



Optical Spectroscopy of Graphene and Topological Insulators



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University of Northern Iowa
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Outline

Graphene

Introduction

Graphene on Cu single crystal surfaces

Nitrogen doped graphene

Twisted bilayer graphene

Graphene

Introduction

Graphene on Cu single crystal surfaces

Nitrogen doped graphene

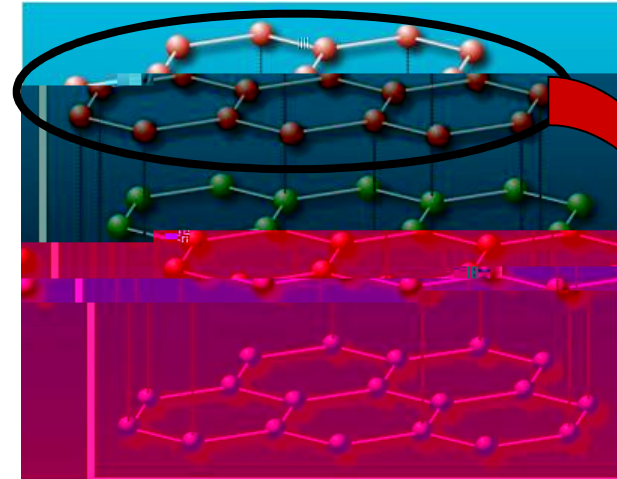
Twisted bilayer graphene

Graphite

Graphite pencils

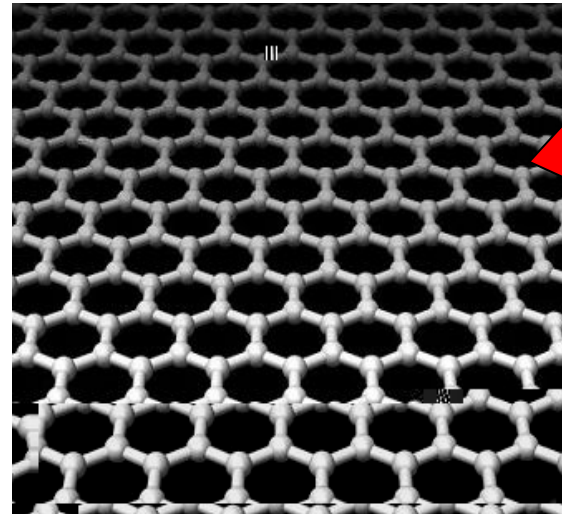


Graphene



3D graphite crystal

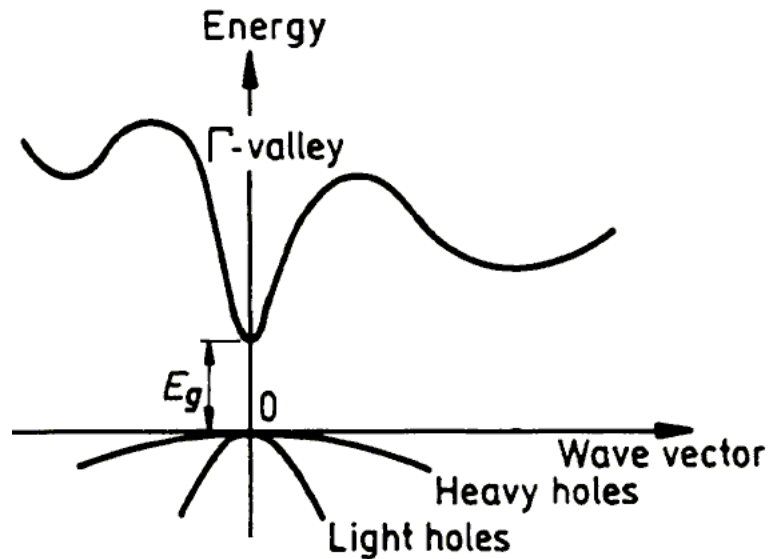
2D graphene



Discovered in
2004
Nobel Prize
awarded in
2010

Graphene: a new condensed-matter system

Electron band structure in conventional



Graphene: Linear dispersion near the Dirac points

Novel properties

Low electrical resistivity $1\mu\Omega\cdot\text{cm}$ at room temperature

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

Room temperature **mobility** up to $200,000\text{cm}^2/\text{Vs}$

electrons in graphene travel more than 100 times faster than those in Si ($\mu\sim 1400\text{cm}^2/\text{Vs}$)

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, Uniaxial Graphene

Yan Li, S. Dimitrakopoulos, K. A. Jenkins, G. B. Farmer, H. Y. Chen,
A. G. Rinzler

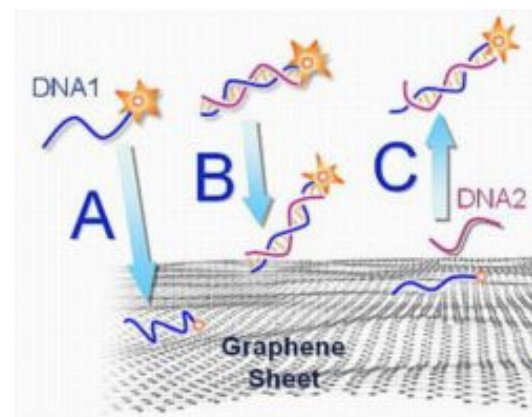
optoelectronic devices
(displays, touch screens, etc.)



stronger composite materials
(lighter but more crack-resistant aircraft)



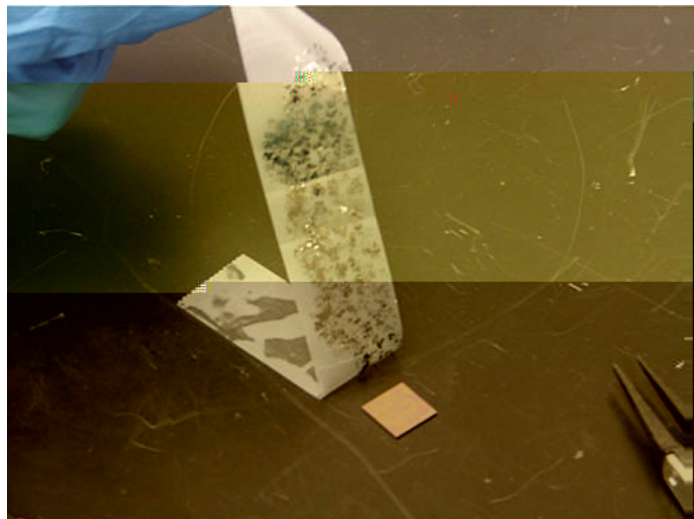
biosensors
(disease diagnosis)



How to make graphene?

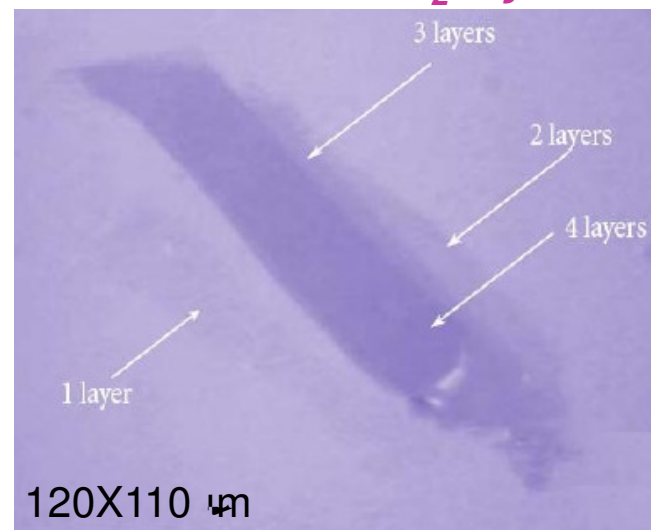
Scotch-tape method

Mechanical exfoliation



Scientific American

Observable color contrast
on 300 nm SiO_2 layer



Advantages:

- * high quality graphene flakes
- * low cost

Drawbacks:

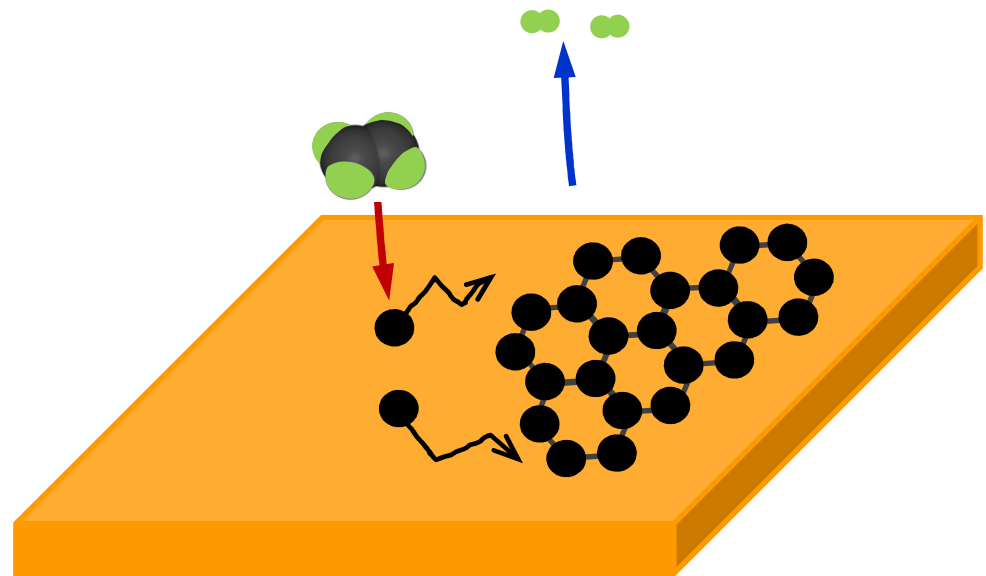
- * low efficiency (tiny flakes)
- * not suitable for large area production required by electronic applications

How to make large area graphene?

Growth on transition metal by chemical vapor deposition (CVD)

- Growth temperature 900-1000°C
- Ethylene or methane is used as C source
- Cu is a catalyst for graphene growth

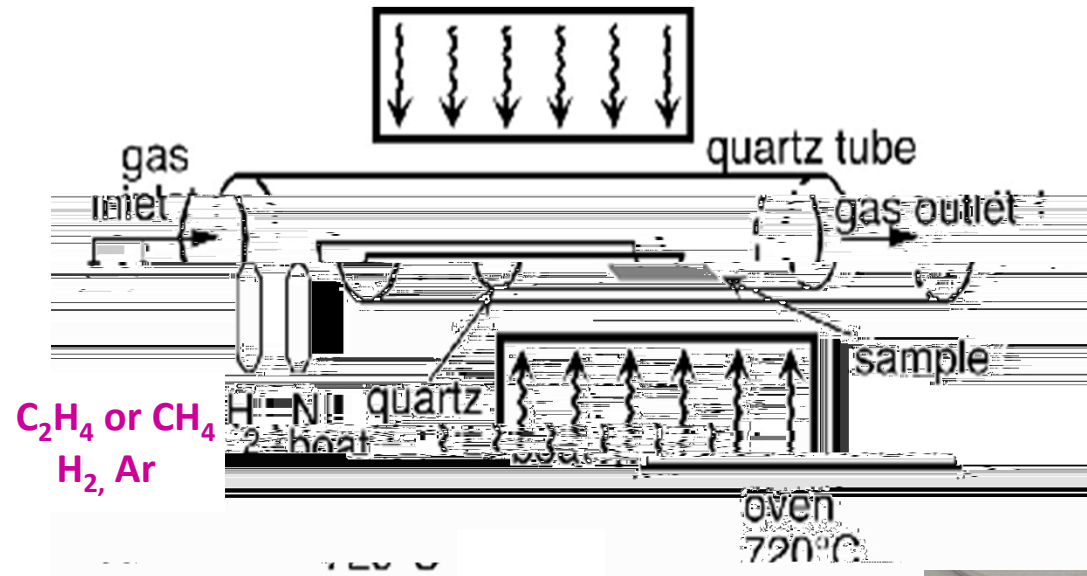
*hydrocarbon molecules
crack on hot Cu surface*



