Electronic and Transport properties of 2D Semiconductors

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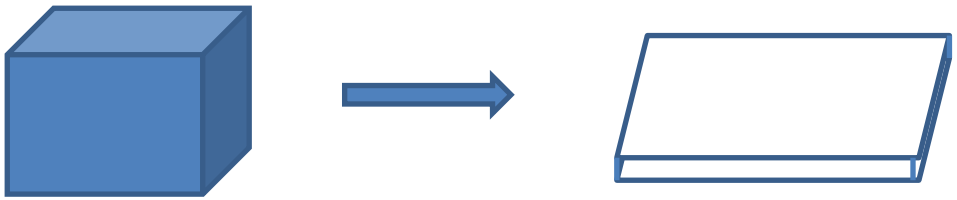
Outline

- Introduction
- Overview of new 2D materials
- Electronic properties
- Transport properties
- Conclusion

Introduction

- **What are 2D materials?**
- **How to define 2D materials?**

→ One dimension in the nanometer range?



→ GaAs or Si (~100nm)

- Properties of Metals (Al, Au, Ag) for different thickness → significant qualitative changes (considered as different dimensions) – few monolayers (10 Å)
- Liquid helium – 3 monolayer considered as a 2D system because we find significant physical properties (unexpected phenomena or novel features)

Introduction

- **The properties of a materials are identified by a specific length scale.**

→We can consider electronically confined in one direction if the confinement length is smaller than or comparable to the length scale we consider.

→ Conventional (or physical) length scale: smaller than the exciton Bohr radius (exciton=electron-hole bound state)

$$a_B^* = \frac{\epsilon \hbar^2}{me^2} = \frac{\varepsilon}{m} a_B$$

Si: $a_B^* = 30$ Å, GaAs: $a_B^* \sim 100$ Å

Metals: $a_B^* \sim 1$ Å

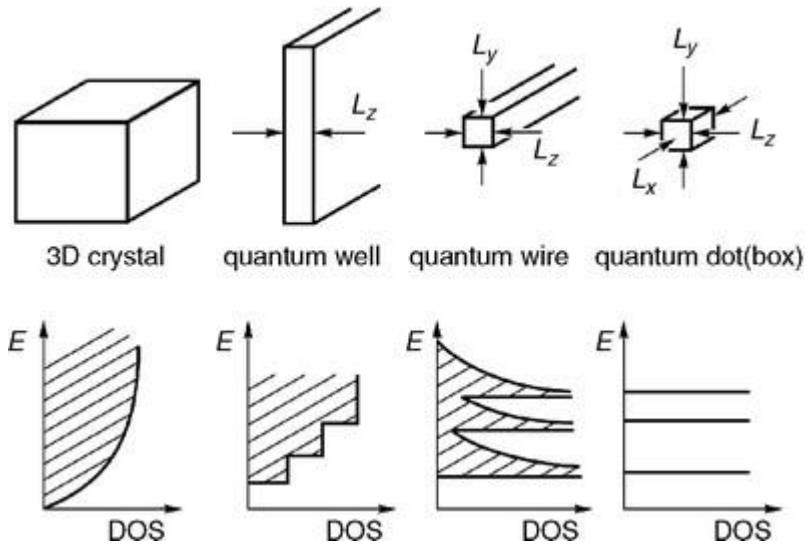
Introduction

- Quasi-2D systems: depending on our interest
- → various length scales: scattering length, mean free path, Fermi wavelength, thermal mean free path, screening length …
- → energy scale: thermal energy $k_B T$, subband energy: $\frac{\hbar^2}{2m}\left(\frac{\pi}{d}\right)^2$
- → In semiconductor Quasi-2D systems: large length, energy scale
- → As the same reason, thin metals (Au, Ag, Al foils) are not 2D materials.

Introduction

Why 2D materials are important?

- Parameters (density) can be tuned.
- **Their properties can be modified by external gate voltage.**
- Density of states are enhanced.
- → many physical properties are proportional to the density of states (e.g., scattering times, absorption (band-band transition), …)



Introduction

Why 2D materials are important?

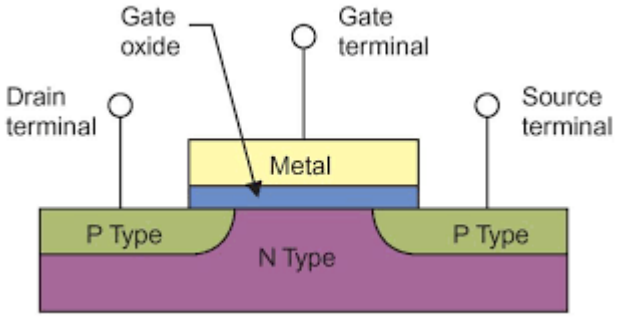
- Science – novel physics

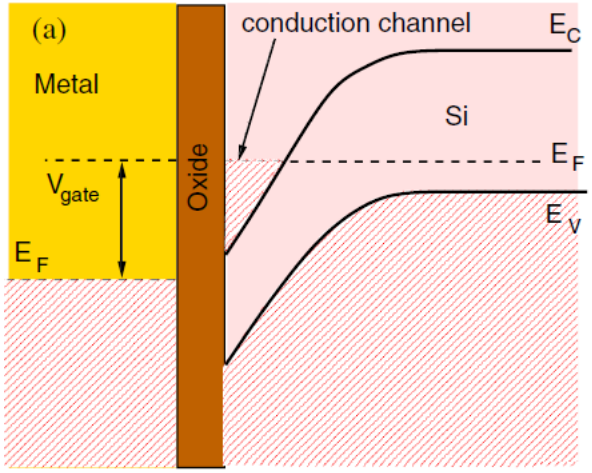
  - Novel physical phenomena, QHE, FQHE, which leads to the Nobel prize

- Engineering – multifunctional devices, overcome scaling limit
- they can be combined with different 2D materials.

Introduction

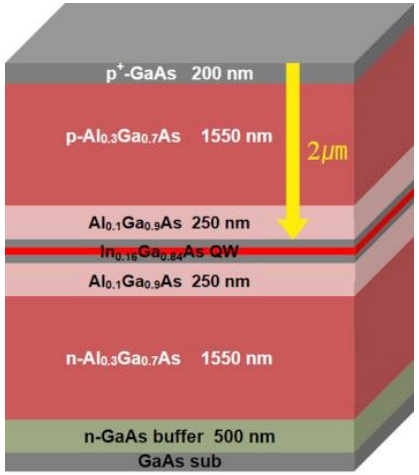
- First 2D systems – Si-MOSFET, Kahng and Atalla (1960)
- MOSFET (metal–oxide–semiconductor field-effect transistor): insulating layer + semiconductor + metallic gate electrode

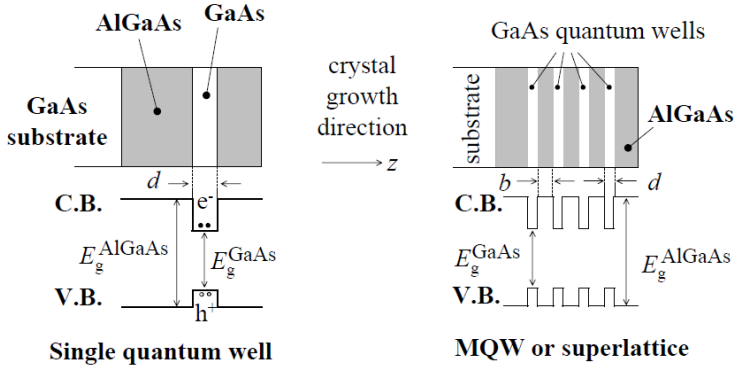




Introduction

- Semiconductor superlattice is also considered as a 2D system. GaAs : $a_B^* \sim 100$ Å
- Superlattices: narrow-bandgap semiconductor (GaAs)+wide-bandgap semiconductor (AlGaAs).
- quantum well: A thin layer of GaAs between two layers of AlGaAs creates a potential well for an electron, where its motion is restricted.





Introduction

- Quasi-2D systems based on semiconductors have limitations arising from length scale (e.g., low temperature).

→Need real 2D systems

→Atomically thin 2D materials (the actual confinement length in z-direction is smaller than all other physical length.

2D materials

- Why realizing 2D materials is difficult?

→Thermodynamically unstable

- There are many layered materials with strong in-plane chemical bonds and weak coupling between the layers. These layered structures provide the opportunity to be cleaved into individual freestanding atomic layers. These layers with one dimension strictly restricted to a single layer are called two-dimensional (2D) material.

2D materials

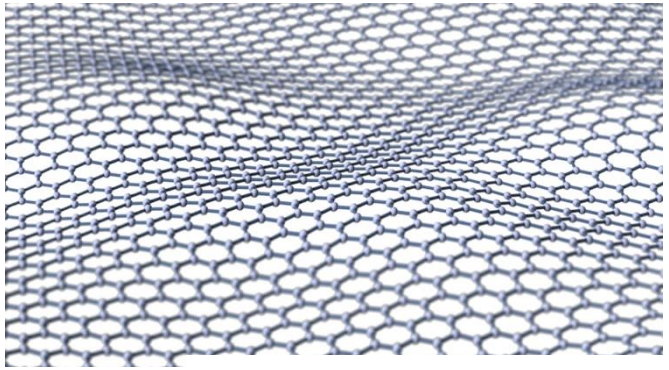
- Stable single layer graphene (2004)
- Why it is stable?
- Emerged during the last decade as one of the most active research topics
- Recently, research has been expanded to other layered van der Waals materials.

2D materials

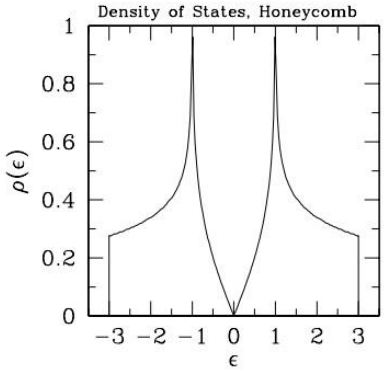
- Properties of 2D materials are usually very different from their 3D counterparts.
- Offer a huge flexibility in tuning of their electronic properties.
- Band gap engineering can be done by changing the number of layers.
- Heterostructures of 2D materials offer not only a way to study novel phenomena, but open unprecedented possibilities of combining them for technological use.

2D materials

Graphene



- The most well-known 2D material:
- First 2D material studied in detail.
- Long history, realized experimentally by the works of Novoselov & Geim in 2004.
- High mobilities (>100 000 cm2/Vs @ 300K) raised expectations regarding electronic applications (possible successor of Si).

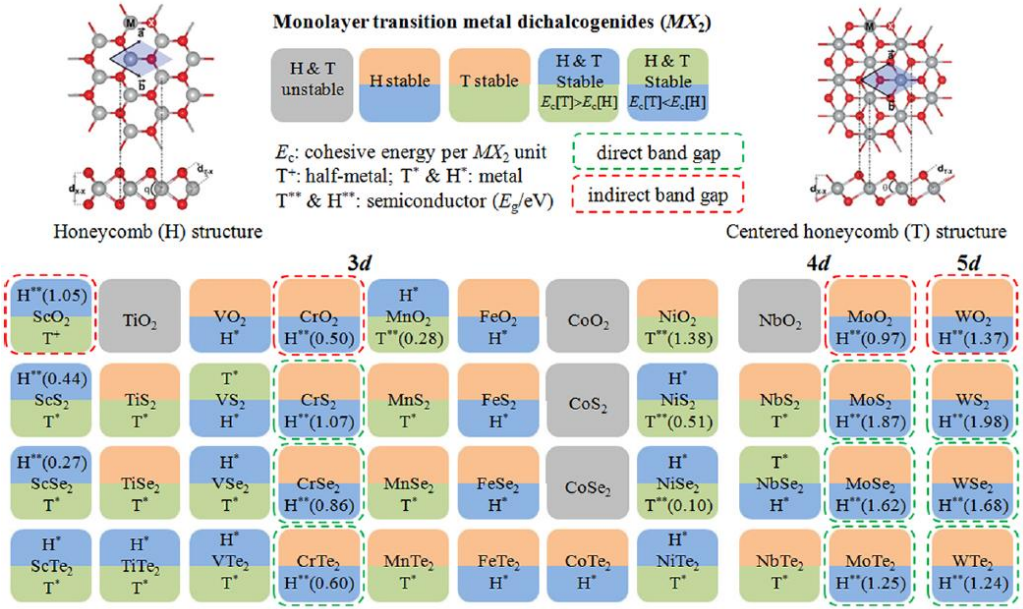


- The prospects of graphene electronics are considered less optimistic.
- However, significant attention for 2D materials beyond graphene.
- So far, more than 500 layered materials discovered.
- Many of them semiconducting and possibly useful for electronics.

2D materials

TMDC

- **TMDC (MX_2)** – M: transition metal, X: chalcogen
  -- insulating or semiconducting (Ti, Hf, Zr, **Mo and W)**
  -- metals or semimetals (V, **Nb** and Ta)
- The different electronic behavior arises from the progressive filling of the non-bonding *d* bands by the transition metal electrons.

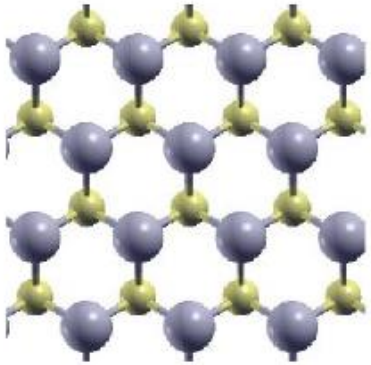


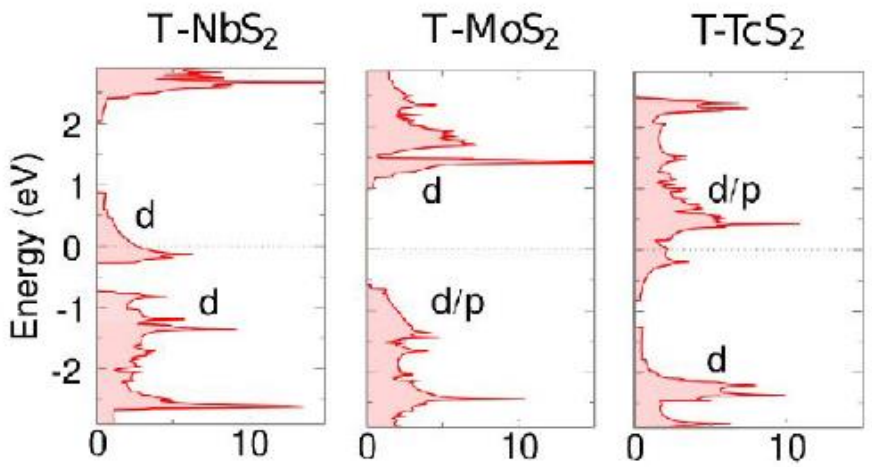
21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg
**	104 Rf	105 Db	106 Sg	10d7 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn

