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1997 J. Phys.: Condens. Matter 9 747

(http://iopscience.iop.org/0953-8984/9/3/014)

J. Phys.: Condens. Matter **9** (1997) 747–752. Printed in the UK PII: S0953-8984(97)73735-4

A change in domain morphology in optical superlattice $LiNbO_3$ induced by thermal annealing

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Received 17 April 1996, in final form 8 August 1996

Abstract. Optical superlattice $LiNbO_3$ crystals were grown by the Czochralski method. The effect of thermal annealing below the Curie temperature on domain structures of a sample with good periodicity was studied. It was found that the periodic domain structure remained unchanged at annealing temperature lower that 1000 °C and began to deteriorate when annealed at above 1000 °C. A sample at 1100 °C for an hour almost changed to a single-domain structure except that a 60 μm single-domain layer with reversed spontaneous polarization was formed at the edge of the sample. These results are useful for revealing the mechanism of formation of the periodic domain structure and designing a more favourable temperature field to improve the crystals' quality. A space-charge-field model was proposed to explain the phenomena.

Compact visible sources based on nonlinear frequency conversion of infrared laser beams are of interest for a number of applications including optical storage, laser printing and laser display. Optical superlattice crystals, namely nonlinear optical crystals with periodic ferroelectric domain structures, allow quasi-phase-matched [1] (QPM) frequency doubling using the largest nonlinear coefficient at an arbitrary temperature over the crystals' entire transparency range. So they are attracting more and more attention.

The optical superlattice $LiNbO_3$ was first grown at the beginning of the 1980s by the Czochralski method [2]. Since that time, a variety of techniques have been developed to fabricate the domain-inverted structure in $LiNbO_3$ and $LiTaO_3$ crystals, for example the laser-heated pedestal technique [3], applying an external electric field at room temperature [4, 5], Ti in-diffusion [6, 7] and heat treatment after proton exchange [8–10]. However, some of these methods are only suitable for waveguide preparation, which is inconvenient for the high-power second-harmonic generation (SHG) and resonator-enhanced frequency-doubling applications. Although the laser-heated pedestal technique has been used to grow bulk optical superlattice $LiNbO_3$ crystals with modulation period as thin as 2 μm, the domain had curvature and the crystal diameter was too small. The method of applying an external field also has the disadvantage of incomplete domain reversal. The 0.5 mm thickness of samples is also insufficient for angle-turning operation in some applications. The Czochralski method is still the most effective and economical ways to prepare optical superlattice $LiNbO_3$ crystals with practical sample dimensions and modulation periods in

0953-8984/97/030747+06$19.50

the range 2.0–15.0 μm [11]. Thus far, efficient picosecond-pulsed blue [11], green [12] and violet [12] light sources have been obtained with optical superlattice $LiNbO_3$ samples grown by this method. Continuous wave (CW) 0.35 mW, 405 nm blue light [13] and CW 1.34 mW, 489 nm blue light [14] generation by directly doubling an 810 nm GaAlAs laser diode and a 978 nm InGaAs laser diode, respectively, have also been reported. However, some problems still remain unsolved regarding the periodicity and the morphology of domain structures. Among them, domain criss-crossing is one of the main defects of the periodic domains structures, which hampers the improvement of conversion efficiency. Since the crystals are grown from the $LiNbO_3$ melt and must undergo a period of high-temperature treatment, which may influence the domain structures, investigating the effects of thermal annealing on the domain morphology of the as-grown optical superlattice $LiNbO_3$ crystal may be beneficial in revealing the physical mechanism associated with the domain inversion, clarifying the characters of the periodic domain structures and improving the crystal growth technology.

In this paper, we report our studies on the effect of annealing on domain structures at different treatment temperatures in an optical superlattice $LiNbO_3$ sample. The morphological change of the ferroelectric domains on the *b* face was observed with an optical microscope.

A $LiNbO_3$ crystal doped with 0.4 wt% yttrium (Y) was grown along the *a* axis by the Czochralski method, as we described early [2]. A particular asymmetrical temperature field was used, which led to a periodic temperature fluctuation on the solid–liquid interface (SLI) during the crystal-growing process. This temperature fluctuation caused a periodic Y^{3+} concentration fluctuation along the growing direction, whence resulted a periodic space-charge field (SCF). When the crystal was cooled through the Curie temperature (T_c), the periodic ferroelectric domain structure was written in the crystal by the periodic SCF.

