CARACTÉRISATION EX-SITU DE LA DIFFUSION: MESURE PAR FAISCEAU D'IONS ET D'ÉLECTRONS

Ecole thématique du CNRS, Verres et diffusion 4-8 octobre 2021, Fréjus

Hervé Montigaud

SVI - Saint-Gobain Research Paris

AGENDA

INTRODUCTION - SPECIFICATION

TECHNIQUE 1

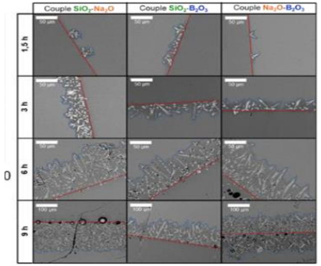
TECHNIQUE 2

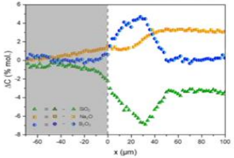
TECHNIQUE 3

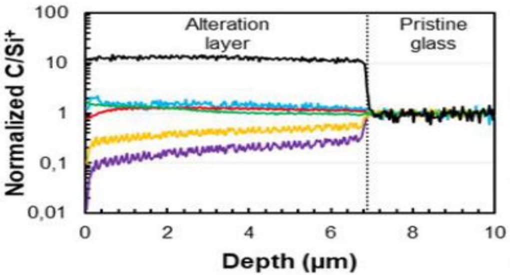
TECHNIQUE 4

OTHERS TECHNIQUES…

CONCLUSION







INTRODUCTION

1D characterization

Isotope selectivity
^{16}O, ^{18}O

Multi-elements analysis (wide range of sensivity?)
72,2%at. …. 0,3%at.

Combining with other characteristics
$[Fe] / {}^{VI}Fe^{2+}$

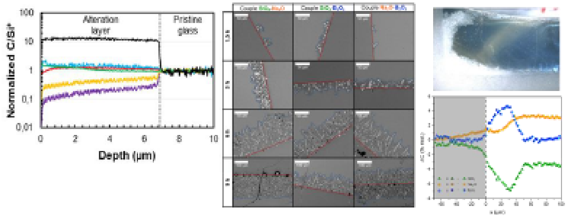
ECOLE THEMATIQUE DU CNRS

« Verres et diffusion »
Diffusion chimique dans les phases vitreuses et liquides

03 au 08 octobre 2021 - La Villa Clythia Fréjus

Public attendu : académique et industriel - Etudiants en doctorat et jeunes chercheurs, ingénieurs, chercheurs CNRS et enseignant-chercheurs, Ingénieurs R&D - Domaines (INC, INP, INSU) : verres, matériaux, archéomatériaux (verres, glaçures, phases amorphes dans les céramiques et métaux), minéralogie et volcanologie

Date limite d'inscription : 30 juin 2021 - Inscription en ligne : https://verre-diffusion.sciencesconf.org



Enjeux

La diffusion est un processus physico-chimique majeur et déterminant pour les verres et les amorphes (oxydes, chalchogénures, verres métalliques), qui influence la plupart de leurs propriétés, de l'élaboration à la mise en service et au vieillissement. Les processus de diffusion chimique sont par ailleurs complexes, avec autant de mécanismes différents (autodiffusion, diffusion multi-composante avec échange ionique ou réactions d'oxydation/réduction, diffusion des traceurs ou des défauts), que de types de milieux de diffusion (liquide, solide cristallin et amorphe, phase gazeuse) et de conditions (haute et basse température, échelles de temps allant de quelques secondes aux temps géologiques). Dans ce contexte, la recherche verrière a

High sensitivity (traces)
<0,1%at.

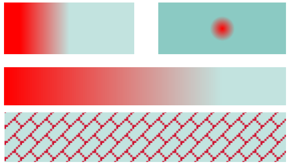
3D characterization

3D characterization with high lateral resolution

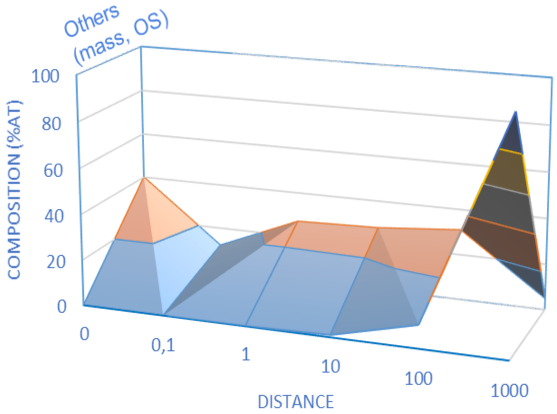
Wide range of probed areas

INTRODUCTION

list of specifications



- Over a wide range of distances,
- Through the 3D directions,
- Among heterogeneities (specific path)



72,2%at. ... 0,3%at.
<0,1%at.

- The major components,
- And the traces too,

^{16}O, ^{18}O

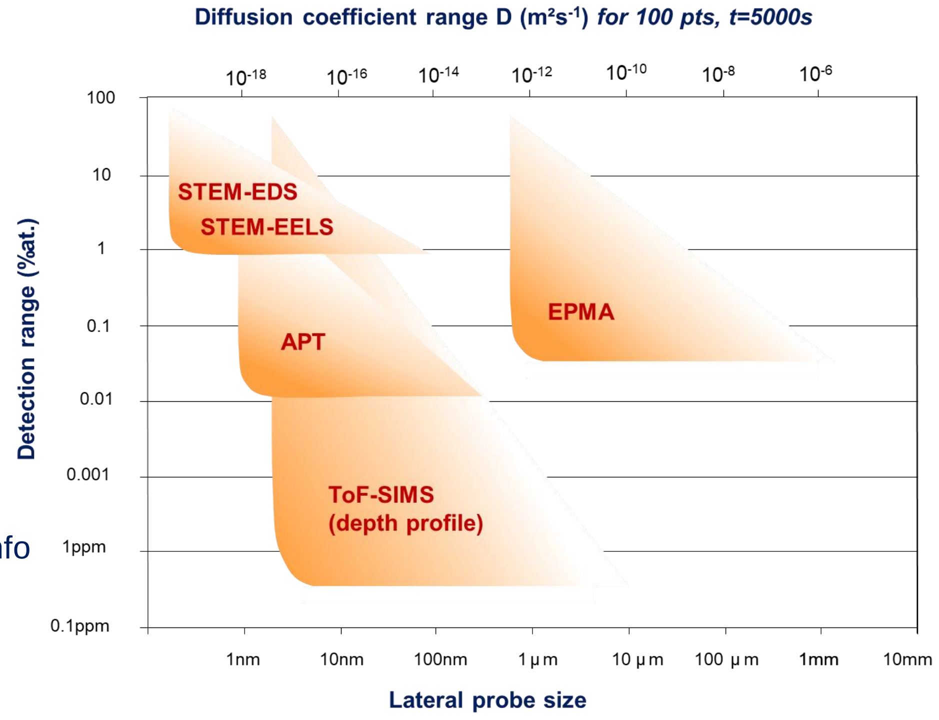
- Every isotopes are concerned,

[Fe] / $^{VI}Fe^{2+}$

- Other characteristics
  (oxidation state, site…)

INTRODUCTION: SELECTION OF RELEVANT TECHNIQUE FOR THE ANALYSIS OF COMPOSITION GRADIENT

- **Electron Probe MicroAnalysis**
  - Wide range of detection and distances (µm to nm)
  - Only elements (Boron=>)
- **Time of Flight-Secondary Ion Mass Spectro.**
  - Major and traces, large distances (nm to several µm)
  - Isotope (H =>)
- **Scanning Transmission Electron Microscopy**
  - 0,1nm to 1µm
  - **Energy Dispersive Spectro**: elements (Boron =>)
  - **Energy Electron Loss Spectro**: elements and binding info
- **Atom Probe Tomography**
  - 1nm to 100nm
  - Isotope (H =>)



AGENDA

INTRODUCTION - SPECIFICATION

ELECTRON PROBE MICRO ANALYSIS (EPMA)

- Principle - history
- Device description
- Acquisition, quantification and artifacts
- Example of gradient analysis within glass

SECONDARY IONS MASS SPECTROMETRY (SIMS / ToF-SIMS)

ATOM PROBE TOMOGRAPHY (APT)

SCANNING TRANSMISSION ELECTRON MICROSCOPY (STEM-EDS, EELS)

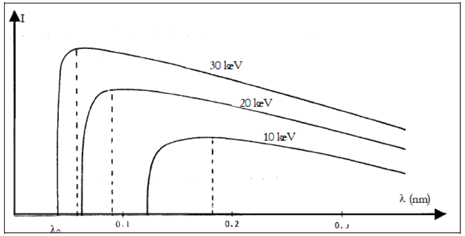
OTHERS TECHNIQUES: XPS, AUGER, XAS DEPTH PROFILING

CONCLUSION

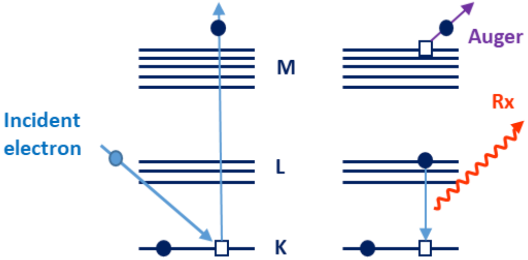
EPMA PRINCIPLE

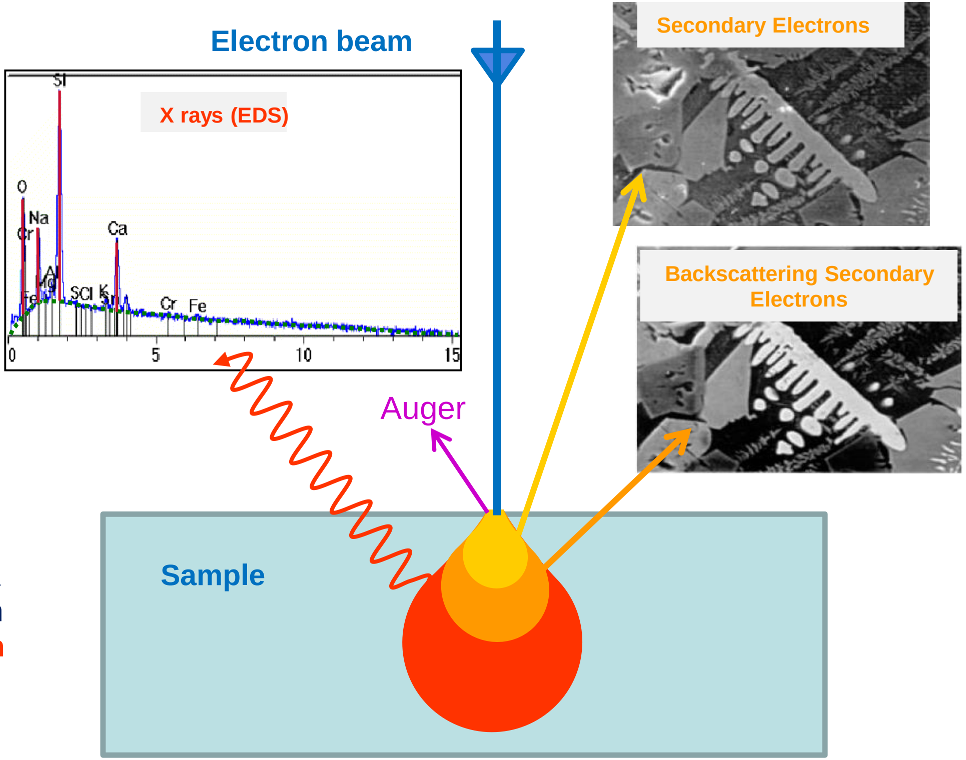
Electron / material interaction

- 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).**

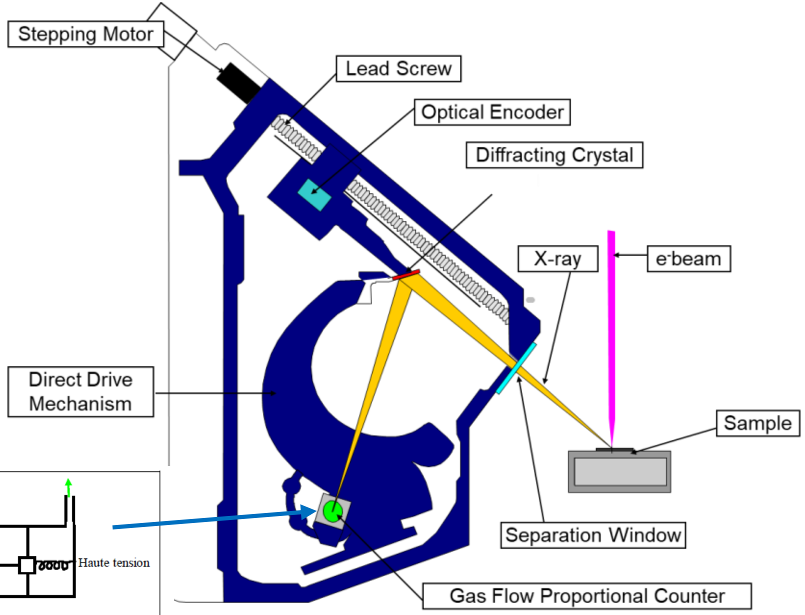




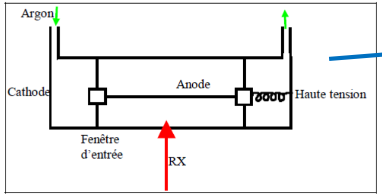
EPMA : TECHNICAL POINT VIEW

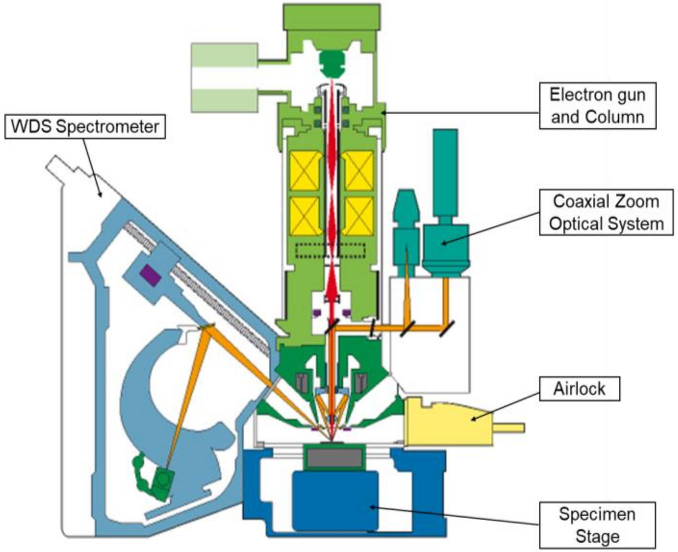
Wavelength Dispersive X-ray Spectrometer

- The key part of EPMA
- Associated to gas-flow counter (photoelectrical effect)



Gas-flow counter





Crystal used in WDS

Nom du Cristal	2d (nm)	*Domaine d'analyse* [4]		Raies X analysables (ordre 1)		
		Longueur d'onde (nm)	*Energie (keV)*	Raie K	Raie L	Raie M
LiF [1]	0.4026	*0.08 à 0.33*	*14.76 à 3.75*	Sc à Sr	Te à U	X
PET [2]	0.874	*0.18 à 0.72*	*6.81 à 1.73*	Si à Fe	Sr à Ho	W à U
TAP [3]	2.575	*0.54 à 2.11*	*2.31 à 0.59*	F à P	Mn à Mo	La à Hg
PC1(W/Si)	6.100	*1.83 à 4.42*	*0.68 à 0.28*	C, N, O, F	K à Ni	La à Ce
PC2 (Ni/C)	9.500	*2.36 à 6.74*	*0.53 à 0.19*	B, C, N, O	S à Cr	X
PC3 (Mo/B_4C)	14.000	*3.10 à 11.62*	*0.40 à 0.10*	Be, B	Si à Sc	X

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

EPMA: SOME DATES

R Castaing (1921-1998)
the « Father » of EPMA

1944 : J. Hillier, RF Baker (RCA-USA)

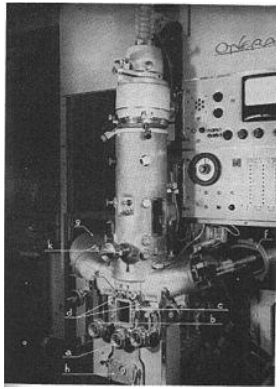
- First electron microprobe, combining an electron microscope and an energy loss spectrometer and proposed WDS design (but never constructed).

