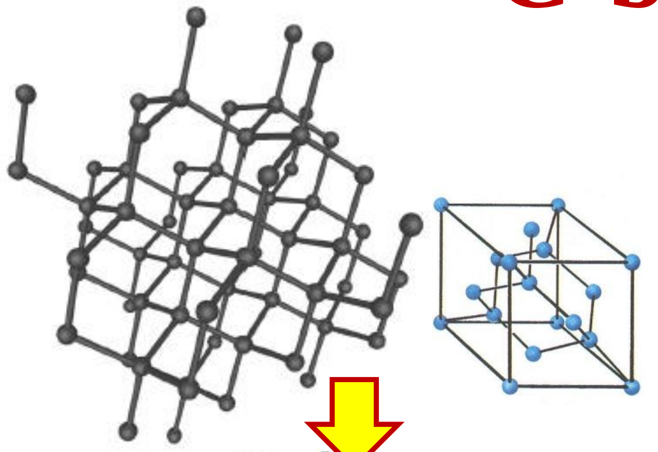
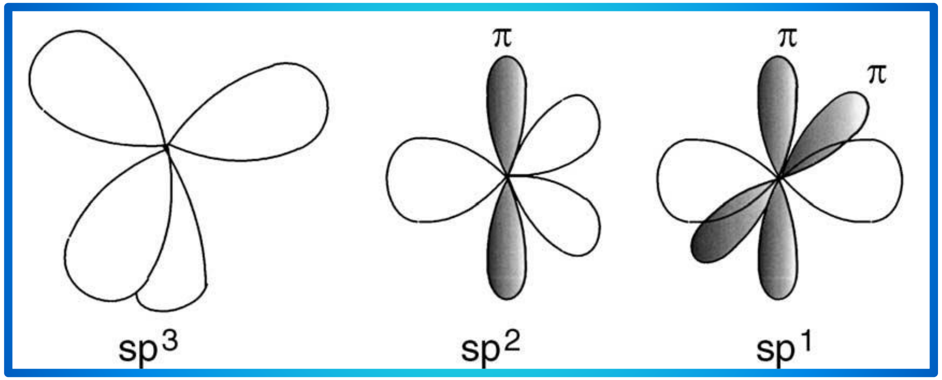
Diamond-like Carbon (DLC) films deposited by Pulsed Laser Deposition (PLD)

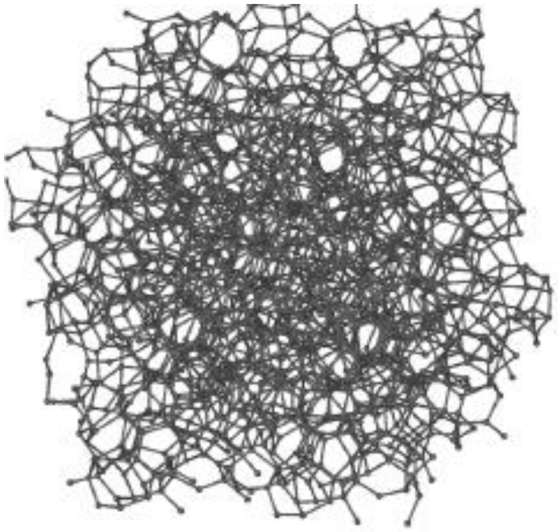
C-based materials

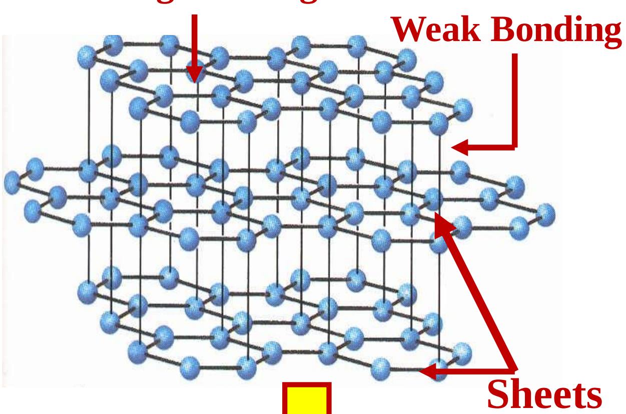




Diamond: 100 % sp^3 bonded carbon

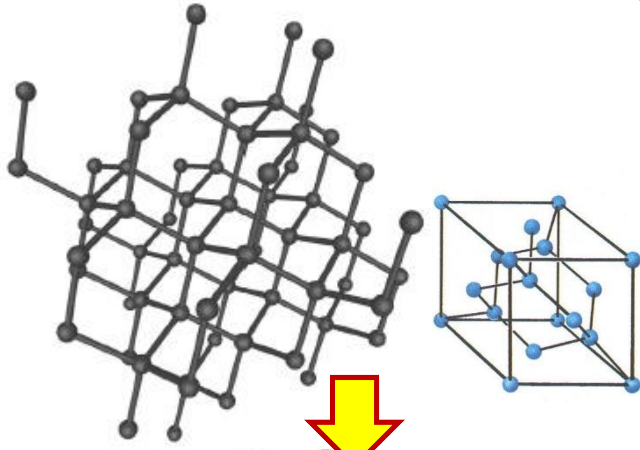
Amorphous C: sp^3 + sp^2



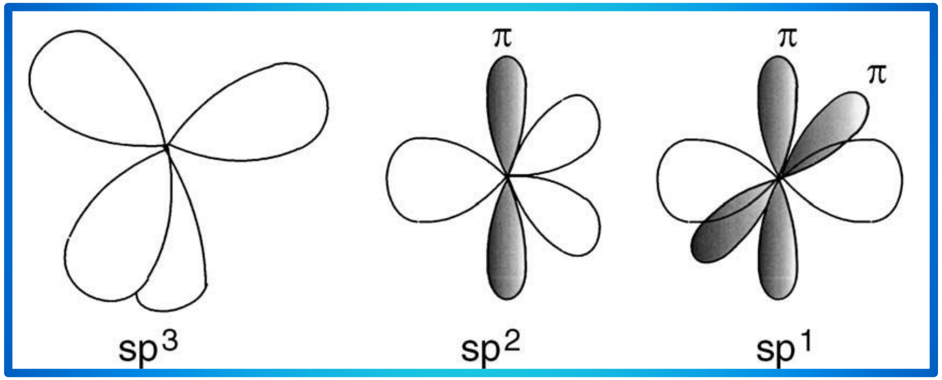


Graphite: 100 % sp^2 bonded carbon

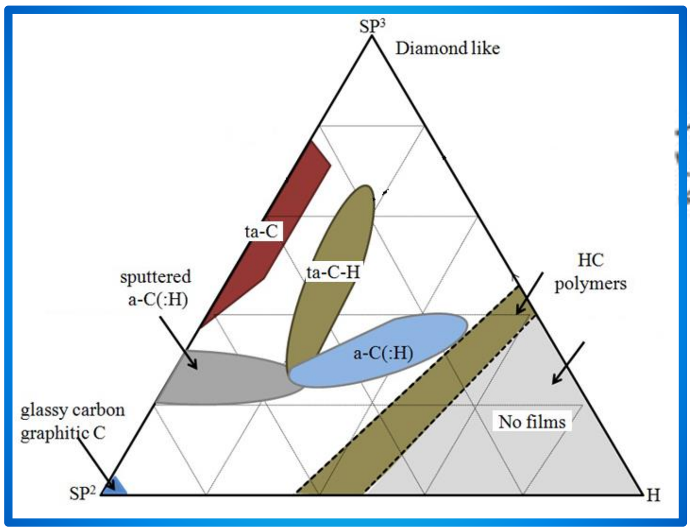
DLC: general properties

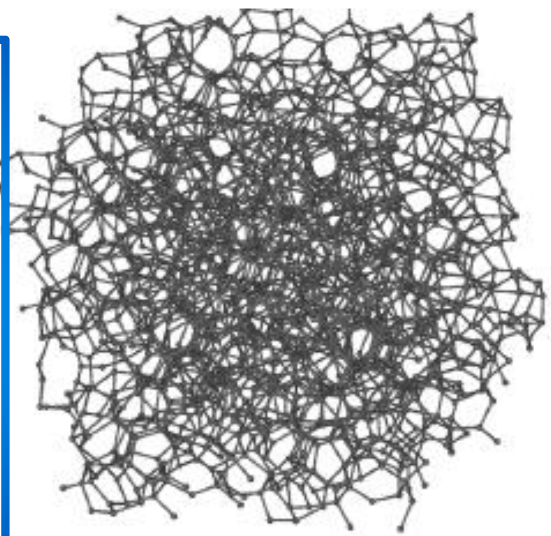


Diamond: 100 % sp^3 bonded carbon



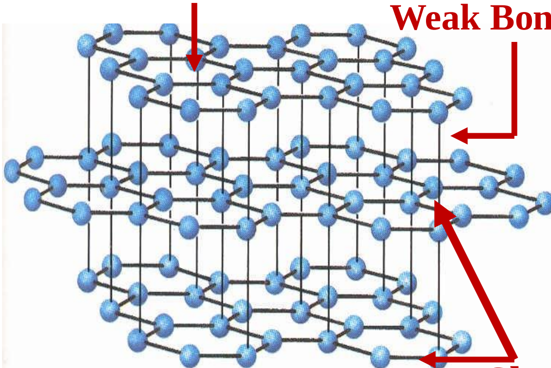
Amorphous C: sp^3 + sp^2





σ bonds
Strong Bonding

π bonds
Weak Bonding

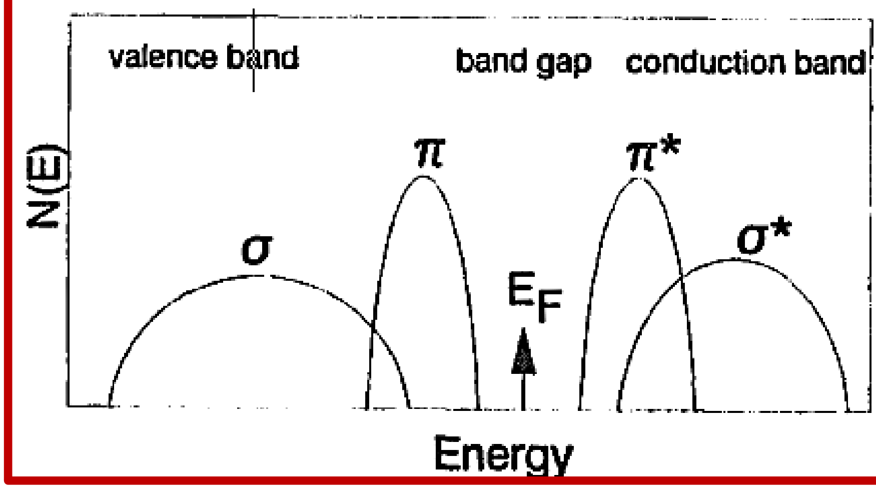


Sheets

Graphite: 100 % sp^2 bonded carbon

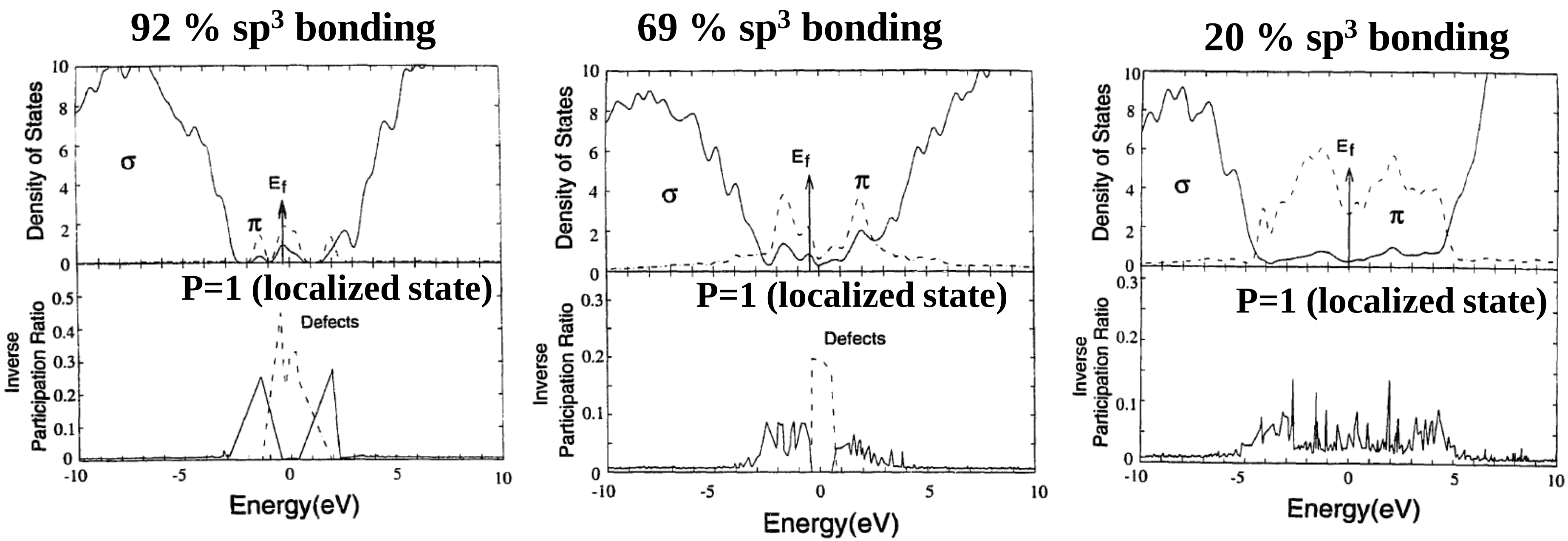
DLC: metastable C-phase containing a mixture of sp^3 (> 60%) and sp^2 C-C bonds

C-based materials: band structure



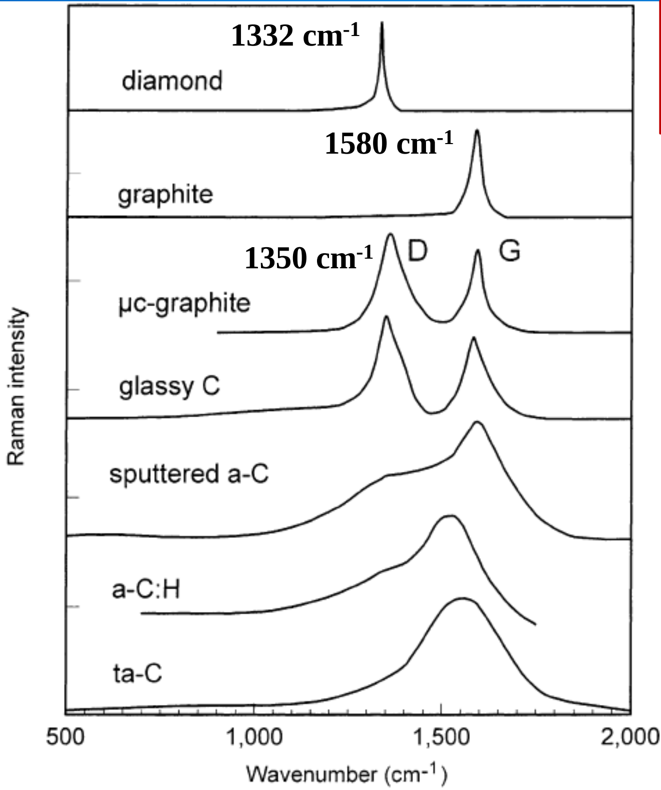
sp^3 → tetrahedral σ bonds
sp^2 → trigonal σ bonds and weak π bonds

σ, σ* → deep valence and conduction (extended) states
π, π * → band edge valence and conduction (localized) states
Band gap is formed by π and π * states



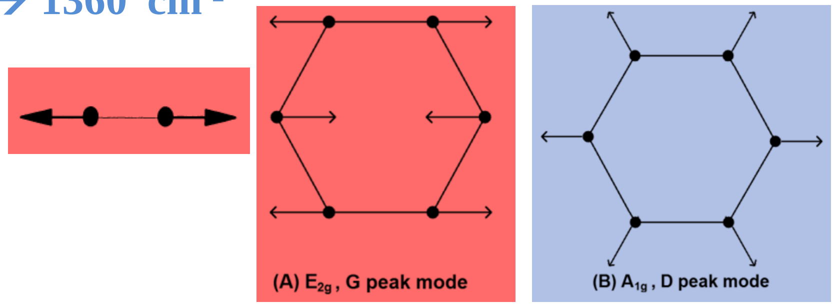
J. Robertson, Electronic structure of diamond-like carbon, Diamond and Related Materials 6 (1997) 212-218

DLC: Raman spectroscopy



Under visible laser excitation:

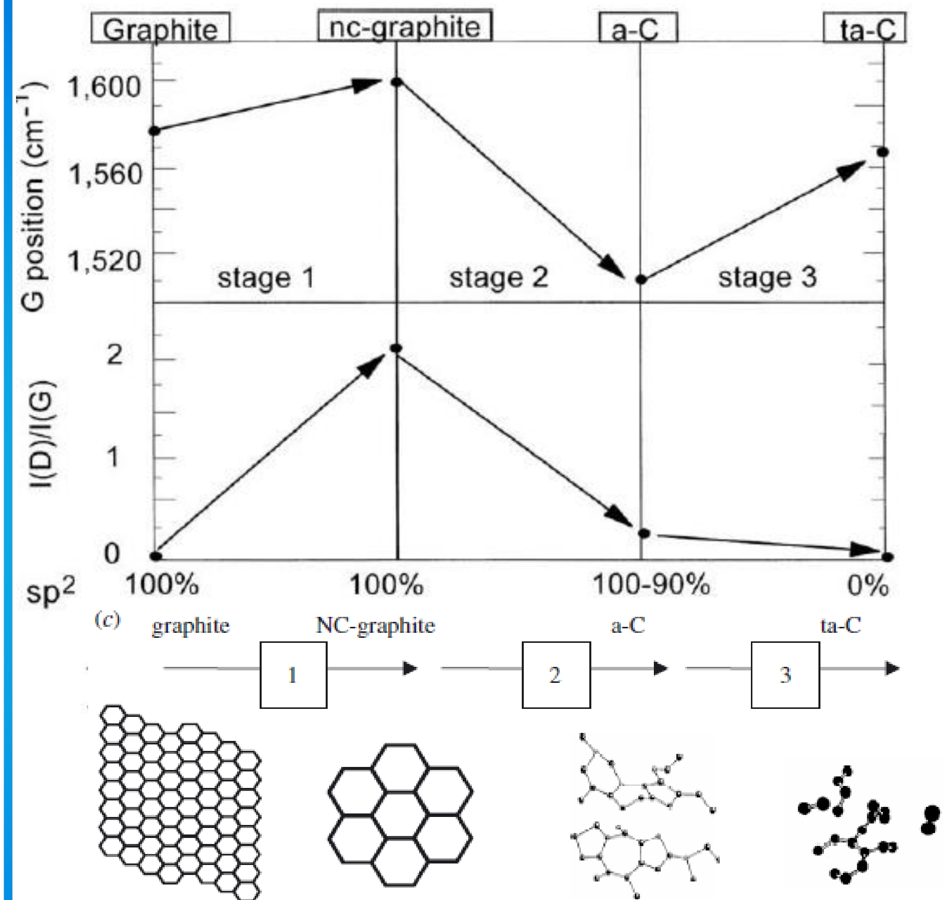
- **G peak** (bond stretching of all pairs of sp^2 atoms in both **rings** and **chains**) → **1560 cm^{-1}**
- **D peak** (breathing modes of sp^2 atoms in **rings**) → **1360 cm^{-1}**



Under UV laser excitation

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

Three-stage model



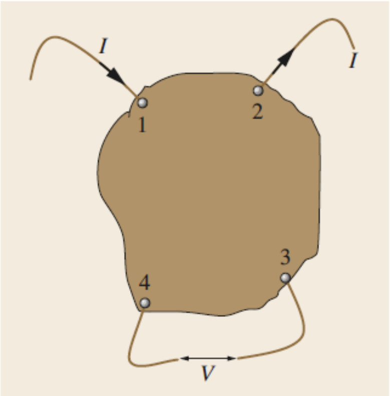
A. C. Ferrari and J. Robertson,
Phil. Trans. R. Soc. Lond. A 2004 362, 2477-2512

Decreasing I_D/I_G→ increasing sp_3

DLC by PLD: electrical measurement technique

Van der Pauw Method to measure electrical resistivity on bulk/films

4-probe technique that involves applying a current and measuring a voltage using four small contacts on a circumference of a flat, arbitrarily shaped sample.



