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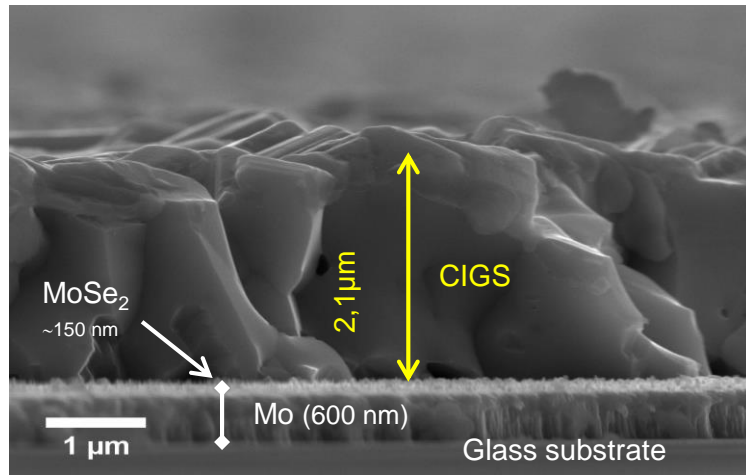
Using X-ray induced Auger electron spectroscopy transitions to explore the surface reactivity of CIGS: In and Ga degradation kinetics at different probing depths

Anna Gagliardi,¹ Neal Fairley,² Solène Béchu¹





¹ *Institut Lavoisier de Versailles (ILV), Versailles Saint-Quentin-en-Yvelines University, CNRS, UMR 8180, Versailles, France.*

² *Casa Software Ltd, Bay House, 5 Grosvenor Terrace, Teignmouth, Devon TQ14 8NE, United Kingdom.*

CuIn_{0.7}Ga_{0.3}Se₂: a solar device material

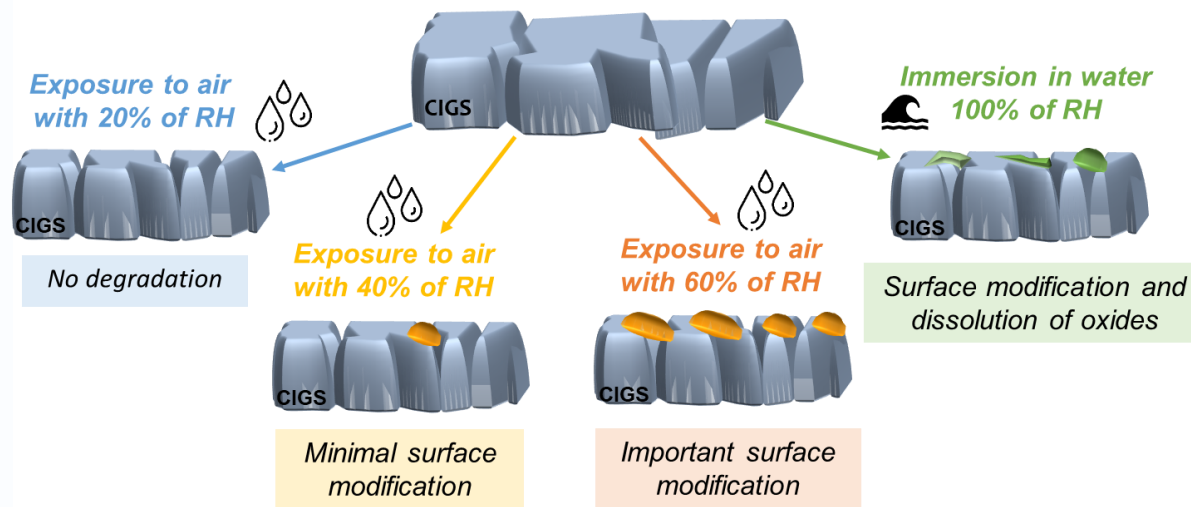


- Cu(In_xGa_{1-x})Se₂ (CIGS): solar absorber with efficiencies up to 23.6%
- **Long-term stability of the cell:** main factors responsible for degradation

- Relative humidity 
- Temperature 
- Illumination 
- Gaseous environment 

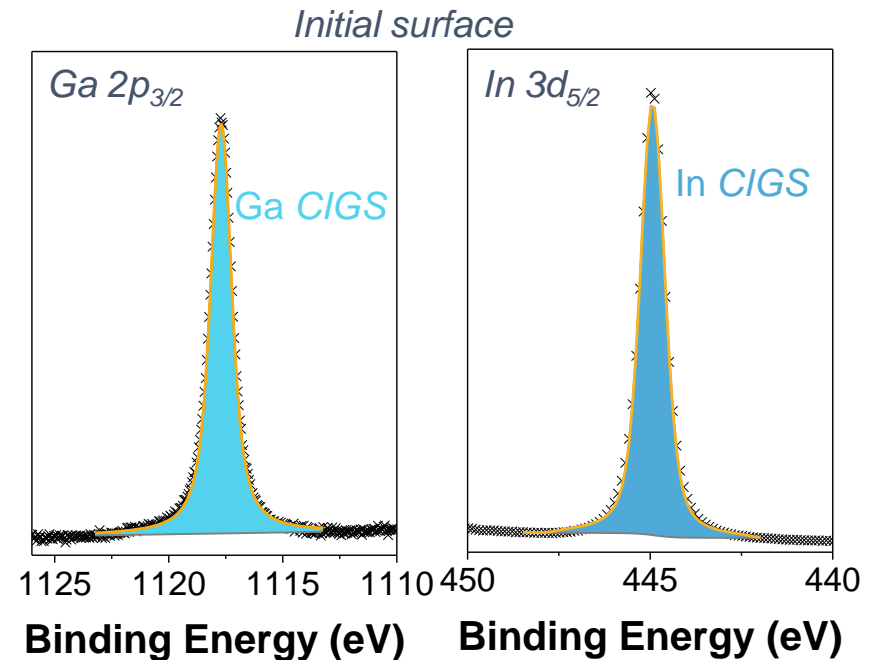
M. Theelen, F. Daume, *Sol. Energy.*, **2016**, 133, 586–627

Degradation of CIGS material itself?



Influence of RH for CIGS surface reactivity

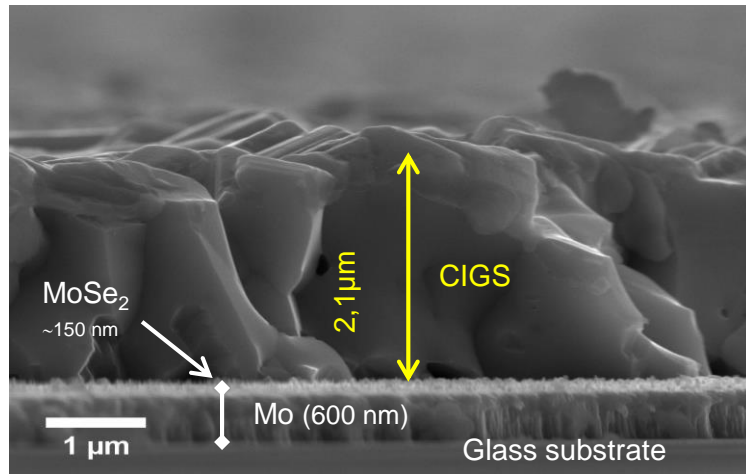
Surface modifications?



Kinetics of degradation?

