Effect of Atomic H on a-C:H surfaces

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Workshop ARCHES - 27/10/2008

OUTLINE

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- ► DECR deposition process of a:CH films
- ► H atoms – a:CH film interaction
    - 1- Experimental set-up
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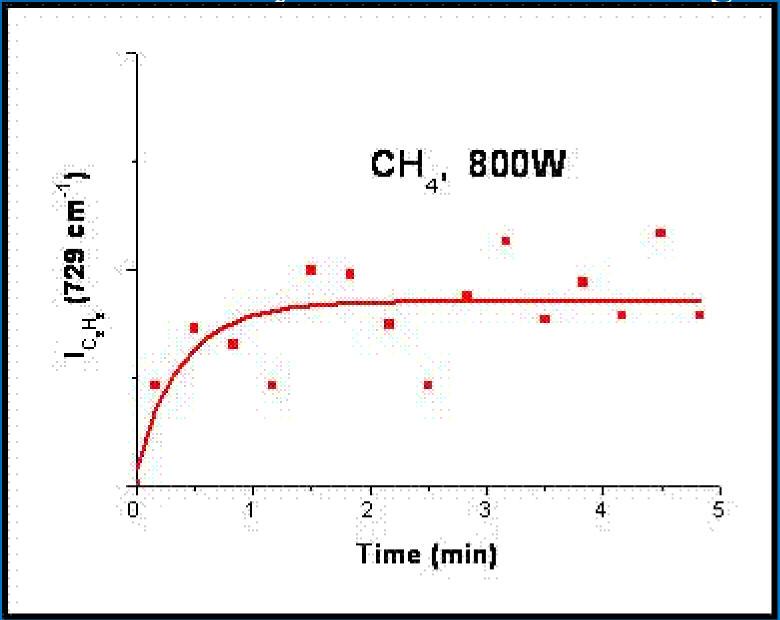
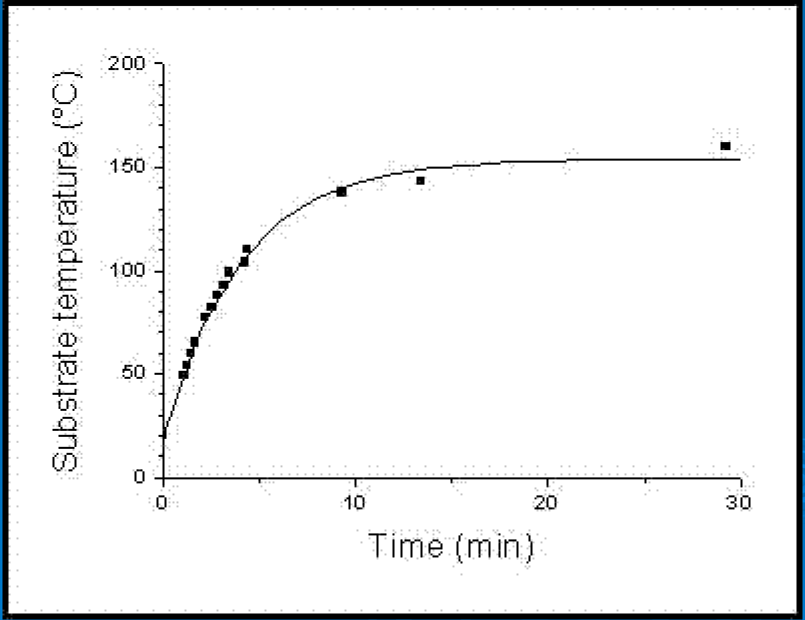
    - 4- H interaction with H rich a:CH
- ► Back to DECR process
- ► Conclusion

INTRODUCTION

- **Formation of C_2H_2 molecules in CH_4 DECR plasmas.**
- **Mean free path of neutral species >> dimension of the reactor.**
  - ⇒ Acetylene formed on the reactor walls.
  - ⇒ Acetylene formed due to high wall temperature.



