Ion-beam induced nano-sized Ag-metal clusters in glass

H.-E. Mahnkea,b,*, I. Zizak a,1, P. Schubert-Bischoffa, V. Koteskia,c

a Hahn-Meitner-Institut Berlin GmbH, Bereich SF, Glienicker Str. 100, D-14109 Berlin, Germany
b FU Berlin, D-14195 Berlin, Germany
c VINČA, POB 522, 11001 Belgrade, Serbia

Received 22 October 2007; received in revised form 23 November 2007; accepted 27 November 2007

Abstract

The formation of silver-metal clusters has been studied in ion-exchanged soda-lime glass following swift heavy ion irradiation at ISL. While the transformation into a metallic chemical form was detected with X-ray absorption spectroscopy (EXAFS) the shape and geometrical arrangement was studied both by transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS). A chain-like arrangement of nanoclusters of approximately 7 nm in diameter observed in TEM was further investigated with in situ SAXS during the subsequent annealing process. © 2007 Elsevier B.V. All rights reserved.

Keywords: Metallic nanoclusters in glass; Small angle X-ray scattering (SAXS); Ion beam modification; Ion tracks; Transmission electron microscopy (TEM); X-ray absorption spectroscopy (XAS)

1. Introduction

Glasses containing transition metal clusters have attracted attention both in cluster research and in possible applications of such clusters for magnetic or optoelectronic purposes. Nanometer-sized clusters of the noble metals Au and Ag in glasses exhibit strong absorption in the visible spectral range. The light absorption, in addition, may be highly sensitive to the polarization depending on size and shape of the clusters [1,2]. Special arrangements of the nanoclusters, their alignment in particular, may be used for waveguiding as already discussed and studied (e.g. Refs. [3,4]).

The new possible applications of such metallic nanoclusters have led to a renewed interest in investigating the binary exchange technique for introducing the respective metals into the glass, already used since centuries in making colourful glasses. Various steps must be understood for a better control: the introduction of the metal atoms into the glass which typically results in a non-metallic chemical environment (step i), the transformation into metal (step ii) and cluster formation with a control of size, shape, and arrangement (step iii). It is obvious that these steps are interrelated and interdependent. They are strongly influenced by the presence of reducing constituents or impurities in the glass. The means by which the energy is brought in, needed for reducing the elements typically incorporated in the glass in oxidic environment to metal, are, besides heat (annealing) treatment, laser (light) or ion irradiation. Studies using laser irradiation and irradiations with light or low energy ions with only little energy transfer to the electrons in the material (“electronic stopping”) combined with annealing procedures already showed some influence on the cluster formation and size distribution [5,6]. In the most recent studies using swift heavy ions, a “directionality” showed up as a special feature of the metallic cluster formation in glass: metallic silver clusters were observed in a chain-like arrangement along the direction of the ion beam [7,8]. This finding has to be attributed to the higher energy density being transferred to the electronic system of the material which seems to be sufficiently high enough above the threshold for ion track formation in these glasses in the case of irradiation with Si ions used in Ref. [7] and well above the threshold in the case of the Au ion irradiation used in our previous [8] and present investigation.

Starting from soda-lime glass into which silver was introduced by ion exchange, Ag-metal clusters were observed in transmission electron microscopy (TEM) images which were induced by heavy ion irradiation and subsequent annealing under reducing atmosphere. The transformation of Ag from the oxidic chemical configuration after the ion-exchange process into the metallic form was detected with X-ray absorption spectroscopy.
(XAS, in particular EXAFS). In the case of Ag (Au and Cu) a very sensitive indication for the transformation into metallic clusters already is the change of the optical absorption spectra depending on the wavelength even before visible colour changes become obvious. For other transition metals (e.g. Co) such a criterion is not sufficient evidence, a good signature for metallic clusters is the occurrence of surface plasmon resonances as observed in simple optical spectroscopy or the metallic coordination as seen in EXAFS experiments. The transmission electron microscopy experiments revealed the chain-like arrangement of the metallic clusters over a length of a few hundred nanometers consistent with the diffusion length of the Ag ions according to the parameters chosen in the ion-exchange process. Such finding prompted us to follow the process of formation with in situ small angle X-ray scattering experiments (SAXS) while annealing the ion-irradiated glass samples, of which first results are presented.

2. Experimental

We have used the ion-exchange process to incorporate Ag into borosilicate glass as described already in [8]. Glass plates, typically 0.1 mm [9], were immersed in a molten salt bath of a mixture of 1 mol% AgNO3 and NaNO3 at a temperature of 340°C for typically 30 min. The samples were mounted, self-supporting in Cu-frames, onto a cold Cu plate kept at LN2 temperature and irradiated with 600-MeV Au ions from the ISL accelerator facility of the HMI with fluences of $1 \times 10^{11} - 1 \times 10^{13}$ ions/cm$^2$. In one experiment 350-MeV Au ions were used. The ion flux was kept below $10^{10}$ ions/cm$^2$/s. In addition, glass samples ion-exchanged for a much longer time of 310 h to obtain a more homogeneous profile [10] were also studied. The same fluences were applied onto both sides of the plates since the projected range is approximately only half the thickness of the glass plates. For further details on the handling, mounting, and treating (annealing) of the samples after the irradiation see Ref. [8].

