Structural characterization of bimetallic Ag-Au nanoparticles in glass

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Abstract. Metal nanoparticles embedded in glass have been thoroughly studied because of their specific optical properties. The present work is directed to the fabrication of bimetallic Ag/Au nanoparticles by double ion implantation and their structural investigation. Ion-implanted samples were measured at the Ag K- and Au L$_3$-edge at HASYLAB/Hamburg and ESRF/Grenoble, respectively, in fluorescence mode (at 10 and 20 K). The Fourier transformed spectra 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. At the Au L$_3$-edge, the high-dose implantation creates an additional Au-Ag correlation visible in the Fourier transformed spectra. These results indicate the formation of Ag-Au alloy nanoparticles for high-dose sequential implantation of Ag and Au ions (4x10$^{16}$ ions/cm$^2$ in each case) whereas for lower doses mainly the ionic state of implanted ions should exist. Transmission electron microscopy characterization revealed the formation of smaller homogeneous particles of ≈5 nm mean size and larger ones of ≈15 nm that exhibit an internal void, i.e. hollow core-shell particles. EXAFS data prove bimetallic structures for all nanoparticles.

1. Introduction
Nanosized metal particles embedded in surfaces regions of glass are of great interest because of their potential application [1,2]. Specific linear and non-linear optical properties have been achieved already for Au, Ag or Cu nanoparticles in silica glasses [3,4,5]. The resulting macroscopic properties are based on a surface plasmon resonance (SPR). The frequency of this resonance strongly depends on the materials and their composition. The preparation of bimetallic Au-Ag nanoparticles allows the shift of SPR in between the position of resonance of Ag and Au particles [6]. Such bimetallic nanoparticles have already been produced by double ion implantation in silica glass already. The structure of such nanoparticles has been investigated by transmission electron microscopy (TEM), X-ray absorption fine structure (EXAFS) spectroscopy and X-ray diffraction [7,8,9]. In all these studies, pure nanoparticles of both elements or bimetallic alloys were found. Hannemann [10] studied the structure and formation of Au-Ag nanoparticles prepared by flame spray pyrolysis on substrates with electron microscopy and EXAFS. Shibata [11] investigated the alloying of Au-Ag core-shell nanoparticles in aqueous solution with EXAFS and molecular dynamics simulation. In the present work, we investigated double-implanted Ag/Au nanoparticles prepared by different implantation sequences and implantation doses.
in soda-lime glasses [12] to characterize their structure using EXAFS experiments at the Au L$_3$- and Ag K-edges, respectively.

2. Experimental details

2.1. Sample preparation
Soda-lime glasses containing (in mol%) 72.4% SiO$_2$, 14.4% Na$_2$O, 6.4% CaO, 6.0% MgO, 0.5% Al$_2$O$_3$, 0.20% K$_2$O, 0.3% SO$_3$ and 0.04% Fe$_2$O$_3$ were exposed to Ag$^+$ and/or Au$^+$ ion implantation at room temperature using energies between 200 and 300 keV so as to achieve the same penetration depth for both ions. On glass sheets of 1mm thickness areas of 20x20 mm$^2$ have been subjected to implantation for each type of ions at doses ranging from 2x$10^{16}$ to 4x$10^{16}$ ions/cm$^2$. The beam current density was 1 A/cm$^2$. Charge buildup reduction at the glass surface during implantation was achieved by electron beam irradiation onto the surface. Samples with different implantation sequence and ion dose were produced: 4x$10^{16}$ Ag$^+$ (sample name: 4Ag), 4x$10^{16}$ Au$^+$ (sample name: 4Au), 2x$10^{16}$ Ag$^+$ + 4x$10^{16}$ Au$^+$ (sample name: 2Ag4Au), 4x$10^{16}$ Au$^+$ + 4x$10^{16}$ Ag$^+$ (sample name: 4Au4Ag).

2.2. X-ray absorption spectroscopy
EXAFS spectroscopy was performed at the ESRF/Grenoble and the HASYLAB/Hamburg, respectively, at the Ag K- and Au L$_3$-edges. The samples were measured simultaneously in transmission and fluorescence mode. For the calibration silver and gold foils were measured at room temperature. Because of the thin nanoparticle layer (some 100 nm) and thus a low concentration of metal in the whole samples the fluorescence data were used for the data evaluation. The EXAFS oscillations ($\chi(k)$) were extracted by standard procedures using the program package Athena [13].

