Raman Spectroscopy: a non-destructive, non-contact and simple technique to characterize carbon materials

Sergej Shashkov[1]

[1]SOL instruments Ltd, 58-10, Nezavisimosti ave, P.O. Box 235,
Minsk 220005, Republic of Belarus

sales@solinstruments.com

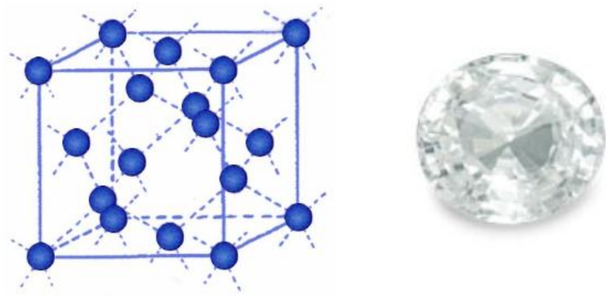
Characterization of carbon materials

Due to carbon's three hybridization states (*sp3*, *sp2*, and *sp*), many carbon allotropes, such as graphite (*sp2*), diamond (*sp3*), fullerene (*sp2*), carbon nanotube (*sp2*), and graphene (*sp2*), are synthesized.

There are still a large number of new forms of carbon to be discovered!

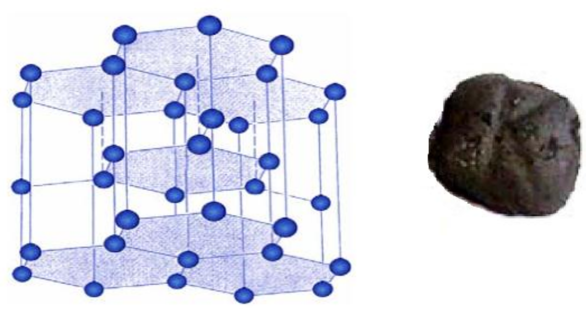
There are possibility to generate networks of combinations of *sp2* and *sp,* or *sp3* and *sp* hybridized carbons.

DIAMOND

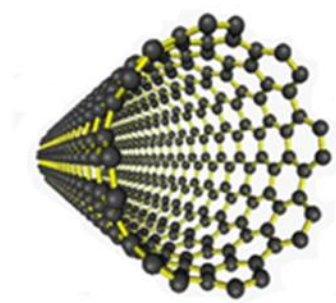


FULLERENE

GRAPHITE



CARBON NANOTUBE



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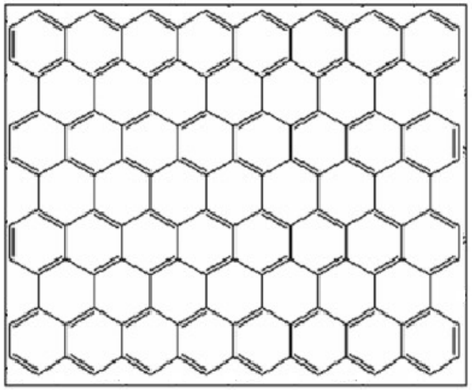
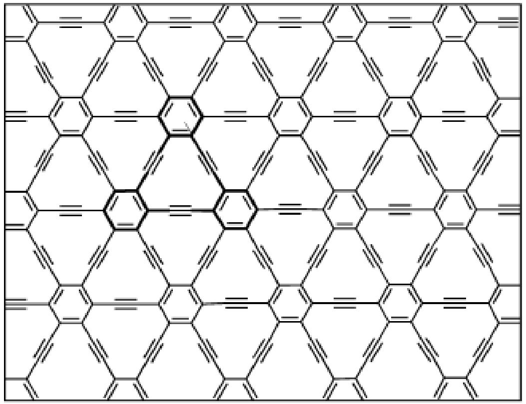
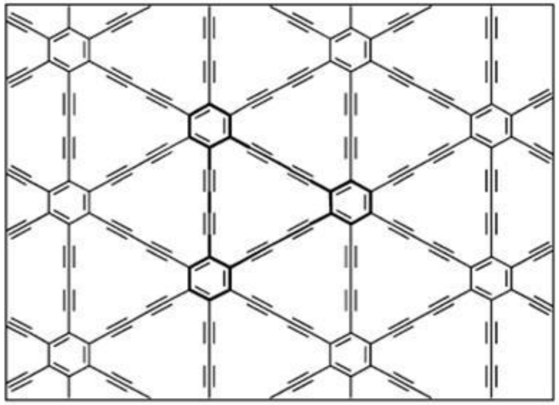
GRAPHENE



GRAPHYNE

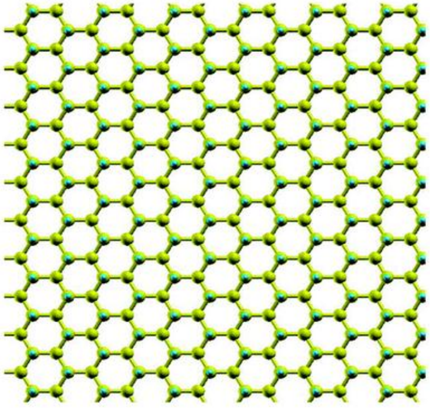


GRAPHDIYNE



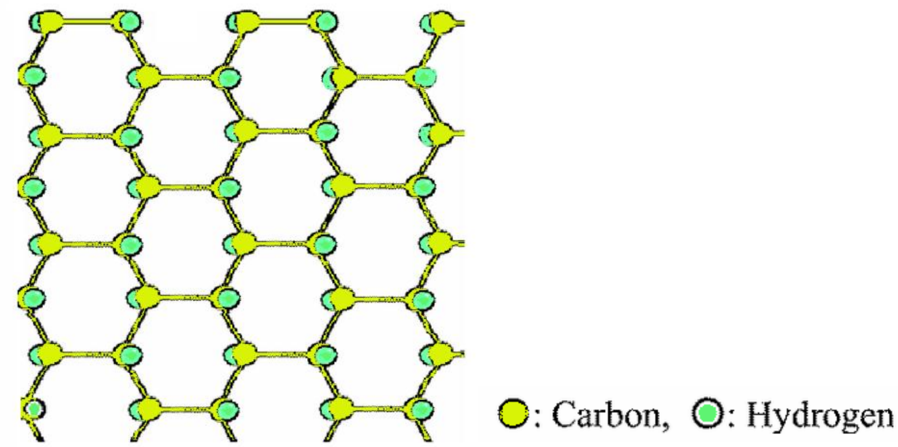
GRAPHONE

Graphone is a half-hydrogenated graphene



GRAPHANE

Graphane is a fully hydrogenated form of graphene



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Why carbon allotropes are interesting?

Graphene has been recognized as promising candidates for use in next-generation electronic and optoelectronic devices.

Why Raman spectroscopy has been used?

Advantages of Raman spectroscopy

- Very small samples
- No special preparation of samples
- Ease of use
- Non-destructive and non-contact analysis
- Measurement of various types of samples (liquids, solids, powders, etc.)
- It can be used for studies of material properties under extreme conditions of high pressure and low temperature
- Depth analysis

Information obtained from Raman spectra

Raman spectroscopy	Information
Peak position shift	Stress Strain Phase transition
Peak polarization	Crystal orientation Polymer orientation Symmetry
Peak width	Crystal quality Degree of crystallinity
Intensity	Material content Concentration
Characteristic frequencies	Material recognition Chemical analysis

Raman Spectroscopy. History.

The Raman effect, the phenomenon of inelastic scattering of light (Raman scattering), was discovered by Dr. C.V.Raman in 1928.

The Raman spectroscopy is based on the Raman effect.
In 1960s, Raman spectroscopy has been practically used due to the invention of Laser system.

In the late 1970s, Raman spectroscopy with optical microscope has been came to use for microanalysis in many fields
In 1990, the first confocal Raman scanning instrument demonstrated
in 1998, a Raman 3D scanning confocal microscope (Nanofinder) was developed by SOLAR TII (SOL Instruments) jointly with Tokyo Instruments (TII) and NT-MDT.

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Instrumentation
3D Raman Confocal Microscope Confotec™

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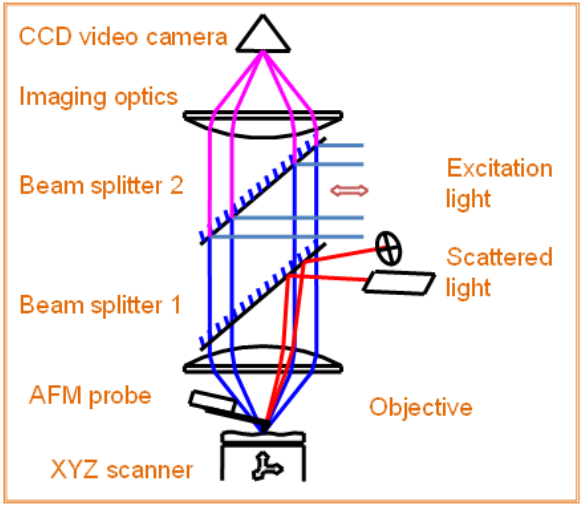
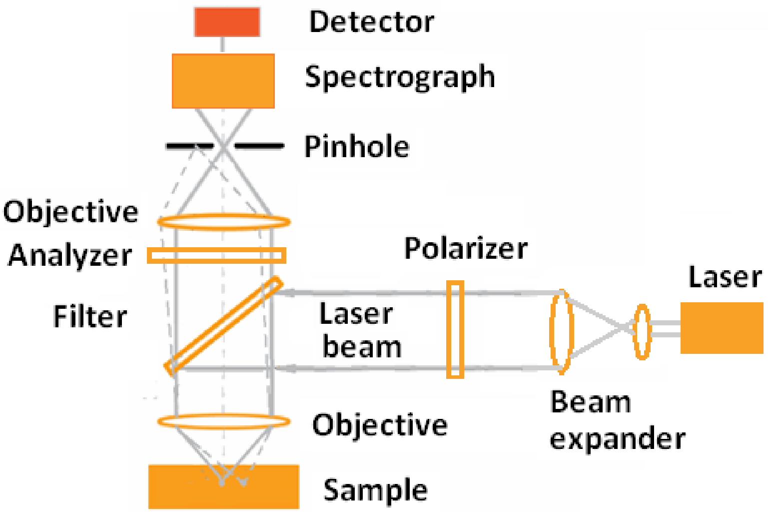
Raman Confocal System with NT-MDT AFM



http://www.ntmdt.ru/afm-raman/ntegra-spectra

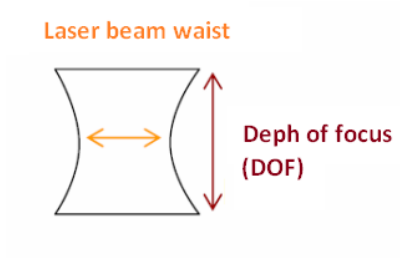
Confocal Raman Microscopy. Principles.

