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WINTER COLLEGE ON
LASER PHYSICS: SEMICONDUCTOR LASERS
AND INTEGRATED OPTICS

(22 February - 11 March 1988)

PROTON - EXCHANGE IN LITHIUM NIOBATE & LITHIUM TANTALATE

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Proton-Exchange in Lithium Niobate and Lithium Tantalate

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1. Introduction

The proton-exchange process for optical waveguide fabrication in litnium niobate was announced by Jackel, Rice and Veselka in 1982 [1,2]. The simplicity of the process, by means of which large refractive index difference waveguides could be made by immersing lithium niobate samples in molten benzoic acid for periods of a few minutes to produce single-mode guides or for longer times to give highly multimode guides, was an obvious attraction and has led to considerable activity in a number of laboratories. Reports soon followed of successful device realisations[3,4] and of several major variations on the basic proton-exchange process[5-7]. The objects of this paper are to review briefly, but not exhaustively, developments in the understanding and application of the proton-exchange process since 1982, to describe some recent work carried out at Glasgow University and elsewhere and to assess the contribution which proton-exchange can make to the development of integrated optics.

2. Review

Early work on proton-exchange lithium niobate confirmed the considerable promise of this technique. It was shown that lithographic masking procedures could be used to define regions of high refractive index with good resolution and accuracy, yielding efficient and compact grating beam-splitting[3]. It was also shown that electro-optic devices could be realised[4,8], although there were significant stability problems and evidence of a substantial reduction in the electro-optic effect. The remarkable time variations of waveguide properties reported by Yi Yan[9] have been widely noted, but procedures for obtaining long term stability have been found[10].

Proton-exchange has been used to make a wide range of integrated optical devices[11]. These include various types of planar lens and grating structure[12-15], electro-optic devices[4,8,16], acousto-optic devices[17-22], ring resonators[23], interferometric temperature sensors[24], non-linear optical devices[25,26] and polarizing components[27]. For many of these device applications, the large refractive index difference ($\Delta n \sim 0.12$ at $\lambda = 0.6328\mu m$) obtained using proton-exchange and not available with titanium in-diffusion is an essential aspect. Furthermore the fact that only the extraordinary refractive index, n_e, is increased, while there is a significant decrease in the ordinary refractive index ($n_o \sim -0.04$ at $\lambda = 0.6328\mu m$), is also vital in the operation of leaky wave polarizing devices and devices involving guided-mode polarisation rotation.

3. Structural Studies

Provided that the required device performance is obtainable, there may be little demand from the device engineer for a full understanding of the underlying materials science. However, there is a strong fundamental case for such studies and the continuing but contradictory evidence of significant problems, particularly in respect of the electrooptic effect[4,8,16], provides considerable justification. In early work[28] inorganic acids such as nitric acid were used together with powdered lithium niobate and lithium tantalate to obtain complete exchange between lithium in the powder and hydrogen in the acid. A more recent study of this reaction using X-ray diffractometry[29], has shown both evidence for the formation of an intermediate $Li_{1-x}H_xNbO_3$ phase on single crystal lithium niobate samples and evidence for the completely $HNbO_3$ phase. Practical waveguides on single crystal substrates have almost invariably been formed from partial exchange in organic acids such as the carboxylic acids - notably benzoic acid, but often with 'dilution' involving the addition of small percentages of the related compound lithium benzoate.

A comprehensive study of proton-exchanged waveguides formed in pure benzoic acid, using the techniques of Rutherford back scattering spectrometry (RBS), X-ray diffractometry and topography, resonant and non-resonant nuclear interactions and SIMS, has been described by Canali et al[30,31]. Close agreement between waveguide depths estimated from optical measurements and estimates from RBS and resonant nuclear interactions was found. X-ray diffractometry on X-cut crystals indicated that the proton-exchanged region had undergone a positive lattice strain $\Delta a/a$ of about 0.8%. Related work on Y-cut lithium niobate[32] shows that even larger positive strains ($\Delta a/a$ of about 1.6%) are developed and that the consequent stress is the cause of the substantial surface damage which develops once the exchanged layer exceeds about 2000A. A more recent study by Minakata et al [16] on Z-cut lithium niobate with dilute benzoic acid melts showed negligible lattice strain $\Delta a/a$ but substantial strain $\Delta c/c$ - up to 0.46%. Canali et al [30] have pointed out that the lattice strain observed is normal to the surface in each case for all three crystallographic cuts, ie it is a function of substrate orientation and so will naturally take the form of a change $\Delta c/c$ on Z-cut lithium niobate.