2D materials

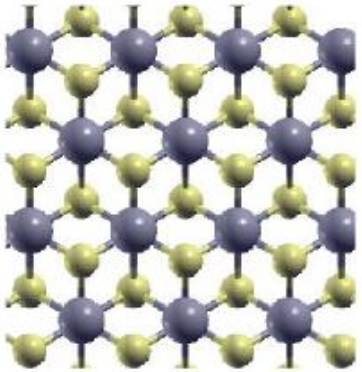
TMDC – semiconductors, metals

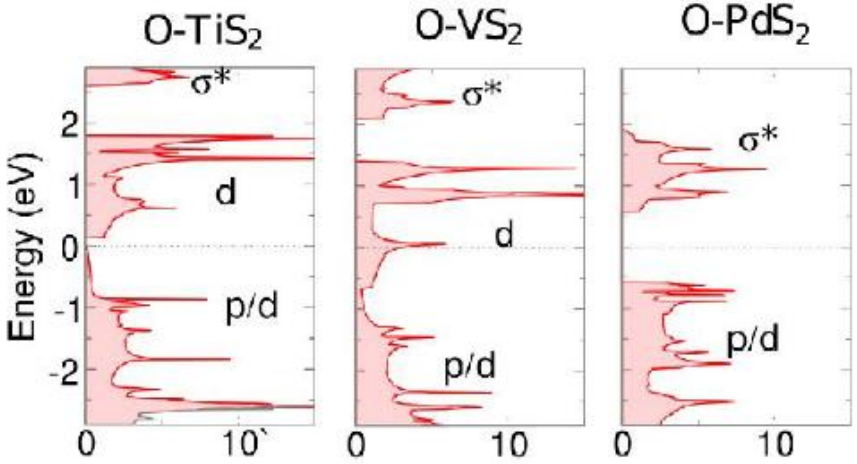
TMDCs-trigonal prismatic





TMDCs-octahedral



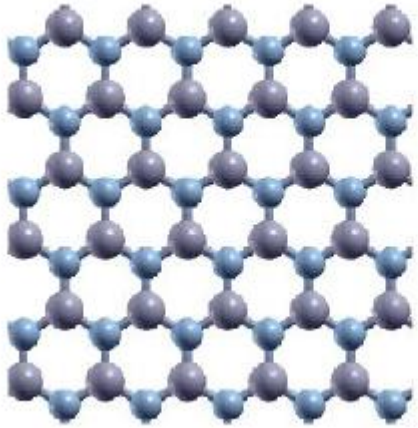


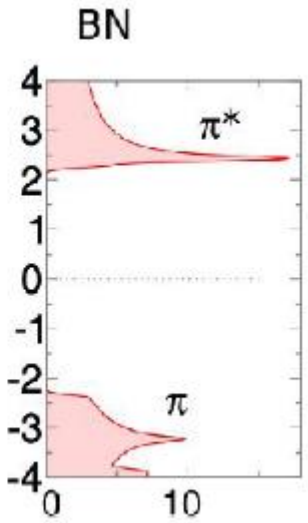
2D materials

h-BN - insulator

- h-BN: large bandgap (~6eV), low number of impurity states within the barrier and high breakdown field

Boron nitride



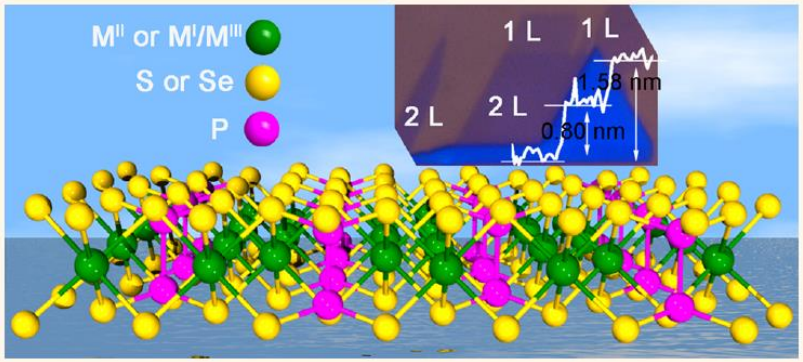


Comparison of h-BN and SiO_2

	Band Gap	Dielectric Constant	Optical Phonon Energy	Structure
BN	5.5 eV	~4	>150 meV	Layered crystal
SiO2	8.9 eV	3.9	59 meV	Amorphous

2D materials

MPX3 - magnetic 2D semiconductors



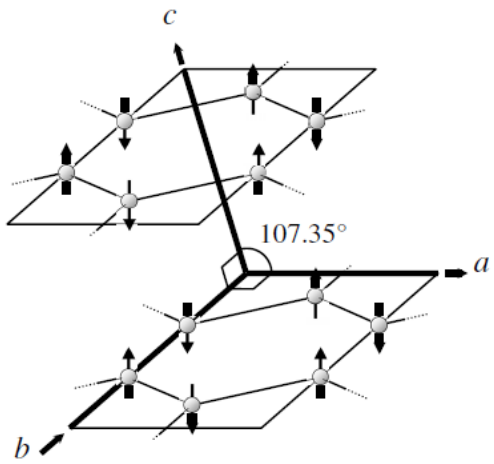
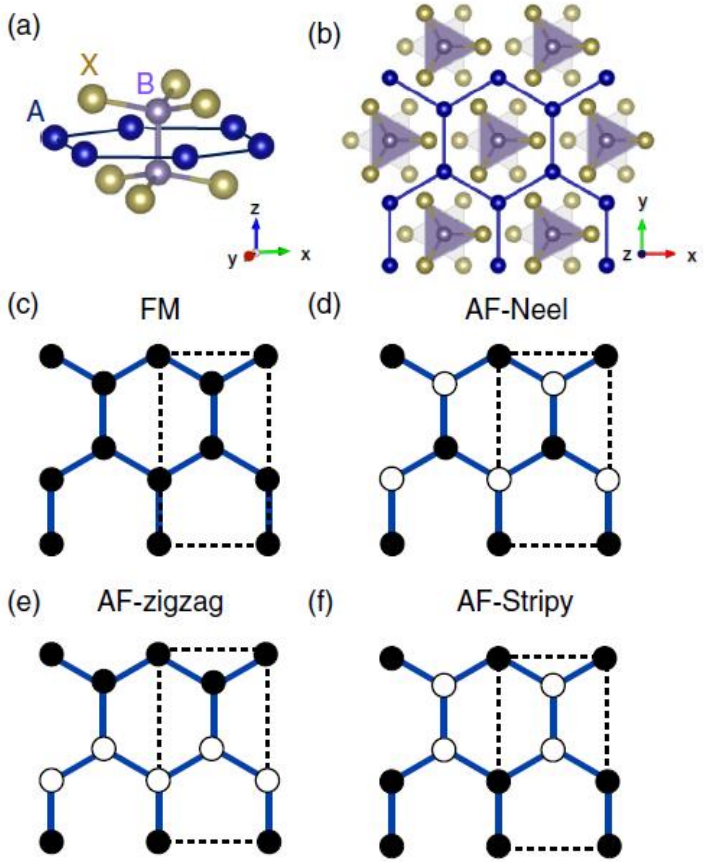
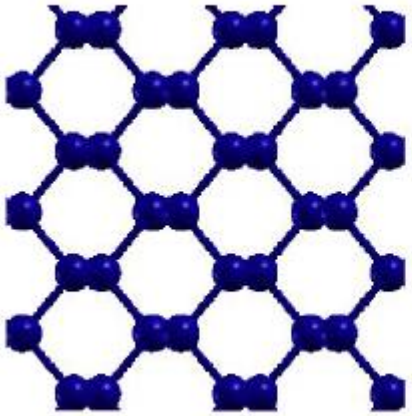


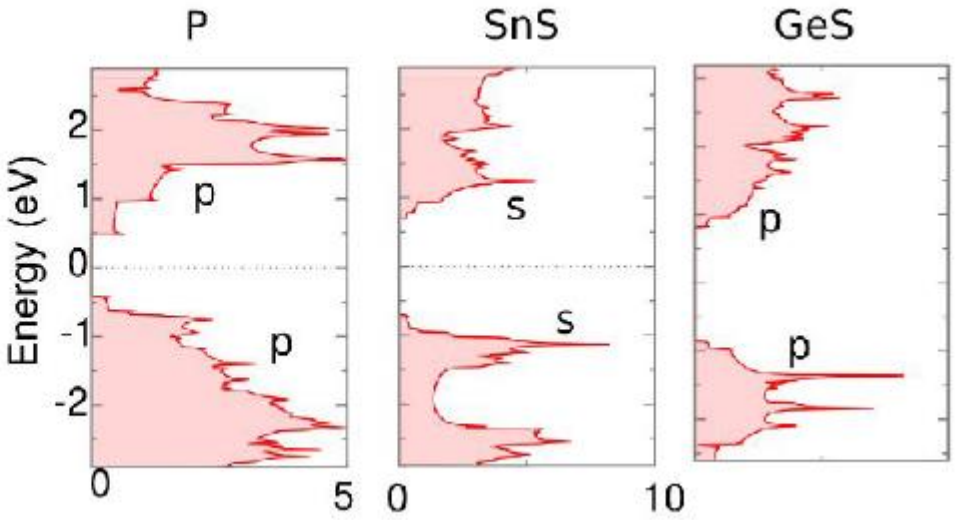
FIG. 1. Schematic showing the magnetic structure of $MnPS_3$. The magnetic moments, given by $S=5/2$, point normal to the *ab* planes.



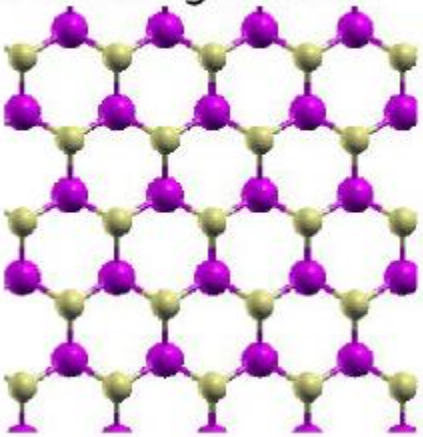
2D materials

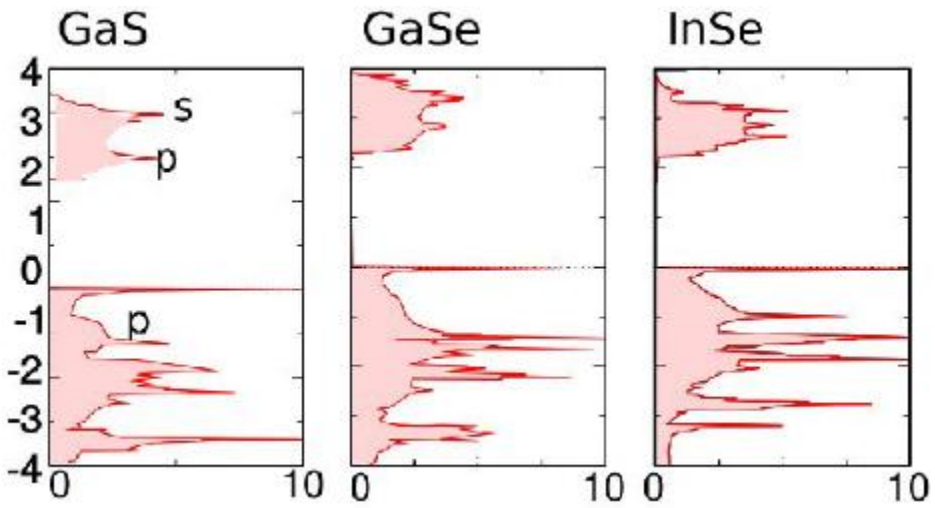
Phosphorene and IV-VI





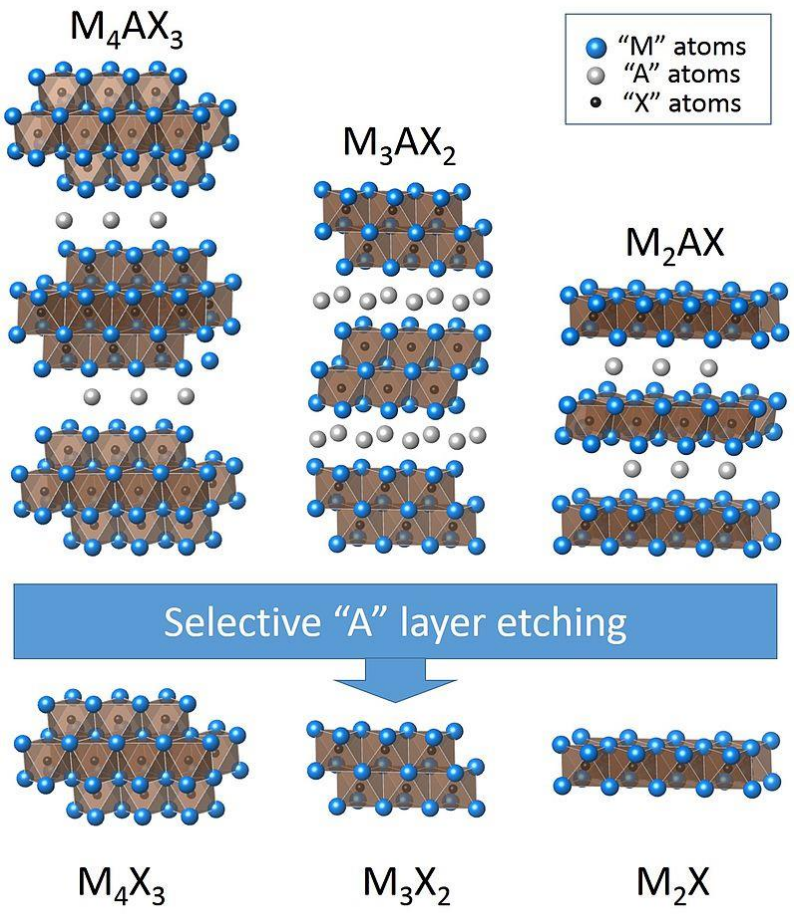
Group III chalcogenides

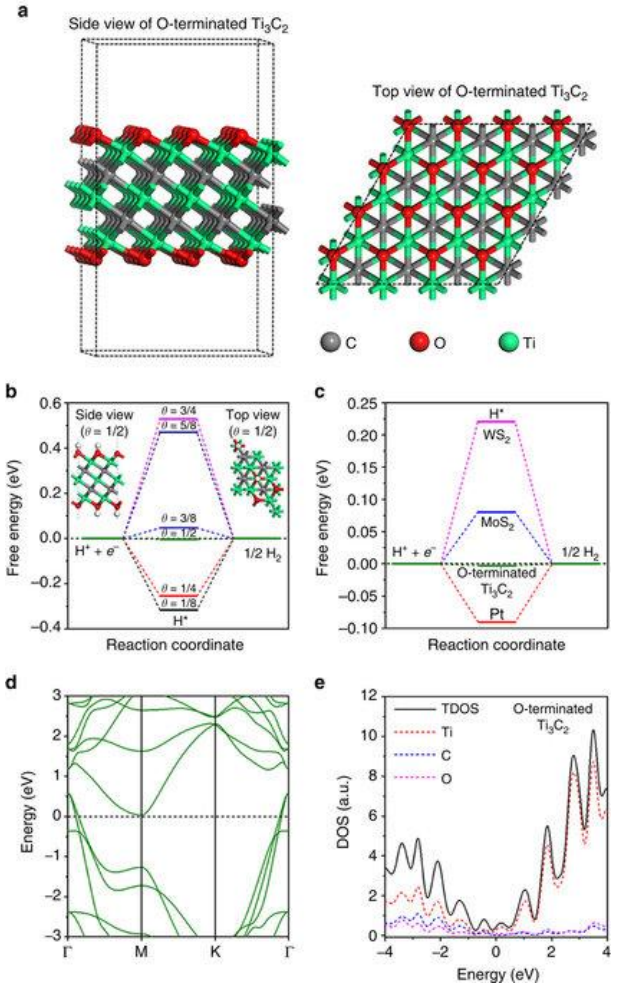




2D materials

Mxenes –narrow band gaps or metals

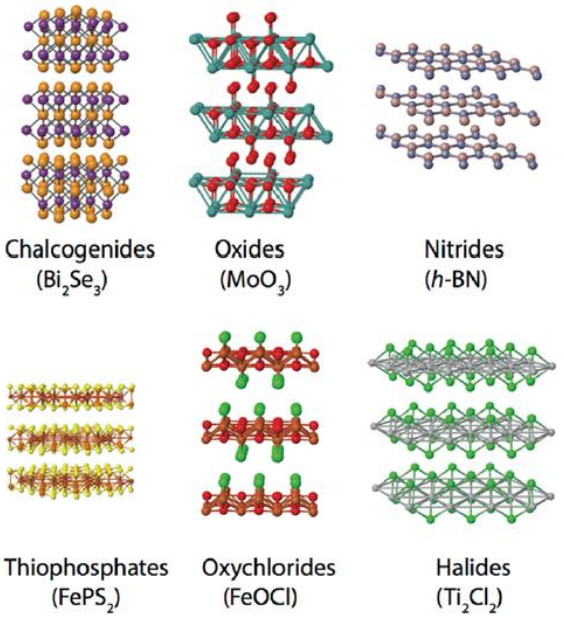




2D materials

TABLE 1. Layered Crystal Structures That Have Been or May Potentially Be Mechanically Exfoliated

Group IV	Dichalcogenides	Trichalcogenides	Oxides	Halides	Potential 2D Zintl Hosts
Graphene C	VSe_2, $NbSe_2$,	Bi_2Se3, Bi_2Te_3,	MoO_3, V_2O_5,	$FeCl_3$,	$CaSi_2$, $CaGe_2$,
Graphane CH	TiS_2, ZrS_2, HfS_2,	Sb_2Te3, Bi_2S_3,	WO_3, ...	$FeBr_3$,	$Ca(Si_{1-x}Ge_x)_2$
Fluorographene CF	ReS_2, PtS_2,	In_2Se3, As_2S_3,		$CrCl_3$,	$Ba_3Sn_4As_6$
Silicene Si	$TiSe_2$, $ZrSe_2$,	As_2Se_3, $NbSe_3$,	**Nitrides**	$CrBr_3$,	$CaMg_2N_2$
Germanane GeH	$HfSe_2$, $ReSe_2$,	TiS_3, ZrS_3, $ZrSe_3$,	BN	$MoCl_3$,	$CaIn_2$
	$PtSe_2$, $SnSe_2$,	$ZrTe_3$, HfS_3,		$MoBr_3$,	$CaNi_2P_2$
	$TiTe_2$, $ZrTe_2$,	$HfSe_3$, $HfTe_3$,	**Oxychlorides**	$TiCl_2$,	$CaAuGa$, ...
MXenes	VTe_2,$NbTe_2$,	NbS_3, TaS_3,	BiOCl, FeOCl,	$TiBr_3$,	
Ti_3C2,Ti_2C, Ta_4C_3,	$TaTe_2$, $MoTe_2$,	$TaSe_3$, ...	HoOCl, ErOCl,	$InBr_3$,	
$Ti_3(Co._5No.5)2$, ...	WTe_2, $CoTe_2$,		ErOCl, TmOCl,	PbI_2,	
	$RhTe_2$, $IrTe_2$,	**Mono-Chalcogenides**	YbOCl, LnOCl, ...	$A1C1_33$,	
	$NiTe_2$, $PdTe_2$,	GeSe, GeTe,	**Layered Silicate**	$InBr_33$,	
	$PtTe_2$, $SiTe_2$,	GaSe, GaS	**Minerals**	$CrBr_33$,	
	NbS_2, TaS_2,		Egyptian Blue, ...	$FeCl_2$,	
	MoS_2, WS_2,	**Thiophosphates**		$MgCl_2$,	
	$TaSe_2$, $MoSe_2$,	FePS3, MnPS3,		$CoCl_2$,	
	WSe_2, $MoTe_2$,	NiPS3, ...		$VC1_2$,	
	$SnSe_2$, SnS_2, ...			VBr_2, VI_2	
				$CdCl_2$,	
				CdI_2, ...	



