Peculiarities of ion-exchange in poled glasses

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Abstract. We demonstrate for the first time that the results of ion exchange processing of thermally poled soda-lime glass essentially depend on the poling conditions. In particular, the processing of vacuum-poled soda-lime glass in silver-sodium nitrate melt results in the diffusion and reduction of silver ions followed by clustering silver nanoparticles in the subsurface layer of the glass after either ion-exchange or additional heat treatment of the ion-exchanged samples. Poling in air atmosphere with deposited gold film anode prevents silver ions penetration in the glass, but electric field stimulated diffusion of gold in this configuration leads to the formation of gold nanoparticles in the glass after heat treatment. It is also shown that corona poling of the glass in air atmosphere does not completely block silver penetration.

1. Introduction
The study of the processes taking place in thermal poling of glasses is of interest in connection with the possibility to use thermal poling for producing micro- and nanostructures for photonics, microfluidics and integrated optics [1]. It is known that the poling results in the redistribution of positive ions, the main charge carriers in glasses, which leads to the formation of spatial charge under the anodic surface of the poled glass [2]. Thermal poling of multicomponent glasses can differently modify the composition and structure of the subanodic region of glass, the modification being dependent on the poling mode. In the case of closed anode poling, which prevents access of atmospheric species to the anodic surface of glass, the subanodic region of the glass becomes depleted with alkali and alkali earth ions, and the latter form a peak of concentration beneath the depleted layer [3]. If open anode poling is used, the subanodic region of the glass is enriched with hydronium ions generated from atmospheric water vapor in the vicinity of the anodic electrode and penetrating into the glass during the poling [4]. Experimental data [5] indicate that the hydronium ions are more mobile than alkaline earth metal ions, and they occupy positions of alkali ions which shift in the glass bulk towards the cathode, while alkaline earth ions retain their position. Previous studies have shown that poling changes the resistance of glasses to chemical etching [6], allows the formation of phase patterns [7] or dissolves metal nanoparticles in glasses [8]. In this paper, we present the studies of the influence of thermal poling regime on silver ion exchange in soda-lime glass.
2. Experiments and results

We used 1 mm thick soda-lime glass slides “Menzel” purchased from Agar Scientific. The glass composition is presented in Table 1.

Table 1. Composition of Menzel glass in wt % of oxides.

|     | SiO₂  | Al₂O₃ | Na₂O  | K₂O  | MgO  | CaO  | Others |
|-----|-------|-------|-------|------|------|------|--------|
|     | 72.2  | 1.2   | 14.3  | 1.2  | 4.3  | 6.4  | 0.33   |

We thermally poled the glass samples with electrodes presenting 1) pressed glassy-carbon plates, 2) deposited metal (55 nm gold and 200 nm chromium) films on the both sides of the slides, and poled using 3) corona discharge in air atmosphere. This is illustrated with figure 1. The list of the samples and the conditions of their poling, following ion exchange and thermal processing are presented in table 2. Further, we put main attention to the anodic electrodes, for they essentially influence results of glass poling.

![Figure 1. Three different types of anodic electrode.](image)

Table 2. Prepared samples.

| Anode type                   | Pressed anode, vacuum poling | Deposited anode, vacuum poling | Deposited anode, air poling | Corona poling |
|------------------------------|------------------------------|-------------------------------|-----------------------------|---------------|
| Voltage (V)                  | Glassy carbon                | Chromium                      | Gold                        |               |
|                              | 500                          | 800                           | 800                         | 800           |
| Ion Exchange                 | Ag₀.₀₅ Na₀.₉₅NO₃ (in wt.%)   | 20 min 325 °C                 | 10 h 325 °C                 |               |
| Annealing, 1 h 600 °C       | -                            | -                             | +                           | +             |

All samples were poled at the temperature of 300 °C. Duration of the poling with anodic electrodes corresponded to 90% drop of the poling current. The corona poling was performed for 3 h. It has been found that vacuum poling with pressed electrodes results in the coloration of the samples after the ion exchange. Measurements of the optical absorption spectra of the sample poled with pressed electrodes (figure 2a) showed wide absorption peaks centered at ~375 nm in 500 V-poled and a narrower peak at ~420 nm in 800 V-poled glass (yellowish-colored sample). We attributed the first peak at ~375 nm to the absorption of Ag₆-Ag₉ neutral clusters [9] and the second peak - to the surface plasmon resonance absorption of a polydispersed ensemble of silver nanoparticles [10]. Thus, vacuum poling with pressed electrodes resulted in the reduction of silver ions penetrated into the glass during the ion exchange. Vacuum poling with deposited chromium electrodes under 800 V similarly led to the
formation of polydisperse silver nanoparticles after the ion exchange, however, their number, which correlates to the height of optical absorption peak (see figure 2b), essentially increased. We associate the reduction of silver with the presence of negatively charged non-bridging oxygen atoms in the subanodic layer of the poled glasses [2]. Supposedly, the non-bridging oxygen atoms donate electrons to silver ions, and thermal diffusion of reduced silver atoms leads to their clustering and the growth of silver nanoparticles. The higher poling voltage and poling in “closed anode” configuration results in the generation of higher spatial charge and, correspondingly, in an increased number of silver atoms, which facilitates the formation of the nanoparticles.

