Optical Spectroscopy of Graphene and Topological Insulators

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Outline

Graphene

- Introduction
- Graphene on Cu single crystal surfaces
- Nitrogen doped graphene
- Twisted bilayer graphene

Topological insulator nanostructures

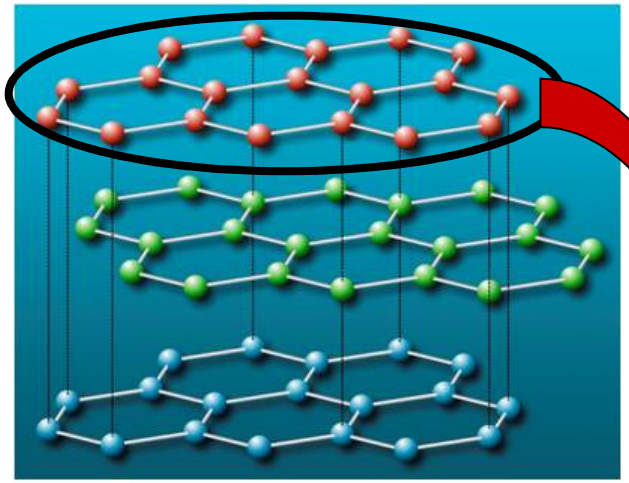
- Bi_2Te_3 nanoplates

Graphene

- **Introduction**
- Graphene on Cu single crystal surfaces
- Nitrogen doped graphene
- Twisted bilayer graphene

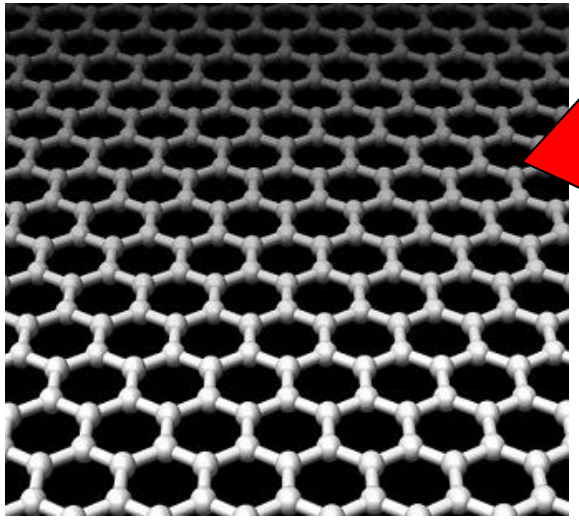
Graphite → Graphene

Graphite pencils



3D graphite crystal

2D graphene

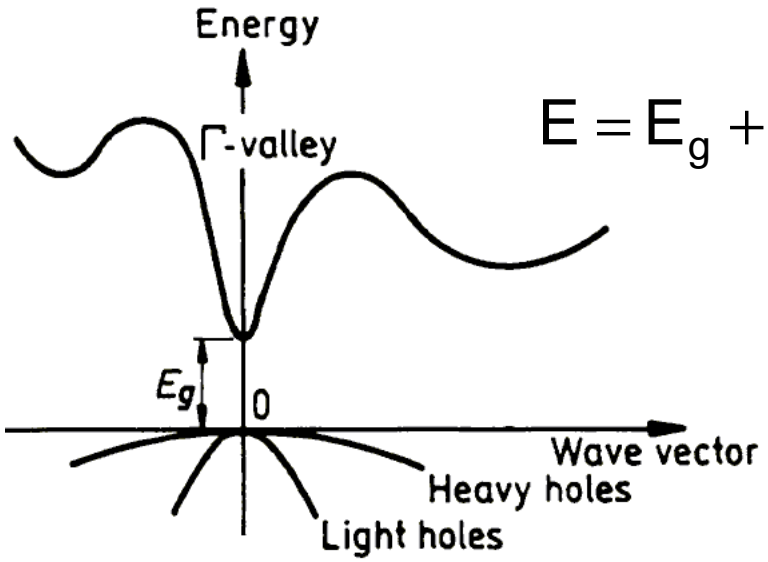


Graphene is a **one-atom-thick** (~3.35Å) planar sheet of carbon atoms that are packed in a **honeycomb** crystal lattice

Discovered in 2004
Nobel Prize awarded in 2010

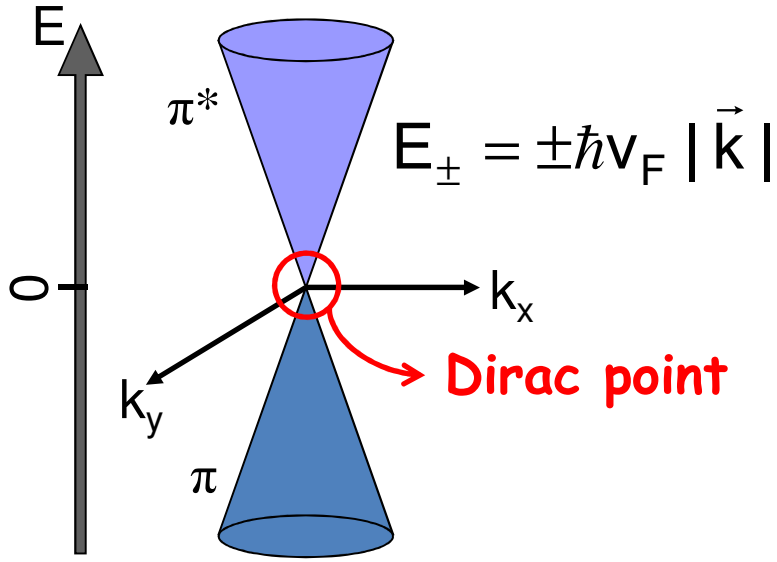
Graphene: a new condensed-matter system

Electron band structure in conventional condensed-matter system



$$E = E_g + \frac{\hbar^2 k^2}{2m^*}$$

Electron band structure in graphene



$$E_{\pm} = \pm \hbar v_F |\vec{k}|$$

Graphene: Linear dispersion near the Dirac points

Novel properties

- **Low electrical resistivity** 1μΩ·cm at room temperature

  ~33% less than Cu and Ag, the lowest-resistivity metallic materials

- Room temperature **mobility** up to 200,000cm^2/Vs

  electrons in graphene travel more than 100 times faster than those in Si (μ~1400cm^2/Vs)

- Superb mechanical strength

  breaking strength comparable to that of the diamond

- Superior thermal conductivity

  Heat transfer ability ~10 times higher than Cu and Ag

- Optically transparent in the visible range: **transparent conductor**

Significant potential applications

high-frequency electronics

BREVIA

Science, **327**, 662 (2010)

100-GHz Transistors from Wafer-Scale Epitaxial Graphene

Y.-M. Lin,* C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H.-Y. Chiu, A. Grill, Ph. Avouris*

stronger composite materials

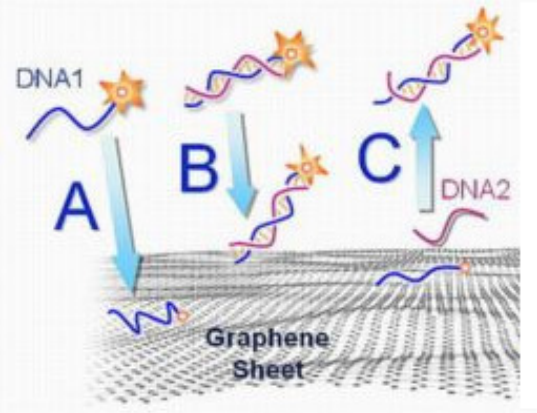
(lighter but more crack-resistant aircraft)

optoelectronic devices

(displays, touch screens, etc.)

biosensors

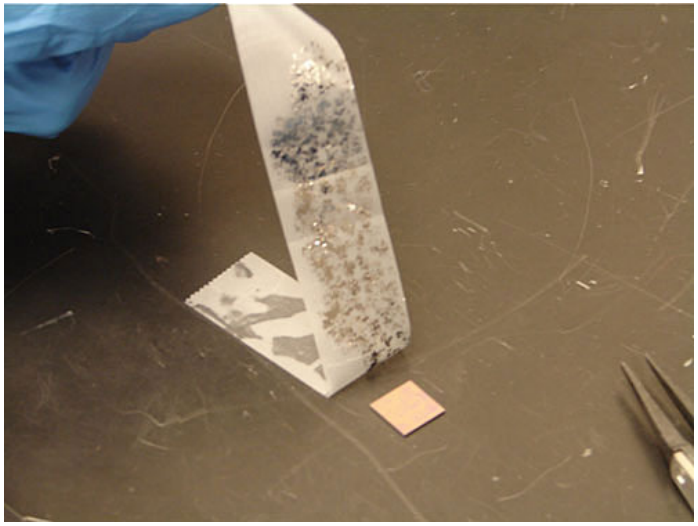
(disease diagnosis)



How to make graphene?

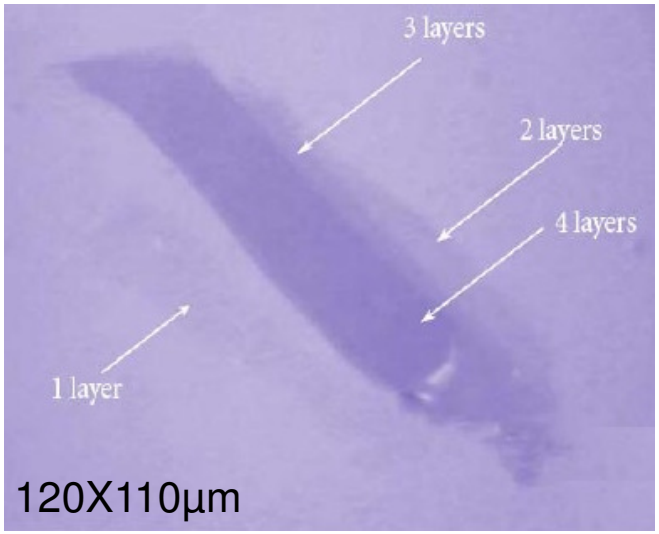
Scotch-tape method

Mechanical exfoliation



Scientific American

Observable color contrast on 300 nm SiO_2 layer



NT-MDT

- **Advantages:**
  - * high quality graphene flakes
  - * low cost

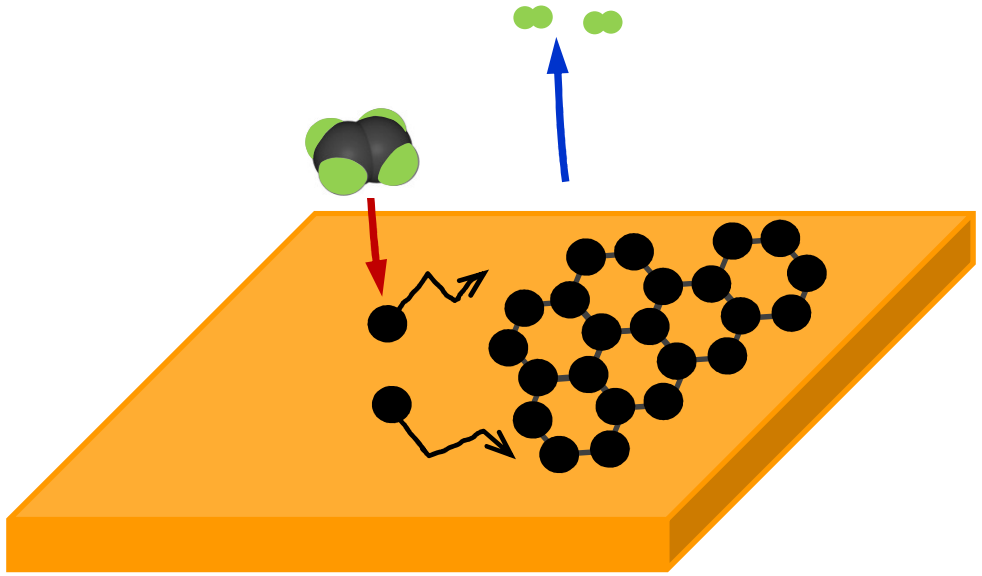
- **Drawbacks:**
  - * low efficiency (tiny flakes)
  - * not suitable for large area production required by electronic applications

How to make large area graphene?

Growth on transition metal by chemical vapor deposition (CVD)

- **Growth temperature 900-1000^{o}C**
- **Ethylene or methane is used as C source**
- **Cu is a catalyst for graphene growth**

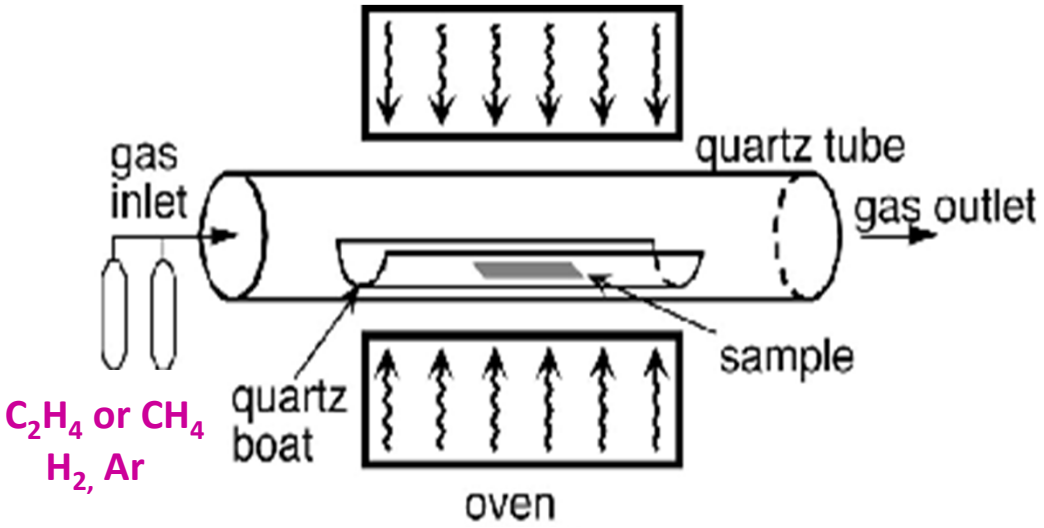
hydrocarbon molecules crack on hot Cu surface



How to make large area graphene?

