Study on domain inversion in proton-exchanged and heat-treated LiNbO$_3$

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Abstract. Domain inversion in LiNbO$_3$ was obtained by proton-exchange and heat treatment. The calculation of the internal electric field resulting from the proton concentration gradient was performed, the result of which can explain well our four-layered domain structure.

1. Introduction

Ferroelectric crystals have a spontaneous polarization direction which can be reversed by an electric field. There are numerous methods for the reversal of spontaneous polarization direction (i.e. the so-called domain inversion), e.g. the application of an external electric field [1, 2], electric beam writing [3–5], high-temperature annealing [6, 7] and proton exchange followed by rapid heat treatment [8–11]. These methods are most effective for domain inversion in LiNbO$_3$ and LiTaO$_3$. The structures of the inverted domains show different morphologies for different methods, and even for the same method but with different processing conditions, thus shedding some light on the mechanism of domain inversion. Several models have been proposed to explain the inversion mechanism. All, except for the application of an external electric field and electron beam writing, are related to an internal electric field, the origin of which may vary. Nakamura *et al* [8] and Mizuuchi *et al* [9] proposed an internal-electric-field model to explain the mechanism of domain inversion at the $-c$ face of LiTaO$_3$. Nakamura *et al* suggested that the field may be attributed to excess protons diffused into the crystal and the negative charges adsorbed onto the surface for electroneutrality. Mizuuchi *et al* believed that the field is built up owing to proton in-diffusion and lithium out-diffusion with protons diffusing more rapidly than lithium. Kugel and Posenman [12] and Huang and Jaeger [13] both suggested a mechanism for domain inversion in LiNbO$_3$ that is based on the defect (oxygen vacancies or Nb$_{Li}$ defects) gradient resulting from lithium out-diffusion at high temperatures. With this model, they calculated the electric field numerically. In order to explain the single-domain layer formed in heat-treated LiTaO$_3$ Ahlfeldt [4] and Ahlfeldt and Webjorn [15] believed that the gradient of Li vacancies plays an important role in the single-domain formation process. According to these models, domain inversion can take place only at the $-c$ face of LiTaO$_3$ and the $+c$ face of LiNbO$_3$.

Previously we studied domain inversion in LiNbO$_3$ by proton exchange followed by rapid heat treatment [10, 11]. A four-layered structure was found. Based on the proton
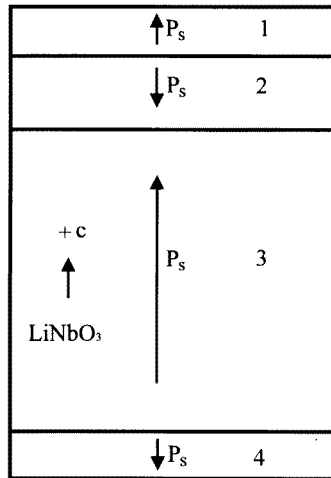
Figure 1. A schematic diagram of the four-layered structure. The arrows indicate the directions of spontaneous polarizations.

concentration measured by SIMS, a modified diffusion model was proposed [16]. The four-layered domain inversion structure was explained by an internal-electric-field model related to the proton concentration gradient [11, 17]. Here, in this paper, we report our further studies on domain inversion in LiNbO$_3$ by proton exchange followed by heat treatment. A calculation of the electric field based on the proton concentration gradient is performed, and the result is consistent with the domain structure observed in our experiment.

2. Experiment

Domain inversion in a z-cut LiNbO$_3$ 0.5 mm thick was obtained by proton exchange followed by heat treatment. Proton exchange was carried out in benzoic acid at 225 °C for 3 h. Then, heat treatment was performed at 1100 °C for several minutes. The inverted domain was observed from an etched y face of LiNbO$_3$. As expected [11], a four-layered structure was obtained. Figure 1 is a schematic diagram of the four-layered structure. The arrows represent the directions of the spontaneous polarization in each layer. Apart from the bulk, three layers form. At the $+c$ face of the virgin crystal (the spontaneous polarization of the third layer points to it), there are two layers. The upper layer, denoted 1, has its polarization direction upwards. The second layer, just below the upper layer (denoted 2), has its polarization direction downwards. At the $-c$ face, a layer (denoted 4) with polarization direction downwards appears. The measured results of the domain structure are listed in table 1.

