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The effect of electron beam irradiation on silver–sodium ion exchange in silicate glasses

Alexander I. Sidorov [a,b,*], Mikhail A. Prosnikov [c]

[a] ITMO University, Kronverksky Ave., 49, St. Petersburg 197101, Russian Federation
[b] St. Petersburg Electrotechnical University "LETI", Prof. Popova Str., 5, St. Petersburg 197376, Russian Federation
[c] Ioffe Physical-Technical Institute, Russian Academy of Sciences, Politechnicheskaja St., 26, St. Petersburg 194021, Russian Federation

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ABSTRACT

It is shown experimentally that electron irradiation of sodium–silicate glasses makes possible the control of the subsequent ion exchange $Ag^+ \leftrightarrow Na^+$ process in a salt melt. The reason of this effect is the negatively charged regions formation in a glass volume during electron irradiation. The electric field, produced by these regions in glass volume, results in positive Na^+ ions field migration into them. The spatial redistribution of Na^+ ions results in the decrease of the ion exchange efficiency, or the ion exchange can be even blocked. This led to the decrease of the luminescence intensity of neutral silver molecular clusters in the irradiated zone, and effect on the silver nanoparticles formation during the subsequent thermal treatment. The observed effects can be used for the control of ion exchange processes during integrated optics devices fabrication, and for the electron-beam recording of optical information.

1. Introduction

The electron-beam materials processing is widely used in precise technologies – in the electron-beam lithography [1], surface modification [2], optical waveguides writing [3,4], materials evaporation etc. The action of electron beam results not only in materials surface heating, but in the sequence of more complicated effects. Some of them are the following:

- ionization of material components by the fast electrons;
- breaking of chemical bonds of material by fast electrons and the formation of new bonds [4];
- initialization of crystallization processes in glasses [5–7];
- formation of negatively charged region under the substrate surface by thermalized electrons [6,8];
- field migration of positive mobile ions to the negatively charged region and their reduction by the thermalized electrons [2,6,9];
- dissolution of the metal films and metal nanoparticles in glasses in strong electric field produced by the negatively charged regions [10,11].

The ion exchange (IE) is the effective method of glasses doping by the mobile metal ions [12–14]. This method consists in the exchange of metal ions (ex., Na^+ in sodium-containing glasses) by some other ions (ex., Ag^+) from the salt melt. The diffusion of metal ions during IE process takes place mainly through the defects of glass network. The IE method is used to produce in glasses an optical waveguides, gradient lenses, etc. For example, the IE $Ag^+ \leftrightarrow Na^+$ results in gradient optical waveguide formation under the glass surface, because of the higher polarisability of silver ions [12]. The IE method can be also used for the strengthening of glass surfaces [14]. It was shown in [15] that during such process silver appear in a glass not only in the state of ions, but also in the states of neutral atoms and neutral silver molecular clusters (MCs) – Ag_2, Ag_3, and Ag_4. Neutral silver MCs possess intense luminescence in a visible spectral region when excited by UV radiation [15,16]. This can be used for fabrication of luminescent waveguides in glasses by the IE method. The ability of the local formation of charged regions in glass by electron irradiation and spatial redistribution of mobile metal ions will make possible the control of the subsequent IE process.

The goal of the present work was the investigation of the effect of preliminary electron-beam irradiation on the $Ag^+ \leftrightarrow Na^+$ IE processes in sodium-containing glasses.

2. Materials and methods

In our experiment we used the plates of the commercial sodium–silicate (soda-lime) glass of the composition

* Corresponding author at: ITMO University, Kronverksky Ave., 49, St. Petersburg 197101, Russian Federation. Tel.: +7 911 920 5938.
E-mail address: sidorov@oi.ifmo.ru (A.I. Sidorov).

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$76SiO_2$–$14Na_2O$–$10MgO$–$0.1Al_2O_3$. The glass samples were the polished plates with the size 10 × 10 mm and 1 mm thick. The glass transition temperature (T_g) of this glass measured with STA6000 (Perkin-Elmer) differential scanning calorimeter was equal 560 °C. Electron irradiation was carried out in a JEBD-2 electron microscope with electron energy $E = 35$ keV with doses $Q = 50$ mC/cm^2 (relatively low dose) and 600 mC/cm^2 (high dose) for electron current density $j = 40$–200 μA/cm^2. The irradiation was carried out at room temperature, but it must be noted that during the irradiation the temperature of glass surface increases up to approximately 150 °C. The electron beam diameter on the glass surface was 1.5 mm. It must be mentioned that electron beam can be focused to the spot of 10 nm. The large beam diameter was used for the convenience of optical measurements. At one of the samples one of the irradiated zones was formed as a line by electron beam scanning. The 100 nm thick Al film was deposited on a glass surface for removing the surface charge appearing on a glass surface during the electron irradiation. After the irradiation the Al film was removed by etching in aqueous solution of KOH.

The interval between electron irradiation and IE was varied from several days up to several months. It is evident that negatively charged regions in a glass volume produced by the thermalized electrons during these periods absolutely disappear. IE was performed in a molten mixture of $AgNO_3$ (5 mol.%) and $NaNO_3$ (95 mol.%) at a temperature of 350 °C for 30 min. The calculated depth of Ag ions penetration for the mentioned IE mode is approximately 20 μm. For the calculations we used the expression which describes IE process from [12] with Ag diffusion coefficient $D_{Ag} = 2.6 \cdot 10^{-15}$ m^2/s and $D_{Ag}/D_{Na} = 0.1$ [17]. Thermal treatment of the samples after the IE was carried out in air at temperatures $t = 500$ °C and 580 °C in program-controlled muffle furnace (Nabertherm). The optical density spectra were measured using the Cary500 (Varian) spectrophotometer. Optical density spectra were measured with the diaphragm 0.7 mm in diameter, which was put on the irradiated zone. Luminescence and luminescence excitation spectra were recorded on an SL55 (Perkin Elmer) spectrofluorimeter. Spectral measurements were performed with the steps 1 nm. Luminescence and optical density spectra were measured at room temperature.

