Diamond-Like Carbons

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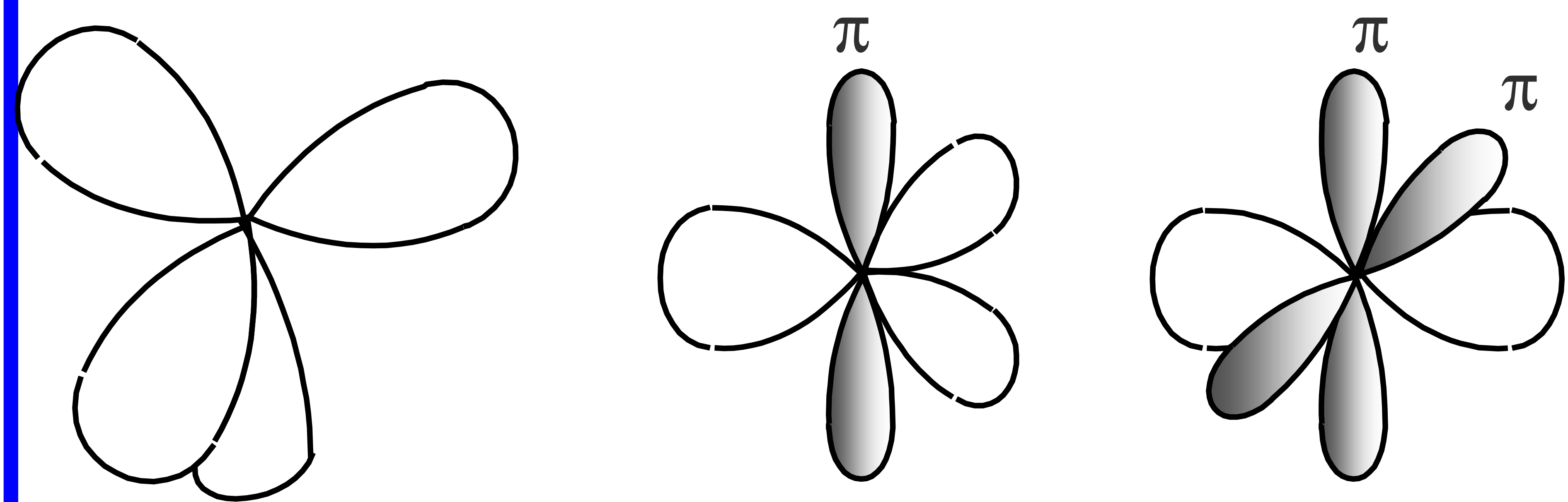
Carbon sp^3, sp^2, sp^1 hybridization



sp^3 sp^2 sp^1

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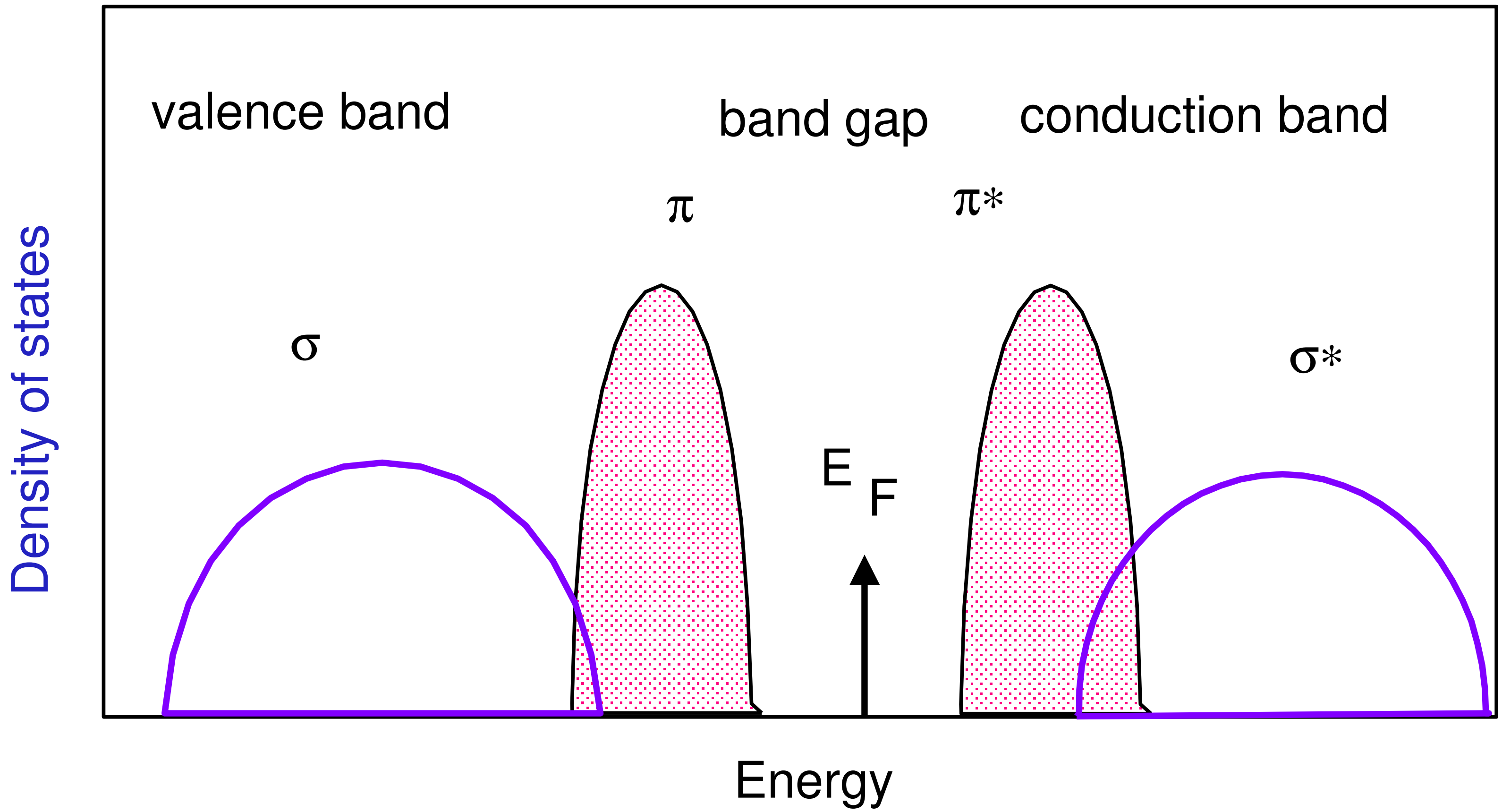
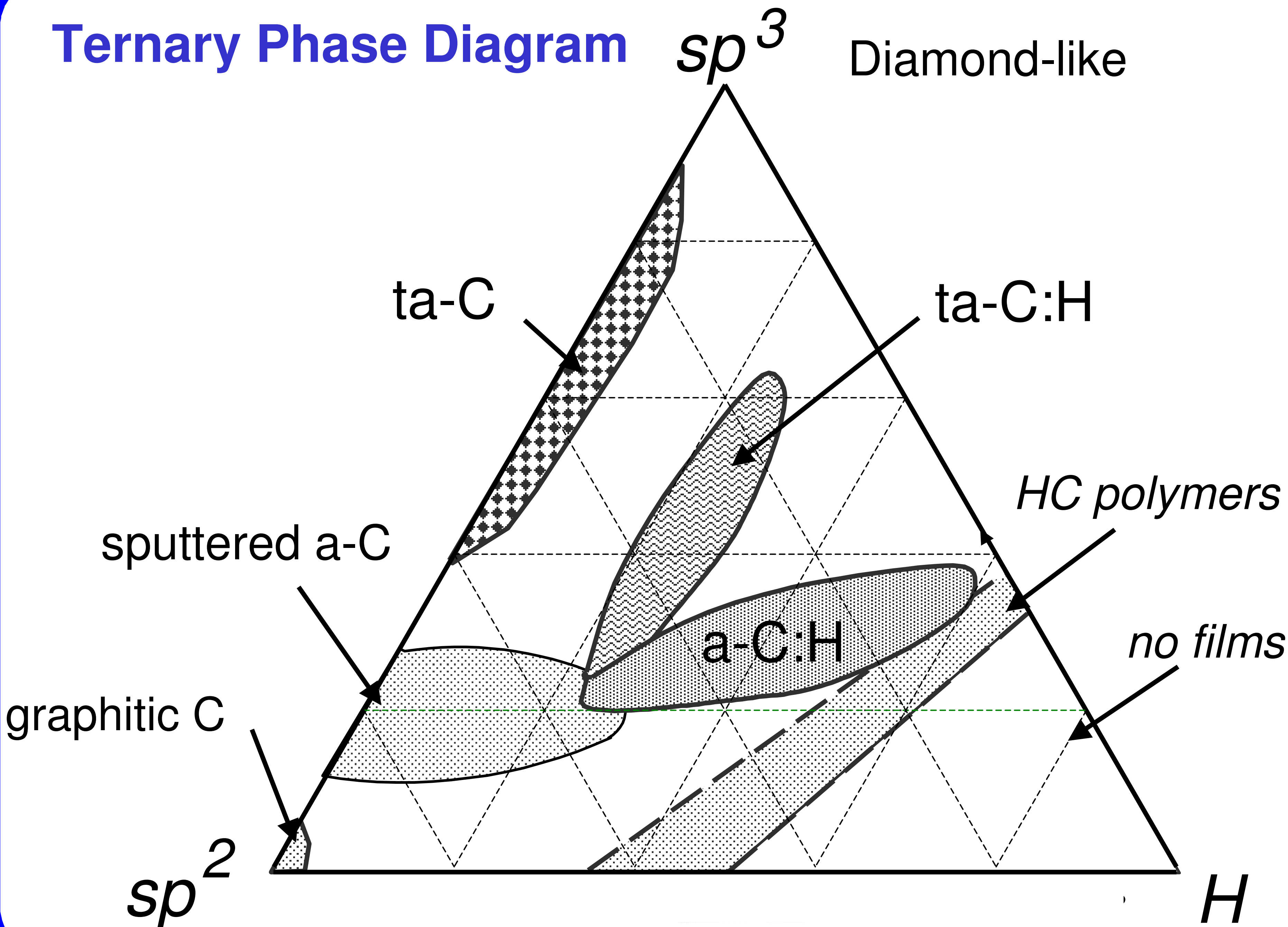

valence band
band gap
conduction band
π
π*
σ
σ*
E F
Density of states
Energy

Ternary Phase Diagram



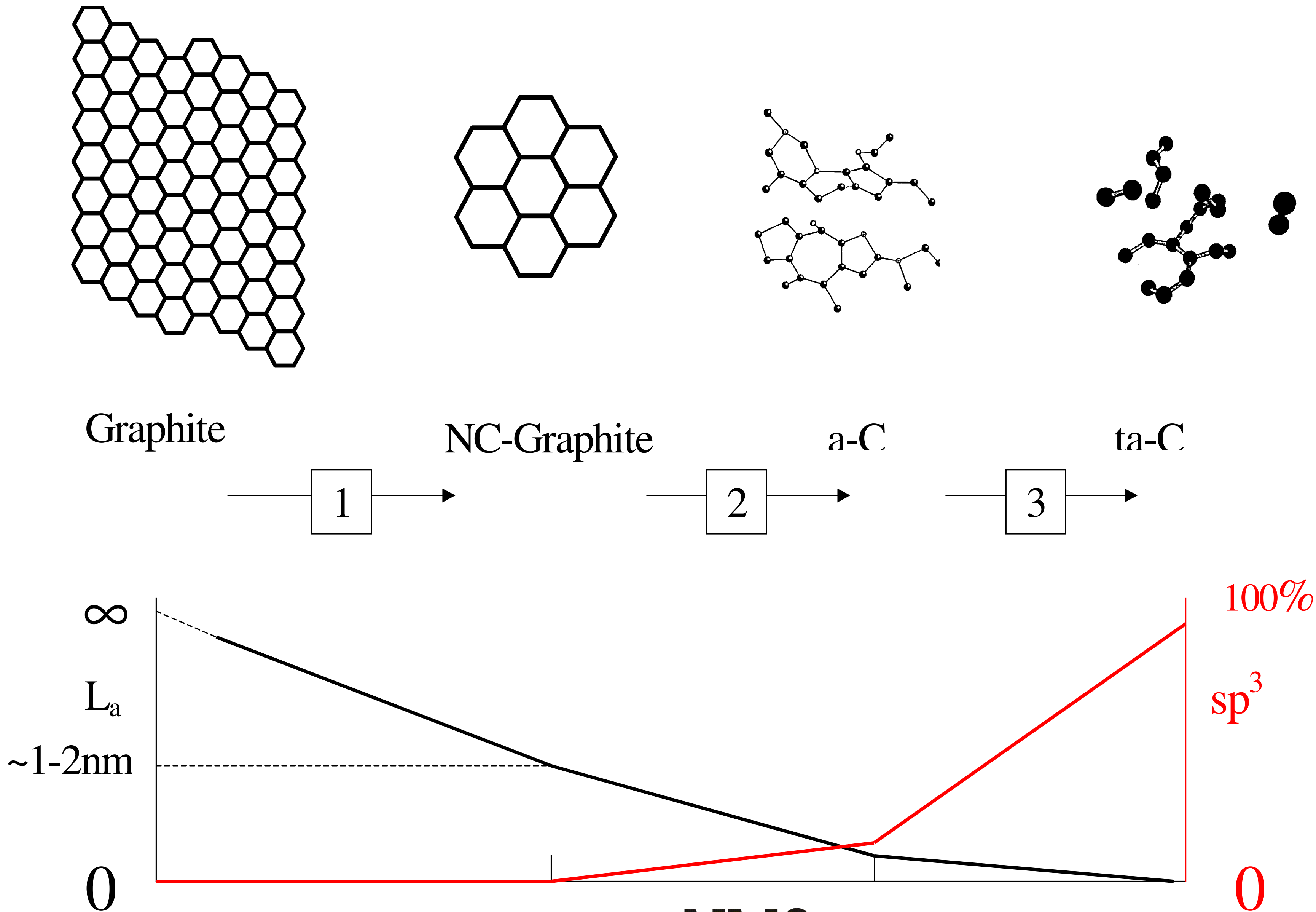
Key parameters:

- sp^3 content
- Clustering of the sp^2 phase
- Orientation of the sp^2 phase
- Cross Sectional Nano-structure

•Note: CLUSTERING OF THE SP^2 PHASE SHOULD BE 4TH DIMENSION In Diagram

•Same H and sp^3 content but different clustering ⇒ different, optical, electronic and mechanical properties.

⇒ Three stages of amorphisation



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Deposition Systems

•Sputtering (a-C)

•Supersonic Cluster Beam Deposition (SCBD) (nanostructured a-C)

•Mass Selected Ion Beam (MSIB) (a-C->ta-C)

•Cathodic Arc (a-C->ta-C)

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Deposition Systems

- Pulsed Laser Deposition (PLD) (a-C->ta-C)

- Plasma Enhanced Chemical Vapour Deposition (PECVD)   (a-C:H)

- Plasma Beam Source (PBS) (a-C:H->ta-C:H)

- Electron Cyclotron Wave Resonance (ECWR) (a-C:H->ta-C:H)

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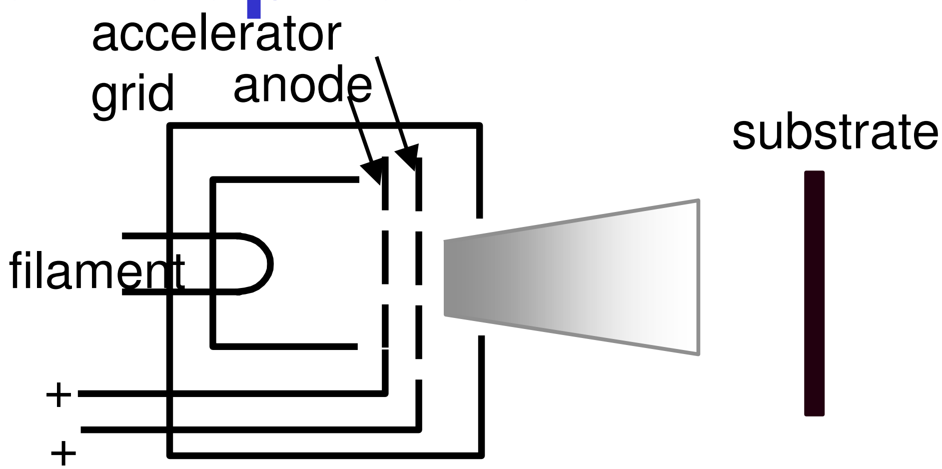
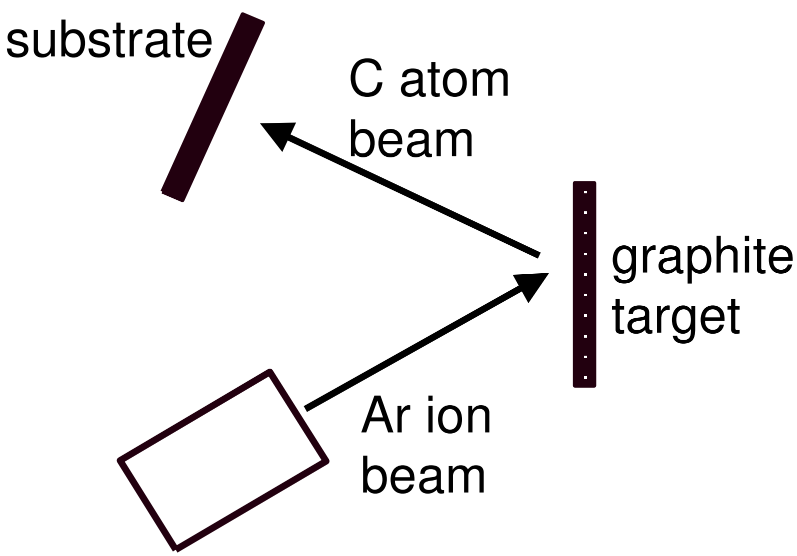
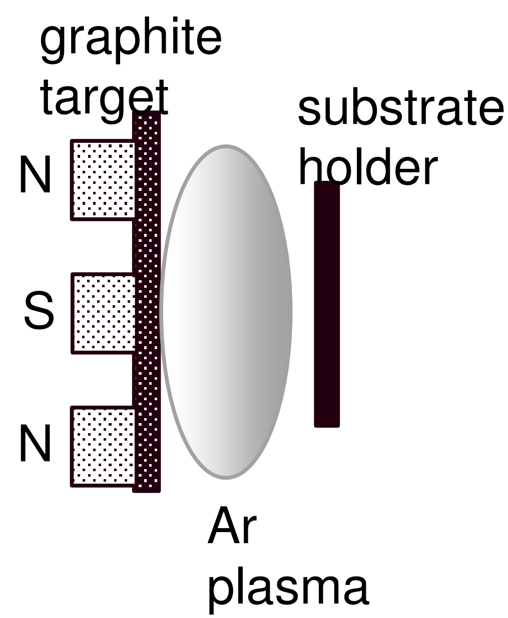
Ion deposition