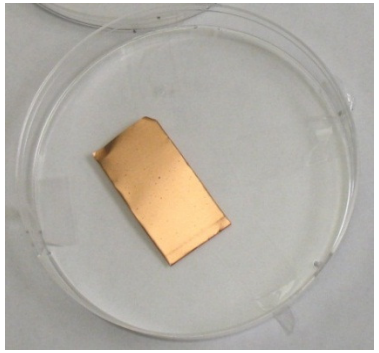
chemical vapor deposition (CVD)

apparatus

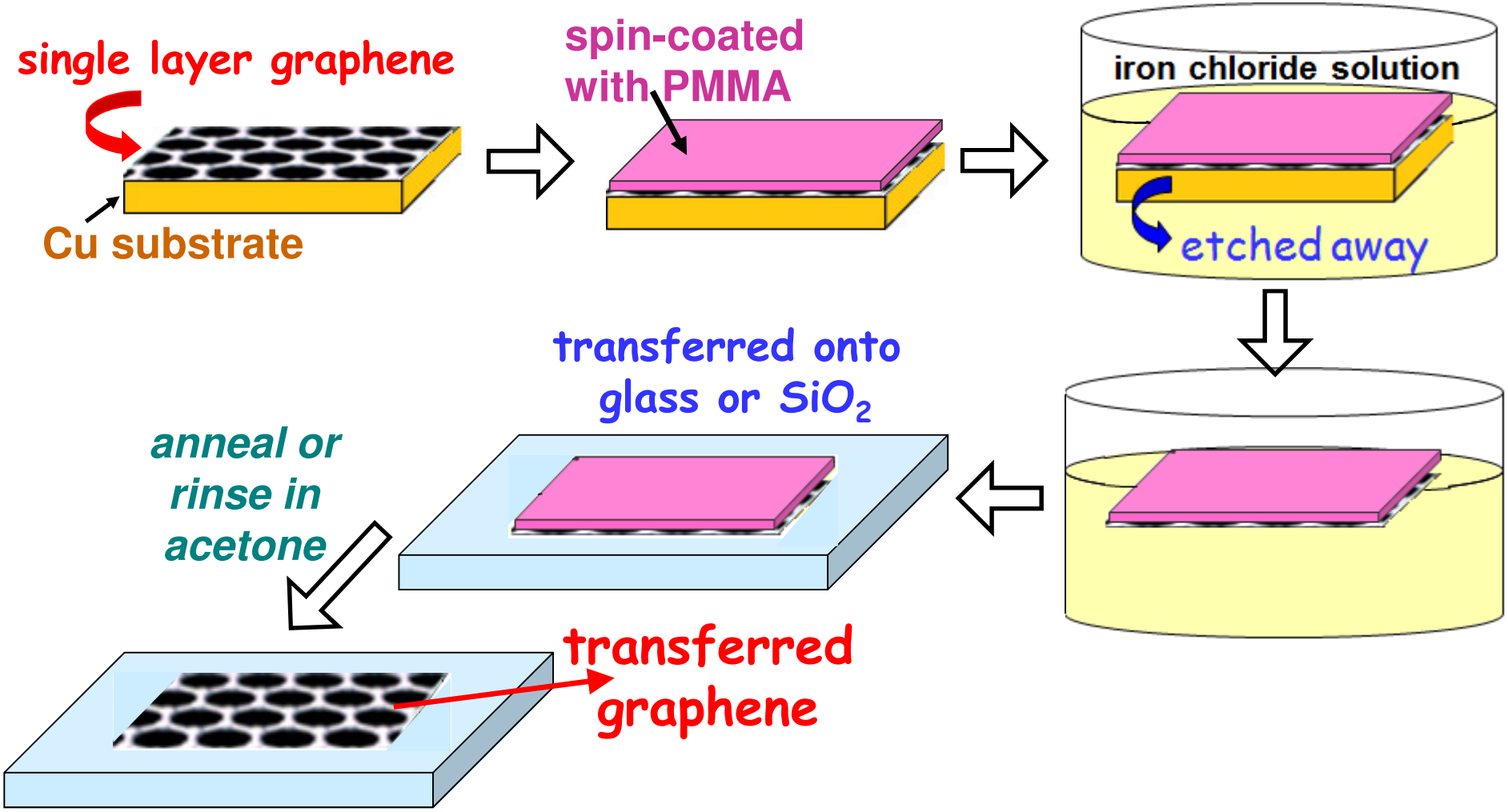


- **Advantages:**
  - * large area graphene
  - * reasonably low cost
  - * ease of processing

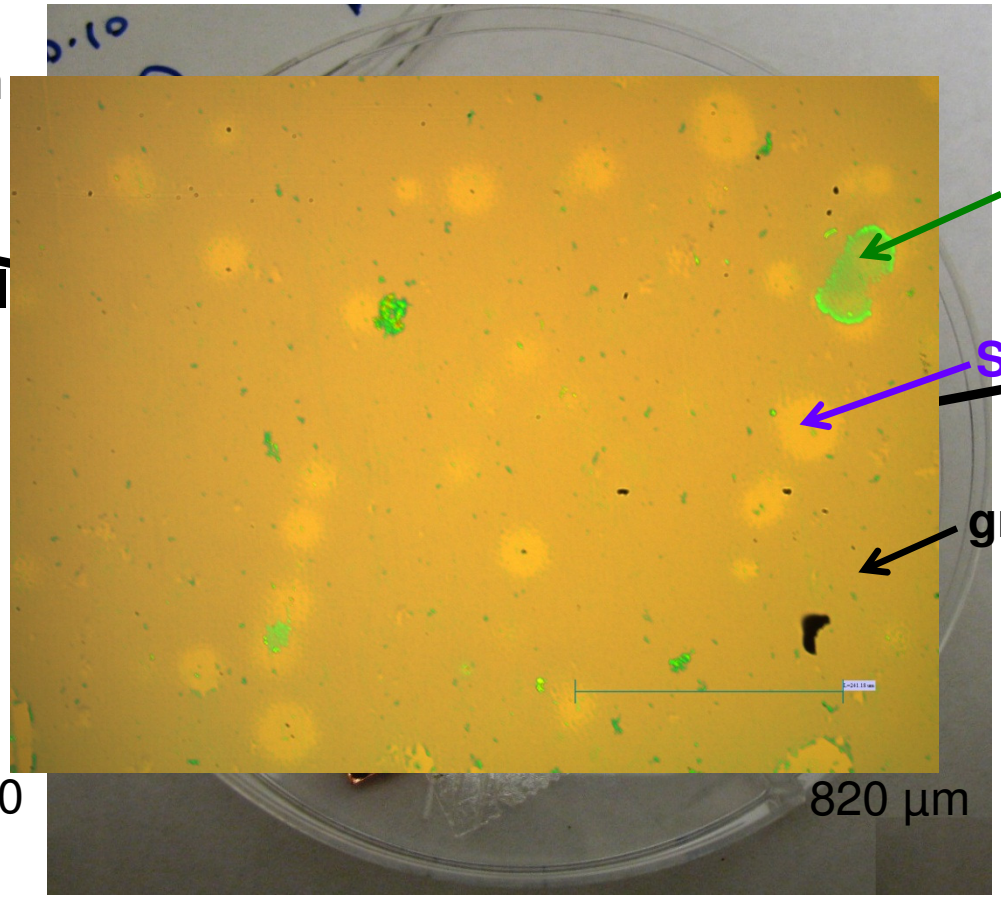
- **Drawbacks:**
  - * lower quality than exfoliated flakes (natural graphene)
  - * have to transfer to dielectric substrates for electronic applications



Transfer of graphene from metal surfaces onto dielectric substrates

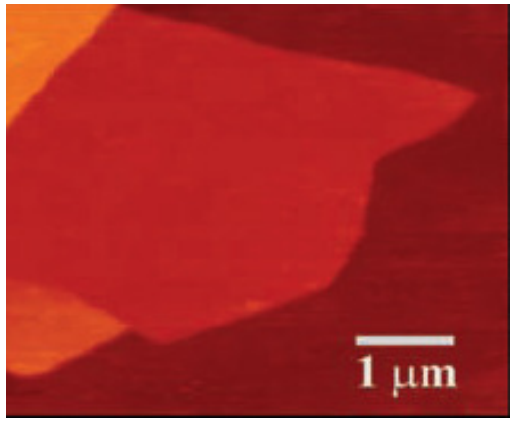


Graphene after transfer
large area

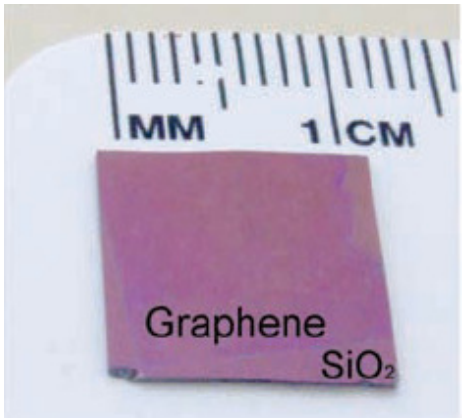


The transfer process introduces impurities, defects, and mechanical damages in graphene

Natural graphene flake has higher quality than CVD graphene



K. Novoselov, *et al.,* Science, **306**, 666 (2004)



X. Li, *et al.,* Science, **324**, 1312 (2009)

Natural graphene flake on SiO_2:
μ~10,000-25,000cm^2/Vs

CVD graphene on Cu foil transferred onto SiO_2:
μ~2000-5000cm^2/Vs

We study CVD growth on single crystal Cu

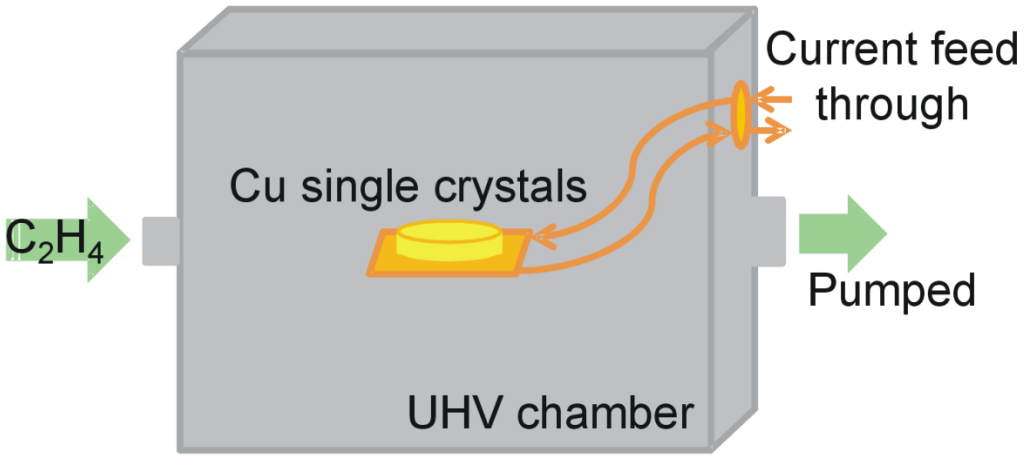
Graphene

- Introduction
- **Graphene on Cu single crystal surfaces**
- Nitrogen doped graphene
- Twisted bilayer graphene

Graphene growth on Cu single crystal

Chemical vapor deposition (CVD) in UHV (STM) environment

- **Growth temperature 900°C**
- **Ethylene was used as C source**
- **Cu is a catalyst for graphene growth**



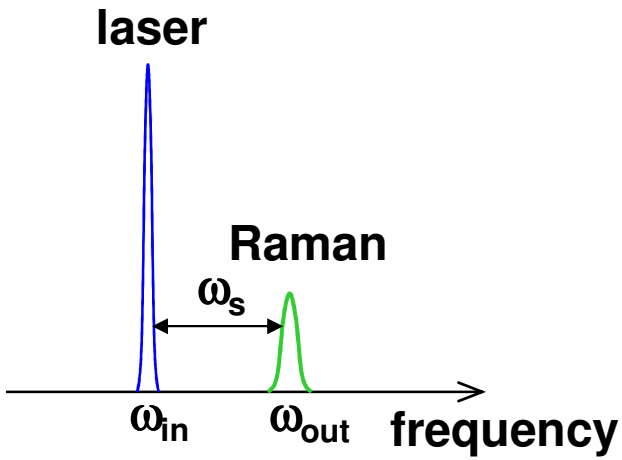
Graphene on Cu single crystal surfaces

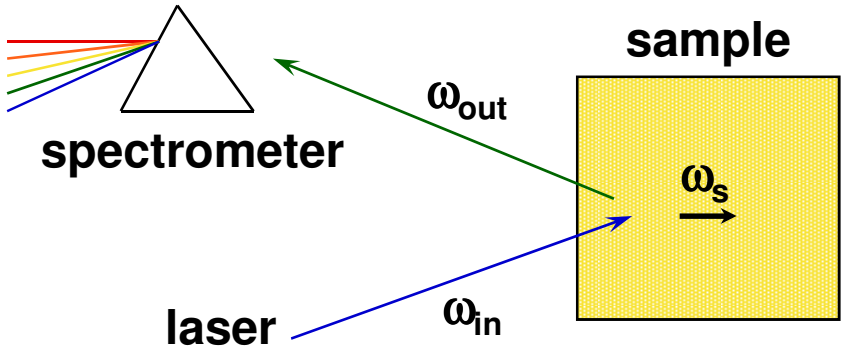
Graphene layers on Cu surfaces are strained

- **strains in graphene on Cu single crystal (111) and (100) surfaces are very different**
- **strain is released after transfer**

The quality of CVD graphene on Cu single crystal is high

Inelastic light scattering:
Raman scattering



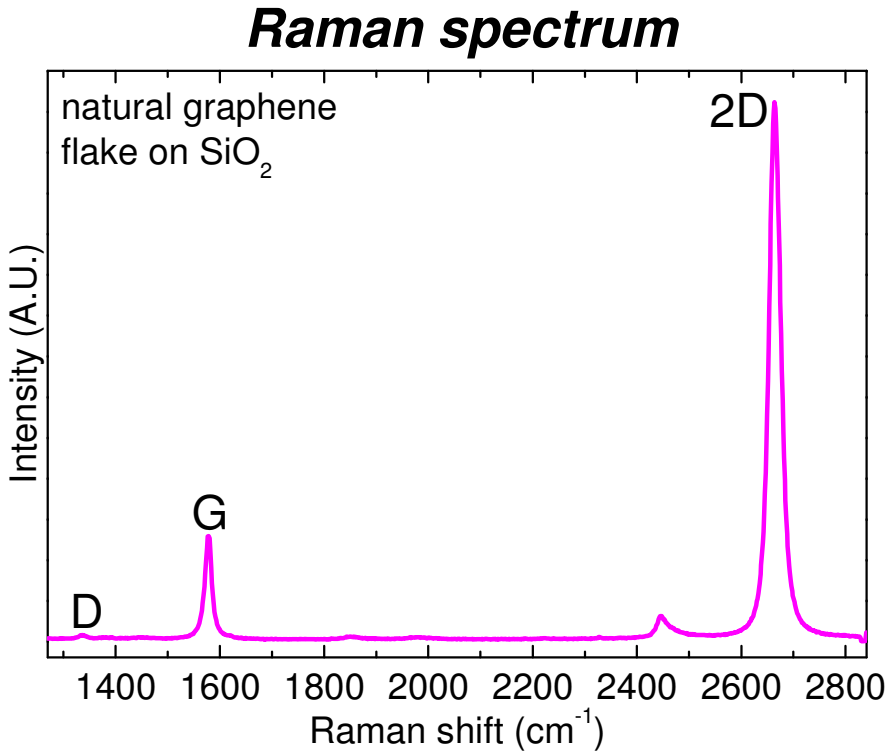


scattering frequency $\omega_s = \omega_{in} - \omega_{out}$

scattering wave vector $\vec{k}_s = \vec{k}_{in} - \vec{k}_{out}$

Raman scattering probes elementary excitations: phonons, vibrations, electronic excitations, etc.

