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Deep Structures Wet Etched into Lithium Niobate using a Physical Mask

by

Andrew Randles

A Thesis Submitted in
Partial Fulfillment of the
Requirements for the

**MASTER OF SCIENCE
IN
MECHANICAL ENGINEERING**

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December, 2002

Deep Structures Wet Etched into Lithium Niobate using a Physical Mask

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Andrew Randles

Date: 12/16/2002

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Nomenclature

Ar	- Argon
Au	- Gold
Cr	- Chrome
LiNbO ₃	- Lithium Niobate
PR	- photoresist
Ti	- Titanium

1. Abstract

The present work is an investigation and characterization of a new technique for etching and masking Lithium niobate (LiNbO_3) to realize high aspect ratio trenches. LiNbO_3 is a single crystal optically clear (from 350 nm to 5 μm wavelength), piezoelectric material. It is also inert to most reactants and has a high curie temperature (the temperature that a material loses its piezoelectric effect). These properties allow LiNbO_3 to be used as a sensor or actuator in harsh environments. To realize this actuator/sensor a multilevel lithium niobate deep etching technique is currently unavailable. The present work uses a chrome gold mask and a solution of hydrofluoric acid and nitric acid at 90 °C to etch the LiNbO_3 . The new wet etch method developed yields a an etch rate of 50 μm per hour on the -z face and a 250 nm per hour on the +z face.

2. Introduction

Lithium Niobate (LiNbO_3) is a single crystal, optically clear, piezoelectric material. Its curie temperature ranges from 1362 K to 1435 K (1992 °F to 2124 °F) (Abrahams, 2002) which is an order of magnitude higher than most PZT. For example Navy type II lead zirconate titanate's curie temperature is 350 °C. This gives LiNbO_3 devices the ability to work in harsher conditions and higher temperatures than conventional PZT. LiNbO_3 is chemically stable and inert to most reactants, with few wet etches. The most prevalent (LiNbO_3) wet etch used with LiNbO_3 is a solution of one part HF and two parts HNO_3 (Nassau et al., 1965), which is used in the research presented in this paper. LiNbO_3 properties allow use in harsh environments such as under the hood of a car, in the petroleum industry, in jet engines, and in other applications where actuators or sensors with fine precision must operate under harsh conditions. LiNbO_3 is typically implemented in devices for its nonlinear optical properties and its piezoelectric properties, but in the past the LiNbO_3 has not been etched than 2 μm deep. These devices included ridge waveguides, surface acoustic wave (SAWs), and optical modulators (Cheng et al., 1997; Madou, 1997).

The goal of this research is to characterize and demonstrate a conventional ultraviolet lithography method of masking and etching LiNbO_3 capable of multilevel lithography. Several masking techniques and materials such as gold, Cytop, polyimide, and Su-8, will be investigated.

3. Czochralski growth of LiNbO_3

Lithium niobate is a man made material, typically made by Czochralski pulling, similar to silicon wafer processing (Madou, 1997). A seed crystal is dipped into a LiNbO_3 melt and then slowly pulled out, forming a single crystal ingot of LiNbO_3 as it is pulled. For LiNbO_3 , obtaining a single ferroelectric domain was historically one of the largest challenges to fabricating wafers. A single domain LiNbO_3 crystal was needed so that the crystal properties are consistent for optical and piezoelectric applications. Most PZT's are poled in their solid state, however all the data before 1965 indicated that the Curie temperature of LiNbO_3 was above its melting temperature (Nassau, 1989). In 1965, K. Nassau attempted to reduce platinum impurities in LiNbO_3 from the crucible by applying 1000 volts to the pulled crystal with respect to the melt. This caused the crystal to grow with a single domain. To make single domain crystals nine parameters for the growth of the crystal need to be controlled (Nassau, 1989). Without this work the current research would not have been possible.

4. Physical Properties of LiNbO_3

The physical properties of LiNbO_3 are what make it an interesting and challenging material to work with. In this section the crystal structure and the piezoelectric and electro-optic properties are discussed. The piezoelectric and electro-optic properties of LiNbO_3 are important in industry and commercial applications.

4.1. Crystal Structure

The crystal structure of LiNbO_3 is distorted perovskite structure below its curie temperature and perovskite structure above its curie temperature. Figure 1 is a diagram of the unit cell for perovskite unit cell.

Figure 1: Unit cell for LiNbO_3 in paraelectric phase

Figure 2 is a diagram of a distorted perovskite structure. The paraelectric phase only occurs above the curie temperature for LiNbO_3 . Below the curie temperature the structure is the

distorted perovskite structure. The distorted perovskite structure is what gives LiNbO_3 its ferroelectric properties.

Figure 2: Unit cell for LiNbO_3 in the ferroelectric phase

In Figure 3 through Figure 6 are diagrams of the crystal lattice viewed from different angles.

Figure 3: LiNbO_3 crystal viewed along z axis

Figure 4: LiNbO_3 crystal viewed along x axis

Figure 5: LiNbO₃ crystal

Figure 6: LiNbO₃ crystal looking from the y axis

In Figure 3 through Figure 6 are diagrams of the LiNbO₃ crystal structure in its distorted perovskite structure. The positive z direction is determined by taking the crystal and applying a compressive pressure along the z axis. The +z face will have a negative charge on it as a result of the pressure (Barry, 2000 p. 7).

4.2. Piezoelectric Properties

Lithium niobate's piezoelectric matrix is in the form shown below,

$$\begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & -d_{22} \\ -d_{22} & d_{22} & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix}$$

Figure 7: Piezoelectric strain coefficient matrix

This matrix is used to transform forces applied to the LiNbO₃ crystal into charge generated from the piezoelectric effect. Table 1 Is the preferred set of piezoelectric strain coefficients according to Ballto.

Table 1: Piezoelectric strain coefficients (10^{-12} C/N) Ballato, A. "Second-order Piezoelectric Constants of LiNbO_3 ." *Properties of Lithium Niobate*. 2nd ed. Ed. K. K. Wong. London: INSPEC, The Institution of Electrical Engineers, 2002. 101-4.

d_{15}	d_{22}	d_{31}	d_{33}	T ($^{\circ}\text{C}$)
69.2	20.8	-0.85	6.0	25

As it can be seen in Table 1 the highest coefficient is for the d_{15} . The d_{15} represents one of the shear modes for the crystal. However the d_{22} coefficient is for strain applied in the y direction and the resulting charge produced on the y face. In Table 2 are the strain coefficients for Navy Type II PZT.

