Nitrogen doping of 2D transition metal carbide multilayers (MXenes) by in situ ion implantation in the TEM

Marie-Laure David[1]

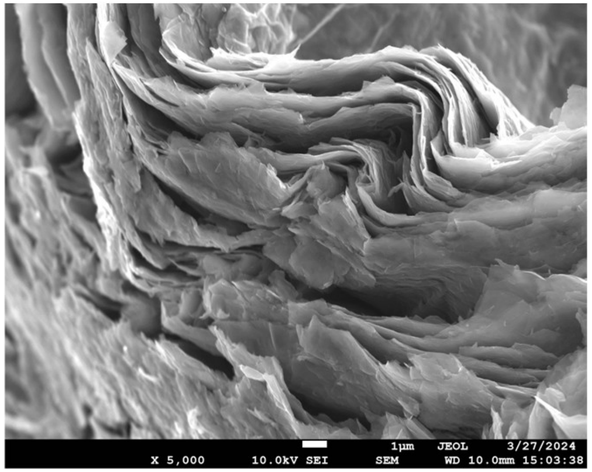
Noé Condé[1], Ayoub Benmoumen[1,2], Cédric Baumier[3], Stéphanie Jublot-Leclerc[3], Aurélie Gentils[3], Sophie Morisset[4], Stéphane Célérier[4], Luc Pichon[1], Michel Drouet[1], Philippe Moreau[2] and Vincent Mauchamp[1]

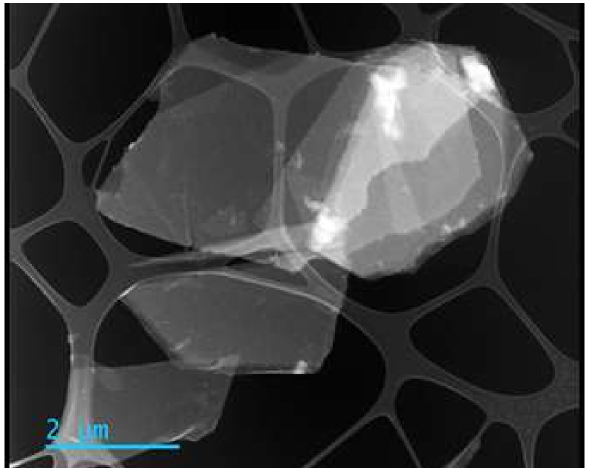
[1]Université de Poitiers, ISAE-ENSMA, CNRS, PPRIME, Poitiers, France
[2]Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, Nantes, France
[3]IJCLab, Université Paris-Saclay, CNRS, Orsay
[4]Université de Poitiers, CNRS, IC2MP, Poitiers, France

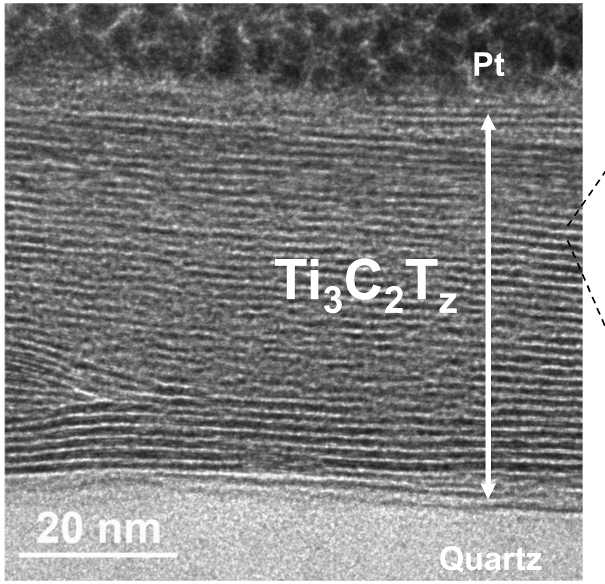
Motivation

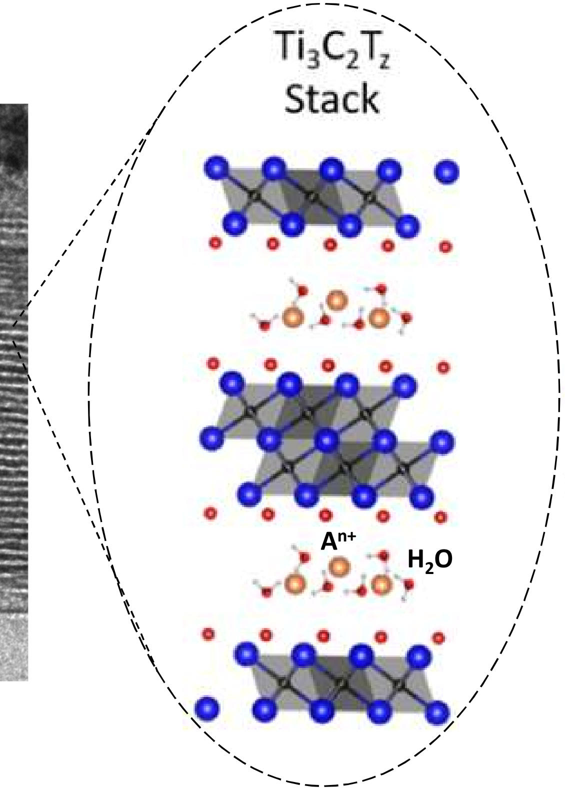
MXenes properties and applications

- Emerging class of 2D materials : single flakes or **multilayers**









Transition metal carbides or nitrides

$M_{n+1}X_nT_z$

➡ $Ti_3C_2T_z$

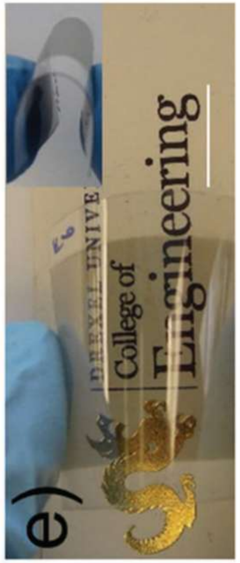
- M = Transition metal (Ti, V, Cr, Mo,…)
- X = C or/and N
- T_z = surface groups : O(H), F, Cl …
- n=1-3

Motivation

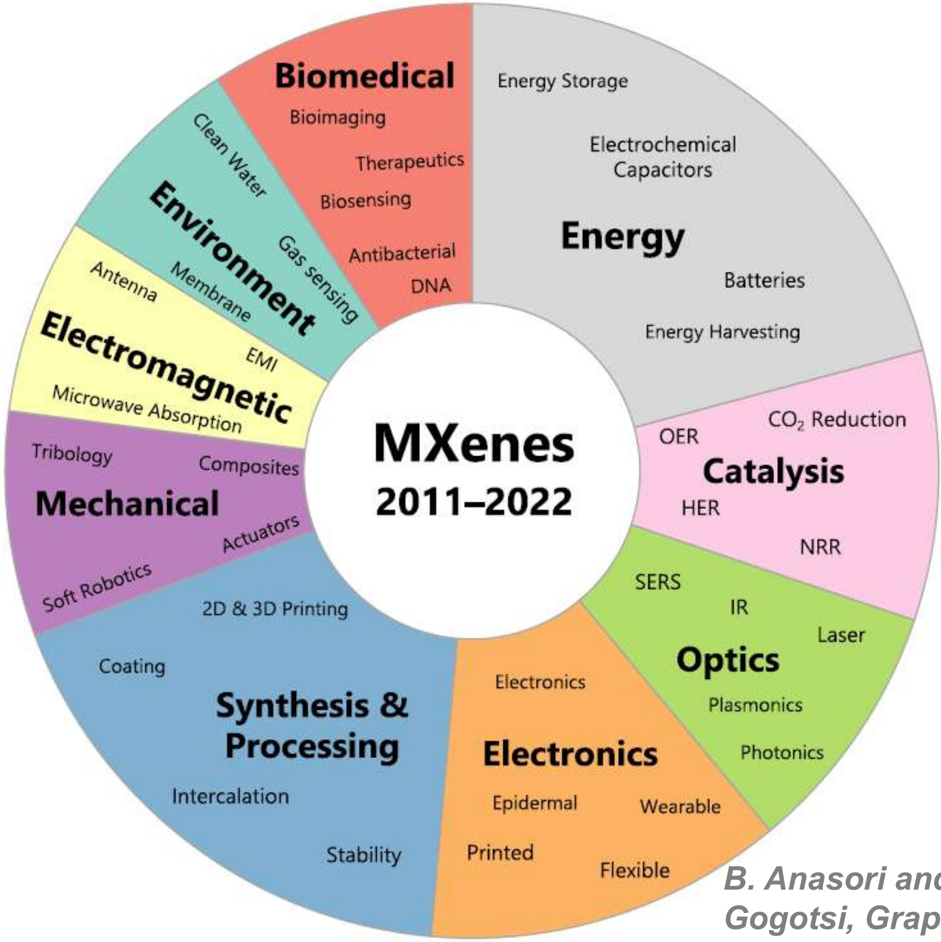
MXenes properties and applications

Conductive clays – complex architecture
Flexible structure and chemistry
⇨ Tune the properties
⇨ Applications

