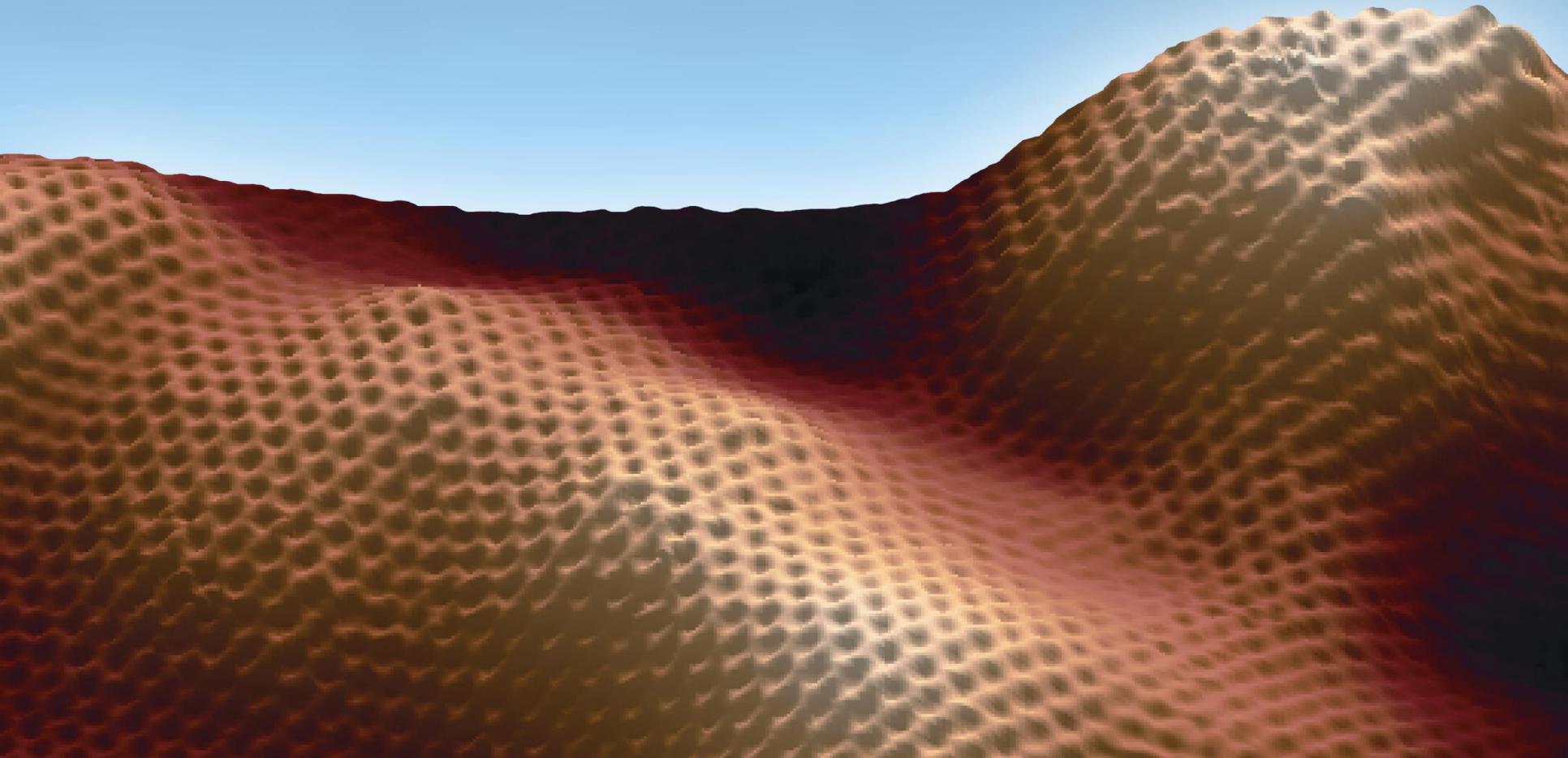


New Opportunities in Two-dimensional Materials

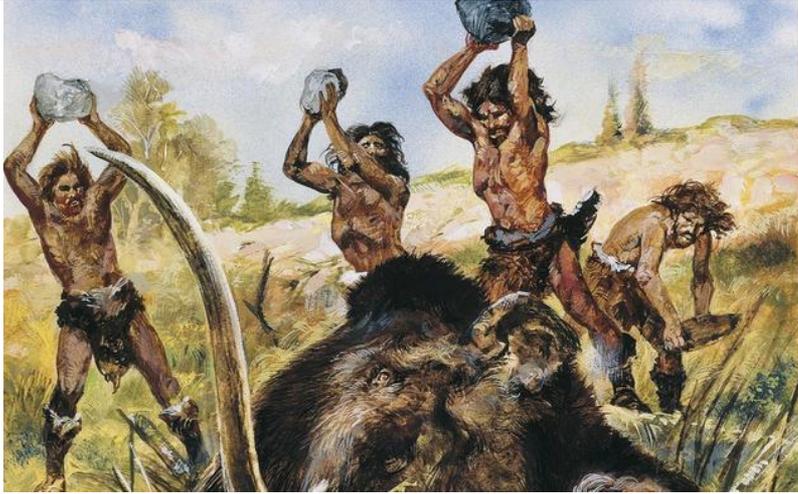
Yuanbo Zhang (张远波)

Dept. of Physics, Fudan University, China

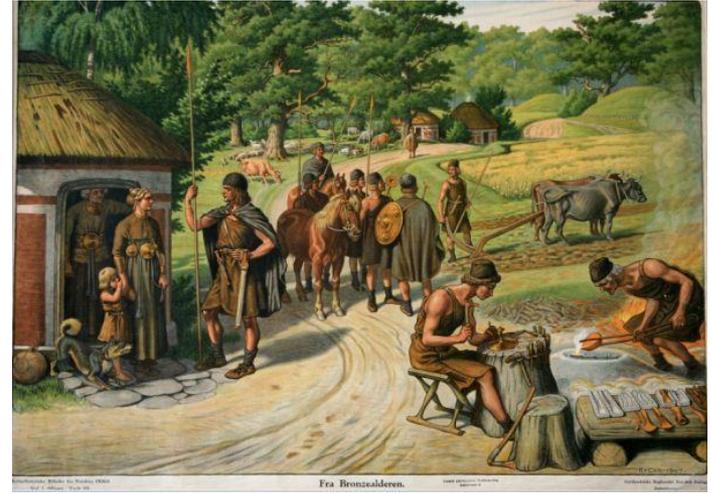


A Brief History of Materials

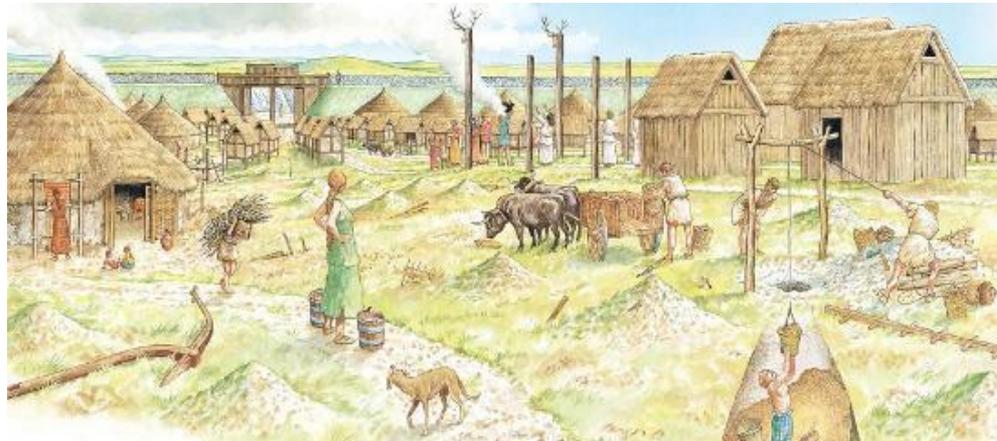
The Stone Age



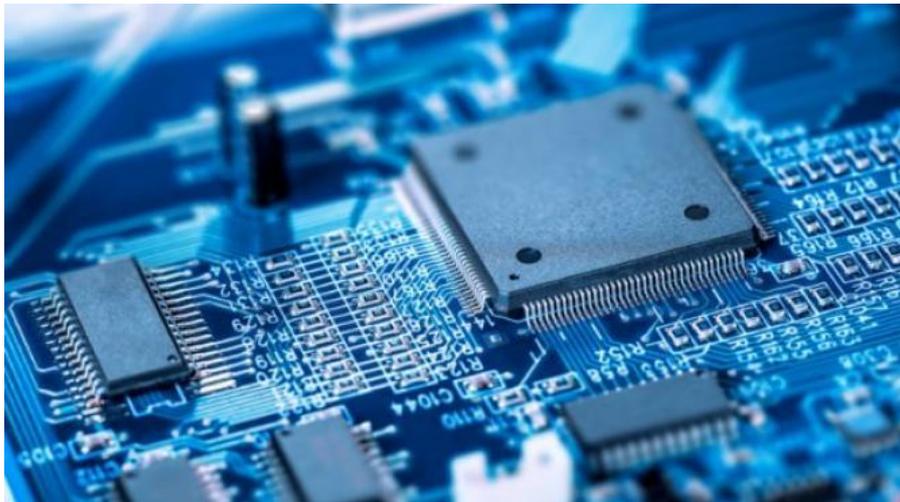
The Bronze Age



The Iron Age



The Silicon Age?

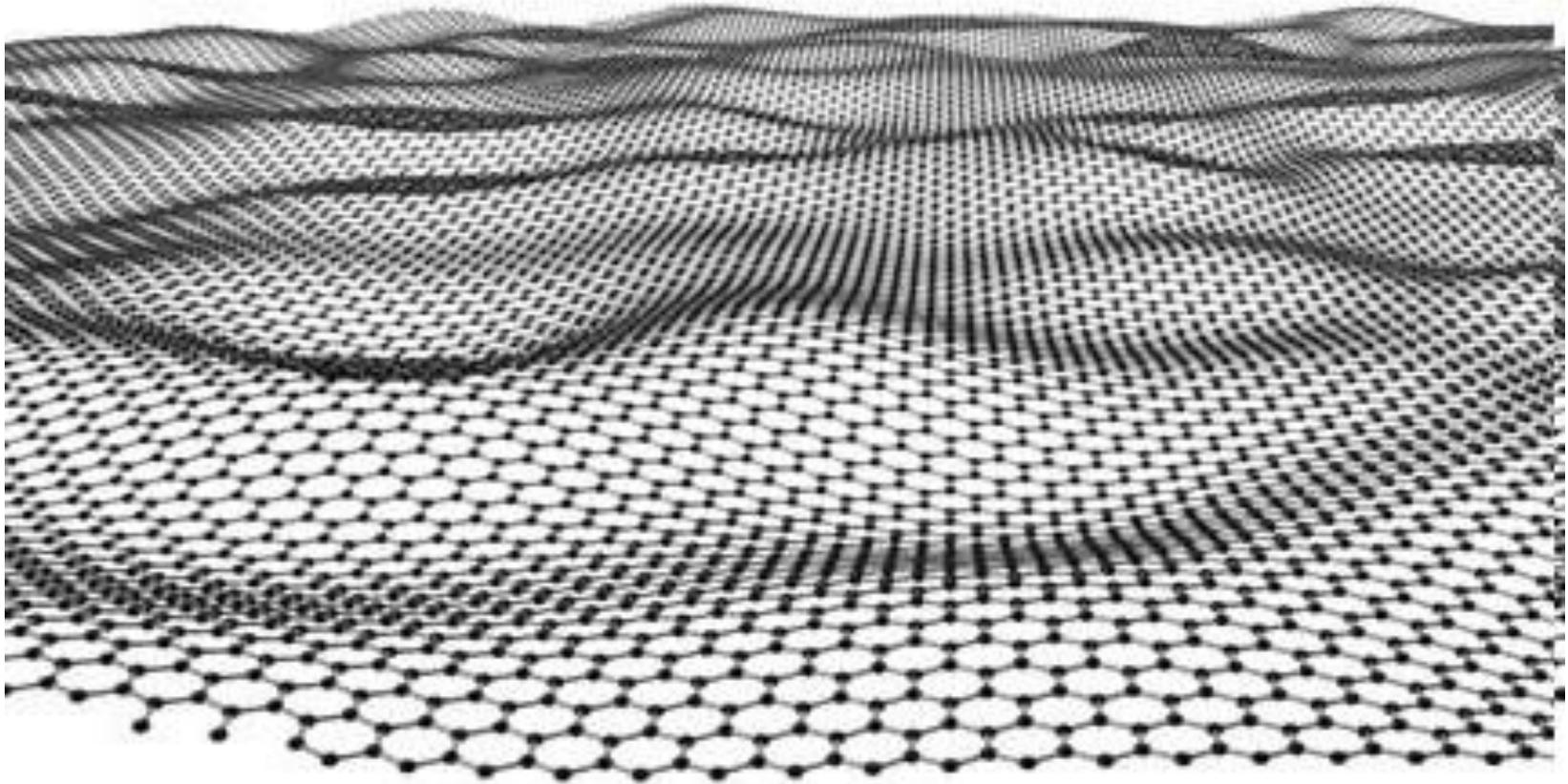


“Interface is the Device”



The first transistor, Bell Lab, 1947

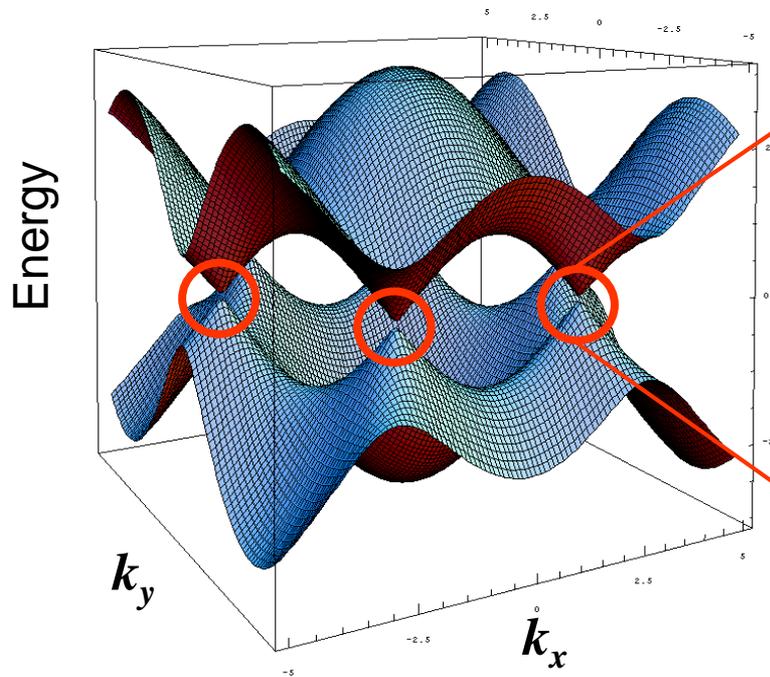
Graphene: The Beginning of 2D Material Research



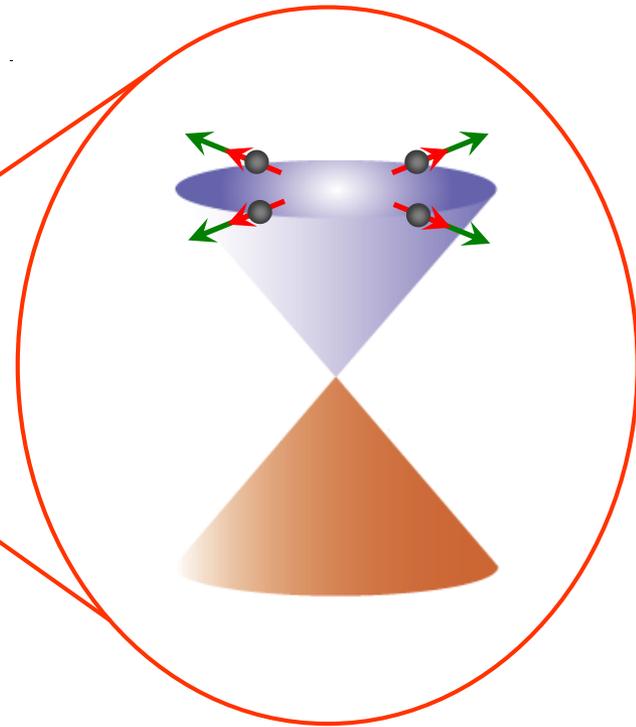
Geim group (2004)

Graphene : Dirac Fermions in 2D

Band Structure of Graphene

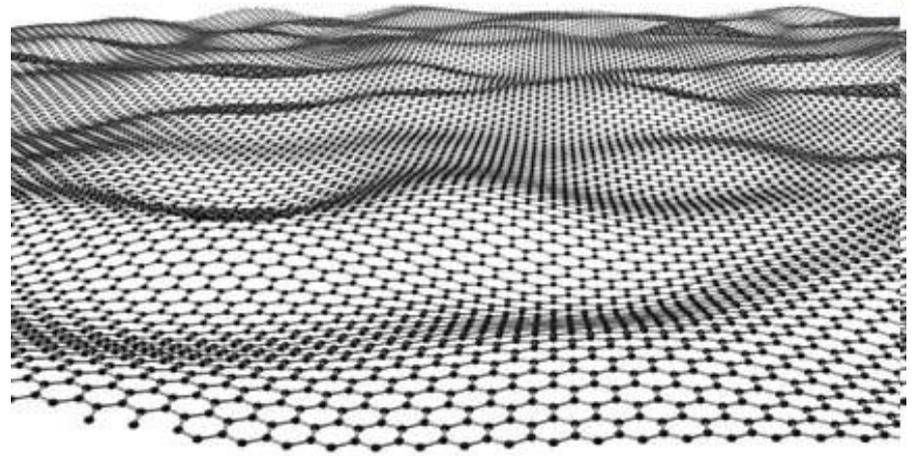


→ Momentum, $\hbar\mathbf{k}$
→ Pseudo-spin



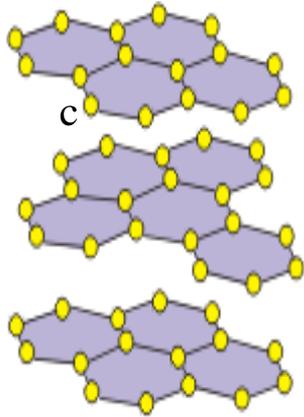
P. R. Wallace, *Phys. Rev.* 71, 622 (1947).
T. Ando et al, *J. Phys. Soc. Jpn* 67, 2857 (1998).

$$E = \hbar k v_F$$
$$E = pc$$

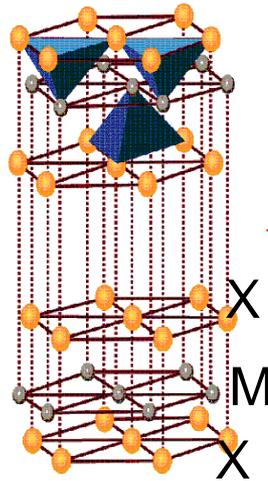


Less is different

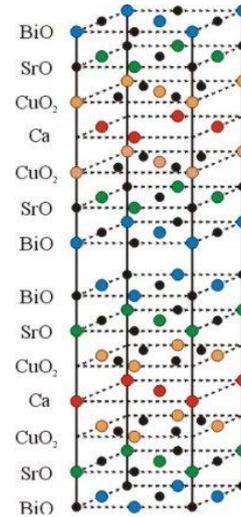
Families of New Materials in 2D



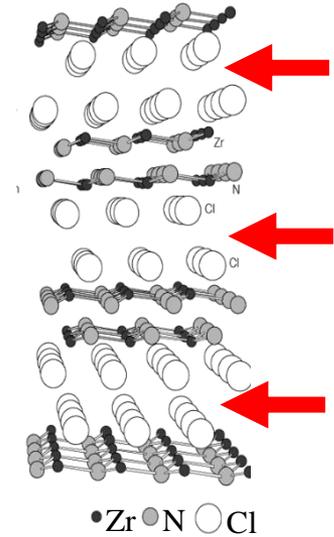
Graphite



Metal
Chalcogenides
(M= Nb, Ta, Va, ...
X= S, Se, Te)



High Tc Materials
Such as
 $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-x}$



β - ZrNCl

Hundreds of 2D crystals waiting to be explored

Opportunities to Tune the Material Properties in 2D



New device paradigm?

