

## Supporting information

### Nanosized Surface Films on Brass Alloys by XPS and XAES

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#### Details on the curve fitting procedure of XAES data:

The spectra of pure reference compounds were acquired applying the same analysis conditions applied for the real samples: i.e. for sputtered, mechanically polished and as received CuZn37. The line-shapes of the various components were thus obtained on samples having a very well defined stoichiometry and they were exploited for the curve synthesis of the signals acquired on the brass samples following different surface treatments.

Here, some examples of the spectra acquired on pure copper and zinc and on their commercial high purity oxides are shown (Figures S.I. 1 – 5), together with their curve fitting parameters.

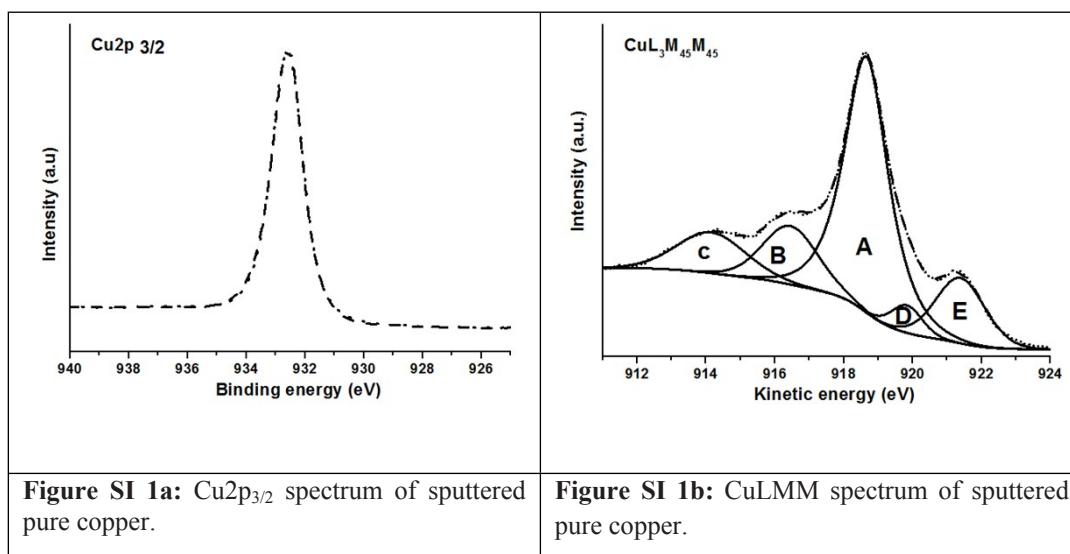
Following the usual XPS curve fitting procedure, the line-shapes of copper and zinc in the as received, mechanically polished and sputtered alloys were fixed in agreement with the line-shapes empirically determined in the reference compounds (Tables S.I.1 – S.I. 5).

The different line-shapes observed for the same element in different compounds are due to differences in the electronic configuration of the atoms involved in the electron emission process: ZnLMM signals acquired on pure Zn and ZnO (Figure SI 2b and SI 5b respectively), for example, show different Gaussian/Lorentzian ratio, due to the different electronic structure.

Not only the line-shape vary with the electronic structure of the atoms, but also the full-width at half maximum (FWHM). The broadening of the signal is due to instrumental factors (which in our case should be the same for all the samples since both the reference compounds and the brass samples were acquired under the same instrument set-up) and to the natural width of the electron level, which is inversely proportional to the lifetime of excited state.

For example, the different lifetime of the two holes final state determines the differences in the FWHM values of the CuLMM signals in CuO and Cu metal. Different lifetimes are related to different electronic configuration of the valence levels: Cu met and Cu (I) are  $3d^{10}$ , while Cu (II) is a  $3d^9$ . According to literature such a difference in the valence electrons may justify both the peak broadening of Cu LMM components in CuO (Table S.I. 3) compared to Cu met (Table S.I. 1) (and  $\text{Cu}_2\text{O}$ , Table S.I. 2) and the appearance of the Cu2p shake up satellites in Cu(II) compounds (Figure S.I. 3a).

