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

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Brief introduction to 2D materials

Graphene

✓ 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


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

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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∙s**

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![Graphene structure](image1)

**Science** 306.5696 (2004).

**Nature Nanotechnology** 6, 147–150 (2011)


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

**Nano Lett. 2013, 13, 1852–1857**
2D materials beyond graphene

**Black phosphorous (phosphorene)**

- 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 $2.0\text{eV (monolayer)}$ to $0.35\text{eV (bulk)}$

Thickness dependent band structure

Scientific Reports 4, 6677, (2014)
Characteristics of black phosphorous devices

- Black phosphorus usually shows intrinsic p-type semiconducting characteristic with high average carrier mobility range from $100$ to $300 \text{cm}^2/\text{V} \cdot \text{s}$ at room temperature (highest value of $1000 \text{cm}^2/\text{V} \cdot \text{s}$ 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

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

![Images and graphs from nanolett 2014 and 2D Mater. 2015]

◆ 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 TiO\textsubscript{x} as N-type dopant**

- In recent graphene-related research, TiO\textsubscript{x} exhibits *n-type doping* property

![Graphene and TiO\textsubscript{x} diagram](image)

- TiO\textsubscript{x} is also a *Photoactive material* with *light-sensitized n-type doping* property

ACS Nano, 2012, 6 (7), pp 6215–6221

Stability testing

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

![Pristine BP](Image)

- **With TiO$_x$ capped on black phosphorus, it seems BP could be protected well**

![TiOx/BP](Image)
Roughness measurement

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

◆ Pristine black phosphorus

◆ TiO\textsubscript{x}-capped black phosphorus

- Under ambient atmosphere, pristine BP surface roughness decay with time, but the surface roughness of TiO\textsubscript{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\textsubscript{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

• As we expected, the electron mobility has slightly enhanced
  - TiOx also serve as good **n-type dopant** in black phosphorus system
  -> Reduce the effective Schottky barrier height
  - Fewer defect sites (electron traps) due to TiOx passivation
The originally p-type transport characteristic has been suppressed. 

$\textbf{TiO}_x$ 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*

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Summary

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