Outline

- ❑ Black phosphorus (semiconductor)
- ❑ 1T-TaS₂ (metal)
 - ❑ Gate-controlled intercalation
 - ❑ Tunable Phase in 1T-TaS₂

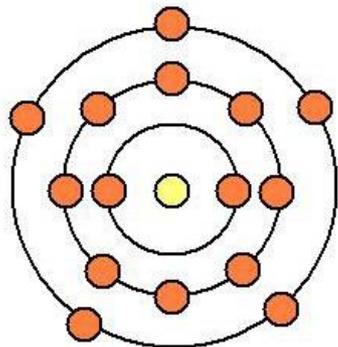
Allotropes of Phosphorus

15

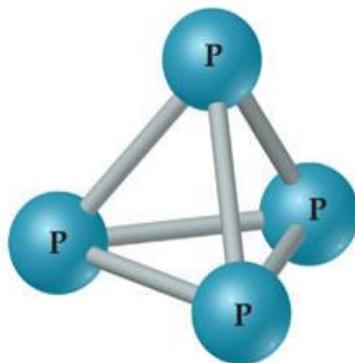
P

Phosphorus

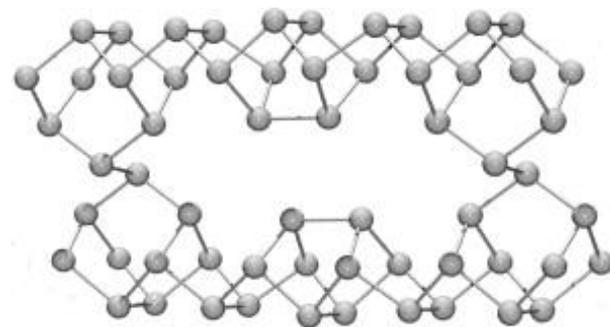
30.974



White Phosphorus



Red Phosphorus



Allotropes of Phosphorus: Black Phosphorus

Black Phosphorus



P. W. Bridgman, JACS 36,1344 (1914)

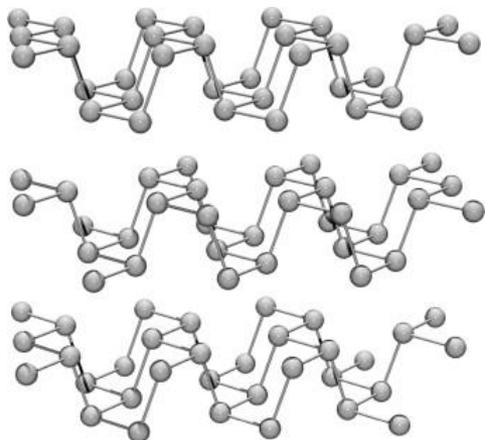
TWO NEW MODIFICATIONS OF PHOSPHORUS.

By P. W. BRIDGMAN.

Received May 4, 1914.

The two new modifications of phosphorus to be described here were obtained during an investigation of the effect of high pressure on the melting point of ordinary white phosphorus. The two new forms have perfectly distinct characteristics; in this they are different from the questionable modifications of red phosphorus often announced. The first of these modifications is a new form of white phosphorus, which changes

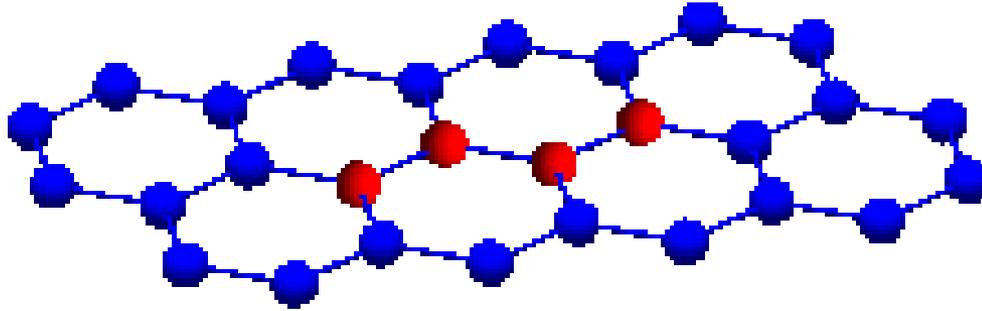
Layered crystal structure



Review:

Morita, *Applied Physics A* **39**, 227–242 (1986).

Phosphorene v.s. Graphene



Graphene

- **Planar** honey-comb lattice
- **4** valence electrons
- **Half-filled** conduction band
- **Zero-gap** semiconductor

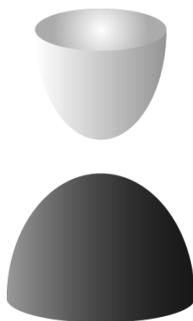
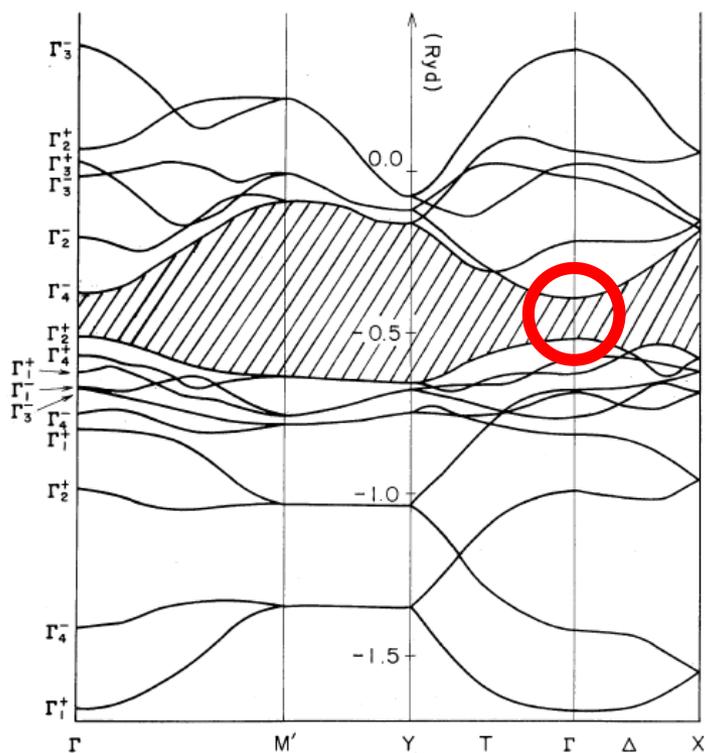
Phosphorene

- **Puckered** honey-comb lattice
- **5** valence electrons
- **Fully filled** valence band
- **Gapped** semiconductor

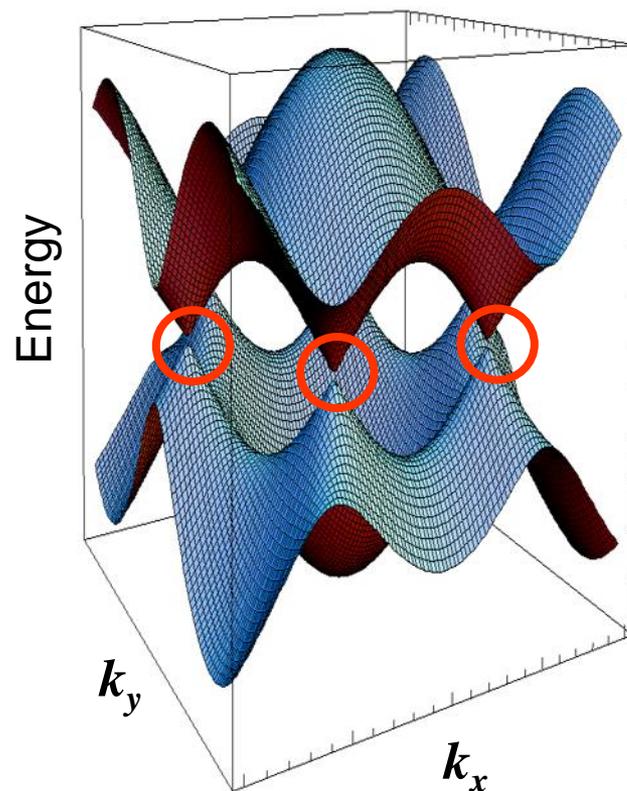
Phosphorene v.s. Graphene

Phosphorene

Band gap ~ 2 eV



Graphene



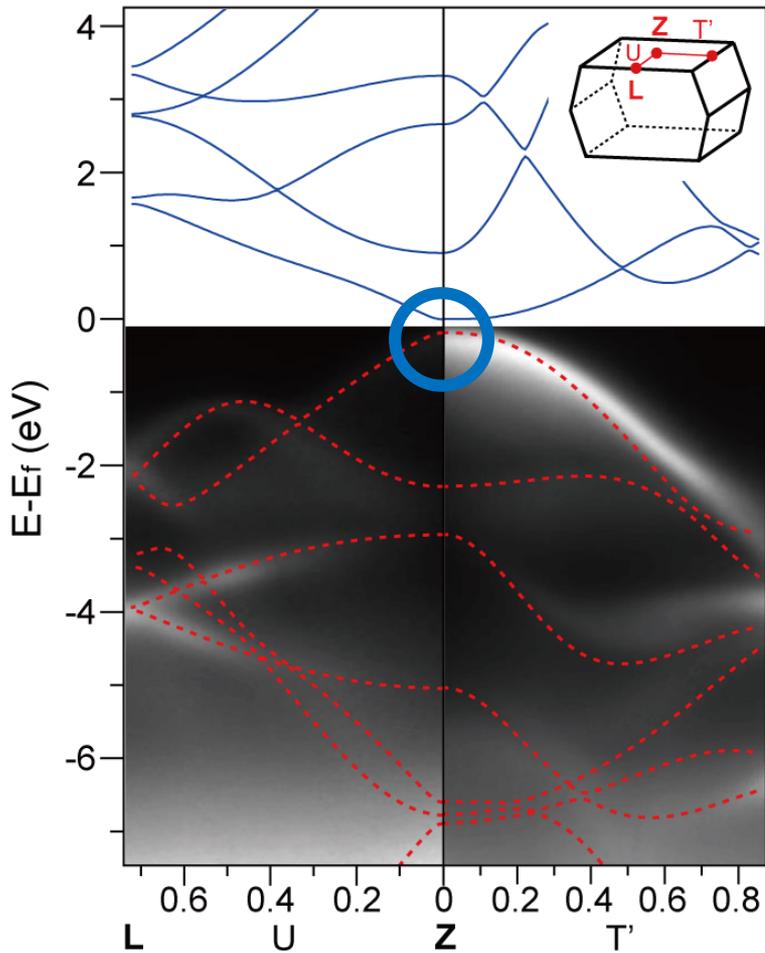
Y. Takao, et al., *J. Phys. Soc. Jpn.* 50, 3362 (1981)

P. R. Wallace, *Phys. Rev.* 71, 622 (1947).

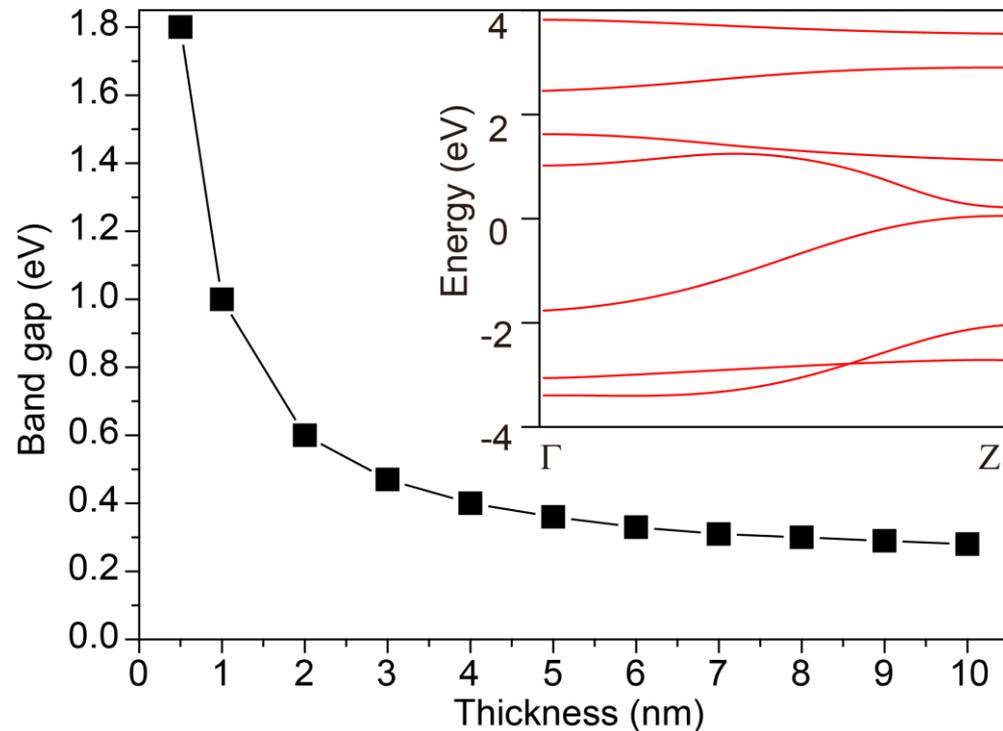
Thickness-dependent Bandgap in few-layer Phosphorene

Band structure of the bulk

Direct band gap ~ 0.3 eV



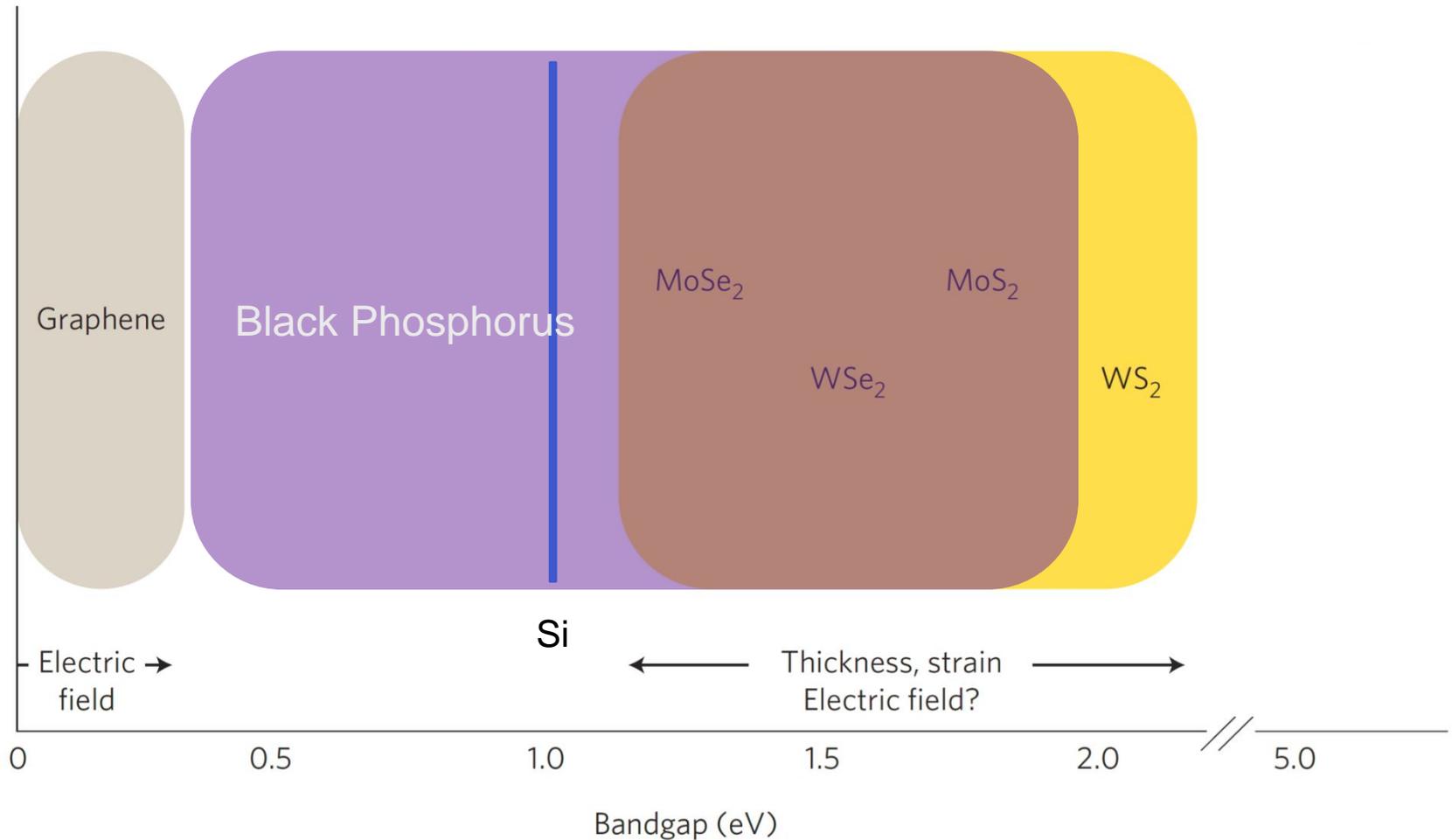
Thickness-dependent bandgap



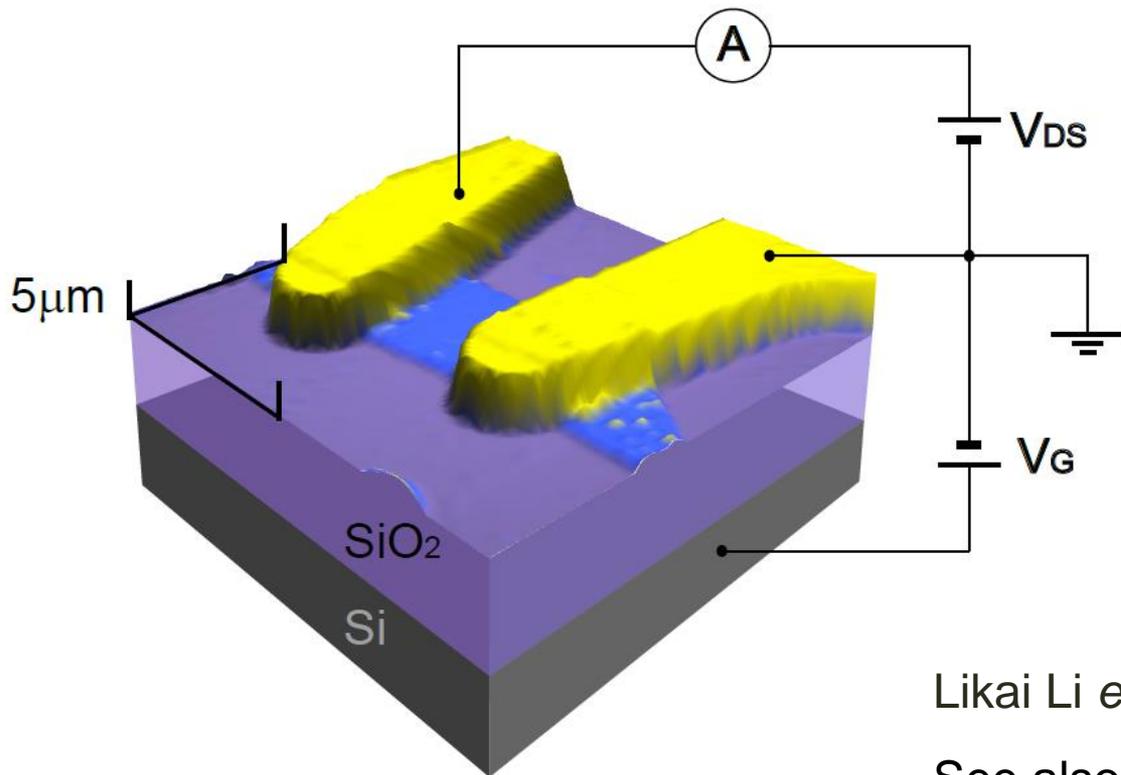
Direct bandgap tunable by varying thickness

Thickness-dependent Band Gap

Bridging the gap



Black Phosphorus Field-effect Transistor



Likai Li



Fangyuan Yang

Likai Li *et al.* Nature Nano. **9**, 372 (2014).

