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Sinclair et al.

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(54) **TECHNIQUES FOR PROCESSING PHOTORESIST FEATURES USING IONS**

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G03F 7/00 (2006.01)

(52) **U.S. Cl.**
CPC ***G03F 7/00*** (2013.01)
USPC .... **250/492.3**; 250/492.1; 250/492.2; 250/396 R; 250/397

(58) **Field of Classification Search**
CPC C23C 14/00; C23C 14/48; H01J 37/36; H01J 37/317; H01J 37/3171; H01J 37/32412; H01J 2237/31701; H01J 2237/3365
USPC .... 250/492.1, 492.2, 492.22, 492.23, 250/492.3, 396 R, 397
See application file for complete search history.

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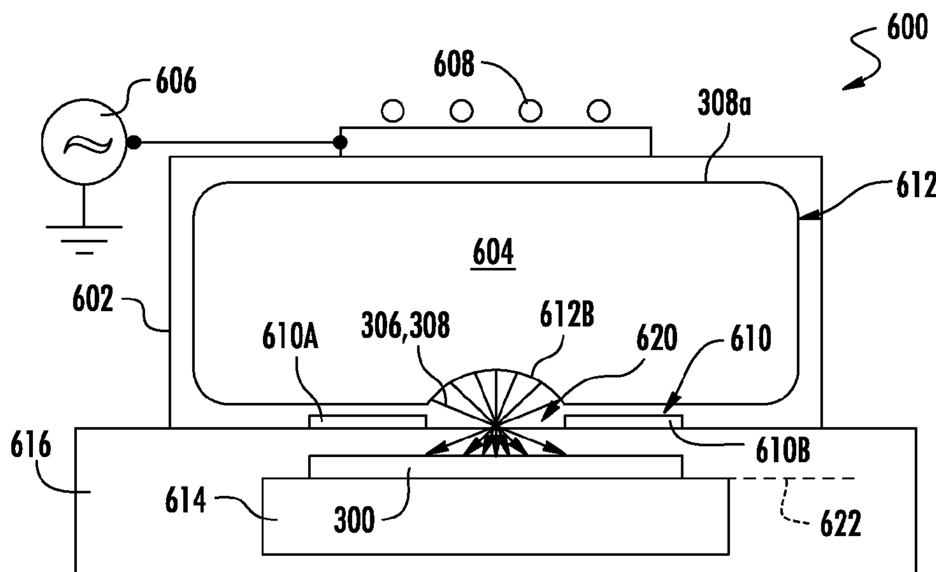
(57) **ABSTRACT**

A method of treating a substrate includes directing first ions over a first range of angles to one or more photoresist features disposed on the substrate, the first ions effective to generate an altered layer in the one or more photoresist features, the altered surface layer encapsulating an inner portion of the one or more photoresist features, and directing second ions different from the first ions over a second range of angles to the one or more photoresist features, the second ions effective to generate gaseous species in the inner regions of the one or more photoresist features.

