Graphene

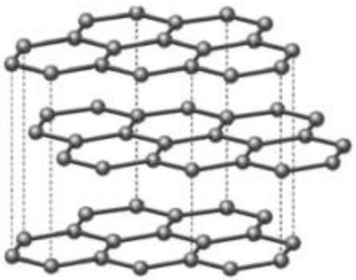
2.674

Jeehwan Kim

Carbon-based nanomaterials

Basic building block

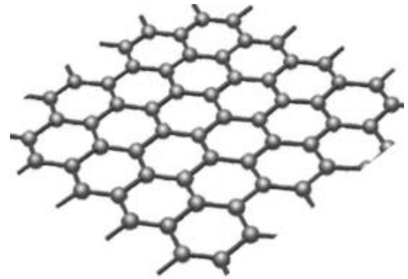
Stack



Graphite (3D)

van der Waals stack of graphene

Conductor



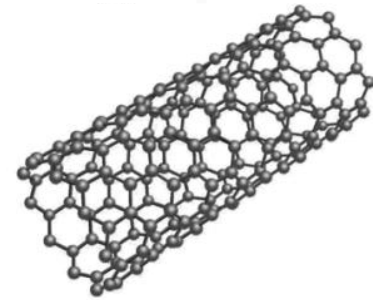
Graphene (2D)

Single-atom-thick carbon layer

sp2 bonding of carbons

Semi-metal

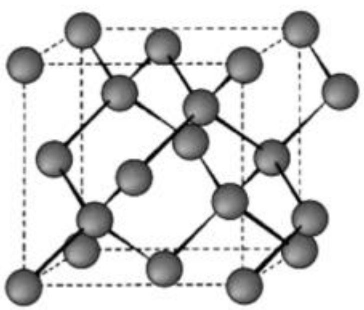
Roll



Carbon nanotube (1D)

Rolled graphene

Semiconductor (2/3) or metal (1/3)

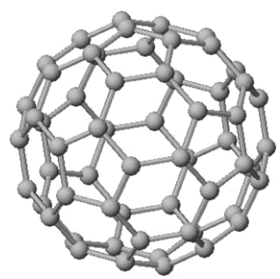


Diamond (3D)

sp3 bonding of carbons

Wide band gap (5.5 eV)

Ball

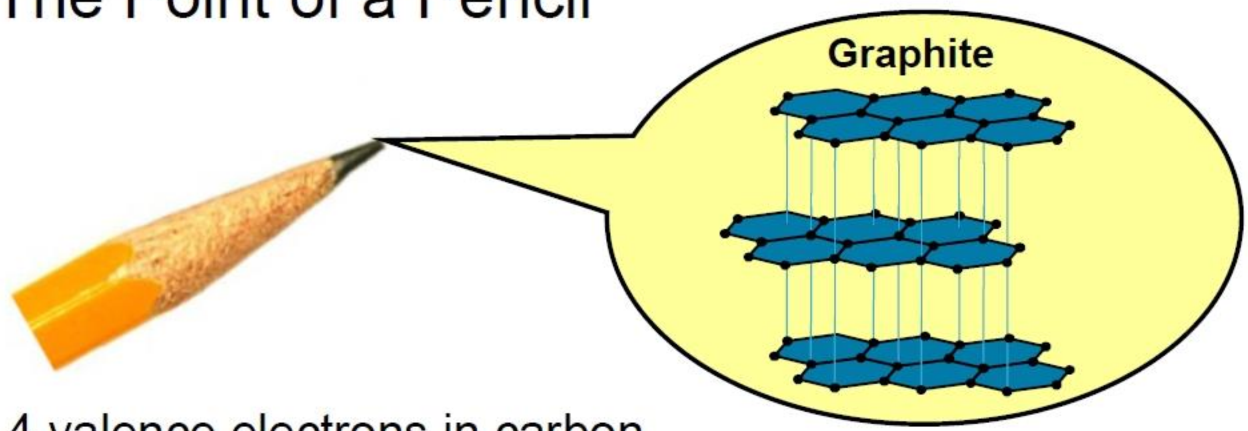


Fullerene (0D)

Wide band gap (5.5 eV)

What is graphene?

The Point of a Pencil



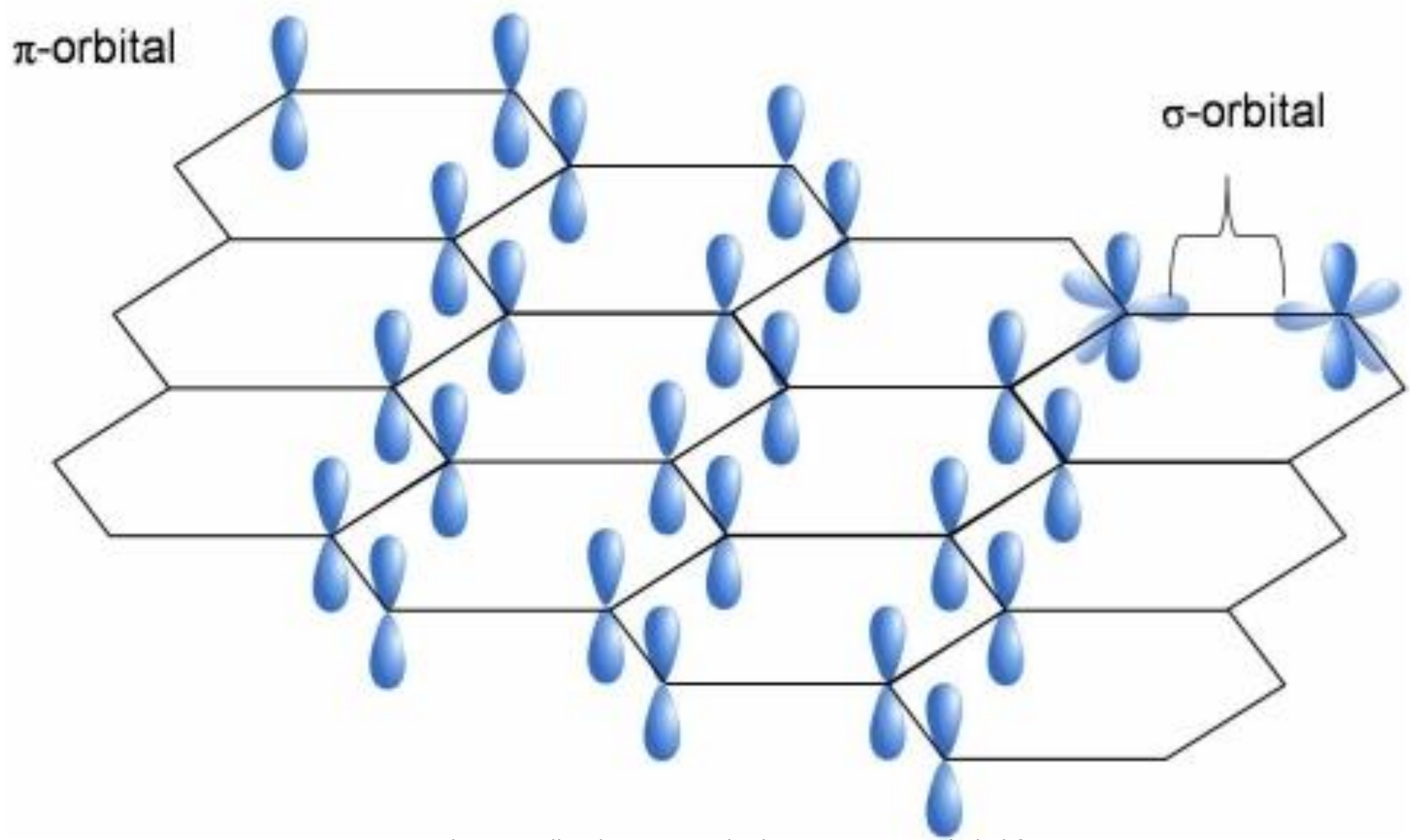
4 valence electrons in carbon

- 3 bonds to neighbors (sp^2 σ bonds)
  - Structural Rigidity within planes
  - Weak Van der Waals attraction between planes
- 1 delocalized π electron
  - Electrical Conductivity

