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Godet et al.

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(54) **3D MATERIAL MODIFICATION FOR ADVANCED PROCESSING**

(71) Applicant: **Applied Materials, Inc.**, Santa Clara, CA (US)

(72) Inventors: **Ludovic Godet**, Sunnyvale, CA (US); **Srinivas D. Nemani**, Sunnyvale, CA (US); **Erica Chen**, Cupertino, CA (US); **Jun Xue**, San Jose, CA (US); **Ellie Y. Yieh**, San Jose, CA (US); **Gary E. Dickerson**, Gloucester, MA (US)

(73) Assignee: **APPLIED MATERIALS, INC.**, Santa Clara, CA (US)

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H01L 27/092	(2006.01)
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H01L 21/3105	(2006.01)

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CPC H01L 21/0337; H01L 21/033; H01L 21/0332; H01L 21/3105; H01L 21/31; H01L 21/02678; H01L 21/027; H01L 21/0465; H01L 21/845; H01L 21/823431; H01L 27/0886; H01L 27/0924; H01L 27/10879; H01L 27/1211; H01L 29/66795; H01L 29/7831

See application file for complete search history.

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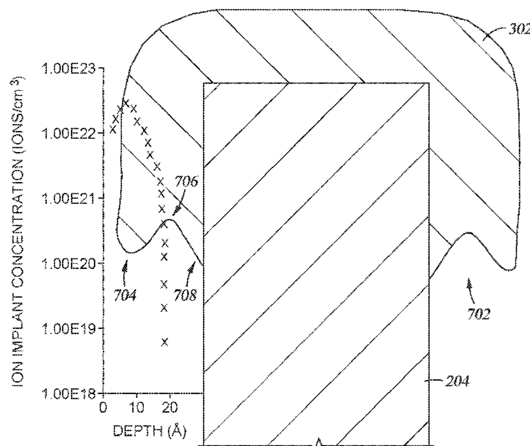
Primary Examiner — Thanhha Pham
(74) *Attorney, Agent, or Firm* — Patterson+Sheridan LLP

(57) **ABSTRACT**

Embodiments of the present disclosure relate to precision material modification of three dimensional (3D) features or advanced processing techniques. Directional ion implantation methods are utilized to selectively modify desired regions of a material layer to improve etch characteristics of the modified material. For example, a modified region of a material layer may exhibit improved etch selectivity relative to an unmodified region of the material layer. Methods described herein are useful for manufacturing 3D hardmasks which may be advantageously utilized in various integration schemes, such as fin isolation and gate-all-around, among others. Multiple directional ion implantation processes may also be utilized to form dopant gradient profiles within a modified layer to further influence etching processes.

20 Claims, 6 Drawing Sheets



Related U.S. Application Data

(60) Provisional application No. 62/089,081, filed on Dec. 8, 2014.

(51) **Int. Cl.**
H01L 27/108 (2006.01)
H01L 27/12 (2006.01)

(52) **U.S. Cl.**
CPC ***H01L 27/10879*** (2013.01); ***H01L 27/1211*** (2013.01); ***H01L 29/7831*** (2013.01)

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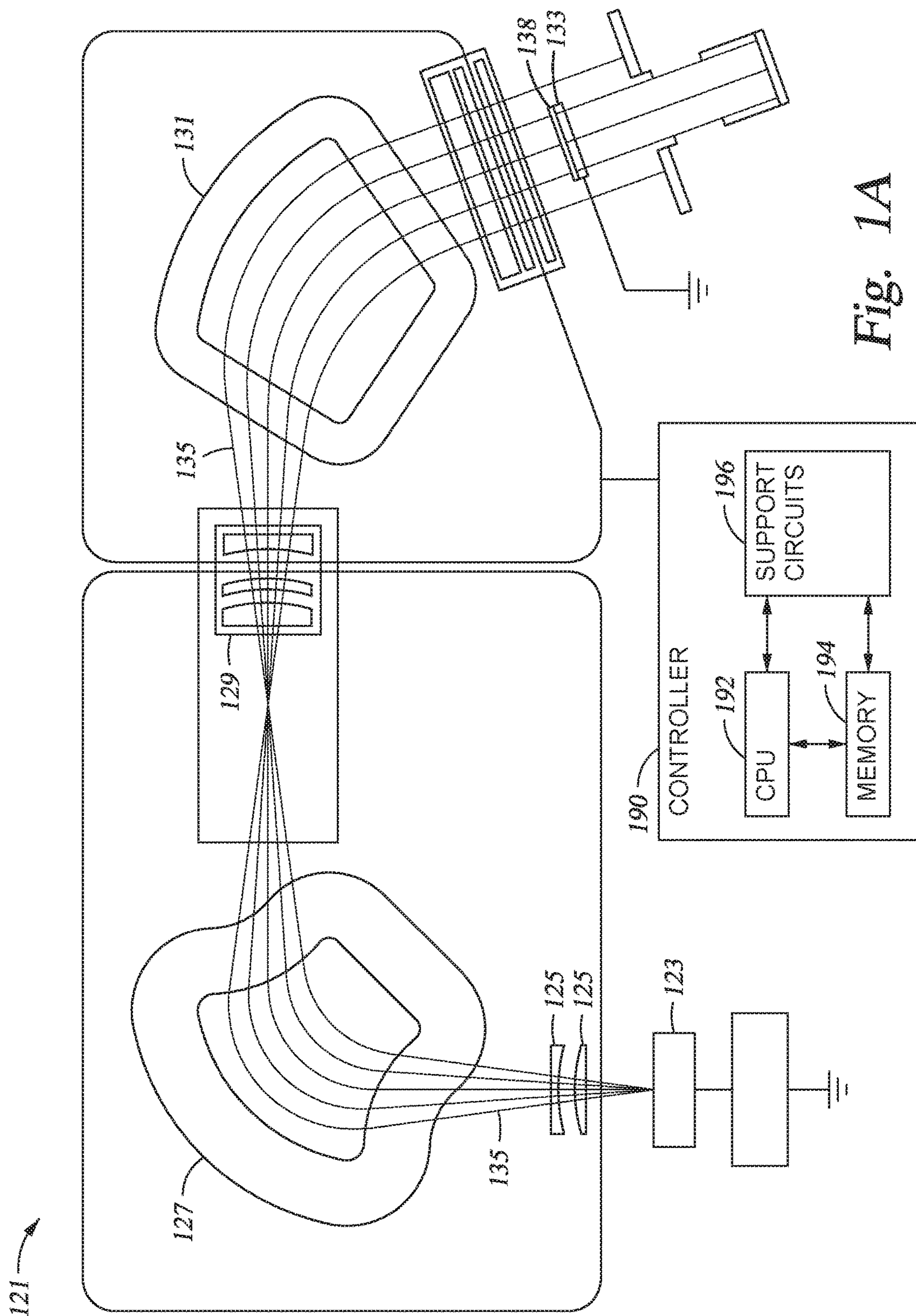

Fig. 1A

GAS SOURCE
188
102
140
114
138
134
101
141
147
144
113
171
169
142
106
112
108
151
189
BIAS SOURCE
100
190
CONTOLLER
SUPPORT CIRCUITS
196
CPU
192
194
MEMORY