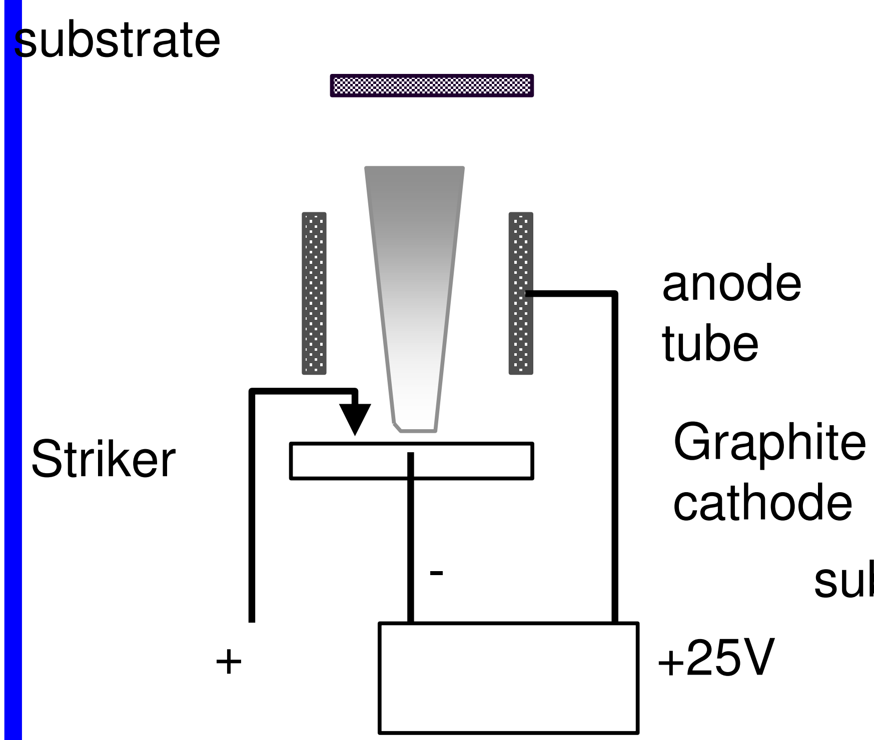
Ion assisted Sputtering



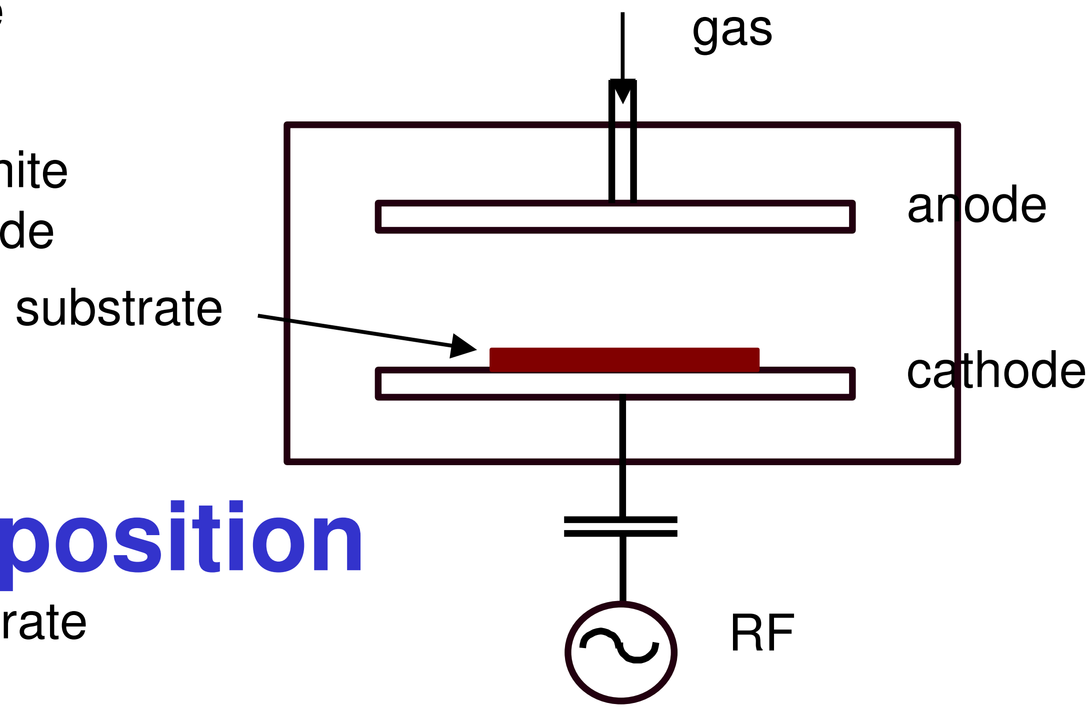
Sputtering



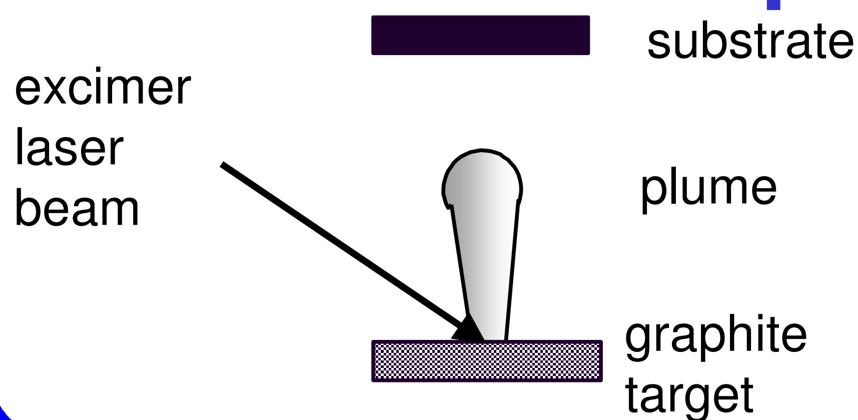
Cathodic Vacuum Arc



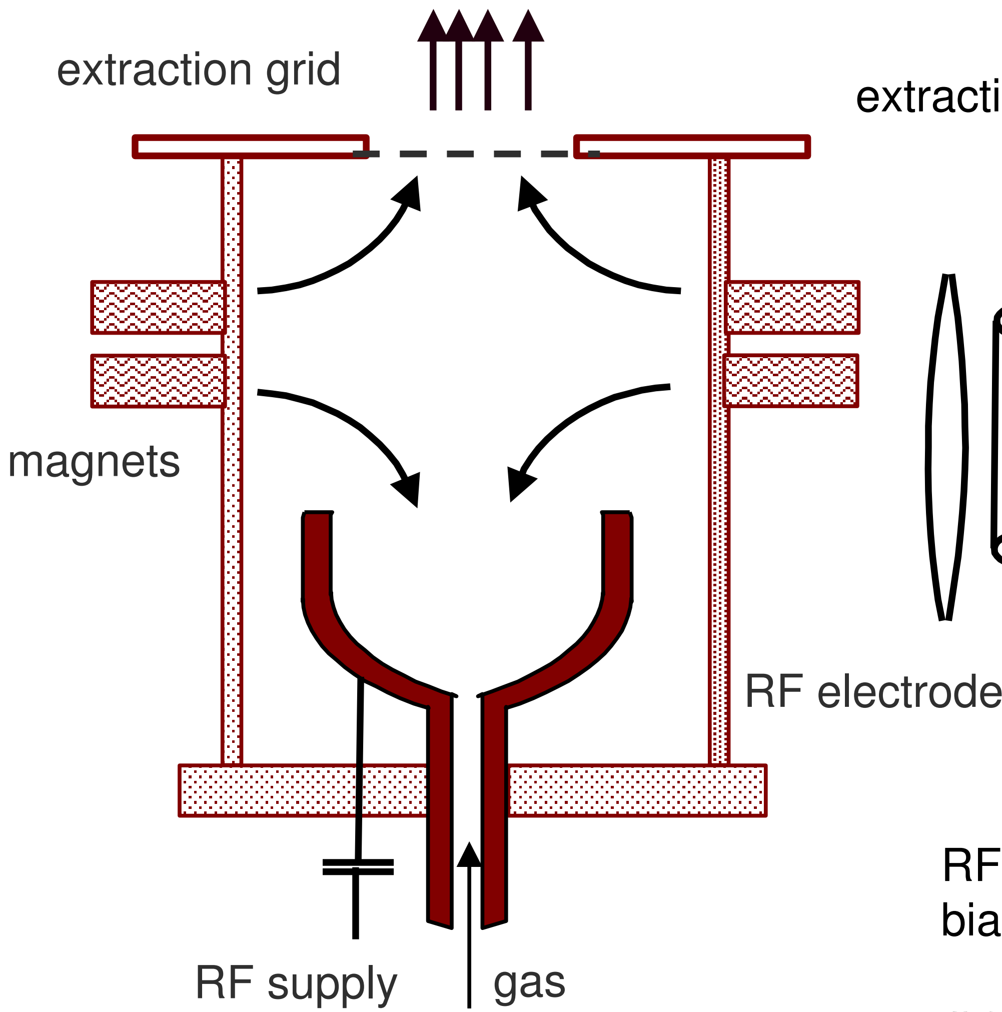
Plasma Deposition

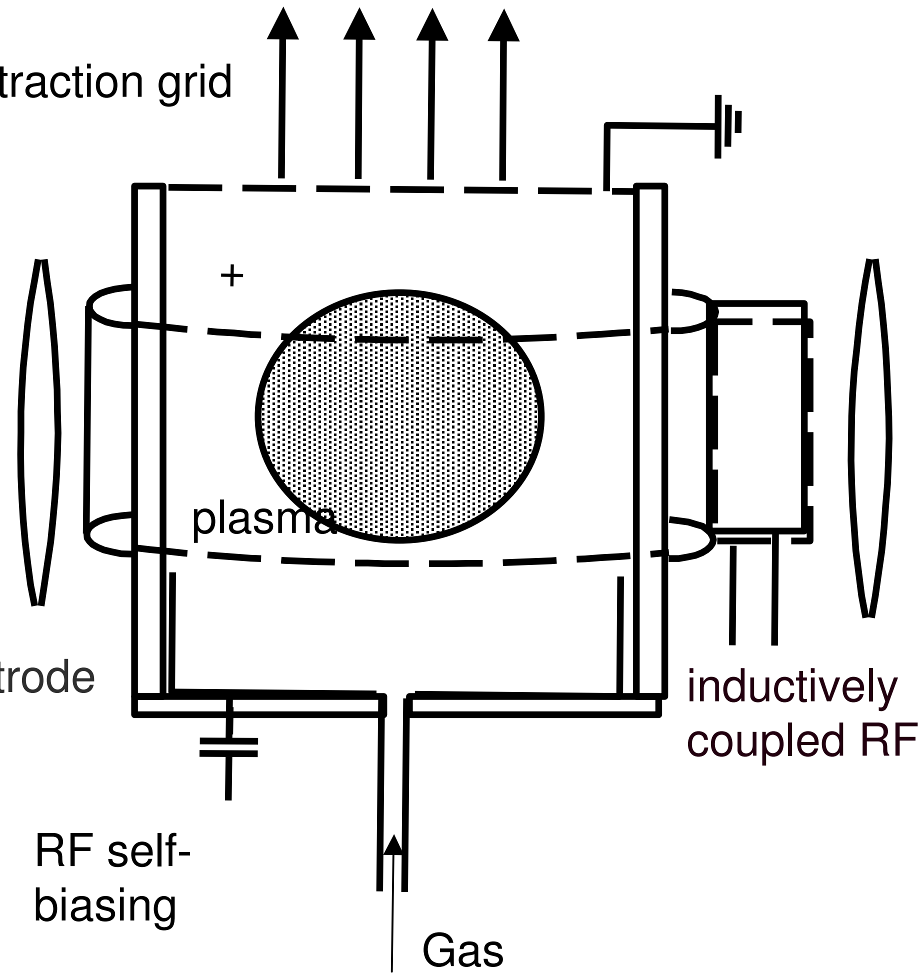


Pulsed Laser Deposition

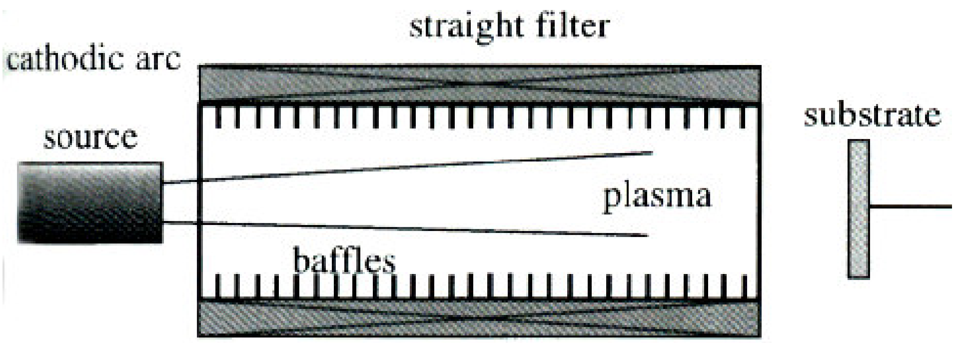


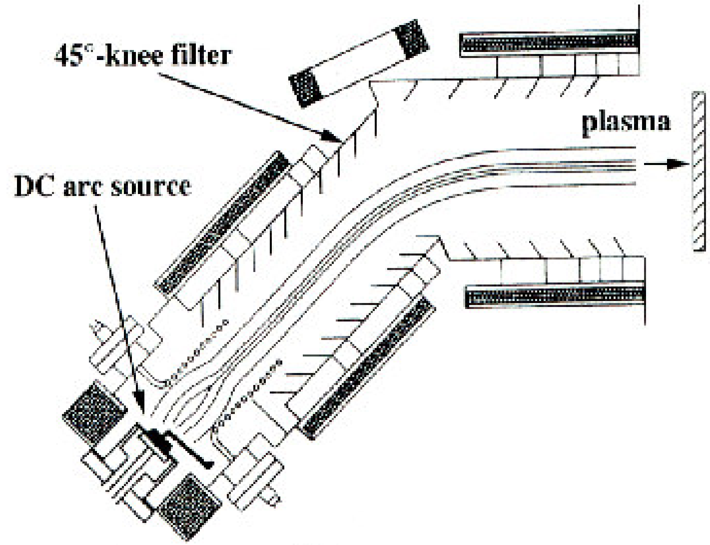
Plasma Beam Source ECWR

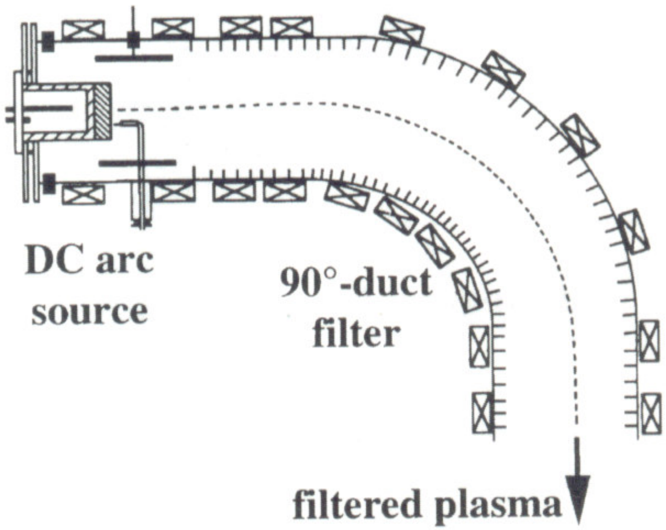


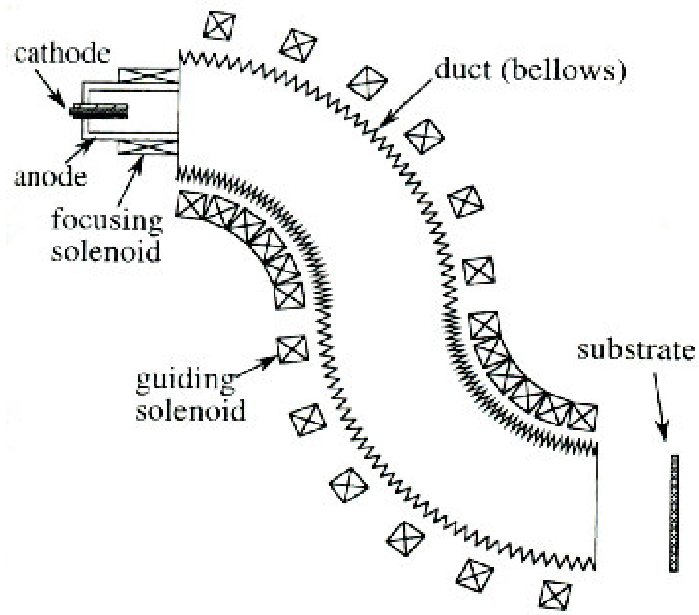


Filtered cathodic vacuum arcs



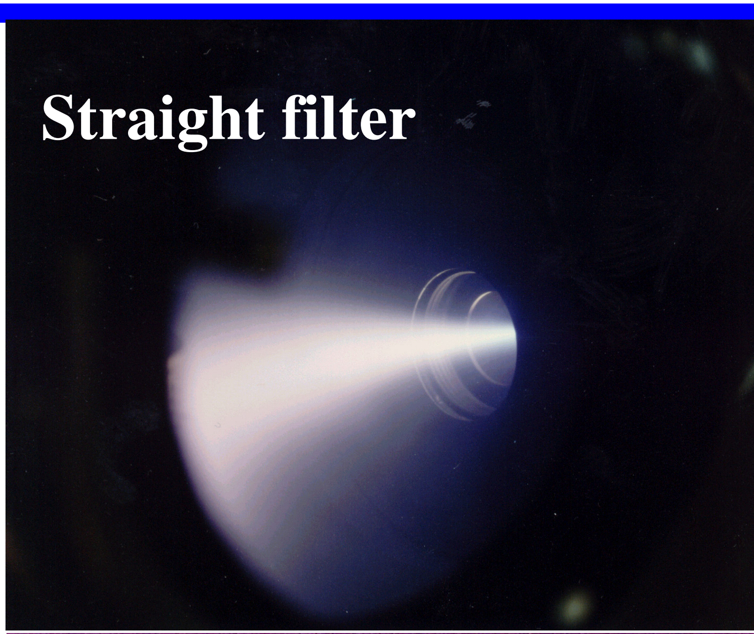


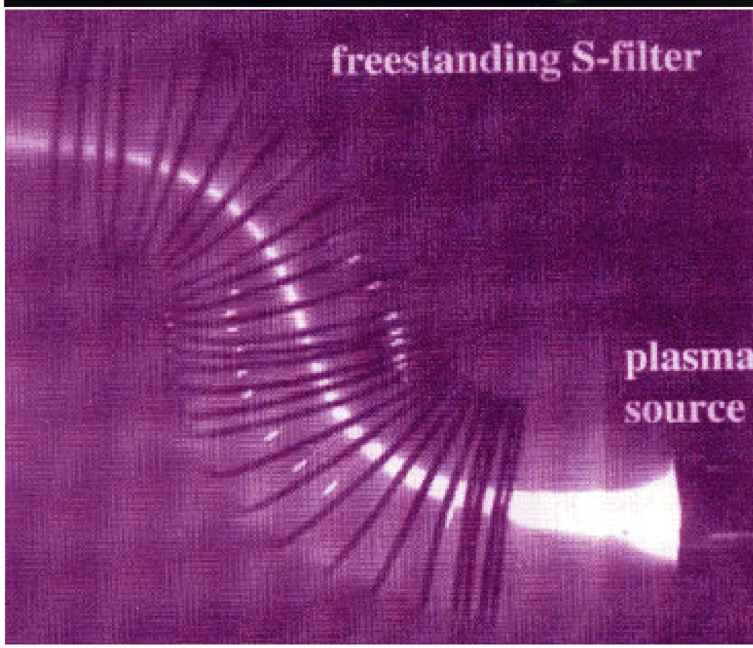


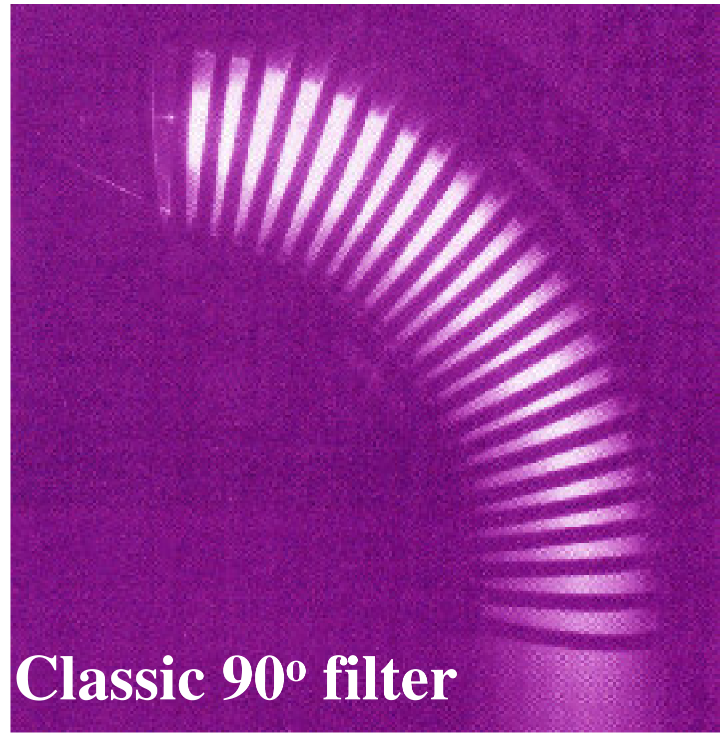


A. Anders, Surf. Coat. Technol., 1999.

FCVA







A. Anders, Surf. Coat. Technol., 1999

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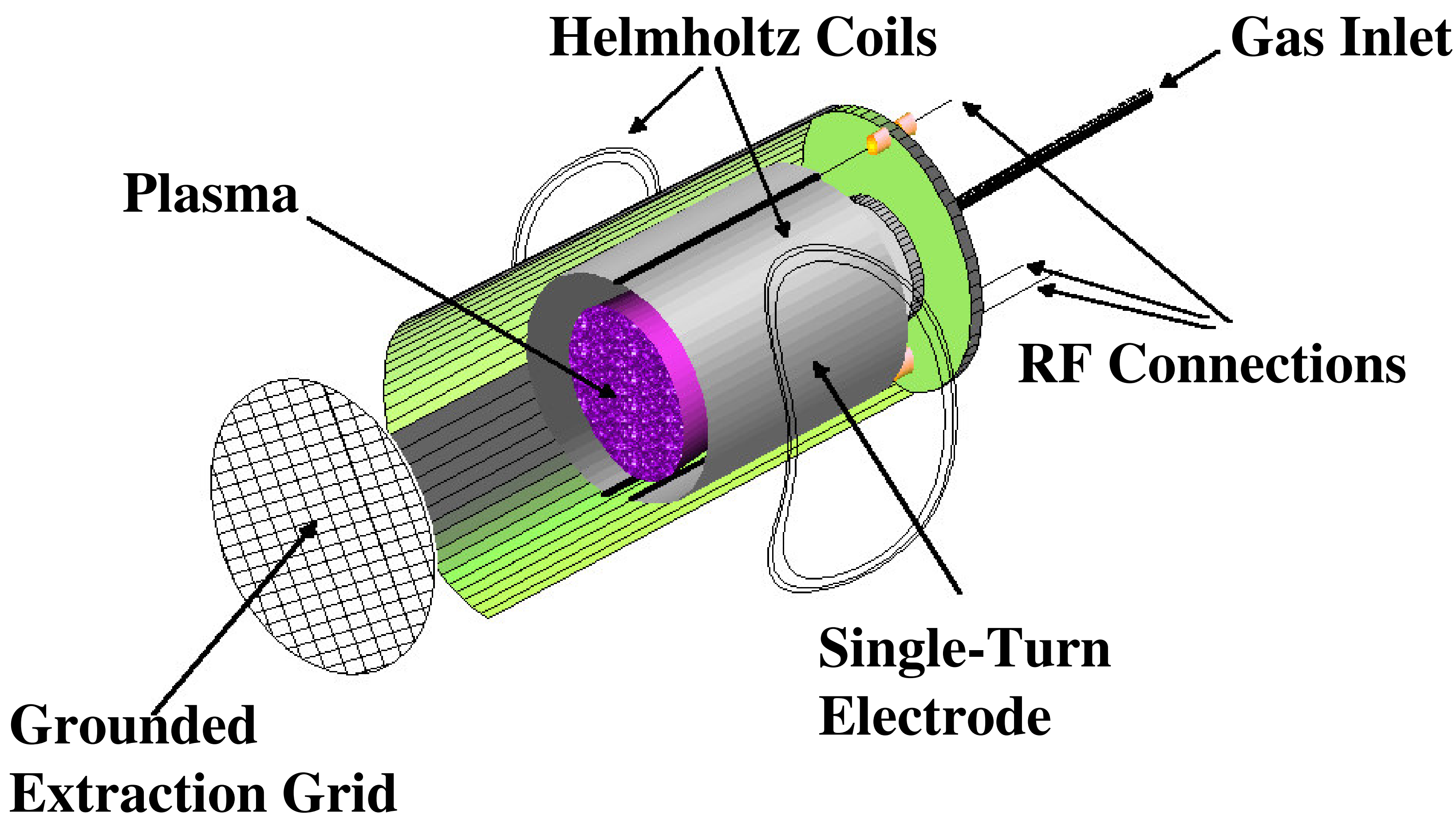
The ECWR Plasma Beam Source



ECWR

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CLASSES OF CARBON NITRIDES

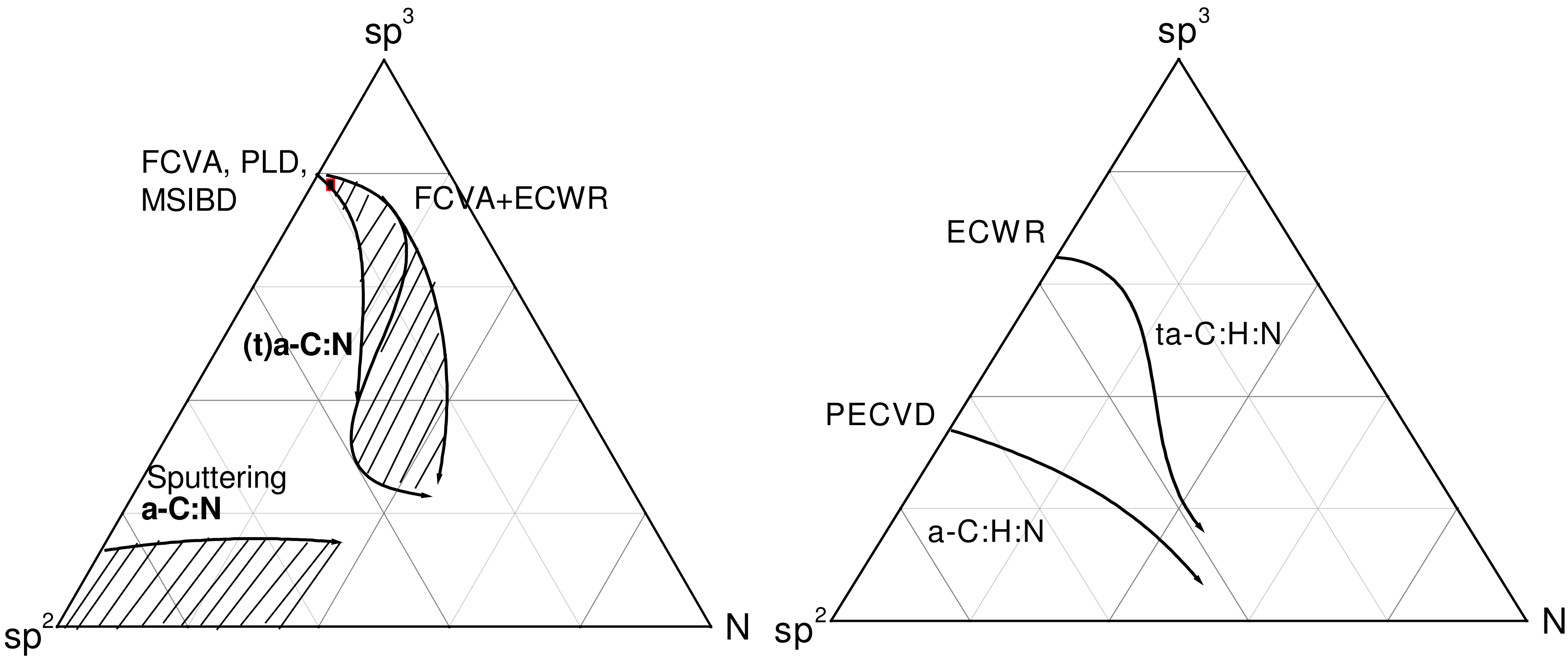
1) Mainly sp^2 a-C:N by sputtering

2) Mainly sp^3 ta-C:N by FCVA, PLD, MSIBD

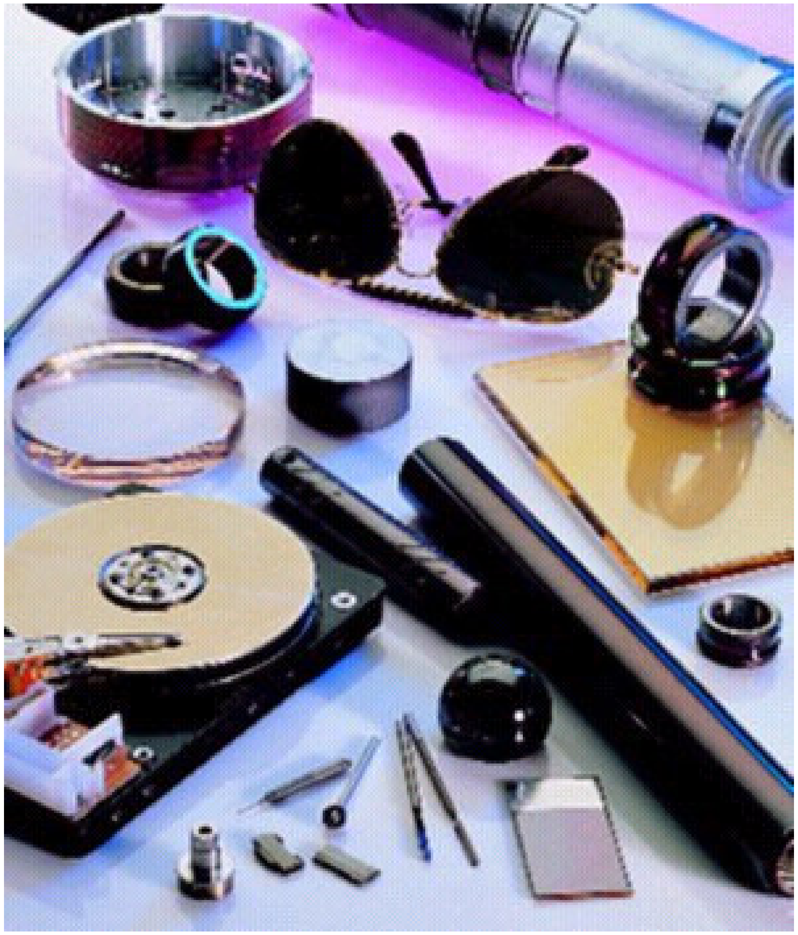
3) Plasma deposited a-C:H:N with moderate sp^3 content

4) ta-C:H:N by high plasma density sources, with higher sp^3 content and lower H content

Amorphous Carbon Nitrides



Commercial applications of DLC



- Aerospace
- Automotive
- Bearings
- Electronics
- Industrial Wear Parts
- Instruments
- Medical/Dental
- Metalworking
- Textiles
- Tools/Dies/Molds
- Bar Code Windows

Diamond-like carbon for data and beer storage

Carbon is a very versatile element that can crystallize in the forms of diamond or graphite. There are many noncrystalline carbons, known as amorphous carbons. An amorphous carbon with a high fraction of diamond-like (sp^3) bonds is named diamond-like carbon (DLC). Unlike diamond, DLC can be deposited at room temperature. Furthermore, its properties can be tuned by changing the sp^3 content, the organization of the sp^2 sites and the hydrogen content. This makes DLC ideal for a variety of different applications. We review the use of ultrathin DLC films for ultrahigh density data storage in magnetic and optical disks and ultralong beer storage in plastic bottles.

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Materials Today Feb 07

Characterization

•AFM (Roughness Evolution)

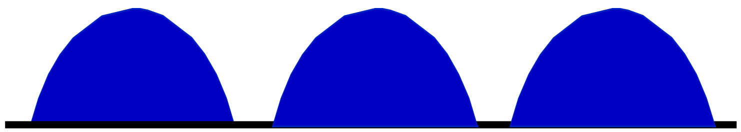
•X-Ray Reflectivity

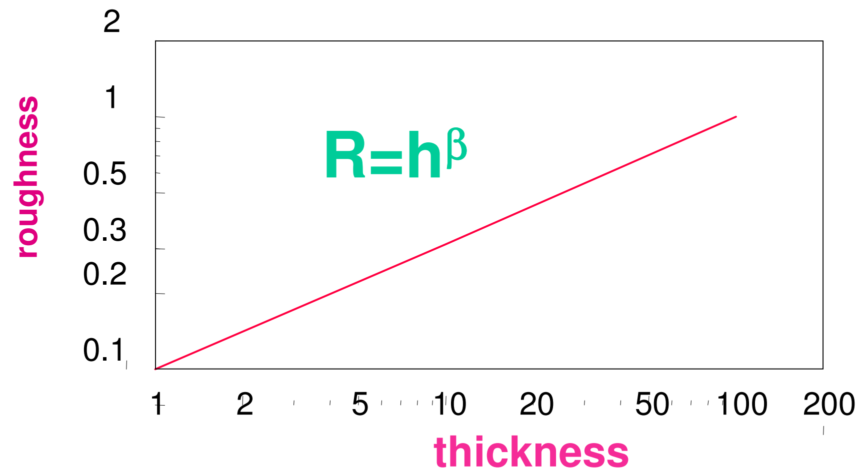
•Surface Acoustic Waves (LAW, SBS)

•Resonant Raman Spectroscopy

COVERAGE is fundamental parameter

- Pin-holes
- Extrinsic
  - filtering, cleaning
- Intrinsic
  - Interface energy between phases - *wetting*
  - Surface mobility helps islanding
- Roughness - fractal growth (Lower β, smoother films)





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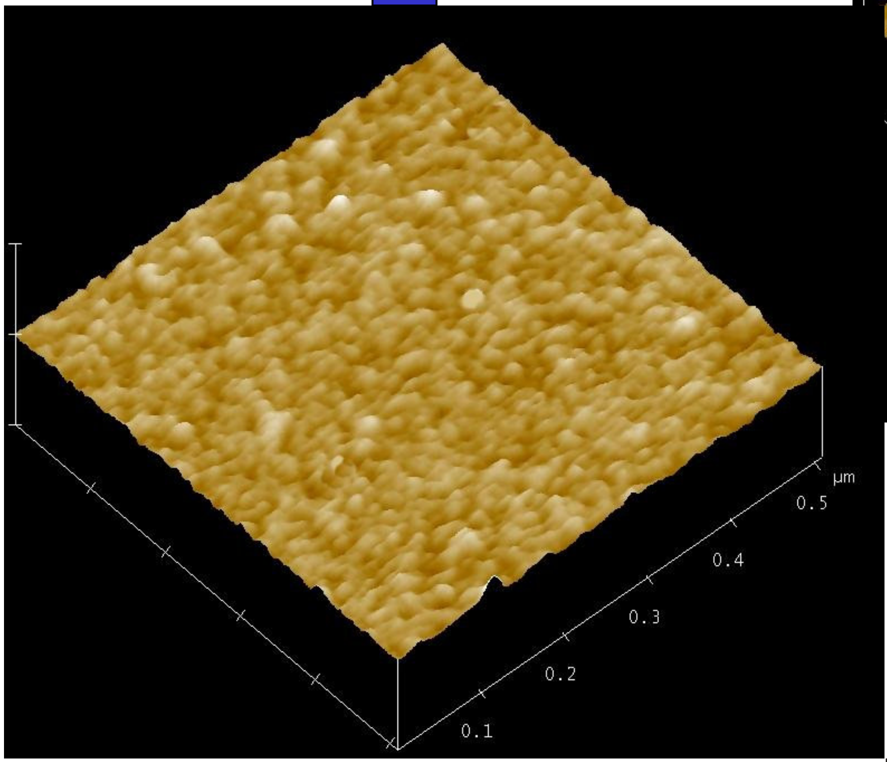
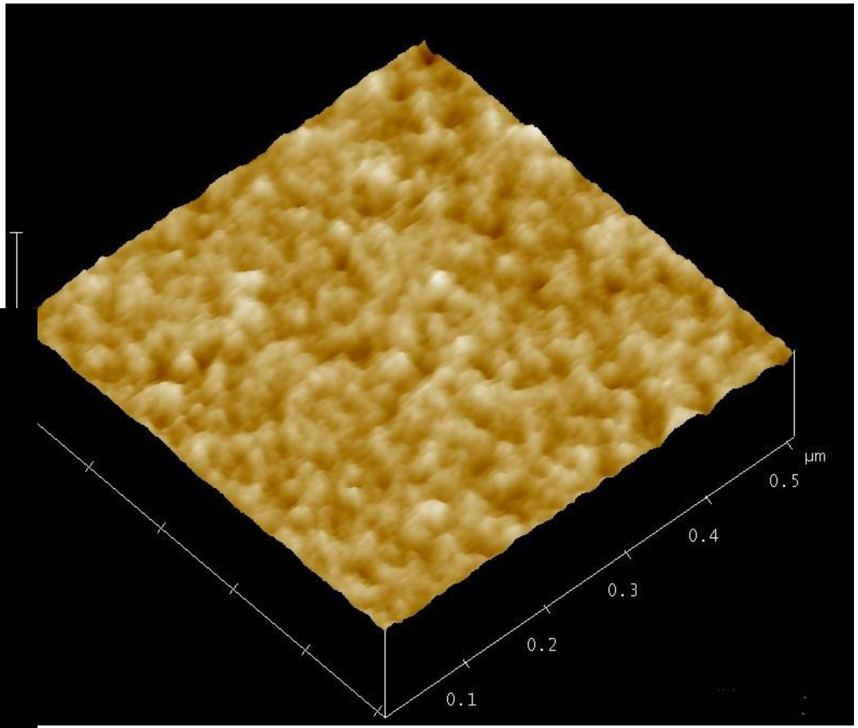
ROUGHNESS EVOLUTION IN TA-C

z = 0.9 nm

R =0.124 nm





z = 15 nm

R =0.12 m

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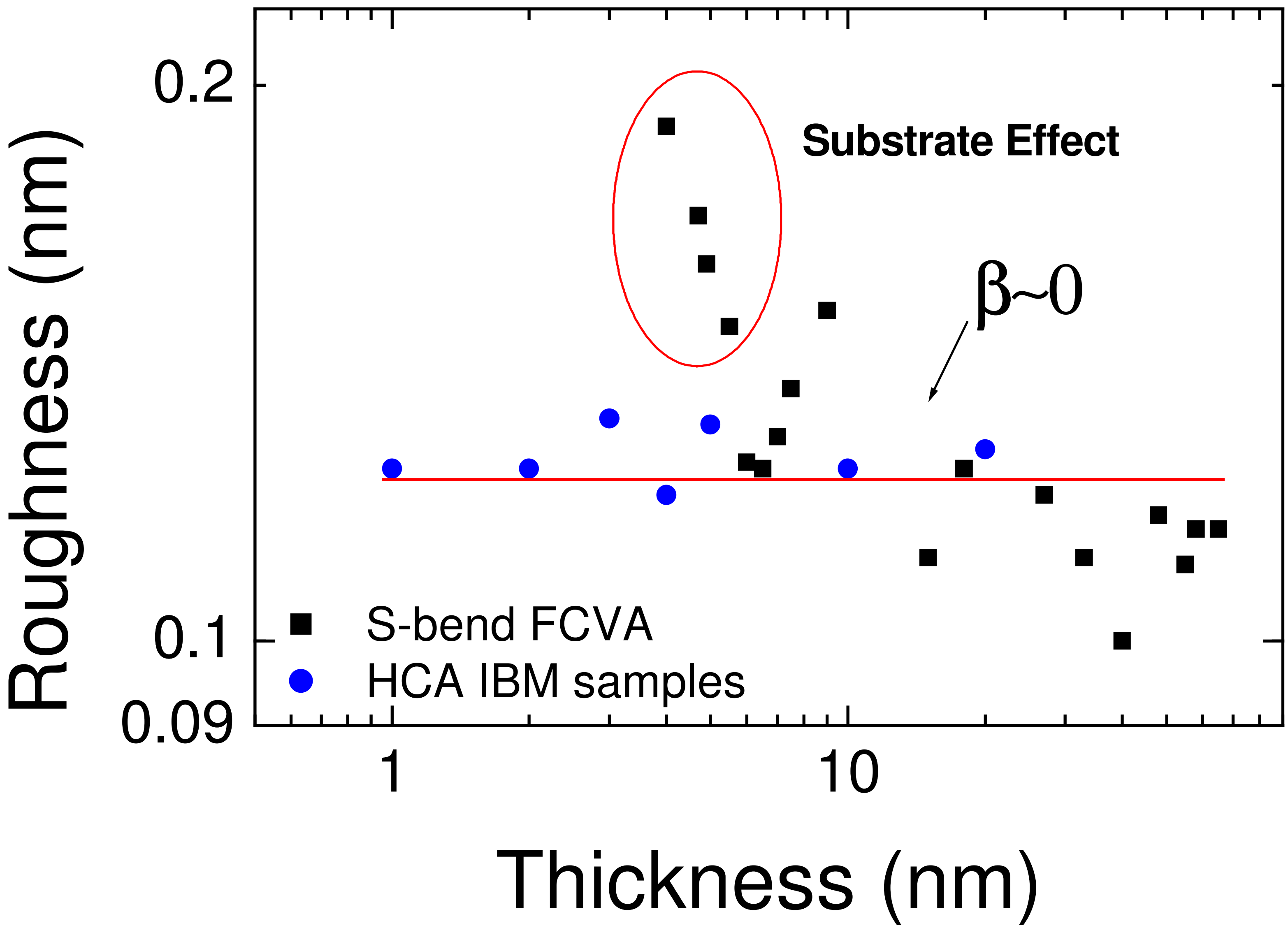


