二维原子晶体的光电性能

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2014年4月10日

提　　纲

- 二维原子晶体的基本物性
- 石墨烯与光相互作用
- 光电子器件

——激光锁模

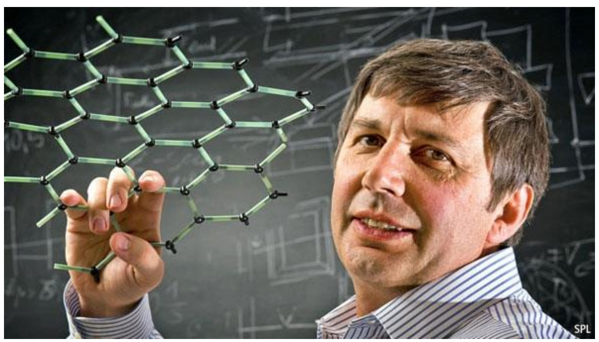
——光调制器

——光探测器件

——光发射器件

——光伏器件

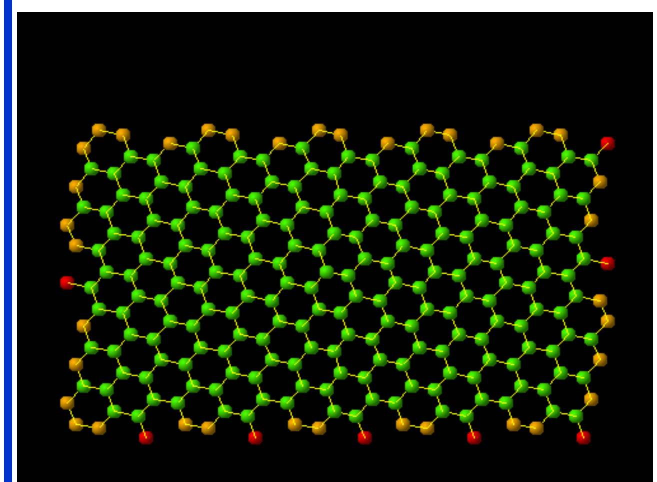
石墨烯的发现



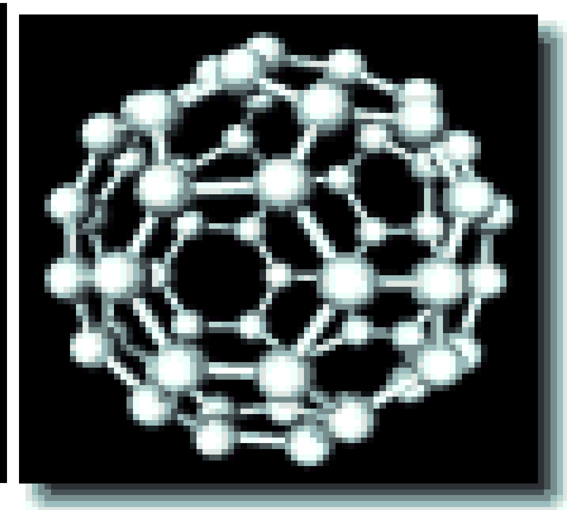
Andre Geim

Kostya Novoselov

Novoselov KS, Geim A K, *et al.* **Science** 2004, **306**, 666
Zhang YB *et al.* **Nature** 2005, **438**, 201
Geim AK and Novoselov KS **Nature Materials** 2007, **6**, 183

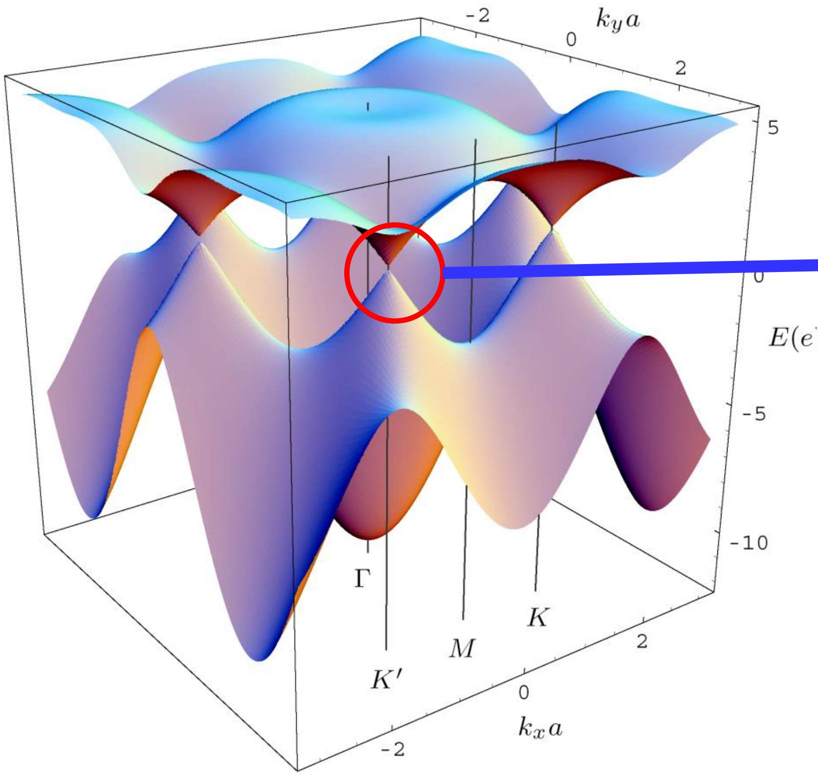


碳纳米管

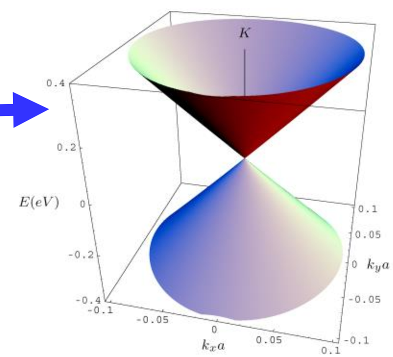


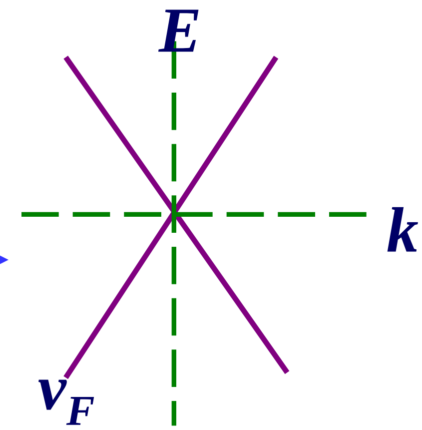
碳60

石墨烯能带结构



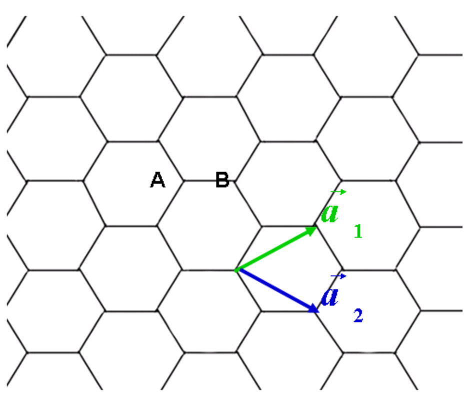
狄拉克点





$$E = \hbar k v_F$$

$$v_F \approx 10^6\ ms^{-1} = c/300$$



与传统半导体材料对比

- 超高迁移率（$2x10^5 cm^2/Vs$）
- 零带隙材料
- 线性色散关系
- 电子有效质量为零
- 对界面非常敏感

石墨烯能带结构

$$H = H_{at} + H_{\text{int}}(\vec{k})$$

Tight-binding calculation on π bands:

$$H\begin{pmatrix} u_1 \\ u_2 \end{pmatrix} = \begin{pmatrix} E_p, & f(\vec{k}) \\ f^*(\vec{k}), & E_p \end{pmatrix}\begin{pmatrix} u_1 \\ u_2 \end{pmatrix}$$

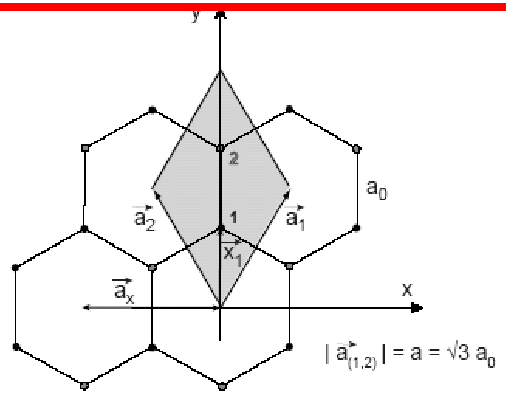
$$f(\vec{k}) = \gamma[1 + e^{i\vec{k}\cdot\vec{a}_1} + e^{i\vec{k}\cdot\vec{a}_2}]$$

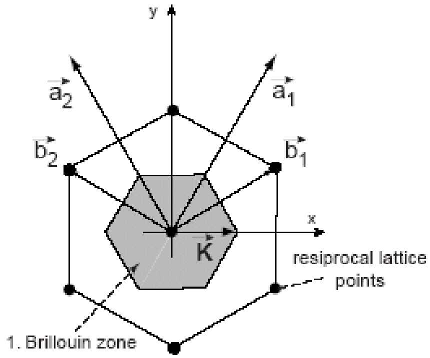
$$E_\pi(\vec{k}) = E_p \pm |f(\vec{k})|$$

$$= E_p \pm \sqrt{3 + 2\cos\vec{k}\cdot\vec{a}_1 + 2\cos\vec{k}\cdot\vec{a}_2 + 2\cos k(\vec{a}_2 - \vec{a}_1)}$$

$$= E_p \pm \sqrt{1 + 4\cos^2(\sqrt{3}k_x a/2) + 4\cos(\sqrt{3}k_x a/2)\cos(3k_y a/2)}$$

$$= E_p \pm v_F k' \qquad \text{near K points}$$





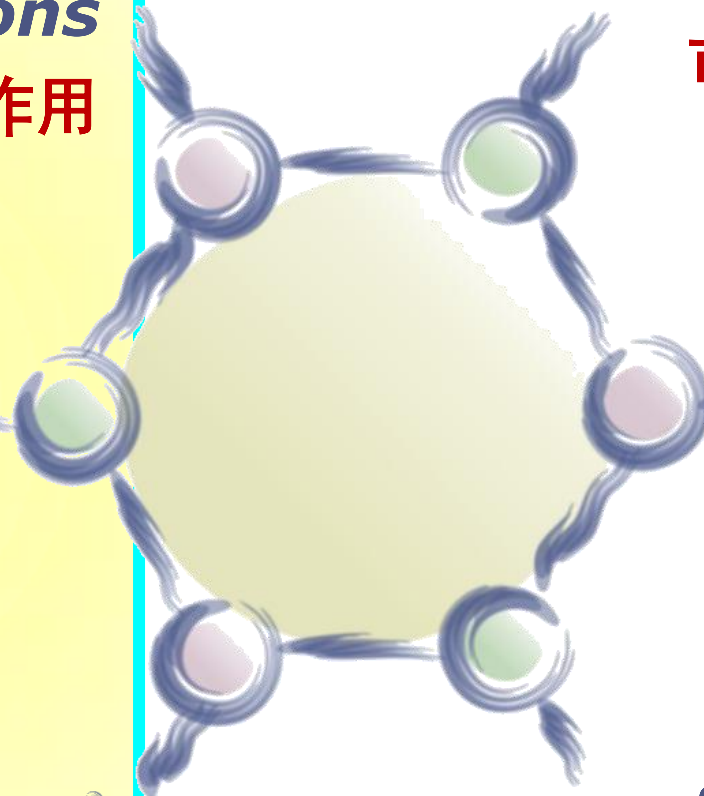
P.R.Wallace, Phys.Rev.71,(1947)