Table 2: Navy type II coefficients. *Navy Type II*. 25 June, 2002 . Piezo Kinetics. 10 Oct. 2002. <<http://www.piezo-kinetics.com/navytype2.htm>>.

<i>Piezoelectric Coefficient</i>	<i>(*10^{-12} C/N)</i>
d_{31}	-175
d_{33}	400
d_{15}	580

Even though LiNbO_3 piezoelectric coefficients are an order of magnitude less than PZT's as shown in Table 1 and Table 2, LiNbO_3 has some distinct advantages over PZT. LiNbO_3 has a higher curie temperature than PZT which makes it suitable for high temperature use. LiNbO_3 does not show much, if any, hysteresis when used as a sensor as shown by Nakamura. PZT has some hysteresis and creep because of domain reorientation within the PZT at room temperature (1989).

4.3. Electro-Optic Properties

The electro-optic properties of LiNbO_3 give LiNbO_3 the capability to be used as an optical modulator. When an electric field is induced in the LiNbO_3 crystal, the crystal's refractive index will change. The matrix describing this phenomenon is shown below.

$$\begin{bmatrix} 0 & -r_{22} & r_{13} \\ 0 & r_{22} & r_{13} \\ 0 & 0 & r_{33} \\ 0 & r_{42} & 0 \\ r_{42} & 0 & 0 \\ -r_{22} & 0 & 0 \end{bmatrix}$$

Figure 8: Electro-Optic properties of LiNbO₃ matrix

Kirkby compiled a list of the Electro-optic coefficients and tabulated them. In the table below is a summary of Kirkby's data.

Table 3: Electro-Optic coefficients for LiNbO₃. Averaged values from Kirkby, C. J. G.; updated by C. Florea. "Electro-optic Coefficients of LiNbO₃." *Properties of Lithium Niobate*. 2nd ed. Ed. K. K. Wong. London: INSPEC, The Institution of Electrical Engineers, 2002. 131-40. p 134

<i>Coefficient</i>	<i>Value (pm/V)</i>
r_{42}	32.2
r_{22}	5.96
r_{13}	10.25
r_{33}	31.31

The optical properties of LiNbO₃ are used with optical modulators and with ridge waveguides. A further discussion of optical modulators is in the next section.

5. Devices made with LiNbO_3

The applications of LiNbO_3 make use of its optical properties or its piezoelectric properties. A brief list of the products made with LiNbO_3 are discussed in this section.

5.1. Optical Modulator

An optical modulator is a device that takes light, splits it and then to one of the beams changes the phase of the beam. When the beams of light are combined back together if one beam is 180° out of phase with respect to the other beam, they will cancel out and result in darkness. LiNbO_3 is an excellent material for this application because of its electro-optical properties and that when a metal such as titanium (Ti) is diffused into the crystal lattice the LiNbO_3 can be used as a wave guide. In Figure 9 is a diagram of an optical modulator.

Figure 9: Optical Modulator

The electric field applied by the electrodes would be similar to what is shown in Figure 10.

Figure 10: Surface micromachined electrodes for optical switching (Barry, 2000 p. 24)

An improved design for the portion of the modulator shown in Figure 10 is shown in Figure 11.

Figure 11: Deep waveguide for optical modulators (Barry, 2000 p. 24)

Figure 11 shows a waveguide with the electrodes on the sidewalls of the LiNbO_3 , which results in field lines that are more uniform than the ones that are shown in Figure 10. This could lead to devices that are more efficient and have better switching characteristics. This present research presents a method of etching deep structures in LiNbO_3 that could be used to fabricate this device.

5.2. Surface Acoustic Wave Devices

Surface acoustic wave devices (SAWs) work by sending an input signal into one set of interdigitated fingers as shown in Figure 12. The electronic signal is converted into a physical wave, by the piezoelectric effect. This wave then propagates across the crystal to another set of interdigitated fingers. This second set of fingers converts the wave back to an electrical signal

by the piezoelectric effect in the crystal. These devices have been used as band pass filters, signal convolvers and lag elements.

Figure 12: Diagram of a Surface Acoustic Wave Device

SAWs are made by depositing a metal on the surface of the crystal and then patterning the fingers. Potentially with the etching technique described by this research it will be a possible to make SAWs by etching into LiNbO_3 which may give better characteristics compared with conventional surface micromachined techniques.

5.3. Domain Inversion for a Bimorph Actuator

One unique application of LiNbO_3 involved making an actuator, by inducing a domain inversion in one half of the crystal and applying a voltage over the domain inversion (Nakamura and Shimizu, 1989). This actuator is similar to a bimorph actuator in that it deflects

by causing one half of the cantilever to expand and the other half of the cantilever to contract. A diagram of this actuator is shown in Figure 13.

Figure 13: Diagram of bimorph actuator (Nakamura and Shimizu, 1989)

To induce the domain inversion the LiNbO₃ wafers were put in a furnace at a temperature close to the curie temperature. Then argon gas flowed over the top of the LiNbO₃. After 10 hours the domain inversion in the LiNbO₃ crystal would reach the mid plane of the crystal (Nakamura and Shimizu, 1989). This actuator demonstrated no creep or hysteresis. This is an advantage over most PZTs because most PZT actuators will display some creep or hysteresis (Nakamura and Shimizu, 1989).

6. Past Processing of Lithium Niobate

Optical system construction has been the focus of processing lithium niobate. Most studies have concentrated on making ridge waveguides in LiNbO_3 , however these structures were typically less than $2\text{ }\mu\text{m}$ tall. A ridge waveguide is used to guide light through a confined area. In LiNbO_3 these devices are areas of LiNbO_3 that have not been etched while the surrounding crystal has been etched. The limit of most methods is the etch rate or the etch depth. These techniques are cataloged in the following sections.