2D materials

- Graphene, silicene, germanene
- Graphene nanoribbons (GNR)
- Bilayer graphene (BLG)
- Phosphorene, stanene

X-enes

- MQ_2: M = transition metal, Q = chalcogene (S, Se, Te)
- Mo-based TMDs, e.g., MoS_2
- W-based TMDs, e.g., WS_2

2D TMDs

X-anes

- Graphane
- Silicane
- Germanane
- Stanane

MX-enes

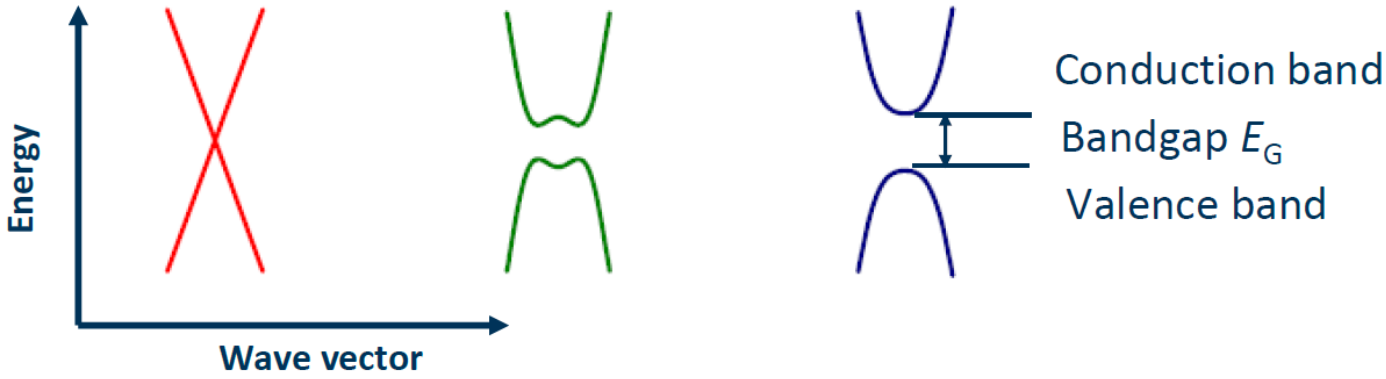
- M_2X: M = early transition metal, X = C or N
- M_2X plus F_2, $(OH)_2$, O_2 e.g. Ti_2CO_2, Sc_2CF_2, …

Many Further 2Ds

Flouro-X-enes, Chloro-X-enes, SMCs, 2D III-Vs, 2D IV-IVs, 2D elementals, etc.

2D materials

Band gaps of 2D materials



X-enes
- Graphene
- Silicene
- Germanene

No gap, E_G = 0! This is really a pitty, since the missing gap causes serious problems for transistors.

BLG

$E_G \leq 130$ meV
Too narrow for logic transistors.

X-enes
- Phosphorene
- Stanene
- GNRs

X-anes
- Graphane
- Silicane
- Germanane

MX-enes
- Sc_2CF_2
- $TiCO_2$

2D TMDs
- MoS_2, $MoSe_2$, $MoTe_2$
- WS_2, WSe_2, WTe_2

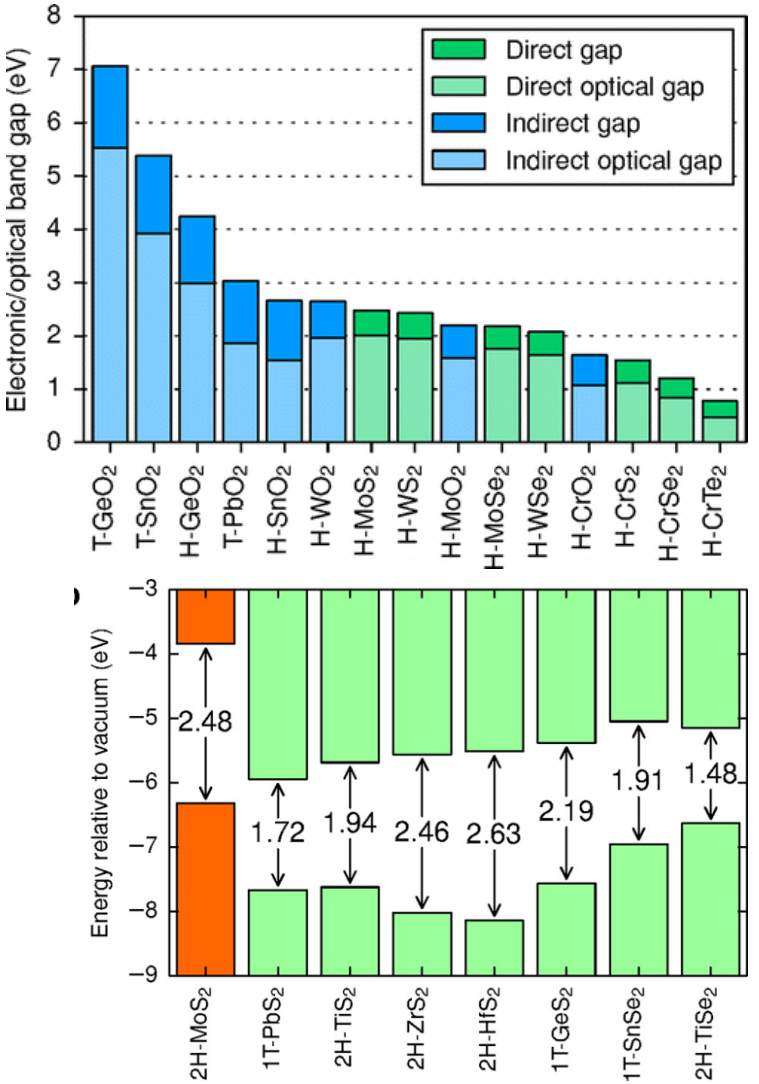
etc., etc.

Many of these materials have a gap E_G = 0.5... 2.5 eV, perfect for transistors.

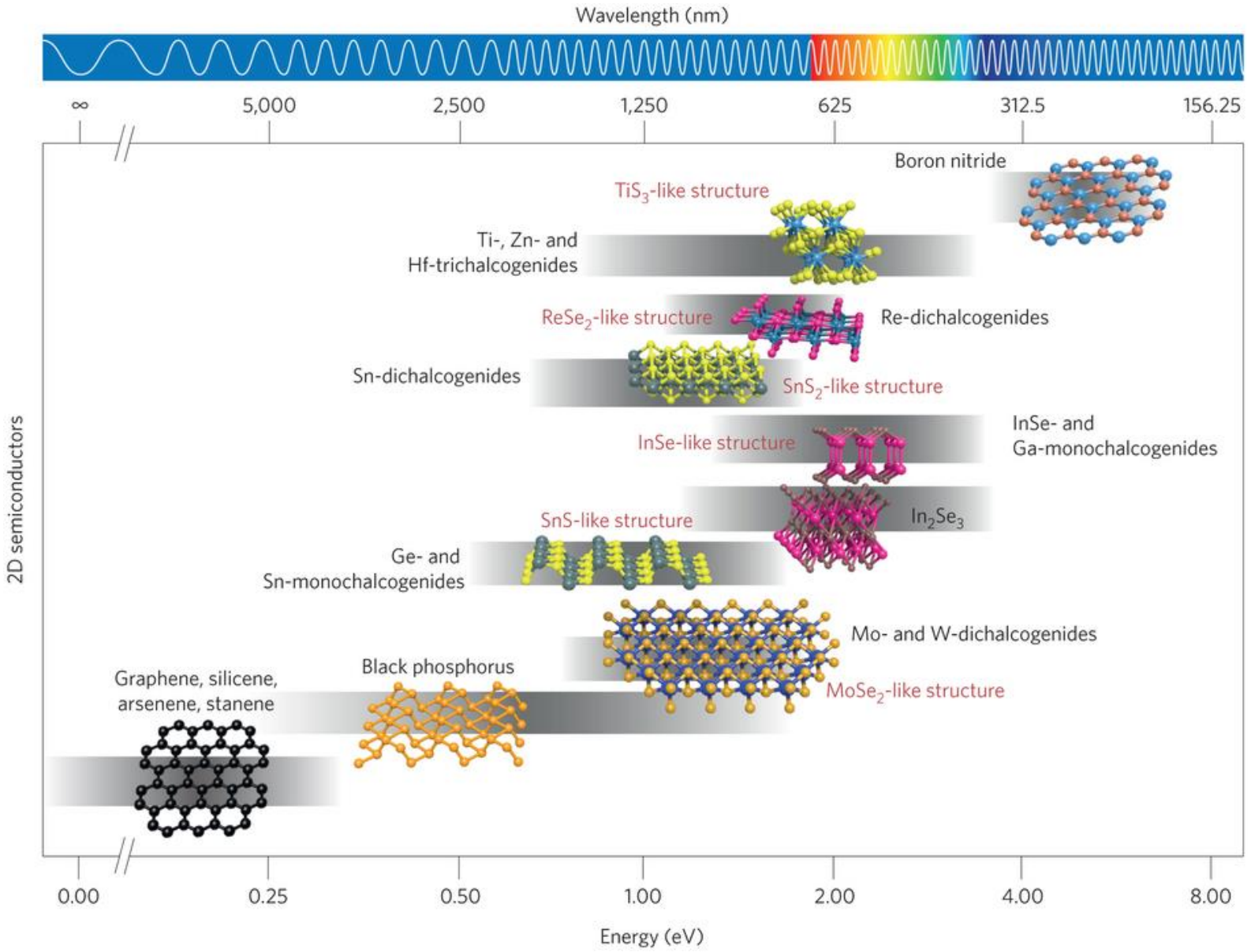
2D materials

Band gaps of TMDC

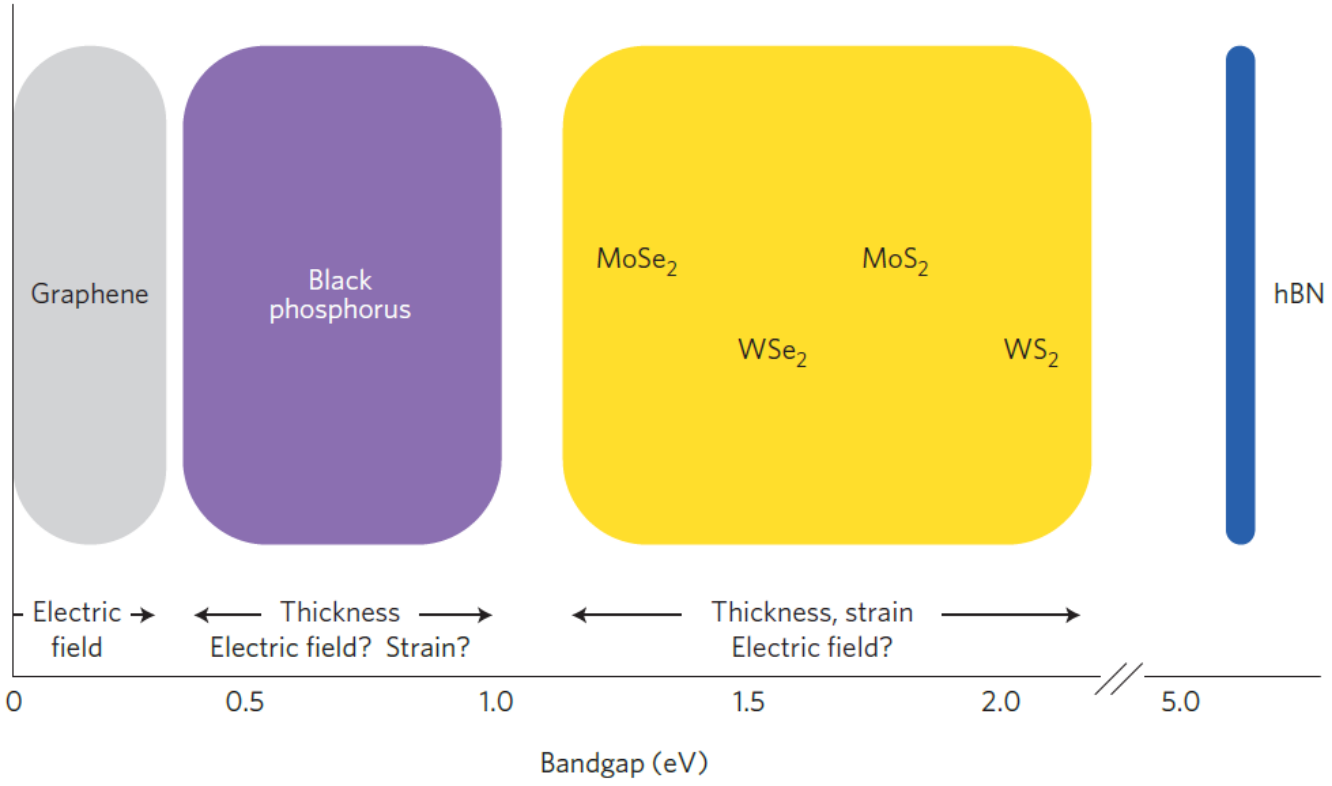
2D sheets	theoretical E_g (eV)	experimental E_g (eV)
graphene	0	0
bilayer graphene	0	0
bulk *h*-BN		5.97 [ref 52]
monolayer *h*-BN		6.07 [ref 65]
fully hydrogenized *h*-BN	3.05 [ref 66]	
2−5 layers *h*-BN		5.92 [ref 105.]
bulk MoS_2	1.20 (indirect[b]) [refs 35, 139]	1.0−1.29 (indirect) [refs 35, 139]
monolayer MoS_2[a]	~1.90 (direct[b]) [ref 140]	~1.90 (direct) [ref 140]
bulk WS_2	~1.30 (indirect[b]) [refs 35, 147]	~1.35 (indirect) [refs 35, 147]
monolayer WS_2[a]	~2.10 (direct[b]) [ref 147]	
	~1.80 (direct[c]) [ref 148]	
monolayer $MoSe_2$	~1.44 (direct[c]) [ref 148]	
monolayer $MoTe_2$	~1.07 (direct[c]) [ref 148]	



