Kinetics and mechanisms of network modifiers migration from glass substrates to silica thin films

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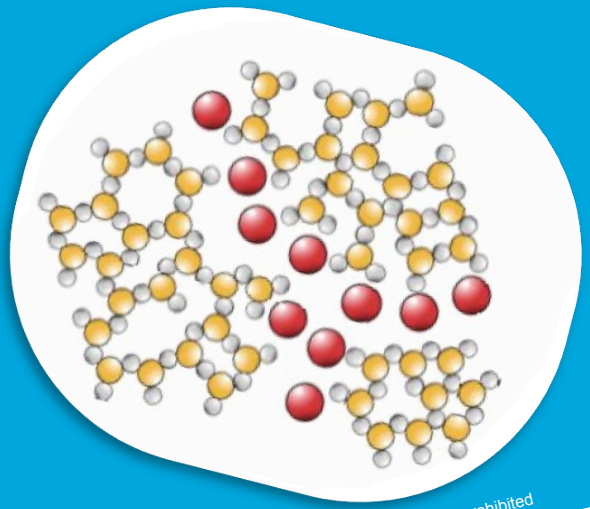

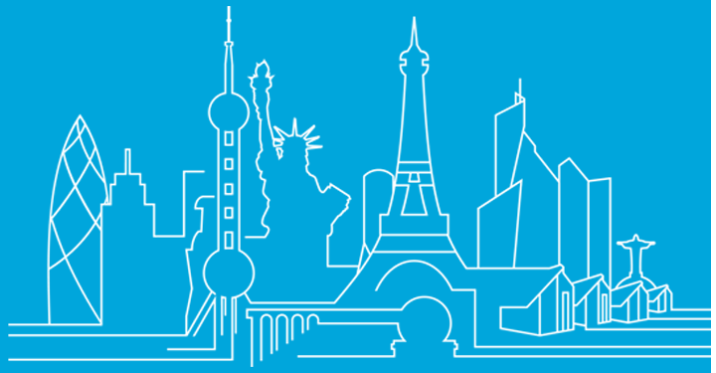

SAINT-GOBAIN 350 RAISONS DE CROIRE EN L'AVENIR

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Diffusion et séparation de phases à la surface du verre

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1. Contexte

- La surface du verre est fonctionnalisée par des couches minces métalliques et/ou diélectriques déposées par pulvérisation cathodique magnétron.

- Le développement de couches minces nanostructurées pourrait permettre d'obtenir de nouvelles :
  - ➲ *propriétés optiques,*
  - ➲ *propriétés de mouillage, …*

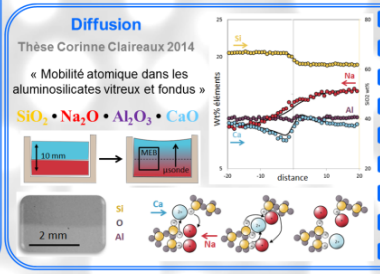
2. Laboratoire SVI

Diffusion

Thèse Corinne Claireaux 2014

« Mobilité atomique dans les aluminosilicates vitreux et fondus »

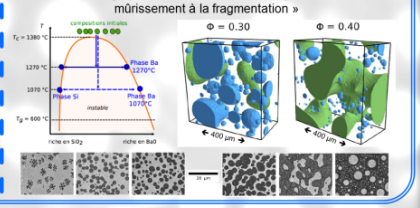
$SiO_2 \bullet Na_2O \bullet Al_2O_3 \bullet CaO$



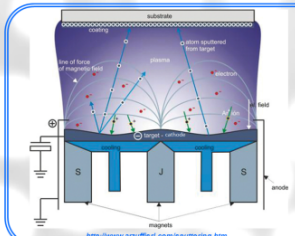
Séparation de phases

Thèse David Bouttes 2014

« Micro-tomographie d'un borosilicate de baryum démixé : du mûrissement à la fragmentation »



3. Pulvérisation cathodique magnétron



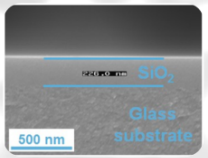
http://www.arzoffiarl.com/sputtering.htm

➲ **Dépôts PVD (*Physical Vapor Deposition*) de couches minces de verre ou de silice .**

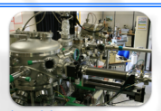
Cibles :
- Si / Si:Al / SiO_2 / Al_2O_3 / …
- Verres de différentes compositions

Gaz :
- Ar
- Ar + O_2

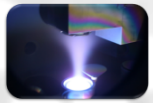
Paramètres :
- Pression de dépôt :
  - ↳ Densité des couches
  - ↳ Stœchiométrie des couches
- Puissance sur la cible :
  - ↳ Vitesse de dépôt
- Temps de dépôt :
  - ↳ Épaisseur des couches



Couche de silice de 220 nm d'épaisseur après dépôt (coupe en tranche - MEB)



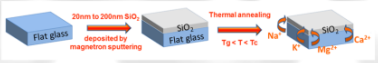
Bâti de dépôt "MISSTIC" au laboratoire Surface du Verre et Interfaces



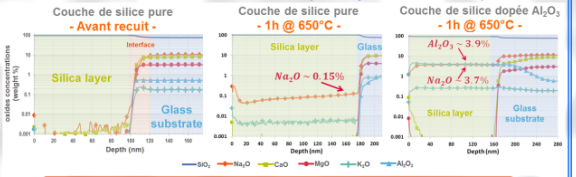
Plasma d'Ar pendant le dépôt

4. Etude de la diffusion du verre vers la silice

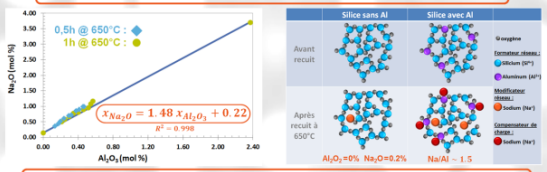
… par dépôt de couches minces de SiO_2 sur substrats de verre et traitements thermiques au-dessus de la Tg du substrat.



Etude de la diffusion des modificateurs de réseau par analyses SIMS avant et après recuits :



Quelle est la relation entre le dopage en aluminium et la diffusion du sodium ?

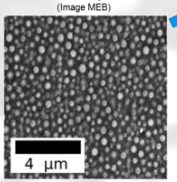


$\frac{Na}{Al} > 1$ → Na peut être compensateur de charge ou modificateur de réseau après diffusion.

5. Séparation de phases à la surface

… par dépôt de couches minces de verre sur substrats de verre ou silicium

cible de verre pour PVD
(Image MEB)



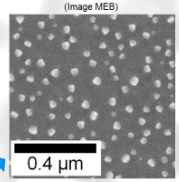
Gouttelettes riches en Baryum
Ø : 200 nm à 400 nm

❶ Dépôt PVD mode RF

❷ Traitement thermique

10x plus petit

Couche mince de verre
(Image MEB)



Gouttelettes riches en Baryum
Ø : 20 nm à 40 nm

Perspectives :

Etudier et comprendre l'influence des différents paramètres sur la morphologie de la couche après séparation de phases :

- ➲ *Épaisseur du dépôt,*
- ➲ *Composition de la couche,*
- ➲ *Température de traitement thermique,*
- ➲ *Durée du recuit, …*

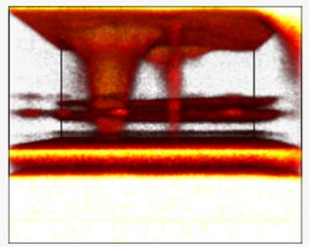
Introduction - context

- Flat glass surface is functionalized with metallic and/or dielectric thin films deposited by magnetron sputtering.

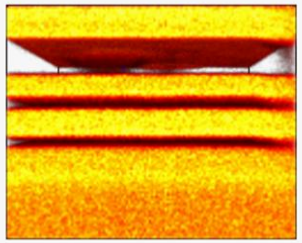
- Sodium migration can be observed from glass substrate to active layers in industrial processes, for example during thermal treatments above Tg (annealing, shaping, ...)

