國立臺灣大學
National Taiwan University

Graphene 2017
March 28-31
Barcelona (Spain)

# Air stable n-type black phosphorus transistor with photoactive doping layer

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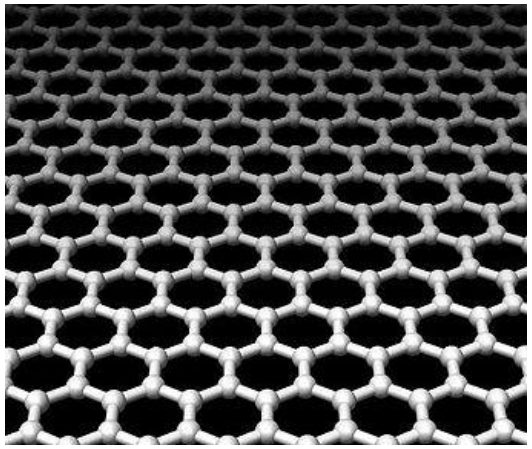
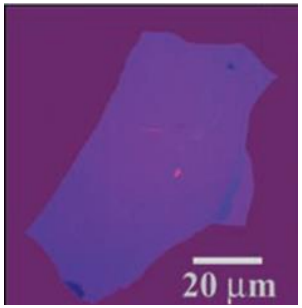
7th edition of Graphene Conference, Mar. 30 , 2017

# Brief introduction to 2D materials

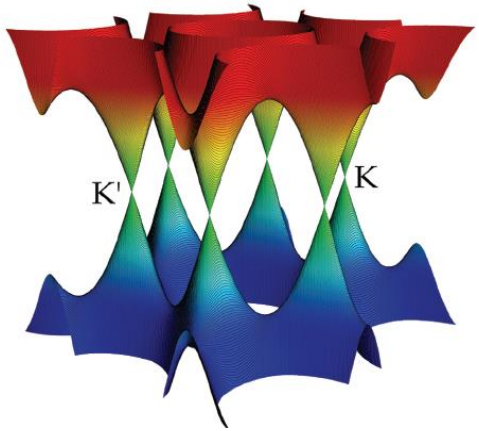
## Graphene







Novoselov et al., *Science* 306.5696 (2004).

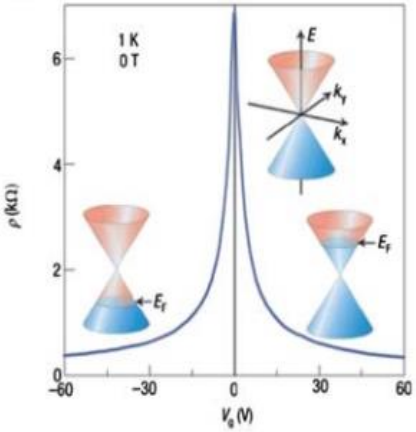



- ✓ ***Atomic-thick monolayer** of **carbon atoms** in **honeycomb shape***

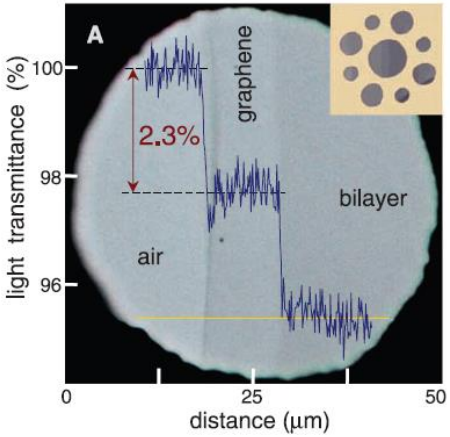
- *Unique band structure*

- *Extraordinary **electrical** and **optical** properties*

➢ ***Zero effective mass** near the Dirac point*
➢ ***High carrier mobility***
➢ ***Sensitive and tunable fermi level***
➢ ***High transparency***

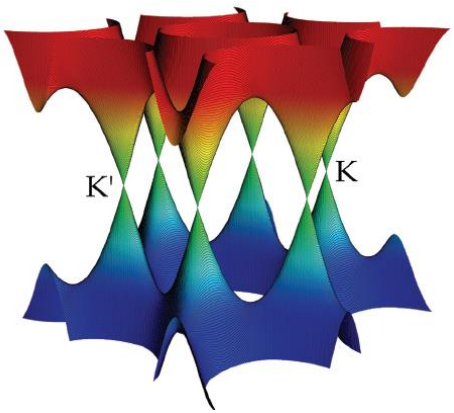



**J. Mater. Chem., 21, 3335–3345(2011)**



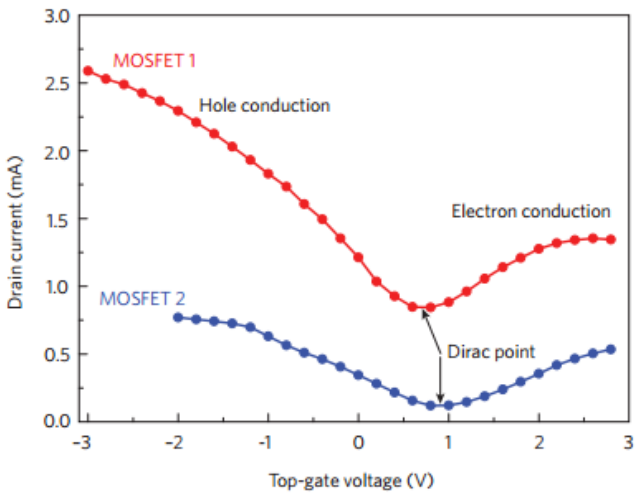

*Science*, **2008**, *320*, 1308–1308

# Restriction against graphene

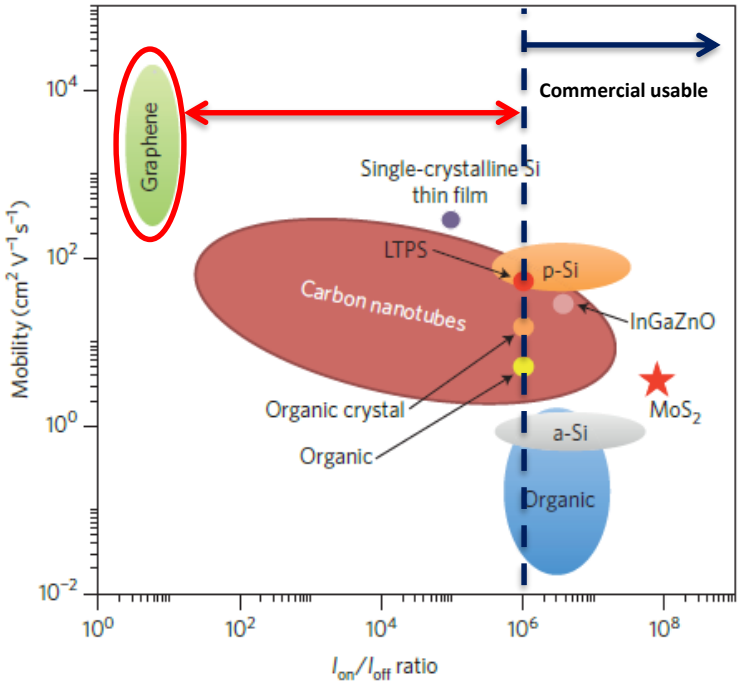



- ***Absence of a bandgap!***
  - *Graphene transistors are difficult to turn "off"*
  - ***Low on/off ratio (usually < 10)***

- *On/off current ratio is usually far below what is needed for applications in logic circuits*




Nature Nanotechnology 5, 487–496 (2010)

