ESRF	**Experiment title:** Structural characterization of very small Ag and Ag/Au nanoparticles in soda-lime glasses by EXAFS spectroscopy	**Experiment number**: HS-3314
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Shifts: 12	**Local contact(s)**: Dr Giuliana AQUILANTI	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*Doz.Dr. Manfred DUBIEL

*Dr. Jörg HAUG

*Holger KRUTH

Martin-Luther-Universität Halle-Wittenberg
Friedemann Bach Platz 6
D-06108 Halle
Germany

Report:

The aim of the experiments was the characterization of the atomic structure of very small Ag and Ag/Au nanoparticles by means of temperature-dependent EXAFS experiments. Therefore, samples prepared by three different experimental procedures (ion exchange, ion irradiation, ion implantation of Ag and Au) were measured in fluorescence mode.

Fig. 1 shows the EXAFS measurements for ion-exchanged samples and for a Ag foil. Here, it can be shown that it is possible to investigate samples with short times of ion exchange (10 to 60h) in fluorescence mode. The formation of silver nanoparticles is indicated by a shoulder in the normalized EXAFS spectra at about 25560 eV as well as in the Fourier transformed spectra at about 2.8 Å. The presence of Ag-O bonds shows that the formation process of the nanoparticles is not complete.

Ion-implanted samples were measured at the Ag K- and Au L3-edge. In Fig. 2, the normalized EXAFS spectras of the Ag K-edge show differences depending on the ion dose. For smaller Ag ion doses ($2x10^{16}$ ions/cm^2) only a shoulder is present (comparable to the ion-exchanged samples in Fig. 1) whereas for $4x10^{16}$ ions/cm^2 a sharp peak comparable to that of the Ag foil can be seen. The Fourier transformed spectras show Ag-Ag and Ag-O bonds for small ion doses, for high ion doses two different correlations (Ag-Ag and Ag-Au) can be found between 2 and 3 Å. Similar results were reported in literature for flame sprayed gold-silver nanoparticles [1].

At the Au L3-edge, the sample with a reduced ion dose was not measured because of the limited time. The samples with high ion dose show differences to the Au foil. That indicates that for a fit of the Fourier transformed spectras two bonds (Au-Au and Au-Ag) has to be considered.

With this first experiments, we proved that it is possible to get information on the formation of very small silver nanoparticle (some nm in size). For this, EXAFS fluorescence measurements with a high photon flux are necessary. With these measurements, we can investigate the formation of the nanoparticles as well as their growth during ion exchange as result of additional heat treatment. Also structural changes of the nanoparticles during heating can be observed.
For ion implanted samples, measurements at the Ag- and Au-edges lead to information on the structure of Ag/Au nanoparticles. In this case, bimetallic nanoparticles, core-shell particles or silver and gold nanoparticles are possible. Because of the low concentration of metal ions in this samples an extended time for the measurements is necessary.
All measurements were carried out at 20K. The aim of the experiment was also to investigate the temperature-dependent lattice parameters to calculate the Einstein temperature and the thermal expansion coefficients on the basis of cumulant expansion method. Therefore, additional experiments with more shifts are necessary.

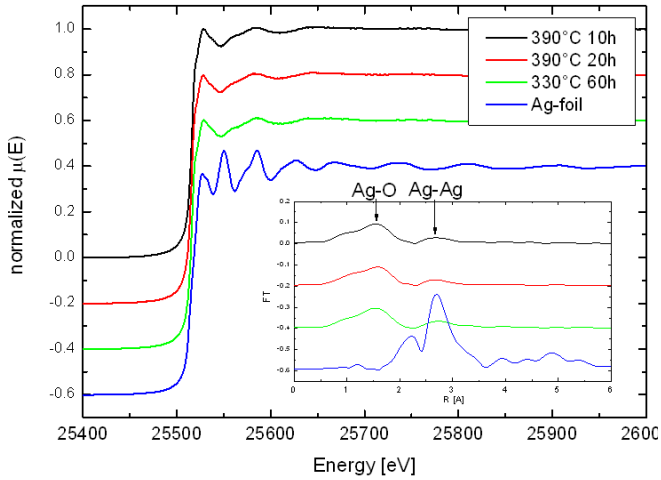

Fig. 1: Normalized EXAFS spectra collected at the Ag K-edge for different ion-exchanged samples at 20K. The inset shows the Fourier transformed spectras.

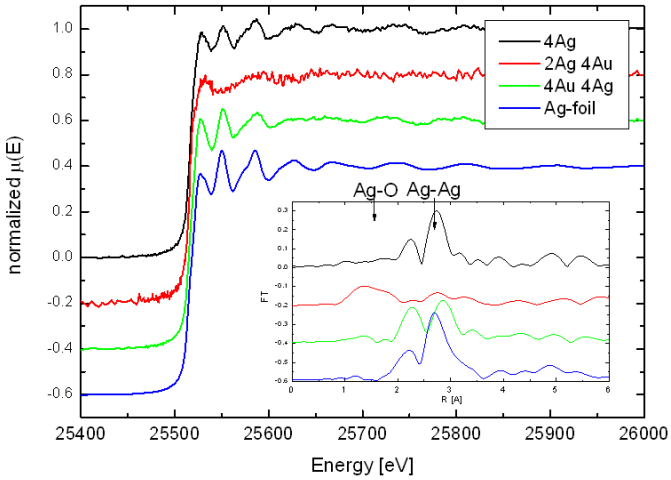

Fig. 2: Normalized EXAFS spectra collected at the Ag K-edge for different ion-implanted samples at 20K. The inset shows the Fourier transformed spectras.
2: $2x10^{16}$ ions/cm^2 ; 4: $4x10^{16}$ ions/cm^2

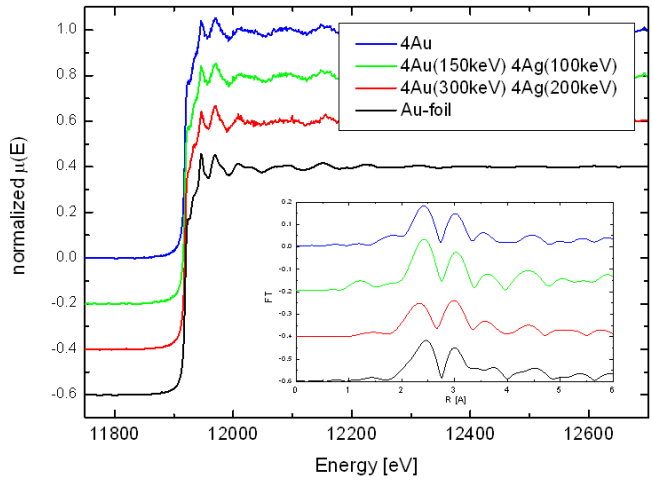

Fig. 3: Normalized EXAFS spectra collected at the Au L3-edge for different ion-implanted samples at 20K. The inset shows the Fourier transformed spectras.

[1] S. Hannemann, J-D. Grunwaldt, F. Krumeich, P. Kappen, A. Baiker, *"Electron microscopy and EXAFS studies on oxide-supported gold-silver nanoparticles prepared by flame sprayed pyrolysis"*, Appl. Surf. Sci. 252 (2006) 7862-7873