2D materials



2D materials

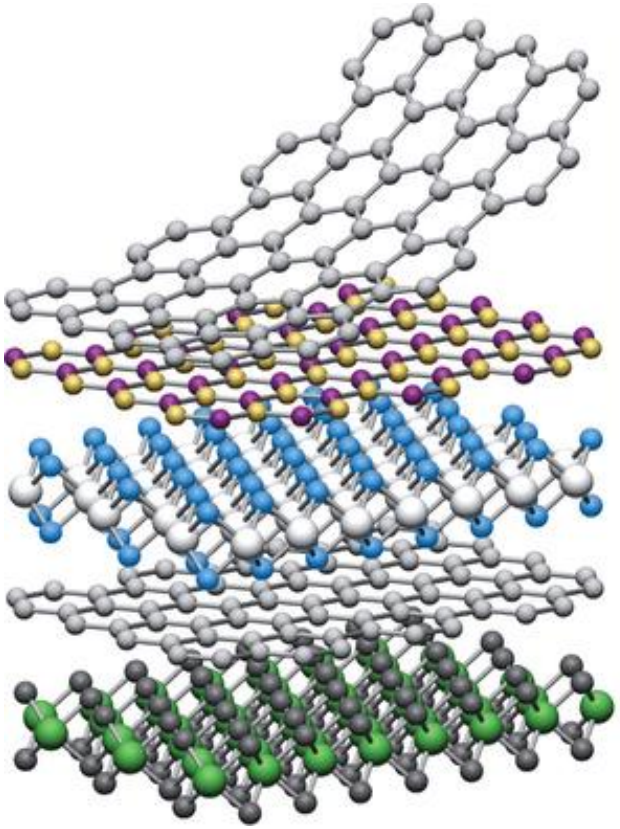


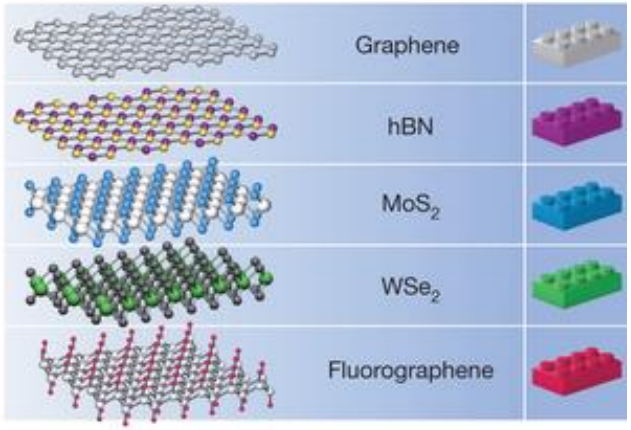
2D materials

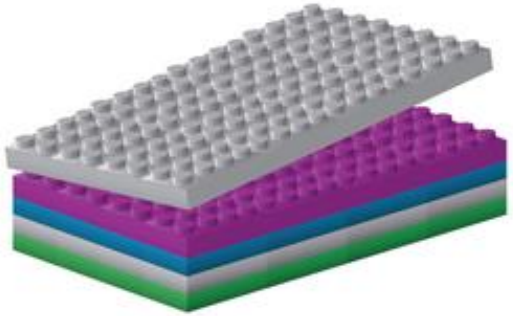
Van der Waals heterostructures

A. K. Geim[1,2] & I. V. Grigorieva[1]

2D crystals can be assembled into heterostructures, where the monolayers are hold together by the van der Waals forces.

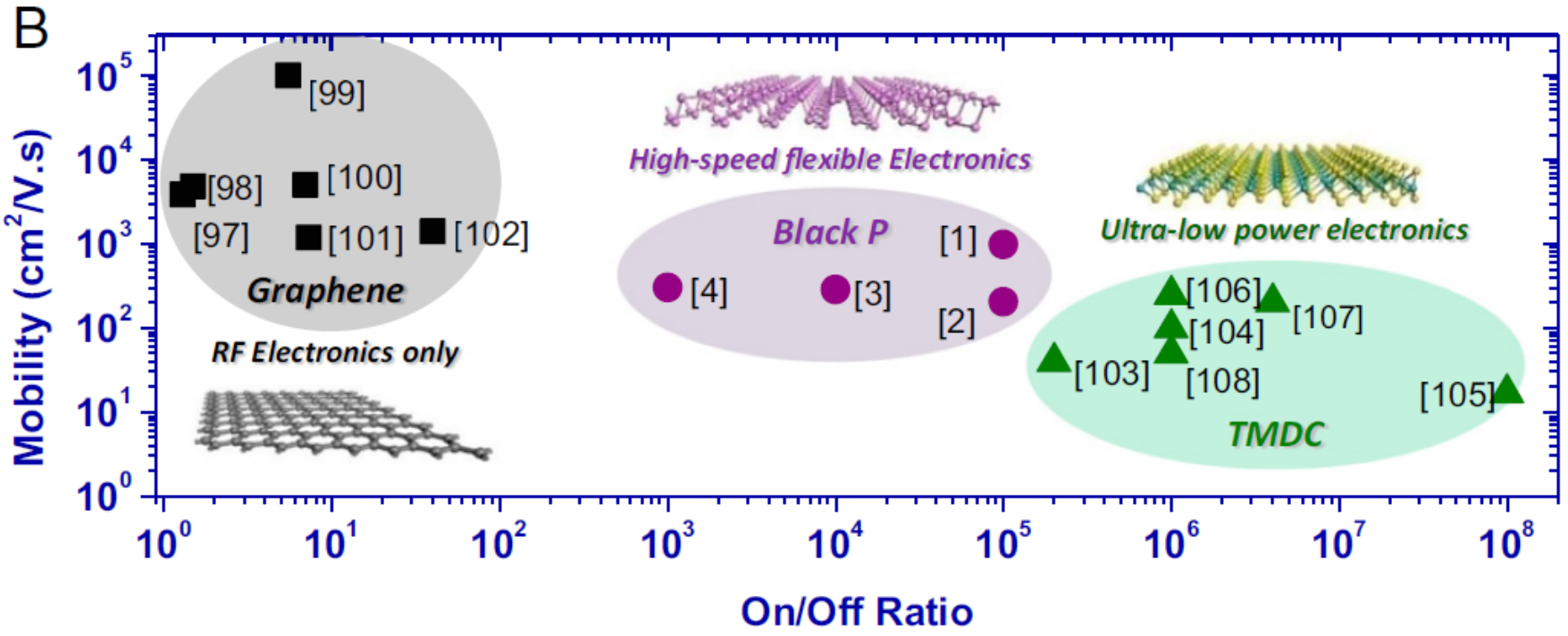






Transport properties

- Channel (in-plane) transport
- Tunneling (out-of-plane) transport



Transport properties

Channel (in-plane) transport

What limits mobility of 2D materials?

To understand the observed transport data
To identify the main scattering mechanism

→ Improve sample quality (high mobility)

→ Device applications

New physics (IQHE, FQHS, SLL, TQC …)

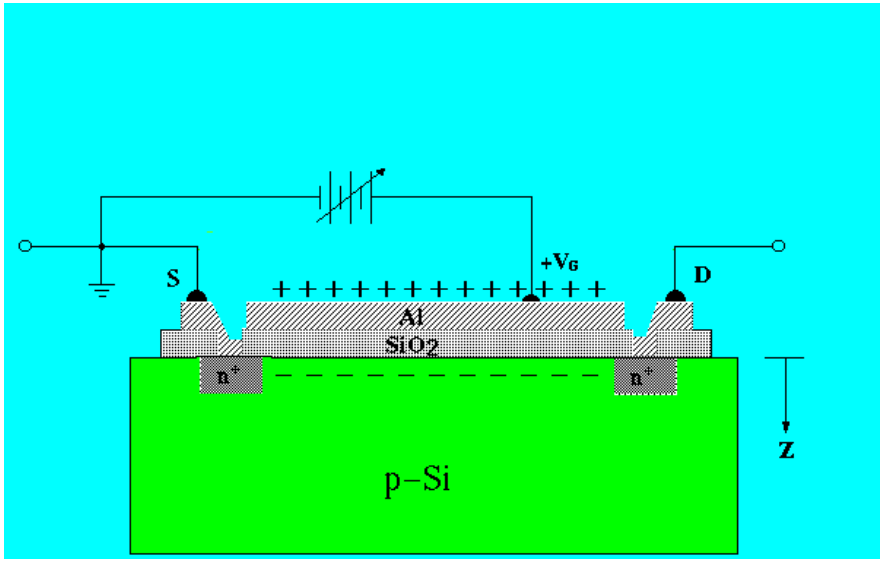
$m \sim 10,000\ cm^2/Vs$ $m \sim 100,000\ cm^2/Vs$ $m \sim 1,000,000\ cm^2/Vs$

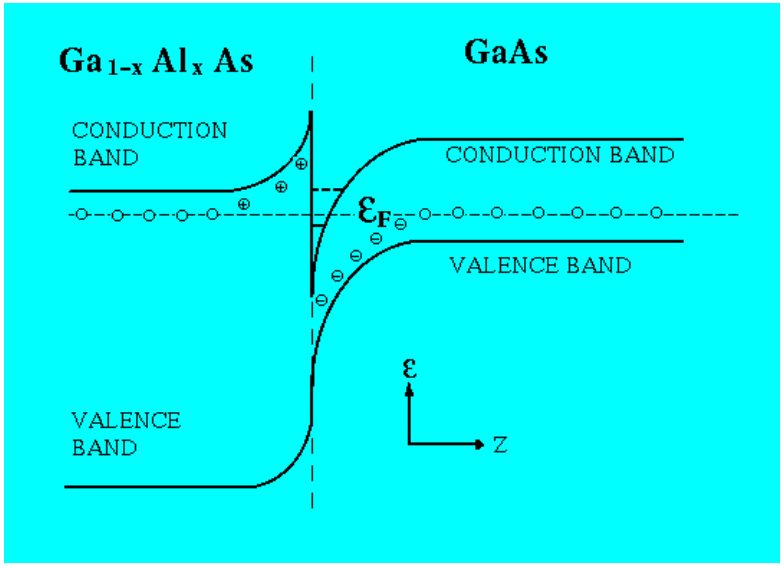
Transport properties

Si-MOSFET vs. Modulation doping in GaAs

Si-MOSFET $\mu \sim 20{,}000\ cm^2/Vs$

Modulation doping in GaAs
$\mu \sim 36{,}000{,}000\ cm^2/Vs$





Transport properties

Theoretical Approach

- **Semi-classical Boltzmann transport (**relaxation time approximation)
- **Long-range screened disorder potential**
- **Wave-vector and Temp dependent screening**
- **Quantum-mechanical scattering**
- **Physically motivated**
- **Gives correct (T,n,κ) dependence**
- **Low-density inhomogeneity (screening-failure)**
- **The ensemble Monte Carlo technique**
- **Non-Equilibrium Green's Function Method**

Compare with experimentally measured density and temperature dependent mobility.

Transport properties

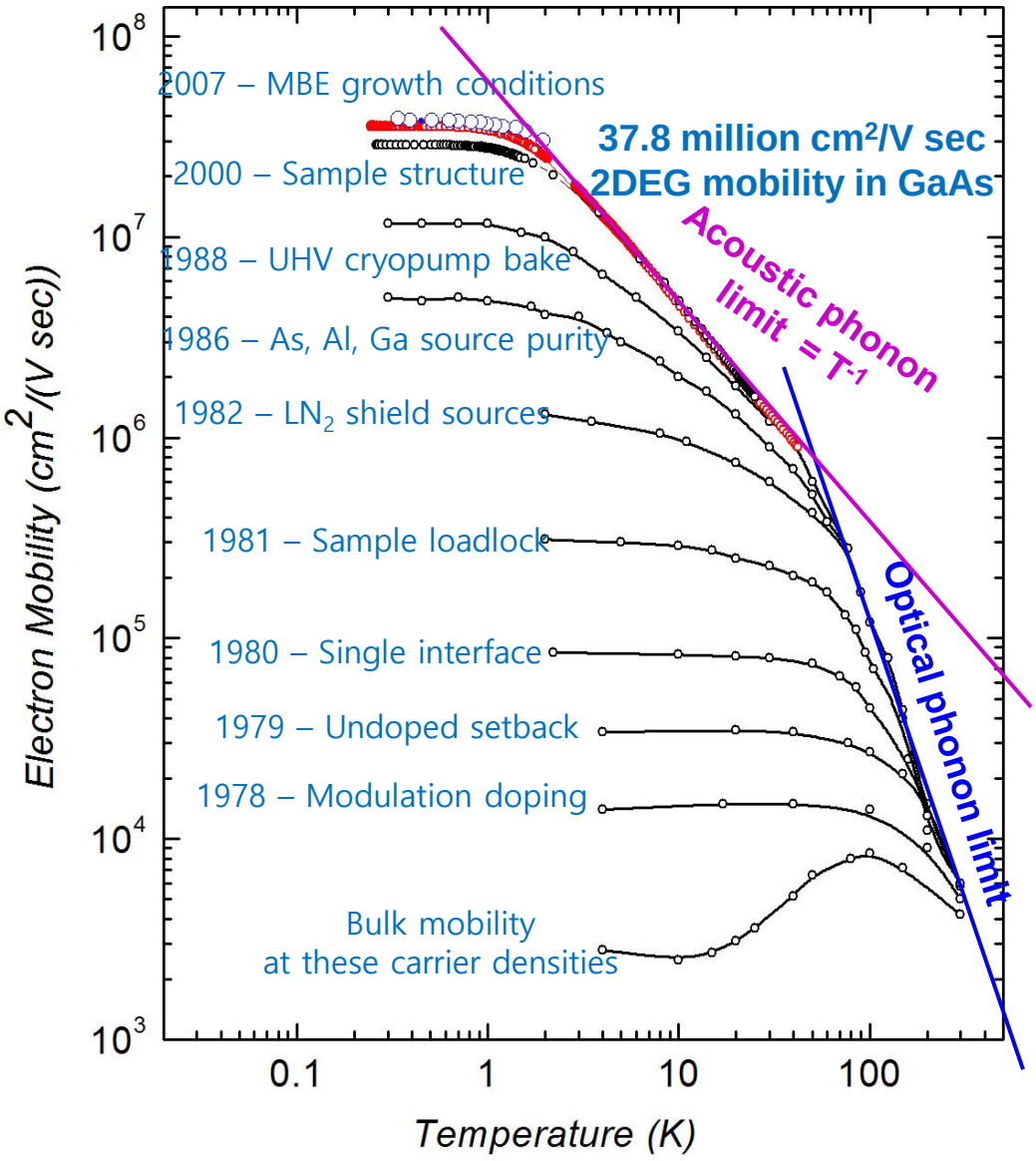
GaAs/AlGaAs

There are many independent contributions that can adversely affect the carrier mobility in modulation-doped AlGaAs/GaAs 2DEG systems.