See also:

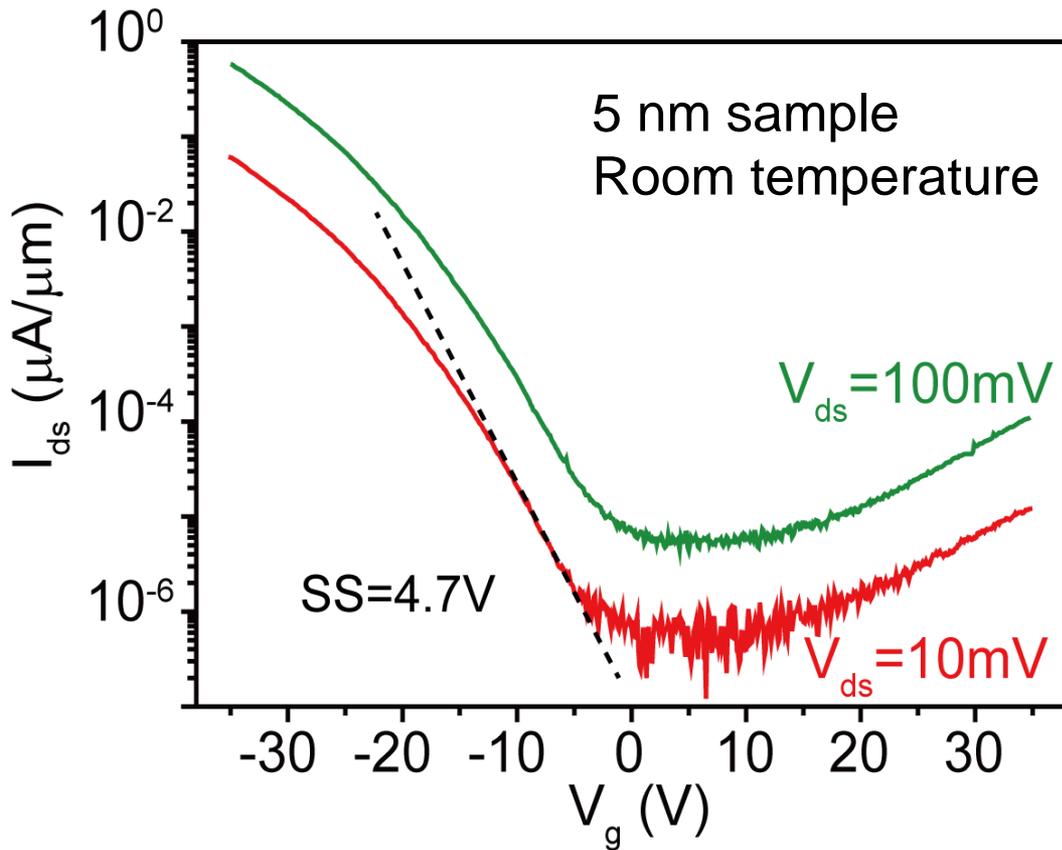
Liu, H. *et al.* ACS Nano **8**, 4033 (2014).

Koenig, S. P. *et al.*, APL **104**, 103106 (2014).

Xia, F. *et al.*, Nature Comm. **5**, 4458 (2014).

Black Phosphorus FET

Highest on-off ratio $\sim 10^5$

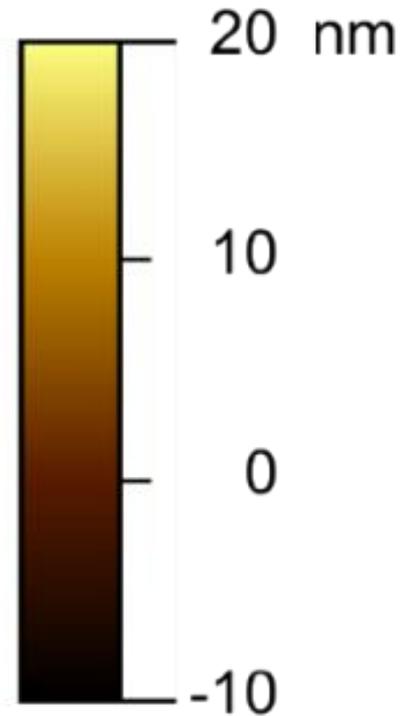
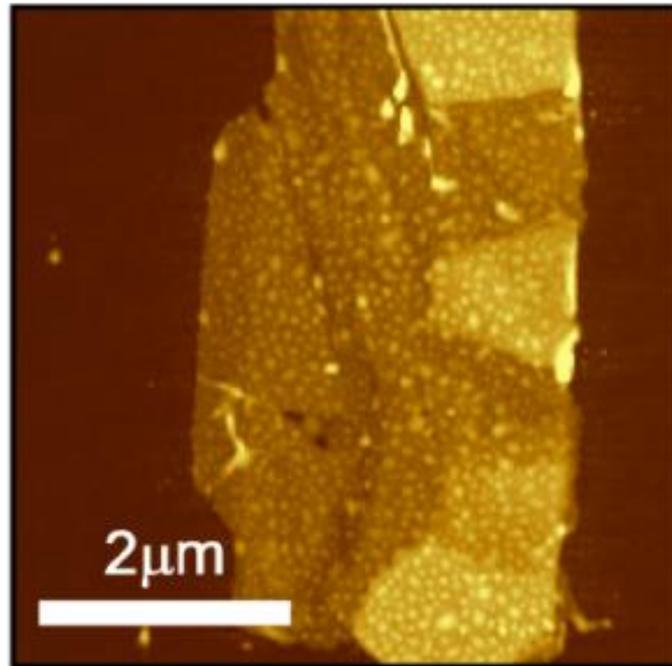
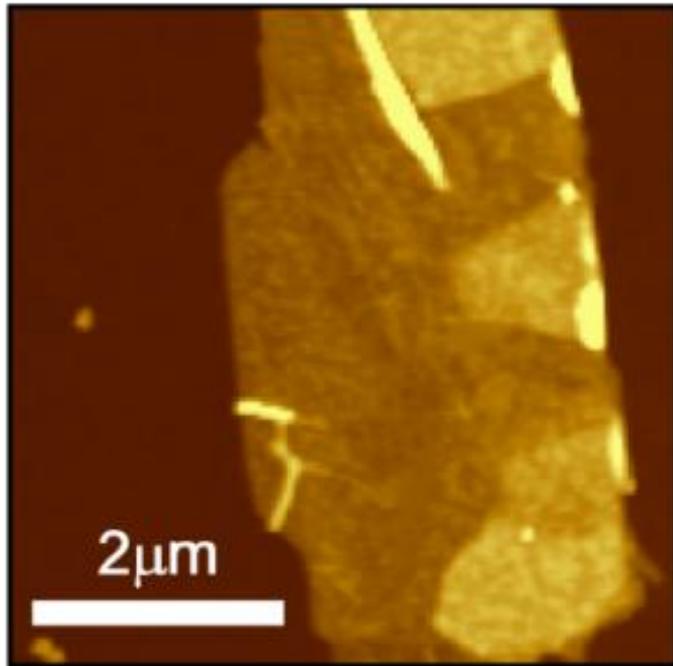


- High mobility up to $1000 \text{ cm}^2/\text{Vs}$
- Saturation in I-V Characteristics

Limiting Factors of Carrier Mobility

Before

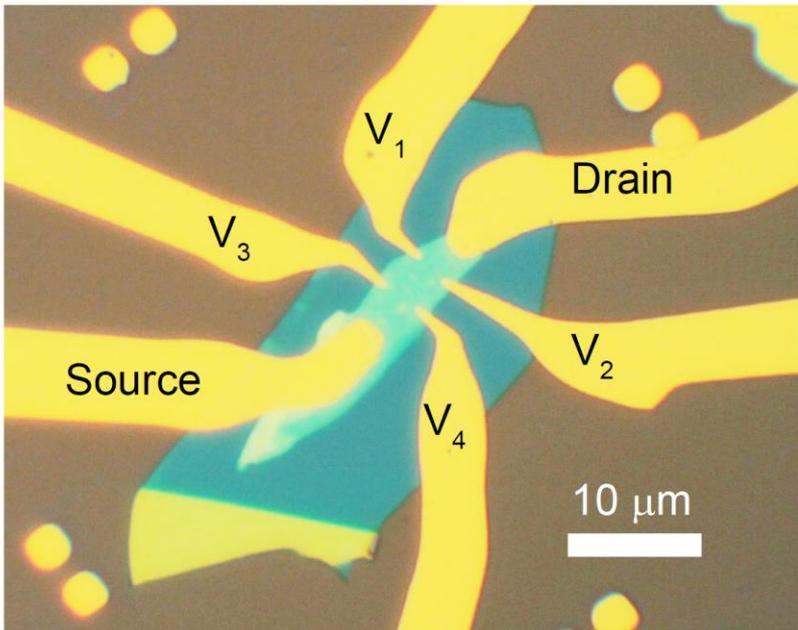
After



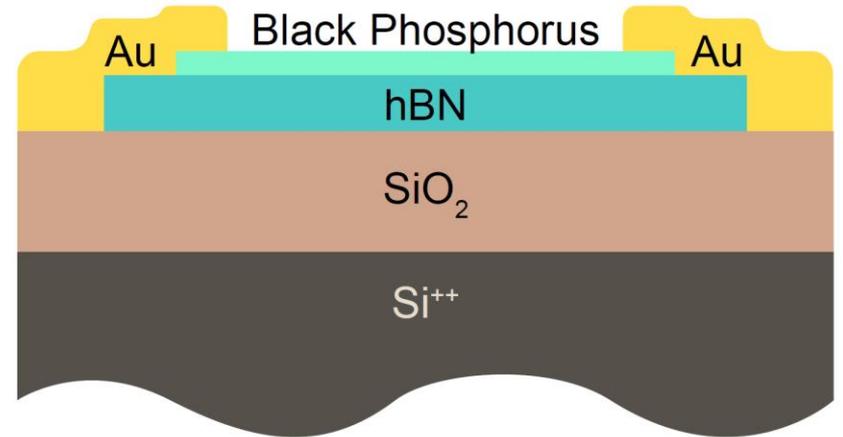
Sample left in air for 3 days

Black Phosphorus on Hexagonal Boron Nitride

Optic Image of
Black Phosphorus on BN



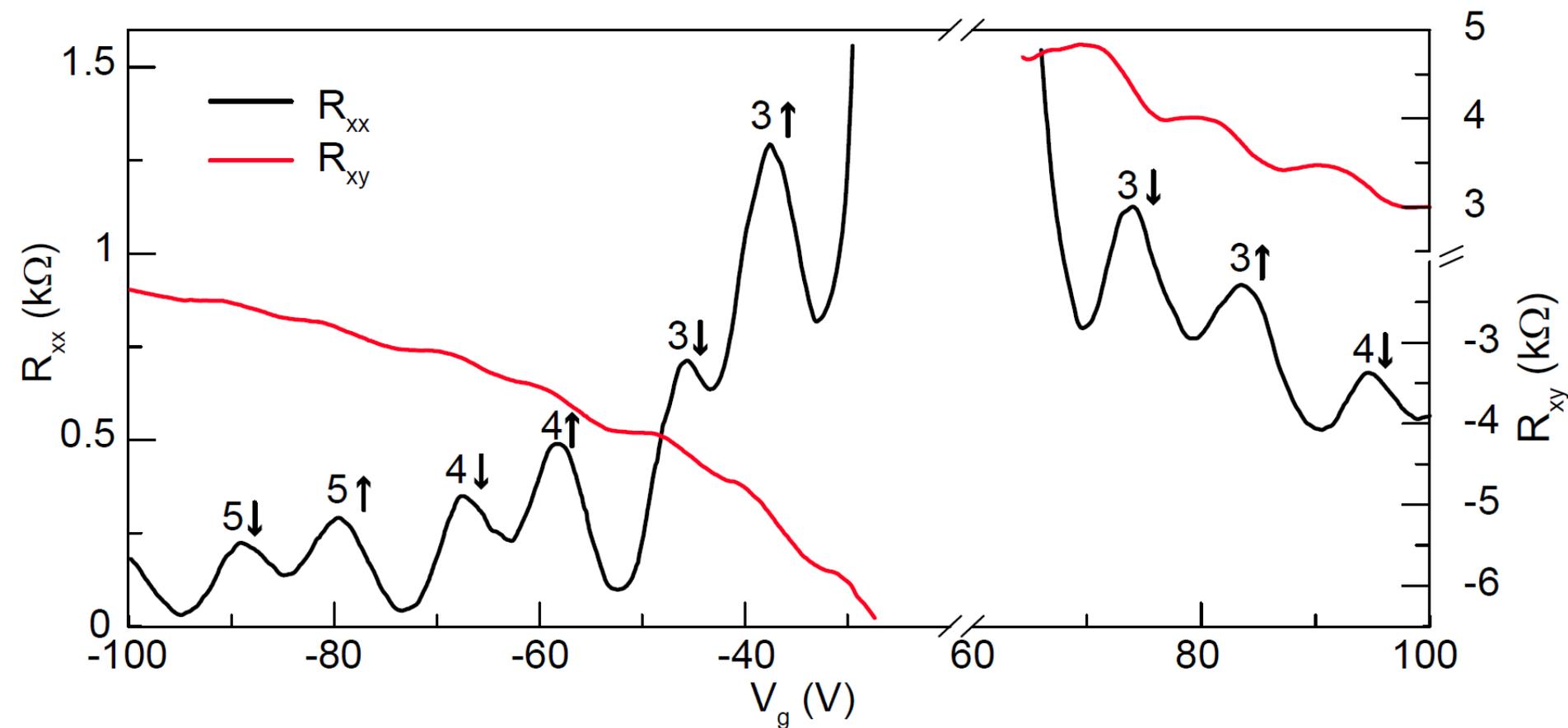
Cross-sectional View



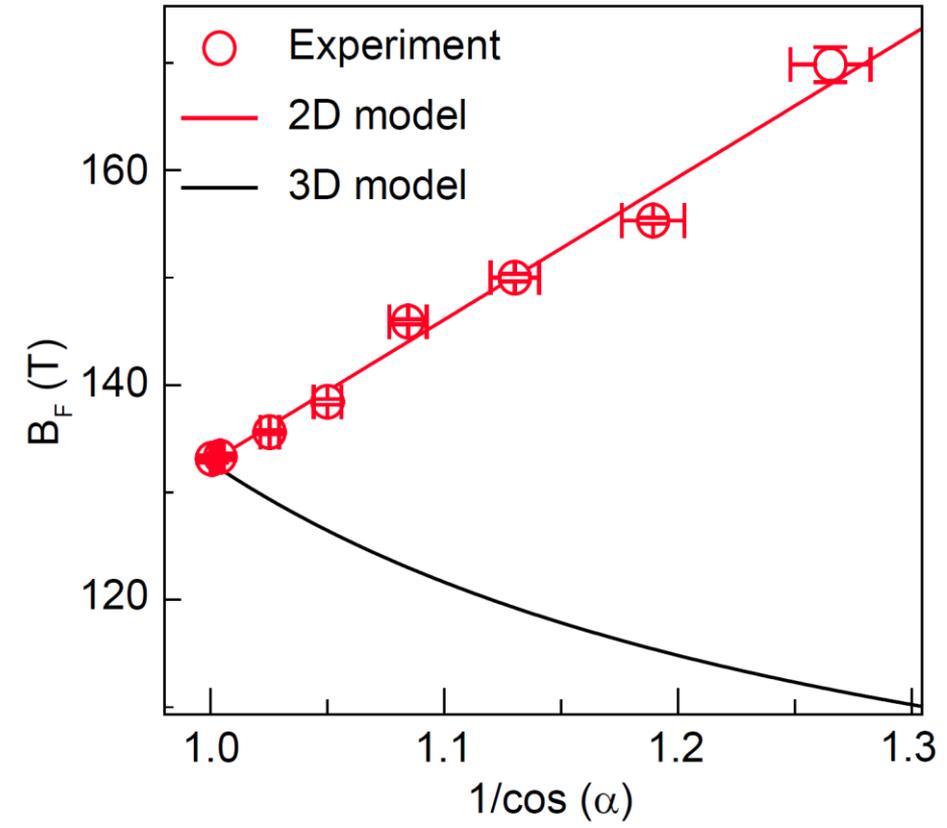
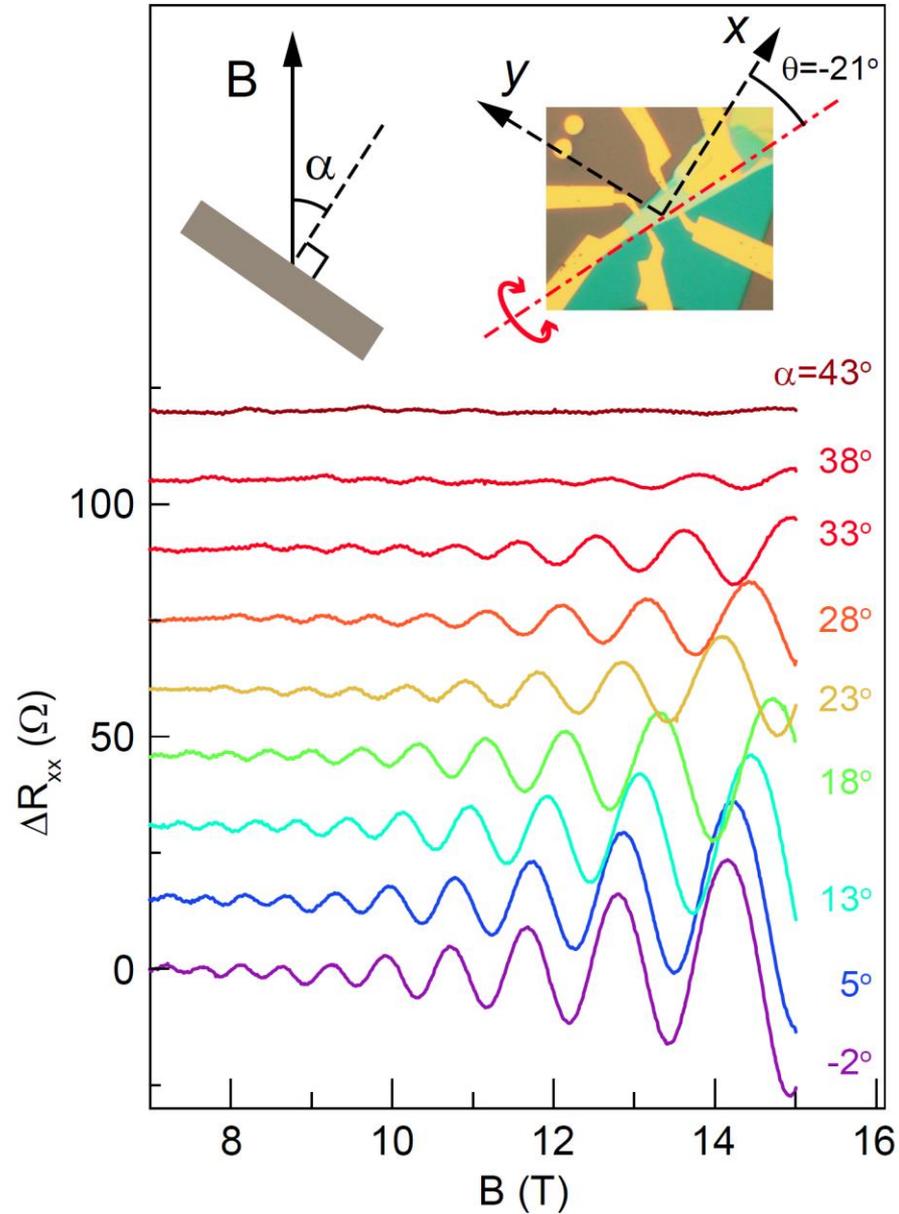
Protecting the bottom surface with hBN

Quantum Oscillations in Black Phosphorus on hBN

$B = 31\text{T}, T = 0.3\text{K}$



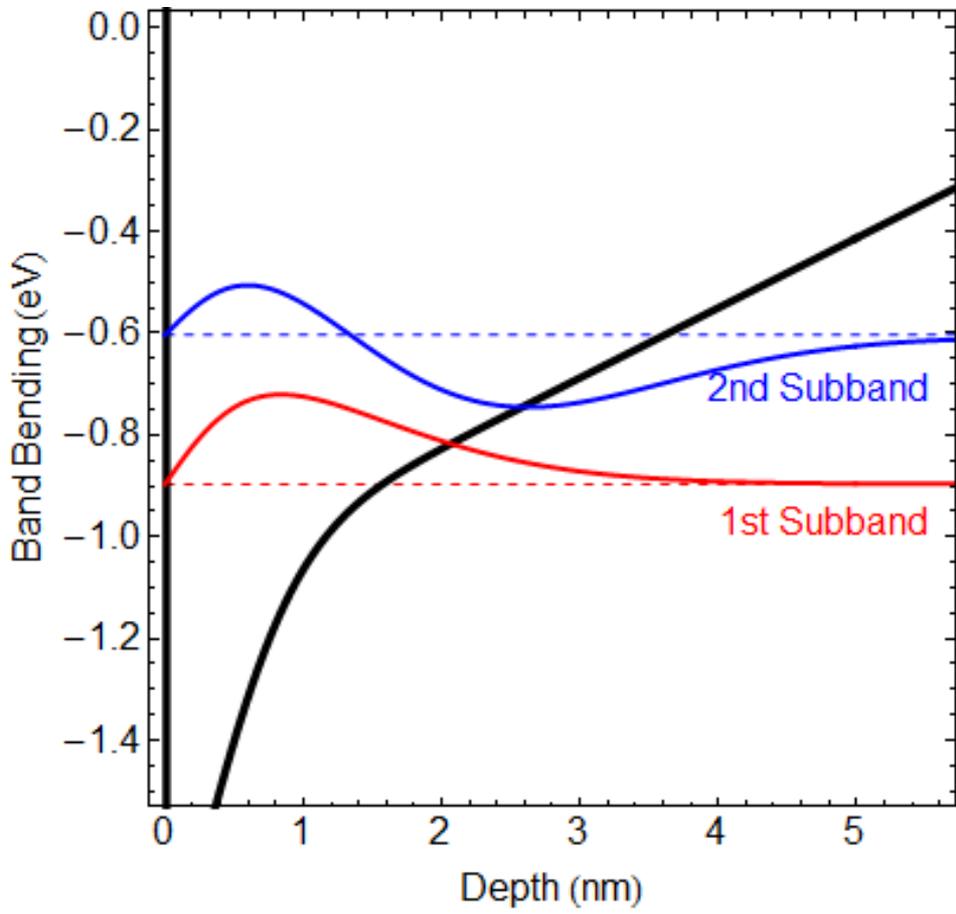
2D Electron and Hole Gases in Black Phosphorus