Scaling Law ⇒ β ~ 0

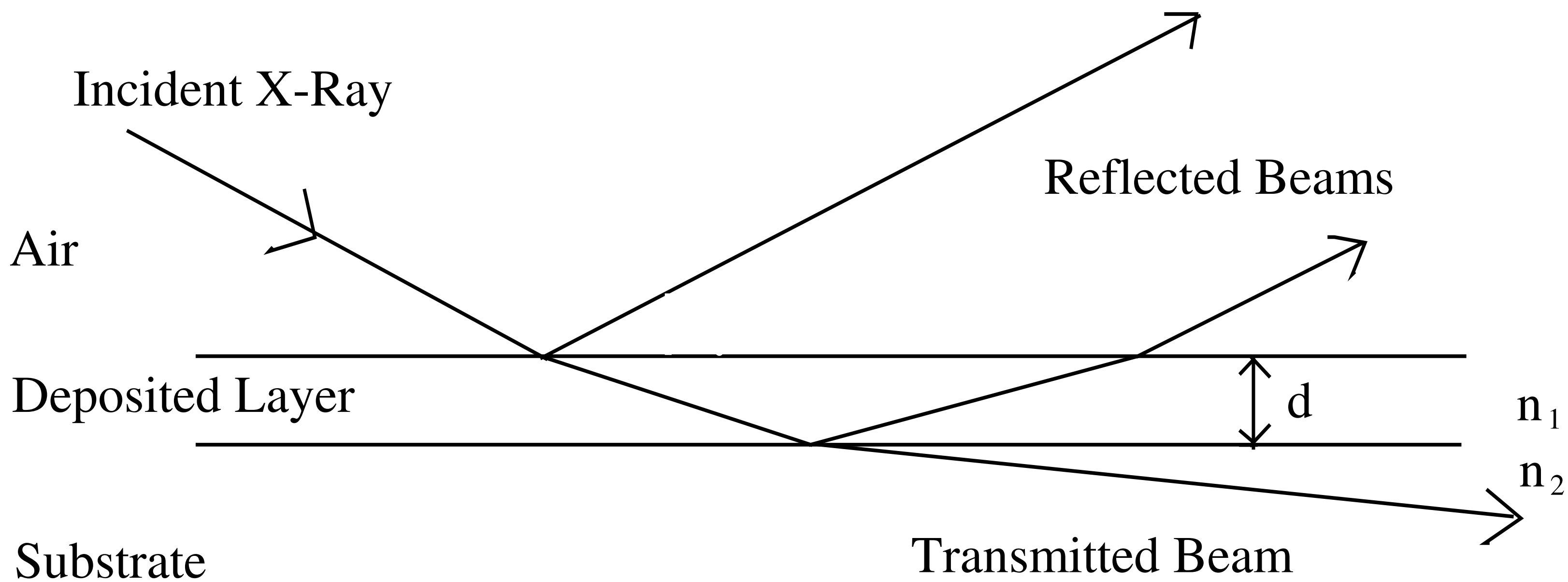
X-Ray Reflectivity (XRR)

XRR is a simple, fast and non- destructive technique to determine:

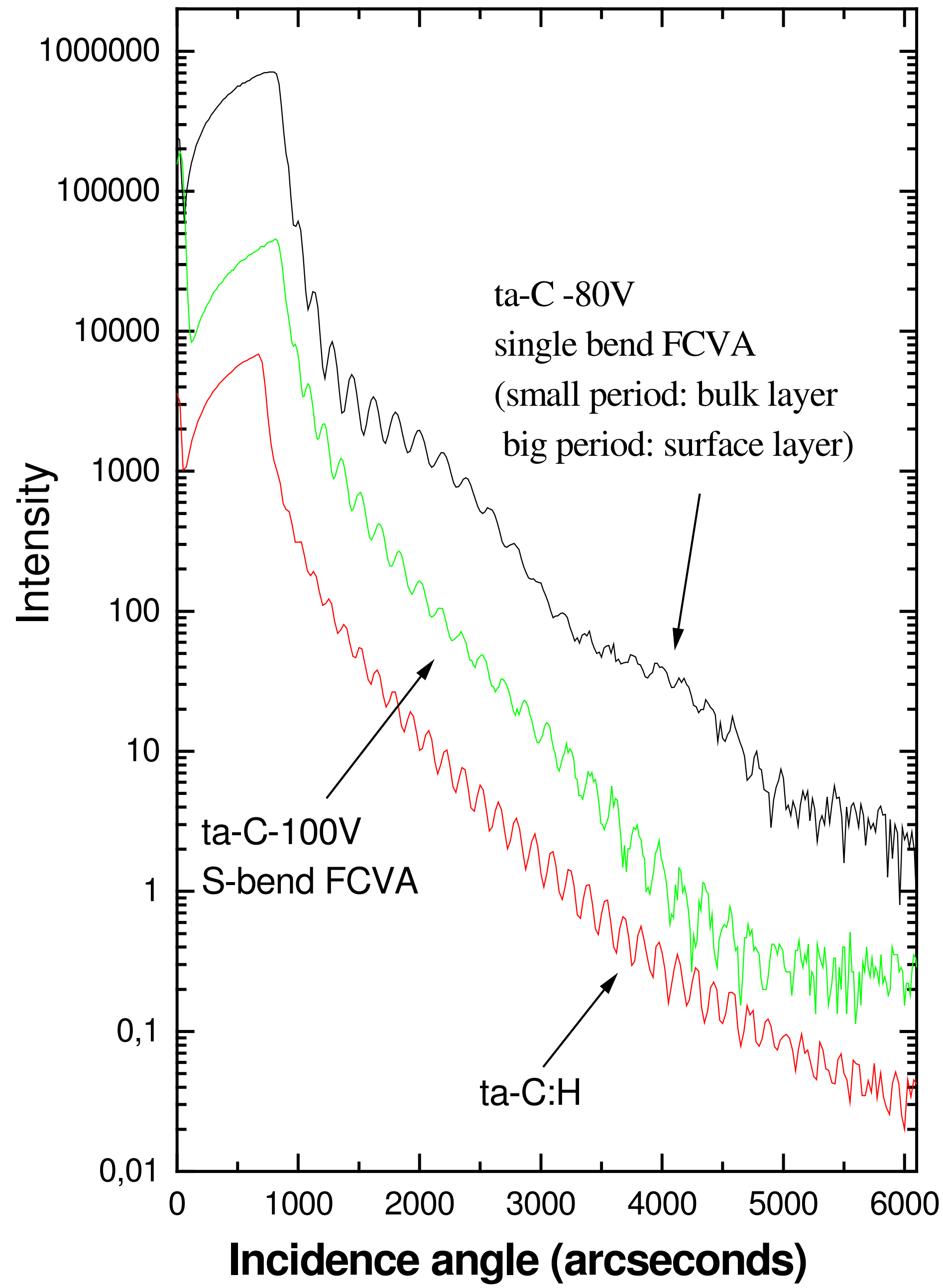
- density
- thickness
- internal layering
- surface roughness

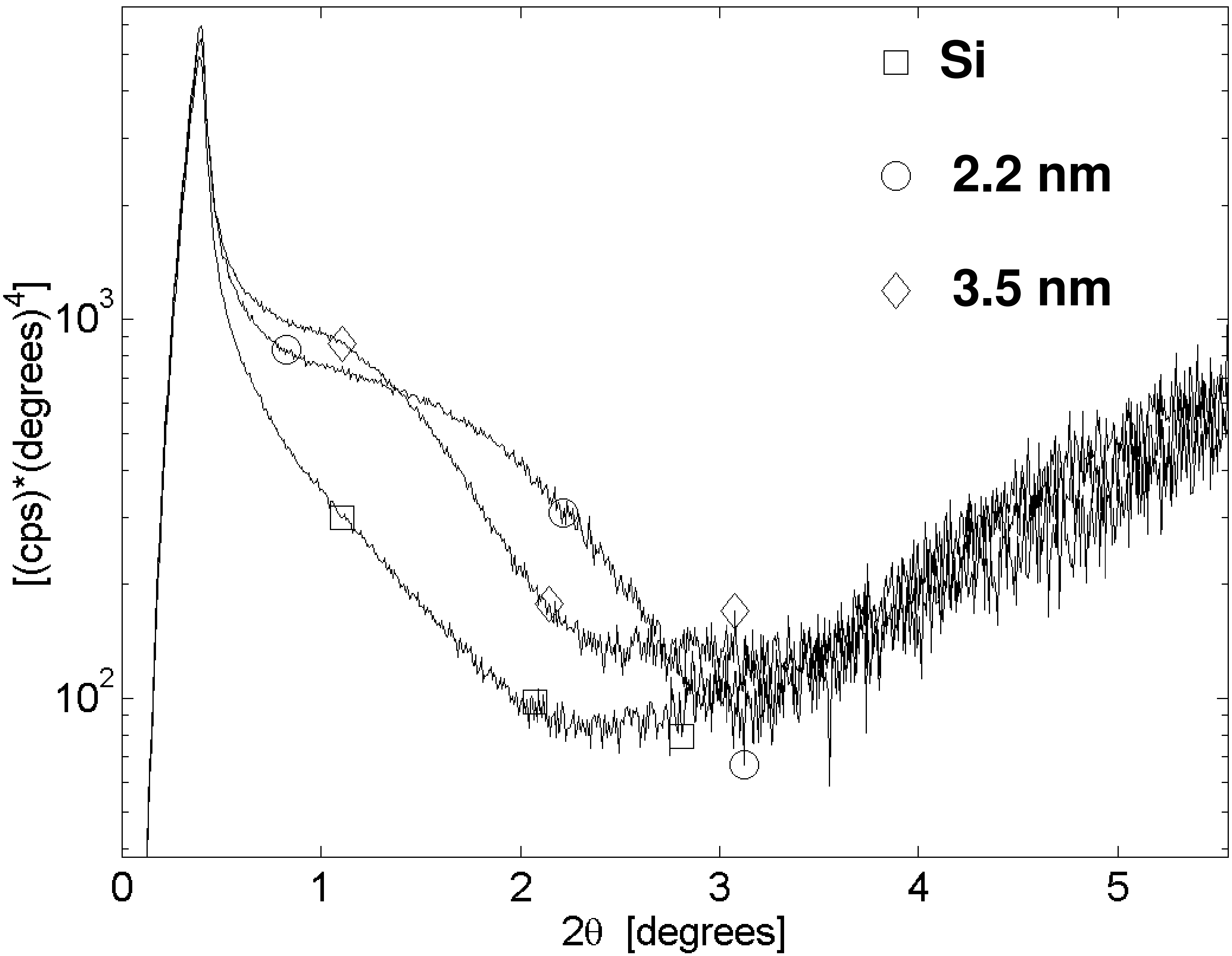
- **non destructive** technique
- **no sample preparation** required

XRR can be used as a **standard method** for amorphous carbon films characterization

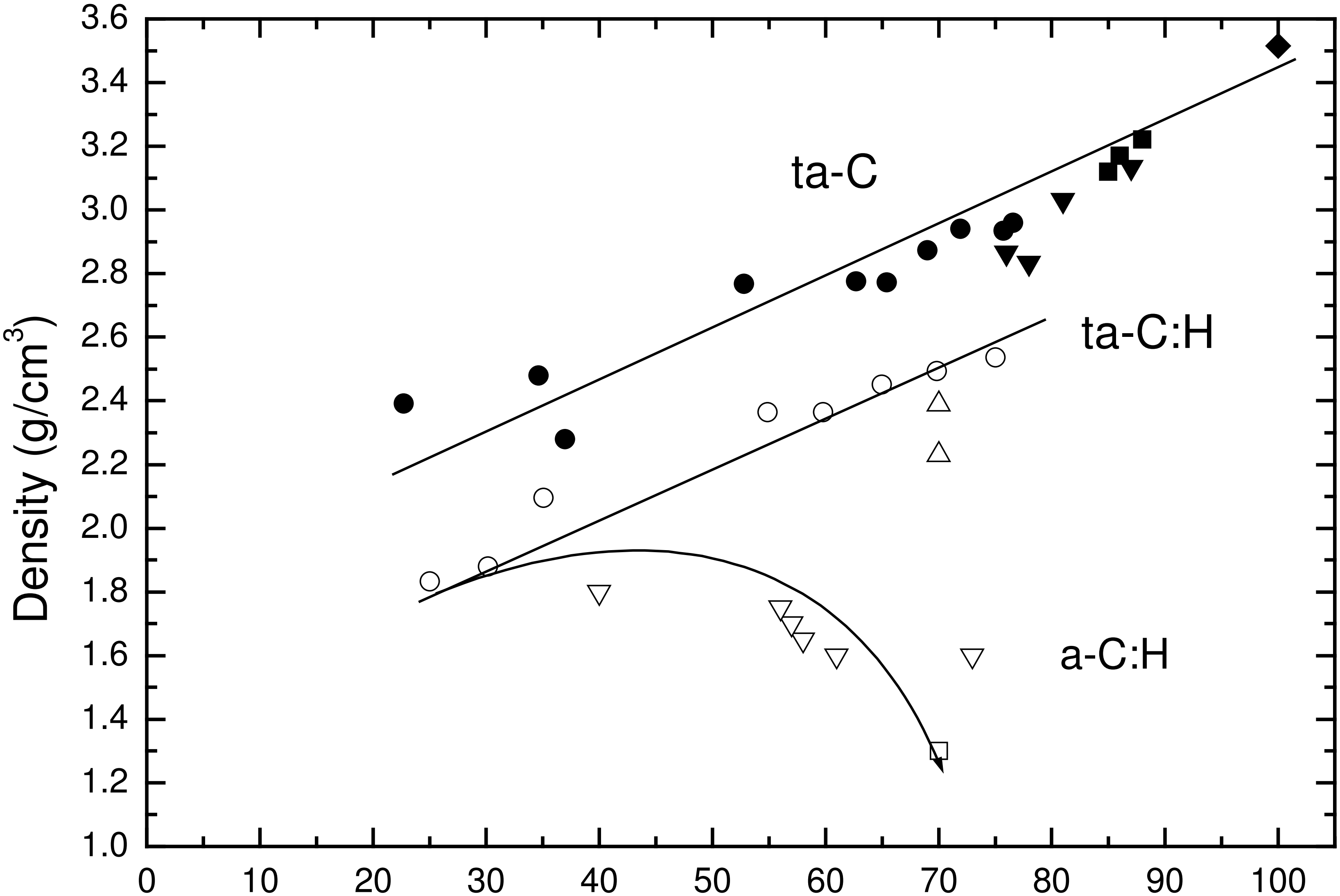


- θ_c gives density
- Fast interference fringes give thickness
  Period $\Delta\theta$ gives the Film thickness:
  $\Delta\theta \cong \lambda/2d$
  d = thickness
- **Longer fringe periods $\Rightarrow$ layering**
  The longest period corresponds to the smallest layer
- **Decay slope gives roughness**





Si
2.2 nm
3.5 nm
[(cps)*(degrees)^4]
10^3
10^2
0
1
2
3
4
5
2θ [degrees]



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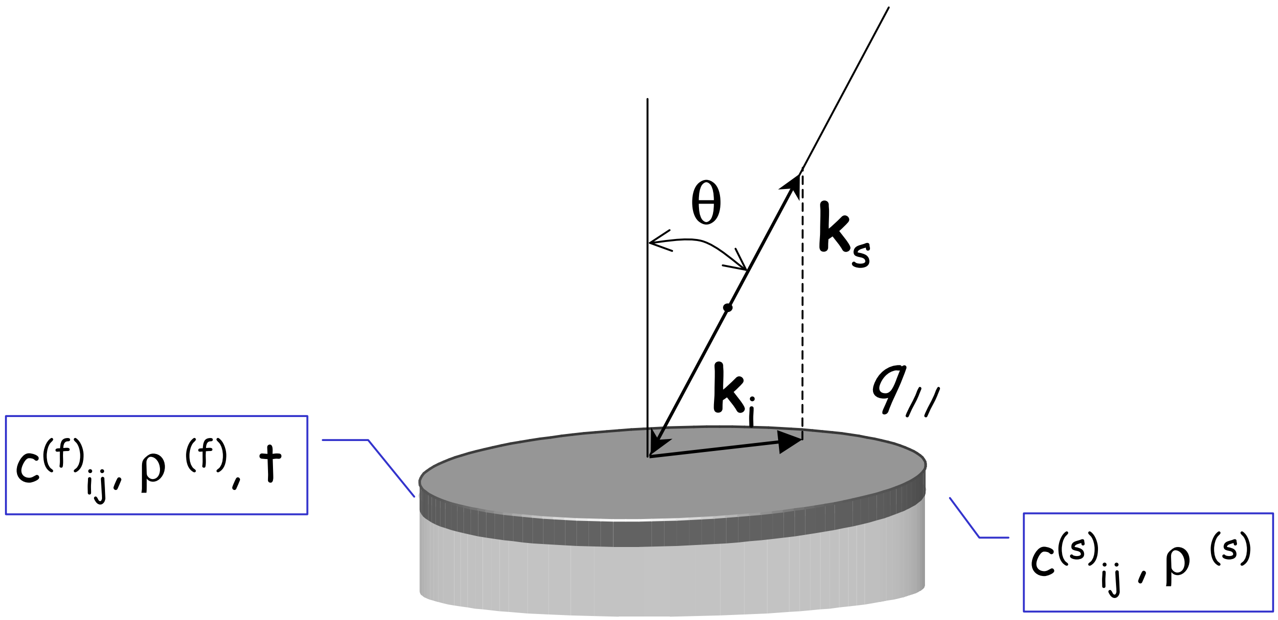
Surface Brillouin Spectroscopy (SBS)



Film (f)
and substrate (s)
properties:
c_{ij}: elastic constants
ρ: density
t: thickness

Back-scattering configuration:

θ: incidence angle
k: incident (i) and scattered (s) wave-vector
$\mathbf{q}_{//}$: parallel component of the acoustic phonon wave-vector

Laser Acoustic Waves

Fraunhofer Institut Werkstoff- und Strahltechnik

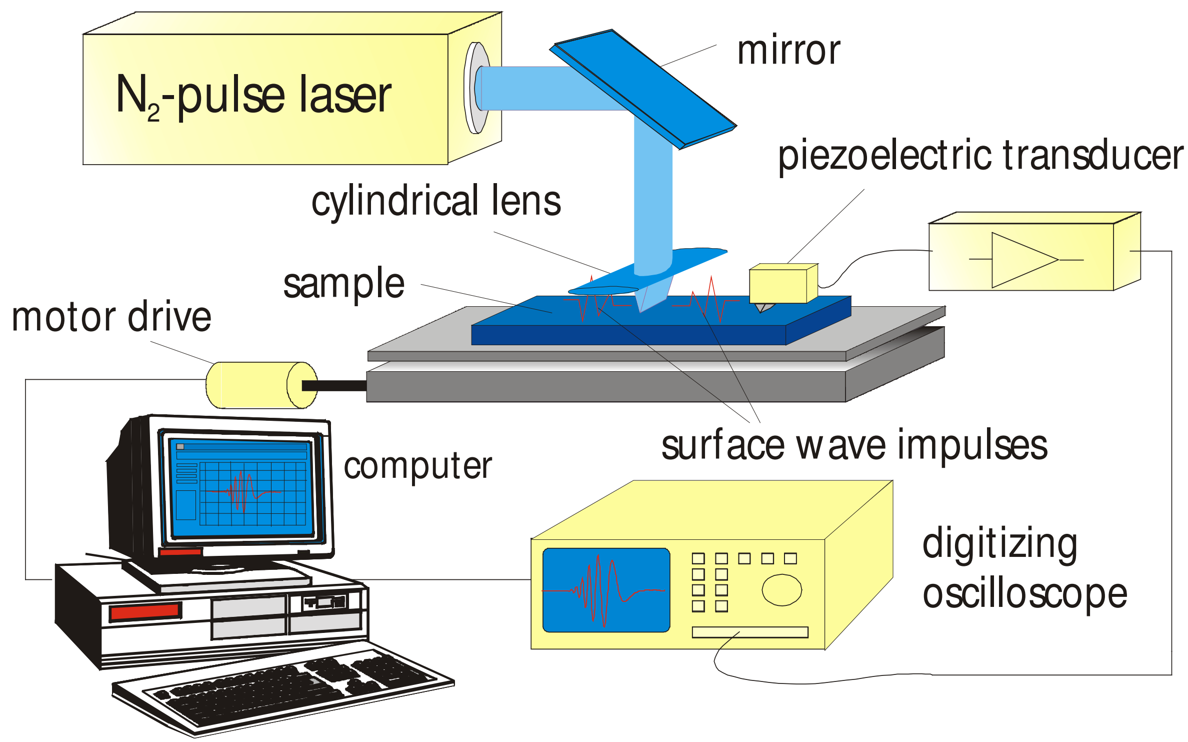
Technical specification

Nitrogen laser
pulse length: 0.5 ns
pulse energy: 400 µJ

Detector
piezoelectric foil
(Hess, u.a. Heidelberg)

Translation stage
accuracy: ±1 µm

Digital oscilloscope
sampling rate: 2 GSa/s



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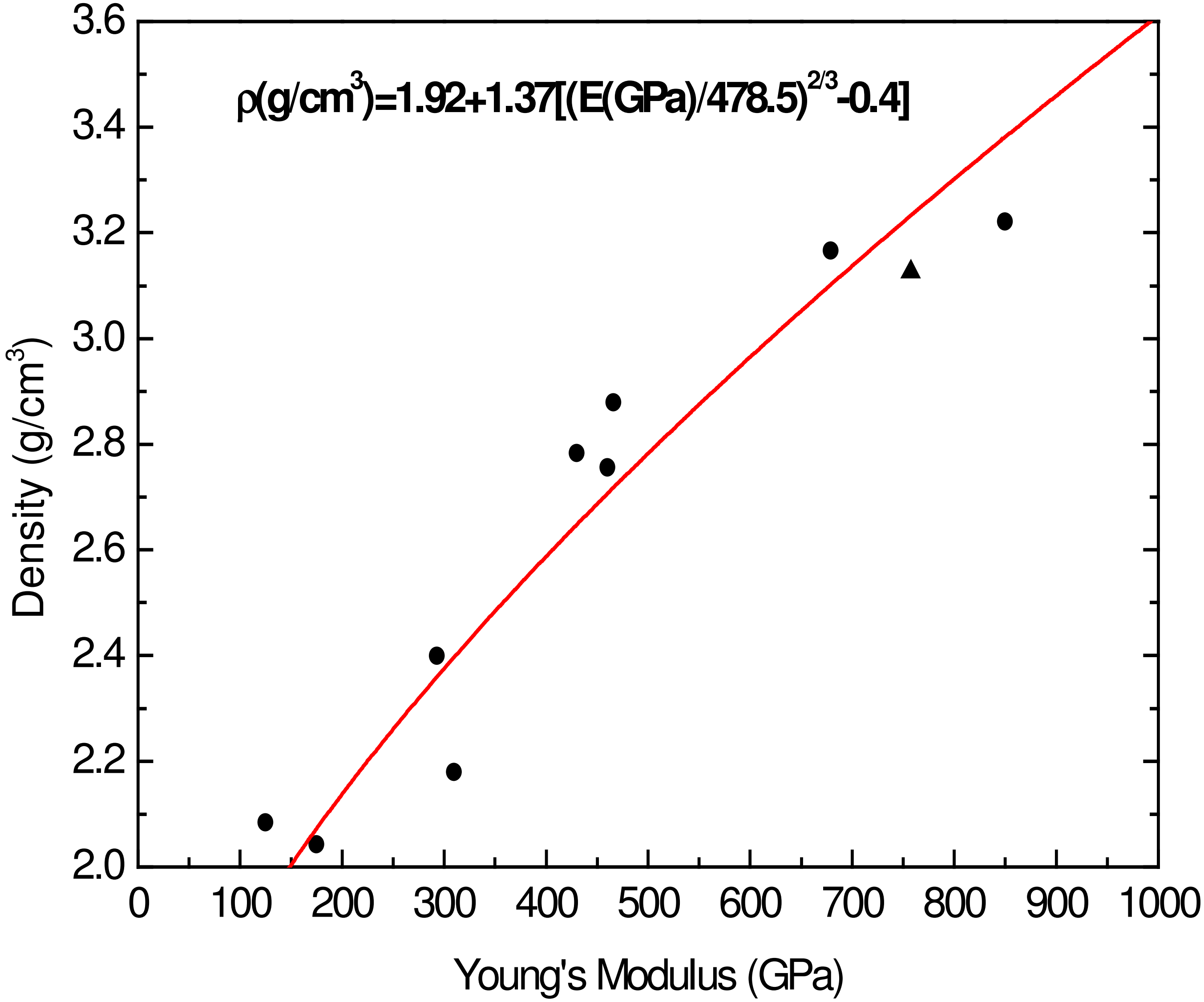
LAW	SBS
excited SAWs →	relies on thermally excited SAWs →
high amplitude – fast measurements (minutes)	small amplitude – slow measurements (several hours)
frequency is determined	wavelength is determined
f = 50 – 250 MHz → λ = 10 – 250 μm	λ = 300 – 800 nm → f = 3 – 25 GHz
longer wavelength → lower sensitivity to thin films	shorter wavelength → higher sensitivity to thin films
but higher precision (< 1/1000)	but lower precision (~ 1/100)
requires ~ 20 mm propagation	local: < 1 mm
	possible low scattering cross-section
piezoelectric sensing	contact-less: one optical access
only vertically polarized waves	in non-metallic materials: also other types of waves

