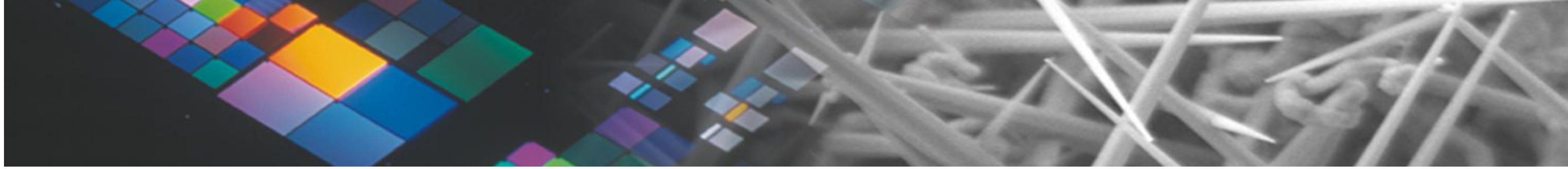


UV absorption spectroscopy to study the role of CF radicals during cryogenic etching of Si in CF_4 plasmas

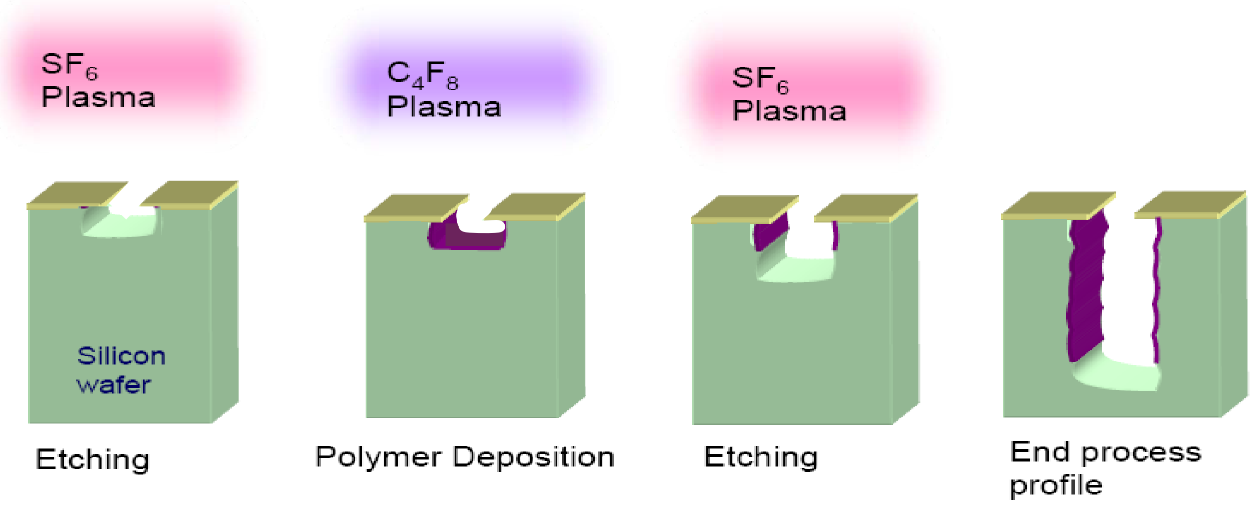
M. Kogelschatz[1], J. Nos[2], S. Iséni[2], G. Cunge[1], P. Lefaucheux[2], R. Dussart[2], T. Tillocher[2], E. Despiau-Pujo[1]

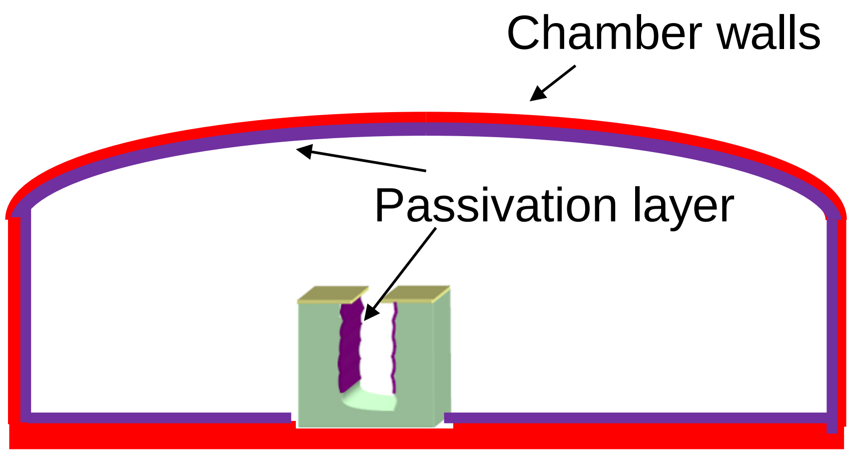
[1]*University Grenoble Alpes, CNRS, CEA/LETI-Minatec, Grenoble INP, LTM, 38000 Grenoble*

