2D Materials

Outline:

- Graphene fabrication
- Possible applications
- Van der Waals Heterostructures

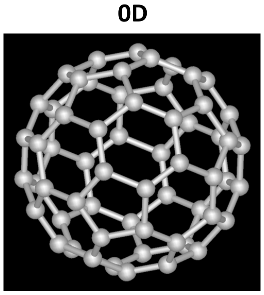
References:

- E. McCann Graphene monolayers Lancaster University, UK Tight-binding model, QHE
- C. Beenakker, Reviews of Modern Physics, 80, 1337 (2008)
- L. Tapaszto & J. Cserti talks, MAFIHE Teli Iskola a Grafenrol 2011, ELTE
- A. Geim talk, TNT Conference 2010 http://www.tntconf.org/2010/Presentaciones/TNT2010_Geim.pdf
- A. C. Ferrari http://ec.europa.eu/research/industrial_technologies/pdf/graphene-presentations/0-3-ferrari-21032011_en.pdf

More info in Halbritter, Csonka, Makk: Fundamentals of Nanoelectronics

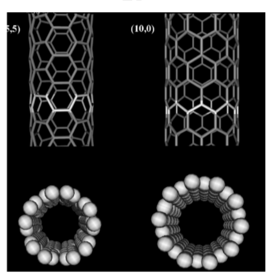
Carbon nanostructures

Fullerene
0D



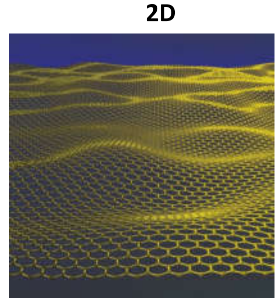
1985
H.W.Kroto
Mass spectrometer

Nanotube
1D



1991
S Iijima
Electron microscope

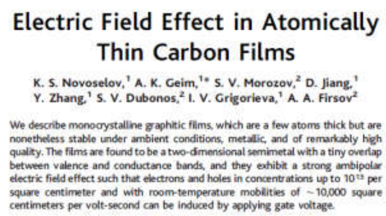
Graphene
2D



2004
K. S. Novoselov
Optical microscope

Graphene – Nobel Prize in Physics 2010

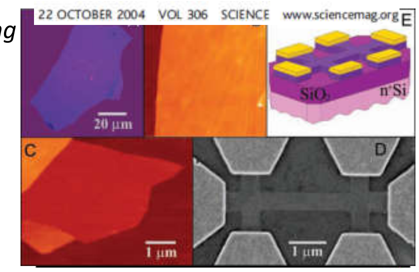
Andre Geim **Kostya Novoselov**


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]

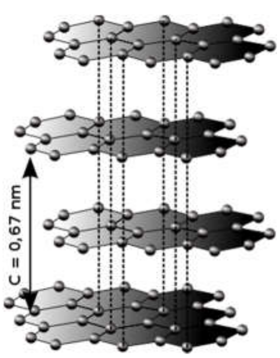
We describe monocrystalline graphitic films, which are a few atoms thick but are nonetheless stable under ambient conditions, metallic, and of remarkably high quality. The films are found to be a two-dimensional semimetal with a tiny overlap between valence and conductance bands, and they exhibit a strong ambipolar electric field effect such that electrons and holes in concentrations up to 10^{13} per square centimeter and with room-temperature mobilities of ~10,000 square centimeters per volt-second can be induced by applying gate voltage.

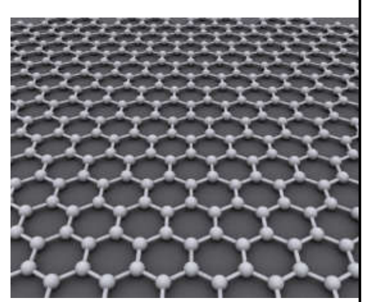
"for groundbreaking experiments regarding the two dimensional material graphene"



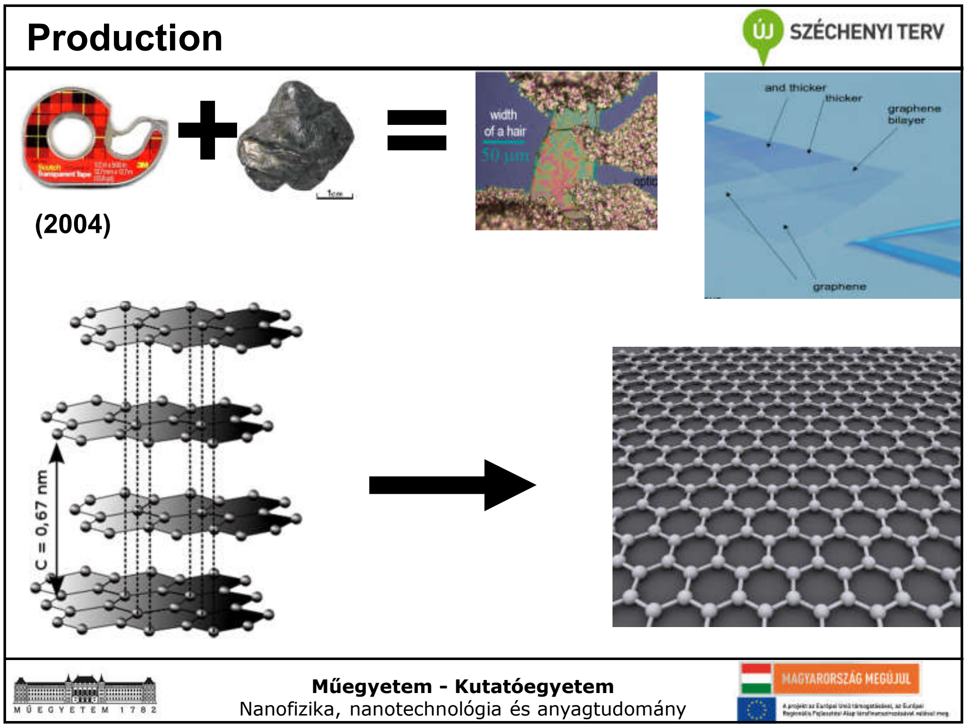
Surprising, since growth of macroscopic 2D objects is strictly forbidden due to phonons (Mermin Wagner)

