



US008815720B2

(12) **United States Patent**  
**Godet et al.**

(10) **Patent No.:** **US 8,815,720 B2**  
(45) **Date of Patent:** **Aug. 26, 2014**

(54) **METHOD OF ETCHING A WORKPIECE**  
(75) Inventors: **Ludovic Godet**, Boston, MA (US);  
**Morgan D. Evans**, Manchester, MA  
(US); **Chi-Chun Chen**, Gloucester, MA  
(US)  
(73) Assignee: **Varian Semiconductor Equipment  
Associates, Inc.**, Gloucester, MA (US)

6,930,030	B2 *	8/2005	Rausch et al.	438/589
7,807,583	B2	10/2010	Van Aelst et al.	
2002/0096496	A1 *	7/2002	Molnar et al.	216/87
2010/0252531	A1	10/2010	Godet et al.	
2011/0151610	A1	6/2011	Ramappa et al.	
2011/0309049	A1	12/2011	Papasouliotis et al.	
2012/0098087	A1 *	4/2012	Abadeer et al.	257/507
2012/0276658	A1 *	11/2012	Godet et al.	438/3

(\* ) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 155 days.

**FOREIGN PATENT DOCUMENTS**

EP	0363099	A1	4/1990
EP	1079424	A1	2/2001
FR	2905516	A1	3/2008

(21) Appl. No.: **13/440,678**

(22) Filed: **Apr. 5, 2012**

**Prior Publication Data**

US 2012/0276658 A1 Nov. 1, 2012

**Related U.S. Application Data**

(60) Provisional application No. 61/474,564, filed on Apr. 12, 2011.

(51) **Int. Cl.**  
**H01L 21/302** (2006.01)  
**H01L 21/322** (2006.01)

(52) **U.S. Cl.**  
USPC ..... **438/524**; 438/705; 438/718

(58) **Field of Classification Search**  
USPC ..... 438/524, 705, 718, FOR. 118;  
257/E21.22

See application file for complete search history.

**References Cited**

**U.S. PATENT DOCUMENTS**

4,735,920	A *	4/1988	Stephani et al.	438/718
5,436,174	A *	7/1995	Baliga et al.	438/705

**OTHER PUBLICATIONS**

Ladroue et al., Deep GaN Etching by Inductively Coupled Plasma and Induced Surface Defects, J. Vac. Sci. Tech. A, Sep./Oct. 2010, pp. 1226-1233, vol. 28(5), American Vacuum Society.  
Yang et al, Fabrication of Mesa Shaped InGaN-Based Light-Emitting Process, J. of Electronic Materials. 2009, pp. 145-152, vol. 38, No. 1.  
Qiu et al, Optimization of Inductively Coupled Plasma Deep Etching of GaN and Etching Damage Analysis, Applied Surface Sci., 2011, pp. 2700-2706, vol. 257, Elsevier B.V.

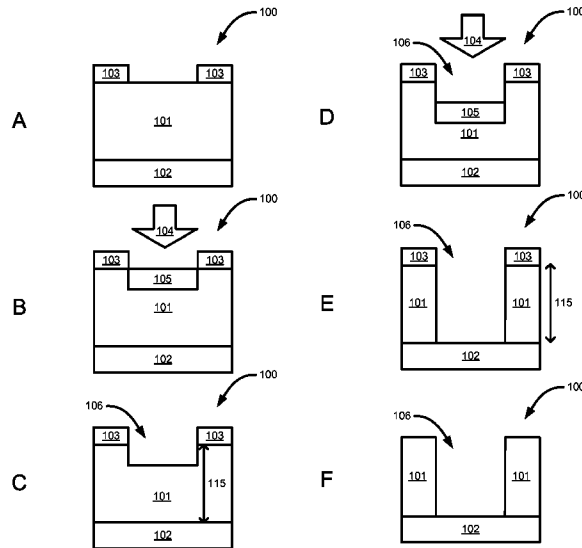
\* cited by examiner

*Primary Examiner* — George Fourson, III

(57) **ABSTRACT**

A workpiece is implanted to a first depth to form a first amorphized region. This amorphized region is then etched to the first depth. After etching, the workpiece is implanted to a second depth to form a second amorphized region below a location of the first amorphized region. The second amorphized region is then etched to the second depth. The implant and etch steps may be repeated until structure is formed to the desired depth. The workpiece may be, for example, a compound semiconductor, such as GaN, a magnetic material, silicon, or other materials.