[2]GREMI, Université d'Orléans-CNRS, 14 Rue d'Issoudun, BP 6744, 45067 Orléans

Context: Bosch process

F chemistry at room temperature – sidewall passivation with gas modulation





***Time-multiplexed* process for deep silicon etching**

➢ Cycles composed of SF_6 etch plasma followed by C_4F_8 deposition plasma

➢ Passivation layer = Fluoropolymer (C_xF_y) produced by the decomposition of the injected gas

Advantages

➢ Process usually at room temperature

➢ Robust process, repeatable

Drawbacks

➢ « Scalloping » at the sidewalls

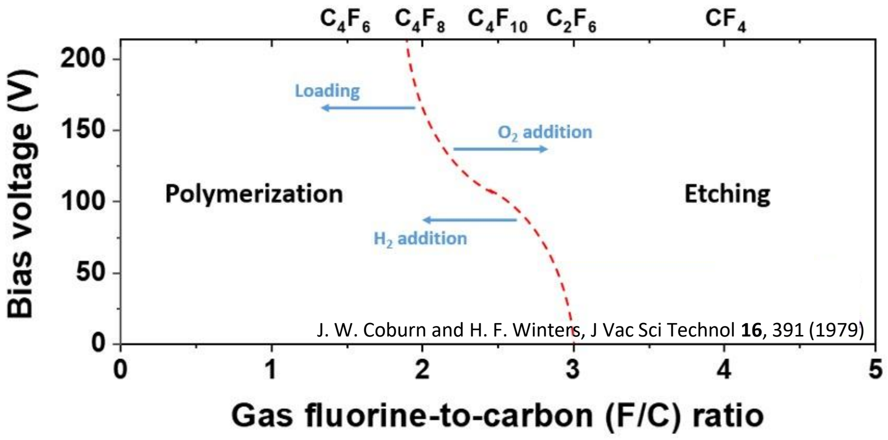
➢ Deposition of fluorocarbon layer on chamber walls -> Chamber cleaning necessary to prevent process drifts

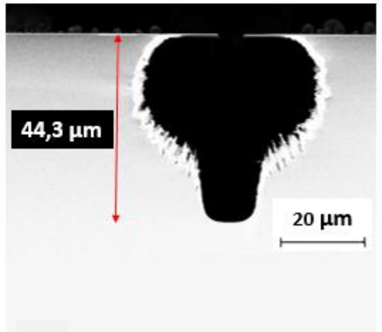
➢ Global warming potential of C_4F_8

Switching to less polymerizing gas ?

- Low F/C ratio gases are highly polymerizing

⇒ Deposition regime whatever the substrate temperature





+20°C
CF_4
➔ Isotropic profile

Nos et al, Appl. Phys. Lett. 126, 031602 (2025)

- High F/C ratio gas-based plasmas lead to an etch regime at room temperature

⇒ Is it possible to promote deposition on feature sidewalls by only decreasing the substrate temperature while keeping chamber walls clean ?

→ Bosch process at cryogenic temperature with CF_4 ?

LTM LABORATOIRE DES TECHNOLOGIES DE LA MICROÉLECTRONIQUE

Cryogenic etching

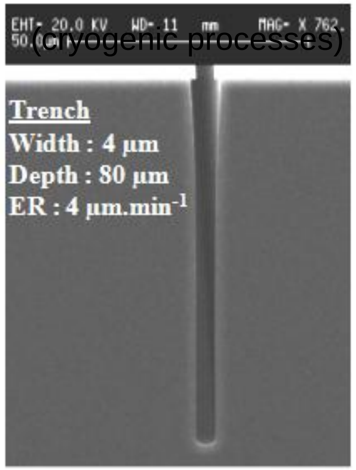
Benefits of substrate cryogenic cooling for plasma etching

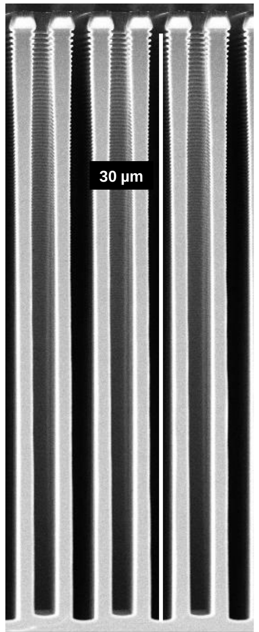
⇨ Increased surface residence time of species => passivation, capillary condensation, physisorption…

