Reversible microstructuring of lithium niobate by direct laser write technique

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ABSTRACT

Versatility of femtosecond direct laser writing (DLW) technique for non-destructive and reversible micro-structuring of lithium niobate crystals is demonstrated. Persistent photorefractive modification induced by the focused laser beam without structural damage to the host crystal has refractive index modulation on the order of $10^{-5} - 10^{-2}$, and can be optically erased or modified. Application of this mechanism for realization of diffractive optical elements is demonstrated.

Keywords: Laser microfabrication, direct laser write, photorefractive effect, lithium niobate, diffractive optical elements

1. INTRODUCTION

Lithium niobate (LiNbO$_3$) is an attractive material for photonics applications due to rich variety of physical properties, such as ferroelectricity, piezoelectricity, photoelasticity, uniaxial birefringency, and strong optical nonlinearity.\textsuperscript{1–4} Bulk crystals as well as periodically-polled and microstructured lithium niobate find applications in optical modulators, Q-switches, optical harmonics generators, and diffractive optical elements (DOE).\textsuperscript{5} Realization of these functionalities often require application of microstructuring techniques. Typically this is done by modification of sub-surface regions of bulk crystals using proton exchange, titanium in-diffusion, or radiation damage through planar masks.\textsuperscript{4,6} As a result, permanent modification of crystal's refractive index by an amount of $\Delta n \approx 10^{-4}$ is achieved, allowing realization of permanent wave-guides, DOE, etc. in a wide spectral range corresponding to the optical transparency window of undoped lithium niobate crystals. An interesting alternative to permanent structuring techniques can be inferred from another popular application area of lithium niobate – optical information recording and processing by holographic technique. In this approach, doped LiNbO$_3$: (Fe,Mn,Zn) crystals are exposed to periodic 2D or 3D light interference patterns created by spatially overlapping laser beams. The role of doping is to introduce deep donors centers which photosensitize the crystal at visible wavelengths and are responsible for creation of space-charge field between stationary ionized donors and charge of mobile electrons, diffused away from the donors and subsequently trapped.\textsuperscript{1,2} Spatial distribution of the space-charge field closely follows the intensity distribution of interference pattern, and results in local modulation of the refractive index via electro-optic effect. Photorefractive modification offers the possibility to form meta-stable index modulation structures in the bulk of the crystal without permanent optical damage. The recording is reversible, since it can be erased by spatially uniform exposure, and a new structure can be recorded in the same volume of the crystal, or another structure can be directly recorded on top of the previous one, as is often used in angular multiplexing approach. This approach has been widely used in optical memories and for formation of narrowband spectral filters in lithium niobate.\textsuperscript{3,7,8} However, holographic recording requires lengthy exposure and allows recording of periodic patterns only. Here we demonstrate that the same physical mechanism...
Figure 1. Photoexcitation in the bulk of lithium niobate by focused laser beam (a), build up of the space-charge near the focus (b), modification of the refractive index (c).

can be fruitfully exploited for Direct Laser Write (DLW), which uses translation of a tightly focused femtosecond laser beam in the bulk of the sample and allows formation of almost any periodic or non-periodic structure quickly and efficiently. The advantages of nearly-arbitrary 2D and 3D patterning by DLW non-destructive photorefractive photomodification can be combined to obtain optically modifiable diffractive optical elements and optical networks.

2. PHOTOREFRACTIVE PHOTOMODIFICATION OF LITHIUM NIOBATE BY A FOCUSED LASER BEAM

Photorefractive modification of iron-doped lithium niobate by tightly focused femtosecond laser beam pulses is illustrated schematically in Fig. 1(a,b). Processes leading to photorefractive photomodification of lithium niobate by femtosecond laser pulses\textsuperscript{9,10} and their application for discrete optical memories\textsuperscript{11} have been addressed in the literature. However, previous applications of DLW technique for micro fabrication of lithium niobate were mostly focused on irreversible fabrication using optical damage by high power laser pulses.\textsuperscript{12–14}

