Thermal H-content evolution of a-C:H characterized by *in situ* Raman microspectroscopy:

Application to Tore Supra deposits

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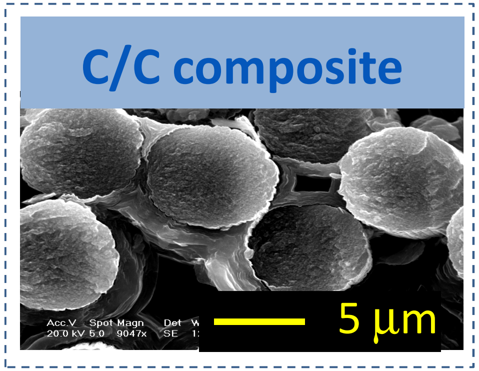
[3]MPI für Plasmaphysik/ EURATOM Association, Garching (GERMANY)

I - Introduction

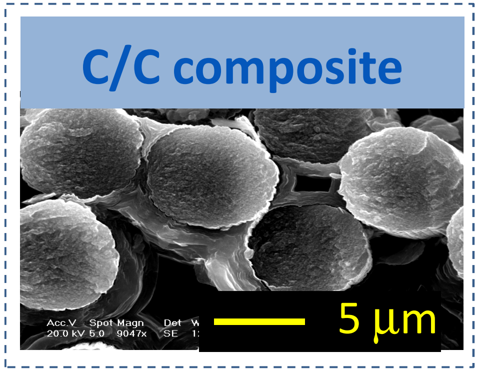
→Plasma wall interactions

*Tore Supra **Tokamak** (C.E.A., FRANCE)*



Actively cooled→ longer plasma shots

*Tore Supra **Tokamak** (C.E.A., FRANCE)*



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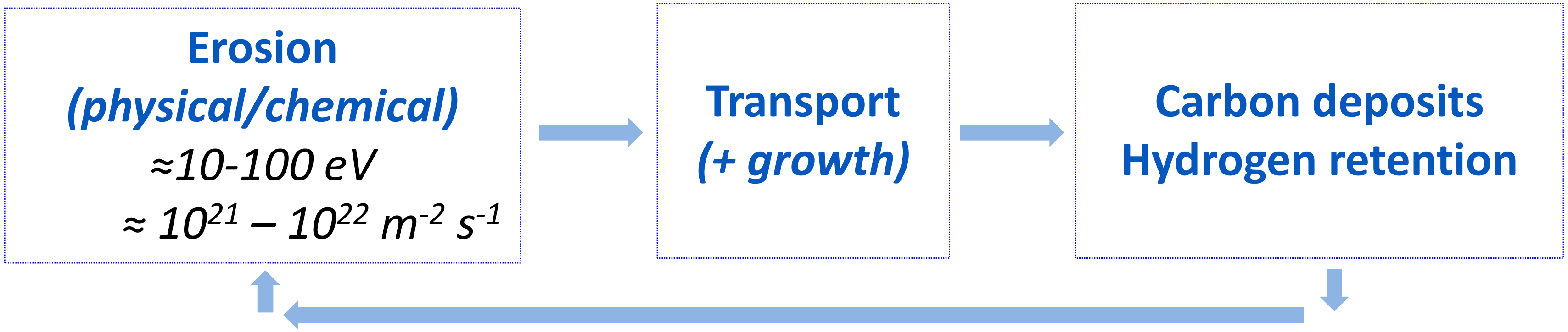


Erosion
(physical/chemical)
≈10-100 eV
≈ $10^{21} – 10^{22}$ m^{-2} s^{-1}

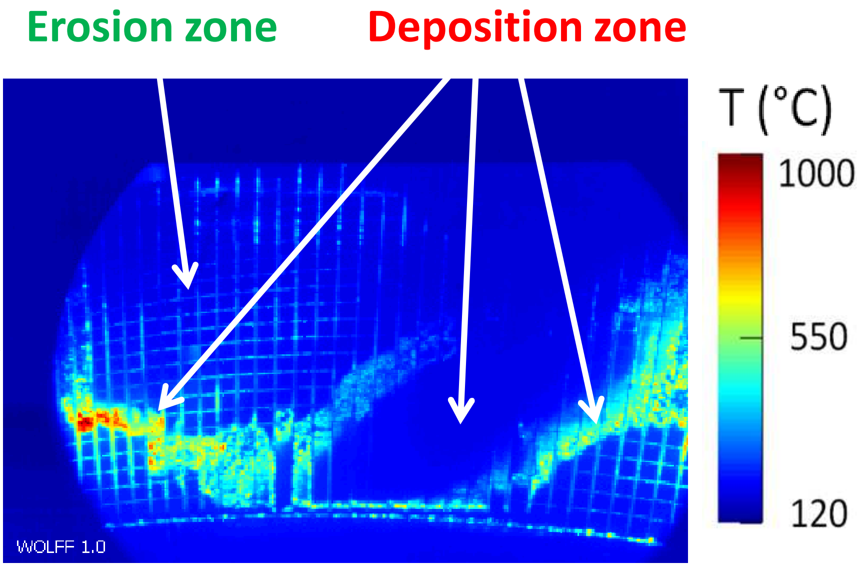
Transport
(+ growth)

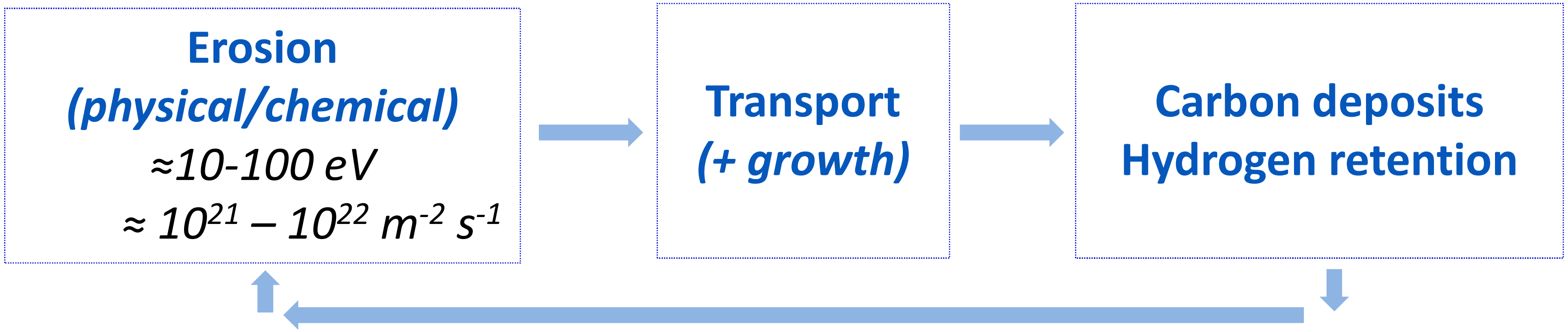
Carbon deposits
Hydrogen retention

For ITER: Safety issue

Tsitrone *et al.*, Nuclear Fusion (2009)
Pegourie *et al.*, J. Nucl. Mater (2009)
Dittmar *et al.*, Physica Scripta (2009)
Pardanaud *et al.*, J. Nucl. Mater (2010)
Martin *et al.*, J. Nucl. Mater (2011)

Tore Supra ***Tokamak*** *(C.E.A., FRANCE)*





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II - Context

→ The D.I.T.S. campaign

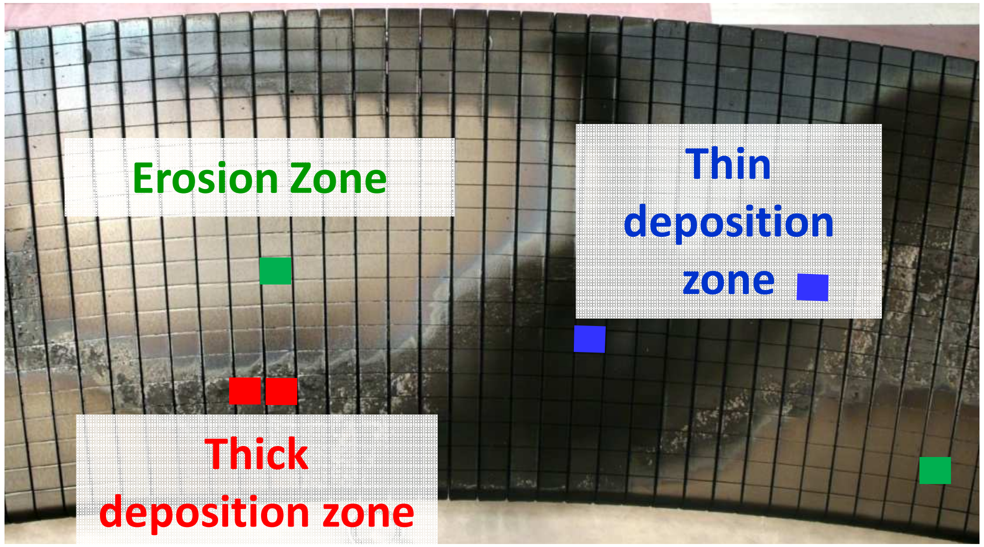
The D.I.T.S. campaign

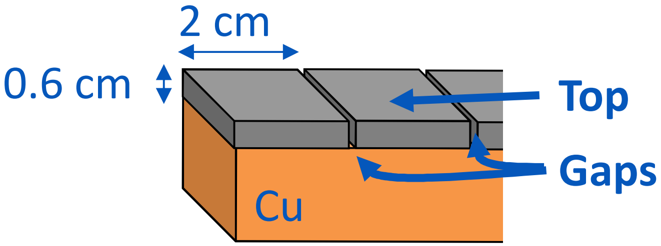
Aim:

- **Load** Plasma Facing Components in Deuterium
- **D-inventory**

How:

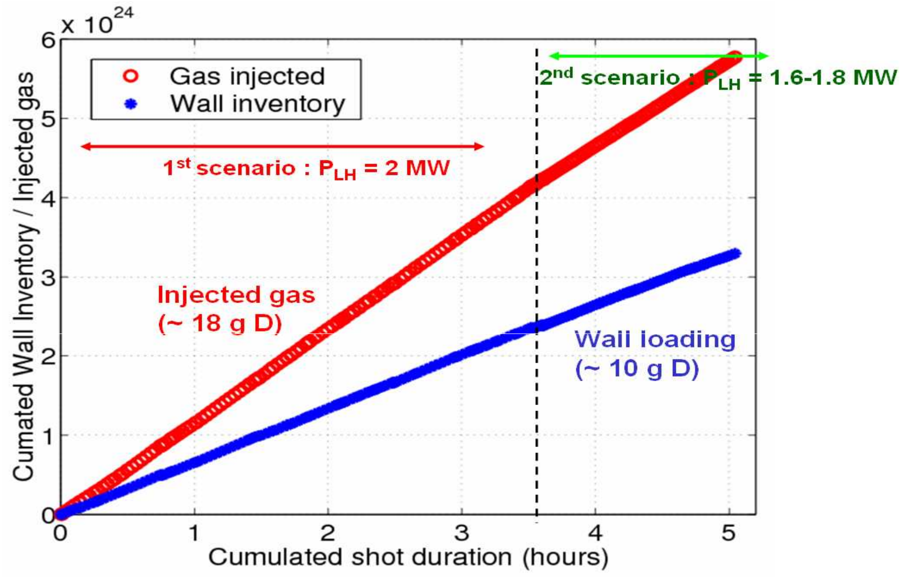
- ***In-situ*** *gas balance*
- One section of the Limiter dismanteled for ***post-mortem*** *analysis*
- **Compare** *post-mortem* analysis and *in-situ* gas balance





In-situ gas balance

>160 plasma shot
(1 min each)



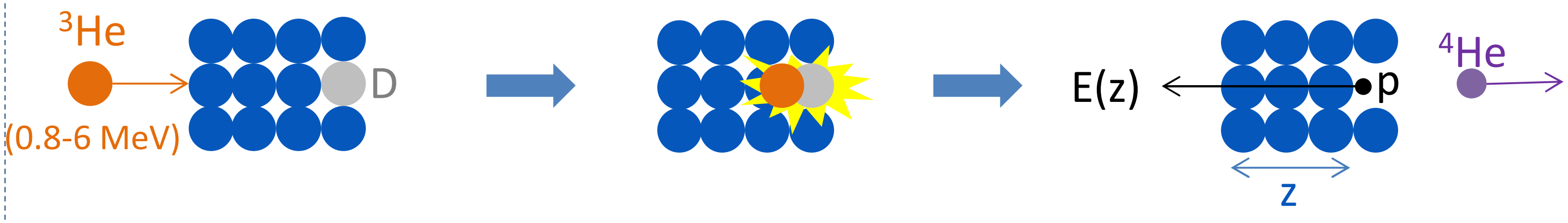
- No saturation
- 10 g of D trapped in the walls during the DITS campaign

Tsitrone *et al.*, Nuclear Fusion (2009)
Pegourie *et al.*, J. Nucl. Mater (2009)

Post-mortem analysis

Aim: find the 10 g

One example: Nuclear **R**eaction **A**nalysis

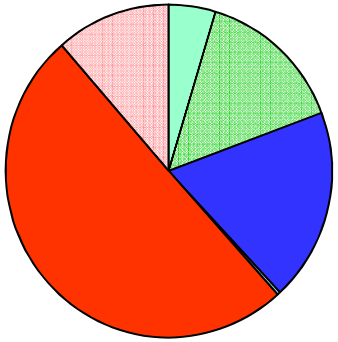


- Absolute measurment of D
-D/C in function of z
(down to ≈35-40 µm)

Post-mortem analysis

D-content / surface unit

D-content total



Extrapolation to the limiter →

?

🟥 ▨ **Thick deposits**
tiles / gaps

🟦 ▨ **Thin deposits**
tiles / gaps

🟩 ▨ **Erosion zones**
tiles / gaps

Tsitrone *et al.*, Nuclear Fusion (2009)
Pegourie *et al.*, J. Nucl. Mater (2009)

Post-mortem analysis

Extrapolation to the limiter

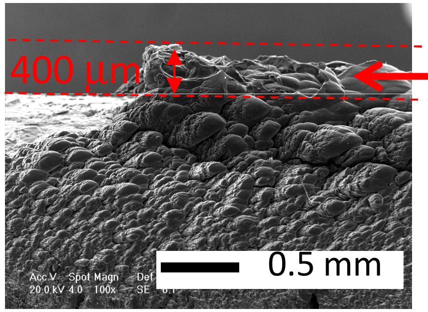
Methodology:
1) Identifying zones

Post-mortem analysis

Methodology:
1) Identifying zones
2) Measuring thickness of relevant tiles

Extrapolation to the limiter

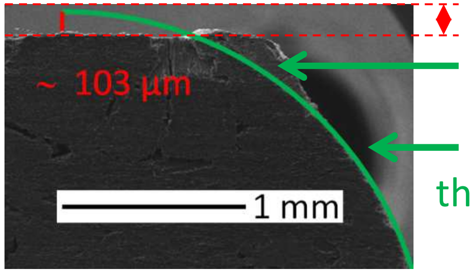
Thick deposition zone



Deposited carbon

Gap side view

Erosion zone



Eroded carbon

Gap deposits

Profile of the virgin tile

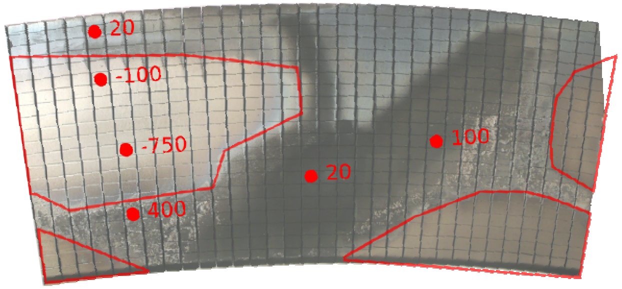
Cross section view

Post-mortem analysis

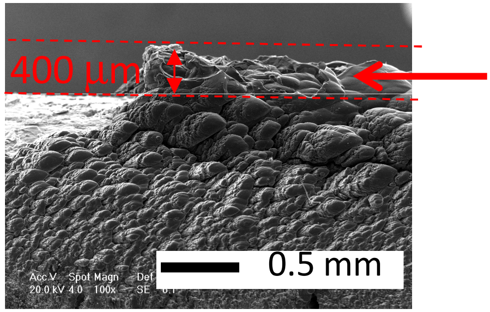
Methodology:

1) Identifying zones
2) Measuring thickness of relevant tiles
3) Identifying frontier of zones

Extrapolation to the limiter

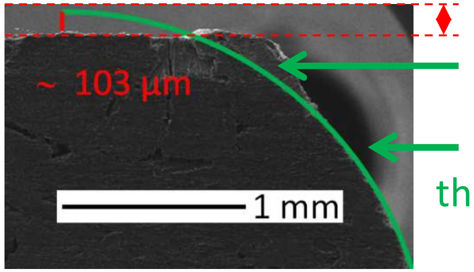


Thick deposition zone



Gap side view

Erosion zone



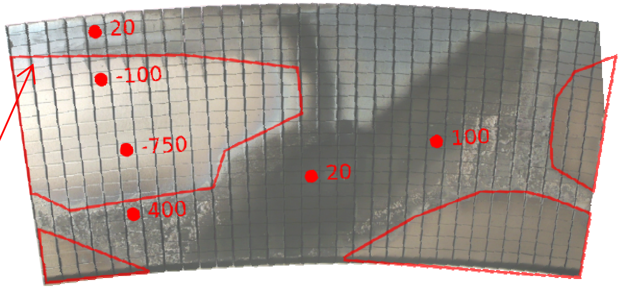
Cross section view

Post-mortem analysis

Methodology:

