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19RCGD

Workshop on Resistive Coatings for Gaseous Detectors

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INFN Bari
Europe/Rome timezone

DLC films deposited by Laser Ablation for gaseous detectors: first experiments

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SEZIONE DI LECCE

Outline

Introduction

PLD for DLC films

DLC properties for MPGD

DLC films deposited in Lecce

- First set of samples: properties and discussion
- Second set of samples: properties and discussion
- Third set of samples: properties and discussion

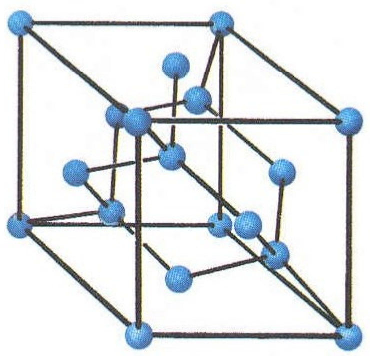
Conclusions and Future work

Introduction

Carbon forms different hybridizations (sp^3, sp^2 and sp^1)

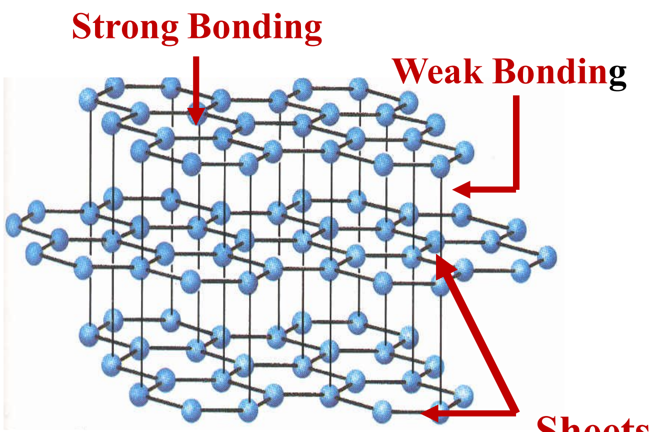
Diamond and Graphite are forms of pure carbon, however, the physical properties, hardness and cleavage are quite different for the two minerals

Diamond



- Tetrahedral atomic arrangement of C atoms: stable atomic structure
- C-C bonding is strong in all directions

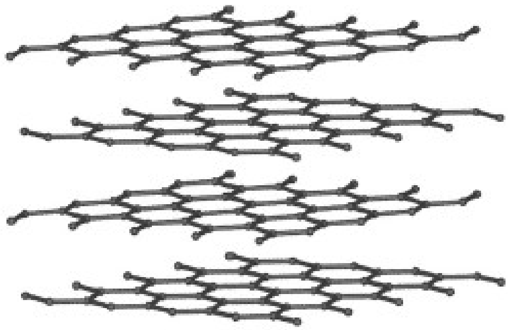
Graphite



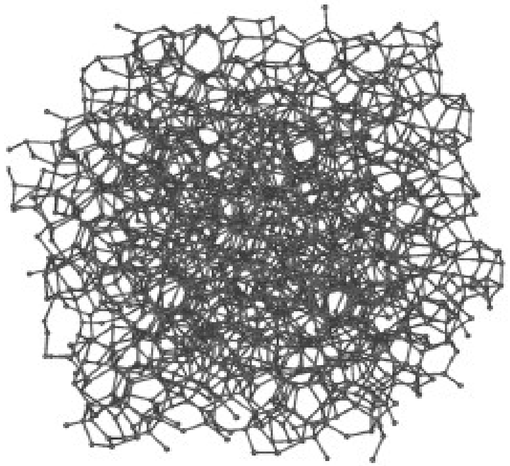
- C atoms arranged in sheets or layers
- C-C bonding is strong within the layers and is weak between the layers

Introduction

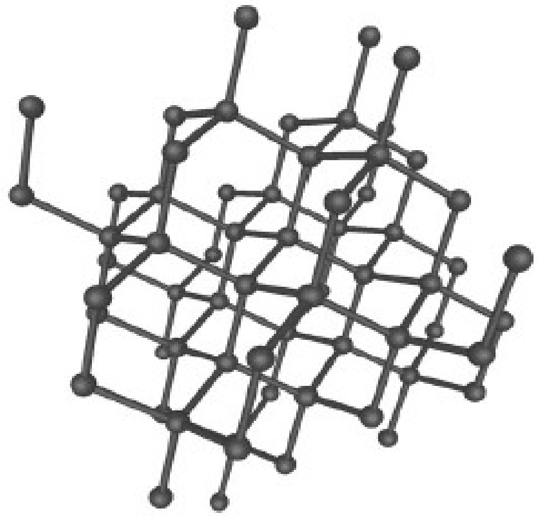
DLC is characterized by clusters of sp^2 and sp^3 bonded atoms in the material. The size and distribution of these clusters depend on the sp^3/sp^2 fraction.



Graphite. 100% sp^2 bonded carbon.



Amorphous carbon. Mix between sp^2 and sp^3 bonded carbon atoms

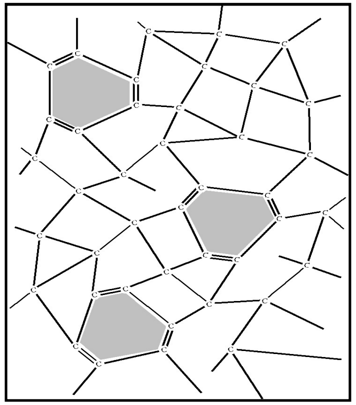


Diamond. 100% sp^3 bonded carbon.

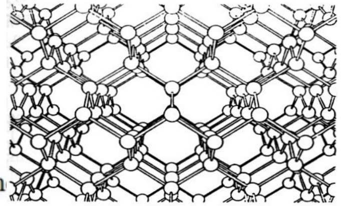
This bond configuration is such to confer to DLC particular properties intermediate between that ones of diamond and graphite which can be modulated by the sp^3/sp^2 fraction.

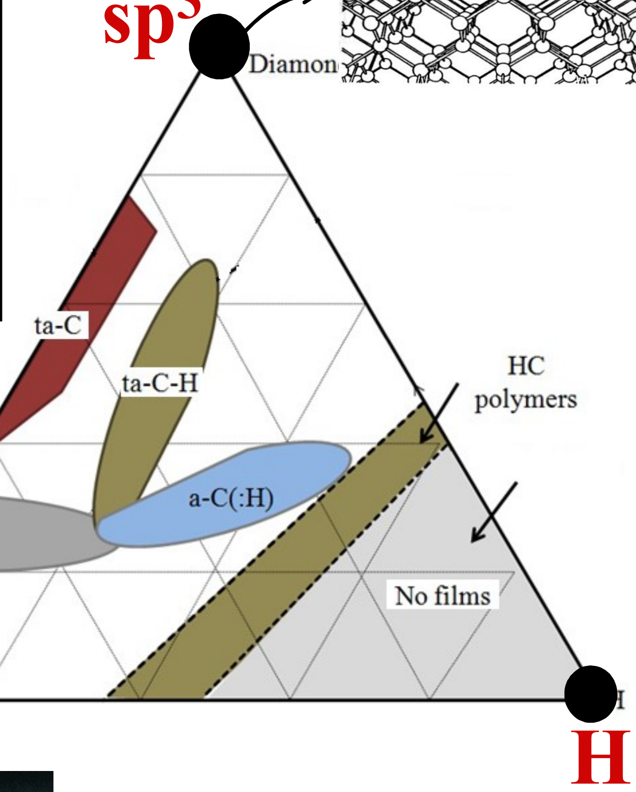
DLC main properties: high hardness, scratch resistance, smooth surface morphology, chemical inertness, good thermal conductivity, high electrical resistance, and optical transparency

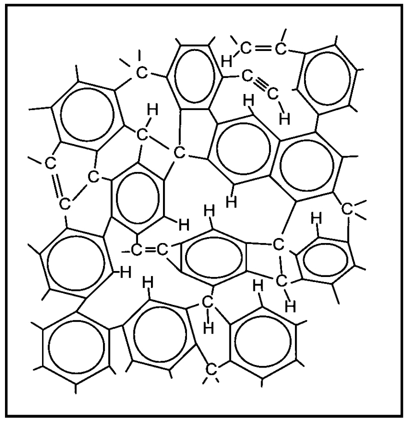
Introduction



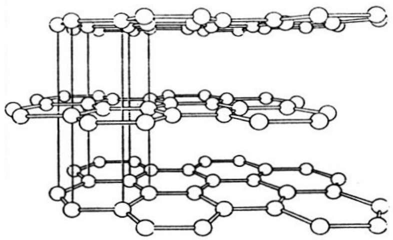
Diamond







Graphite



Ternary phase diagram of bonding in amorphous C-H alloys: the physical properties of DLC films depend on H-concentration and the sp3/sp2 ratio

PLD for DLC films growth

The DLC (ta-C) formation requires very high energy carbon species: 100 eV

Low-energy atoms preferentially condense into the thermodynamically favored, *sp*^{2} coordinated, graphitic structure. High-energy atoms can penetrate the surface, and condense under a compressive stress into the metastable *sp*^{3} coordinated, tetrahedral geometry