A. Vahidmohammadi *et al.*, Science 372, abf1581 (2021)



ACS Nano (2019),13, 8491

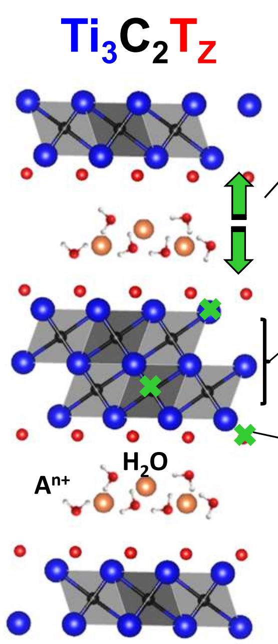


B. Anasori and Y. Gogotsi, Graphene and 2D Materials 7, 75 (2022)

Motivation

MXenes properties and applications

To play with the structure and chemistry of MXenes
- Modify the elemental constitution
- **Modify a given composition**



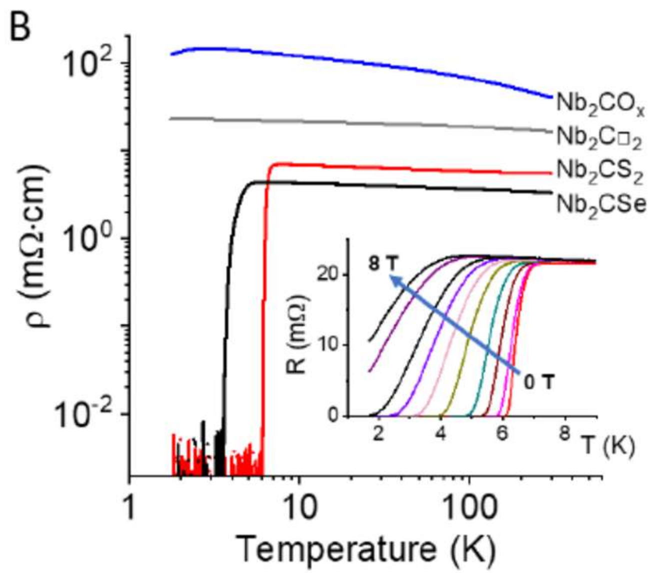
At the mutlilayer level

Modification of the interlayer space

At the flake level

In the TiC skeleton
- Structural disorder (M vacancies)
- Foreign species (N doping…)

At the flake surface
- Modification of the surface groups



Kamysbayev et al., Science 369 (2020)

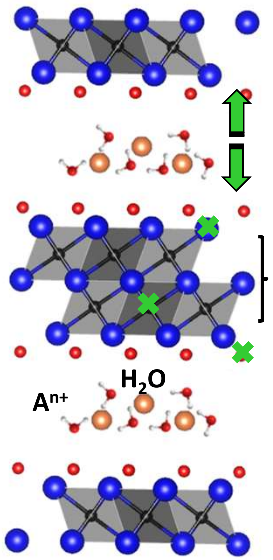
Motivation

MXenes properties and applications

To play with the structure and chemistry of MXenes

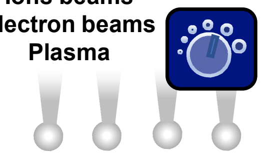
- Modify the elemental constitution
- **Modify a given composition**

$Ti_3C_2T_z$



State of the art
Chemical synthesis steps or post-synthesis annealing
⇨ Lack of control, flexibility and reproducibility on the as-obtained functionalisation

Ions beams
Electron beams
Plasma



Introduction of defects
⇩
Manipulate the structure and chemistry of MXene multilayers in a controlled way

Motivation

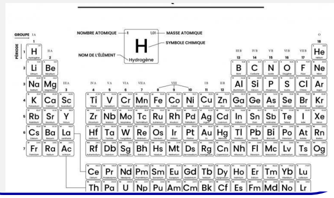
Defect engineering by ion implantation/irradiation

Ion implantation/irradiation : versatile tool to introduce the desired amount of defects in a given material

CONTROL

- Mass selection

⇨ **Implanted ion**

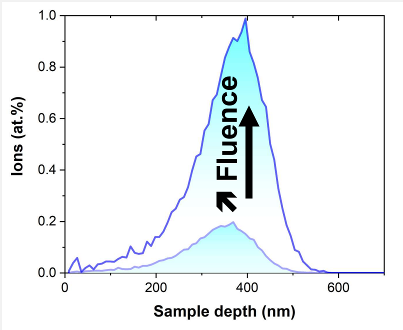


- Dose rate
- Substrate temperature

⇨ **Defect formation**

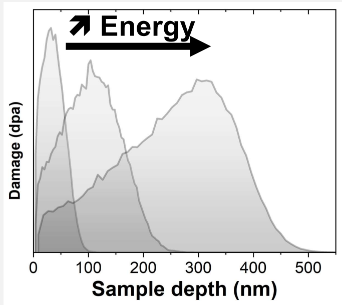
- Fluence

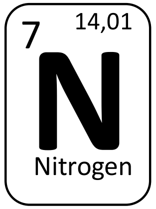
⇨ **Ion /damage concentration**



- Energy

⇨ **Ion/damage profile**





Nanomaterials (2D)

- **MoS_2** *K. Xu et al., Semicond. Sc. Tech (2017)*
- **Graphene** *H. Wang et al., Nano Lett. (2012), G. Lopez-Polin et al., Nature Physics (2015)*
- **MXenes**

Ion implantation ⇨ approach for structural modifications and functionalization of $Ti_3C_2T_Z$

H. Pazniak et al., ACS Nano 15 (2021) 4245

He ion irradiation ⇨ Modification of optical properties

A. Benmoumen et al., App. Surf. Sci. 652 (2024) 159206

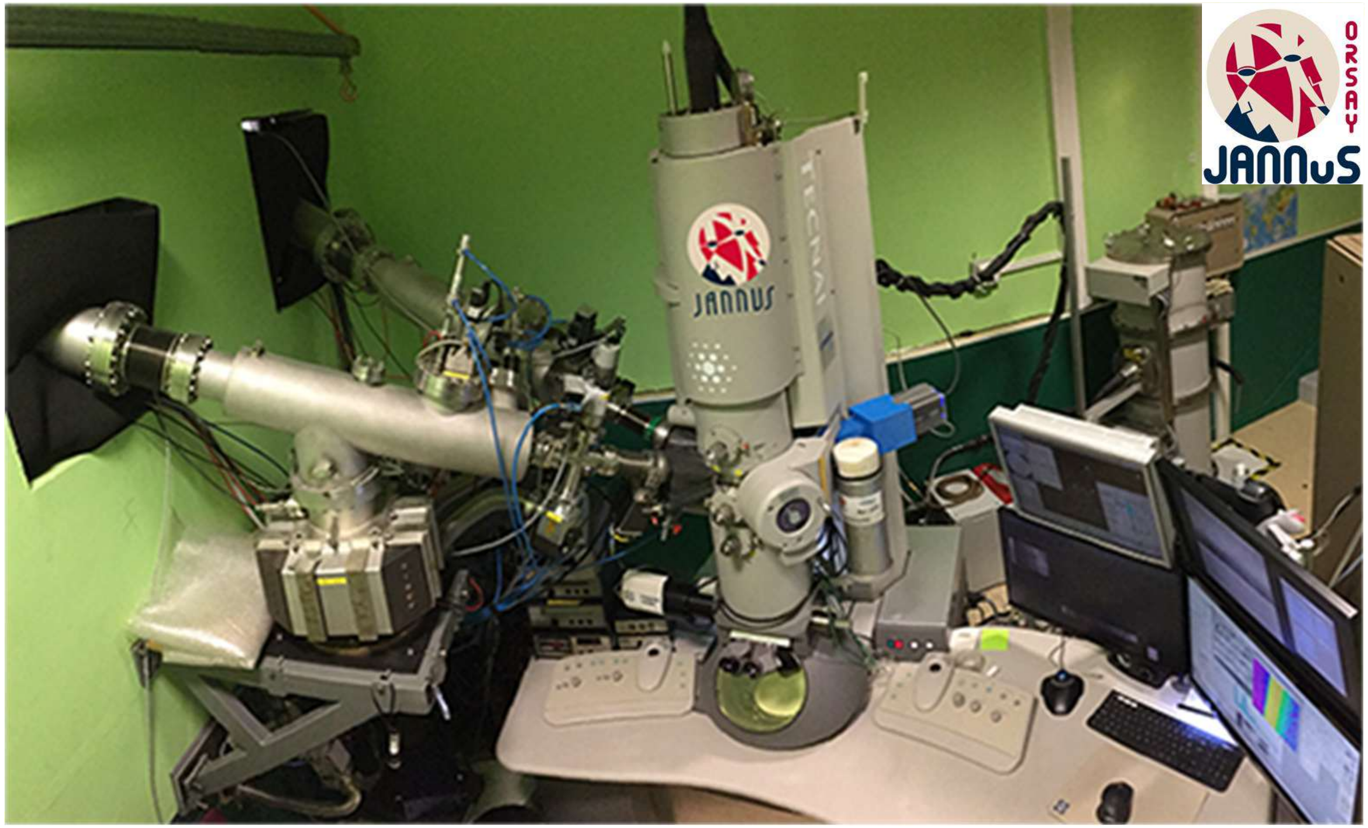
Motivation

In situ nitrogen implantation in the TEM

Why Nitrogen ?

