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(54) **METHOD OF ETCHING FERROELECTRIC MATERIAL**

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(57) **ABSTRACT**

A method of etching a ferrolectric material is disclosed whereby a single layer of ions is implanted into a surface of the film and then, without first annealing the substrate, the material between that surface and the layer of ion implantation is etched away. Such a method has the benefit of being faster and much less costly as compared to prior art methods. A single ion implantation of sufficient energy causes a high level of electronic damage near the surface of the material and a high level of crystalline damage at the ion implant level. While it is well known that crystalline damage greatly increases the etch rate of a ferroelectric material, the inventors have discovered that the aforementioned electronic damage also substantially increases the etch rate of the material. Since damaged lithium niobate etches at a much faster rate then undamaged lithium niobate, no annealing is necessary to create an etch stop. Additionally, since there is sufficient damage, either electronic or nuclear, continuously from the surface of the material to the implant layer, multiple ion layer implantations are not necessary.

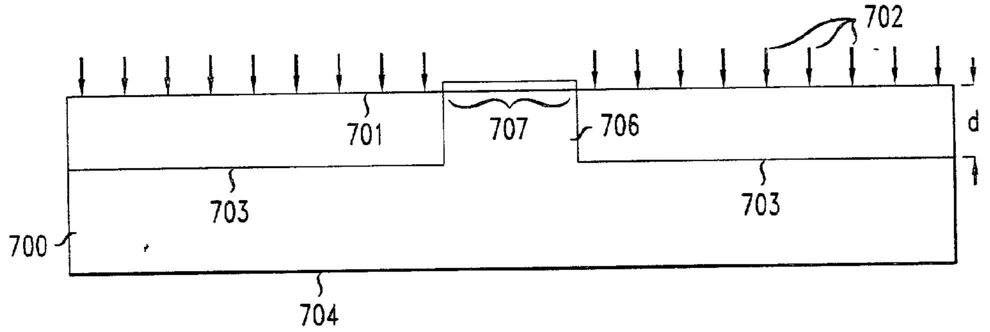


FIG. 1
(PRIOR ART)

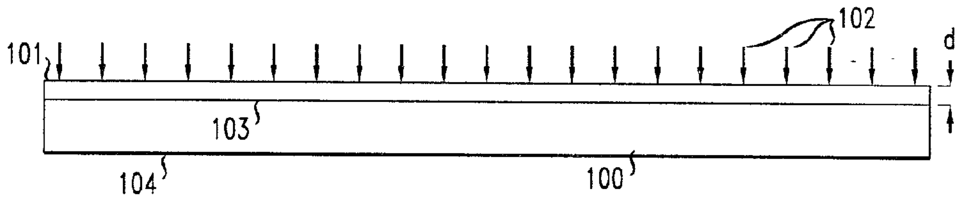


FIG. 2
(PRIOR ART)

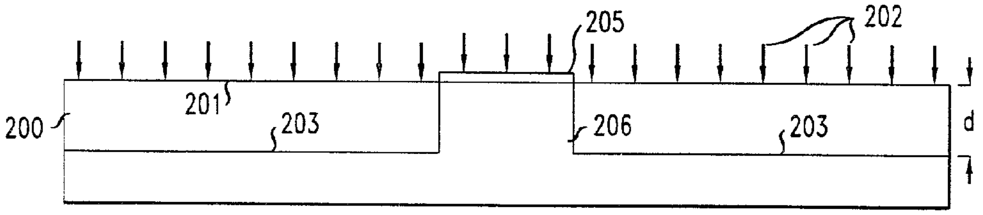


FIG. 3
(PRIOR ART)