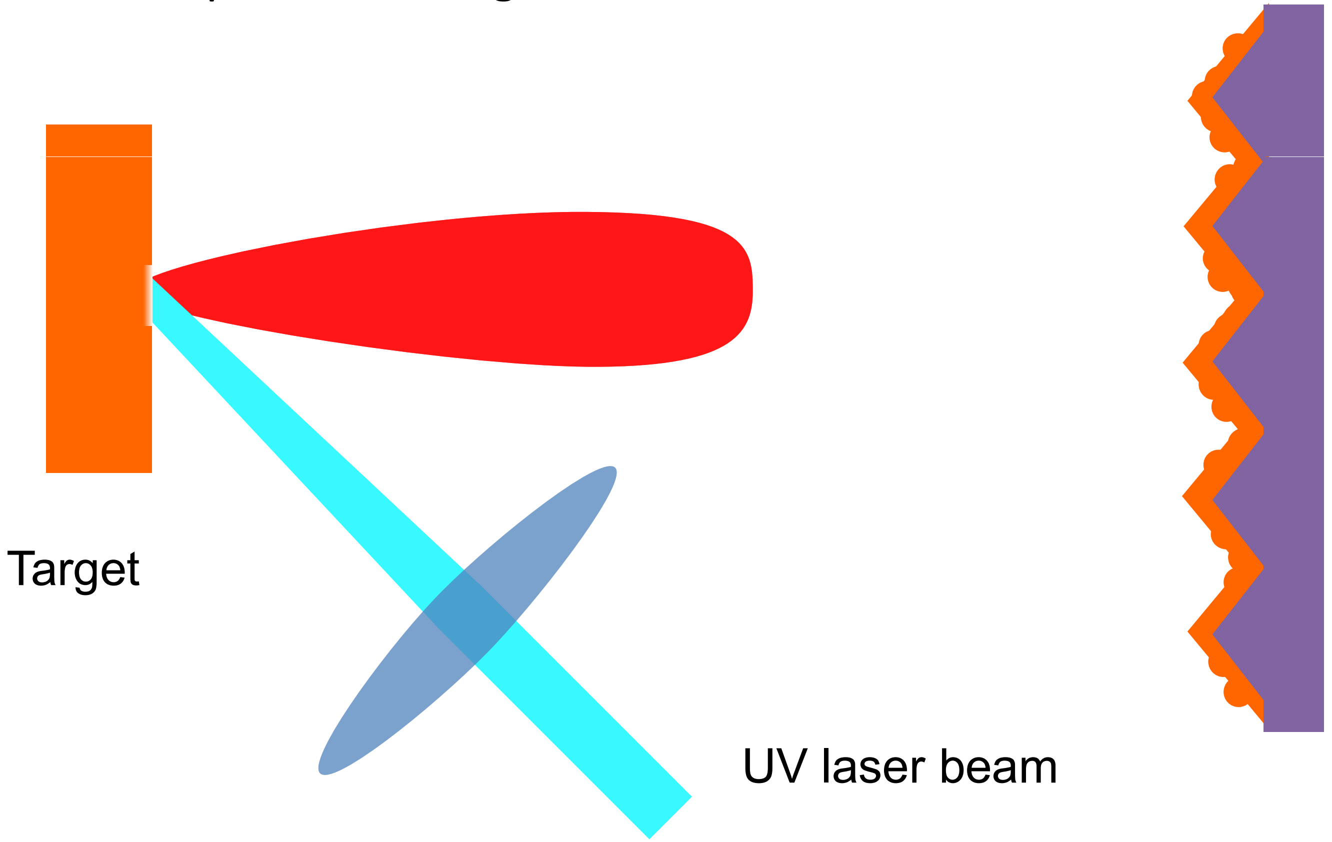
High-energy atoms, already condensed into the *sp*^{3}-coordinated system, may relax back to the *sp*^{2}-coordinated system if the excess energy is not quickly removed from the system

Low substrate temperatures and high thermal diffusivity of the substrate are essential for DLC film growth.

PLD for DLC films

Pulsed laser deposition is a "unique" technique for the deposition of hydrogen-free diamond-like carbon films.

During deposition, amorphous carbon is evaporated from a solid target by a high-energy laser beam, ionized, and ejected as a plasma plume. The plume expands outwards and deposits the target material on a substrate.

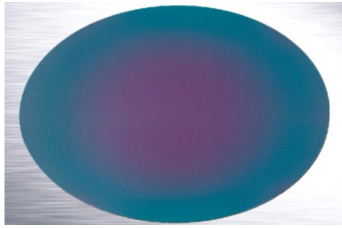


PLD for DLC films

Advantages

- ✓ Stoichiometric transfer of material from target to substrate;
- ✓ Good control of the thickness (0.1 monolayer/pulse);
- ✓ Very few contaminants;
- ✓ High particles energies - Low substrate temperatures;
- ✓ Multilayer deposition in a single step;
- ✓ Deposition on flat and rough substrates;
- ✓ Many independent parameters

Drawbacks



- ✓ Low uniformity of the deposited film;
- ✓ Presence of droplets and particulates on the film surface.

DLC films by PLD for MPGD

GOALS TO REACH

- ✓ Uniformity on a 2×2 cm^2
- ✓ Good adhesion on polyimide substrates
- ✓ Sheet resistance values in the range 10 ÷ 100 MΩ/sq

Experimental (first set of samples)

Target: pyrolytic graphite

KrF excimer laser: wavelength λ = 248 nm, pulse width τ = 20 ns, frequency: f=10 Hz

Laser Fluence: 2,5 $\div$ 5,5 J/cm^2

Target-substrate distance: d_{TS}: 55 $\div$ 45 mm

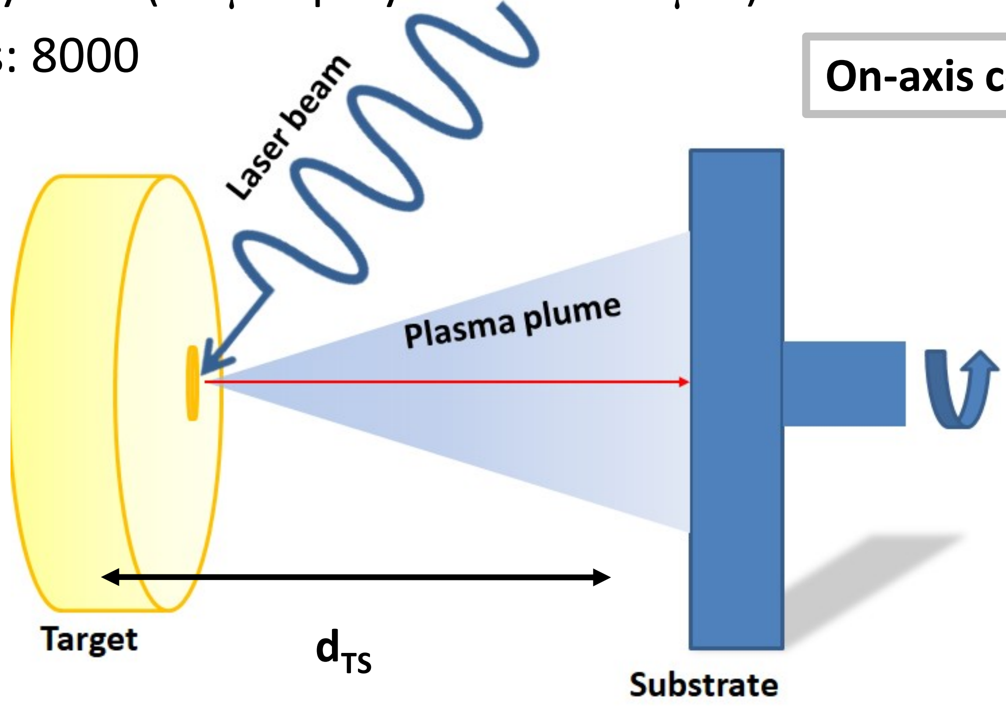
Background pressure: ~ 10^{-5} Pa

Laser spot area: ~ 4 mm^2

Substrates: Si/SiO_2, Polymide (50 µm polymide + 5 Cu µm)

Number of laser pulses: 8000

On-axis configuration



Experimental: Charatcerization techniques

Raman spectroscopy (excitation wavelength: 514 nm 20 mW)

Electrical characterization (Four Point Probe Van der Pauw Biorad 5500)

Transmission electron microscopy (TEM Hitachi 7700 120 keV)