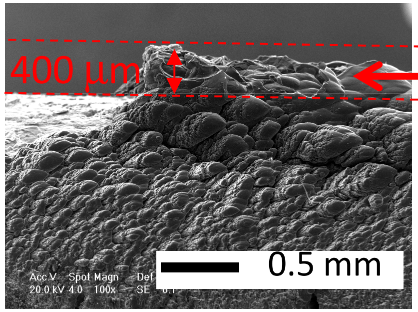
1) Identifying zones
2) Measuring thickness of relevant tiles
3) Identifying frontier of zones
4) Linear interpolation

Extrapolation to the limiter



z_0: at the edge of erosion zone

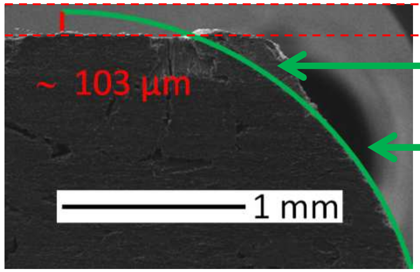
Thick deposition zone



Deposited carbon

Gap side view

Erosion zone



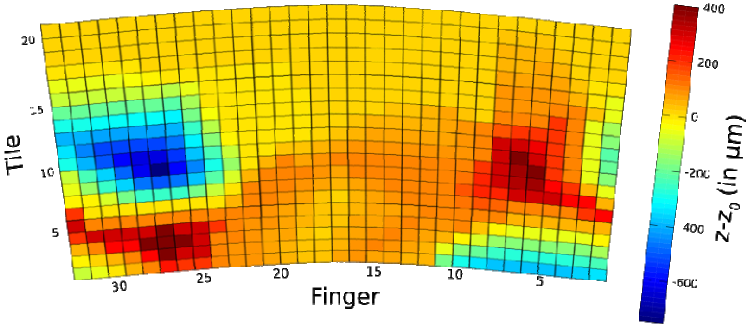
Eroded carbon

Gap deposits

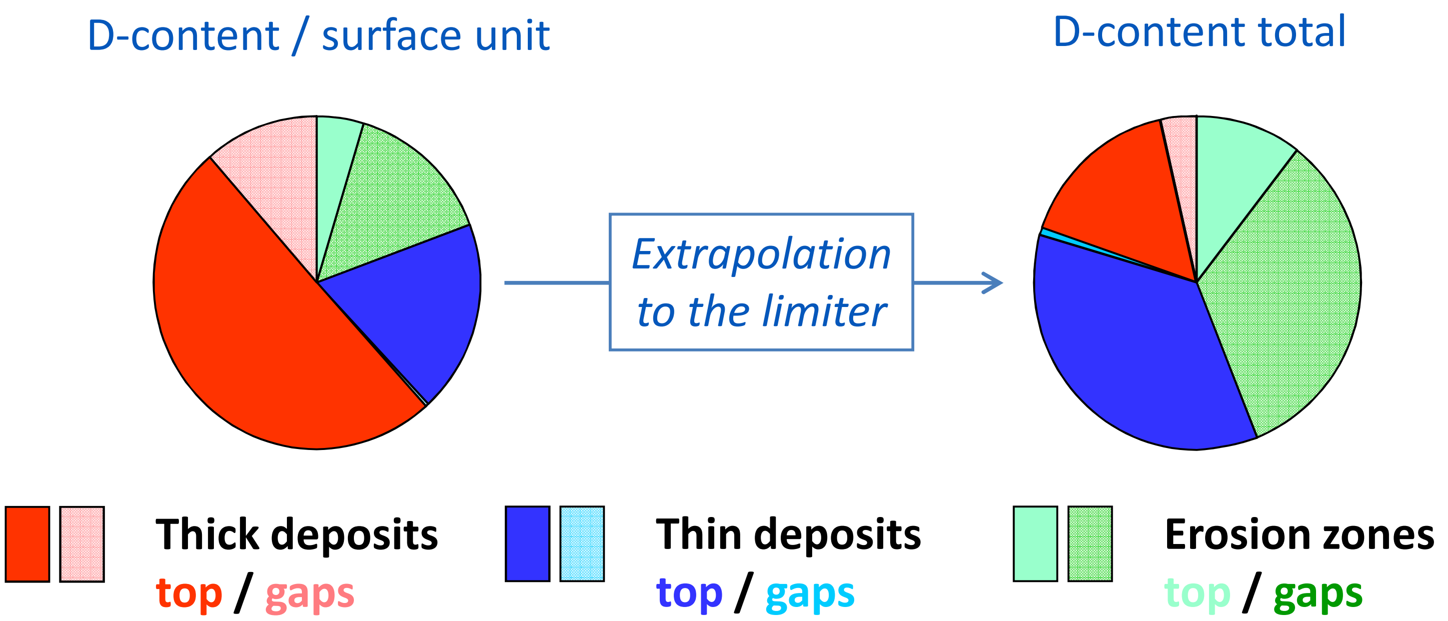
Profile of the virgin tile

Cross section view

Mapping of the dismanteled section of the LIMITER



Post-mortem analysis



D-content / surface unit

Extrapolation to the limiter

D-content total

🟥 ▨ **Thick deposits**
top / gaps

🟦 ▨ **Thin deposits**
top / gaps

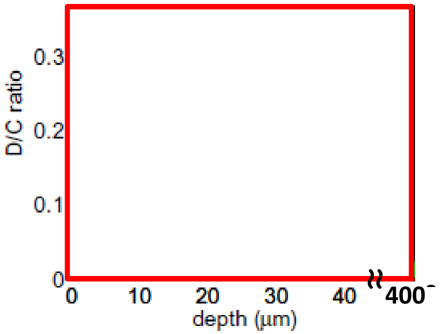
🟩 ▨ **Erosion zones**
top / gaps

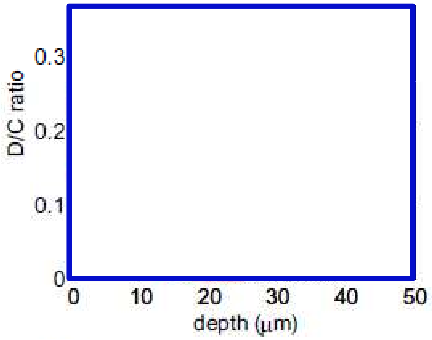
2-3 g of D retained in all the limiter
Where is the missing D ?

Tsitrone *et al.*, Nuclear Fusion (2009)
Pegourie *et al.*, J. Nucl. Mater (2009)

Post-mortem analysis

In-depth profiles

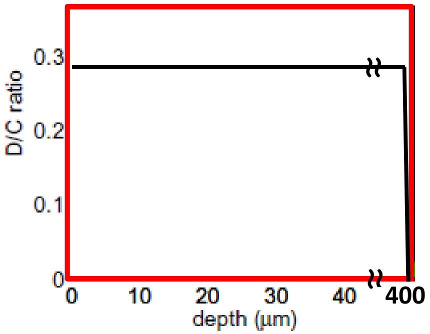


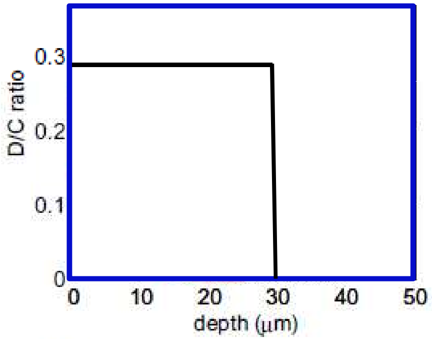


-Deposition rate is ≈ constant with time

Post-mortem analysis

In-depth profiles



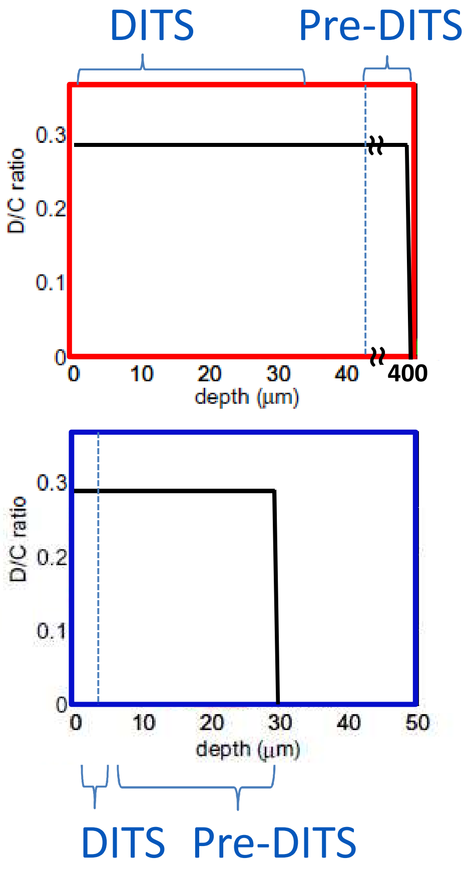


-Deposition rate is ≈ constant with time

≈ Constant in-depth profiles

Post-mortem analysis

In-depth profiles



-Fuelling: DITS ↔ 1.8 10^4 s

pre-DITS ↔ 1.4 10^5 s

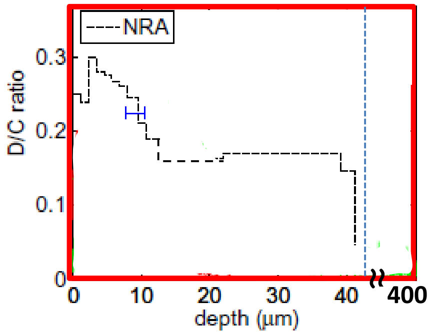
≈ 13 %

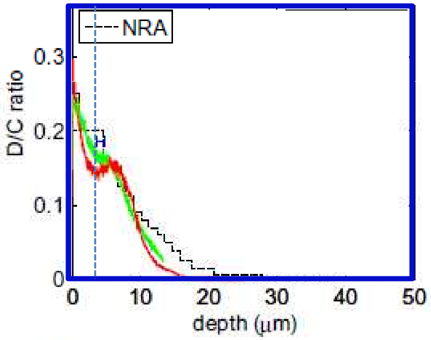
-Deposition rate is ≈ constant with time

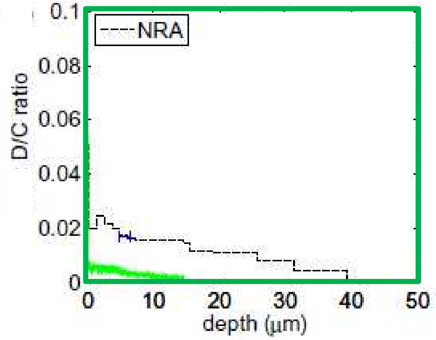
≈ Constant in-depth profiles

Post-mortem analysis

In-depth profiles







Decreasing profiles

↓

Slow D-release !

Dittmar *et al.*, Physica Scripta (2009)

Aim:

→ Characterizing this slow D-release

Technique:

→ Raman spectroscopy

Methodology:

→ Refined understanding of Raman spectroscopy on « well-known » samples

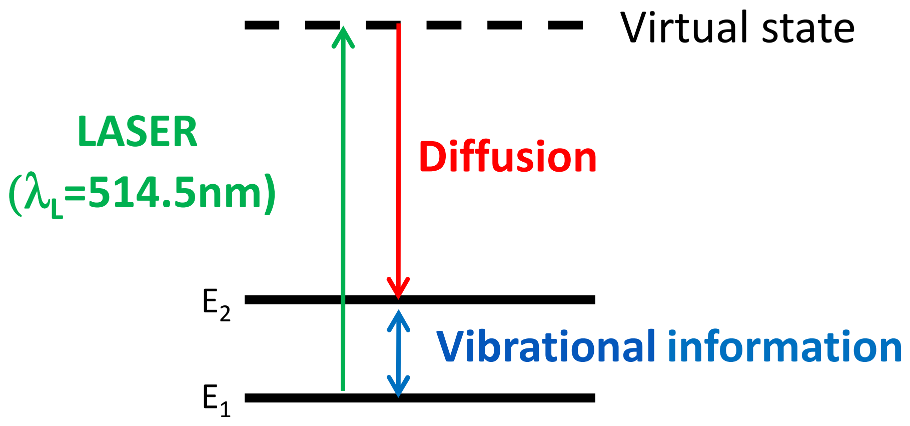
→ Comparative study with Tore Supra samples

III – Raman spectroscopy as a tool

→ *Structural characterization*

→ *H-content estimator*

Raman spectroscopy



- ***Local probe*** *(surface ≈ 1μm^2, depth ≈ 10-500 nm)*

- ***Fast technique*** *(1 spectrum in ≈ 100 s or less)*

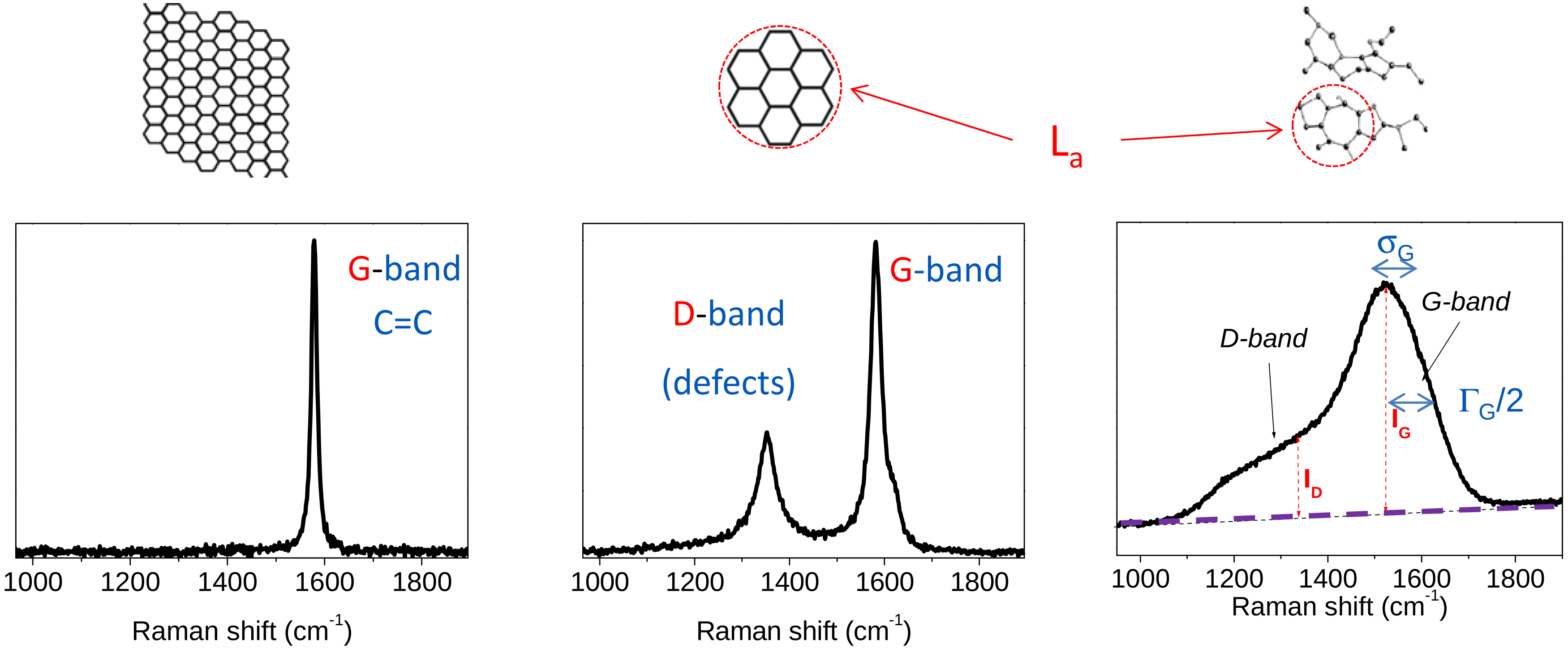
- ***« Non destructive » technique***

Raman spectroscopy of carbons

Graphite

Nanocrystalline graphite

Amorphous carbon

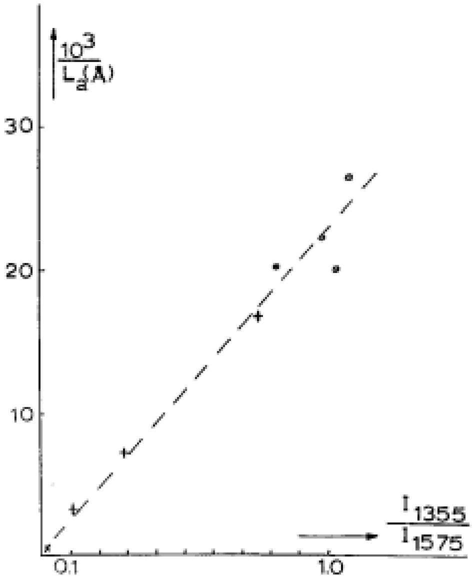


- Spectrum dominated by sp^2 C
- Influence of sp^3 C
- **D band**: probe of **aromatic domains**

Local ordering

Local ordering in nc-G

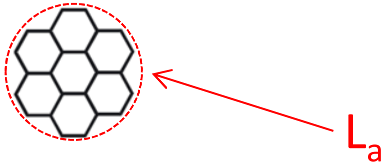
Experimental evidence



X-ray data

L_a → obtained by the width diffraction peaks

Raman data



$$\frac{I_D}{I_G} \propto \frac{1}{L_a}$$

Tuinstra and Koenig
J. Chem. Phys. **53**, 1126 (1970)

Local ordering in a-C

Experimental evidence

$$\frac{I_D}{I_G} \propto \frac{1}{E_g^2}$$

Chhowalla and co.
Appl. Phys. Lett.**76**, 1419 (2000)

+

In aromatic clusters:

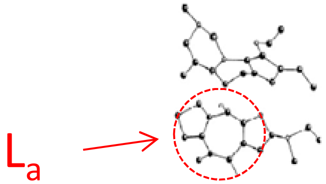
$$E_g \propto \sqrt{\text{number of rings}} \propto \frac{1}{L_a}$$

