Ultraviolet laser induced sub-micron periodic domain formation in congruent undoped lithium niobate crystals

C.L. Sones[*], C.E. Valdivia, J.G. Scott, S. Mailis, R.W. Eason

Optoelectronics Research Centre, University of Southampton, Southampton, SO171BJ

U.K

D.A. Scrymgeour, V. Gopalan

Materials Research Laboratory, Pennsylvania State University, University Park,

Pennsylvania 16802, U.S.A

T. Jungk, E. Soergel

Institute of Physics, University of Bonn, Wegelerstraße 8, D 53115, Bonn, Germany

Abstract

We report the formation of ordered sub-micron periodic surface domains on the −z face of congruent undoped lithium niobate single crystals induced by pulsed ultraviolet laser illumination of the sample faces under specific irradiation conditions. We demonstrate the utility of this simple light-induced technique for achieving periodic domain inversion and investigate the nature and spatial structure of these nano-domains by scanning force microscopy. We also demonstrate subsequent re-inversion of a small region of these light induced nano-domains using scanning force microscopy.

1. Introduction

Fabrication of periodically inverted domain patterns in ferroelectric materials such as lithium niobate has been widely researched for the realisation of applications as diverse as quasi-phase-matched (QPM) non-linear devices [1], electro-optic Bragg deflectors [2], photonic band-gap structures [3], and piezoelectric devices such as micro-resonators, atom traps and micro-cavities.

While several techniques such as Li_2O out-diffusion [4], proton-exchange followed by heat treatment [5], Ti-indiffusion [6], scanning force microscopy [7], e-beams [8,9] and electric field poling [10] have been successfully demonstrated for achieving domain inversion over the past years, even perhaps the most routinely used technique of electric field induced domain inversion (E-field poling) becomes problematic when periodicities of a few microns and below are desired for first-order QPM non-linear processes.

In order to overcome the limitations associated with E-field poling, we have been investigating the feasibility of a relatively simple single-step technique, which exploits the interaction of intense laser light with ferroelectric lithium niobate to engineer domains at micron and sub-micron scale-lengths. Some light-assisted poling experiments which take advantage of the ultraviolet light-induced transient change in the coercive field of the illuminated ferroelectric material to transfer a patterned light distribution into an equivalent domain structure in bulk crystals have already been reported for lithium tantalate [11,12] and lithium niobate [13,14] crystals. In this letter we report a direct *optical poling* technique that employs ultraviolet laser light to induce surface domain inversion in undoped lithium niobate in a single step. We further show characterisation

and analysis of the domain structures produced, using scanning force microscopy, and subsequent manipulation (re-poling) of the light-induced domains using the same technique.

2. Experimental Procedure

The experimental procedure to achieve domain inversion involved the illumination of the optically polished −z faces of 500μm thick congruent undoped lithium niobate single crystals, obtained from Crystal Technology, USA, by pulsed ultraviolet laser light from a KrF excimer laser. The illuminating laser wavelength was 248nm and the duration of the irradiating laser pulses was approximately 20ns. To investigate the feasibility of achieving domain inversion with sub-micron periodicities, and nano-scale domain sizes, we utilized a phase mask in the irradiation process. The length scale over which domain inversion was achievable was limited only by the size of the phase mask employed in the illumination procedure and the spatial extent of the excimer laser spot size.

The phase mask was optimised for an illuminating laser wavelength of 248nm and had a grating period of 726nm. To achieve consistency in the illumination procedure the phase mask was held above the crystal sample face at a distance of 125μm using two standard telecommunication fibres with identical diameters. With their polymer jackets stripped off, the fibres served as precision spacers maintaining the distance between the phase mask and the sample face.