=> decrease of thin films properties

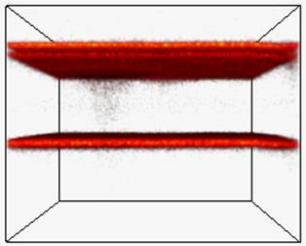
SIMS measurement - 3D Reconstruction



Na 3D Image



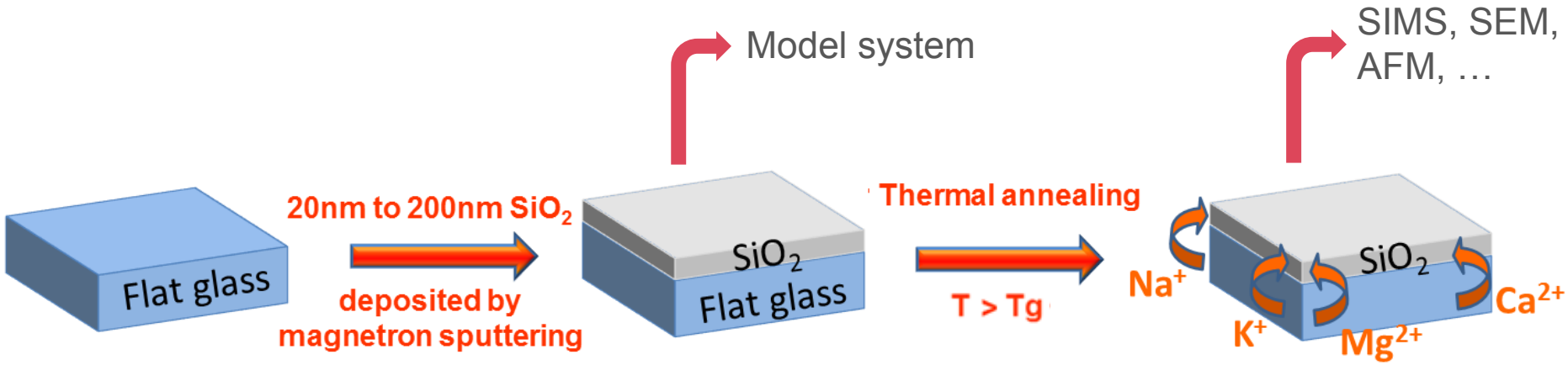
Si 3D Image

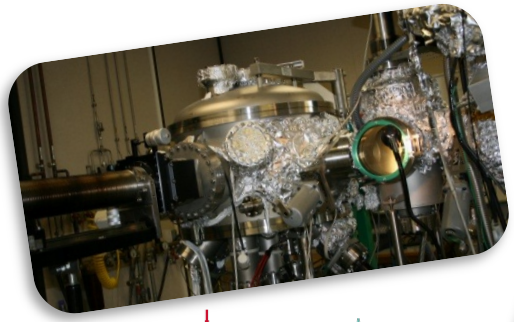


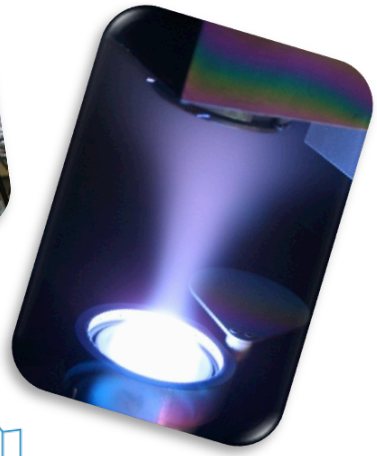
Ag 3D Image

Introduction

Aim : understand the kinetics and mechanisms of this phenomenon

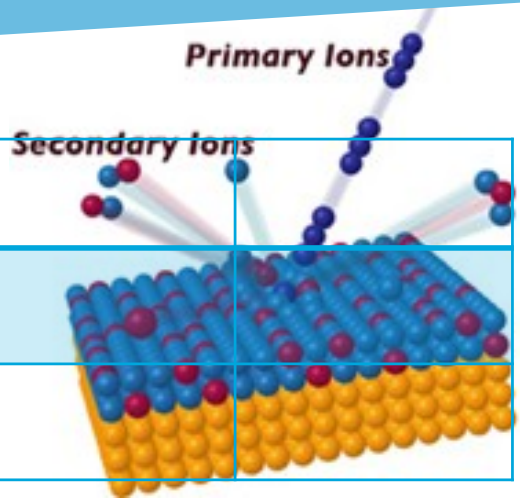


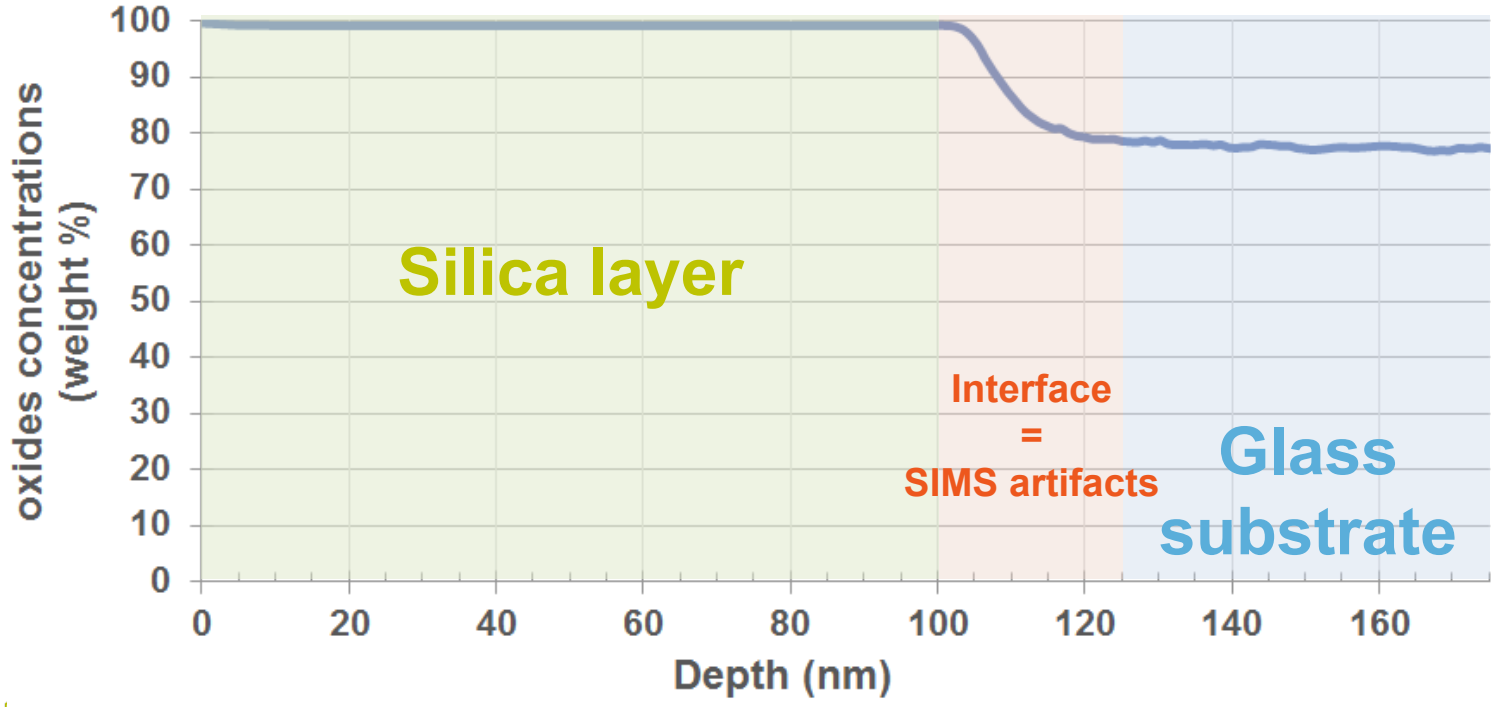




SIMS measurement - before annealing