Robertson and O'Reilly
Phys. Rev. B **35**, 2946(1987)

=

$$\frac{I_D}{I_G} \propto L_a^2$$

Ferrari and Robertson
Phys. Rev. B **61**, 14095(2000)



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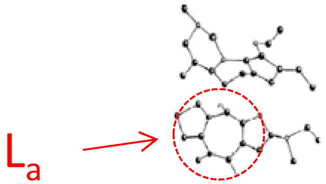
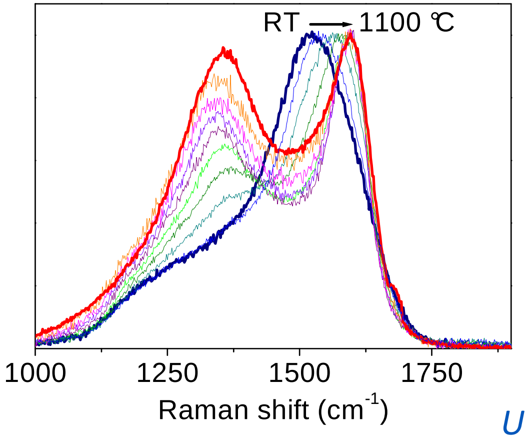


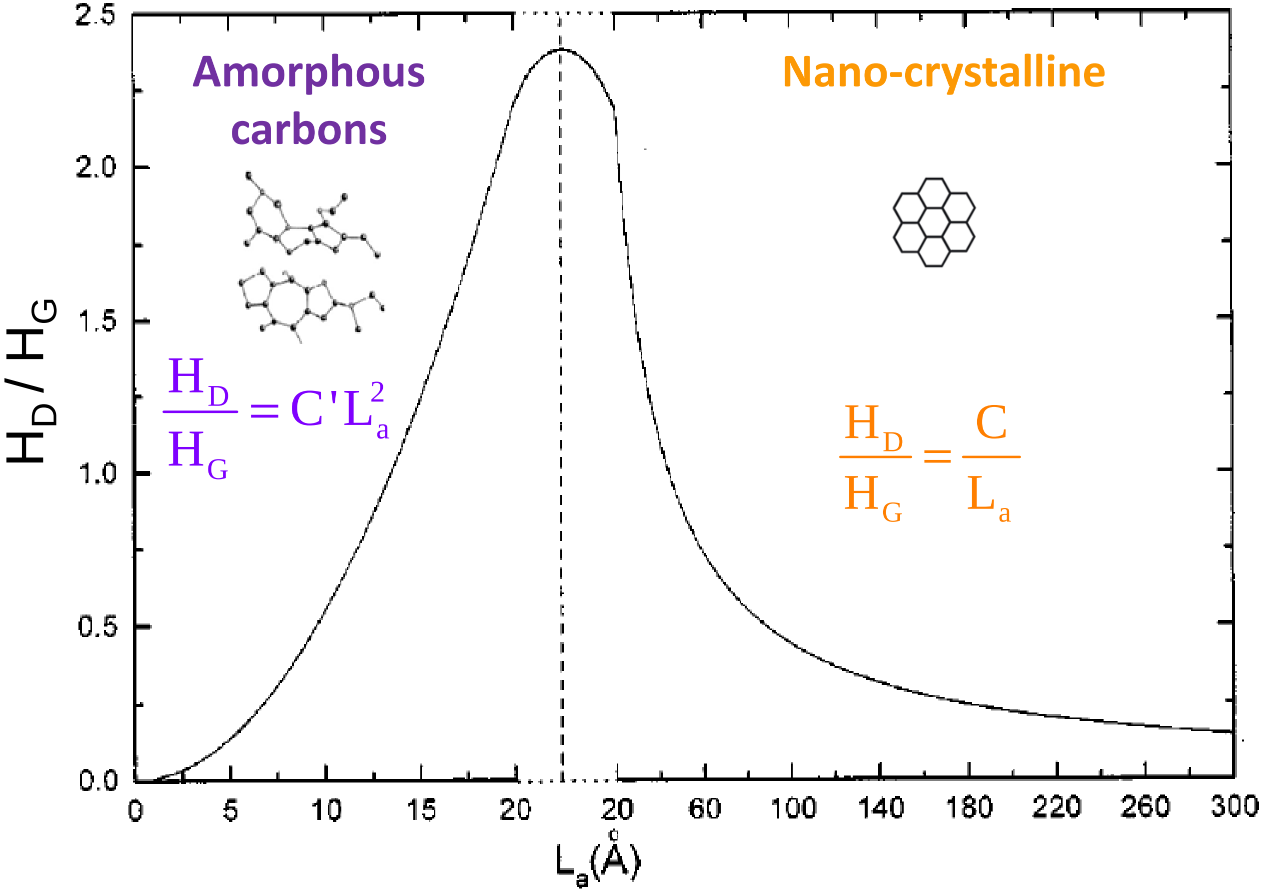


UHV conditions

$\frac{I_D}{I_G}$ increases
σ_G shifts
Γ_G narrowing

} organization increases

Raman spectroscopy of carbons

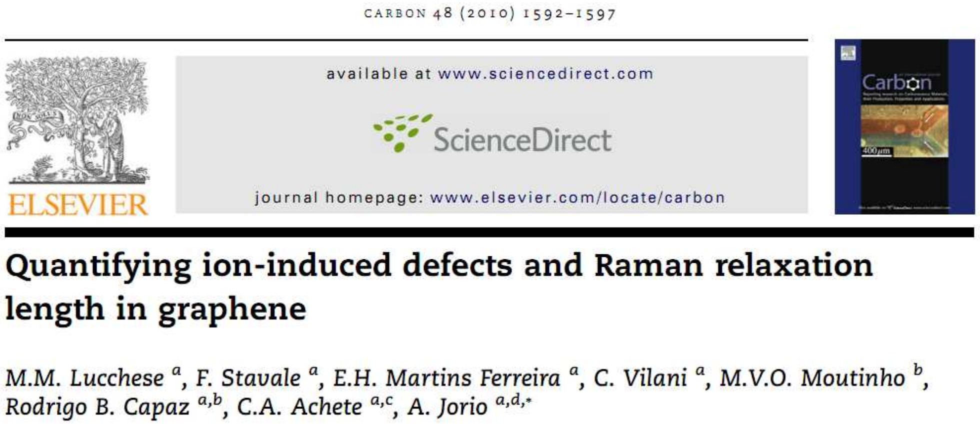


$$\frac{H_D}{H_G} = C'L_a^2$$

$$\frac{H_D}{H_G} = \frac{C}{L_a}$$

Ferrari and Robertson
Phys. Rev. B **61**, 14095(2000)

Transition ≈ 2 nm



CARBON 48 (2010) 1592–1597

available at www.sciencedirect.com

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journal homepage: www.elsevier.com/locate/carbon

Quantifying ion-induced defects and Raman relaxation length in graphene

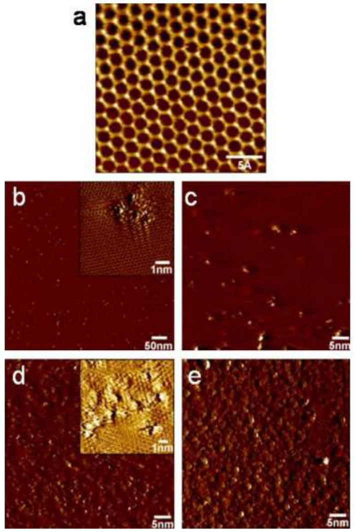
M.M. Lucchese [a], F. Stavale [a], E.H. Martins Ferreira [a], C. Vilani [a], M.V.O. Moutinho [b], Rodrigo B. Capaz [a,b], C.A. Achete [a,c], A. Jorio [a,d,*]

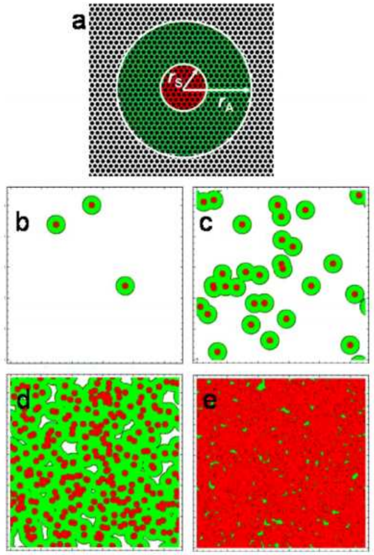
STM/Raman on exfoliated Graphene

Modelisation of the defects: 2 zones

→*Strutural disorder occuring after ion impact*

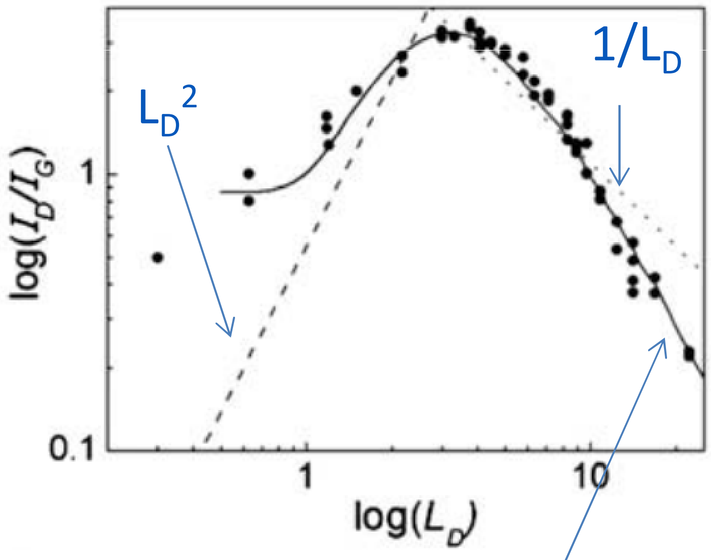
→*Selection rules relaxation (activated region)*





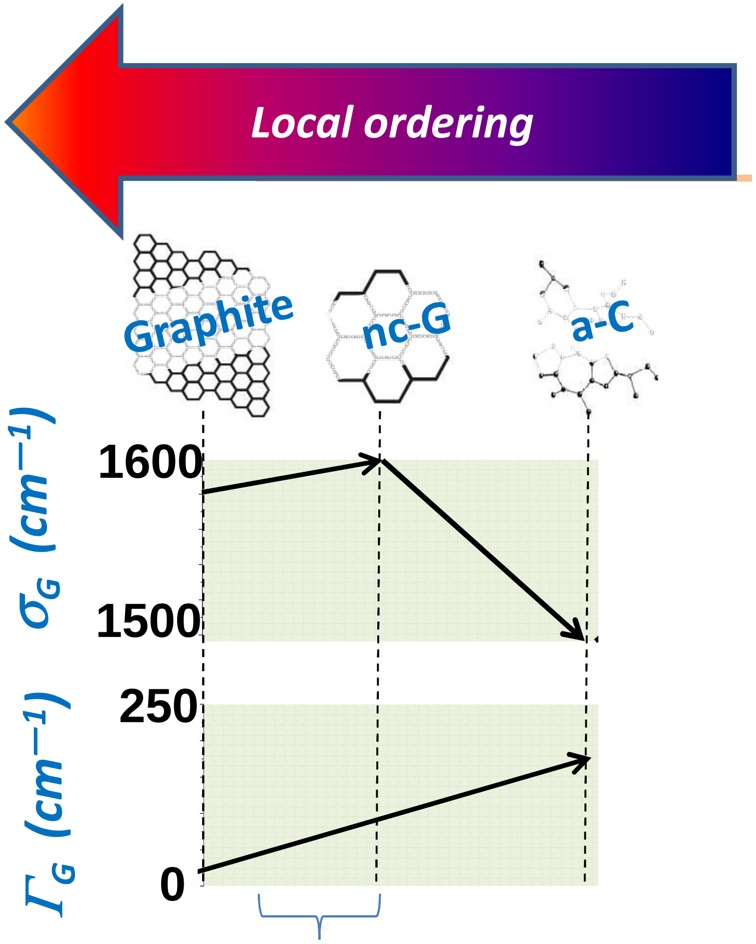
From b to e: 10^{11} →10^{14} Ar^+ (90 eV) cm^{-2}

