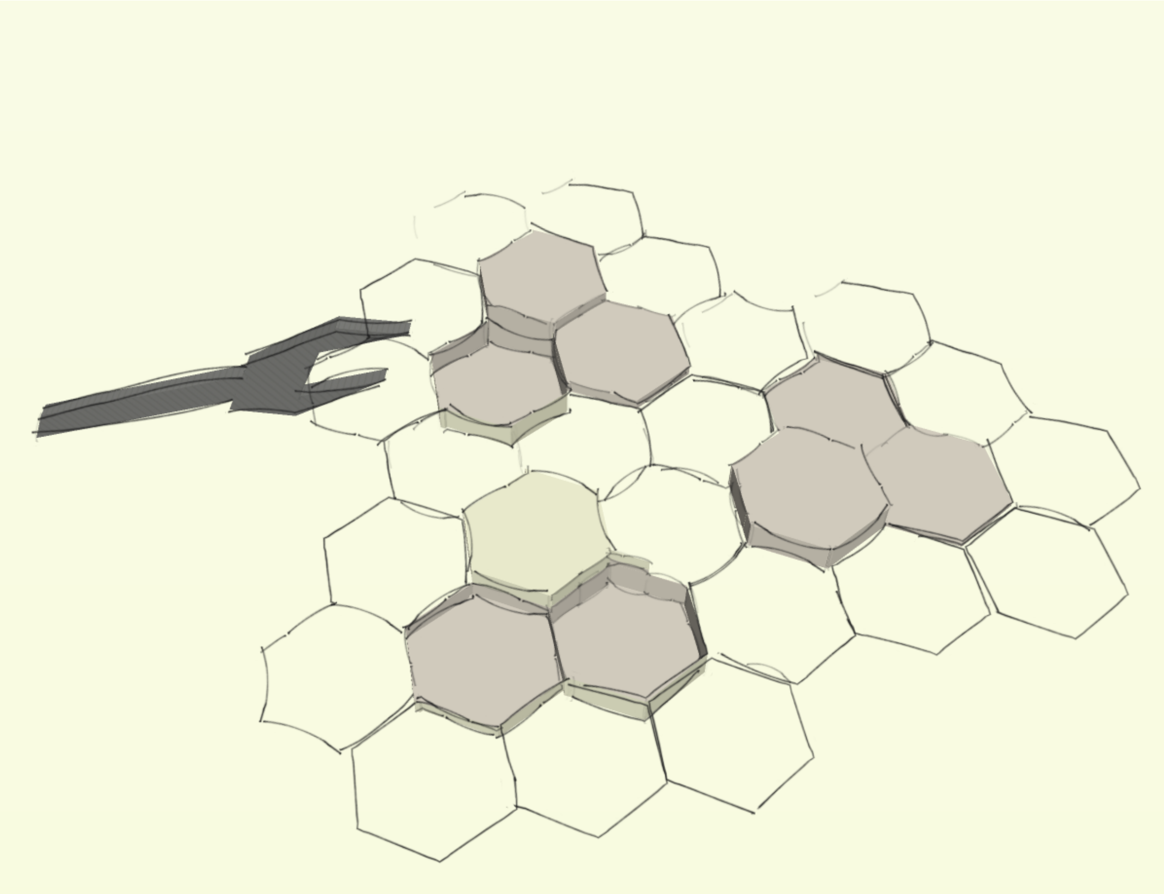
Modification of Graphene Films by Laser-Generated High Energy Particles



Elena Stolyarova (Polyakova), Ph.D.

ATF Program Advisory and ATF Users' Meeting
April 2-3, 2009, Berkner Hall, Room B, BNL

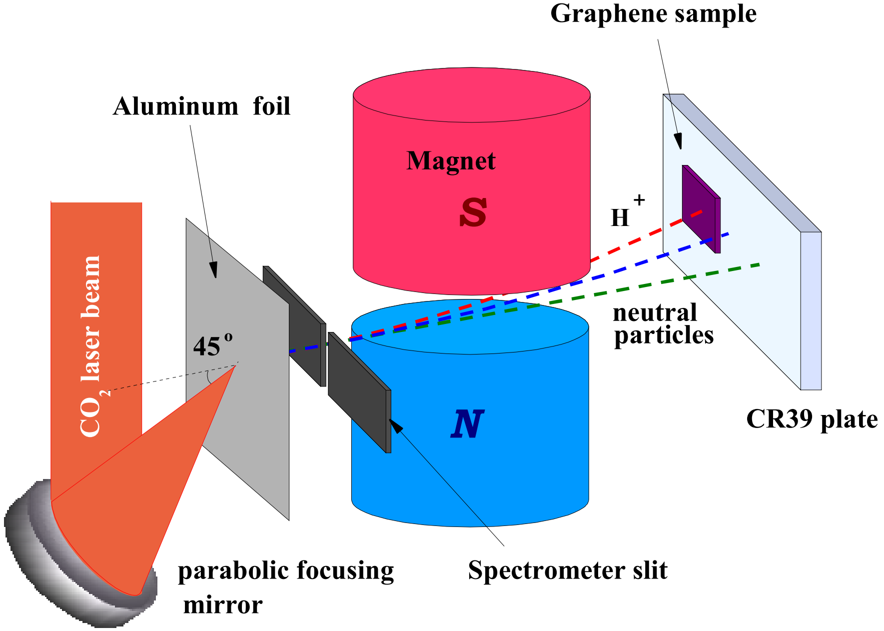
Columbia University in the City of New York

Department of Chemistry
Center for Electron Transport in Molecular Nanostructures, Columbia University, New York

Columbia University and the National Science Foundation
Center for Electron Transport in Molecular Nanostructures

Modification of Graphene Films by Laser-Generated High Energy Particles

- The world of sp² carbon
- What is graphene?
- Graphene: the thinnest impermeable membrane



- High energy particles and nanotechnology
- Possible applications and future plans

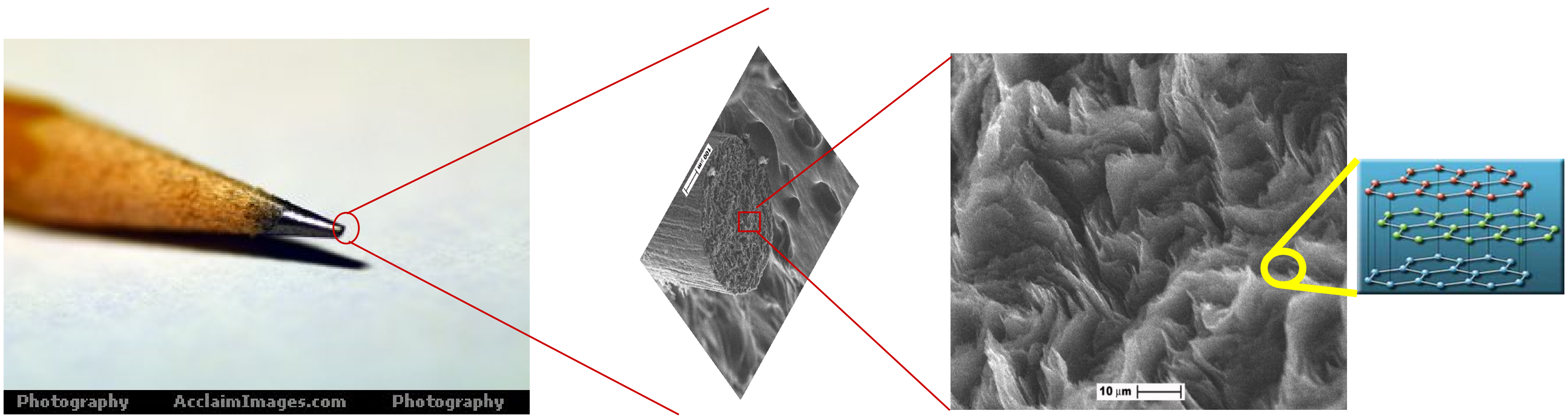
Observation of Graphene Bubbles and Effective Mass Transport under Graphene Films

E. Stolyarova, D. Stolyarov, K. Bolotin, S. Ryu, L. Liu, K. T. Rim, M. Klima, M. Hybertsen, I. Pogorelsky, I. Pavlishin, K. Kusche, J. Hone, P. Kim, H. L. Stormer, V. Yakimenko, and G. Flynn

Nano Lett., **2009**, 9 (1), 332-337• DOI: 10.1021/nl803087x • Publication Date (Web): 23 December 2008

