To be published in the Proceedings of the Materials Research Society Symposium on "Beam-Solid Interactions: Physical Phenomena," held in Boston, Massachusetts, November 27 – December 1, 1989.

OPTICAL WAVEGUIDE FABRICATION BY STOICHIOMETRIC IMPLANTATION OF Ti AND O INTO $LiNbO_3$

CONF-891119--45

DE90 004238

D. B. Poker
Solid State Division
Oak Ridge National Laboratory

and

W. Xia
Department of Electrical and Computer Engineering
University of California at San Diego

SOLID STATE DIVISION
OAK RIDGE NATIONAL LABORATORY
Operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
under
Contract No. DE-AC05-84OR21400
for the
U.S. DEPARTMENT OF ENERGY
OAK RIDGE, TENNESSEE 37831

November 1989

OPTICAL WAVEGUIDE FABRICATION BY STOICHIOMETRIC IMPLANTATION OF Ti AND O INTO $LiNbO_3$ *

D. B. POKER† and W. XIA‡
†Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6057
‡Department of Electrical and Computer Engineering, University of California at San Diego, La Jolla, CA 92093-0407

ABSTRACT

X-cut substrates of $LiNbO_3$ have been implanted at 500°C with Ti and O to doses of 2.5 and 7.5×10^{17} ions/cm^2, respectively. The high substrate temperature during implantation ensures dynamic recrystallization, preserving the crystallinity of the $LiNbO_3$. The stability of the stoichiometric implants is enhanced sufficiently that annealing at 1000°C proceeds with no surface degradation of the substrate. Annealing under identical conditions without the O implant usually results in phase separation of an oxide at the surface, even when annealing is performed immediately following implantation. Samples implanted with Ti and O to preserve the stoichiometric metal:oxygen ratio of the substrate can be stored at room temperature for several months without phase separation. Planar optical waveguides have been produced by stoichiometric implantation followed by annealing in water-saturated oxygen for one hour at temperatures of 900 and 1000°C. The sample annealed at 900°C supported a single lossy mode, while the 1000°C sample supported two propagating modes and one lossy mode at λ=0.6 μm.

INTRODUCTION

The introduction of Ti into $LiNbO_3$ can be used to modify the index of refraction near the surface, forming a region capable of sustaining a propogating mode of light transmission. Ion implantation of Ti has been shown to exhibit several advantages over thermal diffusion, namely: shallower waveguides, a higher concentration of Ti, steeper concentration gradients, and better lateral control of the Ti concentration.[1] However, the implantation process produces damage at room temperature sufficient to drive the $LiNbO_3$ amorphous. The samples must then be annealed in an oxygen atmosphere to restore the oxygen stoichiometry and to regrow the crystal via solid-phase epitaxy (SPE). In addition, the as-implanted, amorphous state of the $LiNbO_3$ is relatively unstable. Allowing the samples to remain at room temperature for a period longer than a few days results in degradation of the surface during SPE and annealing.[2] To produce a successful waveguide, the samples are usually implanted and stored at liquid-nitrogen temperature before annealing.[3]

Ion implantation of $LiNbO_3$ at high temperatures would offer advantages over low-temperature implantation. If the implantation were performed at temperatures above the crystallization temperature, then the formation of the amorphous phase might be avoided. This would eliminate the need for regrowth via SPE. However, when $LiNbO_3$ is implanted at high temperatures with Ti alone and subsequently annealed in oxygen, segregation of Li and Ti oxides occurs at the surface.[4] This surface segregation can be mechanically removed, but represents a disadvantage in the fabrication of optical waveguides. The purpose of this study was to determine whether high-temperature, stoichiometric implantation of Ti and O could be used to produce optical waveguides, and whether the process offers advantages over other techniques.

---

* Sponsored by the Division of Materials Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

EXPERIMENTAL PROCEDURE

Samples of X-cut optical grade $LiNbO_3$ were implanted at 500°C with 360-keV ^{48}Ti to a dose of 2.5×10^{17} ions/cm^2. Half of the samples were additionally implanted with 7.5×10^{17} ions/cm^2 of 110-keV ^{16}O at the same temperature. Implantations were performed at pressures below 10^{-6} Torr. The implantation temperature was chosen to be slightly higher than the recrystallization temperature of $LiNbO_3$.[5] It was hoped that this would prevent the formation of an amorphous implanted layer. The ratio of O to Ti in the dual implantations was chosen to restore the stoichiometry of metal to oxygen that was originally present in the $LiNbO_3$.

