



## Data Article

# A dataset of high-resolution synchrotron x-ray photoelectron spectra of tarnished silver-copper surfaces before and after reduction with a remote helium plasma at atmospheric pressure



Olivier Schalm<sup>a,b,\*</sup>, Alessandro Patelli<sup>c</sup>, Patrick Storme<sup>a</sup>,  
Amandine Crabbé<sup>d</sup>, Stefano Voltolina<sup>e</sup>, Vitaliy Feyrer<sup>f</sup>,  
Herman Terryn<sup>d</sup>

<sup>a</sup> University of Antwerp, Conservation Studies, Blindestraat 9, B-2000 Antwerp, Belgium

<sup>b</sup> Antwerp Maritime Academy, Noordkasteel Oost 6, B-2030 Antwerpen, Belgium

<sup>c</sup> Department of Physics and Astronomy, Padova University, Via Marzolo 8, 35131 Padova, Italy

<sup>d</sup> Vrije Universiteit Brussel (VUB), Research Group of Electrochemical and Surface Engineering, Pleinlaan 2, B-1050 Brussels, Belgium

<sup>e</sup> Veneto Nanotech, Nano Fabrication Facility, Via delle Industrie 9, 30175 Venezia-Marghera, Italy

<sup>f</sup> Peter Grünberg Institute (PGI-6) and JARA-FIT, Research Center Jülich, 52425 Jülich, Germany

## ARTICLE INFO

## Article history:

Received 5 January 2021

Revised 5 February 2021

Accepted 10 February 2021

Available online 13 February 2021

## Keywords:

Silver

Silver alloy

Copper

Sulphide

Plasma afterglow cleaning

XPS

Heritage

## ABSTRACT

The data presented in this article are related to the measurements in the contribution titled: 'Tarnished silver-copper surfaces reduction using remote helium plasma at atmospheric pressure studied by means of high-resolution synchrotron x-ray photoelectron microscopy' published in Corrosion Science. X-ray photoelectron spectra were collected from pure silver, sterling silver (92.5 w% Ag and 7.5 w% Cu) alloy and pure copper. These metals were artificially sulphidised. A remote helium plasma at atmospheric pressure was applied on the metallic and sulphidised state. Then the top layer of the 4 surface states were analysed at the NanoESCA beamline (Electron Spectroscopy for Chemical Analysis at the Nanoscale) at Elettra Sincrotrone Trieste. The instrument

DOI of original article: [10.1016/j.corsci.2020.109074](https://doi.org/10.1016/j.corsci.2020.109074)

\* Corresponding author at: Antwerp Maritime Academy, Noordkasteel Oost 6, B-2030 Antwerpen, Belgium.

E-mail address: [Olivier.schalm@hzs.be](mailto:Olivier.schalm@hzs.be) (O. Schalm).

<https://doi.org/10.1016/j.dib.2021.106872>

2352-3409/© 2021 The Authors. Published by Elsevier Inc. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

installed as an end station at the NanoESCA beamline of the Elettra storage ring combines an electrostatic Photo Electron Emission Microscope (PEEM) with a double-hemispherical ('IDEA') analyser, allowing the collection of photoemission electron microscopy (PEEM) images, X-ray photo electron-energy-filtered images and XPS spectra. The NanoESCA beamline provides electromagnetic radiation with variable polarization (linear, circular) and energies up to 1000 eV. Information for Cu3p, Cl2p, S2p, C1s and Ag3d were obtained by collecting spectra at 450 eV. The goal of the analyses was to determine how the plasma treatment changed the top layer of the metallic and sulphidised surface of pure silver, sterling silver and pure copper. This contribution focuses on the calibration of the collected XPS spectra, as well as the impact of the plasma treatment on the surface states.

© 2021 The Authors. Published by Elsevier Inc.

This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

## Specifications Table

Subject	Material science, Surfaces
Specific subject area	Plasma cleaning
Type of data	Graph
How data were acquired	X-ray photoelectron spectra collected at the NanoESCA beamline of the Elettra storage ring
Data format	Raw and analysed
Parameters for data collection	Spectra collected from pure silver, sterling silver (92.5w% Ag and 7.5 w% Cu) and pure copper plates before and after artificial sulphidation, and before and after a reductive plasma treatment with a remote helium plasma at atmospheric pressure. Reference spectra were collected from Ag <sub>2</sub> S, Cu <sub>2</sub> S and CuS powders pressed into pellets.
Description of data collection	Information about Cu3p, Cl2p, S2p, C1s and Ag3d were obtained by collecting XPS spectra at 450 eV. For sulphidised copper after plasma treatment, additional spectra were collected after the removal of the top layer by applying 2 subsequent Ar <sup>+</sup> ion sputtering cycles (kinetic energy 2.0 keV, 13–15 μA on the sample, 10–20 min per cycle) in the preparation chamber of the XPS instrument.
Data source location	University of Antwerp, Conservation Studies Antwerp Belgium
Data accessibility	1. Raw and processed spectra are deposited at Mendeley Database with the following link: <a href="http://dx.doi.org/10.17632/zyzzt2xyxj.1">http://dx.doi.org/10.17632/zyzzt2xyxj.1</a> 2. Part of the data is also accessible via this article 3. Interpretation of the data and context: With the related research article
Related research article	O. Schalm, A. Patelli, P. Storme, A. Crabbé, S. Voltolina, V. Feyer, H. Terryn, Tarnished silver-copper surfaces reduction using remote helium plasma at atmospheric pressure studied by means of high-resolution synchrotron x-ray photoelectron microscopy, <i>Corros. Sci.</i> , 178 (2021), 109,074

## Value of the Data

- XPS spectra give an insight in the modifications of the first nanometres of the surface layer of metallic and sulphidised silver, sterling silver and copper caused by a reductive plasma treatment.
- Applicable for comparing surface changes induced by other corrosion conditions, other cleaning methods and other silver alloys.
- Data can provide a foundation for further investigation of improved cleaning methods of tarnished silver.