$$\frac{Ga_{ox}}{Ga_{CIGS}} \quad \& \quad \frac{In_{ox}}{In_{CIGS}}$$

CuIn_{0.7}Ga_{0.3}Se₂: a solar device material

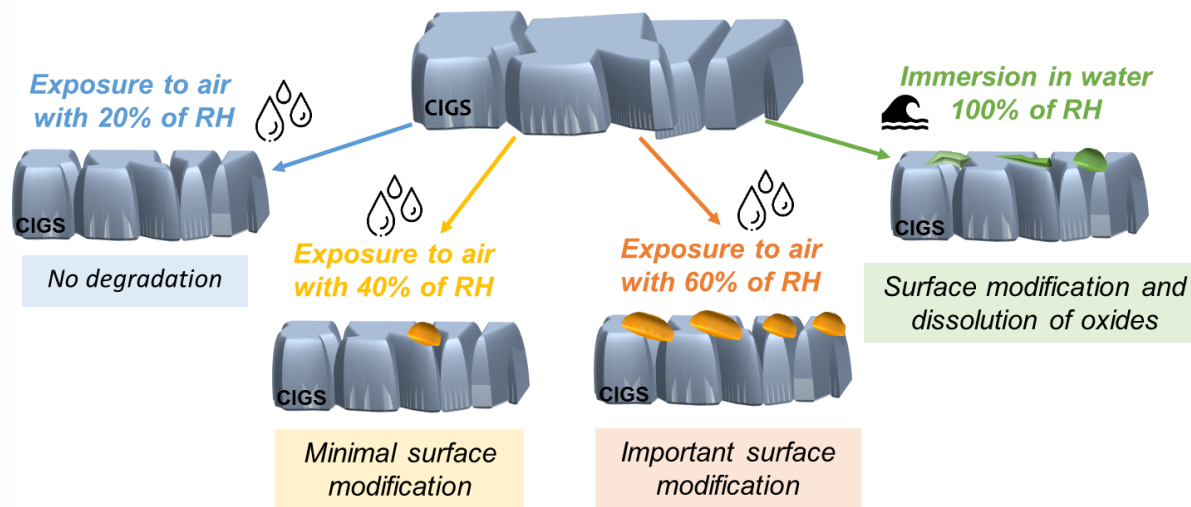


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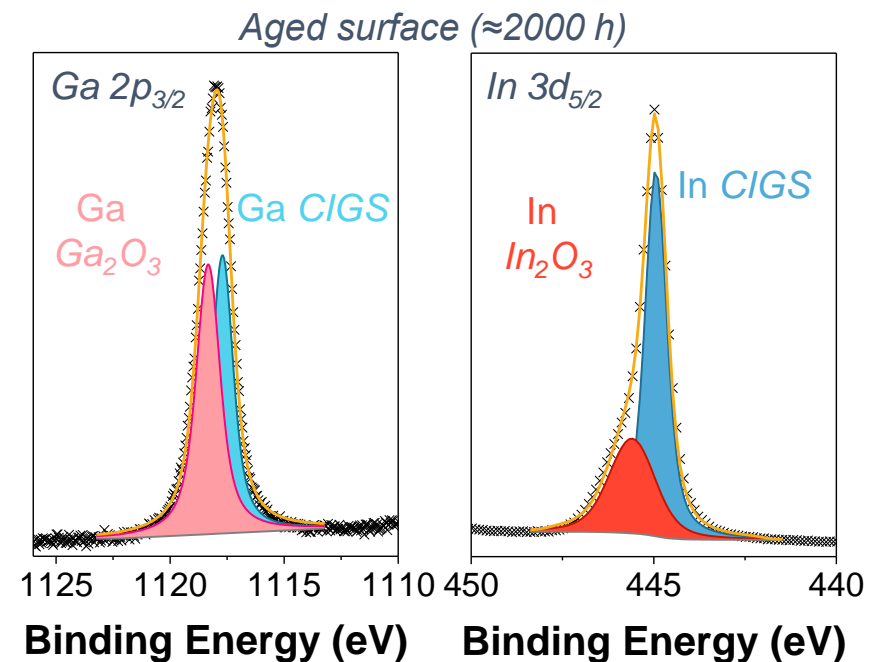
M. Theelen, F. Daume, *Sol. Energy.*, **2016**, 133, 586–627

Degradation of CIGS material itself?



Influence of RH for CIGS surface reactivity

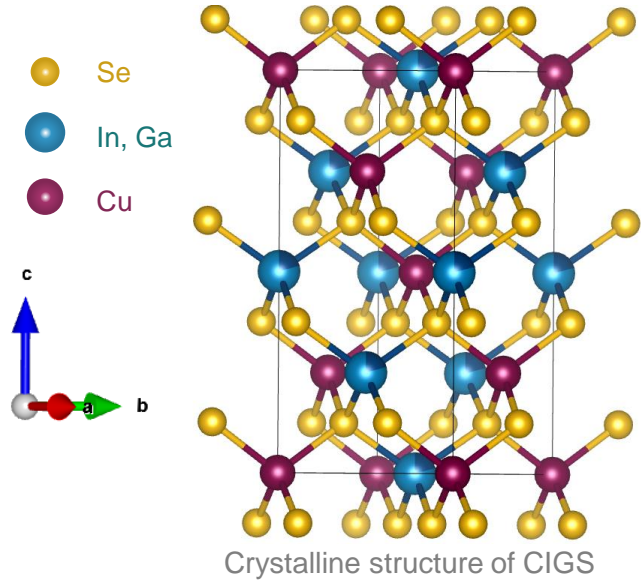
Surface modifications?



Kinetics of degradation?

$$\frac{Ga_{ox}}{Ga_{CIGS}} \quad \& \quad \frac{In_{ox}}{In_{CIGS}}$$

Why using X-AES transitions? The case of $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$

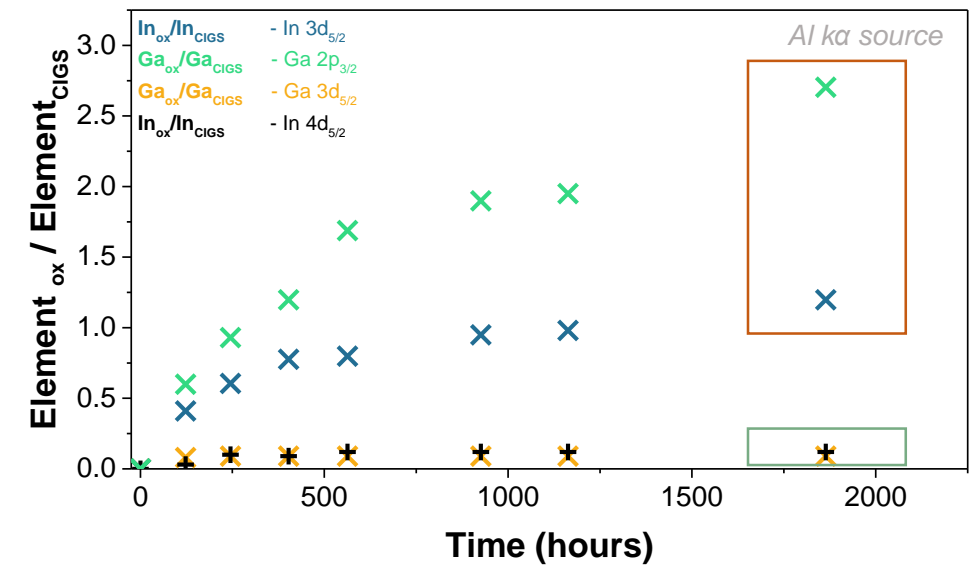


Evolution of In and Ga under aging?



most decomposed photopeaks

photopeaks with the same probing depth



S. Béchu et al., Appl. Surf. Sci., 2022, 576, 151898

Atomic level
Binding Energy
Kinetic Energy
Depth probed

In $M_{4,5}N_{4,5}N_{4,5}$
1105 - 1068
381 - 417
≈ 3 nm

In 3s
826
660.6
≈ 4 nm

In 3p
702 - 664
822.6
≈ 5 nm

In 3d
451 - 443
1035.6 - 1043.6
≈ 6 nm

In 4s
122
1364.6
≈ 7 nm

Similar kinetics

In 4d
16
1470.6
≈ 8 nm

Ga 2s
1298
188.6
≈ 2 nm

Ga 2p
1143 - 1116
343.6 - 370.6
≈ 3 nm

Different kinetics due to the different probing depths

Ga $L_3M_{4,5}M_{4,5}$
430 - 410
1058 - 1075
≈ 6 nm

Ga 3s
158
1328.6
≈ 7 nm

Ga 3p
107 - 103
1379.6 - 1383.6
≈ 8 nm

Ga 3d
18
1468.6
≈ 8 nm

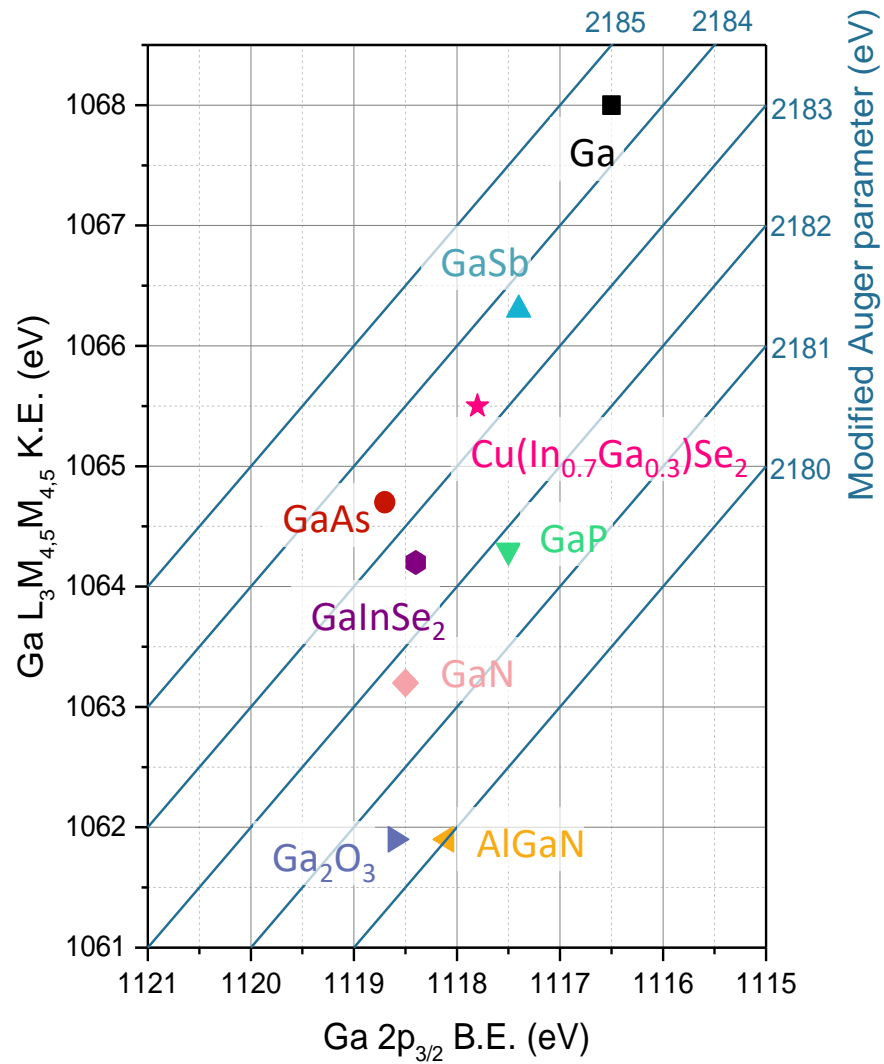
Extreme surface (≈2 - 3 nm)

Sub surface (≈8 nm)

B.E and K.E of In and Ga elements for an Al Kα source
Probing depths are calculated with the TPP2M formula for CIGS