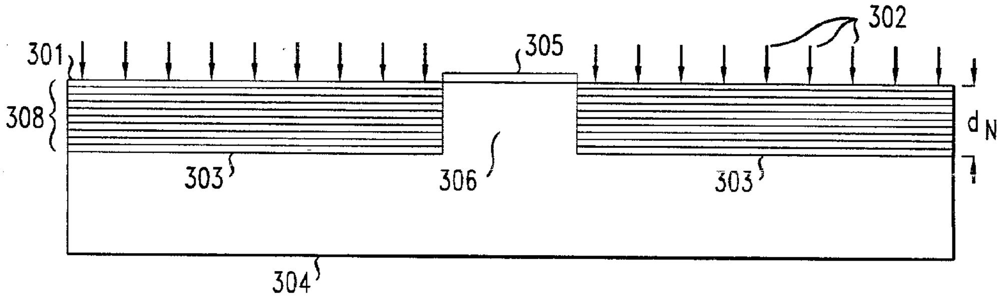


FIG. 4

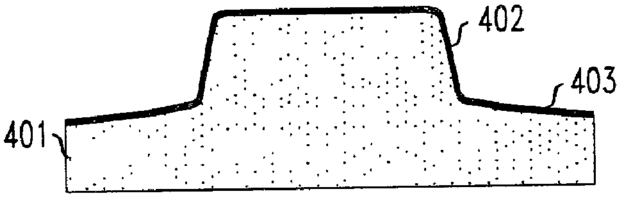


FIG. 5

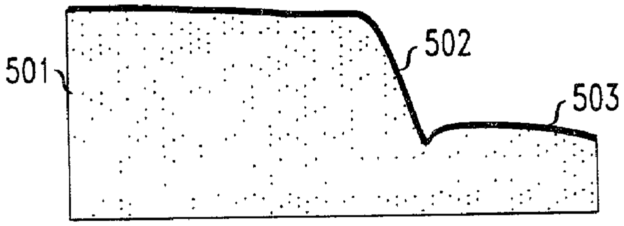


FIG. 6

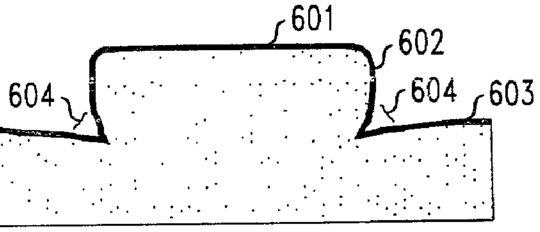


FIG. 7

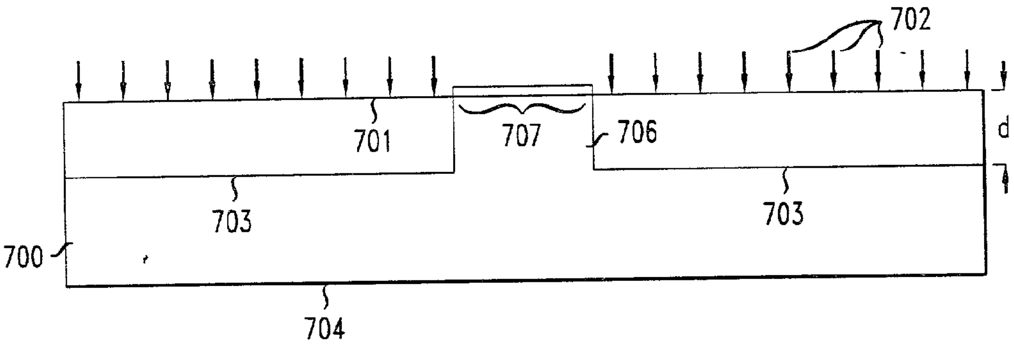

702
d
701
707
706
703
703
700
704

FIG. 8

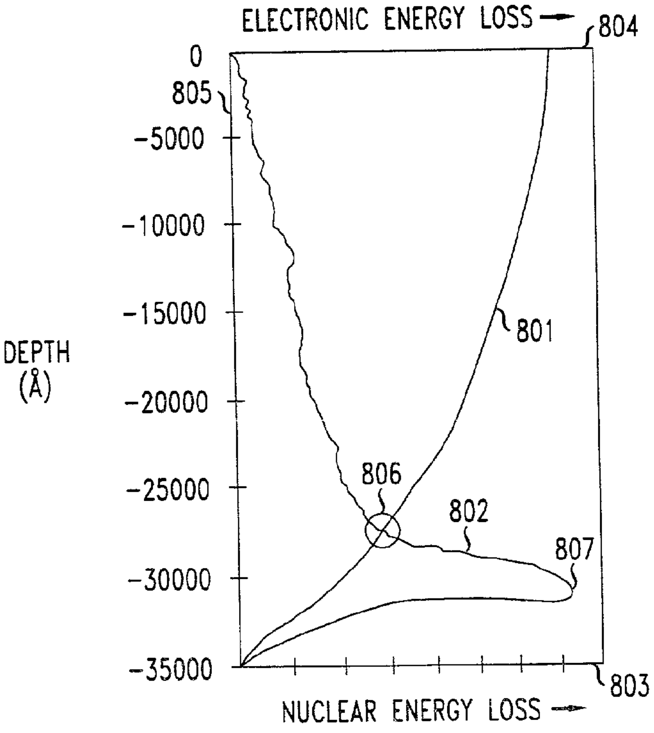
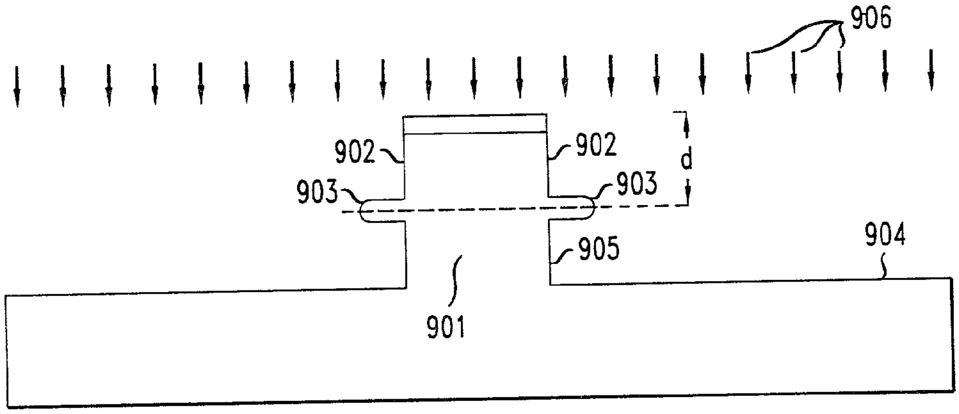

ELECTRONIC ENERGY LOSS →
804
0
805
-5000
-10000
-15000
-20000
-25000
-30000
-35000
DEPTH (Å)
801
806
802
807
803
NUCLEAR ENERGY LOSS →

FIG. 9



METHOD OF ETCHING FERROELECTRIC MATERIAL

FIELD OF THE INVENTION

[0001] The present invention relates to etching structures into ferroelectric materials.

BACKGROUND OF THE INVENTION

[0002] Lithium nobate ($LiNbO_3$) and other ferroelectric materials are often used as hosts for waveguides in various optical devices such as optical switches, electro-optic modulators, and optical wavelength conversion devices. In these applications, it can be particularly advantageous to be able to form either a relatively thin (i.e., <10 μm) film layer of such material, due to its strong optical confinement properties and large optical nonlinearities, and/or to etch structures into the surface of the ferroelectric material, such as ridges or gratings.