⇨ Less plasma-induced damage

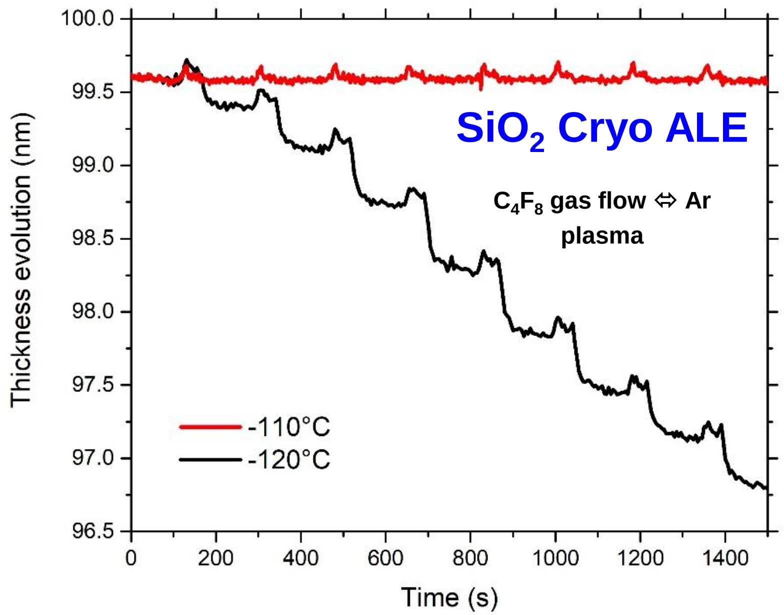
⇨ Less contamination of chamber walls (layers deposited only on cooled surfaces)

Deep silicon etching (cryogenic processes)





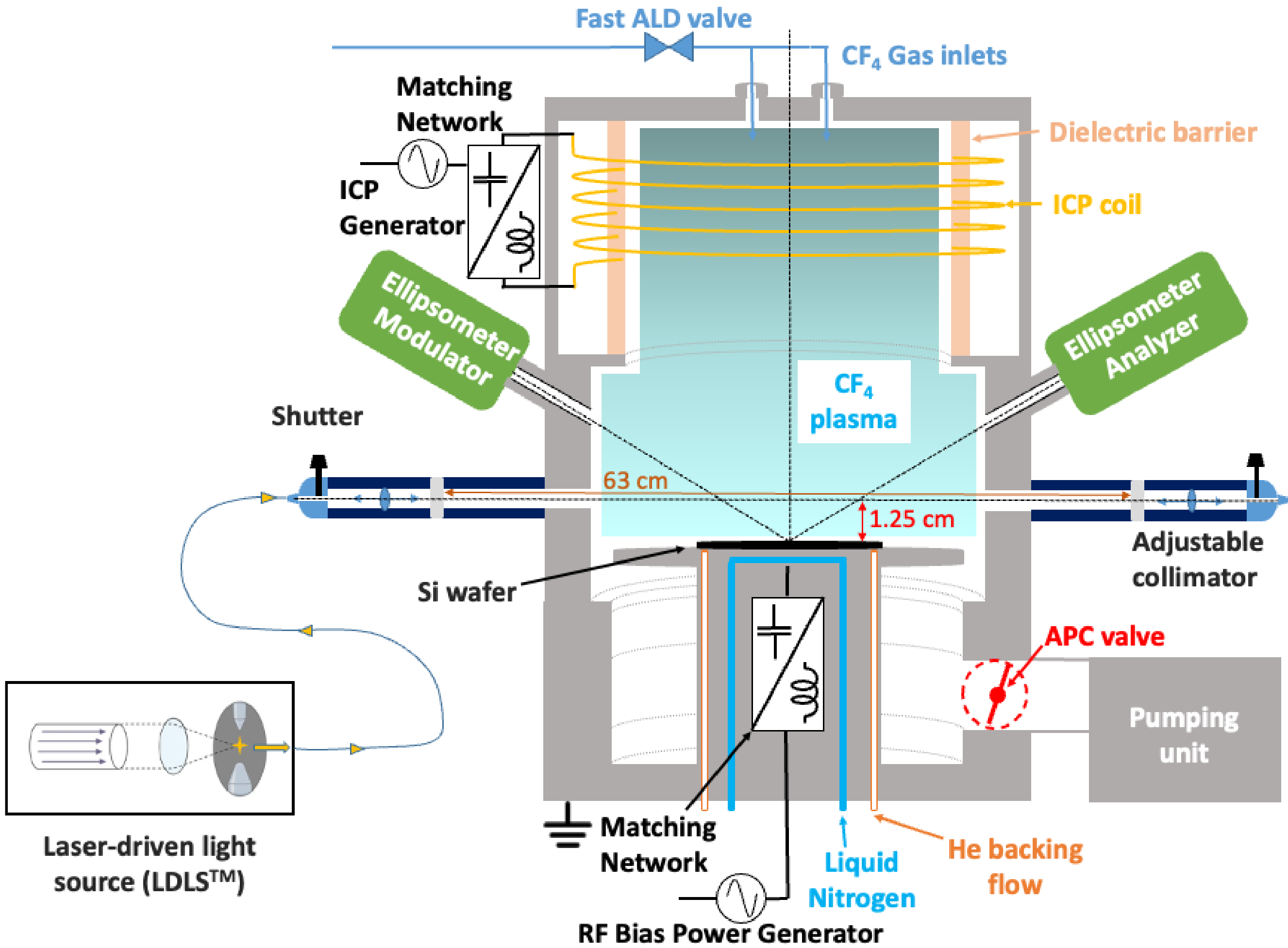
R. Dussart *et al.*, J. Phys. D: Applied Physics, 47 (2014) 123001



