Submicron Surface Relief Formation Using Thermal Poling of Glasses

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(Received 13 October 2008; Accepted 20 February 2009; Published 16 May 2009)

Imprinting the relief of anodic electrode in glass surface in the course of DC electric field polarization of the glass is studied using atomic force microscopy. Square grid with rectangular relief produced on silicon by e-beam lithography and ion etching (relief height 120 nm, line width 0.5 μm, and periodicity 1 μm), and lead-silicate glass microchannel plate (channel diameter 9.5 μm and distance between the channels 12.5 μm) possessing electronic conductivity along the channels walls were used as anodic electrodes. The height of the relief formed on glass surface after polarization varied from 5 to 15 nm depending on the conditions of the processing. The mechanism of relief formation is discussed. [DOI: 10.1380/ejssnt.2009.617]

Keywords: Glasses; Electrical transport; Poling; Surface relief; Atomic force microscopy

I. INTRODUCTION

As known, the conductivity of alkali-silica glasses is due to ionic mobility of alkaline ions, which are the main charge carriers in such glasses. If a glass plate placed between two metallic electrodes is heated up to a temperature sufficient to activate ionic conductivity (250-300°C for usual alkali-silicate glasses), and several kV voltage is applied to the electrodes, the electric field forces the cations (positive alkaline ions) to migrate from anodic surface towards cathode, i.e. in glass bulk. This migration leads to the formation of negative spatial charge and in a strong electric field arising in the subanodic region of the glass. Cooling the glass under the voltage applied results in the formation of “frozen” electric field, for the mobility of ions - charge carriers in glass is negligible at room temperature. The process of thermal polarization of glasses in strong electric field is presently referred to as thermal poling, and the glasses with strong frozen electric field are treated as a prospective material for second optical harmonic generation [1–3]. Field-induced compositional change of the subsurface layer of a glass in thermal poling [4–6] is followed by the glass index change, and this is in use for the producing of optical waveguides [7–9]. Additionally, the arising of a relief on the surface of glasses poled with the electrodes having surface relief has recently been observed, and the formation of relief structures with submicron spatial resolution on the glass surface was demonstrated [10, 11]. It is necessary to note the essential difference of the relief formation in thermal poling and in thermal stamping of glass. As thermal stamping of materials requires their low viscosity, the temperature of glasses under stamping should exceed glass transition temperature, while thermal poling can occur at 150-300°C, when viscous flow of glass is not possible, also the stamping technique does not allow producing submicron structures [10]. Imprinting of the relief of electrode on glass surface is of interest for diffraction optics and submicron lithography.

II. EXPERIMENTAL

The present study is aimed at the formation of the relief on the surface of glass in thermal poling with the use of relief electrodes. We used commercial soda-lime glass with composition 72SiO₂−15Na₂O−6.8CaO−4MgO−1.6Al₂O₃−0.2Fe₂O₃−0.4SO₃ (wt.%). Square grid with the height of rectangular relief 120 nm, line width 0.5 μm, and periodicity 1 μm produced with e-beam lithography and ion etching on the surface of n-silicon wafer and protected with 10 nm chromium film, and lead-silicate glass made microchannel plate with the diameter of hexagonally packed channels equal to 9.5 μm and channels spacing 12.5 μm, possessing electronic conductivity in channels walls [12], were used as the anode electrodes for thermal poling of the soda-lime glass plates. The glass plate of 1 mm thickness was placed between the anode and the flat cathode made from stainless steel. Then the whole structure was put in a furnace and heated up to 300°C, and 400-750 DC volts were applied to the electrodes for 5-20 min. The relief of glass surface formed in the thermal poling was characterized with atomic force microscope (AFM) Dimension 3100 (Veeco) in air using semi-contact mode and NSG01 (NT-MDT) probes with pin curvature ~10 nm.

III. RESULTS AND DISCUSSION

3D AFM-image of the anode electrode with square grid and its spatial profile are presented in Figs. 1(a) and (b), respectively, and 3D AFM image of the surface of the glass plate after 20 min of thermal poling at 300°C with 750 V applied to the electrodes and its spatial profile are illustrated by Figs. 1(c) and (d), respectively. As it is seen
FIG. 1: 3D AFM image of the part of anodic electrode with square grid (a), its spatial profile (b), 3D AFM image of the part of glass surface after poling with this electrode (c), and its spatial profile (d). The profiles are measured along the straight lines marked in the AFM images.

from Fig. 1, glass surface dips correspond to the electrode relief feathers, and the glass surface relief height is about 15 nm that is about eight times less than the anodic electrode relief height. The shape of the imprinted in glass relief also differs with the shape of the anodic electrode, and the walls of imprinted dips are not vertical. It was observed that the height of imprinted relief essentially depends on the conditions of the glass poling. For example, the decrease of poling voltage down to 400 V and poling time down to 5 min led to the formation of glass surface relief of 5-6 nm in height.