1950 : R. Castaing, *A Guinier* (Onera-Fr)

- First electron microprobe with crystal (quartz) for wavelength discrimination (PhD in 1951)

1956 : CAMECA (Fr)

- First commercial electron microprobe MS85 →



1957 : P Duncumb (Microscan-UK)

- First commercial electron microprobe with scanning electron bean

EMPA examples: CAMECA SXFive and JEOL 8530

J. Hillier, RF Baker, Microanalysis by Means of Electrons". *J. of Appl Phys*. 15 (1944)

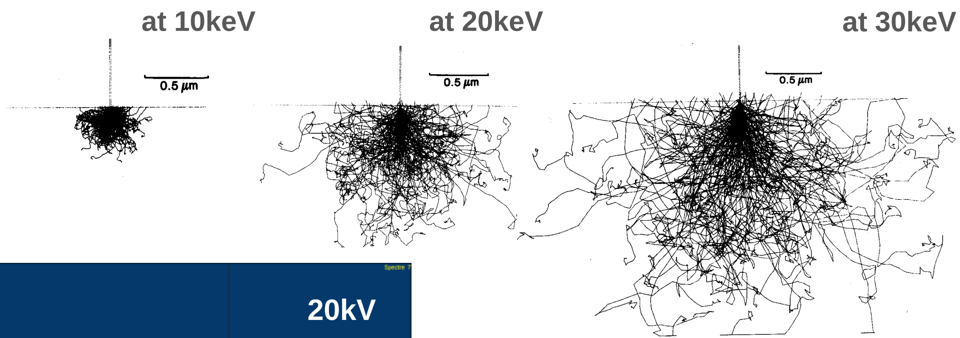
https://commons.wikimedia.org/

EPMA: KEY PARAMETERS

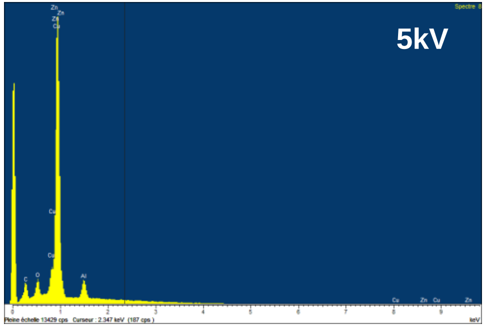
Choice of the incident electron energy

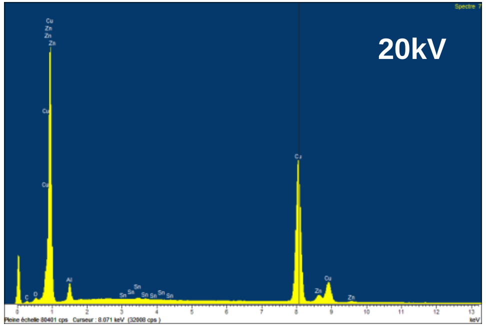
- A compromise between
  - Lateral / depth resolution
  - Element analysis ($E_{electron} > 2{,}5 \times E_{peak}$ for I_{max})

Electron paths in Fe



Example of CuAlZnSn alloy

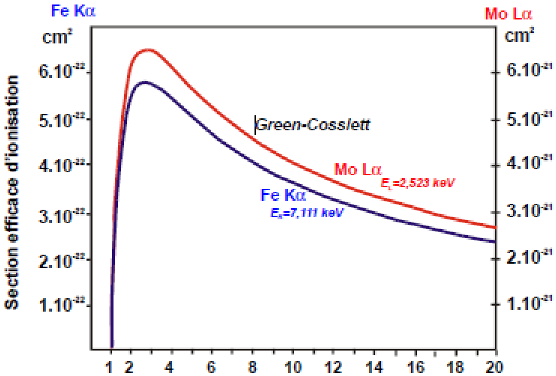




Choice of optimal X-ray characteristic peak

- Depending of the element of interest and its amount

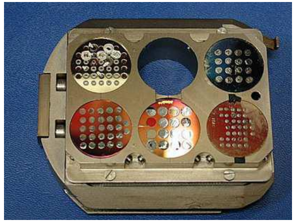
$$U = \frac{E}{E_j}$$

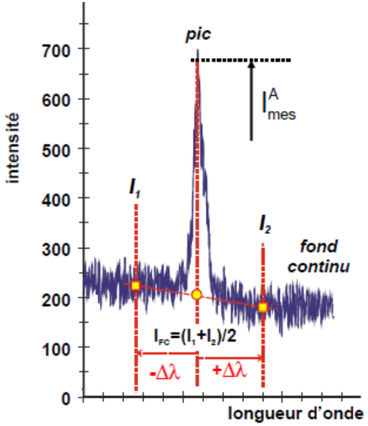


AND FINALLY QUANTIFICATION BY EPMA

- **Acquisition on sample**
  - Centering at peak max => acquisition during tx
  - Background measurement at $-\Delta\lambda$ and $+\Delta\lambda$

- **Acquisition on standard**
  - Centering at peak max => acquisition during tx
  - Background measurement at $-\Delta\lambda$ and $+\Delta\lambda$





- **k-ratio estimation**
  - Using correction protocol
    - ZAF
    - Phi(roz)

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

Note : *if $E_{electron\ incident}$ >10keV, for element ≠ light ones peak energie>5keV => $K_A \sim C_A$*

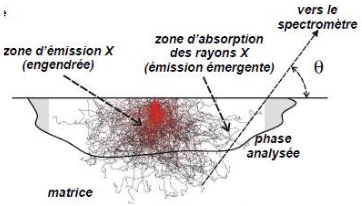
if light Elements or samples with elements with different Z => absorption high => $K_A \neq C_A$ =>modelization!!

SAINT-GOBAIN RESEARCH PARIS

BUT ARTEFACTS POSSIBLE (FOR EVERY SOLIDS AND GLASS)

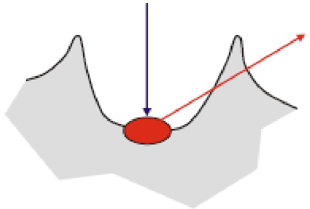
- **Surface heterogeneities > emission volume**
  - Probed volume ~1µm³

=> Reduction of $E_{Electron}$



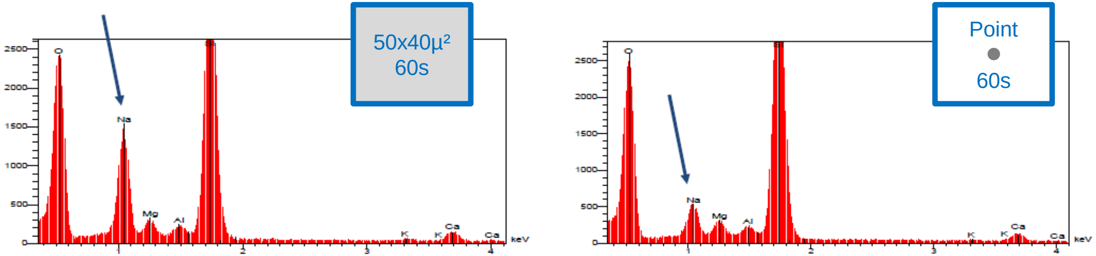
- **Surface roughness**
  - X-ray absoprtion

=> Reduction of roughness (< 1µm)



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

=> reduction of electron dose

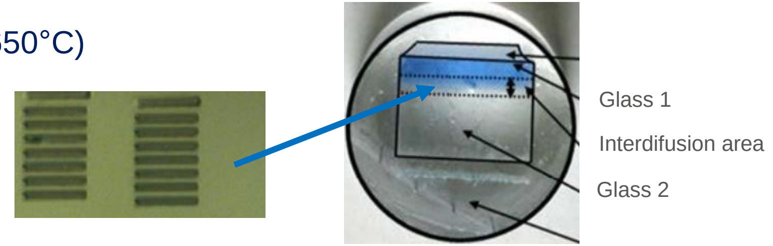


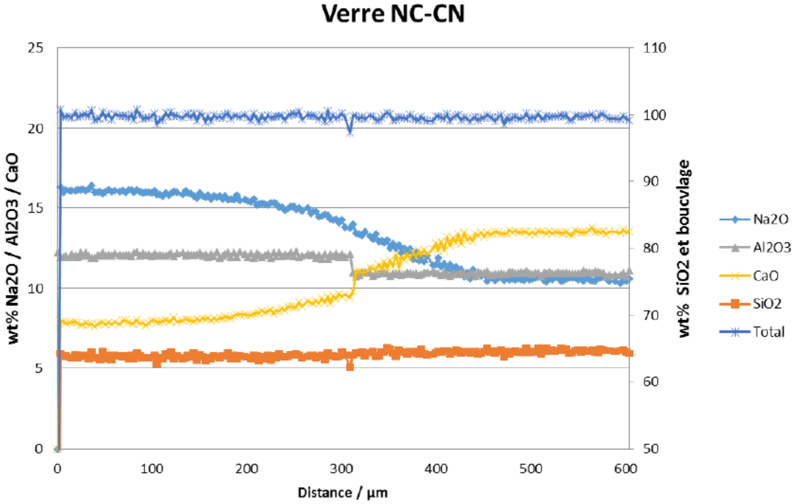
- **Samples (glass) preparation**
  - Polishing (optical quality)
  - Deposition of conductive layer (carbon)

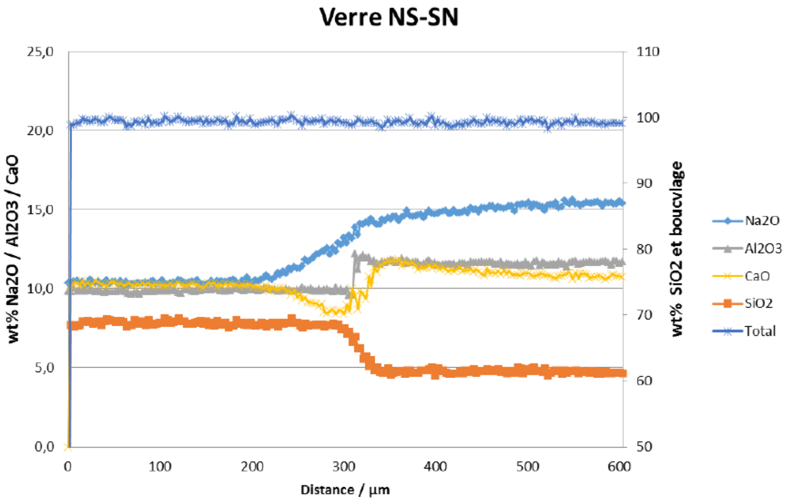
Microanalyse X quantitative, J Ruste, GNMEBA

ANALYSIS OF DIFFUSION BETWEEN GLASS

- **Atomic mobility in silicate glasses**
  - Interdiffusion within Na, Ca, Al, Si system (annealing at 650°C)
- **EPMA Acquisition**
  - Line mode 1µm x 40µm
  - Na-Ka, Al-Ka, Si-Ka, Ca-Ka at 10nA
  - 2 rows of lines (steps=5µm) with offset of 2,5µm





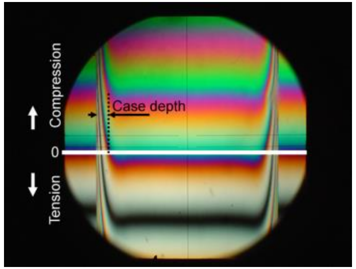


C Claireaux JNCS (2019)
C Claireaux PhD, Univ Sorbonne (2014)

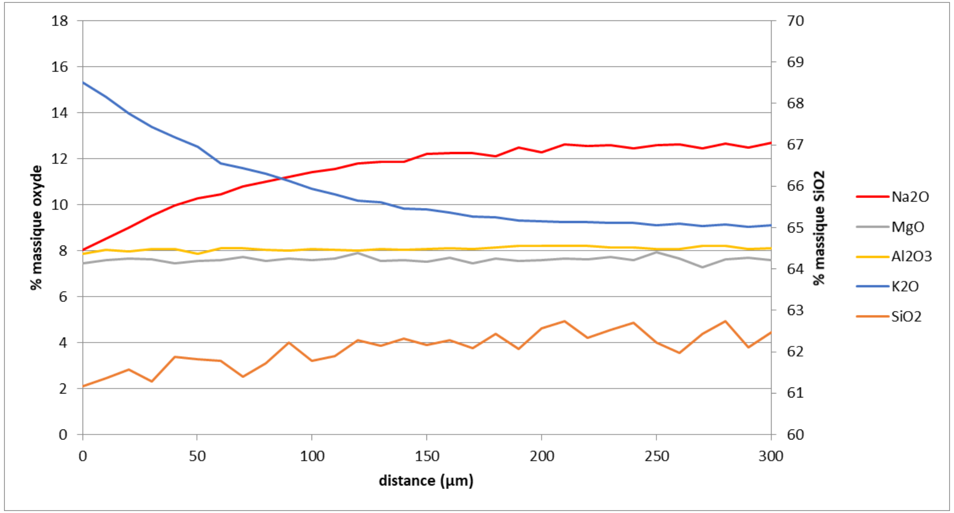
ANALYSIS AT SURFACE: CHEMICAL TEMPERED GLASS

- **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



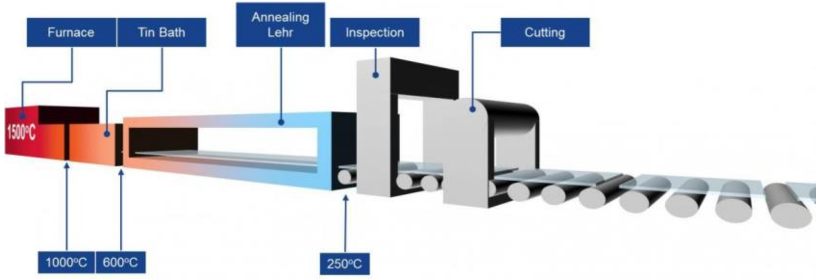
R Gy, Mat. Sci.Eng. B, 149 (2007)

ANALYSIS OF GLASS DEFECT

TRANSVERSAL R&D CENTERS BY SAINT-GOBAIN

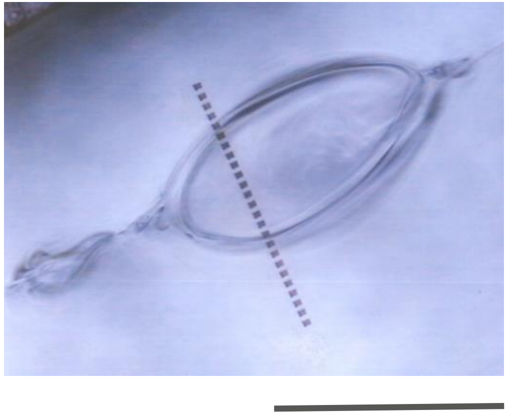
Float Glass : quality control

- Example of “gum” defect (refractories)

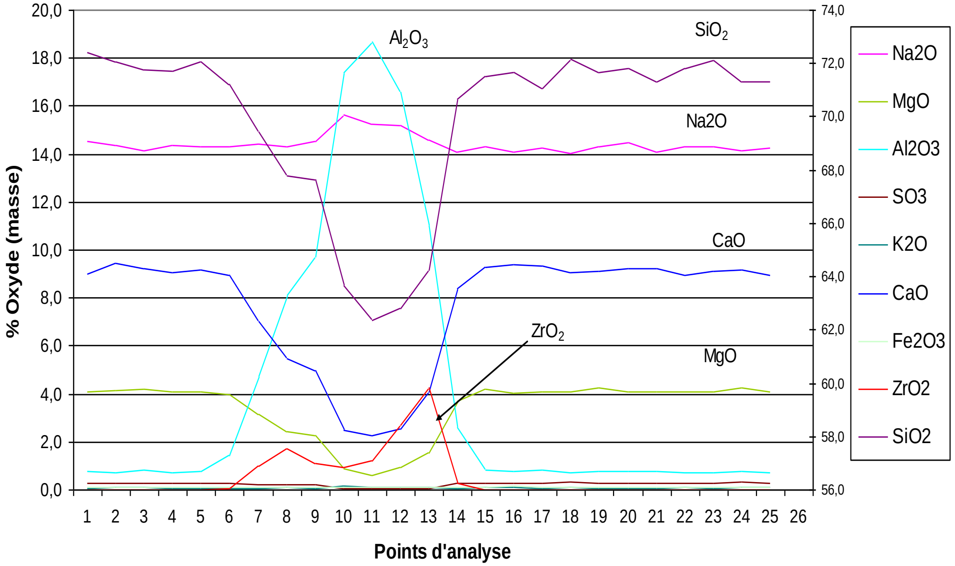


EPMA Acquisition

- 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



1mm



P Lehuedé pers. Com. (2007)

AGENDA

INTRODUCTION - SPECIFICATION

ELECTRON PROBE MICRO ANALYSIS (EPMA)

SECONDARY IONS MASS SPECTROMETRY (SIMS / ToF-SIMS)

- Some elements of history
- Principle (from incident ions to secondary ions)
- ToF-SIMS compared to other sputtering-based techniques
- ToF-SIMS equipement
- Performances (resolution, sensitivity, key paremeters artifacts)
- Case of glasses

ATOM PROBE TOMOGRAPHY (APT)

SCANNING TRANSMISSION ELECTRON MICROSCOPY (STEM-EDS, EELS)

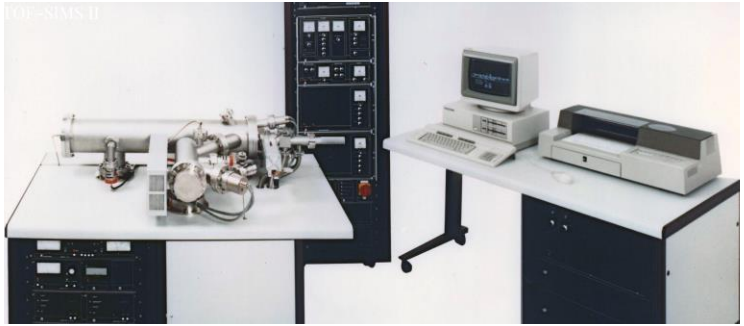
OTHERS TECHNIQUES: XPS, AUGER, XAS DEPTH PROFILING

CONCLUSION

SIMS : A QUITE RECENT TECHNIQUE

Some dates concerning SIMS

- **1910-3** : J.J. Thomson studied the interactions cations / metal
- **1949** : Herzog et Viehbock built the first prototype (Univ. Wien)
- **1960** : 2 SIMS instruments were developed : 1 in USA by Liebel and Herzog for the analysis of Moon rocks and the second by R Castaing and his PhD, G Slodzian. This latter was developed by CAMECA.
- **1969** : A. Benninghoven introduced the method of Static SIMS using Time-of Flight mass spectrometer
- **1982** : Briggs developed the surface analysis of polymers
- **~1982** : First commercial Static SIMS



A Benninghoven
the « Father » of SSIMS

ION – SOLID INTERACTION

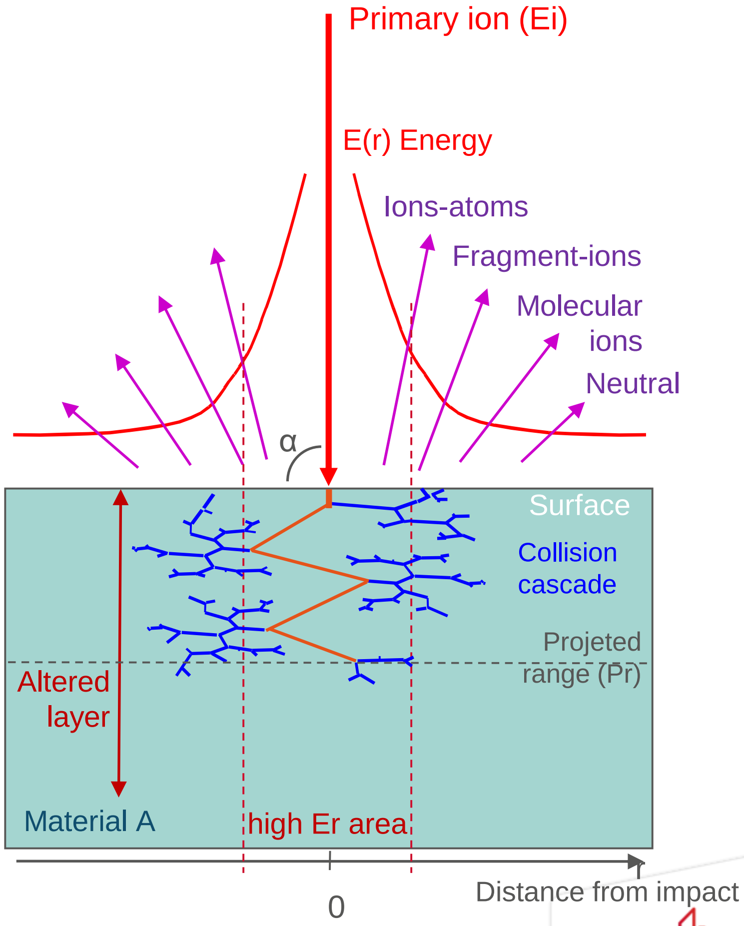
▶ Phenomena occurring at the surface (Ei>100eV> E_{th})

- Mainly nuclear interactions (electron stopping power weak)
- Energy and momentum transfer from I => A
- Amount of transfer = f(Mi, M_A, α)
- After 1[rst] interaction, ion and atom hit interact with more atoms of the material => cascade initiated
- Projected range =f(Ei $^{2/3}$)