N doped MXene have better performances than C-MXene:

- Electrocatalysis *Y. Yoon et al., J. Mater Chem. A (2018), P. Urbankowski et al., Nanoscale (2017)*
- Charge storage F. Yang, J. Mater Chem (2021), *M. Cai et al., Chem Eng. J. (2023)*
- Electrical conductivity (DFT) *Y. Wen et al., Nano Energy (2017)*



Why *in situ* ?

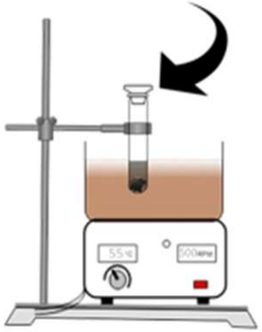
- Study the evolution of the very same flake
- No oxydation from the ambient air

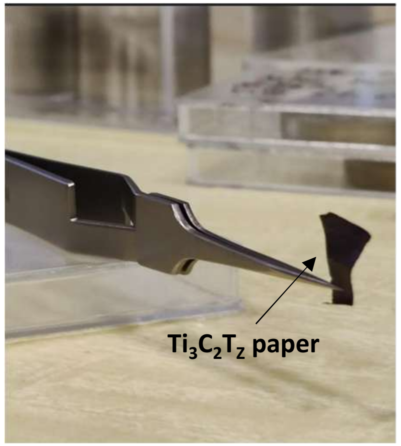
Materials and Methods

Sample synthesis and TEM grid preparation

Chemical exfoliation and delamination of Ti_3AlC_2
⇨ **$Ti_3C_2T_z$ powder**

Ti_3AlC_2
in LiF + HCl
at 40°C 24h





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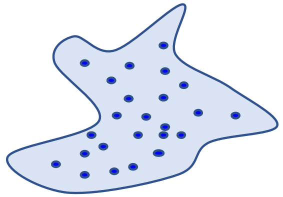
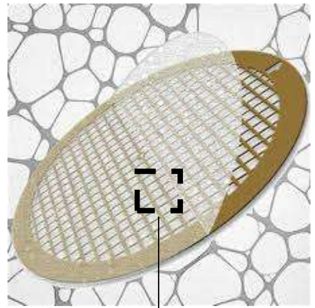
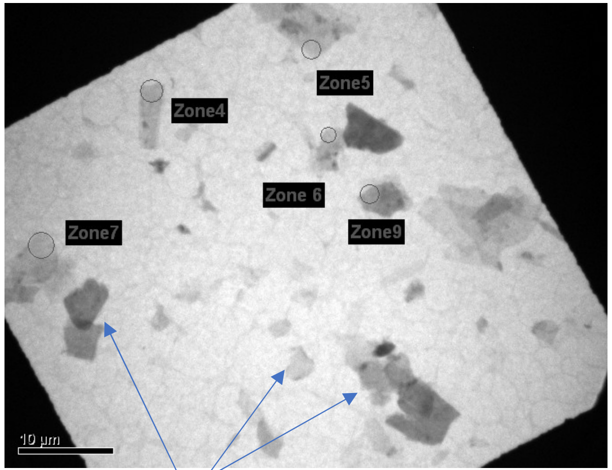


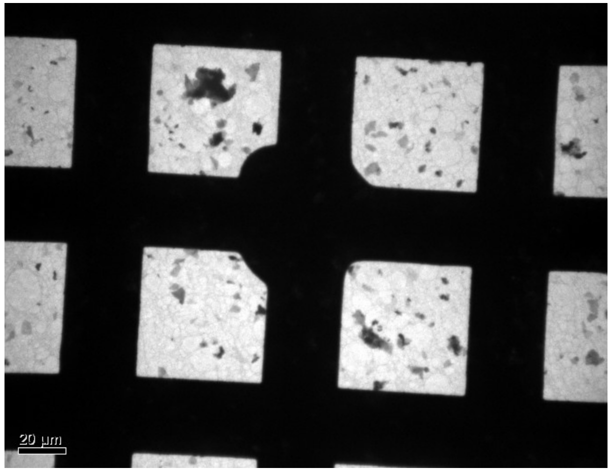
+ deionized water

Colloidal solution



Lacey carbon copper TEM grid





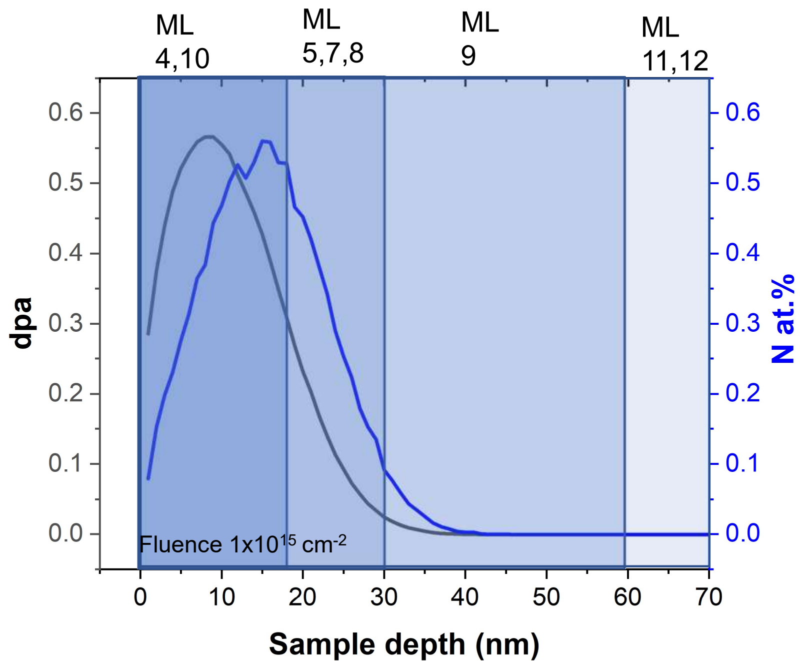
Multilayers -> tens of nm thick
Few microns wide

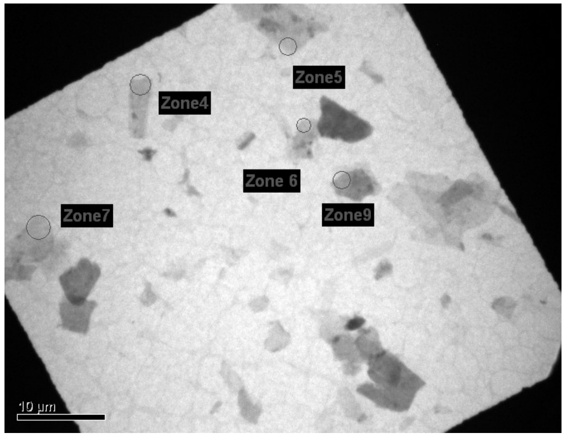
N implantation

In situ ion implantation conditions

Goal: N incorporation ? Structural damage ?

- **Multilayer thickness**: 15 – 70 nm (8 multilayers)
- **Ion, energy**: N^+, 7.5 keV (N_2^+, 15 keV), R_p=18 nm
- **Fluence**
  - 7 steps of irradiation (1 week experiment)
  - Cumulated fluence : 1×10^{14} ⇨ 2×10^{16} N^+/cm^2
  - Damage at max : 0.05 – 10 dpa





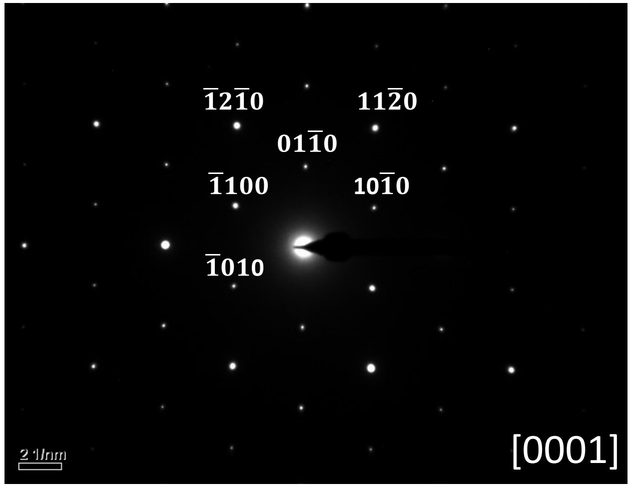
- **Dose rate:** 3.9-9.2x10^{11} ions/cm^2/s
- **Characterization (FEI TECNAI G^2, 200 kV, LaB_6)**
  - Bright-field TEM
  - Electron diffraction
  - Electron Energy Loss Spectroscopy (EELS)