Many samples were exposed through the phase mask over a range of different incident energy densities from around 50-150mJ/cm^2 per pulse and a varied number of pulses that ranged from 2-100 pulses. The ablation threshold of lithium niobate had

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previously been determined by a separate set of experiments, and was known to vary with the number of pulses used in the illumination procedure. The single pulse ablation threshold for nanosecond pulsed excimer laser was of the order $500mJ/cm^2$, and hence above the range of energy densities used here. The central more uniform region of a rectangular excimer laser beam was used to illuminate the sample faces. Excimer laser beams are known to have poor spatial uniformity and even the central portion of the beam ($\sim5\times5mm^2$), which was used in the illumination process, possessed some unavoidable spatial non-uniformity in the intensity profile. The spatial extent and selection of the laser light incident on the sample was defined by the size and positioning of an aperture placed in the path of the laser beam, for subsequent imaging onto the sample face through the phase mask.

The –z faces of several samples had been previously illuminated directly without the use of phase masks to establish the exposure conditions which lead to ultraviolet light-induced etch-frustration [15,16] of the illuminated lithium niobate faces, and it was believed that similar conditions might be ideally suited to induce domain inversion within the illuminated areas. As etch-frustration had previously been observed for a narrow range of incident energy densities around $70mJ/cm^2$ per pulse, energy densities around this value were subsequently used for the exposures through the phase mask.

To reveal domain inversion within the illuminated areas several techniques can be used. Samples were firstly etched briefly at room temperature in HF acid which is known to differentially etch the +z and –z faces of lithium niobate. The surface topography of the etched samples was then examined with a surface profilometer and a scanning electron microscope (SEM). Figure 1 shows a typical SEM image in which it is clear that

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sub-micron periodicity has been achieved, with individual surface feature sizes of ~100nm. Few studies explaining the involved etch-chemistry in wet etching procedures for lithium niobate have been reported in the literature to date however, and the observed modifications in the etch-behaviour of illuminated samples could also be a result of other physical mechanisms such as localisation of surface charge. To further characterise these features, and to demonstrate their domain nature, a second and more conclusive non-destructive technique was adopted, and we have used a scanning force microscopy (SFM) imaging technique. These scanning force microscopy techniques, sensitive to the presence of domains, employ similar principles of operation, and are identified by several related names such as "dynamic contact electrostatic force microscopy" (DC-EFM) and "piezoelectric force microscopy" (PFM). Scanning force microscopy, available at the University of Bonn, Germany, and at Pennsylvania State University, USA, was used to study identical previously unetched samples.

This well-established approach has previously been employed [17-22] in the visualisation of ferroelectric domains, and is well-suited for conclusively distinguishing between anti-parallel domain orientations. The one complication relevant to the light-induced domain structuring reported here concerns their possible surface nature. Prior to mapping with SFM we had no knowledge of the depth of any domain features produced. Although this technique is suitable for surface characterisation, it is possible that the domains created are very shallow, and may extend to depths of less than one micron. In this case, there can be a convolution of surface and bulk response; however this potential complication did not impede our successful imaging of the surface features.

Ferroelectric domain structures and their relative orientations were visualised by operating the scanning force microscope in contact mode with an AC voltage (10V peak to peak and 35-38kHz) applied to an electrically conductive gold-coated silicon tip, which results in a mechanical vibration of the sample/tip via the piezoelectric effect. The observed image contrast for samples with anti-parallel oriented domain structures, acquired by the scanning force microscopy approach, results from the alternate signs of electromechanical/piezoelectric response of the oppositely orientated domains.

The higher stiffness constants (14-20N/m) of the cantilevers that carry the probe tips employed in such scanning force microscopy ensure that the scanning tip is sensitive to the mechanical response [23,24] from the oscillating sample surface rather than vibrations generated via an electrostatic force between the tip and the scanned surface. Moreover, scanning with the probe tip at various angles to the sample surface should change the capacitance between the tip and the sample. However no variation in the measured signal was observed for these differing angles, further confirming that the measured signal is dominated by mechanical rather than electrostatic forces.

3. Results and discussion

The SFM piezoresponse image in figure 2, for a sample prepared under the same irradiation conditions as in figure 1, shows a periodic dotted domain-inverted structure with a periodicity that matches the fundamental period of the phase mask. The periodic arrangement of the dark spots seen in figure 2 corresponds exactly to the periodic image of the etch-resistant features of figure 1. As discussed in earlier references [17,22], this image contrast is a clear indication of the presence of anti-parallel domains.