20 Claims, 7 Drawing Sheets



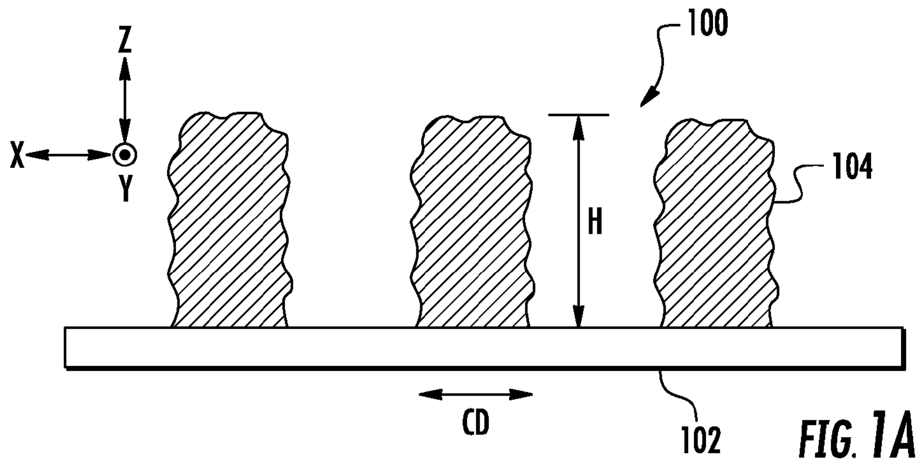


FIG. 1A

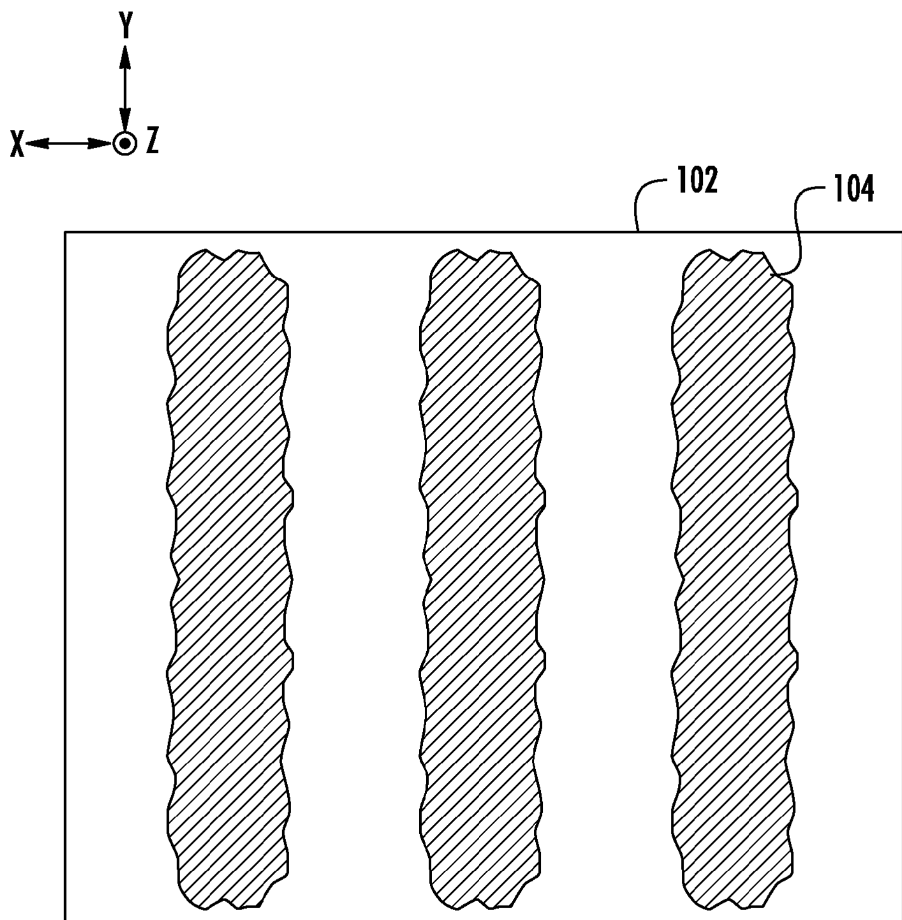


FIG. 1B

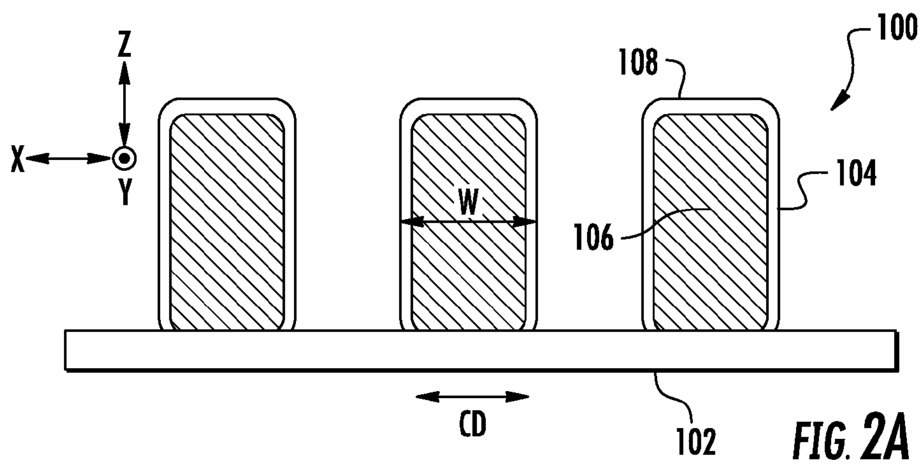


FIG. 2A

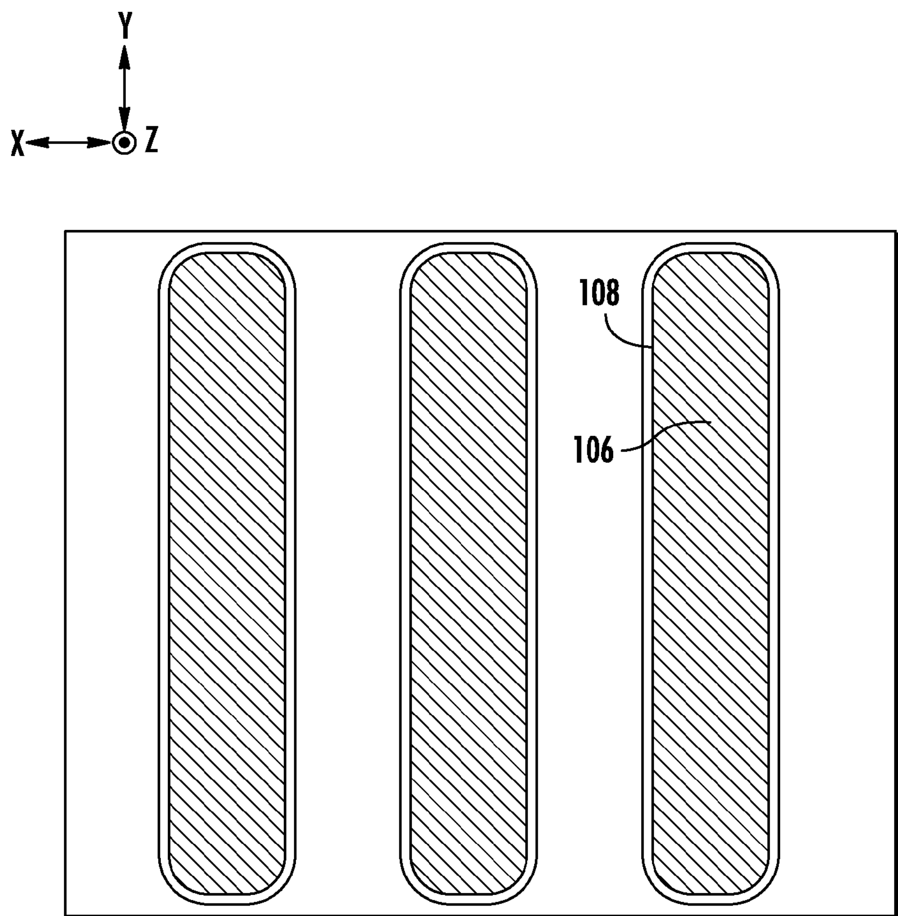


FIG. 2B

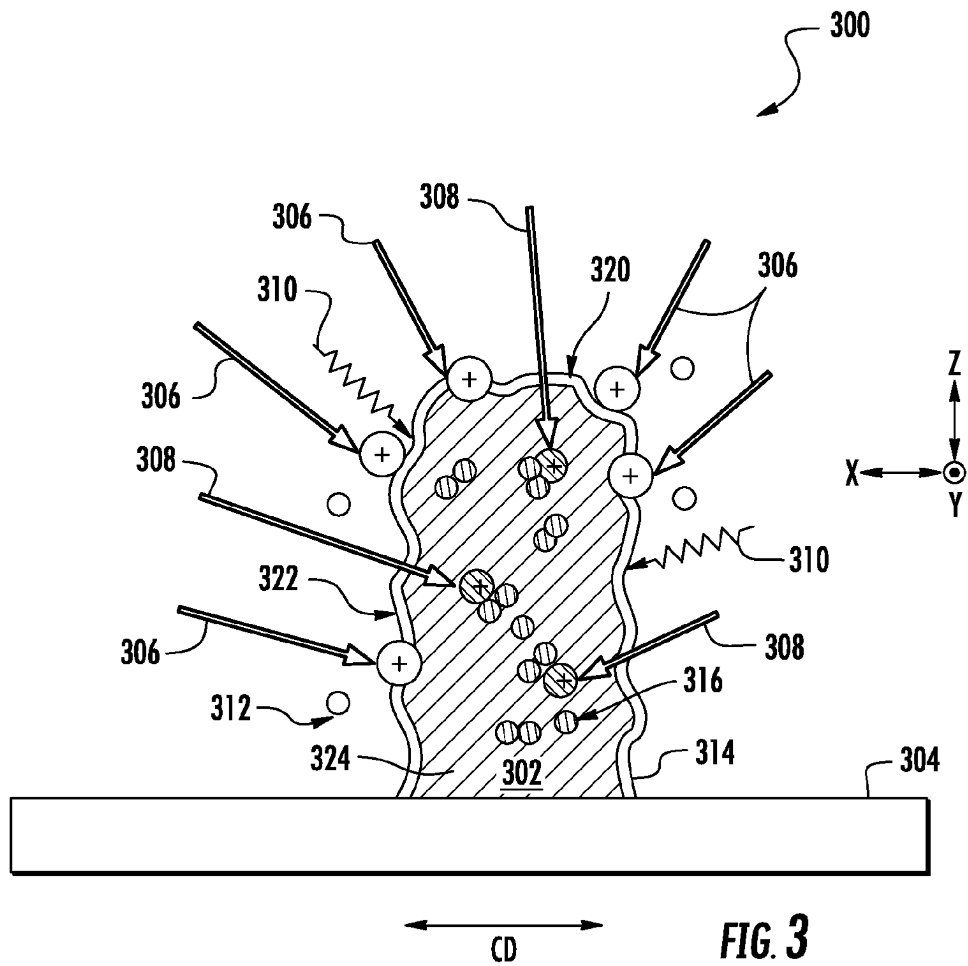


FIG. 3

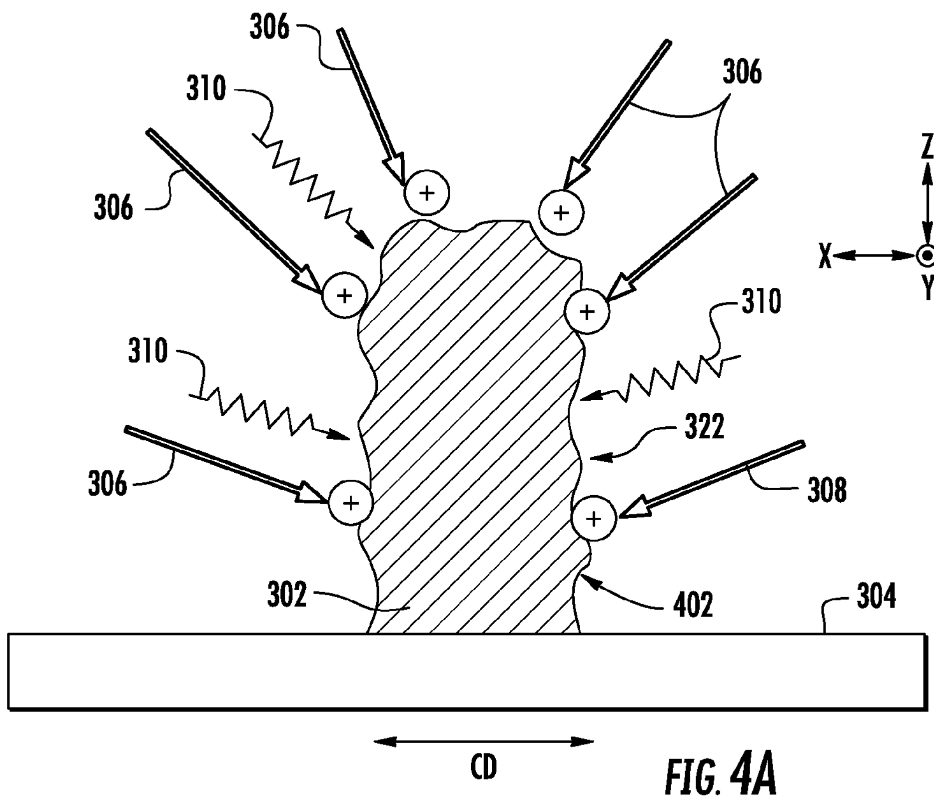


FIG. 4A

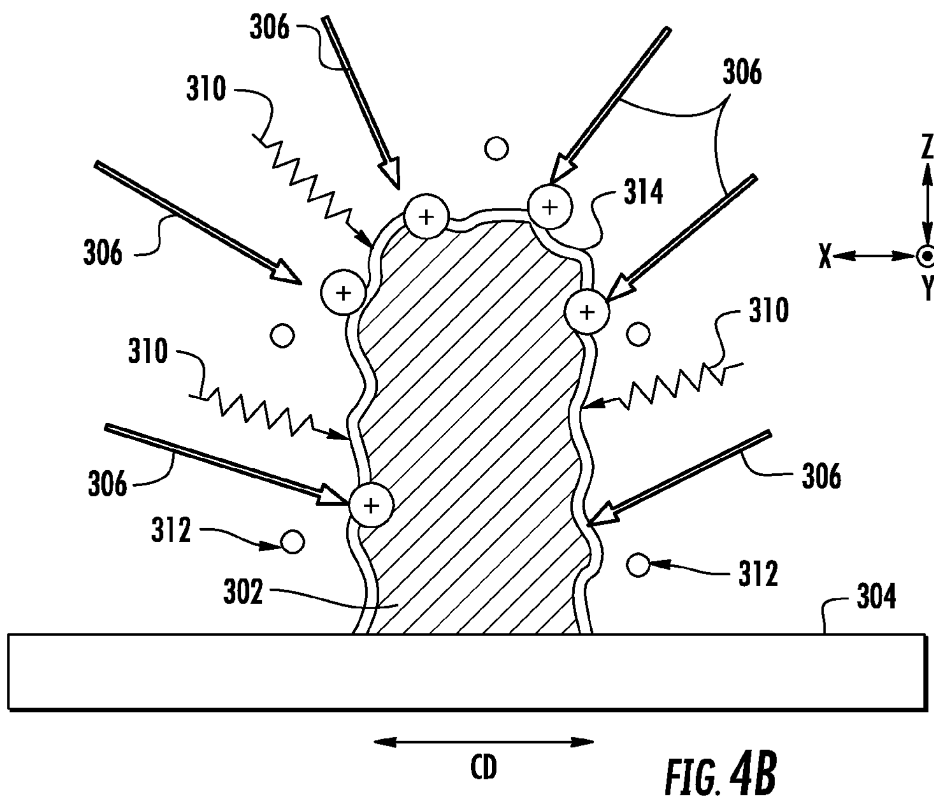


FIG. 4B

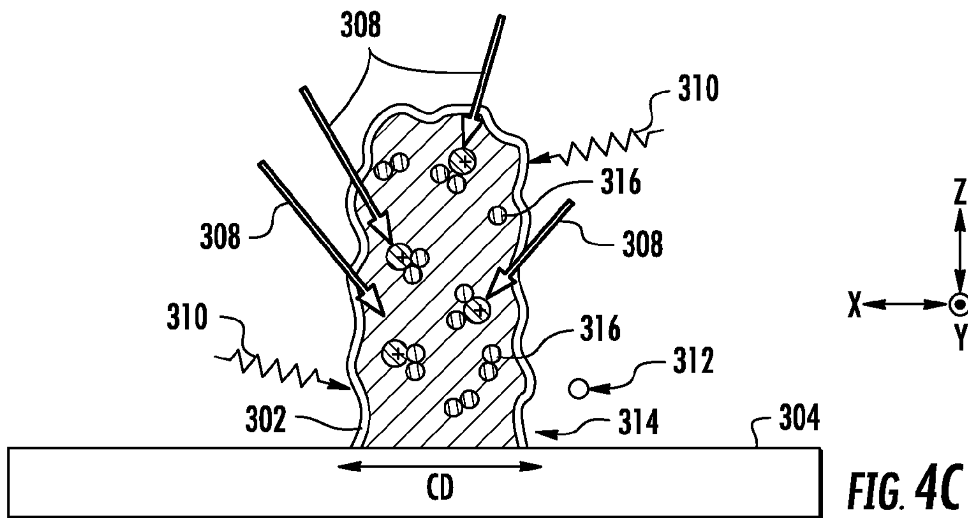


FIG. 4C

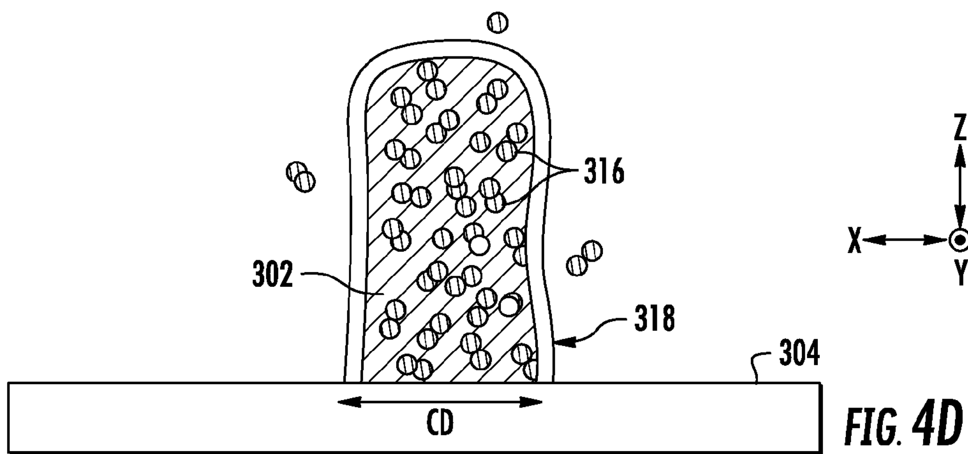


FIG. 4D

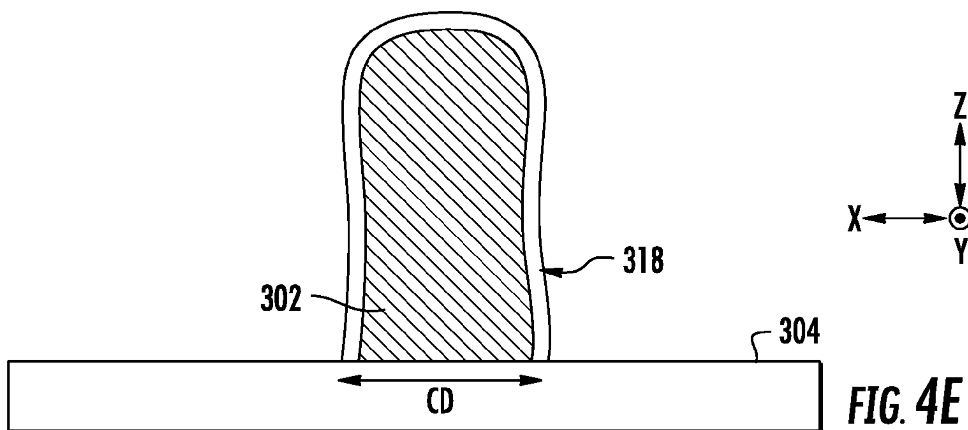


FIG. 4E

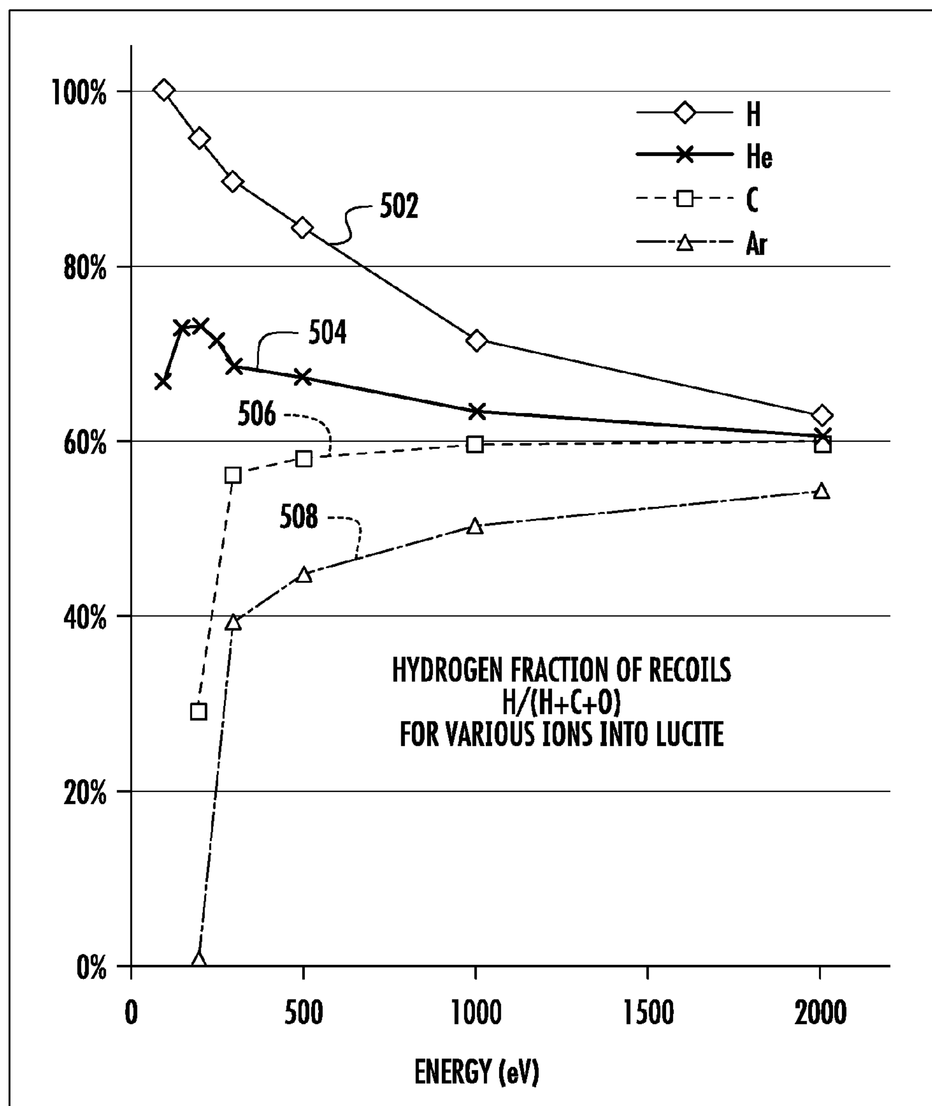


FIG. 5

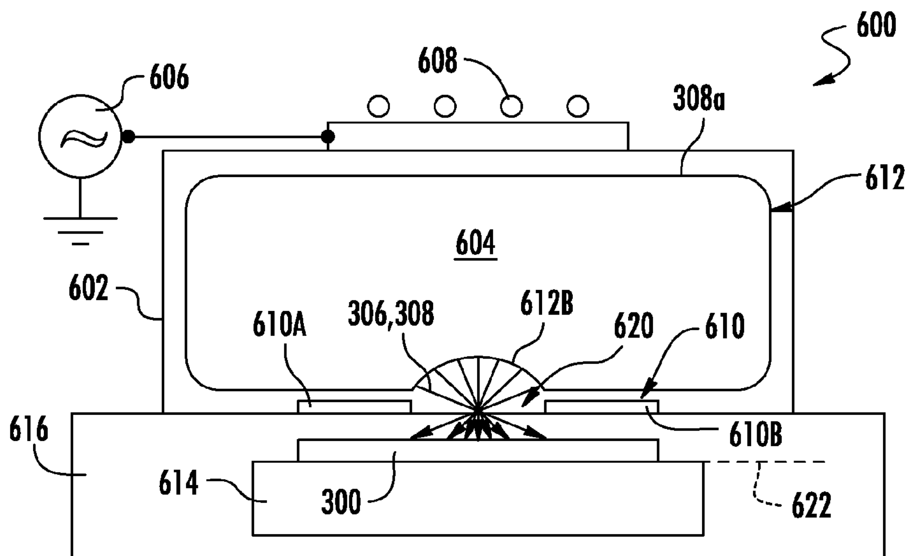


FIG. 6A

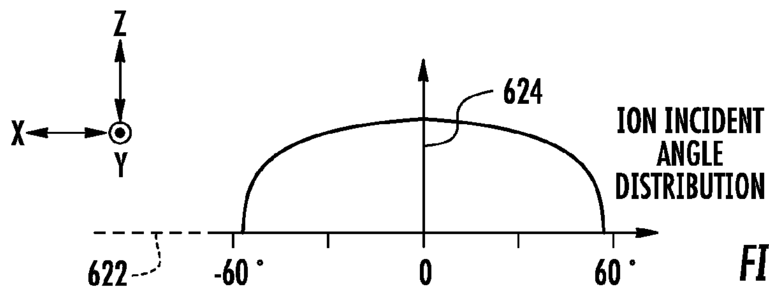


FIG. 6B

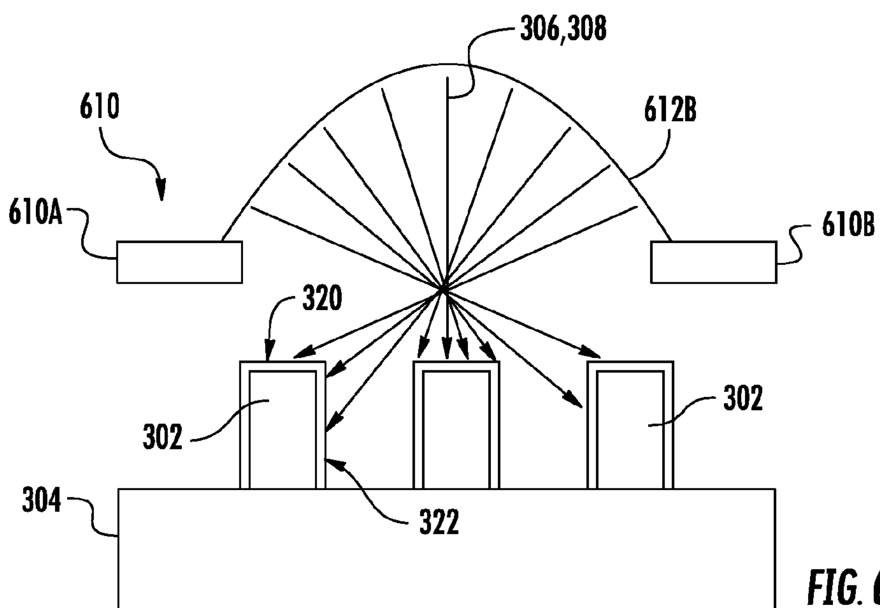


FIG. 6C

TECHNIQUES FOR PROCESSING PHOTORESIST FEATURES USING IONS

FIELD

This invention relates to fabrication of patterned substrates and more particularly to the use of ions to process patterned photoresist.

BACKGROUND

In present day electronic devices, continued scaling of integrated circuit features to smaller dimensions places continued pressure on patterning technology to define device features with required fidelity. Lithography is used to define patterns in mask material such as photoresist in order to provide a means to transfer desired patterns into permanent features of the device to be fabricated. For device critical dimensions (CD) smaller than about 50 nm, line edge roughness (LER) has emerged as a fundamental limiter to patterning devices.

Several features associated with lithographic patterning of photoresist contribute to LER and related problems. For one, the use of high molecular weight polymers has increased in recent technology generations because of smaller exposure doses required for patterning using such photoresists, resulting in higher substrate throughput. However, clustering that is inherent in high molecular