Hard limits → phonons

A. LO-Phonon Scattering (Long-Range Polar Fröhlich Coupling)

B. Acoustic Phonon Scattering
   i. Via Deformation Coupling
   ii. Via Piezoelectric Coupling

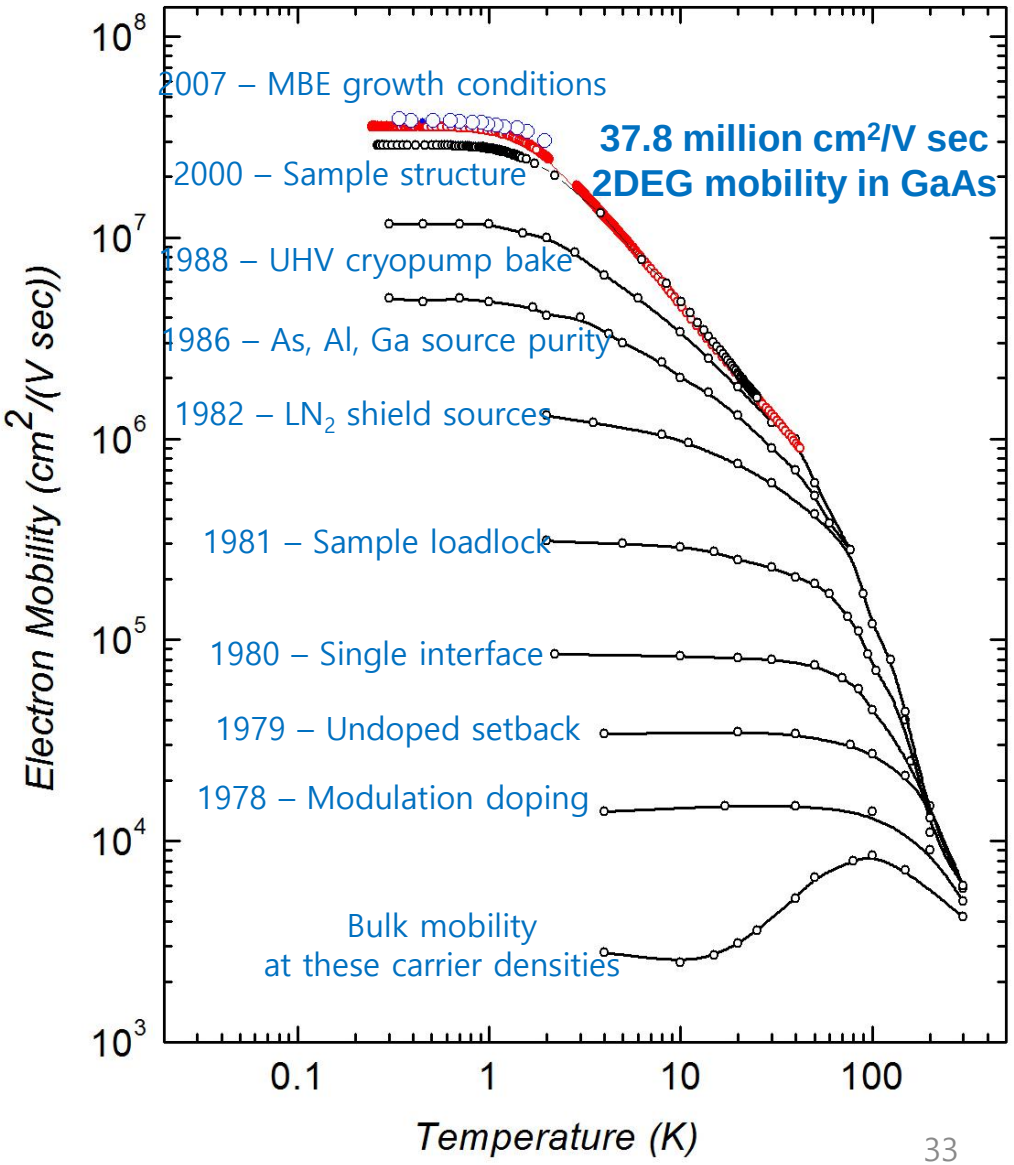


Transport properties

There are many independent contributions that can adversely affect the carrier mobility in modulation-doped AlGaAs/GaAs 2DEG systems.

Soft limits → disorders

C. Short Range Scattering by Neutral Defects and Impurities
D. Interface Roughness Scattering at AlGaAs-GaAs Interface
E. Alloy Disorder Scattering in AlGaAs



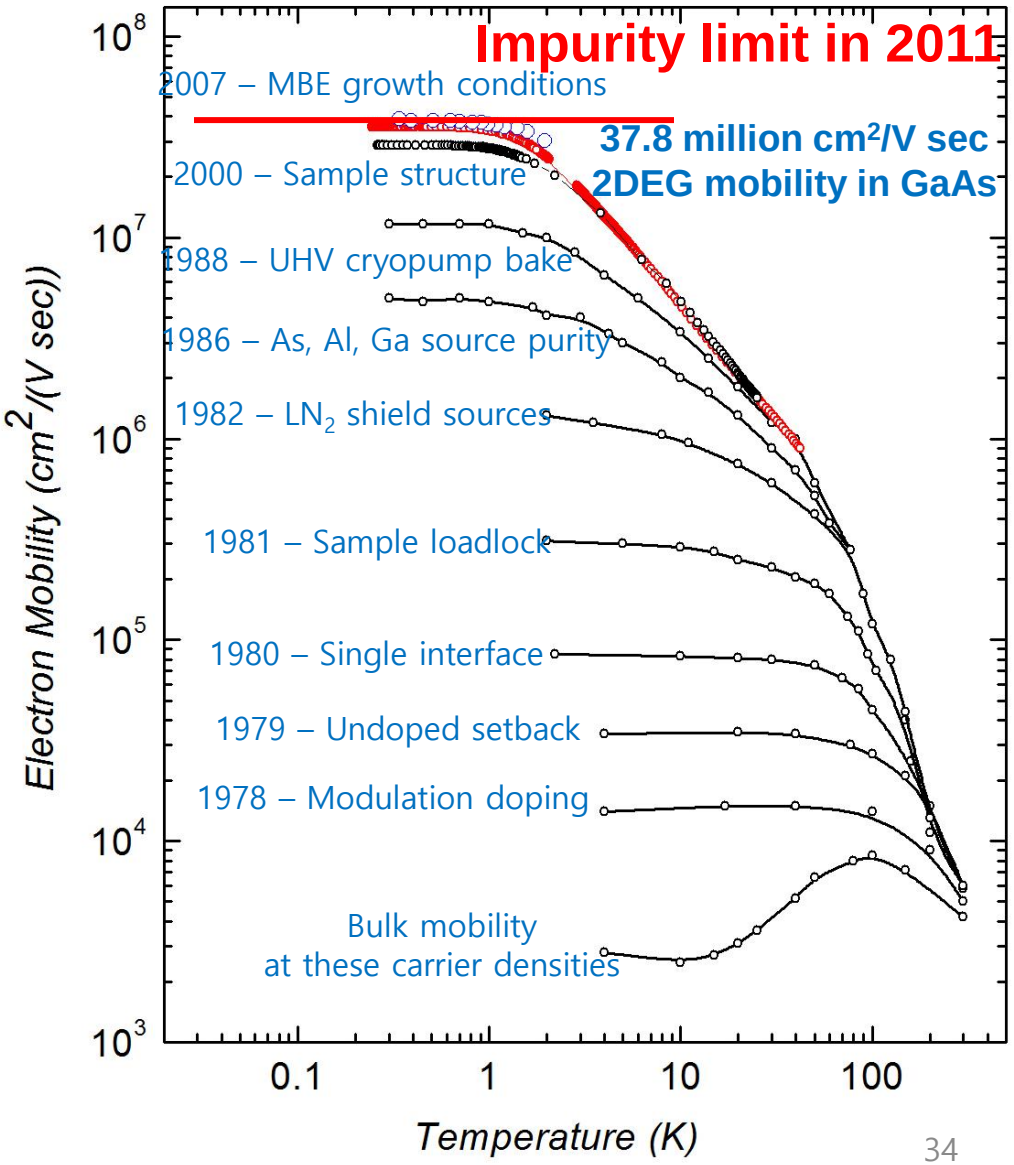
Transport properties

There are many independent contributions that can adversely affect the carrier mobility in modulation-doped AlGaAs/GaAs 2DEG systems.

F. Coulomb Scattering

i. From Unintentional Background Charged Impurities in AlGaAs and GaAs

ii. Scattering by Intentional Dopants in the Silicon Modulation Doped Layer



Transport properties

What limits the 2-D mobility?

The history of this field is the raising of the limit imposed by impurities.

2D mobility increased from 10^3 in 1978 to 10^7 in 1988

But only by another factor of 3 during 1988-2002

Has not increased in the 2002-2007 period

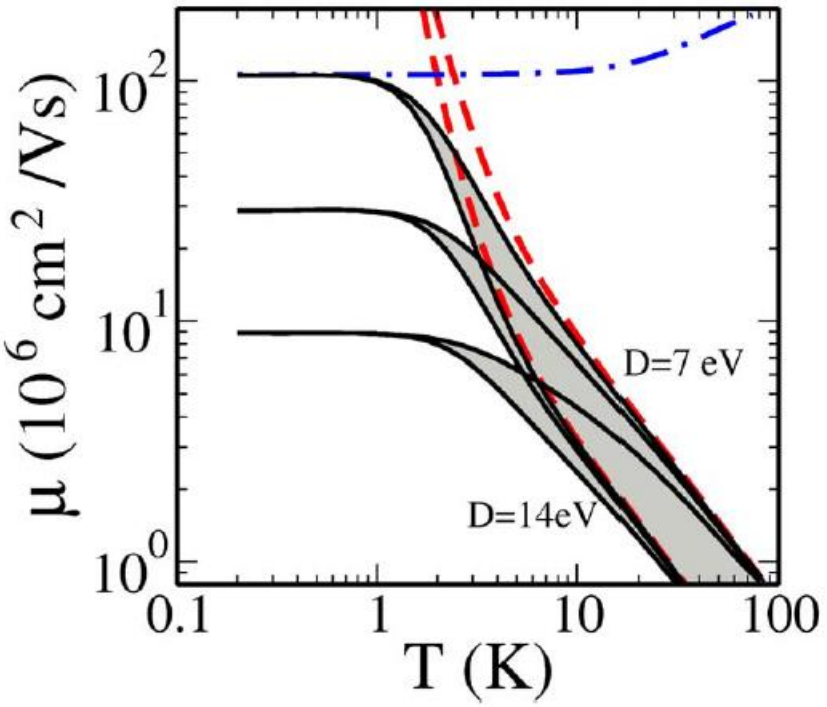
Current record~ 36.10^6

(2008)

REASON?

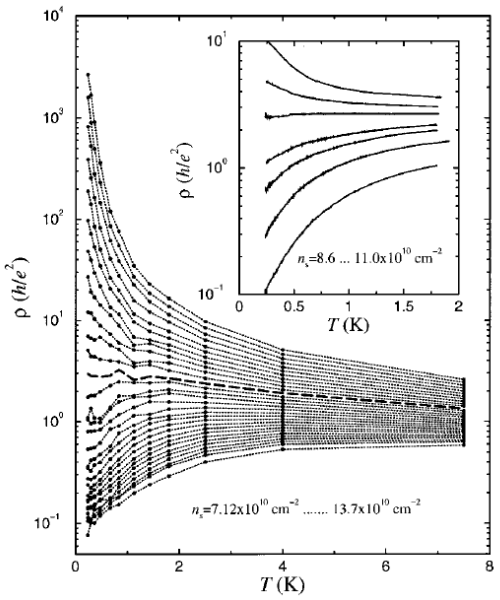
BACKGROUND CHARGED IMPURITIES

100 million mobility → background charged impurity (Hwang & Das Sarma PRB 77, 235437 (2008))

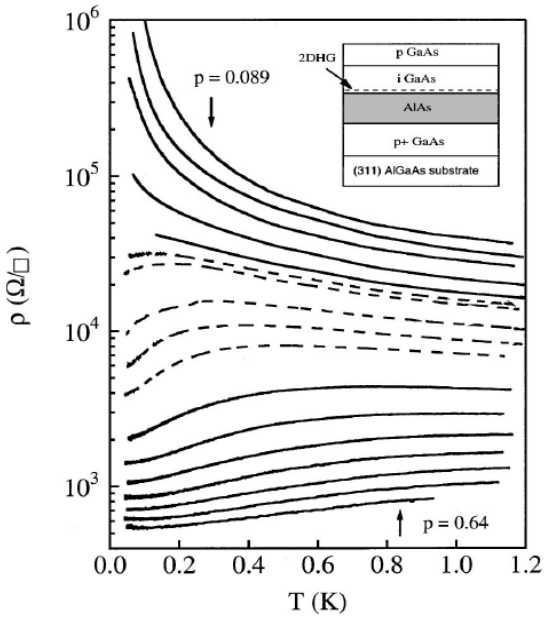


Transport properties

Strong temperature dependent resistivity → Metal-Insulator transition



Si MOSFET, Kravchenko (1994)



p-GaAs, Hanein (1998)

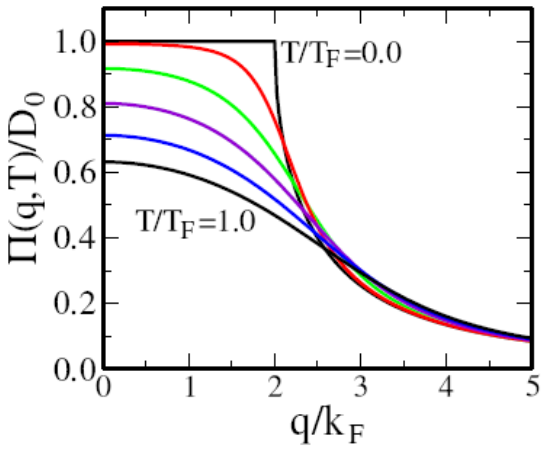
Observed in many different 2D semiconductor systems : Si-MOSFET, p-GaAs, n-GaAs, SiGe, AlAs, …

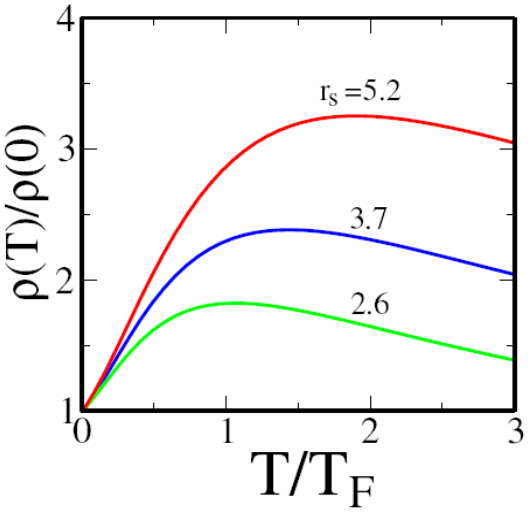
Strong temperature dependent screening of charged impurity scattering g ives rise to the strong temperature dependent metallic behavior.

→ Screening theroy (Das Sarma & Hwang)

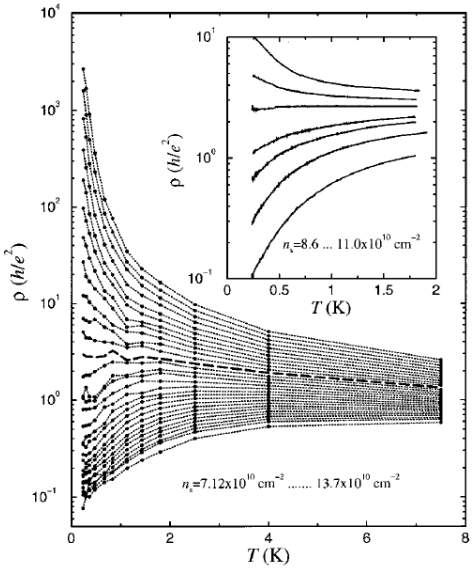
Transport properties

Role of screening

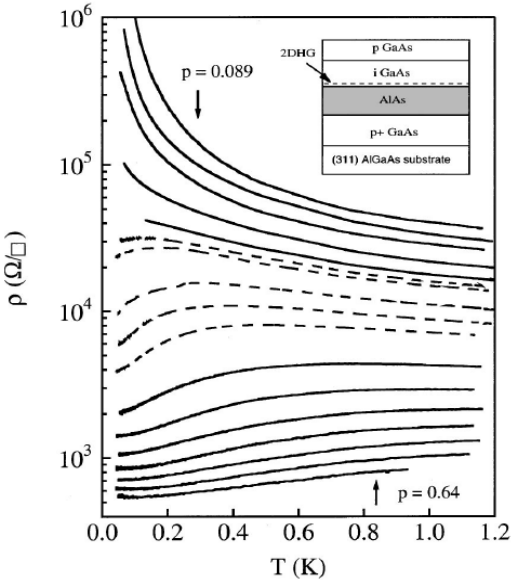




$$T_F \sim 10K$$



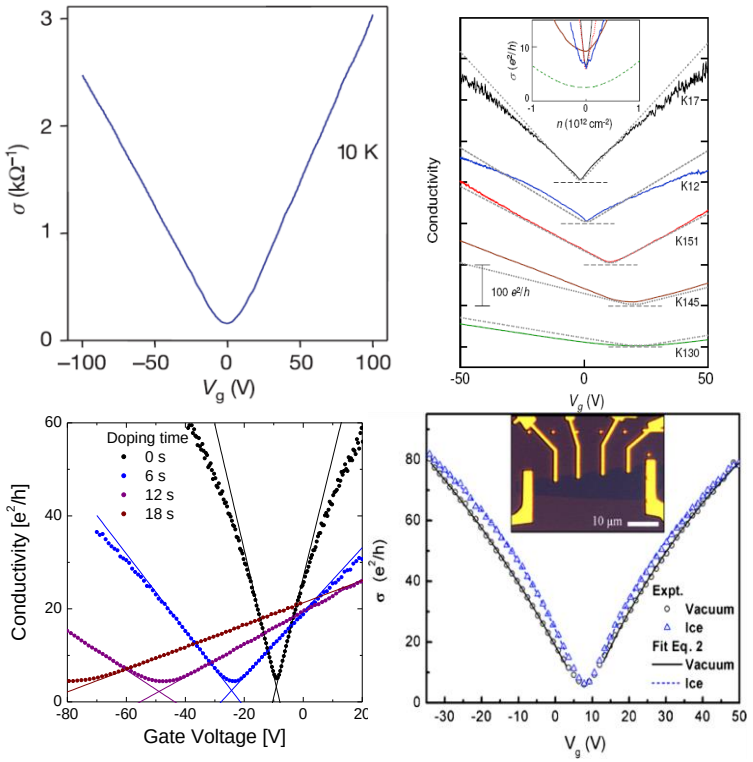
Si MOSFET, Kravchenko (1994)