A typical Raman spectroscopy set-up is shown in the next Figure.
A pinhole blocks the scattered light which is coming from the out-of-focus points.
A suitable light source and efficient detection system are necessary for Raman measurements.



3D Raman Confocal Microscope Confotec™

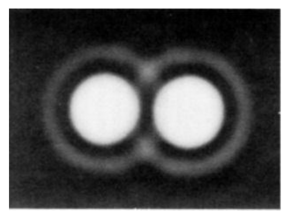
Confocal Raman signal is collected only with a diffraction limited volume:



Focused spot diameter: $d \sim 0.61\,\lambda\ /\ NA$

Depth of focus: $\sim 4\,\lambda\ /\ NA^2$

Lateral resolution (XY)



$$R_{Lateral} = \frac{0.61 \cdot \lambda}{NA}$$

(Rayleigh Criteria)

Axial resolution (Z)

The next formula is used for axial resolution calculation

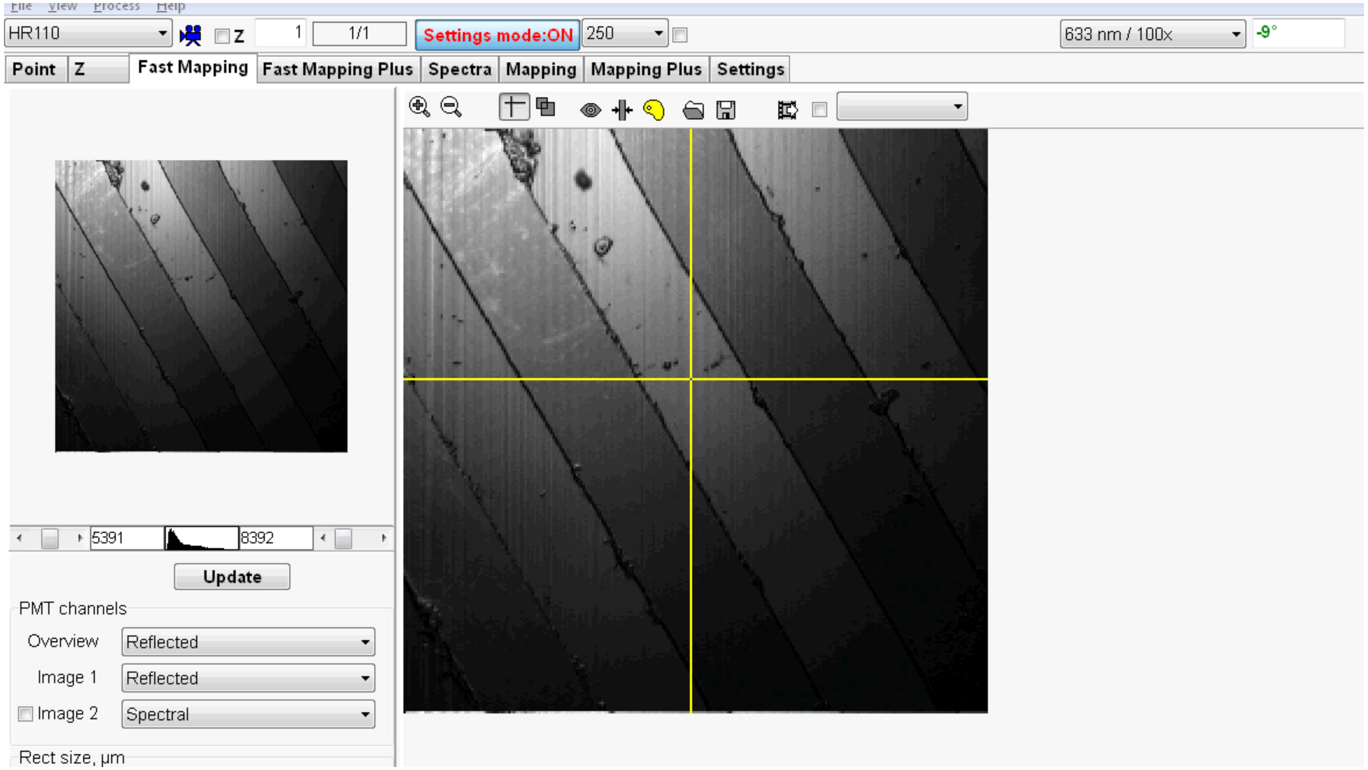
$$R_{Axial} = \frac{0.88 \cdot \lambda}{n - \sqrt{n^2 - (NA)^2}}$$

(n – refractive index of medium)

Thus, the spatial resolution is determined by the wavelength of light (λ), medium (n) and the lens numerical aperture (NA).

High speed mapping with
3D Raman Confocal Microscope Confotec™

Video:



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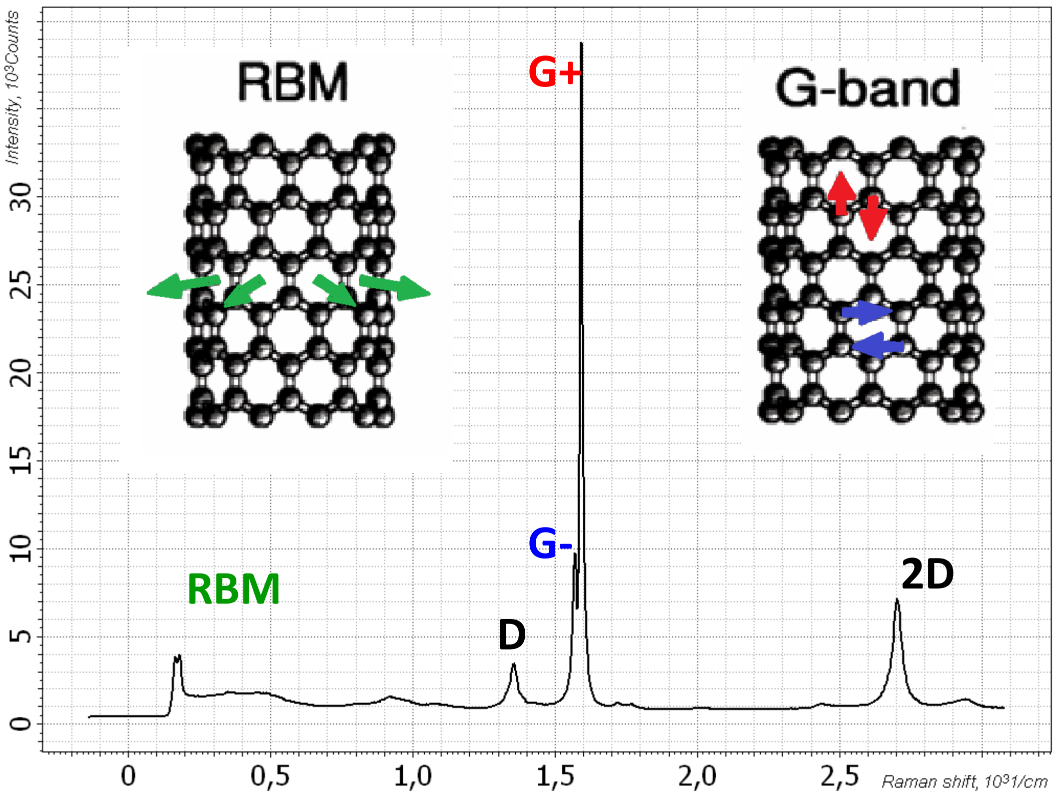
Carbon nanotubes

Carbon nanotubes (CNTs) have drawn much attention due to their unique structural, mechanical, thermal, and electrical properties.

Applications for nanotubes:

- Semiconductor devices
- STM/AFM tips
- New materials
- Battery additives
- Polymer composites

Single walled carbon nanotubes (SWCNs). Raman spectrum.



