# Planar THz Devices and Graphene Tunnelling Diodes


Aimin Song

Department of Electrical Engineering and Electronics

University of Manchester

# Acknowledgements


**Gregory Auton, Arun Singh, Hu Li, Tianye Wei, Josh Wilson, Joseph Brownless**

*Department of Electrical and Electronic Engineering, University of Manchester, UK*

**Baoqing Zhang, Zihao Zhang, Mingyang Wang, Qian Xin, Jiawei Zhang**

*Center of Nanoelectronics, School of Microelectronics, Shandong University, China*

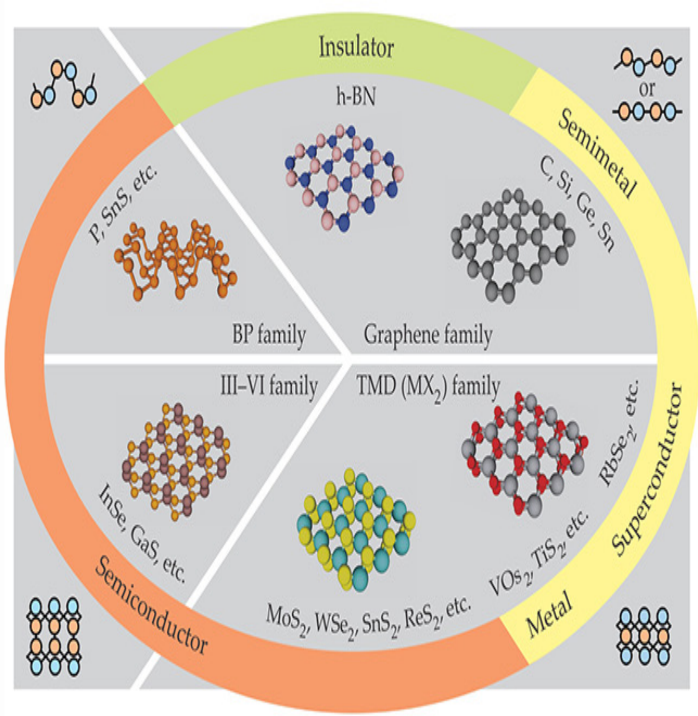
# Planar THz Devices and Graphene Tunnelling Diodes

- **Background**
- **How to determine 2D material thickness**
- **Graphene tunnelling transistors**
- **Planar THz nanodevices**
- **Semiconducting graphene nanoribbons**
- **Summary**

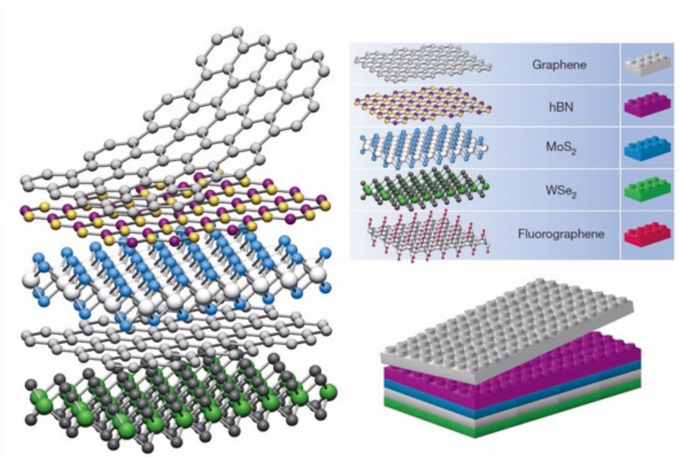
# Graphene:  A Super Material

- Nobel Prize in Physics 2010
- Thinnest imaginable material
- Strongest material ever measured (theoretical limit)
- Stiffest known material (stiffer than diamond)
- Most stretchable crystal (up to 20% elastically)
- Record thermal conductivity (outperforming diamond)
- Highest current density at room T (million times of that in copper)
- Lightest charge carriers (zero rest mass)
- Most impermeable (even He atoms cannot squeeze through)
- Highest intrinsic mobility (>100 times that of Silicon)
- Longest mean free path at room temperature (micron range)

# 2D materials: a huge family




| | | | | | |
|---|---|---|---|---|---|
| Graphene family | Graphene | hBN 'white graphene' | BCN | Fluorographene | Graphene oxide |
| 2D chalcogenides | $MoS_2$, $WS_2$, $MoSe_2$, $WSe_2$ | Semiconducting dichalcogenides: $MoTe_2$, $WTe_2$, $ZrS_2$, $ZrSe_2$ and so on | Metallic dichalcogenides: $NbSe_2$, $NbS_2$, $TaS_2$, $TiS_2$, $NiSe_2$ and so on | Layered semiconductors: GaSe, GaTe, InSe, $Bi_2Se_3$ and so on | |
| 2D oxides | Micas, BSCCO | $MoO_3$, $WO_3$ | Perovskite-type: $LaNb_2O_7$, $(Ca,Sr)_2Nb_3O_{10}$, $Bi_4Ti_3O_{12}$, $Ca_2Ta_2TiO_{10}$ and so on | Hydroxides: $Ni(OH)_2$, $Eu(OH)_2$ and so on | |
| | Layered Cu oxides | $TiO_2$, $MnO_2$, $V_2O_5$, $TaO_3$, $RuO_2$ and so on | | Others | |




**More than 1800 types of 2D materials**

*Nature Nanotech* 5, 487–496 (2010).
*Nature* 490, 192–200 (2012)
*Nature* 499, 419–425 (2013).

# 2D materials: Problem 1

**Too thin!**

**Difficult to identify atomic layer numbers!**

**But the first thing in any experiment is to identify the exact thickness.**

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# Properties sensitive to thickness

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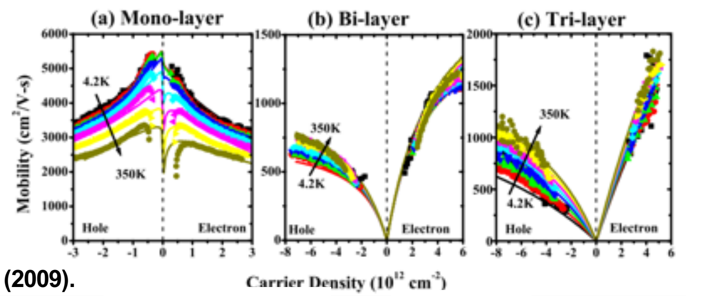
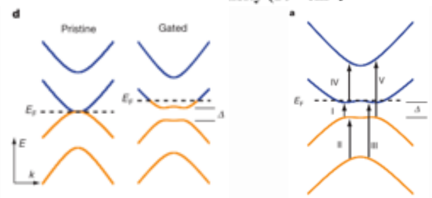
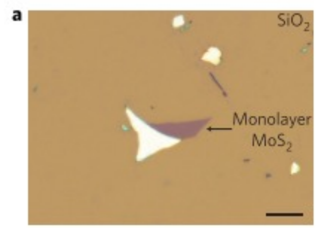



Phy. Rev. B 80, 235402 (2009).

*Nature* 459, 820-823 (2009).

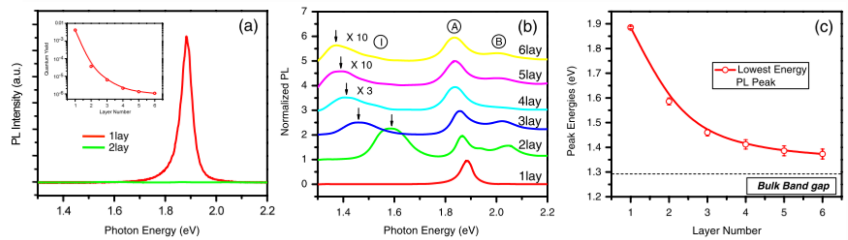



**Monolayer-Bilayer-Trilayer Graphene**

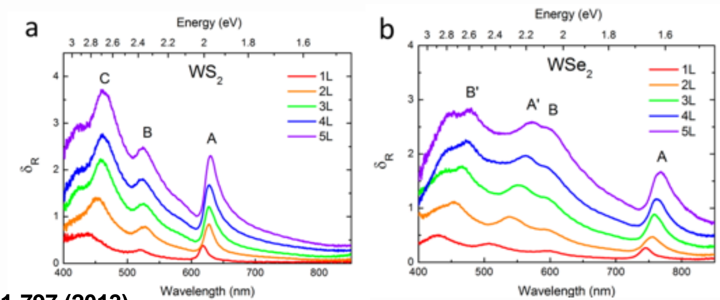



Nat. Nanotech. 6, 147–150 (2010).

*Phy. Rev. Lett.* 105, 136805 (2010).

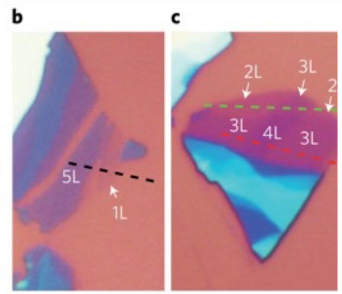


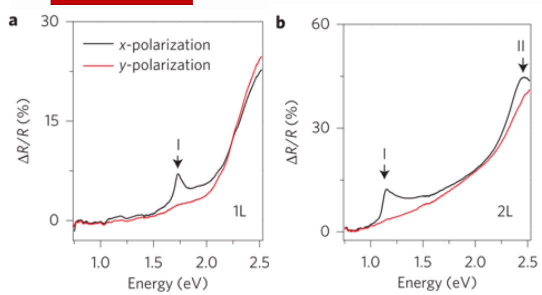

**$MoS_2$**




*ACS Nano* 7, 791-797 (2013).

**$WS_2$; $WSe_2$**




**Black phosphorus**

Nat. Nanotechnol. 12, 21-25 (2017)

IEEE SSCS Electron Devices Society

GreEnergy

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# Properties sensitive to thickness

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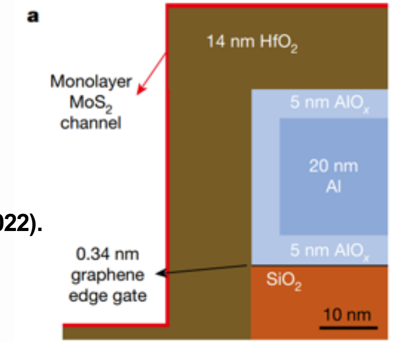
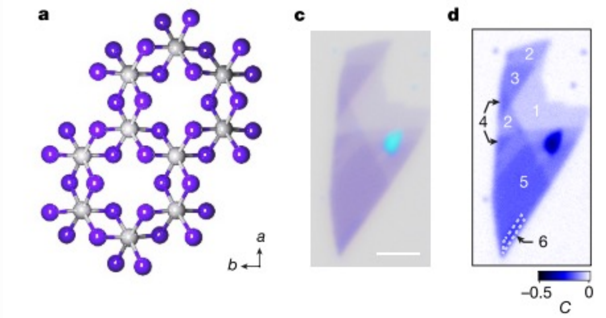
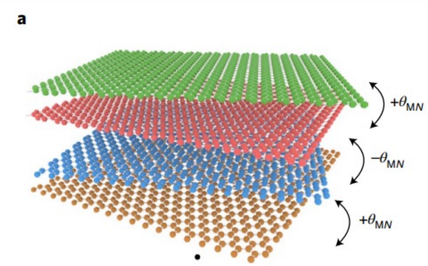
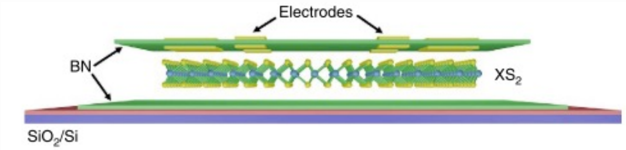



*Nature* 603, 259-264 (2022).

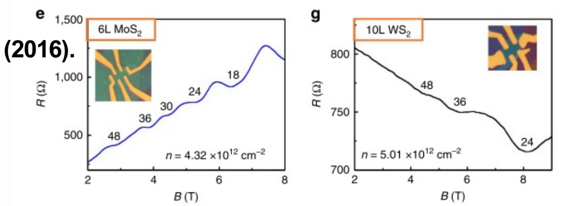
**Sub-1 nm Channel**



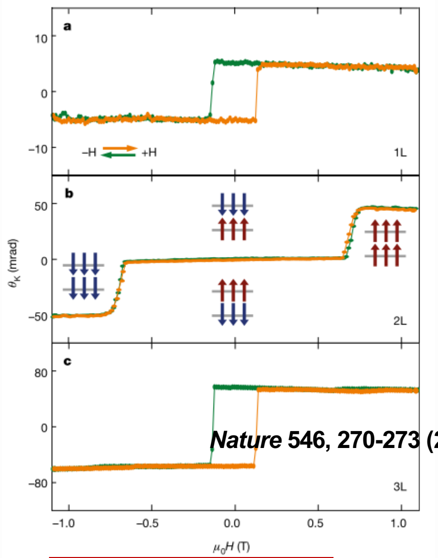




*Nat. Commun.* 7, 12955 (2016).

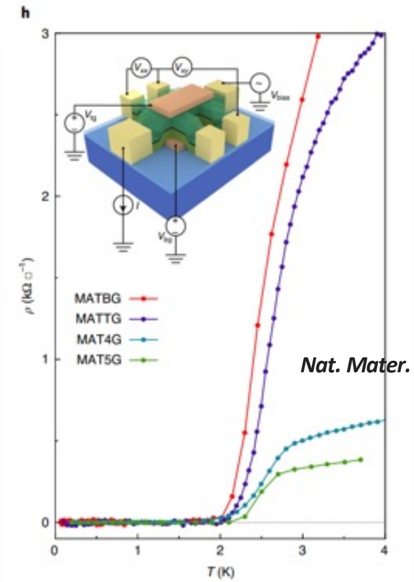



**Q-valley electron**




*Nature* 546, 270-273 (2017).

**Ferromagnetism**




*Nat. Mater.* 21, 877–883 (2022).

**Magic-angle twisted Graphene**

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# Graphene: Problem 2

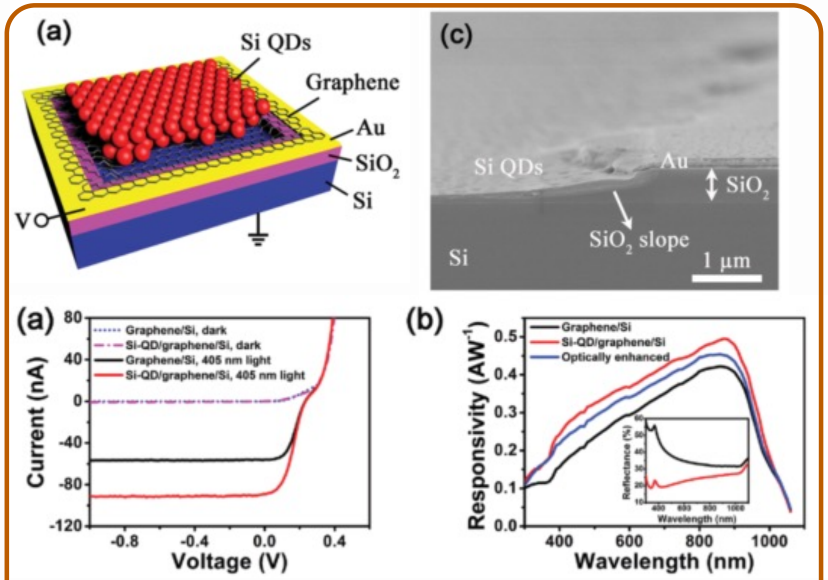
Zero bandgap semimetal

It is not a semiconductor!