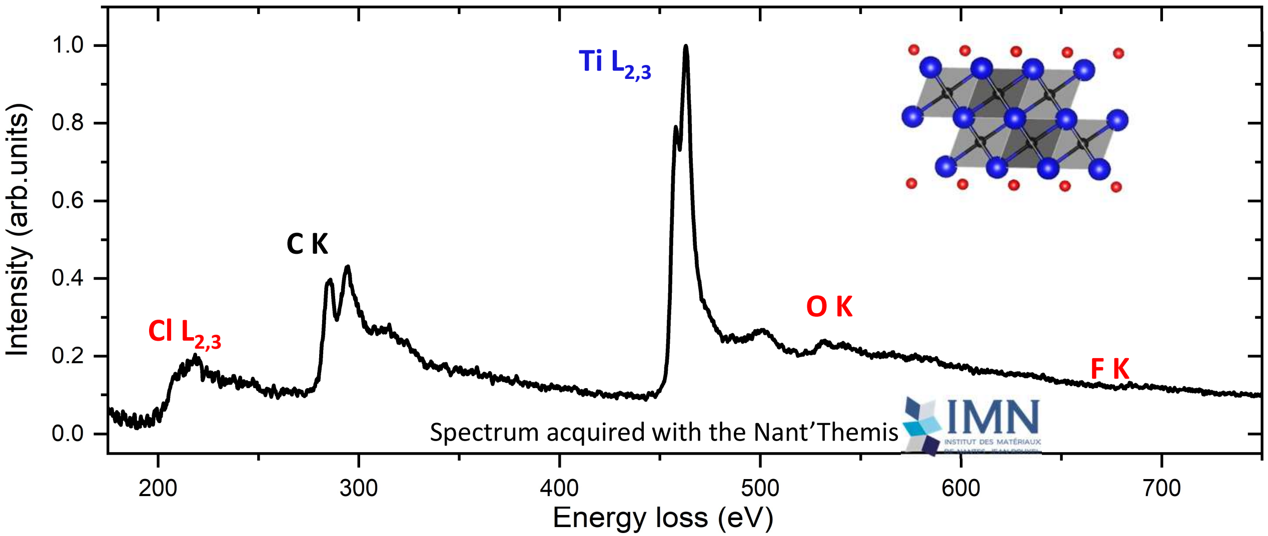
N implantation

Ex situ ion implantation conditions

- **Ion, energy:** N^+, 5 keV (N_2^+, 10 keV)
- **Flake thickness** : ~2 nm – 70 nm (50 multilayers)
- **Fluence:**
  - Fluence : 1×10^{16}, 2×10^{16} N^+/cm^2
  - Damage at max : 5, 10 dpa
- **Dose rate:** 1.8×10^{13} ions/cm²/s

- **Characterization (JEOL 2200 FS, 200 kV, Ω filter)**
  - Bright-field TEM
  - Energy-filtered electron diffraction
  - EELS

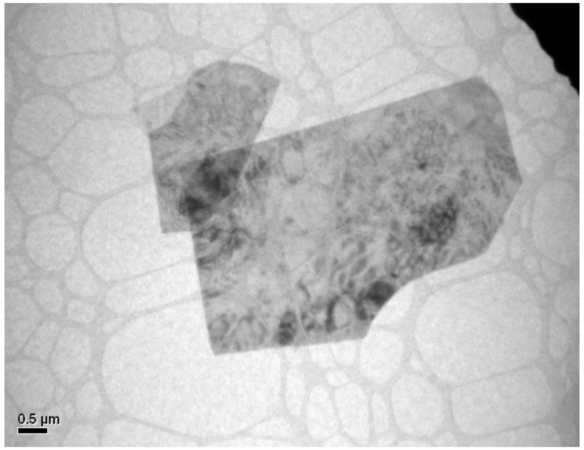




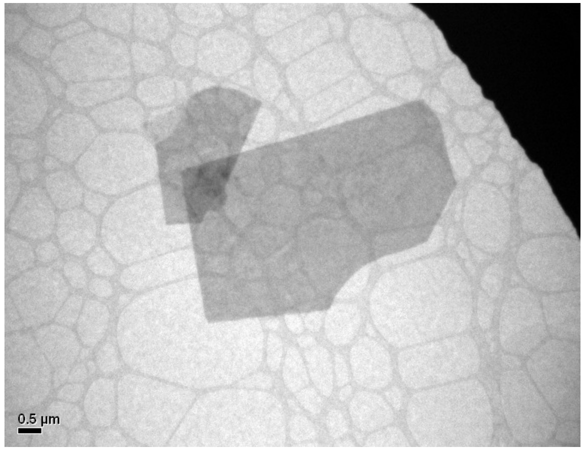
Results and discussion

Morphological evolution

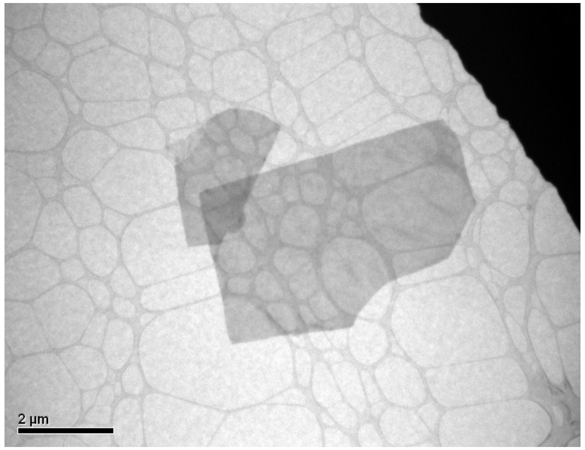
Pristine



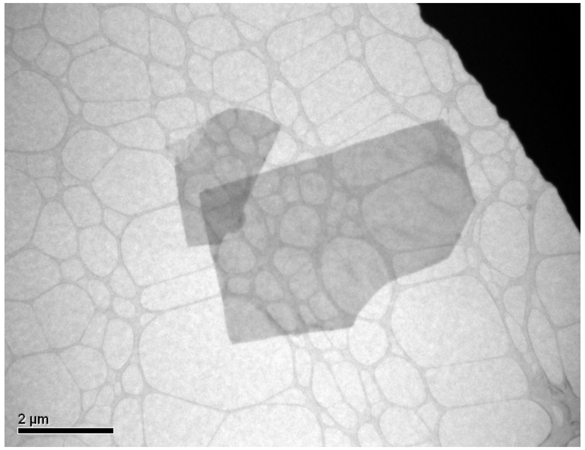
$5x10^{14}$ cm^{-2}

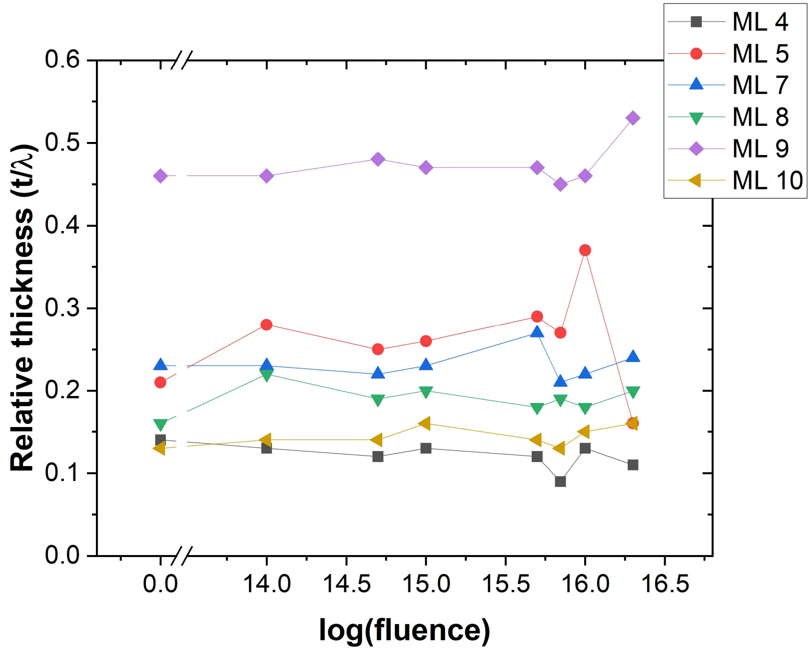


$5x10^{15}$ cm^{-2}



$2x10^{16}$ cm^{-2}



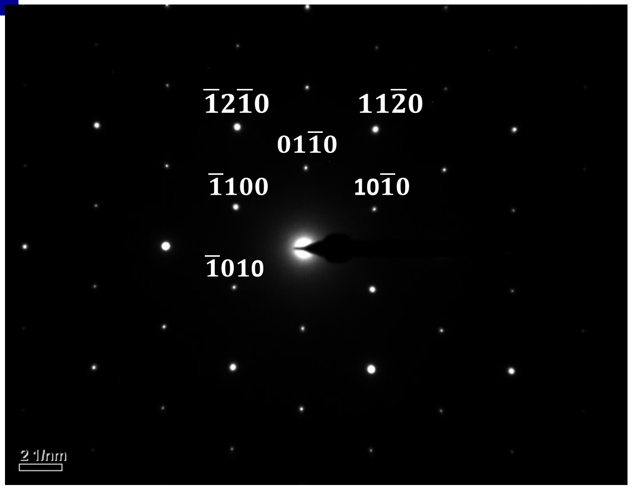


- No shape modification
- No sputtering

Flake 7 (0.23)