4. Electro-optic devices

An electro-optic stripe waveguide frequency-shifter device using proton-exchange waveguides on X-cut lithium niobate was successfully demonstrated by Wong et al[4]. However, there was also clear evidence of problems which were thought to be due possibly to ionic conductivity. Becker[8] subsequently compared the performance of similar waveguide Mach-Zehnder modulators fabricated using titanium in-diffusion and pure melt benzoic acid proton-exchange respectively. He concluded that there was a factor of three reduction in the electrooptic effect. More recently, Minakata et al[16] have reported an approximately ten-fold reduction in the electrooptic coefficient r_{33} on dilute-melt proton-exhange waveguides Z-cut lithium niobate. In marked contrast, Wong[33] has obtained V_π values for Mach-Zehnder modulators as small as those on comparable titanium in-diffused structures with operation essentially at d.c. He noted, however, that annealing had probably occurred during deposition of a silica buffer layer.

Clearly the electrooptic effect of $LiNbO_3$ is at least partially retained in $Li_{1-x}H_x NbO_3$. Our view is that a combination of melt dilution and annealing should provide the route to substantial retention of the electrooptic effect, albeit with the likelihood of Δn values below the maximum available without annealing. There is still considerable scope for work to investigate the relationship between the electrooptic effect and device fabrication procedure. Our preliminary observations of devices using strip electrodes deposited directly on to dilute melt planar proton-exchange waveguides have shown several interesting features, including possibly full electrooptic effect below the guide region - indicating negligible ionic conductivity - but also apparently hysteretic behaviour. More details will be given in the conference presentation.

5. Proton-exchange in Y-cut lithium niobate

Despite the early onset of surface damage, Y-cut guides can successfully be formed in pure benzoic acid[34]. Moreover, any of (a) titanium in-diffusion and proton-exchange (TIPE process), (b) a short exchange in pure acid followed by annealing or (c) benzoic acid with lithium benzoate dilute melts can produce guides free of the surface damage problem - albeit still possibly with substantial lattice strain. Chen and Chang[35] have observed remarkable anomalous attenuation and depolarisation scattering effects on Y-cut waveguides produced in dilute melts. Our own observations on a single mode Y-cut guide verify these observations. However, we have also found that after annealing for ten minutes at 400°C these effects disappear completely. This result clearly supports the view that the anomalous attenuation and depolarisation effects are due to very large lattice strain and this view differs from that of Chen and Chang - probably because they have concentrated on a highly multimode - and therefore much deeper - waveguide.

6. Acousto-optic devices

Investigation of the acousto-optic device possibilities of proton-exchange waveguides has been a natural extension of earlier work[17-22]. Hinkov and co-workers[18] have made highly multimoded guides by the TIPE process to obtain the controlled birefringence required for a collinear waveguide polarisation rotating device and have also observed[36] substantial changes in the surface acoustic wave velocity. Because of waveguide problems initially encountered with acousto-optic devices on Y-cut lithium niobate[22], we have also investigated devices on X-cut material, obtaining 87% diffraction efficiency in an electrically tuned device with a centre frequency of 425MHz at a drive power level of 640mW. For this device, exchange was carried out for 12 minutes at 220°C with 0.5% lithium benzoate dilution followed by 5 minutes annealing at 400°C. With the improved understanding of the guide formation process now obtained, it is clear that efficient interaction together with good quality waveguides can also be obtained on Y-cut lithium niobate.

