Surface des verres et durabilité chimique

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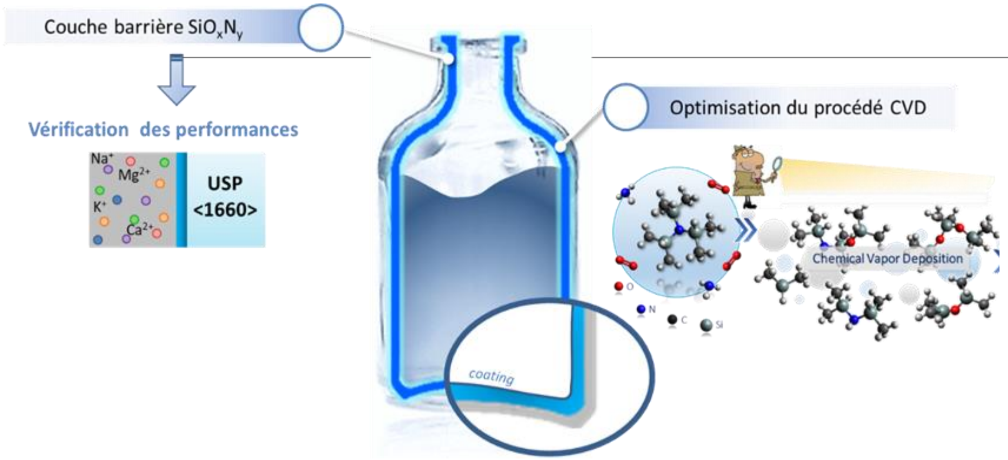
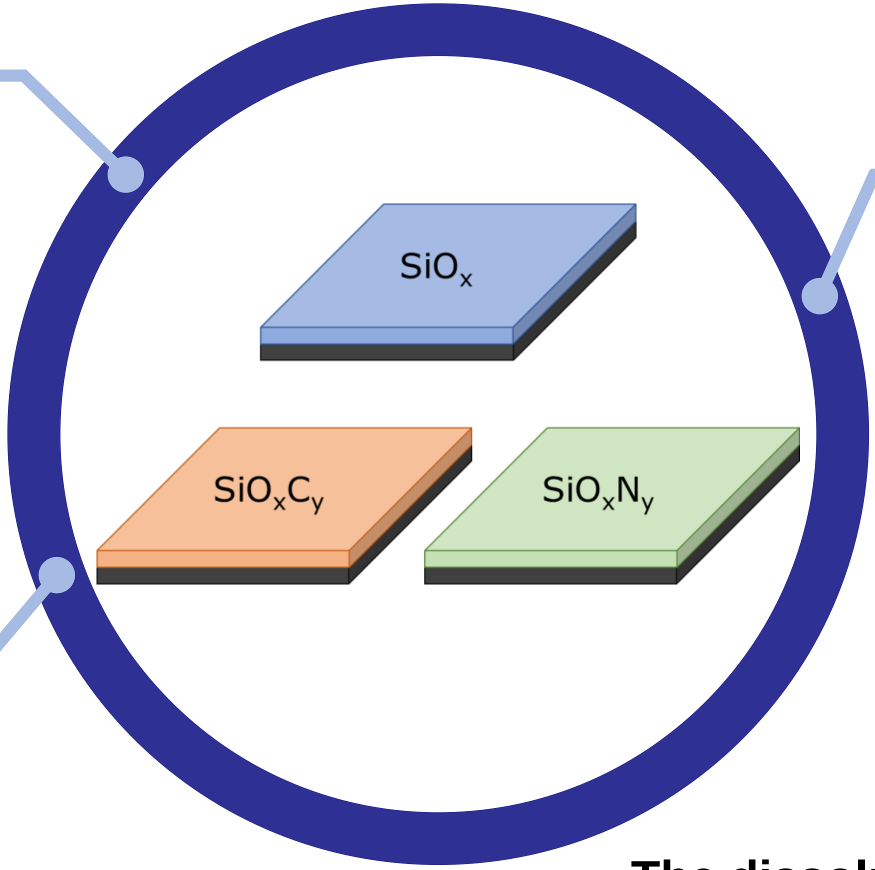


Processable by :
- Sol-gel
- PVD
- CVD

Tunable properties :
- Optical
- Mechanical : high fracture toughness
- Electrical : high dielectric constant
- Biocompatibility
- Chemical and thermal stability, corrosion resistance



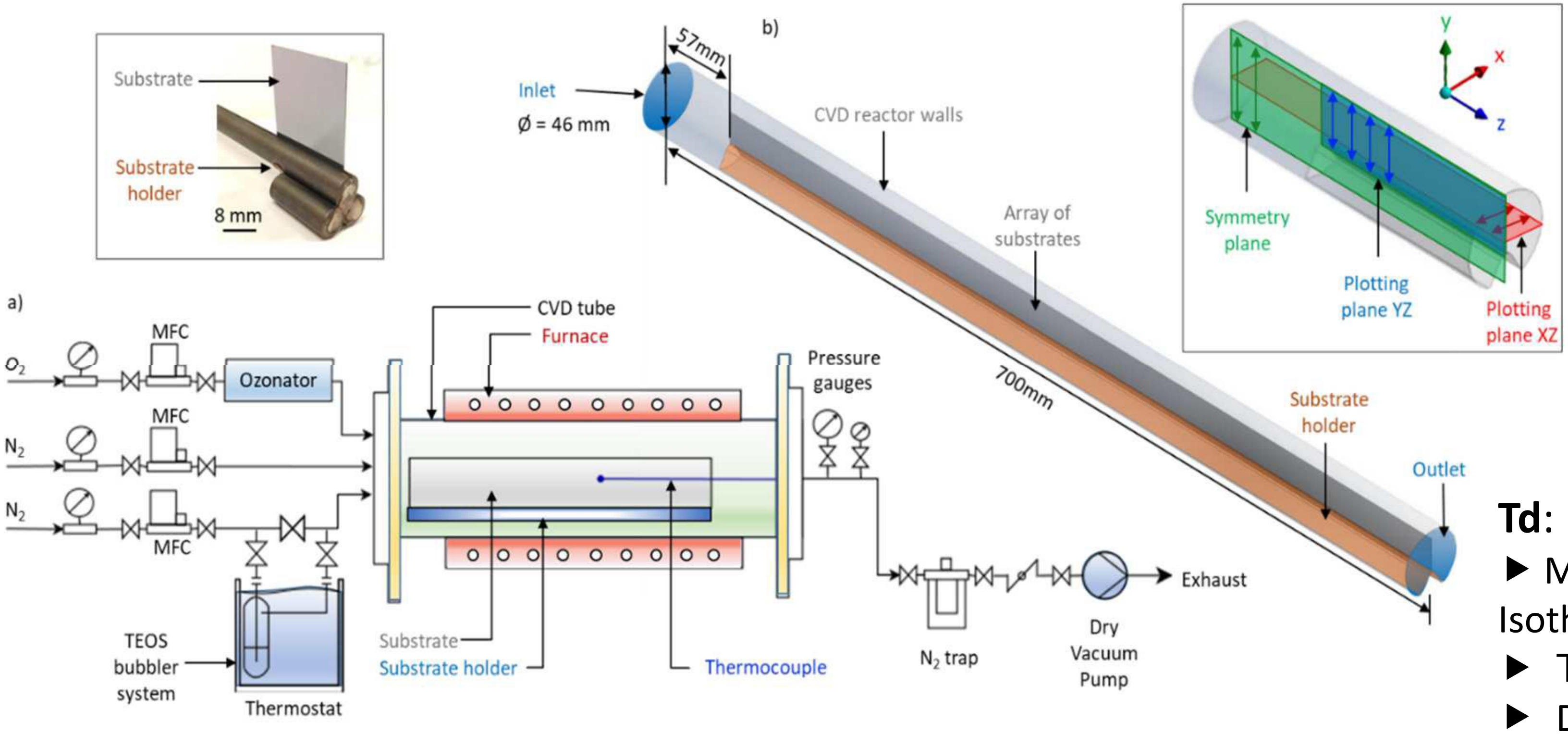
Applied as :
- Anti-wear coatings
- Ion-diffusion barrier (Na,B) in LED
- Low water vapor transmission rate : food packing, electronic devices
- Gas diffusion barrier on various plastic packaging materials
- Encapsulation of carbon dots
- Optical waveguides
- Structural layers for MEMS

The dissolution rates in pure water

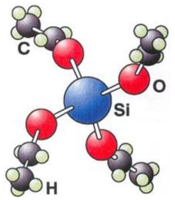
Quartz	Amorphous silica	
$4.2\ 10^{-14}$	$9.0\ 10^{-13}$	$mol/m^2\ s$

Solubility stays very low for pH < 9

CVD reactor



Oxygen-Ozone O2/O3 mixture assisted atmospheric pressure Chemical Vapor Deposition (CVD) from tetraethyl orthosilicate **$Si(OC_2H_5)_4$**,TEOS precursor



flow rates :