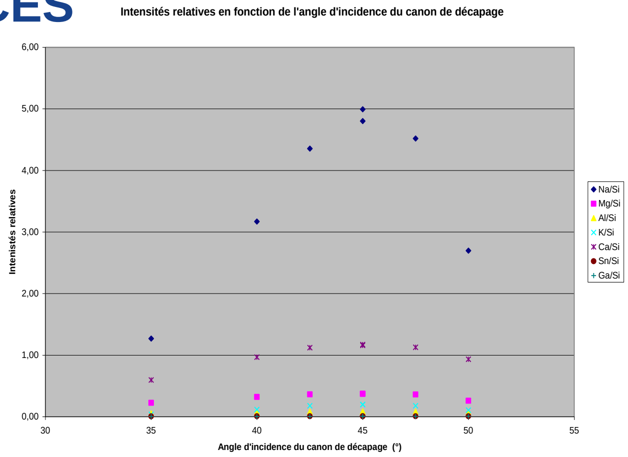
▶ Consequence from the surface

- Implantation of the impinging ion
- Modification of the material, amorphization, oxidation modification => altered layer ~ 2 x Pr
- Fraction of the momentum directed back to the surface

  => **SPUTTERING of different species**
- Origin depth < ~1nm
- Major part of neutral (90%)



SPUTTERING YIELD: DEFINITION AND INFLUENCES

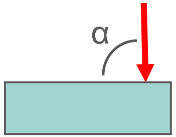


Definition

- Number of sputtered particles per incident ion
- The total sputtered Yield => sum of Y_x of individual species

  => Challenge: estimation of Y_x => Approximation Y_{matrix}

$$Y_{tot} = \sum_i Y_i$$



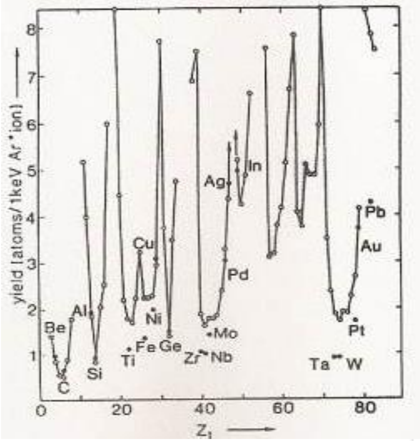
Dependence

- Angle of incidence

  0-45° => Y=f($\cos^{-b}$ α) with b=1-2 and depend of Mi and M_A

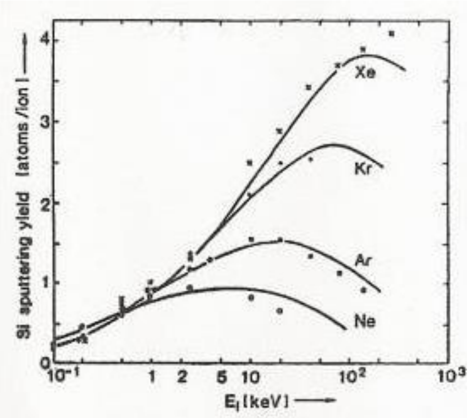
  45-60° => Ymax

  >60° => Y decreases rapidly to 0
- Mass of the target atom (example with Ar^+ 1keV)



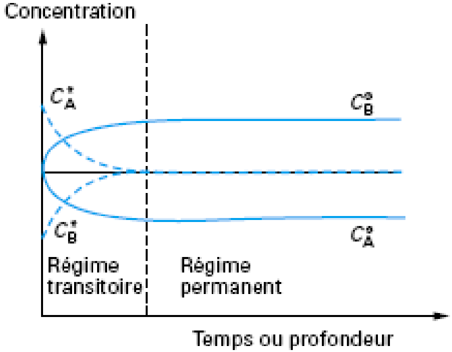
- Mass of the incident ion Mi

  (example of Si target)



Courtesy T Crétin SGR Paris (2010)

SPUTTERING YIELD: UNEXPECTED PHENOMENA



Preferential sputtering

- In case of $Y_A \neq Y_B$ => the surface composition evoles

  Example of material with C_A=C_B but Y_A > Y_B

Implantation

Surface roughening

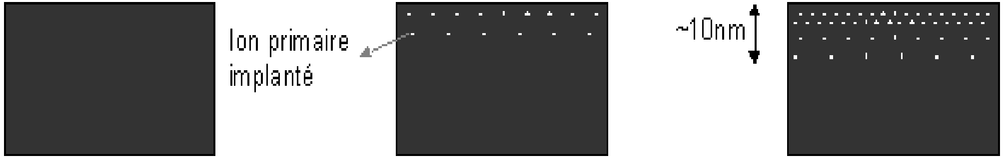
- Ripples can occured (favoured in high α)
- Phenomema pronounced for polycristallized surface

ⓑ image d'électrons secondaires de la même zone

The transient width

- Definition: Depth over which all material changes (roughness, amorphization, bounding…) take place. => Yield is biaised !

Starting surface **first ionic bombardment** **stationnary regim**

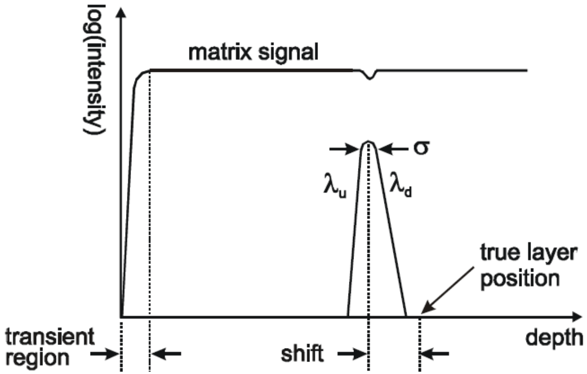


Techniques de l'ingénieur (2010)

UNEXPECTED PHENOMENA: CONSEQUENCE ON DEPTH PROFILING

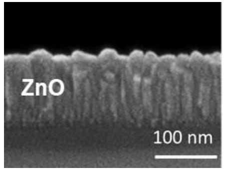
The transient width/depth profiling

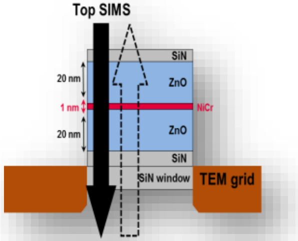
- Impact at layer interface
- Amplitude varies with the differences between the 2 layers.

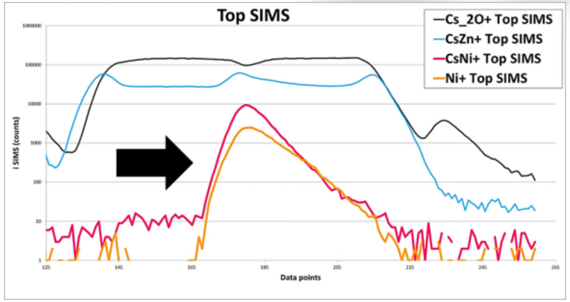


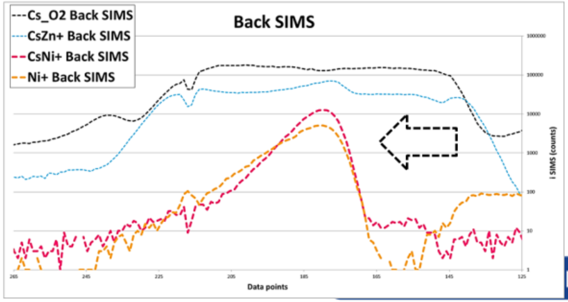
J Voronkoff, SIMS Europe (2018)
Techniques de l'Ingénieur (2010)
T Grehl, PhD (2003)

ZnO/NiCr/ZnO stack

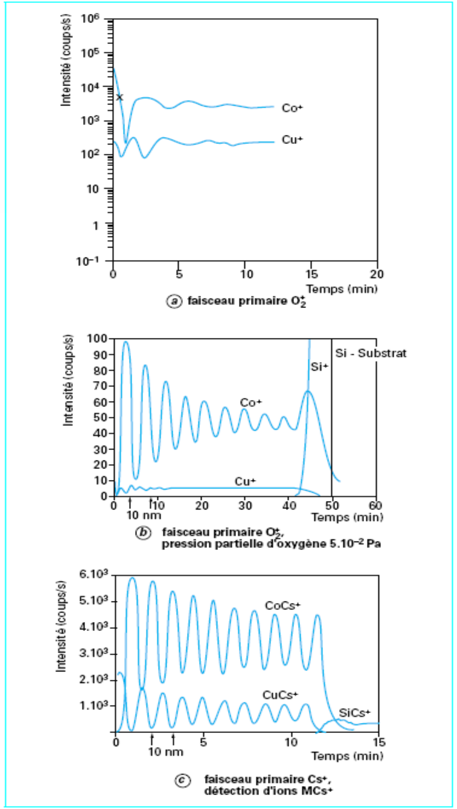








Cu/Co/Cu/… stack



SIMS : SECONDARY IONS MASS SPECTROMETRY

- **Technique based on the detection of ions emitted from sputtered surface**
  - Cations and anions detected (separately, *see technical chapter*)
  - Formalism

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

  - 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

Measured or table

Usually goal of analysis

To be calibrated

- **Calibration of Y_M and $Y^{\pm}$: what for?**
  - For quantification **BUT** only if they are **EQUAL between references and samples**

IONIZATION YIELD (*IONIZATION PROBABILITY*)

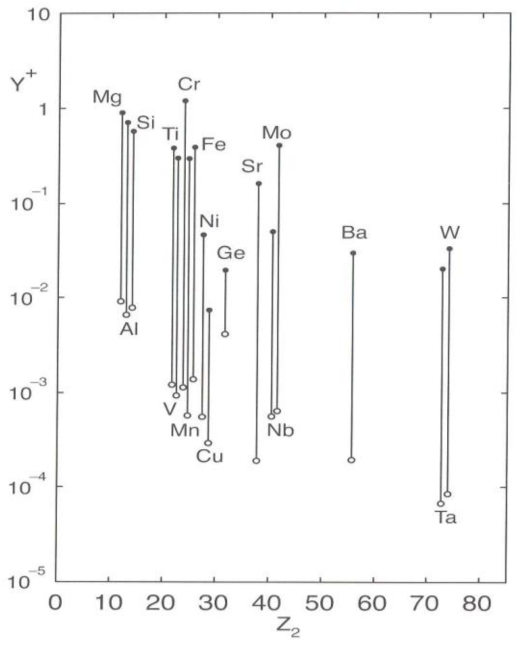
- **It is THE key parameter**
  - Strongly depends on the nature of the species
  - Varies over several orders of magnitude for the same combination of incident ions and target material
  - “Matrix effect”

- **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
● metallic surface
○ oxidized surface

M. Py, PHD (2011)

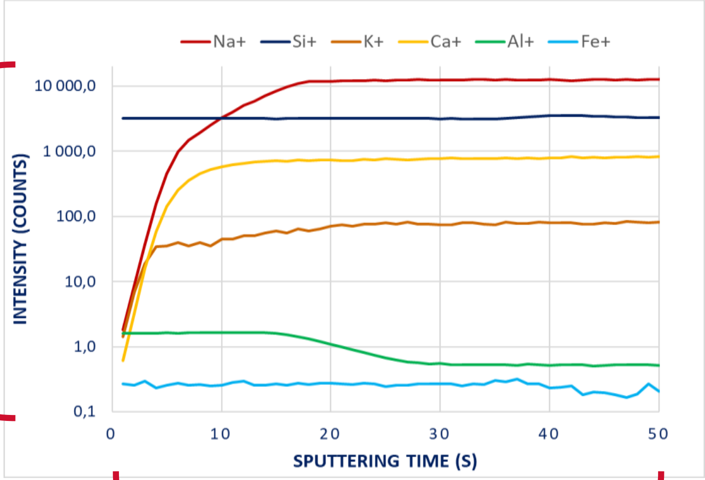
DEPTH PROFILE: *“WELCOME TO THE REAL WORLD”*

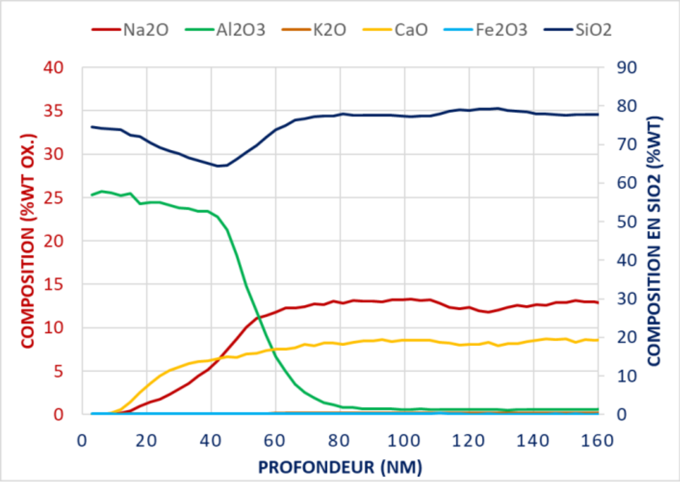
Conversion Intensity to composition (% wt ox)

- Calibration of the intensity using reference sample

BUT

- Same characteristics for the element /**Matrix** :
  - same acquisition parameters (incident ions, energy, vacuum…)
  - Same matrix
  - Same oxidation state, same microstructure and crystallization.



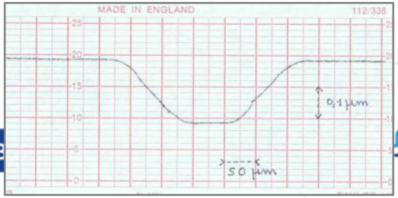


Conversion sput. time (s) to depth (nm)

- Calibration of the abrasion rate

BUT

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



CONCENTRATION EVALUATION IN DEPTH PROFILE

Definition of RSF

- Normalization of the intensity of the selected ions for the element of interest with the intensity of the ions representative of the matrix.
- For instance : Na^+ for sodium and Si^+ for silica

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

ELEMENT	facteur s	ELEMENT	facteur s
Li2O	2,5	MnO	3
B2O3	0,37	Fe2O3	2,5
C	0,0042	CoO	3,2
F	0,0085	NiO	0,63
Cl	0,0046	CuO	1,45
Na2O	12,5	ZnO	0,25
MgO	4,4	ZrO2	0,75
Al2O3	4,8	Ag	0,15
SiO2	1	SnO2	0,6
K2O	20	Sb2O5	0,038
CaO	9,2	BaO	6,5
TiO2	2,3	PbO	1,25
V2O5	1,5	Bi2O3	2,9
Cr2O3	2,1	SrO	7,4

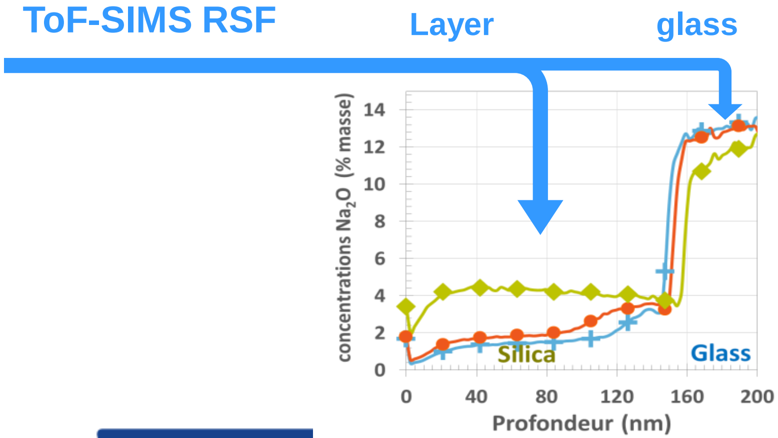
Composition analysis of the glass

- From EPMA and/ or Chemistry

oxides	SiO_2	Na_2O	CaO	MgO	K_2O	Al_2O_3
substrate (wt %)	73.3	13.3	9.6	3.1	0.2	0.5

- Depth profile of bulk glass (polished cross section),

ToF-SIMS RSF

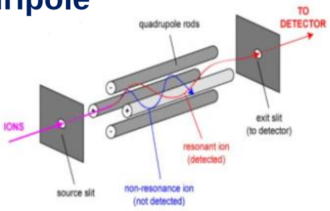


THE SIMS FAMILY

- **The detection system in mass**
  - Perfomances

	Resolution	Mass Range	Transmission	detection mode	Sensivity
Quadripole	10^2 to 10^3	< 10^3	0,01 to 0,1	sequential	1
Magnetic sector	10^4	> 10^3	0,05 to 0,5	sequential & parallel	10^4
Time of Flight	10^4	until 10^4	0,5	parallel	10^4

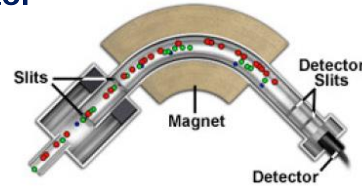
Quadripole



Millbrooks MiniSIMS alpha

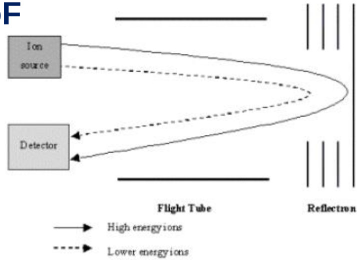
Cameca SIMS 4550

Magnetic sector



Cameca IMS 7F

ToF



IonTOF TOFSIMS 5

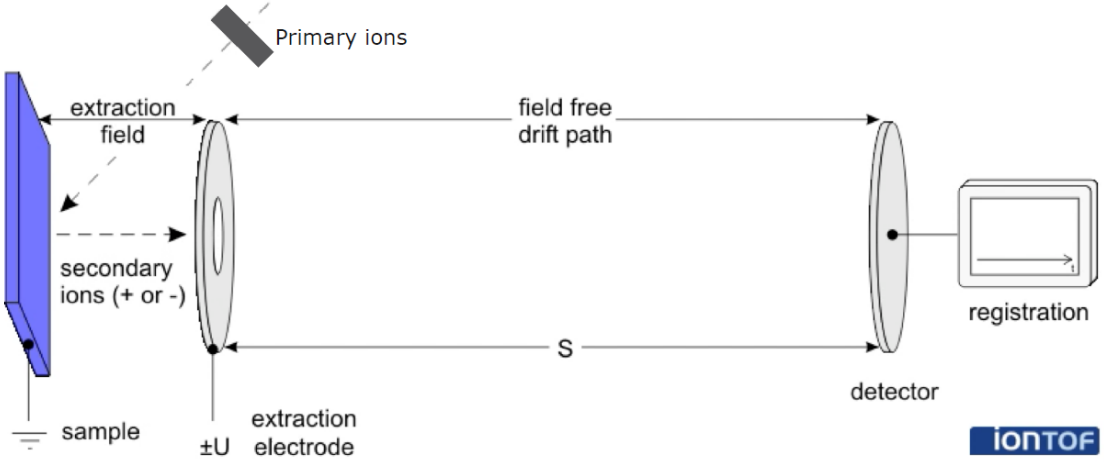
- **SNMS: a solution to counterbalance the fact that ions are the minor part of the species emitted under sputtering**