Density vs. Young's Modulus for ta-C



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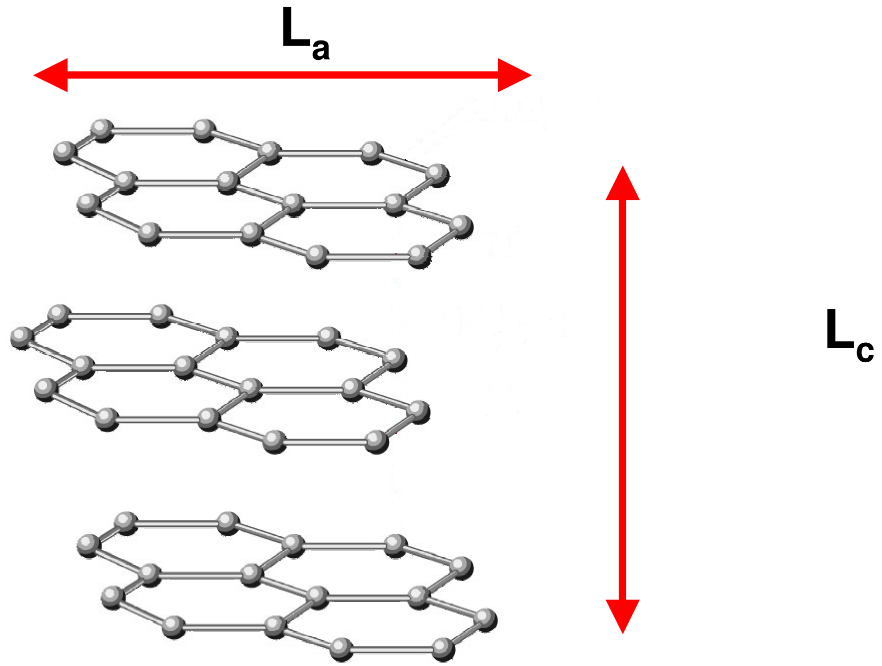
Raman Fingerprints Carbons

In graphites: L_a, L_c, disorder, doping



Poly-aromatic hydrocarbons

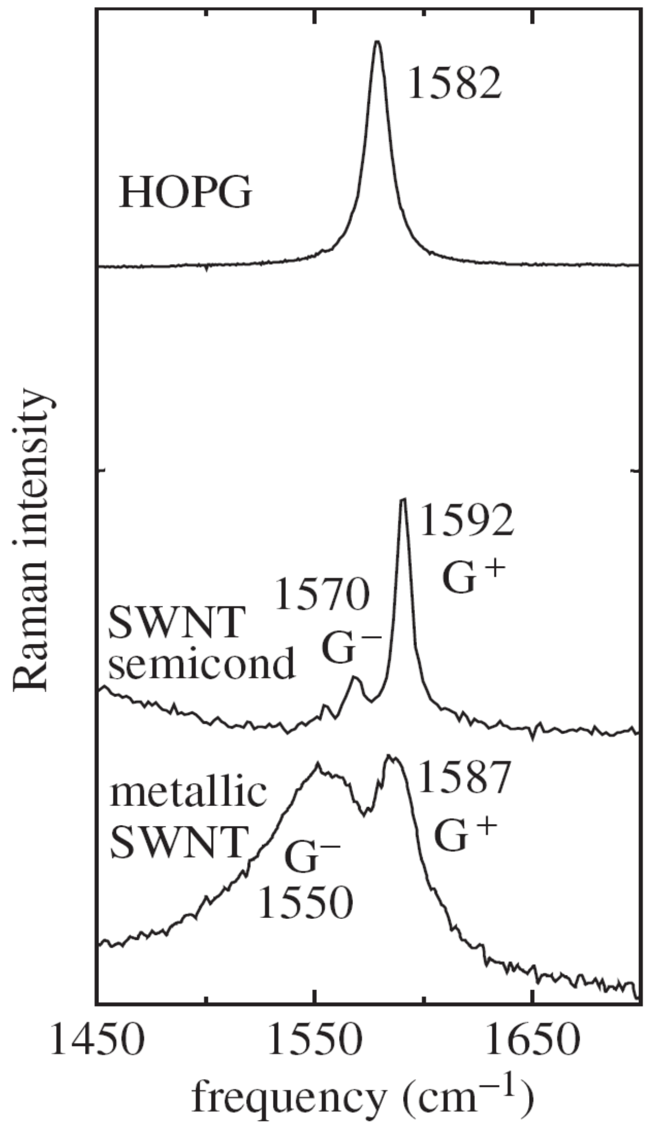
size, gap

In amorphous carbons:

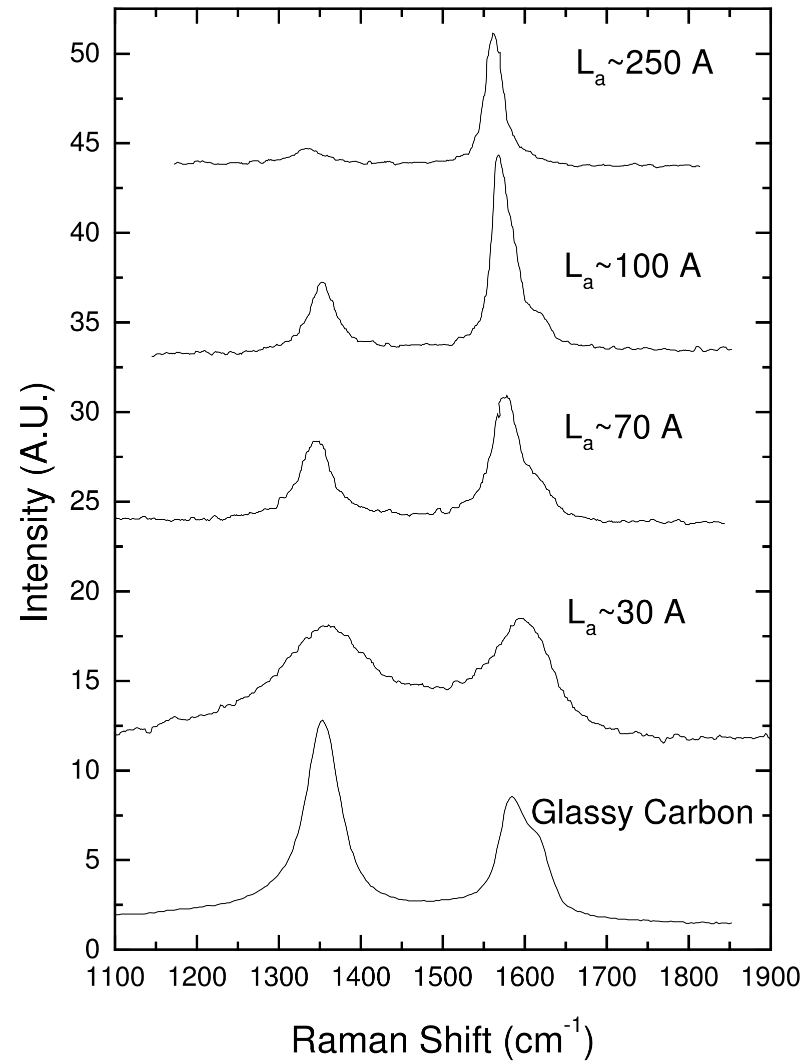
Composition, clustering of sp^2 phase, density, optical gap, elastic constants, ect.

In nanotubes:

Metallic, Semiconductors,
Diameter, chirality, number of walls, doping



1582
HOPG
1592
G+
1570
G−
SWNT
semicond
1587
G+
metallic
SWNT
G−
1550
Raman intensity
1450
1550
1650
frequency (cm−1)



La~250 A
La~100 A
La~70 A
La~30 A
Glassy Carbon
Intensity (A.U.)
0
5
10
15
20
25
30
35
40
45
50
1100
1200
1300
1400
1500
1600
1700
1800
1900
Raman Shift (cm-1)

Resonant Raman Scattering-DLCs

sp^2/sp^3 ratio is NOT THE MAJOR parameter ruling evolution of visible Raman spectra

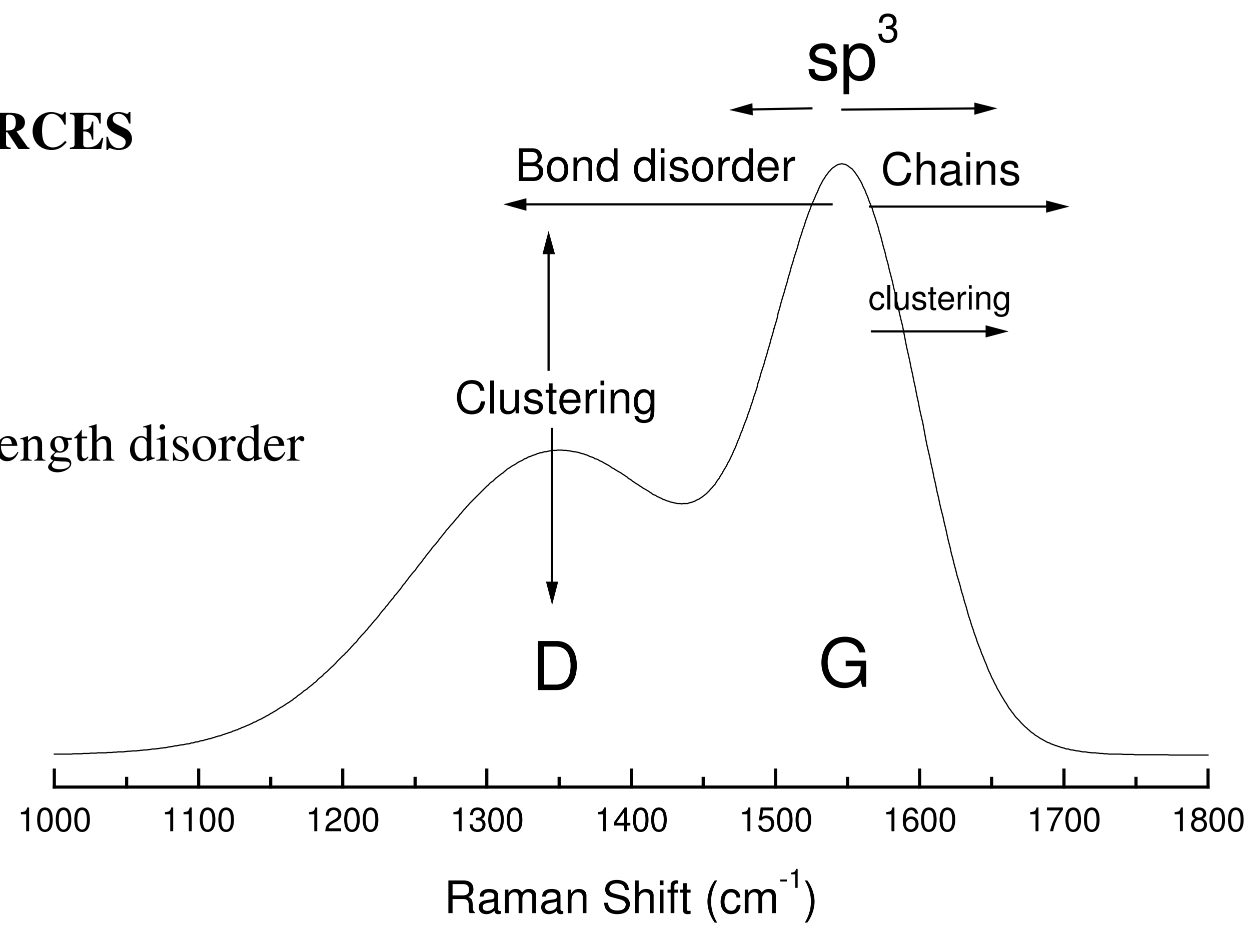
⇒ 4 COMPETING FORCES

1) sp^2 clustering (L_a)

2) bond angle and bond length disorder

3) Rings or Chains

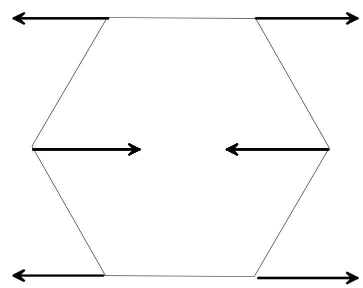
4) sp^2/sp^3 ratio



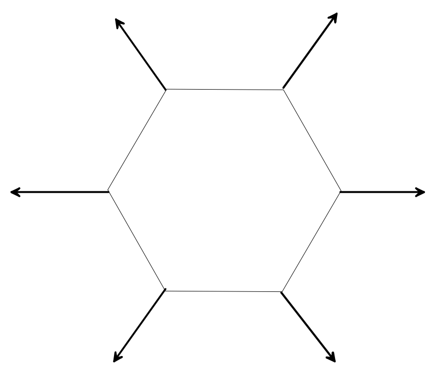
Key parameter is sp^2 QUALITY, NOT sp^2 QUANTITY

Origin of D and G peaks

G: E_{2g} mode of sp^2 rings and chains



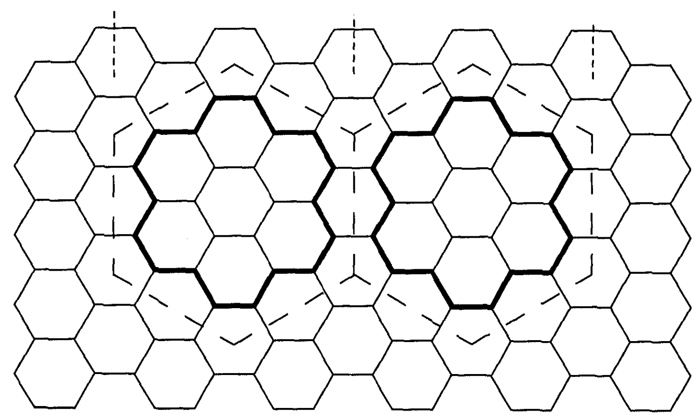
D: A_{1g}-Breathing mode in *rings*



Double Resonance Effects

Energy levels and vibrational modes of clusters map onto graphite

Clusters≡graphite superlattice



Clusters:

$E_g \approx \pm 2\beta \quad \Rightarrow 1+2\cos(ka) = -\dfrac{a}{L_a}$

Graphite:

$E \approx \pm 2\beta |1+2\cos(ka)|$

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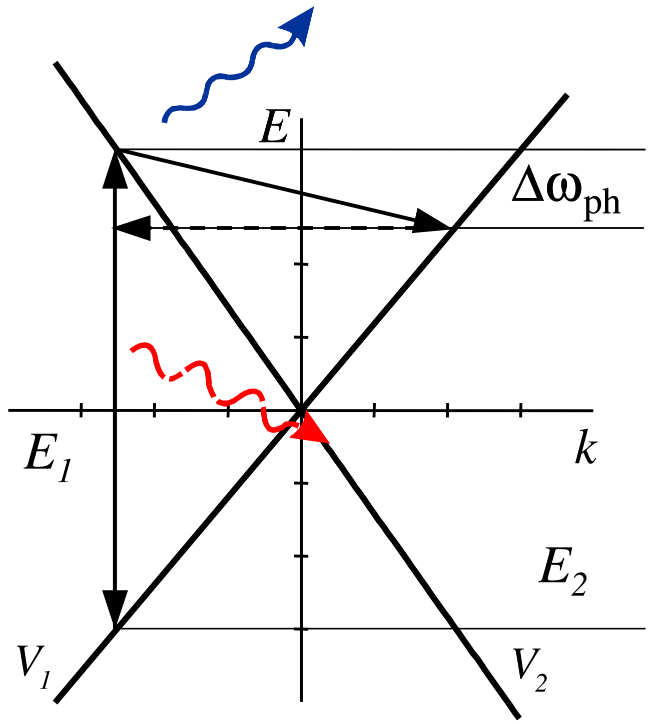
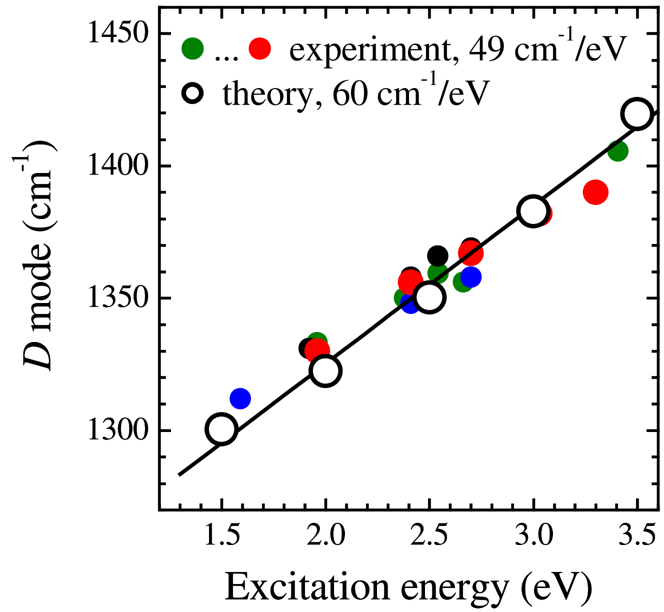
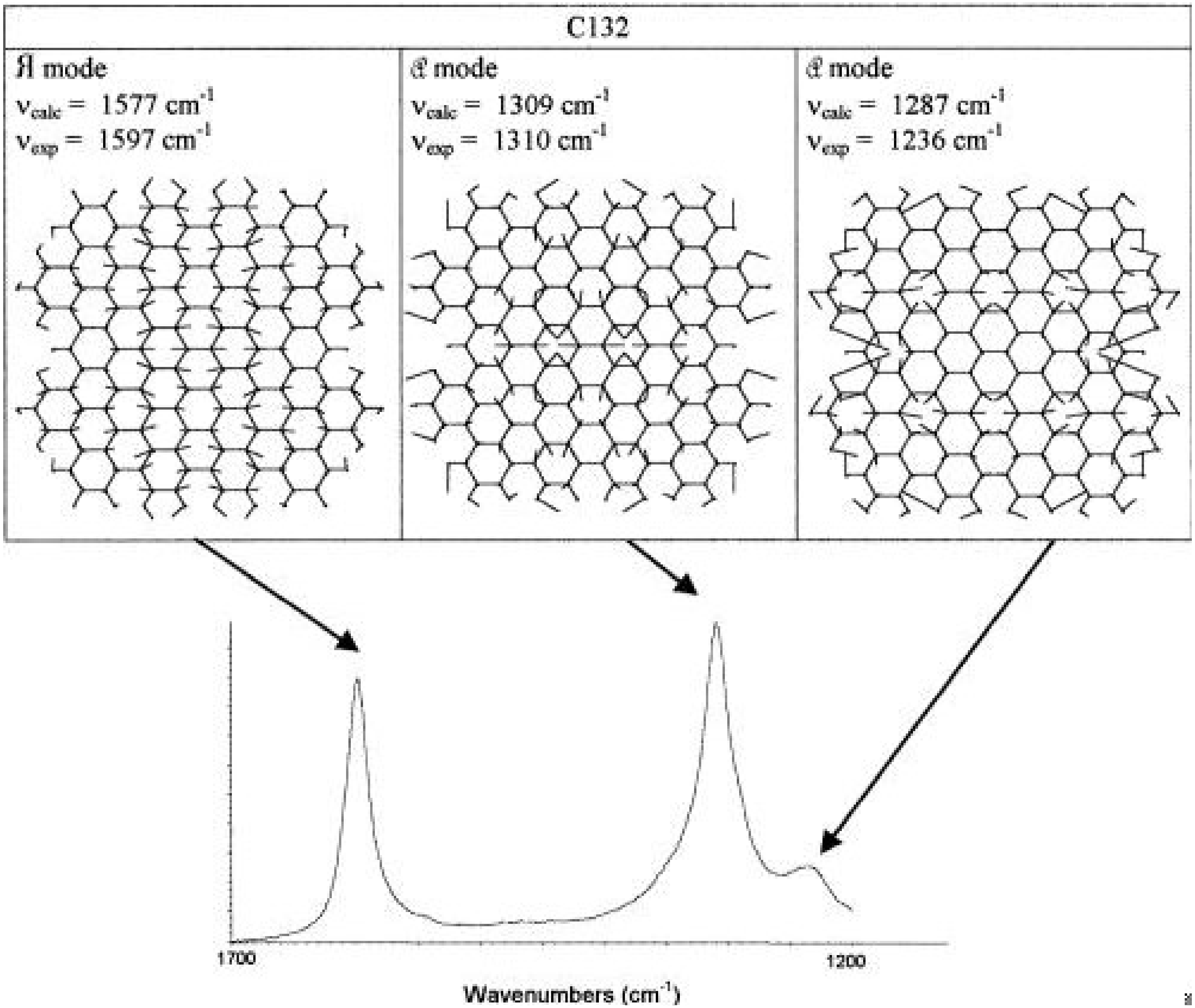
Double resonant Raman scattering



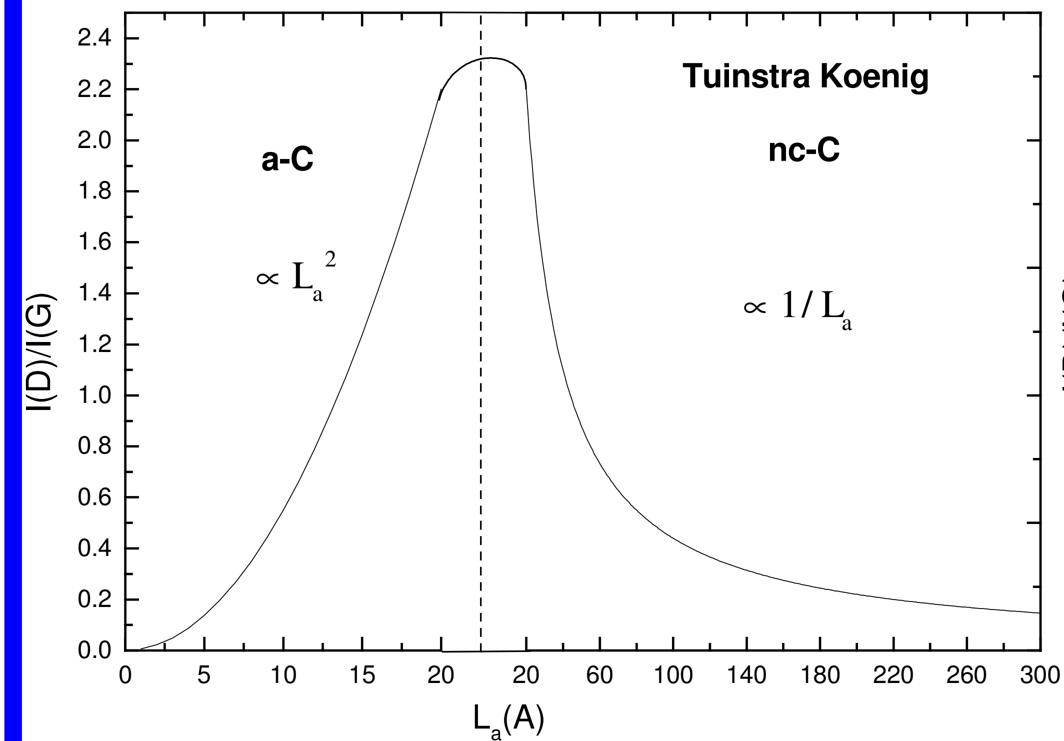
graphite band structure

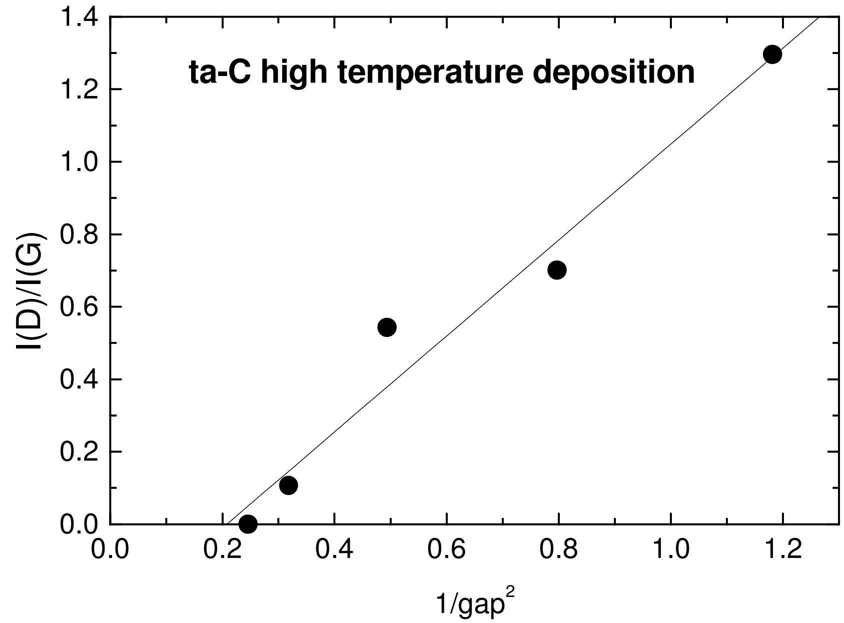


C. Thomsen & S.Reich. PRL **61**, 5214 (2000)


C132
𝔄 mode
ν_{calc} = 1577 cm^{-1}
ν_{exp} = 1597 cm^{-1}
𝔈 mode
ν_{calc} = 1309 cm^{-1}
ν_{exp} = 1310 cm^{-1}
𝔈 mode
ν_{calc} = 1287 cm^{-1}
ν_{exp} = 1236 cm^{-1}
1700
1200
Wavenumbers (cm^{-1})

I(D)/I(G) vs. cluster size



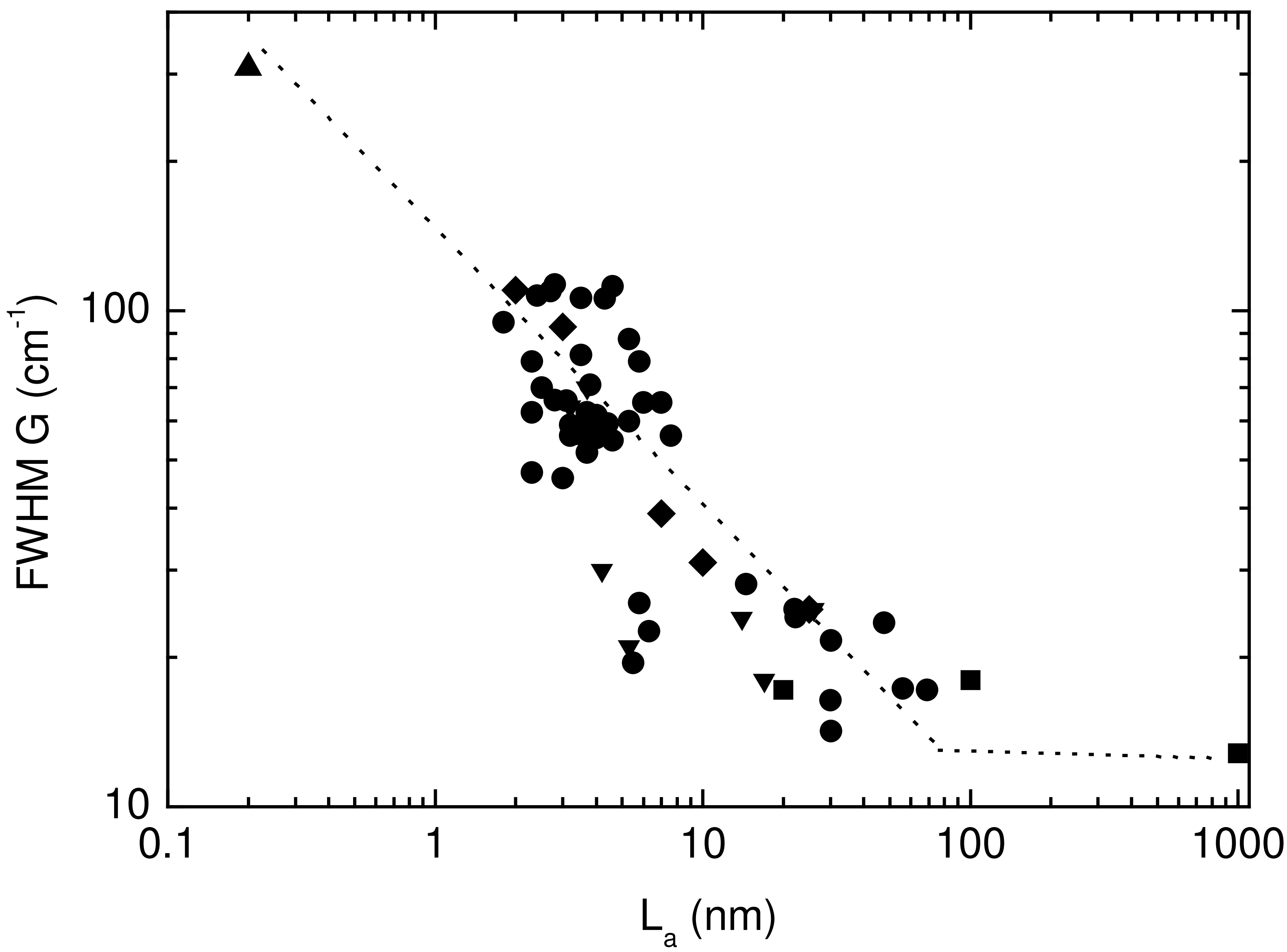


D → **Disordering** in graphites

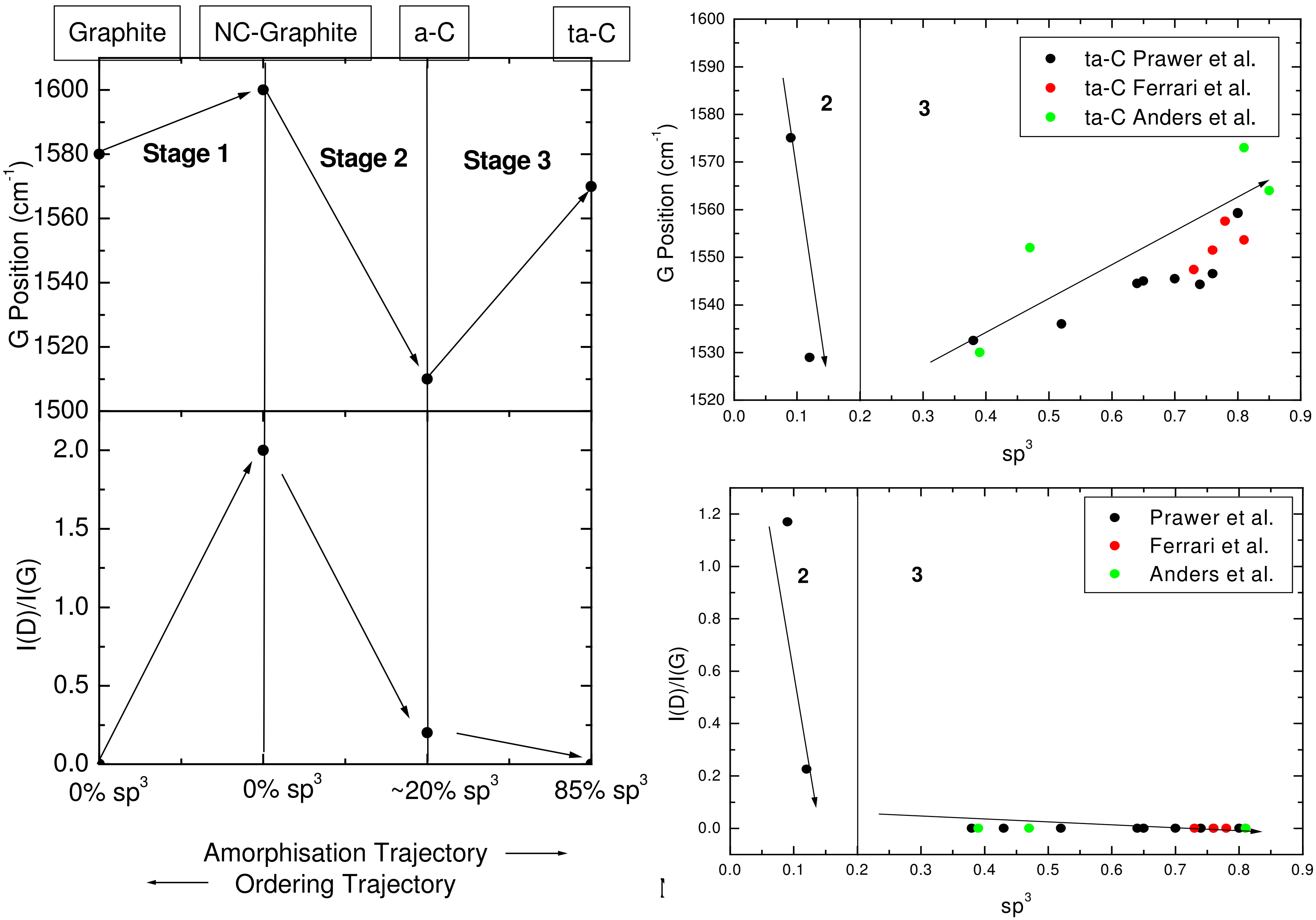
D → **Ordering** in a-C's

$$\Rightarrow \frac{I(D)}{I(G)} \propto M \propto L_a^2 \Rightarrow \frac{I(D)}{I(G)} \propto \frac{1}{gap^2}$$

FWHM G vs. cluster size



Three Stage Model



HYSTERESIS-NON-UNIQUENESS

What happens if we follow **an ordering trajectory**, from ta-C to graphite?