TEOS : 2 sccm ; O_2/O_3 1960 sccm
O_3 concentration of 60 mg/L
sccm: *standard cubic centimeters per minute*

Td: **Deposition Temperature**

- Measured at the middle of the reactor

Isothermal region : **140 mm** long from 360 to 500 mm

- Td between **320** and **550 °C**
- Deposition time of 30 min: film thickness of ≅ 100 nm

Numerical simulations (FLUENT®)

- Apparent chemical reactions and kinetic laws at atmospheric pressure
- Computational Fluid Dynamics (CFD) codes

SUBSTRATE

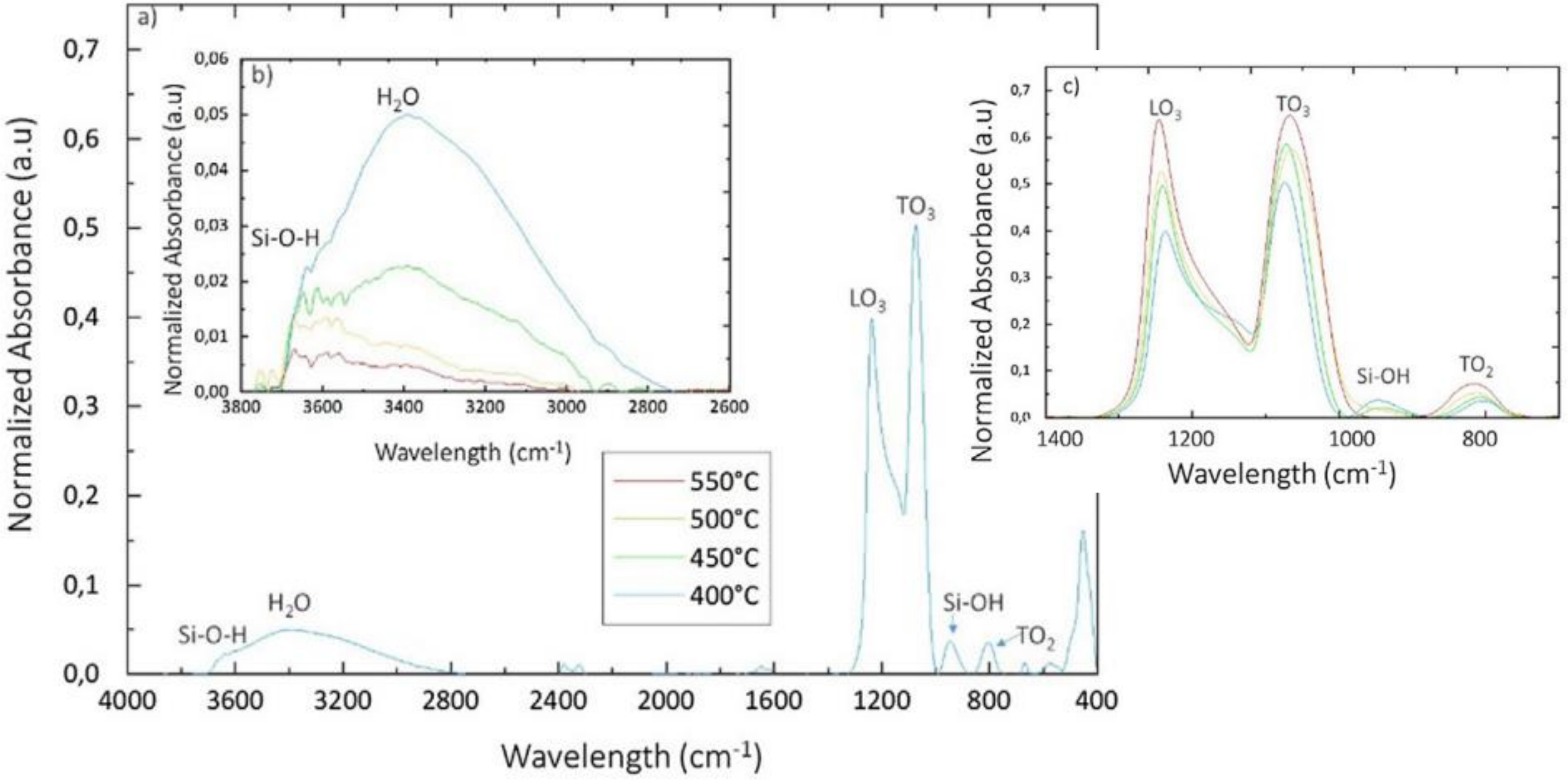
monocrystalline silicon (100)
wafers, 280 µm thick, 32×24 mm²

Glass plate

Glass vial

LABORATOIRE DE GÉNIE CHIMIQUE
TOULOUSE • UMR 5503

K.C. Topka et al, Chemical Engineering Research and Design, 161:2020, 146-158



Si – O – Si bond :
480 cm^{-1} : rocking mode TO_1
780 cm^{-1} : bending mode TO_2
1050 cm^{-1} : asymmetric stretching mode TO_3 and LO_3

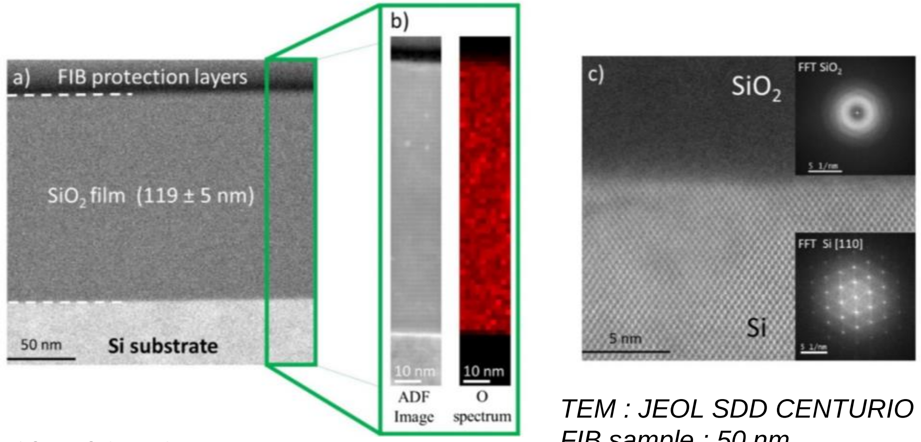
Adsorbed water and silanols :
940, 1600 cm^{-1}
2600 – 3800 cm^{-1}
3200, 3400 cm^{-1} : symmetric and asymmetric OH stretching in H_2O
3550, 3600, 3650 cm^{-1} : OH stretching of silanols

When Td ↗
- ↗ TO_2 band, shift
  ➔↗ **medium range order, connectivity**
- ↗ TO_3/LO_3 and shift
  ➔ ↗ **polymerisation**
- ↘ Si-OH mode 940 cm^{-1}
- ↘ high ν band (H_2O steeper than Si-OH)

►Network polymerisation : enhanced at high Td through a **dehydration-condensation mechanism**.

- STEM image : very homogeneous coating with no specific defect, texture or nanoporosity
- ADF, EELS : chemical homogeneity
- Sharp interface ~ 8 nm; amorphus nature of silica

a) STEM-HAADF image
b) ADF: Annular Dark Field image and oxygen spectrum obtained from EELS spectroscopy (STEM)



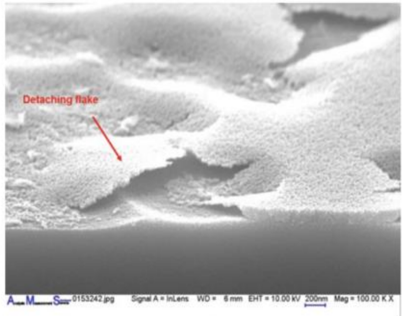
TEM : JEOL SDD CENTURIO
FIB sample : 50 nm

B. Diallo et al, Journal of Materials Research and Technology 2021 ; 13 : 534 - 547

ALTERATION PROCESSES

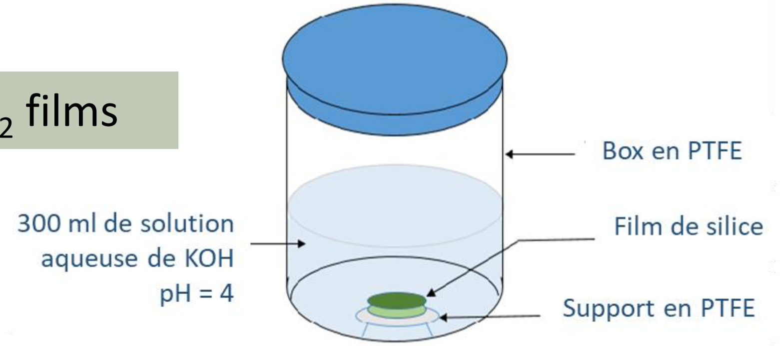
Alteration protocols :

- Very fast test (15 - 60s) : P-etch / BOE test
- Short standardized tests USP (pharmacopeia)
- Classical method by immersion on the longest term at different pH and T
- Long term atmospheric conditions