weight polymers tends to increase LER in patterned high molecular weight photoresists, as opposed to lower molecular weight photoresists. LER is also exacerbated because of the fewer number of photons used to expose a photoresist material to be patterned, especially for high molecular weight photoresists. Each photon that strikes a photoresist material may induce photoacid diffusion into a spherical zone characteristic of the photoacid diffusion length. When only a small number of photons are used to expose a photoresist, as in high molecular weight photoresists, the overlapping spherical regions define rough boundaries at the edge of diffusion zones after the unexposed resist is removed. This so-called shot noise may define roughness on a scale that is a significant fraction of a CD for small photoresist features less than about 50 nm in CD.

The increased LER in patterned photoresist typically leads to increased LER in underlying substrate layers into which the photoresist pattern is subsequently transferred. In particular, during an etch step (pattern transfer) of an underlying layer, the LER from the photoresist is transferred at least in part to the material of the underlying layer being etched. While the etching used for the pattern transfer process, typically a reactive ion etch, may exhibit some capability of reducing LER, this is typically limited.

In the present day, reduction of LER remains an active area of efforts for most device manufacturers. Several additional processes have been tested to address this problem with marginal results. For example, dry chemical etch processes have the ability to remove material from the resist image but suffer pattern dependent loading effects from different exposed area to isolated to dense biases. In addition, it is important to maintain the photoresist CD within a tight tolerance. Hence it is desirable that any secondary