Eur. Phys. J. D **43**, 291–294 (2007)
DOI: 10.1140/epjd/e2007-00090-0

THE EUROPEAN
PHYSICAL JOURNAL D

Formation of argentic clusters and small Ag nanoparticles in soda-lime silicate glass

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Received 24 July 2006

Abstract. The formation of argentic clusters and very small Ag nanoparticles of 0.5 to 2 nm size in commercial soda-lime glass silver-doped by Ag/Na ion exchange in a mixed nitrate melt has been studied by electron microscopy and EXAFS. Particles formation was induced already during the ion exchange procedure, or by subsequent ion irradiation with 1.5 MeV He^+ or 3 MeV Au^+. The presence of nanoparticles was also macroscopically revealed by their surface plasmon resonance. The structural characterization indicates that specific configurations of silver oxide-like structures, so-called argentic clusters, are involved in the initial stage of nanoparticles formation.

PACS. 61.10.Ht X-ray absorption spectroscopy: EXAFS, NEXAFS, XANES, etc. – 61.43.Fs Glasses – 68.37.lp Transmission electron microscopy (TEM) (including STEM, HRTEM, etc.) – 61.46.Df Nanoparticles

1 Introduction

Nanosized metal particles embedded in glass have attracted much interest as material with potential applications because of their specific linear and non-linear optical properties [1]. Especially, strong variations of the properties are expected for particle sizes much less than 10 nm [2]. Therefore, we tested a number of experimental procedures in order to produce Ag nanoparticles of approximately 1 nm size in commercial soda-lime glasses. Because of this small dimensions several experimental methods for identification and characterization of such species were needed. In particular this is valid for particles embedded in a disordered dielectric matrix like the glasses are. Since silver is introduced into the matrix in ionic form, as first step of the formation of metal precipitates the reduction of silver ions is required [3]. This can be achieved either by polyvalent ions already present in the glass, or by a treatment generating negatively charged defects. Here, ion exchange processes of soda-lime glasses containing enhanced amounts of polyvalent Fe ions serving as thermosensitive reductive were investigated successfully as well as the irradiation of ion-exchanged glasses having less internal reductive content to generate charged defects within the matrix due to electronic excitations.

In both cases electron microscopy enabled a direct proof of the presence of Ag particles and the evaluation of their crystalline structure. The surface plasmon resonance as typical characteristic of metal nanoparticles was investigated by optical spectroscopy. Furthermore, the extended X-ray absorption fine structure (EXAFS) was used for in-depth structural characterization because of its ability to identify crystalline coordination without any size limitations.

2 Experimental

Commercial soda-lime glass containing (in weight %) 71.9% SiO_2 and 13.3% Na_2O as main components and 0.865% Fe_2O_3 as Fe ion component (glass 1) and 72.6% SiO_2 and 14.4% Na_2O as main components and 0.13% Fe_2O_3 (glass 2), respectively, were used as base glass materials. The Ag ions were incorporated into the glass in both cases by immersing into $NaNO_3/AgNO_3$ mixed melt at 330 °C, but for different duration. The depth distribution of Ag species was determined by energy-dispersive X-ray spectroscopy (EDX) using an analytical electron microscope ESEM-E3. Optical spectroscopy was performed by means of a microspectralphotometer (MPM 800D/UV) and a Perkin-Elmer Lambda 900 spectrometer. Glasses were irradiated with 1.5 MeV He ions or 3 MeV Au ions provided by ARMIS accelerator of CSNSM using currents up to 0.1 $\mu A/cm^2$ to prevent sample heating [4].

Electron microscopy examination to evaluate size and size distribution of silver particles was done by means of a JEM 1010 operating at 100 kV. To this aim both, planar and cross-section preparation, were performed including

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mechanical grinding, polishing and ion-beam etching. For advanced structural characterisation high-resolution electron microscopy (HREM) using a 400 kV JEM 4010 was applied. Lattice parameters of individual Ag particles were determined from digitised HREM micrographs by image processing and diffractogram analysis.