The samples were stored in air at room temperature for 174 days to determine the relative stability of the stoichiometric and nonstoichiometric phases. The samples were then annealed in a water-saturated oxygen atmosphere at 500, 800, or 1000°C for one hour. It is known that at 500°C some of the residual lattice damage due to implantation will anneal, but the regions of high Ti concentration would still be highly damaged.[5] The lattice damage in the regions of high Ti concentration begins to anneal at 800°C, as does the solution of Ti oxides into the $LiNbO_3$.[6] At 1000°C the annealing is completed, and annealing times on the order of an hour are sufficient to produce an optical waveguide.

The samples were analyzed with Rutherford backscattering spectroscopy (RBS) of 2.5 MeV alpha particles along the X-axis channel, which was normal to the surface. The Li and O signals were generally invisible, due to their low masses and scattering cross sections compared to Nb and Ti. The Nb signal was useful for indicating the relative crystallinity of the lattice. Amorphous or highly damaged regions produce RBS scattering equivalent to a randomly-oriented lattice, whereas regions of high quality are effective at channeling the ions, resulting in a reduction in the scattering yield.

RESULTS

The unannealed condition of stoichiometric and nonstoichiometric samples can be seen in Fig. 1. The step near 2.1 MeV is due to scattering from Nb at the surface. The yield at lower energies corresponds to scattering from deeper within the sample. The Ti yield is smaller and appears on top of the Nb yield, starting at 1.8 MeV and continuing to lower energies. The deficit in the random yield near 2.0 MeV is due to the reduction in density of the Nb from the implanted Ti and O, and gives a rough indication of the concentration of Ti.

The nonstoichiometric sample showed little channeling, indicating a large amount of lattice damage, especially near 2.0 MeV, which is the middle of the implanted region. There was still some alignment in the regions deeper and shallower, indicating a lower level of lattice damage there. The stoichiometric implant showed a much greater yield deficit in the Nb, due to the extra O implant. The increased channeling below 1.8 MeV suggests a lower level of dechanneling in the implanted region. The broadness of the Ti yield, centered around 1.7 MeV, suggests that the Ti has been dispersed by the additional O implantation, whether by ion beam mixing or other effects.

The color of the samples following implantation and before annealing gave an indication of the state of the implanted species and defects present. The nonstoichiometric sample showed an opaque silver color, with a slight blue tinge near the corners, even in the unimplanted region. The blue color is thought to be due to the introduction of O vacancies during the exposure to vacuum at high temperature.[7] The silver color is probably the result of segregation of the implanted Ti into metallic colloids. The stoichiometric sample was quite transparent, except for the blue tinge near the corners, as in the nonstoichiometric sample. The transparency is a result of the introduction of sufficient oxygen to react with and oxidize the implanted Ti.

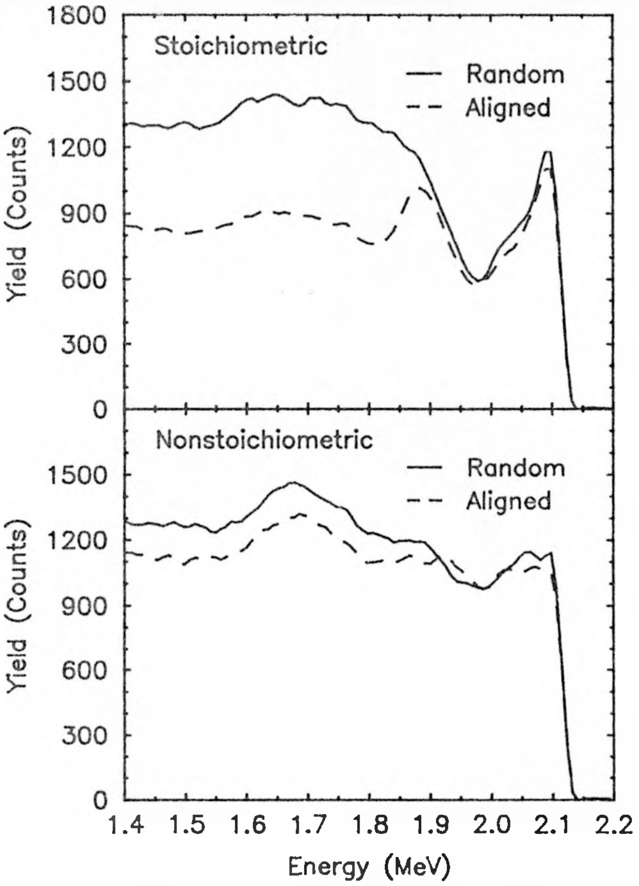

Fig. 1. RBS channeling spectra of Ti (nonstoichiometric) and Ti+O (stoichiometric) implants prior to annealing. The yield deficit near 2.0 MeV results from depletion of Nb due to the implanted ions. The Ti signal is very broad and occurs atop the Nb signal near 1.7 MeV.