3. Results and Discussion
Figure 1 shows the normalized Ag K-edge EXAFS spectra measured at 20 K for the samples 4Ag, 2Ag4Au, 4Au4Ag and for the reference foil. The spectra show differences which depend on the ion dose, e.g. for smaller Ag ion dose (2Ag4Au) only a shoulder at about 25550 eV is present whereas for 4Ag and 4Au4Ag a sharp peak comparable to that of the Ag foil can be seen. The different configuration of the white line of sample 2Ag4Au indicates that in this case one part of the silver is in an oxidized state. Implantation of silver only (4Ag) results in an EXAFS spectrum nearly identical to that of the Ag-foil, whereas for double-implanted sample 4Au4Ag a variation can be seen. This variation leads to a shift in $\chi(k)$ for k values higher than 5 Å$^{-1}$ and therefore, also in the Fourier transformed spectra of $\chi(k)$ depicted in figure 2. These spectra show Ag-Ag and Ag-O bonds for small ion doses (sample 2Ag4Au) indicating that the silver is partially oxidized. For high ion doses (4Au4Ag) two different correlations (Ag-Ag and Ag-Au) can be found between 2 and 3 Å. The peak at 2.2 Å is more intense and the second one at about 2.8 Å is shifted to higher values compared to pure silver. These characteristics can be explained by bimetallic Ag-Au particles. The simulation of spectra of bimetallic particles with 50 at.% Au and 50 at.% Ag were performed by means of FEFF6.0 code [14] by an exchange of Ag atomic positions with Au. Such structure leads to an increase in intensity for the first peak and a shift of the second one as obtained in the Fourier transformed spectra of our experiment. These changes result from the different backscattering function of Ag and Au atoms, respectively. Similar results were reported in the literature for flame sprayed gold-silver nanoparticles [10]. These findings indicate that in the sample 4Au4Ag a significant amount of Au is arranged in the nearest neighbour shell around Ag and therefore, bimetallic nanoparticles exist.

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At the Au L₃-edge, the sample with reduced ion dose was not measured because of the low intensity of EXAFS oscillations also in fluorescence mode. The normalized EXAFS spectra for high ion dose are shown in figure 3 together with the Au foil. The absence of the typical white line for oxidized Au (e.g. Au₂O₃) demonstrates that no Au-O correlations are present in the samples 4Au and 4Au4Ag. Also the Fourier transformed spectra in figure 4 do not indicate any oxides. The monometallic sample 4Au as well as the bimetallic sample 4Au4Ag show two peaks in the Fourier transforms at 2.4 and 3.0 Å, but, the spectrum of 4Au4Ag shows differences to 4Au and the Au foil. The first peak is shifted to smaller values and the intensity of the second peak is increased as compared to the first one. This indicates that for a fit of the Fourier transformed spectra two bonds (Au-Au and Au-Ag) must be considered. Calculations by the FEFF6.0 code demonstrate that the increase of the second peak is characteristic for Au-Ag alloys. Therefore, also the measurements at the Au L₃-edge prove the bimetallic composition of the double-implanted sample 4Au4Ag.

TEM experiments at the sample 4Au4Ag revealed the formation of small homogeneous nanoparticles with about 5 nm diameter and larger particles with about 15 nm in size. The larger nanoparticles show a reduced TEM contrast in the central region. This points to a core-shell structure of these particles.
To get detailed information on the composition of the nanoparticles, the Fourier transformed EXAFS oscillations at the Au L$_3$-edge as well as Ag K-edge should be fitted together in future work. Other methods like anomalous small angle scattering (ASAXS) also can be used to determine the composition [14].

4. Conclusions
EXAFS experiments at the Ag K-edge demonstrated that for low ion dose ($2 \times 10^{16}$ ions/cm$^2$) the most part of the ions still exist in the ionic state whereas for higher dose ($4 \times 10^{16}$ ions/cm$^2$) two separate peaks in the Fourier transformed spectra between 2 and 3 Å can be seen. For sample 4Au4Ag these two peaks indicate the presence of backscattering from Au atoms. Therefore, the nanoparticles consist of bimetallic alloy. No Ag-O bonds were found in this sample. Also at the Au L$_3$-edge, no oxidized Au is indicated for the sample 4Au4Ag.

In comparison to EXAFS data, TEM investigations showed small homogeneous particles and larger core-shell structures. The contrast of TEM images indicates the formation of hollow nanoparticles.

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References