Ag K-spectra (25.514 keV) were recorded in transmission mode at 10 K by means of a liquid-helium vapour flow cryostat at beam line X1 in HASYLAB. EXAFS data processing was done using the UWXAFS program package with the theoretical amplitude and phase functions calculated by FEFF 7 [5]. Crystalline bulk samples were used as reference standard. The Fourier transform of EXAFS oscillations yield the interesting structural parameters like atomic distances, coordination numbers and the distribution of distances described by a Debye-Waller factor.

3 Results and discussion

3.1 Particle formation upon ion exchange

Thin samples of glass 1 (thickness of 150 μm) were prepared for the ion exchange experiments at 330 °C. At this temperature, the formation of crystalline nuclei should be favoured compared with the growth of particles. Such conditions were chosen to achieve very small particles. The incorporation of silver as monitored by EDX occurs at nearly constant interdiffusion coefficient for all samples in the range of 20 to 600 h ion exchange duration. Already after 20 h a slight coloration can be observed due to surface plasmon absorption in the range of 410 to 420 nm being typical for Ag particles of a few nanometres size. Electron microscopy determination of particle sizes in a surface near region reveals a nearly constant mean size of about 1.5 nm for ion exchange duration not above 400 h as it is shown in Figure 1. Upon longer ion exchange, or upon subsequent heat treatment at temperatures above 400 °C a distinct particle growth accompanied by an increase of the optical absorption can be observed. That means, Ag nanoparticles distinctly smaller than 1.5 nm could not be obtained by this route of synthesis.

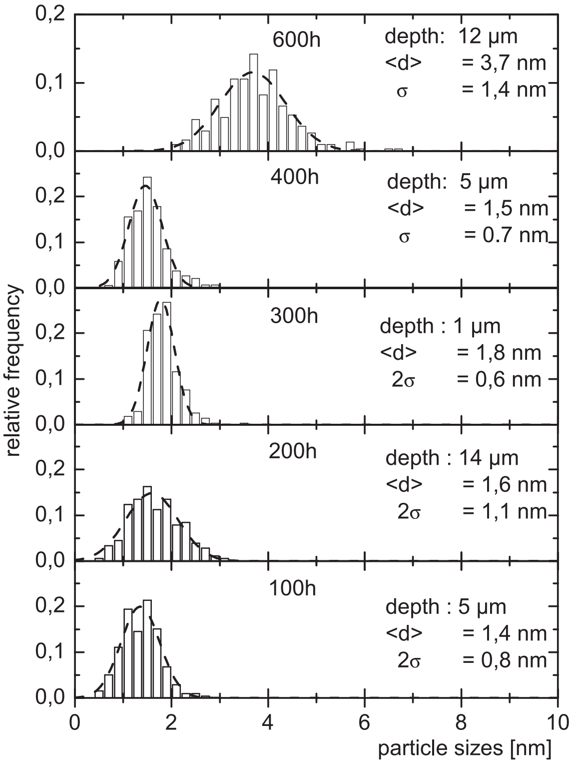

Fig. 1. Sizes and size distributions as determined by TEM for different periods of ion exchange.

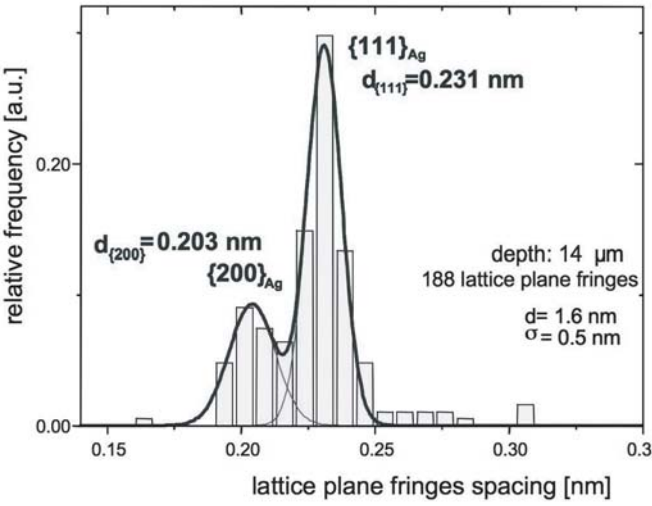

Fig. 2. Distribution of lattice fringe spacings after 200 h ion exchange based on the evaluation by HREM analysis.