How to make large area graphene?



apparatus

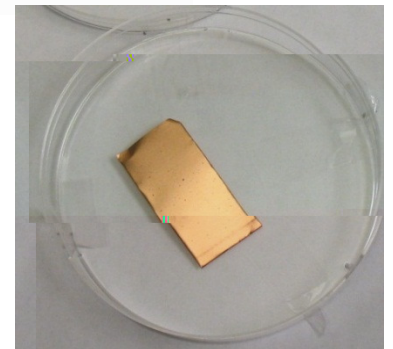


Advantages:

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

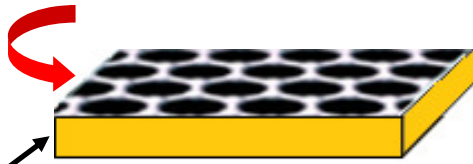
Drawbacks:

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



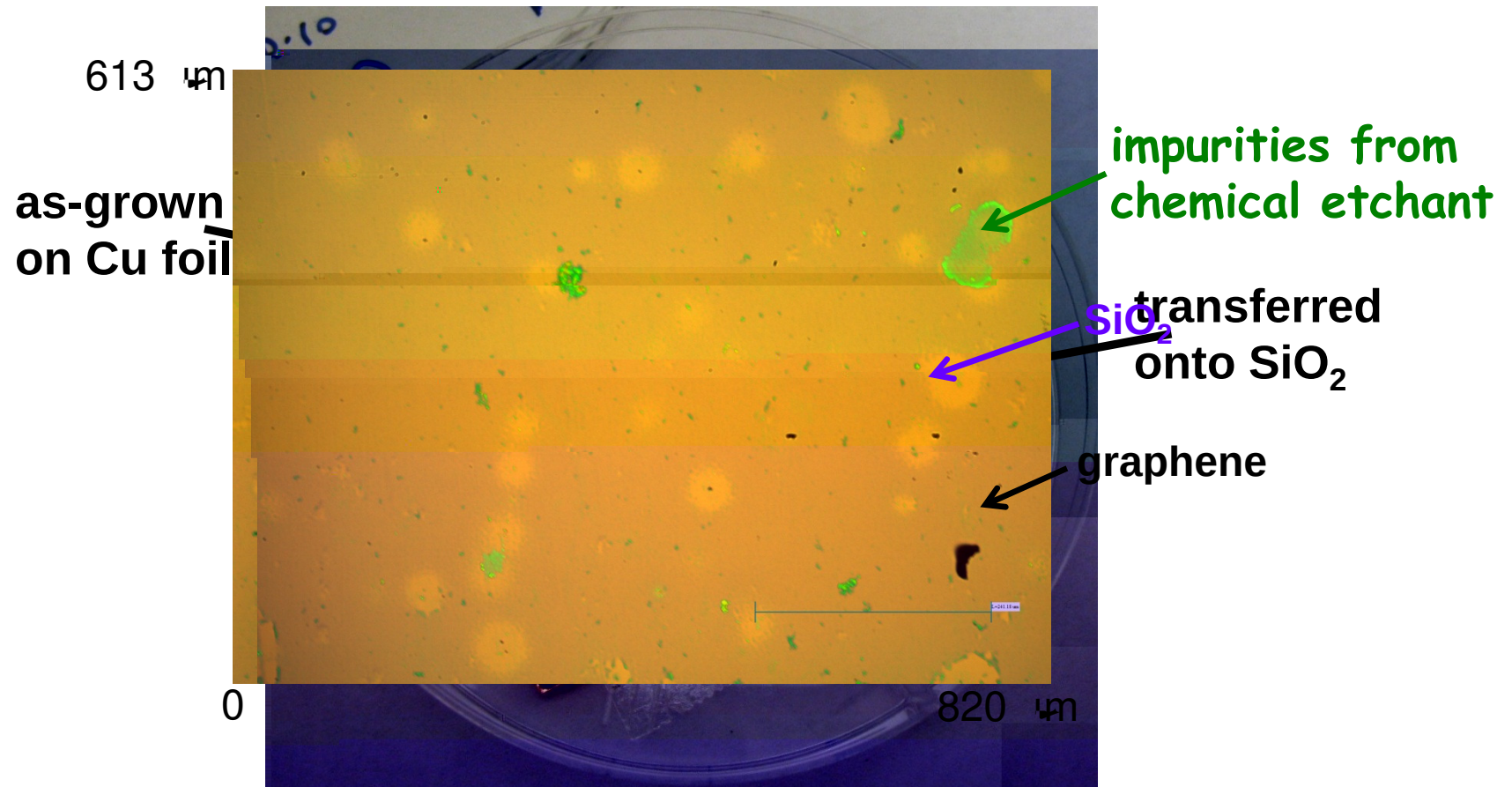
Transfer of graphene from metal surfaces onto dielectric substrates

single layer graphene



Cu substrate

Graphene after transfer large area

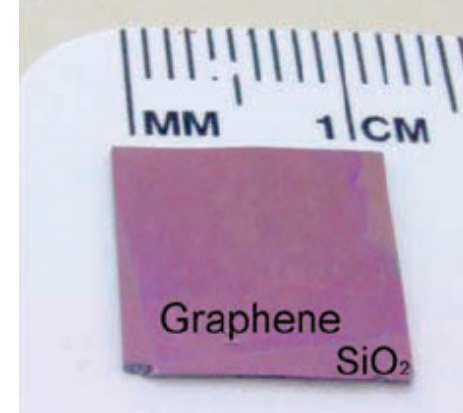


The transfer process introduces impurities, defects, and mechanical damages in graphene

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 :
 $\mu \sim 10,000\text{-}25,000 \text{ cm}^2/\text{Vs}$

CVD graphene on Cu foil
transferred onto SiO_2 :
 $\mu \sim 2000\text{-}5000 \text{ cm}^2/\text{Vs}$

We study CVD growth on single crystal Cu

Graphene

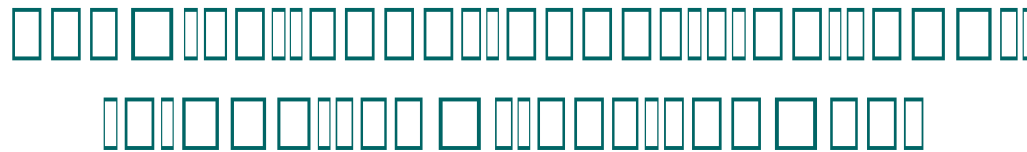
Introduction

Graphene on Cu single crystal surfaces

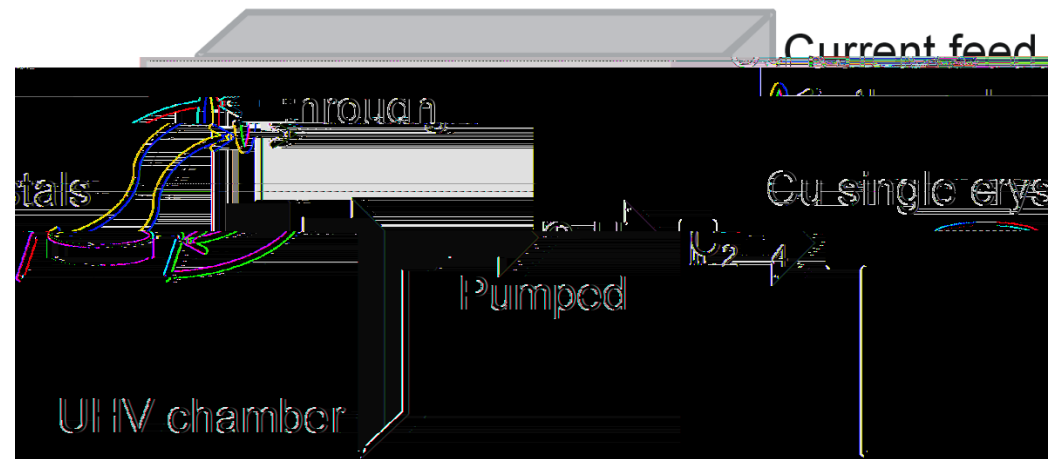
Nitrogen doped graphene

Twisted bilayer graphene

Graphene growth on Cu single crystal



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



Graphene on Cu single crystal surfaces

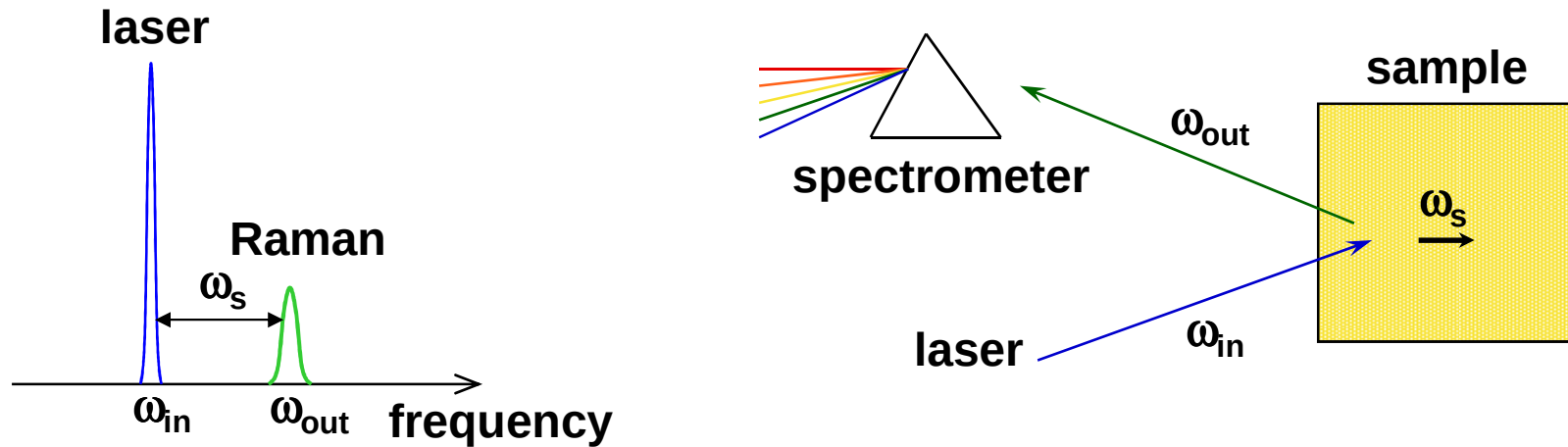
Graphene layers on Cu surfaces are strained

