	Experiment title: Local atomic and electronic structure of Ag clusters deposited on SiO ₂ substrates, in SiO ₂ aerogel and of partly sulfidised Ag clusters	Experiment number: Si-2567
Beamline: ID 26	Date of experiment: from: 07.11.2012 to: 11.11.2012	Date of report: 05.03.2013 <i>Received at ESRF:</i>
Shifts:12	Local contact(s): Kristina Kvashnina	
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Report:

The purpose of the experiment Si-2567 was to study the electronic and atomic structure of Ag clusters deposited in SiO₂ aerogel with x-ray absorption near edge structure spectroscopy (XANES) at the Ag L₁ and L₂ (3.80 keV, 3.52 keV) absorption edges and the changes which occur due to oxidation and sulfidation. Our findings yield new information on a size dependent change in electronic and atomic structures of Ag clusters compared to bulk Ag as well as on the process of oxide and sulfide formation at the cluster surface. This is of utmost relevance to the use of Ag in nano optical applications.

XANES measurements at the Ag L₁ and L₂ absorption edges of precharacterised samples with different Ag cluster coverages were performed at beamline ID26 of the ESRF using fluorescence detection. The Ag clusters were produced in a supersonic nozzle expansion and deposited into silica aerogel, a highly porous network of SiO₂ molecules with up to 99 vol.-% empty space [1]. After cluster deposition the samples have been characterised before and after contact with air by measuring the plasmon resonances using optical absorption spectroscopy [2]. The cluster coverages were measured by a quartz crystal monitor. Using silica aerogel as matrix material it is possible to deposit more than one cluster monolayer without risking coalescence or film formation. The XANES measurements were performed at the Ag L₁ absorption edge (3.79-3.88 keV) and at the Ag L₂ absorption edge (3.51-3.60 keV). The samples were installed in a custom build vacuum chamber ($p \leq 2$ mbar) during the experiment. The samples were exposed to H₂S produced by the reaction of Na₂S with H₃PO₄ in the Chemistry Laboratory. Using an UV/VIS spectrometer available at the ID26 the Ag cluster plasmon could be measured for different sulfidation steps. Reference measurements of an 100nm Ag film, an Ag₂S pellet, an AgO pellet and an Ag₂O pellet were performed at both absorption edges.

Figure 1 depicts the Ag L₁ absorption edge measured for the Ag clusters in SiO₂ aerogel with a coverage from 1.25 up to 2.76 cluster monolayers compared to the reference spectrum of a 100nm Ag film. With a mean cluster diameter of 2 nm one cluster monolayer corresponds to an effective film thickness of approx. 1.2 nm. The spectra have only few differences in relation to the Ag reference spectrum. The most characteristic divergence is the suppressed peak at an energy of about 3.826 keV (denoted with A).

Figure 2 depicts the Ag L₂ absorption edge of the same sample. Clear differences between the reference spectrum and the cluster spectra are visible from the absorption edge up to an energy of about 3.55 keV. The cluster spectra exhibit considerably less structures at this region. The relative height of the absorption edge differs from the reference spectrum. The pre-edge structures of the absorption spectra shows no significant indication [3] for oxide formation despite air contact during removal from cluster apparatus in our laboratory and montage at the beamline.