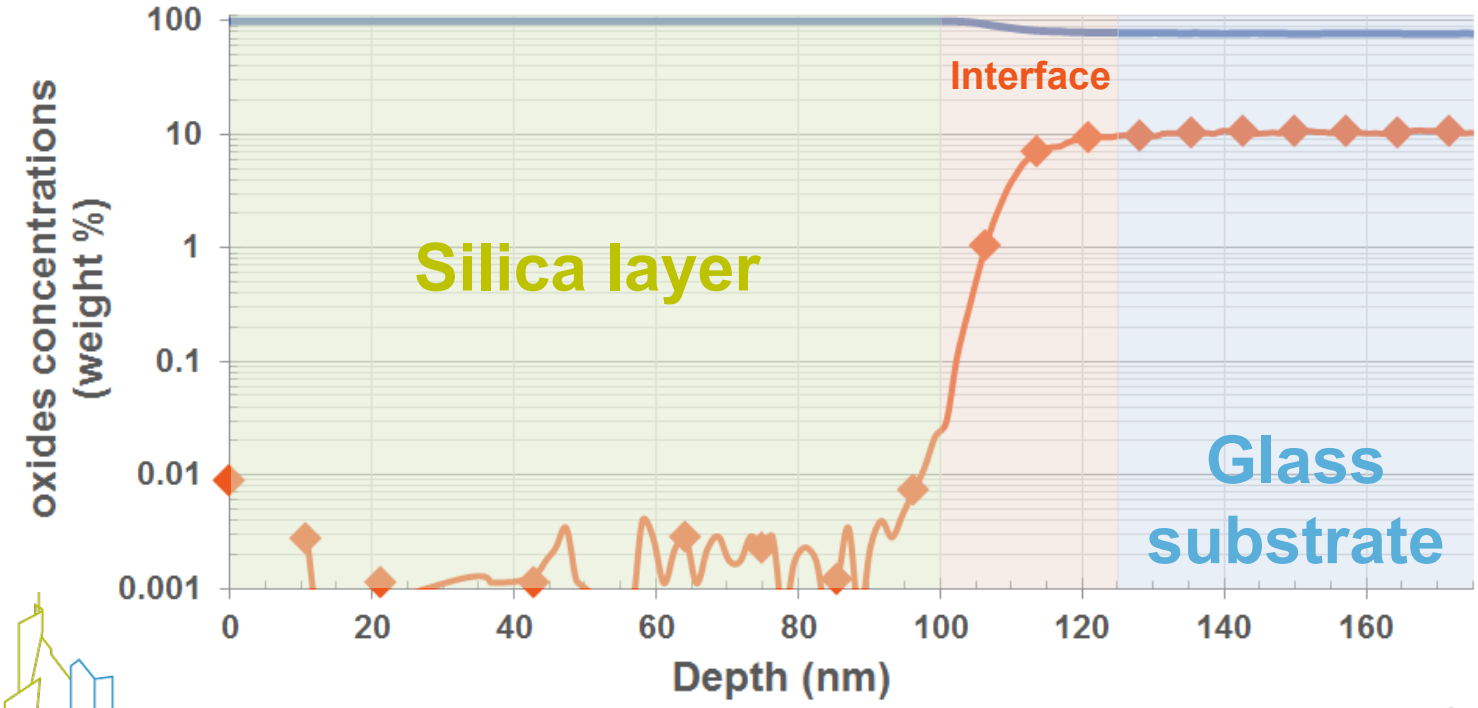
oxides	SiO_2				
Glass substrate (weight %)	73.3				
Silica layer (weight %)	<99,99				





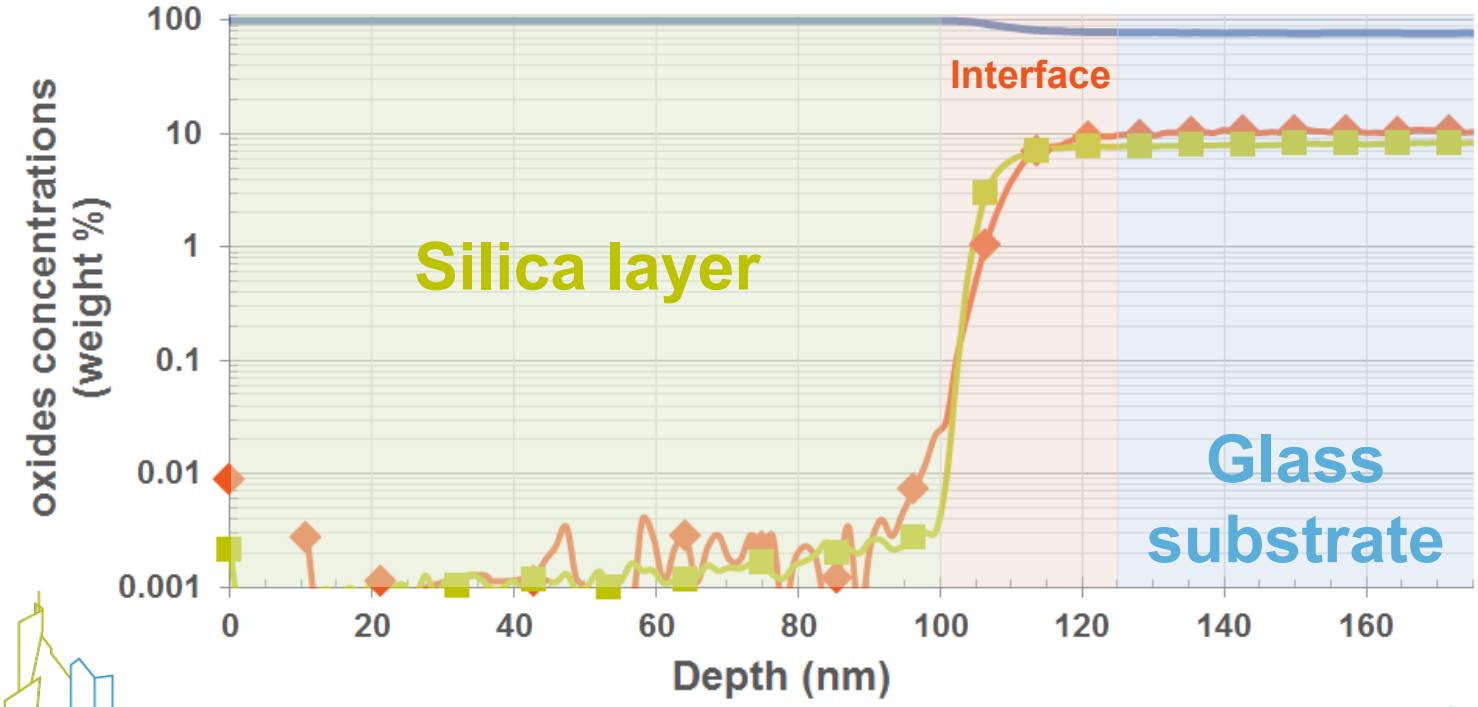
SIMS measurement - before annealing

oxides	SiO_2	Na_2O				
Glass substrate (weight %)	73.3	13.3				
Silica layer (weight %)	<99,99	<0.003				



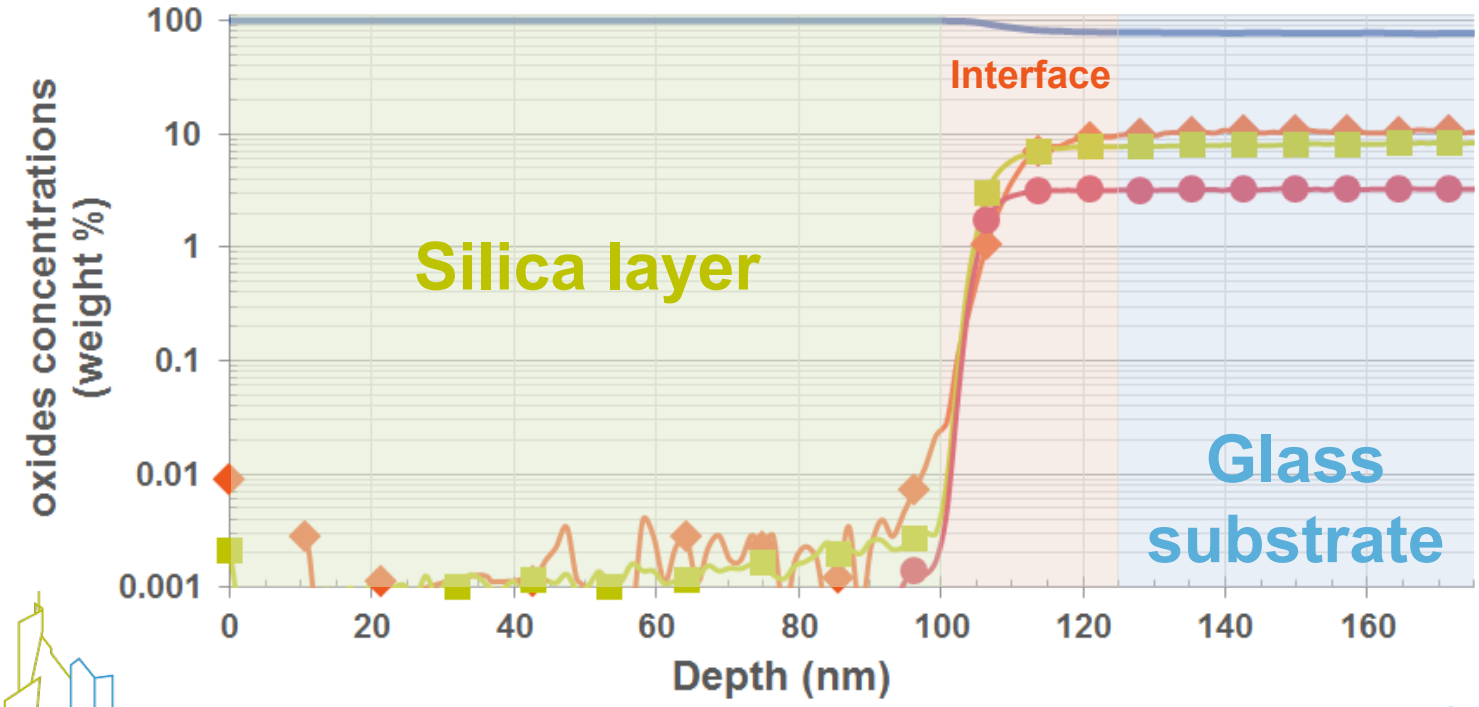
SIMS measurement - before annealing

oxides	SiO_2	Na_2O	CaO			
Glass substrate (weight %)	73.3	13.3	9.6			
Silica layer (weight %)	<99,99	<0.003	<0.003			



