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Formation of silver nanoparticles in glass by vacuum thermal poling

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Abstract. It is shown that the vacuum poling of soda-lime silicate glass followed by silver-for-sodium ion exchange results in the formation of silver nanoparticles (NPs) in subcathode region of the glass. The latter was confirmed by the presence of silver NPs' localized surface plasmon resonance peak in optical absorption spectra of the samples. The NPs had grown in 2 μm thick subsurface region of the glass, which was confirmed by etching the cathode side of the sample. The possibility of forming a 2D-structured pattern from silver NPs that repeats the relief of the cathode electrode used for poling, has also been demonstrated. A hypothesis about the reduction of silver ions during the ion exchange by sodium atoms penetrated the glass from the cathode during poling in vacuum is proposed.

Keywords: soda-lime glass, thermal poling, silver nanoparticles

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Образование серебряных наночастиц в стекле с помощью термического полинга в вакууме

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Аннотация. Показано, что вакуумный полинг щелочно-силикатного стекла и последующий серебряно-натриевый обмен приводят к образованию серебряных наночастиц (НЧ) в подкатодной области стекла. Продемонстрирована возможность создания 2D-структурированных паттернов, образованных серебряными НЧ, повторяющих рельеф катодного электрода, используемого при полинге. Предложена гипотеза о восстановлении ионов серебра в процессе ионного обмена атомами натрия, проникшими в стекло с катодной стороны в процессе вакуумного полинга.

Ключевые слова: щелочно-силикатное стекло, термический полинг, серебряные наночастицы

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Introduction

Thermal poling of glasses consists in the application of a DC voltage to a heated glass plate. This process leads to compositional [1] and structural [2, 3] changes in the subanode layer of a glass and, accordingly, alternates physical properties of such layer. When soda-lime glass is poled in air, electric current through the sample occurs due to the influx of positive hydrogen/hydronium ions (H_3O^+) from atmosphere [4]. This results in a displacement of alkaline ions contained in it towards the bulk of the glass and the formation of alkaline-depleted and hydronium-enriched layer in the subanode region of the glass, which significantly slows down or even prevents ionic exchange [5]. This allows creating 2D-structured pattern from silver NPs in the subanode layer of the glass by poling silver-for-sodium exchanged glass with structured (relief) anode electrode and subsequent thermal treatment in reducing atmosphere. However, recent studies have also shown that the thermal poling of silver-for-sodium exchanged glasses being performed in air leads to the growth of silver dendrites in the subcathode layer of the glasses without the use of reducing atmosphere [6]. This allows us to conclude that poling itself creates reducing centers there. Indeed, when poled soda-lime glass in vacuum, we recorded an electric current through the glass, despite the absence of the penetration of positive species into it, the current being only several times less compared to the case of air-poling. This current arises partly because of the reduction of sodium ions near the cathode side of glass. Sodium ions drift is possible due to the local repolymerization of glassy network in subanode layer that compensate negative subanode charge [7]. We hypothesized that formed sodium atoms can act as reducing agents for silver ions, and we tested their presence in the subcathode layer of soda-lime glass poled in vacuum by performing silver-for sodium ion exchange. This work is devoted to the description of related experiments and demonstration of the possibility to form 2D-structured patterns from silver NPs by combination of vacuum thermal poling and silver-for-sodium ion exchange without using additional thermal treatment.

Experimental and results

In the experiments we used slides of a soda-lime glass, which composition in wt.% is: 72.2% SiO_2, 14.3% Na_2O, 6.4% CaO, 4.3% MgO, 1.2% K_2O, 1.2% Al_2O_3 and 0.4% other oxides. 1 mm thick glass slides were placed between two electrodes, heated to 300 °C and subjected to 800 V DC voltage in a vacuum chamber at about 2×10^{-5} mmHg pressure. After poling, we performed silver-for-sodium ion exchange by immersion the samples for 20 min in $Ag_{0.05}Na_{0.95}NO_3$ (in wt.%) melt heated to 325 °C.

To characterize quantity and depth distribution of silver nanoparticles we etched in several stages one of the samples in a solution of 80 ml H_2O, 10 ml NH_4F and 10 μl HF and measured the optical absorption at each stage. Evaluated etching rate was ~ 90 nm per min. The corresponding spectra are shown in Figure 1. The presence of localized surface plasmon (LSP) peak at ~ 410 nm confirmed the formation of silver NPs in poled glasses after the ion exchange [8]. From the dependence of integral absorbance (330–483 nm) on the etching depth we calculated the depth distribution of silver nanoparticles, which is shown in Figure 2.

