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(54) **PULSED PLASMA FOR FILM DEPOSITION**

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H01L 21/02 (2006.01)
H01L 21/768 (2006.01)

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CPC ***H01L 21/02274*** (2013.01); ***H01L 21/0217*** (2013.01); ***H01L 21/0234*** (2013.01); ***H01L 21/02329*** (2013.01); ***H01L 21/76826*** (2013.01); ***H01L 21/76829*** (2013.01); ***H01L 21/76831*** (2013.01)

(58) **Field of Classification Search**
CPC H01L 21/0234; H01L 21/02274; H01L 21/02329; H01L 21/0217; H01L 21/02
See application file for complete search history.

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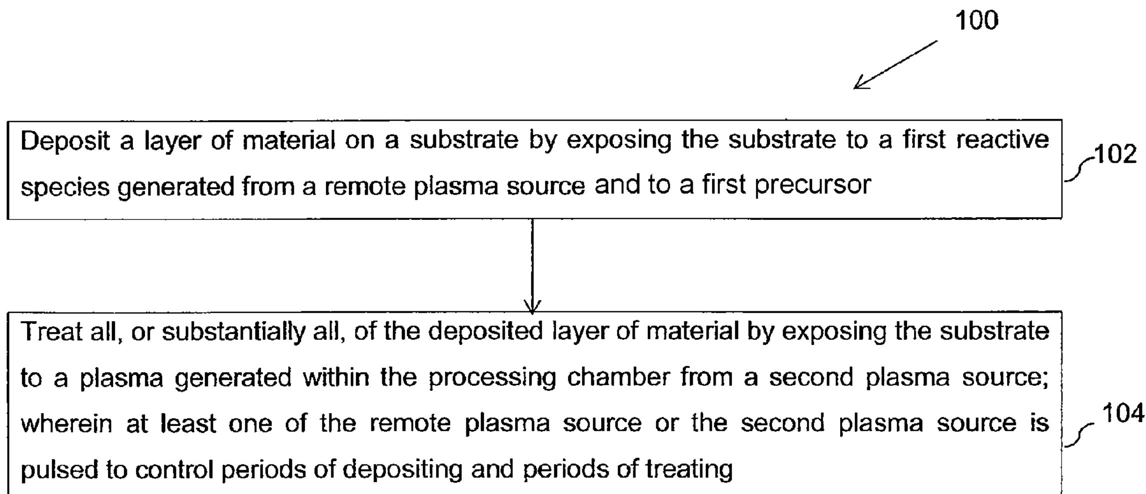
(57) **ABSTRACT**

Methods of processing a substrate are provided herein. In some embodiments, a method of processing a substrate disposed in a processing chamber includes: (a) depositing a layer of material on a substrate by exposing the substrate to a first reactive species generated from a remote plasma source and to a first precursor, wherein the first reactive species reacts with the first precursor; and (b) treating all, or substantially all, of the deposited layer of material by exposing the substrate to a plasma generated within the processing chamber from a second plasma source; wherein at least one of the remote plasma source or the second plasma source is pulsed to control periods of depositing and periods of treating.