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

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

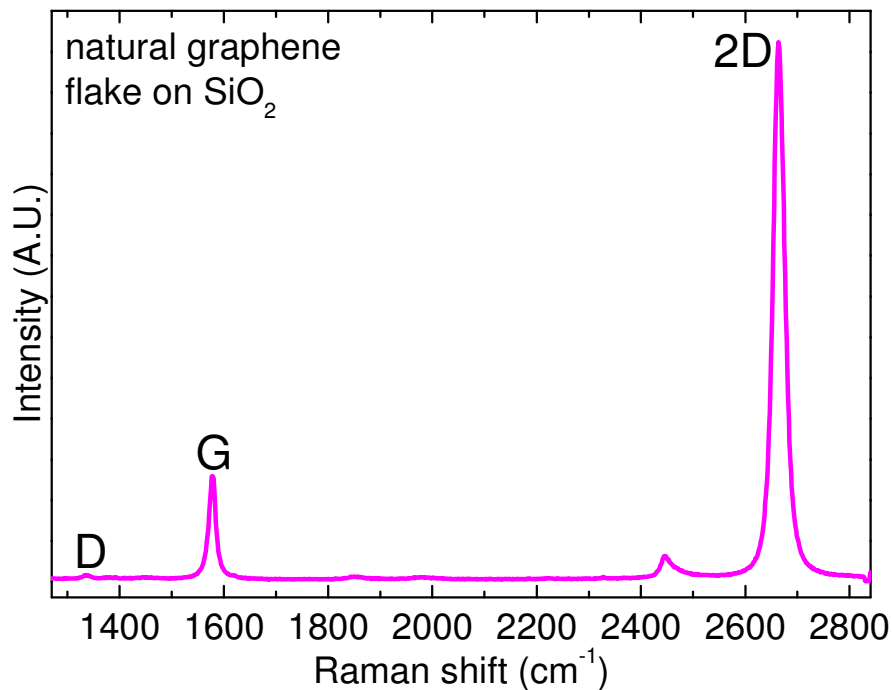
scattering wave vector

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

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

Characterization of graphene by Raman scattering

Raman spectrum



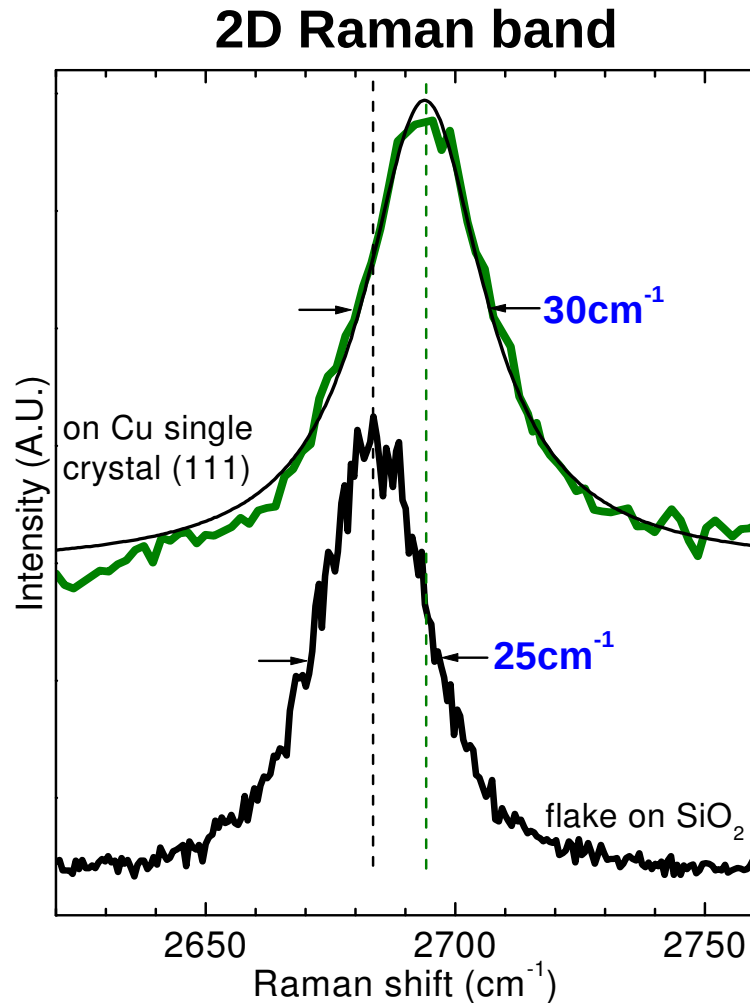
Measure optical phonons

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

2D-band (two-phonon mode) at $\sim 2680\text{cm}^{-1}$ (monitors strain)

D-band at $\sim 1350\text{cm}^{-1}$ (due to disorder)

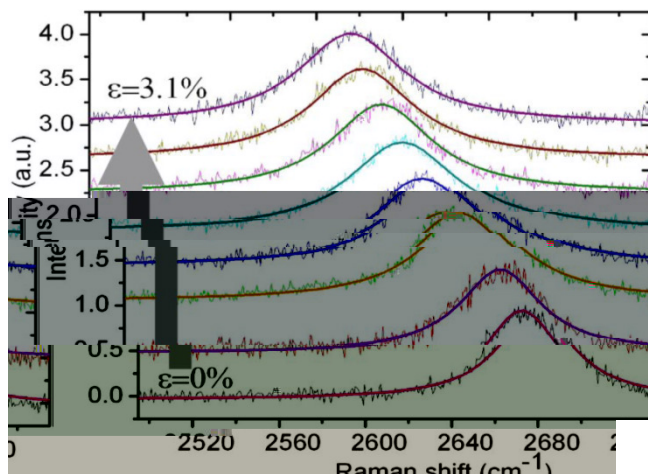
CVD graphene on (111) Cu single crystal



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

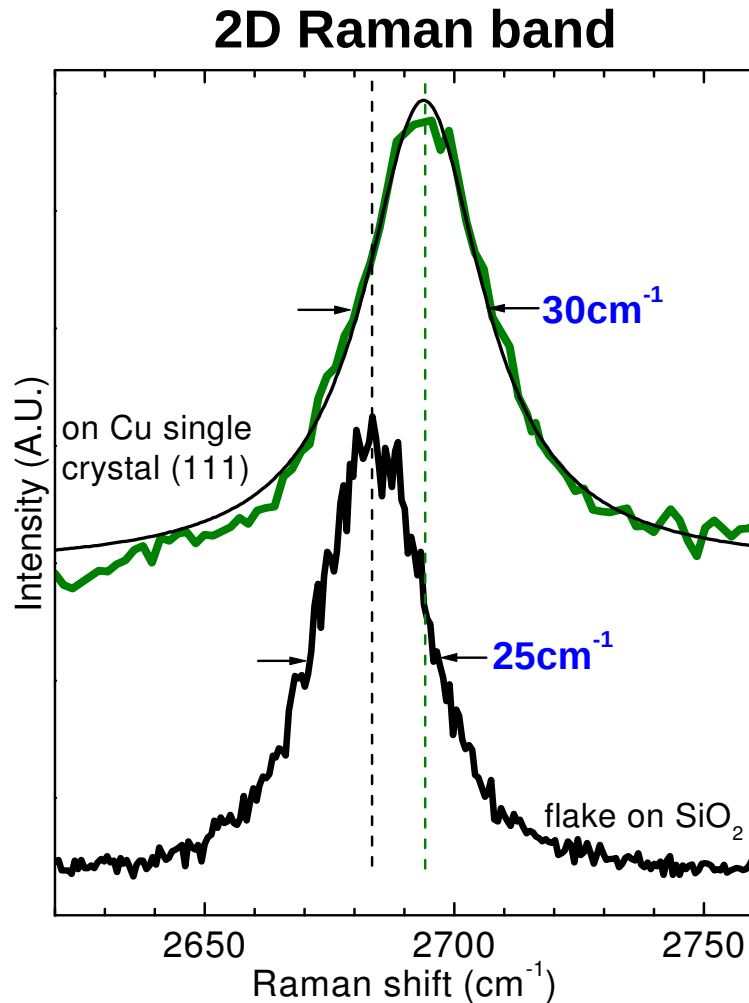
2D Raman band is very sensitive to strain

mode softens under tensile strain



**Blue-shifts indicate
compressive physisorption strain**

CVD graphene on (111) Cu single crystal

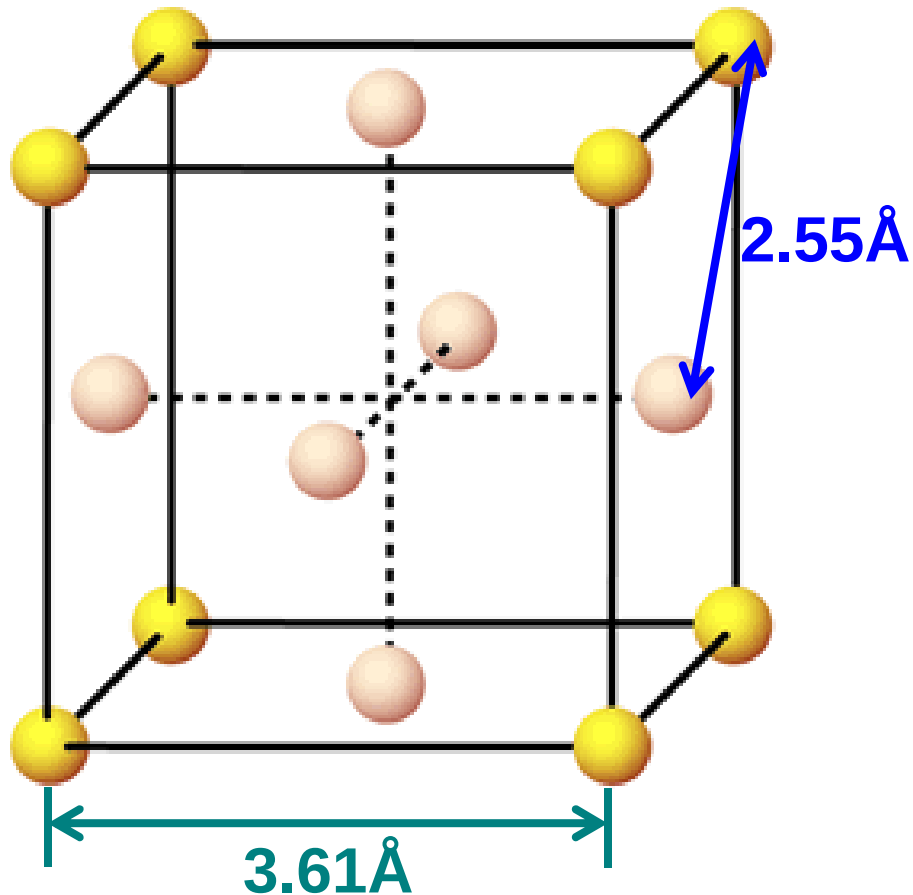


- 2D Raman band is **blue-shifted**
- The **blue-shift** indicates compressive strain due to physisorption of graphene on Cu

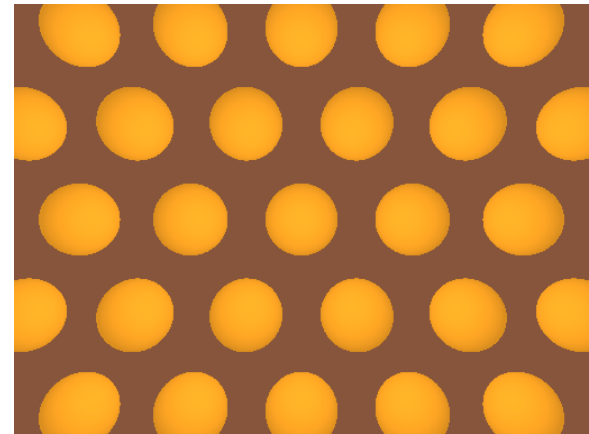
***Graphene on Cu (111) surface has
higher quality***