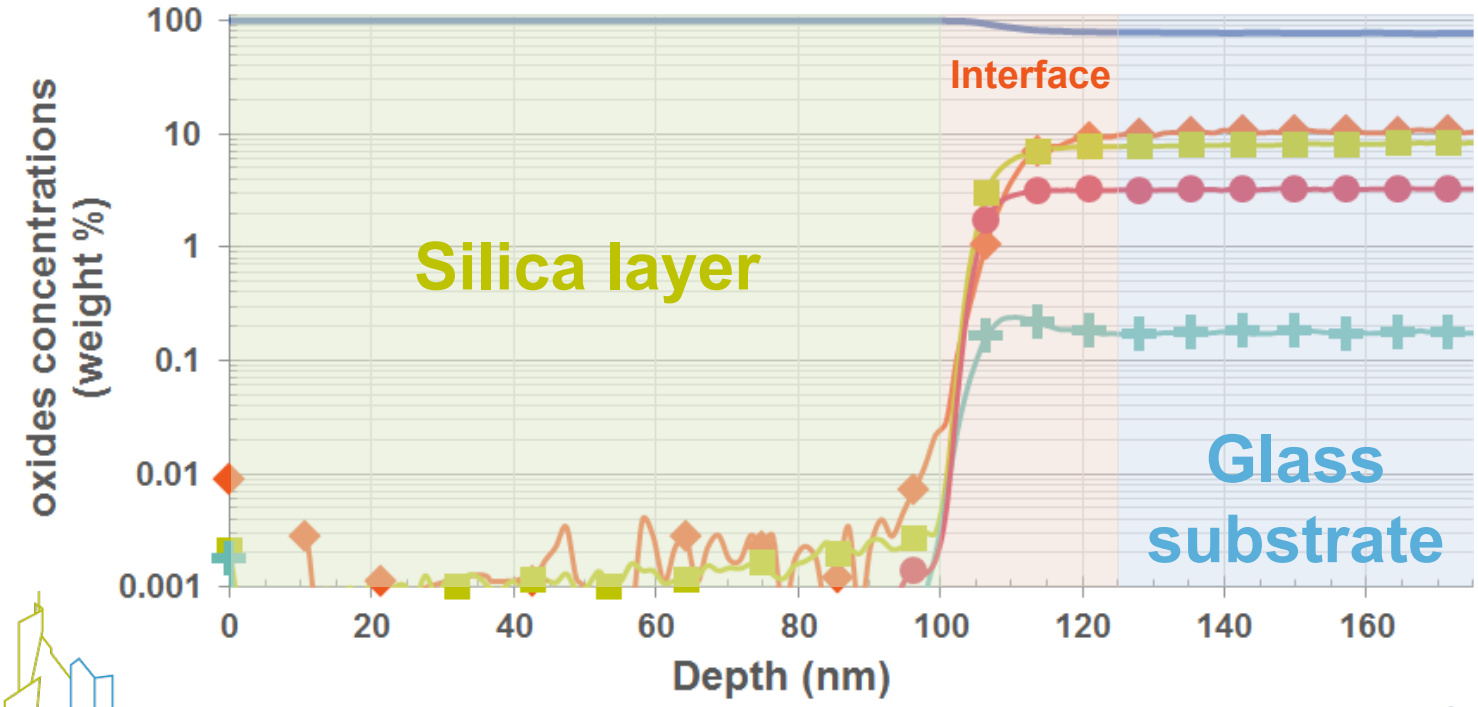
SIMS measurement - before annealing

oxides	SiO_2	Na_2O	CaO	MgO		
Glass substrate (weight %)	73.3	13.3	9.6	3.1		
Silica layer (weight %)	<99,99	<0.003	<0.003	<0.001		



SIMS measurement - before annealing

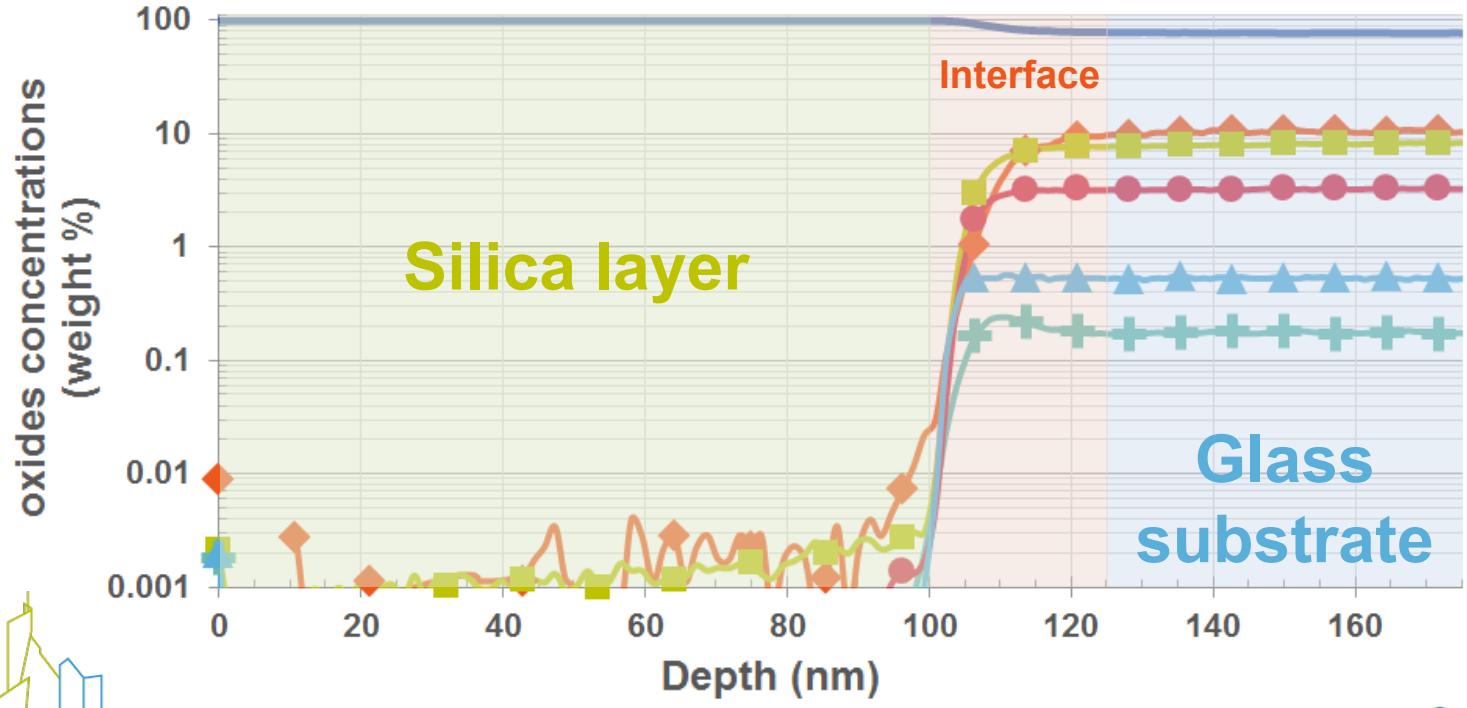
oxides	SiO_2	Na_2O	CaO	MgO	K_2O	
Glass substrate (weight %)	73.3	13.3	9.6	3.1	0.2	
Silica layer (weight %)	<99,99	<0.003	<0.003	<0.001	<0.001	



SIMS measurement - before annealing

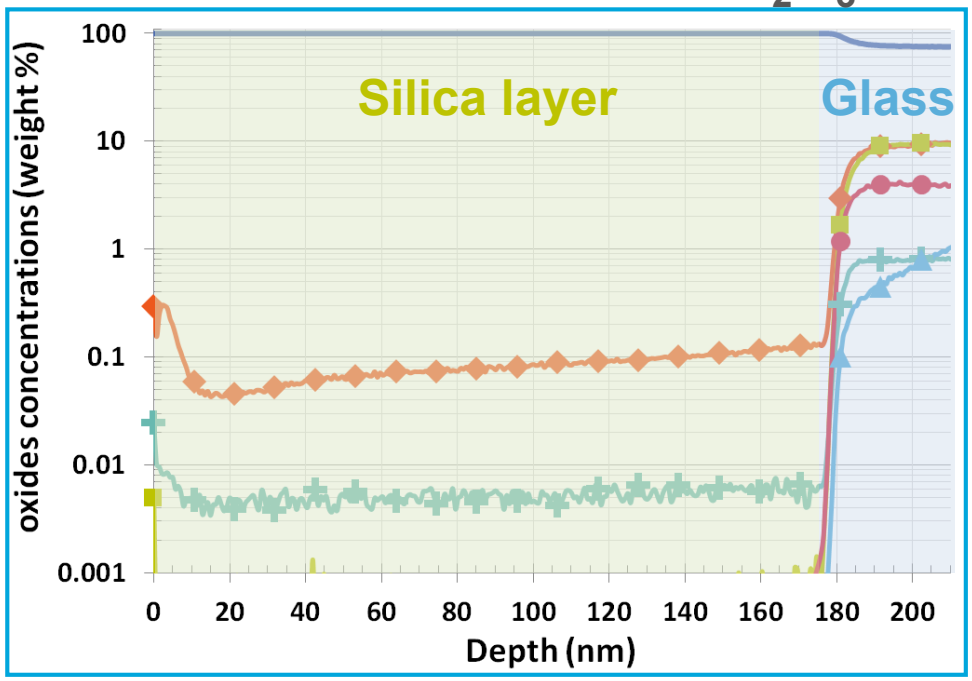
oxides	SiO_2	Na_2O	CaO	MgO	K_2O	Al_2O_3
Glass substrate (weight %)	73.3	13.3	9.6	3.1	0.2	0.5
Silica layer (weight %)	<99,99	<0.003	<0.003	<0.001	<0.001	<0.001