石墨烯的优异特性

Strong interaction with photons
强光子互作用

High Mobility
高载流子迁移率

Linear Spectrum
线性能谱关系

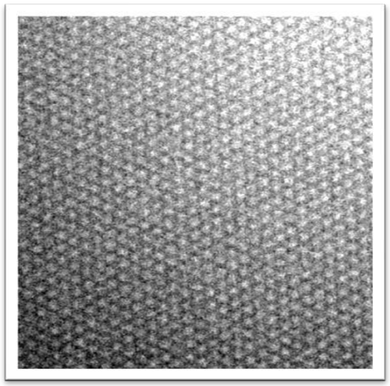


Highly Stretchable
可延展性

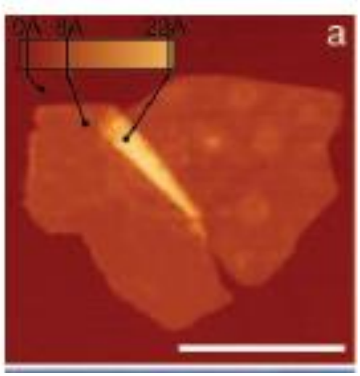
One Atom Thin
二维单原子层

Strength
机械强度

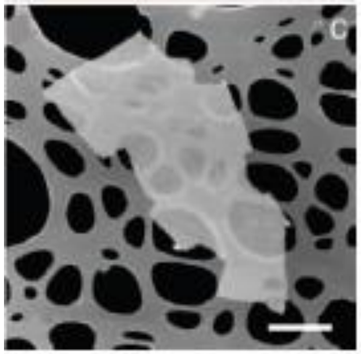
二维原子晶体材料



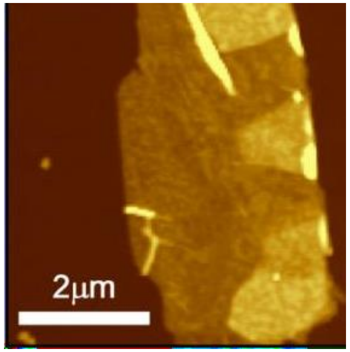
Graphene



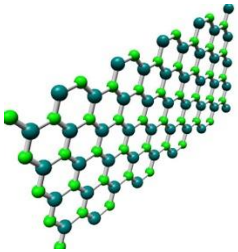
$NbSe_2$

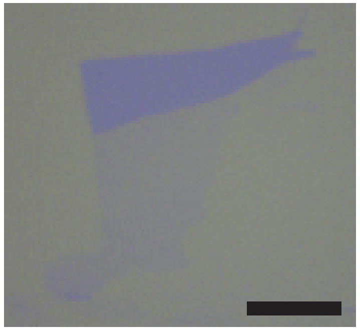


BiSrCaCuO

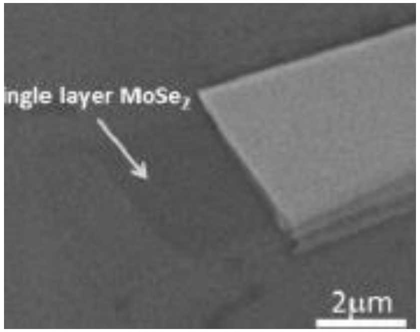


Black phosphorus

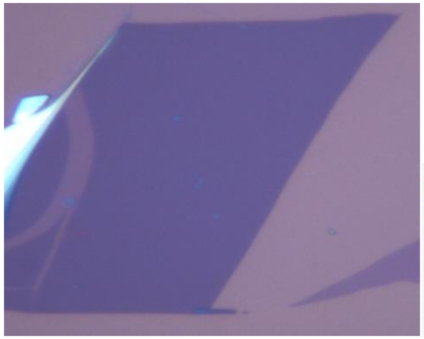


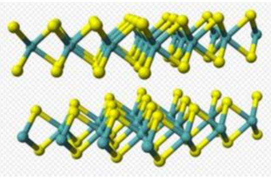


BN



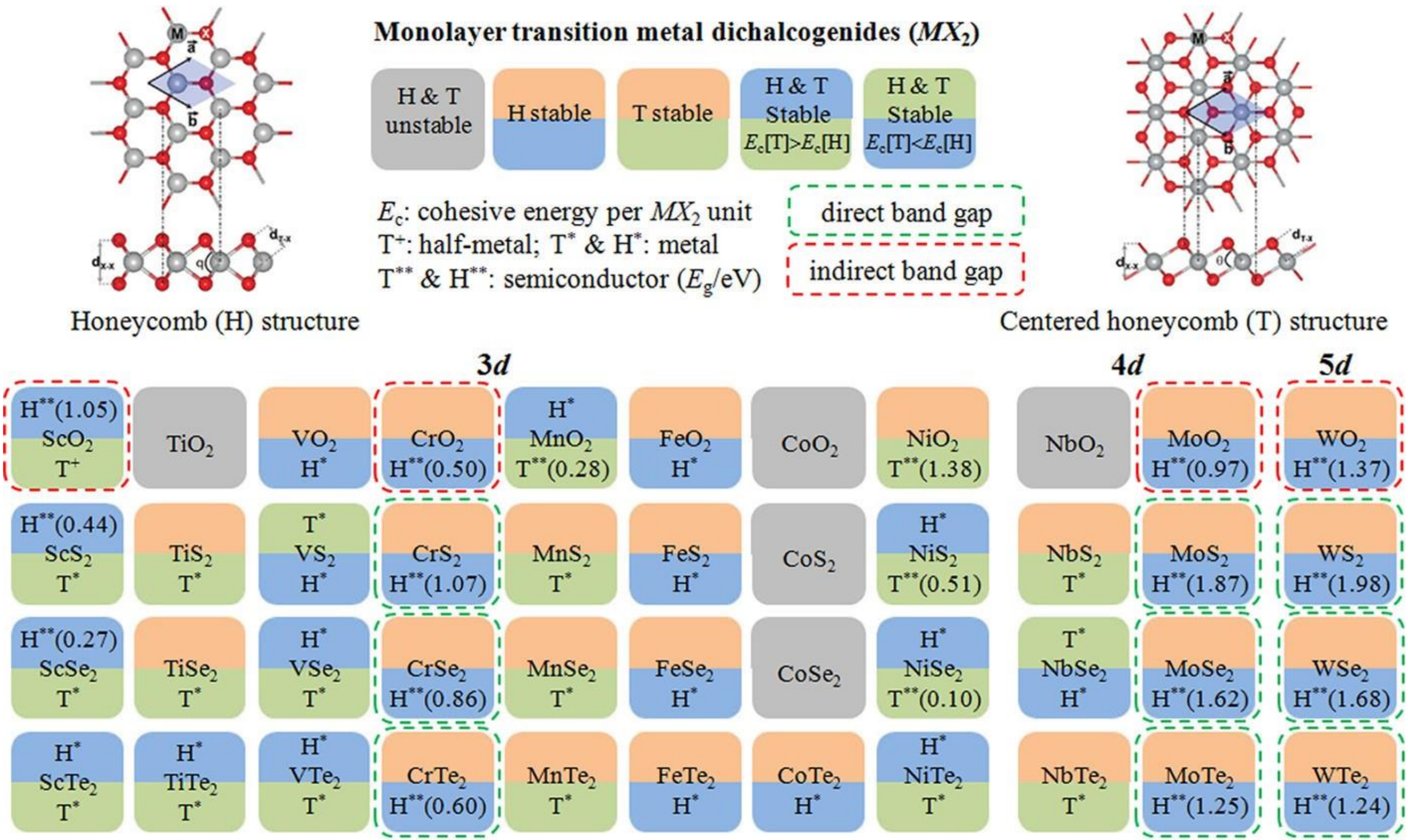
$MoSe_2$





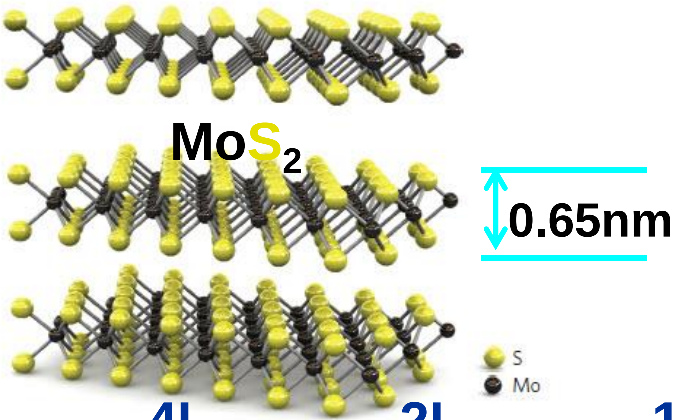
MoS_2

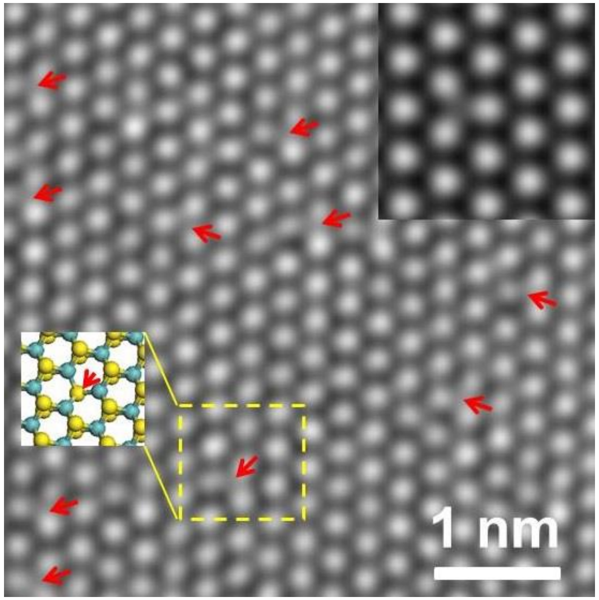
层状过渡金属二硫属化物

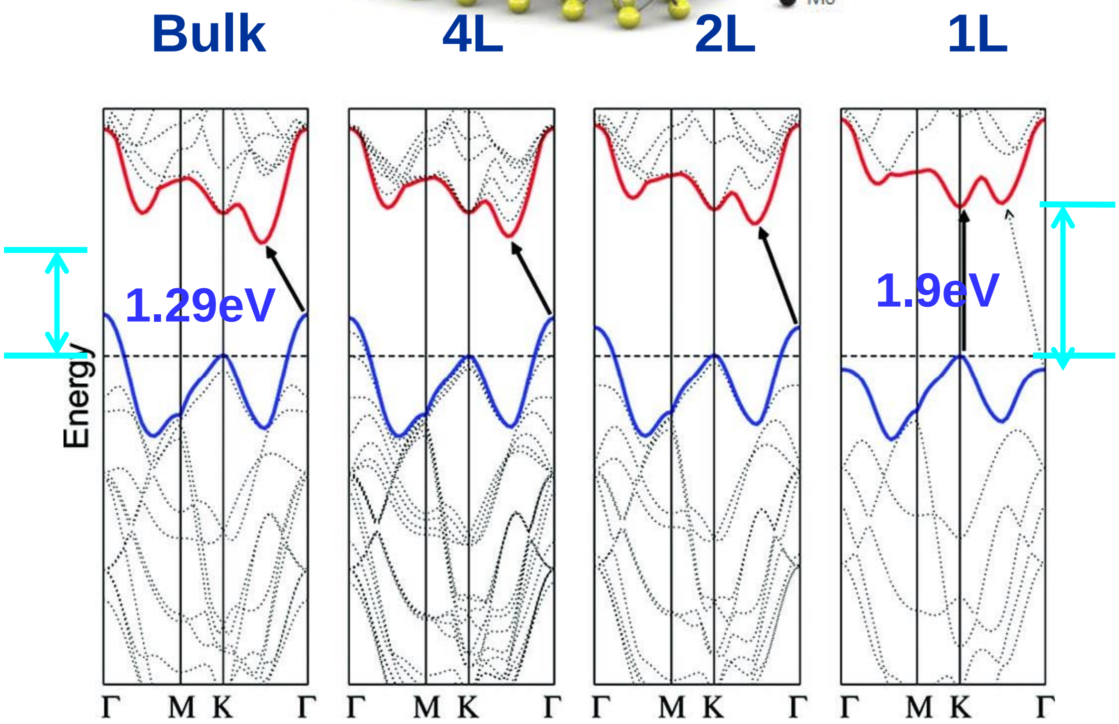


MoS_2 能带结构

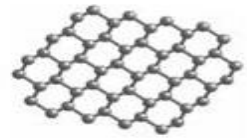
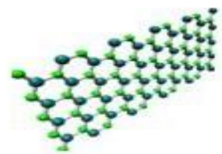
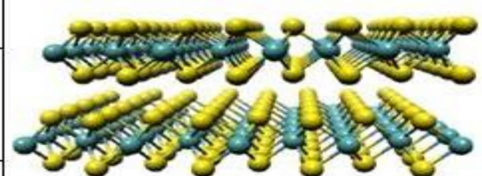
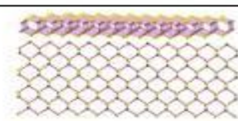
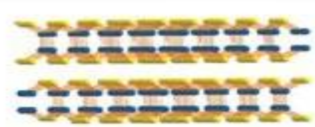

Natural MoS_2 crystal,
Canada


MoS2
0.65nm
S
Mo

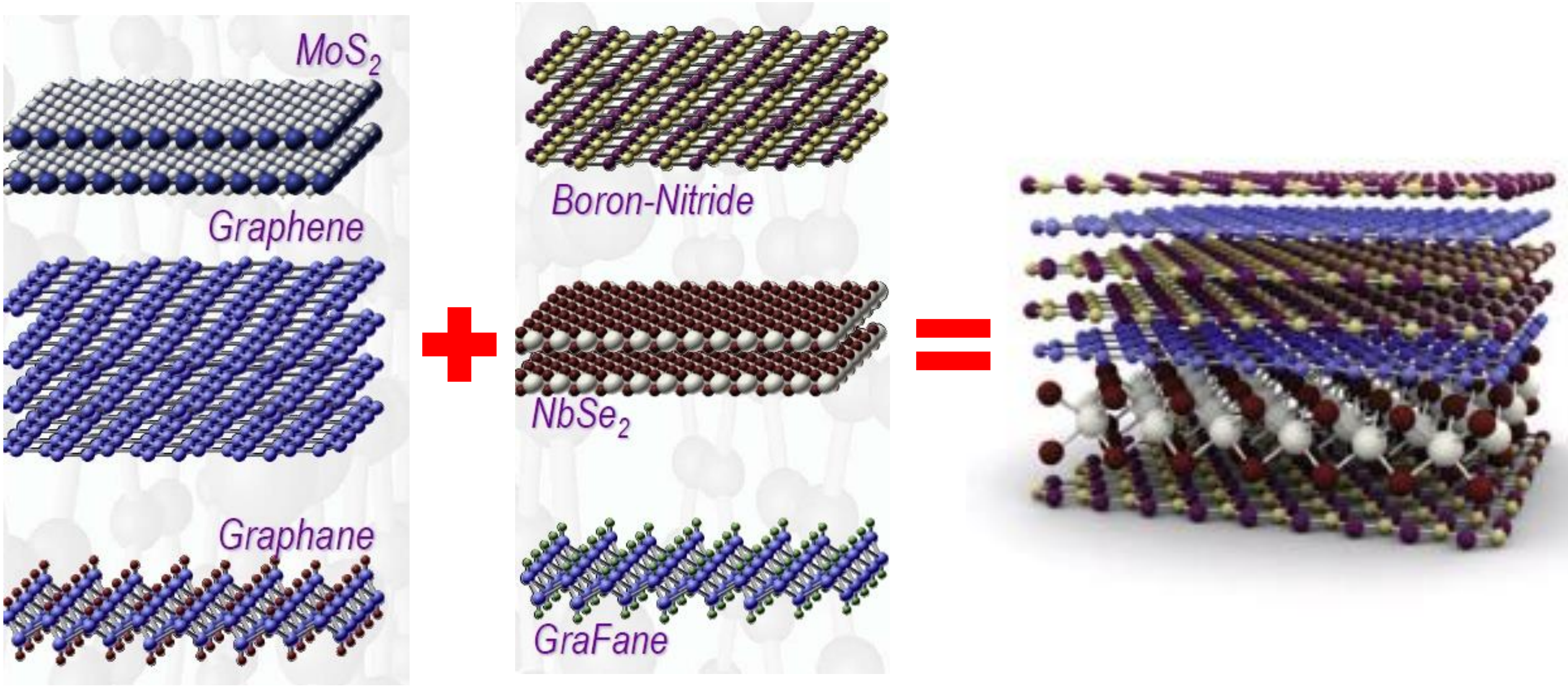

1 nm


Bulk
4L
2L
1L
1.29eV
1.9eV
Energy
Γ M K Γ
Γ M K Γ
Γ M K Γ
Γ M K Γ

二维原子晶体材料的能带结构

二维原子晶体材料	结构模型	能带隙 (eV)	载流子迁移率
单层石墨烯 (C)		0	超高
单层 *h*氮化硼 (BN)		~ 6.07	低
单层硫化钼 (MoS_2)		~1.90 (直接带隙)	低
单层硫化钨 (WS_2)		~2.10 (直接带隙)	
单层硒化钨 (WSe_2)		~1.44 (直接带隙)	
单层碲化钼 (WTe_2)		~1.07 (直接带隙)	
单层硫化镓 (GaS)		~ 3.04(直接带隙) ~ 2.59(间接带隙)	低
单层硒化镓 (GaSe)		~ 2.1(直接带隙) ~ 2.0(间接带隙)	

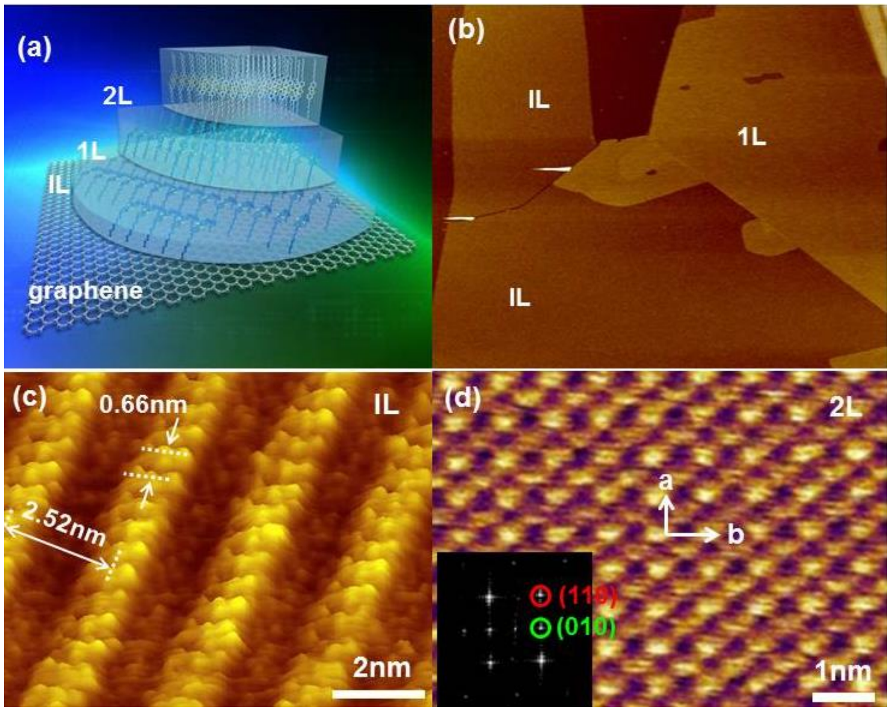
范德瓦尔斯（Van der Waals）异质结构

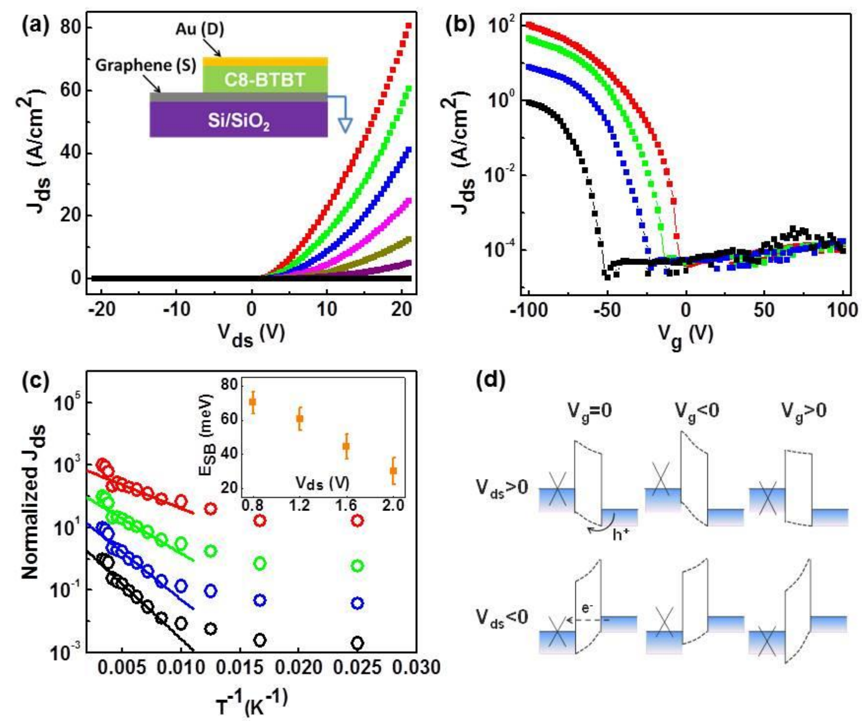


各种组合的异质结构更加丰富物理性能和器件应用

S.K.Novoselov, Nobel Prize Lecture (2010)