6.1. Reactive Ion Etching

An, reactive ion etching (RIE) of LiNbO_3 used a mixture of CHF_3 , CF_4 , CCl_2F_2 , O_2 and Ar. The etch rate for this was approximately $500\text{ }\text{\AA}$ per minute (Jackel et al., 1981). Pitt and Florea report an etch rate of $2000\text{ }\text{\AA}$ per minute using CF_4 at 15 Pa in a Parallel plate hollow cathode chamber with 1800 V peak to peak of RF running at 8 MHz (2002).

6.2. Laser Ablation

Laser processing can be used to remove LiNbO_3 by imparting enough energy into a small volume of material vaporize it. Christensen and Müllenborn used a KrF laser to remove LiNbO_3 and then moved the wafer to pattern the LiNbO_3 (1994). With this process they were able to achieve etch rates of $10^6\text{ }\mu\text{m}^3/\text{s}$. Barry also used a KrF laser which gave 1.46 Joules per cm^2 . With a shot frequency of 10 Hz and 3000 shots a trench $150\text{ }\mu\text{m}$ by $14\text{ }\mu\text{m}$ was obtained that was $70\text{ }\mu\text{m}$ deep (Barry, 2000 p. 146). This results in an etch rate of $490\text{ }\mu\text{m}^3/\text{s}$. This process is able to produce deep structures in LiNbO_3 .

6.3. Wet etching Techniques

Wet etch techniques have some advantages over dry systems. A wet etch, typically does not require expensive equipment besides etchants. To wet etch LiNbO_3 , either defects are introduced into the crystal lattice to improve the etching or a bulk wet etching is done. This section discusses these two methods of etching LiNbO_3 .

6.3.1. Proton Exchange

Proton exchange (PE) is the process of replacing Li^+ ions in the crystal lattice with H^+ ions. Next the wafers with proton exchange regions are etched. The etchant will selectively attack the areas with the crystal defects resulting from the PE. This method of etching is typically used to make ridge wave guides because the etch depth is typically less than $2\text{ }\mu\text{m}$ because that is the depth needed for ridge waveguides.

When PE is used, benzoic acid is typically the source of protons. The samples are left in contact with LiNbO_3 for one to six hours at elevated temperatures ($\sim 200\text{ }^\circ\text{C}$) (Cheng et al., 1997; Laurell et al., 1992; Lee and Shin 1995). The time for PE determined how deep the PE layer was. The PE layer is removed when the samples were put into the a solution of hydrofluoric and nitric acid. For a sample of LiNbO_3 placed in benzoic acid for six hours at $240\text{ }^\circ\text{C}$ followed by one hour of etching in HF and HNO_3 , the resulting etch depth was $1.6\text{ }\mu\text{m}$ on the +z face(Cheng et al., 1997).

The reason that the PE technique was not used in the present research was that the PE region only extends a finite depth into the wafer. In this research the goal was to etch into LiNbO_3 to a depth at least $200\text{ }\mu\text{m}$. To do this with the method described by Cheng et al. it would take 125 PE steps for a total time of 875 hours to etch into the LiNbO_3 $200\text{ }\mu\text{m}$.

6.3.2. Bulk etching with Hydrofluoric and Nitric Acid

Hydrofluoric (HF) and Nitric Acid (HNO_3) was originally used as a tool to reveal the domain inversion in LiNbO_3 (Nassau, 1965). Typically a solution of one part concentrated HF and two parts concentrated HNO_3 would be used at elevated temperatures (50°C to 110°C) to increase the etch rate. The etch would attack the -z face and would only attack local domain inversion regions on the +z face.

6.4. Domain Inversion and wet etch.

Another studied used HF and HNO_3 to make tall structures in lithium niobate that had an etch rate of approximately $1\ \mu\text{m}$ per minute, with a pattern created by domain inversion (Barry, 2000 p.48). Barry took advantage of the preferential etching of the -z face by HNO_3 and HF. As stated above, areas of the LiNbO_3 will not be etched because of local domain inversions in the crystal structure (Nassau, 1965). To invert certain section of the LiNbO_3 , Barry patterned photoresist on one side of the LiNbO_3 and applied a 22.5kV per mm field across the LiNbO_3 with liquid electrodes. A diagram of Barry's setup is shown in Figure 14.

Figure 14: Setup for inducing domain inversion (Barry, 2000 p. 48)

The poling in the LiNbO_3 was only inverted in the areas exposed by the photoresist (PR) as can be seen in Figure 14. Next, Barry put the sample in a solution of one part HF and two parts HNO_3 . Barry used solutions at various temperatures to determine the etch rate as a function of temperature. An etch rate of $55 \mu\text{m}$ per hour was theorized to occur if the etch solution would have been boiling (110°C) (Barry, 2000 (p.60)).

Figure 15: Dual etching in Barry's experiment. Barry, Ian. E. "Microstructuring of Lithium Niobate." Dissertation. University of Southampton, 2000. (p.52)

Figure 15 shows the cross section of a sample that was patterned and etched using Barry's domain inversion method. The sample used was scratched on one side and then snapped. That is the reason for the diagonal lines in the LiNbO_3 . One of the results from using the domain inversion is that the negative of the image is etched on one side and etched on the other (Figure 15).

7. New Wet Etching and Physical Masking Process for Lithium Niobate

As stated in the previous section the etching done with LiNbO_3 was typically less than $2\text{ }\mu\text{m}$. In Barry's research was able to produce tall structures however the ability to make multilevel lithography. In the research presented here fast etch rates with tall structures and multilevel lithography is demonstrated.

7.1. Wet Etch Processes

The first mask and etch combination, tested a photoresist (PR) mask and 49% HF solution. The result was that the PR mask peeled off and the LiNbO_3 was not etched. Next, dilute HF and BHF solutions were tested. In this case, the PR mask adhered to the surface with these etches, but the LiNbO_3 was not etched. A sample was then etched with HF and HNO_3 was prepared with Su-8 patterned on it and it was put in the HF and HNO_3 etch. The Su-8 did not adhere to the LiNbO_3 , but the LiNbO_3 was etched. A picture of the results from this etch are shown in Figure 16.