No network modifiers in silica layers after deposition

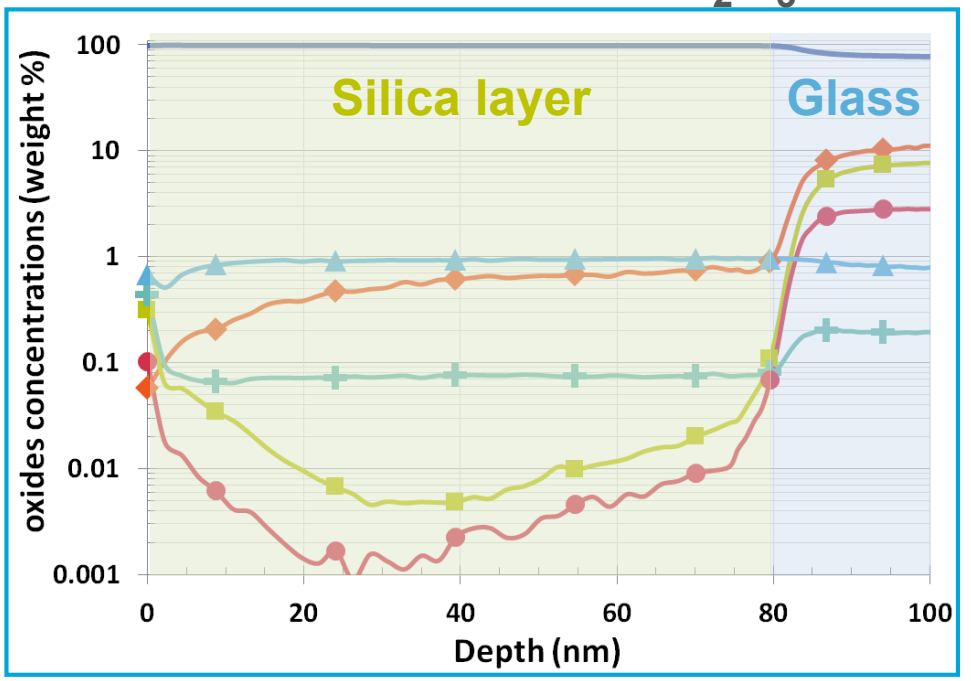


SIMS measurement - after annealing 1h @ 650°C

Silica thin film without Al_2O_3



Silica thin film with 1% Al_2O_3 (weight %)

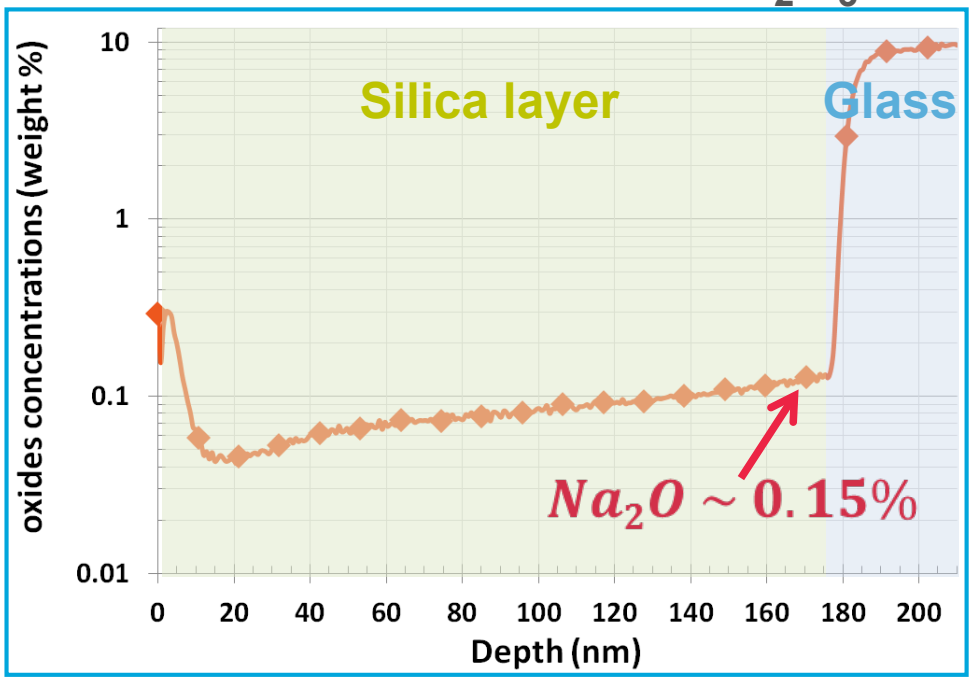


SiO_2 Na_2O CaO MgO K_2O Al_2O_3

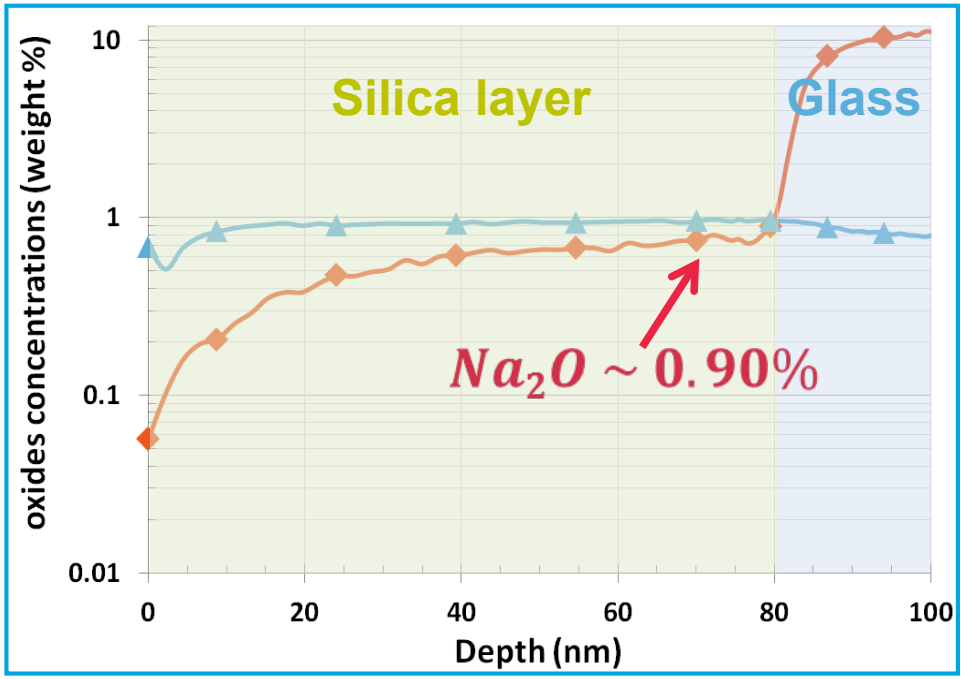
CaO, MgO and K_2O concentrations after annealing < 0.1 % in silica layers.