范德瓦尔斯（Van der Waals）异质结构

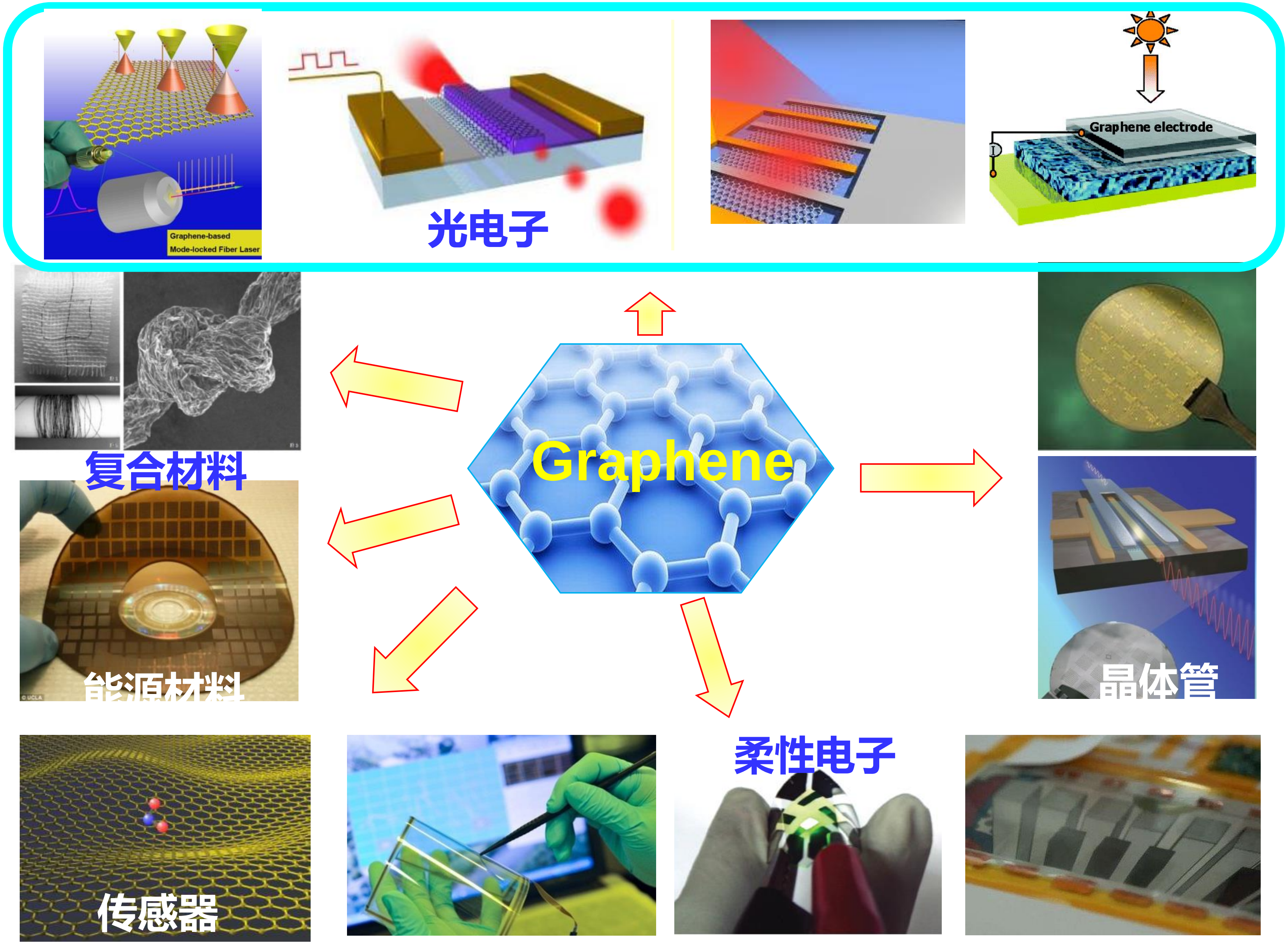




单层、多层有机材料C8-BTBT在石墨烯外延，垂直电输运实验反映出石墨烯势垒二极管整流特性。

Nature Nano. under review

以石墨烯为代表的2D材料潜在应用



A Roadmap for Graphene：光电子学

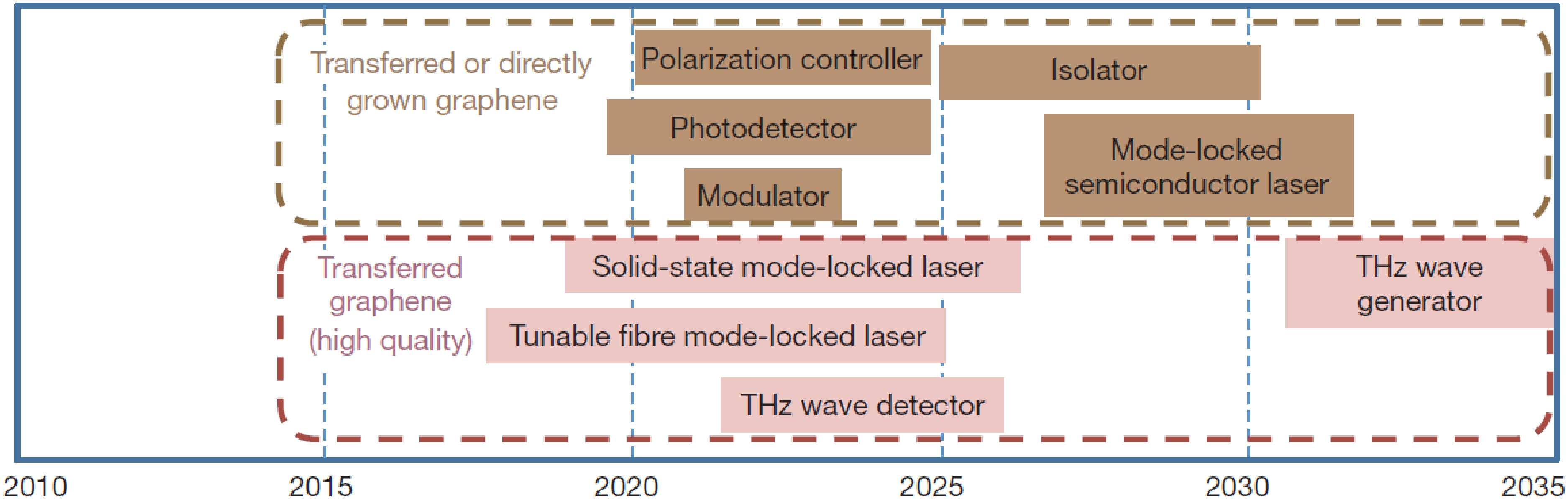


Table 3 | Photonic applications of graphene

Application	Drivers	Issues to be addressed
Tunable fibre mode-locked laser	Graphene's wide spectral range	Requires a cost-effective graphene-transferring technology
Solid-state mode-locked laser	Graphene-saturable absorber would be cheaper and easy to integrate into the laser system	Requires a cost-effective graphene-transferring technology
Photodetector	Graphene can supply bandwidth per wavelength of 640 GHz for chip-to-chip or intrachip communications (not possible with IV or III–V detectors)	Need to increase responsivity, which might require a new structure and/or doping control, and the modulator bandwidth must follow suit
Polarization controller	Current polarization controlling devices are bulky or difficult to integrate but graphene is compact and easy to integrate with Si	Need to gain full control of parameters of high-quality graphene
Optical modulator	Graphene could increase operating speed (Si operation bandwidth is currently limited to about 50 GHz), thus avoiding the use of complicated III–V epitaxial growth or bonding on Si	High-quality graphene with low sheet resistance is needed to increase bandwidth to over 100 GHz
Isolator	Graphene can provide both integrated and compact isolators on a Si substrate, dramatically aiding miniaturization	Decreasing magnetic field strength and optimization of process architecture are important for the products
Passively mode-locked semiconductor laser	Core-to-core and core-to-memory bandwidth increase requires a dense wavelength-division-multiplexing optical interconnect (which a graphene-saturable absorber can provide) with over 50 wavelengths, not achievable with a laser array	Competing technologies are actively mode-locked semiconductor lasers or external mode-lock lasers but the graphene market will open in the 2020s; however, interconnect architecture needs to consume low power

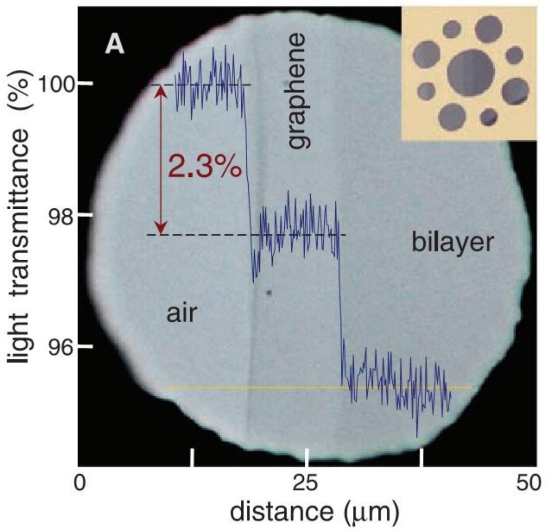
K. S. Novoselov *et al.* *Nature*, 2012

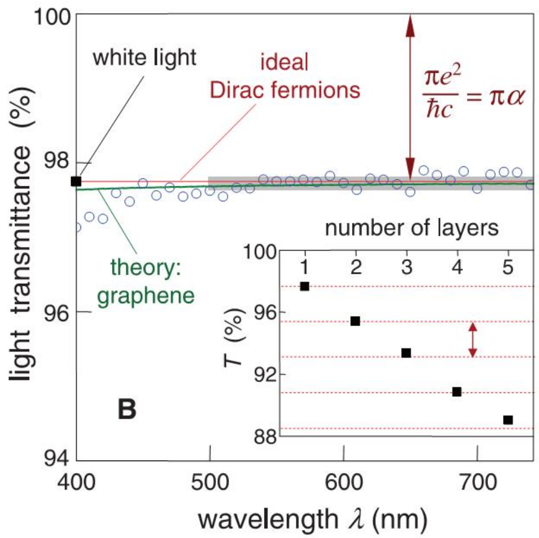
二维原子晶体材料应用的挑战

- **MATERIALS:**
  - Complete control: domain size, impurities, defects, number of layers, etc.
  - Low cost: low temperature, substrate re-use, etc.
  - Characterization: comprehensive information in large scale, in situ, high resolution.
- **PROCESSING:**
  - Transfer to arbitrary substrate at low cost without creating defects.
  - Create structures with controlled edge and orientation.
  - Compatibility with Si CMOS process.
- **STRUCTURES:**
  - Passive vs active components.
  - New devices structures that exploit the intrinsic properties of 2D materials is needed.

石墨烯与光相互作用特征

任何物质的光学性质都与其电子结构直接相关



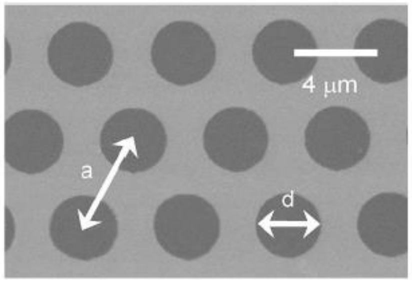


如何更“强”？

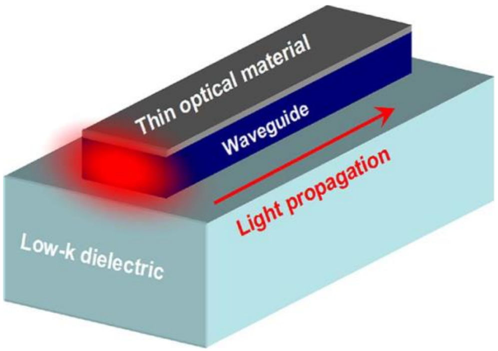
多层结构

（类似二维电子气模型）

强的光吸收 (πα~2.3% per layer)



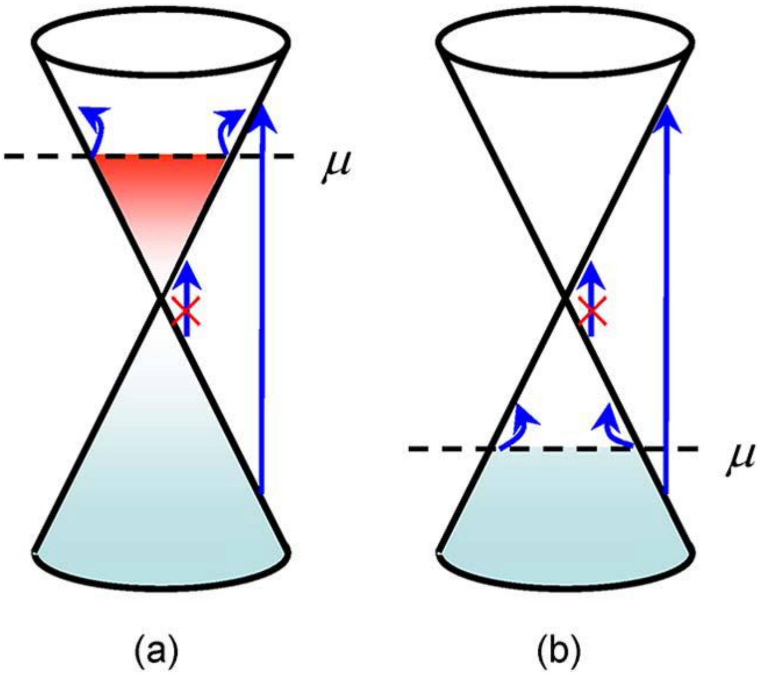
等离子激元



光波导结构

石墨烯与光相互作用特征

任何物质的光学性质都与其电子结构直接相关



带间载流子复合时间，约0.4-1.7ps
带内载流子热平衡时间，约0.07-0.12ps

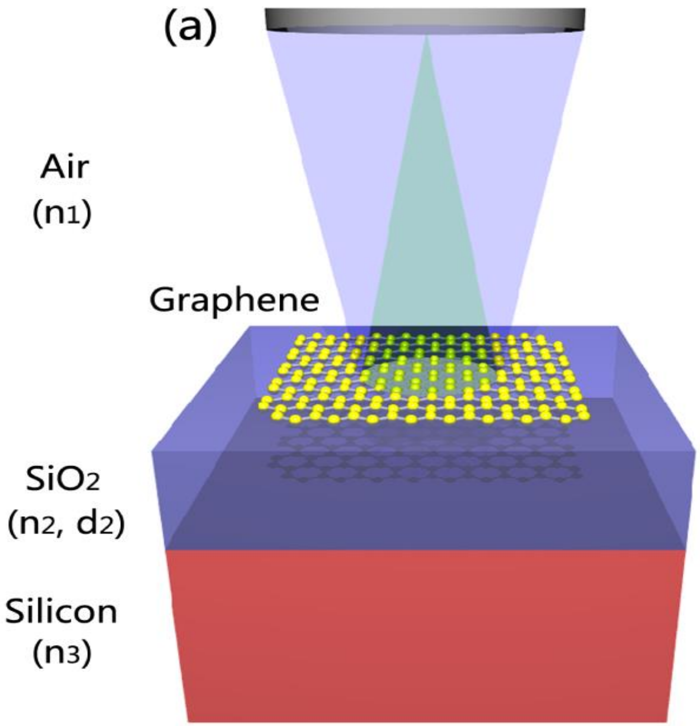
→ 光学过程和应用

通常在单电子理论框架内处理

石墨烯圆锥形能带结构和光学跃迁。
- 带间跃迁（ 直蓝线箭头）
- 带内跃迁占（弯蓝线箭头）

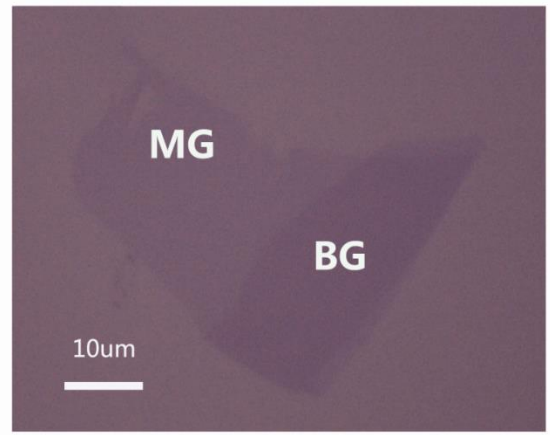
石墨烯与光相互作用特征

- 光学反射对比谱应用于石墨烯电子结构特性研究

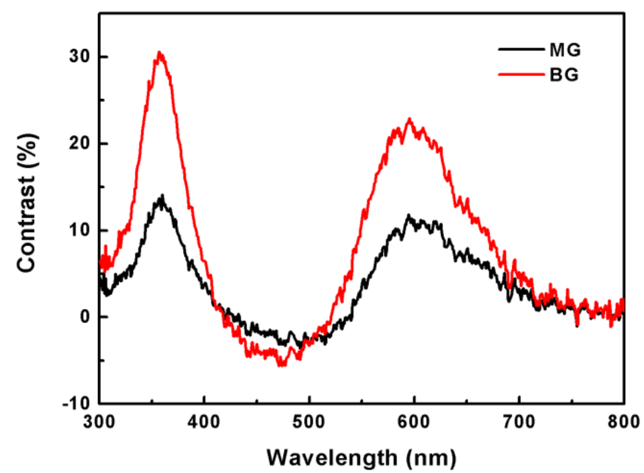


对比度

$$Contrast = \frac{R_{substrate} - R_{graphene}}{R_{substrate}}$$



光学显微照片



反射对比光谱

Z.Fei, Phys. Rev. B (2008)