- High temperature deposition
- Annealing after deposition
- Ion implantation in ta-C
- "unfiltered" deposition processes
- N introduction

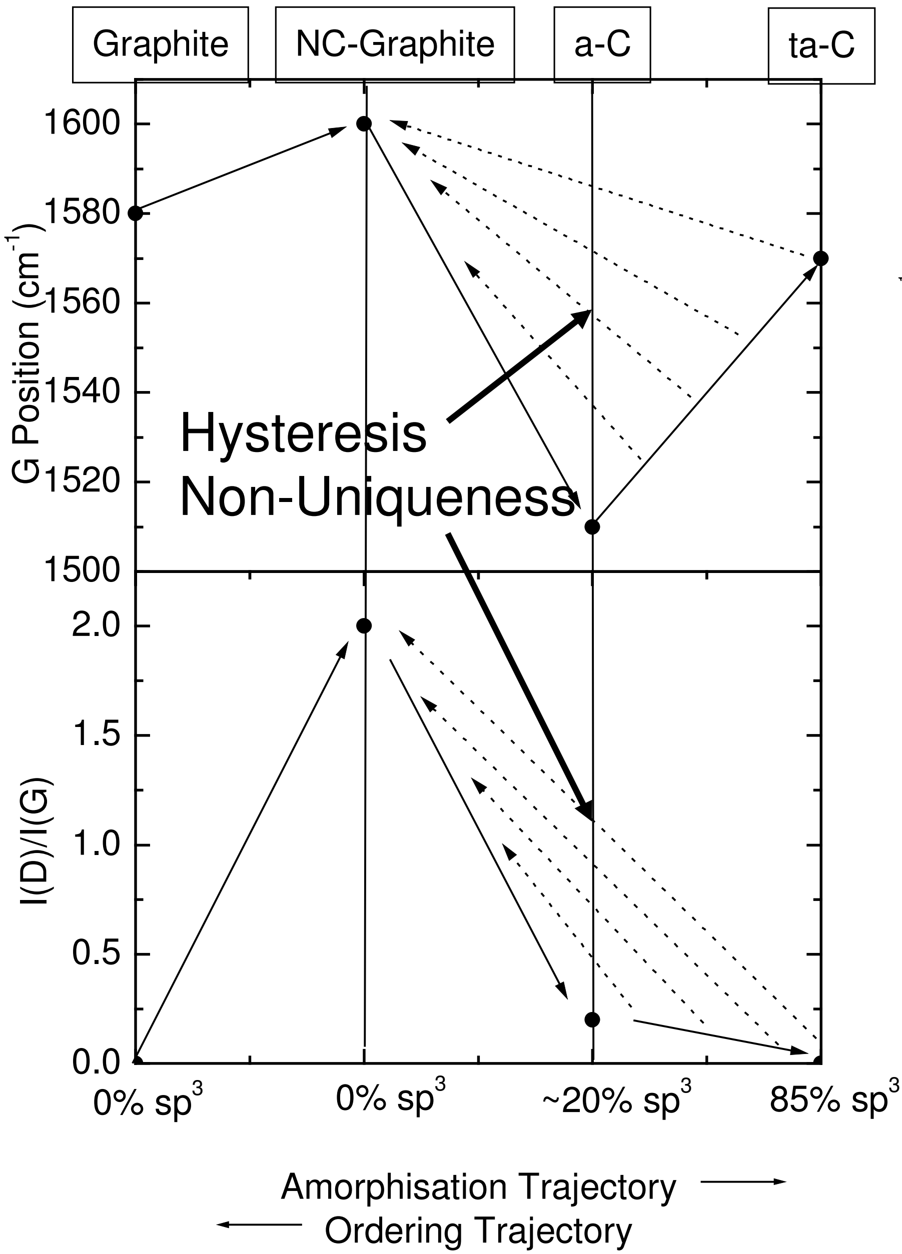
This splits the evolution of sp^2 and sp^3 phases:

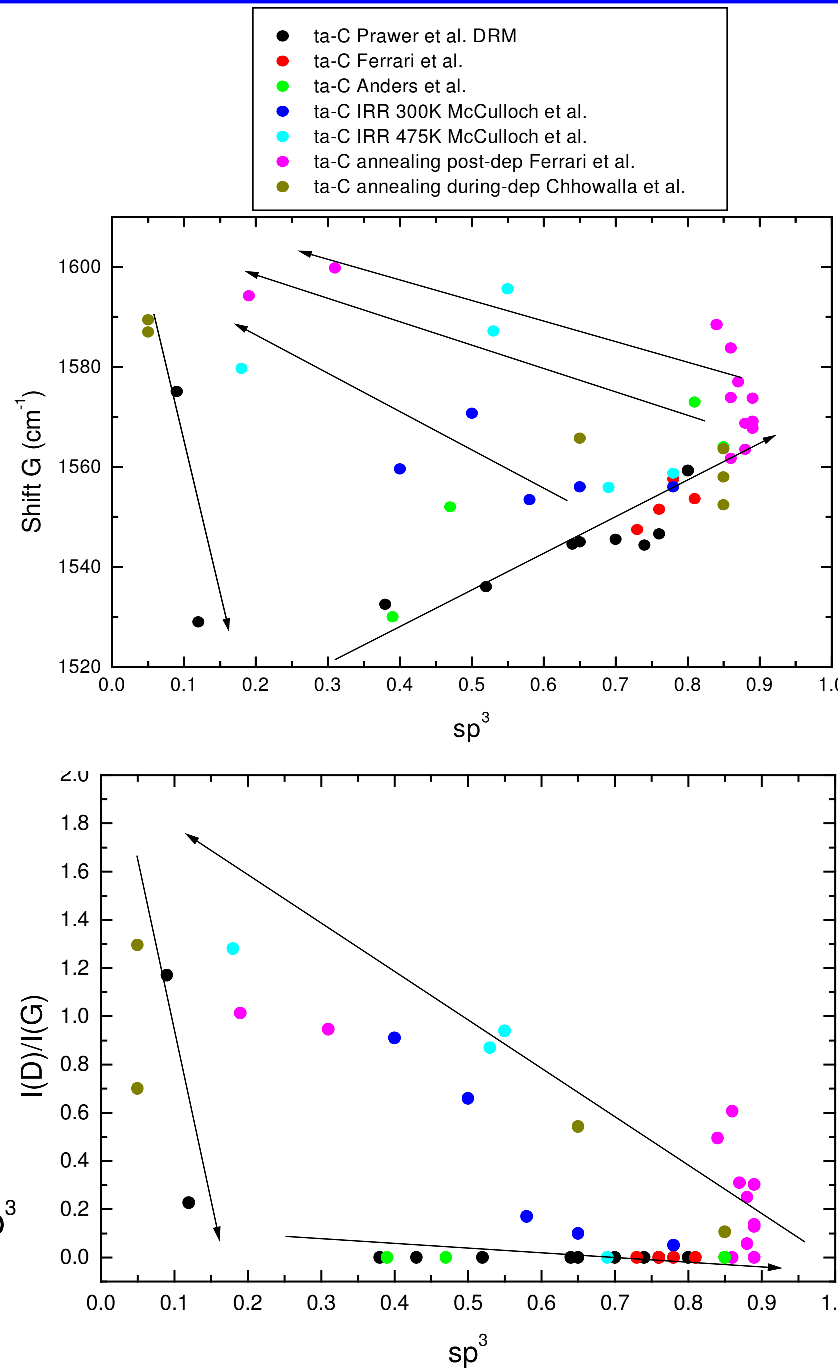
a) sp^2 orders in rings
b) sp^3 converts to sp^2.

Visible Raman spectra and optical gaps are much more sensitive to process a than b $\Rightarrow$ **Non-Uniqueness**

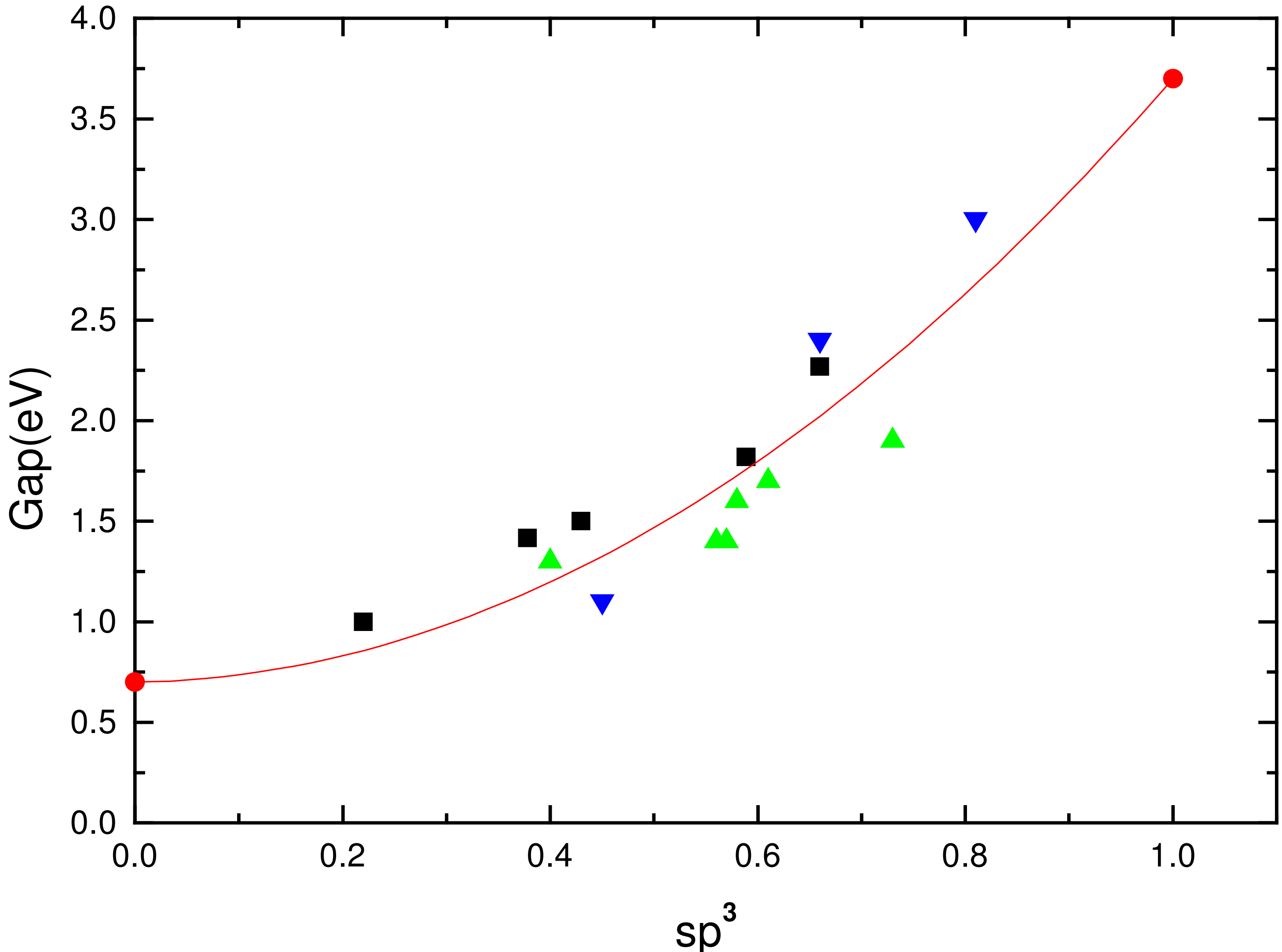
EFFECTS: Any I(D)/I(G) and G position combined with any sp^3 fraction.

Three Stage Model





PECVD a-C:H; gap vs. sp^3 content



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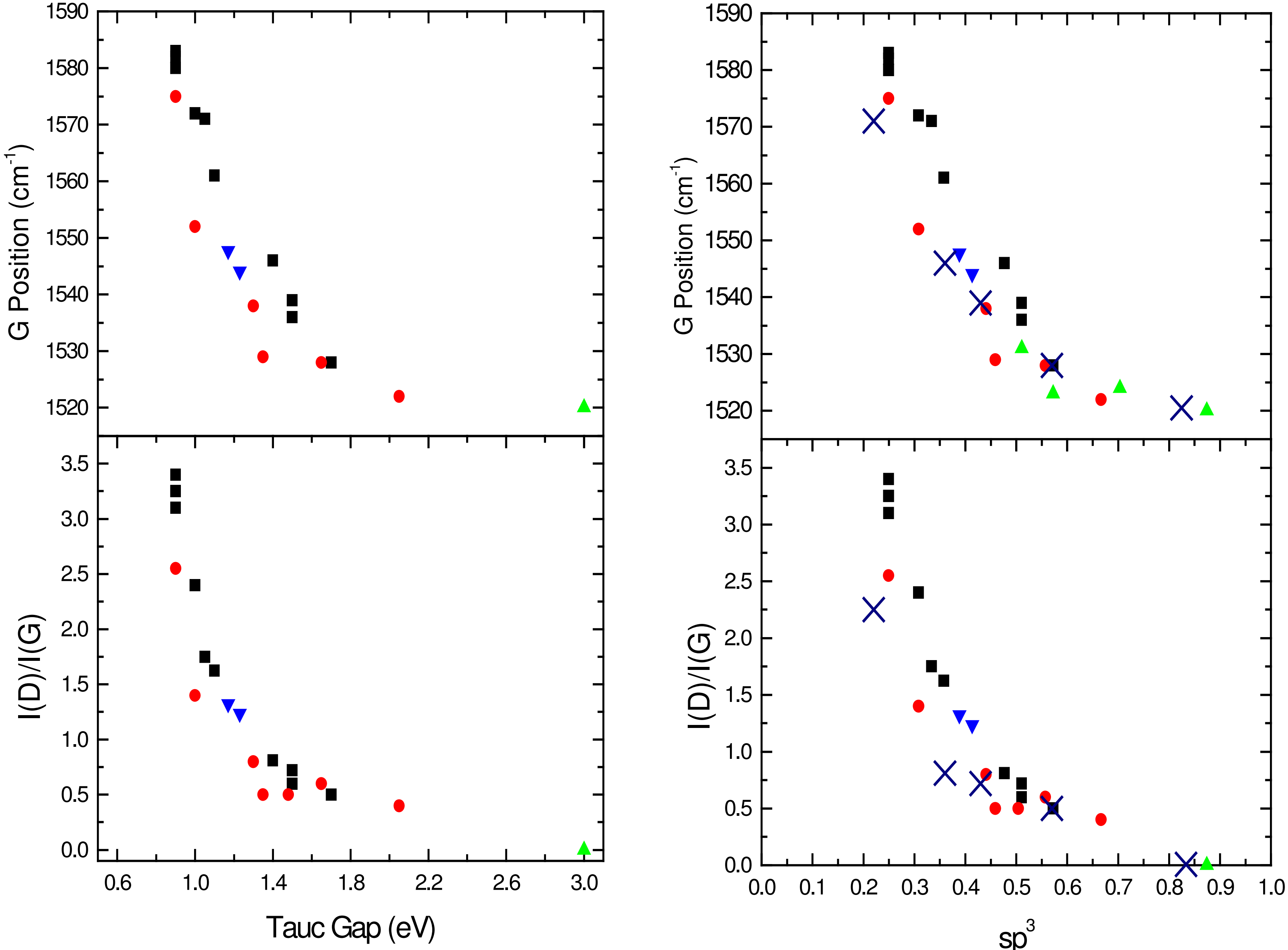
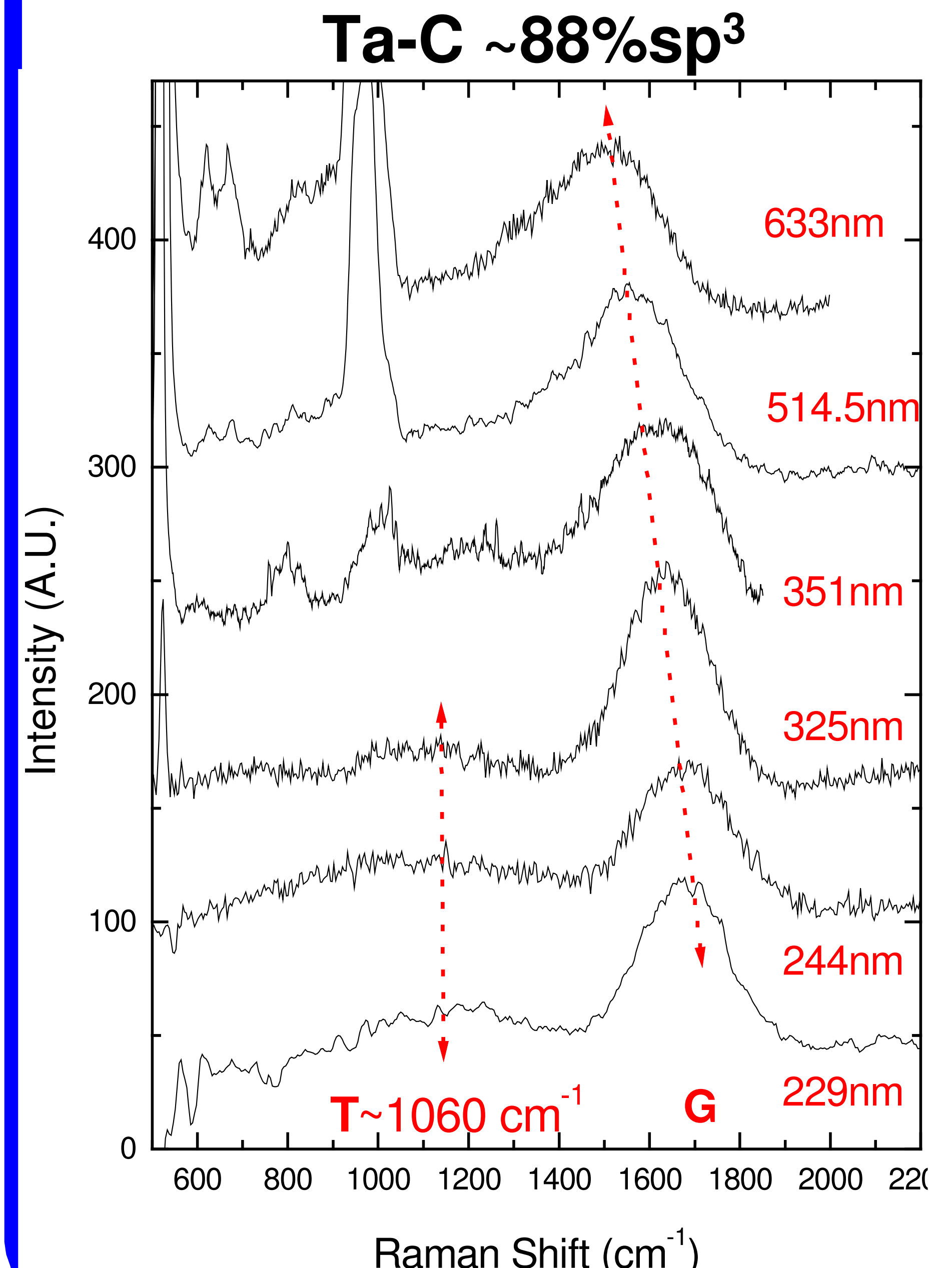
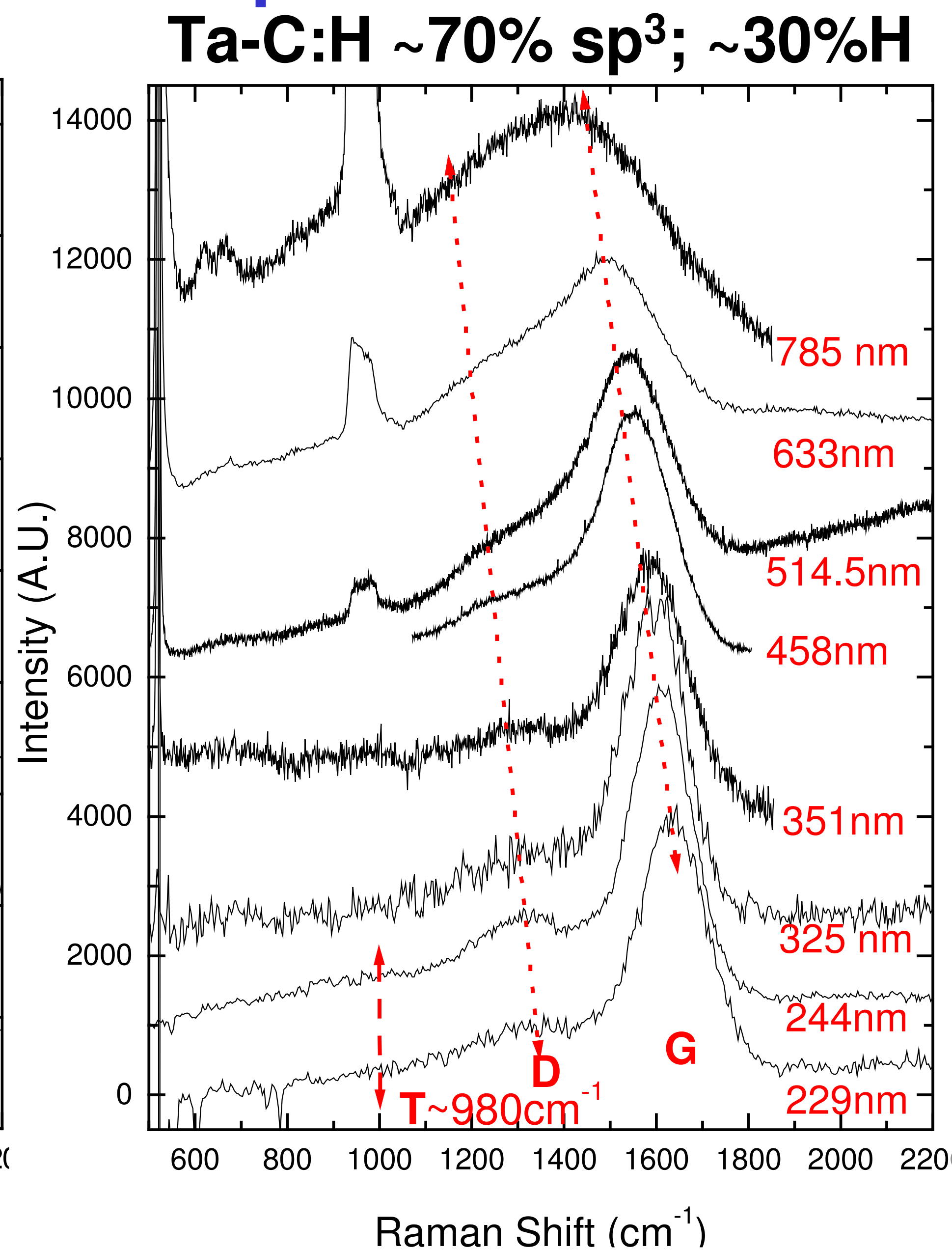
PECVD a-C:H

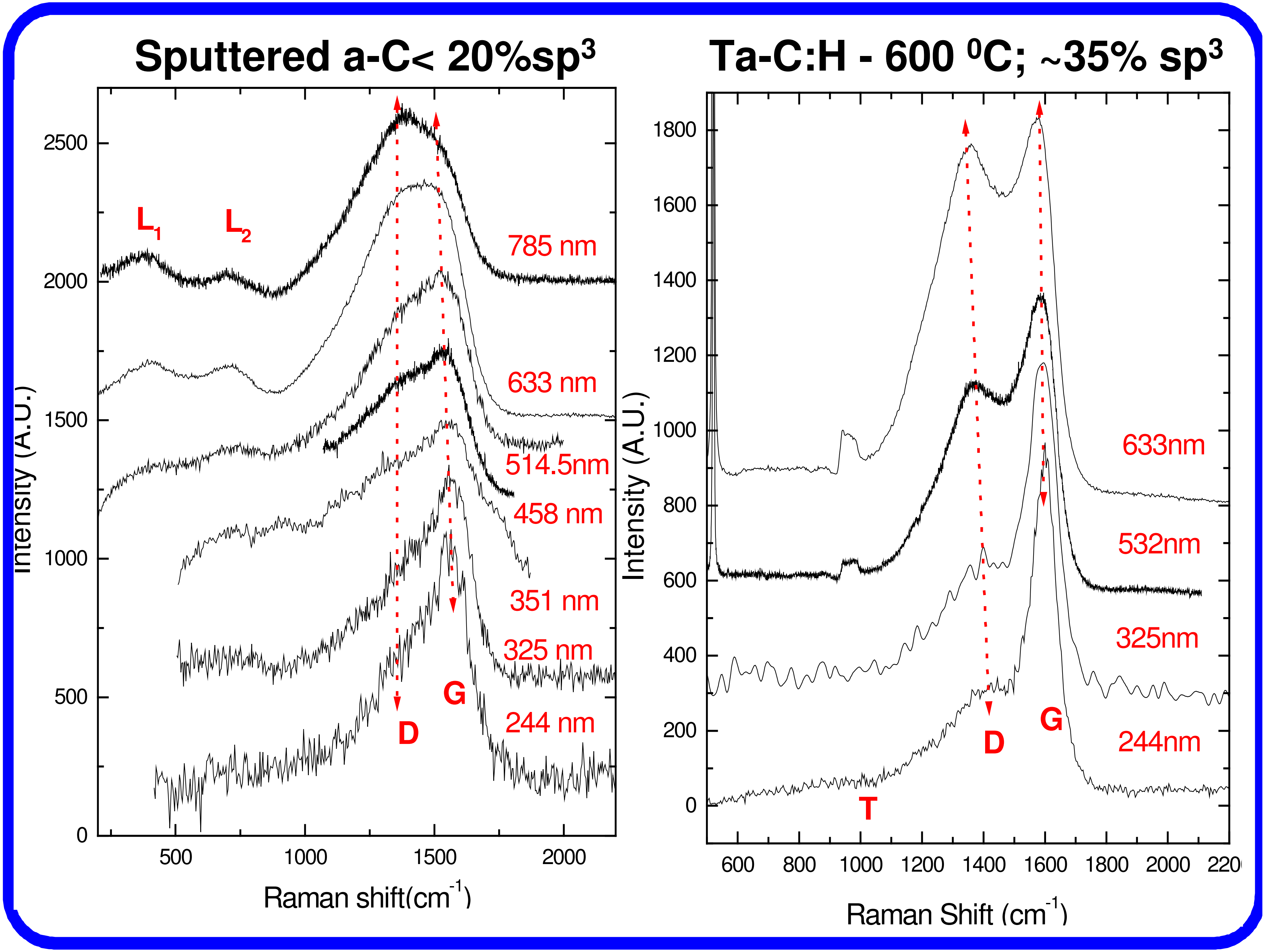


Tamor and Vassel, JAP (1994)