Test Procedure:

- **Force Current (I) on adjacent terminals**
- **Measure Voltage (V) on an opposite pair of adjacent termin**
- **Repeat measurements around sample**
- **Calculate resistivity**

$$\rho = \frac{\pi\delta}{\ln 2}\left(\frac{R_{12,43} + R_{23,14}}{2}\right) f\left(\frac{R_{12,43}}{R_{23,14}}\right)$$

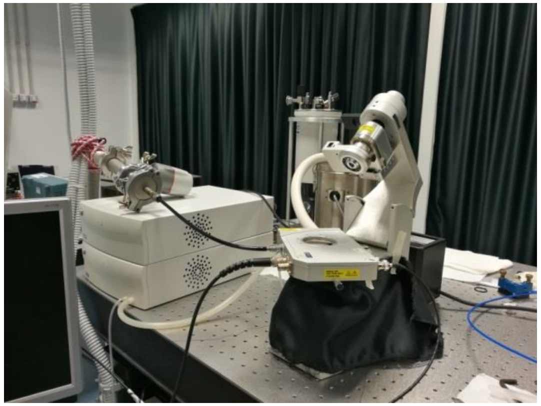
The van der Pauw contact configuration is also used to measure carrier mobility and concentration by Hall effect (in a magnetic field).

Ohmic contacts are implicitely required ! This can be tricky on high resistivity samples.

Electrical Resistivity at ELPHO
(ELectrical and PHOtoelectrical Laboratory, a CNR joint lab)

- **In the ELPHO Lab it is available a Hall Measurement System (Ecopia HMS-3000): van der Pauw system for measuring electrical resistivity from 10^{-4} to 10^{7} Ω cm, and, in a B=0.5T, the carrier concentration and mobility**.

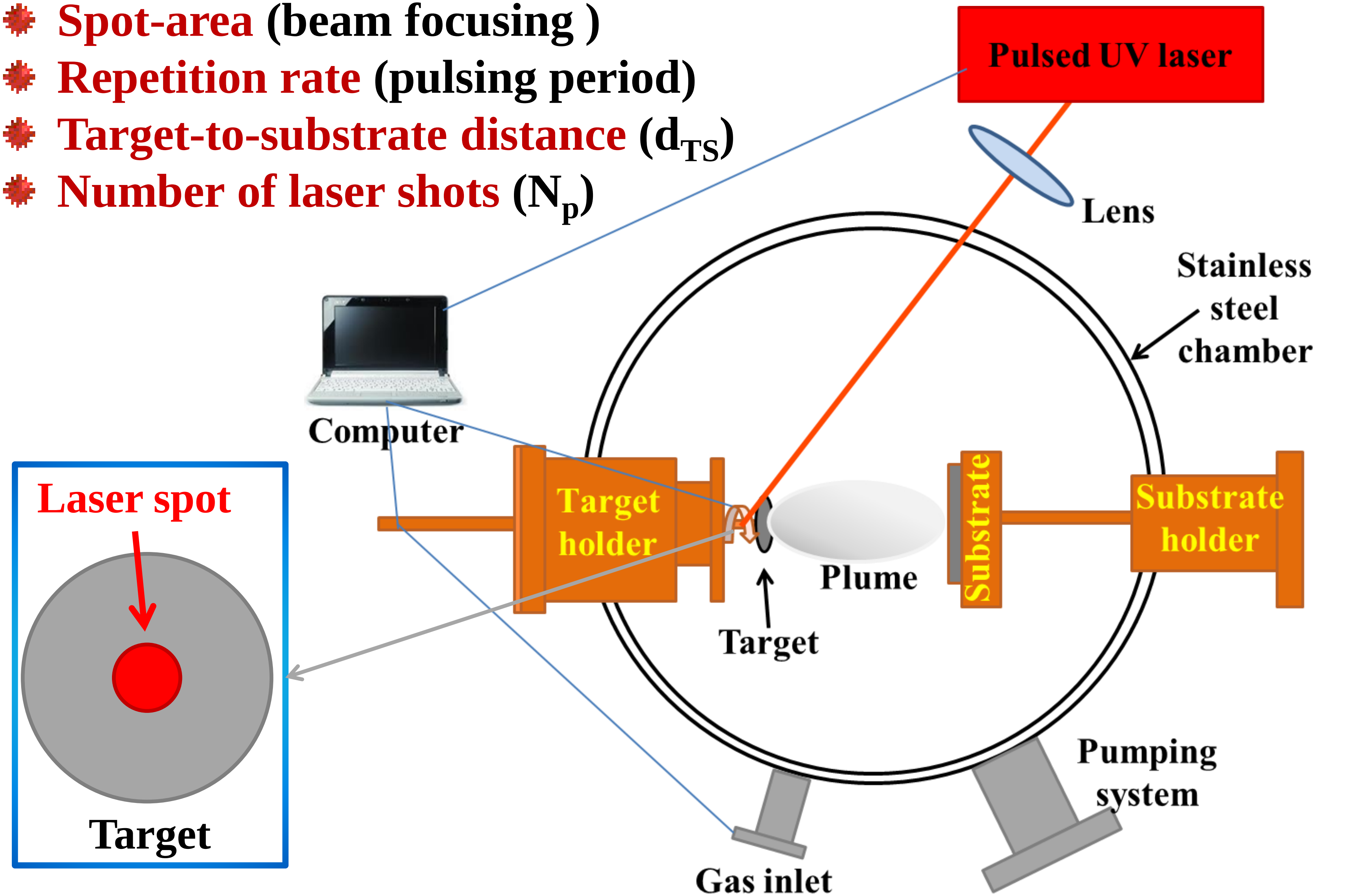
- **In the temperature range 77K-600K we use a liquid nitrogen thermal stage and a vacuum chamber (Linkam)**



- **To measure high resistivity we use multi Source-Monitor-Unit system Agilent B1500 (input resistance >10^{13} Ω) with guarded (Triax) cables.**

PLD: working principle and apparatus

- **Fluence** (energy per unit surface)
- **Spot-area** (beam focusing)
- **Repetition rate** (pulsing period)
- **Target-to-substrate distance** (d_{TS})
- **Number of laser shots** (N_p)



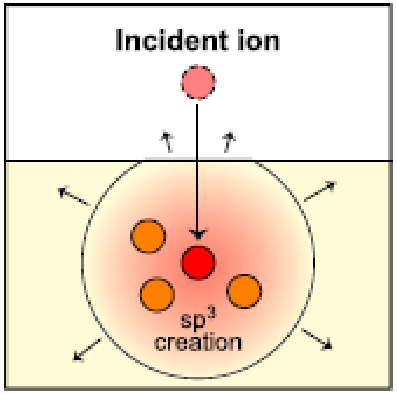
DLC: why PLD?

Hydrogen-free C-materials

The incorporation of H passivates the dangling covalent bonds of C (C-H bonds) and forms defect states close to E_F
H:DLC is thermally and electrically less stable than hydrogen-free DLC (above 250-300 °C evolution of H from the film and conversion of sp^3 C-C bonds to sp^2 C-C bonds).

Hyper-thermal deposition flux in high-vacuum

PLD avoids precursor gases containing H and lets grow at low temperature (25-100 °C) by exploiting energetic (60–100 eV) deposition flux containing C-species (ions, neutrals, dimers, clusters) favoring the formation of sp^3-C bonds (→ C^+).
PLD allows to produce the highest percentage of sp^3 bonds (up to 85-90%) *[Diam. Relat. Mater. 8, 1659 (1999)]* **→ high degree of diamond-like properties.**

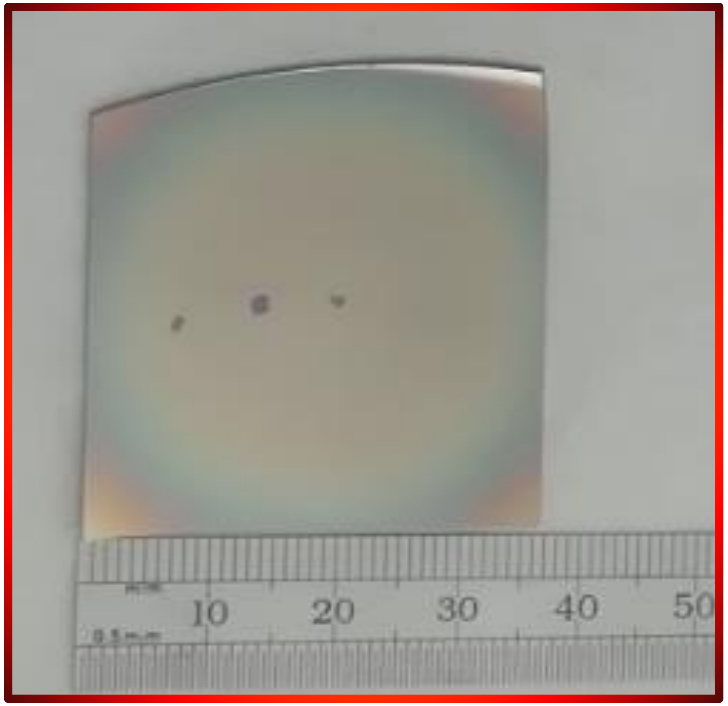


DLC by PLD: aims and characterizations

- **Deposition over a large area & film uniformity**
- **Desired resistivity values**

  Sheet resistance: 10 ÷ 100 MΩ/sqr

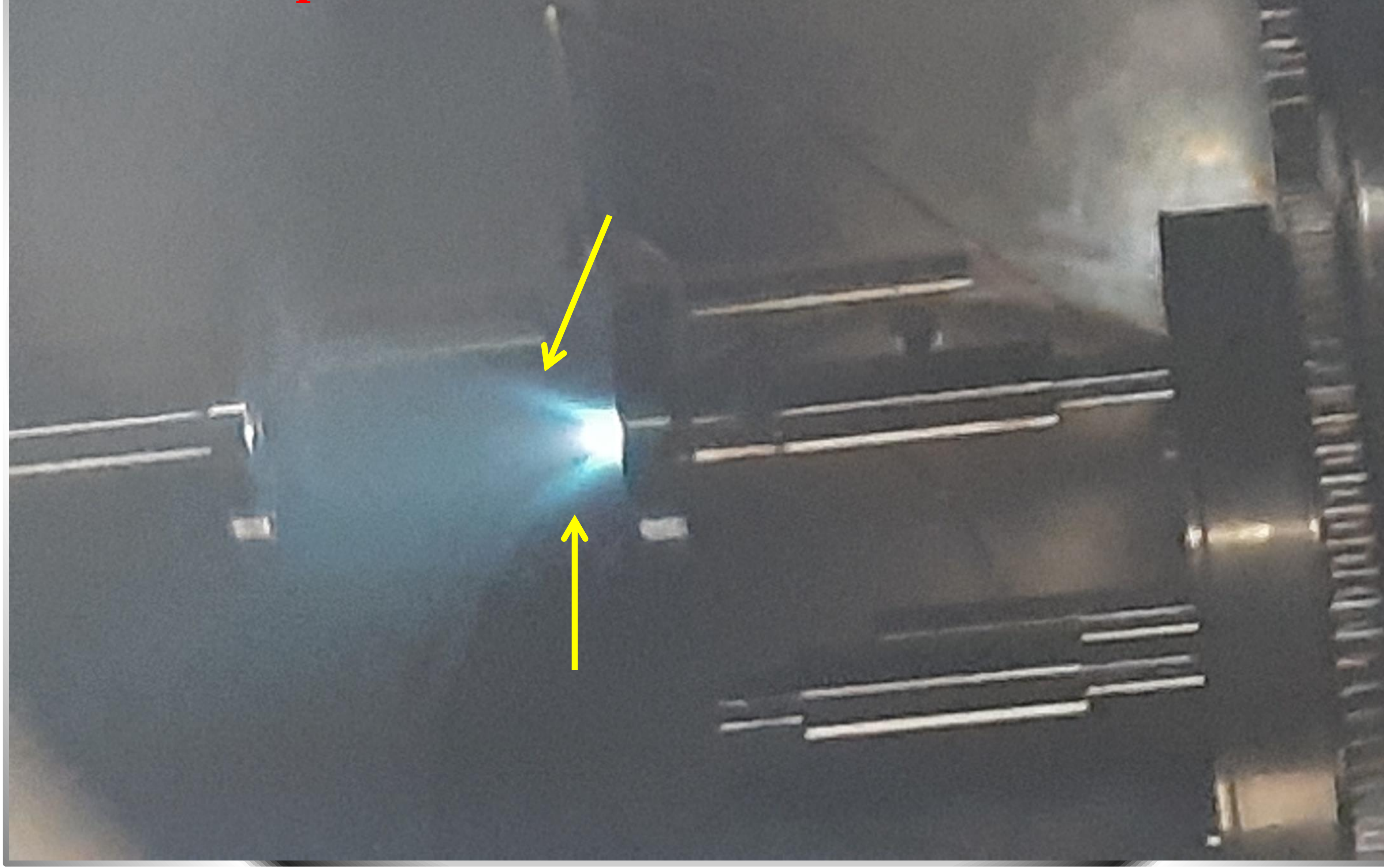
- **Deposition geometry**
- **Spot area**
- **Fluence tuning**



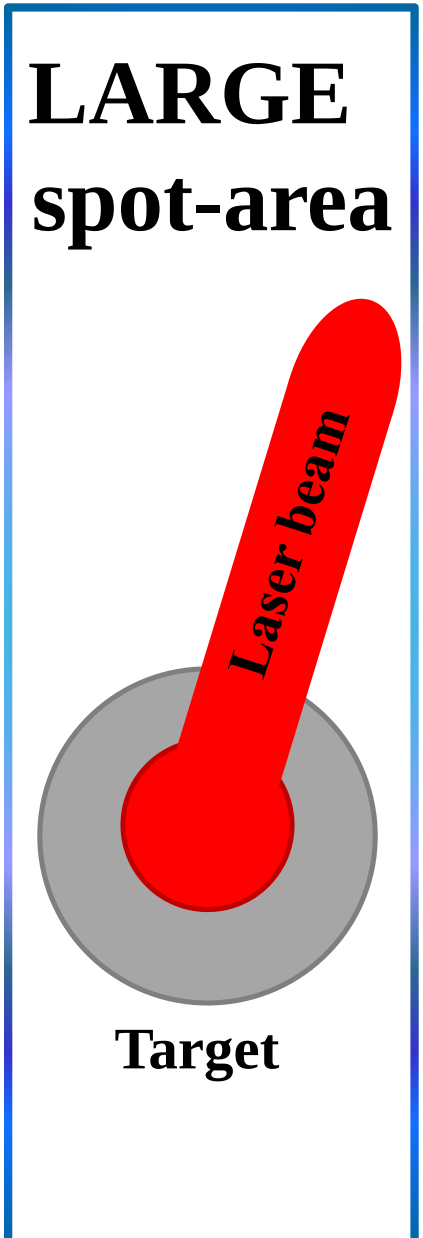
- **Characterizations**
- **Raman spectroscopy**
- **SEM and TEM**
- **XPS analysis**
- **Spectrophotometric analysis**
- **Electrical properties**