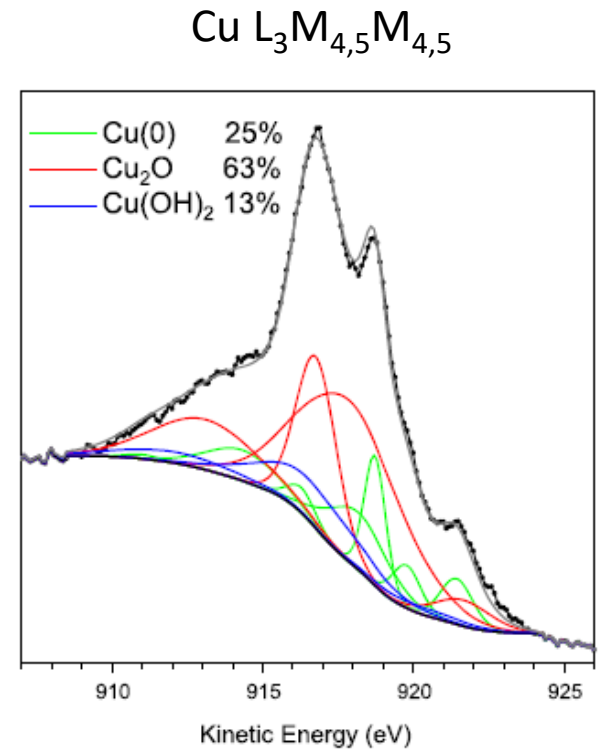
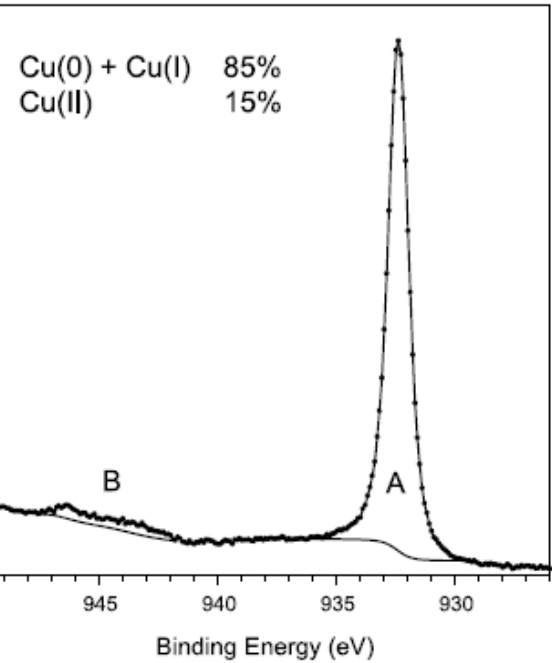
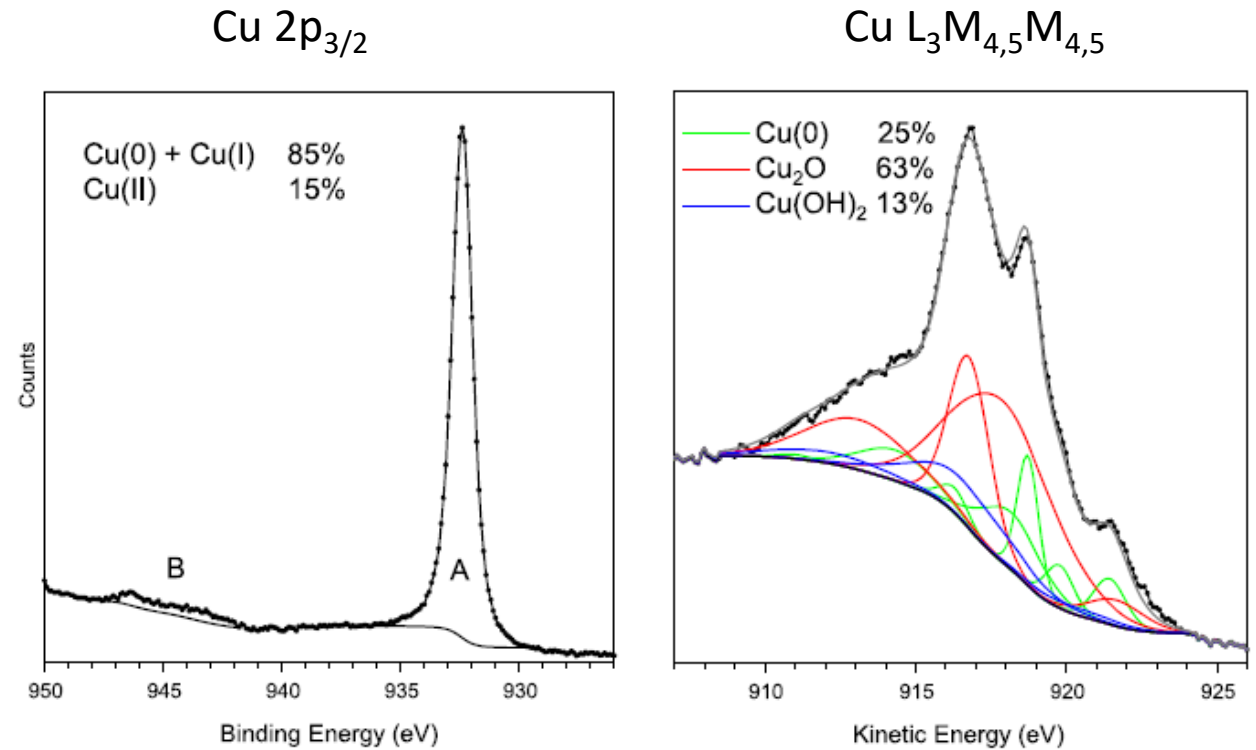
The X-AES transitions: phase identifications and quantification

Wagner plot and modified auger parameter



Ga 2p_{3/2} – Ga LMM Wagner plot

Quantifications with X-AES lines



Advanced analysis of copper X-ray photoelectron spectra

Mark C. Biesinger*

SURFACE and
INTERFACE
ANALYSIS

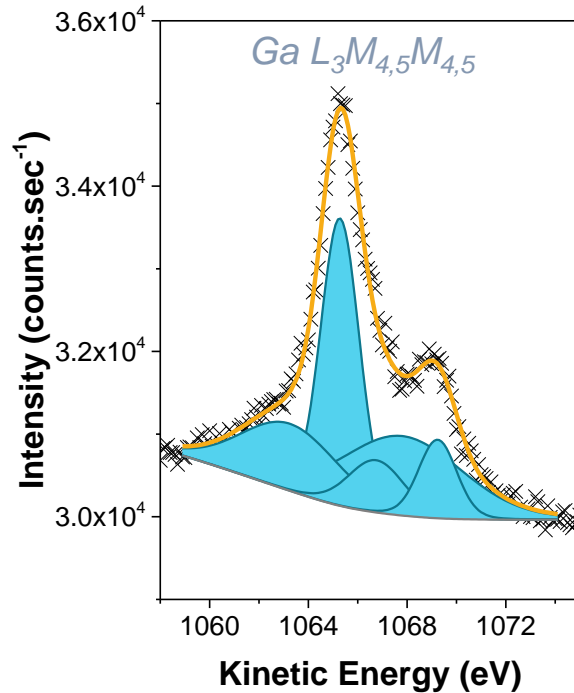
Surf. Interface Anal. 2017, 49, 1325–1334

Non-linear versus linear least square decomposition

2 methods to decompose the X-AES transitions

Non-linear least square decomposition

Arbitrary use of Gaussian Lorentzian curves to simulate one chemical environment



NLLS

Ga L₃M_{4,5}M_{4,5} non-linear least square decomposition for CIGS

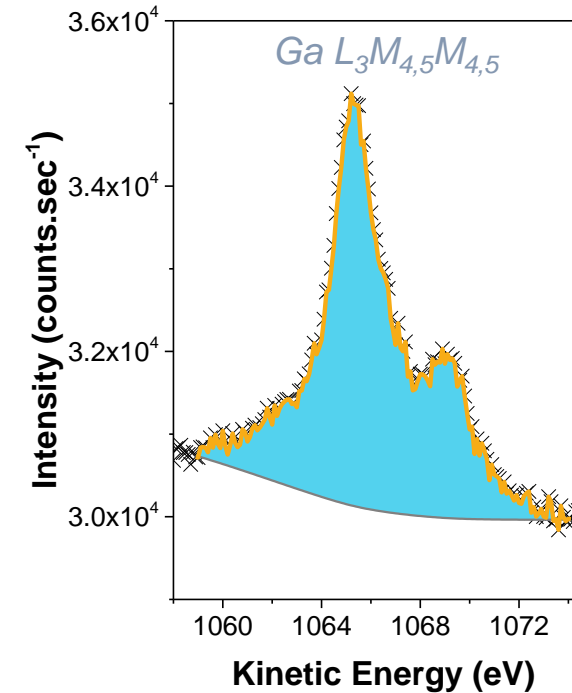
✓ Possibility of slight adjustments for the positions, the FWHM values

✗ For a mix of chemical environments, necessity of many arbitrary peaks → possible error

J. J. Moré, *Numer. Anal.*, **1978**, 630, 105

Linear least square decomposition

Implementation of a spectral shape



LLS

Ga L₃M_{4,5}M_{4,5} linear least square decomposition for CIGS

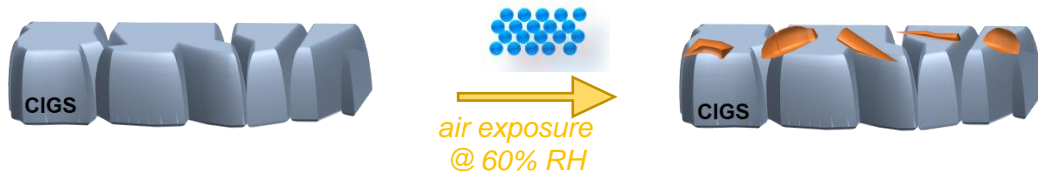
✓ Easy to implement with different chemical environments