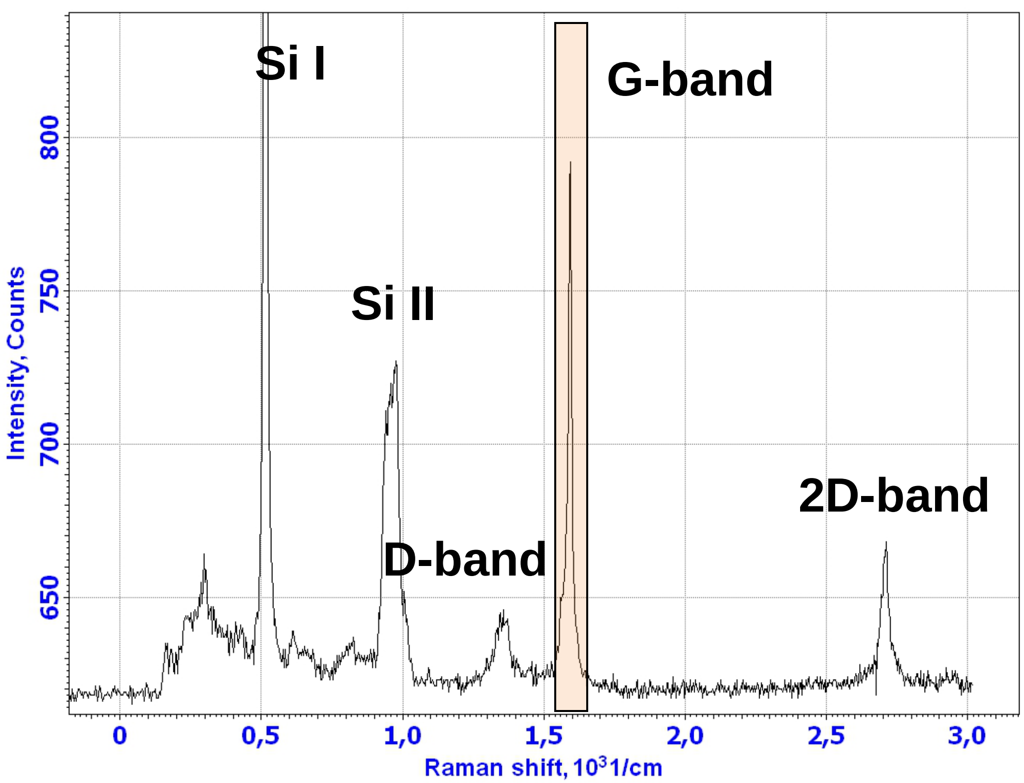
The **D (defect-activated)-mode** peak is associated with the defects in the nanotube structure.
The greater the relative intensity of this peak, the more defects in the structure appears.

The strong Raman peak at ~1582 cm^{-1} is related to the tangential C-C stretching vibrations **(G-band).**

The **RBM peak** correspond to the radial breathing mode.

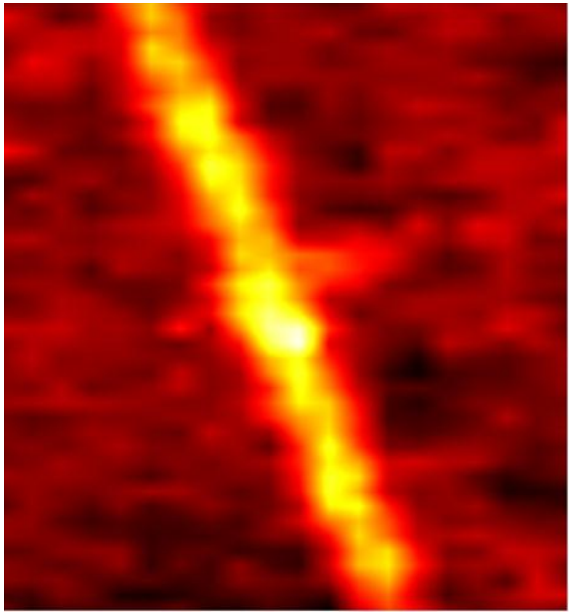
SWNT on Si substrate

Single walled carbon nanotubes have been deposited on a Si substrate by spin casting of their solution in ethyl alcohol.



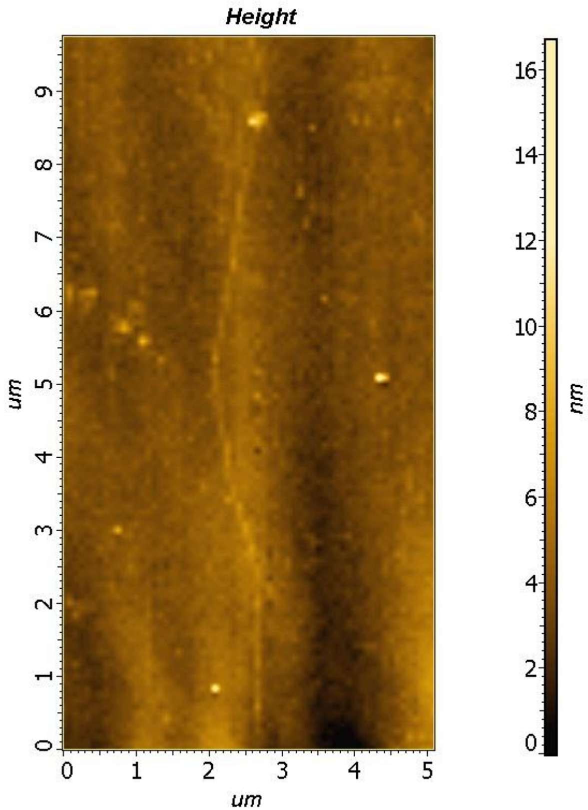
Raman image of a CN

532 nm laser, 100 x NA0.95 objective, scanning step is 40 nm

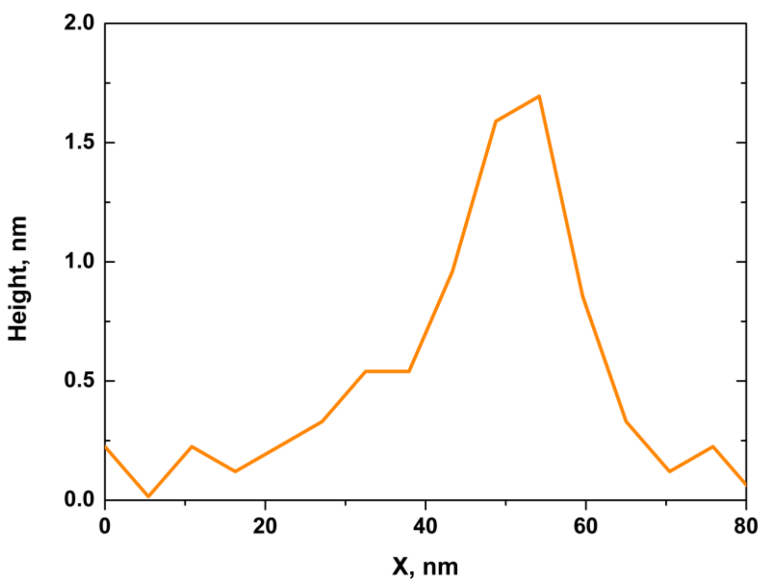


Carbon nanotubes in the bent state

AFM topography
(NT-MDT NTEGRA Prima)



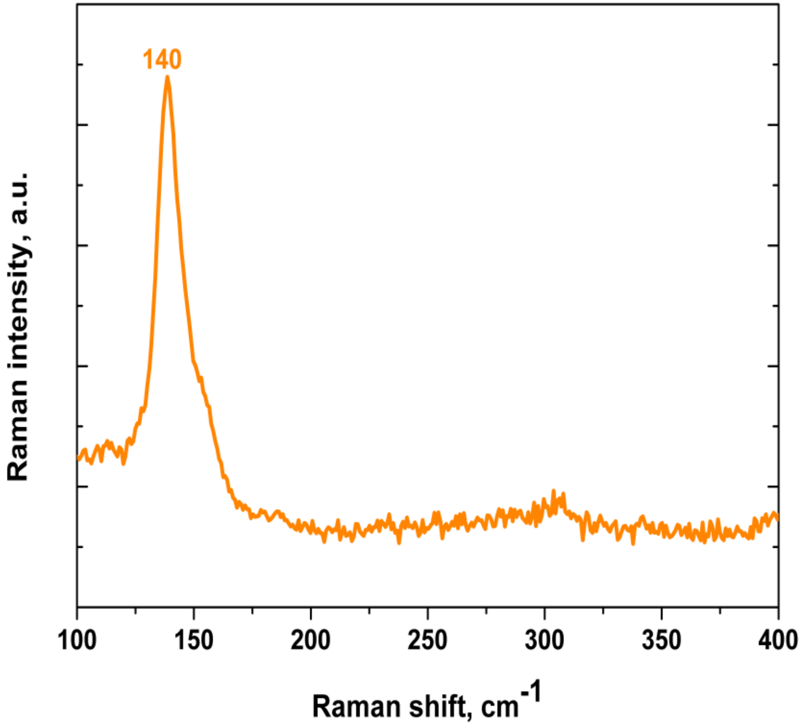
AFM cross section



According to atomic force microscopy characterization, the carbon nanotube diameters is 1.7 nm

Raman spectroscopy of a bent SWCN (RBM mode)

The radial breathing mode (RBM) is very sensitive to the diameter of SWCN.



The diameter of the nanotube is 1.75 nm (approximately) according to the relation

$$\nu_{RBM}(\mathrm{cm}^{-1}) = \frac{223.5}{d_t\,(\mathrm{nm})} + 12.5$$

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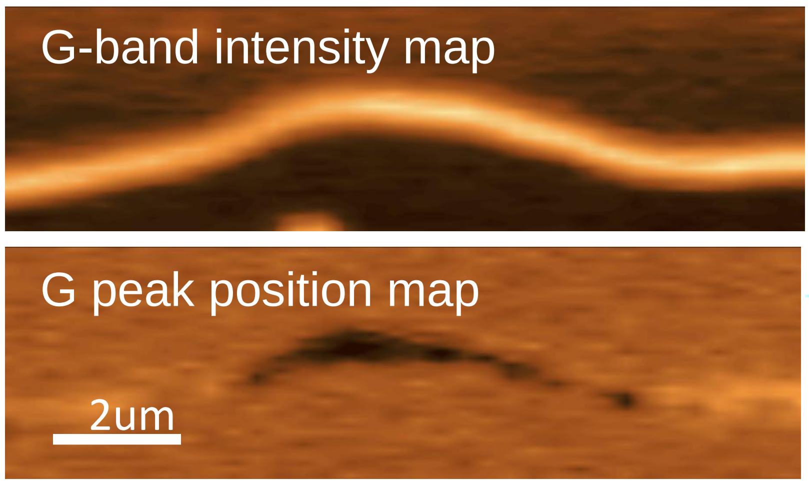
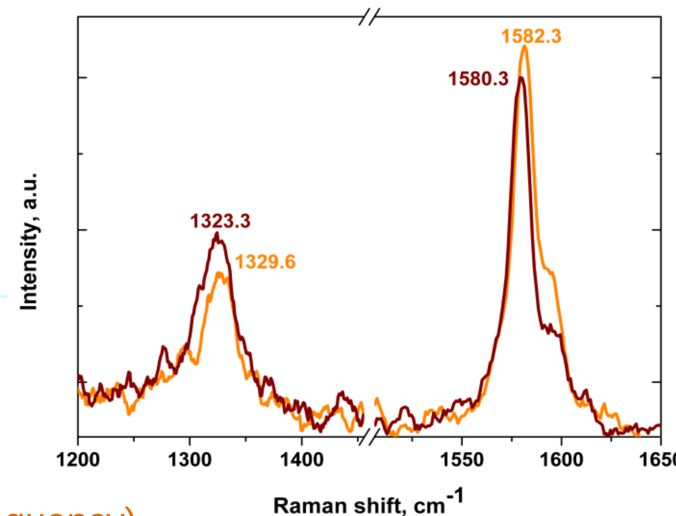
Raman microscopy of a bent SWCN (G and D modes)





(The brighter the color corresponds to the higher frequency)

The tangential stretching mode is highly sensitive to strain and the local structural changes in CNs. The local structural changes and strain may occur due to curvature effects.