applied technique to improve LER maintain the original photoresist attributes for profile, height, and CD. Dry chemical etch systems may also impart unwanted defects to the pattern resulting in yield loss. Another alternative approach that has been investigated in the use of a Deep Ultraviolet (DUV) cure where a rough pattern of photoresist lines or other small features is exposed to a lamp based platform in which heating through radiation exposure is used to smooth the photoresist lines. A drawback to this technique is a feature found in the corner of line segments where pattern pull back occurs, resulting in line deformation in such a way to render the device to be patterned useless.

BRIEF SUMMARY

In view of the foregoing, it will be apparent that improved methods and apparatus are desirable to reduce LER without otherwise compromising pattern integrity. Various embodiments involve treating patterned photoresist to reduce line roughness. In one embodiment, a method of treating a substrate comprises directing first ions over a first range of angles to one or more photoresist features disposed on the substrate, the first ions effective to generate an altered layer in the one or more photoresist features, where the altered surface layer encapsulates an inner portion of the one or more photoresist features. The method further includes directing second ions different from the first ions over a second range of angles to the one or more photoresist features, the second ions effective to generate gaseous species in the inner regions of the one or more photoresist features.

In another embodiment a method of reducing roughness in patterned photoresist layers on a substrate includes directing first ions over a first range of angles to one or more photoresist features disposed on the substrate, the first ions effective to generate an altered layer in the one or more photoresist features, the