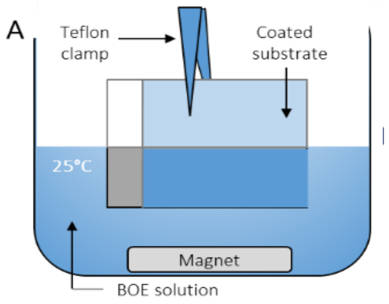


SCHOTT AG, « Glass delamination »

SiO_2 films

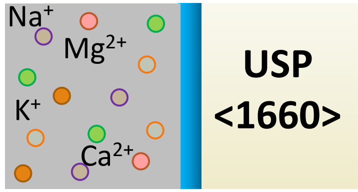


90°C

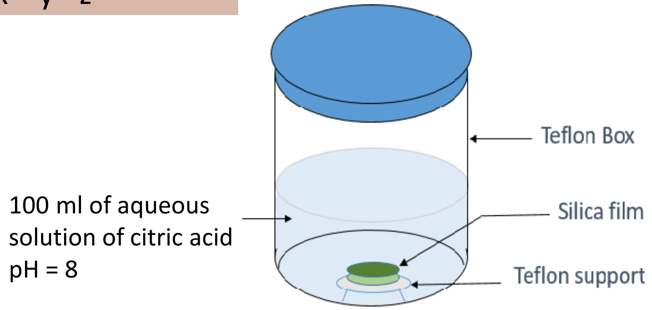


P-etch test : pH 1.5 solution of 3 parts of HF, 2 parts of nitric acid and 60 parts of water
Pliskin J Vac Sci Technol 1977; 14:1064-81

BOE test : 6 parts NH_4F (40 wt %) + 1 part of HF (49 wt %)



$SiO_xN_yC_z$ films



80°C
1 month

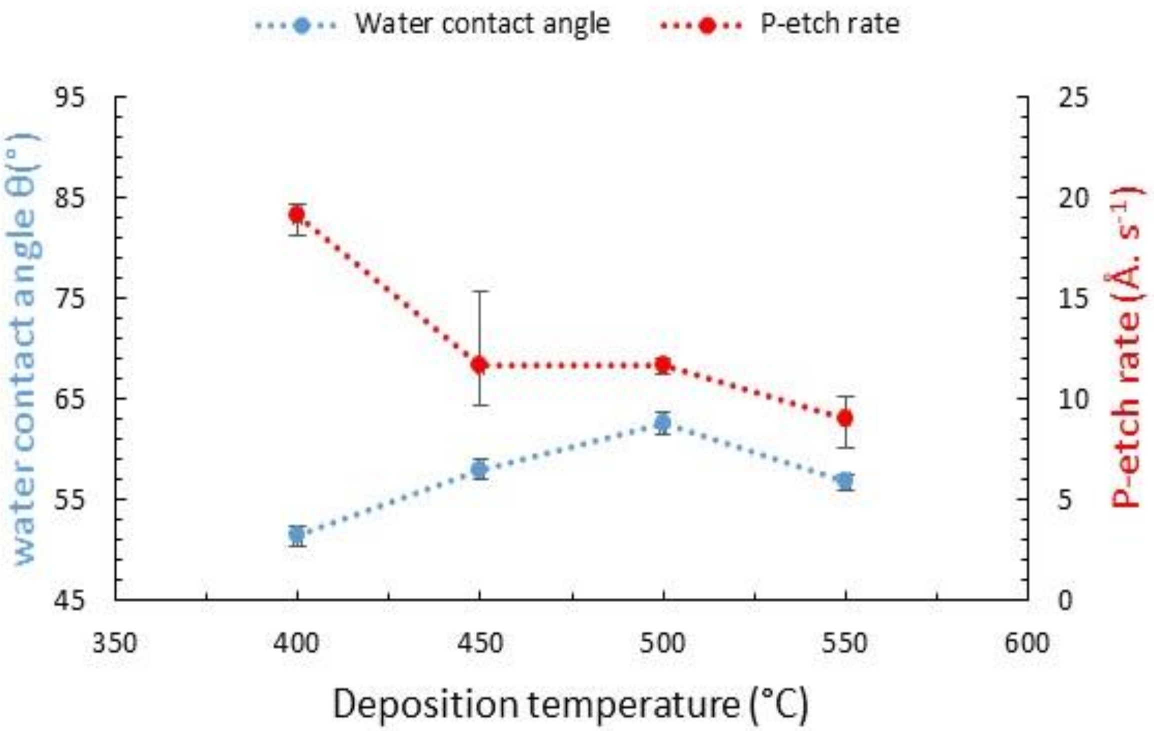
Formulations and Conditions Used to Accelerate Delamination

Formulation	0.9% KCl pH 8.0	3% Citric Acid pH 8.0	20 mM Glycine pH 10.0
Conditions	2 h at 121°	24 h at 80°	24 h at 50°

SiO_2 films

$SiO_xN_yC_z$ films

- **IBA techniques** : RBS and ERDA
- IR, XPS
- TOF-SIMS
- AFM
- SEM, TEM



▶ *Etching rate according to thickness measurements (ellipsometry)*

Etching in standard hydrofluoric acid (HF) solutions at **pH = 1.5**
Immersion maintained for **30 s** at 25°C

$$r\ (mol/m^2.s) = 10^{0.48} e^{\frac{-34243}{RT}}\ a_{HF}^{1.5}\ a_{H+}^{-0.46}$$

Empirical dissolution rate low of Mitra and Rimstidt for bulk silica

[Geochem Cosmochim Acta 2009; 73:7045-59]

where $10^{-2.37} < a_{HF} < 10^{1.61}$ (a_{HF}: HF chemical activity),
0.32 < pH < 4.76 and 296 < T < 343 K.

Water contact angle :
Confirms the hydrophilic character of the silica surface
fused silica (SQ-1 SCHOTT®, hydroxyl content 1200 ppm) [54] : 81 ± 8° [55].

Wettability : GBX apparatus using 0.35 ± 0.01 µL of distilled-water droplets

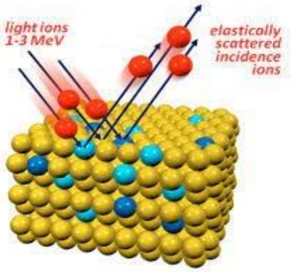
P-etch rate with T_d :

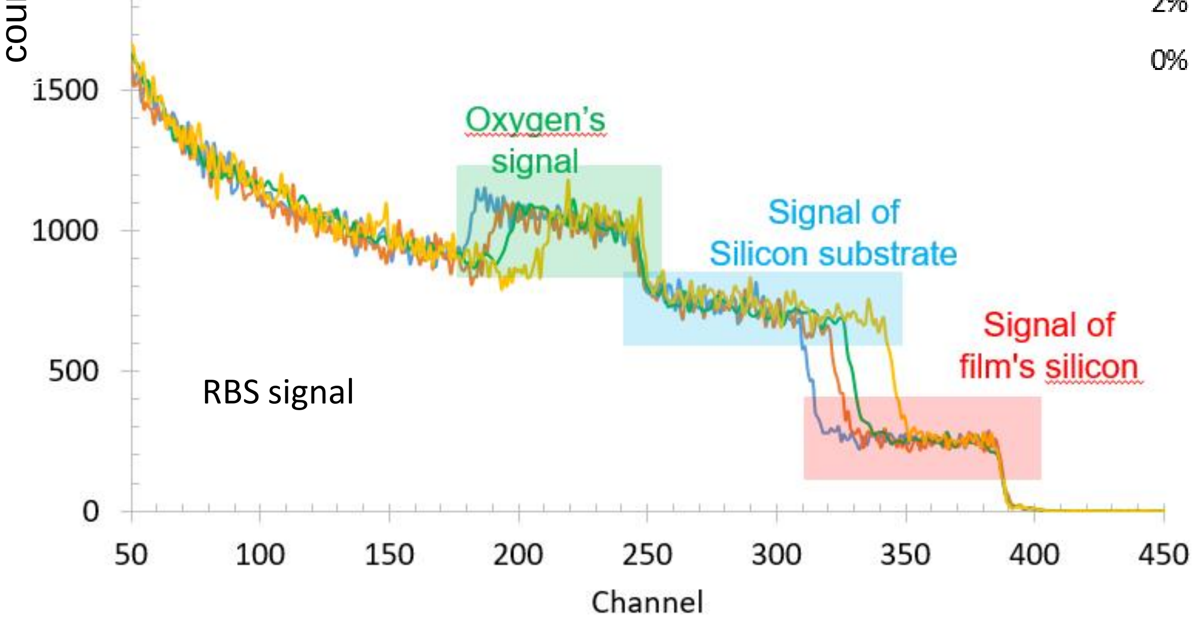
At 400°C : 19 Å/s
At 450°C : 11 Å/s
At 550°C : 9 Å/s
} As processed

after annealing 2h at 550°C under N_2 flow :
4.0 ± 0.1 Å/s (in excellent agreement with Mitra law)

