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Ferroelectric domain engineering by focused infrared femtosecond pulses

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We demonstrate *infrared* femtosecond laser-induced inversion of ferroelectric domains. This process can be realised solely by using tightly focused laser pulses without application of any electric field prior to, in conjunction with, or subsequent to the laser irradiation. As most ferroelectric crystals like $LiNbO_3$, $LiTaO_3$, and $KTiOPO_4$ are transparent in the infrared, this optical poling method allows one to form ferroelectric domain patterns much deeper inside a ferroelectric crystal than by using ultraviolet light and hence can be used to fabricate practical devices. We also propose *in situ* diagnostics of the ferroelectric domain inversion process by monitoring the Čerenkov second harmonic signal, which is sensitive to the appearance of ferroelectric domain walls. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4932199]

Domain-engineered ferroelectric crystals with periodic variations in the second-order nonlinearity $\chi^{(2)}$ create a valuable class of materials to realize quasi-phase matching (QPM) for applications involving laser frequency conversion,[1–3] generation of entangled photons,[4] and optical solitary wave devices.[5,6] While electric poling[7] by means of periodic electrodes is at present conventionally applied to ferroelectric domain engineering, there has been growing interest to produce domain structures using light patterns,[8] which can be manipulated more accurately with a resolution up to the diffraction limit. Therefore, it enables one to fabricate fine ferroelectric domains with better defined details than those produced by electric-field poling alone. Light-mediated poling can also overcome the sensitivity of electric poling to the crystallographic orientation of the medium including the situation when the latter technique cannot be used at all.[9]

So far, the light field has been employed in ferroelectric domain engineering in two ways. In the first approach, referred to as light-assisted poling, the crystal is irradiated in conjunction with or prior to application of an external, homogeneous electric field.[10,11] It is generally believed that selective illumination of the ferroelectric crystal by weakly absorbed light leads to a spatially modulated coercive field E_c. This, in turn, results in spatially selective domain inversion,[12,13] thereby eliminating the need for structured electrodes, which are used in traditional electric poling. The second approach represents the optical poling, where the illumination of a ferroelectric crystal with intense UV radiation (244–308 nm, c.w., and pulsed) leads to local domain inversion via pyroelectric field, without applying any external electric field.[14–19] The optical poling allows one to overcome a number of drawbacks of electric poling, in particular, the fundamental restriction that the electric field must be applied along the polar axis (i.e., Z-axis) of the crystal. Consequently, all optical poling allows one to create domain patterns in X- or Y-cut wafers, which is otherwise difficult by using electric poling.[20,21] However, as UV light is strongly absorbed by most ferroelectrics, the resulting ferroelectric domain inversion is restricted to a shallow surface layer (few hundred nanometers).[22] This severely limits the application of such optically created domain structures.

In this letter, we present an experimental study on optical ferroelectric domain engineering using near-infrared femtosecond laser pulses. We show that the illumination of a $LiNbO_3$ crystal by focused ultrashort infrared pulses results in ferroelectric domain inversion, without applying any external electric field. Since the $LiNbO_3$ crystal is transparent in the infrared,[23] the inverted ferroelectric domains are not confined to the surface, but extend deep into the crystal ($\approx$60 μm below the $-$Z-surface).

The experimental setup of our optical poling is shown in Fig. 1(a). We used a 500-μm-thick Z-cut congruent $LiNbO_3$ wafer. The sample was mounted on a translational stage that can be positioned in three orthogonal directions with a resolution of $\sim$100 nm. The infrared light was generated by a femtosecond oscillator (MIRA, Coherent) operating at 800 nm, with a pulse duration of 180 fs and a repetition rate of 76 MHz. The pulse energy can be continuously varied from 0 to 5 nJ by using a half wave plate followed by a polarizer.

A linearly polarized beam was focused inside a $LiNbO_3$ wafer with a microscope objective of numerical aperture NA = 0.65. The resulting focus spot is about 1.5 μm in diameter. The beam was incident normally to the surface of the crystal. The beam was initially focused on the front ($-$Z) surface of the crystal. Then, the sample was translated along the Z-direction so that the position of the focal region moved