altered surface layer forming an encapsulating layer that surrounds an inner portion of the one or more photoresist features. The method also includes, after the directing the first ions, directing second ions different from the first ions over a second range of angles different from the first range of angles to the one or more photoresist features, where the second ions are effective to generate gaseous species in the inner regions of the one or more photoresist features.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1**A depicts a side view of photoresist features with significant LER;

FIG. **1**B depicts a top plan view of the photoresist features of FIG. **1**A;

FIG. **2**A depicts a side view of photoresist features of FIG. **1**A after dual mode implantation to reduce LER consistent with the present embodiments;

FIG. **2**B depicts a top plan view of photoresist features of FIG. **2**A;

FIG. **3** depicts various features of dual mode implantation;

FIG. **4**A depicts a first instance of dual mode implantation consistent with the present embodiments;

FIG. **4**B depicts a second instance of the dual mode implantation of FIG. **4**A;

FIG. **4**C depicts a third instance of dual mode implantation of FIG. **4**A-**4**B;

FIG. **4**D depicts a fourth instance of the dual mode implantation of FIGS. **4**A-**4**C;

FIG. **4**E depicts a fifth instance of the dual mode implantation of FIGS. **4**A-**4**D;

FIG. **5** depicts simulated hydrogen yield from ion implantation into polymethyl methacrylate photoresist as a function of ion species;

FIG. **6**A depicts an exemplary processing system that may be used for dual mode implantation;

FIG. **6**B depicts an exemplary distribution of ion angles of implantation ions consistent with the present embodiments; and

FIG. **6**C depicts details of geometry of the processing system of FIG. **6**A and a substrate.