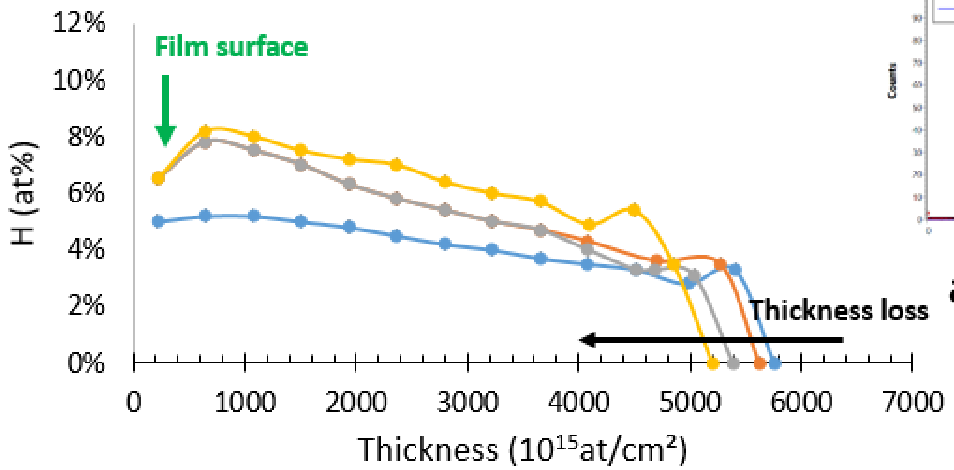
RBS: Rutherford Backscattering Spectroscopy
ERDA: Elastic Recoil Detection Analysis

PELLETRON accelerator 3MV – 3 lines of beam analysis
($^4He^+$ – $^3He^+$ – $^2H^+$ - H^+)

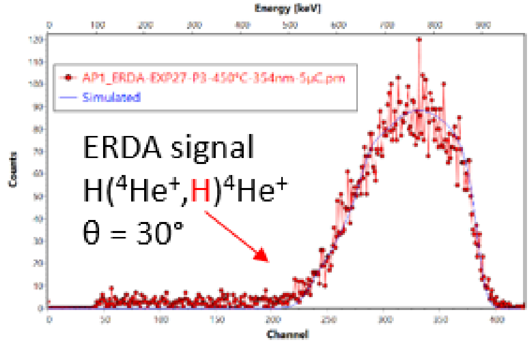




ERDA spectra evolution throught alteration (550°C)



ERDA depth resolution



δx_H = 430.10^{15} at/cm² ≈ 60 nm

- RBS and ERDA spectra simulation by SIMNRA*
- Film thickness in 10^{15}at/cm^2 and **Atomic concentration (at.%) for Si, O, H** → **Thickness loss calculations**

*M. Mayer, American Institute of Physics Conference Proceedings 475, p. 541 (1999)

t0 → t1 → t3

0.3 – 0.5 nm/day

Silica hydrolysis : ≡Si-O-Si ≡ + H_2O ⇌ 2 ≡Si-OH → H_4SiO_4

CHEMISTRY :

Precursor **tris(dimethylsilyl)amine TDMSA**, O_2 and/or NH_3

Atmospheric pressure CVD, at moderate temperature **600–650 °C**

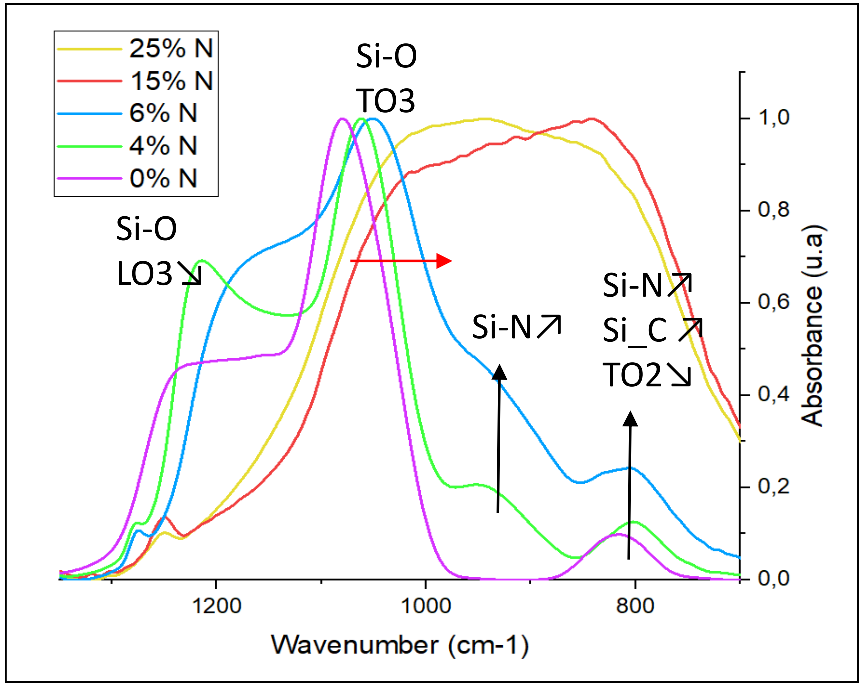
***S**tate of the art: 760-820°C!! with conventional disilazane precursors*

Air Liquide Precursor **sylilamine derivative BMDSD**

(N,N-bis(1-methylethyl)-N',N'-disilyl-silanediamine)

Atmospheric pressure CVD, **below 580°C**

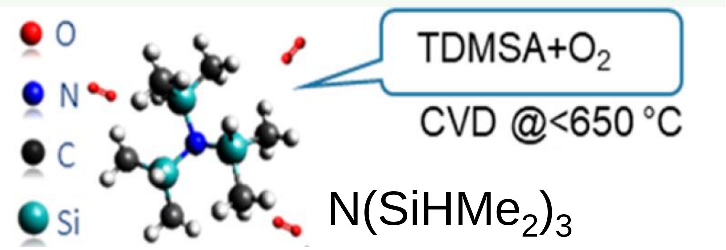
➲ Large range of N and C (up to 30 at.%) substitution