## 1. Data Description

The article focuses on the data collection and analysis of some of the synchrotron X-ray photoelectron spectra collected from sulphidised silver (Ag999), sterling silver alloy with an amount of 7.5 w% of Cu (Ag925), and pure copper (Cu999) before and after the application of a reducing plasma afterglow at atmospheric pressure can be found in the related research article [1]. The XPS-spectra were collected with the instrument installed as an endstation at the NanoESCA beamline of the Elettra storage ring combines an electrostatic Photo Electron Emission Microscope (PEEM) with a double-hemispherical ('IDEA') analyser (more information in [1]). An overview of the acquired spectra is given in Table 1. For every metal type, 4 surface states are distinguished. The surface states of the samples are denoted by the following abbreviations: (1) metallic state before plasma treatment (BP: Before Plasma), (2) metallic state after plasma treatment using a remote helium plasma at atmospheric pressure (APH: After Plasma Helium), (3) sulphidised surface before plasma treatment (SBP: Sulphide Before Plasma), and (4) the sulphidised state after the plasma treatment (SAPH: Sulphide After Plasma Helium). The published XPS-spectra are raw spectra without background removal but where normalization was applied by shifting the spectra in the vertical direction by adding a constant to the intensities and by stretching/compressing the spectra by multiplying the intensities with a constant. In the following paragraphs, the calibration of these spectra will be discussed as well as the impact of the plasma treatment on the metallic states.

### 1.1. Energy calibration of XPS spectra

Due to the variability of surface composition among the samples, the plasma treatments and the resulting surface changes, the C1s peak changes in shape and in intensity among the samples. This hinders the identification of the binding energy (BE) of the C1s peak. It means that the C1s peak related to adventitious carbon could not be used as reference as already pointed out by the recent literature [2]. Therefore, the spectra are calibrated in energy with respect to the Fermi level position. To perform such procedure, least-squares fitting was applied on the Fermi edge using the CasaXPS software version 2.3.15 (CasaXPS Software Ltd. UK [CasaCook-Book; [www.casaxps.com](http://www.casaxps.com)]). However, for some samples the identification of the Fermi edge is problematic due to the low density of states close to the edge or due to the presence of a band gap. Therefore, an additional refinement of the energy calibration is performed using (specific features of) the overall shape of the valence band (VB) spectra. This is done by comparing the shape of the complete valence band spectrum with valence band spectra of similar shape that could be calibrated with least square fitting. In the list below, the calibration method used for

**Table 1**  
Overview of the collected spectra.

Nr.	File name	Analysed materials	Surface states
1	Ag999 – spectra	Silver plate	BP, APH, SBP, SAPH
2	Ag925 – spectra	Sterling silver plate	BP, APH, SBP, SAPH
3	Ag925 - reference and spectra	Sterling plate + Ag <sub>2</sub> S, Cu <sub>2</sub> S and CuS pellet	Same SBP, SAPH as in 2
4	Ag925 BP - before and after sputtering	Sterling plate	BP before and after Ar <sup>+</sup> sputtering
5	Cu999 - spectra	Copper plate	BP, APH, SBP, SAPH
6	Cu999 - reference and spectra	Copper plate + Ag <sub>2</sub> S, Cu <sub>2</sub> S and CuS pellet	Same BP, APH, SBP, SAPH as in 5
7	Cu999 - effect of sputtering	Copper plate	SBP before and after Ar <sup>+</sup> sputtering

BP: Metallic surface before plasma treatment; APH: Metal surface after plasma treatment; SBP: Sulphidised surface before plasma treatment; SAPH: Sulphidised surface after plasma treatment.

**Table 2**

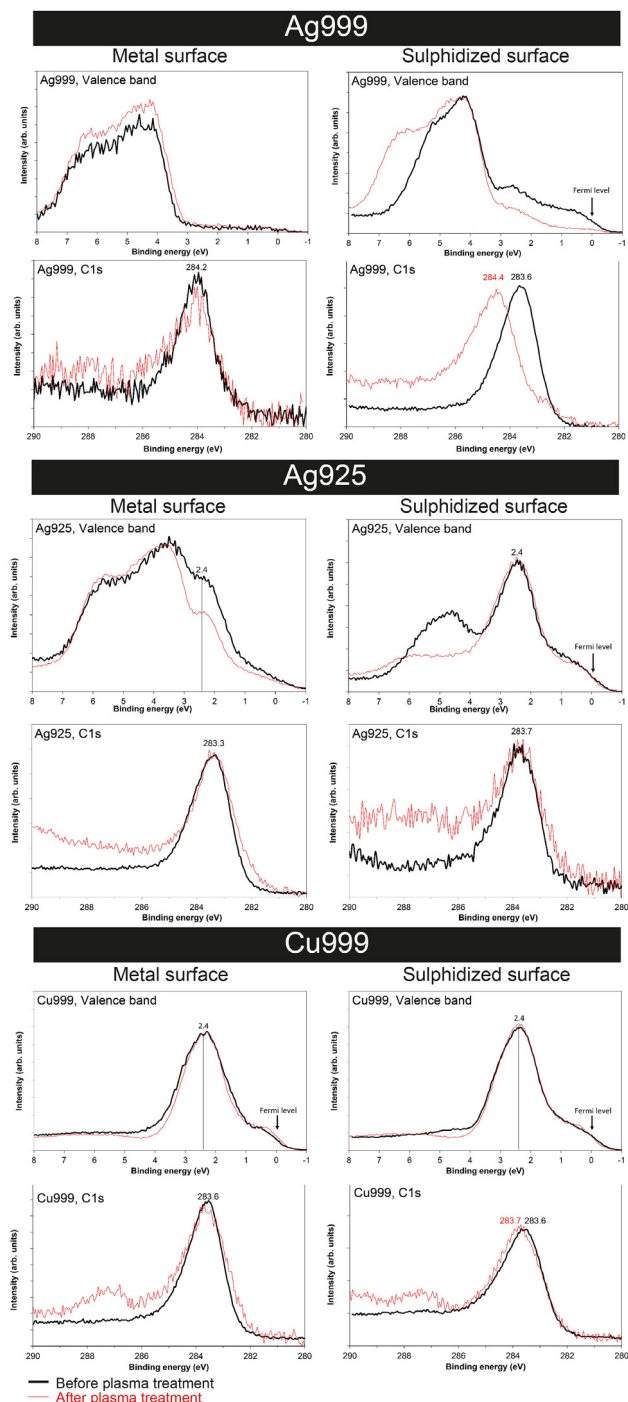
Features used to perform the energy calibration and the energy calibration method that was used.