A laser beam with central wavelength in the optical transparency window of the crystal focused into the bulk of the sample can induces nonlinear absorption in the focal region. For a typical Ti:Sapphire laser wavelength of \(\approx 800\) nm, the absorption is predominantly associated with photexcitation of electrons from deep iron donor levels located about 2 eV below the conductance band. The mobile electrons diffuse away from the static ionized donors till diffusion-drift equilibrium is established. Subsequently, electrons recombine or are trapped on other defects and dopants, and a strong space-charge field builds up between the positively and negatively charged regions. Correspondingly, local modulation of the refractive index is induced via electro-optic effect, which is most pronounced along the crystallographic \(c\)–axis due to the dominant value of electro-optic coefficient along this direction.\textsuperscript{15} Qualitative spatial index modulation profile induced by the focused laser beam is shown
schematically in Fig. 1(c), and comprises negative index change region near the center of the focus and positive change region in the periphery. The space charge field and refractive index modulation may remain stable from days to months after the irradiation, till background exposure and dark current erase the space charge inhomogeneities and refractive index modulation. The refractive index modification is reversible, and the recordings can be optically erased using spatially-uniform exposure, and re-written many times.

This description of photorefractivity in lithium niobate is rather simplified, and more accurate models are often employed for interpretation of various holographic recording applications. Nevertheless, it provides basic understanding of the main underlying physical mechanisms. Holographic recording applications typically employ linear absorption, and prolonged exposure times (tens of minutes or hours) are required to complete recording of large index modulation structures ($\Delta n \sim 10^{-4}$) in the bulk of the crystal. A method to increase life time of the holograms to hundreds of years using simple thermal fixing process was suggested and is in principle applicable for structures written by DLW technique. Photorefractive photomodification by single laser pulses and beams is much faster and occurs on a millisecond time scale with index modulation amplitude easily reaching $\Delta n \sim 10^{-3}$. Hence, fast drawing of various optical structures in reversible regime in lithium niobate crystals is possible.

3. EXPERIMENTAL DETAILS AND SAMPLES

3.1 DLW optical setup

Optical setup used for the fabrication is shown schematically in Fig. 2(a). The laser source is a femtosecond MaiTai oscillator (Spectra-Physics) with a pulse duration of $< 100$ fs, a central wavelength of 800 nm, and a repetition of 80MHz. The laser beam is attenuated by a variable attenuator, and coupled into a custom-made DLW optical setup which houses a dielectric mirror highly reflective at the laser wavelength but transparent in the visible range (for coupling the laser beam into the focusing optics), a microscope lens (for beam focusing and sample imaging), and a stacked pair of high-accuracy translation stages (for sample translation), as well as an illuminator and a video camera (for in situ imaging of the writing process. Olympus microscope lenses with various magnifications and numerical apertures were used as focusing/imaging optics. The sample translation was achieved using Physik Instrumente stages M-686.D64 (for rough XY positioning within the $(25 \times 25)\text{mm}^2$ area) and P-563.3CD (for high resolution drawing within the $(300 \times 300 \times 250 \mu\text{m})^3$ region), controlled by a Poli3D software package.
3.2 Lithium niobate samples

Both doped and undoped samples were used in experiments. The samples were polished slabs with a size of \((10 \times 10 \times 1)\) mm\(^3\). The doped lithium niobate samples were Y-cut (the crystalline \(c\)-axis parallel to the polished faces of the sample) single crystals of near-stoichiometric (Li/Nb = 49.85/50.15) Fe-doped (400 ppm) LiNbO\(_3\). Refractive index of lithium niobate is \(n_o = 2.3\) and \(n_e = 2.21\). The undoped samples were polished slabs of pure congruent LiNbO\(_3\). Linear absorption of doped and undoped samples is compared in Fig. 2(b). The undoped samples have negligible absorption at wavelengths longer than 370 nm. The doped samples have an absorption band at visible wavelengths due to deep iron donors. Since both samples are transparent at the laser wavelength \(\lambda_{\text{laser}} = 800\) nm, laser structuring should be attributed to two-photon or other non-linear absorption processes occurring at the focus of the laser beam.