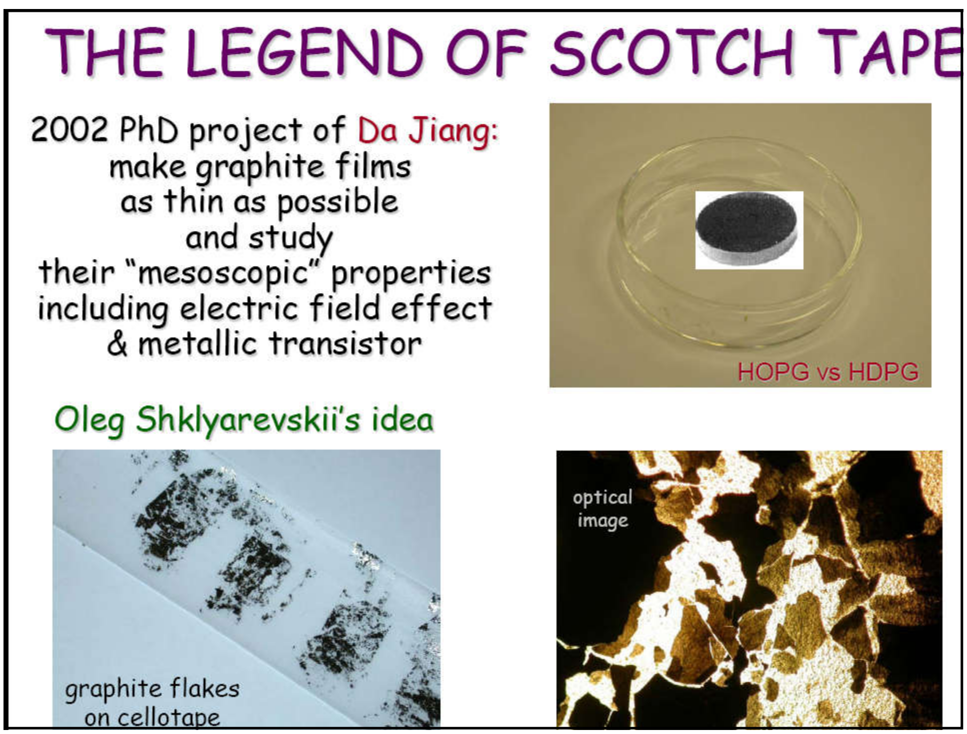
Production

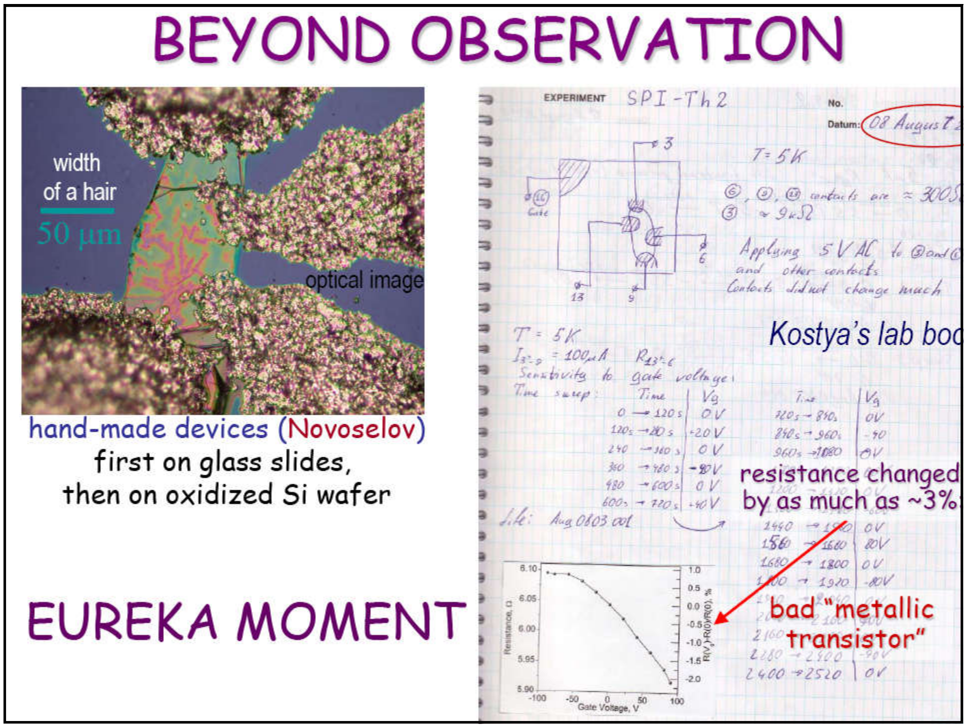


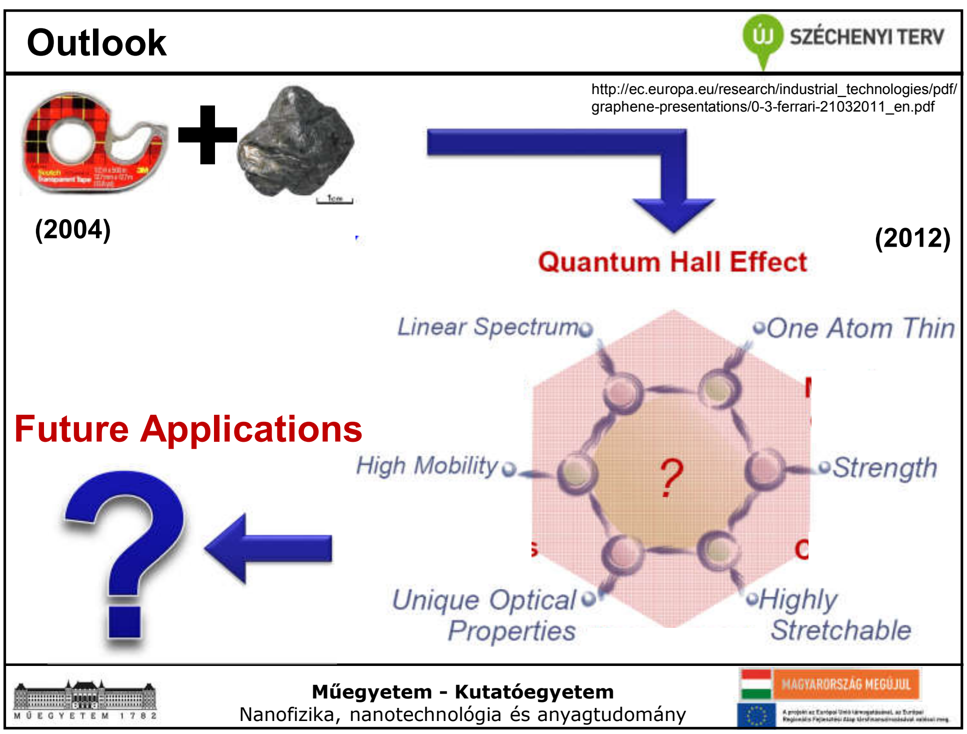


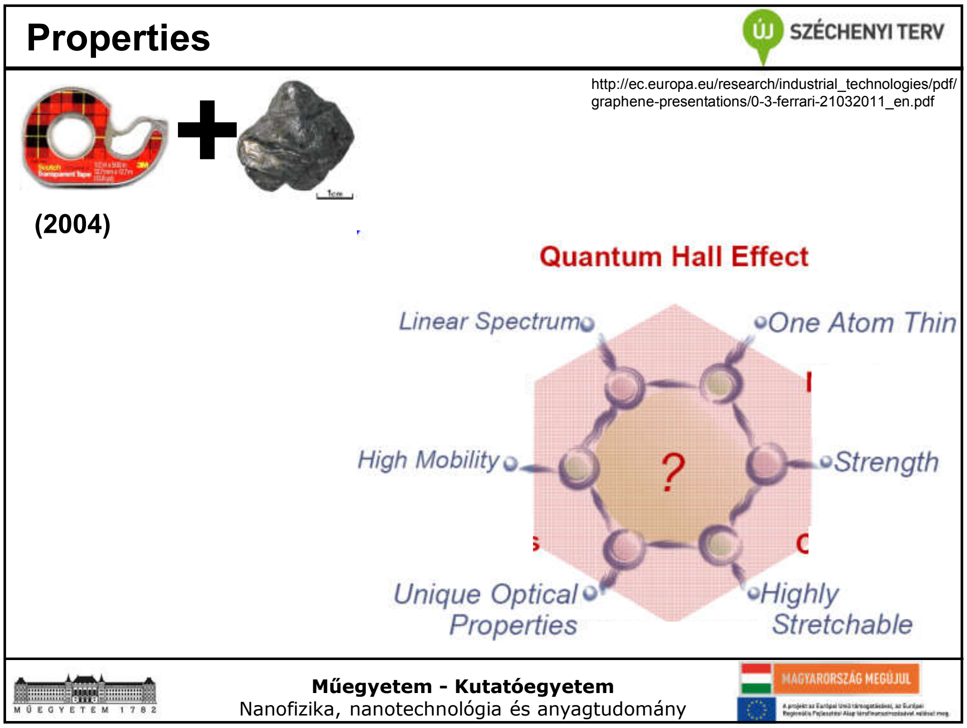
Műegyetem - Kutatóegyetem
Nanofizika, nanotechnológia és anyagtudomány

