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Precise, reproducible nano-domain engineering in lithium niobate crystals

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We present a technique for domain engineering the surface of lithium niobate crystals with features as small as 100 nm. A film of chromium (Cr) is deposited on the lithium niobate surface and patterned using electron beam lithography and lift-off and then irradiated with a wide diameter beam of intense visible laser light. The regions patterned with chromium are domain inverted while the uncoated regions are not affected by the irradiation. With the ability to realize nanoscale surface domains, this technique could offer an avenue for fabrication of nano-photonic and phononic devices. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4926910>]

Lithium niobate (LiNbO₃) is a ferroelectric crystal that is used in a variety of acoustic and optical applications due to its excellent piezoelectric, acousto-optic, electro-optical, and nonlinear optical properties.¹ In particular, domain engineering of LiNbO₃ has attracted attention, which can be attributed to the use of periodically poled LiNbO₃ for nonlinear optical applications, applying the concept of quasi-phase matching.² The most common technique for fabricating periodically poled LiNbO₃ is electric field poling, where a spatially modulated electric field is applied along the polar crystal axis.³ The crystal polarization inverts where the applied electric field exceeds the coercive field (E_c). Although electric field poling has been proven to achieve domain periods down to the micrometer regime, it is difficult to reliably generate sub-micron domain engineered features.⁴ However, domains with sub-micron feature scales are of particular interest, since they are required for the generation of counter propagating photons in nonlinear optical applications.⁵ Unique properties of counter propagating parametric interaction are an inherent feedback and a narrow bandwidth, enabling the realization of classical optical devices such as mirrorless optical parametric oscillator (MOPO)⁵ or permitting the generation of quantum states that possess discrete-frequency entanglement in quantum optics.⁶ Therefore, research into techniques for reliable sub-micron domain engineering of LiNbO₃ is in demand.

Recently, strongly absorbed UV laser light was employed to directly write domains into the surface of LiNbO₃ by scanning a focused UV laser beam across the surface.^{7–9} It has been proposed that the domain inversion process is likely due to a steep temperature gradient, which induces an electric field via the thermoelectric effect. Similar to the physics of electric field poling, domain inversion occurs when the thermoelectric field becomes strong enough to exceed the coercive field of the crystal.^{8,10} The need for strongly localized temperature gradients, however, results in mechanical stress, which often results in surface damage.^{7–9}

Progress in suppressing the surface damage has been achieved by combining UV direct writing with a diffusion process that takes place at a lower temperature in which the diffusion process is activated by coating the surface of the crystal with a thin chromium (Cr) layer prior to the UV irradiation.¹¹ The Cr layer partially absorbs the UV laser light and locally heats up the crystal. This results in a diffusion process in which the Cr acts as an oxygen sink when reacting with the LiNbO₃ oxygen ions, thus forming Cr₂O₃.¹¹ The generated defect gradient induces an electric field, which can invert the crystal polarization when exceeding the coercive field.^{11,12} By employing this domain engineering technique, a domain pattern was generated in LiNbO₃, which was used for exciting surface acoustic waves (SAWs), indicating that the crystal properties are preserved after the domain inversion process.¹³ Although this domain engineering technique offers the flexibility to direct write domains with suppressed surface damage, the domain width was found to be wider than the focal beam diameter,¹¹ therefore limiting the smallest achievable domain size.

In this paper, we report the use of patterned Cr on the surface of LiNbO₃ and visible ($\lambda = 532$ nm) laser light irradiation for generating surface domain patterns with sub-micron domain periods. The resulting nano-domain patterns are revealed by hydrofluoric acid (HF) etching to demonstrate its existence. The green laser light is only partially absorbed at the Cr coated areas (reflectivity $R = 0.55$),¹⁴ whereas at the uncoated areas it is either reflected or transmitted (undoped lithium niobate is transparent in the visible spectral range). As a result, diffusion-based domain engineering takes place at the Cr coated areas only with minimal heating occurring in regions that are un-coated. This domain engineering method was used for the generation of pre-designed domain patterns with features as small as 100 nm.