This allowed us to assume that vacuum poling with structured cathode electrode should result

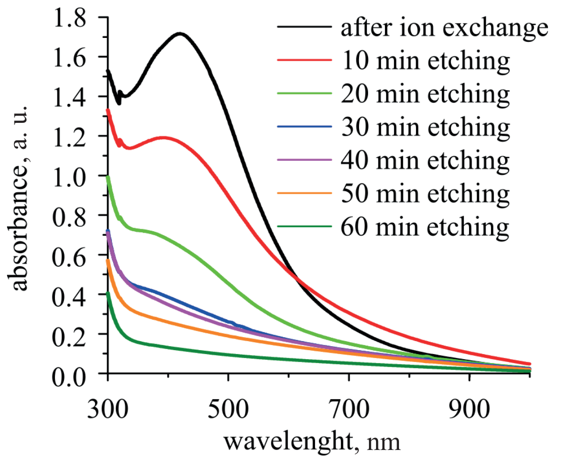

Fig. 1. Optical absorption spectra before and after etching of soda-lime glass after vacuum thermal poling and silver-for-sodium ion exchange

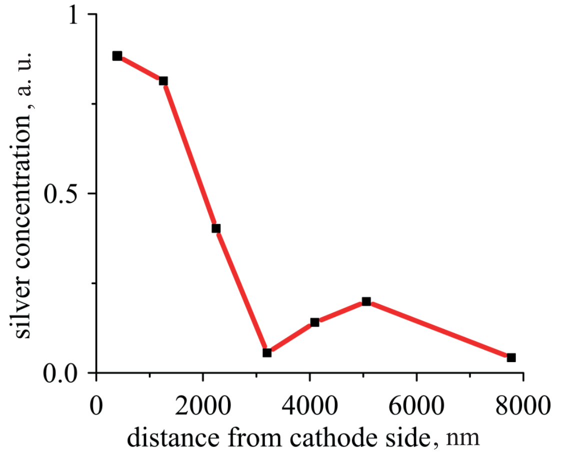

Fig. 2. Depth distribution of silver in soda-lime glass after vacuum thermal poling and silver-for-sodium ion exchange

in the formation of 2D patterns from silver NPs. The result of poling experiment with a bronze grid pressed to the glass slide and used as cathode electrode is shown in Figure 3. One can see that the dark strips, which correspond to the glass regions containing silver NPs, replicate the structure of the cathode electrode.

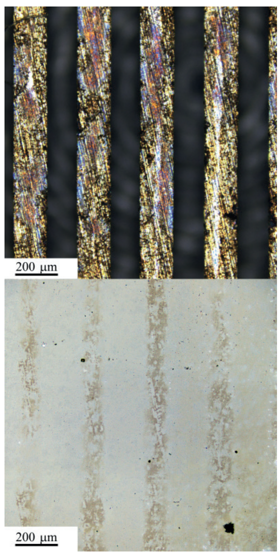

Fig. 3. Photos of the cathode electrode (top) and its replica formed by silver NPs in the subcathode layer of a sample (bottom)

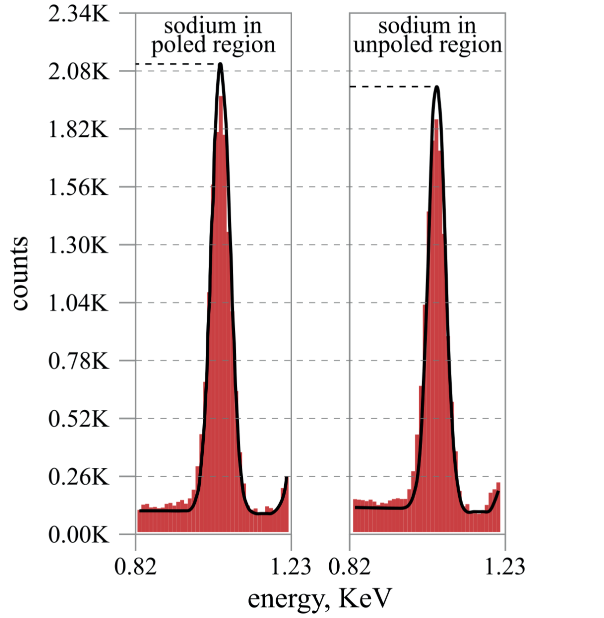

Fig. 4. EDX spectra in poled and unpoled regions of soda-lime glass

To interpret the difference the formation of nanoparticles in the subcathode layer of soda-lime glass poled in vacuum we measured sodium concentration in poled and unpoled regions under the cathode surface of the sample using energy-dispersive X-ray spectroscopy (EDX). The thickness of the analyzed region was about 1 μm. The corresponding data is shown in Figure 4. Calculated weight percentage gave 10.91 wt.% of sodium in poled region and 10.50 wt.% of sodium in unpoled region of the sample that is excess sodium in the poled subcathode region.