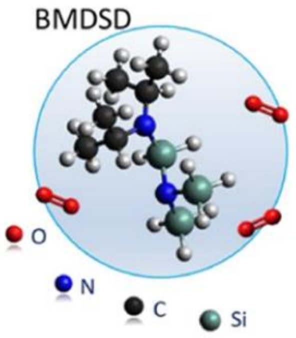


Si – N : streching vibration at 936 cm^{-1}, 840 cm^{-1}, 470 cm^{-1}

CHEMICAL ETCHING

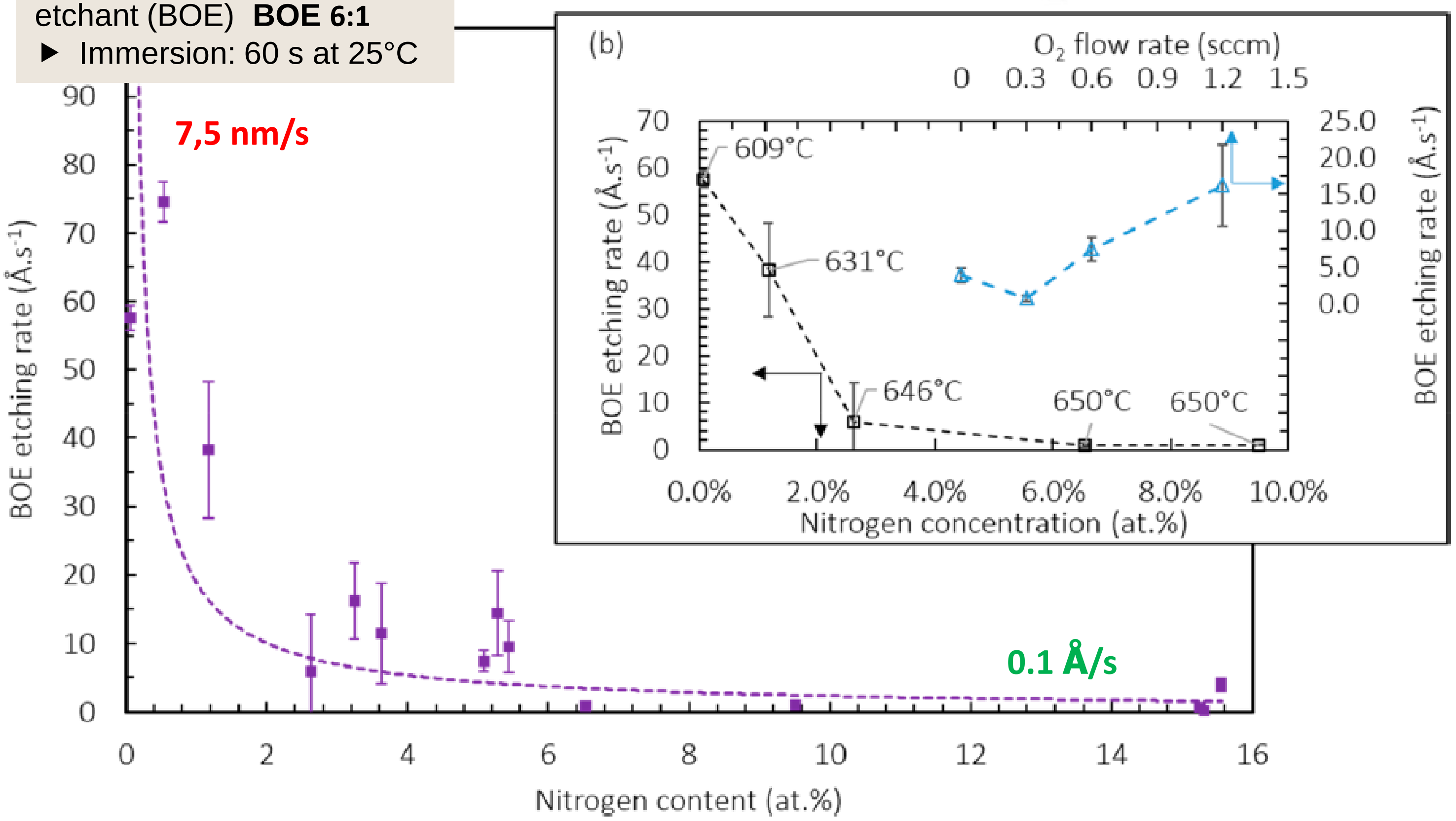
SiO_xN_y





Hydrofluoric buffer oxide etchant (BOE) **BOE 6:1**

▶ Immersion: 60 s at 25°C



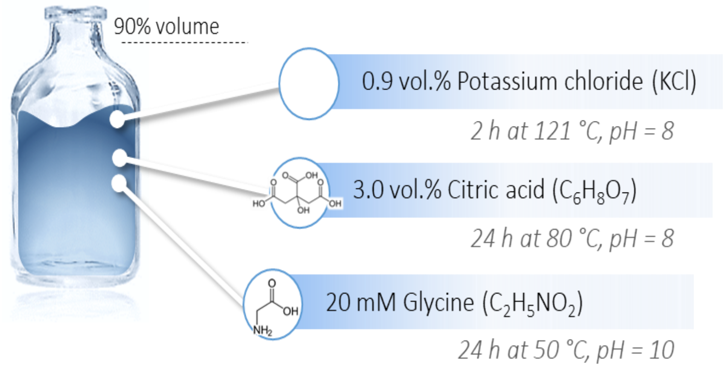
Konstantina Topka et al. ACS Applied Electronic Materials, 2022, 4 (4), pp.1741 - 1755

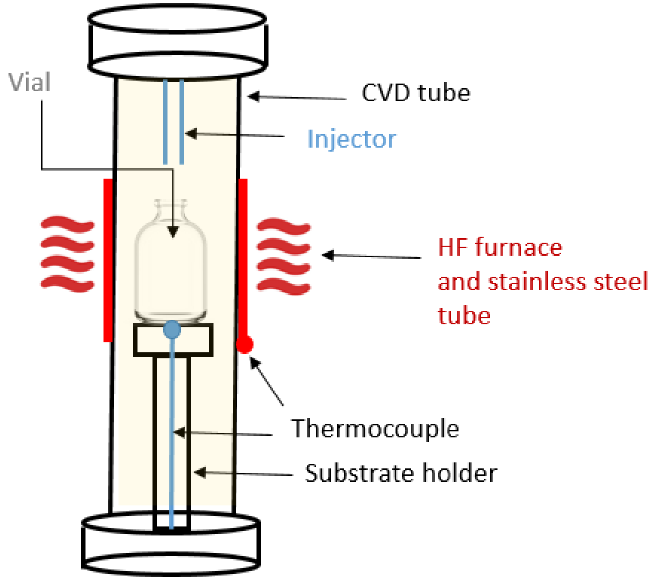
CHEMICAL ETCHING

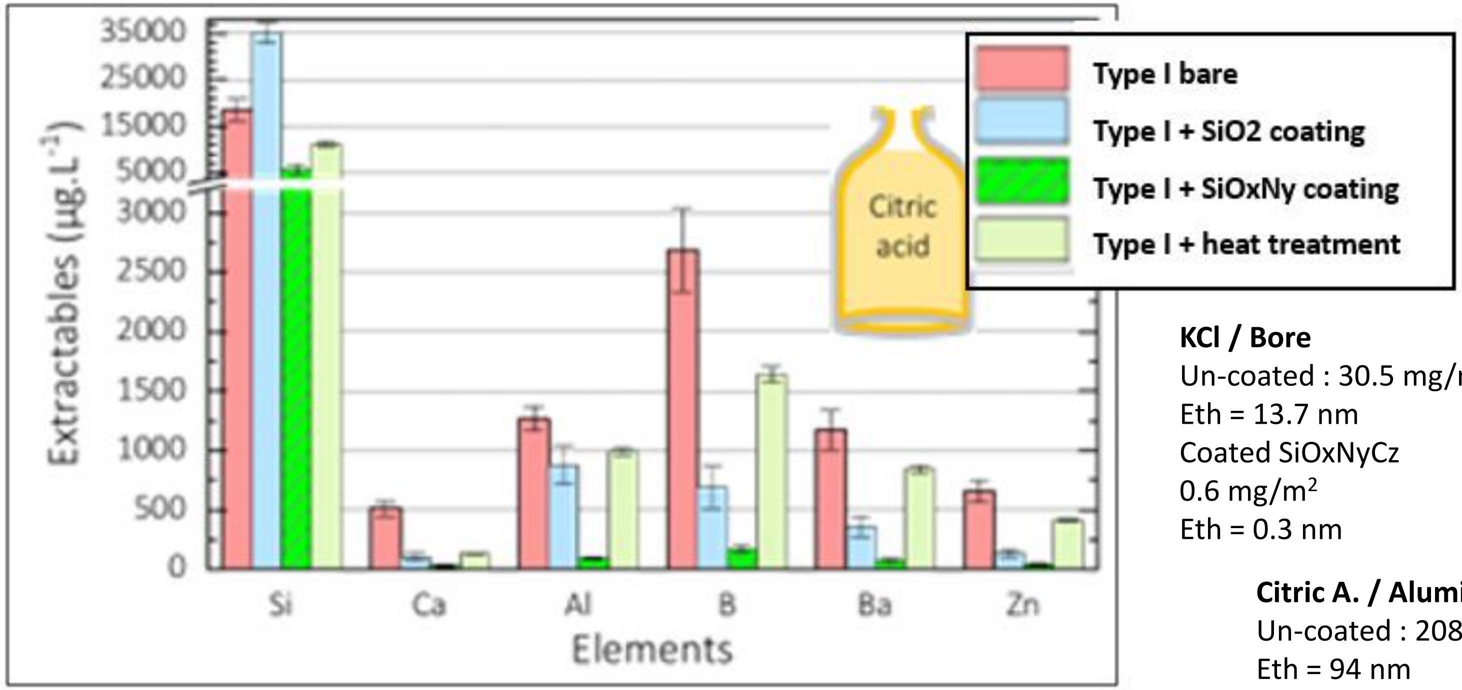
SiO_xN_y

USP : United States Pharmacopeia

The 1660 chapter suggest procedures of testing the compatibility between container and stored drug by utilizing wet corrosion tests under extreme thermal and chemical conditions that aim to replicate the prolonged exposure of the glass surface to aggressive pharmaceutical substances







KCl / Bore
Un-coated : 30.5 mg/m²
Eth = 13.7 nm
Coated SiOxNyCz
0.6 mg/m²
Eth = 0.3 nm

Citric A. / Aluminium
Un-coated : 208 mg/m²
Eth = 94 nm
Coated SiOxNyCz
14.8 mg/m²
Eth = 6.6 nm

$$Improvement\ Factor\ (FI) = \frac{([\sum conc]uncoated - [\sum conc]\ coated) \times 100}{[\sum conc]uncoated}$$

►SiOxNy coating contributes in limitting interaction between vial vitreous matrix and solutions