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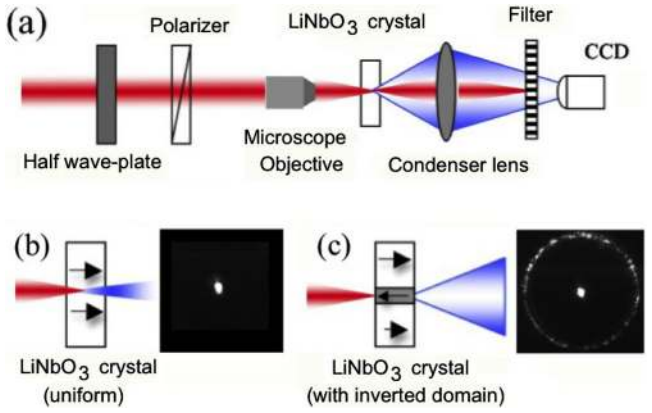

FIG. 1. (a) Experimental setup for femtosecond laser optical poling and *in situ* monitoring of ferroelectric domain inversion via Čerenkov second harmonic generation. (b) Only a collinear (forward) second harmonic signal is generated in a homogeneous sample; (c) in addition to the collinear second harmonic signal, a conical Čerenkov signal is generated when ferroelectric domain walls are produced.

from the −Z toward the +Z-surface with an average speed of $v = 10\,\mu m/s$.

For an *in situ* monitoring of the ferroelectric domain inversion, we used Čerenkov second harmonic generation (ČSHG). In this process, the fundamental infrared beam generates two second harmonic signals. The first one, a non phase-matched wave propagates collinearly with the fundamental beam. In addition, there is a non-collinear second harmonic signal emitted conically at the angle determined by the longitudinal phase matching condition. This so-called Čerenkov signal is generated only when the fundamental beam illuminates a region, where $\chi^{(2)}$ is spatially modulated, for instance, a wall separating oppositely oriented ferroelectric domains.[24–28] In other words, ČSHG, which is normally not observable in a homogeneous ferroelectric crystal, will appear if a focused fundamental beam locally induces the domain inversion. To monitor the appearance of ferroelectric domain we therefore used a lens and a CCD camera to collect and record the emitted Čerenkov second harmonic signal [see Fig. 1(a)]. We found that illumination of the crystal with a femtosecond beam led to the appearance of ČSHG indicating the formation of spatially localized ferroelectric domains. The graphs in Figs. 1(b) and 1(c) display typical images of second harmonic signals recorded before and after the ferroelectric domain inversion, respectively.

The reported here femtosecond domain inversion bears close similarities with the UV light poling technique.[10,18] Therefore, it seems that in both cases we deal with the same underlying physical mechanism. We found, for instance, that domain inversion takes place only when the focus of the beam moves along the polar Z-axis from the −Z toward the +Z-surface. In fact, we could not observe any domain formation if the beam was tightly focused on the +Z-surface of the sample while efficient domain formation was taking place on the −Z-surface. These observations indicate the presence of thermoelectric or/and pyroelectric field in the focal volume of the femtosecond beam as a possible cause of domain inversion. In case of UV poling this field was induced by strong absorption of the UV light just below the surface of the crystal. The asymmetry of the thermal profile induces electric field of either thermoelectric or pyroelectric nature, which can locally invert the domain if it is oriented opposite to the direction of spontaneous polarization and its strength exceeds the coercive field. Since the thermal profiles at +Z and −Z surfaces are exactly opposite, only the profile near the latter surface results in thermoelectric field oriented against the direction of spontaneous polarization and hence is capable of domain inversion. As lithium niobate is transparent in the infrared, the multi-photon absorption of the high intensity light would heat the crystal in the focal area. While our fundamental wavelength 800 nm is too long for band to band two photon absorption (the band gap of lithium niobate is ≈4 eV) the process could involve two or higher order photon absorption as well as defects or impurity states within the gap.[29] The tight focusing within the crystal ensures high temperature gradient and, consequently, high strength of the poling field. In the region where this field exceeds the coercive field, the domain inversion takes place. Moving the focal spot toward the +Z-surface promotes the ferroelectric domain growth along the same direction.

It is worth mentioning that a different mechanism of domain reversal with ultrashort pulses has been proposed by Fahy and Merlin.[30] According to their theory the strong electric field of ultrashort pulses may accelerate ions in ferroelectric crystal increasing their kinetic energy such that they would be able to switch between their two stable positions and subsequently flip the direction of spontaneous polarization. Lao *et al.* paper[31] claims experimental confirmation of this process. However, no systematic studies of inverted domain structure had been presented in that work. We want to stress that this mechanism is entirely different from the one reported in our paper. First, in order to accelerate ions, the incoming beam has to be polarized along the polar axis of the crystal (Z). In our experiments, the fundamental beam actually propagates along the Z axis and is polarized along one of the other principal directions. Second, according to Fahy and Merlin, domain switching process should be very fast, on a picosecond time scale. In our experiments, the process of domain inversion was rather slow, so the crystal was illuminated with millions of pulses and this behavior clearly points towards time integrated process such as heating.