TIME OF FLIGHT DETECTION

Principle

- Extract the ions emitted by the sputtered surface
  => same kinetic energy ***q.U***
- Measure the duration ***t*** for ions to reach detector

$$t = S.\sqrt{\frac{m}{2.q.U}}$$



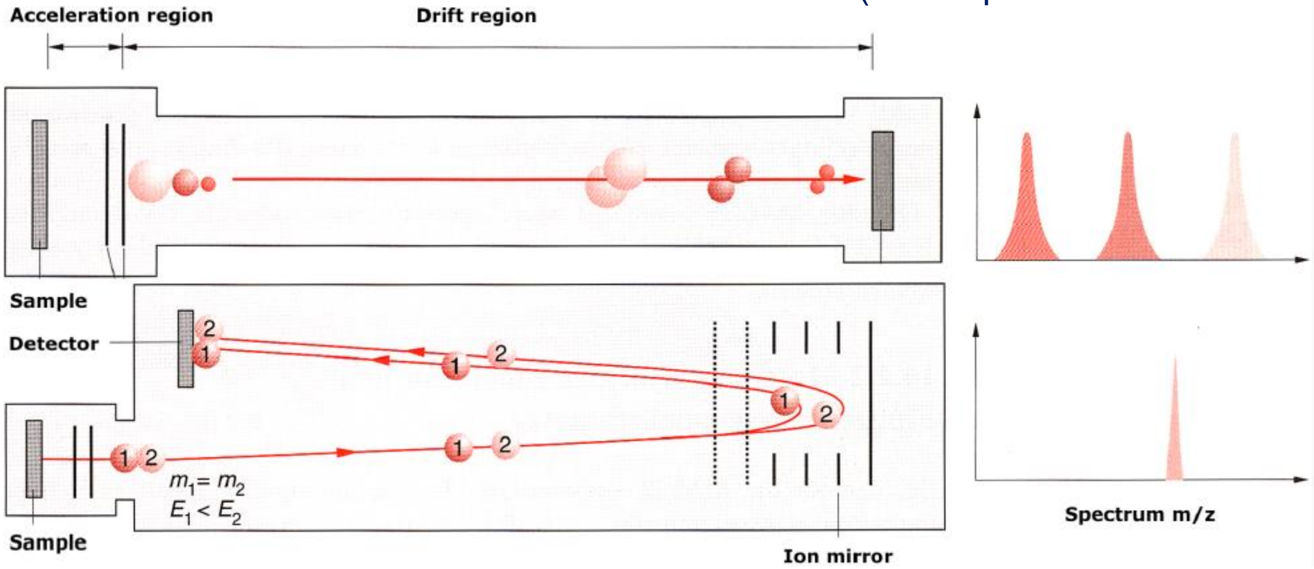
Specifications

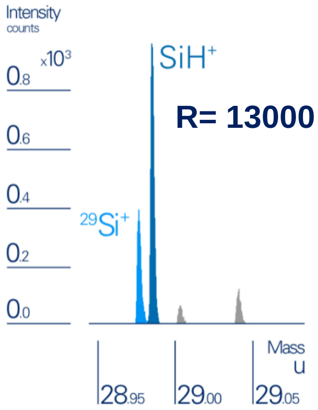
- Start signal?
- Ions charge difference
- Sample surface potential
  (charging effect / isolators)
- Duration of the fight of the heaviest ions: 600D ~100µs

TIME OF FLIGHT DETECTION

The added-value of the reflectron

- Correction of the peak broadening due to kinetic energies differences (consequence of surface roughness, loss…)





R= 13000

$$R = \frac{m}{\Delta m} = \frac{t}{2\Delta t}$$

$$\Delta t = \sqrt{\Delta t_{prim}^2 + \Delta t_{ToF}^2 + \Delta t_{det}^2}$$

(with Δt_{prim}<1ns, Δt_{ToF} some 1ns, Δt_{det}~0,2ns)

TOF-SIMS

Constraint imposed by the ToF

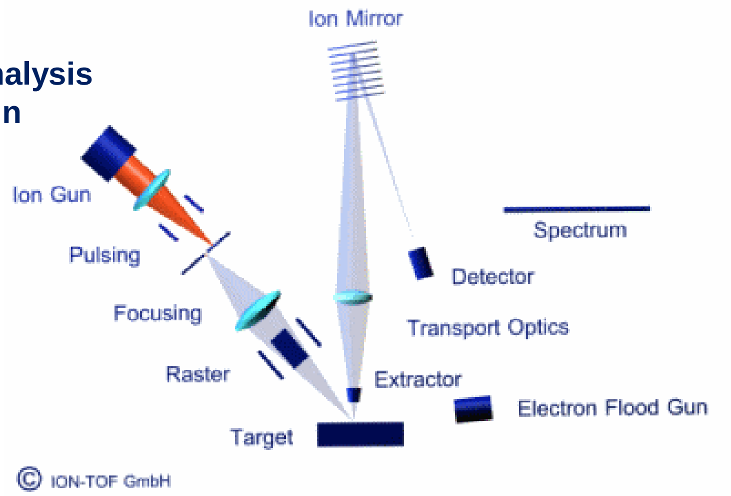
- Secondary ions separated by their time of fight until sensor

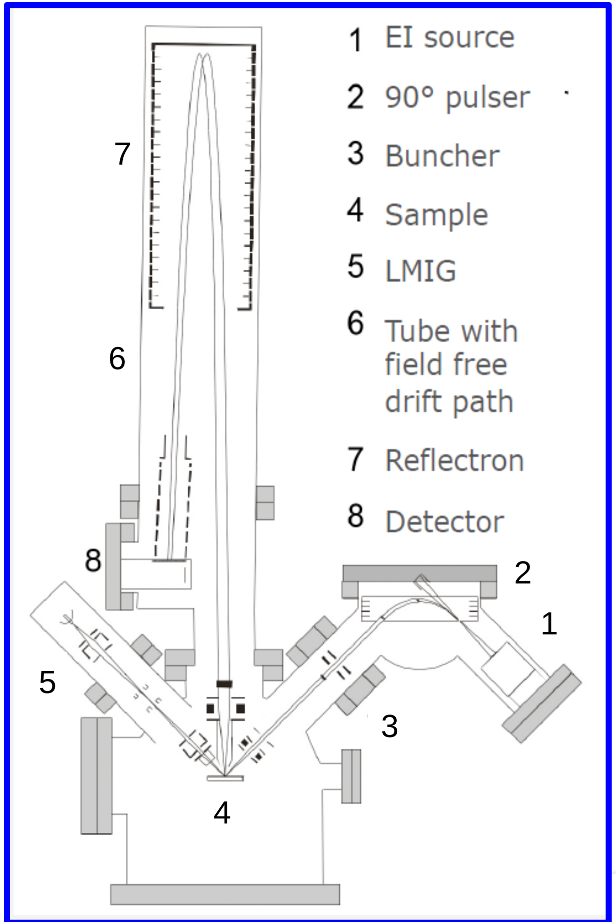
THUS

- Pulsed primary ions impact
- Focalized ions (/extraction)

Second primary ions beam for abrasion is required !

Analysis gun



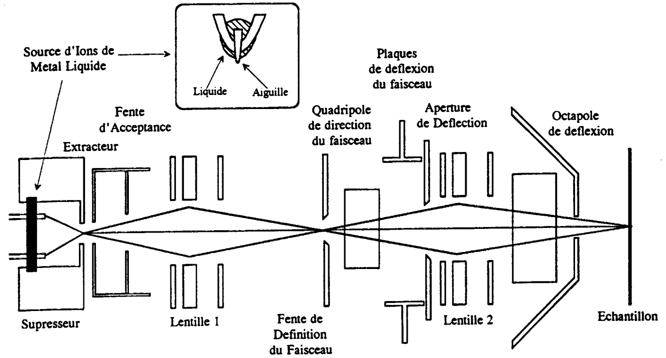


Ion ToF source

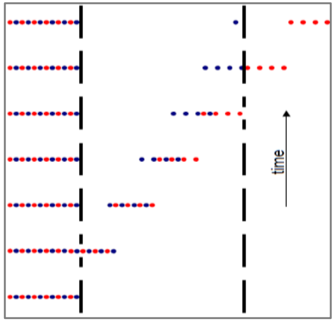
PRIMARY SOURCES

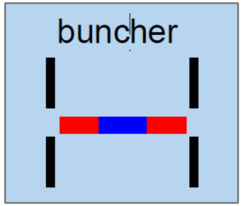
For Analysis

- Liquid Metal Ion Gun (Ga, Bi)



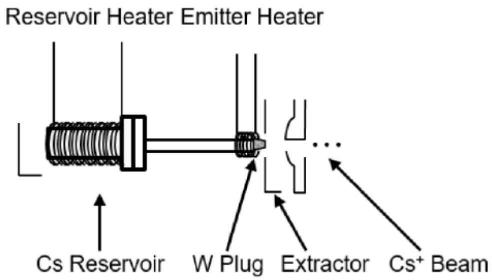
« It's a chopper baby »





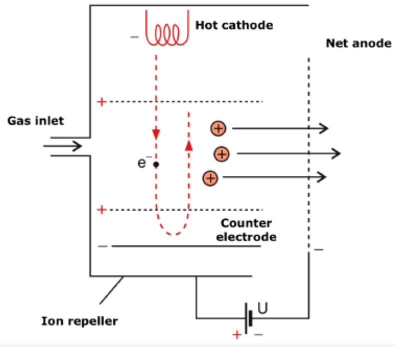
For Abrasion

- Thermal Ionization source (Cs)



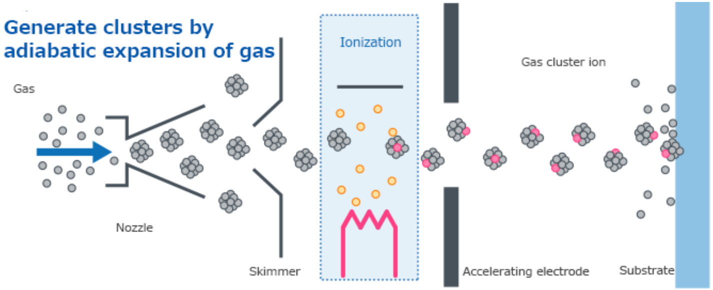
For Abrasion

- Electron Ionization source (O_2^+)



For Abrasion

- Gas Cluster Ion Beam
- (Ar, O2)

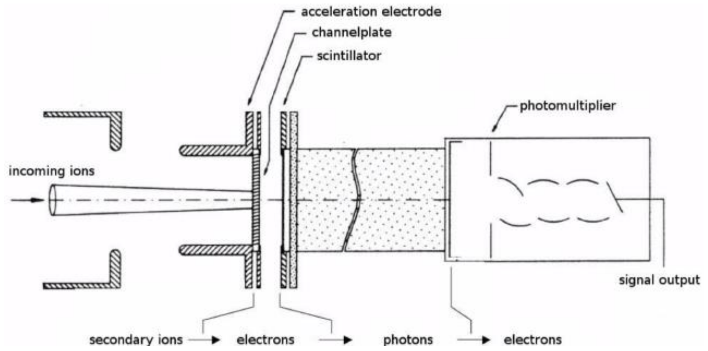


D Rading , IontoF (2016)
Ulvac-phi.com

OTHER PART OF INTEREST

Ions Detection

- The channeltron
- Conversion ions => electrons (signal)



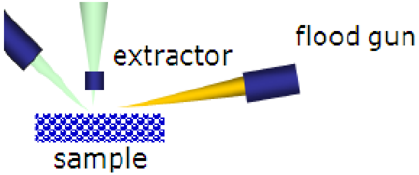
Sample surface specifications

- Flat surface with reduced roughness
- Isolator, metal…
- UHV compatible (<10^{-8}mbar).

Electron Flood Gun

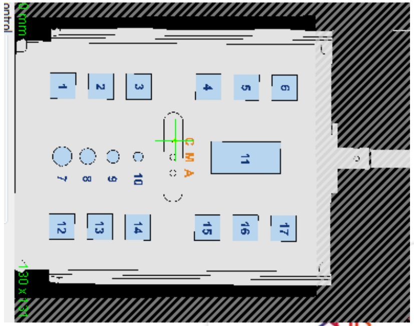
- For Surface charges neutralization
- Low energy electron 0-20eV,

Warning: sensitive material (polymer,,,)



Sample holder

- Connected to earth (charge neutralization).
- Parts for current (ions/e-)and focus adjustments
- Temperature control (-100°C / +600°C)

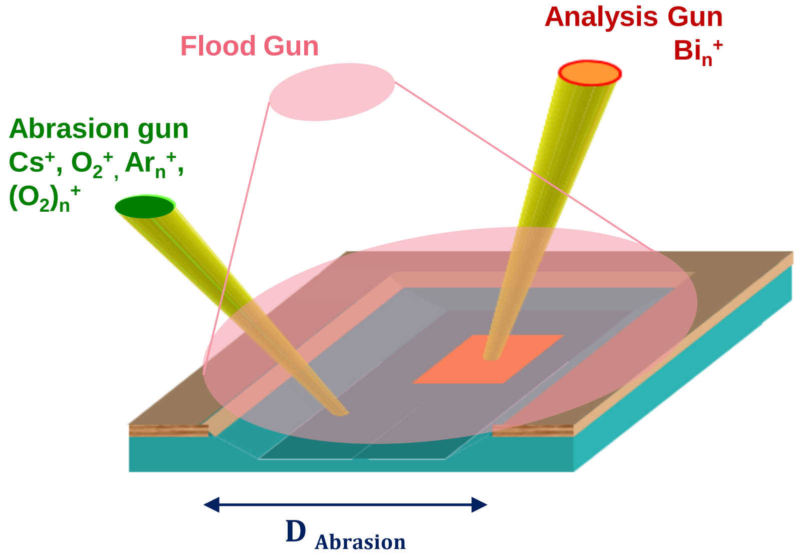


SAINT-GOBAIN RESEARCH PARIS

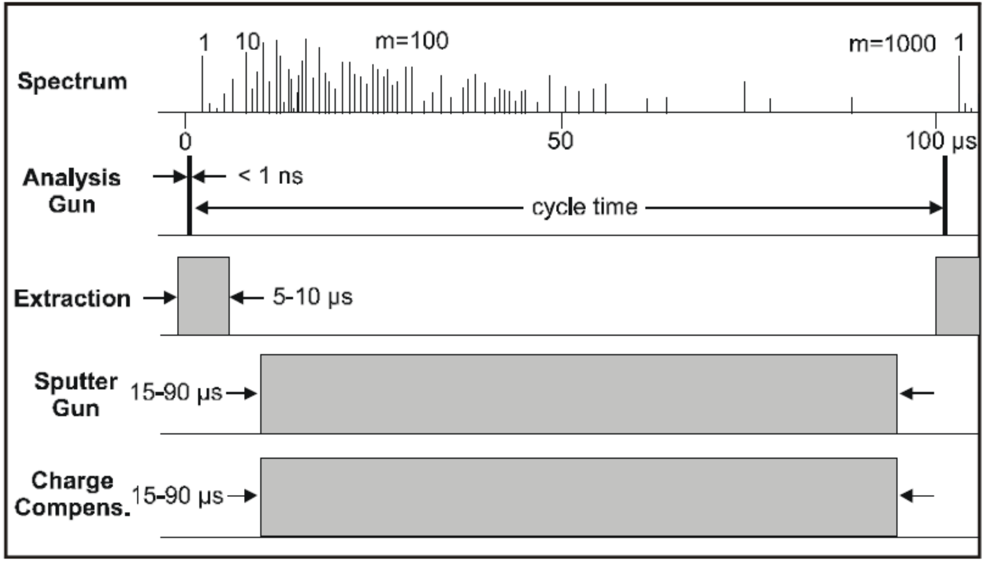
ANALYSIS SEQUENCE AND CONFIGURATION DURING DEPTH PROFILE

▶ Area configuration

- $D_{Analysis} < \frac{D_{Abrasion}}{3}$



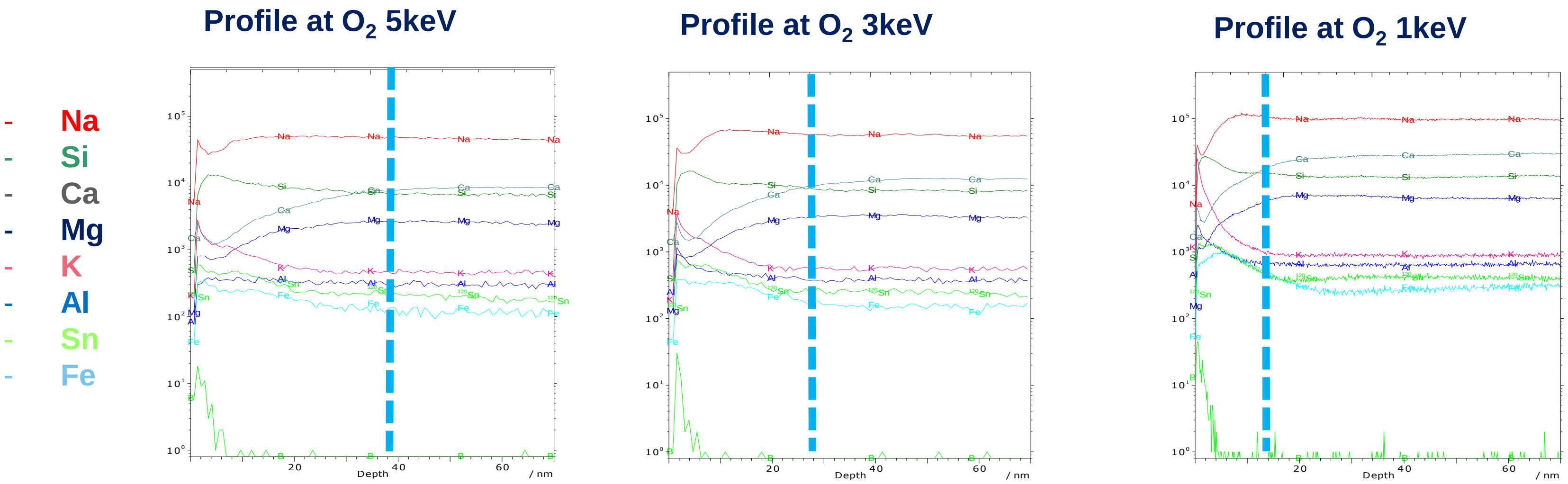
▶ Analysis/ Abrasion sequence – interlaced mode



CASE OF GLASS: REVIEW OF KEY PARAMETER BEFORE ANALYSIS (1/3)

Impact of the abrasion ions Energy

- Surface of fresh Soda lime glass (reduced surface gradient)
- ION ToF IV : Analysis Ga^+ / Abrasion O_2



SAINT-GOBAIN RESEARCH PARIS

CASE OF GLASS: REVIEW OF KEY PARAMETER BEFORE ANALYSIS (2/3)

