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Erasure of thermally poled second-order nonlinearity in fused silica by electron implantation

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We show that implantation of electrons erases the second-order nonlinearity in thermally poled silica. This technique provides a versatile new means of realizing quasi-phase-matching structures for parametric frequency conversion in glass optical fibers and planar waveguides.

In this Letter we report the first observation, to our knowledge, of electron-beam erasure of the second-order nonlinearity induced in silica by thermal poling and record new results on the location of the nonlinearity. The report by Myers *et al.*[1] that a second-order nonlinearity of the order of 1 pm/V can be induced in fused silica by thermal poling has excited considerable interest, because it offers the prospect of linear electro-optic modulators and frequency converters monolithically integrated into optical fibers or planar glass waveguides. Since then, two other techniques resulting in similar levels of nonlinearity have been reported, i.e., corona poling[2] and electron-beam irradiation.[3] Despite the plethora of techniques, the mechanisms behind the formation of the second-order nonlinearity are not yet fully understood. For example, during thermal poling in fused silica, the sample has to be heated to ~250–300 °C with an applied field of 3–5 kV/cm, and the second-order nonlinearity is observed only near the anodic surface. Probing of the depth profile of the nonlinearity (with a chemical etching process) showed that it was exponential with a $1/e$ decay length of a few micrometers. Myers *et al.* suggested that fields E_{sc} of the order of 10^7 V/cm are generated in a surface layer by charge separation at the higher temperature and then frozen in by trapping as the temperature is lowered. By means of the third-order susceptibility $\chi^{(3)}$, this field then creates a second-order susceptibility $\chi^{(2)}$ proportional to $\chi^{(3)}E_{sc}$. Although this explanation is feasible, it does not explain why no such field is induced near the cathodic surface of the substrate. Moreover, the distribution of second-order nonlinearity measured in the sample by use of an etching process (inevitably destructive) may be difficult to relate to its actual form after poling, because the removal of one layer of buried charge can strongly affect the measured nonlinearity in the whole layer. We have therefore used a nondestructive technique to probe the distribution of the nonlinearity in the poled layer. In a previous Letter we reported the use of electron-beam irradiation to create a second-order nonlinearity in lead silicate glass,[3] and it is, of course, interesting to investigate whether this technique also works for fused silica and whether lead silicate glass [which has high $\chi^{(3)}$] responds to thermal poling.

Our experiments were carried out in fused silica and lead silicate glass. We heated the samples to ~300 °C in an oven while applying a voltage of 4 kV across 1.3-mm-thick silica disks with an approximate 20-mm diameter (Fig. 1). After ~20 min of poling, the samples were cooled to room temperature. The anode dimension was 2 mm × 20 mm, the cathode extended over the whole disk, and both were pressed against the sample. After cooling to room temperature, the electrodes were removed from the sample. Q-switched (1-kHz repetition rate, 200-ns envelope duration) and mode-locked (76-MHz repetition rate, 3-ns pulse duration) Nd:YAG laser pulses at 1064 nm were used to probe the second-order nonlinearity, with average powers of ~1.2 W. The pump laser beam (polarized in the plane of incidence) was focused by a lens (10-cm focal length) on the anodic surface. The angle of incidence (~60°) was chosen to lie close to the Brewster angle. No second-harmonic (SH) signal was observed in the poled lead silicate samples, whereas a strong signal (compared with the value observed in electron-beam-irradiated lead silicate samples[3]) was observed in samples of fused natural quartz. We were surprised to discover, while scanning the focused laser beam along the surface of the sample, that a SH signal was observed outside the electrode region (Fig. 2). The poled second-order nonlinearity extended beyond the anode, covering an area ~1.8 times wider than the anode width.

The distribution of the nonlinearity perpendicular to the plane of the anode was characterized by the same nondestructive technique that was used to measure the depth profile of he nonlinearity induced by electron-beam irradiation in lead silicate glasses.[3] A 1-mm-wide piece was cut from the 1.3-mm-thick poled

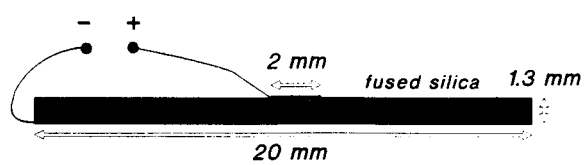

Fig. 1. Schematic of the side view of the poling geometry. Silica disks of ~20-mm diameter and 1.3-mm thickness were sandwiched between the anode (2 mm × 20 mm) and the cathode.

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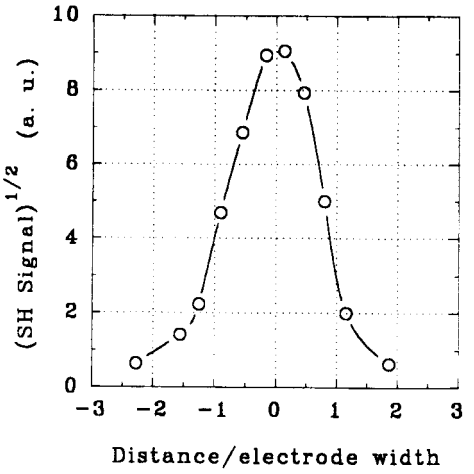

Fig. 2. Square root of the SH signal versus the distance from the center of the positive electrode.