[0003] Many techniques have been used in the past to form suitable waveguide structures in lithium niobate, such as thin film waveguides and ridge waveguides. When forming such waveguides, the lithium niobate is commonly etched, i.e., parts of the lithium niobate are removed in order to form the desired structure. Specific well-known etching techniques used in the past include ion milling, plasma etching, and ion implant wet etching. Ion milling and plasma etching both involve bombarding lithium niobate with ions and either a) physically sputtering away portions of that surface (i.e., ion milling), or b) causing a chemical reaction between the ions and the surface of the material such that volatile species are formed, resulting in etching of that surface (i.e., plasma etching). On the other hand, prior processes characterized by ion implantation followed by wet etching formed waveguides by bombarding either the −z crystal surface or the +z crystal surface of the lithium niobate with a single implant of ions, for example oxygen ions. Depending upon the structure to be created, various areas of the bombarded surface could be masked to prevent ion implantation in those areas. The depth at which the ions are implanted is dependent upon the energy to which the ions are accelerated and is typically <10 μm. When accelerated to a particular energy, the ions are implanted into the lithium niobate at a particular depth, hereafter referred to as the implant layer, that is proportional to that particular energy with little damage to the crystalline structure of the lithium niobate between the bombarded surface and that depth. For example, oxygen ions implanted at an energy of 3.6 MeV have been found to produce an implanted layer approximately 2 μm below the surface.

[0004] While the majority of the damage to the crystalline structure is near the implant layer in such implanting methods, it has been noted that electronic damage may occur in the region between the surface and that implant layer. To remedy this electronic damage, prior processes annealed (heated) the ion-implanted material. Such annealing also had the simultaneous effect of creating, at the oxygen ion implant layer, a layer of material that was highly resistant to etching, known as an "etch stop." After this annealing, mechanical polishing and/or a chemical wet etchant was applied to the −z side of the lithium niobate and the lithium niobate between the −z surface and the ion-implant etch stop was removed, leaving either a thin film or a more complex structure formed as a result of the aforementioned masking.

[0005] Variations in the ion implant process to create a structure in lithium niobate, for example a ridge waveguide, have been developed. For example, the aforementioned plasma etching method has been used in conjunction with a single oxygen ion implant step with no annealing step between the implant step and the etching step. Additionally, one prior art process known as crystal slicing utilizes a single hydrogen or helium ion implant, as opposed to an oxygen ion implant, followed by a rapid thermal annealing process. Such rapid annealing is characterized by a rapid temperature increase to a specific temperature (e.g., 800° C.) followed by a rapid decrease back to the starting temperature. Instead of producing an etch stop at the ion implant layer, the damaged material at that layer after the annealing is characterized by a much faster etch rate than the surrounding material. By then immersing the ion-implanted layer in a chemical etchant, the damaged material is etched away, thereby undercutting the material between the ion-implanted surface and the ion implant layer. That material can then be readily removed thereby exposing the desired structure in the ferroelectric material.

[0006] Another ion-implant method of creating a structure in lithium niobate, for example a ridge waveguide, masks the ridge portion of the lithium niobate and, instead of performing a single ion implant, uses several ion implants at various depths to create a relatively continuous volume of nuclear damage which, in turn, results in significant damage to the crystalline structure of the lithium niobate. Either surface (the +z or the −z crystal surface) may be used in this process. The wet etchant is then applied to the implanted surface to etch away the damaged material, leaving a ridge of undamaged lithium niobate. This method has the advantage of eliminating the need for annealing the lithium niobate after ion implantation to reduce electronic damage. While annealing the material after implantation was used in prior processes to form an etch stop, such an etch stop is unnecessary when multiple layers of crystalline damage are created. By knowing the etch rate of the chemical when applied to the crystalline-damaged lithium niobate, and emersing the material into the chemical etchant for a specific time, a given etch depth can be achieved. Since undamaged lithium niobate is etched at a much slower rate than is crystalline damaged lithium niobate, it is not necessary when using these prior processes to precisely control the etch time. Therefore, it would appear that such a method of performing ion implants at multiple levels without subsequent annealing, followed by chemical etching, would have benefits over prior processes that use an intermediate step of annealing. However, such multiple-level ion implants are very costly and take a great deal of time to accomplish as compared to single-layer implant methods.

SUMMARY OF THE INVENTION

[0007] The present inventors have discovered that various optical waveguide structures may be formed in a ferroelectric material, such as lithium niobate, by implanting only a single layer of ions into a surface of the film and then, without first annealing the substrate, etching away the material between that surface and the single layer of ion implantation. Such a method has the benefit of being faster and much less costly as compared to prior art methods.