**9 Claims, 5 Drawing Sheets**



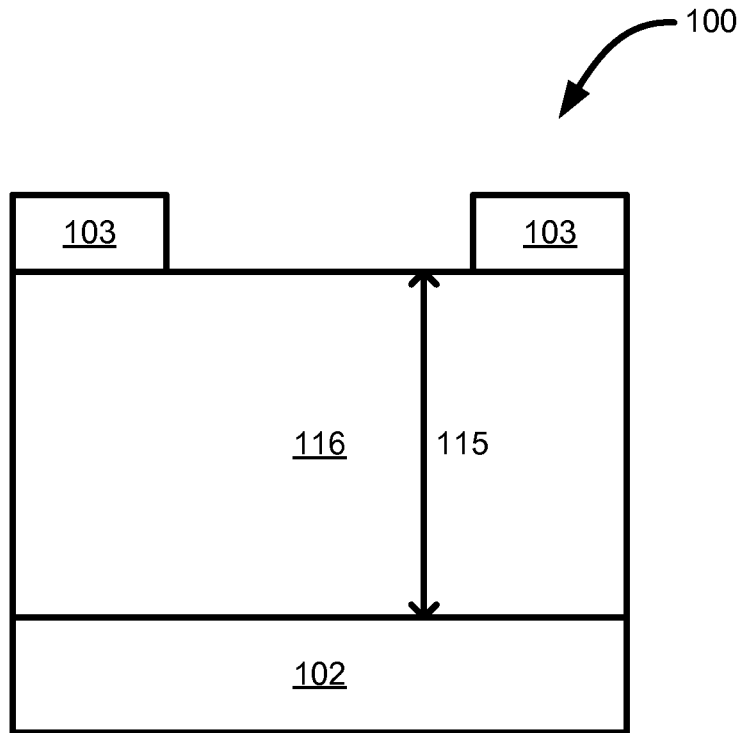


FIG. 1  
(Prior Art)