So, it is not of much use for electronics as the active layer.

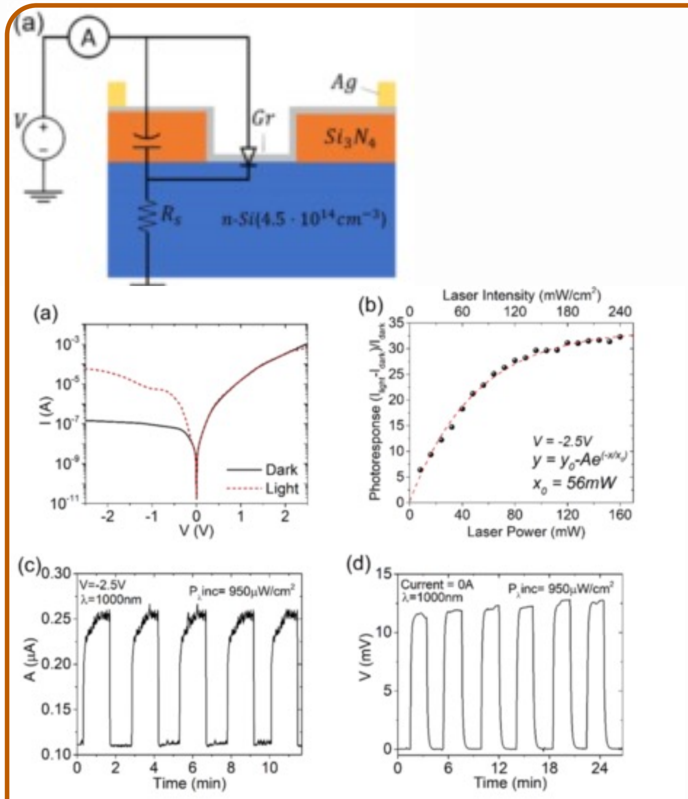
# Use of Graphene in Devices

✓Used as transparent electrode




**Responsivity: 0.495 A/W**
**Detectivity: 7×10$^9$ Jones**

*Adv. Mater. 2016, 28, 4912–4919*

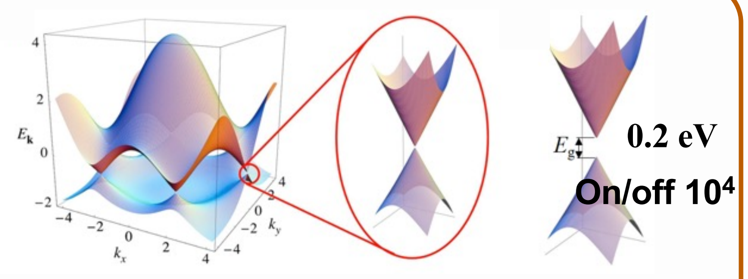



**Responsivity: 0.35 A/W**

*ACS Appl. Mater. Interfaces 2021, 13, 47895*

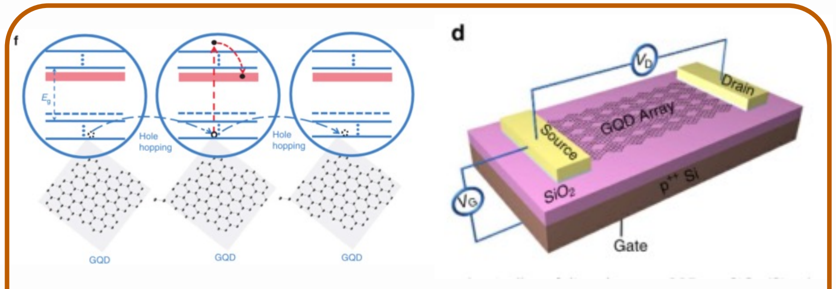
# Use of Graphene in Devices

✓Try to generate a bandgap




*Phys. Rev. Lett. 2007, 98 (20), 206805*

Graphene nanoribbon




Responsivity: 8.61 A/W

*Nat. Commun. 2013, 4, 1811*

Graphene quantum dots

- Only very small bandgap achieved
- Edge imperfection due to lithography limitation

# Planar THz Devices and Graphene Tunnelling Diodes

- Background
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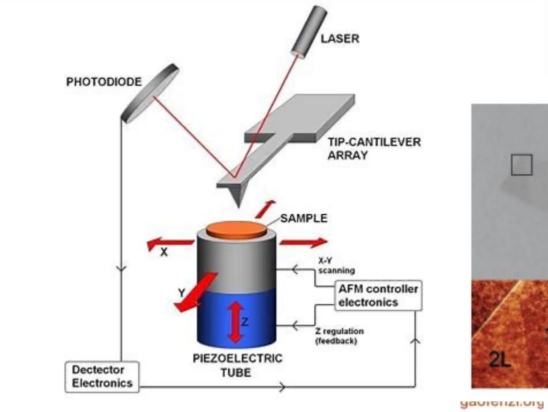
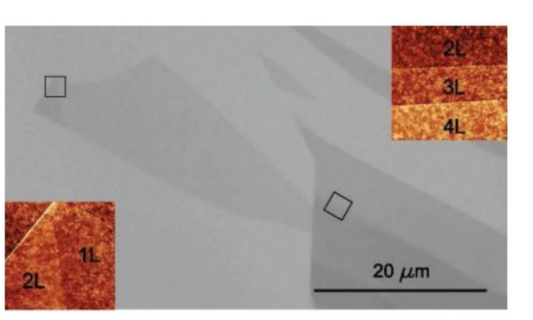
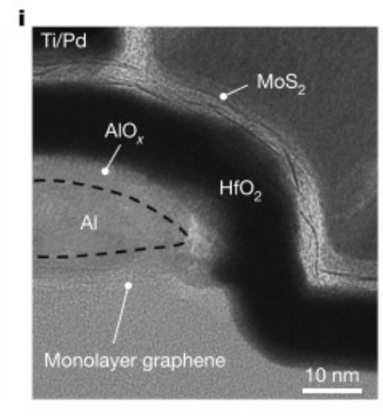
- Planar THz nanodevices
- Semiconducting graphene nanoribbons
- Summary

# Methods to identify the number of atomic layers




*Small 7, 465–468 (2011).*




*Nature* 603, 259-264 (2022)

**Atomic force microscope (AFM)**

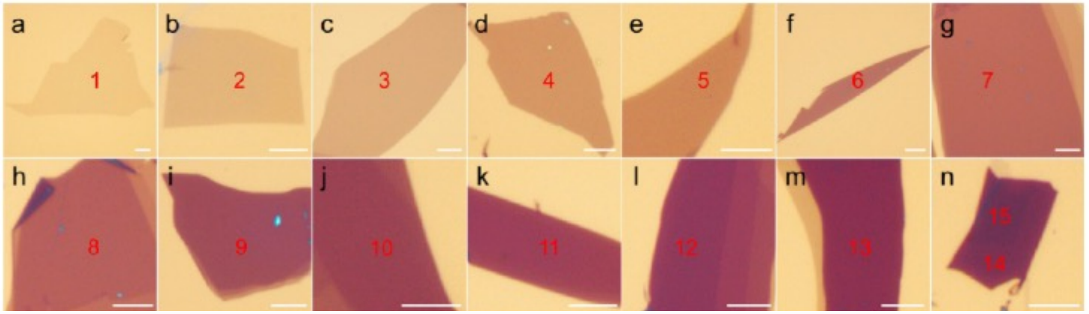
**Tunneling electron microscopy (TEM)**

**Highly time consuming and expensive**

# Optical reflection method



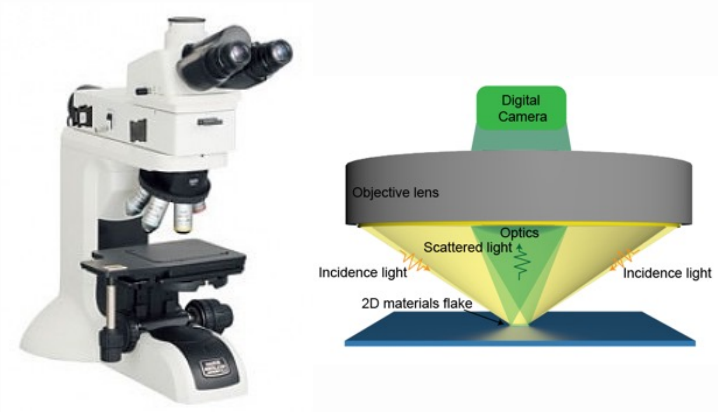
## Most commonly used in labs



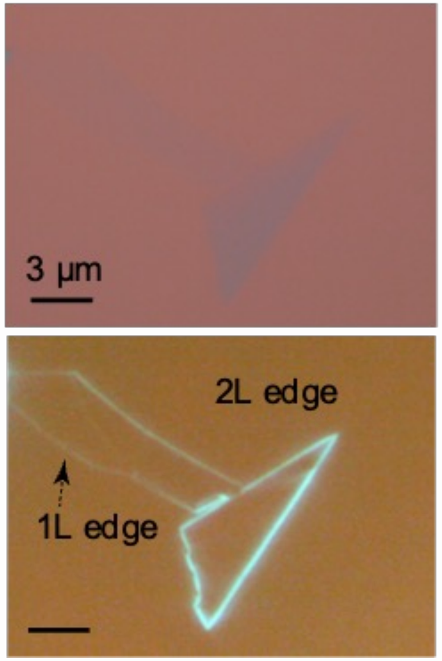

*ACS Nano* 7, 10344-10353 (2013).

- Very low contrast
- Sensitive to wavelength, substrate thickness, incapable on transparent substrate….
- Contrast usually < 10 % for single-layered graphene
  < 2% for single-layer h-BN (transparent)
- Very rare to see single-layered h-BN based devices

# Dark-field method for BN flakes




**Standard microscope with dark field**




**H-BN exfoliated on Si/$SiO_2$**

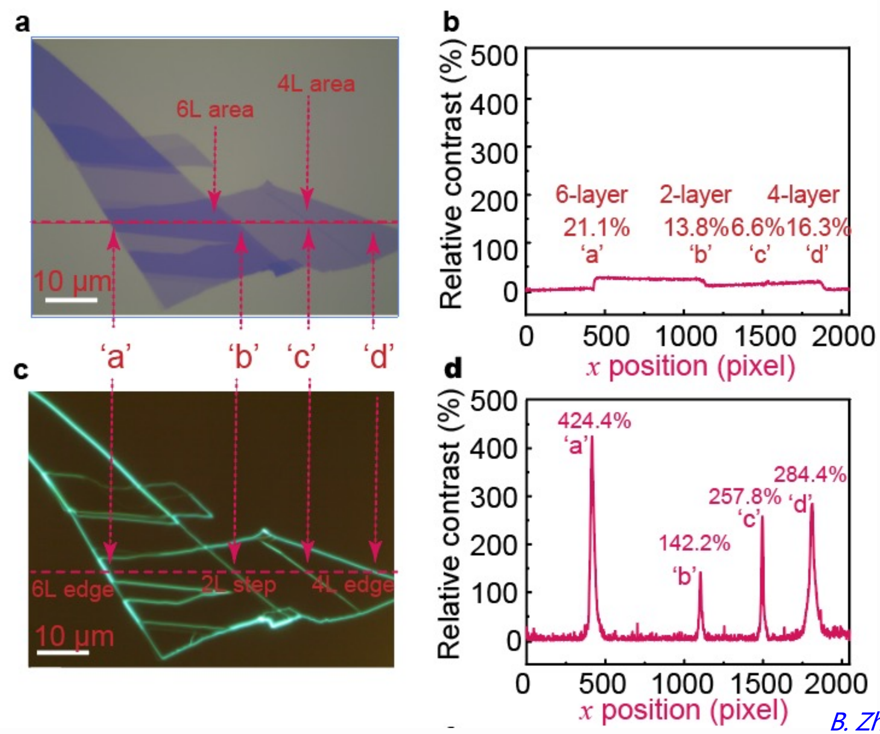
*B. Zhang, et al., Nano Letters* 23, 9170 (2023)

- **High contrast at the edge of atomically thin h-BN flake**
- **Single layered BN is now very visible**

# Dark-field method for graphene flakes

Optical reflection method
White light

Dark-field method
White light




*B. Zhang, et al., Nano Letters* 23, 9170 (2023)

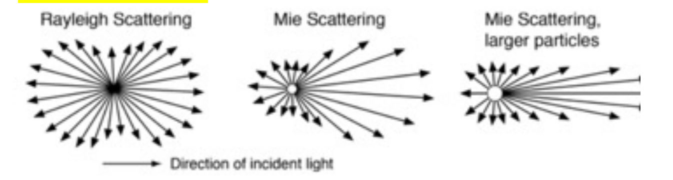
**Per-layer contrast increased from 5% to 70%**

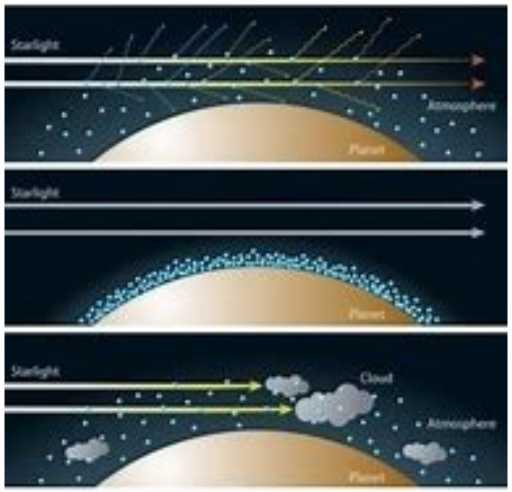
# Rayleigh scattering and charge-dipole model