3.3 Characterization of the recorded structures

Single refractive index modulation features (dots, lines, etc.) as well as extended structures (diffraction gratings) recorded by DLW were characterized using wide-field and phase contrast optical microscopies to assess their shape and size as well as to monitor local modification of refractive index. Performance of extended DOE structures and magnitude of refractive index modulation was assessed by monitoring diffraction of laser beams passed through the structures and by measurements of their diffraction efficiency.

4. RESULTS AND DISCUSSION

4.1 Magnitude of refractive index modulation

Diffraction efficiency of a DOE depends on the magnitude of refractive index modulation. One-dimensional diffraction grating formed by parallel straight lines is a simple DOE simple to record and characterize. From its measured diffraction efficiency and some structural parameters refractive index modulation can be easily determined.

Figure 3(a) shows optical image of a grating with a lattice period \(\Lambda = 13\) \(\mu\)m recorded using \(NA = 0.35\) focusing lens, an average power of the writing laser beam of 35 mW, and a sample translation velocity of 100 \(\mu\)m. During the DLW, the laser beam was focused about 50 \(\mu\)m below the sample surface. Polarization of the writing beam was along the \(c\)-axis. According to \(in situ\) observation of the writing process, optical contrast of lines did not depend sensitively on the polarization orientate of the writing beam. It means that instantaneous interaction between the linearly polarized field of the writing laser and the internal space charge field does not affect the writing efficiency. At the same time it indicates that refractive index modification arises primarily due to (initially nearly isotropical) gradient of the photoexcited carrier density in the focal region. On the other hand, optical
contrast of the recorded lines is strongly anisotropic, and is strongest when the lines are perpendicular to the crystalline \( c \)-axis, because photorefractive effect is strongest along that direction. Hence, writing along the lines parallel to \( c \)-axis direction does not induce observable photomodification along the path of translation. Diffraction pattern of the linear grating observed for a \( \lambda = 650 \) nm probing laser beam (strongly attenuated to minimize erasure during probing) is shown in the same figure.

It is possible to record linear and curved features having segments tilted (but not strictly parallel) with respect to the \( c \)-axis direction. An example of such structuring is shown in Fig. 3(b) where two-dimensional diffraction grating recorded by drawing of two mutually perpendicular sets of parallel lines, each set oriented at an angle of \( 45^\circ \) with respect to the \( c \)-axis is shown. As can be seen, optical contrast of the tilted lines is as strong as that of the on-dimensional grating. Diffraction pattern of this grating is also shown in the figure. An example of more complex pattern composed of smooth wavy lines is also shown in Fig. 3(c). Its optical contrast and refractive index modulation is also strong.

From the measured first-order diffraction efficiency of a grating, magnitude of refractive index modulation can be determined. First-order diffraction efficiency of a thin sinusoidal phase grating can be expressed as

\[
\eta = J_1^2(\Delta \phi),
\]

(1)

where \( J_1 \) is Bessel function of the first kind, and \( \Delta \phi \) is the optical phase difference arising due to the refractive index modulation. The phase difference can be approximately expressed via the magnitude of index modulation \( \Delta n \) as

\[
\Delta \phi = \frac{2\pi \Delta n \Delta z}{\lambda},
\]

(2)

where \( \Delta z \) is geometrical thickness of the grating and \( \lambda \) is the probing wavelength. Approximate geometrical thickness of gratings was determined using side-view observations of photomodification areas by an optical microscope (see Fig. 4(a)). According to these observations, the measured thickness was considerably longer than expected from thin lens approximation and numerical simulations. For the grating structures shown in Fig. 3, \( \Delta z \approx 60 \mu m \) was found as illustrated in Fig. 4(a). Even when tight focusing and high numerical aperture oil-immersion lenses were used for DLW experiments, axial extension of photomodification reached \( \Delta z \approx 10\, \text{to} \, 20 \mu m \), far more than expected theoretically. The most likely reason for such elongation are spherical aberrations due to refractive index mismatch\(^{21}\) and strong optical nonlinearity of lithium niobate.\(^4\) Although axial elongation limits resolution of DLW, in some cases it may be helpful for fast processing of large crystal volumes. In the future it may be possible to suppress the elongation using a recently proposed temporal focusing technique, which has proven successful in achieving symmetrical shape of the focal spot in glasses.\(^{22}\)
Despite significant geometrical thickness, the recorded gratings diffract light in Raman-Nath regime characteristic to thin gratings,\textsuperscript{19,23} since multiple diffracted orders can be seen in diffraction patterns in Fig. 3. This fact indicates that optical thickness gratings ($\Delta n \Delta z$) is low due to moderate values of $\Delta n$. In the Bragg regime characteristic to thick gratings, only a single diffracted order would be visible.

