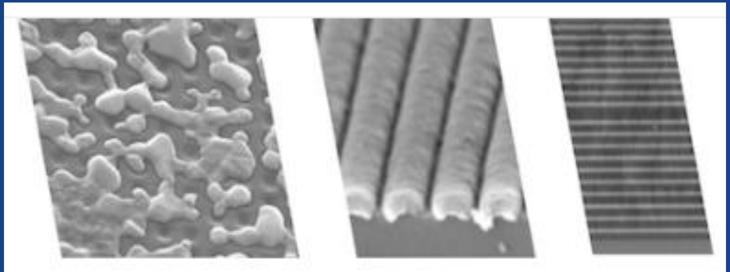
SURFACES ET INTERFACES DU VERRE : ETAT DE L'ART DE LEUR CARACTÉRISATION (PART 1)



Ecole thématique du CNRS, Surfaces et Interfaces du verre

Hervé Montigaud

SVI - Saint-Gobain Research Paris

Oléron, 15-20 octobre 2023

TRANSVERSAL R&D CENTERS BY SAINT-GOBAIN

UNION POUR LA SCIENCE ET LA TECHNOLOGIE VERRIÈRES

SVI SURFACE DU VERRE ET INTERFACES

CNRS advancing the frontiers

SAINT-GOBAIN RESEARCH PARIS

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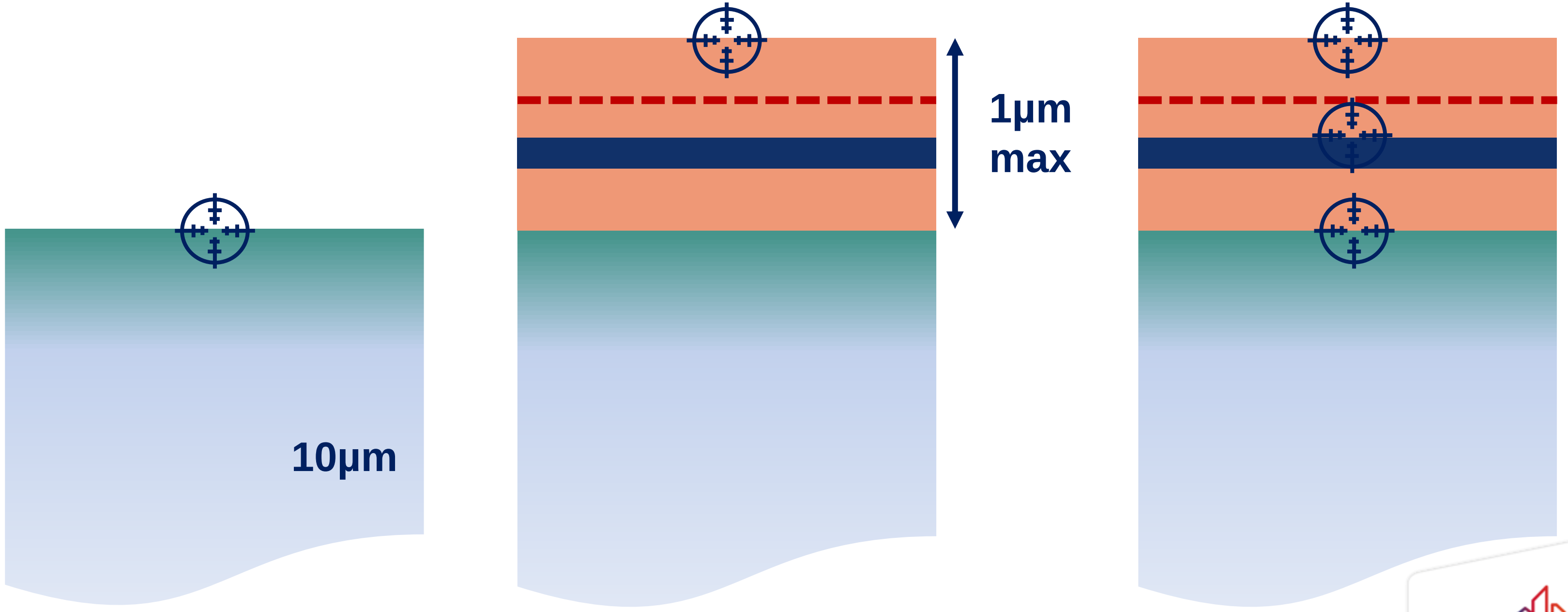
SURFACES AND INTERFACES OF GLASS

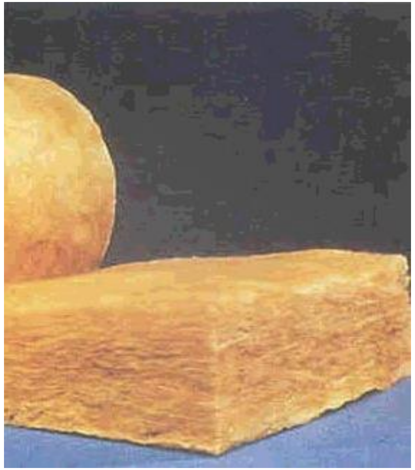
Glass surface | **Thin layer stack** | **Thin layer surface & interface**

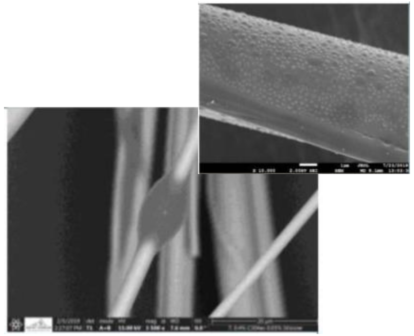


SAINT-GOBAIN RESEARCH PARIS

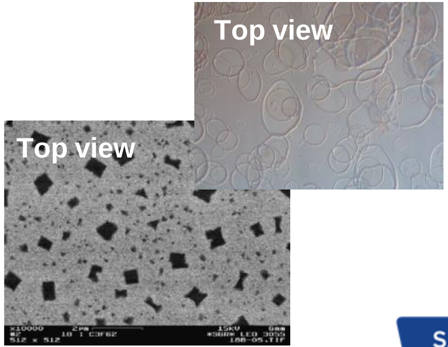
CONTEXT OF THE GLASS SURFACE

Wool

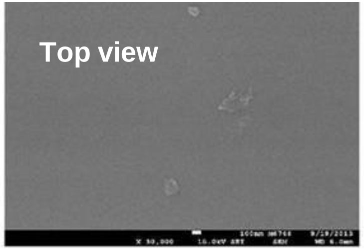




Bottle



Flat Glass

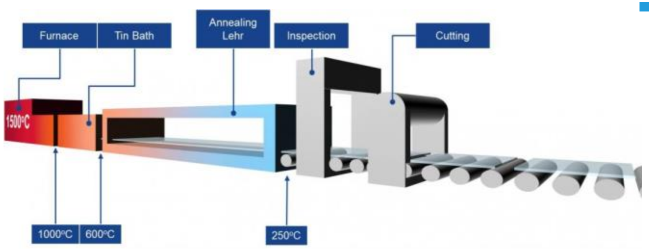


(scale bar : 100nm)

[…]

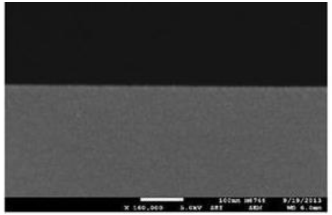
Focus on the surface

CONTEXT OF FLOAT GLASS



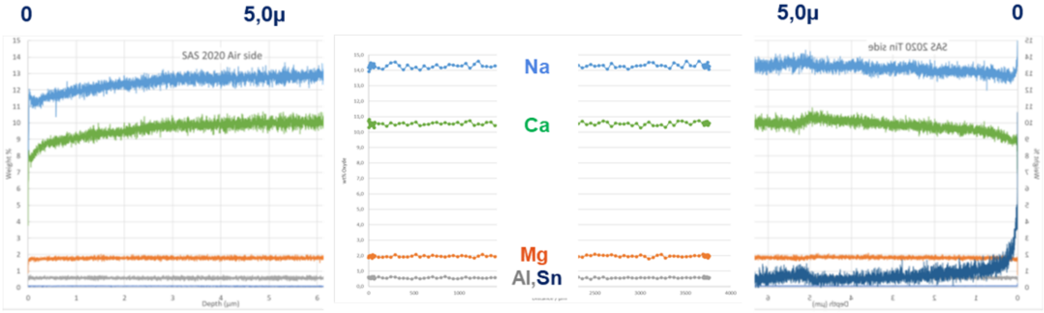
A very flat surface

- Both side (as produced)



Gradient of composition through the glass thickness

- Example of 4mm thick float glass



- **Atm side:**
  - Na and Ca amount reduction
- **Bath side:**
  - Sn enrichment
  - Na and Ca amount reduction

https://zbindendesign.wordpress.com/category/trucks/

Application

- Glazing

Saint-Gobain confidential & proprietary

FUNCTIONALIZED GLAZING / COATINGS

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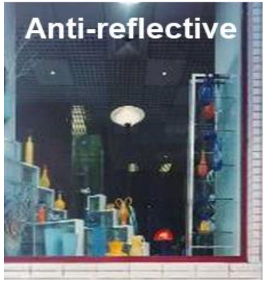
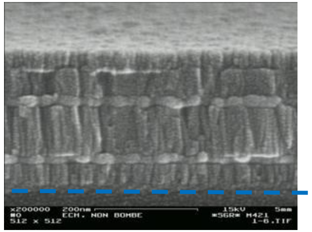
Float glass substrate

PVD coater

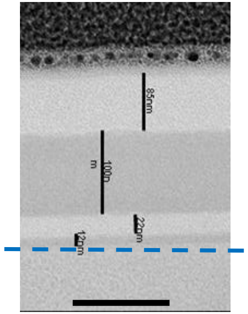


Layer stack

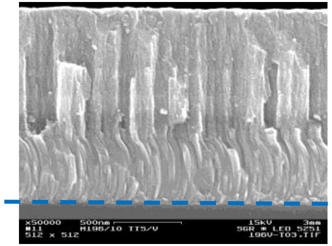
Float glass substrate



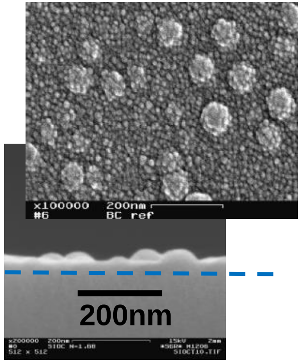
200nm



100nm



500nm



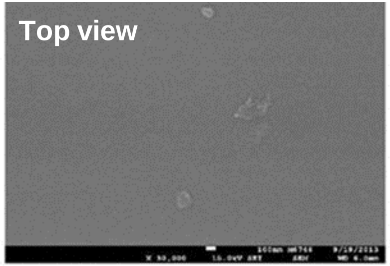
200nm

The glazing performances are correlated to the <u>glass (surface included) + thin film characteristics</u>

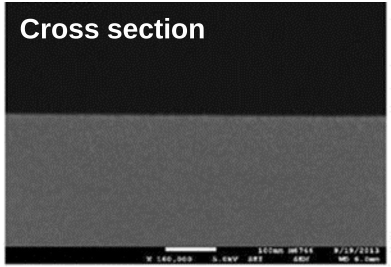
THE FLAT GLASS EVOLUTION

Float Glass surface

- Atmospheric side, just produced and cleaned



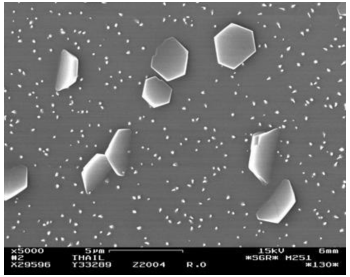
(scale bar : 100nm)



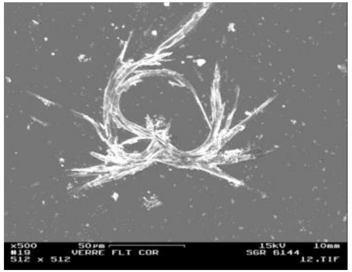
(scale bar : 100nm)

Float Glass surface

- After few time (ageing)

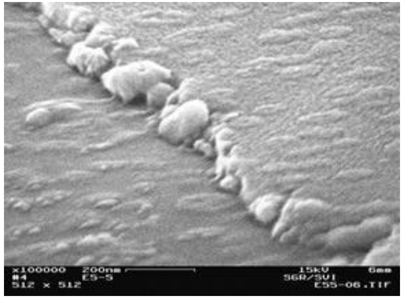


(scale bar : 5µm)



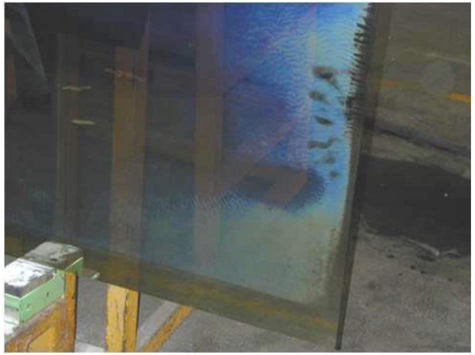
(scale bar : 50µm)

Corroded Float Glass + coating



Com. A lelarge (scale bar : 200nm)

Corroded Flat Glass



The ageing phenomena occurring start at the nanoscale

See O Majerus lecture (thu)

Com. P Lehuédé

SPECIFICATIONS OF THE CHARACTERIZATION

- **All these phenomena require to select the appropriate tool to access the relevant information**

- **The definition of the relevant information**
  - A size (dimension)
  - The nature of the atoms present within defined area
  - The atom arrangement

- **When the relevant information is selected, further specifications have to be defined**
  - Probed resolution (0,1nm => 1µm…)
  - Probed range (1nm => 1µm…)
  - 1D, 2D, 3D.

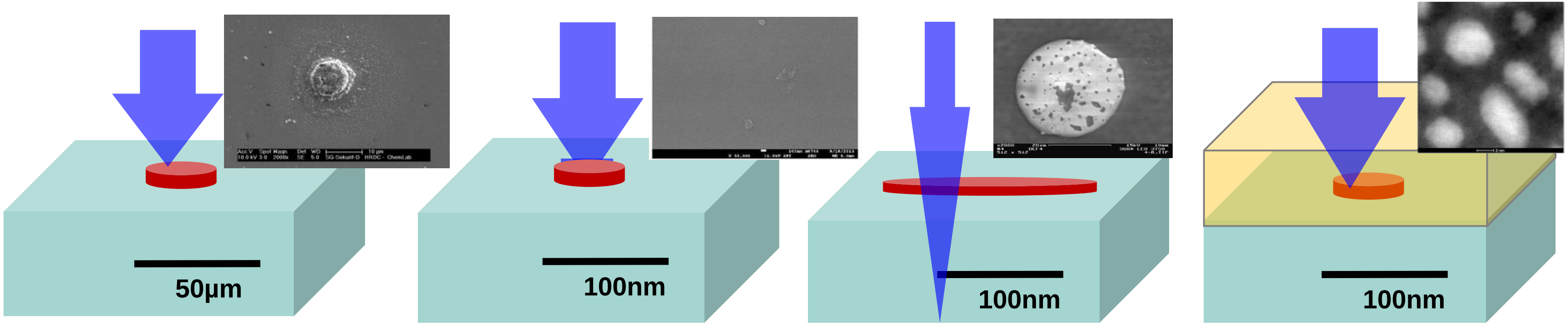
SPECIFICATIONS OF THE CHARACTERIZATION

Relevant information

- A size (dimension)
- The nature of the atoms
- The atom arrangement

Additional Specifications

- Probed resolution (0,1nm => 1µm…)
- Probed range (1nm => 1µm…)
- 1D, 2D, 3D.



Specifications concerning the technique have to be taken into account:

- Sufficient sensitivity (1%at, 1ppb…)
- Ease of accessibility
- Impact of the preparation and/or the signal acquisition on the result
- The stability (time evolution, ageing)

SPECIFICATIONS OF THE CHARACTERIZATION

List of characteristics evaluated

- A singularity size
- Surface morphology and roughness
- Thickness (layer)
- Composition and gradient
- Bondings
- Structure (Microstructure)
- Density
- Stress (and strain)

Technical specifications:

- Sufficient sensitivity (1%at, 1ppb…)
- Ease of accessibility
- Impact preparation/acquisition.
- stability

AGENDA

INTRODUCTION

- **CONTEXT FLAT GLASS, COATING AND SPECIFICATIONS**

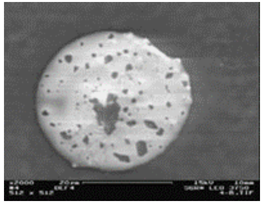
HOW TO MEASURE :

- **A SINGULARITY SIZE**
- **SURFACE MORPHOLOGY AND ROUGHNESS**
- **THICKNESS (LAYER)**
- **COMPOSITION AND GRADIENT**
- **BONDING**
- **STRUCTURE (MICROSTRUCTURE)**
- **DENSITY**
- **STRESS (AND STRAIN)**

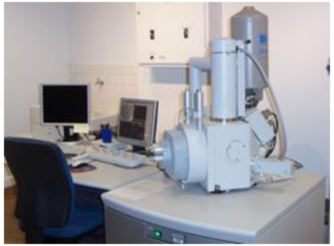
CONCLUSION

SINGULARITY SIZE

- **In plane 1 or 2 or 3 dimension(s)**
- **Examples**
  - Particles at the surface (contrast of topography and/or composition)
  - Area (local thin layer)
  - Glass inclusion
  - Local variation of the surface morphology (hole, dome, scratch…)



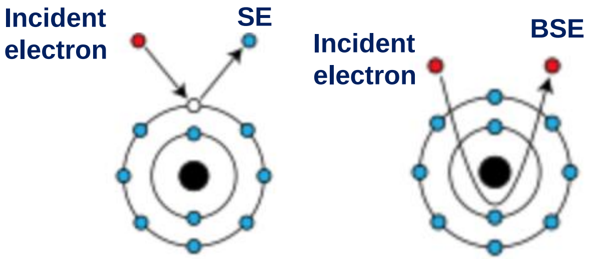
- **Techniques used**
  - Scanning Electron Microscopy collecting Secondary electrons : SEM-SE or BSE
  - Scanning Electron Microscopy collecting RX : SEM-EDS
  - Electron Probe MicroAnalysis : EPMA
  - Atomic Force Microscope

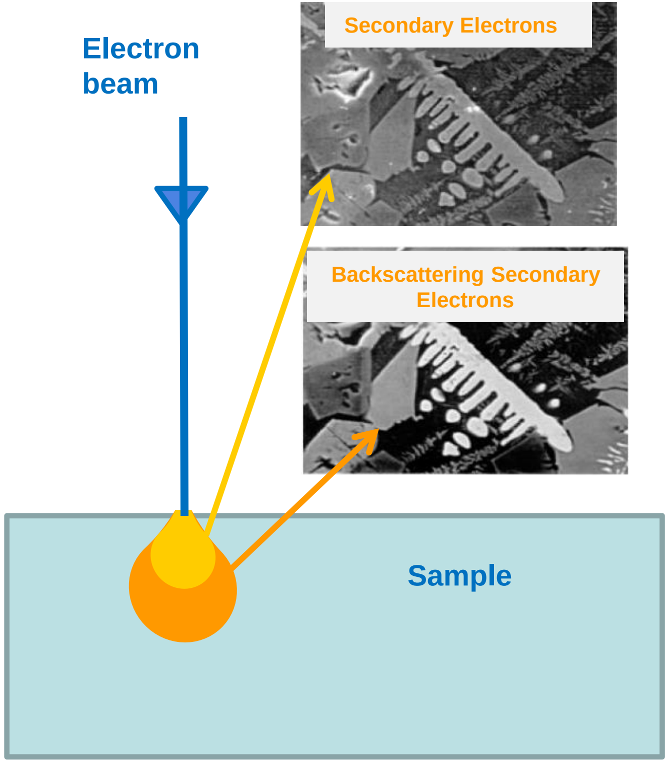


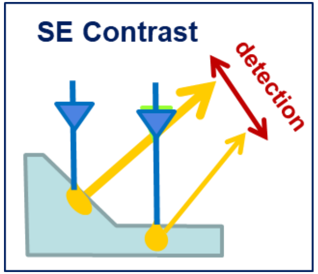
SEM PRINCIPLE

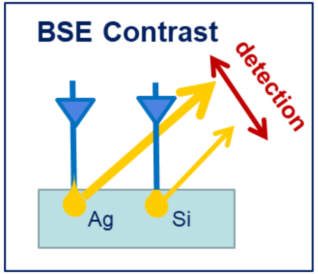
Electron / material interaction

- Under high energy (few kV to 30kV) incident electrons impact, the atoms close the surface of the sample release
  - - secondary electrons (SE) that the intensity depend on the local surface orientation.
  - - back scattered electrons (BSE with E / E_{SE}) due to quasi elastic interactions. The corresponding intensity depend on the local average Z of the atoms close to the surface.