## Rayleigh scattering

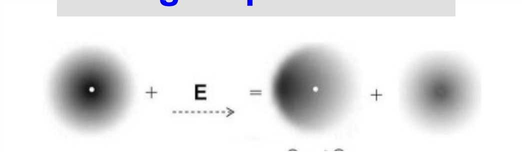
**d < 0.1 λ**

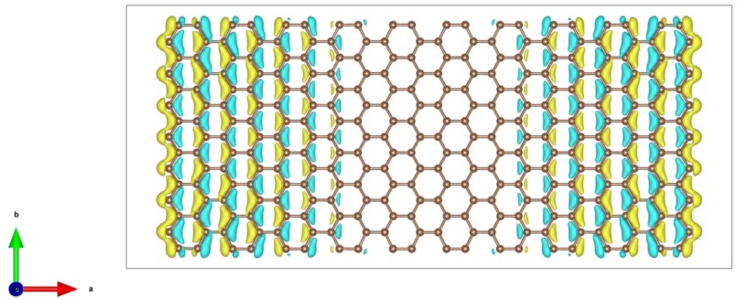
**d > 0.1 λ**

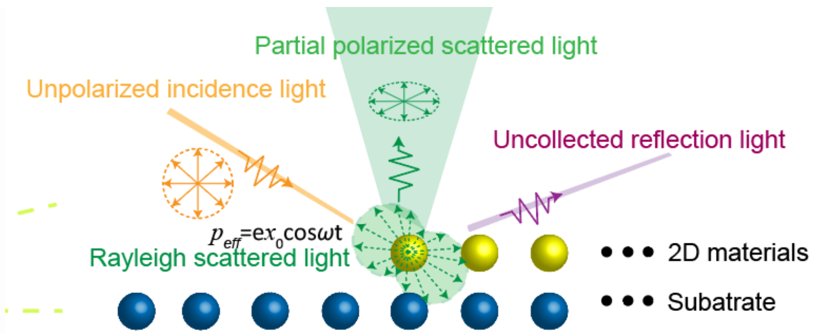


## Charge-dipole model



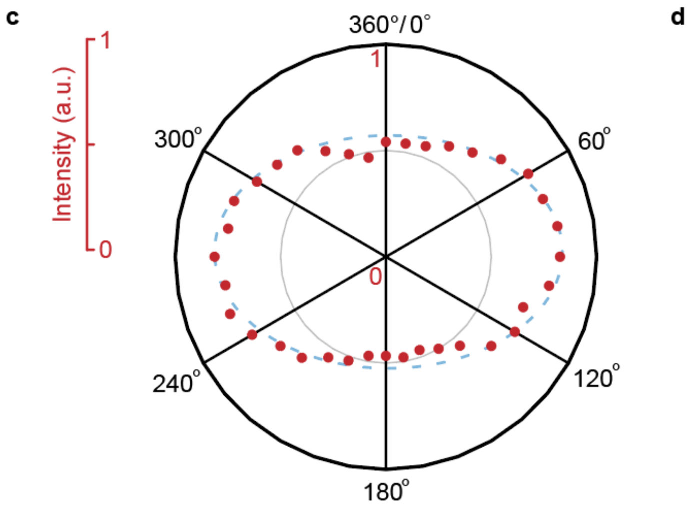





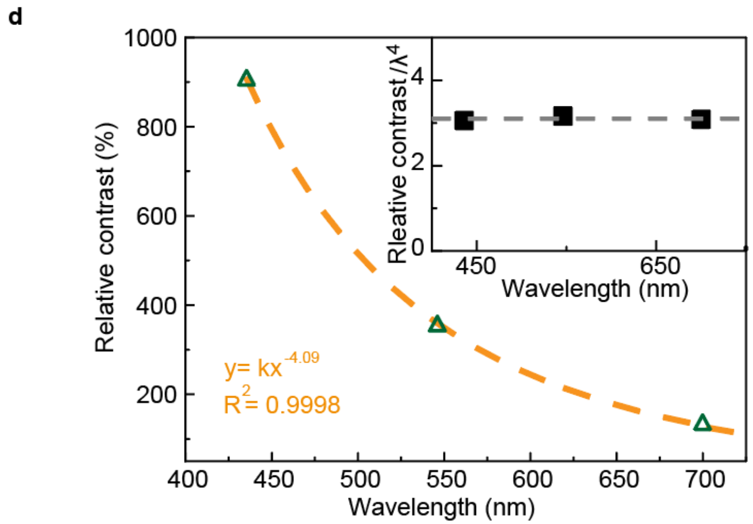
# Polarization distribution and wavelength dependence of Rayleigh scattering

$$\overline{S} = \frac{c\pi^2 |\boldsymbol{p_{eff}}|^2}{2\varepsilon_0 r^2 \lambda^4}(1 + \cos^2\theta)$$

**Our model**




**Fitting the partial polarization distribution**

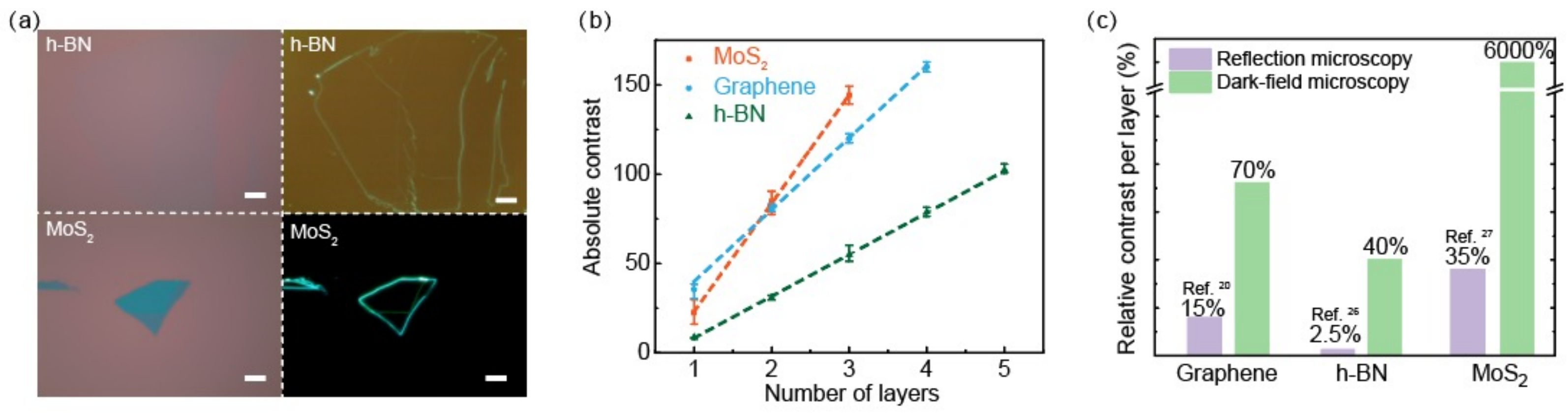



**Fitting the $\lambda^{-4}$ relationship**

**Good agreement between our model and experiment**

*B. Zhang, et al., Nano Letters* 23, 9170 (2023)

# Application to other 2D materials

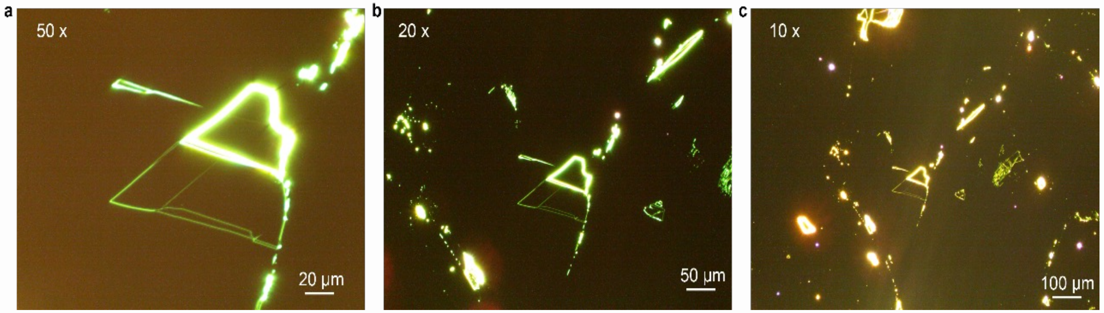



- **Highly linear dependence of the contrast on the number of layers**

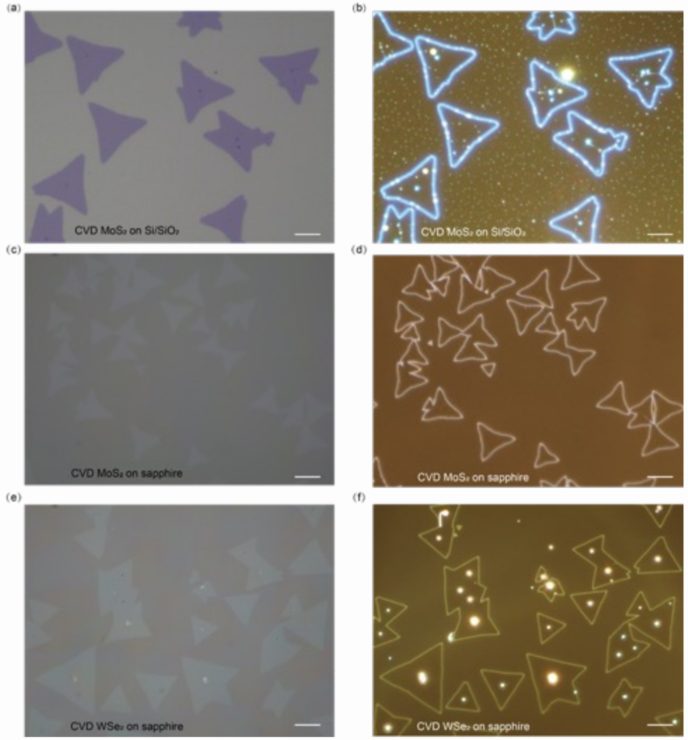
*B. Zhang, et al., Nano Letters* 23, 9170 (2023)

# Large-area identification, transparent substrate






**Large field of vision achieved, up to 0.8 x 1.2 $mm^2$**




CVD-$MoS_2$ on Si/$SiO_2$

CVD-$MoS_2$ on Sapphire

CVD-$WSe_2$ on Sapphire

**Feasible on transparent substates!**

*B. Zhang, et al., Nano Letters* 23, 9170 (2023)

# Comparison with optical reflection method

| | Materials | Method | Per layer contrast | Detection range | Optimized wavelenth of the incident light | Optimized thickness of the $SiO_2$ layer | Reference |
|---|---|---|---|---|---|---|---|
| 1 | graphene | ORC | 15% | 2 - 4 L | 550 - 600 nm | 285 nm | Ref.S1 |
| 2 | Graphene;$MoS_2$ | Deep learning;ORC | N.A. | 2 -5 L | White light | 300 nm | Ref.S2 |
| 3 | graphene | ORC | 6% | 1 - 10 L | 550 nm | 285 nm | Ref.S3 |
| 4 | graphene | ORC | 7.70% | 2 - 5 L | 550 nm | 300 nm | Ref.S4 |
| 5 | h-BN | ORC | 2.50% | 1 - 100 L | 516 nm | 282 nm | Ref.S5 |
| 6 | h-BN | Raman;ORC | 1.50% | 7 -38 L | 525 nm | 290 nm | Ref.S6 |
| 7 | h-BN | Raman;ORC | 2.50% | 2 - 4 L | 500 or 570 nm | 290 nm | Ref.S7 |
| 8 | $MoS_2$ | Deep learning;ORC | N.A. | 1 - 5 L | 470 - 850 nm | 270 nm | Ref.S8 |
| 9 | $MoS_2$ | ORC | 9% | 1 - 15 L | White light, with RGB channel | 300 nm | Ref.S9 |
| | $WSe_2$ | ORC | 14% | 1 - 14 L | White light, with RGB channel | 300 nm | |
| | $MoS_2$ | ORC | 35% | 1 - 15 L | White light, with RGB channel | 90 nm | |
| | $WSe_2$ | ORC | 38% | 1 - 14 L | White light, with RGB channel | 90 nm | |
| 10 | **Graphene** | **Dark-field** | **70%** | **1 - >100 L** | **White light, better at shorter wavelength** | **Not required** | **This work** |
| | **h-BN** | **Dark-field** | **40%** | **1 - >100 L** | | | |
| | **$MoS_2$** | **Dark-field** | **6000%** | **1 - >100 L** | | | |

- **Contrast for graphene increased by a factor ~ 10**
- **Contrast for BN increased by a factor ~ 20**
- **Contrast for $MoS_2$ increased by a factor ~ 200**

*B. Zhang, et al., Nano Letters* 23, 9170 (2023)

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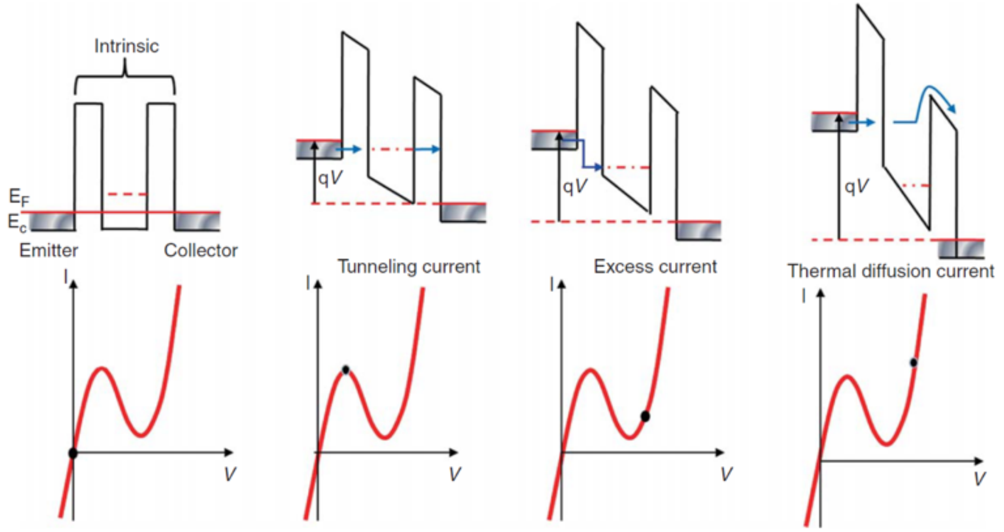
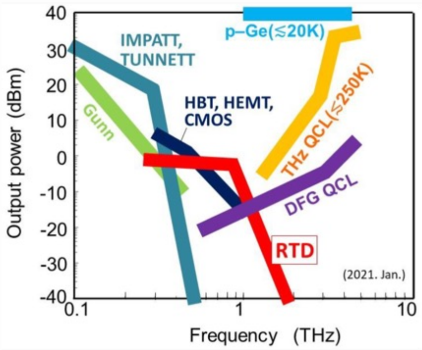
# Resonant tunnelling diode

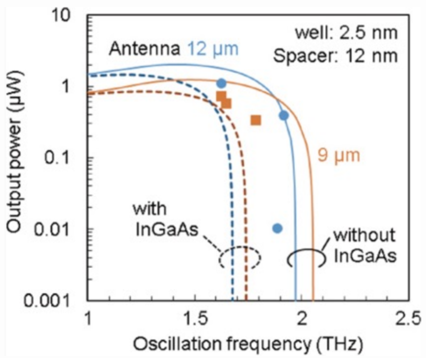
- Predicted by Tsu and Esaki in 1973
- Demonstrated by Chang, Esaki and Tsu in 1974
- Room-temperature quantum device
- Negative differential resistance
- Applications: high-frequency oscillators (>1 THz), multi-value logic, memory, etc