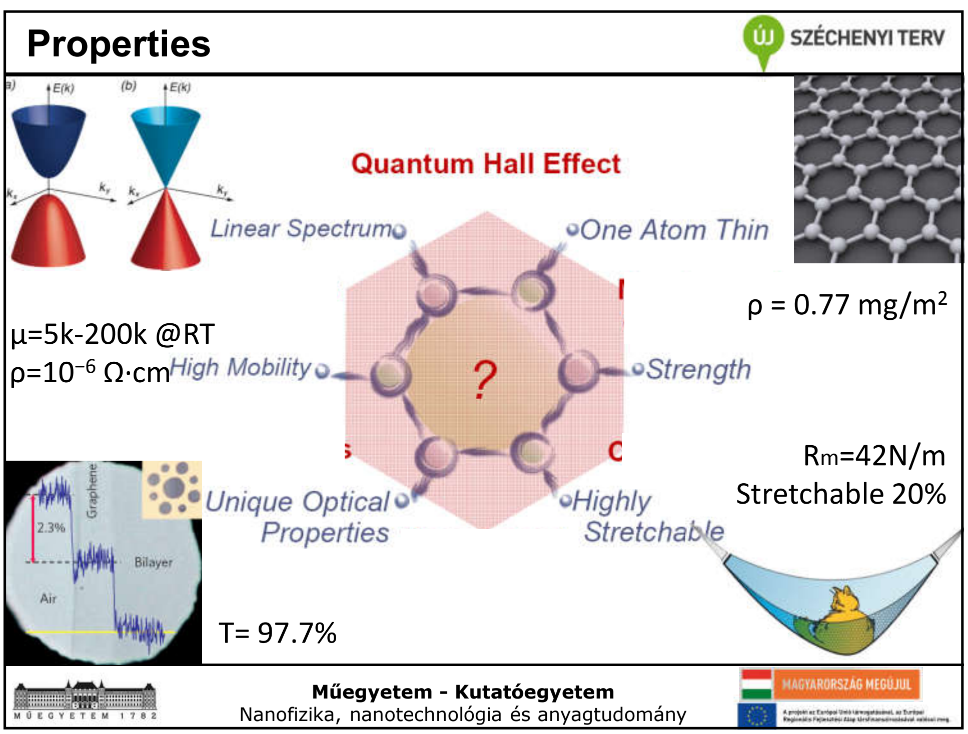

Production
ÚJ SZÉCHENYI TERV
(2004)
width
of a hair
50 µm
and thicker
thicker
graphene
bilayer
graphene
C = 0,67 nm
MŰEGYETEM 1782
Műegyetem - Kutatóegyetem
Nanofizika, nanotechnológia és anyagtudomány
MAGYARORSZÁG MEGÚJUL


THE LEGEND OF SCOTCH TAPE
2002 PhD project of Da Jiang:
make graphite films
as thin as possible
and study
their "mesoscopic" properties
including electric field effect
& metallic transistor
HOPG vs HDPG
Oleg Shklyarevskii's idea
graphite flakes
on cellotape
optical
image


BEYOND OBSERVATION
width
of a hair
50 μm
optical image
hand-made devices (Novoselov)
first on glass slides,
then on oxidized Si wafer
EUREKA MOMENT
EXPERIMENT SPI-Th2
Datum: 08 August
T = 5K
Kostya's lab book
resistance changed
by as much as ~3%
bad "metallic
transistor"
Resistance, Ω
Gate Voltage, V

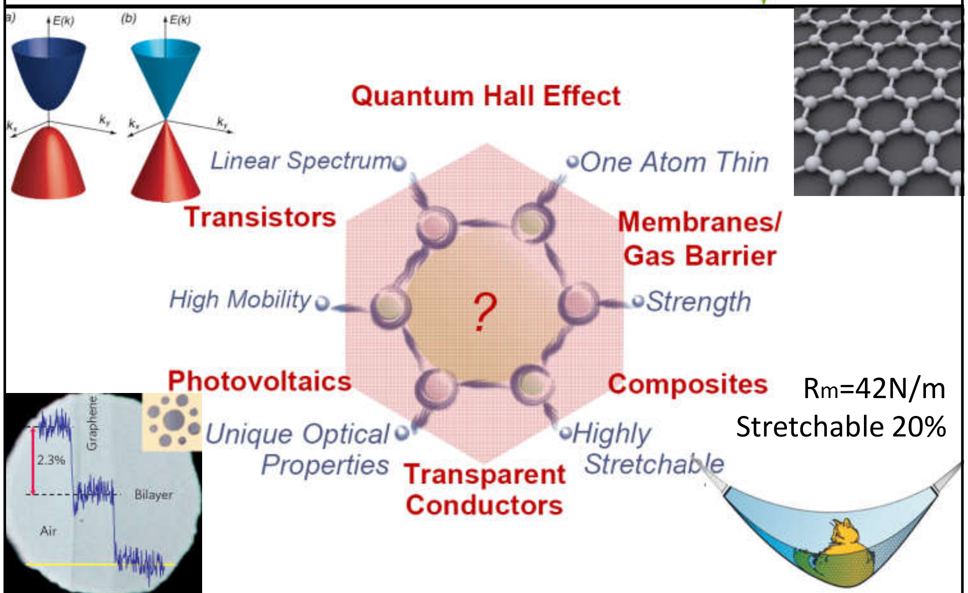

Outlook
SZÉCHENYI TERV
http://ec.europa.eu/research/industrial_technologies/pdf/graphene-presentations/0-3-ferrari-21032011_en.pdf
(2004)
(2012)
Quantum Hall Effect
Linear Spectrum
One Atom Thin
High Mobility
Strength
Unique Optical Properties
Highly Stretchable
Future Applications
?
MŰEGYETEM 1782
Műegyetem - Kutatóegyetem
Nanofizika, nanotechnológia és anyagtudomány
MAGYARORSZÁG MEGÚJUL


Properties
SZÉCHENYI TERV
http://ec.europa.eu/research/industrial_technologies/pdf/graphene-presentations/0-3-ferrari-21032011_en.pdf
(2004)
Quantum Hall Effect
Linear Spectrum
One Atom Thin
High Mobility
?
Strength
Unique Optical Properties
Highly Stretchable
Műegyetem - Kutatóegyetem
Nanofizika, nanotechnológia és anyagtudomány
MAGYARORSZÁG MEGÚJUL


Properties
SZÉCHENYI TERV
E(k)
Quantum Hall Effect
Linear Spectrum
One Atom Thin
ρ = 0.77 mg/m²
μ=5k-200k @RT
ρ=10⁻⁶ Ω·cm
High Mobility
?
Strength
Rm=42N/m
Stretchable 20%
Graphene
2.3%
Bilayer
Air
Unique Optical Properties
Highly Stretchable
T= 97.7%
Műegyetem - Kutatóegyetem
Nanofizika, nanotechnológia és anyagtudomány
MAGYARORSZÁG MEGÚJUL

Properties

SZÉCHENYI TERV



Műegyetem - Kutatóegyetem
Nanofizika, nanotechnológia és anyagtudomány

Production

SZÉCHENYI TERV

(2004)

- **Exfoliation**

Műegyetem - Kutatóegyetem
Nanofizika, nanotechnológia és anyagtudomány

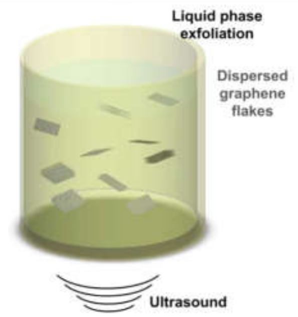
Production

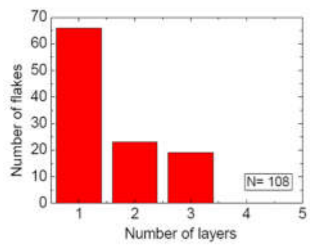
SZÉCHENYI TERV

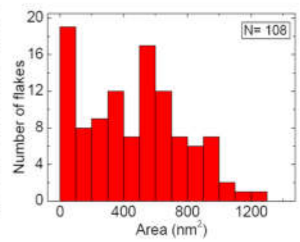
(2004)

- **Exfoliation**
- **LPE (Liquid phase exfolation):**

E.g. in organic solvent with high surface tension to avoid re-aggregation OR water surfactant solution







http://www.vorbeck.com/

Műegyetem - Kutatóegyetem
Nanofizika, nanotechnológia és anyagtudomány

MAGYARORSZÁG MEGÚJUL

Production

SZÉCHENYI TERV

(2004)

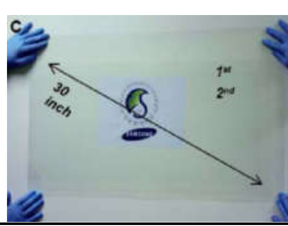
- **Exfoliation**
- **LPE (Liquid phase exfolation):**

E.g. in organic solvent with high surface tension to avoid re-aggregation OR water surfactant solution

- **CVD growth e.g. on Cu**

Self terminating process.
Result: single layer, - polycrystalline graphene.

