

The mechanism for domain inversion in LiNbO_3 by proton exchange and rapid heat treatment

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1995 J. Phys.: Condens. Matter 7 1437

(<http://iopscience.iop.org/0953-8984/7/7/023>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.179

The article was downloaded on 13/05/2010 at 11:58

Please note that [terms and conditions apply](#).

The mechanism for domain inversion in LiNbO_3 by proton exchange and rapid heat treatment

Shi-ning Zhu, Yong-yuan Zhu, Zhi-yong Zhang, Hong Shu, Jing-fen Hong, Chuan-zhen Ge and Nai-ben Ming

National Laboratory of Solid State Microstructures, Nanjing University, Centre for Advanced Studies in Science and Technology of Microstructures, Nanjing 210093, People's Republic of China

Received 21 July 1994, in final form 13 September 1994

Abstract. Domain-inverted structures in LiNbO_3 are fabricated by proton exchange followed by rapid heat treatment. The domain inversion mechanism is discussed in relationship to the pyroelectric field and to the concentration gradient of protons.

Recently there has been great interest in the study of domain inversion in LiNbO_3 because of its practical importance in quasi-phase-matched second-harmonic generation [1-19]. Many techniques have been developed to fabricate such structures. However, several problems related to the quality of domain-inverted structures remain unsolved. Therefore, it is important to understand the domain inversion mechanism.

This article reports the fabrication of domain inversion in LiNbO_3 . The fabrication process consists of proton exchange followed by rapid heat treatment. The effect of heat treatment conditions on domain inversion profiles was studied experimentally. The domain inversion mechanism is discussed in relationship to the pyroelectric field and to the concentration gradient of protons. This method may be useful to the study of the domain inversion mechanism.

The domain inversion in a polished *z*-cut LiNbO_3 single crystal, which was grown by the Czochralski method from a congruent melt (48.6% Li_2O +51.4% Nb_2O_5), is formed by proton exchange followed by rapid heat treatment. Proton exchange was carried out in a melt of benzoic acid held constant at 225 °C for a few hours. Then the samples were heat treated for several minutes in air at temperatures between 950 and 1100 °C. The inverted region was observed from a cross-sectional view of the domain-inverted structure corresponding to the *y* face of LiNbO_3 which was etched in a mixture of HF and HNO_3 . Figure 1 is a photograph of the *y* face of etched sample, which was proton exchanged for 2.5 h and rapidly heat treated for 5 min at 1100 °C. A layer with reversed spontaneous polarization can be seen on the original +*c* face side.

It was found [11] that domain inversion could take place even in LiNbO_3 plates without proton exchange when they underwent heat treatment at high temperatures. To see whether domain inversion in our case has any relation to the proton exchange process, samples with proton exchange and without proton exchange were subjected to rapid heat treatment. Experiments show that domain inversion takes place on the +*c* face of samples with proton exchange. Under a given rapid heat treatment condition (say at 1100 °C for about 3 min), the longer the proton exchange time, the thicker are the inverted domains. For example,

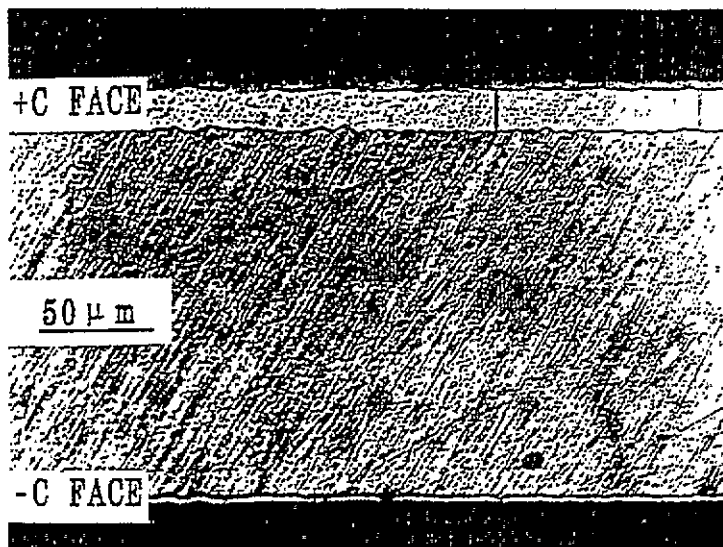


Figure 1. Domain inversion formed on both the $+c$ and the $-c$ faces of a LiNbO_3 plate. A four-layered structure can be seen.