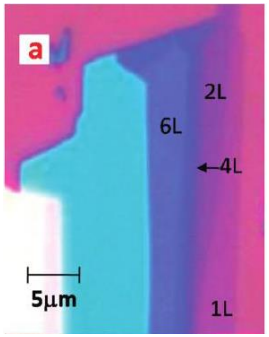



Nature Nanotechnology 9, 768–779 (2014)

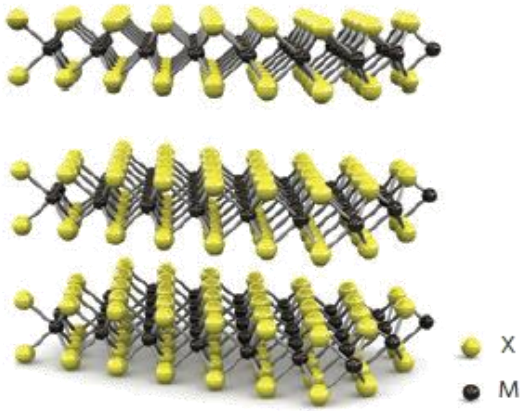
# 2D materials beyond graphene

- *Transition metal dichalcogenide (TMD)*
  - *Exfoliated by scotch tape method*
  - *Layered structure*
  - *$MoS_2$, $MoSe_2$, $WS_2$…*
  - *1~2eV direct bandgap*
  - ✓ ***Much higher on/off ratio***
  - ✓ ***Inferior mobility ~1-10 $cm^2/V{\cdot}s$***

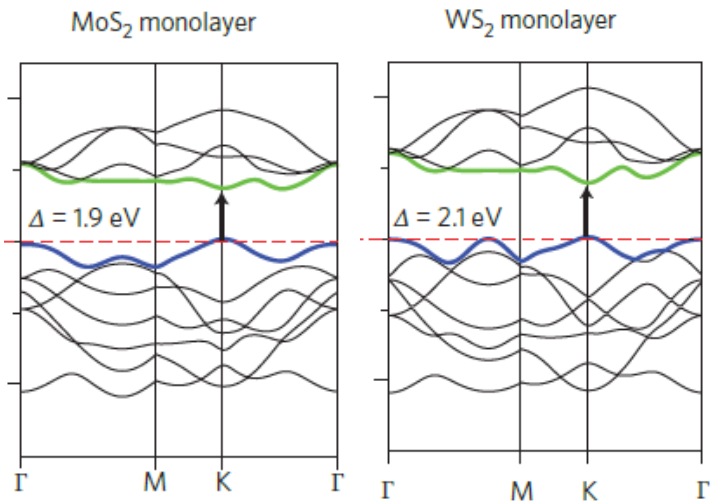

*Science* 306.5696 (2004).



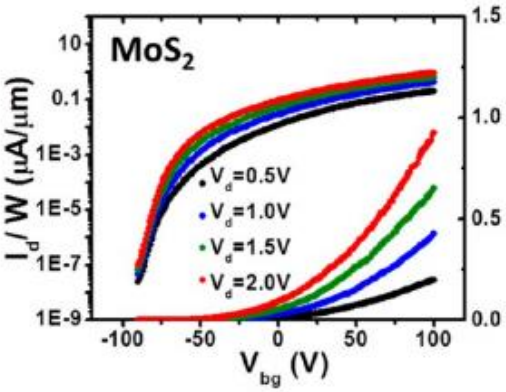

*Nano Lett.*, **2010**, *10* (4), 1271–1275

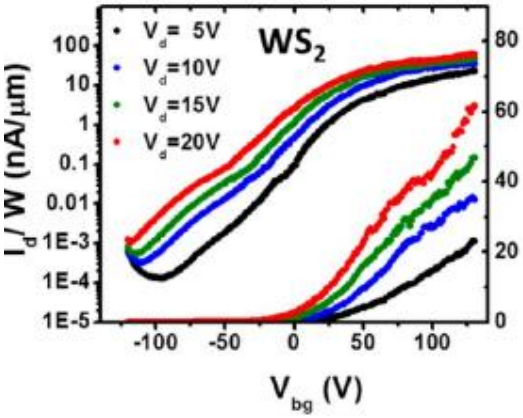



Nature Nanotechnology 6, 147–150 (2011)




*Phys. Rev. B* **83,** 245213 (2011)




Nano Lett. 2013, 13, 1852−1857

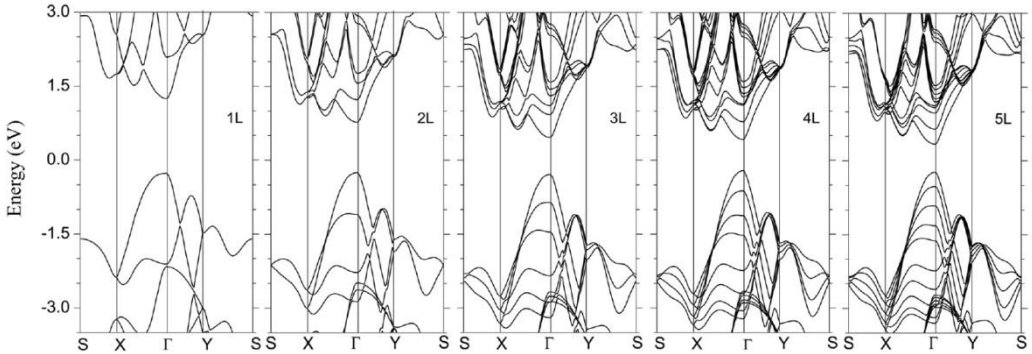
# 2D materials beyond graphene

***Black phosphorous ( phosphorene)***

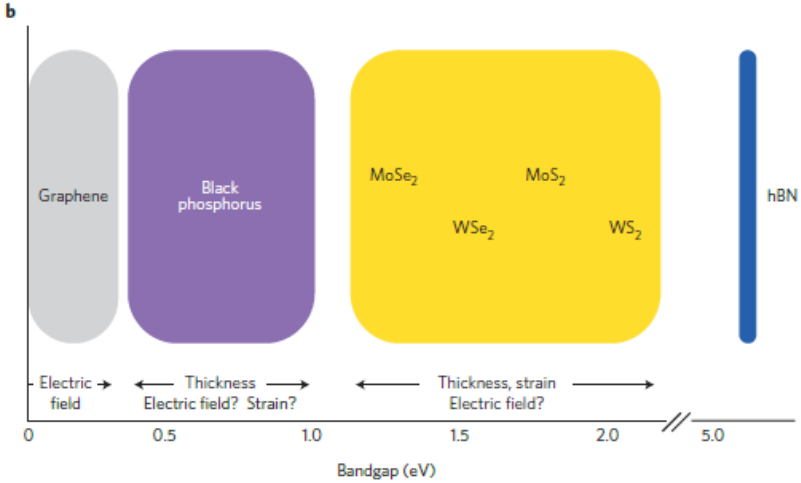

Nature Nanotechnology 9, 330–331 (2014) DOI: 10.1038/nnano.2014.85

- *The most stable phosphorus (P) allotrope, also known as **phosphorene** or **BP***
- *The second known two-dimensional material formed by only single element*
  - ***Chair configuration***
- *Thickness-dependent **direct bandgap***
  - *Bandgap changes from about 2.0eV(monolayer) to 0.35eV(bulk)*

- Thickness dependent band structure




Scientific Reports 4, 6677, (2014)