G. Antoun *et al.*, Appl. Phys. Lett. 115 (2019) 153109

Experimental setup

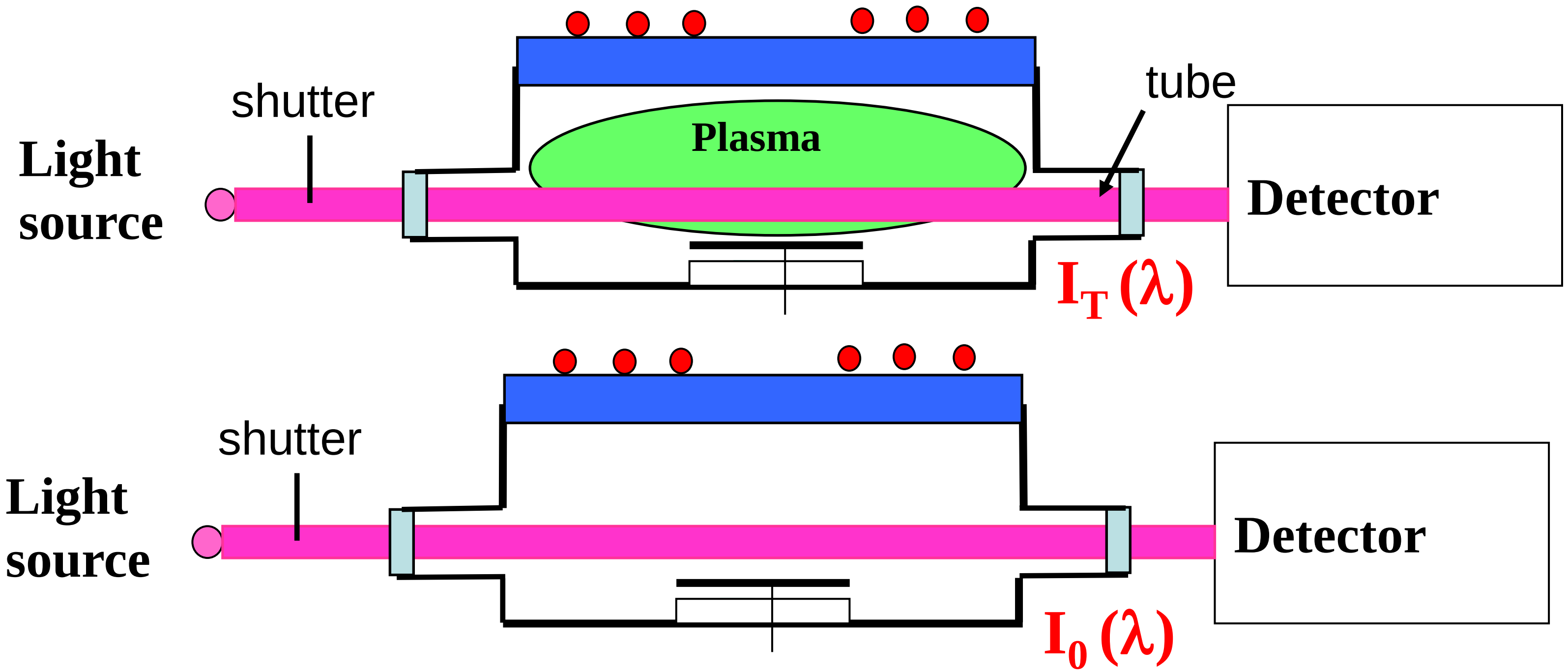
Oxford Instruments ICP reactor



Equipement:
- Hamamatsu Energetiq LDLS
=> 170 – 2500 nm
- Additional tubes on the viewports
=> Connection du optical fiber, collimation, protection of windows
- Princeton Instruments Acton Spectrometer, 750 mm, 3 gratings
- Pylon CCD detector (200 – 1050 nm)