石墨烯与光相互作用特征

光学反射对比谱 → 光电导率 → 电子结构

狄拉克色散关系在~3 eV处终结

区域A

恒定的光电导

↑

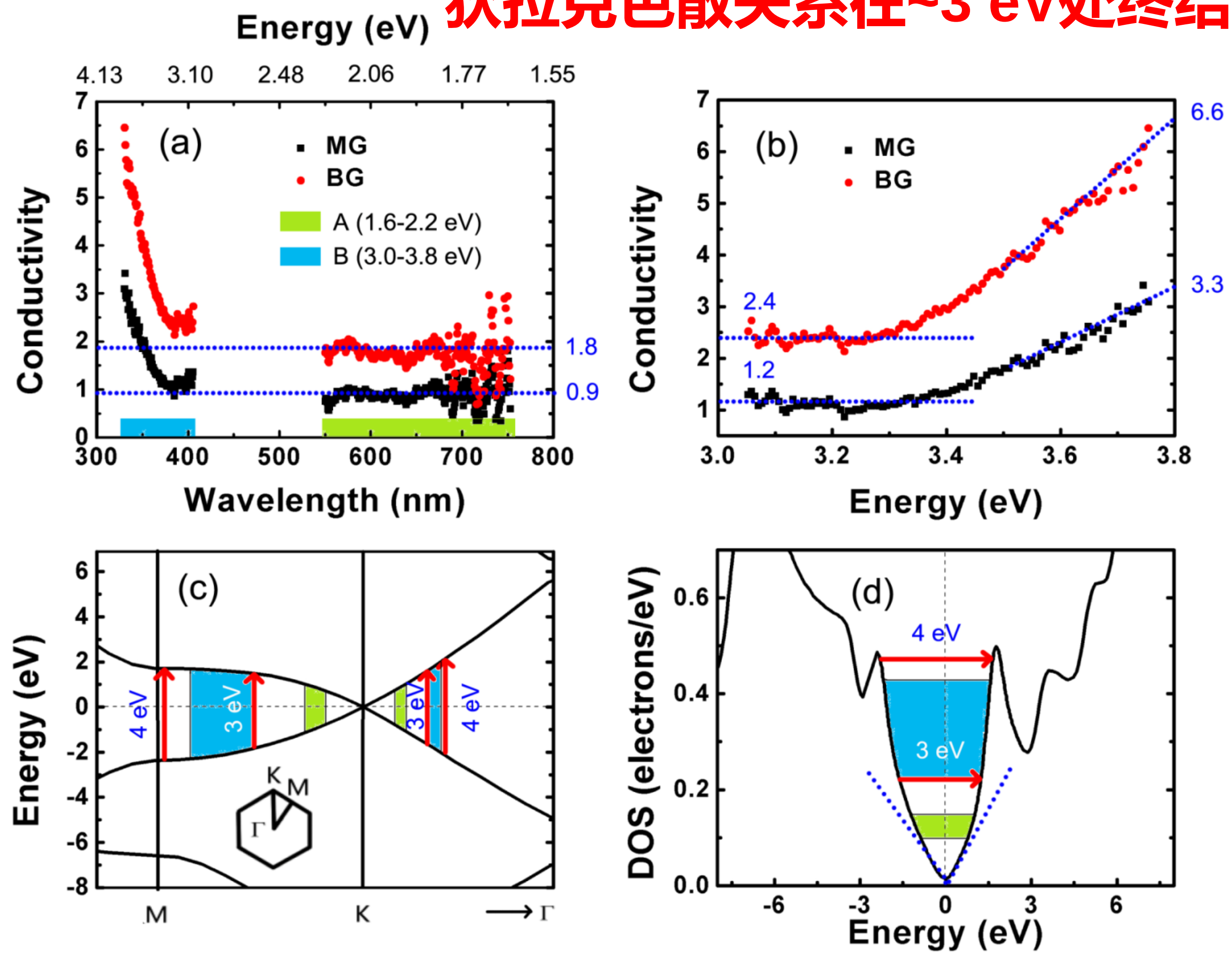
狄拉克色散关系线形的态密度

区域B

高速增长光电导

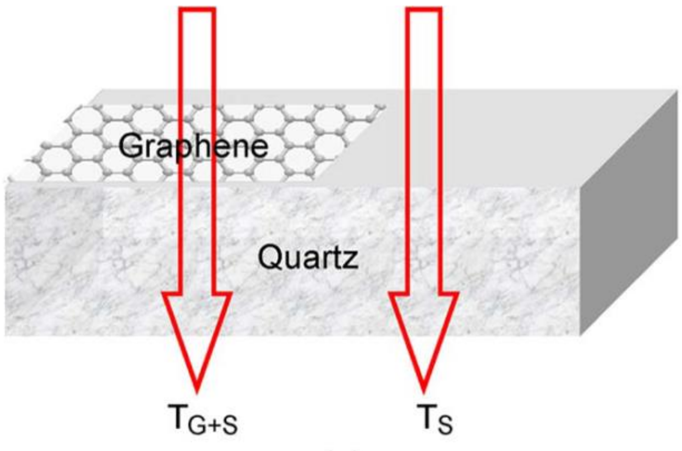
↑

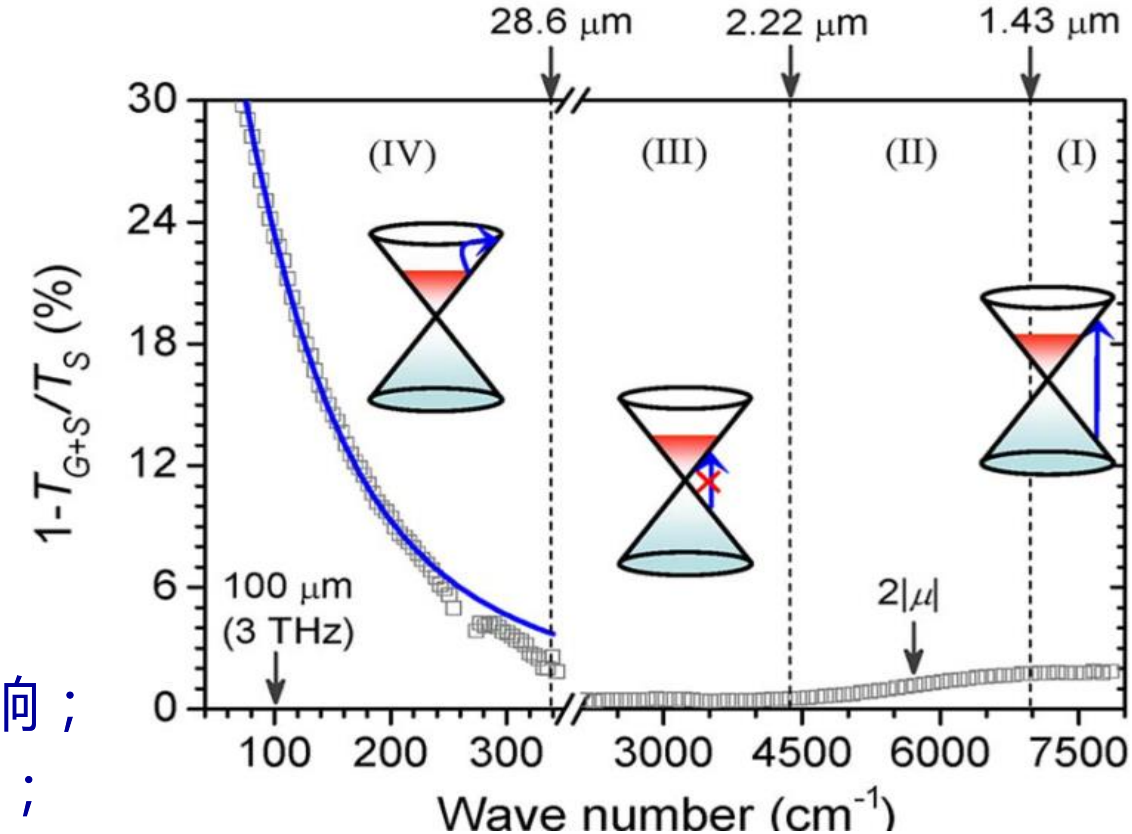
平的色散关系快速增长的态密度



石墨烯与光相互作用特征

- 红外、太赫兹区光吸收的能谱依赖关系



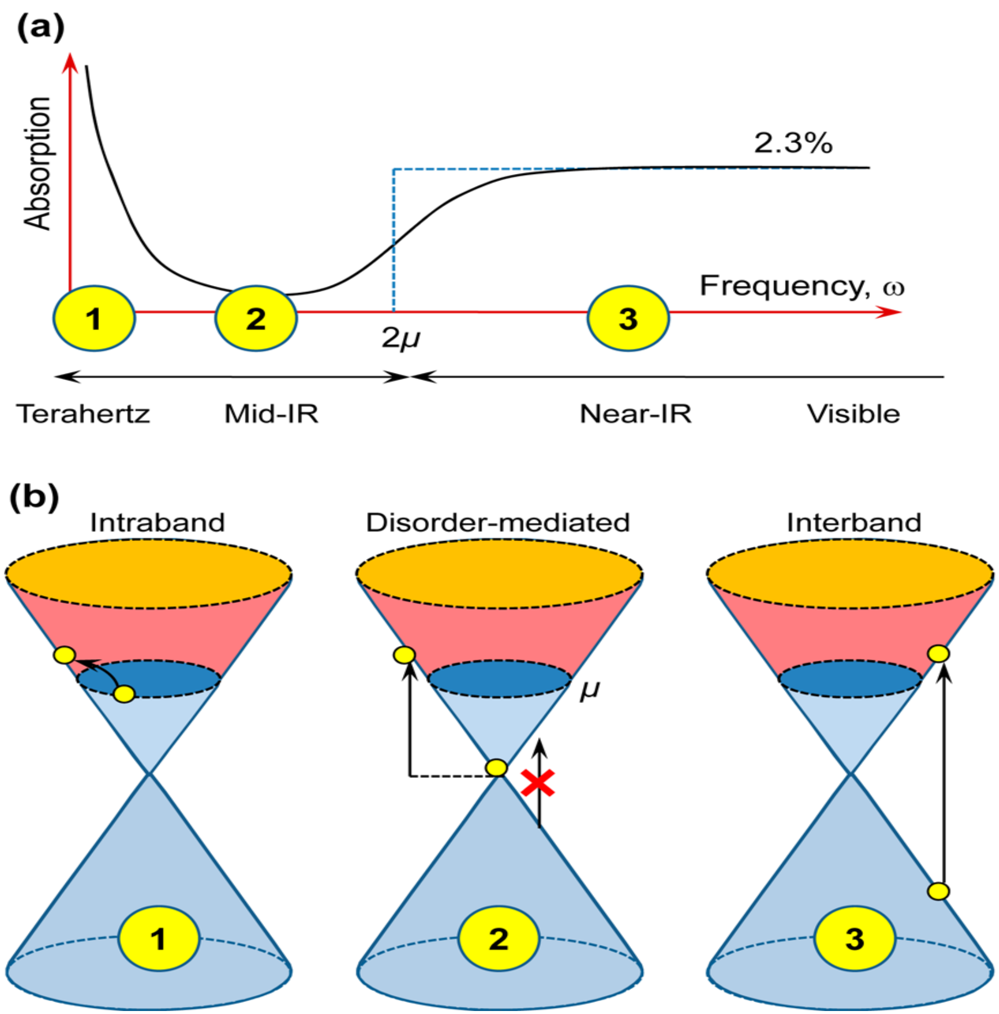


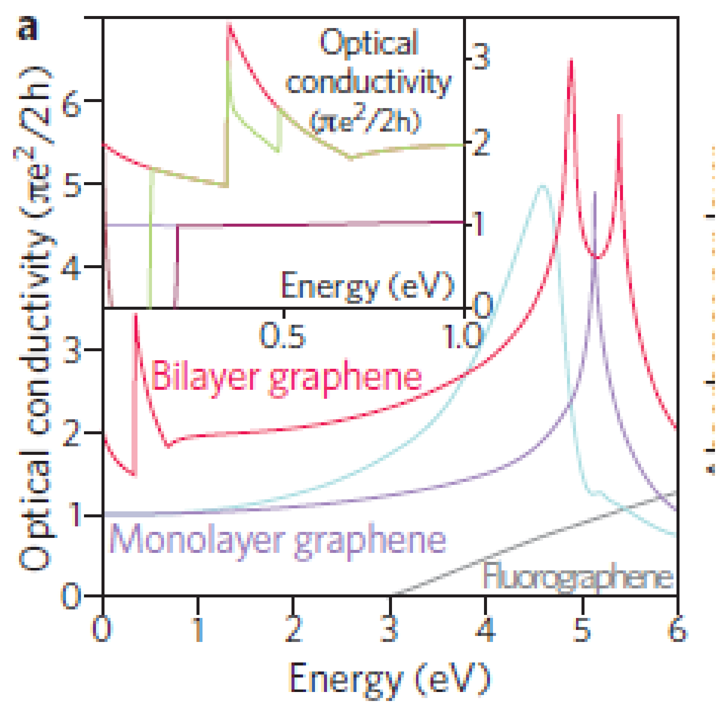
- ✓ I区：带间跃迁，界面影响；
- ✓ II区：逐渐出现泡利阻塞；
- ✓ III区：泡利阻塞（化学势移动）；
- ✓ IV区：带内跃迁导致光吸收迅速增强。

可通过栅电场等方法调节化学势位置

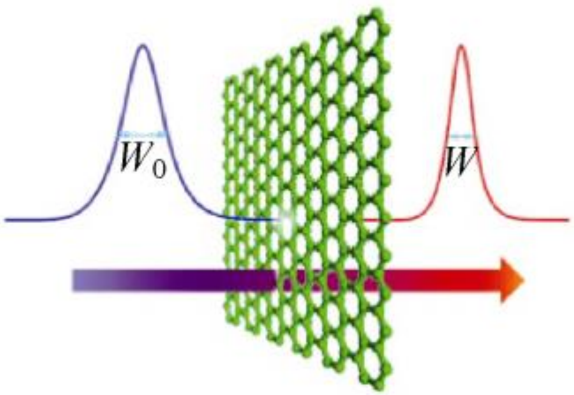
石墨烯与光相互作用特征

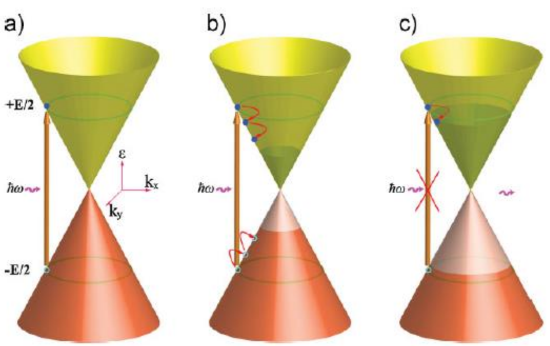
总结：掺杂石墨烯的典型光吸收谱





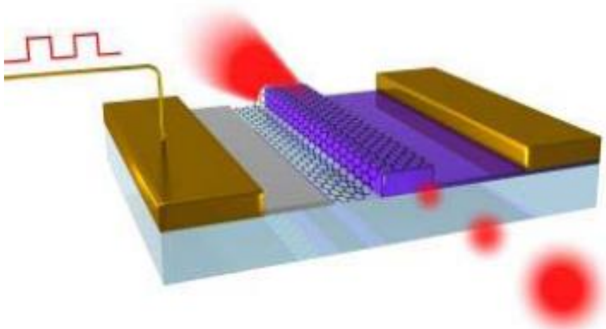
主要光电子器件

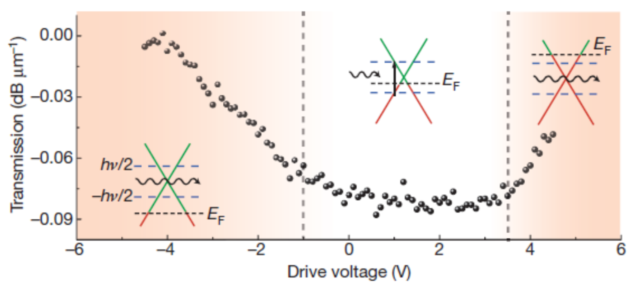




激光锁模

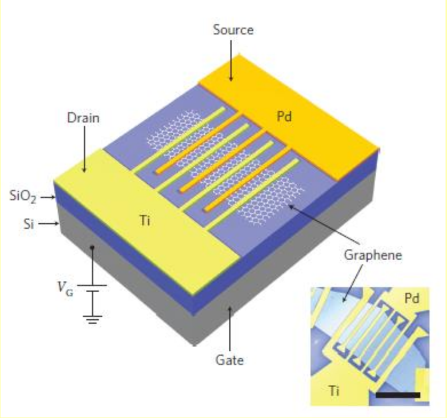
Adv Mater 19，(2009)

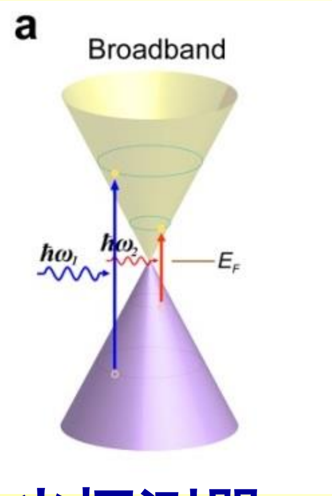




光调制器

Nature 474, (2011)

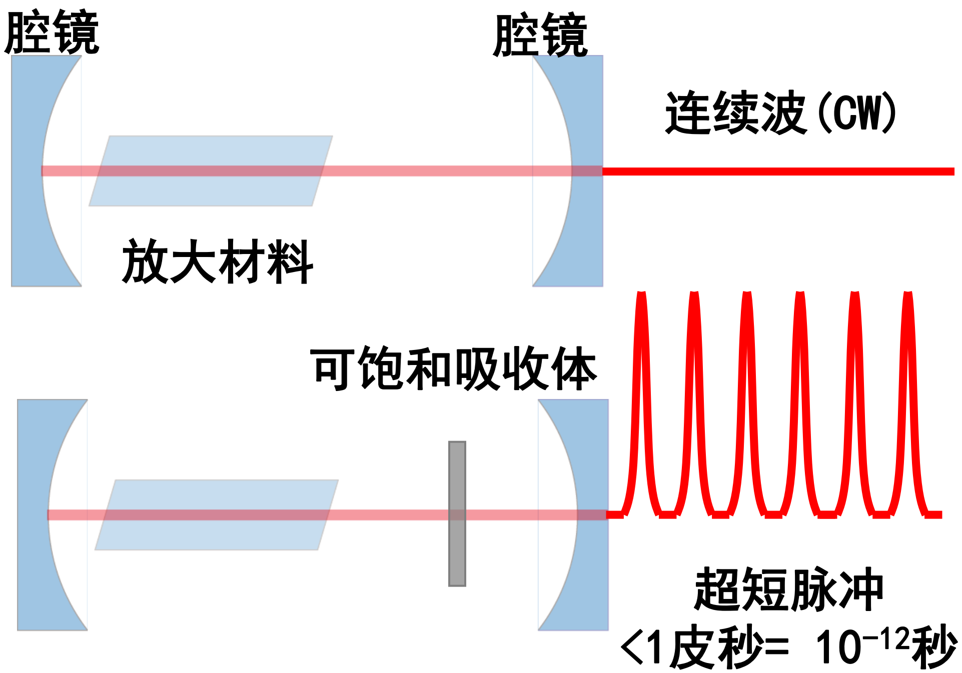




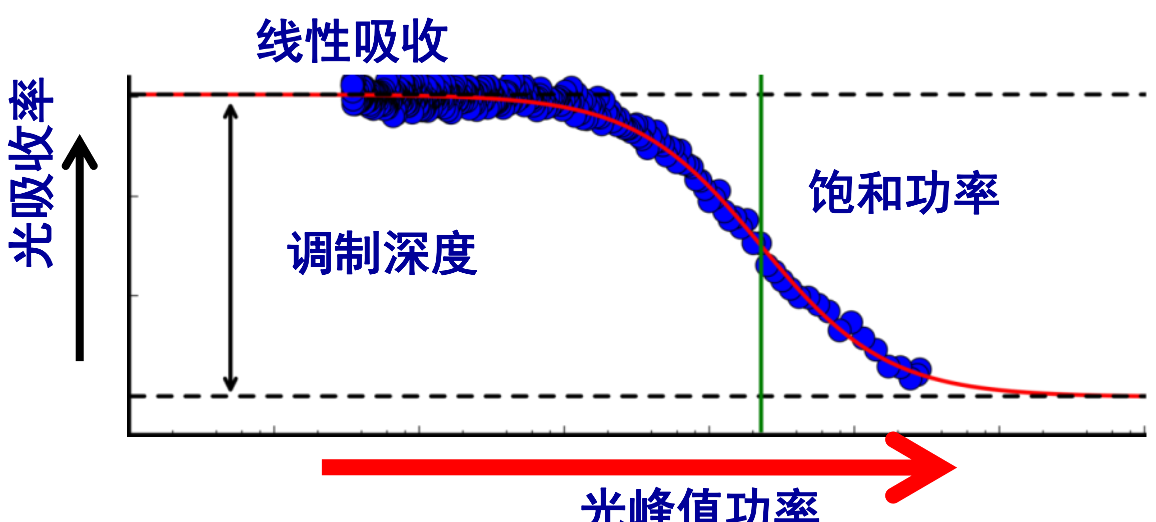
光探测器

Nat Photonics 4, (2010)