SKKU Process
Bae Nature Nano (2010)



www.graphenesq.com/

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Nanofizika, nanotechnológia és anyagtudomány

MAGYARORSZÁG MEGÚJUL

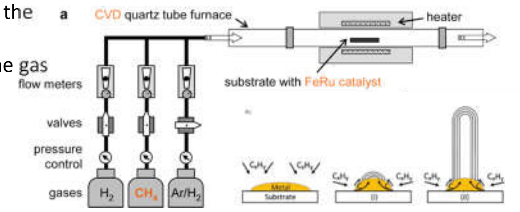
Chemical Vapour Deposition (CVD)

Creation of reactive chemical species close to the surface to be coated

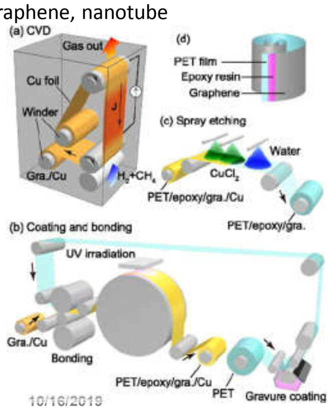
E.g. growth of polycrystaline silicon from silene gas (600C and 1mbar)

$$SiH_4 \rightarrow Si + 2H_2$$

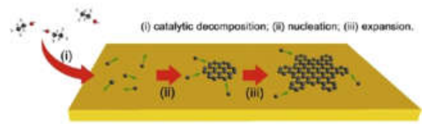
E.g.2: Growth of carbon nanostructures: graphene, nanotube



(Up) Typical CVD system to grow carbon nanostructures. Calayst particles with e.g. CH4 gas creates carbon nanotubes. The schematic growth process is shown bellow.
https://www.nano.physik.uni-muenchen.de/nanophysics/research/rep11.html
https://www.semanticscholar.org/paper/Chemical-vapor-deposition-of-carbon-nanotubes%3A-a-on-Kumar-Ando/8cad65216fe922b14c5c947330cc791341f621fb



(Down) Basic process of CVD growth of graphene on Cu substrate from CH4.
(Left) Continous roll-to-roll CVD growth and transfer of large area graphene
https://www.sciencedirect.com/science/article/abs/pii/S0379677915300138
https://www.researchgate.net/figure/Schematic-of-continous-roll-to-roll-CVD-growth-and-transfer-of-large-area-graphene_fig5_249286739



22

Lindsay : Intro to Nanoscience, Chapter 5 *see more detail in Gabor Kiss: Micro and Nanotechnology*

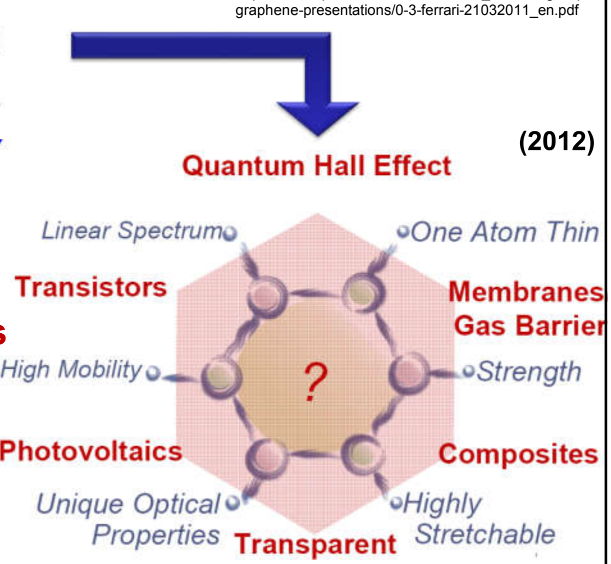
Towards applications

SZÉCHENYI TERV

(2004)

http://ec.europa.eu/research/industrial_technologies/pdf/graphene-presentations/0-3-ferrari-21032011_en.pdf

(2012)



Műegyetem - Kutatóegyetem
Nanofizika, nanotechnológia és anyagtudomány

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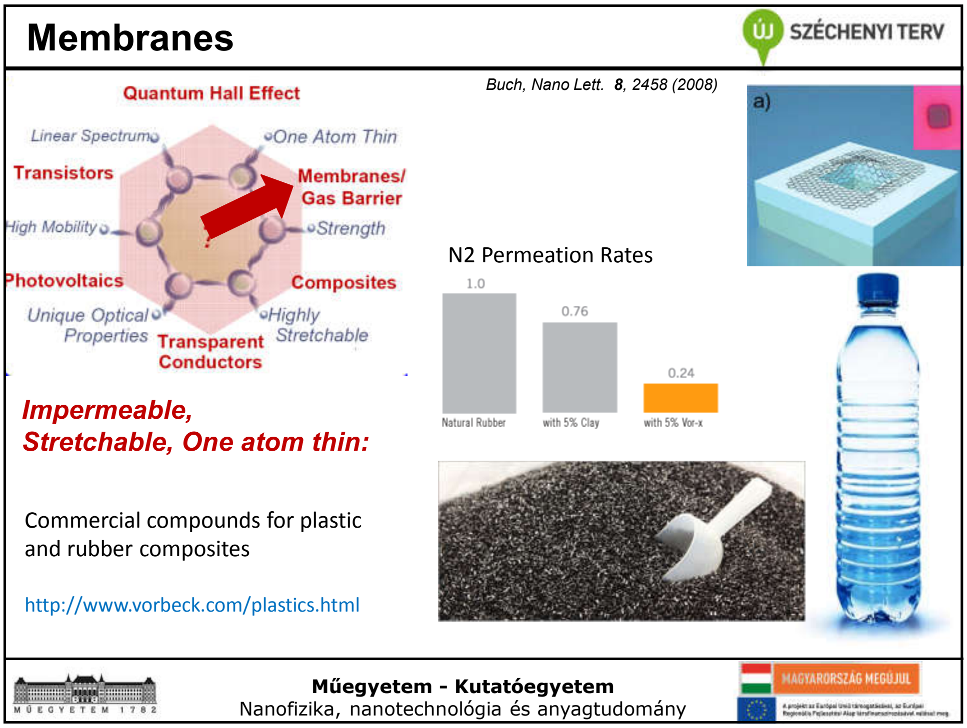
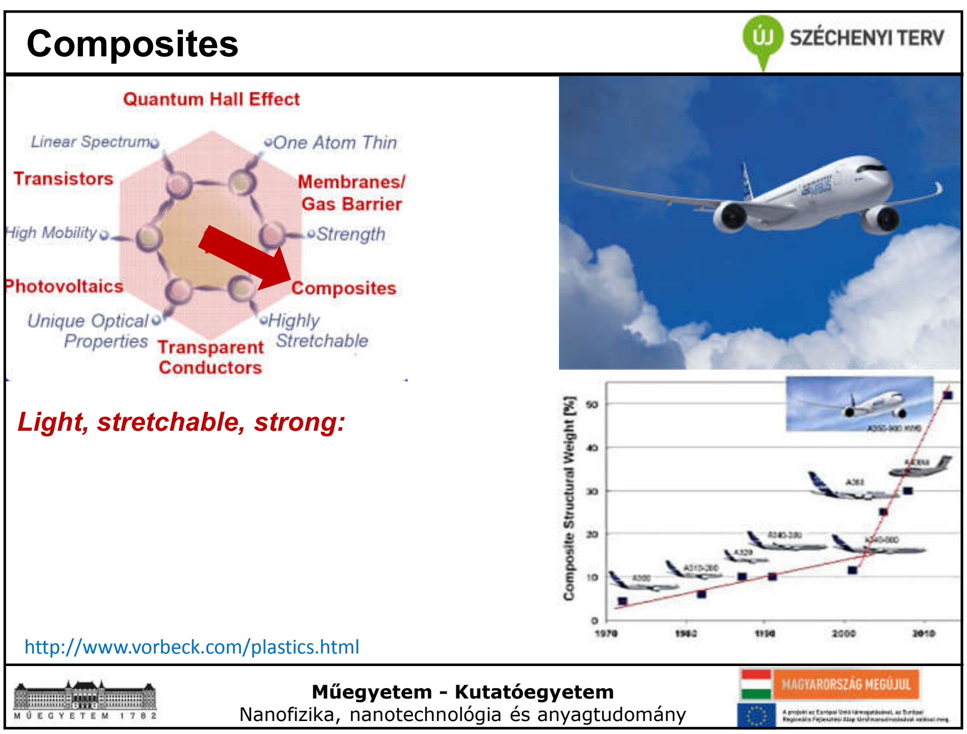
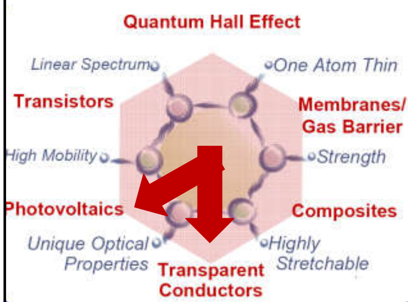
MAGYARORSZÁG MEGÚJUL