[0008] When ions are implanted into a ferroelectric material, two different types of damage occur: nuclear and electronic. When ions are implanted with sufficient energy into lithium niobate and other ferrolectric materials, crystalline damage due to nuclear interaction associated with this implantation is very low until the ions begin to slow. At this point the ions begin to collide with the atoms of the physical crystalline structure of the material and cause a layer of nuclear damage at a depth dependent upon the initial energy of the ion bombardment. This relationship is such that the higher the initial energy of the ions, the deeper those ions travel within the substrate prior to creating the layer of nuclear damage.

[**0009**] While the crystalline damage is low until the energy of the ions begins to dissipate, electronic damage is at its maximum near the surface into which the ions are implanted. This electronic damage gradually declines in magnitude as the energy of the ions declines. Therefore, after ion implantation, the resultant structure is characterized by a relatively high level of electronic damage and low crystalline damage near the ion-implanted surface. However, as one goes deeper into the substrate away from the bombarded surface, the electronic damage decreases and the crystalline damage increases until, at the implant layer, the electronic damage is at a minimum and the crystalline damage is at its maximum.

[**0010**] While it is well known that crystalline damage greatly increases the etch rate of a ferroelectric material, the inventors have discovered that the aforementioned electronic damage also substantially increases the etch rate of the material. Thus, a single implant layer of ions to a specific depth results in damage that facilitates the etching process without requiring an intermediate annealing step between the implant and etching steps, and also obviates the need for multiple layers of ion implantations.

BRIEF DESCRIPTION OF THE DRAWING

[**0011**] **FIG. 1** shows a prior art method of producing a thin film waveguide;

[**0012**] **FIG. 2** shows the method of **FIG. 1** used to produce a ridge waveguide;

[**0013**] **FIG. 3** shows a prior art method of producing a ridge waveguide wherein multiple ion implants are made to cause multiple layers of crystalline damage in the substrate;

[**0014**] **FIG. 4** shows a ridge waveguide in cross section produced using a prior art ion milling method;

[**0015**] **FIG. 5** shows a ridge waveguide in cross section produced using a prior art plasma etching method;

[**0016**] **FIG. 6** shows a ridge waveguide in cross section produced using ion implantation followed by chemical wet etching;

[**0017**] **FIG. 7** shows the method of the present invention whereby a single ion implant is made;

[**0018**] **FIG. 8** shows a graph of the nuclear and the electronic damage caused by the method of **FIG. 7**; and

[**0019**] **FIG. 9** shows a ridge waveguide formed by the method of **FIG. 7** when it is prematurely removed from the chemical wet etchant.

DETAILED DESCRIPTION OF THE INVENTION

[**0020**] **FIG. 1** shows a prior art method of producing a thin film waveguide. With reference to that figure, the +z crystal surface **101** of a ferroelectric film **100**, here exemplified by lithium niobate ($LiNbO_3$), is bombarded with ions, for example oxygen ions, shown as arrows **102**, with a particular energy such that they are implanted at level **103**, which is a distance d from surface **101**. Level **103** is proportional to the level of energy with which the ions are implanted into the lithium niobate. The bombarded material is then heated (at 400° C., for example) to partially restore the etch rate of the implant region between surface **101** and level **103** and the material at level **103** becomes an etch stop. This etch stop is a layer of lithium niobate with a much higher resistance to etching than the surrounding material. Next, the −z surface **104** of the substrate is removed by mechanical and/or chemical etching using a chemical etchant such as HNO_3:HF (2:1), or RCA1. During this etching, the lithium niobate between the −z surface **104** and etch stop **103** is removed, leaving a slab waveguide of lithium niobate of thickness d.

[**0021**] **FIG. 2** shows how the above-described process is used in the prior art to form a waveguide structure known as a ridge waveguide. Referring to that figure, mask **205** is applied to the −z surface **201** of the lithium niobate **200** prior to ion bombardment. When bombarded with ions **202**, the ions are implanted at depth d below surface **201**, forming implant layer **203**. The ions bombarding the masked portion of surface **201**, however, do not penetrate the surface of the lithium niobate thus forming a region **206** of undisturbed material. By then annealing the material an etch stop is formed at the implant layer **203** such that a subsequent chemically etch will remove material from surface **201**, thereby forming ridge **206** on a lithium niobate base.