Measurements of lattice plane spacings of {111} and {200} type from HREM images show slightly diminished values (about 2%) as compared to the bulk. The distribution of lattice plane spacings of the 200 h sample shown in Figure 1 can be seen in Figure 2. This result points to a certain lattice contraction owing to an interface stress of about 2 N/m [6]. By means of EXAFS spectroscopy measured at 10 K the lattice parameters are available with higher accuracy. The presence of Ag-Ag correlations as prerequisite for Ag particle formation can be recognized from the Fourier transformed EXAFS oscillations at the Ag K-edge upon ion exchange shown in Figure 3. Besides, there are also Ag-O correlations present reflecting the oxygen environment of silver ions in the glass matrix. From this measurements, an Ag-Ag distance less than 3.4% as compared to the bulk (see Tab. 1) was calculated. This value, exceeding that of the HREM results, can not be explained by the lattice contraction alone, but requires to consider also the presence of clusters having structures similar to those of Ag-O compounds. In fact, such strongly reduced Ag-Ag distances can be found in crystalline silver oxides, for example at 2.751 Å in Ag_6O_2 [7]. This view is supported by the distinctly higher Debye-Waller factor (see Tab. 1) indicating a larger static disorder due to the high number of surface atoms of such clusters. Therefore, we assume the formation of silver oxide-like clusters as predecessors or intermediates in the formation of crystalline Ag nanoparticles.

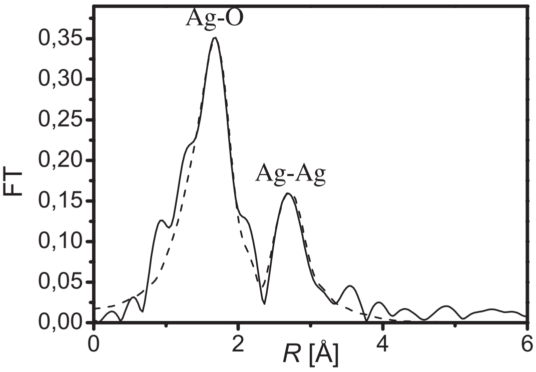

Fig. 3. Fourier transforms calculated on the basis of EXAFS oscillations measured at the Ag K-edge in transmission mode at 10 K for ion-exchanged sample of glass 2. The dashed line represents the result of fitting procedure.

Table 1. EXAFS parameters of Ag-Ag correlations measured at 10 K together with the respective particle sizes.

Sample	Size of particles	Ag-Ag distance	Debye-Waller factor
Glass 1 ion exchange (330 °C, 200 h)	1.5 nm	2.7809 Å	0.0141 Å^2
Glass 1 ion exchange (330 °C, 200 h) + annealing (410 °C, 459 h)	2.8 nm	2.879 Å	0.0049 Å^2
Glass 2 ion exchange + ion irradiation by Au$^+$	0.5 nm	2.8331 Å	0.0089 Å^2
Glass 2 ion exchange + ion irradiation by He$^+$	-	-	-
Ag crystal structure	∞	2.8786 Å	0.0027 Å^2

In the case of extended duration of ion exchange (>600 h) or a subsequent thermal treatment, i.e. for larger particles, the Ag-Ag distance is similar or slightly larger than that of bulk silver [8] and the Debye-Waller decreases. An example is given in Table 1 for particles of 2.8 nm in size.

