



Experiment title: Local atomic and electronic structure of mass separated Ag clusters deposited on SiO ₂ substrates	Experiment number: MA-1298	
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Report:

The purpose of the experiment MA-1298 was to study the electronic and atomic structure of partly oxidised and sulfidised Ag clusters deposited on SiO₂, in SiO₂ aerogel and in polydimethylsiloxane (PDMS) by x-ray absorption near edge structure spectroscopy (XANES) at the Ag L₁ and L₂ (3.80 keV, 3.52 keV) absorption edges. 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 the influence of sulfide formation on 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 onto an SiO₂ substrate or into a PDMS matrix [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 a polymer as matrix material it is possible to deposit more clusters without risking coalescence [3]. The XANES measurements were performed at the Ag L₁ absorption edge in an energy range of 3.79-3.88 keV for Ag clusters in PDMS and at the Ag L₂ absorption edge in an energy range of 3.51-3.60 keV for Ag clusters in PDMS and on a SiO₂ substrate. The resolution of incident energy was 0.1 eV. Reference measurements of both absorption edges were performed at an Ag film, a sulfidised Ag film and an Ag₂O tablet.

Figure 1 depicts the Ag L₂ absorption edge measured for the Ag clusters on SiO₂ for coverages of 0.17, 0.45 and 1 cluster monolayers compared to the reference spectrum of a Ag film. With a mean cluster diameter of 2 nm one cluster monolayer corresponds to a height of approx. 1.2 nm. While for the highest coverage of one cluster monolayer the shape of the L₂ edge still looks quite similar to the Ag reference, there are more and more pronounced differences for lower cluster coverages. The similarity for the highest coverage is a result of beginning coalescence of the closely packed clusters on the surface, which was also visible in the optical absorption spectra. Thus the investigated particles grow to larger islands while for the smallest cluster coverage of 0.17 monolayers the Ag clusters are still separated from each other, meaning that there are significant differences in local and electronic structure between the 2 nm clusters and the

bulk reference. The pre-edge structure of the absorption spectra shows no significant indication for oxide formation. To reveal the origin of the differences, calculations of absorption spectra for different Ag cluster sizes and different geometrical structures are being performed at the moment.

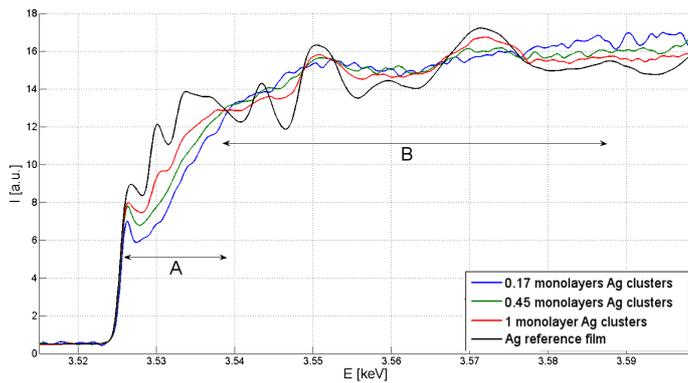


Figure 1: Ag L_2 absorption edge of Ag clusters on SiO_2 compared to Ag reference signal (black line)

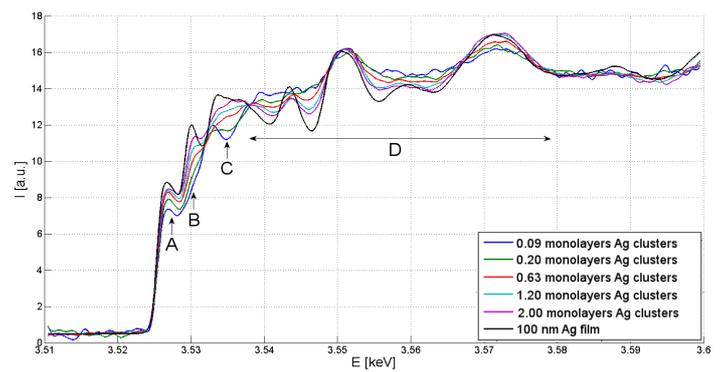


Figure 2: Ag L_2 absorption edge of Ag clusters in PDMS matrix compared to Ag reference signal (black line)

Figure 2 depicts the Ag L_2 absorption edge measured for the Ag clusters in a PDMS Matrix for different cluster coverages. There are clearly visible changes in different edge features (marked A, B, C, D) which become more similar to the Ag reference edge feature with increasing cluster coverage.

Figure 3 depicts the Ag L_1 absorption edge measured for the Ag clusters in a PDMS Matrix for different cluster coverage. Here, in contrast to the L_2 edge different excited states are probed yielding complementary information about the unoccupied density of states. Similar to the findings for the L_2 edge remarkable differences (marked with A) between the cluster signals and the Ag bulk reference are observed for low cluster coverage.

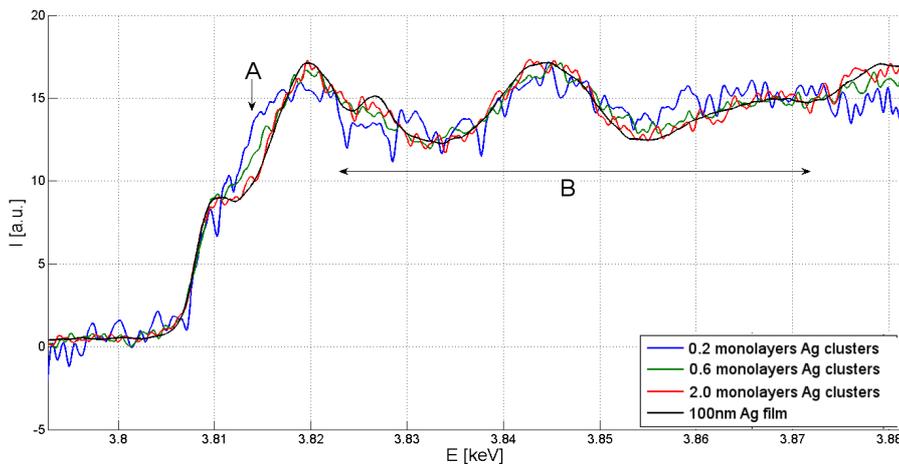


Figure 3: Ag L_1 absorption edge of Ag clusters in PDMS matrix compared to Ag reference signal

As the data analysis is still in progress, a full interpretation of the data can not be given here yet. However, it is already clear that there are remarkable differences in the absorption spectra of small Ag clusters on SiO_2 as well as in a PDMS matrix compared to the bulk reference. A significant oxidation of the clusters seems to be unlikely, when comparing the edge onset with Ag_2O reference [5]. Calculations of the absorption edges are in progress to understand the changes in geometric and electronic structure of the clusters dependent on cluster size.

References:

- [1] H. Hövel, S. Fritz, A. Hilger, and U. Kreibig, Phys. Rev. B **48**, 18178 (1993).
- [2] H. Hövel, A. Hilger, I. Nusch, and U. Kreibig, Z. Phys. D **42**, 203 (1997).
- [3] L. Ravagnan, G. Divitini, S. Rebasti, M. Marelli, P. Piseri and P. Milani, J. Phys. D **42**, 082002 (2009).
- [4] P. Behrens, S. Amann, U. Bilow, C. Linke, M. Jansen, Z. anorg. allg. Chem. **625**, 111 (1999).
- [5] T. Miyamoto, H. Niimi, Y. Kitajima, T. Naito and K. Asakura, J. Phys. Chem. A **114**, No.12, 4093 (2010).