## 1. Example of Metallic Copper spectra.



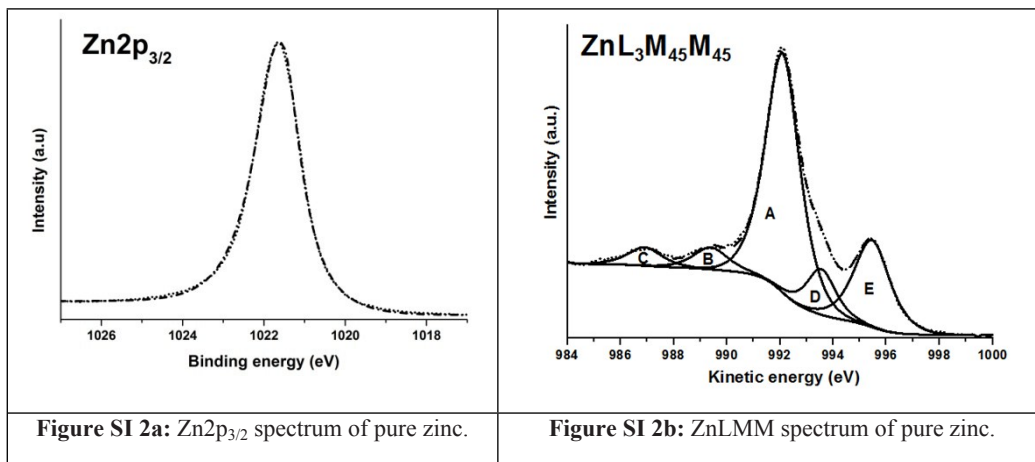
**Table SI 1:** BE, KE, FWHM of the peaks, line shape (GL ratio and tail function) of the Cu<sub>2p<sub>3/2</sub></sub> and CuL<sub>3</sub>M<sub>45</sub>M<sub>45</sub> signals from sputtered pure copper. Spectra were acquired using the Thetaprobe.

Peak	BE (eV ± 0.1)	FWHM (eV ± 0.1)	Line Shape
<b>Cu<sub>2p<sub>3/2</sub></sub></b>	932.5	1.1	GL(85)T(2.5)

	KE (eV ± 0.1)	Assignment	Intensity ratio	FWHM (eV ± 0.1)	Line Shape
<b>CuLMM</b>					
<b>A</b>	918.6	<sup>1</sup> G	1	1.5	GL(80)
<b>B</b>	916.5		0,3	1.9	GL(30)
<b>C</b>	914.1	<sup>1</sup> S	0,2	2.3	GL(30)
<b>D</b>	919.8	<sup>3</sup> P/ <sup>1</sup> D	0,1	1.1	GL(30)
<b>E</b>	921.4	<sup>3</sup> F	0,3	1.7	GL(30)

## 2. Example of Metallic Zinc spectra



**Table SI 2:** BE, KE, FWHM, line shape (GL ratio and tail function) of the Zn $2p_{3/2}$  and ZnL $_3$ M $_{45}$ M $_{45}$  signals from sputtered pure metallic zinc. Spectra were acquired using the Thetaprobe.

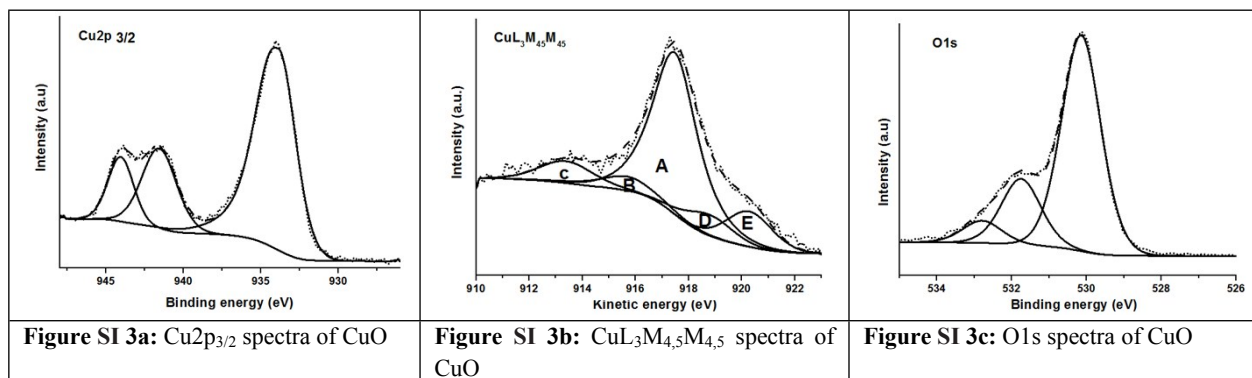
Peak	BE (eV $\pm$ 0.1)	FWHM (eV $\pm$ 0.1)	Line Shape
Zn $2p_{3/2}$	1021.6	1.1	GL(92)T(2)