24 Claims, 5 Drawing Sheets



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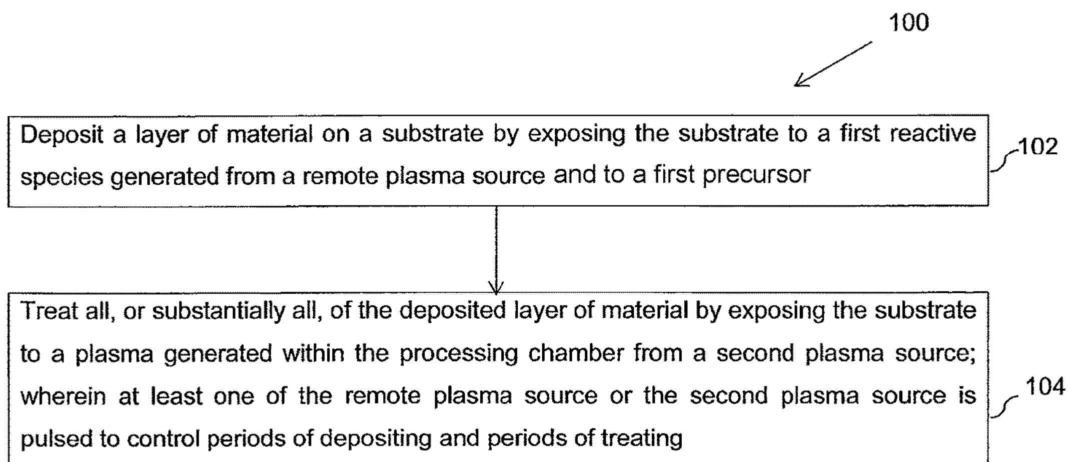


