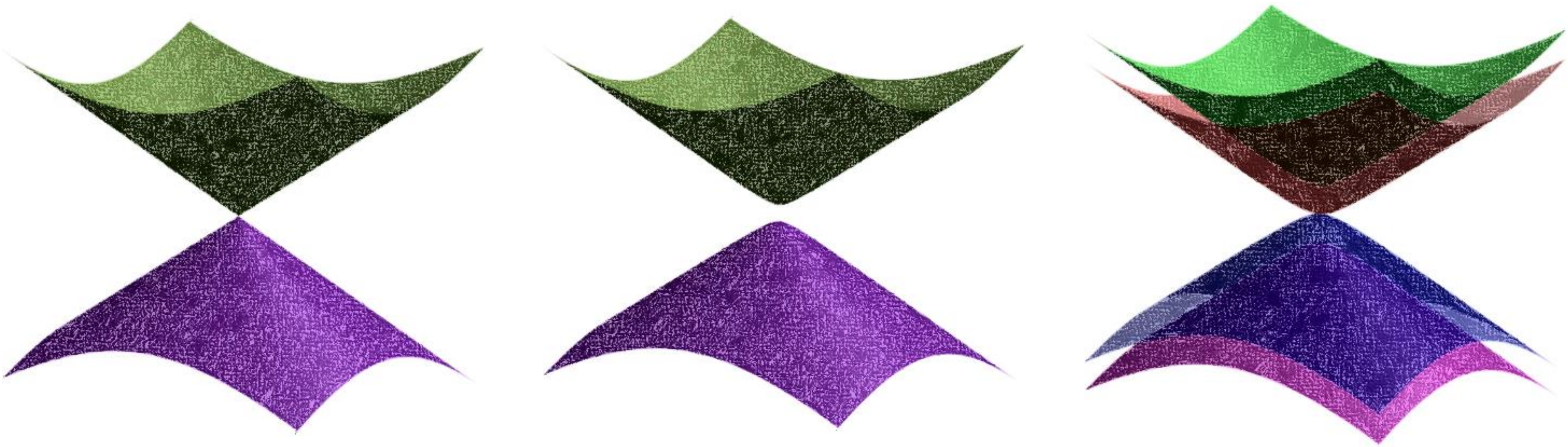
2D materials: An introduction



Alessandro Cresti

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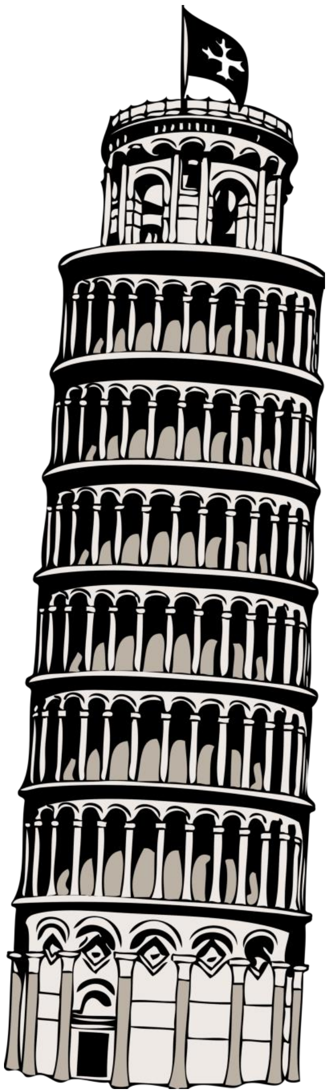
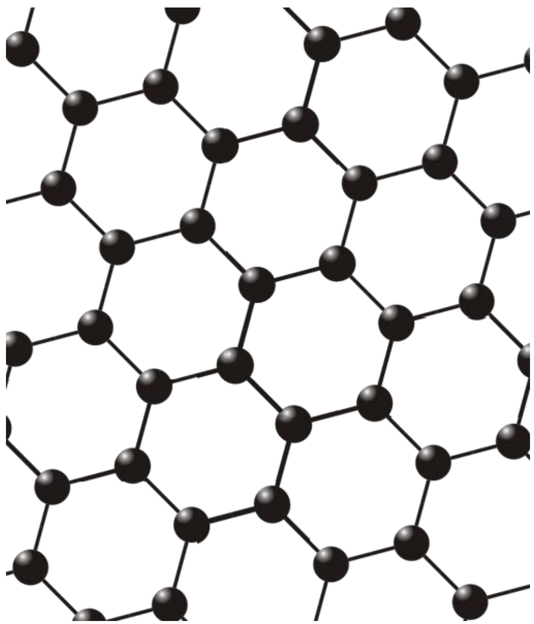
IMEP-LaHC / Grenoble INP / CNRS / Univ. Grenoble Alpes / Univ. Savoie Mont Blanc

Some years ago in Pisa…



…I was a PhD student and my advisor told me…



2005

Band Structure and Optical Properties of Graphite and of the Layer Compounds GaS and GaSe (*).

F. Bassani (**) and G. Pastori Parravicini (**)

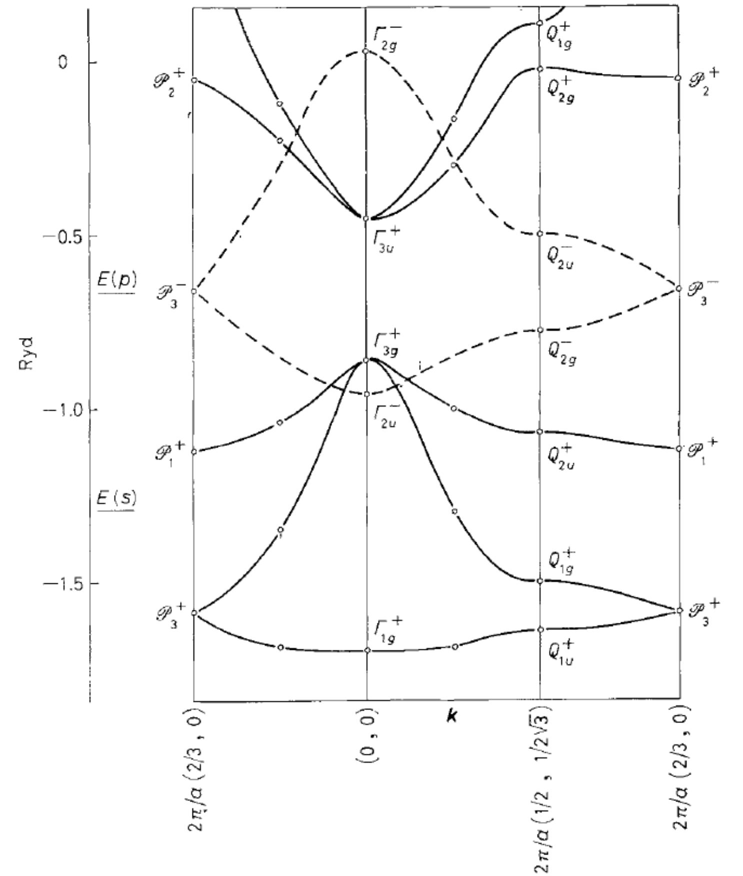


Fig. 5. – Band structure of two-dimensional graphite.

[Nuovo Cim. B 50, 95 (1967)]

1967

Foreword: The discovery of graphene

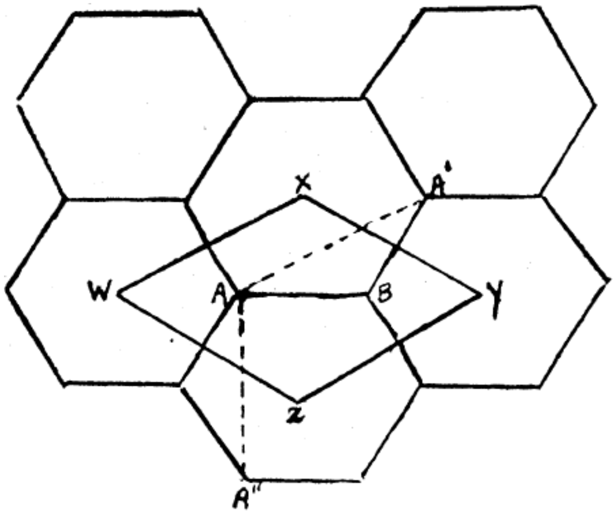
PHYSICAL REVIEW VOLUME 71, NUMBER 9 MAY 1, 1947

The Band Theory of Graphite

1947

P. R. WALLACE*
National Research Council of Canada, Chalk River Laboratory, Chalk River, Ontario

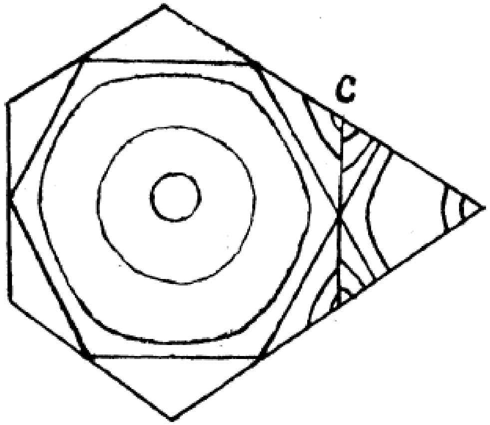
Philip R. Wallace



3. NUMBER OF FREE ELECTRONS AND CONDUCTIVITY OF A SINGLE HEXAGONAL LAYER

$$|E-E_c| \approx \sqrt{3}\pi\gamma_0 a\,|\mathbf{k}-\mathbf{k}_c|$$

Linear mass-less relativistic dispersion



Foreword: The discovery of graphene

PHYSICAL REVIEW VOLUME 104, NUMBER 3 NOVEMBER 1, 1956

Diamagnetism of Graphite

J. W. McClure

1956

Using the abbreviation $s = eH/\hbar c$, we may then write

$$\kappa_n = [(2n+1)s]^{\frac{1}{2}}, \quad \epsilon_n = \pm \hbar v [(2n+1)s]^{\frac{1}{2}}. \quad (2.3)$$

Relativistic Landau levels in graphene

Results for graphene were just a side product of those for graphite... graphene should not exist!

Landau and Peierls predicted strictly 2D and infinitely extended materials to be unstable due to thermal fluctuations.

R. Peierls *1935*

Quelques propriétés typiques des corps solides

Annales de l'I. H. P., tome 5, nº 3 (1935), p. 177-222

Indeed, real 2D materials have a finite size and may show 3D warping!

Foreword: The discovery of graphene

Electric Field Effect in Atomically Thin Carbon Films

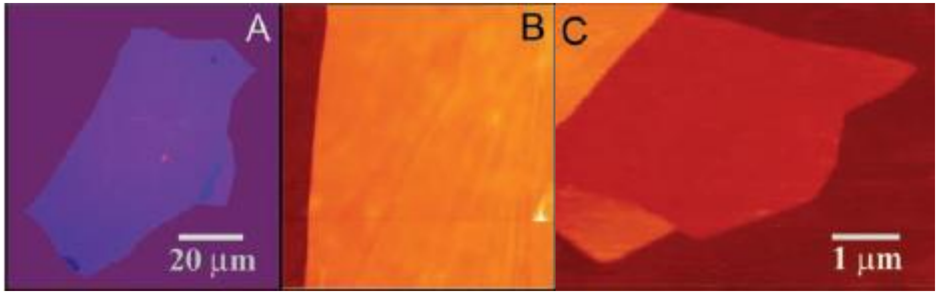
K. S. Novoselov,[1] A. K. Geim,[1*] S. V. Morozov,[2] D. Jiang,[1] Y. Zhang,[1] S. V. Dubonos,[2] I. V. Grigorieva,[1] A. A. Firsov[2]

22 OCTOBER 2004 VOL 306 SCIENCE

2004

A. Geim

K. Novoselov



2010 Nobel Prize

"for groundbreaking experiments regarding the two-dimensional material graphene"

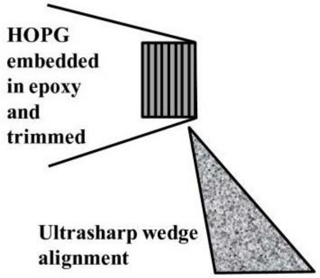
Foreword: The discovery of graphene

Ozyilmaz's Group, National University of Singapore - **https://www.youtube.com/watch?v=rphiCdR68TE**

Foreword: The discovery of graphene

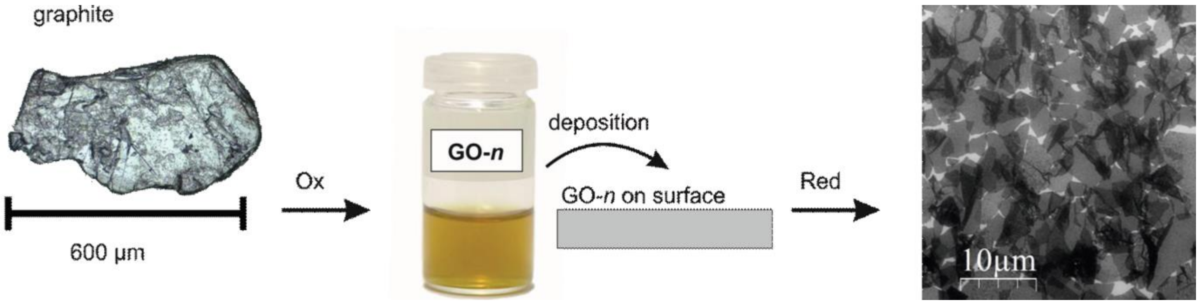
Exfoliated graphene

Mechanical cleavage



[Nanoscale Res. Lett. 6, 95 (2011)]

Graphite oxide reduction

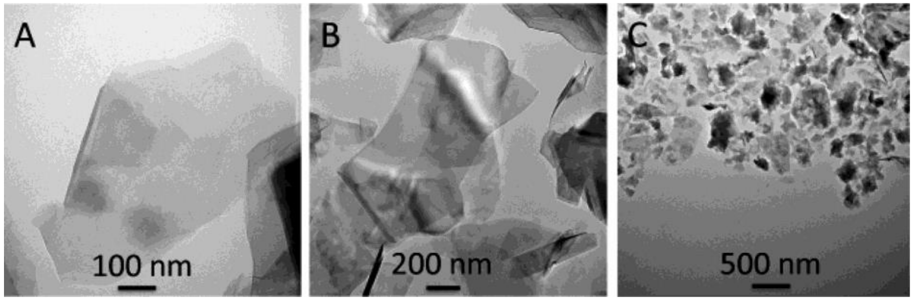


[S. Eigler et al., Adv. Mat. 25, 3583 (2013)]

Shearing in liquid

[Nat. Mat. 13, 624 (2014)]

Sonication

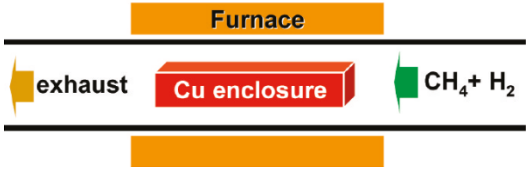


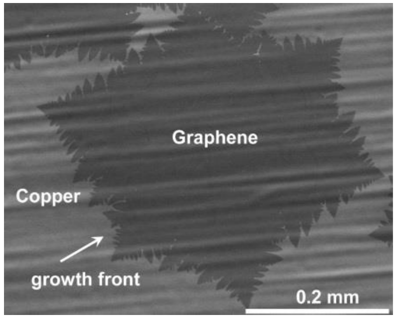
[S. J. Woltornist et al., ACS Nano 7, 7062 (2013)]

Foreword: The discovery of graphene

Epitaxial graphene

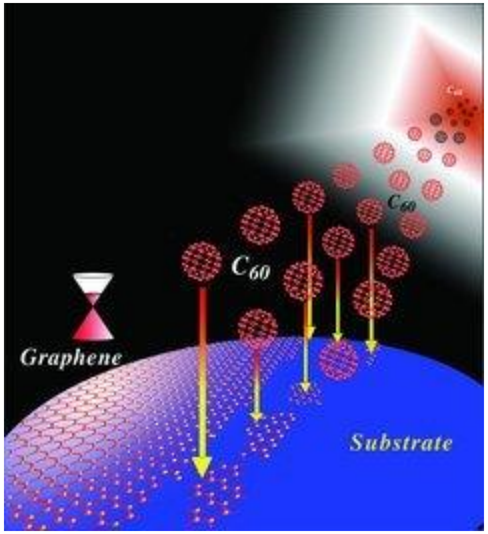
Chemical vapor deposition (CVD)





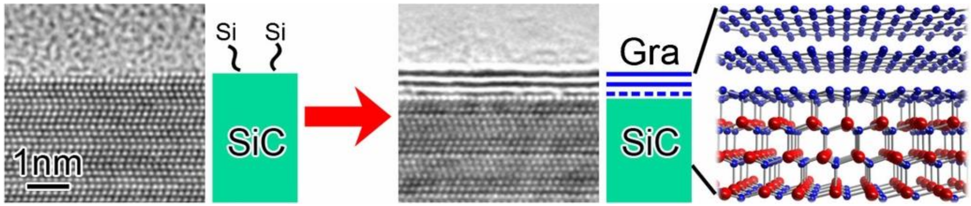
[X. Li et al., J. Am. Chem. Soc. 133, 2816 (2011)]

Molecular beam epitaxy (MBE)

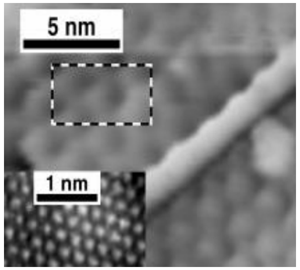


[J. Park et al., Adv. Mater. 22, 4140 (2010)]

Thermal decomposition on the (0001)surface of 6H-SiC



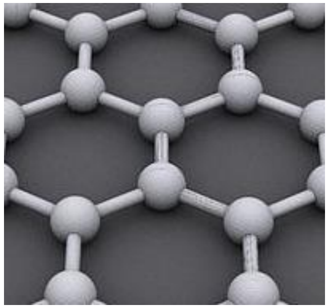
[W. Norimatsu et al., Semicond. Sci. Technol. 29, 064009 (2014)]

