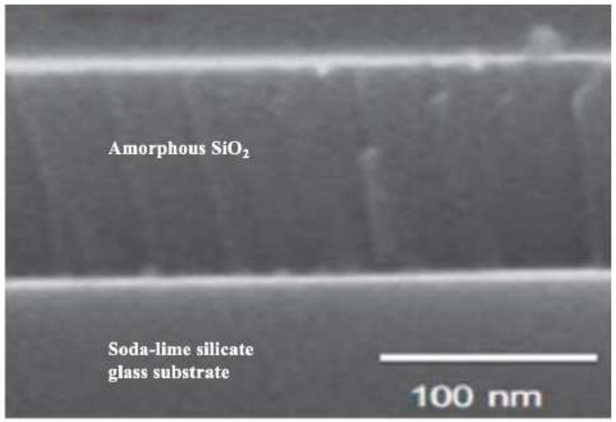
Comparaison structure du verre et couche mince amorphe

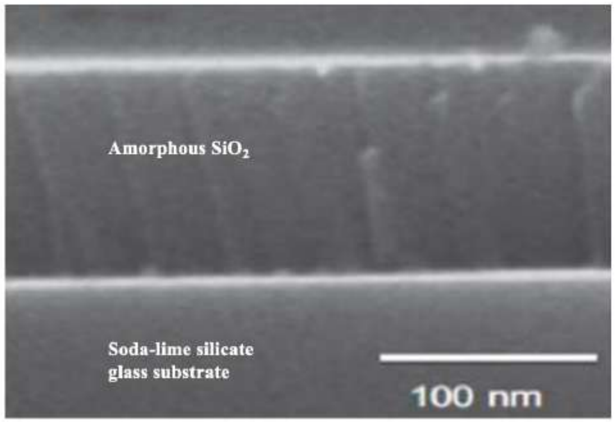
Laurent Cormier



Comparaison structure du verre et couche mince amorphe

Laurent Cormier

Katia Burov
Hervé Montigaud
Sirine Ben Khemis



Basics of glass structure

Structure of the surface

Structure of an amorphous thin film

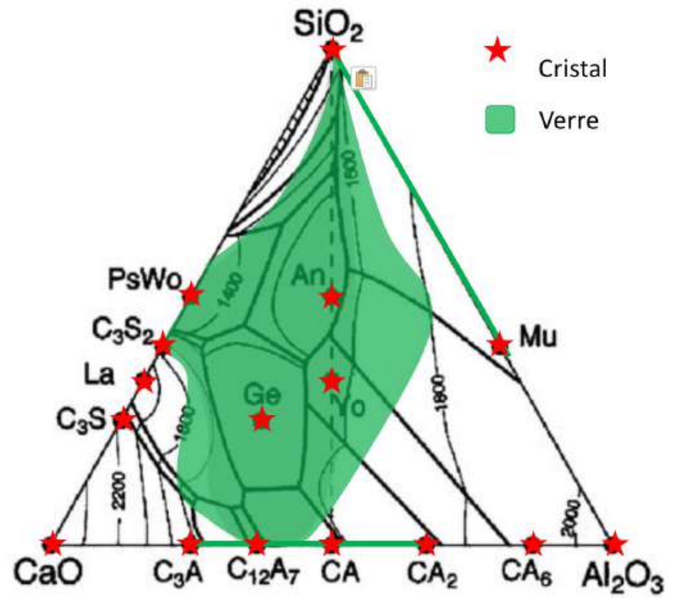
Structure of a non-crystalline solid

- Non-crystalline solids do not have the long-range order (periodicity) of the crystal

Structural complexity:

- Compositions
- Bonding (ionic, covalent, van der Waals)
- History (quenching rate)

- Infinite primitive cell



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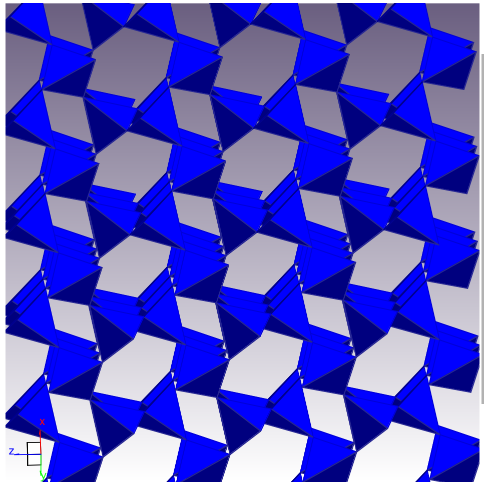
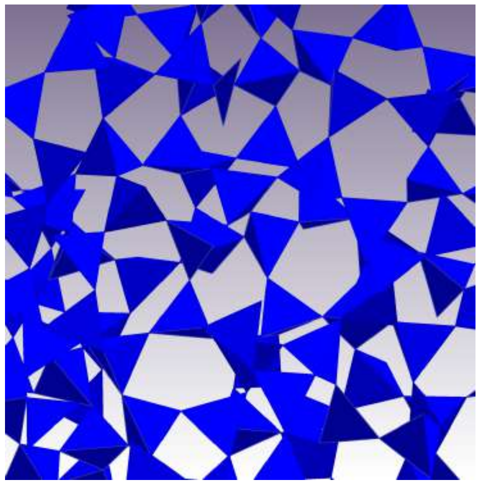


Crystal SiO_2 Quartz plan (110)

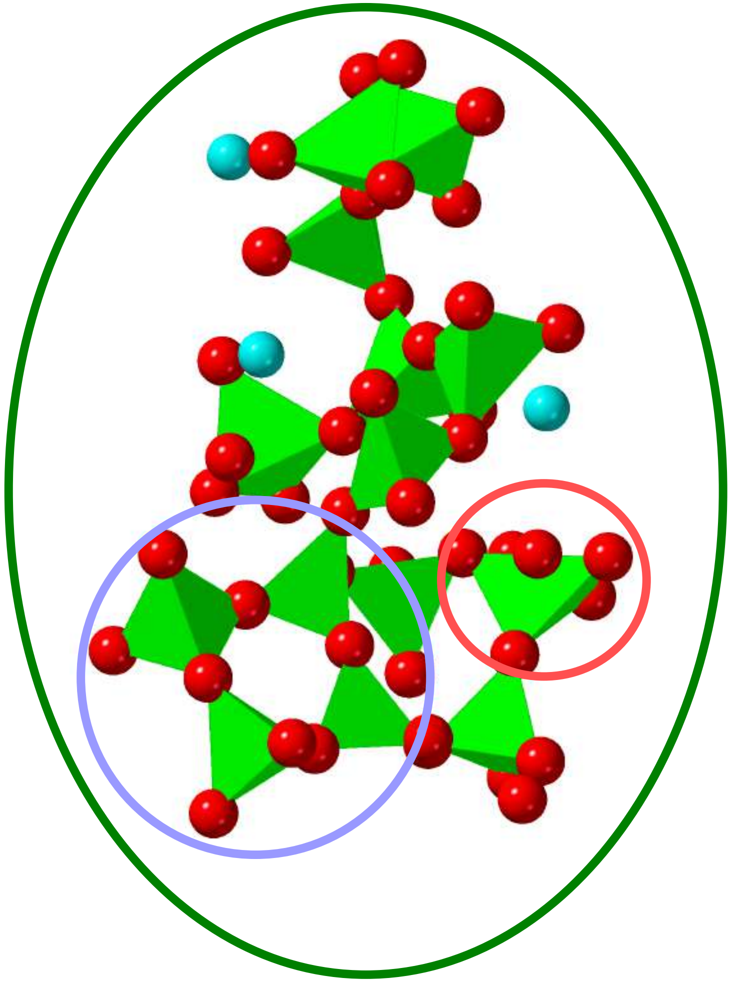
- Infinite primitive cell

The structure of non-crystalline solids is not known precisely: structural models, numerical simulations
Non-uniqueness
Averaged information



Glass model SiO_2

Different structural ranges



Short range structure (<3 Å):

– coordination, bond lengths, bonding angles

– linkages homo (-Se - Se- , -C - C-, -As - As) vs. heteropolar (Si - O, B - O, Ge - S)

Medium range structure (3-15 Å):

– angles between structural units

– connectivity between structural units(corner-, edge-sharing…)

– dimensionnality, rings

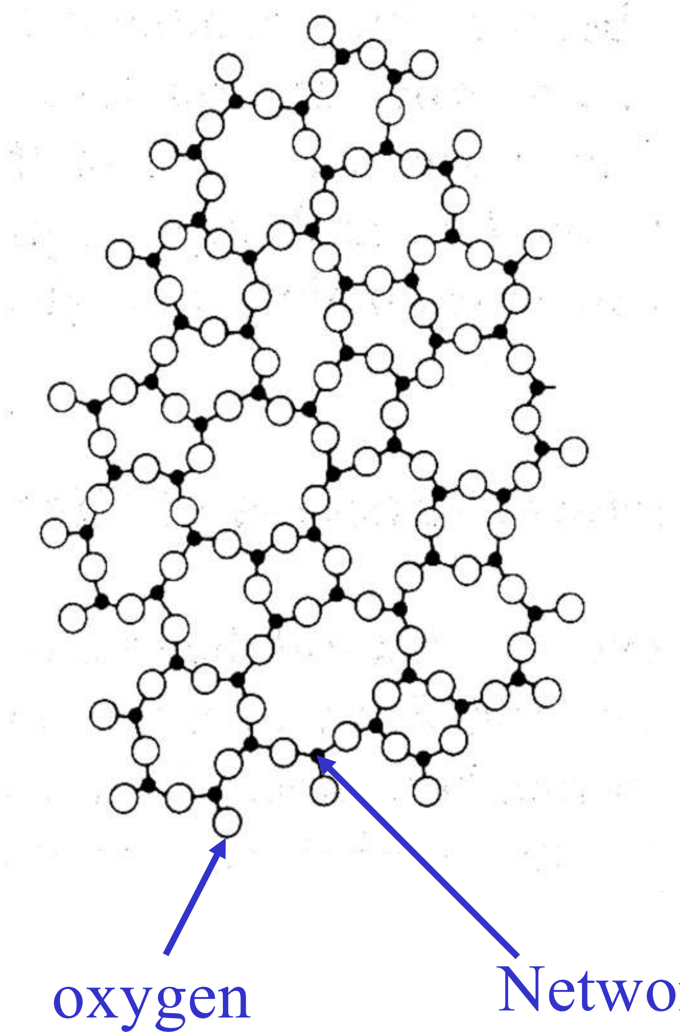
– heterogeneities

Long range structure, almost absent (no periodicity!) :

– phase separation

Structural models of covalent glasses

Continuous random network



Oxyde glasses

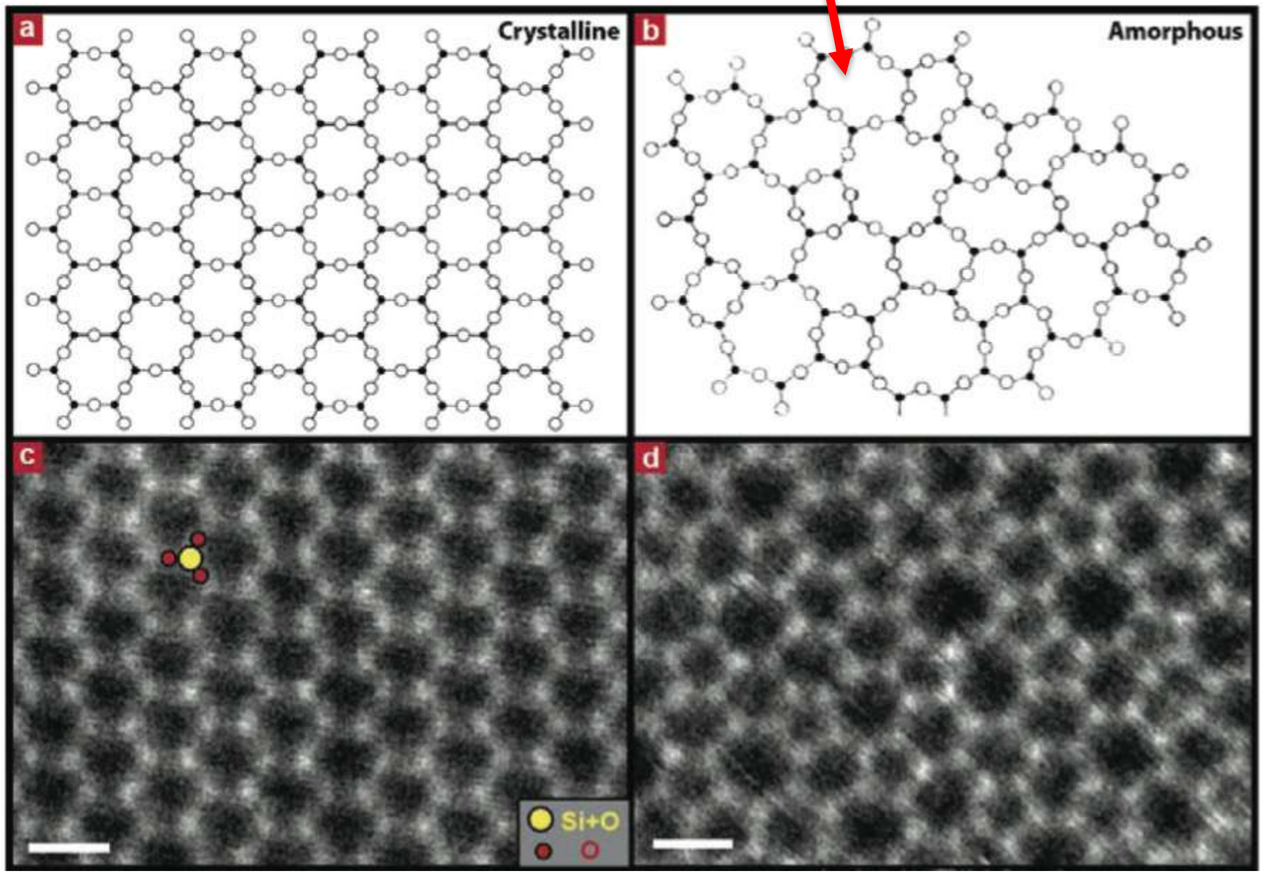
Zachariasen model (1932)
=> Define network formers

Rules for glass formation

1. No O atoms linked to more than 2 cations
2. Cation coordination is low (3, 4)
3. O polyhedra share corners, no faces or edges
4. For 3D networks, at least 3 corners must be shared

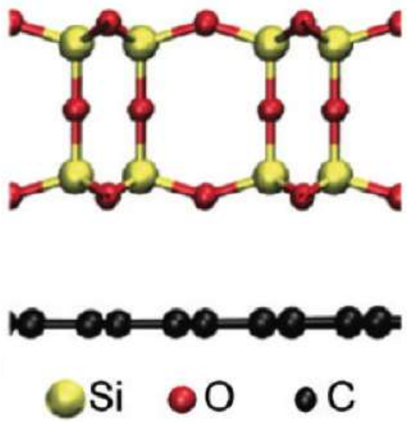
Zachariasen, W.H., 1932. The atomic arrangement in glass. J. Am. Ceram. Soc., 54,3841-3851.

Zachariasen model (1932)



