ESRF	**Experiment title:** Arrays of plasmonic AgAu nanoparticles prepared in glass by UV laser: dependence of particles atomic structure, size and degree of agglomeration upon irradiation parameters	**Experiment number**: MA-3438
Beamline: BM-23	**Date of experiment**: from: 12 Jul 2017 to: 16 Jul 2017	**Date of report**: 27 Feb 2018
Shifts: 12	**Local contact(s)**: Kirill Lomachenko (email: kirill.lomachenko@esrf.fr)	*Received at ESRF:*

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Report:

Monotonic changes in Au L3-edge X-ray absorption near-edge structure (XANES) spectra can be observed for gold coated ion-exchanged glass with the increasing number of the applied laser pulses (Figure 1a). These changes are best appreciated in difference spectra (Figure 1b) where a spectrum of non-irradiated gold coated glass has been subtracted from each spectrum of the irradiated samples. Difference in XANES is caused by the formation of alloyed gold-silver nanoparticles. No such changes were observed in the case of pure gold particle formation, when the glass without Ag-Na ion exchange procedure was used.

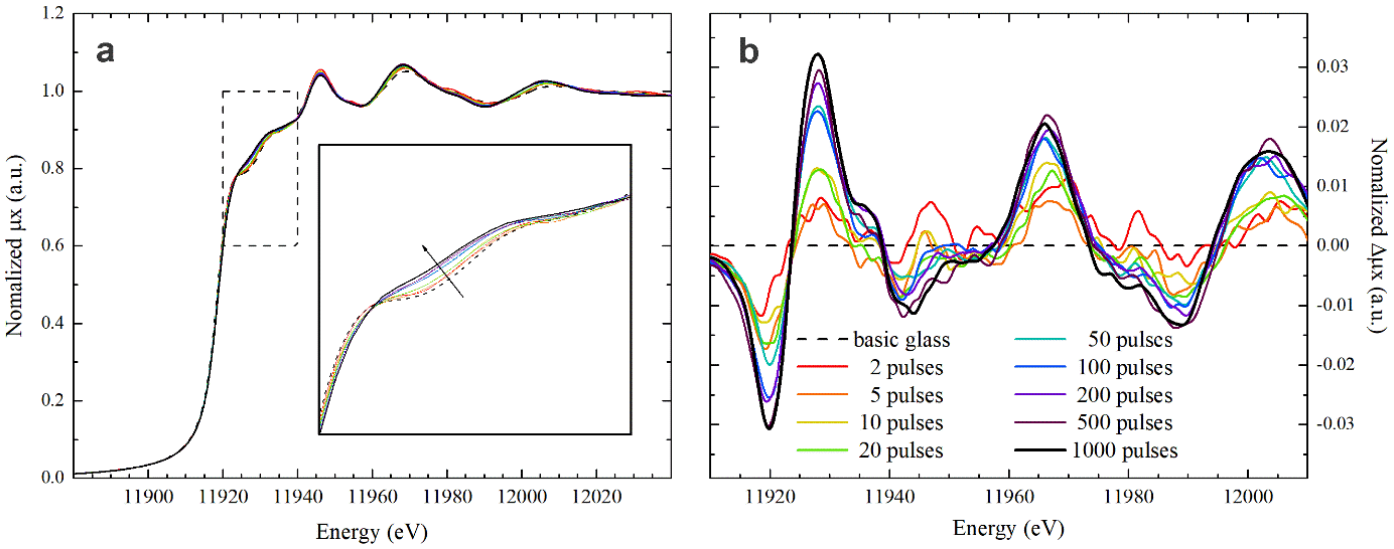

Figure 1. XANES spectra (part a) of the ion-exchanged gold coated glass irradiated by different number of laser pulses (colored curves) from 0 (dashed black line) to 1000 (solid black line) and corresponding difference spectra (part b).

The quantitave analysis of Au L3-edge EXAFS spectra provided information about local atomic structure of Au atoms in the glasses irradiated by different number of laser pulses.

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Au-Au and Au-Ag coordination details are shown in the following Table and one of the fittings of Fourier-transformed signal is shown on Figure 2.