Zn LMM	KE (eV $\pm$ 0.1)	Assignment	Intensity ratio	FWHM (eV $\pm$ 0.1)	Line Shape
A	992.1	$^1G$	1	1.4	GL(70)
B	989.6		0.1	2.4	GL(70)
C	986.8	$^1S$	0.1	1.9	GL(70)
D	993.5	$^3P/^1D$	0.2	1.5	GL(70)
E	995.5	$^3F$	0.4	1.5	GL(70)

### 3. Copper oxides

#### 3.1 Example of CuO spectra



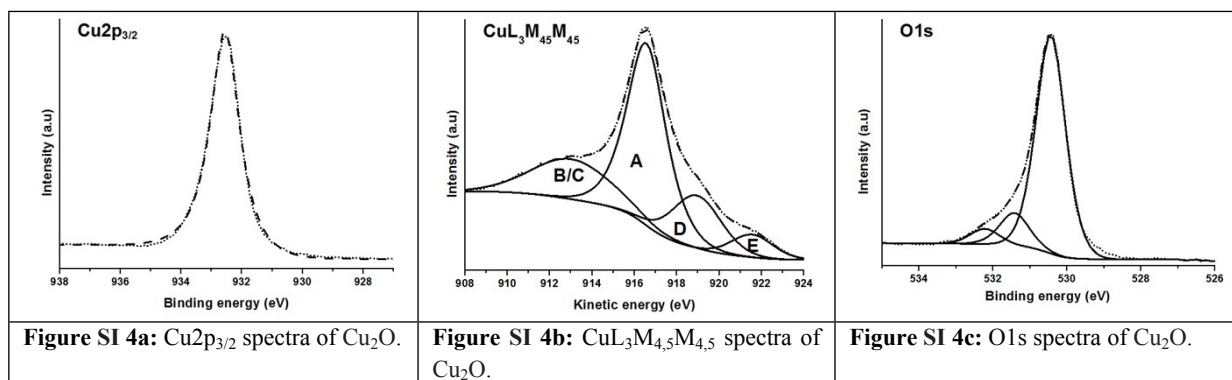
**Table SI 3:** BE, KE, FWHM, line shape (GL ratio and tail function) of the Cu2p<sub>3/2</sub> and CuL<sub>3</sub>M<sub>4,5</sub>M<sub>4,5</sub> signal from CuO. Spectra were acquired using the Thetaprobe.

Peak	BE (eV ± 0.1)	FWHM (eV ± 0.1)	Line Shape
<b>Cu2p<sub>3/2</sub></b>	933.8	2.4	GL(70)T(1.5)
<b>Sat 1</b>	941.6	2.6	GL(30)
<b>Sat 2</b>	944.1	1.9	GL(30)
<b>O1s</b>	530.1	1.2	GL(40)
<b>O1s</b>	531.7	1.2	GL(40)
<b>O1s</b>	532.8	1.2	GL(40)

	KE (eV ± 0.1)	Attribution	Intensity ratio	FWHM (eV ± 0.1)	Line Shape
<b>Cu LMM</b>					
<b>A</b>	917.8	<sup>1</sup> G	1	1.8	GL(30)
<b>B</b>	916.0		0.1	2.4	GL(30)
<b>C</b>	913.3	<sup>1</sup> S	0.2	2.4	GL(30)
<b>D</b>	919.1	<sup>3</sup> P/ <sup>1</sup> D	0.1	1.8	GL(30)
<b>E</b>	920.6	<sup>3</sup> F	0.2	1.9	GL(30)