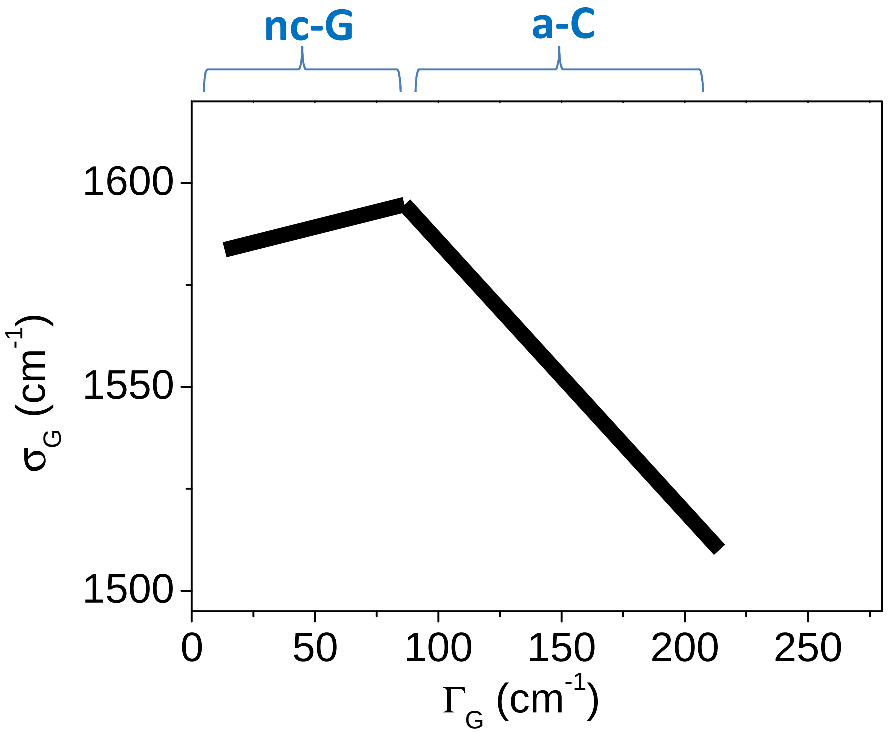
L_D: Average distance between defects



→r_a=3nm, r_s=1nm

Raman spectroscopy of carbons

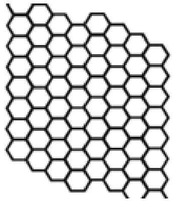




Ferrari, and Robertson, Phys. Rev. B **(2001)**

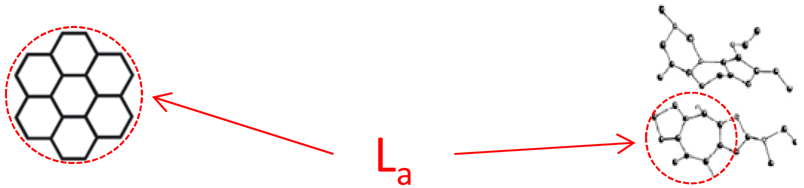
Raman spectroscopy of carbons

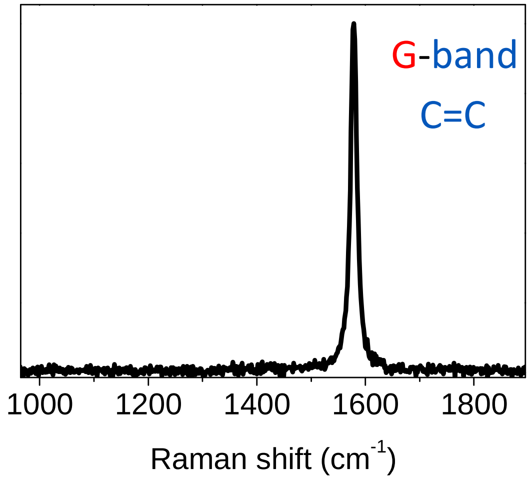
Graphite

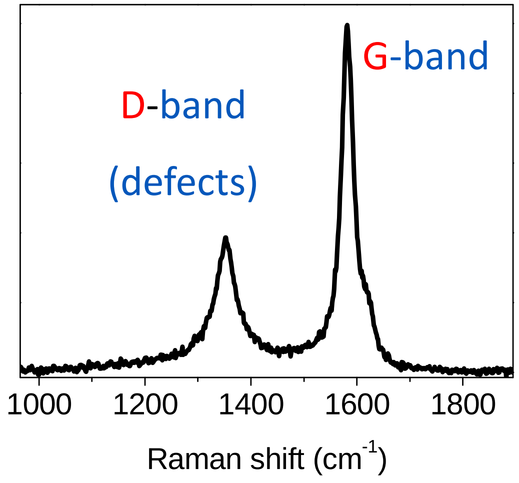


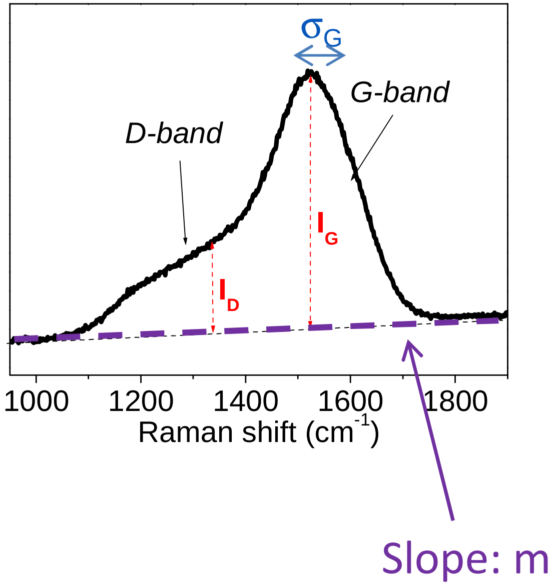
Nanocrystalline graphite

Amorphous carbon





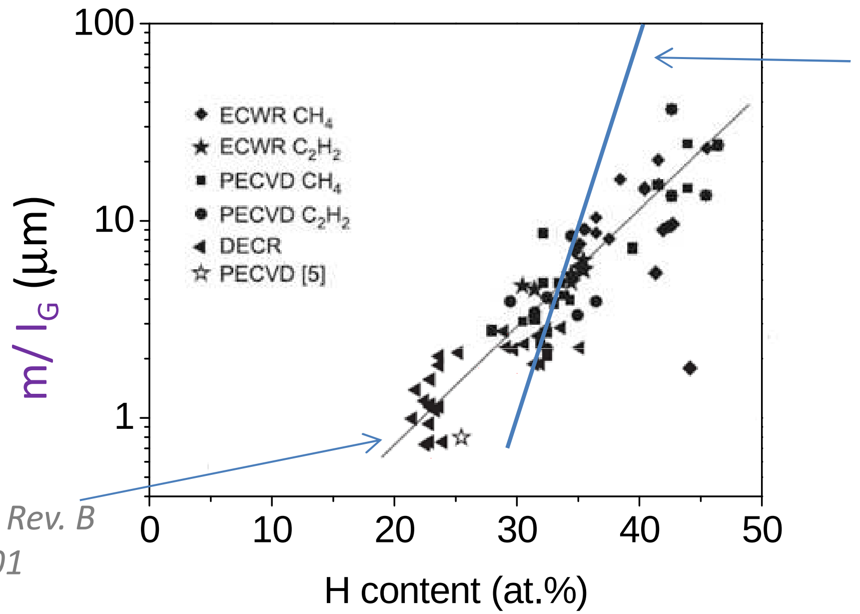




Photoluminescence background → Hydrogen content

Hydrogen content

For as-deposited a-C



Buijnsters et al, J. App. Phys. ***105*** *(2009) 093510*

Casiraghi et al, Phys. Rev. B ***72*** *(2005) 085401*

Modification of the band tail luminescence model of a-Si:H

→Radiative recombination occurs in sp^2 clusters

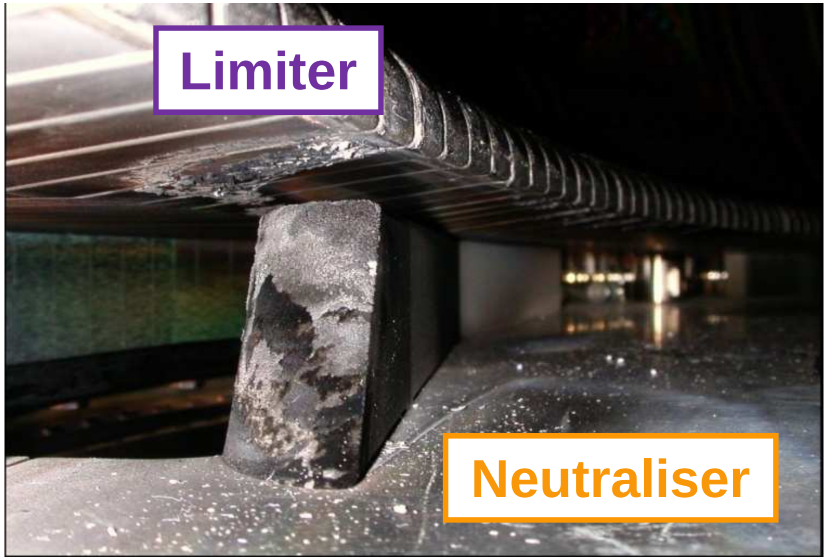
→Non radiative recombination centers are paramagnetic defects

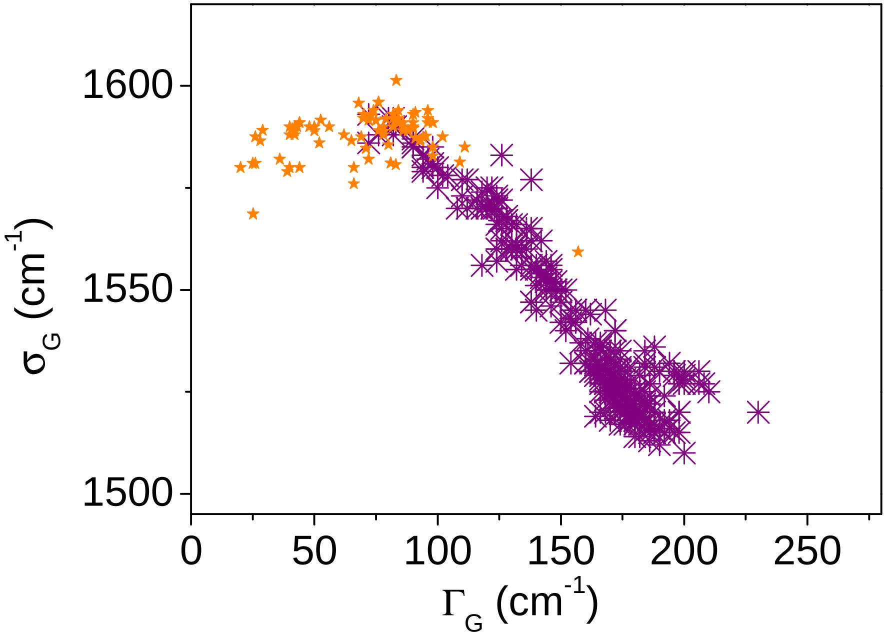
Robertson, Phys. Rev. B ***53*** *(1996) 16302*

IV - Results

→Raman spectroscopy of TS samples

Raman spectroscopy of Tore supra deposits





Neutraliser

↓

Nano-crystalline

Limiter

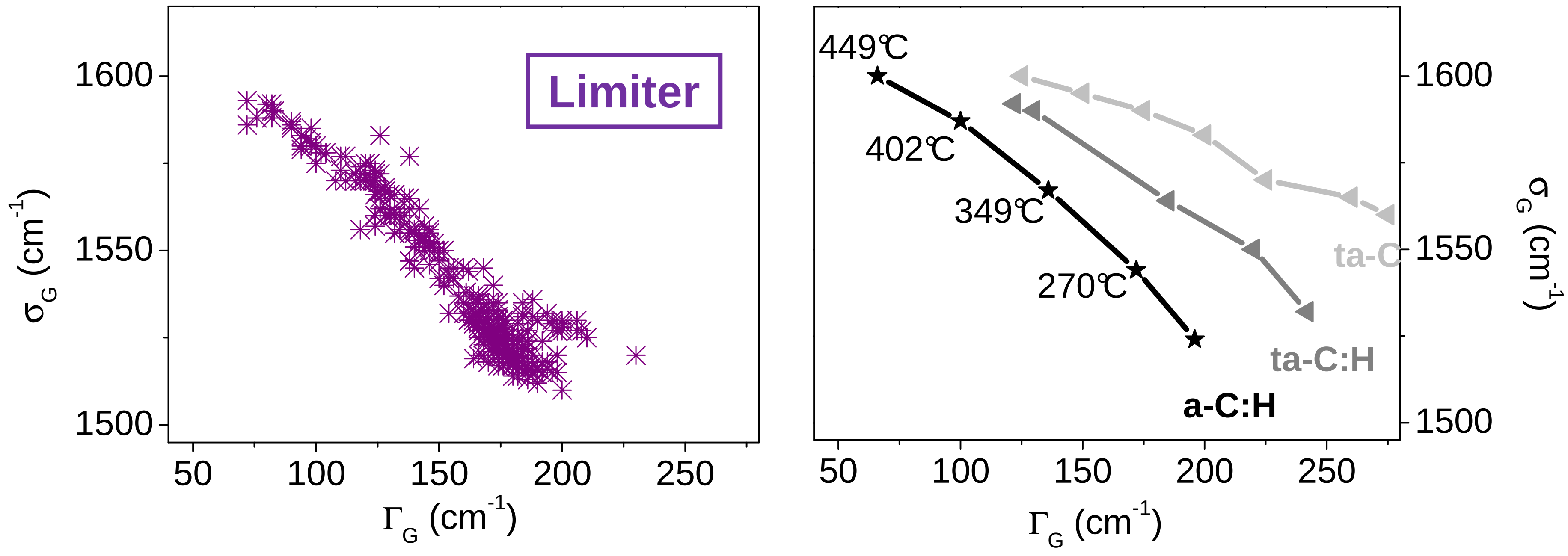
↓

Amorphous carbons

Heterogeneity on both Neutraliser and Limiter → Statistical treatment

Raman spectroscopy of Tore supra deposits

→Focus on the limiter

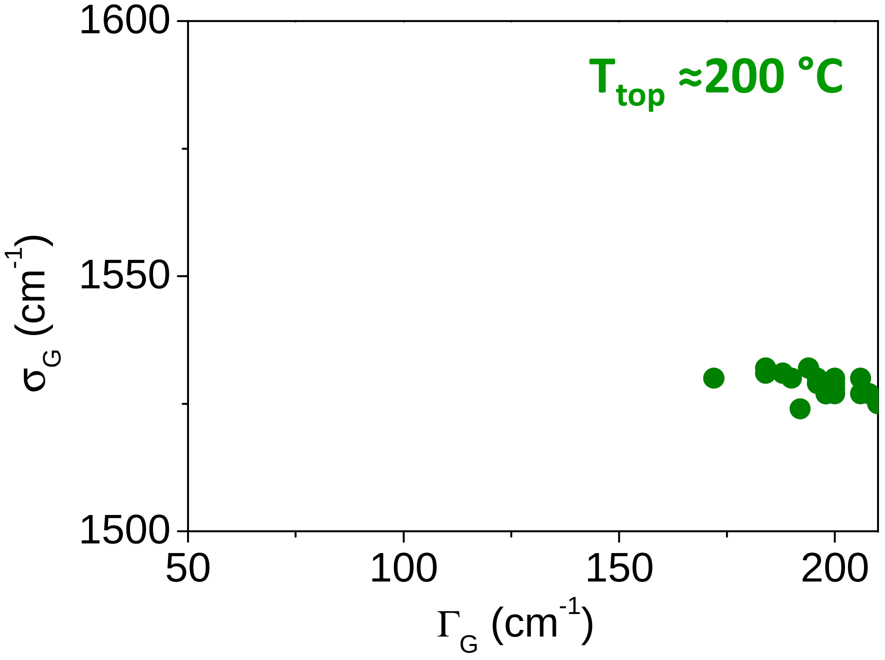


On the limiter : of « a-C:H type»
Local organization→ **Role of surface T ?**

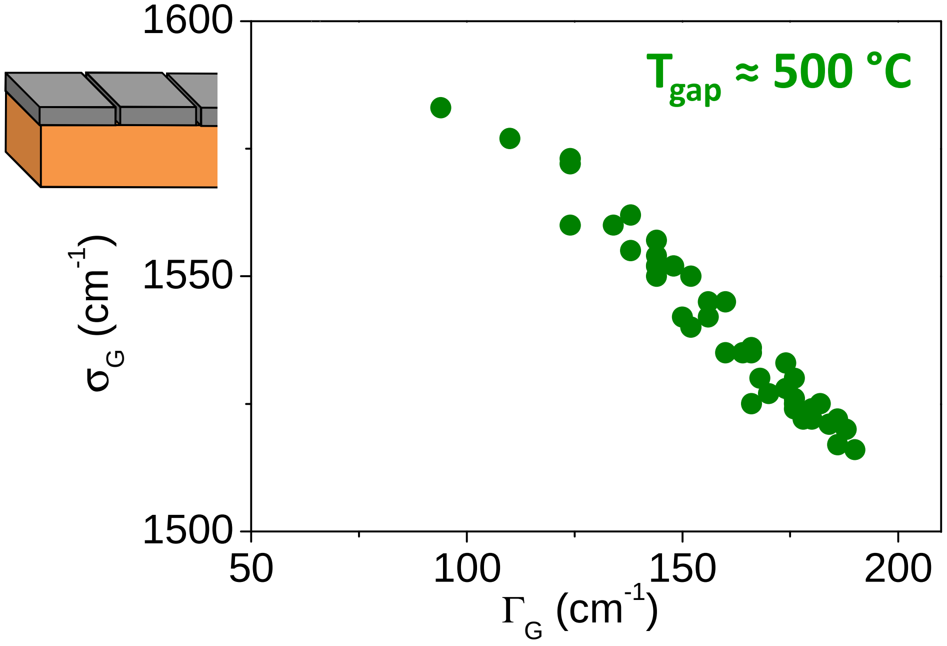
Raman spectroscopy of Tore supra deposits