Cu single crystal

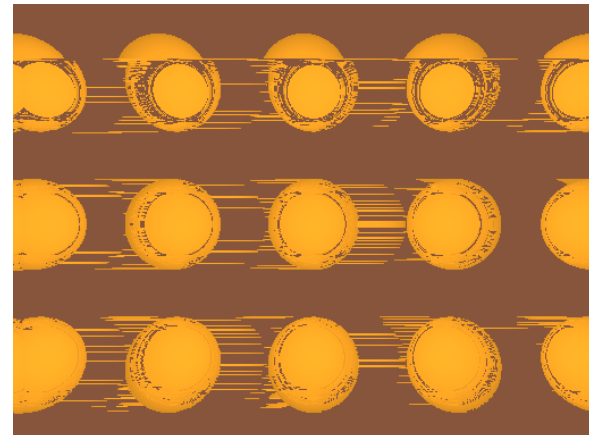
Face-centered cubic
(FCC) structure



Cu (111) hexagonal



Cu (100) square



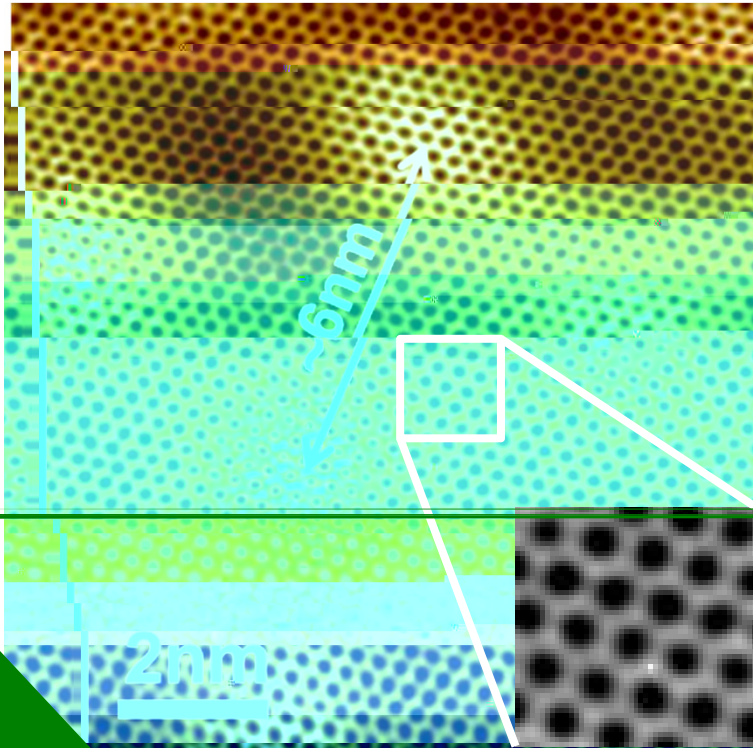
Characterization by scanning tunneling microscopy (STM)

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

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

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

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

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

$$\rightarrow \theta \approx 0^\circ$$

Rotational angle θ is almost zero



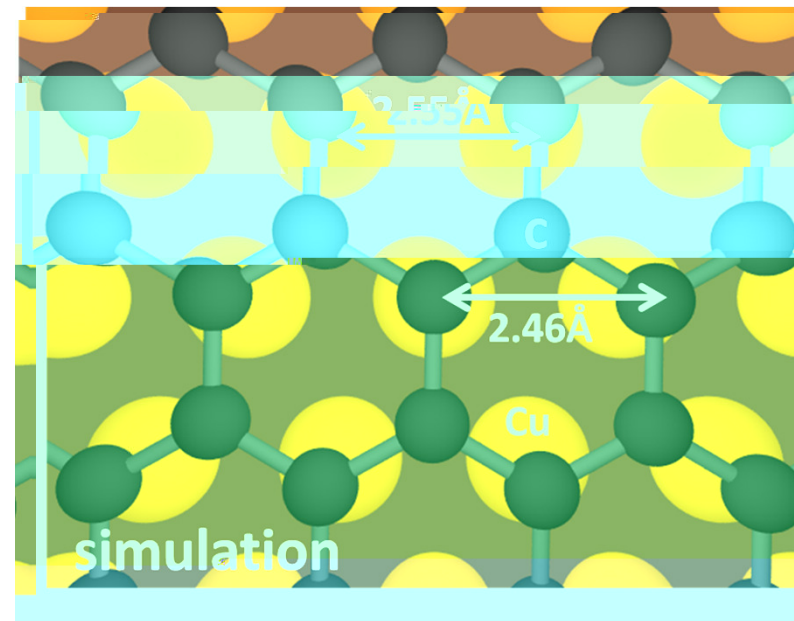
Graphene on Cu (111) single crystal

Graphene *honeycomb* lattice with lattice constant of **2.46Å**

Cu (111) *hexagonal* lattice with lattice constant of **2.55Å**

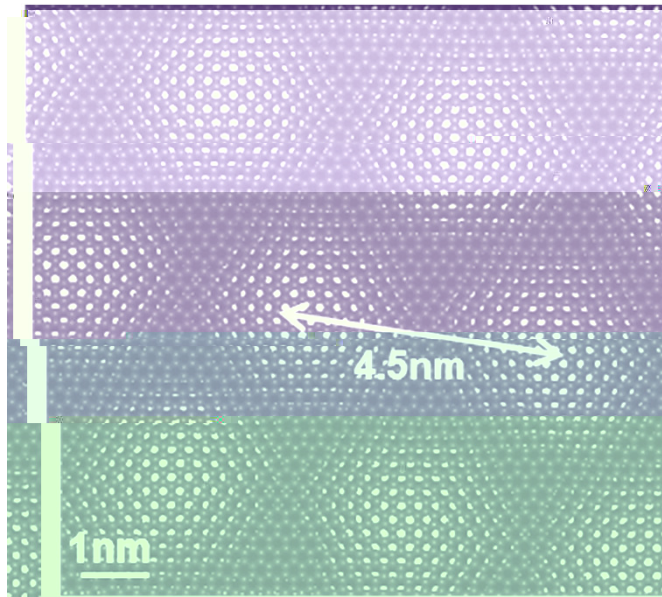
Rotational angle θ is almost zero

Quasi-epitaxial
growth

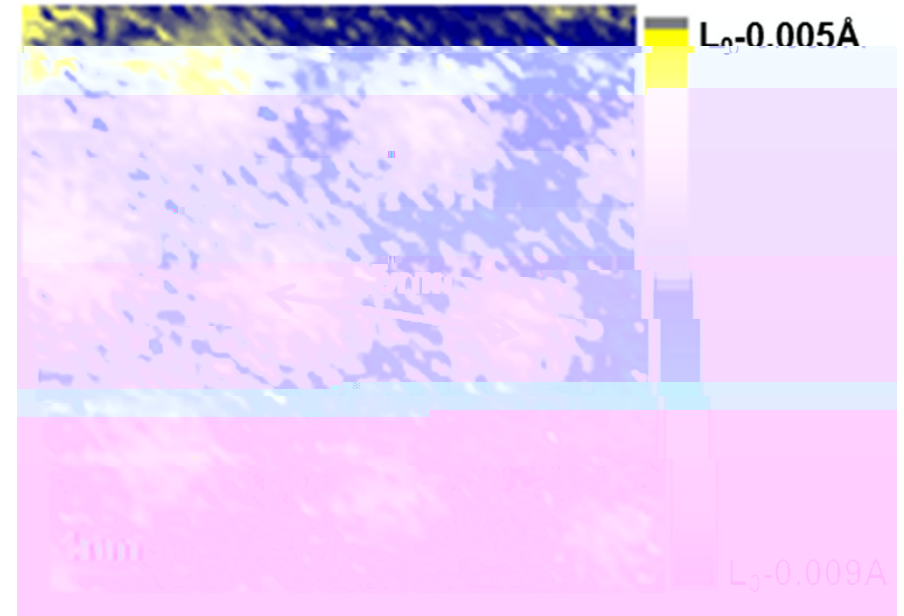


Molecular dynamics (MD) simulations of graphene on Cu (111) single crystal

Simulated superstructure



C-C bond length simulation

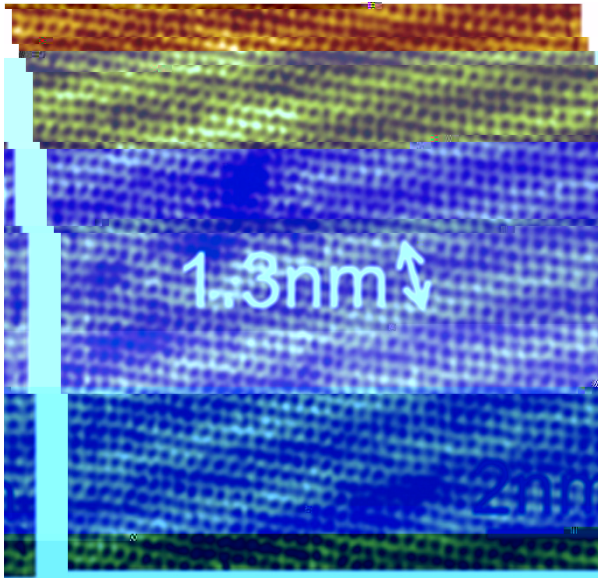


Compressive strain over the entire surface
Strain varies between 0.3% and 0.6%
Domain walls are highly compressed