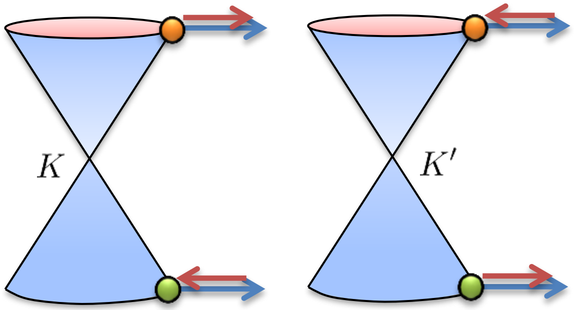


[C. Berger et al., J. Phys. Chem. B 108, 19913 (2004)]

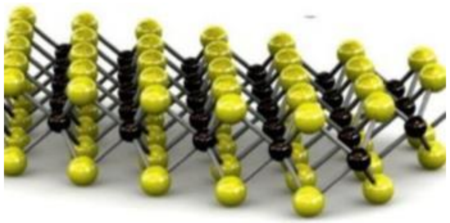
Plan

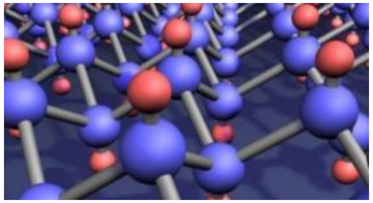
- Graphene: structure and properties

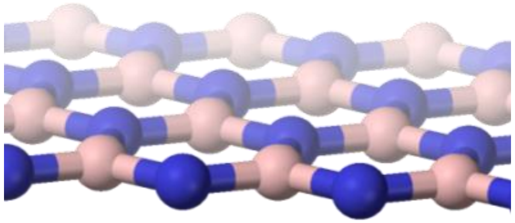




- Other 2D materials: TMDs, SMCs, X-enes, X-anes…



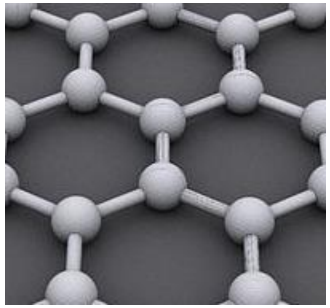


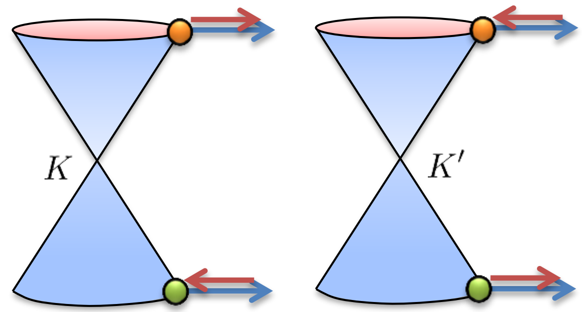


- Applications of 2D materials: electronics, optoelectronics, spintronics and many more

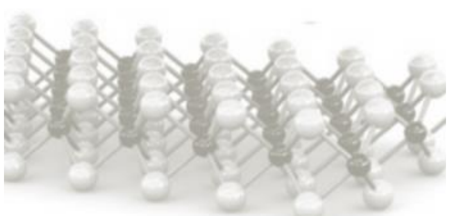
Plan

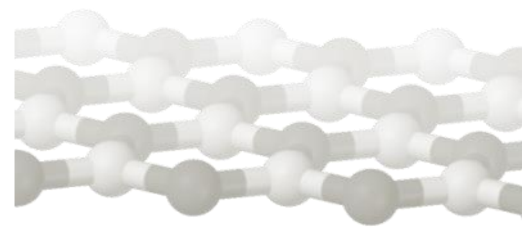
- Graphene: structure and properties





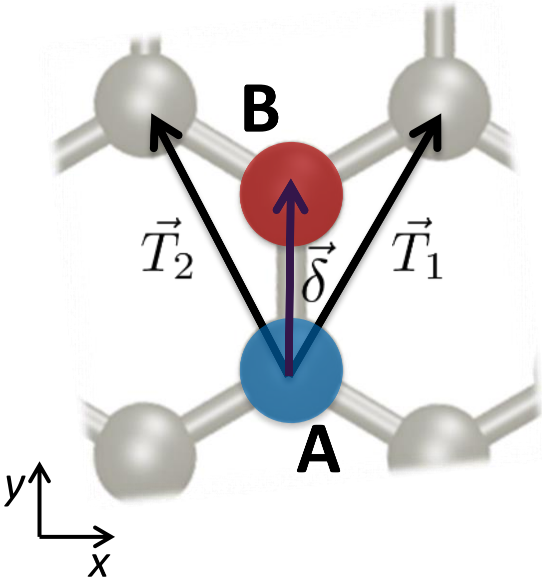
- Other 2D materials: TMDs, SMCs, X-enes, X-anes…





- Applications of 2D materials: electronics, optoelectronics, spintronics and many more

Graphene lattice and reciprocal space



triangular lattice with basis (2 atoms per unit cell)

$$\vec{T}_1 = \begin{bmatrix} \frac{\sqrt{3}}{2}a \\ \frac{3}{2}a \end{bmatrix} \qquad \vec{T}_2 = \begin{bmatrix} -\frac{\sqrt{3}}{2}a \\ \frac{3}{2}a \end{bmatrix} \qquad \vec{\delta} = \begin{bmatrix} 0 \\ a \end{bmatrix}$$

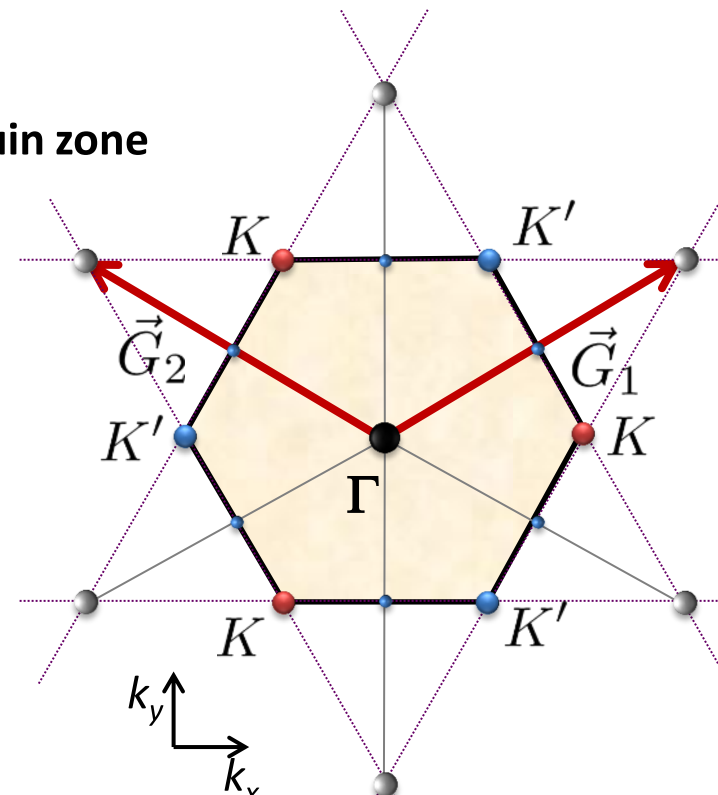
Reciprocal space

hexagonal Brillouin zone

$$\vec{G}_i \cdot \vec{T}_j = 2\pi\delta_{ij}$$

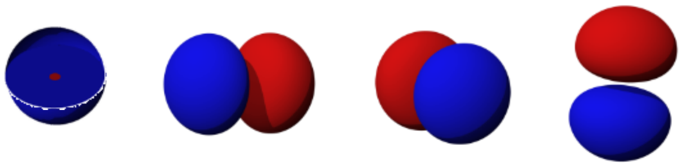
$$\vec{G}_1 = \begin{bmatrix} \frac{2\pi}{\sqrt{3}a} \\ \frac{2\pi}{3a} \end{bmatrix} \qquad \vec{G}_2 = \begin{bmatrix} -\frac{2\pi}{\sqrt{3}a} \\ \frac{2\pi}{3a} \end{bmatrix}$$

$$\Gamma = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \qquad K = \begin{bmatrix} \frac{4\pi}{3\sqrt{3}a} \\ 0 \end{bmatrix} \qquad K' = \begin{bmatrix} \frac{-4\pi}{3\sqrt{3}a} \\ 0 \end{bmatrix}$$

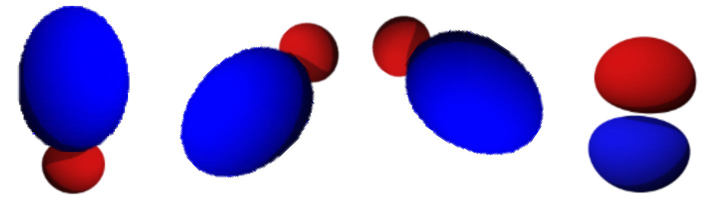


A convenient orbital basis for graphene

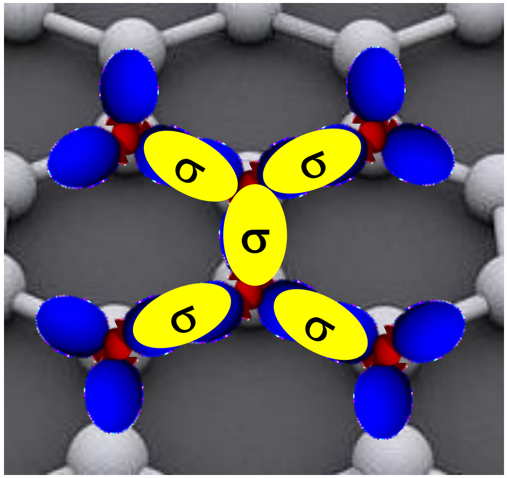
carbon electronic configuration [He] $2s^2\,2p^2$



sp^2 hybridization



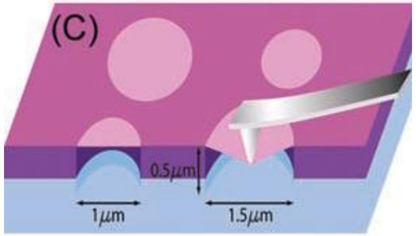
σ bonds

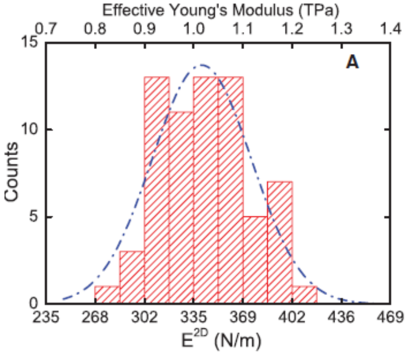


Stiff → Young's modulus 1.0 ± 0.1 TPa

Strong → tensile strength 130 GPa → 42 N/m

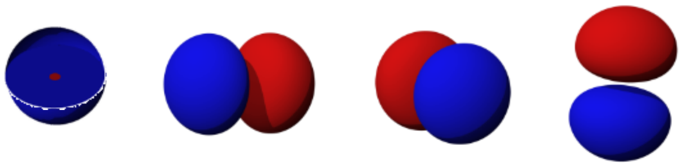
Stretchable → up to 20%



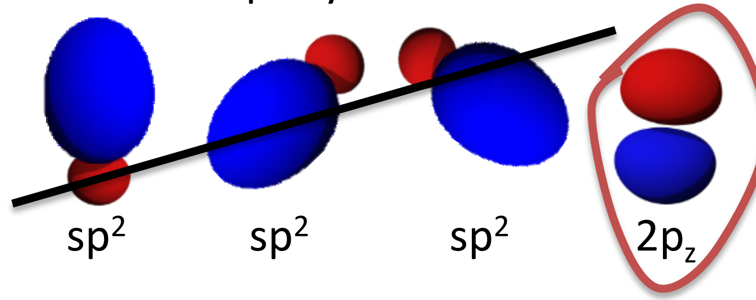


The sp^2 orbitals form strong covalent σ bonds, which give mechanical stability to graphene and have high energy.

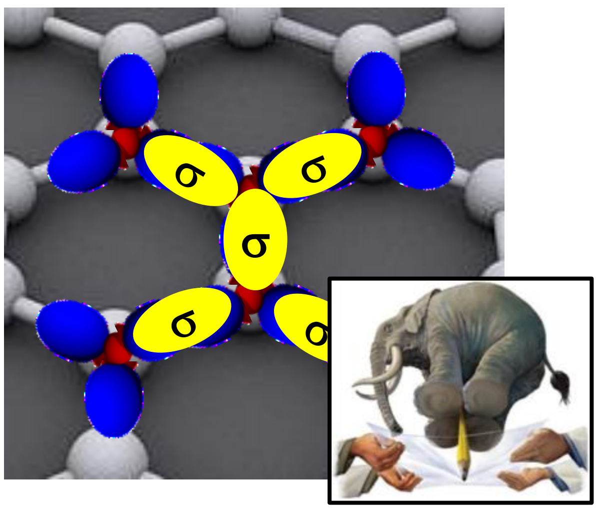
[D. G. Papageorgiou et al., Prog. Mat. Science 90, 75 (2017)] carbon electronic configuration [He] $2s^2\,2p^2$



sp^2 hybridization

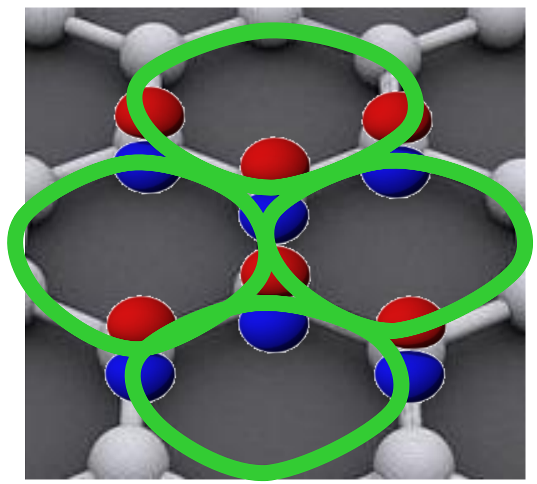


σ bonds



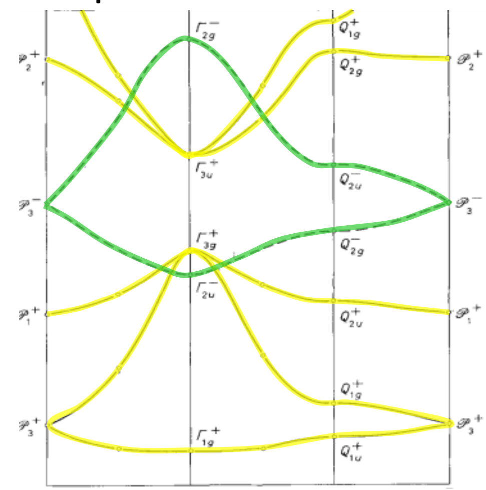
The sp^2 orbitals form strong covalent σ bonds, which give mechanical stability to graphene and have high energy.

π bonds



The 2p$_z$ orbitals form weaker and delocalized π bonds, which have low energy and determine the electronic properties.

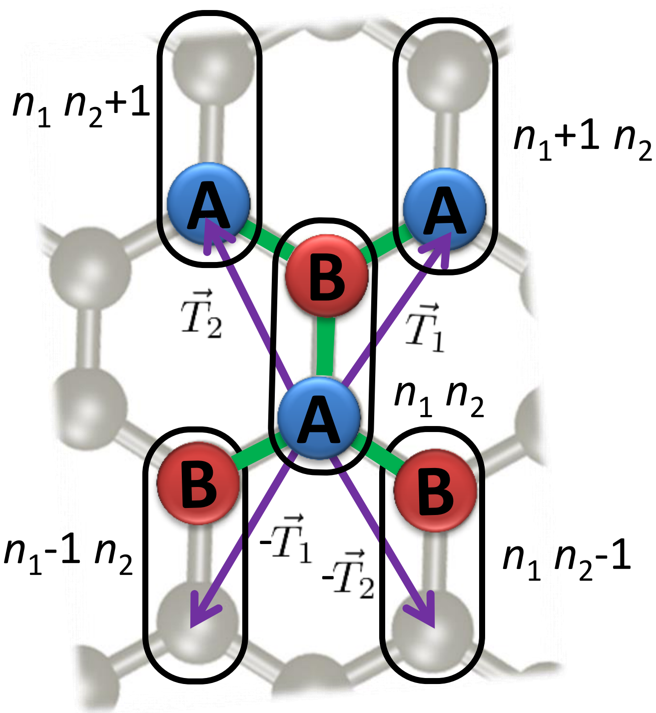
complete band structure



[Pastori Parravicini et al., Nuovo Cim. B 50, 95 (1967)]

For the description of the electron properties around the charge neutrality point, we can limit to 2p$_z$ orbitals.