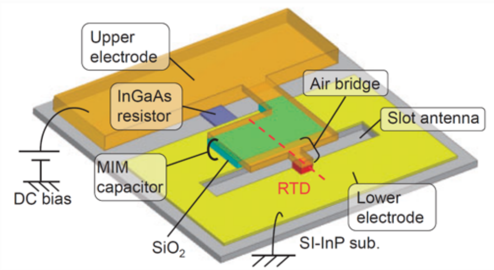


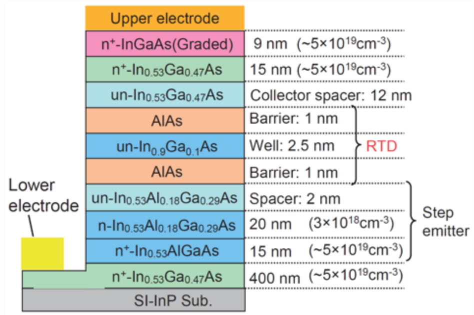

*Tsu R, Esaki L. APL, 1973, 22: 562*
*Chang L L, Esaki L, Tsu R. APL, 1974, 24: 593*

# Resonant tunnelling diode for THz



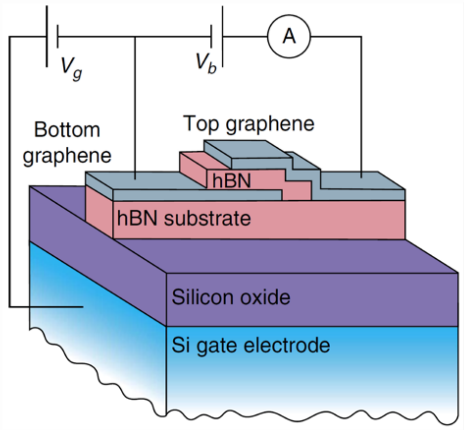

*Maekawa T, Kanaya H, Suzuki S, Asada M. Applied Physics Express, 2016, 9(2): 024101.*

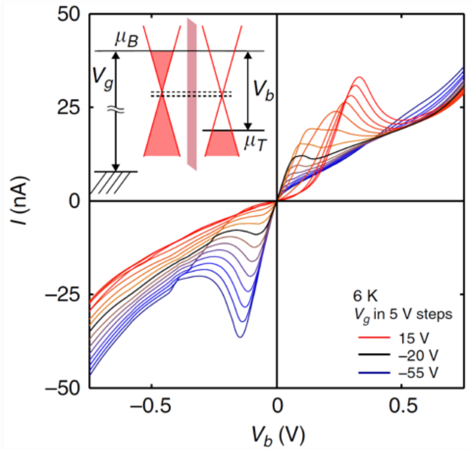
*Izumi R, Suzuki S, Asada M. 2017 42nd International Conference on Infrared, Millimeter, and Terahertz Waves (IRMMW-THz). 2017.*

*Asada M, Suzuki S. Sensors (Switzerland), 2021, 21(4): 1384.*

- **Oscillators up to 1.98 THz**
- **Currently used as solid-state THz emitter at 300K**

# Graphene resonant tunnelling diode

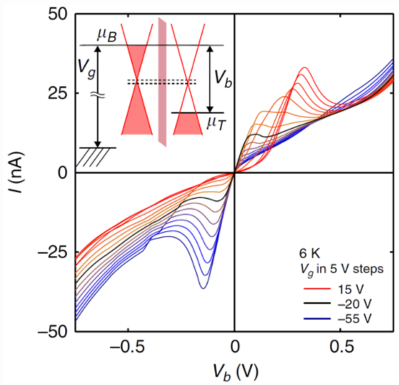



*Britnell L et al. Nature Communications, 2013, 4: 1794.*

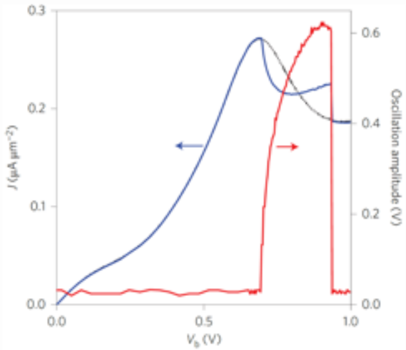
- **Atomically flat 2D materials extremely suitable for tunnelling diodes**
- **2D-to-2D tunnelling is much more ideal than conventional 3D-2D-3D tunnelling**
- **Single-barrier graphene/BN/graphene diode demonstrated in 2013**
- **Potentially even higher speed without the so-called dwell time limitation**
- **Difficulty: identify the atomic-layer numbers of very thin 2D materials**

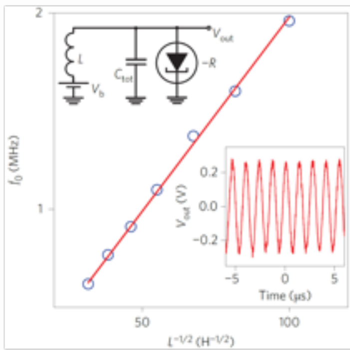
# State of the art




**Highest peak-to-valley current ratio: 3.9**

**Highest peak current density: 2 µA/µm²**

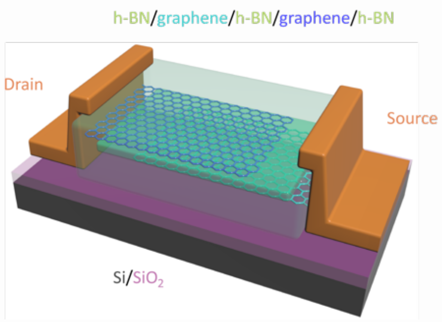


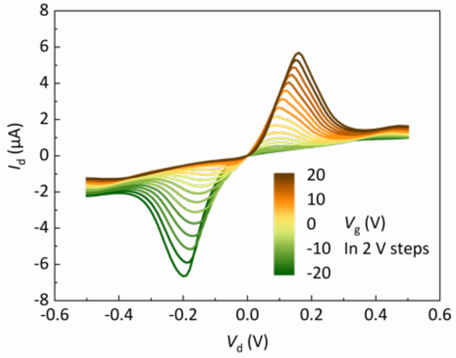



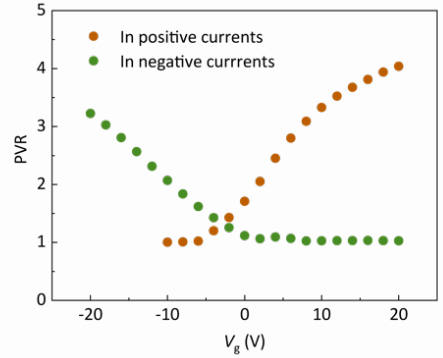

**Highest oscillation frequency: 2 MHz**


*Berger P R, Ramesh A. Amsterdam: Elsevier, Comprehensive Semiconductor Science and Technology, 2011, 5:176-241.*
*Burg G W, Prasad N, Fallahazad B, et al. Nano Letters, 2017, 17(6): 3919–3925.*
*Kinoshita K, Moriya R, Okazaki S, et al. Nano Letters, 2022, 22(12): 4640–4645.*
*Srivastava P K, Hassan Y, de Sousa D J P, et al. Nature Electronics, 2021, 4(4): 269–276.*
*Al-Khalidi A et al. IEEE Transactions on Terahertz Science and Technology, 2020, 10(2): 150-157.*

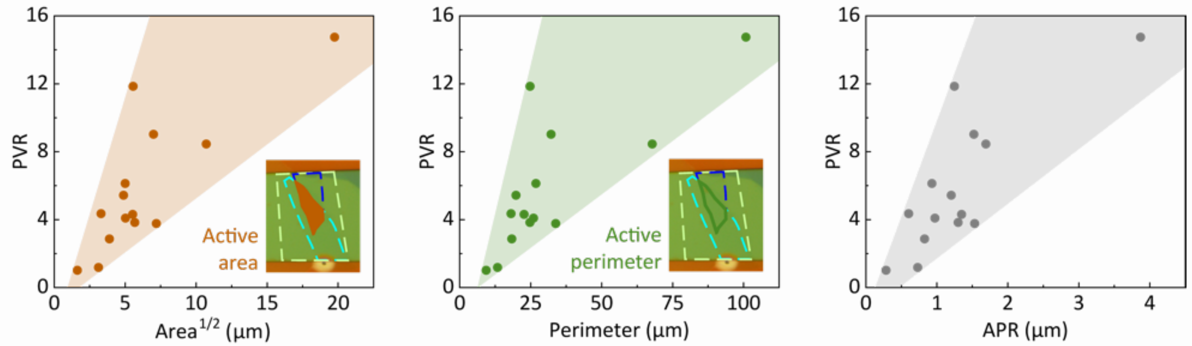
# Unexpected size/geometry dependence



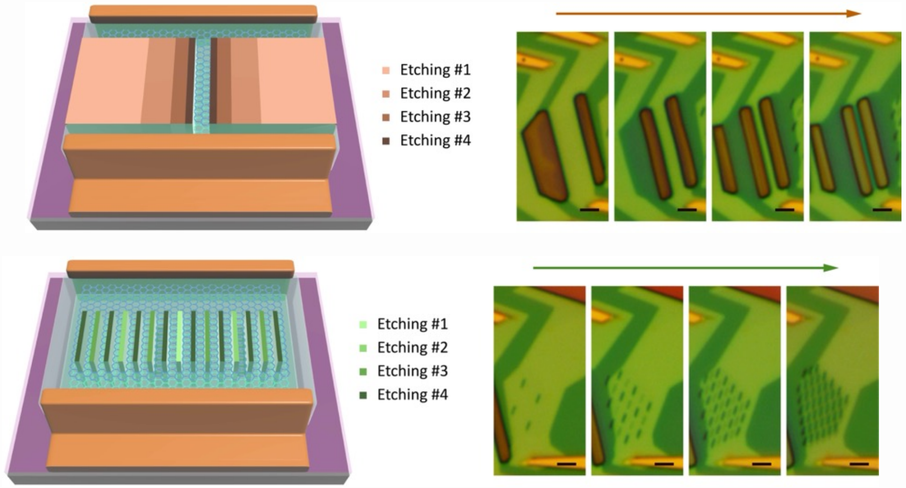

**Statistics**




*Zihao Zhang et al. Nano Letters, 23, 8132 (2023)*

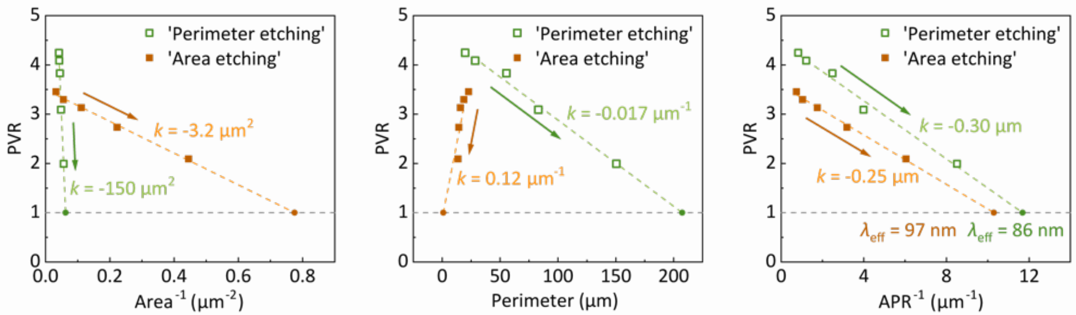
- **Helped by the dark field method to identify thin 2D material thickness**
- **Peak to valley ratio (PVR) depends on area, perimeter and area/perimeter**

# Controlled tests on the same device




**Different areas but perimeter almost the same**

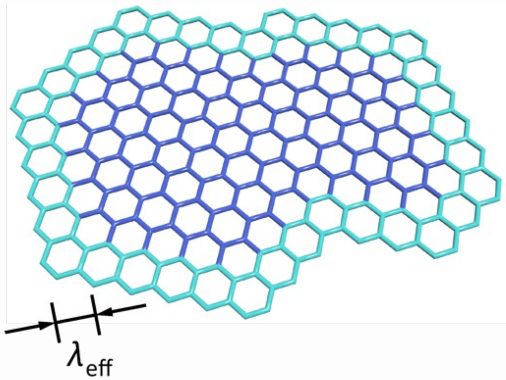
**Different perimeters but area almost the same**




**Area/perimeter is the key!**

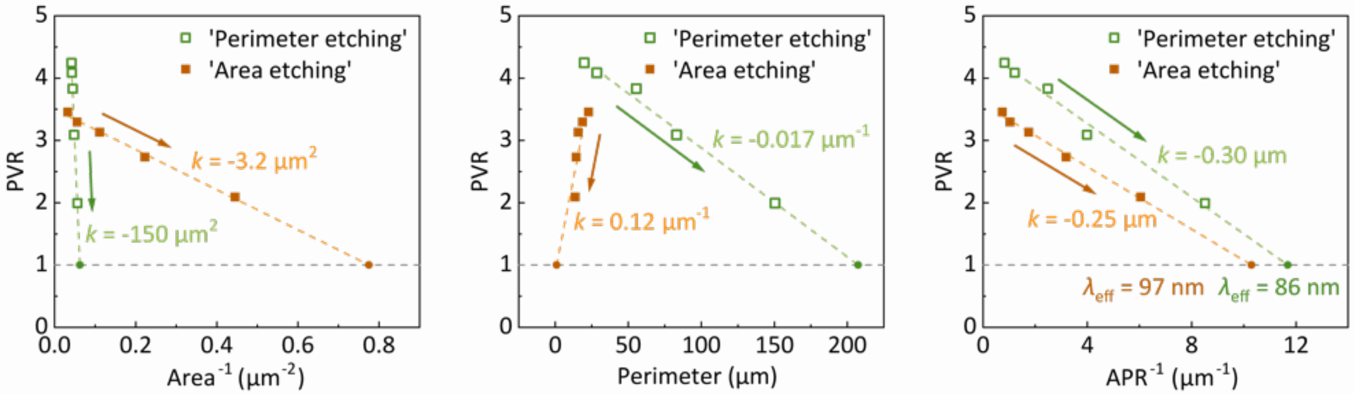
*Zihao Zhang et al. Nano Letters, 23, 8132 (2023)*