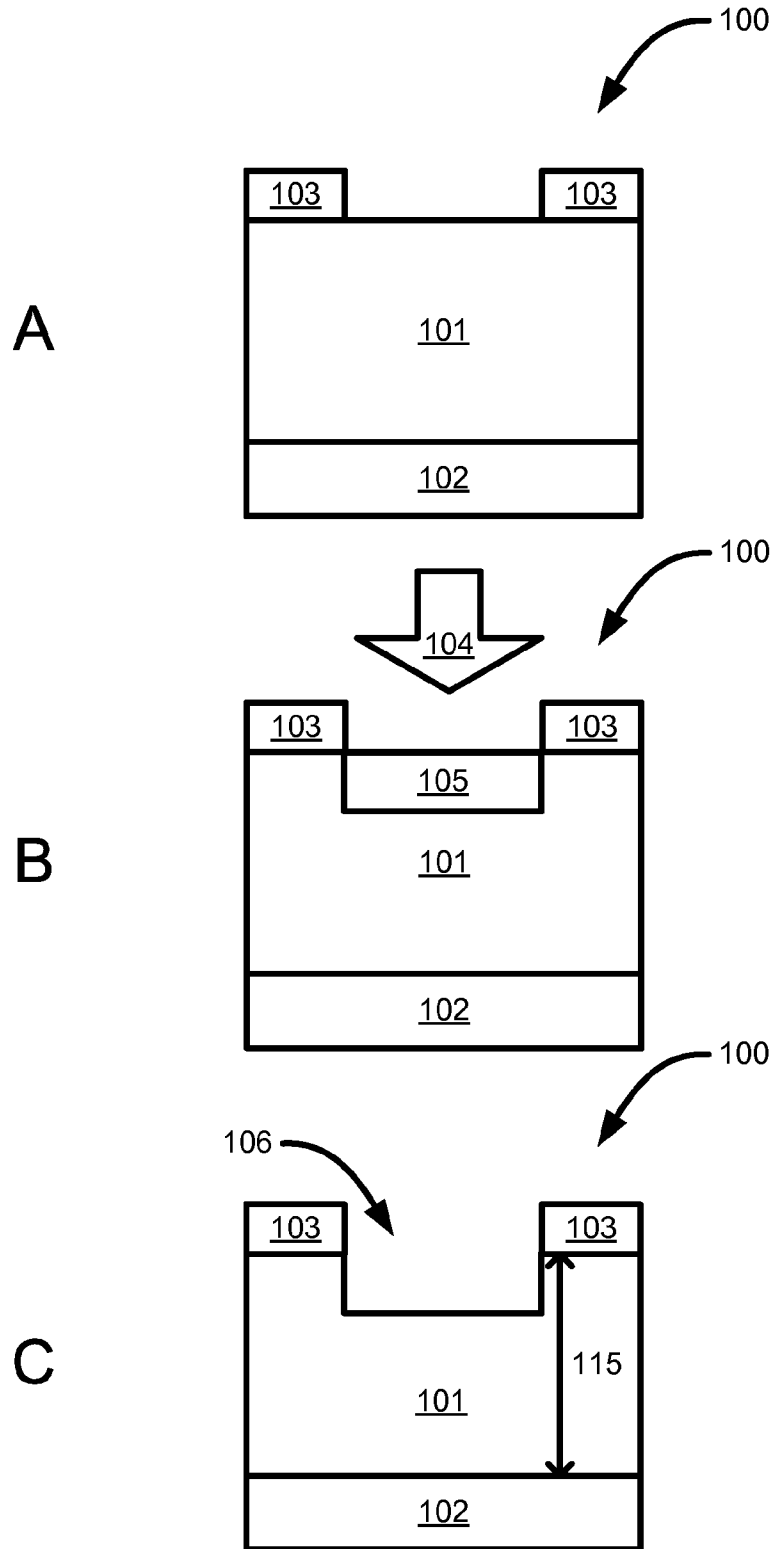
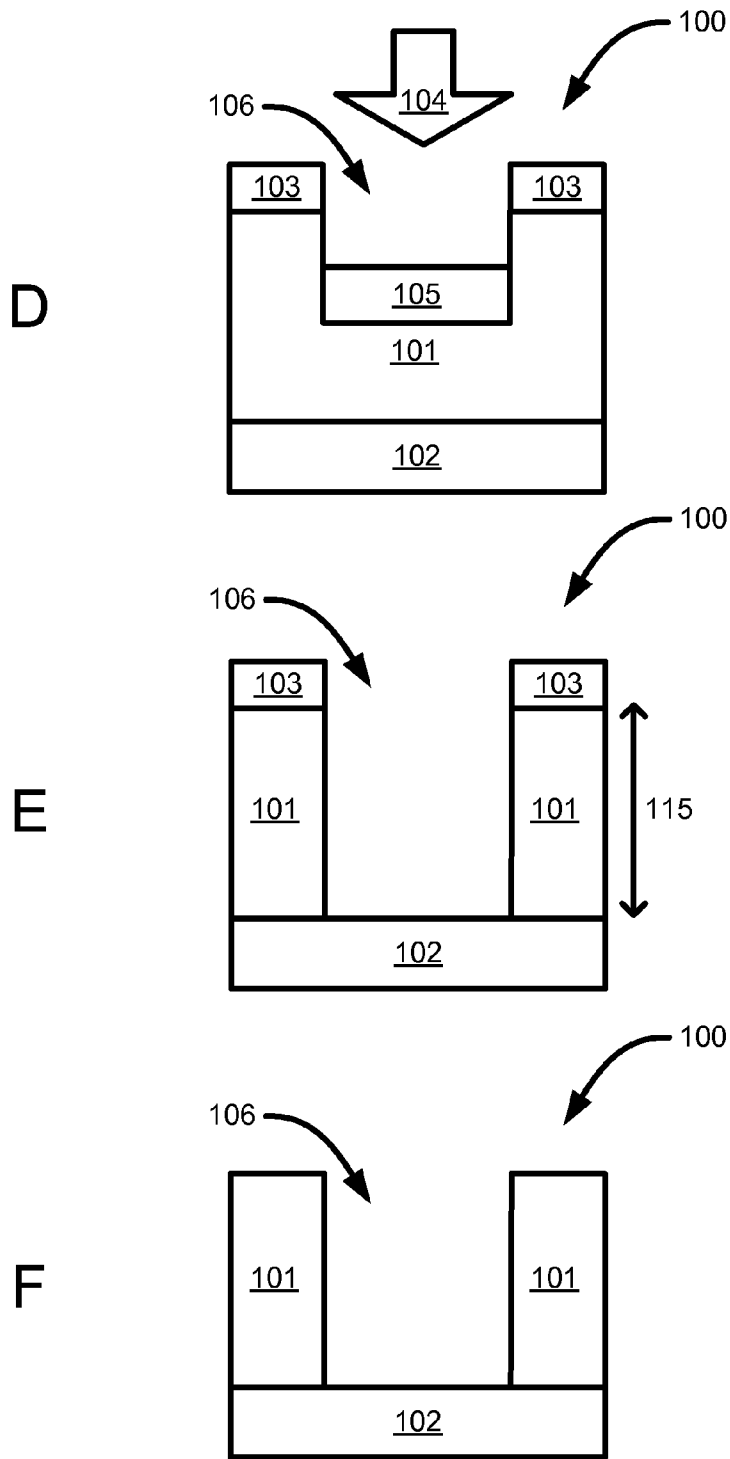