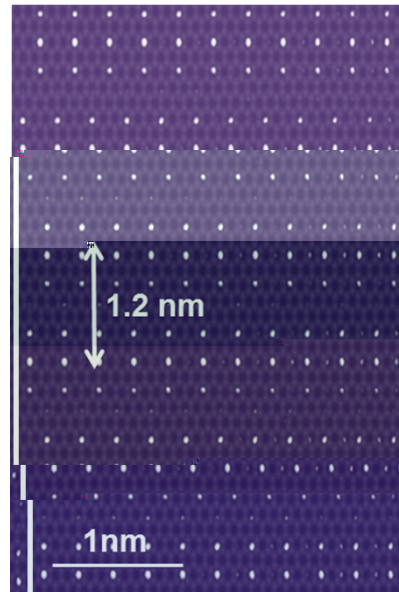
Graphene on Cu (100) single crystal

Molecular Dynamics simulations

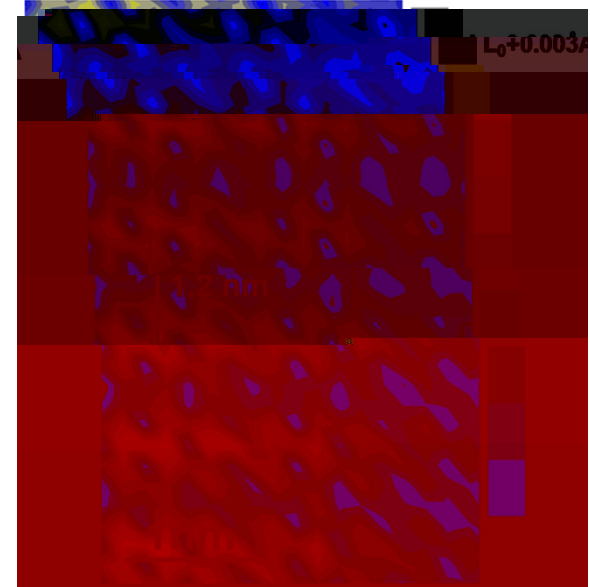
STM



Superstructure



C-C bond length

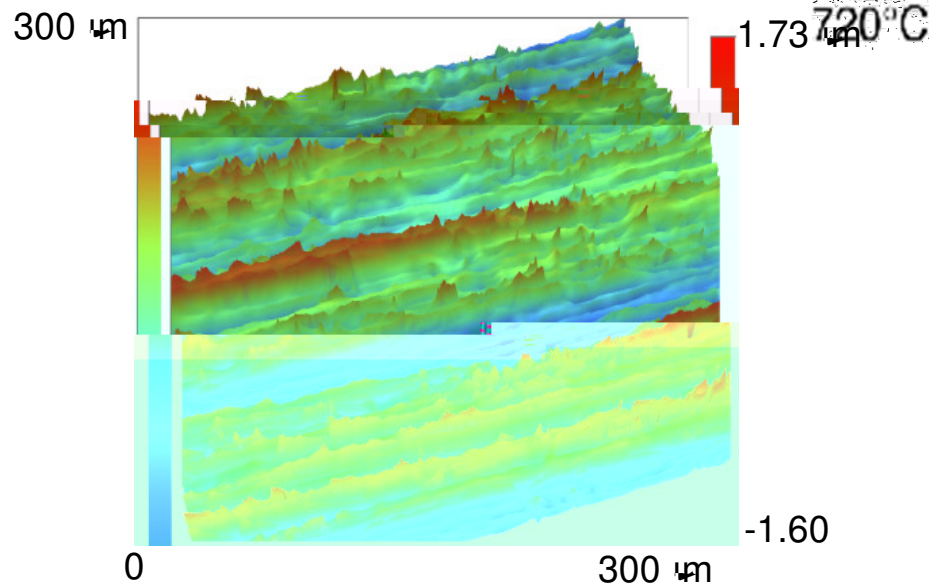
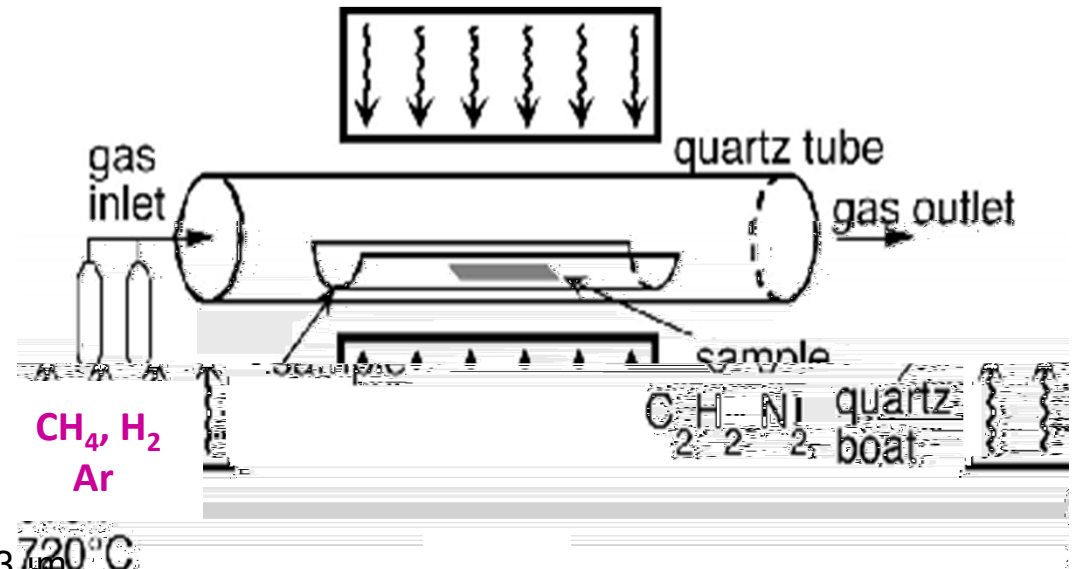


No epitaxy: honeycomb graphene lattice on Cu (100) square lattice

Highly nonuniform strain that varies from 0.3% compressive to 0.2% tensile

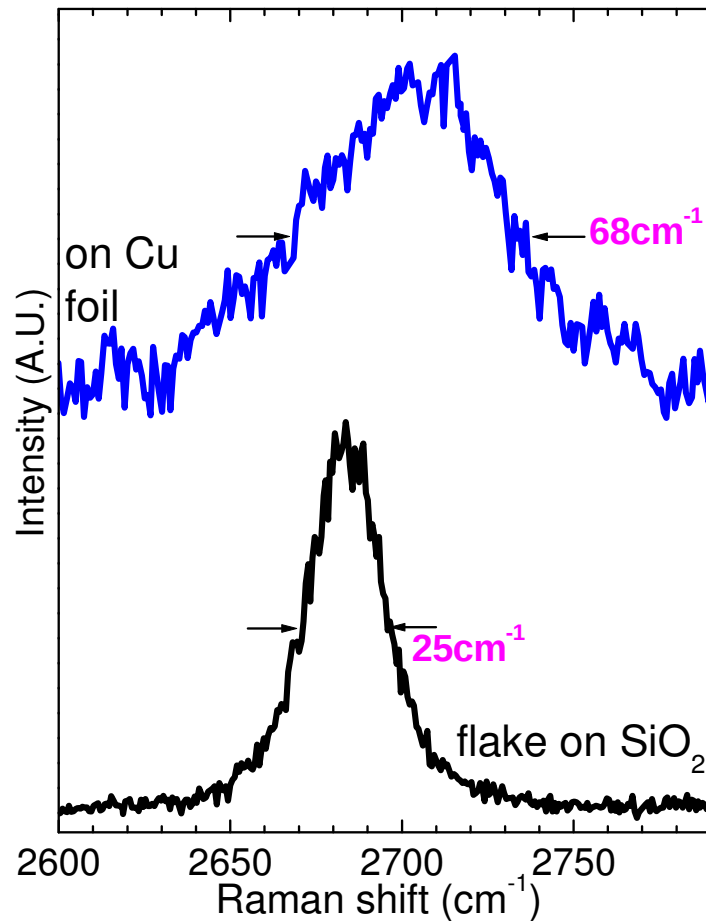
CVD growth on Cu foil

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



*polycrystalline and
rough surface*

CVD graphene on Cu foil



after transfer onto SiO_2

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 SiO₂ substrate

Nano Letters 12, 2408 (2012)

Graphene

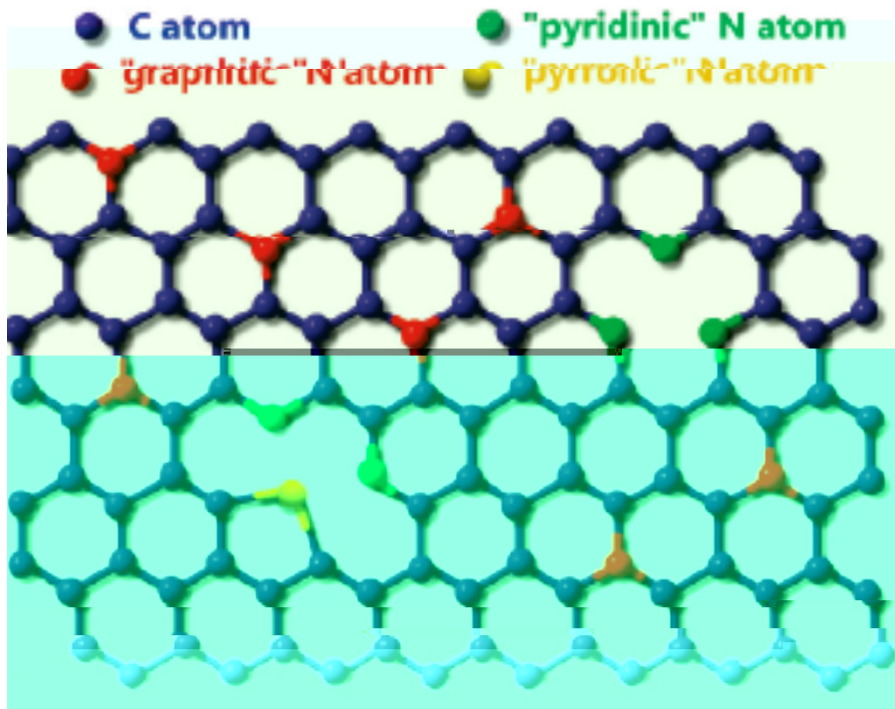
Introduction

Graphene on Cu single crystal surfaces

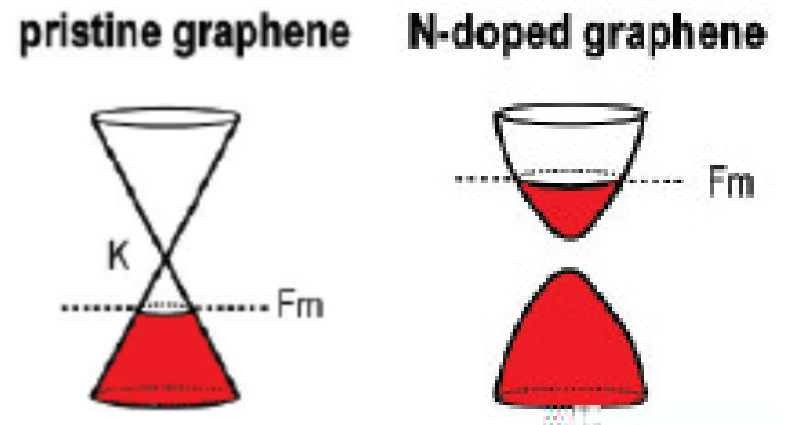
Nitrogen doped graphene

Twisted bilayer graphene

Nitrogen doped graphene



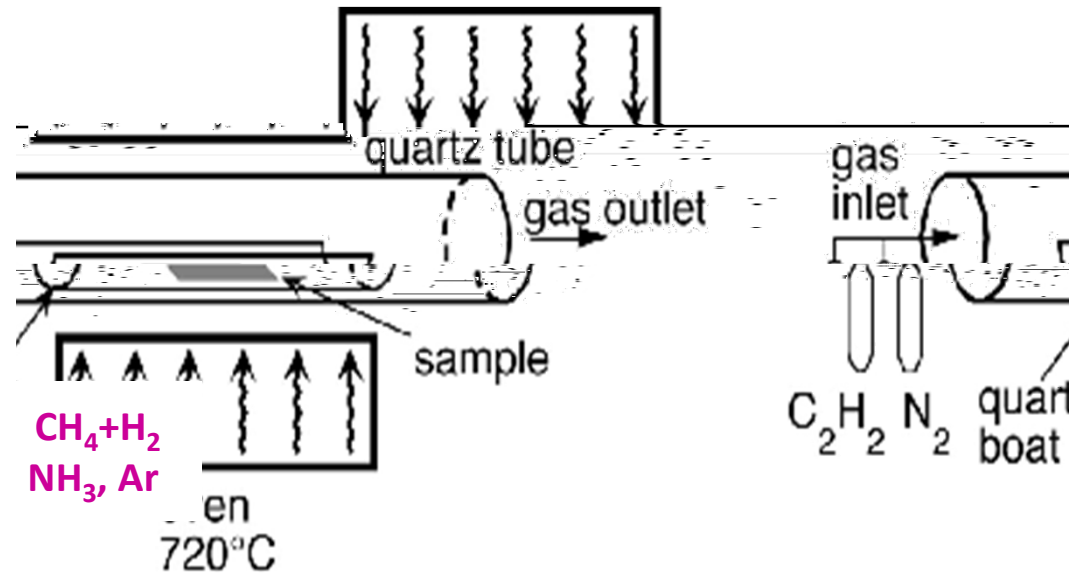
Doping: control electronic properties of graphene



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

Nitrogen doped graphene

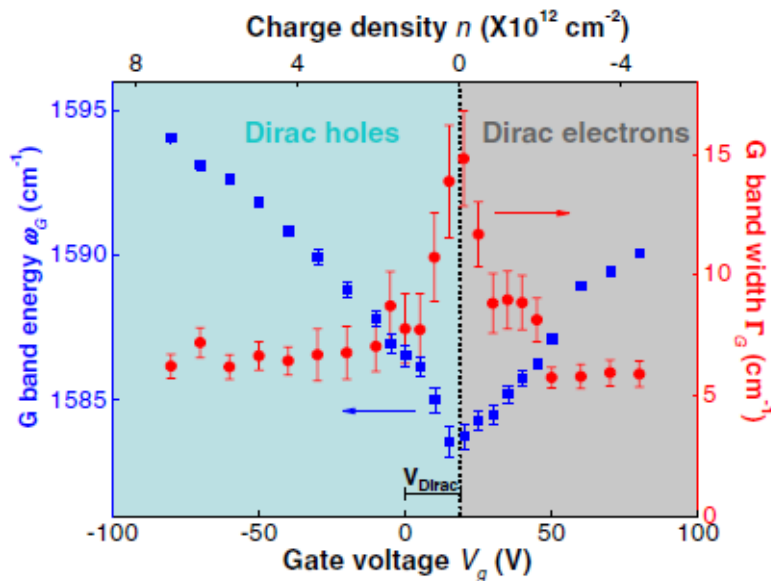
chemical vapor deposition (CVD)



- Copper foil is heated to $\sim 1000^\circ\text{C}$
- 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