Metal	Surface state	Plasma treatment	Sample code	Feature	Calibration method
Ag999	Metal	No	BP	Spectrum shape	Shift spectrum to match SAPH-spectrum & peak at 4.3 eV
		Yes	APH	Spectrum shape	Shift spectrum to match SAPH-spectrum & peak at 4.3 eV
	Sulphide	No	SBP	Fermi Level	Spectrum fitting using least-squares fitting
		Yes	SAPH	Fermi Level	Spectrum fitting using least-squares fitting
Ag925	Metal	No	BP	Peak at 2.4 eV	Shift spectrum to match peak in SAPH-spectrum
		Yes	APH	Peak at 2.4 eV	Shift spectrum to match peak in SAPH-spectrum
	Sulphide	No	SBP	Peak at 2.4 eV	Shift spectrum to match peak in SAPH-spectrum
		Yes	SAPH	Fermi Level	Spectrum fitting using least-squares fitting
Cu999	Metal	No	BP	Fermi Level	Spectrum fitting using least-squares fitting
		Yes	APH	Fermi Level	Spectrum fitting using least-squares fitting
	Sulphide	No	SBP	Fermi Level	Spectrum fitting using least-squares fitting
		Yes	SAPH	Fermi Level	Spectrum fitting using least-squares fitting
Reference – products		No	Cu <sub>2</sub> S	Fermi Level	Spectrum fitting using least-squares fitting
		No	CuS	Fermi Level	Spectrum fitting using least-squares fitting
		No	Ag <sub>2</sub> S	Fermi Level	Spectrum fitting using least-squares fitting

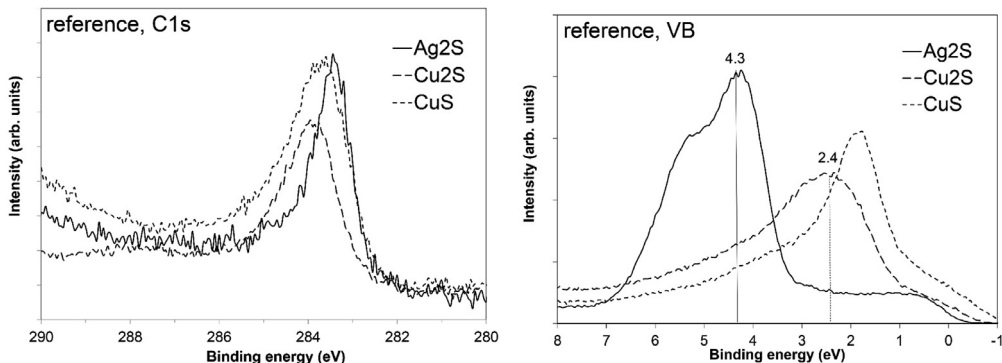
the collected spectra is described for the 3 metal types. Table 2 gives an overview of the methods used for each spectrum.

- **Ag999:** Of the 4 surface states, only 2 of them have a pronounced Fermi level: the sulphidised surface state (i.e., SBP) and the sulphide surface state that is transformed into the metallic surface state due to plasma treatment (i.e., SAPH). This means that energy calibration of both spectra can be performed by least-squares fitting using the CasaXPS software version 2.3.15. Due to a weak Fermi level of the other 2 surface states, the valence band (VB) spectra of metallic Ag999 before (BP) and after plasma treatment (APH) must be calibrated in another way. The VB-spectra of the metallic surface states, (see Fig. 1: SAPH, BP and APH of Ag999) are very similar in shape and in agreement with the general shape of published VB spectra of metallic silver: a faint jump at the Fermi level, the energy of the VB band ranging from 4 eV to 8 eV, and a dip at about 6 eV [3-5]. Therefore, the energy calibration of these 2 spectra is obtained by shifting the spectrum until the shape coincide with that of the VB-spectrum of sulphidised Ag999 after plasma treatment (SAPH) which was previously calibrated by least-squares fitting. The peak at 4.3 eV of the SAPH spectrum is a useful feature to perform the energy calibration. After this refinement, the BE of Ag3d5/2 and Ag3d3/2 for the spectra collected of metallic silver are located at 367.9–368.0 eV and 373.9–374.0 eV, which are close to published BE obtained from high-resolution XPS: 368.0 eV and 374.3 eV respectively [6].