c-SiO_2 a-SiO_2

STEM images

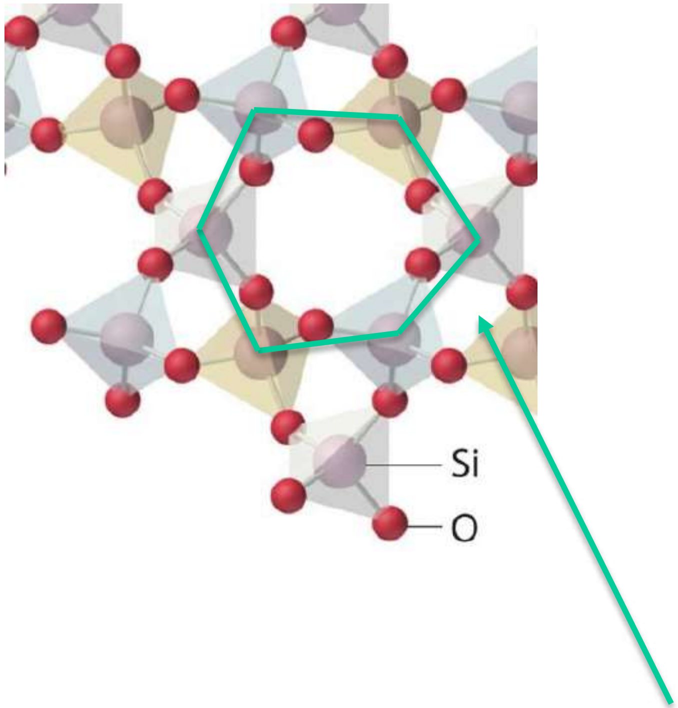


Huang et al., Nano Lett. 12 (2012)1081

Structure of silica glass

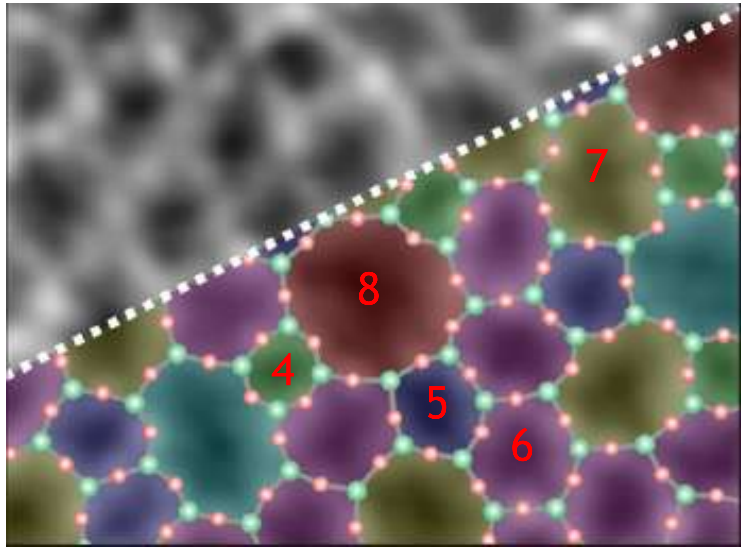
Silica glass

Amorphous material
Random network of SiO_4 tetrahedron



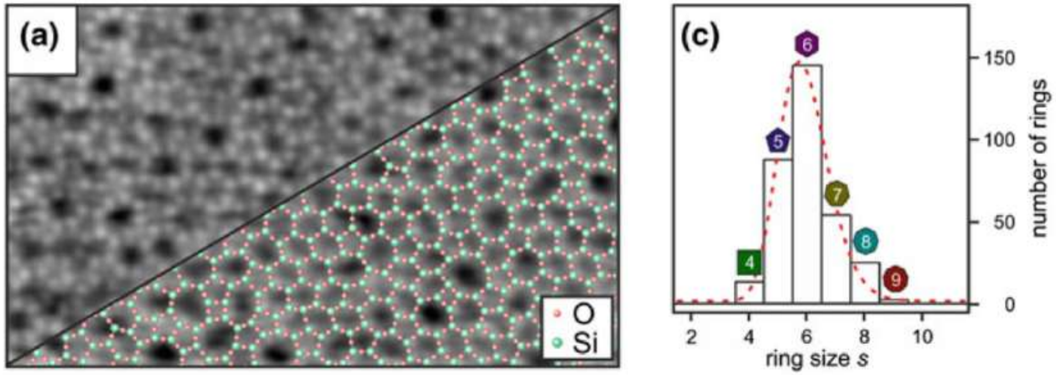
6-membered ring of SiO_4 tetrahedra

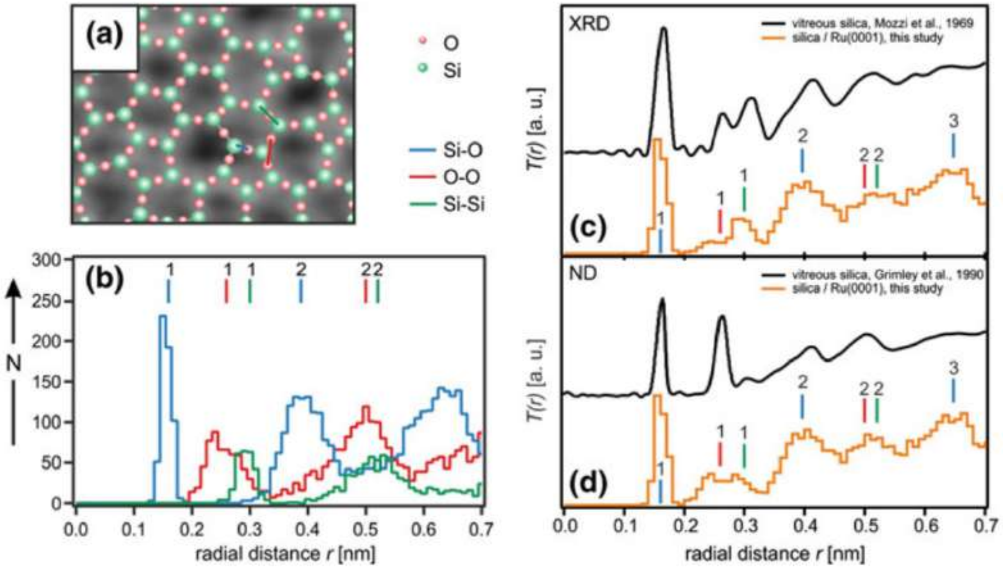
Rings of different size



Lichtenstein et al., J. Phys. Chem. C 116 (2012) 20426

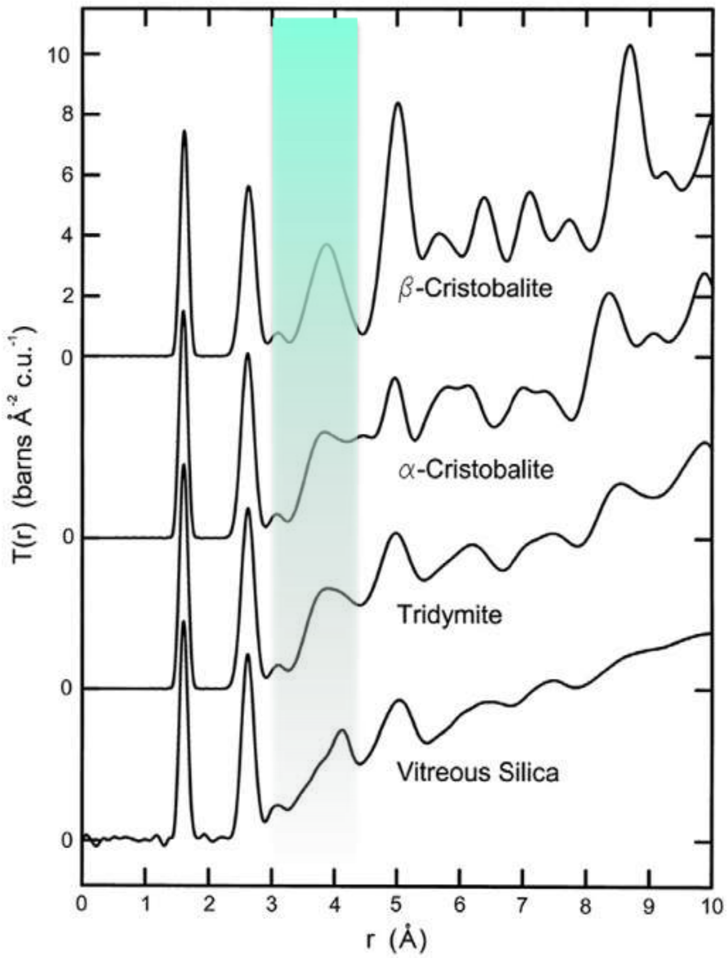
Structure of 2D silica glass





Büchner et al., (2015) 325

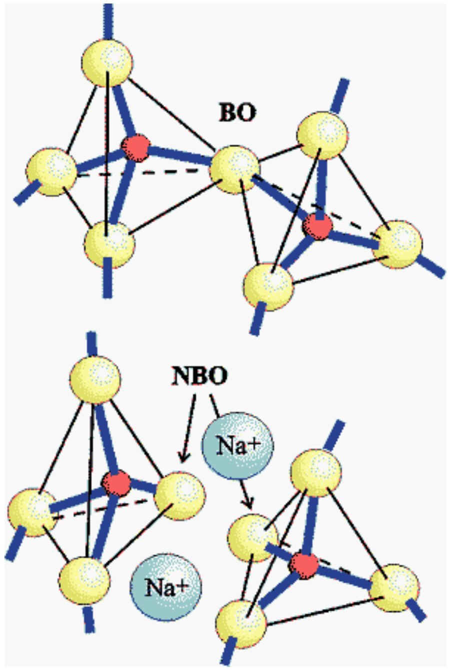
Structure of fused silica glass



Wright, J. Non-Cryst. Solids 410 (2014) 1

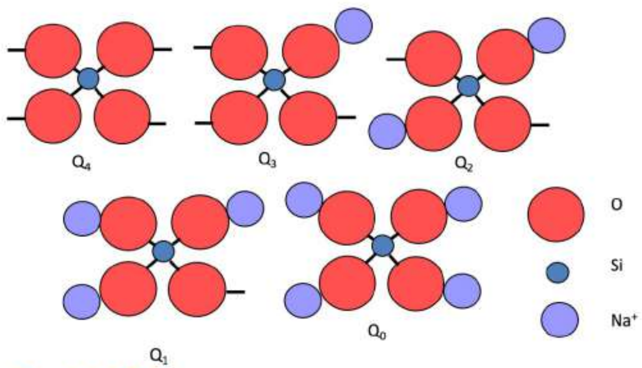
Multicomponent oxide glasses

Alkali silicate glasses



Non-network former cations (alkali, alkaline-earth, transition elements) depolymerize the network by forming **non-bridging oxygens**

Network modifiers



Q_n species

n = number of bridging oxygens by tetrahedra

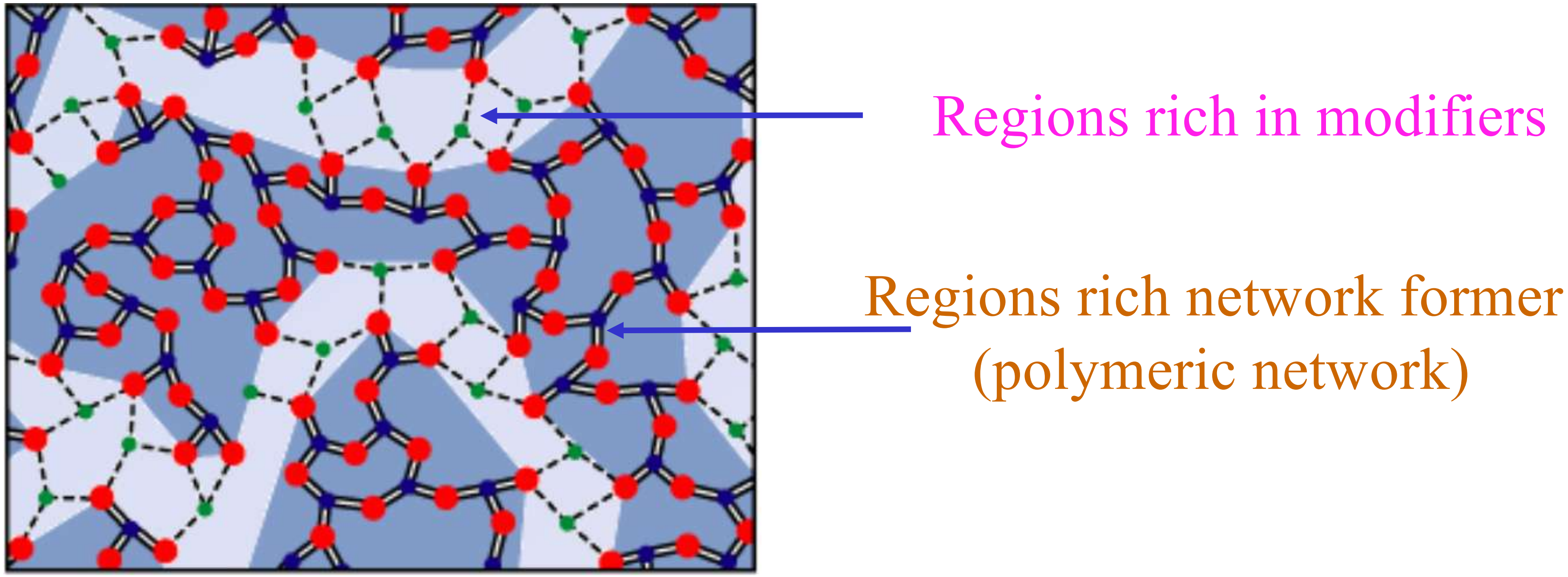
The modifying elements

- higher coordinence
- non-homogeneous distribution in glass

Structural models of covalent glasses

Modified random network model (Greaves, 1985)
=> Extension of the Zachariasen's model with regions rich in network formers and regions rich in modifiers

Deduced from EXAFS, neutron scattering data



Relationships with conduction properties, alteration...

Glass may have heterogeneities (at the nanometer scale)

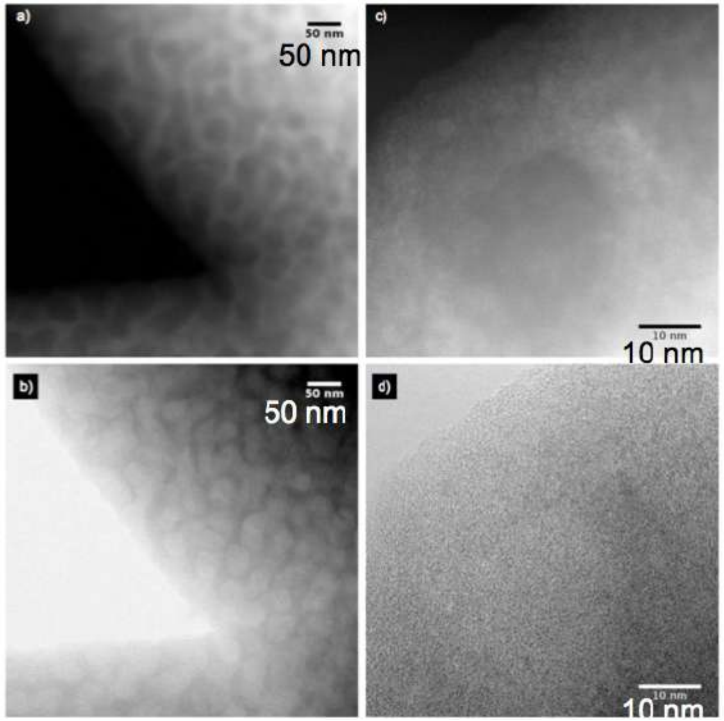
Amorphous-amorphous separation (A-A)

Glass MAS+Zr+Zn

➪ Macroscopic A-A separation

STEM HAADF

STEM



Dargaud et al., JNCS 358, 1257 (2012)

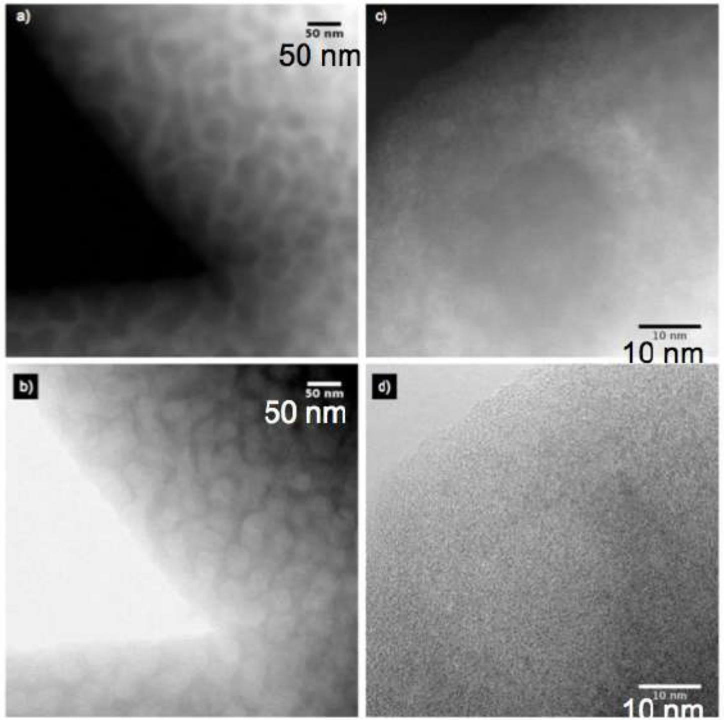
Amorphous-amorphous separation (A-A) and heterogeneities

Glass MAS+Zr+Zn

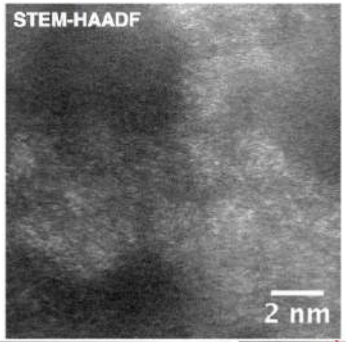
➪ Macroscopic A-A separation

STEM HAADF

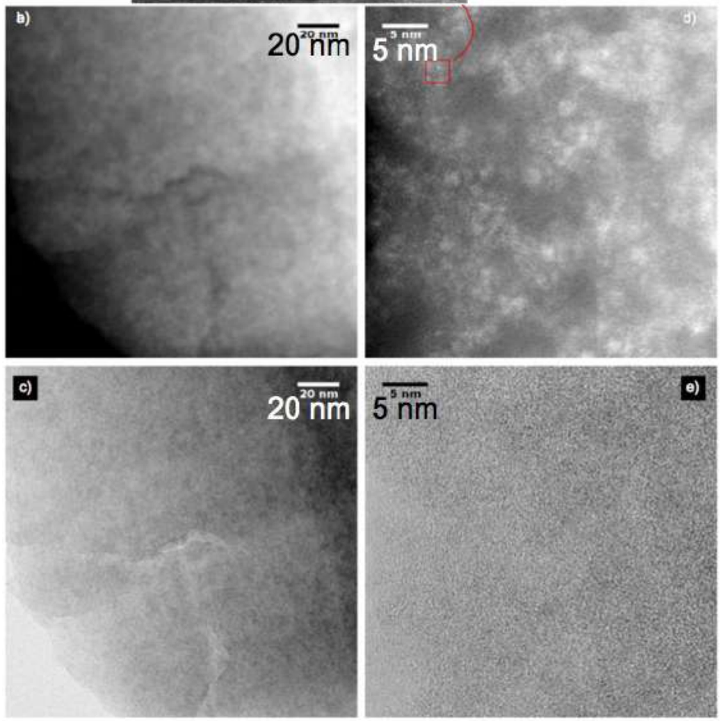
STEM



Dargaud et al., JNCS 358, 1257 (2012)



➪ No macroscopic A-A separation



STEM HAADF

STEM

➪ Heterogeneities visible even without macroscopic A-A separation

➪ At which scale is there an A-A separation?

Kirchner et al., Chem. Rev. 123 (2022) 1774

Surface of a silicate glass

Is it the same than the structure of the bulk glass ?