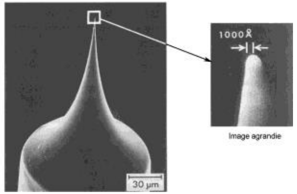




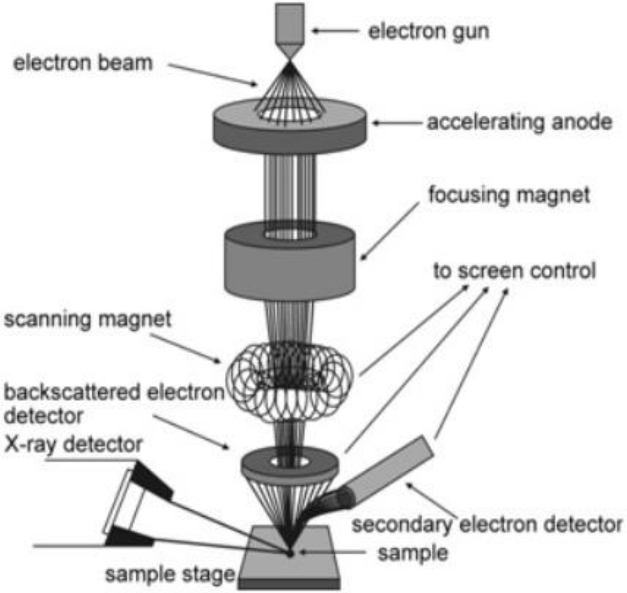
SEM: TECHNICAL POINT OF VIEW

- **Electron gun**
  - Field emission gun

  (to achieve the best lateral resolution)

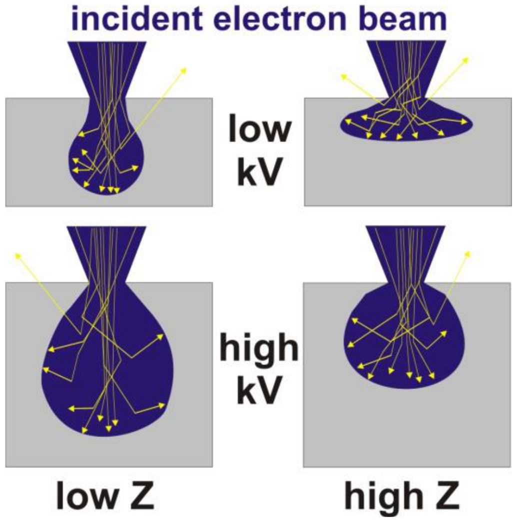


- **Focusing and scanning (lens)**
  - To focus the beam at sample surface
  - To scan the surface
- **Secondary electron detection**
  - Emitted from the sample surface
  - Detection In lens : BSE and SE
  - Lateral detection : SE
- **Sample stage**
  - x, y, z, rotation, tilt
  - Heating, cooling…



https://www.technoorg.hu/

SEM: THE KEY PARAMETERS AND LIMITATIONS



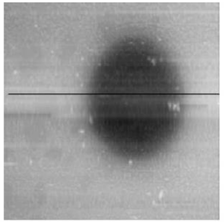
Choice of the key operating parameters

- Electrons energy (1 – 30kV) : the lateral and depth resolution
- Electrons flux : sensitivity and artifacts!

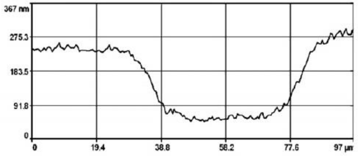
Limitations and artifacts (in case of glass)

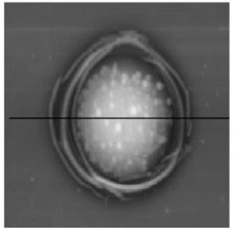
- Isolator => necessary of conductive layer at the surface in order to eliminate surface charges.
- Compromise : conductive / conformant
  (to limit the impact on surface morphology)
- If electron dose is too large => alkaline migration

Example: SiO_2, 15%K_2O, 50kV, spot size 60µm

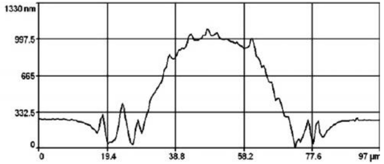


Dose= 1,3kC/m²





Dose= 64kC/m²



Gedeon, JNCS 353 (2007) 1946–1950

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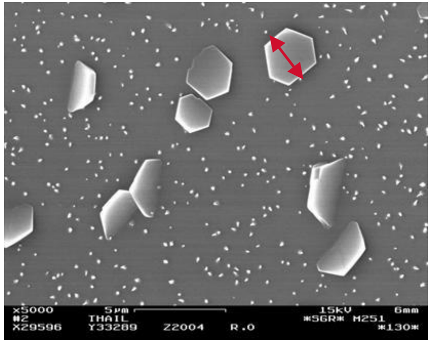
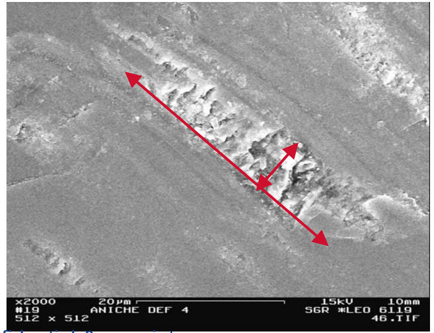
EX. CONCERNING GLASS SURFACE ANALYSE BY SEM (SE)

▶ Contrast due to surface topography

- Cristal growth after ageing (carbonate)



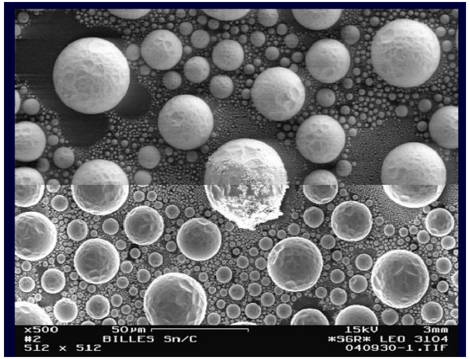
- Scratch



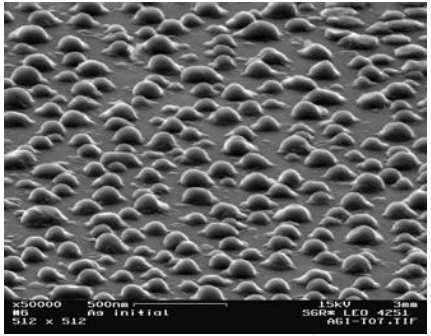
▶ Surface topography

Normal acquisition (plan view)

- lateral detector (ETD)
- In-lens



- Tilted

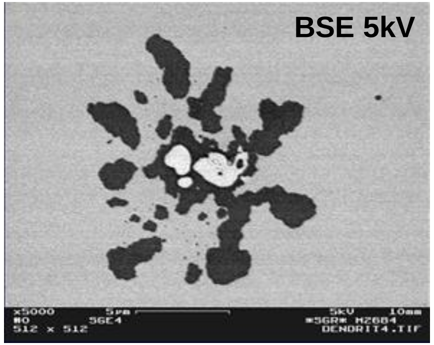


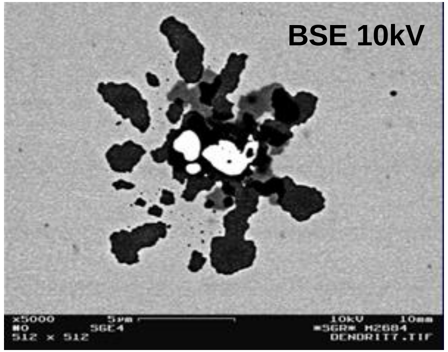
Lack of height information

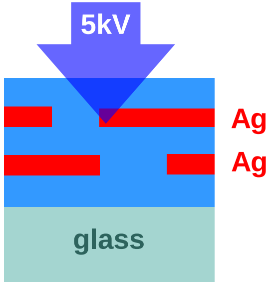
EX. CONCERNING GLASS SURFACE ANALYSE BY SEM (BSE / SE)

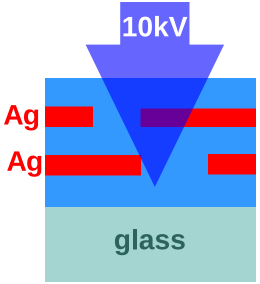
▶ BSE pictures at different E electrons

- Ag layers defects within stack



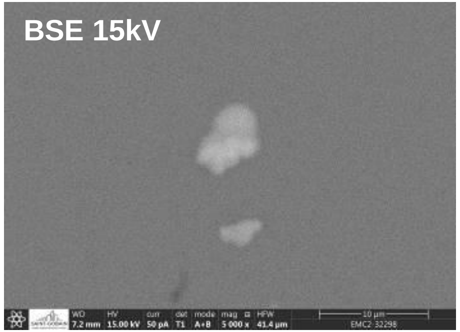


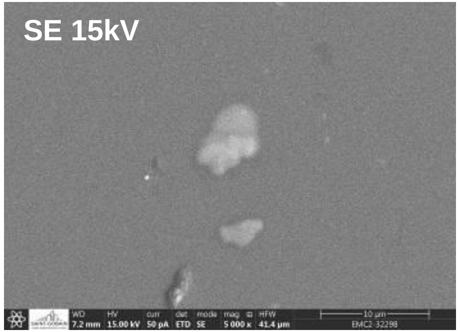


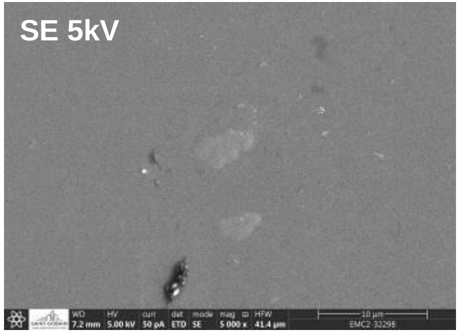


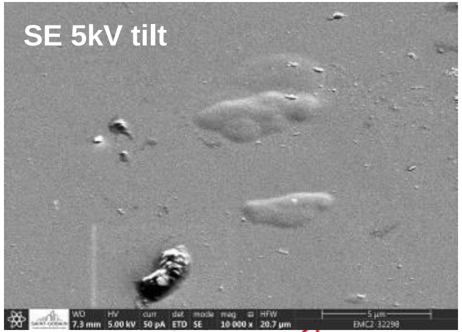
▶ BSE, SE pictures at different E electrons

- Ag layers defects at upper part of stack









Com. D Abriou, C Papret

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SURFACE SINGULARITY SIZE ASSESSMENT

Technique	Resolution lateral (depth)	Range (min-max)	Sensitivity	Materials	Sample preparation	Other (artifact, limitation…)
SEM - SE	1nm (few nm)	few nm / few mm	topography	All (compatible vacuum and e beam)	Conductive layer at surface	Alkaline migration, charging effect
SEM - BSE	>1nm (few 10 nm)	few nm / few mm	topography, Z element	All (compatible vacuum and e beam)	Conductive layer at surface	Alkaline migration, charging effect
SEM - EDS	~1µm (1µm)	few µm / few mm	Composition, B=<	All (compatible vacuum and e beam)	Conductive layer at surface	Alkaline migration, charging effect
EPMA	~1µm (1µm)	few µm / few mm	composition B=<	All (compatible vacuum and e beam)	Conductive layer at surface	Alkaline migration, charging effect
ToF-SIMS (carto)	100nm (0.1nm)	few µm / few mm	Composition all	All (compatible vacuum and ion beam)	none	destructive, alkaline migration
Raman	~1µm (1µm)	few µm / few mm	Structure, composition	All compatible with laser	none	fluorescence (laser)
AFM	0,1nm (0.1nm)	few nm / 100µm	topography / material	All	none	Tip apex radius

+ APT, STEM (BF, HAADF, EDS)

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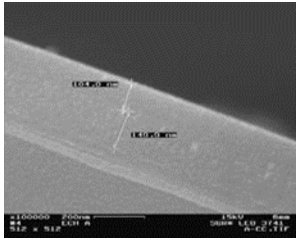
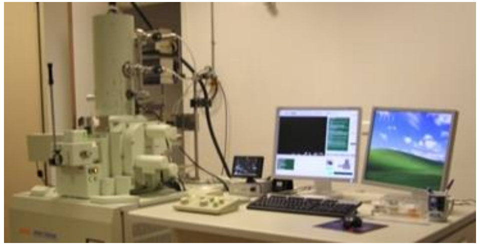
LAYER THICKNESS

- **Dimension 1D perpendicular glass surface**
- **Examples**
  - Continuous thin layers of functionalized glass (< 2µm)
  - thick layers



- **Techniques used**
  - Scanning Electron Microscopy collecting Secondary electrons : SEM-SE or BSE
  - Scanning Electron Microscopy collecting RX : SEM-EDS
  - Transmission Electron Microscopy collecting electrons (BF, HAADF)
  - Transmission Electron Microscopy collecting RX
  - Electron Probe MicroAnalysis : EPMA
  - X Ray Reflectometry : XRR
  - Secondary ion Mass Spectrometry : SIMS, ToF-SIMS
  - XPS (HAXPES)
  - Ellipsometry



LAYER THICKNESS: SAMPLE PREPARATION FOR CROSS SECTION

Objective

- Necessary to prepare a well defined cross section of the substrate and the layer

Fracture

- Simple to process when the optimum protocol is defined
- For thin layer : hot spot assisted fracture leads to better defined cross section
- Material depending (impossible for glass ceramic, tempered glass…)

Mechanical Polishing

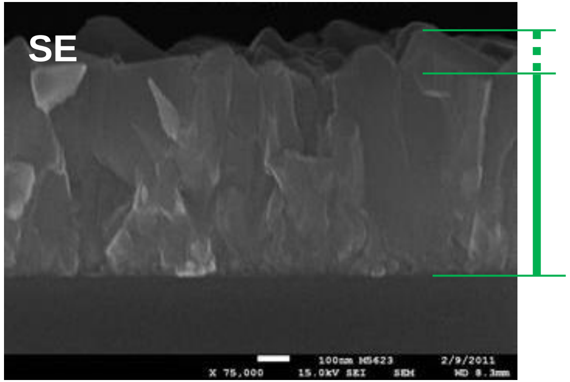
- Only useful for thick layer thick >> 1µm
- Material depending (fragile, water sensitive…)
- Time consuming

Ion Polishing

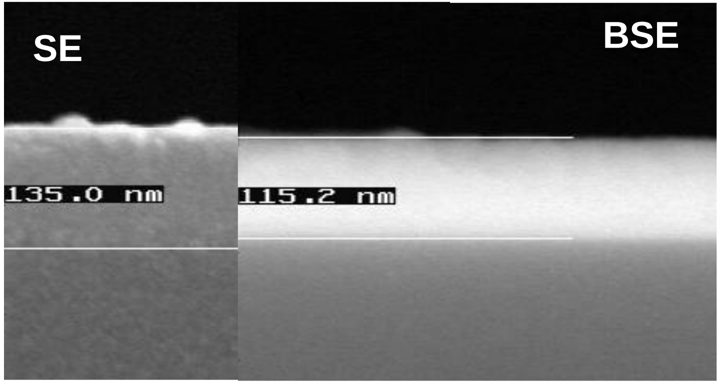
- Compatible with wide range of material (including glass ceramic)
- Available for thin layer
- Time consuming

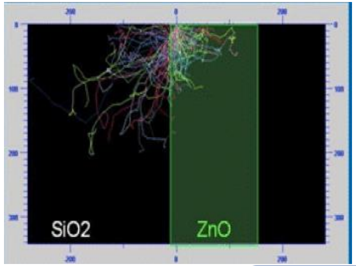
EX. OF LAYER THICKNESS EVALUATION BY SEM (SE, BSE)

- **Thick and rough layer**
  - Thickness ?

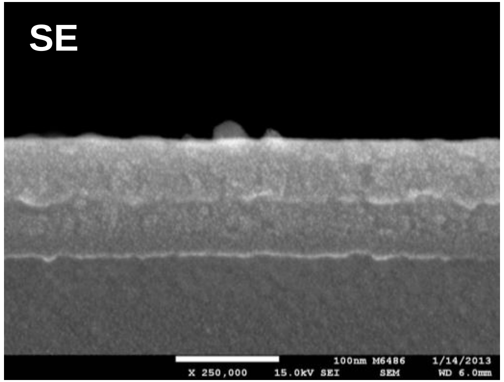


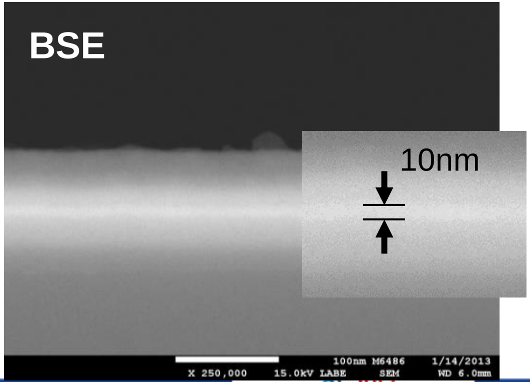
- **Thin layer**
  - SnO_2/glass: SE / BSE comparison





- **Very thin layer**
  - Low E stack





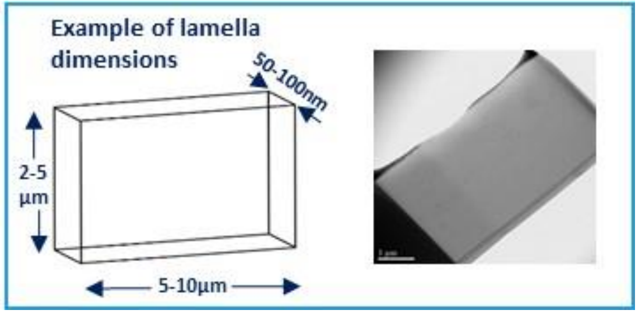
Key parameter : select the relevant signal for the best contrast

Thin layer : Lack of resolution due to electron penetration (depth >> layer thickness) => thin lamella

LAMELLA PREPARATION BY FIB FOR STEM

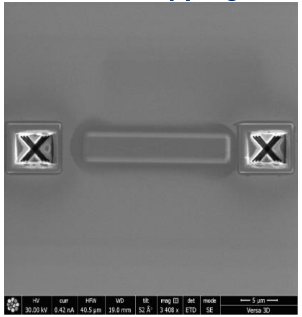
STEM Lamella specifications

- Thickness very weak : few tens of nm
- Wide : few µm (enough statistic)
- Stable during STEM acquisition

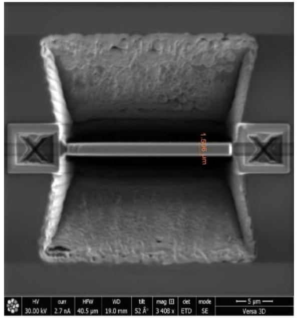


The different steps of lamella preparation

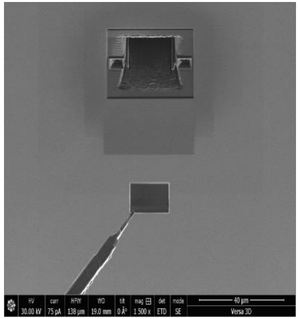
area selection + surf. capping



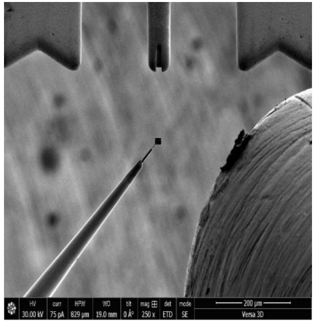
Rough milling



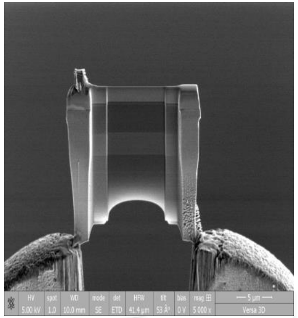
welding on probe +cut +extraction



Transfer + Cu support approach



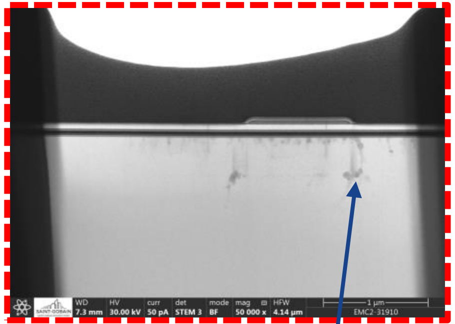
Welding on Cu + final refining

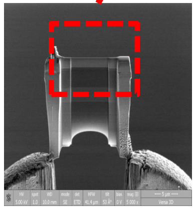


EX. LAYER THICKNESS EVALUATION BY SEM/STEM ON FIB LAMELLA

Lamella

- Ag stack on PLC

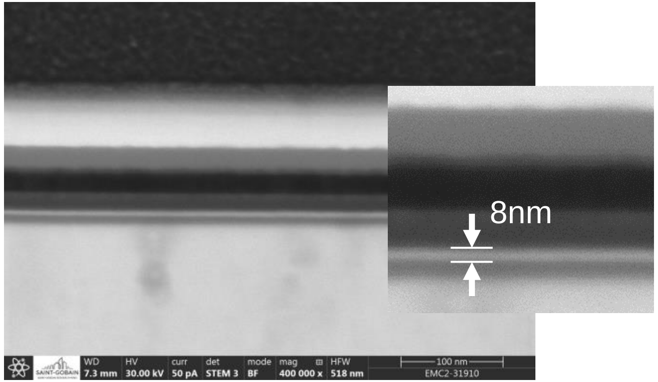




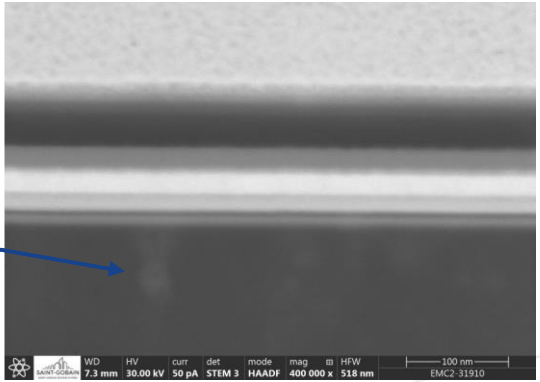
Impact of e beam on glass
=> Na migration

