Nonlinear-optical characterization of planar domain patterns written in LiNbO₃ by electron-beam irradiation


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Using the combination of atomic-force microscopy (AFM), SHG confocal microscopy (SHGCM) and selective chemical etching we investigated domain patterns written on the non-polar surfaces of LiNbO₃ crystals by electron-beam of SEM. The SHG intensity along the domain axis \( I_2(z) \) is nonmonotonic and discontinuous. It has been shown experimentally that in agreement with the approach proposed recently, the coordinate dependences \( I_2(z) \) are related to variations of the domain thickness \( T_d \). Assuming the wedge-like shape of domains, supported by the chemical etching data, a general expression for \( I_2(z) \) is proposed taking into account both the domain depth \( T_d \) in the irradiation point and the domain length \( L_d \) along the polar axis. This permits to calculate the period of \( I_2(z) \) oscillations for different irradiation conditions, since \( T_d \) and \( L_d \) are determined by the accelerating voltage \( U \) of SEM and irradiation time \( t_p \), respectively.

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1. Introduction

Ferroelectric domain patterning in LiNbO₃-based optical devices, in particular in integrated optical schemes, is of interest for optical frequency conversion based on the quasi phase-matching (QPM) principle ([1]). Traditionally, periodically-poled LiNbO₃ (PPLN) elements are produced by application of external fields to an electrode pattern deposited onto the crystal surfaces. At the same time, alternative noncontact methods such as domain patterning by dc voltages of an AFM-tip or electron-beam (EB) of SEM are developed. These methods provide certain advantages over the field-writing method, since they permit to achieve, relatively easily, the pattern periods at a scale of sub-to few microns. Additionally, using these methods one can write domain patterns on the nonpolar crystal faces, which is of interest for certain integrated schemes on LiNbO₃. There is a large amount of publications on domain EB writing (DEBW) in LiNbO₃ crystals, starting from the pioneering works [2–5]. A detailed description of papers on DEBW in pure and doped LiNbO₃ crystals, published before 2008 one can find in the monograph [6]. In view of a special interest to nonlinear photonic crystals [7], mention should be made of 2D domain patterning using DEBW [8–13].

DEBW method seems to be especially appropriate for thin waveguide layers, in which an undesirable effect of decreasing domain lateral dimensions along the EB trajectory observed in thicker plates [5,9], can be neglected. Application of DEBW for Ti-indiffused and proton-exchanged optical waveguides on LiNbO₃ was reported in Refs. [14–17] and [18], respectively.

With time, the number of materials subjected to DEBW is increasing. The authors of [12] reported on DEBW in BaMgF₄ crystals; we applied DEBW to SBN crystals [19]. Our recent works concerned DEBW on the LiNbO₃ nonpolar surfaces [20–26], and in Ti-indiffused [21] and He-implanted [27] optical waveguides fabricated on the LiNbO₃ nonpolar surfaces.

A general problem of domain engineering is 3D characterization of fabricated patterns. A promising method is the use of second harmonic generation (SHG) microscopy; the basics of this method derived from the Kleinman-Boyd theory [28] and developed in Refs. [29–31] can be found in recent reviews [32,33]. The confocal interference SHG microscopy (denoted below as SHGCM) for
observations of domain patterns, proposed in Refs. [29–32] is based on the interference of SH waves transmitting through a pattern of 180° domains and a reference single-domain plate. Similar approach was utilized in Ref. [34] for visualization of domains fabricated by external fields on the X-cut LiNbO3 crystals. The SHGFM method approved for domain observations in LiNbO3 [28–31], was applied to other ferroelectrics as well [32]. Note that the non-interference SHG microscopy can detect domain walls (DW) only and not antiparallel domains themselves [31]. An example of visualization of DWs with the aid of SHG microscopy is presented in Ref. [35]. Another possibility is provided by an enhanced emission of Cerenkov SHG on DWs [36].

In Ref. [24] we applied a combination of scanning probe microscopy and SHGCM for characterization of domain patterns written by EB on the non-polar surfaces of LiNbO3 crystals. The confocal SHG microscopy developed in Refs. [31–34], was extended to the case of thin (planar) domain patterns. The given paper continues our studies in the nonlinear-optical diagnostics of planar domain patterns, started in Ref. [24].