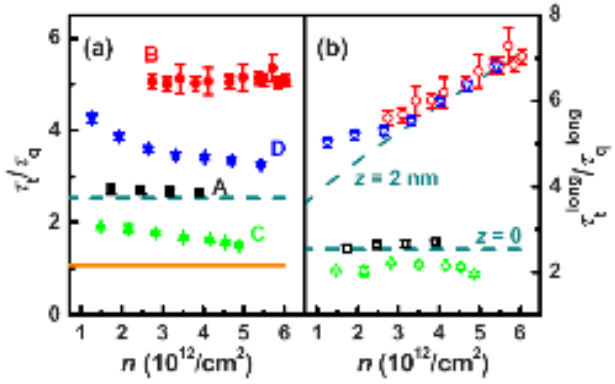
p-GaAs

Transport properties

Graphene



(a) Novoselov et al. (b) Tan et al. PRL 2008
(c) Chen et al. Nphys 2008 (d) Jang et al. PRL 2008



Hong et al. PRB 2009

Linear-in-density conductivity
(constant mobility)
Non-universal minimum conductivity
Dielectric constant dependence
Ratio of transport scattering time to quantum (t_t/t_q) scattering time
Impurity dependent mobility

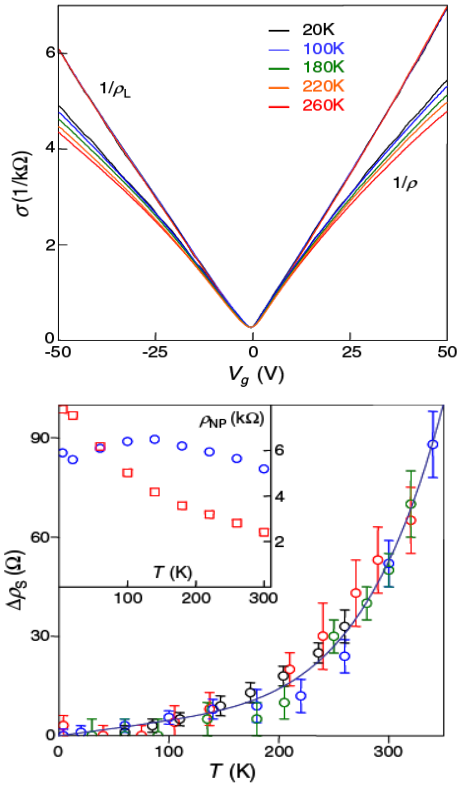
Screened random charged impurity

$s(n) \mu n$ SLG $m=1/n_i$

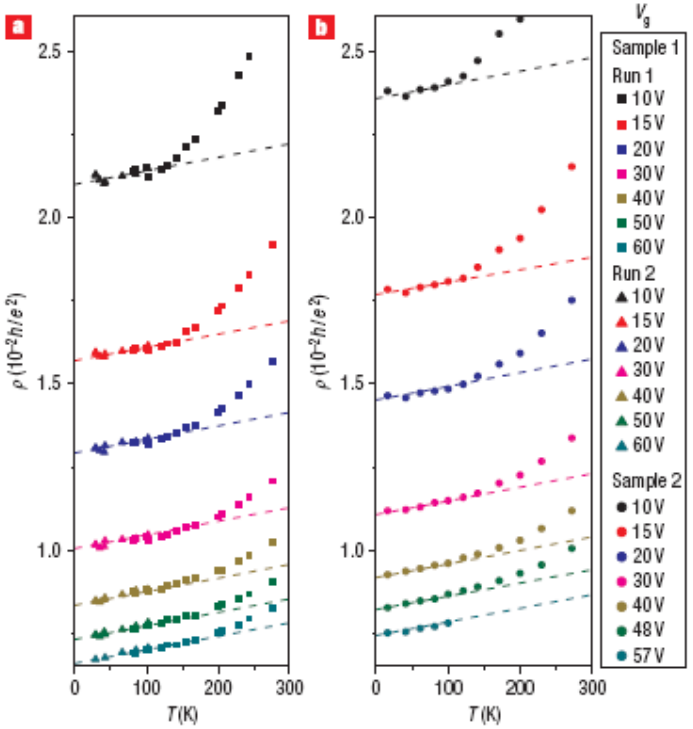
Transport properties

Higher mobility sample μ ~ 20,000 cm²/Vs

Morozov, Geim (2008)



Chen, Fuhrer (2008)



Weak temp. dependence at high density and near Dirac point.
No Temp dependent at Dirac point.

→ **Phonons (deformation potential , remote optical polar phonons, flexural), ripple**

Transport properties

Graphene transport limited by el-ph scattering

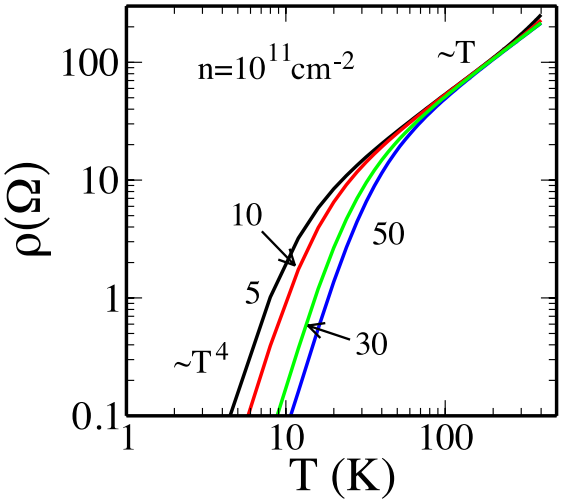
- acoustic phonon scattering

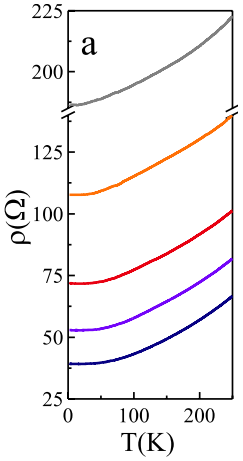
$$r = gT \qquad T > T_{BG} \qquad g = \frac{pD^2 k_B}{4e^2 \hbar r_0 v_{ph}^2 v_F^2}$$

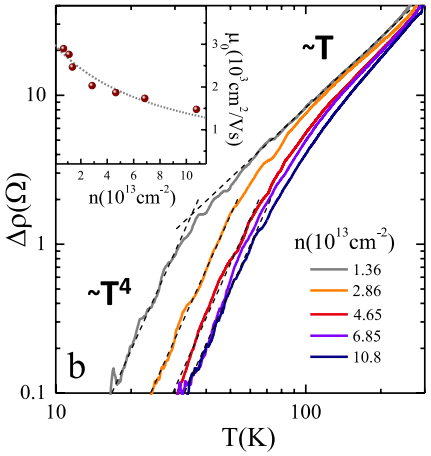
$$r = aT^4 \qquad T < T_{BG} \qquad a = \frac{12\zeta(4) D^2 k_B^4}{e^2 \hbar^4 r_0 v_{ph}^5 v_F^2} \frac{1}{k_F^3}$$

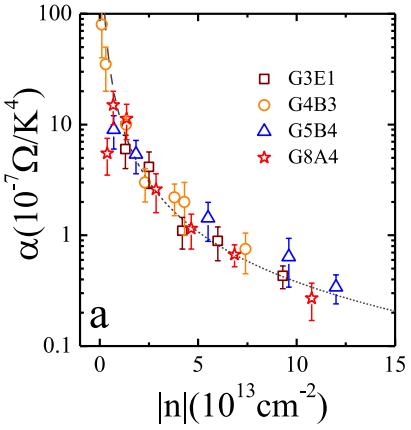
$$T_{BG} = 2k_F v_{ph}$$

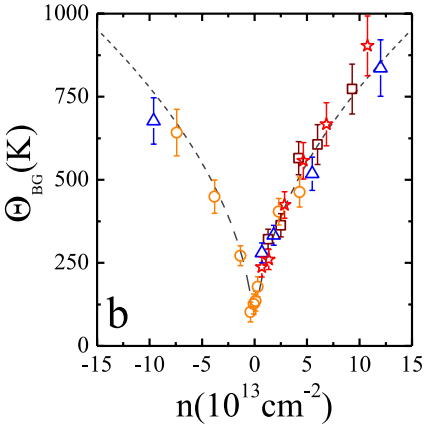
Hwang & Das Sarma, PRB (2008)







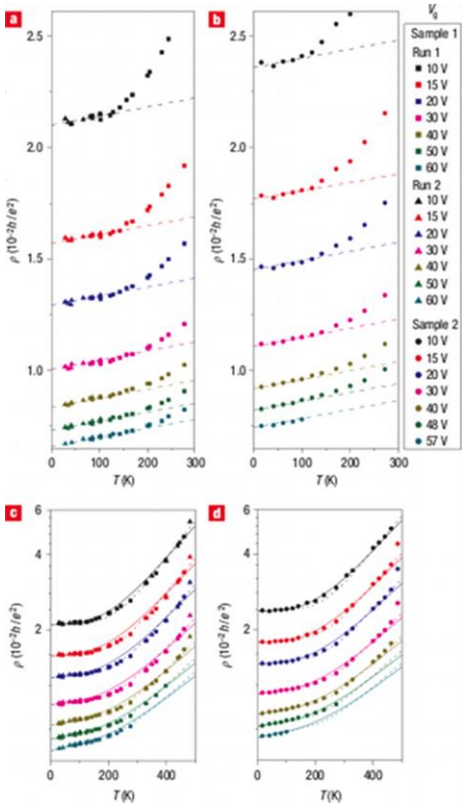




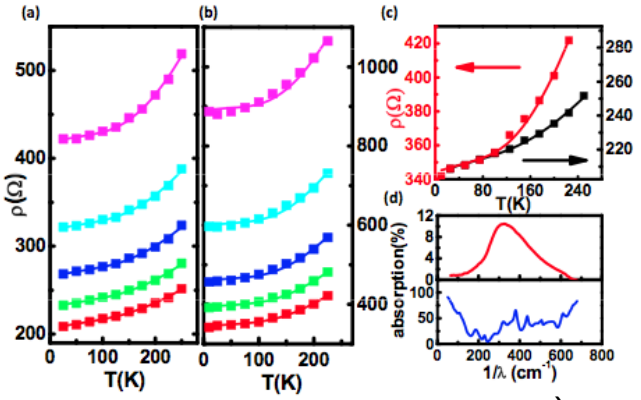
Efetov & Kim (PRL)

Transport properties

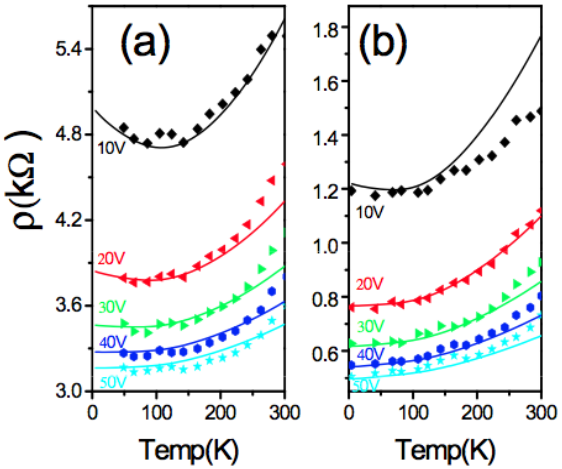
Graphene transport limited by el-ph scattering



Chen et al. Nnono (2008)



Hong et al. PRL (2010)

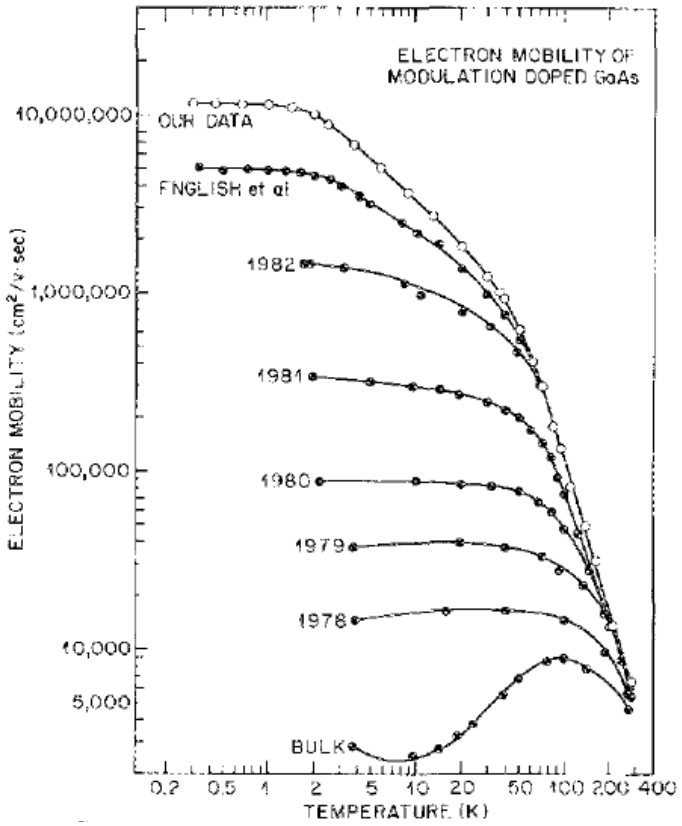


Heo et al. arXiv (2010)

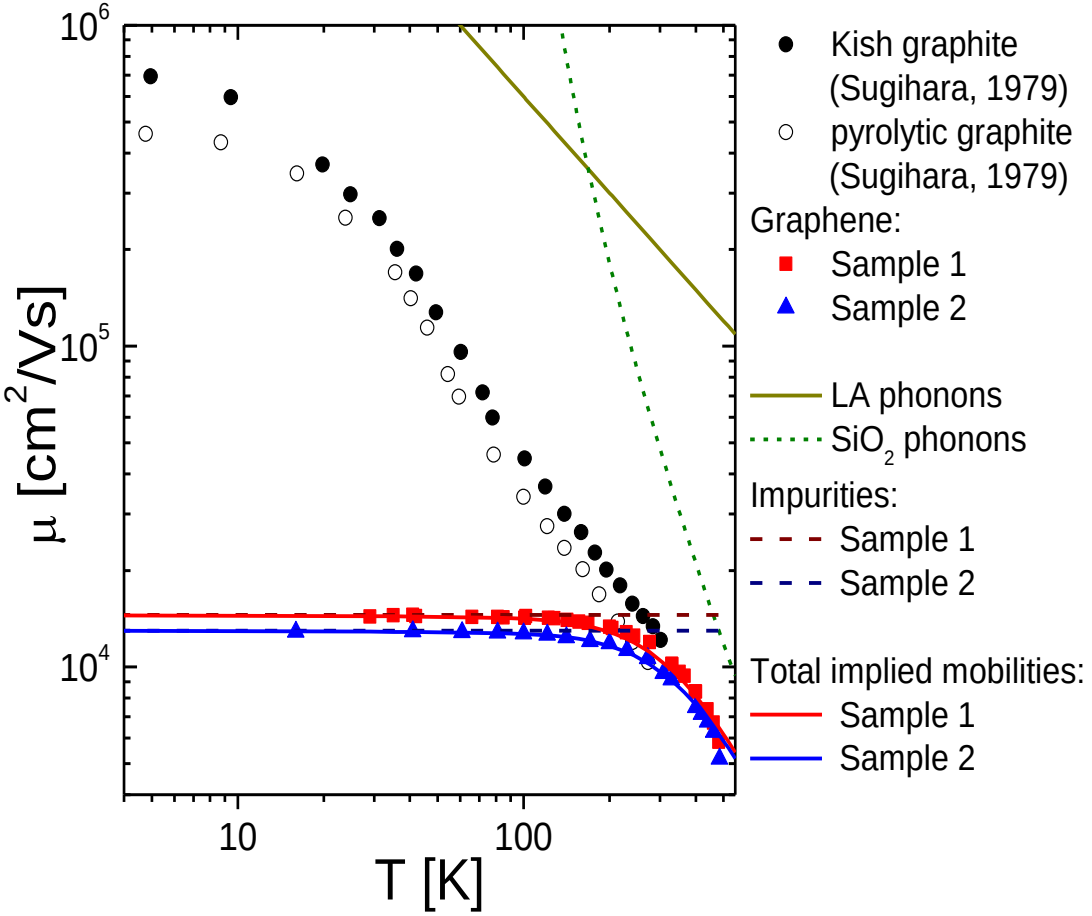
Graphene on a polar substrate
→ surface optical phonons scattering dominates over all other scatterings at room temperature