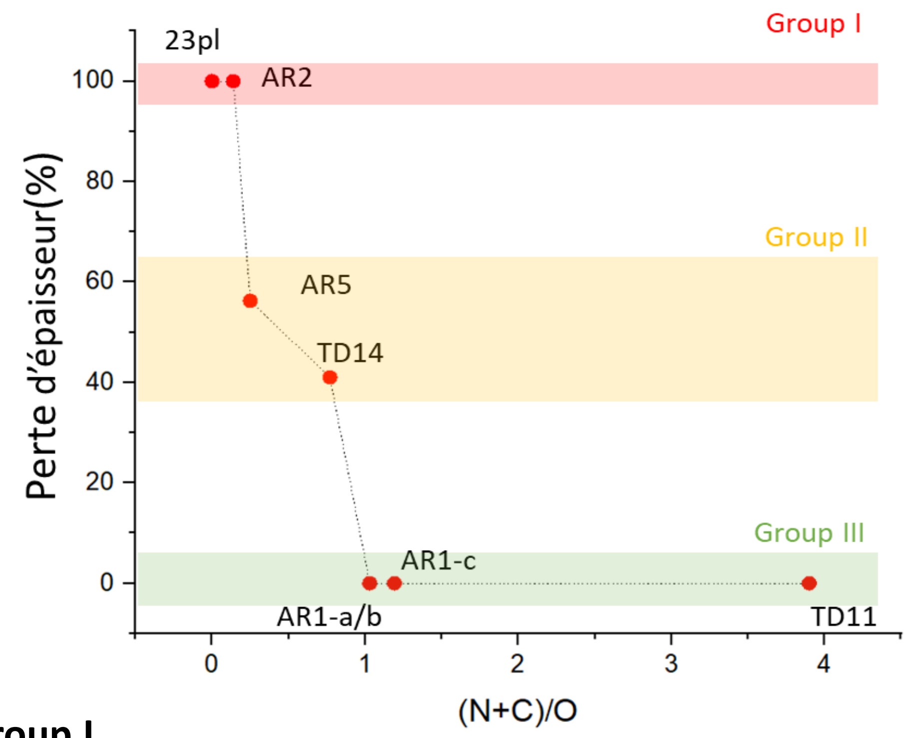
Chemical solution	Citric acid	KCl	Glycine
IF of SiOxNy coating	92%	98%	95%

*K.C. Topka et al. ACS Appl. Eng. Mater. **1**, 3268-3283 (2023).*

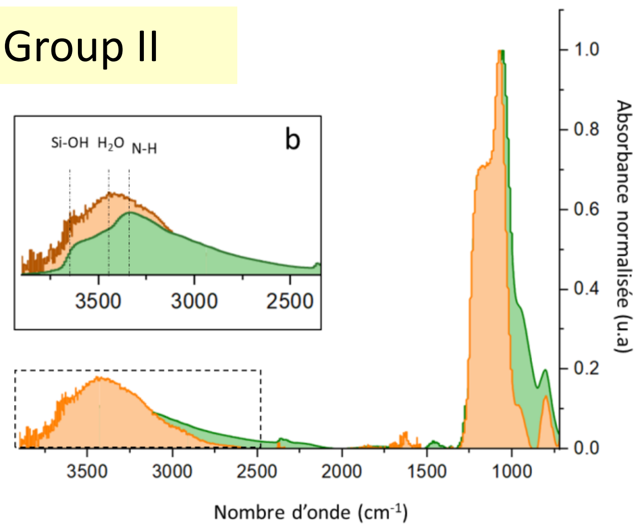
Citric Acid pH 8
▸ Immersion: 1 month at 80°C

CHEMICAL ETCHING

$SiO_xN_yC_z$

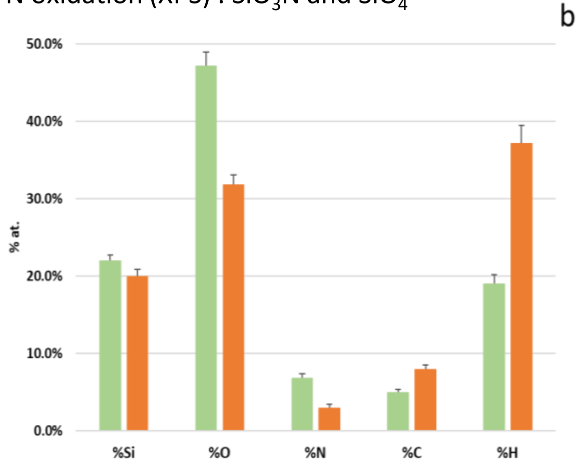


Group II

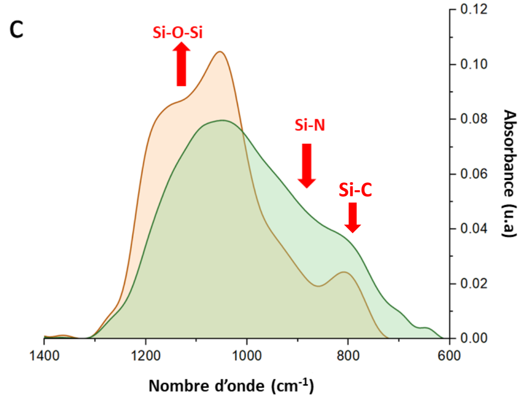


O➘ (XPS) : SiO_4 and SiO_3N environments more sensitive to alteration

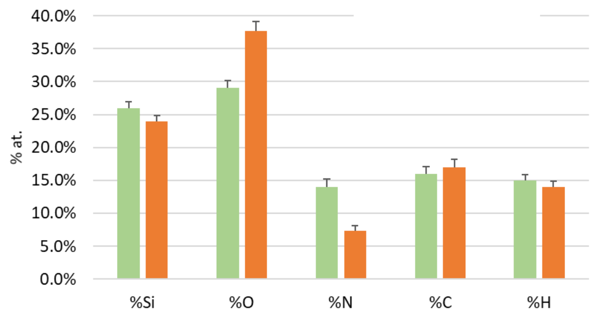
Si-N oxidation (XPS) : SiO_3N and SiO_4



Group III



Si-N hydrolysis (XPS) : SiO_3N ↗



Group I

Alteration dominates by Si-O-Si hydrolysis

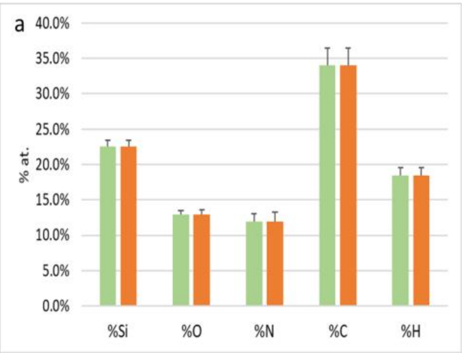
$$\equiv Si - O - Si \equiv \; + OH^- \rightleftharpoons \; \equiv Si - OH \; + \; \equiv Si - O^-$$

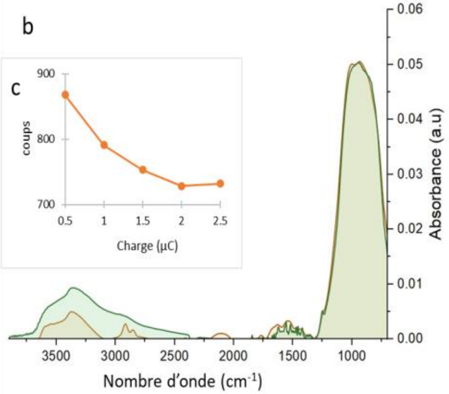
Group II, III

- Oxygen substitution by trivalent N and tetravalent C is more efficient: network more compact, void size reduced
- Increase of the covalent part of the chemical bond for Si-N# and Si-C*

