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Effective diffraction gratings via acidic etching of thermally poled glass

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ABSTRACT

Relief diffraction gratings are formed via acidic chemical etching of a periodically poled soda-lime glass. The thermal poling under 1000 V DC is performed at 325 °C using a thermally stable glassy-carbon anodic electrode with periodic grooves, the depth of the grooves being of ~650 nm. Poling-induced modification of the glass results in deepening the glass anodic surface in the regions under the ribs of the anodic electrode due to volume relaxation and in increasing chemical durability of these regions in acidic media comparatively to the virgin glass. Chemical etching of the poled glass in $NH_4F:8H_2O$ solution allows additional to the thermal poling shaping of the glass surface via faster dissolution of unpoled/less poled glass regions. The morphology of the glass surface before and after the etching is characterized with atomic force and scanning electron microscopy. About 30 min etching provides the formation of ~0.9 μm in height relief diffraction gratings with the diffraction efficiency close to the theoretically achievable ~30% for multi-order diffraction. In vivo measuring of the diffraction efficiency in the course of the etching allows precise fabrication of the gratings.

1. Introduction

The phenomenon of glass thermal poling was being under study during last four decades [1–3]. In the poling process, DC voltage from hundreds of volts to several kilovolts is applied to a heated glass plate, and the redistribution of charge carriers in the glass and following depletion of the subanodic glass volume with charge carriers results in the formation of ultra-high, up to 0.1 V/nm, local electric field in the subanodic region [4]. After cooling the glass becomes poled that is it contains “frozen” spatial charge, and, respectively, internal electric field exists in the glass. Thermally poled region of glasses demonstrates losing optical isotropy and a set of other features never observed in virgin glasses. In spite of preferable attention of the researches to silica glasses, essential achievements were demonstrating in the studies of thermally poled soft (multicomponent) glasses. In particular, poling-resulted structural and compositional modification of subanodic glass region [5], poling-induced second harmonic generation [6], development of surface relief [7] and a change in chemical resistivity in the poled region of soft glasses [8,9] were reported. The physics of processes taking place in multicomponent glasses subjected to thermal poling is still under discussion, and such topics as transport of negative charge carriers, relief formation on the anodic surface of poled glasses, relation of structural and compositional modifications, and chemical durability change still stay poorly explained. Nevertheless, thermal poling was effectively used for microstructuring of second harmonic generation along glass surface [10], for the formation of channel optical waveguides [11], 500 nm in period 2D structures in nanocomposite glasses [12], relief diffraction gratings up to 40 nm in height [13], and, being combined with chemical etching in KOH, for the manufacturing of relief diffraction gratings as high as 280 nm [14].

After the difference in HF etching rates of poled and unpoled glasses had been reported for the first time [8], the etching was multiply applied to evaluate the thickness of poled layers in glasses. In silica glass the poled region is more etching resistive, and this difference is about 2 times for the etching in 40% fluoric acid and poling conditions used in Ref. [9]. According to Ref. [15], the difference in fluorine acid etching rates of virgin and poled silica glasses is directly proportional to electric field used in poling. In the case of soda-lime glass the poled region is similarly more acid-resistive to HF. The difference in etching rates of poled and unpoled soda-lime glass in KOH used for the formation of 280 nm in height relief grating was not indicated by the authors of Ref. [14],

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but that height was achieved after 12 h etching in 55% water solution of KOH at the temperature of 70 °C. According to Ref. [14], the glass surface relief formed after the thermal poling with periodic electrode was continuously growing in the course of the chemical etching. This corresponds to faster etching of the poled region in alkalic etching contrary to the case of acidic etching reported in Refs. [9,15]. In the present paper we report our results related to the formation of diffraction gratings with the relief as high as ~0.9 μm using acidic etching of poled soda-lime glass. It is essential that during the etching the relief formed in the poling procedure topples, and the grooves in the finally etched structure correspond to the ribs of the structure formed after the poling. In vivo measurements of the gratings diffraction efficiency allow us precise control of the grating efficiency, which provides the efficiency close to the theoretical limit.

2. Experimental

We poled glass slides with a profiled anodic electrode that resulted in the formation of a weak relief on the glass surface and chemically etched the poled glass in an acidic etchant to strengthen the relief. The whole process of manufacturing the diffraction gratings is illustrated in Fig. 1.

The glassy carbon anodic electrode contained 2 and 20 μm periodic systems of 650 nm deep (see Fig. 2) grooves formed on the polished surface of the electrode using e-beam lithography and reactive ion etching, the widths of the grooves being equal to their spacing. Three mm thick glassy carbon plates were produced by Svensk Specialgrafit AB, and a rectangular piece of 20 × 25 mm^2 was used to fabricate the electrode. In the electron beam lithography, a 50 nm thick chromium film was deposited onto the carbon plate in Kurt J. Lesker Company Lab 18 thin film deposition system. Then it was coated with electron resist, baked and exposed using Vistec Lithography Ebeam EBPG5000 and developed with SSE OPTIspin SST 120 setup. The chromium film was etched through the formed mask using Plasmalab 100 machine, and resulting chromium mask allowed profiling of the glassy carbon surface via the etching in Plasmalab 80 machine. After the removal of the chromium mask and cleaning the profiled glassy carbon plate, the anodic electrode was ready for usage. The choice of these two periods was based on supposed depth of our chemical etching, ~1 μm: 20 μm period was large enough to exclude the influence of lateral etching, and 2 μm period was comparable with that depth.