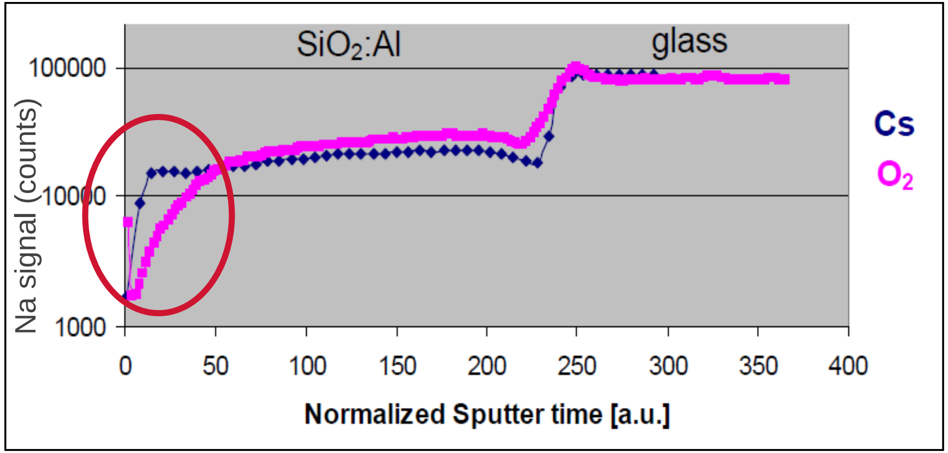
TRANSVERSAL R&D CENTERS BY SAINT-GOBAIN

Impact of the nature of Abrasive species

- Na saturated SiO_2:Al layer deposited on glass

Comparison O_2 at 20°C / Cs at 20°C

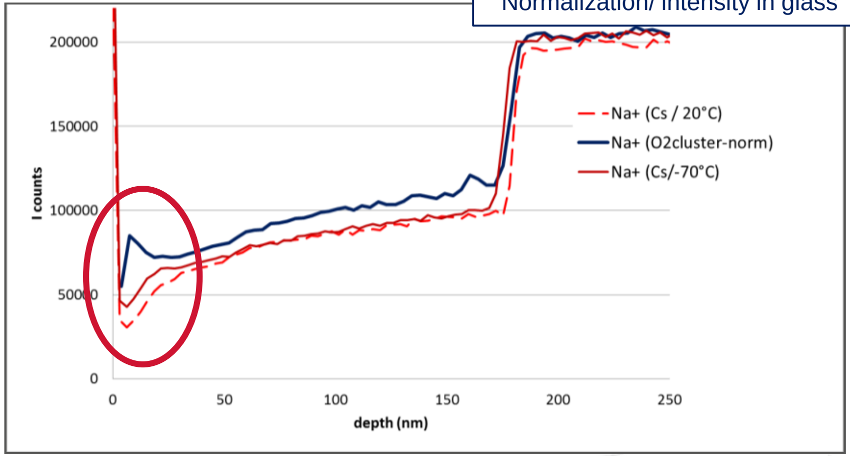
- TOF.SIMS IV Analysis Ga^+ 15keV
- Abrasion O_2^+ 2keV and Cs^+ 2keV



Comparison O_2 cluster at 20°C / Cs at 20, -70°C

- TOF.SIMS 5 Analysis Bi^+ 15keV
- Abrasion $(O_2)_{1500}^+$ 20keV (O_2 Flood, EDR)

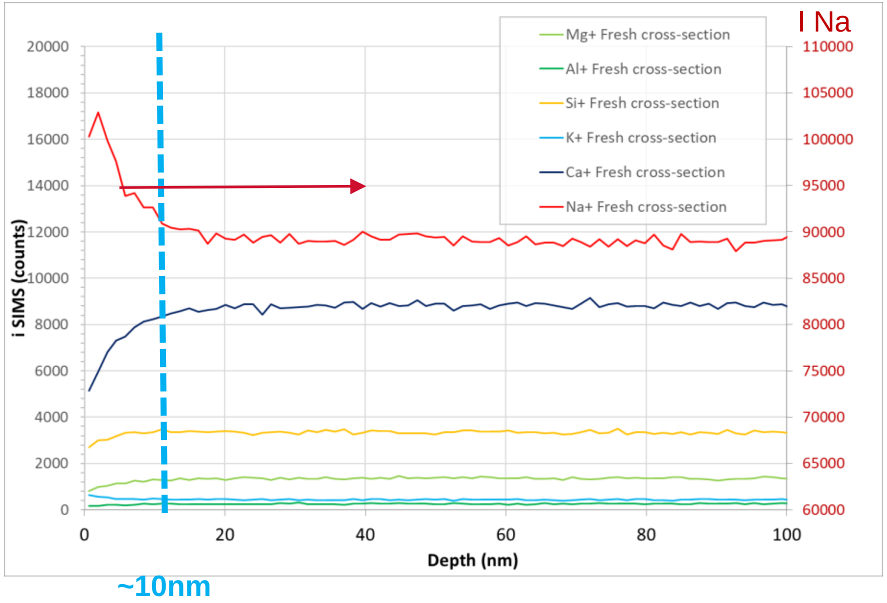
Normalization/ intensity in glass



O2-Cluster perfomed by IONTOF :
Thanks to S Kayser, M Kleine-Boymann

CASE OF GLASS: REVIEW OF KEY PARAMETER BEFORE ANALYSIS (3/3)

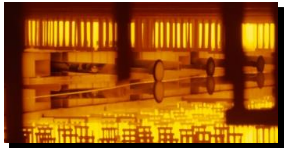
- **Is perfect depth profiling exist ?**
  - Standard fresh Soda lime glass
  - TOF.SIMS 5 Analysis Bi^+ 15keV, Abrasion $(O_2)_{1500}$ 20keV

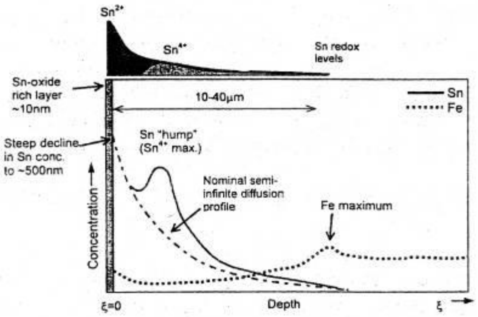


ANALYSIS OF GRADIENT IN GLASS (1/3)

Case of industrial Float Glass : the bath side

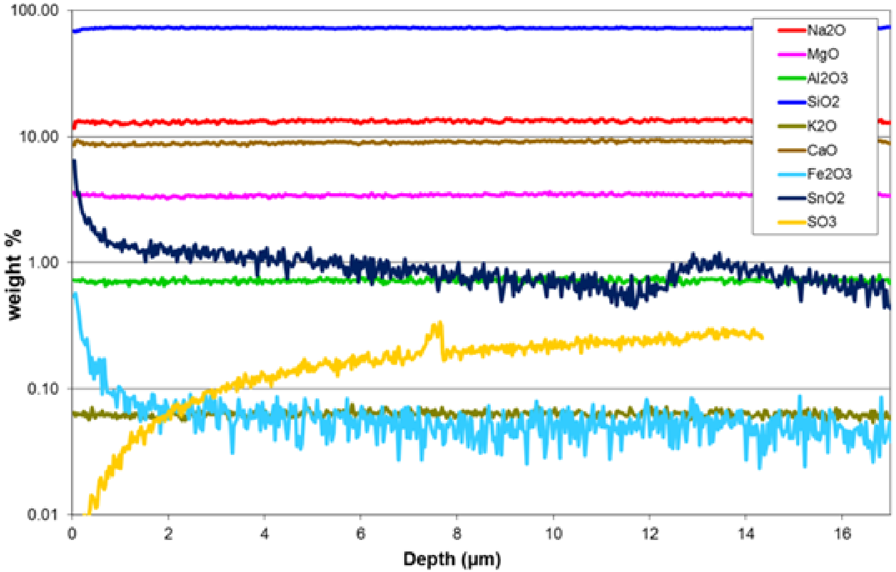
- Exchange between Na and Tin in the tin bath.
- Behavior of Sn^{2+}/Sn^{4+} => tin hump



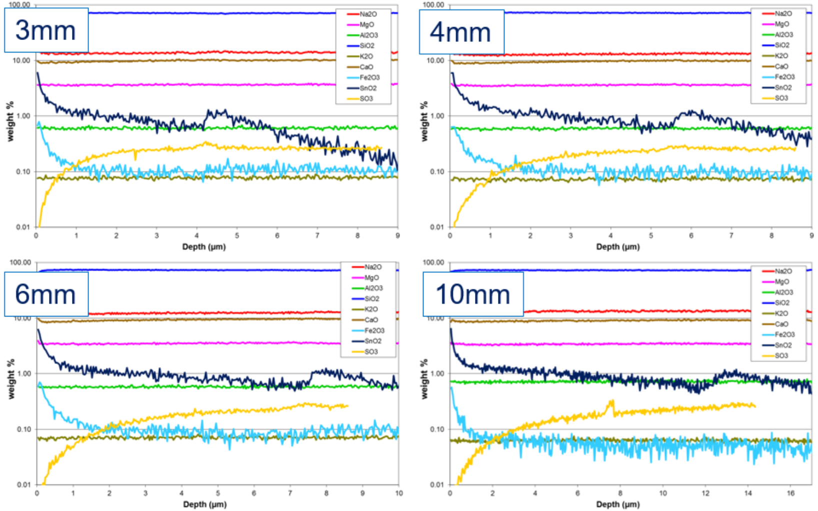


ToF SIMS depth profiling (Float glass 10mm thick)

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



Impact of the glass thickness,
Interaction with others elements S, Fe



SAINT-GOBAIN RESEARCH PARIS

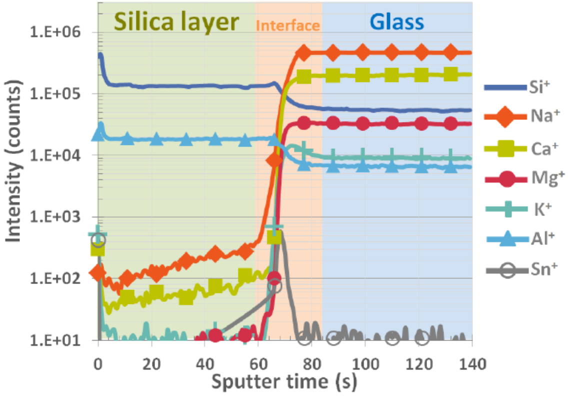
SAINT-GOBAIN

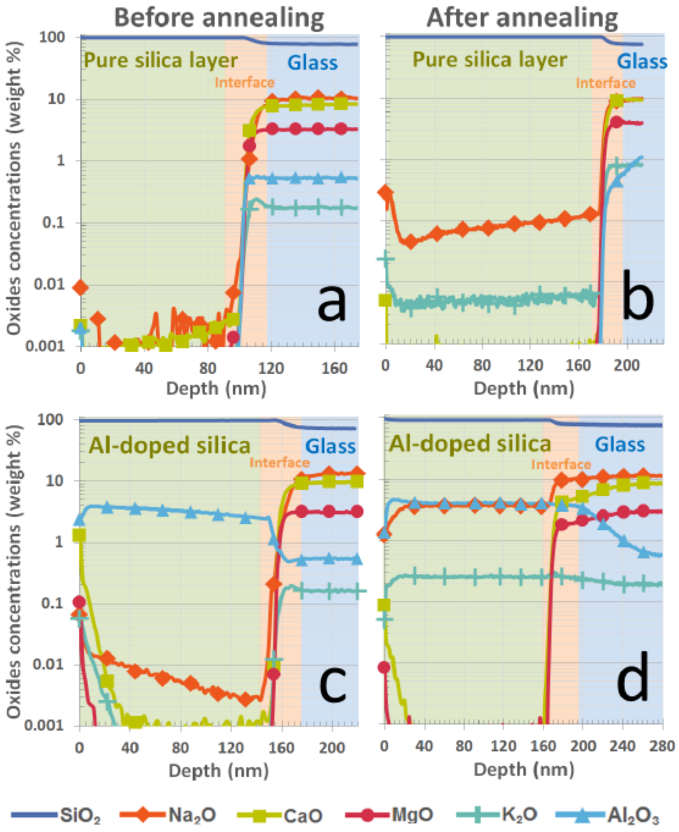
H Montigaud, ICG-yokohama (2018)
GB Cook JNCS (1999)

ANALYSIS OF GRADIENT IN GLASS (2/3)

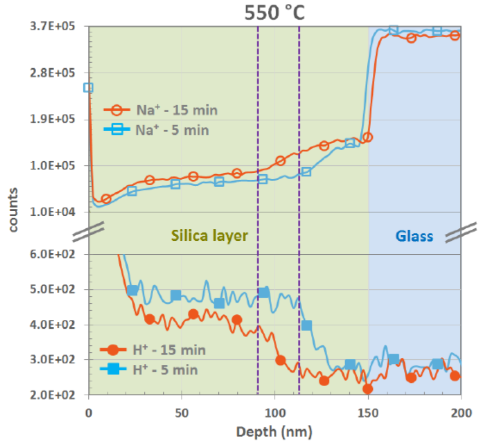
▶ Silica layer deposited by PVD on glass and then annealed

- ToF.SIMS5
- Anal. Bi^+30kV, Abr, Cs^+ 2kV
- Calibrated depth profiles
- Raw data





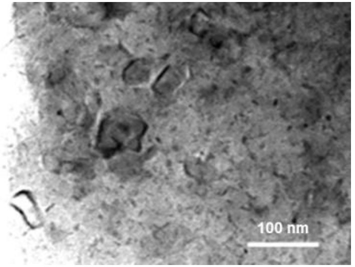
Comparison Na / H (raw datas)

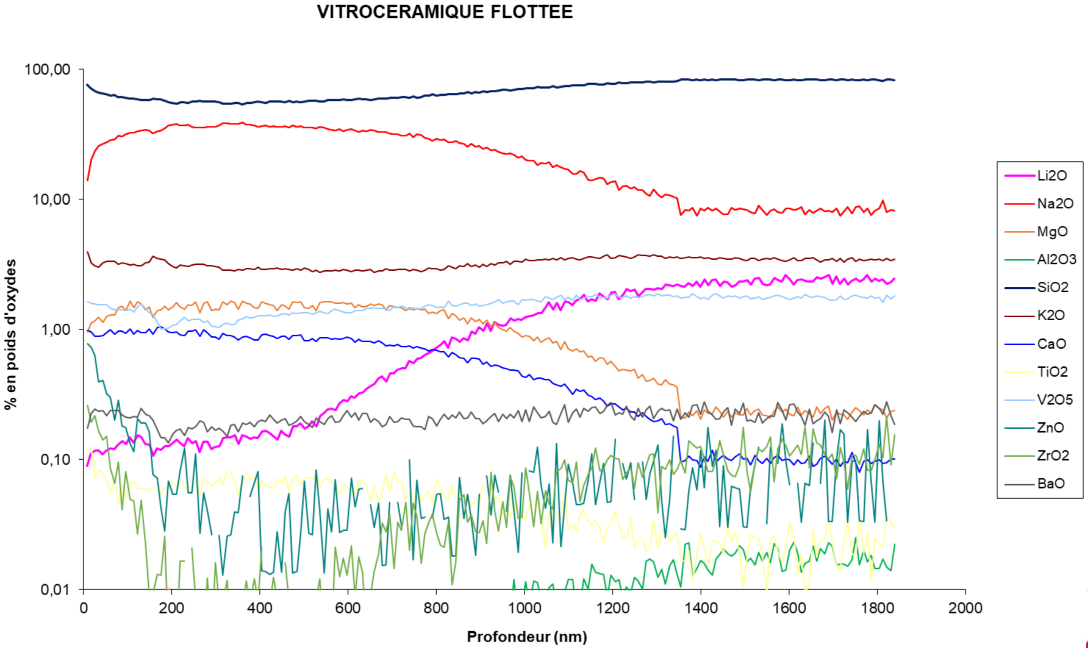


JT Fonné et al. JACS (2019)
S Ben Khemis, PhD (2020)

ANALYSIS OF GRADIENT IN GLASS (3/3)

- **Case of glass ceramic**
  - Li_2O, SiO_2 + TiO_2, ZrO_2 (nucleation)
  - Nucleation: virgilite, spodumène
  - Annealing at HT (>800°C)





SAINT-GOBAIN RESEARCH PARIS

SAINT-GOBAIN

AGENDA

INTRODUCTION - SPECIFICATION

ELECTRON PROBE MICRO ANALYSIS (EPMA)

SECONDARY IONS MASS SPECTROMETRY (SIMS / ToF-SIMS)

ATOM PROBE TOMOGRAPHY (APT)

- Principle and added-values
- Sample preparation
- Results concerning glass

SCANNING TRANSMISSION ELECTRON MICROSCOPY (STEM-EDS, EELS)

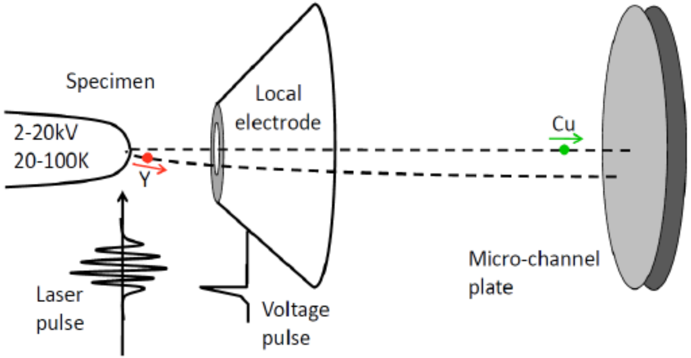
OTHERS TECHNIQUES: XPS, AUGER, XAS DEPTH PROFILING

CONCLUSION

ATOM PROBE TOMOGRAPHY

Principle

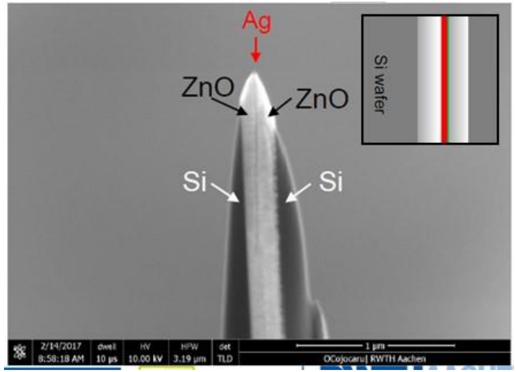
- Field emission from a tip assisted by laser.
- Tip at reduced T to limited migration under HV.
- Elemental analysis (isotope)

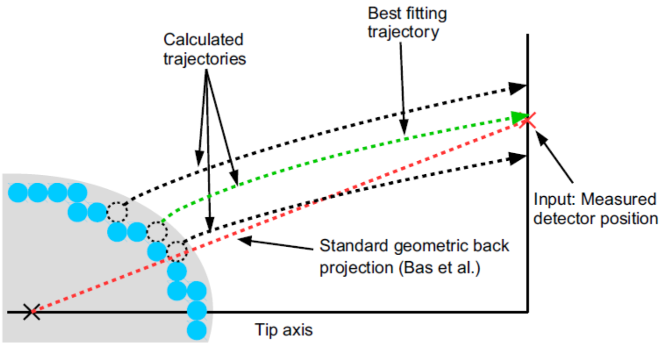


The key parameters

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

Example (LEAP)