For the experiments, we used Z-cut congruent LiNbO₃ crystals supplied by “Gooch & Housego.” Fig. 1 illustrates the fabrication steps to achieve surface nano-domains. First, a nanostructured Cr film is defined on the $-Z$ face of the

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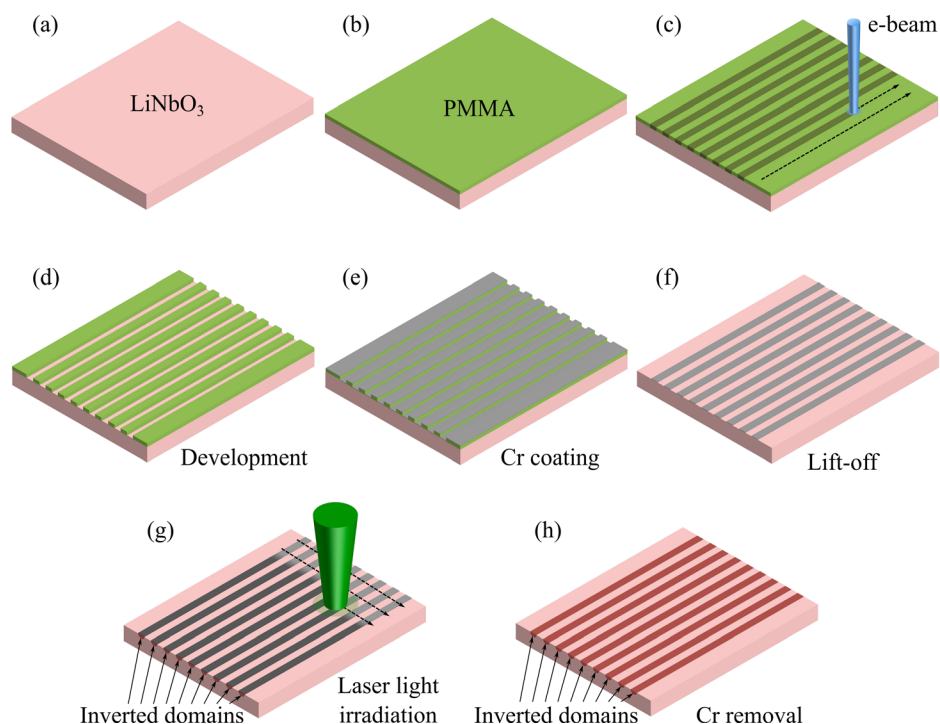


FIG. 1. Fabrication steps for the generation of nano-domains: (a) Bare LiNbO₃ crystal; (b) $-Z$ face of the crystal coated with PMMA; (c) EBL writing procedure; (d) development of the exposed PMMA; (e) coating of the structure with 30 nm of Cr; (f) lift-off process to reveal the Cr pattern; (g) generation of the surface domains by laser light irradiation; and (h) Cr pattern removal by Cr etchant.

LiNbO₃ crystal by coating the surface with an electron beam lithography (EBL) resist (PMMA) as shown in Fig. 1(b). The EBL resist was coated with a thin metal layer to reduce charging of the non-conductive LiNbO₃ during the EBL process. The desired pattern is then transferred onto the EBL resist by scanning an electron beam across the surface (Fig. 1(c), here a 1D line pattern). The EBL resist is developed to remove the exposed areas as illustrated in Fig. 1(d). The crystal is then coated with a 30 nm thin layer of Cr (Fig. 1(e)) by the means of e-beam evaporation. Cr was chosen because the coating layer has to be reactive at elevated temperatures at which the oxygen ions become mobile in lithium niobate as well as having a reasonable absorption at the laser irradiation wavelength. The last step, which defines the Cr pattern, is a lift-off process that removes the PMMA and leaves the desired pattern of Cr that is in contact with the surface of the crystal (Fig. 1(f)).

Nano-domains are generated by scanning a focused green laser beam from a Verdi G-series laser (“Coherent,” $\lambda = 532$ nm) across Cr pattern (Fig. 1(g)) with a velocity of 0.5 mm/s. The crystal was placed in a gas chamber and on a computer controlled translation stage for regulating the atmosphere during the scanning procedure and for controlling the velocity and the laser beam position on the crystal, respectively. The irradiation was conducted in a nitrogen atmosphere to avoid any oxidization of the Cr layer by ambient oxygen from the air.¹¹ The laser beam was attenuated and focused to yield a beam with a diameter of ~ 6 μ m and an intensity of $4.2\text{--}7.1 \times 10^5$ W/cm². Since the focused laser beam diameter is wider than the Cr pattern structures, multiple structures were irradiated at the same time with a spacing of 1 μ m as indicated by dashed lines in Fig. 1(g). Finally, the Cr was removed using a ceric ammonium nitrate mixture, which is a standard Cr etchant (Fig. 1(h)).

To reveal the domain, we treated the sample under HF solution.¹⁵ This uses the differential etching rates between

the two polar faces to transfer the domain pattern into a surface relief pattern, which can be imaged using an scanning electron microscope (SEM).