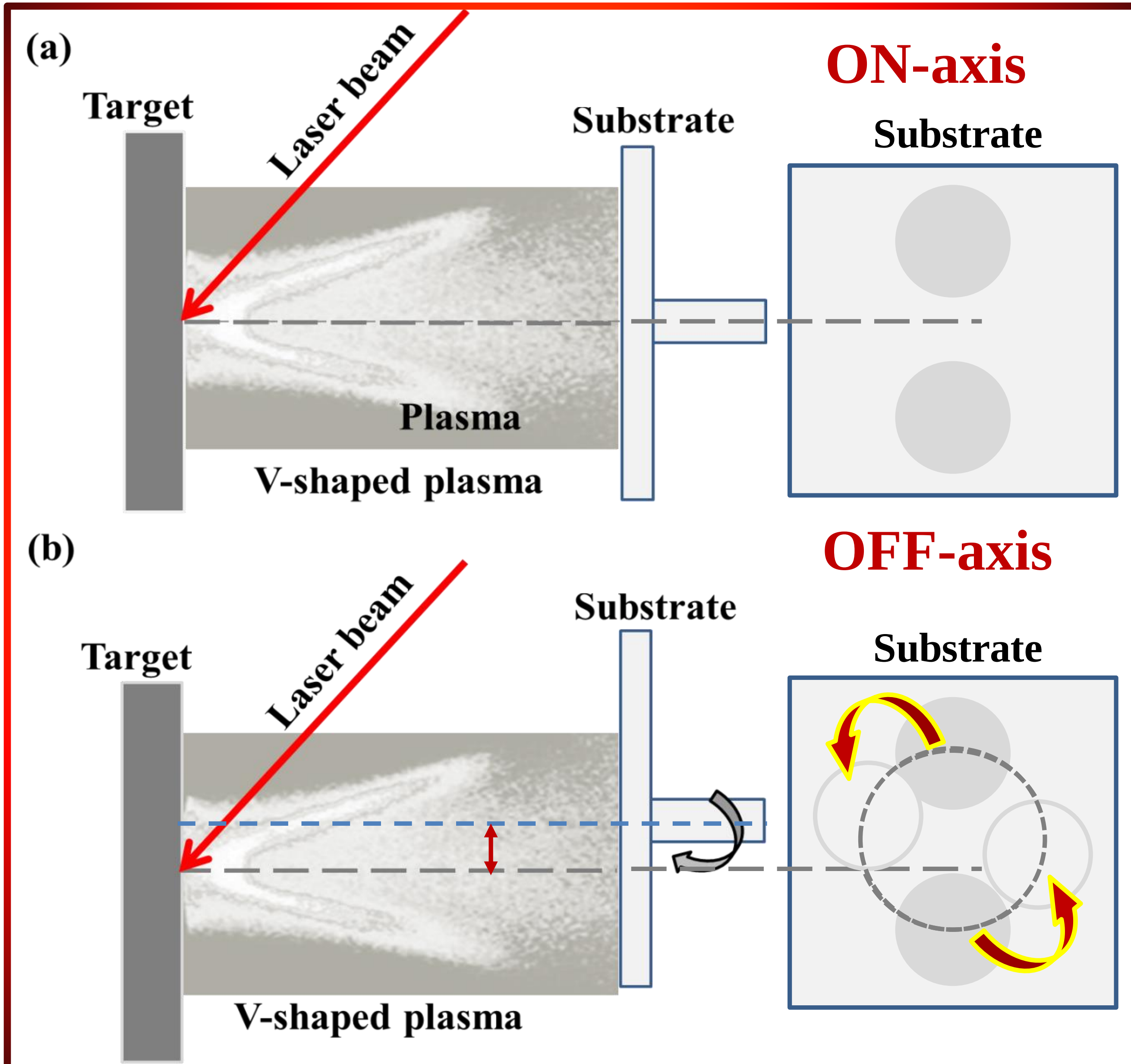
PLD-deposited DLC: V-shaped plume

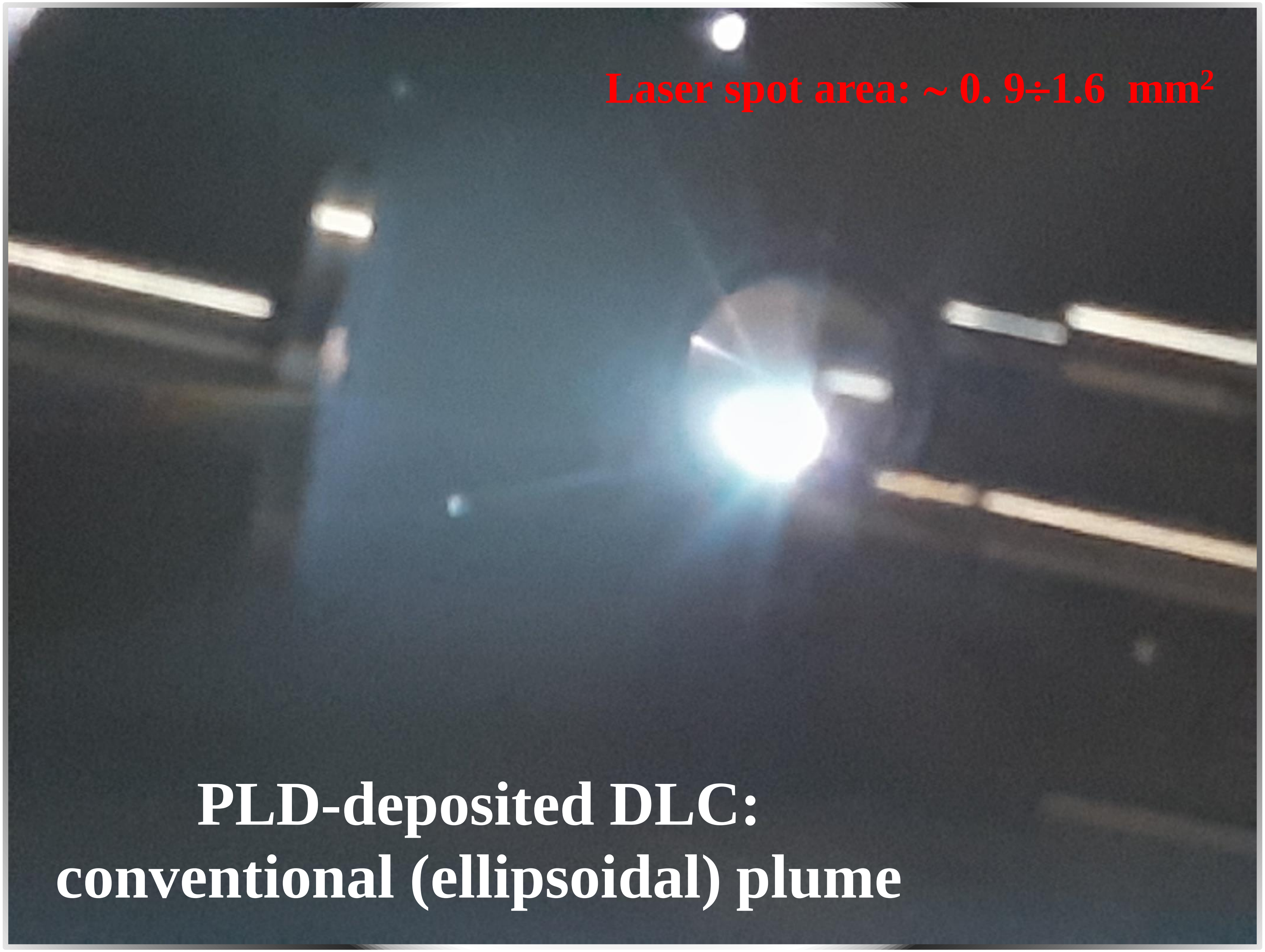
Laser spot area: ~ 3 ÷ 4 mm^2



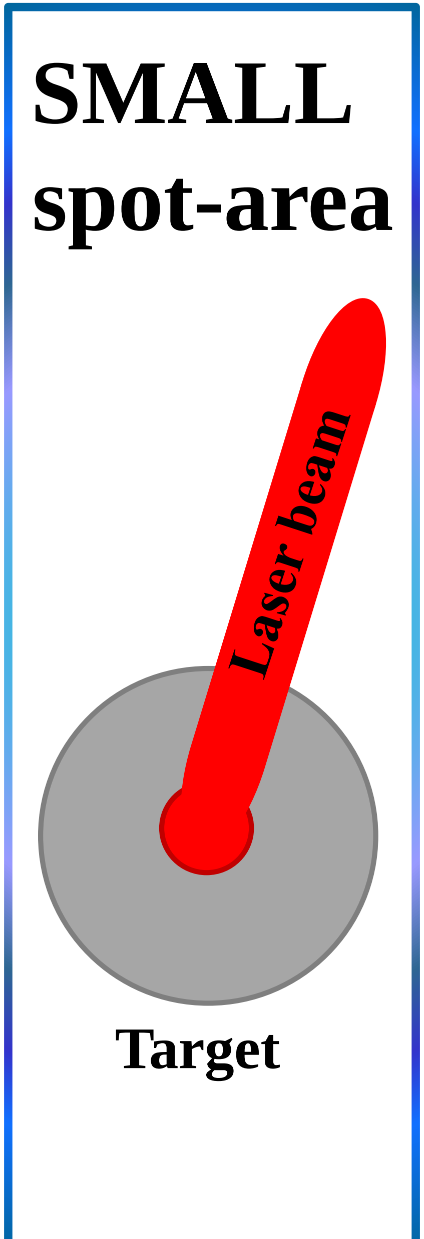
PLD: OFF-axis vs ON-axis

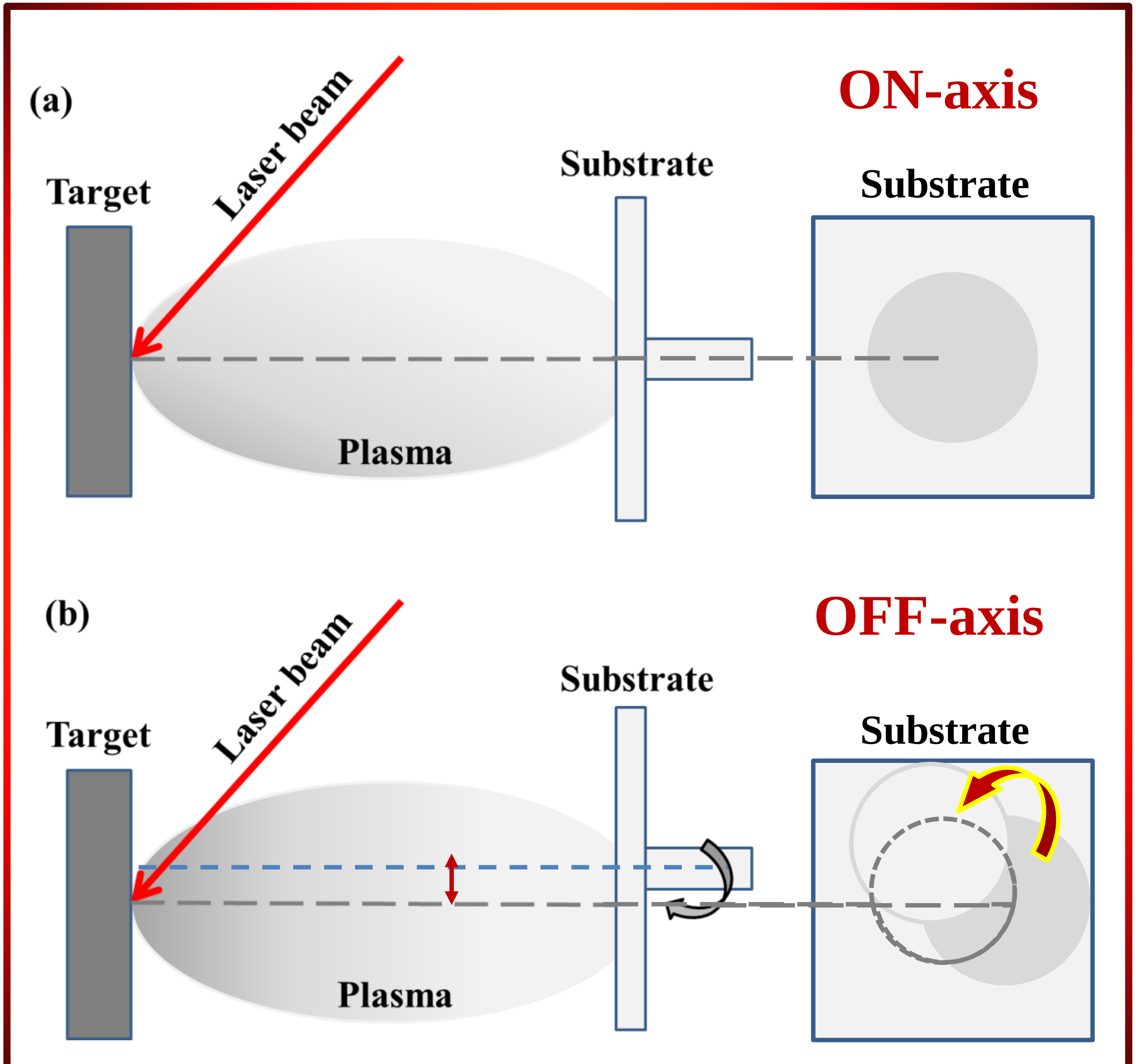


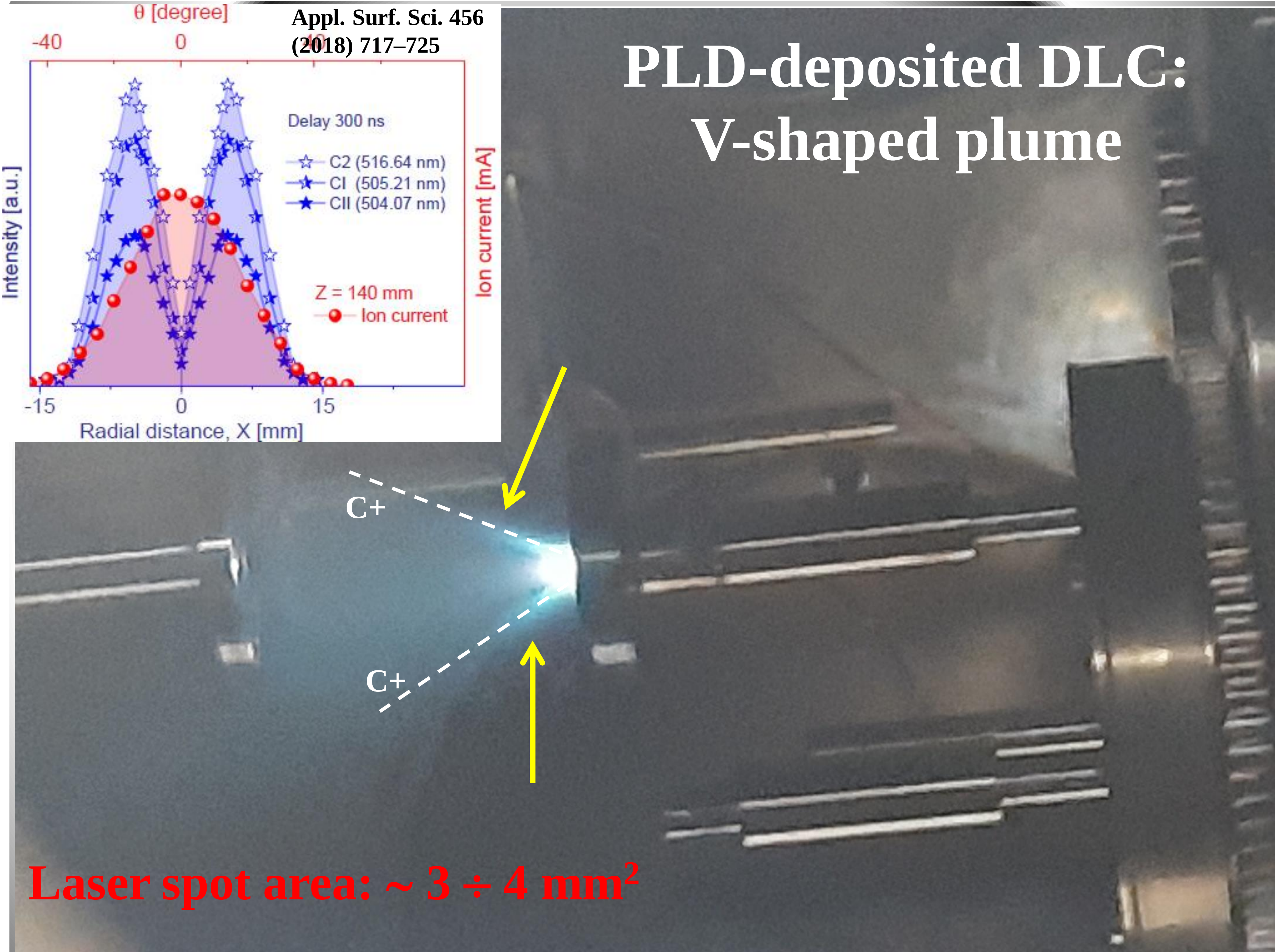



Laser spot area: ~ 0. 9÷1.6 mm²
PLD-deposited DLC:
conventional (ellipsoidal) plume

PLD: OFF-axis vs ON-axis







PLD-deposited DLC:
V-shaped plume
Appl. Surf. Sci. 456 (2018) 717–725
θ [degree]
-40
0
40
Intensity [a.u.]
Ion current [mA]
Delay 300 ns
C2 (516.64 nm)
CI (505.21 nm)
CII (504.07 nm)
Z = 140 mm
Ion current
-15
0
15
Radial distance, X [mm]
C+
C+
Laser spot area: ~ 3 ÷ 4 mm²