Raman spectroscopy

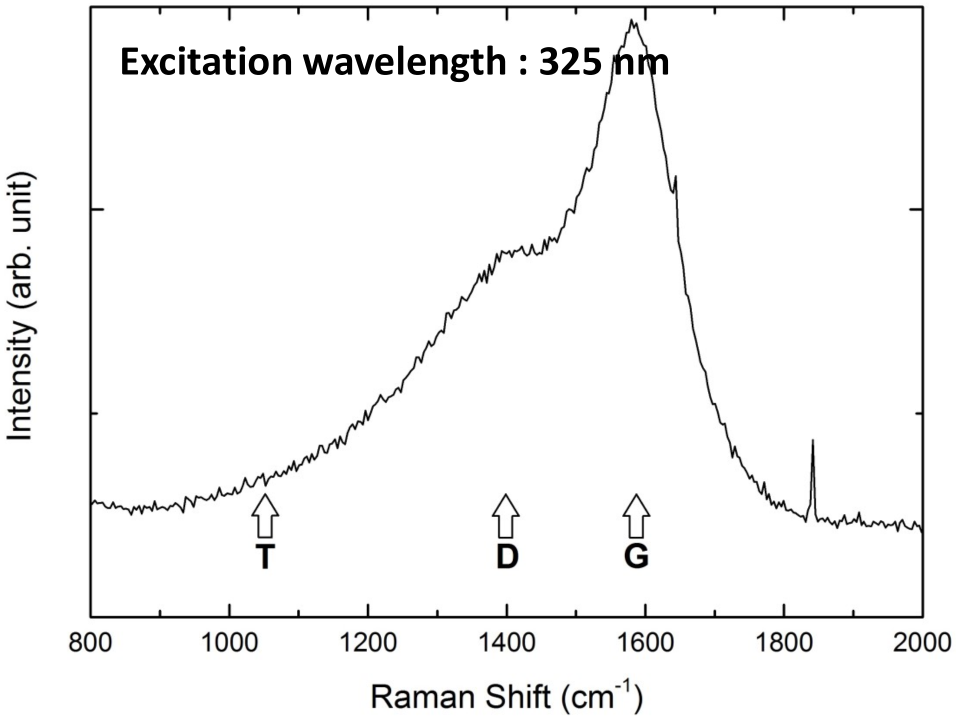
Under visible laser excitation

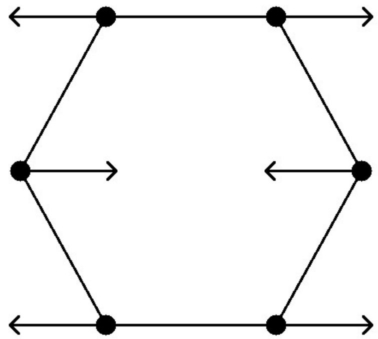
G peak (bond stretching of all pairs of sp^2 atoms in both rings and chains) → 1560 cm^{-1}

D peak (breathing modes of sp^2 atoms in rings) → 1360 cm^{-1}

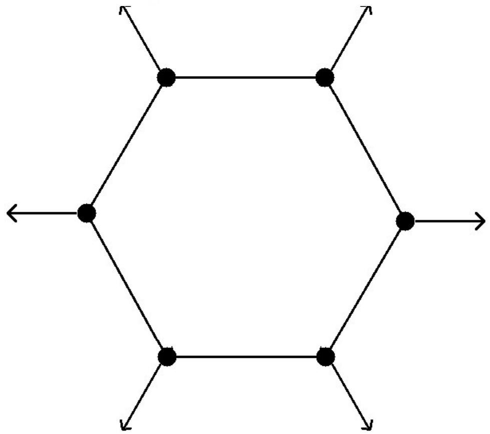
Under UV laser excitation

T peak (C–C sp^3 vibrations)→1060 cm^{-1}





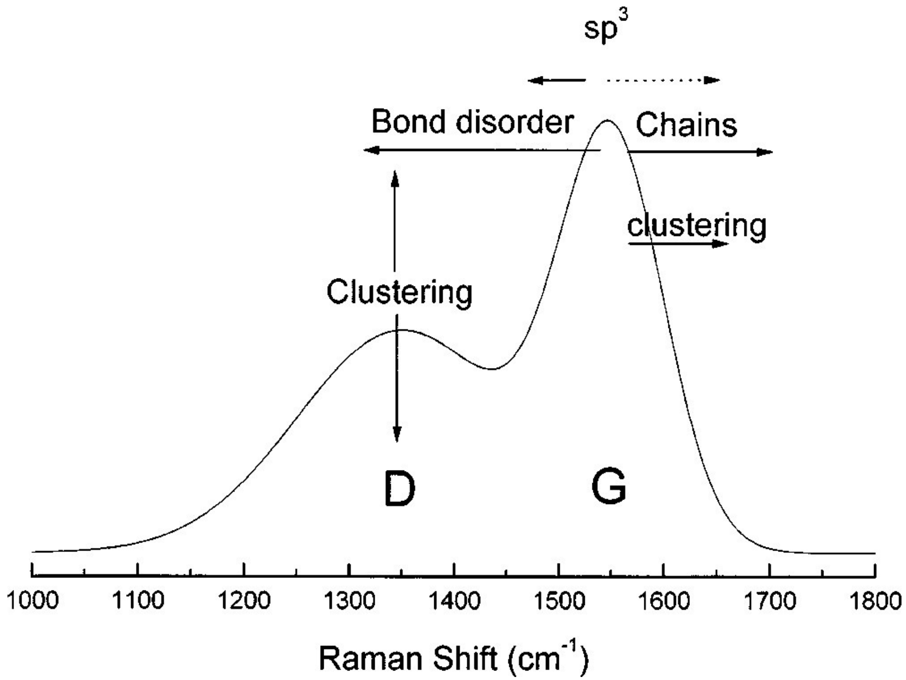
(A) E_{2g} , G peak mode

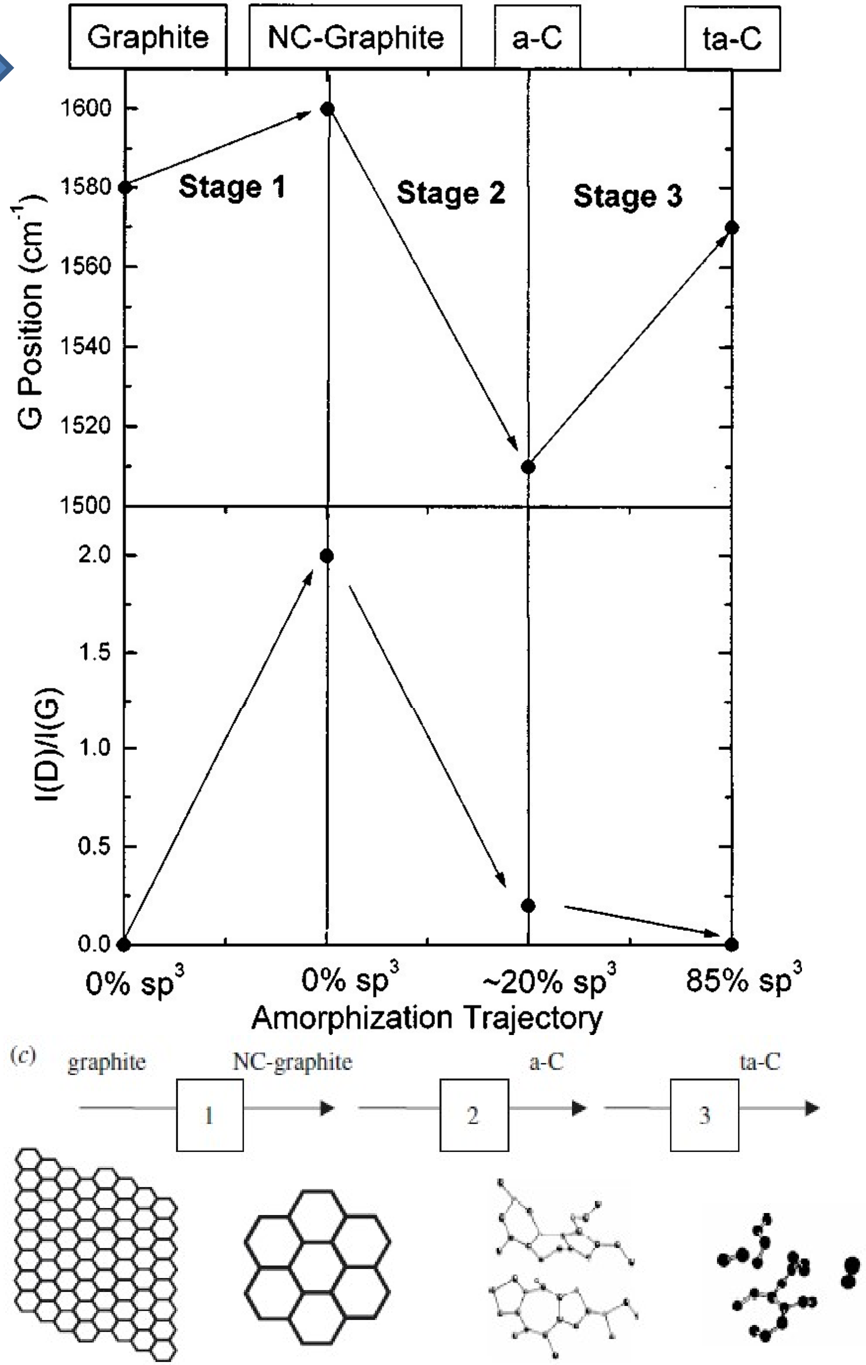


(B) A_{1g} , D peak mode

Three-stage model

Schematic model of how the D/G-peak cluster obtained with Raman spectroscopy changes with properties of the film.





sp^3 content
sp^2 clusters size
sp^2 cluster orientation

A. C. Ferrari and J. Robertson, Phil. Trans. R. Soc. Lond. A 2004 362, 2477-2512

First set of samples (on-axis; big spot area)

First problem: which fluence to reach the desidered sheet resistence value!