### 3.2 Example of Cu<sub>2</sub>O



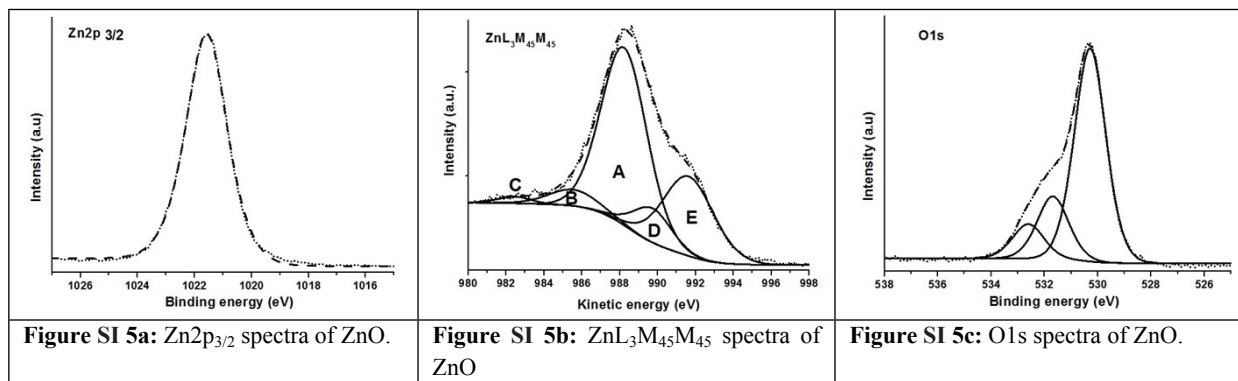
**Table SI 4:** BE, KE, FWHM, line shape (GL ratio) of the Cu<sub>2</sub>p<sub>3/2</sub> and CuL<sub>3</sub>M<sub>4,5</sub>M<sub>4,5</sub> signal from Cu<sub>2</sub>O. Spectra were acquired using the Thetaprobe.

Peak	BE (eV ± 0.1)	FWHM (eV ± 0.1)	Line Shape
<b>Cu<sub>2</sub>p<sub>3/2</sub></b>	932.4	1.1	GL(90)
<b>O1s</b>	530.3	0.9	GL(50)
<b>O1s</b>	531.3	0.9	GL(50)
<b>O1s</b>	532.1	0.9	GL(50)

	KE (eV ± 0.1)	Assignment	Intensity ratio	FWHM (eV ± 0.1)	Line Shape
<b>Cu LMM</b>					
<b>A</b>	916.8	<sup>1</sup> G	1	2.1	GL(70)
<b>B/C</b>	913.7	<sup>1</sup> S	0.6	5.4	GL(30)
<b>D</b>	919.2	<sup>3</sup> P/ <sup>1</sup> D	0.4	2.4	GL(30)
<b>E</b>	921.8	<sup>3</sup> F	0.1	2.5	GL(30)

## 4. Zinc oxide ZnO



**Table SI 5:** BE, KE, FWHM, line shape (GL ratio) of the Zn2p<sub>3/2</sub> and ZnL<sub>3</sub>M<sub>45</sub>M<sub>45</sub> signals from ZnO - Spectra were acquired using the Thetaprobe.

Peak	BE (eV ± 0.1)	FWHM (eV ± 0.1)	Line Shape
Zn2p <sub>3/2</sub>	1021.6	1.7	GL(70)
O1s	530.3	1.4	GL(40)
O1s	531.6	1.4	GL(40)
O1s	532.6	1.4	GL(40)