#S. Sakka, *J. Non-Cryst. Solids*, vol. 181, nº 3, p. 215-224, 1995

*G. D. Sorarù et al, *J. Am. Ceram. Soc.*, vol. 85, nº 6, p. 1529-1536, 2002

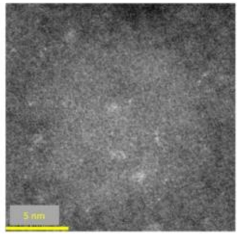




CHEMICAL ETCHING

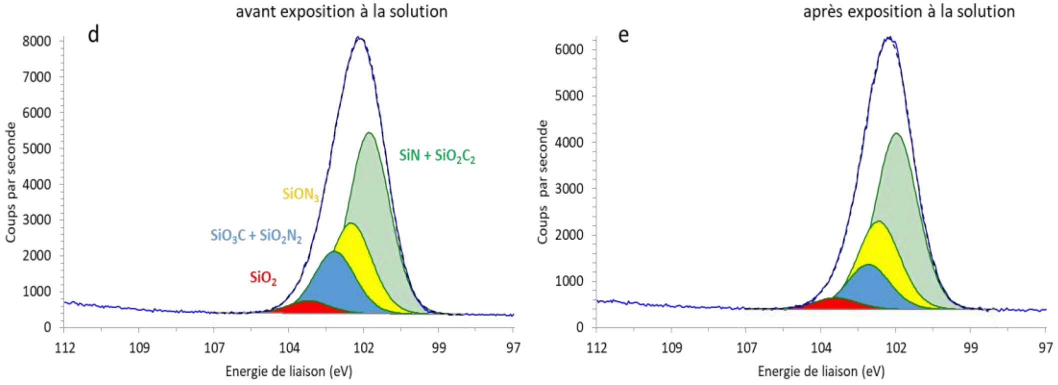
$SiO_xN_yC_z$

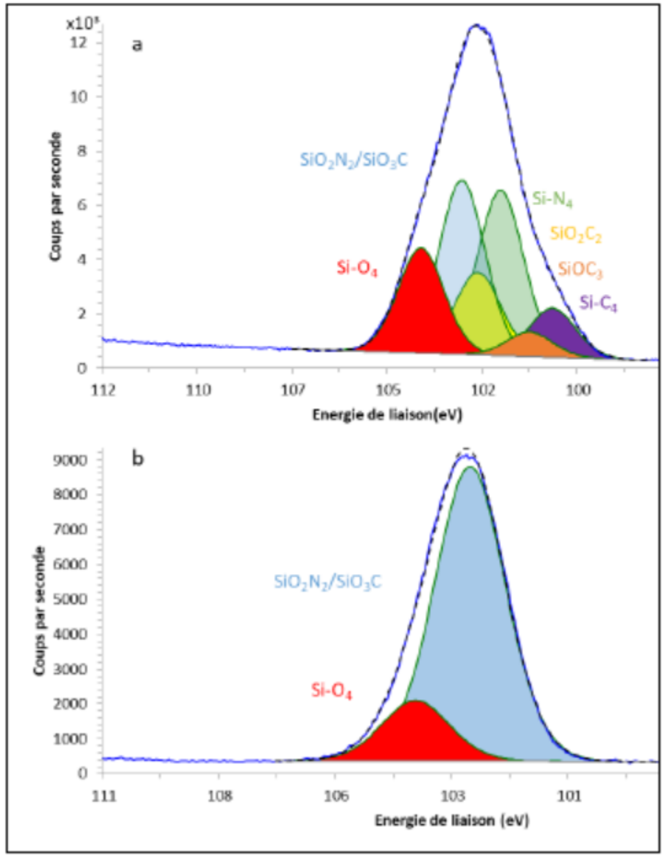
AR6 – N content: 27 at.%
Thickness loss: 31%
Alteration: strong loss of Si-N and Si-C, and strong oxidation



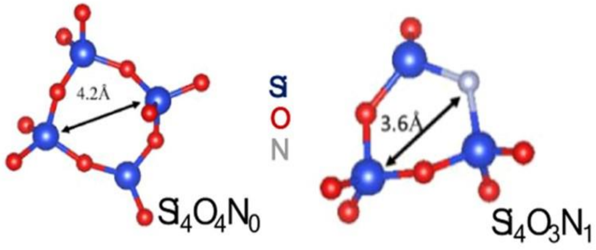
STEM-HAADF

Nanodomains enriched in Si or N



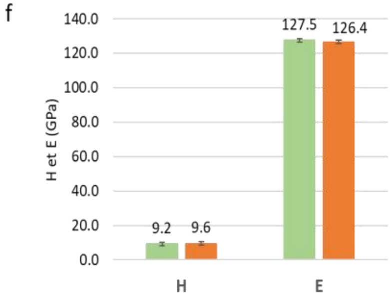


MD and DFT calculations on $SiO_{2-x}N_y$ systems (Nmax: 12 at.%) - Box 16 Å



Absence of SiN_4
SiO_3N ↗ with N content
SiO3N is the major specie for 12 at.% N
N induces the ring size reduction and occupies the smallest rings
➘ Si-O-Si angle : 147° → 133° (12 at.% N)

► RBM model
► Void size reduction



Group III

RBM* microstructure
Random Binding Model
Favors the mixing O/N/C around Si according to the five different configurations of SiOxN4-x, extrapolated to C
➲ Most efficient against chemical attack

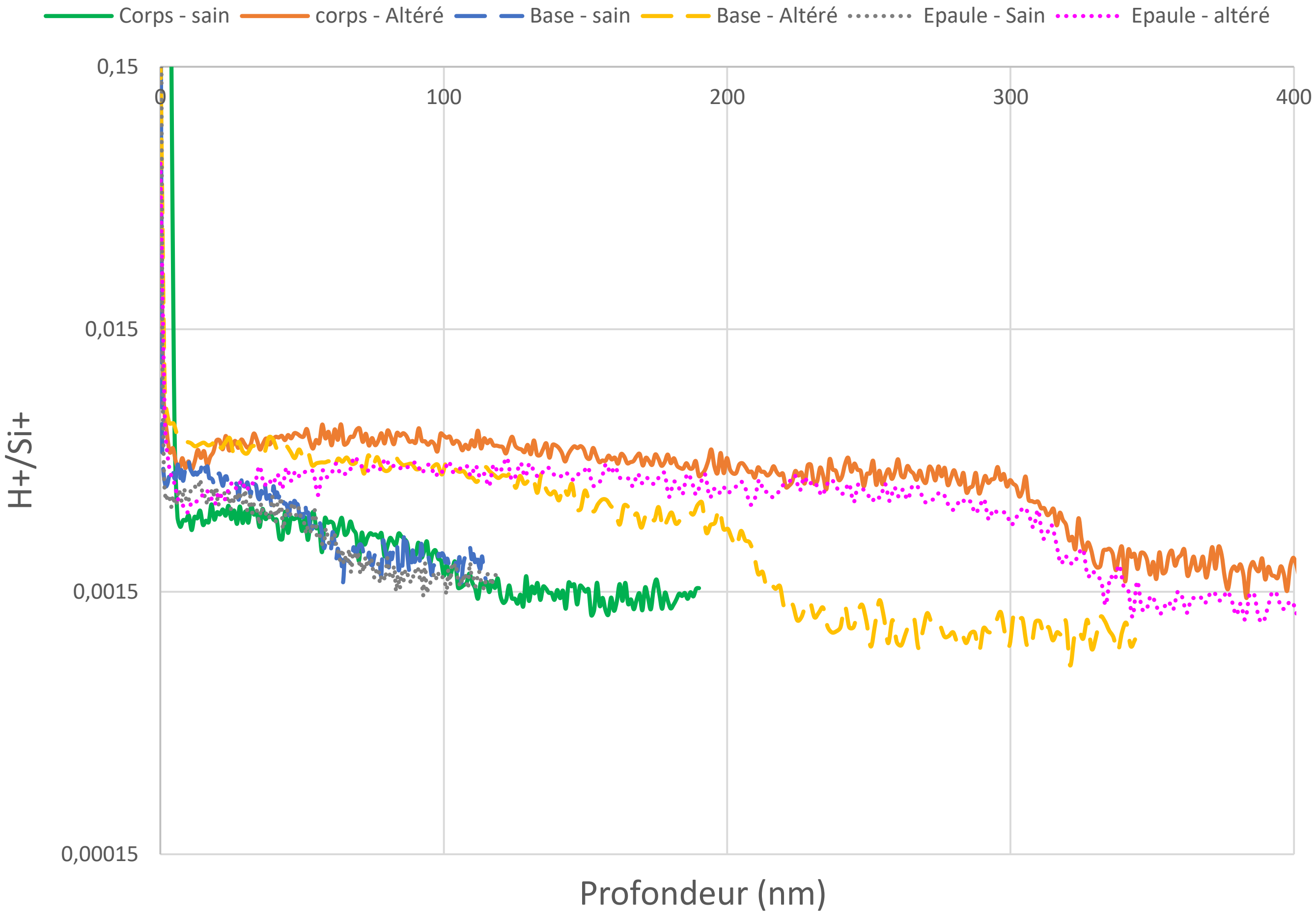
RMM* microstructure : ***Random Mixture Model***
microdomains: randomly distributed SiO2 and Si3N4 - extrapolation to SiC

