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Reduto, I

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RIE for structuring E-field processed glasses

I Reduto[1,2,3], D Raskhodchikov[2,3], E Gangrskaia[3], V Kaasik[3], Yu Svirko[1], A Lipovskii[2,3]

[1] Institute of Photonics, University of Eastern Finland, Joensuu 80101, Finland
[2] St. Petersburg Academic University RAS, St. Petersburg 194021, Russia
[3] Peter the Great St. Petersburg Polytechnic University, St. Petersburg 195251, Russia

Abstract. We present studies of reactive ion etching of glasses modified by electric field applied to the glasses at elevated temperature. Voltage dependence of the thickness of the modified glass layers is revealed. Secondary ion mass spectrometry data are used to establish the relation between the ion etching rate of the electric field modified glasses and their local composition resulted from the modification. Using structured anodic electrodes allows formation of nanoscale relief structures on the glass surface because of the volume relaxation of the modified regions. This is thermal electric field imprinting procedure. It is shown that the reactive ion etching allows effective deepening the glass surface relief formed in the course of the imprinting. The reactive ion etching allows keeping a high lateral resolution of the surface relief formed in the imprinting. The formation of gratings with micron-scale periodicity is demonstrated.

Introduction

Glasses are widely used for the formation of devices for photonics and sensing, like phase diffraction gratings and microfluidic channels. Many of these applications require formation of a given relief pattern on the surface of a glass plate. Apart from conventionally used techniques for the patterning, like laser micromachining, moulding and lithography followed by an etching, a novel one-step thermal-electric-field imprinting (TEFI) technique has recently been developed [1]. TEFI is based on the modification of a glass at elevated (but below glass transition) temperature by shaped electric field (E-field) generated using a structured anodic electrode. Occurring structural/compositional changes of the glass result in the formation surface relief reproducing the electrode pattern and define patterned chemical stability, respectively. Importantly, the surface relief of the E-field modified glass, which results from the volume relaxation (shrinkage) of the structurally/compositionally modified layer [3], presents height-scaled stamp of the anodic electrode. In conjunction with acidic [3] or alkalic [4] chemical etching TEFI allows fabricating relief structures as high as several microns, the pattern of the etched structure being direct or reversed profile to the electrode relief, respectively. Applicability of plasma-chemical etching to TEFI-processed glasses for deepening their surface relief has recently been demonstrated [5]. Here we present our studies of the reactive ion etching (RIE) of similarly modified glasses.

Thermal Electric Field Imprinting

In the experiments we used one millimeter thick "Menzel" soda-lime glass microscope slides (chemical composition is presented in the Table 1). Surface-structured glassy carbon plate pressed to the glass surface or deposited Cr-Au films were used as the anodic electrodes. The TEFI was carried out at 300˚C under 300-1000 V voltage. In the TEFI, the processing stopped when the current through the samples dropped down to 10% of initial (maximal) current and the slides were cooled under the voltage applied. Processed slides were characterized with secondary ion mass spectrometry (IMS-7f, Cameca, France),

stylus (Dektak 150, Veeco Instruments, USA) and optical (Wyko NT9300, Veeco Instruments, USA) profilometry, atomic force microscopy (Dimension 3100, Veeco, USA) using RTESP tips and subjected to $12HCF_3$:38Ar gas mixture RIE (Plasmalab 80, Oxford Plasma Technology, UK). Schematic of the slides processing is presented in Figure 1.
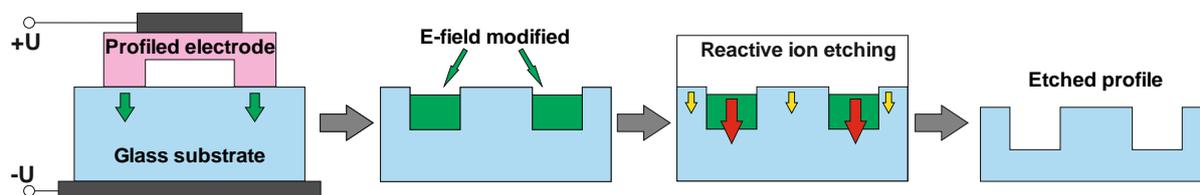

Figure 1. Schematics of thermal electric-field modification and reactive ion etching.

Table 1. Chemical composition of the Menzel glass microscope slides [6].

Oxide	SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	Fe_2O_3	SO_3
wt%	72.20	14.30	1.20	6.40	4.30	1.20	0.03	0.30

Secondary-ion mass spectrometry

Data obtained using secondary-ion mass spectrometry (SIMS) showed essential changes in the glass composition (relatively to deeper region of the virgin glass) up to one micron depth, which resulted from the TEFI modification. Importantly, the SIMS data showed strong depth dependence of the concentrations of all constituents of the glass slides including silicon. Since the current depths were calculated basing on the final depth of the crater formed in the slide by ions in the SIMS and the duration of the measurements, registered depth dependence of silicon concentration data allowed us presuming that the rate of ion etching in the course of the SIMS measurements was depth-dependent. This is because silicon, which is glass network former in silicate glasses, is not capable of drifting under electric field. This allowed us calculating the SIMS etching rate assuming silicon concentration has to be constant. (Fig. 2a). Using this rate we nonlinearly changed the depth scale of the SIMS data and accounted for this in the concentrations data in Figure 2b. Comparing Figures 2a and 2b we established that the absence of movable (Na^+, K^+, Ca^{2+}) ions, which makes this initially multicomponent glass to be closer to fused silica, essentially influences the etching rate. This stimulated us to perform RIE processing of the glass slides subjected to the TEFI with $12HCF_3$:38Ar gas mixture conventionally used for RIE of silica [7].