Figure 16: LiNbO₃ surface after four hours of etching. The scale is 0.1 mm and 5.3kV excitement voltage.

Once an effective etchant was found then a masking material was needed.

7.2. Masking

The harsh etchants used in this project require a mask to withstand as much as four hours of etching time and still protect the LiNbO₃. The mask needed to be processable with standard photolithography techniques such as wet etches or RIE patterning.

Several different masks were used with the LiNbO₃ with varying degrees of success. A summary of the masks and how they worked in the LiNbO₃ etch is shown in Table 4.

Table 4: Summary of masks used and the results of each mask

<i>Masking Material</i>	<i>Result</i>
photoresist (PMER AZ 900)	Was consumed by the HNO_3
Cytop	Withstood the etch but did not adhere
Polyimide	Withstood the etch but did not adhere
Su-8	Withstood the etch but did not adhere
Cr/Au	Gold mask survived with some undercutting of the Cr adhesion layer.
Au alone	Gold mask survived and in some areas adhered however in others there was sever underetching.

Each of the materials in Table 4 were deposited onto the surface of the LiNbO_3 and then patterned. Details of the results are listed with each material. Each mask, after patterning by photolithography, was put in a solution of one part of HF in a 50% solution in water and two parts HNO_3 at 70 % solution in water at 90 °C for thirty minutes. A diagram of the experimental setup is shown in Figure 17.

Figure 17: Setup for Etching LiNbO_3 . (Barry 2000 p. 49)

The etch solution was brought up to temperature on the hotplate, typically after an hour. Once the etch solution was at the desired temperature the LiNbO_3 samples were put in.

7.2.1. Cytop

Cytop is an amorphous fluorocarbon polymer distributed by Bellex International Corporation. Cytop was investigated because it has similar characteristics to PTFE, which was used as the material for the beaker and other parts in the etching setup shown in Figure 17.

Therefore the expectation is that it would stand up the LiNbO_3 etch.

The processing of Cytop is described below as suggested by Asahi Glass Company.

1. Spin OPR (HMDS) 2000 rpms 30 seconds
2. Put in 145°C oven for three minutes
3. Spin on Cytop - 811NMD at 500 rpms for 20 seconds
4. 2000 rpms 40 seconds
5. The following steps are using a hotplate, the times indicate the time spent at that temperature not the time to ramp up to it.
 - a. 60 °C 1 minute
 - b. 150 °C 1 minute
 - c. 240 °C 60 minutes
6. Ash for two minutes in auto asher at 130 watts
7. Spin on photoresist PMER AR 900 at 3000 rpms for 20 seconds
8. Bake at 90°C in oven for 1 hour
9. Expose with 770 mJ/cm²
10. Develop PMER P-6G for 2 minutes 40 seconds
11. Rinse in water twice for thirty seconds
12. Bake at 145 °C for 60 minutes
13. Ash the Cytop for one hour at 150 watts

In Figure 18 is a picture of the processed Cytop.

Figure 18: Cytop Mask after ashing for one hour.

In Figure 18 the PR mask is still on the surface of the Cytop after ashing. As stated in Table 4, the Cytop did not adhere to the surface of the LiNbO_3 when it was put in the LiNbO_3 etch. The reason that the CYTOP did not adhere is most likely due to the fact that there was little if any atomic interaction between the CYTOP and the LiNbO_3 surface. HMDS was used to try and improve the adhesion, but it did not. An adhesion promoter that was designed to work with fluoropolymers would might improve the adhesion between CYTOP and other inorganic substrates.

One possible method for improving adhesion was to apply a compressive stress on the Cytop film while it is being cured (Oh et al., 2002). On one borosilicate glass plate Cytop was patterned and another glass plate was brought into contact with each other at 160°C . A pressure of 7 MPa was applied for 30 minutes to the glass and Cytop sandwich. With a $1\ \mu\text{m}$ film of Cytop the glass glass interface had a bond strength of 2.2 MPa (Oh et al., 2002). The use

of this technique to increase the adhesion of the Cytop to the LiNbO_3 surface may make Cytop a viable option in the future as a masking material.

7.2.2. Polyimide

Polyimide is another name for nylon. The advantage of using polyimide is that it has good heat resistance and it is chemically stable. The polyimide used was made by Toray with the trade name of Photoneece. The Photoneece used in this research was a negative resist.

Process steps

1. Put four drops onto sample.
2. Spin on at 2000 RPMs for 20 seconds
3. Let sample sit for 10 minutes
4. Put on hot plate at 80 °C for 90 minutes covered
5. Expose with 4480 mJ/cm²
6. Develop for 6 minutes in Toray developer (DEV 505)
7. Rinse in IPA for 30 seconds x2
8. Put on hot plate at 150 °C for 30 minutes covered
9. Hot plate at 180 °C for 30 minutes covered
10. Hot plate at 270 °C for 30 minutes covered
11. Hot plate at 360 °C for 60 minutes covered

The polyimide mask that came from these process steps worked well, as seen in Figure 19.

Figure 19: Polyimide mask

Figure 20: Result from polyimide mask

The polyimide mask did survive the etch, however it did not adhere. With the proper surface treatment the polyimide may be able to adhere well to the LiNbO_3 , however with this experiment it did not work well. As stated with the CYTOP an adhesion promoter made for polyimide with inorganic substrates would improve adhesion.

7.2.3. Su-8 Mask

Su-8 was the first mask used with LiNbO_3 in LiNbO_3 etch. As it can be seen in Figure 16 the Su-8 mask did not work at all. Again, with the right surface treatment to the LiNbO_3 the Su-8 might have adhered better.

7.2.4. Chrome/Gold Mask

A Chrome (Cr)/Gold (Au) mask has been used as a mask for HNA etch (Hydrofluoric, Nitric and Acetic acid) which is the same as the etch used to etch the LiNbO_3 except for the acetic acid. To test this LiNbO_3 samples from Yamaju Ceramics Co., LTD. were cleaned with methanol and acetone, then Cr was evaporated with a CVC evaporator and Au sputtered with a Denton Vacuum Desktop II onto the surface surface of the LiNbO_3 . The Cr/Au mask was patterned using photolithography and etched with wet etches. The sample was put in LiNbO_3 etch for two hours at 90°C . The resulting structure is shown in Figure 21.