# Edge doping model




$$\mathrm{PVR} \approx \frac{J_l\left(V_{\mathrm{d,peak}}\right) \times (\mathrm{Area} - \mathrm{Perimeter} \times \lambda_{\mathrm{eff}}) + J_h\left(V_{\mathrm{d,peak}}\right) \times \mathrm{Perimeter} \times \lambda_{\mathrm{eff}}}{J_l\left(V_{\mathrm{d,valley}}\right) \times (\mathrm{Area} - \mathrm{Perimeter} \times \lambda_{\mathrm{eff}}) + J_h\left(V_{\mathrm{d,valley}}\right) \times \mathrm{Perimeter} \times \lambda_{\mathrm{eff}}}$$

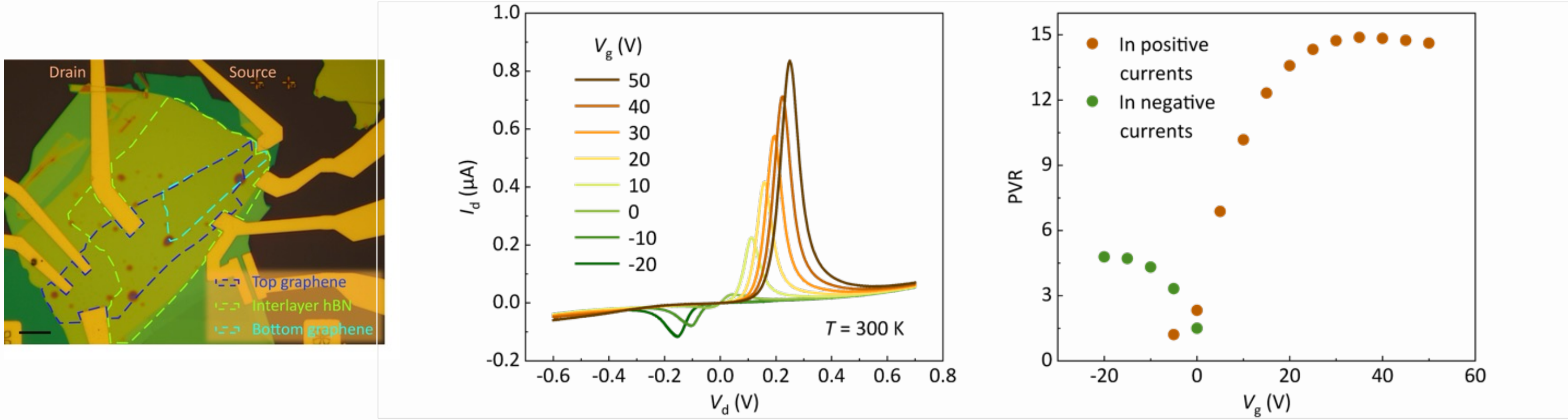
$$\mathrm{PVR} \approx \frac{J_l\left(V_{\mathrm{d,peak}}\right)}{J_l\left(V_{\mathrm{d,valley}}\right)} - \left(\frac{J_l\left(V_{\mathrm{d,peak}}\right)}{J_l\left(V_{\mathrm{d,valley}}\right)} - 1\right)\frac{\lambda_{\mathrm{eff}}}{\mathrm{APR}}$$




**Fitting:**
**$\lambda_{eff}$ = 97 nm**

*Zihao Zhang et al. Nano Letters, 23, 8132 (2023)*

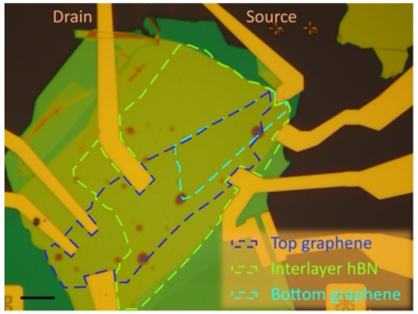
# Optimized resonant tunnelling diode

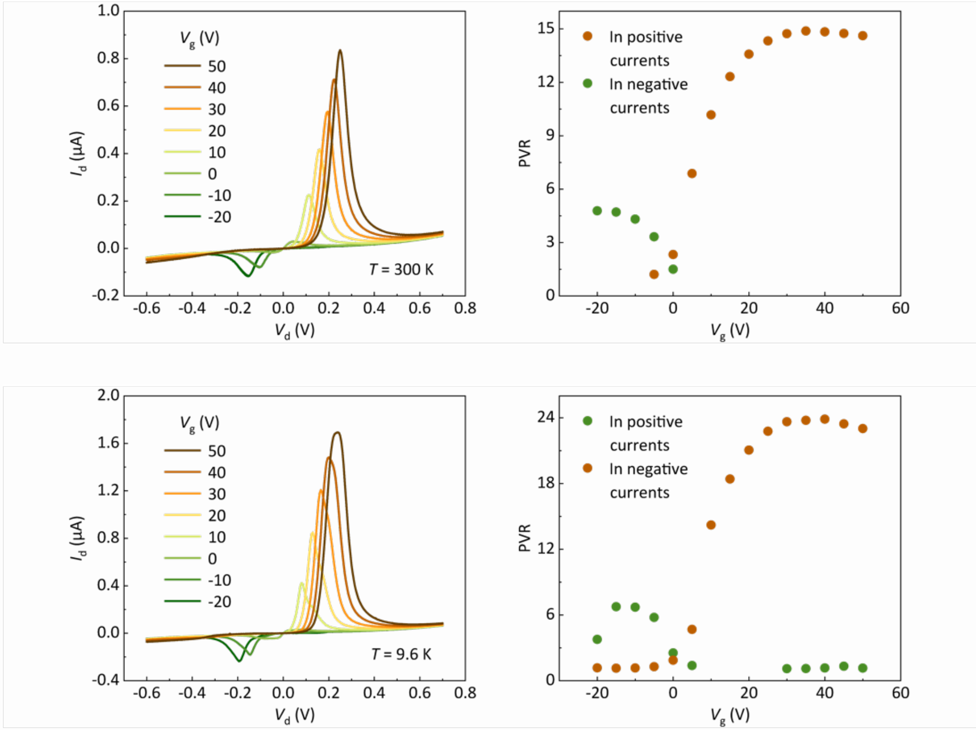



- **Room temperature PVR = 14.9**
- **A factor of 380% increase from the previous record**

*Zihao Zhang et al. Nano Letters, 23, 8132 (2023)*

# Optimized resonant tunnelling diode

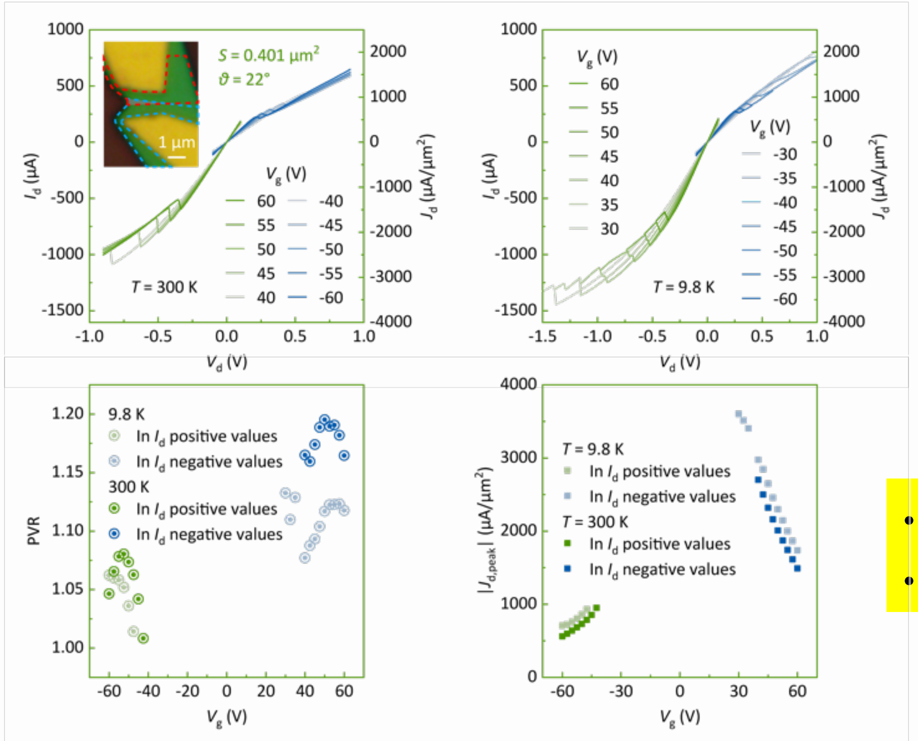



- **PVR=23.9 @ 9.6 K**

*Zihao Zhang et al. Nano Letters, 23, 8132 (2023)*

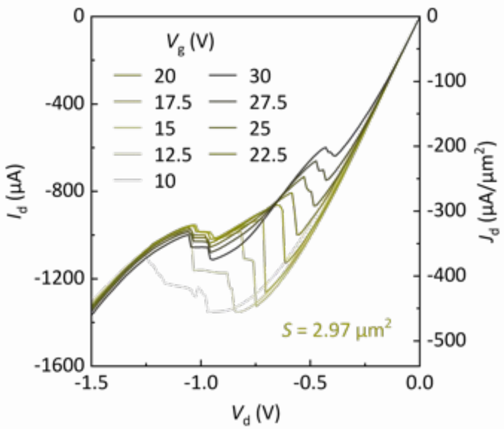
# Optimized resonant tunnelling diode

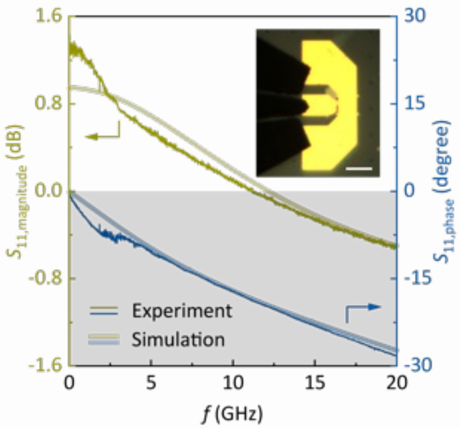



- **Peak current density: 2700 μA/μm$^2$**
- **Improved by 3 orders of magnitude**

*Zihao Zhang et al. To be published*

# Optimized resonant tunnelling diode




- **Oscillation frequency: 11 GHz**
- **Previous highest: 2 MHz**
- **Increased by 3 orders of magnitude**

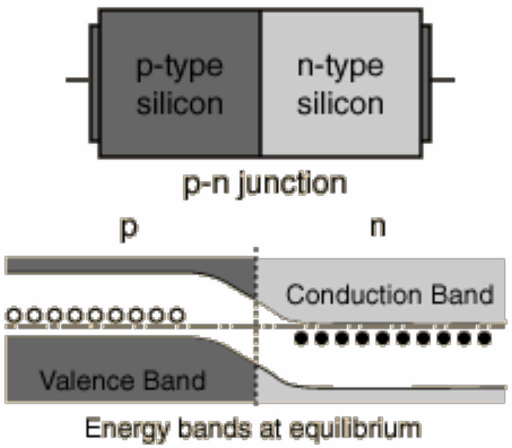
*Zihao Zhang et al. To be published*

# Planar THz Devices and Graphene Tunnelling Diodes

- Background
- How to determine 2D material thickness
- Graphene tunnelling transistors
- Planar THz nanodevices
- Semiconducting graphene nanoribbons
- Summary

# Diode that layman can understand

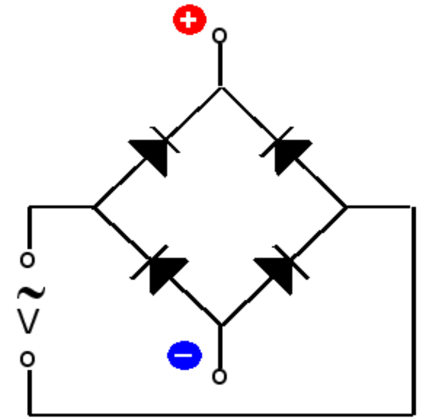
## Conventional diode




**Only experts understand!**

## Ballistic Rectifier

**Working principle in the semi-classical regime.**

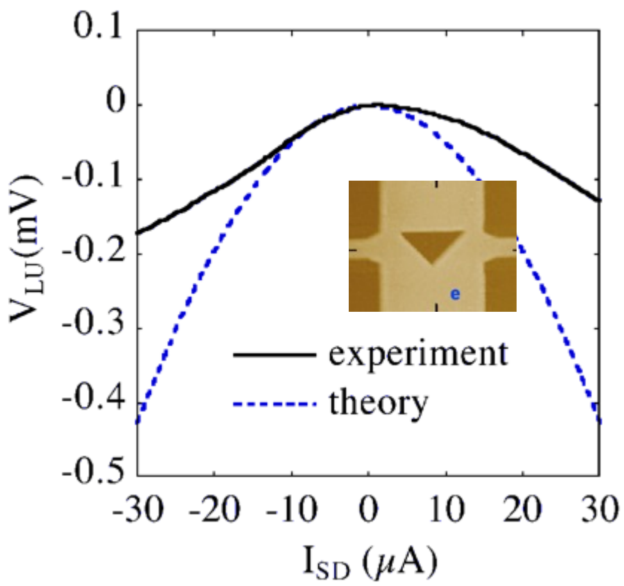



Functions like a **Bridge Rectifier!**

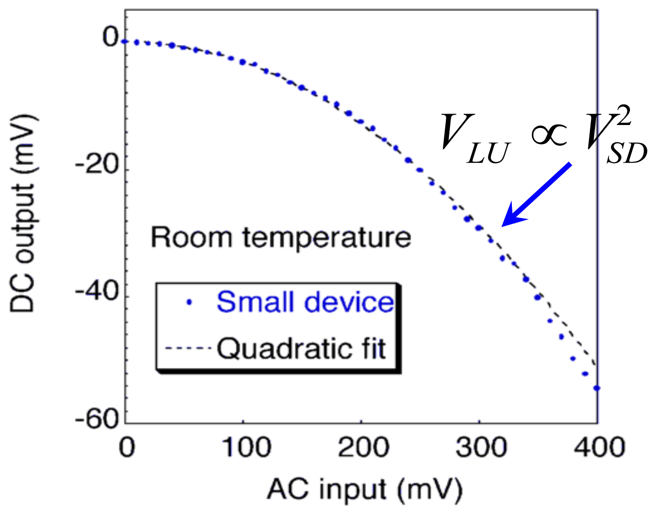
**1st diode that layman can understand!**

