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MODIFICATION OF GLASS SURFACE BY A HIGH ELECTRIC FIELD

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The work has studied an effect of a high DC field on the composition and properties of the subsurface region of a multicomponent silicate glass. The concentration of alkali ions in the subsurface glass region was shown to drastically decrease under the high electric field. This led to a change in the ion-exchange characteristics of glasses and their resistance to etching. The effect allows employing the poled regions of the glass surface as dielectric masks in the formation of gradient optical structures, as well as relief microstructures, e.g., grooves for microfluidics, in glass substrates. The advantage of this approach is that there is no need in multiple lithography using liquid chemicals. This reduces the cost and makes this technological process environment friendly.

Keywords: high electric field, chemical etching, ion etching, ion-exchange

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Introduction

In recent years, glasses have been actively used to fabricate integral elements of waveguide optics and photonics: lenses, multiplexers, modulators, optical amplifiers, as well as microfluidics and lab-on-a-chip devices [1]. In most cases, the change in the optical characteristics of glass is achieved by ion-exchange (thermal or electrostimulated), in which ions from the glass matrix are replaced by ions from the salt melt [2]. Chemical or reactive ion etching is used to change the morphology of the glass surface, for example to form microgrooves. Both the ion-exchange process and the etching process require masks, which are usually formed from dielectric or metallic films deposited on the surface of the glass substrate by lithographic methods. The advantage of dielectric masks is the absence of a contact potential difference [3], so that they do not affect the ion distribution during ion-exchange. However, metal masks are widely used for technological reasons.

This paper presents a new approach to forming a dielectric mask on the glass surface, namely, local modification of its near-surface region by a high electric field. The electric field is applied by means of a relief electrode, which is produced using lithography. The proposed approach has an advantage over the traditional one due to its low cost, since the same electrode can be used multiple times to modify an almost unlimited number of substrates, i.e., to form masks on their surface for ion-exchange or etching.

Experimental

We have considered thermal poling of glass, that is, modification of multicomponent silicate glass by high electric field at elevated temperature with the help of a pressed anode electrode [4]. The process is shown schematically in Fig. 1. A flat (*1*) or comb-shaped (*2*) structure made of glass graphite was used as the anode electrode [5]. After anode *1* (or *2*) and cathode *3* were pressed to glass *4*, it was heated and a DC voltage was applied to it. Patterned electrode *2* was used to form alternating poled (*5*) and unpoled (*6*) regions in the sample.

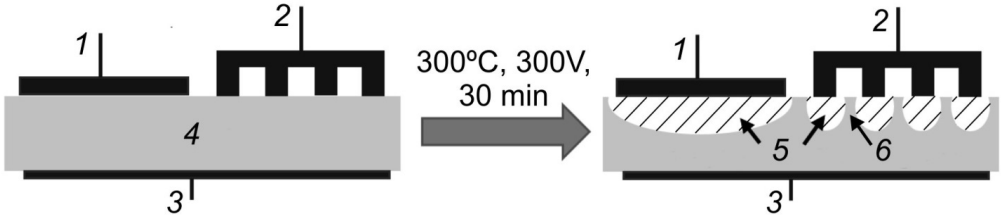

Fig. 1. Schematic of thermal poling:
flat (*1*) and comb-shaped (*2*) anode, respectively; cathode *3*; glass sample *4*;
the same sample with alternating poled (*5*) and non-poled (*6*) regions, respectively

During the thermal poling, the electric field in the sub-anode region of the glass can reach values of tenths of a volt per nanometer [6]. The alkaline ions (sodium ions in our case) located near the glass surface are displaced deep into the bulk under the influence of such a high field. In addition, water vapor penetrating into the sample from the atmosphere partially decomposes to form hydronium ions [7], and replaces the alkaline ions in the near-surface region. As a result, the near-surface region is depleted of alkaline ions and there is subsequently a local change in the physical properties of glass and its chemical resistance. For example, a periodic change of glass properties is observed for a comb-shaped electrode: the non-poled region under the electrode hollow retains the original properties, and the poled region changes its characteristics.

In the experiment, 1 mm thick soda-lime glass plates were used. The content of the main network-modifying oxide in the glass was as follows (wt%): 14.3 Na_2O, 6.4 CaO and 4.3 MgO. Poling was carried out at atmospheric pressure, temperature of 300°C and an applied DC voltage of 300 V; the process duration was 30 min (see Fig. 1). The concentration of sodium, calcium and magnesium in the poled glass was measured by energy dispersive X-ray spectroscopy (EDS) using an automated EDS Oxford Instruments AZtecLive system, installed on a TESCAN LYRA3 scanning electron microscope (SEM) [8]. The measurements showed that sodium ions were absent in the area about 2 μm deep from the glass surface, while the concentration of calcium and magnesium ions remains unchanged (Fig. 2, *a*). EDS is not sensitive to hydronium/hydrogen, but a bright line can be seen in the SEM image (Fig. 2,*b*) at the depth corresponding to the sodium concentration step. Presumably, this corresponds to electrons scattered by the spatial charge accumulated at the interface between hydronium and sodium ions. This charge arises due to the difference in the mobility of hydronium and sodium ions: the mobility of the former is more than three orders of magnitude lower than that of the latter [7]. Together with the known data on detecting the recoil of helium ions (ERDA) by poled glass [9], this allows to conclude that the deficit of sodium ions is mainly compensated by hydronium ions.