FIG. 2



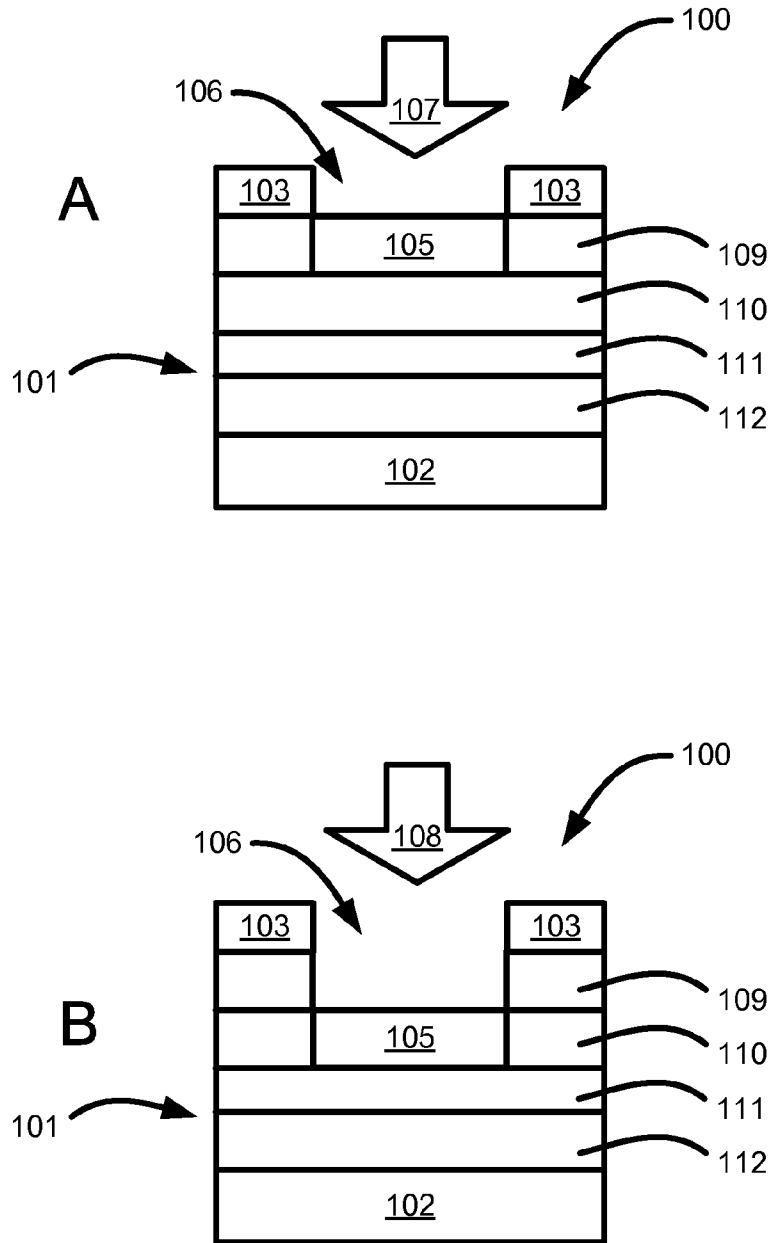


FIG. 3

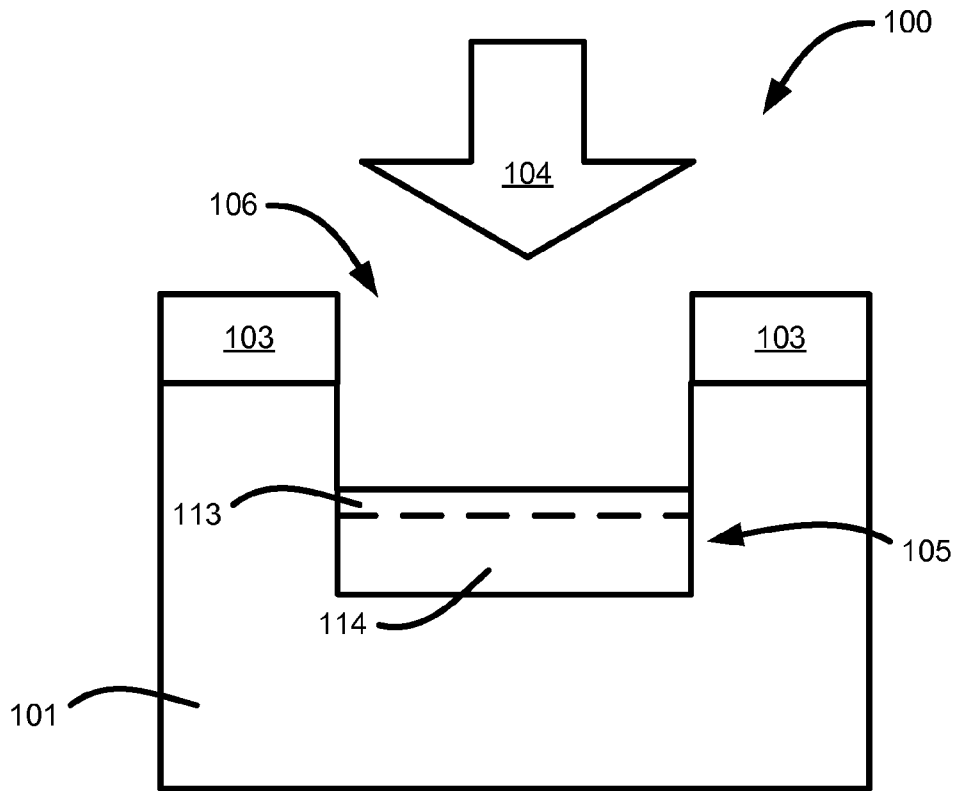


FIG. 4

## METHOD OF ETCHING A WORKPIECE

## CROSS-REFERENCE TO RELATED APPLICATIONS

This claims priority to the provisional patent application entitled "Defect-Free Etching of a Compound Semiconductor," filed Apr. 12, 2011 and assigned U.S. App. No. 61/474,564, the disclosure of which is hereby incorporated by reference.

## FIELD

This invention relates to ion implantation and, more particularly, to ion implantation of a workpiece to improve etching.

## BACKGROUND

Ion implantation is a standard technique for introducing conductivity-altering impurities into a workpiece. A desired impurity material is ionized in an ion source, the ions are accelerated to form an ion beam of prescribed energy, and the ion beam is directed at the surface of the workpiece. The energetic ions in the beam penetrate into the bulk of the workpiece material and are embedded into the crystalline lattice of the workpiece material to form a region of desired conductivity.

In order for light-emitting diodes (LEDs) to gain more of the lighting market, improvements in efficiency and manufacturing cost may be required. In many processes, etching is used to form mesas between LEDs. This etching step is one area that can be improved. Defects and dislocations in the GaN of an LED create centers for etch rate enhancement or reduction. These centers result in cavities, nano-pillars/nano-columns, roughness, or other etch imperfections. In addition, different crystal orientations result in different etch rates. Furthermore, the etch rate of GaN or other compound semiconductors may be slow or provide paths for leakage in a device.