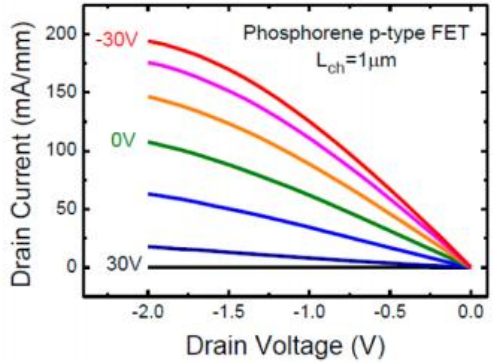


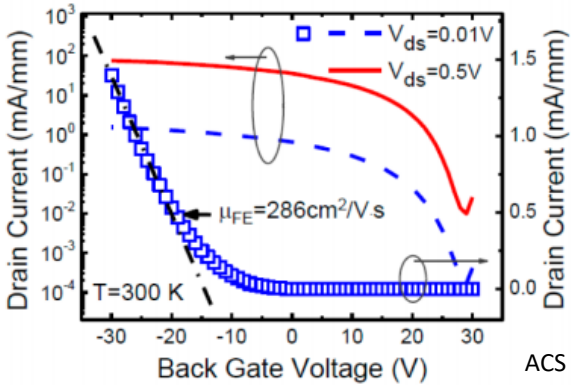

*Nature Nanotechnology 9, 330–331 (2014)*

# Characteristics of black phosphorous devices

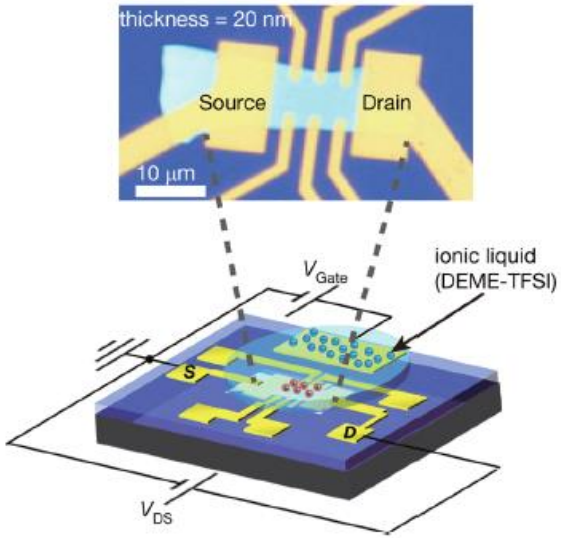

Nature Nanotechnology 9, 330–331 (2014) DOI: 10.1038/nnano.2014.85

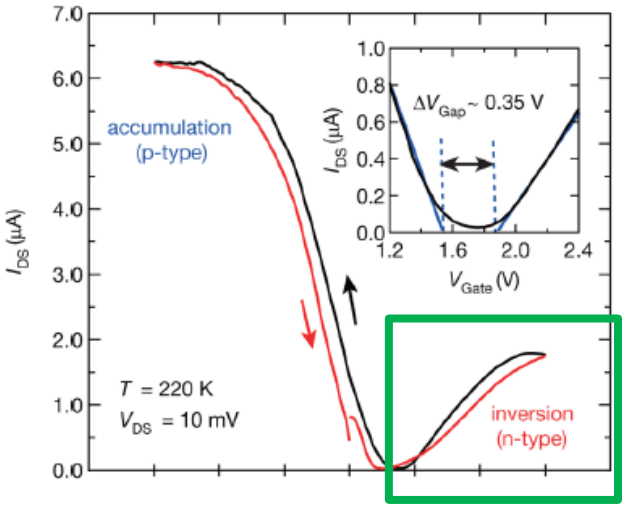
- *Black phosphorus usually shows intrinsic **p-type** semiconducting characteristic with **high average carrier mobility** range from **100** to **300cm$^2$V$^{-1}$s$^{-1}$** at room temperature*
  *(highest value of **1000 cm$^2$/V·s** has been reported)*
- *On/off ratio of **$10^5$** can be achieved*
- ***Ambipolar** transport properties was also reported*
- ***Weaker n-type** transport properties than **p-type***
- ***effective n-type doping technique** is needed*




ACS Nano, 2014, 8 (4), pp 4033–40413

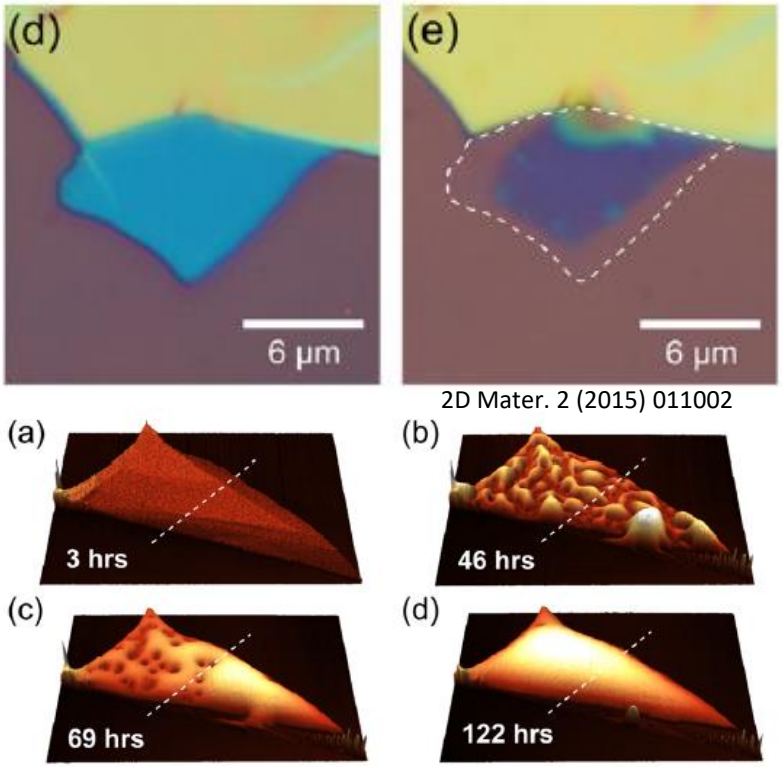



*ACS Nano*, *9* (3), pp 3192–3198 (2015)

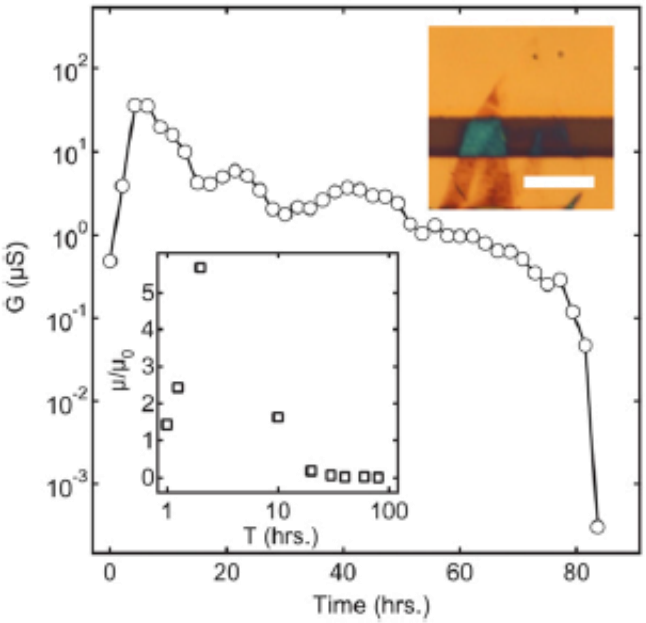
# *Instability in ambient atmosphere*

- *Few-layer black phosphorus is extremely* ***unstable in ambient atmosphere***
  - *Degradation occurs at the* ***surface*** *and would even damage the* ***electronic performance***