Resonant Raman Spectra

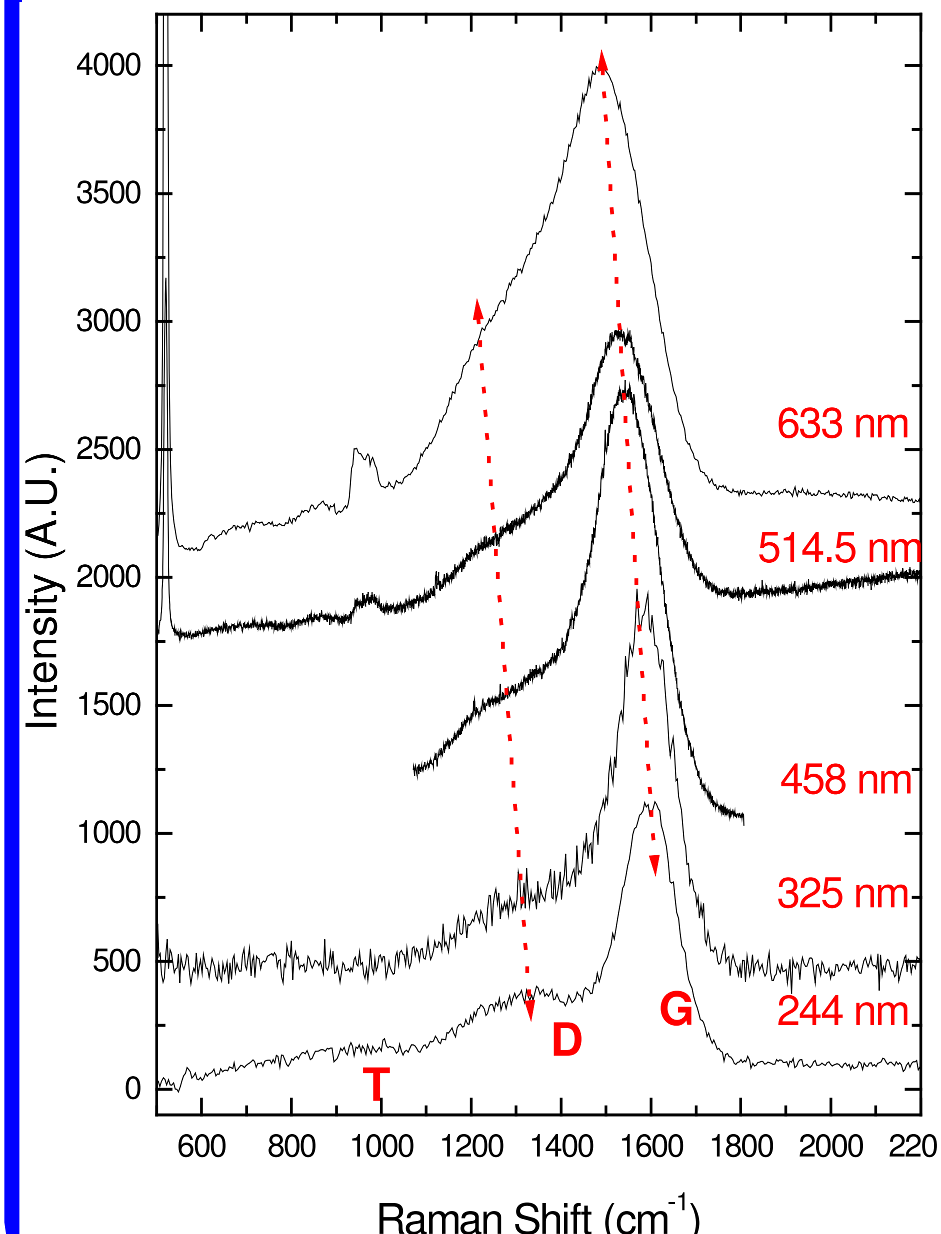




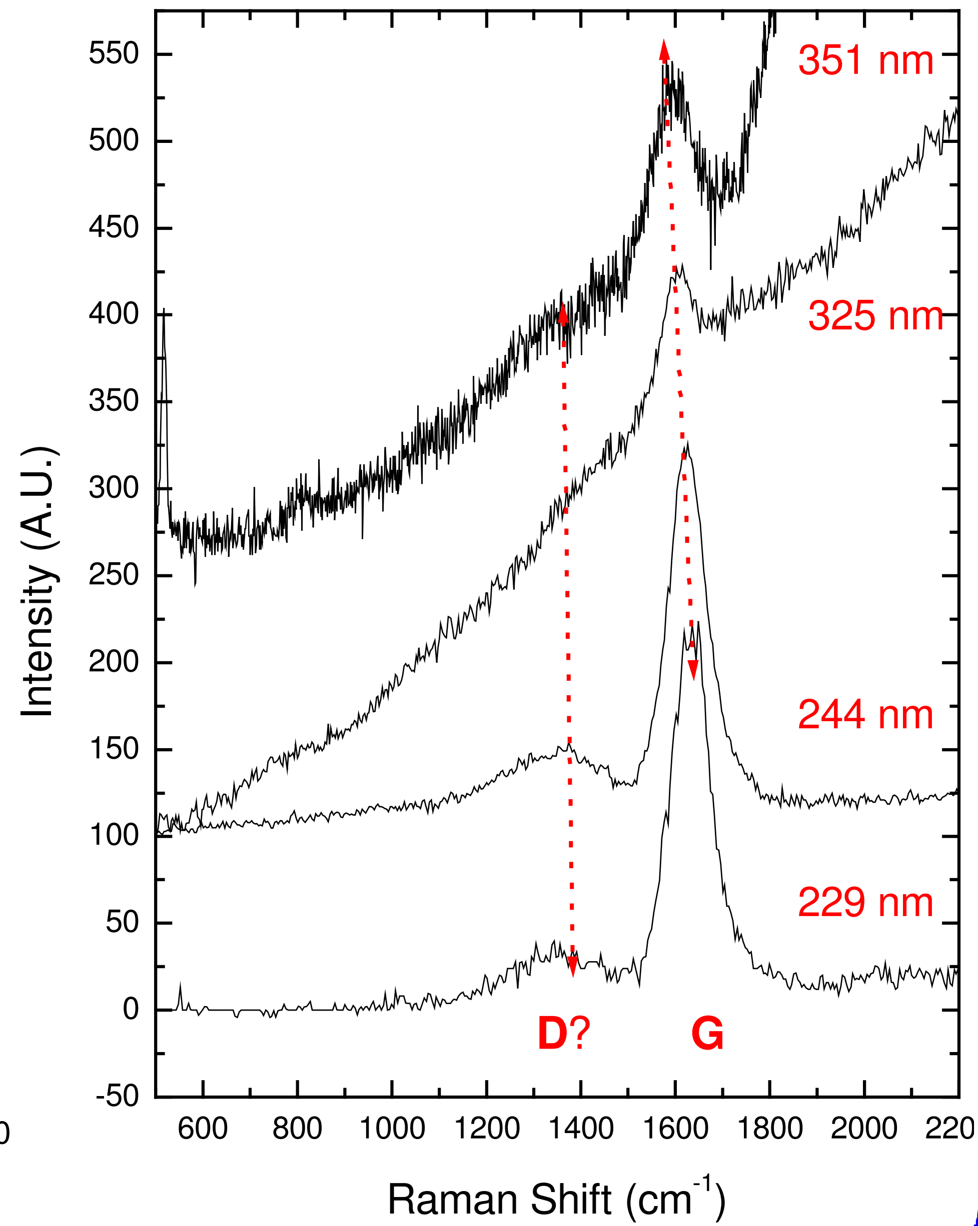


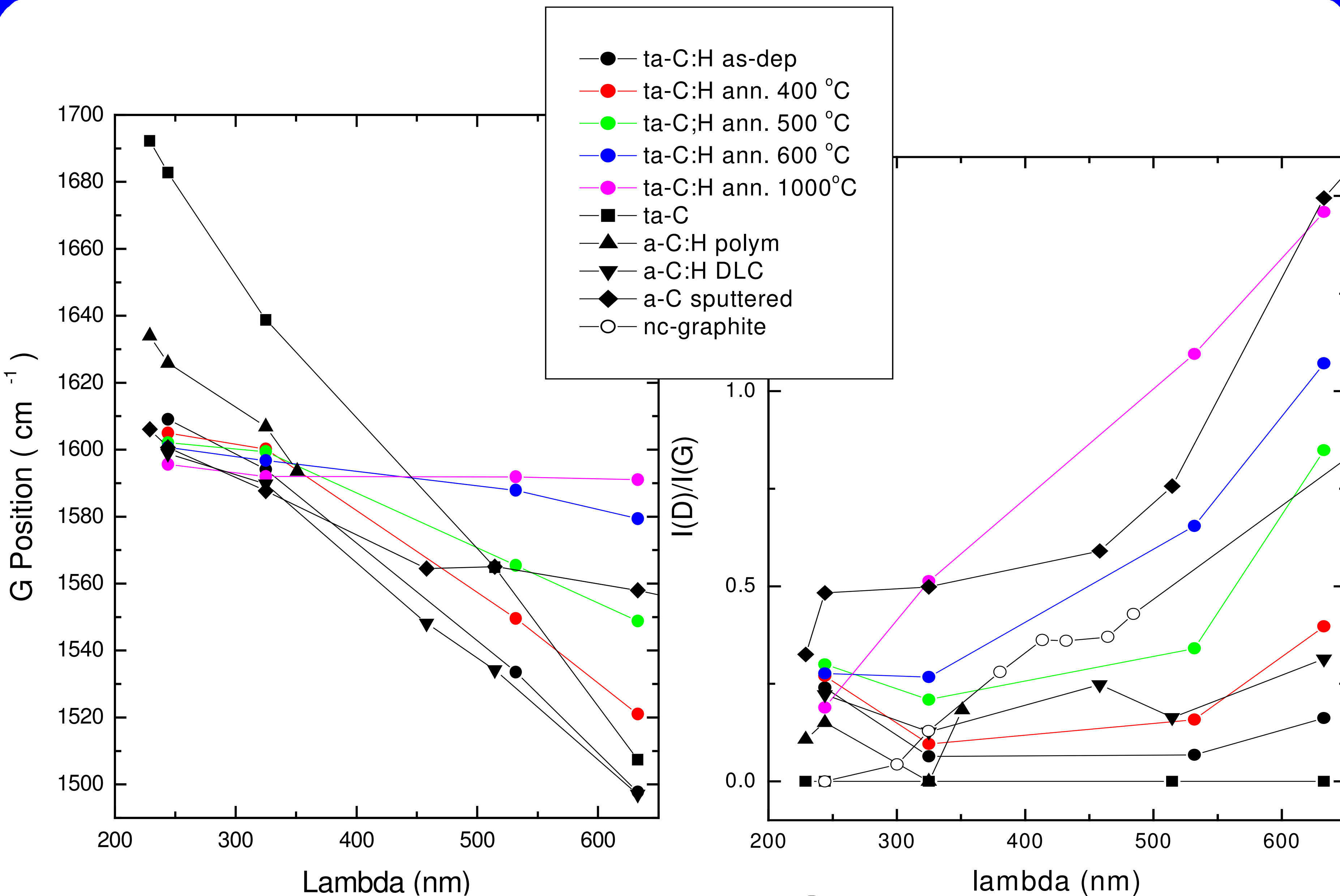
Sputtered a-C< 20%sp3
Ta-C:H - 600 0C; ~35% sp3
L1
L2
785 nm
633 nm
514.5nm
458 nm
351 nm
325 nm
244 nm
D
G
Intensity (A.U.)
Raman shift(cm-1)
633nm
532nm
325nm
244nm
T
Raman Shift (cm-1)

Diamond-like a-C:H~60% sp^3



A-C:H polym., E_{gap}~3-3.5 eV





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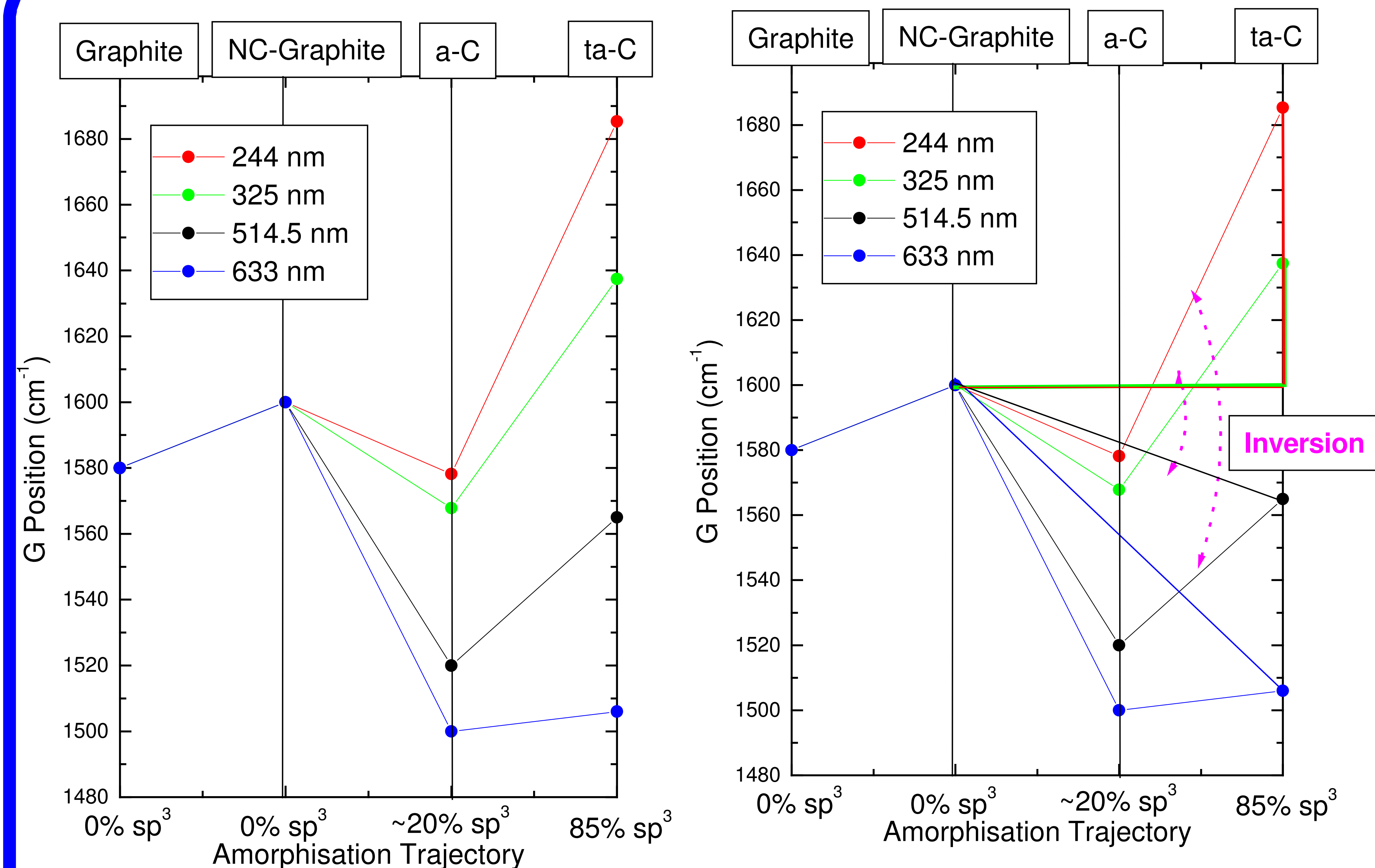

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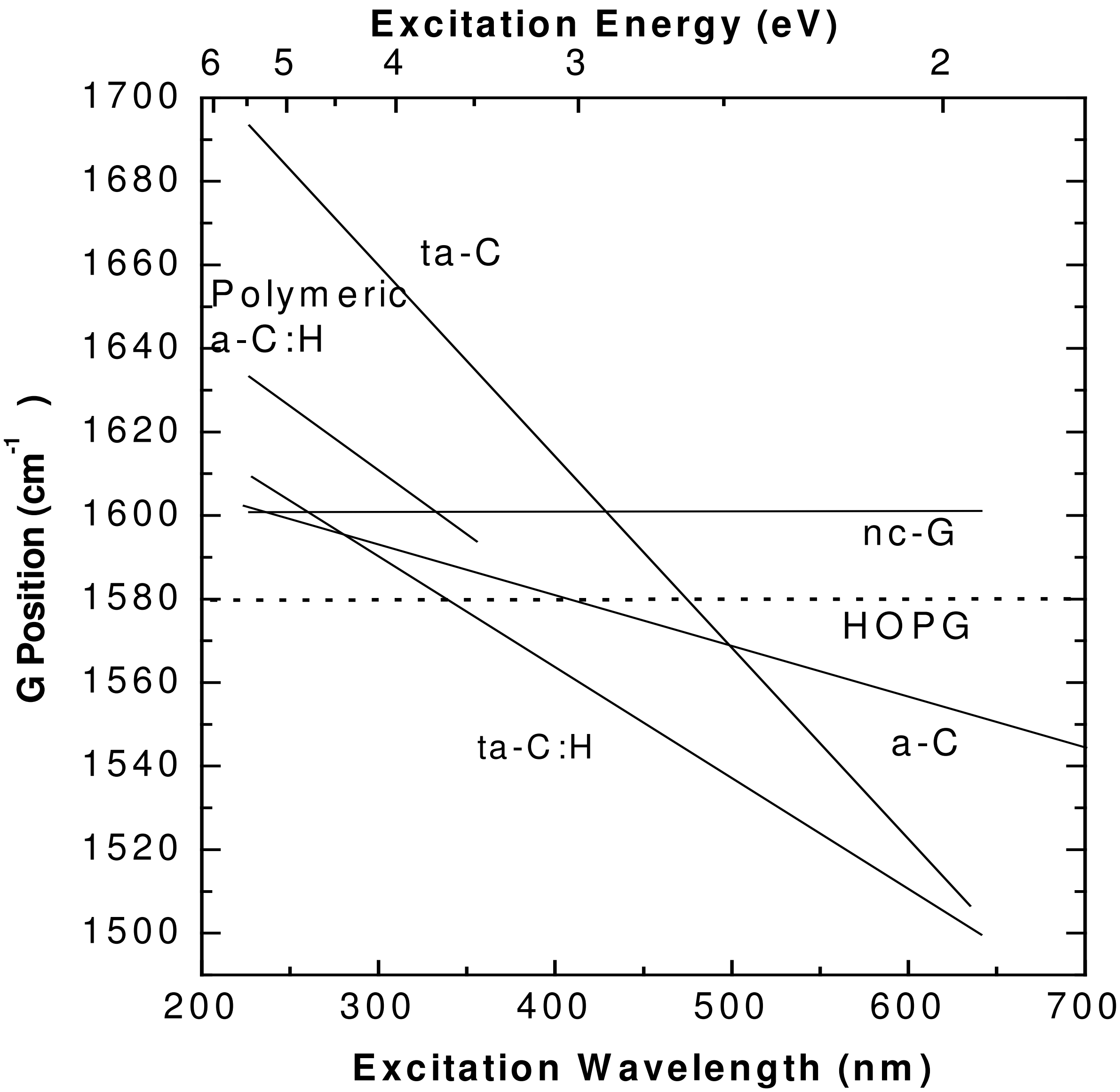
G Peak Dispersion



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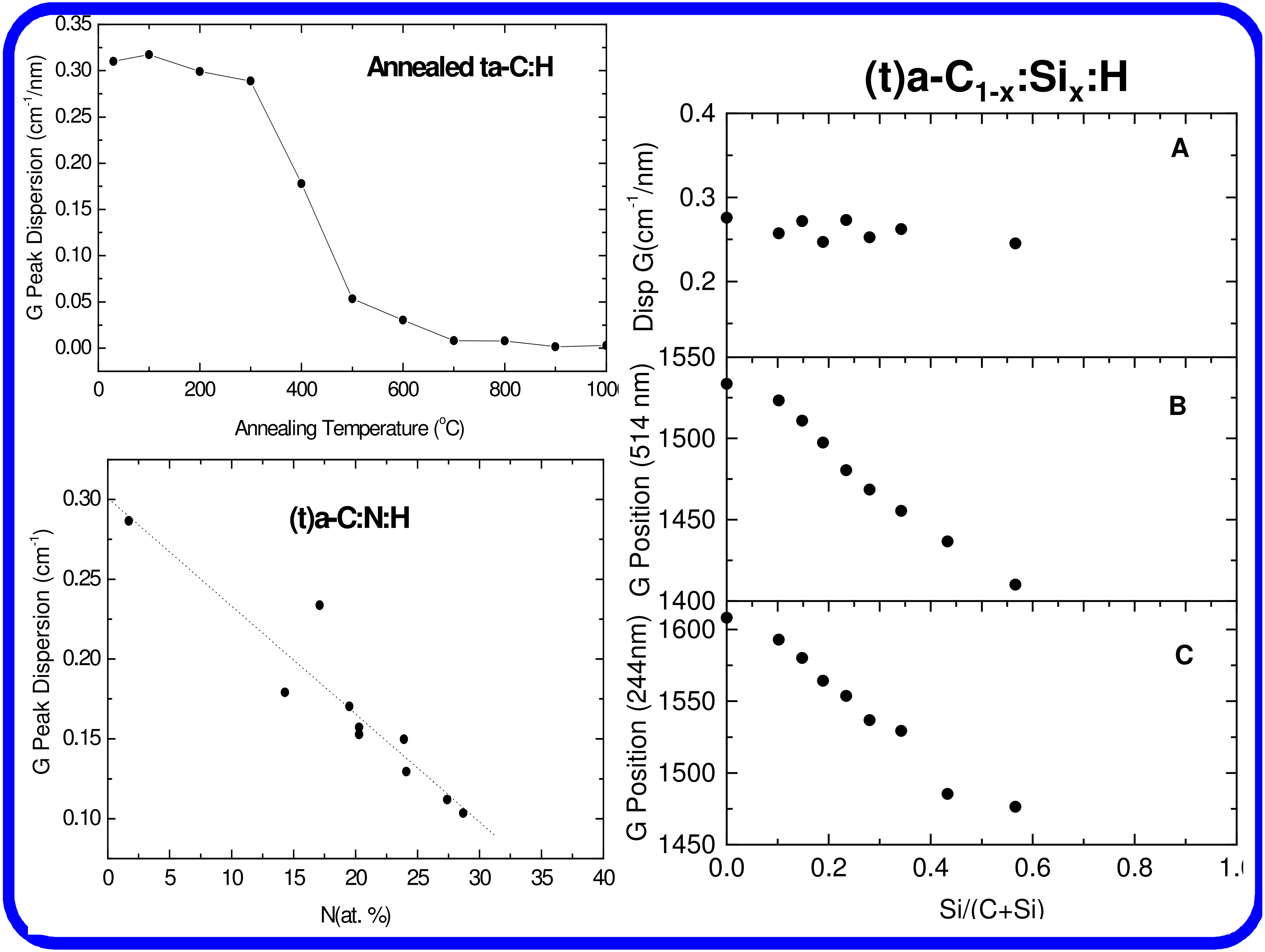
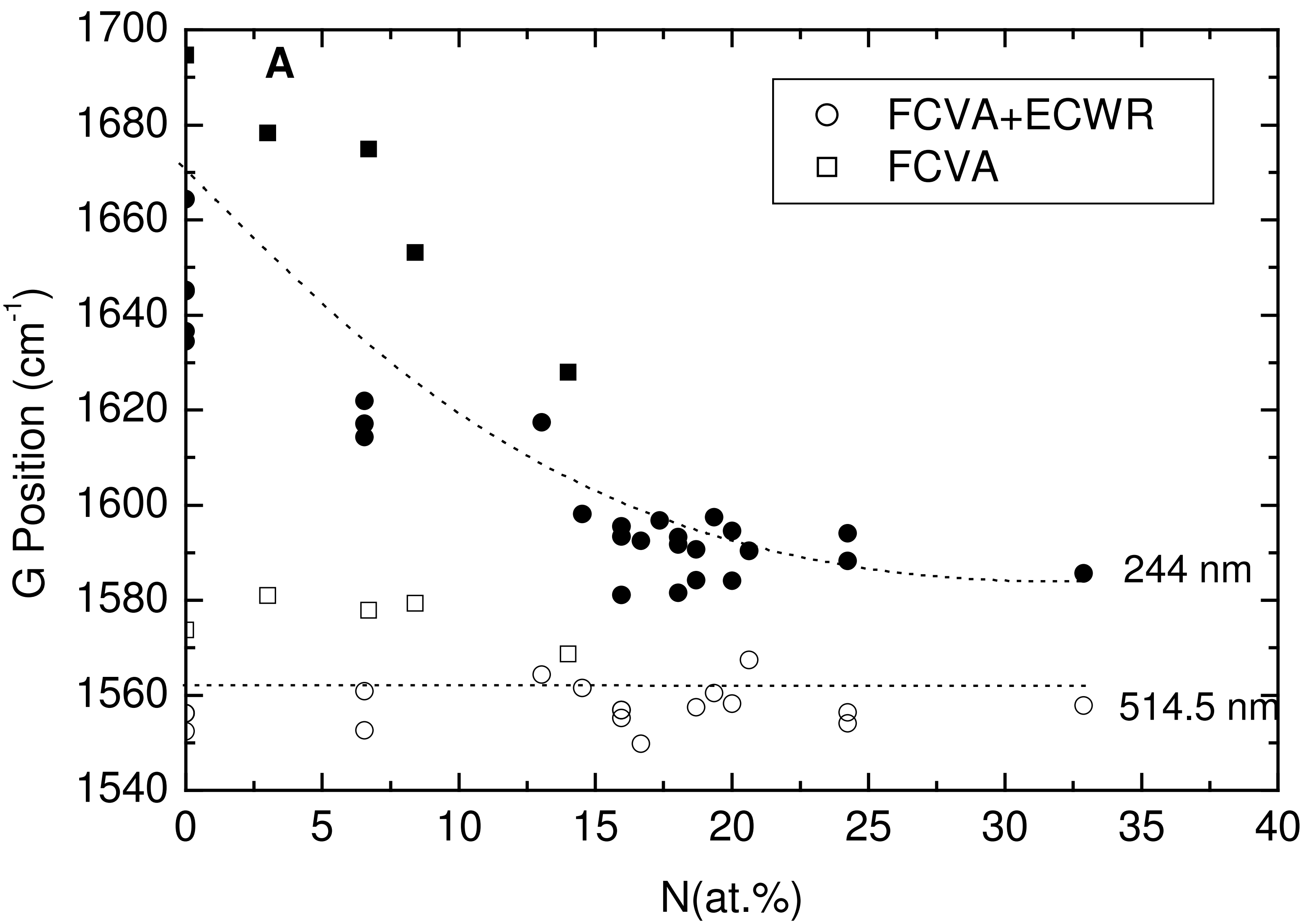


Annealed ta-C:H
G Peak Dispersion (cm^{-1}/nm)
Annealing Temperature (^{o}C)
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
200
400
600
800
1000
(t)a-C:N:H
G Peak Dispersion (cm^{-1})
N(at. %)
0.30
0.25
0.20
0.15
0.10
0
5
10
15
20
25
30
35
40
(t)a-C_{1-x}:Si_x:H
A
B
C
Disp G(cm^{-1}/nm)
G Position (514 nm)
G Position (244nm)
Si/(C+Si)
0.4
0.3
0.2
1550
1500
1450
1400
1600
1550
1500
1450
0.0
0.2
0.4
0.6
0.8