In the place of the greatest curvature, a decrease in the G-band frequency is clearly observed. The G-mode shifts downward upon nanotube bending, and it attributed to the tensile stress.

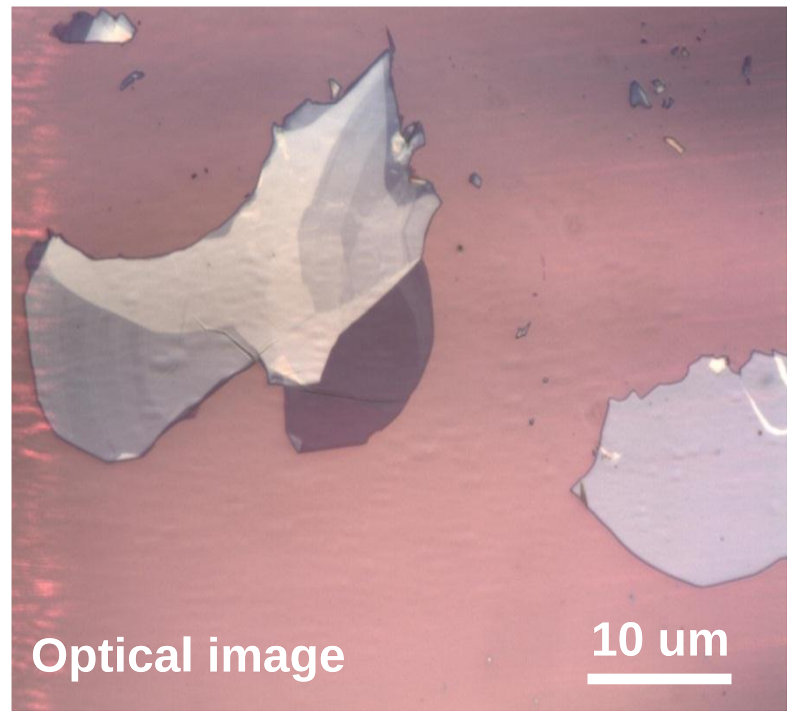
Additionally, an increase of the D-band relative intensity at the given location of the carbon nanotube is also observed.

Graphene properties

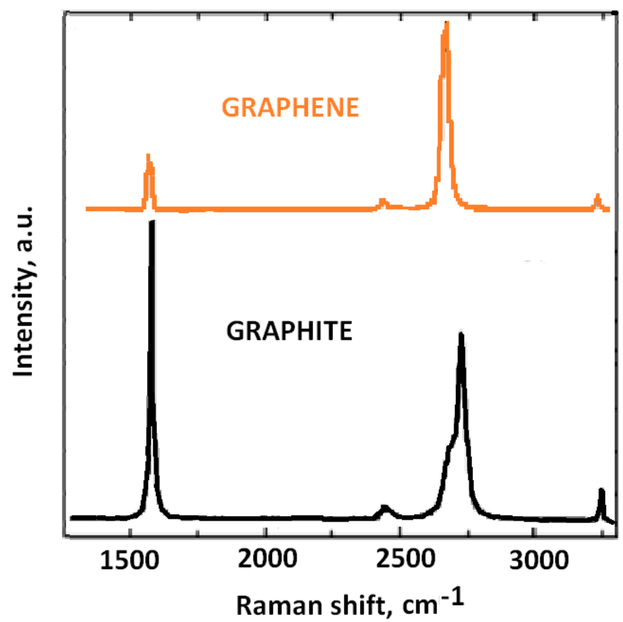
- Hardness
- Significant thermal conductivity
- Significant electrical conductivity
- Optical transparency
- Chemical stability
- etc.

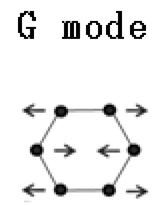
Graphene Production

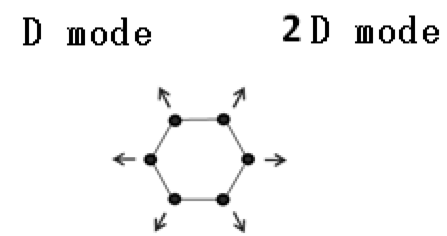
Graphene has been obtained by mechanical exfoliation of graphite and transferred it onto Si/SiO_2 or gold substrates.



Raman spectroscopy of Graphene



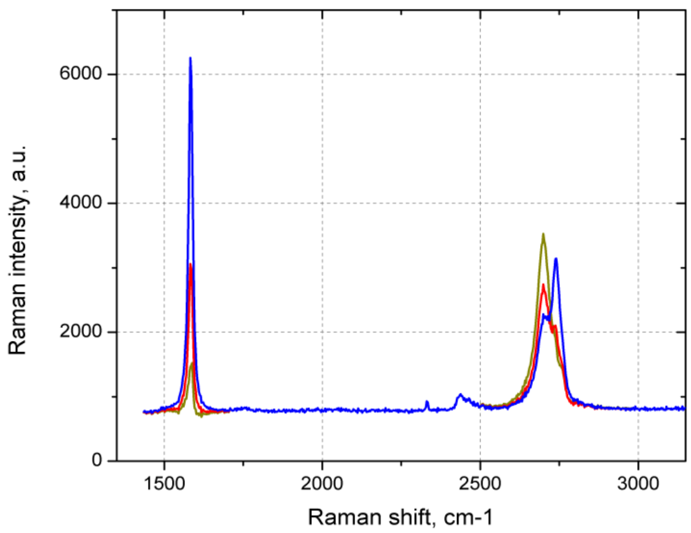




1580 см$^{-1}$ 1360 см$^{-1}$ 2700 -2745 см$^{-1}$

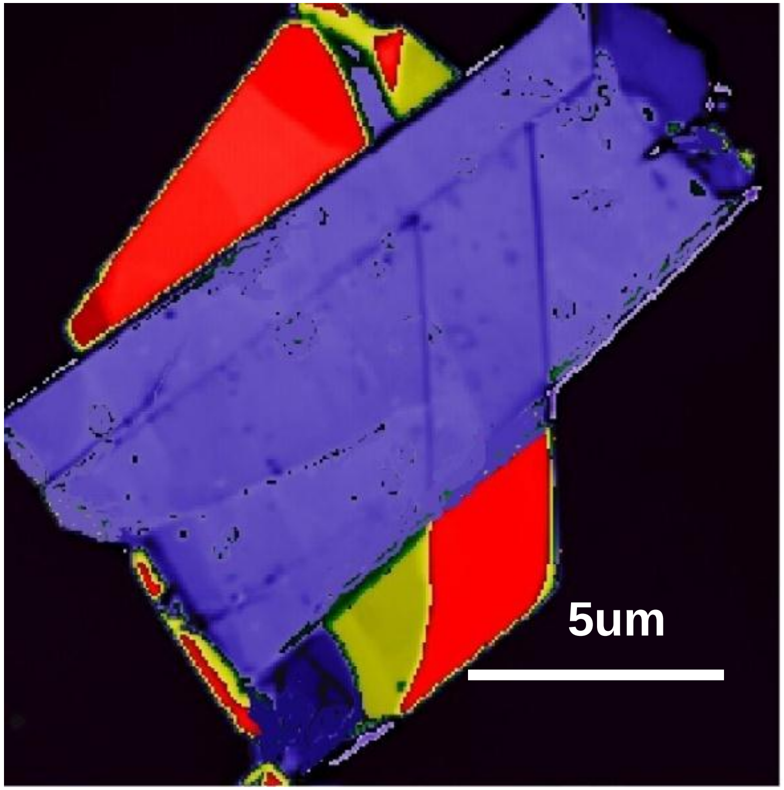
Relative Intensity of G band enhances with the number of layers.
Identification of single, bi or many layers can be done with 2D line.

Raman spectroscopy of Graphene Layers



Yellow color corresponds
to a single layer,
red color - 2 layers,
blue color – 3 layers and more.