2D Mater. 2 (2015) 011002

*Nano Lett.*, **2014**, *14* (12), pp 6964–6970




*Nano Lett.*, **2014**, *14* (12), pp 6964–6970

◆ ***A big challenge for device fabrication and practical applications***

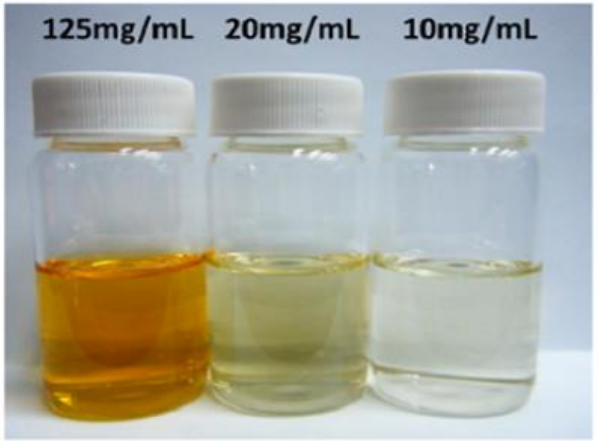
# Motivation

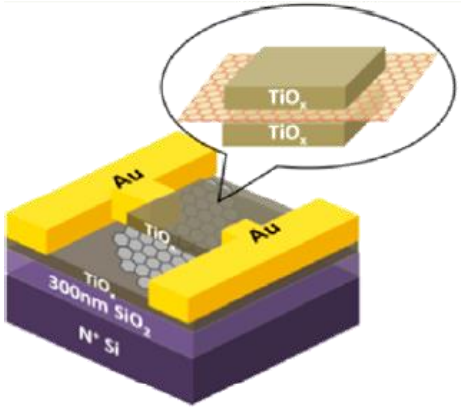
## ◻ *Stable* and *n-type* ***black phosphorus transistor***

- *Critical for further applications of black phosphorus electronic devices, like* ***CMOS*** *or* ***p-n diodes***

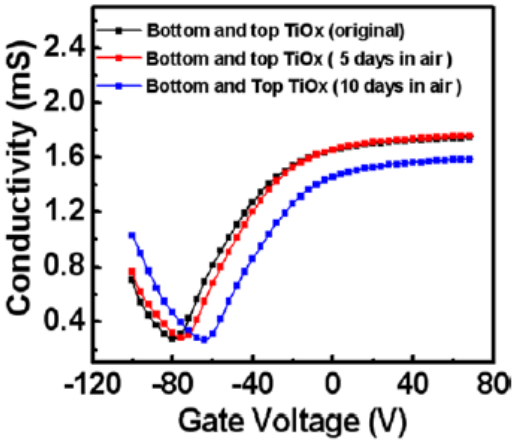
➢ *TiOx might be a suitable candidate to achieve our target*

- ✓ ***Solution processable*** *=> convenient application*
- ✓ ***Promising passivation layer*** *in* ***organic electronic*** *and* ***graphene-based transistor***
- ➢ ***Provide high air stability***



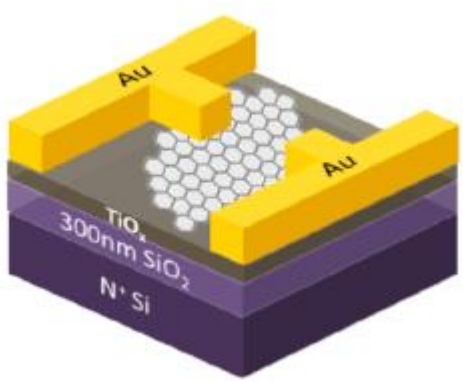



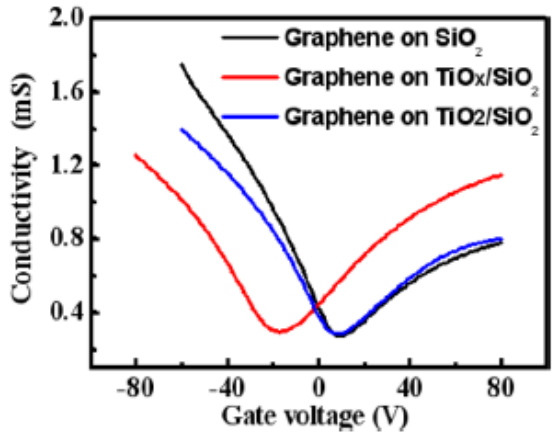

ACS Nano, 2012, 6 (7), pp 6215–6221

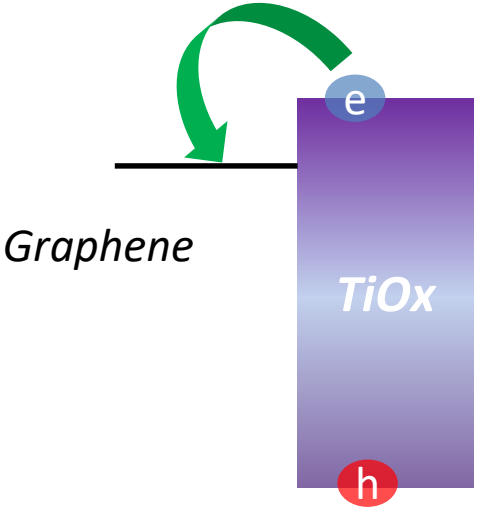


# Characteristics of TiOx as N-type dopant

- *In recent graphene-related research, $TiO_x$ exhibits **n-type doping** property*

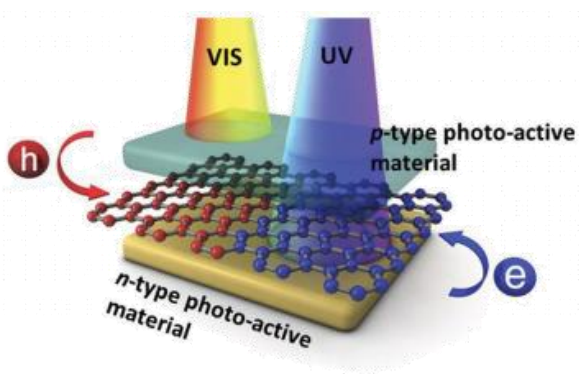


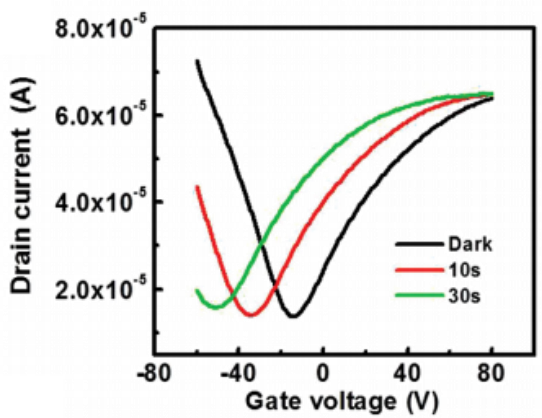



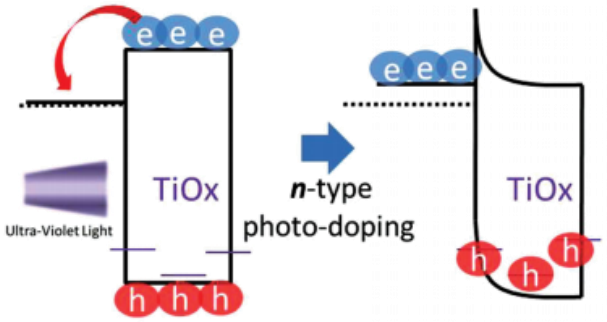




ACS Nano, 2012, 6 (7), pp 6215–6221

- *$TiO_x$ is also a **Photoactive material** with **light-sensitized n-type doping** property*