**Ag925:** The shape of the VB-spectra of the 4 surface states of Ag925 show substantial differences. Moreover, none of the spectra resemble the VB-spectra of Ag999. The differences between both alloys can be explained by the small copper amounts in Ag925 and



**Fig. 1.** High resolution spectra of the valence band of metallic and sulphidised Ag999, Ag925 and Cu999 before and after plasma treatment using a soft-x-ray excitation of 450 eV together with the high resolution spectra of C1s. Spectra were normalized to by shifting and stretching to facilitate comparison.



**Fig. 2.** High-resolution spectra of the valence band and of C1s of Ag<sub>2</sub>S (99.9%), Cu<sub>2</sub>S (99.5%) and CuS (99.8%) powders pressed into pellets using a soft-x-ray excitation of 450 eV. Spectra were normalized by shifting and stretching to facilitate comparison.

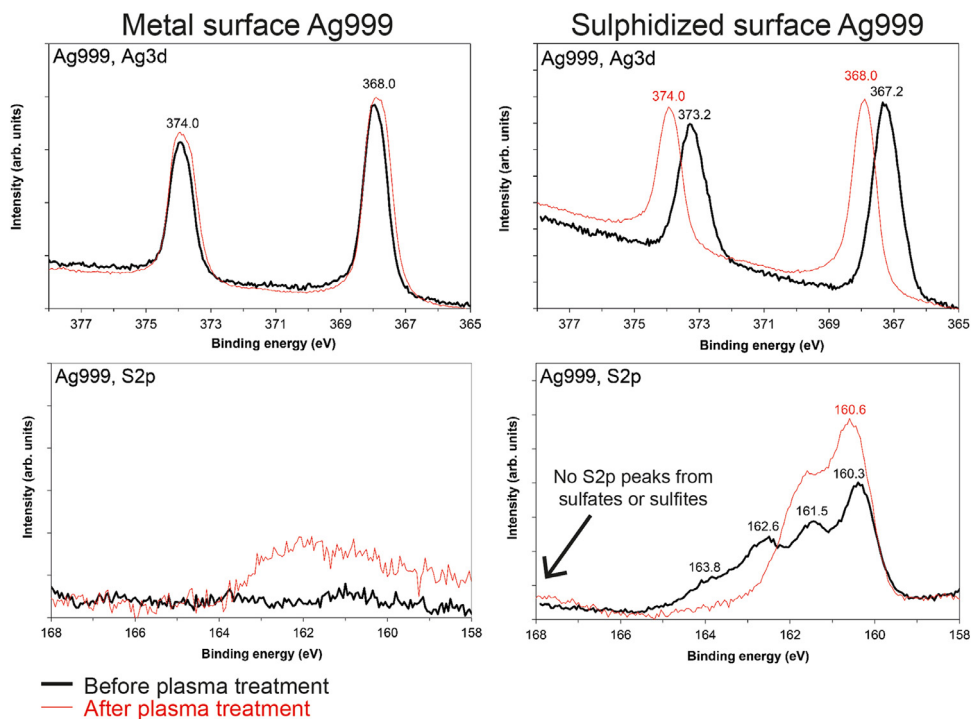
by a different mixture of corrosion products. It is known that corrosion layers on top of Ag<sub>925</sub> consist of a complex mixture of stromeyerite (AgCuS), acanthite (Ag<sub>2</sub>S), chlorargyrite (AgCl), cuprite (Cu<sub>2</sub>O) or covellite (CuS) [7,8]. From the 4 surface states, sulphidised Ag<sub>925</sub> after plasma treatment (SAPH) has the best resolved Fermi level and is calibrated by least-squares fitting. The VB spectrum of that surface state is similar to that of metallic Cu999 (Fig. 1, metal surface before plasma treatment). The peak maximum at 2.4 eV is chosen as reference since it is related to the metallic copper and used to refine the energy calibration of all the other Ag<sub>925</sub> samples. As a result of this calibration procedure, the Cu3p signals for the 4 surface states coincided at 74.3 eV.

- **Cu999:** As can be seen in Fig. 1, the VB-spectra of Cu999 for the 4 different surface states are much more similar than the ones for Ag999 and Ag<sub>925</sub>. Published VB-spectra of metallic copper show a pronounced Fermi level while the peaks start at about 1 eV [3]. The clearly resolved Fermi level allows an accurate calibration of the VB-spectra of all the 4 surface states using least-squares fitting. To evaluate the refining method based on the general shape of the spectrum, the VB-spectrum of metallic Cu999 before plasma treatment is calibrated by the Fermi level while the other ones are calibrated using the general shape of the spectra. Between the refining method and the least-squares fitting method, the average difference in energy shift is equal to  $0.06 \text{ eV} \pm 0.04 \text{ eV}$ , which is smaller than the energy shifts observed in the XPS-spectra. This strengthens our refined fitting method based on the general shape of the VB spectra.

Fig. 2 reports the VB and C1s spectra of the sulphide pellets used as reference materials. The sulphides are semiconductors. Therefore, the attribution of the Fermi level may lead to errors due to the presence of the band gap. However, at high photon energies the compounds Ag<sub>2</sub>S, Cu<sub>2</sub>S and CuS show the valence band, which is very close to the Fermi level [9,10]. In addition, for Ag<sub>2</sub>S the most prominent peak in the VB-spectrum is related to the Ag4d states. This feature is used as a reference for energy calibration.