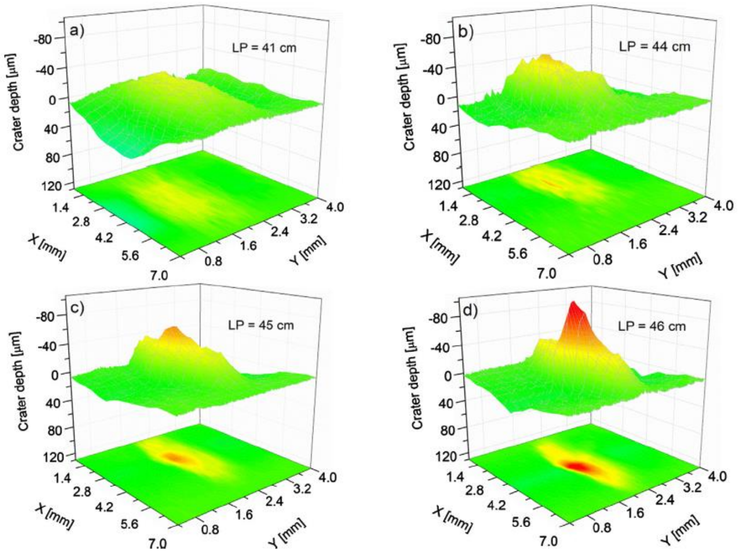
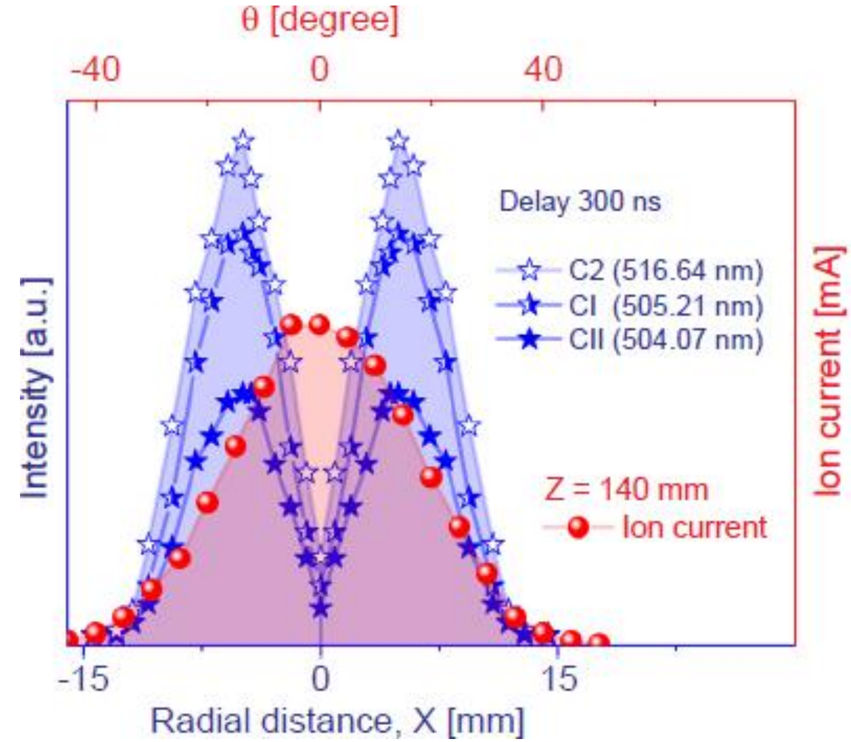
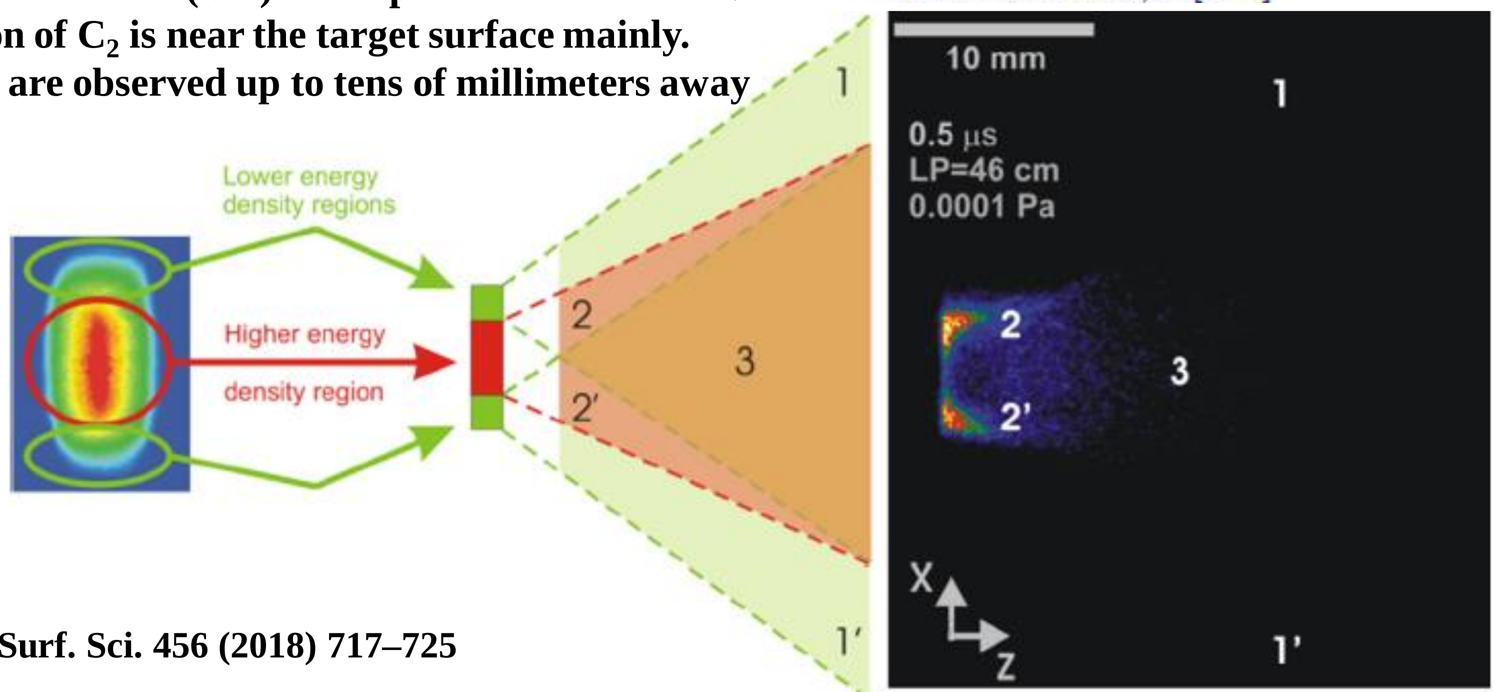


Fig. 4. Laser ablation crater depth profiles as a function of the beam focusing.



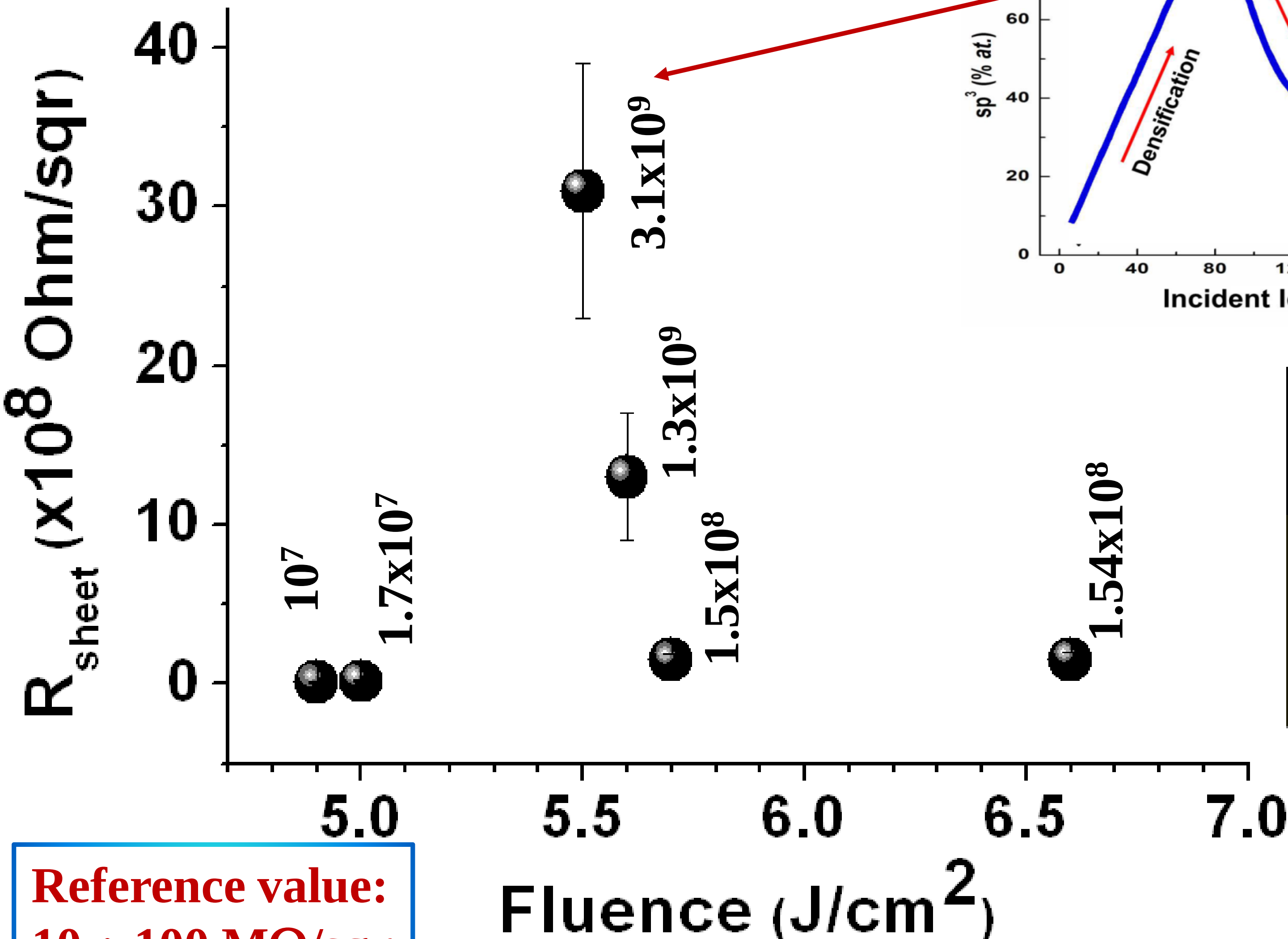
Dominance of C_2 molecules over neutral (CI) and singly-ionized atoms (CII) in the plasma lateral arms. Emission of C_2 is near the target surface mainly. CI and CII are observed up to tens of millimeters away

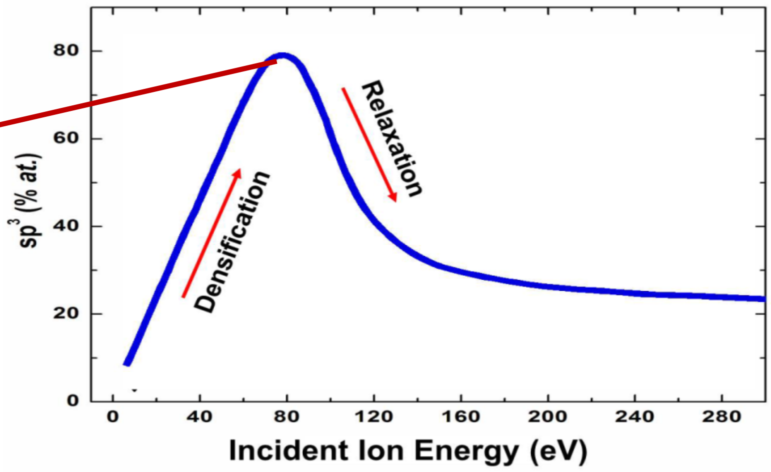


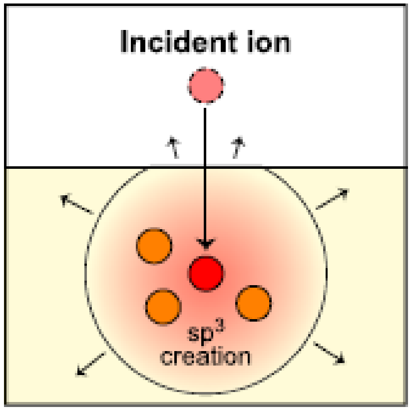
Appl. Surf. Sci. 456 (2018) 717–725

DLC by PLD: large spot, OFF-axis/rot, Cu/Kapton substrate

Threshold fluence: F = 5.5 J/cm^2



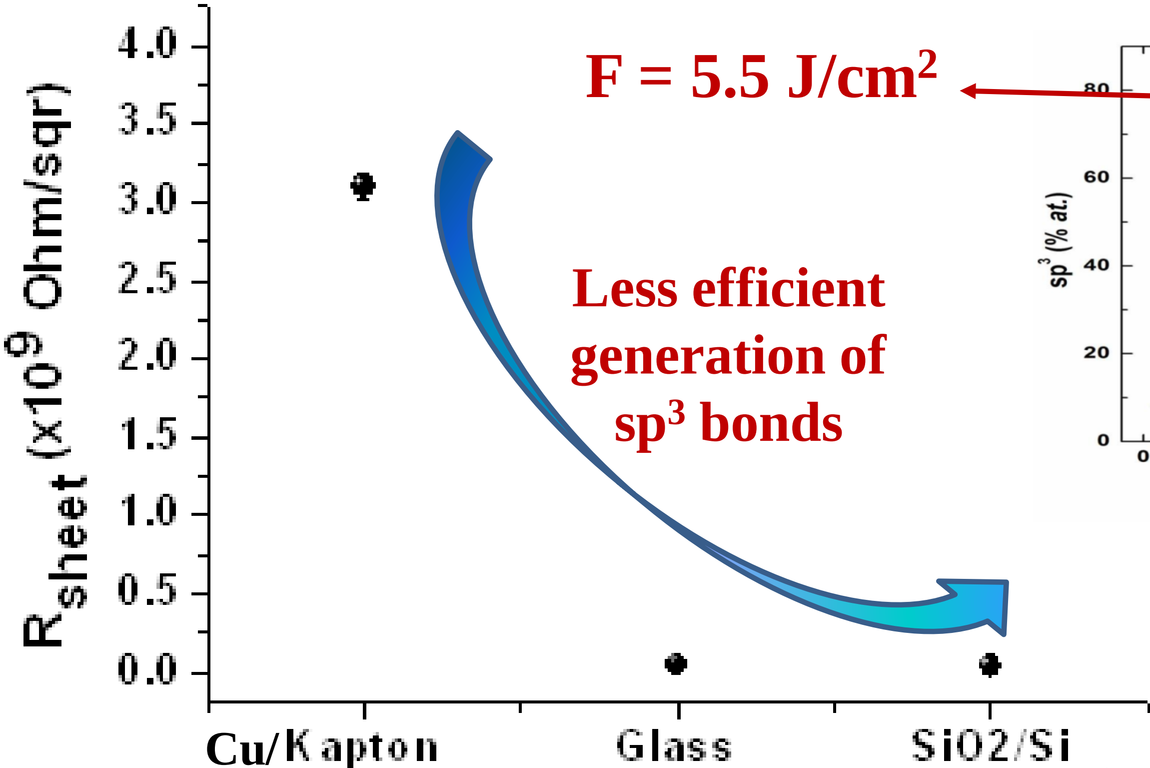


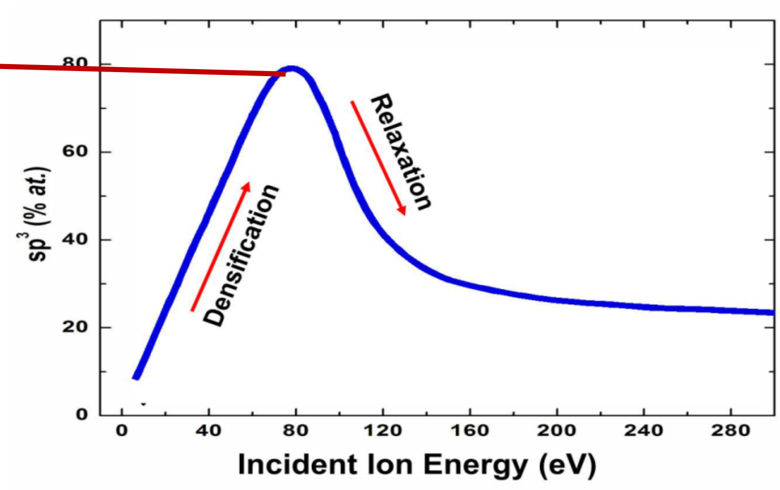


J. Robertson. Japanese Journal of Applied Physics, 50:01AF01, 2011.

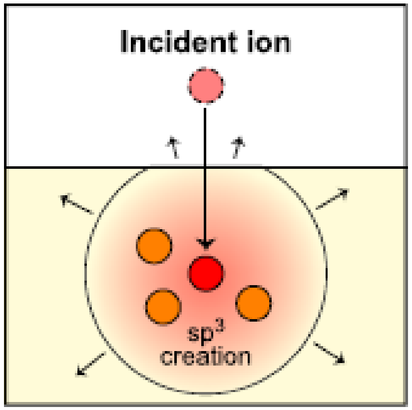
Reference value:
10 ÷ 100 MΩ/sqr

DLC by PLD (large spot, OFF-axis): SUBSTRATE





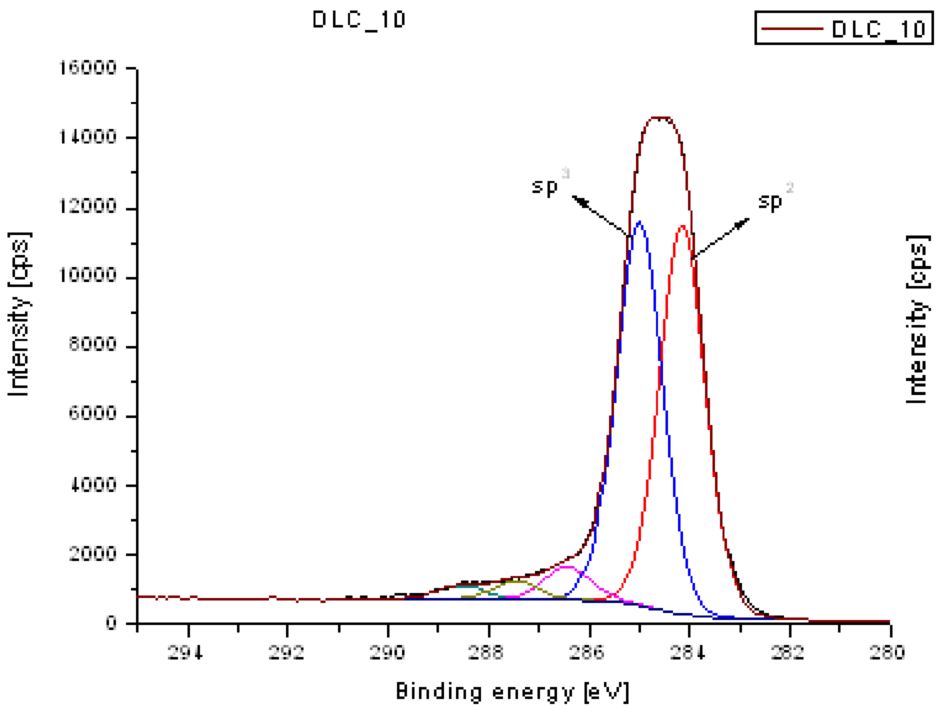
Decreasing thermal conductivity

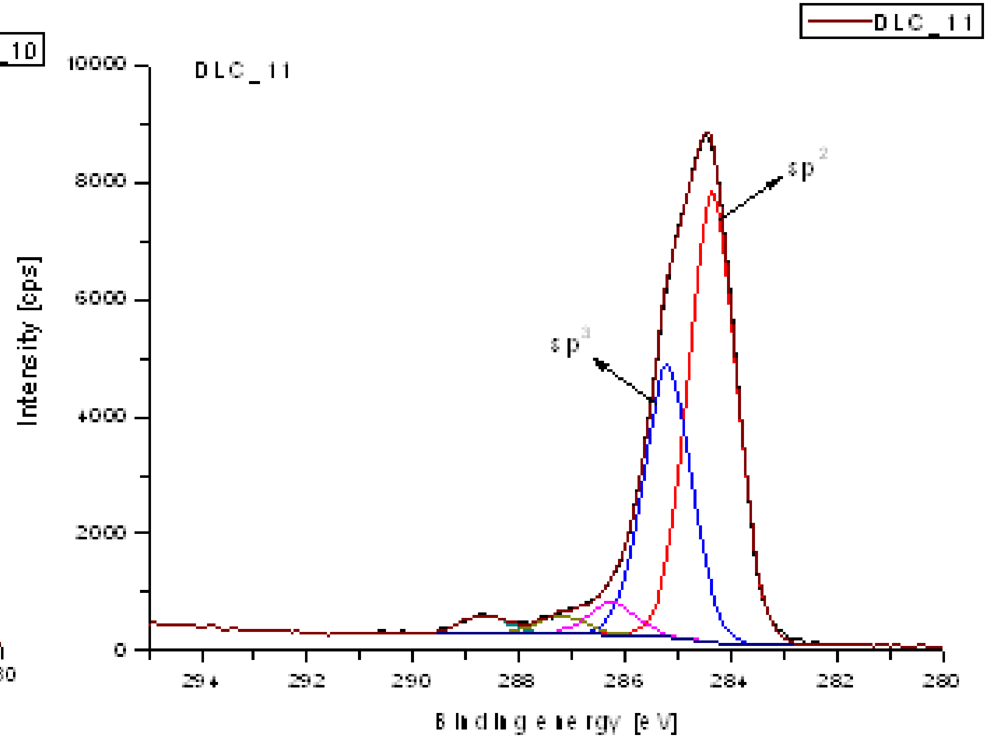


Shots	Spot	d_{TS}	Substrate	R_{sheet} (Ω/sqr)
8000	3.9 mm^2	5.5 cm	Kapton (50µm)/Cu(5µm)	3.1×10^9
7116	3.9 mm^2	5 cm	Silica-glass	6.5×10^7
7000	3.6 mm^2	5.5 cm	SiO_2(100 nm)//Si	3.1×10^6