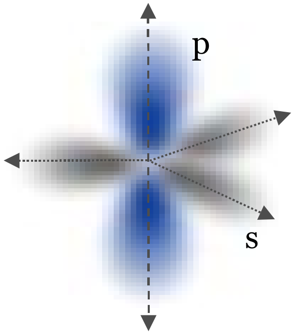
Carbon: remarkable element

Carbon: remarkable element



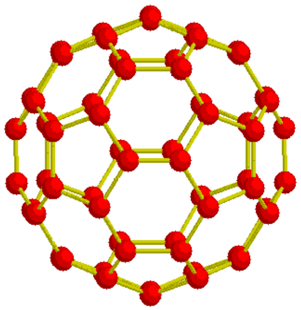
SP$_2$ Carbon: 0-D to 3-D

Atomic orbital sp$_2$

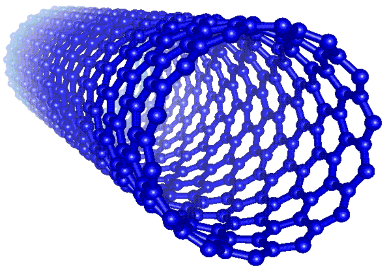


0D **1D** **2D** **3D**

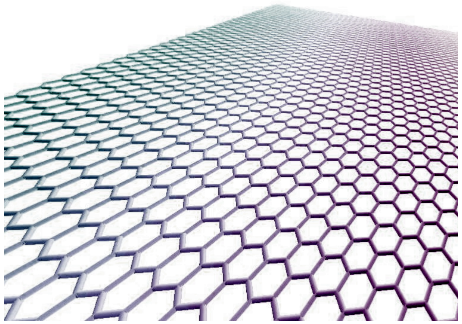
Fullerenes



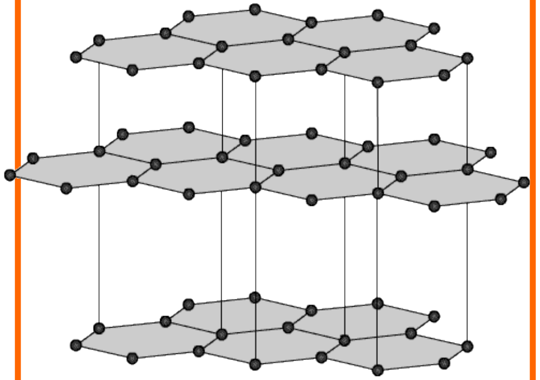
Carbon Nanotubes

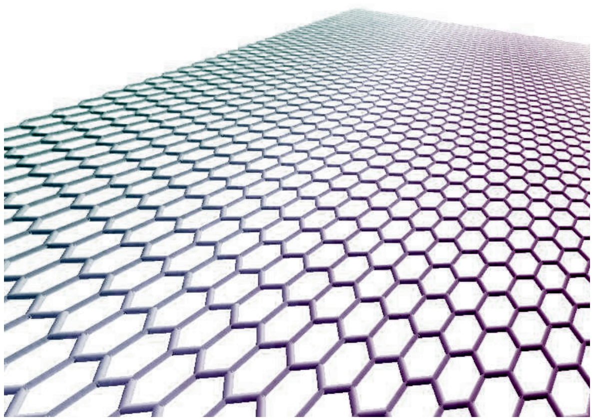


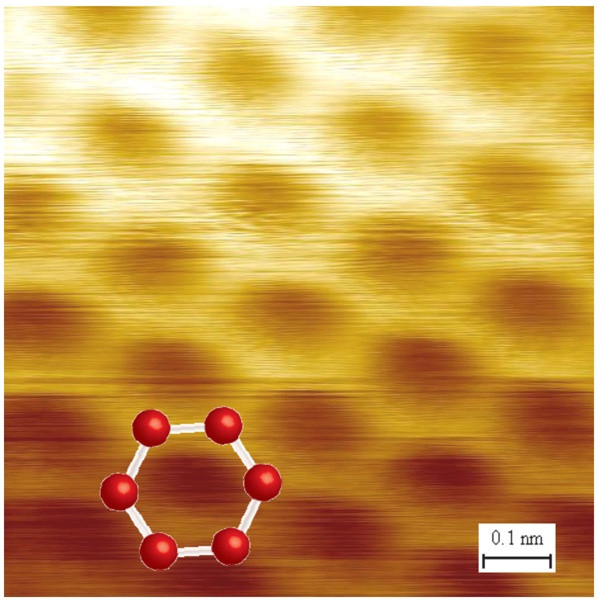
Graphene



Graphite



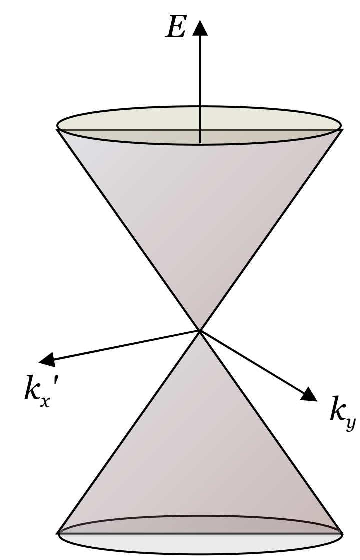




STM image of graphene

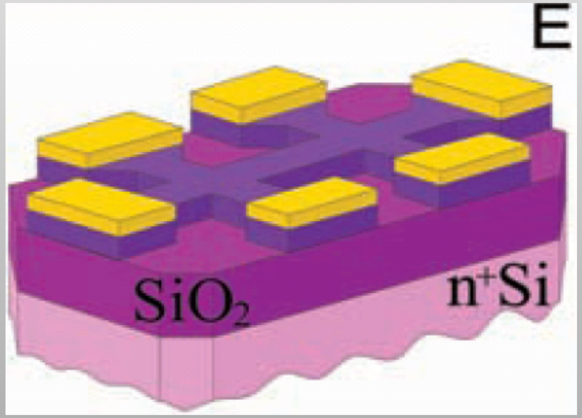
Graphene: a novel exciting material

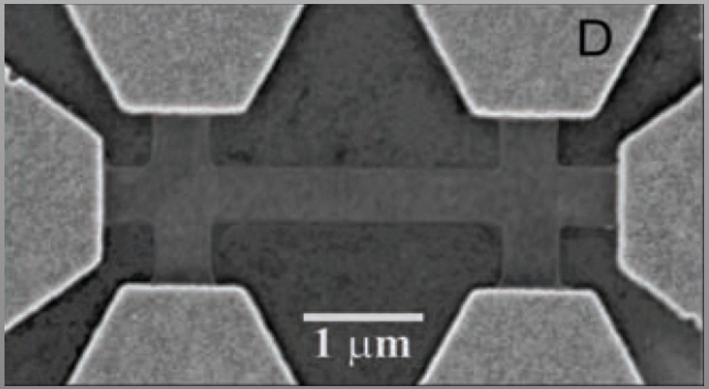
- One atom thick crystal
- Conductive (High Mobility)
- Unusual electronic properties
- Stable, chemically inert
- Stiff
- Gas-impermeable

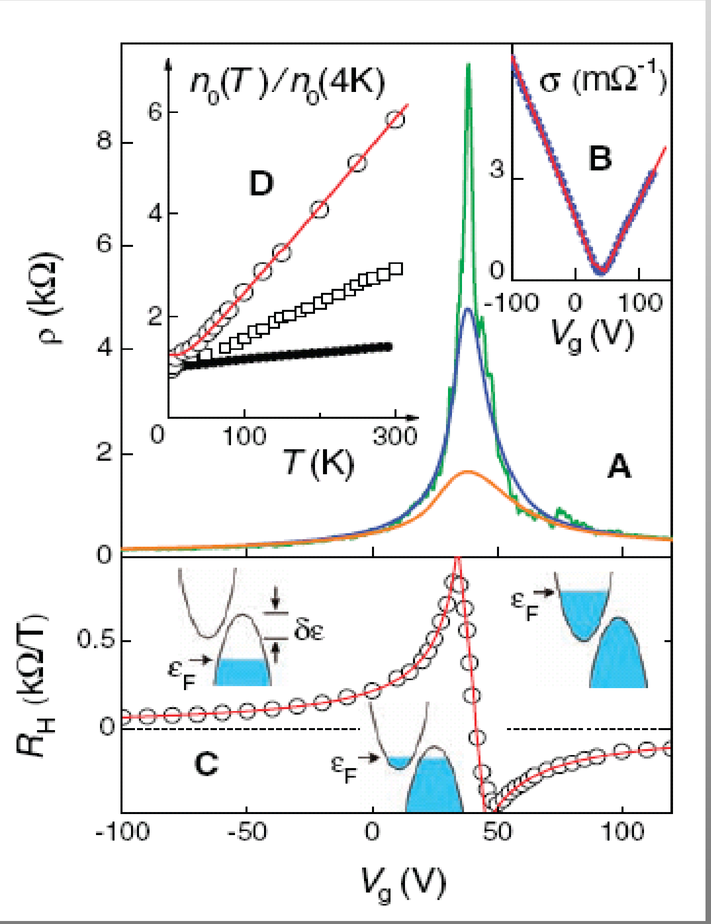


Electric Field Effect in Atomically Thin Carbon Films

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]



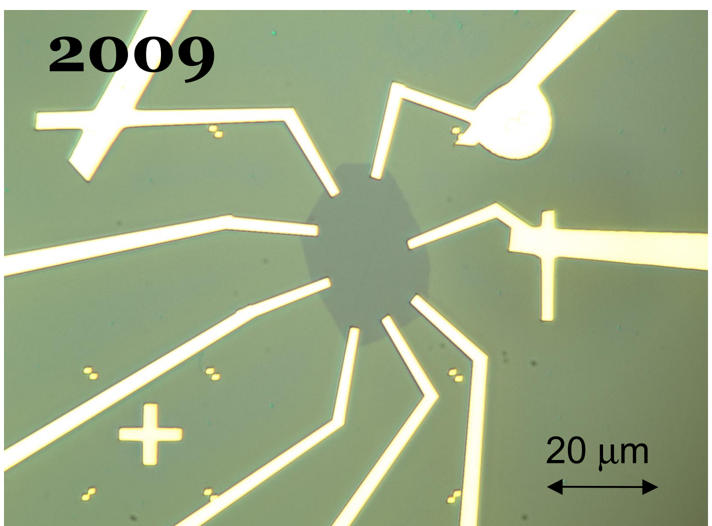




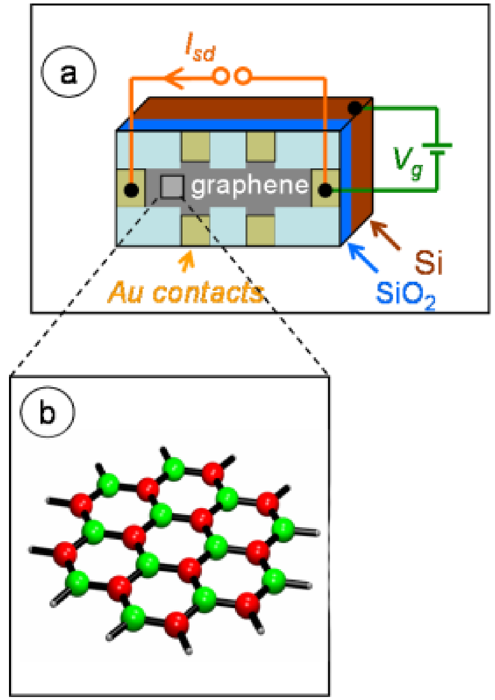
Science 306, 666 (2004)

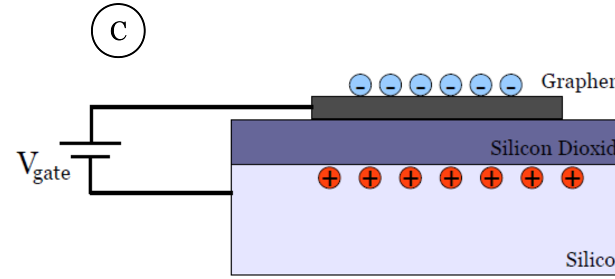
Graphene Field-Effect Transistors

A replica of the first transistor

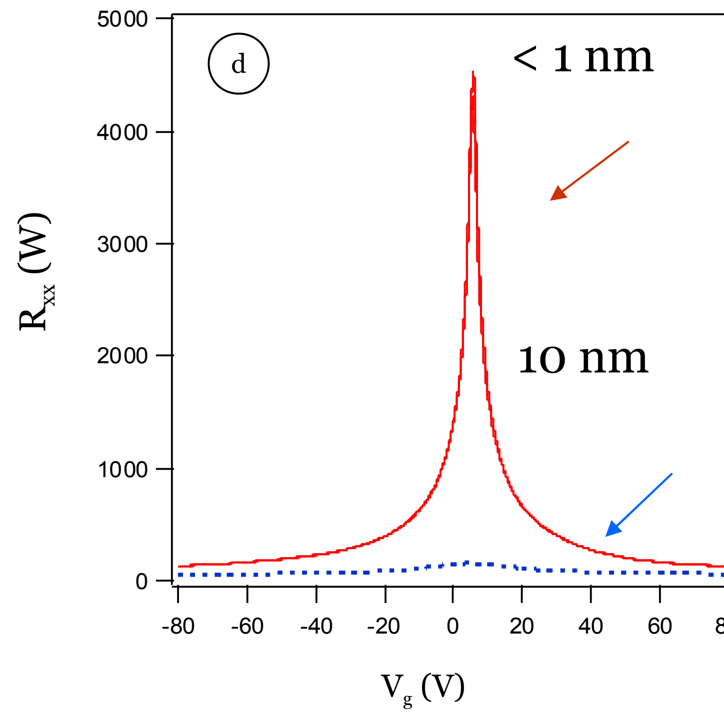


Single layer graphene device



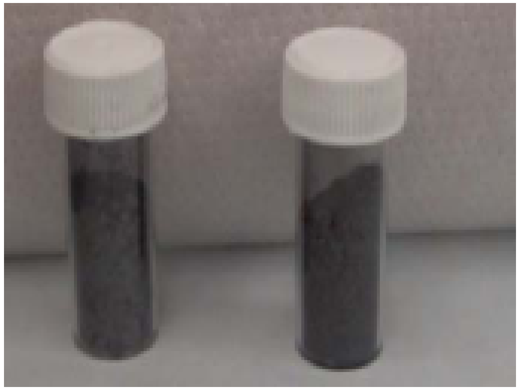


Resistance vs Gate Voltage

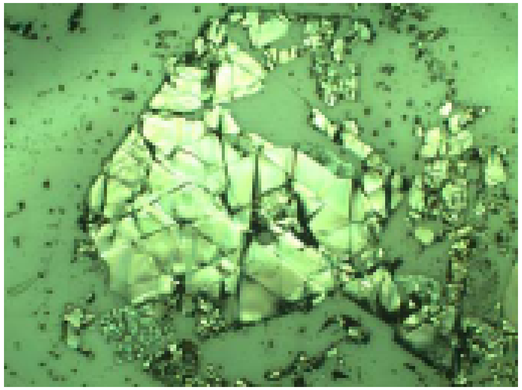


www.hfml.ru.nl/highlights/RT_QHeffect.shtml

Mechanical Exfoliation of Graphene



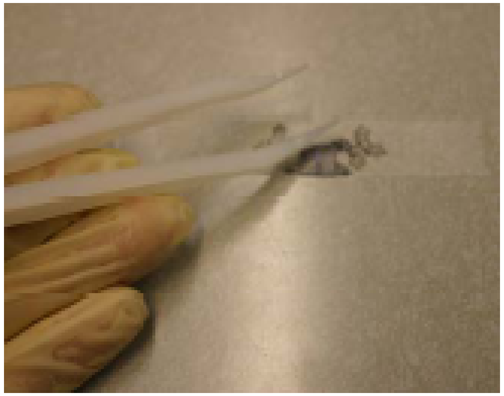
Graphite Flakes (Kish, Toshiba Ceramics)