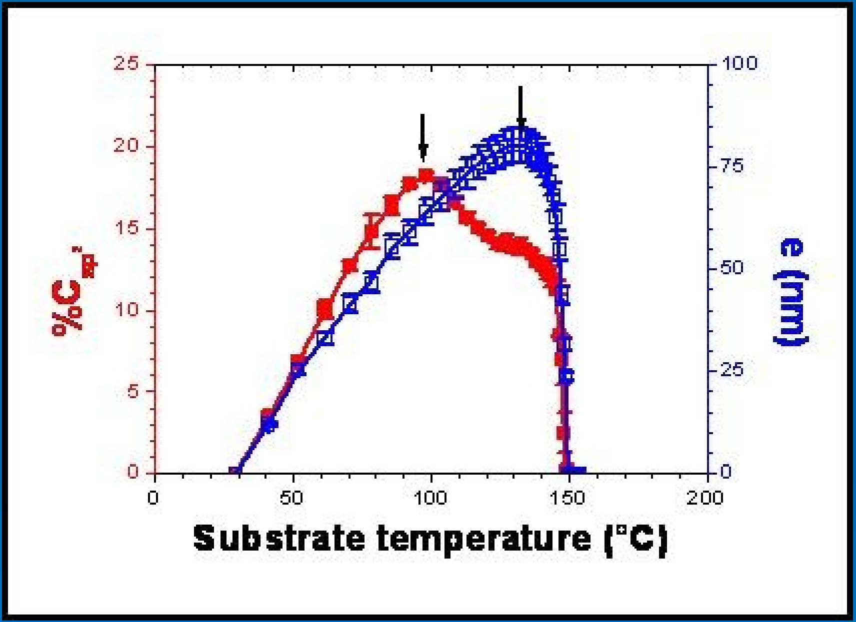


- **Key parameters : Exposure time and Wall temperature**

Temperature effect on a:CH film growth

► **Simulation of reactor walls**

⇒ substrate holder at uncontrolled temperature during CH_4 DECR plasma



Measure of substrate temperature

In-situ spectroscopic ellipsometry

⇒ film thickness

⇒ optical indexes

⇒ C sp^2

Ex-situ FTIR spectroscopy

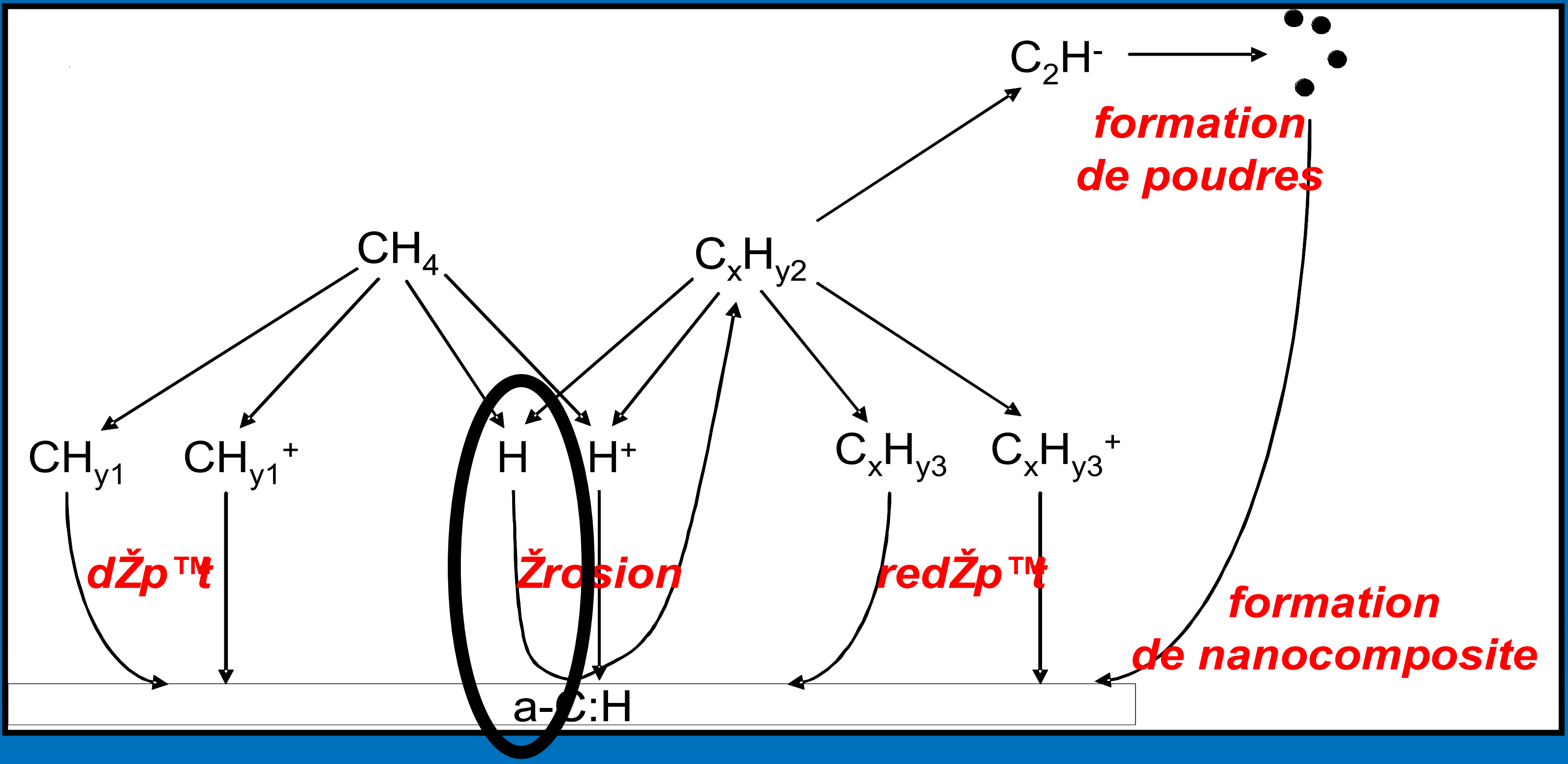
⇒ [H]