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

DLC by PLD: XPS elemental-bonding analysis





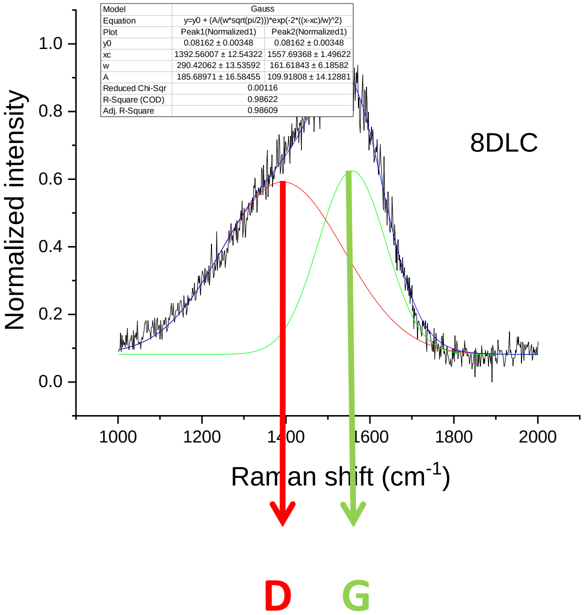
Sample	d_{TS} (cm)	A_{Spot} (mm^2)	N_p	F(J/cm^2)	Substrate	Energy (J)	sp^3
# 10	5	4.0	8000	**4.8**	Cu/Kapton	0.192	**49.7 %**
# 11	5.5	3.4	8000	**5.2**	Cu/Kapton	0.177	**37.5 %**

Energy delivered per pulse → fraction of sp^3 bonds

DLC by PLD: visible RAMAN spectroscopy

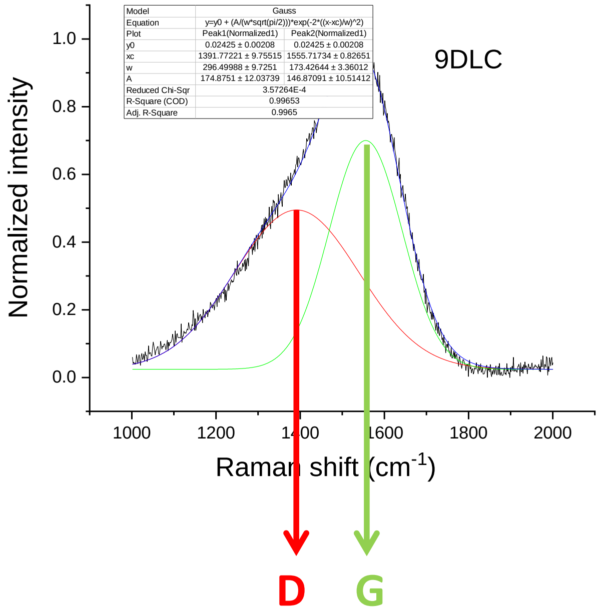
Fluence dependence of I_D/I_G (sp^3 bonding /resistivity)

Cu/Kapton substrate



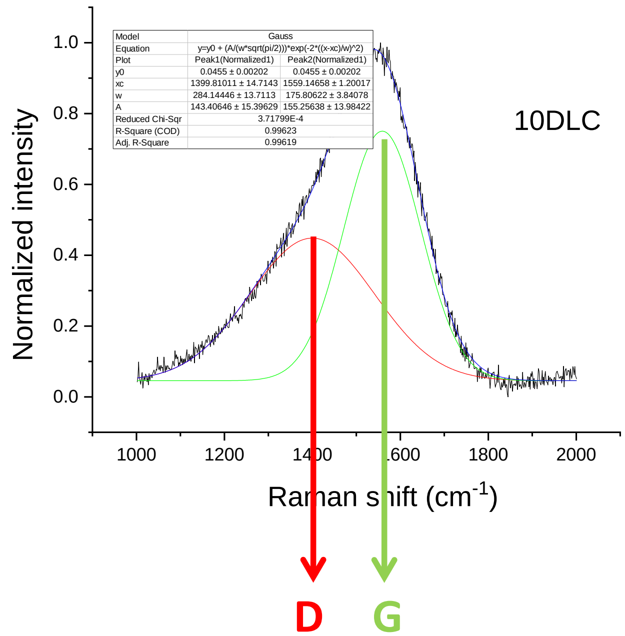
F = 3.3 J/cm²

R_{sheet} = 1.2x10⁵ Ω/sqr



F = 5 J/cm²

R_{sheet} = 1.0x10⁸ Ω/sqr



F = 5.5 J/cm²

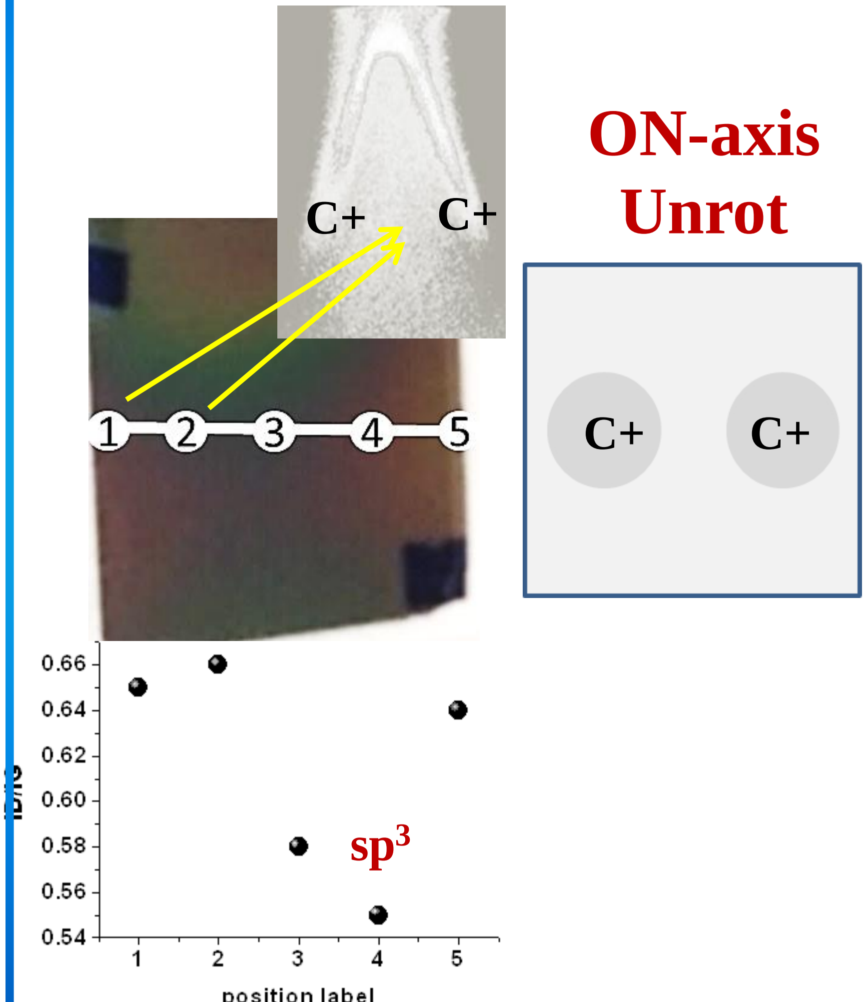
R_{sheet} = 1.2x10⁹ Ω/sqr

Decreasing I_D/I_G → increasing sp_3

DLC by PLD: large spot /ON-axis vs OFF-axis

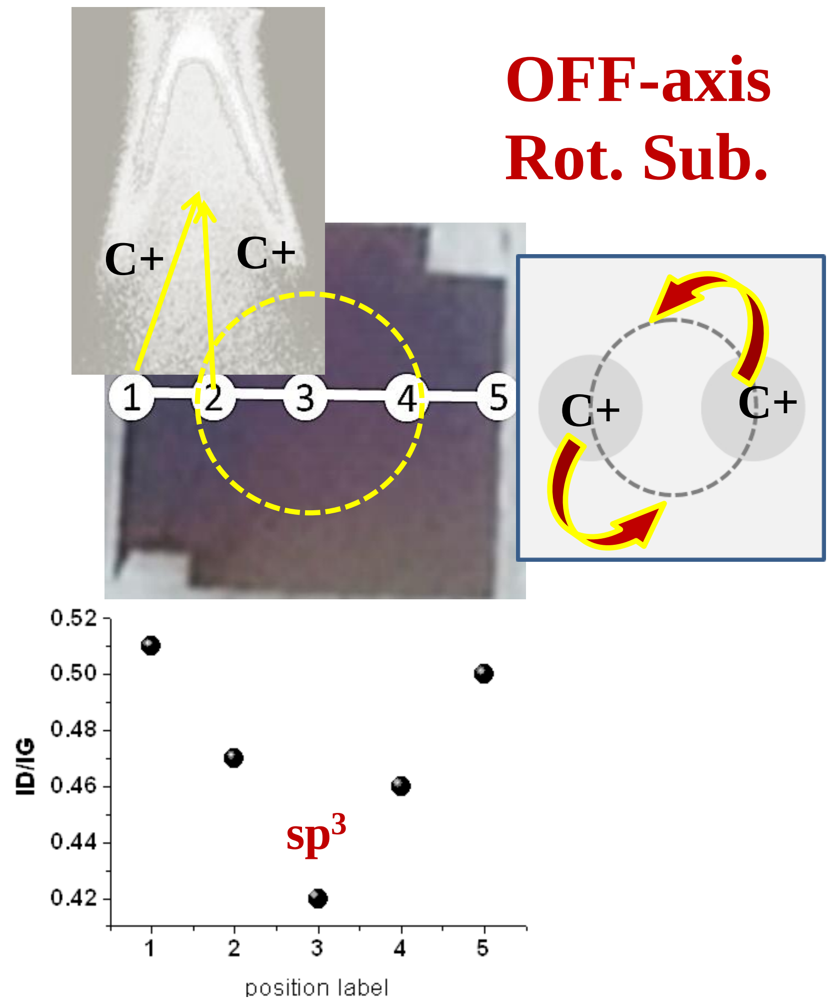
DLC-28 (Si/SiO_2 (100 nm))
F=5.5 J/cm^2 N_p= 7000
d_{TS}=5.5 cm Spot=3.6 mm^2

ON-axis
Unrot



DLC-25 (Si/SiO2 (100 nm))
F=5.5 J/cm^2 N_p= 7116
d_{TS}=5 cm Spot=3.9 mm^2

OFF-axis
Rot. Sub.

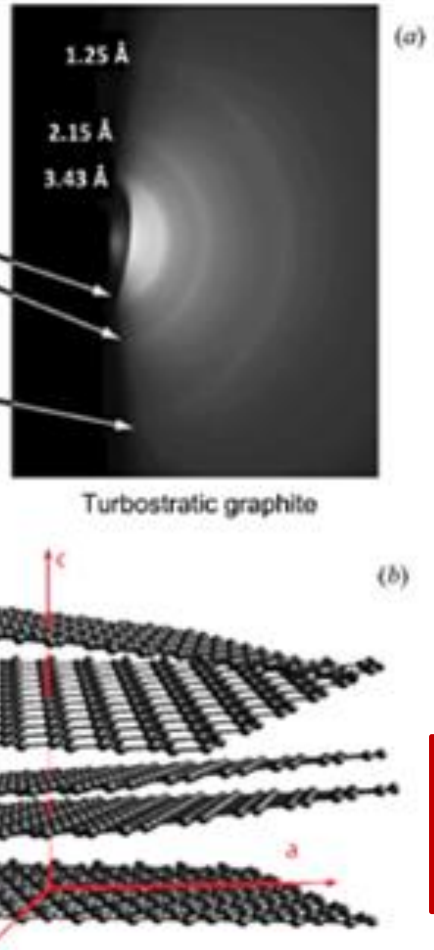


R_{sheet} =(3.1±0.3)x10^6 Ω/sqr → R_{sheet} =(6.5±2.3)x10^7 Ω/sqr

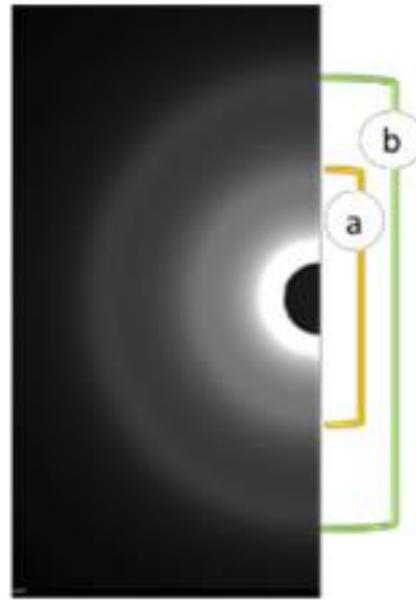
DLC by PLD: structural TEM analysis

GRAPHITE
hexagonal, P63/mmc (194)
JCPDS card 41 - 1487

d spacing (Å)	hkl
3.3756	002
2.1387	100
2.0390	101
1.8074	102
1.6811	004
1.5478	103
1.2341	110
1.1604	112
1.1208	006
1.0567	201



Turbostratic graphite



DIAMOND
Fd3m
JCPDS card 79-1467

	d spacing (Å)	hkl
a	2.059	1 1 1
b	1.261	2 2 0

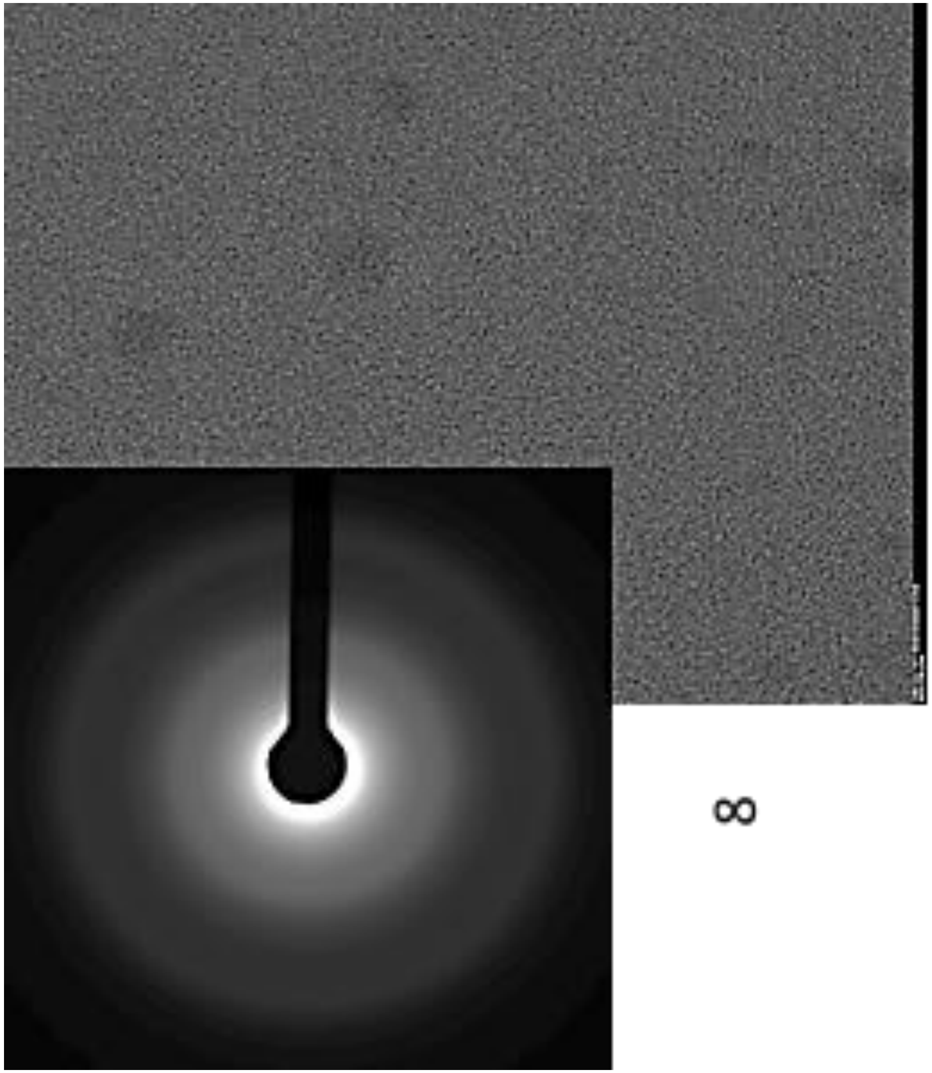
GRAPHITE
P63/mmc
JCPDS card 41-1487

	d spacing (Å)	hkl
	3.357	0 0 2
a	2.023	1 0 1
	1.678	0 0 4
	1.540	1 0 3
b	1.225	1 1 0

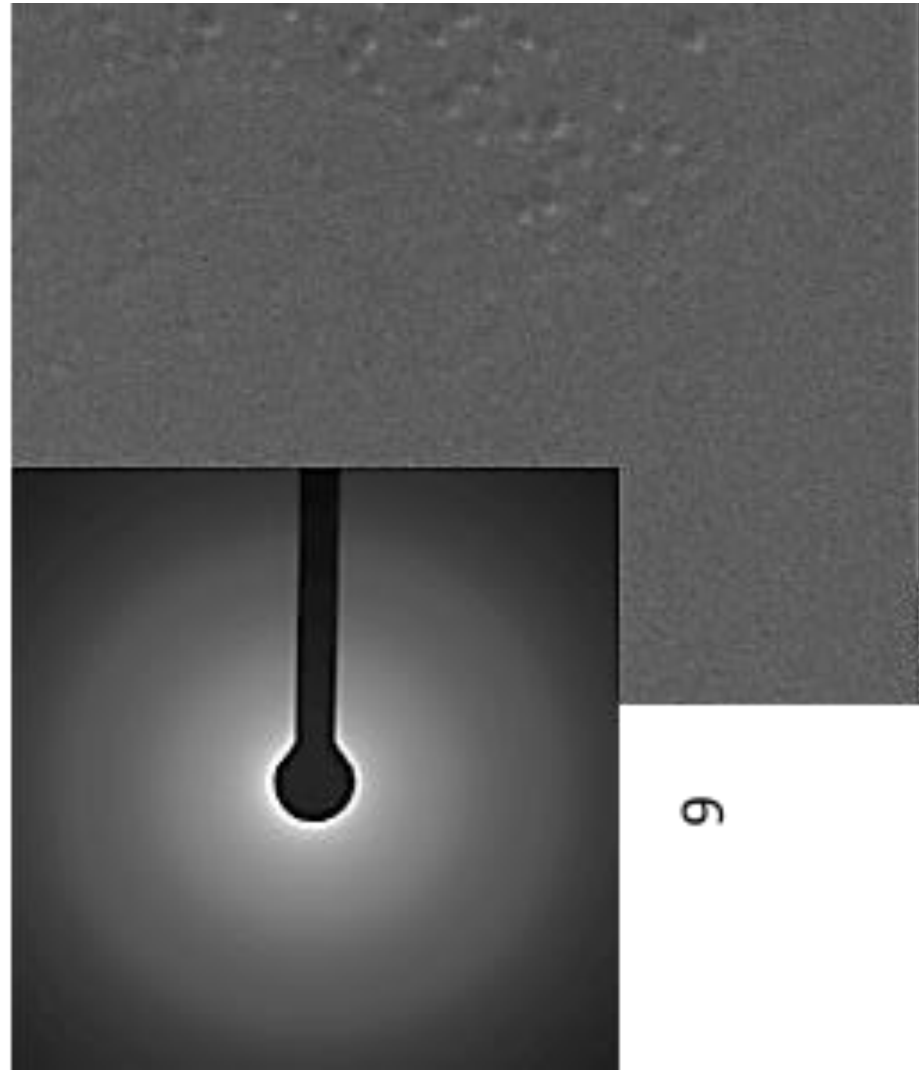
DLC-9 (Cu/Kapton)
F= 4.8 J/cm^2 N_p= 4000
d_{TS} = 5 cm Spot=4.1 mm^2

Two rings are clearly visible compatible with both the diffraction maxima 111 and 220 of diamond, and with the diffraction maxima 101 and 110 of graphite. Overlapping of nano-graphene (missing the ring corresponding to the planes 002 of the graphite) and nano-diamond.