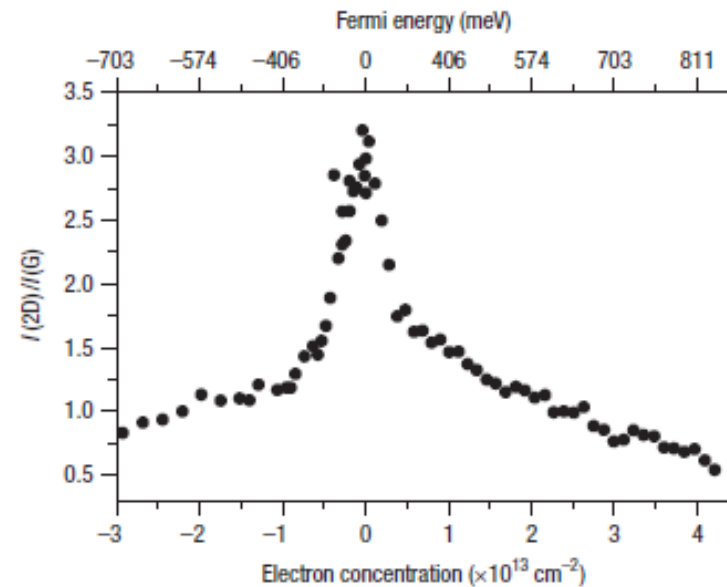
Raman characterization of carrier density in graphene

G peak position



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

2D/G ratio

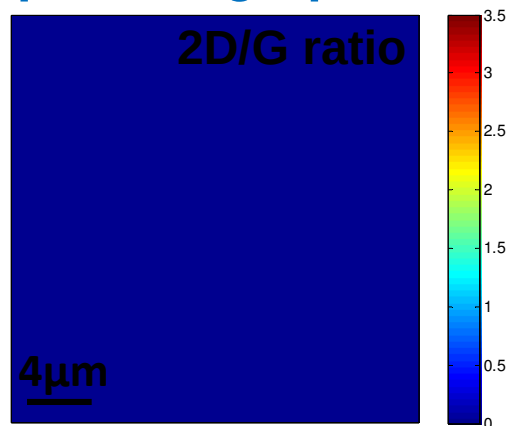


Das *et al.*, *Nature Nanotechnology*
3, 210 (2008)

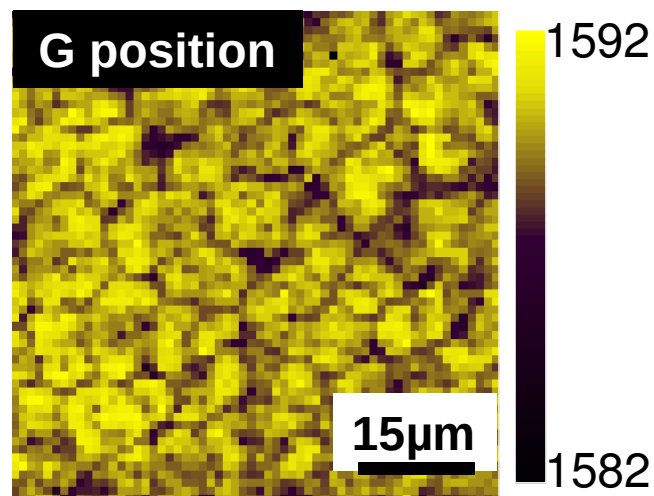
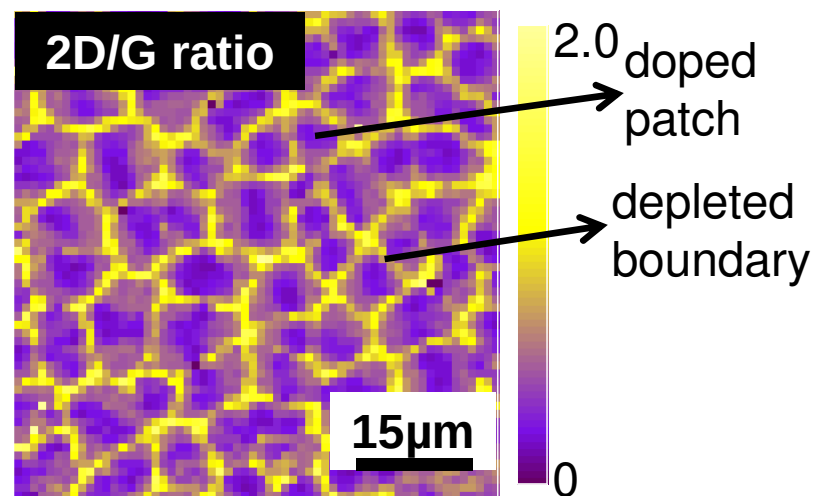
**lower electron (hole) density $\longleftrightarrow$
lower G peak frequency and higher 2D/G ratio**

Raman mapping of nitrogen doped graphene

pristine graphene

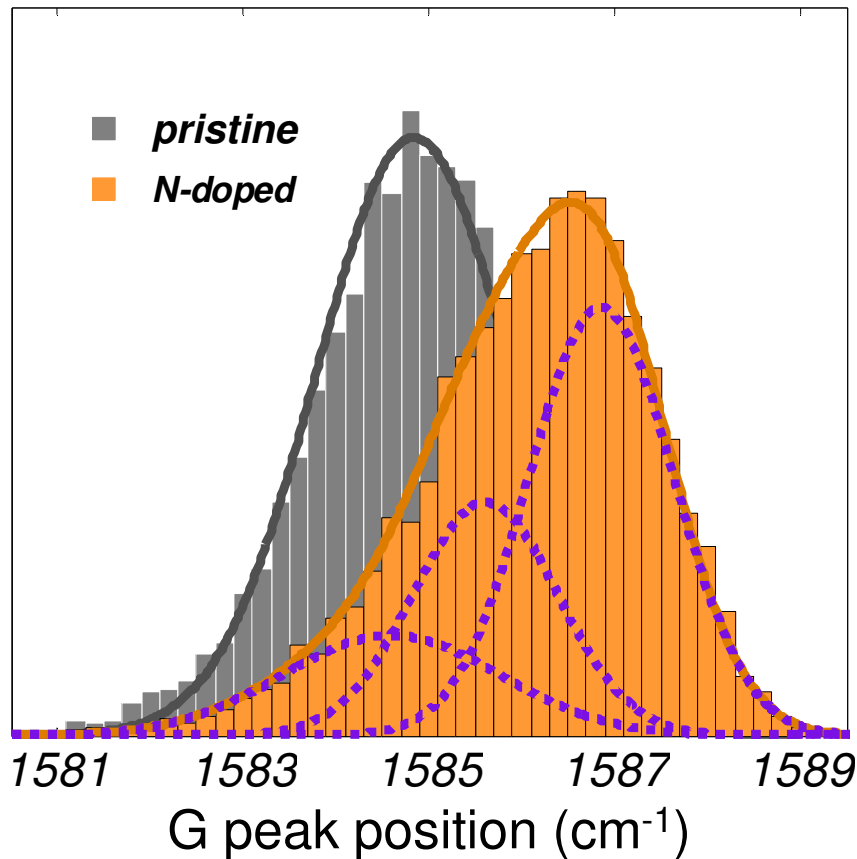


Lower dopant (nitrogen) concentration at the grain boundaries



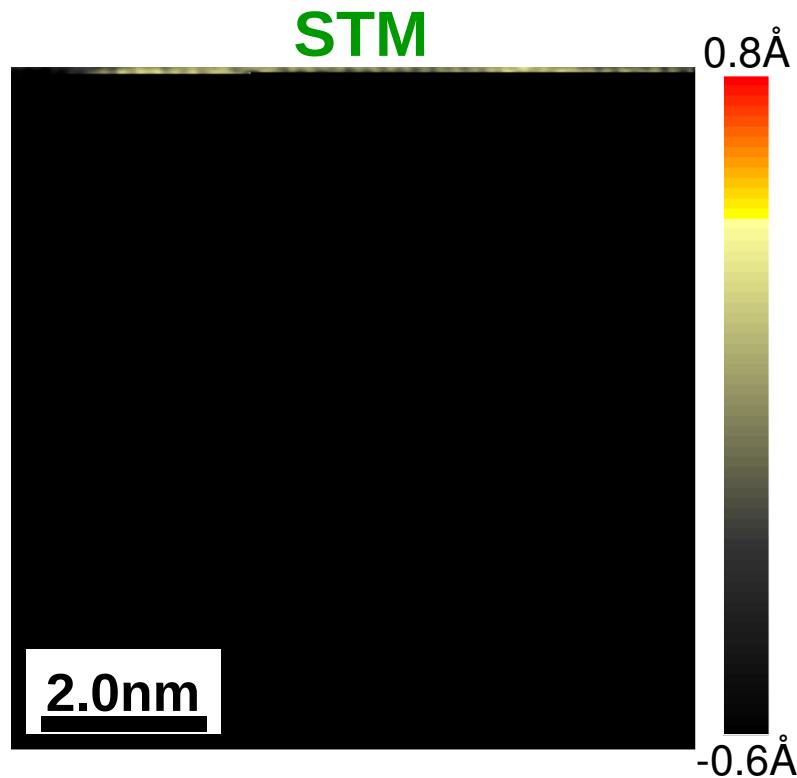
Estimation of average carrier concentration

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 $5 \pm 1.5 \times 10^{12} \text{ cm}^{-2}$

Mobile carriers contributed by nitrogen dopants



Nitrogen dopants are randomly distributed in the honeycomb lattice

N atom density $\sim 1.3 \times 10^{13} \text{ cm}^{-2}$

Carrier concentration (estimated by Raman) is $5 \pm 1.5 \times 10^{12} \text{ cm}^{-2}$

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)

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Graphene on Cu single crystal surfaces

