Towards second-harmonic generation micropatterning of glass surface

Aurelien Delestre,[1] Michel Lahaye,[1] Evelyne Fargin,[1,a)] Matthieu Bellec,[2] Arnaud Royon,[2] Lionel Canioni,[2] Marc Dussauze,[3] Frederic Adamietz,[3] and Vincent Rodriguez[3]
[1]*Institut de Chimie de la Matière Condensée de Bordeaux, UPR 9048 CNRS, Université de Bordeaux, Avenue du Dr. Schweitzer, 33608 Pessac Cedex, France*
[2]*Centre de Physique Moléculaire Optique et Hertzienne, UMR 5798 CNRS, Université de Bordeaux, 351 cours de la Libération, 33405 Talence Cedex, France*
[3]*Institut des Sciences Moléculaires, UMR 5255 CNRS, Université de Bordeaux, 351 cours de la Libération, 33405 Talence Cedex, France*

(Received 6 January 2010; accepted 11 February 2010; published online 3 March 2010)

Thermal poling of sodium borophosphate niobium glasses, previously coated with a thin silver layer micropatterned by femtosecond laser irradiation, is demonstrated. The field-assisted ion-exchange process for fabricating planar surface in this glass substrate is analyzed. Inside the silver ablated lines obtained by femtosecond laser irradiation, we clearly observe a change in the distribution of the frozen electrostatic field that is modulated by the Ag^+/Na^+ ion-exchange process during the thermal poling. © *2010 American Institute of Physics*. [doi:10.1063/1.3350895]

Optical technologies development concerning communication has triggered a real interest about materials with nonlinear properties. Glasses are promising materials in optoelectronics because of their good optical properties and their low production cost. Actually, to gain second-order nonlinear responses in a glass, one has to break its natural centrosymmetry. Thermal poling offers a simple and reproducible way to induce permanent second-order nonlinearities in many oxide glasses, and notably in borophosphate niobium glasses on which we focus. In that case, the space charge created during the poling process generates an efficient macroscopic electrostatic field trapped under the anodic surface of the glass ($E_{int} \sim 10^8$ V/m). Actually, the combination of a high voltage (1–3 kV) and the poling temperature (230–280 °C) causes the migration of mobile ions from the anode, resulting in a depletion zone negatively charged under the anode surface related to the trapped electrostatic field.[1,2] Thus an effective electric field induced second-harmonic generation (EFISHG), $\chi^{(2)}=3\chi^{(3)}E_{int}$, is obtained in a 2–5 μm-thick layer.

More recently, monovalent silver ions, resulting from a thin silver layer initially deposited at the anode surface, have been introduced by field-assisted ion-exchange technique in similar glasses.[3] A more complex space-charge-migration process is involved during the poling treatment. The ions profile under the anode surface confirmed that the introduction of silver was achieved with ions piled-up behind the sodium depletion front. Hence, a space charge at a lower spatial extent could be achieved in a thinner layer characterized by less efficient second-order nonlinearity. The ability of these borophosphate niobium glasses to generate a relative efficient nonlinear optical (NLO) response that can be tuned through field-assisted ion-exchange is the first requirement to spatially pattern the chemical and the optical properties of thin layers for optical or electro-optical applications at the micrometer scale.

Besides, it is known that SHG efficiency can be improved when efficient quasi-phase-matching (QPM) conditions are achieved, leading to applications for frequency mixing devices, in lasers, for example.[4] Various techniques have been used for $\chi^{(2)}$ grating fabrication for QPM, including the use of periodical electrodes, erasure by UV or femtosecond laser irradiation before and after poling.[5–7] Also, femtosecond laser sources have already been used in order to inscribe microstructures on silver thin films by metal ablation.[8,9]

Thus, a silver film deposited onto a glass surface micropatterned with a femtosecond laser to fabricate periodical anodes using thermal poling seems to be an attractive pathway to the fabrication of planar architectures which local $\chi^{(2)}$ responses could be dressed. In this letter, we report on the ability of this technique for the fabrication of $\chi^{(2)}$ micropatterning using borophosphate niobium containing glasses.

A 1-mm-thick sodium and niobium borophosphate oxide glass with composition 0.58 [0.95 $NaPO_3$+0.05 $Na_2B_4O_7$] +0.42 Nb_2O_5 (called hereafter BPN42) was elaborated by a solid phase route and polished on both sides to gain optical quality. A ~200-nm-thick silver layer was deposited by sputtering on the top surface (anode) of the glass. Silver ablated lines were obtained using a femtosecond Yb:KGW (potassium garnet tungsten) laser, operating at 1030 nm at a repetition rate of 9.45 MHz, focused with an objective (36×, numerical aperature NA=0.5) onto the sample surface. The beam waist was approximately 1 μm and the pulse energy at the sample was 210 nJ. A grating with a period of 30 μm was fabricated at the surface by scanning (at a speed of 1 mm/s) the sample relatively to the stationary focused beam.