DLC by PLD: structural TEM analysis



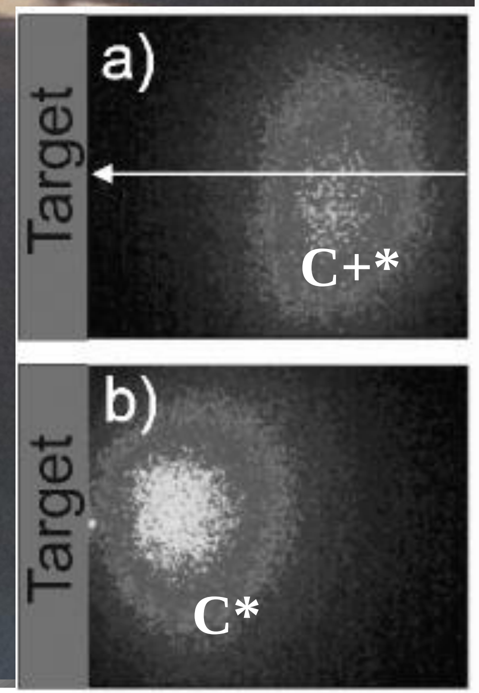
DLC-8 (Cu/Kapton)
F= 3.3 J/cm^2 N$_p$= 8000
d$_{TS}$ = 5 cm Spot = 5.4 mm^2



DLC-9 (Cu/Kapton)
F= 4.8 J/cm^2 N$_p$= 4000
d$_{TS}$ = 5 cm Spot = 4.1 mm^2

PLD-deposited DLC: conventional (ellipsoidal) plume

Chem. Soc. Rev. 33, 23 – 31 (2004)



$$n(r,\theta) = \frac{C}{r^2}(\cos\theta)^m$$

Laser spot area: ~ 1 mm^2

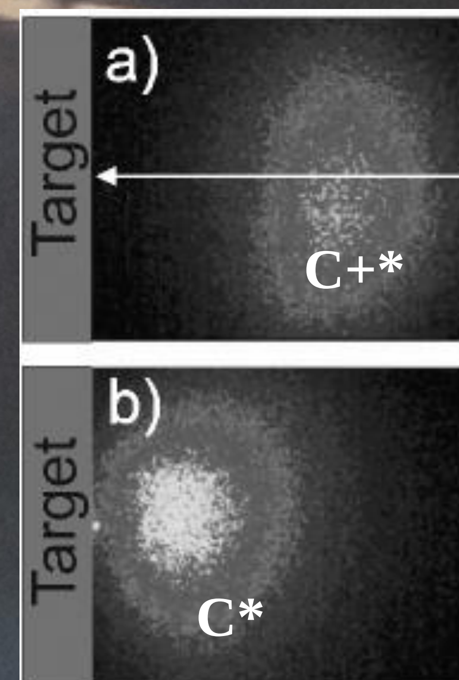
Laser Fluence: 5.5 ÷ 18 J/cm^2

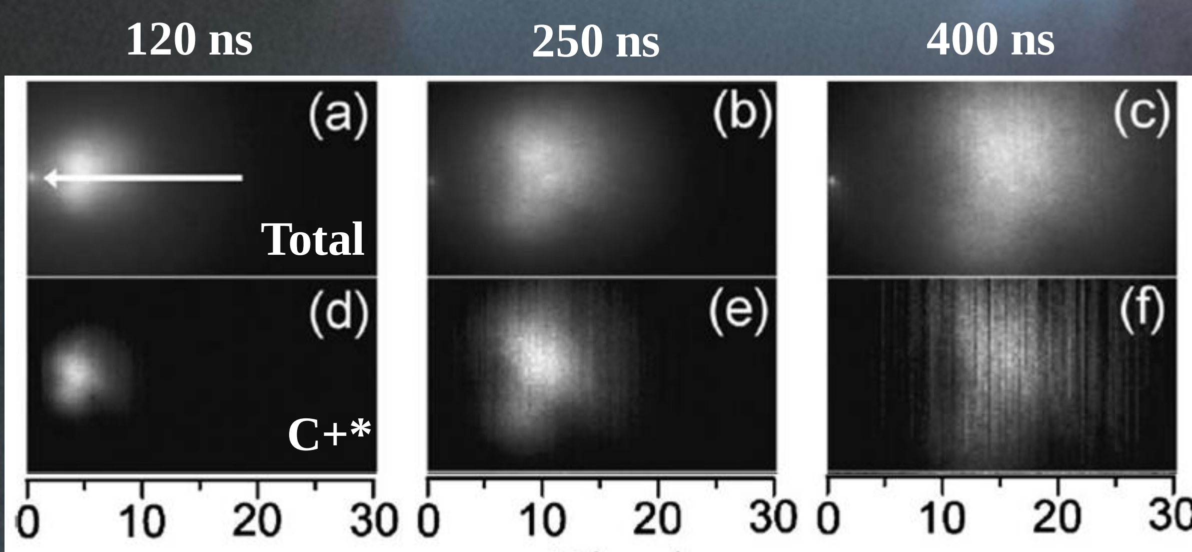
Number of laser pulses: 28000 ÷ 35000

Target-to- substrate distance: d_{TS}: 55 ÷ 45 mm

PLD-deposited DLC: conventional (ellipsoidal) plume

Chem. Soc. Rev. 33, 23–31 (2004)

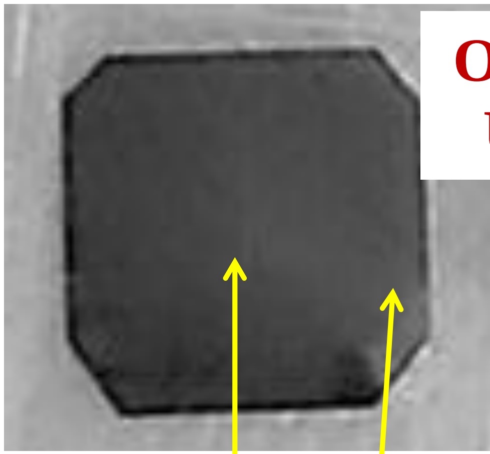


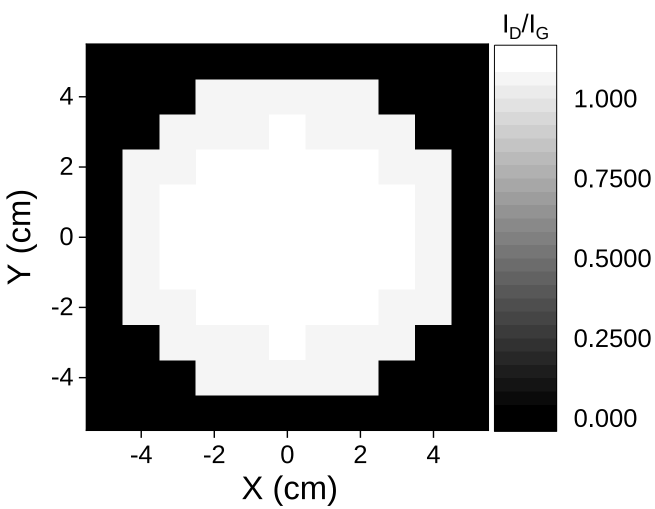


Phys. Rev. B 72, 205413 (2005)

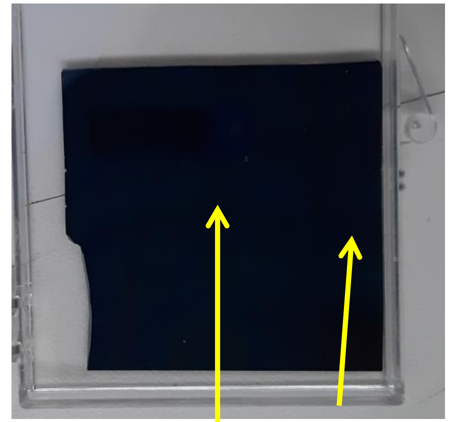
DLC by PLD: small spot /ON-axis vs OFF-axis

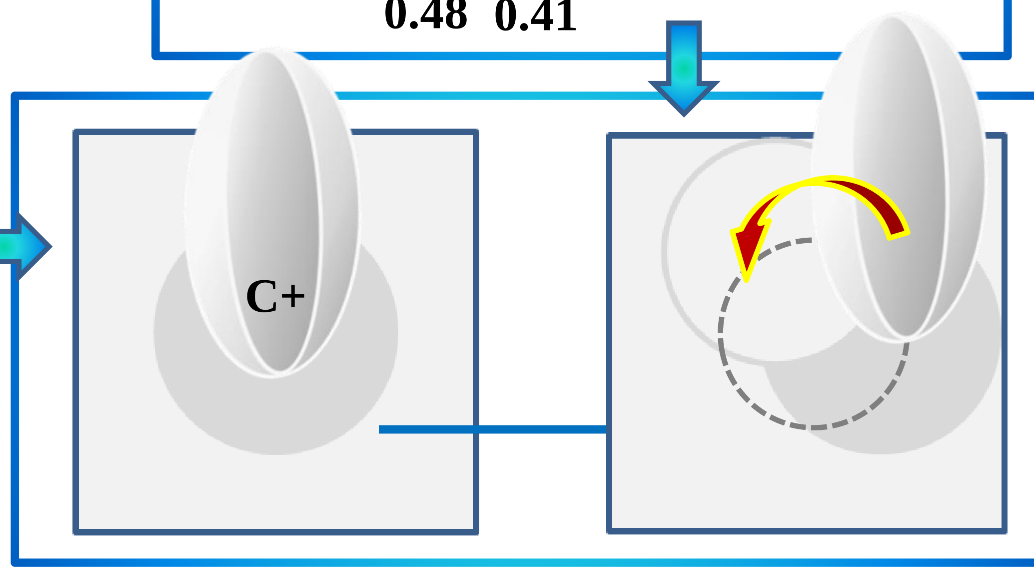
DLC-30 (Si/SiO_2 (100 nm))
F = 5.5 J/cm^2 N_p= 7000
d_{TS} = 5.5 cm Spot=0.9 mm^2





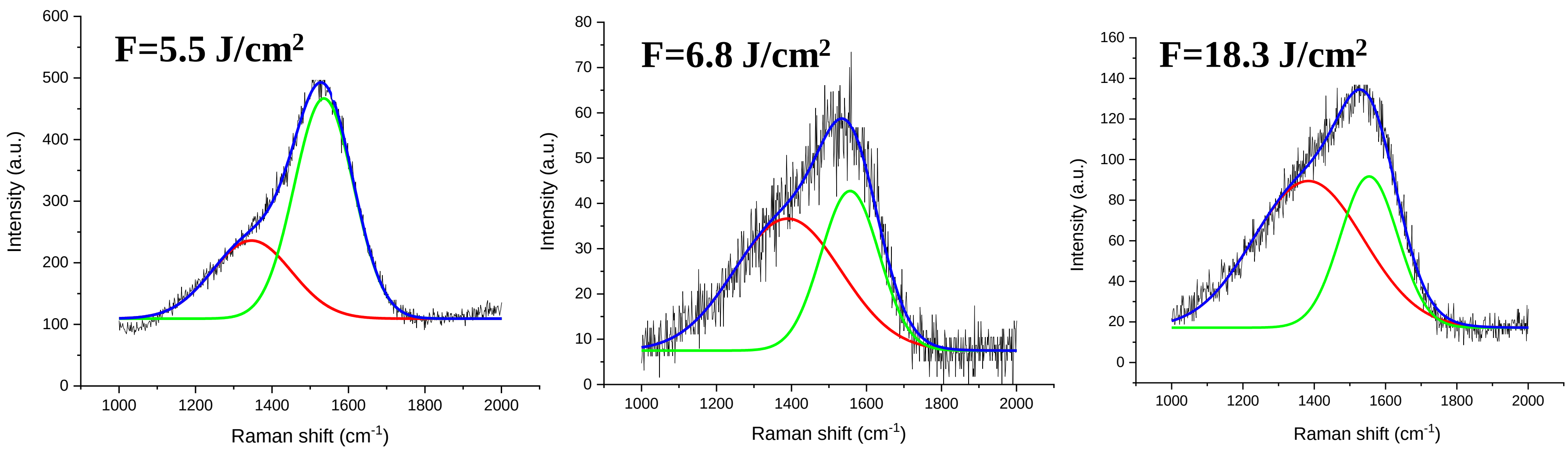
DLC-36 (Si/SiO_2 (100 nm))
F = 5.5 J/cm^2 N_p= 7000
d_{TS} = 4.4 cm Spot=1.5 mm^2