Comparison

- STEM –BF



- STEM-HAADF

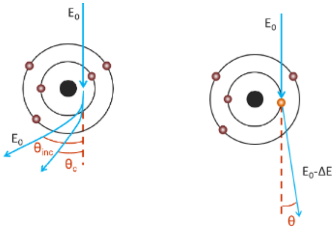


Lack of resolution due to probed size
=> STEM/TEM

TRANSMISSION ELECTRON MICROSCOPY (TEM)

Principle

- Analysis of the transmitted electrons from
  - (a) elastic interaction
  - (b) inelastic interaction



TEM mode

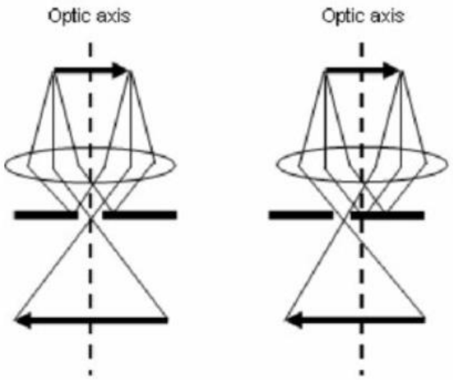
- TEM : parallel electron beam projected through the sample and collection the transmitted electrons

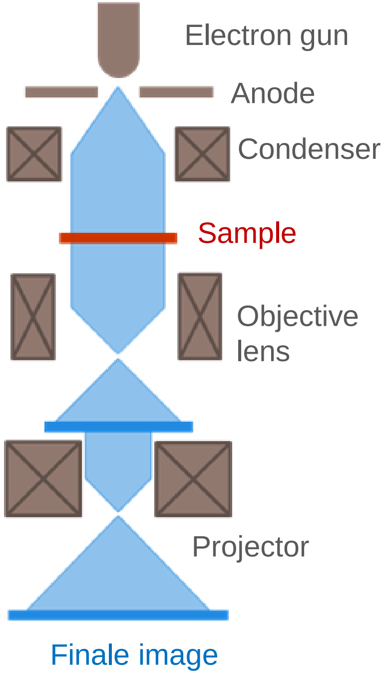
TEM – Bright Field (a)

- Transmitted electron collection
- Contrast due to density, composition, phase

TEM – Dark Field (b)

- Diffracted electron collection
- Contrast due to cristallized volume





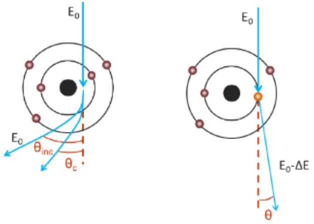
D Williams, C Carter, TEM, 2nd Edition, Springer

T. Barres, PhD, Sorbonne Univ. (2017)

SCANNING TRANSMISSION ELECTRON MICROSCOPY (STEM)

Principle

- Analysis of the transmitted electrons from
  - (a) elastic interaction
  - (b) inelastic interaction



STEM mode

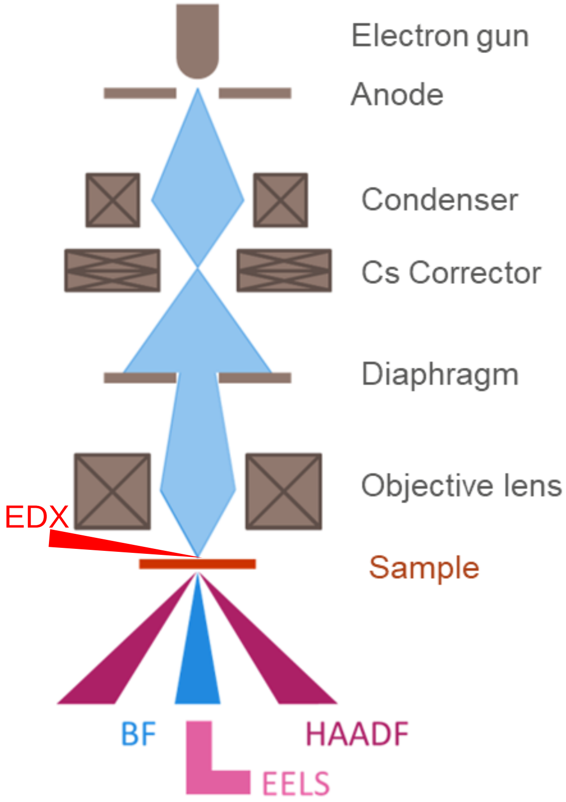
- STEM : electrons beam is focused and scanned the sample.
- Probe size : 0;08nm (Cs correction)

STEM – BF

- Transmitted electron collection Bright Field
- Contrast due to density, composition, phase

STEM – HAADF

- High Angle Annular Dark Field image of transmitted electron
- Contrast due to composition



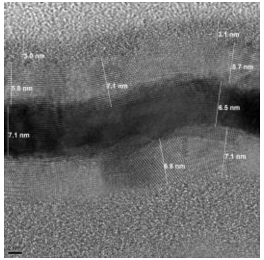
D Williams, C Carter, TEM, 2nd Edition, Springer

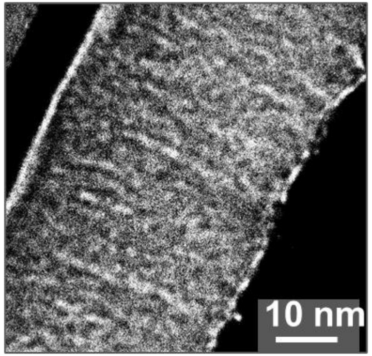
T. Barres, PhD, Sorbonne Univ. (2017)

EX. OF LAYER THICKNESS EVALUATION BY TEM AND STEM

TEM - BF

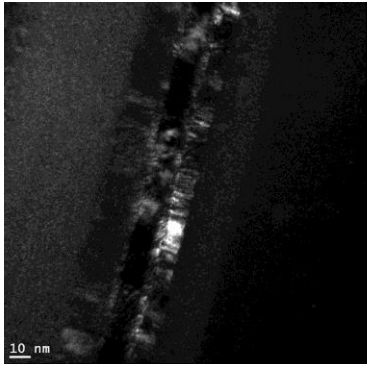
- Amorphous SiNx layer with pores





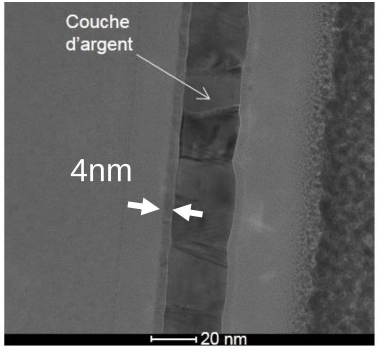
TEM – DF

- Thin layer stack including crystallized ZnO and Ag layer



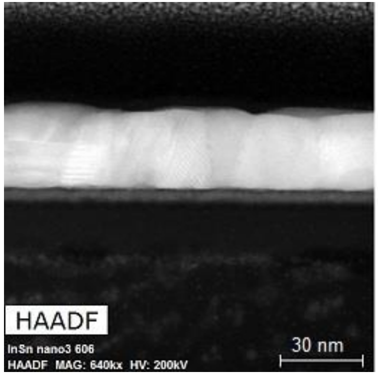
STEM - BF

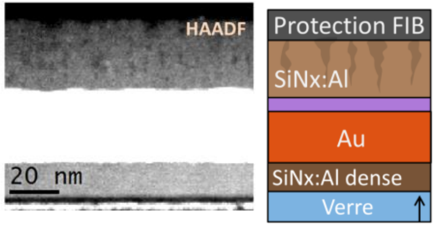
- Thin layer stack including Ag layer



STEM - HAADF

- Thin layer stack including Ag layer





What about very thin layer at the interface of rough thicker layer ??
=> see composition part

LAYER THICKNESS ASSESSMENT

Technique	Resolution lateral (depth)	Range (min - max)	sensitivity	materials	Sample preparation	Other (limitations , artifacts…)
SEM - SE	1.5nm	few 10 nm / few mm	Topography, Z element	All (compatible vacuum and e beam)	Cross section + Conductive layer	Alkaline migration, charging effect
SEM - BSE	>1nm	few nm / few mm	Z element	All (compatible vacuum and e beam)	Cross section + Conductive layer	Alkaline migration, charging effect
SEM – EDS and EPMA	~1µm	few µm / few mm	Composition, B=<	All (compatible vacuum and e beam)	Cross section + Conductive layer	Alkaline migration, charging effect
STEM (SEM) (BF, HAADF)	1.5nm	few 10 nm / few mm	Topography, Z element	All (compatible vacuum and e beam)	lamella	Alkaline migration, charging effect, lamella thickness
STEM (TEM) (DF, BF, HAADF, EDX)	0.1nm	few 1 nm / few µm	Z element, B=< microstructure,	All (compatible vacuum and e beam)	lamella	Alkaline migration, charging effect, lamella thickness
ToF-SIMS (carto)	100nm	few µm / few mm	composition	All compatible vacuum and ion beam	Cross section	alkaline migration
ToF-SIMS (profiling)	~1nm	few nm / ~10µm	composition	All compatible vacuum and ion beam	none	Sputtering, alkaline migration
EPMA/ToF-SIMS	0.5nm	few nm / ~500nm	composition	All compatible vacuum and e and ion beam	Conductive layer at surface	Hypothesis on density
XPS (HAXPES)	0.1nm	few nm / 30nm	Composition Li=<	All (compatible vacuum and RX)	none	charging effect,
XRR	1nm	1nm / ~200nm	Electron density	All	none	Very flat sample, number of layers
Ellipsometry	1nm	few nm / 1µm	Optical index	All	none	Transparent, roughness

+ Raman, APT

SAINT-GOBAIN RESEARCH PARIS
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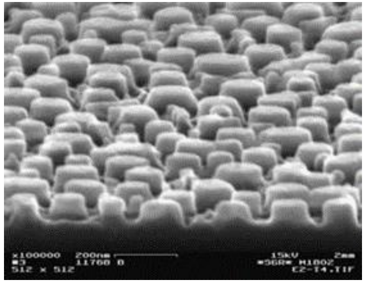
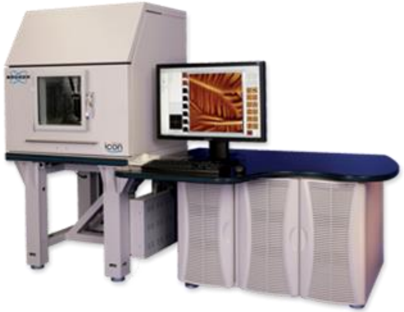
SURFACE MORPHOLOGY AND ROUGHNESS

- **Surface: 3D dimensions over an extended area**
- **Examples**
  - Particles and morphology (hole, dome, scratch…) at the surface (contrast of topography)
  - Rough glass surface (ageing, grafting, deposition)
  - Rough layer surface

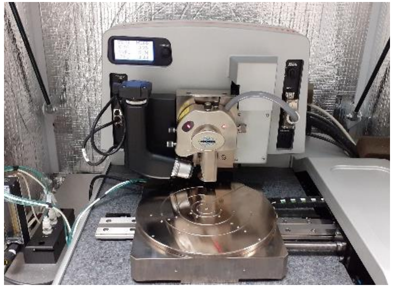


- **Techniques used**
  - Scanning Electron Microscopy collecting Secondary electrons : SEM-SE
  - Atomic Force Microscope AFM
  - X Ray Reflectometry (XRR, in case of layer)



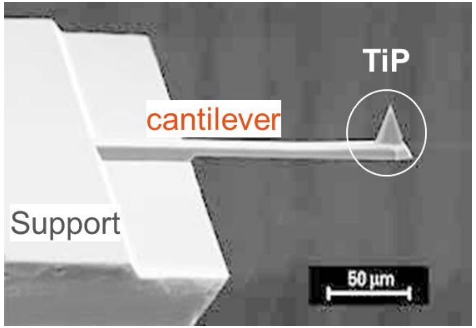
SAINT-GOBAIN RESEARCH PARIS

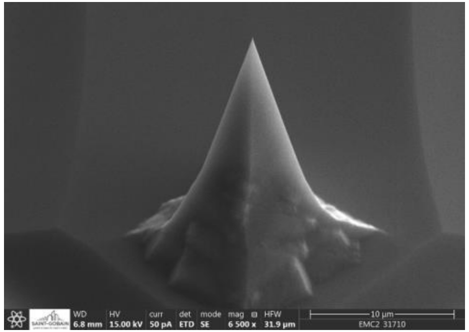
AFM PRINCIPLE AND TECHNICAL ASPECT

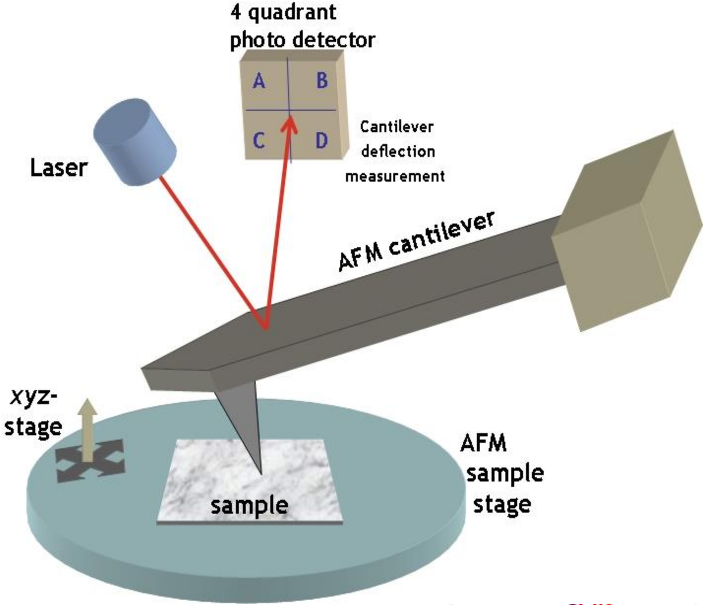


Tip / surface interaction

- AFM is based on the measurement of the forces (attraction and repulsion) between the surface atoms and the apex of a tip scanning the surface of the sample.
- This measurement is obtained from the deflection of the cantilever which is monitored by the reflection of a laser beam positioned on the upper face of the cantilever.
- The xyz displacement (at nm scale) are operated using piezoelectric ceramic.







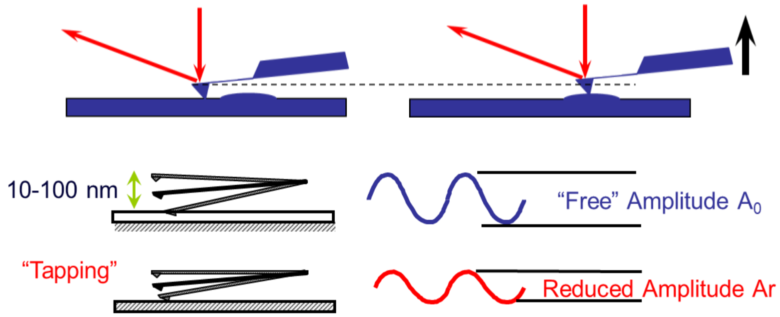
See D Vandembroucq lecture (Mo)

SAINT-GOBAIN RESEARCH PARIS

AFM: OPERATING PARAMETERS AND LIMITATIONS

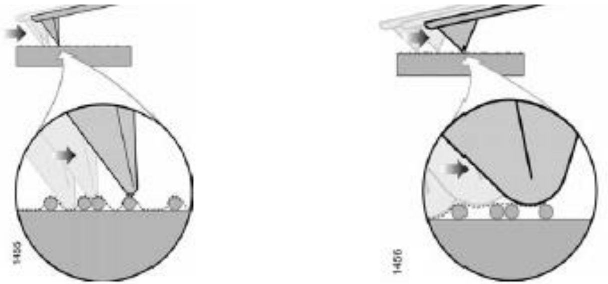
Different operating modes available

- **Contact mode :** the tip is in contact with the sample surface, and the feedback loop maintains a constant deflection (constant force).
- **Tapping mode** : the cantilever oscillates at its resonant frequency with the A_0 amplitude : close to the surface, A_0 is reduced to Ar by the force Field.
- **Peak Force**,
- **Conductive AFM**, **KPFM**…

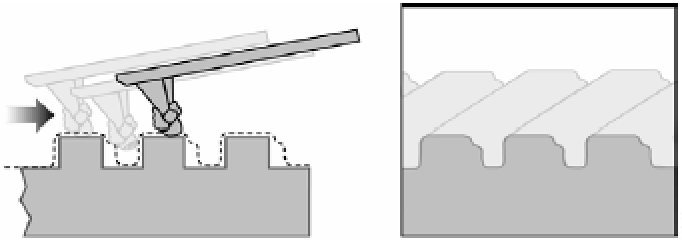


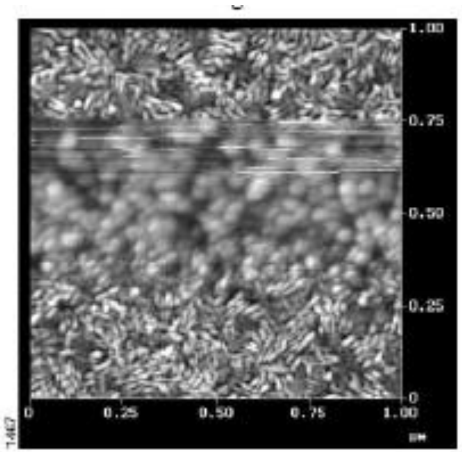
Limitations and artifacts

- The apex radius/roughness



- The apex evolution (break, dust)





SAINT-GOBAIN RESEARCH PARIS
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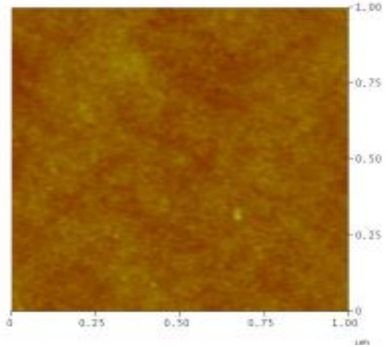
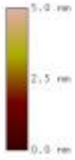
EXAMPLES CONCERNING GLASS SURFACE ANALYSE BY AFM

Float glass

- Atm side, fresh and just cleaned

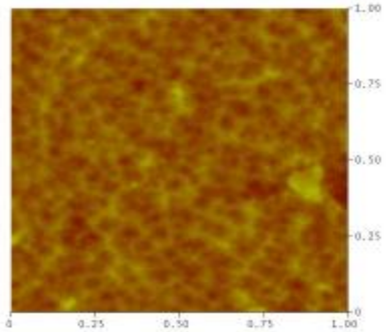


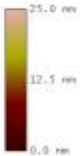


RMS: 0.12 nm

Float glass

- Atm side, corroded and just cleaned

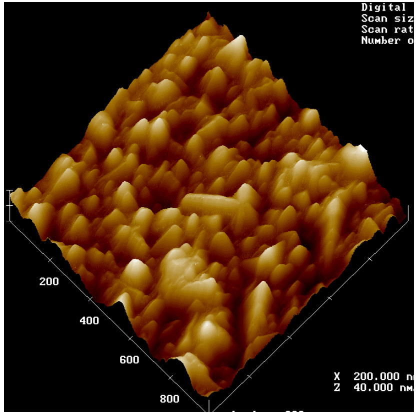




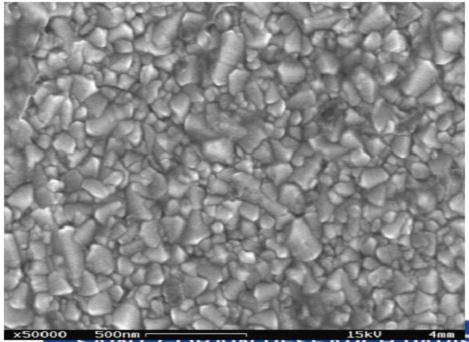
Rms : 0.94nm

Layer surface

- SnO_2 crystallized



SEM-SE comparison (top plan view)



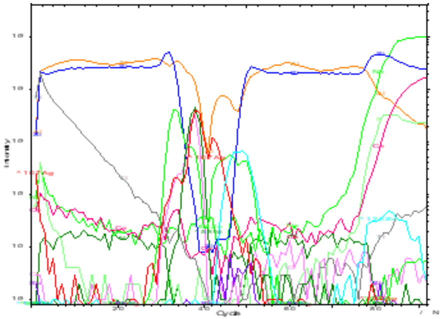
SAINT-GOBAIN

ASSESSMENT OF THE SURFACE MORPHOLOGY (AND INTERFACE)