► **competition between deposition and erosion mechanisms**

deposition: graphitization (up to 100°C) and H incorporation

erosion: formation of volatile species

Surface mechanisms on reactor walls

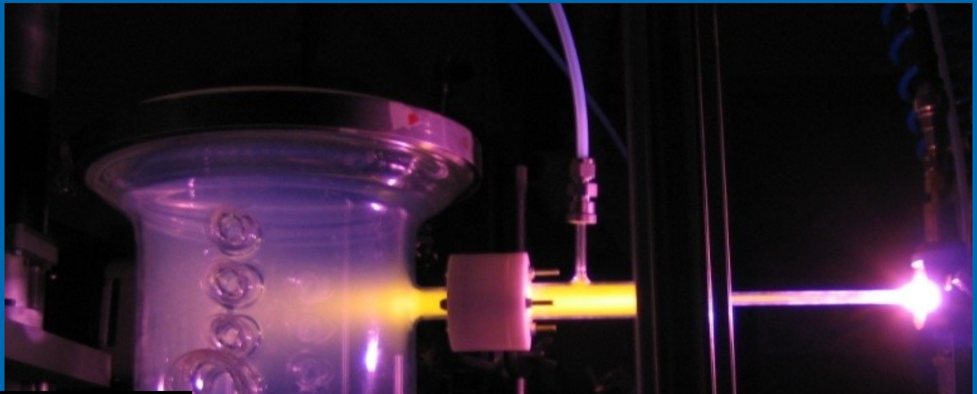


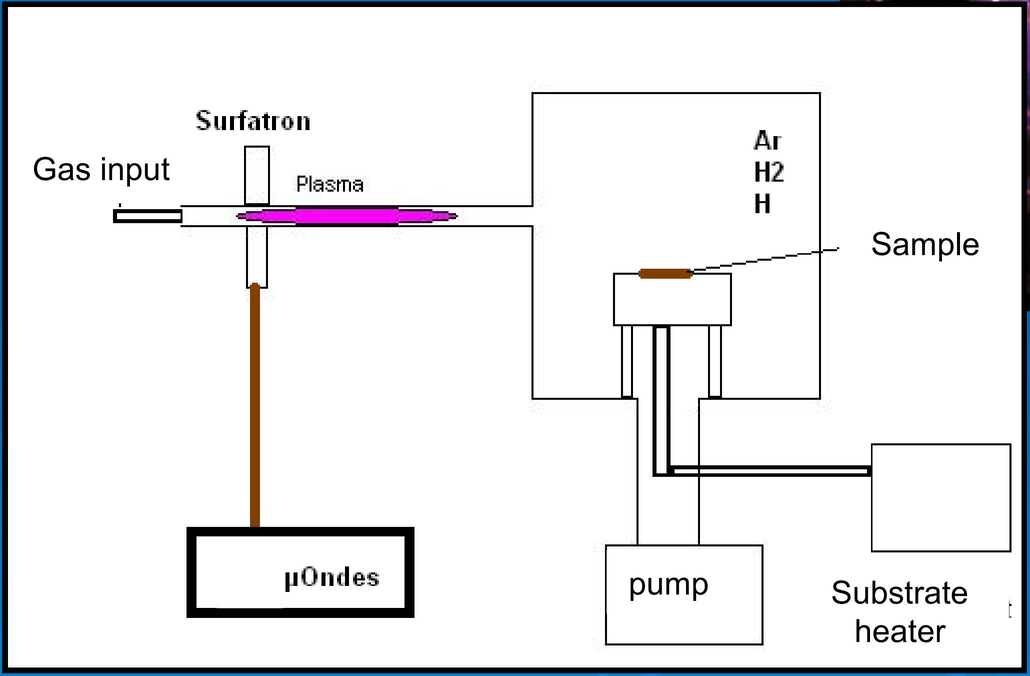
- ► **We focus on H interaction on a:CH films deposited in DECR plasmas**

  effect of temperature and exposure time

H production - Experimental set-up

- Plasma H_2/Ar
  - 2 Torr
  - 100 W
  - [H] = 4.10^{15} cm^{-3}





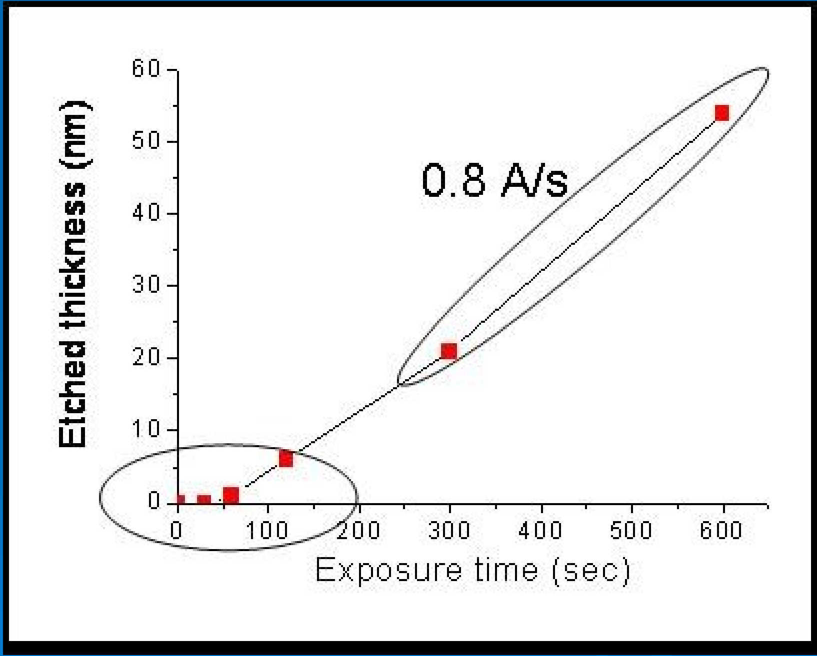
- a:CH films
  - DECR process
  - C sp^2 = 6.3 %
  - [H] = 6.1 10^{22} cm^{-3}