The domain nature of the dotted features shown in figure 2 was further confirmed by a subsequent domain reversal procedure, achieved by application of an electric field through the tip of the scanning force microscope [21,25,26]. Figure 3b for an illuminated −z face shows a $7 \times 7 \mu m^2$ region, which has been re-poled by application of a voltage of the order of -100V through the same tip used to acquire the first image shown in figure3a. The relatively small value of the applied voltage compared to that required for the bulk poling of crystals, sufficient to re-pole the dotted domain features formed by ultraviolet laser illumination, indicates that the domain features are probably shallow and may extend to depths of the order one micron or less. These repoling results are consistent with our other experiments to erase electric field bulk-poled domains in thicker samples with this technique. It is not possible at this stage to specify the exact depth of these optically-poled domains but we are currently investigating this and shall report it in future publications once we have quantitative measurements.

On illumination via phase-mask addressing at higher energy densities, the surface features seen in figure 2 change from individually separated dots, to more densely packed dots, to filled-in features in an effectively continuous line, as seen in the SFM piezoresponse images in figure 4 for a sample illuminated with 25 pulses at $\sim 140 mJ/cm^2$. For higher energy densities ablation is an additional possibility, but up to the energy densities used we do not believe ablation plays any significant role.

We may now conclude that within the energy densities used for these exposures, the evidence for optically-poled domain inversion is strong. We have characterised the domain nature of the optically-induced features using the destructive wet etching procedure, and further confirmed their presence using the established non-destructive

SFM approach to image, and then repole, a specific domain region. Domains have been identified for samples that do not show any appreciable existing surface topography or damage. We may further conclude that there is an interesting comparison to be made between those features that have shown etch-resistance in previous published work [15, 16], and those structures in this present work that have been identified as domains via SFM characterisation. The energy densities are approximately equal for nanosecond exposures, and the resultant etch-resistant features have all the characteristics of domains via their differential etching characteristics. While we do not yet know the exact mechanism behind etch-resistance or direct poling, there may well be a commonality in the light-material interaction process.

4. Summary

In summary we have used a direct optical illumination technique for the creation of domain inverted structures in single crystal undoped congruent lithium niobate using pulsed UV laser light at 248nm. There is no evidence to suggest that this is an optimum wavelength, and we have results [27] that will be published elsewhere that show the parametric dependence of domain formation versus addressing laser wavelength for $+ z$ face irradiated samples. The sub-micron periodicities achieved so far opens up the possibility for the realisation of useful optical devices in the near future. Due to the surface nature of this domain formation mechanism, all such devices would be waveguide structures, although this may not necessarily apply for longer laser wavelength interaction processes.

References

1. M.M Fejer, G.A Magel, D.H Jundt, R.L Byer, IEEE J.Quantum Electron, **28(11)**, 2631, (1992)

2. S.J Barrington, A.J Boyland, R.W Eason, Appl.Opt, **43(5)**, 1038, (2004) / J.A Abernethy, C.B.E Gawith, R.W Eason, P.G.R Smith, Appl.Phys.Lett, **81(14)**, 2514, (2002)

3. B Shi, Z.M Jiang, X.F Zhou, X Wang, J.Appl.Phys, **91(10)**,6769,(2002) / N.G.R Broderick, G.W Ross, H.L Offerhaus, D.J Richardson, D.C Hanna, Phys.Rev.Lett, **84(19)**, 4345, (2000)