[**0022**] **FIG. 3** shows a prior art method of forming a ridge waveguide through etching that does not require annealing to form an etch stop at depth d_N below the surface **301** of the lithium niobate slab. Here, mask **305** is affixed over a portion of the surface **301** that will form the ridge **306**. Surface **301** is then bombarded with appropriate energies to implant ions at multiple depths d_1-d_N from surface **301** down to depth d_N to form layer **303**. Such multiple implantation depths are achieved by varying the energy of the ions from low, to cause crystalline damage near surface **301** at depth d_1, to high, to cause damage down to depth d_N at layer **303**. The effect of such multiple implantations is to create a relatively continuous amount of crystalline damage throughout the ion-bombarded material from surface **301** down to layer **303**, except below mask **305**. Instead of etching surface **304**, mask **305** remains in place while surface **301** is exposed to a chemical etchant. The crystalline damage in the ion-implanted lithium niobate greatly increases the etch rate of the material. By knowing the approximate rate of etching of the chemical used on the damaged lithium niobate, the approximate etch time required to reach layer **303** can be determined. A precise timing of such etching is not necessary as the undamaged lithium niobate between layer **303** and surface **304** is highly resistant to etching relative to the crystalline-damaged lithium niobate. Therefore, if left exposed to the chemical etchant for a period modestly longer than necessary to remove the damaged material, very little undamaged lithium niobate would be etched away. For example, a typical rate of etching crystalline damaged lithium niobate using HNO_3:HF (2:1) is approximately 300 nanometers per minute. This rate is merely exemplary as the etch rate greatly depends on the magnitude of crystalline damage, the concentration of the etchant, and the temperature of the etchant. The etch rate of undamaged lithium niobate is approximately 10 nanometers per minute in HNO_3:HF (2:1). Therefore, using the above numbers, even if left exposed to the chemical etchant for one minute longer than necessary, only approximately 10 nanometers will be etched from the undamaged material, which will have a negligible impact on the ridge waveguide structure.

[**0023**] **FIG. 4** shows an example of a ridge in cross section that results from an alternative method of forming structures in ferroelectric material, known as ion milling. In this method, ions are not implanted into the ferroelectric material but, rather, bombard the surface of the material with a lower energy such that they impact the surface of the material and physically destroy portions of that surface to remove material therefrom. This is referred to as sputtering. Referring to **FIG. 4**, sides **402** of ridge **401** do not form a 90 degree angle with base **403** but, instead, form an angle of approximately 80 degrees, which is typical of ridge structures produced with ion milling. A 90 degree angle is desireable for ridges used in electro-optic waveguide devices as it facilitates concentration of the electrical field applied to such waveguides and assists RF/optical velocity matching in the interaction region of the electro-optic device

[**0024**] **FIG. 5** shows an example of yet another method of producing a ridge, shown here in cross section, known as plasma etching. In this method, a gas is partially ionized, thereby forming ions and radicals that are more chemically reactive with the lithium niobate than the inital gas molecule. The ions are accelerated to the substrate surface where, facilitated by the chemically reactive radicals, they can react with that surface and sputter away portions thereof. Fluorocarbon gases have been shown to be effective in this process to etch ridges in lithium niobate. Once again, however, the side walls **502** of ridge **501** form an angle of less than 90 degrees with base **503**, in this case approximately 70 degrees. This angle is typical of waveguides produced with this method and, for the aformentioned reasons, is not as desirable as a 90 degree angle between the side walls and the base.