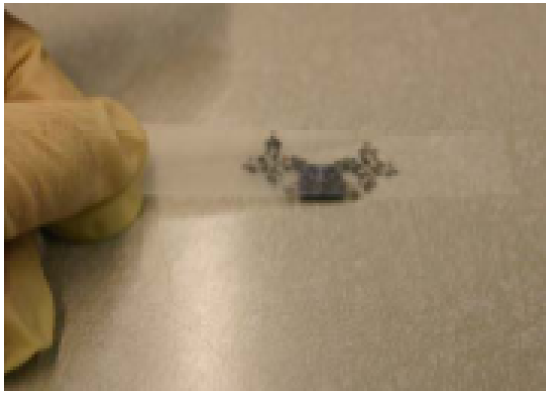
Graphite Flake

Peeling a Graphite Flake

Cleaving to a SiO_2/Si waver

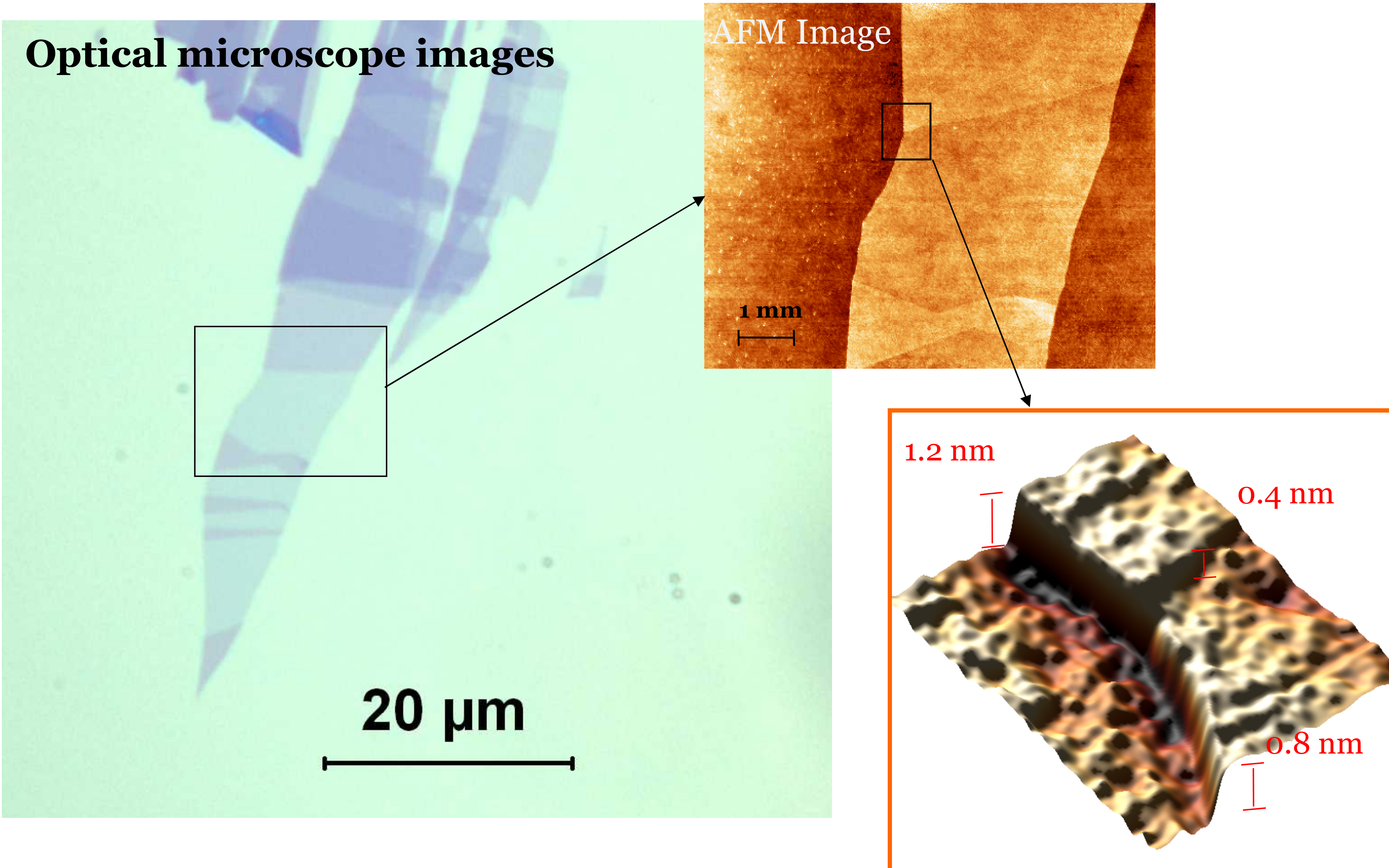


Gentle Rubbing with plastic Tweezers

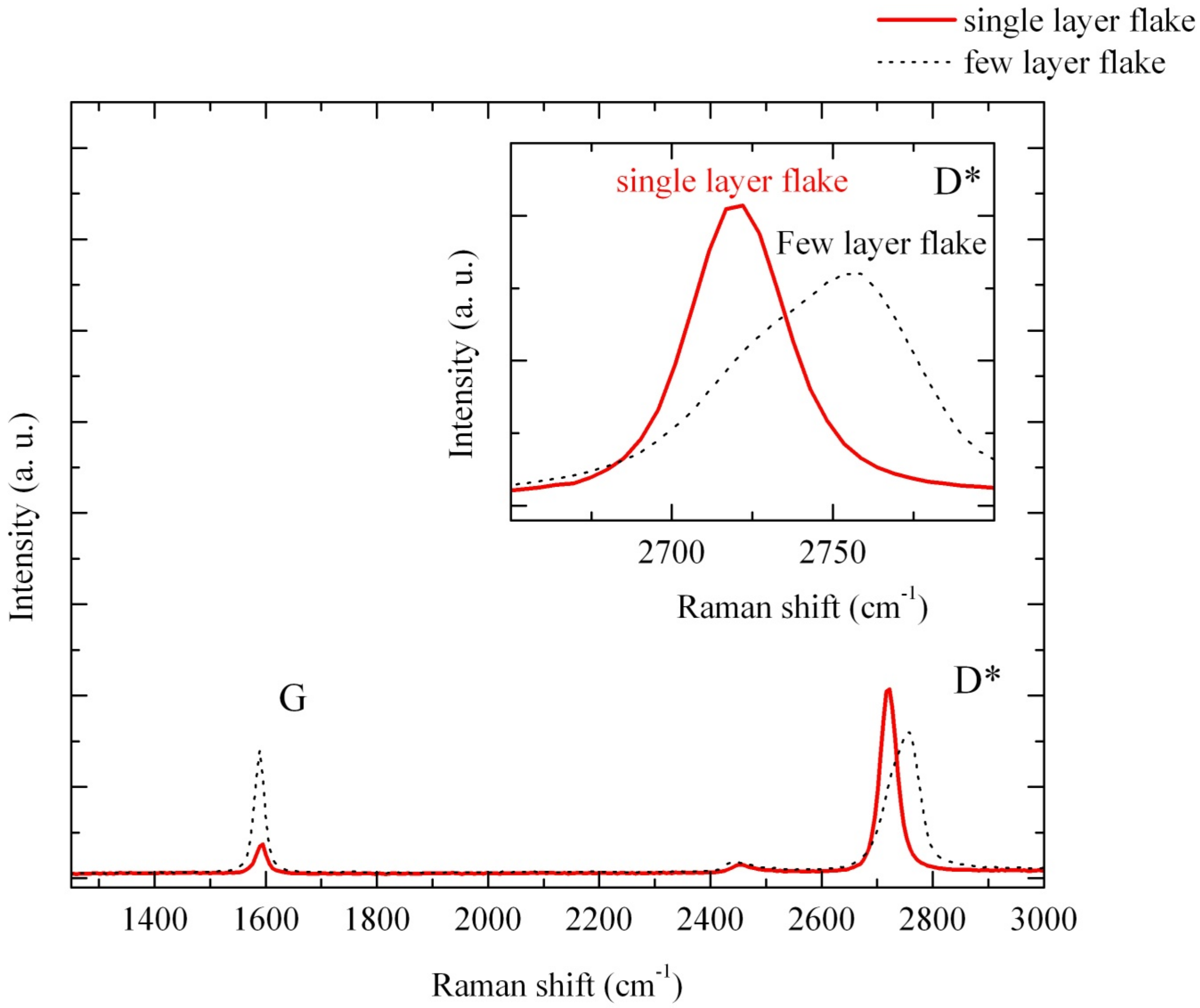


Removing the Scotch Tape

A Few Layer Graphene on SiO_2/Si Substrate

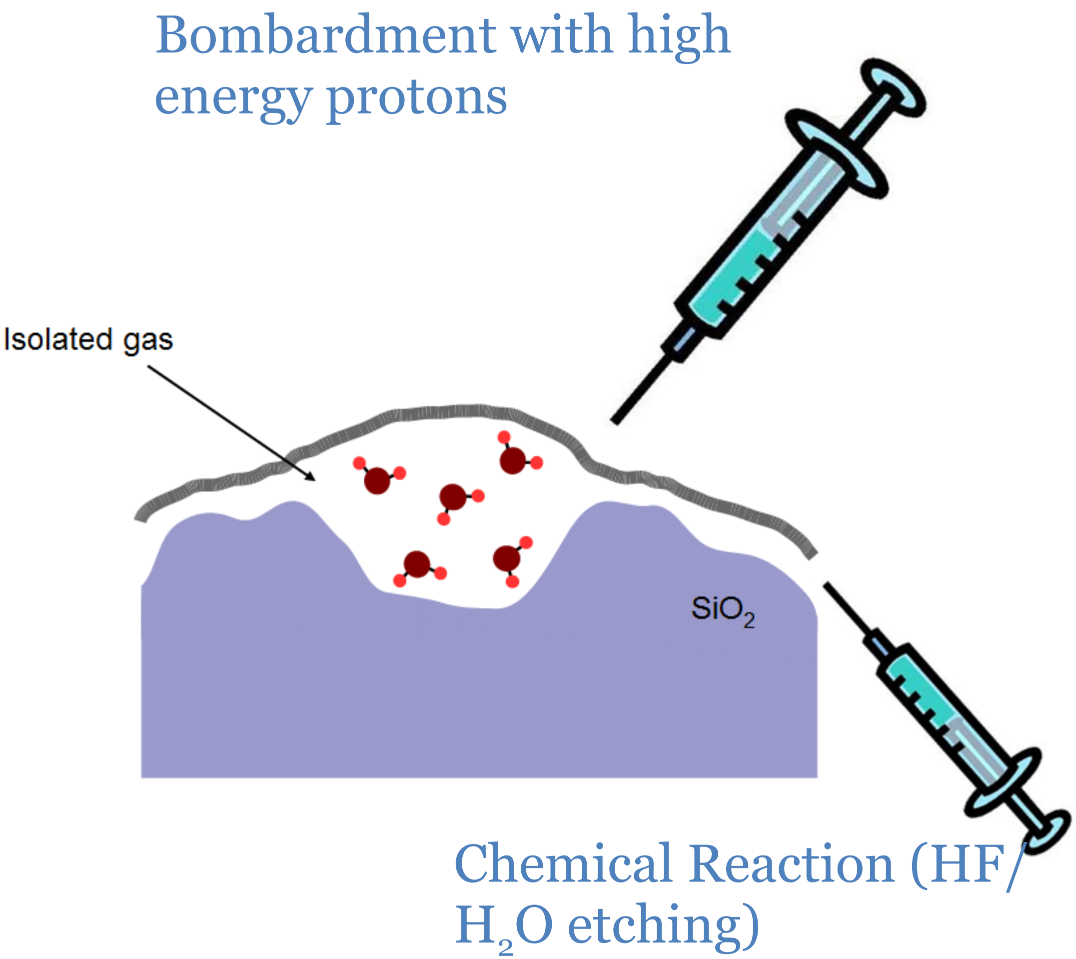


Raman Spectroscopy is a reliable tool for single layer identification



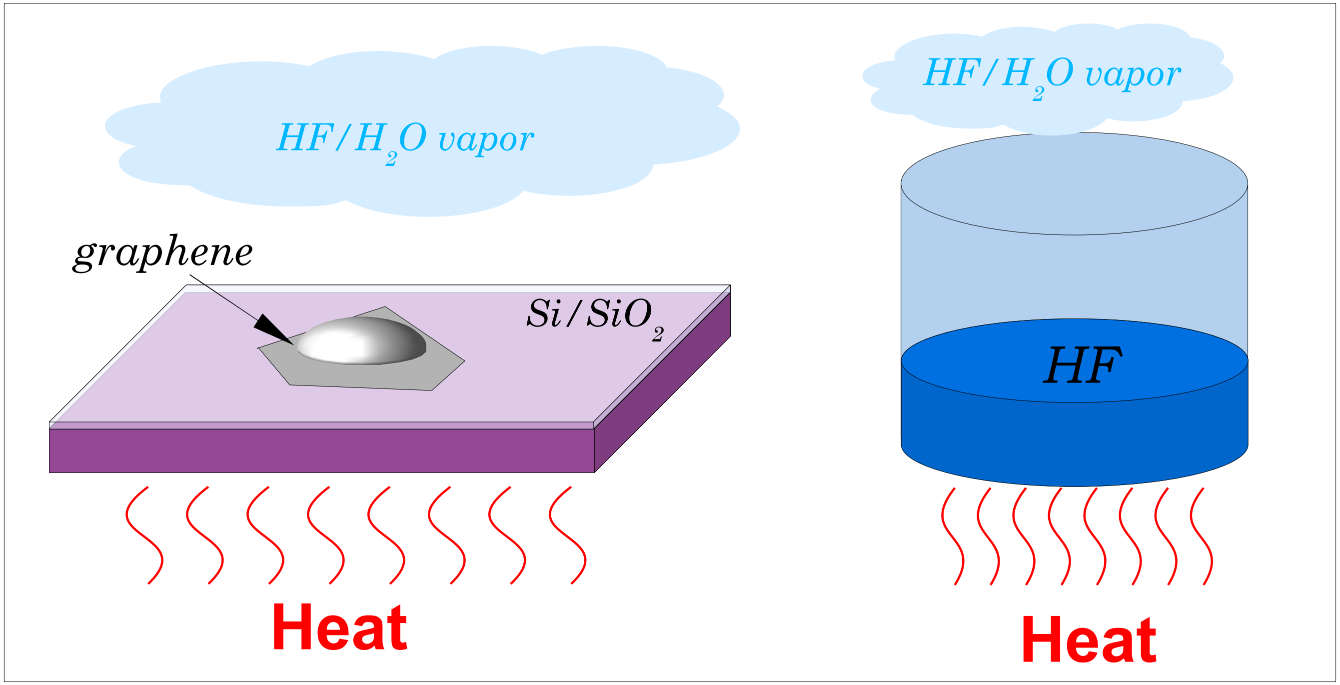
Ferrari, A.C., et al., Phys. Rev. Lett., 2006. ***97(18)***

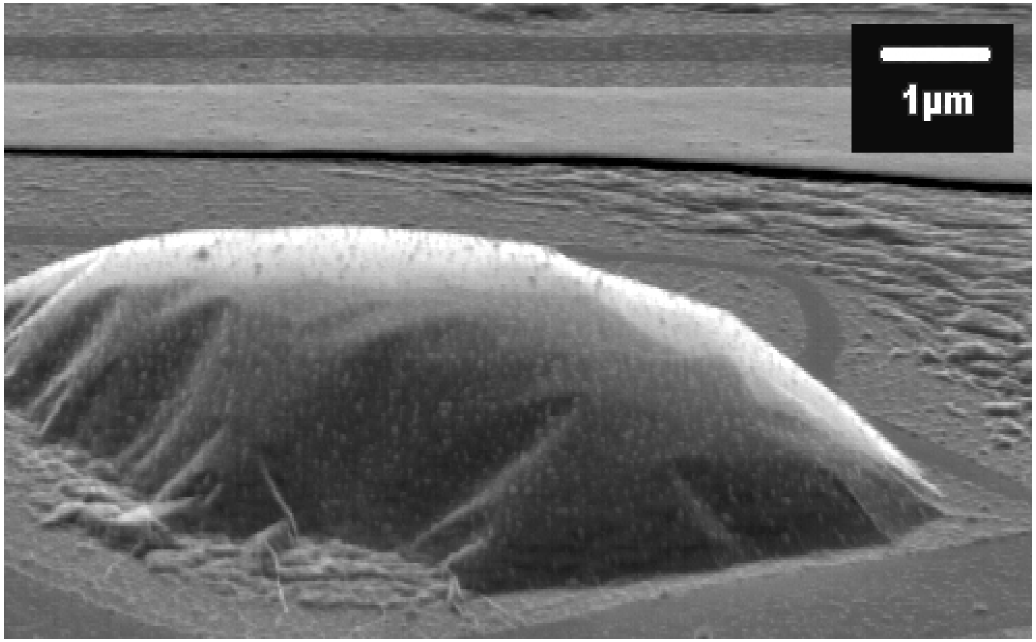