A Veeco optical profilometer (WYKO NT1200, 50× objective) was used to check the silver ablated lines on the glass surface (Fig. 1). The lines were 3-mm-long, 2-μm-wide, and 200-nm-deep, and silver was totally removed from the surface in these areas. No SHG signal could be detected inside and outside the lines after laser irradiation. The glass sample was placed between two electrodes with the silver layer under the anode to proceed to field-assisted ion-exchange during thermal poling. A high voltage of 1.25 kV at 230 °C under air was applied. The sample was cooled down to room temperature before removing the dc bias. After one hour of poling, the whole patterned silver layer was

a)Author to whom correspondence should be addressed. Electronic mail: fargin@icmcb-bordeaux.cnrs.fr. Tel.: +33 (0)5 40 00 84 33.

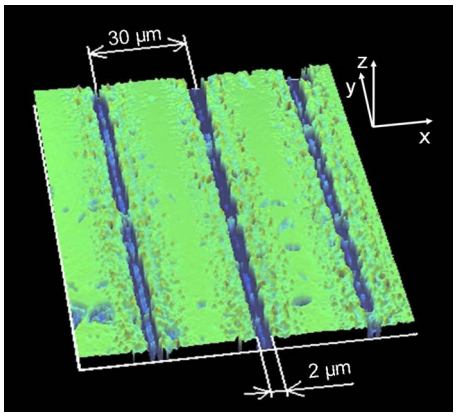

FIG. 1. (Color online) Initial patterned silver film observed on the glass surface.

totally injected inside the glass through the ion-exchange poling process.

SHG from the poled glass was first investigated outside the patterned area. Polarized transmitted *p-p* and *s-p* Maker fringe patterns were recorded with a nanosecond Nd:YAG (yttrium aluminium garnet) laser operating at 1064 nm. The $\chi^{(2)}$ components were obtained from simulations of the Maker fringe data, using an α-quartz z-cut plate ($2d_{11}=\chi^{(2)}_{xxx}=0.6$ pm/V) as a reference for the calibration of the setup.[10] Hence, out of the patterned area, a uniform EFISHG response, provided by a frozen electrostatic field normal to the surface (along z), is generated in a layer with thickness $l=(3\pm0.5)$ μm and $2d_{33}=\chi^{(2)}_{zzz}=3\chi^{(2)}_{xzz}=(2\pm0.2)$ pm/V as expected.[3]

Polarized SHG images (4×4 μm^2) of the patterned area, with a spatial resolution of 0.5 μm, are reported in Fig. 2. The source was a 1064 nm diode pumped laser (EKSPLA PL2200: pulse duration 65 ps, repetition rate 2 kHz) focused at the surface of the patterned area with a 100× NIR objective (NA=0.5). The energy per pulse was less than 100 nJ. More details about the setup are given elsewhere.[11] The four SHG images gave a homogeneous response outside the silver

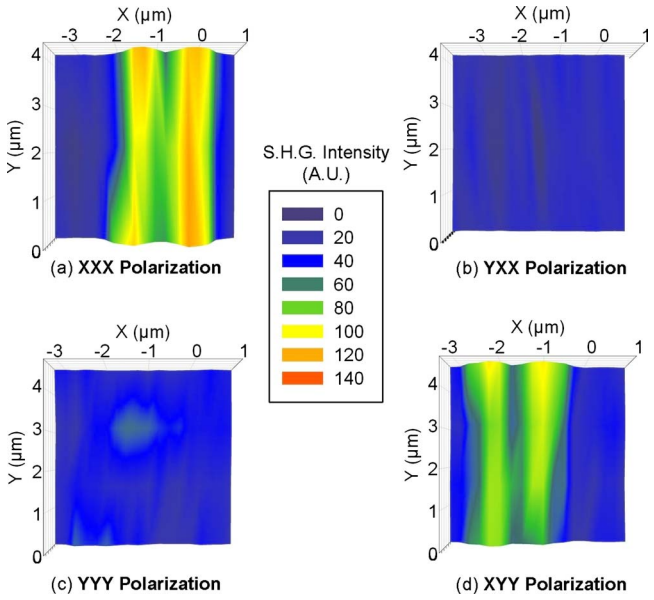

FIG. 2. (Color online) Polarized SHG images of the patterned area after thermal poling.

ablated lines with an intensity approximately 20 in arbitrary unit (see Fig. 2). Indeed, such an effect, which originates from the EFISHG process along the z axis, is expected with beams focused using high numerical aperture objectives. A scan analysis along the z direction, outside the lines with XXX polarization, revealed a SHG profile compatible with a NLO layer of 3 μm under the anode surface as observed previously. Additionally, images with cross polarization [Figs. 2(b) and 2(d)] gave a signal typically less than half the response (not detailed here) of images with parallel polarization [Figs. 2(a) and 2(c)]. Focusing now on the silver ablated lines, we obviously remark that the XXX and XYY polarized images highlight a modulated SHG profile along the X direction which is quite comparable for both polarizations, in shape and intensity, and with two maxima at the edges of the line that is ~2 μm wide. Hence, polarized SHG images obtained across the lines are compatible with C_s symmetry (xz plane), while the symmetry remains classically $C_{\infty v}$ (z-axis) outside the lines.