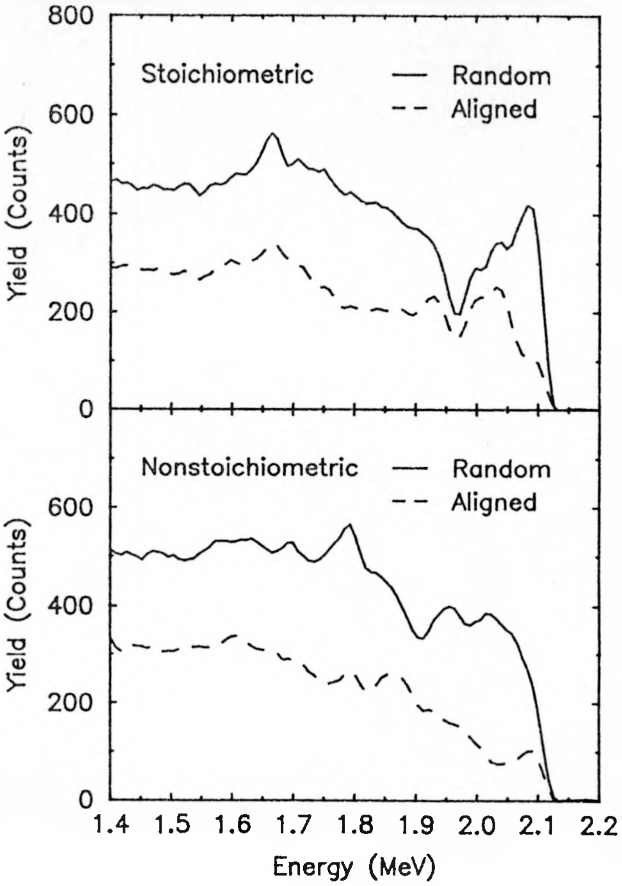

Fig. 2. RBS channeling spectra of Ti and Ti+O implants following an anneal at 800°C for one hour. The nonstoichiometric sample shows a significant yield deficit at 2.1 MeV, due to segregation of various oxides to the surface.

After the 500°C anneal, there was little change in the RBS channeling spectra of the stoichiometric implants, reflecting the stability of the material under stoichiometric implant conditions. The channeling in the nonstoichiometric sample improved slightly outside of the implanted region. This is consistent with studies showing that $LiNbO_3$ with low concentrations of implanted Ti regrows quickly at temperatures above 400°C.[5] The blue color of the stoichiometric implant was reduced, due to the reduction of oxygen vacancies during the anneal, so the stoichiometric sample was quite clear and colorless. The nonstoichiometric sample still showed a significant degree of blue color, but the silver appearance was gone, suggesting the reaction of the metallic colloids with oxygen.

After the 800°C anneal, (Fig. 2) there was noticeable improvement in the channeling of both types of implants. There was a large yield deficit in the Nb signal near the surface of the nonstoichiometric sample, which was probably due to segregation of oxides to the surface during annealing. The stoichiometric sample showed a much steeper surface transition, with correspondingly less segregation. Both samples showed yield deficits in the Nb signal due to Ti, indicating that the Ti had not migrated significantly at 800°C.

After the 1000°C anneal, both samples were clear, but the nonstoichiometric sample exhibited a white-frosted precipitation on the surface. The yield deficits in both samples had disappeared, which was a result of the diffusion of the Ti deeper into the substrate. The channeling spectra (Fig. 3) showed a high degree of channeling, indicating good crystalline quality. An enlargement of the RBS yields in the surface region (Fig. 4) showed a much larger surface peak and a higher yield below the surface in the nonstoichiometric sample