Transport properties

GaAs (Pfeiffer and West, 1989)



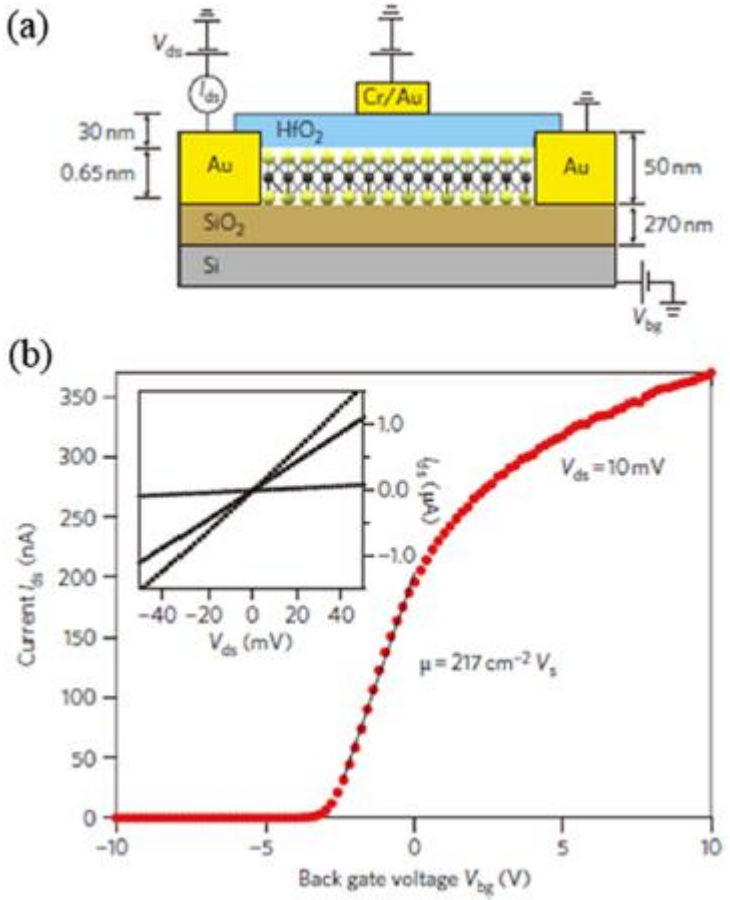
Bulk Graphite and Graphene on SiO_2

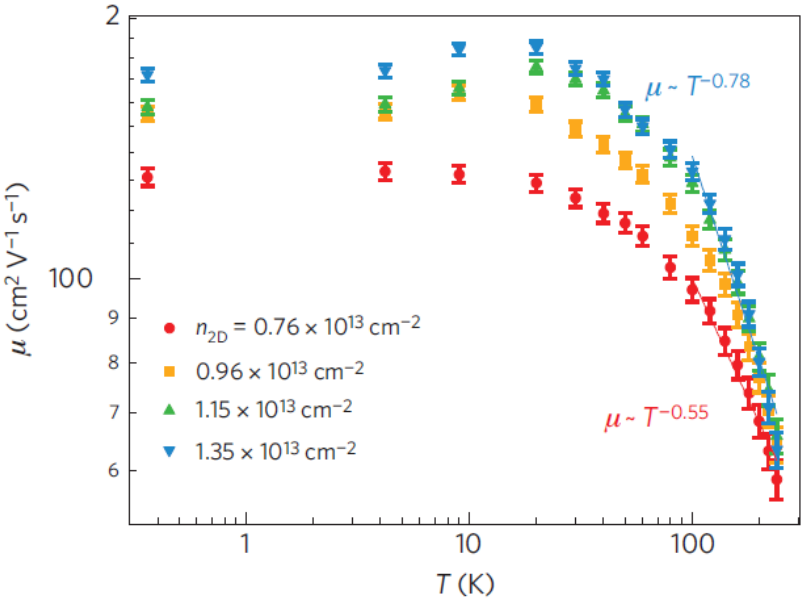


h-BN and suspended graphene

Transport properties

MoS2

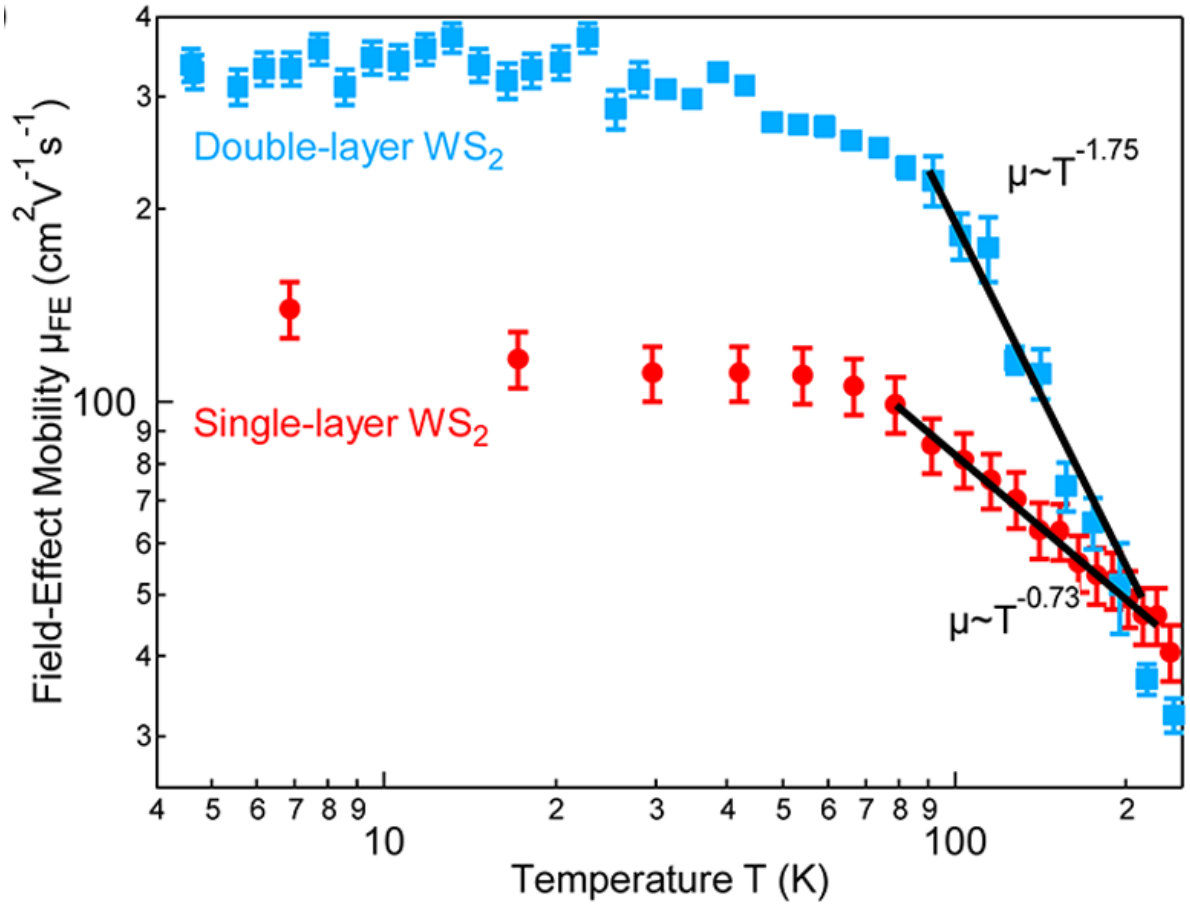




Kis, Nat. Mat. (2013)

Transport properties

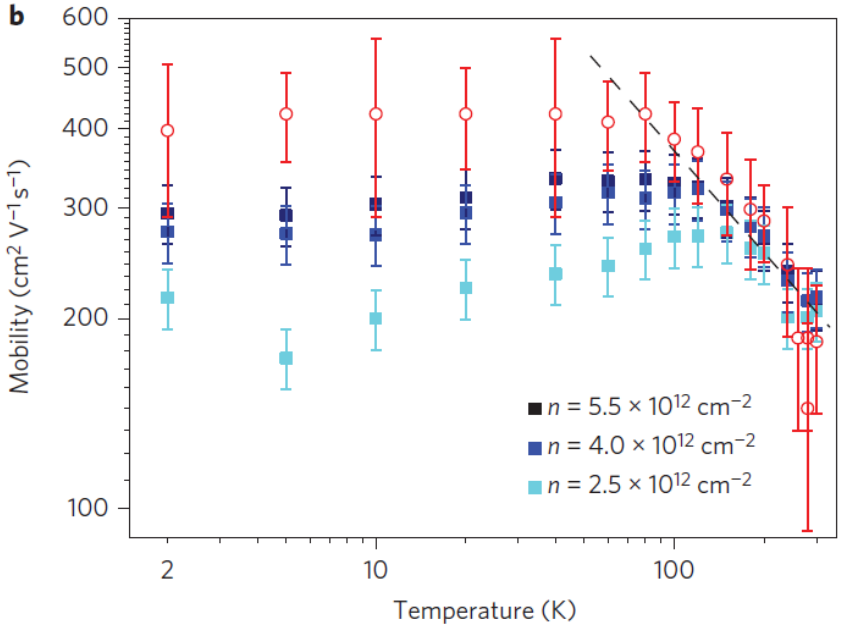
WS2



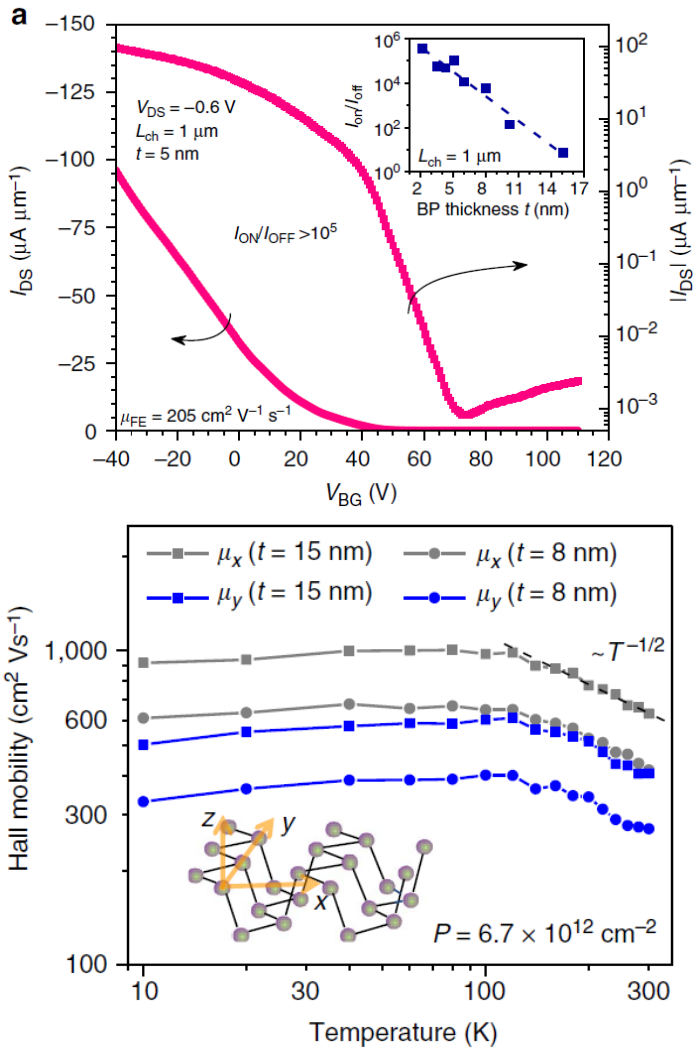
Ovchinnikov et al, ACS Nano (2014)

Transport properties

BP



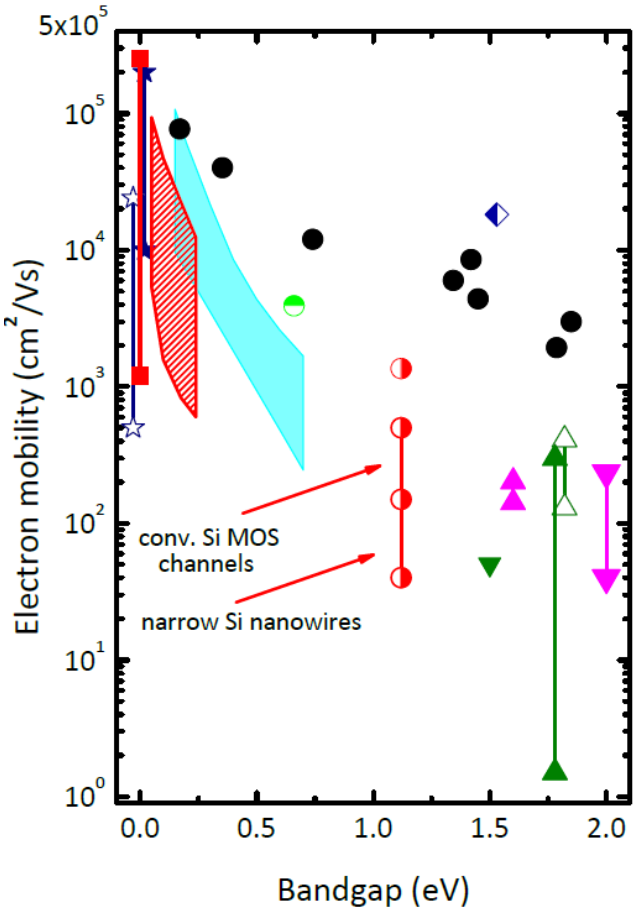
Li et al., Nat. Nanotech. (2014)

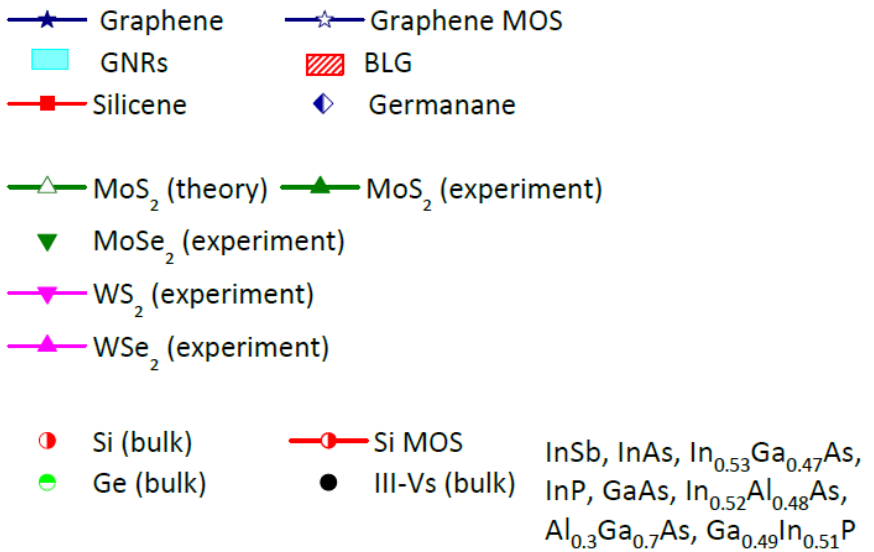


Xia et al., Nat. Commun. (2014)

Transport properties

Mobility vs Bandgap





- The hole mobility (not shown) exhibits a similar trend.
- Regarding mobility, the 2Ds do not show a distinct advantage over the conventional 3D bulk materials. HOWEVER, …

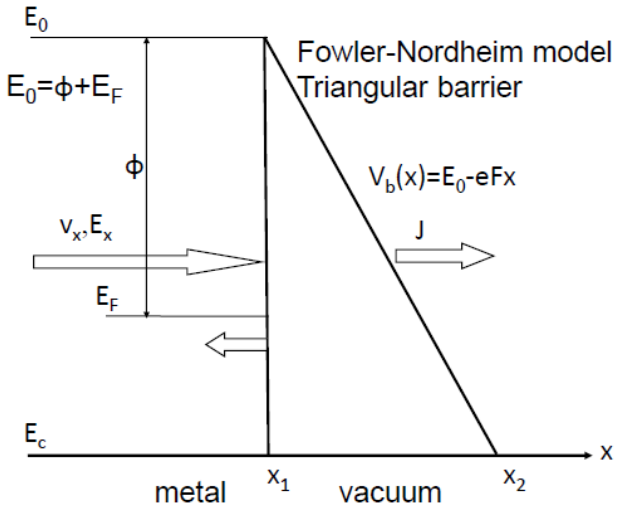
Electron mobility of different semiconductors vs bandgap.
FS, Proc. IEEE 101, 1567 (2013), updated; FS, Nature Nanotechnol. 5, 487 (2010), updated.