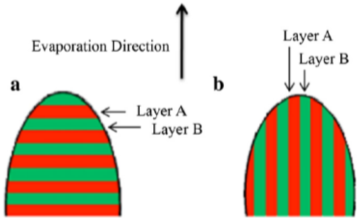


D Beinke Ultramicroscopy 165 (2016)

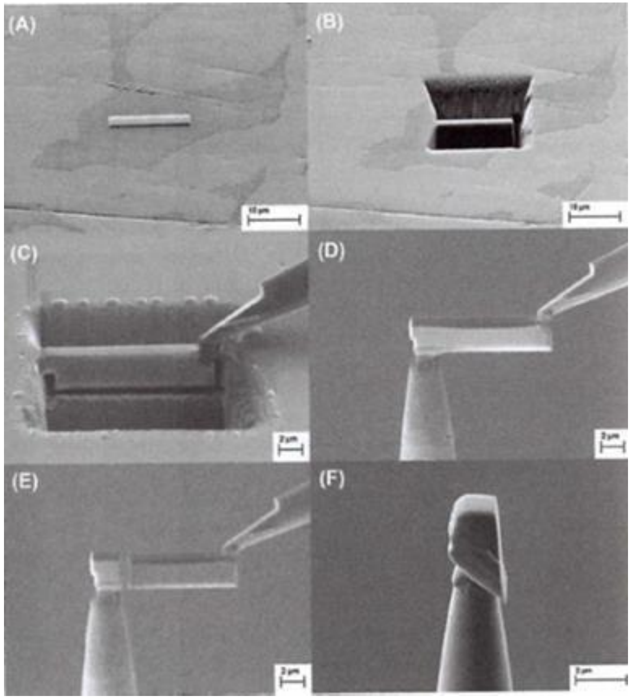
WR Mc Kenzie, Microscopy: Science, Technology (2010)

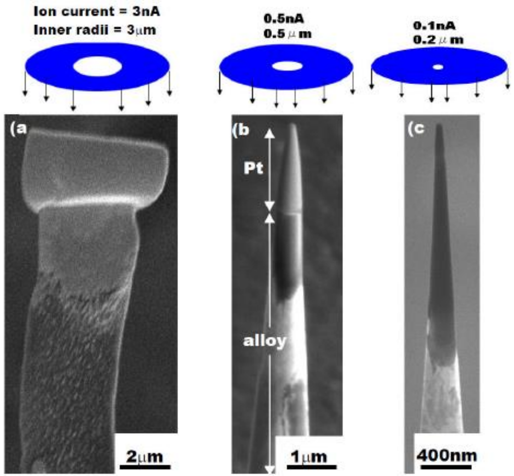
SAMPLE CONFIGURATION AND PREPARATION FOR APT

- **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)

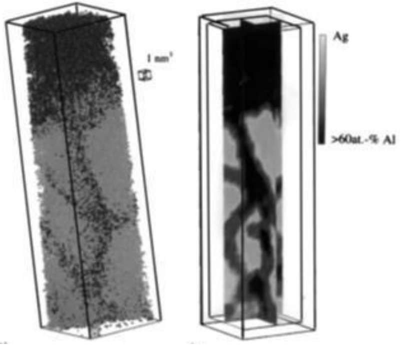
J.G. Brons et al. , TSF 551 (2014)

ATOM PROBE TOMOGRAPHY ADDED VALUES

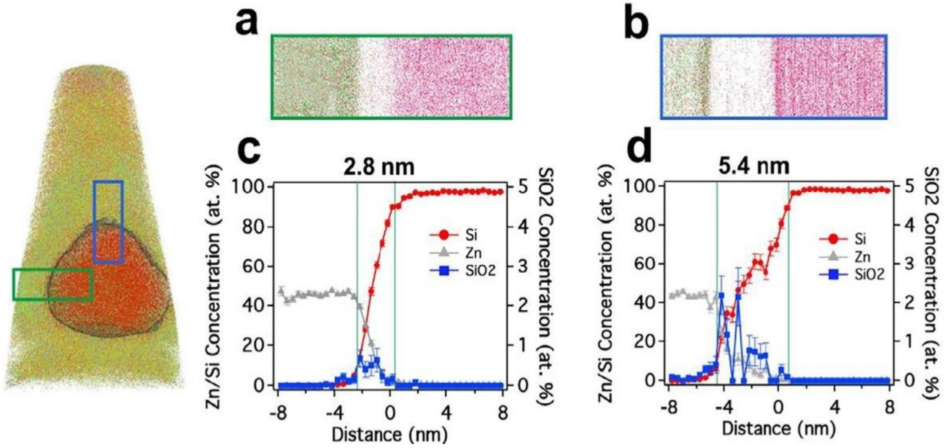
advantages / disadvantages

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

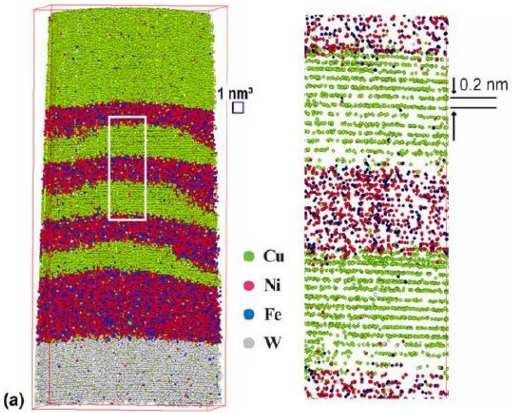
Al/Ag bilayer after annealing at 100°C : Al diffusion in Ag layer through GB



Si nanowires embedded within ZnO



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



Zhiyuan Sun et al. Ultramicroscopy 184 (2018)

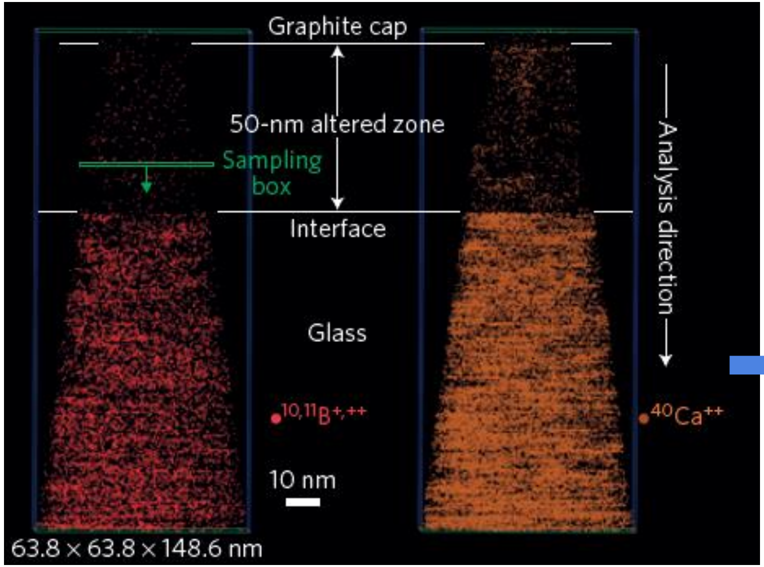
C.B. Ene, Acta Materialia 53 (2005)

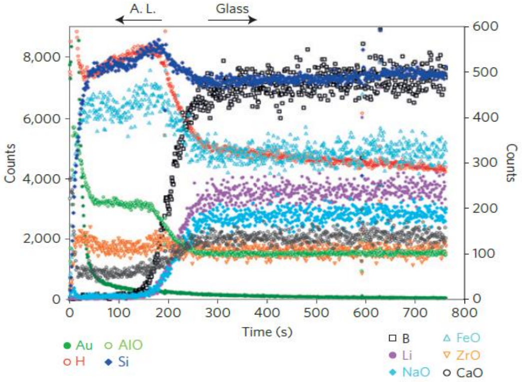
J. Schleiwies et al. Mat. Sci. and Eng. A327 (2002)

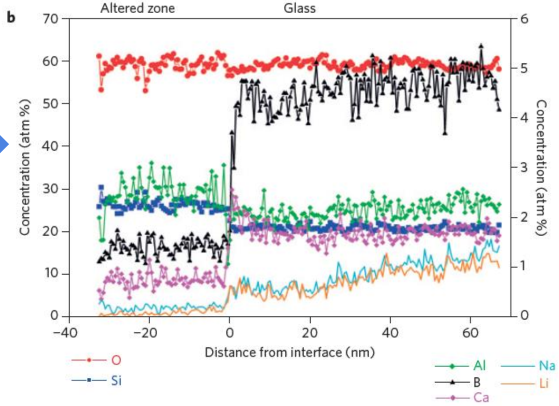
RESULTS CONCERNING GLASS (1/2)

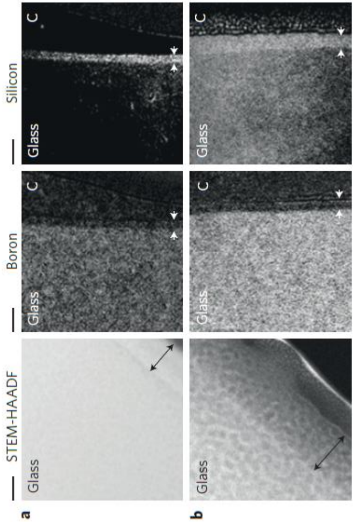
Case of glass surface corrosion

- Silica sodo calcique glass
- Analysis after 1 month ageing
- Comparison APT, ToF-SIMS and EFTEM









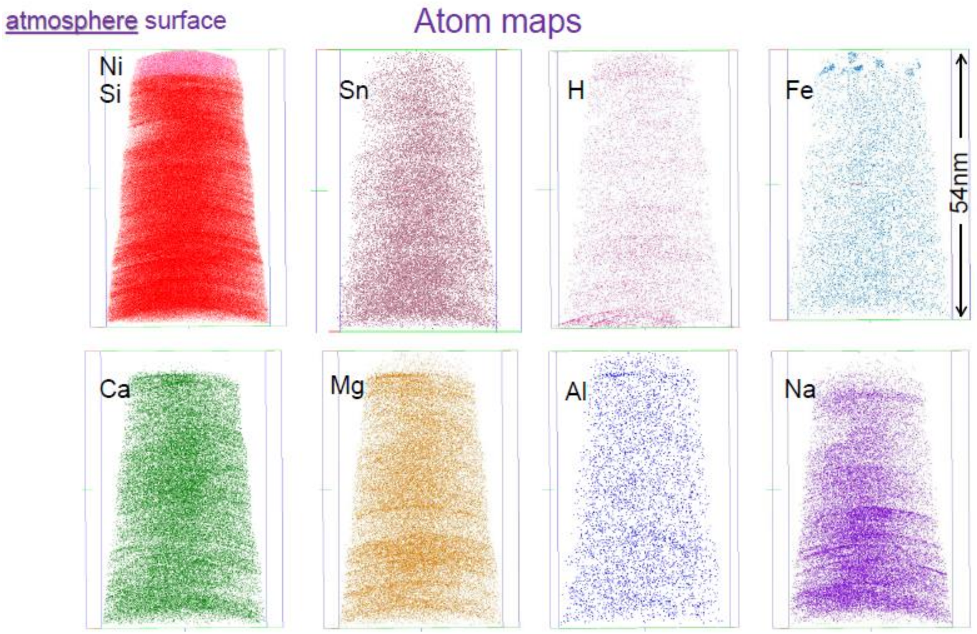
After 4d **After 1month**

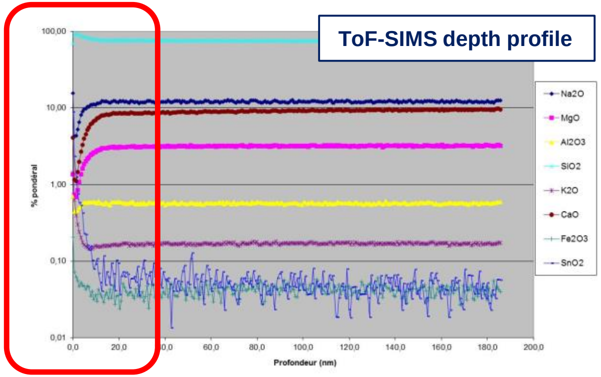
STEM images: scale bar= 25nm
EFTEM maps: scale bar= 100nm

R Hellmann, Nature Materials (2015)

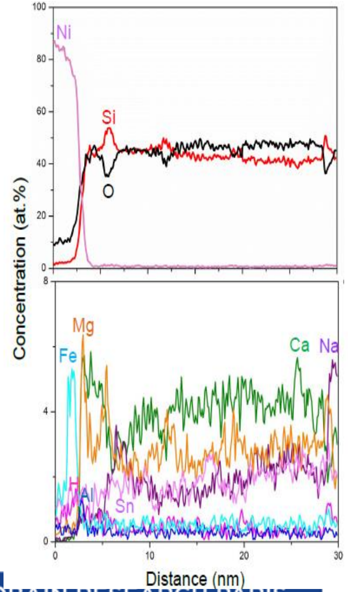
RESULTS CONCERNING GLASS (2/2)

- **Atmospheric side of Float Glass**
  - Early stage of alteration layer
    (Na depletion, Sn traces)





Profiles extracted



OTHER WORKS CONCERNING GLASS

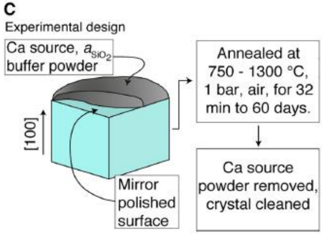
Diffusion of calcium in forsterite

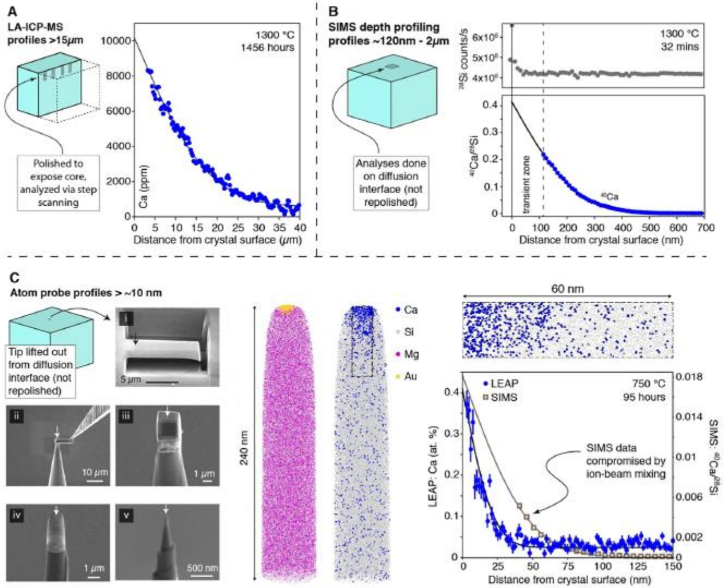
ELSEVIER
Geochimica et Cosmochimica Acta 265 (2019) 85–95
www.elsevier.com/locate/gca

Diffusion of calcium in forsterite and ultra-high resolution of experimental diffusion profiles in minerals using local electrode atom probe tomography

E.M. Bloch [a,*], M.C. Jollands [a], S.S.A. Gerstl [b], A-S Bouvier [a], F. Plane [a]
L.P. Baumgartner [a]
[a] Institute of Earth Sciences, Faculty of Geosciences and Environment, University of Lausanne, Lausanne 1004, Switzerland
[b] Scientific Center of Optical and Electron Microscopy, ETH Zürich, Zürich 8093, Switzerland

Received 28 March 2019; accepted in revised form 2 September 2019; Available online 10 September 2019





APT of glass + ice for the analysis of corroded surface

npj | Materials Degradation
www.nature.com/npjmatdeg

ARTICLE OPEN

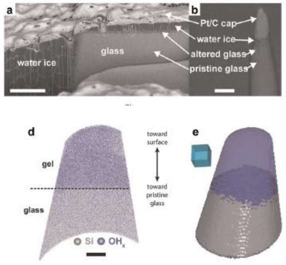
Check for updates

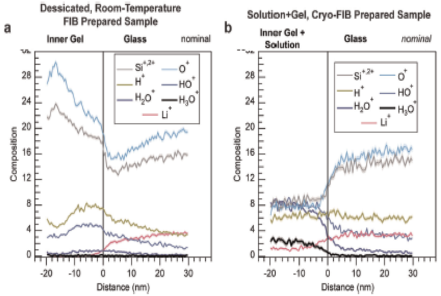
Tomographic mapping of the nanoscale water-filled pore structure in corroded borosilicate glass

Daniel E. Perea [1,4✉], Daniel K. Schreiber [2,4✉], Joseph V. Ryan [2], Mark G. Wirth [1], Lu Deng [3], Xiaonan Lu [3], Jincheng Du [3] and John D. Vienna [2]

Cryo-based atom probe tomography has been applied to directly reveal the water-solid interface and hydrated corrosion layers making up the nanoscale porous structure of a corroded borosilicate glass in its native aqueous environment. The analysis includes morphology and compositional mapping of the inner gel/glass interface, isolation of a tomographic sub-volume of the tortuous water-filled gel, and comparison of the gel structure with simulations. The nanoscale porous structure is qualitatively consistent with that of the molecular dynamics simulation, enabling in greater confidence in both interrogations. Comparison of the gel/glass interface between desiccated and cryogenically preserved samples reveals consistently abrupt B dissolution behavior and quantitative differences in the apparent H ingress into the glass. These comparisons give some guidance to future experimental approaches to understanding glass corrosion behavior. More broadly, the cryogenic preservation and 3D visualization of the native water/solid structure in 3D at the nanoscale has direct relevance to a wide range of materials systems beyond glass science.

npj Materials Degradation (2020)4:8 ; https://doi.org/10.1038/s41529-020-0110-5





__Review:__ D.W. Saxey et al., Atomic worlds: Current state and future of APT in geoscience, Scripta Materialia (2017)

AGENDA

INTRODUCTION - SPECIFICATION

ELECTRON PROBE MICRO ANALYSIS (EPMA)

SECONDARY IONS MASS SPECTROMETRY (SIMS / ToF-SIMS)

ATOM PROBE TOMOGRAPHY (APT)

SCANNING TRANSMISSION ELECTRON MICROSCOPY (STEM-EDS, EELS)

- Principle and some dates
- Sample preparation
- Examples of analysis on amorphous material

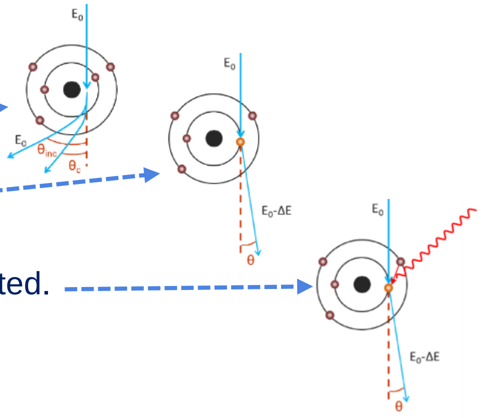
OTHERS TECHNIQUES: XPS, AUGER, XAS DEPTH PROFILES

CONCLUSION

SCANNING TRANSMISSION ELECTRON MICROSCOPY

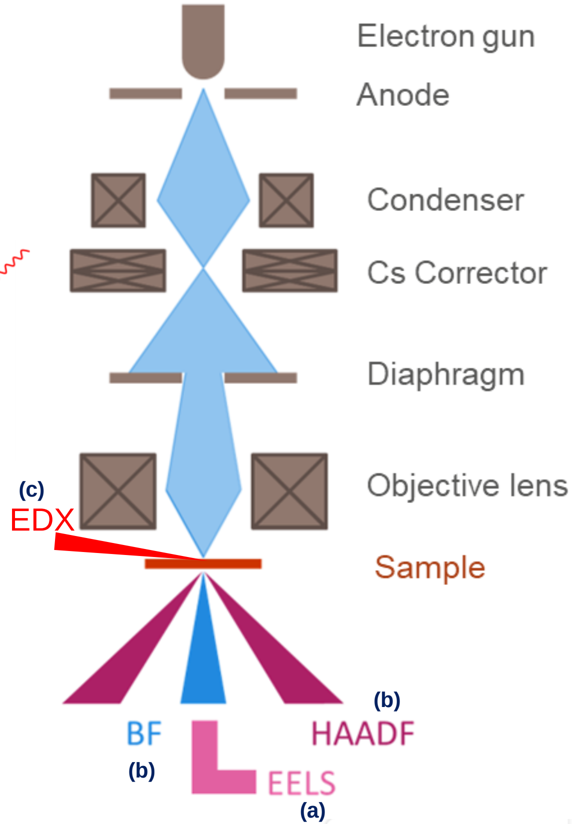
Principle

- Analysis of the transmitted electrons from
  - (a) elastic interaction
  - (b) inelastic interaction
  - (c) inelastic interaction with RX emitted.