EXAFS experiments on the glass platelets were performed at the X1 beamline of HASYLAB with the samples kept close to LN2 temperature (for details see Ref. [8]). The absorption was measured at the absorption edges of Ag in the ion-exchanged glasses as well as in silver oxide and silver metal for comparison. Details are given and results are presented in Ref. [8] already. The EXAFS spectra clearly revealed the transformation from oxidic to metallic coordination. They also showed that both fractions not only depend on details of the composition of the glasses but also on the post-irradiation treatment. One obviously influencing factor is the content of reducing agents in the glass, even at fractions below the 1% level, such as Fe-(2+)-compounds or Sb2O3. When the samples were annealed following the ion irradiation, it was done under a reducing atmosphere (5% H2–Ar mixture) at 340°C for 30 min.

First information on the shape of the formed clusters was obtained by transmission electron microscopy on thin slices of some 10 nm cut out of the samples parallel to the ion impact and deposed onto a fine grid. The TEM was operated at 120 kV.

The SAXS experiments were performed at the recently installed 7-T multipole wiggler beamline for small angle scattering at BESSY using a photon energy of 8 keV. Sample and detector distance and the size of the detector (approximately 20 cm × 20 cm with a resolution of 0.2 mm) allowed to cover a range in the transferred wave vector $q$ from 0.1 to 1.3 nm$^{-1}$. The beam intensity in this setup now allows in situ experiments to follow the annealing of the ion-induced clusters after the ion irradiation.

3. Results and discussion

Earlier EXAFS studies already illustrated the complementary approach to optical absorption to follow the transformation from the oxidic to the metallic coordination of Ag in silicate glasses. TEM images showed that the irradiation with swift heavy ions with much higher energy density input than in earlier ion experiments resulted not only in a more uniform distribution of the size of the metallic nanoclusters but also in a chain-like arrangement of the clusters parallel to the ion direction. Such an arrangement can be seen in Fig. 1, an image with a higher magnification than presented in Ref. [8]. The unidirectional arrangement is consistently observed in a SAXS experiment presented in Fig. 2. For this SAXS study glasses with a deeper in-diffusion length (ion-exchange process for 120 min) were ion irradiated with a total fluence of $1 \times 10^{11}$ ions/cm$^2$ to avoid overlapping or influencing ion tracks. In these samples, the depth of the Ag profile with a diffusion length of only a few micrometers is much shorter than the ion range. In this very first experiment of the newly installed small angle scattering setup at BESSY slit scattering could not be
Fig. 2. SAXS images of ion-irradiated, annealed (right) and non-annealed (left) Ag containing glass samples revealing a column-like structure by the disc-like image. The image to the right was obtained after subtracting events from air scattering and diffuse scattering (see the non-annealed image on the left). The size of the images represents approximately 90% of the total detector area. The direction of the ions was 45° against the normal of the surface while the X-ray beam was parallel to the normal. The length of the streak translates into a diameter of the “cylindrical structure”, the arrangement of Ag droplets in chains along the ion direction, of around 7 nm in accordance to the diameter of the droplets seen in Fig. 1. (Note: We can only speculate on the origin of the non-symmetric streak at the left side, it may result from parasitic reflections on a beam line component or on the edge of the sample.)

Avoided totally. Therefore, the right part of Fig. 2 was obtained by subtracting events from air scattering and from the mostly diffuse scattering from the glass and randomly distributed clusters in the non-annealed sample (left part) from the original image. The shown result reflects the arrangement in accordance with the TEM image. The treatment of the scattering events (when subtracting “non-annealed” from the “annealed”) clearly establishes a dependence on the post-irradiation treatment for the development of the chain-like arrangement.

Since these experiments revealed that the extent to which the transformation into the metallic form is achieved in the ion irradiation depends on the post-irradiation treatment, an in situ SAXS experiment was set up to follow the development of the clusters during the annealing process. Using glass samples (according to Ref. [10]) with an almost homogeneous Ag profile after the ion-exchange process we tried to match the ion range with the Ag concentration profile. In Fig. 3 we present a comparison for ion-irradiated and non-ion-irradiated glass samples containing Ag at the beginning of the in situ annealing procedure and at the end of the annealing. Although the procedure was not fully analogous for both samples (for technical reasons) the effect of ion irradiation is fairly obvious. For the non-ion-irradiated sample the annealing was followed up to 340 °C, while for the ion-irradiated sample the procedure was stopped at 280 °C. The radially integrated intensity given in dependence of the azimuthal angle ϕ clearly shows the 2 maxima, 180° apart, of the columnar directional arrangement. Since the ion irradiation was done from both sides turning the samples by 180°, the turning was obviously not absolutely perfect, the 2 maxima are split due to the small misalignment.

Besides some ambiguities due to some variations in the choice of the samples in the different experiments (because
of technical difficulties) it is obvious from this preliminary in situ SAXS experiment that there are at least 3 contributions to the scattering signal: “normal” background (from the base glass), scattered intensity from spherical or randomly distributed objects, and scattered intensity originating from aligned chain-like or columnar structures of the metallic Ag clusters. A more complete analysis to untangle the different contributions and further experiments to gain control over the influencing parameters are under way.

Acknowledgements

The authors are grateful to the HASYLAB staff at DESY, in particular to J. Wienold and E. Welter. We very much appreciate P. Szimkowiak’s help in sample preparation. Special thanks are expressed to the colleagues from the department SF3 of the HMI, A. Höll, S. Haas, and D. Tachev, who helped as scientists at the HMI SAXS 7-T MPW beam line at BESSY.

References

[9] Schott AG, type D263.