Note that a blank sample has been prepared, i.e., it has been submitted to femtosecond laser irradiation using the same experimental conditions but with no silver layer previously deposited. Again, no SHG signal could be detected after laser irradiation. After thermal poling, the blank sample was found homogeneously poled with an EFISHG response along z. This is an indication that the femtosecond laser irradiation does not affect significantly the SHG response, in regards to what has been observed in poled silica glass.[7]

Here, because of the high repetition rate of the femtosecond laser and probably through a multiphoton process that occurs in the presence of silver,[12] the thermal energy brought by the pulsed irradiations ablates silver and also partially thermally injects some amount of silver ions inside the glass.[13] These assumptions seem to be confirmed using wavelength dispersive x-ray spectroscopy (WDS), imaged with a scanning electron microscope, on the cross-section of the BPN42 sample at the anode side (xz plane) where concentration profiles of Ag^+ and Na^+ have been recorded (Fig. 3).

The concentration profile of Ag^+, piled up onto the Na^+ depleted front, outside the silver ablated line [Fig. 3(a)] is typical of the field-assisted ion-exchange technique in BPN42 sample.[3] However, we clearly evidence a different profile inside the silver ablated lines [Fig. 3(b)] that suggests that some amount of silver has been thermally injected during the femtosecond laser irradiation, before Ag^+ is piled up again onto the Na^+ depleted front during thermal poling. As a result, a periodical silver ion concentration is observed along the x direction [see Fig. 3(c)]. The silver concentration map in the xz plane nicely indicates a first layer at the interface, free from any ion and 2 μm wide, as indicated by the concentration profiles inside and outside the silver ablated line. In addition, note that the distance between successive areas with low Ag^+ content fits nicely that one between two ablated lines (Fig. 1).

In conclusion, we have demonstrated a technique for SHG micropatterning of glass surface that involves the effect of silver and femtosecond laser ablation of silver to micropattern glass surfaces with subsequent thermal poling. Through high resolution SHG images and WDS analyses, we have observed a change in the distribution of the frozen electrostatic field embedded in the NLO active layer, with components along z and x directions compatible with a local

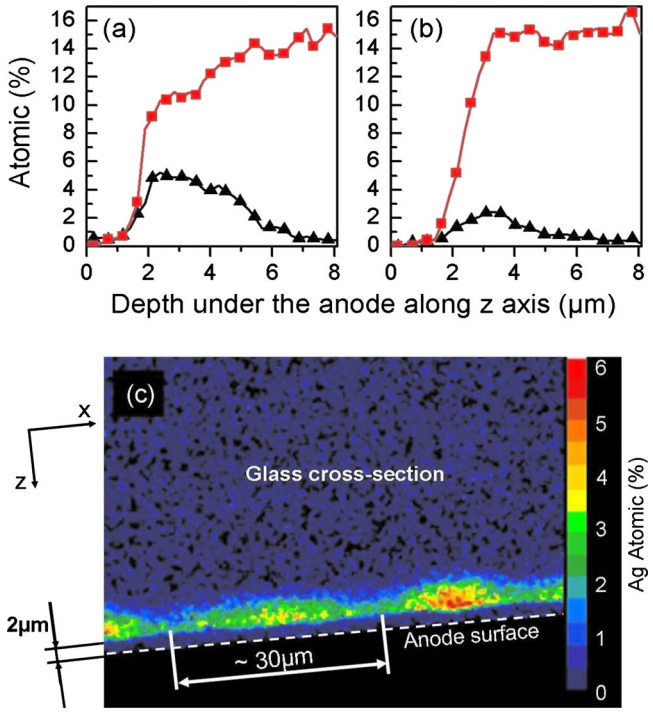

FIG. 3. (Color online) Top: sodium ions (red squares) and silver ions (black triangles) concentration profiles (cross-section) outside (a) and inside (b) a silver ablated line. Bottom: silver ionic concentration (c).

C_s symmetry. The electrostatic field is modulated by the Ag^+/Na^+ ion-exchange process during the thermal poling. Further experiments are scheduled to clarify the field-assisted ion-exchange mechanisms at the level of the local glass structure, key aspects of silver and femtosecond laser irradiation.

M.D., F.A., and V.R. thank David Talaga and Jean-Luc Bruneel for technical assistance for the μ-SHG setup. This research has been partially supported by Région Aquitaine (Advanced Materials in Aquitaine), the Agence Nationale de la Recherche ANR (Grant No. ANR-05-BLAN-0212-01).

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