Characterization of graphene by Raman scattering



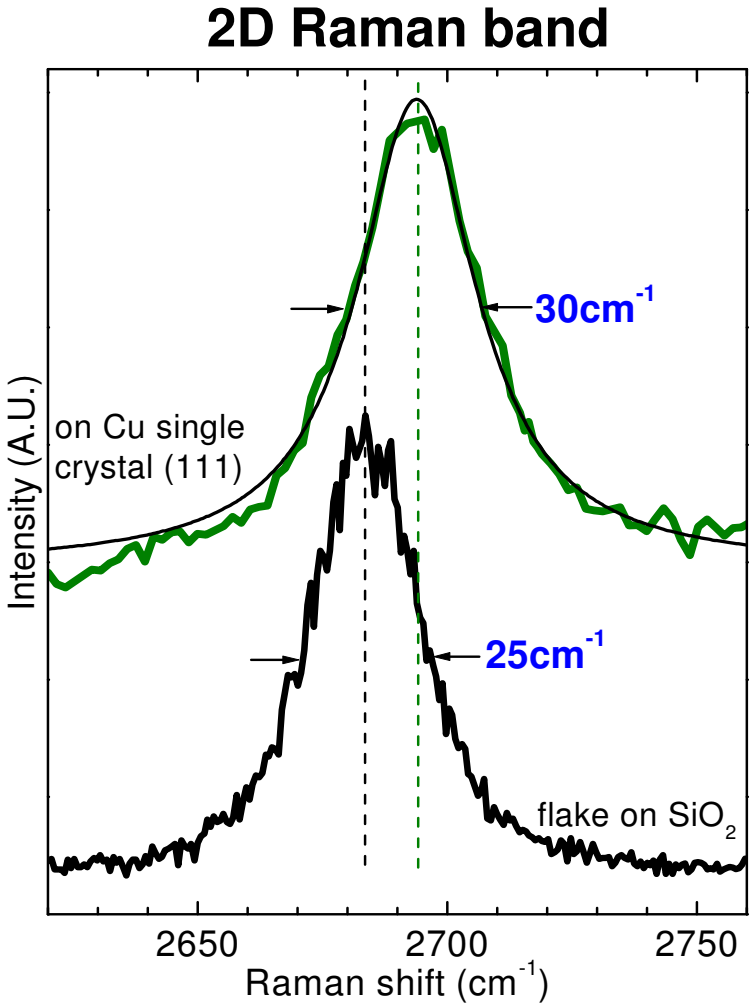
Measure optical phonons

G-band ($q \rightarrow 0$ mode) at ~1580cm^{-1} (electron-phonon coupling)

2D-band (two-phonon mode) at ~2680cm^{-1} (monitors strain)

D-band at ~1350cm^{-1} (due to disorder)

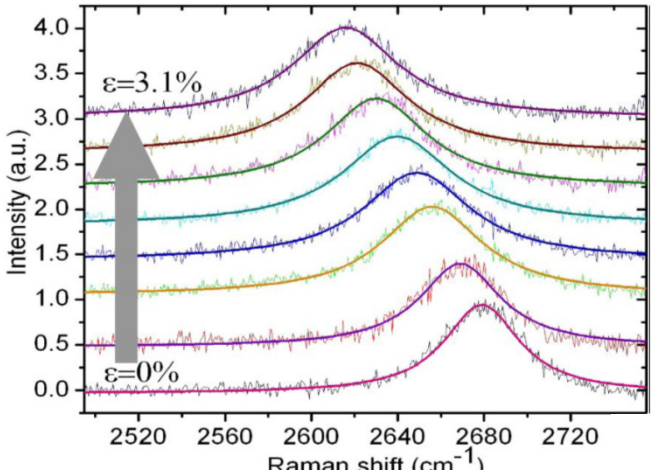
CVD graphene on (111) Cu single crystal



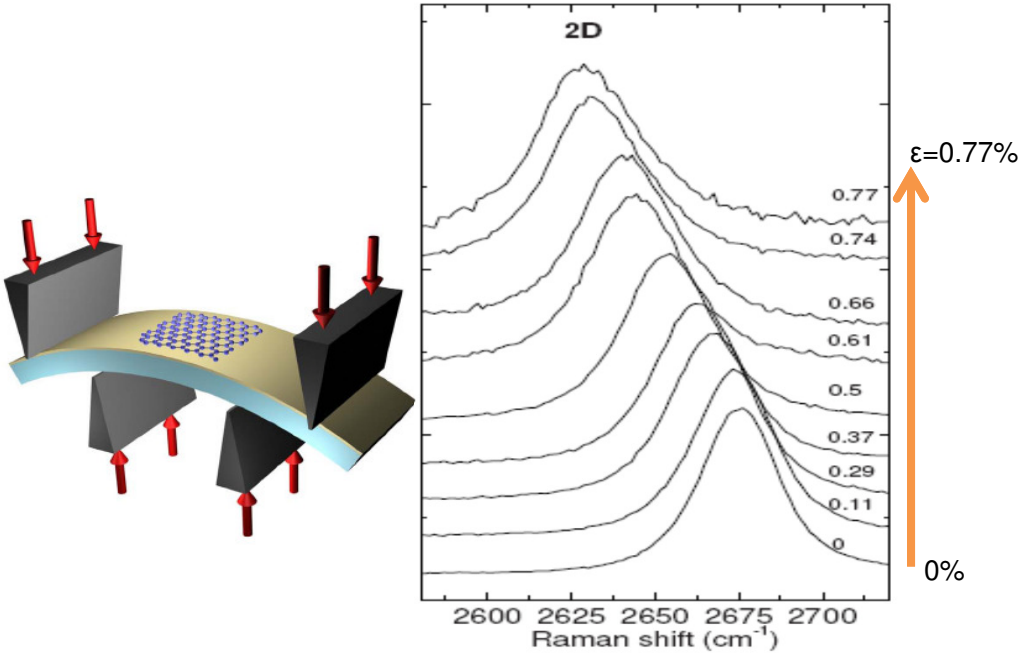
- **2D Raman band is blue-shifted**
- **quality comparable to natural graphene! *(similar FWHM)***

2D Raman band is very sensitive to strain

mode softens under tensile strain



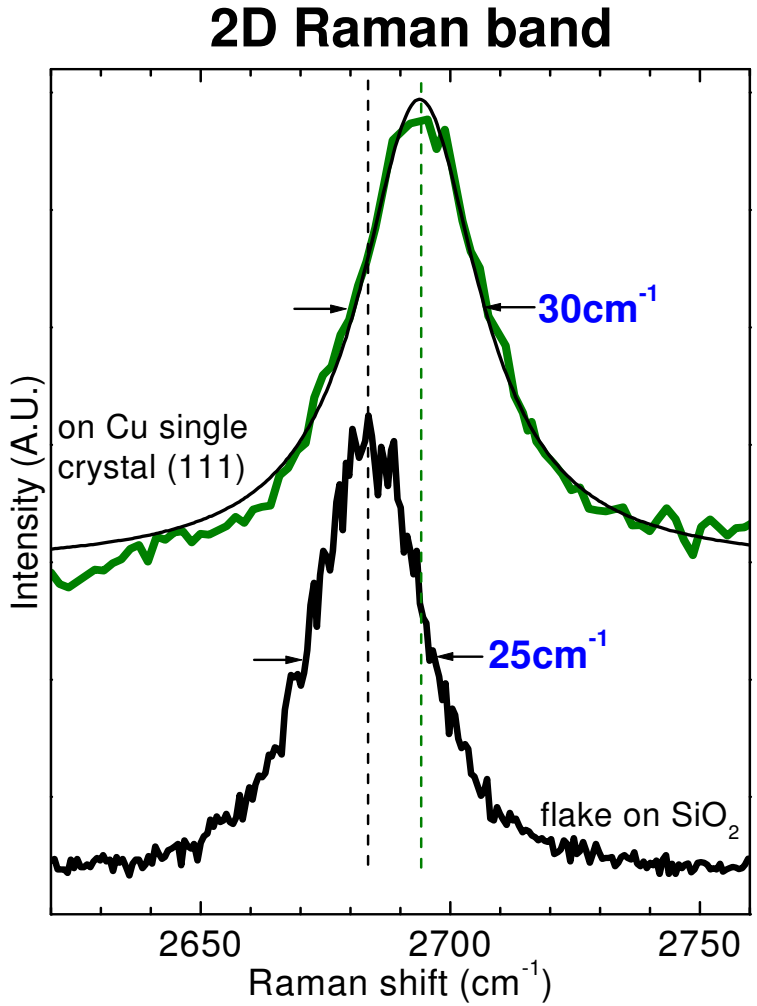
M. Huang, *et al.,* PNAS, **106**, 7304 (2009)



T. Mohiuddin, *et al.*, PRB, **79**, 205433 (2009)

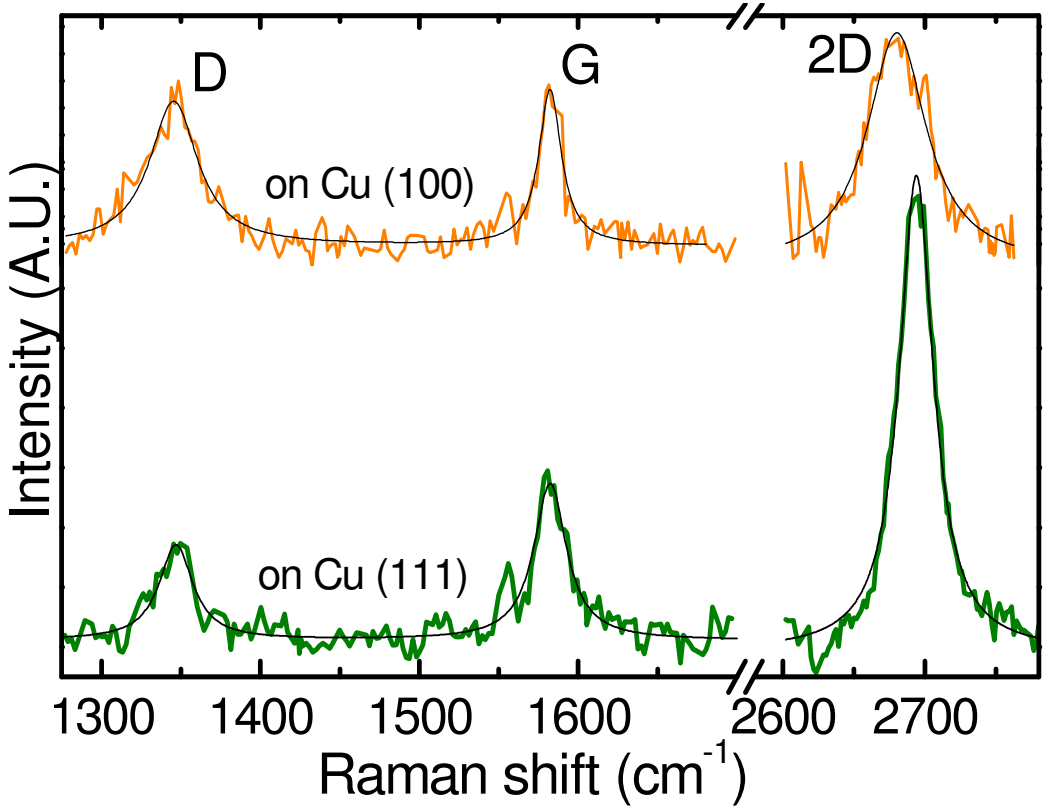
Blue-shifts indicate compressive physisorption strain

CVD graphene on (111) Cu single crystal



- **2D Raman band is blue-shifted**
- **The blue-shift indicates compressive strain due to physisorption of graphene on Cu**

Growths on Cu (111) and (100) are vastly different

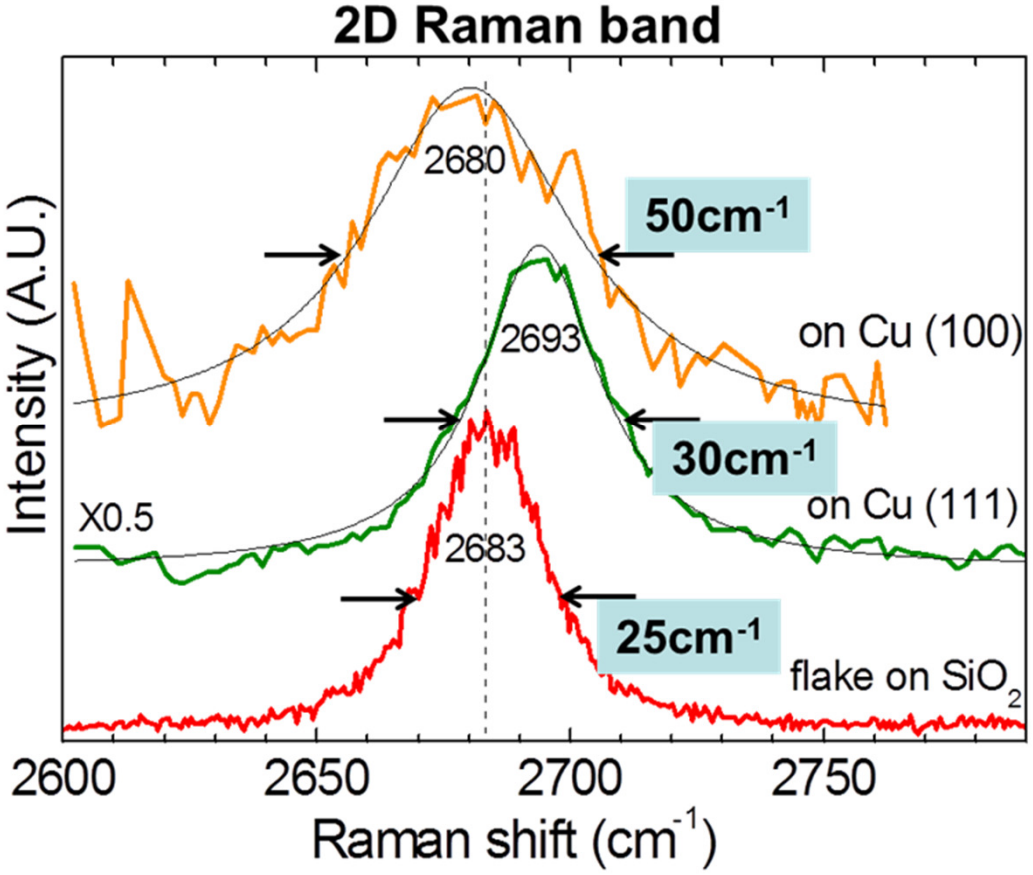


Graphene on Cu (111):