3. Experimental results

The as-prepared samples and the electron irradiated samples were colorless. After the IE the samples became pale-yellow and the luminescence appeared in not-irradiated regions. In the irradiated zones the luminescence was weak or absent. After that, thermal treatment at temperatures lower (500 °C) and higher (580 °C) then the glass transition temperature of the samples was carried out. At temperatures lower than glass transition temperature one can expect the formation of silver molecular clusters, while at temperatures higher than T_g – the formation of the nanoparticles, due to significant increasing of the diffusion coefficient of Ag ions and atoms. The thermal treatment at 500 °C during 1 h increases the yellow color of the samples especially in the irradiated regions (Fig. 1a). It can be seen that in the region 2 the color at the perimeter of the region is more intense than in its center. The thermal treatment also results in the increase of the luminescence intensity in the not-irradiated regions (Fig. 1b). Fig. 1c shows the luminescence intensity distribution in the regions irradiated with $Q = 50$ mC/cm^2 and $j = 40$ μA/cm^2 and 60 μA/cm^2. It can be seen that the increase of the electron current density led to the decrease of the luminescence intensity.

Fig. 2 shows the luminescence spectra of the zone 3 at Fig. 1a for different excitation wavelengths. It can be seen that the luminescence occupies the spectral region 450–750 nm with maximum

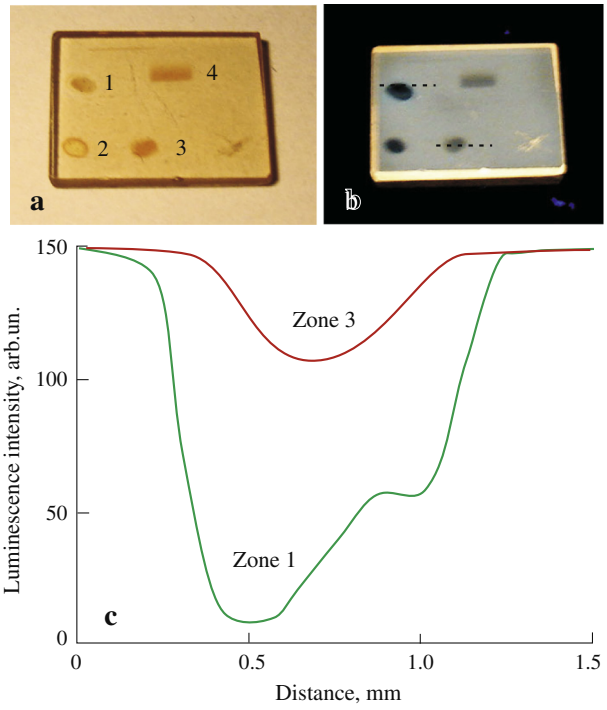

Fig. 1. Photos of the sample (a) and its luminescence (b) after electron irradiation, IE and thermal treatment at 500 °C during 1 h. $E = 35$ keV. a: 1 – $Q = 50$ mC/cm^2 and $j = 60$ μA/cm^2, 2 – $Q = 600$ mC/cm^2 and $j = 200$ μA/cm^2, 3 – $Q = 50$ mC/cm^2 and $j = 40$ μA/cm^2, 4 – $Q = 50$ mC/cm^2 and $j = 40$ μA/cm^2. (c) Luminescence intensity distribution along the dashed lines at Fig. 1b. Excitation wavelength is 365 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

intensity at 500–530 nm. For the excitation wavelengths 360 and 400 nm the luminescence is caused by neutral molecular silver clusters Ag_2, Ag_3, and Ag_4 [16–19]. The luminescence of the not-irradiated region has the similar band, but its intensity is much higher (see also Fig. 1a). The excitation bands of Ag^+, Ag^0 and charged silver dimers Ag^+–Ag^+ are located in the spectral range 230–330 nm [20], so their luminescence is absent in the spectra shown at Fig. 2.

Optical density spectra in the zone 3 at Fig. 1a before and after electron irradiation, after IE, and after thermal treatment at 500 °C

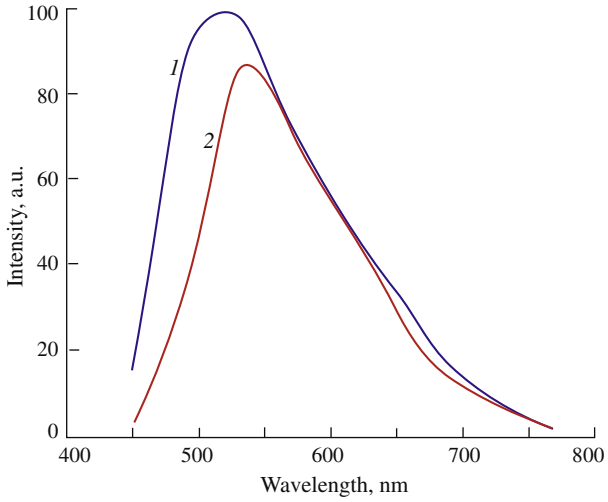

Fig. 2. Luminescence spectra of the zone 3 at Fig. 1a. Excitation wavelengths are 360 nm (1) and 400 nm (2).