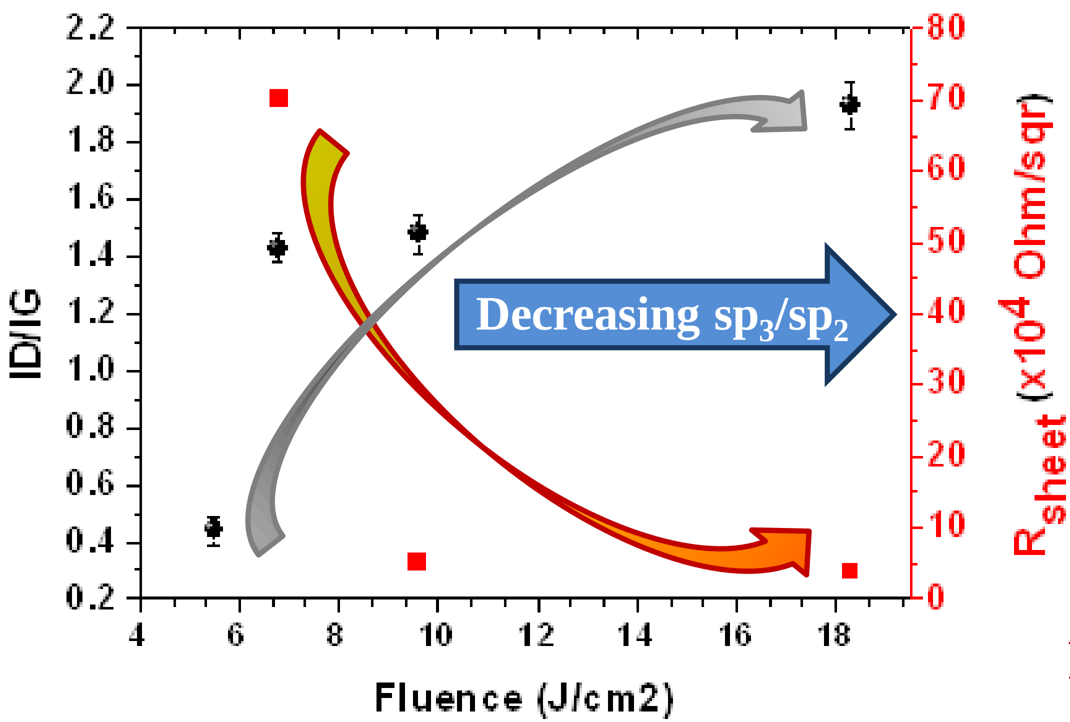




R_{sheet} ~10^{11} → R_{sheet} >10^{12}

DLC by PLD: fluence-dependent sp^3 bonding



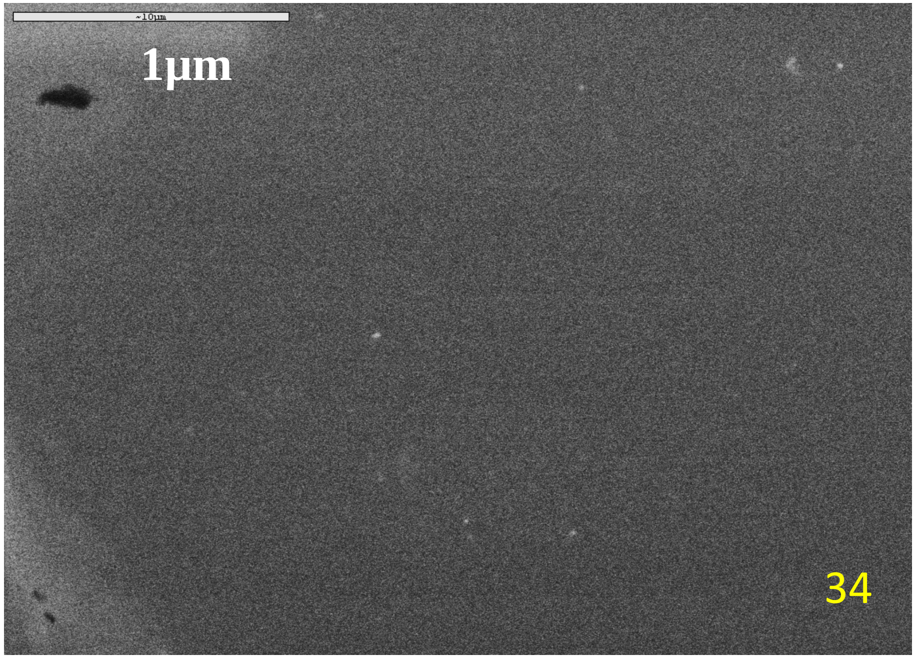


For increasing fluence: sp_3/sp_2 ratio and R_{sheet} decrease

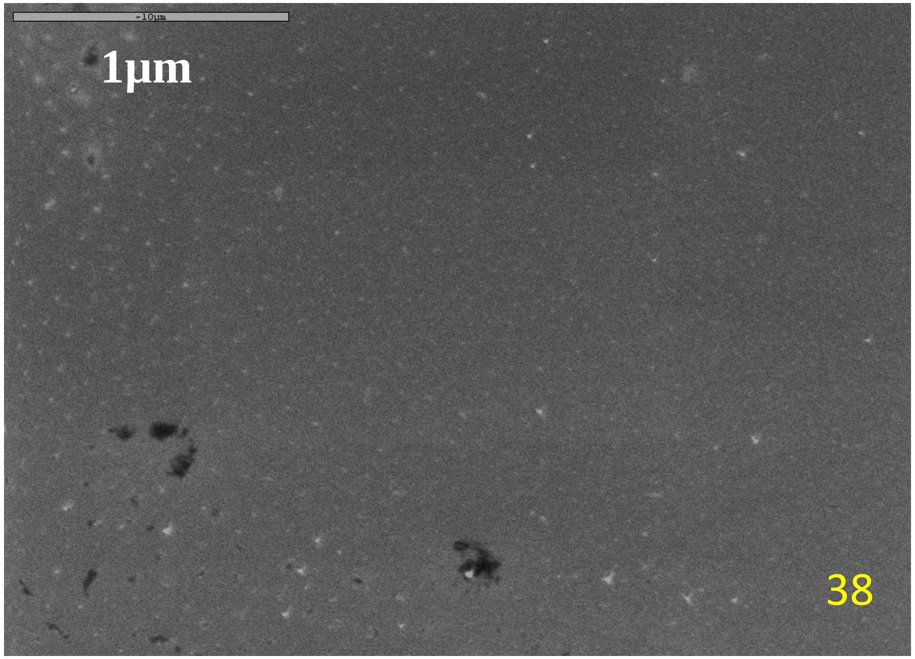
R_{sheet} (5.5 J/cm²) ~10^{12} Ω/sqr

DLC by PLD: XPS and SEM analyses

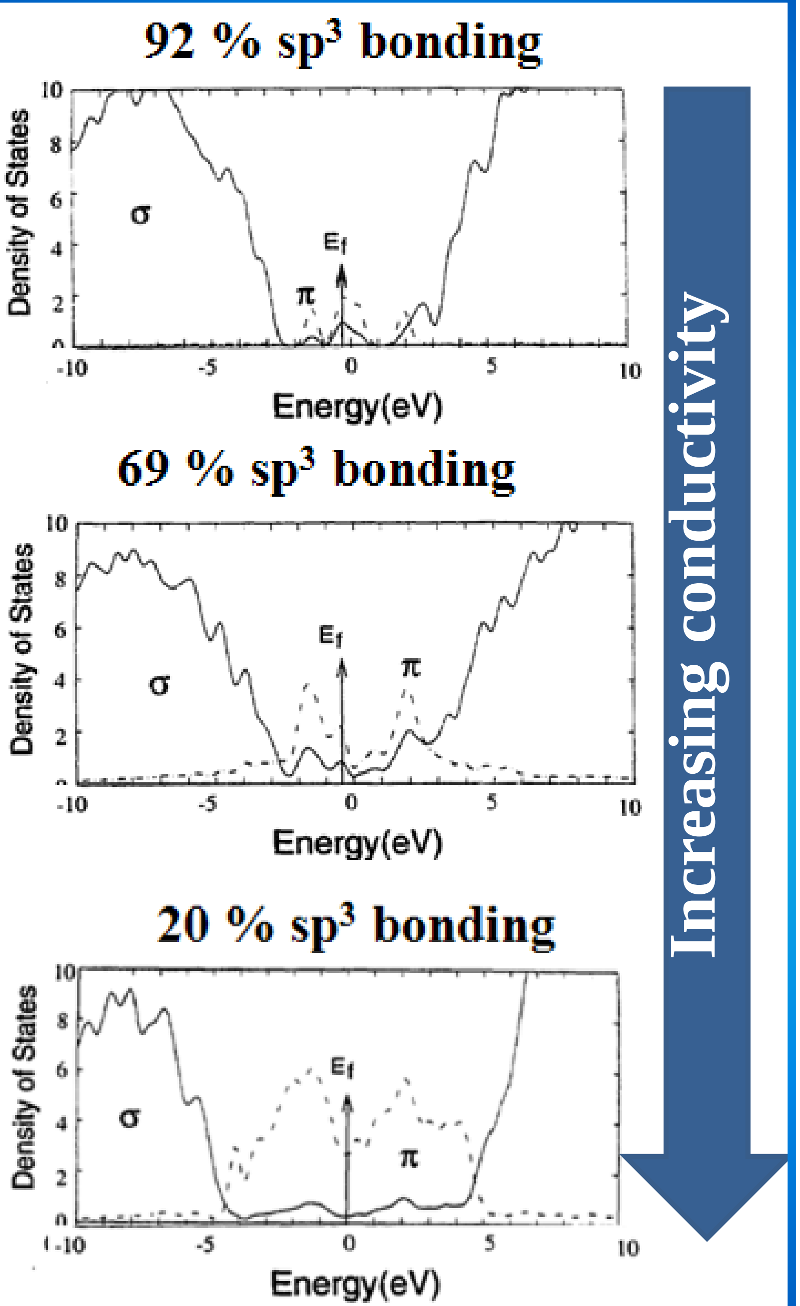
DLC-34 (Si/SiO_2 (100 nm))
F=18.3 J/cm^2 N_p= 28000
d_{TS}=4.2 cm Spot=1.3 mm^2
Thickness = (175±10) nm

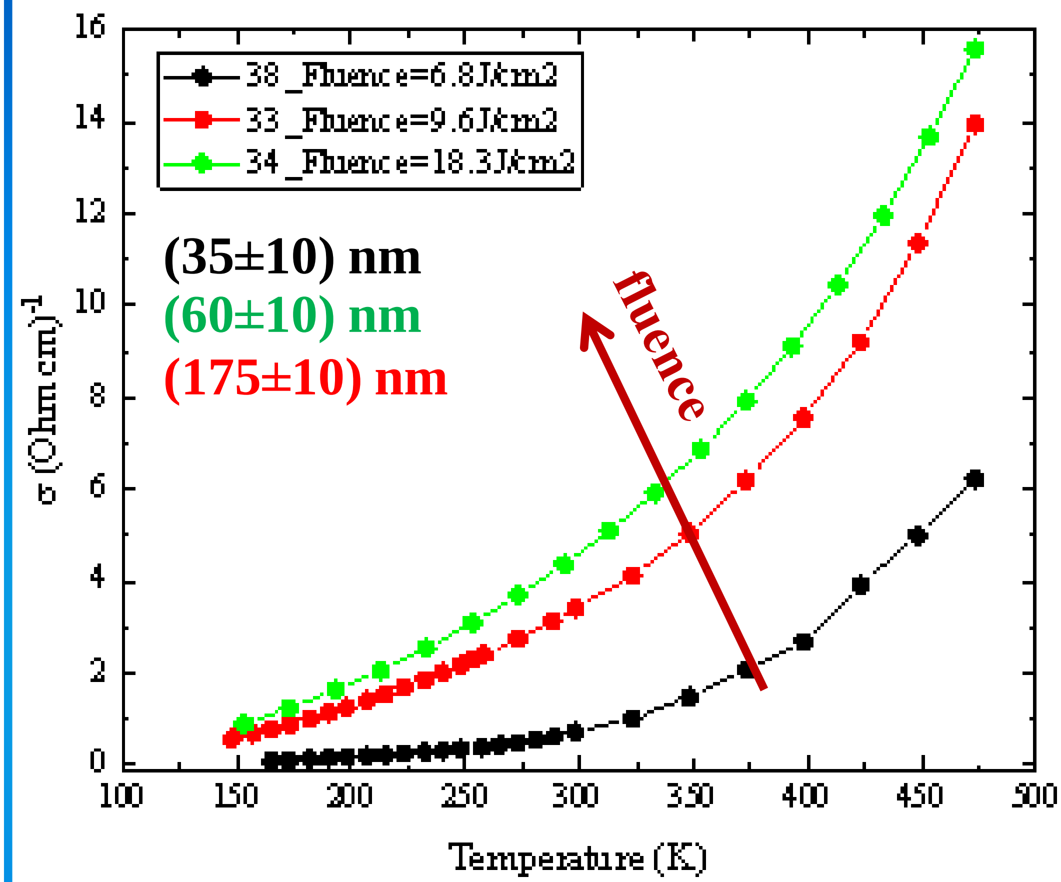


DLC-38 (Si/SiO_2 (100 nm))
F = 6.8 J/cm^2 N_p= 35000
d_{TS}=3.8 cm Spot=1.6 mm^2
Thickness = (35±10) nm
XPS: sp^3 -→29.6 %
sp^2 -→ 70.4 %



DLC by PLD: electrical properties





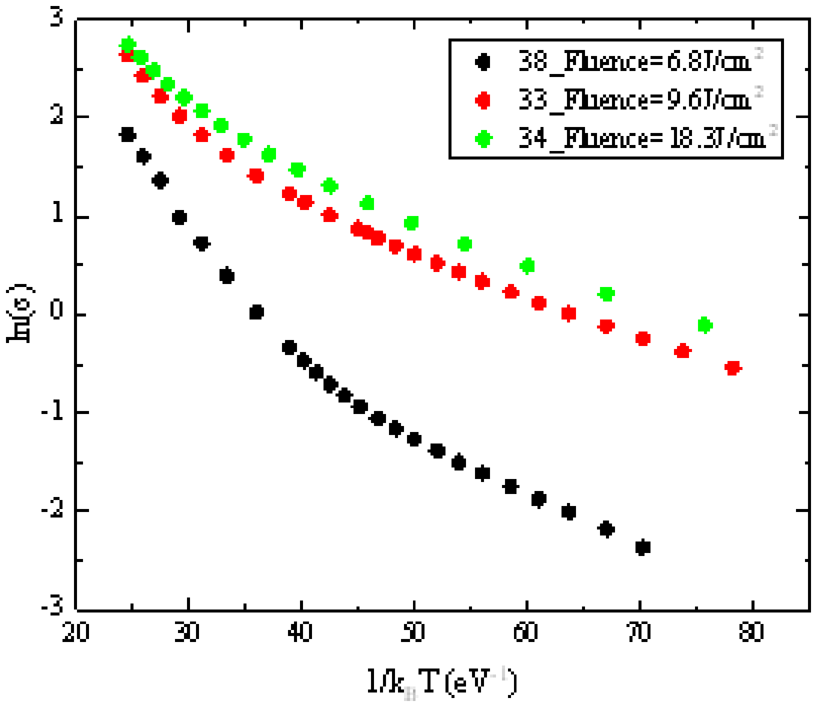
Room temperature conductivity

σ (6.8 J/cm^2) = 8.77 x 10 $^{-1}$ (Ω cm)$^{-1}$

σ (9.6 J/cm^2) = 3.22 (Ω cm)$^{-1}$

σ (18.3 J/cm^2) = 4.42 (Ω cm)$^{-1}$

DLC by PLD: electrical properties

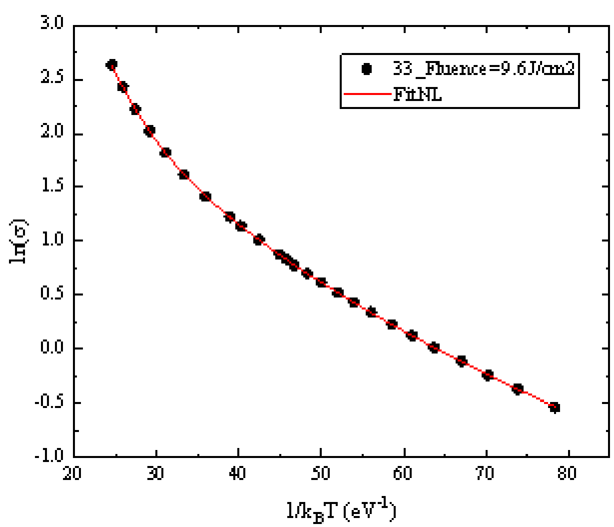


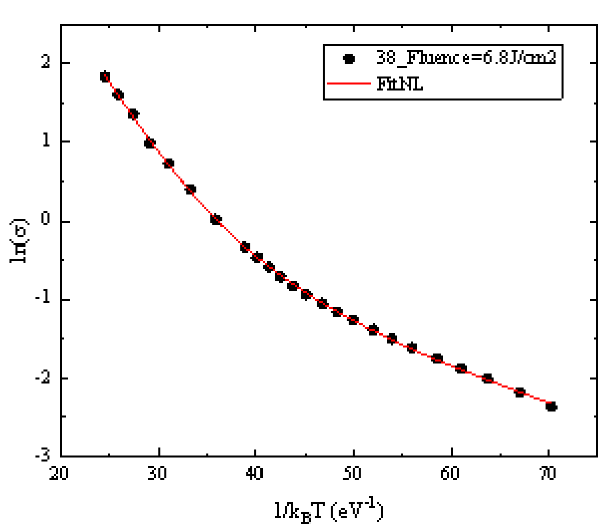
Conduction mechanisms: thermal activation involving localized and tail states

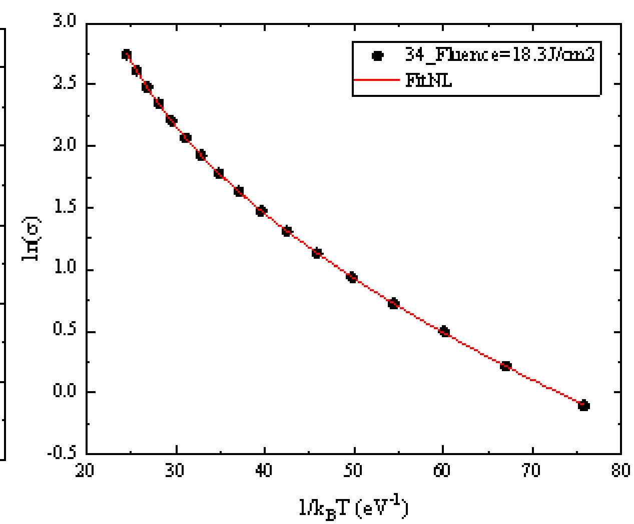
High T $\sigma_{dc}(T) = \sigma_o \exp(-E_\sigma/k_B T)$