**1st diode having intrinsic zero threshold!**

# InGaAs ballistic rectifier characteristics



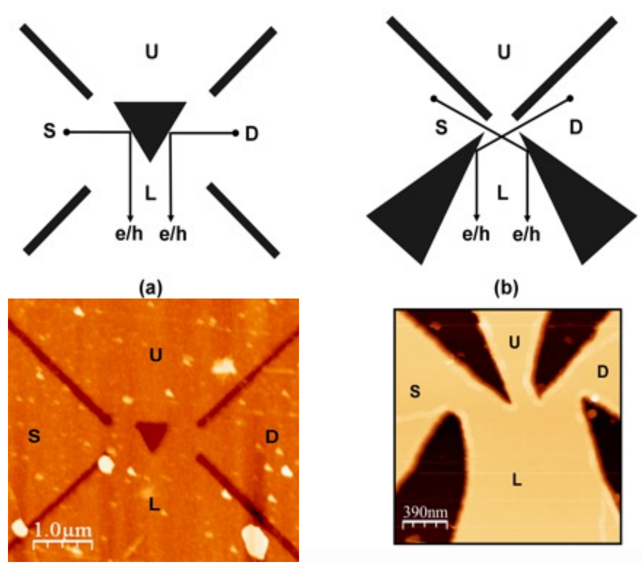

*Phys. Rev. Lett. 80, 3831; Phys. Rev. B59, 9806*



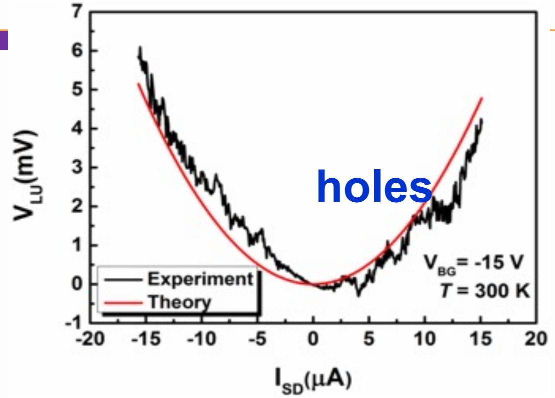

*Japn. J. Appl. Phys. 40, L909; Appl. Phys. Lett. 79, 1357*

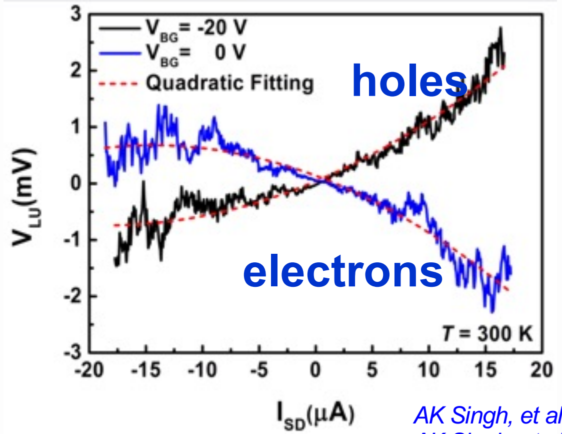
- ✓ **New device concept and working principle**
- ✓ **Zero threshold, no need of DC biasing**
- ✓ **Parabolic (not exponential), quadratic response**

# Graphene Ballistic Rectifier




- Graphene flake directly placed on $SiO_2$
- Low mobility: ~2000 $cm^2/Vs$
- Device size > mean free path

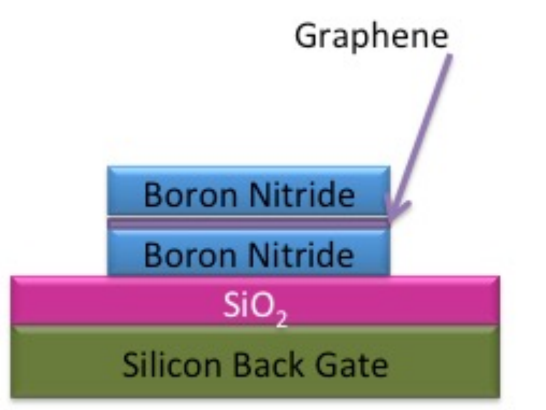


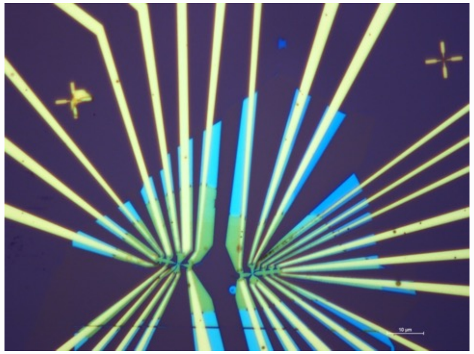




*AK Singh, et al, 2D Materials 5 (3), 035023 (2018)*
*AK Singh, et al, Carbon 84, 124-129 (2015)*

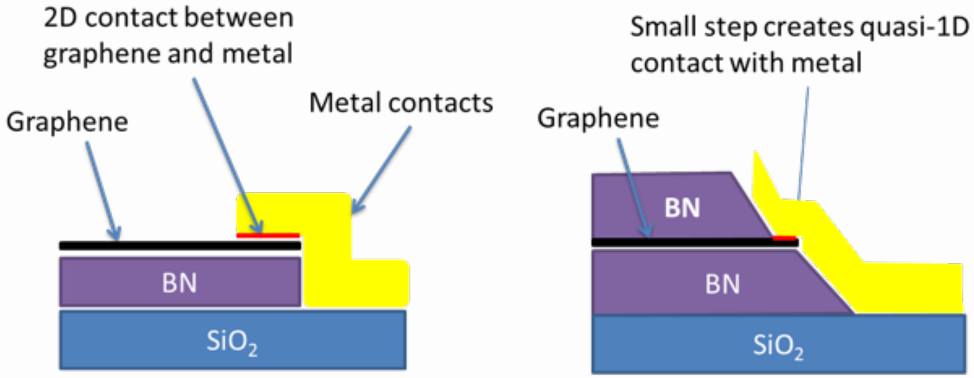
✓ Both devices worked at 300K
✓ Thermoelectric effect ruled out due to opposite output

# High mobility graphene & 1D contact



**Hall bars by e-beam lithography**

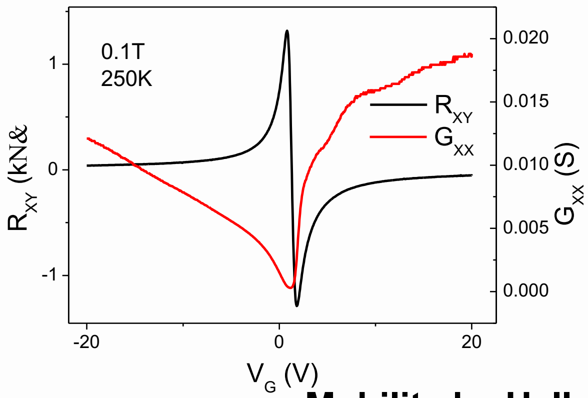


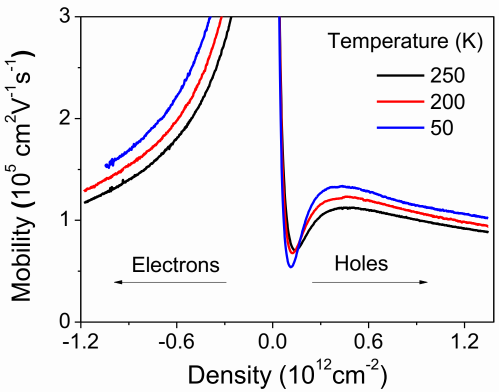

*L. Wang, et al. Science 342, 614 (2013).*

**BN enables ultralow surface states/traps**

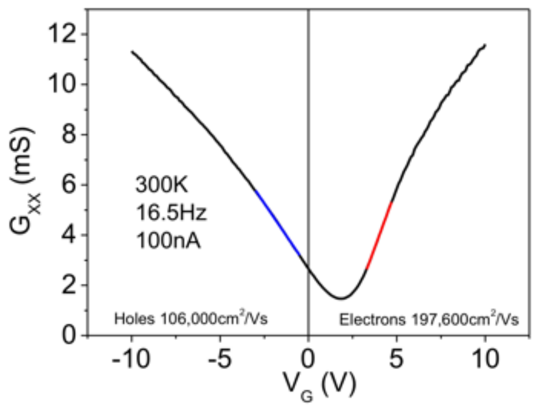
**1D contact to reduce series resistance**

# High-mobility graphene

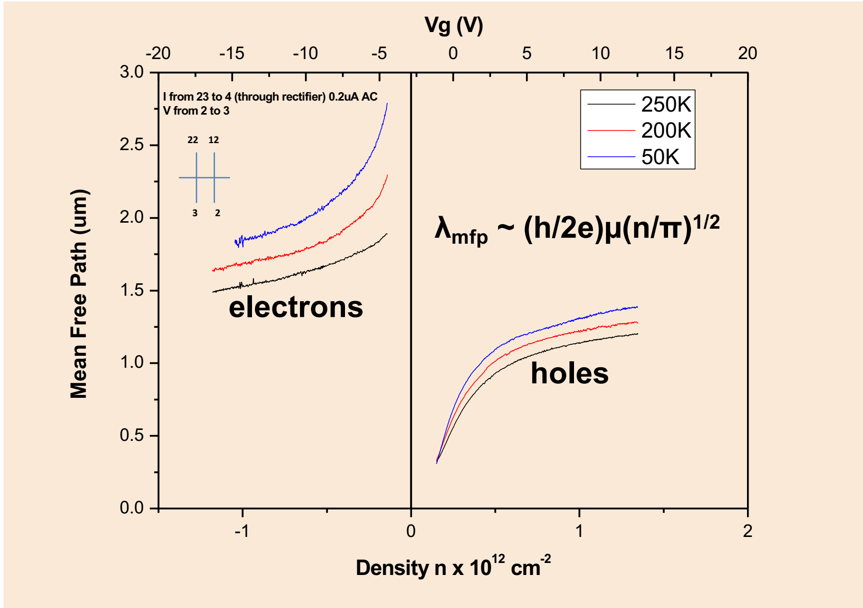



**Mobility by Hall measurement**



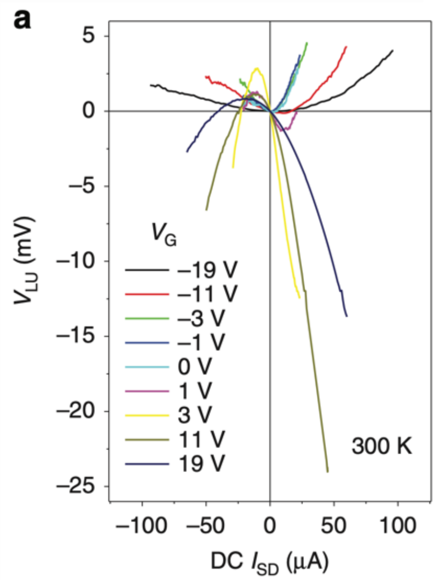

**Mobility by field-effect measurement**




- ➢ **Mobility ~ 200,000 $cm^2/Vs$ at 300 K**
- ➢ **Close to theoretical limit**
- ➢ **Mean free path: 1-2 microns**

*G. Auton, et al, Nature Communications, 7:11670 (2016)*

# Record microwave detection sensitivity

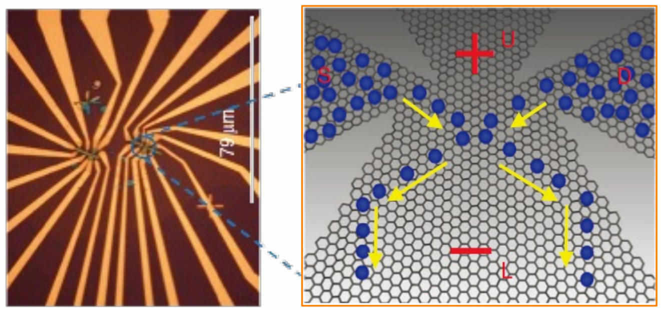


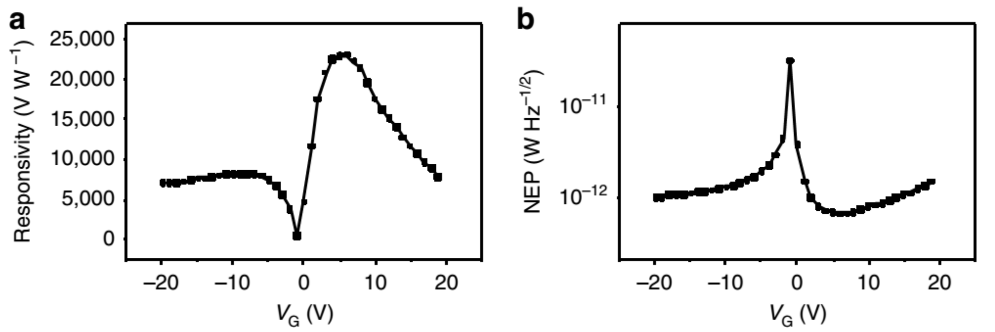

nature COMMUNICATIONS

ARTICLE

Received 15 Dec 2015 | Accepted 18 Apr 2016 | Published 31 May 2016 DOI: 10.1038/ncomms11670 OPEN

## Graphene ballistic nano-rectifier with very high responsivity

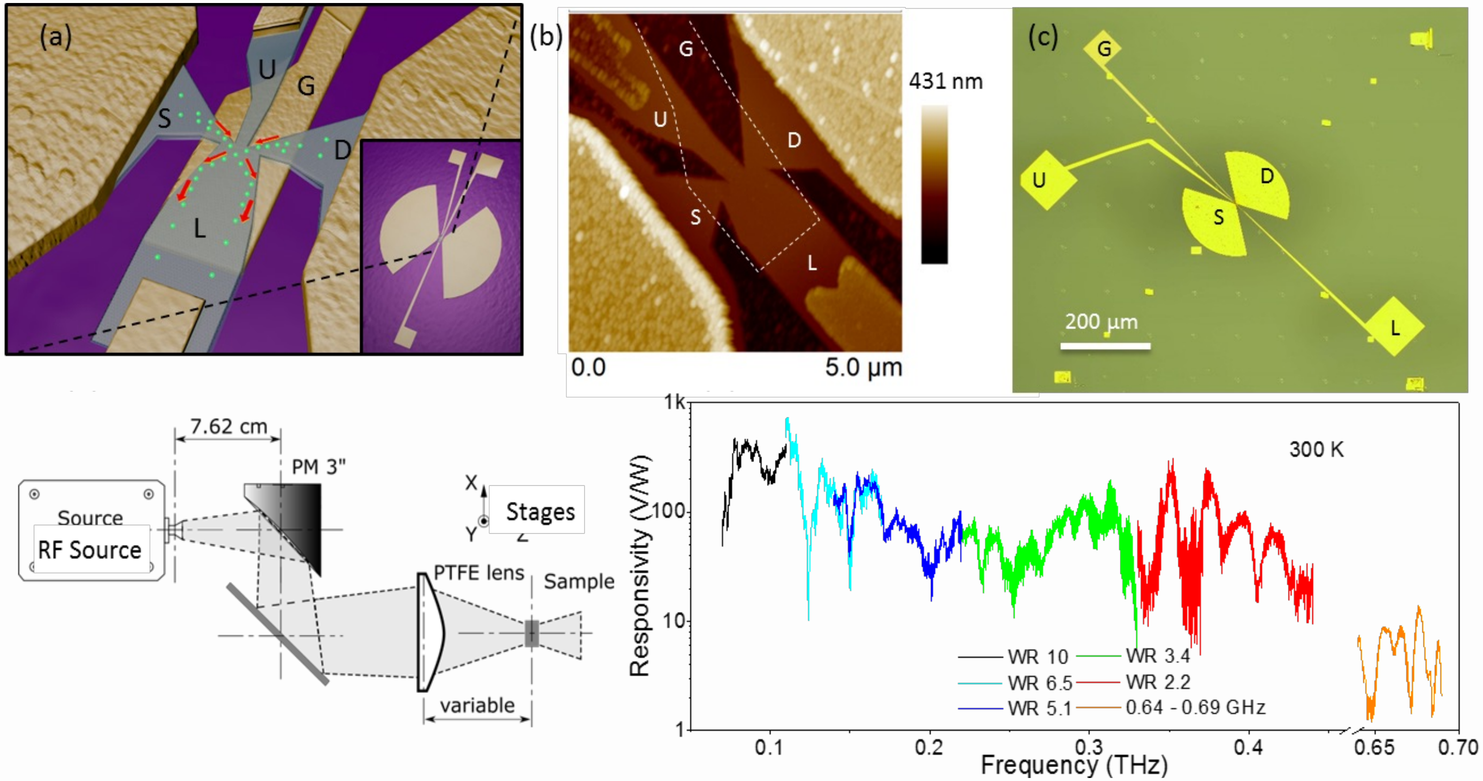



- **Room temp responsivity: 23,000 V/W**
- **Record sensitivity (NEP) for microwave detection at 300 K, <1 pW/Hz$^{1/2}$**
- **Comparable to superconductor bolometer (-270°C)**