The sample with good periodic domain structure was cut out from a high-quality as-grown crystal and annealed successively at different temperatures. After each annealing, the *b* face was finely polished and then etched in $1HF{:}2HN0_3$ at 100 °C for 10 min. Since the negative domains are more susceptible to attack by the solution, they show black contrast under the optical microscope, whereas the positive domains are white. Thus the morphology of the domain structures was observed.

The annealing treatment consisted of a 3 h ramping up from room temperature to the set point and the sample was held at this temperature for 1 h; then the oven was turned off and cooled to room temperature. The oven had an initial cooling rate of about 10 K min^{-1} and the annealing treatment was performed in air.

Figure 1 shows the domain morphology changing on the surface of the sample after it had been annealed at different temperatures. Figure 1(*a*) shows the result after heat treatment below 1000 °C (for example 850 and 950 °C). It was found that, under this condition, even though the annealing time was prolonged, the domain structures remained unchanged. We can see that the domains are of regular periodicity and that the domain walls are all sharp and clear. When the annealing temperature increased to 1000 °C, the domain structures began to change in a few regions, as can be seen in figure 1(*b*). Two negative-domain laminae came into contact with each other. The situation became worse and worse when the sample was annealed much above 1000 °C. Figure 1(*c*) shows the result of annealing at 1050 °C. In some regions, some domain laminae criss-crossed and the area of negative domains increased. This picture is similar to the domain morphology of some low-quality crystals, indicating that it is just the high temperature that makes the periodic structure deteriorate. Finally, after the sample had been treated at 1100 °C (below the T_c of 1160 °C), almost the whole sample changed to a single negative-domain structure, as shown in figure 1(*d*). However,

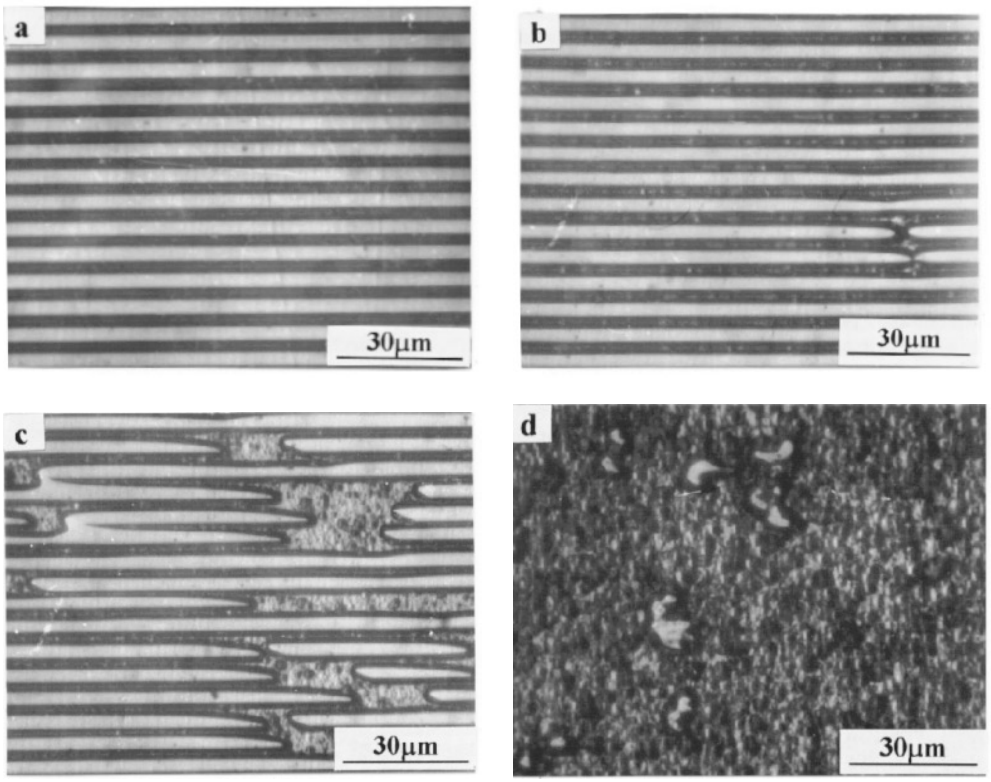

Figure 1. Ferroelectric domain structures on the etched *b* face after the sample had been annealed at (*a*) below 1000 °C, (*b*) 1000 °C, (*c*) 1050 °C and (*d*) 1100 °C.