Technique	Resolution lateral (depth)	Range (min - max)	sensitivity	materials	Sample preparation	Other (limitations , artifacts…)
SEM - SE	1.5nm	few 10 nm / few mm	Topography, Z element, surface	All (compatible vacuum and e beam)	Cross section, tilt + Conductive layer	Alkaline migration, charging effect
STEM (SEM) (BF, HAADF)	1.5nm	few 10 nm / few mm	Topography, Z element, interface	All (compatible vacuum and e beam)	lamella	Alkaline migration, charging effect, lamella thickness
STEM (TEM) (DF, BF, HAADF, EDX)	0.1nm	few 10 nm / 1µm	Z element, interface	All (compatible vacuum and e beam)	lamella	Alkaline migration, charging effect, lamella thickness
XRR	1nm	1nm / 200nm	Electron density, interface	All	none	Very flat sample, number of layers
AFM	0.1nm	few nm / 100µm	Topography	All	none	charging

SAINT-GOBAIN RESEARCH PARIS

COMPOSITION AND GRADIENT



- **Surface: 3D informations**
- **Examples**
  - Glass inclusions
  - Chemically tempered glass
  - Multilayer stack (low E)
  - Aged glass surface

- **Techniques used**
  - X ray Photoelectrons Spectroscopy: XPS (carto/depth profiling)
  - Scanning Electron Microscopy collecting RX : SEM-EDS
  - Electron Probe MicroAnalysis : EPMA
  - Rutherford Backscattering spectrometry : RBS
  - Auger spectrometry
  - Secondary ion Mass Spectrometry : SIMS, ToF-SIMS
  - Atom Probe Tomography: APT
  - Scanning Transmission Electron Microscopy collecting RX : STEM-EDX or EELS

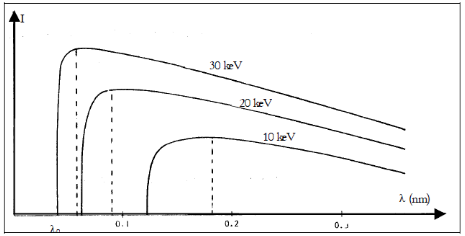
  - *Elastic Recoil Diffusion Analysis : ERDA (hydrogen)*

Probed size/volume

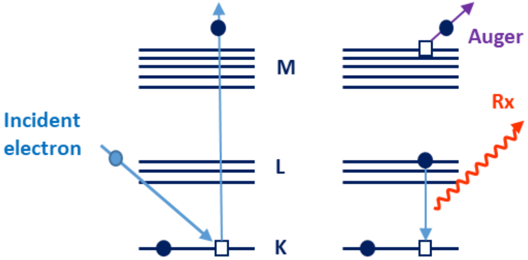
EPMA AND SEM-EDX PRINCIPLE

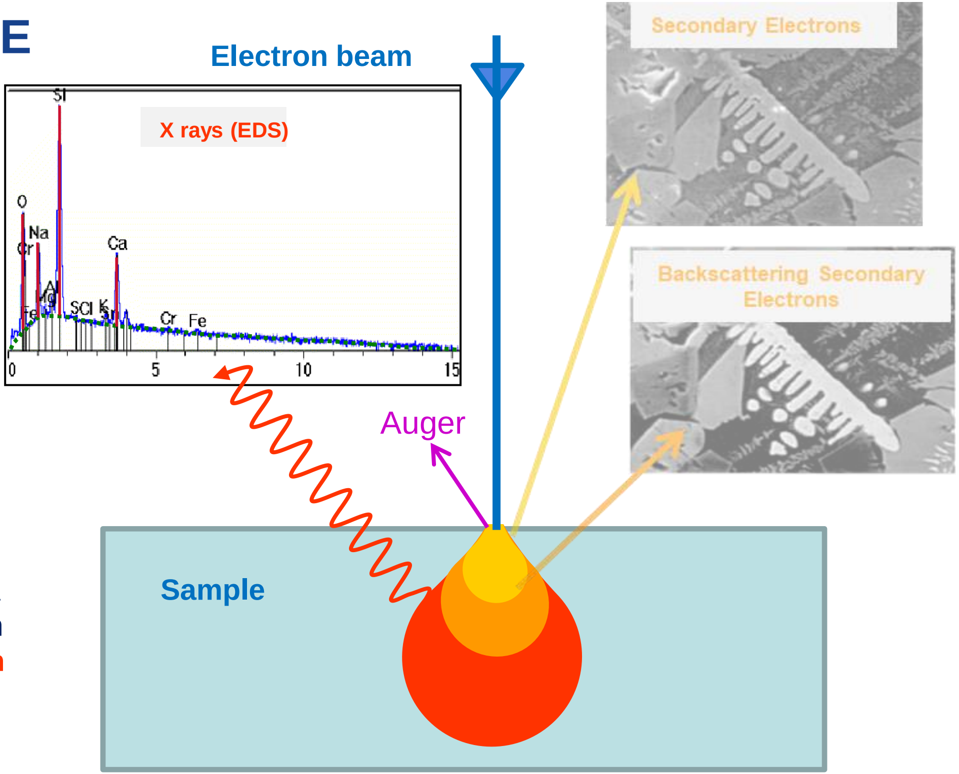
Electron / material interaction

- Among the numerous emission, X-ray emitted are due to
  - Electron deceleration => **Bremsstrahlung**



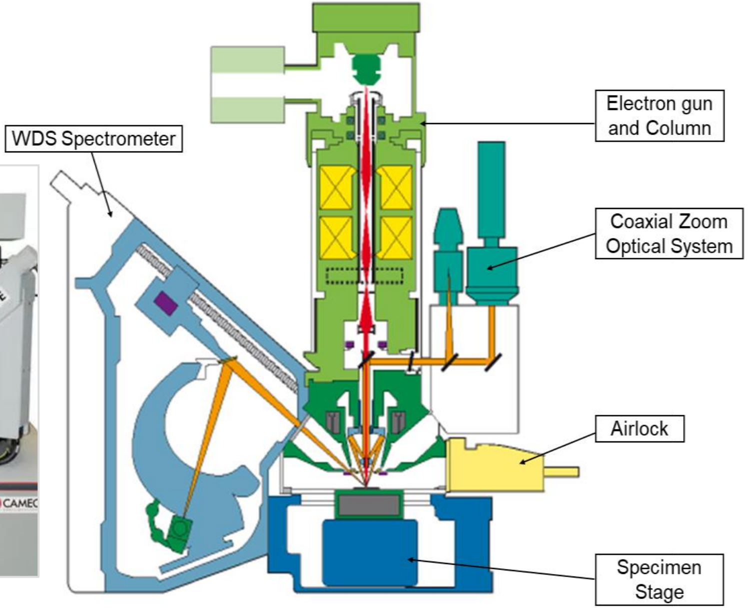
  - Interaction with innermost electrons shells, producing a vacancy (unstable). Then, it is filled by electron from higher energy bound shells with **X-ray emission** characteristic of the levels **(+ Auger electron).**





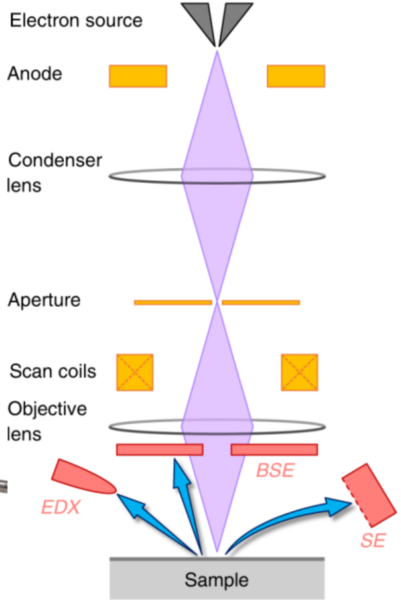
EPMA AND EDX : TECHNICAL POINT VIEW

- **Wavelength Dispersive X-ray Spectrometer**
  - The key part of EPMA
  - Associated to gas-flow counter (photoelectrical effect)



EPMA course, Univ. Montpellier-CNRS
CAMECA Sx Five description

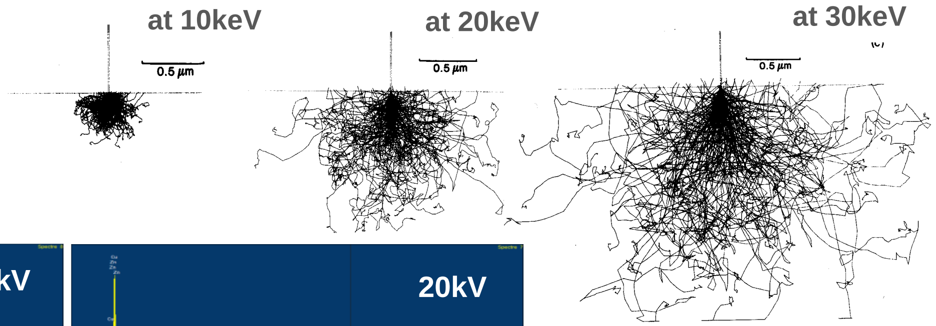
- **Energy Dispersive X-ray Spectrometer**
  - Diode detector



Shah, Bone Research 2019

EPMA AND EDX: KEY PARAMETERS

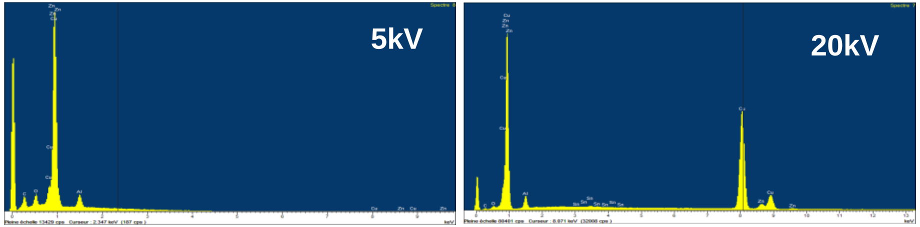
Electron paths in Fe



Choice of the incident electron energy

- A compromise between
  - Lateral / depth resolution
  - Element analysis ($E_{electron}$ > 2,5 x E_{peak} for I_{max})

Example of CuAlZnSn alloy



Calibration for quantification: k-ratio estimation

- Background measurement at -Δλ and +Δλ (EPMA)
- Using correction protocol
  - ZAF
  - Phi(roz)

$$K_A = \frac{I_{mes}}{I_{std}} = \frac{C_A.\left(\int \phi_A(\rho z).\exp(\chi_A \rho z).d\rho z\right).\left(1+\sum f_{cA} + f_{FC_A}\right)}{\left(\int \phi_S(\rho z).\exp(\chi_S \rho z).d\rho z\right).\left(1+\sum f_{cS} + f_{FC_S}\right)}$$

Note : *if $E_{electron\ incident}$ >10keV,*

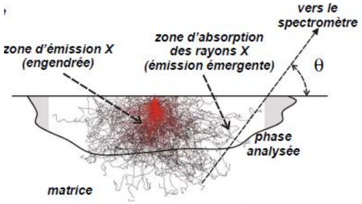
for element ≠ light ones => K_A ~C_A

for light elements or samples with elements with different Z => absorption high => $K_A \neq C_A$ =>modelization!!

EPMA / EDS ARTEFACTS (ESPECIALLY FOR GLASS)

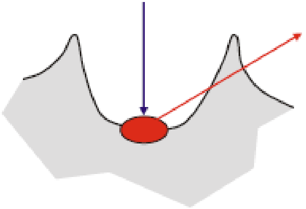
- **Surface heterogeneities > emission volume**
  - Probed volume ~1µm^3

=> Reduction of $E_{Electron}$



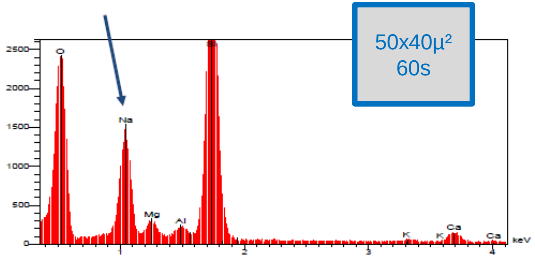
- **Surface roughness**
  - X-ray absoprtion

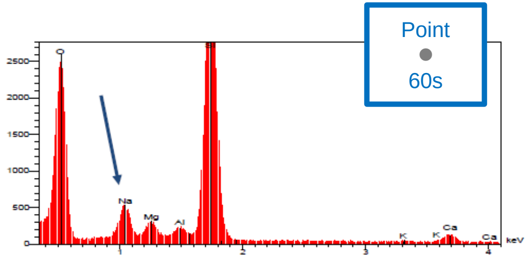
=> Reduction of roughness (< 1µm)



- **Case of glass**
  - The main one : alkaline migration under electron irradiation

=> reduction of electron dose





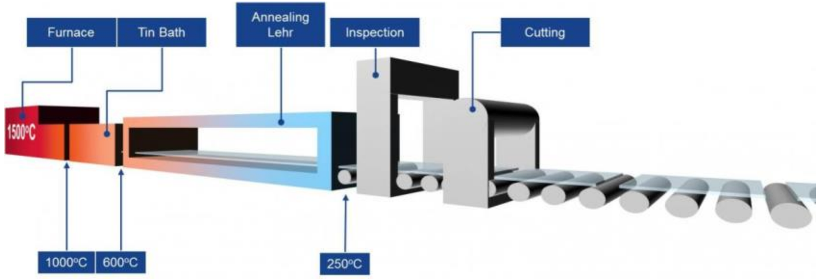
- **Samples (glass) preparation**
  - Polishing (optical quality)
  - Deposition of conductive layer (carbon)

Microanalyse X quantitative, J Ruste, GNMEBA

ANALYSIS OF GLASS INCLUSION

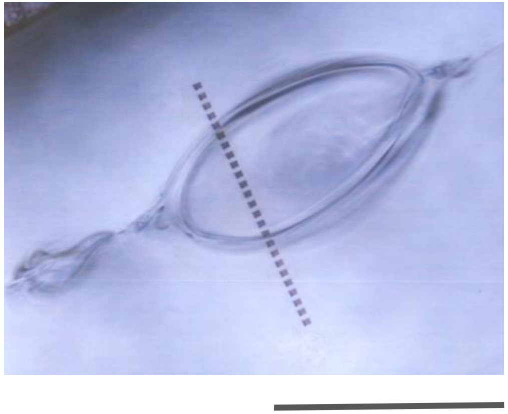
Float Glass : quality control

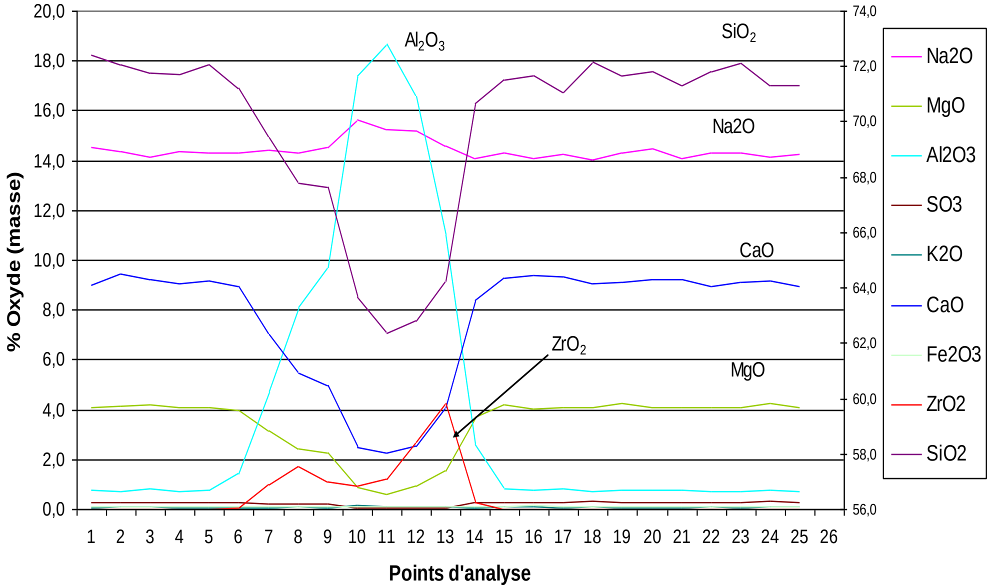
- Example of "gum" defect (refractories)



EPMA Acquisition

- Line mode 10µm x 20µm, step of 40µm
- Na-Kα, Al-Kα, K-Kα, Si-Kα, Ca-Kα at 10nA
- Zr-Kα, Fe-Kα, S-Kα at 150nA



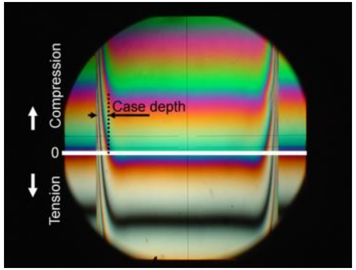


© WordPress.com https://zbindendesign.wordpress.com/category/trucks/

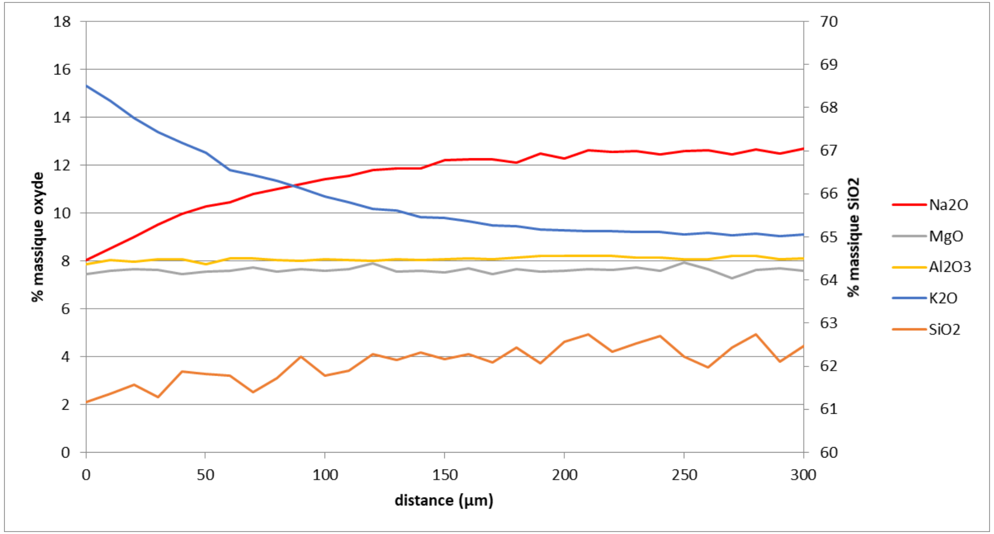
P Lehuedé pers. Com. (2007)

ANALYSIS AT SURFACE: CHEMICAL TEMPERED GLASS

- **Na / K exchange for glass strenghtening**
  - 420-490°C during ~70h
- **EPMA Acquisition**
  - Line mode 2µm x 40µm, step of 10µm
  - Na-Kα, Al-Kα, K-Kα, Si-Kα, Ca-Kα at 10nA



Stress pattern from polariscope



If profile resolution needed is < 1µm with range of 10µm.