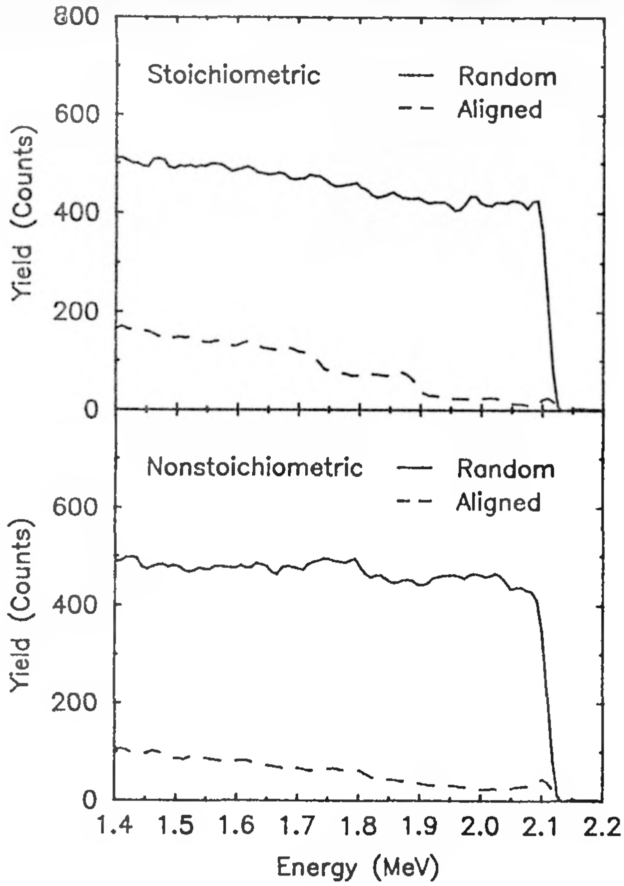

Fig. 3. RBS channeling spectra of Ti and Ti+O implants following an anneal at 1000°C for one hour. Nearly complete annealing of the implantation damage has occurred in both samples.

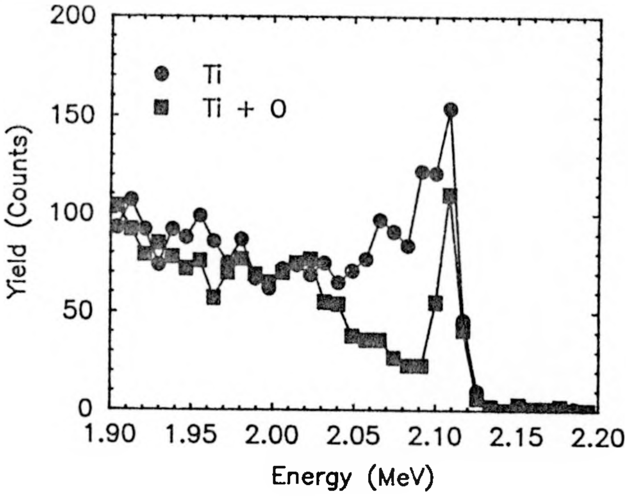

Fig. 4. Enlargement of the surface region of Fig. 3. The stoichiometric implant exhibits a normal surface peak, indicating a clean surface. The surface peak of the nonstoichiometric implant is higher and broader, indicating a large amount of material at the surface that is not in registry with the substrate.

compared to the stoichiometric one. SEM analysis of the surfaces showed the cause of the higher yield (Fig. 5). The surface of the stoichiometric implant was relatively smooth, while the nonstoichiometric sample showed a large amount of surface segregation of an unknown material, which was responsible for the frosted appearance of the surface. By analogy with low-temperature implantation results[2], it is assumed that the precipitation is primarily Li oxides. This is consistent with the low level of dechanneling observed by RBS compared to the amount visible by the SEM, since the light elements Li and O would produce much less dechanneling than the heavier elements.

An optical transmission analysis at λ=0.6 μm of the stoichiometric samples annealed at various temperatures was performed by polishing the ends of the samples and using a microscope objective to couple light into the planar implanted region in an end-fire configuration. After the 800°C anneal, no waveguiding was observed; after the 900°C anneal, one lossy mode was observed; and after the 1000°C anneal, two well-guided modes and one lossy mode were observed. These preliminary results indicate success in fabricating optical waveguides by high-temperature stoichiometric implantation.