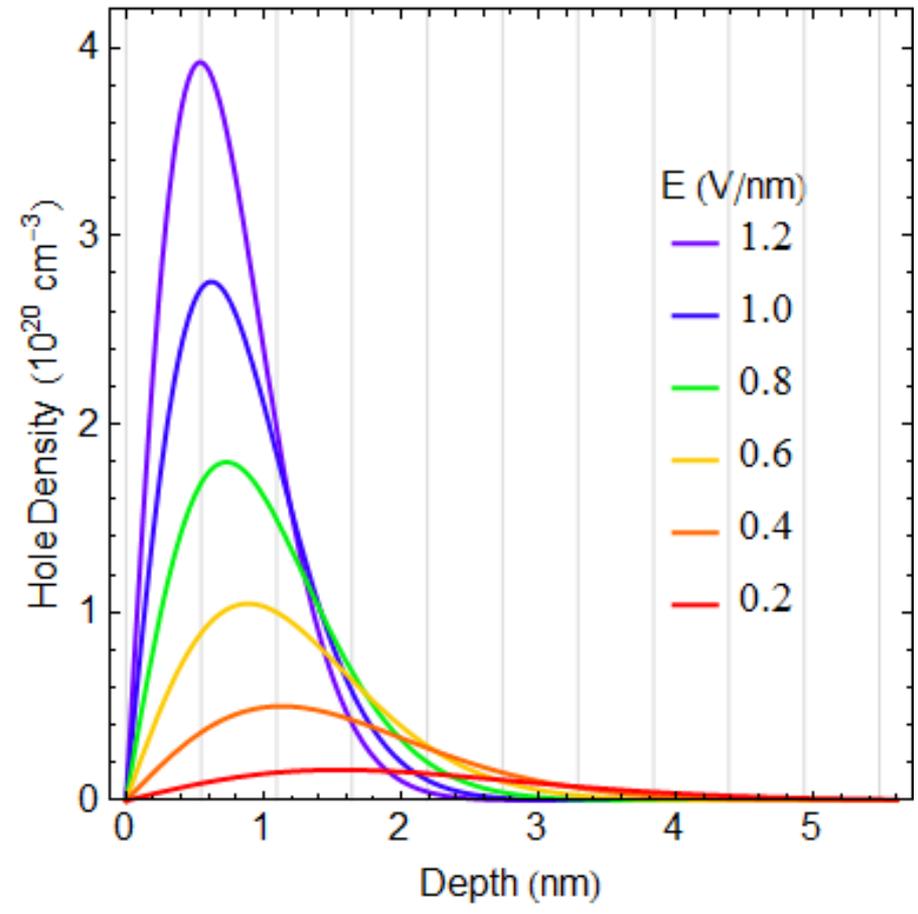
2D instead of 3D Fermi surface

2D Electron and Hole Gases in Black Phosphorus

2D confinement at the surfave

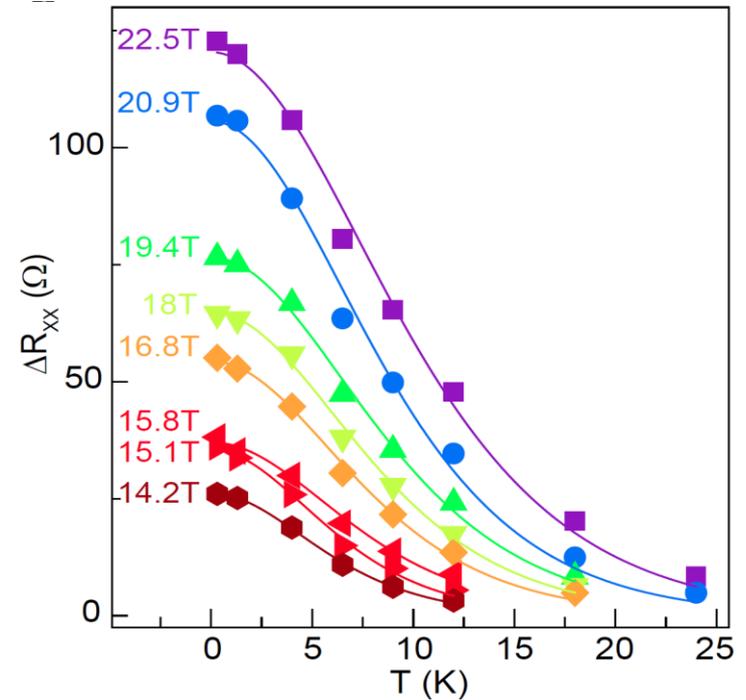
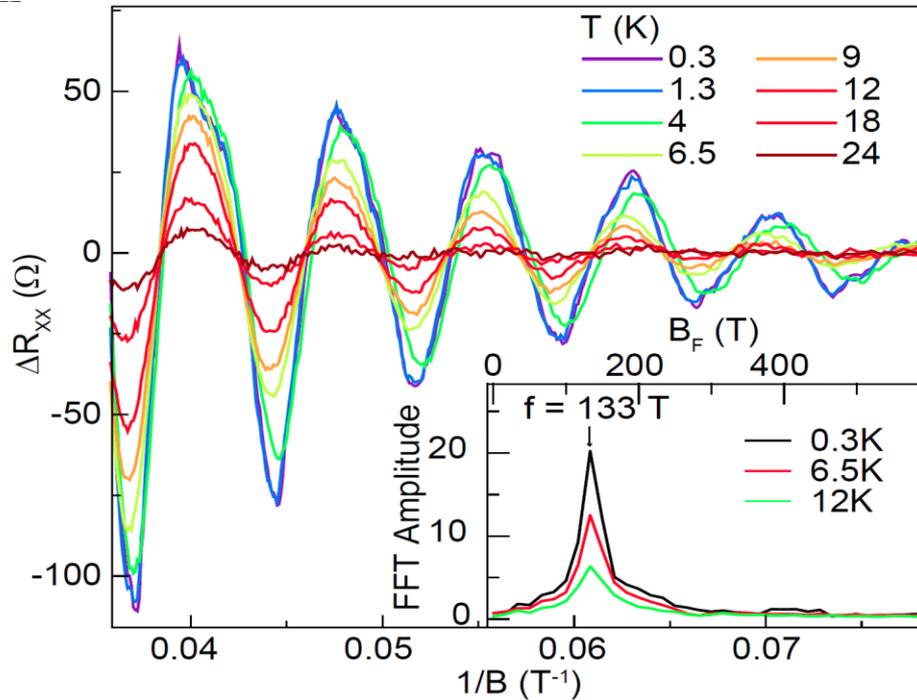


Charge distribution



2D electron and hole gases are confined to ~ 2 atomic layers

2D Electron and Hole Gases in Black Phosphorus



Crucial information obtained from the quantum oscillations

Likai Li *et al.* Nature Nano., Advance Online Publication (arXiv:1411.6572).

See also:

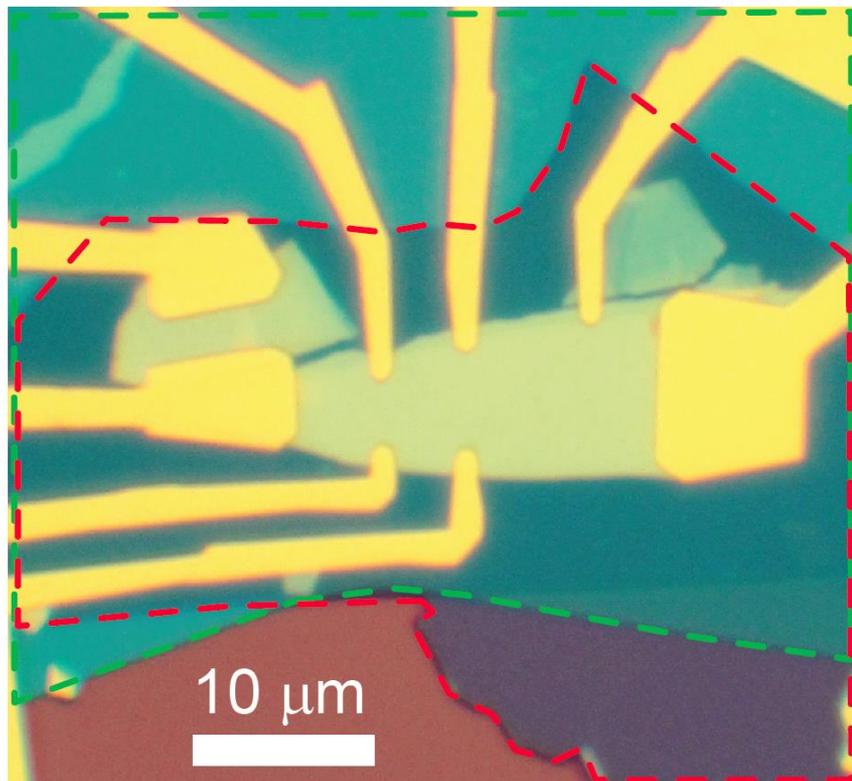
Tayari, V. *et al.*, arXiv:1412.0259 (2014).

Chen, X. *et al.*, arXiv:1412.1357 (2014).

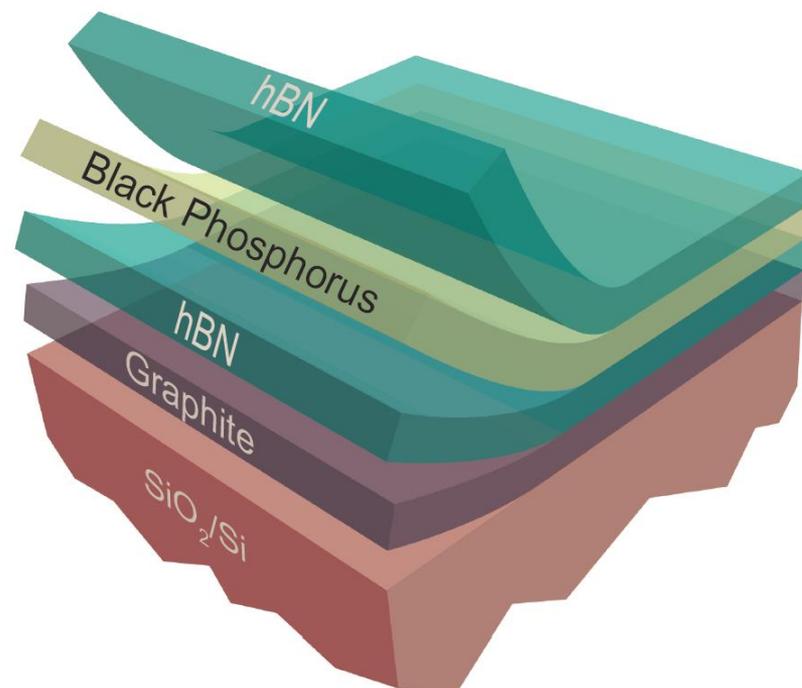
Gillgren, N. *et al.*, 2D Mater. 2, 011001 (2015).

Even Higher Mobility?

Top View

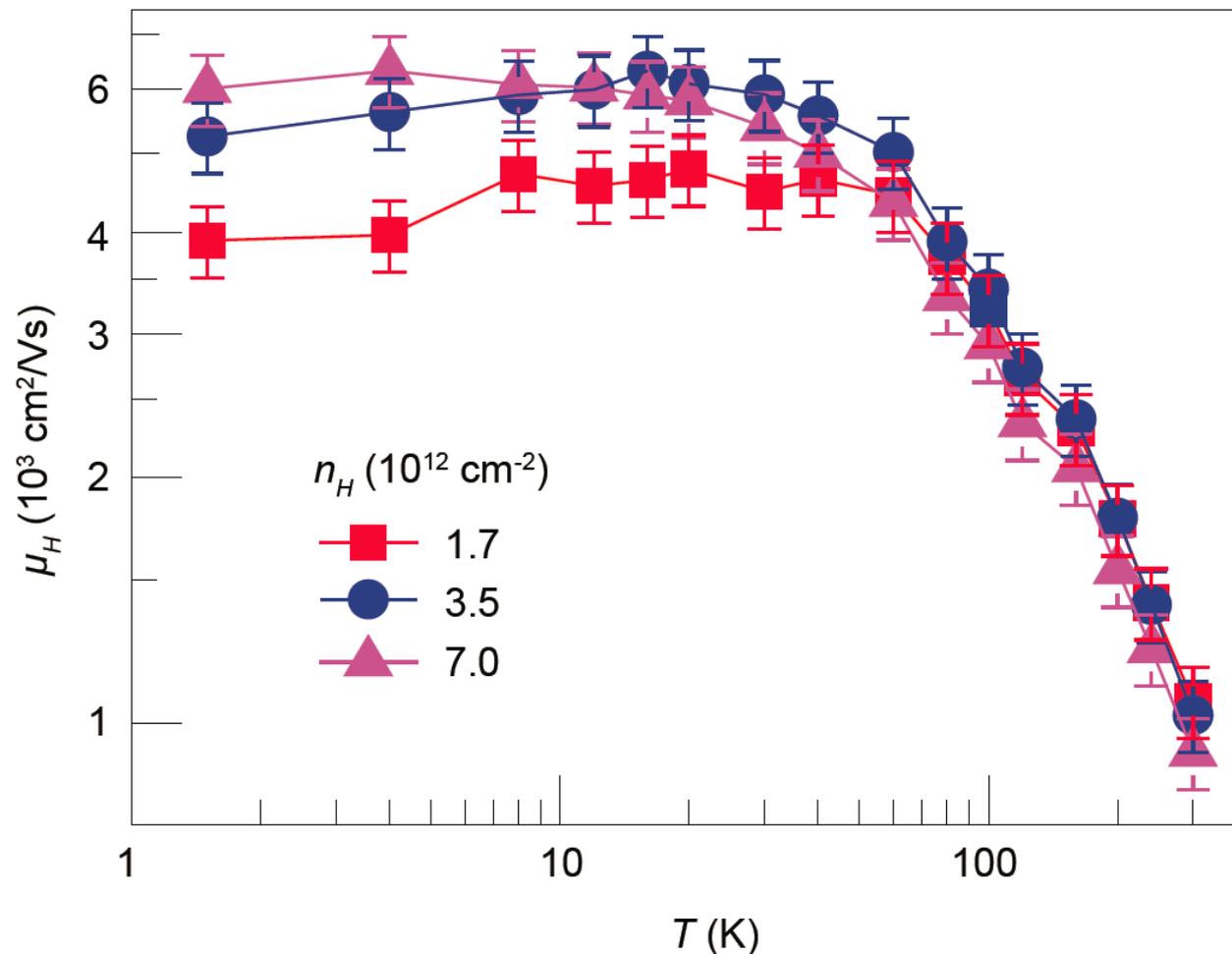


Side View



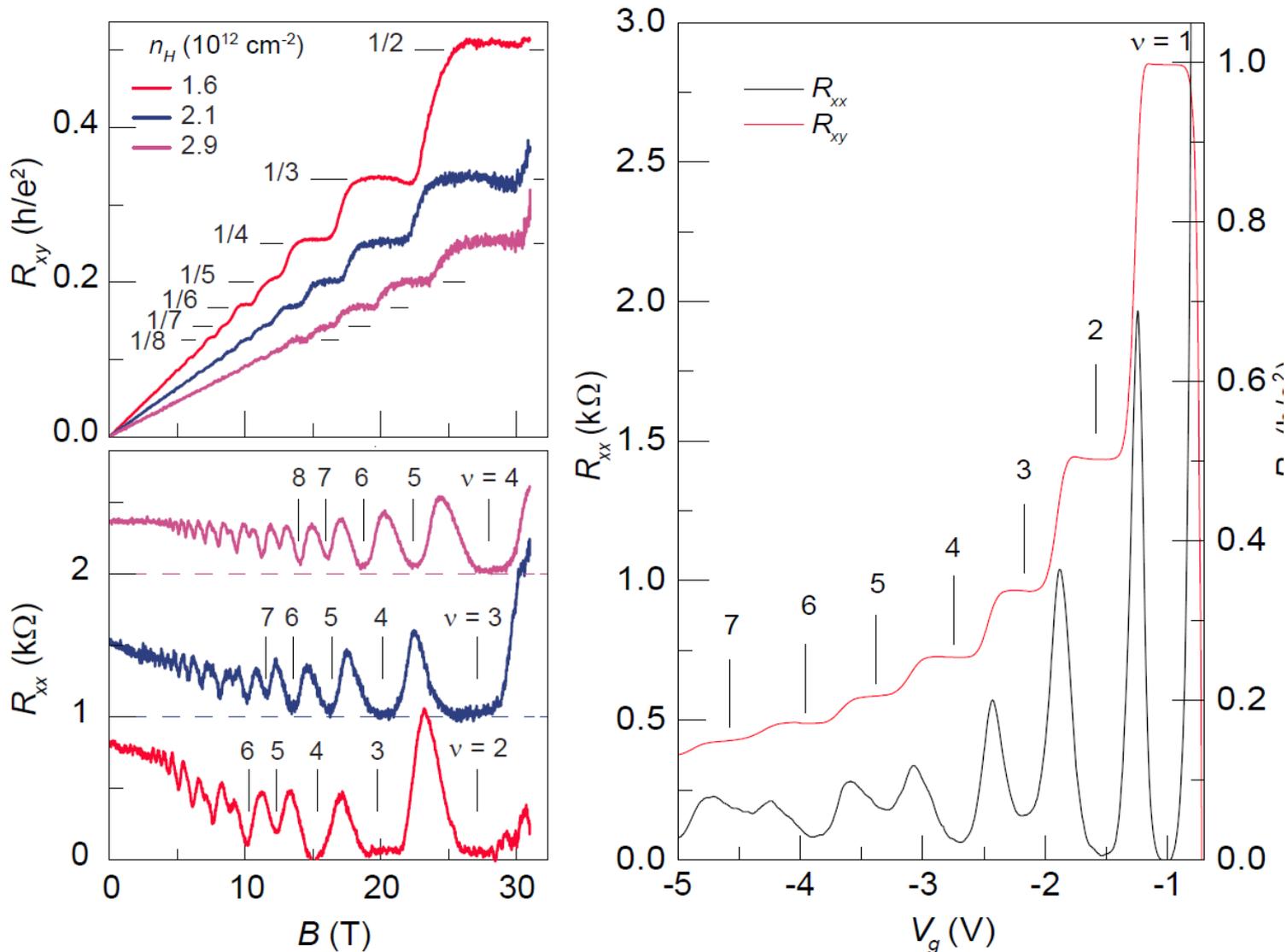
Graphite local gate screens impurity potential, leads to high mobility