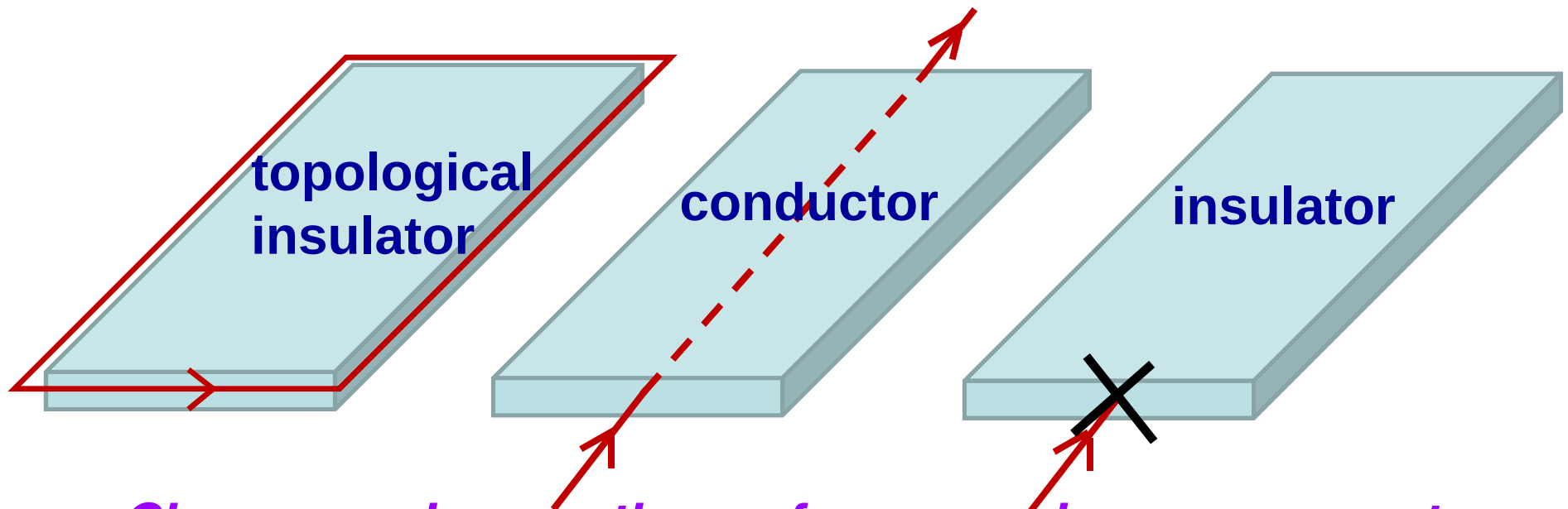
Nitrogen doped graphene

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

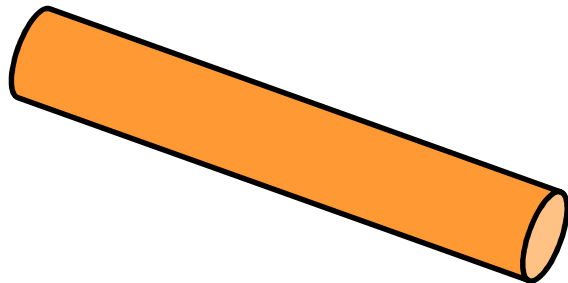
Challenges in TI research



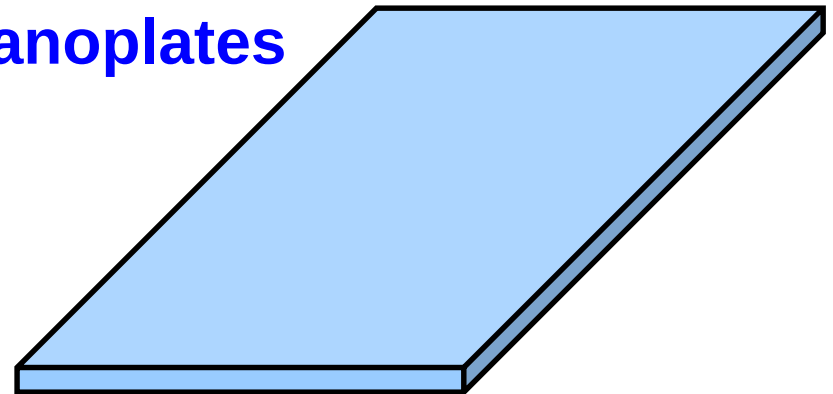
In 3D TIs, bulk characteristics dominate their properties

Reduce its dimension:
enhance surface-to-bulk ratio

1D nanowires



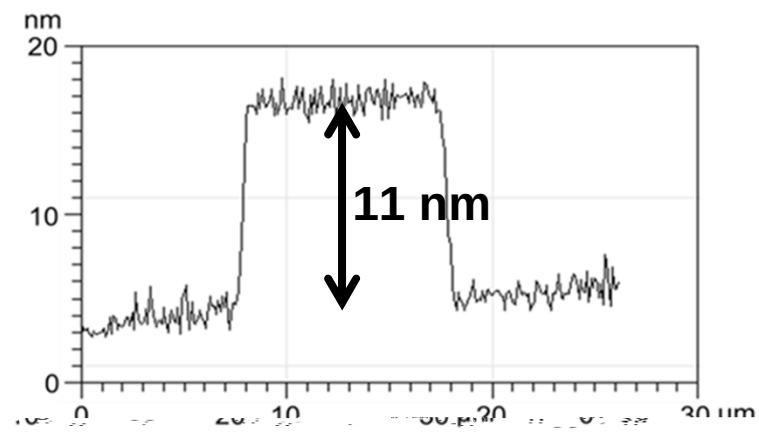
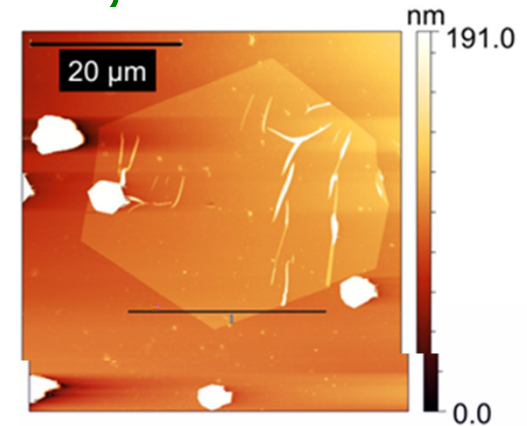
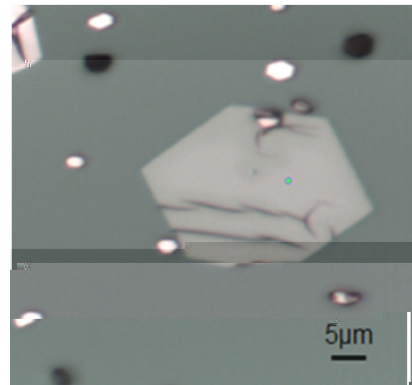
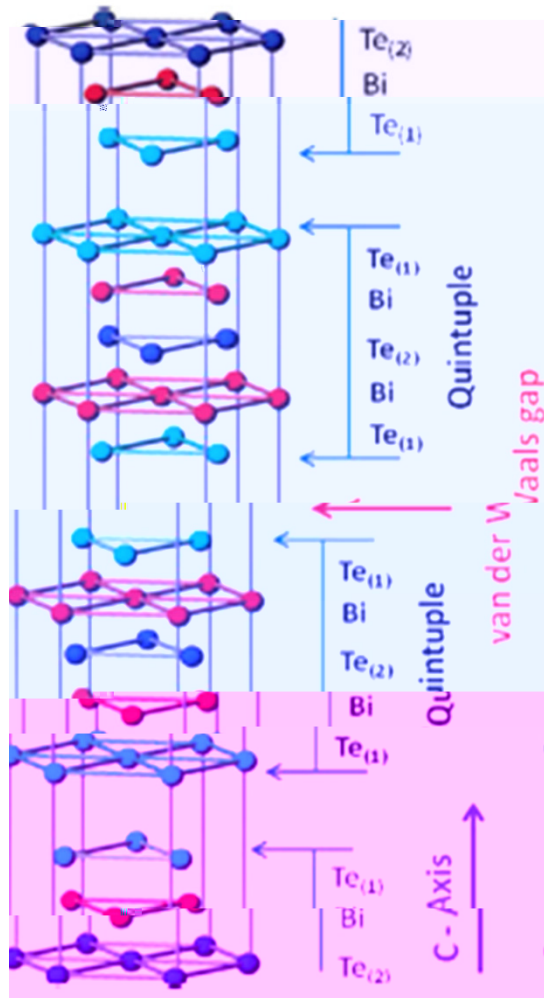
2D nanoplates