Ion implantation may be used to amorphize or damage the defects or dislocations of a compound semiconductor, such as GaN, or some other material. The etch rate is affected if the material being etched is amorphized. FIG. 1 is a cross-sectional side view of a GaN workpiece. The workpiece **100** has a GaN layer **116** and substrate **102** composed of sapphire. A mask **103**, which may be photoresist or some other hard mask, is disposed on the surface of the GaN layer **116**. The distance between the top surface of the GaN layer **116** with the mask **103** to the sapphire substrate **102** may be at least 1  $\mu\text{m}$ , as seen by length **115** in FIG. 1. In another example, the length **115** may be at least 10  $\mu\text{m}$ . Implantation from the surface to the desired depth in GaN layer **116** may be costly and time consuming and require multi-energy implantation as high as 10 MeV and a dose as high as  $1\text{E}18$ . This may be too slow or expensive for commercial manufacturing. Lateral straggle also may occur, which could potentially damage the material of the GaN layer **116**. Furthermore, point defects and dislocations formed during GaN growth may cause defects at the bottom of any trench that is formed in the GaN layer **116**. This may be at least partly due to the lattice mismatch between the GaN layer **116** and the substrate **102**, which will be worse closest to the intersection of the GaN layer **116** and substrate **102**. What is needed is an improved method of implanting a workpiece to improve etching.