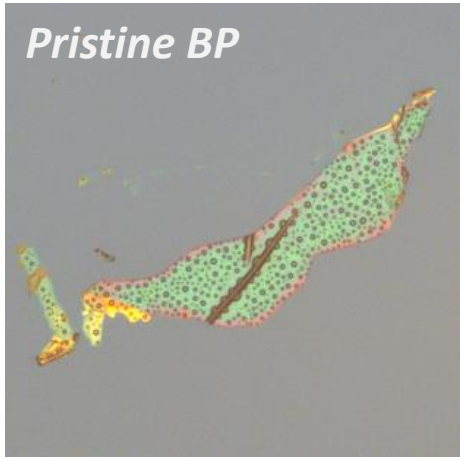




Adv. Mater. 2015, 27, 282–287

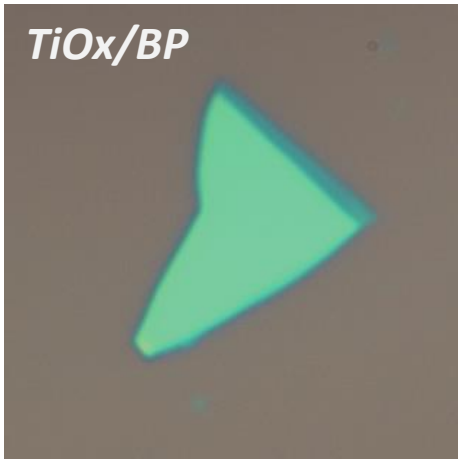
# *Stability testing*

- *Pristine black phosphorus in ambient atmosphere*
  - *The **degradation** could easy be observed under optical microscopy*

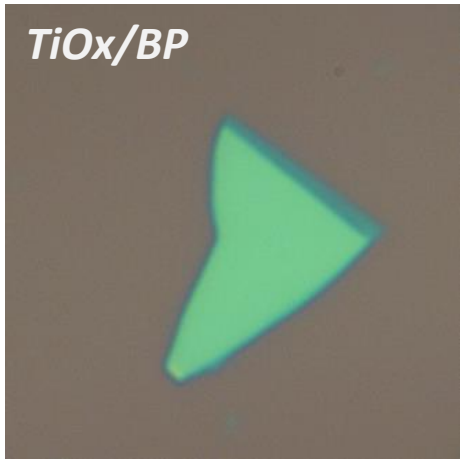

*After 1 day in air*




- *With $TiO_x$ capped on black phosphorus, it seems BP could be protect well*



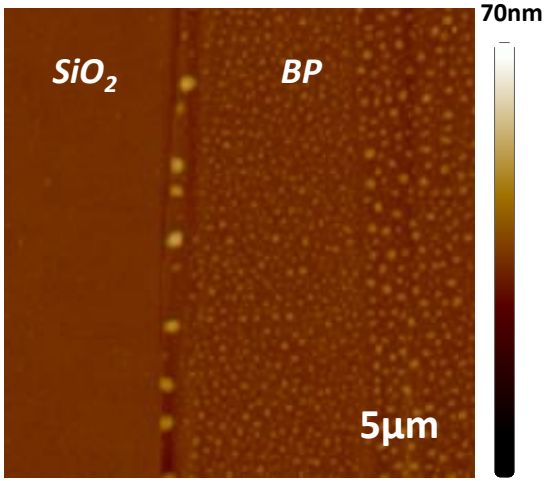

*After 1 day in air*



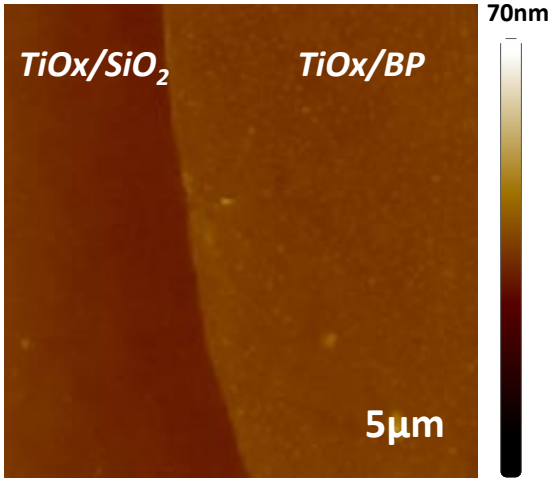
# Roughness measurement

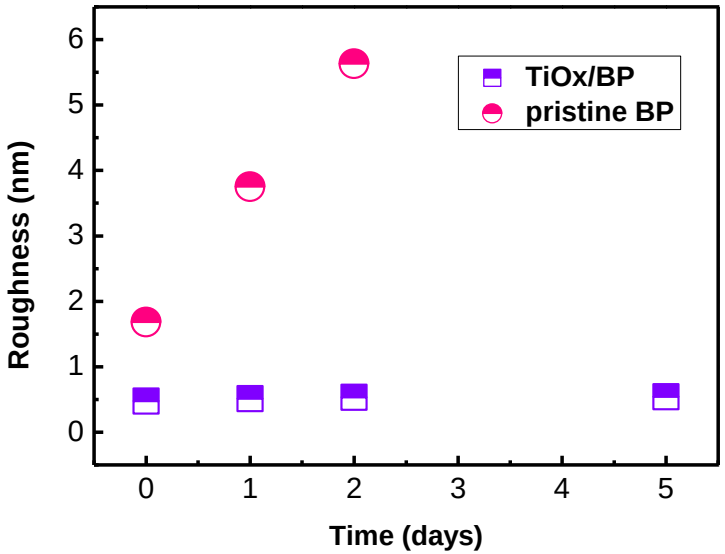
- *Use atomic force microscopy to measure the **roughness variation** with time*

◆ ***Pristine black phosphorus***




◆ ***$TiO_x$-capped black phosphorus***



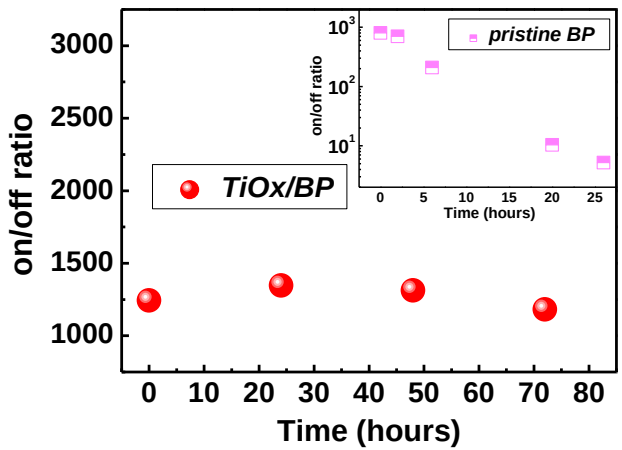



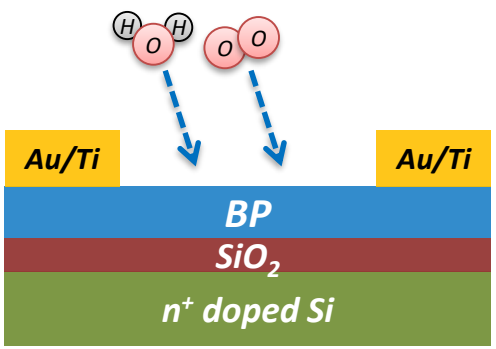

- *Under ambient atmosphere, pristine BP **surface roughness** **decay with time**, but the surface roughness of $TiO_x$ coated BP keeps flat*