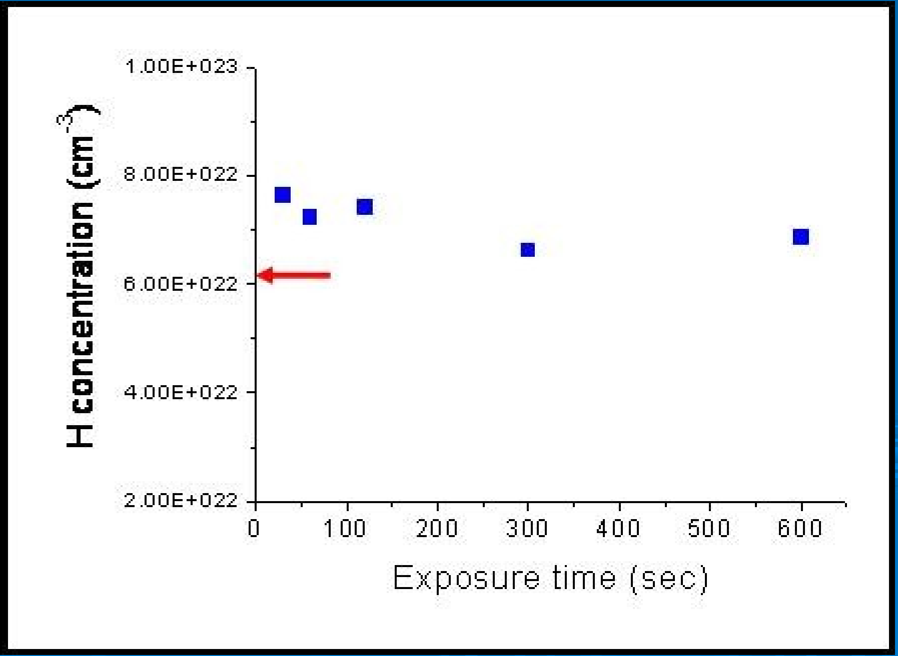
Exposure time effect

► **Substrate temperature 100°C**

constant etching rate after 100s

modification of hydrogen bonded concentration





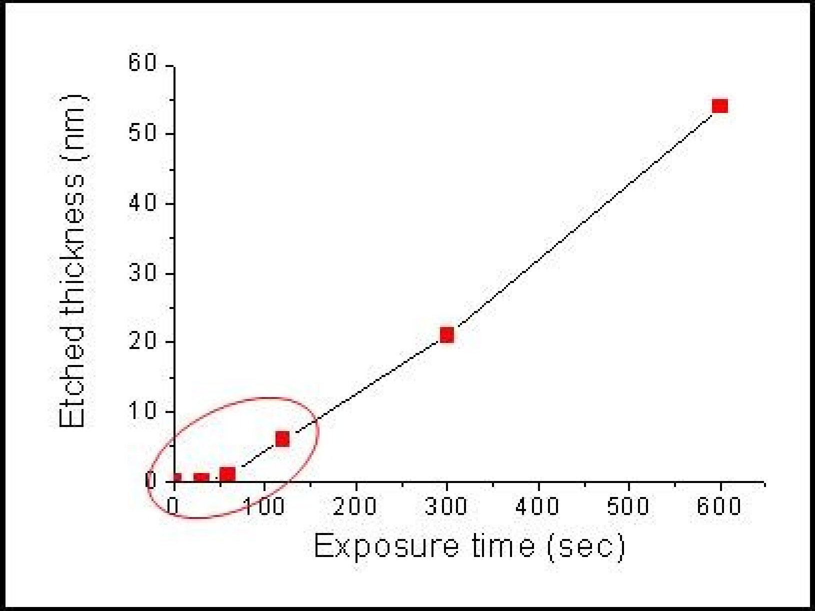
Description of the film / Spectroscopic Ellipsometry

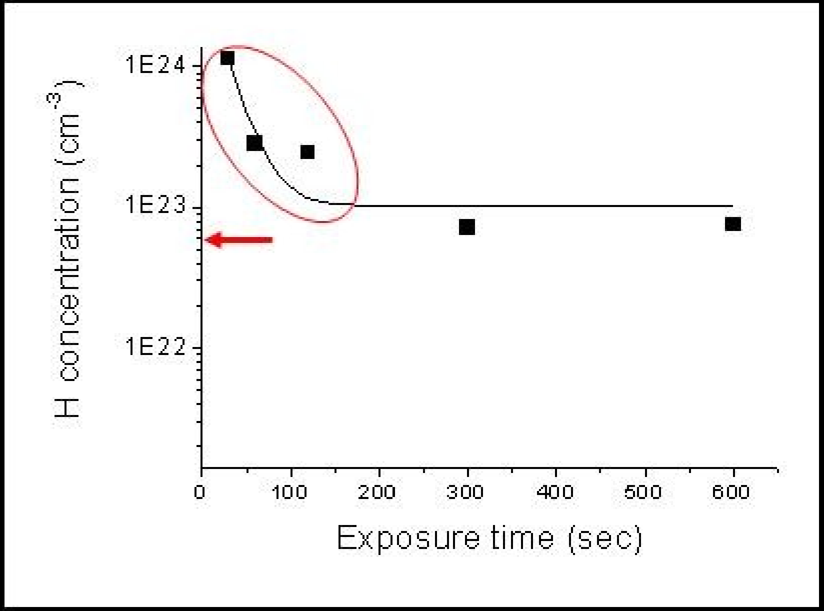
Before exposure

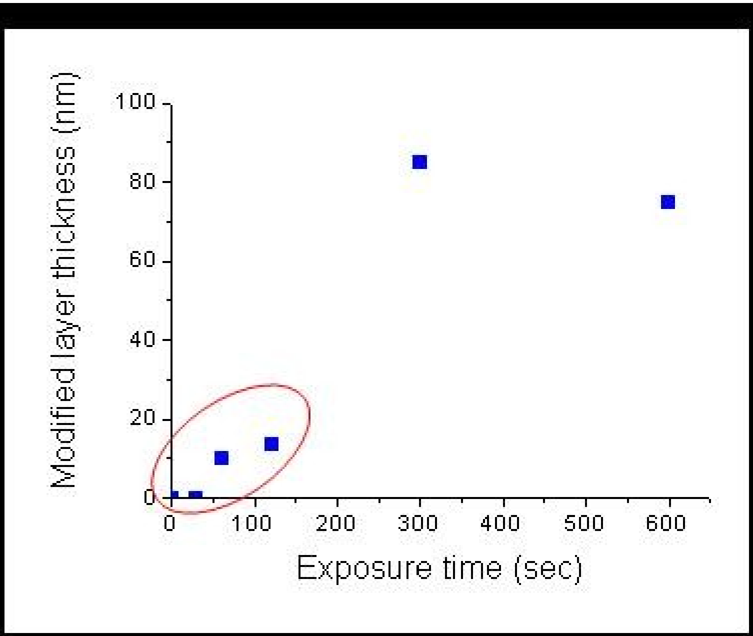
After exposure

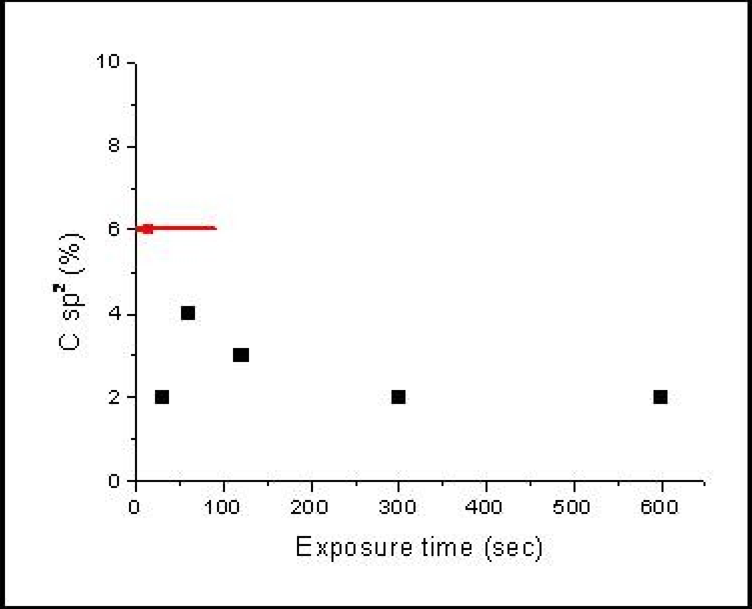
- characterization of the modified layer
  - thickness
  - H concentration
  - C sp^2 percentage

