Self-arrangement of periodic layers of silver nanoparticles in silicate glass

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Abstract. We studied the influence of hydrogen-reducible metal ions concentration profile under the surface of ion exchanged glass on the behavior of the layered glass-metal nanocomposite which can be formed via self-arranging in the course of thermal processing of the glass in hydrogen atmosphere. The modeling shows that depending of the ascending or descending type of the concentration profile the layered nanocomposite with decreasing or increasing gaps between the layers of nanoparticles can be formed. In certain cases the mean radius and the particle size-distribution function may be the same among the subsequent layers. A proper choice of the ascending concentration profile can provide practically equidistant layers of the nanocomposite applicable for photonic crystals and Bragg gratings.

1. Introduction
Since famous R. Feymann’s talk “There's Plenty of Room at the Bottom” at the annual meeting of the American Physical Society at the California Institute of Technology in 1959 a lot of regular nanostructures were formed using the bottom-up approach. Firstly presented in 1981 [1] the self-arrangement, both spontaneous and externally stimulated, has been demonstrated in the systems of different nature. Below we concentrate on metal nanoparticles whose plasmonic properties [2] have attracted a lot of attention because of application potential [3]. Additionally to regular arrangements of metal nanoparticles under electric charging [4], with electron beam [5] or laser [6] irradiation, and with the use of organic templates [7], the self-arranging of multiple layers of silver [8] and copper [9] nanoparticles within glasses have been reported. The latter experiments consisted in hydrogen processing of glasses containing metal ions introduced in the glasses using ion exchange techniques. This kind of processing, being the conventional one for the formation of glass-metal nanocomposites (GMN), has resulted [8,9] in an irregular layered spatial distributions of the nanoparticles contrary to usually observed monotonic decrease [10,11] in nanoparticles concentration with the distance from the glass substrate surface. Modification of the existing theory of the nanoparticles formation [12] have allowed us to present the first model of the layering [13], which is capable of description of available experimental data [8,9], and the mechanism to control the gap between the GMN layers via varying the pressure of hydrogen in the course of the processing. Here we present another approach to govern the GMN layering, which is based on the formation of prescribed metal ions concentration profile in glasses to be processed in hydrogen.
2. Formation of layers

The problem under consideration is illustrated with figure 1. Hydrogen penetrates into heated glass containing positive ions capable of hydrogen reduction, and the probability of the reduction is proportional to the product of the ions and hydrogen concentrations. The glass contains one more type of positive ions, usually sodium, which possesses mobility comparable with the mobility of reducible ions. The mobilities of neutral hydrogen and reduced metal are also accounted for, while the mobility of oxidized hydrogen is low [14]. The set of equations describing the problem is presented in Appendix.

It is worth to note that proper relation of ionic mobilities and concentrations of species participating in the formation of metal nanoparticles (ionic and molecular hydrogen, ionic and atomic metal, e.g. silver, and ionic sodium initially presenting in glass) can provide non-monotonous profile of nanoparticles concentration in the glass due to the concurrence of two processes occurring in the glass enriched with reducible ions [13]. The first one is the formation of metal nuclei in the oversaturated solid solution of hydrogen-reduced metal in the glass, and the second is the growth of metal nanoparticles after the nucleation stage. This concurrence is because growing nanoparticles “consume” metal atoms via diffusion flow from the surrounding glass and, thus, decrease the concentration of the solid solution, while the size of critical nuclei increases with the solution drop [15]. That is why the probability of nucleation and, respectively, formation of new nanoparticles is hardly possible in the vicinity of existing ones.

