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To cite this article: M Dubiel *et al* 2016 *J. Phys.: Conf. Ser.* **712** 012110

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Silver nanoparticles in silicate glass prepared by UV laser irradiation: dependences of size and atomic structure of particles upon irradiation parameters

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Abstract. Plasmonic Ag nanostructures were generated in glass surfaces by means of UV laser irradiation (193 nm). The aim of the work was to identify the correlations between the atomic structure of such nanoparticles and their optical properties. The structural characterization of the samples, prepared with different number of laser pulses was performed by Ag *K*-edge EXAFS. The processing of the spectra by the Fourier-transform analysis gave the values of Ag-Ag and Ag-O interactions averaged over ionic and neutral states of silver in the sample. The consistent analysis of the behavior of features in optical spectra and the obtained dependencies of Ag-Ag and Ag-O structural parameters upon the number of laser pulses enabled to suggest the mechanism of plasmonic Ag nanoparticles formation in silicate glass, which is influenced by the interaction with polyvalent ions (for example Fe²⁺) and by defect centers (for example HTC and NBOHC centers) generated by UV irradiation.

1. Introduction

The formation of metal nanoparticles, especially silver particles in dielectric matrixes, is extensively studied. These nanocomposite materials exhibit linear and non-linear optical properties, which are determined by the surface plasmon resonance (SPR) of the nanoparticles [1]. Generally, silver nanoparticles in sodium silicate glasses are prepared by the Ag⁺↔Na⁺ ion exchange process and subsequent thermal treatments [2, 3]. However, this method does not allow creating nanoscaled arrays of particles localized in a certain way. In our previous work [4] to obtain spatially specific precipitation of nanoparticles (line structures) in Ag⁺↔Na⁺ ion exchanged glass surfaces the laser irradiation below the ablation threshold of the glass was implemented. By means of UV laser irradiation high resolution patterning could be realized. However, the UV laser irradiation, depending on the laser parameters, can lead to the reduction of the size or to the dissolution of nanoparticles [5] and to their instability even at room temperature. These processes can occur since the UV irradiation of glass induces the creation of various defect centers [6], which results both in the enhancement of particles formation and in the recombination processes giving a decrease in the particles concentration. In some cases it was also shown that the formation of stable nanoparticles can be obtained without

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additional thermal treatments [7]. Therefore, to obtain stable nanoparticles with certain characteristics of SPR, for example peak position and full width at half maximum (FWHM), it is necessary to reveal the dependences of these characteristics upon the parameters of the laser irradiation and to obtain the values of these parameters that provide the stability of the nanoparticles.

In this paper the formation of stable silver nanoparticles in $\text{Ag}^+ \leftrightarrow \text{Na}^+$ ion exchanged glass surfaces by means of ArF-excimer laser irradiation (193 nm) without additional thermal treatments is succeeded. Experimental methods to characterize the nanoparticles are optical spectroscopy to determine the size of the nanoparticles using Mie theory, and Ag *K*-edge extended X-ray absorption fine structure (EXAFS) to reveal the dependences of the structural parameters of Ag-Ag and Ag-O interactions upon the number of laser pulses.

2. Experimental results

The basic glass was soda-lime silicate glass (float glass). The $\text{Ag}^+ \leftrightarrow \text{Na}^+$ ion exchange has been performed by immersing the glass slides into a molten $\text{NaNO}_3 / 5 \text{ wt.-% AgNO}_3$ salt bath at a temperature of 330 °C for 20 minutes. Then the ion exchanged glass slides have been irradiated by the ArF-excimer laser (Lambda Physik LPX 315; wavelength 193 nm, 20 ns pulse duration) at the tin bath side. The laser fluence was approximately 100 mJ/cm^2 and the repetition rate was 10 Hz. The number of laser pulses has been varied from 2 to 5000. The size of the laser spots was 5 to 10 mm. For simplicity of notations, the sample obtained using 2 laser pulses will be referred to as Sample 2, the other one using 10 laser pulses will be referred to as Sample 10 and so on.