Figure 21: After two hours of etching at 90°C . The gray area on the right is the gold mask.

Figure 21 shows where the gold was still on the surface of the LiNbO_3 sample after etching. Looking at the crystal through the +z face, all that could be seen was the gold mask. This meant that the Cr adhesion layer had been completely undercut. Figure 22 is another area of the same sample shown in Figure 21, but shows part of the pattern where the gold adhered for some of the etching.

Figure 22: Area of working pattern partially protected by the Cr/Au mask

This indicated was that the surface of the LiNbO_3 was not clean enough. Also, the Denton Vacuum Desktop II did not produce a good Au layer because it is not capable of maintaining a good vacuum for sputtering. The process used here the LiNbO_3 sample is moved from the CVC evaporator to the sputtering tool in open air. A better method would for the Cr and Au to deposited in the same tool and not have the tool out gassed.

The rest of the samples used in this research followed this basic procedure. Three inch diameter, $400\ \mu\text{m}$ thick LiNbO_3 wafers were purchased from Crystal Technology, Inc. The wafers were Z cut wafers with an optical polish on both sides of the wafer. These wafers were diced into 20 mm squares on a Disco DAD 522 automatic dicing saw. The wafers were scratched with a diamond tipped pen to mark the +z face and the direction of the y axis. They were then cleaned using a combination of organic cleaning and RCA (refer to appendix 13.1 for details).

Approximately 20 nm of Cr and 800 nm of Au were sputtered onto the -z surface LiNbO_3 samples using an Eiko ES 350 multi target sputter. Photolithography was done and the

gold and was patterned using an noble metal RIE system (Abe et al., 2002). The chrome was patterned by the ion impacts on its surface during the etching of the gold. Next the sample was put in the LiNbO_3 etch for 30 minutes at 90 °C. The apparatus used to etch LiNbO_3 is shown in Figure 17. This was to etch into the lithium niobate approximately 25 μm . The results of this etch is shown below.

Figure 23: Trench etched in LiNbO_3 after etching for 30 minutes

To do the second level photo lithography, the Cr/Au mask was then removed and the substrate cleaned again. Another layer of Cr/Au was sputtered using the same procedure as listed above. This mask was patterned using AR 900 photoresist. The area to be patterned is shown in green in Figure 24. The first level photo lithography is shown in blue.

Figure 24: Two level mask design for an actuator. The green represents photo level two with an etch of approximately 200 μm deep trenches and the blue is photo layer one with an etch of 25 μm deep trenches.

The PR effectively fills in the trenches from the first level protecting the Cr/Au mask. The PR is patterned and then the Cr/Au mask underneath is etched. This is shown in Figure 25.

Figure 25: After etch for photo level 2. The photo level still has Cr/Au mask and PR mask in the trench. This represents an area in Figure 24 where the blue and green boxes come together.

Figure 25 shows that the two etched sections of LiNbO_3 come together. Figure 25 demonstrates multilevel masking using a Cr/Au mask.

7.3. Gold sputtered directly onto LiNbO_3

One of the advantages of using this type of mask is that it would remove the chrome adhesion layer which is etched by the LiNbO_3 etch. Because there are two dissimilar metal in contact with each other and in contact with an ionic solution, an electrolytic cell is setup between the Au and Cr. This electrolytic cell accelerates the etching of Cr. When this happens, it exposes more of the LiNbO_3 to the etch solution.

Gold was sputtered using two different methods to test how it adhered to the LiNbO_3 during the LiNbO_3 etch. First, Au was sputtered in a heated chamber and in the second method Au was sputtered in an argon (Ar) and oxygen (O_2) atmosphere. Mattox found that adhesion strength of Au films on silica substrates was significantly increased by sputtering Au in a partial atmosphere of O_2 (1966).

7.3.1. Gold sputtered onto a heated substrate

For the gold sputtered at an elevated temperature test, LiNbO_3 substrates were cleaned and then put in the Eiko sputtering machine. The substrate holder temp was set to 150 °C, the chamber pressure was 5 mTorr, and the Ar gas flow rate was 5 sccm. With these settings, 800 nm of gold was sputtered on to the -z face of the LiNbO_3 . photoresist was patterned and then the gold was etched using an iodine-based gold etch. The sample was then put in the lithium niobate etch for 45 minutes. The resulting etched sample is shown in Figure 26.

Figure 26: Results of Au mask sputtered with the substrate heating. Gold mask peeled off during etching. The semi transparent blue box represents the original opening in the mask. (not to scale)

Figure 26 is an area where the gold completely peeled off the LiNbO_3 . Figure 27 shows where the gold pattern remained on the surface of the LiNbO_3 .

Figure 27: Section of gold mask that adhered. The brown color is the PR after etching.

The brownish color on top of the gold is what is left of the PR in Figure 27. It can also be seen in Figure 27 that the gold film is falling into the areas where LiNbO_3 has been undercut because there is nothing under the Au film.

A profile of the area etched after mask removal shows the LiNbO_3 was undercut.

Figure 28: Etch Profile of the Au mask after the removal of the Au.

The blue line in Figure 27 indicates the path of this scan. As can be seen, the LiNbO_3 was severely undercut by the LiNbO_3 etch because the gold mask did not adhere to the surface of the LiNbO_3 .

7.3.2. Gold sputtered in an O_2 Atmosphere

The Au sputtered in a partial oxygen environment was processed in the same way as the gold film was processed above except an Anevla Multi Target was used as the sputtering tool. Figure 29 is the sputtered film with the patterned PR on top.

Figure 29: Picture of the surface of Au mask sputtered in oxygen atmosphere with patterned PR.

Because the black dots were unidentifiable features, the sample was put in and SEM to determine what the black dots were.

Figure 30: SEM of gold sputtered in oxygen atmosphere after patterning the Au film with a wet etch

The bumps in the film are most likely the different grains of the Au film. These grains were grown in a more prominent manner because of the O_2 in the sputter chamber. Figure 30 also showed that the black dots in Figure 29 were not pin holes.