Erosion zone

Top



Gap



Homogeneous structure

Amorphous

Inhomogeneous structure

Local organization

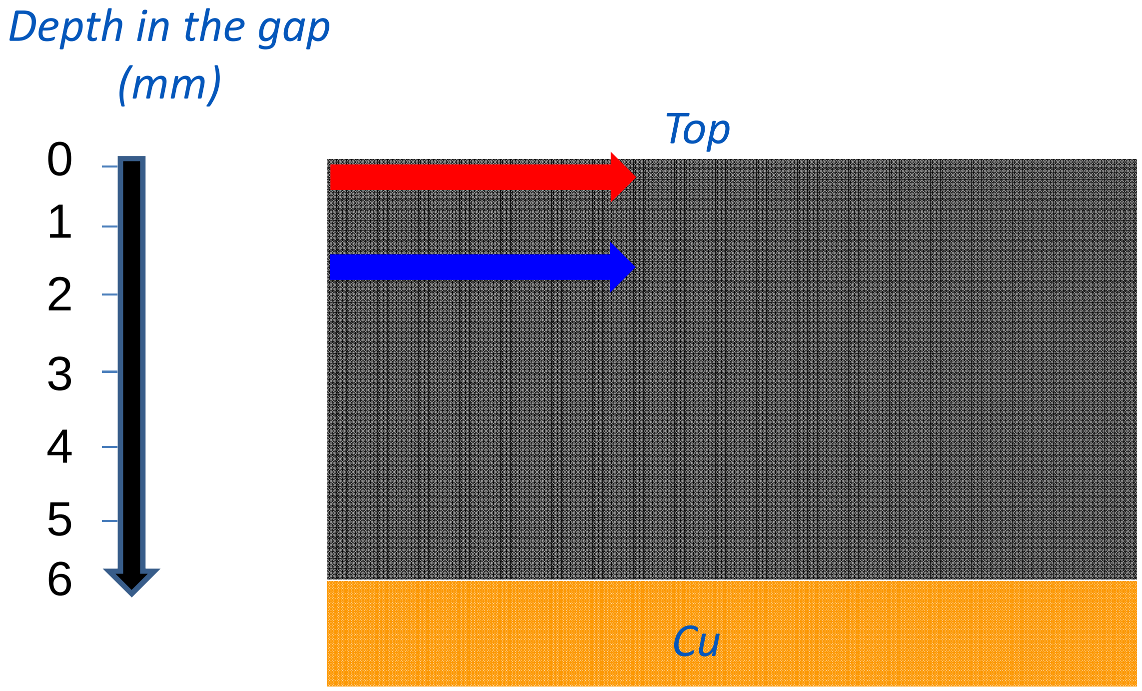
Top bombarded

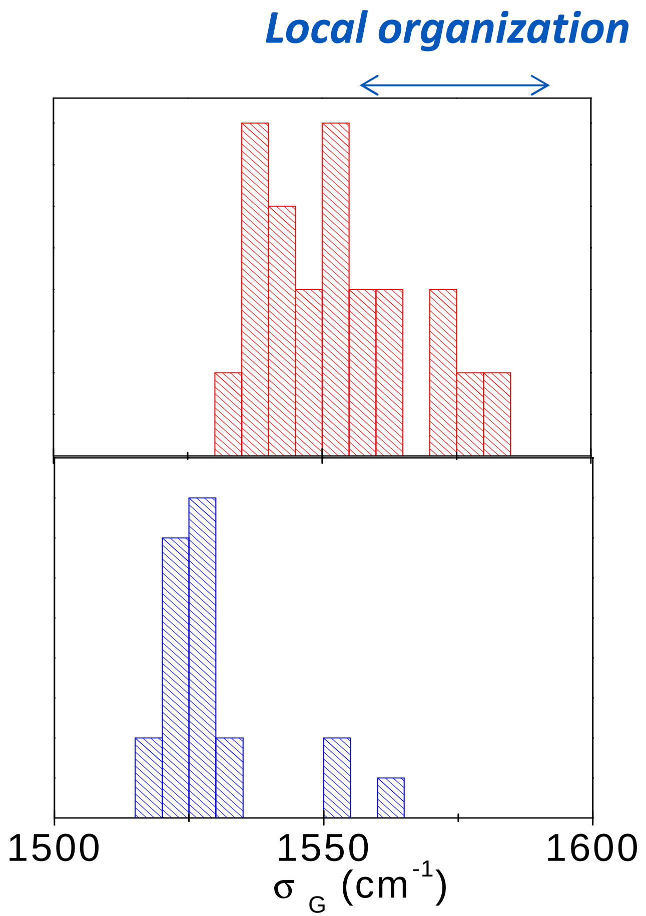
→ C/C amorphised

Deposit

Raman spectroscopy of Tore supra deposits

Erosion zone

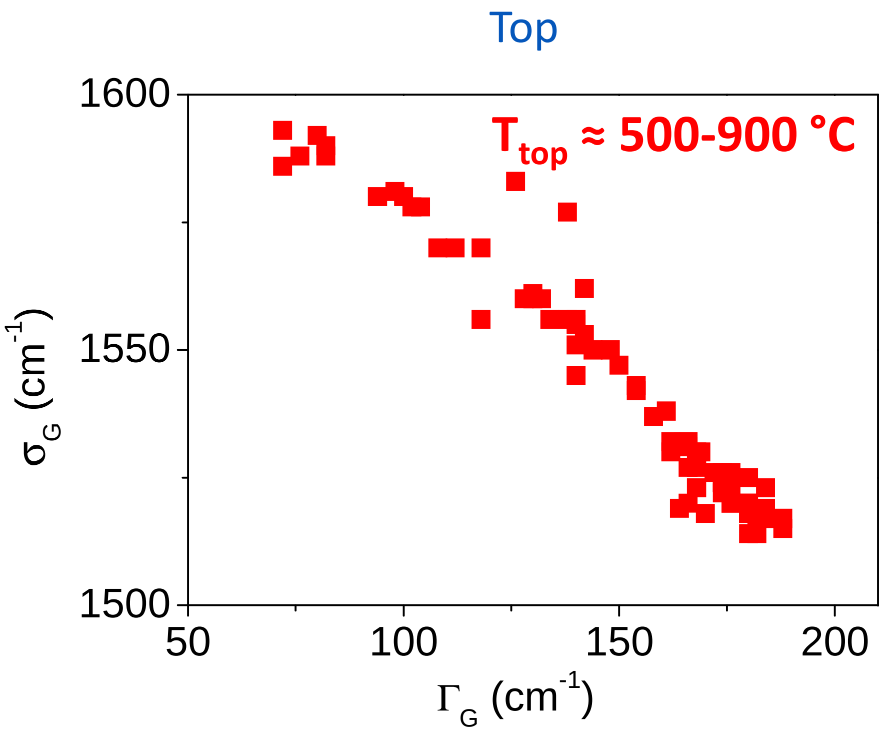


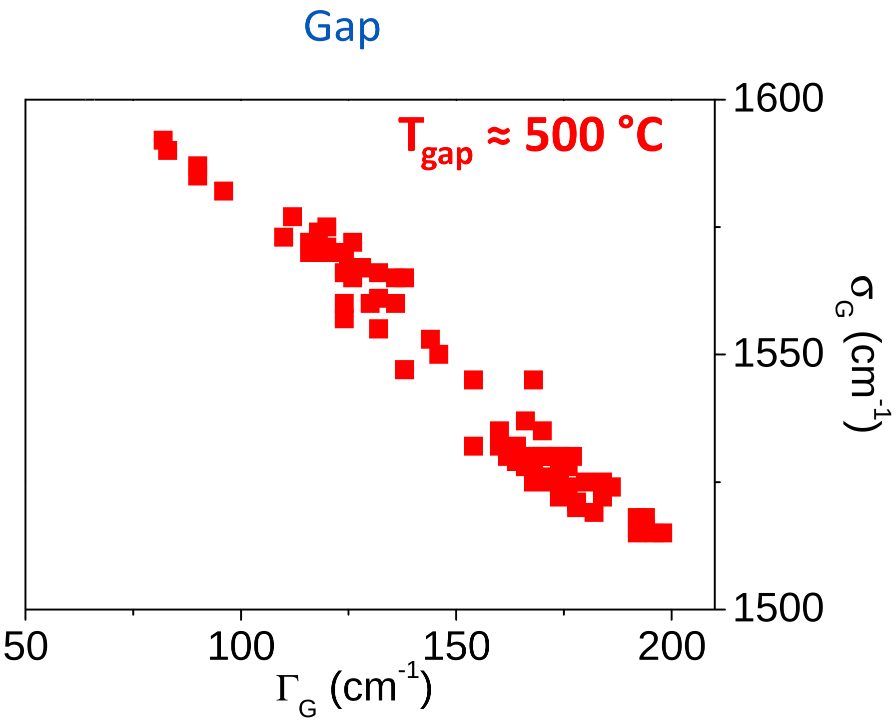


Thermal gradient in the gap

Raman spectroscopy of Tore supra deposits

Thick deposit zone





Inhomogeneous structure

Local organization

Inhomogeneous structure

Local organization

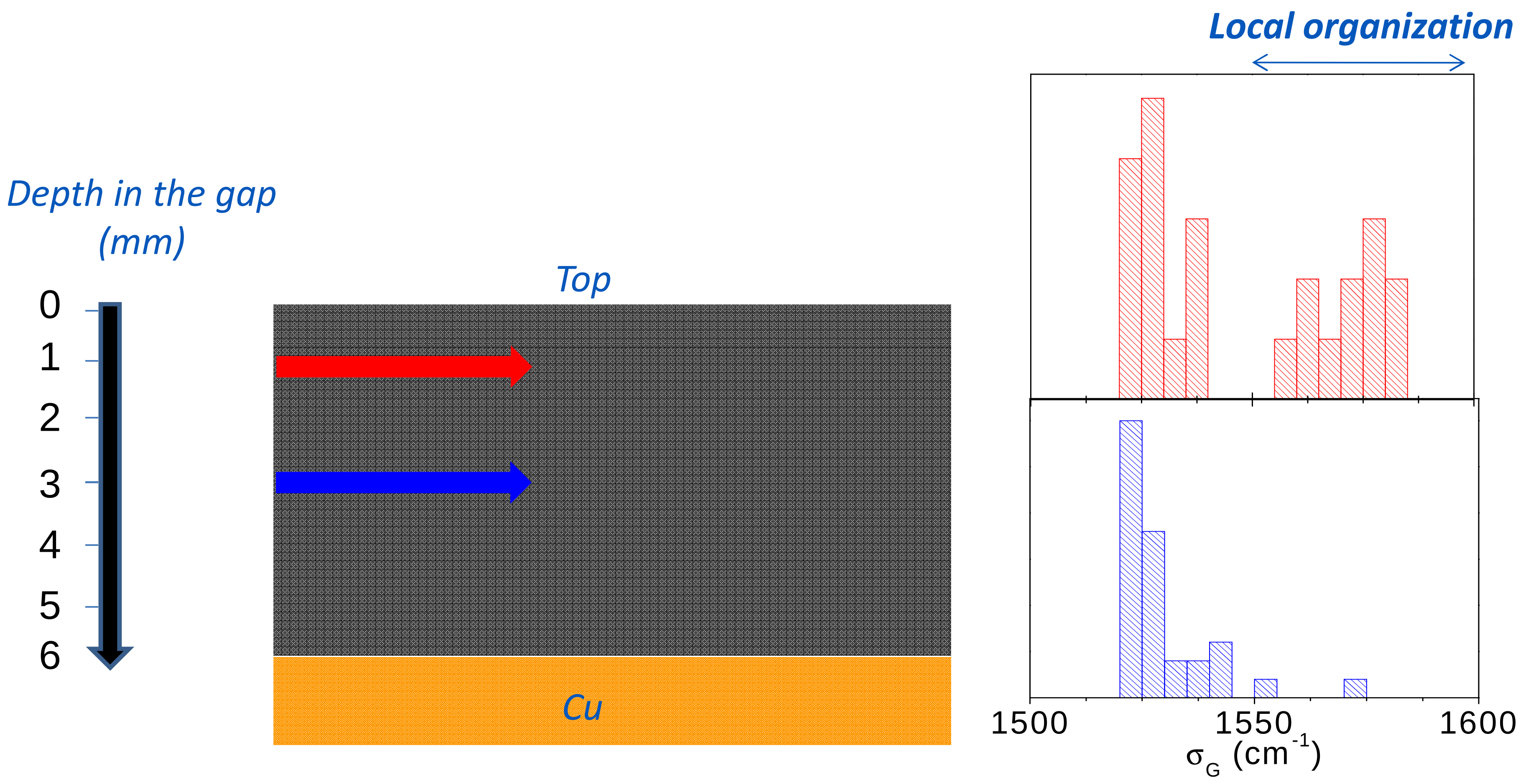
Caused by: →**Surface temperature inhomogeneity?**

→ **Precursor and/or ion energy?**

Tamor et al., J. Appl. Phys. 76 (1994) 3823

Raman spectroscopy of Tore supra deposits

Thick deposit zone

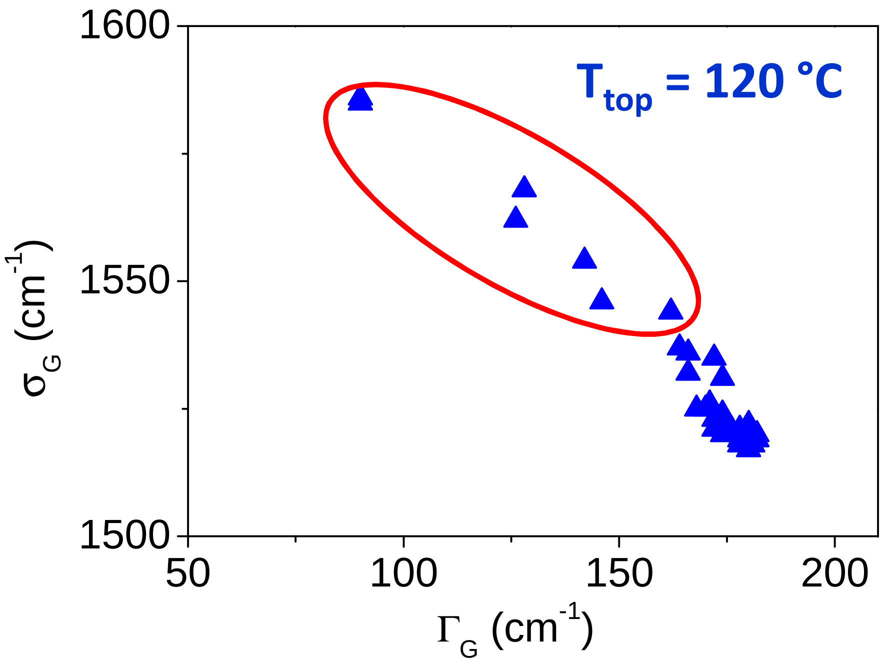


Thermal gradient in the gap

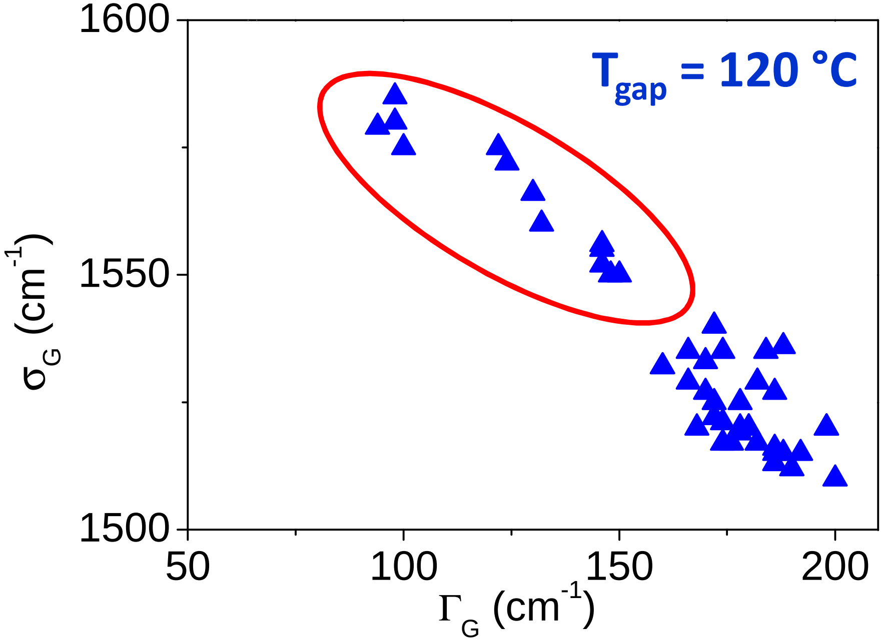
Raman spectroscopy of Tore supra deposits

Thin deposit zone

Top



Gap



Inhomogeneous structure

Inhomogeneous structure

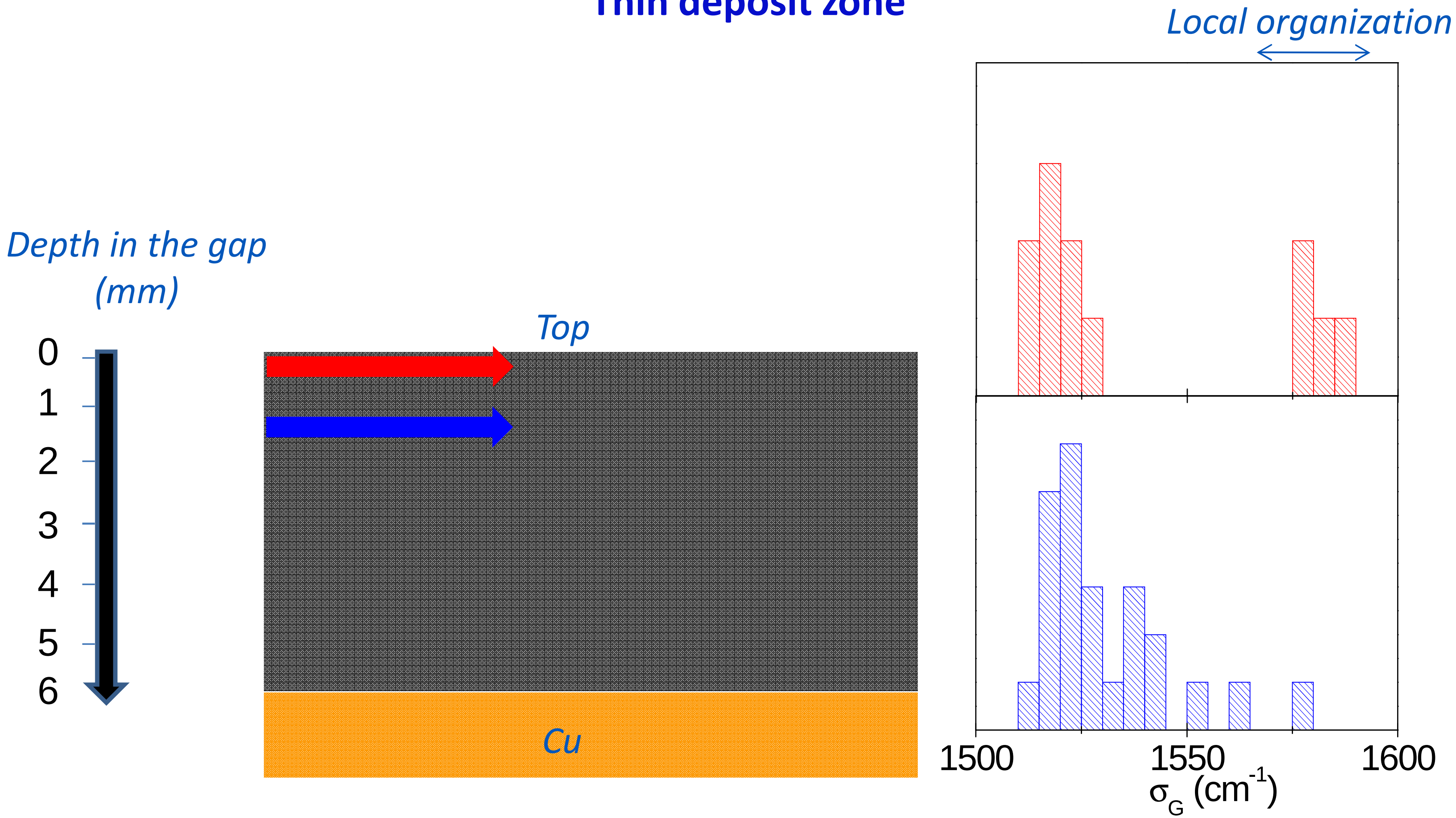
Local organization even if T=120°C

→ Precursor local organisation or ion energy influence ?

Tamor et al., J. Appl. Phys. 76 (1994) 3823

Raman spectroscopy of Tore supra deposits

Thin deposit zone

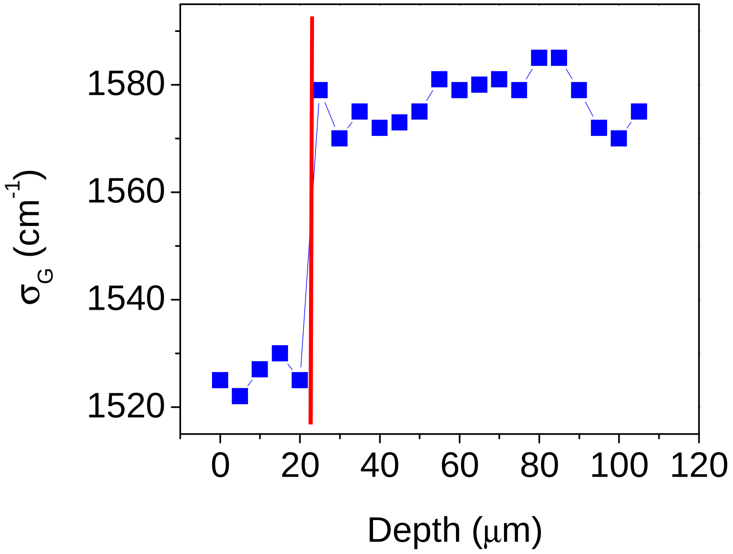


→ Precursor local organisation or ion energy influence ?