[**0025**] **FIG. 6** shows an illustrative ridge **601** in cross section produced using the ion implant etching process exemplified in FIGS. **1-3**, and discussed above. Such a ridge is characterized by side walls **602** that are at approximately the desirable 90 degree angles from base **603**. Such a ridge is also characterized by reentrant side wall angles **604** where sides **602** meet base **603**. Such side wall angles can have the advantage in electro-optic devices of beneficially further concentrating an electric field within the waveguide. This advantage is directly related to the size of angle **604** such that, as angle **604** decreases (i.e., the side walls become more reentrant), the concentration of the electric field beneficially increases.

[**0026**] **FIG. 7** shows the ion implant etch process of the present invention whereby a single ion implantation **702** is performed on lithium niobate **700** through surface **701** with sufficient energy to penetrate to depth d to form a single implant layer **703** and wherein, without performing an intermediate annealing step, the ion-implanted lithium niobate **700** is then subjected to a chemical wet etch. By masking the portion **707** of surface **701** over the region that will form ridge **706**, ions are prevented from penetrating this region. Referring to **FIG. 8**, the result of a single ion implant to depth d below surface **701** in **FIG. 7** is graphically illustrated as the electronic damage, represented by line **801**, and nuclear (crystalline) damage, represented by line **802**, caused by this implant. Axis **804** represents the electronic energy loss represented by line **801** at a depth from the surface represented by axis **805**. High levels of electronic energy loss equate to high levels of electronic damage within the lithium niobate structure. Thus, the highest level of electronic damage is near the surface, and declines according to graph **801** until it reaches a minimum at a depth, in this case, of approximately 35000 Å. Axis **803** represents the nuclear energy loss represented by line **802** at a depth from the surface by axis **805**. For a given implant ion, target material and energy applied to ion implantation, the axes **803** and **804** have a relationship with each other. Nuclear energy loss occurs as the ions interact with, and damage, the crystalline structure of the lithium niobate. Such damage also varies with the depth into the lithium niobate. However, in this case, a minimum level of damage is incurred when the energy of the implanted ions is at a maximum near the surface **701**. As the depth increases and the ion energy begins to dissipate, the ions begin to have a greater degree of nuclear interaction with the crystalline structure of the material. As such interaction increases, crystal damage increases (i.e., the crystal structure is significantly disrupted). Finally, as the ions reach their implant depth, the nuclear energy loss of the ions greatly increases. The result is a peak level of interaction, equating to a maximum level of disruption to the crystalline structure at point **807** on line **802**. The nuclear energy loss drops off quickly after the ions slow upon reaching the implant layer between −30000 Å and −35000 Å. Both aforementioned types of damage, crystalline and electronic, enhance the etch rate of lithium niobate in such a way that no intermediate anealing step is required after the ions are implanted and before the material is etched. Of special note in **FIG. 8** is that total structural damage to the lithium niobate, consisting of a combination of crytalline and/or electronic damage, is at a minimum at point **806**.

[**0027**] **FIG. 9** shows a ridge waveguide **901** on base **904** that exemplifies the potential effect of a minimum energy-occurring at point **806** in **FIG. 8**. The ridge profile of **FIG. 9** results from chemical wet etching lithium niobate that was implanted with ions **906** to achieve the electronic and nuclear damage represented by **FIG. 8**. In **FIG. 9**, the etch rate along ridge side walls **902** of the lithium niobate is increased by the electronic damage represented by line **801** in **FIG. 8**. Thus the damaged lithium niobate is readily etched away leaving side walls **902**. When total damage to the lithium niobate is at a minimum, however, represented by point **806** in **FIG. 8**, the etch rate is also at a corresponding minimum. Therefore, if the material is removed from the chemical wet etchant prematurely, proboscises **903** of lithium niobate may remain because the etch rate at depth d, corresponding to the depth of point **806** in **FIG. 8**, is lower than that of the surrounding material that is characterized by greater electronic and/or nuclear damage. As the depth into the lithium niobate increases past the point of minimum total damage **806** in **FIG. 8**, crystalline damage increases and, correspondingly, the etch rate increases and forms side walls **905**, where crystalline damage is at its maximum, represented by point **807** in **FIG. 8**. Thus, for a given amount of time exposed to a chemical wet etchant, the material at depth d will etch less than surrounding areas, which will etch relatively quickly to form side walls **902** and **905** before proboscis **903** is etched away. Therefore, the minimum amount of etching time required to produce a ridge waveguide using the process of the present invention is that time necessary to etch away proboscis **903**.