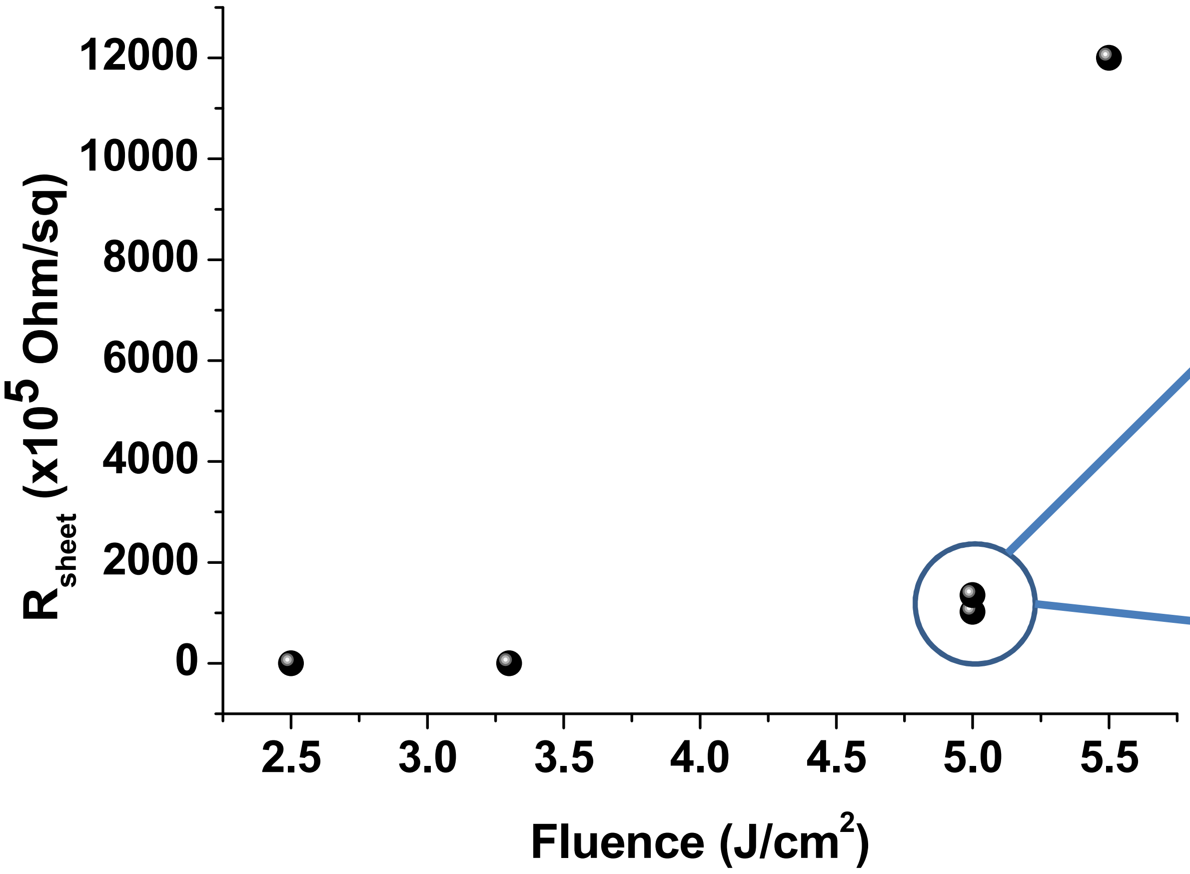
Influence of laser fluence (J/cm^2)

Samples	ρ_{sheet} (Ω/sq)	Fluence (J/cm^2)
#7	9.62×10^4	2,5
#8	1.2×10^5	3,3
#9	**1.02×10^8**	**5**
#10	1.2×10^9	5.5
#11	**1.35×10^8**	**5**

First set of samples (on-axis; big spot area)

First problem: which fluence to reach the desidered sheet resistence value!

Influence of laser fluence (J/cm^2): laser fluence vs sheet resistence



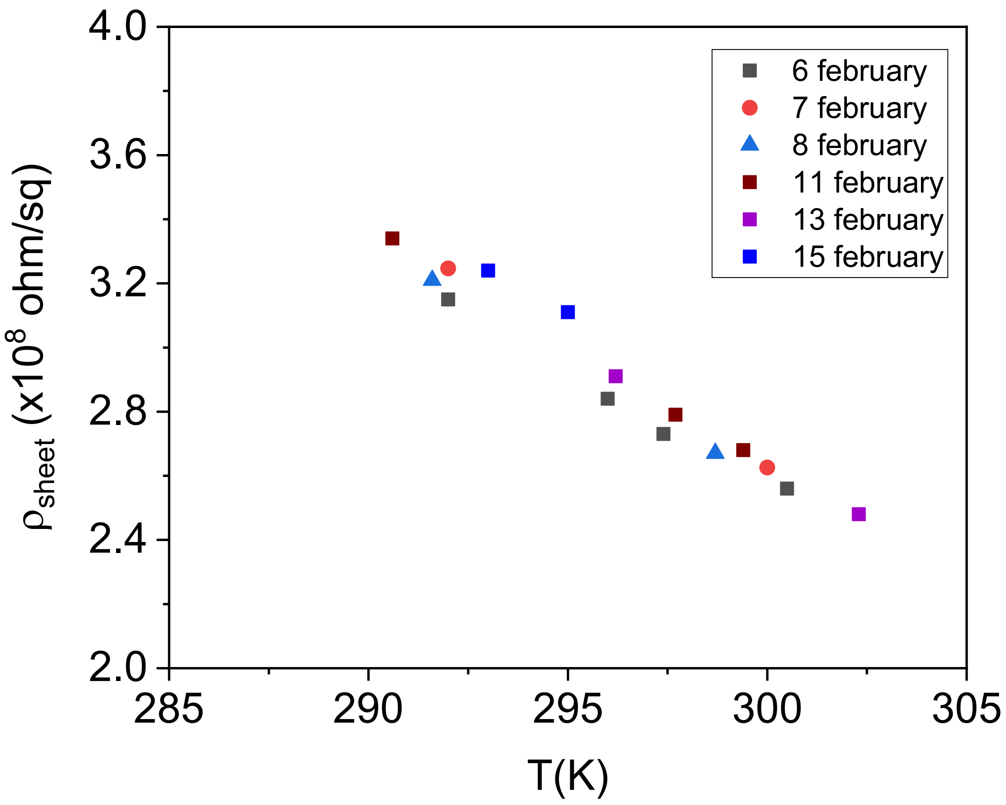
Right sheet resistance value (although a very narrow fluence window)!

Reproducible results

First set of samples (on-axis; big spot area)

First problem: which fluence to reach the desidered sheet resistence value!

sheet resistence stability

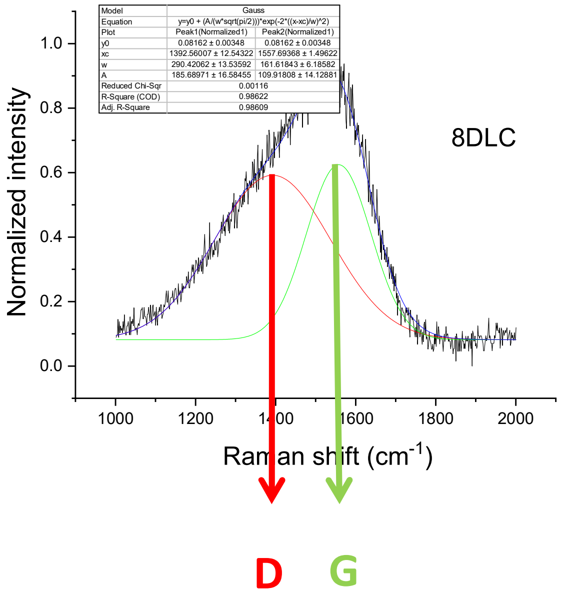


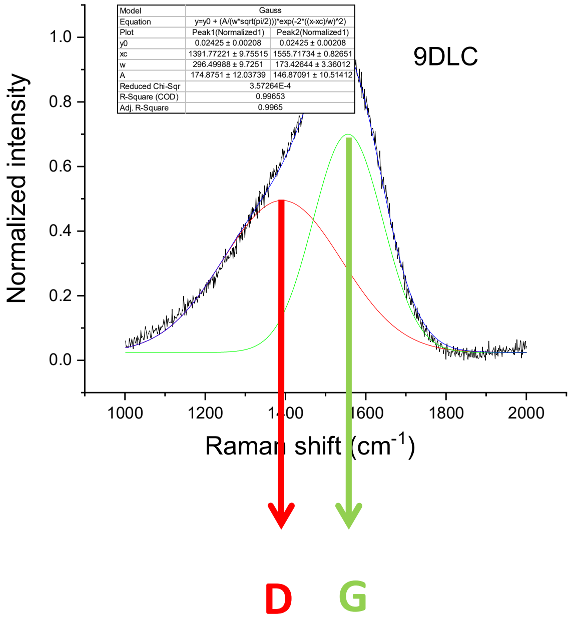
Good stability in time!

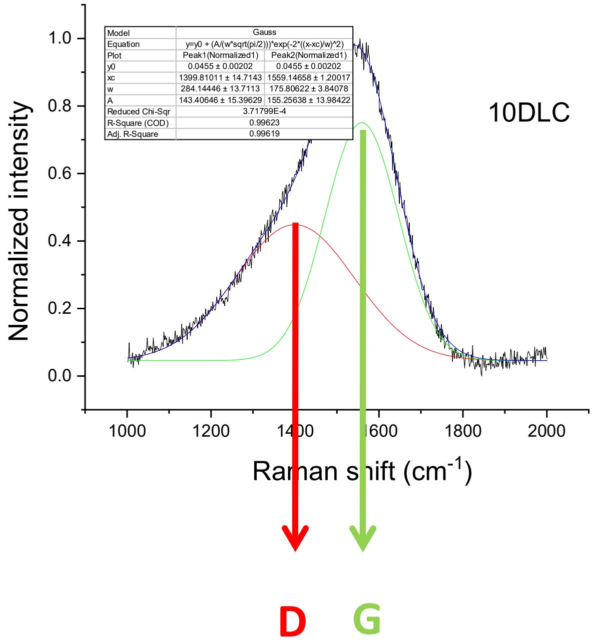
First set of samples (on-axis; big spot area)

First problem: which fluence to reach the desidered sheet resistence value!