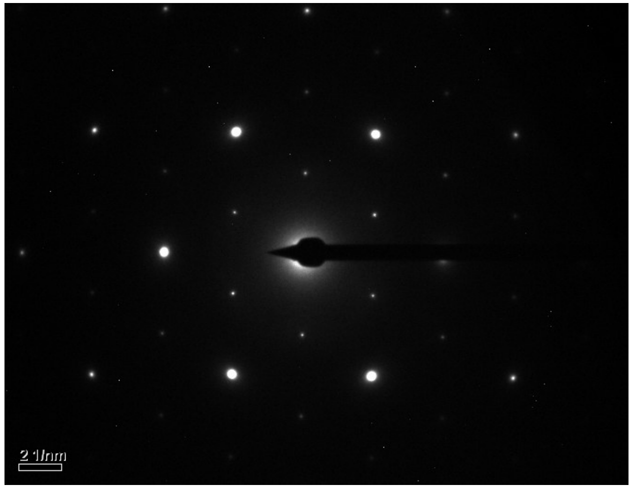
Microstructural evolution

Pristine

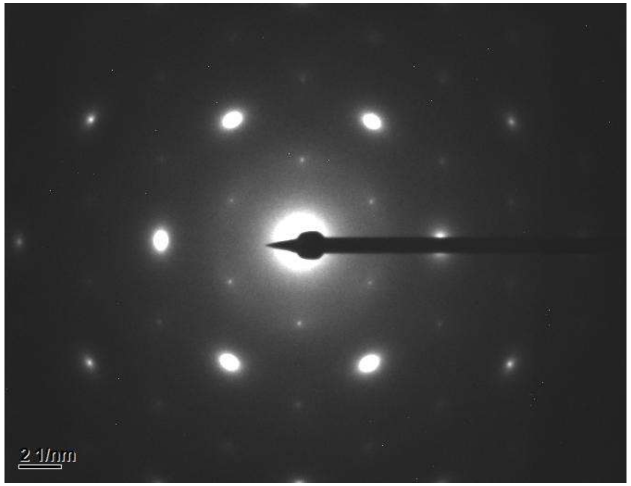


5x10^{14} cm^{-2}

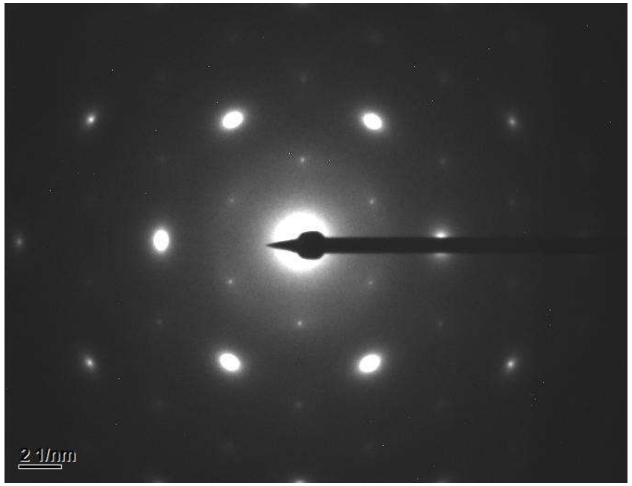
1x10^{15} cm^{-2}



5x10^{15} cm^{-2}



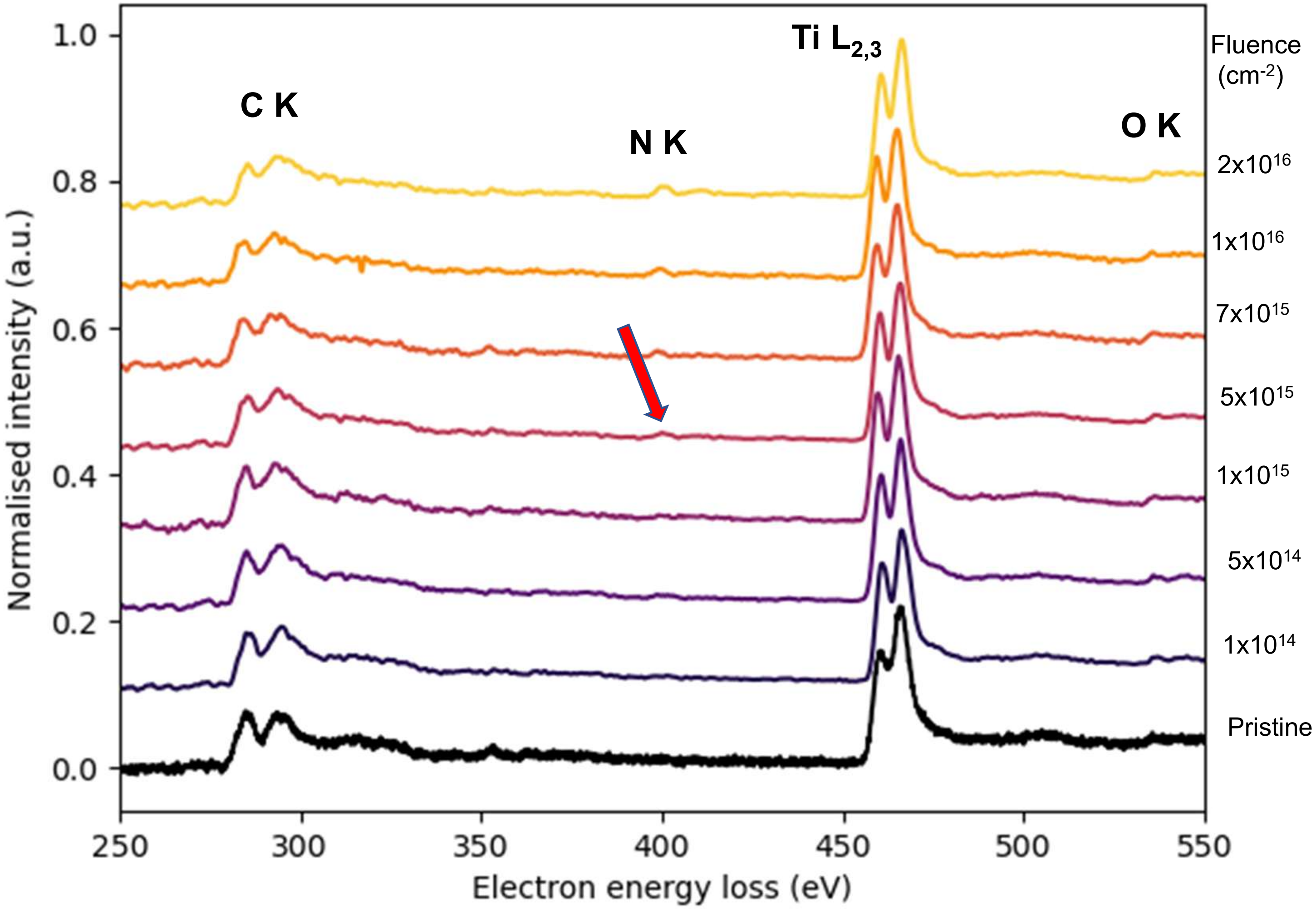
2x10^{16} cm^{-2}



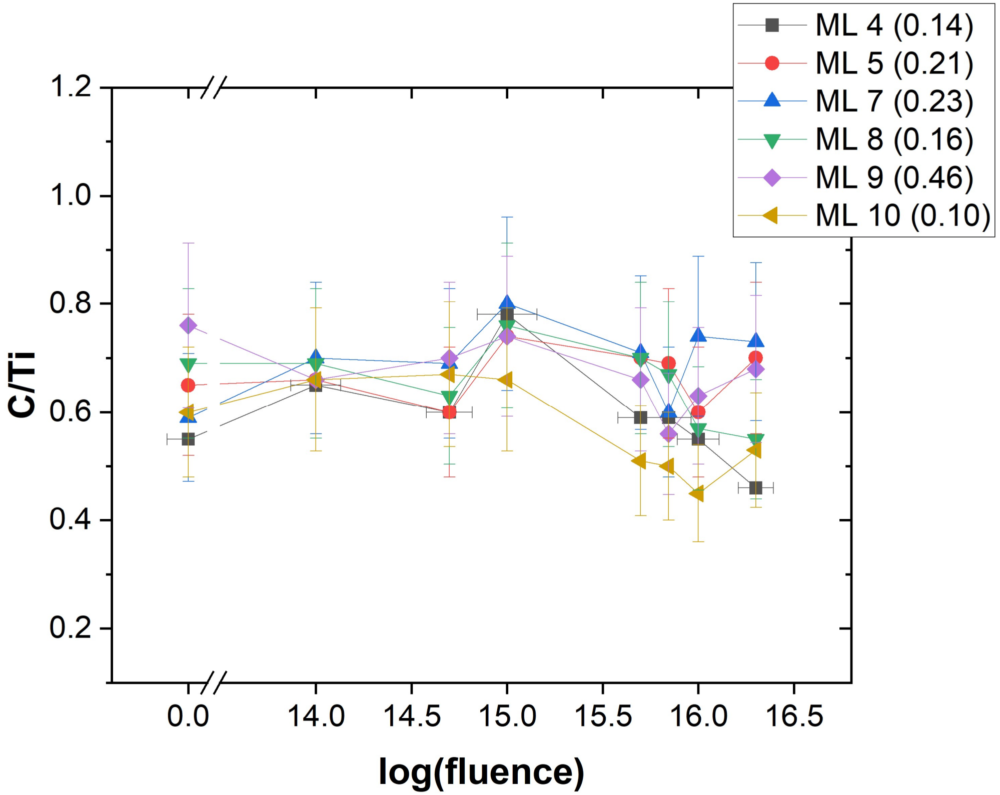
- Structural disorder ↑ with fluence
- No sign of oxydation