DETAILED DESCRIPTION

The present embodiments are generally directed toward novel methods to treat patterned photoresist features. Various embodiments are effective to reduce line edge roughness while maintaining critical dimension in small photoresist features, such as those having a CD of less than 100 nm. The present embodiments in particular facilitate a control over the balance between LER reduction and maintaining CD within a tight margin.

In various embodiments techniques for treating photoresist features involve a so-called "bimode" ion implantation operation (also referred to herein as "bimode implantation"). The technique of bimode ion implantation includes at least two different ion treatments of photoresist features in which the ions are directed at photoresist features over a range of angles. The angular range provides ions that may strike a photoresist feature in a manner that treats all exposed surfaces of the photoresist feature. The two different ion treatments allow the different treatments to be tailored to different portions of the photoresist feature in a manner that may enhance smoothening of the photoresist features, and in particular may reduce LER and related roughness. In particular, the bimode ion implantation may facilitate treatment of a surface portion of the photoresist using a first set of ions independently of treatment of interior portions using a second set of ions. The independent treatment of surface and inner portions facilitates the creation of an optimum structure for photoresist features that reduces LER.

FIG. **1**A and FIG. **1**B depict a side view and a top plan view of a substrate **100** after formation of a pattern of photoresist features on a surface of the substrate. The base portion **102** may include any number of layers and structures (not explicitly shown. The photoresist features **104** are formed on the base portion using any known lithography technique. In some examples, the photolithography technique may be an optical lithography technique that induces line edge roughness as illustrated schematically by the undulating features shown. In some examples, the CD may have a nominal value of 5 nm to 100 nm, and the height H may range from about 10 nm to 300 nm. The LER represents deviation in the edge of a resist feature from an ideal smooth shape. LER is typically quantified as a linear dimension that reflects deviations in dimension along a line or other feature. For example, a photoresist line having a nominal width or CD of 22 nm may exhibit an LER of 3 to 5 nm. Such an LER may be subsequently transferred into device structures in the underlying substrate resulting in poor performance, a large variability in performance or failure of devices in some instances because of the wide variation in actual device dimensions within a device and deviation from designed dimensions.

Consistent with the present embodiments, a bimode implantation operation is performed to reduce photoresist roughness in patterned photoresist features. FIGS. **2**A and **2**B depict a side view and a top plan view of the substrate **100** shown in FIGS. **1**A and **1**B after being treated with a bimode implantation process, whose details are discussed below. After exposure to the bimode implantation process, the photoresist features **104** develop an altered region **108** that surrounds and encapsulates an inner portion **106**. Both the altered region **108** and the inner portion **106** are subjected to interaction with ions during the bimode implantation process. One component (set of ions) of the bimode implantation process discussed below is tailored to develop the altered region **108**, while another component of the bimode implantation process is tailored to induce gas formation within the inner portion **106** that results in the structure shown in FIGS. **2**A and **2**B. In particular, not only is line edge roughness reduced, but the actual width W of photoresist features **104** after bimode implantation is maintained at about the value of CD as shown. Accordingly, the bimode implantation process of the present embodiments provides a mechanism to reduce roughness in resist features without unwanted reduction in CD.

FIG. **3** depicts a schematic illustration of features of bimode implantation consistent with various embodiments. The substrate **300** is depicted as having a single photoresist feature **302** disposed on a substrate base **304**, which resist feature represents multiple such resist features in some cases. The bimode implantation is performed upon the substrate **300** by directing two sets of ions **306** and **308** to the substrate **300**. Although depicted together in FIG. **3**, the ions **306** and **308** may be directed to the substrate at separate instances in various embodiments, while in other embodiments the ions **306** and **308** may be directed concurrently to the substrate **300**. The ions **306** and ions **308** are directed generally over a range of angles so that top surface **320** and sidewalls **322** are exposed to the ions **306**, **308**. The ions **306** are generally directed to the substrate **300** before or concurrently with the ions **308**. The ions **306** are configured to interact with the outer portions of the photoresist feature **302** including the outer surface region of the photoresist. The ions **306** in particular are configured to implant into the surface region of the photoresist feature to produce an altered layer **314**. During the implantation the interaction of the ions **306** with polymer material of the photoresist may produce chemical alteration of the polymer, may induce the production of volatile species **312**, and may yield an altered material in the altered layer **314** that is carbon rich as compared to the inner portion **324**. In some embodiments, ultraviolet (UV) radiation **310** may also be directed to photoresist features **302**, which may induce chemical reactions in the surface of the photoresist features **302**, contributing to polymer chain scission, cross-linking or other chemical changes. Moreover, in some embodiments, ions **306** may include a chemically active species such as N, C, or F, which facilitate cross-linking and creation of a tensile stress in the altered layer.

The sum of exposure to ions **306** and optional UV radiation **310** contributes to imparting a different character to the altered layer **314** as compared to the inner portion **324**. Because all exposed surfaces, that is, top surface **320**, and sidewalls **322**, receive exposure to the ions **306**, the altered layer **314** may thereby extend over the entire exposed surfaces of the photoresist feature **302** and thereby encapsulate the inner portions **324** of the photoresist feature **302**. The encapsulation of the inner portion **324** facilitates smoothening of the photoresist features as detailed in the FIGs. to follow.

In contrast to the ions **306**, the ions **308** are configured to penetrate into the inner portion **324** of the photoresist feature **302**. In the inner portion, the implantation of the ions **308** may cause the release of gas species **316** when the ions **308** interact with polymers of the photoresist feature **302**. This gas may exert a pressure on the inside of the altered layer **314** that tends to inflate the photoresist feature **302** as detailed below. In so doing the roughness of the photoresist feature may be reduced while the inflation of the photoresist feature **302** compensates for loss of any photoresist material that is removed from the photoresist feature **302** by sputtering or evaporation during the exposure to ions **306**, **308**.

As further detailed below, by proper selection of processing conditions, the smoothened photoresist features may be

retained and the photoresist critical dimension maintained at a desired value. In various embodiments, whether ions **306** and **308** are provided simultaneously or in succession to one another, the ions **306** generally have greater mass than ions **308**. This facilitates the ability to direct the different ions **306**, **308** to different parts of a photoresist feature and thereby produce an optimum photoresist feature structure. In one particular example, experiments have shown that employing a dual mode ion implantation process using an Ar/Ne mixture provides a significant improvement in control of CD and reduction of LER in narrow photoresist lines as compared to the use of "monomode" implantation using either Ar alone or Ne alone.

In various embodiments one or more apparatus performs bimode implantation in two or more operations. FIG. **4**A-**4**E depict various operations involved in a bimode operation in which two different implantation operations are performed separately. The first operation directs ions over a range of angles, and with an ion energy designed such that the ions penetrate at most only to a shallow distance from the outer surface of the photoresist, which may typically be less than about 5 nm. FIG. **4**A depicts a first instance during an initial period in which such "shallow ions" impinge upon the photoresist feature **302**. The photoresist feature has a width that is approximately that of a design CD, which design CD is indicated in the FIGS. **4**A-**4**E as "CD" alongside an arrow whose length is indicative of the design CD. In this instance the total dose of ions **306** that has been received is low and the outer surface **402** has not yet developed a substantial altered layer. Subsequently, as shown in FIG. **4**B as ion exposure continues the ions **306** transform the outer regions of the photoresist feature **302** such that an altered layer **314** or "skin" is formed that surrounds the formerly exposed surfaces of the photoresist feature **302**. Examples of species that may be suitable to produce the ions **306** include Ar, Xe or a combination thereof; a chemically reactive species such as N_2, O_2, F_2, NF_3, or P. As suggested by FIG. **4**B, the ion energy of ions **306** is tailored to locate the implant depth within a range that extends from the surface of the photoresist feature only partially into the photoresist feature so that the inner portion **324** remains unimplanted by the ions **306**.