4. K Yamamoto, K Mizuuchi, K Takeshige, Y Sasi, T Taniuchi, J.Appl.Phys, **70(4)**, 1947, (1991)

5. K Nakamura, H Shimizu, Appl.Phys.Lett, **56(16)**, 1535, (1990)

6. S Miyazawa, J.Appl.Phys, **50(7)** ,4599, (1979)

7. K Terabe, M Nakamura, S Takekawa, K Kitamura, S Higuchi, Y Gotoh, Y Cho, Appl.Phys.Lett, **82 (3)**, 433, (2003)

8. M Yamada, K Kishima, Electron.Lett, **27(10)**, 828, (1991)

9. H Ito, C Takyu, H Inaba, Electron.Lett, **27(14)**, 1221, (1991)

10. M Yamada, N Nada, M Saitoh, K Watanabe, Appl.Phys.Lett, **62(5)**, 435, (1993)

11. S Chao, W Davis, D.D Tuschel, R Nichols, M Gupta, H.C Cheng, Appl.Phys.Lett, **67**, 1066, (1995)

12. P.T Brown, G.W Ross, R.W Eason, A.R Pogosyan, Opt.Commun, **163**, 310, (1999)

13. M Müller, E Soergel, K Buse, Appl.Phys.Lett, **83(9)**, 1824, (2003)

14. A Fujimura, T Sohmura, T Suhara, Electron.Lett, **39 (9)**, 719, (2003)

15. S Mailis, P.T Brown, C.L Sones, I Zergioti, R.W Eason, Appl.Phys-A Mater.Sci.Process, **74(2)**, 135, (2002)

16. P.T Brown, S Mailis, I Zergioti, R.W Eason, Opt.Mater, **20(2)**, 125, (2002)

17. R Lüthi, H Haefke, E Meyer, L Howald, H.J Güntherodt, J.Appl.Phys, **74(12)**, 7461, (1993)

18. L.M Eng, M Friedrich, J Fousek, P Gunter, Ferroelectr, **186** (1-4), 49-52 (1996).

19. A Gruverman, O Auciello, R Ramesh, H Tokumoto, Nanotechnology, **8(3A)**, A38-43, (1997)

20. A Gruverman, O Auciello, H Tokumoto, Integr.Ferroelectr, **19(1-4),** 49, (1998)

21. L.M Eng, H.J Güntherodt, G Rosenman, A Skliar, M Oron, M Katz, D Eger, J.Appl.Phys, **83(11),** 5973 (1998)

22. S.V Kalinin, D.A Bonnell, Phys.Rev.B, **65(12),** 125408, (2002)

23. G Hu., T Tang, J Xu, Jap.J.Appl.Phys.Part-1,**41(11B)**,6793,(2002)

24. S Hong, H Shin, J Woo, K No, Appl.Phys.Lett, **80(8)**,1453,(2002)

25. K Terabe, S Takekawa, M Nakamura, K Kitamura, S Higuchi, Y Gotoh, A Gruverman, Appl.Phys.Lett, **81(11)**, 2044, (2002)

26. K Terabe, M Nakamura, S Takekawa, K Kitamura, S Higuchi, Y Gotoh, Y Cho, Appl.Phys.Lett, **82(3),** 433, (2003)

27. C.E Valdivia, C.L Sones, J.G Scott, S Mailis, R.W Eason, D.A Scrymgeour, V Gopalan, T Jungk, E Soergel, I Clark, Submitted to Appl.Phys.Lett in Sept'04.

Figure Captions

Fig.1. SEM image of an etched –z face, showing the etch-frustrated grating structure with periodicity at the fundamental period (Λ=726nm) of the phase mask. The irradiation conditions were 25 pulses at ~70mJ/cm^2.

Figure 2 SFM piezoresponse response image of a 10×10μm^2 area for an *unetched* sample exposed under the same conditions as that for the sample shown in figure 1.

Figure 3 SFM images showing the same region of a sample before (a) and after (b) domain erasure in the central region of the image. Domain erasure of the 7×7μm^2 central region was achieved on application of an electric field by the scanning tip.

Figure 4 SFM piezoresponse response image of a –ve z face illuminated through a phase mask with 25 pulses at ~140mJ/cm^2.

