Kinetics of Bulk Nano-Clustering in Silver-Doped Glasses during Reactive Hydrogen Diffusion

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1. Introduction

Glasses embedded with metal nanoclusters are prospective materials which can be used in optical recording [1, 2] and laser microfabrication [3]. The conventional way to produce such nanoclusters in a glass consists in doping the glass by metals using ion exchange and subsequent reducing metallic ions to neutral metals [4, 5]. Annealing of metal-doped glasses in a hydrogen atmosphere leads to hydrogen diffusion accompanied by chemical reaction in the doped layer, in which metal ions are reduced to neutral state whereas neutral hydrogen atoms form OH groups and become ions. As solubility of neutral metal atoms in the glass matrix is negligible compared to the ion concentration in the doped layer, reduced metal atoms create high supersaturation in the glass matrix and form nanoclusters.

In spite of seeming understanding, quantitative description of the clustering kinetics is rather complicate. First, hydrogen ions H^+ appearing in the glass due to chemical reaction are rather mobile, with diffusion coefficient, D_{H+}, comparable with D_{Ag+}. As the total number of positive ions per unit volume should stay constant, diffusion fluxes of H^+ and Ag^+ ions are not independent. Inequality of D_{H+} and D_{Ag+} leads to the formation of internal electric field, which accelerates slower flux and reduces faster flux. Second, diffusion of Ag^0 atoms is accompanied by their birth due to chemical reaction and their leaving to sinks (clusters). Such diffusion is also a non-linear process because kinetics of leaving to sinks depends on the current silver concentration. Previously [6] we analyzed the kinetics of silver clustering in a Ag^+-doped glass matrix in the course of hydrogen diffusion by rigorous numerical solution of the appropriate diffusion equations and modeled how the clustering kinetics varied with the variation of diffusion coefficients.

In this paper we present experimental results on the clustering kinetics with the purpose to compare them with the results of modeling and to get information about diffusion coefficients of hydrogen (D_{H0}) and neutral silver (D_{Ag0}), which are presently unknown.

2. Experimental

The kinetics of clustering was studied by optical spectrometry and high-resolution SEM. Optical absorption spectra were measured after each successive stage of annealing. They contained a peak near 410 nm corresponding to the surface plasmon resonance in Ag clusters. The peak height grew with annealing time. To separate contributions of bulk clusters in the optical absorption, we removed surface clusters after each stage of annealing.

3. Resuts

The experiments were carried out at 160, 180, and 200°C. The plasmon peak height grew with time due to thickening of the layer filled by growing clusters and increase of the cluster size. A theoretical analysis of the reactive hydrogen diffusion accompanied by interdiffusion of H^+ and Ag^+ ions and neutral silver allowed us to get the average cluster size and spatial cluster distribution in the bulk of the glass and thus to calculate optical absorption caused by clusters.

Analysis of optical spectra showed rather good qualitative agreement between our experimental result and calculations made on the basis of our previous modeling [6] (Fig. 1). Fitting of calculated curves to experimental spectra by choosing of appropriate parameters allows us to determine diffusion coefficients D_{H0} and D_{Ag0}, which define kinetics of clustering.
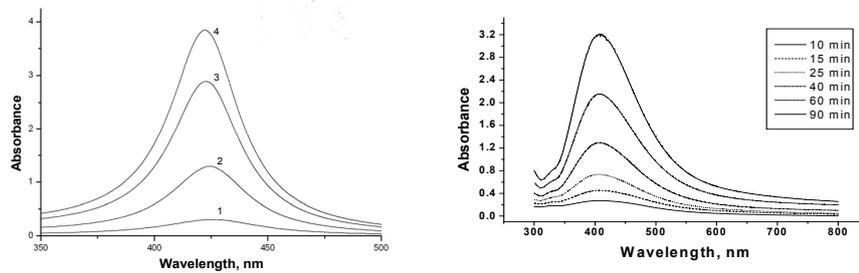

Fig. 1. Calculated (a) and experimental (b) optical absorption spectra for various times of annealing. (a) – $D_{H0} = 10^{-3}$ μm²/s; $D_{Ag0} = 10^{-4}$ μm²/s; 1 – t =5 min; 2 – 10 min; 3 – 20 min; 4 – 30 min; (b) – T = 200°C; annealing times are indicated in the plot.

4. Conclusion

We obtained qualitative agreement between our experimental data and calculations made on the basis of our previous model. This shows that the model is valid and by variation of diffusion coefficients we can find quantitative agreement and determine diffusion coefficients by optical method.

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