) and after formation of the 2D Si adlayer (right), taken along the Ag  $\overline{\Gamma} - \overline{K}$  direction through the silicene  $\overline{K}(h\nu)$  126 eV). (b) Brillouin-zone (BZ) scheme of the 2D Si layer with respect to the Ag(111)-(1 × 1) surface. The red arrow indicates the ARPES measurement direction.

#### Linear dispesion

P. Vogt et al. PRL 108, 155501 (2012)

#### PHYSICAL REVIEW B 87, 245430 (2013)

#### Absence of a Dirac cone in silicene on Ag(111): First-principles density functional calculations with a modified effective band structure technique

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We investigate the currently debated issue of the existence of the Dirac cone in silicene on an Ag(111) surface, using first-principles calculations based on density functional theory to obtain the band structure. By unfolding the band structure in the Brillouin zone of a supercell to that of a primitive cell, followed by projecting onto Ag and silicene subsystems, we demonstrate that the Dirac cone in silicene on Ag(111) is destroyed. Our results clearly indicate that the linear dispersions observed in both angular-resolved photoemission spectroscopy [P. Vogt et al Phys. Rev. Lett. 108, 155501 (2012)] and scanning tunneling spectroscopy [L. Chen et al., Phys. Rev. Lett. 10.06804 (2012)] come from the Ag substrate and not from silicene. It ac cone

<u>???</u>

Y. Peng et al. Phys. Rev. B. 87 245430 (2013)

### **Demonstration of Germanene:**

### Germanene grown on Pb (111) on Ge (111)





#### First observation of Dirac cone

First observation of "real" Honeycomb

Prof. Shu-jung Tang et al, NTHU, 2015



- Tin (*Sn*) with its large spin-orbit coupling offers rich electronic structures
- Predicted to exhibit highly efficient thermoelectrics, topological superconductivity, high-temperature quantum spin Hall, and quantum anomalous Hall effects.
- Stanene could support a large gap (~ 0.3 V) 2-D quantum spin Hall (QSH) state, thus enable the dissipationless electric conduction at RT.
  Y. Xu et al. PRL 111, 136804 (2013).
- Integrability with conventional semiconductor industry.
  - $\checkmark$  With its elemental nature, *Sn* is free from the stoichiometry and related defects.
  - $\checkmark$  Sn is commonly used in many group-IV MBE system and is easy to tackle.
- In this 2-D materials, outstanding properties : The Fermi velocity near Dirac point approaches 7.3x10<sup>5</sup> m/s, much larger than that of typical 3-D TI, and close to that of graphene (1x10<sup>6</sup> m/s).
- stanene/Bi<sub>2</sub>Te<sub>3</sub> crystal structure



F. Zhu *et al*. *Nature Materials*, **14**, 1020–1025 (2015).

- α-Sn film was grown on *InSb*(001) as a 3-D TI, with nearly massless electron dispersion with a bandgap of 230 mV, showing spin helical band by ARPES.
- One monolayer (111) orientated α- Sn is a buckled-honeycomb structure, similar to graphene.

# Stanene grown on Bi<sub>2</sub>Te<sub>3</sub>(111)

- Monolayer stanene was fabricated by MBE on  $Bi_2Te_3(111)$  substrate.
- Obvious discrepancies :

--According to ARPES, the valence bands of stanene are pinned in the conduction band of  $Bi_2Te_3$  (111), giving metallic interface states. The inverted-bandgap at  $\Gamma$  point, the key to QSH state, was not obtained.

--Dirac-cone-like features at K point are expected in a honeycomb structure; Stanene, with a larger SOC, leads to a bandgap of 0.1 eV at the Dirac-cone. However, Dirac-cone at the K-point of stanene  $/Bi_2Te_3(111)$  was not obtained.



F. Zhu *et al*. *Nature Materials*, **14**, 1020–1025 (2015).

(a) ARPES spectra of  $Bi_2Te_3(111)$ , (b) stanene on  $Bi_2Te_3$  along K-F-K direction. The orange dashed lines mark the bulk band dispersions of  $Bi_2Te_3$ . The blue dotted lines mark the hole band of stanene. SS marks the surface state and CB marks the conduction band of  $Bi_2Te_3$ . (c) Comparison of experimental results with DFT calculation of stanene/ $Bi_2Te_3$ . Red dots above the Fermi level are obtained by in-situ potassium deposition that provides the film with electrons.

### **Progress on Stanene**

 Discover superconductivity in few-layer stanene down to a bilayer grown on PbTe, while bulk α -tin is not superconductive.

a trilayer Sn on top of PbTe/Bi<sub>2</sub>Te<sub>3</sub>/Si(111)

 Stanene on Cu(111) by low-T MBE. Discovered an unusually flat stanene showing an in-plane *s*-*p* band inversion with a SOC-induced topological gap (~0.3 eV) at the Γ point, which represents a group-IV graphene-like material displaying topological features.





Nature Physics, 14, 344, 2018.

Nature Materials, 17, 1081, 2018

### Borophene

The  $\beta_{12}$  sheet, a borophene structure that can form spontaneously on a Ag(111) surface.



FIG. 1. Schematic drawing of the Dirac cones and lattices. (a) Honeycomb structure. (b)  $\beta_{12}$  sheet. (c) The  $\beta_{12}$  sheet with a  $3 \times 1$  perturbation. The blue and green balls indicate the boron atoms with different on-site energies in our TB analysis. The top and bottom panels are the band structures and atomic structures, respectively. The basic vectors of the primitive unit cell are indicated by the blue arrows.

I. Matsuda group, PRL 118, 096401 (2017)