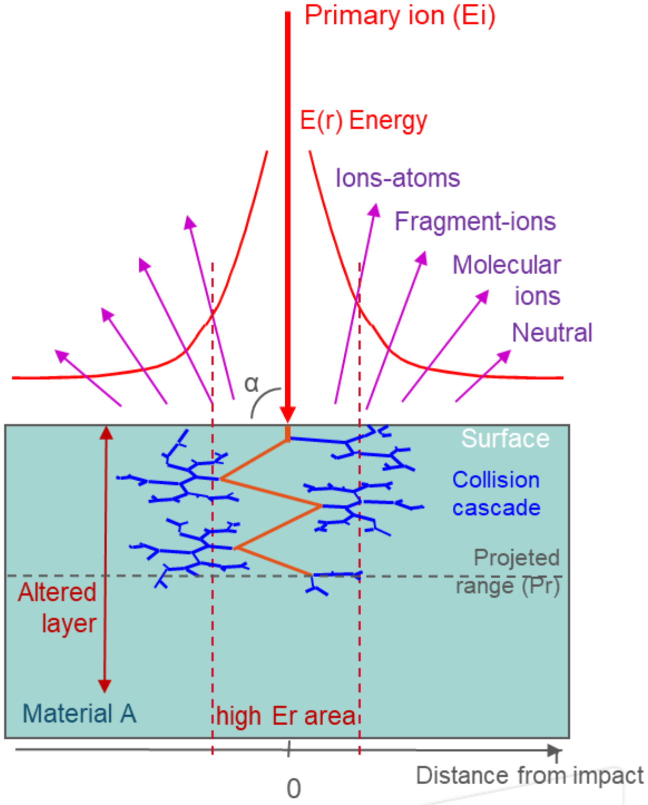
=> SIMS

R Gy, Mat. Sci.Eng. B, 149 (2007)

SIMS PRINCIPLE

▶ Ion – Solid interaction (for Ei >100eV)

- Modification of the material, amorphization,
  => altered layer ~ 2 x Projected range =f(Ei $^{2/3}$)
- Fraction of the momentum directed back to the surface => **SPUTTERING of different species**
  Origin depth < ~1nm
- Major part of neutral (90%)



▶ Detection of anions/cations emitted from sputtered surface

$$I(A^{\pm}) = f_A \,.\, D_A \,.\, C_A \,.\, I_i \,.\, Y_M \,.\, Y^{\pm}_{A(M)}$$

- f_A= isotopic abundance of the element A
- D_A= detection efficiency (transmission… of sensor)
- C_A=concentration of the element A within the matrix M
- I_i = intensity of the primary incident ions
- Y_M= sputtering yield of the matrix
- $Y^{\pm}_{A(M)}$= ionization yield of A within Matrix

SPUTTERING ISSUES WITH GLASS

Surface charging effect

- Example of Ar^+ on Na

$$\equiv Si - O^- Na^+ + Ar^+ \rightarrow Ar^0 + \equiv Si - O + Na^+,$$

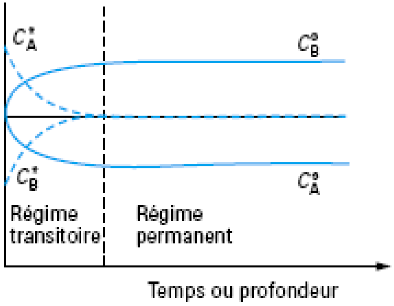
RK Brow JNCS 107 (1988) 1-10

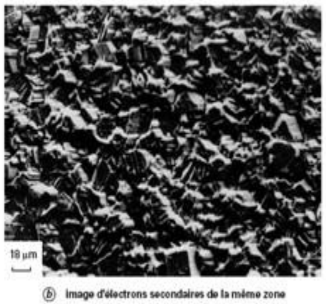
Solution :
⇒ reduction of the charge density
⇒ Decrease sample T

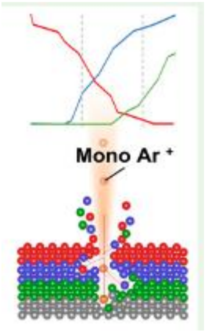
To Reduce of Na mobility

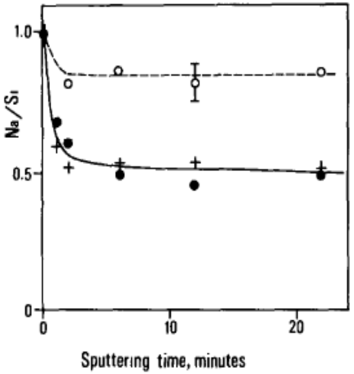
Sputtering artifacts

- Preferential sputtering
- Surface roughening
- implantation
- Segregation









Solution : => increase the size of incident ions

Techniques de l'ingénieur (2010)

HY Chang et al. Appl. Nano Let. 2022

A Torristi et al. Nucl. Instr. and Meth. in Phy. Res. B32 (1988) 283

IONIZATION YIELD (*IONIZATION PROBABILITY*)

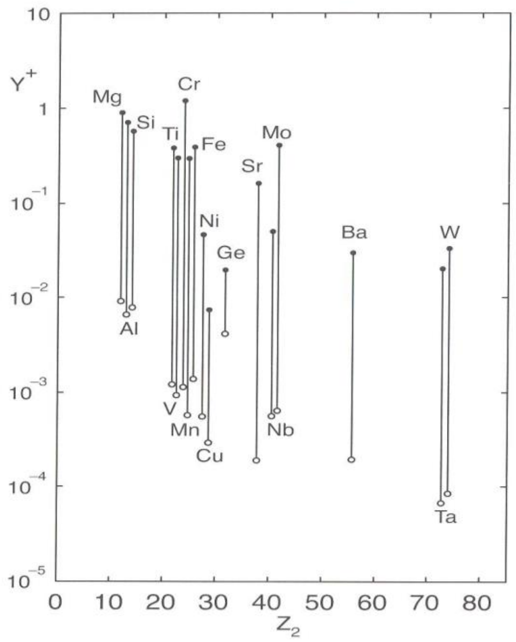
- **It is THE key parameter**
  - Strongly depends on the nature of the species
  - Varies over few orders of magnitude for the same combination of incident ions and target material
  - "Matrix effect"

- **How to take advantage of it? : some recipes**
  - Oxidation of the surface favor the electropositive secondary ions

    => oxygen bombardment and/or oxygen flooding

  - the presence of Cs at the surface enhanced negative secondary ions

    => use Cs gun and/or Cs deposition prior analysis.



Ar^+ 8keV / cations collection from

● oxidized surface

○ metallic surface

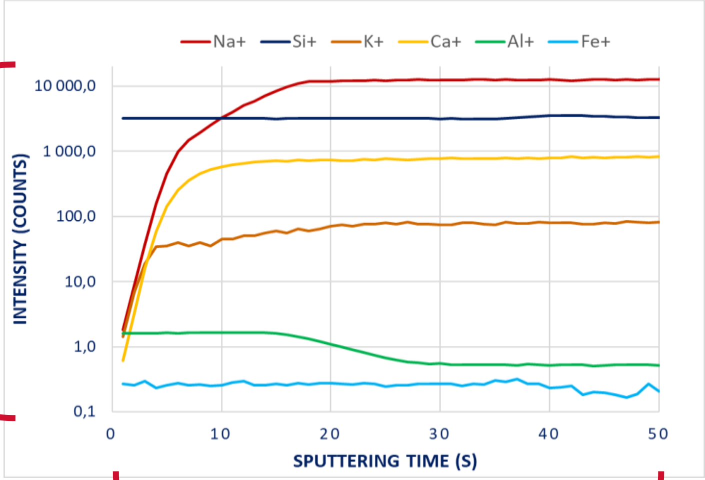
SIMS DEPTH PROFILE : FROM SIGNAL TO QUANTIFICATION

Conversion Intensity to composition (% wt ox)

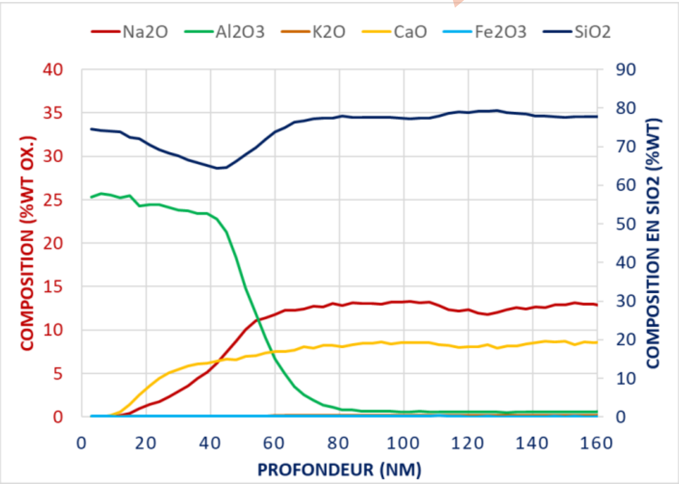
- Calibration of the intensity using reference sample

=> Normalization of the intensity of the selected ions for the element of interest with the intensity of the matrix ions.

$$\frac{C\,Na_2O}{C\,SiO_2} = RSF_{Na.Si}\,\frac{I\,Na^+}{I\,Si^+}$$



See K Burov lecture (Tu)

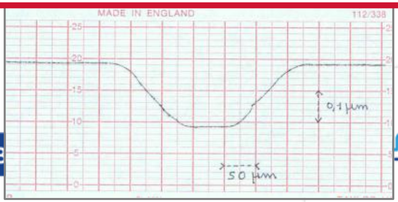


Conversion sput. time (s) to depth (nm)

- Calibration of the abrasion rate

BUT

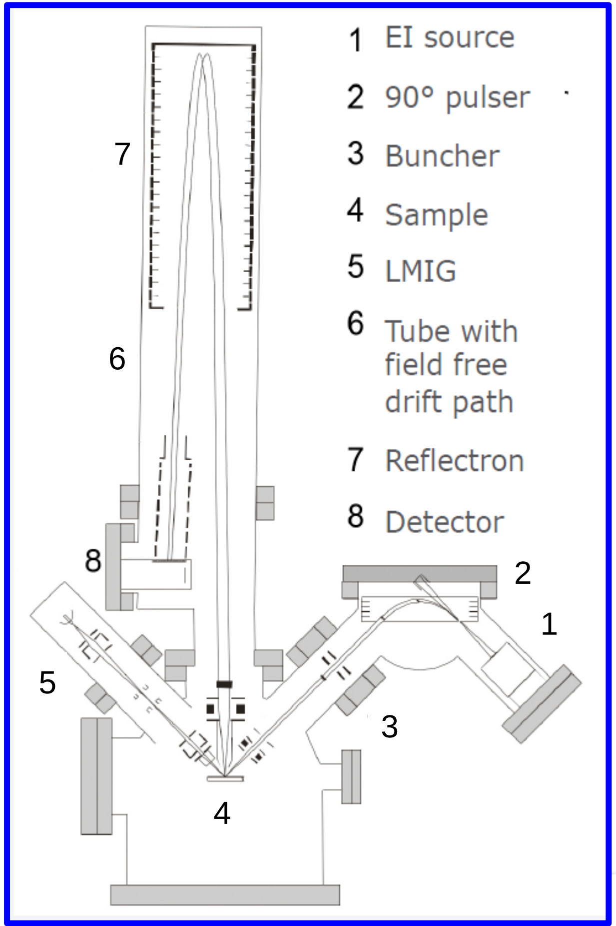
- Hypothesis: it is homogenous during the whole depth profile! (excepted transient width)



SAINT-GOBAIN

TOF-SIMS PRINCIPLE

- **how it works**
  - 1 gun generating pulse ions for analysis (LMIG)
  - 1 gun for abrasion for efficient depth profiling (EI, Clusters…)
  - Analysis on the secondary ions using Time of Flight mass spectrometer



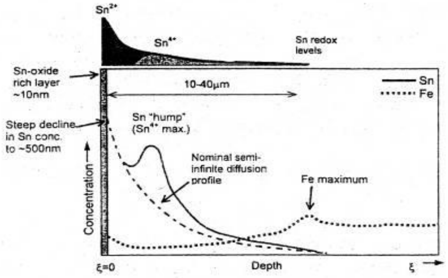
Ion ToF source

ANALYSIS OF GRADIENT IN FLOAT GLASS

TRANSVERSAL R&D CENTERS

▶ Case of industrial Float Glass : the bath side

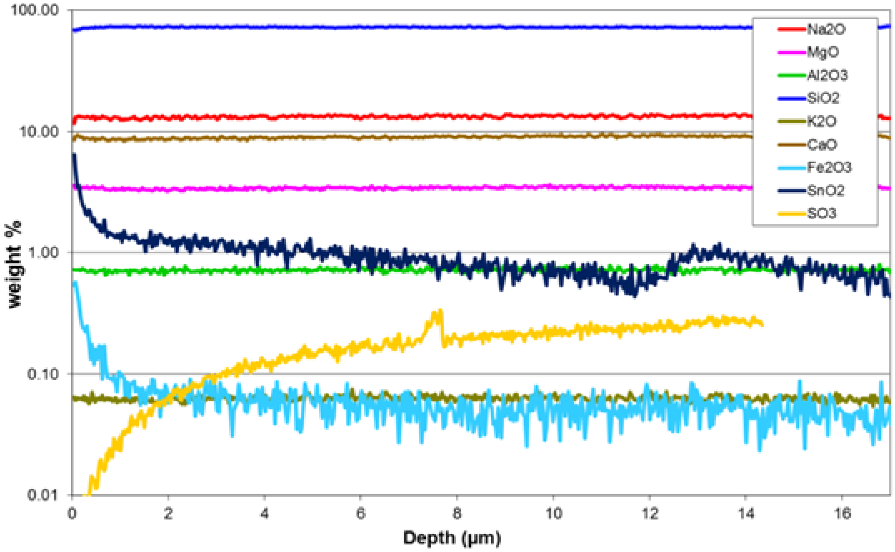
- Exchange between Na and Tin in the tin bath.
- Behavior of Sn^{2+}/Sn^{4+} => tin hump



GB Cook JNCS (1999)

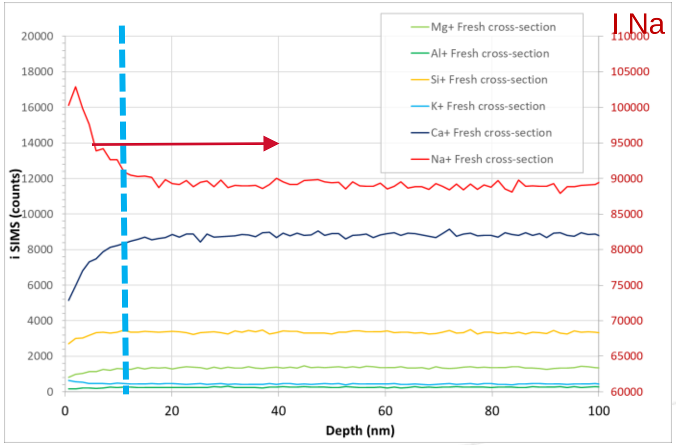
ToF SIMS depth profiling (Float glass 10mm thick)

- TOF.SIMS 5, Anal, Bi^+ 30keV, Abr, $^+O_2$ 1keV, ^-Cs 2keV



Transitory regime : example of glass fresh fracture

- TOF.SIMS 5, Anal, Bi^+ 15keV, Abr $(O_2)_{1500}$ 20keV



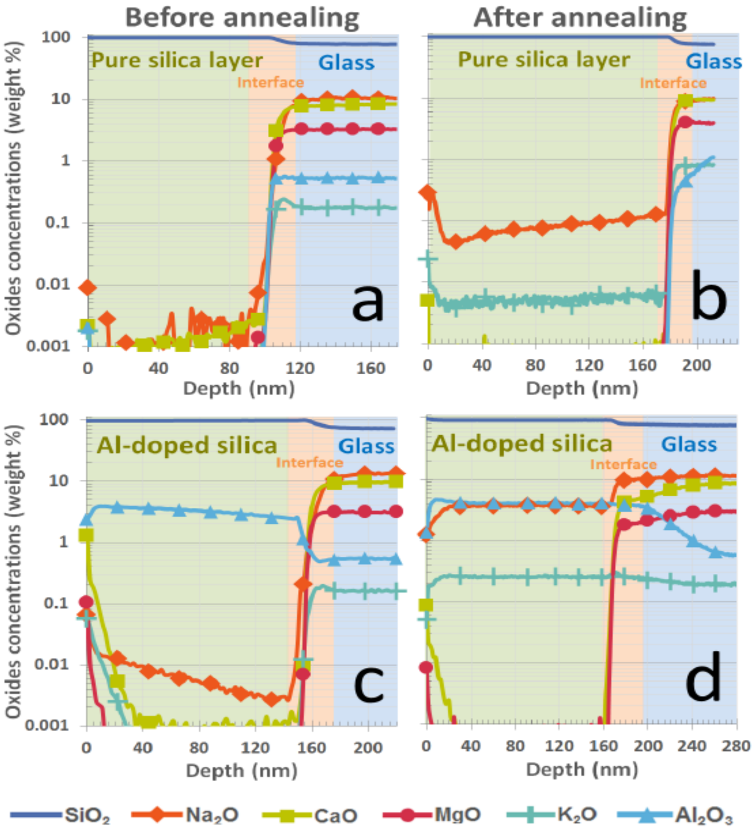
~10nm

H Montigaud, ICG-yokohama (2018), ICG Boston(2019)

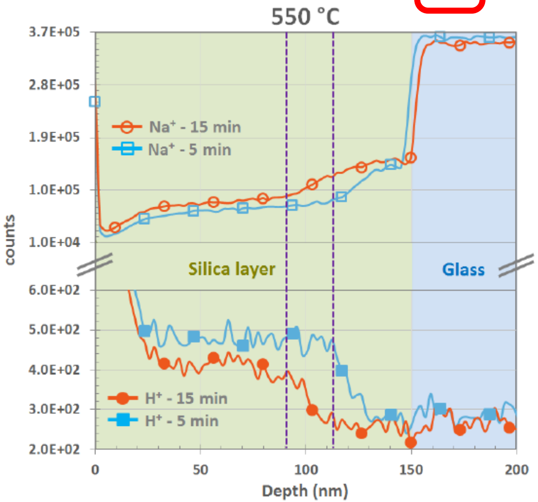
SAINT-GOBAIN

ANALYSIS OF GRADIENT WITHIN LAYER (SILICA / GLASS)

- **Silica layer deposited by PVD on glass and then annealed**
  - ToF.SIMS5
  - Analysis Bi^+30kV,
  - Abrasion, Cs^+ 2kV



Comparison Na / H



See K Burov lecture (Tue)

1D composition gradient within homogenous thin thin : what about heterogeneous material

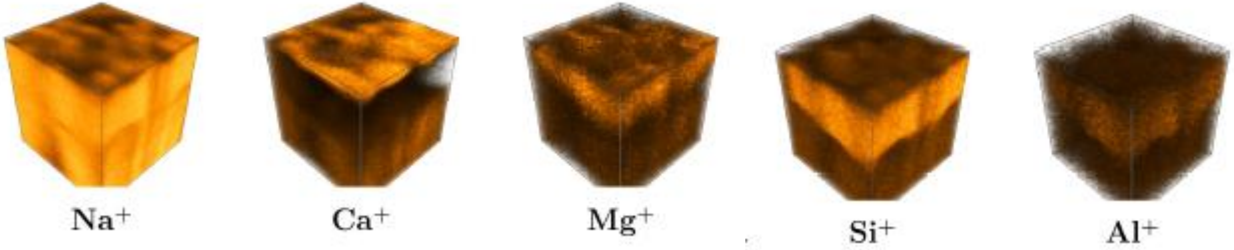
=> ToF-SIMS, STEM-EDS, **APT**

JT Fonné et al. JACS (2019)
S Ben Khemis, PhD (2021)

SAINT-GOBAIN RESEARCH PARIS

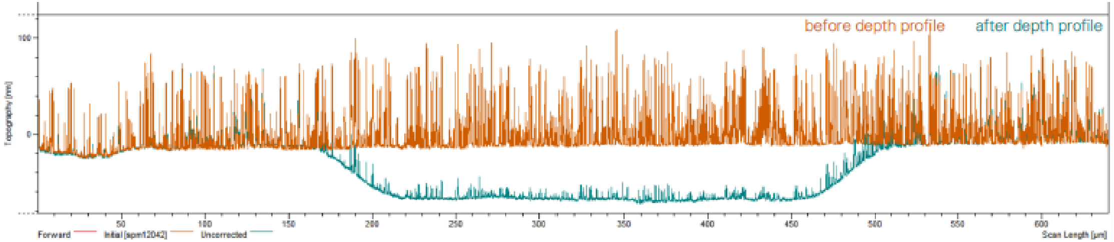
ANALYSIS OF GRADIENT WITHIN HETEROGENEOUS LAYER

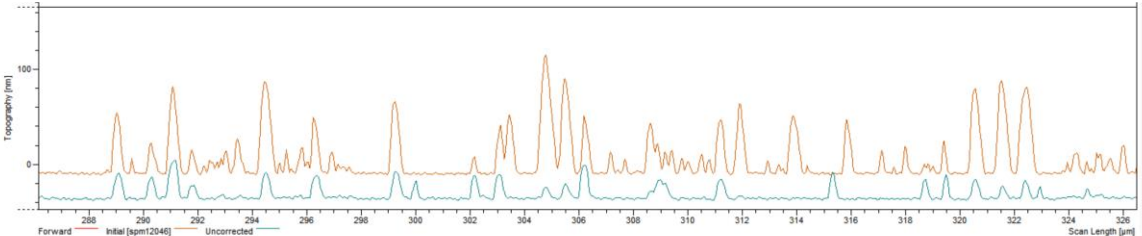
- **ToF-SIMS 4D depth profile**
  - Glass surface corroded



- **ToF-SIMS depth profile**
  - Glass surface corroded with local height information

A Serve, PhD (2023)



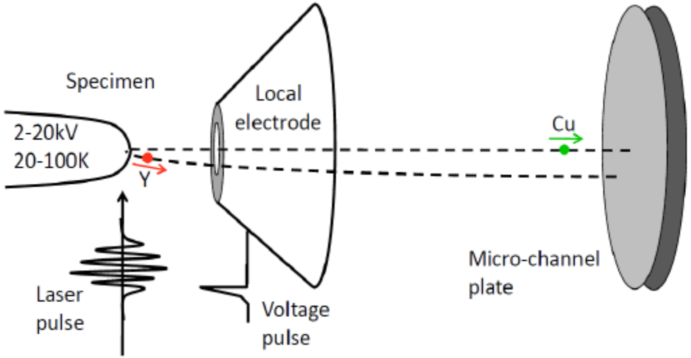


ToF-SIMS + AFM

ATOM PROBE TOMOGRAPHY

Principle

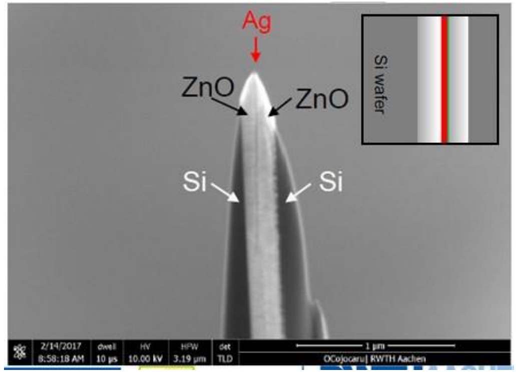
- Field emission from a tip assisted by laser.
- Tip at reduced T to limited migration under HV.
- Elemental analysis (isotope)