Optical spectrometer
+
CCD detector

Optical absorption spectroscopy



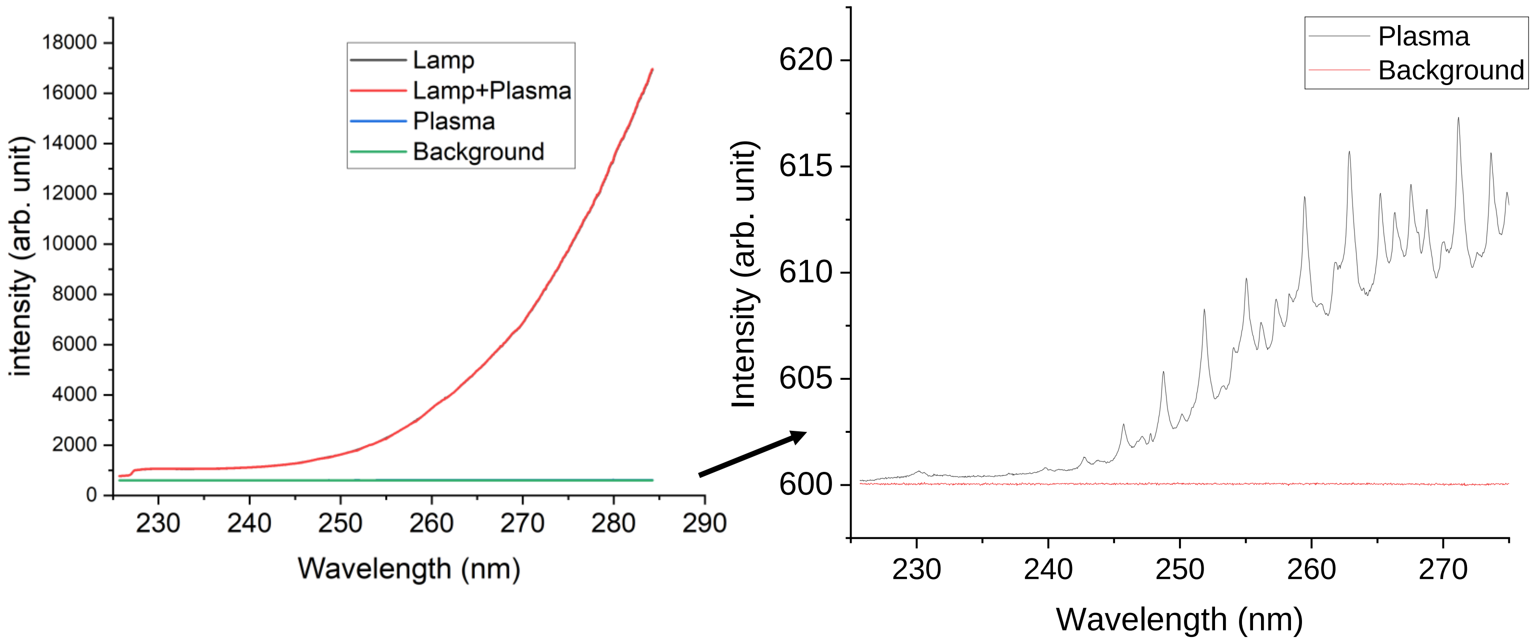
Beer-Lambert law: $I_T(\lambda) = I_o(\lambda)\, e^{-n.\sigma(\lambda)L}$

By measuring $I_o(\lambda)$ and $I_T(\lambda)$:

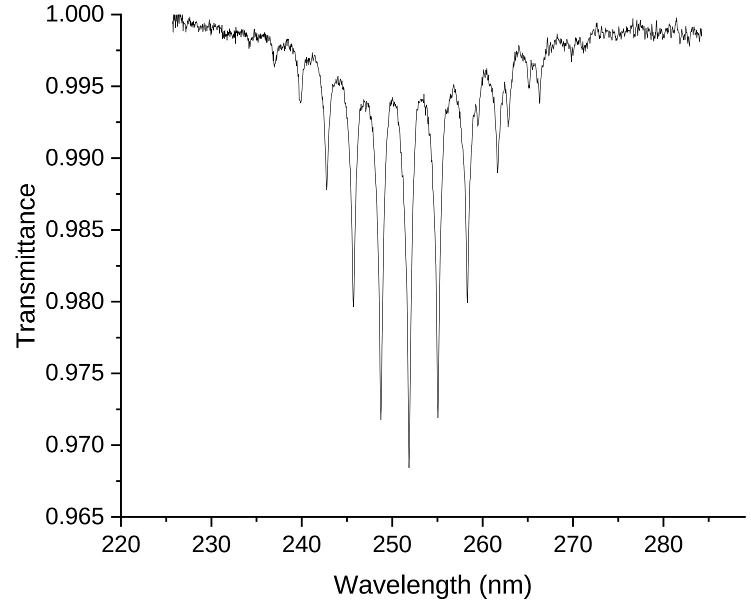
- **1) Shape of $\sigma(\lambda) \Rightarrow$ species temperature**
- **2) Absolute concentration of n**

$\Rightarrow$ Flux of radicals incident on the substrate: $\Phi = \frac{1}{4} n \sqrt{\frac{8kT}{\pi m}}$

Optical absorption spectroscopy



CF_2 A(0,v',0)-X(0,0,0)
Absorption spectrum



I_{LP}: Lamp on – plasma on, shutter open
I_P: Lamp off – plasma on, shutter closed
I_L: Lamp on – plasma off, shutter open
I_{BG}: Lamp off – plasma off, shutter closed

$$\text{Transmittance} = \left(\frac{I_{LP} - I_P}{I_L - I_{BG}}\right)$$

Thanks to multichannel detector, a large wavelength range can be detected simultaneously