Pulse	Au-Au			Au-Ag		
s	*R*, Å	*N*	σ^2, Å^2	*R*, Å	*N*	σ^2, Å^2
10	2.855	9.9	0.0098	2.889	2.1	0.010
50	2.854	7.8	0.0084	2.861	3.3	0.009
100	2.852	7.7	0.0079	2.857	3.1	0.008
200	2.860	6.8	0.0077	2.864	3.3	0.007
1000	2.852	5.7	0.0084	2.860	4.2	0.009

Obtained high total coordination number of Au atoms in the sample corresponding to 10 pulses is the evidense of the core-shell architecture of the nanoparticles (or very big particles, whichm however, should not be expected).

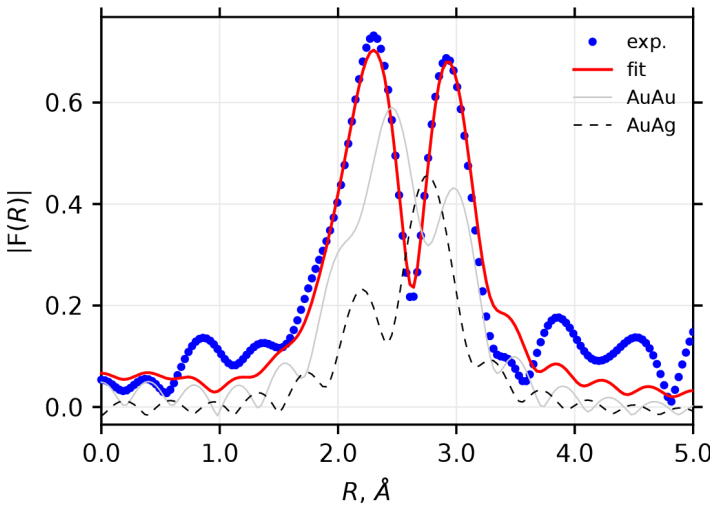

Figure 2. The quality of the fitting for the sample obtianed after 50 pulses.

XRD results are partly published in:

Heinz, M., Srabionyan, V., Avakyan, L., Bugaev, A., Skidanenko, A.V., Pryadchenko, V., Ihlemann, J., Meinertz, J., Patzig, C., Dubiel, M., Bugev, L.

Formation and implantation of gold nanoparticles by ArF-excimer laser irradiation of gold-coated float glass (2018) J. Alloys Compd. 736(5) 152-162 http://dx.doi.org/10.1016/j.jallcom.2017.11.122

Abstract: To develop a technique for the production of submicron line patterns and directed arrays of plasmonic nanoparticles, the generation and implantation of gold nanoparticles into float glass surfaces was studied by means of ArF-excimer laser irradiation (193 nm) below the ablation threshold of the glass which was sputter coated with a gold layer with a thickness of 70 nm. The formation of gold particles was confirmed by the characteristic surface plasmon resonance (SPR) peak at ~550 nm. The intensity of the SPR peak of gold particles embedded in the glass matrix increases with the number of applied laser pulses, indicating a different degree of implantation of the gold nanoparticles into the glass surface. It was revealed that the laser implantation of the generated gold particles into the glass is supported on the tin-bath side by the enhanced absorption of tin ions. The dependences of SPR parameters upon the number of laser pulses at different fluences were obtained. Using the methods of X-ray diffraction and extended X-ray absorption fine structure, the mean size of implanted gold particles was estimated at 15–20 nm. This particle size was confirmed by analytical (scanning) transmission electron microscopy, but a small fraction of single particles with a size of ~50 nm have also been observed. The particles arrangement was further examined by the fitting of experimental optical extinction spectra, varying the particles sizes and interparticle distances within the direct calculations of spectra by the multi-spheres T-matrix method, considering the possible agglomerations of particles. The applied experimental technique provides the creation of arrays of gold nanoparticles in the near-surface region of the glass, which can be used as the substrates or nuclei in the glass for producing bimetallic nanoparticles with gold as the core and SPR characteristics varied in a wide range of visual wavelengths.

EXAFS and XANES results are preparing for publication in J. Alloys Compd:

M Heinz, VV Srabionyan, LA Avakyan, AL Bugaev, AV Skidanenko, VV Pryadchenko, SYu. Kaptelinin, J Ihlemann, J Meinertz, Ch Patzig, M Dubiel, LA Bugaev

Formation of bimetallic silver-gold nanoparticles in glasses by UV laser irradiation: X-ray absorption spectroscopy study