G-band Raman Intensity Map
of a graphene flake



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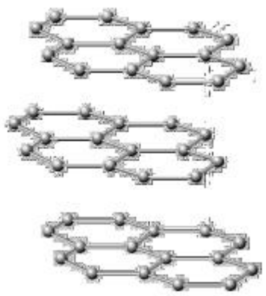
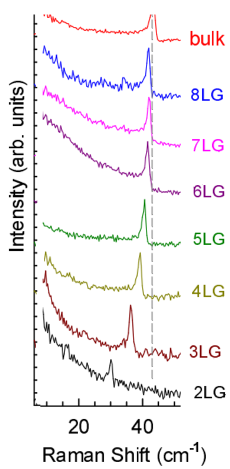
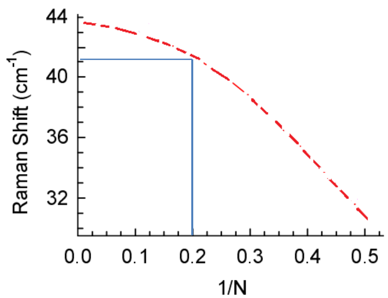
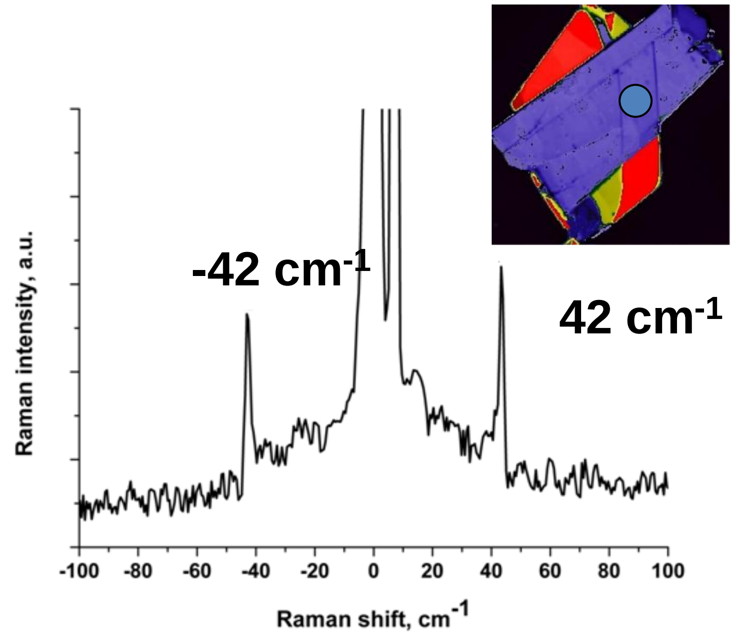
C-band



The interlayer shear Raman mode of few layer graphene (C-band) can be observed from 44 cm^{-1} (in bulk graphene) to 32 cm^{-1} (in bilayer graphene).

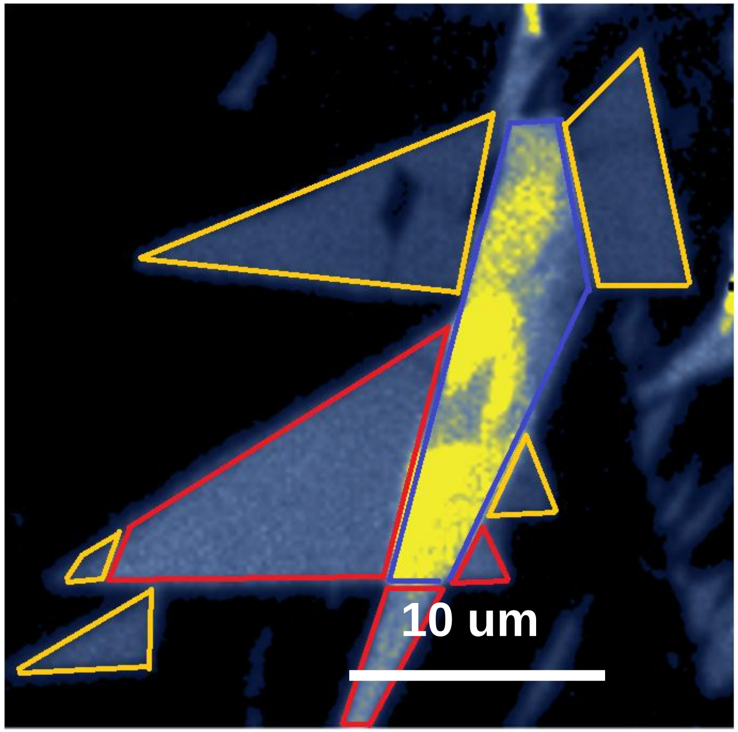






P.H. Tan, The shear mode of multi-layer graphene

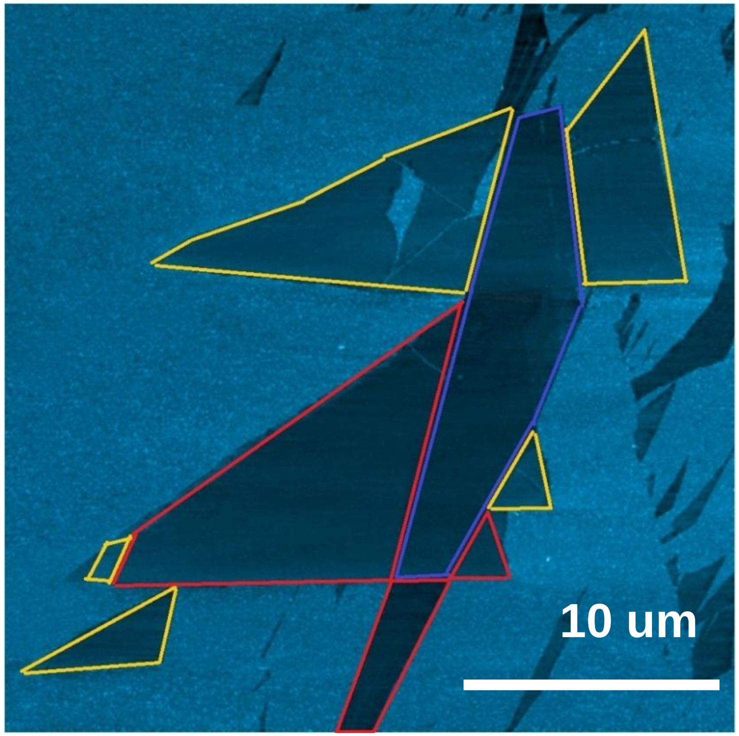
Raman Map of Graphene (2D band position)



Yellow color corresponds
to a single layer,
red color - 2 layers,
blue color – 3 layers and more.

E. Kuznetsov, S. Timofeev, P. Dorozhkin, NT-MDT

Lateral Force Map



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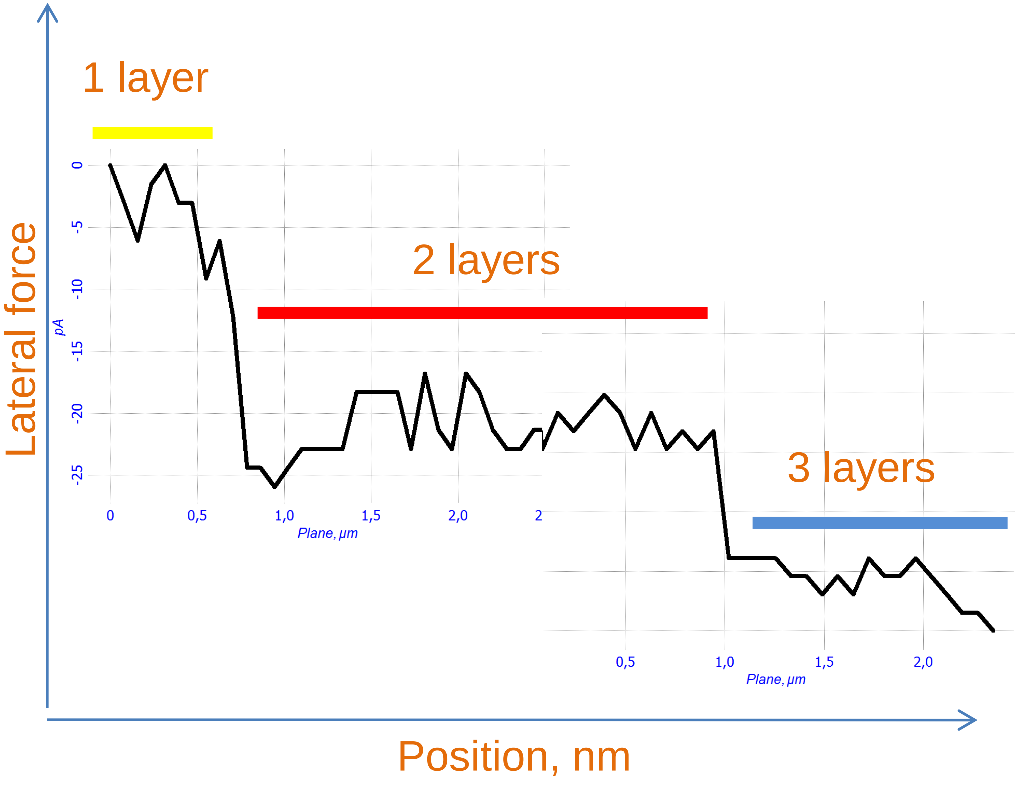
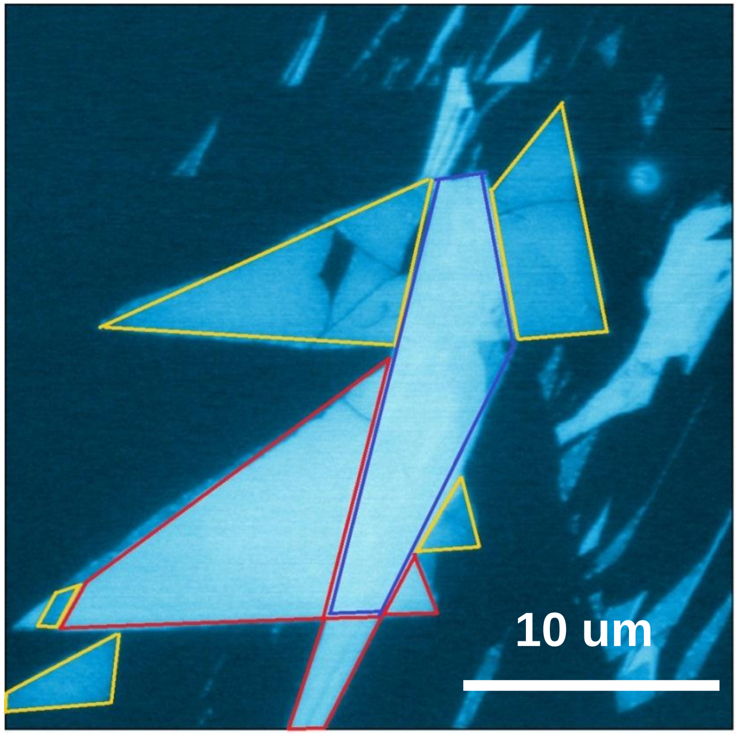


Local friction of graphene is smaller than of the gold substrate.
Friction decreases monotonically with increasing number of layers.