Extinction spectra have been measured at a UV/Vis/NIR spectrometer (Perkin Elmer, Lambda 900). Figure 1 shows the extinction spectra of Samples 10, 100, 500, 1000 and 5000 (here the extinction coefficient is represented). It can be seen, that up to 100 pulses (Samples 10 and 100) the spectra are characterized by a wide absorption band with a maximum at $\sim 450 \text{ nm}$. In the spectra of Samples 500, 1000 and 5000 (more than 500 pulses), this absorption band takes the form of a SPR band with a maximum shifted from $\sim 450 \text{ nm}$ in Sample 10 to $\sim 435 \text{ nm}$ in Sample 5000. Concerning the SPR bands Mie theory simulations have been performed (dashed lines in Figure 1) assuming that the absorption in the visible region occurs only owing to the SPR of silver nanoparticles which are described by a log-normal size distribution. This results in average particle sizes of $D = 28, 20$ and 14 nm in Samples 500, 1000 and 5000, respectively. Required equations for the simulations are taken from [8]. Deviations in the UV region can be explained by atomic and ionic silver in the glass, which were not taken into account by the simulations. Probably, the calculated average sizes of nanoparticles are not exactly determined because of the neglect of absorption contributions of any other Ag centers. The concentration of such structural units is not known.

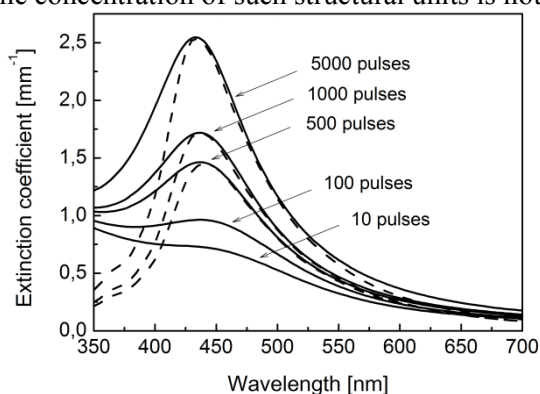


Figure 1. Extinction spectra of samples 10, 100, 500, 1000 and 5000; the solid lines represent the experimentally obtained spectra and the dashed lines refer to the Mie theory simulations.

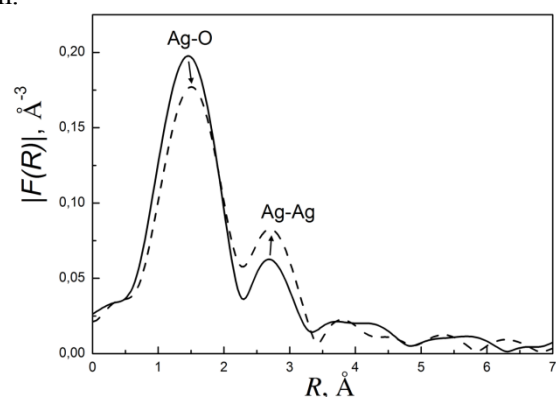


Figure 2. FT magnitudes $|F(R)|$ of experimental Ag *K*-edge EXAFS in Sample 20 (solid curve) and in Sample 5000 (dashed curve).

In Figure 2 the magnitudes of the Fourier-transforms $|F(R)|$ of experimental Ag *K*-edge EXAFS in Sample 20 (low number of pulses) and in Sample 5000 (largest number of pulses) are compared. The magnitude of the first peak, which corresponds to the contribution of Ag-O interactions, decreases with the increasing of the number of laser pulses, while the magnitude of the second peak, attributed to the contribution of Ag-Ag bonds, increases. To confirm these qualitative conclusions, experimental Ag *K*-edge EXAFS in Samples 2 – 5000 were processed by the technique of [9], which enables to reduce the effect of correlations among fitting parameters on the determined values of structural parameters by using interdependencies between all correlating parameters of a fitting model, which were obtained at different weights k^n for oscillatory part $\chi^{exp}(k)$ and at different Δk intervals for FT. The fit of $F(R)$ of EXAFS spectrum can be performed using the following expression for $\chi(k)$:

$$\chi(k) = A_{\text{Ag-Ag}} \cdot \chi_{\text{Ag-Ag}} + A_{\text{Ag-O}} \cdot \chi_{\text{Ag-O}} + \tilde{\chi}_{\text{Ag}} \quad (1)$$

where $\chi_{\text{Ag-Ag}}$ – is the contribution of one atomic pair Ag-Ag without the reduction factor $S_0^2(\text{Ag-Ag})$ [10]; $\chi_{\text{Ag-O}}$ – is the contribution of one atomic pair Ag-O without $S_0^2(\text{Ag-O})$. These reduction factors are included into the amplitudes $A_{\text{Ag-Ag}} = C_{\text{Ag-Ag}} \cdot N_{\text{Ag-Ag}} \cdot S_0^2(\text{Ag-Ag})$ and $A_{\text{Ag-O}} = C_{\text{Ag-O}} \cdot N_{\text{Ag-O}} \cdot S_0^2(\text{Ag-O})$, where $C_{\text{Ag-Ag}}$ and $C_{\text{Ag-O}}$ are the fractions of Ag atoms in the sample bonded respectively with Ag and O atoms; $N_{\text{Ag-Ag}}$ and $N_{\text{Ag-O}}$ are respectively the number of Ag and O atoms neighboring to the absorbing Ag atom. $\tilde{\chi}_{\text{Ag}}$ in (1) is the contribution of photoelectron scattering processes on the second and more distant shells of the absorbing Ag atom. Determining the structural parameters for the nearest neighbors of Ag atoms using FT of EXAFS enables to neglect the contribution of the term $\tilde{\chi}_{\text{Ag}}$ in (1). This can be done because of the strong spread of Ag-Ag and Ag-O distances for the second neighbors of the absorbing Ag atoms in glass and hence, in the reduction of their contributions in relation to the nearest neighbors one. The fit of $F(R)$ of Ag *K*-edge EXAFS in the samples was performed by such a “nearest neighbors” approximation of (1). The functions $\chi(k)$ of the Samples 2 – 5000 were obtained in the k -scales with the zero at the inflection point $E_0 = 25513$ eV. The fit gave the average values of structural and non-structural parameters: amplitudes $A_{\text{Ag-Ag}}$, $A_{\text{Ag-O}}$ and corresponding Debye-Waller (DW) parameters $\sigma^2_{\text{Ag-Ag}}$, $\sigma^2_{\text{Ag-O}}$, interatomic distances $R_{\text{Ag-Ag}}$, $R_{\text{Ag-O}}$, and energy-shift parameters $e_0(\text{Ag-Ag})$, $e_0(\text{Ag-O})$ [10].

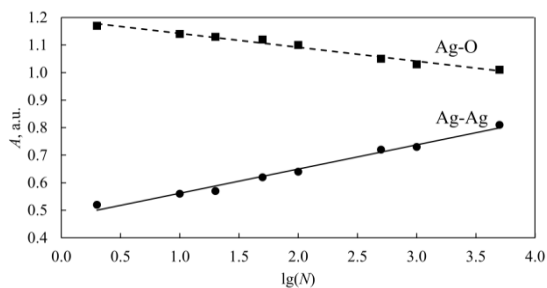


Figure 3. Dependences of amplitudes (A) of Ag-Ag (solid curve) and Ag-O (dashed curve) interactions upon the number N of laser pulses.