Observation of graphene bubbles and effective mass transport under graphene films



- Can we insert molecules under the graphene film?
- Can a molecule penetrate through a graphene?
- Do molecules move across graphene-silicon dioxide interface?

"Chemical" method for making bubbles





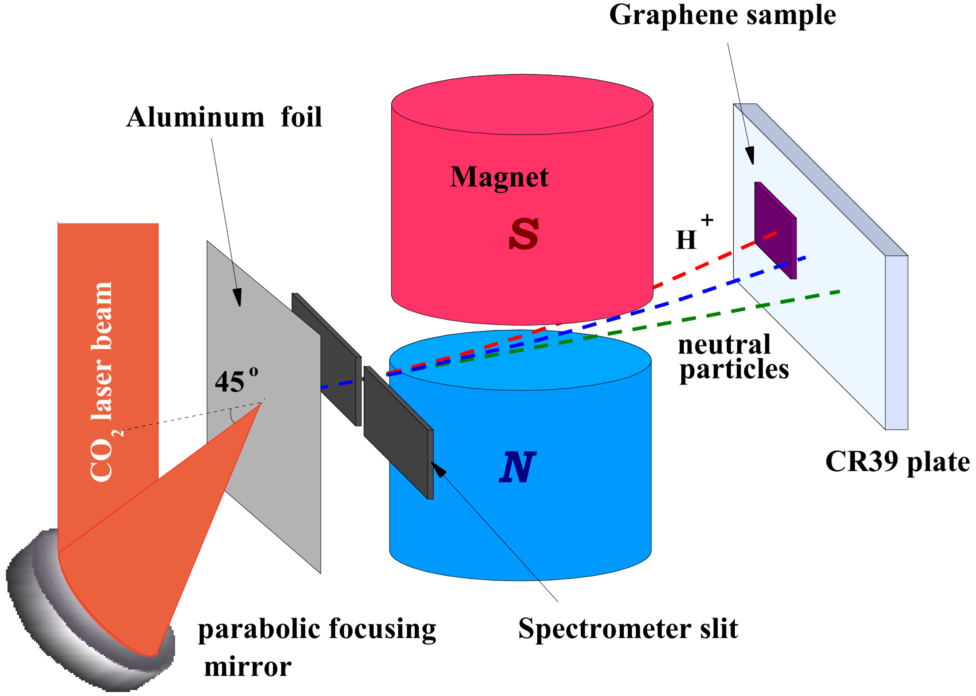
$$SiO_2 + 4HF \xrightarrow{water} SiF_4 + 2H_2O$$

Huge graphene bubbles

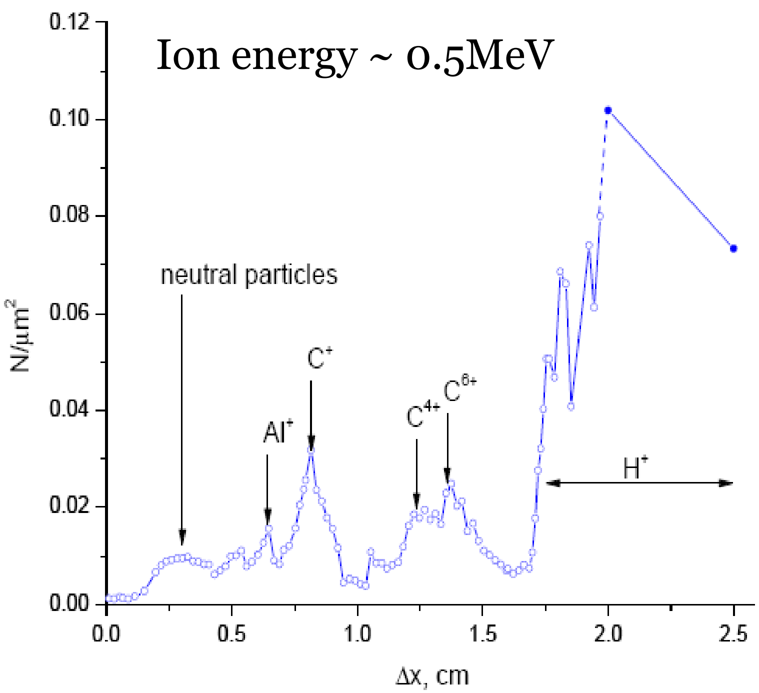
Stable for months
Raman spectrum is similar to supported graphene
Can be destroyed by AFM tip
Formed only if SiO_2 is etched completely