- **Narrower 2D band**
- **Larger 2D/G ratio**
- **Smaller D/G ratio**

Graphene on Cu (111) surface has higher quality

Graphene on Cu single crystal
Nonuniform strain

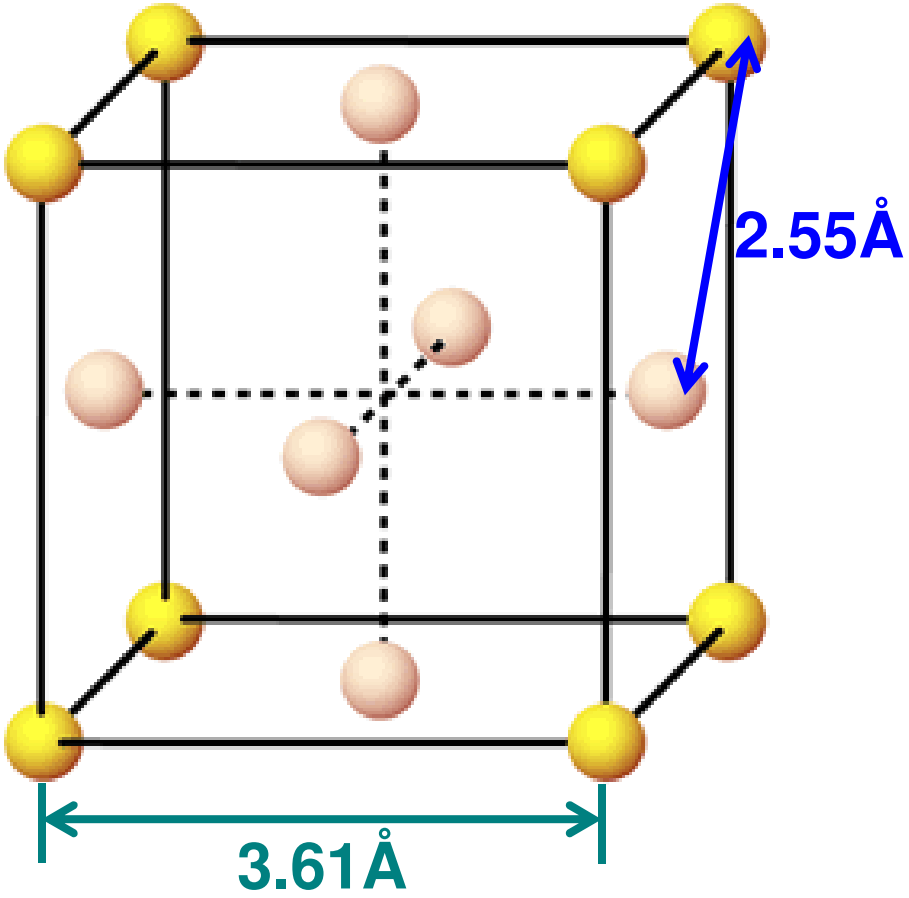


- **graphene on Cu (111): 2D band is broadened by 20%**
- **graphene on Cu (100): 2D band is broadened by a factor of 2**

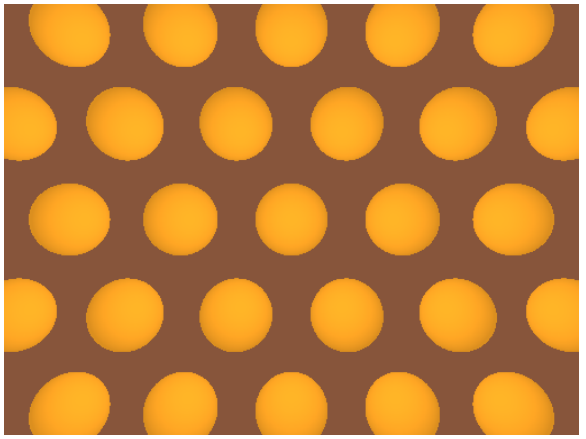
Strain is more uniform on Cu (111) surface

Cu single crystal

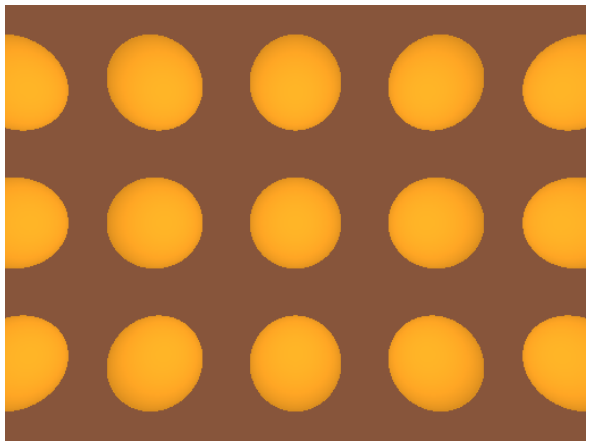
Face-centered cubic
(FCC) structure



Cu (111) hexagonal



Cu (100) square



Characterization by scanning tunneling microscopy (STM)

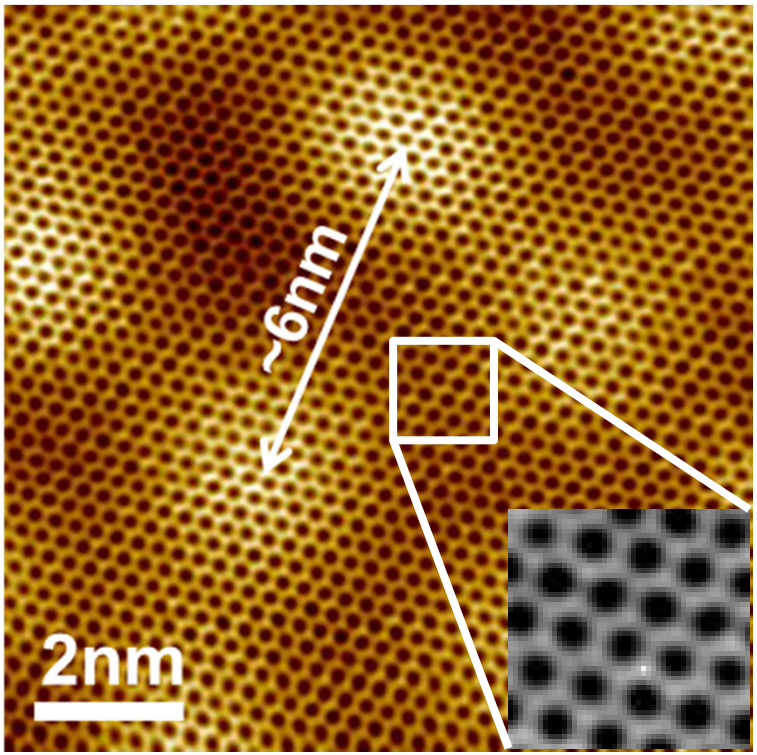
- ***Image graphene surface at the atomic level***

- ***Moire patterns (superstructure) appear when***

  * **two periodic grids with different lattice constants are overlaid**

  * **two periodic grids are rotated with each other**

STM of graphene on Cu (111) single crystal



In *k*-space $\vec{k}_{Moire} = \vec{k}_{Cu} - \vec{k}_{gr}$

$$k_{Moire}^2 = k_{Cu}^2 + k_{gr}^2 - 2k_{Moire}k_{gr}\cos\theta$$

$$\left|\vec{k}_{Moire}\right| = \frac{1}{6nm}$$

$$\left|\vec{k}_{Cu}\right| = \frac{1}{0.255nm}$$

$$\left|\vec{k}_{gr}\right| = \frac{1}{0.246nm}$$

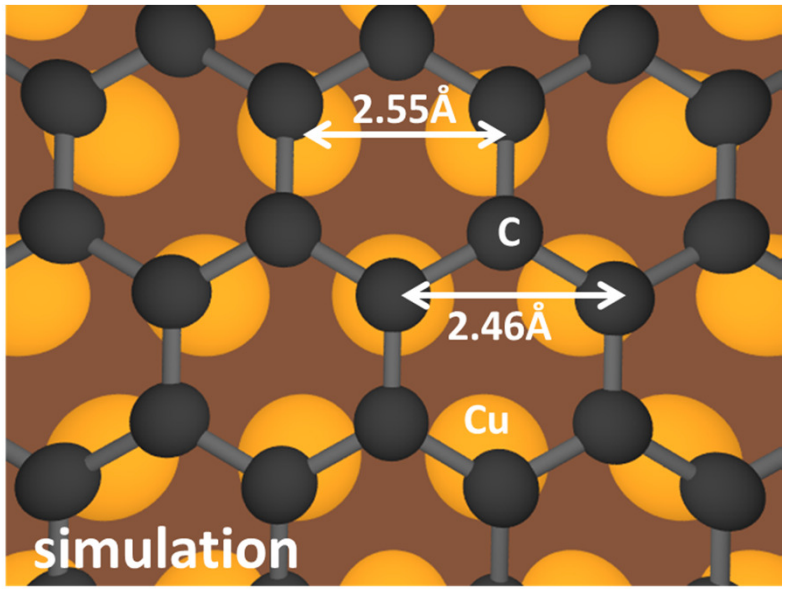
$$\rightarrow \quad \theta \approx 0^o$$

Rotational angle θ is almost zero

Graphene on Cu (111) single crystal

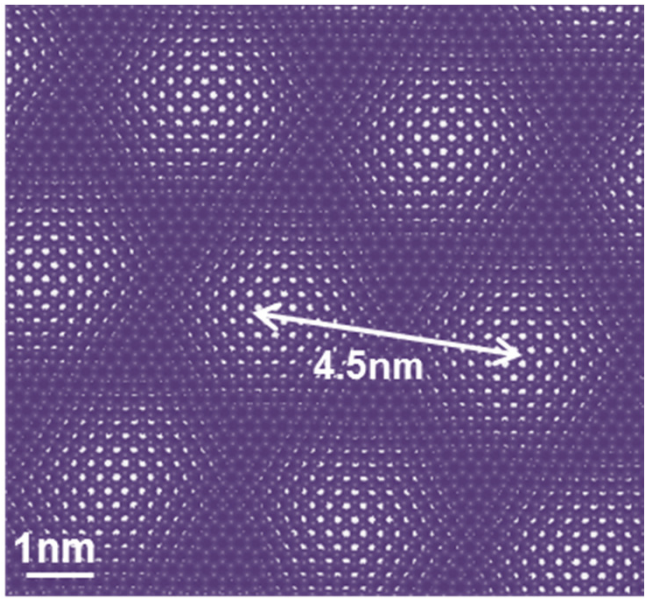
- *Graphene honeycomb lattice with lattice constant of 2.46Å*
- *Cu (111) hexagonal lattice with lattice constant of 2.55Å*
- *Rotational angle θ is almost zero*

Quasi-epitaxial growth

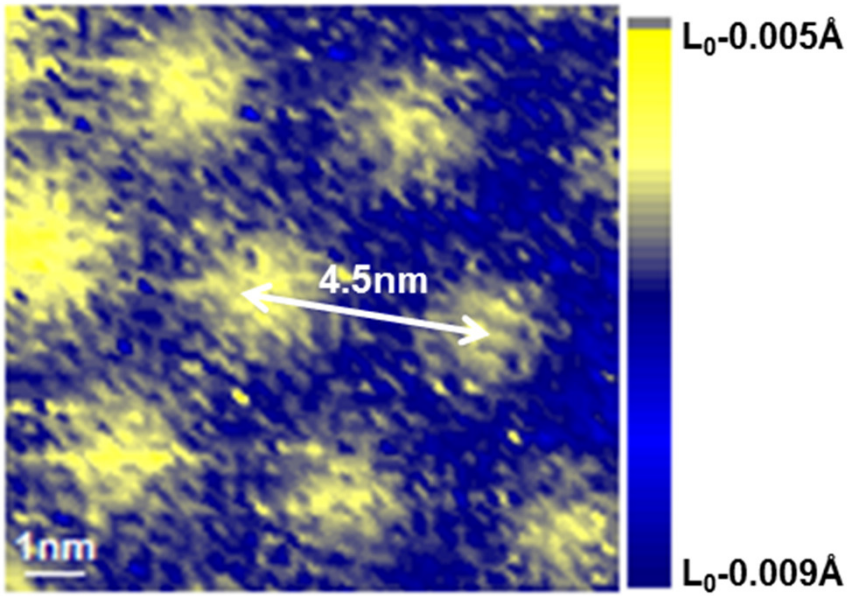


Molecular dynamics (MD) simulations of graphene on Cu (111) single crystal

Simulated superstructure



C-C bond length simulation

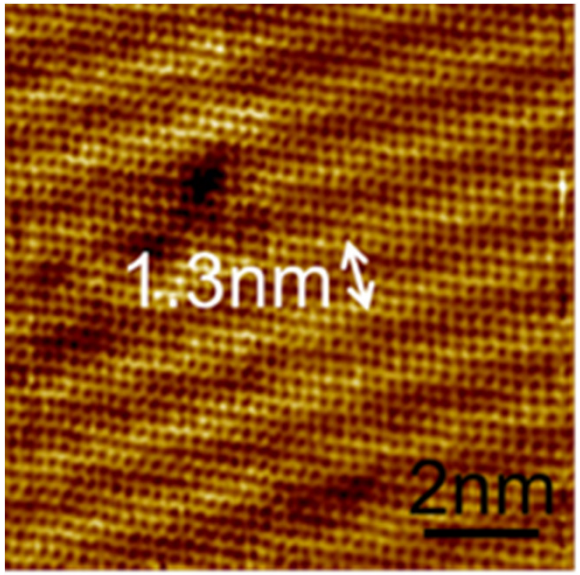


- Compressive strain over the entire surface
- Strain varies between 0.3% and 0.6%
- Domain walls are highly compressed