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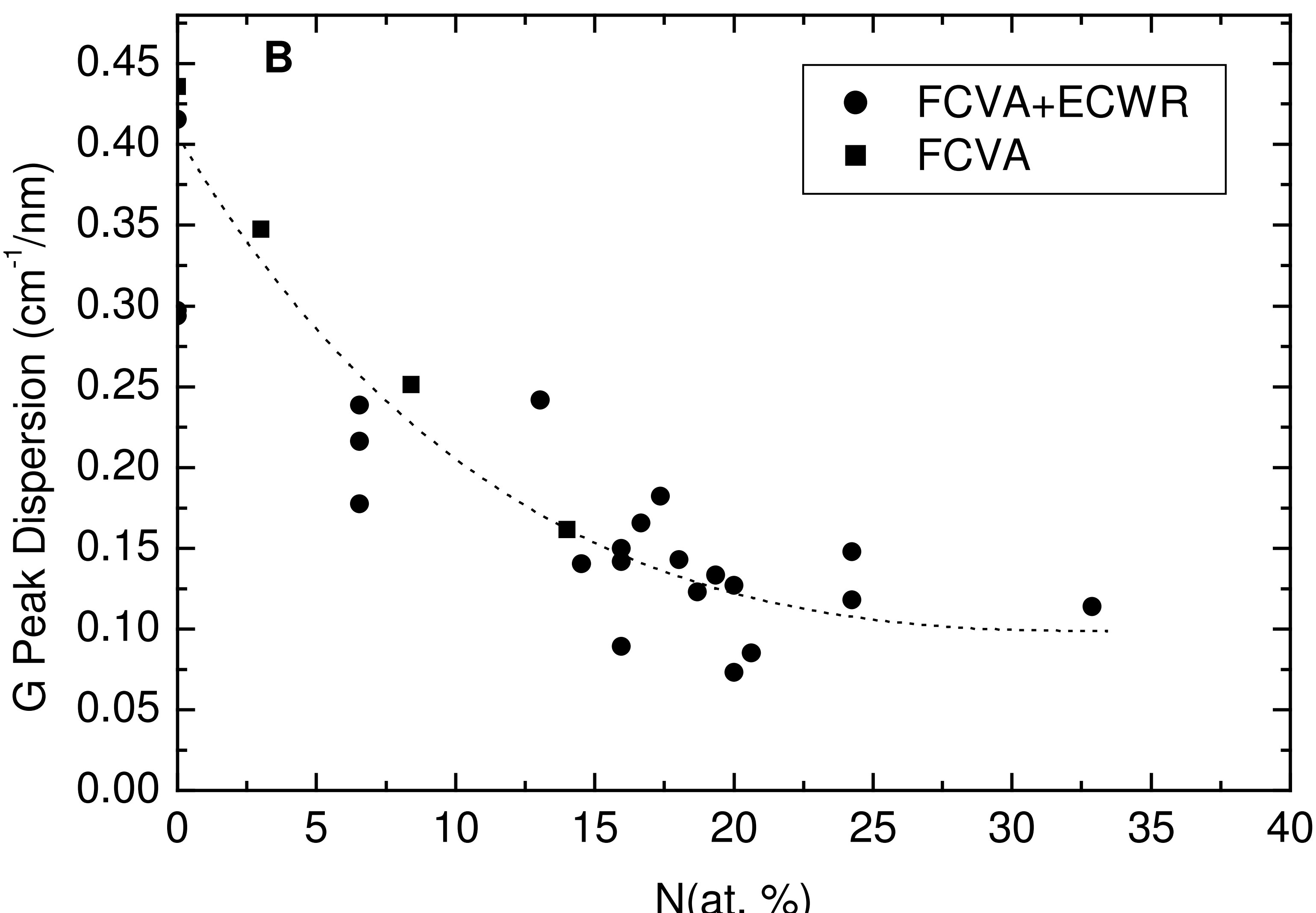
G Peak Dispersion



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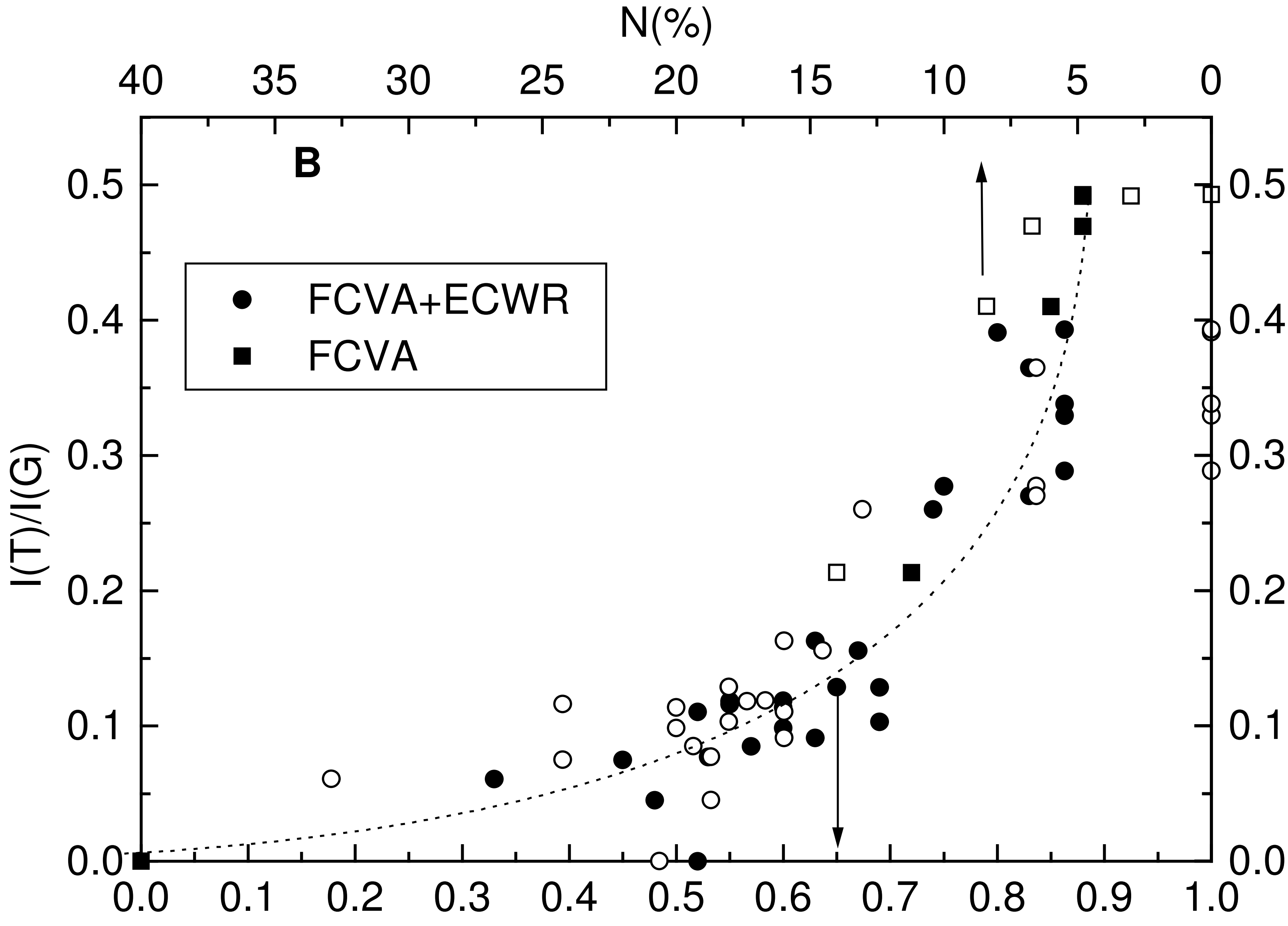

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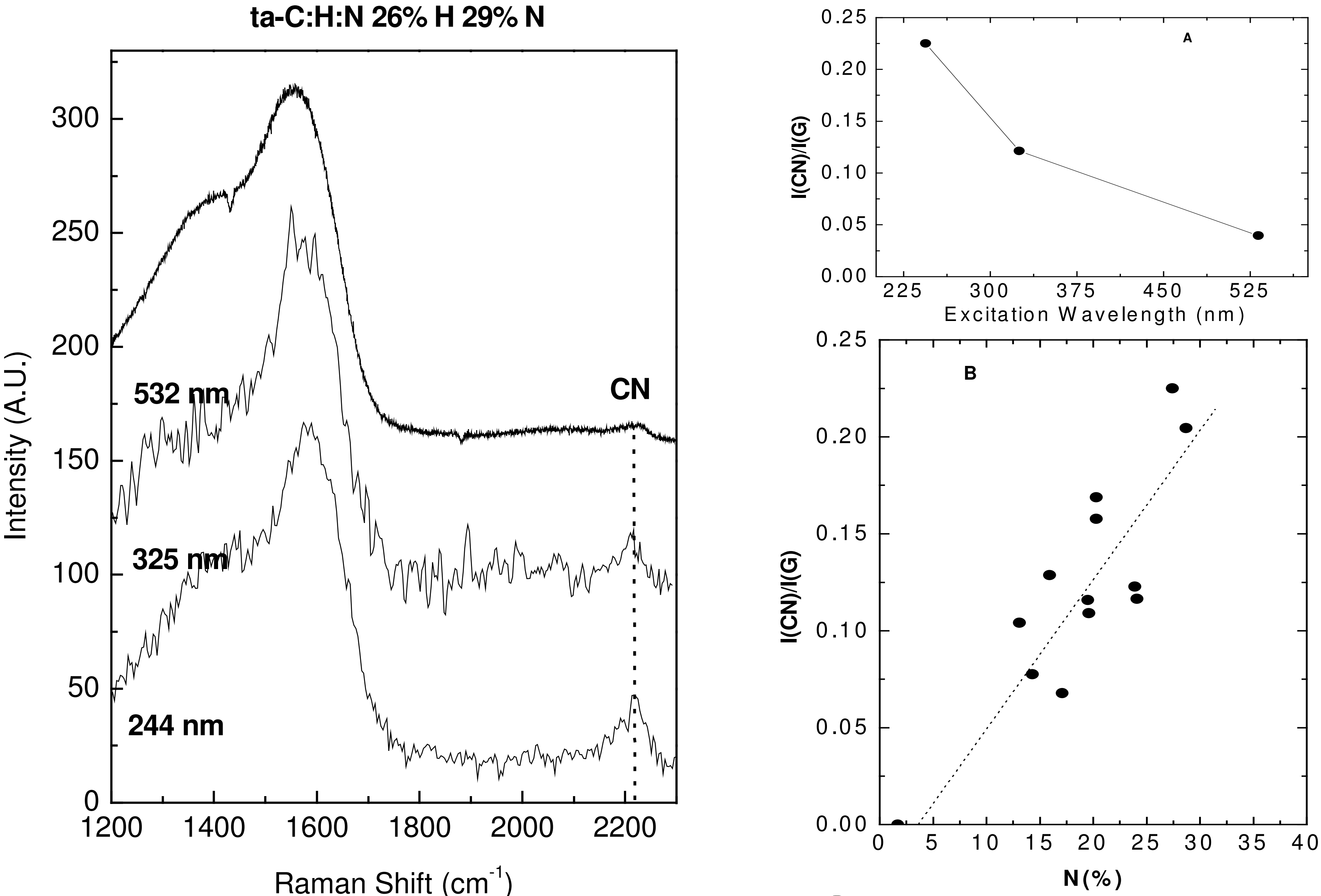

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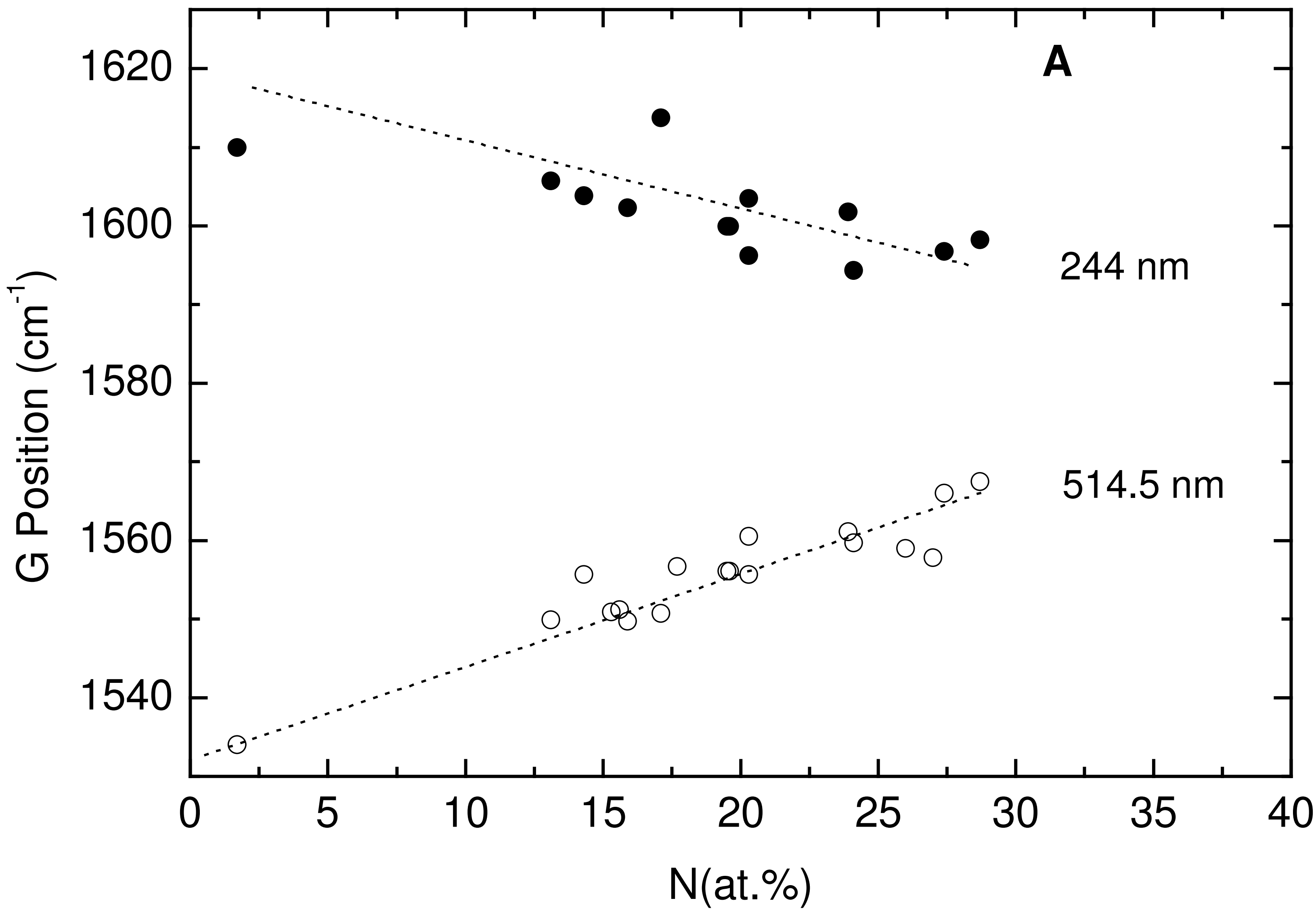

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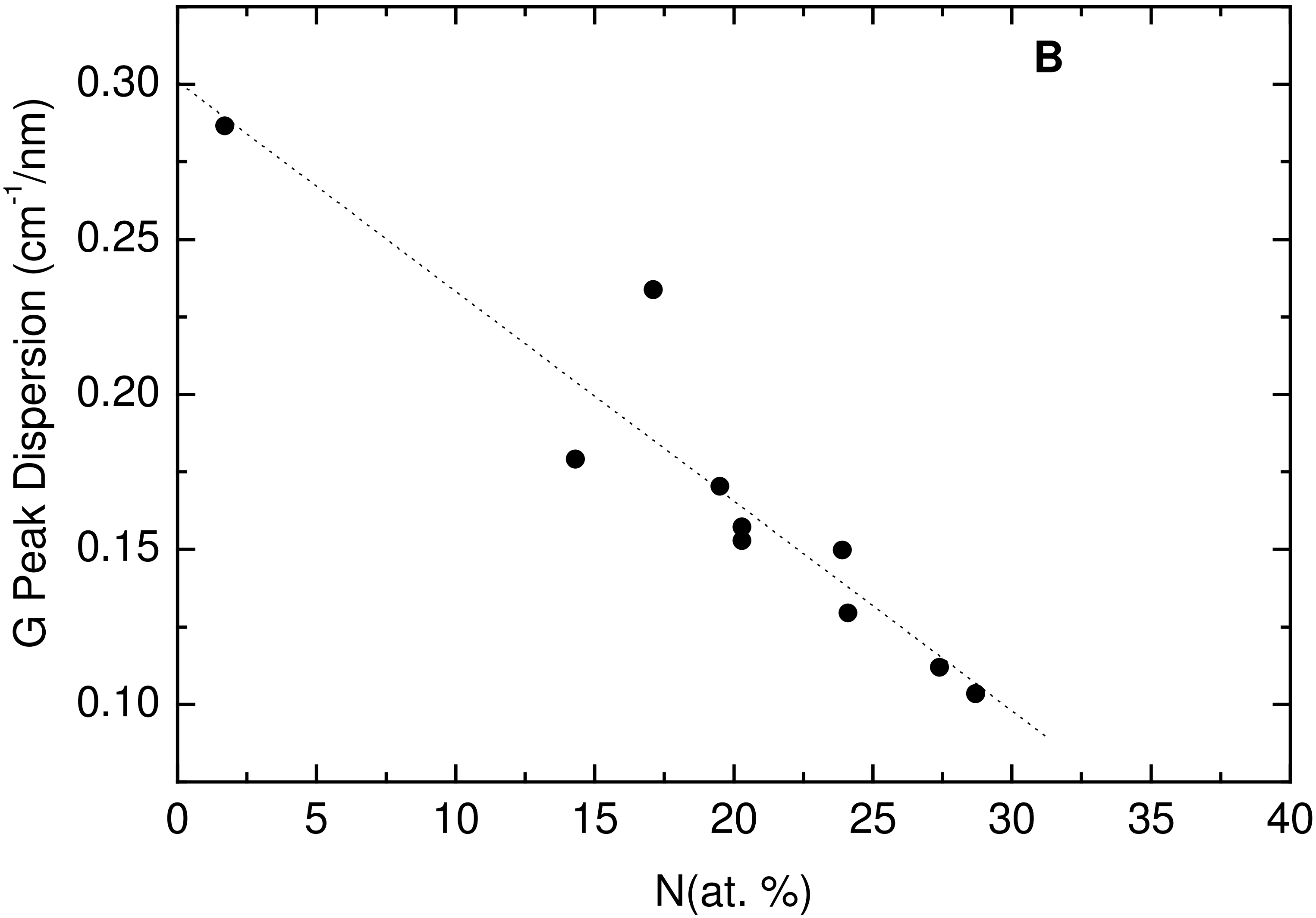
G Peak Dispersion



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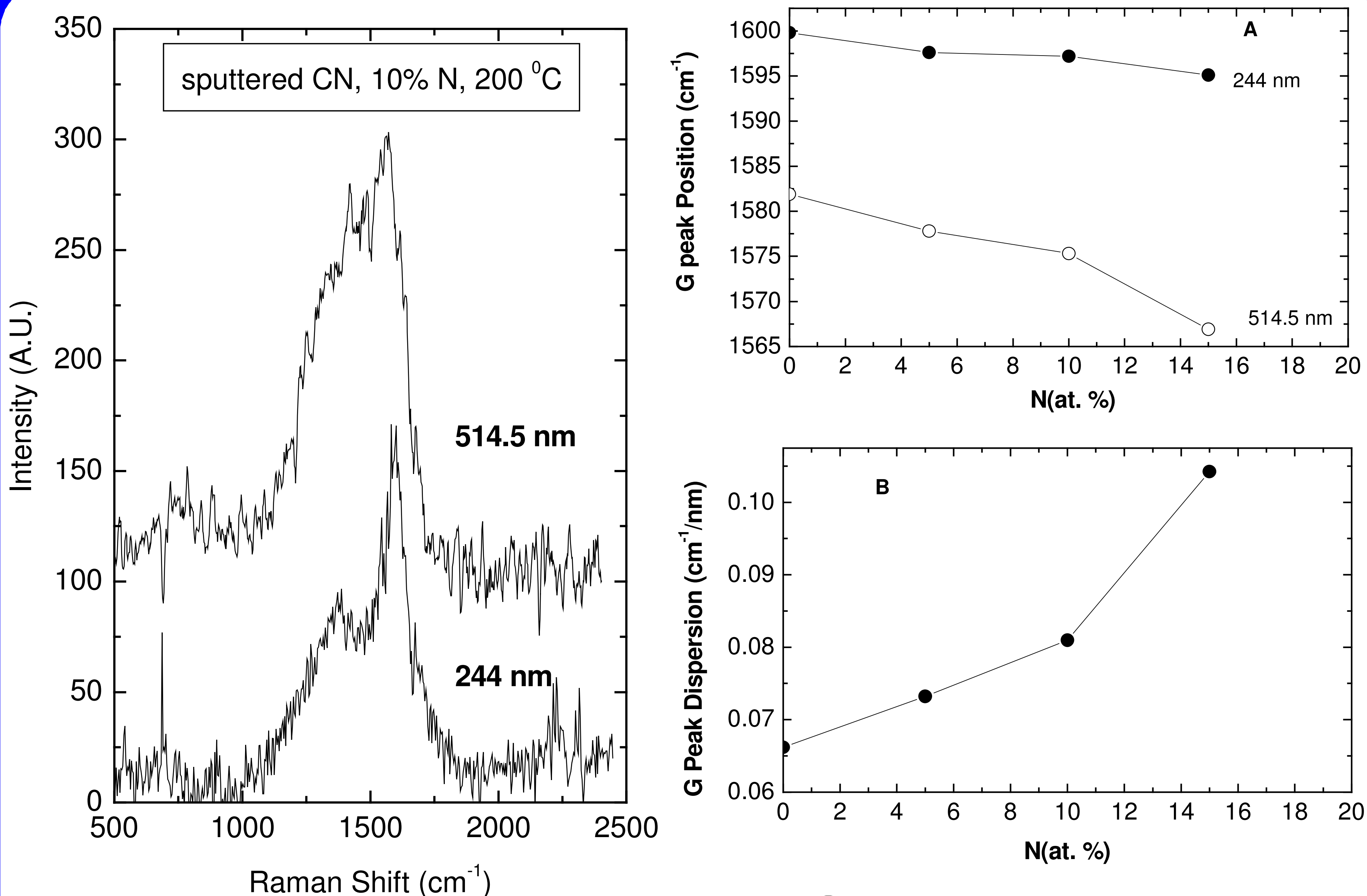

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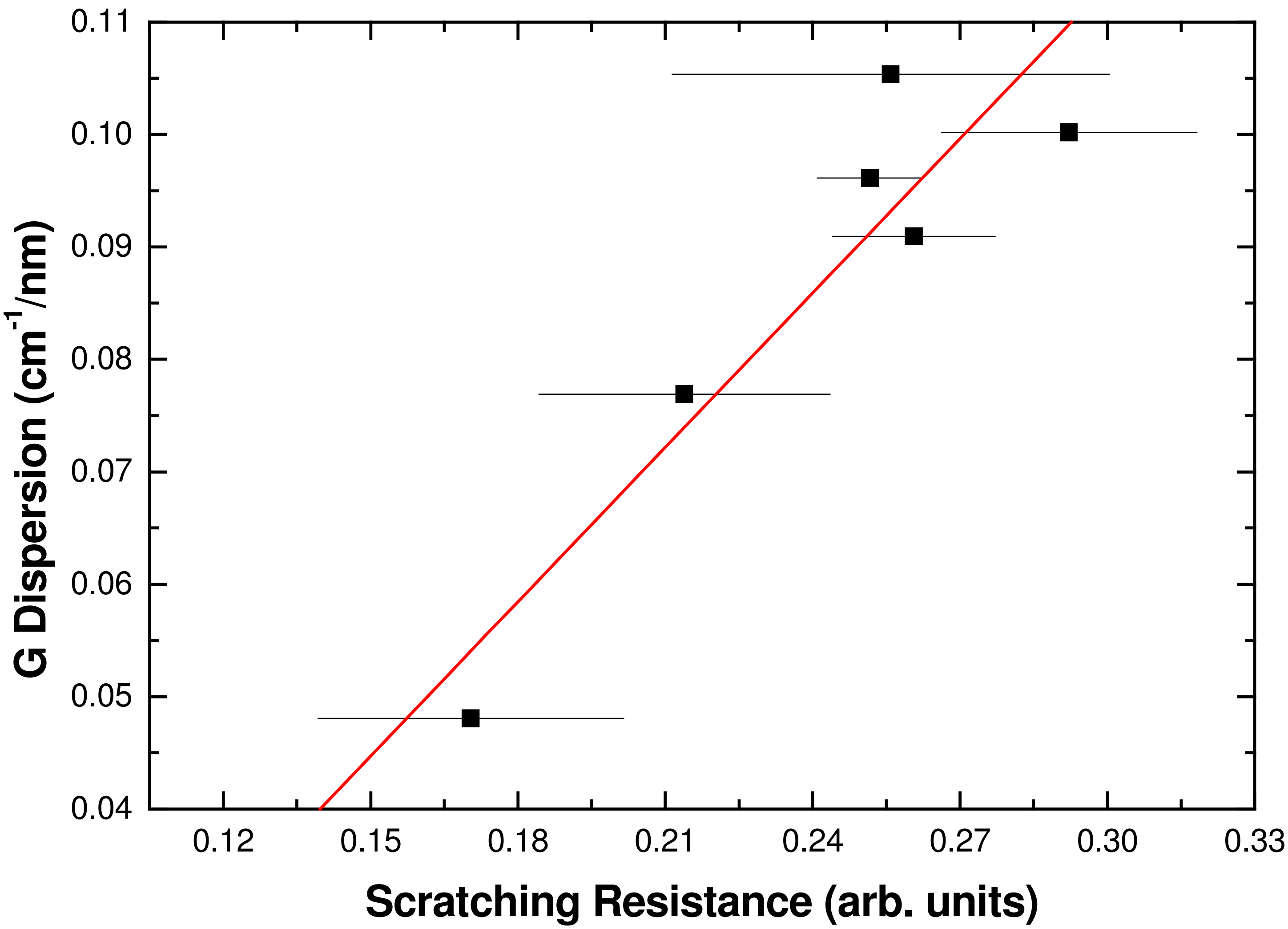
G Peak Dispersion