The initial Cr pattern and the corresponding domain distribution are shown for comparison in Fig. 2. Fig. 2(a) shows an SEM image of the 1D Cr pattern with a period of 600 nm prior to laser irradiation (corresponds to Fig. 1(f)). The 1D Cr line pattern and uncoated LiNbO₃ are indicated with arrows in Fig. 2(a). The Cr stripes appear to be straight with little sidewall roughness. The duty cycle of the Cr pattern is close to 0.6 (duty cycle is defined as Cr or inverted domain width divided the pattern period). Fig. 2(b) shows an SEM image surface, after irradiation Cr removal, and brief HF etching. The HF has etched trenches in the regions, which were un-coated during irradiation, but has left the regions, which were coated with Cr un-etched. This indicates that uncoated regions retain that $-Z$ characteristics, while the coated regions have converted to the $+Z$ domain orientation. The domains have relatively straight sidewalls and a duty cycle that is also close to 0.6, suggesting that the domain formation process strongly follows the Cr covered area prior to laser irradiation. However, the domain pattern was observed

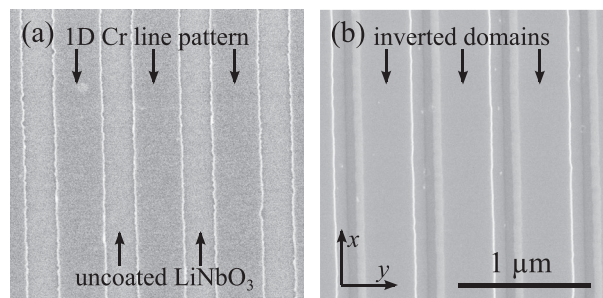


FIG. 2. (a) SEM image of a periodic Cr pattern, with a period of 600 nm, on the $-Z$ surface of a LiNbO₃ crystal; (b) SEM image of the HF etched surface showing the inverted domain stripes after the completion of the laser irradiation and Cr removal process.

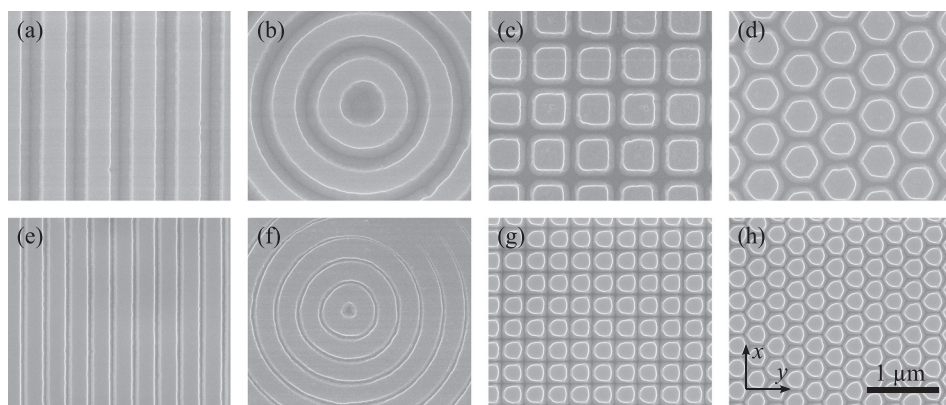


FIG. 3. SEM images of different domain patterns (line, circular, 2D rectangular, and 2D hexagonal domain patterns) that were achieved by this domain engineering technique. Domain patterns with a period of 600 nm are shown in (a)–(d), whereas the domain patterns with a period of 300 nm are shown in (e)–(h).

to be strongly dependent on the irradiation laser intensity; as at very low laser intensities resulted in no domain inversion, while at very high laser intensities the whole crystal surface was uniformly domain inverted. Hence, it is required to choose an optimum laser intensity at which the crystal temperature is just high enough to render the oxygen ions mobile in the crystal lattice and the Cr reactive. Therefore, the oxygen ions will selectively out-diffuse only into the reactive oxygen “sink” regions coated by Cr, so that only these areas are domain inverted.