Raman spectroscopy of Tore supra deposits

Thin deposit zone: In-depth profile

20 µm ≈ 1 hour of plasma



→ Structural changes

Consistent with NRA
Showing a D-diminution in depth

Dittmar *et al.*, Physica Scripta (2009)
Dittmar *et al.*, J. Nucl. Mater (2010)

Even at T=120°C
→ Slow processes leading to H-loss

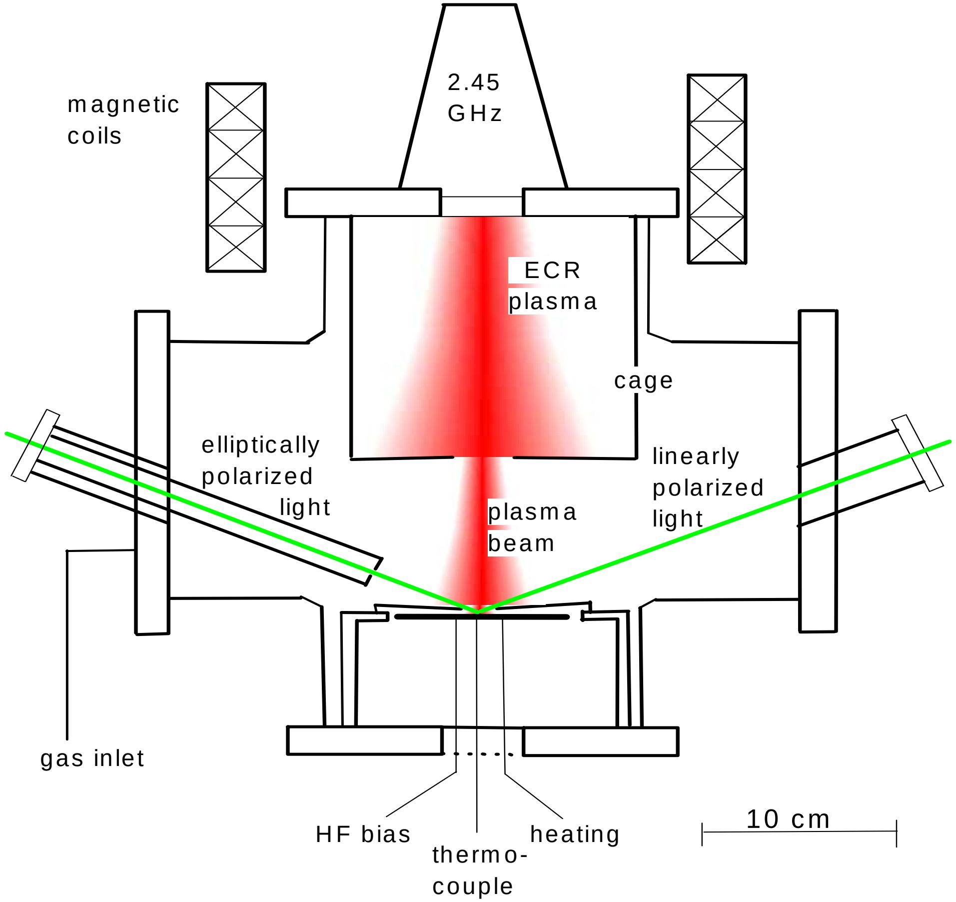
IV - Results

→Raman spectroscopy of TS samples

→Raman spectroscopy of « well known » a-C:H
→Kinetic effect and slow H-release

→Comparative study

Hydrogenated amorphous carbons



Plasma deposited

- Precursor: CH_4
- On silicon wafer
- e ≈ 200 nm
- 1.7-1.9 $g.cm^{-3}$
- E_{ions}≈100-300 eV
- H/H+C ≈ 30-40% (NRA)

A. von Keudell and W. Jacob, Journal of Applied Physics 79, 1092–1098 (1996)
B. Landkammer, A. von Keudell, and W. Jacob, Journal of Nuclear Materials 264, 48–55 (1999)

a-C:H growth

Plasma

H

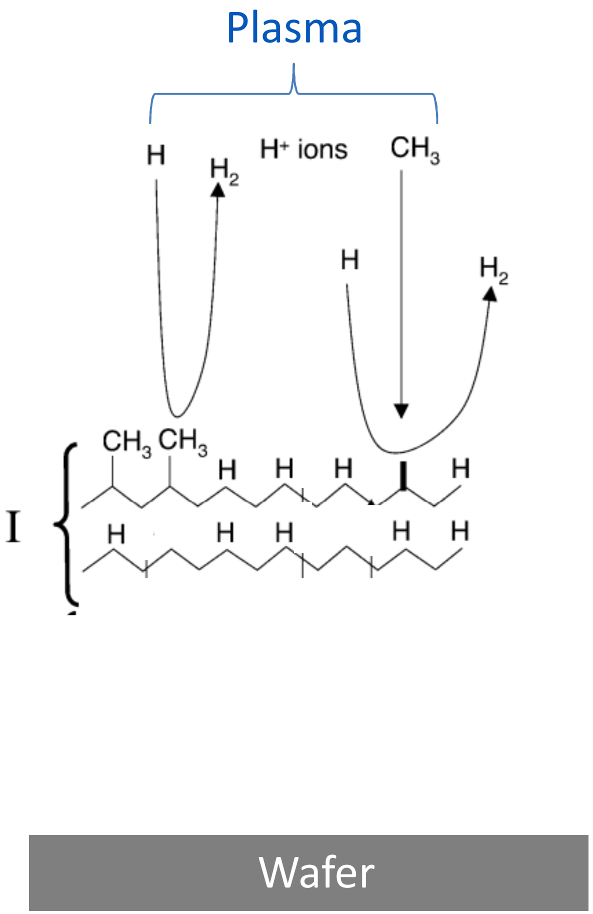
H^+ ions

CH_3

Wafer

Von Keudell, M. Meier, C. Hopf, Diamond and Related Materials 11 (2002) 969

a-C:H growth

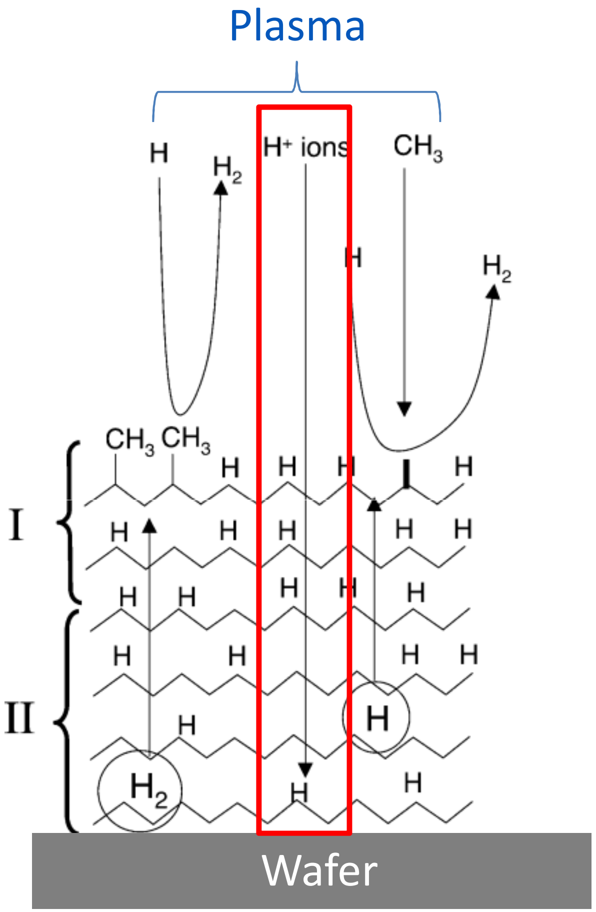


Chemistry dominated growth zone (≈2 nm)

- Incident atomic H governs the surface activation

Von Keudell, M. Meier, C. Hopf, Diamond and Related Materials 11 (2002) 969

a-C:H growth



Chemistry dominated growth zone (≈2 nm)

- Incident atomic H governs the surface activation

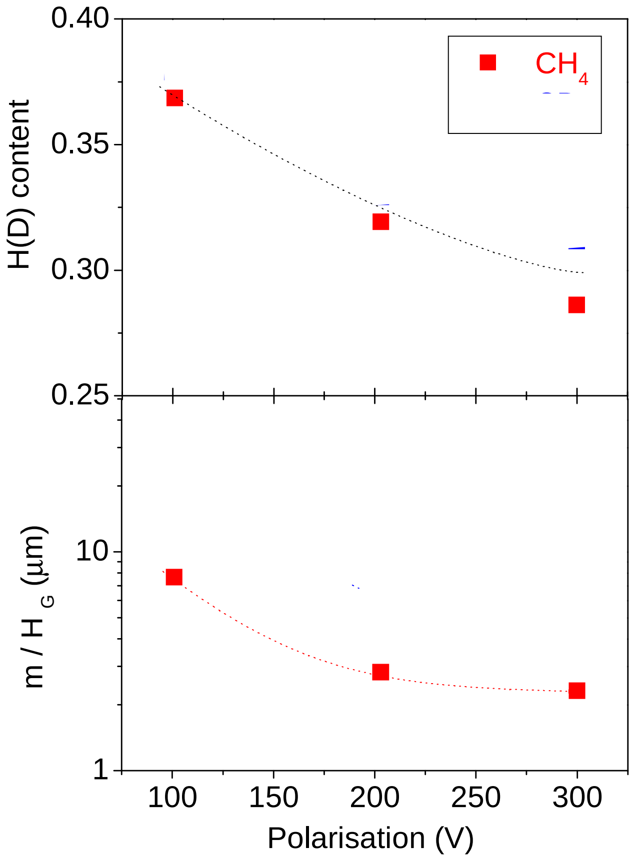
Ion-dominated zone

-H^+ implantation → bonding in the film

-Displaced H atoms can recombine to form H_2

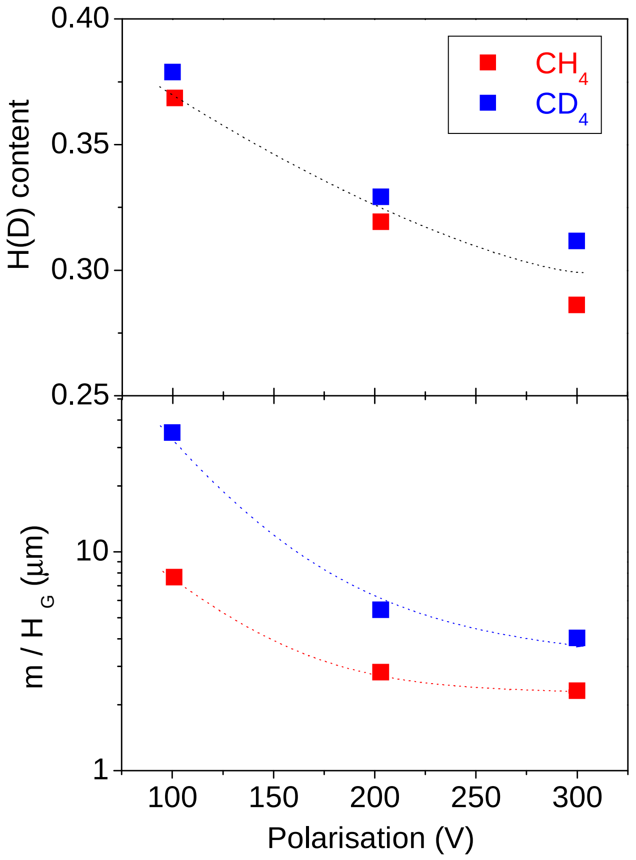
Von Keudell, M. Meier, C. Hopf, Diamond and Related Materials 11 (2002) 969

Defect density in the layer: isotopic effect



-H content decreases with polarisation

Defect density in the layer: isotopic effect



-H(D) content decreases with polarisation

- For a given polarisation: H and D content ≈

-m/H_G(D) > m/H_G (H)

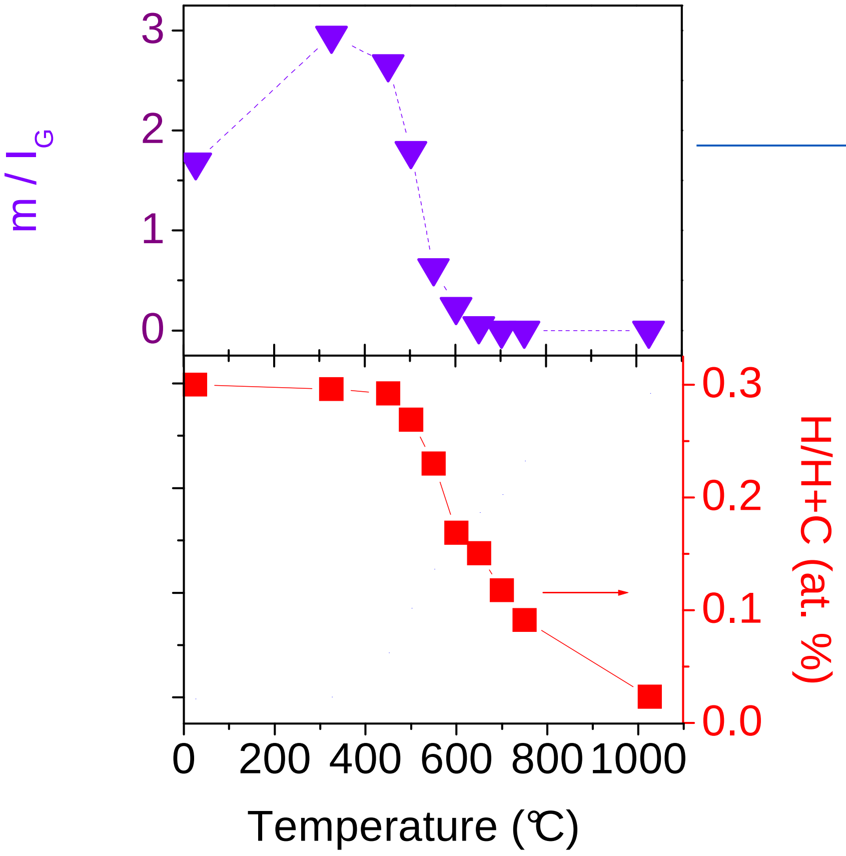
$$\left.\begin{aligned} P_H &= m_H V_H \\ P_D &= m_D V_D \\ E_H &= E_D \end{aligned}\right\} \frac{P_D}{P_H} = \sqrt{\frac{m_D}{m_H}} > 1$$

For the same ion kinetic energy, D produces more defects than H

→ **m/H_G also depends on the number of defects**

Heat treated a-C:H

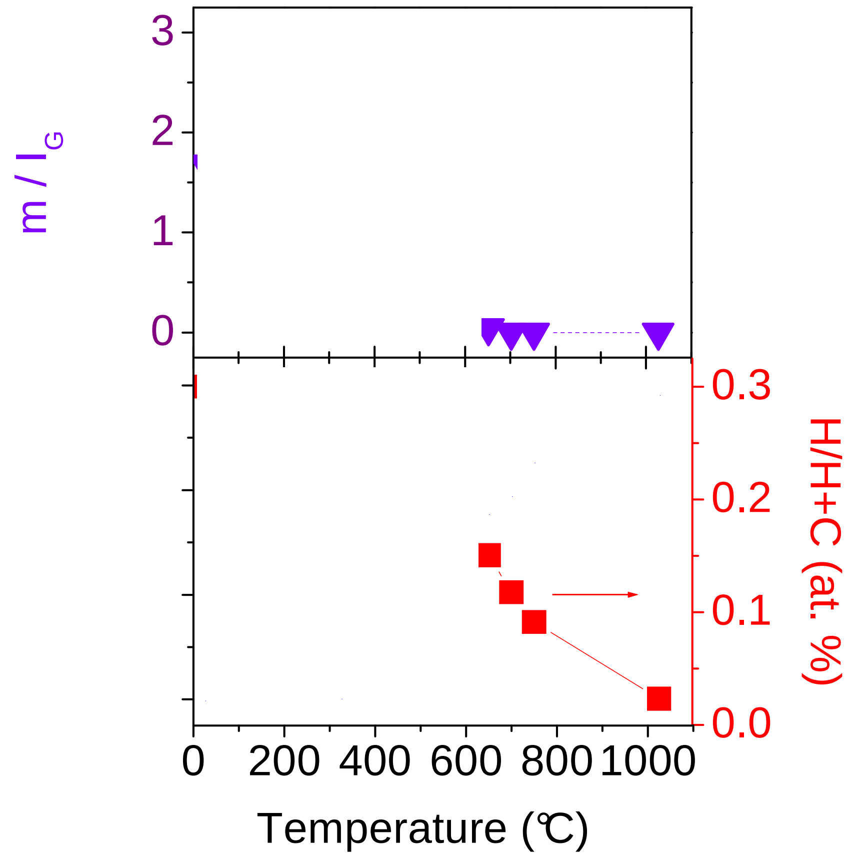
Under UHV conditions
(≈45 min)