In the thermal poling, we used home-made setup allowing to apply DC voltage to heated glass plates and to control current and electric charge passing through the samples. In this experiment we used 1 kV voltage applied to 325 °C heated glass plate. A nickel plate was used as the cathodic electrode, and both electrodes were pressed to the sample surface with springs. It is worth to note that in our experiments more than one hundred of samples can be processed without any degradation of the anodic electrode. We poled 1 mm thick Menzel soda-lime glass slides the composition of which can be presented as SiO_2-72.20%, Na_2O-14.30%, K_2O-1.20%, CaO-6.40%, MgO-4.30%, Al_2O_3-1.20%, Fe_2O_3-0.03%, SO_3-0.30% (in weight %) [16]. The poling was stopped when poling current reached the maximum. After the poling the morphology of the glass surface was characterized using Veeco Dimension-3100 atomic force microscope (AFM) with Bruker RTESP/TESP-SS tips in tapping mode. We characterized structural changes in the poled glass using Micro-Raman Witec Alpha 300R spectrometer equipped with confocal optical microscope.

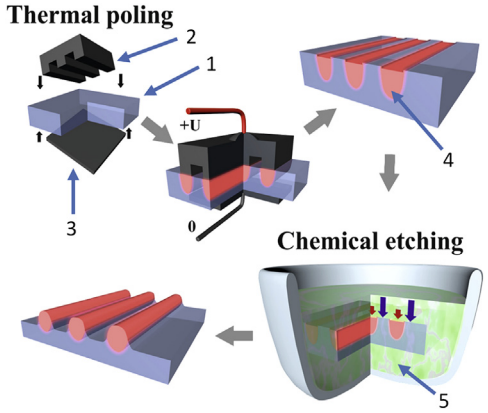

Fig. 1. Schematic of the grating formation process. 1 – glass, 2 – anodic electrode, 3 – cathodic electrode, 4 – stronger poled region, 5 – acidic etchant.

To etch the poled glasses we used acidic NH_4F:$8H_2O$ polishing etching agent [17]. The poled slide was vertically immersed in a transparent cuvette and the structure formed in the poling was illuminated with He-Ne laser beam as shown in Fig. 3. As soon as the poling with a periodic electrode results in the formation of periodic surface relief on the anodic surface of the poled glass, the diffraction of the laser beam by this grating allows evaluating the grating efficiency in the course of the etching. In the experiments, we measured the signal from the first diffraction order using a photodiode, and the dynamics of this signal was recorded with a computer. In addition, differently etched samples were removed from the etching solution and the efficiency of the diffraction in the first order was measured. It should be mentioned that the latter differs with the efficiency measured online in the cuvette because of the difference in the phase shifts provided by the diffraction gratings in the solution and in the air environment corresponding to ~0.17 and ~0.5 index difference, respectively. We also used Zeiss Supra 25 scanning electron microscope (SEM) to observe cleaved cuts of the poled and etched samples.

3. Results and discussion

The origin of the difference in etching rates of poled and unpoled glass regions are a structural modification of the poled glass, which is illustrated by Raman spectra tending to the spectrum of silica glass and indicating the formation of interstitial oxygen molecules [18], see Fig. 4, and reported redistribution of positive charge carriers under poling [19] that is a compositional modification. In Fig. 5, one can see AFM profiles of the manufactured structures. Fig. 5a, c presents the profiles of 20 μm in period diffraction gratings formed in thermal poling step and after the acidic etching respectively, parameters of the processing are in Fig. 5 caption, the profiles of 2 μm in period grating measured after poling and after chemical etching are presented in Fig. 5b, d, respectively. Measured first order diffraction efficiencies corresponding to the gratings presented in Fig. 5c and d are equal to 28% and 9%, respectively. It should be noted that 28% diffraction efficiency is close to maximal diffraction efficiency in Raman-Nath mode, which corresponds to the square of the first order Bessel function maximum, $(J_1)^2 = 0.34$. The results of in-vivo diffraction measurements are presented in Fig. 6a and b for 20 μm and 2 μm grating, respectively. It is worth to note that the vertical axes show diffraction efficiency in the etchant which is less than the efficiency in the air surrounding because of less index contrast between the glass and the surrounding. To calculate the first order diffraction efficiency in the air η_{air} using the data on the diffraction efficiency in the etchant η_{etch} one should use the relation $\eta_{air}=(J_1(a))^2$, where the a is the root of the equation $\eta_{etch} = (J_1(\beta a))^2$, $\beta = \frac{n_{glass}-1}{n_{glass}-n_{etch}}$ and n_{glass}, n_{etch} are refractive indices of the used glass and etchant, respectively.