Figure 4(b) shows dependence of the first-order diffraction efficiency on the writing laser power for a one-dimensional grating with period $\Lambda = 5 \mu m$ recorded with $NA=0.35$ focusing at a velocity of $100 \mu m/s$. For these gratings slightly shorter period was chosen in order to create quasi-sinusoidal refractive index modulation. At low laser powers diffraction efficiency increases steeply, and tends to saturate at elevated power levels. The saturation most likely reflects population depletion of optically active iron donors by optical exposure. At the same time no optical damage in the entire range of recording beam powers used in the experiments, and all recorded structures were erasable by spatially uniform UV irradiation. This is due to the fact that the present DLW experiments used low pulse energy, high repetition rate femtosecond laser source. In these circumstances, neither instantaneous power of individual pulses ($>\sim 0.1$ nJ) nor possible accumulation of photoexcitation-induced heating between the pulses (12 ns) could exceed threshold of permanent damage of lithium niobate. Most of the previous DLW experiments in lithium niobate used high pulse energy, low repetition rate laser sources with pulse energies on the order of $\sim 10 – 100$ nJ, sufficient for inducing permanent modification via optical breakdown in single-shot regime.\textsuperscript{12,13}

To estimate the refractive index modulation using measured diffraction efficiency and thickness of the grating, we have selected data points corresponding to low laser power in Fig. 4(b). For example, the measured grating thickness $\Delta z \approx 60 \mu m$ at the recording power of $I = 24$ mW yields index modulation by $\Delta n \approx 6 \times 10^{-4}$ This estimate was obtained for extraordinary probing laser beam (polarization along the $c$–axis). For ordinary beam (polarization normal to $c$–axis), $\Delta n \approx 2 \times 10^{-4}$ was smaller about three times, reflecting lower value of electro-optical coefficient of lithium niobate along that direction. The estimated refractive index photo modification is comparable to what was achieved previously in lithium niobate using other microfabrication techniques, and approaches saturation values determined previously for holographic recording in strongly doped lithium niobate.\textsuperscript{1,7,24}

4.2 Reversibility, erasure, and recording of binary patterns

Reversible photomodification allows one to erase and re-write micro-structures in the same volume of crystal many times. Natural decay of photorefractive features in lithium niobate occurs due to dark conductivity, but this process is fairly slow,\textsuperscript{24} and lifetime of recordings may reach months. Thermal fixing technique allows one to further increase the lifetime to hundreds of years,\textsuperscript{25} and is expected to be applicable to photorefractive structures recorded by DLW. Below we will describe various erasure techniques, and also exploitation of the erasure process for recording of binary photorefractive structures.

Erasure of the entire crystal volume can be achieved by spatially uniform short-wavelength illumination. Figure 5(a) shows optical image of as-recorded features: one-dimensional grating and a rectangular region formed by dense linear scan of laser focus as indicated schematically by arrows immediately after the recording (a), after exposure to a spatially uniform irradiation (b).

Figure 5. Global erasure of photorefractive structures in lithium niobate. A grating and a rectangular area formed by dense linear scan of laser focus as indicated schematically by arrows immediately after the recording (a), after exposure to a spatially uniform UV irradiation (b).
by a dense scan of the focus. To erase these structures, the crystal was irradiated by a frequency-doubled beam of a nanosecond Nd:YAG laser defocused to deliver irradiance of about 10 mW/cm\(^2\). Optical contrast of the microstructures becomes weak after 40 minutes' exposure as illustrated in Fig. 5(b), and completely disappears after 1 h exposure. This observation indicates absence of any permanent photomodification mechanisms, for example due to optical or thermal damage in the crystal during DLW. Faster erasure is possible using higher irradiance levels.