The deficit of sodium ions in the near-surface region of glass has a significant impact on the process where sodium ions are displaced by silver ions from the molten salt (ion-exchange). This process is most often used for formation of integral optical structures: due to higher polarizability of silver ions as compared to sodium ions, the $Ag^+ \rightarrow Na^+$ exchange leads to an increase in the refractive index by Δn in the ion-exchange region and formation of optical waveguides [2].

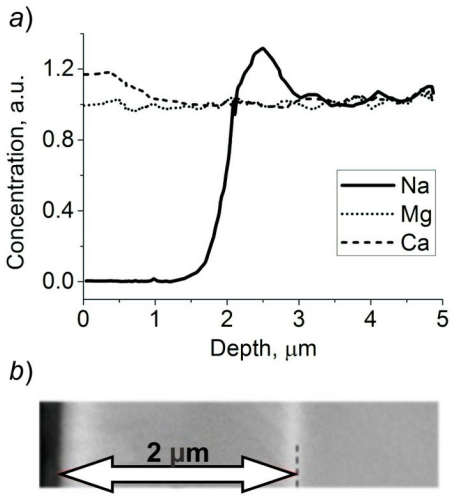

Fig. 2. Distributions of normalized metal concentration along the depth near the surface of poled glass sample (*a*) and SEM-image of its cross section (*b*)

To study the effect of thermal poling on the ion-exchange properties of glass, we placed poled glass in a melt of $Ag_{0.05}Na_{0.95}NO_3$ at 325°C. The treatment lasted for 60 min. The refractive index behavior in the poled and non-poled regions of the glass was investigated after ion-exchange. For this purpose, the modal spectra of gradient optical waveguides formed as a result of ion-exchange in the corresponding glass regions were measured on the MetriconM-2010 setup using prism coupling of light. Both poled and non-poled glass regions exhibited light wave grooveing after ion-exchange, but the modal spectra of these waveguides differed significantly. We calculated the refractive index profiles from the measured modal spectra using the Heidrich-White algorithm [9]. The results of the calculations are presented in Fig. 3.

Fig. 3 shows significant differences both in the magnitude of the change in the refractive index and in the depth of the area with increased refractive index for poled and non-poled glasses. It should be noted that the magnitude of the change in the refractive index linearly depends on the concentration of silver in the glass [11]. Thus, it can be concluded that the maximum concentration of silver in the poled region of glass is about 3.5–4 times less compared to the non-poled region, and the depth of silver penetration is about 4 times less (with the ion-exchange duration of 60 minutes). Since the ion penetration depth is proportional to the square root of the diffusion coefficient, the difference in depths allows to conclude that the diffusion coefficient of silver ions in poled glass is at least 10–15 times smaller than in virgin glass. The decrease of both concentration and depth of penetration of silver ions is presumably due to replacement of sodium ions by less mobile hydronium ions and structural changes caused by thermal poling. Thus, poled regions of glass are more stable with respect to ion-exchange treatment. This makes it possible to use them as dielectric masks for producing gradient integral optical structures on glass substrates or diffraction gratings.

The change in the glass structure after treatment with a high electric field is also confirmed by Raman scattering (RS) data. Fig. 4 shows Raman spectra of the virgin glass and glass after thermal poling (the spectra were obtained on a WITec Alpha 300R Raman microscope with a laser excitation wavelength of 532 nm). Fig. 4 shows that the poled glass lacks a peak in the 1100 cm^{-1} region, whose intensity is determined by the presence of modifying ions in

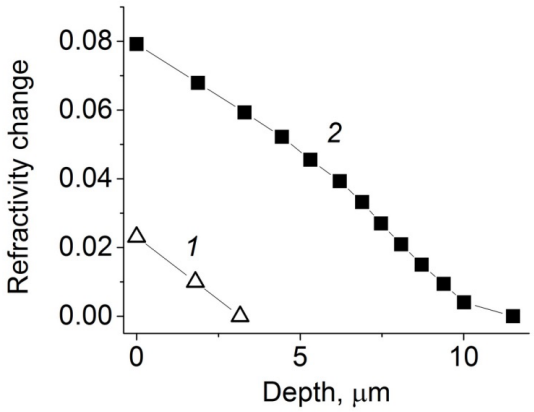

Fig. 3. Calculated profiles of refractive index increase in the ion-exchanged region of poled (*1*) and non-poled (*2*) glasses.
The duration of ion-exchange was 60 min