# Extended lifetime of BP FET

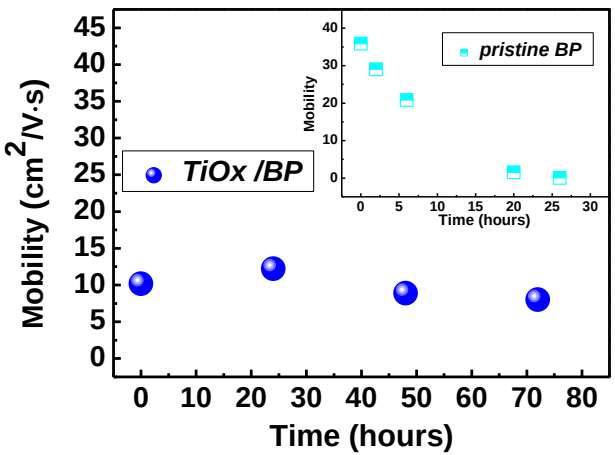
- *It also **extends the lifetime** of the device in ambient condition*

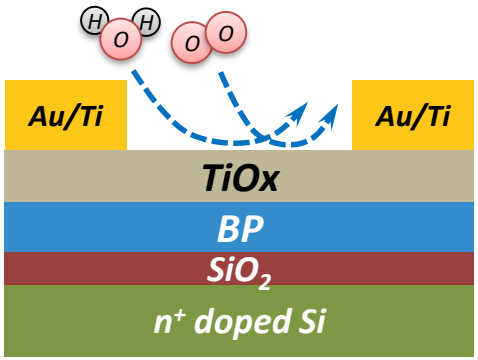
◆ ***Pristine black phosphorus FET***




◆ ***$TiO_x$-capped black phosphorus FET***

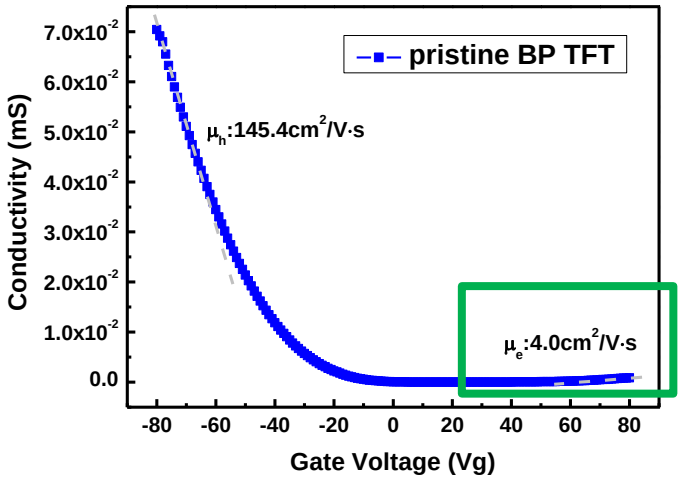


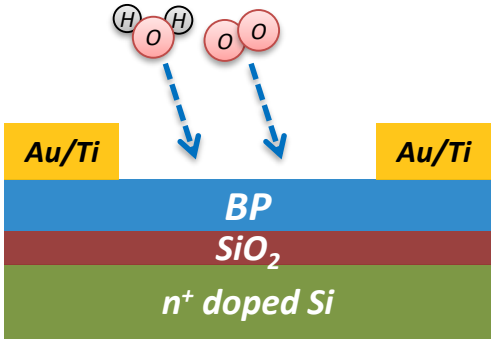




- *Both of the **mobility** and **on/off ratio** would decay under exposure to air, but they could maintain well with the protect of thin film TiOx*

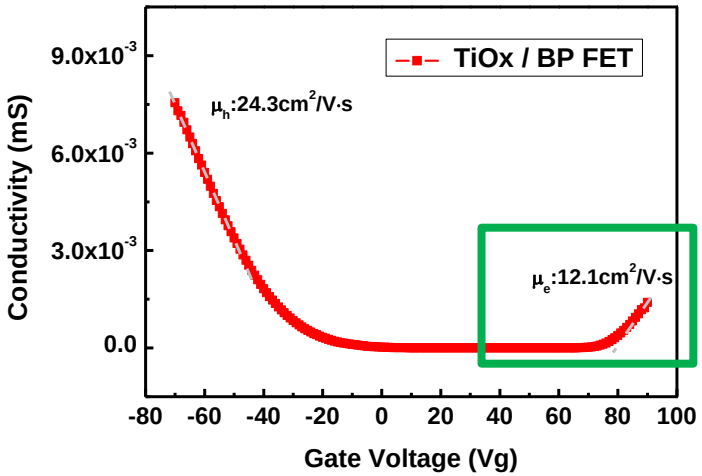
# Measurement of TiOx passivated BP FET

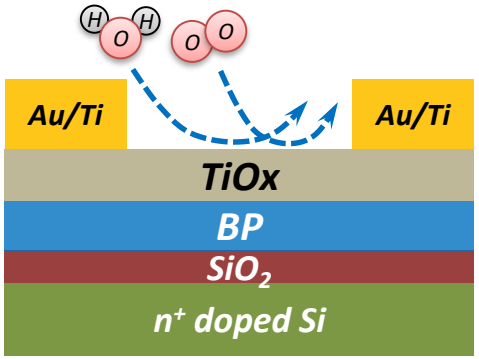
◆ ***Pristine BP FET***




◆ ***TiOx / BP FET***

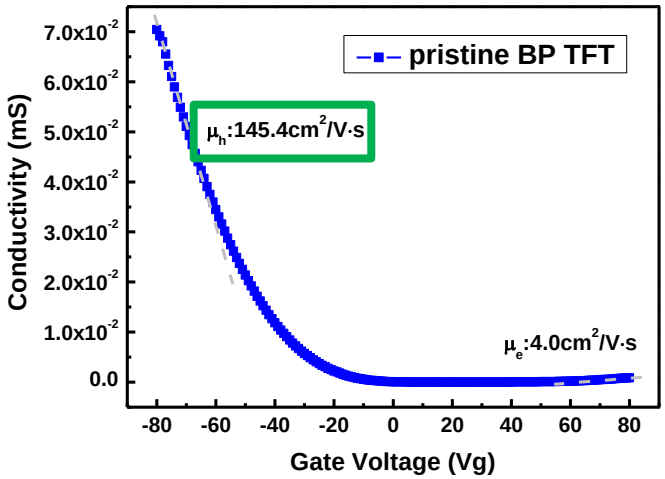


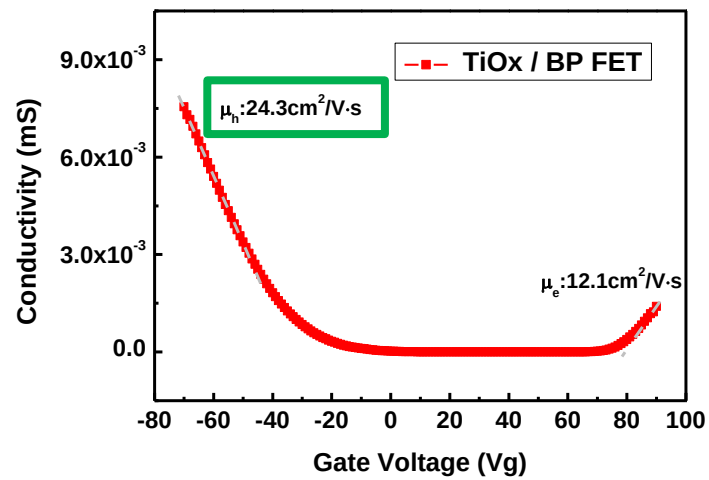

- *As we expected, the **electron mobility** has slightly enhanced*
  - ☐ *$TiO_x$ also serve as good **n-type dopant** in black phosphorus system*
    *=> Reduce the effective Schottky barrier height*
  - ☐ *Fewer defect sites (electron traps) due to **$TiO_x$ passivation***

