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

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Glasses containing metal clusters have attracted quite some attention both in cluster research and in possible applications of such clusters for magnetic or optoelectronic purposes. So exhibit nanometer-sized clusters of noble metals in glasses strong absorption of visible light which, in addition, may be highly polarization dependant depending on size and shape with special alignment of the clusters [1, 2]. Various preparation methods are pursued to obtain control of the mechanisms to form such clusters. A promising approach is the irradiation of glasses containing the wanted metal as a metal oxide with heavy-ion beams at MeV energies [3,4,5].

Fig. 1 (left): Radial distribution function (Fourier transform) of the k^2-weighted EXAFS spectrum of the ion irradiated Ag exchanged glass (bottom) compared with spectra for Ag metal (center) and for Ag_2O (top).

Fig. 2 (right): TEM images of Ag ion exchanged glass, annealed only (top) and Au ion irradiated (fluence 1·10^{12} ions/cm^2) and subsequently annealed for 30 min at 340 °C (bottom), the surface being at the left side. The TEM was operated at 120 kV.

We have studied the formation of Ag-metal clusters in soda lime glass induced by heavy ion irradiation with x-ray absorption spectroscopy (XAS), complemented with transmission electron microscopy (TEM). Silver was introduced by ion exchange into 0.1-mm thick glass platelets (see [4]). While annealing under a reducing atmosphere of Ar with a few % H_2 already leads to the formation of metal clusters, such clusters are not very uniform in size and are randomly distributed over the Ag-containing glass volume. We have irradiated these Ag-containing glass platelets kept at LN_2 temperature with 600-MeV Au ions with fluences around 10^{12} ions/cm^2 at ISL. The ion flux was kept below 10^{10} ions/cm^2/s.
Following the ion irradiation, the samples were investigated with X-ray absorption spectroscopy at the Ag K-edge (25.514 keV) either with or without further annealing at the same temperature as for the ion-exchange preparation under a reducing atmosphere (5% H2-Ar mixture) for 30 min (see ref. [4]). The EXAFS experiment was performed at the X1 beamline of HASYLAB with the samples kept close to LN2 temperature. The absorption was measured in fluorescence mode using a 7-element Ge detector. For comparison, the absorption was measured for samples of Ag metal and a sample of Ag2O powder, mixed with graphite and polyethylene and pressed into a pill, too. The EXAFS spectra were analysed using the standard FEFF procedures [6,7,8] by which the coordination numbers and distances at least for the first and second coordination shells could be derived.

In Fig.1 the ion-induced transformation from Ag oxide into Ag metal is illustrated by the comparison of the different EXAFS signals. The extracted bond lengths correspond to the respective values known for the pure chemical systems. The bond length of Ag to O in the glass is slightly larger than in pure Ag2O. This difference may reflect the substitution of Na by Ag as an impurity (details are presented in [9]).

As illustrated with the EXAFS spectrum the transformation is not complete. Approximately 30% of the Ag is surrounded by Ag, while the major part of Ag atoms is ambiented by oxygen. With no post-irradiation heat treatment the metal fraction is at the detection limit. Obviously, the metal fraction strongly depends on the treatment following the ion irradiation.

Complementary information on the distribution within the platelets, the shape and the sizes, was obtained from transmission electron microscopy (TEM) on thin slices of some 10 nm cut out of the samples parallel to the ion impact and deposed onto a fine grid. The comparison presented in Fig.2 illustrates the significant influence of the ion irradiation: (i) the metal clusters have grown and their size distribution has become more uniform, but the most remarkable feature is that (ii) the clusters are arranged in chains parallel to the direction of the ion beam. Since some of the chains consist of clusters very similar in diameter and almost in contact, one is tempted to speculate that a totally columnar structure may be obtained by controlling the influencing parameters such as the ion fluence and the annealing parameters.

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References
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