High Mobility Black Phosphorus 2DEG

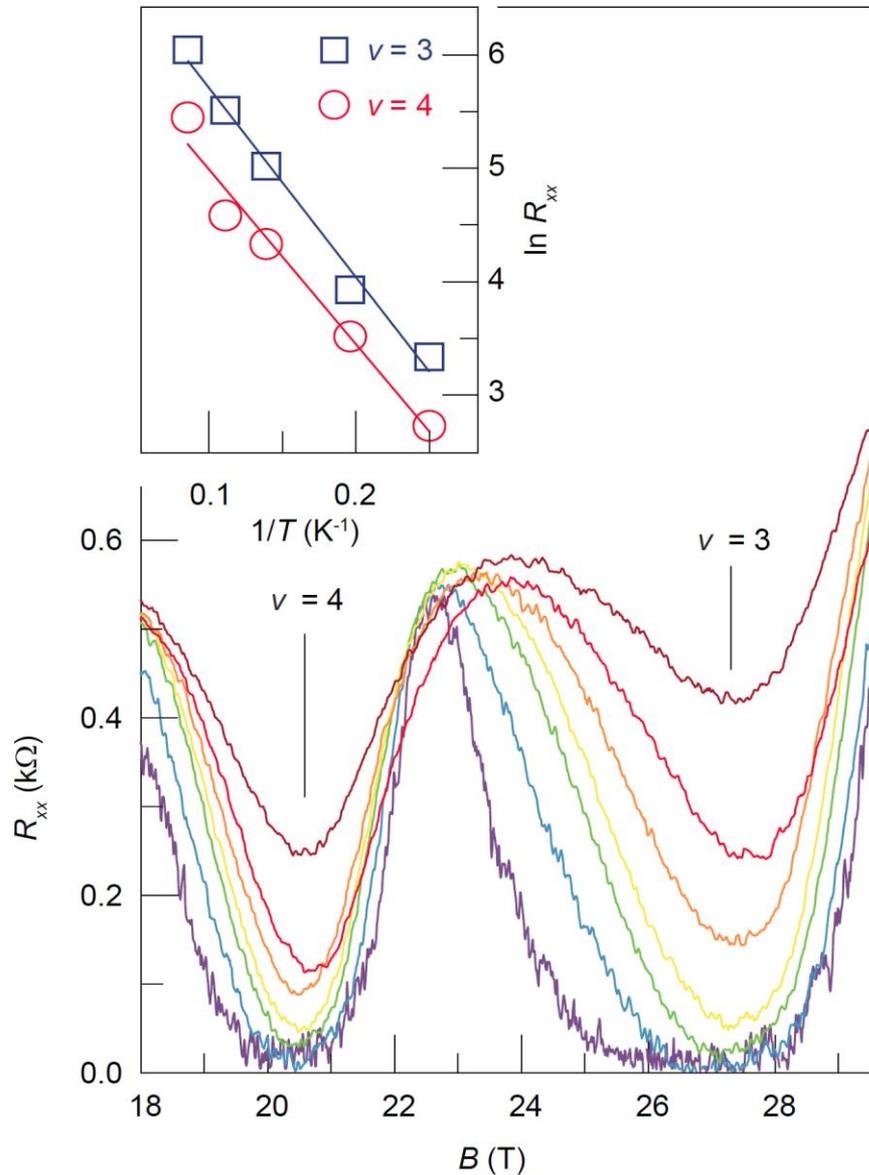


Factor of 3 increase in mobility

Quantum Hall Effect in Black Phosphorus 2DEG



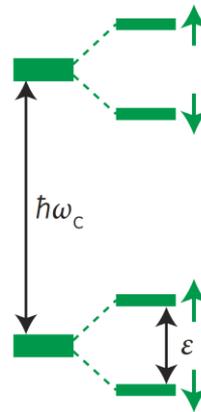
Landau Level Energy Landscape



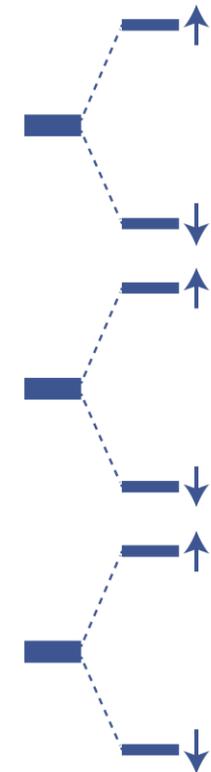
$$E_Z/E_C = m^* g^* / 2 m_0$$

$$E_Z/E_C = 0.35$$

$$E_Z/E_C > 0.5$$



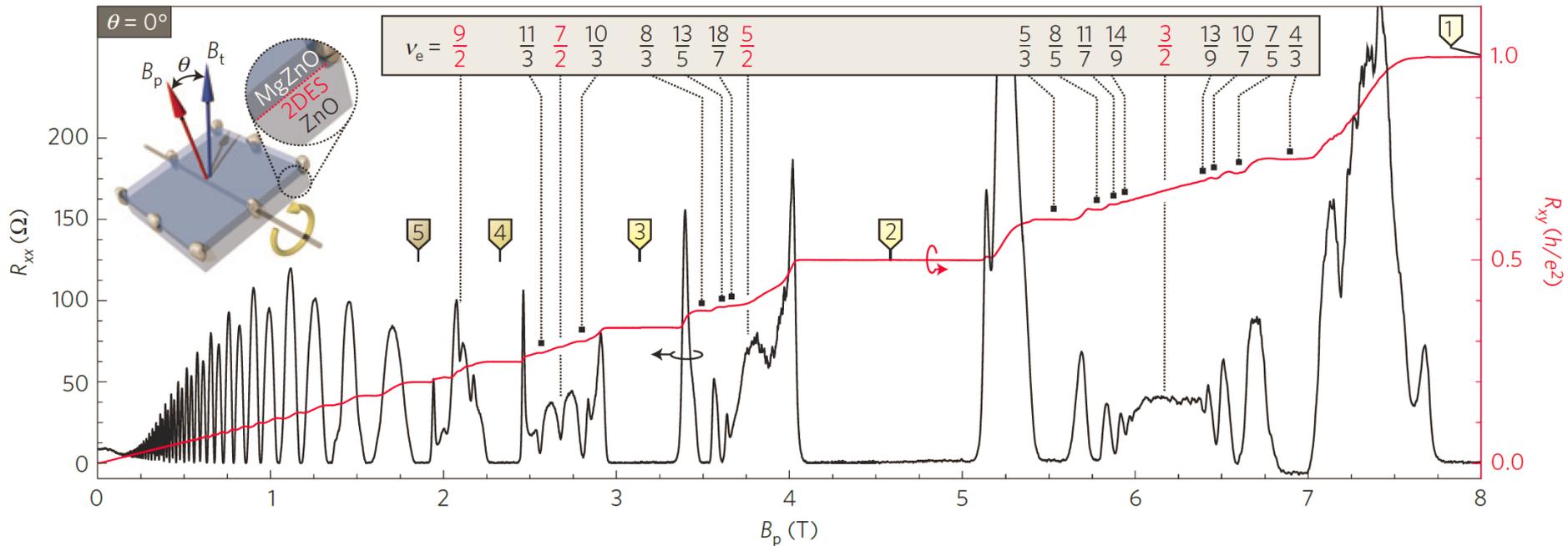
Holes



Electrons

Anyons in Black Phosphorus 2DEG?

Even-denominator fractional quantum Hall states in ZnO



Falson, J. *et al.* Nature Physics **11**, 347 (2015)

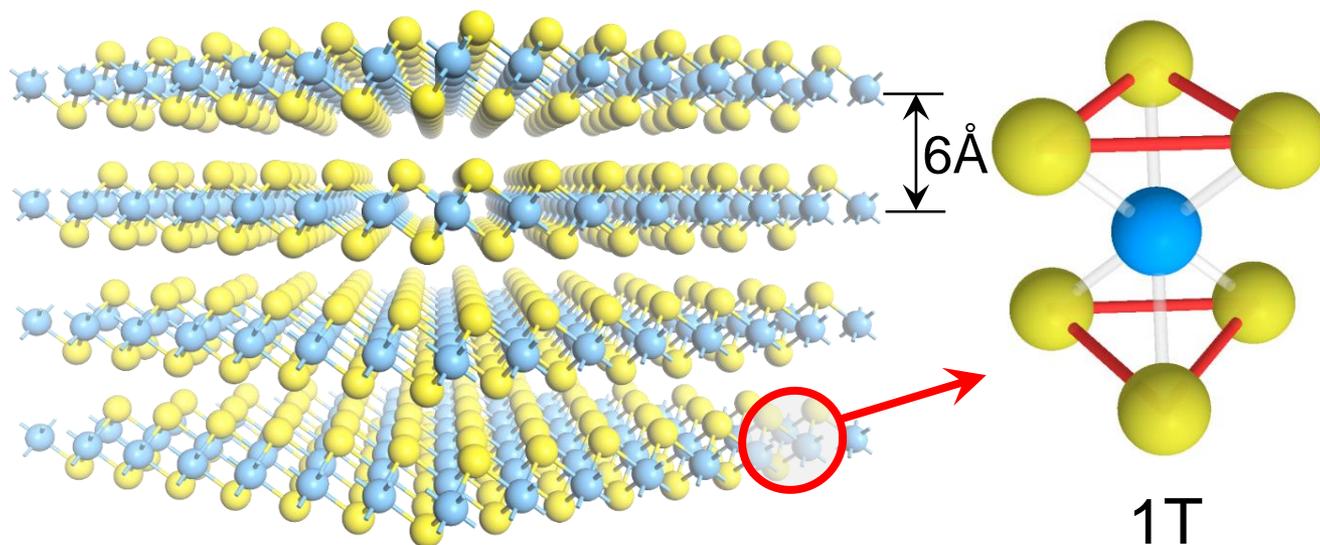
Black phosphorus potentially harbors similar FQH states

1T-TaS₂ : a Strongly Correlated 2D Material

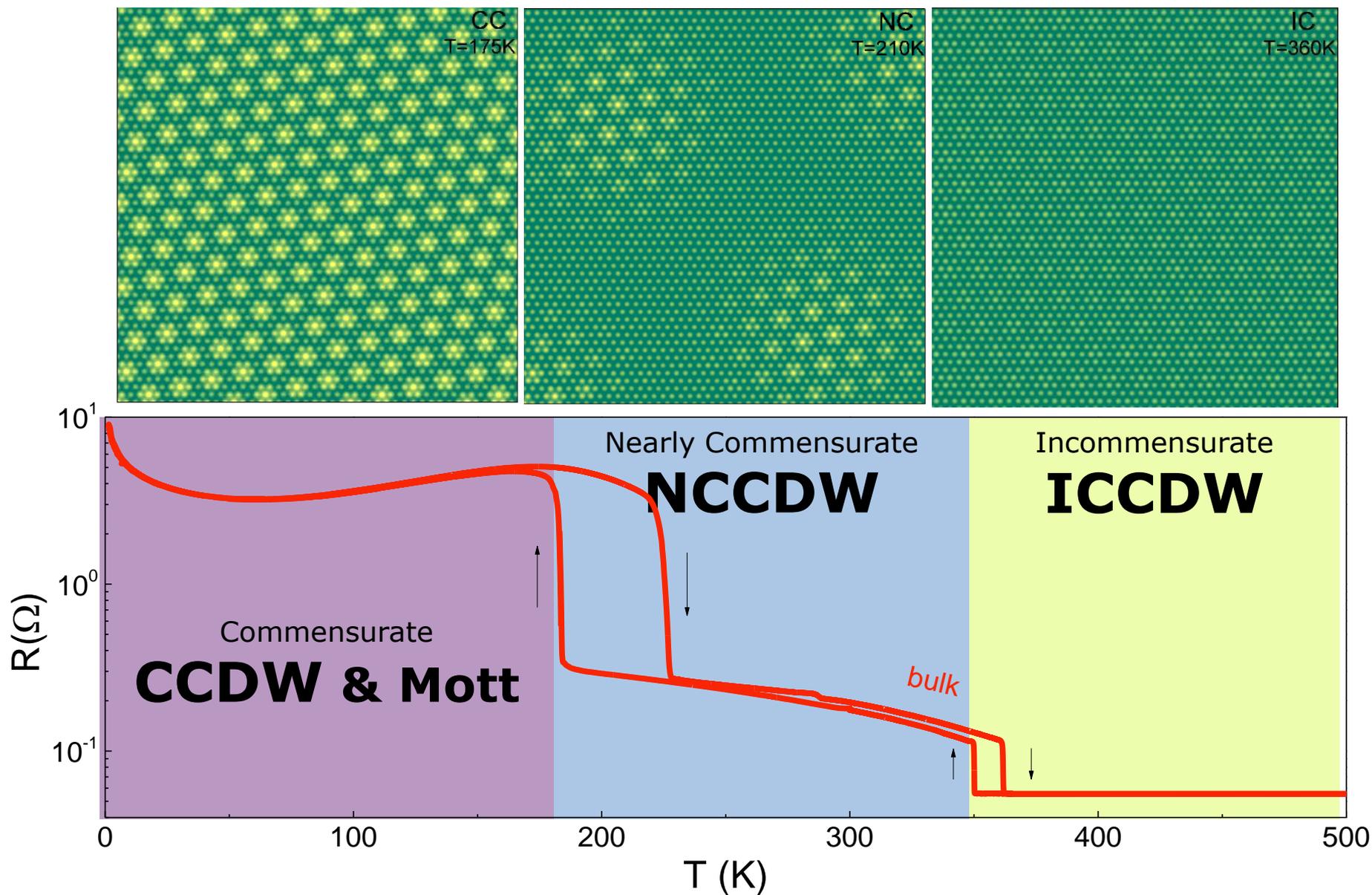


Yijun Yu

Crystal structure of 1T-TaS₂

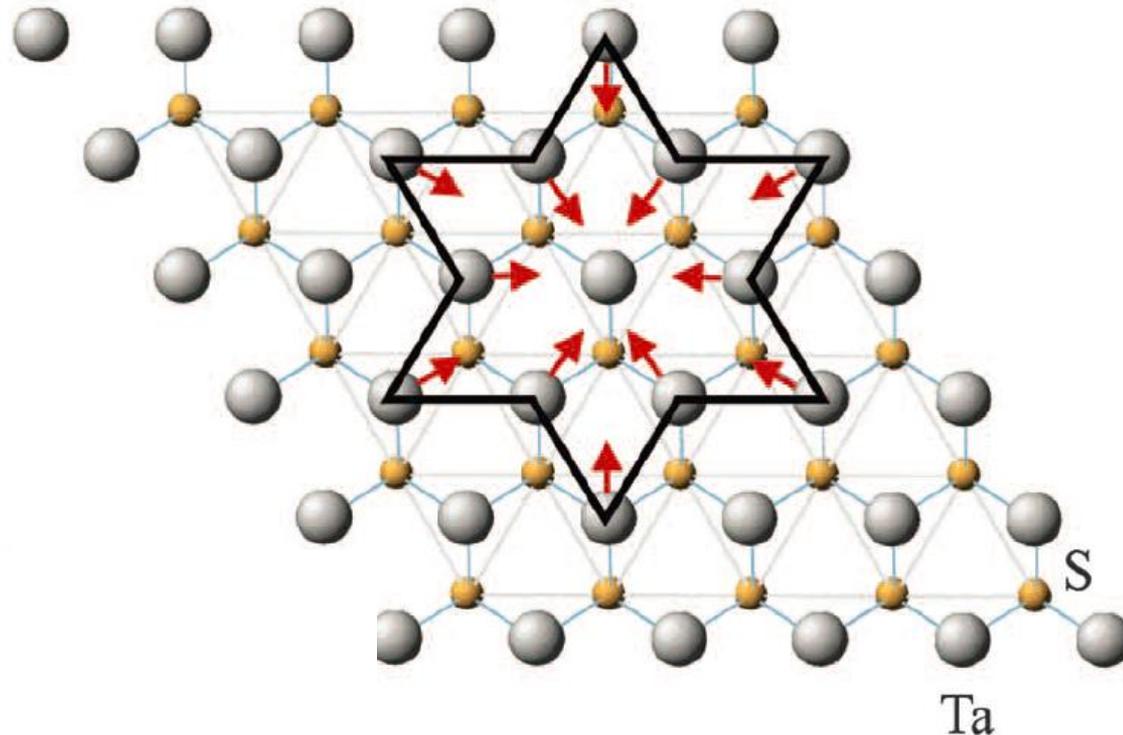


Various CDW Phases in 1T-TaS₂



Various CDW Phases in 1T-TaS₂

Commensurate CDW and Mott Insulator State



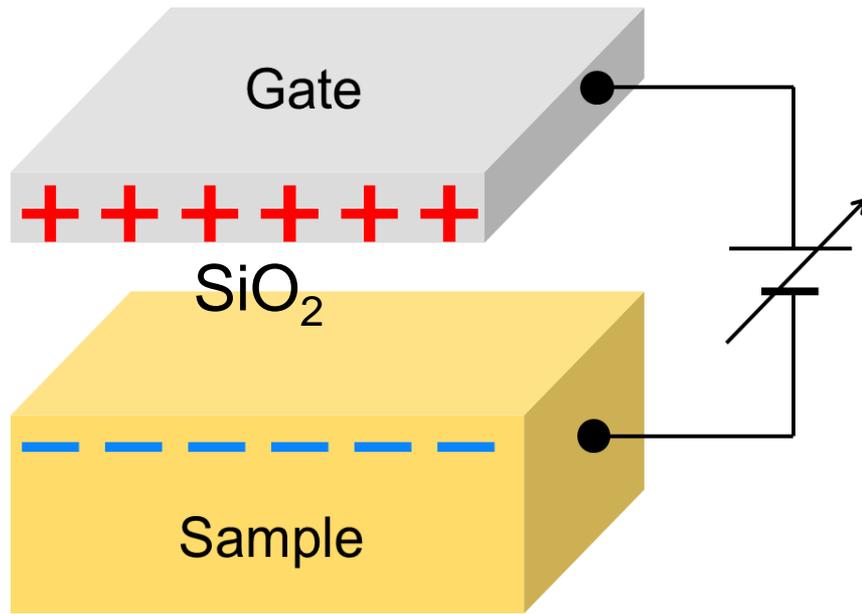
Wilson et al., *Adv. Phys.* (1975)

Fazekas, P. & Tosatti, E. *Philos. Mag. B* (1979)

Sipos, et al. *Nat. Mater.* (2008).

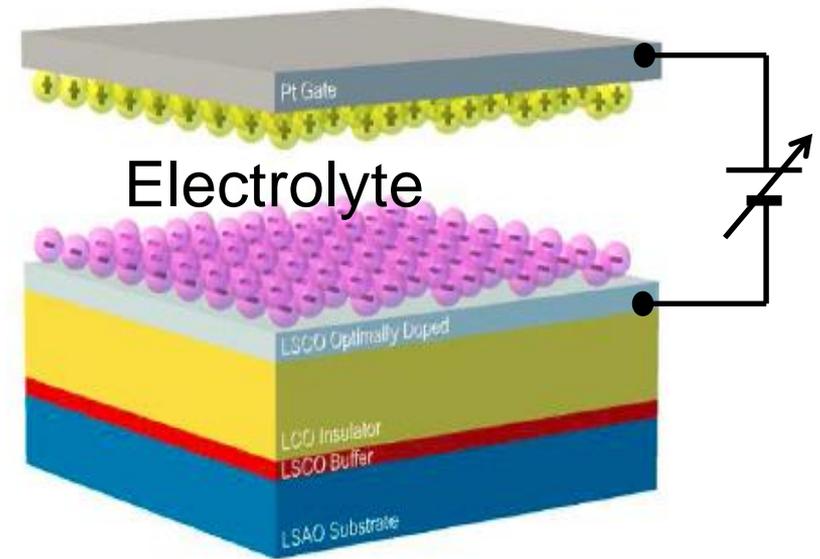
Gate Doping Limits

Conventional Dielectric Gating



Maximum $n \sim 10^{13} \text{ cm}^{-2}$

Ion Liquid Gating

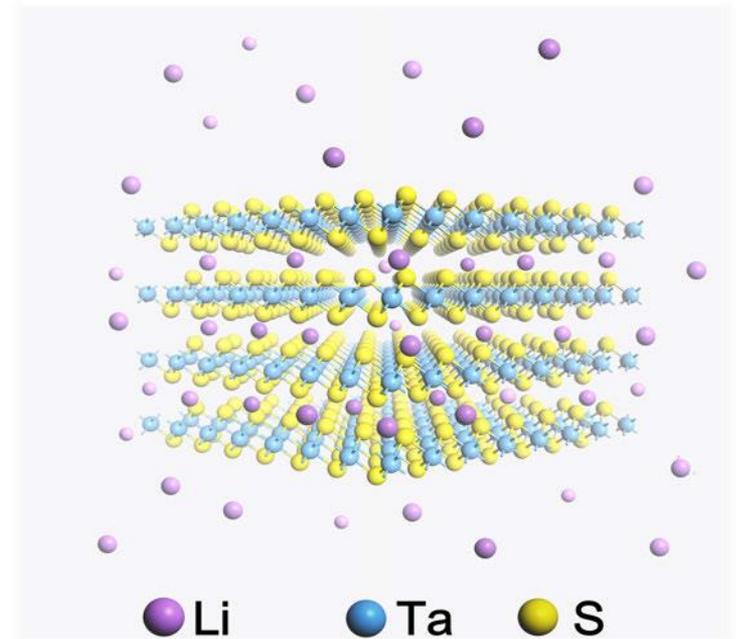
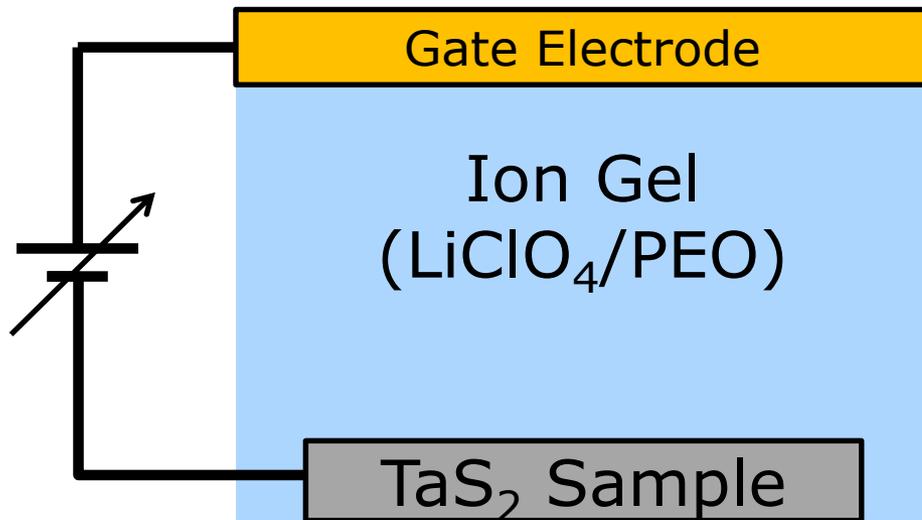