DISCUSSION

These results indicate that high-temperature stoichiometric implantation is capable of producing an optical waveguide. Several aspects of the technique differ from the use of nonstoichiometric implantation at high or low temperature. The-low temperature

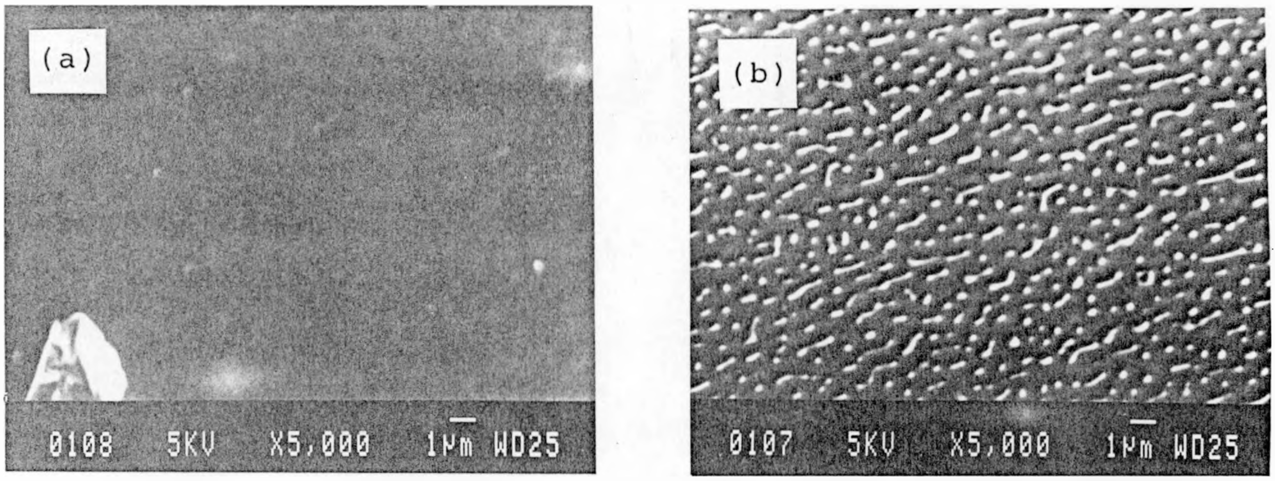

Fig. 5. SEM micrographs of the surface of the a) stoichiometric and b) nonstoichiometric samples following annealing at 1000°C. The object to the lower left in a) is an extraneous dust particle used for focusing.

process is very successful at producing good quality waveguides, but an amorphous layer results from the implantation that must be regrown via SPE soon after the implantation. Storage for periods longer than a few days at room temperature or a few weeks at liquid-nitrogen temperature result in degradation of the implanted region during annealing, namely, segregation of Li oxides on the surface. The implanted Ti also undergoes a high degree of segregation to the surface of the sample during SPE, which disrupts the initial concentration profile. Much of the segregated Ti eventually diffuses back into the substrate during annealing, however, which mitigates the severity of the effect.

The implant process can be performed at high temperatures (>400°C), where the amorphization of the substrate is hindered by dynamic recrystallization during implantation. This offers the advantage that no amorphous layer is formed, no SPE is required, and consequently no segregation of Ti occurs during SPE. However, the stability of the implanted state is questionable and leads to degradation similar to that observed with the low-temperature implants. The use of a stoichiometric Ti plus O implant appears to produce sufficient stability in the resulting phase so that further annealing does not lead to degradation. The main advantage in using stoichiometric implants currently lies in the insensitivity of the implanted samples to storage time. The fundamental processes involved in the different techniques are not clear, but further work may elucidate these points and reveal other advantages of the technique.

REFERENCES

[1.] P. R. Ashley, W. S. C. Chang, Ch. Buchal, and D. K. Thomas, *J. Lightwave Technol.* **7**, 855 (1989).
[2.] B. R. Appleton, G. M. Beardsley, G. C. Farlow, W. H. Christie, and P. R. Ashley, *J. Mater. Res.* **1**, 104 (1986).
[3.] Ch. Buchal, P. R. Ashley, D. K. Thomas, and B. R. Appleton, *Mat. Res. Soc. Symp. Proc.* **88**, 93 (1988).
[4.] Ch. Buchal, KFA Jülich, and T. Bremer, Univ. Osnabrück, (private communication).
[5.] D. B. Poker and D. K. Thomas, *J. Mater. Res.* **4**, 412 (1989).
[6.] M. A. McCoy, S. A. Dregia, W. E. Lee, and N. A. Sanford, *Mat. Res. Soc. Symp. Proc.* **152**, 271 (1989).
[7.] K. L. Sweeney and L. E. Halliburton, *Appl. Phys. Lett.* **43**, 336 (1983).