The result from the gold mask sputtered in an oxygen environment is that the gold did not adhere well in the patterned areas. This can be seen in Figure 31, which is a picture of the etched area of the $LiNbO_3$ looking through the +z face of the sample so that the gold mask and the etched areas of the $LiNbO_3$ can be seen.

Figure 31: Severe undercut of the gold mask sputtered in a oxygen environment

In this area it can be seen that there is significant undercut of the LiNbO_3 by the etchant. The reason that this gold film did not adhere because gold requires an adhesion layer (chrome or titanium) to stick to most substrates.

7.3.3. Gold Adhesion Promotion by Low Energy Ion Bombardment

To increase the adhesion of gold films deposited directly on to the surface of LiNbO_3 one could use procedure similar to what Pedraza suggested for the adhesion of gold films to sapphire (Pedraza, 1999 p. 266). Pedraza cleaned sapphire substrates and bombarded them with 7-keV Ar^+ ions and then annealed them in air. Pedraza found that the adhesion strength of the Au film was stronger than the epoxy used in the testing (70.4 MPa) compared to samples in which Au was deposited without the ion bombardment (4.7 MPa) (Pedraza, 1999 p.

268). In the future this method may allow directly deposited gold films to adhere to the surface of LiNbO_3 .

7.4. Cr/Au/Au

With this mask the idea was that a second layer of gold after patterning the Au/Cr would protect the Cr and prevent lateral etching of Cr while in the LiNbO_3 etch. As the Cr is being laterally etched by the LiNbO_3 etch the LiNbO_3 etch is also etching the LiNbO_3 , causing the LiNbO_3 to be undercut. Because Au does not adhere directly to LiNbO_3 the Au would come off the substrate but would adhere to the sidewalls of the Cr. The process steps for this mask are the same as the Cr/Au mask used for the main process until the sample is put the LiNbO_3 etch.

The extra process steps are as follows.

1. Strip PR
2. Clean with typical procedure using only the organic solvents
 - a. Gold and H_2O_2 reaction produce excess gases (O_2 and H_2) (Explosion hazard).
3. Put in Eiko Sputter to sputter Au
 - a. 5 sccms of Ar
 - b. 300 Watts of RF power
 - c. 160 nm (1 minute)
4. Put in LiNbO_3 etch

The Cr/Au/Au mask gave similar results as the Cr/Au mask. The only noticeable difference was how straight the side wall of the trench was as can be seen in Figure 32 for the Cr/Au/Au vs.

Figure 23 or Figure 44 for Cr/Au.

Figure 32: Results of Cr/Au/Au mask

Figure 32 shows one example of the etch pits caused by pin holes in the Au mask seen during the research. Further discussion of pinholes in the Au mask is in section 7.7. The extra Au layer does not reduce the undercut of the LiNbO_3 in the LiNbO_3 etch.

7.5. The z^+ face etching

As it has been stated before the $+z$ face is etched much slower than the $-z$ face. In Figure 33 is the profile of the $+z$ face after four hours of etching at 90°C . As it can be seen in the figure there is approximately a $1\ \mu\text{m}$ step between the protected area and the unprotected area. This puts the etch rate at approximately $250\ \text{nm}$ per hour or $42\ \text{\AA}$ per minute.

Figure 33: Profile of the +z face etch

The second way that +z face is affected by the LiNbO_3 etch is that local areas of domain inversion are attached preferentially. These areas act the same as the -z face. This is shown in Figure 34.

Figure 34: +z face after two hours of etching

This SEM picture of the +z face of the lithium niobate shows the affect of the LiNbO_3 etch for two hours at 90 °C.

7.6. RIE Etching of LiNbO_3

It was found while using the RIE system for etching gold discussed previously, that LiNbO_3 was etched. A sample of LiNbO_3 had one micrometer of gold sputtered in a partial oxygen atmosphere and PR was patterned on the surface. After 23 minutes of etching in the RIE system, in some areas the gold and the PR mask were completely removed. The sample was put in a proflometer to determine how much LiNbO_3 had been removed. After 23 minutes of etching the 1 μm of gold was removed plus 500 Å of LiNbO_3 was also removed. The typical etch time for gold that thick is ten minutes, so the approximate etch rate of the LiNbO_3 is less than 50 Å per minute. The etching was most likely do to the physical removal of the LiNbO_3 rather than by chemical action.

8. Challenges with using a Cr/Au Mask

There were several unique challenges to using a Cr/Au mask and processing that mask. The method used to process the Cr/Au mask had a significant implications with the results from etching the LiNbO_3 . The two challenges with processing the Cr/Au mask found while doing the research for this paper were the undercut of the Cr adhesion layer before being put in the LiNbO_3 etch. The second problem was with pin holes in the Cr/Au mask.

8.1. Undercut of Cr Adhesion during Mask Processing

During this research, one of the initial problems encountered was that the LiNbO_3 was being undercut more than expected. An example of this can be seen in Figure 35. Figure 36 is the design of the mask where the shaded green areas are where the mask opening are.

Figure 35: Etched LiNbO_3 showing the results of the undercut Cr after the Au mask has been removed

Figure 36: Mask design, areas in green are openings in the mask.

Nemirovsky et al. explained the reason for the undercut of the Cr adhesion layer. To pattern the Au mask an iodine based Au etch was used. When this etch reaches the Cr layer it sets up an electrolytic cell between the Cr/Au and the gold etch. This causes the Au to be etched approximately an order of magnitude faster at the interface between the Cr/Au layers than if only Au was being etched (Nemirovsky et al., 1978). The result of this can be seen Figure 37.

Figure 37: Demonstration of Cr undercut

Figure 37 the Cr/Au mask looking through the +z face of the LiNbO_3 . The gray area is the Cr and the yellow is the Au. The brown area is the patterned area of the Au. As shown in Figure 37 the Cr has been undercut. When this was put in the LiNbO_3 etch the result is as shown in Figure 35.

Another related problem, is that larger patterns take longer to etch in the gold etch than smaller patterns, as shown in Figure 38.