石墨烯的可饱和吸收与激光锁模



- ✓ 超短脉冲宽度
- ✓ 增强的峰值功率
- ✓ 频谱丰富

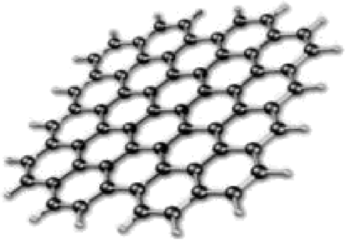


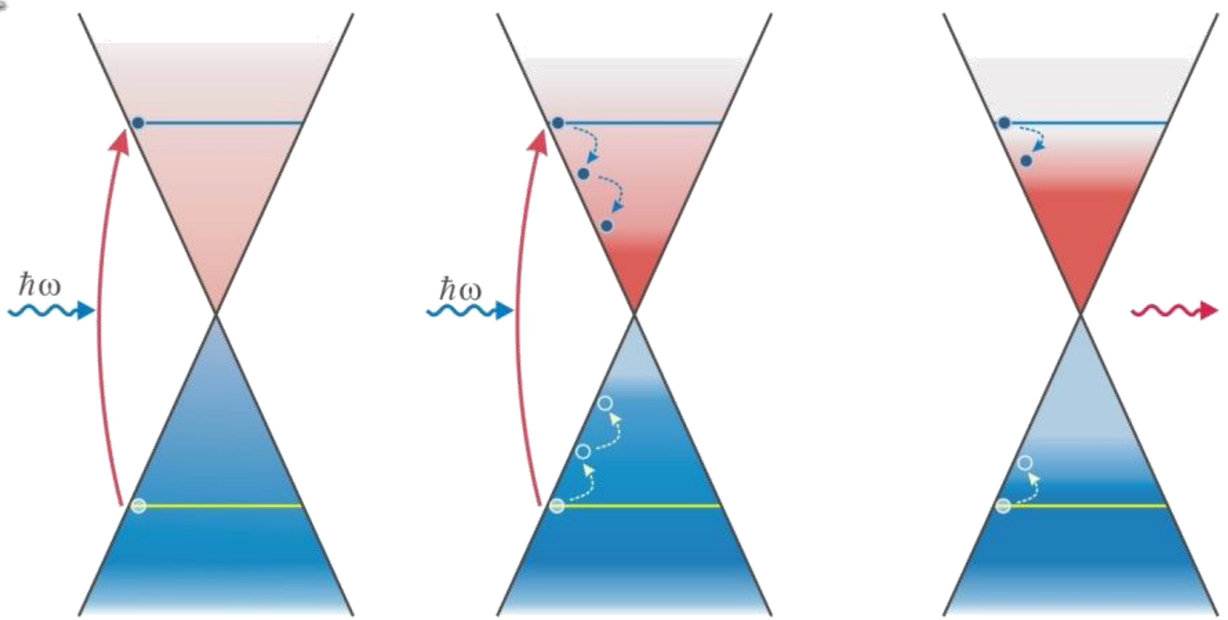
$$\alpha = \alpha_{ns} + \frac{\alpha_0}{1 + I / I_{sat}}$$

剩余吸收

石墨烯的可饱和吸收与激光锁模

石墨烯可饱和吸收机理





不断增加的入射光强
提高光生载流子浓度

载流子填充狄拉克点
附近导带价带电子态

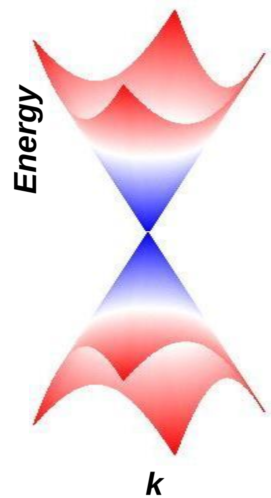
不断填满的电子态
阻塞进一步光吸收

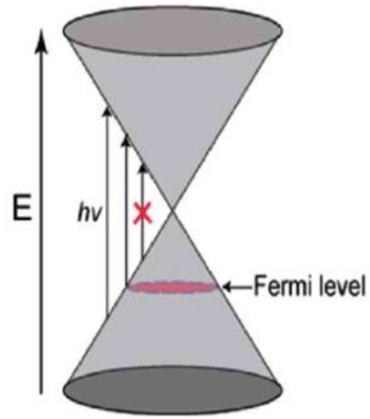
超快的恢复时间(Relaxation time)是否能够实现锁模？

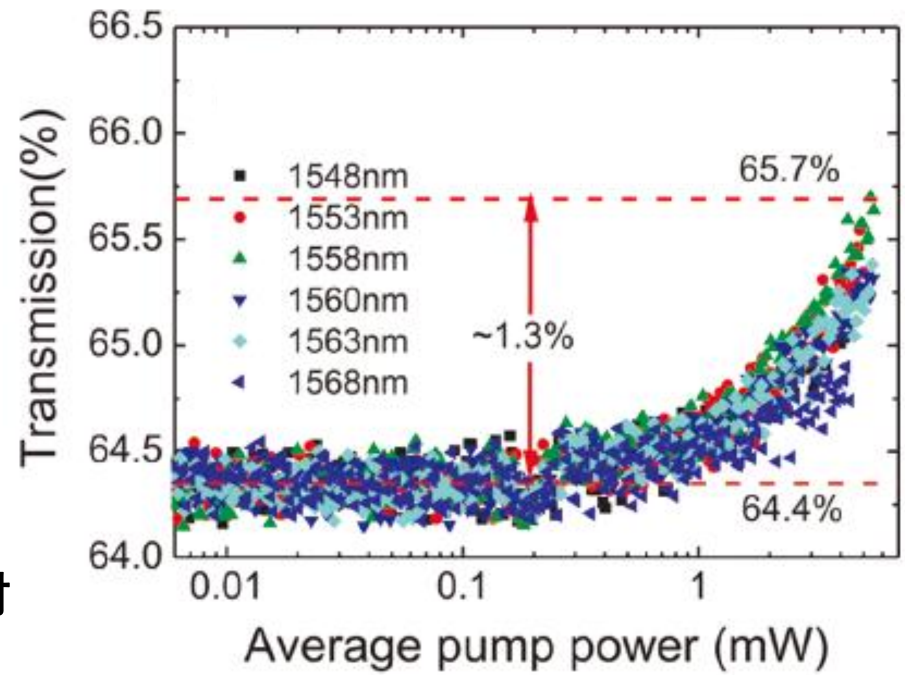
- 带内载流子热平衡时间是非常小的，可以非常有效的稳定锁模，以产生飞秒脉冲；
- 带间载流子复合时间则相对较长，可以发挥启动锁模的作用。

石墨烯的可饱和吸收与激光锁模

无需带隙工程的超宽带锁模体，UV-to-FIR



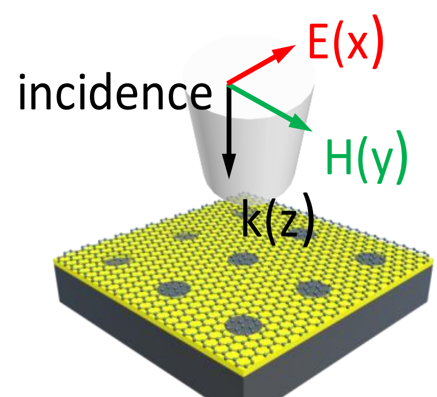




- ✓ 波长无选择性吸收
- ✓ 任何激发波长都能产生电子–空穴对
- ✓ 电子向导带跃迁产生泡利阻塞

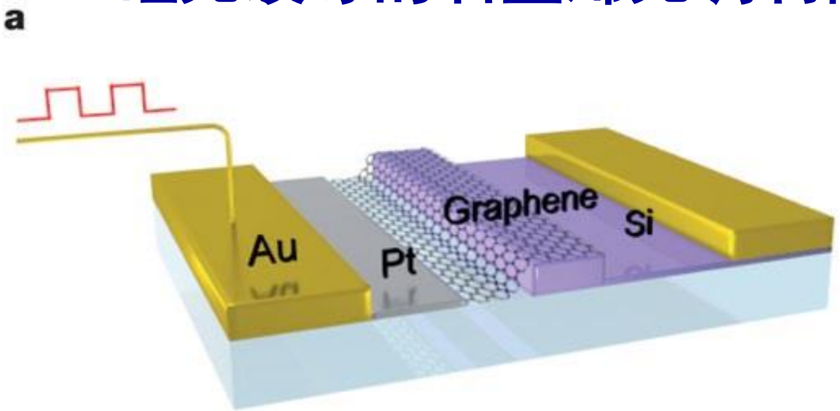
主要难点

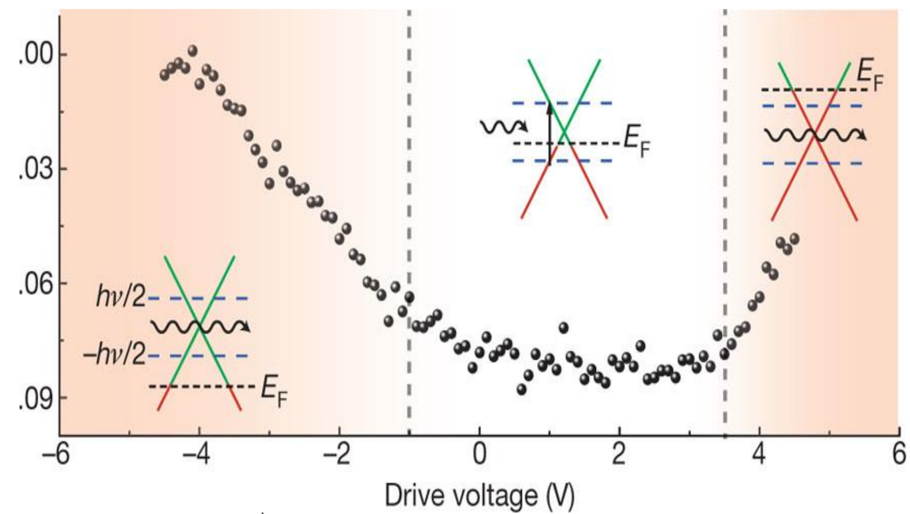
- ✓ 器件结构的精细表征
- ✓ 器件主要参数的独立调控
- ✓ 层数工程 layer engineering

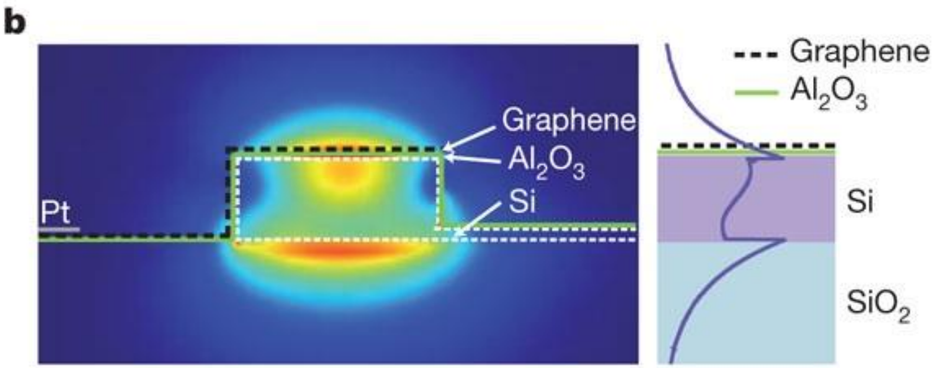


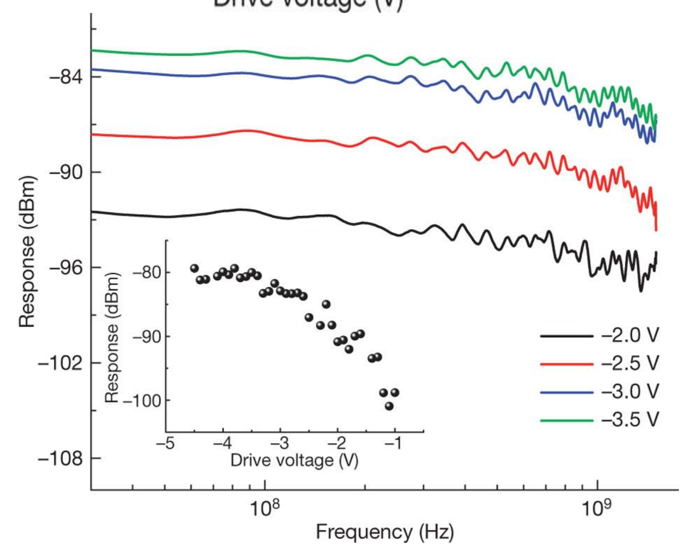
基于石墨烯的宽带光调制器

◆ 硅光波导的石墨烯光调制器







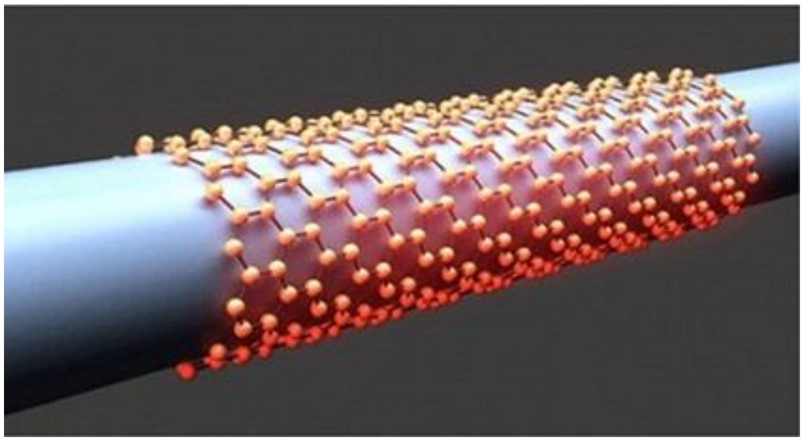


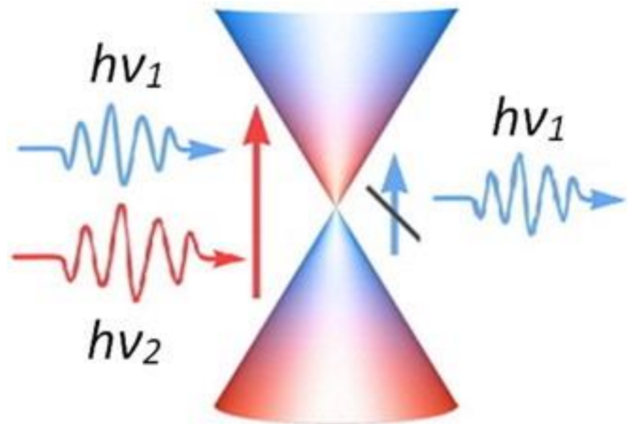
石墨烯下方的掺杂硅不仅作为光波导，也作为化学势的调整背栅。

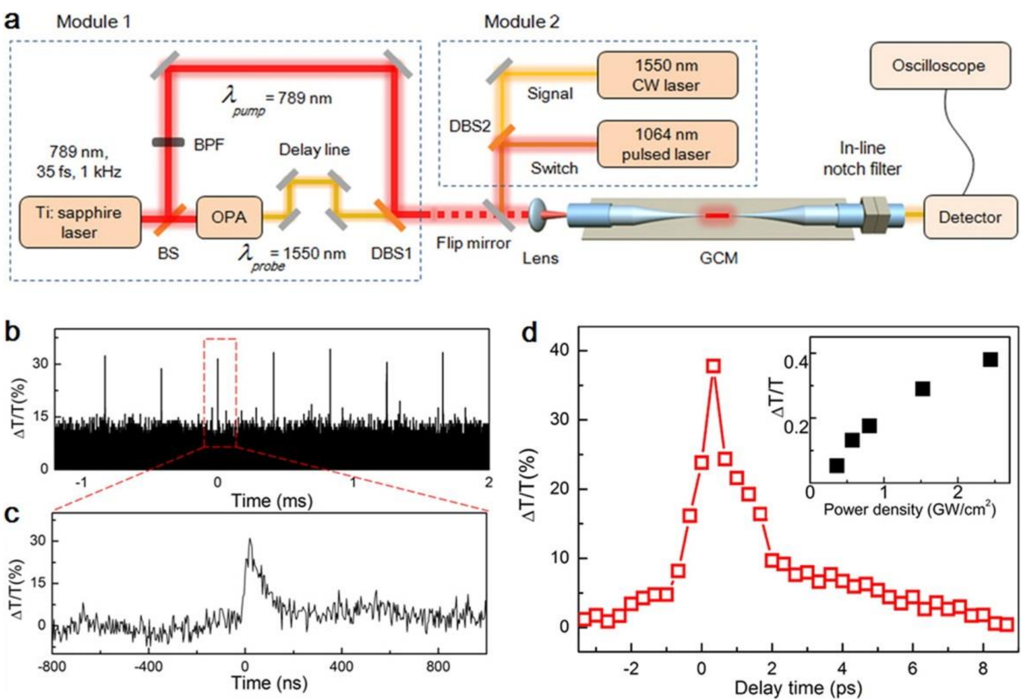
M.Liu, et al. Nature 474,(2011)

基于石墨烯的宽带光调制器

◆ 超快全光石墨烯调制器



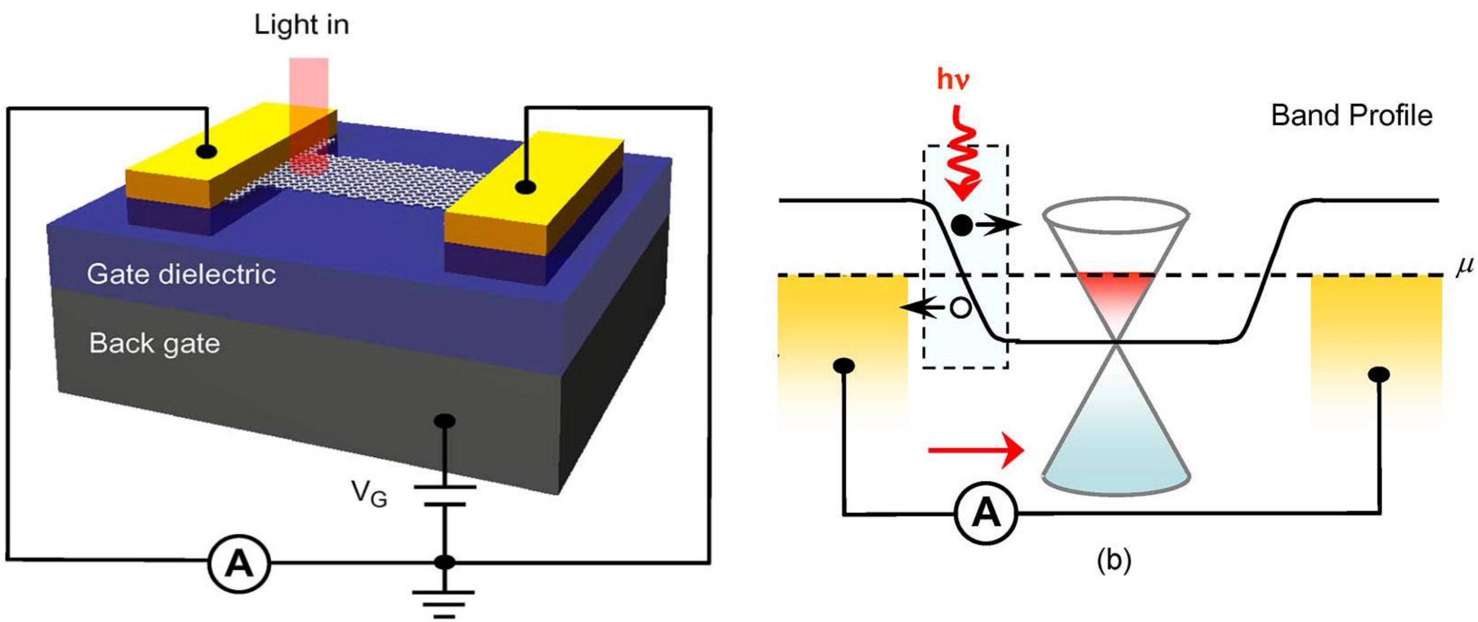




W.Li, et al. Nano Lett. 14,(2014)