Proton Irradiation of Graphene Flakes

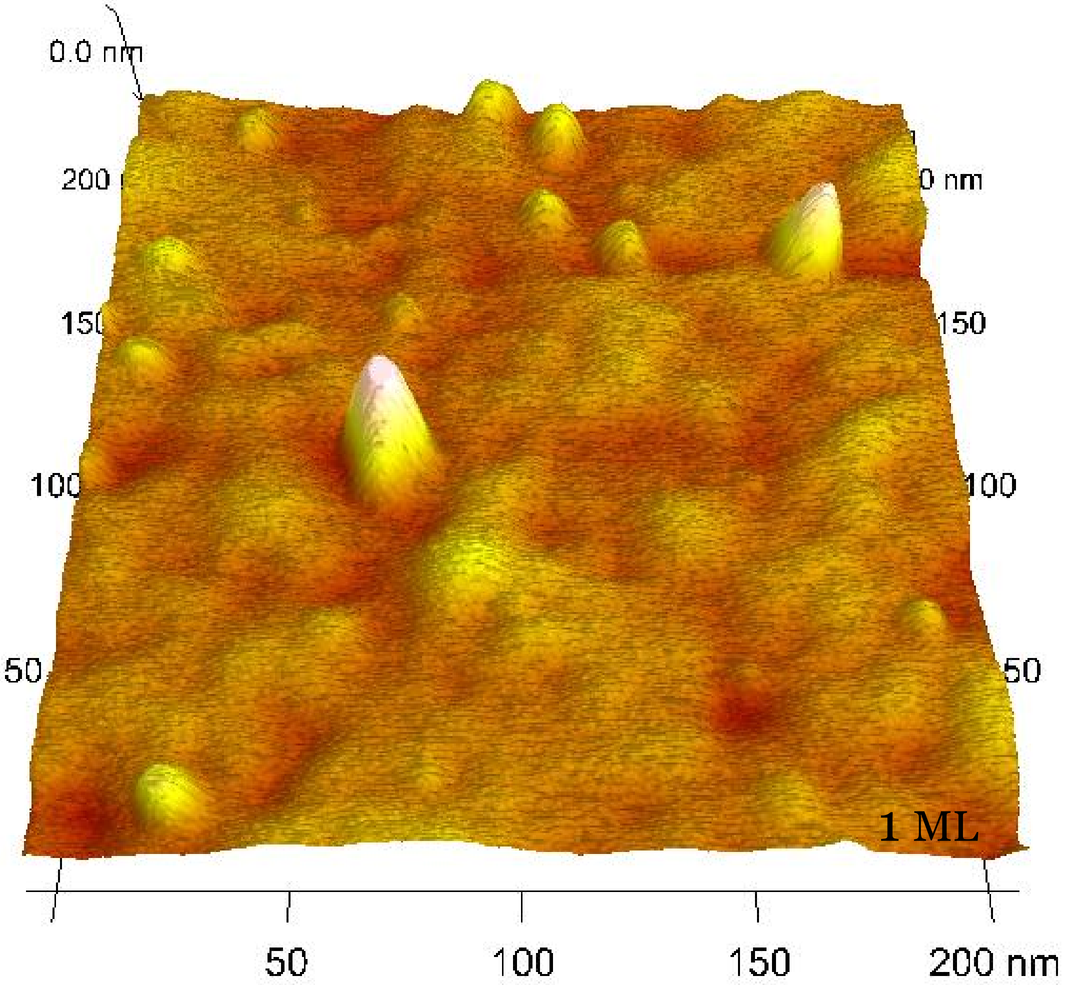
ATF TNSA Source

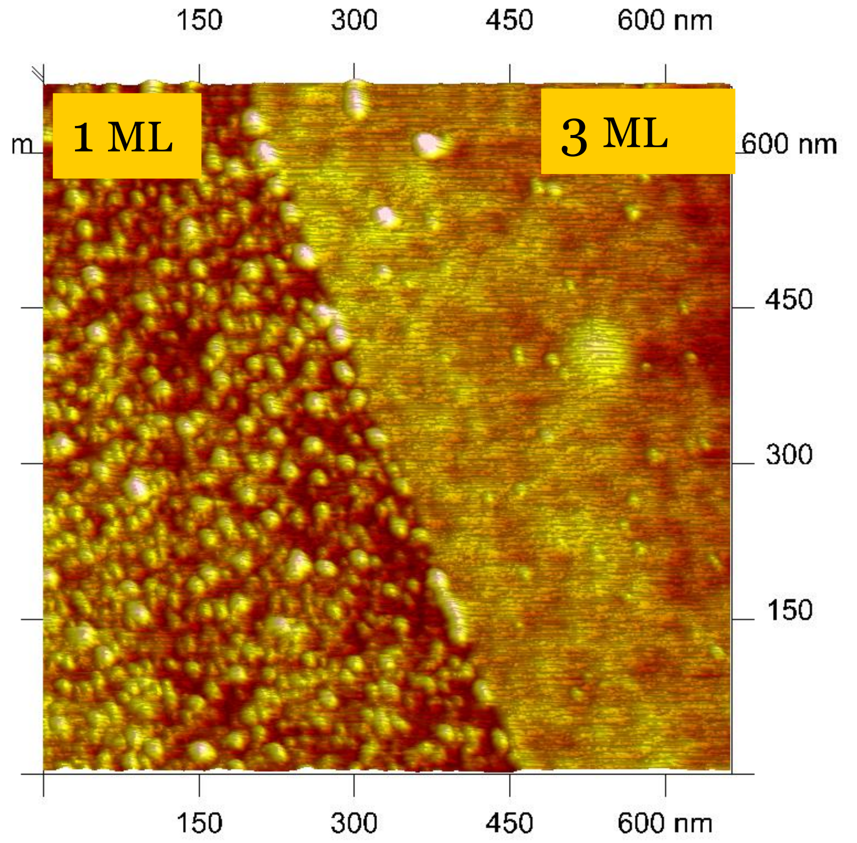


CR39 track density vs deflection distance



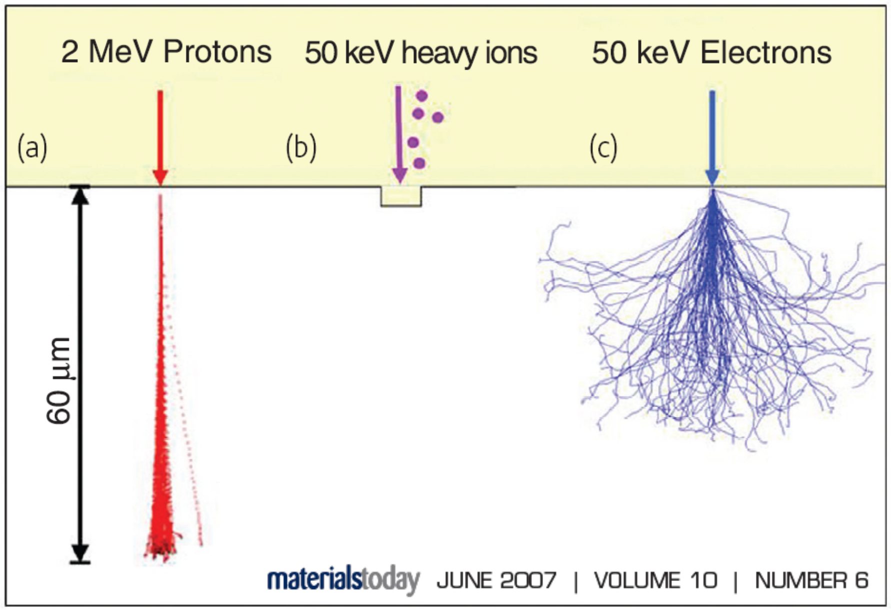
AFM Images of irradiated graphene samples: Nanoscale bubbles





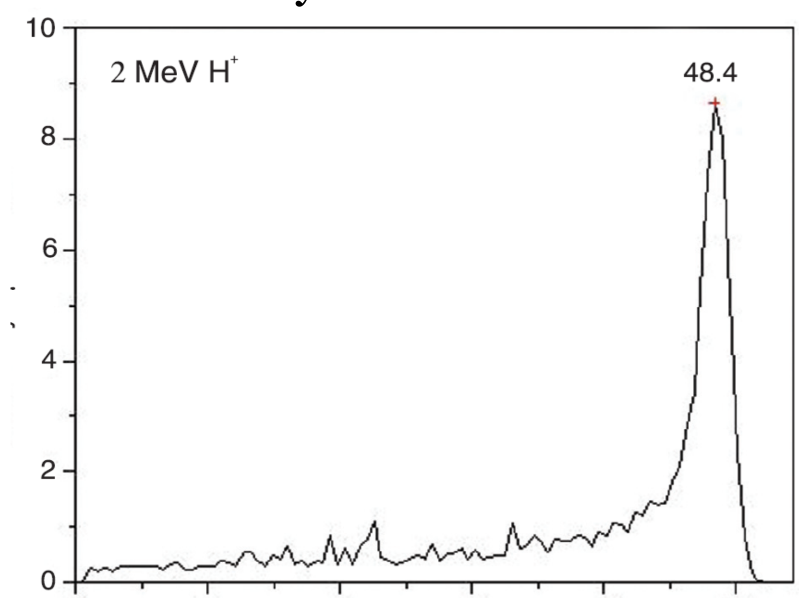
- Small gas bubbles are formed
- Gas molecules are trapped between graphene and SiO_2

Propagation of a proton through the solid target



- Protons are only weakly deviated from the straight path
- Nuclear knock-off damage is significant only in the end of the track
- Energy loss per distance traveled is nearly uniform

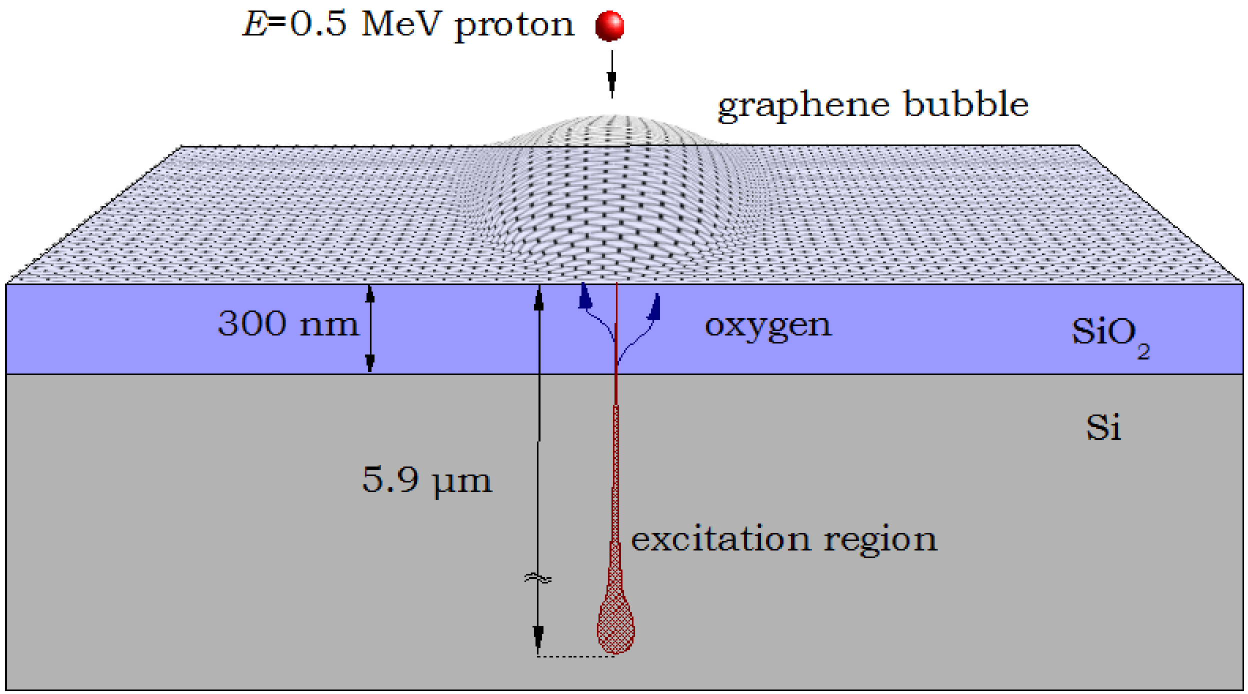
Probability of nuclear knock-off



Applications of proton beams

- Cancer therapy
- 3D lithography
- Magnetic carbon

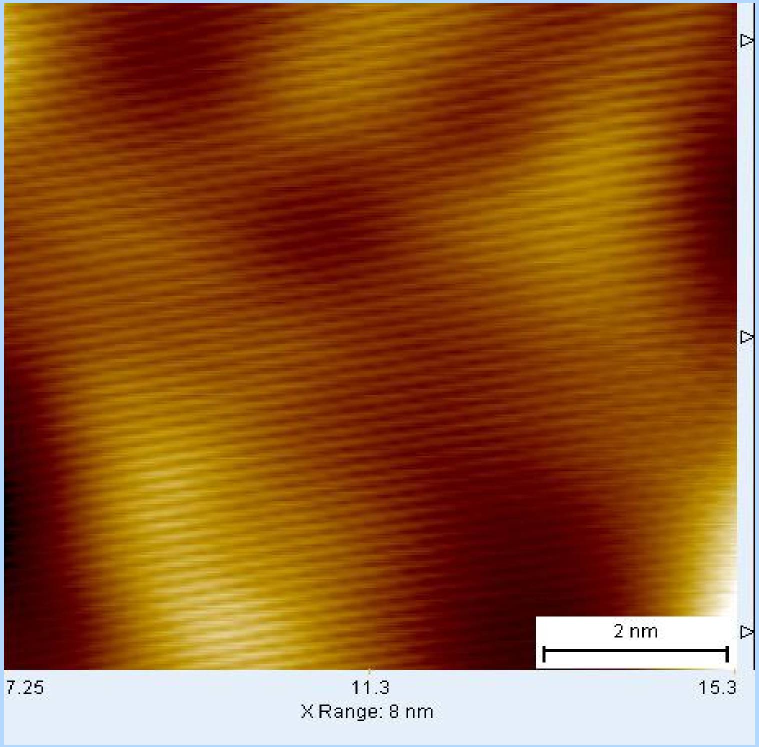
Propagation of a proton through the graphene sample