✗ No FWHM or position adjustments for a series of fits

G. H. Golub and C. Reinsch, *Numer. Math.*, **1970**, 14, 403

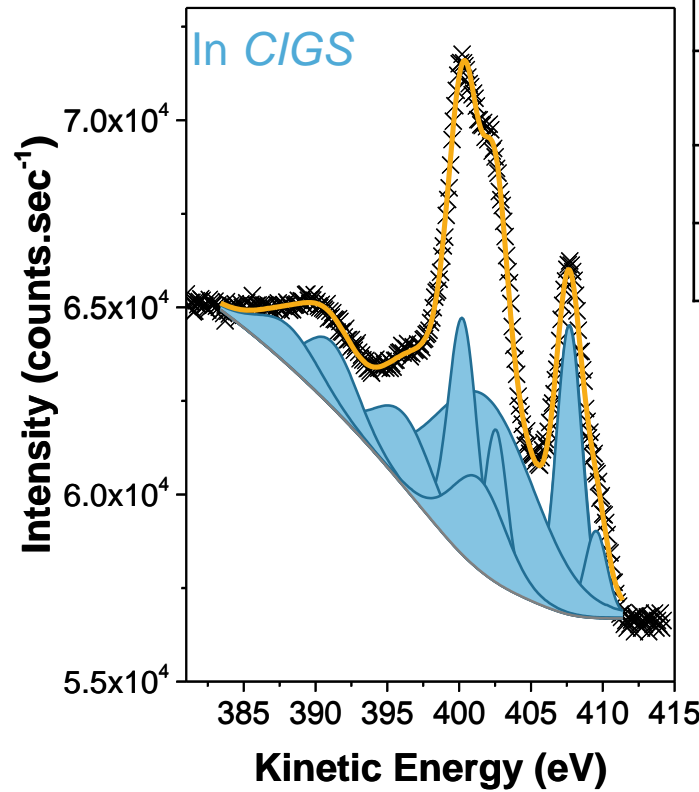
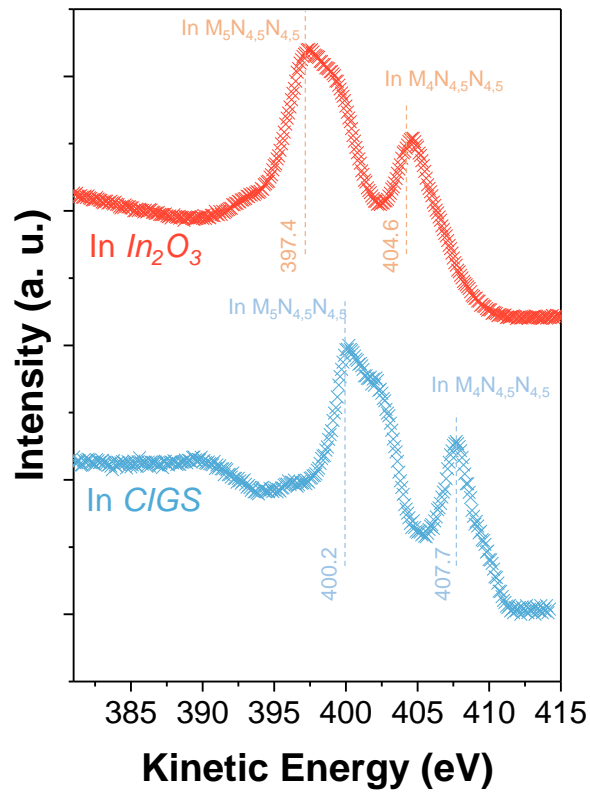
NLLS decomposition of CIGS X-AES transitions

Modifications induced by the aging



Growth of In_2O_3 and Ga_2O_3 phases in addition to the CIGS one
Identified with the modified Auger parameter

$\text{In } M_{4,5}N_{4,5}N_{4,5}$ X-AES line



	PP
Position	407.7 ± 0.1
FWHM	2.10 ± 0.05
Area	/

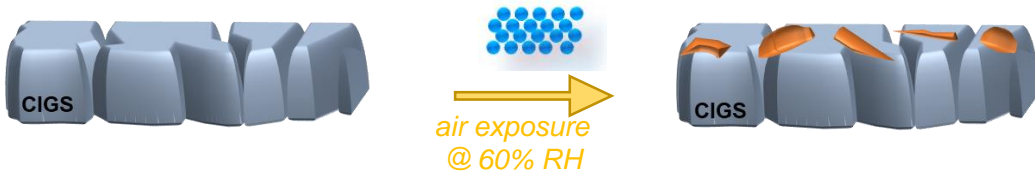
Peak 6	Peak 7	Peak 8	Peak 9
PP-7.4	PP-11.5	PP-16.5	PP-19.5
PP*1.11	PP*2.34	PP*2.04	PP*2.45
PP*0.91	PP*0.59	PP*0.46	PP*0.34

Thermo Nexsa
P.E. 20 eV; step size: 0.1 eV; dwell time: 100 ms
Bckg: U2 Tougaard – resolution 0.52 eV

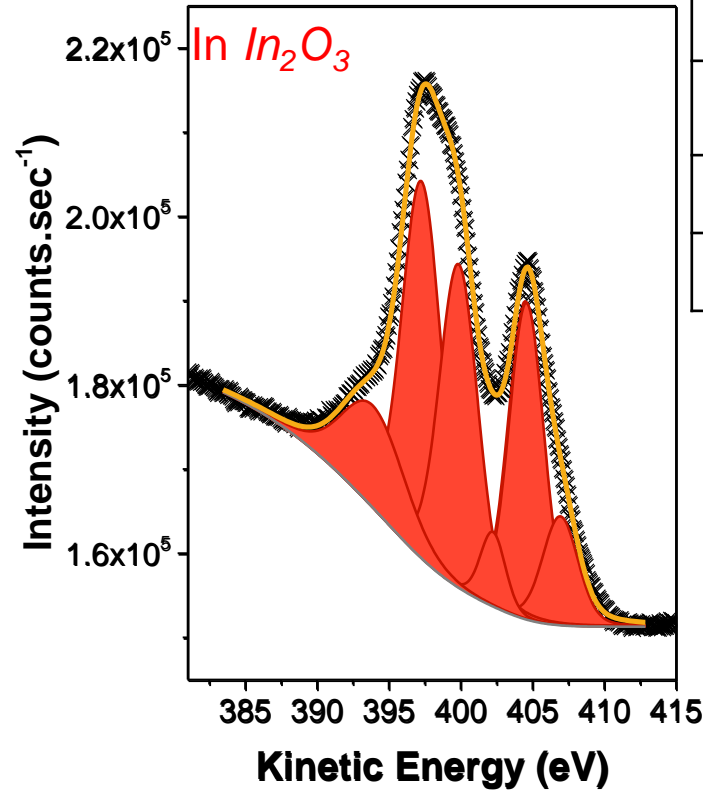
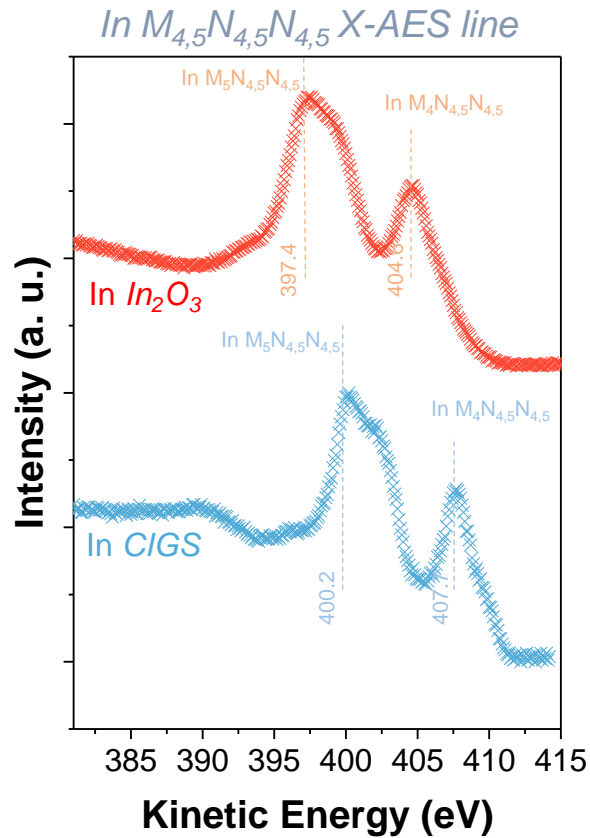
9 arbitrary peaks to decompose the $\text{In } M_{4,5}N_{4,5}N_{4,5}$ X-AES transition of CIGS
→ 5 for the $\text{Ga } L_3M_{4,5}M_{4,5}$ X-AES transition of CIGS

NLLS decomposition of CIGS X-AES transitions

Modifications induced by the aging



Growth of In_2O_3 and Ga_2O_3 phases in addition to the CIGS one
Identified with the modified Auger parameter



	PP
Position	404.5 ± 0.1
FWHM	2.85 ± 0.05
Area	/

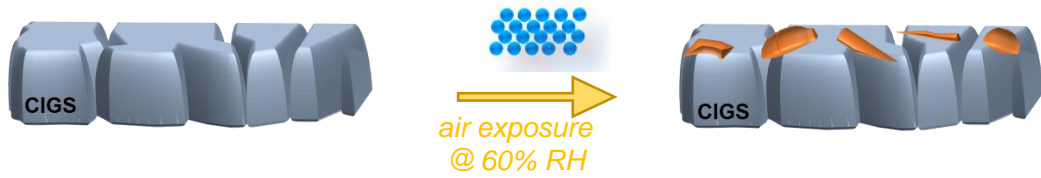
Peak 5	Peak 6
PP-7.3	PP+10.7
PP*1.13	PP*1.81
PP*1.34	PP*0.58

Thermo Nexsa
P.E. 20 eV; step size: 0.1 eV; dwell time: 100 ms
Bckg: U2 Tougaard – resolution 0.52 eV