SIMS measurement - after annealing 1h @ 650°C

Silica thin film without Al_2O_3



Silica thin film with 1% Al_2O_3 (weight %)

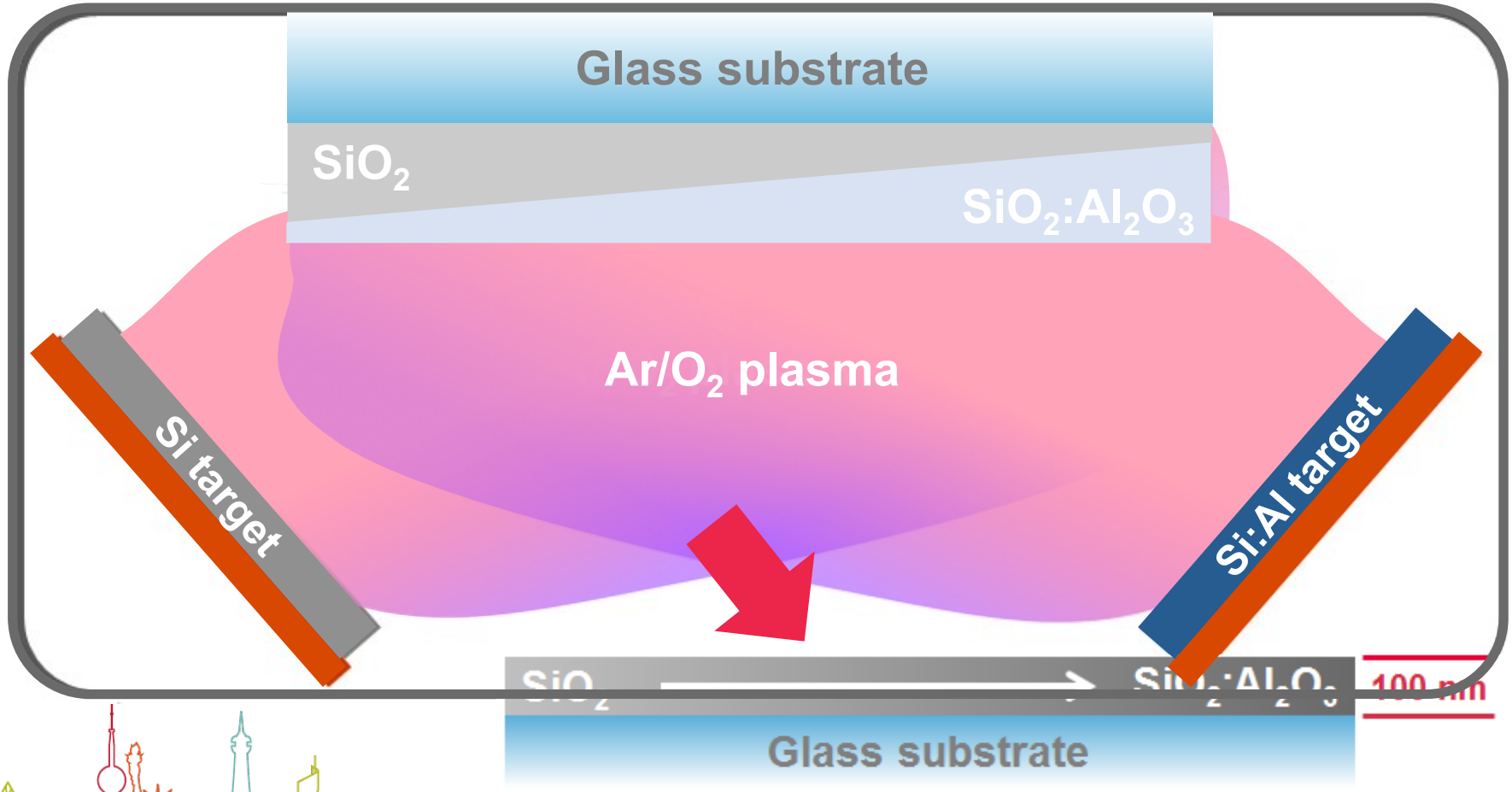


Na_2O Al_2O_3

Na_2O concentration ~ 6x higher in silica layer with 1% in weight of Al_2O_3

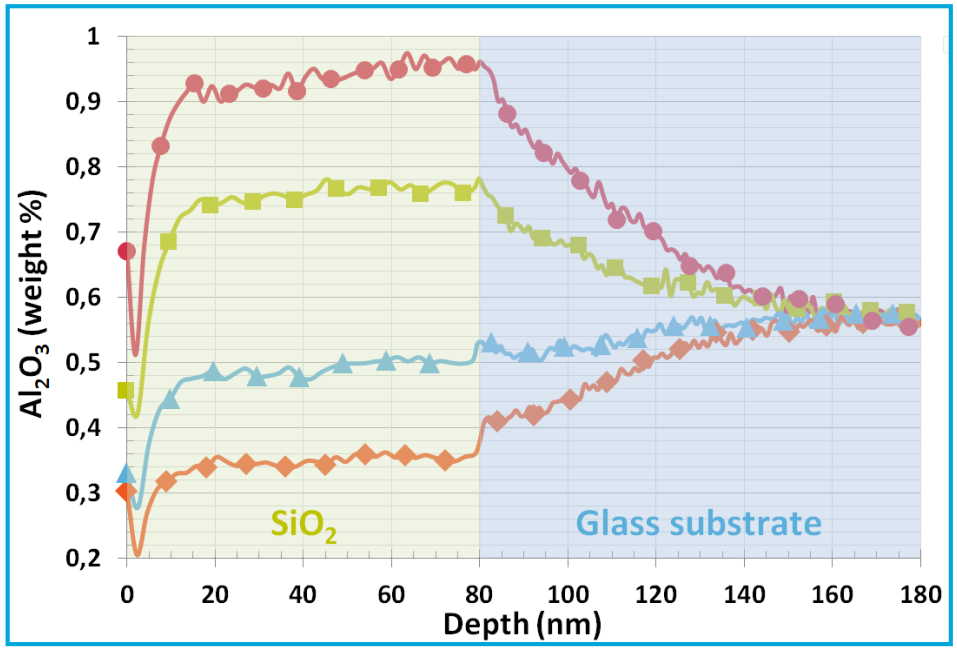
Influence of Al_2O_3 concentration on Na_2O migration

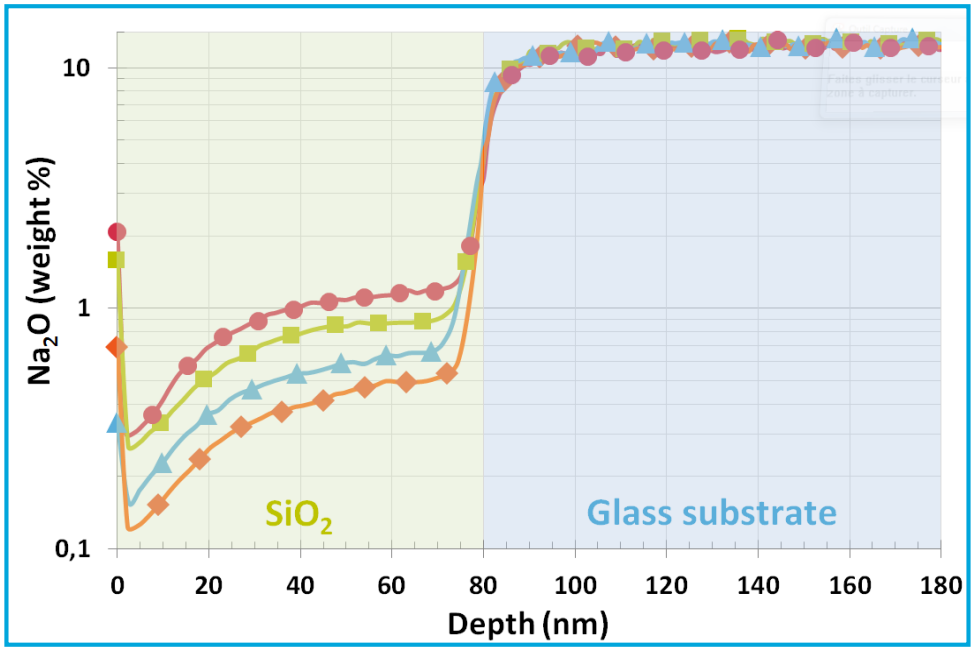
- Elaboration of a 100nm thick SiO_2 layer with a gradient of Al_2O_3