Fig. 1B

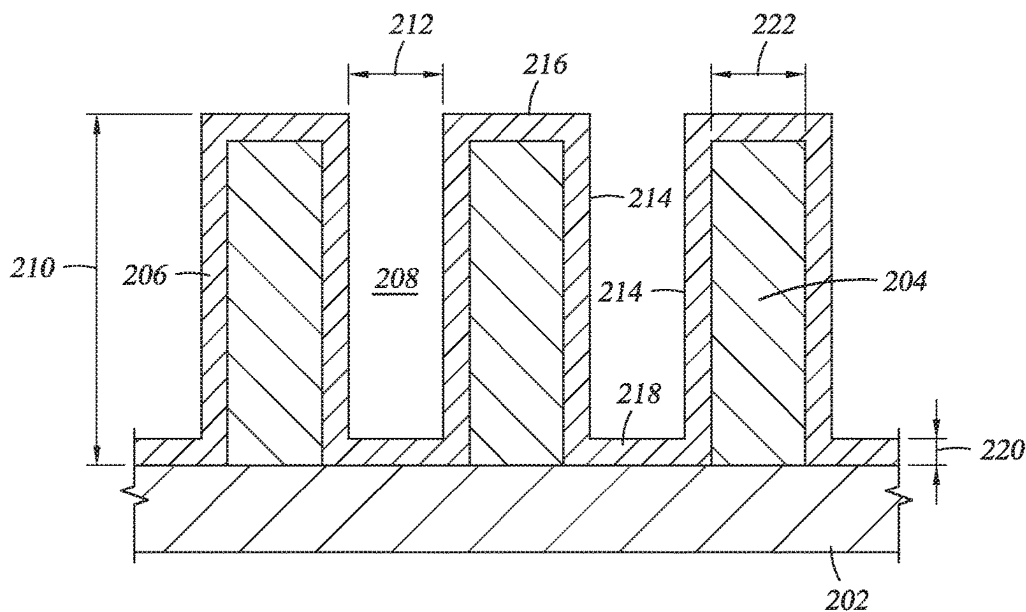

Fig. 2

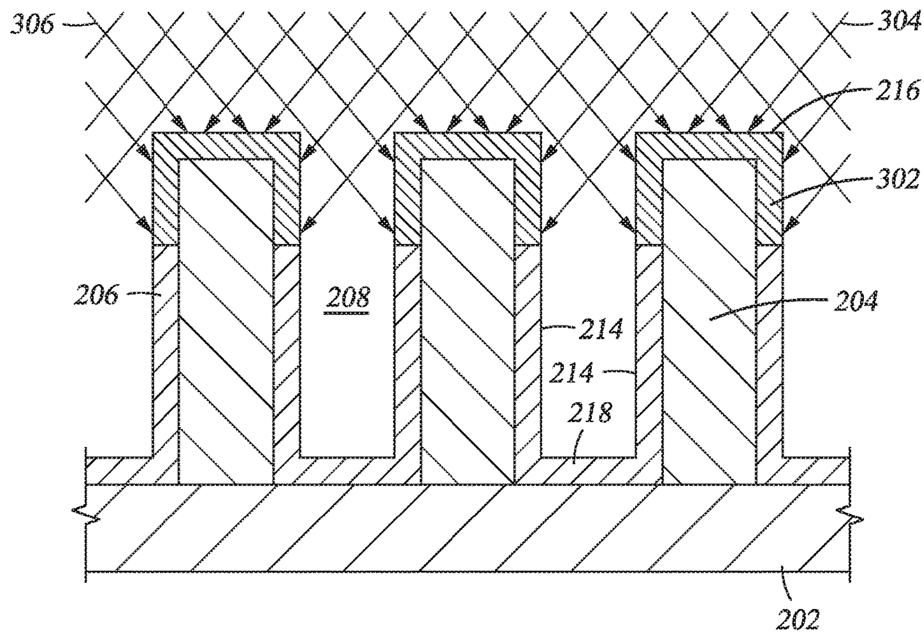

Fig. 3

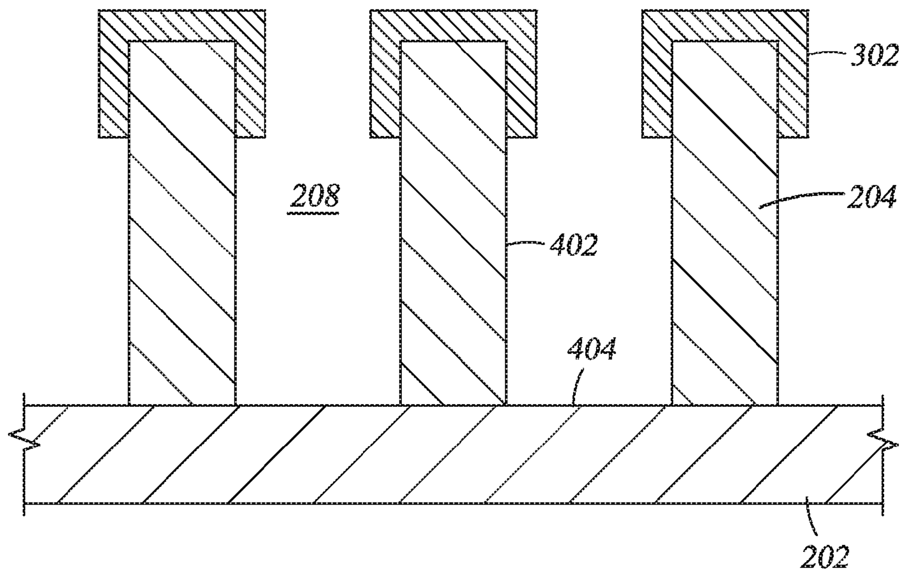

Fig. 4

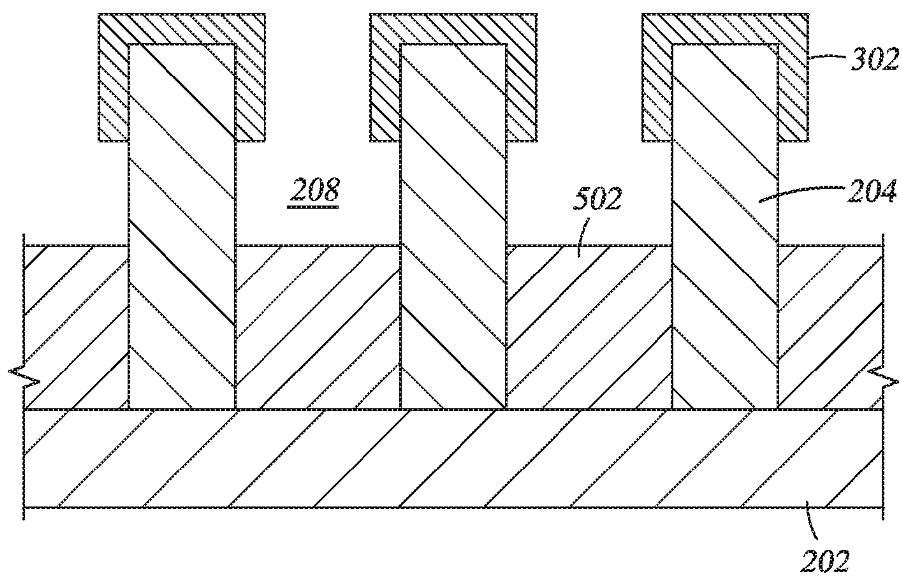

Fig. 5

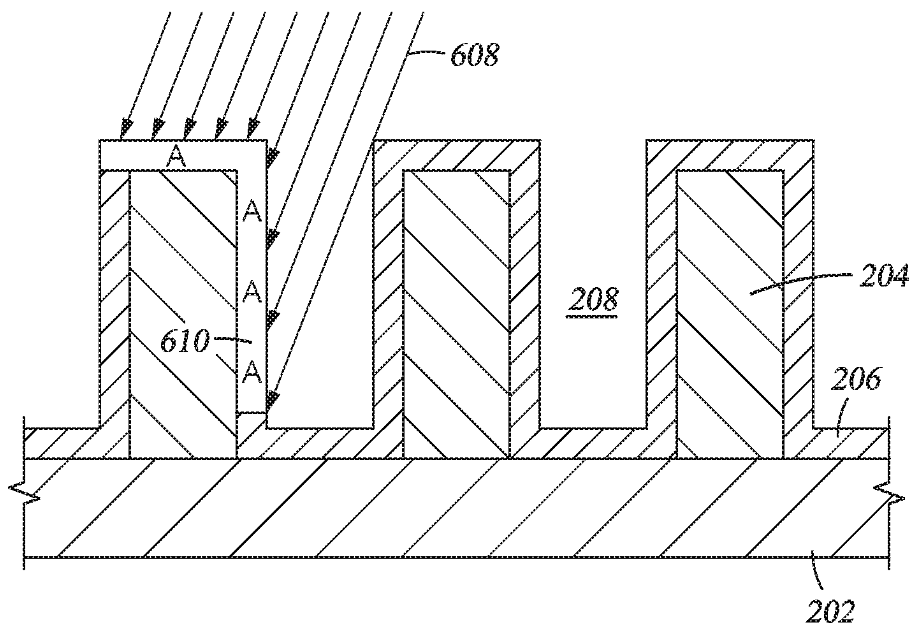

Fig. 6A

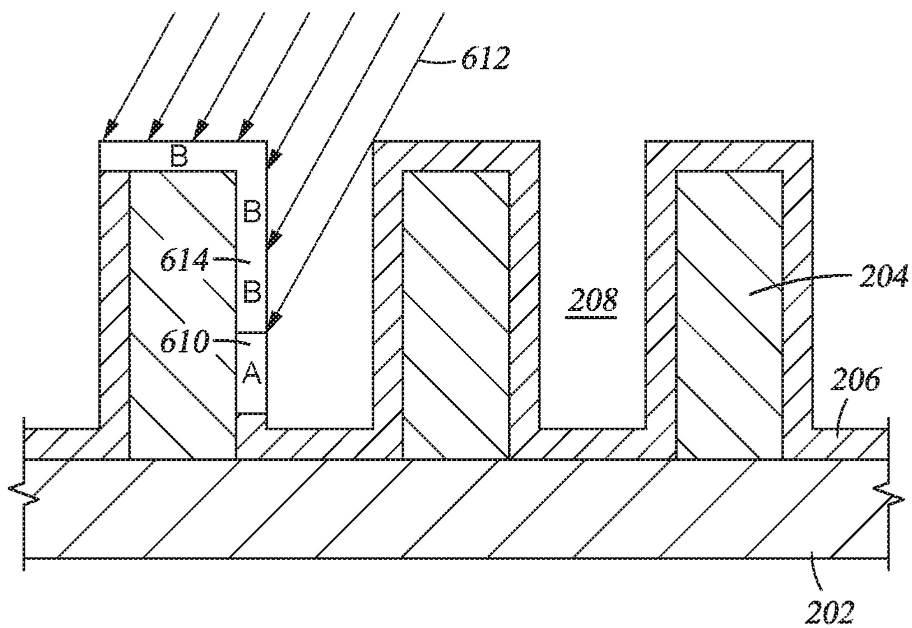

Fig. 6B

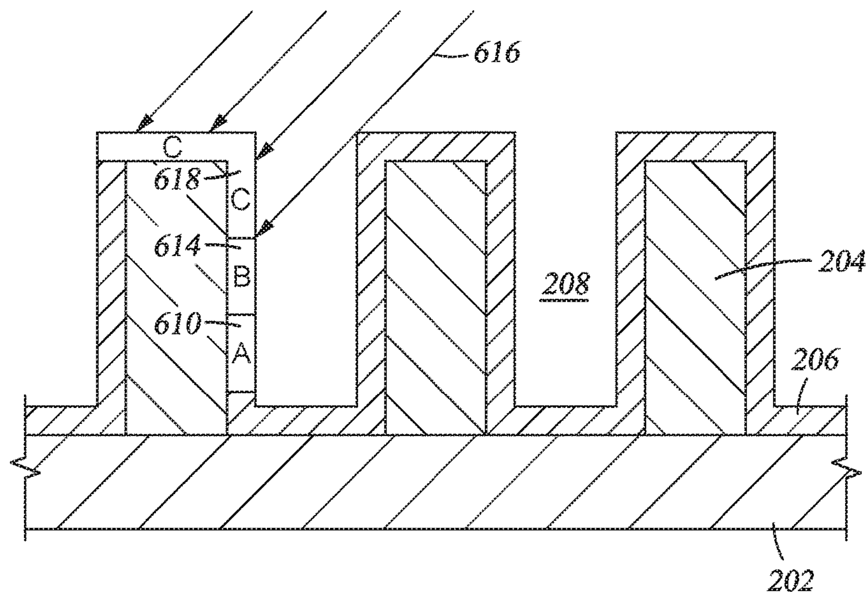

Fig. 6C

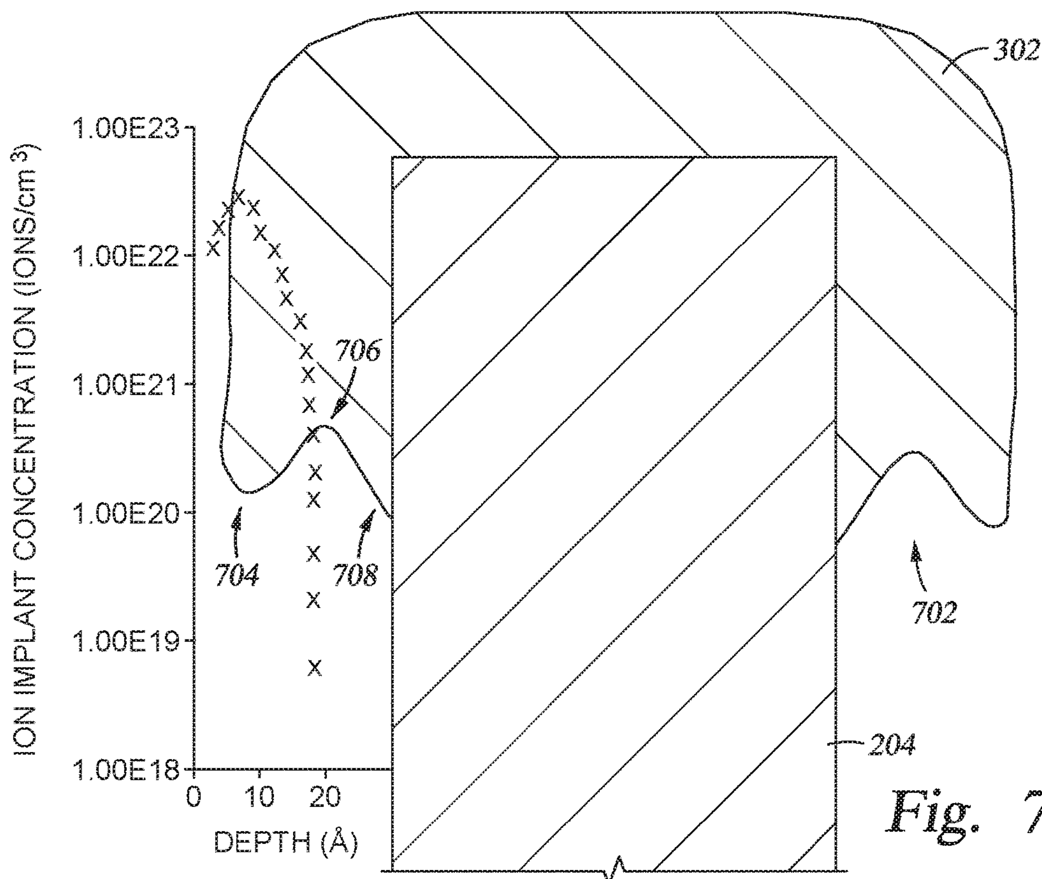

Fig. 7

3D MATERIAL MODIFICATION FOR ADVANCED PROCESSING

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a divisional of U.S. patent application Ser. No. 14/613,545, filed Feb. 4, 2015, which claims benefit to U.S. Provisional Patent Application No. 62/089,081, filed Dec. 8, 2014, both of which are herein incorporated by reference in their entirety.

BACKGROUND

Field

Embodiments of the present disclosure generally relate to methods and device structures which may be utilized in advanced patterning schemes. More specifically, embodiments described herein relate to three dimensional (3D) material modification for advanced processing methods.

Description of the Related Art

In response to an increased need for smaller electronic devices with denser circuits, devices with three dimensional (3D) structures have been developed. An example of such devices may include FinFETs having conductive fin-like structures that are raised vertically above a horizontally extending substrate. Conventional FinFETs may be formed on a substrate, such as a semiconducting substrate or silicon-on-insulator (SOI). The substrate may comprise a semiconducting substrate and an oxide layer disposed on the semiconducting substrate.