Kelvin Probe Microscopy map: Surface potential



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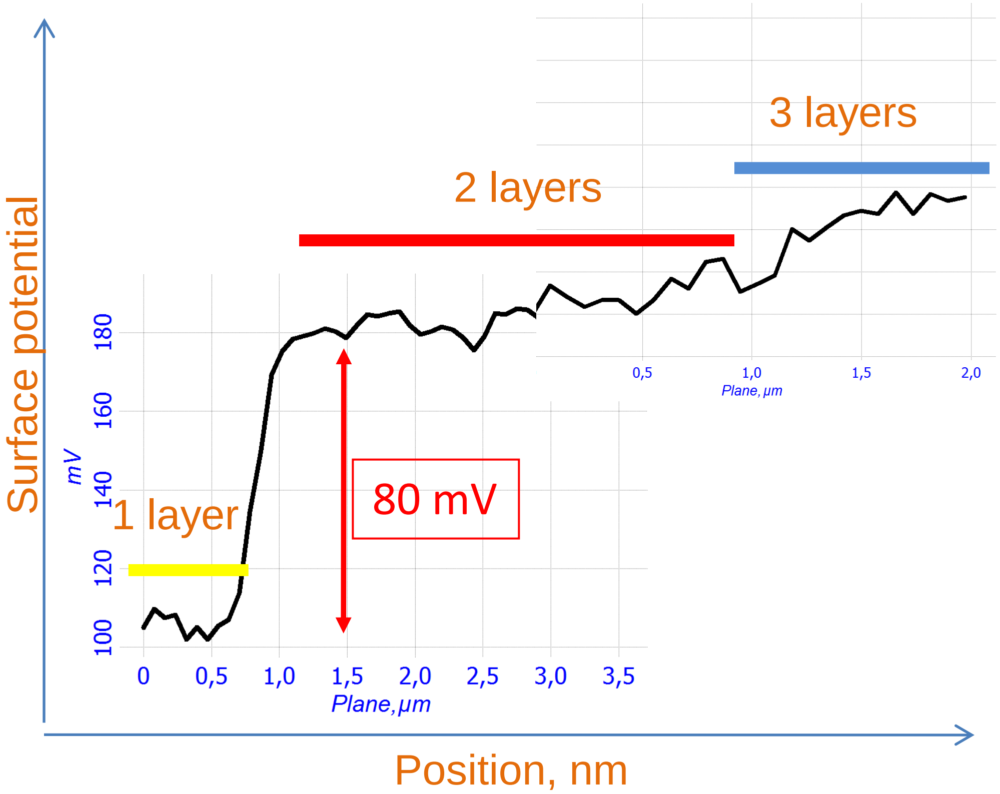


Surface potential increases monotonically with increasing number of layers.
Surface potential difference is about 80 mV between single layer and bi-layer and it is about 20 mV between bi-layer and triple layer.

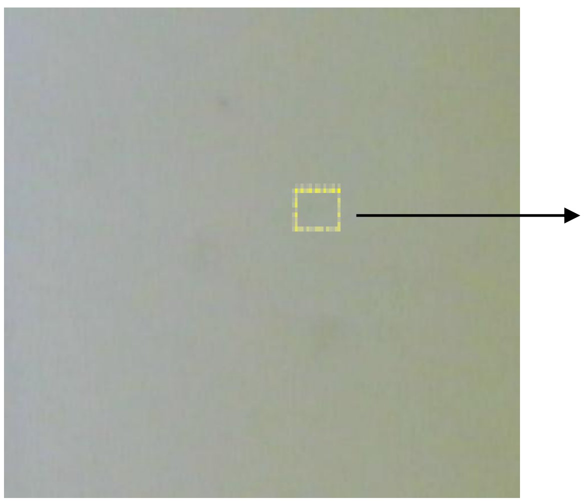
Properties and applications of Graphite
(a crystalline form of carbon):

- High thermal stability and electrical conductivity
- Graphite are used to construct the anode of all major battery technologies
- Pencils (the ability to leave marks on paper)
- Neutron moderator
- etc.

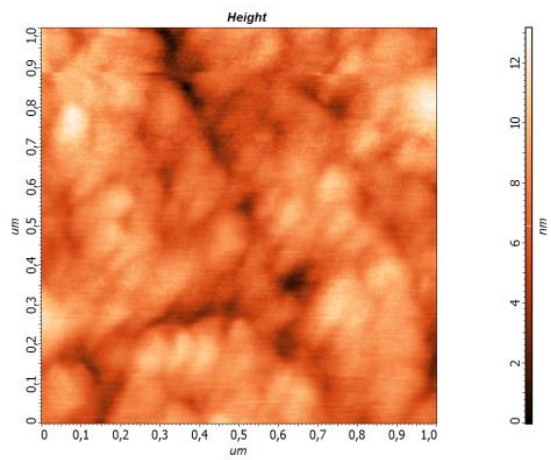
Microcrystalline Graphite

Amorphous (microcrystalline) graphite is used in many lubricant products especially greases.

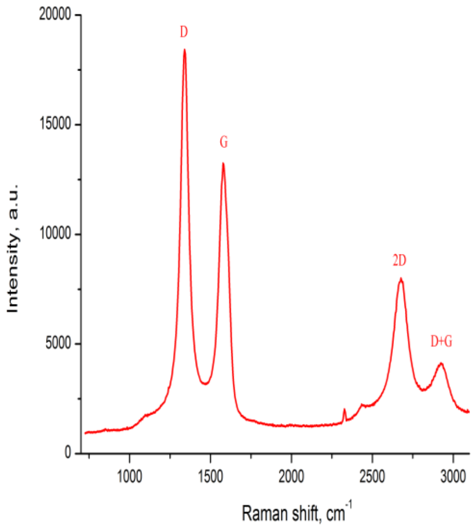
Optical image



AFM topography



Raman spectrum



Properties of Carbon Fibers

Carbon (graphite) fiber is a new material consisting of fibers about 5–10 μm in diameter and composed mostly of carbon atoms. Carbon fibers are produced from Polyacrylonitrile (PAN) commonly.

The properties of carbon fibers, such as high stiffness, high tensile strength, low weight, high chemical resistance, high temperature tolerance and low thermal expansion, make them very popular in aerospace, civil engineering, military, and motor sports, etc.

Carbon fibers are usually combined with other materials to form a composite.

Applications

1. Composite materials

Carbon fiber is most notably used to reinforce composite materials. The increasing use of carbon fiber composites is displacing aluminum from aerospace applications in favor of other metals because of galvanic corrosion issues.

2. Textiles

Carbon fiber filament yarns are used in several processing techniques: the direct uses are for prepregging, filament winding, pultrusion, weaving, braiding, etc.

3. Microelectrodes

Carbon fibers are used for fabrication of carbon-fiber microelectrodes.

4. Catalysis

PAN-based nanofibers can efficiently catalyze the first step in the making of synthetic gasoline and other energy-rich products out of carbon dioxide.

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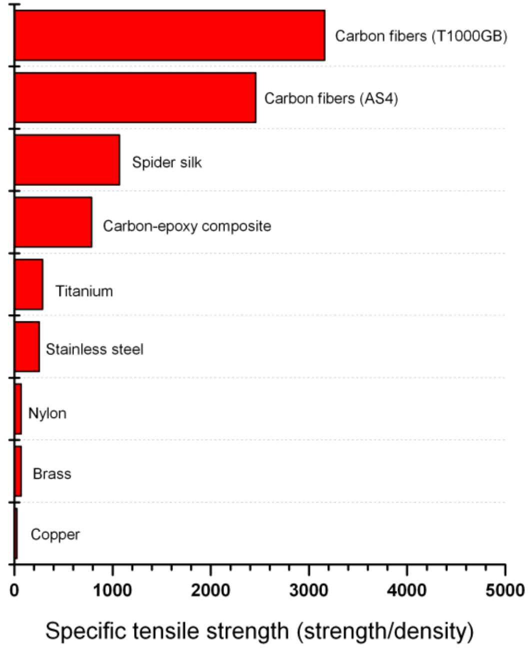
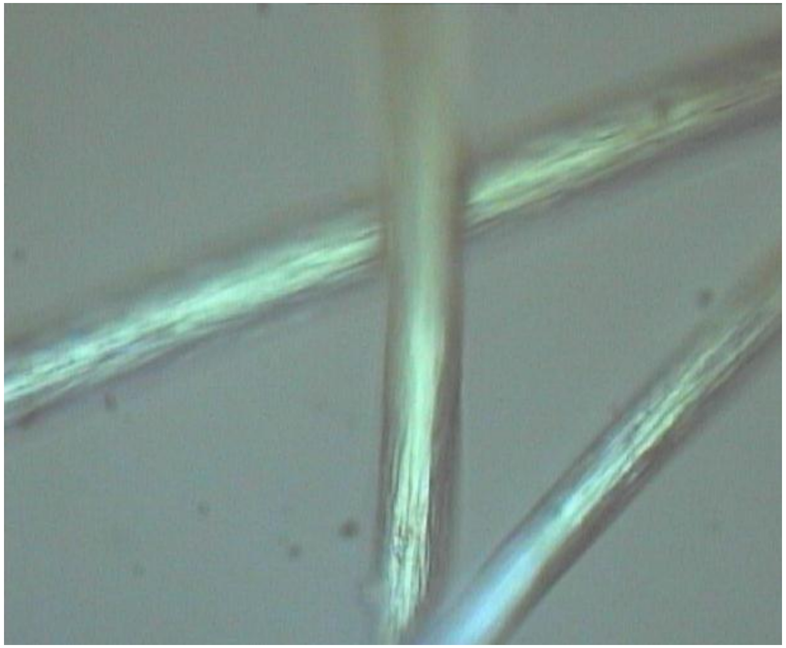
Carbon fibers

The specific strength is a material's strength (force per unit area at failure) divided by its density.
It is also known as the strength-to-weight ratio.