Structure at the surface of an oxide glass differs from that of the bulk glass

Layer a the surface depend on a large number of factors

- interdiffusion coefficients between the glass elements and the environmental elements
- possibility of secondary phase precipitation on the surface, depending on the elements available

Important for

- crack propagation
- surface dissolution or atmospheric alteration
- ion exchange

Surface of a silicate glass

MD Simulations

(Zeitler & Cormack, 2022,
https://onlinelibrary.wiley.com/doi/abs/10.1002/9781118939079.ch14)

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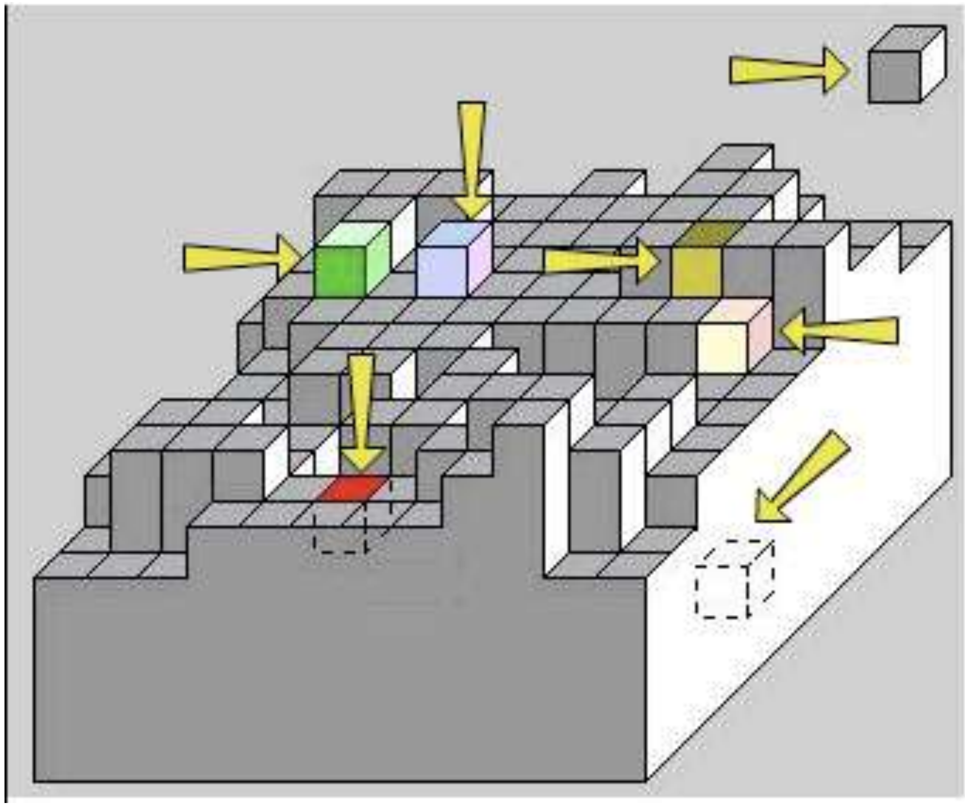


Energetically frustrated bonds at the surface

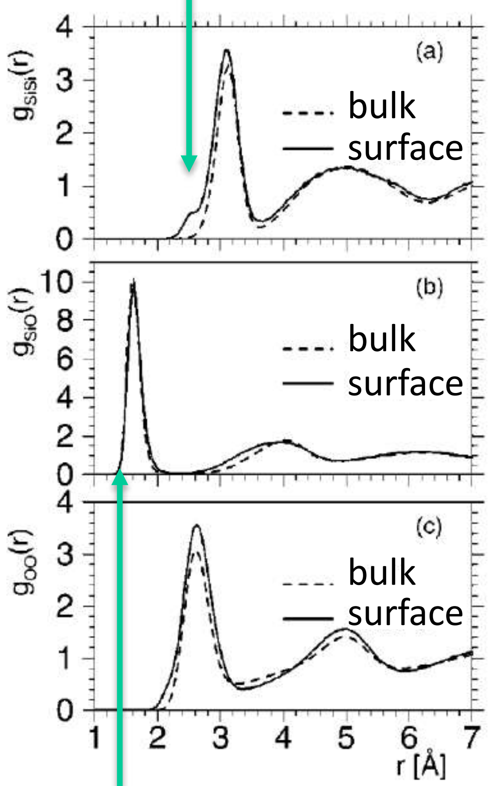
Surface of a pure SiO_2 glass

Defects (top ~3Å surface) :

More NBO => enrichment of O at the surface and increased concentration of Si under the surface

under coordinated Si (artefact from MD simulation ?), small-membered rings (2-membered rings)

small rings

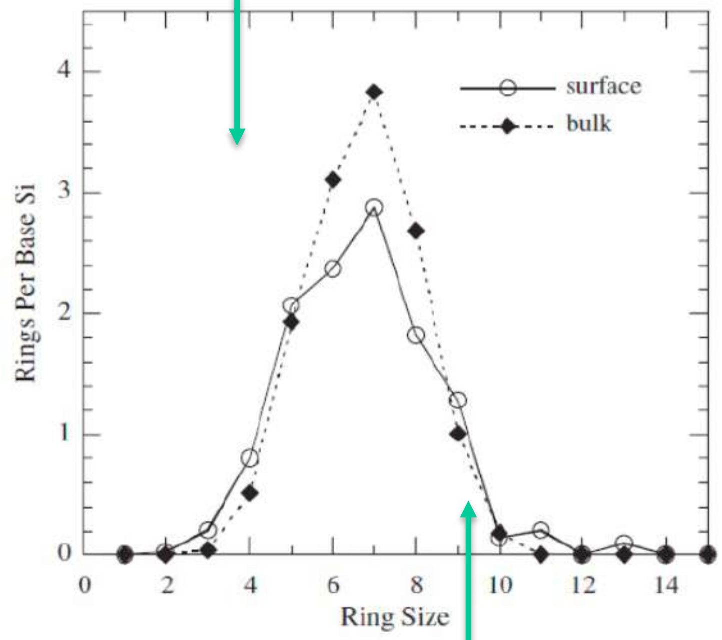


NBO

undercoordinated Si

Roder et al., J. Chem. Phys. 114 (2001) 7602

small rings



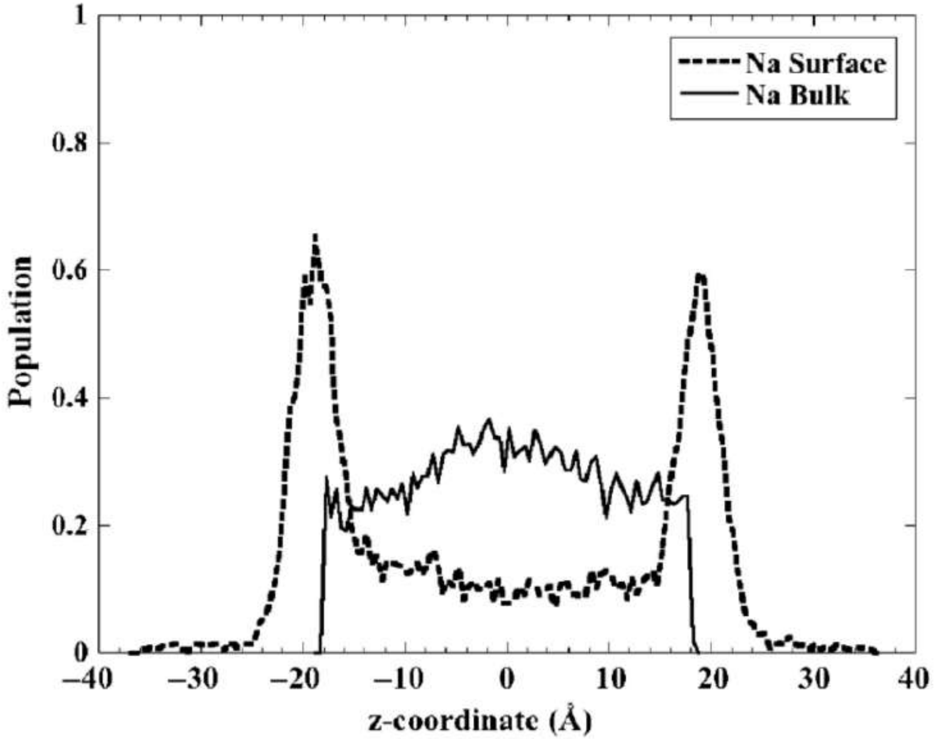
large rings

Zeitler & Cormack, J. Chem. Phys. (2022)

Surface of a (soda-lime) silicate glass

Surface concerns ~100 nm:

Enrichment of alkalis (Na and K but not Li) and NBO, depolymerization leading to larger surface rings

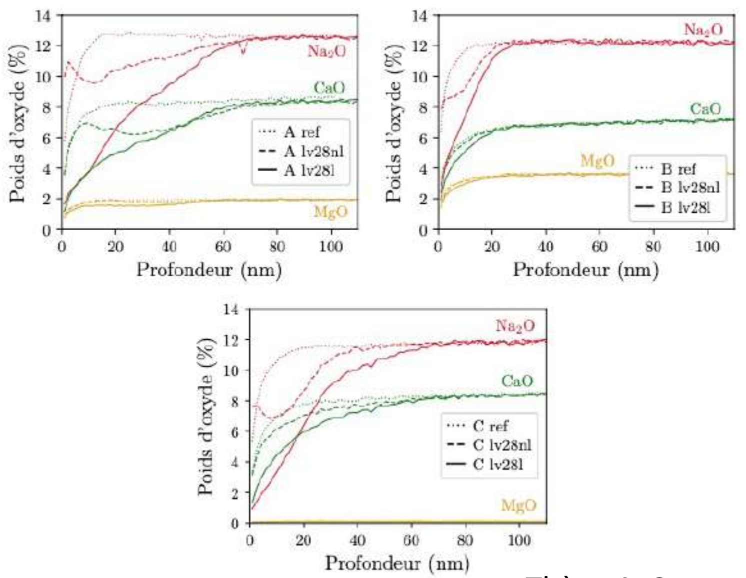


MD simulations
Zeitler & Cormack, 2022

Surface of a (soda-lime) silicate glass

Surface concerns ~50-100 nm:

Enrichment of alkalis (Na and K but not Li) and NBO, depolymerization leading to larger surface rings
Depletion of Na in the subsurface



Thèse A. Serve, 2023

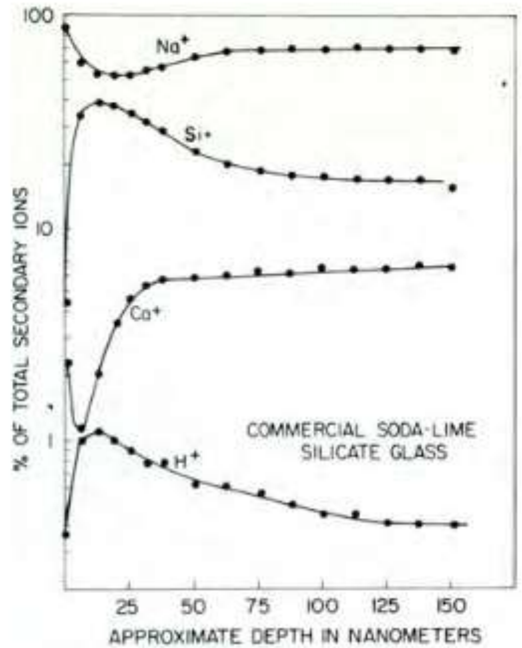


Fig. 5. SIMS depth profiles for commercial soda-lime silicate glass (1500 eV Ne at 10 μA/cm^2).

Pantano, Am. Ceram. Soc Bull. 60 (1981) 1154

Surface of a (soda-lime) silicate glass

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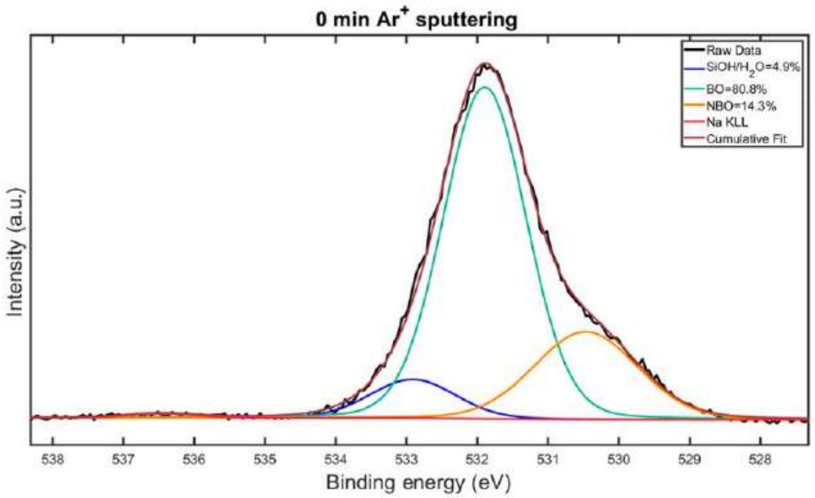
Depletion of Na in the subsurface
free oxygen O^{2-} / Si-OH bonds



O 1s XPS spectra
Roy et al., Int. J. Appl. Glass Sc. 14(2023)229

Surface of a (soda-lime) silicate glass

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Enrichment of alkalis (Na and K but not Li) and NBO, depolymerization leading to larger surface rings
Depletion of Na in the subsurface
free oxygen O^{2-} / Si-OH bonds

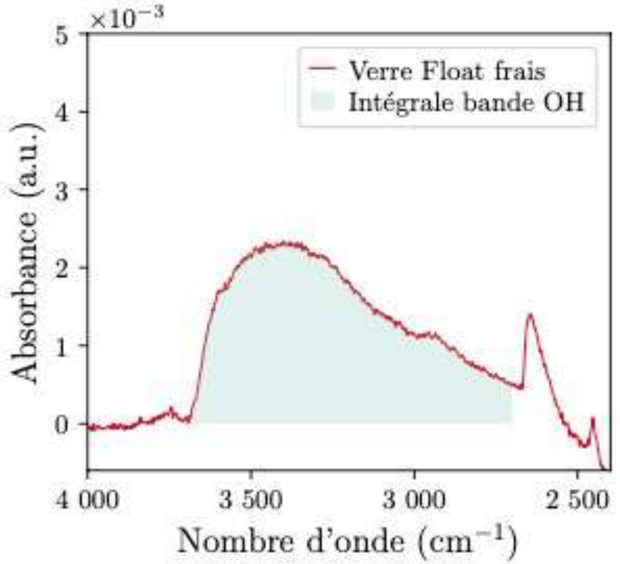
Less migration of Na in aluminosilicate glasses
More BO_3 units

affect crack initiation and leaching behavior

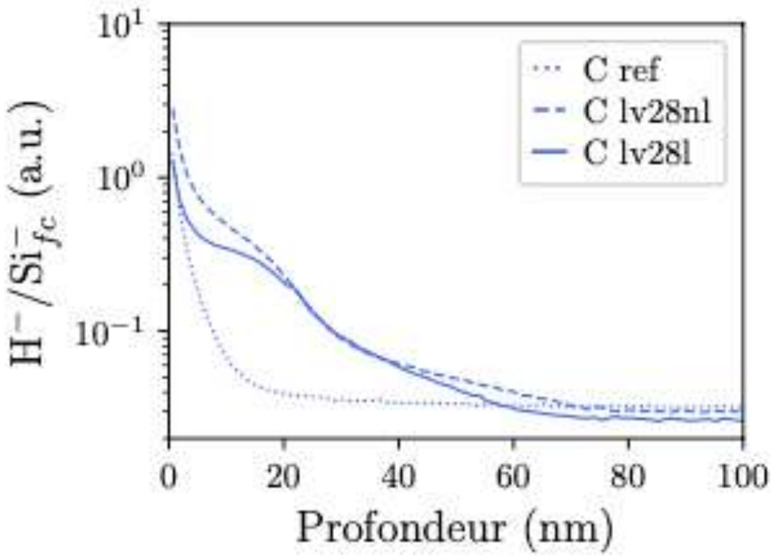
Surface of a (soda-lime) silicate glass

Always water on the surface => water molecules or hydroxyls present
can be studied by vibrational spectroscopies, ion beam analysis (ERDA), TOF-SIMS, IR-ATR

IR-ATR



TOF-SIMS



Thèse A. Serve, 2023

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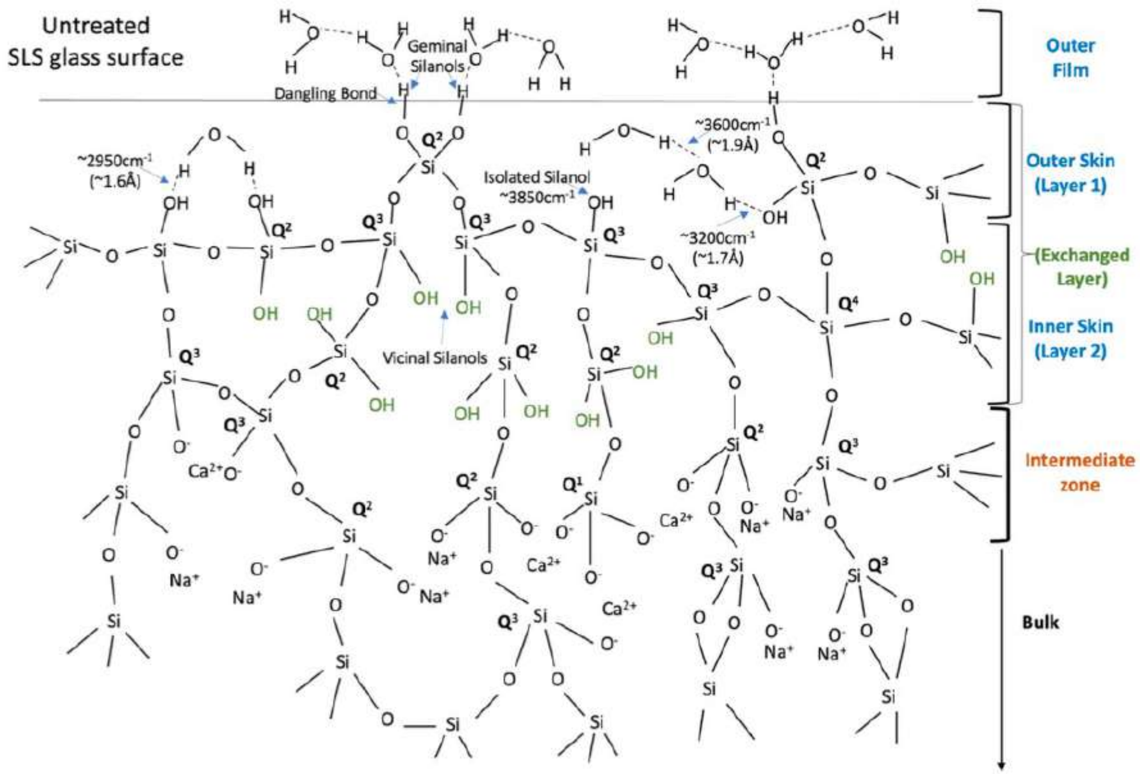
Silanol bonds Si-OH
Modifiying cations could have a sphere of solvatation