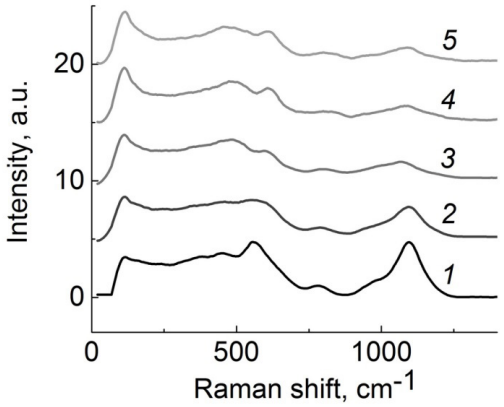

Fig. 4. Raman scattering spectra of virgin (*1*) and poled (*2–5*) glasses.
As the passed charge increases (this is reflected in the numbering of curves, *2* → *5*), the glass structure becomes more silica-like

the glass. Comparing the Raman spectra for the samples of the virgin glass and the glass poled at different applied voltages shows that the higher the electric field or the duration of thermal poling, the closer the structure of the poled region to that of fused glass without modifying alkali oxides [12]. Consequently, the number of non-bridging oxygen atoms decreases in poled regions [12]. The latter are associated in particular with alkaline ions which are capable of exchange, so the number of positions in the glass structure that can be occupied by ions involved in the process also decreases. This confirms the conclusion made above that thermal poling increases the resistance of glass to ion-exchange.

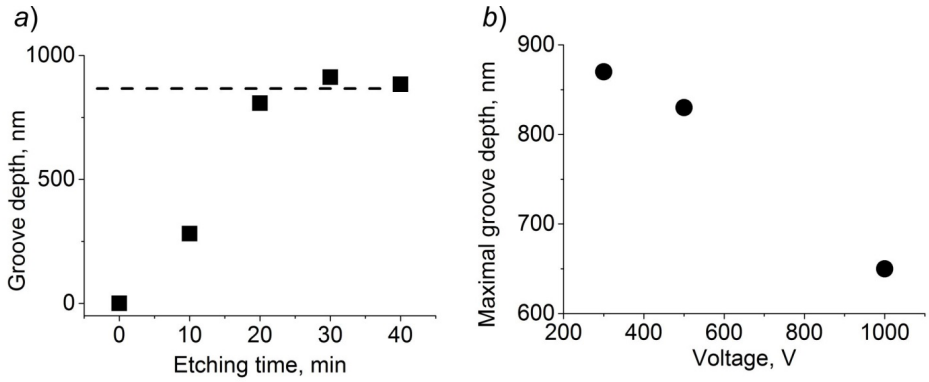

Fig. 5. Dependences of depth on the glass surface on the etching time in $NH_4F : 8H_2O$ solution (*a*) and the maximum depth of this groove on the applied voltage (*b*). The width of the groove is 60 μm; its maximum depth corresponds to complete etching of the poled layer

It has recently been shown that poled regions of soda-lime glass have better resistance to acid etchants and worse resistance to ion etching compared to non-poled regions [13].

We considered chemical etching of glass poled with a comb-shaped electrode (see Fig. 1) in an aqueous solution of ammonium fluoride ($NH_4F : 8H_2O$). It was found that etching of non-poled areas of glass under the electrode hollow occurs faster than that of poled ones, and grooves form on the glass surface as a result. The maximum depth of grooves is determined by the difference of etching rates of poled and non-poled regions and the thickness of the poled layer. The etching dynamics of poled and non-poled regions was studied by plotting the dependence of the groove depth on the etching time (Fig. 5, *a*); the groove width corresponding to the hollow width in the electrode was 60 μm. Fig. 5,*a* shows that the groove depth first increases linearly with time, and the dependence reaches saturation after 20 minutes of etching, at a depth of about 900 nm. Thus, the poled region in the given sample is completely etched after 20 minutes.

Notably, the glass in the region below the electrode hollow is not poled for grooves wider than 10 μm. Reducing the groove width leads to substantial edge effects and, consequently, glass poling even under the electrode hollow. A similar effect is observed when the applied voltage is increased (Fig. 5,*b*).

The picture will be reversed for reactive ion etching: poled regions are etched faster than non-poled ones, and the relief formed on the glass surface repeats the geometry of the electrode [13]. The maximum depth of the grooves is also determined by the depth of the poled region.

Thus, thermal poling of glass with a patterned electrode makes it possible to form a dielectric mask on the glass surface for chemical or ion etching. Depending on the task, forward or reverse (mirror) relief of the electrode can be formed in the glass. This method can be used to form, for example, lab-on-a-chip devices, as well as grooves for microfluidics.

Conclusion

Based on the results obtained, we can conclude that the changes in the composition and structure of multicomponent silicate glasses induced by thermal poling can be used to form dielectric masks on their surface for silver-sodium ion-exchange, chemical and reactive ion etching. The reason for this is that the escape of mobile alkaline ions from the sub-anode glass region during its thermal poling significantly slows down the process of ion-exchange, while increasing the cohesion of the glass network makes its structure more ‘silica-like’. This property increases the resistance of poled glass regions to chemical etchants used for multicomponent glasses and decreases the resistance of these regions to the process of reactive ion etching traditionally used for quartz glass.

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