Influence of laser fluence (J/cm^2): laser fluence vs I_D/I_G







$F = 3{,}3\ J/cm^2$
$\rho^* = 1.2 \times 10^5\ \Omega/sq$

$F = 5\ J/cm^2$
$\rho^* = 1.0 \times 10^8\ \Omega/sq$

$F = 5{,}5\ J/cm^2$
$\rho^* = 1.2 \times 10^9\ \Omega/sq$

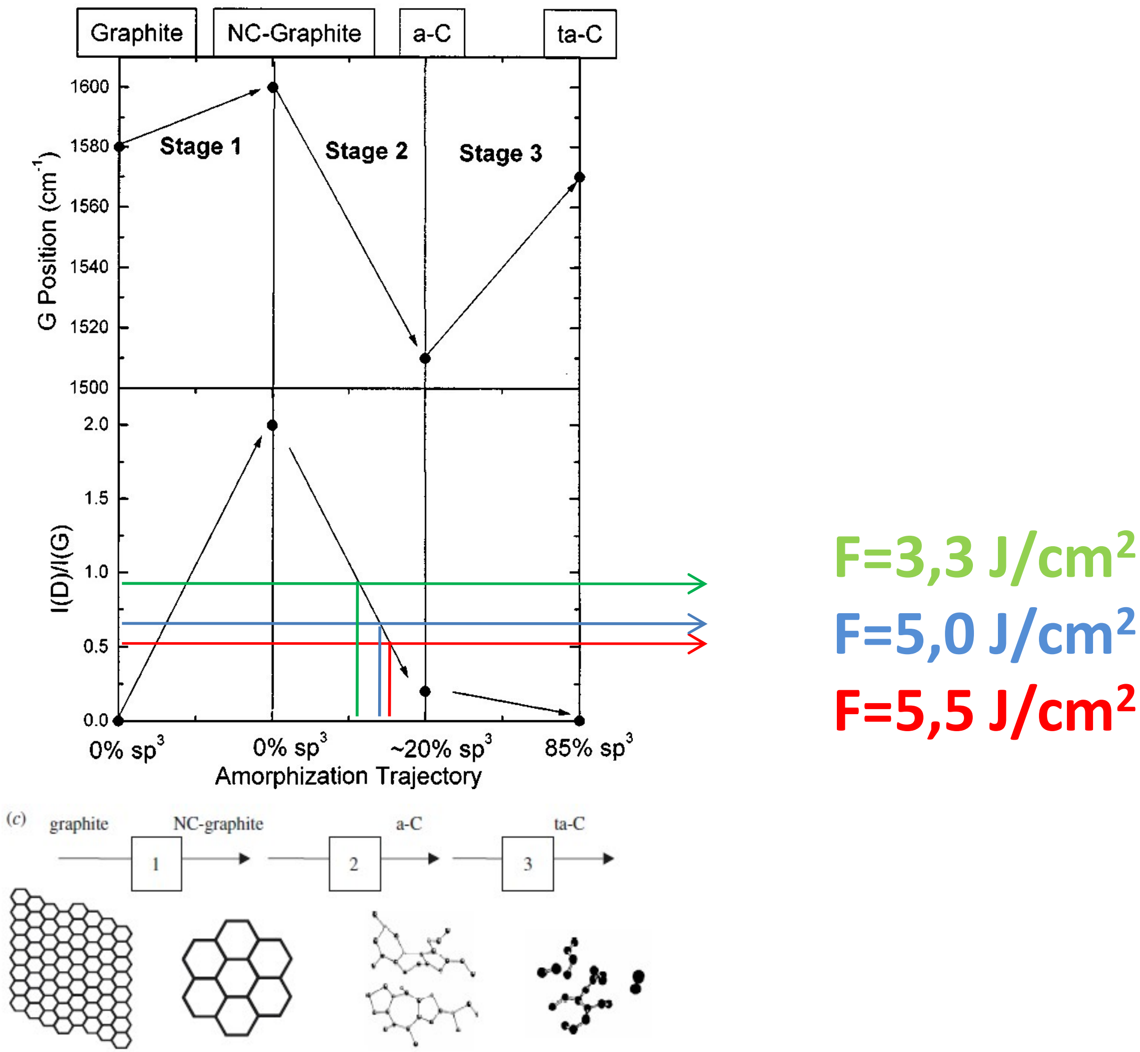
The intensity of I_G increases compatible with the presence of bigger sp_3 concentration

$^*\rho$= sheet resistence

First set of samples (on-axis; big spot area)

Influence of laser fluence (J/cm^2): laser fluence vs I_D/I_G

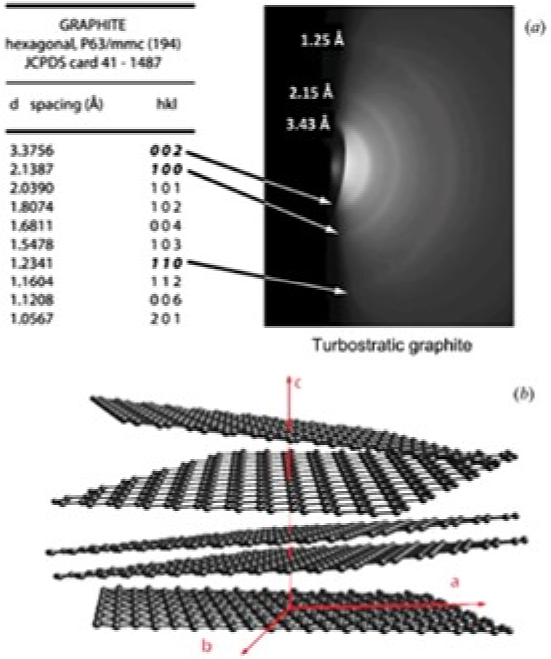
The sheet resistence desidered values are obtained with small percentage of sp^3 bonds

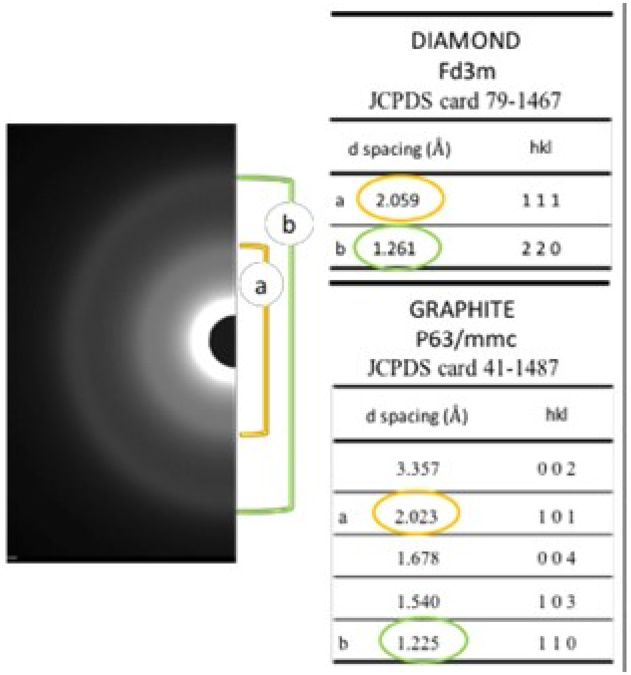


First set of samples (on-axis; big spot area)

First problem: which fluence to reach the desidered sheet resistence value!

Film structures (sample #9)