Discussion

According to figure 1, 40 min etching results in the complete degradation of LSP resonance that is to the removal of silver nanoparticles. Thus, the first peak in figure 2 mainly corresponds to silver NPs while the second – to ionic silver.

The correlation between the formation of silver nanoparticles in the poled region, that is, the reduction of silver ions, and the detected excess sodium suggested that it is responsible for the reduction.

In poling, atomic sodium forms at the cathode because of reduction of Na^+ ions. In the case of poling in air, neutral sodium immediately oxidizes and forms NaOH because of atmospheric humidity, while in vacuum poling it can preserve in atomic state at the cathode. Then, in a vacuum, sodium can be desorbed directly from the cathode surface into the glass either through vapor or even from a liquid layer between the glass and the cathode, the layer being formed due to the low melting temperature of sodium 98 °C. Thus, we suppose that the portion of sodium atoms not intercalated at the cathode penetrates from the cathode into the glass (the diffusion of sodium atoms into glass up to a depth of 10 microns was recorded [9]. Then penetrated sodium atoms serve as a reducing agent for silver ions against the background of conventional ion exchange:

$$Na^0 + ...Si\text{-}O\text{-}Ag^+ \rightarrow ...Si\text{-}O\text{-}Na^+ + Ag^0.$$

The possibility of the existence of neutral atoms and even sodium nanoparticles in glass has been confirmed experimentally [10, 11]. Reduced silver atoms, in turn, are clustering in silver nanoparticles at the temperature of the ion exchange (300 °C):

$$nAg \rightarrow Ag_n.$$

Conclusion

We demonstrate that vacuum poling of a soda-lime glass and subsequent silver-for-sodium ion exchange results in the formation of silver nanoparticles in the subcathode layer within 2 microns. This approach can be used to create 2D-structured glass metal composites without using thermal treatment in reducing atmosphere. A hypothesis about the reduction of silver ions during the ion exchange by sodium atoms penetrated the glass from the cathode during poling in vacuum is proposed.

REFERENCES

1. **Lepienski C.M., Giacometti J.A., Ferreira G.L., Freire Jr F.L., Achete C.A.,** Electric field disctribution and near-surface modifications in soda-lime glass submitted to a dc potential, Journal of Non-Crystalline Solids. 159 (3) (1993) 204–212.
2. **An H., Fleming S.,** Second-order optical nonlinearity and accompanying near-surface structural modifications in thermally poled soda-lime silicate glasses, JOSA B. 23 (11) (2006) 2303–2309.
3. **Ziemath E.C., Araujo V.D., Escanhoela C.A.,** Compositional and structural changes at the anodic surface of thermally poled soda-lime float glass, Journal of Applied Physics. 104 (5) (2008).
4. **Doremus R.H.,** Mechanism of electrical polarization of silica glass, Applied Physics Letters. 87 (23) (2005) 1–2.
5. **Babich E., Reduto I., Redkov A., Reshetov I., Zhurikhina V, Lipovskii A.,** Thermal poling of glasses to fabricate masks for ion exchange, Journal of Physics: Conference Series. 1695 (1) (2020) 012107.
6. **Brunkov P.N., Lipovskii A.A., Melehin V.G., Red'kov A.V., Statsenko V.V.,** Formation of silver fractal structures in ion-exchange under poling, Technical Physics. 60 (2015) 270–274.
7. **Redkov A.V., Melehin V.G., Lipovskii A.A.,** How Does Thermal Poling Produce Interstitial Molecular Oxygen in Silicate Glasses, The Journal of Physical Chemistry C. 119 (30) (2015) 17298–17307.
8. **Hlaing M., Gebear-Eigzabher B., Roa A., Marcano A., Radu D., Lai C.Y.,** Absorption and scattering cross-section extinction values of silver nanoparticles. 58 (2016) 439–444.
9. **Samuneva B., Djambaski P., Avramova K.,** Interaction between glasses and alkali metal vapours. Journal of Non-Crystalline Solids. 112 (1989) 385–391.
10. **Iliescu B., Enculescu I., Pera I., Alexe G., Polosan S., Stanculescu A.,** Chemical composition of structures obtained inside quartz crystal by sodium electrodiffusion, Crystal Research and Technology. 36 (4-5) (2001) 403–410.
11. **Bochkareva E.S., Nikonorov N.V., Podsvirov O.A., Prosnikov M.A., Sidorov A.I.,** The Formation of Sodium Nanoparticles in Alkali-Silicate Glass Under the Action of the Electron Beam and Thermal Treatments, Plasmonics. 11 (2016) 241–246.

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