Exposure time effect



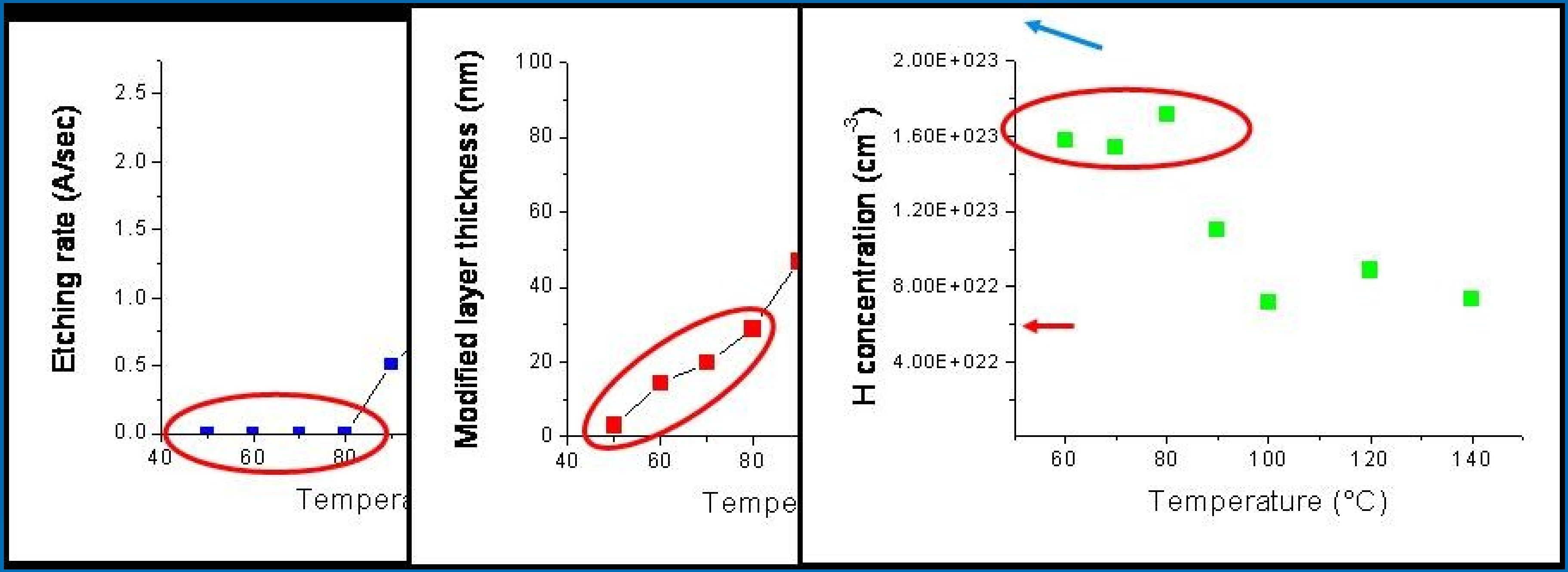






Temperature effect

► **5 min exposure time – Low temperature**

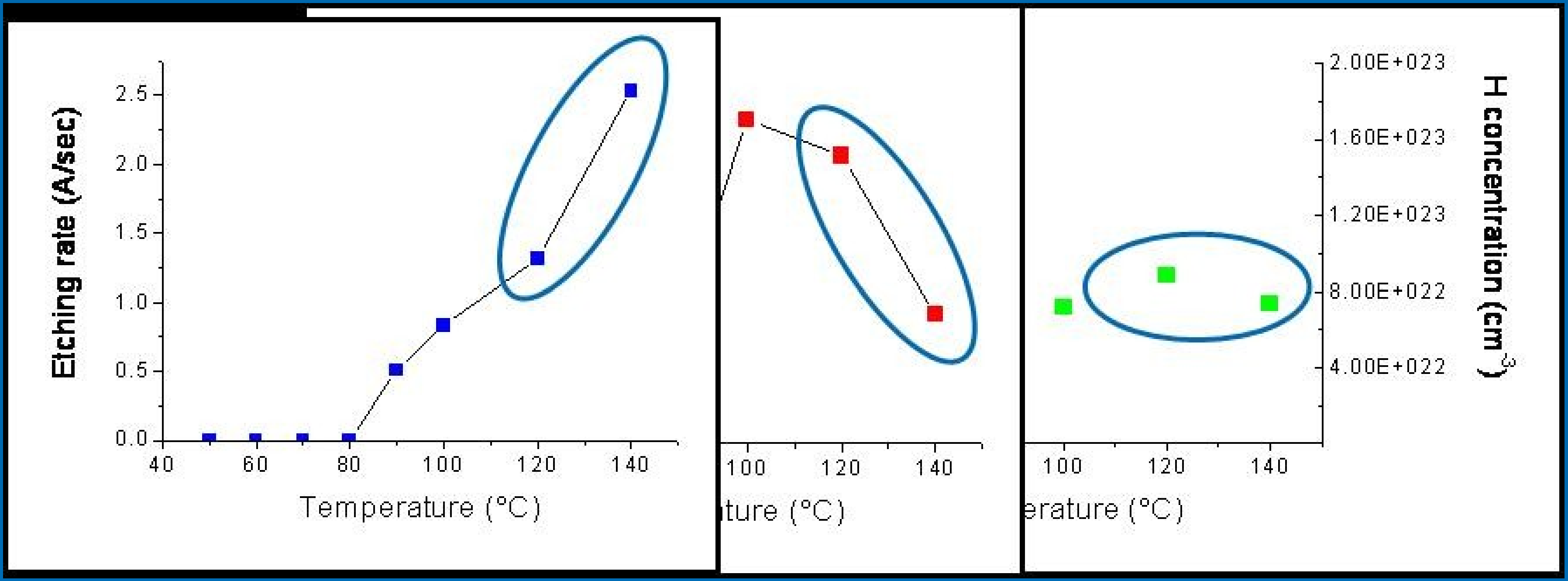


- No desorption
- Diffusion
- Storage

- Temperature is high enough for sufficient H storage
- Temperature is not high enough for desorption