Remind the scenario of domain formation under an EB incident onto a nonpolar crystal surface (Fig. 1) [20–27]. A single domain induced by EB in an irradiation point grows frontally in the +Z direction parallel to the sample surface. The driving force is the tangential component \( E_{d}(r) \) of the space-charge field \( E_{sc} \) pumped by EB. An elementary domain grating is fabricated by means of point-to-point discrete displacement of EB along the direction normal to \( Z \) (the X-one in our case) with a specified distance \( \lambda \) between the points; a grating with the period \( \lambda \) is formed by elongated domains of the opposite sign embedded in a single-domain matrix. These domains are within few microns thick, thus, by several orders of magnitude thinner than the crystal plate. As shown in Refs. [24,25], their thickness \( T_{d} \) along the EB propagation direction is controlled by the accelerating voltage \( U \). Based on this approach, the following relation was experimentally proved for the congruently melting LiNbO3 samples under study [24,25]:

\[
T_{d} = 78.9U^{1.7} / \rho \tag{1}
\]

(where \( \rho = 4.65 \text{ g/cm}^{3} \) is the LiNbO3 crystal density). This dependence \( T_{d}(U) \) permits one to vary \( T_{d} \) from (200–300) nm to (3–4) \( \mu \text{m} \) in the range of \( U \) from 5 to 25 kV, respectively.

When examination of EB-written domain gratings by SHGCM [24], the SH intensity vs \( U \) was found to be nonmonotonic and discontinuous along the domain axis. The \( T_{d} \) values given by Eq. (1) characterize the maximum domain thickness; at the same time, a decrease of the field \( E_{d} \) with distance from the irradiation point [22] leads to a decrease of \( T_{d} \) along the Z-axis. In Ref. [24] we supposed this domain thinning to be responsible for the observed discontinuity of SH intensity. The calculations [24] performed in the framework of the Kleinman-Boyd theory [28] and Y. Uesu approach [29–32] extended to reflection geometry, predicted the dependence of SHG conversion efficiency \( \eta \) on the domain thickness.

The aim of the present work was to analyze the applicability of the approach proposed in Ref. [24] for description of coordinate dependences of SH intensity in planar domain patterns. This approach may be helpful for characterization of domain patterning in planar optical waveguides.

2. Experimental details

The samples under study were Y-cut optically polished LiNbO3 plates 1 mm thick. Domain gratings with the period \( \Lambda = 4 \mu \text{m} \) were written using the procedure described above and illustrated by Fig. 1. Domains were written in a JSM-840A SEM by an EB incident normally onto the positive (+Y)-surface. The opposite side of the crystals was covered by a grounded Au layer. The NanoMaker program allowed us to control EB scanning over the surface. The accelerating voltages were varied from 10 to 25 kV, the EB current \( I = 0.1 \text{ nA} \), the specified area of local irradiation was \( S_{0} = 0.5 \text{ \mu m}^{2} \). The details can be found in Refs. [21–26] and references therein. The written patterns were characterized by the combination of SHGCM on reflection, lateral piezo-response force microscopy (PFM), and selective chemical etching. The reflection geometry of SHGCM was applied taking into account the small thickness of the gratings of about microns; the transmission method used in Refs. [29–31] would not detect their contrast against the background of the crystal plate thickness. The pump was generated by a Ti-sapphire laser (TiF-100, Avesta project, Russia) with the wavelength 800 nm at the repetition rate 100 MHz; the pulse average power and duration were 70 mW (on the sample) and 100 fs, respectively. Focusing of the pumping beam and detection of the reflected SH beam were performed with a confocal microscope (alpha300xs+, WITec, Germany). The focal position of the objective was determined at the sample surface at 800 nm within the linear-optical image. To observe SHG images we used an objective lens x40 (NA = 0.65). PFM images were obtained by means of measuring the electromechanical response signal:

\[
H_{m} = \left[ \frac{1}{k} \frac{dC}{dZ} \left( \frac{V'}{2} + \frac{V}{2} \right) + d_{15} \right] U_{dc} \tag{2}
\]

where \( k \) is the force constant of the tip, \( C \) is the tip-sample capacity, \( \left( \frac{V'}{2} + \frac{V}{2} \right) \) is the average contact potential difference between the tip and the crystal surface, and \( U_{dc} \) is the ac voltage between the tip and the electrode and counter surface of the crystal. Si probes with Pt/Ti conducting coating (CSC21, MikroMasch, Estonia) were used; tip radius \( R \leq 40 \text{ nm} \), cantilever stiffness \( k \approx 0.12 \text{ N/m} \) (A lever) and \( k \approx 2 \text{ N/m} \) (B lever) and resonance frequencies \( f = 12 \text{ kHz} \) (A lever) and \( f = 105 \text{ kHz} \) (B lever). All AFM experiments were carried out with a NTegra PRIMA AFM (NT–MDT, Russia).