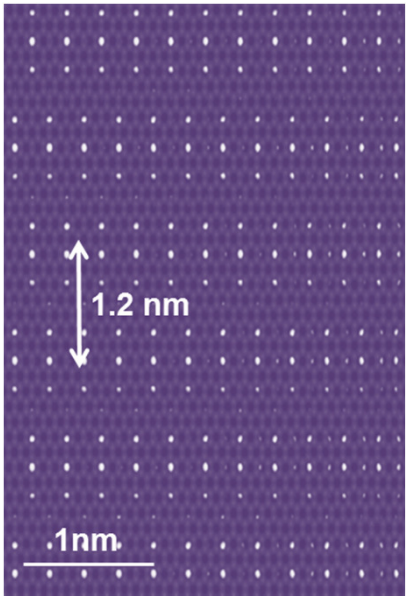
Graphene on Cu (100) single crystal

Molecular Dynamics simulations

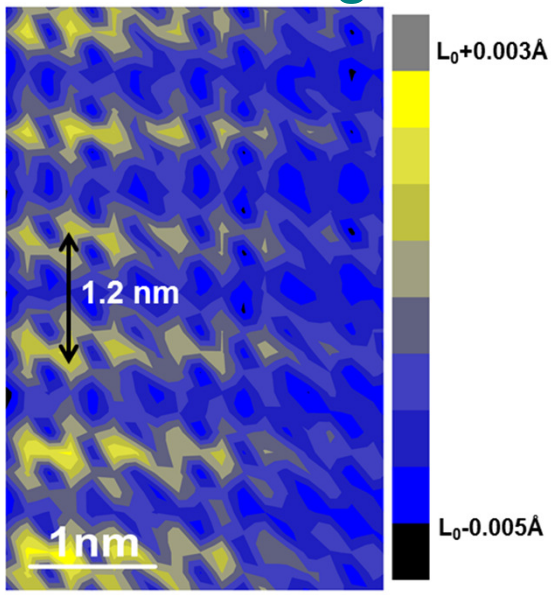
STM



Superstructure



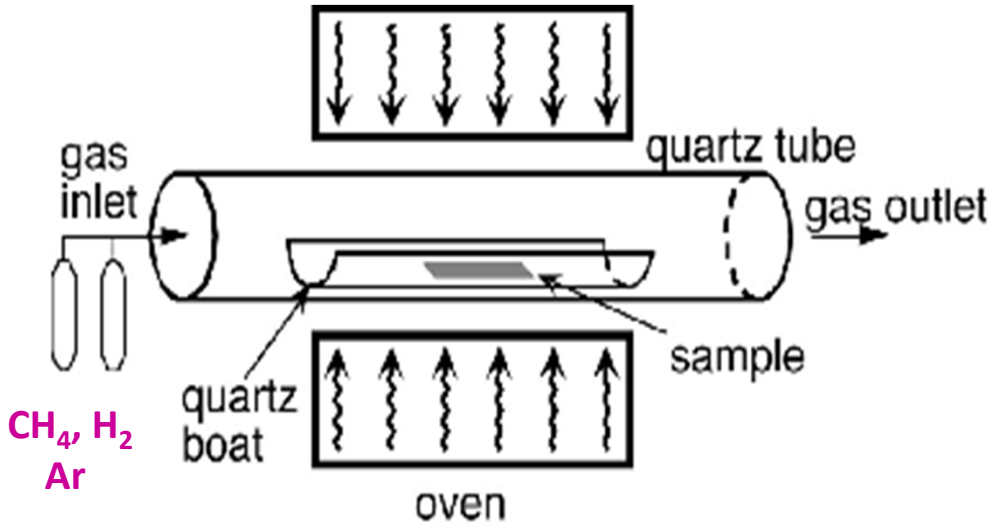
C-C bond length

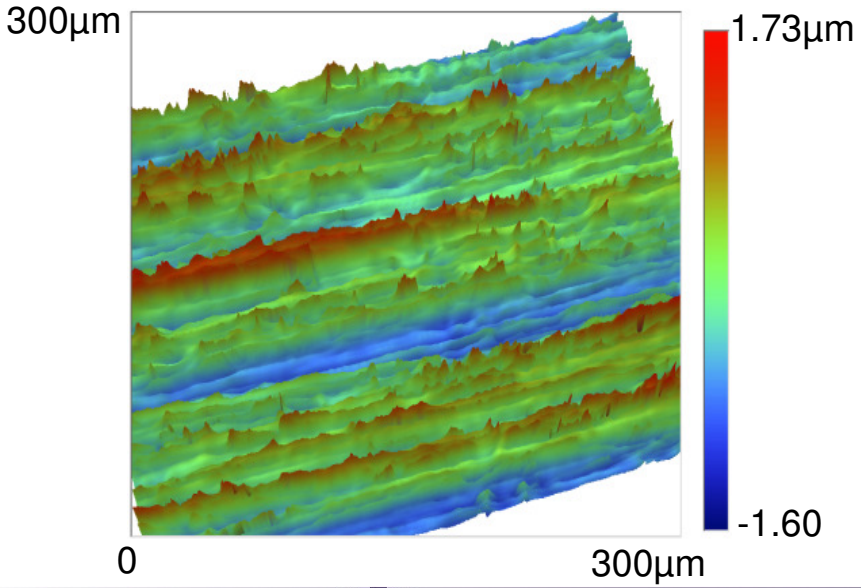


- **No epitaxy:** honeycomb graphene lattice on Cu (100) square lattice
- Highly nonuniform strain that varies from 0.3% compressive to 0.2% tensile

CVD growth on Cu foil

- **Growth temperature 1000°C**
- **Methane was used as C source**

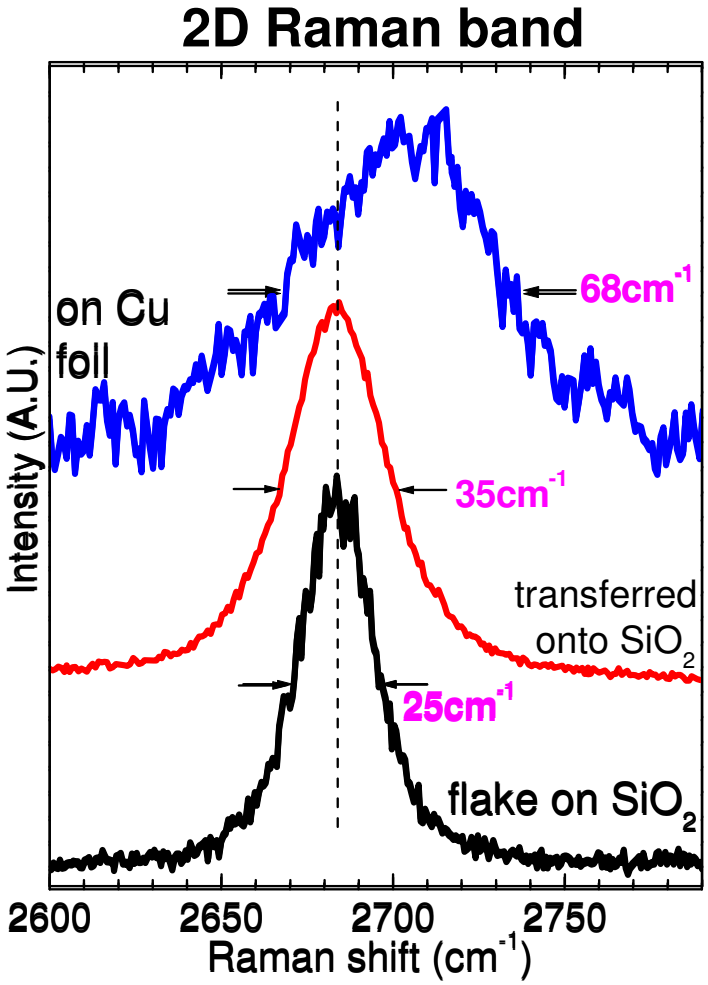




polycrystalline and rough surface

CVD graphene on Cu foil

Release of strain



after transfer onto SiO_2:

- ***2D band overlaps that of natural graphene***
- ***broadening related to residual strain***

CVD graphene on copper substrates

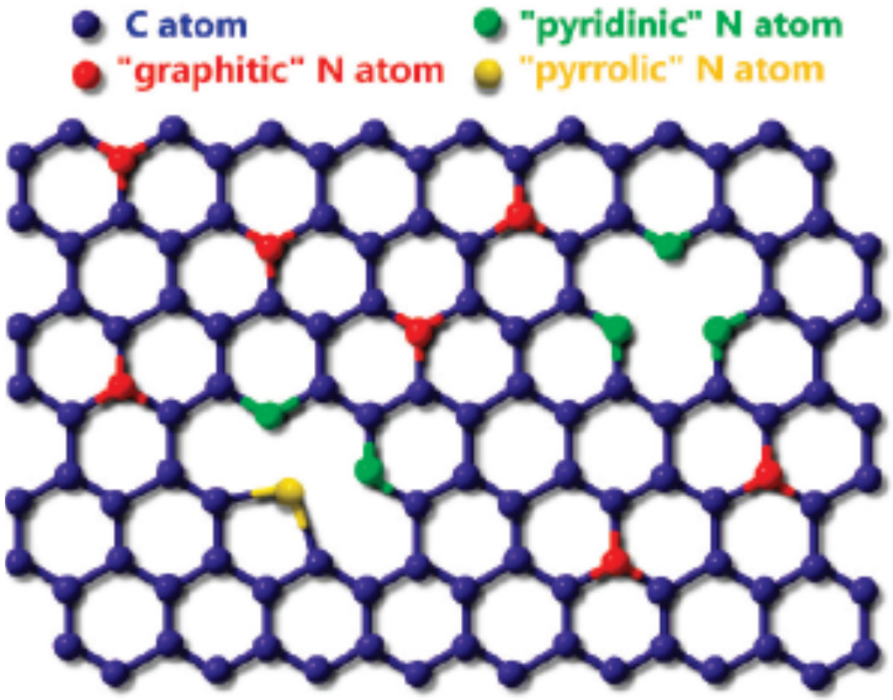
- Raman and STM reveal degree of perfection and strain
- Strain is dependent on Cu surface orientation
- Release of strain after graphene is transferred onto SiO_2 substrate

Nano Letters 12, 2408 (2012)

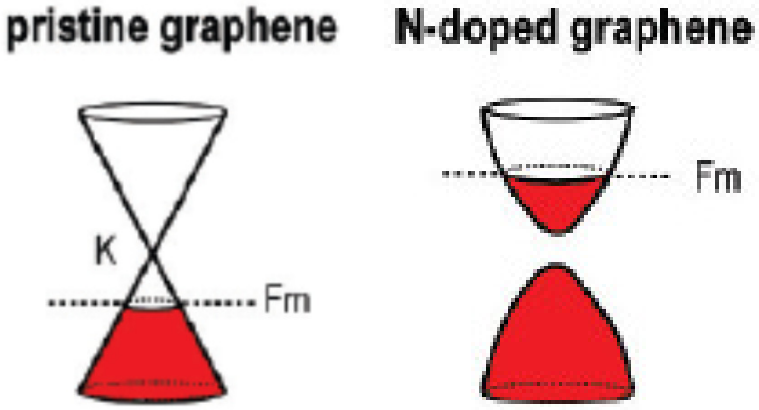
Graphene

- Introduction
- Graphene on Cu single crystal surfaces
- **Nitrogen doped graphene**
- Twisted bilayer graphene

Nitrogen doped graphene



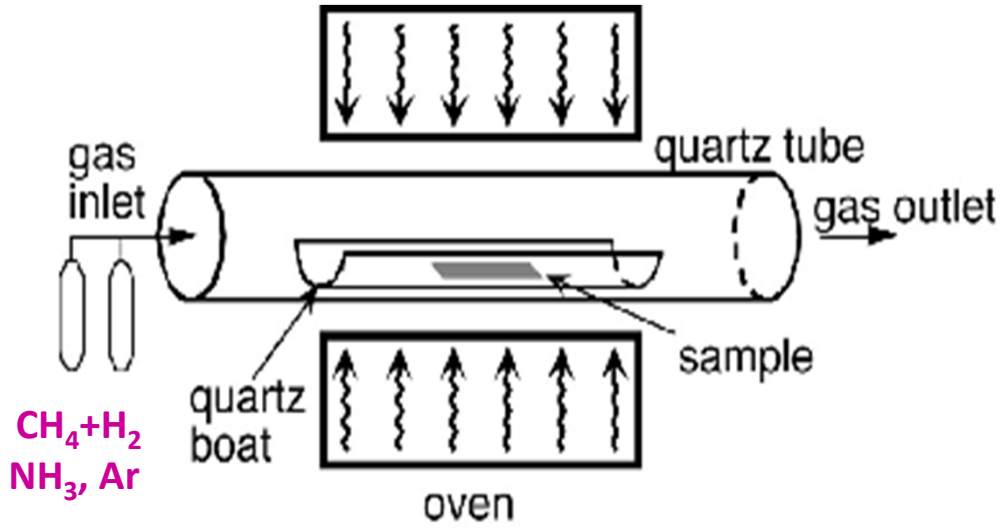
Doping: control electronic properties of graphene



Wei *et al. Nano Lett.* **9**, 1752 (2009)

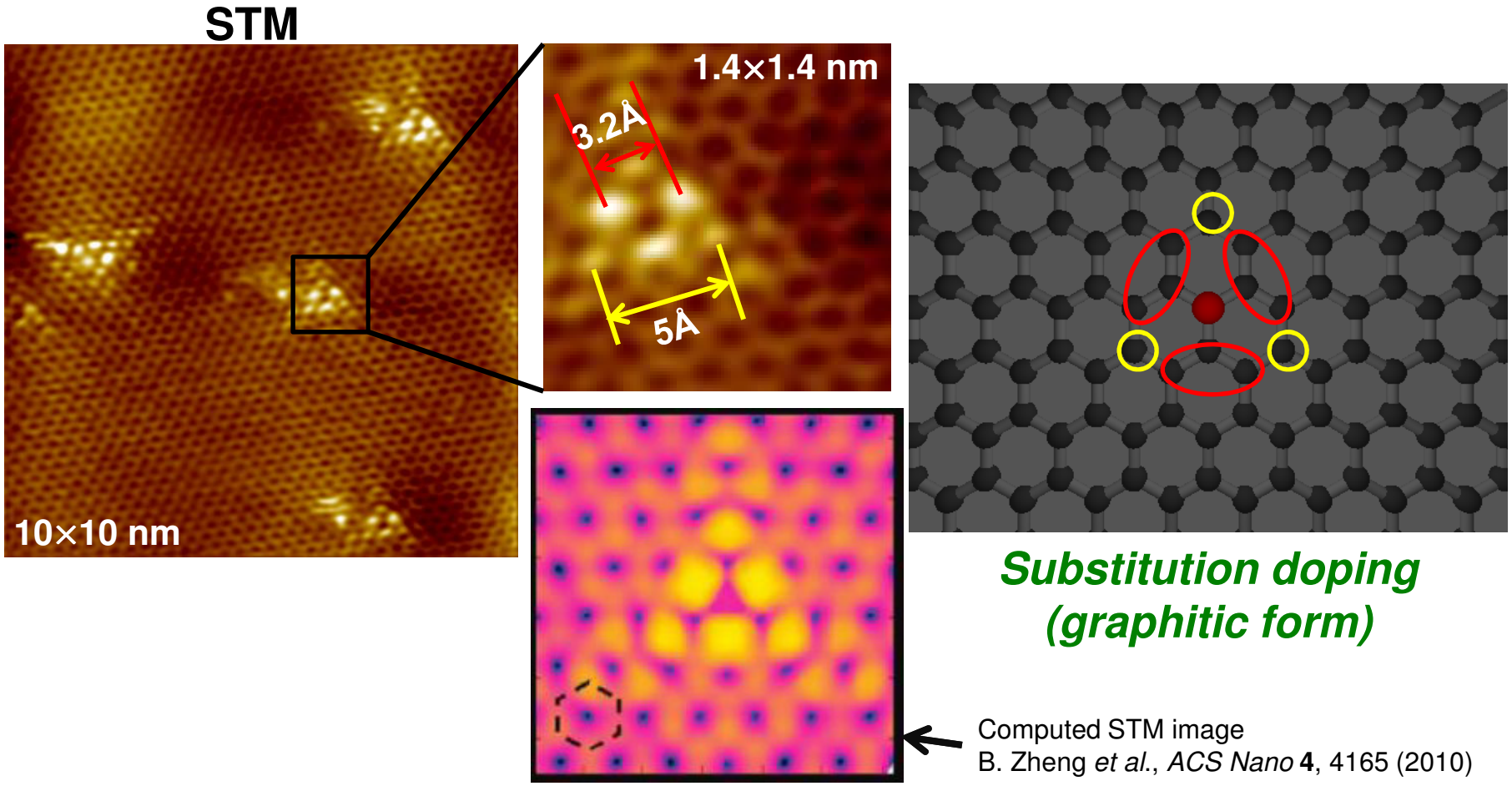
Nitrogen doped graphene

chemical vapor deposition (CVD)



- **Copper foil is heated to ~1000^{o}C**
- **NH_3, CH_4, H_2, and argon gas are passed in with appropriate ratio**
- **Doping level is controlled by the pressure of ammonia gas**

