Application Note #230401

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

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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 online NAP-XPS monitoring of a plasma-enhanced surface cleaning process on a polycrystalline silver sample. Changes of the surface chemistry were studied directly under working conditions (*operando*) using an ambient air plasma at a pressure of 0.05 mbar (5 Pa) in the EnviroESCA (SPECS GmbH). This laboratory NAP-XPS photoelectron spectrometer is equipped with an EM-KLEEN in-situ downstream plasma cleaner (PIE Scientific LLC) with a rf power of 75 W at 13.56 MHz.[1]

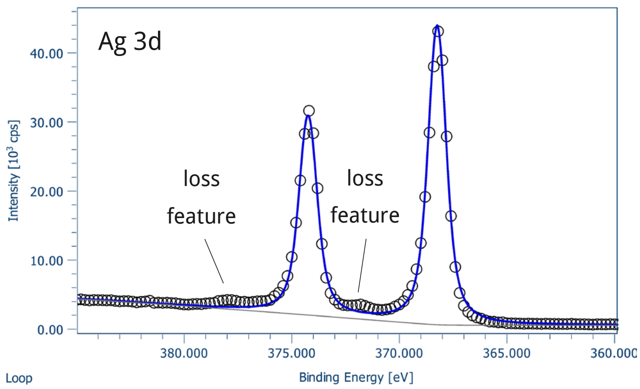

Fig. 1. High-resolution Ag 3d core-level spectra of a native polycrystalline silver sample. The metallic silver species (Ag^0) is reflected by its Ag $3d_{5/2}$ peak position and the characteristic loss features at higher binding energies.

Fig. 1 shows the Ag 3d core-level spectrum before the plasma cleaning. The metallic silver species (Ag^0) is reflected by the Ag $3d_{5/2}$ peak position at a binding energy of 368.3 eV and the characteristic loss features at higher binding energies.[2]

After that the plasma cleaner was started and high-resolution Ag 3d, O 1s, and C 1s core-level spectra (5 scans each) were taken in four loops (5 min each) over a time of 20 minutes.

Fig. 2 shows exemplarily a picture of the ignited air plasma in the sample environment of the EnviroESCA.

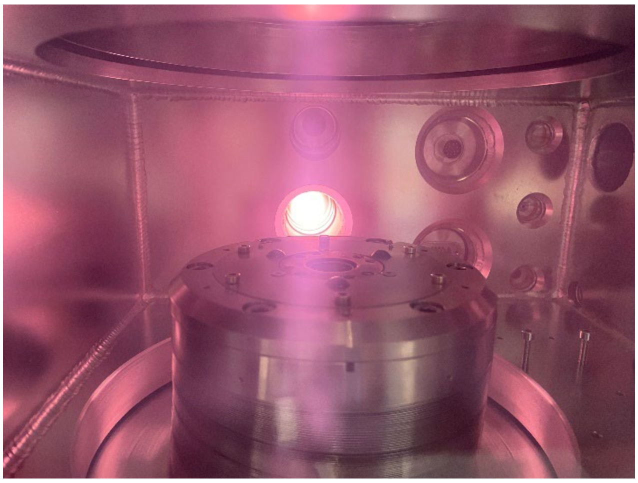

Fig. 2. Picture of the ignited air plasma in the sample environment at a pressure of 0.05 mbar and 75 W rf power at 13.56 MHz.

Fig. 3 shows the high-resolution Ag $3d_{5/2}$ XP spectra acquired live directly while the air plasma was ignited, and the plasma cleaner was in operation.

The metallic silver species (Ag^0) is still observable at around 368 eV. Additionally, a second peak component at binding energies between 367.1 eV and 367.3 eV is now present on the silver surface. This peak component at lower binding energy can be correlated to silver oxide species, e.g., AgO that is formed on the sample during air plasma treatment. This finding is corroborated by an increasing O 1s peak at 530.3 eV, cf. Fig. 4 (left panel).