## 1.2. Ag 999

The XPS spectra of the polished silver Ag999 samples presented the same features before (BP) and after (APH) the plasma treatments, with a small shift of 0.1 eV in binding energy of the Ag3d peaks (Fig. 2) and an increase in FWHM of about 0.05 eV. This may be due to a small surface

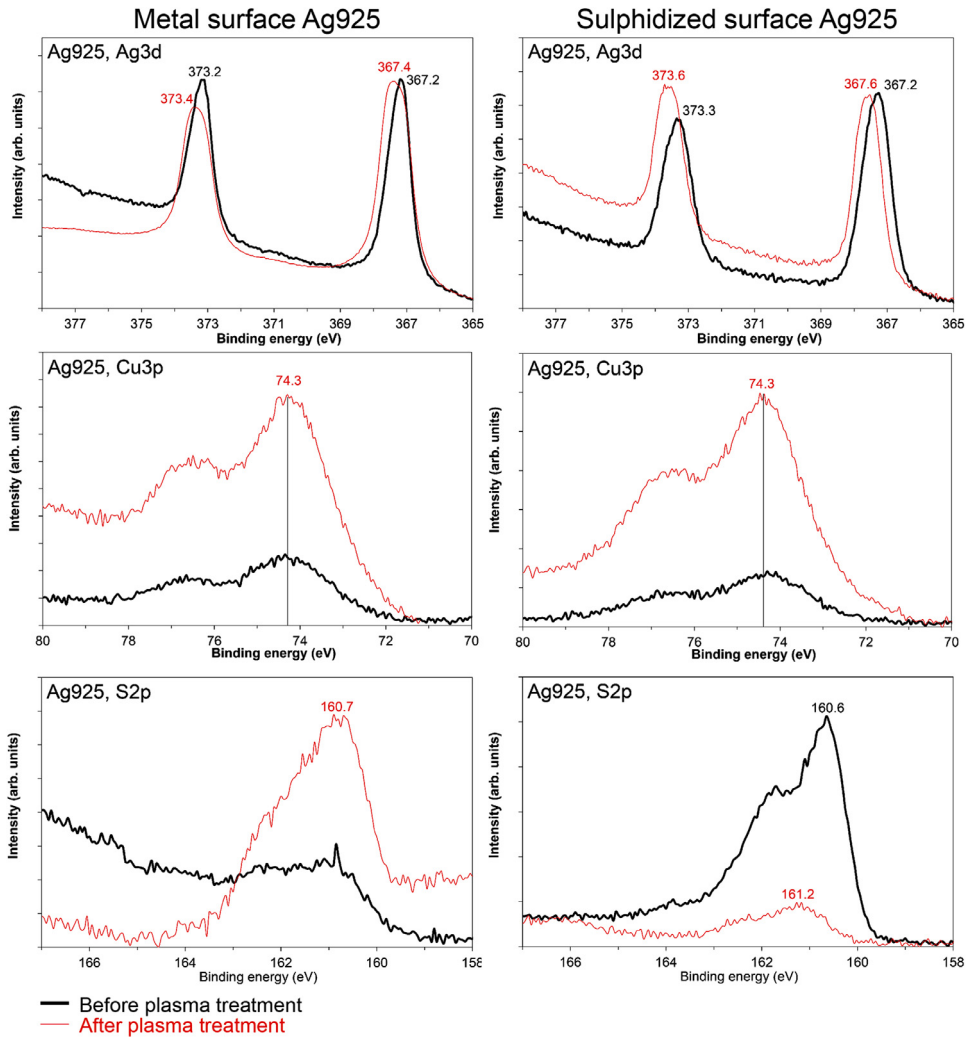


**Fig. 3.** High resolution spectra of Ag3d and S2p using a soft-x-ray excitation of 450 eV collected of Ag999 from a region of 90  $\mu\text{m}$  diameter without background removal. The spectra at the left were collected from the metal surface; the spectra at the right were collected from the sulphidised surface.

oxidation or resulphidization after the cleaning process. A strong variation in the intensity of the peaks could be detected, which increased with a factor of 5 after the plasma treatment. However due to the different history of the samples and their re-exposure to air in the period between plasma treatment and XPS analyses, it is difficult to draw conclusions from the peaks height. In addition, carbon was present before and after the plasma treated surface (Fig. 1). After the plasma treatment of the metal (Fig. 3) only a faint bump in the range of S2p BE can be seen, meaning that the sulphur presence was hardly detectable. The shiny appearance of the metal sample was maintained after the plasma treatment. The sulphided samples showed the presence of sulphur before and after the plasma cleaning, even if after the treatment the silver Ag3d peak shifted to metallic binding energies. The sulphur presence on SAPH is probably linked to its re-exposure to air after the treatment.