Temperature effect

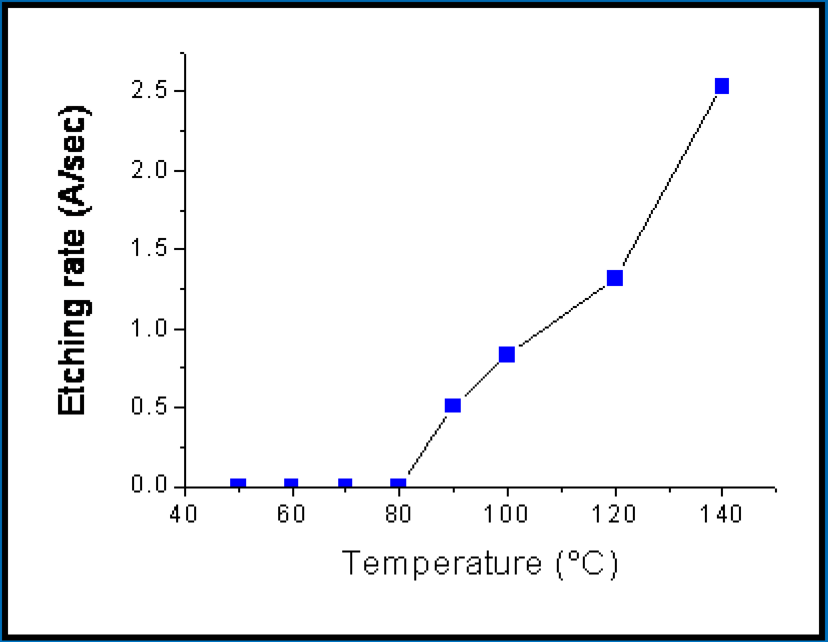
► **5 min exposure time – higher temperature**

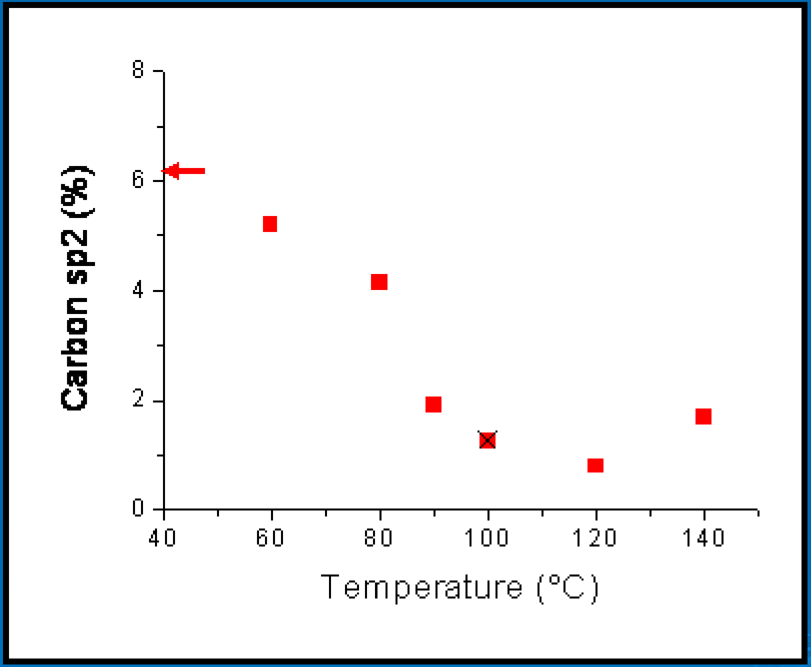


- Desorption - Diffusion

- Temperature is high enough for desorption even if the storage of H is low in the modified layer
- Desorption limits the diffusion of H in the a:CH coating