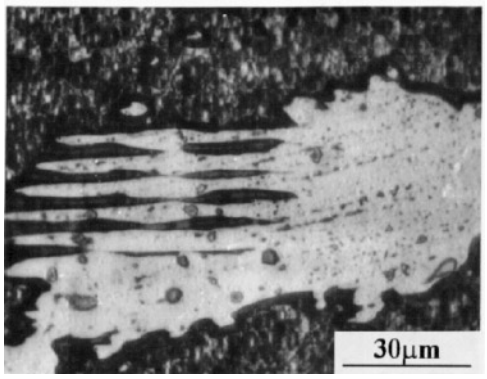

Figure 2. A special region showing the original periodic domain structures after the sample had been at 1100 °C for an hour.

when the sample was carefully checked under the microscope, a small area showing the original periodic domains was observed, which is shown in figure 2.

Figure 3 shows the variation of domain structures at the edge (nearly *c* face) of the sample. Since usually the SLI is arc-shaped, the domain walls near the edge are not perpendicular to the *c* face as indicated in figure 3. In figure 3(*a*) (heat-treated below

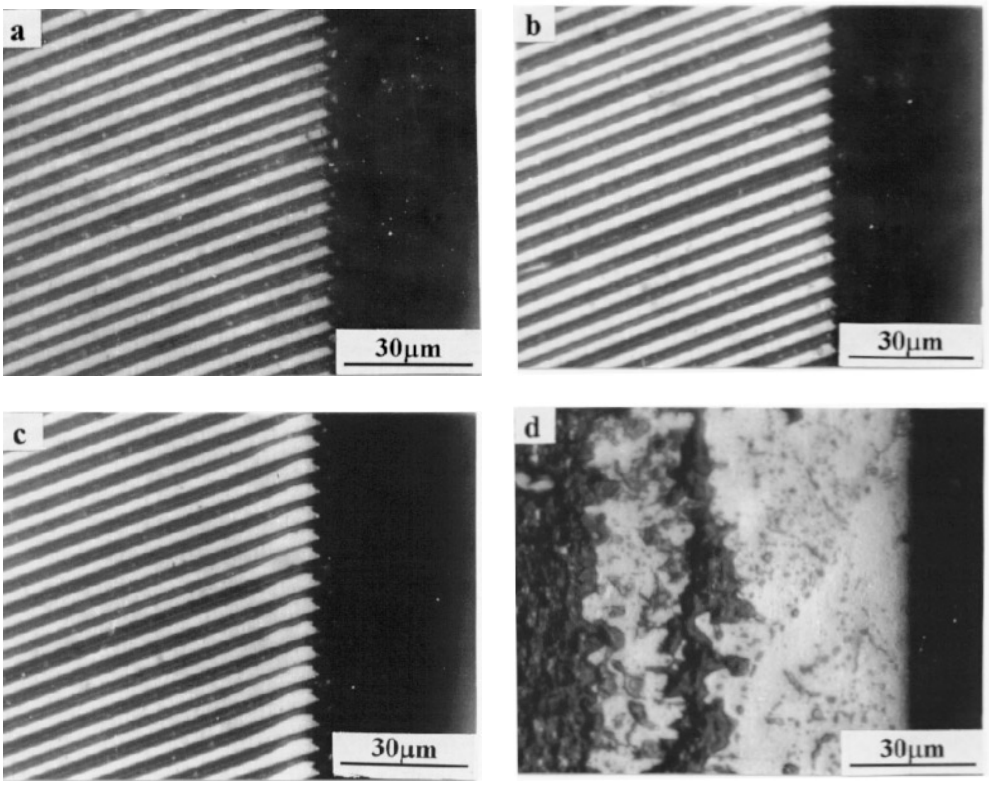

Figure 3. Ferroelectric domain structures near the edge of the sample at different annealing temperatures: (*a*) below 1000 °C, (*b*) 1000 °C, (*c*) 1050 °C and (*d*) 1100 °C.