- Probability of the defect formation in graphene is extremely low
- 99.9% of proton's kinetic energy is deposited in electronic excitations
- The 0.5 MeV protons stops deep inside the Si wafer
- Gas is expected to be released from the substrate
- Irradiation causes desorption / rearrangement of surface impurities

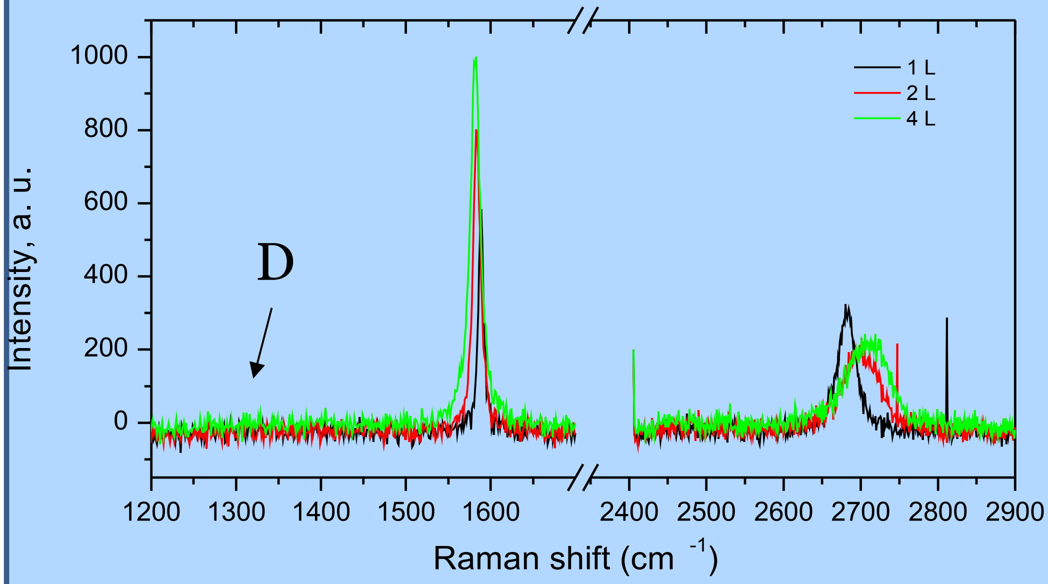
STM and Raman study of graphene samples exposed to high energy protons

STM Imaging



STM imaging of the samples exposed to high energy protons shows no atomic scale defects

Raman Spectroscopy

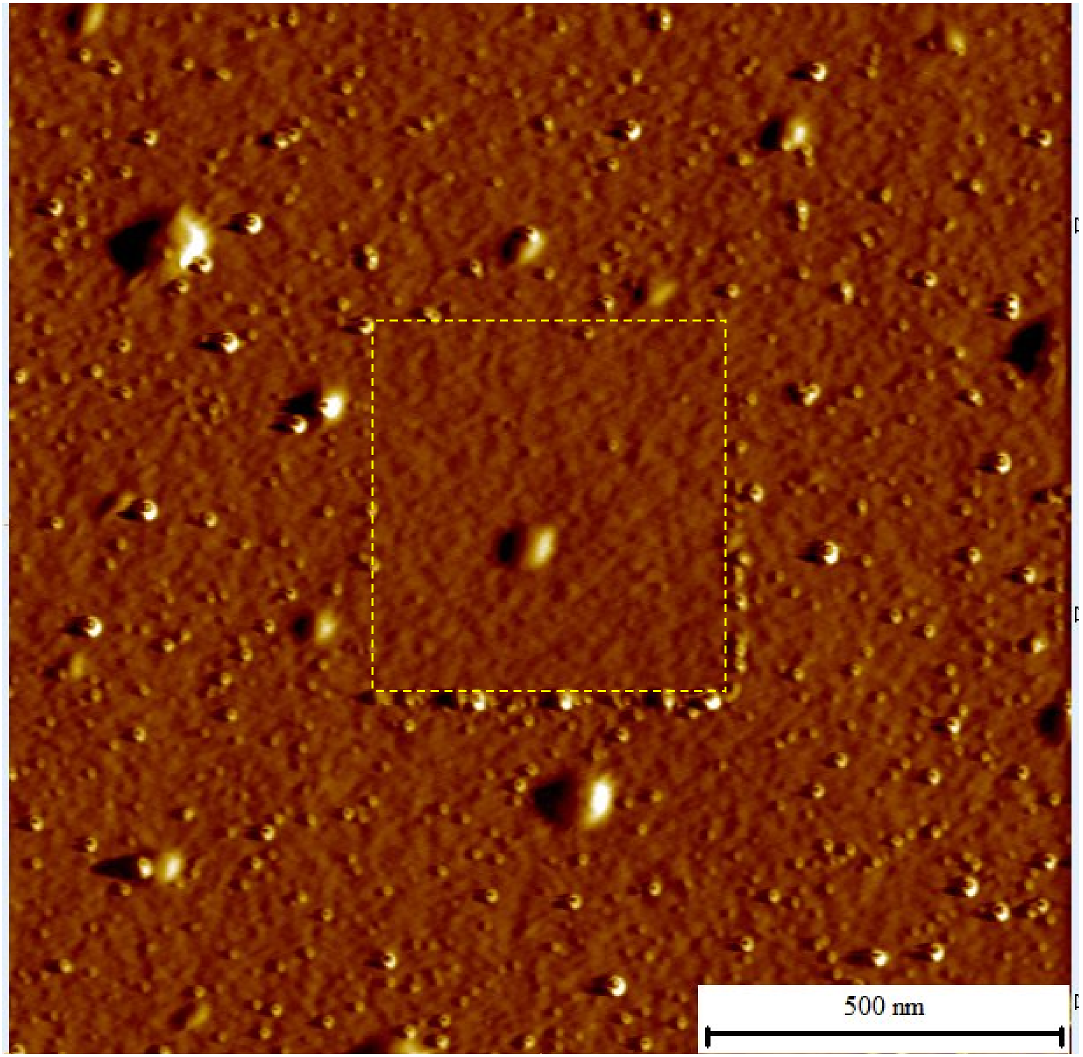


- G band is blue-shifted by 10 cm^{-1}, indicating significant chemical doping
- There is no signature of the D "defect" band → no structural damage

Brookhaven National Laboratory

Accelerator Test Facility

Mobility of the graphene bubbles



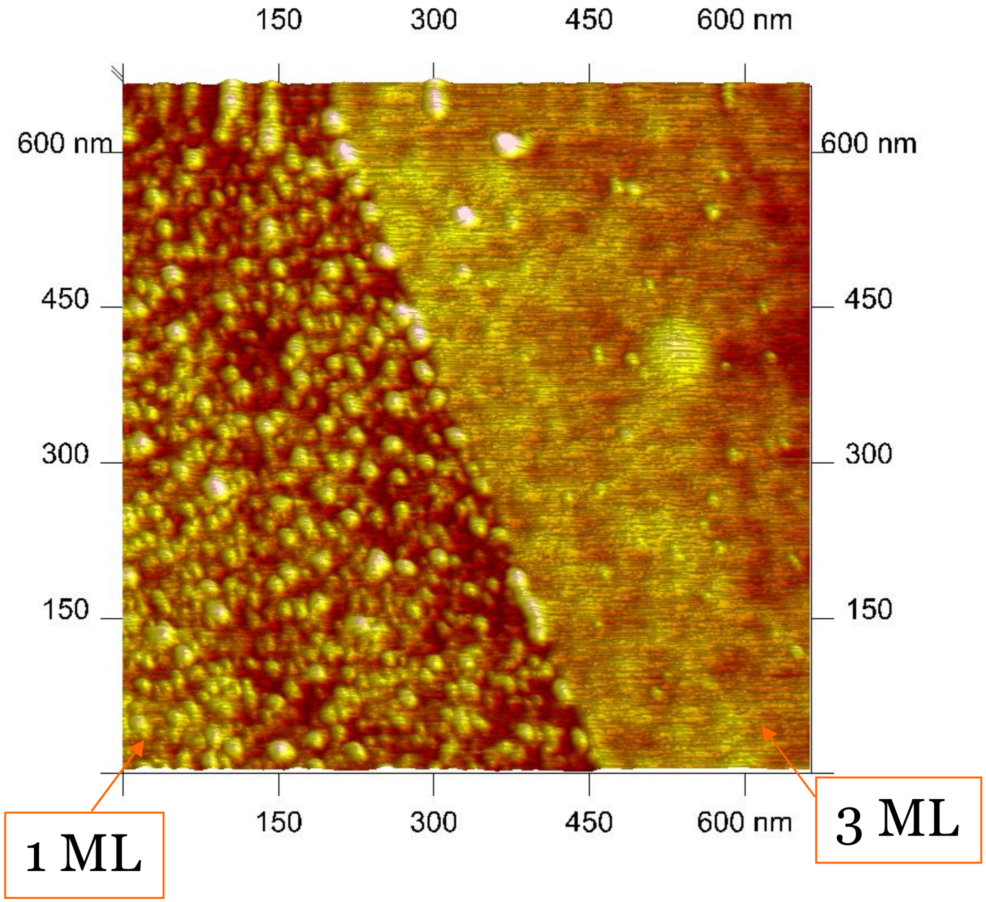
- The center region marked by a dashed square was scanned previously with a lower value of set point in the tapping mode (stronger tip-sample interactions)