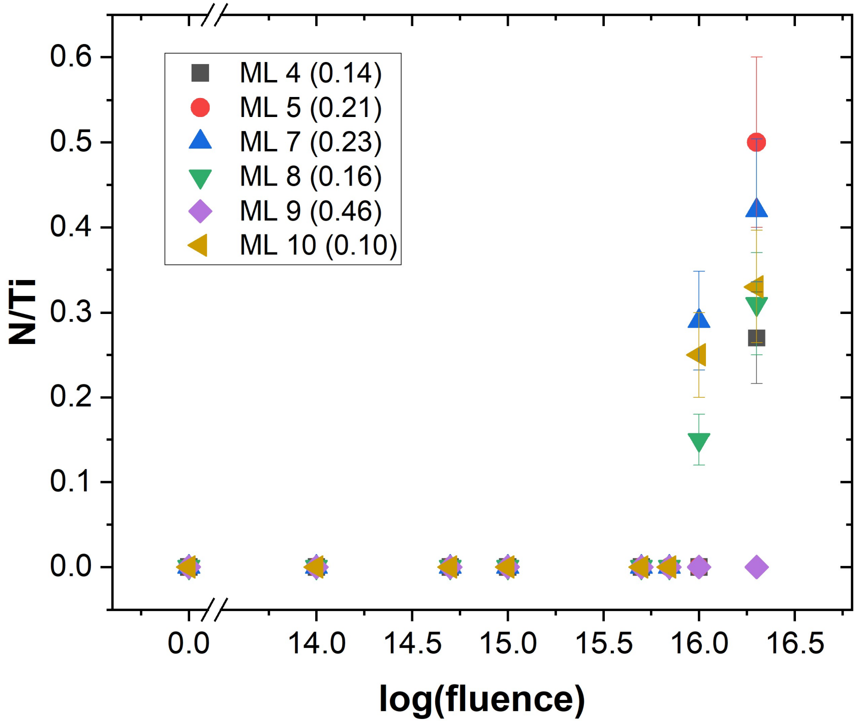
Flake 7 (t/λ=0.23)

Elemental analysis (EELS)



Elemental quantification (EELS)

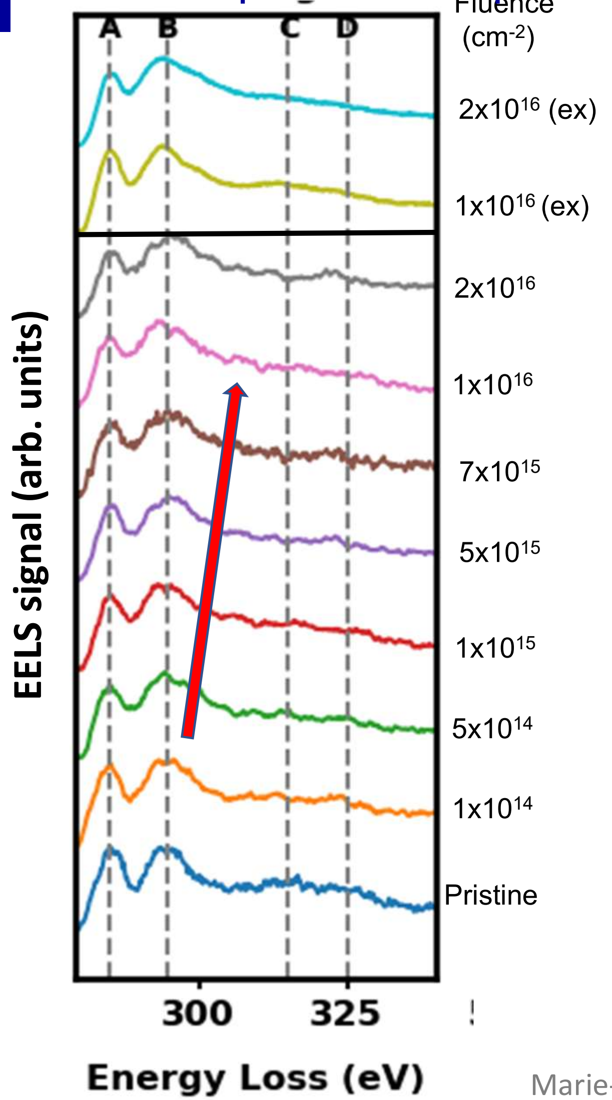


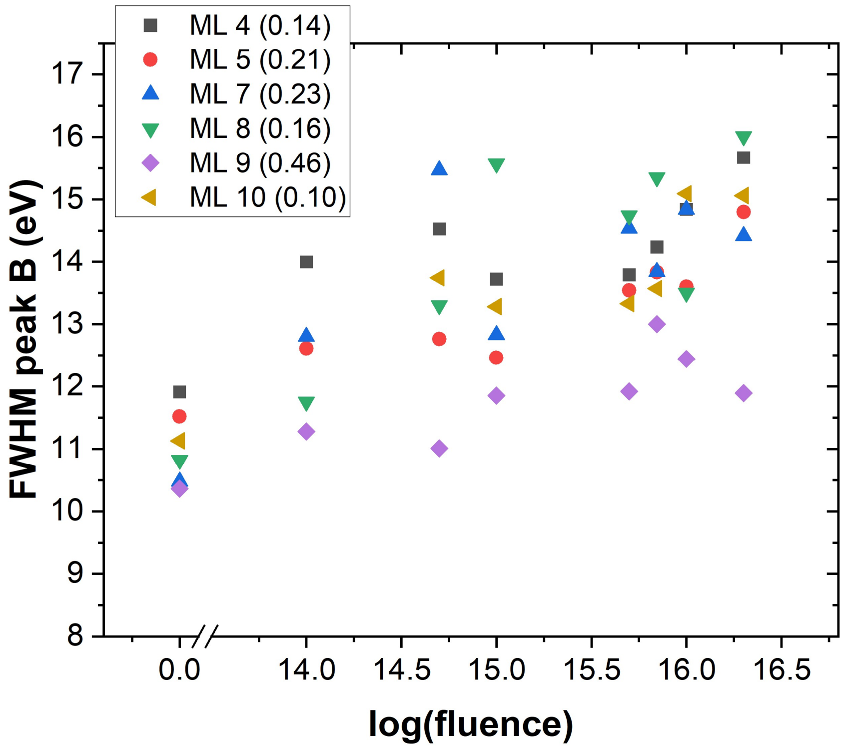


- No visible modification of the C/Ti ratio
- Detection of N for a fluence of $5\text{x}10^{15}$ cm^{-2}
- Successful incorporation of N up to 15 at%
- No correlation between C/Ti and N/Ti

EELS-fine structure analysis : C K-edge

N ion implanted samples

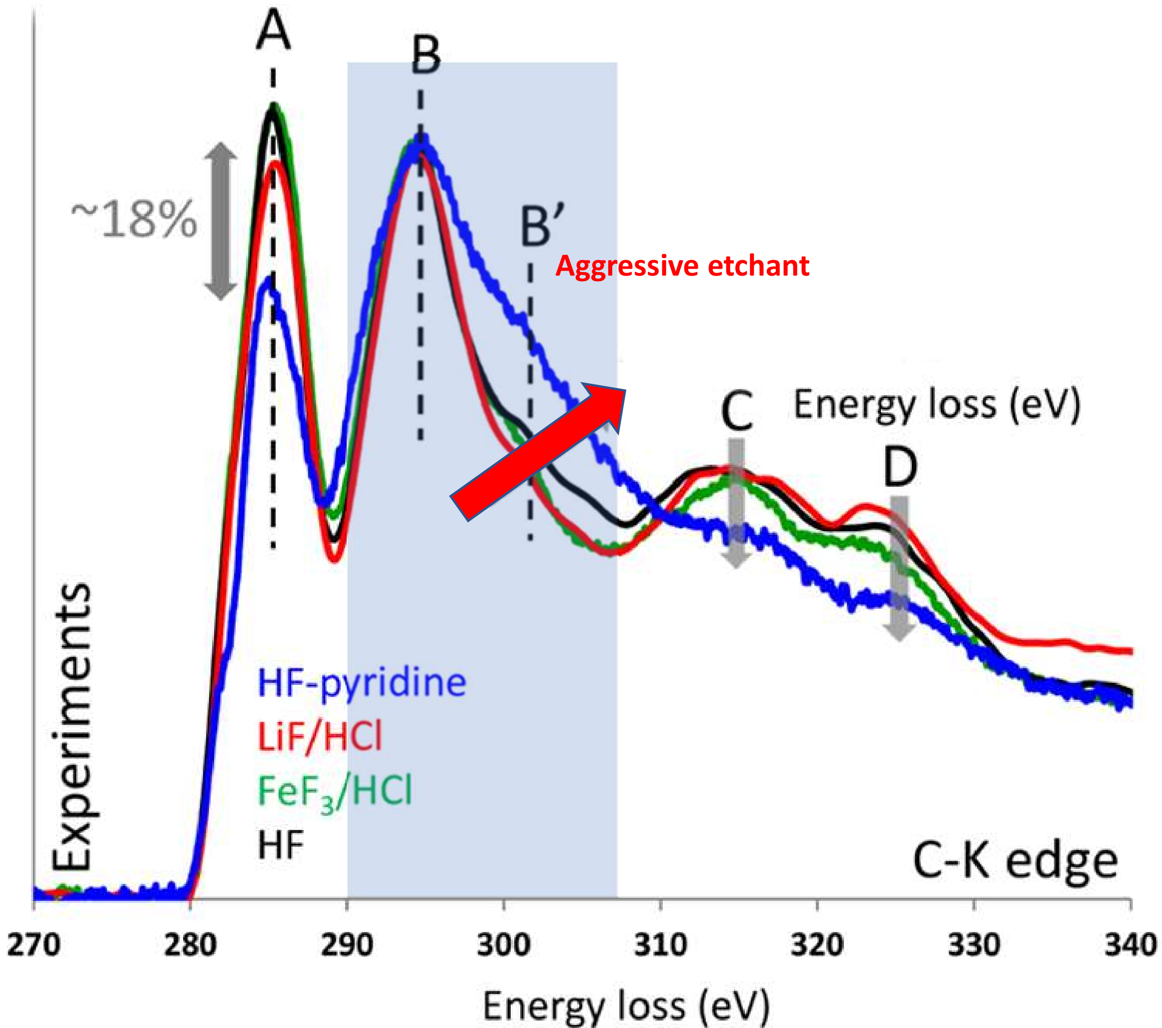




- Broadening of peak B of the C K-edge with the fluence
- ⇨ gradual increase of defect amount in the **Ti_3C_2 skeleton**