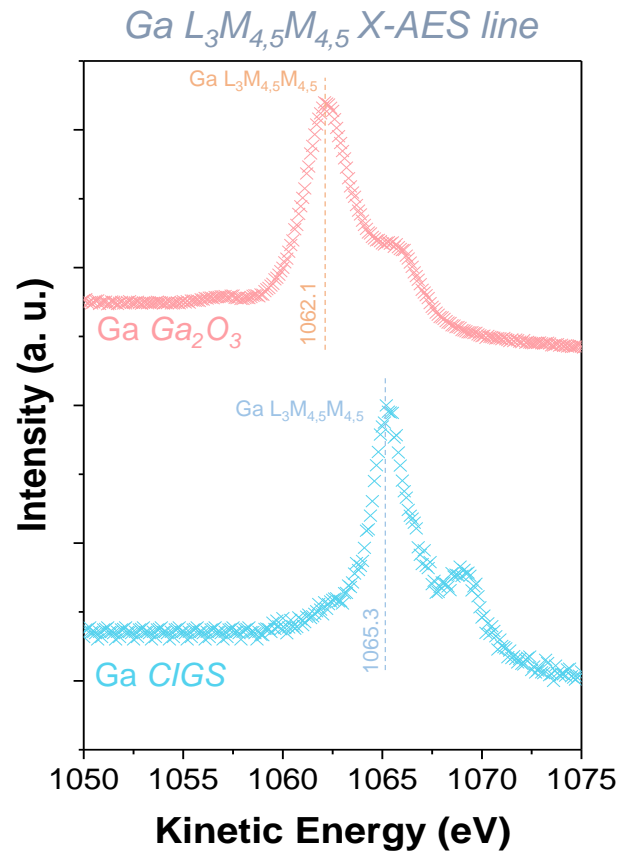
6 arbitrary peaks to decompose the
 $\text{In } M_{4,5}N_{4,5}N_{4,5}$ X-AES transition of In_2O_3
→ 5 for the $\text{Ga } L_3M_{4,5}M_{4,5}$ X-AES transition of Ga_2O_3

LLS decomposition of CIGS X-AES transitions

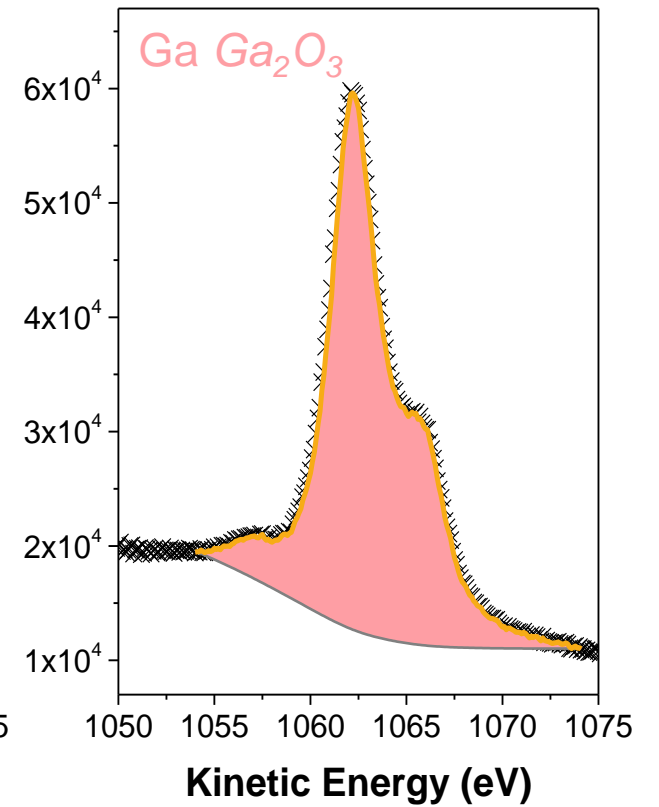
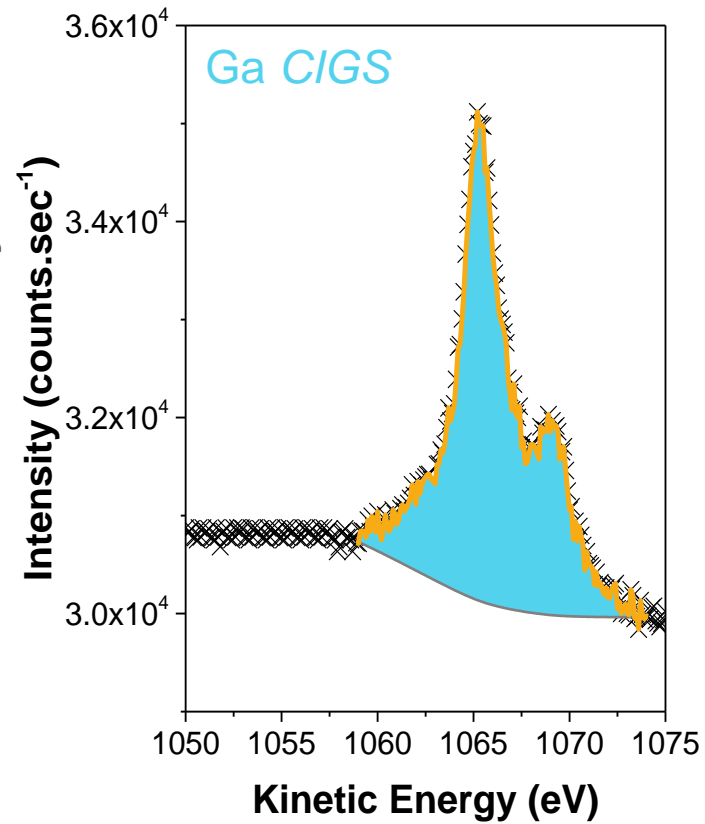
Modifications induced by the aging



Growth of In_2O_3 and Ga_2O_3 phases in addition to the CIGS one
Identified with the modified Auger parameter

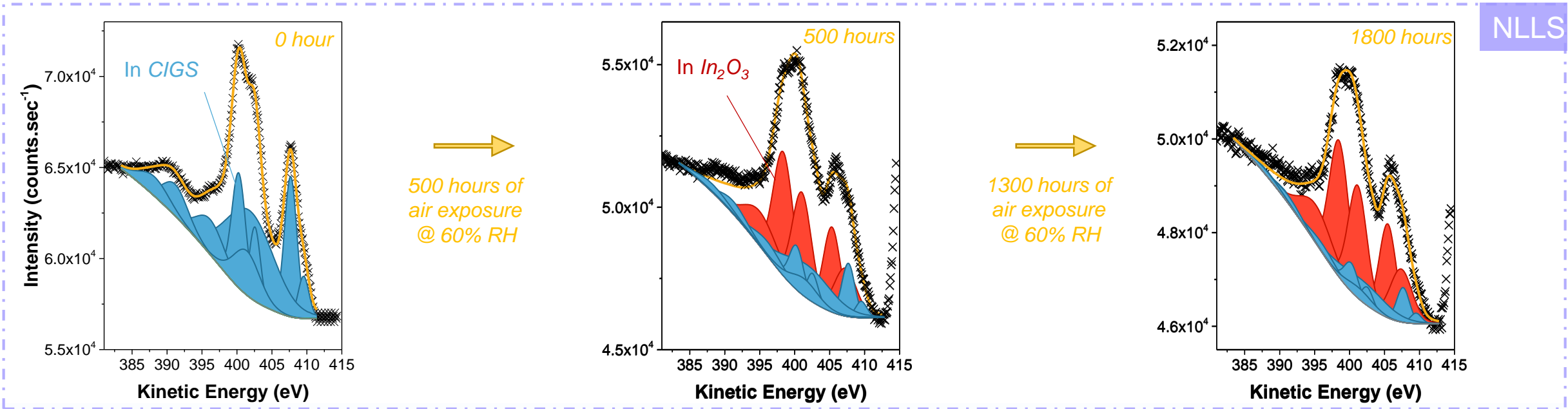
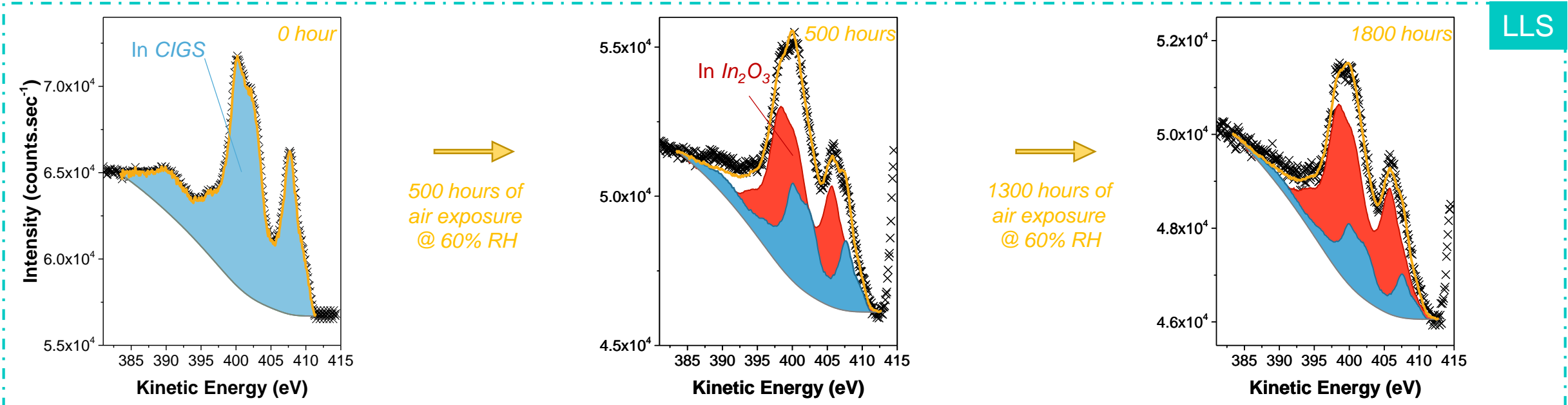