- Bubbles can be moved by the AFM tip

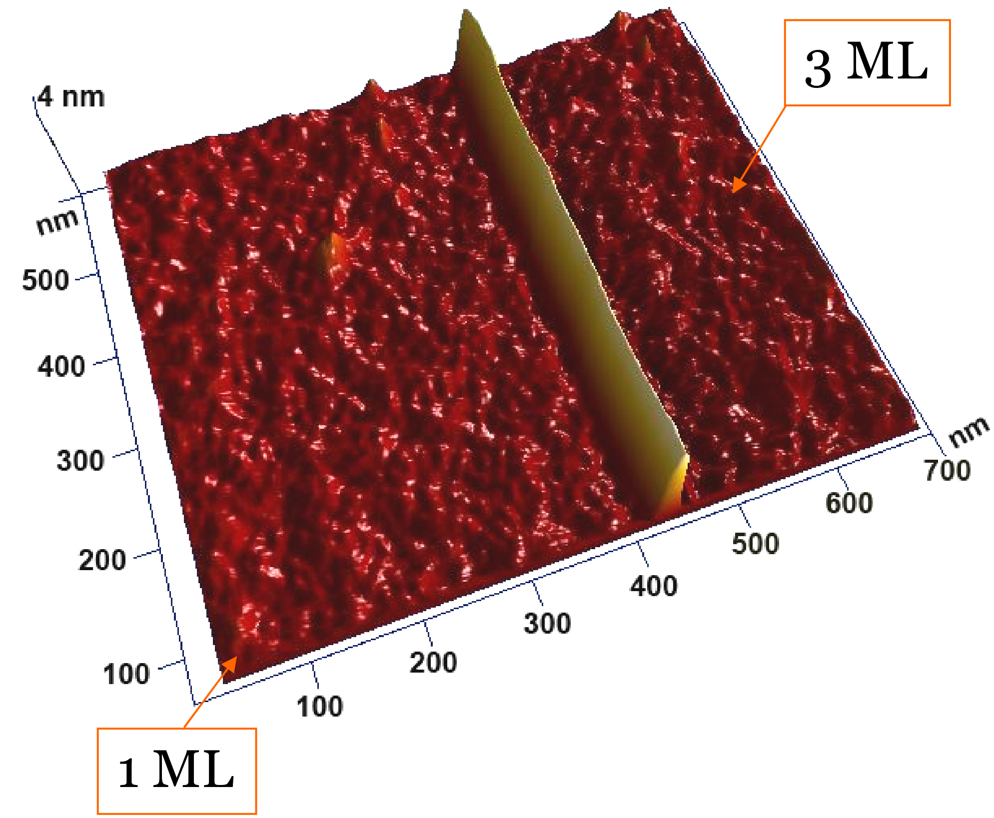
Coalescence of the Bubbles

AFM images of irradiated graphene flakes

Before annealing



After annealing (12 h at 350°C)



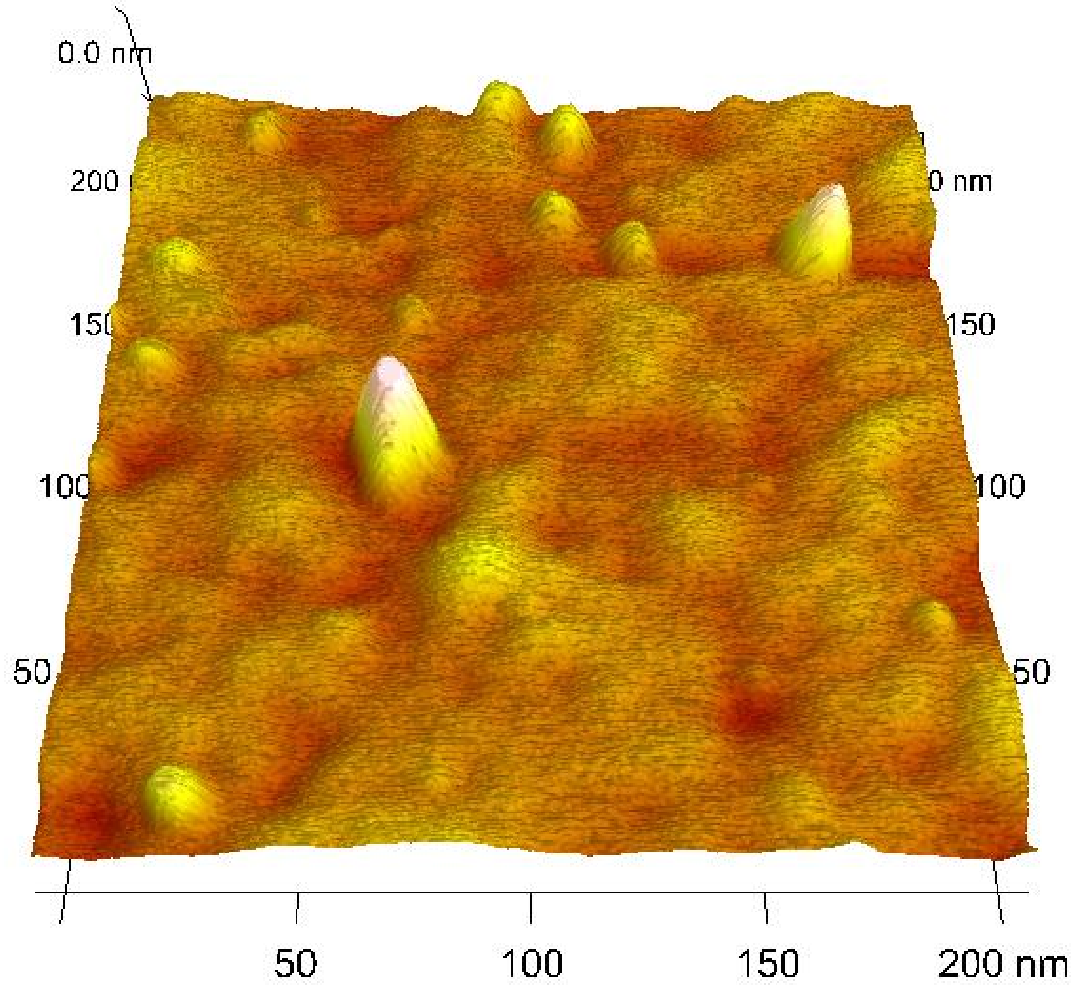
- Annealing causes coalescence of the bubbles
- Transport is possible underneath a graphene film

Summary

Graphene, being only one atom thick, is stable and stiff material.

Graphene membranes can capture mesoscopic volumes of gas.

Graphene acts as an impermeable membrane



Observation of Graphene Bubbles and Effective Mass Transport under Graphene Films

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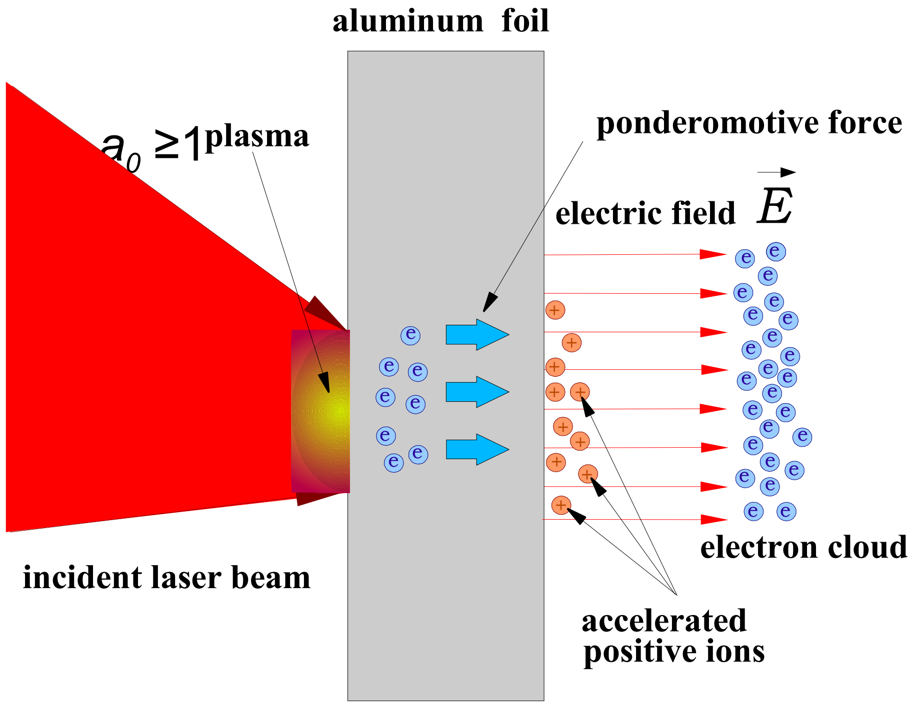
Nano Lett., **2009**, 9 (1), 332-337• DOI: 10.1021/nl803087x • Publication Date (Web): 23 December 2008

Advantages of laser-driven ion source for applications in nanotechnology

Target Normal Sheath Acceleration



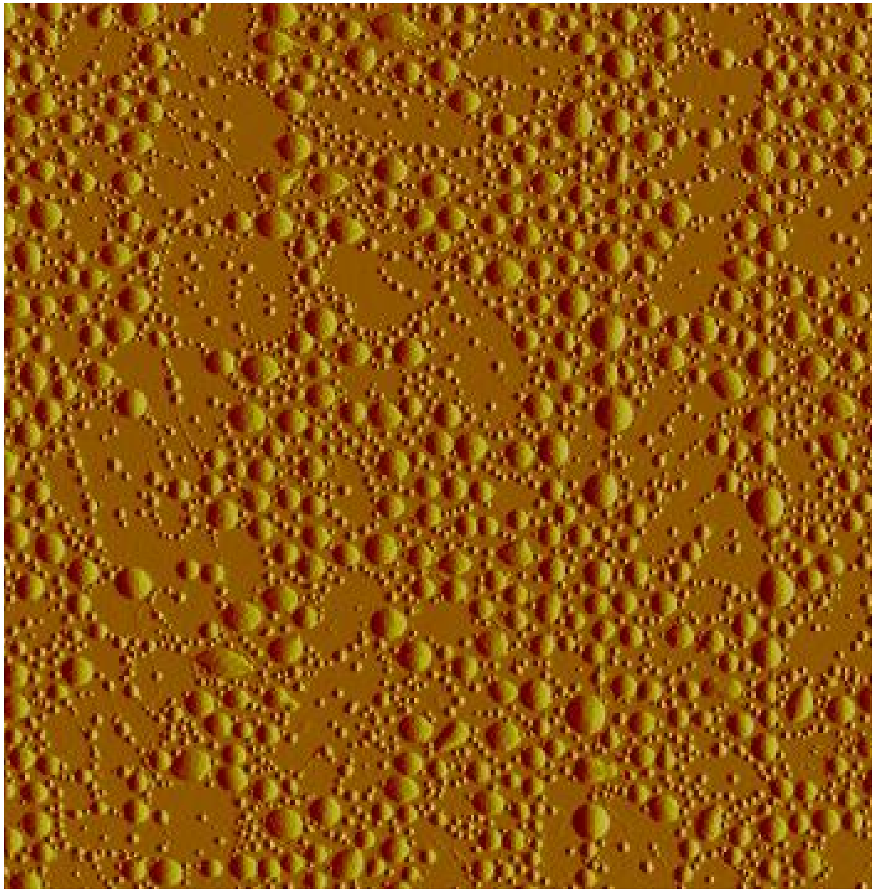
- Material modification under extreme conditions (New physics and chemistry)
- Reimaging/ion writing
- 3D lithography

Compact and inexpensive source of high-energy ions.

Easy switching between different ions by changing the target material.