→ *Post-mortem* Raman measurment

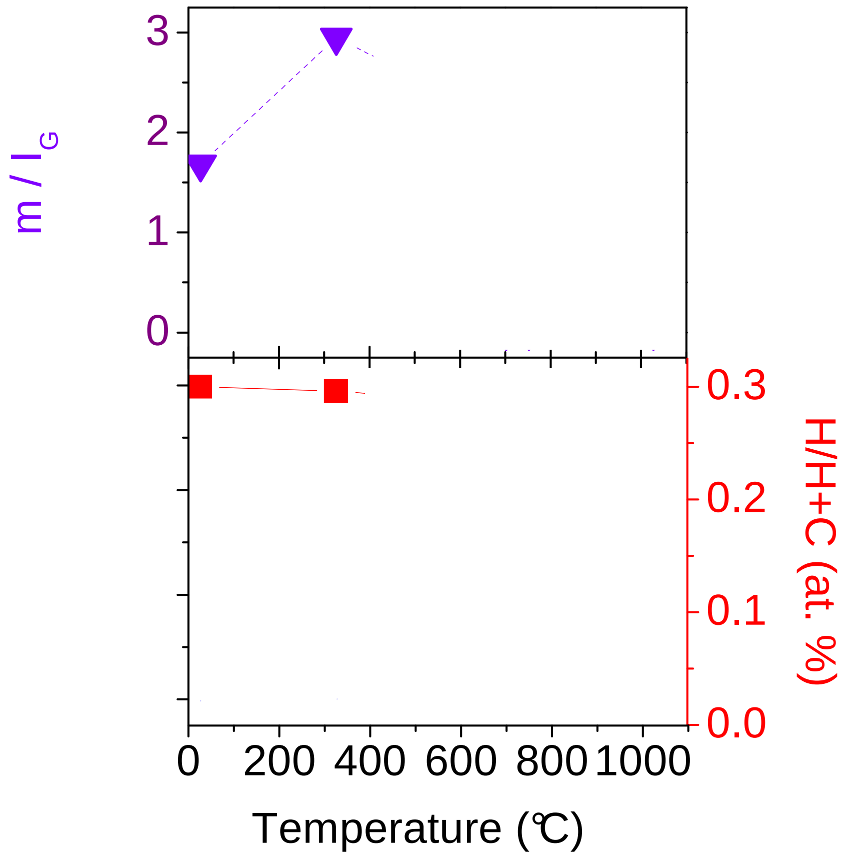
→ Determined by ion beam analysis

Heat treated a-C:H



- m/I_G not sensitive if H/H+C<10-15 %

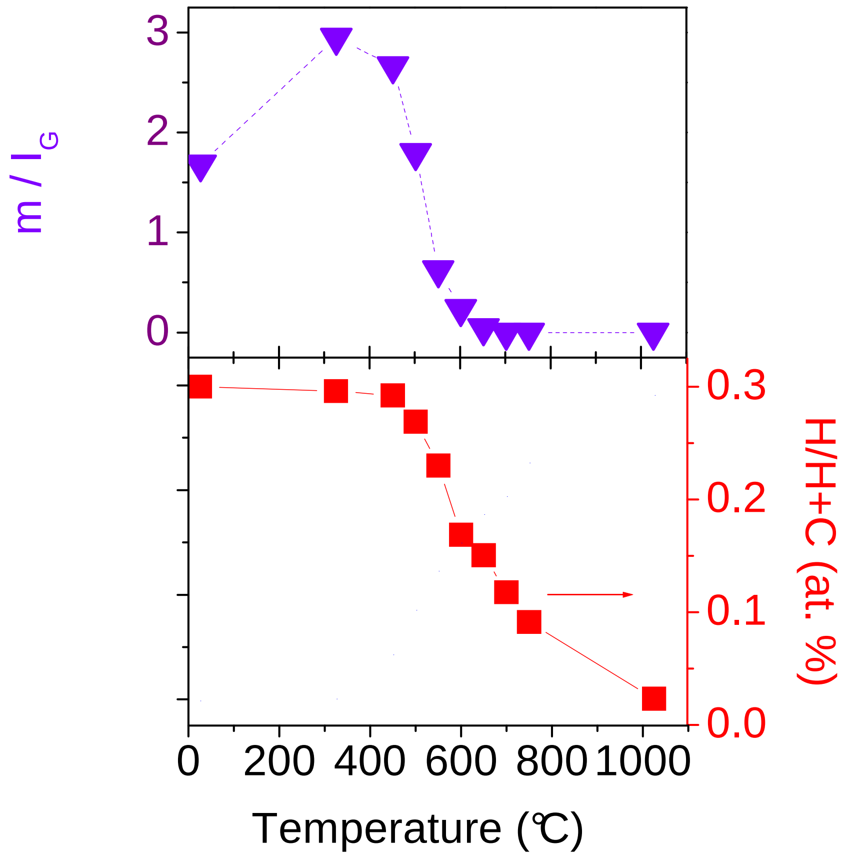
Heat treated a-C:H

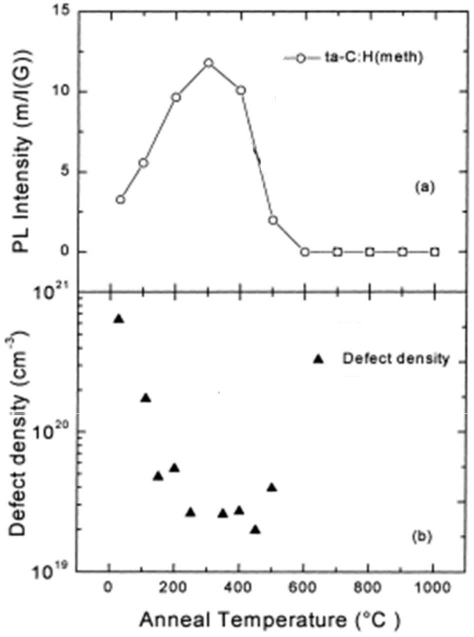


- m/I_G not sensitive if H/H+C<10-15 %
- m/I_G vary whereas H/H+C is constant

Is m/I_G still relevant ?

Heat treated a-C:H





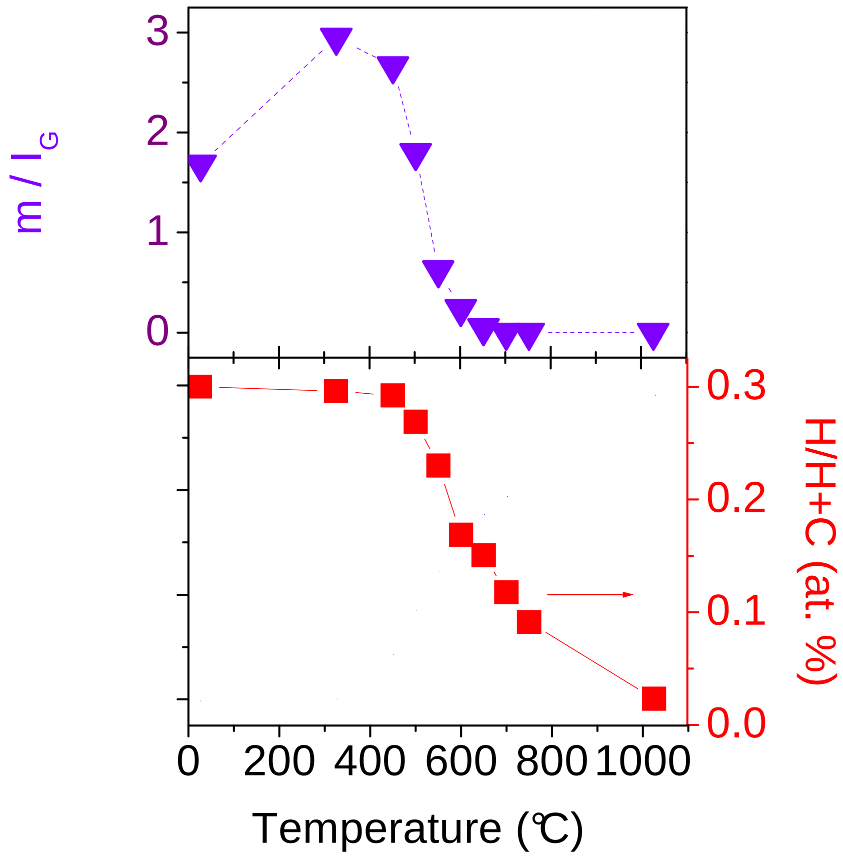
Conway *et al*,
Diamond Relat. Mater.
9, 765 (2000)

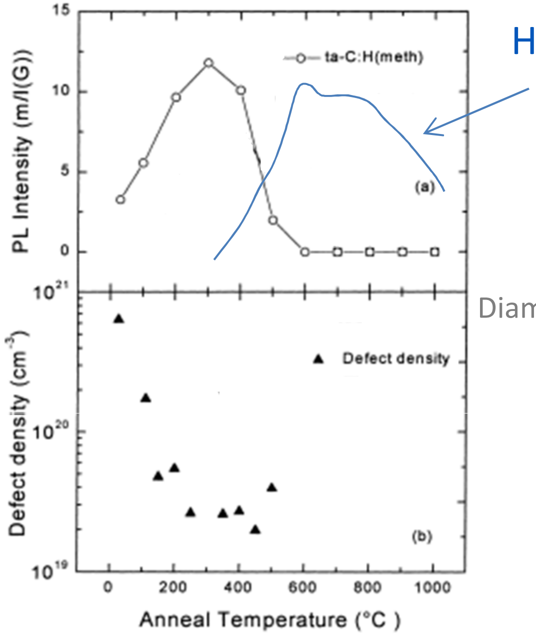
Non radiative recombination centers passivated by hydrogen migration under heat treatment

Photoluminescence is quenched for as deposited samples

→2nd experimental evidence of the m/H$_G$ defects dependency

Heat treated a-C:H





H_2 mass signal
(log scale)

Conway *et al*,
Diamond Relat. Mater.
9, 765 (2000)

Non radiative recombination centers passivated by hydrogen migration under heat treatment

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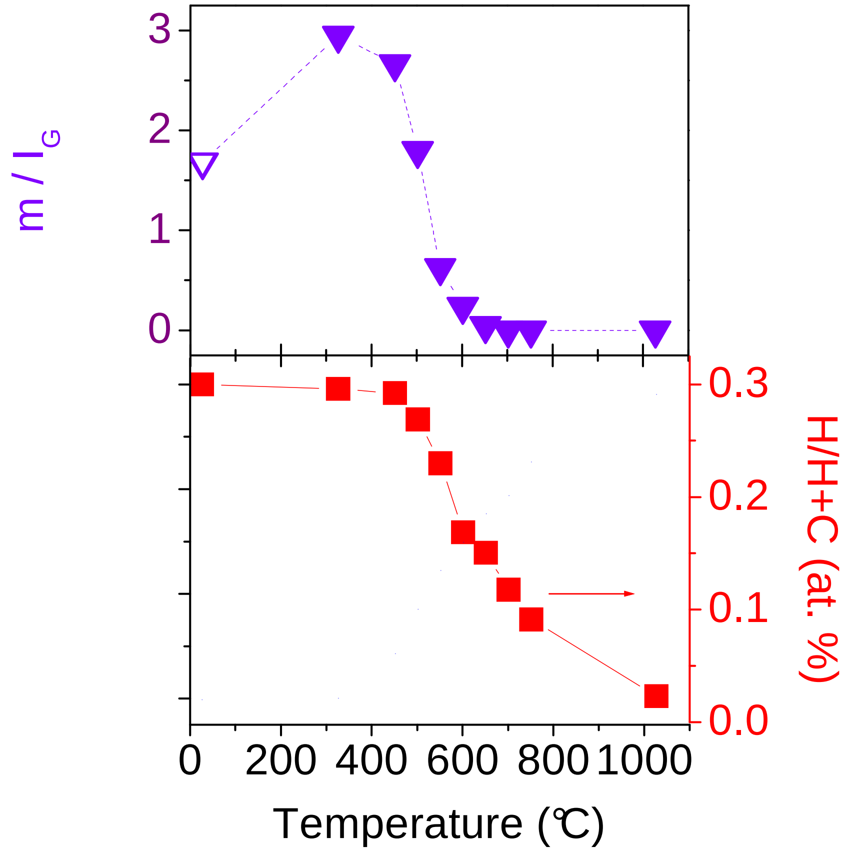
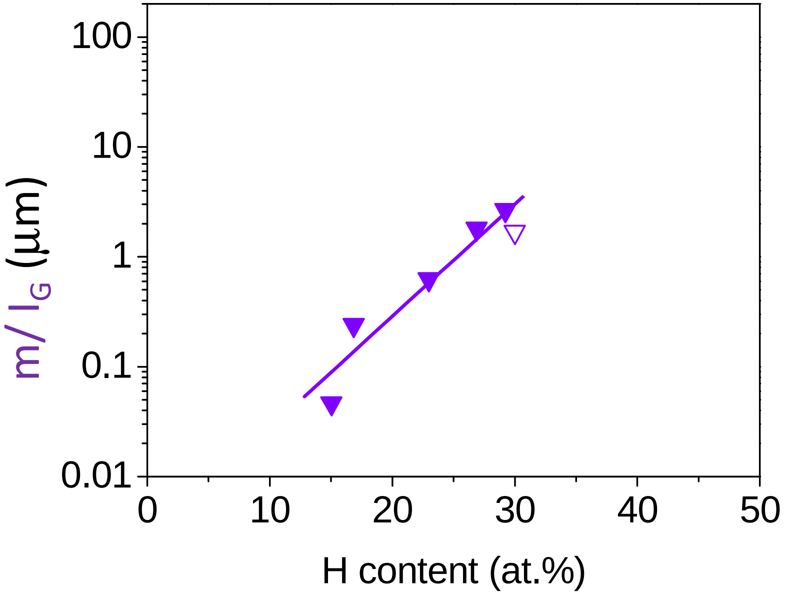
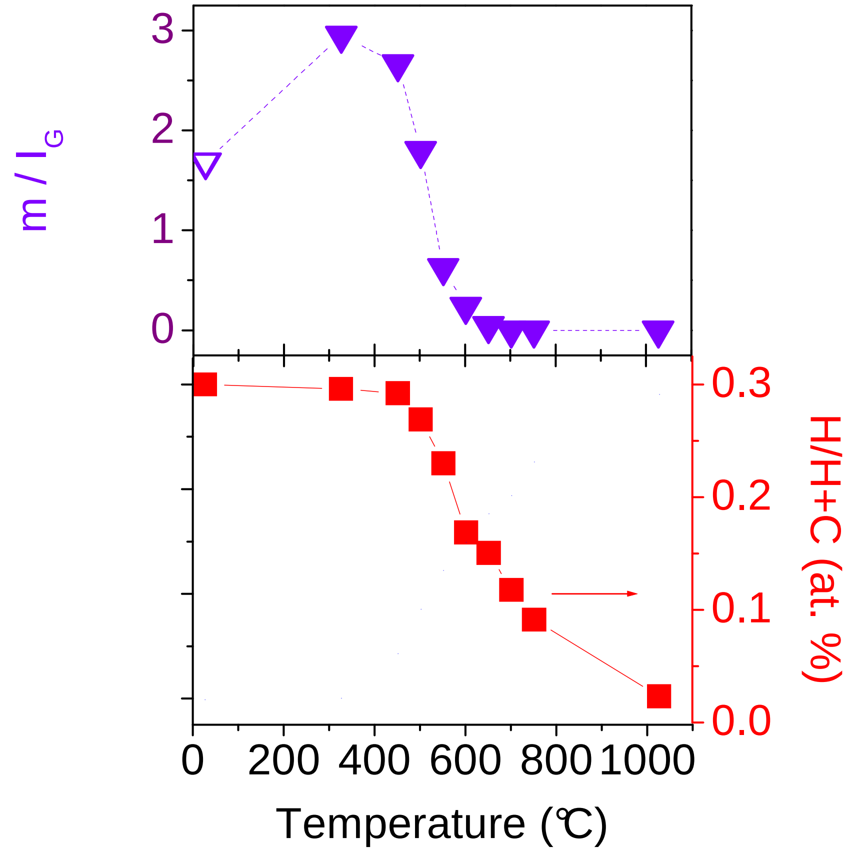
Heat treated a-C:H