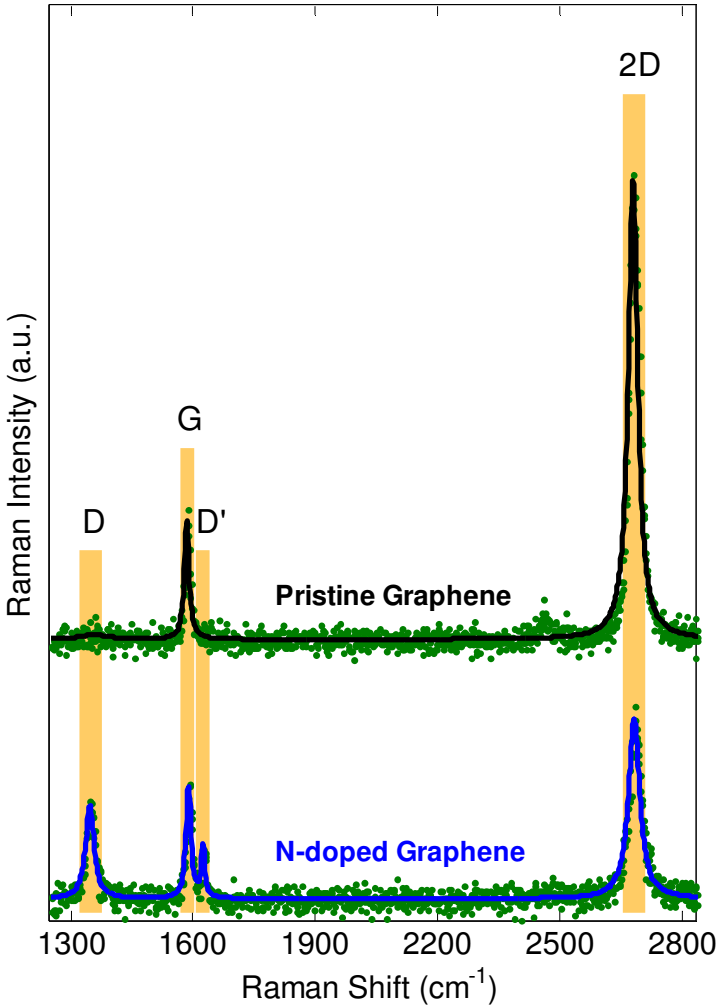
Visualizing individual nitrogen dopants in honeycomb lattice

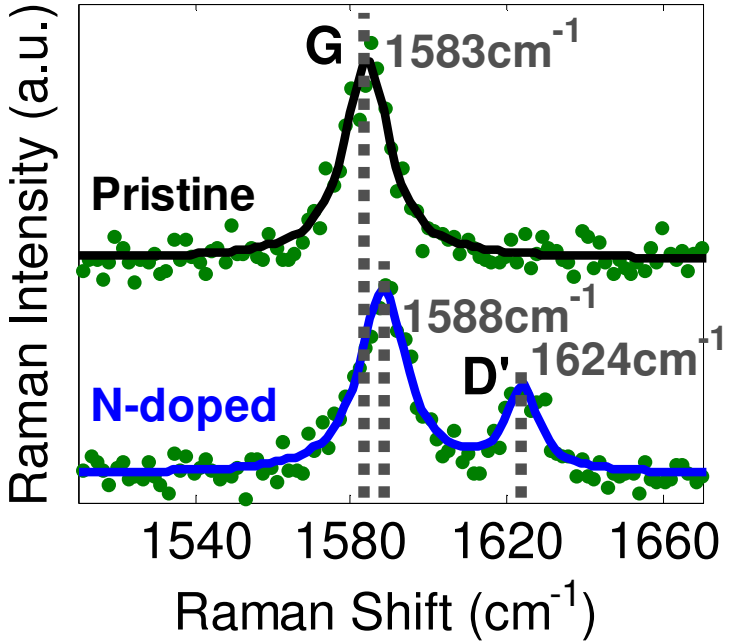


Substitution doping (graphitic form)

Computed STM image
B. Zheng *et al.*, *ACS Nano* **4**, 4165 (2010)

Raman scattering from nitrogen doped graphene

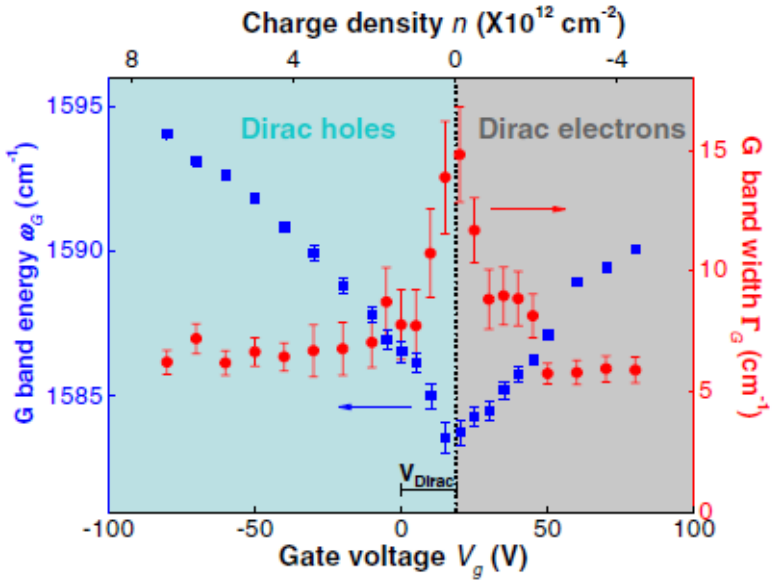




- strong defect bands D and D'
- lower 2D/G ratio
- blueshift of G peak

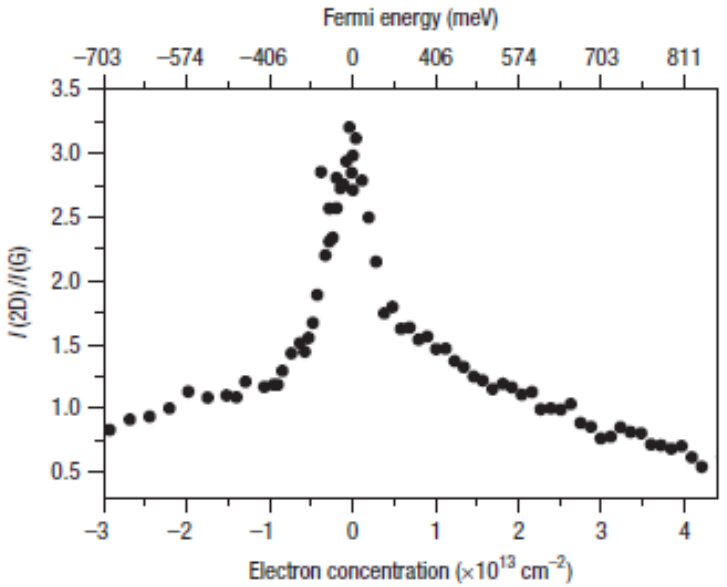
Raman characterization of carrier density in graphene

G peak position



Yan *et al.*, *Physical Review Letters* 98, 166802 (2007)

2D/G ratio

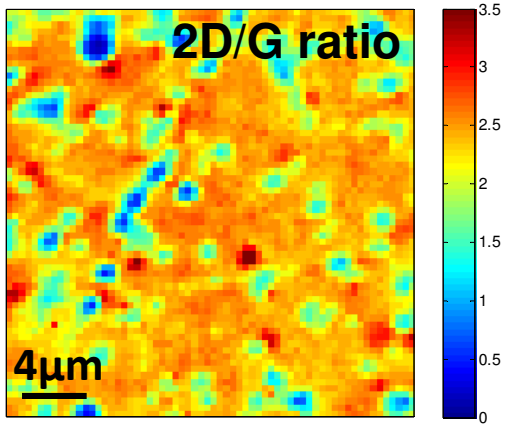


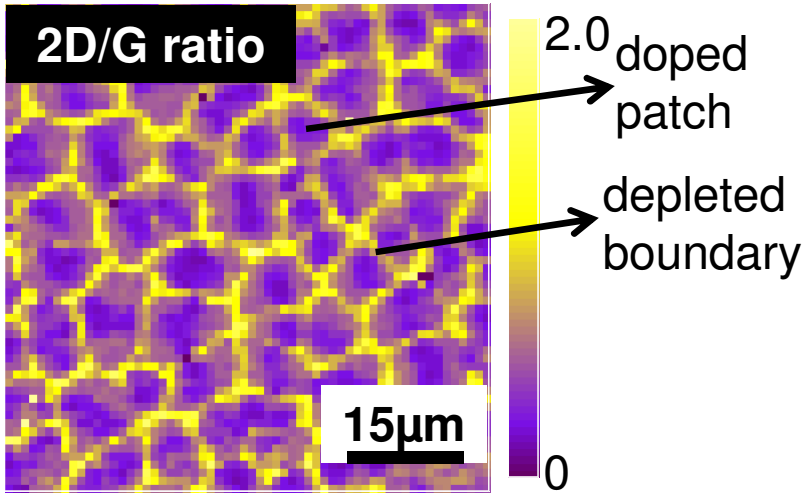
Das *et al.*, *Nature Nanotechnology* 3, 210 (2008)

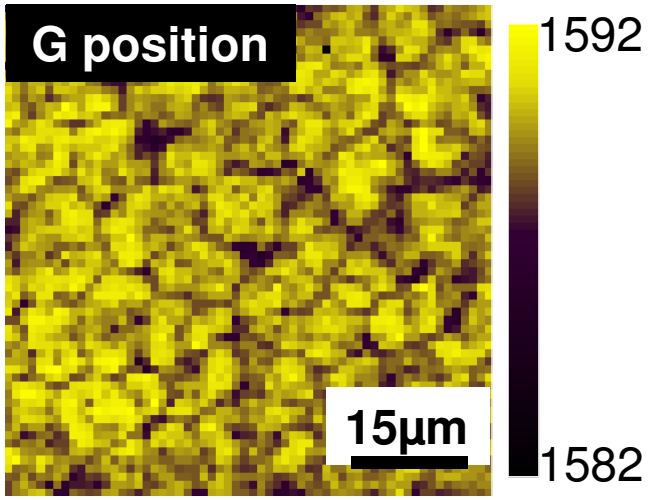
lower electron (hole) density ⟷
lower G peak frequency and higher 2D/G ratio

Raman mapping of nitrogen doped graphene

pristine graphene



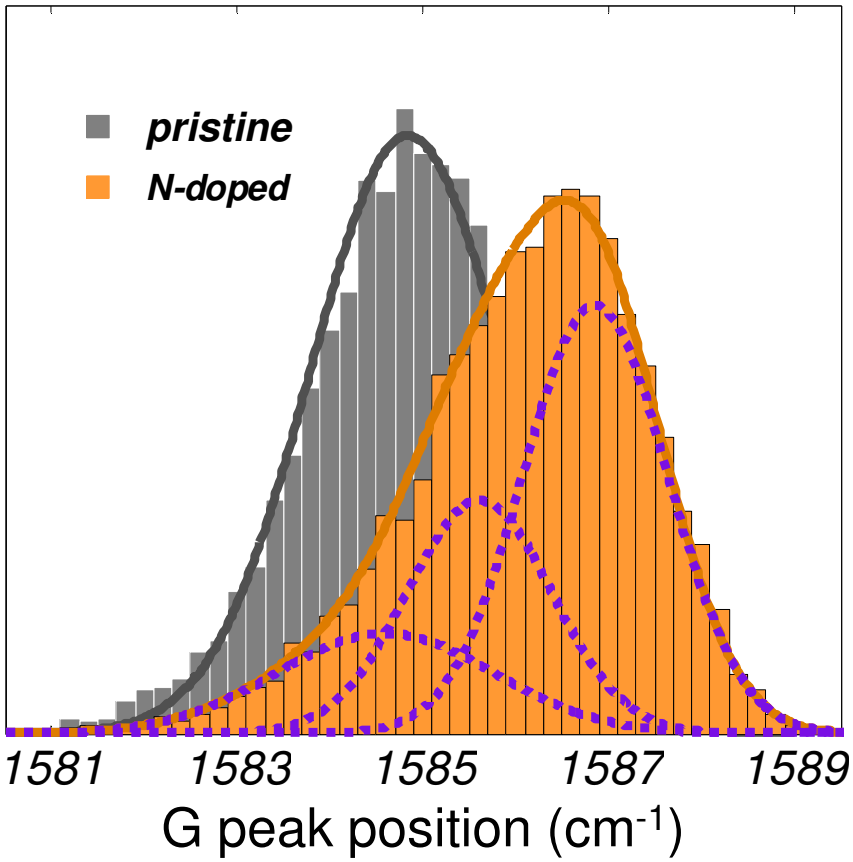




Lower dopant (nitrogen) concentration at the grain boundaries

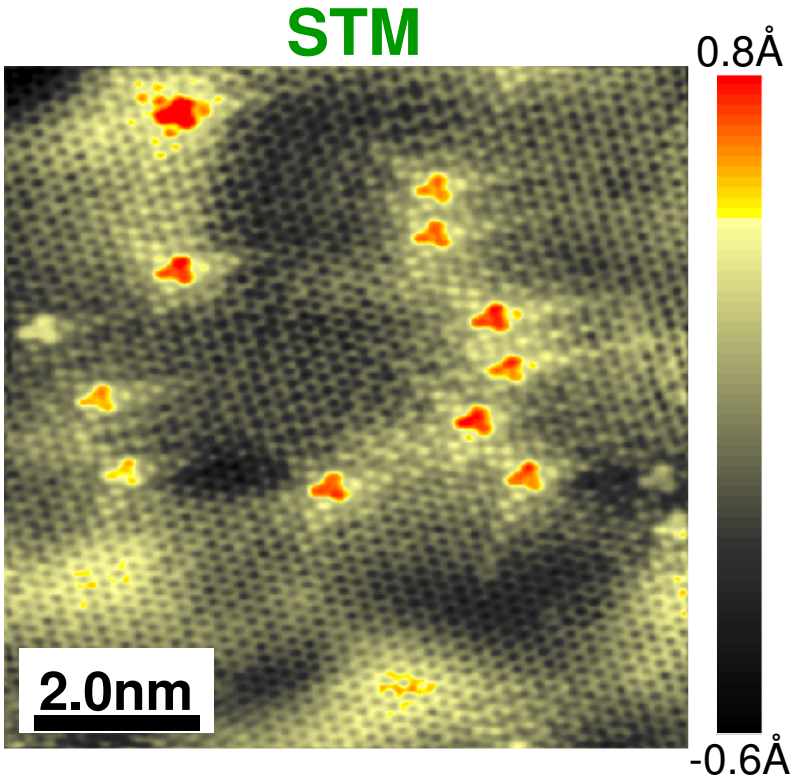
Estimation of average carrier concentration

Distribution of G peak position



Based on the shift in the position of the G peak in the Raman spectra induced by doping, we estimate that the carrier concentration is 5 ± 1.5 × 10^{12} cm^{-2}

Mobile carriers contributed by nitrogen dopants



- Nitrogen dopants are randomly distributed in the honeycomb lattice
- N atom density ~1.3×10^{13} cm^{-2}
- Carrier concentration (estimated by Raman) is $5 \pm 1.5 \times 10^{12}$ cm^{-2}

Each graphitic N dopant contributes (on average) ~0.4 mobile carriers to the graphene lattice

Nitrogen doped graphene

- Individual nitrogen dopant was observed in real space by STM. Most of the dopants are graphitic forms
- Nitrogen concentration is lower at grain boundaries
- Each graphitic nitrogen atom contributes ~0.4 mobile charge carrier (electron) into graphene lattice

Science 333, 999 (2011)