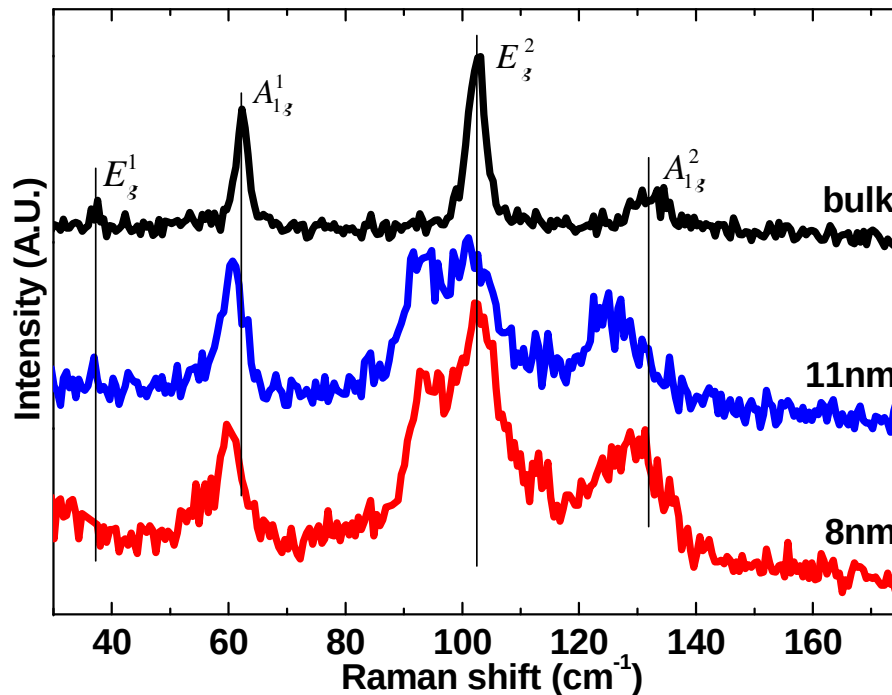
TI nanoplates

representative TI material: Bi_2Te_3

As-grown NP, 11 nm

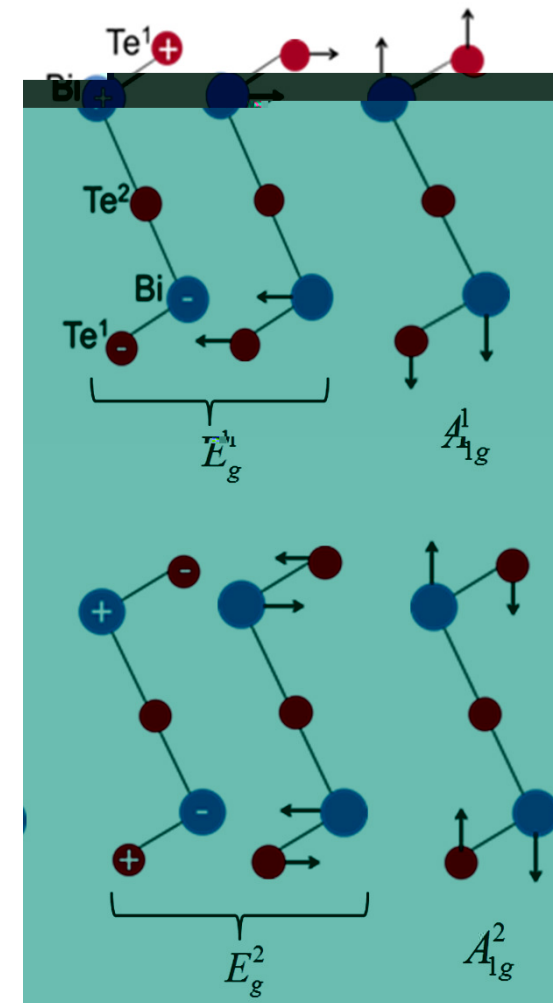


Raman scattering from bulk Bi_2Te_3 and as-grown Bi_2Te_3 NPs

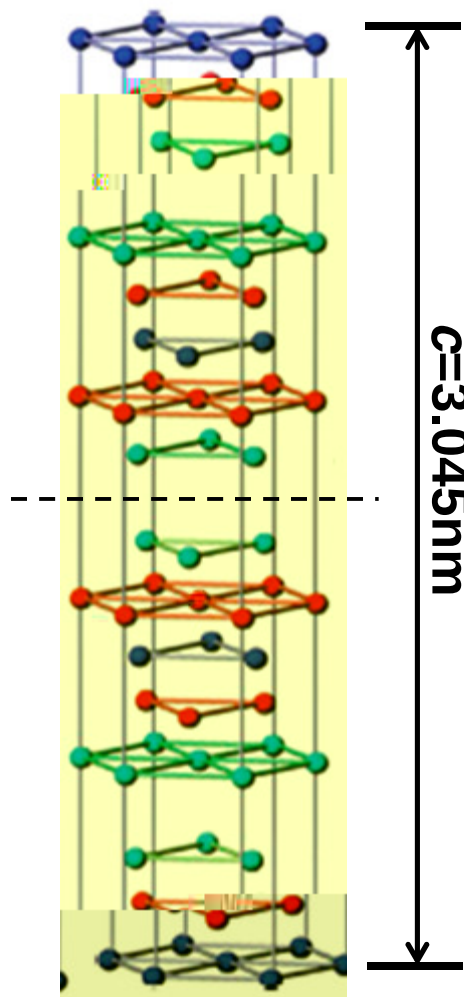


4 Raman-active modes from bulk Bi_2Te_3

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



Raman selection rules in crystals with inversion symmetry



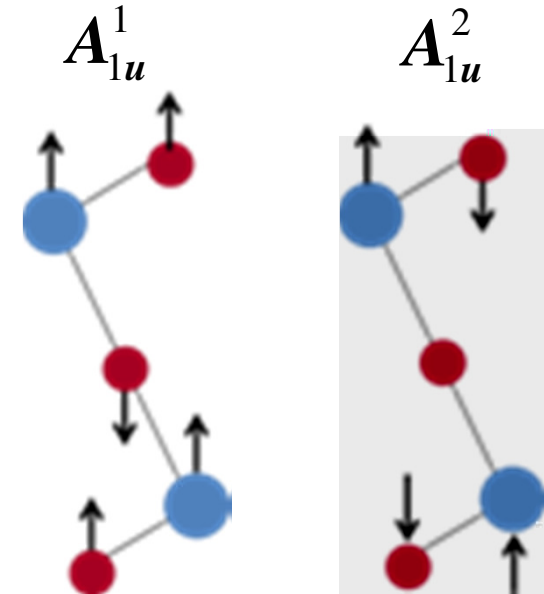
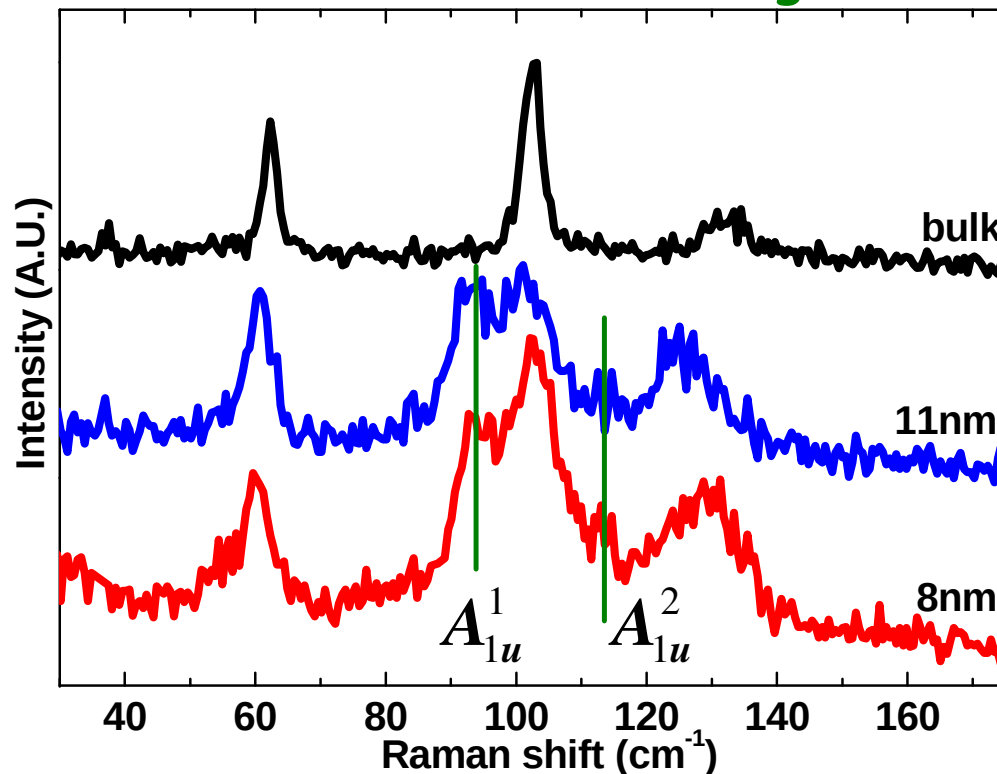
Bi₂Te₃ crystal lattice

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

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

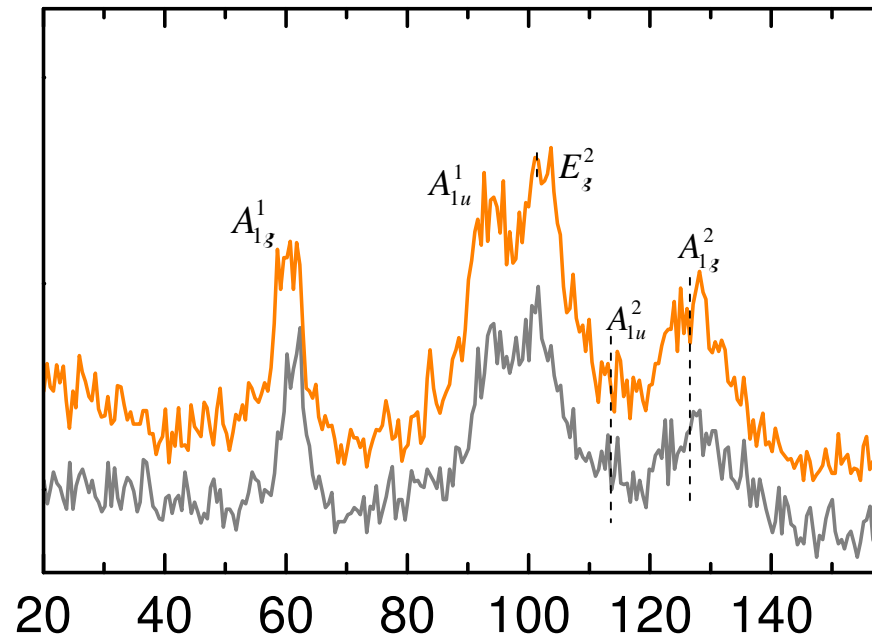
Infrared-active modes observed in Raman scattering from Bi_2Te_3 NPs

Two new modes emerge



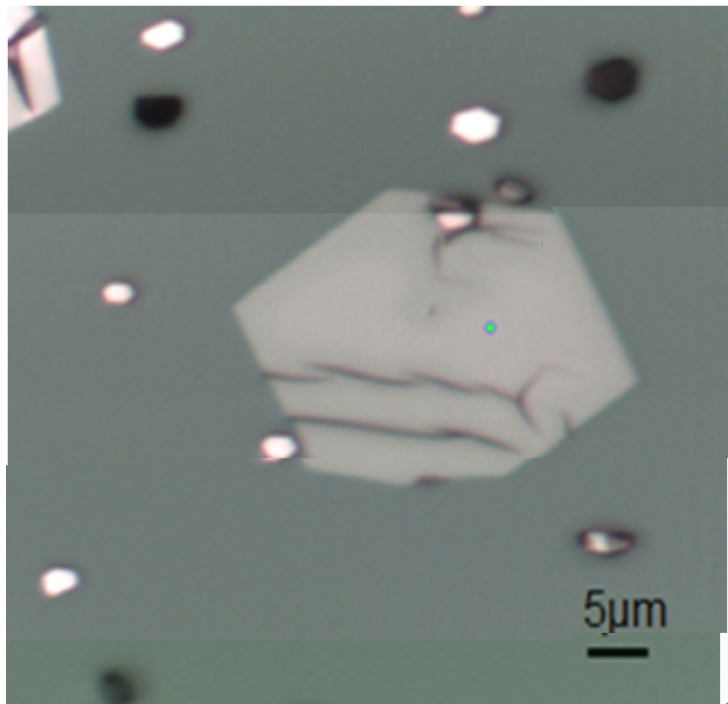
The emergence of *IR-active* modes in *Raman spectra* reveals a *breakdown of inversion symmetry* in TI nanostructures

Robustness of vibrational properties of Bi_2Te_3 NPs

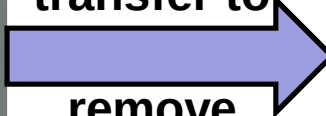


Transferred Bi_2Te_3 NPs

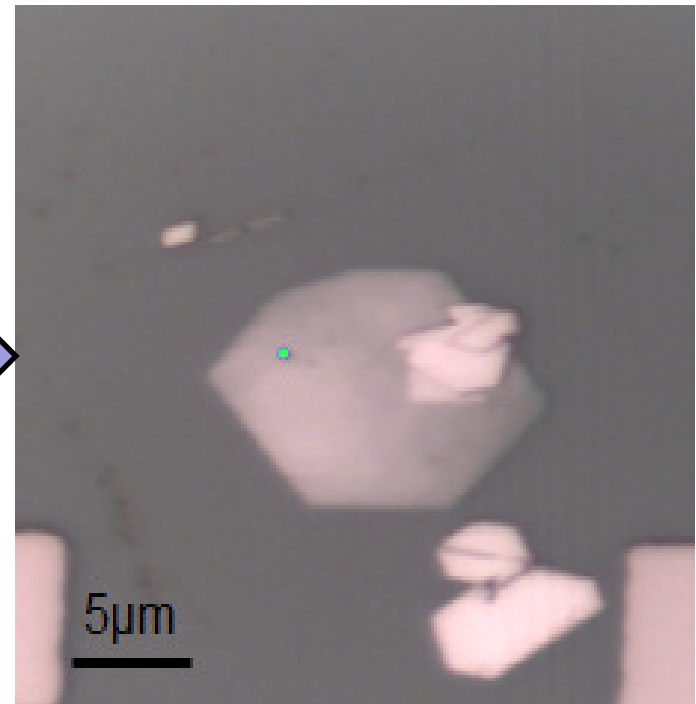
As-grown 11 nm



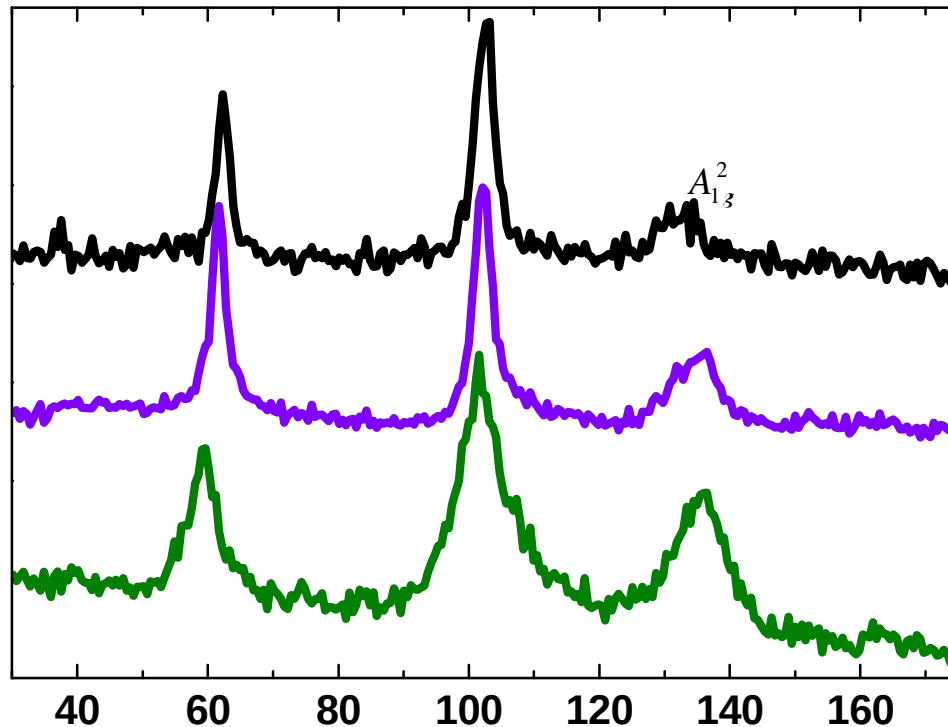
Mechanical
transfer to
remove
impurities



Transferred 12 nm



Raman scattering from transferred Bi_2Te_3 NPs



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)

Acknowledgments

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Columbia University:

Aron Pinczuk, Liuyan Zhao, Nicholas Petrone,
Abhay Pasupathy, James Hone, Philip Kim,
George W. Flynn

Purdue University:

Ting-Fung Chung, Yong Chen

Case Western Reserve University:

Zhenhua Wang, Richard L. J. Qiu, Xuan Gao

Many thanks to all

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 - The New York State Office of Science, Technology, and Academic Research (NYSTAR)

Thank you!