Roy et al., Sc. Rep. 12 (2022) 2681

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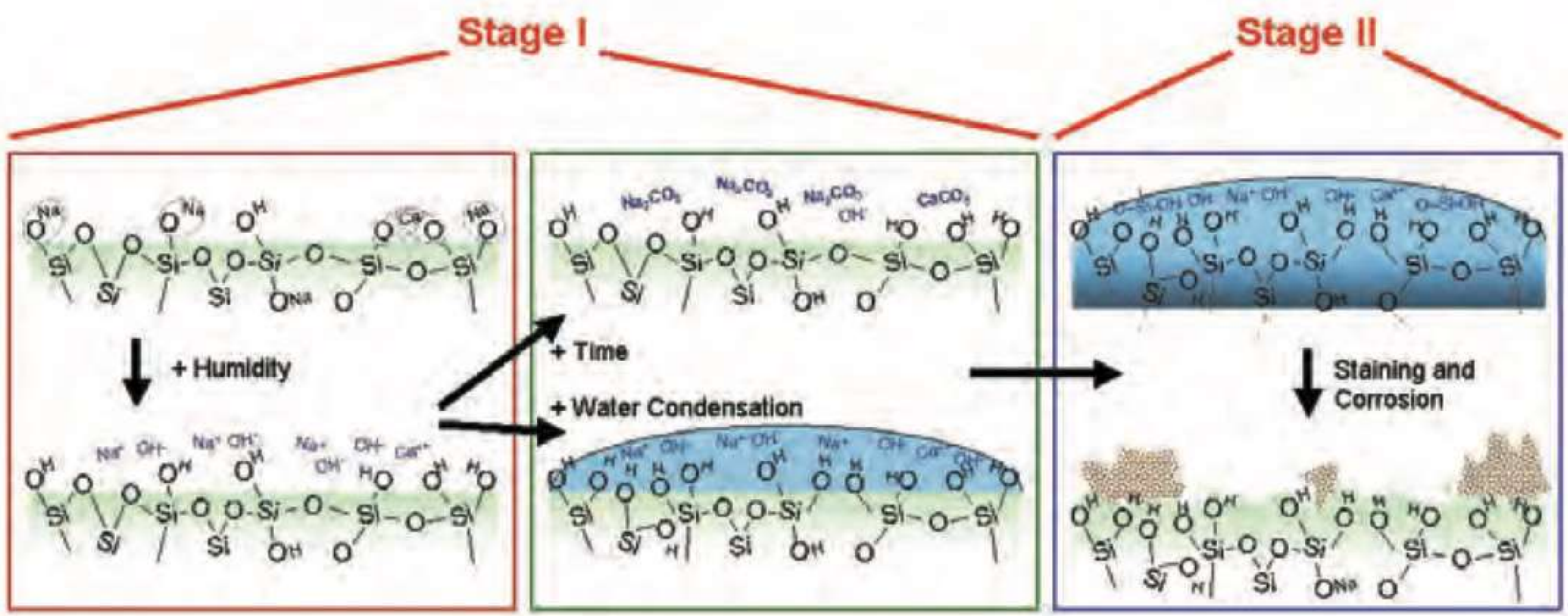
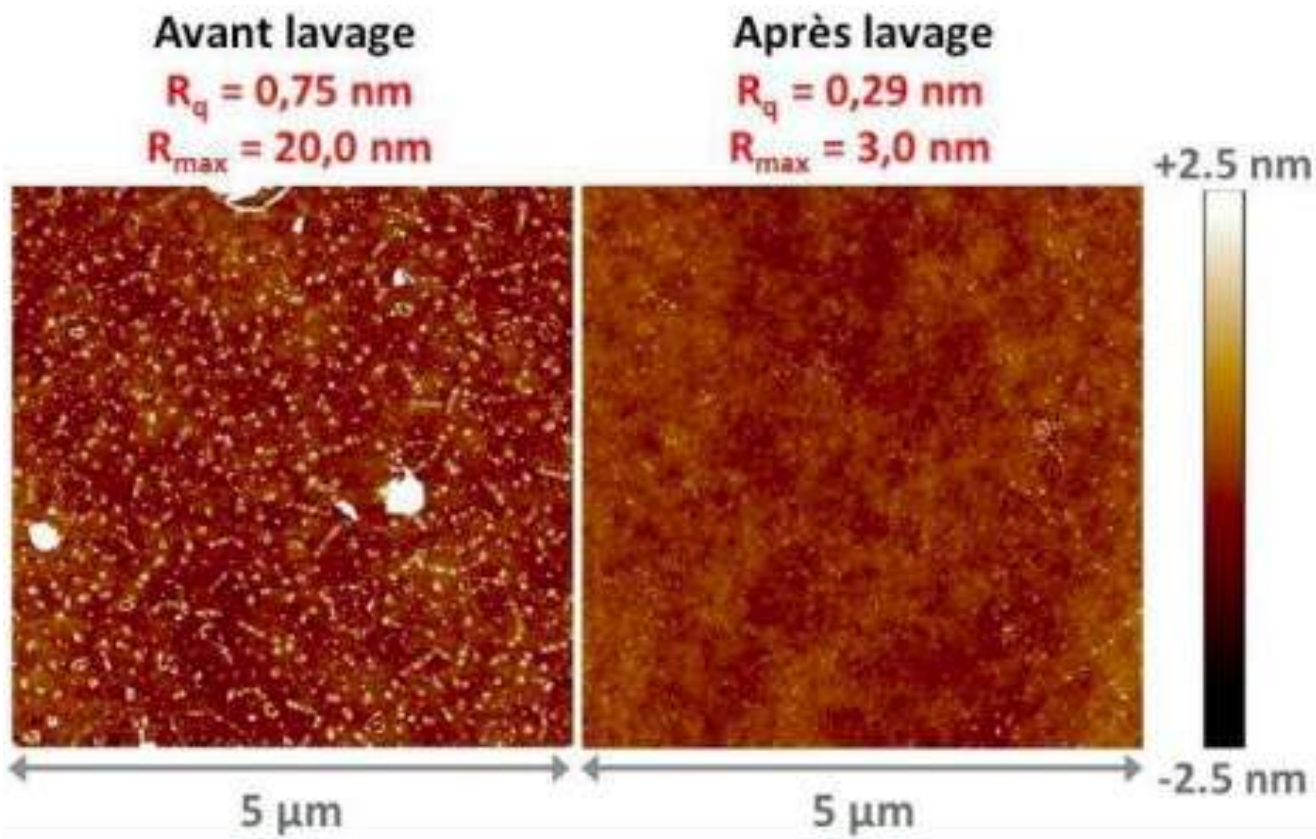


Schaut & Pantano., Amer. Ceram. Soc. Bull. 84 (2005) 44

Surface of a silicate glass

Surface morphology

rugosity of the surface (optical profilometer, AFM)
=> Reduced surface roughness, with mean square value (Rq) less than nanometer

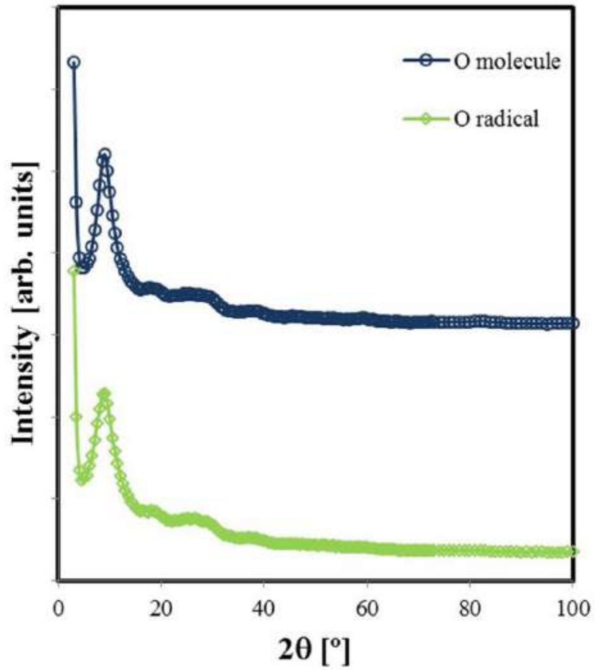


Thèse J-T. Fonne, 2017

How to determine the amorphous structure of thin films?

Grazing incidence Wide angle X-ray scattering

ultra-thin (<10 nm) SiO_2 films formed on Si substrates



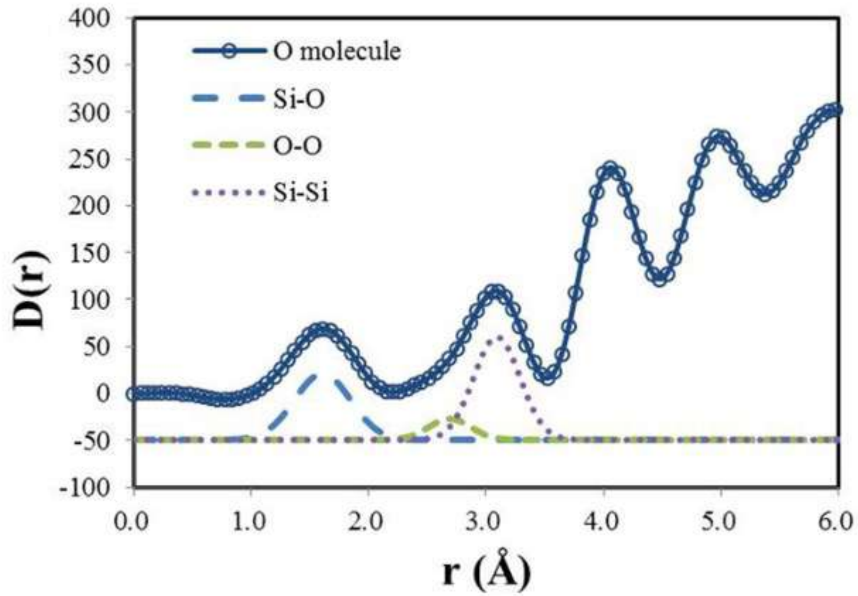
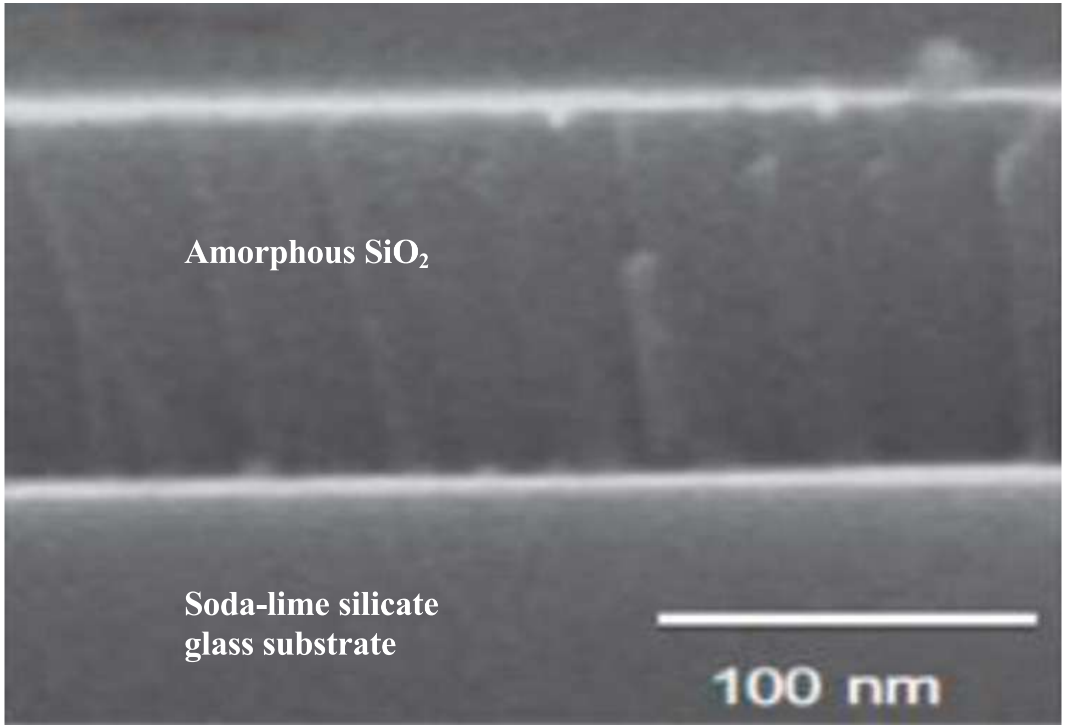


TABLE I. SRO parameters estimated from GI-WAXS measurements.

	Bond angle (°)		Distance (Å)			FWHM (Å)		
	Si-O-Si	O-Si-O	Si-O	O-O	Si-Si	Si-O	O-O	Si-Si
O molecules	148.7	113.8	1.60	2.69	3.09	0.56	0.42	0.47
O radicals	146.3	91.42	1.60	2.29	3.07	0.62	0.55	0.70

Nagata et al., J. Appl. Phys. 119 (2016) 154103

How to determine the amorphous structure of thin films?



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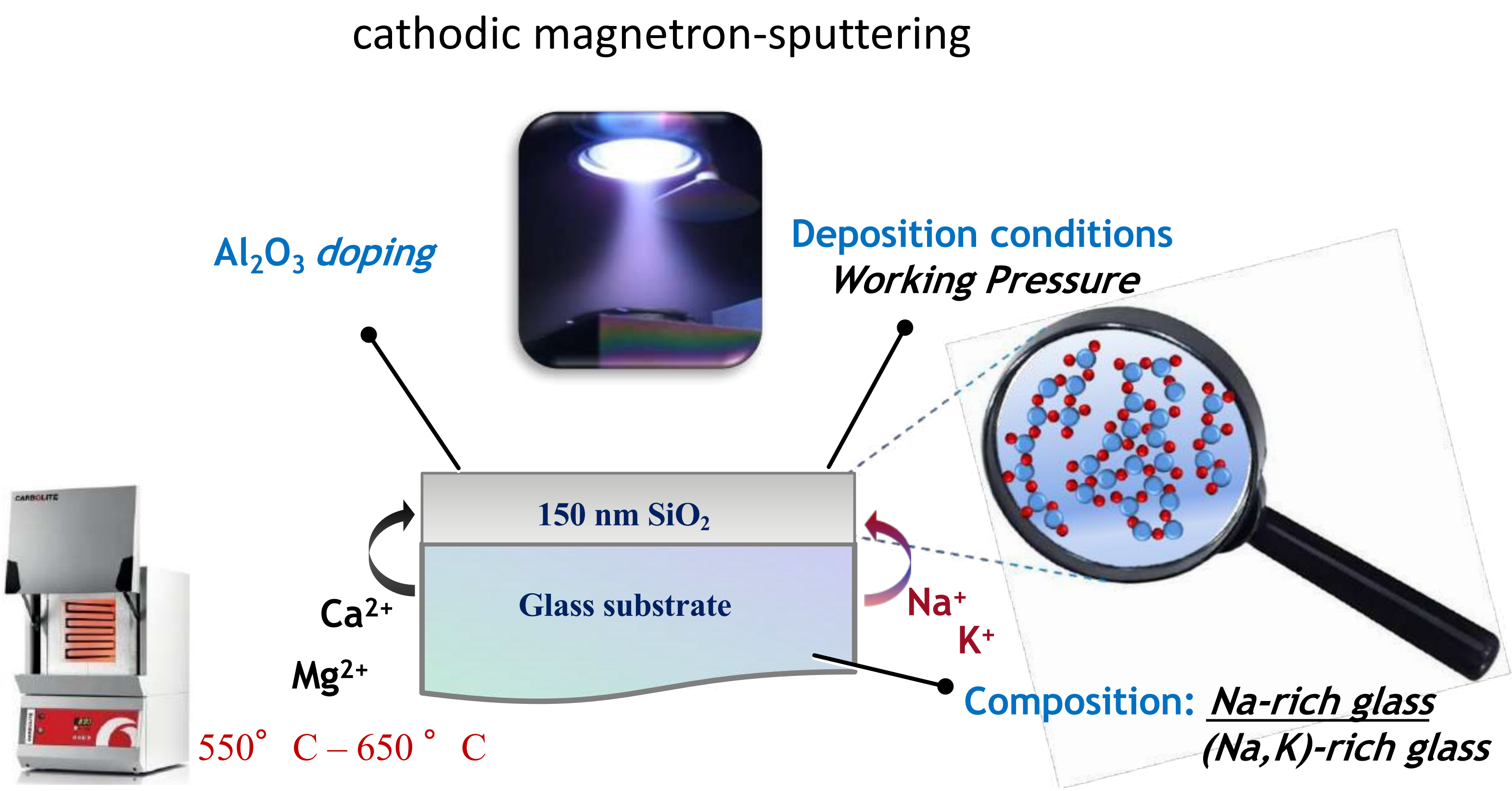
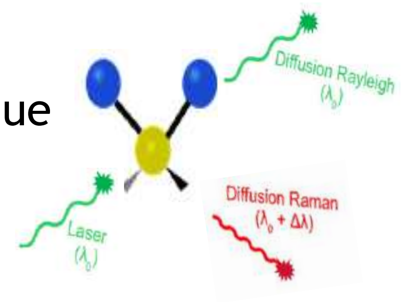


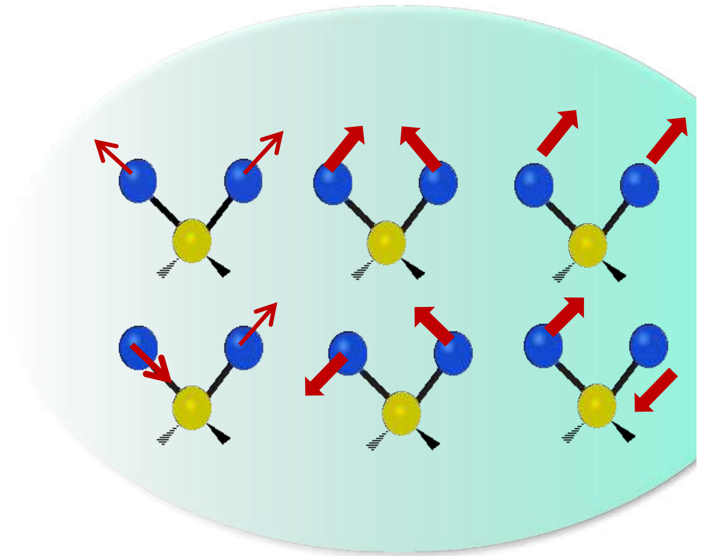
Thèse S. Ben Kemis, 2021

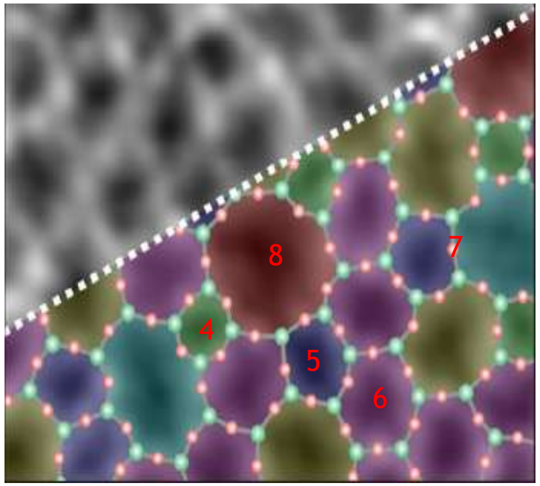
Raman structural characterization of the fused silica glass