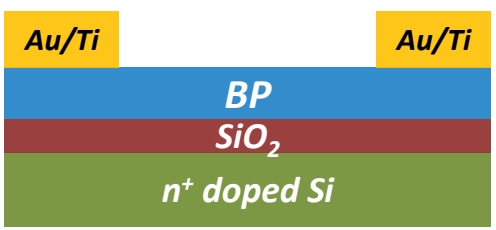
# Measurement of TiOx passivated BP FET

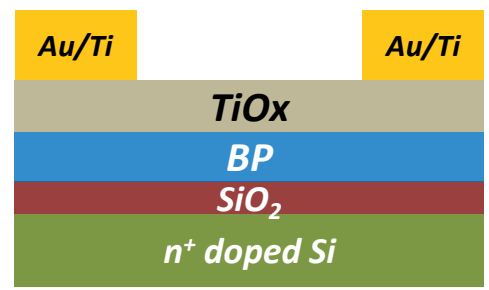
◆ ***Pristine BP FET***




◆ ***TiOx / BP FET***



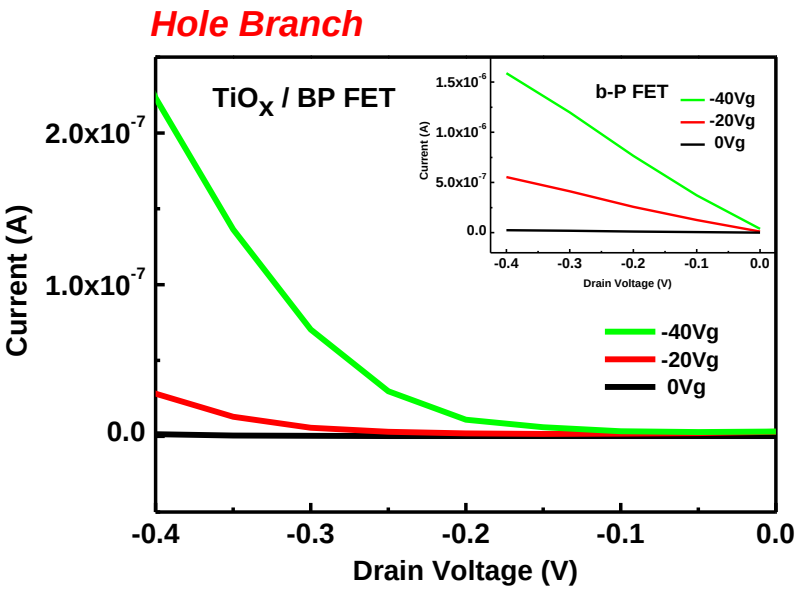



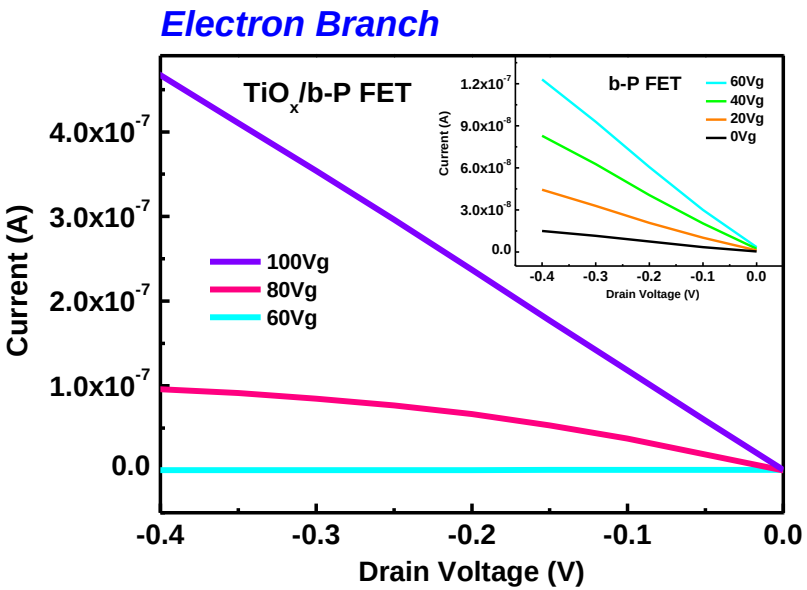




- *The originally **p-type** transport characteristic has been **suppressed***
  - ➢ *$TiO_x$ acts as **hole blocking layer** in this system*

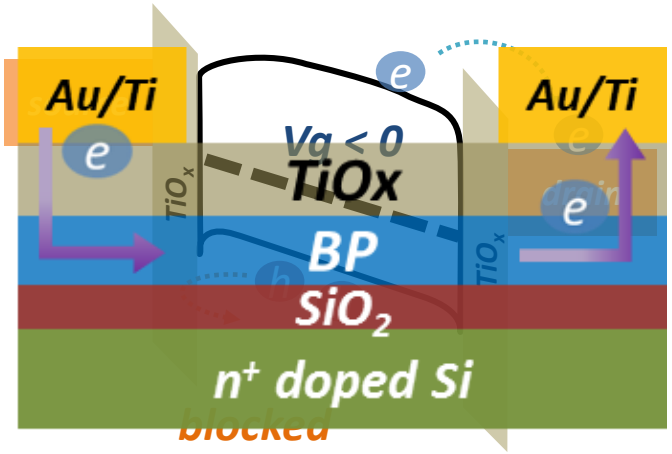
# TiOx as hole blocking layer

◆ ***Id-Vd measurement of TiOx / BP FET and BP FET***




- *From the IV curve of **hole branch**, we found TiOx would block hole carriers*
  - *Hole transport behavior turns into a **non-ohmic manner***
  - *This phenomenon didn't happen in electron branch*
  - ***Charge transport layer***



# *Photo active n-type doping in TiOx/BP system*

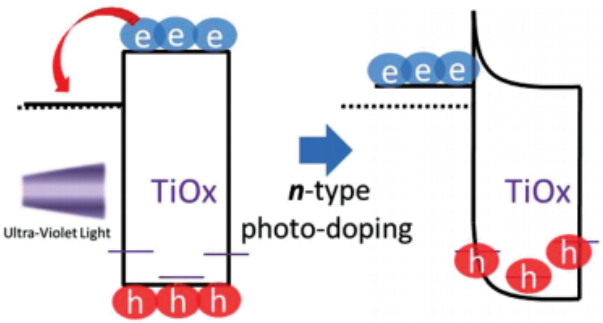
- ***Trap-assisted photo-induced doping***
- *Photo-excited holes* ***trapped by defects in TiOx***