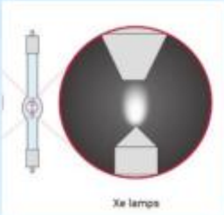
Challenge: light source has to be stable to avoid baseline fluctuation

⇒ High sensitivity needed for some species (10^{-4} absorbance with few sec acquisition)

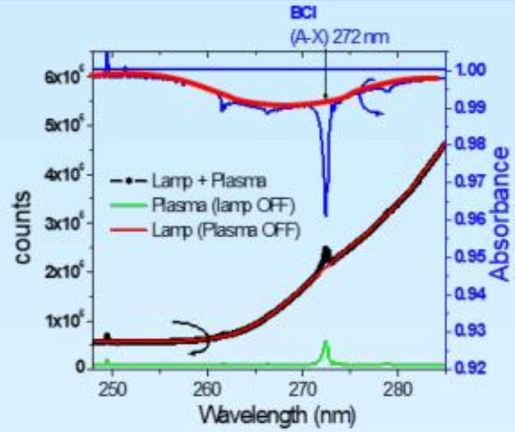
Improvement of lamp source stability over 20 years

➢ Xe arc

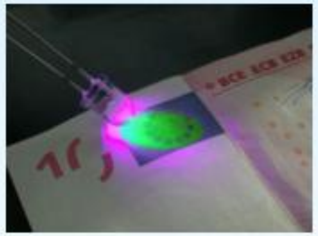
Arc = spatial + intensity fluctuations → the unabsorbed baseline $I_0(t1)/I_0(t2)$ oscillates

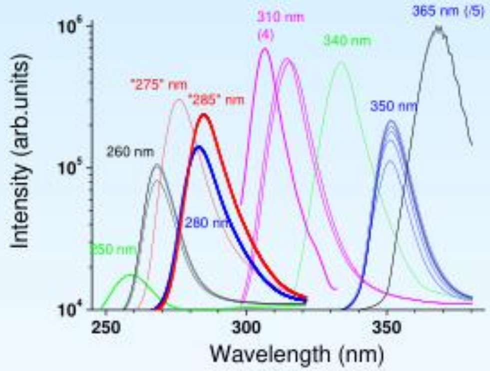


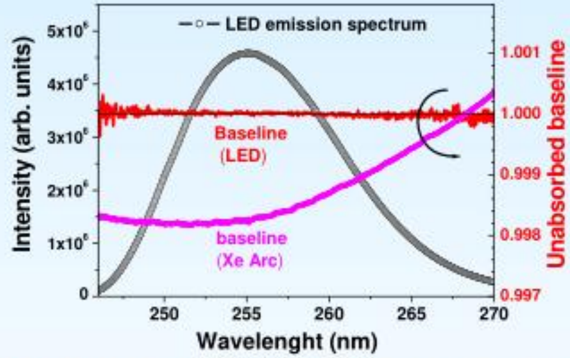
→ Sensitivity limited by baseline oscillations (> 10^{-3})



➢ UV LED

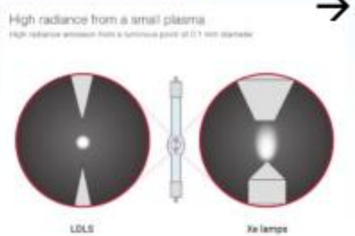






→ Sensitivity is limited by the baseline noise (< 10^{-4}) → gain factor 10 in sensitivity…but spectral range of each LED restricted

➢ Laser driven light sources (LDLS)



→ stability almost as good as LED but wider spectral range (180 nm → visible)

→ A good choice to detect <u>small polyatomic radicals</u>…

LTM LABORATOIRE DES TECHNOLOGIES DE LA MICROÉLECTRONIQUE

Optical absorption spectroscopy: experimental protocol

Influence of the substrate temperature on the CF and CF_2 radical densities

- Broadband UV absorption spectroscopy: measurement procedure

x3

1) Plasma OFF – Lamp OFF (shutter closed) - Acquisition of background spectrum (I_{BG})
2) Plasma OFF – Lamp ON (shutter open) - Acquisition of lamp emission spectrum (I_L) x2
3) Plasma ON – Lamp OFF (shutter closed) – Acquisition of plasma emission spectrum (I_P) X2
4) Plasma ON – Lamp ON (shutter open) – Acquisition transmission spectrum (I_{LP})

- Experiment performed at two substrate temperatures: 20 °C and -130 °C
- Absorption spectra plotted from the average of 3 separate measurements
- Absorbance A is given by Beer Lambert's law:

$$-ln\left(\frac{I_{LP}-I_P}{I_L-I_{BG}}\right) = -ln\left(\frac{I_T}{I_0}\right) = \boldsymbol{A} = \sigma.n.L$$

L = absorption path
σ = absorption cross section
n = species density

J. Luque et al., J Chem Phys **118**, 622 (2003)

LTM LABORATOIRE DES TECHNOLOGIES DE LA MICROÉLECTRONIQUE

Influence of the substrate temperature on gas phase CF and CF_2 radical densities