Graphene = A single layer of graphite

A unique 2D electronic material

Graphene overall orbital structure



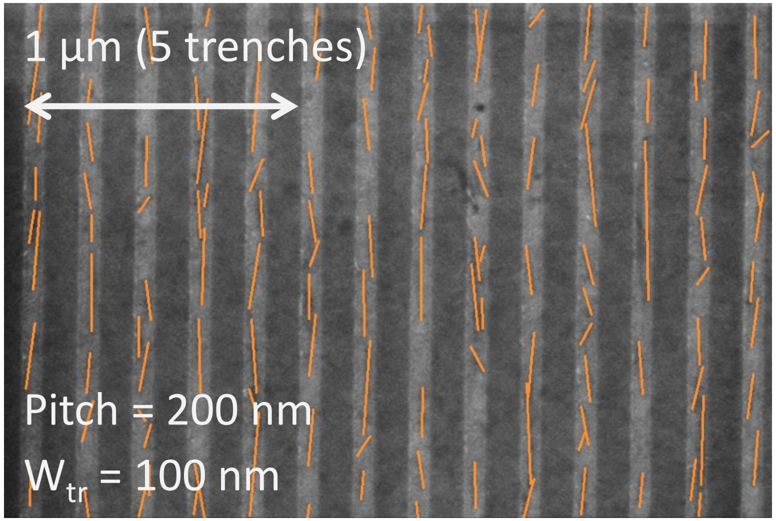
CNT vs Graphene

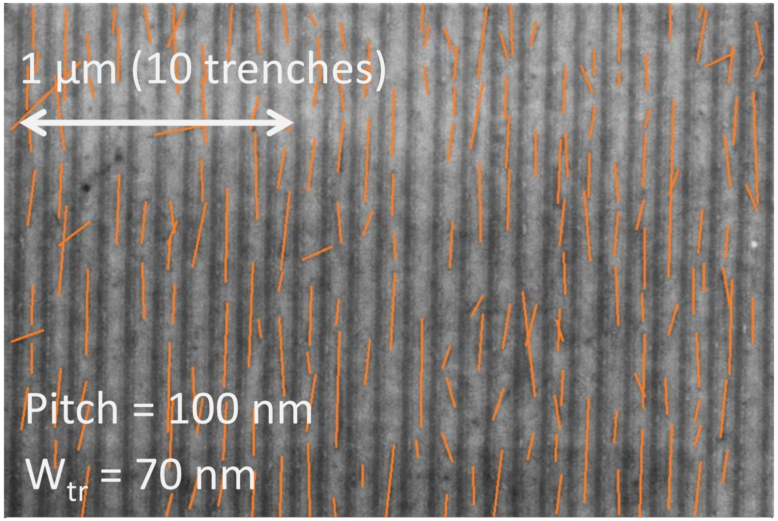
	CNT	Graphene
Electrical conductivity	~100,000 cm^2/VS	>100,000 cm^2/VS
Thermal conductivity	~5000W/K.m	~5000W/K.m
Young's modulus	0.9 ~1.1TPa	1 TPa
Transparency	O	O
Flexibility	O	O

	Electron mobility (cm^2/Vs)	Electrical characteristics
Copper	5,770	Conductor
Silver	9,490	Conductor
GaAs	6,000	Semiconductor
Si	1,350	Semiconductor
Graphene/CNT	>100,000	Semi-metal

Challenges for Carbon Nanotube Applications

- Control the diameter of nanotubes and chirality.
  - Purification/sorting methods required for uniform CNT
- Large scale integration
  - Placement/alignment methods required for **long-range order**



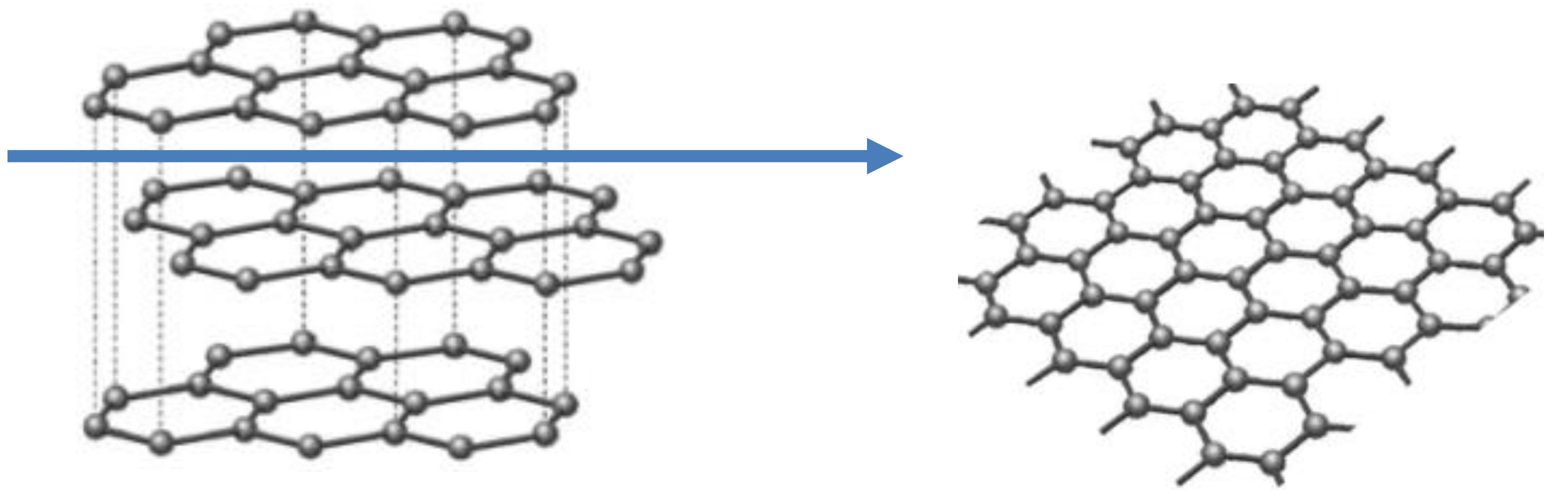


H. Park *et al.*, *Nature Nanotechnology* 7, 787(2012)

- **ASSEMBLY, ASSEMBLY, ASSEMBLY!!!**
- **Graphene → Lab 11**

Discovery of carbon allotropes

- 1985: Curl, Kroto, Smalley discovered fullerene (Nobel, Physics 1996)
- 1991: Iijima discovered single wall carbon nanotubes.
- 2010 A. Geim and K. Novoselov (Nobel physics on Graphene)→ **Scotch tape method**



Why so difficult?

Graphene fabrication method

- Scotch Tape Method (Top down)
  - Exfoliation of random thickness graphene from graphite
- Growth method (Bottom up)
  - CVD growth on Cu foils
  - Graphitization of SiC wafer
- Layer resolved transfer (Bottom up + Top down)
  - Exfoliation of graphene on SiC wafer/transfer

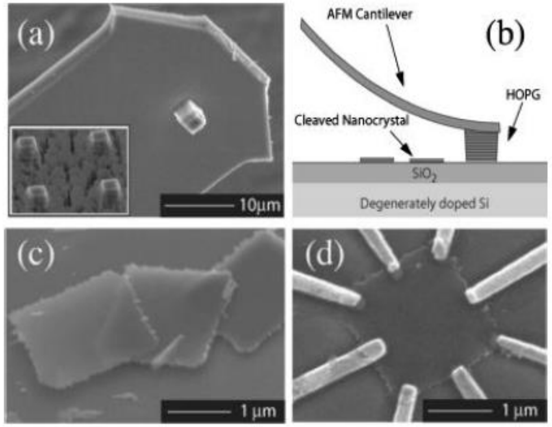
Pioneers in graphene

Andre Geim (Manchester)
Novoselov et al. Science 2004

Individual layers on SiO_2 prepared by mechanical exfoliation.

Philip Kim (Columbia)
Zhang et al. APL 2004

"Nanopencil" on AFM cantilever deposits ~ 15 layer graphite films



Scotch tape process

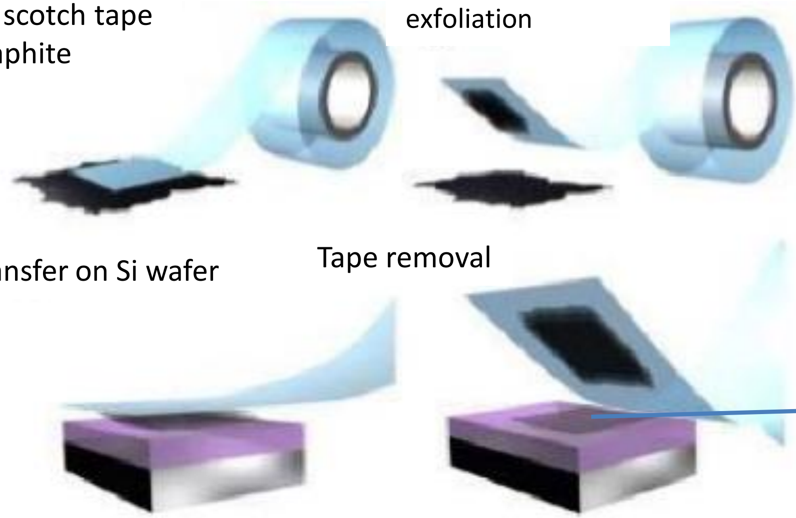
http://phelafel.technion.ac.il/~tzipora/graphene.html

Apply scotch tape on graphite

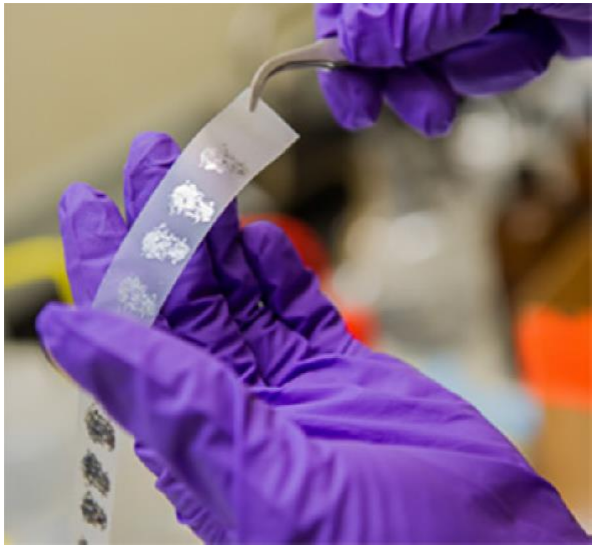
Multilayer graphene exfoliation

Transfer on Si wafer

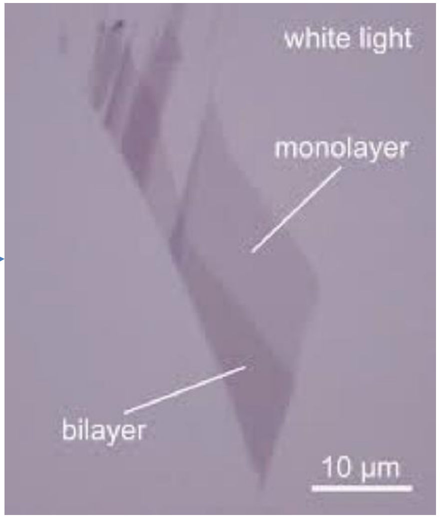
Tape removal



Novoselov et al., Phys. Sci. 014006 (2012)