EELS-fine structure analysis : C K-edge

$Ti_3C_2T_z$ synthetized using different etchants

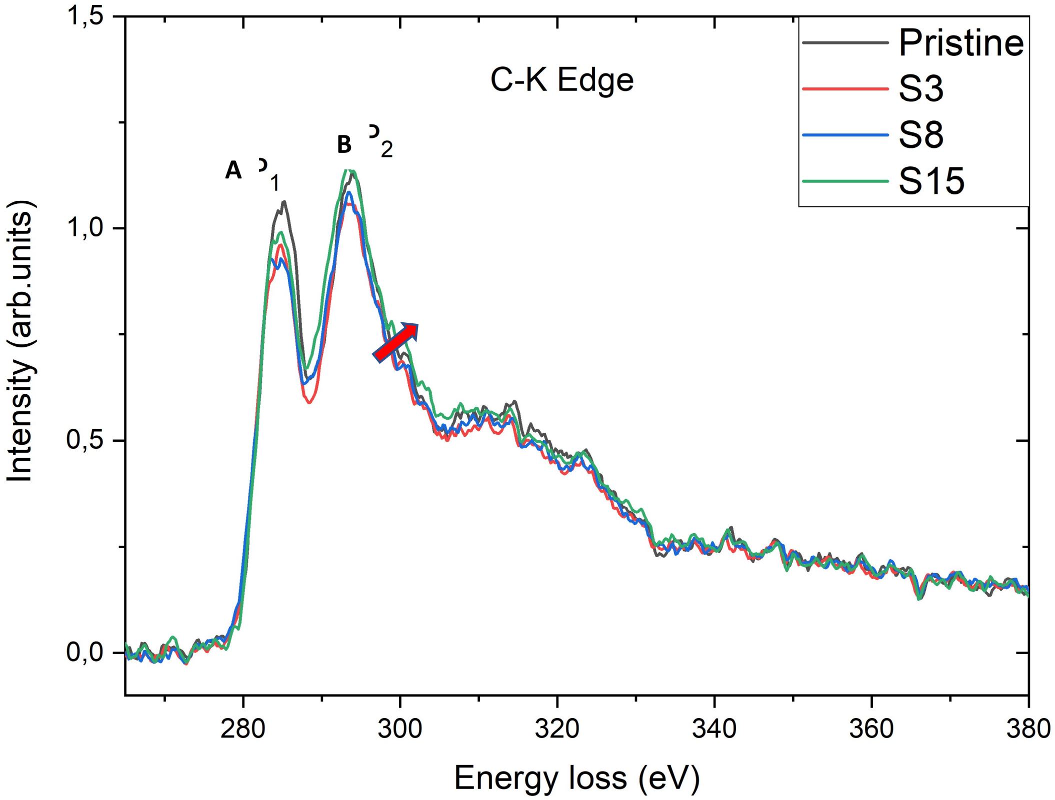


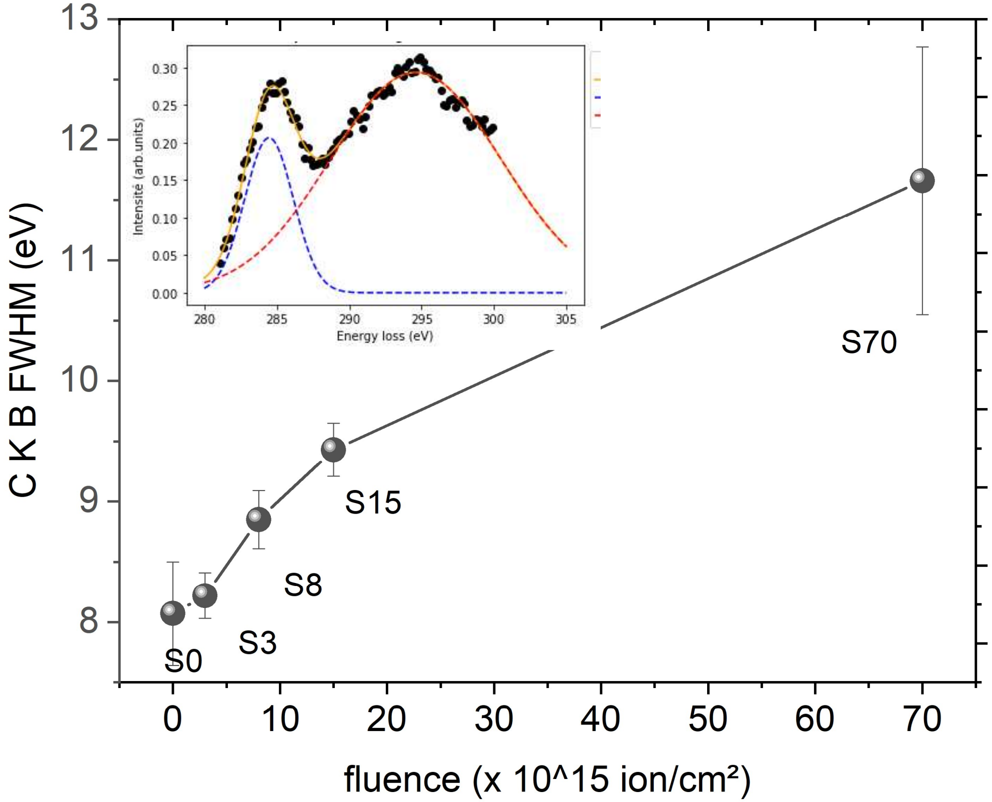
➡ Peak B (B') of the C K-edge: structural disorder in the Ti_3C_2 skeleton