### 1.3. Ag 925

For metallic Ag925 before plasma treatment, the Ag3d5/2 binding energy (BE) was 367.2 eV (see Fig. 4) while the same signal for metallic Ag999 after the plasma treatment had a BE of 368.0 eV. For metallic Ag925 after plasma treatment, the Ag3d5/2 peak underwent an energy shift of 0.2 eV towards higher energies suggesting a reducing action. The Cu3p peaks for Ag925 and Cu999 for the 4 surface states did not endure any shift. The shift in Ag3d5/2 is due to the presence of sulphides as highlighted also by the evidence of the S2p signal. The sulphur recontamination is most probably due to the natural corrosion process after the re-exposure to



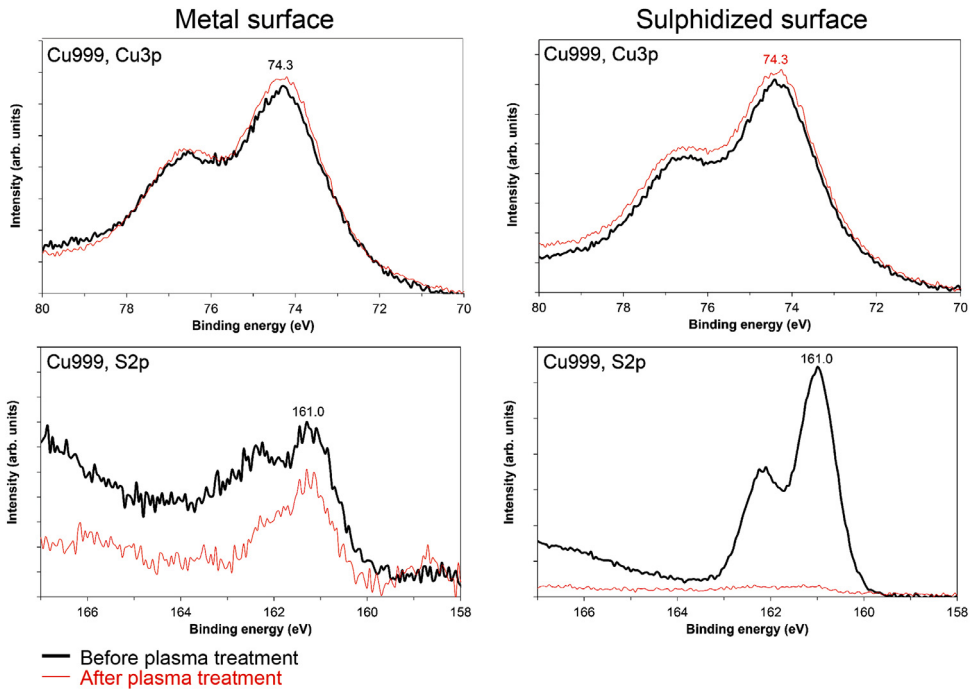
**Fig. 4.** High resolution spectra of Ag3d, Cu3p and S2p using a soft-x-ray excitation of 450 eV without background removal. The spectra at the left were collected from the metal surface; the spectra at the right were collected from the sulphidised surface.

air between the plasma treatment and the XPS-analyses. Finally, the valence band spectra of metallic Ag925 suggested that the plasma afterglow caused a transformation of the surface.

#### 1.4. Cu999

For metallic Cu999 without corrosion layer, the plasma treatment had a limited effect (see Fig. 5). The clearest change induced by plasma was the increase of the copper signal and a higher VB-signal. The faint signal of sulphur suggested that almost no sulphides were present at the surface. For the sulphidized surface, a similar observation could be made for the copper signal, although the copper is reduced to its metallic state during the plasma treatment (i.e.,





**Fig. 5.** High resolution spectra of Cu3p and S2p using a soft-x-ray excitation of 450 eV without background removal. Spectra were collected of metallic and sulphidised Cu999 before and after plasma treatment. In the right column, high resolution XPS spectra collected from sulphidised Cu999 before and after plasma treatment are compared with reference spectra.

the sulphide signal almost completely vanished). During the plasma treatment of the sulphide surface, the oxygen content increased to some extent (O1s spectra can be found in the dataset).

## 2. Experimental Design, Materials and Methods

### 2.1. Sample preparation

Coupons (20 mm × 50 mm) were cut from larger sheets of Ag999 (i.e., 99.9 w% Ag), Ag925 (i.e., 7.5 w% Cu and 92.5 w% Ag) and Cu999 (i.e., 99.9 w% Cu) using a parallel metal cutting guillotine. The silver sheets Ag925 and Ag999 were purchased at Schöne Edelmetaal B.V. (Netherlands), which retrieves its metal from Degussa, Germany. The Cu999 sheets were obtained from Dejong Metals nv, Antwerp (Belgium). An inventory number was engraved at the backside of the coupons. The front side was grinded and polished with a fixed procedure to obtain as close as possible identical surface states. On the surface of the coupon, a small amount of water soluble polishing pastes (3M™ Finesse-it™ Finishing Material, followed by 3MTM Imperial™ Machine Glaze) was applied and the surface was brought into contact with a soft cotton rotating wheel for approximately 1 min. Cleaning of the polished surface was performed by immersing the coupon in an ultrasonic bath with ethanol for 2 min. Afterwards, the coupons were rinsed with deionised water and dried with oil- and water-free compressed air. The mirror-like appearance of the surface was very similar to that of historical ‘silver’ objects finished with a traditional mechanical and abrasive polishing technique.