Maximum $n \sim 10^{14}-10^{15} \text{ cm}^{-2}$
Only top atomic layer

K.Ueno, *Nat. Mater.* (2008); D.K.Efetov, *Phys. Rev. Lett.* (2010); J.T.Ye, *Nat. Mater.* (2010); J.G.Checkelsky, *Nat. Phys.* (2012); Nakano, *Nature* (2012); J.T.Ye, *Science* (2013)

Tuning TaS₂ through Gate-controlled intercalation

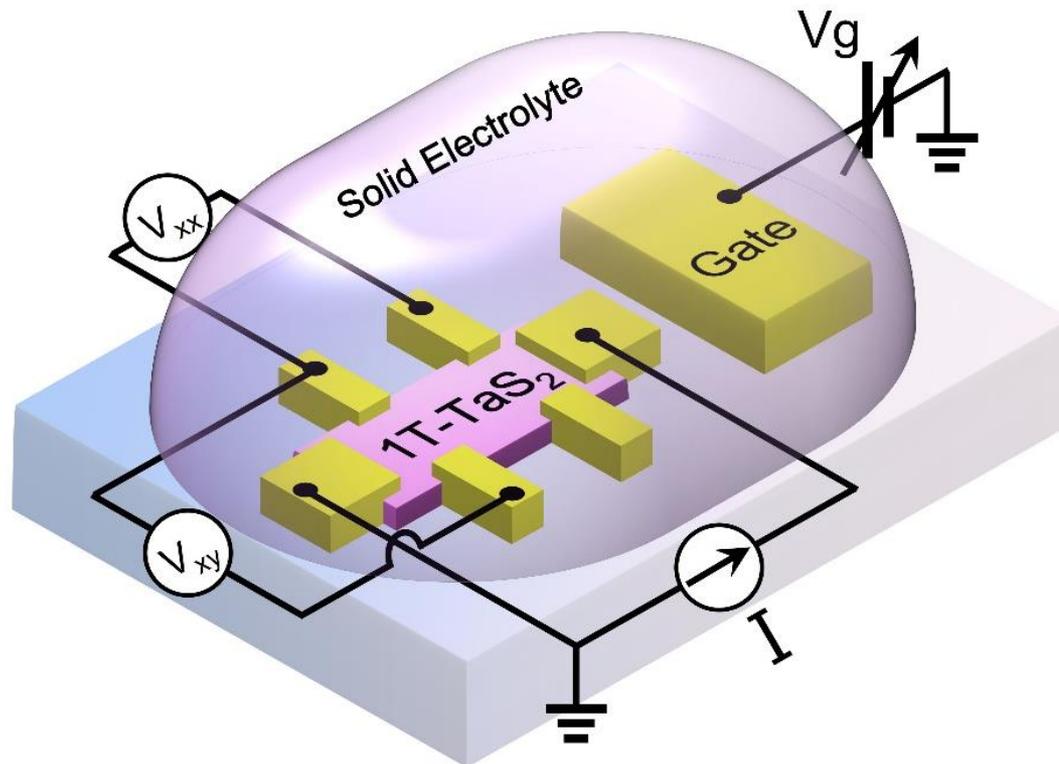
Gate-controlled intercalation in TaS₂



$n \sim 10^{15} \text{ cm}^{-2}$ for EACH atomic layer

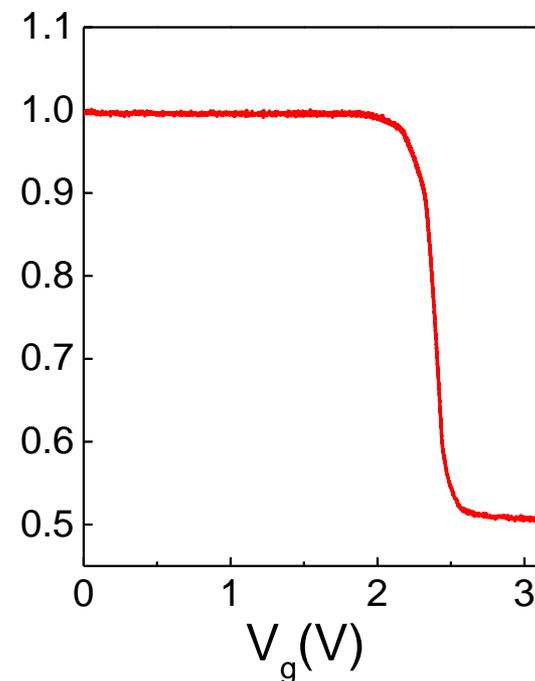
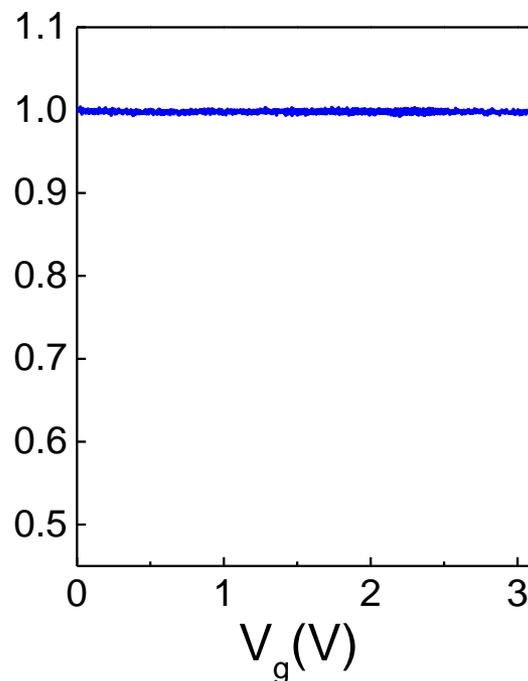
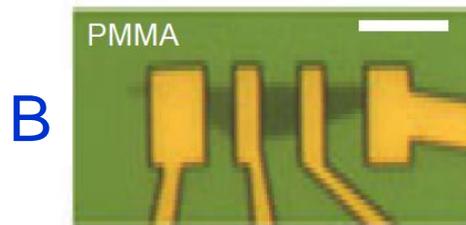
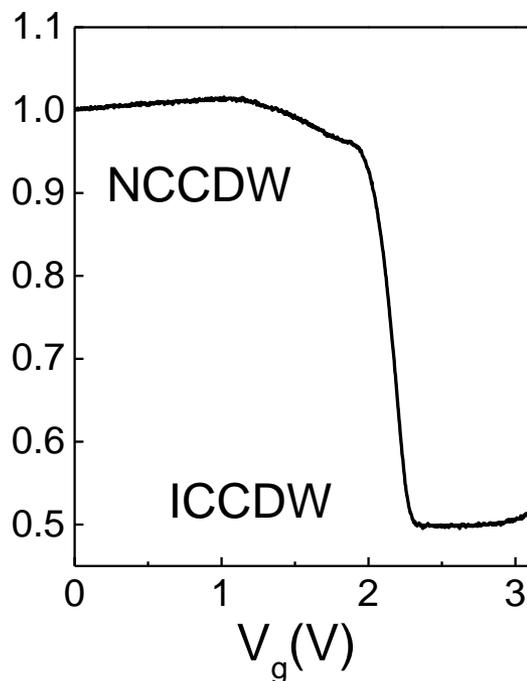
Gate-controlled Doping by Intercalation

Device Structure



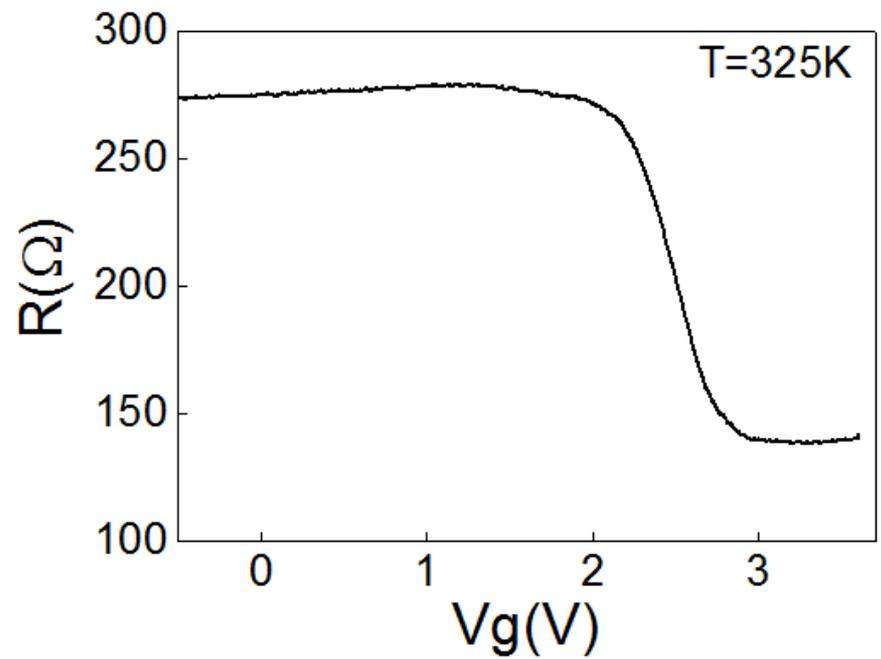
Yijun Yu *et al.* Nature Nano., 10, 270 (2015).

1T-TaS₂ Ionic Field-effect Transistors (iFET)

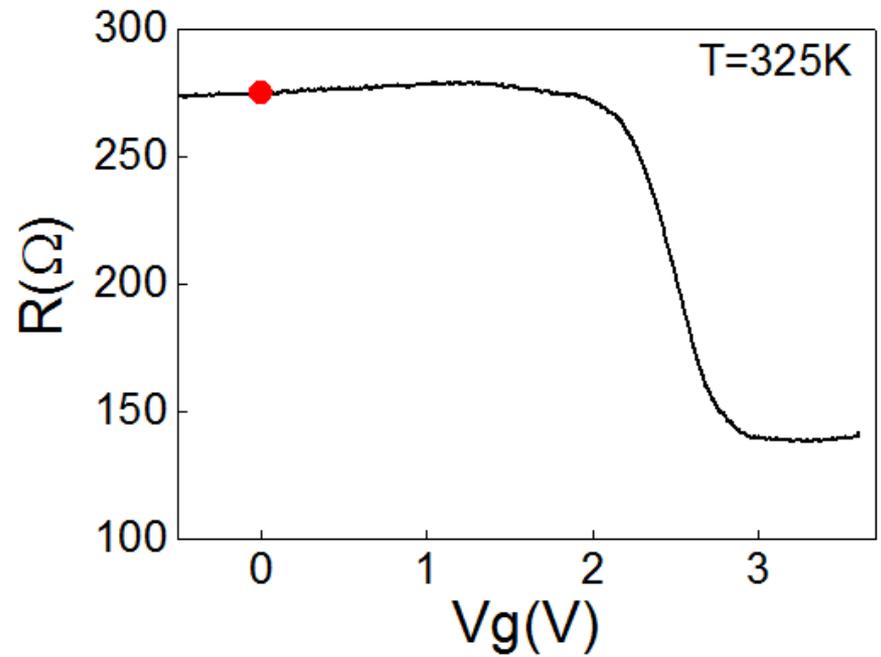
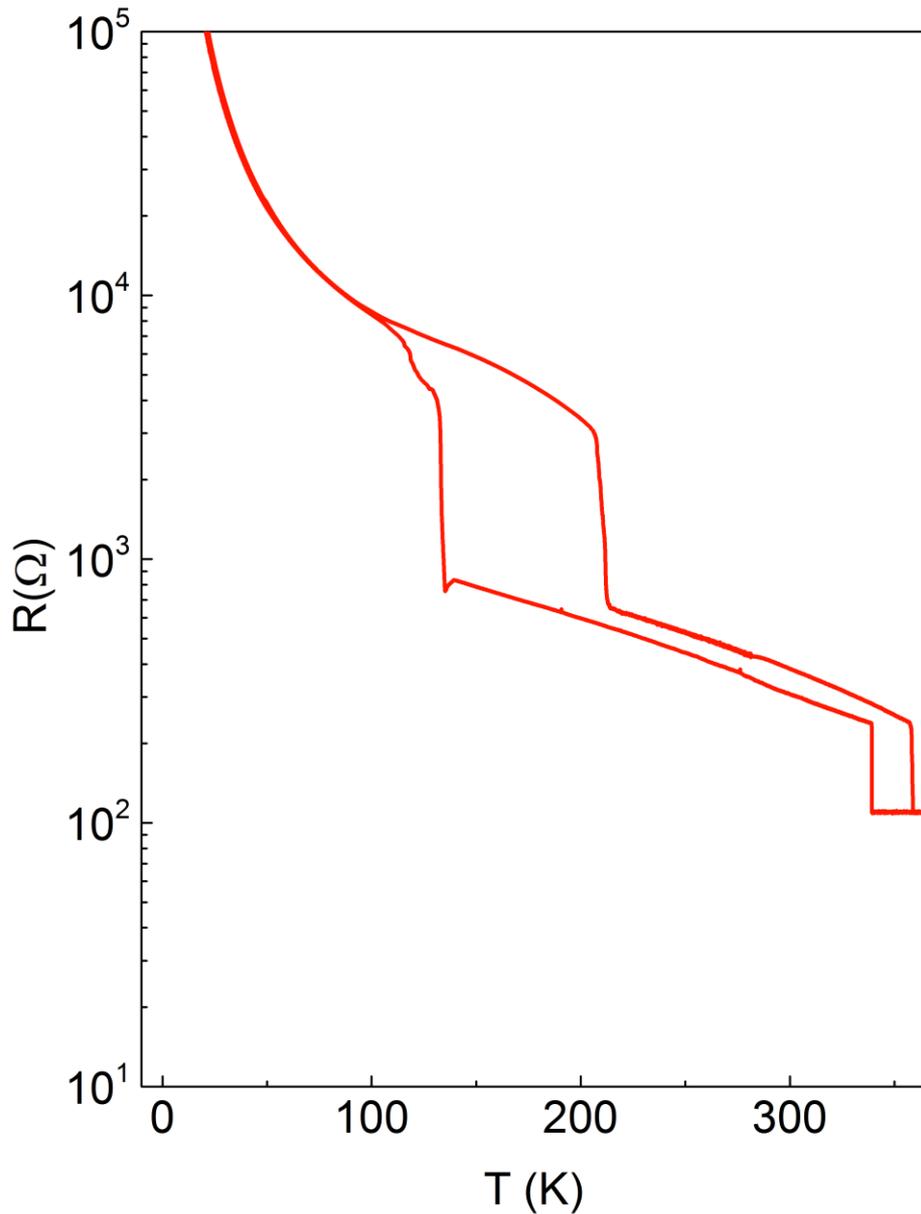


iFET operates through ion diffusion

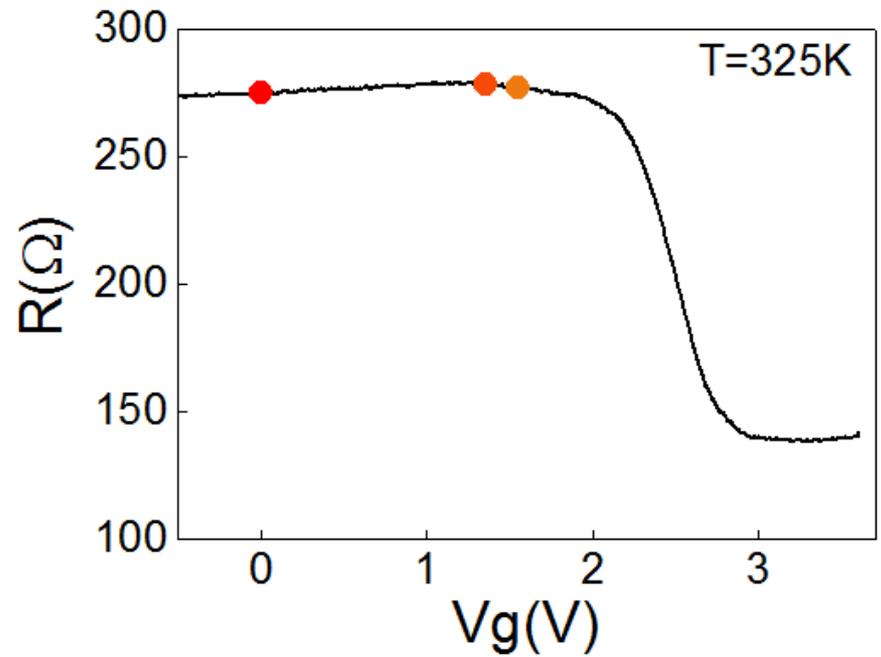
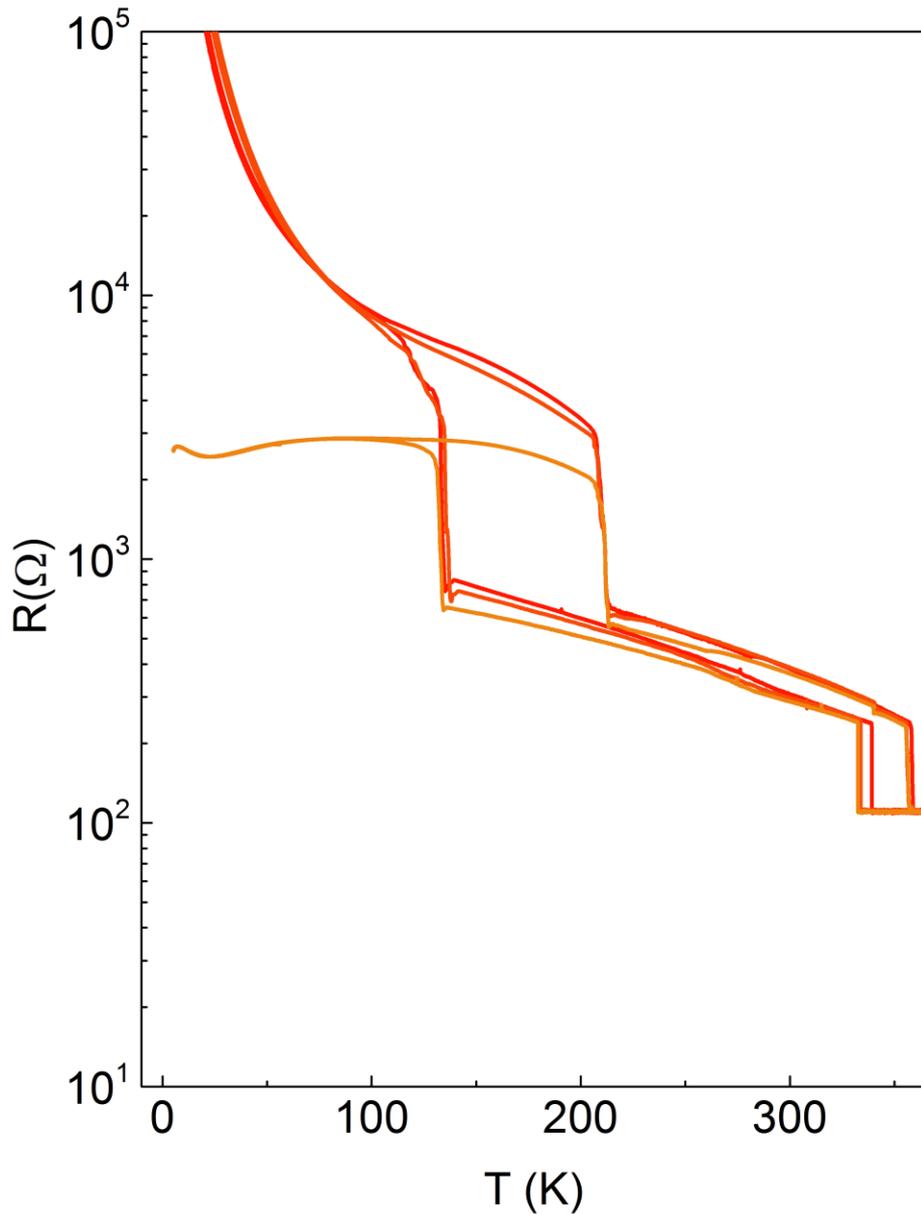
Gate-controlled Doping by Intercalation