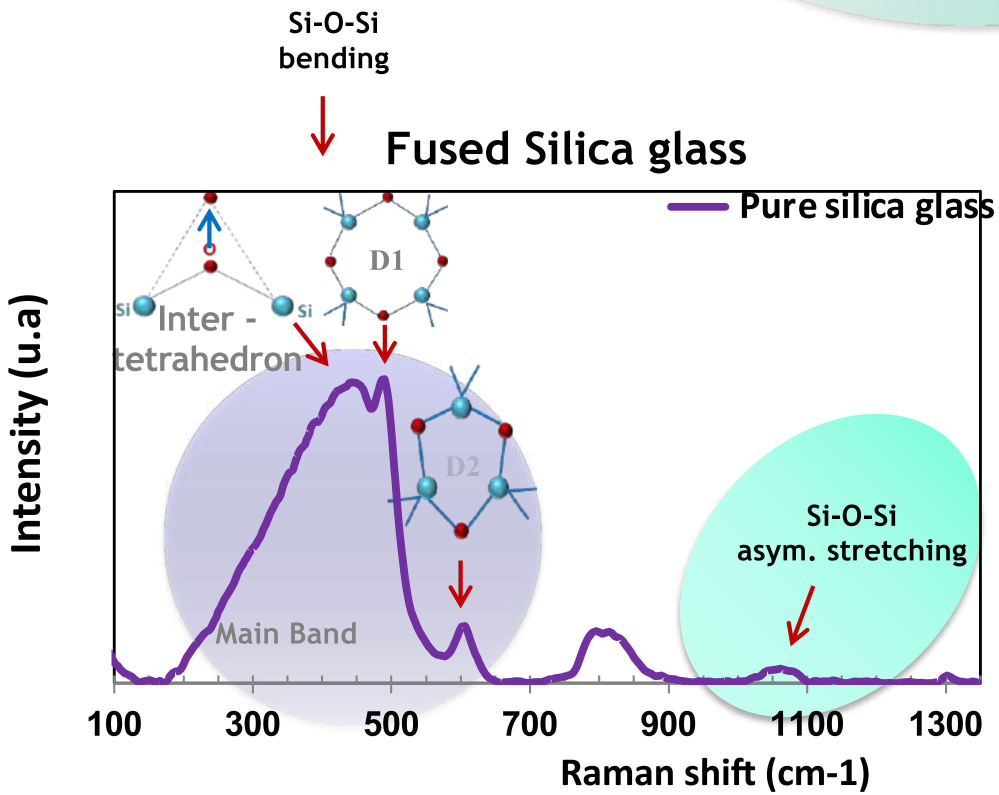
- **Raman spectroscopy**

Raman is a light scattering technique





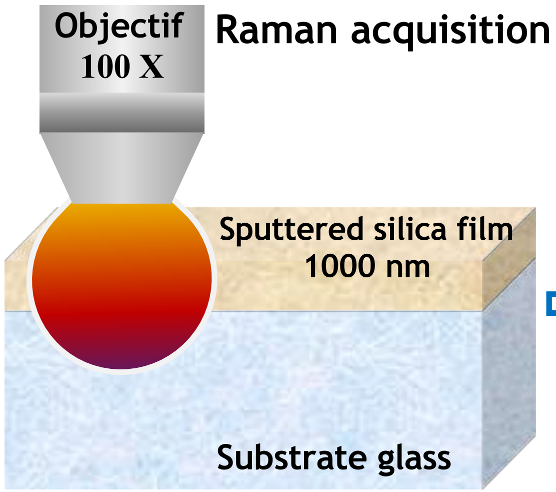




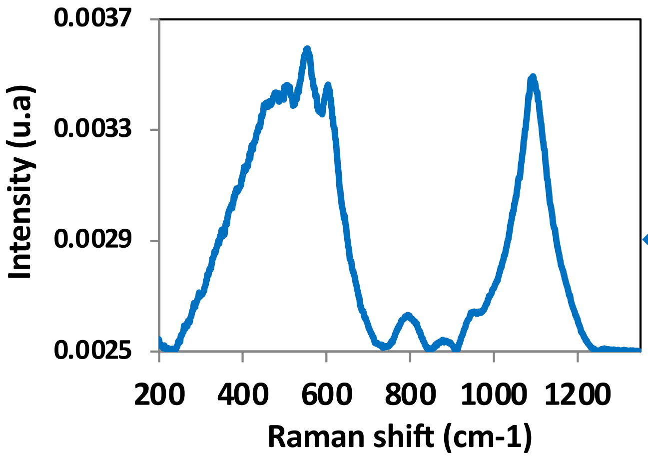
Raman structural characterization of the sputtered silica films

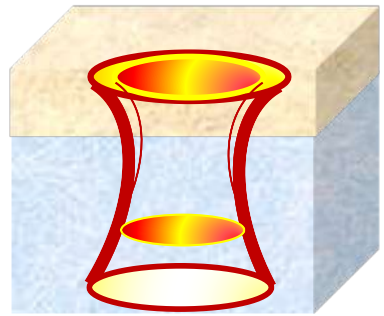
Aim:

- ✓ Investigate the medium range characterization of a sputtered silica film



Mixing of the both signatures of the silica film and the substrate!!!





Overlapping of the Raman signal of the substrate and the silica film

Difficulties

- × Thin amorphous film ➔ Small signal to noise ratio
- × Raman signal of the substrate and silica

Raman structural characterization of the sputtered silica films

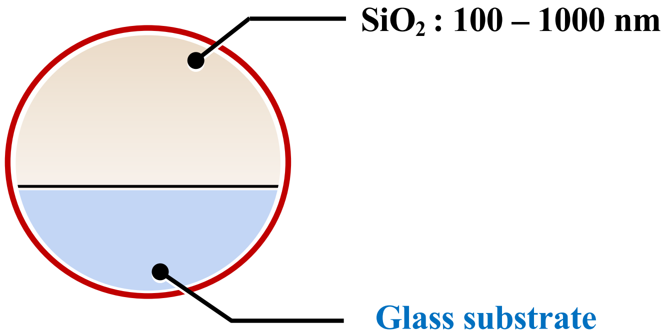
Solution:

✓ Developing of different processes for extracting the Raman signature of silica film

➢ Method 1

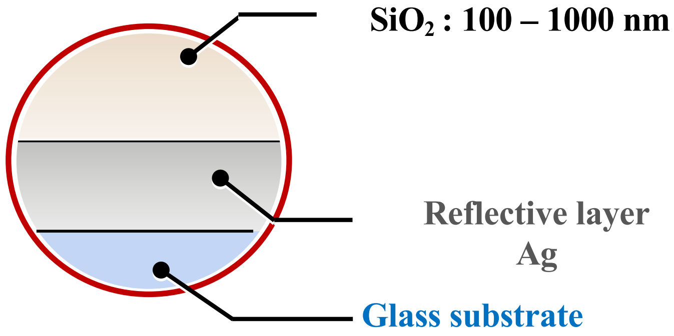
Statistical analysis

Non-negative-Matrix Factorization (NMF)



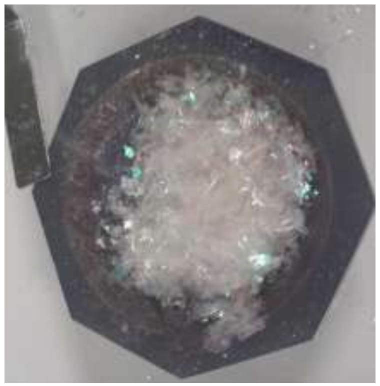
➢ Method 2

Reflective mask substrate



➢ Method 3

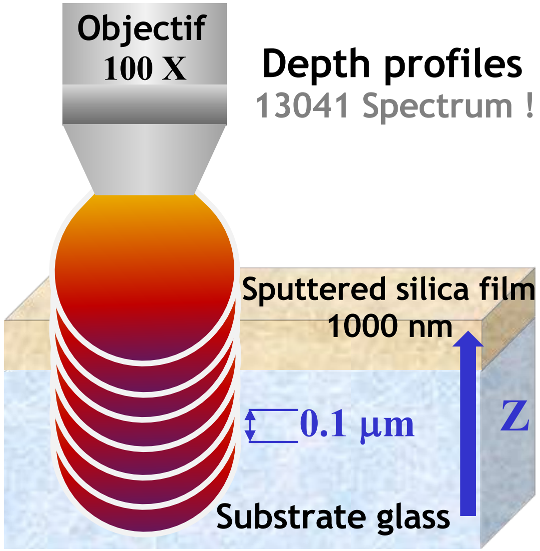
Delamination of the silica film

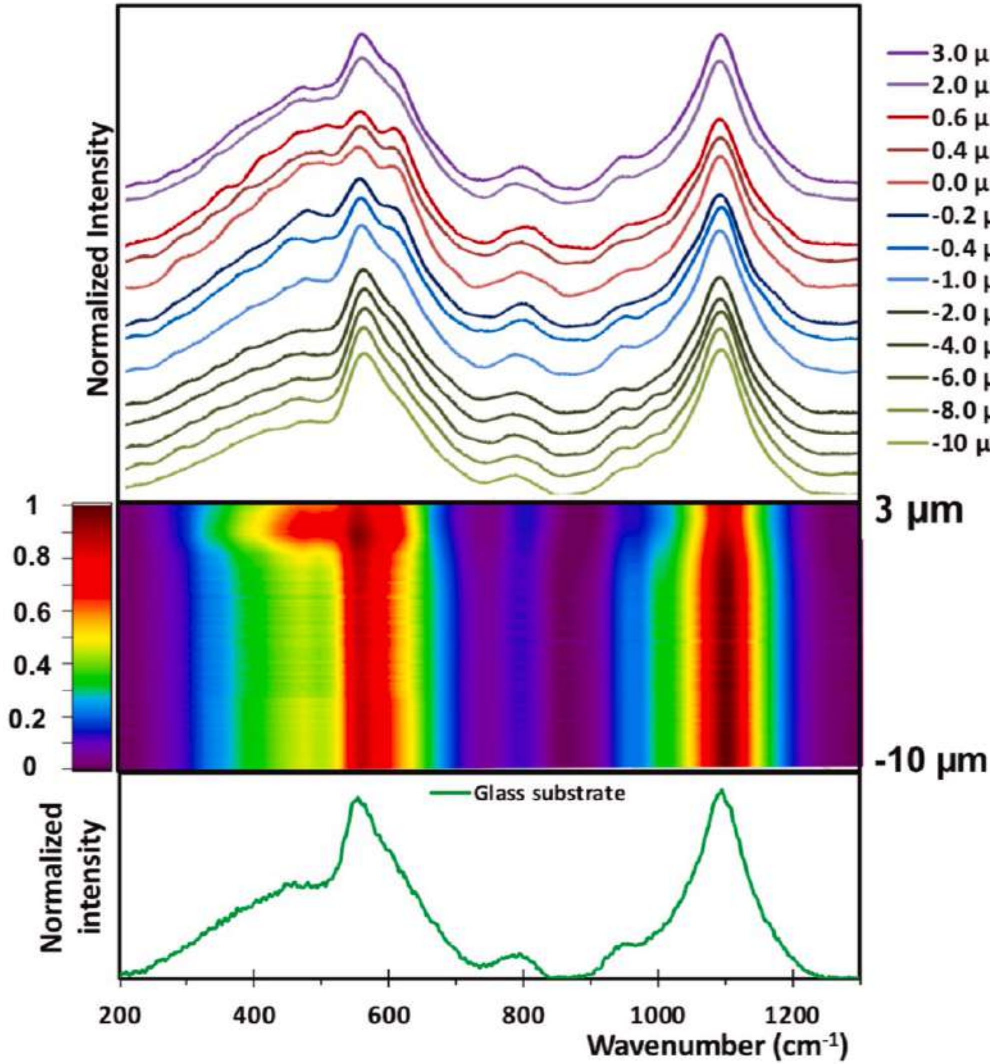


Depth Raman profiles of the sputtered silica films

Challenges:

- ✓ Extract the Raman signature of the amorphous silica film





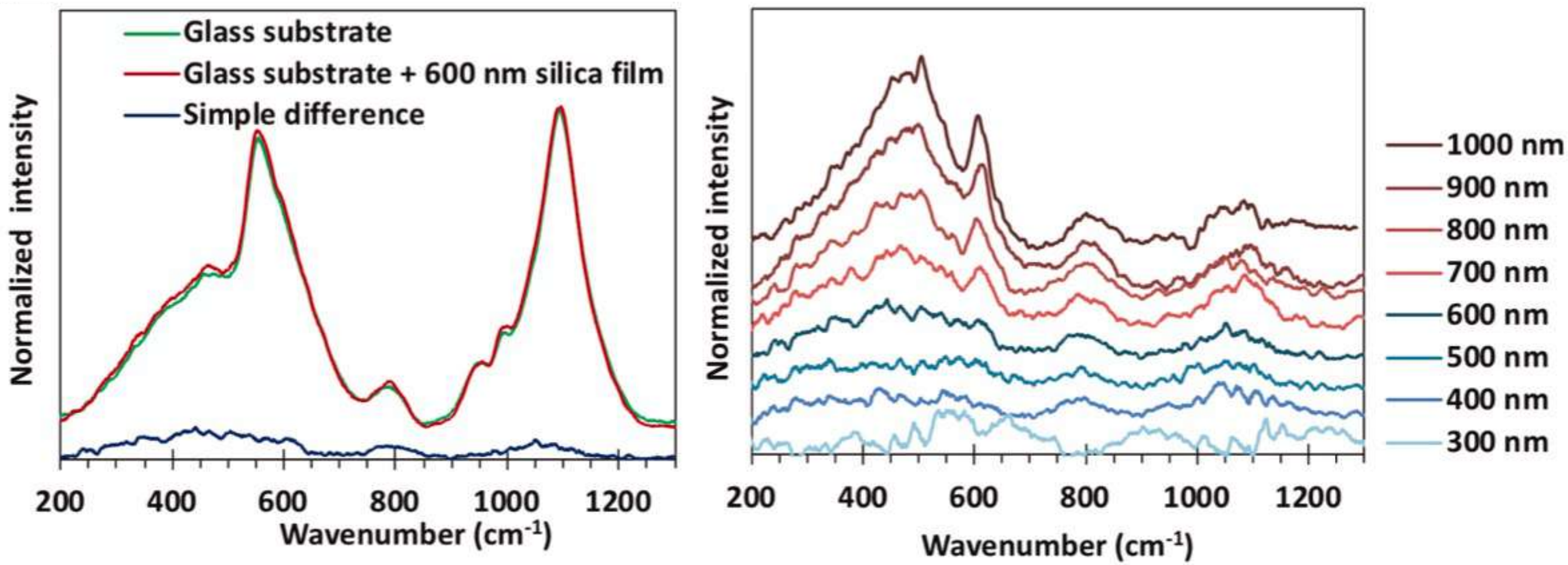
Signal variations during a depth profile

=> Mixing of the silica film Raman signal with those of the substrate

Depth Raman profiles of the sputtered silica films

Challenges:

- ✓ Extract the Raman signature of the amorphous silica film



between 300 nm to 600 nm, no discernible signal from the thin film

subtraction method of an arbitrary fraction of the glass substrate signal is an uncertain and inaccurate analysis protocol

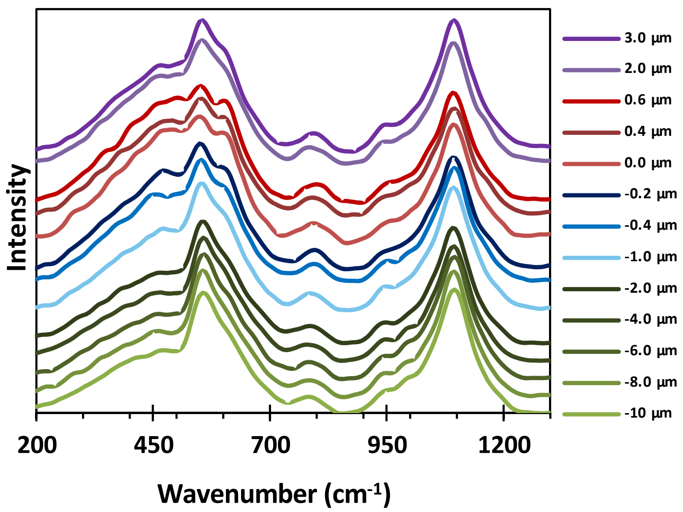
Non-negative Matrix Factorization (NMF)

Decompose a set of Raman spectra as a weighted sum of characteristic components

$Y_i = \Sigma H_i X_i = H_{substrate} X_{substrate} + H_{film} X_{film}$

⇔ Solve $\min_{H,X} ||Y - HX||$

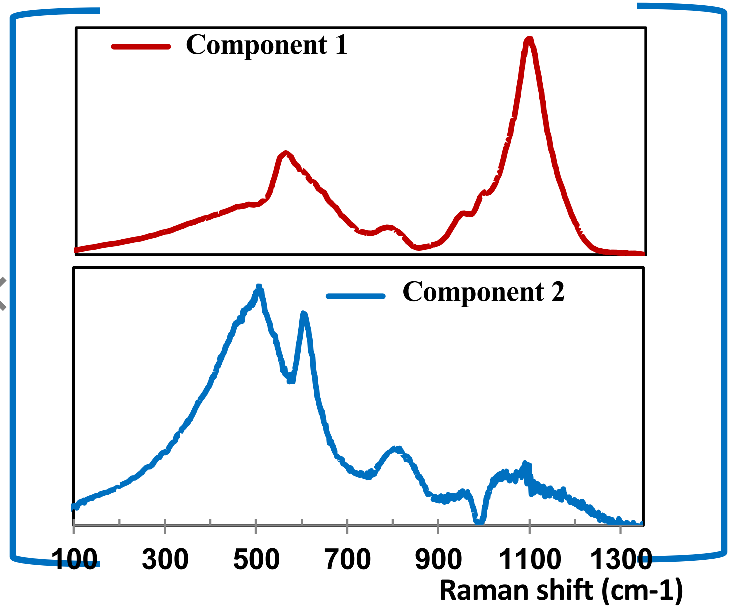
Raman depth spectra Y	Contributions H	Component X
Experimental data	Weight of the component	Raman spectra of each species

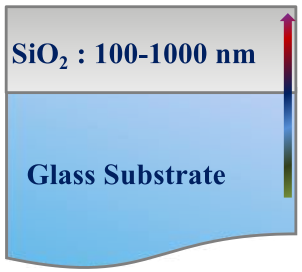


=

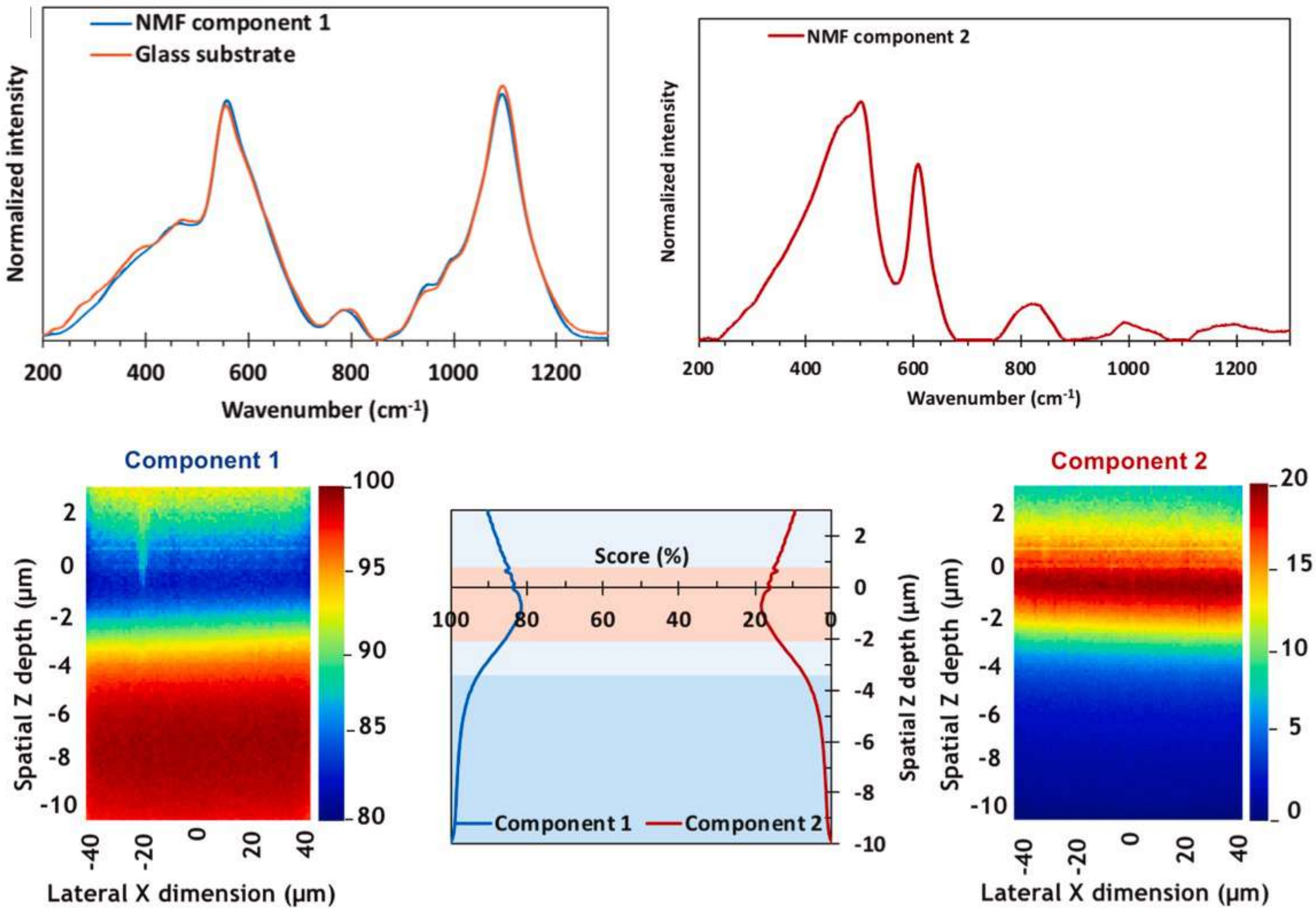
$H_{1,substrate}$	$H_{1, film}$
$H_{2,substrate}$	$H_{2, film}$
$H_{3,substrate}$	$H_{3, film}$
⋮	⋮
$H_{n, substrate}$	$H_{n, film}$