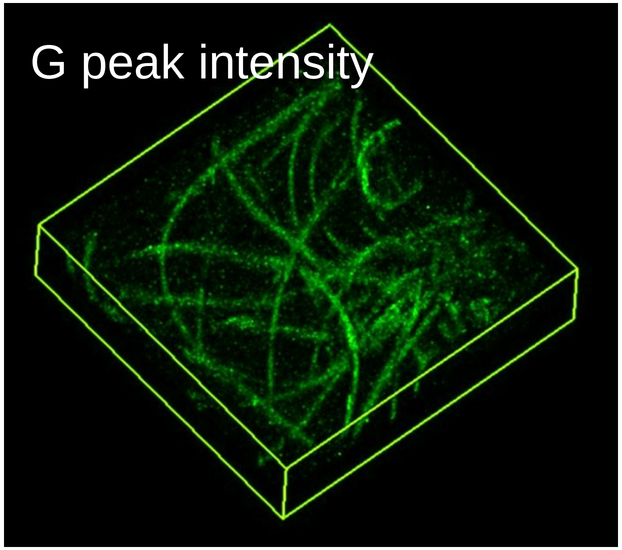
Comparison of carbon fiber properties with other engineering materials

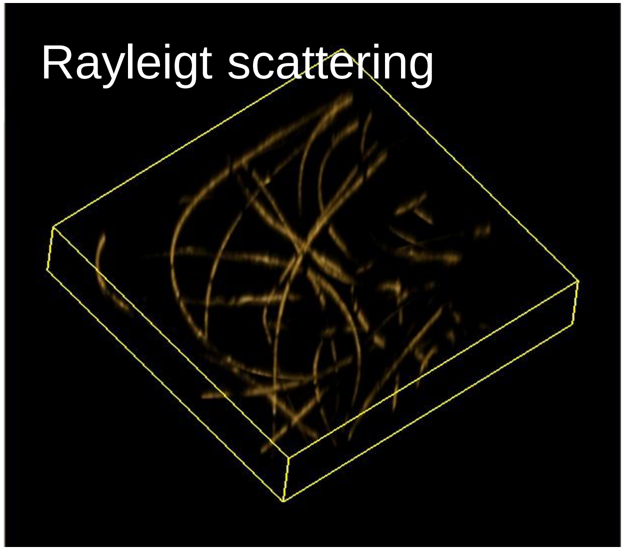




Carbon fibers. Raman Microscopy

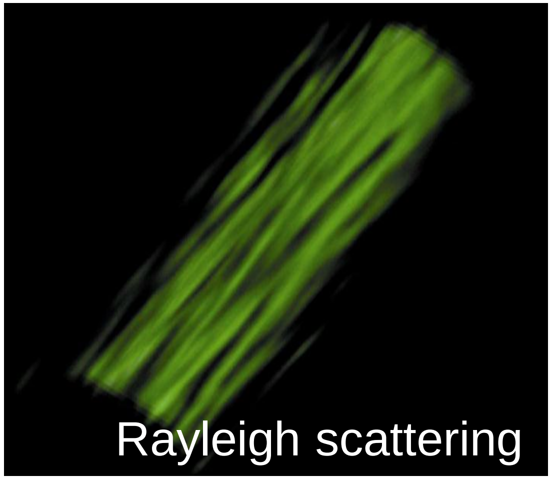
G peak(1580 cm-1): Graphite structure
D peak (1380 cm-1): Disorder

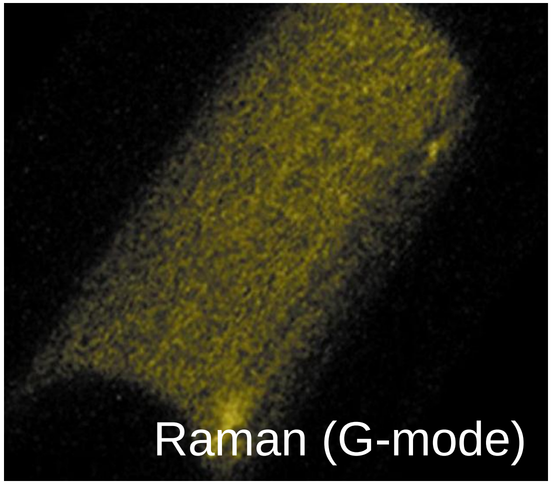


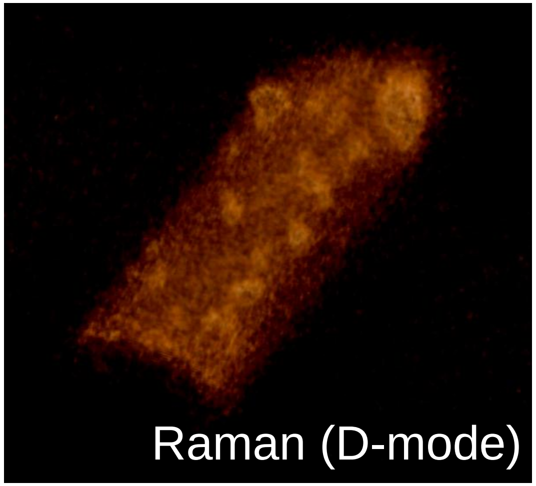


680 x 680 x 30 µm (250 x 250 x 70 points)

A carbon fiber. Raman Microscopy







21 x 21x 7 μm (250 x 250 x70 pixels), total imaging time is 90 sec (4,375,000 acquisitions)

Raman imaging with G band (vibration mode of graphite structure) of carbon fibers can be used for the structural characterization of fibers and their graphitization level.

Properties and applications of Diamond

- Hardness
- Pressure resistance
- Significant thermal conductivity
- Significant electrical conductivity
- Optical transparency
- Chemical stability
- Color (gem diamonds)
- etc.

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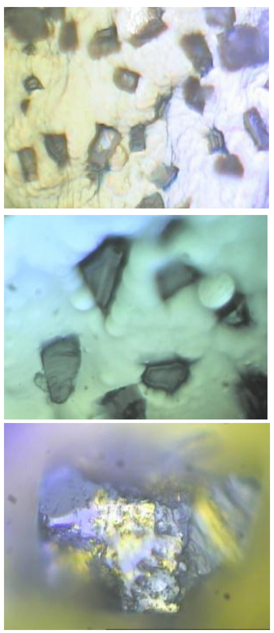
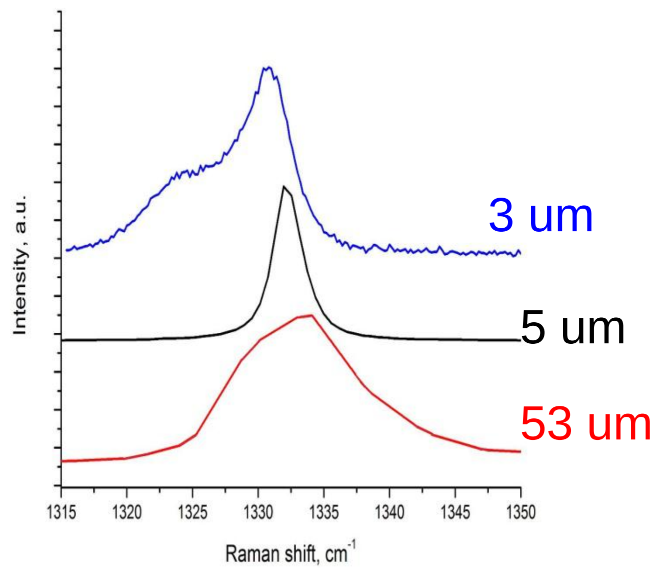
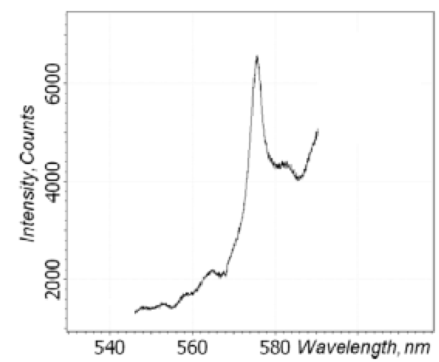
Raman spectroscopy



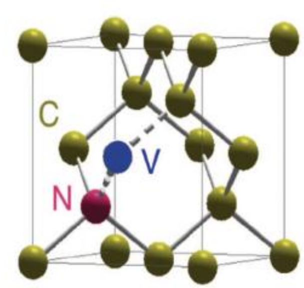
Raman spectra of synthetic diamonds



Luminescent peak at 575 nm (NV peak)