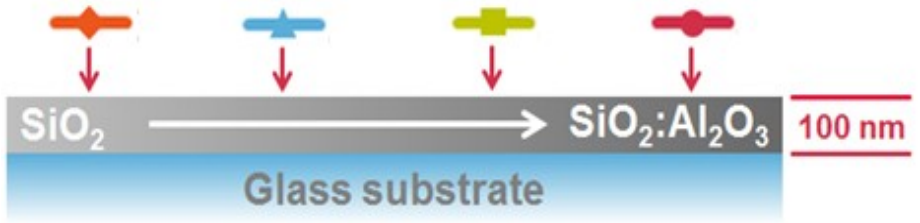


Influence of Al_2O_3 concentration on Na_2O migration

100 nm silica thin film after 1h @ 650°C



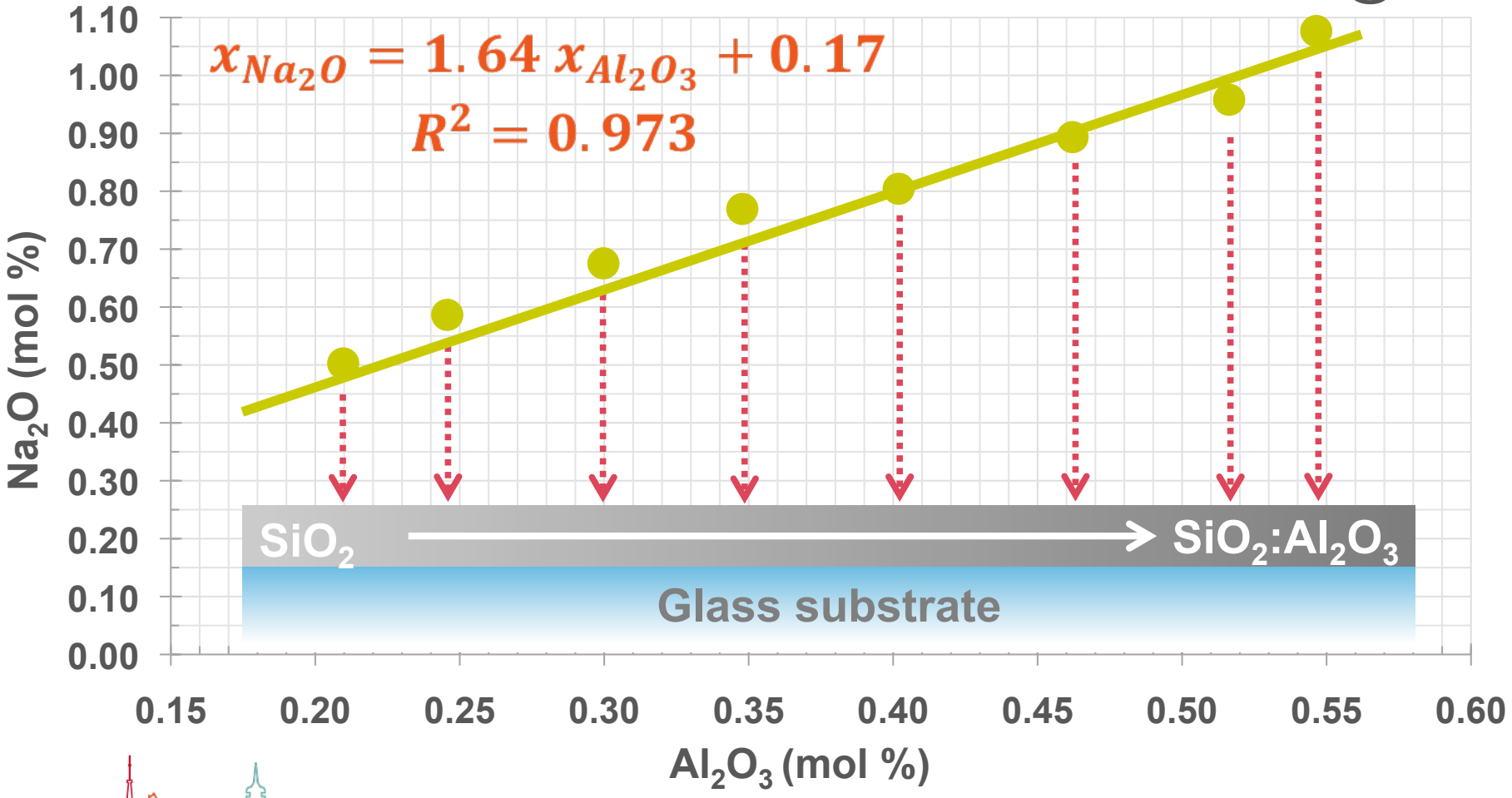




Which relationship between Na_2O and Al_2O_3 ?

Influence of Al_2O_3 concentration on Na_2O migration

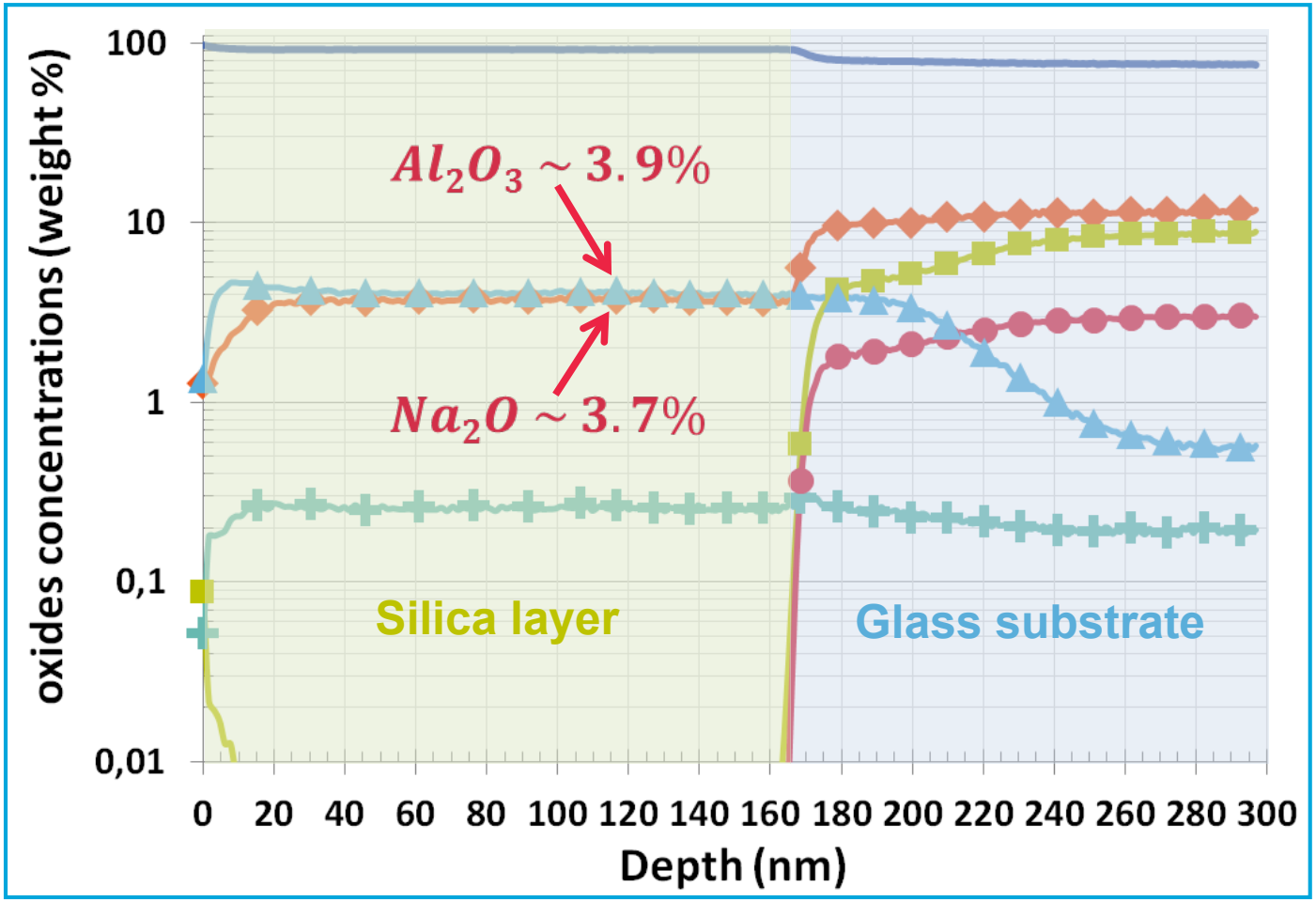
100 nm silica thin film after 1h @ 650°C



Is this linear relationship also true for silica thin films with more alumina?