In a subsequent operation shown in FIG. **4**C the ions **308** are directed to the photoresist feature **302** that already contains the altered layer **314**. The ions **306** may be different from the ions **308** and may have a different ion energy than those of ions **306**. In particular, the ions **308** are directed with an energy that has a longer implantation range within the photoresist feature **302** than that of ions **306**, which longer implantation range may be up to 50 nm in some cases. The ions **308** may in particular have a lower mass than ions **306**. Suitable species for ions **308** include He, Ne, H_2 among others.

In the instance shown in FIG. **4**C, which may represent an initial period of exposure to ions **308** the photoresist feature **302** still retains a rough shape. However, the implantation of ions **308** into the inner portion **324** produces species including the gas species **316** as illustrated. One example of gas species **316** is H_2 which may be generated when ions **308** interact with polymers within the photoresist feature **302**. Residual gas analysis (RGA) of photoresist subject to ion implantation has shown that a predominant species released from the photoresist is H_2 with smaller amounts of low molecular weight hydrocarbons and possibly nitrogen-containing species also evident. As the gas species **316** builds up within the inner portion **324** the gas may diffuse in all directions including toward the altered layer **314**.

In accordance with various embodiments, the ion species and ion energy for ions **308** are tailored to optimize yield of gas species **316**. For example, the ion species can be selected with a mass that better matches that of hydrogen in order to ensure that a large fraction of momentum transfer caused by implanting ions **308** is imparted into the hydrogen species within the photoresist feature **302**. In this manner, the likelihood increases of dislodging hydrogen from the photoresist polymer during implantation. FIG. **5** depicts simulation of hydrogen yield for implantation into a photoresist material for four different ion species including hydrogen (curve **502**), helium (curve **504**), carbon (curve **506**), and argon (curve **508**). The photoresist is a known polymethyl methacrylate (Lucite) material. As shown, in the energy range at least up to 2000 eV the yield of hydrogen is above 60% for both hydrogen and helium ions. The yield using carbon ions is also in the range of 60% for the ion energy range between 500 and 2000 eV, while the yield for argon ions is lower. Accordingly, ions having a lower mass are more appropriate for use as ions **308** to yield a high fraction of gas.

FIG. **4**D depicts the structure of the photoresist feature at an instance subsequent to the exposure to the ions **308** shown in FIG. **4**C. As illustrated a large number of gas species **316** have been produced, which gas species exert a pressure within the photoresist feature **302**. This pressure tends to inflate the photoresist feature **302**. The altered layer **314** presents a barrier to outdiffusion of the gas species **316**, which results in an expansion of the photoresist feature **302** in response to the pressure created by the gas species **316**. The expansion may result in an increase in width (along the X-direction) of the photoresist feature, which may counteract a reduction in CD that takes place during the exposure to ions **306** and **308**. In addition, the expansion may reduce the roughness of the photoresist feature **302**.

FIG. **4**E shows the structure of the photoresist feature **302** after completion of bimode implantation. The photoresist feature **302** retains the altered layer **314** and inner portion **324**. The roughness of the photoresist feature **302** is reduced as compared to before bimode implantation, while the width is maintained at a value of the CD. The gas species **316** may also gradually outdiffuse from the photoresist feature **302**. In order to optimize the bimode implantation process, an elevated temperature may be imparted into the substrate **300** during operations generally shown in FIGS. **4**A to **4**D. The substrate **300** including photoresist features **302** may be heated to an elevated temperature using a heat source and/or may experience a rise in temperature during the implantation processes. At elevated temperature plastic deformation of the photoresist features **302** is facilitated, which deformation results in the expanded and smoothed shape of the photoresist feature **302** shown in FIG. **4**D. Subsequently, the photoresist feature **302** may be cooled and may retain its expanded and smoothed shape as shown in FIG. **4**E.

In the bimode implantation operations shown in FIGS. **4**A-*to* **4**C because ions **306** are provided at a separate instance from ions **308**, the distribution of angles of incidence for the ions **306** may be different than that of ions **308**. In some cases the ions **306** may be provided over a wider angular range than that used for implantation of ions **308**. This may be particularly useful to ensure that all surfaces of the photoresist features **302** are adequately exposed to the ions **306** to generate a complete continuous altered layer **314** that acts as a barrier to outgassing of the gas species **316**. The ions **306**, on the other hand, may be directed to the substrate over a narrower range of angles, which may be closer to perpendicular to a plane of the substrate base **304**, as suggested by FIG. **4**C. This is because a purpose of the exposure to ions **308** is the gen-

eration of gas species **316** within the inner portion **324** of the photoresist feature **302**. The generation of gas species **316** in inner portion **324**, in turn, does not require that all regions of the surface of the photoresist feature **302** are impacted by ions **308**. The bimode implantation shown in FIGS. **4**A-**4**E provides the further advantage that the first dose of ions **306** to form an optimal encapsulating layer (altered layer **314**) can be separately tailored from the second dose of ions **308** used to develop gas species **316**. In general the optimum dose for ions **306** and **308** may differ and therefore are more readily achieved when provided in separate operations.

Consistent with further embodiments, FIG. **6**A depicts an exemplary processing system **600** for performing bimode implantation. The processing system **600** includes a plasma chamber **602** in which a plasma **604** may be generated. A plasma source for the plasma **604** may, in various embodiments, be an in situ or remote, inductively coupled plasma source, capacitively coupled plasma source, helicon source, microwave source, or any other type of plasma source. In the specific embodiment depicted in FIG. **6**A, a radio frequency (RF) generator **606** is coupled to RF coils **608** to generate the plasma **604**. Ions for performing bimode implantation, such as ions **306**, **308** are extracted from the plasma **604** in a manner described below to implant into the substrate **300** that is disposed on a substrate holder **614** located in the process chamber **616**. over a range of angles

The processing system **600** includes a plasma sheath modifier (PSM) **610** adjacent to a portion of the plasma chamber **602** that is proximate the process chamber **616**. Consistent with the present embodiments, the PSM **610** defines one or more apertures **620** that are used to direct the ions **306**, **308** over a range of angles to the substrate **300**. The PSM **610** acts to cause a local perturbation in the edge of a plasma sheath of plasma **604**, as illustrated in more detail in an embodiment illustrated in FIG. **6**C, for example. By doing so, the shape of plasma sheath proximate the aperture can be controlled in a manner that causes ions **306**,**308** to exit the plasma **604** and impinge on the substrate **300** over a range of angles. By changing experimental conditions such as chamber pressure, plasma power, and so forth, the exact distribution of angle of incidence of ions **306**, **308** can be altered. FIG. **6**B depicts an exemplary distribution of angles of incidence that may be provided by the processing system **600**. As illustrated, ions may impinge upon the substrate over a range of about −60 to +60 degrees with respect to a perpendicular **624** to a substrate plane **622**. Thus, referring to FIG. **6**C, ions **306**, **308** impinge upon both top surface **320** and sidewalls **322**. Additional description of general features of a processing system with a PSM can be found in co-pending U.S. patent application Ser. No. 12/417,929, filed Apr. 3, 2009, and issued as U.S. Pat. No. 7,767,977; Ser. No. 12/418,120, filed Apr. 3, 2010; Ser. No. 12/644,103, filed Dec. 22, 2009; and Ser. No. 12/848,354, filed Aug. 2, 2010, each of which is herein incorporated in its entirety by reference.