  *=> electrons accumulated*

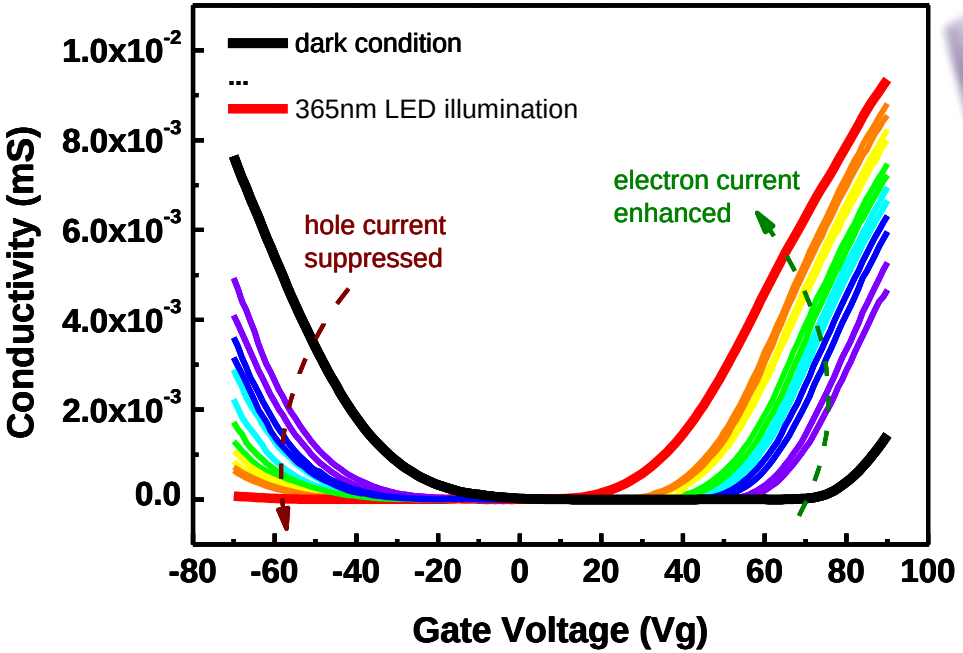
  *=> excess electron transfer along band alignment*

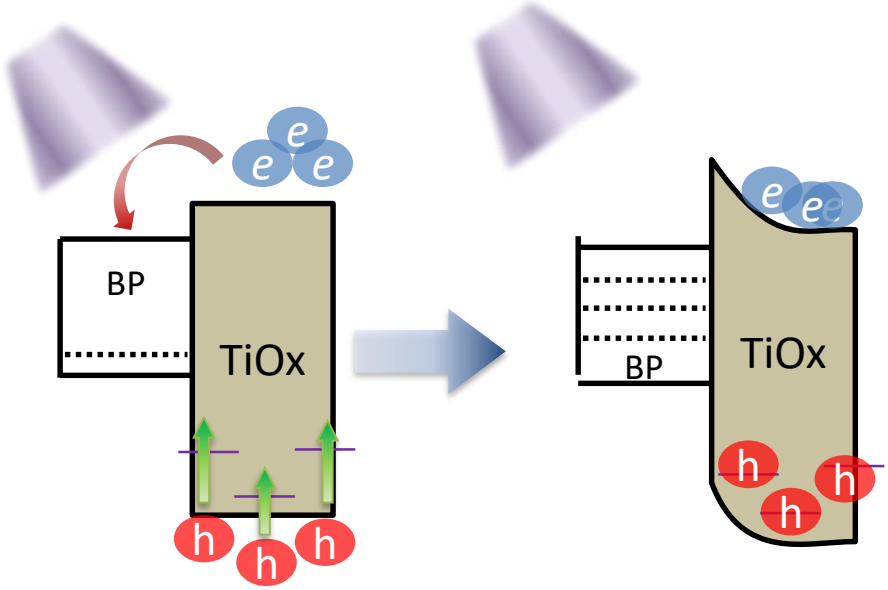
  *=> photo-induced n-type doping*

  *=> **precisely controllable***




Adv. Mater. 2015, 27, 282–287

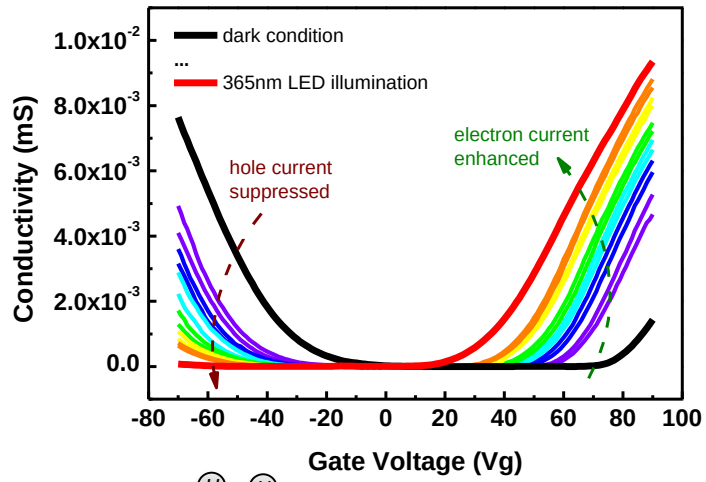


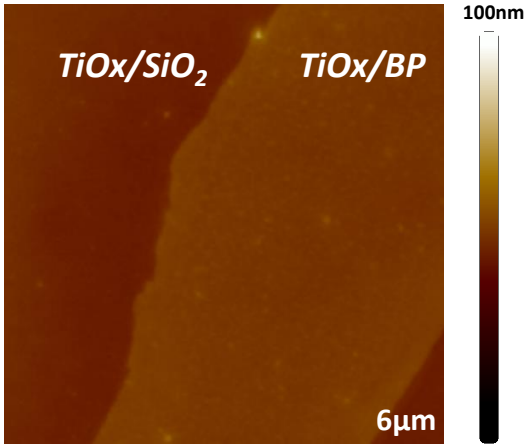
# Summary

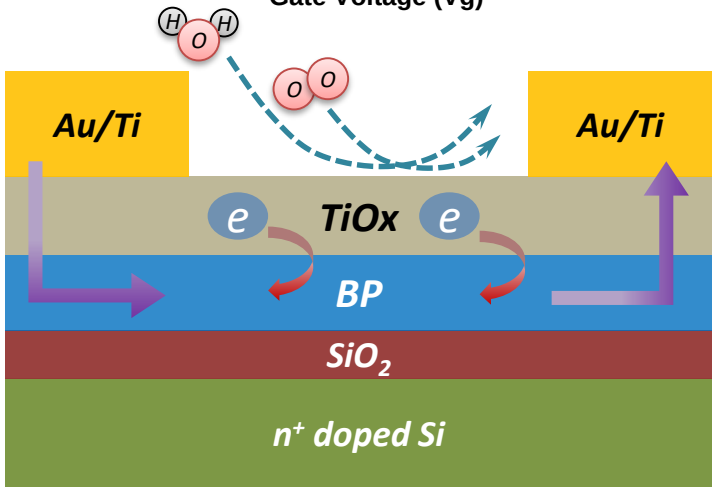
- *With the **self-encapsulated photoactive doping layers**, **TiOx**, **stable** and **high performance n-type** **black phosphorus transistor** has been fabricated*

## Controllable photoactive N-type dopant

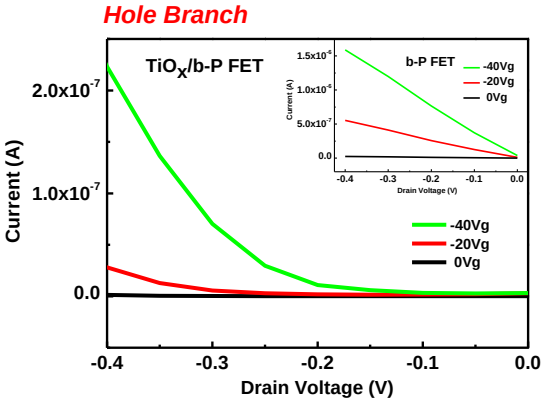



## Passivation layer




## Charge transport layer



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***Thanks for your attention***