Figure 1

Fig 2A

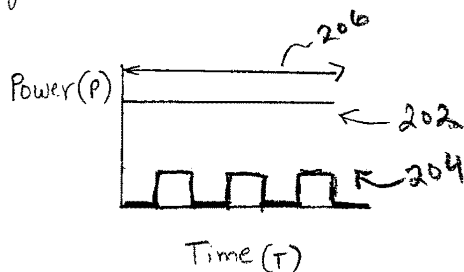


Fig 2B

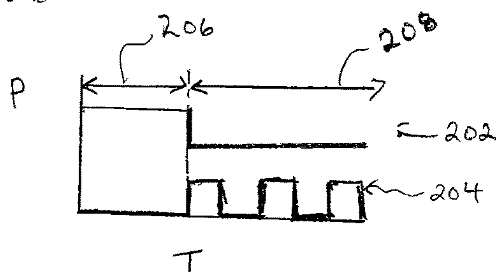


Fig. 2C

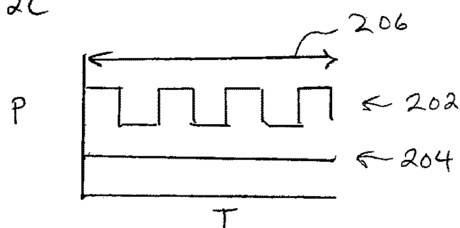


Fig 2D

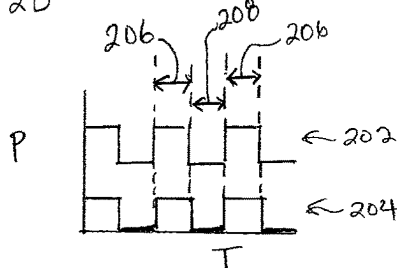


Fig 2E

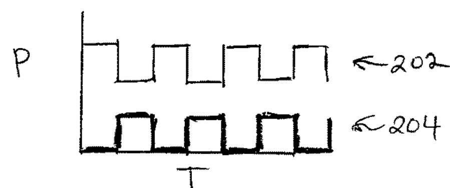


Fig 2F

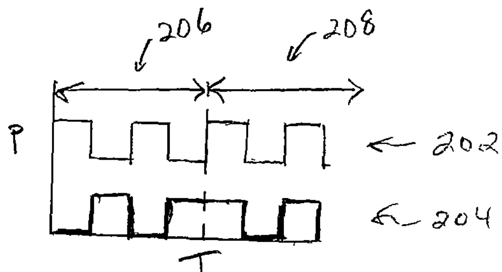


Fig. 2G

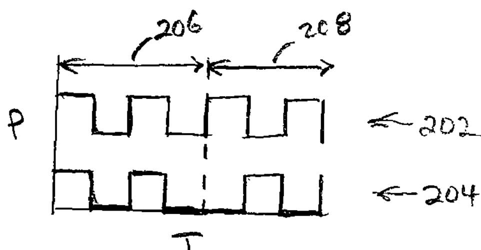


Fig 2H

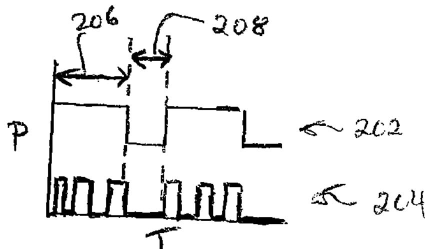
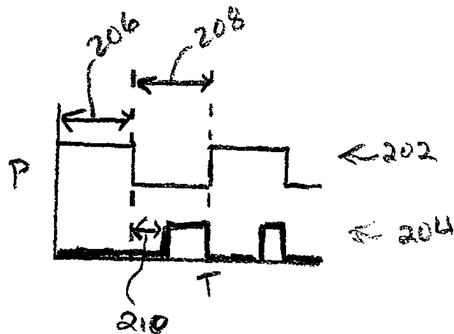


Fig. 2I



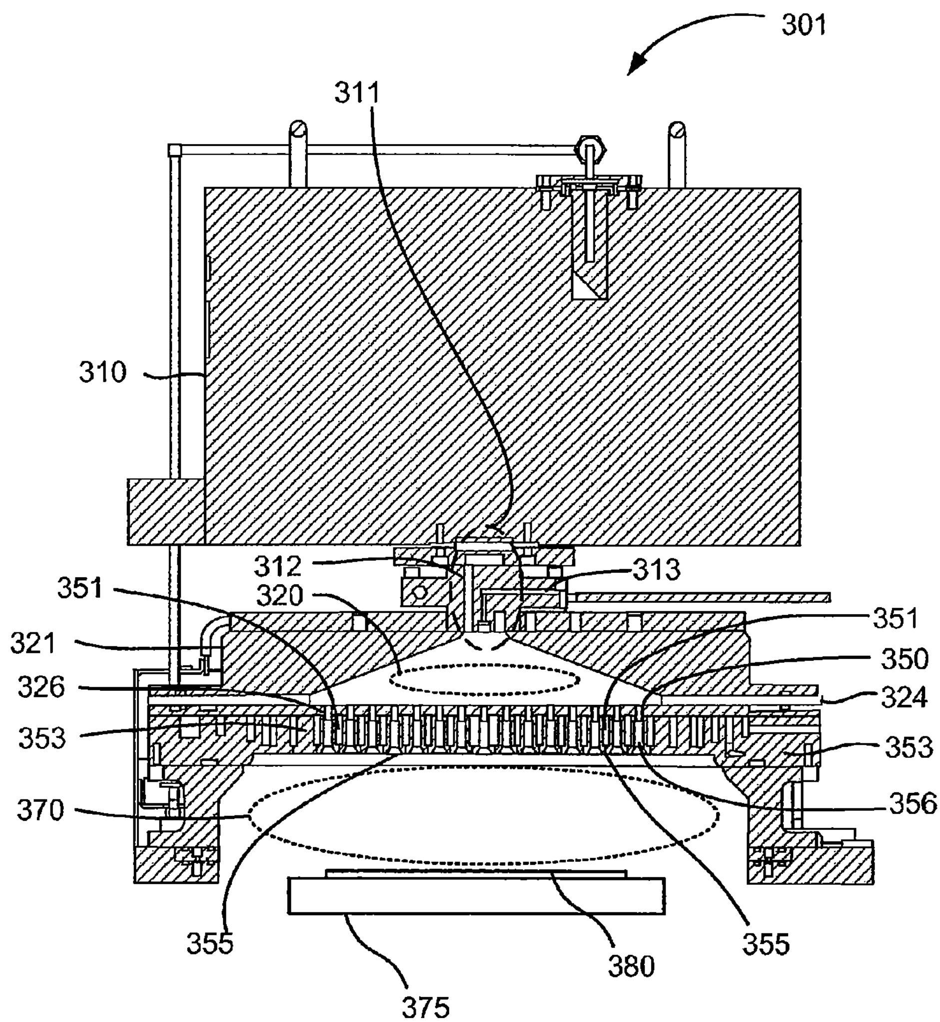


FIG. 3.