In light of the continued demand for continually smaller devices, various integration and advanced patterning schemes have been proposed. Examples of advanced applications include fin isolation, gate-all-around and 3D capping, among others. These 3D integration schemes generally demand precise processing capabilities which are operable at increasingly reduced technology nodes. For example, 3D hardmasks are often required to protect fin structures. However, various challenges arise in the manufacture of such features. Etch selectivity often limits the usefulness of many conventional hardmask formation processes and conventional processing schemes may lack the ability to be implemented efficiently and economically at advanced technology nodes.

Thus, what is needed are improved 3D processing methods and device structures.

SUMMARY

In one embodiment, a method of manufacturing a 3D hardmask is provided. The method includes depositing a film on a substrate having one or more fin structures formed thereon and selecting an ion implantation angle in response to an aspect ratio defined by the one or more fin structures. An ion dosage concentration and implantation energy may be selected and configured to modify compositional characteristics of the film and an implantation temperature may also be selected. Ions may be accelerated toward the film along the angle and bombard at least one surface of the film with the ions to form a modified portion of the film. An unmodified portion of the film may also be removed from the substrate.

In another embodiment, a method of manufacturing a 3D hardmask is provided. The method includes depositing a silicon nitride film on a silicon substrate having one or more fin structures formed thereon and selecting an ion implan-

tation angle in response to an aspect ratio defined by the one or more fin structures. An ion dosage concentration greater than about 5E15 (ions/cm^3) and an implantation energy may be selected and configured to modify compositional characteristics of the film and an implantation temperature of between about 15° C. and about 400° C. may also be selected. Ions may be accelerated toward the film along the angle and bombard sidewalls and a top surface of the film with the ions to form a modified cap portion of the film. An unmodified portion of the film may be etched from the substrate using a fluorine containing etching process and exposed surfaces of the substrate and fin structures may be oxidized.

In yet another embodiment, a 3D hardmask structure is provided. The 3D hardmask structure includes a modified film layer disposed on a fin structure. The modified film layer may have a top portion disposed over the fin structure and sidewall portions that extend adjacent to sidewalls of the fin structure. The modified film layer may further include an outer region having a first dopant concentration, an intermediate region having a second dopant concentration less than the first dopant concentration and an inner region having a third dopant concentration less than the second dopant concentration.

BRIEF DESCRIPTION OF THE DRAWINGS

So that the manner in which the above recited features of the present disclosure can be understood in detail, a more particular description of the disclosure, briefly summarized above, may be had by reference to embodiments, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only exemplary embodiments and are therefore not to be considered limiting of its scope, may admit to other equally effective embodiments.

FIG. **1**A illustrates a schematic diagram of a directional implantation apparatus useful to perform the methods described herein.

FIG. **1**B illustrates a schematic diagram of a directional implantation apparatus useful to perform the methods described herein.

FIG. **2** illustrates a partial, cross-sectional view of a substrate with a film deposited thereon.

FIG. **3** is a partial, cross-sectional view of the substrate illustrating a directional implantation process performed on the substrate and the film of FIG. **2**.

FIG. **4** is a partial, cross-sectional view of the substrate illustrating a 3D hardmask formed on the substrate of FIG. **3**.

FIG. **5** is a partial, cross-sectional view of the substrate illustrating an insulator layer formed on the substrate of FIG. **4**.

FIGS. **6**A-**6**C are partial, cross-sectional views of a substrate illustrating a directional implantation sequence.

FIG. **7** illustrates a partial, cross-sectional view of a 3D hardmask formed on a fin structure and a graphically represented dopant gradient profile.

To facilitate understanding, identical reference numerals have been used, where possible, to designate identical elements that are common to the figures. It is contemplated that elements and features of one embodiment may be beneficially incorporated in other embodiments without further recitation.

DETAILED DESCRIPTION

Embodiments of the present disclosure relate to material modification of three dimensional (3D) features for

advanced processing techniques. Directional ion implantation methods may be utilized to selectively modify desired regions of a material layer to improve etch characteristics of the modified material. For example, a modified region of a material layer may exhibit improved etch selectivity relative to an unmodified region of the material layer. Methods described herein may be useful for manufacturing 3D hard-masks which may be advantageously utilized in various integration schemes, such as fin isolation and gate-all-around, among others. Multiple directional ion implantation processes may also be utilized to form dopant gradient profiles within a modified layer to further influence etching processes.

The utilization of directional ion implantation methods described herein modify film properties to advantageously affect an etching rate of the film. More specifically, localized etching rates within a specific region of a film may be modified to selectively remove a desired portion of the film relative to unmodified regions of the film. In addition, ion species and film material selection may be tailored to provide more precise etching characteristics. Various other processing parameters, such as implantation angle and temperature, may enhance selective etching processes and may be suitable for utilization in advanced integration schemes.

FIG. **1**A illustrates a schematic diagram of a processing apparatus **121** useful to perform processes described herein. One example of a beam-line ion implantation apparatus is the Varian VIISTA® Trident, available from Applied Materials, Inc., Santa Clara, Calif. The processing apparatus **121** is representative of a beam-line ion implantation apparatus. In addition to the apparatus **121** described below and the apparatus **100** described with regard to FIG. **1**B, other ion implantation apparatuses, such as plasma immersion ion implantation apparatus or plasma assisted doping apparatus, may be used to perform the methods described herein.

The processing apparatus **121** may include an ion source **123** for generating ions. The processing apparatus **121** may also include a series of beam-line components. Examples of beam-line components may include extraction electrodes **125**, a magnetic mass analyzer **127**, a plurality of lenses **129**, and a beam parallelizer **131**. The processing apparatus **121** may also include a platen **133** for supporting a substrate **138** to be processed. The substrate **138** may be moved in one or more dimensions (e.g. translate, rotate, tilt, etc.) by a component sometimes referred to as a "roplat" (not shown). It is also contemplated that the processing apparatus **121** may be configured to perform heated implantation processes to provide for improved control of implantation characteristics, such as the ion trajectory and implantation energy utilized to dope the substrate.

In operation, ions of the desired species, for example, dopant ions, are generated and extracted from the ion source **123**. Thereafter, the extracted ions **135** travel in a beam-like state along the beam-line components and may be implanted in the substrate **138**. Similar to a series of optical lenses that manipulate a light beam, the beam-line components manipulate the extracted ions **135** along the ion beam. In such a manner, the extracted ions **135** are manipulated by the beam-line components while the extracted ions **135** are directed toward the substrate **138**. It is contemplated that the apparatus **121** may provide for improved mass selection to implant desired ions while reducing the probability of undesirable ions (impurities) being implanted in the substrate **138**.

The above-described processing apparatus **121** can be controlled by a processor based system controller such a controller **190**. For example, the controller **190** may be configured to control beam-line components and processing parameters associated with beam-line ion implantation processes. The controller **190** includes a programmable central processing unit (CPU) **192** that is operable with a memory **194** and a mass storage device, an input control unit, and a display unit (not shown), such as power supplies, clocks, cache, input/output (I/O) circuits, and the like, coupled to the various components of the processing apparatus **121** to facilitate control of the substrate processing. The controller **190** also includes hardware for monitoring substrate processing through sensors in the processing apparatus **121**, including sensors monitoring the substrate position and sensors configured to receive feedback from and control heating apparatus coupled to the processing apparatus **121**. Other sensors that measure system parameters such as substrate temperature and the like, may also provide information to the controller **190**.

To facilitate control of the processing apparatus **121** described above, the CPU **192** may be one of any form of general purpose computer processor that can be used in an industrial setting, such as a programmable logic controller (PLC), for controlling various chambers and sub-processors. The memory **194** is coupled to the CPU **192** and the memory **194** is non-transitory and may be one or more of readily available memory such as random access memory (RAM), read only memory (ROM), floppy disk drive, hard disk, or any other form of digital storage, local or remote. Support circuits **196** are coupled to the CPU **192** for supporting the processor in a conventional manner. Implantation and other processes are generally stored in the memory **194**, typically as a software routine. The software routine may also be stored and/or executed by a second CPU (not shown) that is remotely located from the hardware being controlled by the CPU **192**.