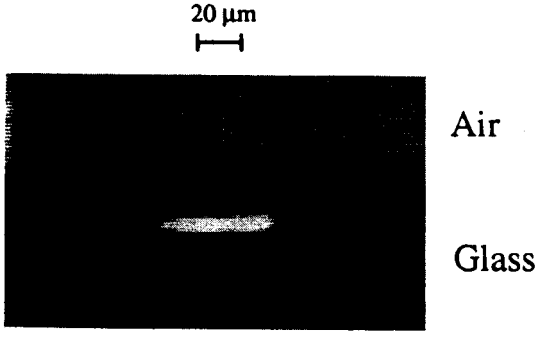

Fig. 3. SH near-field pattern in a thermally poled fused-silica sample photographed from the screen of the TV monitor. The nonlinearity was confined to a 7-μm-wide region that was located ~12 μm below the air–glass interface.

substrate shown in Fig. 1. The two faces parallel to the direction of the applied electric field were polished, and an *s*-polarized pump beam was focused on one of these faces near the edge where the anode had been placed during the poling process. The pump beam was perpendicular to the polished end, and the spot size of the focused beam was ~50 μm. The near-field pattern of the SH signal was imaged by a microscope objective and a video camera. As illustrated in Fig. 3, the SH spot was localized at a depth of 12 μm below the anodic surface, and the width of the spot was ~7 μm.

The above results have important implications for device fabrication. In particular, realization of fine-pitch $\chi^{(2)}$ gratings (with periods of ~40 μm), which are needed for quasi-phase-matched (QPM) SH generation, may be difficult because of the extensive spreading of the nonlinearity beyond the boundaries of the positive electrode. Although this effect could be eliminated by use of identical upper and lower electrodes, it will have a deleterious effect on the formation of QPM structures that use a periodic upper electrode. One possibility for localizing the $\chi^{(2)}$ would be to decrease the distance between the electrodes to a value smaller than the QPM grating period. This would, however, significantly complicate the practical realization of the method, and, anyway, surface conductivity may cause spreading out of the $\chi^{(2)}$ region even for small gap distances.

We have investigated another technique that can circumvent the problem of spreading fields in a fairly simple manner. The technique involves the use of focused electron beams to erase the $\chi^{(2)}$ in the thermally poled regions. A scanning electron microscope was used for irradiation of the samples. The beam current used was 3 nA, and the electron energy ranged between 5 and 40 keV. The electron-beam spot size was less than 0.1 μm. The TV scanning mode of the electron microscope (horizontal scanning rate 0.064 ms/line and vertical scanning rate of 0.017 s/frame) was used. Areas of approximately 1 mm × 1 mm on the surface of the samples were irradiated in the electron microscope for ~1 min.

First, we tried to induce a $\chi^{(2)}$ by electron-beam irradiation in fresh silica glass samples. No signal was observed in irradiated samples from synthetic silica. Relatively weak signals were observed in irradiated samples of fused natural silica. This signal was, however, approximately 2 orders of magnitude smaller than the signal from irradiated lead silicate samples.[3] On the other hand, the $\chi^{(2)}$ was erased by the electron beam in thermally poled fused-silica samples. An exponential decrease in the second-order nonlinearity was observed with increasing electron-beam energy (Fig. 4).

A possible explanation of this erasure process runs as follows. Electrons of energy E (keV), implanted at a depth R_e (μm) = $0.018E^{1.75}$ (where R_e is the average electron penetration depth[4]), cause neutralization of the layer of positive charge located just near the surface (this positively charged surface layer may arise owing to the ionization of negatively charged defects in the strong electrostatic field that forms near the anodic surface). This may, in some respects, be similar to the etching process reported by Myers *et al.* that removes a charged layer from the surface. Conductivity induced by the implanted electrons might also lead to neutralization of the frozen-in field created by thermal poling. No matter what the explanation of the erasure process, the

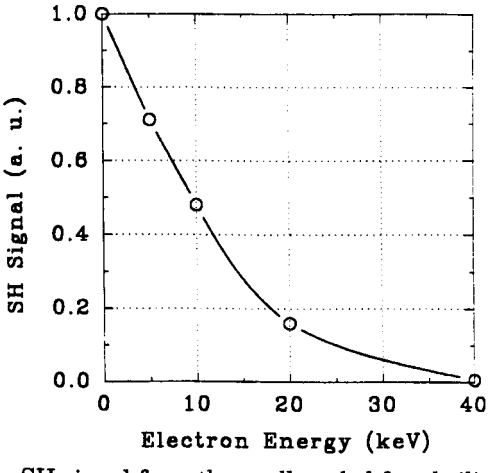

Fig. 4. SH signal from thermally poled fused silica after electron-beam irradiation as a function of electron energy. The electron current and exposure time were fixed at 3 nA and 1 min, respectively.

erasure of the nonlinearity is limited to the total interaction volume or the region to which the electrons spread out inside the substrate. The size of this interaction volume is determined by the radial spreading of electrons owing to various scattering effects. This radial spread is of the same order as the penetration depth of the electrons.[5,6] The resolution, however, is limited by the variations in the radial spread about the mean value. This standard deviation can be smaller than 1 μm, which is sufficient to write QPM structures of 40-μm pitch. It should be mentioned here that the temperature rise in a region irradiated by a scanning electron beam at currents of a few nanoamperes is only 10 °C.[7] Such minor increases in temperature over a time scale of 1 min cannot erase the induced second-order nonlinearity.[1]

In conclusion, we have used a nondestructive method to measure the thickness of the nonlinear layer created by thermal poling and to determine its location. Substantial spreading out of second-order nonlinearity beyond the boundaries of the positive electrode is observed. This may present an obstacle to the creation of QPM $\chi^{(2)}$ gratings by the thermal poling technique. The problem can, however, be circumvented by use of a focused electron beam to erase the nonlinearity selectively in the thermally poled silica glass. The great flexibility offered by high-resolution electron-beam direct-write machines suggests that this technique may have important applications in glass-based optoelectronic devices.

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