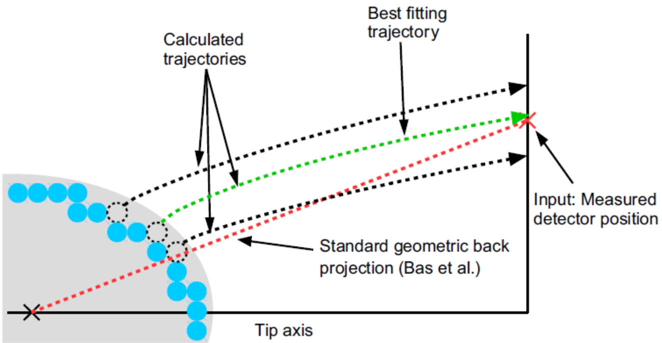


The key parameters

- The tip size (/ sample volume to be probed)
- The secondary ions trajectories reconstruction

Example (LEAP)



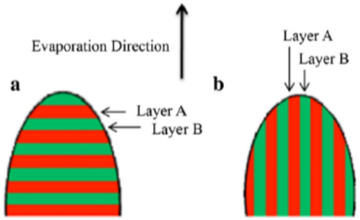


D Beinke Ultramicroscopy 165 (2016)

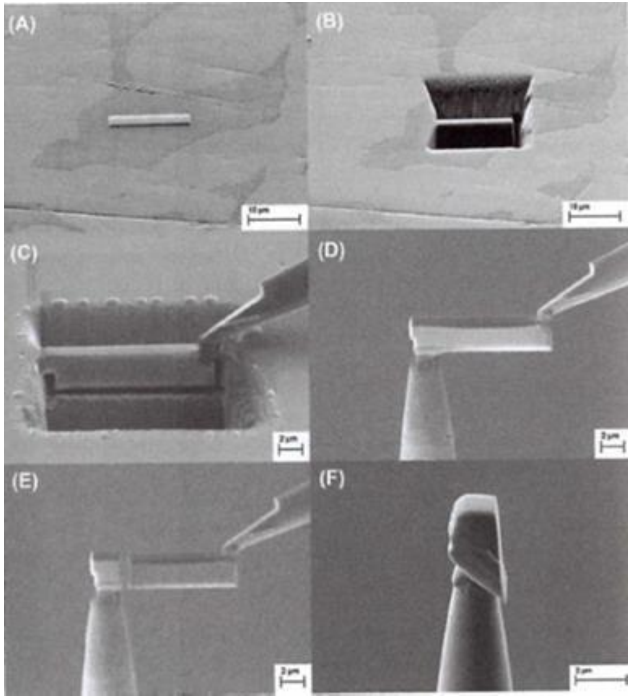
WR Mc Kenzie, Microscopy: Science, Technology (2010)

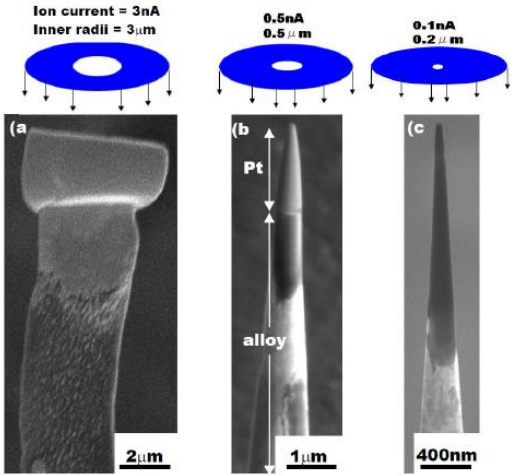
SAMPLE CONFIGURATION AND PREPARATION FOR APT

- **Configuration**
  - Strong impact in case of conductive/isolation parts of the probed volume.



- **Tip preparation by FIB**
  - Extraction of the “pyramid” from the sample surface
  - Final milling for the tip preparation





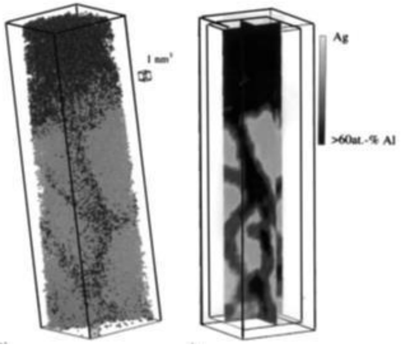
Lefebvre-Ulrikson et al, APT Put Theory Into Practice, Ac. Press, (2016)

J.G. Brons et al. , TSF 551 (2014)

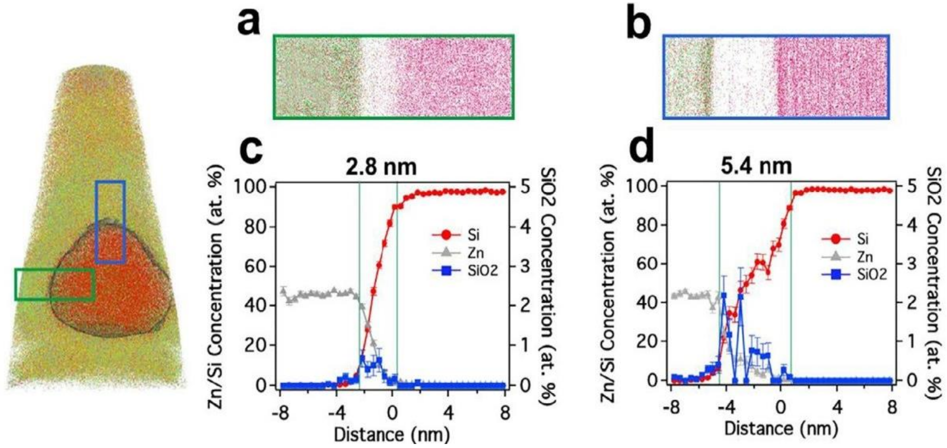
ATOM PROBE TOMOGRAPHY ADDED VALUES

- **advantages / disadvantages**
  - ☺ Until atomic scale (positive case)
  - ☺ 3D information
  - ☹ Possible migration during acquisition
  - ☹ Reduced mass resolution.

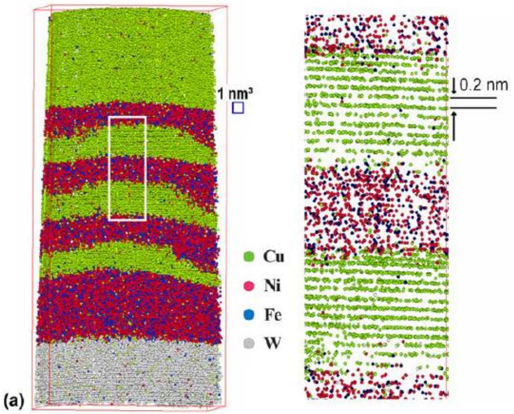
Al/Ag bilayer after annealing at 100°C : Al diffusion in Ag layer through GB



Si nanowires embedded within ZnO



Py 5nm/(Cu 2.5nm/Py 2nm)3/Cu 7nm multilayer



Zhiyuan Sun et al. Ultramicroscopy 184 (2018)

C.B. Ene, Acta Materialia 53 (2005)

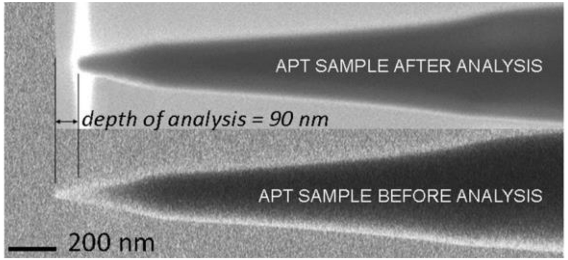
J. Schleiwies et al. Mat. Sci. and Eng. A327 (2002)

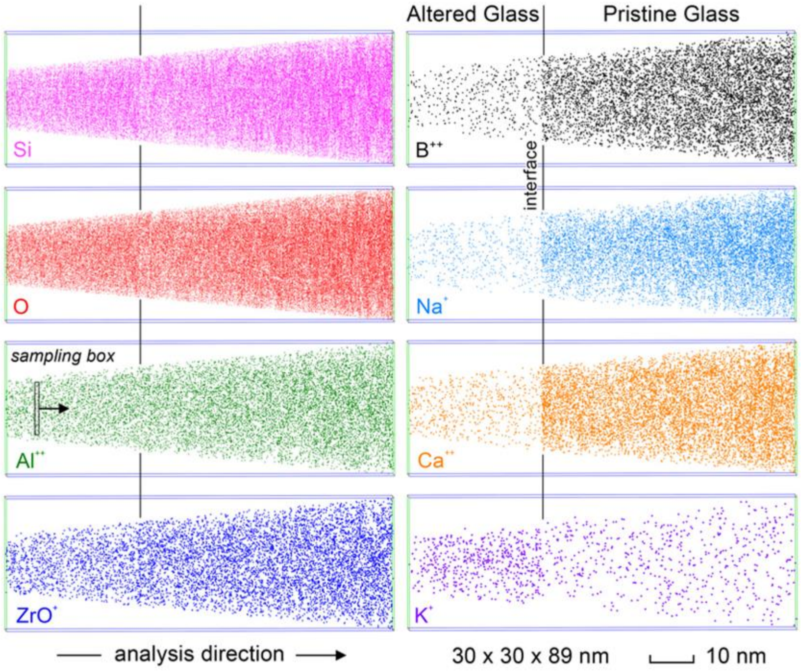
APT RESULTS CONCERNING GLASS (CORRODED)

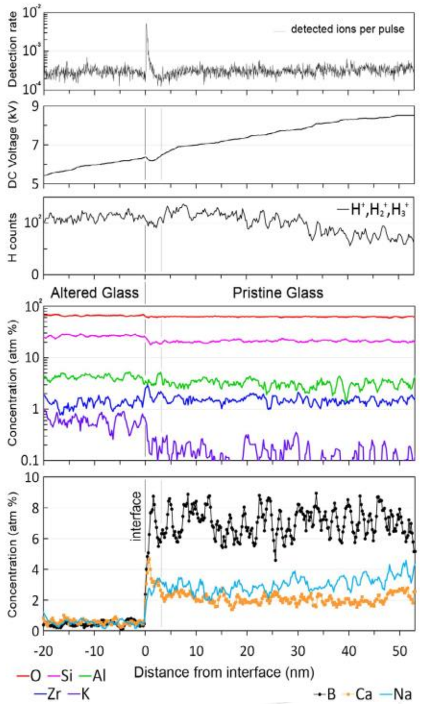
Case of glass surface corrosion

- Borosilicate glass 2.5Y aged
- Comparison APT, ToF-SIMS and EFTEM

Picture of the tip before/after analysis

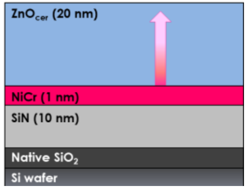






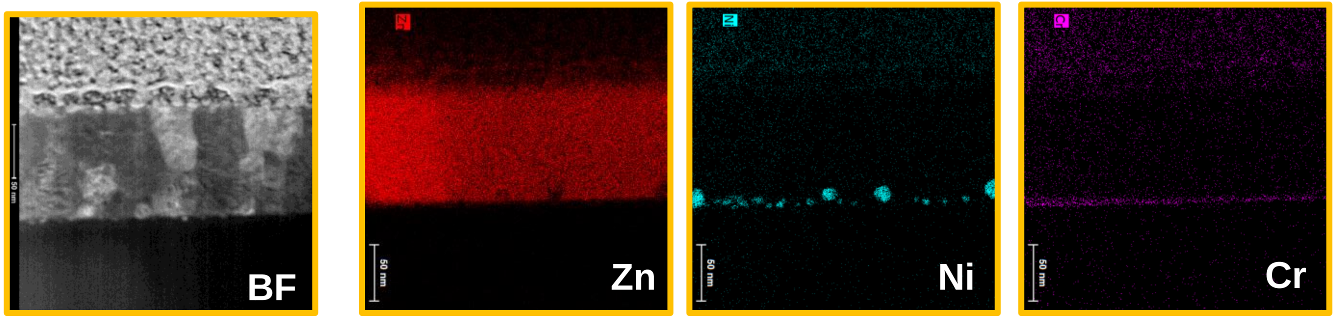
Gin Geochimica et Cosmochimica Acta (2017)

ATP RESULTS CONCERNING HETEROGENOUS LAYER

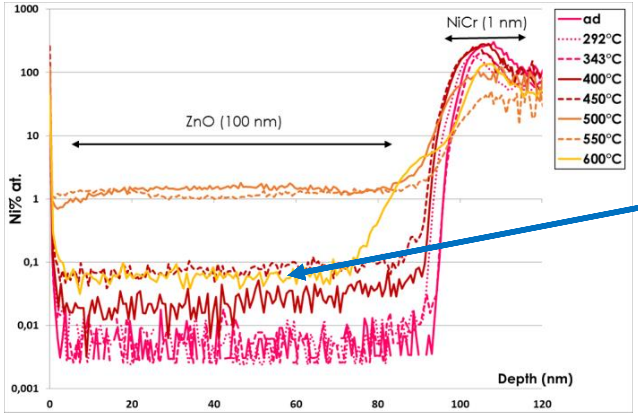


▶ Stack of Siwafer/barrier/NiCr[1nm]/ZnO[100nm]

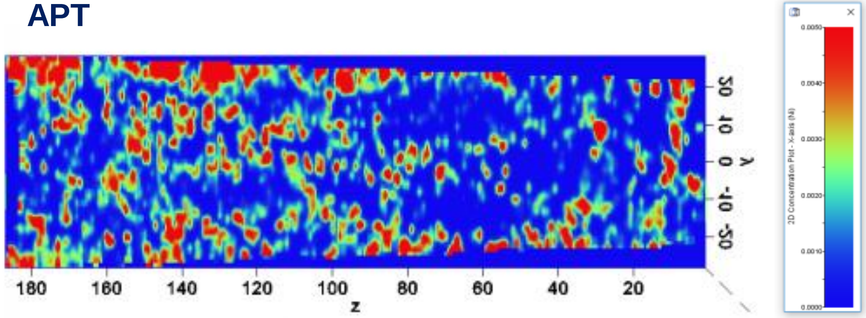
- Annealed 600°C, 1h, under vacuum
- **STEM-BF –EDX**



- **ToF-SIMS**



APT



See K Burov lecture (Tue)

J Voronkoff PhD (2020)

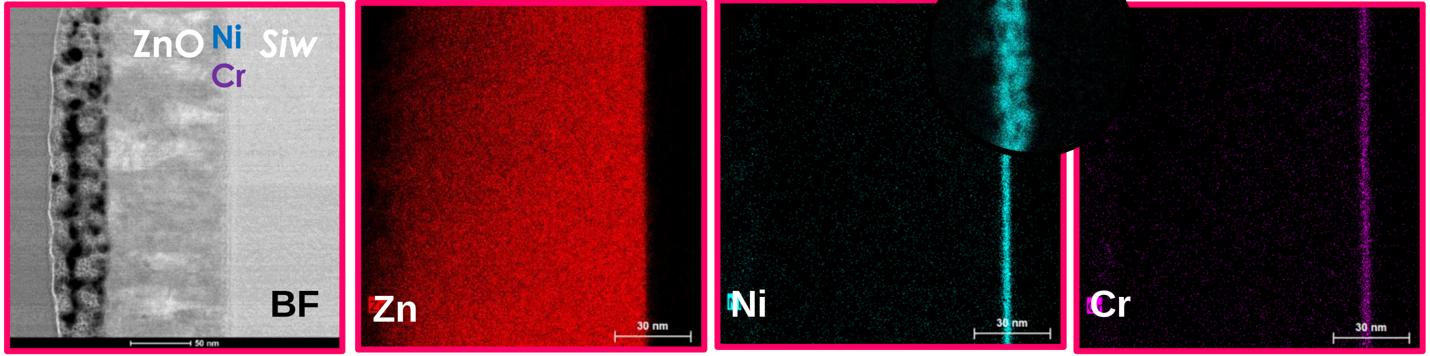
SAINT-GOBAIN RESEARCH PARIS

SAINT-GOBAIN

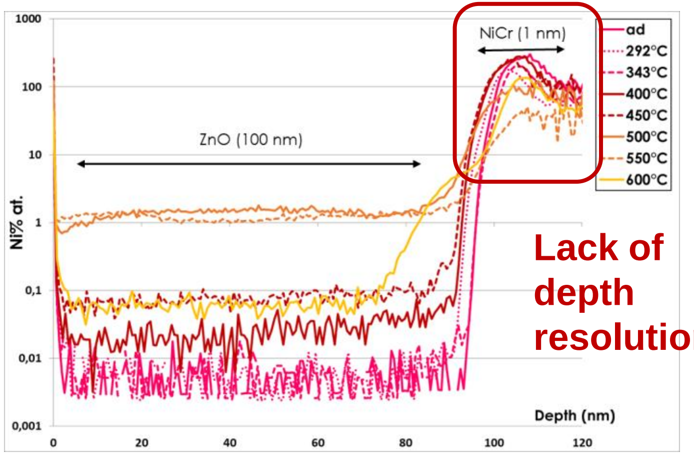
THICKNESS OF NANOLAYER=> TOF-SIMS + EPMA SOLUTION

Stack of Siwafer/barrier/NiCr[1nm]/ZnO[100nm]

- As deposited
- **STEM-BF –EDX**

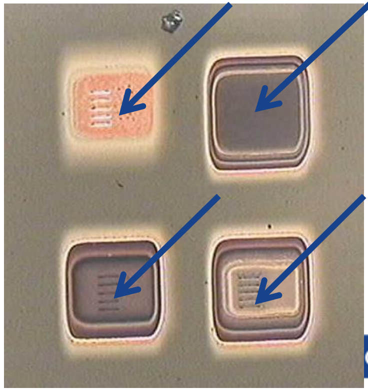


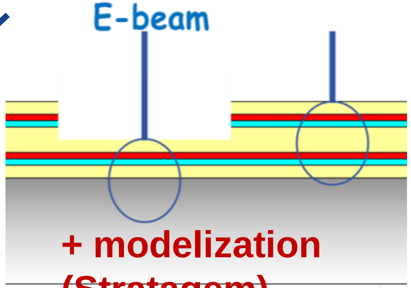
- **ToF-SIMS**



Lack of depth resolution

ToF-SIMS crater + EPMA





+ modelization (Stratagem)

J Voronkoff PhD (2020)

CH PARIS SAINT-GOBAIN

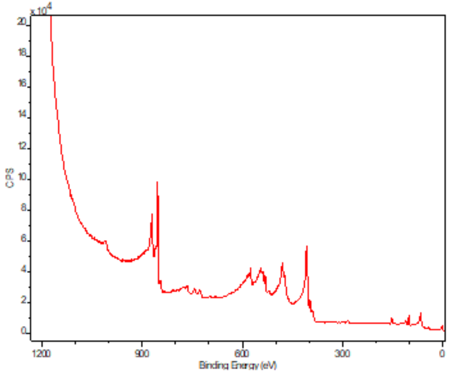
ASSESSMENT OF THE COMPOSITION (3D INFORMATION)

Technique	Resolution lateral (depth)	Range (min / max)	sensitivity	materials	Sample preparation	Other (limitations , artifacts…)
SEM – EDS	~1µm (1µm)	few µm / few mm	B=< ~0.5%at.	All (compatible vacuum and e beam)	Conductive layer	Alkaline migration, charging effect
EPMA	~1µm (1µm)	few µm / few mm	B=< ~500ppm.	All (compatible vacuum and e beam)	Conductive layer	Alkaline migration, charging effect
STEM (TEM) EDX	0.1nm	few 10 nm / 1µm	B=< ~0.5%at.	All (compatible vacuum and e beam)	lamella	Alkaline migration, charging effect, lamella thickness
STEM (TEM) EELS	0.1nm	few 10 nm / 1µm	B=< ~0.5%at. Light element	All (compatible vacuum and e beam)	lamella	Alkaline migration, charging effect, lamella thickness
ToF-SIMS (stat)	100nm (0.1nm)	Lat : few µm / few mm	All (H included) molecule Few ppm	All compatible vacuum and ion beam	none	alkaline migration quantification
ToF-SIMS (profiling)	~1nm (0.1nm)	Depth: few nm / 10µm	All (H included) Few ppm	All compatible vacuum and ion beam	none	Sputtering, alkaline migration, quantification
XPS (HAXPES)	50µm (0.1nm)	Depth: few nm / 30nm	Composition Li=< ~0.5%at.	All (compatible vacuum and RX)	none	charging effect,
XPS (profiling)	50µm (few nm)	Depth: few nm / 200nm	Composition Li=< ~0.5%at.	All (compatible vacuum and RX)	none	charging effect, sputtering
APT	0.1nm	few nm / 100nm	All (H included) Few 100 ppm	All compatible vacuum and ion beam	TiP (FIB)	alkaline migration quantification

+ RBS, GD-OES, Auger

BONDING

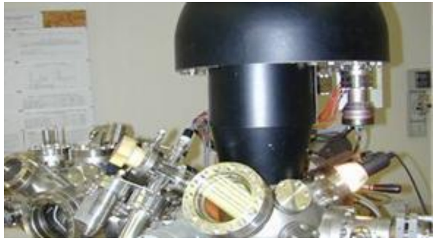
- **3 dimensions (but not selective)**
- **Examples**
  - Oxidation state of metal
  - Environment of oxygen atoms in glass : BO/NPO
  - Carbon contamination : carbonates, carbonaceous species…



- **Techniques used**
  - XPS (HAXPES)
  - XAS-XANES
  - Scanning Transmission Electron Microscopy collecting electrons (EELS)
  - ATR –IR
  - ToF – SIMS (static mode)