The memory **194** is in the form of computer-readable storage media that contains instructions, that when executed by the CPU **192**, facilitates the operation of the apparatus **121**. The instructions in the memory **194** are in the form of a program product such as a program that implements the method of the present disclosure. The program code may conform to any one of a number of different programming languages. In one example, the disclosure may be implemented as a program product stored on computer-readable storage media for use with a computer system. The program(s) of the program product define functions of the embodiments (including the methods described herein). Illustrative computer-readable storage media include, but are not limited to: (i) non-writable storage media (e.g., read-only memory devices within a computer such as CD-ROM disks readable by a CD-ROM drive, flash memory, ROM chips or any type of solid-state non-volatile semiconductor memory) on which information is permanently stored; and (ii) writable storage media (e.g., floppy disks within a diskette drive or hard-disk drive or any type of solid-state random-access semiconductor memory) on which alterable information is stored. Such computer-readable storage media, when carrying computer-readable instructions that direct the functions of the methods described herein, are embodiments of the present disclosure.

FIG. **1**B illustrates a schematic diagram of another processing apparatus **100** useful to perform processes described herein. The plasma processing apparatus **100** is representative of a bi-directional plasma implantation apparatus and the plasma processing apparatus **100** includes a process chamber **102**, a platen **134**, a source **106**, and a modifying element **108**. The platen **134** may be positioned in the processing chamber **102** for supporting the substrate **138**.

The platen **134** may be coupled to an actuator (not shown) which may cause the platen **134** to move in a scanning motion. The scanning motion may be a back and forth movement within a single plane which may be substantially parallel to the modifying element **108**. The source **106** is configured to generate the plasma **140** in the process chamber **102**. The modifying element **108** includes a pair of insulators **112**, **114** which may define a gap therebetween having a horizontal spacing (G). The insulators **112**, **114** may comprise an insulating material, a semi-conducting material, or a conductive material. The modifying element **108** also includes a directional element **113** disposed in a position relative to the insulators **112**, **114** to define a directional pathway for ion **101** delivered toward the substrate **138**.

In operation, a gas source **188** may supply an ionizable gas to the process chamber **102**. Examples of an ionizable gas may include BF_3, BI_3, N_2, Ar, PH_3, AsH_3, B_2H_6, H_2, Xe, Kr, Ne, He, CHF_3, C_2F_6, CH_4, CF_4, CO_2, AsF_5, Carborane, PF_3 and PF_5, among others. More specifically, species of ions may include He+, H_3+, H_2+, H+, Ne+, F+, C+, CF_x+, CH_x+, C_xH_y, N+, B+, BF_2+, B_2H_x+, Xe+ and molecular carbon, boron, or boron carbide ions. The source **106** may generate the plasma **140** by exciting and ionizing the gas provided to the process chamber **102**. The ions **101** are attracted from the plasma **140** across the plasma sheath **142**. For example, a bias source **189** is configured to bias the substrate **138** to attract the ions **101** from the plasma **140** across the plasma sheath **142**. The bias source **189** may be a DC power supply to provide a DC voltage bias signal or an RF power supply to provide an RF bias signal.

The modifying element **108** modifies the electric field within the plasma sheath **142** to control a shape of the boundary **141** between the plasma **140** and the plasma sheath **142**. The modifying element **108** includes the insulators **112**, **114** and directional element **113**. The insulators **112**, **114** and directional element **113** may be fabricated from materials such as quartz, alumina, boron nitride, glass, silicon nitride, silicon, silicon carbide, doped silicon, graphite, and other suitable materials. The boundary **141** between the plasma **140** and the plasma sheath **142** is dependent upon the placement of the directional element **113** relative to the insulators **112**, **114** as the directional element **113** may alter the electric field within the plasma sheath **142**.

Ions following a trajectory path **171** may strike the substrate **138** at about an angle of +θ normal to the plane **151**. Ions following trajectory path **169** may strike the substrate **138** at an angle of about −θ normal to the plane **151**. Accordingly, the range of incident angles normal to the plane **151** may be between about +1° and about +89° and between about −1° and about −89°, excluding 0°. For example, a first range of incident angles normal to the plane **151** may be between about +30° and about +80° and a second range of incident angles may be between about −30° and about −80°. In one embodiment, the first range of incident angles relative to the plane **151** may be between about −40° and about −70° and the second range of incident angles relative to the plane **151** may be between about +40° and about +70°. In addition, some ion trajectories, such as paths **169** and **171**, may cross one another.

Depending on a number of factors including, but not limited to, the positioning of the directional element **113**, horizontal spacing (G) between the insulators **112**, **114**, the vertical spacing (Z) of the insulators **112**, **114** above the plane **151**, the dielectric constant of the directional element **113** and the insulators **112**, **114** and other plasma processing parameters, the range of incident angles (θ) as described above, is between about +89° and about −89°, exclusive of 0°.

The range of incident angles may be selected based upon an aspect ratio of a 3D feature on the substrate **138**. For example, sidewalls **147** of a fin structure **144** having one or more material film layers formed thereon, having an exaggerated size for clarity of illustration, may be more uniformly treated by the ions **101** than with conventional plasma processing apparatuses and procedures. For example, by utilizing a bimodal ion distribution, only desired areas of the features may be modified as a result of shadowing effects and the ion trajectory. The processing apparatus **121** may be configured to perform heated implantation processes. The aspect ratio, which may be defined as the relationship between a pitch between the sidewalls **147** and a height of the sidewalls **147** extending from the substrate **138**, may determine the trajectory at which the ions **101** are directed toward the sidewalls **147**. In one embodiment, the trajectory of the ions **101** and the incident angle relative to the plane **151** may be selected to avoid contact with material below the sidewalls **147**, for example, the substrate **138** in one embodiment, or an insulator in another embodiment. It is also contemplated that different angles and ion trajectories may be selected for different orientations of features disposed on the substrate. For example, treatment of a fin structure and treatment of a gate structure may utilize the same or different ion trajectories, materials, dosages, etc.

The above-described processing apparatus **100** can be controlled by a processor based system controller such as the controller **190**. For example, the controller **190** may be configured to control flow of various precursor and process gases from gas sources and control processing parameters associated with directional ion implantation processes. The controller **190** includes the programmable central processing unit (CPU) **192** that is operable with the memory **194** and a mass storage device, an input control unit, and a display unit (not shown), such as power supplies, clocks, cache, input/output (I/O) circuits, and the like, coupled to the various components of the processing apparatus **100** to facilitate control of the substrate processing. The controller **190** also includes hardware for monitoring substrate processing through sensors in the processing apparatus **100**, including sensors monitoring the substrate position and sensors configured to receive feedback from and control heating apparatus coupled to the processing apparatus **100**. Other sensors that measure system parameters such as substrate temperature, chamber atmosphere pressure and the like, may also provide information to the controller **190**.

To facilitate control of the processing apparatus **100** described above, the CPU **192** may be one of any form of general purpose computer processor that can be used in an industrial setting, such as a programmable logic controller (PLC), for controlling various chambers and sub-processors. The memory **194** is coupled to the CPU **192** and the memory **194** is non-transitory and may be one or more of readily available memory such as random access memory (RAM), read only memory (ROM), floppy disk drive, hard disk, or any other form of digital storage, local or remote. The support circuits **196** are coupled to the CPU **192** for supporting the processor in a conventional manner. Implantation and other processes are generally stored in the memory **194**, typically as a software routine. The software routine may also be stored and/or executed by a second CPU (not shown) that is remotely located from the hardware being controlled by the CPU **192**.