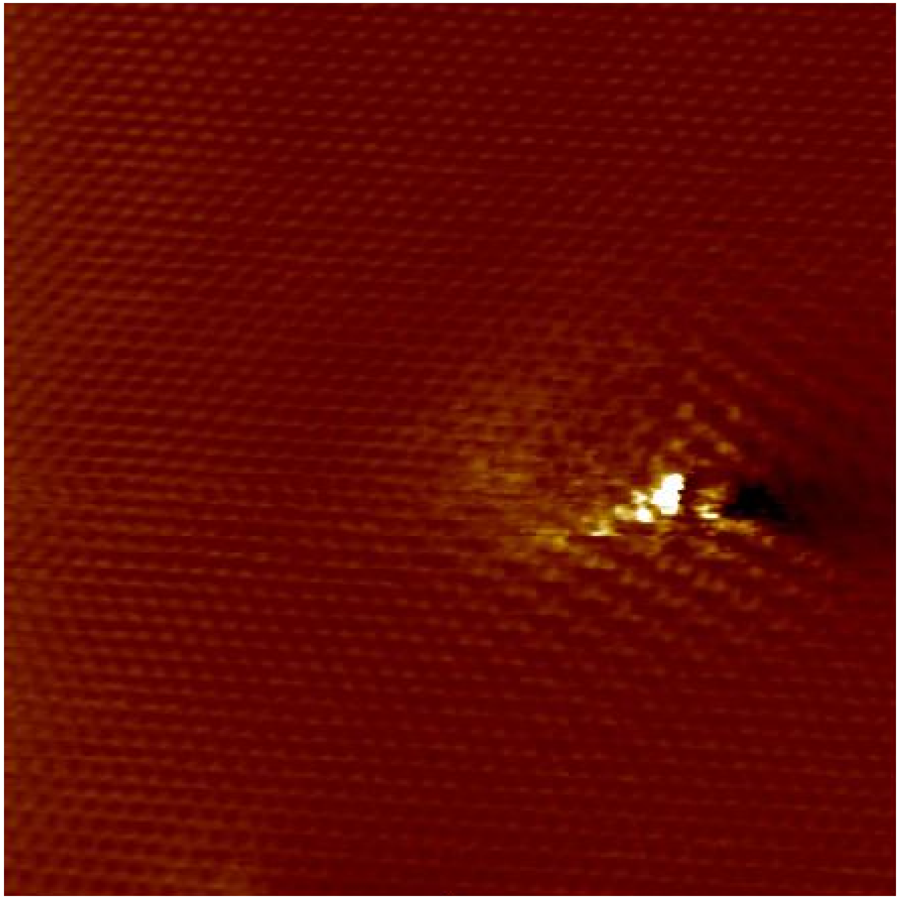
Material modification under extreme conditions

Protons



•Ultrafast heating
•Irradiation with pulsed beams

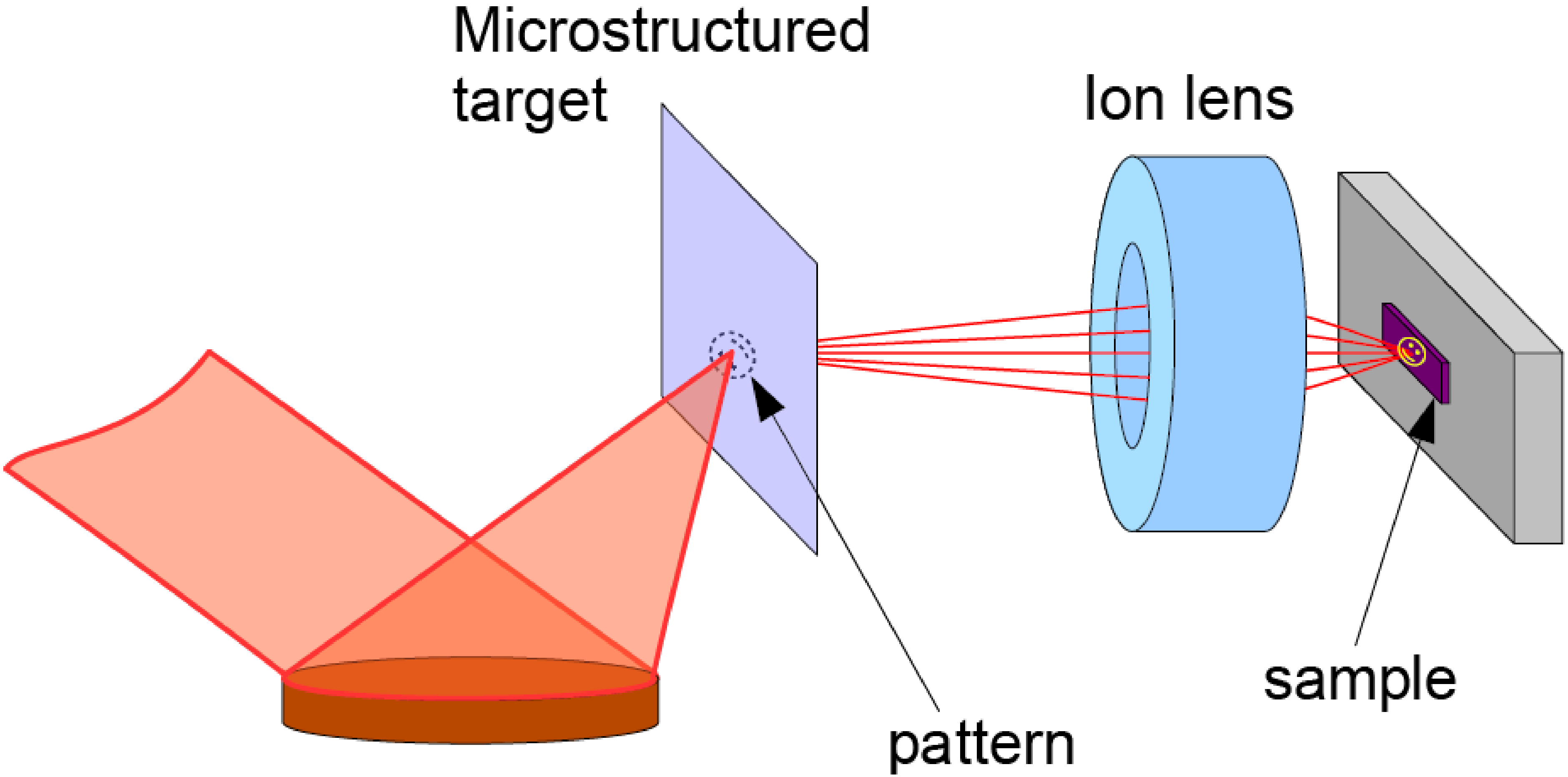
Ions



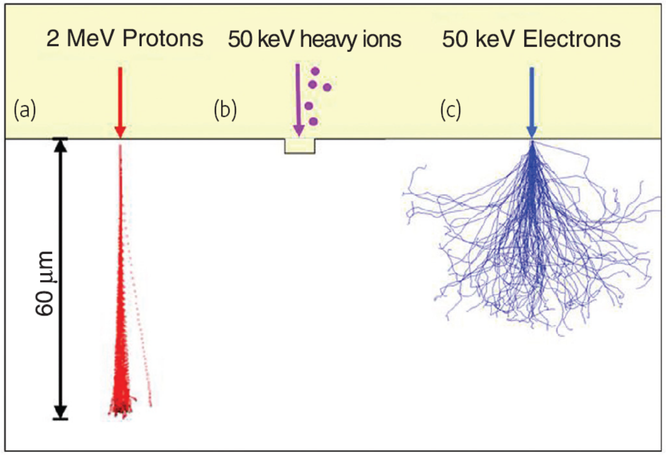
•Defect generation
•Chemical modification of irradiated ares
•Local doping

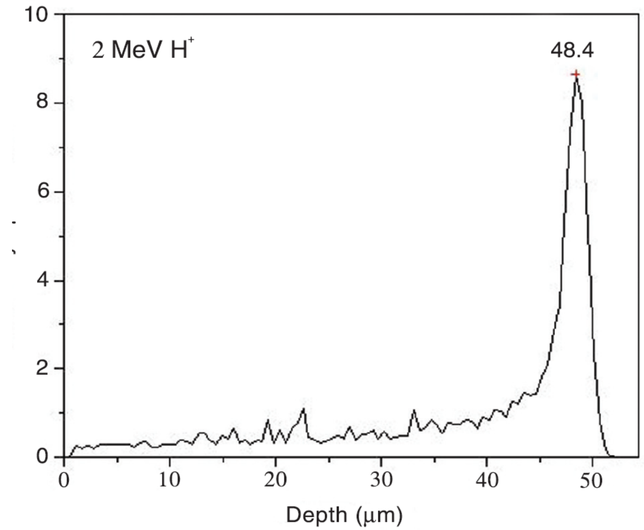
Polyakova (Stolyarova), et. al. unpublished

Reimaging target structure

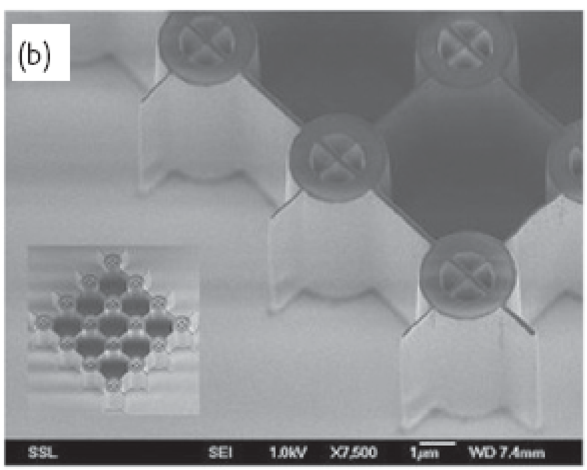


3D proton-beam lithography



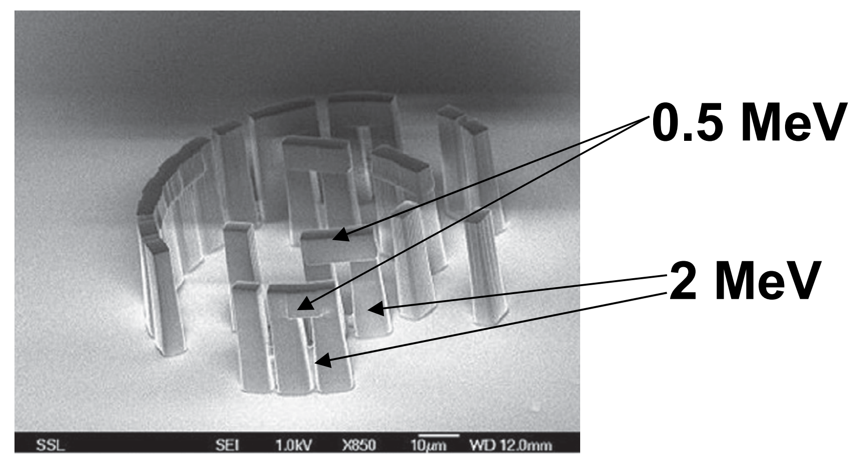


High aspect ratio structures:



p-beam writing in SU-8 negative resist showing 60 nm wall structures that are 10 µm deep

True 3D structures:



Microsized copy of Stonehenge in the UK fabricated using p-beam writing in SU8 resist.

materialstoday JUNE 2007 | VOLUME 10 | NUMBER 6

Thanks

- Prof. George Flynn, Dr. Kwang Rim, Dr. Daejin Eom, Dr. Li Liu (Columbia)
- Prof. Philip Kim, Dr. Kirill Bolotin, Melinda Han, Meninder
- Prof. Horst Stormer, Dr. Etienne De Poortere (Intel), Dr. Erik Henriksen (Caltech)
- Prof. Hone, Martin Klima,
- Prof. Louis Brus , Dr. Sunmin Ryu (Columbia), Prof. Tony Heinz, Dr. Janina Maultzsch
- Dr. Mark S. Hybertsen (CFN, BNL)
- Dr. D. Stolyarov, Dr. I. Pogorelsky, Dr. I. Pavlishin, K. Kusche, Dr. V. Yakimenko (ATF, BNL)

Columbia University IN THE CITY OF NEW YORK
Columbia University and the National Science Foundation Center for Electron Transport in Molecular Nanostructures
Brookhaven National Laboratory Accelerator Test Facility
Center for Functional Nanomaterials