基于石墨烯的光探测器

◆ 光电流结构的石墨烯光探测器

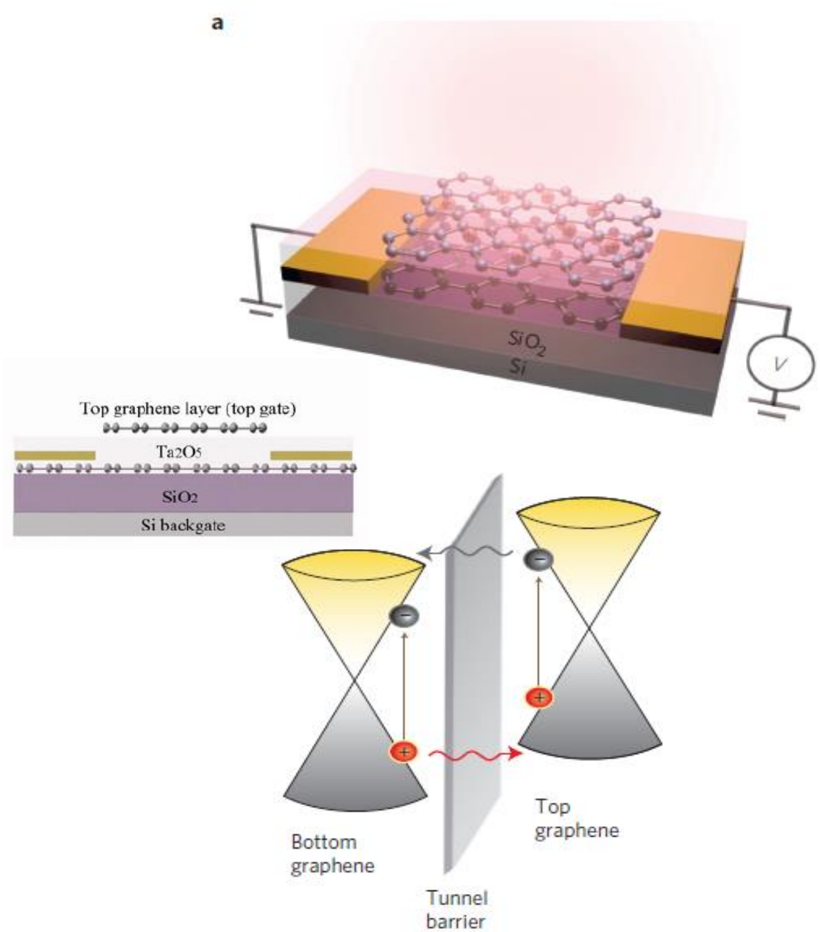


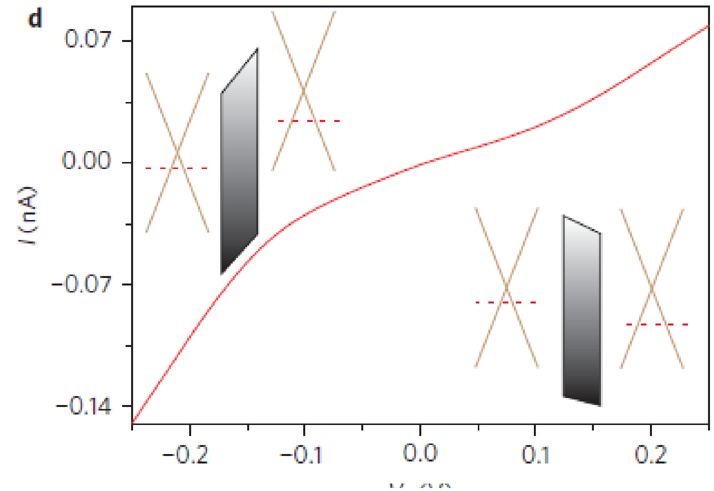
优势与发展方向：

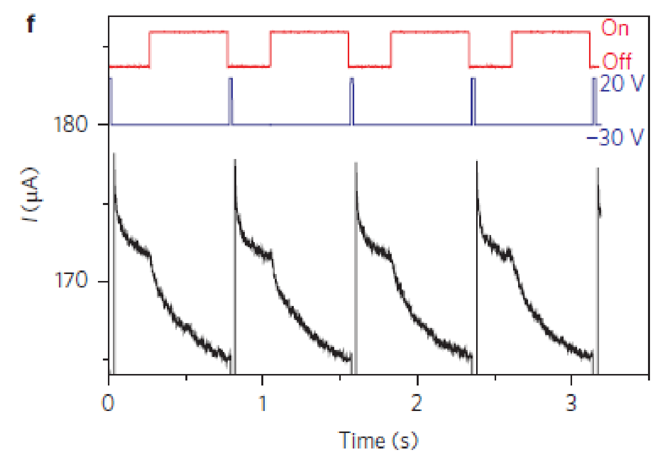
- 超宽带（紫外到太赫兹，石墨烯的零能隙、线性）
- 高速（载流子高迁移率）
- 高增益
- 器件/系统的集成

基于石墨烯的光探测器(超带宽)

◆ 超宽带、高响应光探测器







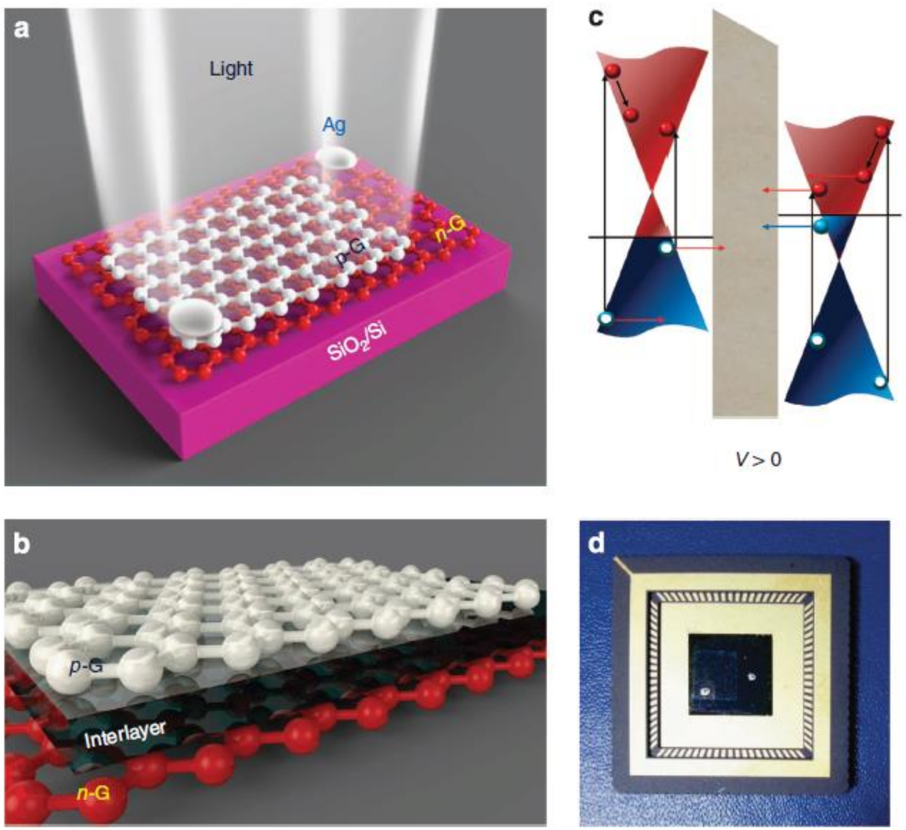
在光照下，光激发的在顶部石墨烯产生热载流子层隧道进入底部层，导致在栅极电荷积聚，在沟道形成强的光栅效果（ Photogating Effect）。

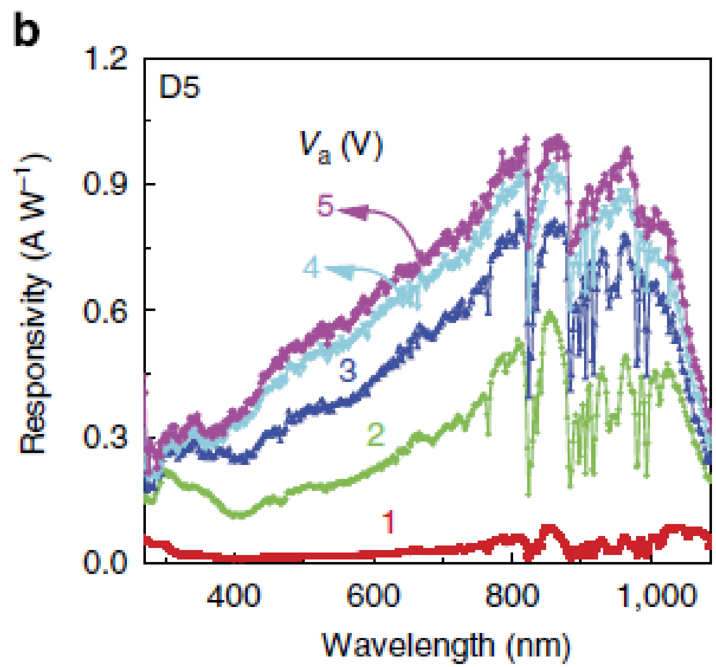
从可见光到中红外波段，光响应>1A/W

C.H..Liu, et al. Nature Nano.,(2014)

基于石墨烯的光探测器（超带宽）

- **High photoresponsivity in an all-graphene p–n vertical junction photodetector**



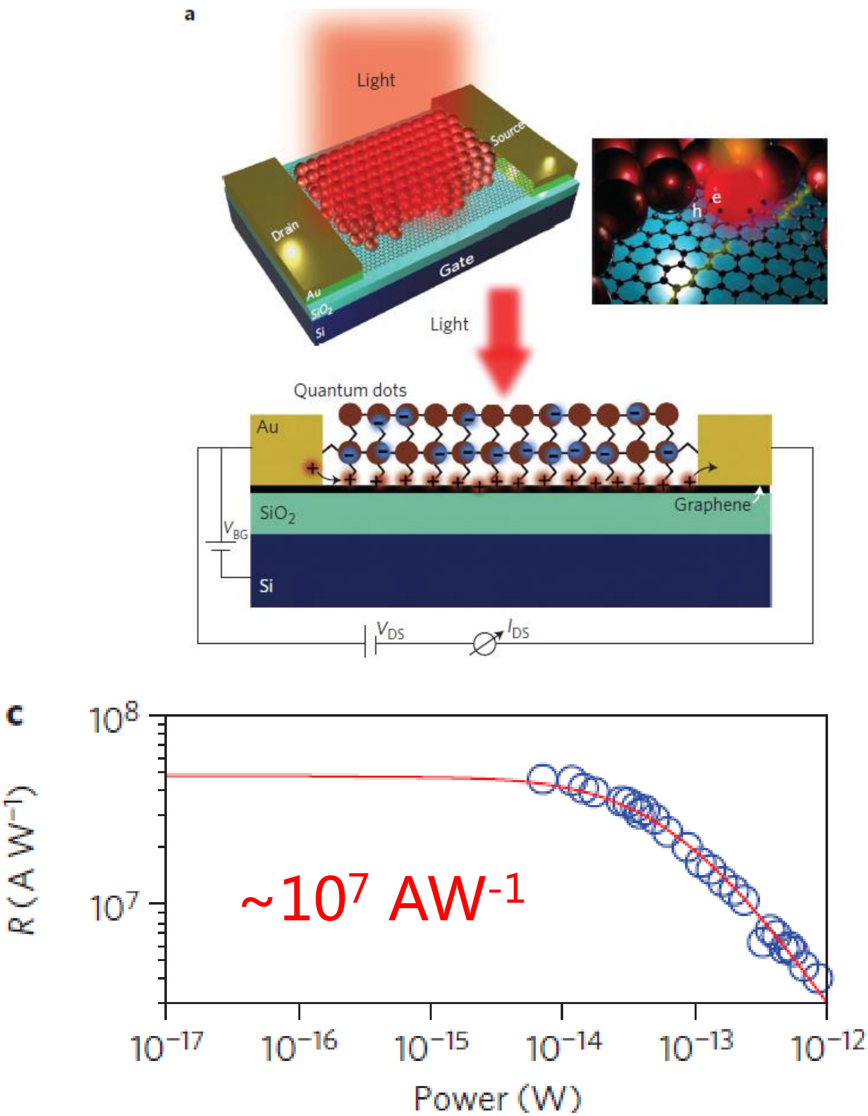


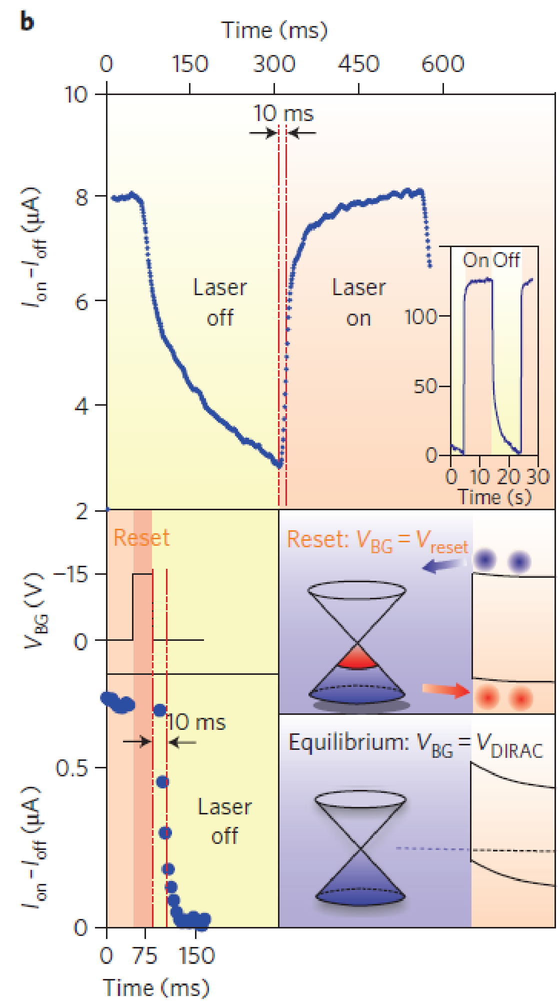
光响应:0.4-1.0A/W

C.O.Kim, et al. Nature comm.,(2014)

基于石墨烯的光探测器（高增益）

◆ 超高增益异质结构光探测器（PbS量子点桥键到石墨烯）

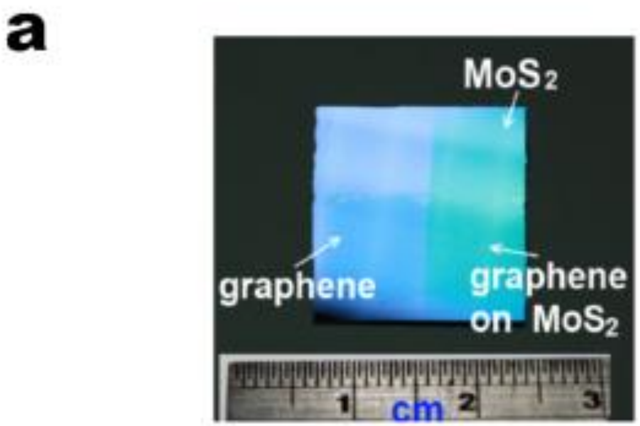


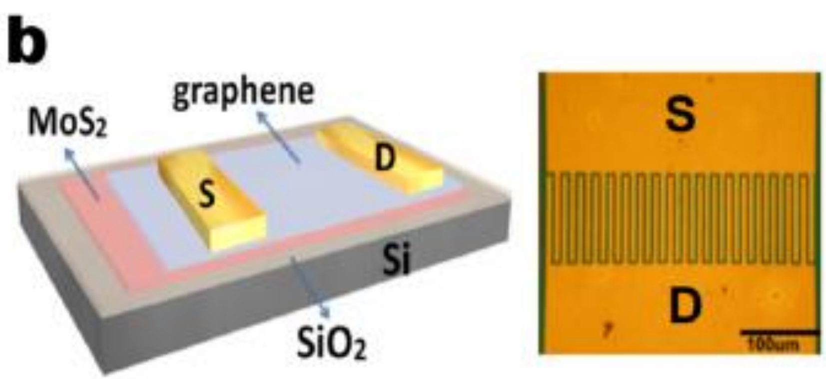


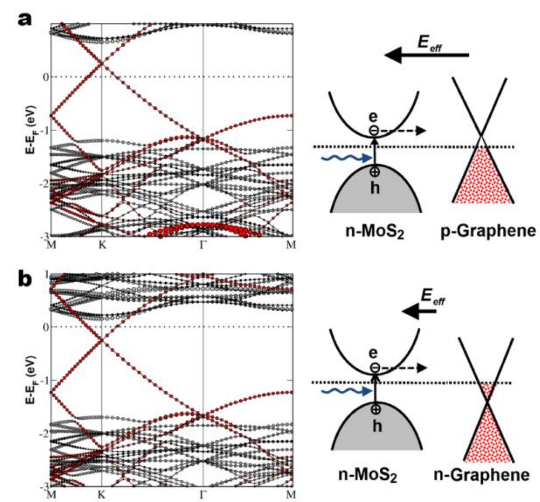
G. Konstantatos, et al. Nature nano (2012)