In addition to the global erasure, it is possible to realize a process that can be informally described as a spatially selective local erasure. This is achievable using translation of the focal spot along the \(c\)-axis direction as shown in Fig. 6. A stationary beam would create intensity distribution and refractive index modulation similar to those shown in Figs. 1 and 6(a), with negative index change at the center, and positive changes in the periphery. When the beam focus is translated along the \(c\)-axis direction, previously unexposed regions of the crystal will be photoexcited along the focus translation path. Photoexcited electrons will be pushed forward by diffusion and by the leading intensity edge of the beam, leaving uncompensated ionized iron ions behind. As a result, nearly spatially uniform drop in the refractive index qualitatively similar to that shown in Fig. 6(b) will be induced along the translation path. Redistribution of the space charge will override the refractive index modulation of any previously recorded features, making them invisible. Such erasure is different from the global erasure described above. The global erasure returns crystal to its original state that existed before the recording, whereas the local erasure creates linear regions in which refractive index is uniformly lowered and previous recordings are overridden. Uniform refractive index makes the erasure lines invisible, except for kinks at both ends. These kinks should be regarded as artifacts and can always be pushed far away from region of interest in the crystal.

Drawing of multiple closely-spaced erasure lines allows one to erase selected areas of the crystal. Figure 6(c) shows schematic layout of such dense scan, and Fig. 6(d) presents practical demonstration this scheme. In the experiments, set of vertical lines to be erased was drawn parallel to the \(c\)-axis at a constant translation velocity of 20 \(\mu\)m/s and various laser powers using NA=0.35 focusing lens. The erasure lines were drawn parallel to the \(c\)-axis at the same velocity as the previous lines and various laser beam powers, with vertical separation step of \(\Delta y = 1.5 \mu\)m. As can be seen from the figure, optical contrast of recorded lines is suppressed by the erasure, and its efficiency of the erasure increases with exposure of the erasure lines (decreasing speed).

Linear sweep of the beam focus along the \(c\)-axis direction creates nearly uniform lowering of refractive index (except for the kinks at the ends of lines). Thus, dense set of erasure lines can be also used for realization of binary refractive index modulation patterns. Figure 7(a) shows phase contrast microscopy image of a diffraction
grating comprised of 10 µm wide stripes recorded using dense scan of erasure lines superimposed schematically on the image. The scanning was done with at a translation speed of 40 µm/s, a vertical line spacing of 0.2 µm, and a laser power of 25 mW using NA=0.4 focusing lens. In the phase contrast image bright regions correspond to negative refractive index change, while dark regions correspond to positive refractive index change. Brightness of the stripes is fairly uniform, with some variations near their edges due to the kinks described above.

Figure 7(b) shows optical images of two diffraction gratings. The first grating is square profile quasi-binary grating with period of Λ = 40 µm composed of 20 µm wide index modulation stripes recorded using densely spaced lines shown in the by arrows in the Figure. Assuming that dominant refractive index modulation occurs just near left and right edges of the stripes, the grating period would become halved, and correspondingly, the diffraction angle would become doubled to Λ = 20 µm. As a reference, a second grating composed of single photomodification lines recorded by vertical translation perpendicular to c-axis and period Λ = 20 µm was also recorded in the nearby area. Diffraction patterns of both gratings are shown in Figure 7(c). It is obvious from the diffraction angles that period of the first grating has not become halved and its refractive index modulation profile is close to square profile, as expected. Realization of binary DOE’s in photorefractive media is of considerable interest to optical applications, but is impossible to achieve using holographic recording technique.

5. CONCLUSIONS

The above results suggest several interesting opportunities for application of femtosecond DLW technique in lithium niobate and other photorefractive materials. Photorefractive effect can be exploited to create reversible structures and achieve more intricate spatial tailoring of the refractive index profile. Thus, binary patterns and discrete diffractive optics can be realized by DLW. This approach may be applicable for realization of dynamical photonic structures, for example waveguides and waveguide arrays, directional couplers, diffractive elements, computer-synthesized holograms, and rewritable optical memories.

REFERENCES