

**KeyWords**

NAP-XPS, operando, plasma, cleaning, ambient air

Operando NAP-XPS study of plasma-enhanced surface reactions

First results of an *operando* NAP-XPS experiment on a silver surface during an air plasma cleaning process are presented. The observed chemical changes are plasma-induced and monitored under working conditions.

In this application note, we present the real-time monitoring of a plasma-enhanced surface cleaning process applied to a polycrystalline silver sample using NAP-XPS (Near Ambient Pressure X-ray Photoelectron Spectroscopy). We examined alterations in surface chemistry while the process was actively running (*operando*). The experiments were conducted in an ambient air plasma environment at a pressure of 0.05 mbar (5 Pa) within a fully automated, laboratory backfilling NAP XPS system provided by SPECS GmbH. This particular NAP-XPS photoelectron spectrometer was equipped with an EM KLEEN in-situ downstream plasma cleaner from PIE Scientific LLC, operating at 75 W and 13.56 MHz radio frequency power.[1]

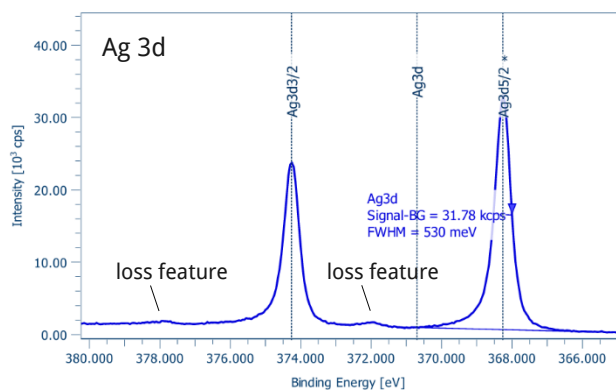


Fig. 1. High-resolution Ag 3d core-level spectra of a native polycrystalline silver sample. The metallic silver species (Ag^0) is reflected by its $\text{Ag } 3d_{5/2}$ peak position and the characteristic loss features at higher binding energies.

Figure 1 illustrates the Ag 3d core-level spectrum observed prior to the plasma cleaning process. The presence of metallic silver species (Ag^0) is evident from the Ag $3d_{5/2}$ peak, located at a binding energy of 368.2 eV, along with its characteristic loss features.[2]

Following this, the plasma cleaner was activated, and high-resolution core-level spectra for Ag 3d, O 1s, and C 1s (5 scans each) were acquired in 15 intervals, each lasting 3 minutes, spanning a total of 45 minutes. Figure 2 provides a visual representation of the ignited air plasma within the load lock.

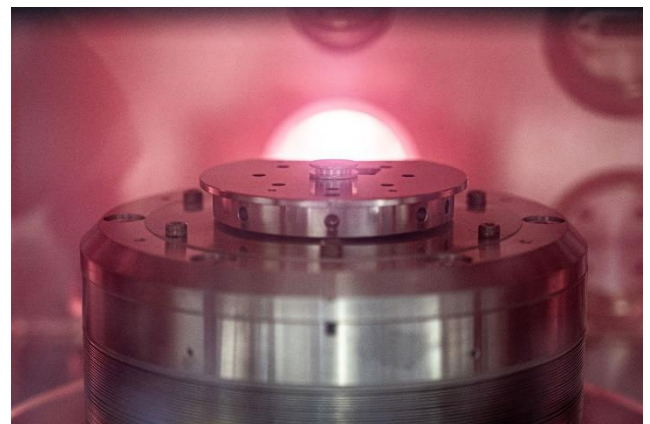


Fig. 2. Picture of the ignited air plasma in the sample environment at a pressure of 0.05 mbar and 75 W rf power at 13.56 MHz.

Figure 3 showcases high-resolution Ag $3d_{5/2}$ XP spectra obtained in real-time while the air plasma was active, and the plasma cleaner was operational. Despite the ongoing plasma treatment, the metallic silver species (Ag^0) remained at approximately 368 eV. Notably, a second peak component, with a binding energy around 367.7 eV, emerged on the silver surface. This lower binding energy component corresponds to Ag(I) species, such as Ag_2O or AgOH , formed during the air plasma treatment.[3] This observation is supported by the increasing O 1s peak at 530.3 eV, as seen in Figure 4 (left panel).

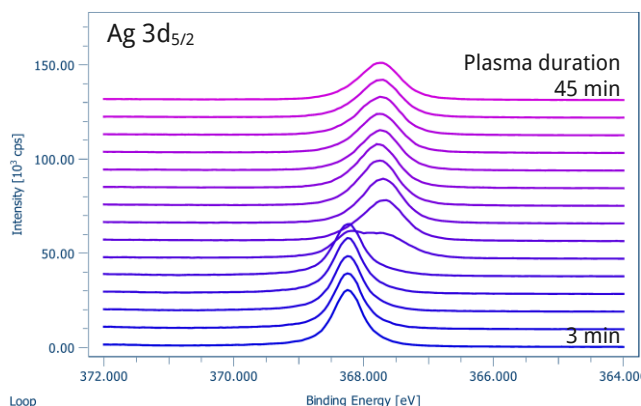


Fig. 3. High-resolution $\text{Ag } 3d_{5/2}$ core-level spectra of the silver sample during air plasma treatment (75 W rf power at 13.56 MHz) over 45 min at a pressure of 0.05 mbar.