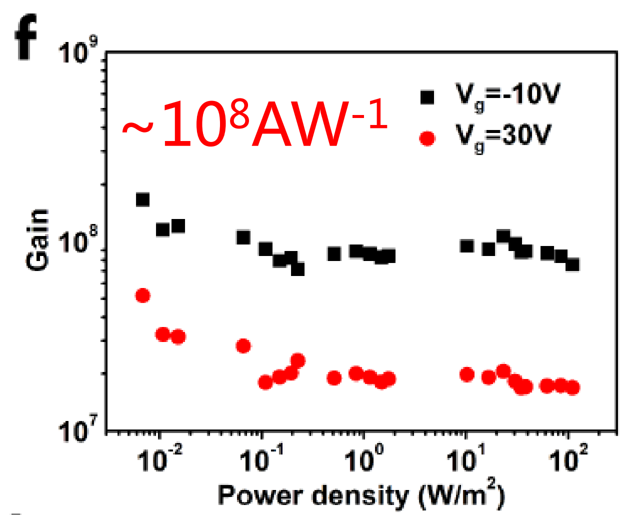
基于石墨烯的光探测器（高增益）

◆ **超高增益异质结构光探测器（MoS2耦合于石墨烯）**



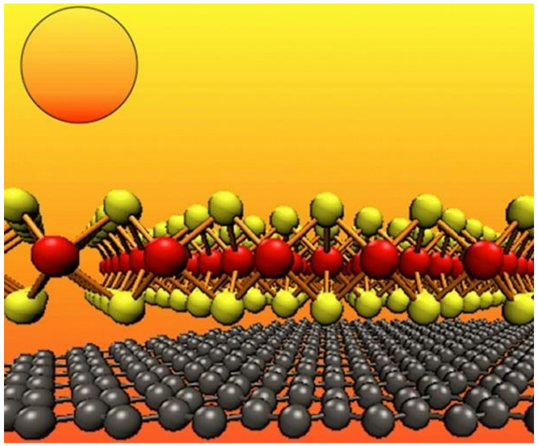




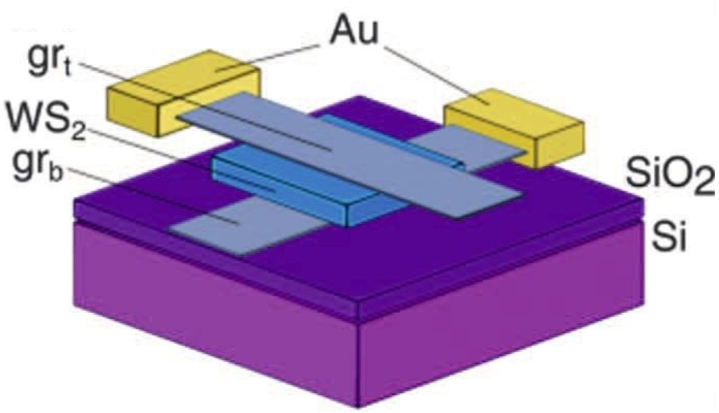


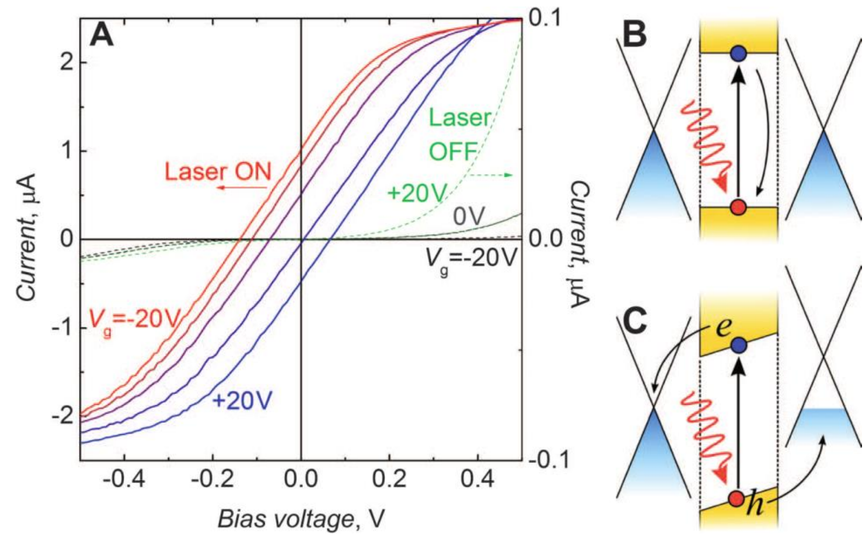
W.J.Zhang, et al. Sci.Rep. (2014)

基于石墨烯的光探测器（高增益）



material	thickness	efficiency	power density (kW/L)
GaAs	1 μm	~29%[38]	290
Si	35 μm	20.6%[39]	5.9
graphene/MoS_2	0.9 nm	0.1−1.0%	1000−10 000
WS_2/MoS_2	1.2 nm	0.4−1.5%	3000−12 000





30% EQE achieved due to enhanced light-matter interaction

Bernardi et al. Nano Lett (2013); Britnell et al. Science (2013)

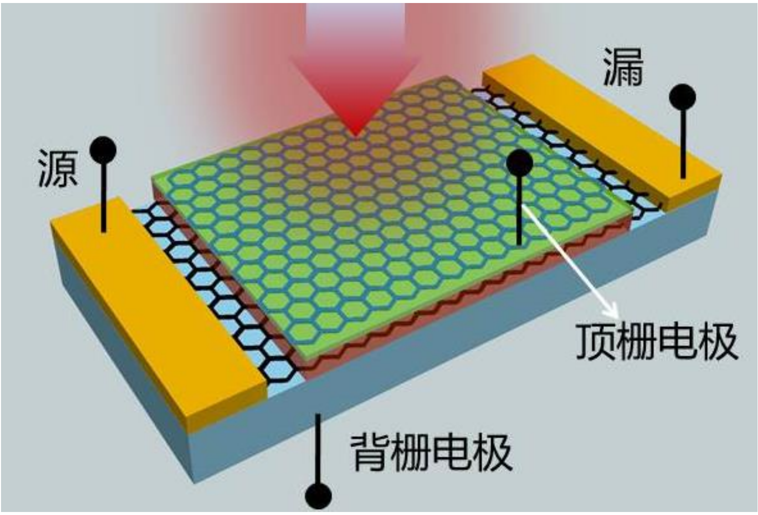
基于石墨烯的光探测器（高增益）

◆ 超高增益异质结构光探测器

石墨烯基异质结构的高增益光电探测器基本结构：

吸收层和增益层分离(SAM，Separate Absorption and Multiplication)

- ✓ 探测波段取决于作为吸收层半导体材料的光学性质
- ✓ 石墨烯的载流子高迁移率作为电流信号倍增
- ✓ 异质结构能带特征、载流子行为、电荷陷阱态和外电场调控等关键问题



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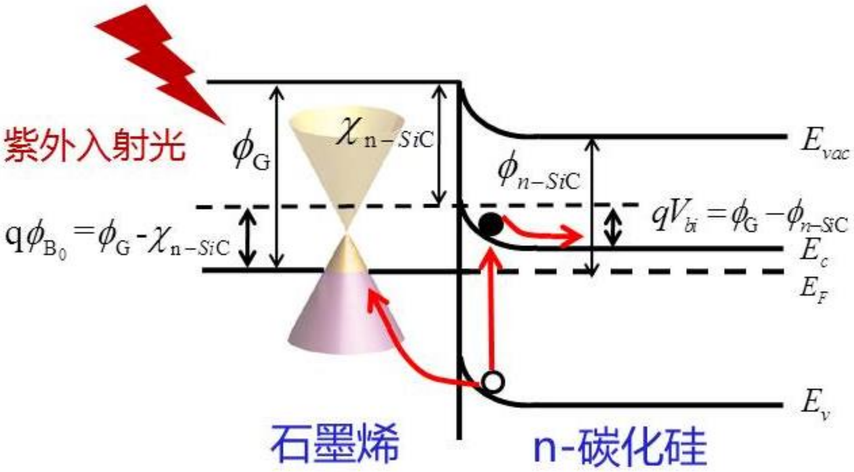


基于石墨烯的光探测器（硅基集成）

LETTERS
PUBLISHED ONLINE: 15 SEPTEMBER 2013 | DOI: 10.1038/NPHOTON.2013.240
nature photonics

CMOS-compatible graphene photodetector covering all optical communication bands

Andr
Thom

LETTERS
PUBLISHED ONLINE: 15 SEPTEMBER 2013 | DOI: 10.1038/NPHOTON.2013.241
nature photonics

High-responsivity graphene/silicon-heterostructure waveguide photodetectors

Xiaomu

nature photonics
LETTERS
PUBLISHED ONLINE: 15 SEPTEMBER 2013 | DOI: 10.1038/NPHOTON.2013.253

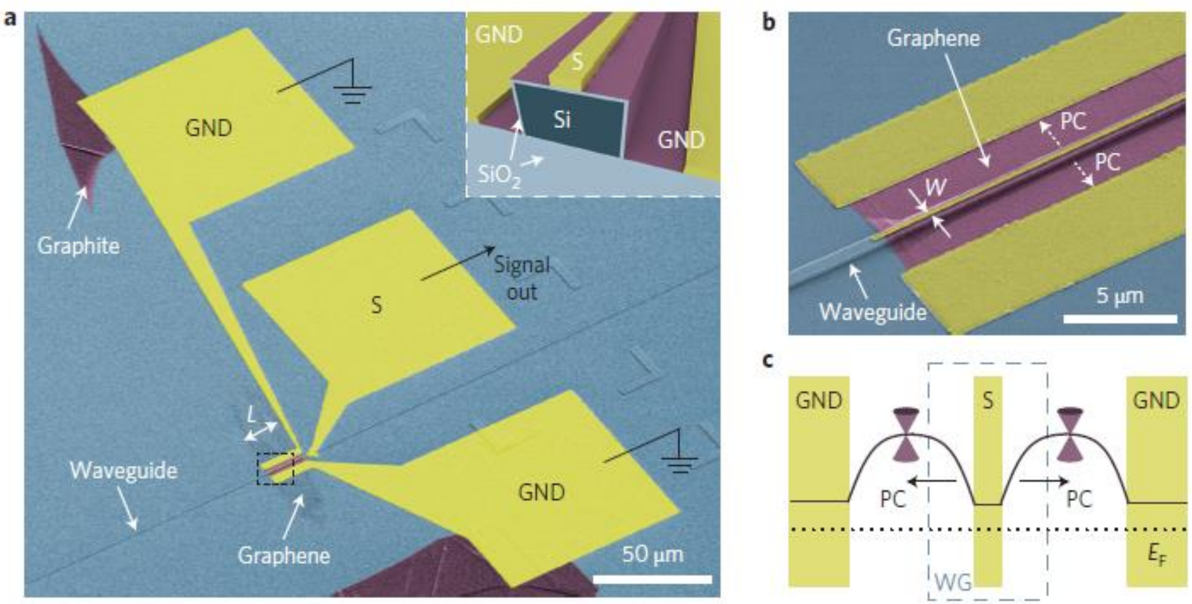
Chip-integrated ultrafast graphene photodetector with high responsivity

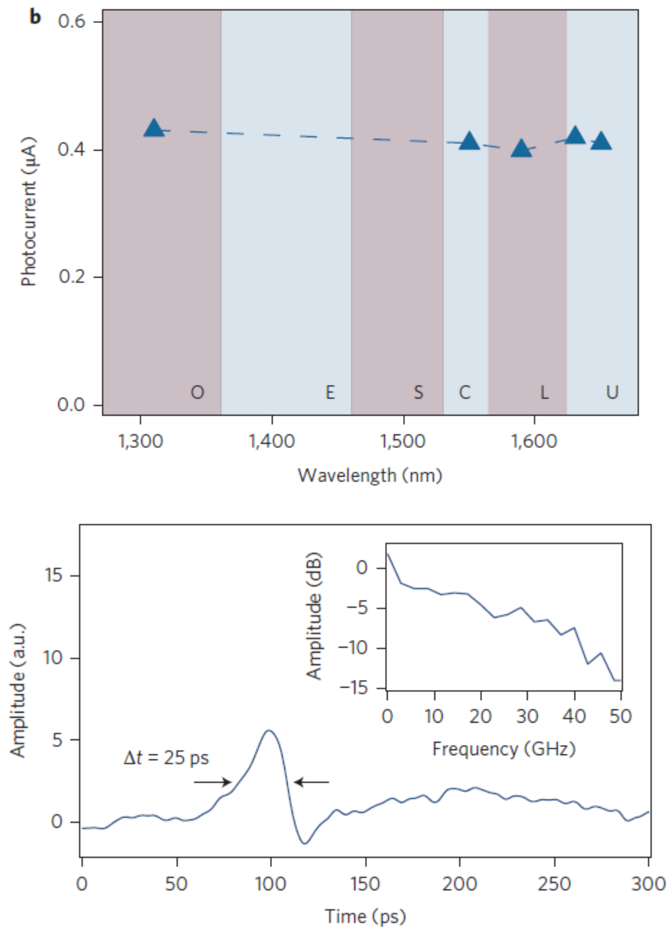
Xuetao Gan[1†], Ren-Jye Shiue[2†], Yuanda Gao[3], Inanc Meric[1], Tony F. Heinz[1,4], Kenneth Shepard[1], James Hone[3], Solomon Assefa[5] and Dirk Englund[1,2]*

2013年，Nature Photonics在同一期中报道了三篇基于硅基集成的超快宽光谱石墨烯红外光波段探测器。

基于石墨烯的光探测器（硅基集成）

Chip-integrated ultrafast graphene photodetector with high responsivity



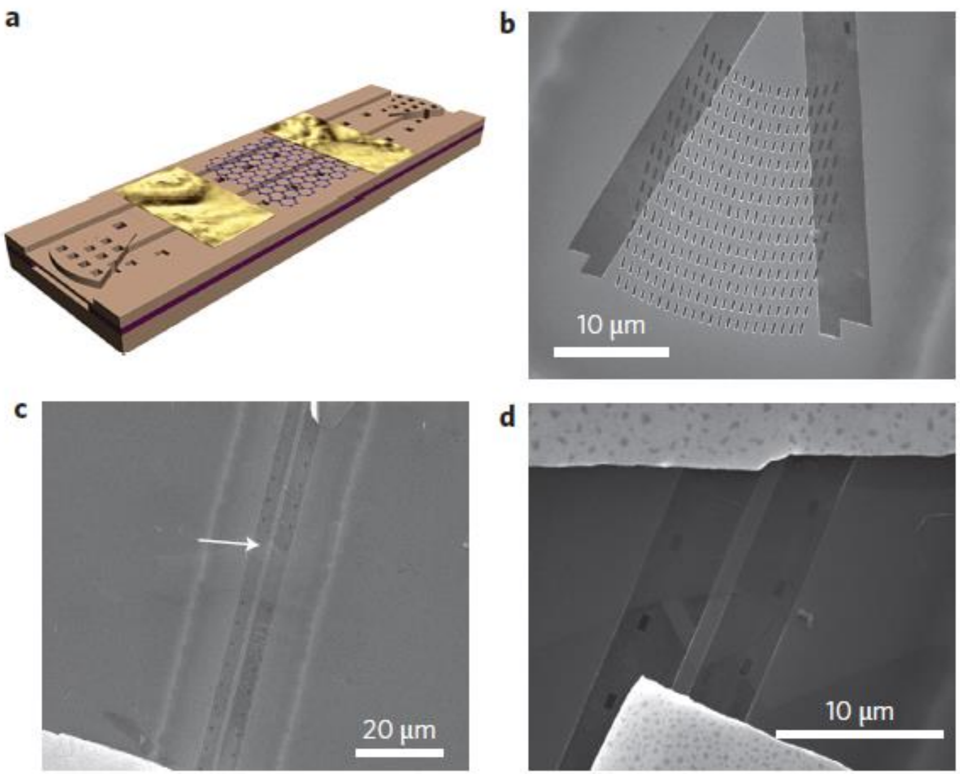


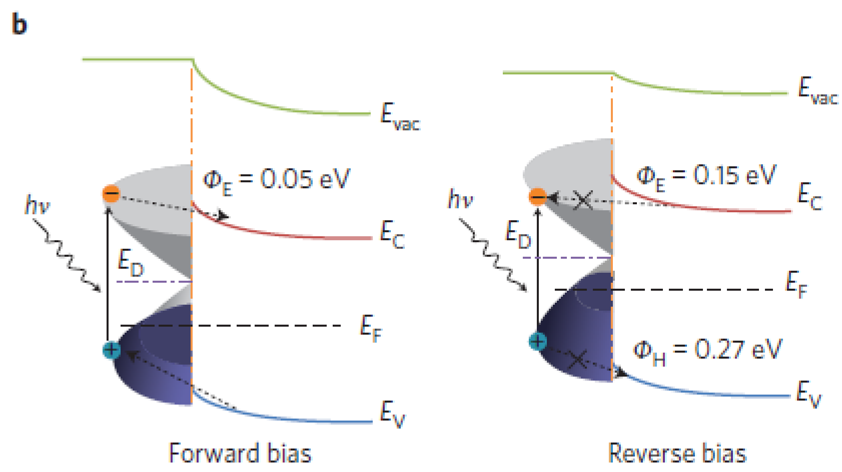
光纤通讯频段，> 20GHz

Gan, X. *et al*. Nature Photon. 7,883 (2013).

基于石墨烯的光探测器（硅基集成）

High-responsivity graphene/silicon-heterostructure waveguide photodetectors



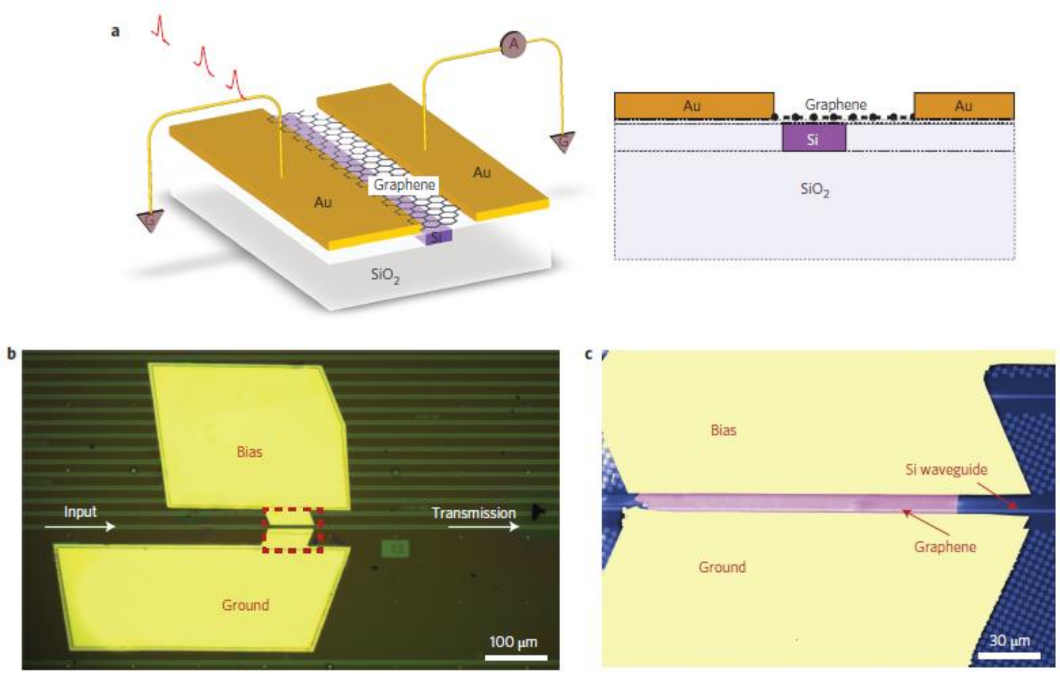


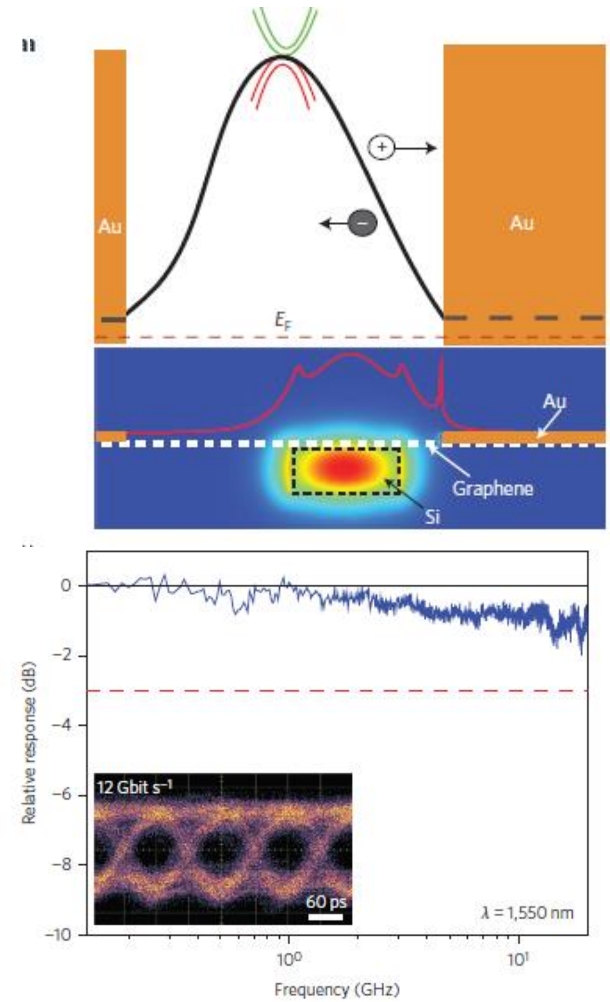
探测波段：1.2~8um

Wang, X. *et al.* Nature Photon. 7,888 (2013).

