

Study on the proton profile in proton-exchanged and heat-treated LiNbO_3 with domain reversal

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

1995 J. Phys.: Condens. Matter 7 7583

(<http://iopscience.iop.org/0953-8984/7/38/015>)

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

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 22:10

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

Study on the proton profile in proton-exchanged and heat-treated LiNbO₃ with domain reversal

Hai-feng Wang[†], Yong-yuan Zhu[†], Zhi-yong Zhang[‡], Shi-ning Zhu[†] and Nai-ben Ming[‡]

[†] Department of Physics, National Laboratory of Solid State Microstructure, Nanjing University, Centre for Advanced Studies in Science and Technology of Microstructures, Nanjing 210093, People's Republic of China

[‡] Chinese Centre of Advanced Science and Technology (World Laboratory), PO Box 8730, Beijing 100080, People's Republic of China

Received 10 April 1995, in final form 2 June 1995

Abstract. The domain inversion in LiNbO₃ is fabricated by proton exchange and rapid heat treatment. The proton concentration is measured by secondary-ion mass spectroscopy. A modified diffusion model is proposed, the result of which agrees well with the measured data. Comparisons with the existing models are made, which suggests that our model may be more extensively applicable.

The method of proton exchange has been widely used for the fabrication of LiNbO₃ and LiTaO₃ optical waveguides as it is effective, cheaper and easier to manipulate [1, 2]. Recently this method has attracted much more attention because periodic domain inversion, which is useful for quasi-phase-matched second-harmonic generation, can be induced by proton exchange followed by rapid heat treatment [3–6]. In both cases, the distribution of protons plays a predominant role.

It is well established that the change in refractive index is related to the proton concentration in the exchanged waveguide. The relation may be nonlinear, stepwise linear or linear [2, 7–9, 21]. The domain reversal in LiTaO₃ by proton exchange and rapid heat treatment was studied by Nakamura *et al* [3] and Mizuuchi *et al* [4]. In order to explain the mechanism of domain inversion at the $-c$ face, they both proposed an internal electric field model. Nakamura *et al* suggested that the field may be attributed to the excess protons diffused into the crystal and the negative charges adsorbed onto the surface for electroneutrality. Mizuuchi *et al* thought differently. On annealing, the protons diffuse from the proton-exchanged surface region into the substrate and the lithium ions diffuse in the opposite direction [8, 10]. If the protons have a greater mobility than the lithium ions, an electric field will build up between diffused protons and the vacancies remaining behind them. Previously we studied domain inversion in LiNbO₃ induced by proton exchange and rapid heat treatment [5, 6]. From the experiment, the following results have been obtained. First, in our case the domain inversion has something to do with the proton exchange. Second, it is inferred that the inverted domain first nucleates near the $+c$ face and then develops deep inside the substrate with the increase of the rapid heat treatment time. When the heat treatment time exceeds some limit (about 10 min), part of the inverted region near the $+c$ surface re-inverts to its original parity. A very thin layer on the $-c$ surface also inverts. Thus a four-layered structure is formed. An internal electric field is proposed [6, 11]

which is related to the proton concentration gradient, to explain the formation mechanism of this structure.

Since protons have such an important effect on the refractive index and domain inversion, much work has been done on the determination of the proton concentration [2, 12, 13]. Meanwhile, a theoretical model has been proposed to explain the proton distribution [2]. Here in this paper, we report our further studies on domain inversion in LiNbO_3 by proton exchange followed by rapid heat treatment. The proton profile has been measured by secondary-ion mass spectroscopy (SIMS). A diffusion model has been suggested to explain the measured result.

The domain inversion in z -cut LiNbO_3 0.5 mm thick is formed by proton exchange followed by heat treatment. Proton exchange was carried out in benzoic acid at 225°C for 3 h. Subsequently, heat treatment was performed at 1100°C for 40 min. Before SIMS measurement, the inverted domain was observed from an etched y face of LiNbO_3 . As expected [6], 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 polarizations 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 by 1) is about $8\ \mu\text{m}$ thick with the polarization direction upwards. The second layer, (denoted by 2), just below the upper layer, is about $30\ \mu\text{m}$ thick with the polarization direction downwards. At the $-c$ face, a layer about $8\ \mu\text{m}$ thick (denoted by 4) can be seen with the polarization direction downwards.