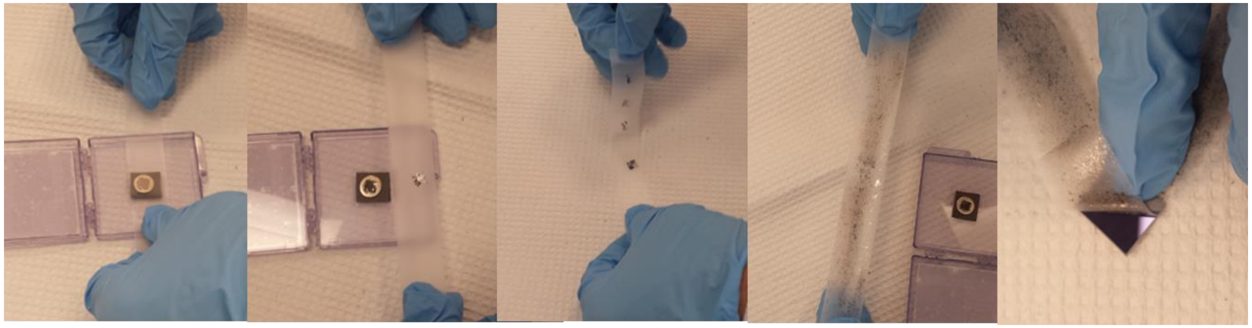


http://www.mccormick.northwestern.edu/magazine/



http://grapheneindustries.com

Scotch tape method (in Lab 11)



The procedure

A. Apply scotch tape on highly ordered pyrolytic graphite (HOPG) and detach the graphite from HOPG surface.

B. Fold over the Scotch tape several times at different locations to make multiple clones of exfoliated graphite all over the sticky side of tape

C. Repeat B for at least 30 times

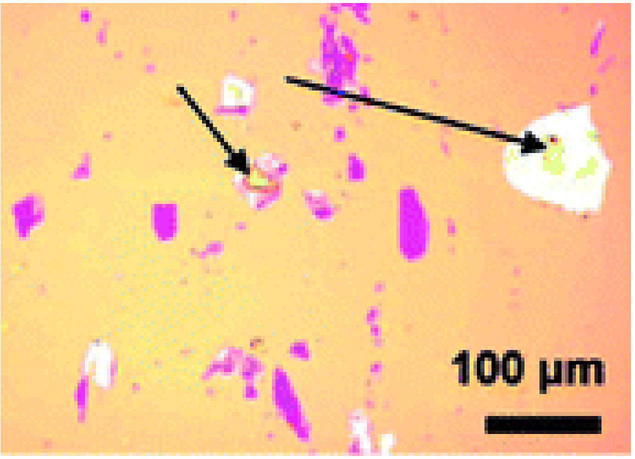
D. Place graphite with reduced number of layers on the tape, on the Si substrate and press it hard

E. Detach the tape

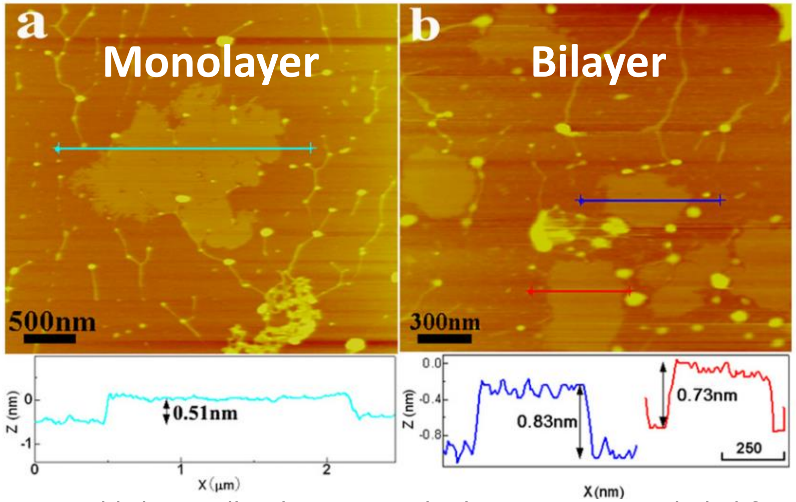
F. Observe your sample under the microscope at AFM to see if you successfully transferred graphene on the Si substrate and save the image

Graphene flakes on oxide

Optical image



Nanoscale, 2012,**4**, 5527-5537



Thickness of monolayer graphene typically measured by AFM
: 0.5-1nm

Theoretical thickness of graphene
: 0.35 nm

Nanotechnology 22 (2011) 365306

CVD growth

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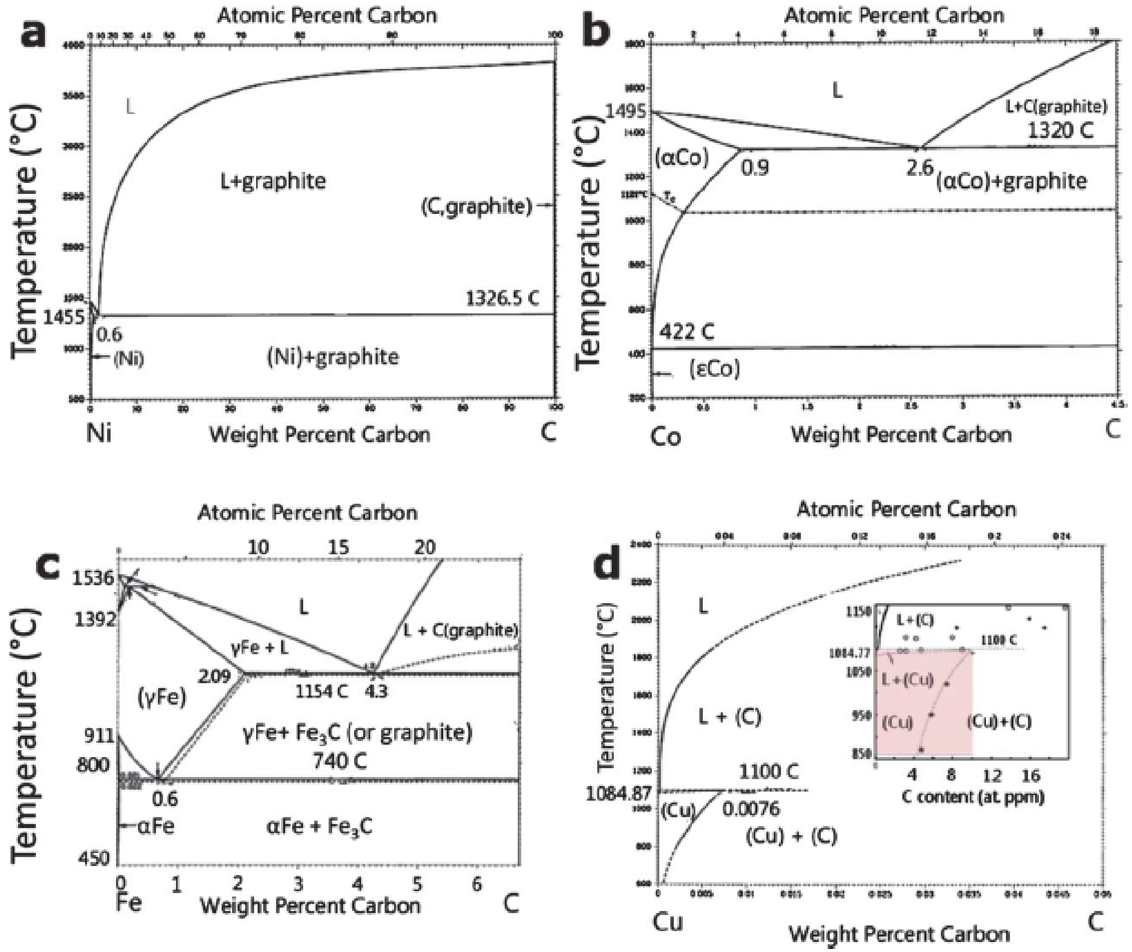
Please see the second image on page https://www.comsol.com/blogs/synthesizing-graphene-chemical-vapor-deposition/.