Transport properties

Tunneling (our-of-plane) transport

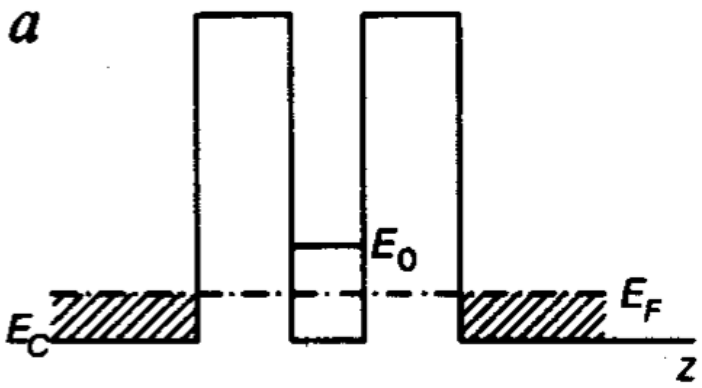
- Thermionic current
- Direct tunneling
- Fowler-Nordheim Theory

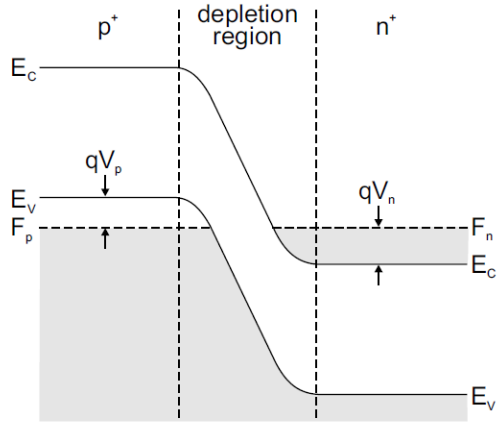
Current ∝ Density of states

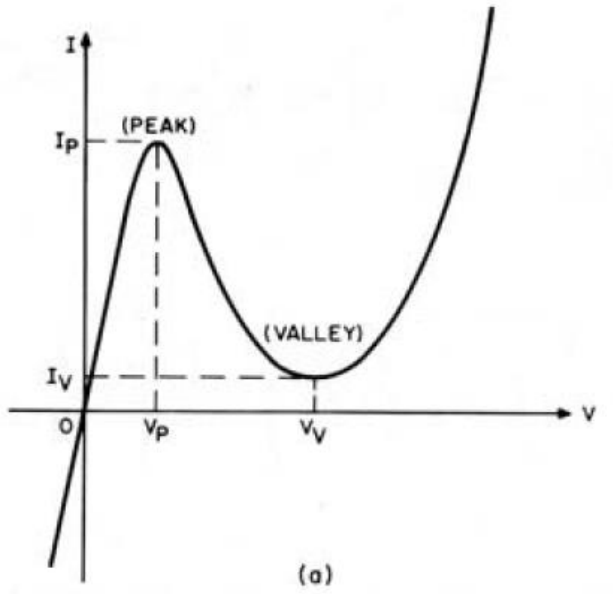


Transport properties

Resonant tunneling







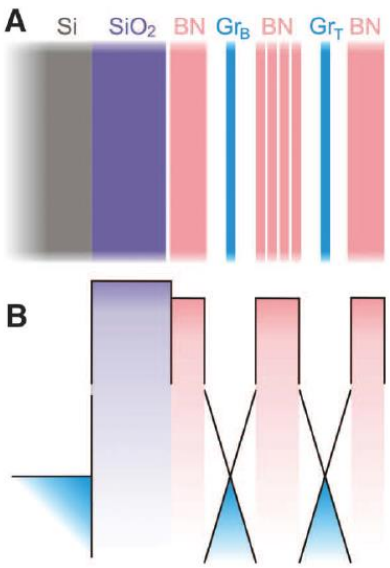
NDR – negative differential resistance

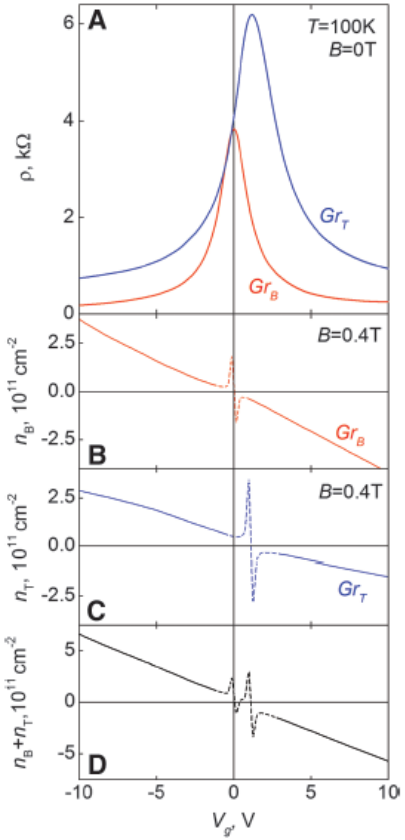
Transport properties

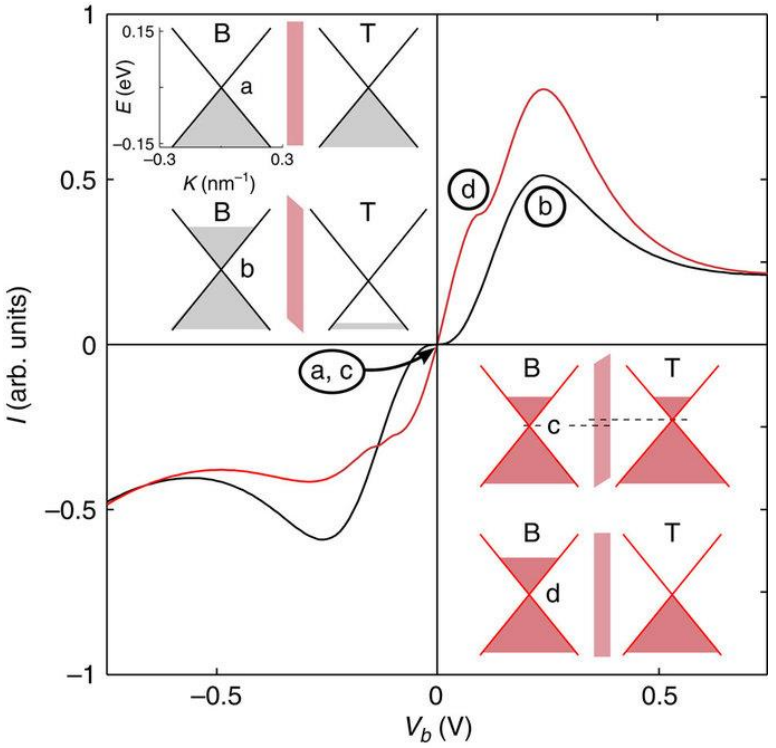
Tunneling (our-of-plane) transport

- Graphene can be combined with semiconductor and insulating 2D crystals to create tunnel junction
- Since the position of the Fermi energy and the DOS in graphene can be varied by external gate, so as the tunneling current, which allows such structures to be used as field effect tunneling transistors (FETT)
- Tunneling → describe the difference between the simple tunneling and the resonant tunneling
- Novel heterostructure devices tunneling
- transistors, resonant tunneling diodes, light emitting diodes

Transport properties



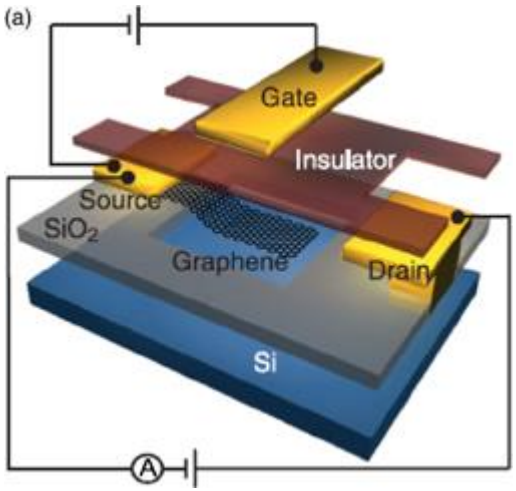


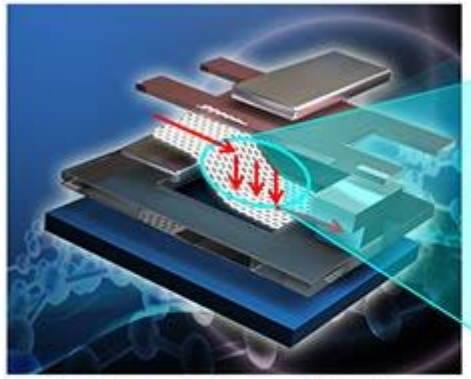


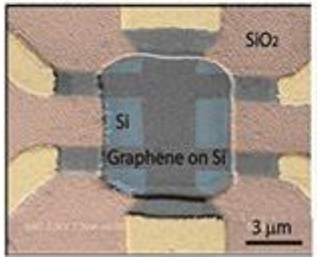
L. Britnell et al., Science 335, 947-950 (2012).

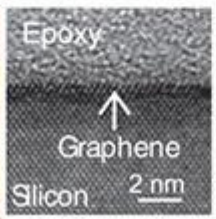
Transport properties

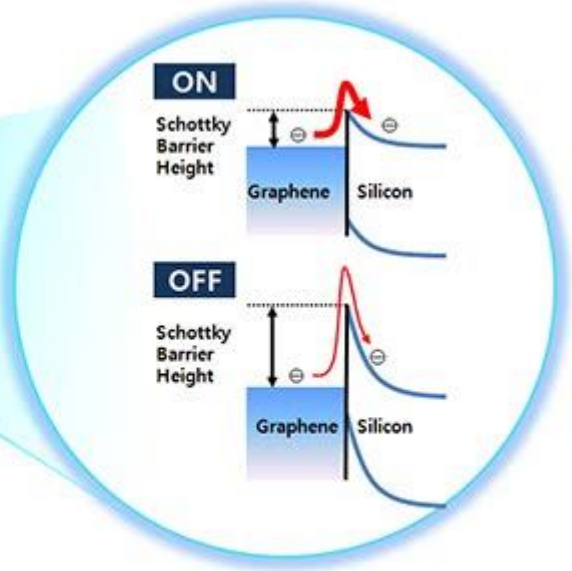
Graphene barristor





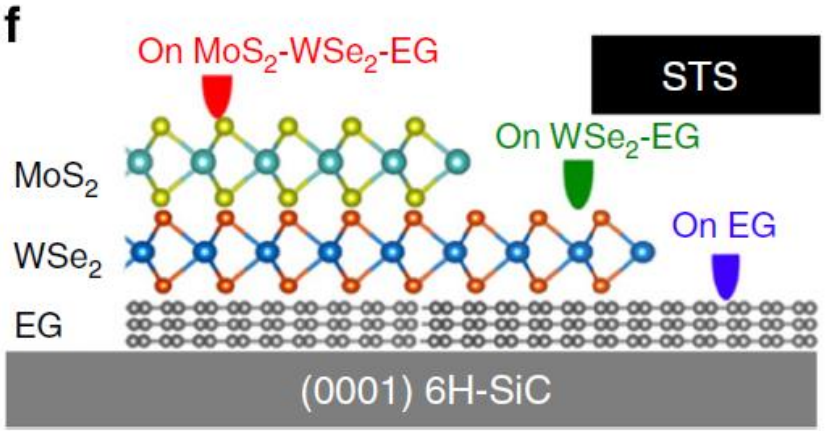


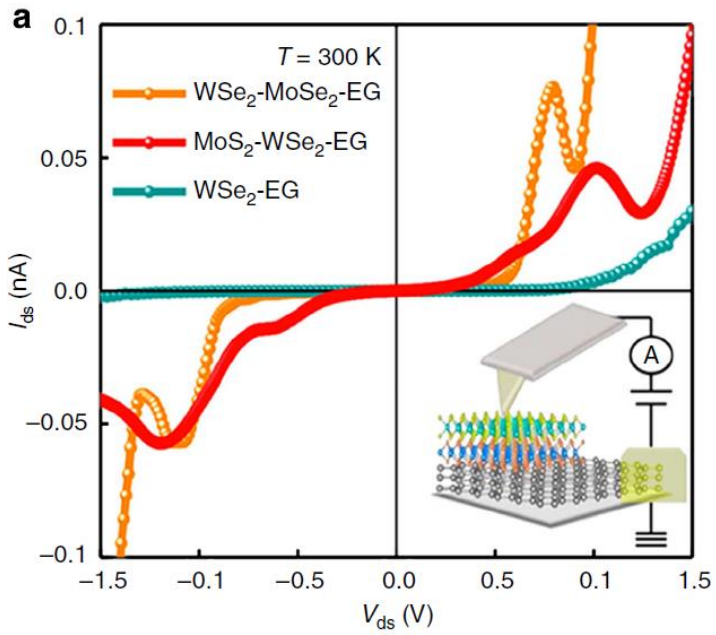


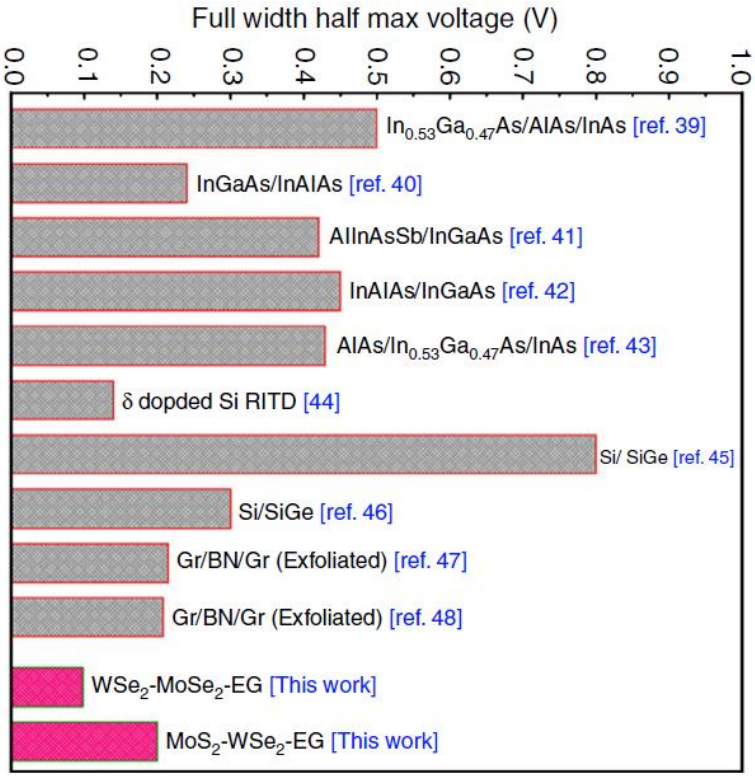


H. Yang, SKKU

Transport properties







Lin et al, Nat. Commun (2015)

Conclusion

- The family of 2D crystals grows both in terms of variety and number of materials.
- Almost every new member brings excitement in terms of the unusual electronic and transport properties.
- The most interesting phenomena can be realized in van der Waals heterostructures.
- Among the unsolved problems is the control of the surface reconstruction, charge transfers and build-in electric fields in such heterostructures.
- The standard band diagrams with quasi-electric fields is not a useful concept in 2D heterostructures, and a new framework has to be developed.
- Novel devices – valleytronics, 2D spintronics