Outline

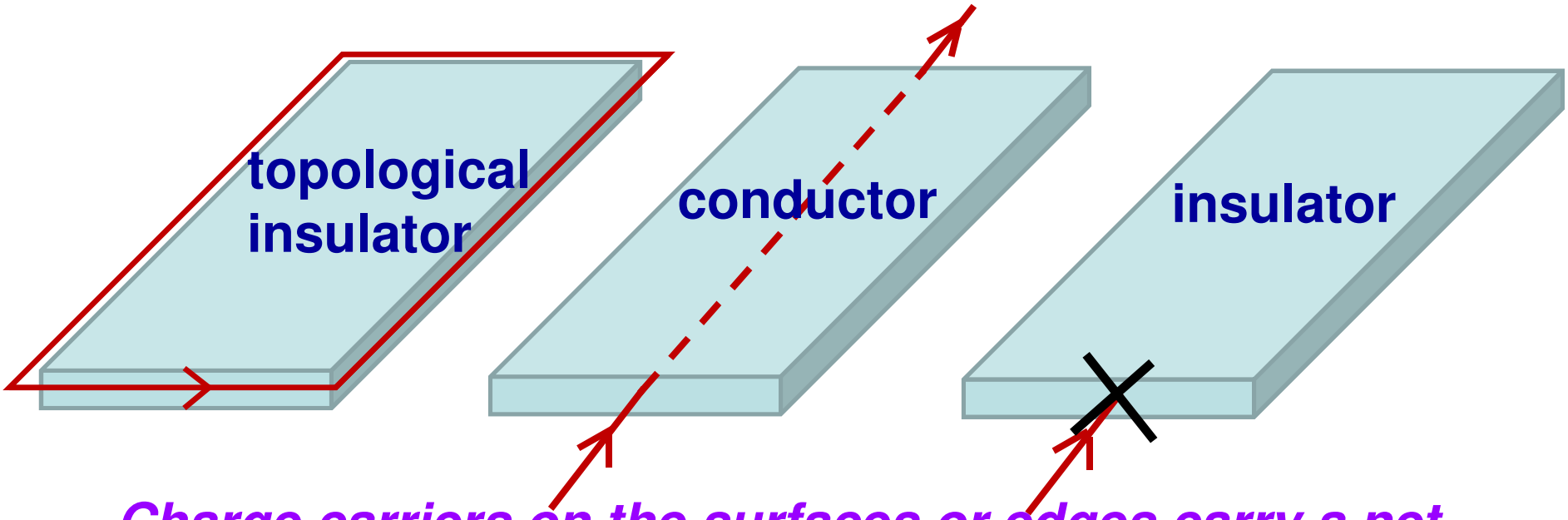
Graphene

- Introduction
- Graphene on Cu single crystal surfaces
- Nitrogen doped graphene
- Twisted bilayer graphene

Topological insulator nanostructures

- **Bi_2Te_3 nanoplates**

Topological insulator (TI)



Charge carriers on the surfaces or edges carry a net spin and conduct electricity without much thermal dissipation

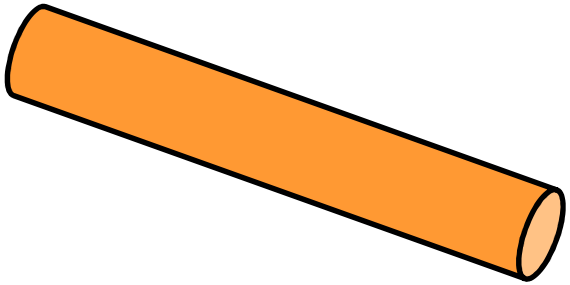
→ **promising candidate for spintronics and quantum computing devices which are based on spin transport**

Challenges in TI research

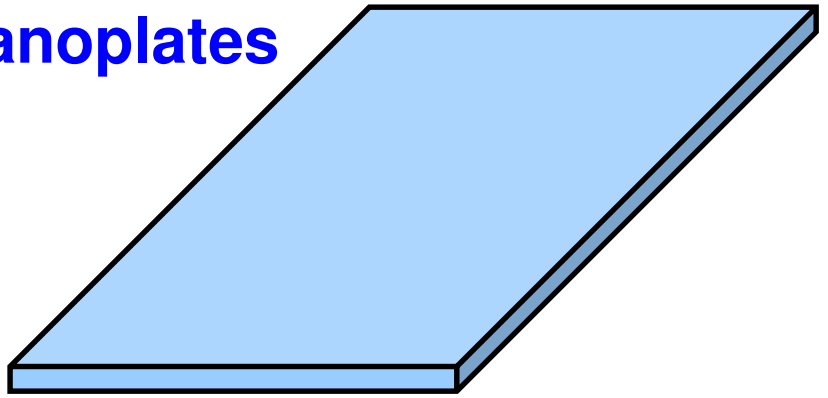
In 3D TIs, bulk characteristics dominate their properties