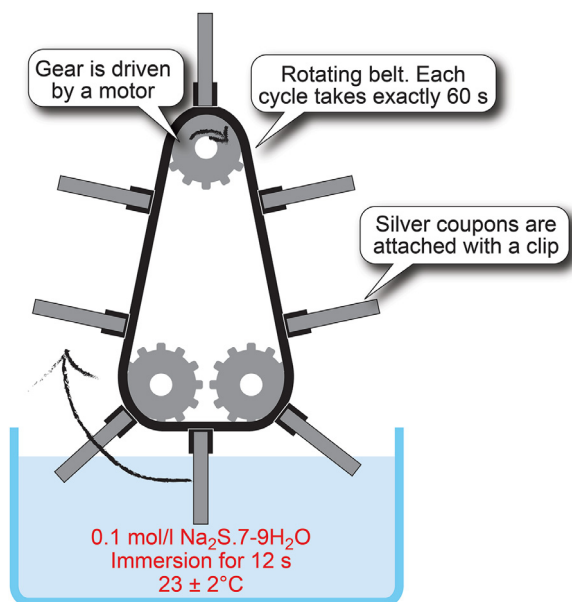


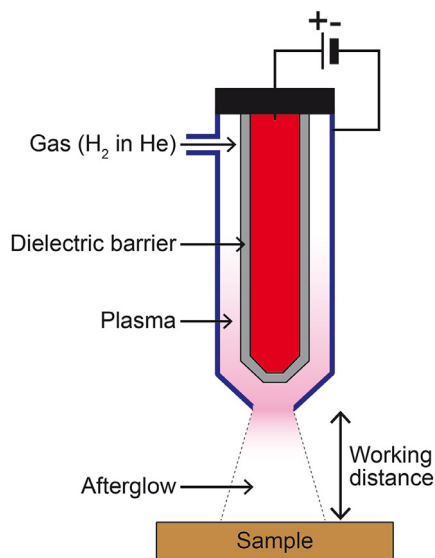
Fig. 6. Device used to immerse the coupons for exactly 12 s in a sodium sulphide solution for every cycle of 60 s.

## 2.2. Artificial corrosion

With a self-developed instrument as illustrated in Fig. 6, the coupons were exposed to subsequent cycles consisting of a short immersion (12 s for every cycle of 60 s) in a  $\text{Na}_2\text{S}$  solution (0.1 mol/L  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ,  $\text{pH} = 14$ ) followed by a longer exposure to air (48 s/60 s cycle) [11]. Dissolved sulphides are known to make the solutions alkaline. For Ag999, Ag925 and Cu999 the exposure time is respectively 300 min, 60 min and 30 min. The exposure time had to be diminished for the metals with higher copper amounts in order to compensate for the higher corrosion rates. XPS analyses of Cu999 only found limited amounts of oxygen (see spectra Cu999SBP in dataset) in the top surface of the sulphide layer. This suggests that (almost) no sulphites or sulfates exist in that top layer. All corrosion tarnish layers had a black and dull appearance and were well attached to the surface. The corrosion method is based on a normalized sodium sulphide test [12].

## 2.3. Atmospheric pressure plasma treatment

A dielectric barrier discharge commercial plasma-jet, type Plasma Spot<sup>®</sup>, was used for the experiments. The power was set to 120 W with a gas flow of 70 slm (standard liter per minute). A schematic representation of this type of torch is shown in Fig. 7. The nozzle of the torch had a circular opening with a diameter of 10 mm. Inside that opening, a central anode of 6 mm diameter was located. For the removal of the tarnish layer, a reducing gas mixture of 5 vol%  $\text{H}_2$  in He was used. The plasma-jet was mounted perpendicular to the coupons with a working distance of 5 mm. The treated area was approximately 15 mm in diameter. The cleaning time varied between 15 s and 120 s. During the treatment, the samples reached a maximum temperature of 50–70 °C [11]. In the remote configuration used in the present plasma setup the sample is not seen as an electrode. This setup was chosen to avoid the reducing effect caused by arc discharges from the plasma, passing through the afterglow and reaching the sample surface.



**Fig. 7.** Schematic representation of a dielectric barrier discharge plasma torch and how it treats material surfaces at atmospheric pressure.

#### 2.4. Preparation for XPS analysis

In order to fit the samples in the sample holder of the XPS instrument, small squared samples of  $10\text{ mm} \times 10\text{ mm}$  were cut from the coupons. This was done with a jeweller's saw, using nitrile gloves and removing saw dust from the surface with purified canned air. The squared samples were taken from the most homogeneous regions of the coupons. The samples were unavoidable exposed to air between the sample preparation (e.g., plasma treatment) and the XPS measurements. Therefore, the adventitious carbon on the surface, which was probably removed by plasma treatment, could be observed for all the plasma treated surfaces.

#### 2.5. Reference materials

To facilitate the interpretation of the XPS analyses, a series of reference materials was analysed as well. The metallic surfaces of Ag999, Ag925 and Cu999 were considered as reference for the metals. For the corrosion products, powders of respectively  $\text{Ag}_2\text{S}$  (99.9%),  $\text{Cu}_2\text{S}$  (99.5%) and  $\text{CuS}$  (99.8%) were purchased at Alfa Aesar and pressed into pellets. About 0.1 g of powder was transformed into a pellet of 8 mm diameter and about 1 mm thickness by means of a hand press using a pressure of 3 to 4.5  $\text{ton}/\text{cm}^2$ . The pellets had a glossy surface and could easily be transported and be manipulated without physical damage. Before these pellets could be analysed with XPS, outgassing was needed. This was done in the preparation chamber of the XPS-instrument. Except for carbonaceous matter, no systematic surface contamination introduced during the sample preparation could be detected. Moreover, no disturbing surface charging occurred during the analyses of the pellets.