×

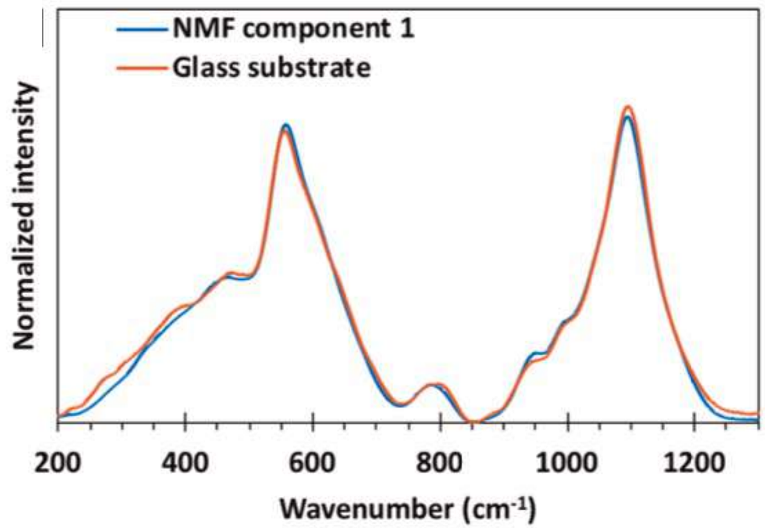


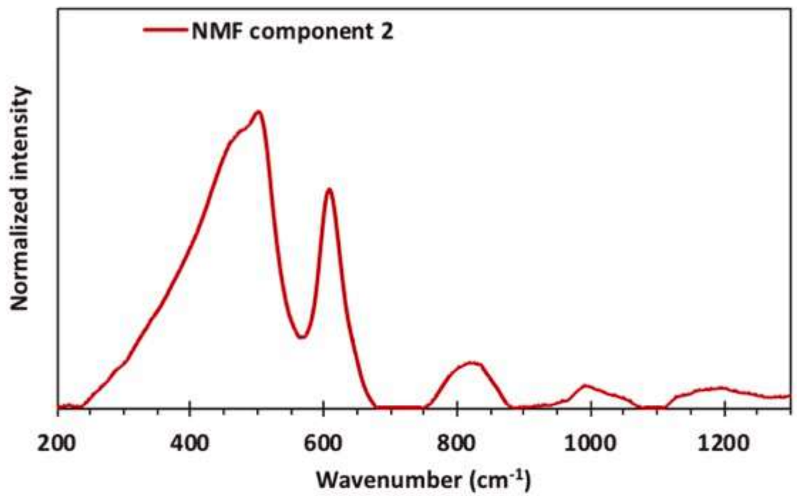


Non-negative Matrix Factorization (NMF)



Non-negative Matrix Factorization (NMF)

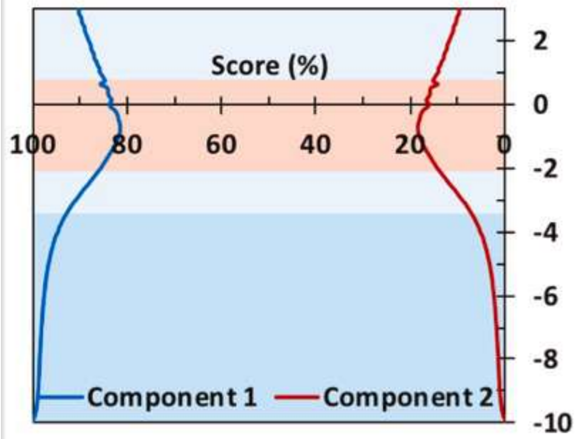


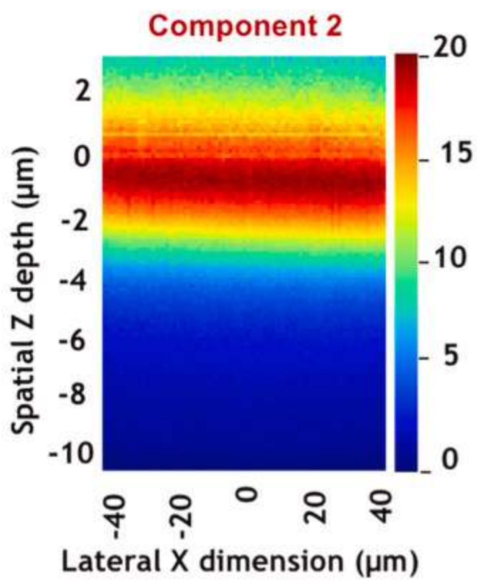


Principal component 1

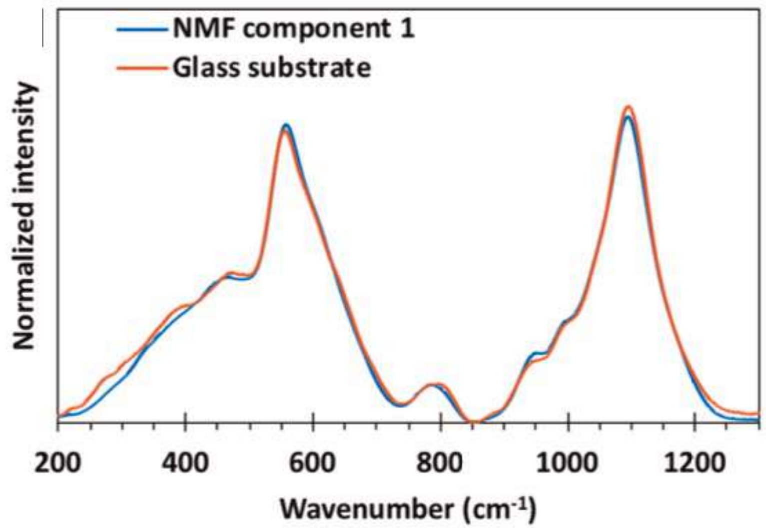
⬍

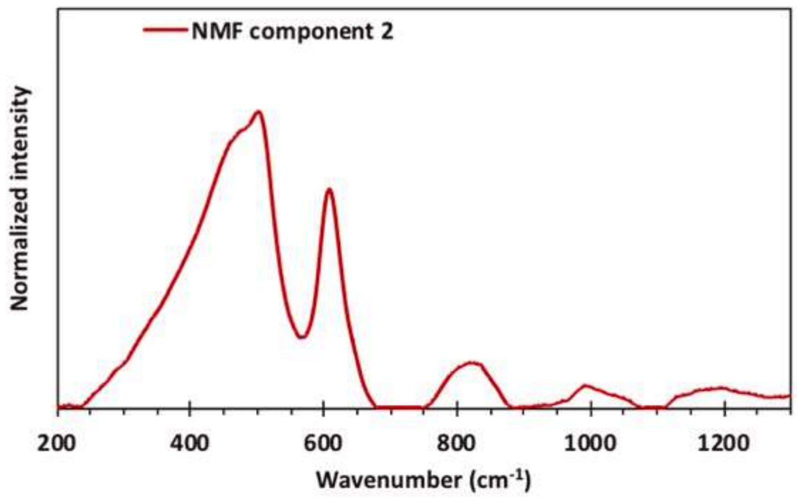
✓ Raman signal of the soda-lime silicate glass substrate





Non-negative Matrix Factorization (NMF)

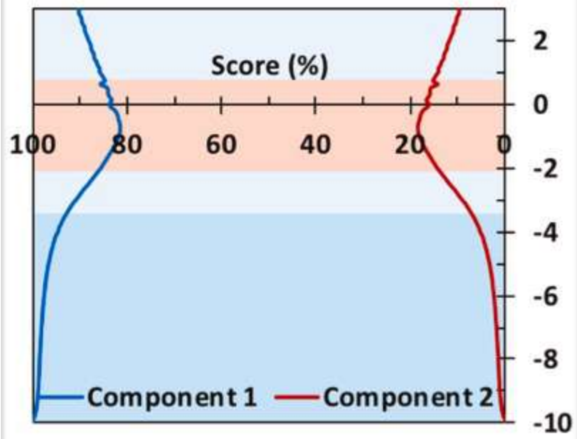




Principal component 1

⬍

✓ Raman signal of the substrate



Principal component 2

⬍

✓ Raman signal of silica film

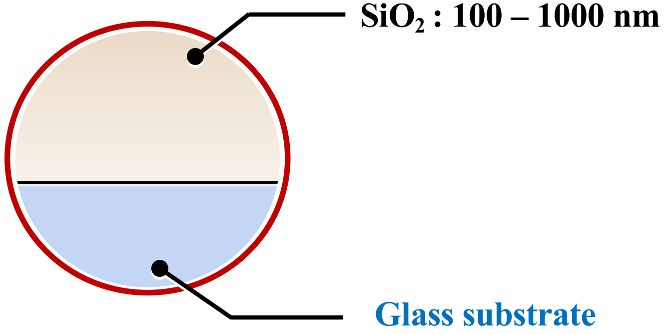
Reliability of this component ?

Raman structural characterization of sputtered silica films deposited on a reflective silver underlayer

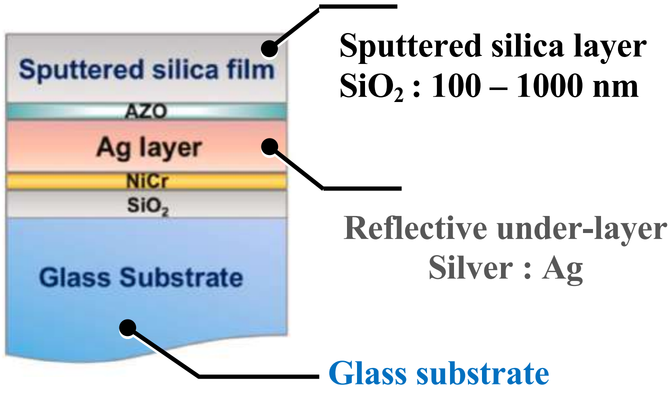
Solution:

✓ Developing of different processes for extracting the Raman signature of silica film

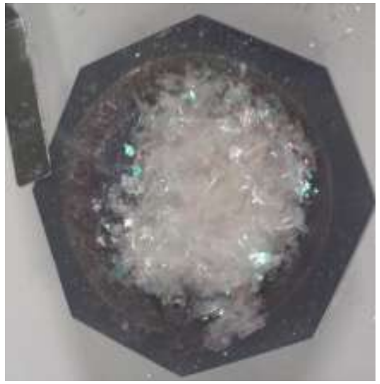
➢ Method 1
Statistical analysis
Non-negative-Matrix Factorization (NMF)



➢ Method 2
Reflective mask substrate



➢ Method 3
Delamination of the silica film



Silver under-layer :

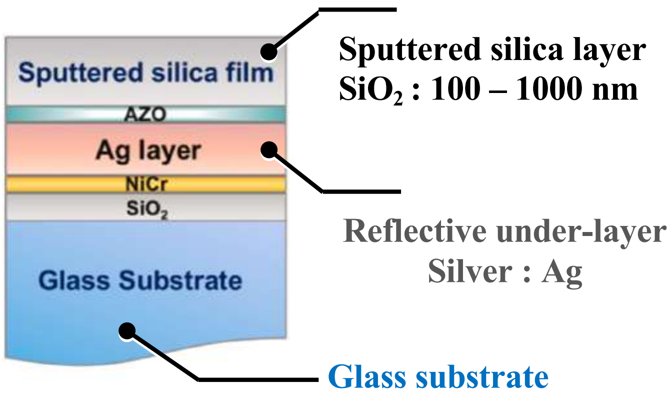
✓ Reflective coating mask the glass substrate

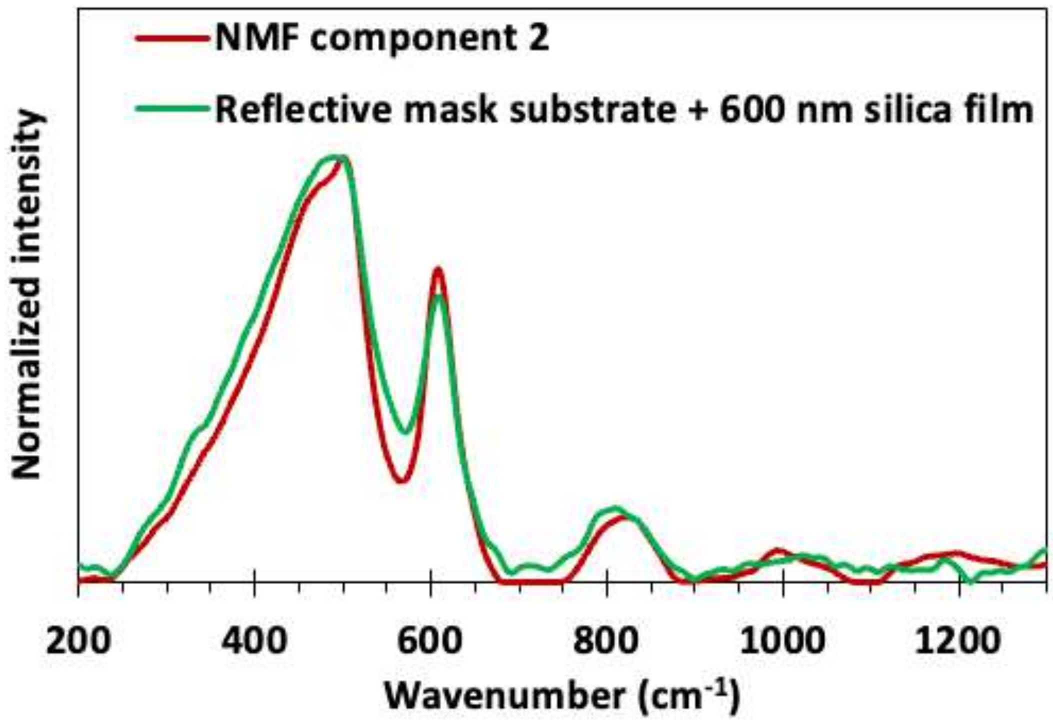
Raman structural characterization of sputtered silica films deposited on a reflective silver underlayer

Deposit of silver under-layer

➢ Method 2

Reflective mask substrate





- ✓ Confirmation of the effectiveness of NMF approach
- ✓ An efficient approach for Raman signal extraction of a film material,

But not applicable for other structural characterization analysis (NMR, PDF…)

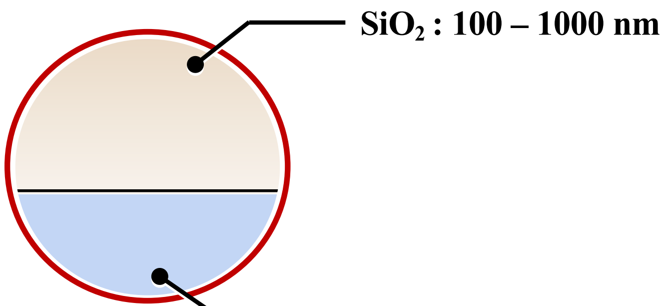
Raman structural characterization of recovered sputtered silica films

Solution:

✓ Developing of different processes for extracting the Raman signature of silica film

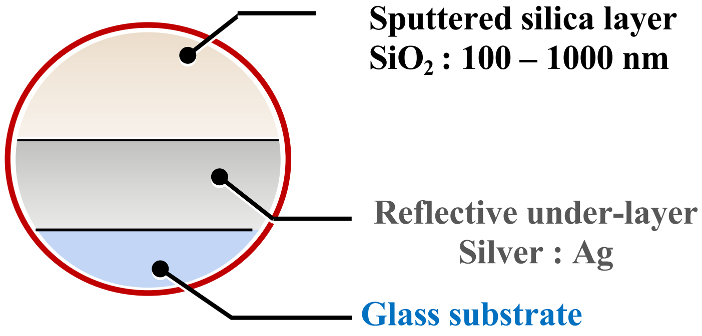
➢ Method 1

Statistical analysis
Non-negative-Matrix Factorization (NMF)