Having established experimental conditions for domain formation, we produced two-dimensional domain patterns with different periods. In particular, Fig. 2 depicts square lattices with periods equal to 2, 1.5, and 1 μm. In all these cases, we used a 0.65 numerical aperture and a 4 nJ pulse energy. The images shown in Fig. 2 depict the −Z-surface of the samples after 5 min of etching in hydrofluoric (HF) acid. It is clearly seen that the inverted domains were uniform over the whole area. In our experiments, almost no domain merging was observed at a 1.5 μm separation between the centers of neighbouring inverted domains [Fig. 2(b)]. The average diameter of the inverted domains was less than 1.5 μm, which is comparable to the focal spot size of the femtosecond beam. The neighbouring ferroelectric domains merge when the distance between them is smaller than 1.5 μm, thus allowing the production of domains of various sizes and shapes [Fig. 2(c)]. Fig. 3 illustrates application of our optical poling technique to fabricate complex domain patterns. In particular, we show the optical microscopy

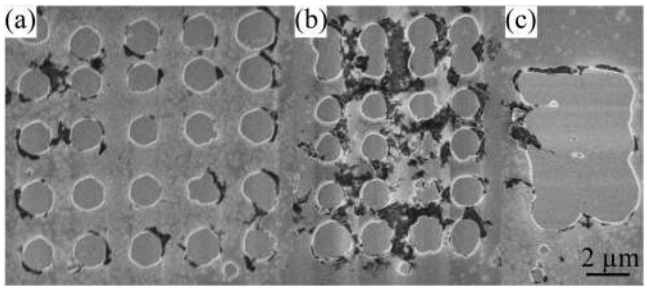

FIG. 2. Scanning electron microscopy images of square two-dimensional ferroelectric domain patterns (after HF etching) formed by infrared femtosecond laser optical poling. The period of the patterns is equal to (a) 2 μm, (b) 1.5 μm, and (c) 1 μm.

images of square and hexagonal ferroelectric lattices, as well as decagonal quasi-periodic and short-range ordered domain structures.

In order to determine the depth of the inverted ferroelectric domain pattern along the Z-direction, we used Čerenkov second harmonic microscopy.[24,25,28] The technique employs a weak, tightly focused fundamental beam that is scanned along the X, Y, and Z-directions inside ferroelectric crystal leading to the emission of Čerenkov second harmonic signal whenever the beam illuminates a ferroelectric domain wall. In this way, two- and three-dimensional maps of ferroelectric domain walls inside the crystal can be obtained. The power of this nondestructive technique is demonstrated in Fig. 4, which compares images of the same ferroelectric domain pattern inside a lithium niobate crystal obtained using traditional optical microscopy after HF etching [Fig. 4(a)] and the Čerenkov nonlinear microscopy [Fig. 4(b)].

The quality of domain reversal process is illustrated in Fig. 5, which depicts three-dimensional images of the section of the square domain pattern in lithium niobate from Fig. 3(a). Figure 5(a) shows the first 15 μm of the structure inside the crystal. It can be seen that our femtosecond optical poling indeed allows one to fabricate a high quality domain structure extending over tens of micrometers inside the crystal. In

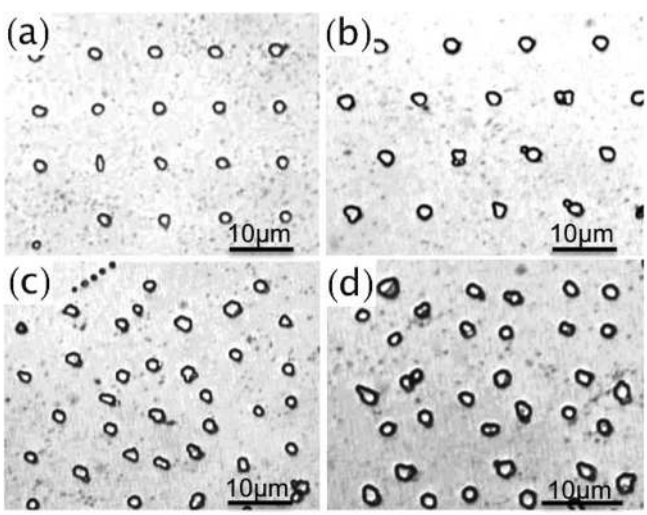

FIG. 3. Optical microscopic images of two-dimensional ferroelectric domain patterns (after HF etching) formed by femtosecond optical poling. (a) Square lattice; (b) hexagonal lattice; (c) decagonal quasi-periodic; and (d) short-range ordered domain structures.