The memory **194** is in the form of computer-readable storage media that contains instructions, that when executed by the CPU **192**, facilitates the operation of the apparatus **100**. The instructions in the memory **194** are in the form of a program product such as a program that implements the method of the present disclosure. The program code may conform to any one of a number of different programming languages. In one example, the disclosure may be implemented as a program product stored on computer-readable storage media for use with a computer system. The program(s) of the program product define functions of the embodiments (including the methods described herein). Illustrative computer-readable storage media include, but are not limited to: (i) non-writable storage media (e.g., read-only memory devices within a computer such as CD-ROM disks readable by a CD-ROM drive, flash memory, ROM chips or any type of solid-state non-volatile semiconductor memory) on which information is permanently stored; and (ii) writable storage media (e.g., floppy disks within a diskette drive or hard-disk drive or any type of solid-state random-access semiconductor memory) on which alterable information is stored. Such computer-readable storage media, when carrying computer-readable instructions that direct the functions of the methods described herein, are embodiments of the present disclosure.

As previously described, the plasma processing apparatus **100** is only one example of an apparatus that may be used. Other apparatus, such as pattern beams, electron beams (e.g., pulsed or continuous), raster scanning, and variable scanning apparatus may be used. Any other method of directionally implanting ions may also be used. According to certain aspects, one or more energetic particle beams may include a cylindrical shaped beam, a plurality of adjacent or overlapping cylindrical beams, or a ribbon shaped beam (e.g., a continuous rectangular shaped beam). The one or more energetic particle beams can be moved relative to the substrate **138** during processing and/or the substrate **138** can be moved relative to the energetic particle beam during processing. Different processing characteristics may be used, such as beam energy, beam angle, beam angle relative to the transfer direction of the substrate **138**, and beam composition (e.g., gas ions), among other processing characteristics, may be utilized to implant one or more features or layers formed on the substrate **138**.

FIG. **2** illustrates a partial, cross-sectional view of a substrate **202** having a film **206** formed thereon. The substrate **202** may be a silicon material, such as monocrystalline silicon, or the substrate may be a silicon-on-insulator type substrate. In the illustrated embodiment, the substrate **202** is a silicon substrate having fin structures **204** formed thereon extending from the substrate **202**. It is contemplated that any number of fin structures **204** may be formed on the substrate **202**. The film **206** may be deposited over the substrate **202** and fin structures **204** and the film **206** may be formed from an insulating material. In one embodiment, the film **206** may be conformally deposited over the substrate **202**. Suitable film deposition processes include chemical vapor deposition (CVD) processes, such as plasma enhanced chemical vapor deposition (PECVD) process, atomic layer deposition (ALD) processes, or epitaxial deposition processes. Examples of suitable film materials include one or more of a silicon nitride containing material, an oxide containing material, and aluminum oxide containing material, an amorphous silicon containing material, or a polysilicon containing material.

In one embodiment, the film **206** is a silicon nitride material deposited by an ALD process, which may be a low temperature ALD process. For example, the ALD process may be performed at temperatures between about 25° C. and about 450° C. The film may be deposited to a thickness **220** of between about 1 nm and about 30 nm, such as between about 2 nm and about 4 nm. Generally the silicon nitride film **206** exhibits low quality etch resistance, but may be modified by the methods described herein to improve etch selectivity of the film **206**. In one embodiment, horizontally disposed portions **216**, **218** of the film **206** may exhibit a greater material density relative to vertically disposed portions **214**. It is believed that differing densities of the film **206** may influence subsequent ion implantation processes and may also influence etch selectivity of the film **206** due to modification profiles of the film **206** across different portions **216**, **218** as a result of ion implantation into the film **206**.

The fin structures **204** define an aspect ratio, for example a height **210** and a width **222**. The height **210** may be between about 30 nm and about 90 nm, such as about 60 nm, and the width **222** may be between about 2 nm and about 20 nm, such as about 10 nm. The aspect ratio may be altered by the presence of the film **206** disposed on the fin structures **204**. For example, the portion **216** of the film **206** may be disposed on a top of the fin structures **204**, the portion **214** of the film **206** may be disposed on sidewalls of the fin structures **204** and the portion **218** of the film **206** may be disposed on the substrate **202** between adjacent fin structures **204**. Generally the portions **216**, **218** may be horizontally disposed on the substrate **202** and the portion **214** may vertically disposed adjacent the fin structure sidewalls. A trench **208** may be defined between adjacent fin structures **204** and the trench **208** may have a width **212**. The width **212** may generally be between about 10 nm and about 30 nm, however other widths are contemplated depending upon desired feature characteristics. Generally, the dimensions of the fin structures **204** may be defined by the feature densities selected for device manufacturing at advanced nodes with reduced critical dimensions. As such, it is contemplated that the aspect ratio of the fin structures **204** and other dimensions, such as the width **212** of the trench **208**, may influence subsequent directional ion implantation processes.

FIG. **3** is a partial, cross-sectional view of the substrate **202** of FIG. **2** illustrating a directional implantation process performed on the film **206**. One or more directional ion implantation angles may be selected in response to the aspect ratio of the one or more fin structures **204**. Ions directed toward the fin structures **204** may modify at least a portion of the film **206** to form a 3D hardmask **302**. The directional implantation process may be a bi-directional process as shown in the illustrated embodiment, or the directional implantation process may be a unidirectional process. A bi-directional process may utilize at least two ion trajectories and a unidirectional process may utilize a single ion trajectory. In one embodiment, the bi-directional process may utilize similar implantation angles, but with different orientations (i.e. +/−). The directional ion implantation process accelerates ions towards the film **206** along the selected implantation trajectories defined by the angles and bombards the film **206** to implant ions therein.

For example, a first angle **304** may be selected to control exposure of the sidewalls **214** of the film **206** to the ions within the trench **208**. Similarly, a second angle **306** may be selected to control exposure of the sidewalls **214** of the film **206** to the ion within the trench **208**. The angles **304**, **306**, in combination with other processing variables, control the depth to which the ions are implanted in the film **206**. The angles **304**, **306** advantageously benefit from a shadowing

effect of adjacent fin structures **204** to prevent implantation of ions below a desired position on the sidewalls **214** of the film **206**. Generally, the first angle **304** may be between about +40° and about +70° and the second angle may be between about −40° and about −70°. Both the first angle **304** and the second angle **306** may be measured relative to a datum line oriented parallel to a horizontal surface of the substrate **202**, which may be similar to the plane **151** illustrated in FIG. **1**.

During the directional ion implantation process, ions propagate predominantly along the selected trajectories defined by the selected angles **304**, **306** and bombard the film **206**. The ion bombardment implants the ions within the film **206** to modify the film **206** by altering the physical composition of the film **206** and/or the chemical composition of the film **206**. The degree to which the physical or chemical composition of the film **206** is modified may be determined by one or more variables, including the species of ion selected, the material properties of the film **206** being modified, the rotational orientation of the substrate **202**, the temperature at which the ions are implanted, the concentration, or dosage, of the ion being implanted and the amount of energy with which the ions are implanted in the film **206**.

The substrate **202** may be rotated to orient the substrate **202** in a first position. If desired, the substrate **202** may be rotated to a second position different from the first position for further directional ion implantation processing. The rotational orientation of the substrate **202** may be utilized to improve the implantation uniformity of ions in the film **206**.

The temperature utilized to perform the ion implantation process may be between about 20° C. and about 1000° C., depending on thermal budgets of the materials present on the substrate **202**. In one embodiment, the temperature may be between about 200° C. and about 500° C., such as between about 300° C. and about 400° C., for example, about 350° C. Utilizing an elevated temperature to perform a heated ion implantation process may improve incorporation of the ions into the film **206** by maintaining bond integrity of the film material. As a result, damage to the film **206** as a result of the ion implantation may be reduced or eliminated.

The ion dosage selected to incorporate ions in the film **206** may be configured to predominantly modify surface regions of the film **206** to avoid implantation in or damage to the underlying fin structures **204**. The ion dosage is dependent upon the species of ion being utilized and the energy with which the ions are implanted, however, the dosage may be greater than about 1E15 (ions/cm^3). In one embodiment, the dosage of carbon ions (subject to the influence of other processing variables) may be between about 5E15 (ions/cm^3) and about 1E22 (ions/cm^3), such as about 1E16 (ions/cm^3). Other ions, such as boron ions and silicon ions, may be implanted with similar dosages.