Bilyk et al., J. Phys. Chem. C, 2020, 124, 49, 27071–27081

EELS-fine structure analysis : C K-edge

He ion irradiation, 180 keV, 3-70x10^{15} cm^{-2}

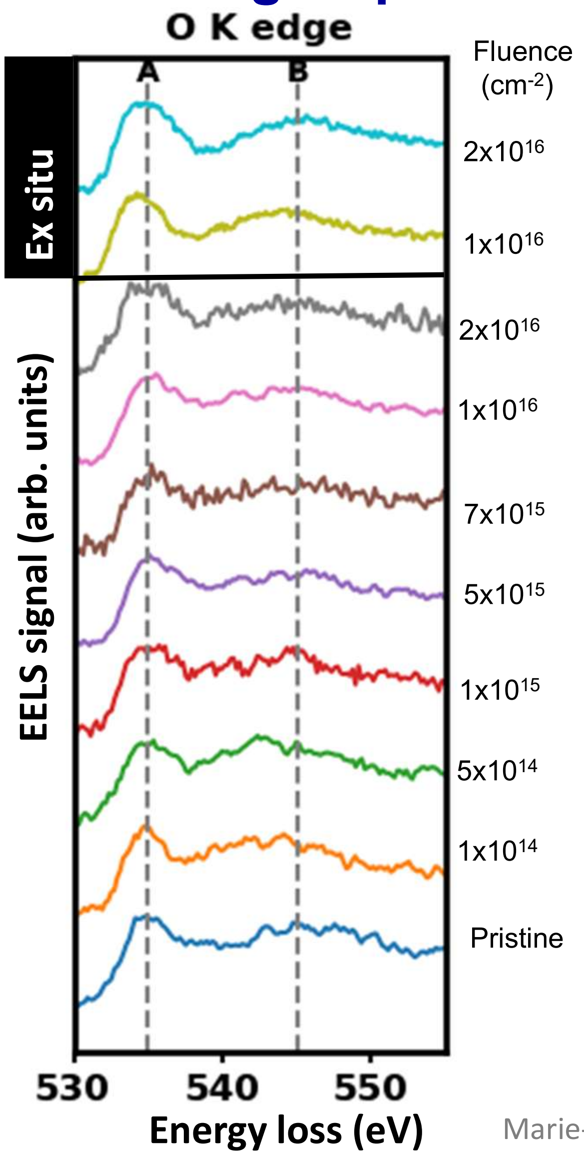


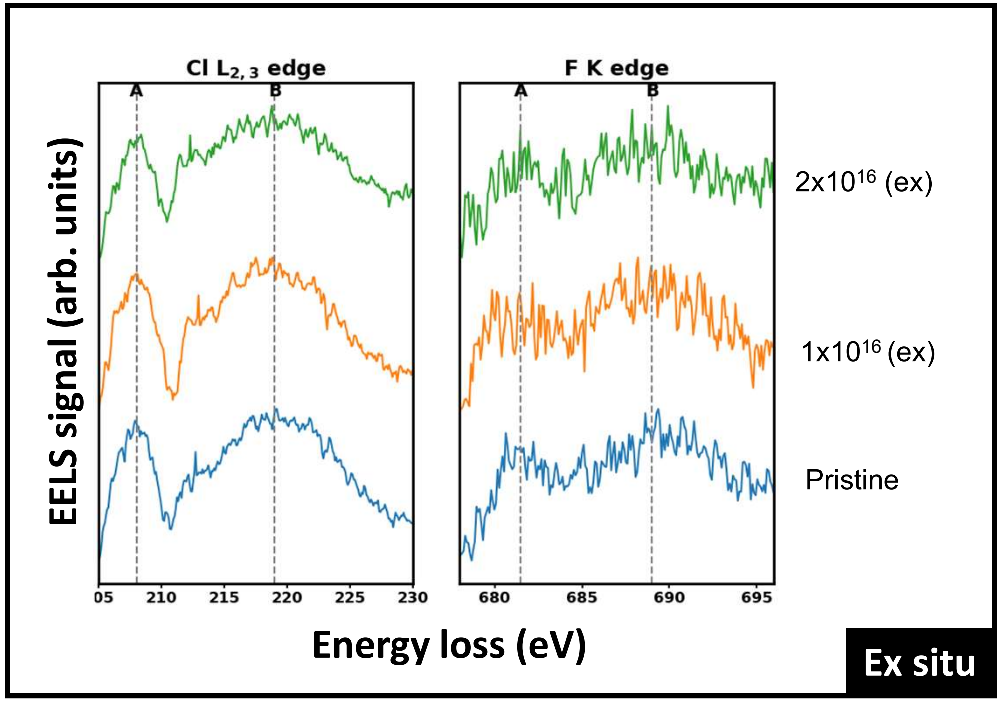


➡ Gradual increase of peak B of the C K-edge as a function of the amount of defects in the **Ti_3C_2 skeleton**

A. Benmoumen et al., App. Surf. Sci. 652 (2024) 159206

Surface groups



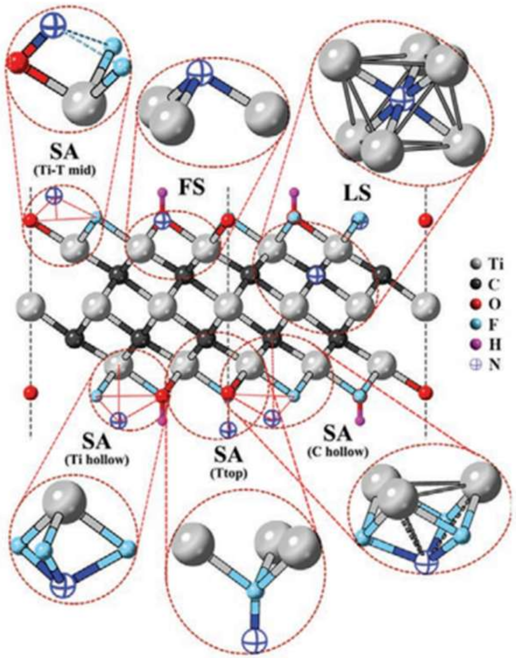


- No sputtering and no modification of the O K-edge revealed
- The same for *ex situ* experiments
- The same for Cl and F (*ex situ*)

⇨ **Surface groups are not sputtered by N ions**

Behavior ≠ from in situ e- irradiation where Cl and F are sputtered.
O content is stable. **A. Benmoumen *et al.*, to be published**

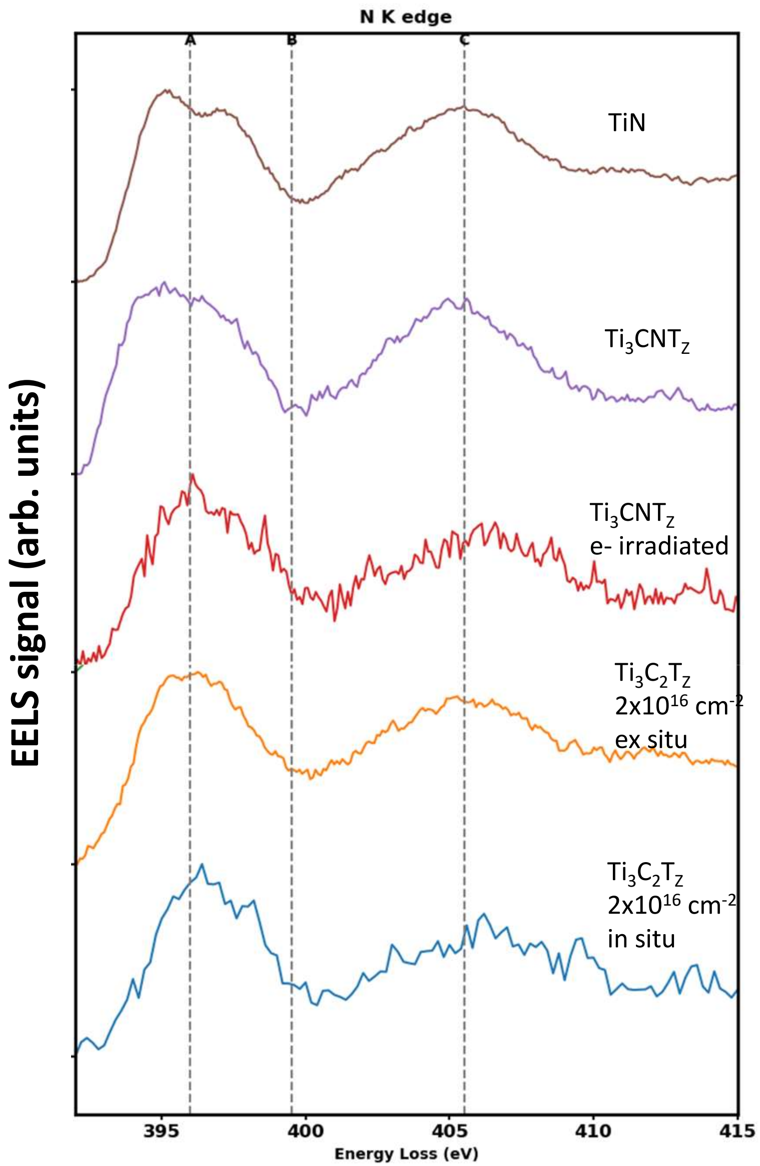
Nitrogen doping



Chengjie Lu *et al.*,
Adv. Funct. Mater. 2020

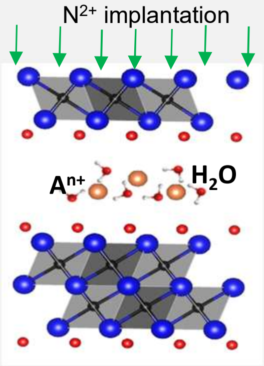
- ~~Surface group substitution ?~~
- ~~Adsorption ?~~
- **Carbon substitution in Ti octahedra with structural disorder ?**

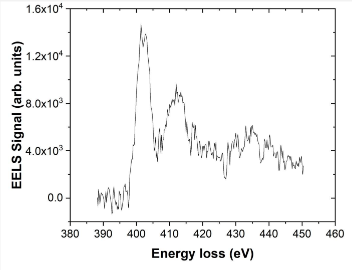
DFT calculations and XPS in progress…



Coll. B. Anasori, A. Thakur, Purdue Univ., USA

Summary and outloook



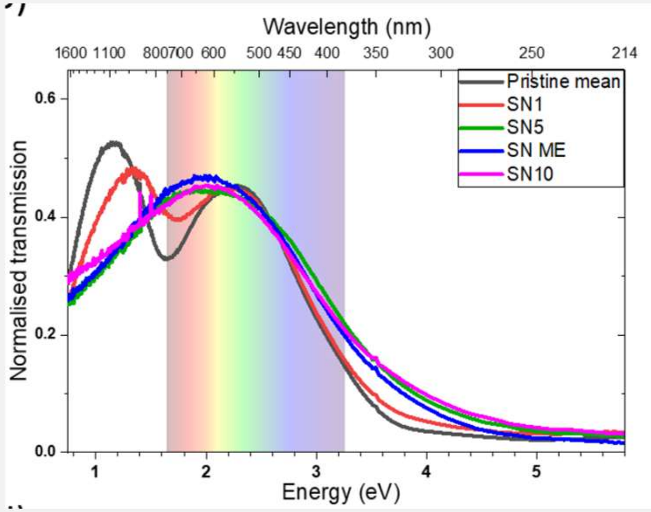


N ion implantation in situ in the TEM (7.5 keV, $1x10^{14}$ – $1x10^{16}$ cm^{-2})

- ⇨ **No sign of oxidation**
- ⇨ **No sputtering of the surface groups**
- ⇨ **Introduction of structural disorder (TiC octahedra)**

- ⇨ **Incorporation of N up to 15 at%**
- ⇨ **N in substitution of C in TiC octahedra (with strutural disorder)?**

- ⇨ **DFT calculations ?**
- ⇨ **Effect of temperature ?**
- ⇨ **How can we relate the microstructural characteristics to the material properties?**



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B. Anasori
A. Thakur

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