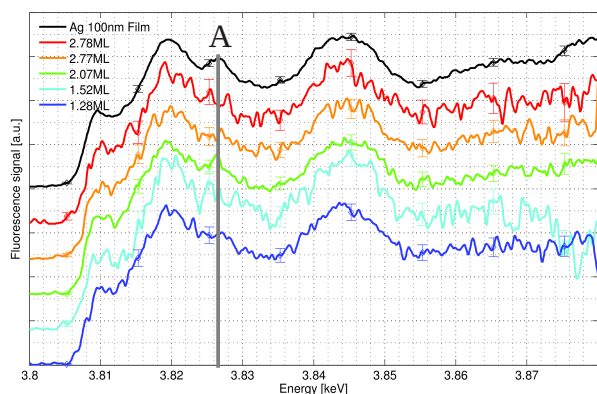


Figure 1: Ag-L₁-absorption edge of Ag clusters deposited in silica aerogel

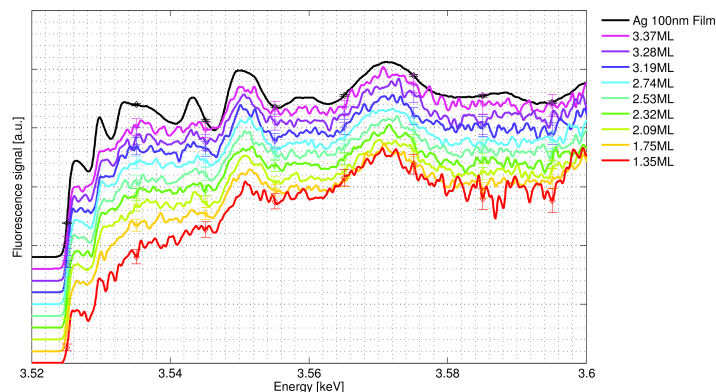


Figure 2: Ag-L₂-absorption edge of Ag clusters deposited in silica aerogel

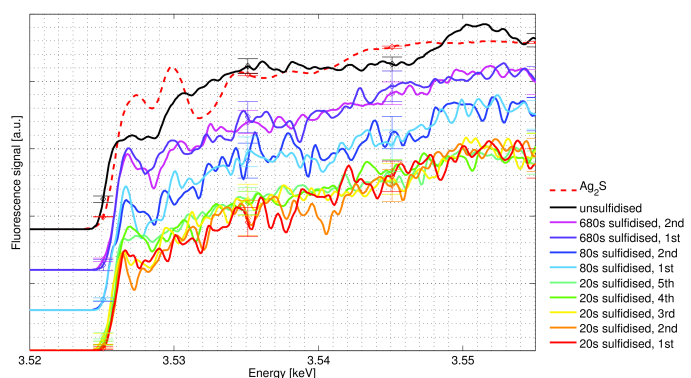


Figure 3: Ag-L₂-absorption edge of Ag clusters deposited in silica aerogel before sulfidation (black), after sulfidation (coloured) and Ag₂S reference spectrum (dashed red)

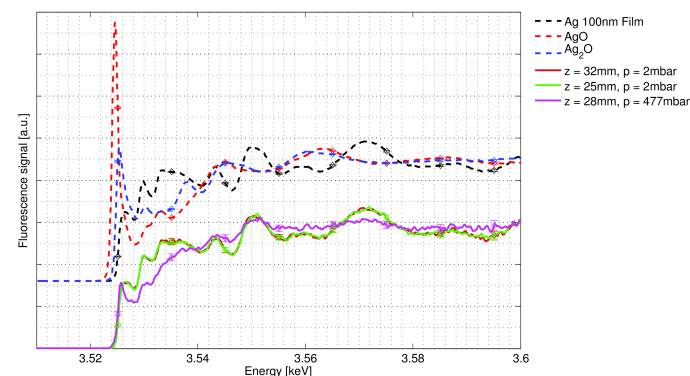


Figure 4: Ag-L₂-absorption edge of Ag clusters deposited in silica aerogel measured at 2 mbar and 477 mbar. Reference spectra measured at 2mbar.

Figure 3 depicts our results of the sulfidation experiments. Here Ag clusters deposited in aerogel were sulfidised with 20, 80 and 680 seconds exposure to H₂S. Measurements with a total integration time of 2400 s were repeated 5 times (20 s sulfidation), 2 times (80 s sulfidation) and 2 times (680 s sulfidation). Comparing the 1st measurement of the 20 s sulfidised clusters (red) with the spectrum of the unsulfidised clusters (black) a shift of the absorption edge to higher energies is visible. Corresponding UV/VIS measurements performed after each sulfidation step showed the disappearance of the cluster plasmon. These observations indicate a chemical reaction of silver and sulphur. An increasing signal (white line) at the absorption edge confirms a chemical reaction like ionic or covalent bonding. After the 2nd to 3rd measurement the absorption edge shifted back to lower energies. A second sulfidation experiment confirmed this. However a recurrency of the plasmon could not be observed. A similar behaviour with an even stronger similarity to the Ag₂S reference spectrum was observed for longer exposure (80 s and 680 s) to H₂S.

Figure 4 depicts the spectra of the oxidation experiments. A sample with a high amount of clusters (and therefore strong similarities to Ag reference spectrum) was measured at two different positions at p = 2 mbar. The spectra were identical. Subsequently a valve of the vacuum chamber was opened to increase the pressure up to 477 mbar. XANES spectroscopy was performed at a new position for 10-180 seconds. The spectrum of the clusters now reveal the formation of silver oxide indicated by the increasing white line. Also the after-edge region exhibits similarities to the AgO and Ag₂O reference spectra. So while no oxidation was observed for clusters which were just exposed to air, silver oxide forms while exposing the clusters to air and simultaneous energy deposition by the incident x-ray beam.

These results were very important to complete the study started with experiment MA-1298. The PhD thesis of Sabrina Hoffmann was finished in December 2012 [4] and the publication of the results will be submitted in near future to the Journal of Physical Chemistry C.

References:

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