Key points

- Electron spot diameter ~0,08nm (FEG source)
- Surface scan (=> no sample shift ! and vibrations)
- Very thin sample (<<100nm thick)
- High vacuum (until 5 10^{-11}mbar within the gun)



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

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

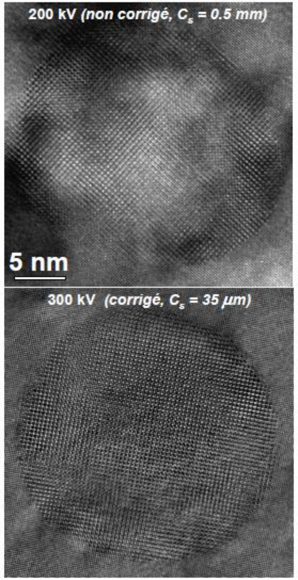
STEM: SOME DATES

▶ TEM-STEM evolution during 20th century

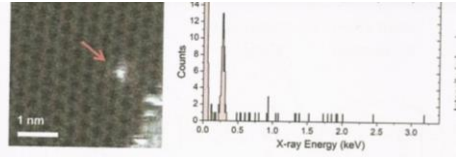
- 1931 : Ruska PhD : **first TEM**

- 1938: M Von Ardenne (Siemens) **First STEM**,
  but performances < TEM + WW2 destruction

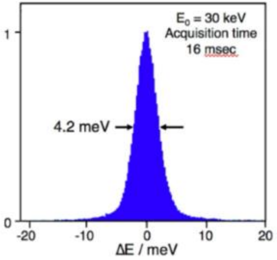
- **Cs corrector**
  1971: Rose => theoretical proposal
  1995: Krivanek => first success of Cs in STEM

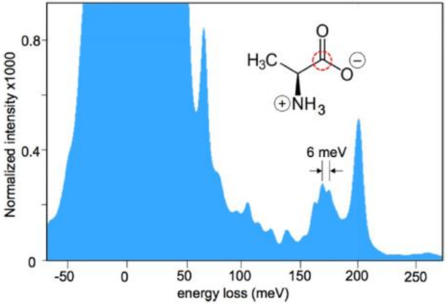


- High efficiency EDS detection
  example of Si single atom EDX



- High resolution spectrometer + monochomator dev.
  2019: Krivanek@Nion => **4,2meV FWHM for** ZLP





T Epicier, Colloque National, Aussois Janvier 2010

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

https://en.wikipedia.org/

O. Krivanek et al. ultramic. 203 (2019)

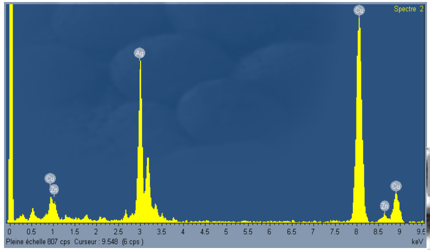
STEM-EDS AND STEM-EELS COMPARISON

STEM-EDS

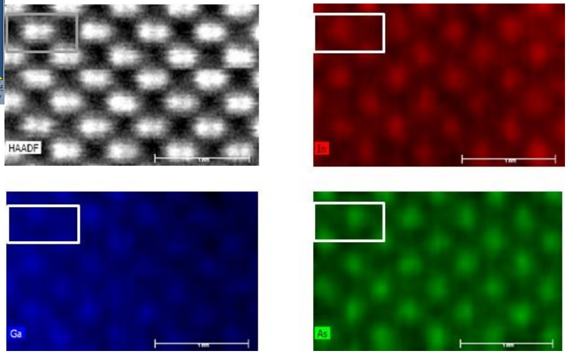
- Probe size => atomic scale
- Elemental analysis (C=>)
- Semi-quantitative analysis

BUT

- Interference with sample holder (Cu)
- Low sensitivity for light elements.



InGaAs/InAlAs sur InP

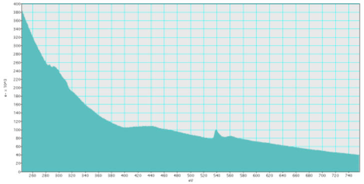


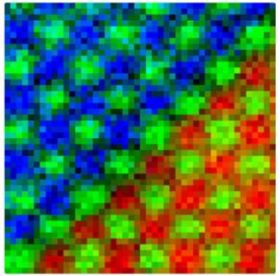
STEM-EELS

- Probed size => atomic scale
- Elemental analysis (B=>)
- Semi-quantitative analysis
- Chemical information (OS)

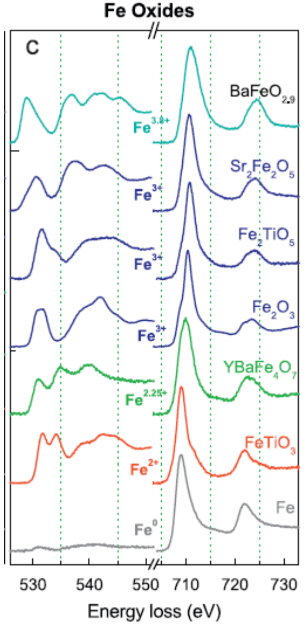
BUT

- Very thin lamella



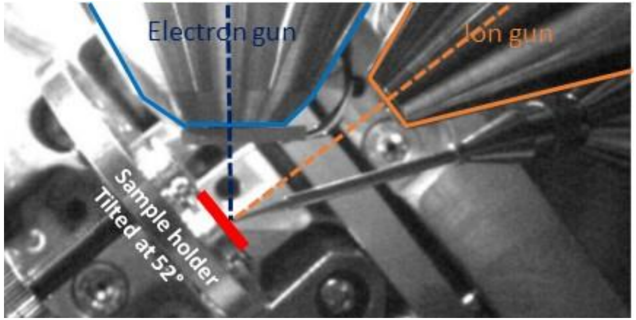


Core-loss EELS atomic-resolution elemental map of a $BaTiO_3/SrTiO_3$
Ba, Sr, Ti



H. Tan Ultramicroscopy 116 (2012)

SAMPLE PREPARATION: A KEY STEP (1/2)

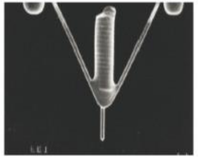


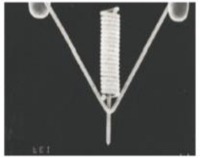
Focused Ion Beam

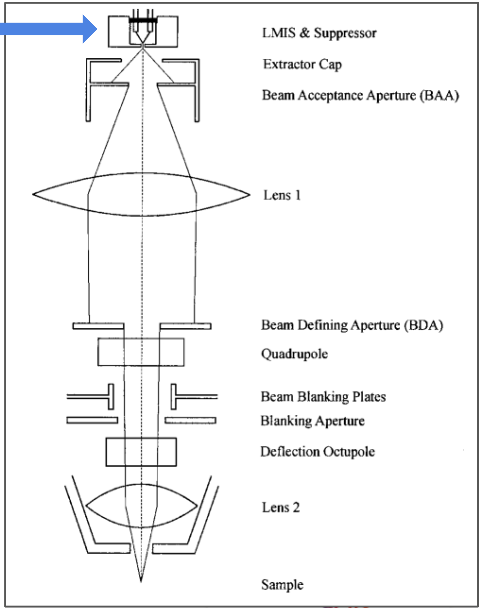
- Selection of the area/volume by SEM-SE, EDS
- Milling the TEM lamella using Focused Ion Beam
- To follow the progress by SEM image

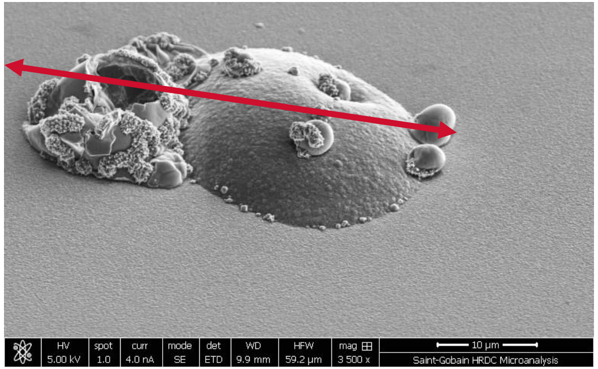
key parameters

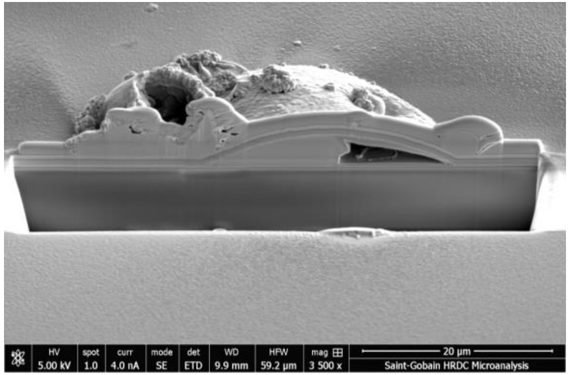
- High lateral resolution for Ga Gun
- Milling efficiency
- Sample (sample holder) stability











T Epicier, Colloque National, Aussois Janvier 2010

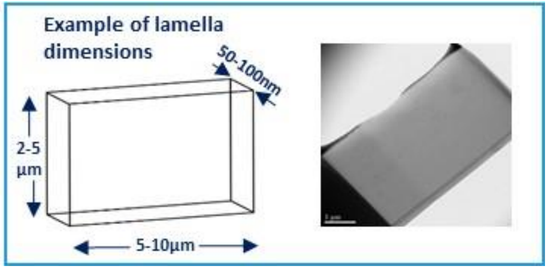
P. Letocart, SGR Germany Pers. Com. (2014)

TRANSVERSAL R&D CENTERS BY SAINT-GOBAIN

SAMPLE PREPARATION: A KEY STEP (2/2)

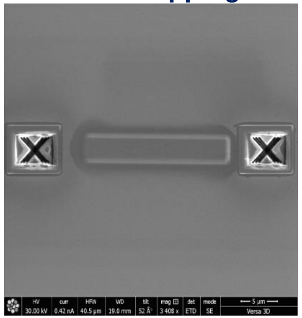
STEM Lamella specifications

- Thickness very weak : several tens of nm
- Wide : several µm (enough statistic)
- Stable under STEM

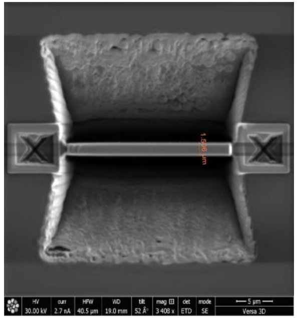


The different steps of lamella preparation

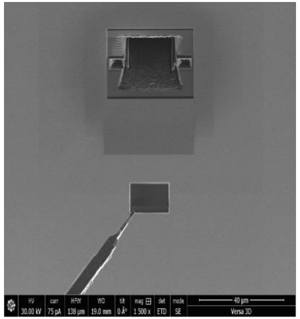
area selection + surf. capping



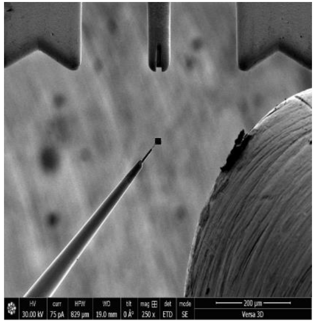
Rough milling



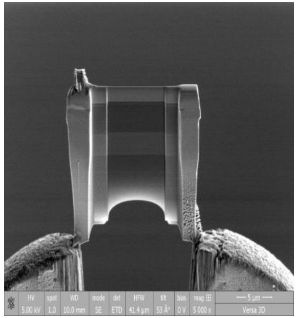
welding on probe +cut +extraction



Transfer + Cu support approach



Welding on Cu + final refining



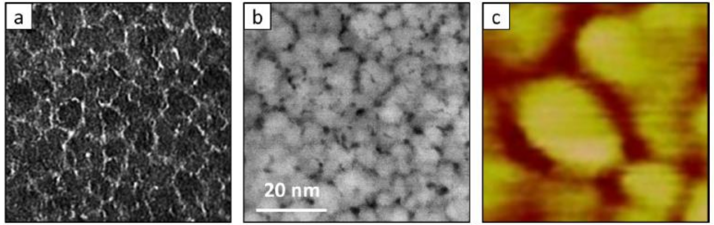
Others techniques used

- Mechanical polishing + ion milling by PIPS

STEM-EELS OF AMORPHOUS SAMPLE (1/3)

Plan-view comparison

TEM-BF (φ contrast) **STEM-HAADF** **AFM (surface)**



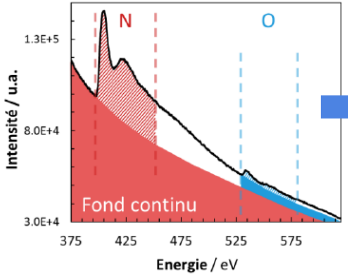
Porous Al-doped silicon nitride layer (30nm thick)

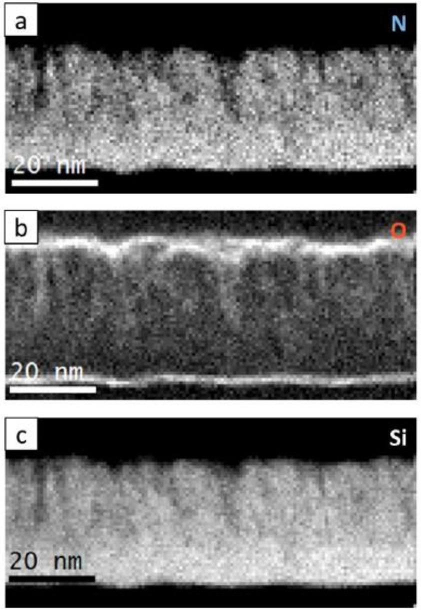
- Deposited by magnetron sputtering in specific conditions.
- Oxidation from the surface (air contact impact)

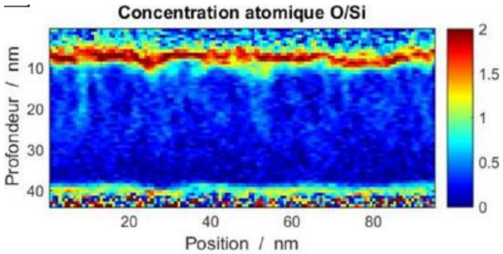
  => depth/distribution

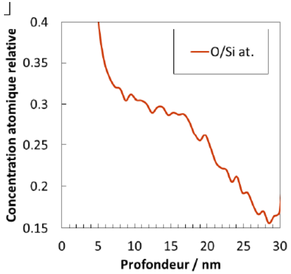
EFTEM in cross section

- N, O, Si maps



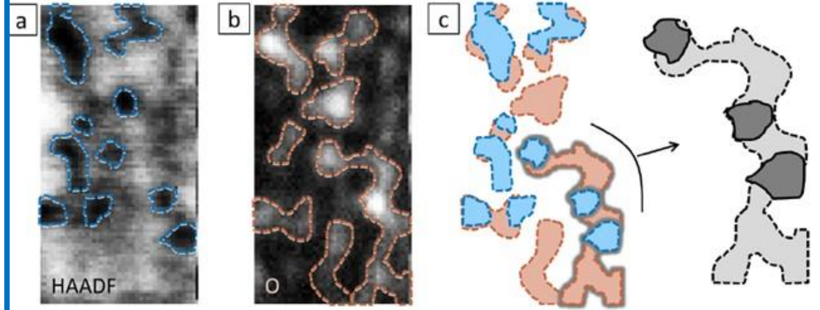






Plan-view comparison

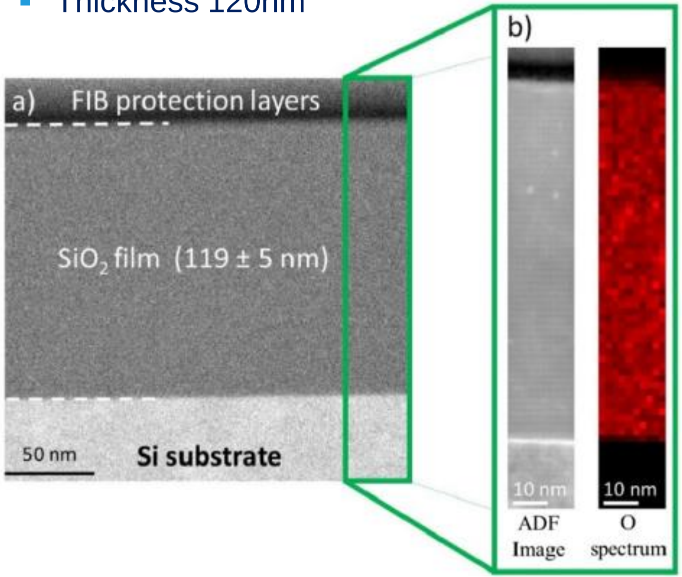
STEM-HAADF **and EELS for O** **for connectivity information**

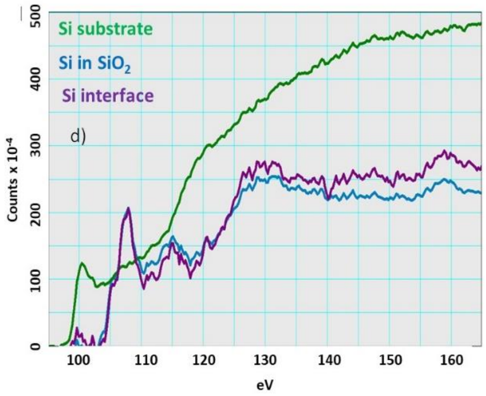


T. Barres, PhD, Sorbonne Univ. (2017)

STEM-EELS FOR AMORPHOUS SAMPLE (2/3)