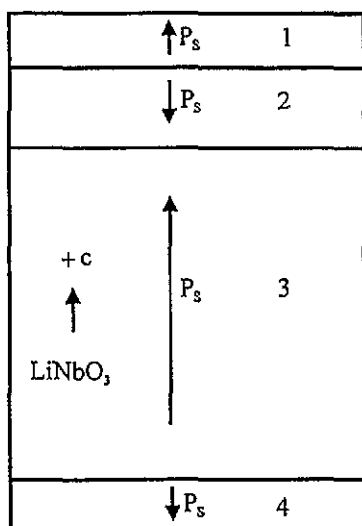


Figure 1. A schematic diagram of the four-layered structure. The arrows indicate the directions of spontaneous polarizations.

The SIMS measurement was performed on a bevelled sample [14] to determine the proton profile. Because LiNbO_3 is a good insulator, the use of charge-compensated SIMS is required to prevent charging and subsequent measurement errors. The charge compensation is achieved by electron beam flooding [15]. Figure 2 shows the result. The proton profile peaks away from the surface. The proton concentration is lower near the surface, next increases towards the inside and then reaches its maximum at about $8\ \mu\text{m}$ below the surface. The position of the maximum coincides with the position of the boundary between the first

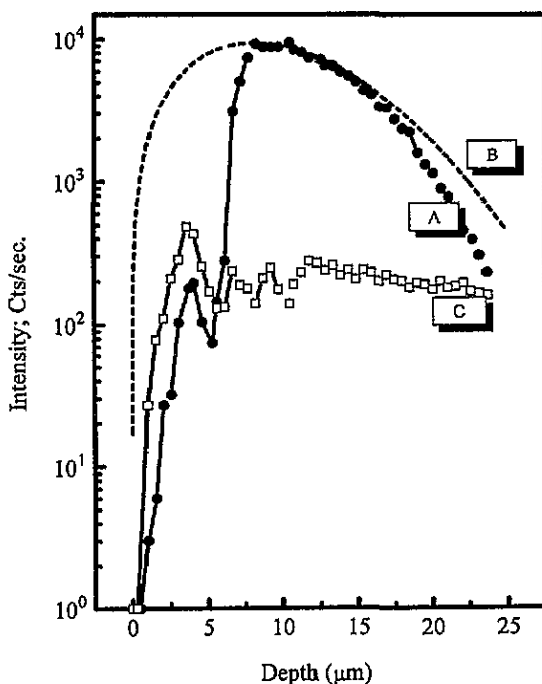


Figure 2. The SIMS measured proton profile (curve A), the calculated proton profile according to equation (5) by varying the value of h (curve B) and the SIMS measured Li profile (curve C).

layer and the second layer just mentioned above.

Our observations are different from those in the previous work, in which the proton profile peaks at the sample surface [2, 8]. For proton-exchanged LiNbO_3 annealed at about 350°C , Vohra *et al* [2] sketched a diffusion model in which the self-diffusion coefficient is concentration independent. An error function solution of the diffusion equation with an impermeable boundary was obtained. Zavada *et al* [8] also measured the proton concentration; two Gaussian functions with different diffusivities and surface concentrations were used to fit the SIMS profile, although they did not propose a model. Considering that the proton out-diffusion is not obvious at low temperatures, although it exists [10], it is not improper that both of them did not take into account the proton out-diffusion at the surface because of the low annealing temperatures (less than 400°C) used. However, it was found that domain inversion takes place only at temperatures higher than 1000°C in LiNbO_3 [6]. At such a high temperature, the proton out-diffusion becomes obvious and cannot be neglected [16]. Thus a modified diffusion model is needed. For simplicity, only proton diffusion is considered here and the diffusion coefficient is taken to be concentration independent.

The initial and boundary conditions are considered as follows. Obviously, the proton concentration profile after the proton exchange process is the initial condition of heat treatment. It has been experimentally proved that the proton concentration in the crystal after the exchange is step like [2, 13] (shown in figure 3) and obeys the standard square root law [17]

$$d = 2\sqrt{D(T)t} \quad (1)$$

where d is the exchanged depth, t is the exchange time and $D(T)$ is the diffusion coefficient.