Graphene first-nearest-neighbor tight-binding Hamiltonian



Bloch states

$$|\Phi^A(\vec{k})\rangle = \frac{1}{\sqrt{N}} \sum_{n_1 n_2} e^{i\vec{k}\cdot(n_1\vec{T}_1+n_2\vec{T}_2)}|\phi^A_{n_1n_2}\rangle$$

$$|\Phi^B(\vec{k})\rangle = \frac{1}{\sqrt{N}} \sum_{n_1 n_2} e^{i\vec{k}\cdot(n_1\vec{T}_1+n_2\vec{T}_2)}|\phi^B_{n_1n_2}\rangle$$

Generic state with vector *k*

$$|\Psi(\vec{k})\rangle = \Psi^A(\vec{k})|\Phi^A(\vec{k})\rangle + \Psi^B(\vec{k})|\Phi^B(\vec{k})\rangle$$

basis : $2p_z$ orbital per carbon atom

$$|\phi^A_{n_1n_2}\rangle = |\phi_{2p_z}(n_1\vec{T}_1 + n_2\vec{T}_2)\rangle$$

$$|\phi^B_{n_1n_2}\rangle = |\phi_{2p_z}(n_1\vec{T}_1 + n_2\vec{T}_2 + \vec{\delta}\,)\rangle$$

first-nearest-neighbor tight-binding Hamiltonian

$$H|\phi^A_{n_1n_2}\rangle = t|\phi^B_{n_1n_2}\rangle + t|\phi^B_{n_1-1,n_2}\rangle + t|\phi^B_{n_1,n_2-1}\rangle$$

$$H|\phi^B_{n_1n_2}\rangle = t|\phi^A_{n_1n_2}\rangle + t|\phi^A_{n_1+1,n_2}\rangle + t|\phi^A_{n_1,n_2+1}\rangle$$

k-dependent Hamiltonian

$$H|\Phi^A(\vec{k})\rangle = t\left(1 + e^{-i\vec{k}\cdot\vec{T}_1} + e^{-i\vec{k}\cdot\vec{T}_2}\right)|\Phi^B(\vec{k})\rangle$$

$$H|\Phi^B(\vec{k})\rangle = t\boxed{\left(1 + e^{i\vec{k}\cdot\vec{T}_1} + e^{i\vec{k}\cdot\vec{T}_2}\right)}|\Phi^A(\vec{k})\rangle$$

$$H(\vec{k}) = t\begin{bmatrix} 0 & f(\vec{k}) \\ f^*(\vec{k}) & 0 \end{bmatrix}$$

$$\boxed{H(\vec{k})\begin{bmatrix} \Psi^A(\vec{k}) \\ \Psi^B(\vec{k}) \end{bmatrix} = E(\vec{k})\begin{bmatrix} \Psi^A(\vec{k}) \\ \Psi^B(\vec{k}) \end{bmatrix}}$$

Graphene energy bands

k-dependent Hamiltonian

$$H(\vec{k}) = t\begin{bmatrix} 0 & f(\vec{k}) \\ f^*(\vec{k}) & 0 \end{bmatrix} \qquad f(\vec{k}) = 1 + 2e^{-i3ak_y/2}\cos(\sqrt{3}ak_x/2)$$

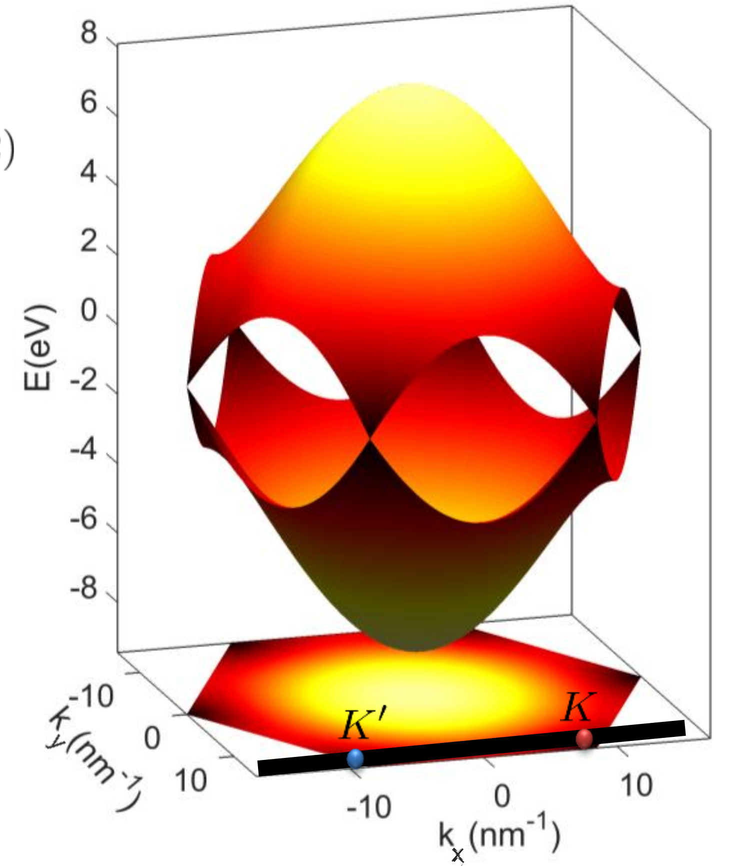
Eigenvalues

$$E(\vec{k}) = t\sqrt{1 + 4\cos(3ak_y/2)\cos(\sqrt{3}ak_x/2) + 4\cos^2(\sqrt{3}ak_x/2)}$$

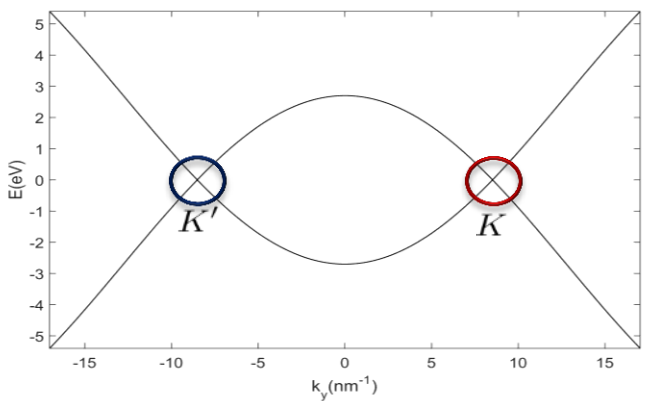
Eigenstates

$$\begin{bmatrix} \Psi^A(\vec{k}) \\ \Psi^B(\vec{k}) \end{bmatrix}_\pm = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ \pm\frac{f(\vec{k})}{|f(\vec{k})|} \end{bmatrix}$$

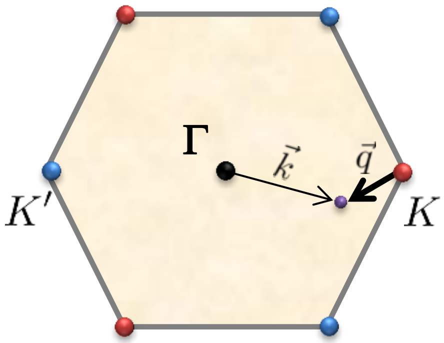
$$|\Psi_\pm(\vec{k})\rangle = \frac{1}{\sqrt{2}}|\Phi^A(\vec{k})\rangle \pm \frac{1}{\sqrt{2}}\frac{f(\vec{k})}{|f(\vec{k})|}|\Phi^B(\vec{k})\rangle$$



- two components (A/B): **pseudospin**
- **semimetal** = zero band-gap semiconductor
- **linear isotropic dispersion (cones) at** K and K' points
- **low-energy** physics around K and K'



Graphene – low energy approximation



For wave vectors close to the K point

$$\vec{k} = \vec{K} + \vec{q} = \left[\frac{4\pi}{3\sqrt{3}a} + q_x \; ; \; q_y \right]$$

$$f(\vec{k}) = f(\vec{K} + \vec{q}) = 1 + 2e^{-i3aq_y/2} \cos(2\pi/3 + \sqrt{3}aq_x/2) \approx -\frac{3}{2}a(q_x - iq_y)$$

Pauli matrices operating on pseudospin

$$H_K(\vec{q}) \equiv H(\vec{K} + \vec{q}) \approx -\frac{3}{2}at \begin{bmatrix} 0 & q_x - iq_y \\ q_x + iq_y & 0 \end{bmatrix} = -\frac{3}{2}at \; \vec{\sigma} \cdot \vec{q}$$


Paul Dirac

2D Dirac equation for relativistic particles with spin 1/2

$$H_{2D}^{\mathrm{Dirac}}(\vec{k}) = \hbar c \; \vec{\sigma} \cdot \vec{k} + mc^2 \sigma_z \qquad E(\vec{k}) = \pm \sqrt{\hbar^2 c^2 k^2 + c^4 m^2}$$

- **spin** (Dirac equation) **↔** **pseudospin** (sublattice degree of freedom for graphene)
- **subluminal velocity** $v = \frac{3}{2} \frac{a|t|}{\hbar} \approx c/300$
- **zero mass** $m = 0$

K and K' = Dirac points
linear energy dispersion = Dirac cones

Consequences of graphene band structure: charge mobility

The Fermi velocity is much larger than in other standard materials as silicon (~100 larger): **high charge mobility**

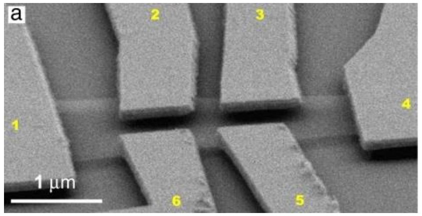
electric field — current density — electron density

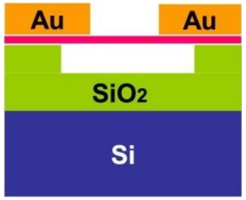
$$v_d = \mu E \;\rightarrow J = e(\, n\, \mu_e + p\, \mu_h\,)\, E$$

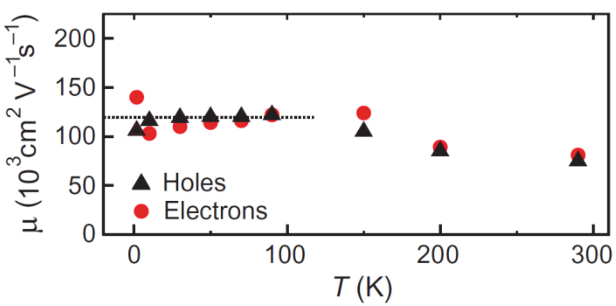
drift velocity

Exfoliated graphene over SiO_2 $\mu \leq 25\,000$ $cm^2/(Vs)$ @ $n = 5 \times 10^{12}$ cm^{-2} [PRL 99, 246803 (2007)]

Suspended exfoliated graphene
$\mu = 230\,0000$ $cm^2/(Vs)$ @ $n = 2 \times 10^{11}$ cm^{-2}
[Sol. State Comm. 146, 351 (2008)]



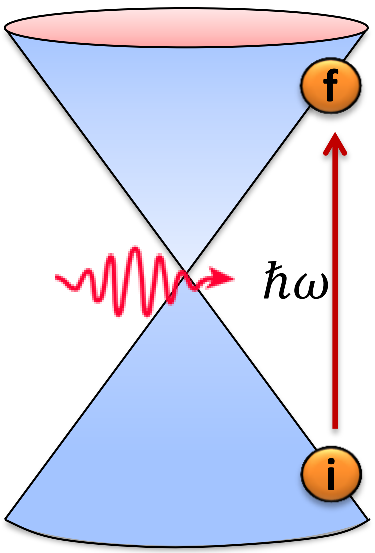




CVD graphene encapsulated in hBN
$\mu > 100\,000$ $cm^2/(Vs)$
[Science Adv. 1, e1500222 (2015)]

Crystalline silicon $\mu \approx 1\,500$ $cm^2/(Vs)$ @300K - AlGaAs/GaAs 2DEGs $\mu \approx 35\,000\,000$ $cm^2/(Vs)$

Consequences of graphene band structure: optical absorption



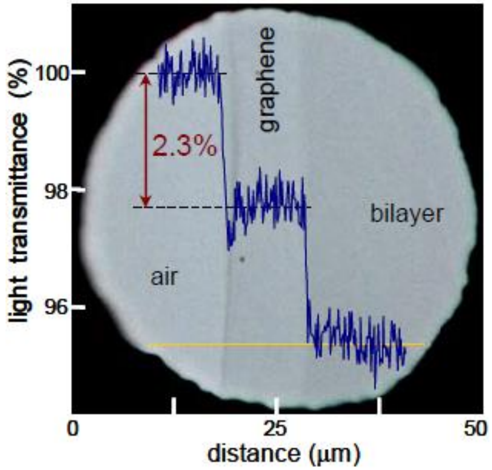
$$\boldsymbol{E} = \boldsymbol{e}Ee^{i\omega t} \qquad W_i = \frac{c}{4\pi}E^2 \qquad W_a = \eta\hbar\omega \qquad \eta = \frac{2\pi}{\hbar}|M|^2\rho\left(\frac{\hbar\omega}{2}\right)$$

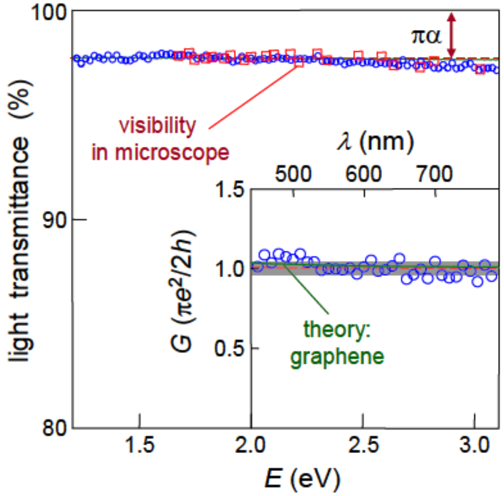
$$\rho\left(\frac{\hbar\omega}{2}\right) = \frac{\hbar\omega}{\pi\hbar^2 v_F^2} \qquad H = v_F\boldsymbol{\sigma}\cdot\boldsymbol{\pi} = v_F\boldsymbol{\sigma}\cdot\left(\boldsymbol{p} - \frac{e}{c}\boldsymbol{A}\right) = H_0 + H_{\text{int}}$$

$$\boldsymbol{A} = \frac{i}{c\omega}\boldsymbol{E} \leftarrow \boldsymbol{E} = c\partial_t\boldsymbol{A} \qquad H_{\text{int}} = -\frac{ev_F}{c}\boldsymbol{\sigma}\cdot\boldsymbol{A} = -i\frac{ev_F}{c\omega}E\boldsymbol{\sigma}\cdot\boldsymbol{e}$$

$$|M|^2 = \left|\left\langle f\left|\frac{ev_F}{i\omega}E\boldsymbol{\sigma}\cdot\boldsymbol{e}\right|i\right\rangle\right|^2 = \frac{e^2v_F^2E^2}{8\omega^2} \qquad W_a = \frac{e^2}{4\hbar}E^2 \rightarrow \frac{W_a}{W_i} = \frac{\pi e^2}{\hbar c} = \pi\alpha$$

Constant optical absorption ~2.3% over a wide spectrum





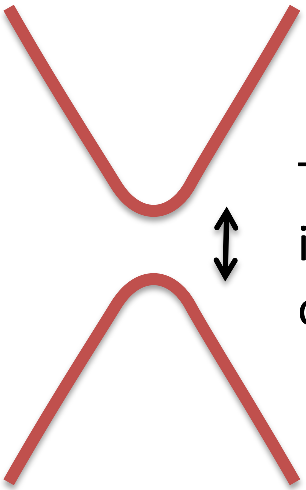
[R.R. Nair et al., Science 320, 1308 (2008)]

Spin-orbit coupling in the graphene

A **moving magnetic dipole generates an electric dipole**, which interacts with the electric field.

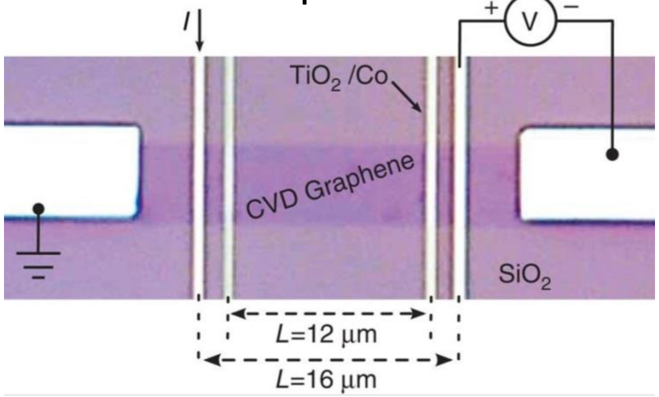
$$H_I = -\frac{e\hbar}{4m^2c^2}\left(\vec{\nabla}V \times \vec{p}\right)\cdot\vec{s} = \begin{cases} -\dfrac{e\hbar}{4m^2c^2}\dfrac{\partial_r V(r)}{r}\vec{L}\cdot\vec{s} & \text{intrinsic SOC} \\ \dfrac{e\hbar}{4m^2c^2}\left(\vec{p}\times\vec{s}\right)\cdot\vec{E} & \text{Rashba SOC} \end{cases}$$

As a consequence, **spin-orbit coupling couples π, σ and higher energy bands**.



The resulting **spin-orbit gap** in graphene is in the order of **20μeV**, i.e. **very small**!