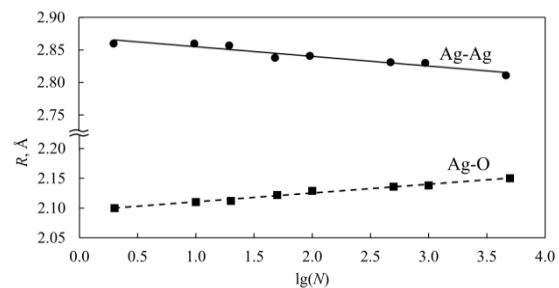


Figure 4. Dependences of interatomic distances (R) of Ag-Ag (solid curve) and Ag-O (dashed curve) bonds upon the number N of laser pulses.

Figure 3 shows the dependences of amplitudes $A_{\text{Ag-Ag}}$ and $A_{\text{Ag-O}}$ upon the number N of laser pulses. Both curves are approximately linear functions of $\lg(N)$, however, $A_{\text{Ag-Ag}}$ increases with N , while $A_{\text{Ag-O}}$

decreases. In Figure 4 the dependences of interatomic distances $R_{\text{Ag-Ag}}$ and $R_{\text{Ag-O}}$ upon the number N of laser radiation pulses are presented.

3. Discussion and conclusions

According to the optical spectra in Figure 1, the samples 10 and 100 exhibit a wide absorption band with a maximum at ~ 450 nm, which can be attributed to different structural units containing silver atoms (e. g. color centers) absorbing in the visible range at $\lambda \sim 420 - 460$ nm. The most suitable constructions are the well-known hole-trap centers (HTC) [11,12] and small clusters of neutral silver atoms Ag^0_n ($n = 2 - 15$ atoms). The increasing number of laser pulses from 500 to 5000 leads to the formation of the distinct SPR line of silver nanoparticles, shifted respectively from ~ 440 nm to ~ 435 nm.

The decrease of $A_{\text{Ag-O}}$ and the increase of $A_{\text{Ag-Ag}}$ amplitudes in Figure 3 agree with the behavior of Ag-O and Ag-Ag peaks of $|F(R)|$ in Figure 2, and reflect the decreasing amount of silver ions in the glass matrix and the simultaneously increasing number of agglomerations of silver atoms (for example nanoparticles) upon the number N of laser pulses. In the glass samples after $\text{Ag}^+ \leftrightarrow \text{Na}^+$ ion exchange and irradiation with small number of laser pulses one can expect the predominance of the Ag-Ag interactions, which can be attributed to the following plausible color centers in glass: $\text{Ag}^+ - \text{Ag}^+$, $\text{Ag}^+ - \text{Ag}^0$ (dimers) and HTC. These centers are characterized by different values of $R_{\text{Ag-Ag}}$ distributed from ~ 2.9 to 3.3 Å [13], which are distinctly longer than $R_{\text{Ag-Ag}}$ between the neighboring neutral Ag^0 atoms. The dependences of $R_{\text{Ag-Ag}}$ and $R_{\text{Ag-O}}$ upon the number N of laser radiation pulses in Figure 4 reflects the decrease of amount of initially dominating silver ions owing to their reduction into Ag^0 atoms according to the reaction $\text{Ag}^+ + e^- \rightarrow \text{Ag}^0$. Thus, considering the behavior of $R_{\text{Ag-O}}$ upon N , one must take into account that the value $R_{\text{Ag-O}} = 2.1$ Å in Sample 10 ($N = 10$ pulses) is typical for the bonds $\text{Ag}^+ - \text{O}$ and $\text{Ag}^{3+} - \text{O}$ in different silver oxides [14]. Meanwhile, the value $R_{\text{Ag-O}} = 2.15$ Å in Sample 5000 is closer to $\text{Ag}^0 - \text{O}$ distances (2.16 Å). The decrease of $R_{\text{Ag-Ag}}$ with the increasing number N of laser pulses can be also explained as the decreasing of contribution from the number of silver ions constructions (like HTC centers) due to the reduction of silver ions, simultaneously with the increasing of contribution of silver nanoparticles, whose size decreases with the increasing number of pulses.

The work was supported by DFG-RFBR project (DFG № DU 214/14-1, RFBR № 14-02-91334)

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