The implantation energy selected to implant the ions in the film **206** may be configured to control the depth of which the ions are implanted into the film **206**. The implantation energy and depth of ion penetration into the film **206** is influenced by the species of ion selected for incorporation into the film **206**, however, the implantation energy may be between about 0.5 keV and about 8.0 keV, such as between about 1 keV and about 3 keV. In one embodiment, the implantation of carbon ions (subject to the influence of other processing variables) may be between about 0.5 keV and about 1.5 keV. Other ions, such as boron ions and silicon ions, may be implanted utilizing the energy ranges described above.

The directional ion implantation process may be performed one or more times to form the 3D hardmask **302**. In one embodiment, the directional ion implantation process may be repeated. For example, the directional ion implantation process may be performed two or more times or even four or more times. Generally, each subsequent repetition of the directional ion implantation process may utilize one or more different processing variables from the previous directional ion implantation process. For example, the directional ion implantation process may be repeated three times utilizing a single ion species, but the implantation energy or the ion dosage may be changed for each subsequent implantation process. While it may be desirable in certain embodiments to repeat the implantation process with differing processing variables, it is contemplated that the repeated processes may utilize the same or similar variables.

FIG. **4** is a partial, cross-sectional view of the substrate **202** illustrating the 3D hardmask **302** formed on the substrate **202** of FIG. **3** after a film removal process. As described above, the 3D hardmask **302** is modified by the directional ion implantation process to improve the etch resistance and selectivity of the 3D hardmask **302** relative to unmodified portions of the film **206** (See FIG. **3**). The unmodified film **206** may be subjected to an etching process to selectively remove the film **206** from the substrate **202** and the fin structures **204**. Removal of the film **206** exposes a sidewall **402** of the fin structure **204** and a bottom surface **404** of the trench **208**.

The etching process utilized to selectively remove unmodified portions of the film **206** may be a wet etching process, a dry etching process, a soft plasma etching process or a directional etching process, among other suitable processes. In one embodiment, a wet etching process utilizing a fluorine containing material, such as a hydrogen fluoride, may be utilized to remove the film **206**. In another embodiment, a low temperature plasma energized by an ion beam may be utilized to remove the unmodified portions of film **206**. It is contemplated that the type of etching process and the associated etch chemistry may be configured to remove predominantly the unmodified portions of the film **206** such that the 3D hardmask **302**, the substrate **202** and fin structures **204** are not etched to a significant degree. Accordingly, the 3D hardmask **302** remains disposed on the fin structures **204** post etch.

FIG. **5** is a partial, cross-sectional view of the substrate **202** of FIG. **4** illustrating the result of an insulator layer deposition process. In one embodiment, subsequent to formation of the 3D hardmask **302** and prior to performing the insulator deposition process, a fin oxidation process may be performed. In this embodiment, portions of the fin structures **204** not protected by the 3D hardmask **302** may be oxidized. The oxidation process may be a thermal oxidation process or an angled oxygen implantation process. The angled oxygen implantation process may be a heated implantation or an unheated process followed by a post implantation annealing process.

An insulator layer **502** may be deposited on the substrate **202** to isolate adjacent fin structures **204** from one another to reduce or eliminate current leakage. The insulator deposition process may be any suitable deposition process, and in one embodiment, a directional deposition process may be utilized to oxidize desired portions of the substrate **202** and fin structures **204**. Generally, the insulator layer **502** may be deposited below the 3D hardmask **302**. The insulator layer **502** is intended to be representative of an oxidizing material, however, other suitable insulating materials compatible with integration schemes such as, fin isolation schemes, gate-all-around schemes, and the like may be utilized. It is also

contemplated that the insulator layer **502** may already be present on the substrate **202** prior to formation of the 3D hardmask **302**.

FIGS. **6**A-**6**C are partial, cross-sectional views of the substrate **202** illustrating a directional implantation sequence according to certain embodiments described herein. Although illustrated as a unidirectional implantation sequence, it is contemplated that the embodiments described with regard to FIGS. **6**A-**6**C may be utilized in a bi-directional implantation sequence or may be utilized in combination with both unidirectional and bi-directional implantation sequences. Various directional implantation processing variables described above with regard to FIG. **3** may be beneficially incorporated, where desirable, into the embodiments described below.

FIG. **6**A illustrates a first directional ion implantation operation adapted to modify a first region **610**. The first implantation operation may utilize a first trajectory defined by a first angle **608** which is determined by the position of the first region **610** and an aspect ratio of the fin structures **204** having the film **206** formed thereon. Ions are accelerated along the first trajectory at the first angle **608** relative to the plane **151** (See FIG. **1**) towards the film **206**. In one embodiment, the first implantation operation may utilize a first ion species to modify the first region **610** with a dopant profile A having unique physical and chemical characteristics as a result of the film modification. The dopant profile A may be unique to the type of ion species utilized, the dosage, the implantation energy, and other processing variables selected when performing the first implantation operation. In one embodiment, the dopant profile A may be configured to provide a unique selective etch signature relative to other regions of the film **206**.

FIG. **6**B illustrates a second directional ion implantation operation adapted to modify a second region **614**. The second implantation operation may utilize a second trajectory defined by a second angle **612** different from the first angle **608** which is determined by the position of the second region **614** and an aspect ratio of the fin structures **204** having the film **206** formed thereon. Ions are accelerated along the second trajectory at the second angle **612** relative to the plane **151**. In one embodiment, the second implantation operation may utilize a second ion species to modify the second region **614** with a dopant profile B having unique physical and chemical characteristics as a result of the film modification. The dopant profile B may be unique to the type of ion species utilized, the dosage, the implantation energy, and other processing variables selected when performing the second implantation operation. In one embodiment, the dopant profile B may be configured to provide a unique selective etch signature relative to other regions of the film **206**, such as the first region **610**.

FIG. **6**C illustrates a third directional ion implantation operation adapted to modify a third region **618**. The third implantation operation may utilize a third trajectory defined by a third angle **616** different from the first angle **608** and the second angle **612** which is determined by the position of the third region **618** and an aspect ratio of the fin structures **204** having the film **206** formed thereon. Ions are accelerated along the third trajectory at the third angle **616** relative to the plane **151**. In one embodiment, the third implantation operation may utilize a third ion species to modify the third region **618** with a dopant profile C having unique physical and chemical characteristics as a result of the film modification. The dopant profile C may be unique to the type of ion species utilized, the dosage, the implantation energy, and other processing variables selected when performing the third implantation operation. In one embodiment, the dopant profile C may be configured to provide a unique selective etch signature relative to other regions of the film **206**, such as the first region **610** and the second region **614**.

The first, second and third directional ion implantation operations may be performed in any desired order and the position of the regions **610**, **614**, **618** may be predominantly determined by the angles **608**, **612**, **616** defining the trajectories utilized to modify the film **206** via dopant implantation. The dopant profiles A, B, C may have similar or different etch characteristics depending upon the numerous processing variables implicit in forming the regions **610**, **614**, **618**. Etch chemistries utilized to ultimately remove either unmodified regions of the film **206** adjacent the regions **610**, **614**, **618** or the regions **610**, **614**, **618** themselves may be selected, at least in part, in response to the dopant profiles A, B, C to enhance etch selectivity. The first, second and third directional ion implantation operations generally provide for improved localized etch selectivity between modified and unmodified films. It is believed that the embodiments described above may be especially advantageous in advanced integration and advanced patterning processes, such as gate-all-around integration schemes.

FIG. **7** illustrates a partial, cross-sectional view of the 3D hardmask **302** formed on one of the fin structures **204** and a graphically represented dopant gradient profile. The 3D hardmask **302**, which is modified by the directional ion implantation embodiments described above, includes an outer region **704**, and intermediate region **706** and an inner region **708**. The inner region **708** may be defined as a region of the 3D hardmask **302** disposed adjacent the sidewalls and top surface of the fin structure **204**. The outer region **704** may be a "skin" region of the 3D hardmask **302** disposed furthest from the fin structure **204**. The intermediate region **706** may be defined as a portion of the 3D hardmask disposed between the inner region **708** and the outer region **704**.