In various embodiments, dual mode implantation is performed using a processing system such as processing system **600** by generating a plasma **604** containing the ions **306** in a first instance and directing the ions **306** to the substrate **300**. Subsequently, the processing system **600** may generate a plasma containing the ions **308** and direct the ions **308** to the substrate **300**. In this operation, besides changing the ion species in plasmas between the two different ion implantation operations, the ion energy, gas pressure, plasma power, and other experimental parameters may be changed between ion implantation operations. This affords the ability to more precisely tailor the location of the ions **306**, **308** and their impact on the photoresist features, to facilitate the different processes shown above in FIGS. **4**A-**4**D in particular.

In embodiments in which dual mode implantation is conducted by directing two different set of ions to a substrate simultaneously, the general features of dual mode implantation shown in FIG. **3** may be achieved. However, because the ions are simultaneously extracted from the same plasma, the ion energy and distribution of angles of incidence is generally not independently controlled between the two sets of ions. In some variants, the range of the ions with the same energy can be controlled by selecting the mass of the ions which is determined by the selection of the gas used. Many possible gases, such as NH_3, CH_4, SiH_4, or $Al_2(CH_3)_6$, produce relatively more massive ions such as N^+, Si^+, C^+ and Al^+ which are suitable candidates for ions **306** and simultaneously less massive ions such as H^+ suitable for ions **308**. In this variant, although the energy of the different ions is the same, the lighter ions will penetrate more deeply and treat the interior of the photoresist features, while the heavier ions will have a shorter range and will treat the superficial regions. Thus, in these variants ions **306** and **308** may be derived from a single gas precursor species such as the aforementioned NH_3, CH_4, SiH_4, or $Al_2(CH_3)_6$. However in other variants, multiple different gas species may be provided simultaneously to generate ions **306** and **308** at the same time.

In one variant of simultaneous dual mode implantation both ions **306** and **308** may be directed to a substrate **300** concurrently during a first period, followed by a second period in which only one of the sets of ions **306**, **308** is directed to the substrate **300**. For example, after an initial period it may be deemed that the ion dose of ions **306** for forming an altered layer **314** of desired thickness has been reached. However, it may be desirable to continue to implant into the photoresist feature **302** to evolve more gaseous species. Accordingly, after the first period, the source of ions **306** may be stopped while ions **308** continue to be implanted into the photoresist.

In additional embodiments, after a dual mode operation is performed, an additional ion implantation is performed at normal incidence, that is, along the perpendicular **624**. The additional ion implantation is performed to create a thicker altered layer **314**. This thicker altered layer provides additional protection of the photoresist feature **302** to subsequent etching processes used to transfer the pattern of the photoresist features **302** into the substrate base **304**.

The present embodiments provide novel techniques and apparatus for reducing photoresist roughness especially in small patterned photoresist features. A dual mode implantation process is disclosed that involves a combination of two different ion implantation operations that together reduce roughness in photoresist features without loss in critical dimension. The dual mode ion implantation process entails directing two different sets of ions over a range of angles to impinge upon all exposed surfaces of photoresist features including tops and sides of such features. A first set of ions produces an encapsulating altered layer or skin on the outer surface region of photoresist features. A second set of ions generates gas species within the encapsulated photoresist features that inflates the encapsulated features and reduces the surface roughness.

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. Thus, such 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 treating a substrate, comprising:

directing first ions over a first range of angles to one or more photoresist features disposed on the substrate, the first ions effective to generate an altered layer in a surface region of the one or more photoresist features, the altered layer encapsulating an inner portion of the one or more photoresist features; and

directing second ions different from the first ions over a second range of angles to the one or more photoresist features, the second ions effective to generate gaseous species in the inner regions of the one or more photoresist features.

2. The method of claim **1**, the first angular range comprising a same angular range as the second angular range.

3. The method of claim **1**, the first angular range comprising a wider angular range than the second angular range.

4. The method of claim **1**, the first ions comprising a first ion energy, and the second ions comprising a second ion energy different from the first ion energy.

5. The method of claim **1**, the first ions comprising one or more of Ar, Xe, N_2, O_2, F_2, NF_3, and PF_3 and the second ions comprising one or more of He, Ne, and H_2.

6. The method of claim **1**, comprising directing the second ions subsequently to the first ions.

7. The method of claim **1**, further comprising:

establishing a substrate temperature at a first temperature greater than room temperature before or during the directing first ions; and

reducing the substrate temperature to a second substrate temperature after the directing the second ions.

8. The method of claim **1**, comprising:

directing the first ions and second ions simultaneously to the substrate during a first period; and

directing only the second ions to the substrate during a second period subsequent to the first period.

9. The method of claim **8**, the first ions comprising one or more of Ar, NH_3, CH_4, Ne, and the second ions comprising one or more of He and H_2.

10. The method of claim **1**, further comprising:

forming the first ions and the second ions from a common precursor gas; and

directing the first ions and second ions simultaneously to the substrate.

11. The method of claim **1**, further comprising, after the directing the first and second ions, directing third ions at an angle of incidence generally perpendicular to a plane of the substrate.

12. The method of claim **11**, the third ions comprising a third ion energy greater than a first ion energy of the first ions and a second ion energy of the second ions.

13. The method of claim **1**, the photoresist comprising a polymer material that generates the gaseous species at least in part as hydrogen gas.

14. The method of claim **1**, wherein diffusivity of the gaseous species through the altered layer is less than diffusivity of the gaseous species through the inner region.

15. A method of reducing roughness in patterned photoresist layers on a substrate, comprising:

directing first ions over a first range of angles to one or more photoresist features disposed on the substrate, the first ions effective to generate an altered layer in the one or more photoresist features, the altered layer forming an encapsulating layer that surrounds an inner portion of the one or more photoresist features; and

after the directing the first ions, directing second ions different from the first ions over a second range of angles different from the first range of angles to the one or more photoresist features, the second ions effective to generate gaseous species in the inner regions of the one or more photoresist features.

16. The method of claim **15**, the first angular range comprising a wider angular range than the second angular range.

17. The method of claim **15**, the first ions comprising a first ion energy, and the second ions comprising a second ion energy different from the first ion energy.

18. The method of claim **15**, further comprising, after the directing the first and second ions, directing third ions at an angle of incidence generally perpendicular to a plane of the substrate, the third ions comprising a third ion energy greater than a first ion energy of the first ions and a second ion energy of the second ions.

19. The method of claim **15**, the photoresist comprising a polymer material that generates the gaseous species at least in part as hydrogen gas, wherein the altered layer comprises a carbon rich composition as compared to composition of the inner portion of the photoresist features.

20. The method of claim **15**, wherein the directing the first ions and second ions comprises:

generating a plasma having a plasma sheath; and

modifying a shape of a boundary between the plasma and the plasma sheath with a plasma sheath modifier so that a portion of the boundary facing a front surface of the substrate is not parallel to a plane defined by the front surface.

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