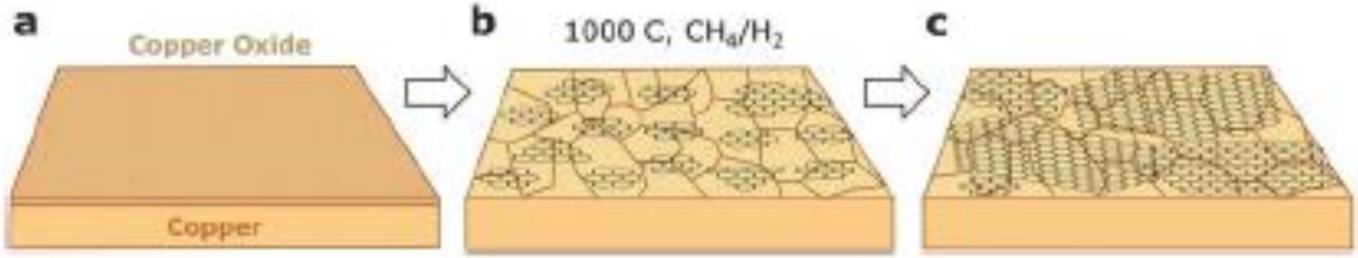
Selection of catalytic metal

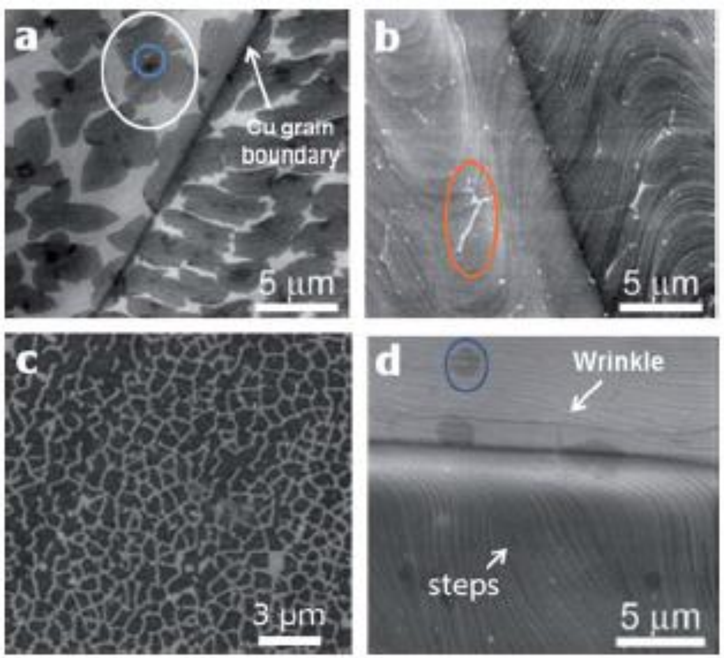


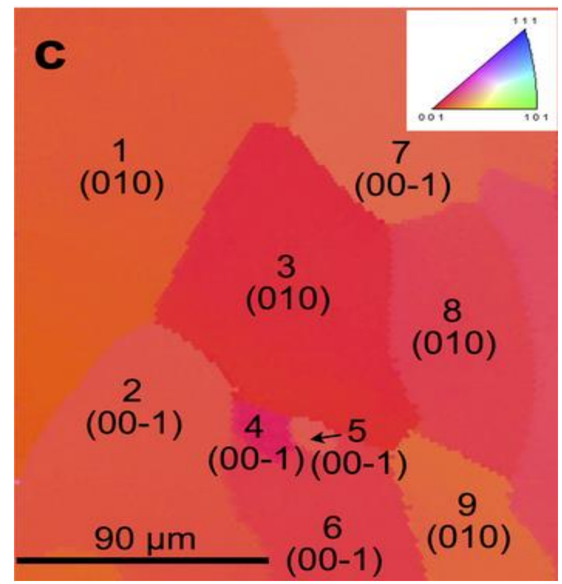
J. Mater. Chem., 2011, 21, 3324–3334

Solubility of carbon in metals determines number of graphene layers : Cu → Monolayer, Ni → mono-bilayers

Growth mechanism



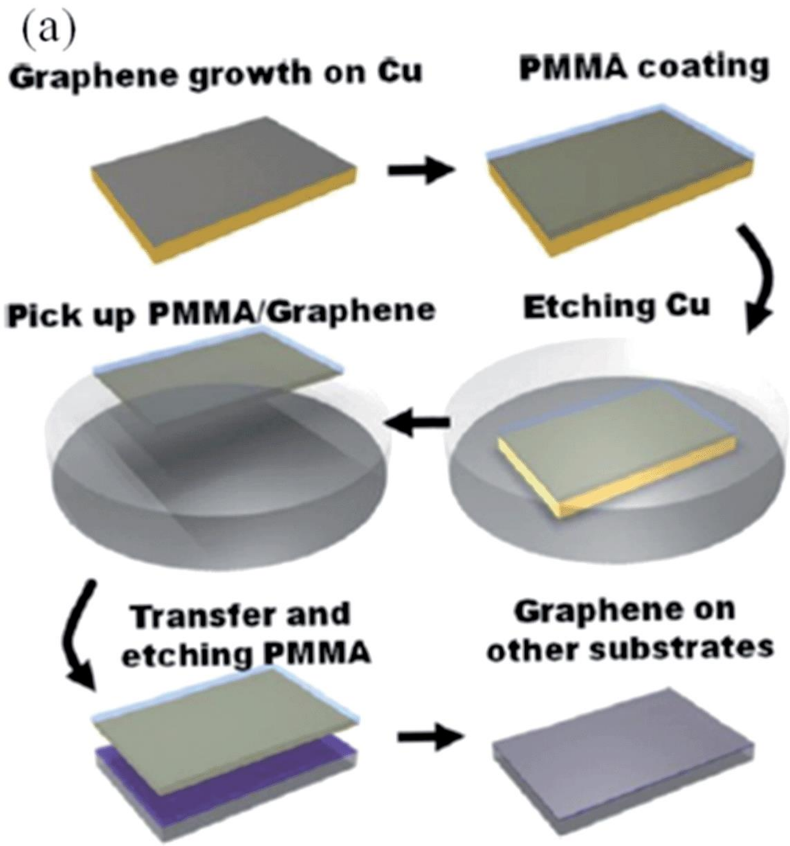




J. Mater. Chem., 2011, 21, 3324–3334

Transfer of CVD graphene

Pick up graphene
From the solution
using a substrate
→ Wrinkle formation



Cu foils etched
Graphene floating on solution

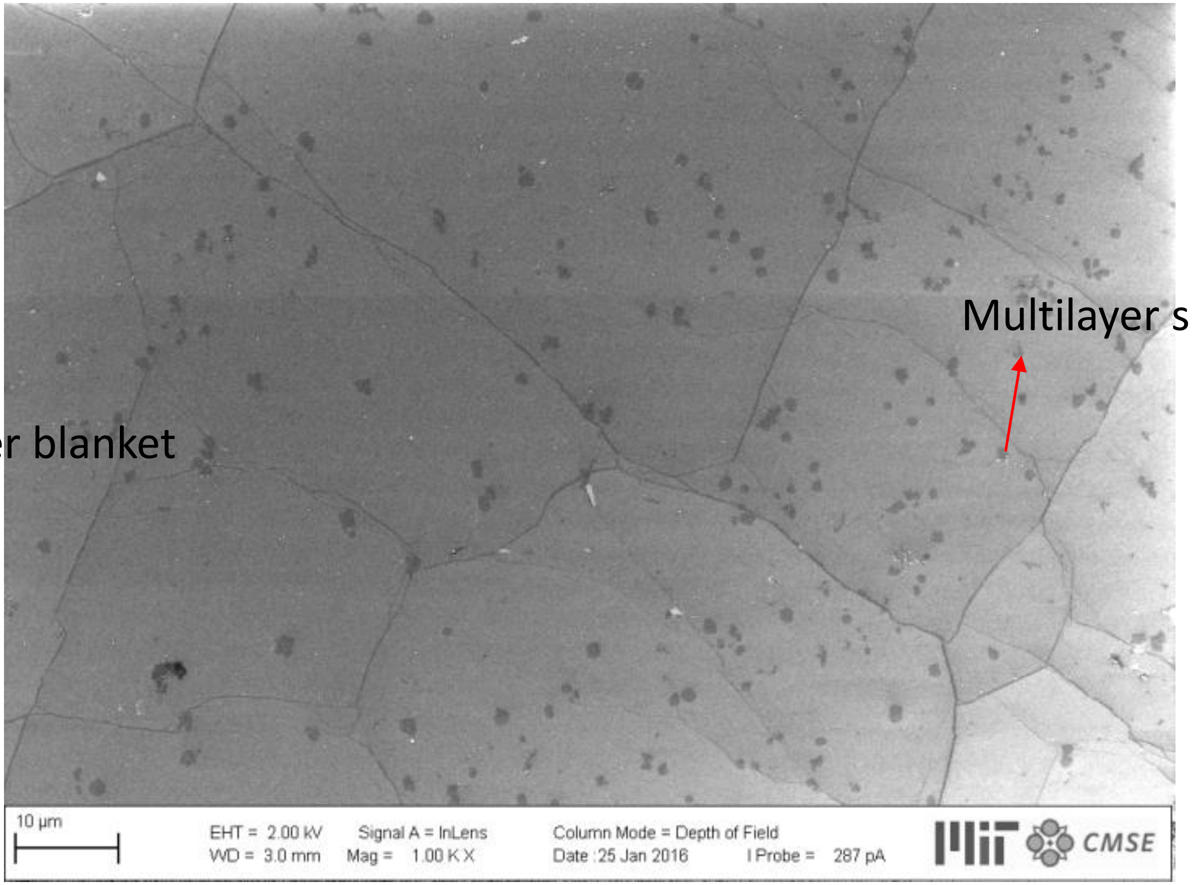
J. Mater. Chem. A, 2014,**2**, 12136-12149