Spin transmission **over 16 μm** at room temperature

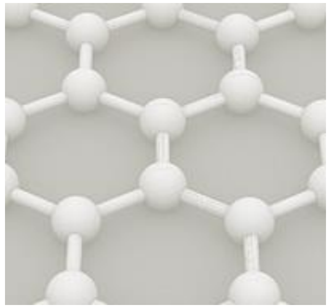


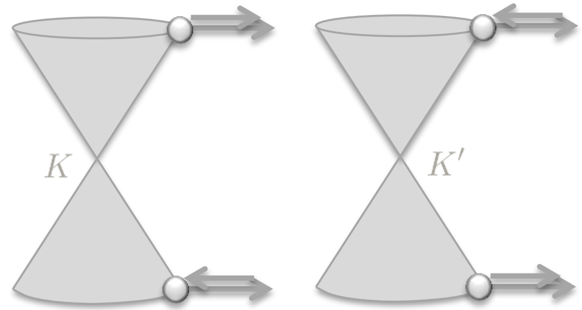
[M. V. Kamalakar et al., Nat. Comm. 6, 6766 (2015)]

[H. Min et al., PRB 74, 165310 (2006); S. Konschuh et al., PRB 82, 245412 (2010)]

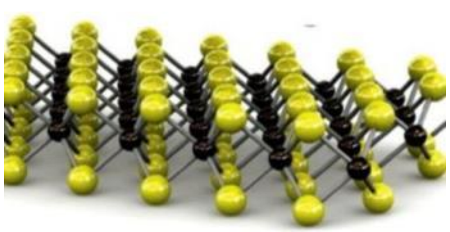
Plan

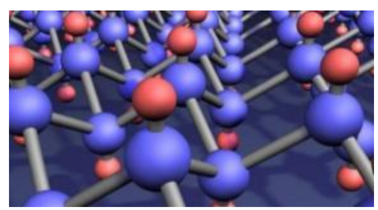
- Graphene: structure and properties

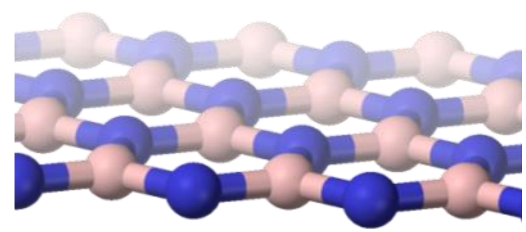




- Other 2D materials: TMDs, SMCs, X-enes, X-anes…





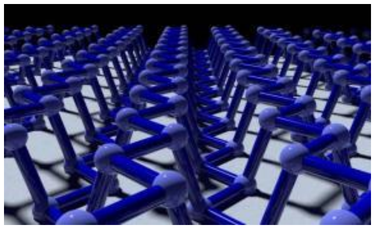


- Applications of 2D materials: electronics, optoelectronics, spintronics and many more

Many 2D materials

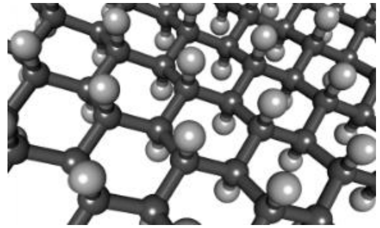
X-enes

graphene, *silicene*, *germanene*,
phosphorene, *stanene*



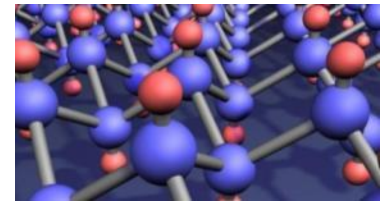
X-anes

*graphane, silicane, germanane,
phosphorane, stanane*

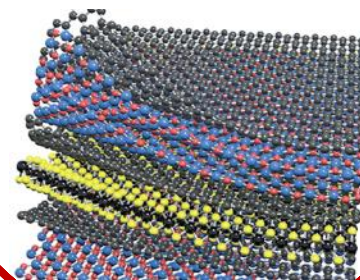


Fluoro-X-enes

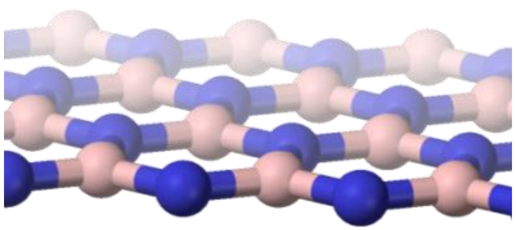
fluorographene, *fluorosilicene*,
fluorogermanene



van der Waals

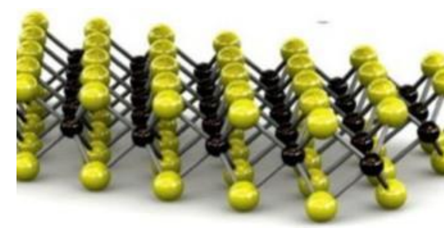


hBN



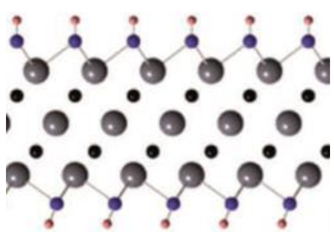
TMDs

transition metal (group IV, V and V)
+ 2 chalcogens (S, Se, Te)



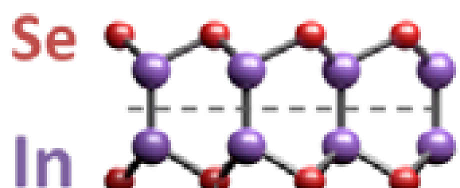
MX-enes

transition metal + C/N



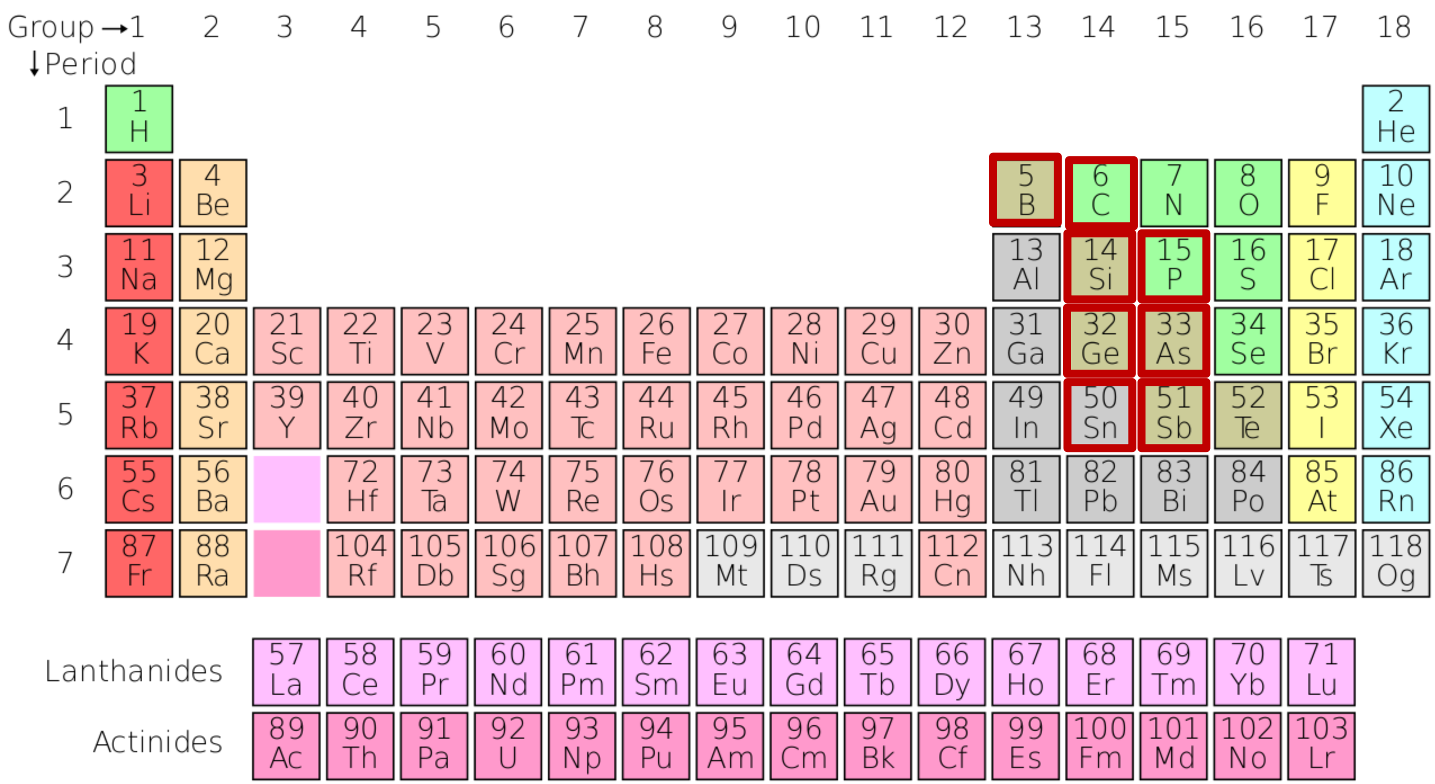
SMCs

semimetal (Ga, In) + chalcogen (S, Se)



[P. Miró, M. Audiffred and T. Heine, *An atlas of two-dimensional materials*, Chem. Soc. Rev. 43, 6537 (2014)]

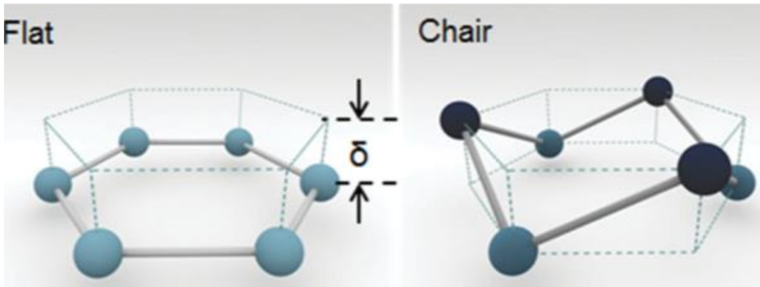
Single-layer single-element materials with hexagonal lattice.

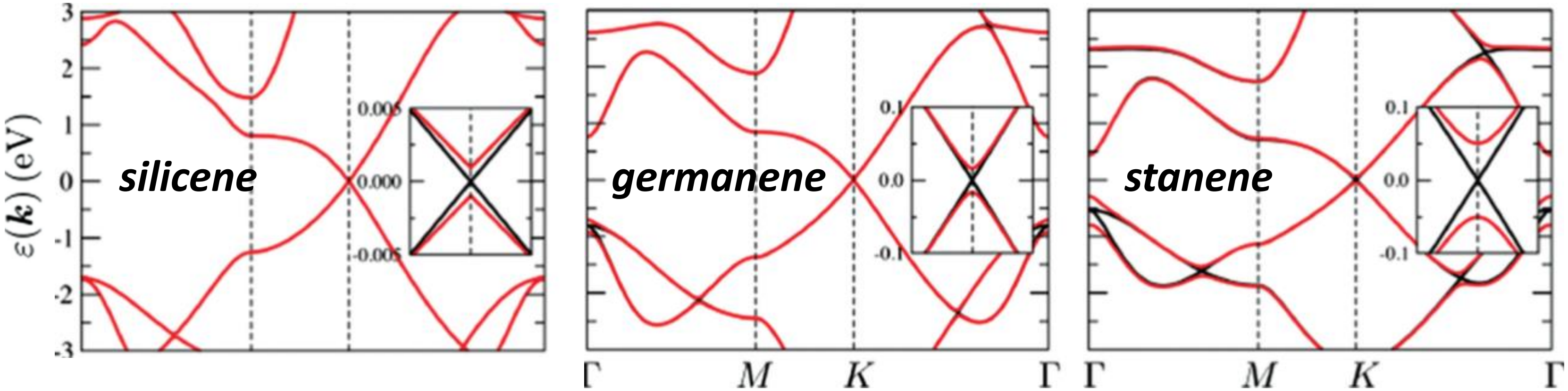


graphene, silicene, germanene, stanene, phosphorene, arsenene, antimonene, borophene…

X-enes group XIV: silicene, germanene, stanene

Si, Ge and Sn have an sp^2-sp^3 hybridization, which leads to a buckled structure.



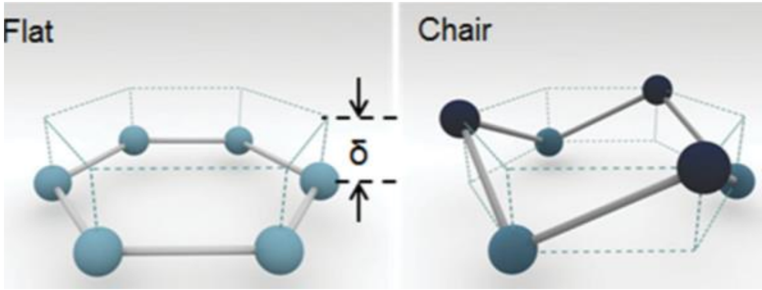


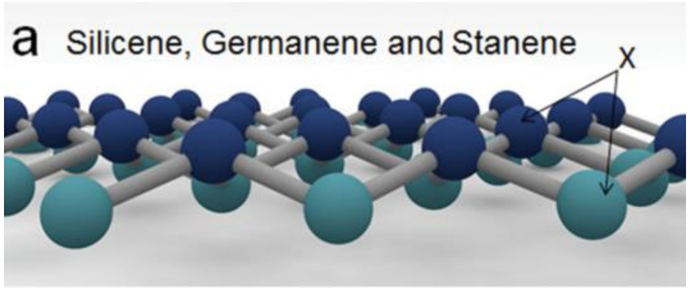
	C	Si	Ge	Sn
Lattice constant a (nm)	0.2468	0.3868	0.4060	0.4673
Bond length d (nm)	0.1425	0.2233	0.2344	0.2698
Buckling parameter δ (nm)	0	0.045	0.069	0.085
Effective electron mass m^* (m_0)	0	0.001	0.007	0.029
Fermi velocity of carriers V_F (10^6 ms^{-1})	1.01	0.65	0.62	0.55
Energy gap E_g (meV)	0.02	1.9	33	101

[Balendhran et al., Small 11, 640 (2015)]
[Matthes et al., J. P.hys. Cond. Mat. 25 , 395305 (2013)]

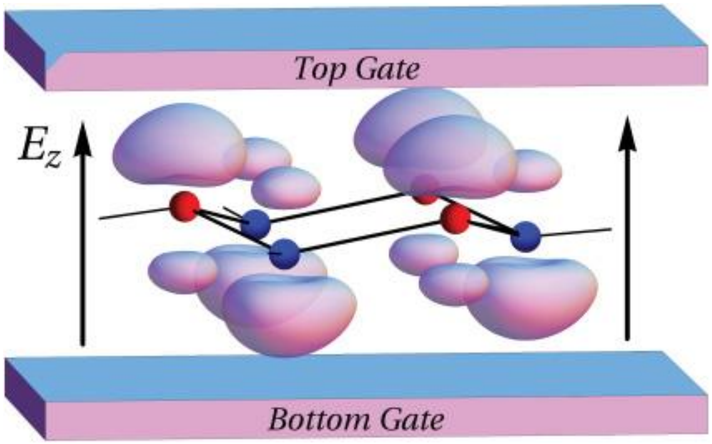
X-enes group XIV: silicene, germanene, stanene

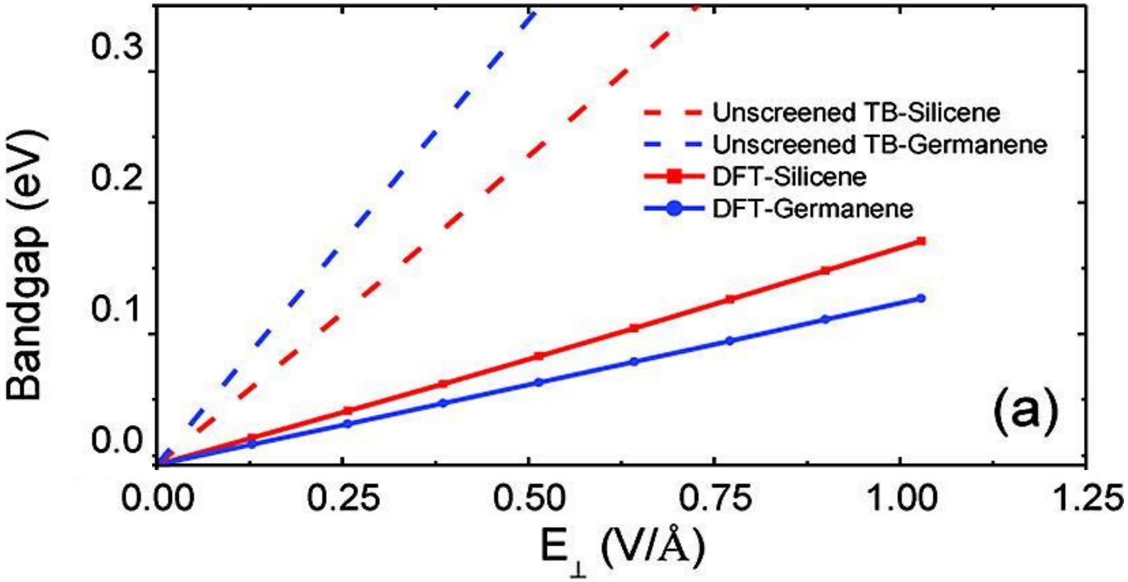
Si, Ge and Sn have an sp^2-sp^3 hybridization, which leads to a buckled structure.





A vertical electric field creates a staggered potential on A/B sublattice and generates a mass term in the Dirac equation!