## SUMMARY

According to a first aspect of the invention, a method of forming a structure in a workpiece is provided. The method

comprises implanting a workpiece to a first depth to form a first amorphized region. The first amorphized region is etched to the first depth. The workpiece is implanted to a second depth to form a second amorphized region below a location of the first amorphized region after the first amorphized region is etched. The second amorphized region is etched to the second depth.

According to a second aspect of the invention, a method of forming a structure in a workpiece is provided. The method comprises alternating between an implant step that forms an amorphized region in a workpiece and an etching step to remove the amorphized region. The implant step and the etching step are each performed at least two times and a structure is formed to a desired depth.

According to a third aspect of the invention, a method of forming a structure in a workpiece is provided. The method comprises placing a workpiece in a chamber. The workpiece is implanted in the chamber to form an amorphized region and etched in the chamber to remove the amorphized region. The implanting and etching is repeated in the chamber until a structure is formed in the workpiece to a desired depth.

## BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of the present disclosure, reference is made to the accompanying drawings, which are incorporated herein by reference and in which:

FIG. 1 is a cross-sectional side view of a GaN workpiece; and

FIGS. 2A-2F are cross-sectional side views of a first embodiment of implanting and etching a workpiece;

FIGS. 3A-3B are cross-sectional side views of a second embodiment of implanting and etching a workpiece; and

FIG. 4 is a cross-sectional side view of another embodiment of implanting a workpiece.

## DETAILED DESCRIPTION

The embodiments are described herein in connection with ion implantation of compound semiconductors such as GaN, but these embodiments also may be used with other III/V compound semiconductors, II/VI compound semiconductors, magnetic materials, silicon, dielectrics, metals, combinations thereof, or other materials known to a person skilled in the art. The workpiece may be part of an LED, magnetoresistive random-access memory (MRAM) stack, microelectromechanical systems (MEMS) device, some other multi-layer stack containing multiple materials, three-dimensional integrated circuits, optoelectronic devices, multi junction solar cells, or other structures. A beam-line ion implanter, plasma doping ion implanter, flood implanter, system that modifies a plasma sheath, or other ion implantation system known to those skilled in the art may be used in the embodiments described herein. A cluster tool of multiple chambers may be used in one particular embodiment. Thus, the invention is not limited to the specific embodiments described below.

A multi-step implant approach will avoid the drawbacks of other implant and etch methods. FIGS. 2A-2F are cross-sectional side views of a first embodiment of implanting and etching a workpiece. In FIG. 2A, a workpiece **100** is provided with a layer **101**, substrate **102**, and a mask **103**. The substrate **102** may be sapphire and the layer **101** may be GaN in one embodiment, but other materials are possible. The substrate **102** may not be present or used in another embodiment.

In FIG. 2B, ions **104** are implanted through an aperture in the mask **103** to form an amorphized region **105** that extends to a first depth in the layer **101**. These ions **104** may be N, but other species may be used.

In FIG. 2C, the amorphized region **105** is etched away to form trench **106**. In one instance, bonds of the material in the amorphized region **105** are broken, which increases the efficiency of the etching. This trench **106** is not the length **115** of the layer **101**. The amorphized region **105** is etched to approximately the first depth in this instance either because the etching is optimized for an amorphous structure or the etching is configured to stop at a particular time. For example, the etching process may be monitored and stopped when the measured concentration of the ions **104** in the amorphized region **105** decreases below a threshold. In another example, the etching may be optimized to be less effective in crystalline material than amorphized material.

In FIG. 2D, the layer **101** is again implanted with ions **104** to form another amorphized region **105** that extends to a second depth in the layer **101**. This implant may be perpendicular to the surface to avoid implanting the sidewalls of the layer **101**. This amorphized region **105** is subsequently etched to approximately the second depth. The process is repeated until the trench **106** is the entire length **115** of the layer **101** as illustrated in FIG. 2E. Of course, other depths or lengths are possible. The mask **103** is then removed in FIG. 2F. This leaves mesas that can be used for, in one example, LEDs separated by the trench **106**.

In one particular embodiment, each implant has a dose between approximately E15 to E16. Each amorphized region **105** may be approximately 20 nm in height or depth, though other dimensions are possible. The overall number of implant and etch steps depends on the dimensions of the amorphized region **105** and the layer **101**. For example, five implant steps may be needed if approximately 20 nm of layer **101** amorphized with each implant and if the layer **101** is approximately 100 nm thick. More implant steps may improve the overall quality because lateral straggle decreases as implant energy decreases. Less sidewall damage may occur due to a lower amorphization energy. The mass of the ions **104** also will affect the lateral straggle. Bigger ions **104** result in a shallower implant and lower dose required to amorphize.