Use of the experimental spectral shape to define the chemical environments

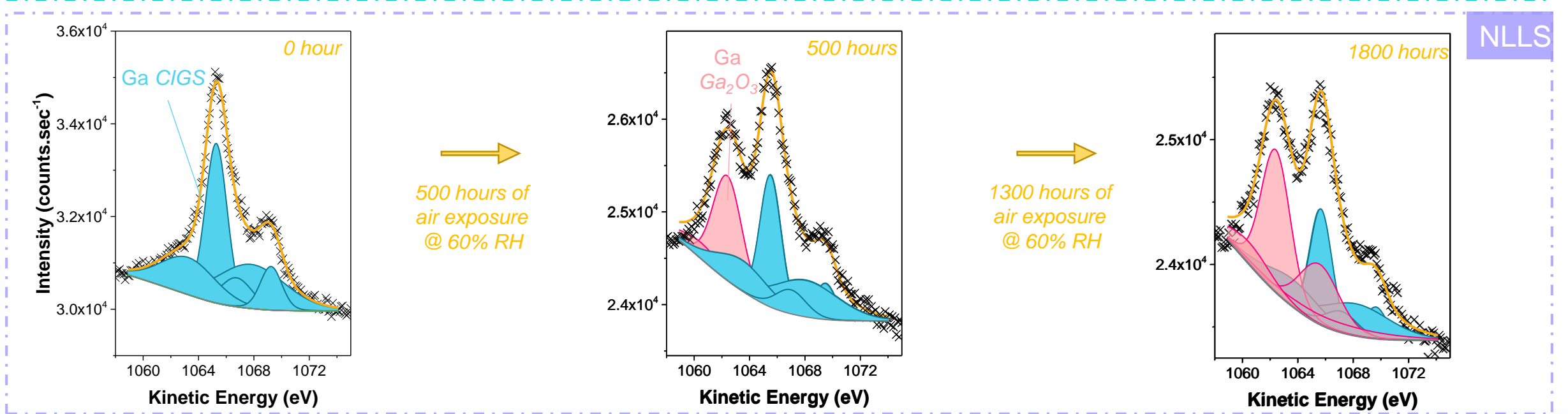
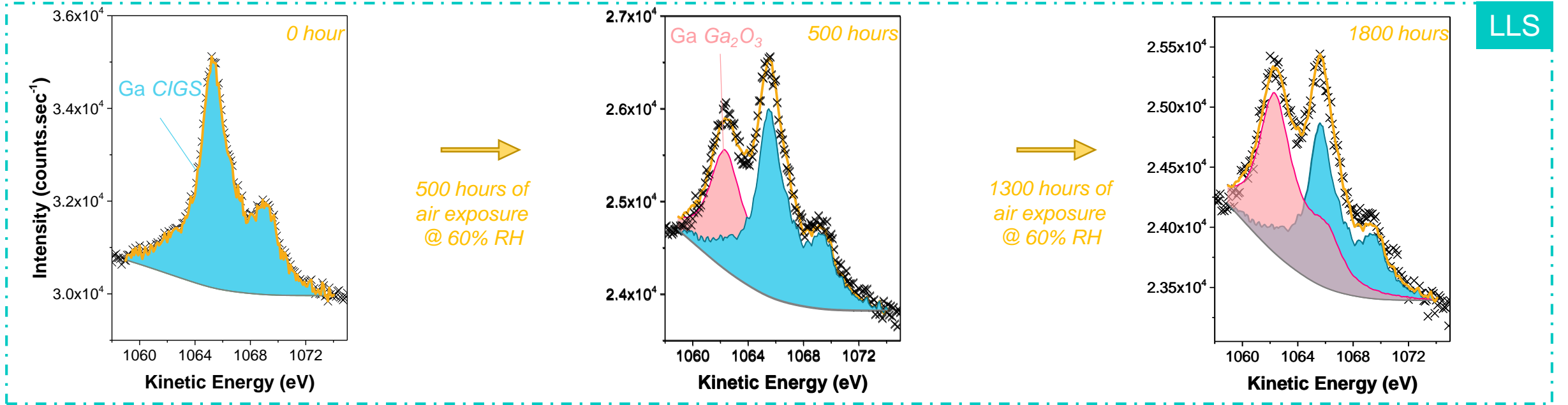


Thermo Nexsa
P.E. 20 eV; step size: 0.1 eV; dwell time: 100 ms
Bckg: U2 Tougaard – resolution 0.52 eV

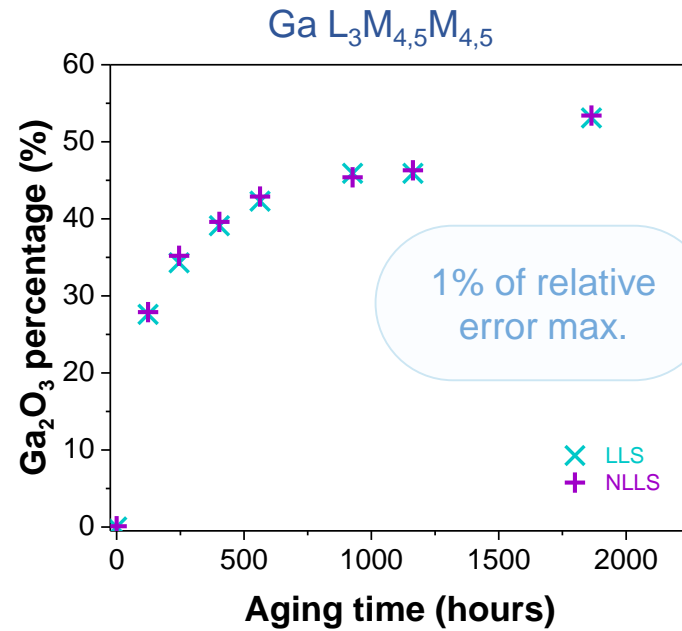
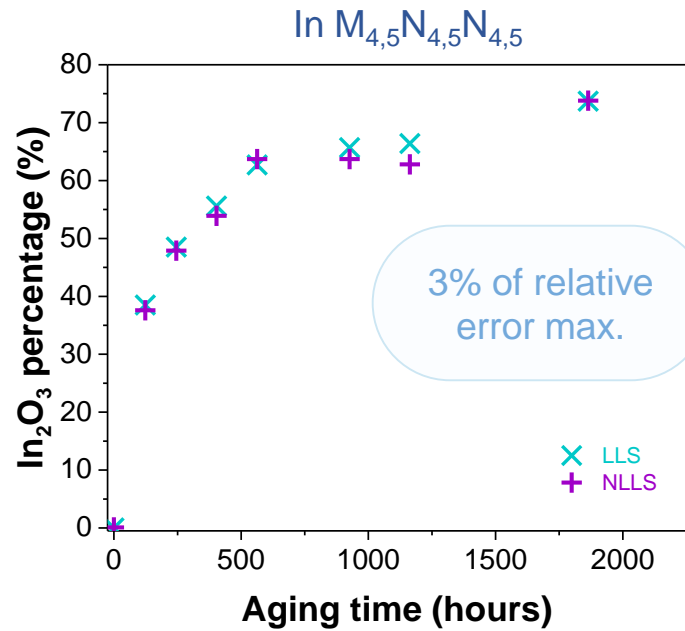
Evolution of the In $M_{4,5}N_{4,5}N_{4,5}$ X-AES transitions over air aging



Evolution of the Ga $L_3M_{4,5}M_{4,5}$ X-AES transitions over air aging

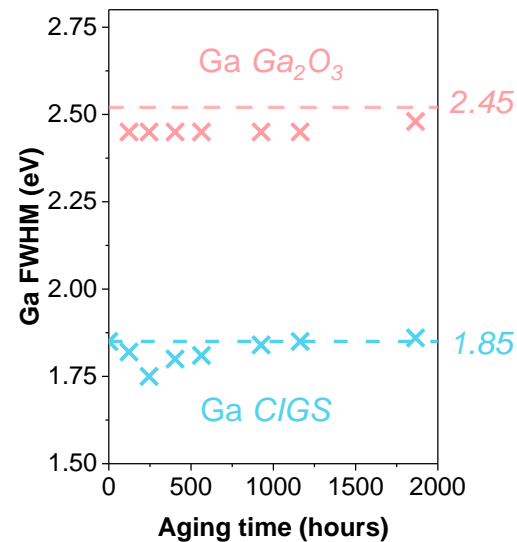
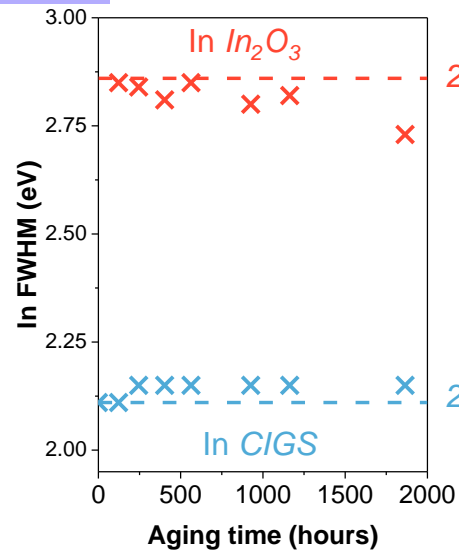