Membranes
SZÉCHENYI TERV
Quantum Hall Effect
Linear Spectrum
One Atom Thin
Transistors
Membranes/ Gas Barrier
High Mobility
Strength
Photovoltaics
Composites
Unique Optical Properties
Transparent Conductors
Highly Stretchable
Buch, Nano Lett. 8, 2458 (2008)
a)
N2 Permeation Rates
1.0
0.76
0.24
Natural Rubber
with 5% Clay
with 5% Vor-x
Impermeable, Stretchable, One atom thin:
Commercial compounds for plastic and rubber composites
http://www.vorbeck.com/plastics.html
Műegyetem - Kutatóegyetem
Nanofizika, nanotechnológia és anyagtudomány
MAGYARORSZÁG MEGÚJUL


Composites
SZÉCHENYI TERV
Quantum Hall Effect
Linear Spectrum
One Atom Thin
Transistors
Membranes/ Gas Barrier
High Mobility
Strength
Photovoltaics
Composites
Unique Optical Properties
Transparent Conductors
Highly Stretchable
Light, stretchable, strong:
Composite Structural Weight [%]
1970
2000
2010
http://www.vorbeck.com/plastics.html
Műegyetem - Kutatóegyetem
Nanofizika, nanotechnológia és anyagtudomány
MAGYARORSZÁG MEGÚJUL

Optoelectronics

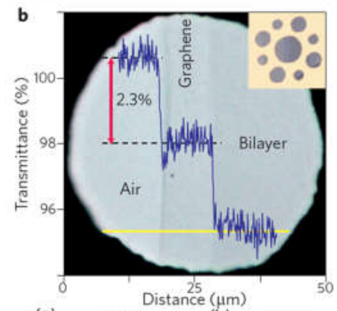
SZÉCHENYI TERV

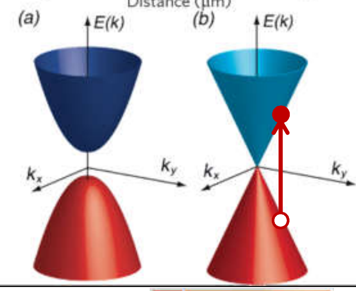


One atom thin:
- Transmittance is high, 97.7%

Linear spectrum:
- For any excitation there is e-h pair → Broad band applications

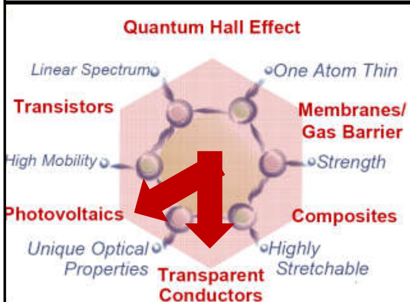
- Pauli blocking→ Saturable absorption



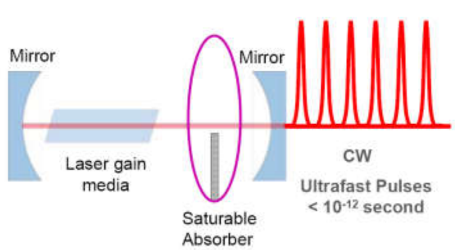


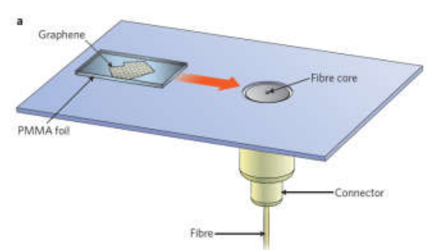
Saturable absorbers, ultrafast laser

SZÉCHENYI TERV



Laser sources with nano to subpicosec pulses
Important in physics, biology, chemistry and also applications: e.g. eye surgery, circuit board manufacturing, trimming electronic components.
Principle: Saturable absorber (SA) turns a continuous wave output to ultrafast pulses
Graphene works as **saturable absorber**
Bilayer graphene promising for **THz generator**, detector due to tunable band gap

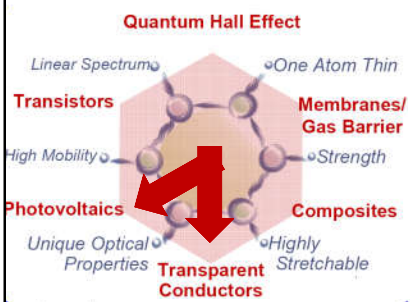




Műegyetem - Kutatóegyetem
Nanofizika, nanotechnológia és anyagtudomány
MAGYARORSZÁG MEGÚJUL

Transparent conductors

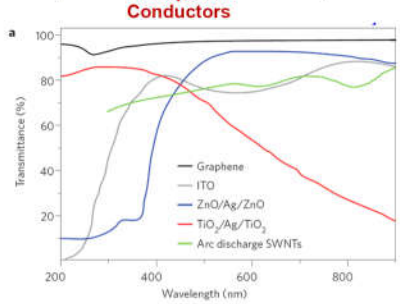
SZÉCHENYI TERV

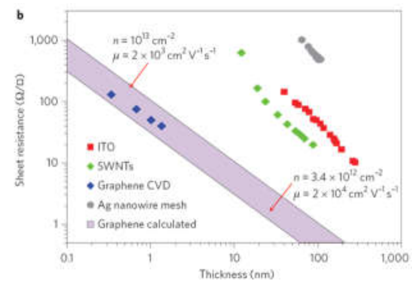


Requirements:
High transparency (T), low sheet resistance (Rs)
Dominant material: ITO (indium tin oxide)
T≈ 80% Rs =10-300Ω
ITOs limitations:

- Scarcity, difficulties in patterning
- Sensitivity to acidic or basic environments
- Brittle, - Wear resistance

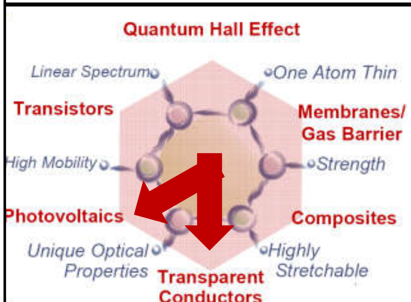
Graphene: T = 97.7%, Rs=6kΩ



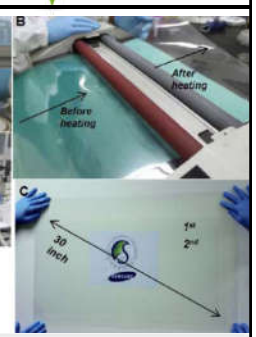


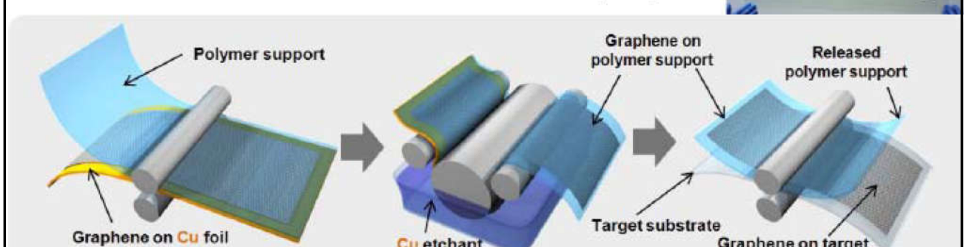
Transparent conductors

SZÉCHENYI TERV



SKKU Process
Bae Nature Nano (2010)