Monolayer graphene | Large scalability

Polycrystalline / Wrinkled | Wet-transfer

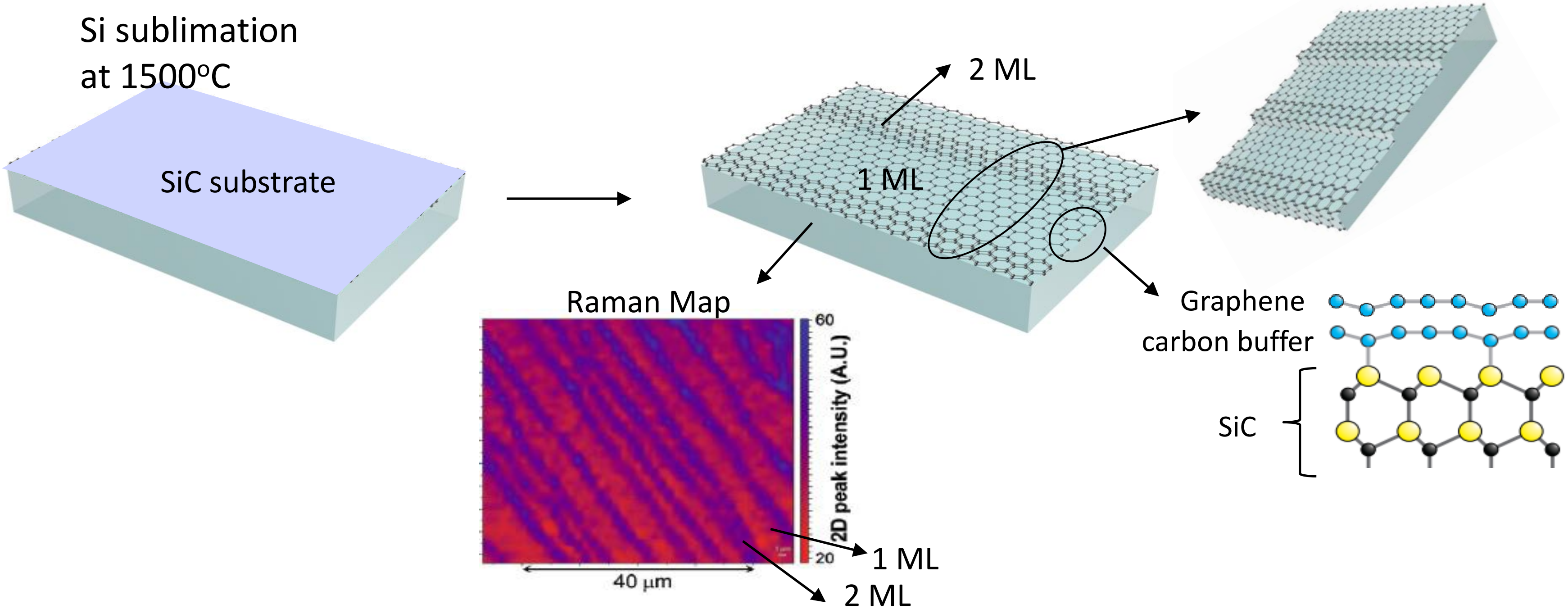
Properties of CVD graphene

Monolayer blanket



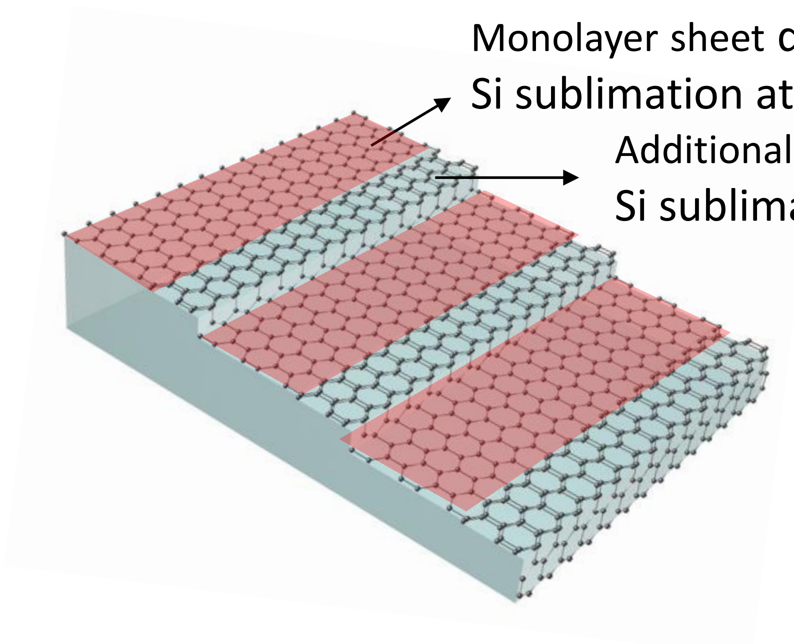
Graphitization of SiC

- When SiC substrates are annealed at high temperature (above 1300 °C), Si atoms selectively desorb from the surface and the C atoms left behind naturally form monolayer graphene
  - Single-oriented flat graphene obtainable



Flat / Single-oriented | **Un-transferrable / Expensive**

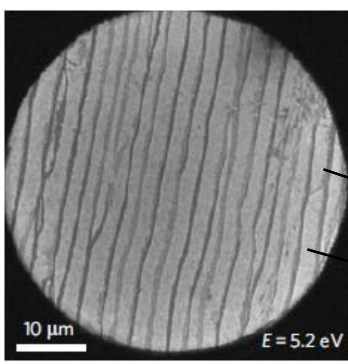
Properties of SiC graphene



Monolayer sheet due to
Si sublimation at surface

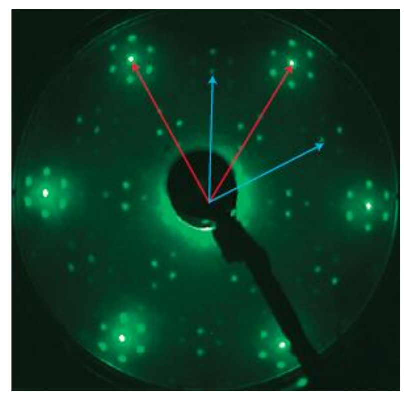
Additional stripe due to
Si sublimation at step edge