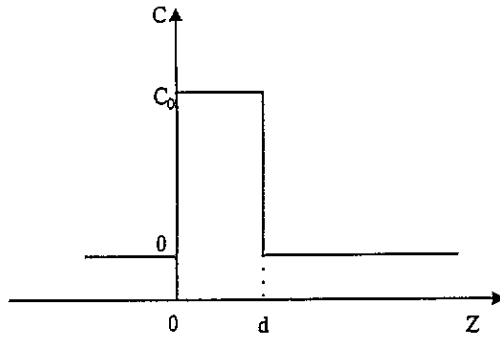


Figure 3. An approximate proton concentration distribution after the proton exchange, which serves as the initial condition of thermal diffusion during heat treatment.

So we have an initial state defined by

$$C = \begin{cases} C_0 & 0 \leq z \leq d \\ 0 & z \geq d. \end{cases} \quad (2)$$

For the boundary condition at the surface ($z = 0$), the proton out-diffusion must be taken into account. The simplest reasonable assumption is that the exchange rate is directly proportional to the difference between the actual concentration C_S at the surface at any time and the concentration C_a in the atmosphere. This means that the boundary condition at the surface in our case is

$$-D\partial C/\partial z = \alpha(C_a - C) \quad z = 0 \quad (3)$$

where α is the constant of proportionality. In our case, C_a approximately equals zero.

Provided that the diffusion coefficient remains constant during the heat treatment process, the equation that needs to be solved in order to calculate the proton profile $C(z, t)$ along the z axis is

$$\begin{aligned} \frac{\partial C(z, t)}{\partial t} &= D \frac{\partial^2 C(z, t)}{\partial z^2} & t > 0 & \quad z > 0 \\ D \frac{\partial C(z, t)}{\partial z} &= \alpha C(z, t) & z = 0 & \end{aligned} \quad (4)$$

$$C(z, t) = \begin{cases} C_0 & t = 0 & 0 \leq z \leq d \\ 0 & t = 0 & z \geq d. \end{cases}$$

By using the Green function method [18], we obtained the solution

$$\begin{aligned} C(z, t) &= -\frac{C_0}{2} \left[\operatorname{erf} \left(\frac{z+d}{2\sqrt{Dt}} \right) + \operatorname{erf} \left(\frac{z-d}{2\sqrt{Dt}} \right) \right] \\ &+ C_0 \left[\operatorname{erf} \left(\frac{z}{2\sqrt{Dt}} \right) + \exp(hz + h^2 Dt) \operatorname{erfc} \left(\frac{z}{2\sqrt{Dt}} + h\sqrt{Dt} \right) \right. \\ &\quad \left. - \exp(hz + h^2 Dt) \operatorname{erfc} \left[\left(\frac{z+d}{2\sqrt{Dt}} + h\sqrt{Dt} \right) \exp(hd) \right] \right] \end{aligned} \quad (5)$$

where $h = \alpha/D$ and $\operatorname{erf}(z)$ and $\operatorname{erfc}(z)$ are the error function and error function complement, respectively.

On the basis of the experimental data of Clark *et al* [17] and Weller and Heidrich [19], $d = 1.7 \mu\text{m}$ and $D = 51 \mu\text{m}^2 \text{h}^{-1}$ are obtained corresponding to the proton exchange

temperature $T_{ex} = 225^\circ\text{C}$, the exchange time $t \approx 3$ h and the heat treatment temperature $T_{heat} = 1100^\circ\text{C}$ in our experiment. The $C(z, t)$ curve is plotted in figure 2 with $h = 20$. On the whole, the fit appears to be fairly good. Both experimental and fitted proton concentration gradients change their sign at nearly the same depth (about $8\ \mu\text{m}$ below the surface). Meanwhile we also notice that the agreement near the surface is not good, which suggests that the proton out-diffusion at such a high temperature may be faster than that assumed in our model, and better agreement can be expected with a boundary condition resulting in faster proton out-diffusion.