PULSED PLASMA FOR FILM DEPOSITION

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims benefit of U.S. provisional patent application Ser. No. 62/134,381, filed Mar. 17, 2015, which is herein incorporated by reference in its entirety.

FIELD

Embodiments of the present disclosure generally relate to deposition processes, such as chemical vapor deposition (CVD), and more particularly, to improvements in the deposition of a material on a substrate.

BACKGROUND

Integrated circuits (ICs) have evolved into complex circuitry that can include millions of components on a chip. The evolution of chip designs continually necessitates faster circuitry and greater circuit densities. The demand for greater circuit densities, in turn, necessitates reductions in the dimensions of integrated circuit components, which includes reductions in the sizes of the features that comprise the integrated circuit components.

The reduced feature sizes of the integrated circuit components have presented new problems in the fabrication of such components. The smaller features often have higher aspect ratios that are more difficult to fill in with materials deposited during subsequent processing. Additionally, the decrease in feature sizes also restricts the total time that the integrated circuit may be subjected to higher temperature (e.g., above 450° C.) processes, known as the thermal budget. The reduced thermal budget limits the time allowed for reflowing of the deposited materials to fill in the higher aspect ratio features.

Therefore, processes have been developed to deposit films having greater flow capability. However, such deposited films often use post-deposition processing to improve the quality of the deposited films. The inventors have observed that the additional post-deposition processing is often carried out at higher temperatures and undesirably consume part of the thermal budget at the expense of the remaining thermal budget available for other steps in the fabrication of the integrated circuit. The inventors have further observed that the post-deposition processing often includes higher energy processes that can damage the structure of the device features.

Accordingly, the inventors have provided improved methods for depositing a material on a substrate with improved film quality.

SUMMARY

Methods of processing a substrate are provided herein. In some embodiments, a method of processing a substrate disposed in a processing chamber includes: (a) depositing a layer of material on a substrate by exposing the substrate to a reactive species generated from a remote plasma source and a first precursor, wherein the reactive species reacts with the first precursor; and (b) treating all, or substantially all, of the deposited layer of material by exposing the substrate to a plasma generated within the processing chamber from a second plasma source; wherein at least one of the remote plasma source or the second plasma source is pulsed to control periods of depositing and periods of treating.

In some embodiments, a method of depositing a material disposed atop a substrate support pedestal on a substrate includes: (a) depositing a layer of material on a substrate by exposing the substrate to a reactive species generated from a remote plasma source and a first precursor, wherein the reactive species reacts with the first precursor; (b) treating all, or substantially all, of the deposited layer of material by exposing the substrate to a plasma generated within the processing chamber from a second plasma source; wherein the remote plasma source is pulsed for a first interval and the second plasma source is pulsed for a second interval concurrent with the first interval; and (c) repeating (a) and (b) until a predetermined thickness of the material is deposited and treated on the substrate, wherein a temperature of the substrate support pedestal during (a)-(c) is controlled from about −150 degrees Celsius to about 500 degrees Celsius.

In some embodiments, a non-transitory computer readable medium having instructions stored thereon that, when executed, cause a method for processing a substrate disposed atop a substrate support pedestal in a processing chamber to be performed. The method may include any of the embodiments disclosed herein.

Other and further embodiments of the present disclosure are described below.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the present disclosure, briefly summarized above and discussed in greater detail below, can be understood by reference to the illustrative embodiments of the disclosure depicted in the appended drawings. However, the appended drawings illustrate only typical embodiments of the disclosure and are therefore not to be considered limiting of scope, for the disclosure may admit to other equally effective embodiments.

FIG. **1** is a flow chart for a method for processing a substrate in accordance with some embodiments of the present disclosure.