The authors of the first paper devoted to the formation of spatial relief on glass surface subjected to thermal poling with relief anodic electrode [10] proposed the deformation of glass under electrostatic forces attracting glass surface to the electrode as the explanation of this phenomenon [10]. Later, in paper [11] it was supposed that the deformation was due to internal stresses arising in the glass matrix after field-induced removal of alkali ions from surface of the sample. The profile of these stresses is defined by spatial distribution of cation vacancies (or, the same, by the distribution of penetrating from atmosphere hydrogen ions occupying the vacancies), which, in its turn, depends on spatial distribution of electric field at the glass surface and in the subsurface region of the glass. The stresses induce a local change of glass volume in the subsurface glass region that results in the formation of the relief on glass surface. Local increase of glass volume was registered earlier in the studies of ion exchange processing of glasses through deposited masks and in the studies of electric field stimulated diffusion of metals from metal films deposited onto glass surface [13–17]. This phenomenon is due to the increase of local glass volume after the replacement of a smaller ion by a bigger one in the glass matrix. The reverse relation of ion dimensions leads to the decrease of glass volume. Contrary to ion exchange and field stimulated diffusion, in thermal poling of glasses the removal and drift of alkaline cations from the glass subsurface layer to the glass bulk and their replacement by hydrogen ions formed at anode electrode due to electrochemical decomposition of atmospheric water vapors [5] take place. As soon as the content of alkali ions in soda-lime glass is high enough, the electric field induced removal of these ions essentially changes the composition of the subsurface glass region. Actually, only the glass skeleton formed by silicon-oxygen tetrahedrons connected
by bridging oxygen atoms is preserved within this region, and alkaline ions connected to non-bridging oxygen atoms are replaced by hydrogen ions. Internal stresses arise in the glass framework after removal the modifier (alkaline ions), and these stresses deform the glass skeleton, i.e. the glass volume changes. The local change of the glass volume is higher in the regions of electric contact of the glass sample and anodic electrode, for electric field there is higher. This results in higher concentration of cationic vacancies arisen in the contact area after thermal poling. Flexion deformation of the glass (along the surface) is negligible due to essential thickness of the sample, and local deformation is mainly directed normally to the glass surface. This deformation results in the formation of the surface relief. Evaluations according to [11] showed that mechanical stresses arising in the subsurface layer in thermal poling of glasses and deforming their silicate skeleton are about an order of magnitude higher than electrostatic pressure arising in glass poling.

This interpretation of the mechanism of the surface relief formation was confirmed by the experiments performed using microchannel plate as anodic electrode for glass poling. 3D AFM image of the part of the microchannel plate and its spatial profile are presented in Figs. 2(a) and (b), respectively. Fig. 2(c) shows 3D AFM image of the part of the glass surface after processing with the microchannel plate as anodic electrode, and spatial profile of the processed glass is presented in Fig. 2(d).

We poled the glass during 20 min at 290°C by 900 DC V applied. As it is seen from Fig. 2, the profile of formed surface relief is inverted relatively to the profile presented in Fig. 1, i.e. the feathers, not dips, on the glass surface correspond to the regions of electric contact, i.e. to the electrode feathers. This is because the walls of conducting channels of the microchannel plate and the end-face of this plate contain essential amount of metallic lead, and in the case of good contact this lead can enter the glass via field-stimulated diffusion. The ionic radius of lead [18] exceeds the ionic radius of sodium, and the sign of the deformation arising in the subsurface layer of the glass due to the difference of ionic volumes is opposite to the sign of deformation arising after the replacement of sodium ions.
by smaller hydrogen ions. The first induces the increase of local volume of the glass and formation hillocks on the glass surface while the latter induces arising caves on the surface of the glass sample.

IV. CONCLUSIONS

Thus the formation of relief on glass surface in thermal poling is due to the local deformation of glass matrix by mechanic stresses arising in the subsurface layer of the glass in the course of field-induced removal of alkali cations and their partial replacement by atmospheric hydrogen ions (or by other cations which enter the glass from anode electrode through electric field stimulated diffusion). The height (depth) and shape of the relief are defined by several cofactors, the main of which are ionic radii of initial and replacing ions, spatial distribution of electric field at the sample surface, concentration and mobility of participating cations, duration of poling process, and its temperature. It is necessary to note that the formation of surface relief was also observed in thermal poling of glass-metal nanocomposites [11, 21]. We suppose this phenomenon to occur in other solids possessing ionic type of electrical conductivity.

Acknowledgments

This study was supported by RFBR (Project No. 08-02-00522-a) and by the Ministry of Education and Science of Russian Federation (Project No. 2.1.1/988), and the facilities of regional JRC “Material science and characterization in advanced technologies” were used.

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[18] Either univalent ($R_{Pb^{1+}} = 106 \text{ pm}$ [19]) or bivalent ($R_{Pb^{2+}} = 126 \text{ pm}$ [20]) lead ions could migrate into the glass substrate. In the most probable case of univalent lead ions replacing the same quantity of sodium ions ($R_{Na} = 95 \text{ pm}$ [19]) the increase of volume is just due to the difference of the radii. In the second case each bivalent lead ion replaces two univalent sodium ions [20], and $0.5 (R_{Pb^{2+}}/R_{Na})^3 > 1$ that is ionic volume increases and hillocks should form in any case.
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