*G. Auton, et al, Nature Communications, 7:11670 (2016)*

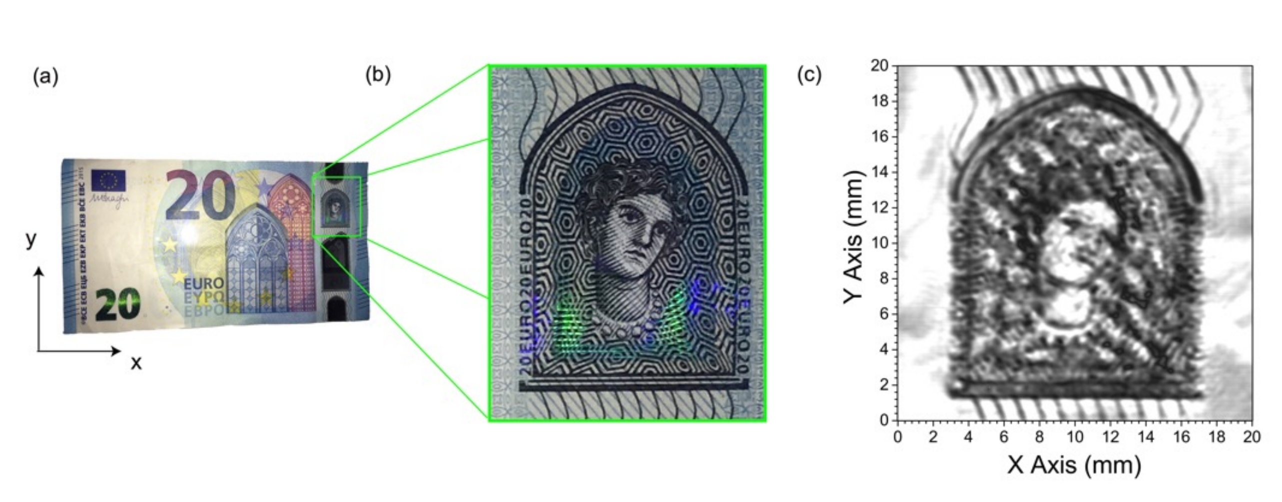
# Microwave detection up to 680 GHz




G. Auton, et al., Nano Letters, 17, 7015 (2017)

**One of the fastest graphene nano-diodes to date**

# Imaging at 640 GHz





- First graphene based THz imaging (resolution ~ 1 mm)
- Collaboration with University of Montpellier
- May be exploited as THz camera for airport security / medical imaging

*G. Auton, et al., Nano Letters, 17, 7015-7020 (2017)*

MANCHESTER 1824

# Planar THz Devices and Graphene Tunnelling Diodes

BRUGES 9-12 SEPTEMBER ESSERC 2024

- Background
- How to determine 2D material thickness
- Graphene tunnelling transistors
- Planar THz nanodevices
- Semiconducting graphene nanoribbons
- Summary

IEEE SSCS Electron Devices Society GreEnergy

# Graphene: Problem 2

**Zero bandgap semimetal**

**It is not a semiconductor!**

**So, it is not of much use for electronics as the active layer.**

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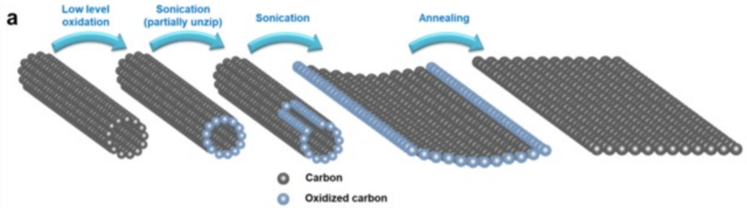
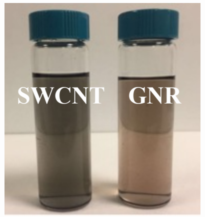
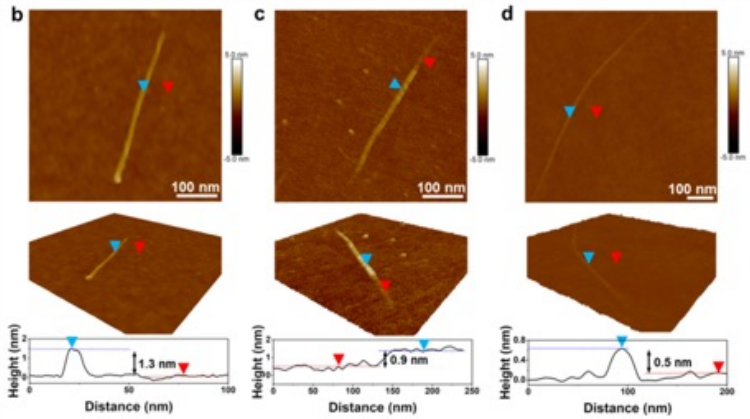
BRUGES 9-12 SEPTEMBER ESSERC 2024

# Graphene nanoribbons (GNRs)

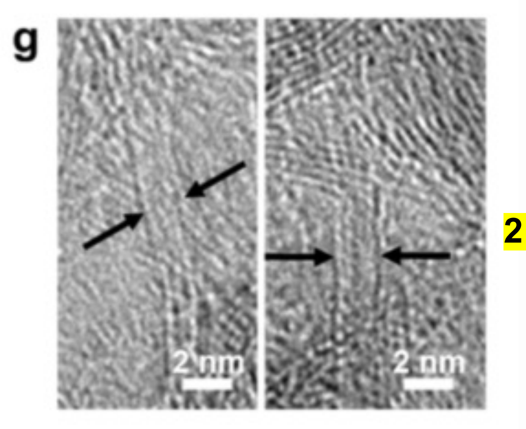



- SWCNT + strong acid
- Generate defects
- Unzip by ultrasonic agitation
- Annealing

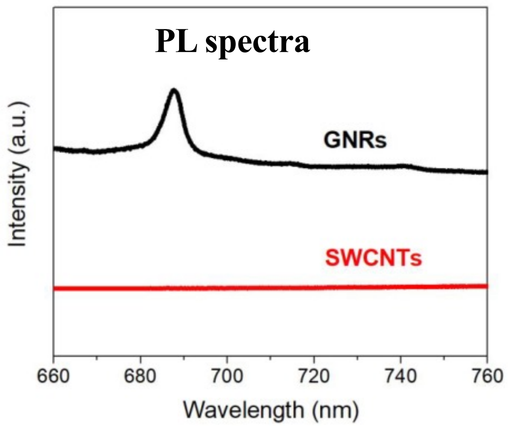



SWCNT | Partially unzipped | Fully unzipped




2 nm wide GNR

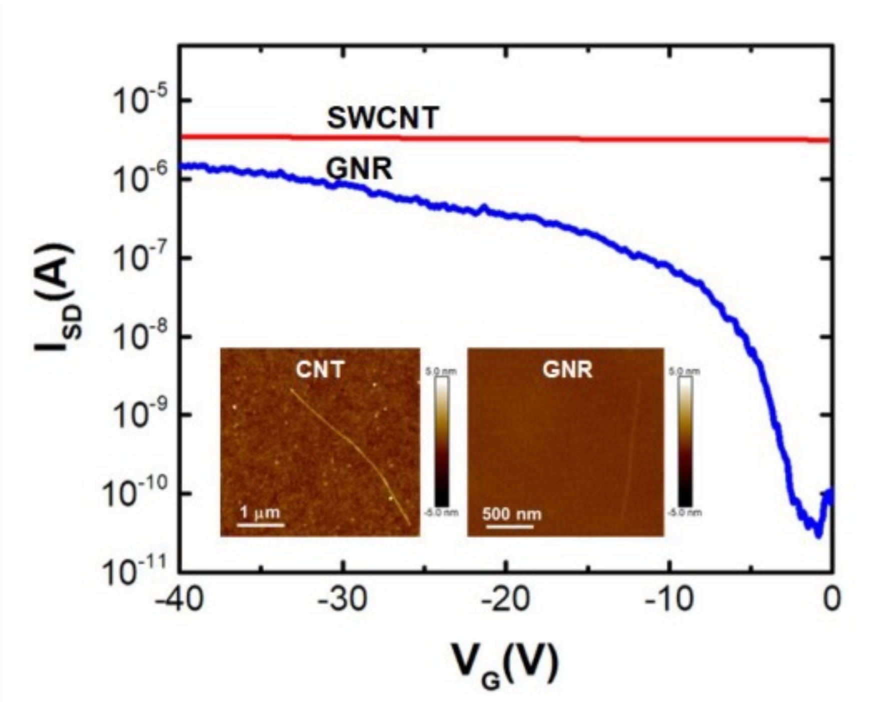



1.8 eV bandgap

*ACS Appl. Mater. Interfaces 13, 52892 (2021)*

IEEE SSCS Electron Devices Society GreEnergy

# Graphene nanoribbons TFTs

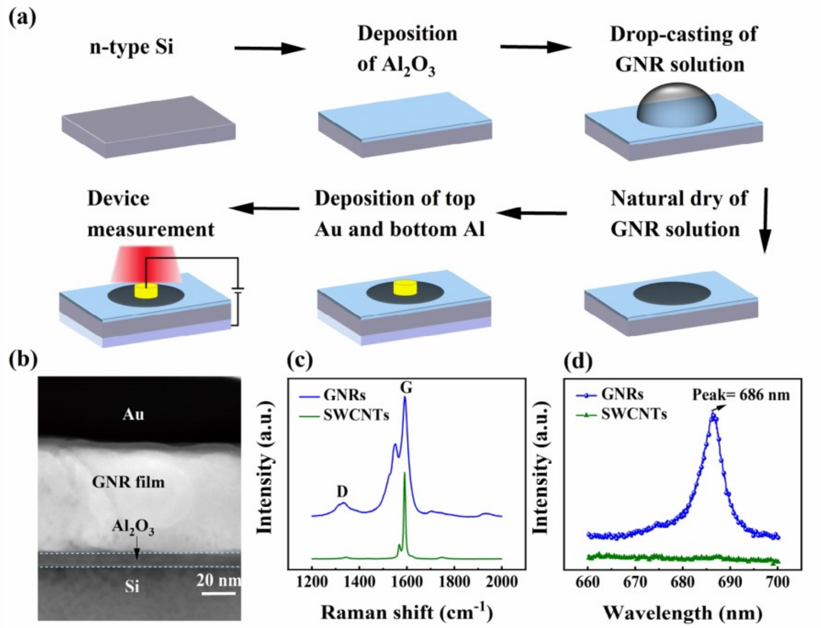


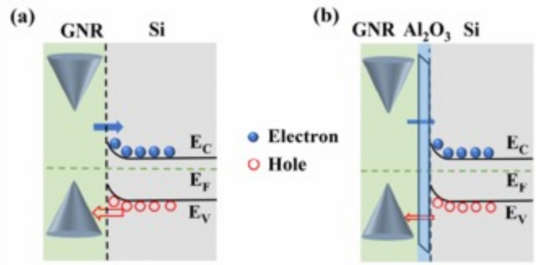

- **GNR TFT on/off ratio >$10^5$**
- **Previous graphene TFT on/off ratio only ~ 10**

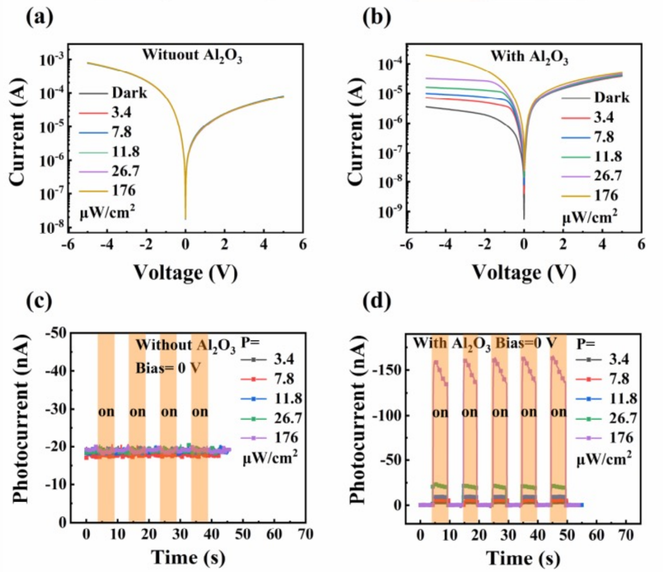
*ACS Appl. Mater. Interfaces 13, 52892−52900 (2021)*