Temperature effect



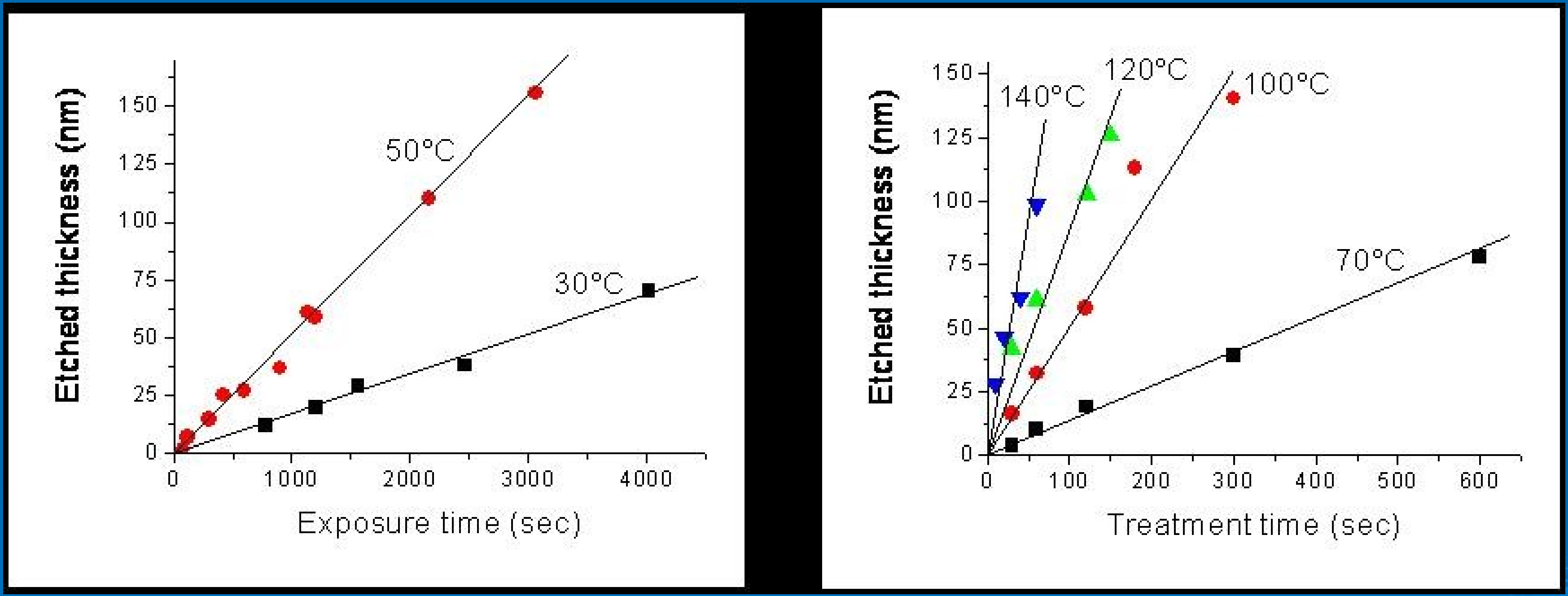


- Competition between graphitization of the coating with temperature and H binding on C sp2

- H concentration and C sp2 evolutions are comparable. C sp2 are not the only sites for H binding

Effect of hydrogen plasma content

- modification of the gas injection
- [H] = 4.10^{15} $cm^{-3} \Rightarrow 10^{16}$ cm^{-3}



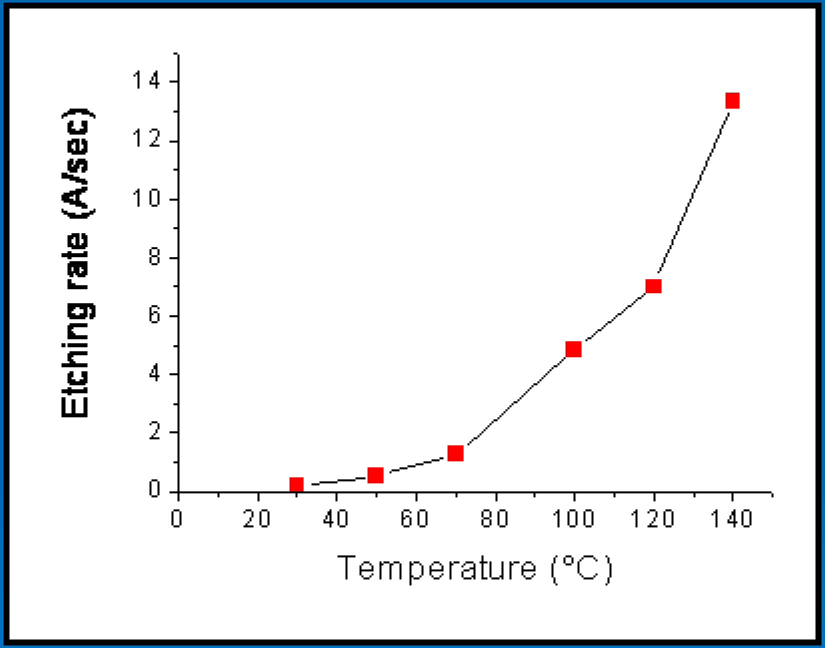
► Linear dependence between etched thickness and exposure time

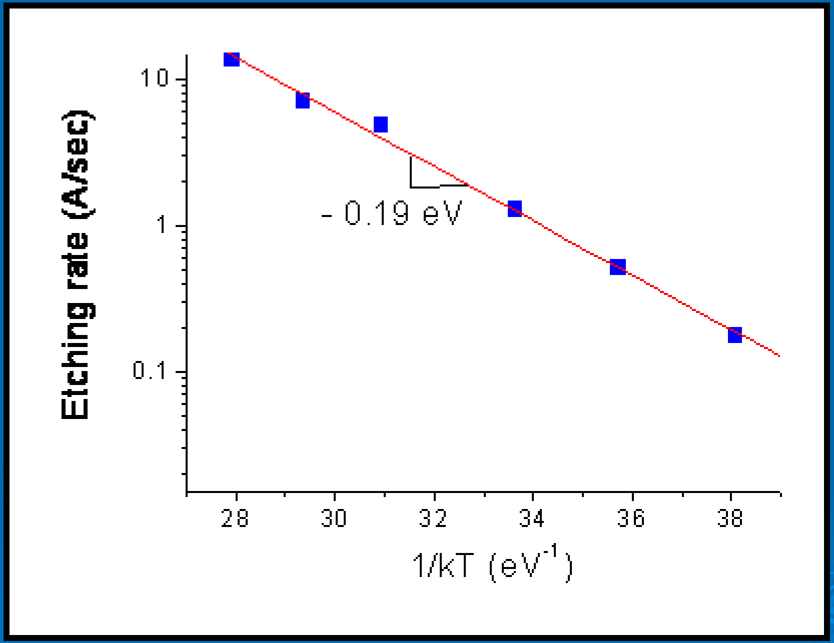
► No modification of the a:CH coating after post-discharge exposure

Temperature effect on H rich plasma

► H diffusion in the material is negligible

► Etch rate is controlled by desorption of volatile species





► when H diffusion in the material is negligible

► for a given composition of a:CH ([H], Csp2…)