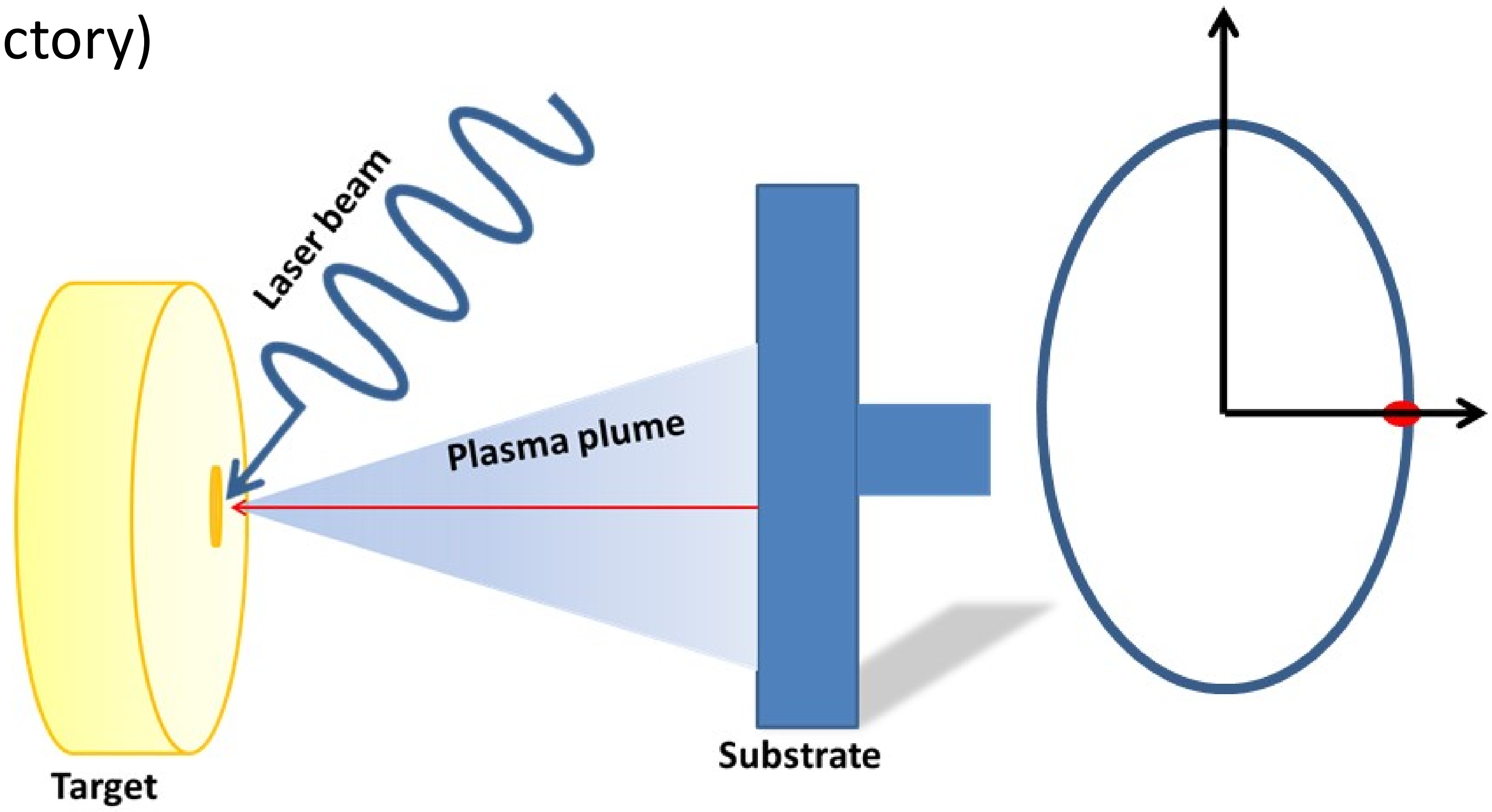
Two rings are clearly visible which are compatible with both the diffraction maxima 111 and 220 of the diamond, and with the diffraction maxima 101 and 110 of the graphite.

This can be interpreted as an overlapping of nano-graphene (missing the ring corresponding to the planes 002 of the graphite) and nanodiamond.

Second set of samples (off-axis + substrate motion; big spot area)

Second problem: how to obtain uniform films?

Off-axis configuration and substrate motion (circular vs elliptical trajectory)



Second set of samples
(off-axis + substrate motion; big spot area)

Samples	ρ_{sheet} (Ω/sq)	Fluence (J/cm²)	Substrate movement
#12	0.128×10^8	5	Circle (diameter: 2 cm)
#13	0.13×10^8	5	Circle (diameter: 2 cm)
#15	3.38×10^6	5	Circle (diameter: 1,6 cm)
#14	9.95×10^{10}	5	Circle (diameter: 1 cm)

For a fixed laser fluence value, the sheet resistence is strongly dependent on the substrate trajectory

Fluence value selected by first set of experiment

Non uniform distribution of elements in the plasma plume produced by the laser-graphite interaction

Second set of samples (off-axis + substrate motion; big spot area)

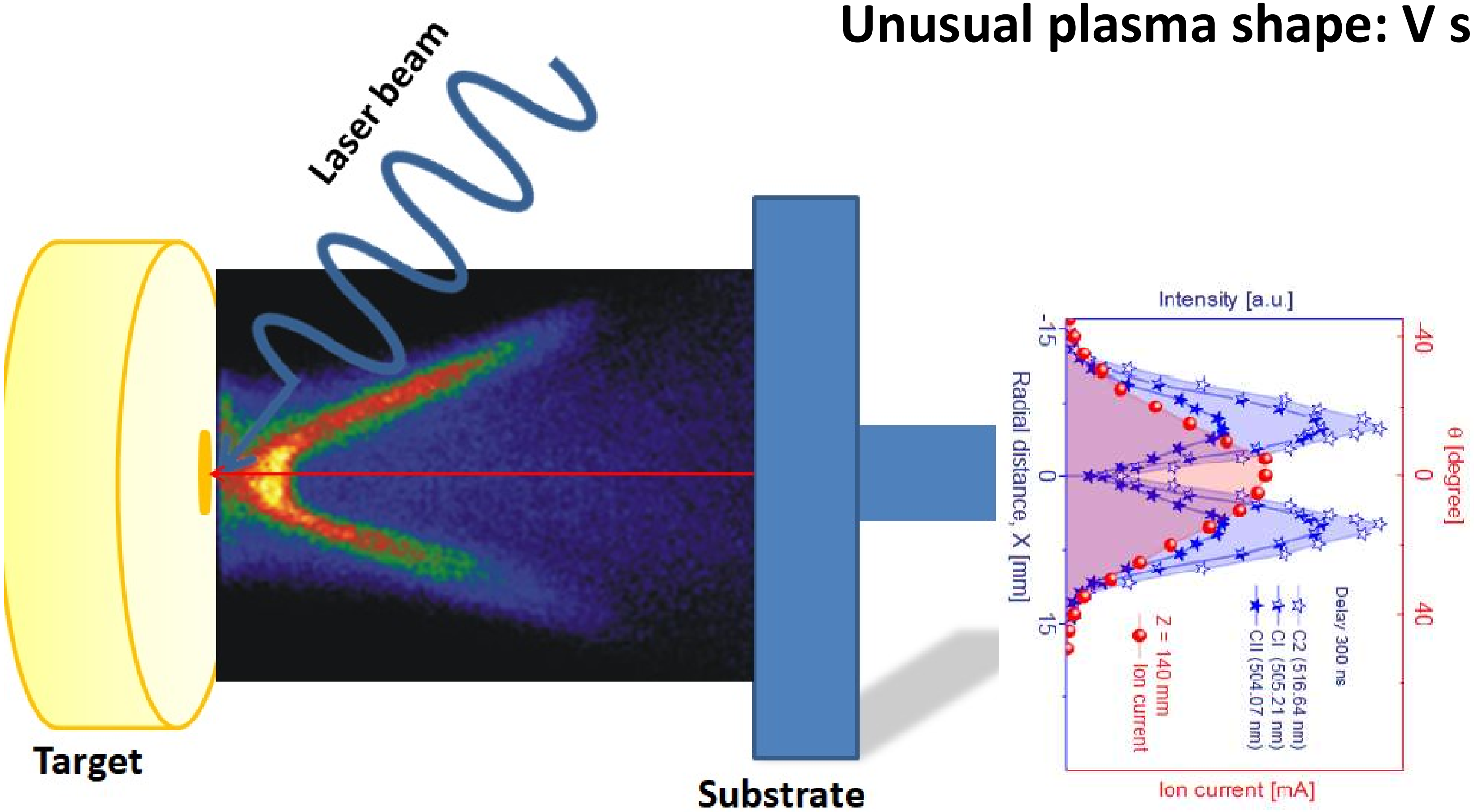
Samples to investigate the behaviour during etching conditions for detectors fabrication with differnt sheet resistence values (10-1000 Mohm/sq)

Sample	Sheet Resistence (Ω/sq)
#20	1.54 x 10^8
#19	1.29 x 10^8
#18	1.1 x10^9
#17	1.01 x 10^9
#16	1.35 x 10^7
#13	7.63 x 10^6

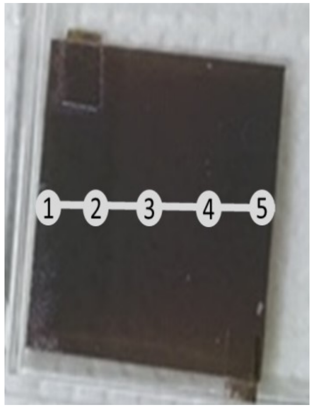
Second set of samples (off-axis + substrate motion; big spot area)