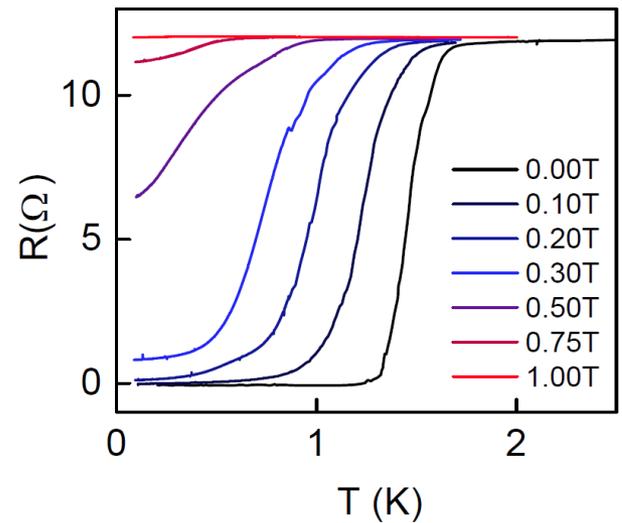
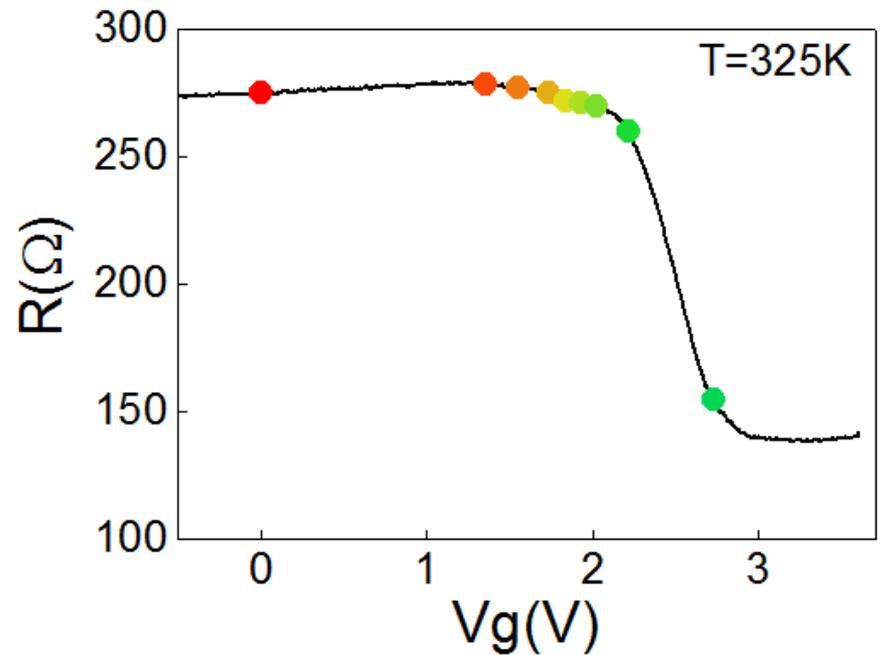
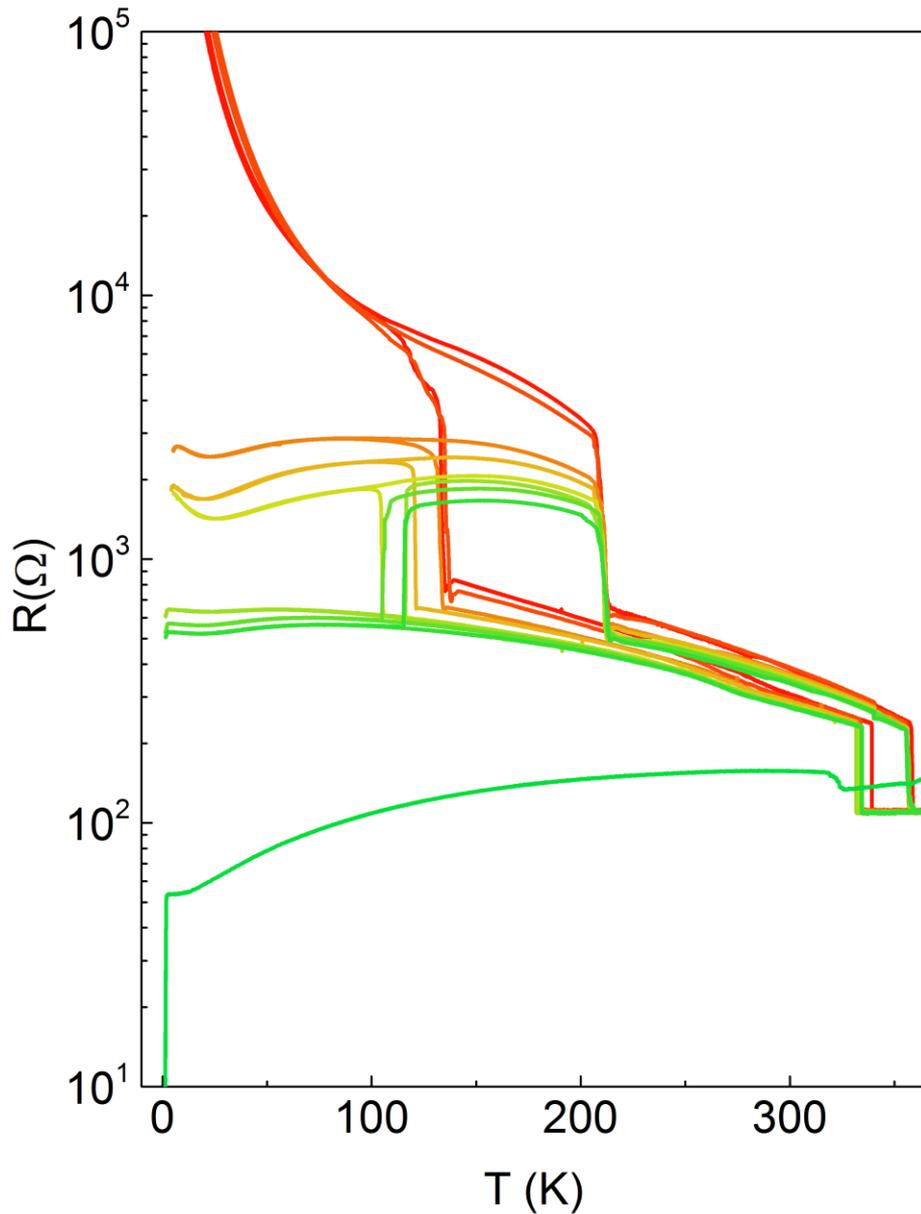
Gate-controlled Doping by Intercalation



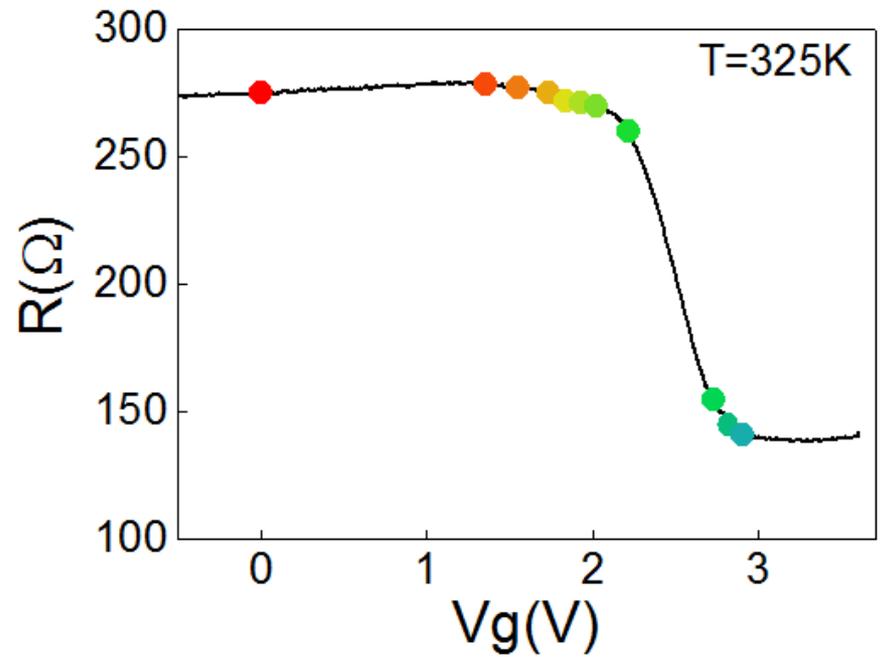
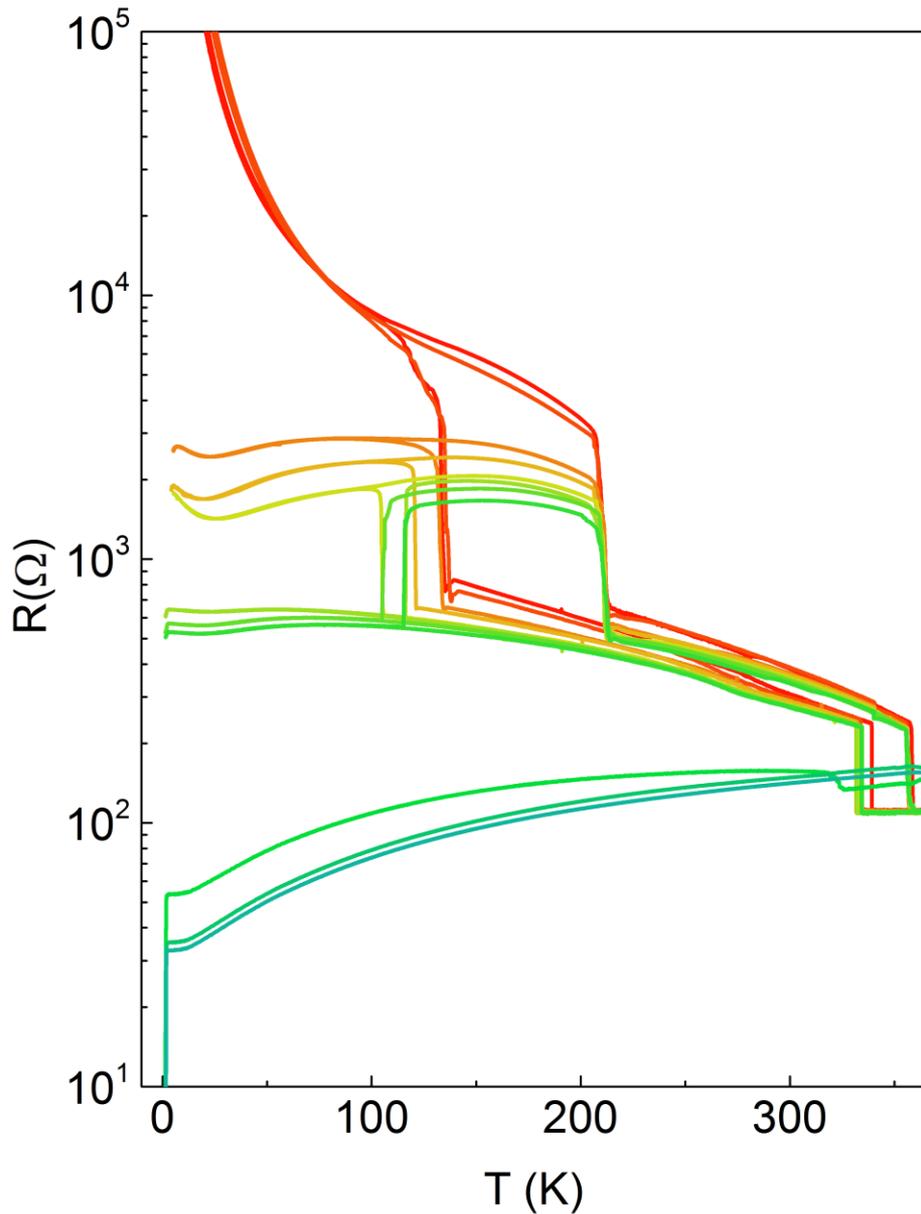
Gate-controlled Doping by Intercalation



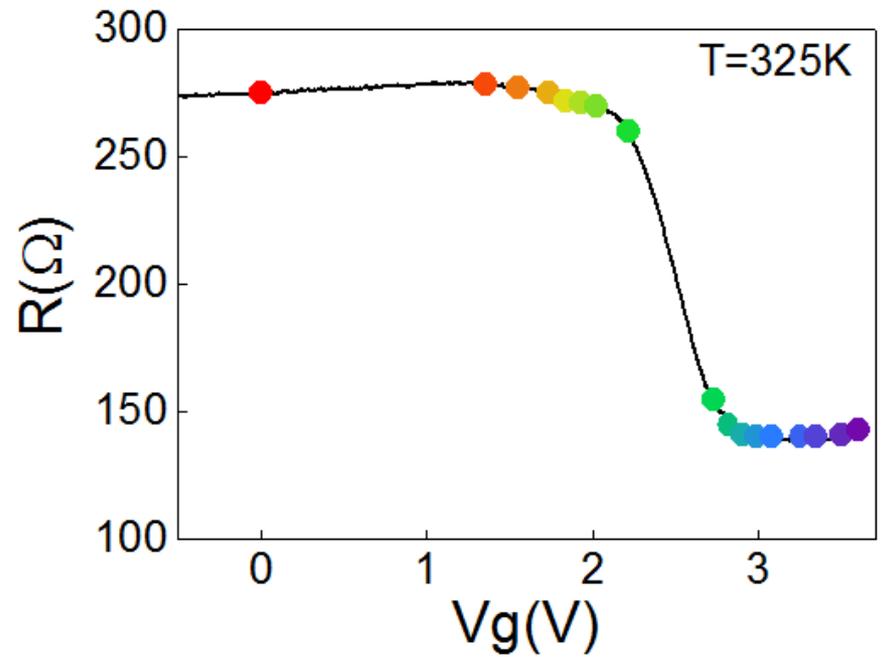
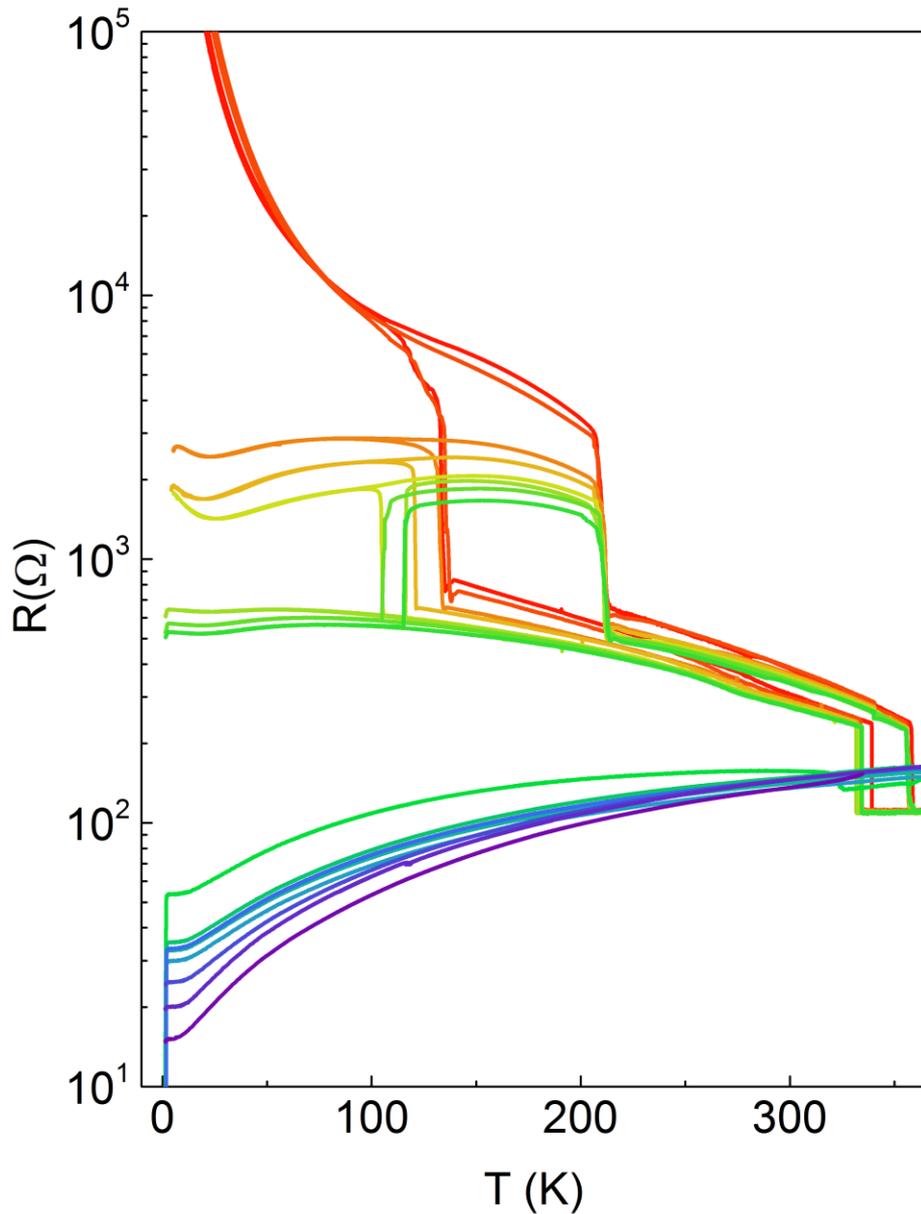
Gate-controlled Doping by Intercalation