The amorphized region **105** removes both point defects and dislocations in the layer **101**. The dislocations, for example, are removed or erased when the layer **101** is amorphized because the lattice is partially or totally destroyed and the dislocations become part of the amorphized material. This reduces the occurrence of defects, cavities, nano-pillars/nano-columns, roughness, or other etch imperfections. The trench **106** also may be more abrupt and less rough than previous methods because amorphizing may prevent lateral etching if the dislocations are near the side of the trench. In one instance, allowing approximately 1 nm amorphization under the mask **103** due to lateral straggle may damage any dislocations near the edge of the trench **106** and reduce the etch species from diffusing inside these dislocations. This leads to better LEDs with better isolation interfaces because, for example, approximately 1 nm of amorphized material may be left on the sidewall under the mask **103**. Of course, all amorphized material may be etched in an alternate embodiment. Subsequent steps, such as a wet etch step, may be used to remove any remaining residue or material in the trench **106**. Furthermore, the process described herein, while using more process steps, may be faster or less expensive than a single implant step because a single implant to the entire depth of the layer **101** may have a very long duration or be at a very high

energy. An abrupt trench **106** will still be formed even if cheaper or lower quality GaN layers **101** are used.

In another particular embodiment, the implanting and etching occurs in a single chamber. The workpiece **100** is placed in the chamber. The workpiece is implanted to form an amorphized region and then etched to remove this amorphized region. The implanting and etching is repeated until a structure or trench is formed with the desired depth. The gas that is ionized during implantation and the gas used for etching may be different and may be purged in between steps. For example, N<sub>2</sub> and Cl<sub>2</sub> or BCl<sub>2</sub> and HCl may be used. If a single plasma is used for implantation and etching, then a halogen such as Cl<sub>2</sub> may be mixed with N<sub>2</sub>, NH<sub>3</sub>, He, or another noble gas. The bias conditions of the workpiece **100** or plasma chamber or the plasma parameters may be varied to preferentially implant or preferentially etch the workpiece **100** using this single plasma. Vacuum around the workpiece **100** may not be broken during this process. Of course, the workpiece **100** may be moved between two or more chambers either breaking vacuum between chambers or maintaining vacuum between chambers.

An implant or plasma process at low energy also may be used after etching to remove any remaining material on the sidewalls of the trench **106**. This may improve performance of the device and may occur in the same chamber as the implant or etching in one instance.

FIGS. 3A-3B are cross-sectional side views of a second embodiment of implanting and etching a workpiece. In this embodiment, the layer **101** is actually made of up different layers **109-112**. Each of the layers **109-112** may be composed of the same material or may be composed of different materials. The workpiece **100** in this example may be, for example, an MRAM stack, a silicon via, an optoelectronic device, a MEMS device, or a multi-junction solar cell. The ions **107**, which may correspond to the ions **104**, are used to form the amorphized region **105** in the layer **109**. After etching the amorphized region **105** in layer **109**, ions **108**, which also may correspond to the ions **104**, are used to form the amorphized region **105** in the layer **110**. The implant energy used to form the amorphized regions **105** in the layer **109** and layer **110** may be different. This may be due to the dimensions of the layer **109** and layer **110** or materials of the layer **109** and layer **110**. Some or all of the layers **109-112** may be implanted with different energies.

In another alternate embodiment, the dose or ion species of the ions **108** and ions **107** are changed to form the amorphized regions **105** in the layer **110** and layer **109**. This may be due to a difference of materials in the layer **110** and layer **109**. Some or all of the layers **109-112** may be implanted with different doses or ion species.

FIG. 4 is a cross-sectional side view of another embodiment of implanting a workpiece. In this embodiment, the ions **104** are used to form the amorphized region **105** in the layer **101** at two different energies. A first implant energy is used to form the region **114** (below the dotted line) and a second implant energy is used to form the region **113** (above the dotted line). The region **113** and region **114** make up the amorphized region **105**. A higher implant energy may be used to form the region **114** and a lower implant energy may be used to form the region **113** closer to the surface. An etch may be used to remove both the region **113** and region **114** of the amorphized region **105**. In one specific example, a higher energy, such as approximately 20 kV, may not amorphize the entire amorphized region **105**. An approximately 5 kV energy may be used to amorphize or fully amorphize the remainder of the region **113**.



While a mask **103** is illustrated, in an alternate embodiment the implantation of ions **104** occurs without a mask **103** on the workpiece **100**. A device that focuses ions, shadow or stencil masks disposed above or a distance away from the workpiece **100**, or a device that modifies the shape of a plasma sheath all may be used for the selective implants into the workpiece **100**. This eliminates the mask **103** application and removal steps and further reduces costs.