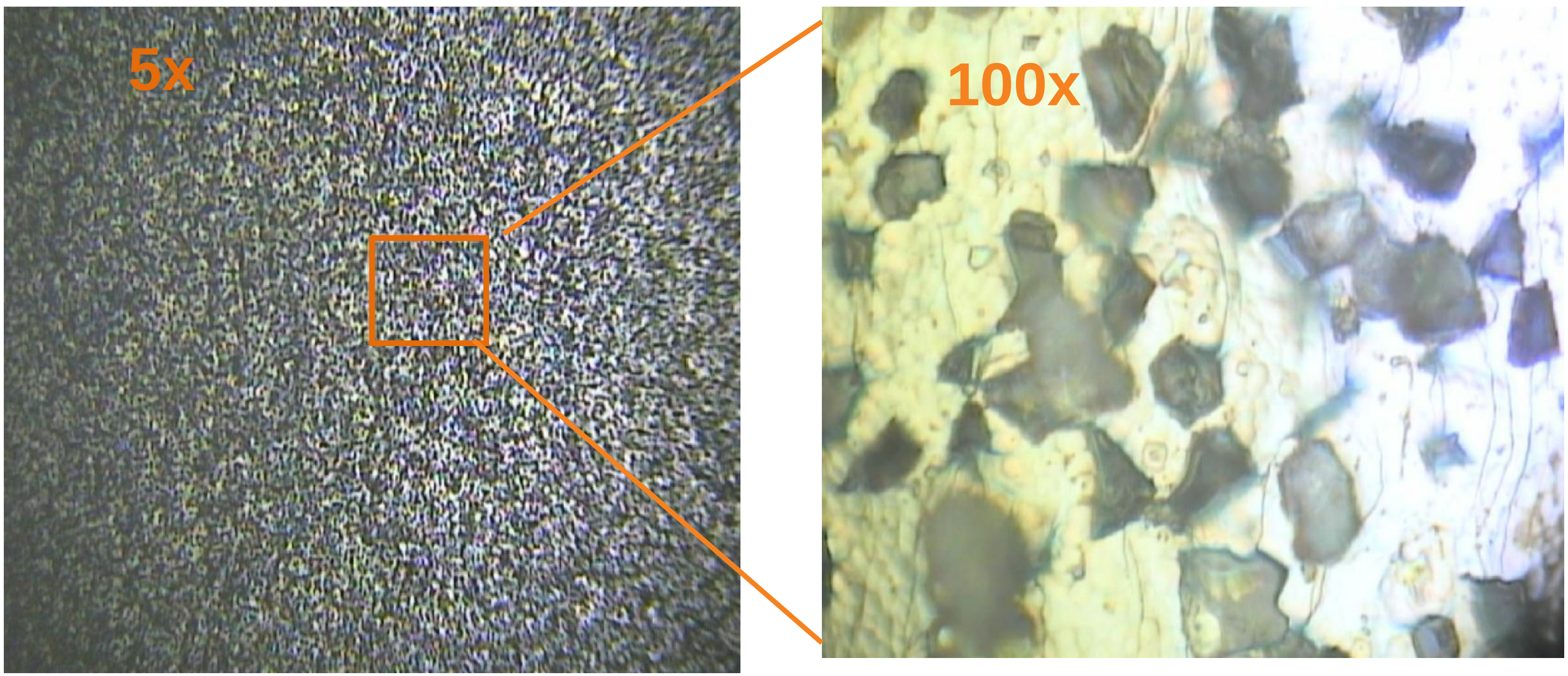


NV center structure



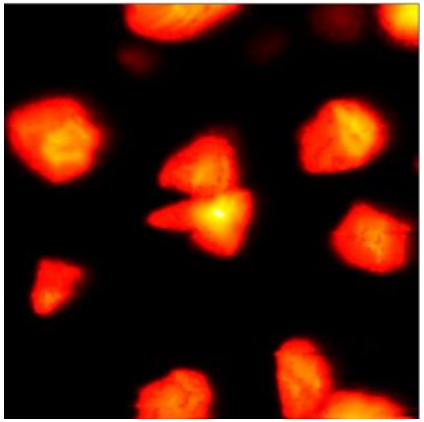
Raman spectra (peak position and peak FWHM) are sensitive to the diamond structure quality.

Diamond coating tools. Optical image

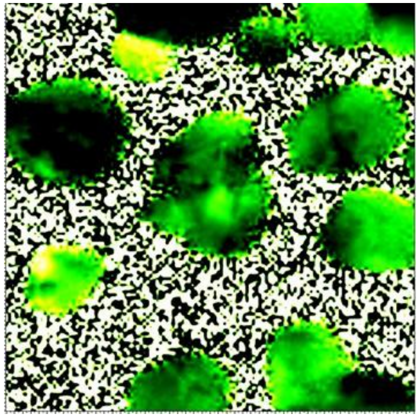


A Diamond coating tool. Raman microscopy

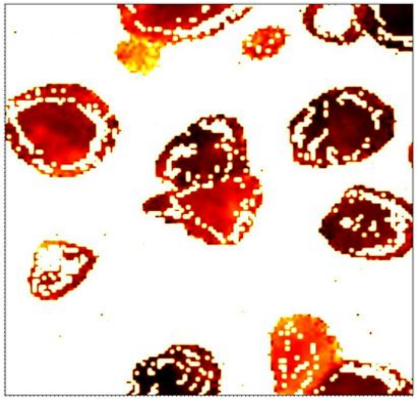
Peak intensity



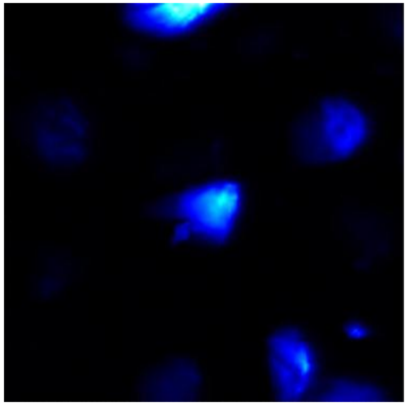
Peak position



FWHM



Luminescence



Diamond-like carbon (DLC)

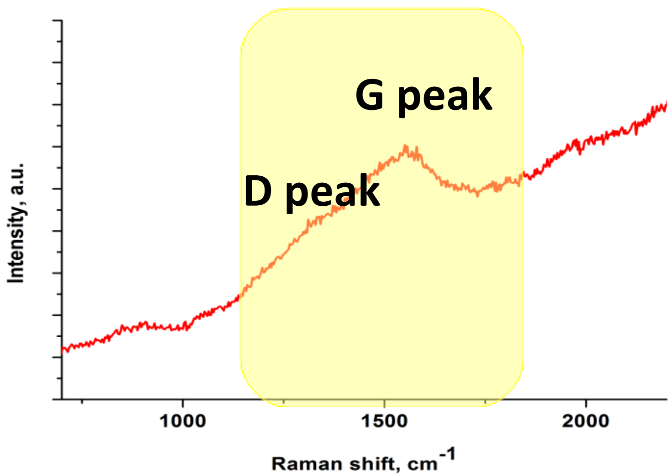
Diamond-like carbon (DLC) is a class of amorphous carbon material that displays some of the typical properties of diamond.

DLC is usually applied as coatings to other materials.

Amorphous carbon. Raman spectroscopy

Amorphose carbon (DLC) has been extensively used in the hard disk drive industry as a wear and corrosion protective overcoat on the magnetic layer.

Raman spectrum of a HDD protective overcoat



633nm laser
100x/NA0.7 obj.

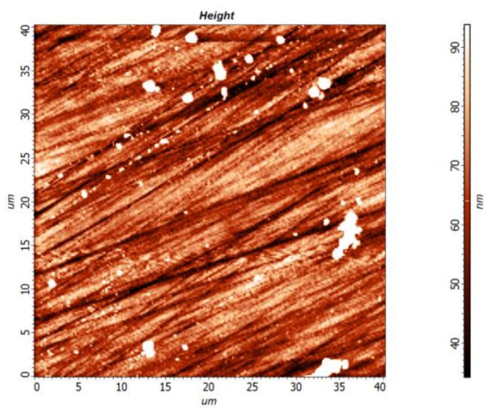
A peak known as the D-peak appears at 1350 cm^{-1}, possibly inherent in the carbon on the boarder of a graphite crystallite.

Another peak known as the G-peak appears near 1570 cm^{-1}, inherent in the planar vibration of the graphite.

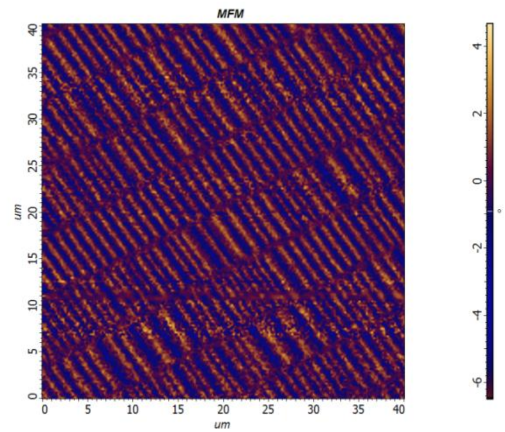
Both peaks superpose on the broadband fluorescent component.

Hard Disk Platter

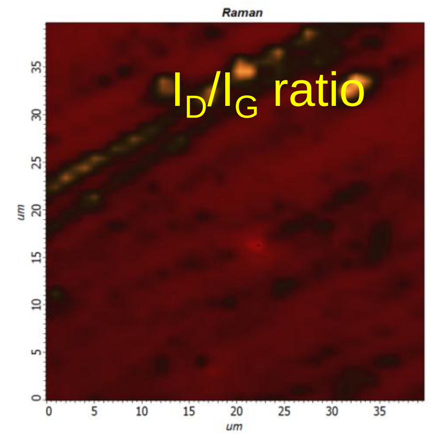
The size of defects varied around an average value of 1 – 2 µm.



Magnetic structures on the disk Platter (MFM measurements)



Analysis of DLC quality on base of Raman spectroscopy



In a completely sp3 network the I_D/I_G ratio will tend to zero

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Summary

Raman spectroscopy and microscopy provide:

- Non-destructive tool useful in the study of different materials
- Powerful tool for characterizing carbon materials with the high spatial resolution
- Raman is particularly well suited to detect changes in structural morphology of carbon nanomaterials
- The method allows study of physical properties at the submicron level

Thank you very much for your attention!

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