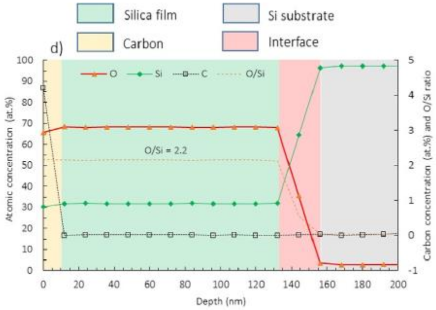
- **Silica layer deposited by CVD**
  - From TEOS at 1atm @ 500°C
  - Thickness 120nm



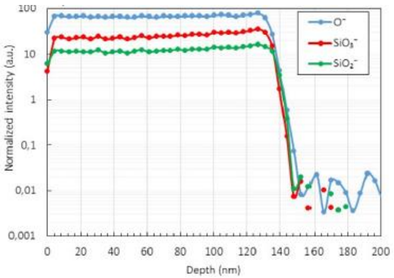


Depth profiles acquired

by XPS



by ToF-SIMS



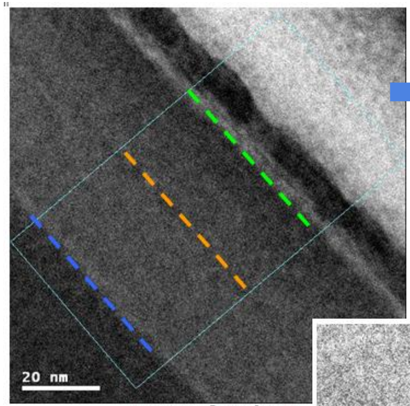
Homogeneous [EELS, ToF-SIMS] composition of $SiO_{2,2}$ layer [XPS, NRA],
No carbon inside [XPS, NRA]

B. Diallo, JMRT, 13 (2021)

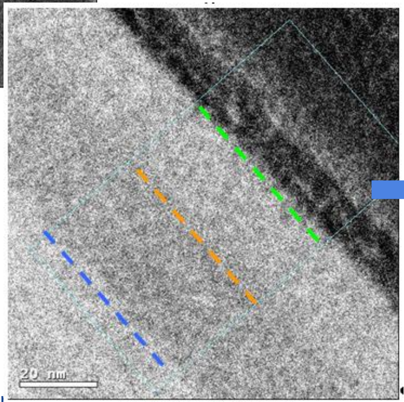
STEM EELS OF AMORPHOUS LAYER (3/3)

Case of SiOC layer

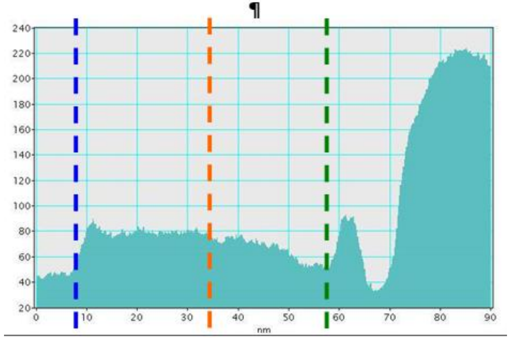
- Deposited by CVD (inside Float)
- 30nm thick, rough surface.



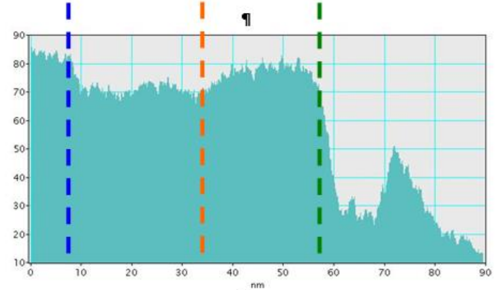
EFTEM of Carbon



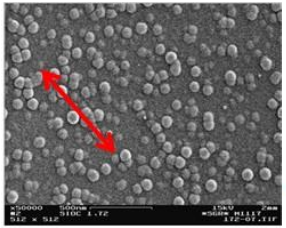
EFTEM of Oxygen



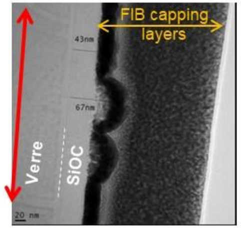
Projected depth profile of Carbon



Projected depth profile of Oxygen

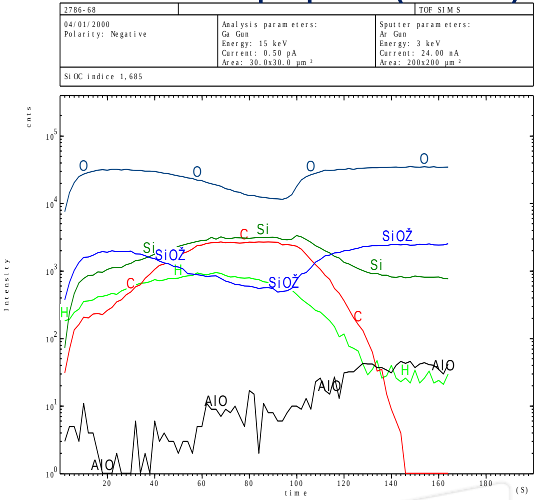


SEM-SE image (surface)



TEM picture (cross section)

ToF-SIMS depth profile (raw data)



TEM thank to M Cabie @CP2M
P Lehuédé, Pers. Com. (2007)

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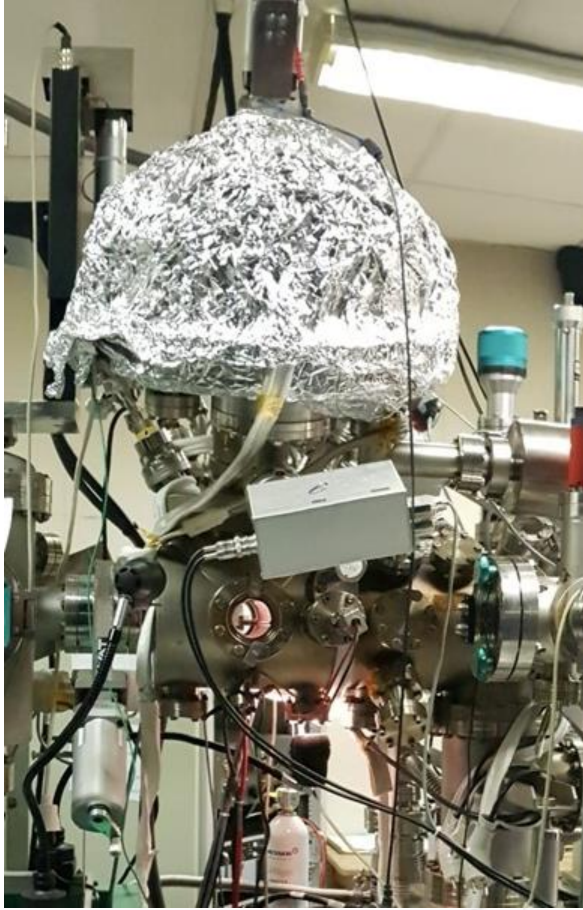
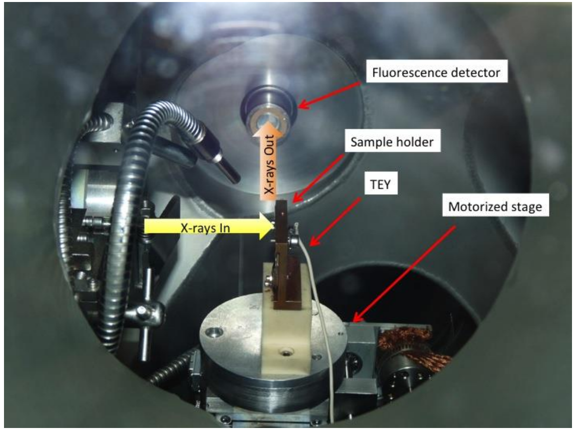
CONCLUSION

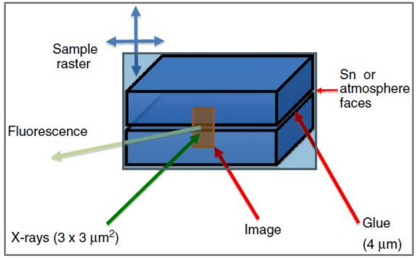


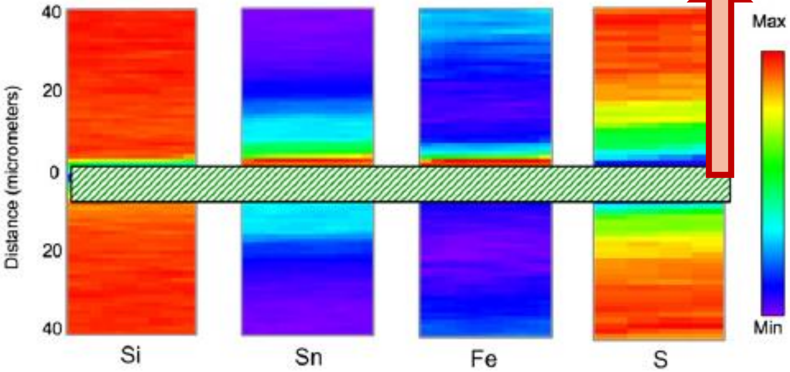
XAS DEPTH PROFILING

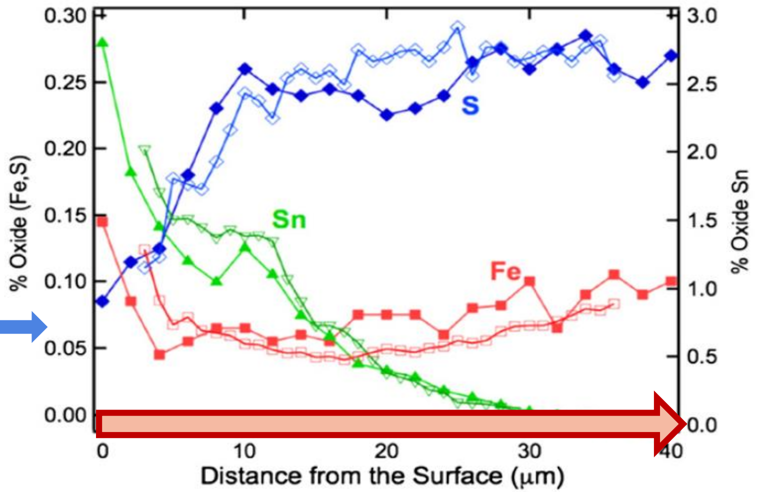


▶ Principle

- X ray monochromatic beam (0,6-8,0keV) of 3x3µm² for µ-XAS, µ-XRF.
- Collection X-ray fluorescence with Si drift diode.
- Chemical map on cross section





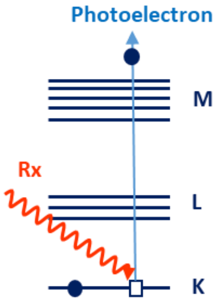


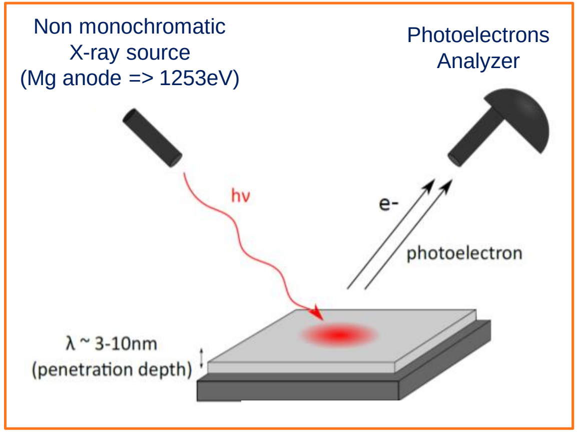
AM Flank, JNCS 357 (2011)

XPS DEPTH PROFILE

Principle

- Based the photoelectric effect under RX irradiation.
- Elemental composition as well as chemical state.





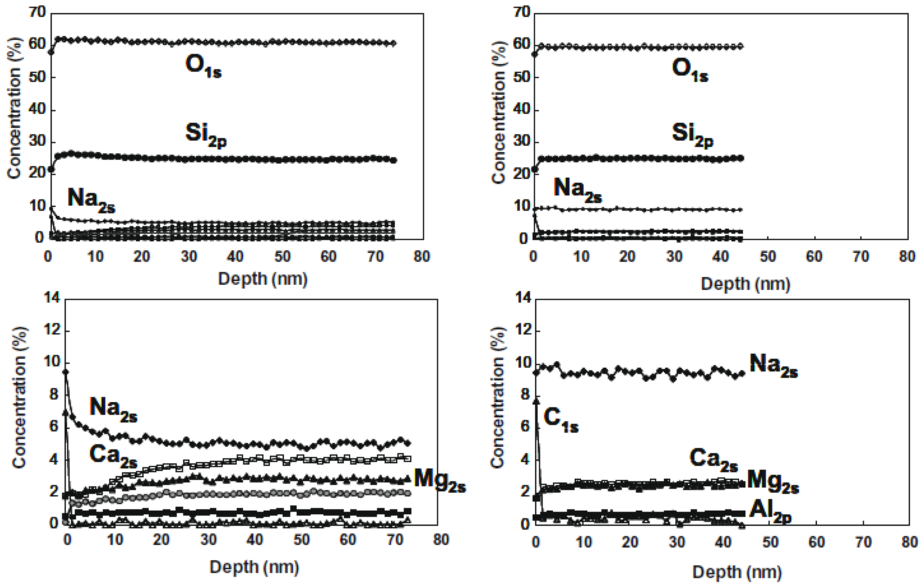
- Depth profiling is obtained combining XPS analysis of the bottom crater with abrasion sequence using ion gun (like ToF-SIMS)

Depth profiling comparison

(Fresh fracture of soda silica glass, settled at -130°C)

Abrasion: Ar^+ 2kV

Abrasion: $C60^+$ 10kV

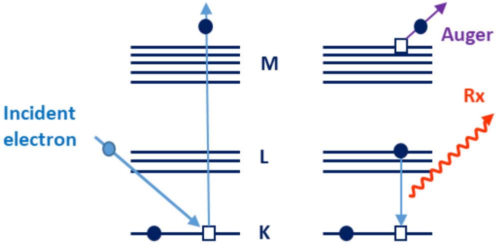


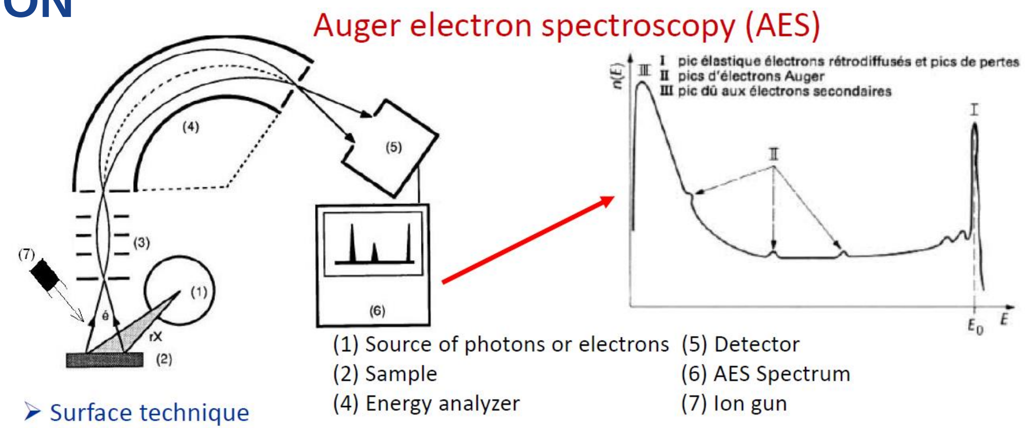
Y Yamamoto, JNCS 356 (2010)

AUGER CHARACTERIZATION

Principle

- Electron emission from excited atom as a consequence of internal relaxation.

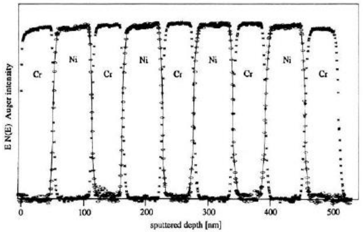




➢ Surface technique

Add-value

- Extreme surface analysis (~2nm)
- Quantitative analysis (~1-2%)
- Depth profile available combined with abrasion gun



Analysis configuration for diffusion at nanoscale

- In situ annealing under UHV + Auger Surface quantification

Advantage

- No sputtering artifact
- Gives access to the exact value of the diffusion coefficient
- Allows diffusion measurements though nanometric films and nanostructures.

A Portavoce DiFSol2 (2021)

CONCLUSIONS

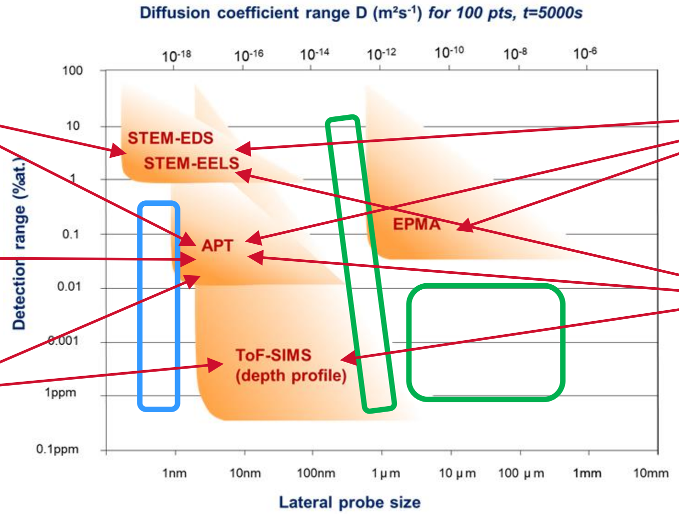
- Sensitivity and lateral resolution are key parameters for the characterization of gradient in glasses

BUT not the only ones

Sample preparation: time consuming

Laborious acquisition

Numerous artifacts (matrix effects)



Gradient modification during the acquisition

Coupling with other structural analysis difficult (destructive analysis)

no solution land

Necessary to adapt solution (ex: SIMS imaging)

CONCLUSIONS

- The tool box for the gradient characterization in glass is very well supplied: EPMA and ToF-SIMS permits to cover a wide range of cases.
- EPMA is adapted for diffusion over distances 0,1mm and more…
- ToF-SIMS depth profiling is well suited to the thin layer stacks
- In case of ToF-SIMS, various artefacts (charging effects, sputtering…) can lead to wrong interpretations but many parameters (nature of abrasions ions, energy, ions collected…) can be used as "leverage" to limit their impacts.

- This presentation lists the techniques sensitive to element **BUT** other techniques can give indirectly information concerning the quantity of some elements (Raman spectroscopy, optical properties, conductivity…)

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ET MERCI POUR VOTRE ATTENTION