Figure 1

Figure 2
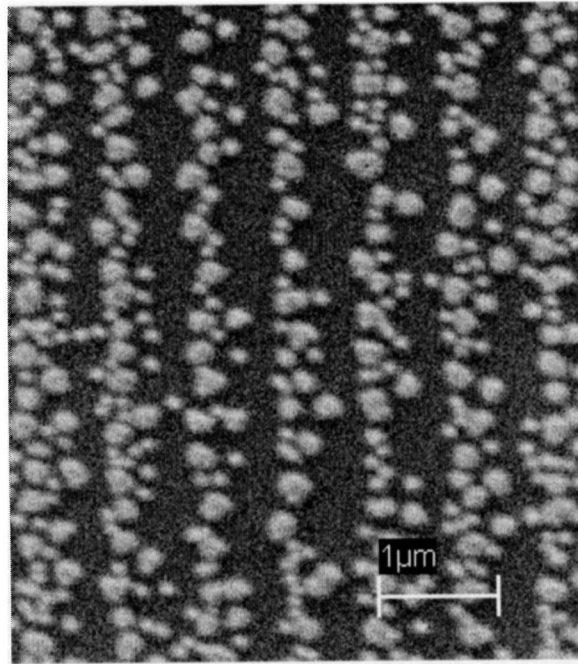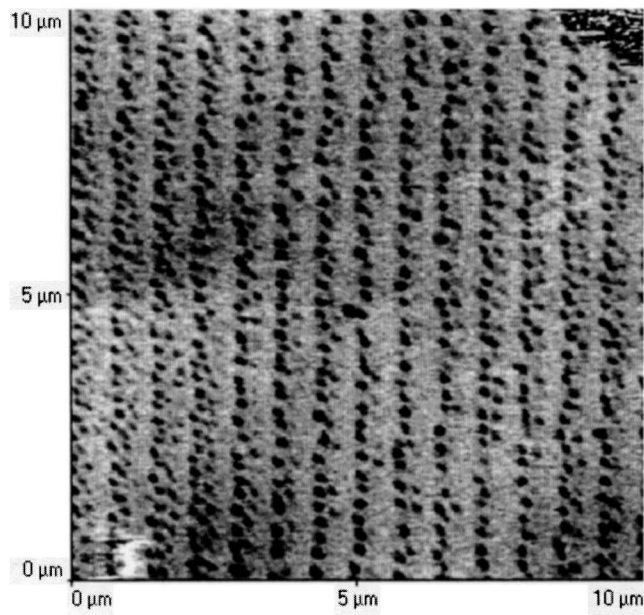
Figure 3

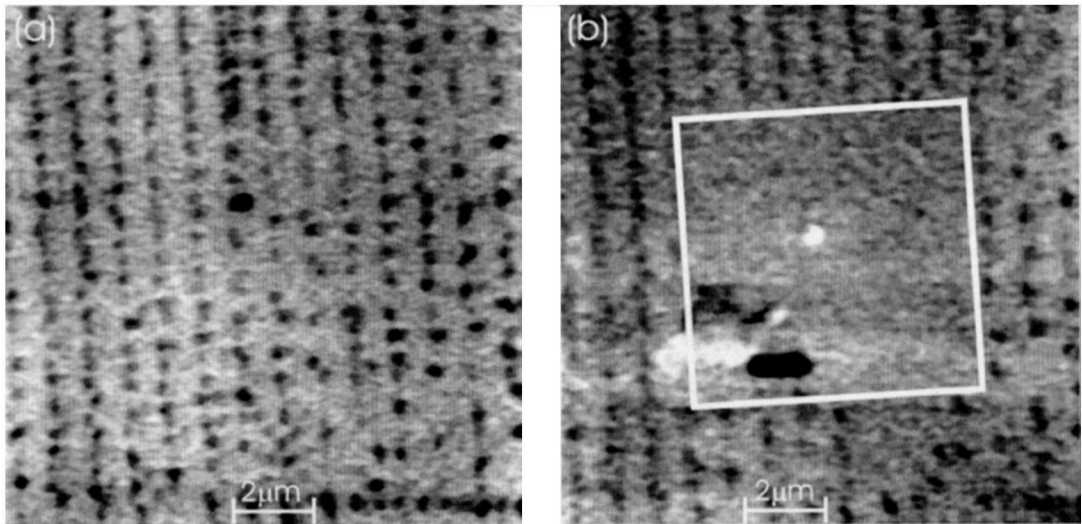**Figure 4**