Reactive Ion Etching

We characterized the surface profile of the TEFI-processed glass slides in the vicinity of the anodic electrode edge before and after the RIE. Measured depth of the steps between TEFI modified and virgin areas of the slides after the RIE and the measured rate of the virgin glass RIE, 6 nm/min, allowed us deducing the thickness of the TEFI modified glass regions, which were 180, 250, 330 and 370 nm for the TEFI processing at 300, 500, 700 and 1000 V, respectively. We supposed the modified glass region completely etched off when the etching rates of both modified and virgin glasses became equal. Note that the actual relief of the slides was deeper because of the etched depths summation with the TEFI-formed relief (80, 130, 150 and 400 nm for the same voltages). Thus, maximal obtained relief steps were 240, 350, 460 and 730 nm, respectively – see Figure 2c, here the decrease in the curves slope corresponds to the etching out of the modified glass region.
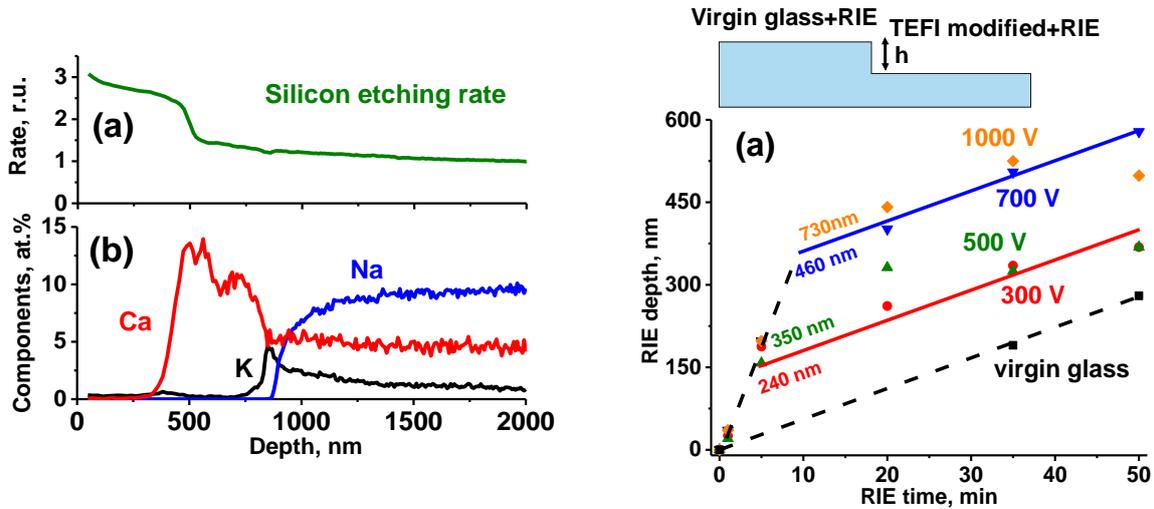
Figure 2. SIMS measured relative etching rate **(a)** and depth dependence of movable ions concentration in the glass **(b)** after 500 V TEFI processing with pressed glassy carbon electrode. Reactive ion etching of the TEFI glasses processed with deposited chromium electrode **(c)**. Inset: schematic of the RIE depth measurements.