In certain embodiments, a dopant gradient profile may be formed in the 3D hardmask **302** as a result of the directional ion implantation processes described above. The dopant gradient profile may generally be defined as a graduated compositional change through a width or thickness of the 3D hardmask **302**. For example, physical and/or chemical characteristics of the 3D hardmask **302**, modified by the implantation of ions therein, may differ in the outer region **704**, the intermediate region **706** and the inner region **708** relative to one another. It is contemplated that the dopant gradient profile may define etch selectivity characteristics of the regions **704**, **706**, **708** resulting in the formation of an engineered feature **702**, such as a notch formed in the 3D hardmask **302**. The engineered feature **702** may also be formed in other shapes depending upon the dopant gradient profile and the processing variables utilized to implant the 3D hardmask **302**.

In the illustrated example, the outer region **704** may be implanted to a depth of up to about 10 Å, the intermediate region **706** may be implanted to a depth of between about 10 Å and about 20 Å, and the inner region **708** may be implanted to a depth of the between about 20 Å and about 30 Å. The depth of ion implantation into the 3D hardmaks **302** may be influenced by one or a combination of the processing variables. Generally a concentration of ions implanted within the 3D hardmask may decrease from the outer region **704** to the inner region **708**. The inner region **708** may even be devoid of implanted ions to prevent modifying or damaging the fin structure **204**. For example, the implanted ion concentration in the outer region **704** may

be between about 1E21 (ions/cm^3) and about 1E23 (ions/cm^3), the ion concentration in the intermediate region **706** may be between about 1E19 (ions/cm^3) and about 1E21 (ions/cm^3), and the implanted ion concentration in the inner region **708** may be less than about 1E19 (ions/cm^3). It is contemplated that other implanted ion concentrations may be achieved depending upon the types of materials utilized and the processing variables used.

In embodiments where the inner region **708** is devoid or predominantly devoid of implanted ions, the material characteristic of the inner region **708** may be determined by the deposition process utilized to form the 3D hardmask **302**. For example, if an ALD or plasma enhanced atomic layer deposition (PEALD) process was utilized the deposit the 3D hardmask, a density of the material in the inner region **708** may be greater on a top surface of the fin structure **204** as opposed to a sidewall of the fin structure **204**. Generally, the density of the regions **704**, **706**, **708** may influence etch selectivity characteristics and the dopant gradient profile of the 3D hardmask, in combination with the film densities, may be utilized to improve selectivity of the 3D hardmask.

In one embodiment, multiple ion implantation processes may be utilized to form a 3D hardmask with an engineered feature **702**. In the illustrated example of FIG. **7**, the engineered feature **702** shaped like a notch is formed in response to the etching of the 3D hardmask **302** having a dopant gradient-profile. Exemplary processing variables include two or more directional ion implantation processes, one or more ion species, implant energies between about 0.5 keV and about 3 keV, dosages between about 5E15 and about 1E17, implant angles of between about +/−30° and about +/−80°, and temperatures of between about 200° C. and about 500° C. After the ion implantation processes have been performed to generate a dopant gradient profile in the 3D hardmask **302**, an etching process may be performed to remove unmodified films which may exist on the fin structure **204**. During the etching process, the engineered feature **702** may be formed in response to the etch rates and etch selectivity of the etchant to the dopant concentration of the 3D hardmask **302** at various regions of the 3D hardmask **302**.

In summation, methods and materials formed utilizing directional ion implantation processes are described herein. The directional ion implantation processes are suitable for improving the creation of hardmask materials with improved etch resistance and etch selectivity. The improved etching characteristics enhance processing performance utilized in advanced integration schemes and the like.

While the foregoing is directed to embodiments of the present disclosure, other and further embodiments of the disclosure may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

What is claimed is:

1. A hardmask structure, comprising:

a modified film layer disposed on a fin structure, the modified film layer having a top portion disposed over the fin structure and sidewall portions that extend adjacent to sidewalls of the fin structure, the modified film layer comprising:

an outer region having a first dopant concentration;

an intermediate region having a second dopant concentration less than the first dopant concentration; and

an inner region having a third dopant concentration less than the second dopant concentration.

2. The hardmask structure of claim **1**, wherein the inner region is disposed adjacent the sidewalls of the fin structure.

3. The hardmask structure of claim **2**, wherein the intermediate region is disposed adjacent the inner region.

4. The hardmask structure of claim **3**, wherein the outer region is disposed adjacent the intermediate region.

5. The hardmask structure of claim **1**, wherein the intermediate region is disposed between the outer region and the inner region.

6. The hardmask structure of claim **1**, wherein the first dopant concentration is between about 1×10^{21} ions/cm^3 and about 1×10^{23} ions/cm^3.

7. The hardmask structure of claim **6**, wherein the second dopant concentration is between about 1×10^{19} ions/cm^3 and about 1×10^{21} ions/cm^3.

8. The hardmask structure of claim **7**, wherein the third dopant concentration is less than about 1×10^{19} ions/cm^3.

9. The hardmask structure of claim **8**, wherein the third dopant concentration is about 0 ions/cm^3.

10. The hardmask structure of claim **1**, wherein the outer region, the intermediate region, and the inner region comprise an engineered feature.

11. The hardmask structure of claim **10**, wherein the engineered feature defines a notched shape.

12. The hardmask structure of claim **1**, wherein the first dopant concentration is present in the outer region of the modified film layer at a depth of up to about 10 Å.

13. The hardmask structure of claim **1**, wherein the second dopant concentration is present in the intermediate region of the modified film layer at a depth of between about 10 Å and about 20 Å.

14. The hardmask structure of claim **1**, wherein the third dopant concentration is present in the inner region of the modified film layer at a depth of between about 20 Å and about 30 Å.

15. The hardmask structure of claim **1**, wherein the top portion of the modified film structure has a density greater than a density of the sidewall portions of the modified film structure.

16. The hardmask structure of claim **1**, wherein the modified film layer comprises an insulative material selected from the group consisting of a silicon nitride containing material, an oxide containing material, an aluminum oxide containing material, an amorphous silicon containing material, a polysilicon containing material, and combinations thereof.

17. A device structure, comprising:

a silicon containing fin structure;

a modified film layer disposed on the silicon containing fin structure, the modified film layer having a top portion disposed over the silicon containing fin structure and sidewall portions that extend adjacent to sidewalls of the silicon containing fin structure, the modified film layer comprising:

an outer region having a first dopant concentration between about 1×10^{21} ions/cm^3 and about 1×10^{23} ions/cm^3;

an intermediate region having a second dopant concentration between about 1×10^{19} ions/cm^3 and about 1×10^{21} ions/cm^3; and

an inner region having a third dopant concentration less than about 1×10^{19} ions/cm^3.

18. The device structure of claim **17**, wherein the modified film layer further comprises:

an engineered feature defining a notched shape.

19. The device of claim **17**, wherein the first dopant concentration is present in the outer region of the modified film layer at a depth of up to about 10 Å, the second dopant concentration is present in the intermediate region of the

modified film layer at a depth of between about 10 Å and about 20 Å, and the third dopant concentration is present in the inner region of the modified film layer at a depth of between about 20 Å and about 30 Å.

20. A device structure, comprising:

a silicon containing fin structure, wherein at least a portion of the silicon containing fin structure is oxidized;

a modified film layer disposed on the silicon containing fin structure, the modified film layer having a top portion disposed over the silicon containing fin structure and sidewall portions that extend adjacent to sidewalls of the silicon containing fin structure, the modified film layer comprising:

an outer region having a first dopant concentration between about 1×10^{21} ions/cm^3 and about 1×10^{23} ions/cm^3;

an intermediate region having a second dopant concentration between about 1×10^{19} ions/cm^3 and about 1×10^{21} ions/cm^3; and

an inner region having a third dopant concentration less than about 1×10^{19} ions/cm^3.

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