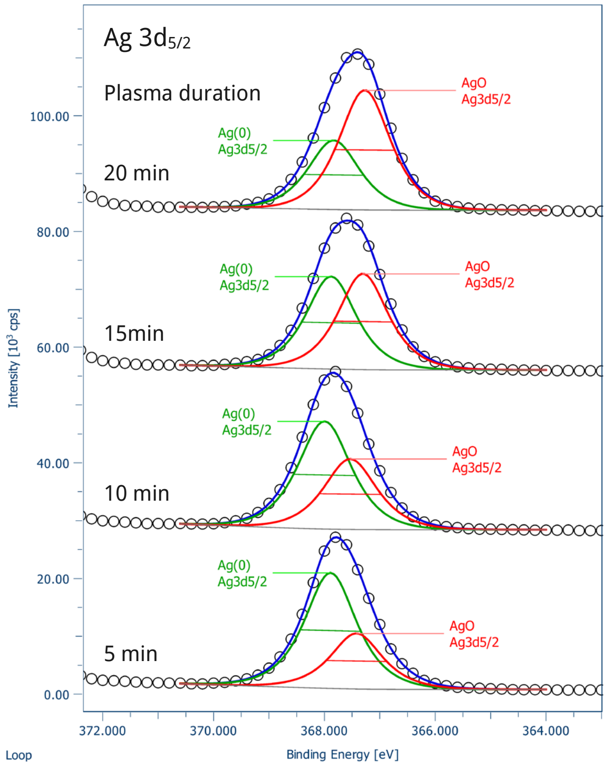

Fig. 3. High-resolution Ag $3d_{5/2}$ core-level spectra of the silver sample during air plasma treatment (75 W rf power at 13.56 MHz) at a pressure of 0.05 mbar.

Further evidence of the plasma-enhanced surface reaction is found in the C 1s core-level spectra. The C 1s peak intensity decreases constantly during the plasma cleaning till it disappears completely after 20 minutes, which proves the effective oxidative removal of the typical adventitious carbon contamination on the silver surface, cf. Fig. 4 (right panel).

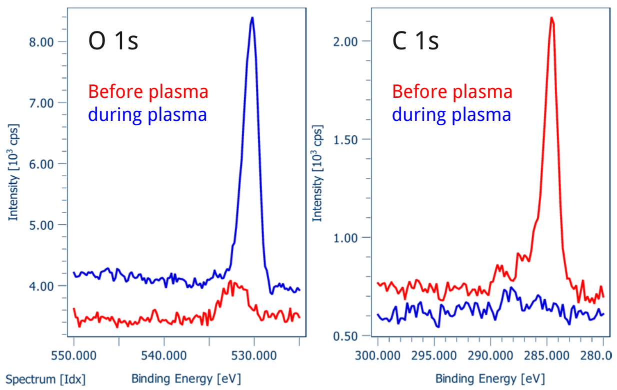

Fig. 4. High-resolution O 1s (left panel) and C 1s (right panel) core-level spectra of the silver sample before (red curve) and during (blue curve) the air plasma treatment (20 min, 75 W rf power, 13.56 MHz) at 0.05 mbar.

The silver oxide is the major surface species after 20 min of plasma cleaning. This can be verified by a fit of the Ag $3d_{5/2}$, yielding an AgO peak component with a relative area of 65 %, which remains on the surface even after the plasma was stopped, see Figs. 3 and 5. The amount of oxygen detected on the silver surface increased from 8 atom-% before to 50 atom-% after the air plasma treatment.

Also, the air plasma cleaning causes a significant Ag $3d_{5/2}$ peak broadening as observed from the corresponding FWHM of 1.0 eV before and 1.4 eV after the plasma cleaning, respectively.

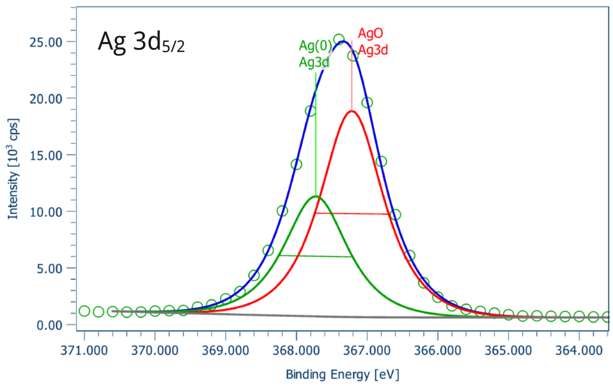

Fig. 5. High-resolution Ag $3d_{5/2}$ core-level spectra of the silver sample after 20 min of air plasma treatment at 0.05 mbar (75 W rf power, 13.56 MHz).

In this short application note we demonstrate the *operando* capabilities of our NAP-XPS equipment to study plasma-enhanced surface reactions directly under working conditions (*operando*).

For this *operando* plasma cleaning study, the EnviroESCA, a fully automated, laboratory NAP-XPS machine was used. The included PHOIBOS 150 NAP photoelectron analyzer has an outstanding NAP-XPS performance that is not to be compromised even when using plasma-based experimental conditions with reactive radicals present in the analysis chamber.

[1] PIE Scientific LLC, EM-KLEEN.

[1] 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**.