# Graphene nanoribbon photodetectors

*Forming GNR film*



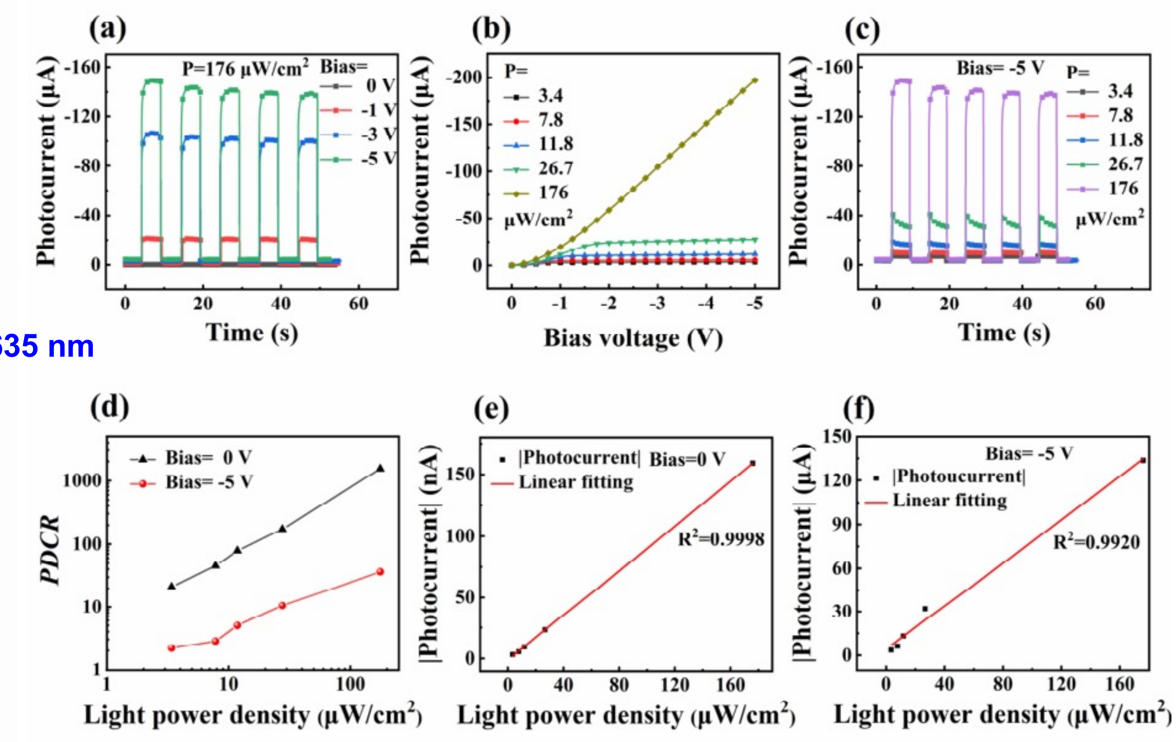




**Introducing $Al_2O_3$ to reduce dark current**

*M.Y. Wang, Nano Lett.* 24, 165 (2024)

# Graphene nanoribbon photodetectors

Light wavelength 635 nm



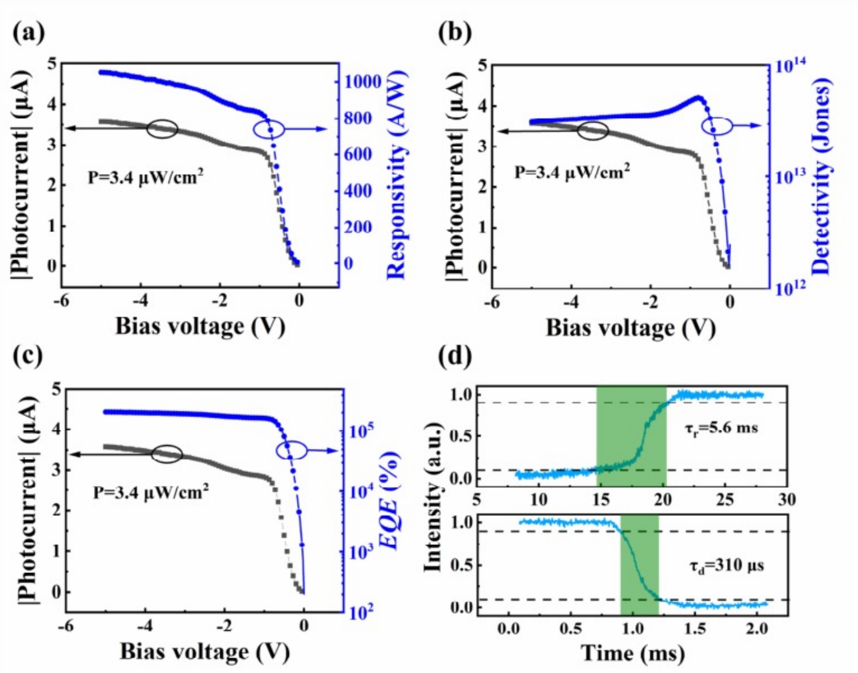

*M.Y. Wang, Nano Lett.* 24, 165 (2024)

**Photo-to-dark current ratio (PDCR) at zero bias: 1.5×$10^3$**



48

# Graphene nanoribbon photodetectors

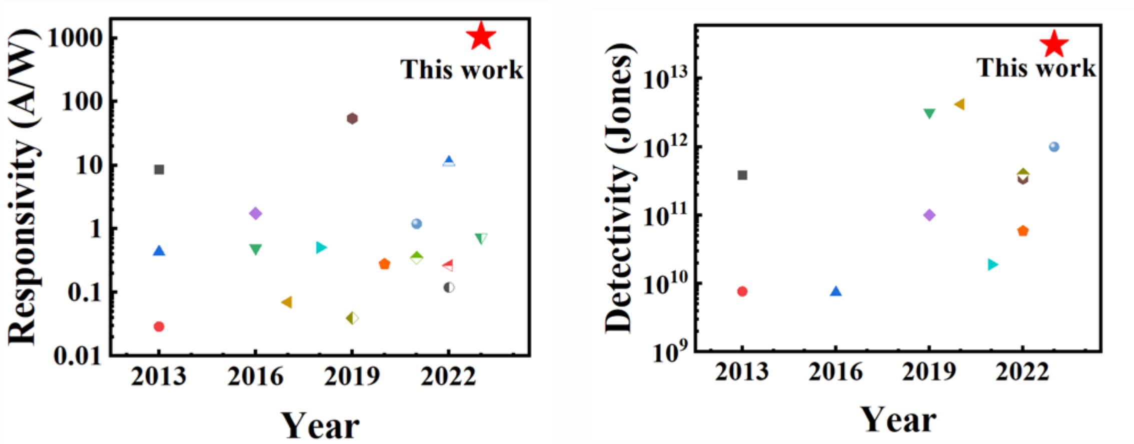



| Bias | R (A/W) | D (Jones) | EQE (%) |
|---|---|---|---|
| -5 V | 1052 | $3.13\times10^{13}$ | $2\times10^{5}$ |
| 0 V | 1.04 | $2.45\times10^{12}$ | 200 |

*M.Y. Wang, Nano Lett.* 24, 165 (2024)

- **Responsivity 1,052 A/W**
- **Response time: 310 μs**

# Comparison with literature



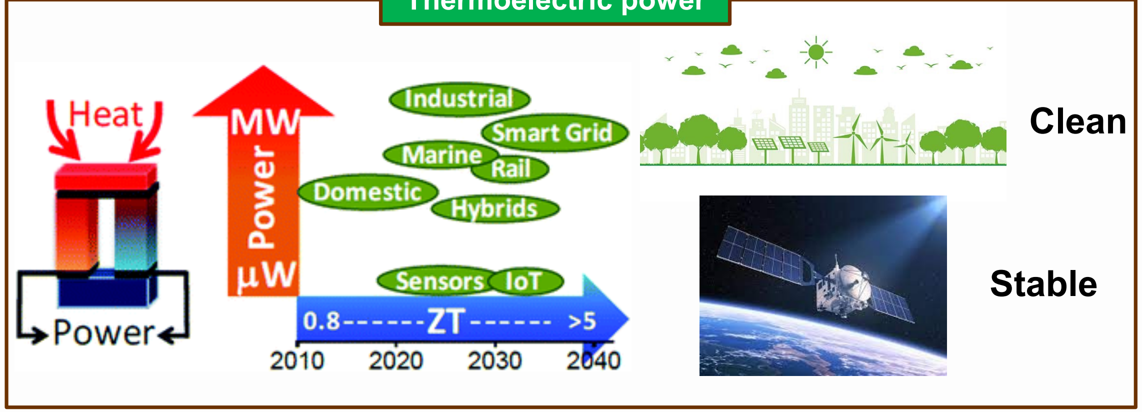


**Highest responsivity and detectivity among graphene-based devices**

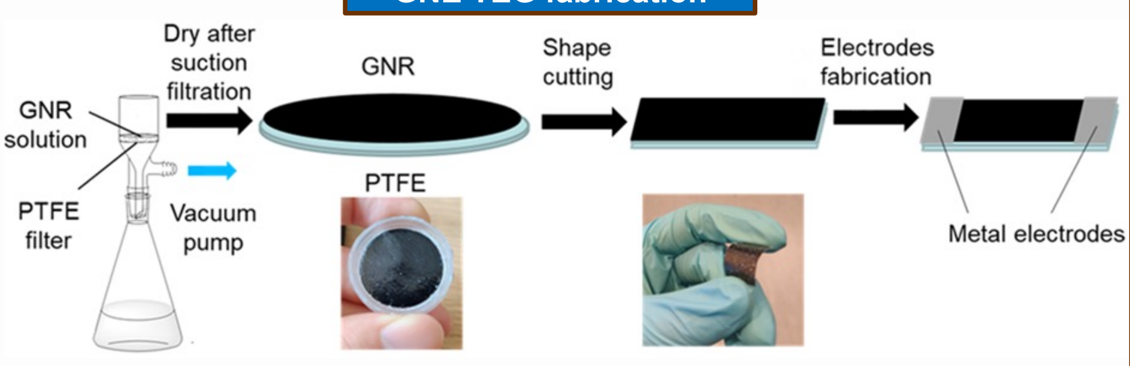
*M.Y. Wang, Nano Lett.* 24, 165 (2024)

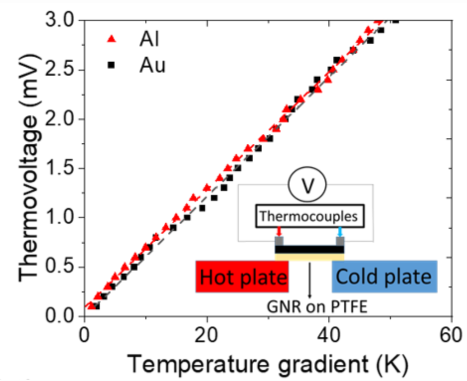
# Graphene nanoribbon thermoelectric generator

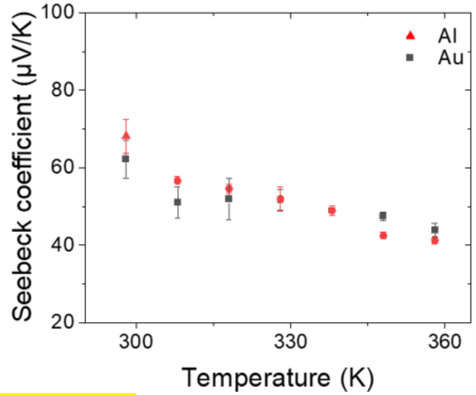
## Thermoelectric power




## GNE TEG fabrication



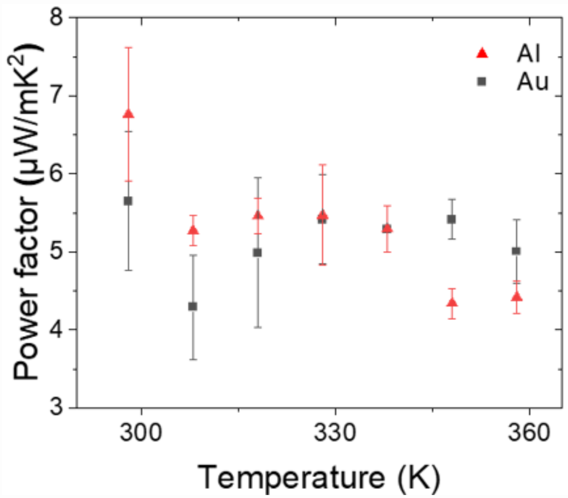



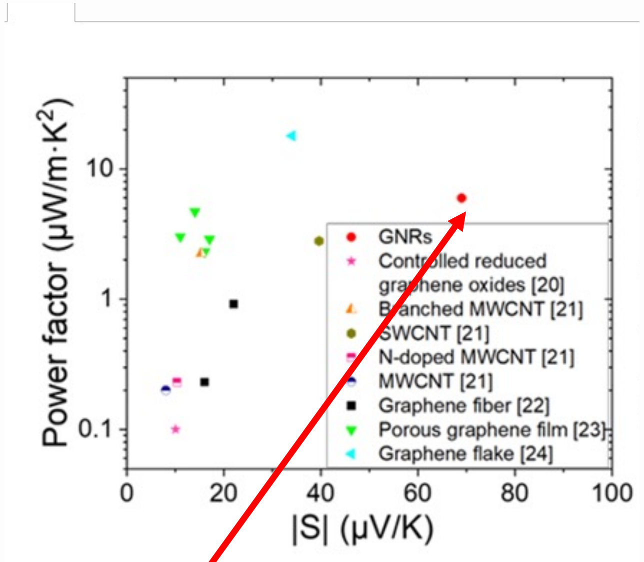



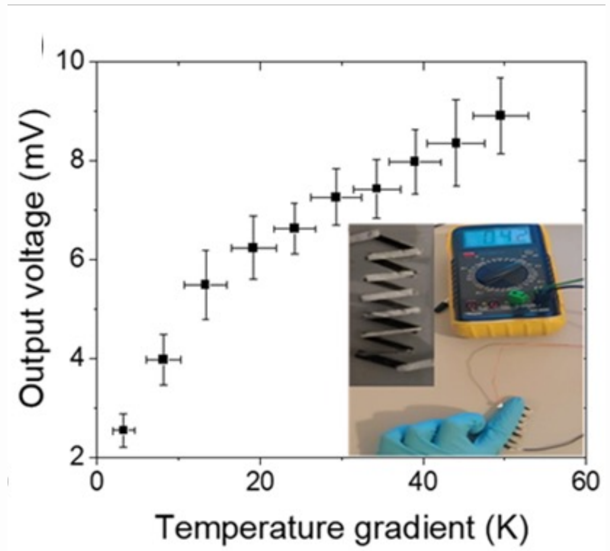

**Average Seebeck coefficient 60 μVK$^{-1}$**

*Wei, et al., Carbon 210, 118053 (2023)*

# Graphene nanoribbon thermoelectric generator




*Wei, et al., Carbon 210, 118053 (2023)*

**Highest Seebeck coefficient in carbon-based devices**

- **Flexible devices**
- **Body heat driven**
- **Voltage output ~ 10 mV**

# Summary

- Background: Graphene too thin and not a semiconductor
- How to determine 2D material thickness?
  - Edge Rayleigh scattering+ dark field
- Graphene tunnelling transistors:
  - Unexpected size and geometry dependence
- Planar THz nanodevices:
  - Device that does not need a bandgap and zero threshold
- Semiconducting graphene nanoribbons
  - Eg=1.8 eV, high on/off FETs, photodiodes, thermoelectric generators

# *Thank you!*