Influence of Al_2O_3 concentration on Na_2O migration

250 nm silica thin film with 4% Al_2O_3 (weight %) - after 1h @ 650°C



Influence of Al_2O_3 concentration on Na_2O migration

- after 1h @ 650°C -

$$x_{Na_2O} = 1.48\, x_{Al_2O_3} + 0.22$$
$$R^2 = 0.998$$

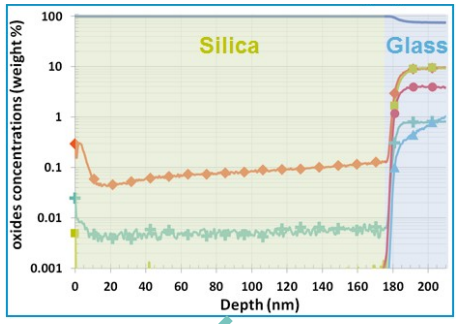
Na_2O (mol %)

4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00

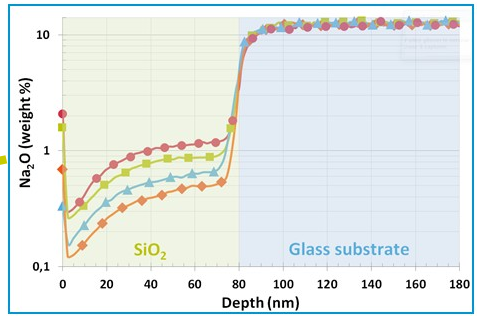
0.00 0.20 0.40 0.60 0.80 1.00 1.20 1.40 1.60 1.80 2.00 2.20 2.40

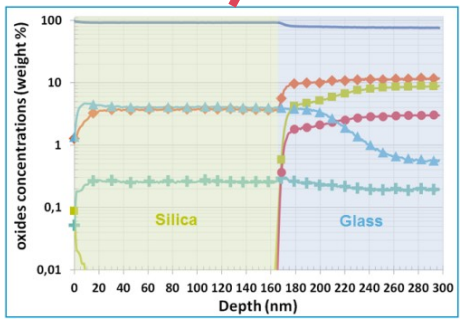
Al_2O_3 (mol %)

Without Al_2O_3



Al_2O_3 gradient



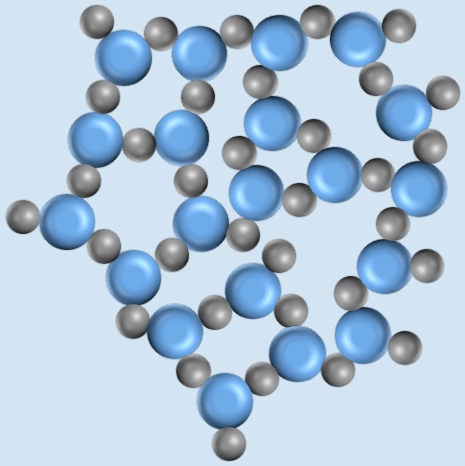
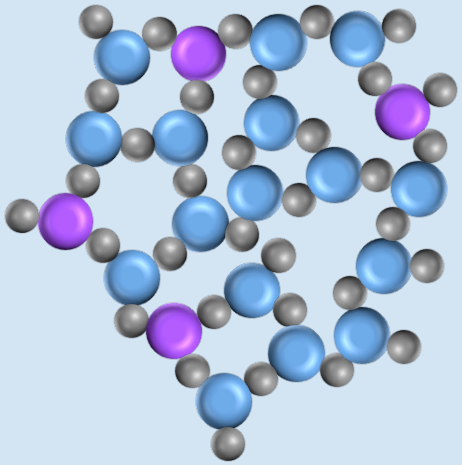
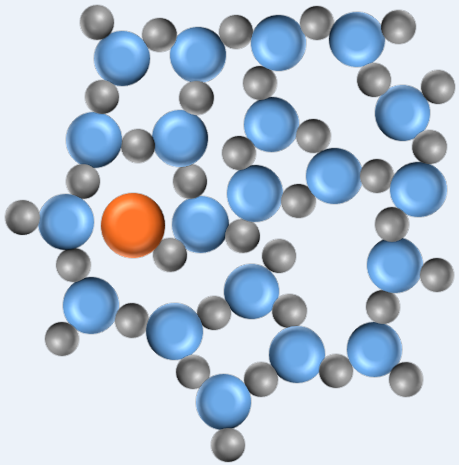
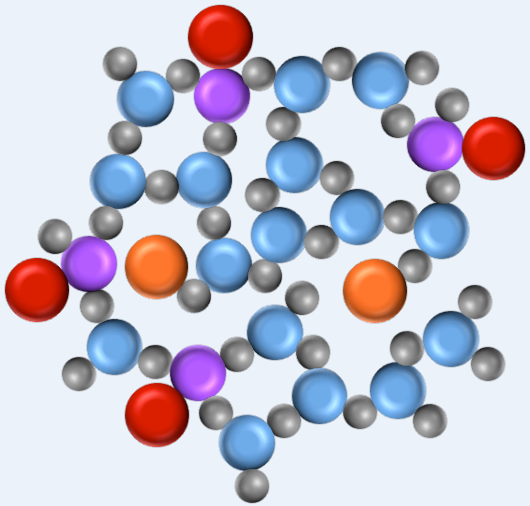


With 4% Al_2O_3

$\frac{Na}{Al} > 1$ → Na charge compensator or modifier ?

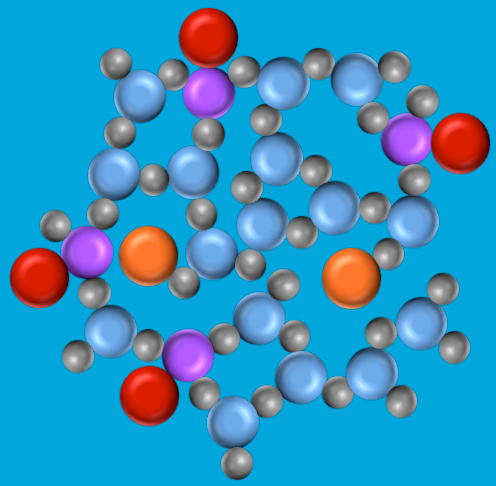
Is sodium charge compensator or network modifier in silica thin films after annealing ?

- 2D structure of silica network -

	Silica without Al	Silica with Al	
Before annealing			oxygen **Network formers:** Silicon (Si^{4+}) Aluminum (Al^{3+})
After annealing 1h@ 650°C	 Al_2O_2 = 0% Na_2O = 0.2%	 Na/Al ~ 1.5	**Network modifier:** Sodium (Na^+) **Charge compensator:** Sodium (Na^+)

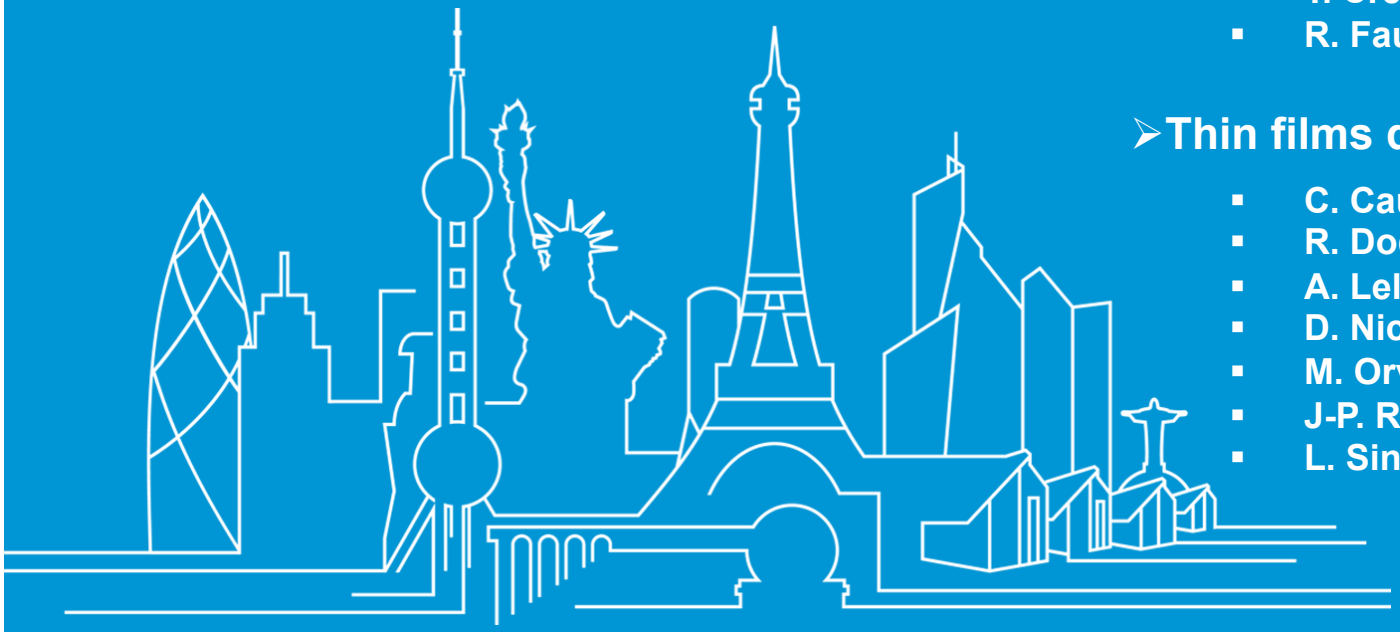
Conclusion

- **Sodium diffusion from glass substrates to silica thin films during annealing above Tg,**
- **Strong influence of Al concentration in silica on sodium migration,**
- **Na/Al ~ 1.5 after annealing :**
  - 1 Na^+ - charge compensator for Aluminum ?
  - 0.5 Na^+ - network modifier ?



- **Sodium concentration after annealing higher than theoretical predictions**
  - Influence of defects in silica thin films on sodium diffusion ?

Acknowledgements



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SAINT-GOBAIN 350 RAISONS DE CROIRE EN L'AVENIR