SAINT-GOBAIN RESEARCH PARIS

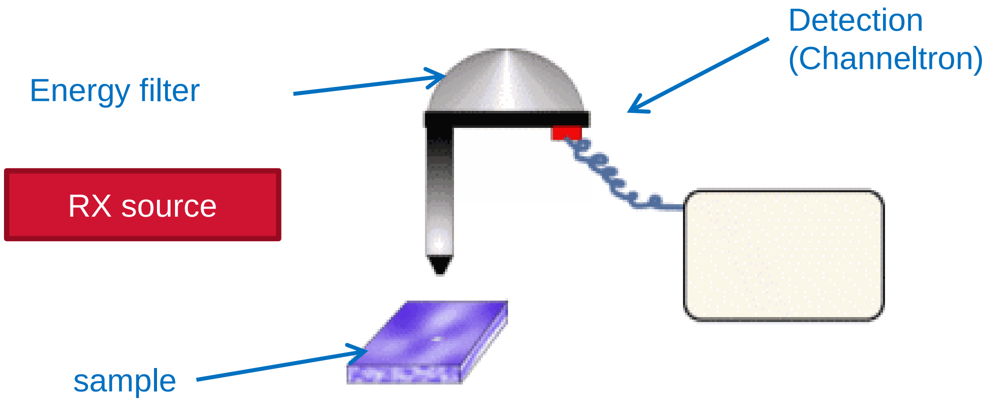
XPS TECHNIQUE



Principle

- By absorbing a photon, the atom receives an energy hν, and emits a photoelectron and, potentially, an Auger electron.
- The energy balance of these photoelectrons is :

$$h\nu = E\ \textbf{cinetic} + E\ \textbf{bonding} + \text{Ø}\ \textbf{working function}$$



The key parameters

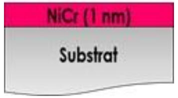
- The probed depth in 1-5nm (depending materials, signal and RX (HAXPES)
- Bonding and composition information
- Possibility to combine with ionic sputtering to perform depth profiling

See R Lazzari lecture (next)

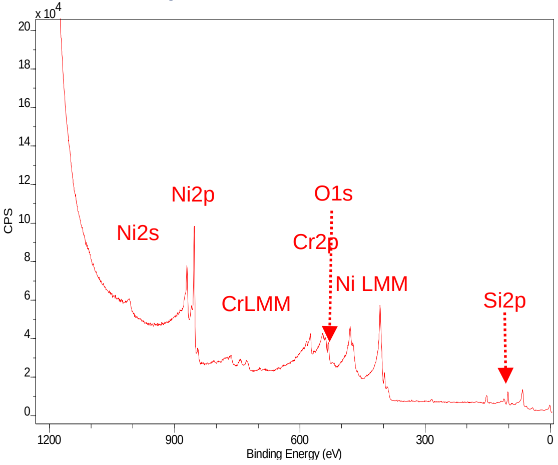
Thanks to www.lasurface.com

EXAMPLES OF BONDING ANALYSIS BY XPS

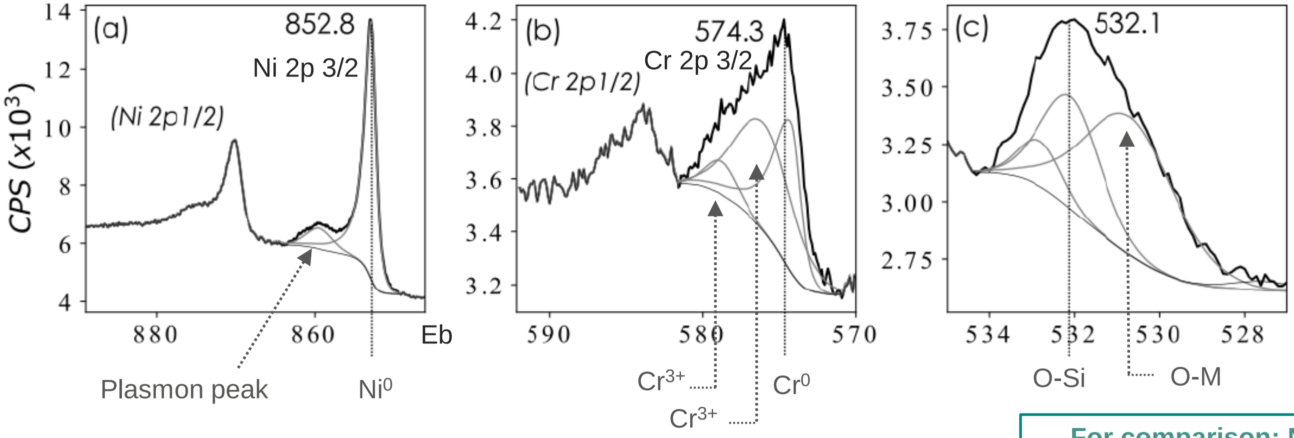
- **Thin [1nm] NiCr layer onto SiNxOy:Al substrate**



survey

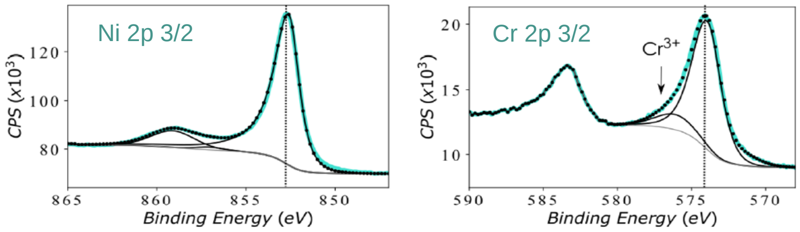


(a) Ni 2p (b) Cr 2p (c) O 1s



- **Oxidation state**
  - Ni => 100% metal
  - Cr => ~60% oxidized: Cr^{3+} type Cr_2O_3, $Cr(OH)_x$
    => consequence of substrate + residual.

For comparison: Ni 2p and Cr 2p of NiCr deposited on metal



J Voronkoff PhD (2020)

B. Payne et al. , JES&RP (2011)

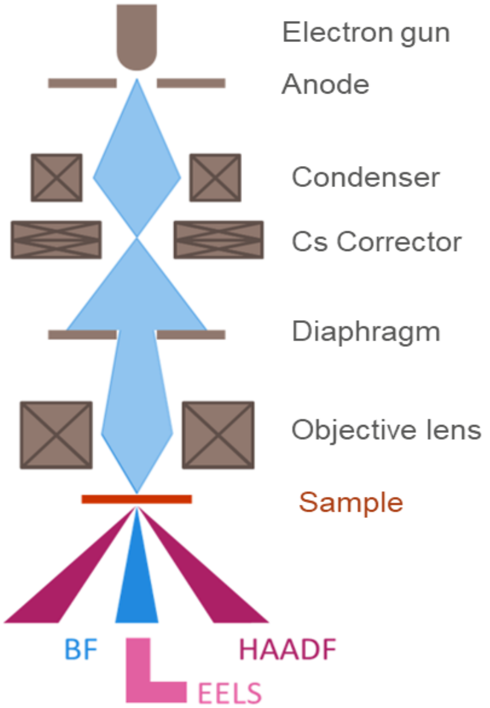
A.P Grosvenor et al., Surf. Sci.(2006)

M. Biesinger, XPSFitting,com

BONDING EXAMPLES BY STEM-EELS

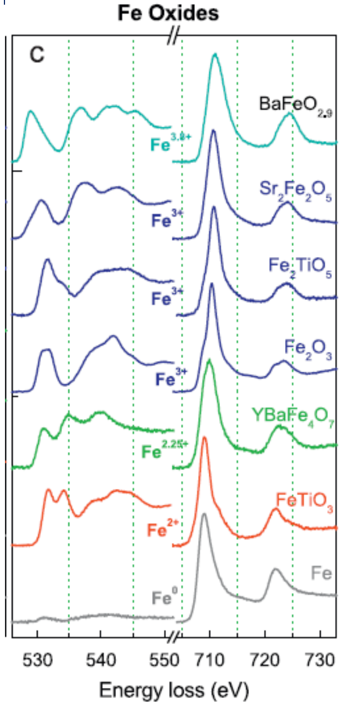
STEM-EELS

- Inelastic absorption



STEM-EELS

- Case of iron oxide type

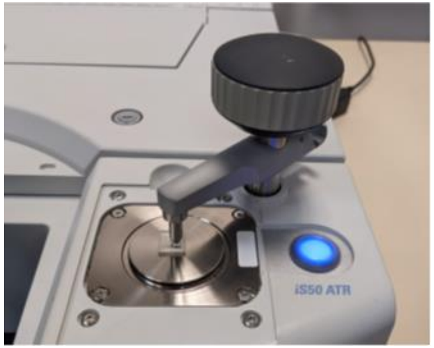


H. Tan Ultramicroscopy 116 (2012)

ATTENUATED TOTAL REFLECTANCE (ATR): PRINCIPLE AND TECHNICAL

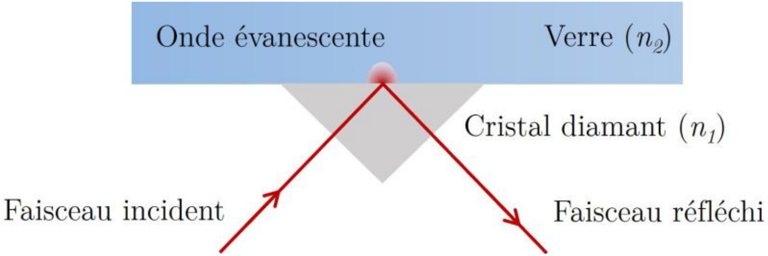
Principle

- The surface of the sample is in contact with high index crystal (Ge, diamond). The incident beam irradiate the sample surface through one side of the crystal and the reflected one is collected from the other one.
- An evanescent wave penetrates the sample.
- The IR spectra collected only concerns the upper part of the sample.



The key parameters

- Probed depth : 0.5 – 2.0 µm
- The pressure applied to the surface (reproductibility)
- The cleanliness of the sample surface analyzed.
- The crystal absorption / relevant signal
  (Diamond : 2400 et 1900 cm−1)



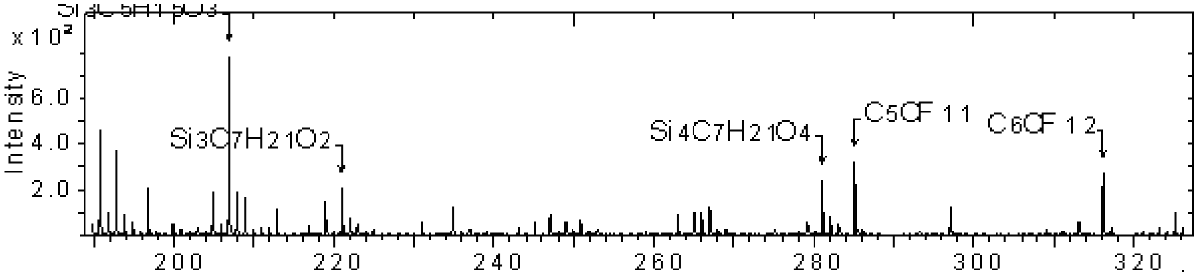
A Serve PhD (2023)

SAINT-GOBAIN RESEARCH PARIS

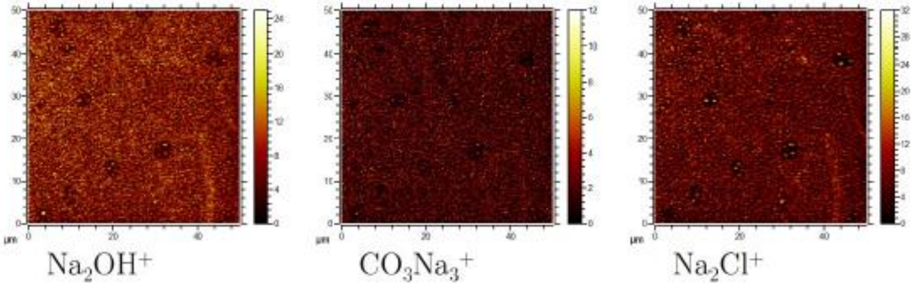
BONDING (MOLECULES) INFORMATION BY TOF-SIMS

- **Example of surface contamination**
  - glass surface

PDMS, fluorosilane contamination



- **Example of glass surface**
  - glass surface salts from corrosion



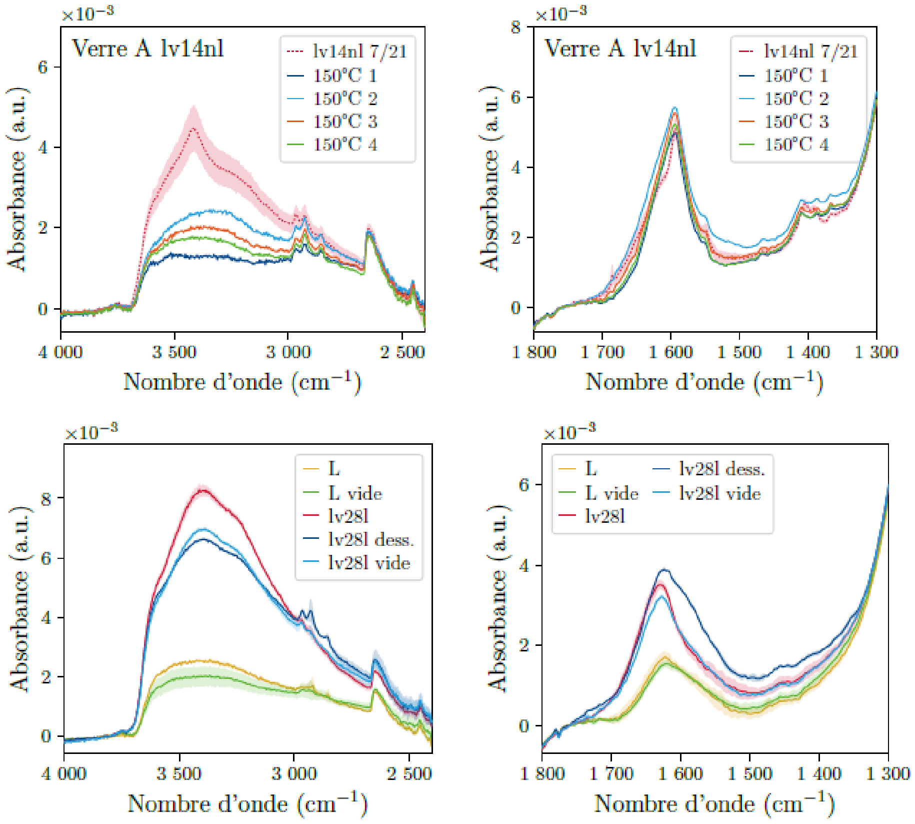
Credit T Cretin, JM Berquier)

EXAMPLES OF BONDING INFORMATION BY ATR-IR

- **Water at the surface of corroded glass (14 / 28days)**
  - Acquisition with sample in contact with atmosphere

a) Impact of heating at 150°C on the water/OH signal (14d aged glass)

b) Impact of desiccant or vacuum post-treatment on 28d aged glass



See O Majerus lecture (thu)

A Serve PhD (2023)

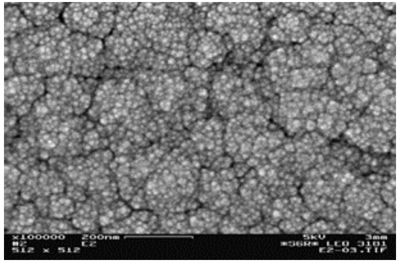
ASSESSMENT OF THE BONDING ANALYSIS

Technique	Resolution lateral (depth)	Range (min / max)	sensitivity	materials	Sample preparation	Other (limitations , artifacts…)
STEM (TEM) EELS	0.1nm	few 10 nm / 1µm	Some binding	All (compatible vacuum and e beam)	lamella	Alkaline migration, charging effect, lamella thickness
ToF-SIMS (stat)	100nm (0.1nm)	Lat : few µm / few mm	Molecules frag.	All compatible vacuum and ion beam	none	alkaline migration quantification
ToF-SIMS (profiling)	~1nm (0.1nm)	Depth: few nm / 10µm	Some binding (from SI cluster)	All compatible vacuum and ion beam	none	Sputtering, alkaline migration, quantification
XPS (HAXPES)	50µm (0.1nm)	Lat : few mm	Composition Li=< ~0.5%at.	All (compatible vacuum and RX)	none	charging effect,
XAS XANES	Few µm (~100nm TEY)	few 10µm / few mm	Some binding	All (compatible vacuum and RX)	none	charging effect
ATR -IR	Few mm (1µm)	few mm	Some binding	All compatible vacuum and ion beam	none	Flat surface

SAINT-GOBAIN RESEARCH PARIS

STRUCTURE (MICROSTRUCTURE)

- **Dimension 3D**
- **Examples**
  - Polycrystalline layer (metal: Ag, Au, oxide: ZnO, ITO, SnO_2, …)
  - Amorphous layer : porosities

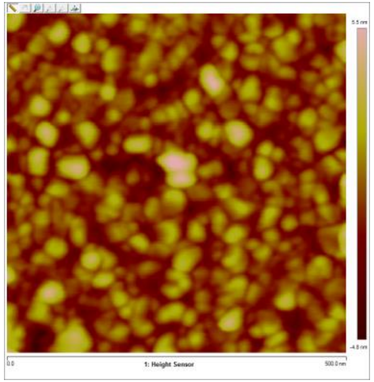


- **Techniques used**
  - Scanning Electron Microscopy -SE
  - AFM
  - Scanning Electron Microscopy coupled with EBSD
  - Transmission Electron Microscopy collecting electrons (diffraction, Dark Field)
  - Scanning Transmission Electron Microscopy collecting electrons (BF, HAADF)
  - PDF
  - X Ray Diffraction : XRD
  - Raman spectroscopy

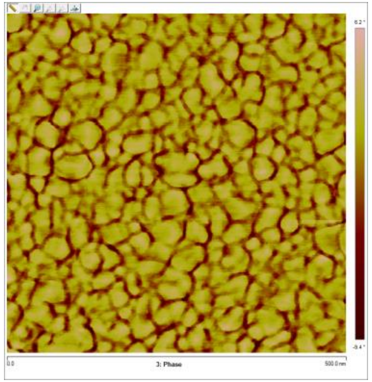
LAYER MICROSTRUCTURE FROM SURFACE SENSITIVE TECHNIQUE

AFM

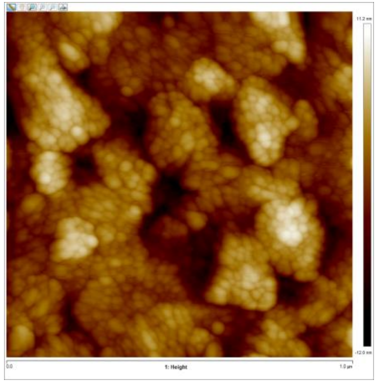
- Ag layer (50nm) : height



phase

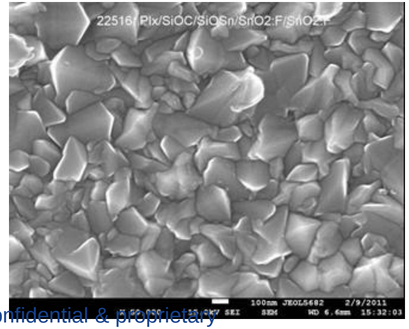


ITO (200nm) : height

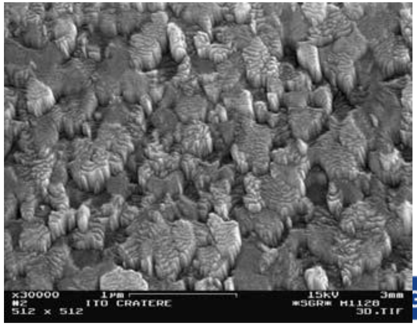


SEM-SE

- SnO2



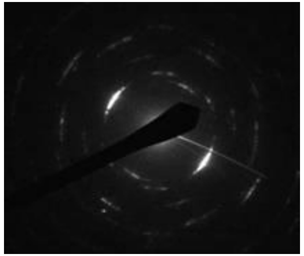
ITO (after ionic sputtering)