when the proton exchange time is increased from 0.5 to 2.5 h at 225 °C, the inverted depth changes from 9.2 to 11.5 μm . In contrast, for samples without proton exchange, no domain inversion was observed after rapid heat treatment at 1100 °C for about 10 min. This implies that the domain inversion has some relation to the proton exchange process.

The domain inversion takes place only at temperatures higher than 1000 °C. The inverted depth increases much more quickly with the rapid heat treatment time than with the proton exchange time. For samples proton exchanged at 225 °C for 2 h, the depth of inverted domains increases from 2 to 53 μm with the increase in the rapid heat treatment time from 1 to 30 min at 1100 °C. The longer the rapid heat treatment time, the thicker are the inverted domains.

In the experiments, we have observed an interesting phenomenon. If the rapid heat treatment time is sufficiently long (about 10 min), a four-layered structure always appears, which can be seen in figure 1. One can see a very thin layer of the same parity as the original crystal on the $+c$ surface. Another very thin layer of opposite parity to the original crystal can also be seen on the $-c$ surface. The same phenomenon has been observed by Nakamura *et al* [11] in LiNbO_3 by heat treatment, but not always.

From these results, it may be inferred that the inverted domain first nucleates near the $+c$ face and then develops deep inside the substrate with increase in the rapid heat treatment time. When the heat treatment time exceeds some limit, part of the inverted region near the $+c$ surface re-inverts into its original parity, and a very thin layer on the $-c$ surface also inverts. The mechanism of domain inversion by this method is not clear at present. It is usually believed [20, 21] that Li deficiency near the surface will lower the Curie temperature T_C in the exchanged region and enable the pyroelectric field, which is induced on the surface by heat treatment, to reverse the polarization in that region. In order to verify whether this is true in our case, the effect of the pyroelectric field is investigated. Two samples were proton exchanged for 2.5 h at 225 °C. Platinum was deposited on the entire surface, including six faces, of one sample by the laser ablation method and then the sample was tightly wrapped with a platinum foil to ensure a short circuit to prevent

a pyroelectric field from being induced on the surface. Subsequently, two samples were rapidly heat treated at 1100°C for 5 min. Domain inversion was observed in both samples. No significant difference between the inverted depths of the two samples was found. This experiment implies that the metallization of the sample surface has no effect on domain inversion and also indicates that the pyroelectric field may not be the main cause of the domain inversion. In the LiTaO_3 crystal, both Nakamura *et al* [21] and Mizuuchi *et al* [22] obtained the same result. An internal electric field model was proposed to explain the mechanism of domain inversion at the $-c$ face in LiTaO_3 , but the domain inversion at the $+c$ face in LiNbO_3 cannot be explained by this model.

Early in the 1980s, we proposed a model, which is related to the impurity concentration gradient [23], to explain the mechanism of periodic laminar ferroelectric domain structures associated with rotational growth striations in LiNbO_3 grown by the Czochralski method. It was proved that, for LiNbO_3 , there exists an internal electric field which is associated with the impurity concentration gradient, and is antiparallel to the gradient. We believe that it is the impurity concentration gradient which determines the spontaneous polarization direction. We think that this model can also be used here.