Vacuum poling of the glass using deposited gold electrodes induced lower (compared to pressed and deposited film chromium electrodes) light absorption after ion exchange. This corresponds to fewer silver clusters formed in the subanodic region of this sample glass during ion exchange (figure 2c). However, annealing (600° C, 1 hour) of the poled and ion-exchanged slide in air led to the formation of numerous nanoparticles on the anode surface of the glass. This is evidenced by the appearance of the absorption peak at the wavelength of surface plasmon resonance of silver nanoparticles in the residual spectrum (figure 2c). Here and below residual spectra were obtained by the subtraction of absorption spectra of slides after anode surface cleaning from the spectra of the slides before cleaning and marked with “R” in figures. We attribute lower silver-related optical absorption of this sample to a lower concentration of silver ions penetrating into glass. Probably, this is because of the limitation of their diffusion due to partial generation and entering of gold ions into the glass and occupying of non-bridging oxygen bonds by these ions. In this poling mode, the gold film anode electrode is the source of some amount of gold ions.

![Figure 2](image.png)

**Figure 2.** Absorption spectra of glass poled in vacuum with (a) pressed anode under 500 and 800 V after the ion exchange, (b) with deposited chromium film anode under 800 V after the ion exchange and (c) glass poled under 500 V with deposited gold film anode after the ion exchange and annealing (residual spectrum, marked with “R”).
Contrary to vacuum poling, poling in air atmosphere using deposited gold film anode (300°C, 500 V) completely prevents silver ions penetration into glass. There is no optical absorption corresponding to silver clusters/nanoparticles in the measured spectrum of the poled glass after both ion exchange and subsequent annealing (also, no surface silver nanoparticles absorption is seen in the residual spectrum in figure 3). We suppose that this is due to blocking of silver penetration by gold ions formed at the anode via some oxidation of the gold film, their drifting into the glass and occupying non-bridging oxygen sites. Occupation of non-bridging oxygen bonds by gold atoms should leave no space for silver ions. Indeed, the heat treatment of the poled sample in air atmosphere at 600°C for 1h has demonstrated the appearance of a peak at ~530 nm in its optical absorption spectrum (see figure 3). This corresponds to the spectral position of surface plasmon resonance in gold nanoparticles [11], and the peak reflects the formation of such nanoparticles inside the glass, not on the surface. The latter was confirmed by the absence of changes in the spectrum after cleaning the slide surface. The appearance of the absorption at the wavelength of surface plasmon resonance of gold nanoparticles indicated the drift of low-mobile gold ions into the glass during poling in this mode. Presumably, thermal poling in the air atmosphere provided some oxidation of the gold film anode, which allowed arising gold ions to penetrate into the glass under the influence of an electric field. In addition, the binding of trivalent gold ions to non-bridging oxygen atoms should block the ion exchange of silver. Gold nanoparticles form at a relatively high temperature, 600°C, at which metal nanoparticles are usually formed in glasses containing noble metal ions [10]. The air poling with deposited chromium film anode (300°C, 800 V) completely prevented silver diffusion into the glass during the ion exchange (see figure 3b). There is no silver clusters/nanoparticles absorption in the spectrum after the ion exchange, and the residual spectrum after additional thermal treatment of the ion exchanged poled glass does not show a presence of nanoparticles on the glass surface. The absence of silver ions penetration into the glass is the result of a strong polymerization of subanodic glass region in this mode of thermal poling.

![Figure 3](image.png)

**Figure 3.** (a) Absorption spectra of the glass poled in air atmosphere under 500 V with deposited gold film anode before and after ion exchange and annealing. (b) Absorption spectra of the glass poled in air atmosphere under 800 V with deposited chromium film anode before and after ion exchange and annealing. Residual spectra are marked with “R”.

### 3. Conclusions

Finally, we have shown that the mode of thermal poling of the soda-lime glass significantly affects results of subsequent ion exchange processing of glass. The most significant results are the formation of silver nanoparticles in the subanodic region of glasses poled in vacuum using pressed or deposited chromium film anode without an additional heat treatment of the glass after the ion exchange. Poling in vacuum with gold film anode allows some penetration of silver ions in the poled glass, but silver nanoparticles do not form in the glass and additional anneal results in their formation on the glass.
Poling in air corona discharge allows silver ion exchange and formation silver nanoparticles after heat treatment of the ion-exchanged glass. Using deposited chromium and gold film anodic electrodes for poling in air prevents silver ions penetration in the poled glasses. However, in the case of gold electrode diffusion of gold in the glass occurred and gold nanoparticles formation took place after additional heat treatment of the glass. Obtained results can be employed in the formation of the metal nanoparticles in glasses, and prescribed 2D distribution of the nanoparticles can be formed if profiled anodic electrodes are used.

Figure 4. Absorption spectra of the glass poled in air corona discharge under 4000 V before and after ion exchange and annealing.

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