LEEM

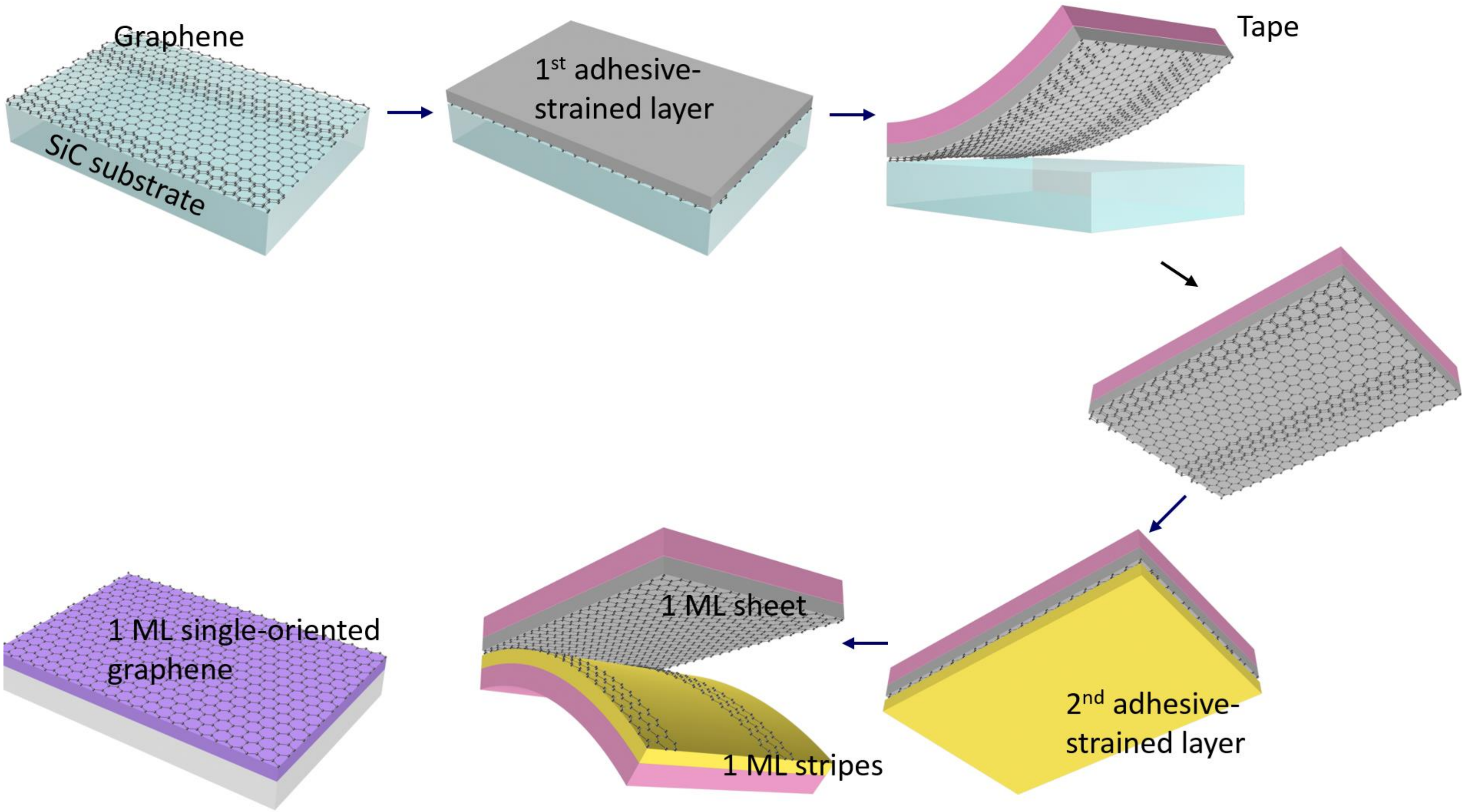


2 ML

1 ML

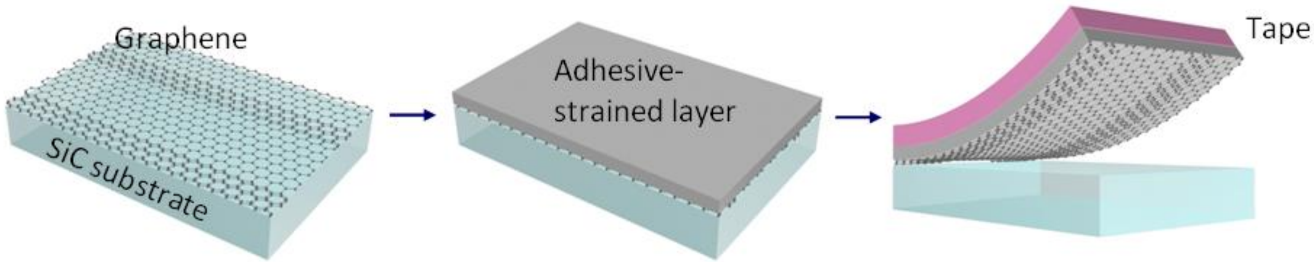


Layer resolved SiC graphene transfer

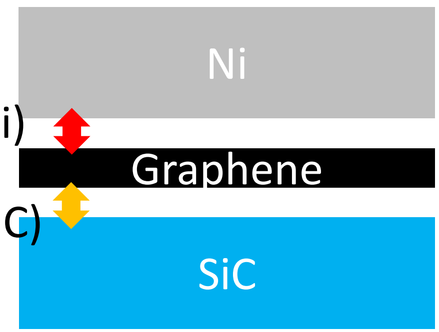


Jeehwan Kim et al., "Layer-resolved graphene transfer via engineered strain-layers", ***Science***, Vol. 342, 833 (2013)

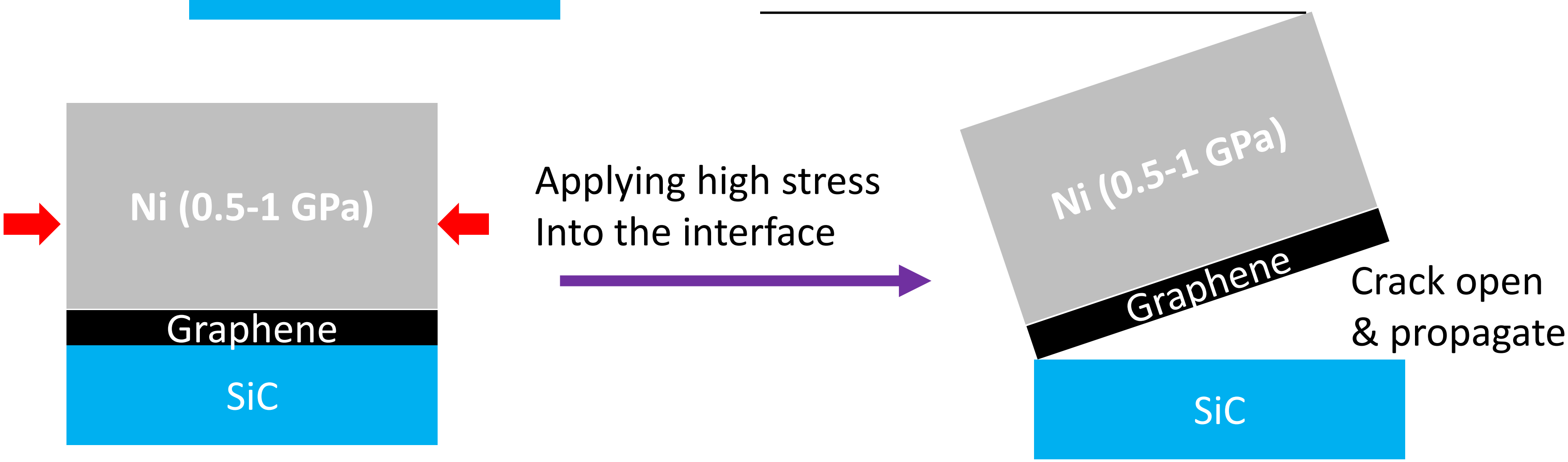
Thin film mechanics



Binding E (G-Ni)
>
Binding E (G-SiC)



	Binding energy (meV/atom)
Ni-G	~ 140
G-SiC	**~100**



Delamination criteria

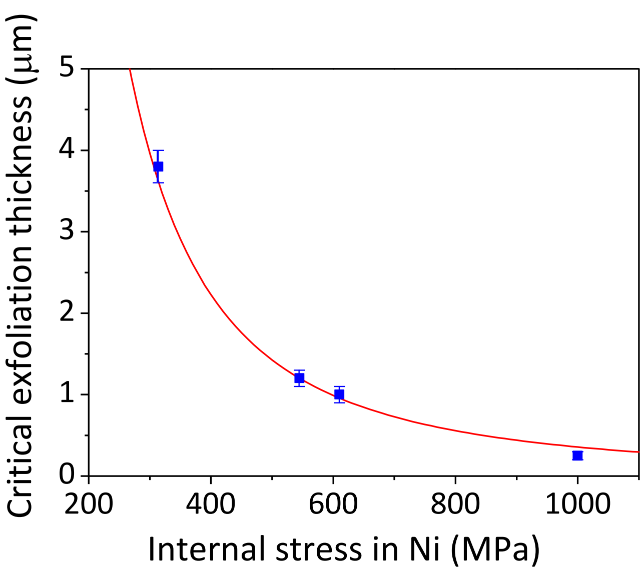
$$E_{G-SiC} = \frac{(1-\nu_{Ni})}{2Y_{Ni}} \sigma_{Ni}{}^{2} t_{Ni}^{c}$$