Figure 38: Excess gold to be etched

This is a sample with 800 nm of gold has been etched in an iodine based gold etch for 7 minutes. The thinner area is a 50 μm gap while the larger brownish area is a 1 mm square contact pad. To fully remove the Au, the sample would have to be left in the Au etch for an extended period of time after the Cr is exposed. This would mean that the undercut of the Au by the mechanism described by Nemirovsky et al. would become an even larger problem. An RIE system for etching Au, Pt and Cu, which uses a combination of $\text{CO}/\text{NH}_3/\text{Xe}$ was used to solve this problem (Abe et al., 2002). With an RIE system there isn't any ionic solution for the electrolytic cell to work with.

8.2. Pin holes in the Mask

During processing, pin holes were observed become a problem with longer etch times (Figure 32). Pinholes in the Cr/Au mask were a problem for two reasons. The first was

discussed in the previous section, the lateral etching of Au at the Cr/Au interface when using an iodine etch for gold. The second, was that in the LiNbO_3 etch the Cr adhesion layer is consumed. As this happens more of the LiNbO_3 is exposed to LiNbO_3 etch. So these pinholes in the Au mask result in etch pit shown in Figure 32.

To solve the pinhole problem a more aggressive cleaning method was used and a thicker PR was used. When pin holes were a problem LiNbO_3 samples were cleaned using the procedure described in Appendix section 13.1. before any metal deposition was done. Originally that procedure had been used but did not include steps 11-15 (organic cleaning and piranha etch). After adding steps 11-15 (RCA cleaning) the number of pinholes in the Cr/Au mask were reduced.

Another change implemented to reduce pinholes in the Au mask, was to reduce the number of pinholes in the PR. To reduce the number of pinholes in the PR a thicker resist was used. This meant that small surface topology would be better covered on the surface of the LiNbO_3 . With thinner PR when it covers protrusions on the surface of the substrate the resist is thinner around the protrusion. With thicker PR protrusions small protrusions do not affect the thickness as much than with thinner PR.

9. Etch Profile

The etch profile is an important characteristic when working with bulk etches. For example the KOH etch of (100) silicon will give sidewalls with 54.7 degree angle. This is because this etch follows the $\langle 111 \rangle$ planes in the silicon. Similarly, LiNbO_3 also etches along crystal planes. Because of the crystal structure of LiNbO_3 and the chemical make up of the crystal and the etch solution, several different crystal planes are revealed during etching. This was demonstrated by Barry (See Figure 15).

During the experimentation for this thesis, the same type of phenomenon was seen. One example of this is shown in Figure 39.

Figure 39: Etch profile for LiNbO_3 after 4 hours in LiNbO_3 etch.

Figure 39 shows the cross section of an area of the LiNbO_3 after being broken that was exposed to the LiNbO_3 etch for four hours. It can be seen that the angle on the side wall changes.

Figure 40: Etch profile in LiNbO_3 . The top of the wafer is along the white dashed line.

Figure 40 depicts the etched cross section of the etched LiNbO_3 . The cross section in Figure 40 is based off the pattern from the photo mask shown in Figure 41. The texture of the walls of the trenches can be seen on the left of Figure 40.

Figure 41: Mask design showing where the samples were broke to look at the cross section

Figure 41 shows the mask that was used to define the etching done in Figure 40 and Figure 39. In Figure 40, on the right is a cross section of how the trenches are etched. As it can be seen the trenches self terminate at a point. The etch rate perpendicular to the trenches is slow compared to parallel. However there is still lateral etching because the Cr mask under the gold is etched in the etching solution. As the Cr is removed the trench gets wider. Figure 40 shows the etch profile for LiNbO_3 with a $50\ \mu\text{m}$ opening and Figure 42 shows the etch profile for an opening of $100\ \mu\text{m}$.

Figure 42: Etch profile after four hours of etching with 100 μm opening in the mask

Figure 42 was obtained using a Tencor P10 profilometer. Figure 43 shows what the LiNbO_3 sample looked like before the gold mask was removed.

Figure 43: 100 μm openings etched for four hours at 90 $^{\circ}\text{C}$

As it can be seen in Figure 43, the gold mask has a opening of 100 μm . However, there is under etching and the gold mask is starting to fall down on the edges. This can be seen from the shadows in the gold mask. Figure 44 is etched LiNbO_3 after the removal of the gold mask. All that remains on the surface is chrome mask.

Figure 44: Same conditions as Figure 43 without the gold mask

When designing these trenches the undercut of the mask needs to be designed into the mask. The undercut of the Au mask in the LiNbO_3 etch was experimentally determined to be 10 μm per hour. In areas where the LiNbO_3 did not self terminate the etch rate was 50 μm per hour. Because the experimental setup did not maintain a constant solution the temperature, the etch rate varied from 40 μm per hour to 70 μm per hour. Barry demonstrated that there is an exponential relationship between the etch rate and the temperature of the solution and for a solution at 90 $^{\circ}\text{C}$ the etch rate would be 50 μm per hour (Barry 2000, p. 60). In the future, a PTFE coated thermocouple for temperature feedback to the the hotplate would give more repeatable results.

10. Future Work

Future work with the etching technique will be applying it to different applications and devices to make harsh environments sensors or optical devices with improved operating characteristics.

10.1. Actuator/Sensor

From the current experimental done in LiNbO_3 the process steps to make high aspect ratio structures in LiNbO_3 are listed below.

1. Clean wafers with organic, piranha etch, RCA cleaning procedures
2. Sputter 20 nm of Cr and 800 nm of Au
3. Do photolithography and pattern Au using Au RIE system
4. Put in solution of 1 part HF and 2 parts HNO_3 at 90 °C

The time that the LiNbO_3 remains in the etch in step four depends on the desired trench depth.

The etch rate for that solution at 90 °C is 50 μm per hour.

The applications of this type of bulk machining in LiNbO_3 would be to make deep three dimensional structures. With the research presented here it would be possible to make an actuator / sensor in LiNbO_3 . Detailed process steps for making this actuator are listed in section

13.1. A figure of what these process steps would look like are shown in Figure 45.

The basic process steps to make the actuator shown in Figure 45 are listed below.

Figure 45: LiNbO₃ actuator process steps

1. Etch in first level, electrical interconnects
2. Etch in the electrodes
3. Electroplate in nickel
4. Dice wafer to release the actuator.