LLS and NLLS decompositions comparison



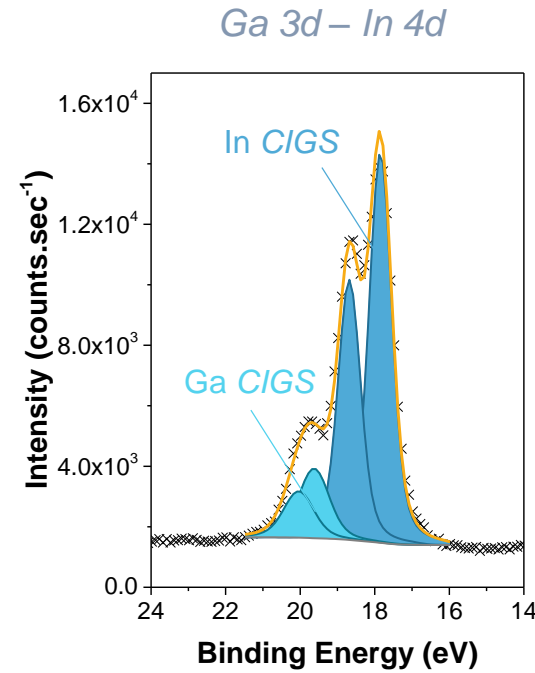
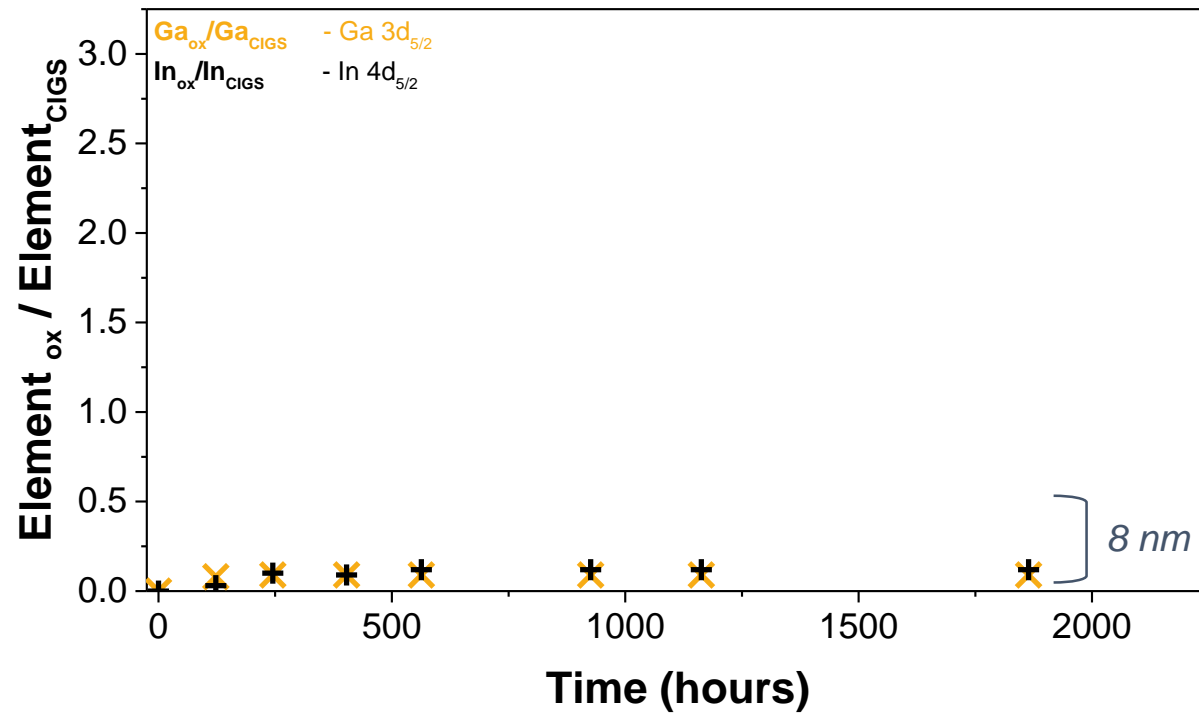
Linear least squares decomposition and non-linear least squares decomposition provide **similar results for X-AES transitions.**

NLLS Evolution of FWHM parameter

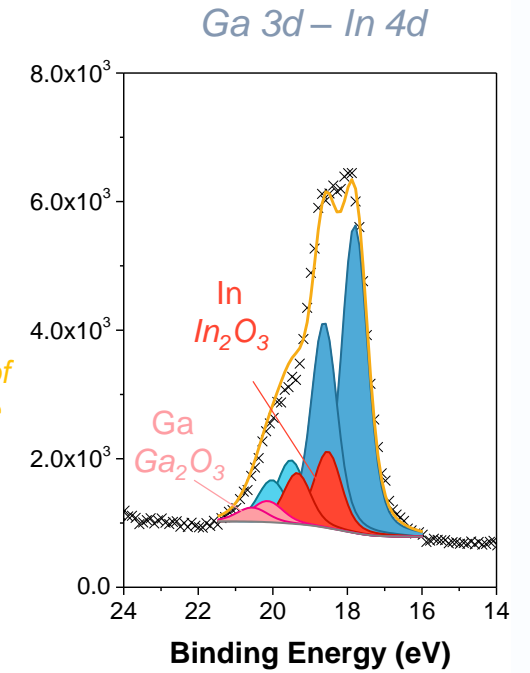


Only small FWHM variations observed during the aging

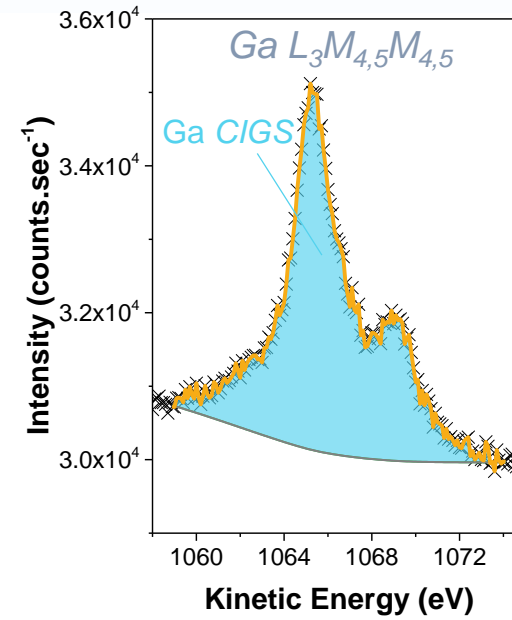
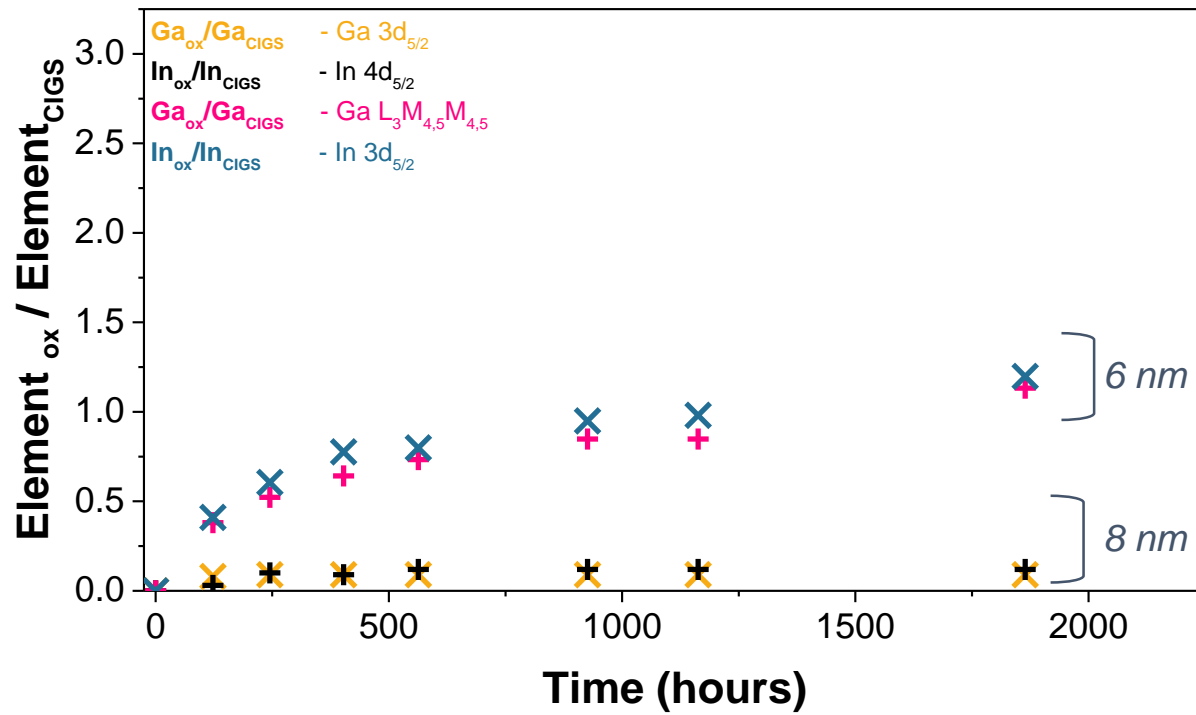
Application to CIGS aging



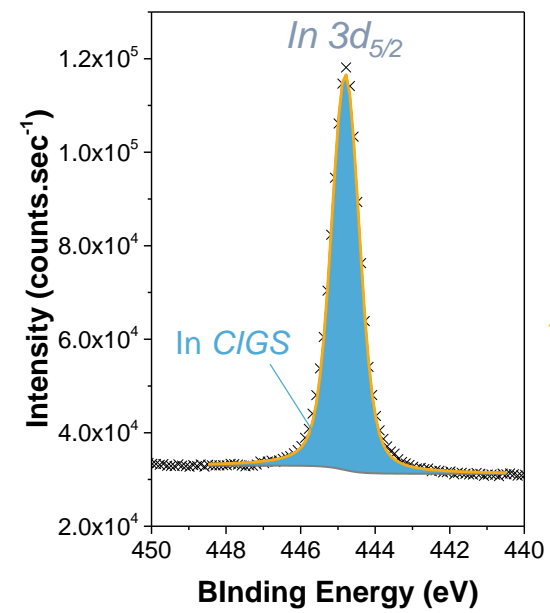
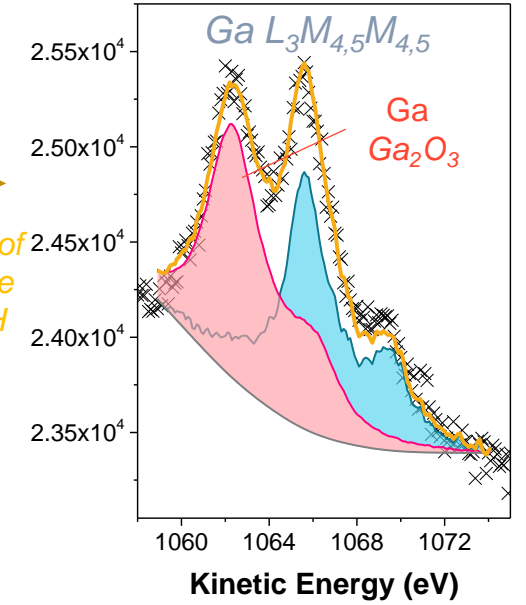
1800 hours of air exposure @ 60% RH