7. Acoustic properties

Burnett et al[37] have carried out an extensive investigation of the acoustic properties of dilute melt proton-exchange regions on lithium niobate, obtaining surface acoustic wave velocity surfaces on all three major crystal cuts. The results are remarkable because substantial changes in propagation velocity are obtained even with layers thin by comparison with the acoustic wavelength and because on X- and Y-cut material the exchanged-region velocity may be either greater than or less than the unmodified substrate velocity, depending on the wave propagation direction, whereas on Z-cut material the velocity is always less in the exchanged region than in the unmodified substrate. Results also indicated that decreases in the propagation velocity were accompanied by an increase in the attenuation.

In seeking to explain these results, it should be remembered that there will be a substantial built-in strain in the proton-exchanged layer, even with dilute-melt fabrication. It would therefore be worthwhile to investigate changes arising from subsequent annealing of the samples. Clearly there is also a potential application for proton-exchange in surface acoustic wave devices utilising, for example, periodic or quasi-periodic grating reflector structures.

8. Lithium Tantalate

Procedures for waveguide fabrication by proton-exchange in lithium tantalate have been described by Kopylov et al[38] and by Spillman et al[39]. Our own work has established several different and reasonably rapid process combinations which yield single-mode or low multi-mode waveguides in lithium tantalate[40]. In all cases, the guides obtained had much smaller refractive index differences than are obtainable with proton-exchange on lithium niobate, the largest values of Δn being 0.0174 on X-cut material and 0.0033 on Z-cut material. While it was found necessary to anneal all waveguides prepared in pure benzoic acid melts, it was possible, with dilute melts, to eliminate the annealing procedure provided that exchange was sufficiently prolonged.

We have recently demonstrated the operation of an acousto-optic guided-wave device on X-cut lithium tantalate. While performance demonstrated was modest - a maximum diffraction efficiency of only 22% with 64 mW rf drive power at 203MHz with an untuned transducer, there is scope for a substantial improvement by appropriate tuning, provided that a relatively narrow bandwidth is acceptable for the particular application. Part of the four-section 10.5 finger-pair interdigital transducer specifically designed for use with lithium tantalate is shown in Figure 1. Figure 2 shows RBS data obtained on a Z-cut lithium tantalate sample, before and after annealing, and gives clear evidence of both the rapid change in the depth of the proton-exchanged region and the significant reduction in lattice deformation resulting from a short annealing period. Proton exchange in lithium tantalate, while currently of lesser interest, could well be valuable at the fundamental science level but also in practical applications, provided that large Δn is not required.

9. Proton-Deuterium exchange in lithium niobate

A recent paper[41] describes our work on pure melt proton-exchanged and deuterium-exchanged waveguides using infra-red absorption spectroscopy and also describes work using atomic absorption spectroscopy to verify that lithium enters the benzoic acid melt in quantities consistent with the measured amounts of hydrogen taken up by the crystal. Infra-red absorption spectroscopy has been used to show that both proton-exchanged and deuterium-exchanged waveguides interact with atmospheric water vapour. Because protons and deuterons are incorporated as hydroxyl groups, but in more than one possible configuration, and there is partial hydrogen bonding, the evolution of infra-red absorption spectra during the isotopic exchange is quite complicated. Figure 3 and 4 illustrate the processes starting from [^{1}H] and [^{2}H] hydrogen-exchanged X-cut material respectively. The fine structure at low absorption levels for $\bar{\nu}$ max ~3500cm^{-1} indicates two slightly different OH environments[42]. Clearly the two evolution processes are not simply opposite to one another and proceed on radically different timescales.

Beaumont et al[43] have noted that finite water vapour pressure substantially affects the stability of titanium in-diffused lithium niobate electro-optic devices using silica buffer layers. Proton-exchanged guides may well suffer from a similar problem. However, proton-exchange and the proton-deuterium exchange processes just described could also help in understanding the role of water vapour during: (i) crystal growth from various melt stoichiometries, (ii) poling of boule-sections and (iii) titanium in-diffusion.