A selection of different 2D domain distributions fabricated using this method is shown in Fig. 3 including simple lines and more complex 2D domain lattices, thus demonstrating the flexibility of this domain engineering method. The period of the domain patterns in Figs. 3(a)–3(d) is 600 nm, whereas a shorter domain period of 300 nm is shown in Figs. 3(e)–3(h). The duty cycle of the domain patterns with a period of 600 nm was measured to be close to 0.6, whereas it was close to 0.8 for the 300 nm period patterns. This increase in the duty cycle is due to the difficulty of performing EBL on the surface of lithium niobate and patterning the chromium, it is not a limitation of the inversion mechanism. It also can be seen that the corners of the rectangular domains are not very distinct in Fig. 3(g). This is most obvious for the corners on the left side of the rectangular domains, which is most probably the consequence of sideways differential etching and the underlying threefold crystalline symmetry.¹⁶ We think that the initial domain is loyal to the Cr pattern, but after etching, it will eventually turn into a triangular shape due to differential etching between the three Y directions.¹⁷ The etched domain pattern in the right top corner of Fig. 3(f) is

not very pronounced, which could be caused by a faulty Cr pattern prior to laser irradiation.

In the following paragraph, the limitations of this domain engineering technique are investigated. The smallest domain period that we generated is 100 nm as presented in Fig. 4, which shows a 2D dot domain pattern. It can be seen that the domain size varies. As with the duty cycle in Fig. 3, we think that the challenging EBL process on lithium niobate is most likely the causes of the difference in domain size rather than the diffusion based domain inversion process driven by laser light irradiation. The shape of the features exposed by HF etching of the domains is predominantly triangular. As mentioned above, we think that the un-etched domain is loyal to the Cr pattern, but differential etching of the crystal facets will eventually result in a triangular shape. This effect is exaggerated for such small domains because the etch range is comparable to the size of the domain features, and therefore the sideways differential etching is more pronounced.

The domain depth is investigated in the following. To analyze the depth of the obtained nano-domains, a line domain pattern with a period of 300 nm was wedge polished at an angle of $\sim 6^\circ$, with respect to the surface.¹⁸ Wedge polishing increases the depth resolution by stretching the depth profile by a factor of ~ 10 . Fig. 5 shows an SEM image of the wedge polished edge after HF etching. From the SEM image, it seems like the domains are in the order of 25 to 30 nm deep; however, further investigations are necessary to be conclusive on this. 25 to 30 nm is quite shallow, but this is perhaps not surprising since the domain inversion process is diffusion based and chrome is only very briefly heated via

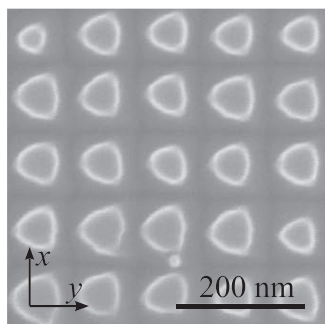


FIG. 4. SEM image of 2D domain inverted structure with a period of 100 nm. It can be observed that not all the domains are formed and that the sizes of the inverted domains are varying.

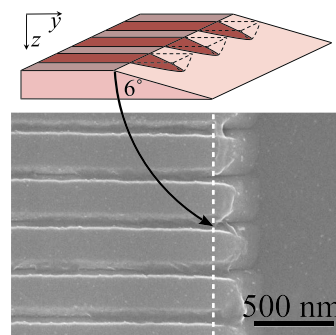


FIG. 5. SEM image of wedge polished domain pattern (period 300 nm) indicating that the domains are approximately 25 to 30 nm deep.

laser irradiation. It may be possible to deepen the domains using longer irradiation duration; however, this would likely come at the expense of increased minimum feature size.

In conclusion, we have introduced a surface domain engineering technique, in which a predefined Cr surface pattern is irradiated with focused visible ($\lambda = 532$ nm) laser light. The laser light is only absorbed at the Cr coated areas, whereas at the uncoated areas no absorption takes place. Therefore, only the Cr coated areas are heated, driving a diffusion process that causes domain inversion only in the areas coated by Cr. This technique has been used for domain engineering of features down to 100 nm. The achievable resolution appears limited by the EBL process on the lithium niobate crystal surface rather than the physical process leading to domain inversion. The depths of the domains achieved in this paper are quite shallow—on the order of 25–30 nm. In spite of the limited depth of the resultant nano-domains, this domain engineering technique could possibly be used for bulk domain engineering by simultaneously applying an electric field during the laser radiation, where the laser irradiation is used for domain nucleation at the surface and the electric field to grow the domains in depth or alternatively by using the surface domains as a template for domain formation when applying multiple electric field poling steps.¹⁹ Another direct application could be for the generation of SAWs in the GHz regime, since the interaction depth of a SAW is in the order of a wavelength.^{13,20–22} Finally, the nano structured LiNbO₃ surfaces that are achieved after etching of the nano-domains can be used for fabricating GHz phononic crystals²⁰ and for photonic or plasmonic applications.²³

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