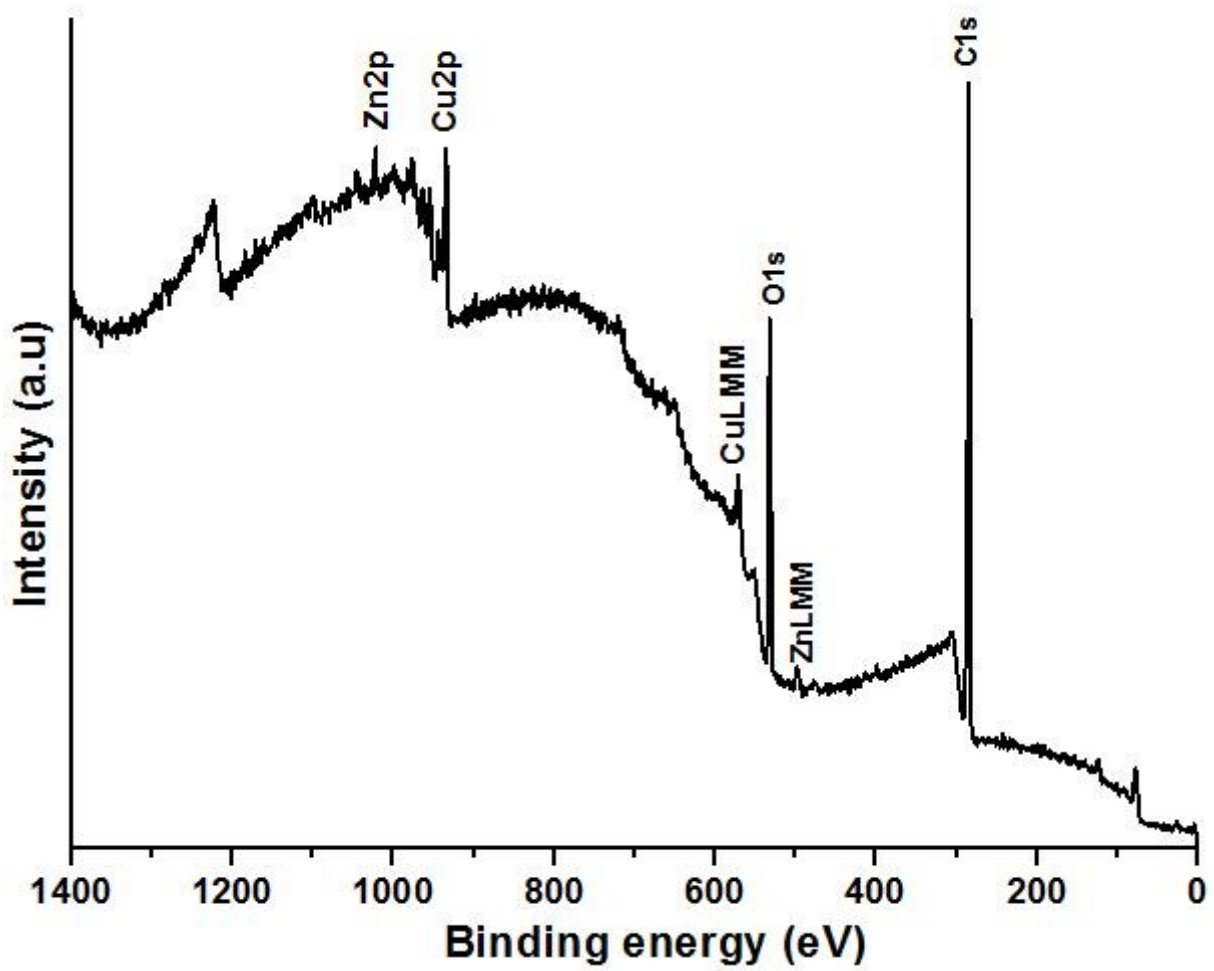
  

	KE (eV ± 0.1)	Attribution	Intensity ratio	FWHM (eV ± 0.1)	Line Shape
<b>Zn LMM</b>					
A	988.2	<sup>1</sup> G	1	2.9	GL(30)
B	985.5		0.1	3.0	GL(30)
C	982.6	<sup>1</sup> S	0.03	2.0	GL(30)
D	989.7	<sup>3</sup> P/ <sup>1</sup> D	0.2	2.4	GL(30)
E	991.6	<sup>3</sup> F	0.5	3.2	GL(30)