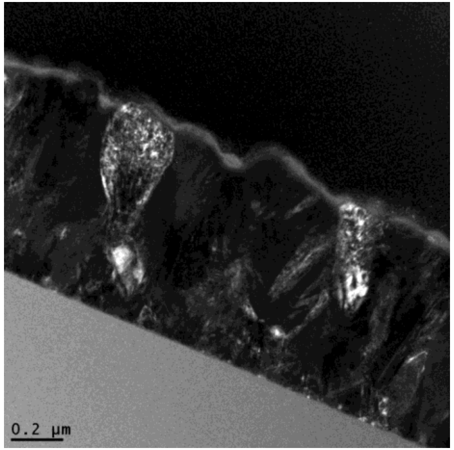
GOBAIN RESEARCH PARIS
SAINT-GOBAIN

MICROSTRUCTURE BY TEM AND STEM

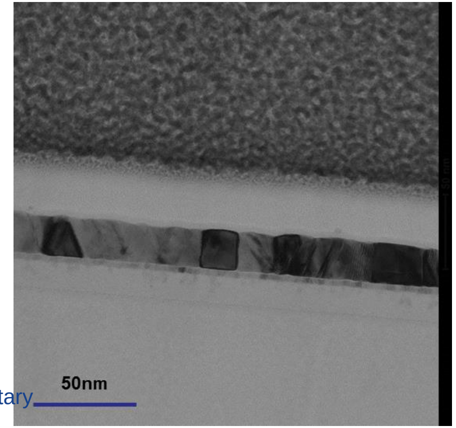
- **TEM - DF**
  - SnO2:F



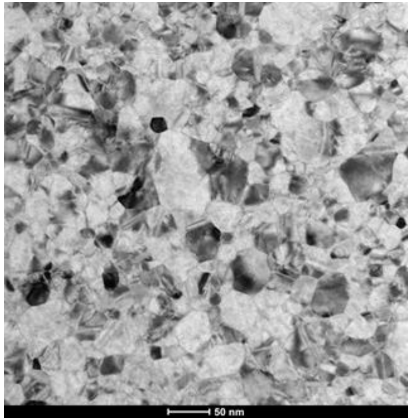
Electron diffraction



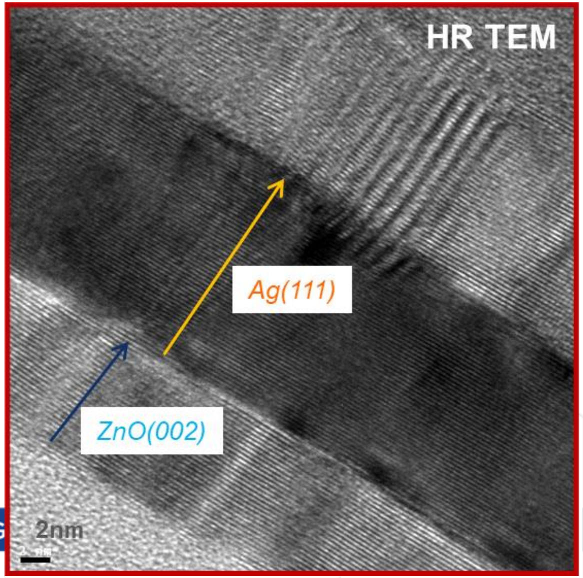
- **TEM - BF**
  - Ag based stack



- **STEM - HAADF**
  - Ag based stack



- **TEM - HR**
  - ZnO/ Ag based stack (epitaxiy)

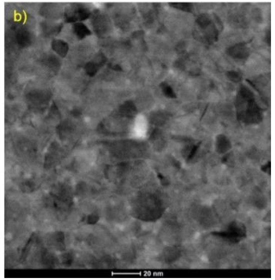


MICROSTRUCTURE BY TEM ASTAR

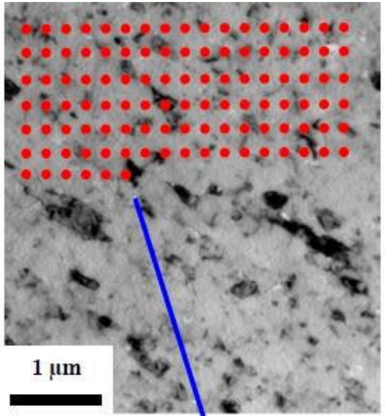
In plane acquisition

- ZnO/Ag/ZnO

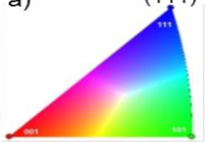
STEM-HAADF

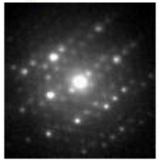


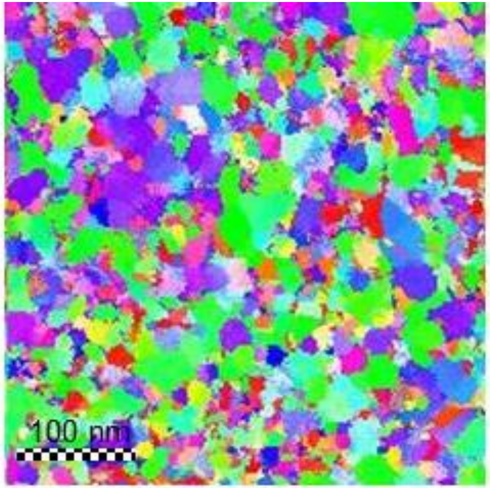
- STEM - ASTAR



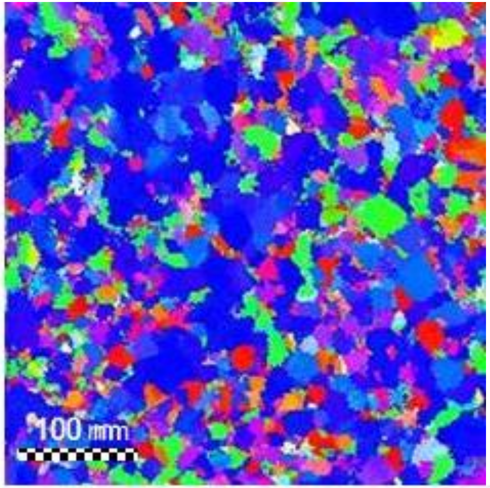
a)







c) Suivant y

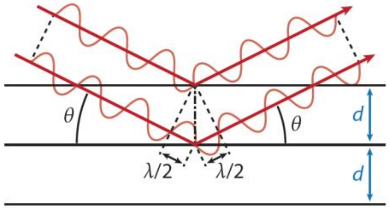


d) Suivant z

MICROSTRUCTURE BY XRD ACQUISITION

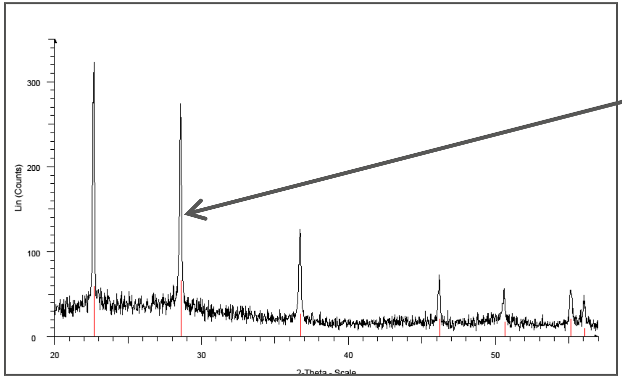
Principe

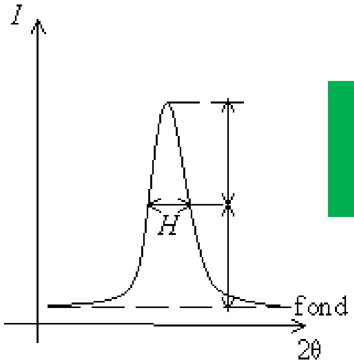
- XRD is based on the interaction of an incident X-ray beam with a material which, if it is crystallized, leads to diffraction phenomena.



Microstructure information

- Peak analysis profile





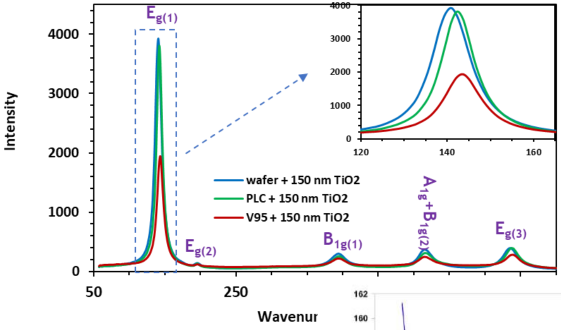
See R Lazzari lecture (next)

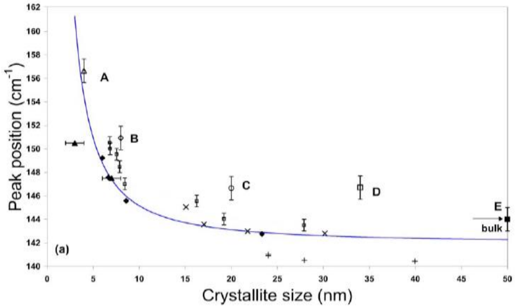
H = k.λ/(τ.cos(θ))

With T = crystal size

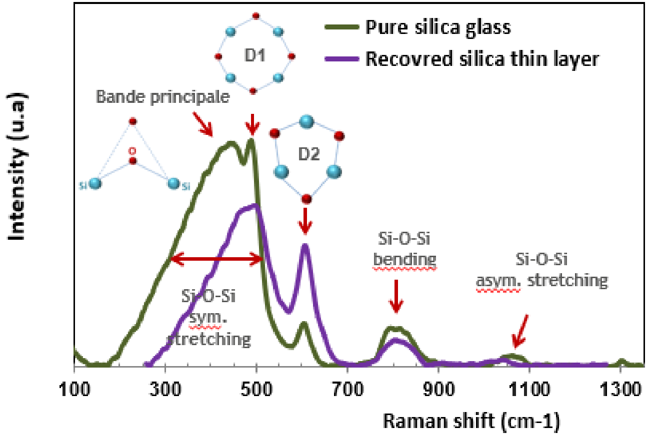
MICROSTRUCTURE BY RAMAN

- crystallized materials
  - TiO2 layer





- Amorphous materials
  - Silica thin film



See K Burov and L Cormier lecture (Tu)

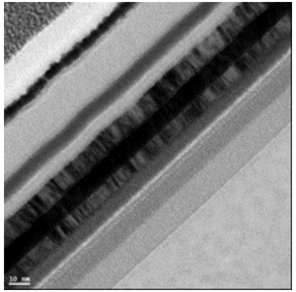
ASSESSMENT OF MICROSTRUCTURE

Technique	Resolution lateral (depth)	Range (min-max)	Sensitivity	Materials	Sample preparation	Other (artifact, limitation…)
SEM - SE	1nm (few nm)	Few nm / few mm	topography	All (compatible vacuum and e beam)	Conductive layer at surface	Alkaline migration, charging effect
SEM - BSE	>1nm (few 10 nm)	few nm / few mm	topography, Z element	All (compatible vacuum and e beam)	Conductive layer at surface	Alkaline migration, charging effect
TEM - Dif	0.1nm	few 10 nm / 1µm	crystallized	All (compatible vacuum and e beam)	lamella	Alkaline migration, charging effect, lamella thickness
STEM (TEM) BF, HAADF	0.1nm	few 10 nm / 1µm	Z element, B=< microstructure,	All (compatible vacuum and e beam)	lamella	Alkaline migration, charging effect, lamella thickness
XRD	50µm	few 10µm / few mm	crystallized	All	none	
Raman	~1µm (1µm)	few µm / few mm	Structure, composition	All compatible with laser	none	fluorescence (laser)
AFM	0,1nm (0.1nm)	few nm / 100µm	topography / material	All	none	Extreme surface

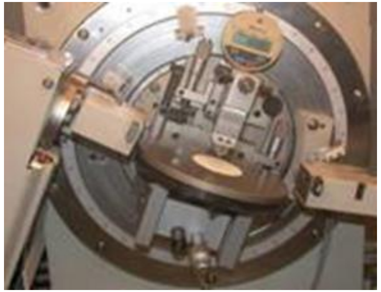
+ APT

DENSITY

- **Dimension …**
- **Examples**
  - Continuous thin layer



- **Techniques used**
  - Scanning Transmission Electron Microscopy collecting electrons (BF, HAADF)
  - X Ray Reflectrometry: XRR

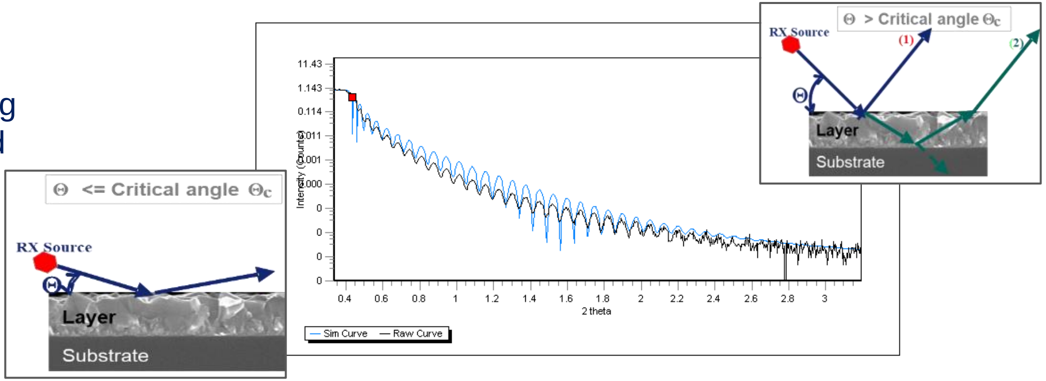


DENSITY EVALUATION BY XRR AND STEM

See R Lazzari lecture (next)

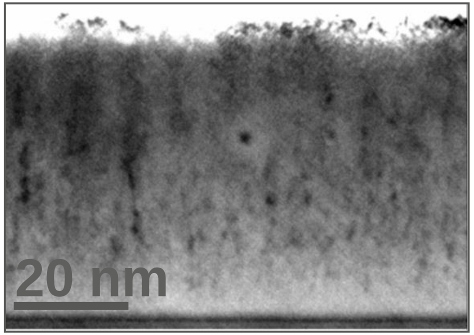
XRR principle

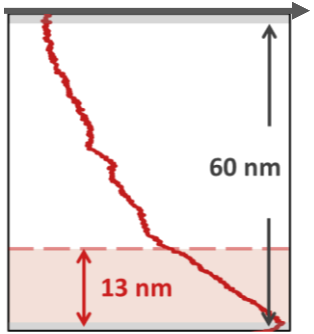
- Based on the sample irradiation by a grazing XR beam and the collection of the reflected beam by the surface and the interface(s).
- Thickness <250nm



Density from STEM-HAADF

- Based on the sample absorption of incident electron.
- Relative information
- Available if lamella thickness = cste





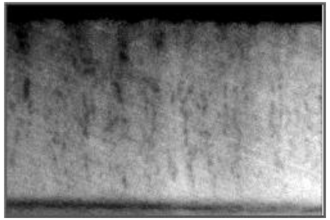
T Barres PhD (2017)

ASSESSMENT OF THE DENSITY

Technique	Resolution lateral (depth)	Range (min - max)	sensitivity	materials	Sample preparation	Other
STEM (TEM) BF, HAADF	0.1nm	few 10 nm / 1µm	Z element, B=< microstructure,	All (compatible vacuum and e beam)	lamella	Alkaline migration, charging effect, lamella thickness
XRR	1nm	1nm / 200nm	Electron density	All	none	Very flat sample, number of layers

STRAIN AND STRESS

- **Dimension 3D**
- **Examples**
  - Crystallized layer
  - Amorphous layer (sputtered SiNx)

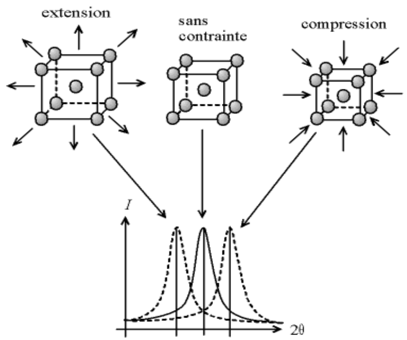


- **Techniques used**
  - Scanning Transmission Electron Microscopy collecting electrons (BF, HAADF)
  - X Ray diffraction : XRD
  - Spectroscopy Raman
  - FIB-SEM + picture analysis

STRAIN EVALUATION BY XRD AND STEM-HAADF (CRYSTALLIZED LAYER)

From XRD

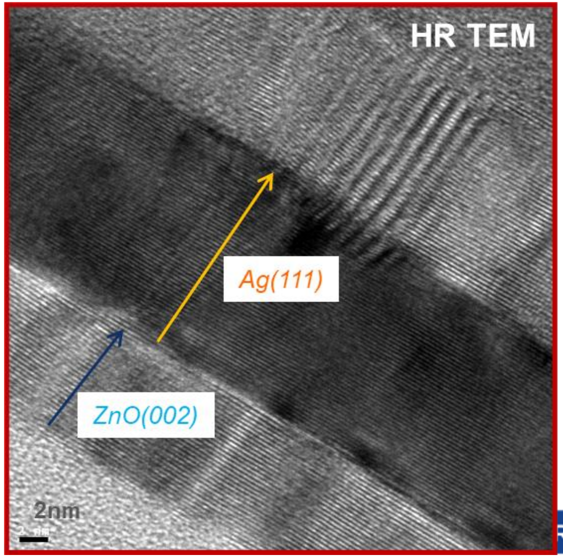
- Principle: Stress induces XRD peak shift due to variation of the lattice parameter



See E Barthel (Mo) R Lazzari lecture (next)

From STEM - HAADF

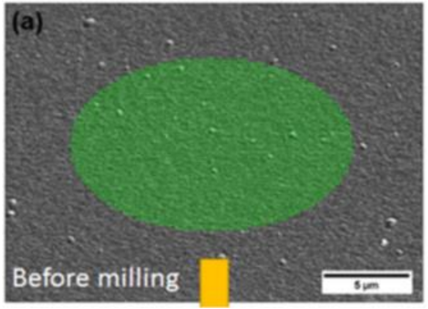
- Principle: Stress induces interplanar distances shift
- Possible to follow gradient



STRESS EVALUATION BY FIB /SEM (CRYSTALLIZED AND AMORPHOUS)

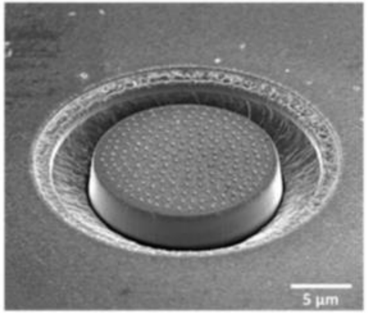
TRANSVERSAL R&D CENTERS BY SAINT-GOBAIN

- **Principle**
  - Sputtered CrN layer deposited with 3 bias voltages -40, -120 and -80V)

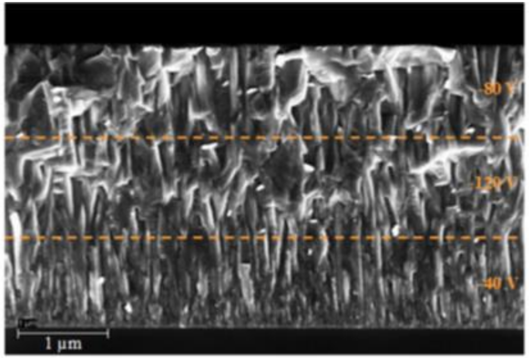


Sequential Milling

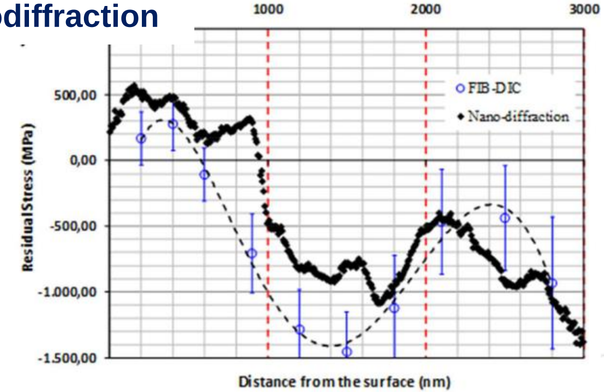
And SEM picture of surface



DIC + FE



Comparison DIC-FE with nanodiffraction



Abadias, Barthel et al. JVSTA (2018)

ASSESSMENT OF THE STRESS AND STRAIN

Technique	Resolution lateral (depth)	Range (min-max)	Sensitivity	Materials	Sample preparation	Other (artifact, limitation…)
TEM - Dif	0.1nm	few 10 nm / 1µm	crystallized	All (compatible vacuum and e beam)	lamella	Alkaline migration, charging effect, lamella thickness
STEM (TEM) BF, HAADF	0.1nm	few 10 nm / 1µm	Z element, B=< microstructure,	All (compatible vacuum and e beam)	lamella	Alkaline migration, charging effect, lamella thickness
XRD	50µm	few 10µm / few mm	crystallized	all	none	
Raman	~1µm (1µm)	few µm / few mm	Structure,	All compatible with laser	none	fluorescence (laser)
FIB-SEM	-	-	crystallized amorphous	All	Particle deposition	Extreme surface

SAINT-GOBAIN RESEARCH PARIS

CONCLUSIONS

- First step : identify the relevant information to answer your question
- Then answer : - Probed resolution (0,1nm => 1µm…) ?
  - Probed range (1nm => 1µm…) ?
  - Sufficient sensitivity (1%at, 1ppb…) ?
  - Is the artifact of the technique and the preparation are compatible with the info?
- Syndrome : “I need SEM pictures !”
- SEM-SE (ETD) SEM-SE(inlens) SEM-BSE SEM-EDX SEM-EBSD SEM-SE(tilt) SEM-SE cross section

MANY THANKS FOR THEIR CONTRIBUTIONS

Thierry Cretin, Patrice Lehuédé, Jacques Perrin-Toinin, Justine Voronkoff,

Sophie Papin, Ludovic Largeau, Nicolas Trcera, Pierre Lagarde, Régine Faure,

Philippe Letocart, Corinne Papret, Sophie Brossard, Jean Thomas Fonné,

Thomas Barres, Sirine Ben Khemis, Amandine Serve, Odile Majerus,

Remi Lazzari, Daniel Caurant, Katia Burov, Odile Stephan

ET MERCI POUR VOTRE ATTENTION