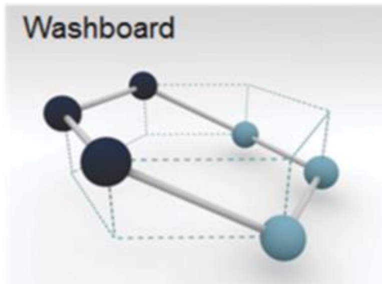


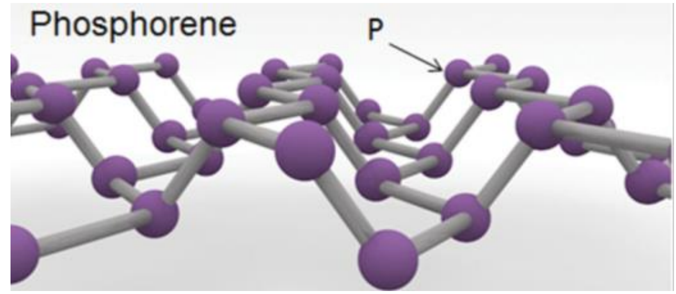
[N. D. Drummond et al., Phys. Rev. B 85, 075423 (2012)]

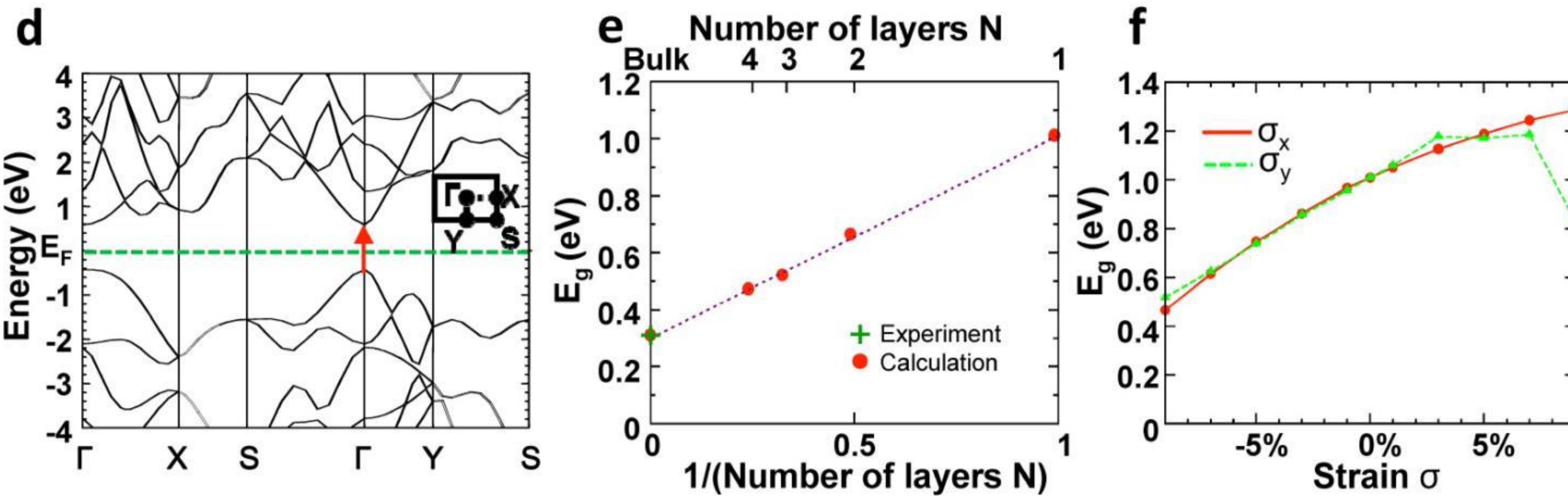
[Z. Ni et al., Nano Lett. 12,113 (2012)]

X-enes group XIV: phosphorene, arsenene, antimonene

Its structure is puckered and it is a semiconductor!

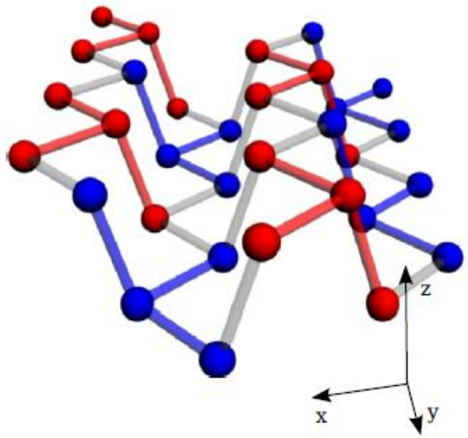


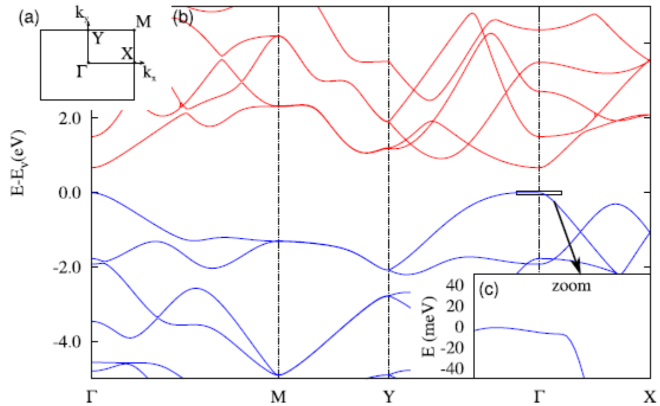




[Balendhran et al., Small 11, 640 (2015)] [H. Liu et al., ACS Nano, 8, 4033 (2014)]

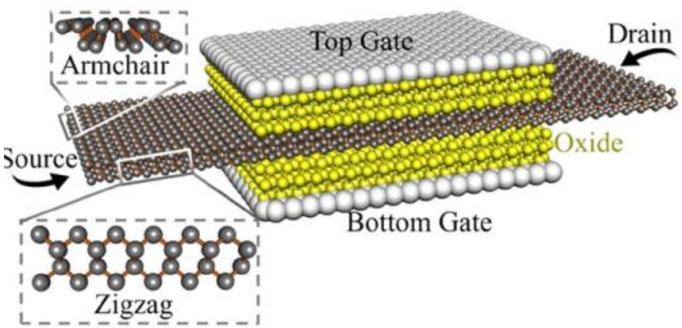
X-enes group XIV: spatial anisotropy in phosphorene

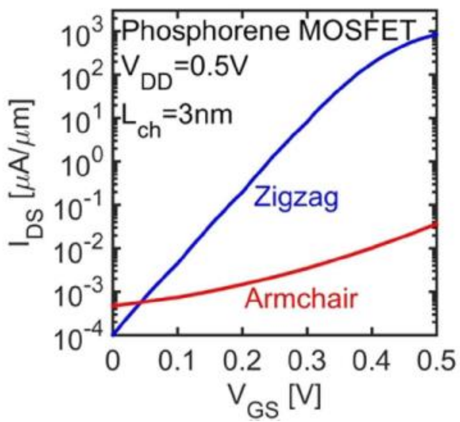




[A. S. Rodin, A. Carvalho, and A. H. Castro Neto., Phys. Rev. Lett. 112, 176801 (2014)]

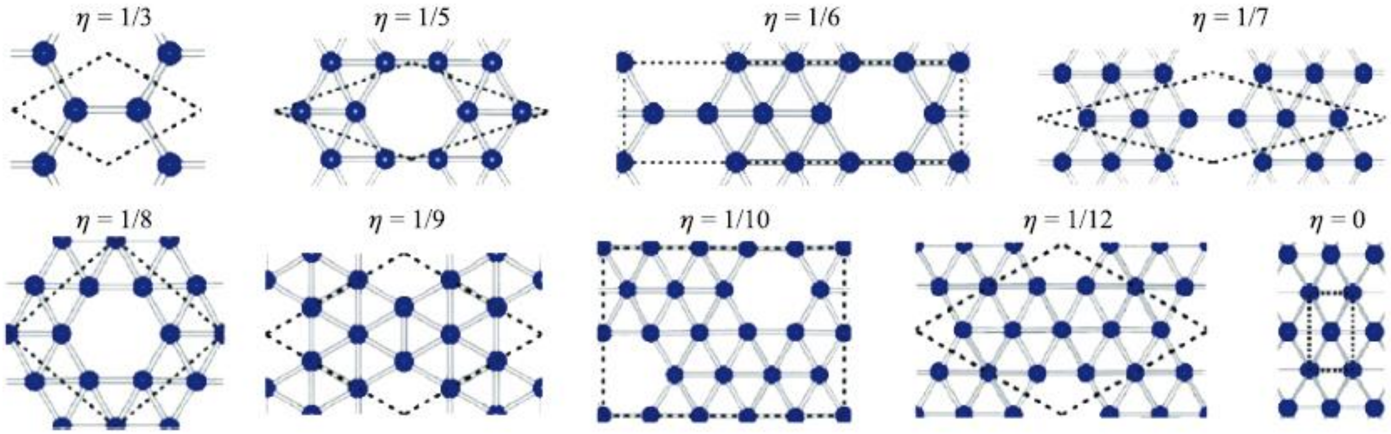
$m^*_{e,arm}$	$m^*_{e,zig}$	$m^*_{h,arm}$	$m^*_{h,zig}$	Ref.
0.17	1.09	0.15	5.84	TB
0.17	1.12	0.15	6.35	HSE06[26]
0.14	1.23	0.13	13.09	PBE[27]



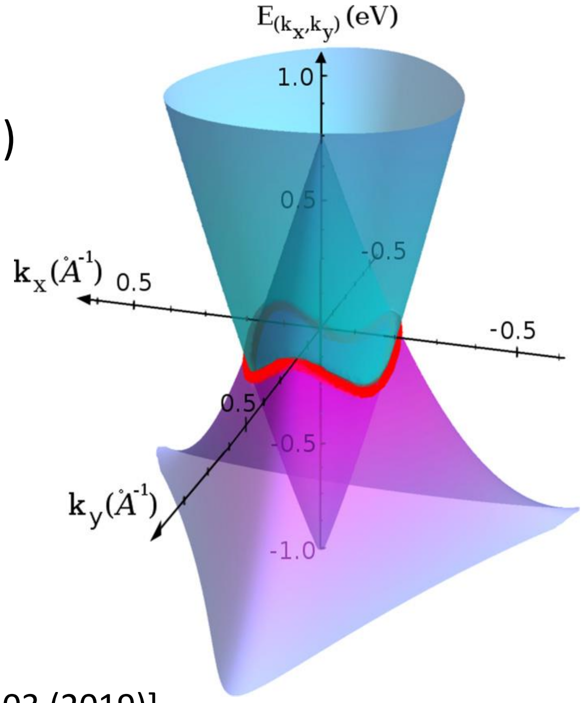


[H. Ilatikhameneh, T. Ameen, B. Novakovic, Y. Tan, G. Klimeck, R. Rahman, *Saving Moore's Law Down To 1 nm Channels With Anisotropic Effective Mass*, Scientific Reports 6, 31501 (2016)]

X-enes group XIII: borophene



- Polymorph material: different phases with different properties
- Large and anisotropic Young's modulus (up to 1.5X graphene)
- Stretchable up to 10-15%
- Large conductivity
- Presence of Dirac cones…



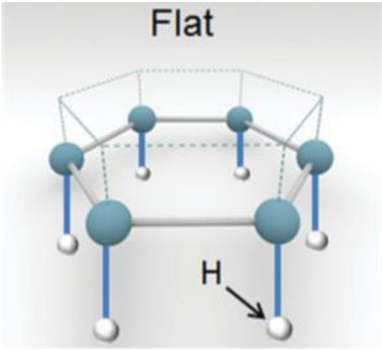
[M. Nakhaee et al., PRB98, 115413 (2018)]

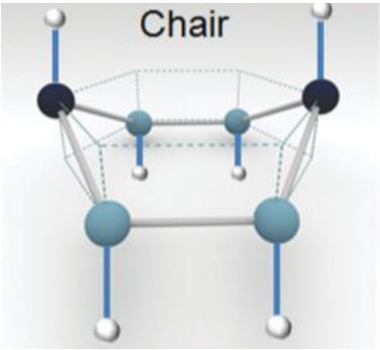
- Transfer from metallic substrate
- Instable due to boron electron deficiency
- Capping as for phosphorene? Hydrogenation? Fluorination?

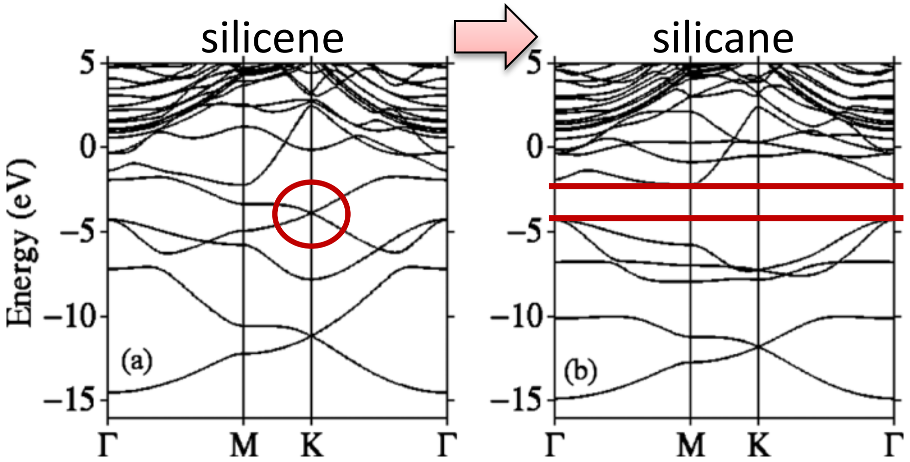
[Zhi-Qiang Wang et al., Front. Phys. 14, 33403 (2019)]

X-anes: hydrogeneted X-enes

X-enes decorated with H covalently bonded to each atom of the layer





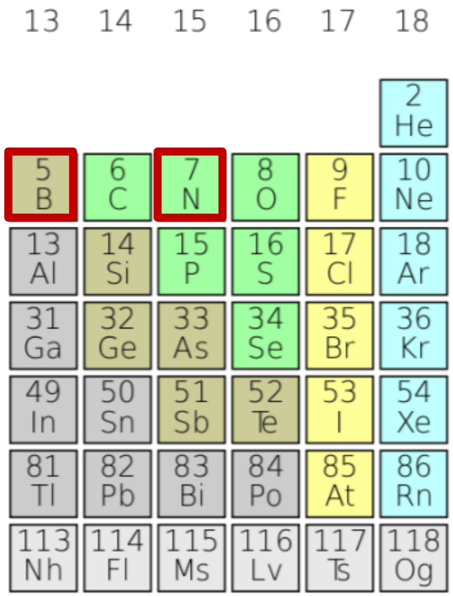


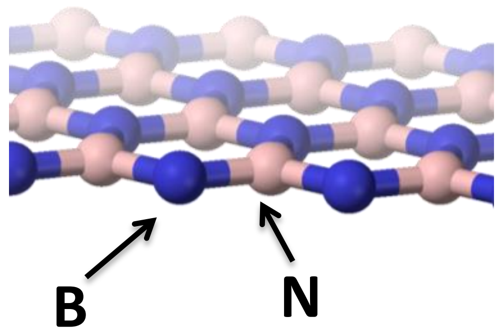
A gap opens due to covalent bonding and the Dirac cones disappear!

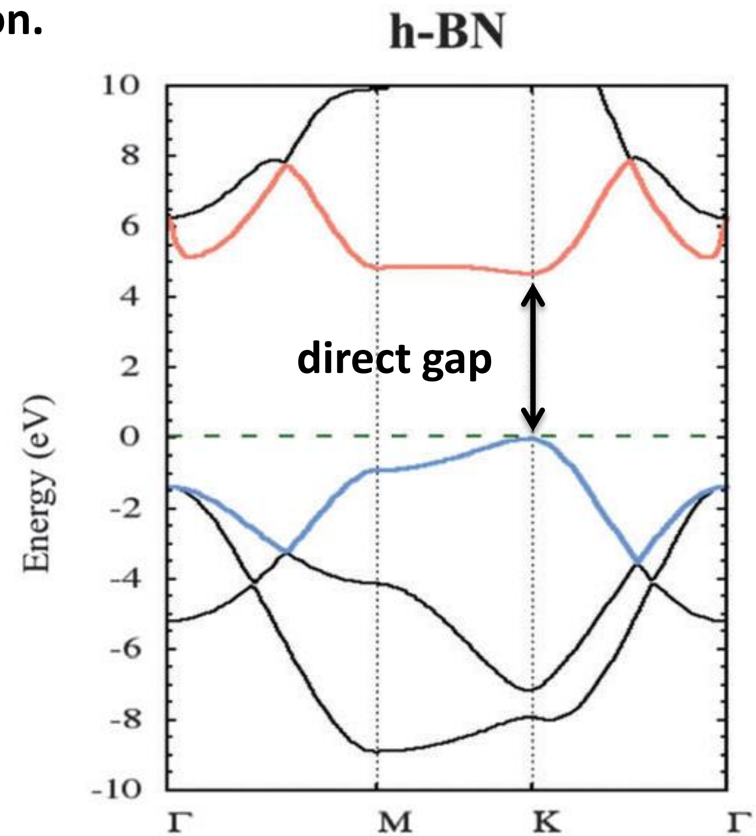
no spin-orbit coupling is considered here	CH	SiH	GeH
Lattice constant a (nm)	0.2514	0.3820	0.4091[21]
Metal-metal length d (nm)	0.1520	0.2319	0.2338
Metal-hydrogen length (nm)	0.1084	0.1502	0.1530
Buckling parameter δ (nm)	0.045	0.072	0.069
Fermi velocity of carriers V_F (10^6 ms^{-1})	0.63	0.51	0.38
Energy gap E_g (eV)	4.9[b)], 5.4[c)][27]	2.9[b)], 4.0[c)][28]	2.9[b)], 3.6[c)][28]

[Balendhran et al., Small 11, 640 (2015)] [H. Liu et al., ACS Nano, 8, 4033 (2014)]
[L. C. Lew Yan Voon et al, Appl. Phys. Lett. 97, 163114 (2010)]

Isoelectronic analog of graphene with sp^2 hybridization.





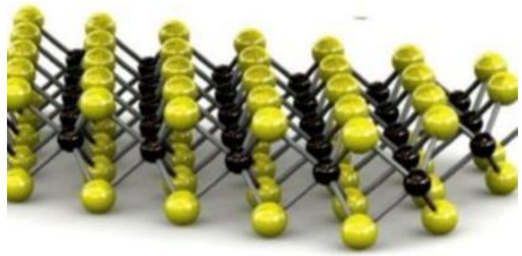


- Due to the different electronegativity of B and N, the two sublattices are no more equivalent and a gap opens!
- The lattice parameter is very similar to that of graphene: excellent substrate

[P. Miró, M. Audiffred and T. Heine, *An atlas of two-dimensional materials*, Chem. Soc. Rev. 43, 6537 (2014)]

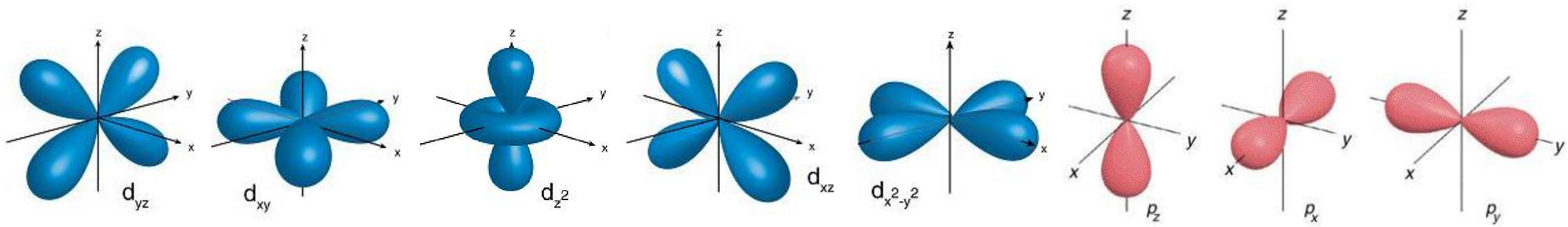
Transition metal dichalcogenides (TMDs)

MX_2 where M is a transition metal (partially filled d sub-shell) and X a chalcogen (S, Se, Te).