3. Theory and results

There is experimental evidence that LiNbO$_3$ is an n-type semiconductor at 1100 °C [18], and it is well known that a non-uniform donor distribution in a semiconductor results in a built-in electric field. In a quasi-neutrality assumption for a one-dimensional ionized donor

Table 1. Experimental data on domain inversion at the $+c$ face of LiNbO$_3$ proton exchanged at 225 °C for 3 h and heat treated at 1100 °C.

Heat treatment time (min)	Depth of total inverted domain (μm)	Depth of re-inverted domain (μm)
2.5	8	$\simeq 0$
10	22	3
40	38	8

gradient, the built-in electric field E_{bi} [19] is given by

$$E_{bi} = -\frac{kT}{q}\frac{1}{N_d^+(z)}\frac{\mathrm{d}N_d^+(z)}{\mathrm{d}z} \tag{1}$$

where k is the Boltzmann constant, T is the heat treatment temperature, q is the charge of the donors and N_d^+ is the ionized donor concentration along the z axis.

For simplicity, in an annealed proton-exchanged LiNbO$_3$, we restrict ourselves to the most important donor, namely a proton, to facilitate calculation. In our previous work [16], considering the proton out-diffusion during heat treatment process, we derived the proton profile in annealed proton-exchanged LiNbO$_3$:

$$N(z) = C(L/2 + z, t) + C(L/2 - z, t) \tag{2}$$

where L is the thickness of the crystal and $C(z, t)$ can be expressed as

$$\begin{aligned}
C(z, t) = &-\frac{C_0}{2}\left[\mathrm{erf}\left(\frac{z+d}{2\sqrt{Dt}}\right) + \mathrm{erf}\left(\frac{z-d}{2\sqrt{Dt}}\right)\right] \\
&+ C_0\left[\mathrm{erf}\left(\frac{z}{2\sqrt{Dt}}\right) + \exp\left(hz + h^2Dt\right)\mathrm{erfc}\left(\frac{z}{2\sqrt{Dt}} + h\sqrt{Dt}\right)\right. \\
&\left. - \exp\left(hz + h^2Dt\right)\mathrm{erfc}\left[\left(\frac{z+d}{2\sqrt{Dt}} + h\sqrt{Dt}\right)\exp\left(hd\right)\right]\right]
\end{aligned} \tag{3}$$

where C_0 is the initial surface concentration, d is the exchanged depth, D is the diffusion constant, t is the diffusion time and h is an adjustable parameter, which satisfies the boundary condition

$$\partial N/\partial z = h^*N \qquad z = \pm L/2. \tag{4}$$

So, to a certain degree, h represents the proton out-diffusion rate; $\mathrm{erf}(z)$ and $\mathrm{erfc}(z)$ are the error function and error function complement, respectively. Here we did not take into account the fact that virgin congruent LiNbO$_3$ contains protons as an impurity [20]. Therefore, the complete expression for the proton concentration is

$$N_{total}(z) = N(z) + N_0 \tag{5}$$

where N_{total} is the total proton concentration in the annealed proton-exchanged LiNbO$_3$ and N_0 is the proton concentration in virgin LiNbO$_3$.

Based on the experimental data of Zavada *et al* [21], Smith *et al* [20] and our previous work [16], $C_0 = 6 \times 10^{18}$ mm^{-3}, $d = 1.7$ μm, $D = 51$ μm h^{-1}, $h = 20$ and $N_0 = 1 \times 10^{12}$ mm^{-3} were obtained. The results of calculations of the built-in electric field E_{bi} distribution along the z axis are shown in figure 2 for sample thickness $L = 0.5$ mm. First, we analyse the behaviour of E_{bi} on the $+c$ face of the sample. From the curves in figure 2, the following results can be obtained. First, the maximum of E_{bi}, whose magnitude is larger than the coercive field, 0.5 V mm^{-1}, of LiNbO$_3$ at 1100 °C [22] and
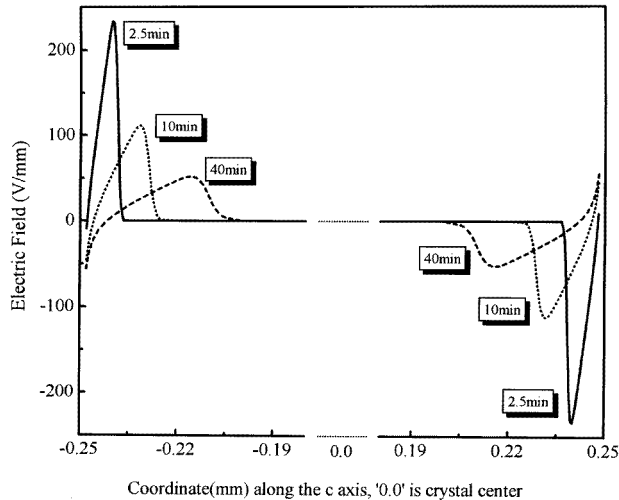
Figure 2. Calculated built-in electric field along the c axis of the LiNbO$_3$ crystal which had undergone proton exchange and heat treatment. The crystal thickness is $L = 0.5$ mm.