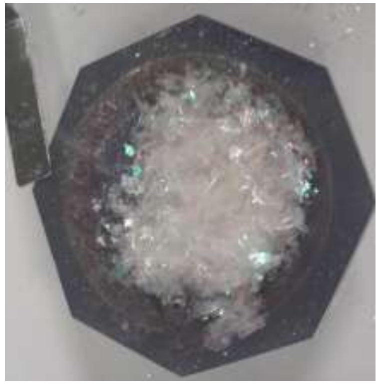
➢ Method 2

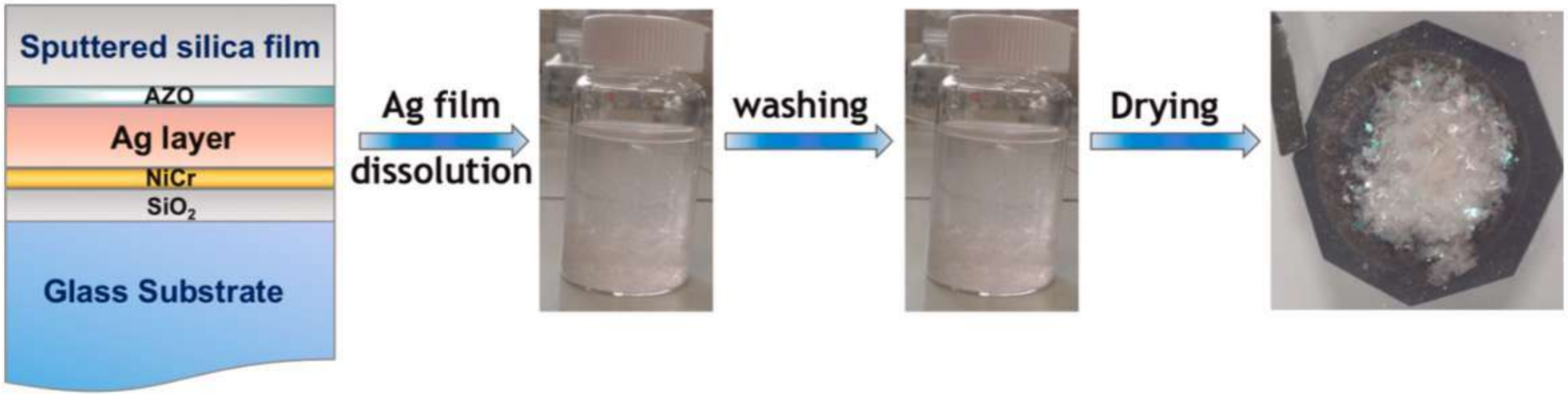
Reflective mask substrate



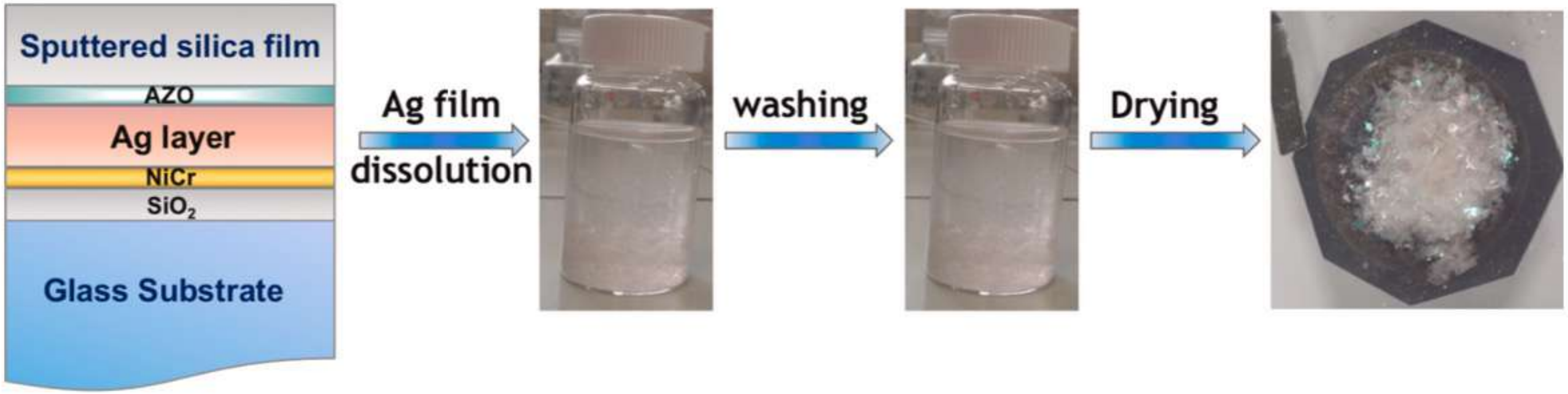
➢ Method 3

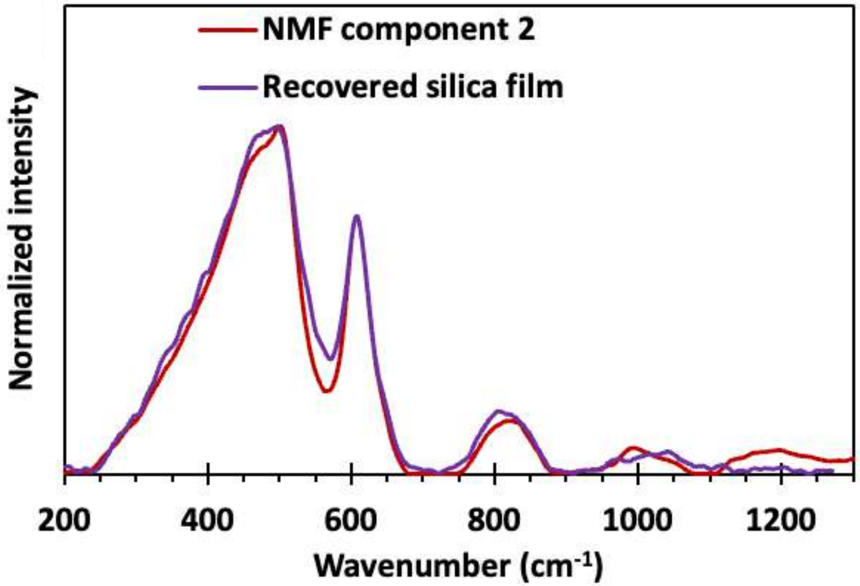
Delamination of the silica film





Raman structural characterization of recovered sputtered silica films



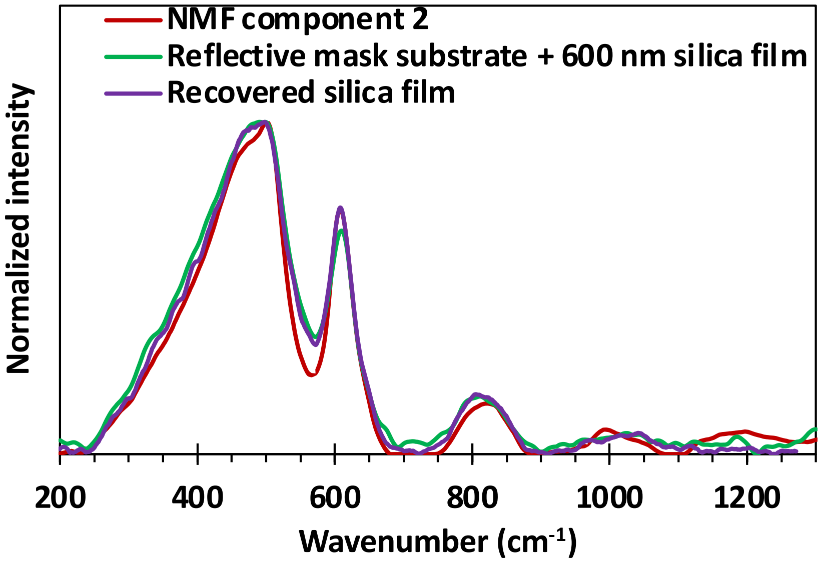


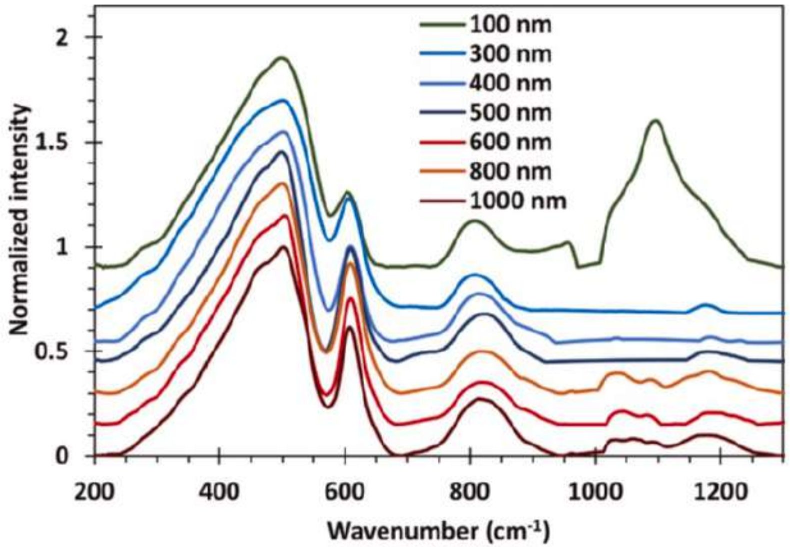
- ✓ Similar Raman signal of the silica film deposited on silver layer and the recovered silica film.
- ✓ No alteration of the structural characterization of the silica film by the acid attack

➔ The acid attack does not impact the structural features of the recovered silica film

Raman structural characterization of recovered sputtered silica films

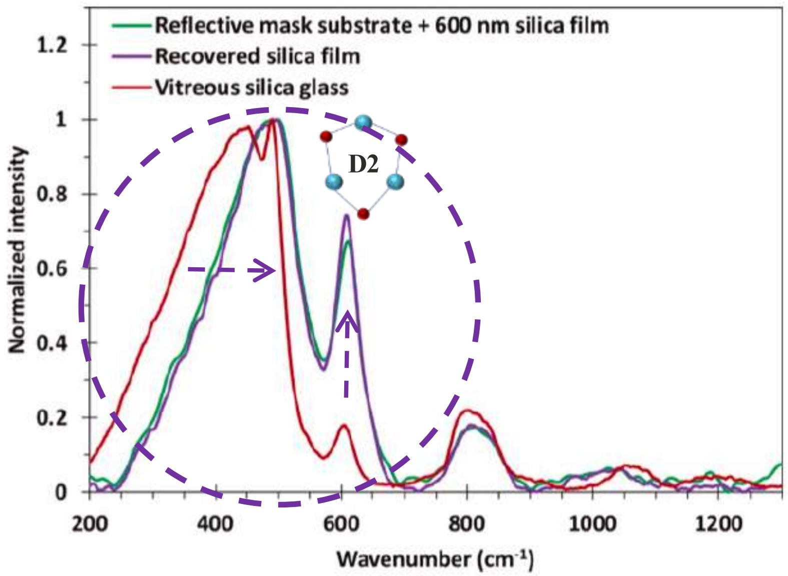
- ✓ Similar Raman signal of the silica film deposited on silver layer and the recovered silica film.
- ✓ No alteration of the structural characterization of the silica film by the acid attack





Revealing the local structural properties of silica film

- Thin silica film versus bulk material



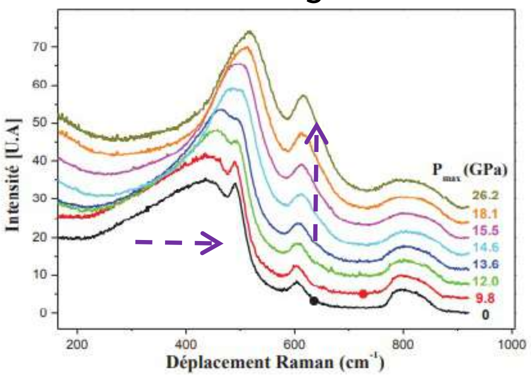
Shift of the main band

=> Decrease of the Si-O-Si intertetrahedral bond (θ)

Increase of D2 band

=> Increase in the number of the threefold-membered rings

- Compressed silica glass
  Densified glass



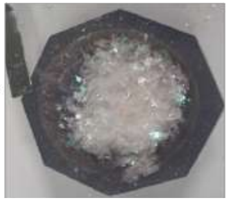
T. Deschamps et al., 2013

➔ **By magnetron sputtering depostion, the deposited silica film is a dense material**

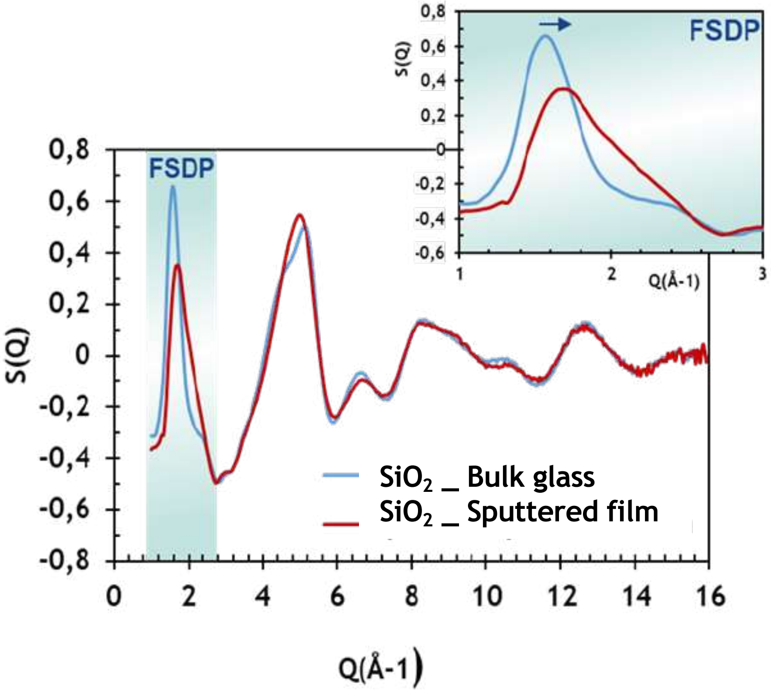
➔ **Densification confirmed by XRR**

Density$_{film}$ = 2.35 g.cm^{-3} >>> Density$_{fused}$ = 2.2 g.cm^{-3}

Determination of Pair Distribution Functions (PDF)

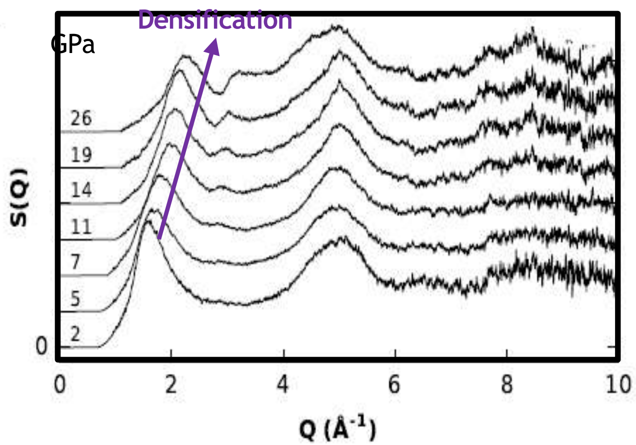


X-ray scattering structure factor S(Q)



Sputtered silica film:

- No/little change in the range of large Q ($Q > 4$ Å^{-1}) ⇔ **Short-range order is mostly preserved**
- Significant evolution of FSDP ⇔ **Medium-range order is modified**

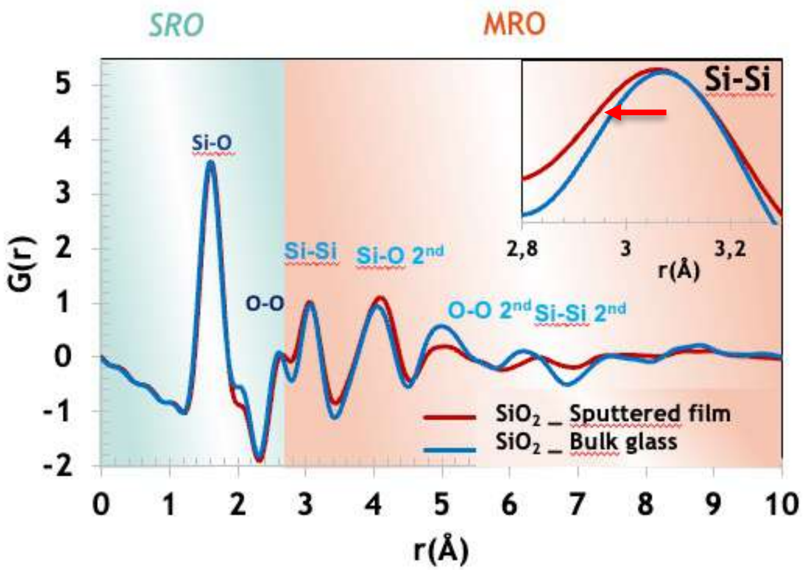


Y Inamura *et al* 2007

➔ **Permanently densified sputtered silica film**

Determination of Pair Distribution Functions (PDF)

➢ Interatomic distances



Sputtered silica film:

➢Preservation of the short-range order

➢ Evolution of the medium-range order:

* Shortening of Si-Si distance ⇔ **a denser packing at MRO**

* Quick vanishing of PDF ⇔ **More pronounced disordered structure at the medium-range scale**

➥ **Sputtered silica film : denser structure with a less organized network**

Sputtered silica film compared to densified silica glass

1

Sputtered silica film

Density 2.35 $g.cm^{-3}$

Magnetron sputtering deposition

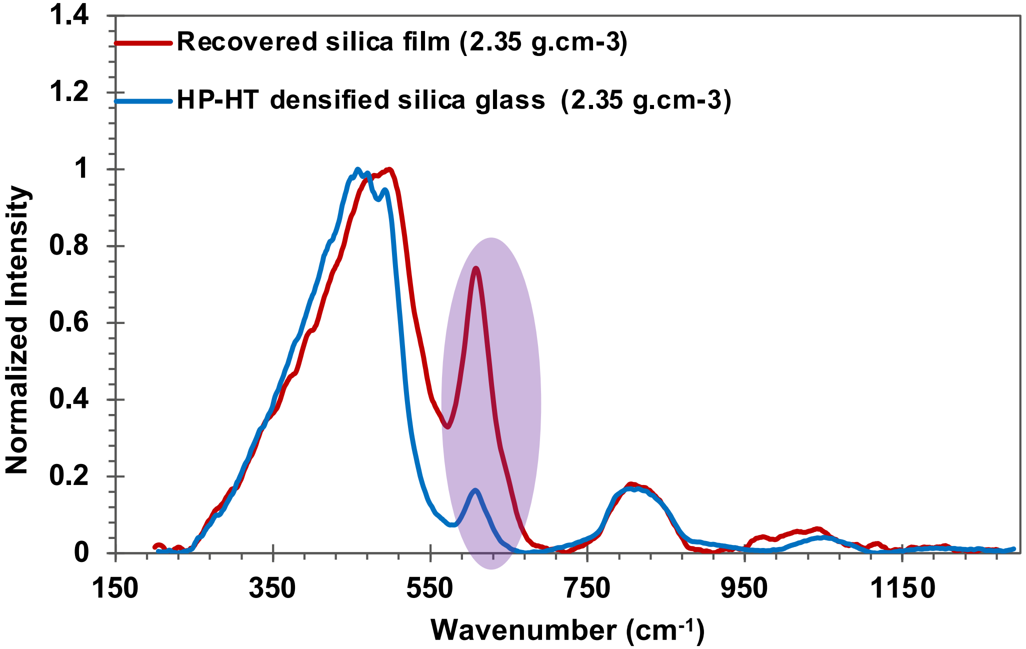
2

Densified silica glass

Density 2.35 $g.cm^{-3}$

Multi-anvil cell

4 GPa - 550° C



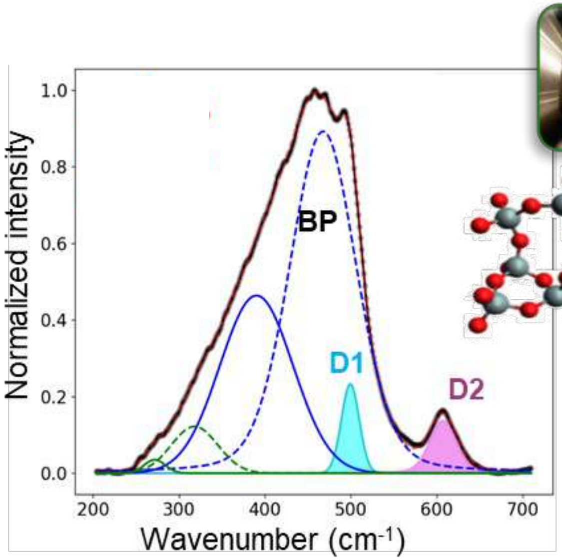
➔ Different Raman features ⇔ Different microscopic organization.