基于石墨烯的光探测器（硅基集成）

CMOS-compatible graphene photodetector covering all optical communication bands





光纤通讯， >20GHz， 0.1A/W

二维原子晶体光发射器件

news & views

OPTOELECTRONIC DEVICES

Monolayer diodes light up

p–n diodes can be fabricated from a single layer of WSe_2 crystal.

Rudolf Bratschitsch

Seventy-five years ago, Russell Ohl of Bell Labs in the US accidentally discovered the p–n junction whilst trying to purify silicon crystals[1]. Today, p–n junctions are essential elements in several devices including diodes and solar cells. Such junctions are boundaries between two regions of a semiconductor — termed p (positive) and n (negative) — that have different levels of impurity atoms. Recently, atomically thin transition-metal dichalcogenides, such as MoS_2, $MoSe_2$, WS_2 and WSe_2, have attracted considerable interest because of their promising electrical and optical properties[2]. These two-dimensional materials are similar to graphene, but differ in one important aspect — they are direct-gap semiconductors. Up to now, MoS_2 was the most studied transition-metal dichalcogenide, but it has proven difficult to obtain hole conduction in this monolayer material[3], hindering fabrication of an atomically thin p–n junction. Writing in *Nature Nanotechnology*, three independent research teams now show that a monolayer

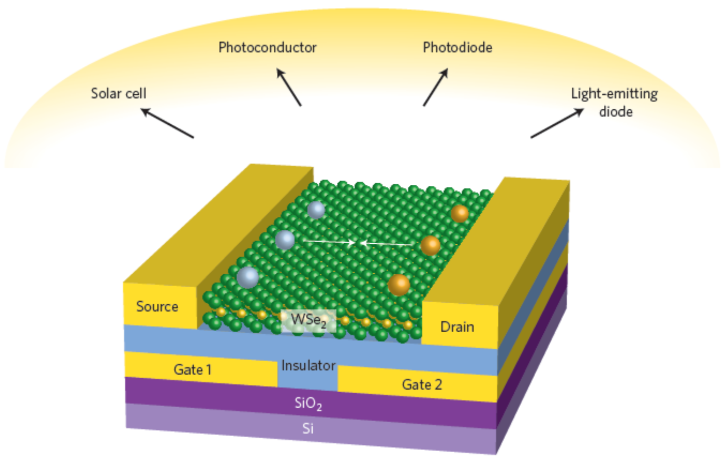


Figure 1 | Schematic drawing of a lateral monolayer WSe_2 p–n diode with split-gate electrodes. The metal back gates are separated from the WSe_2 monolayer by an insulator, which can be SiN, HfO_2 or BN. Blue and orange spheres represent electrons and holes, respectively.

今年4月，Nature Nanotechonlogy在同一期中报道了三篇二维原子晶体材料的PN结光发射器件。

二维原子晶体光发射器件

nature nanotechnology

LETTERS

PUBLISHED ONLINE: 9 MARCH 2014 | DOI: 10.1038/NNANO.2014.14

Solar-energy conversion and light emission in an atomic monolayer p–n diode

Andreas

LETTERS

PUBLISHED ONLINE: 9 MARCH 2014 | DOI: 10.1038/NNANO.2014.25

nature nanotechnology

Optoelectronic devices based on electrically tunable p–n diodes in a monolayer dichalcogenide

Britton

LETTERS

PUBLISHED ONLINE: 9 MARCH 2014 | DOI: 10.1038/NNANO.2014.26

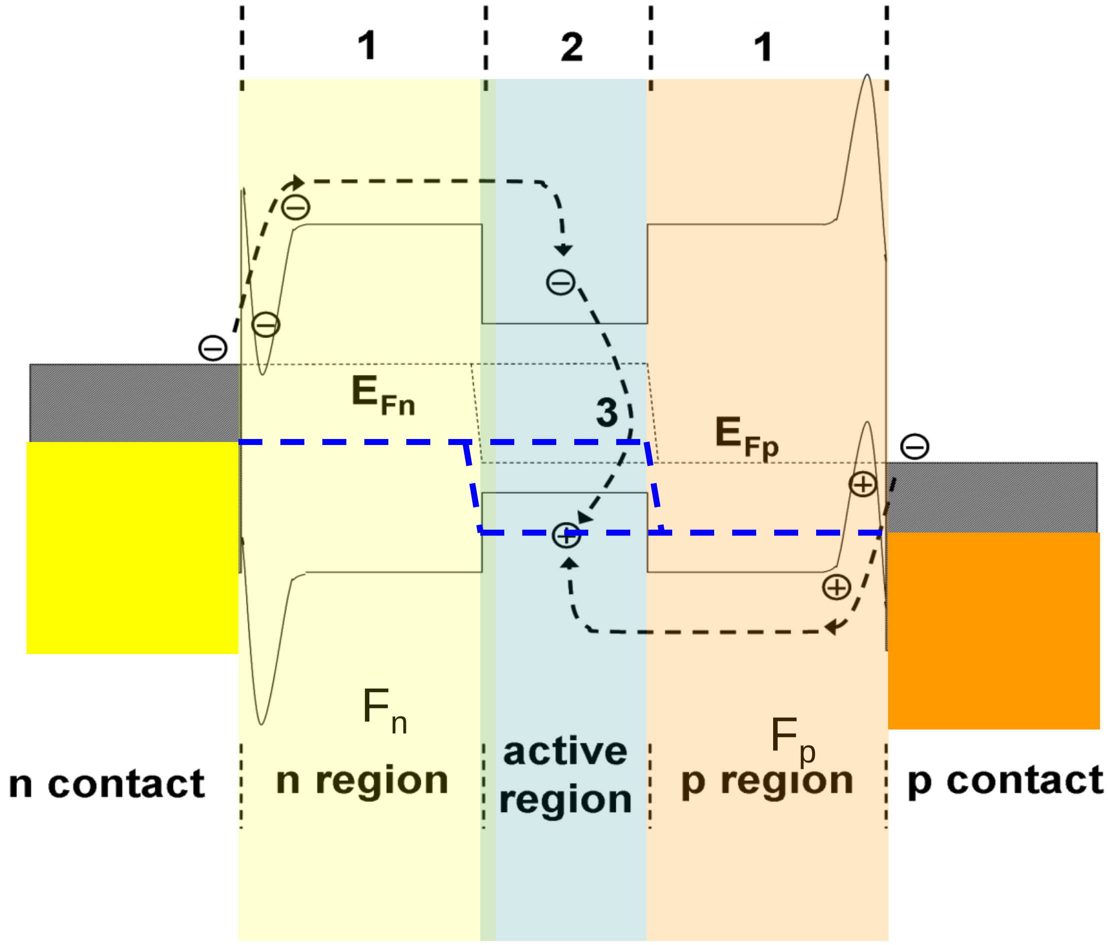
nature nanotechnology

Electrically tunable excitonic light-emitting diodes based on monolayer WSe_2 p–n junctions

Jason S. Ross[1], Philip Klement[2,3], Aaron M. Jones[3], Nirmal J. Ghimire[4,5], Jiaqiang Yan[5,6], D. G. Mandrus[4,5,6], Takashi Taniguchi[7], Kenji Watanabe[7], Kenji Kitamura[7], Wang Yao[8], David H. Cobden[2] and Xiaodong Xu[1,2]*

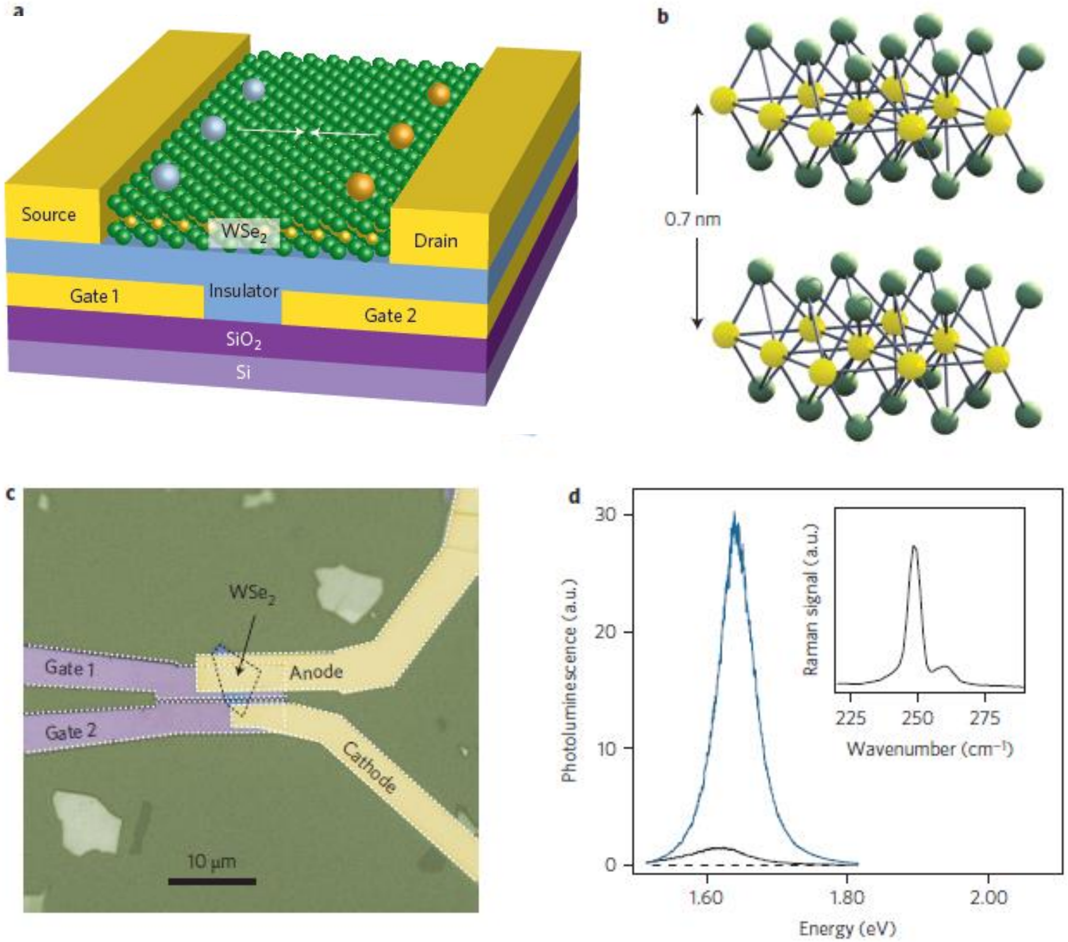
二维原子晶体光发射器件

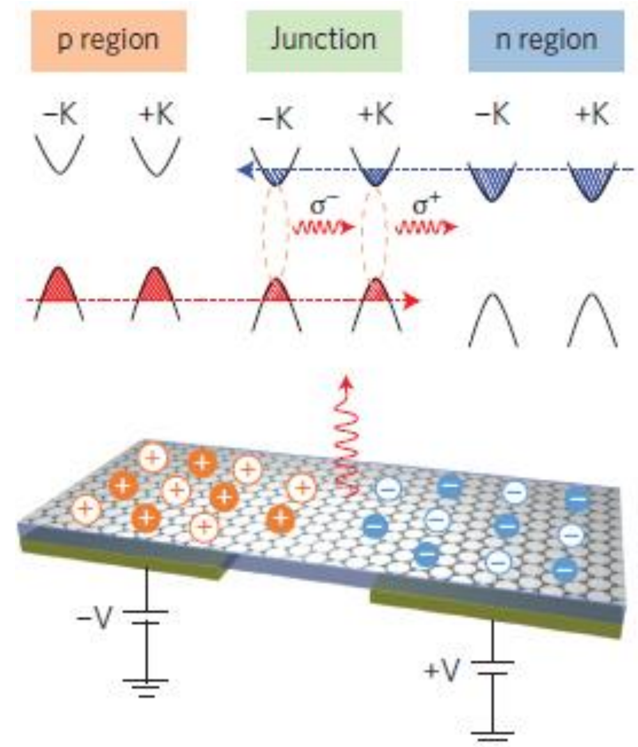
半导体光发射器件基本能带结构



二维原子晶体光发射器件

Optoelectronic devices based on electrically tunable p–n diodes in a monolayer dichalcogenide

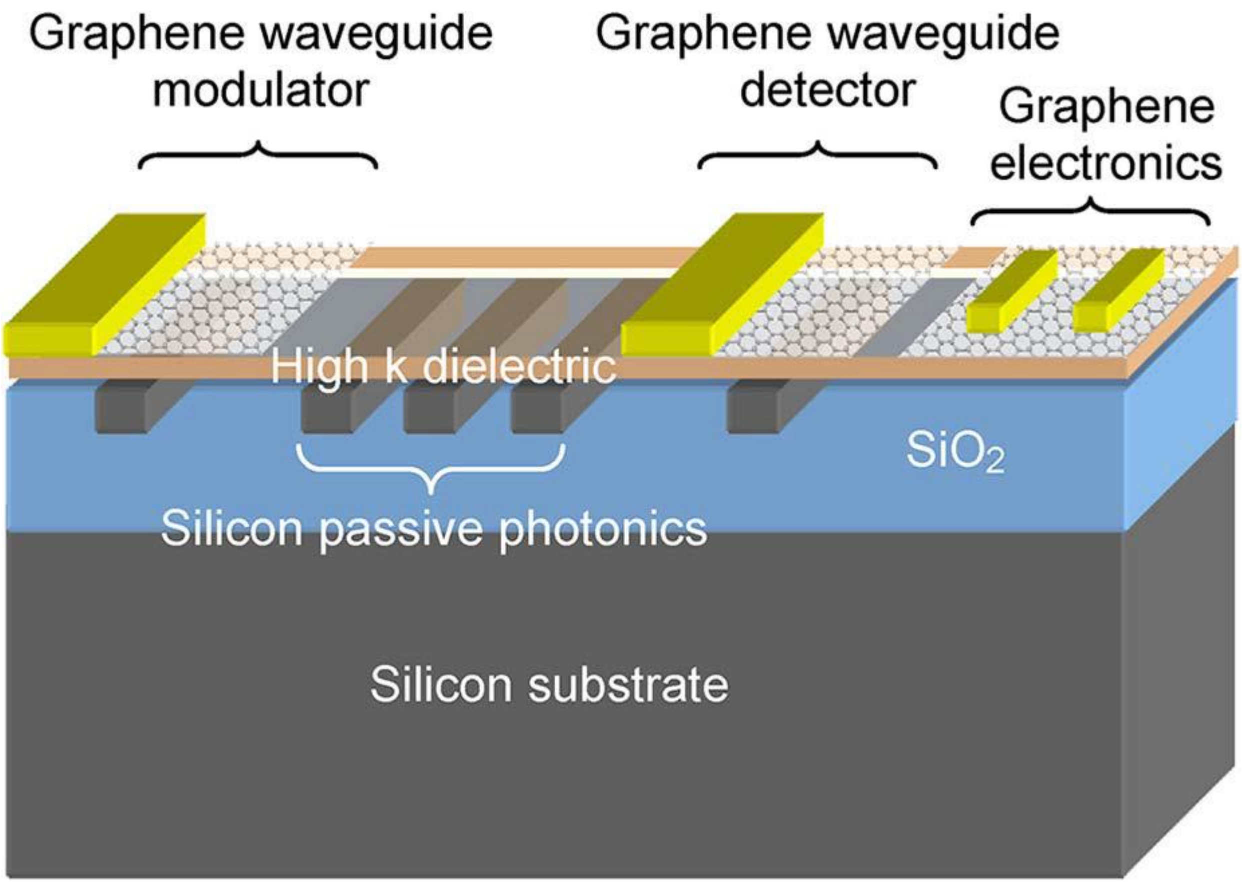




载流子复合过程

基于分裂栅电极的单层WSe_2的p-n结发光器件

展 望



未来的硅基集成的石墨烯光子/电子电路设想：

石墨烯调制器，检测器，硅无源光子学，和石墨烯电子器件。

展 望

十年前，石墨烯被K.S.Novoselov与A.K.Geim成功分离，以其为代表的二维原子晶体立即得到了科学界的极大重视和广泛研究。今天，在研究制备高质量的各类二维原子晶体材料的同时，更关注于其应用。

- 2D materials are promising system for optoelectronic applications.
- Graphene based hybrid is believed to improve its optoelectronic performance.
- The interactions between the materials in hybrid structures are important and deserved detail investigation.

谢谢大家!