## 5. Survey

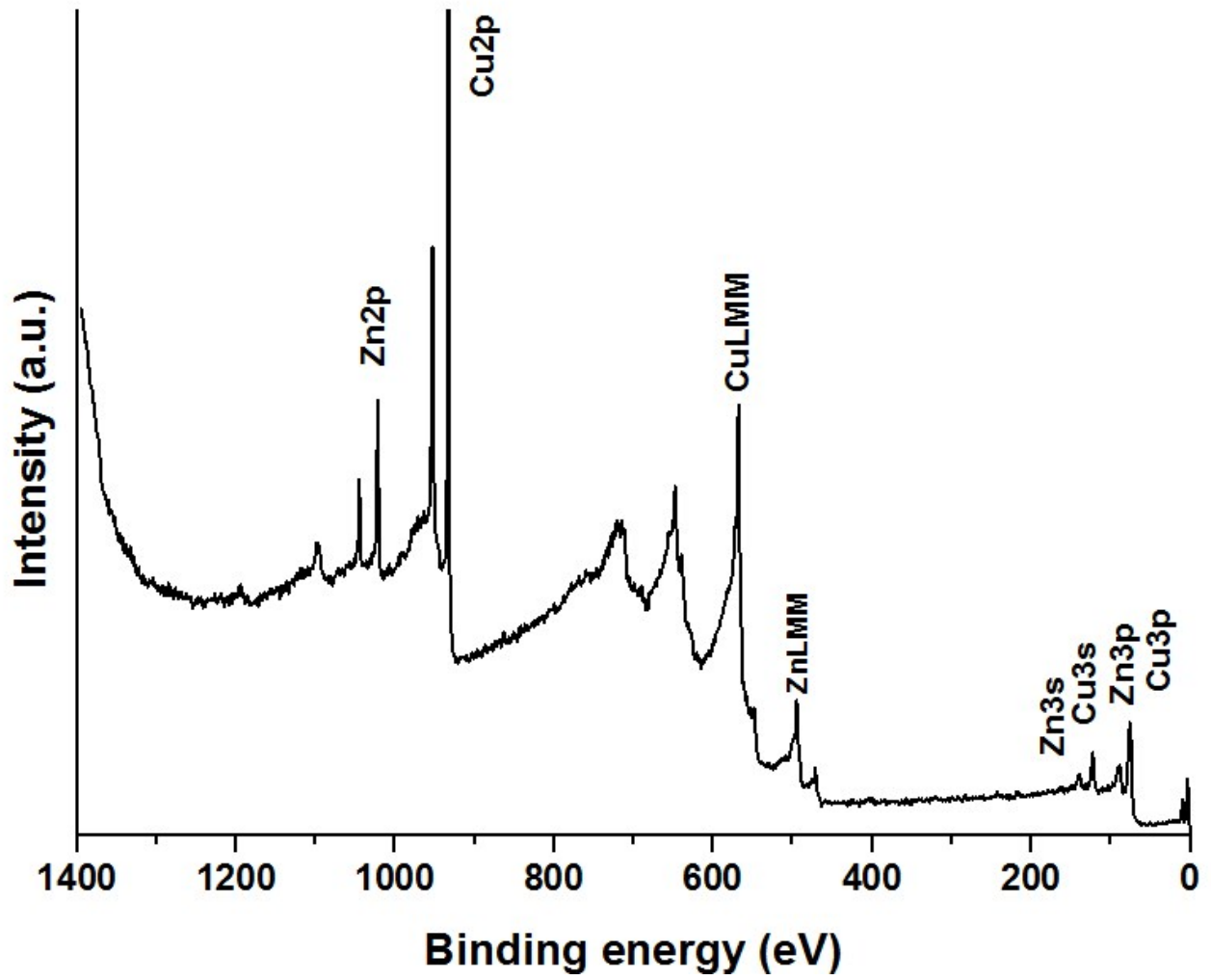
### 5.1 Survey of Cu<sub>37</sub>Zn model alloy “as received” - Spectra were acquired using the Thetaprobe.

Figure SI 6



5.2 Survey of Cu<sub>3</sub>Zn model alloy “sputtered” - Spectra were acquired using the Quantera.

Figure SI 7





5.3 Survey of Cu<sub>3</sub>Zn model alloy “mechanically polished” - Spectra were acquired using the Thetaprobe.

Figure SI 8