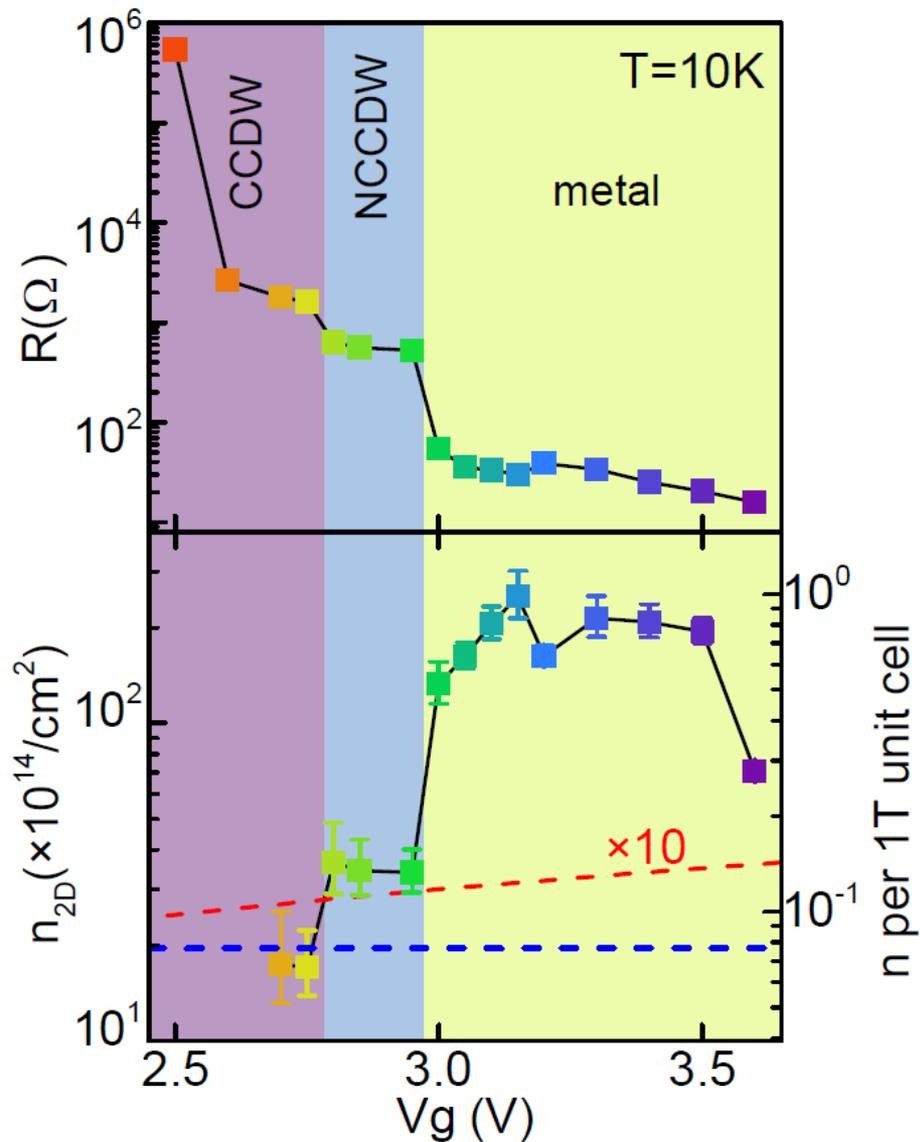
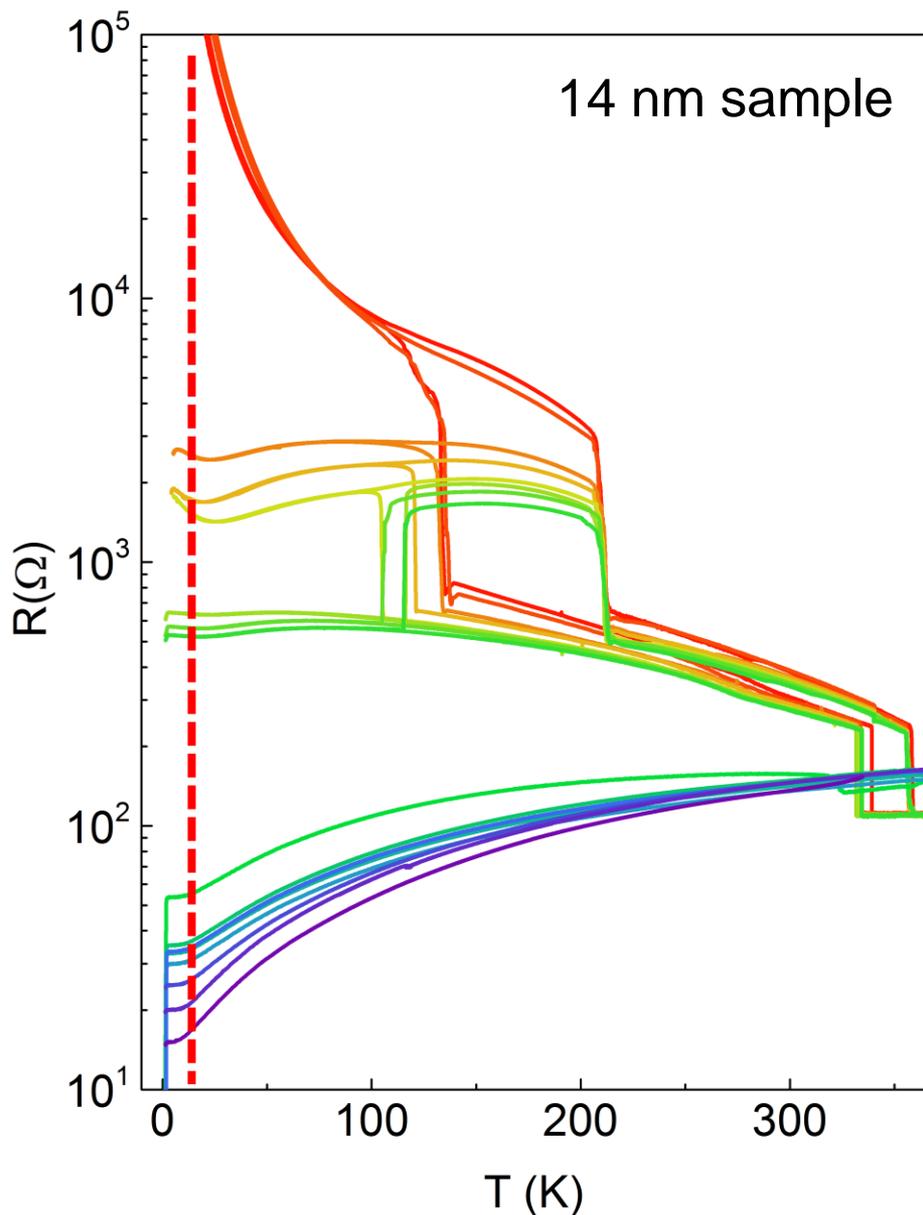
Gate-controlled Doping by Intercalation



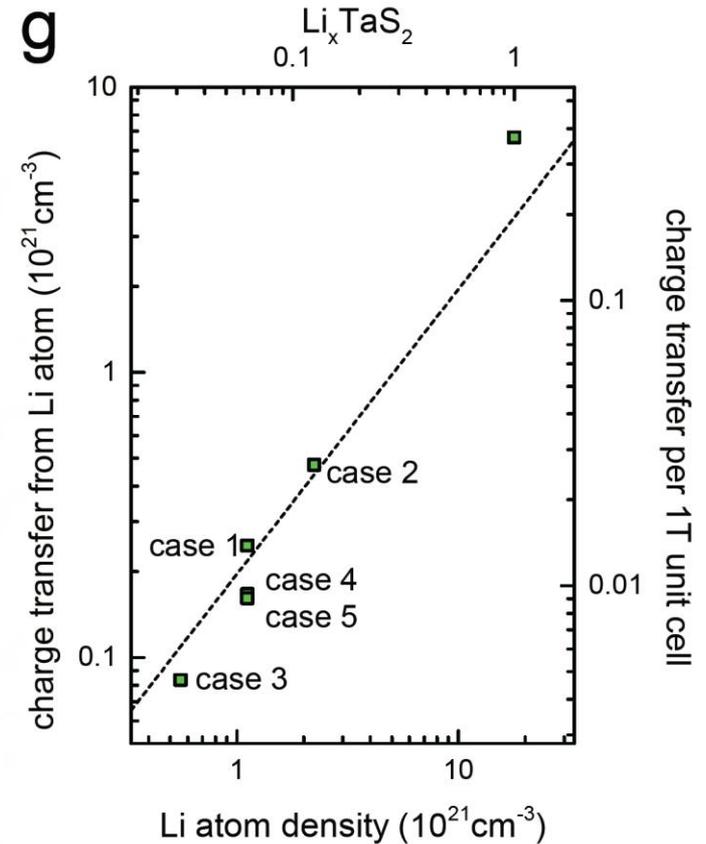
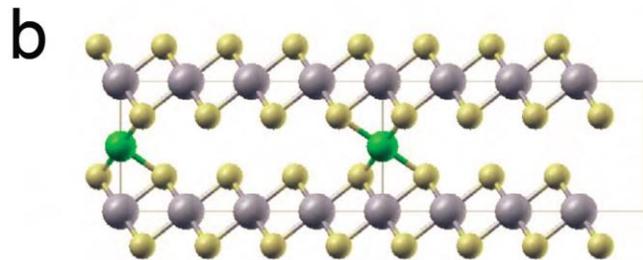
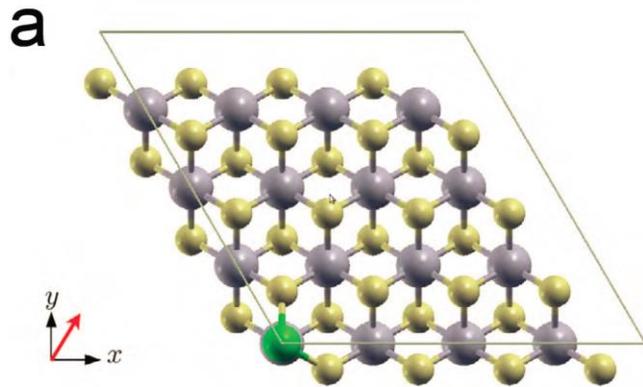
Gate-controlled Doping by Intercalation



Gate-controlled Doping by Intercalation

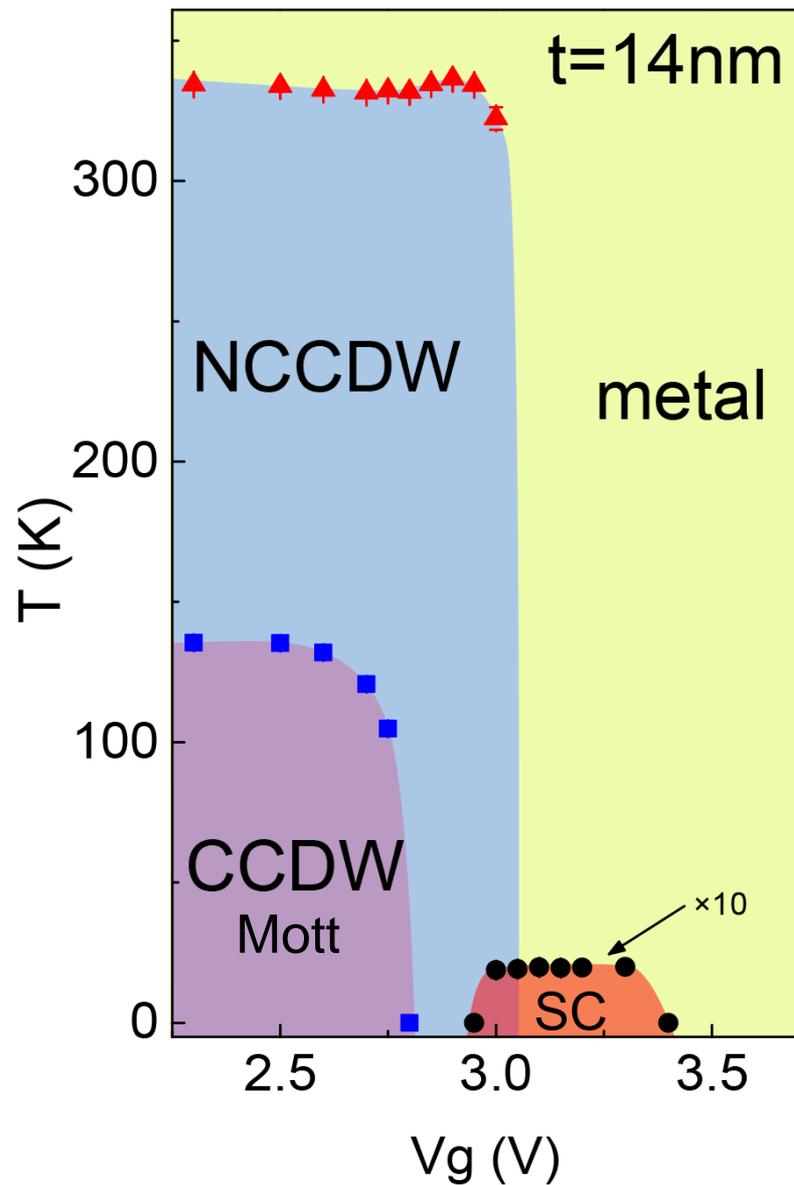
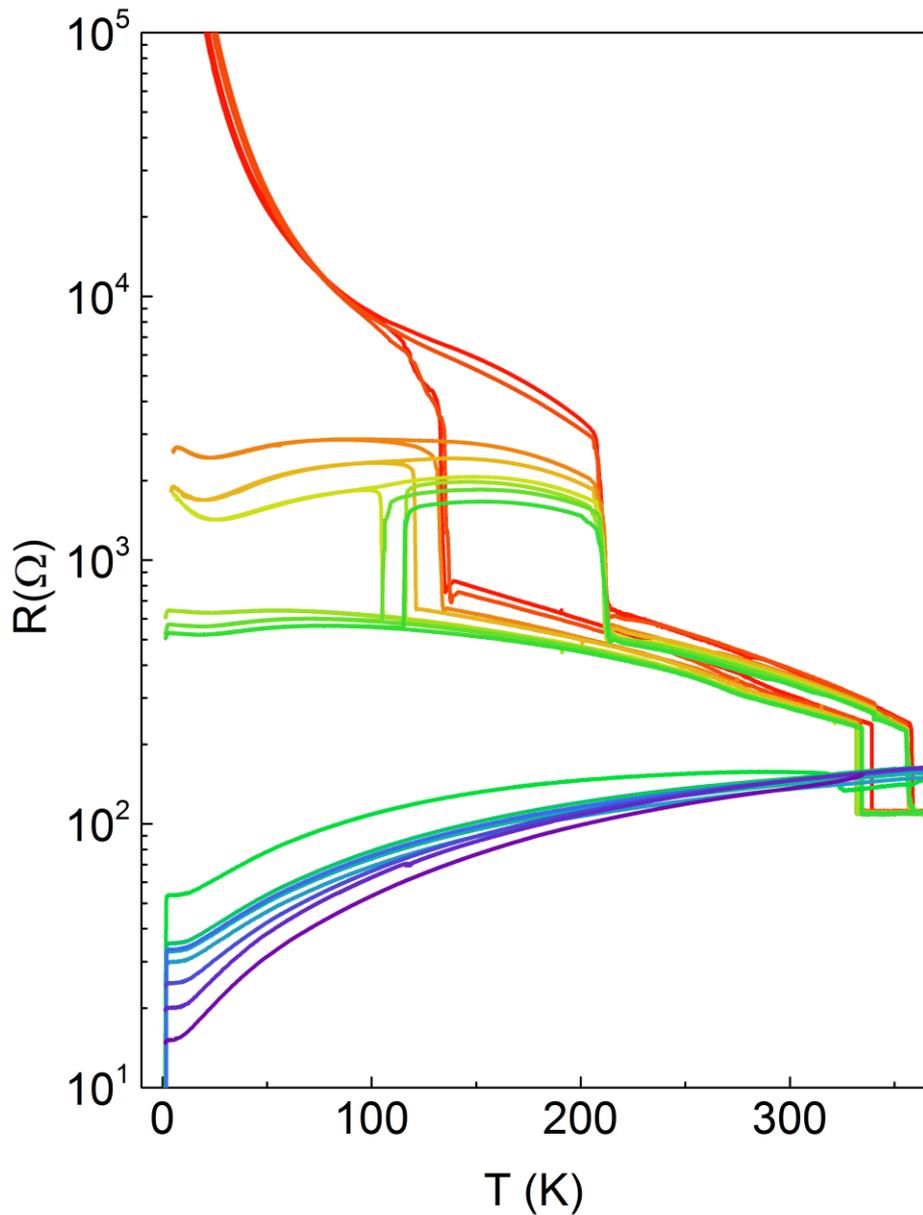


Electron Doping from Charge Transfer

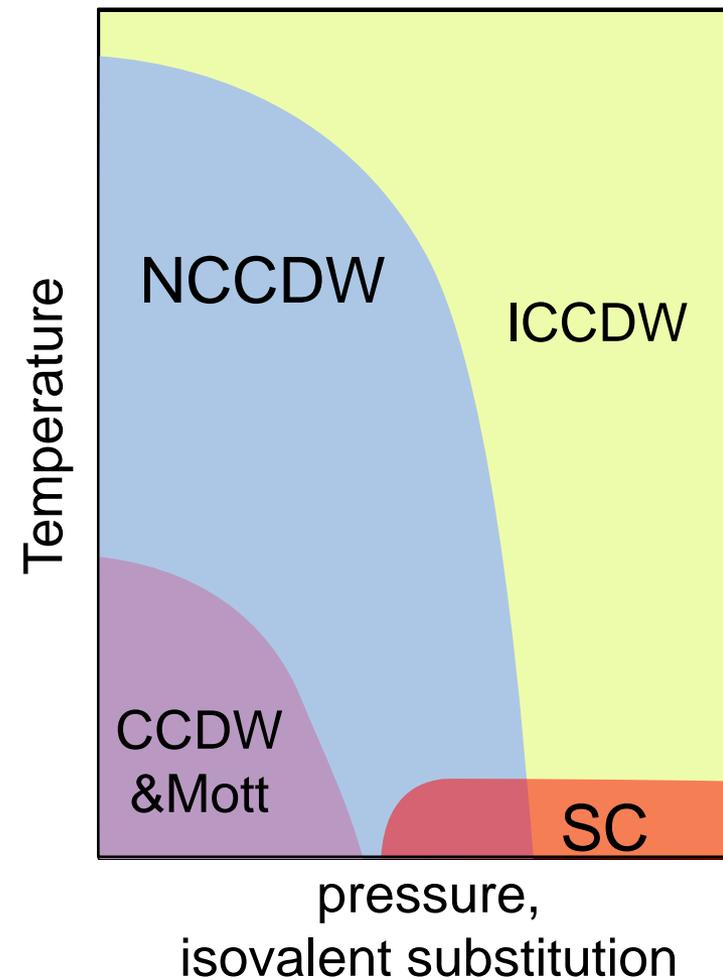
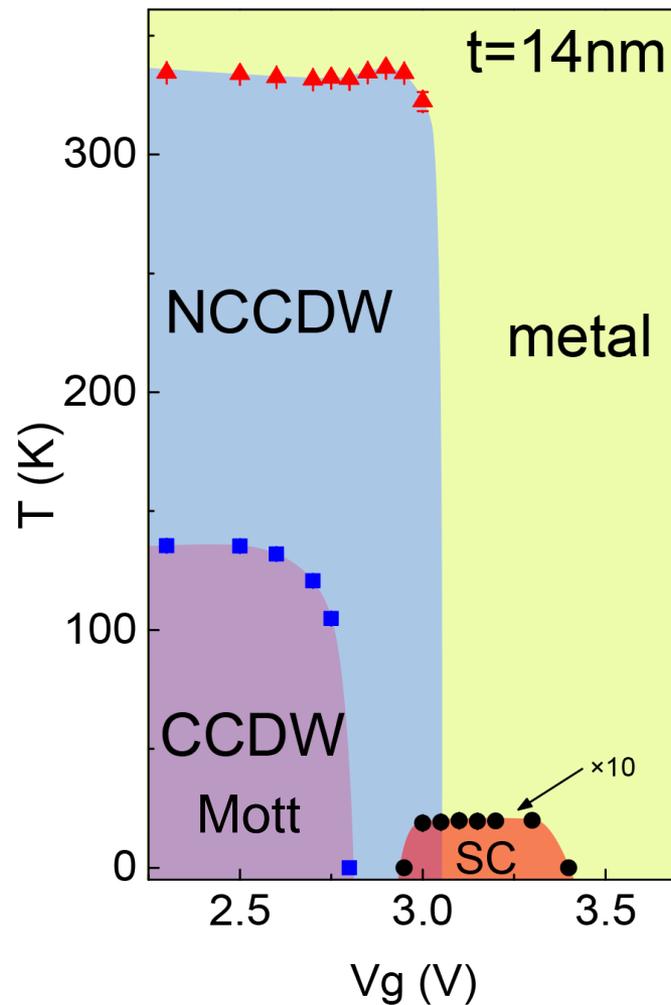


~ 20% electron doping from charge transfer from Li

Tunable Phases in 1T-TaS₂ iFET



Intercalation Compared with Pressure and Isovalent Substitution

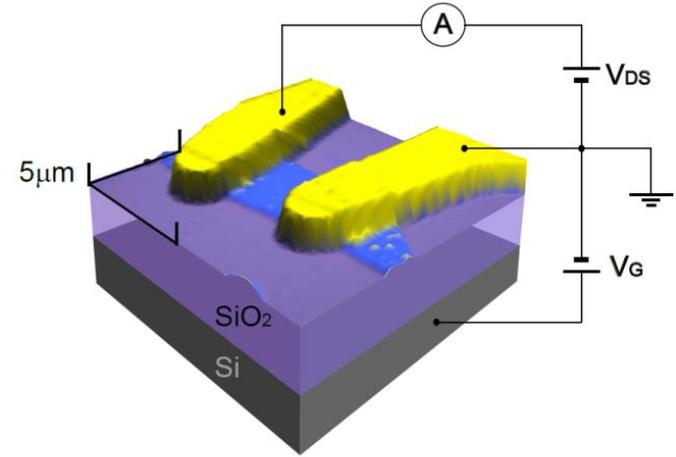


Connection btw intercalation and pressure/isovalent substitution??

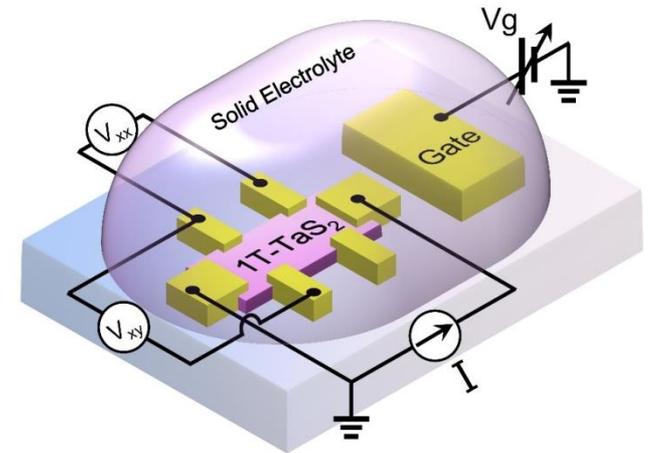
Sipos, *et al.* *Nat. Mater.* (2008).
L. J. Li *et al.* *EPL* (2012)
R. Ang *et al.* *PRL* (2012)

Summary

- Black Phosphorus Transistor



- Tunable Phases in 1T-TaS₂



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