**K.-M. Behrens et al, Surf. Sci., vol. 402-404, 1998*

CHEMICAL ETCHING

GLASS – TYPE I

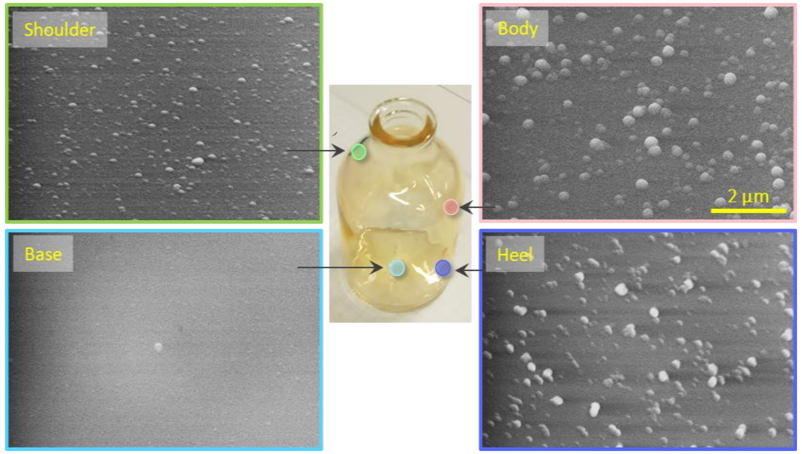
Citric Acid pH 8
▶ Flacon non revêtu



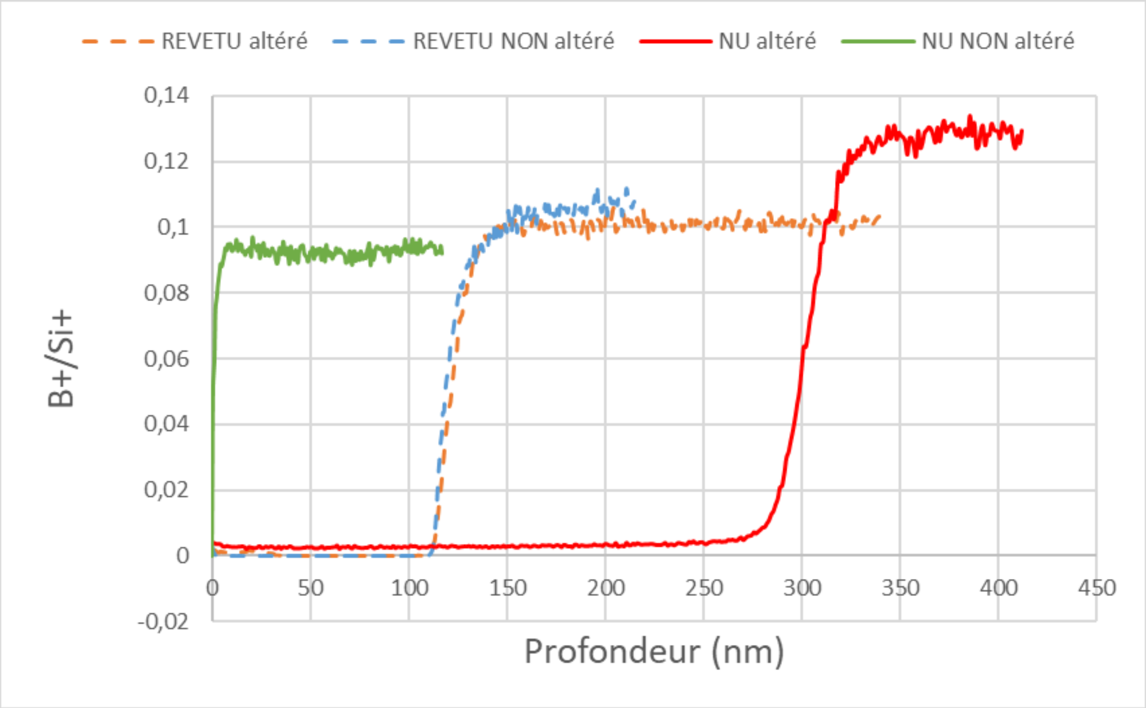
Tof-SIMS profils

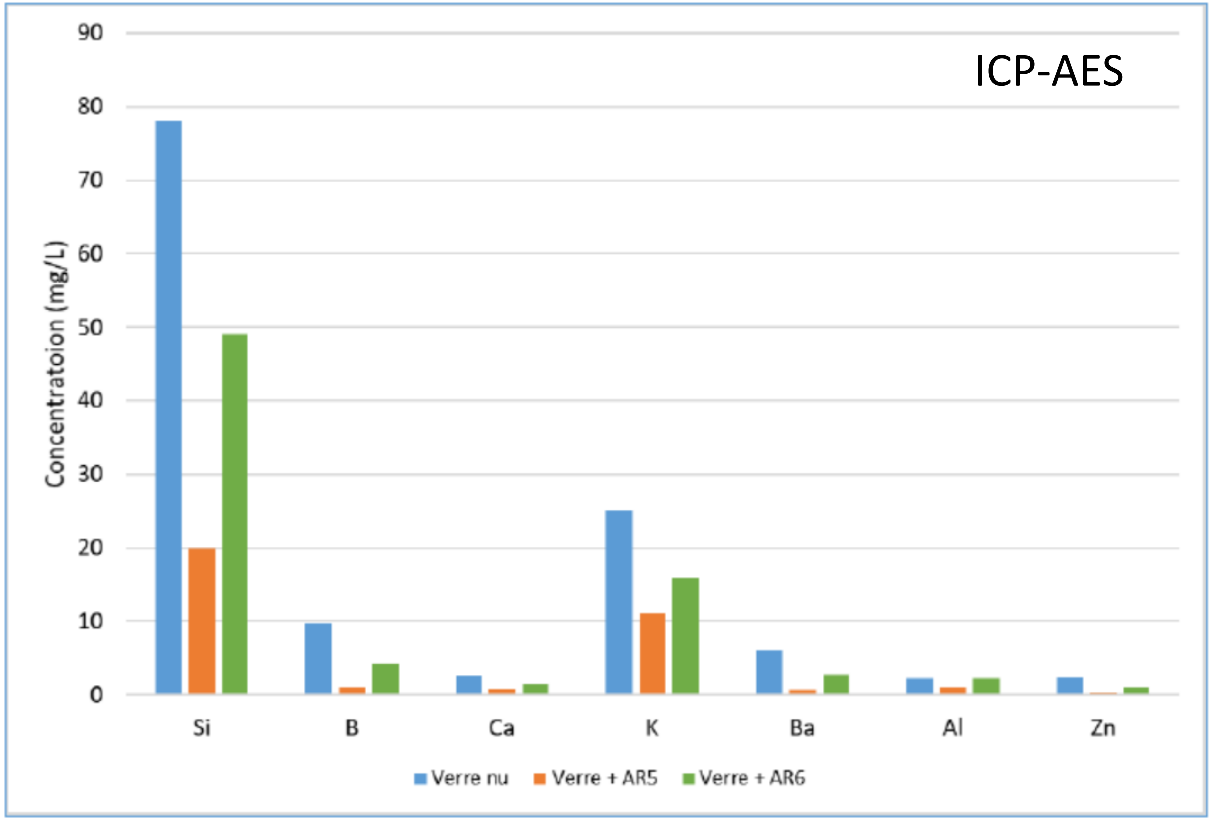
Uncoated type I glass vial

Oxide (wt %)	Clear tubing
SiO_2	72.0–75.0
B_2O_3	10.0–11.5
Al_2O_3	5.0–7.0
$Na_2O + K_2O$	7.0–8.5
CaO + BaO + MgO	0.5–3.0



Citric Acid pH 8
- Flacon revêtu





Group II : AR5 type RBM
'Group II': AR6 type RMM

Tof-SIMS profils

CONCLUSIONS / PERSPECTIVES

Chemical resistance of SiOxNyCz deposits

Strong impact of chemical bonding nature

Si – C > Si – N > Si – O

Strong impact of molecular species nature

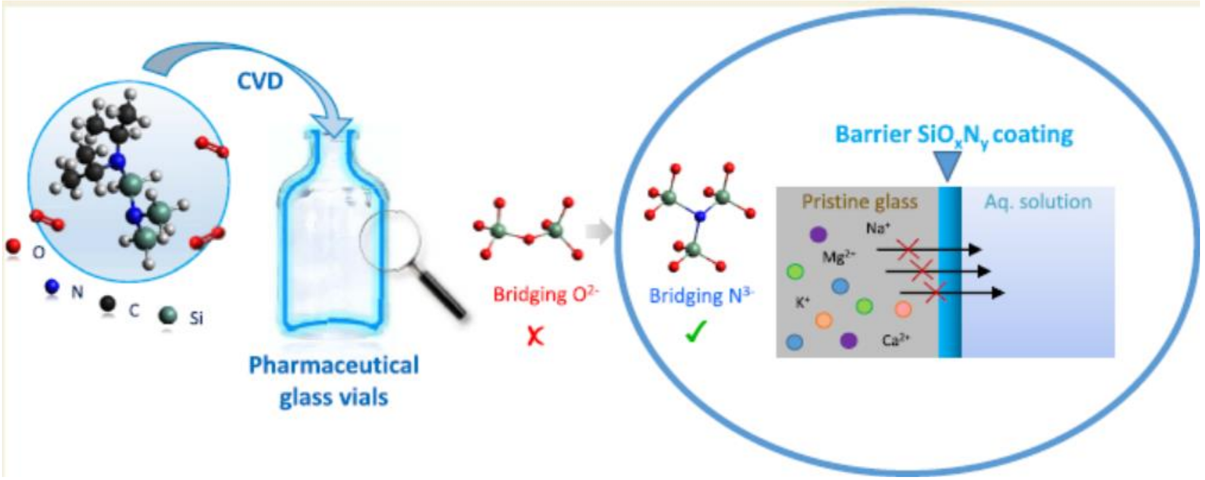
RBM > RMM

Ratio N+C/O optimisation….

TEM observation of the RMM network

MD calculations for SiOxNyCz

Network reticulation and chemical durability



MERCI POUR VOTRE ATTENTION!!

Farah Inoubli, Babacar Diallo, Thierry Sauvage, Cecile Genevois, Emmanuel Véron, Mathieu Allix, Pierre Florian, Vincent Sarou-Kanian

Konstantina C. Topka, Hugues Vergnes, François Senocq, Diane Samelor, Marie-Joëlle Menu, Brigitte Caussat,
Constantin Vahlas

Maxime Puyo, Charlotte Lebesgue, Raphael Laloo, Viviane Turq

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