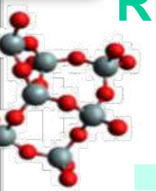
➔ Strong impact of synthesis process on the glass structure especially the intermediate-range order

Quantification of the densification

Densified silica glass_2.35 g.cm^{-3}

Silica film_2.35 g.cm^{-3}

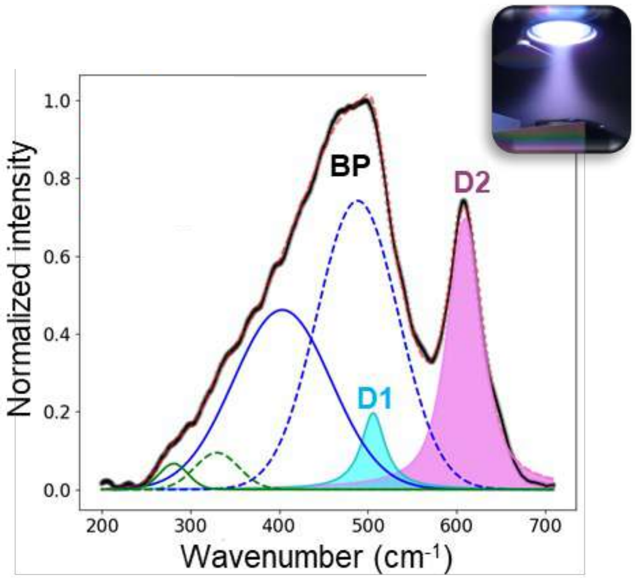


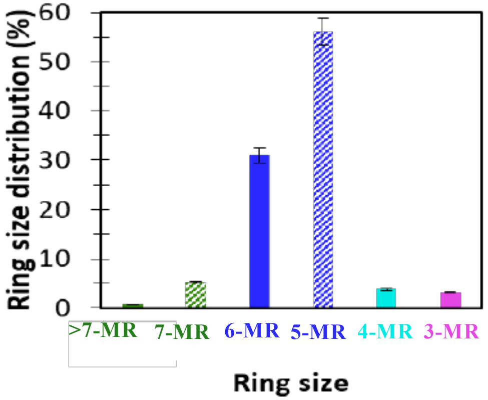


Rings size decrease

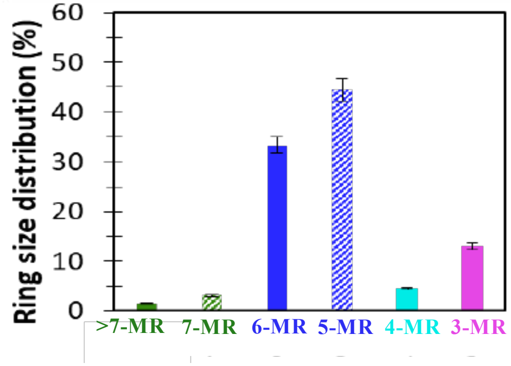
+

Rings deformation



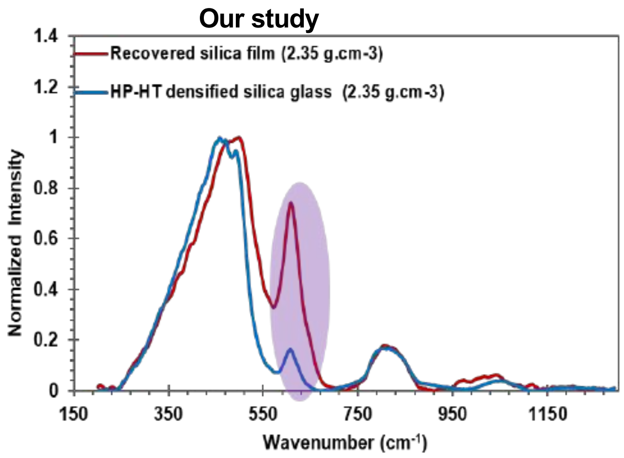


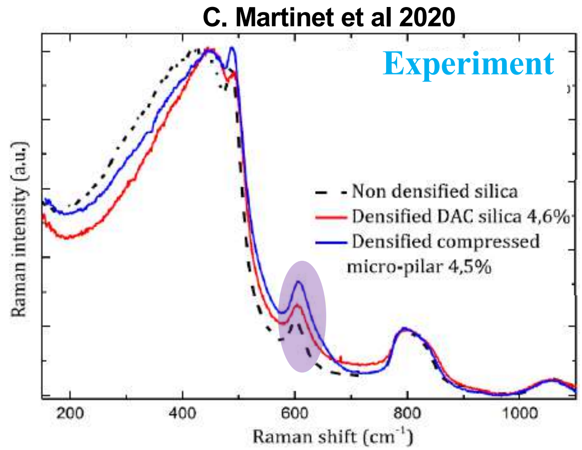
Similar density ≠ Similar structure

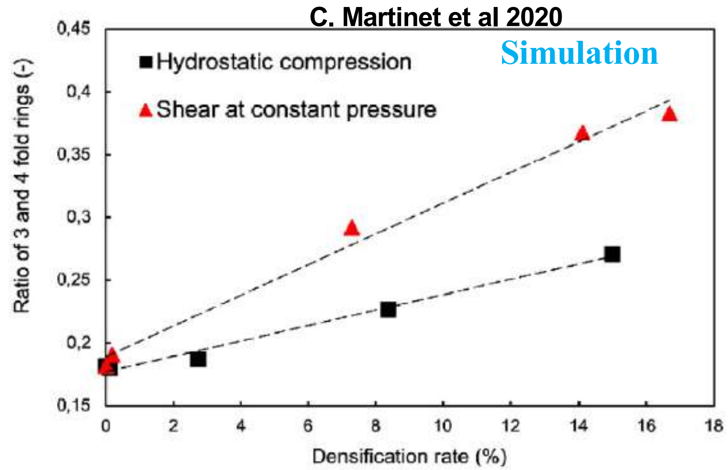


Sputtered silica film compared to densified silica glass

impact of shear strain



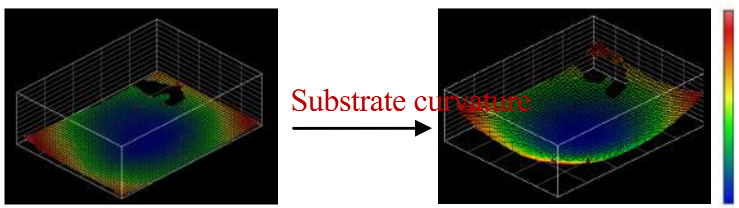




Martinet et al., J. Non-Cryst. Solids 533 (2021) 119898

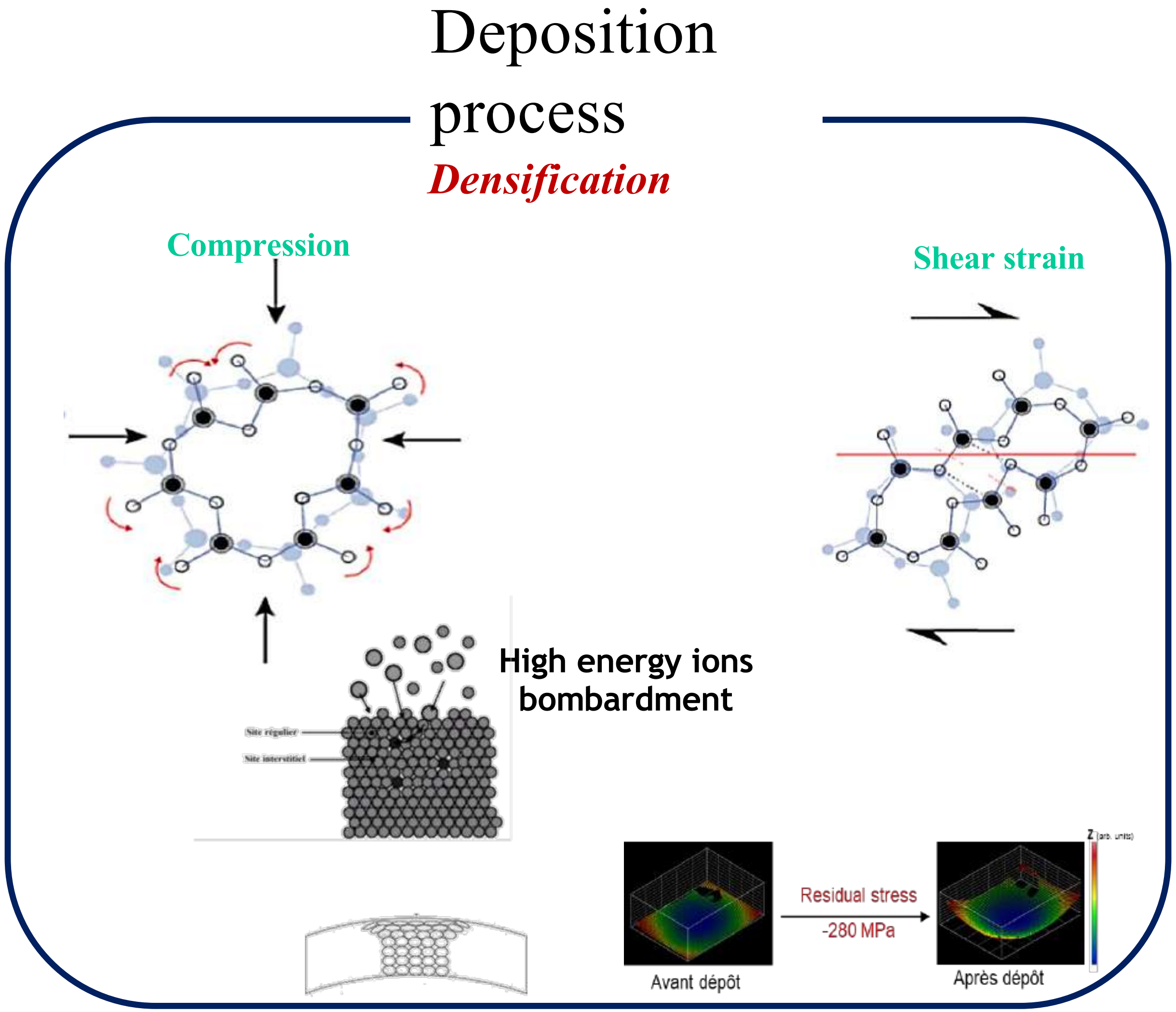
D2 increase ⇔ Impact of the shear stress

Shear stress ↗ => Three-membered rings ↗



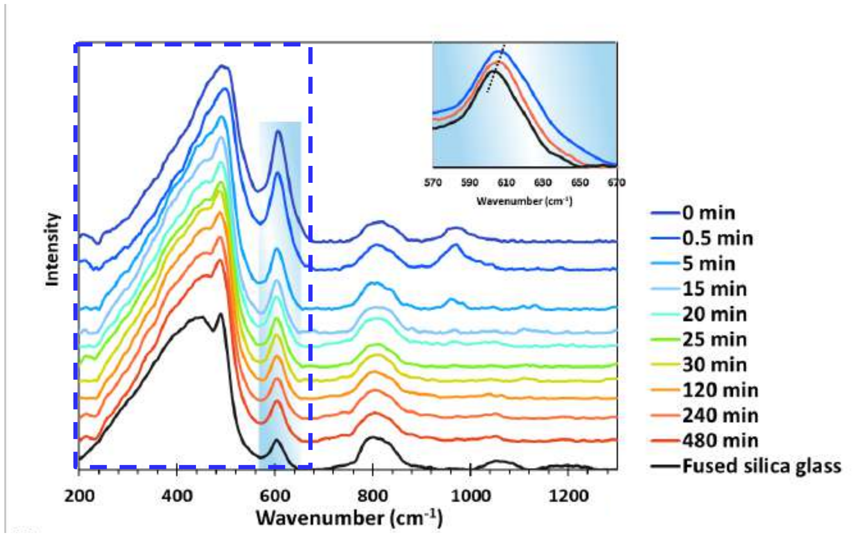
Before deposition   After deposition

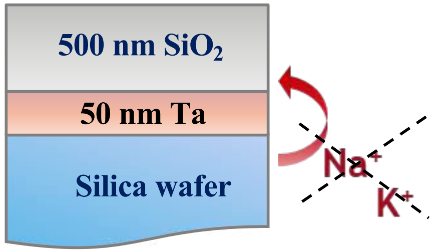
Specificity of the silica film structure



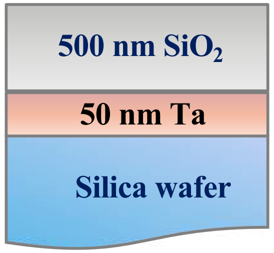
Structure evolution under thermal treatment 650° C

Raman spectroscopy

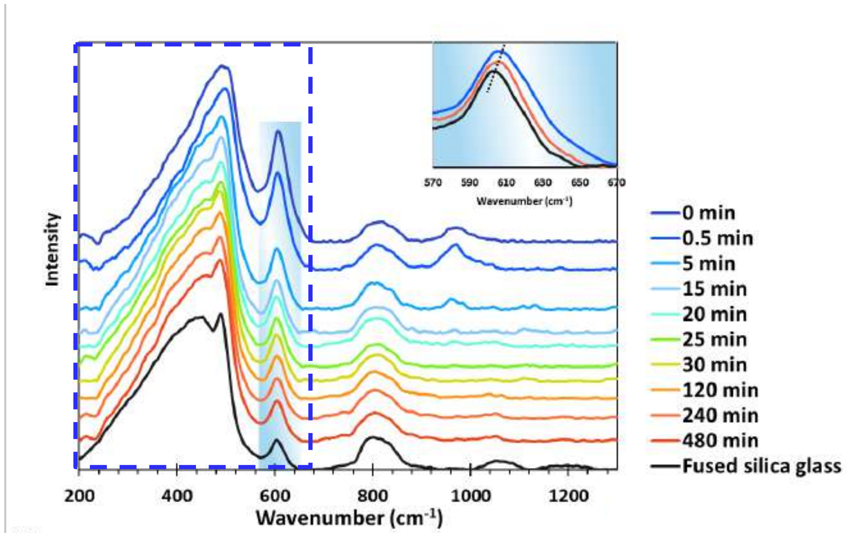




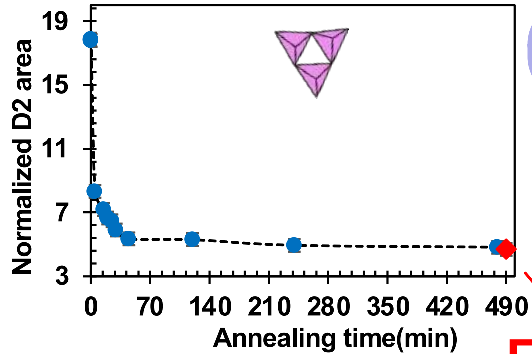
Structure evolution under thermal treatment 650° C



Raman spectroscopy

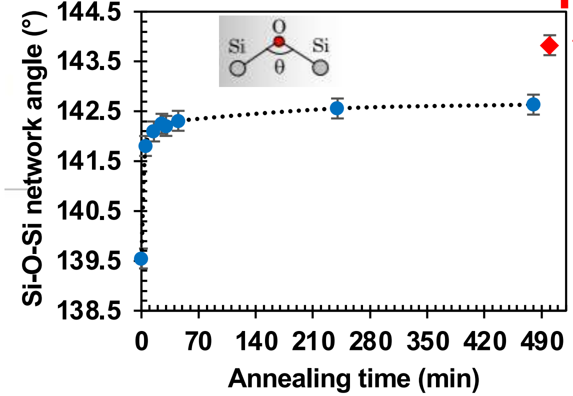


Decrease of D2 band



=> Decrease in the number of the 3-fold membered rings

Fused silica glass



Shift of the main band

=> Increase of Si-O-Si angles

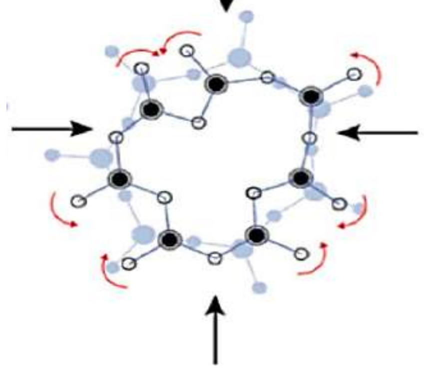
➔ Partial relaxation of the sputtered silica film : 70 %

Specificity of the silica film structure

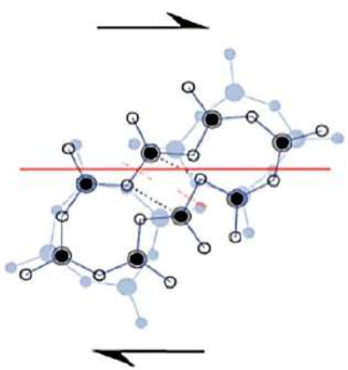
Deposition process

Densification

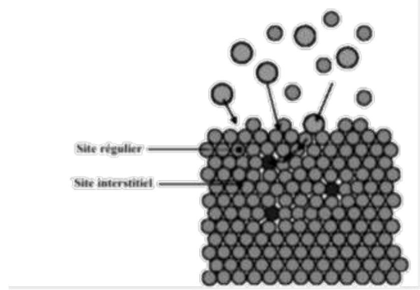
Compression



Shear strain



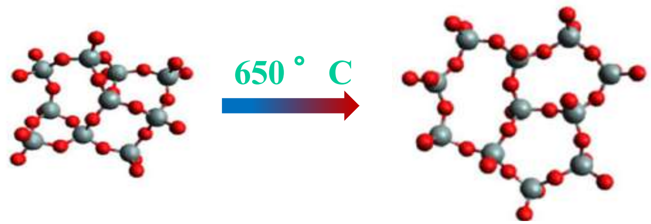
High energy ions bombardment



Thermal treatment

Increase of Si-O-Si angles

Decrease of the small rings proportion



Conclusion

➔ Efficiency of the different developed approaches for Raman signal extraction of the sputtered silica film

➔ Strong impact of synthesis process on the glass structure especially the intermediate-range order

⇨ *By magnetron sputtering depostion, the deposited silica film is permanantly densified*

Short-range transformation:
Decrease of the Si-O-Si intertetrahedral angles

Medium-range evolution:
Change in the ring statistics favoring the formation of smaller rings