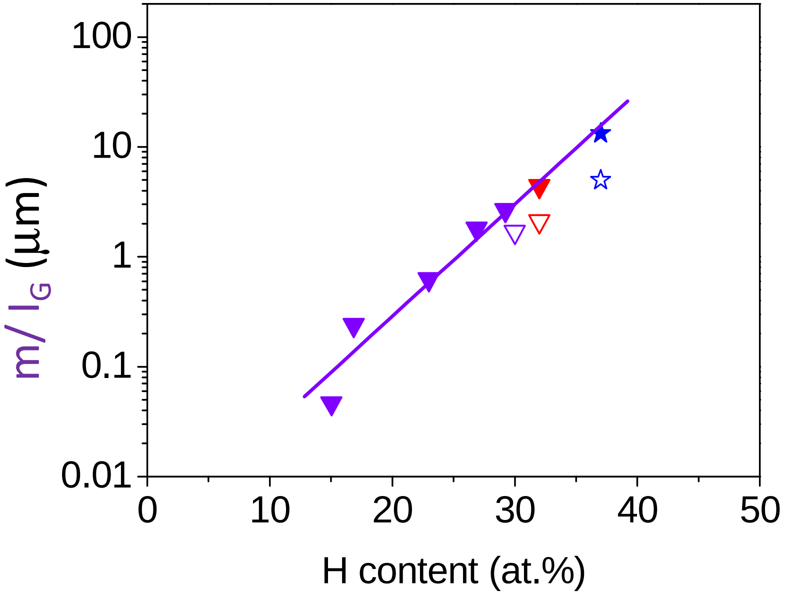




Linear dependency

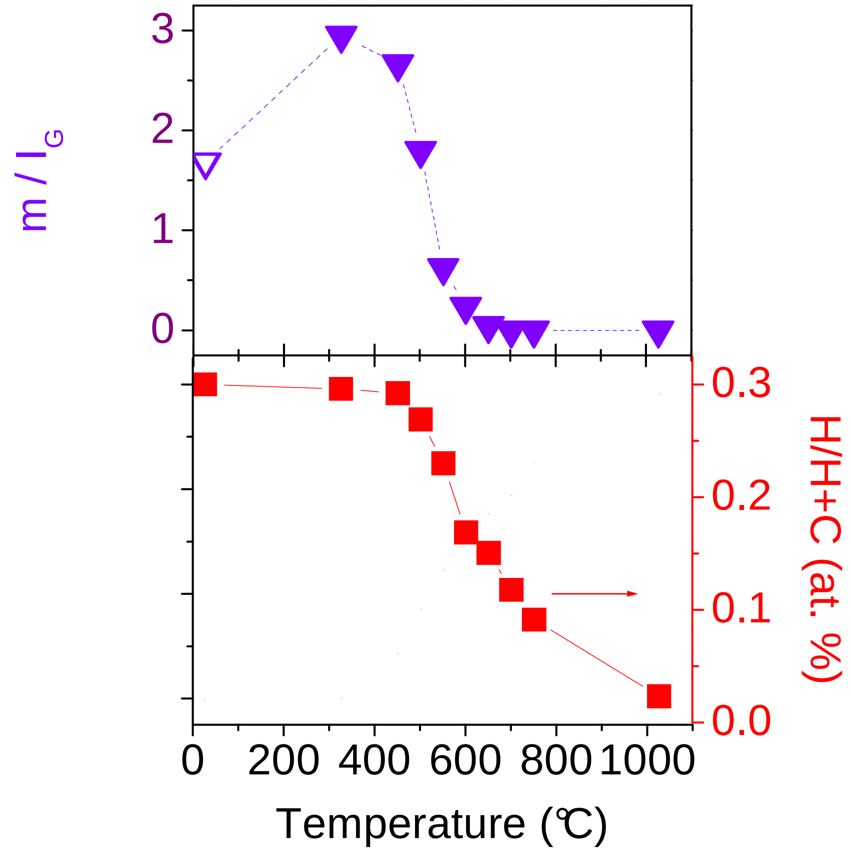
Heat treated a-C:H

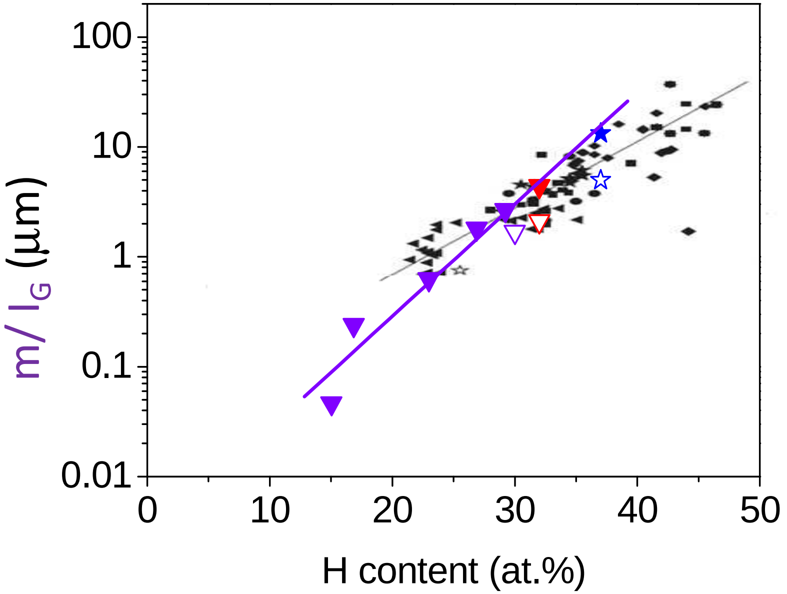




Linear dependency

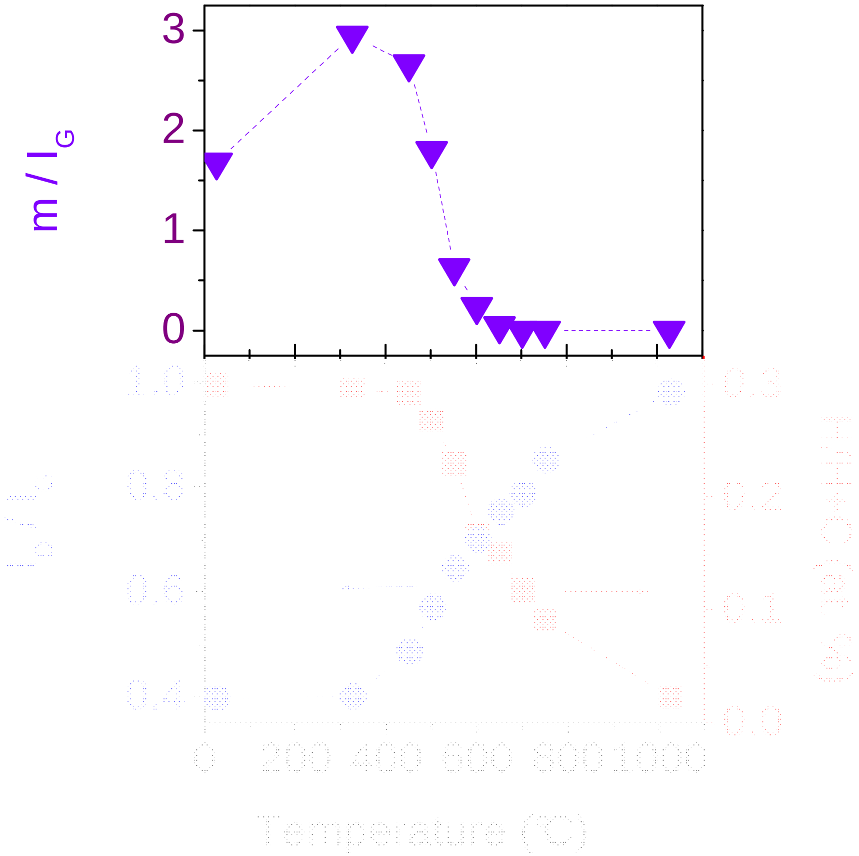
Heat treated a-C:H





Linear dependency even with HT a-C:H
Less dispersed relation

Heat treated a-C:H



- I_D/I_G vary <u>linearly</u> with H/H+C
- I_D/I_G sensitive even if H/H+C ≈ 2 %

→ I_D/I_G as an H content estimator

But…

→ Was known to give information on local order

IV - Results

→Raman spectroscopy of TS samples

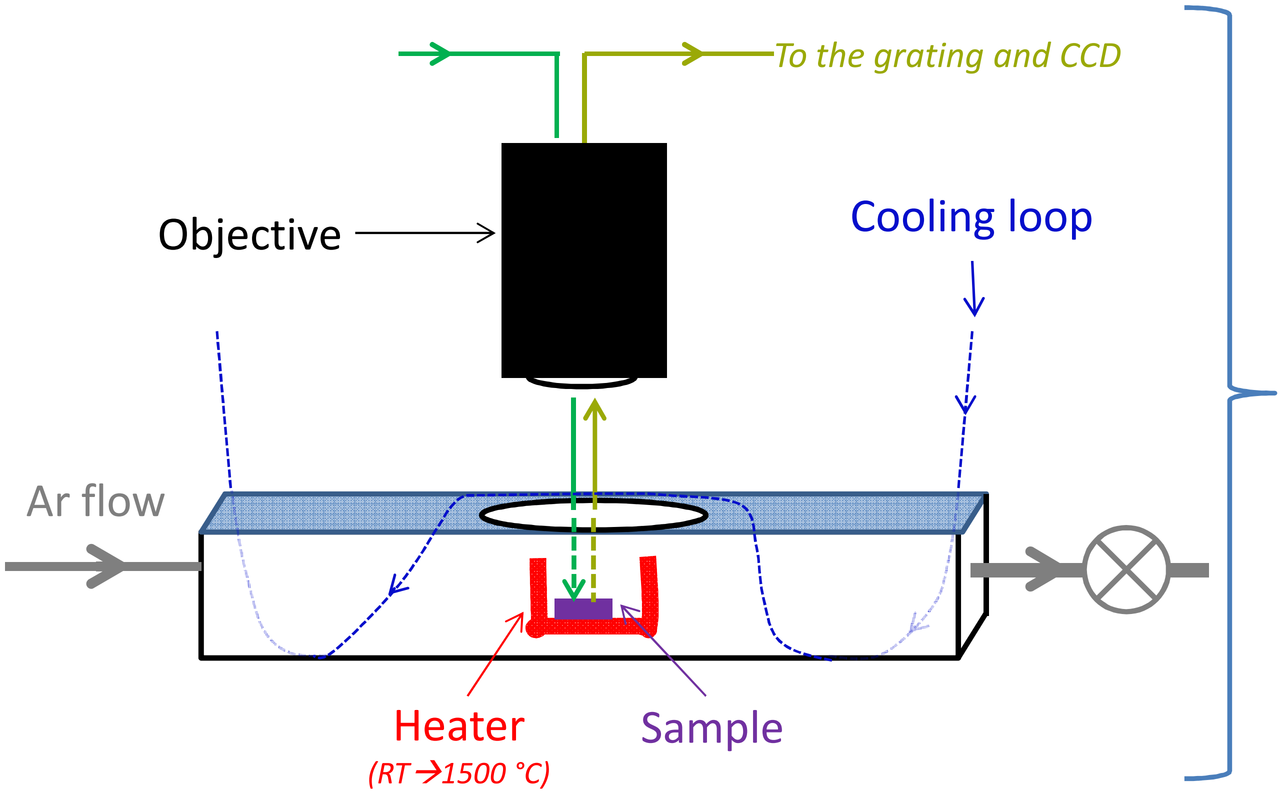
→Raman spectroscopy of « well known » a-C:H
→Kinetic effect and slow H-release

→Comparative study

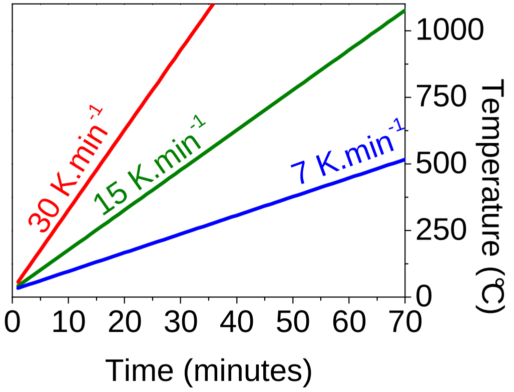
Kinetic effects

Kinetic

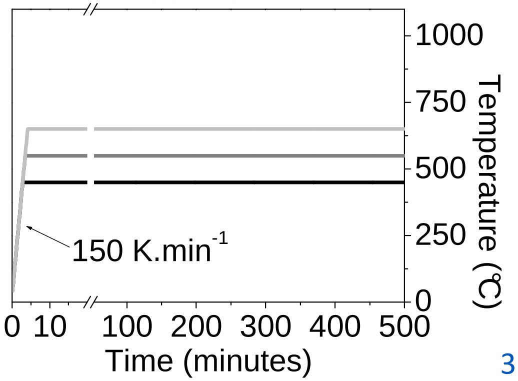
In-situ Raman measurement under Ar atmosphere



Linear variation



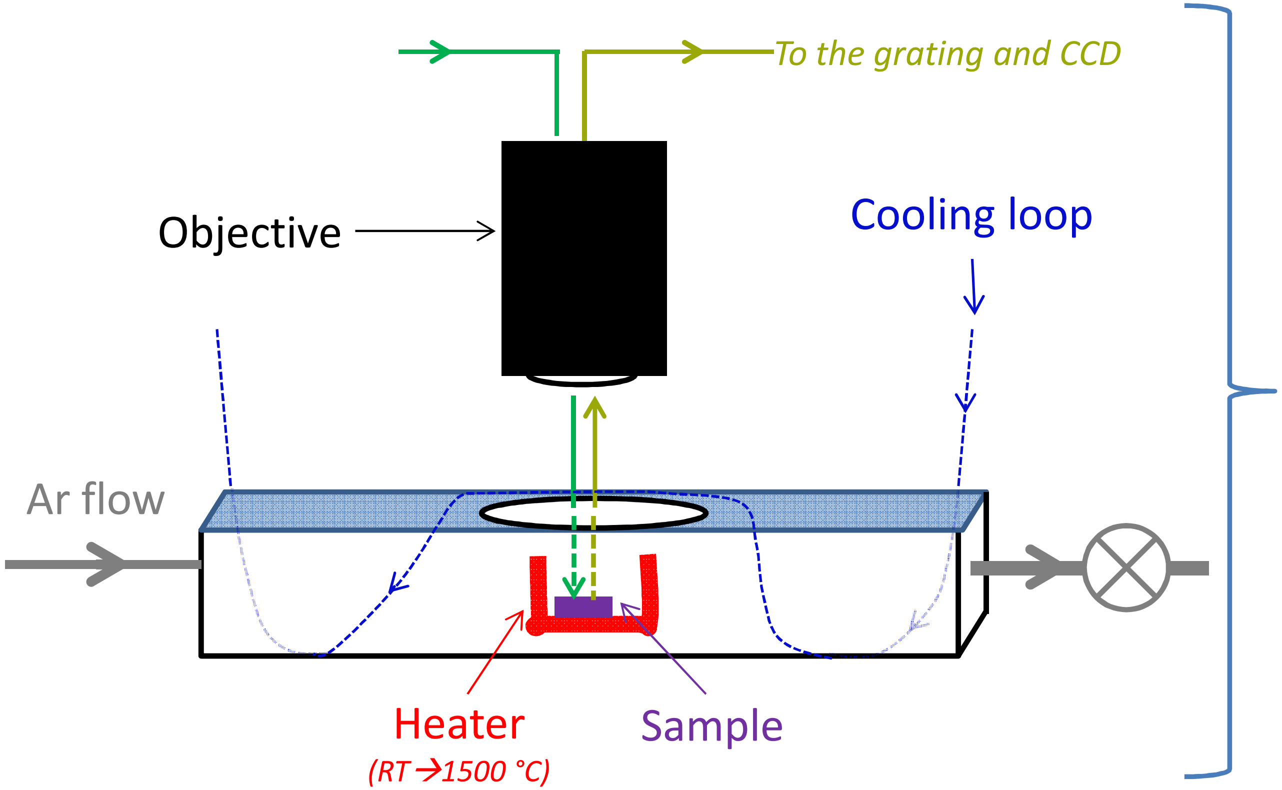
Isotherm



Kinetic effects

Kinetic

In-situ Raman measurement
under Ar atmosphere



To the grating and CCD

Objective

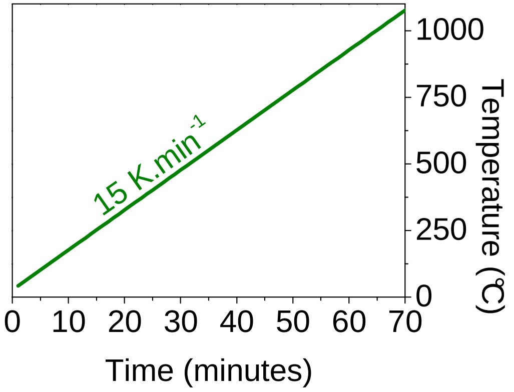
Cooling loop

Ar flow

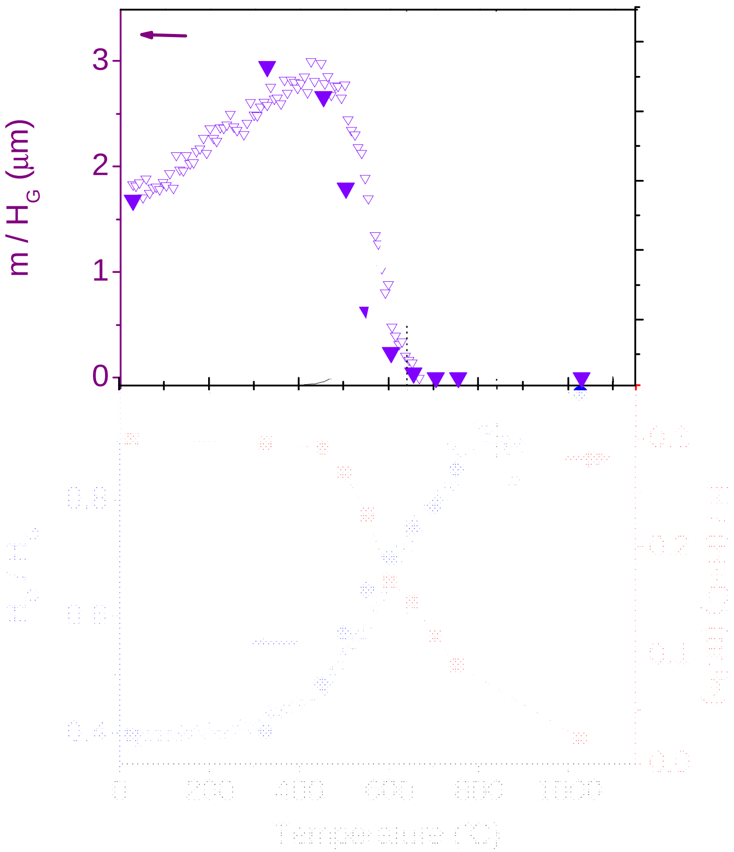
Heater
(RT→1500 °C)

Sample

Linear variation



Kinetic effects



-**Full symbol:**
→*post-mortem* measurement in UHV condition

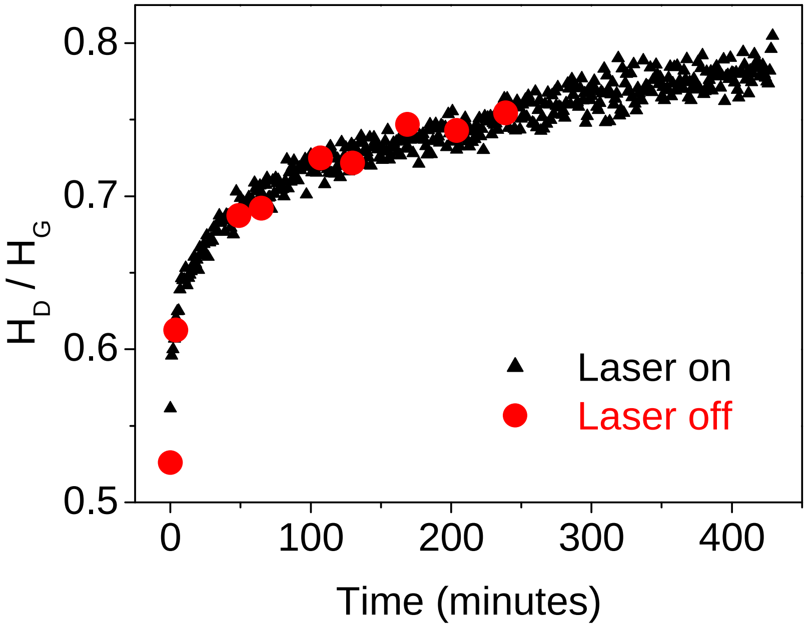
- **Empty symbols:**
→*in-situ* measurements in Ar flow

-UHV and Ar flow measurments give similar thermal evolution

Kinetic effects

Kinetic: isotherm

In-situ Raman measurment
under Ar atmosphere
At **550°C**



No effect of the power LASER on slow H-loss
As H_D/H_G proportional to the H content:→ Linear H-loss observed!

As most of the results in this presentation have not been published yet,
they have not been joined to the GDR website.

However, you can ask for them at:

cedric.pardanaud@univ-provence.fr