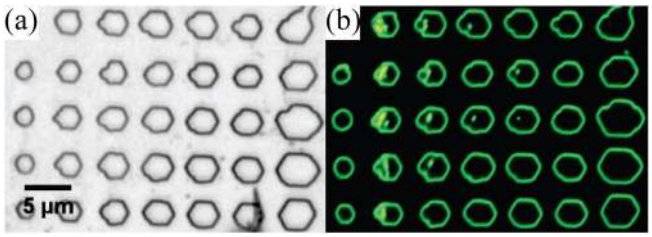

FIG. 4. Images of a square pattern of inverted domains in a lithium niobate crystal obtained (a) using optical microscopy of HF-etched samples and (b) Čerenkov second harmonic microscopy.

fact, we used a series of polishing and HF etching cycles to confirm independently the length of inverted domains inside the samples. It turns out that we were able to fabricate domain structures extending up to 60 μm into the crystal. However, at this depth domains were of rather poor quality. This is illustrated in Fig. 5(b), which depicts the three-dimensional image of the same fragment of the square lattice but extended deep inside of the lithium niobate crystal. The gradual deterioration of the domains is clearly visible. This is a consequence of few factors. First, the process of domain formation deep below the surface is affected by the properties of light focusing inside the crystal. It has been well known that high refractive index mismatch between lithium niobate and surrounding medium introduces spherical aberration, which under focusing conditions, leads to axial deformation of the focal region.[32] Also, when light is tightly focused into a uniaxial crystal along its optical axis, focus splitting occurs.[33] In our experiments, no special measures were undertaken to counteract this effect. In principle, one may use spatial modulation of the incident beam to precompensate for the aberrations.[34] Second, domain reversal could be affected by the temperature-induced stress in the crystal as well as the photorefractive effect. In fact, the refractive index change was observed in the experiment but it disappeared following the annealing of the samples in 200 °C. The role of these and other factors, such as the focal spot size, heat diffusion, and the ambient temperature, on the quality and efficiency of the domain reversal process will be the subject of further investigations.

In conclusion, we demonstrated an optical approach to pole ferroelectric lithium niobate crystals using tightly focused infrared femtosecond pulses. This technique does not involve any external electric field at any stage of the poling

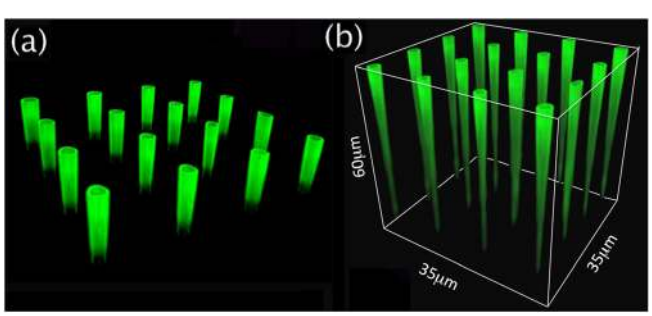

FIG. 5. Three-dimensional visualisation of a section of square pattern of inverted domains by Čerenkov second harmonic microscopy. (a) The first 15 μm-deep layer of the pattern (seen from the −Z surface) illustrating good quality of the inverted domains. (b) Degradation of the domains structure at greater depths inside the crystal.

process. Owing to the high transparency of a lithium niobate crystal in the infrared, we were able to produce inverted domains extending from the surface up to 60 μm inside the crystal. This is a significant result surpassing the capabilities of the optical UV poling technique, which usually enables domain inversion in a shallow layer (few hundreds nanometers below the surface). The separation between the centers of neighbouring inverted domains was as small as 1.5 μm, thus allowing the production of fine two-dimensional structures. In fact, we expect to achieve even higher resolution of domain patterning by using spatial beam shaping and tighter focusing with oil immersed objectives. Finally, we also showed that the process of ferroelectric domain inversion can be monitored via Čerenkov second harmonic generation, which is sensitive to the appearance of ferroelectric domain walls.

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