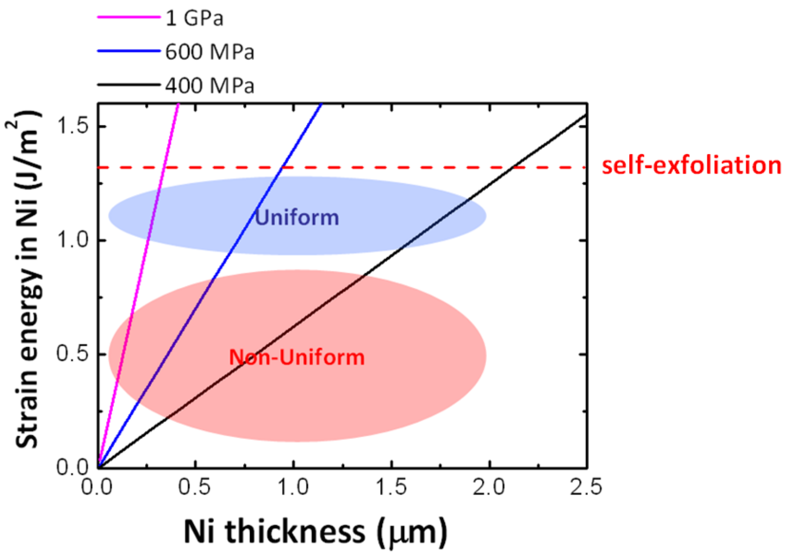
G-SiC binding Energy

Strain energy in Ni

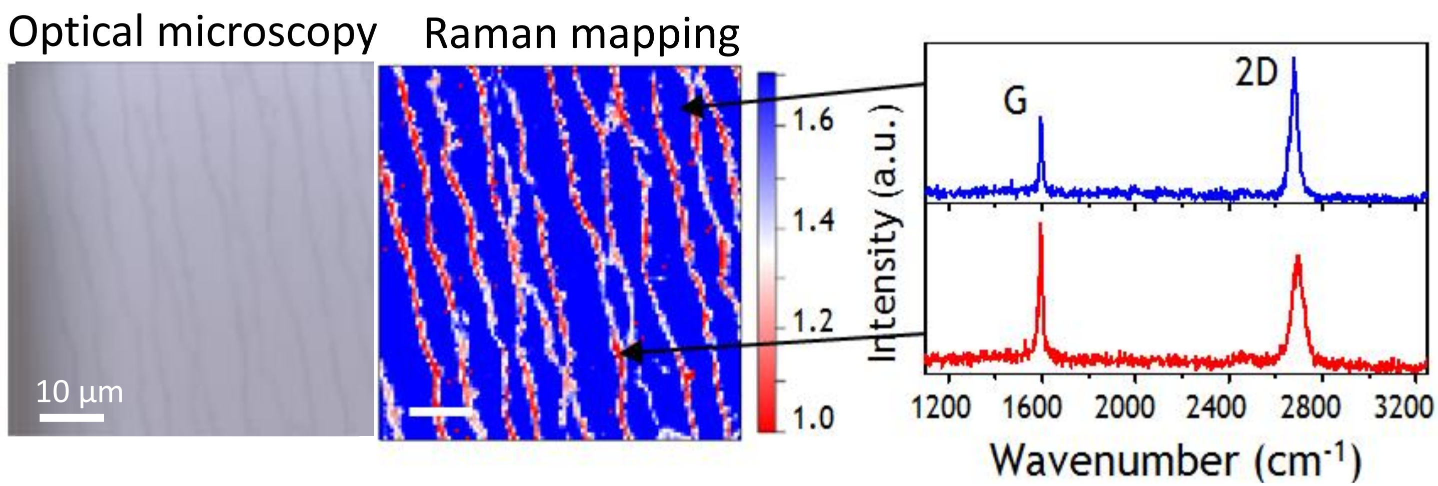
Critical Ni thickness for exfoliation

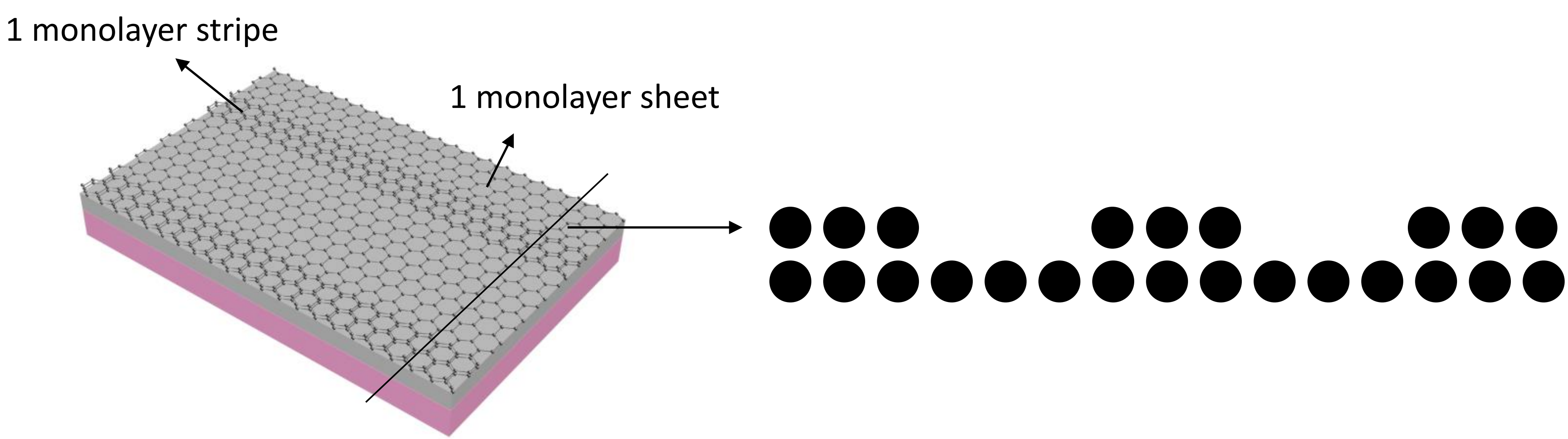
$$t_{Ni}^{c} = E_{G-SiC} \frac{2Y_{Ni}}{(1-\nu_{Ni})} \frac{1}{\sigma_{Ni}{}^{2}}$$



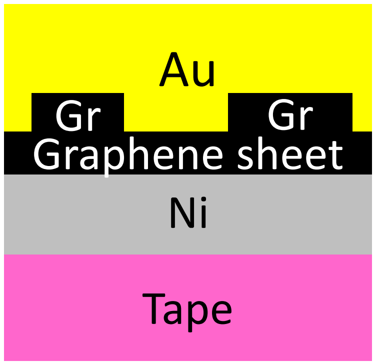


Graphene exfoliated from SiC





Separation of bilayer stripes



	Binding energy (meV/atom)
G-G	~ 45
Ni-G	~ 140
Au-G	~ 60

BE (Au-G) > BE (G-G)
BE (Au-G) << BE (Ni-G)

Manipulation of binding energy contrast among materials

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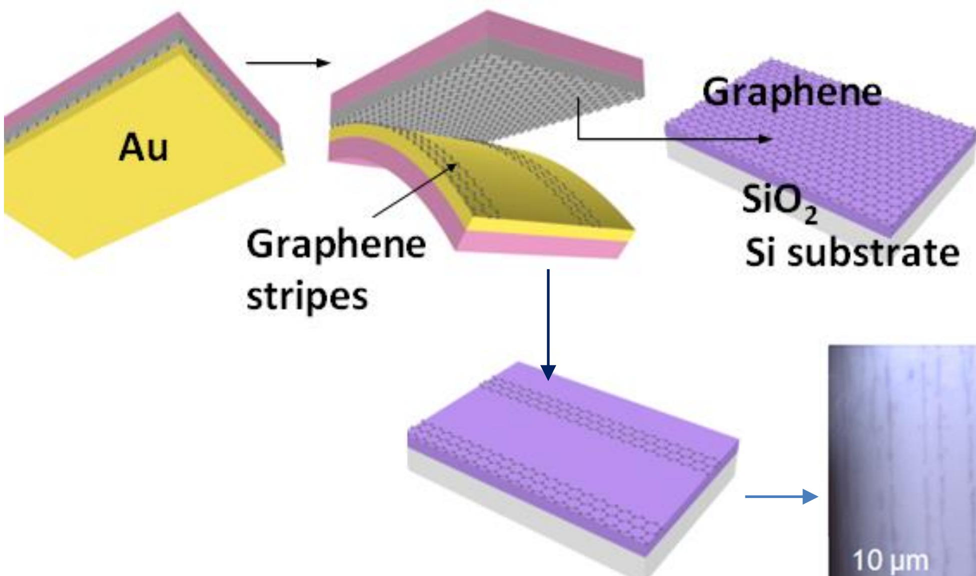
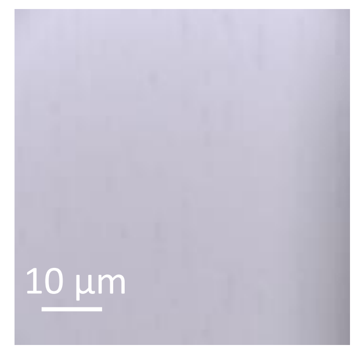
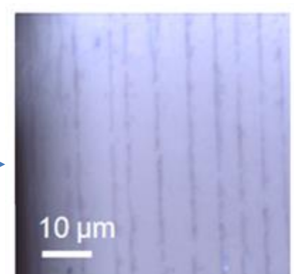
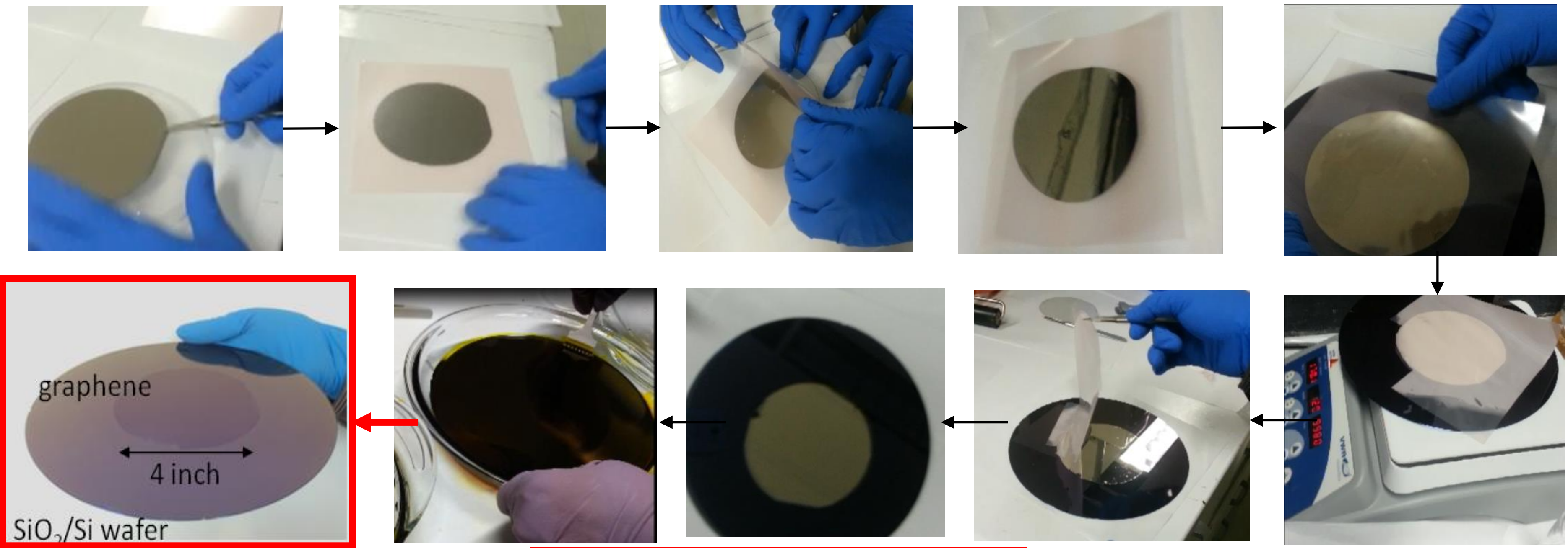
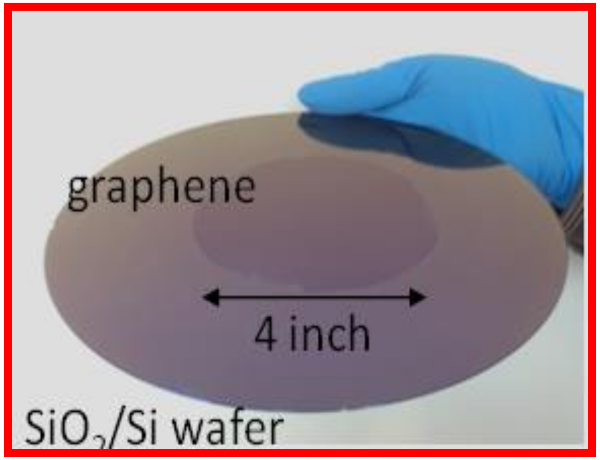