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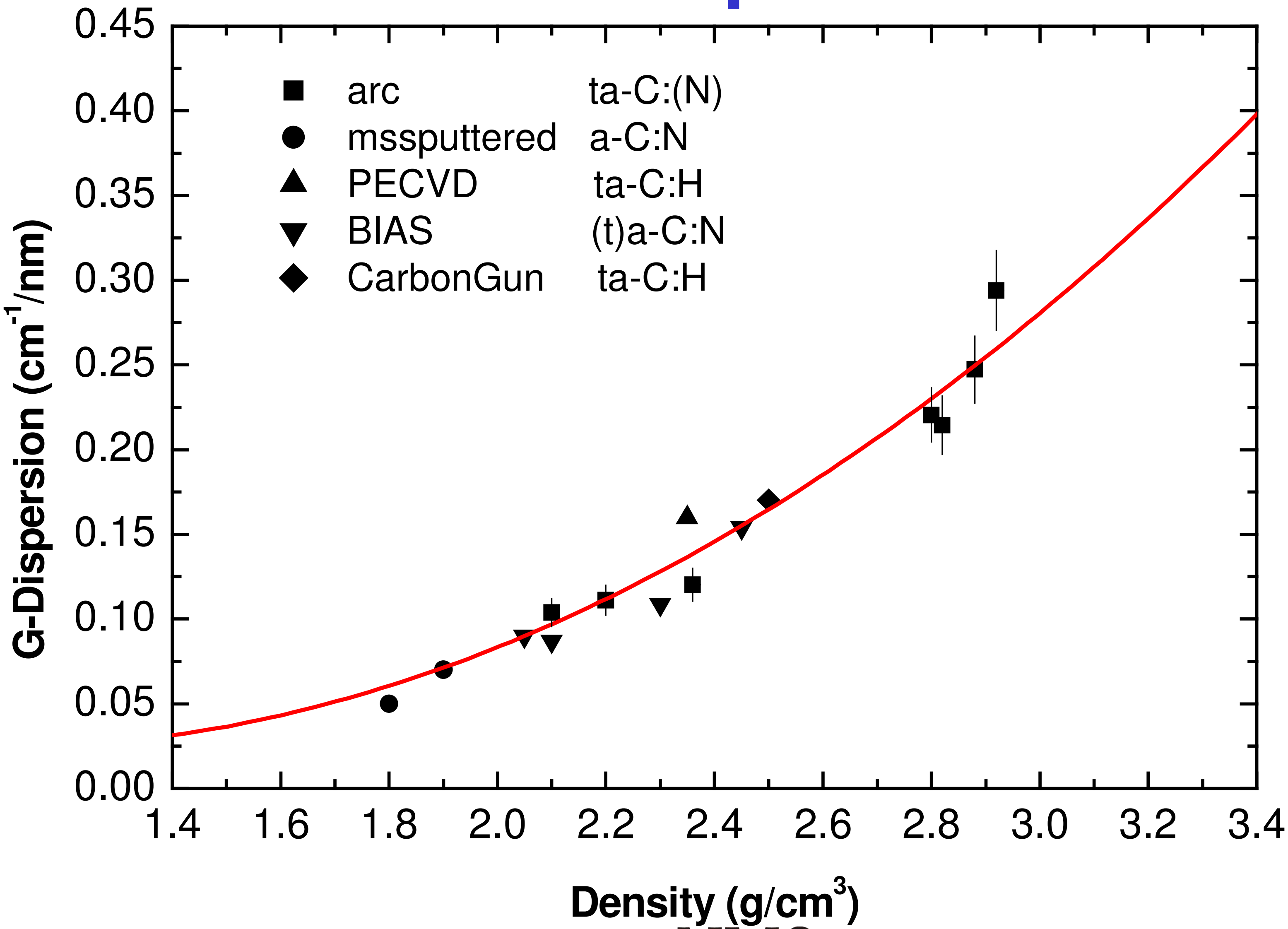
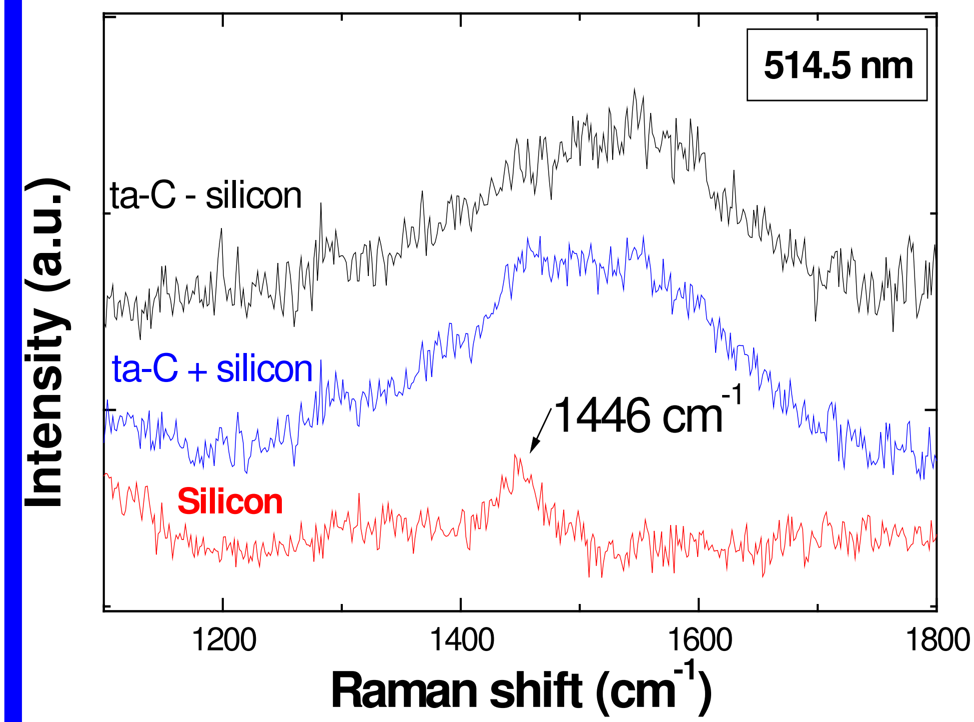
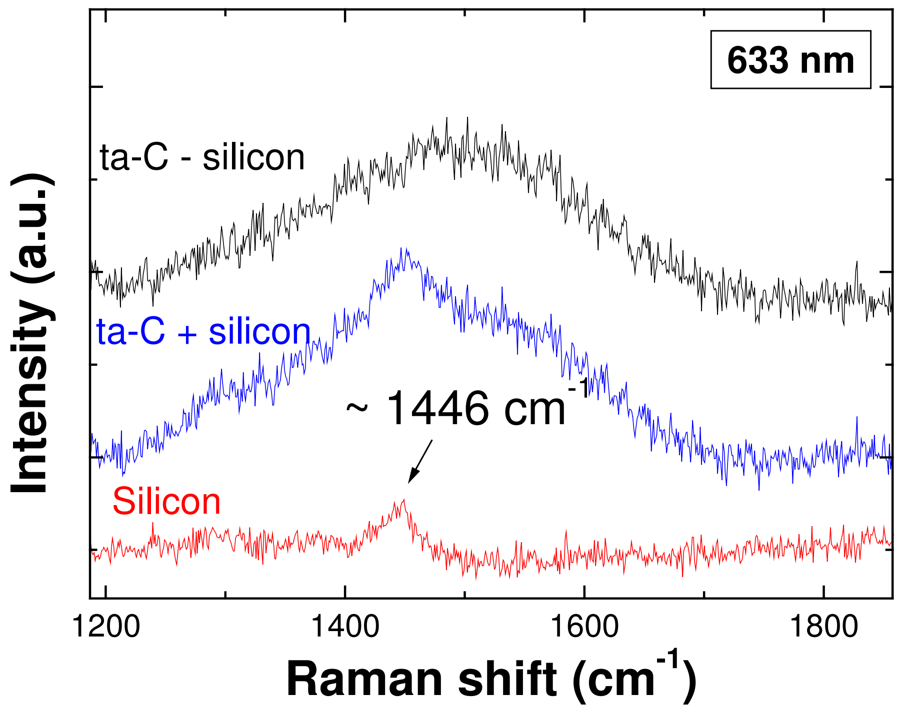


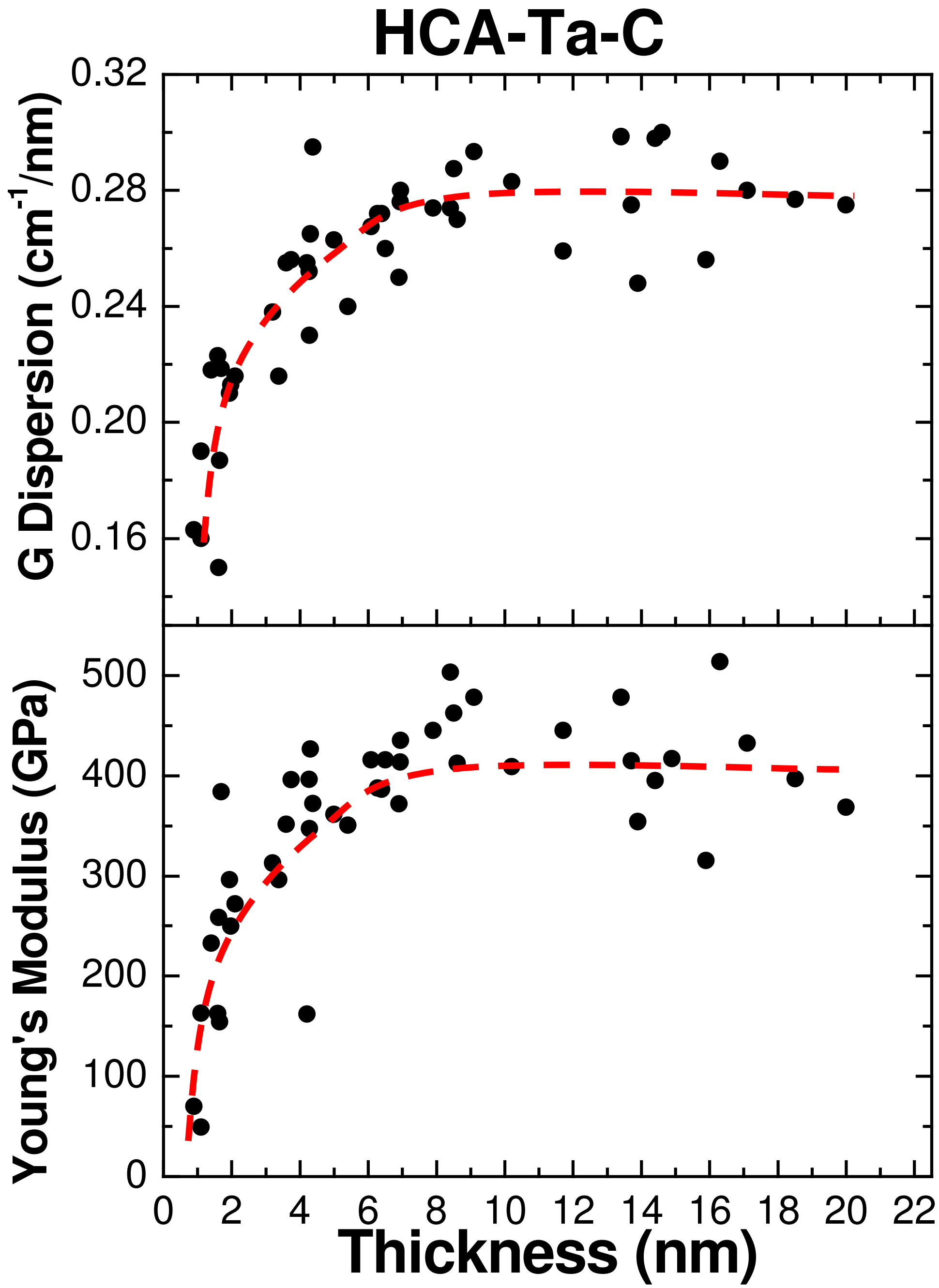
Ultra-thin ta-C films



Substrate Effects:

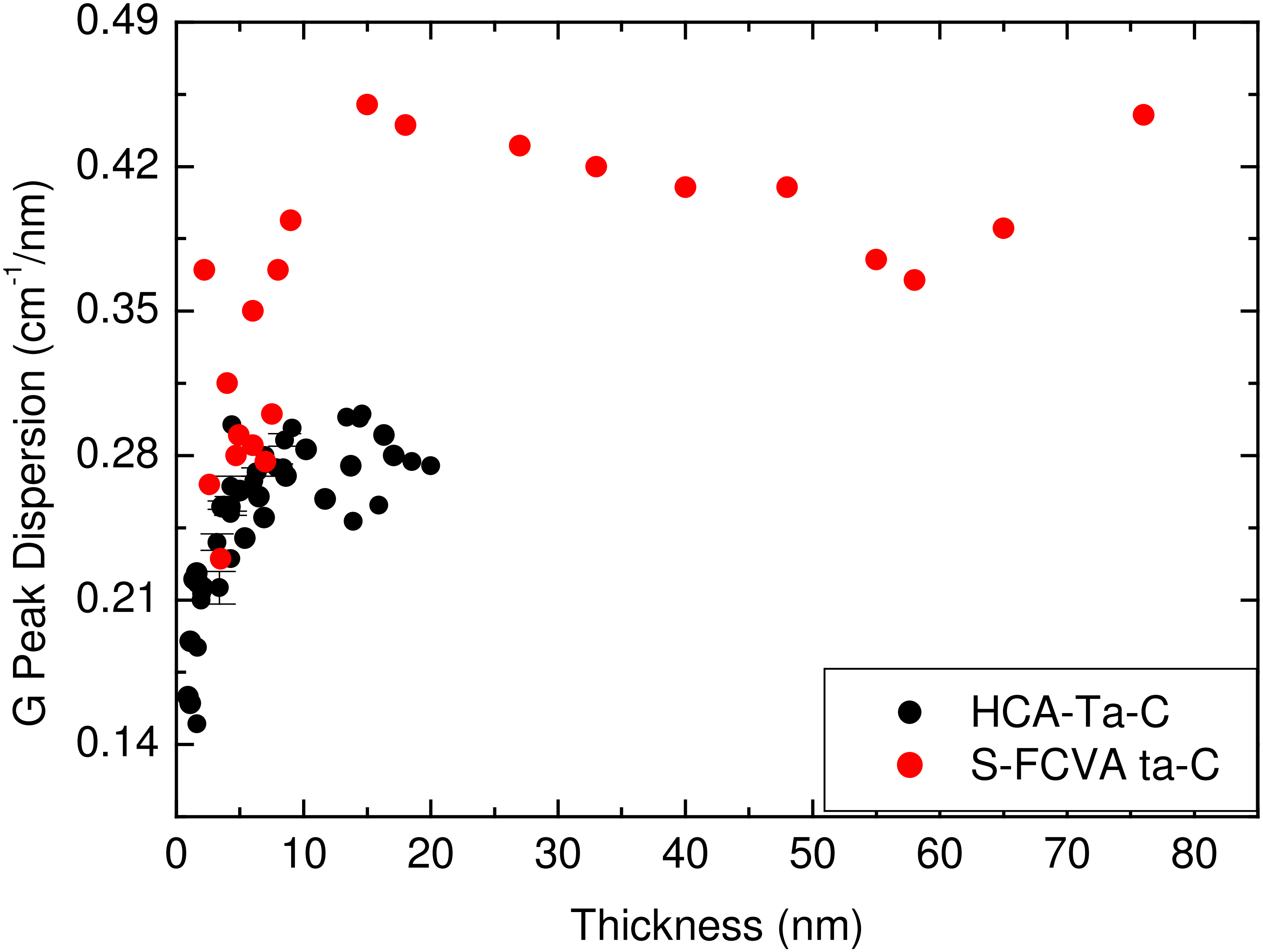
3rd order Si peak



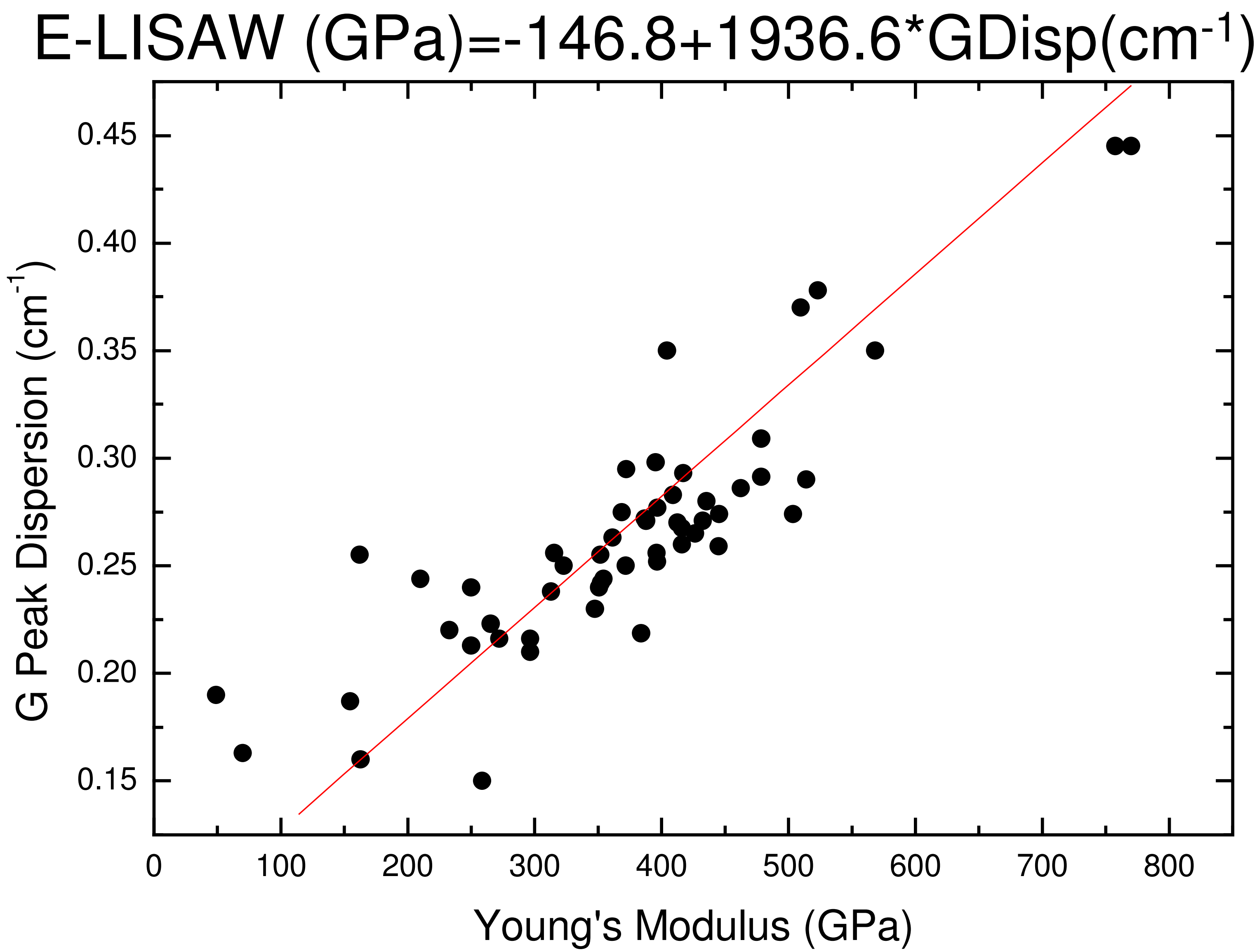

HCA-Ta-C
G Dispersion (cm-1/nm)
0.32
0.28
0.24
0.20
0.16
Young's Modulus (GPa)
500
400
300
200
100
0
0 2 4 6 8 10 12 14 16 18 20 22
Thickness (nm)

)
P

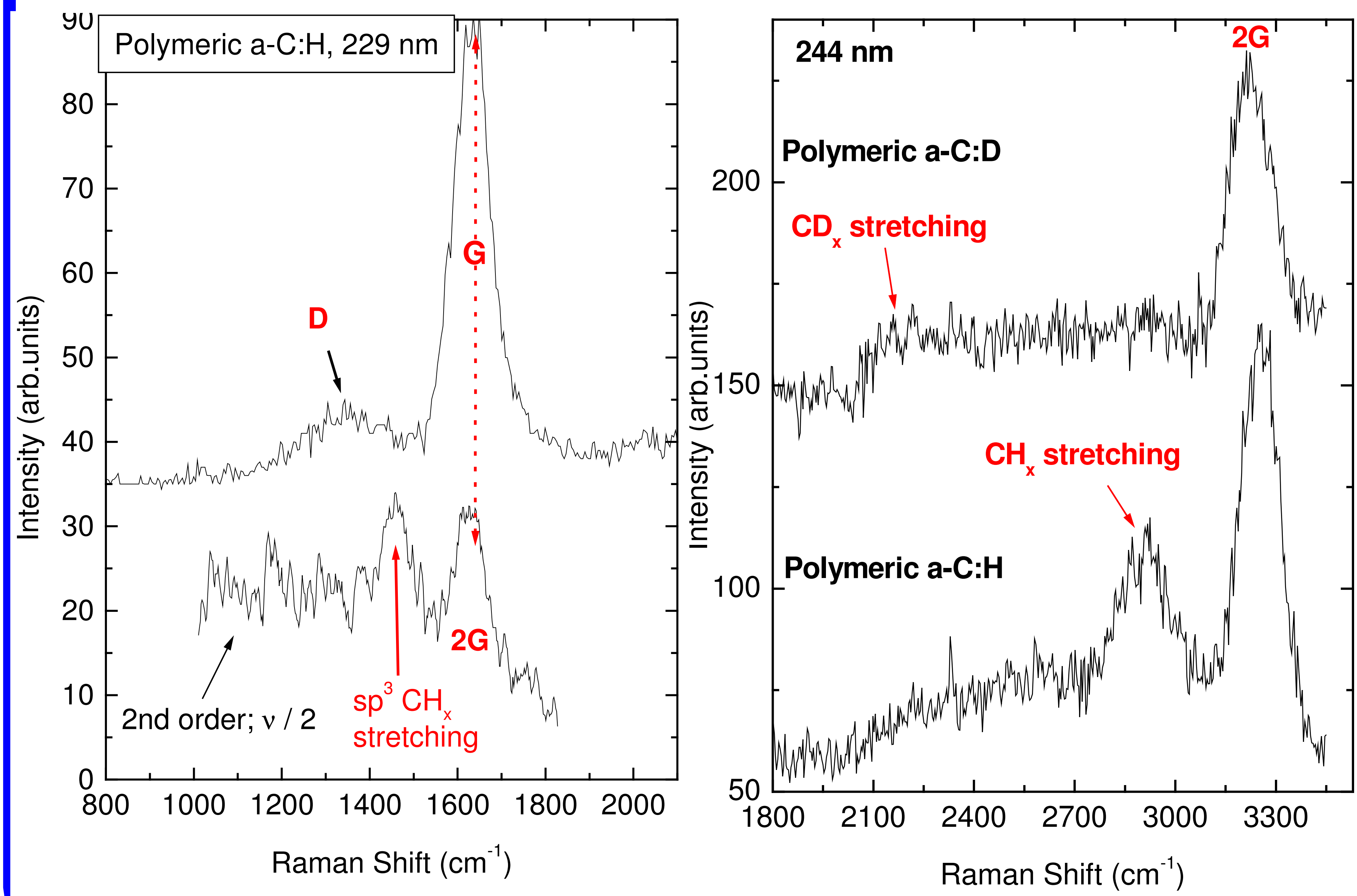
HCA vs S-FCVA Ta-C



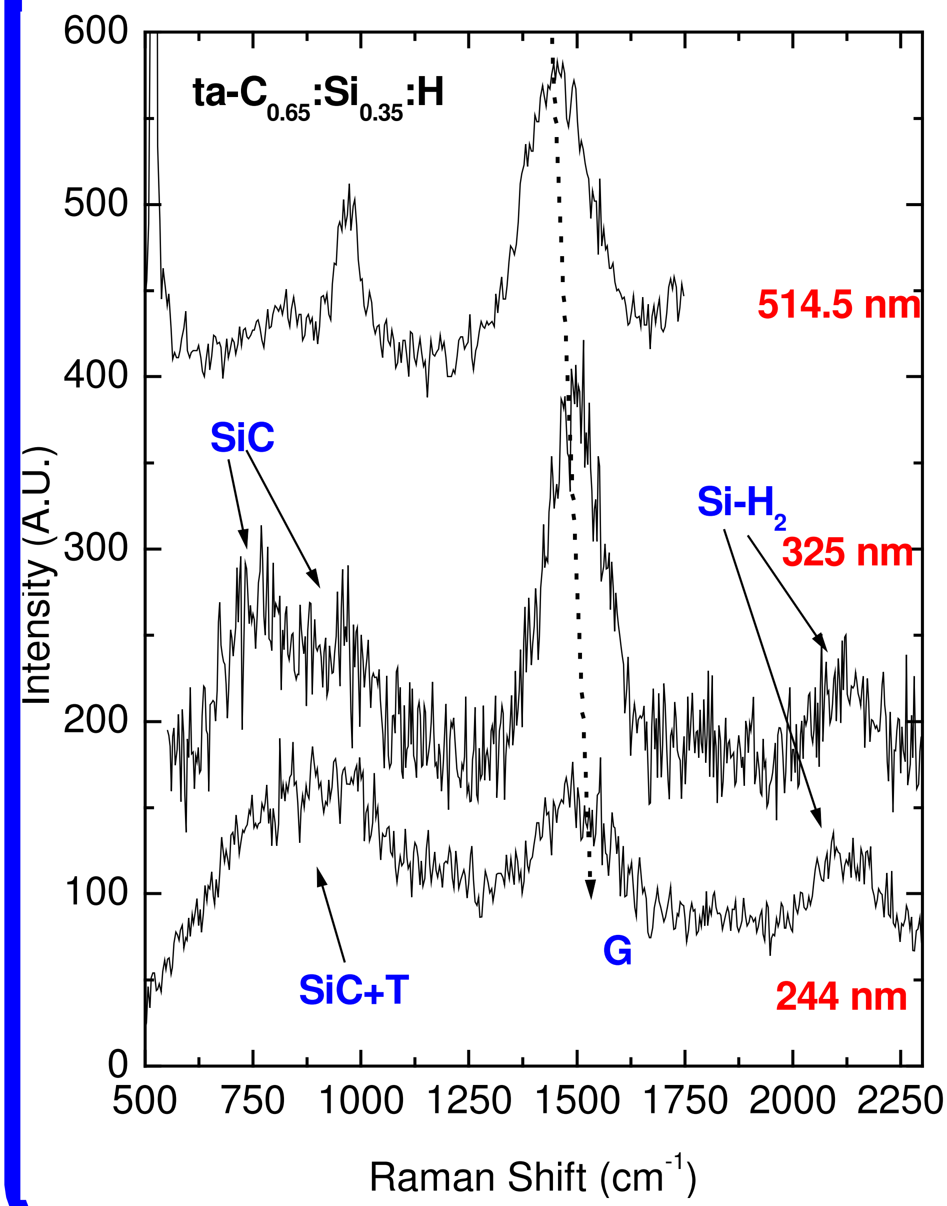
Ta-C: G Dispersion vs. Young's Modulus

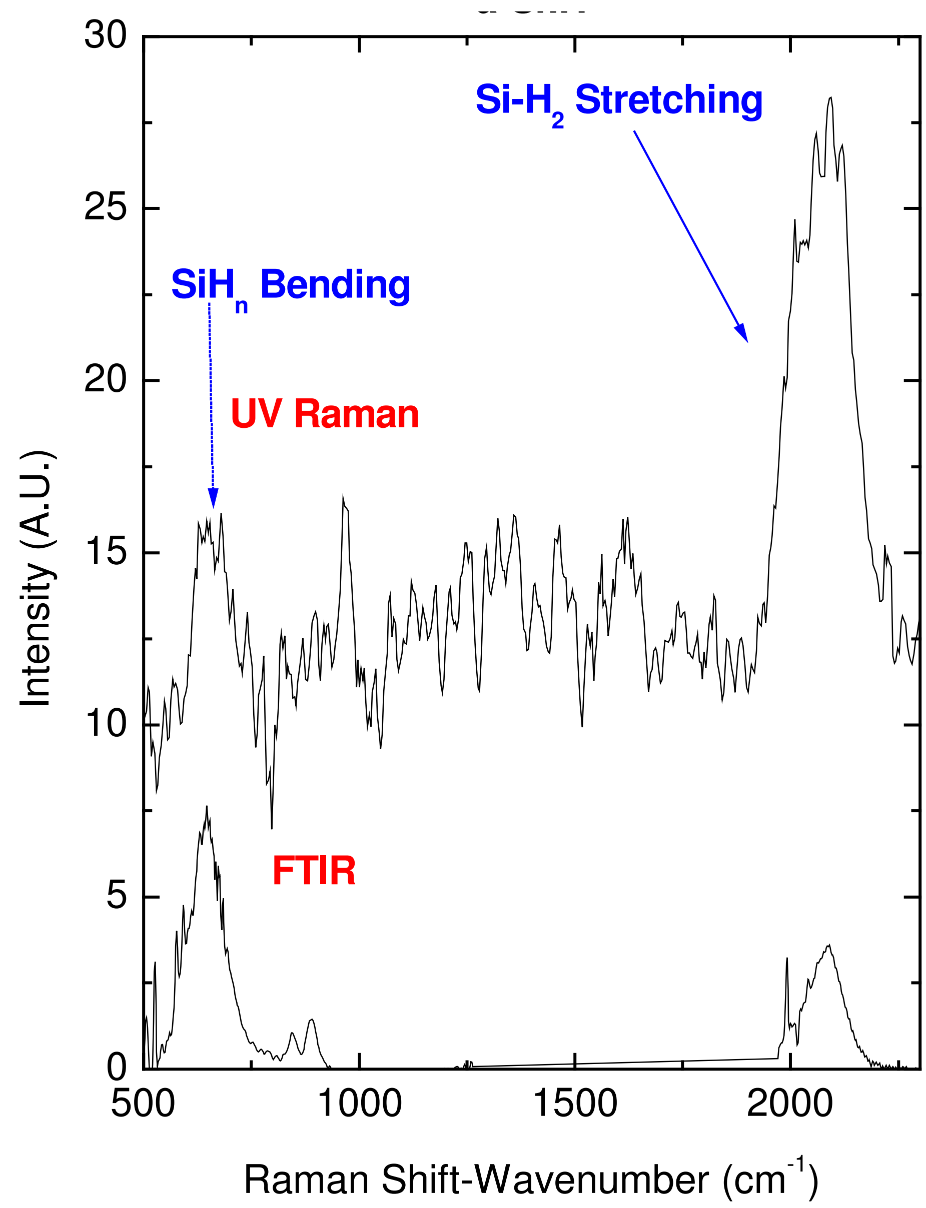


C-H detection by UV-Raman



Si-C and Si-H detection by UV-Raman





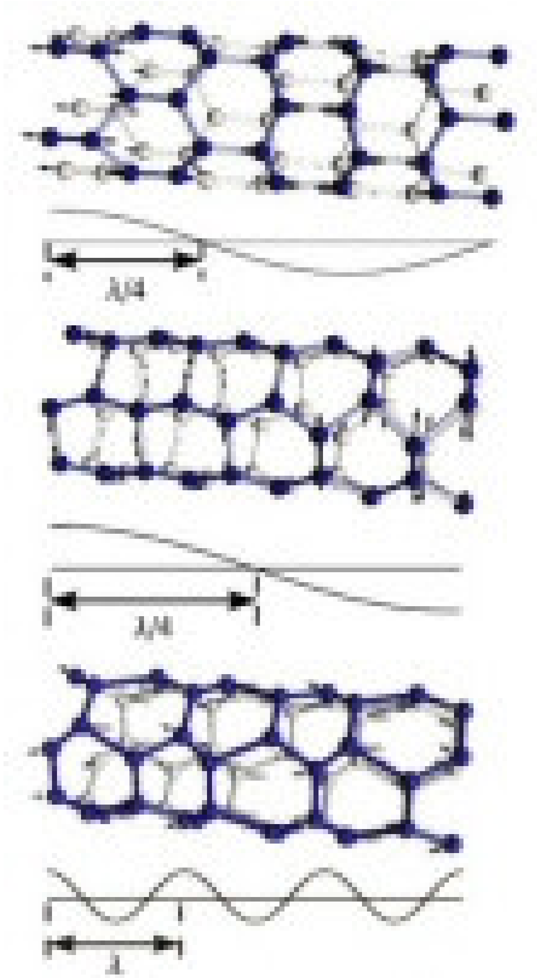
Conclusions

Review DLC properties

Review Characterisations

Review Raman

Useful ref….



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PRB 64, 075414 (2001)
PRB 67, 155306 (2003)
PRB 72, 085401 (2005)
PRB 75, 035427 (2007)
PRL 93, 185503 (2004)
PRL 95, 236802 (2005)
PRL 97, 187401 (2006)
Nano Lett 7, 2711 (2007)
APL 91, 233108 (2007)
Nature Materials 6, 198 (2007)
PRL 91, 226104 (2003)
Science 309, 1545 (2005)
Nature Nano April 2008