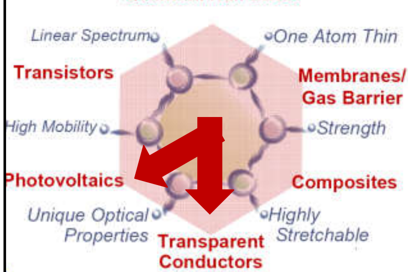




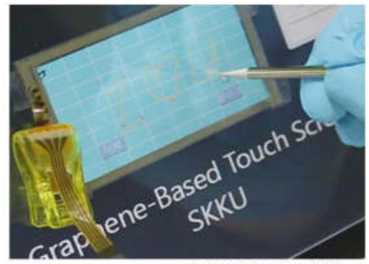
Bonaccorso et al. Nature Photonics 4, 611 (2010)

Transparent conductors

SZÉCHENYI TERV

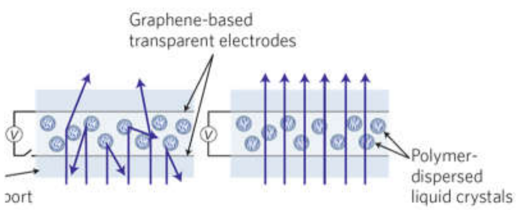


Touch screens (Samsung & SSKU)



Bae, S. *et al.* Nature Nano (2010)

Flexible Smart windows/ bistabile displays



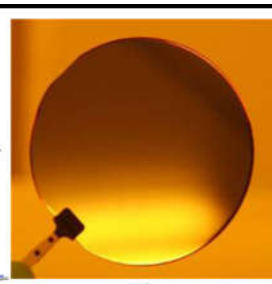
Műegyetem - Kutatóegyetem
Nanofizika, nanotechnológia és anyagtudomány

MAGYARORSZÁG MEGÚJUL

Transparent conductors

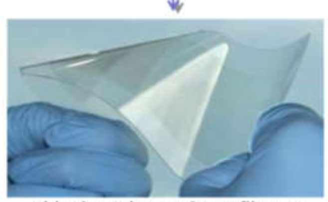
SZÉCHENYI TERV

Transparent graphene film



4 inch scale graphene film on Stretchable Substrate

Patterned Graphene film on PET



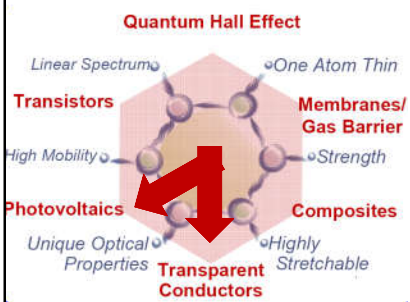
4 inch scale graphene film on Flexible Substrate

SUNG KYUN KWAN UNIVERSITY

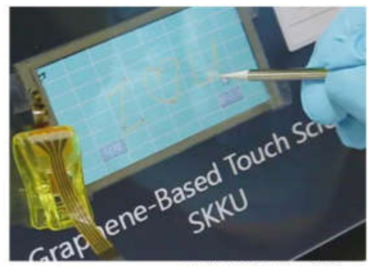
Műegyetem - Kutatóegyetem
Nanofizika, nanotechnológia és anyagtudomány

MAGYARORSZÁG MEGÚJUL

Transparent conductors

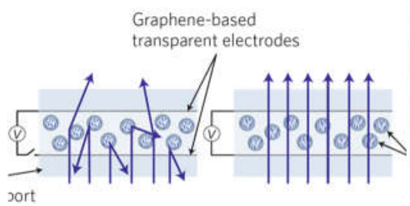


Touch screens (Samsung & SKKU)

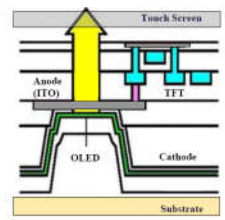


Bae, S. *et al.* Nature Nano (2010)

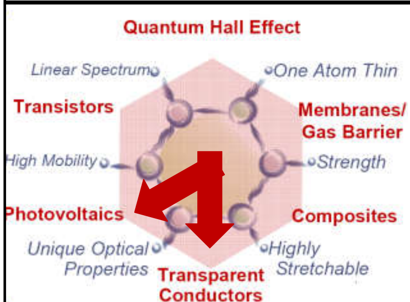
Flexible Smart windows/ bistabile displays



Flexible Foldable displays with OLED



Photovoltaic cells

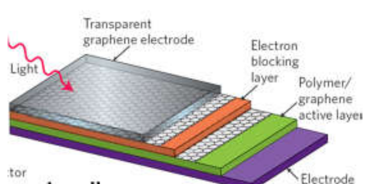


Bonaccorso et al. Nature Photonics 4, 611 (2010)

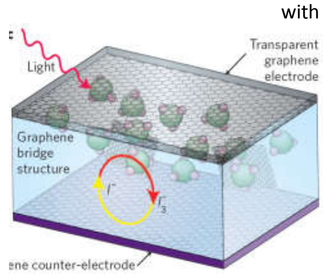
It converts light to electricity.
Silicon cells η ≈ 25%, Organic cells are economic η≈few%

Graphene:

- Transparent conduction window
- Photoactive material (claim η >12% is possible)
- channel for charge transport



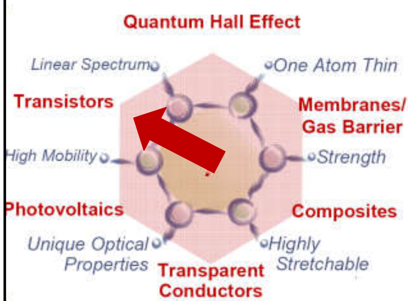
Organic cell
Polimer for light absorp-tion and charge transfer



Dye-sensitized cell
with G as a TiO bridge η ≈ 7%
with G counter electrode η ≈ 4.5% instead of Pt
η ≈ 6.3% → cheaper

Transistors (FET)

SZÉCHENYI TERV

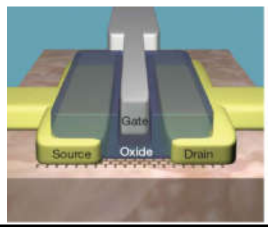


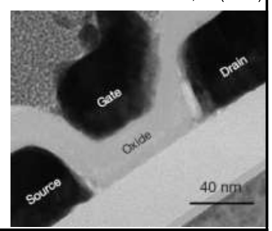
Zero band gap → small on-off ratio
For **Radio frequency** (RF) **transistors** e.g. amplifier, mixers, e.g. in wireless systems not a problem.

High mobility → high frequency (cut off)
f_T = 300GHz exfoilated graphene
f_T = 155GHz with 40nm gate length in industry compatible graphene transistor. (IBM)

With 20nm channel length intrinsic $f_T \approx$ few THz is expected.

Schwierz Nature 472, 41 (2011)



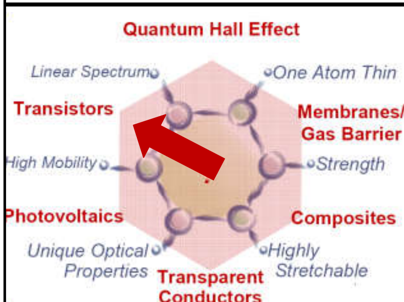


Műegyetem - Kutatóegyetem
Nanofizika, nanotechnológia és anyagtudomány

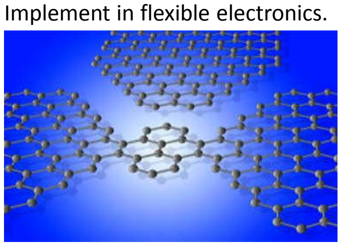
MAGYARORSZÁG MEGÚJUL

Transistors (FET)

SZÉCHENYI TERV



Possible to scale down.
Implement in flexible electronics.