[**0028**] The foregoing merely illustrates the principles of the invention. It will thus be appreciated that those skilled in the art will be able to devise various arrangements that, although not explicitly described or shown herein, embody the principles of the invention and are within its spirit and scope. Furthermore, all examples and conditional language recited herein are intended expressly to be only for pedagogical purposes to aid the reader in understanding the principles of the invention and are to be construed as being without limitation to such specifically recited examples and conditions. Moreover, all statements herein reciting aspects and embodiments of the invention, as well as specific examples thereof, are intended to encompass functional equivalents thereof.

[**0029**] Diagrams herein represent conceptual views of bullk lithium niobate, lithium niobate films and waveguides produced for use in integrated optoelectronics. Diagrams of such ferroelectric films and waveguides are not necessarily shown to scale but are, instead, merely representative of possible physical arrangements of such components. The lithium niobate films depicted in the diagrams represent only one material suitable for use in waveguides. Many other ferroelectric materials are suitable as a substitute for use in the method shown in the diagrams.

[**0030**] Additionally, while in certain prior art methods etching was optimal when accomplished from the −z crystal surface, the method of the present invention does not depend on etching from any specific surface. The electronic and crystalline damage caused by the ion implantation sufficiently enhances the etch rate that even etching the crystal from the +z surface is acceptable.

[**0031**] Other aspects of the disclosed embodiments of the present invention are also merely illustrative in nature. For instance, although the embodiment presented utilizes a single ion implant followed by a chemical wet etch, the inventors realize that a second implant at the level of minimum damage represented by point **806** in **FIG. 8**, could enhance the etch rate at that level, thus minimizing the time necessary to eliminate the proboscis **903** of **FIG. 9** that may result from premature removal of the lithium niobate from the chemical etchant. Additionally, as discussed in the disclosed imbodiments, the inventors recognize that reentrant side walls are advantageous to concentrate the electric field within the waveguide and that such concentration beneficially increases as the reentrant side wall angles decrease. One method of decreasing these angles is to tilt the lithium niobate during the ion implantation process in such a way that the ions penetrate further into the side walls and, accordingly, decrease the angle between the side walls and the base of the material. Any method of increasing the reentrant side wall angles is intended to be encompassed by the present invention. Finally, any method of using a single ion implantation followed by a chemical wet etchant with no prior annealing is intended to be encompassed by the present invention.

What is claimed is:

1. A method for use in etching structures in a substrate, said method comprising the steps of:

implanting a single layer of ions into a substrate top surface using an energy sufficient to drive the ions a predetermined depth into said substrate; and

without performing a preceding annealing step, etching with a chemical wet etchant the substrate through said top surface of the substrate until reaching the layer of ions at said predetermined depth from said surface.

2. The method of claim 1 wherein said substrate is a lithium niobate ($LiNbO_3$) substrate.

3. The method of claim 1 wherein said top surface is the +z crystal surface.

4. The method of claim 1 wherein said top surface is the −z crystal surface.

5. The method of claim 1 further comprising, prior to said etching step, implanting at least a second layer of ions into said substrate top surface using an energy sufficient to drive the ions to a level of minimum combined electronic and nuclear damage within said substrate.

6. The method of claim 1 wherein at least one portion of said top surface of said substrate is masked in such a way that the ions do not penetrate into the substrate underlying said mask.

7. The method of claim 6 wherein said etching step comprises exposing said top surface to a chemical wet etchant for a length of time necessary to etch away at least a portion of the lithium niobate to form a predetermined structure in said lithium niobate.

8. The method of claim 7 wherein said structure is a ridge.

9. The method of claim 1 wherein said implanting step comprises tilting the substrate in such a way that the ions form reentrant angles between the base and the side walls of said substrate.

* * * * *