Reason for non uniform films

Unusual plasma shape: V shape

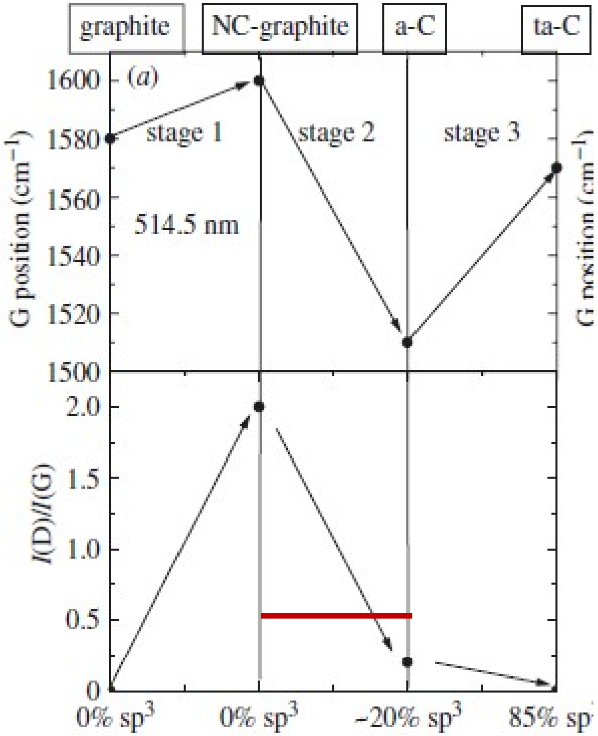


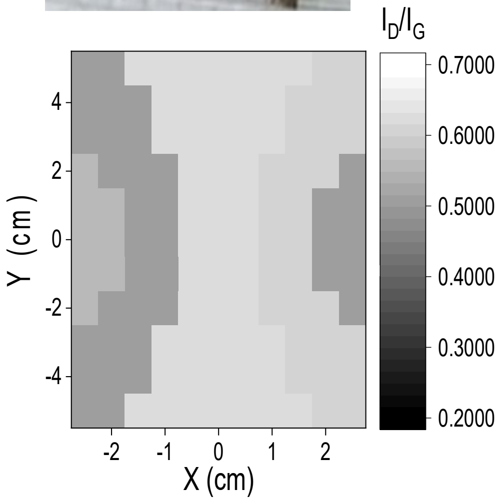
C. Ursu, P. Nica, C. Focsa, Applied Surface Science 456 (2018) 717–725



Raman analysis

Sample region	I_D/I_G	r (Ω/sq)
1	0.56	5.7×10^7
2	0.50	
3	0.63	1.7×10^8
4	0.60	
5	0.51	4.6×10^7





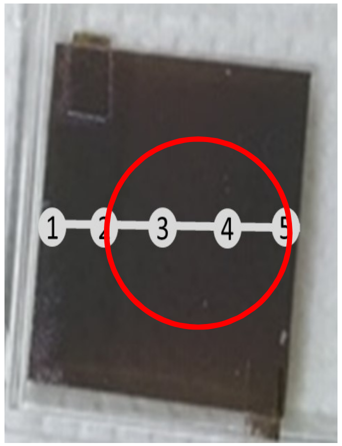
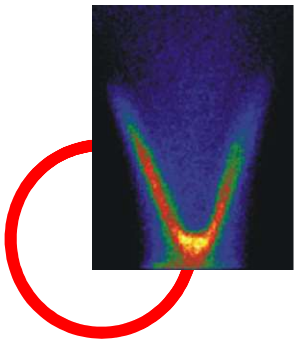
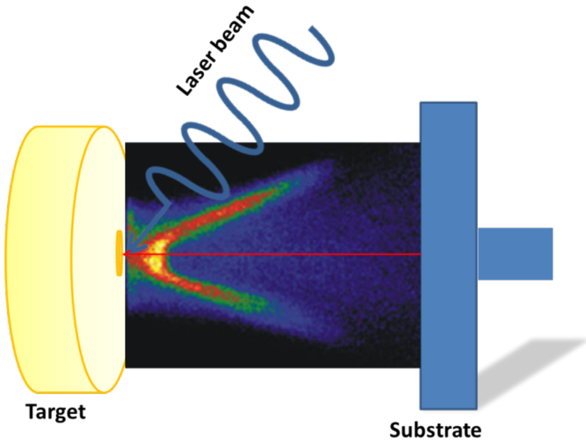


Figura composizione plume



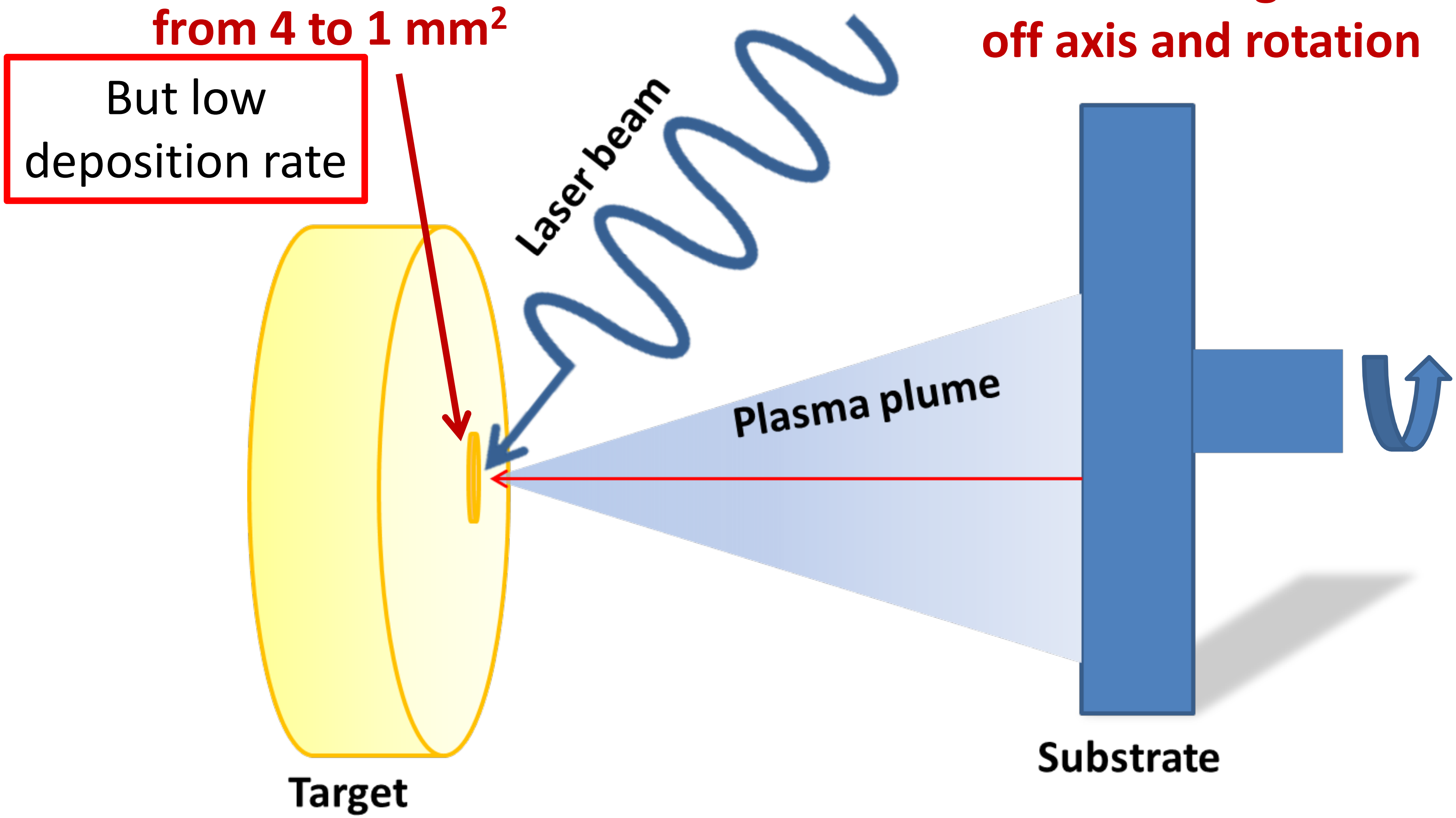


d_{TS}(cm)	A_{Spot} (mm^2)	N_p	F(J/cm^2)
5.5	3.3	7698	6.4

V- shape plasma: how to recover the usual plasma shape?

Decreased laser spot area: from 4 to 1 mm^2

Substrate configuration : off axis and rotation



Third set of samples
(off-axis + substrate rotation; small spot area)

Target: pyrolytic graphite

KrF excimer laser: wavelength λ = 248 nm, pulse width τ = 20 ns, frequency: f=10 Hz

Laser Fluence: 5,5 $\div$ 20 J/cm^2

Target-substrate distance: d_{TS}: 55 $\div$ 45 mm

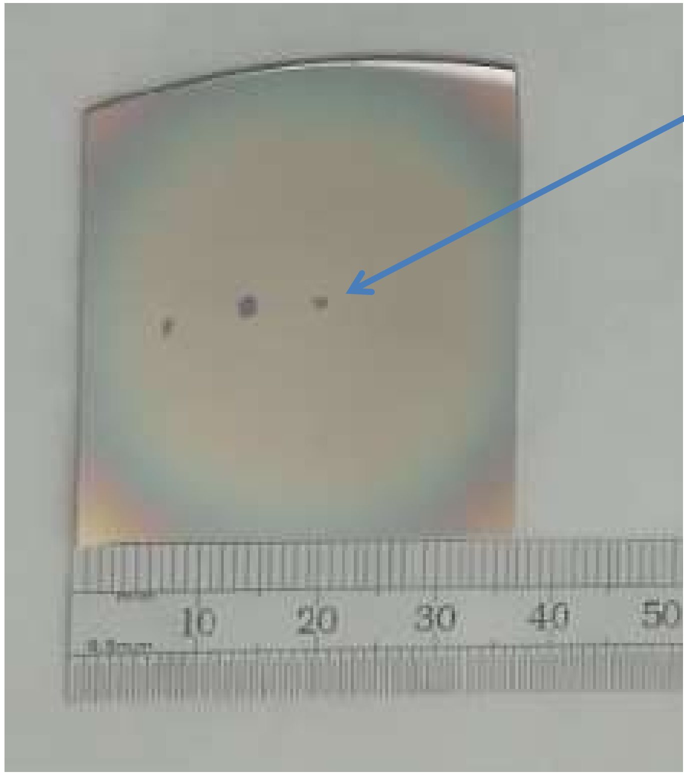
Background pressure: $\sim 10^{-5}$ Pa

Laser spot area: $\sim$ 1 mm^2

Substrates: <100> Si,

Number of laser pulses: 28000 $\div$ 35000

Third set of samples
(off-axis + substrate rotation; small spot area)