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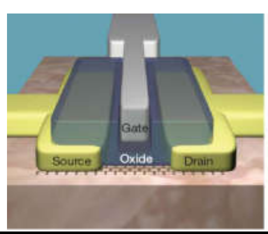
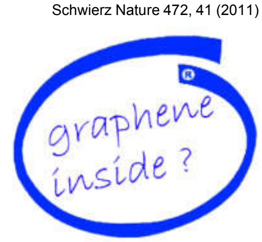
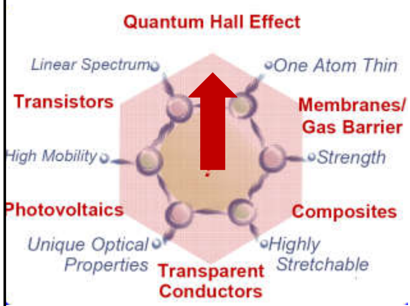


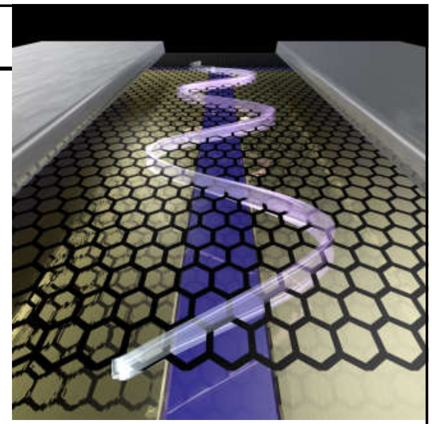


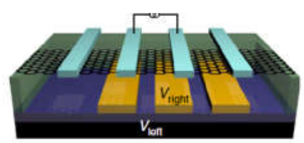
Műegyetem - Kutatóegyetem
Nanofizika, nanotechnológia és anyagtudomány

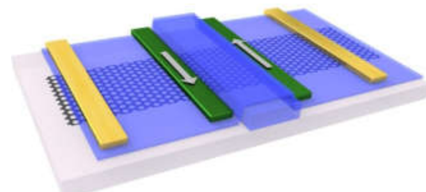
MAGYARORSZÁG MEGÚJUL

Graphene + Hybrid systems









Műegyetem - Kutatóegyetem
Nanofizika, nanotechnológia és anyagtudomány

2D Zoo: Van der Waals heterostructures

Several similar 2D matrials:

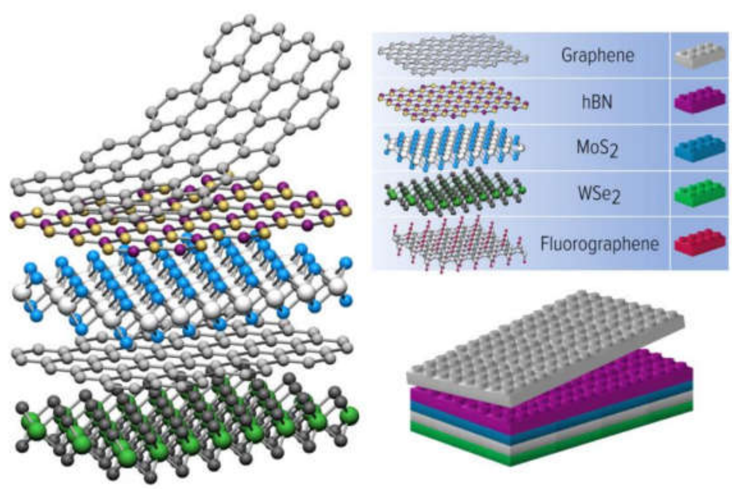


Fig. 1. **Building vdW heterostructures.** If one considers 2D crystals as Lego blocks (right panel), construction of a huge variety of layered structures becomes possible. Conceptually, this atomic-scale Lego resembles molecular beam epitaxy but employs different 'construction' rules and a distinct set of materials.

Geim et al., Nature 499, 419-425 (2013)

2D Zoo: Van der Waals heterostructures

Several similar 2D matrials:

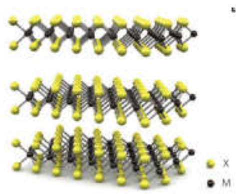
graphene family	graphene	hBN 'white graphene'	BCN	fluorographene	graphene oxide
2D chalcogenides	MoS_2, WS_2, $MoSe_2$, WSe_2		semiconducting dichalcogenides: $MoTe_2$, WTe_2, ZrS_2, $ZrSe_2$, etc.	metallic dichalcogenides: $NbSe_2$, NbS_2, TaS_2, TiS_2, $NiSe_2$, etc.	layered semiconductors: GaSe, GaTe, InSe, Bi_2Se_3, etc.
2D oxides	micas, BSCCO	MoO_3, WO_3	perovskite-type: $LaNb_2O_7$, $(Ca,Sr)_2Nb_3O_{10}$, $Bi_4Ti_3O_{12}$, $Ca_2Ta_2TiO_{10}$, etc.		hydroxides: $Ni(OH)_2$, $Eu(OH)_2$, etc.
	layered Cu oxides	TiO_2, MnO_2, V_2O_5, TaO_3, RuO_2, etc.			**OTHERS**

Table 1. **Current 2D library.** In blue cells are monolayers proven to be stable under ambient conditions (room *T* in air); green – probably stable in air; pink – unstable in air but maybe stable in inert atmosphere. Grey cells indicate 3D compounds which have been successfully exfoliated down to monolayers as evidenced by, e.g., atomic force microscopy but with little further information. Summarized from refs 6-11,42,50. Note that, after intercalation and exfoliation, the oxides and hydroxides may exhibit stoichiometry different from their 3D parents (e.g., TiO_2 exfoliates into a stoichiometric monolayer of $Ti_{0.87}O_2$)[8]. Cell OTHERS indicates that many other 2D crystals including borides, carbides, nitrides, etc. have been[7-11] or can be isolated.

Geim et al., Nature 499, 419-425 (2013)

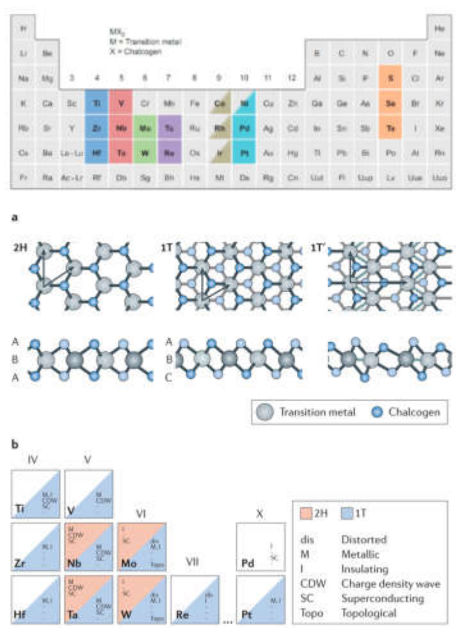
TMDCs

Layered structures with MX_2 structure
Weak interlayer coupling



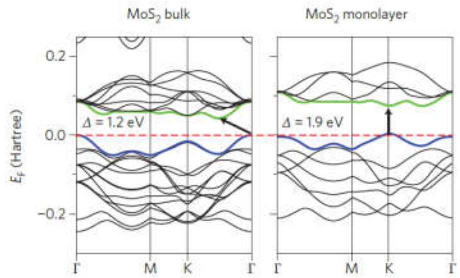
TDMCs have different properties

- Metallic
- Semiconducting
- Superconducting
- Topological
- …



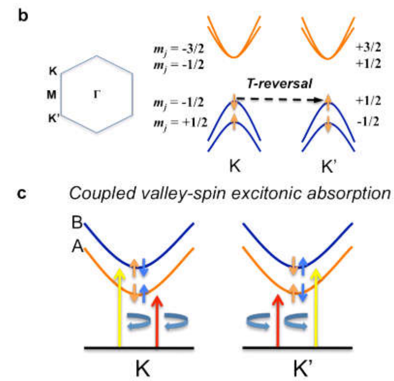
S. Manzeli, S. *et al. Nat. Rev. Mater. 2, 17033* (2017)
D. Zappa et al., Materials 10, 1418 (2017)

Example: MoS2



MoS_2: indirect band gap semiconductor, small gap: 1.3 eV
Single layer MoS_2: direct band gap 1.8 eV

Cond band: localized d orbitals on Mo atom, unaffected by interlayer coupling (K point)
Valance band at (Γ) point p_z orbitals on S, strongly affected by interlayer coupling



- **Inversion symmetry is broken, since, different atoms occupy A and B site**
- **Split valance band due to SO interactions in the lack of inversion (160 meV)**
- **$E_\uparrow(k) \neq E_\uparrow(-k)$ but $E_\uparrow(k)=E_\downarrow(-k)$ (Time Reversal S.)**