Reduce its dimension:
enhance surface-to-bulk ratio

1D nanowires

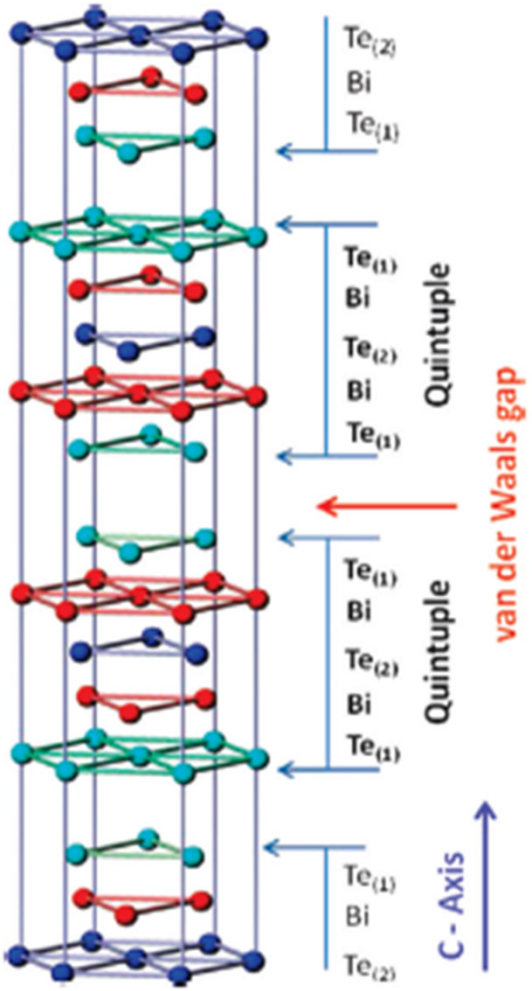


2D nanoplates

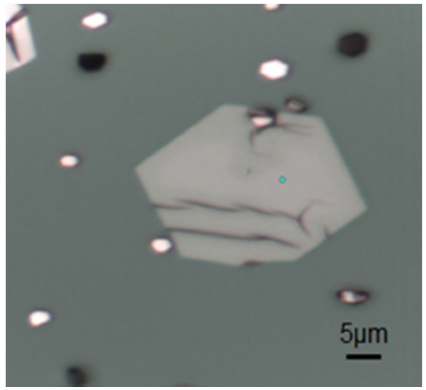


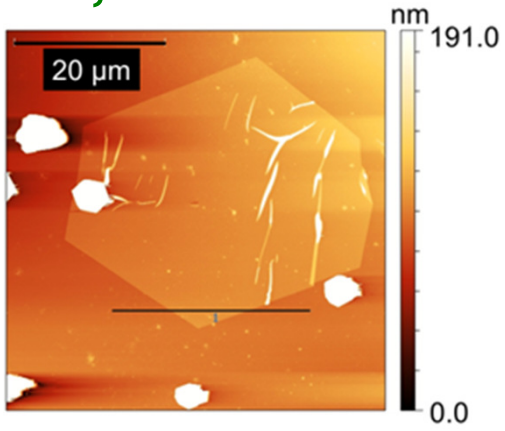
TI nanoplates

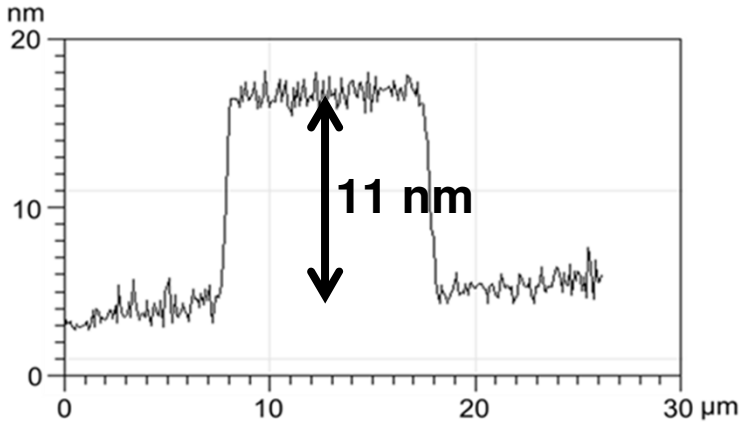
representative TI material: Bi_2Te_3



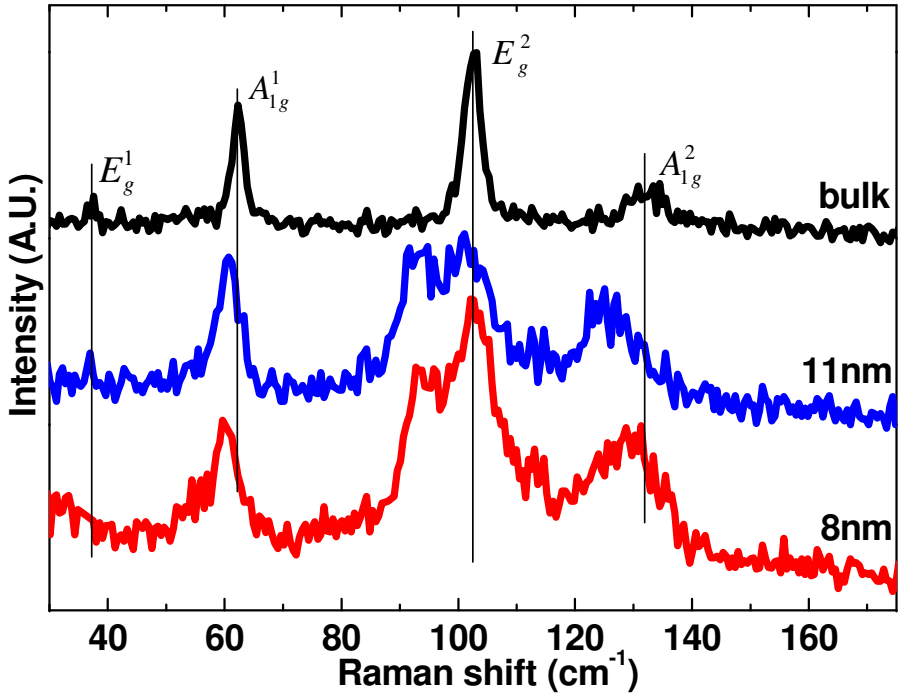
As-grown NP, 11 nm

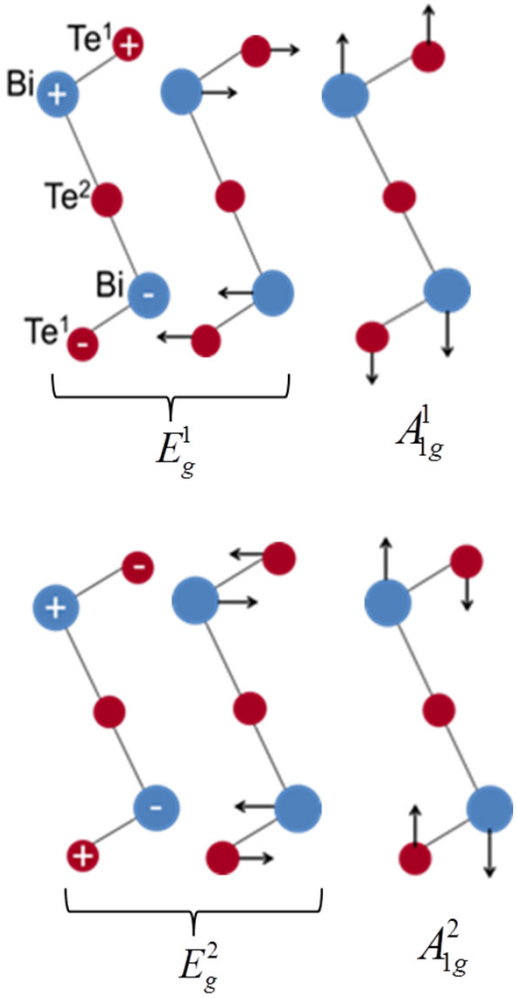






Raman scattering from bulk Bi_2Te_3 and as-grown Bi_2Te_3 NPs

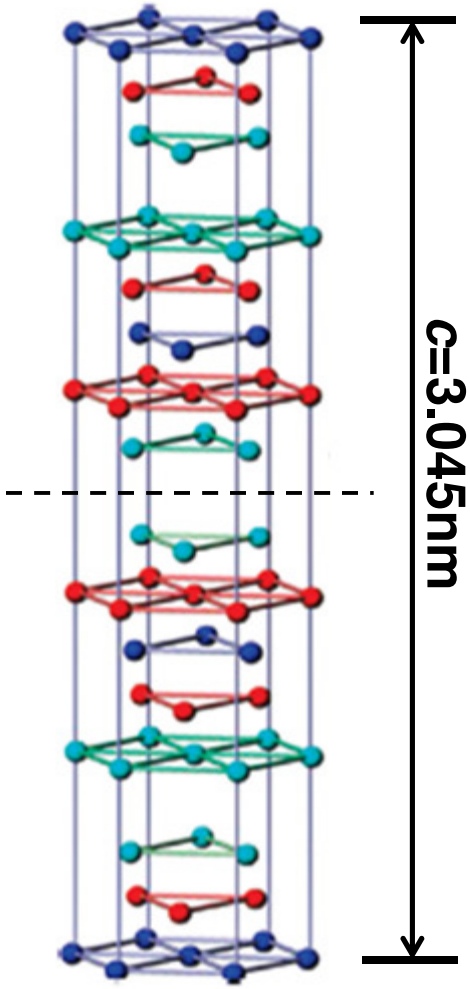




4 Raman-active modes from bulk Bi_2Te_3

The out-of-plane modes are more sensitive to the reduction of thickness

Raman selection rules in crystals with inversion symmetry



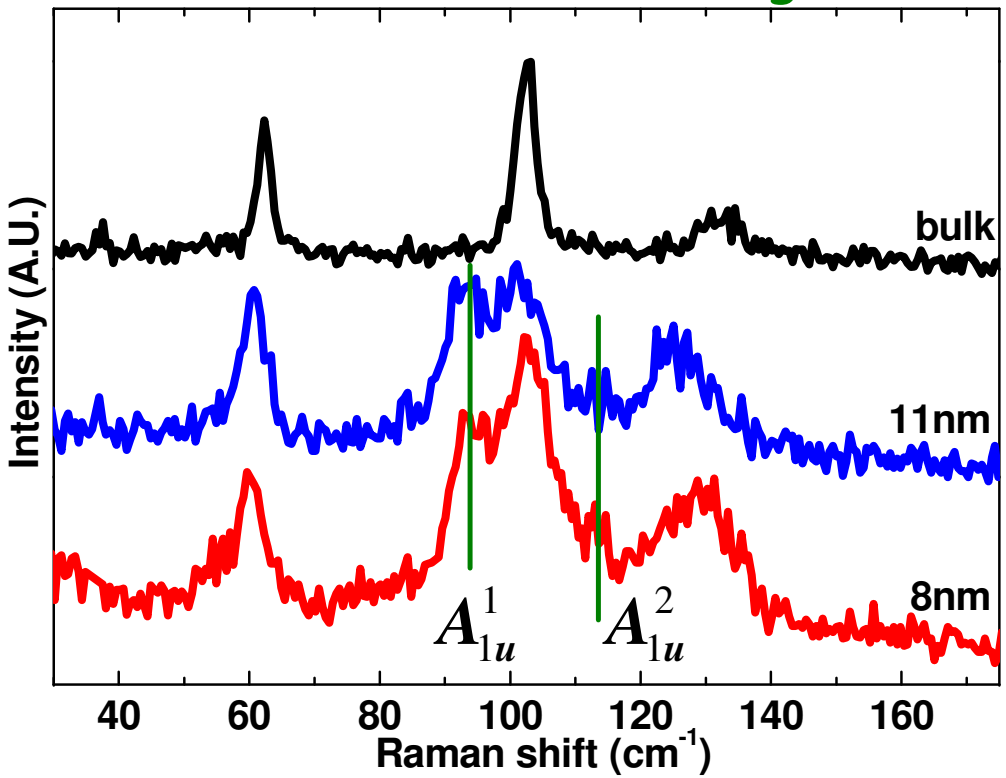
Bi_2Te_3 crystal lattice

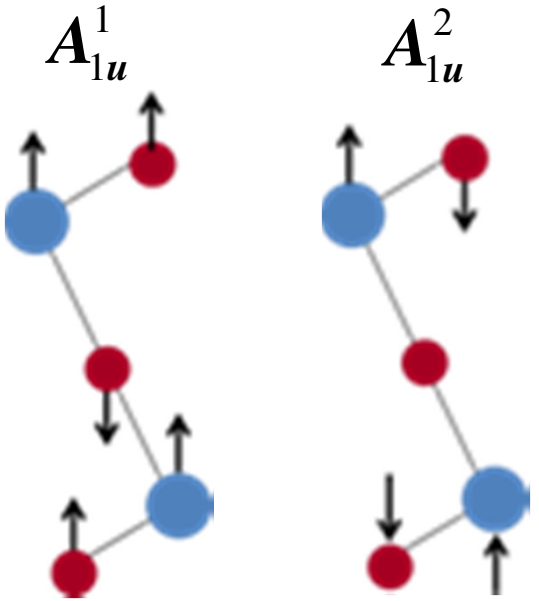
Even-parity phonons (with subscripts "*g*") can be observed in **Raman scattering**

Odd-parity phonons (with subscript "*u*") can be observed in **infrared absorption**

Infrared-active modes observed in Raman scattering from Bi_2Te_3 NPs

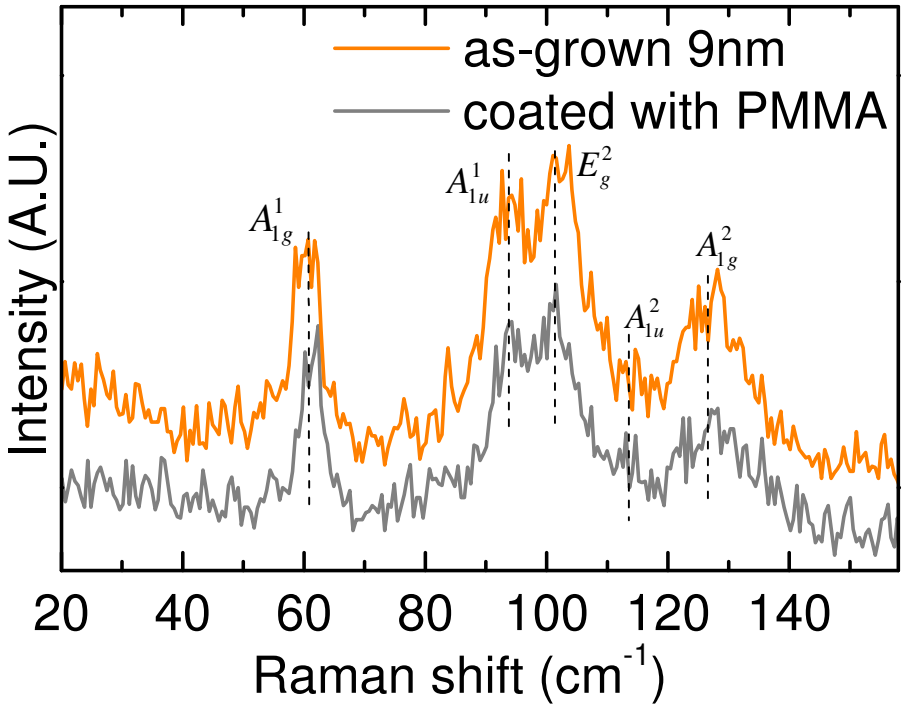
Two new modes emerge

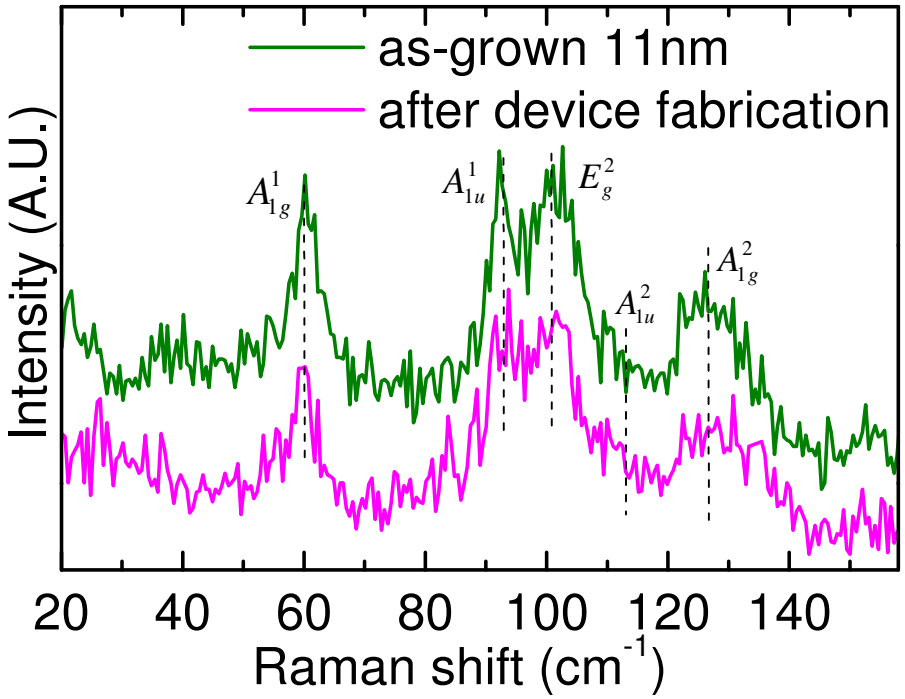




The emergence of *IR-active* modes in *Raman spectra* reveals a breakdown of inversion symmetry in TI nanostructures

Robustness of vibrational properties of Bi_2Te_3 NPs

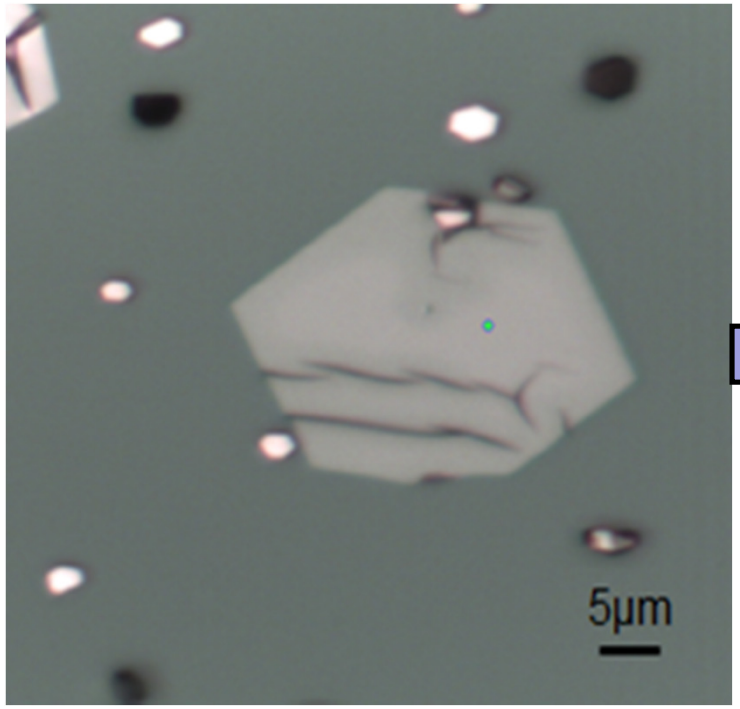




Vibrational properties preserve after device fabrication

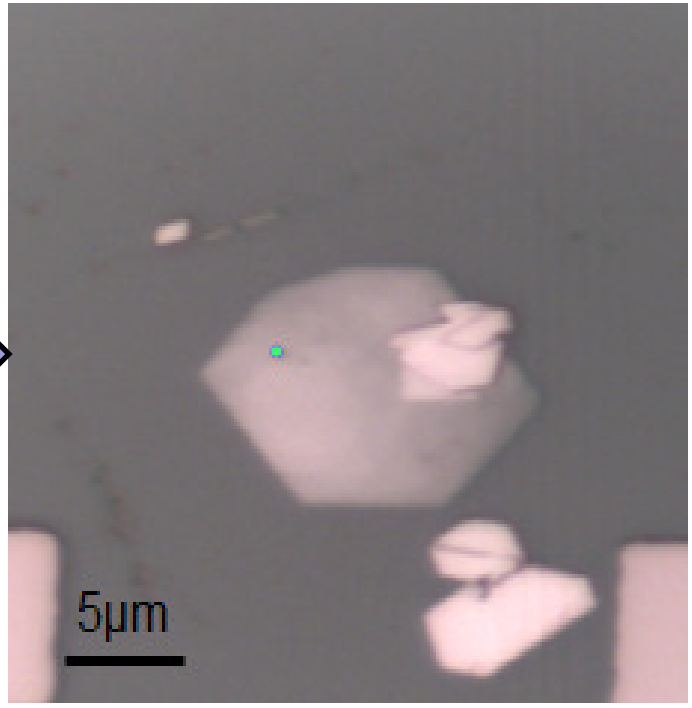
Transferred Bi_2Te_3 NPs

As-grown 11 nm



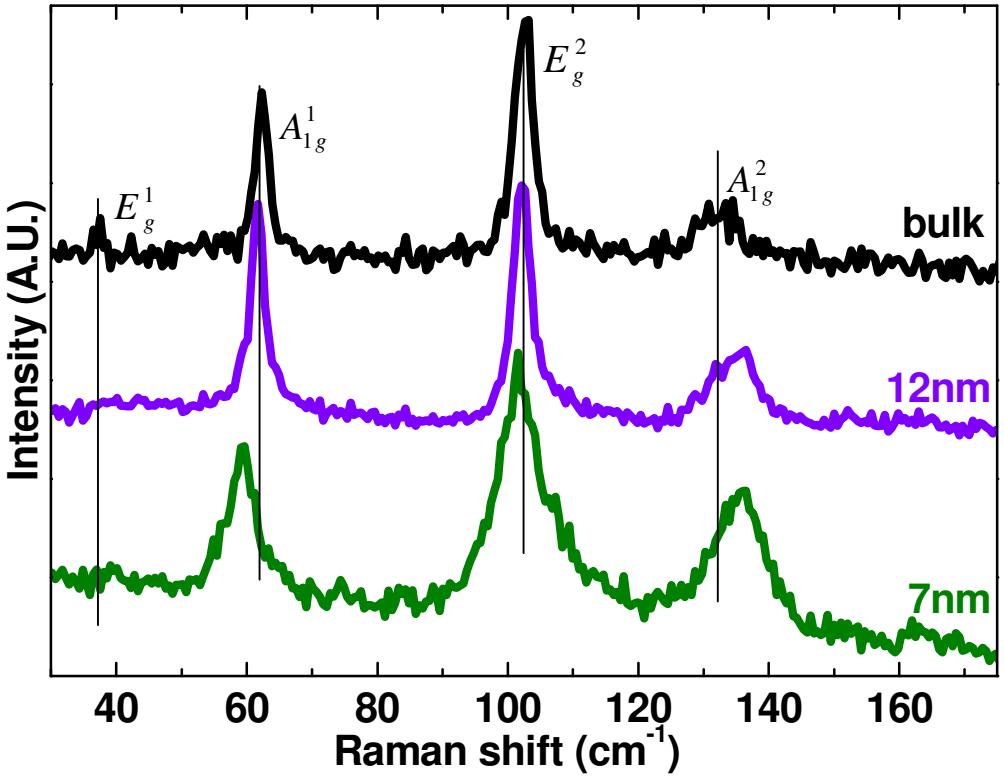
Mechanical transfer to remove impurities

Transferred 12 nm

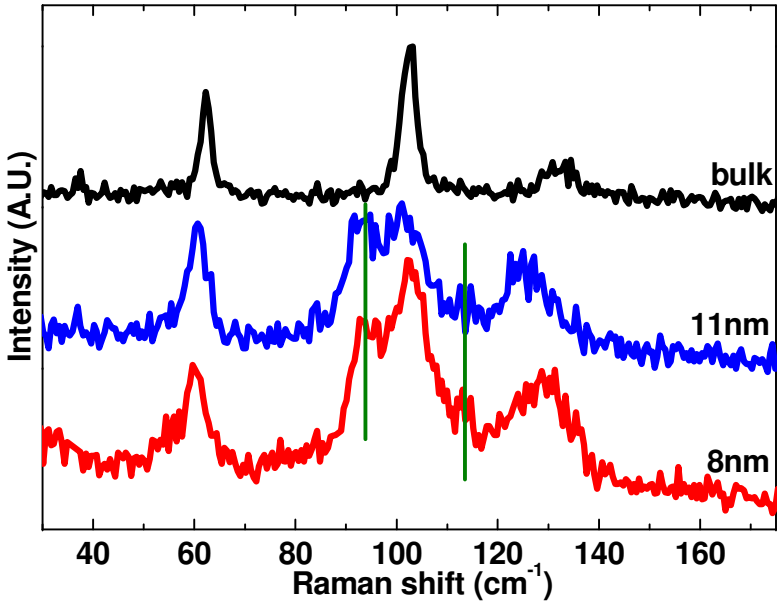


Raman scattering from transferred Bi_2Te_3 NPs

Transferred NPs



As-grown NPs



Infrared-active modes are absent in transferred NPs:

absence of inversion symmetry breaking

Absence of inversion symmetry breaking in transferred NPs

Possible reason:

The transferred NPs are the ones that stand on edge on the substrate

strain applied by the substrate induce inversion symmetry breaking in as-grown NPs

***Nanotechnology* 23, 455703 (2012)**

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Thank you!