- CF_4 plasma: 50 sccm, 4 Pa, 1500 W ICP, no bias power

- Clear decrease in the intensity of absorption signal from 20°C to -130°C

- Calculated CF density at 20°C: 1×10^{13} cm^{-3}

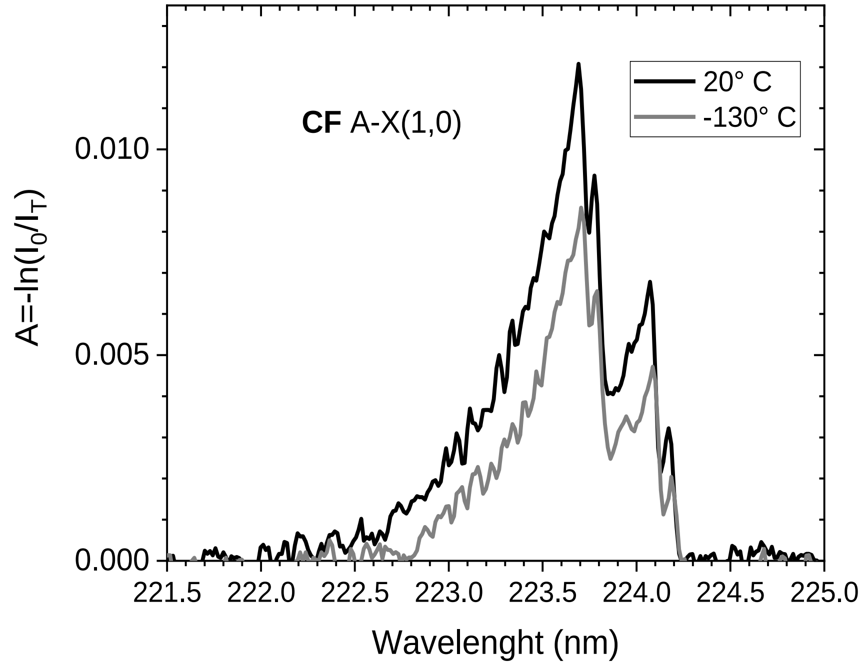
- Calculated CF density at -130°C: 6×10^{12} cm^{-3}

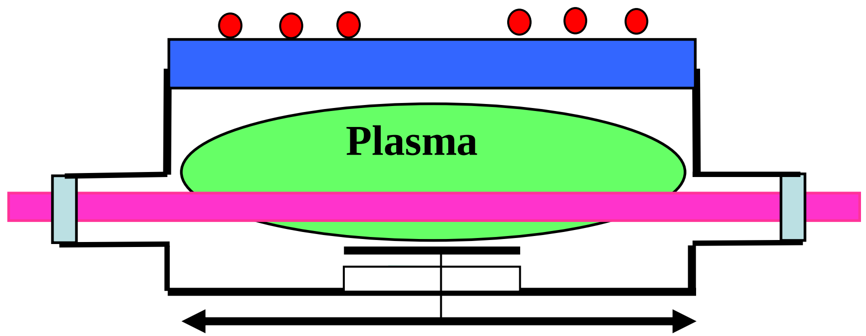
=> Decrease of CF density by 40%

- Cooled wafer area << total chamber wall surface at room T

=> Strong increase of CF loss rate on the surface cooled at -130°C

CF species, A-X(1,0) transition





Absorption path = reactor diameter

Influence of the substrate temperature on gas phase CF and CF_2 radical densities

CF_4 plasma: 50 sccm, 4 Pa, 1500 W ICP, no bias power

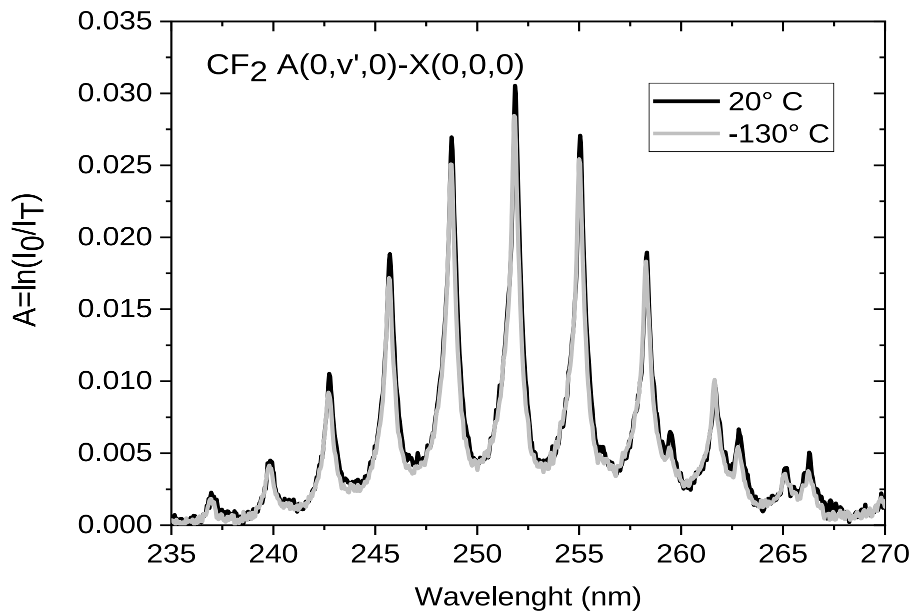
- No significant dependence of CF_2 radical density to the substrate temperature (around 1.7×10^{13} cm^{-3})