To estimate the domain depth, the samples were etched subsequently to EB writing in a boiling solution of HF + 2 HNO3 acids for 60 s. Because the negative (−Y) surface in LiNbO3 etches much faster than the positive (+Y) one [37,38], the selective etching reveal the etched domains written on the +Y- surface as long grooves. Their depth was measured along an etched groove axis using the contact AFM operation mode. The accuracy of \( T_{d} \) estimate is within 10%.
3. Results and discussion

Fig. 2 offers the examples of SHGCM and PFM images of written patterns. Fig. 2a shows SHGCM image of the domain grating written by $U = 10$ kV, $I = 0.5$ nA, $t_p = 200$ ms. The left (unbroken) fragments of images correspond to the areas around the irradiation spots. The rest part of SHGCM images reveals SH discontinuities illustrated by Fig. 2b which displays a fragment of the image together with the corresponding line profiles of SH. The period of SH oscillations estimated in these three parts is of $4.4 \, \mu$m with an accuracy of 15%. On the contrary, PFM images of domains (Fig. 2c) are unbroken, which evidences that domains emerge completely at the surface, so, the SH discontinuity cannot be attributed to a partial subsurface “dip” of domains.

3.1. The domain shape

The domain depth in the irradiation point is given by Eq. (1) [24]. The domain length $L_d$ along the polar axis $Z$ is a linear function of the irradiation time $t_p$ (at a given EB current $I$) [22,23]. Therefore, a written domain can be represented as a wedge with an angle $\alpha$ specified by the ratio $T_d/L_d$. To verify this assumption, isolated domains were written under varied exposure conditions, whereupon the samples were chemically etched. Using the contact AFM, the depth of etched grooves along the domain axis was measured. Fig. 3 a, b exemplify etching profiles obtained by this technique.

The dashed curves in Fig. 3 a and b present the etching profiles for two isolated domains written by $U = 15$ and 10 kV, respectively, at an equal $t_p = 150$ ms and $I = 100$ pA. (The meaning of the insets shown in Fig. 3 will be explained below). The solid gray lines show fitting the plots by linear functions. The upper (right) parts of the etching profiles correspond to the areas around irradiation spots and give the maximum values of domain depth $T_d = 1.1$ and $0.65 \, \mu$m for $U = 15$ and 10 kV, respectively. The maximum deviations from linearity occur close to irradiation spots shown by the dashed circles in Fig. 3 a, b. The $L_d$ values are the same to within 10% for both $U$, thus, in agreement with recent results [22,23] $L_d$ does not depend on $U$ and is controlled primarily by $t_p$. The calculated angles of etching profiles are $\alpha = 3.1^\circ$ and $2.2^\circ$ for $U = 15$ and 10 kV, respectively. These results support the validity of representation of written domains as wedges with an angle determined by the exposure conditions.

As seen from Fig. 3, the plots $T_d$ vs $L_d$ deviate from the linearity in the region of about $5 \, \mu$m around the irradiation spots. This region exceeds significantly the specified area of local irradiation $S_{irr} = 0.5 \, \mu$m², which is obviously caused by EB scattering within the crystal bulk.

3.2. SHGCM studies in written patterns

The small sizes of individual domains (the length of about $L_d \approx 20–25 \, \mu$m and width of about $W_d \leq 1 \, \mu$m) impedes their characterization by SHGCM. At the same time, as shown in Refs. [22,23], the domain sizes $L_d$ and $W_d$ in domain gratings exceed essentially those of individual domains written under the same exposures. This increase is due to the fact that when writing a grating, domains grow under an additive (total) field of space charges induced by EB in all irradiation points. An increase of the domain sizes in gratings facilitates the measurements by SHGCM.

We discuss now the SHGCM images shown in Fig. 2a b. Note that all SHGCM images were obtained in non-etched samples. The unbroken (left) fragments of the SHGCM images are obviously related to the above mentioned broken wedge-shape of domains close to the irradiation areas (Fig. 3), so we disregard them.

Fig. 4 exhibits the scheme of SHG conversion on domains in the reflection geometry. Here $T_d$ and $D$ are the thicknesses of domains and crystal plate, respectively, $D \gg T_d$. In Ref. [24] we discussed the interference phenomena in this optical system on the basis of the approach proposed in Ref. [30] for 3D characterization of the inverted domain patterns using SHGCM. This approach stems from the Kleinman-Boyd theory of SHG in a strongly focused optical system [28]. In Refs. [30,31] the mapping of antiparallel domains was achieved due to interference of SH waves transmitting through
a domain pattern and a reference single-domain plate.