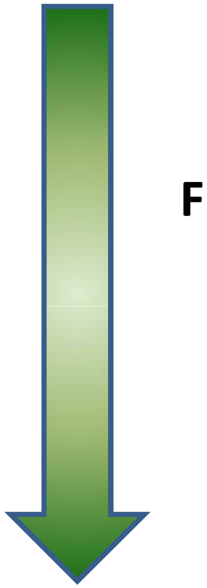


Dot for thickness measurements

GOOD UNIFORMITY ON A "BIG AREA"

Third set of samples
(off-axis + substrate rotation; small spot area)

Samples	Fluence (J/cm^2)	Sheet resistance (Ω/sqr)	I_D/I_G
# 36	5.5	>10^12	0.5
# 38	6.8	7.0*10^5	1.5
# 33	9.6	5.0*10^4	1.54
# 34	18.3	3.8*10^4	2



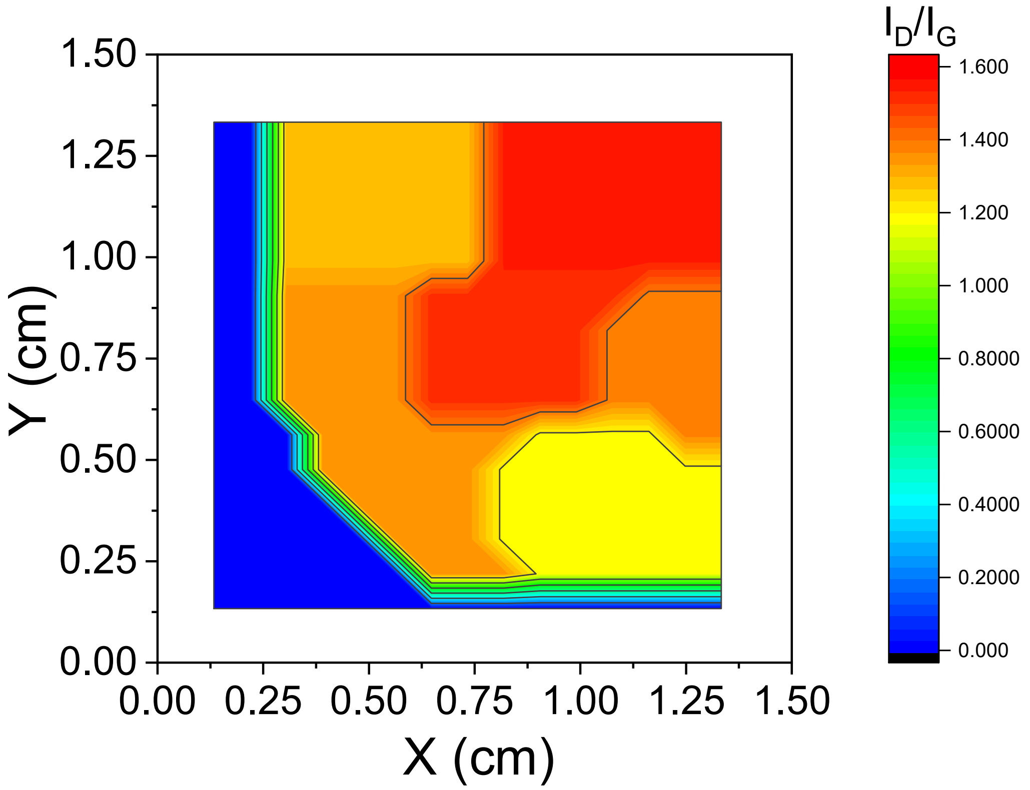
Increasing the laser fluence values sheet resistance and graphite contribution increase

Decreasing the laser fluence values below 5,5 J/cm^2 is such to have very low deposition rate!!

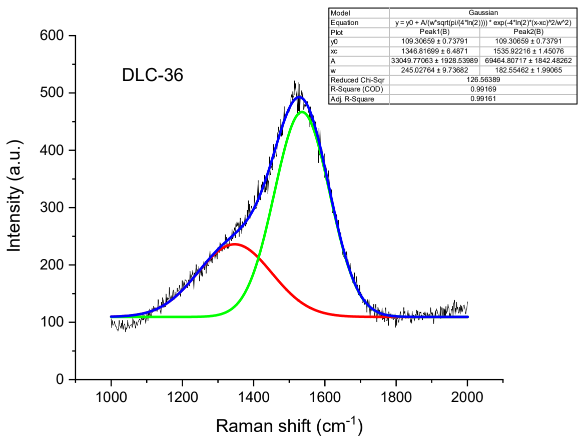
Third set of samples
(off-axis + substrate rotation; small spot area)

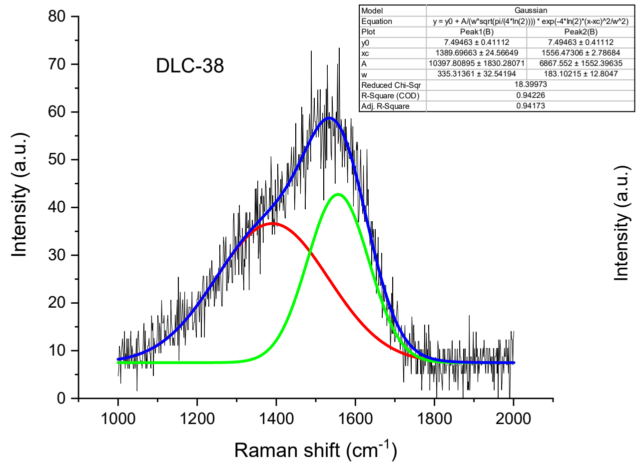
Raman map

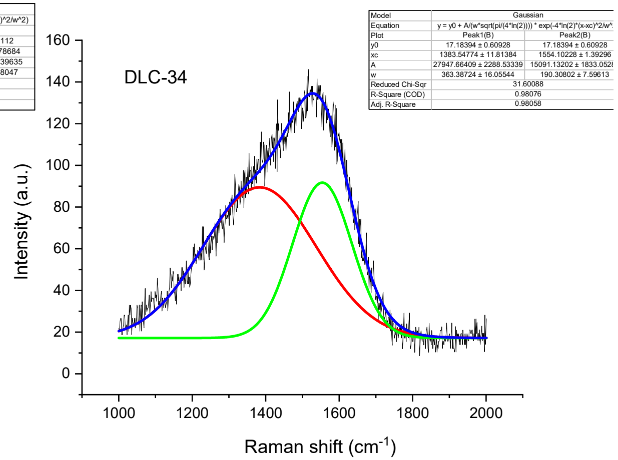
Sample #38
ρ= 7.0*10^5
ID/IG=1,5



Third set of samples
(off-axis + substrate rotation; small spot area)

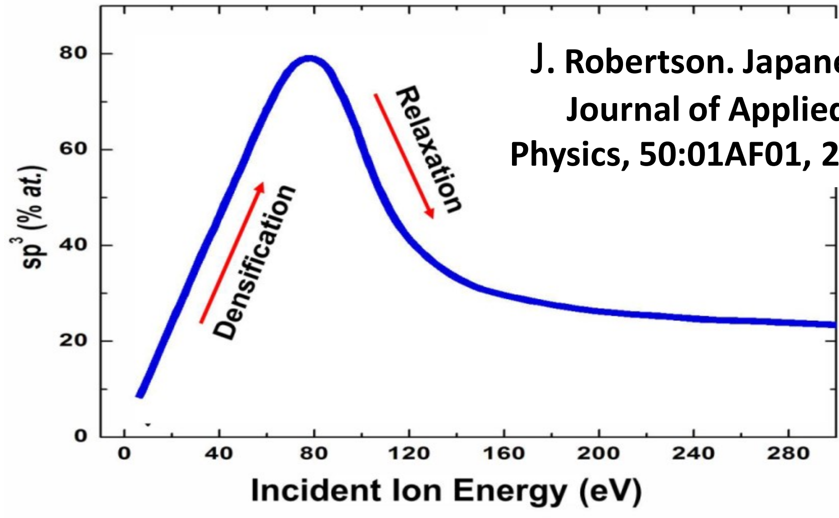






F

Increasing fluence beyond a critical threshold fluence drives sp^3 to sp^2 trasformation according to the subimplantation model



J. Robertson. Japanese Journal of Applied Physics, 50:01AF01, 2011.

Third set of samples
(off-axis + substrate rotation; small spot area)

To better understand film properties:

Electrical measurements (transport measurements);

XPS (X-ray Photoelctron Spectroscopy) to evaluate the exact sp^3 content

Micro Raman;

AFM (Atomic Force Microscopy) to evaluate sample topography

CONCLUSIONS

Films of DLC have been deposited by PLD. The laser fluence is the most critical laser parameters

What about our goals?

- ✓ Uniformity 
- ✓ Adhesion 
- ✓ Sheet resistance values 

Near to the desidered values for MPGD but a very narrow fluence window to obtain the desidered sheet resistence value!

Next depositions changing the laser wavelenght: ArF laser beam (193 nm) + annealing procedure to try to relax the stress