10.2. Pressure Sensor

Another application would be a piezoelectric pressure sensor. A diaphragm could be etched into the lithium niobate. Then electrodes could be patterned onto both sides of the diaphragm to read out a voltage proportional to the pressure differential between both sides of the diaphragm. Before this could be, implemented a study of the uniformity of the crystal thickness at the bottom of trenches would need to be investigated and determine how non

uniformities due to local domain inversions in the crystal would affect the accuracy of the pressure sensor.

10.3. *Optical Modulator*

An optical modulator could be made in the LiNbO_3 , but instead of putting the electrodes on the surface of the LiNbO_3 the electrodes could be in the LiNbO_3 to give improved characteristics for the modulator. Before the device described in Figure 11 can be achieved a method of creating vertical sidewalls in the LiNbO_3 will needed to be investigated.

11. Conclusion

This research has demonstrated the feasibility of creating deep multilevel structures in LiNbO_3 using a Cr/Au mask and a solution of one part HF and two parts HNO_3 at 90 °C. This etched the LiNbO_3 at 50 μm per hour. This etch rate is faster than what Barry reported (2000, p. 60), but this could have been due to slightly different reagent concentrations or not having good temperature control during the present research. Several other masking materials were tested, but in all cases, poor adhesion was the limiting factor. With better adhesion promoters, Cytop, Polyimide or Su-8 could prove to be excellent masks. These mask would not have the inherent problems of the Cr/Au mask with the accelerated etching of the Cr layer due to the electrolytic cell setup between the Cr, Au and LiNbO_3 etching solution.

This research has shown a multilevel etch technique for deep structures in LiNbO_3 . Prior to this the only research that had been done relating to deep structures wet etched into LiNbO_3 was done by Barry. However Barry's work did include multilevel structures because that would be difficult to produce with that method.

Cleaning the surface of the LiNbO_3 was critical to achieving good results from the metal mask. Using a RIE system to pattern the gold eliminated the undercut of the Au when using an iodine based etchants to pattern the Au mask. These steps resulted in a method for patterning and etching deep (~200 μm) multilevel structures into LiNbO_3 with applications to sensors and actuators and optical modulators. The experimental etch rates determined were 50 μm per hour on the -z face and 250 nm per hour on the +z when the etching solution temperature was 90 °C.

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13. Appendix

This appendix describes the process steps required to make the actuator described in section 10. Also included are some precautions for working with LiNbO_3 .

13.1. Procedure for Fabricating LiNbO_3 Actuator

1. Dice wafer
2. Clean wafer
 - (a) Rinse in DI water + ultrasonic 4x20 sec.
 - (b) Used methanol CH_3OH + ultrasonic 30 sec.
 - (c) New methanol + ultrasonic 30 sec.
 - (d) Old trichloroethane $\text{C}_2\text{H}_3\text{Cl}_3$ + ultrasonic 15 min
 - (e) New trichloroethane + ultrasonic 15 min
 - (f) Used methanol + ultrasonic 30 sec.
 - (g) New methanol + ultrasonic 30 sec.
 - (h) DI water + ultrasonic 4x20 sec.
 - (i) H_2SO_4 96% + H_2O_2 30% (10:1) 15 min
 - i. When doing this step Put H_2O_2 in first then H_2SO_4 .
 - ii. Let stand for one minute
 - iii. Lower samples in, be sure that none of the samples are touching
 - (j) DI water + ultrasonic 4x20 sec.
 - (k) NH_4OH + H_2O_2 30% + H_2O (1:1:6) boiling 15 min
 - (l) DI water + ultrasonic 4x20 sec.
 - (m) HCl + H_2O_2 30% + H_2O (1:1:6) boiling 15 min
 - (n) DI water + ultrasonic 4x20 sec.
 - (o) Spin Dry
 - (p) Bake at 145°C 30 min
3. Place sample in 1 part HF 49% and 2 parts HNO_3 60% at 50°C for five minutes. (For micro roughness)
4. Clean wafer (repeat step 2)
5. Mask with Chrome Gold
 - (a) Deposit 500 angstroms of Cr
 - (b) Deposit 1500 angstroms of Au
 - i. Both steps done in the Eiko Sputter
 - ii. 300 watts, 5 sccms of Ar, 5 mTorr pressure
 - iii. 15 seconds of Cr
 - iv. 5 minutes of Au
 - (c) Spin on PR 800 cp 30
 - (d) Bake for 30 minutes at 90°C
 - (e) Expose for 10 seconds

- (f) Develop in NMD-3 developer for 80 seconds, rinse and spin dry
- (g) Hard bake at 145°C for 30 minutes
- (h) Etch Au in CCP RIE
- 6. Lithium niobate etch for thirty minutes at 90°C (25 μm)
- 7. Remove Mask
- 8. Clean wafer (step 2)
- 9. Mask wafer with Cr/Au
- 10. Photolithography
 - (a) Use PR PMER AR 900
 - (b) Spin on at 3000 rpms for 20 seconds
 - (c) Bake at 90°C in oven for 1 hour
 - (d) Expose for 55 seconds
 - (e) Develop PMER P-6G for 2 minutes 40 seconds
 - (f) Rinse twice for thirty seconds
 - (g) Bake at 145 °C for 30 minutes
- 11. Pattern Gold in CCP RIE
- 12. Lithium niobate etch for electrodes, 4 hours at 90°C (200 μm trench)
- 13. Remove mask
- 14. Clean wafer (step 2)
- 15. Electroplate in Nickel
- 16. Dice wafer to release actuators.

13.2. LiNbO_3 Breaking Problems

On several occasions samples broke when they were put in the H_2SO_4 and H_2O_2 solution. The reason was that there were two samples in contact with each other. In the step before this the samples were rinsed in water and in most cases had drops still on the surfaces. If two samples came together and one or both had water on them capillary forces would draw the two together and create a thin film of water in between the samples. When these samples were put in the Piranha Etch they would break because the solution was hot, but the water in between the samples was cool. The water would not warm up uniformly because the Piranha Etch would not be able to flow between the samples. The resulting thermal stress would break the samples.