10. Future Prospects

In a period of approximately five years much has been achieved using the proton-exchange technique, but it is not yet certain that the technique will be used in practical applications. However proton-exchange adds greatly to the flexibility of lithium niobate based integrated optics and it may well be applied as an adjunct of titanium-diffused technology, providing components not readily realised with the titanium in-diffusion technique. In many respects proton-exchange comes closest to providing the optimum technology for planar waveguide lenses on lithium niobate. Should the possibility of really efficient second harmonic generation and other non-linear effects in proton-exchanged guides be properly confirmed, there are a number of interesting potential areas of application. Demonstration of problem-free electro-optic operation at levels comparable to those for unexchanged bulk material would have a major impact and almost certainly lead to widespread use of proton-exchange based integrated optics.

Acknowledgements

We gratefully acknowledge a large number of collaborators - many of whose names appear as authors on references cited. In addition, we acknowledge the encouragement of Professors J Lamb and S J Thomson. This work was supported by the SERC (UK) (in part under JOERS), by Barr & Stroud Ltd, Hughes Microelectronics, Plessey Research and the Royal Society.

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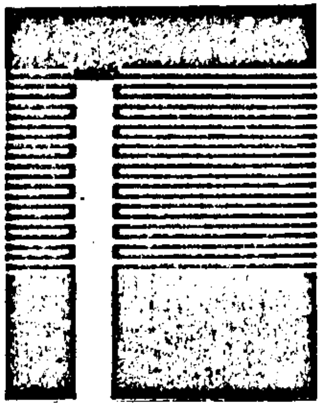

FIG 1: Part of SAW transducer for acousto-optic interaction on lithium tantalate

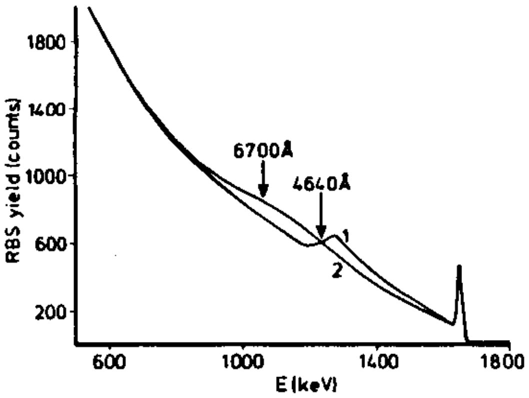

FIG 2: Z-cut $LiTaO_3$ 230°C, RBS data
1. 6 hours diluted melt
2. 6 hours diluted melt ann 15 mins/325°C

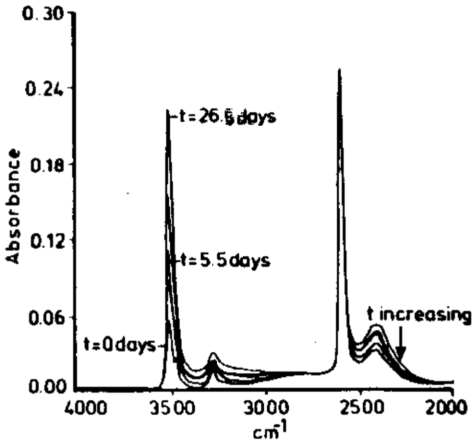

FIG 3: Infrared spectra of [^2H] hydrogen-exchanged x-cut $LiNbO_3$ as a function of exposure time to ambient atmosphere.

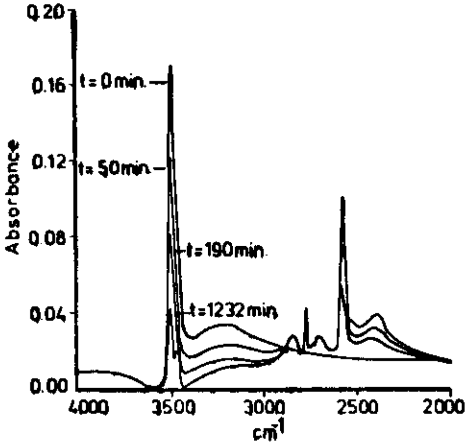

FIG 4: Infrared spectre of [^1H] hydrogen-exchanged x-cut $LiNbO_3$ as a function of exposure time to [^2H] water vapor at room temperature.