1000 °C), the periodic domain structure and the sharp edge of the sample can be seen. This structure remained unchanged until the sample was annealed at 1000 °C (figure 3(*b*)). When the sample was annealed at 1050 °C, some change occured at the edge of the sample. As shown in figure 3(*c*), the positive domains expanded and the negative-domain laminae became thinner. After the sample had been annealed at 1100 °C, together with the disappearance of the periodic domain structures, a positive single-domain layer of about 60 μm was established at the edge, as shown in figure 3(*d*). The boundary between the inner negative-domain region and the single-domain layer at the edge was very obscure.

To summarize the experiment, the effects of annealing on the ferroelectric domain structures in an optical superlattice $LiNbO_3$ sample were studied. The domain structures were stable at the temperatures below 1000 °C. When the annealing temperature increased to 1100 °C, the sample almost entirely changed to a single-domain structure and a single-domain layer at the *c* face with the opposite spontaneous polarization was achieved. Since, during the crystal growth process, the crystals undergo an annealing process, these results are helpful for the design of the temperature field, especially the temperature gradient in the axial direction, to avoid the crystal being exposed to temperatures above 1000 °C for too long a time on order to prevent the deterioration of periodic domain structures. On the other hand, thermal annealing is also one of the procedures involved in the Ti in-diffusion and the heat-treated proton-exchange methods for fabricating optical superlattice $LiNbO_3$ or $LiTaO_3$ waveguides; suitable treating temperature and treating time are the key factors

that may influence the quality of the periodic domain structure. Therefore revealing the characters of the change in domain morphology under thermal annealing and explaining the physical mechanism behind the phenomena are also very important for them.

Early in the 1980s [15], we proposed a SCF model which is related to the impurity concentration gradient. It is assumed that, for $LiNbO_3$ associated with the impurity (Y^{3+}) concentration gradient, there exists a space-charge field, which is antiparallel to this gradient. It is just the periodic SCF that determines the periodic spontaneous polarization. Using this model, we successfully explained the mechanism of periodic ferroelectric domain structures associated with rotational growth striations in $LiNbO_3$. We think that this model can also be used here.

In optical superlattice $LiNbO_3$, the periodic SCF is caused by the periodic distribution of Y^{3+}. We know that the radius of Y^{3+} is about 0.088 nm, which is much larger than those of Nb^{5+} and Li^{+} (0.067 and 0.068 nm, respectively), so the mobility of Y^{3+} substitutions is very low. The periodic Y^{3+} distribution is stable, even at high temperature. However, when the $LiNbO_3$ crystal is heated to a high temperature, it has been found to be an n-type conductor [16, 17]. Large amounts of charged point defects such as oxygen and lithium vacancies can migrate easily. When they are caused to drift by the SCF associated with a periodic Y^{3+} concentration, a periodic point defect distribution will also form in the crystal, which can induce an appending opposite SCF. With the duration of annealing, this opposite SCF will become larger and larger, thus the total intensity of the periodic SCF is weakened. Finally, the Y^{3+} SCF is counterbalanced by the latter one and the periodic domain structure vanishes.

However, the reason why the inner periodic domains change to the single-domain structure rather than to an irregular multi-domain one is not so clear. Since in our experiments concerning growing some impurity-doped $LiNbO_3$ such as MgO:$LiNbO_3$ the crystals also have the tendency to form a monodomain structure, we believe that the single-domain structure here also has something to do with the Y doping. Insofar as for the single-domain layer that appeared at the edge is concerned, a similar result has been reported by Nakamura *et al* [18] and it can be explained in terms of the SCF model. At high temperature, Li ions become mobile and are likely to diffuse out of the crystal because of their low activation energy; thus the concentration of Li is lower near the surface and higher towards the interior. For this reason, a SCF associated with the Li concentration is established at the edge of the sample [19] and caused the formation of the single-domain layer.

In conclusion, we have studied the effects of annealing on domain morphology in an optical superlattice sample. Some interesting phenomena were observed. They are useful for the design of the temperature field to improve the crystal growth quality. A space-charge-field model was proposed to explain the physical origin of the domain changes.

Acknowledgments

The authors would like to thank Dr Luo G P and Dr Hu W S for valuable discussions and help.

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