$$ER(T)\ \alpha\ \exp\left(-\frac{0.19}{kT}\right)$$

Description of mechanisms

► Competition of film hydrogenation and species desorption

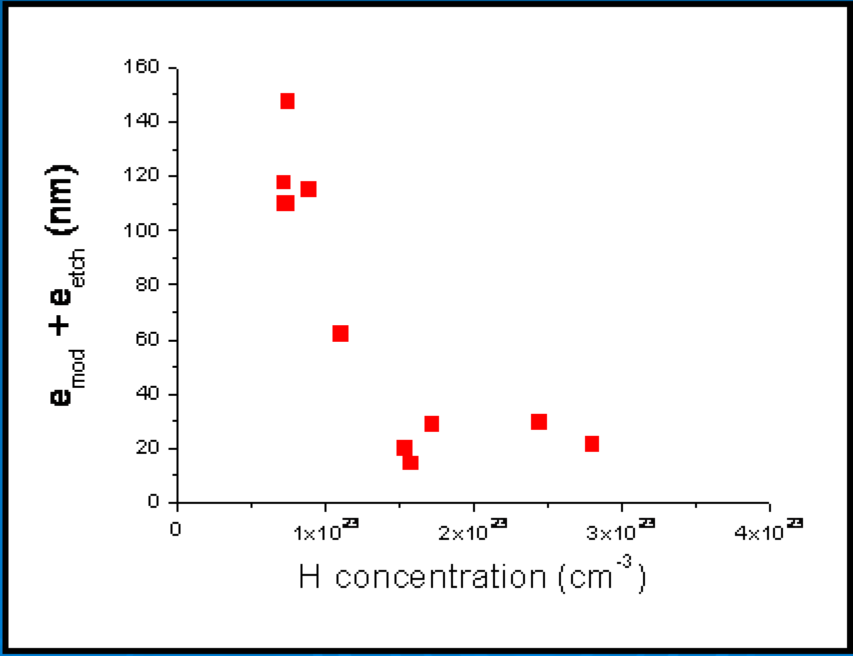
► Mechanisms depends on:

- exposure time
- substrate temperature
- hydrogen plasma

Hydrogen concentration in the film increase

=> modified layer thickness decrease

for low etching rate



=> non modification of film surface

for high etching rate

Back to the DECR plasma deposition process

► Competition of film deposition, film hydrogenation and species desorption

► Mechanisms depends on:

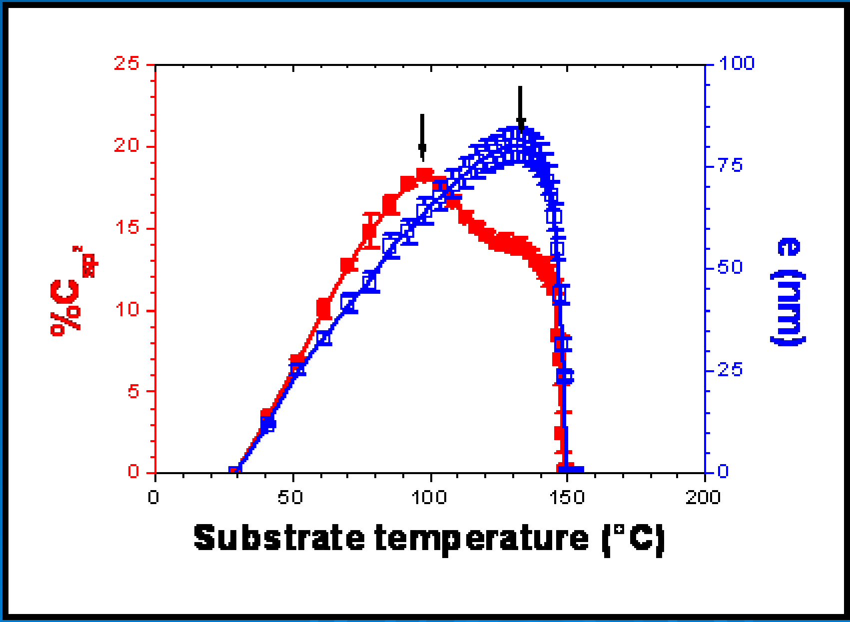
- exposure time
- substrate temperature
- plasma

Modification of the film

=> preparation of volatile species

Erosion

=> desorption



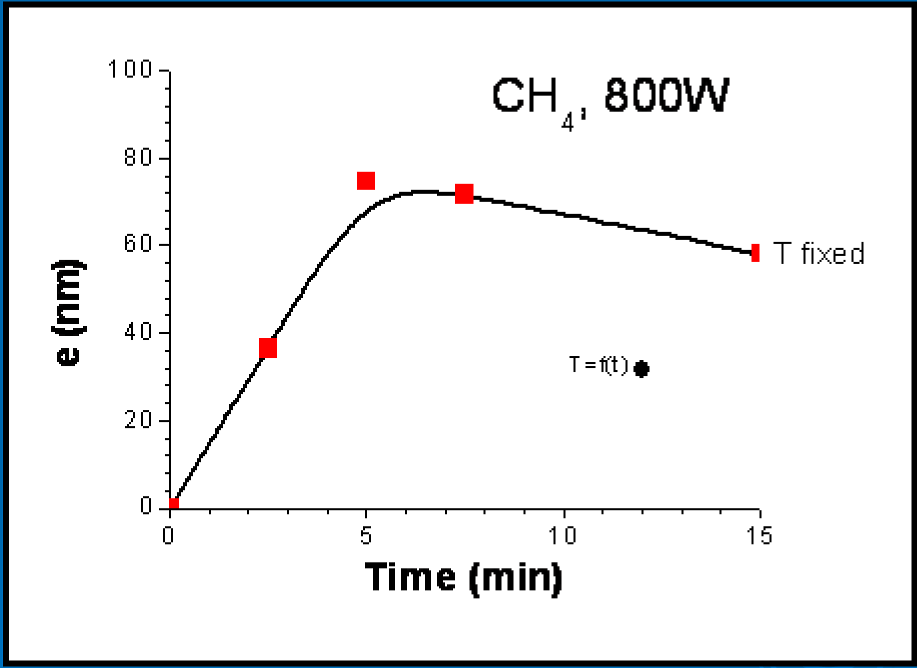
Back to the DECR plasma deposition process

► Film deposition at controlled substrate temperature

Evolution of film deposition rate

⇒Induced by volatile species created from the walls

Film structure evolution



► Volatile species can lead to powder formation in the discharge

=> Important impact of the competition erosion and deposition

Conclusion

► a-C:H film erosion controlled by time exposure and substrate temperature

At low hydrogen density in the plasma

=> low etching rate

=> hydrogen diffusion => modified layer

At high hydrogen density in the plasma

=> high etching rate without surface modifications

⇒Real impact on a-C:H thin film plasma deposition processes

⇒Modification of film structure because of reactor walls

⇒Formation of powder in the plasma volume => nanocomposite thin films