→Coupling of spin and valley and the spin arrangement is different in different valleys

E crystal field (in plane), B_{SO}~k × E out of plane

- **For bilayer, inversion is recovered and $E_\uparrow(k) = E_\uparrow(-k)$**
- **Valley dependent selection rules**

A. Kuc et al., Phys. Rev. B. 83, 245213 (2011)
K. F. Mak et al., Nature Nanotech. 7, 494 (2012)

2D Zoo: Van der Waals heterostructures

Lego game:

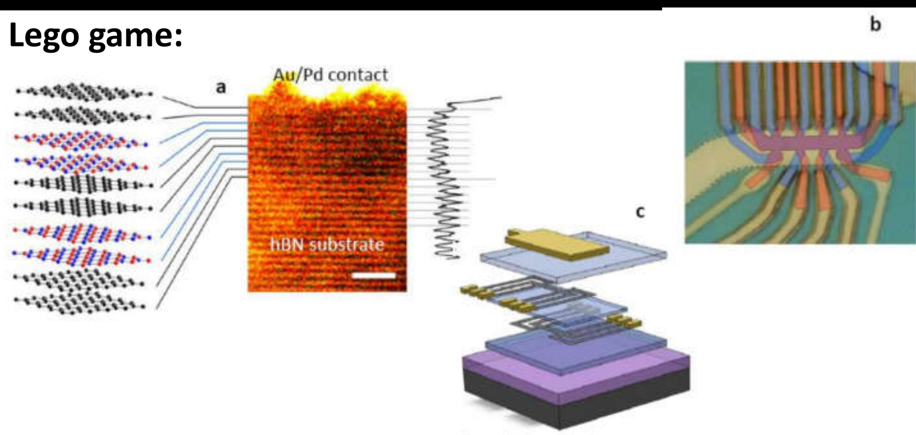


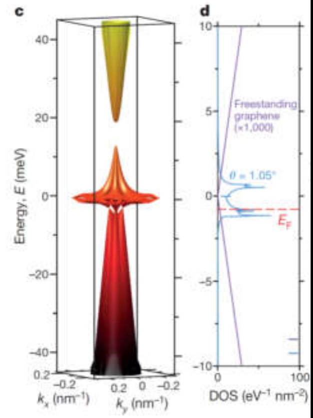
Fig. 2. **State of the art vdW structures and devices**. **a** – Graphene-hBN superlattice consisting of 6 stacked bilayers. Right: Its cross-section and intensity profile as seen by scanning transmission electron microscopy. Left: schematic view of the layer sequence. The topmost hBN bilayer is not visible, being merged with the metallic contact. Scale bar, 2nm. Adapted from ref. 16. **b,c** – Double-layer graphene heterostructures[18]. An optical image of a working device (b) and its schematics (c). Two graphene Hall bars are accurately aligned, separated by a trilayer hBN crystal and encapsulated between relatively thick hBN crystals. Colours in (b) indicate the top (blue) and bottom (orange) Hall bars and their overlapping region in violet. The graphene areas are invisible in the final device image because of the top Au gate outlined by dashes. The scale is given by the width of the Hall bars, 1.5 μm.

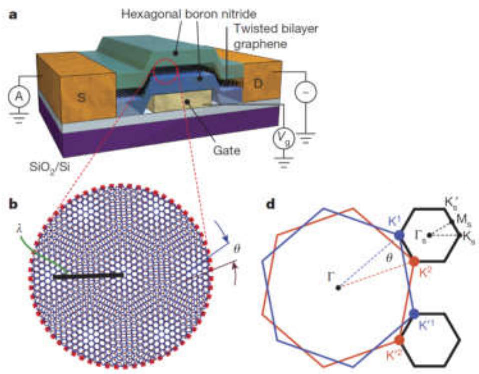
Geim et al., Nature 499, 419-425 (2013)

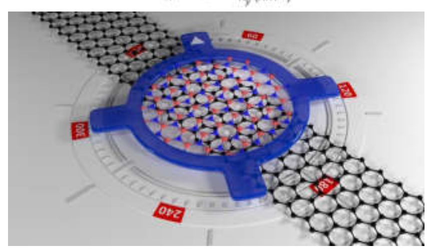
Twistronics

Usually electron-electron interactions can be neglected
Kinetic energy usually dominates and only corrections are given to Fermi liquid theory from e-e interaction
However if narrow bands form (heavy system), correlations might become important
E.g. Mott transition (small t, large U in Hubbard picture)

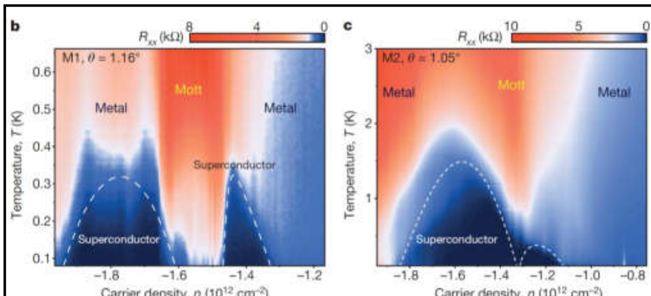
Twisted BLG: Two layers can form a Moiré →band reconstruction.
For certain *magic* angles the bands become flat.





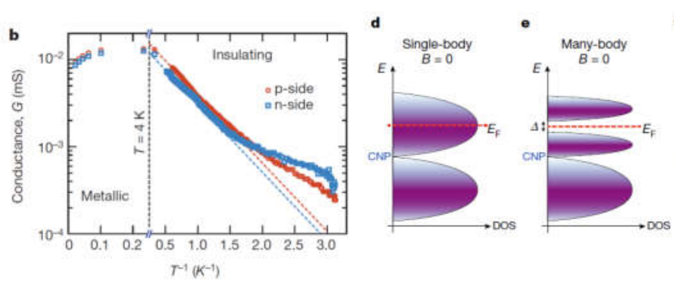


Y. Cao et al., Nature 556, 43 (2018)
Y. Cao et al., Nature 556, 80 (2018)



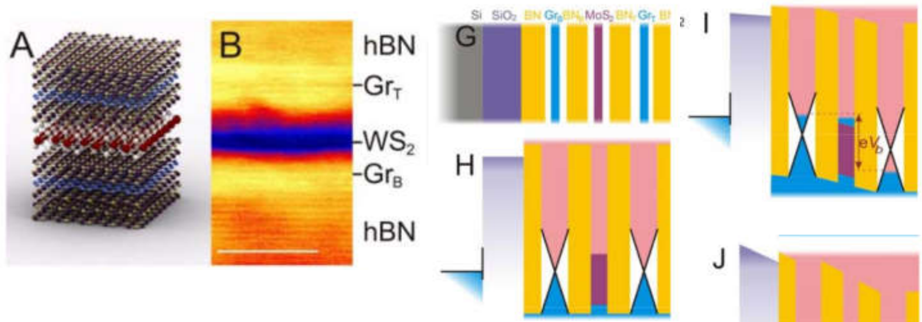
SC phase appears with zero resistance with Tc up to 1-2 K.
It is sourranded insulating phases – „dome" structures
Resambles the phase diagram of high Tc, however now this is gate tunable.
Around 0.4 T, the SC phase vanishes.

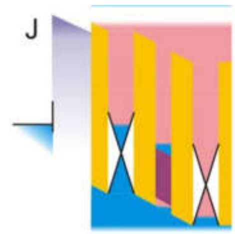
Insulating phase is a Mott phase.
Only appears below 4K.
Many-body gap opens.
It disappears around 6T.



2D Zoo: Van der Waals heterostructures

Various systems. E.g. LED structure





Light-emitting diodes by bandstructure engineering in van der Waals heterostructures

F. Withers[1], O. Del Pozo-Zamudio[2], A. Mishchenko[1], A. P. Rooney[3], A. Gholinia[3], K. Watanabe[4], T. Taniguchi[4], S. J. Haigh[3], A. K. Geim[5], A. I. Tartakovskii[2], K. S. Novoselov[1]

Withers,
Nature Materials, 14, 301-306 (2015)