It was experimentally verified that, for a proton-exchanged LiNbO_3 crystal, there exists a certain distribution of protons [24]. The concentration of protons is higher near the surface and then decreases towards the interior. That is, there exists a proton concentration gradient which is directed outwards from the plate. According to our model, this corresponds to an internal electric field which is opposite to the gradient or directed towards the inside of the crystal. This field may cause domain inversion only at the $+c$ face of LiNbO_3 . When the heat treatment time is sufficiently long (about 10 min), the proton out diffusion [25] at the surface layer leads to a decrease in the proton concentration near the surface, thus reversing the sign of the concentration gradient. This corresponds to an internal electric field that is directed outwards from the crystal. This can account for both the domain inversion at the $-c$ face and the domain re-inversion at the $+c$ surface.

In conclusion, the fabrication of domain inversion in LiNbO_3 by proton exchange followed by rapid heat treatment has been studied experimentally. The domain inversion depends on the rapid heat treatment conditions as well as on the proton exchange conditions. The pyroelectric field has been shown not to be the main cause of the domain inversion. A possible model for domain inversion has been proposed.

Acknowledgment

This work is supported by a grant for the Key Research Project in Climbing Program from the National Science and Technology Commission of China.

References

- [1] Feng D, Ming N B, Hong J F, Yang Y S, Zhu J S, Yang Z and Wang Y N 1980 *Appl. Phys. Lett.* **37** 607
- [2] Lu Y L, Mao L, Cheng S D, Ming N B and Lu Y T 1991 *Appl. Phys. Lett.* **59** 516
- [3] Feisst A and Koidl P 1985 *Appl. Phys. Lett.* **47** 1125
- [4] Magel G A, Fejer M M and Byer R L 1990 *Appl. Phys. Lett.* **56** 108
- [5] Lim E J, Fejer M M, Byer R L and Kozlovski W J 1989 *Electron. Lett.* **25** 731
- [6] Ishigame Y, Suhara T and Nishihara H 1991 *Opt. Lett.* **16** 375
- [7] Cao X, Rose B, Ramaswamy R V and Srivastava R 1992 *Opt. Lett.* **17** 795
- [8] Miyazawa S 1979 *J. Appl. Phys.* **50** 4599
- [9] Webjorn J, Laurell F and Arvidsson G 1989 *IEEE Photon. Technol. Lett.* **1** 316

- [10] Fujimara M, Kintaka K, Suhara T and Nishihara H 1993 *J. Lightwave Technol.* **11** 1360
- [11] Nakamura K, Ando H and Shimizu H 1987 *Appl. Phys. Lett.* **50** 1413
- [12] Endoh H, Sampei Y and Miyagawa Y 1992 *Electron. Lett.* **28** 1594
- [13] Makio S, Nitanda F, Ito K and Sato M 1992 *Appl. Phys. Lett.* **61** 3077
- [14] Yamada M and Kishima K 1991 *Electron. Lett.* **27** 828
- [15] Ito H, Takyu C and Inaba H 1991 *Electron. Lett.* **27** 1221
- [16] Nutt A C G, Gopalan V and Gupta M C 1992 *Appl. Phys. Lett.* **60** 2828
- [17] Fujimura M, Suhara T and Nishihara H 1992 *Electron. Lett.* **28** 721
- [18] Yamada M, Nada N, Saitoh M and Watanabe K 1993 *Appl. Phys. Lett.* **62** 435
- [19] Mizuuchi K, Yamamoto K and Taniuchi T 1991 *Appl. Phys. Lett.* **58** 2732
- [20] Mizuuchi K and Yamamoto K 1992 *J. Appl. Phys.* **72** 5061
- [21] Nakamura K, Hosoya M and Tourlog A 1993 *J. Appl. Phys.* **73** 1390
- [22] Mizuuchi K, Yamamoto K and Sato H 1993 *Appl. Phys. Lett.* **62** 1860
- [23] Ming N B, Hong J F and Feng D 1982 *J. Mater. Sci.* **17** 1663
- [24] Vohra S T, Mickelson A R and Asher S E 1989 *J. Appl. Phys.* **66** 5161
- [25] Son Y S, Lee H J and Shin S Y 1990 *IEEE Photon. Technol. Lett.* **2** 184