![Figure 1. Formation of metal nanoparticles in glass: the scheme and a fragment of cross-sectional view of the glass sample from paper [8], darker regions correspond to GMN layers. The cross sectional view reproduced with the permission of the IOP Publishing Ltd from Ref. 8 (doi:10.1088/0953-8984/13/3/312).](image)

In the course of hydrogen processing the gas diffuses into the glass through the surface and reduces the metal. This reactive diffusion results in hydrogen and reduced metal concentrations decaying with the distance, the same way decays the oversaturation of the glass-metal solid solution. With the account for the depletion of glass with metal atoms under the region where the nanoparticles are already formed, the distance to the next region where the nuclei can arise increases with moving away from the glass surface. This results in the increase in the gap between the layers of GMN for deeper layers. It was both experimentally demonstrated by Mohr [8] and Estournes [9] and theoretically
described in our previous work [13]. The probability of metal reduction is, however, proportional to both metal ions and hydrogen concentration, and a non-uniformity of the ionic concentration can strongly influence mutual position of the GMN layers. This influence is essential if the distance where the concentration of the reducible ions in the glass changes is comparable with the size of the region depleted with the ions in the vicinity of growing metal nanoparticle. Thus relatively sharp concentration profiles are necessary to modify GMN layering and, if the reducible ions are introduced into the glass using ion exchange technique, only short processing duration should be used. According to the measured gap between the GMN layers [8], to modify the layering the concentration of the reducible ions should essentially differ at easily achievable distance of the order of a micron. Descending concentration profile can provide the gap between GMN layers growing with the distance from the glass surface and vice versa.

3. Results
To illustrate the influence of the concentration profile on the formation of the GMN layers we simulated the distribution of nanoparticles in soda-lime glass subjected to silver-sodium ion exchange and subsequent burying of the ion-exchanged layer using reverse sodium-silver ion exchange. Silver ions diffusion coefficient and concentration data were taken from [16] and other parameters from our paper [13]. Calculated for different durations of direct and reverse ion exchange ascending and descending profiles of silver ions in glass are presented in figure 2a.

Figure 2. Concentration profiles of silver ions in glass formed with one-step (solid lines) and two-step (dashed lines) ion exchange (a), 1-5: 0.5 - 8.5 min of ion exchange; 6-10: 20s - 7 min of out-diffusion after 5 min ion exchange; depth distribution of volume fraction of silver nanoparticles calculated for descending silver concentration profile for different ion-exchange duration (b) and for ascending silver concentration profile for different durations of silver ions burying at the second step of ion exchange processing (c); nanoparticles size distribution function in cm, corresponding to profile 10 in (c) (5 min of silver to sodium and then 7 min of sodium to silver ion exchange ). Color denotes the concentration of silver nanoparticles in cm$^{-3}$ (d).
We used these silver ions concentration data to compute spatial distribution of silver nanoparticles resulted from hydrogen processing. In figure 2b,c one can see that shorter ion exchange time provides sharper nanoparticles concentration profiles that are narrower layers of the glass-metal nanocomposite.

For descending concentration of silver ions (solid lines in figure 2a) this corresponds to longer distances between the layers (figure 2b). Contrary, ascending concentration of silver (dashed lines in figure 2a), which can be obtained by two stage ion exchange, short sodium to silver after long silver to sodium, results in decreasing the gaps between the nanocomposite layers with the distance from the glass surface (figure 2c,2d). This phenomenon can be used to form equidistant layers of GMN in glasses. Also the mean radius and the particle size-distribution function are almost the same among the equidistant layers (figure 2d, layers 3-6).

4. Conclusions
Finally we have shown that varying concentration profile of hydrogen-reducible ions in glass allows formation within the glass the layers of GMN which differ in the behavior of spacing between the layers from increasing to decreasing with the distance from the glass surface in the cases of descending and ascending profiles, respectively. Our modeling has demonstrated that bell-shaped profile resulting from silver to sodium and then sodium to silver ion exchange processing of soda-lime glass can provide practically equidistant layers of GMN in the glass that is of interest for variety of optical and plasmonics applications.