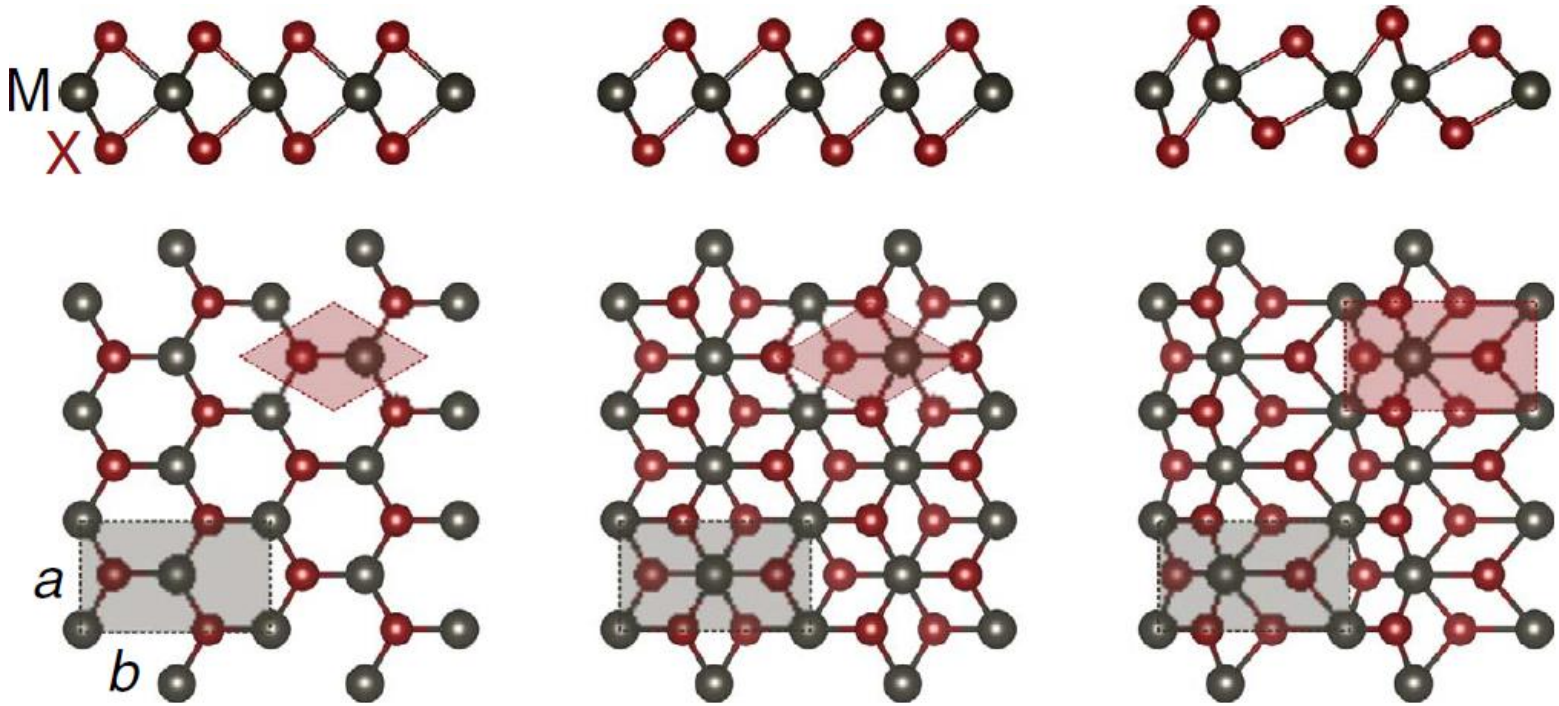
Group → / ↓Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Ms	116 Lv	117 Ts	118 Og

Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

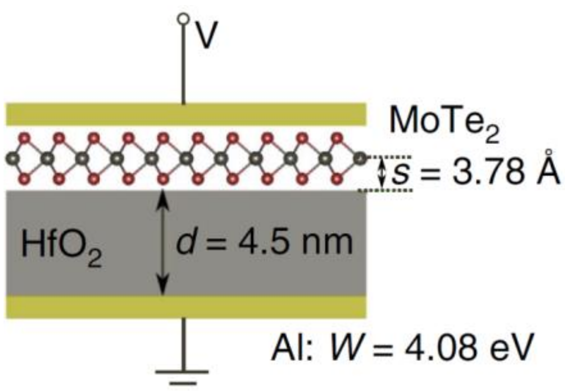


[F. A. Rasmussen and K. S. Thygesen, *Computational 2D Materials Database: Electronic Structure of Transition-Metal Dichalcogenides and Oxides*, J. Phys. Chem. C 119, 13169 (2015)]
[S. Manzeli et al., 2D transition metal dichalcogenides, Nature Reviews Materials 2, 17033 (2017)]

Transition metal dichalcogenides: 2H, 1T and 1T’ phases



2H : trigonal prismatic **1T : distorted octahedral** **1T’ : dimerized 1T**

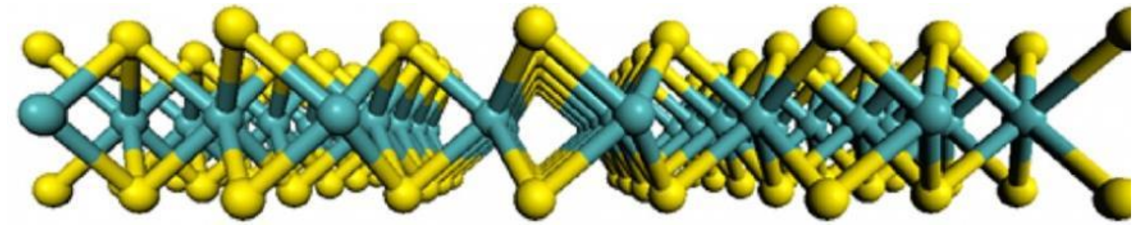


In some materials, the phase is predicted to be **switchable** by an electric field!

[Y. Li et al., Nat. Comm. 7, 10671 (2016)]

Transition metal dichalcogenides: group VI

2H phase, semiconductor
MoS_2 / $MoSe_2$ / WS_2 / WSe_2



- Conduction band minima and valence band maxima at **K and K’** points of the Brillouin zone: **direct gap**
- **Strong spin-orbit** coupling due to heavy atoms

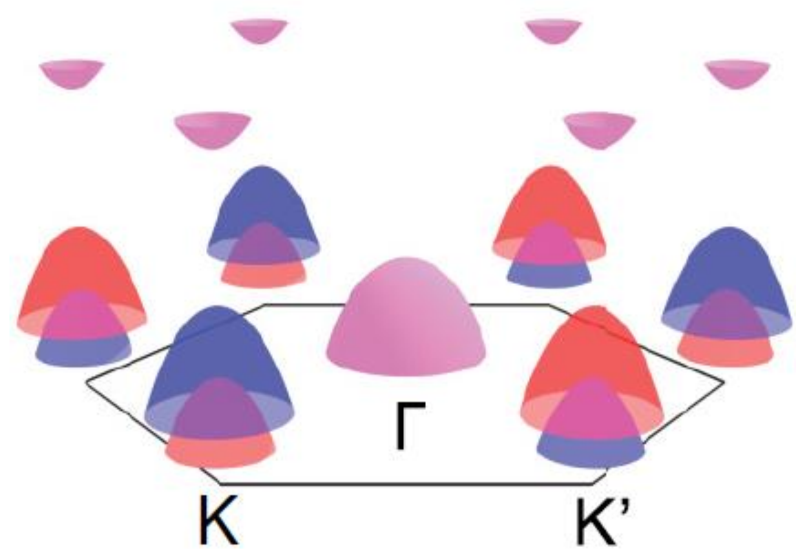
- Lack of inversion symmetry in the 2H phase: **strong spin-splitting at K/K’** points (inversion symmetry recovered for bilayer!)

✔ Time reversal symmetry $E^{\uparrow}(k)=E^{\downarrow}(-k)$

✘ Spatial inversion symmetry $E^{\uparrow}(k)=E^{\uparrow}(-k)$

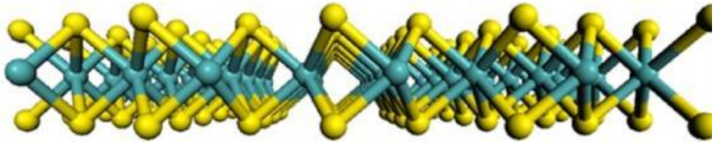
✘ → $E^{\uparrow}(k)=E^{\downarrow}(k)$ *Kramer’s degeneracy*

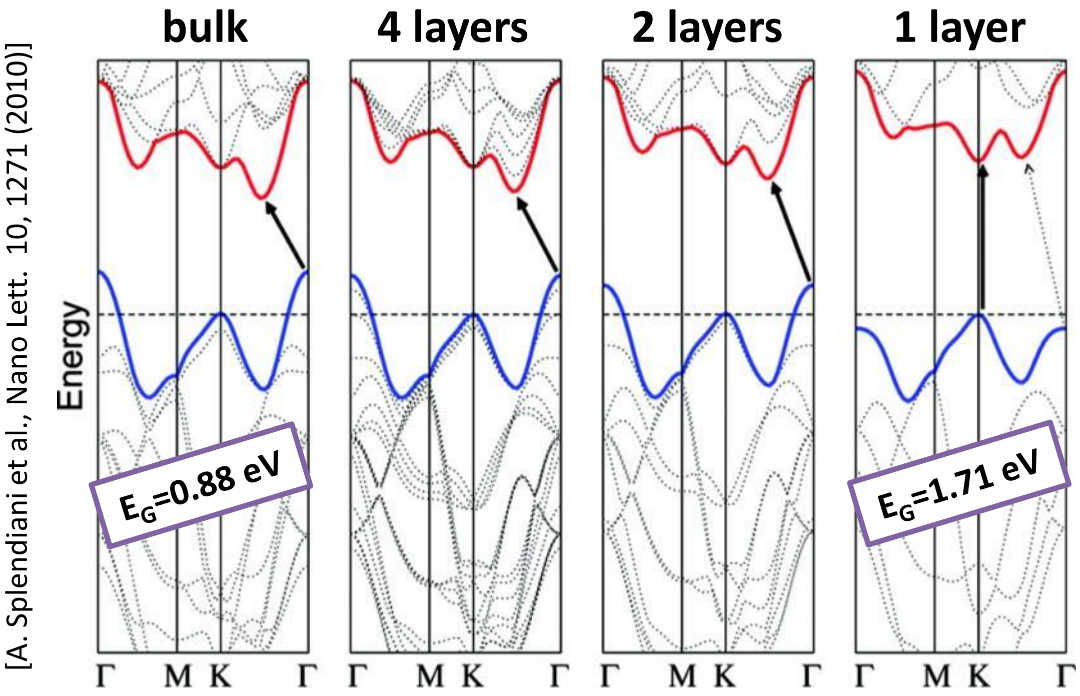
- **Spin-valley coupling**:
  valley polarization = spin polarization

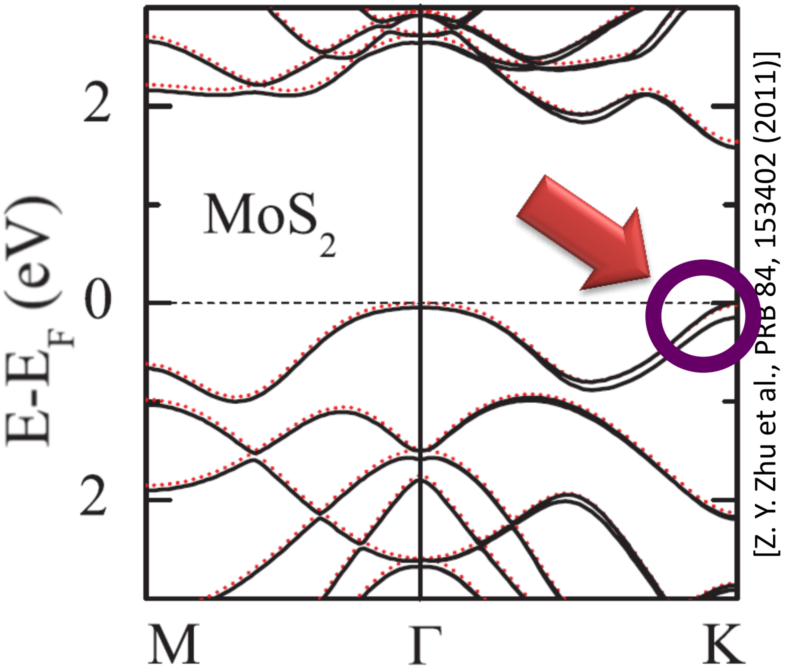


[A. Pulkin and O. V. Yazyev, PRB 93, 041419 (2016)]

MoS_2 molybdenum disulfide (TMDs - group VI)



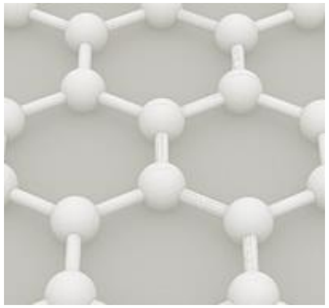


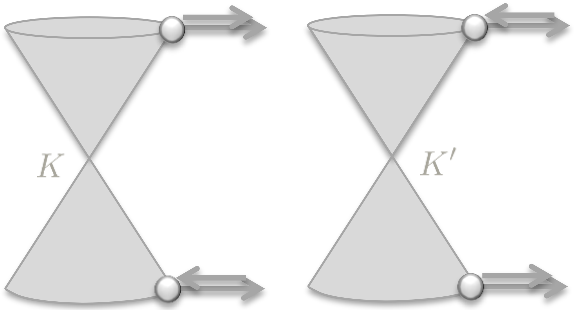


- The gap increases when decreasing the layer number and becomes direct
- The spin-orbit splitting of the valence band is **~150meV**

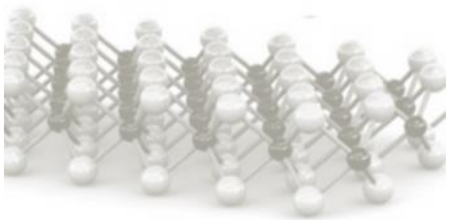
Plan

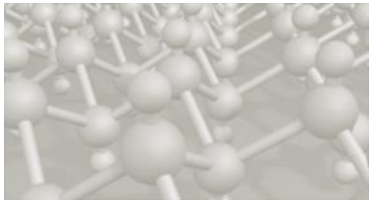
- Graphene: structure and properties

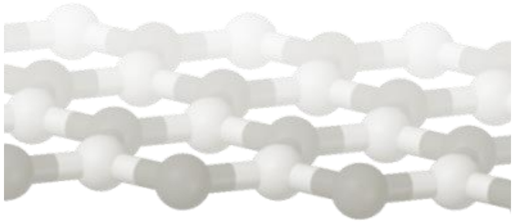




- Other 2D materials: TMDs, SMCs, X-enes, X-anes…







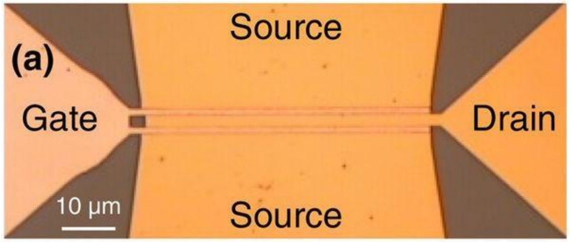
- Applications of 2D materials: electronics, optoelectronics, spintronics and many more

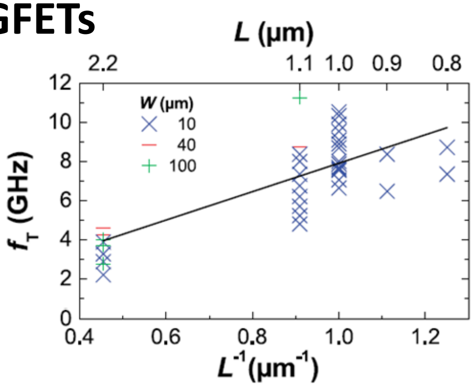
Electronics: field effect transistors

Graphene → **high-frequency analog GFETs**

- ✓ high charge mobility
- ✓ excellent electrostatic control
- ✗ no gap

[E. Guerriero et al., Scient. Rep. 7, 2419 (2017)]

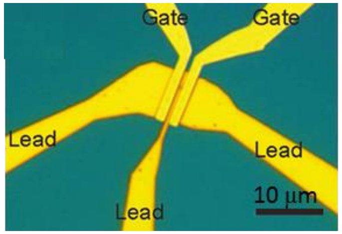


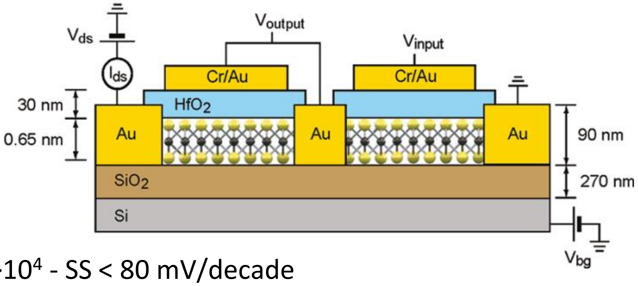


Transition metal dichalcogenides

- ✓ excellent electrostatic control
- ✓ do have a gap
- ✓ self-passivated surface
- ✓ van der Waals heterostructures
- ✗ low mobility (not a problem for ultrascaled channel lengths)