Low T: VRH $\sigma_{dc}(T) = \sigma_o \exp\left[-(T_o/T)^{1/4}\right]$

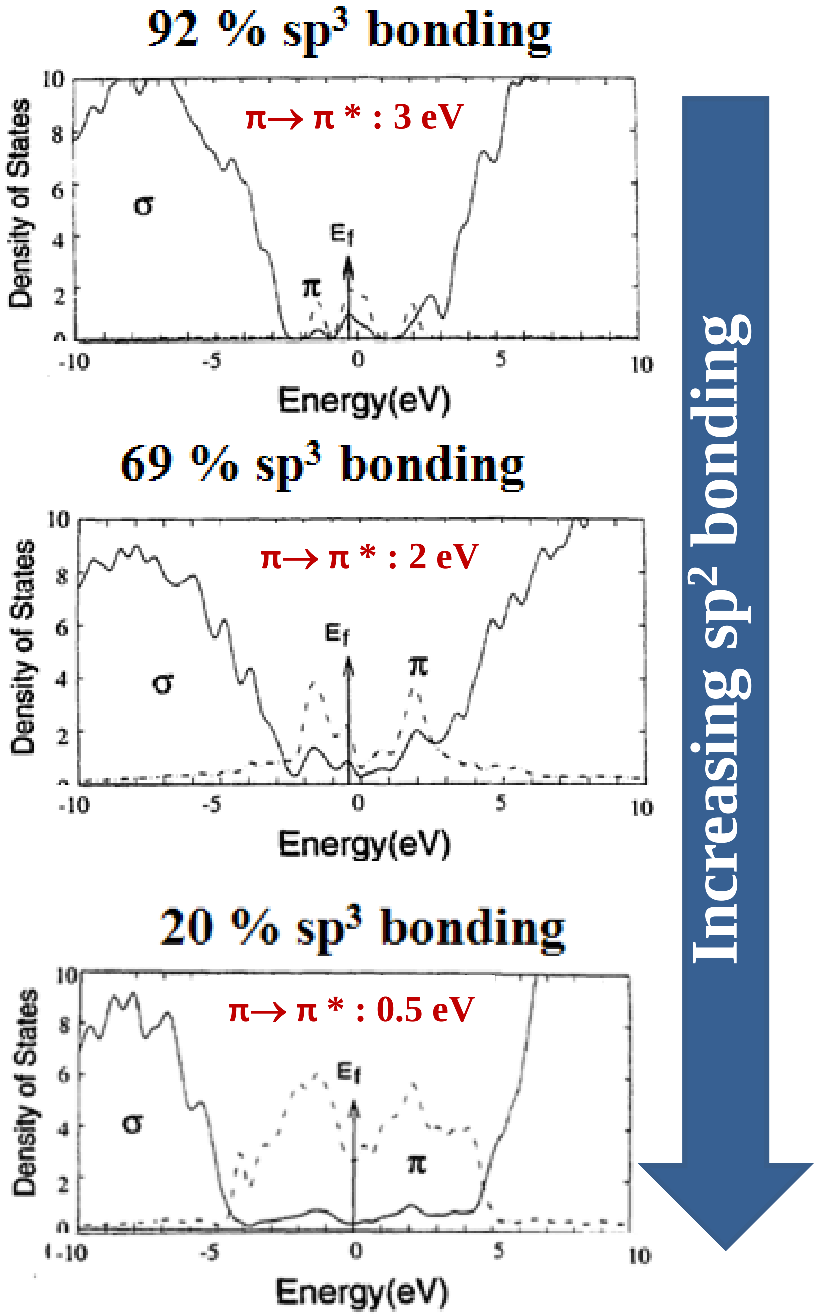
Study in progress…

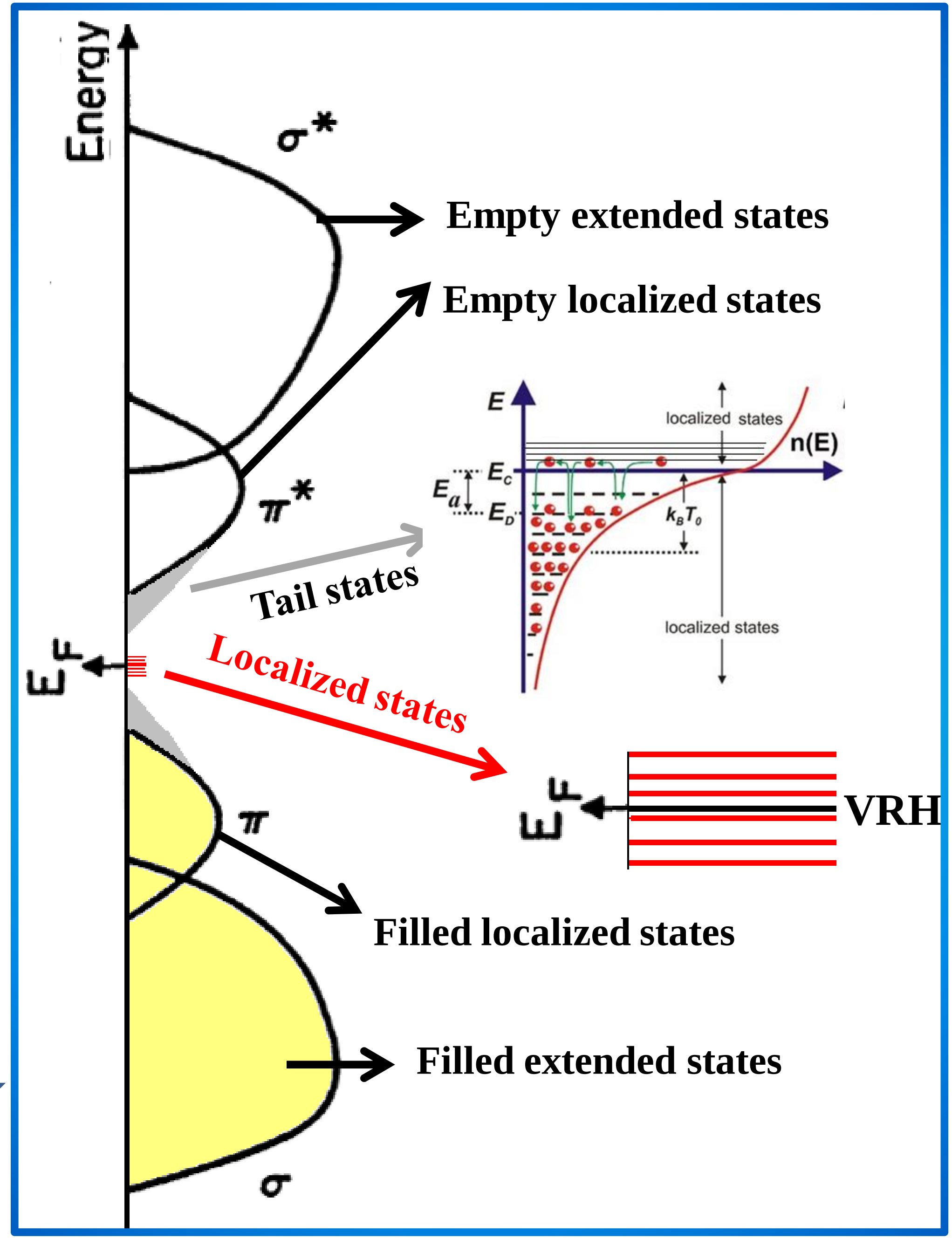




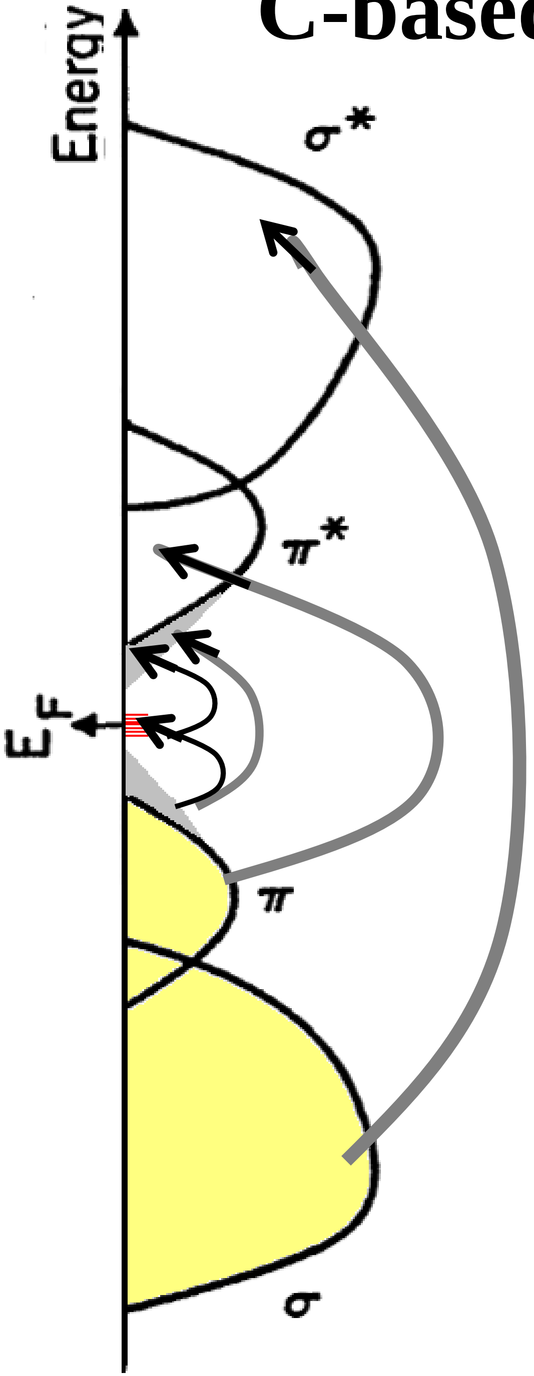


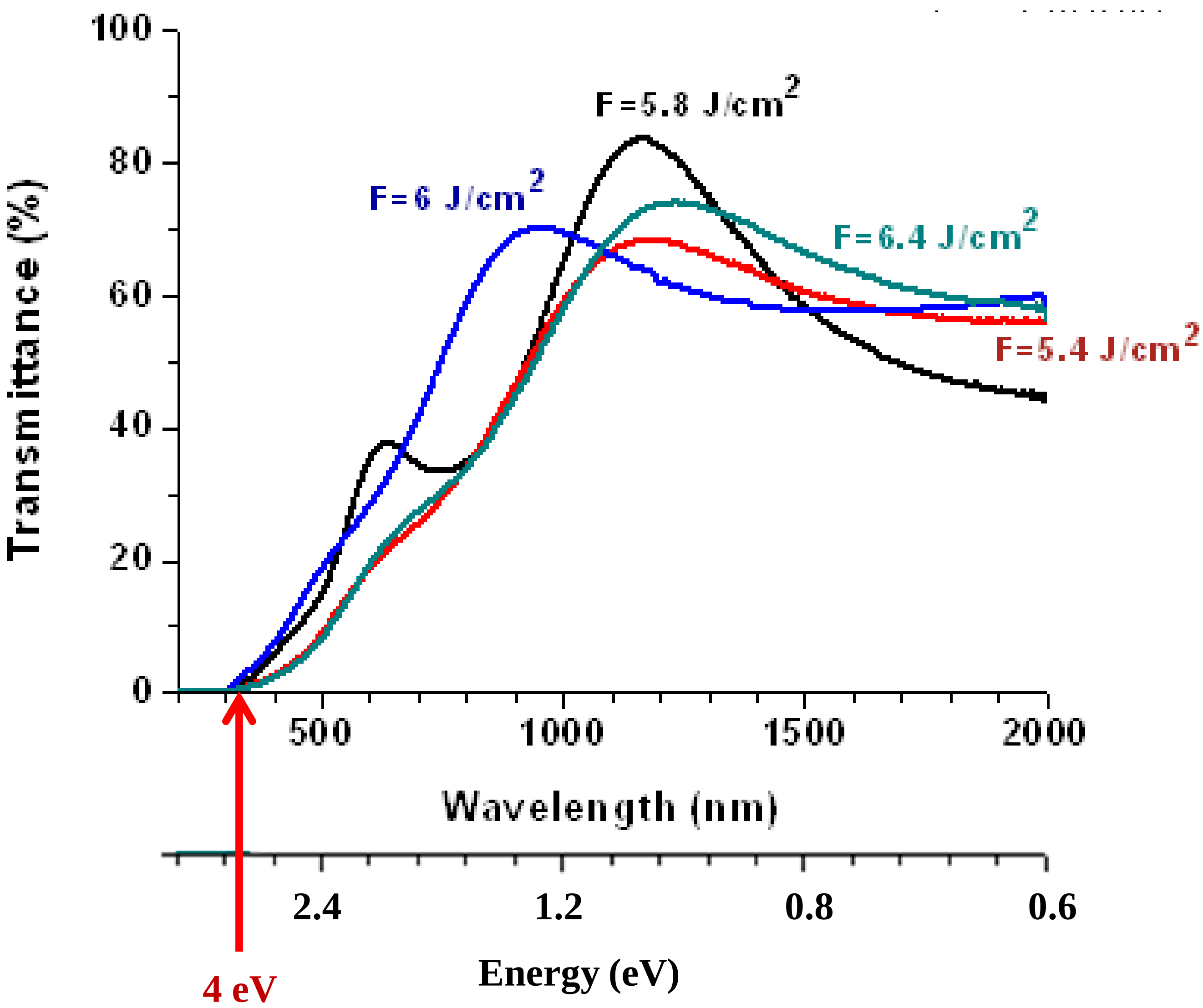
DLC: conduction mechanisms



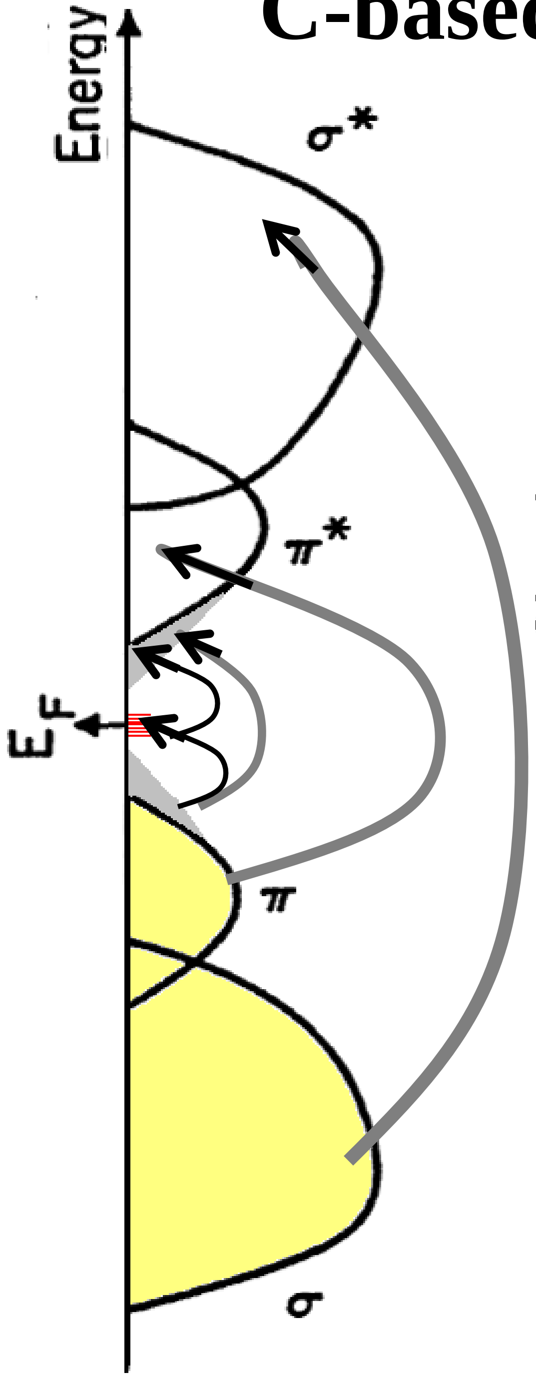


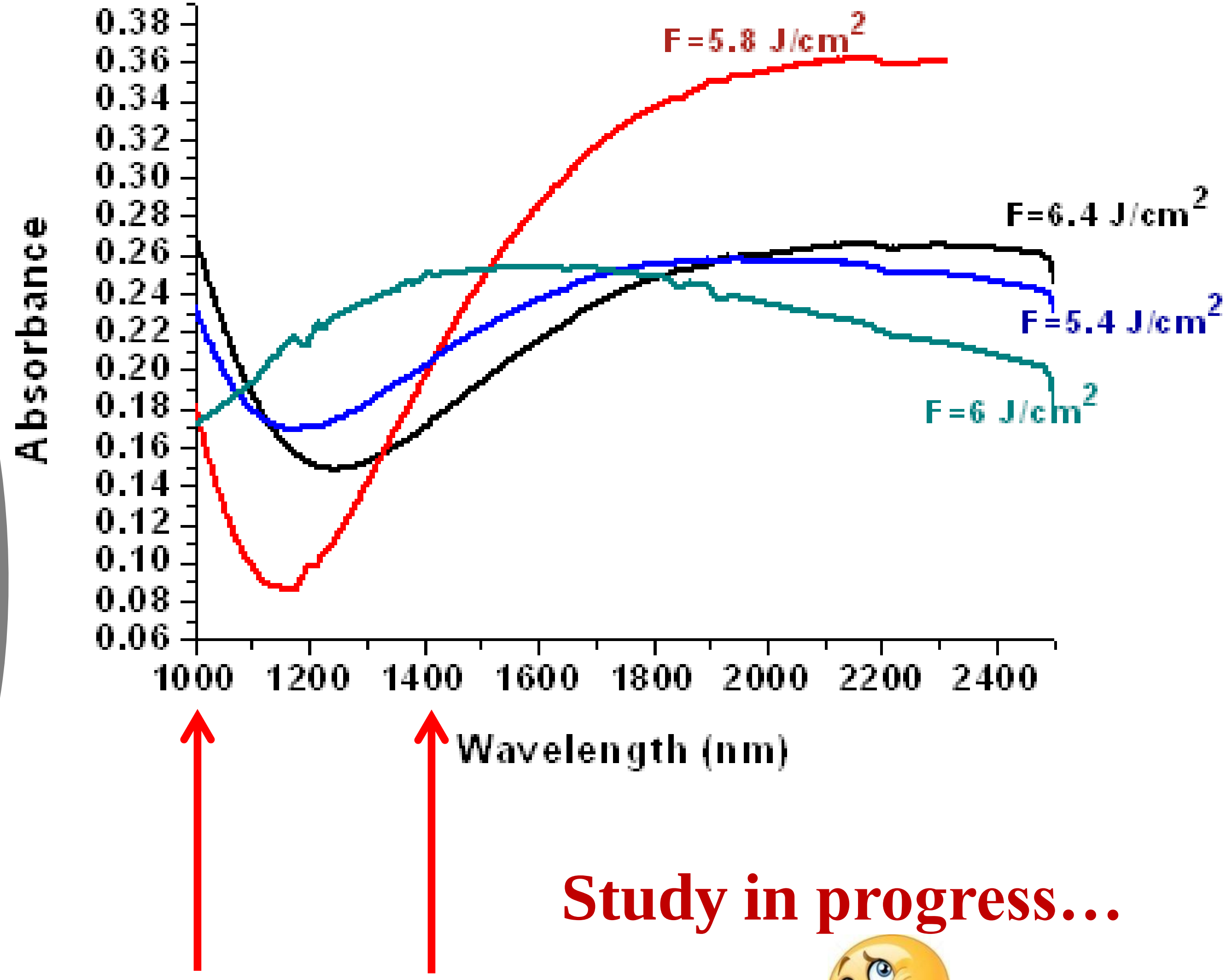
C-based materials: electronic transitions





C-based materials: electronic transitions



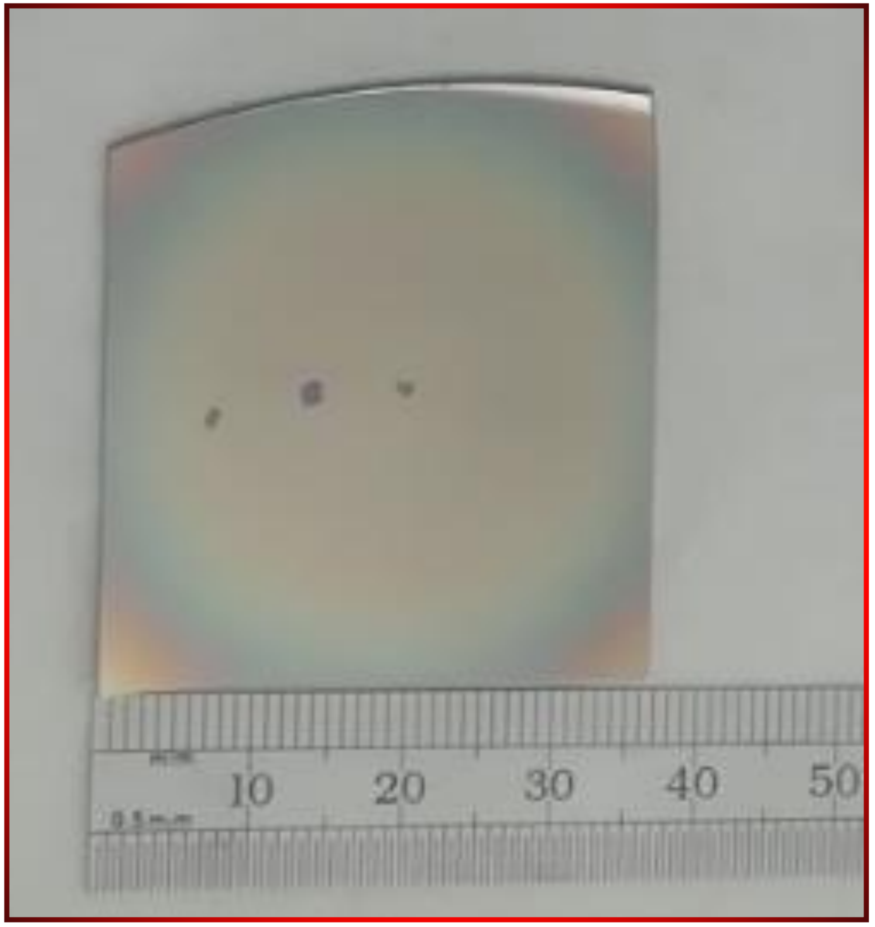


1.24 eV **0.89 eV**

Study in progress…

DLC by PLD: CONCLUSIONS

- **Optimal deposition conditions**
  - OFF-axis configuration
  - Rotating substrate
  - Small spot-area
- **Good UNIFORMITY**
  over a large area
  of film and sp^3 bonds
- **Sheet resistance:**
  $10 \div 10^6$ MΩ/sqr
- **Physical insight**



Thank you very much for your attention!