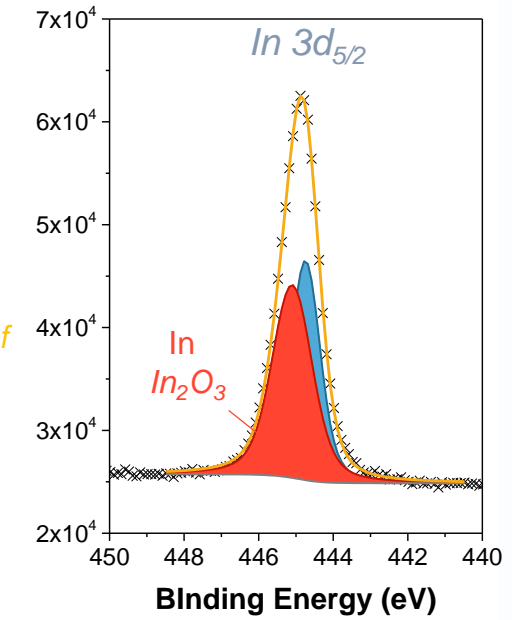
Application to CIGS aging



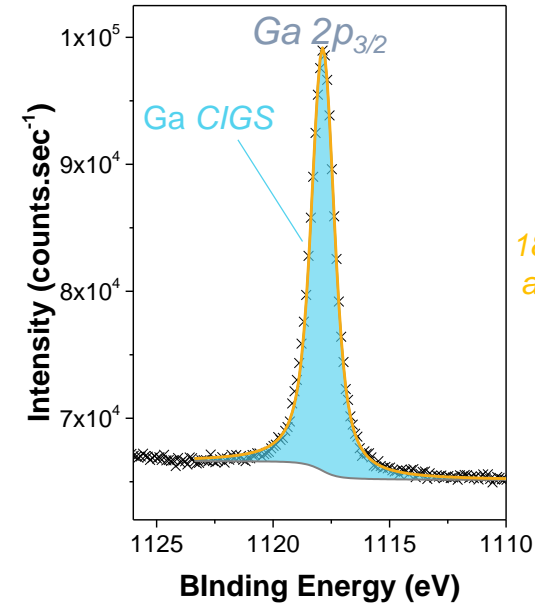
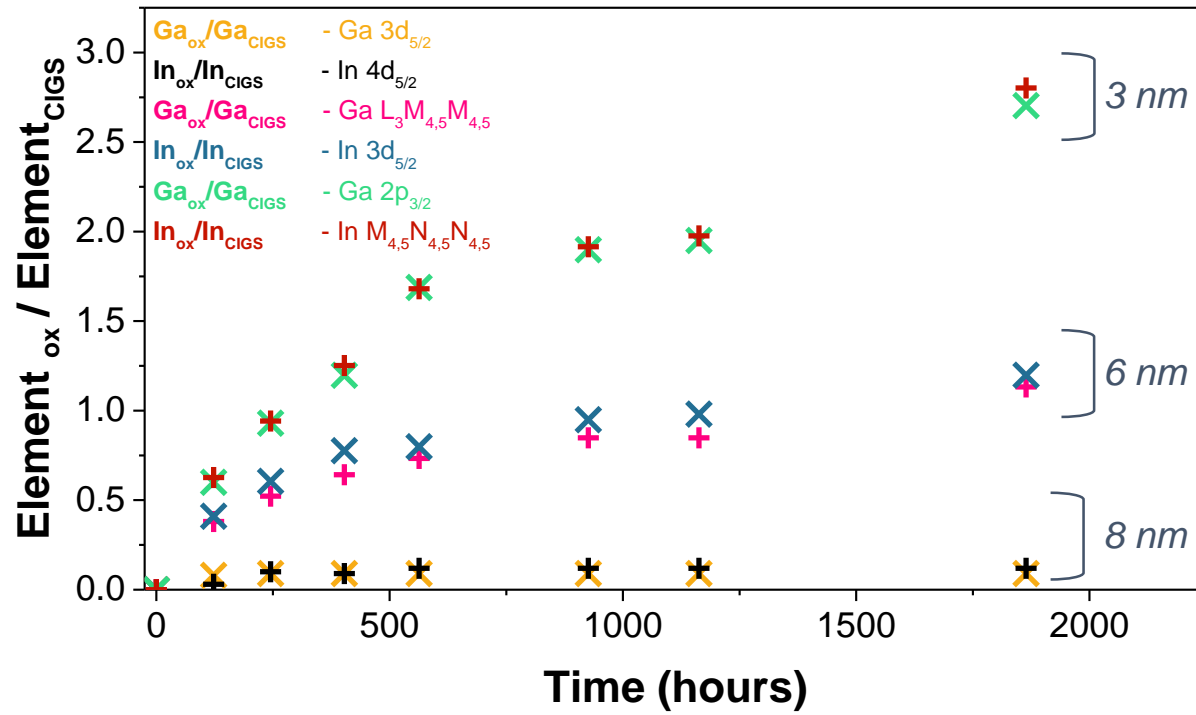
1800 hours of air exposure @ 60% RH



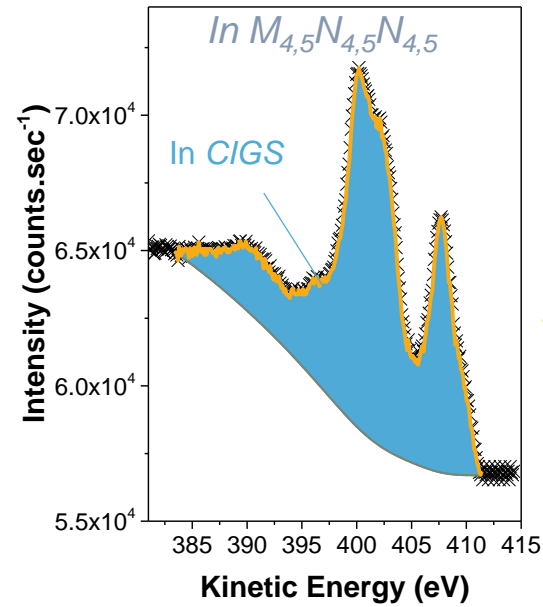
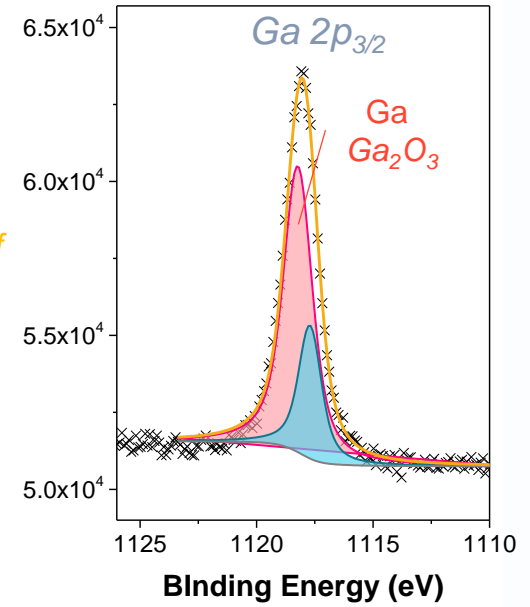
1800 hours of air exposure @ 60% RH



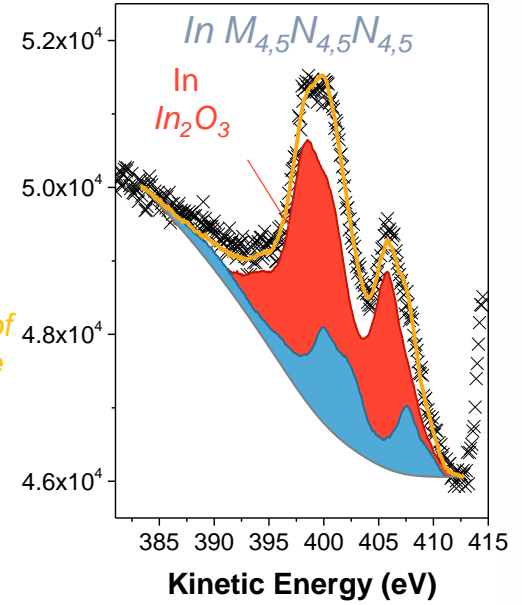
Application to CIGS aging



1800 hours of air exposure @ 60% RH



1800 hours of air exposure @ 60% RH



Conclusions

Decomposition of X-AES lines → 2 methods with advantages and disadvantages giving similar results

LLS

- Easy to use, with only one shape per chemical environment
- No possibility to provide any adjustments with aging (FWHM values...)



NLLS

- Possibility to perform evolution along with air aging (FWHM values, positions...)
- Up to 15 arbitrary peaks to simulate two chemical environments



Application to CIGS aging → access to a depth range probed for 2 elements within the same scale

- 3 different depths probed for Ga and In: 3, 6, and 8 nm using XPS photopeaks and X-AES lines
- Progressive oxidation from the extreme surface to the sub-surface, with a higher level of oxidation on the extreme surface





Neal Fairley



Anna Gagliardi

THANK YOU

Want to know more about the degradation of the sub surface of CIGS?
Don't miss Anna Gagliardi's talk
This afternoon @ 2.50 p.m.
11 NRG

S.B. and A.G. thank the French Agence Nationale de la Recherche for funding under the contract ANR-22-CE50-0008-01