4-inch wafer-scale single-crystalline graphene





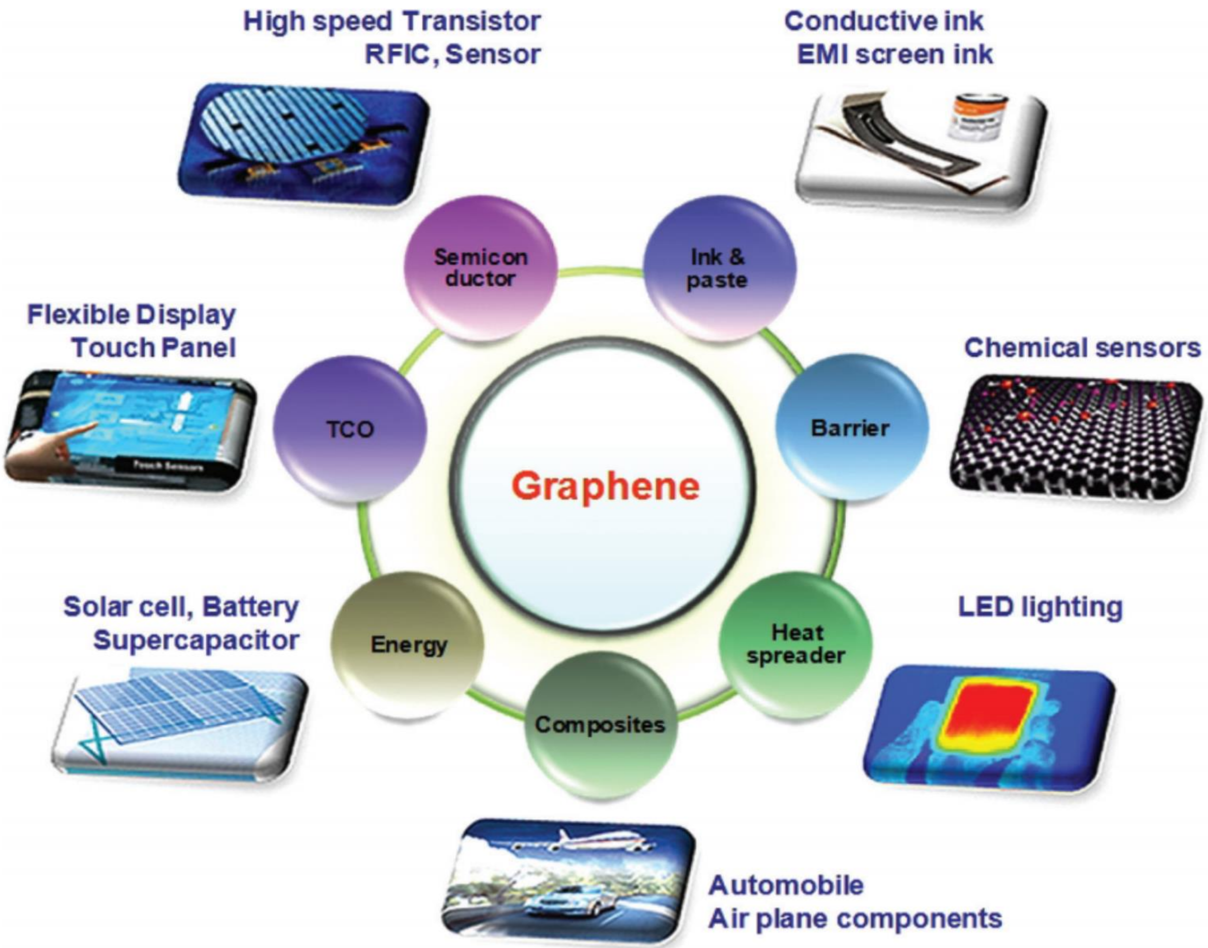
Summary of graphene fabrication methods

Excellent (green) | Good (yellow) | Poor (red)

	Scotch Tape graphene	CVD graphene	SiC graphene	Layer-resolve Transfer
Monolayer Control	Uncontrollable	Self-limiting (>95% ML)	Self-limiting (1.2 ML)	
Crystalline orientation	Single but less than poly grain size	Polycrystal	Single	
Flatness	Pristine	Wrinkle from foils	Same as SiC wafer	
Large-scalability	~50 µm	Depending on CVD reactor size	Wafer size	
Transfer efficiency	Uncontrollable	Wet-transfer	Un-transferrable	
Process cleanliness	Dry-transfer	Wet-transfer	No transfer invovled	
Price	Cheap	Cheap	Extremely expensive	

J. Kim*, H. Park*, J. Hannon, S. Bedell, K. Fogel, D. Sadana, C. Dimitrak
"Layer-resolved graphene transfer via engineered strain-layers", ***Science***, Vol. 342, 833 (2013)

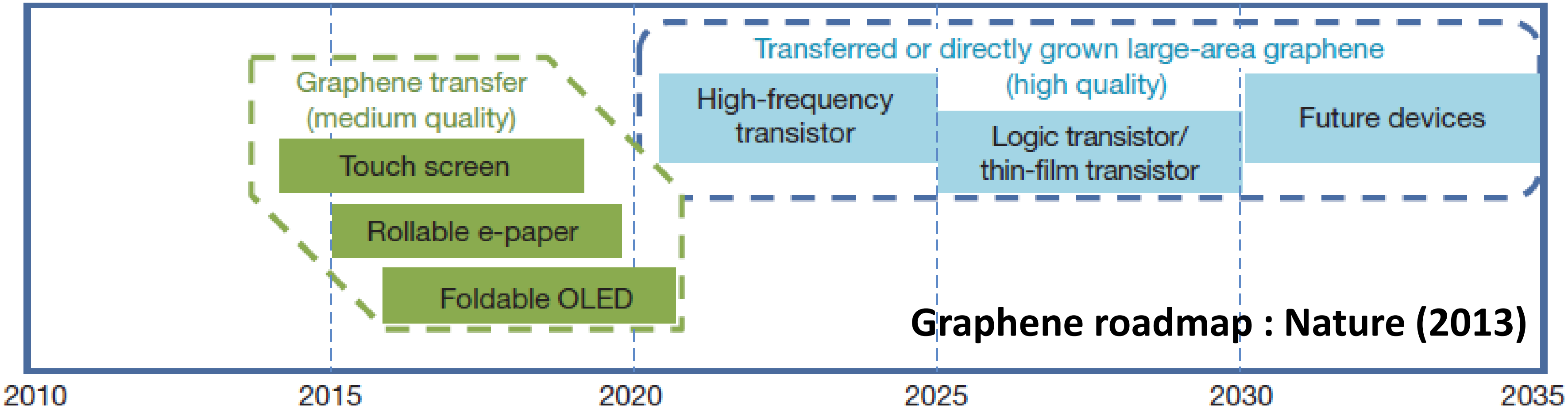
Application of graphene



Nanoscale, 2015, **7**, 4598-4810

Future of graphene electronics

Future of graphene electronics



In Lab 11

1) Experience Nobel Prize winning method to fabricate graphene from graphite

2) Image different types of graphene using AFM

- Measure thickness of monolayer graphene
- Find thinnest graphene among graphene flakes you made

3) Obtain atomic image of graphene using STM

Quiz (May 3)

- Examples
  - Short answer questions
    - What kind of chemical bond between PDMS and glass slide results in after O2 plasma treatment and bonding of the two surfaces?

      Covalent bonding
  - Fill blanks
    - The ratio of inertial force over viscous force defined as, $\rho du/ \mu$. This is (***Reynolds***) number
  - True or False
    - Single atom can be resolved by SEM. ***F***
  - Multiple choices