#### 2.6. NanoESCA beamline

The instrument installed as an endstation at the NanoESCA beamline of the Elettra storage ring combines an electrostatic Photo Electron Emission Microscope (PEEM) with a double-

hemispherical ('IDEA') analyser, allowing the collection of photoemission electron microscopy (PEEM) images, X-ray photo electron-energy-filtered images and XPS spectra as described in the list below. The NanoESCA beamline provides electromagnetic radiation with variable polarization (linear, circular) and energies up to 1000 eV. The main application mode of the NanoESCA is the high lateral resolution (c. 50–150 nm) mapping of core-level photoemission signatures. The fast overview and high-resolution narrow spectra for Cu3p, Cl2p, S2p, C1s, Ag3d were collected from an area with a diameter of 90  $\mu\text{m}$ , using a soft-x-ray source of 450 eV. Spectra for O1s were collected at 600 eV while spectra for Cu2p were obtained at 1250 eV. The total energy resolution (analyser + beamline) was 0.2–0.3 eV. For most analyses, no preceding cleaning procedure by applying Ar<sup>+</sup> ion sputtering (kinetic energy Ar<sup>+</sup> ions 2.0 keV, 13–15  $\mu\text{A}$  on the sample, 10–20 min per cycle) was needed to remove unwanted top layers.

## 2.7. Energy calibration

Energy calibration was performed by localizing the Fermi level position in the valence band spectra and setting that point to zero. For this, least-squares fitting was applied on the step-like jump in the vicinity of the Fermi level using the CasaXPS software version 2.3.15 (CasaXPS Software Ltd. UK [CasaCookBook; [www.casaxps.com](http://www.casaxps.com)]). However, for some surface states the expected step-like jump in the vicinity of the Fermi level was too small for energy calibration. In such cases, the energy calibration was refined by using characteristic features in the shape of the valence band spectra [13]. This was done by comparing the shape of the complete valence band spectrum with valence band spectra of similar shape that could be calibrated with least square fitting.

## Ethics Statement

This work did not involve the use of human subjects, animal experiments or data collected from social media platforms.

## CRedit Author Statement

**Olivier Schalm:** Writing - Original Draft, Conceptualization, Visualization, Investigation; **Alessandro Patelli:** Writing - Original Draft, Visualization, Investigation, Funding acquisition; **Patrick Storme:** Writing - Review & Editing, Conceptualization, Investigation; **Amandine Crabbé:** Writing - Review & Editing, Investigation; **Stefano Voltolina:** Investigation; **Vitaliy Feyer:** Investigation; **Herman Terryn:** Supervision.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships which have, or could be perceived to have, influenced the work reported in this article.

## Acknowledgments

This work was supported by the EU-FP7 grant PANNA no. 282998. The SR-XPS measurements at the NanoESCA beamline of the Elettra storage ring were performed under the approval of the advisory Committee (Proposal no. 20135164).

## References

- [1] O. Schalm, P. Storme, A. Crabbé, S. Voltolina, A. Patelli, V. Feyrer, H. Terryn, Tarnished silver-copper surfaces reduction using remote helium plasma at atmospheric pressure studied by means of high-resolution synchrotron x-ray photoelectron microscopy, *Corros. Sci.* 178 (2021) 109074.
- [2] G. Greczynski, L. Hultman, X-ray photoelectron spectroscopy: towards reliable binding energy referencing, *Prog. Mater. Sci.* 107 (2020) 100591.
- [3] S. Hüfner, G.K. Wertheim, N.V. Smith, M.M. Traum, XPS density of states of copper, silver and nickel, *Solid State Commun.* 11 (1972) 323–326.
- [4] G.K. Wertheim, D.N.E. Buchanan, Core-electron binding energies of adsorbed metallic monolayers: Au/Ag(111), *Phys. Rev. B* 33 (2) (1986) 914–918.
- [5] G.K. Wertheim, S.B. DiCenzo, D.N.E. Buchanan, Noble- and transition-metal clusters: the d bands of silver and palladium, *Phys. Rev. B* 33 (8) (1986) 5384–5390.
- [6] A. Barrie, N.E. Christensen, High-resolution x-ray photoemission spectra of silver, *Phys. Rev. B* 14 (6) (1976) 2442–2447.
- [7] O. Schalm, A. Crabbé, P. Storme, R. Wiesinger, A. Gambirasi, E. Grieten, P. Tack, S. Bauters, Ch. Kleber, M. Favaro, D. Schryvers, L. Vincze, H. Terryn, A. Patelli, The corrosion process of sterling silver exposed to a Na<sub>2</sub>S solution: monitoring and characterizing the complex surface evolution using a multi-analytical approach, *Appl. Phys. A* 122 (10) (2016) 903.
- [8] E. Angelini, T. de Caro, A. Mezzi, C. Riccucci, F. Faraldi, S. Grassini, Degradation mechanisms occurring in precious metallic artefacts, *Surf. Interface Anal.* 44 (2012) 947–952.
- [9] S. Kashida, N. Watanabe, T. Hasegawa, H. Iida, M. Mori, S. Savrasov, Electronic structure of Ag<sub>2</sub>S, band calculation and photoelectron spectroscopy, *Solid State Ion.* 158 (2003) 167–175.
- [10] J. Deng, Z.-Y. Zhao, Effects of non-stoichiometry on electronic structure of Cu<sub>x</sub>S<sub>y</sub> compounds studied by first-principle calculations, *Mater. Res. Express* 6 (2019) 105513.
- [11] O. Schalm, P. Storme, A. Gambirasi, M. Favaro, A. Patelli, How effective were reducing plasma afterglows at atmospheric pressure in removing sulphide layers: application on tarnished silver, sterling silver and copper, *Surf. Interface Anal.* 50 (1) (2018) 32–42.
- [12] International Organization for Standardization, Dental Casting Alloys With Noble Metal Content of at Least 25% But Less Than 75%, 8891, ISO, 1998.
- [13] A.C. Miller, C.J. Powell, U. Gelius, C.R. Anderson, Energy calibration of x-ray photoelectron spectrometers. Part III: location of the zero point on the binding-energy scale, *Surf. Interface Anal.* 26 (1998) 606–614.