Additional confirmation of plasma-enhanced surface reactions is evident in the C 1s core-level spectra. The C 1s peak intensity steadily declined throughout the plasma cleaning process until it completely disappeared after 20 minutes, confirming the effective removal of typical adventitious carbon contamination from the silver surface, as depicted in Figure 4 (right panel).

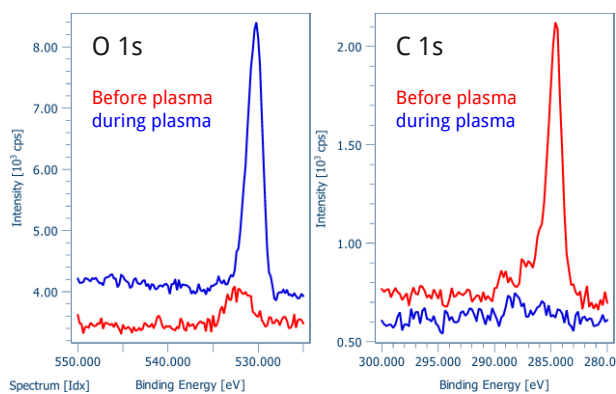


Fig. 4. High-resolution O 1s (left panel) and C 1s (right panel) core-level spectra of the silver sample before (red curve) and during (blue curve) the air plasma treatment (20 min, 75 W rf power, 13.56 MHz) at 0.05 mbar.

After 20 minutes of plasma cleaning, silver oxide became the predominant surface species. This is affirmed by fitting the $\text{Ag } 3d_{5/2}$ spectra, revealing an Ag(I) peak component constituting 65% of the total, which persisted even after the plasma was deactivated. The oxygen content on the silver surface increased from 8 atom-% before the air plasma treatment to 50 atom-% afterward. Additionally, air plasma cleaning led to a notable broadening of the $\text{Ag } 3d_{5/2}$ peak, as evident from

the corresponding Full Width at Half Maximum (FWHM) values, which increased from 530 meV before cleaning to 775 meV post-cleaning, respectively.

The whole process is reversible by a hydrogen plasma treatment of the oxidized silver sample as illustrated in Figure 5. The lower binding energy Ag(I) species at 367.7 eV is reduced back to the metallic Ag(0) species at 368.2 eV during the H_2 plasma treatment. Also, the FWHM of the $\text{Ag } 3d_{5/2}$ peak is reduced from 810 meV to 550 meV.

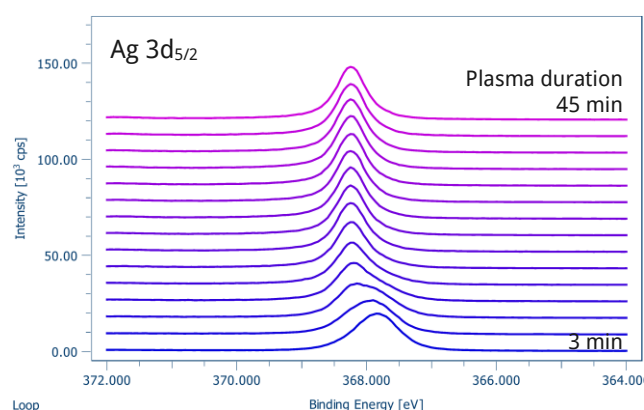


Fig. 5. High-resolution $\text{Ag } 3d_{5/2}$ core-level spectra of an oxidized silver sample during hydrogen plasma treatment (5% H_2 in nitrogen, 75 W rf power at 13.56 MHz) over 45 min at a pressure of 0.05 mbar.

In this application note, we demonstrate the operational capabilities of our NAP-XPS equipment for investigating plasma-enhanced surface reactions directly under working conditions, so called *operando* spectroscopy.

For this study on *operando* plasma cleaning, we utilized a commercial plasma cleaner on a fully automated laboratory NAP-XPS instrument with backfilling configuration. The included PHOIBOS 150 NAP photoelectron analyzer exhibited exceptional NAP-XPS performance, even under plasma-based experimental conditions with reactive radicals present within the analysis chamber.

[1] PIE Scientific LLC, [EM-KLEEN](#).

[2] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder and G.E. Muilenberg *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie, Minnesota, USA, **1979**.

[2] Hoflund, G. B.; Weaver, J. F.; Epling, W. S. Ag_2O XPS Spectra. *Surf. Sci. Spectra* **1994**, *3*, 157.