Acknowledgements
Authors are grateful to S.A. Kukushkin for his valuable advices. The study was supported by RFBR project #14-02-00127

Appendix: Formulation of the problem
Here we formulate the equations describing the whole process which involves diffusion and ion exchange in the presence of sinks and sources, nucleation, growth and repining of nanoparticles. There are six entities involved into the process: ionic and atomic silver and hydrogen, ionic sodium, which diffuses itself and, thus, influences diffusion of ionic silver and ionic hydrogen, and silver nanoparticles. The equation (1) for hydrogen is

$$\frac{\partial C_{H^+}}{\partial t} = D_{H^+} \frac{\partial^2 C_{H^+}}{\partial x^2} - k_1 C_{H^+} C_{Ag^+},$$

(1)

where $C_{H^+}$, $C_{Ag^+}$ are the concentrations of neutral hydrogen and ionic silver, $D_{H^+}$ is hydrogen diffusion coefficient, $k_1$ is the rate of reduction reaction. The equation for ionic silver is

$$\frac{\partial C_{Ag^+}}{\partial t} = D_{Ag^+} \frac{\partial^2 C_{Ag^+}}{\partial x^2} - k_1 C_{H^+} C_{Ag^+} + D_{Ag^+} \left( \frac{C_{Ag^+} \alpha \nabla C_{Ag^+}}{1 - \alpha C_{Ag^+}} \right),$$

(2)
where \( C_i \) is total concentration of ionic silver and sodium, \( D_{Ag^+} \), \( D_{H^+} \) are diffusion coefficients of ionic silver and hydrogen, respectively, \( \alpha = 1 - D_{Ag^+} \cdot \left( D_{H^+} \right)^{-1} \), and we assume that silver and sodium diffusion coefficients are equal. The third term in the right part of equation (2) is responsible for self-consistent process of hydrogen, sodium and silver ions diffusion.

Sodium does not participate in silver reduction but affects the distributions of other charged species, ionic silver and hydrogen. The equation (3) for ionic sodium is

\[
\frac{\partial C_{Na^+}}{\partial t} = D_{Na^+} \frac{\partial^2 C_{Na^+}}{\partial x^2} + D_{Na^+} \frac{\partial}{\partial x} \left[ C_{Na^+} \frac{\partial V C_i}{\partial C_i} \right],
\]

(3)

where \( C_{Na^+} \) is the concentration of sodium, \( D_{Na^+} \) is sodium diffusion coefficient.

The particle critical radius, at which it becomes stable, can be written as [15]

\[
R_{cr}(\xi) = \frac{2\gamma\omega}{k_BT\ln\xi},
\]

(4)

where \( \gamma \) is the coefficient of surface tension, \( \omega \) is the atomic volume of silver, and \( \xi \) is the oversaturation of the solid solution of neutral silver in glass.

Equation (5) for atomic silver accounts for its diffusion, reduction of silver ions, formation and growth of nanoparticles:

\[
\frac{\partial C_{Ag^0}}{\partial t} = D_{Ag^0} \frac{\partial^2 C_{Ag^0}}{\partial x^2} + k_1 C_{H^+} C_{Ag^0} - k_2 C_{Ag^0} \ln \xi \frac{4\pi}{3\omega} R_{cr}^3 \exp \left( -\frac{k_3}{\ln^2(\xi)} \right) \int_0^\infty 4\pi R^2 V_c \cdot N dR
\]

(5)

Here the growth rate \( V_c \) can be described [17] as

\[
V_c(R) = \frac{\partial R}{\partial t} = D_{Ag^0} \left( C_{Ag^0} - S(1 + 2\gamma\omega / k_BT) \right) / R,
\]

and \( k_2 \) and \( k_3 \) are the nucleation rate and a kind of threshold dimensionless nucleation energy, respectively, \( k_3 = 16\pi\gamma / (3k_BT) \). The expression under the exponent equals to the ratio of the energy to create a nanoparticle of critical radius and \( k_BT \). [18]

The last equation is the equation of continuity for particle size-distribution function \( N \). It describes nanoparticle growth and formation [18]

\[
\frac{\partial N}{\partial t} + \frac{\partial}{\partial R} (NV_c) = k_2 C_{Ag^0} \ln \xi \exp \left( -\frac{k_3}{\ln^2(\xi)} \right) \delta(R - R_{cr})
\]

(6)

Here the right part describes the nucleation of particles of critical radius \( R_{cr} \). We solved one-dimensional problem using the boundary conditions of constant hydrogen concentration at the glass surface, the absence of fluxes of other species through the surface, and taking into account that the sample thickness is much larger than the diffusion depths.
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