3.2 Particle formation upon ion exchange and ion irradiation

Processing of ion-exchanged glass 2 by high-energy ion irradiation turned out to be successful for the generation of extremely small Ag nanoparticles in regions near the sample surface. Such nanoparticles as small as 0.5–1 nm formed upon irradiation with 1.5 MeV He$^+$ ions (dose $> 5 \times 10^{14}$ ions/cm^2), or with 3 MeV Au$^+$ ions (dose $> 1 \times 10^{13}$ ions/cm^2) have been detected by optical spectroscopy. For varying Au$^+$ irradiation doses optical density spectra are shown in Figure 4. Evaluation of the surface plasmon absorption according to the Mie theory leads to the above mentioned smallest sizes for silver nanoparticles in case of He$^+$ and of Au$^+$ irradiation, respectively, at the lowest irradiation dose applied. Increasing the dose step by step causes a distinct particle growth [4] that can be understood in terms of successive reduction of silver ions under irradiation.

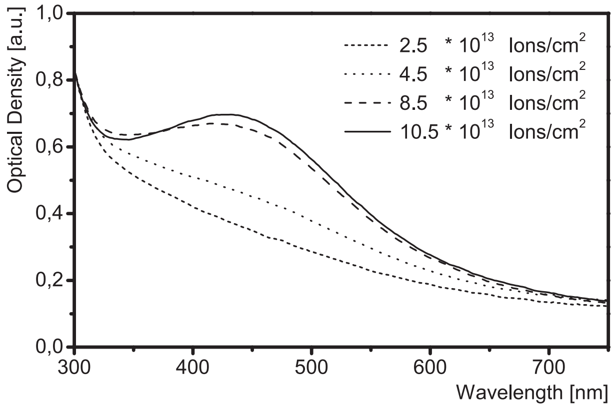

Fig. 4. Optical density measured for different doses of Au$^+$ irradiation.

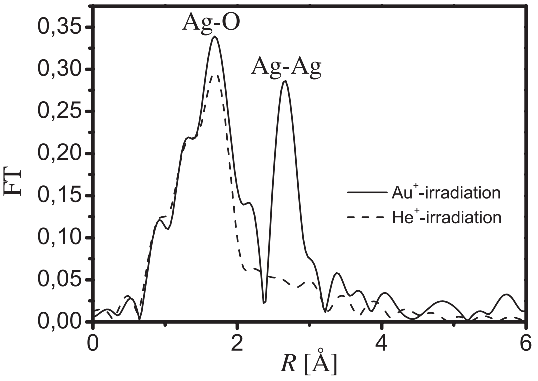

Fig. 5. Fourier transforms of EXAFS data at Ag K-edge of ion irradiated samples.

Since transmission electron microscopy is not capable of imaging the smallest of those Ag nanoparticles as well as the Ag-O clusters presumably also present as in glass 1, EXAFS measurements at 10 K have been done for structural characterization. From Figure 5 representing the Fourier transforms calculated on the basis of EXAFS oscillations it may be recognized that for He$^+$ and for Au$^+$ low dose irradiation Ag-O correlations are present reflecting the local order of silver ions in the glass matrix. For Au$^+$ irradiation, in addition there are Ag-Ag correlations observable. The appearance of the 1st coordination Ag-Ag peak distinctly proves the presence of atomic silver as part of particles. The Ag-Ag distance is similar to that of bulk silver (see Tab. 1). That means, there are nanocrystalline silver particles. However, the reduced height of this peak and fit results including an Ag-Ag coordination number of 1.43 and an interatomic distance of 2.8331 Å (bulk silver has 2.8786 Å at 10 K) point to very small Ag nanoparticles. In the case of He$^+$ irradiation, such correlations can not be detected, possibly due to the low concentration of reduced silver atoms. Obviously, the energy input of this type of ions is too small to promote the generation of Ag particles.

4 Conclusions

The experiments of ion exchange only in glass 1 for a limited period (⩽400 h) lead to the precipitation of Ag nanoparticles of 1.5 nm accompanied by even smaller argentic clusters whereas upon any further treatment the formation of small Ag nanoparticles having a structure similar to the bulk occurs. The ion irradiation of Ag containing glasses (glass 2) results in the generation of very small Ag particles (⩾0.5 nm) where the size was estimated from optical spectra. The structural characterization of such clusters and particles could be realised by HREM for sizes ⩾1 nm and by EXAFS in all cases.

This work has been supported by the Deutsche Forschungsgemeinschaft (SFB 418).

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