Surface structures imprinting

Using the TEFI combined with the RIE we successfully fabricated micron-scale lateral resolution periodic relief structures on the glass surface, which can behave as diffraction gratings (Figure 3). The temporal evolution of the gratings profiles under RIE were characterized with optical profiler (Figure 3a). After TEFI we found surface profiles depth being of 30-40 nm (Figure 3b). Maximal profile depth obtained with the RIE was over 100 nm (Figure 3c). Important to note the existence of "whiskers" at the positions corresponding to the anodic electrode edges after the first 4 minutes of the etching and their complete absence after 10 min RIE. This "whiskers" correspond to stronger electric field treatment in the vicinity of the electrode edges [3,8]. The depth of this "whiskers" is ~110 nm that is also the maximal depth of the etched structure. This means that the etching of stronger modified glass regions is faster, however, finally the glass relief precisely repeats the electrode profile. This is strong distinction in comparison with the wet acidic etching which leaves the "whiskers" untouched [3].
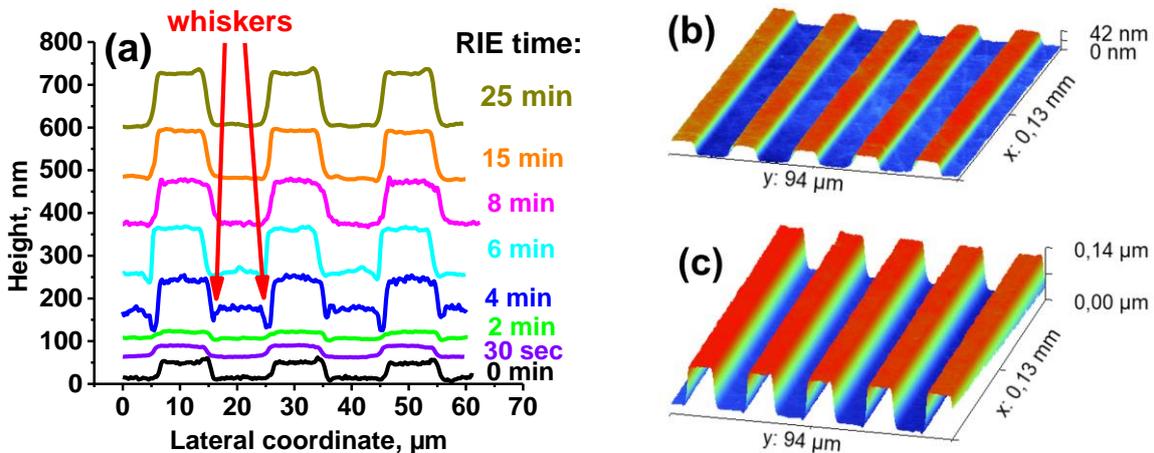

Figure 3. Reactive ion etching of the TEFI glass. Surface profile of RIE TEFI-processed 20 μm in period grating **(a)** and 3D plot of optical profiler data after the TEFI **(b)** and after the RIE **(c)**. The glass was modified at 300°C under 300 V voltage; the TEFI with pressed glassy carbon electrode.

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Figure 4a presents temporal evolution of the RIE-formed gratings. The peculiarities during first 1-2 minutes of the RIE are because of the existence of ~20 nm damaged subsurface layer in the initial glass, which is generally typical for glasses [9]. Degradation of the surface relief at the initial stages of the RIE is also shown in Figure 3a. The thickness of the damaged layer according to our SIMS data is about 20-30 nm, which corresponds to the graph in Fig. 4a. The maximal relief depth was achieved after 10 minutes of the RIE. Importantly, the RIE surface profile was not degrade even after 50 minutes of the treatment. Figure 4b,c illustrates the AFM image and surface profile of fabricated 2 μm in period grating.
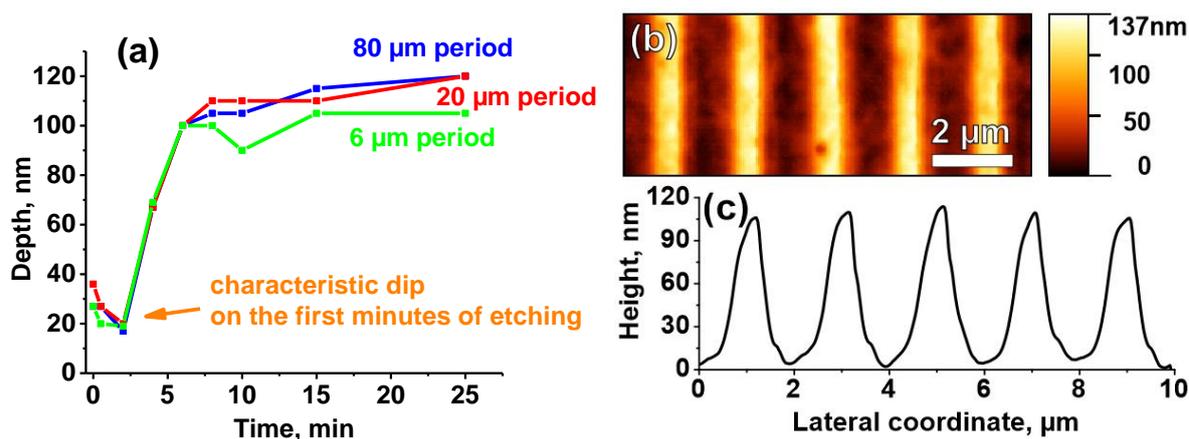

Figure 4. Depth of the gratings during the RIE process **(a)**; AFM image **(b)** and surface profile **(c)** of 2 μm in period grating of glass RIE TEFI-modified at 300˚C under 300 V voltages. TEFI with pressed glassy carbon electrode.

Conclusion

Finally we have characterized the thickness and chemical composition changes in ~1 μm thick region of the TEFI-modified soda-lime glass. Varying the TEFI voltage allows one changing the thickness of the chemically and structurally modified region. Different durability of the virgin and modified glass regions allows using reactive ion etching for the surface profiling of the TEFI-processed glasses. The gratings with the period down to 2 microns were successfully formed. Contrary to wet etching, in the RIE the glass relief precisely repeats the profile of used in the TEFI anodic electrode.

Acknowledgments

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