Field effect transistors/integrated circuits for logic operations





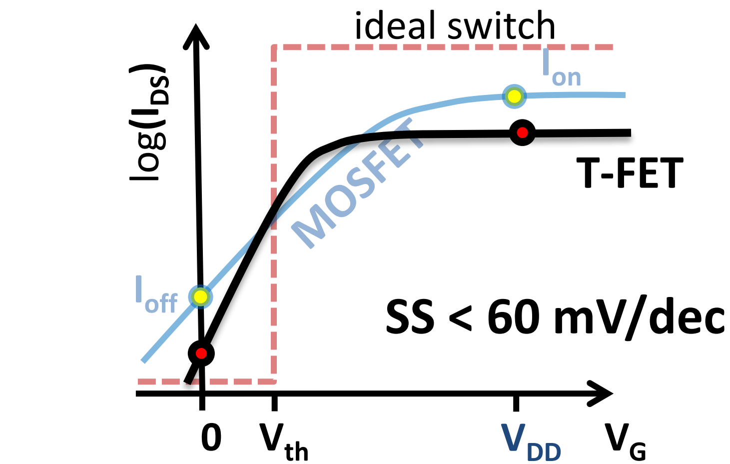
$I_{on}/I_{off} > 10^4$ - SS < 80 mV/decade

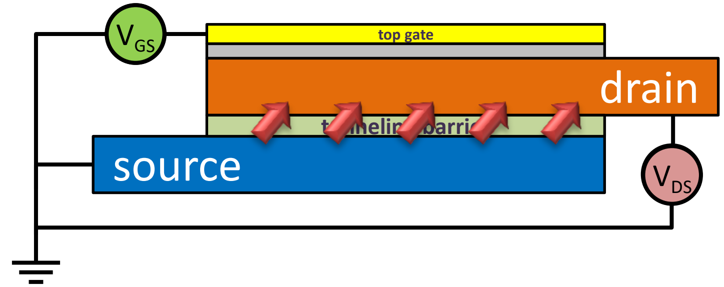
[B. Radisavljevic at al., ACS Nano 5, 9934 (2011)]

However

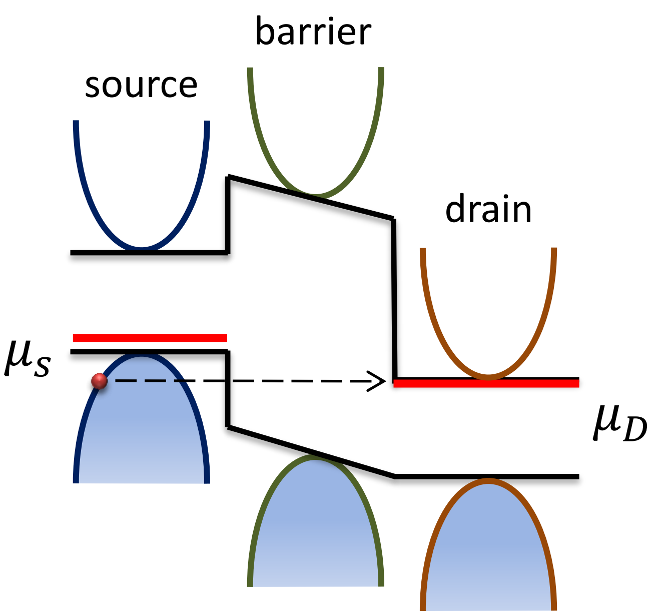
- ✗ not competitive with Si technology for high performance computing
- ✗ Ohmic contacts difficult to obtain

Electronics: low power tunnel field effect transistors

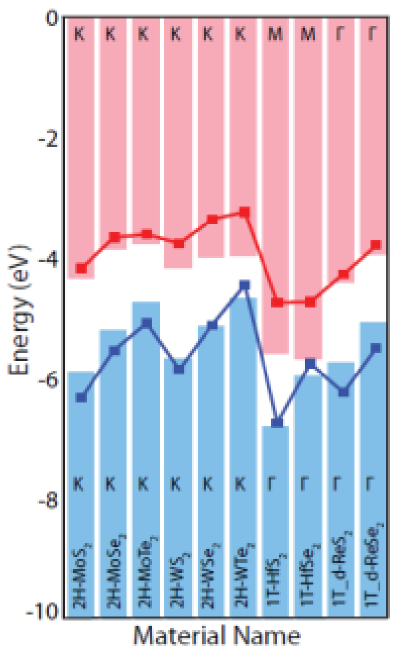




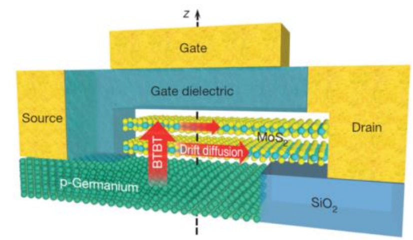
staggered band alignment



vdW heterostructures

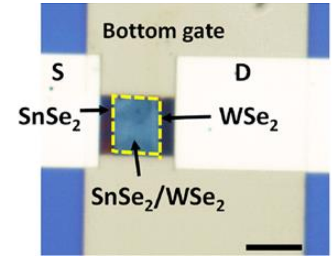


Ge/MoS$_2$ TFET



[D. Sarkar et al., Nature **526**, 91 (2015)]

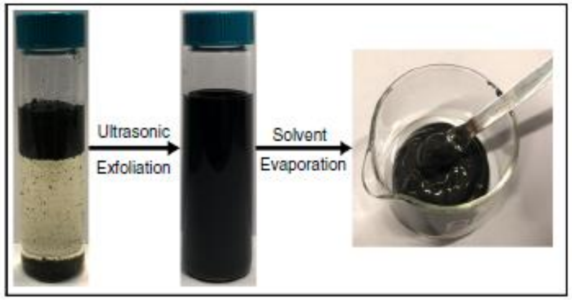
SnSe$_2$/WSe$_2$ vdW TFET

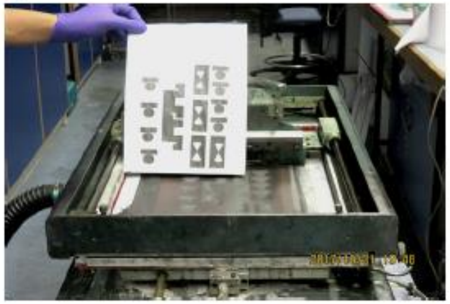


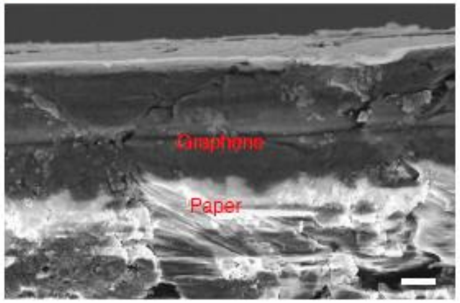
[T. Roy et al., APL **108**, 083111 (2016)]

Printable, low-cost and flexible electronics

Graphene as low-cost printable conductive ink





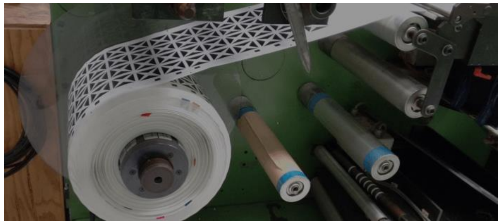


Conductivity up to 7.13×10^4 S m^{-1}, (silver 10^6 S m^{-1})

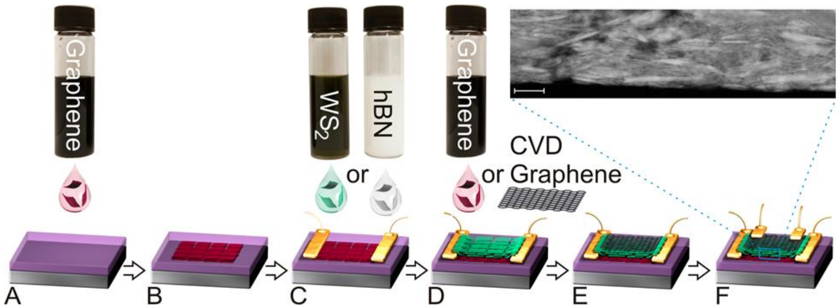
[K. Pan et al., Nat. Comm. 9, 5197 (2018)]

Vorbeck

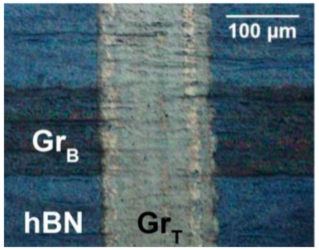
Graphene ink : RFIDs, antenna, wearables…



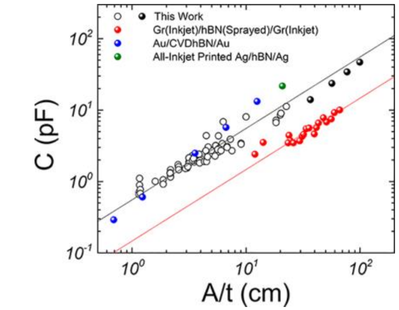
Ink and ink-jet printing of 2D heterostructures



[F. Withers et al., Nano Lett. 14, 3987 (2014)]



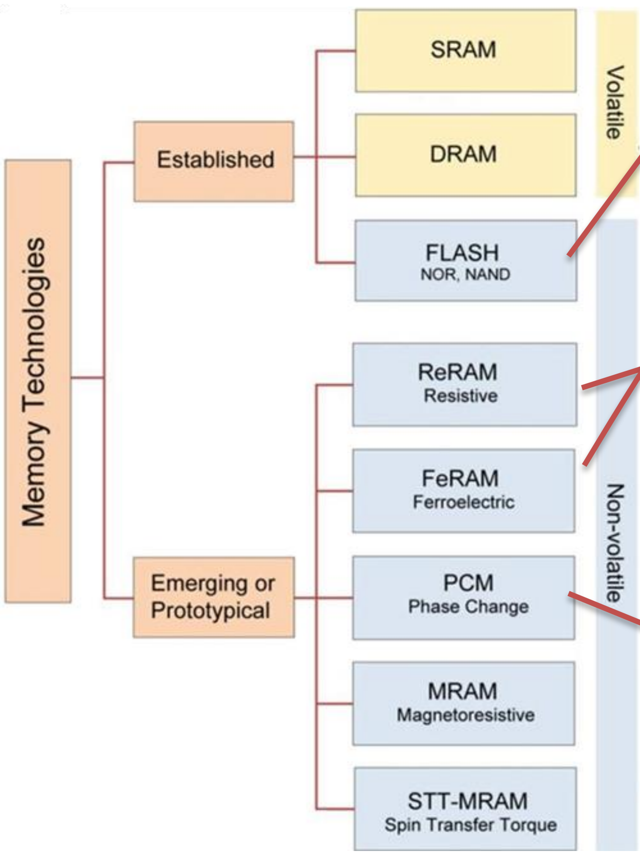
capacitor

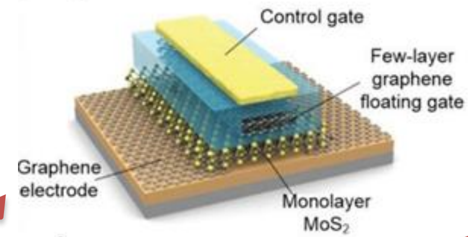


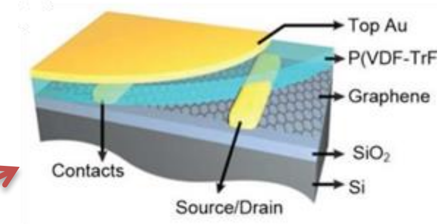
[R. Worsley et al., ACS Nano 13, 54 (2019)]

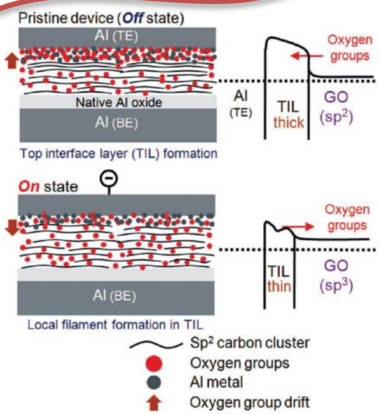
Electronics: non-volatile memories

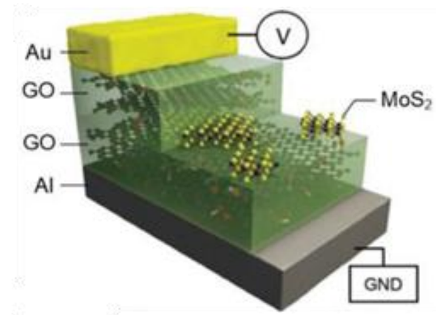
[S. Bertolazzi et al., Adv. Mater. 31, 1806663 (2019)]

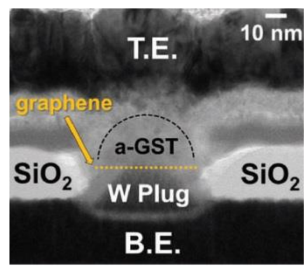


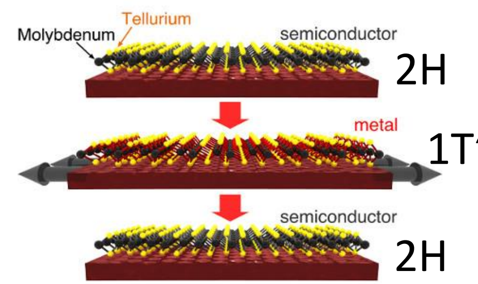






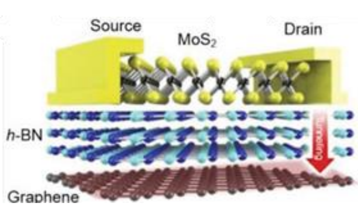


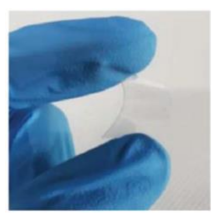




[K.-A. N. Duerloo et al., Nat. Comm. 5, 4214 (2014)]

Tunneling RAM





[Q. A. Vu et al., Nat. Comm. 7, 12725 (2016)]

Strain

Charge doping

Thermal treatment

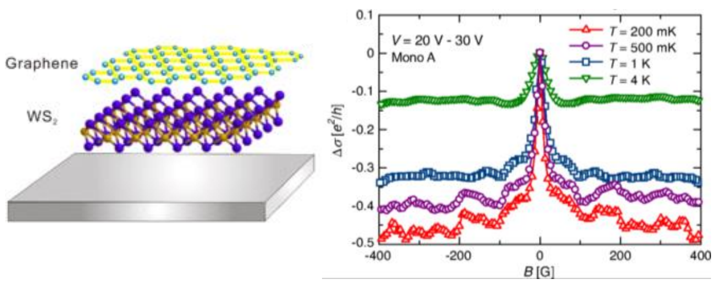
[R. Wang et al., Adv. Funct. Mater. 28, 1802473 (2018)]

Spintronics

Spin length > 10 μm @room temperature for graphene over hBN → **all-graphene-based spintronics**

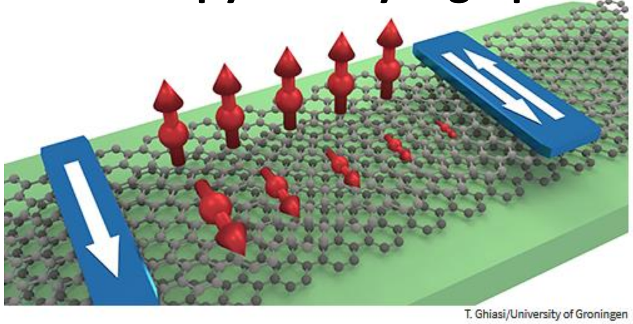
How to manipulate spin?