whose direction is antiparallel to the z axis, shifts from the surface to the interior with increase in the heat treatment time. Second, in the region near the $+c$ face, E_{bi} changes sign, that is to say, its direction is parallel to the z axis, and its magnitude also becomes larger than the coercive field with increase in the heat treatment time. The result is important and interesting, and it is different from the calculated results of Kugel and Posenman [12] and Huang and Jaeger [13] for non-exchanged LiNbO$_3$. From the above results, it can be deduced that the inverted domain first nucleates near the $+c$ face. With increase in the heat treatment time, an inverted domain develops deep inside the substrate and part of the inverted region near the $+c$ face re-inverts into its original parity. According to our calculated results, the total depth of inverted domains 10 μm, 24 μm and 40 μm thick can be obtained with heat treatment times $t = 2.5$ min, 10 min and 40 min, respectively, as indicated in figure 2. The corresponding re-inverted domain depths are about 0 μm, 4 μm and 8 μm, respectively. The results are consistent with our experiment. The domain structure on the $-c$ face can be analysed similarly. From these results, our four-layered domain structure, to an extent, can be quantitatively explained. In our previous paper, we have indicated that proton out-diffusion is neglected when the parameter h equals zero in our diffusion model and it cannot result in a four-layered domain structure. In order to verify this conclusion, the built-in electric field E_{in} with $h = 0$ is calculated. For simplicity, only the result for the heat treatment time $t = 40$ min is shown in figure 3. From this curve, as we expect, it can be easily inferred that domain inversion exists only in the $+c$ face and not in the $-c$ face and there is no re-inverted domain.

Recently Zhao and Engelmann [23] reported a similar domain structure phenomenon in the rapid thermal annealing of proton-exchanged LiTaO$_3$ above the Curie temperature. Interestingly, their double-domain layer has reversed polarizations to those studied in this paper. The H$^+$/Li$^+$ diffusion model was applied to explain that domain structure. They suggested that our four-layered domain structure, based on the Li$_2$O out-diffusion model [13], could possibly be explained by Nb$_{Li}$ depletion from the surface, but NbO$_y$ possesses a much lower diffusion coefficient than Li$_2$O [24]. To date, no measurement has been
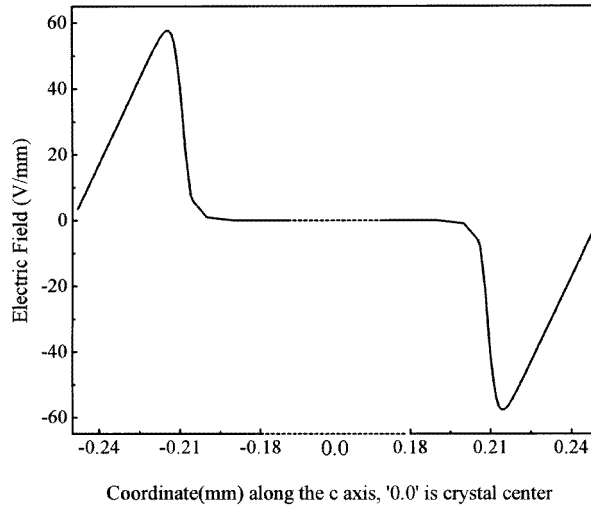
Figure 3. Calculated built-in electric field along the *c* axis of the LiNbO$_3$ crystal which had undergone proton exchange and heat treatment for 40 min with $h = 0$. The crystal thickness is $L = 0.5$ min.

performed to determine the Nb$_{Li}$ distribution. We believe that the microscopic process of domain inversion in LiNbO$_3$ and LiTaO$_3$ is very complex. Much remains to be done to elucidate fully these interesting physical phenomena.

4. Conclusion

In conclusion, the domain inversion in LiNbO$_3$ was fabricated by proton exchange and heat treatment. The calculation of the internal electric field resulting from the proton concentration gradient was performed, the result of which can explain well our four-layered domain structure.

Acknowledgment

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