In order to expand our model to the low-temperature annealing process, we assumed that the value of α in the boundary condition at the surface (equation (3)) approximately equals zero (i.e. the value of h in equation (5) approximately equals zero) because proton out-diffusion is much more difficult on low-temperature annealing than at high temperatures [10]. With this assumption, the proton concentration $C(z, t)$ in equation (5) can be simplified to

$$C(z, t) = \frac{C_0}{2} \left[\operatorname{erf} \left(\frac{d+z}{2\sqrt{Dt}} \right) + \operatorname{erf} \left(\frac{d-z}{2\sqrt{Dt}} \right) \right]. \quad (6)$$

As we expect, the result is in agreement with the solution of the model of Vohra *et al* [2] at low temperatures, in which they did not take into account the proton out-diffusion at the surface. Furthermore, if the initial exchanged depth d is small, we can simplify our diffusion question to a limited-source diffusion equation with an initial δ -function distribution, which results in a Gaussian function solution [17, 20]. This result suggests that, to a degree, our model is consistent with the work of Zavada *et al* [8]. As a consequence, both of these show that our model may have a more extensively applicable scope.

This result, combined with the internal electric field model proposed by us previously, can be used to explain the domain inversion at the $-c$ face and the domain re-inversion at the $+c$ surface in annealed proton-exchanged LiNbO₃ [11].

Acknowledgments

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] Jackel J L, Rice C E and Veselka J J 1982 *Appl. Phys. Lett.* **41** 607
- [2] Vohra S T, Mickelson A R and Asher S E 1989 *J. Appl. Phys.* **66** 5161
- [3] Nakamura K, Hosoya M and Tourlog A 1993 *J. Appl. Phys.* **33** 1390
- [4] Mizuuchi K, Yamamoto K and Sato H 1993 *Appl. Phys. Lett.* **62** 1860
- [5] Zhu Y Y, Zhu S N, Hong J F and Ming N B 1994 *Appl. Phys. Lett.* **65** 558
- [6] Zhu S N, Zhu Y Y, Zhang Z Y, Shu H, Hong J F, Ge C Z and Ming N B 1995 *J. Phys.: Condens. Matter* **7** 1437
- [7] Loni A, De La Rue R M, Zavada J M, Wilson P G and Novak S W 1992 *Electron. Lett.* **27** 1245
- [8] Zavada J M, Casey H C, Chen C H and Loni A 1993 *Appl. Phys. Lett.* **62** 2769
- [9] Howerton M M, Burns W K, Skeath P R and Greenblatt A S 1991 *IEEE J. Quantum Electron* **27** 593
- [10] Loni A, Hay G, De La Rue R M and Winfield J M 1989 *J. Lightwave Technol.* **7** 911
- [11] Ming N B, Hong J F and Feng D 1982 *J. Mater. Sci.* **17** 1663
- [12] Rice C E, Jackel J L and Brown W L 1985 *J. Appl. Phys.* **57** 4437
- [13] Canali C, Carnera A, Mea G D, Mazzoldi P, Alshukri S M, Nutt A C G and De La Rue R M 1986 *J. Appl. Phys.* **59** 2643
- [14] Sanford N A and Robinson W C 1985 *Opt. Lett.* **10** 190
- [15] Wilson R G, Novak S W, Zavada J M, Loni A and De La Rue R M 1989 *J. Appl. Phys.* **66** 6055

- [16] Son Y S, Lee H J and Shin S Y 1990 *IEEE Photon. Technol. Lett.* **2** 184
- [17] Clark D F, Nutt A C G, Wong K K, Laybown P J R and De La Rue R M 1983 *J. Appl. Phys.* **54** 6218
- [18] Crank J 1985 *The Mathematics of Diffusion* (Oxford: Clarendon)
- [19] Weller M T and Hiedrich P F 1987 *J. Solid State Chem.* **60** 139
- [20] Caccavale F, Chakraborty P, Mansour I, Gianello G, Mazzoleni M and Elena M 1994 *J. Appl. Phys.* **76** 7552
- [21] Zevada J M, Casey H C, States R J, Novak S W and Loni A 1995 *J. Appl. Phys.* **77** 2697