Proximity effect: inducing spin-orbit coupling in graphene on TMDs



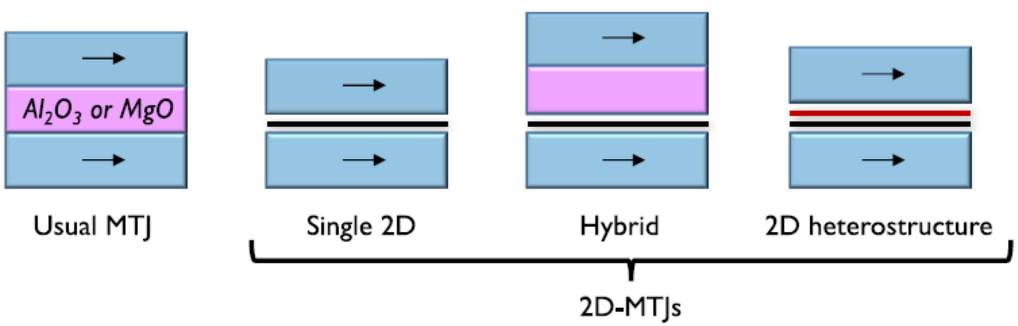
[T. Wakamura et al., Phys. Rev. Lett. 120, 106802 (2018)]

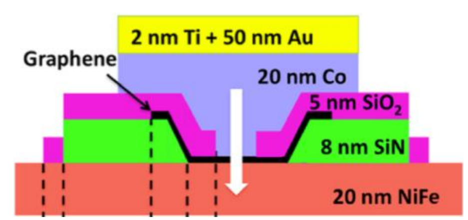
Electric-field induced spin relaxation anisotropy in bilayer graphene



[J. C. Leutenantsmeyer, PRL 121, 127702 (2018)]

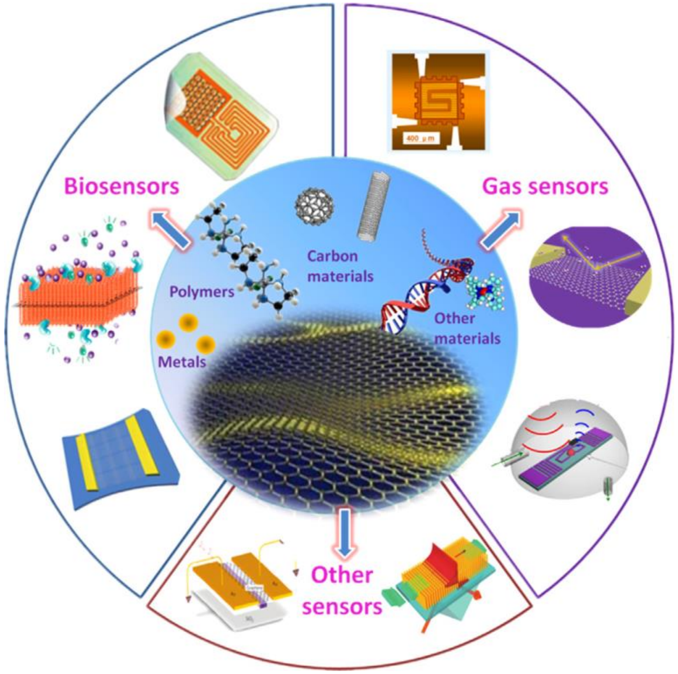
Magnetic tunnel junction for giant magnetoresistance



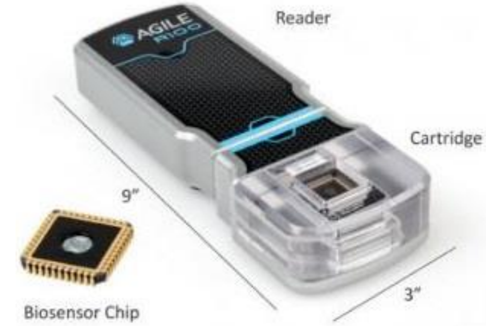


[M. Piquemal-Banci et al., J. Phys. D: Appl. Phys. 50, 203002 (2017)]

Graphene for sensing and health



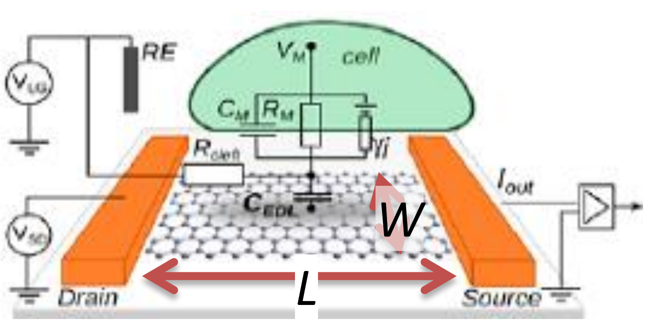
Nanomed



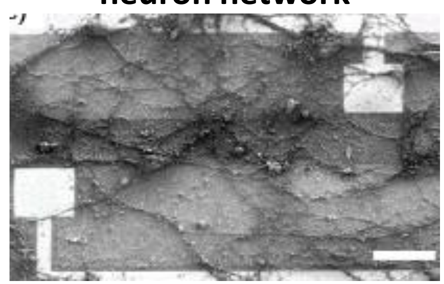
[X. Yu et al., Biosens. and Bioelec. 89, 77 (2017)]
[C. Anichini et al., Chem. Soc. Rev. 47, 4860 (2018)]

In vivo sensing of neuron ion channel activity

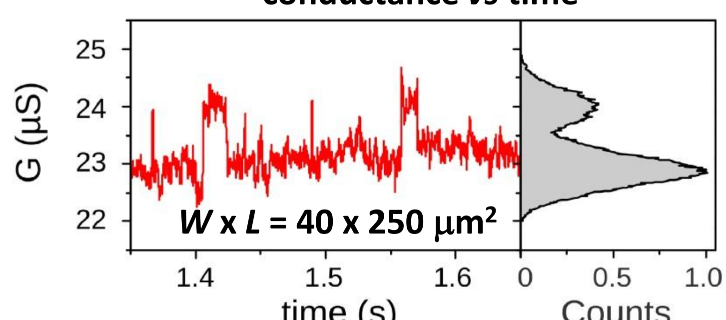
[F. Veliev et al., 2D Materials 5, 045020 (2018)]



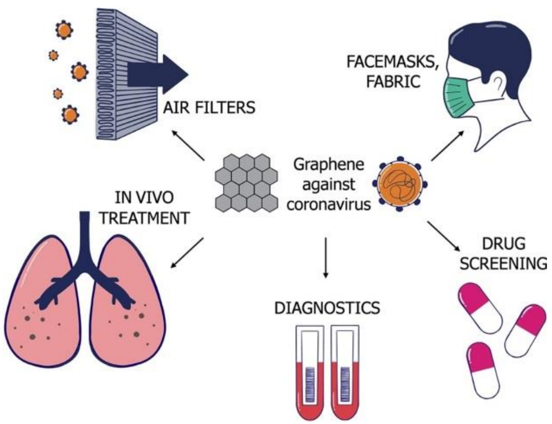
neuron network



conductance *vs* time



Graphene & COVID-19



Can graphene take part in the fight against COVID-19?

V. Palmieri and M.Papi nanotoday *in press*

https://doi.org/10.1016/j.nantod.2020.100883

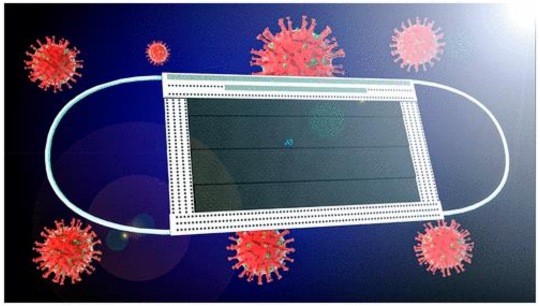
- Functionalized graphene can **capture viruses** and **deliver antiviral drugs**.
- Viruses on graphene can be inactivated by light or heat treatments.
- Graphene can be used as **coating material** for medical devices, personal protective equipment or facemasks to minimize the risk of transmission.
- Graphene-based **sensors c**an be embedded in textiles and environmental filters or used for high-throughput screening of virus helicase inhibitors.

www.acsnano.org

Reusable and Recyclable Graphene Masks with Outstanding Superhydrophobic and Photothermal Performances

Hong Zhong, Zhaoran Zhu, Jing Lin, Chi Fai Cheung, Vivien L. Lu, Feng Yan, Ching-Yuen Chan, and Guijun Li*

Cite This: https://dx.doi.org/10.1021/acsnano.0c02250 Read Online



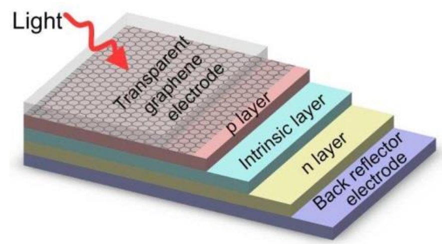
Optoelectronics

Graphene as an electrode

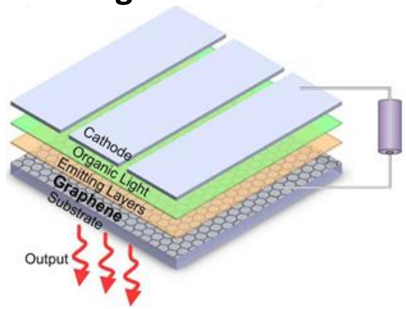
- transparent
- highly conductive
- flexible

[F. Bonaccorso et al., Nat. Phot. 4, 611 (2010)]

silicon solar cell

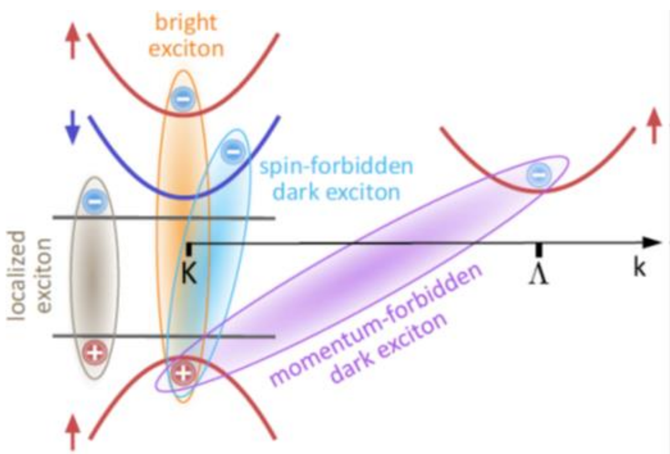


organic LED

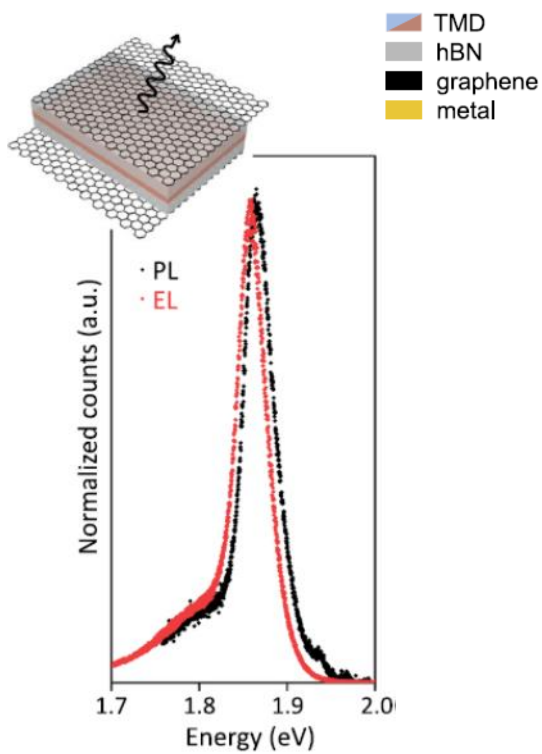


Excitons in transition metal dichalcogenides

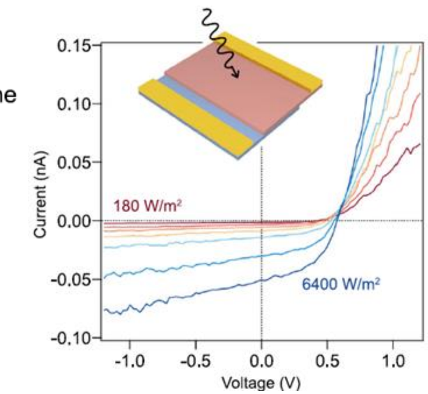
- room temperature (binding energy ~0.5eV)
- reach SOC and multivalley physics
- interlayer excitons in vdW heterostructures



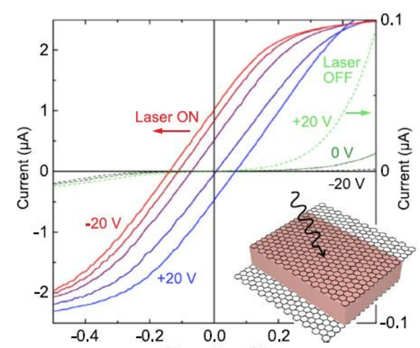
excitonic light emission



photovoltaic solar cells



photodetectors



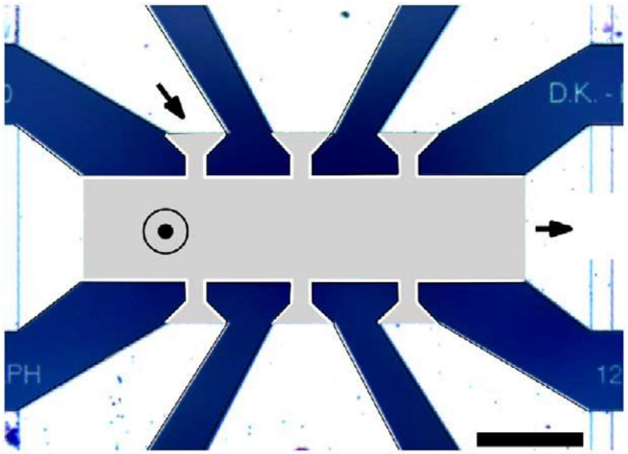
[T. Mueller et al., npj 2D Materials and Applications 2, 29 (2018)]

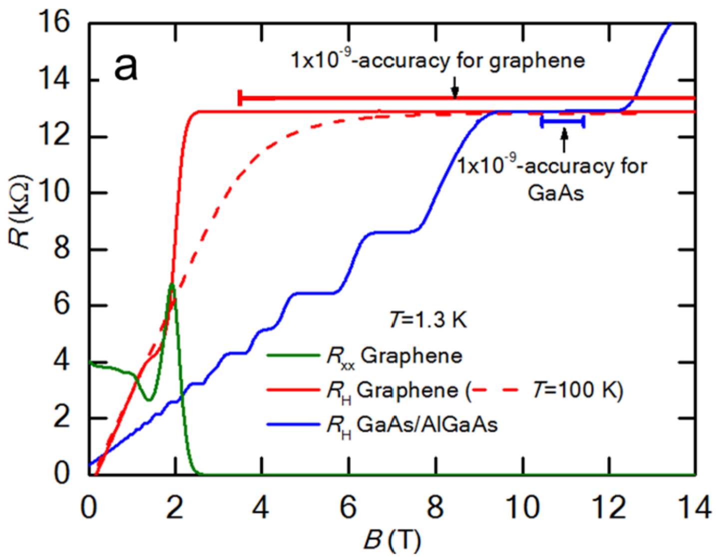
Metrology: graphene as a resistance standard

Energy spacing Landau levels

- GaAs-based Hall bars $\Delta E \approx 1.7B[\mathrm{T}]\mathrm{meV}$
- graphene-based $\Delta E \approx 35\sqrt{B[\mathrm{T}]}$ meV

- low magnetic fields (B<4 T)
- higher temperature (T >4 K)
- higher measurement current (I >100 μA)

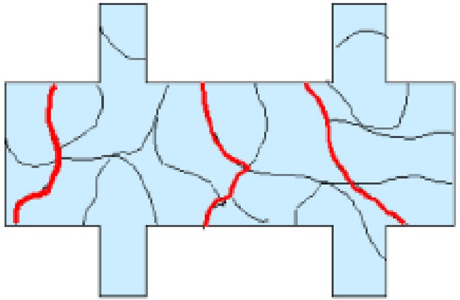




[F. Lafont et al, Nat. Commun. 6, 6806 (2015)]

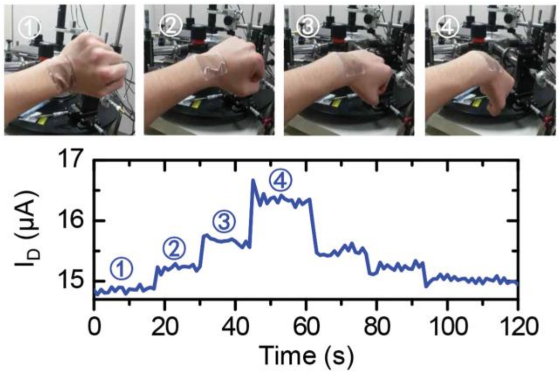
Importance of graphene quality: grain boundaries in CVD graphene can create a network of conductive paths

[A. Cumming et al., PRB 90, 161401 (2014)]



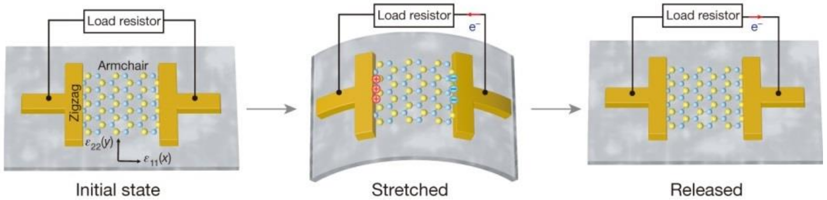
Mechanics

Strain Sensors

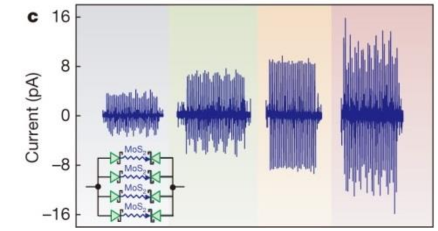


[Q. Sun et al., Adv. Mat. 27, 3411 (2015)]

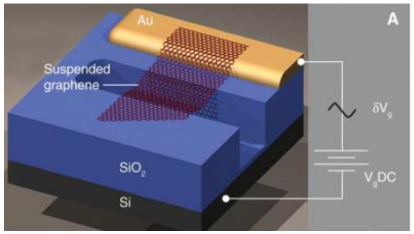
Piezoelectric generators

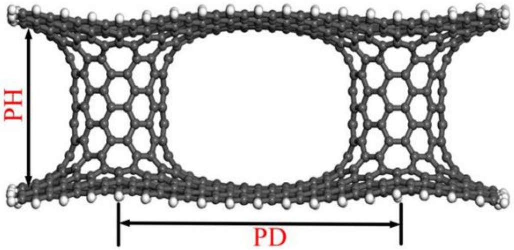


[W. Wu et al., Nature 514, 470 (2014)]



Resonators and mass detection





Sensitivity 1 yg (10^{-24} g)
Mass responsivity 0.34 GHz/yg

[J. S. Bunch et al., Science 315, 490 (2007)]

[K. Duan et al., Scient. Report. 7, 14012 (2017)]

Mechanical reinforcement

Conclusion

- 2D materials represent an **amazing discovery** in material science
- They attracted much interest for both **fundamental physics** and **applications**
- Many new 2D materials are to be predicted, exfoliated or synthetized
- **van der Waals coupling** allows the engineering of vertical heterostructures with specific properties
- Large **variety of applications** in different fields
- **Material quality** and **fabrication techniques** are critical issues for many applications
- …there is still a lot to do

Thanks for your attention!