In an alternate embodiment, inert species, noble gases, p-type species, or n-type species are used instead of N for the ions **104**. He, Ne, Ga, B, P, or As are just some examples and other species known to those skilled in the art also may be used. Different species result in different etch speeds or trench **106** characteristics. For example, implanting B may result in a faster etching rate. In one instance, if silicon in the layer **101** is doped, during etching it may form a volatilized molecule. Other species also may affect etch rate, such as by modifying a material property of the material being etched. In another instance, the ions **104** are an inert species mixed with an active etch species such as Cl or another halogen. If an active etch species is used as at least part of the ions **104**, then the ions **104** may both amorphize and begin to etch the surface of the amorphized region **105**.

In one particular embodiment, different species are used for the ions **104** during different implant steps. For example, a first species is used to amorphize the layer **101** at the beginning of the process, but then a second species is used to amorphize the layer **101** at a slower rate when the etching is closer to the substrate **102** or farther from a surface of the layer **101**, such as the surface of the layer **101** with the mask **103**. This may enable more control of the etching process when needed and prevent unintended damage to the substrate **102**. For example, N and He or B and He may be used.

A vertical trench **106** is illustrated herein. However, the trench **106** may be other shapes or dimensions than that illustrated. For example, the trench **106** may be v-shaped. The embodiment described herein may be used to form many different shaped trenches.

The material of the trench **106** sidewalls may be doped or isolated before, during, or after this process. For example, the ions **104** or subsequent steps, such as an implant step, may be used to isolate the walls of the trench **106**. A surface peak profile may be formed. In one particular embodiment, multiple angled implants or a single implant may treat the sidewalls of the trench **106** after etching is complete. A bimodal angular distribution may be used for the single implant.

The workpiece **100** may be scanned during implantation. This may enable the entire workpiece **100** to be implanted if the workpiece **100** contains multiple structures or devices where etching is desired. The ions used to form the amorphized regions **105** may be, for example, a ribbon beam, a scanned spot beam, or a focused ion beam. Of course, a plasma doping or plasma immersion ion implant system may be used to treat an entire workpiece **100** without scanning. If scanning is used, the workpiece **100** may be rotated during implantation to enable uniformity of the amorphized regions **105** across the workpiece **100**.

The present disclosure is not to be limited in scope by the specific embodiments described herein. Indeed, other various

embodiments of and modifications to the present disclosure, in addition to those described herein, will be apparent to those of ordinary skill in the art from the foregoing description and accompanying drawings. These other embodiments and modifications are intended to fall within the scope of the present disclosure. Furthermore, although the present disclosure has been described herein in the context of a particular implementation in a particular environment for a particular purpose, those of ordinary skill in the art will recognize that its usefulness is not limited thereto and that the present disclosure may be beneficially implemented in any number of environments for any number of purposes. Accordingly, the claims set forth below should be construed in view of the full breadth and spirit of the present disclosure as described herein.

What is claimed is:

1. A method of forming a structure in a workpiece comprising:
  - implanting a workpiece to a first depth to form a first amorphized region;
  - etching said first amorphized region to said first depth;
  - implanting a workpiece to a second depth to form a second amorphized region below a location of said first amorphized region after said etching of said first amorphized region; and
  - etching said second amorphized region to said second depth, wherein said workpiece in said first amorphized region comprises a first material and said workpiece in said second amorphized region comprises a second material different from said first material.
2. The method of claim 1, further comprising:
  - implanting a workpiece to a third depth to form a third amorphized region below a location of said second amorphized region after said etching of said second amorphized region; and
  - etching said third amorphized region to said third depth.
3. The method of claim 1, further comprising forming a mask on said workpiece.
4. The method of claim 1, wherein said workpiece comprises a compound semiconductor.
5. The method of claim 1, wherein said workpiece comprises a magnetic material.
6. The method of claim 1, wherein said workpiece comprises silicon.
7. The method of claim 1, wherein said implanting said workpiece to said first depth occurs at a first energy and wherein said implanting said workpiece to said second depth occurs at a second energy different from said first energy.
8. The method of claim 1, wherein one of said implanting to form said first amorphized region or said implanting to form said second amorphized region comprises two implants at two different energies.
9. The method of claim 1, wherein said implanting said workpiece to said first depth occurs using a first species and wherein said implanting said workpiece to said second depth occurs using a second species different from said first species.

\* \* \* \* \*