In reflection geometry used by us, the vectoral condition for SHG is written as:

\[ \Delta k = k_2 + 2k_1 \]  

(3)

where \( k_1 \) and \( k_2 \) are the wave vectors of the fundamental and SH waves, respectively. Our consideration for the reflection geometry [24] was based on the suggestion that the domain imaging is due to interference of SHG field from a \( D \) thick surface domain with the SHG field from the \( (D - T_d) \) thick rest bulk of the plate. In this case, the rest \( (D - T_d) \) plays the role of the reference plate used in optical schemes described in Refs. [30,31]. Then, the total SHG field can be presented by the classical expression:

\[
E_{2\omega} \propto \left( \chi_1 \int_{-y_f}^{-y_f + T_d} \frac{e^{(i\Delta k y)}}{1 + i \cdot y / y_f} dy \right) + \left( \chi_2 \int_{-y_f - D}^{-y_f} \frac{e^{(i\Delta k y')}}{1 + i \cdot y / y_f} dy \right)
\]

(4)

where \( E_{2\omega} \) is the electric field of a SH wave, \( y_f \) is the distance of the focus position from the crystal surface, \( y_f \) is the Rayleigh length, \( \chi_1 \) and \( \chi_2 \) are nonlinear susceptibilities of the inverted domains and initial (single-domain) crystal matrix, respectively; \( \chi_2 = -\chi_1 = \chi_{33} \) (in the given geometry). The SH intensity is \( I_{2\omega} = |E_{2\omega}|^2 \). The details of this approach are presented in Ref. [4,24].

Based on Eq. (4) the SH intensity vs focal position for various \( T_d \) was calculated [24]. These calculations show that introducing non-zero \( T_d \) in Eq. (4) results in an increase of SH signal up to 2 orders of magnitude with respect to the crystal surface. The curves \( I_{2\omega}(y_f) \) calculated for different \( T_d \) in Ref. [24] were in a reasonable agreement with some experimental data. The calculated curves \( I_{2\omega}(y_f) \) suggested a nonmonotonic dependence of SH signal over a domain with varying thickness. Additionally, these calculated curves demonstrated an extremely high sensitivity of SH intensity to \( T_d \) variations.

Based on Eq. (4) the SH intensity vs domain length \( I_{2\omega}(z) \) was calculated for domains, whose etching profiles are shown in Fig. 3 a, b (with wedge angles \( \alpha = 3.1^\circ \) and \( 2.2^\circ \)). The corresponding \( I_{2\omega}(z) \) curves are shown in Fig. 3 c, d, respectively. So, the observed oscillations of SH intensity along the domain axis can actually be attributed to the variations of domain depth.

To this point, we considered the wedge-angles to be specified by...
with the calculated curve. Experimental data are in a reasonable agreement for three gratings written under different exposure conditions. The parameters of the microscope focusing system (e.g., Nd) practically have no impact on the SH period. In this case, it is 90 nm, so each intensity period in the distribution of the signal of the second optical harmonic corresponds to a thickness change (both a decrease and an increase) of the domain structure by 90 nm. If the domain length is fixed, then we can conclude that the period of SH oscillations along the domain axis vs the wedge-angle takes the form \( A/T_d \).

This consideration was verified experimentally. Fig. 5 presents the experimental data on the periods of SH intensity oscillations in three gratings written under different exposure conditions. The solid curve shows the calculated period of SH oscillations vs the wedge-angle. Experimental data are in a reasonable agreement with the calculated curve.

4. Conclusion

Using atomic-force microscopy (AFM) and SHG confocal microscopy (SHGCM), the effect of domain thickness on the SHG intensity distribution along the polar axis \( L_2(z) \) was investigated in planar domain patterns written on the non-polar surfaces of LiNbO\(_3\) crystals by electron-beam of SEM. AFM measurements together with chemical etching have found the wedge-like shape of written domains, the domain thickness \( T_d \) linearly decreasing with distance from the irradiation point. The observed oscillations of \( L_2(z) \) were accounted for by the wedge-like shape of domains in the framework of the approach based on the Kleinman-Boyd theory and Ueesh approach, extended to the reflection geometry. The results obtained suggest that the distribution of the reflected SH intensity in thin layers characterizes the layer relief.

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