=> No sticking of CF_2 on surfaces (usually produced at surfaces)

→ Absorption path = reactor diameter + tubes

=> CF expected to be the main precursor to CF_x deposition at low temperature

CF_2 species, A(0,v',0)-X(0,0,0) transition



- Competition between etching and deposition in CF_4 plasma turns to deposition at -130°C
- **=> Favored by enhanced sticking of CF radicals on surface cooled at cryogenic temperature**
- By neglecting etching component, sticking probability can be estimated to a minimum of 10%

LTM LABORATOIRE DES TECHNOLOGIES DE LA MICROÉLECTRONIQUE

Cryo-Bosch process with CF_4 passivation

x200

Etching step: 3 s

300 sccm SF_6, 3 Pa, 1500 Ws, -135 Vb

Passivation step: 2 s

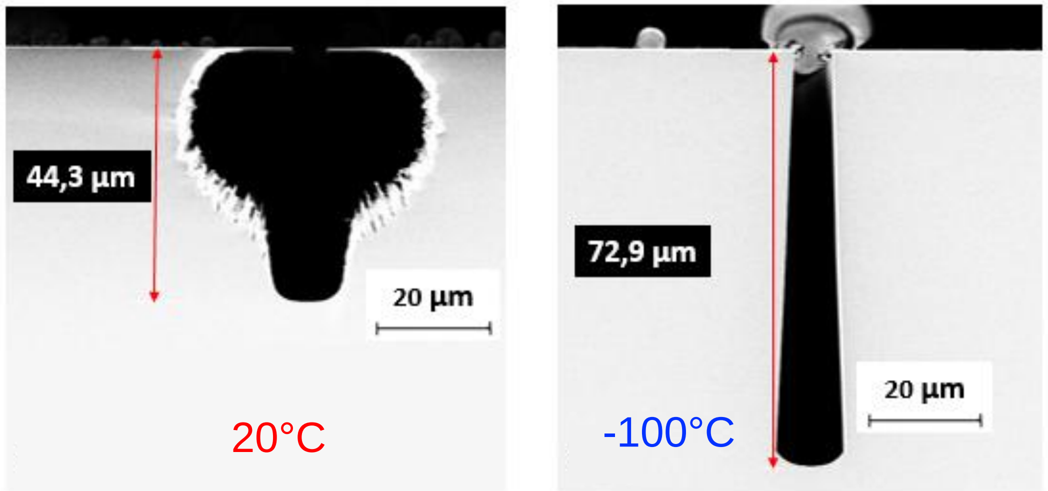
20 sccm CF_4, 1 Pa, 1500 Ws, -65 Vb

- Mostly isotropic profile at 20°C
- Anisotropic profile at -100°C

=> Strong CF_x deposition at -100°C

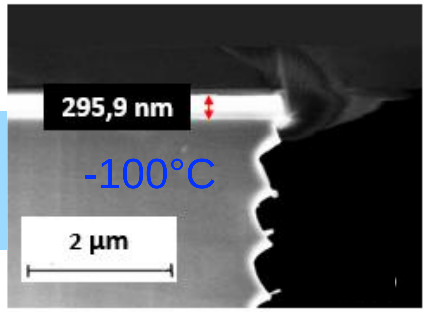
=> Enhanced passivation at -100°C

Trenches cross-section view (CD = 6 µm)



Top view – SiO_2 mask (initial thickness 1.2 µm)

- Selectivity at 20°C: 45:1
- Selectivity at -100°C: 80:1



Nos et al, Appl. Phys. Lett. 126, 031602 (2025)

Conclusions

- **CF_4 plasma:** Transition from Si etching to CF_x deposition by decreasing the substrate temperature from room T to cryogenic T

⇒ Significant decrease of CF radical density observed by UV absorption spectroscopy in cryogenic conditions

⇒ Significant increase of sticking probability of CF radicals on cold surfaces

⇒ CF species are expected to be the main precursor of CF_x layer

- **Bosch process** can be achieved at **cryogenic temperature** by using CF_4 passivation plasma instead of C_4F_8

=>The CF_x layer grows only on cooled surface

=> No deposition on reactor walls at room T

=> Less contamination of chamber walls, less global warming potential

LTM LABORATOIRE DES TECHNOLOGIES DE LA MICROÉLECTRONIQUE

Thank you !

The authors would like to thank ANR for their valuable **financial** support (PSICRYO project)

This research was also supported by CERTeM 5.0 platform, which provides most of the equipment, and funded by the European Union under project no EX004028.