FIG. **2**A-**2**I depict a power vs. time graph of a method for processing a substrate in accordance with some embodiments of the present disclosure.

FIG. **3** is a schematic cross sectional view of an example of a process chamber suitable for performing a method of depositing a material on a substrate in accordance with some embodiments of the present disclosure.

FIG. **4**A-C depict a side cross-sectional view of an interconnect structure formed in a substrate in accordance with some embodiments of the present disclosure.

To facilitate understanding, identical reference numerals have been used, where possible, to designate identical elements that are common to the figures. The figures are not drawn to scale and may be simplified for clarity. Elements and features of one embodiment may be beneficially incorporated in other embodiments without further recitation.

DETAILED DESCRIPTION

Embodiments of the present disclosure advantageously provide improved methods of depositing a material on a substrate. Embodiments of the present disclosure also advantageously provide methods of depositing a material on a substrate with improved film quality. Embodiments of the present disclosure further advantageously provide methods of depositing at a lower temperature a material on a substrate. Embodiments of the present disclosure also advantageously provide methods for lower temperature deposition of a material on a substrate without high temperature post-

deposition processing. Embodiments of the present disclosure also advantageously provide methods for deposition of a material on a substrate with improved film quality without a high temperature or high-energy post-deposition process. As described in greater detail below, a material may be deposited in a process chamber and also treated in the process chamber using a pulsed plasma.

FIG. **1** illustrates a flow chart of a method for processing a substrate in accordance with some embodiments of the present disclosure. The method **100** may be performed in any suitable process chambers configured for one or more of chemical vapor deposition (CVD) or plasma enhanced atomic layer deposition (PEALD). Exemplary processing systems that may be used to perform the inventive methods disclosed herein may include, but are not limited to, those of the ENDURA®, CENTURA®, or PRODUCER® line of processing systems, and the ETERNA® process chambers, all commercially available from Applied Materials, Inc., of Santa Clara, Calif. Other process chambers, including those from other manufacturers, may also be suitably used in connection with the teachings provided herein. The method may be carried out using, for example, the process chamber shown in FIG. **3** described below.

The method **100** may be performed on a substrate **400**, as depicted in FIG. **4**A, having a feature **402** formed in a first surface **404** of the substrate **400** and extending into the substrate **400** towards an opposing second surface **406** of the substrate **400**. The substrate **400** may be any substrate capable of having material deposited on the substrate **400**, such as a silicon substrate, a III-V compound substrate, a silicon germanium (SiGe) substrate, an epi-substrate, a silicon-on-insulator (SOI) substrate, a display substrate such as a liquid crystal display (LCD), a plasma display, an electro luminescence (EL) lamp display, a solar array, solar panel, a light emitting diode (LED) substrate, a semiconductor wafer, or the like.

The substrate **400** may be any suitable substrate having a feature **402** formed in the substrate. For example, the substrate **400** may comprise one or more of a dielectric material, silicon (Si), metals, or the like. In addition, the substrate **400** may include additional layers of materials or may have one or more completed or partially completed structures formed on or in the substrate **400**. For example, the substrate **400** may include a first dielectric layer **412**, such as silicon oxide, a low-k material (e.g., a material having a dielectric constant less than silicon oxide, or less than about 3.9), or the like. The feature **402** may be formed in the first dielectric layer **412**. In some embodiments, the first dielectric layer **412** may be disposed atop a second dielectric layer **414**, such as silicon oxide, silicon nitride, silicon carbide, or the like. A conductive material (e.g., conductive material **420**) may be disposed in the second dielectric layer **414** and may be aligned with the feature **402** such that the feature **402**, when filled with a conductive material, provides an electrical path to and from the conductive material. For example, the conductive material may be part of a line or via to which the interconnect is coupled.

The feature **402** may be any opening, such as a via, trench, dual damascene structure, or the like. In some embodiments, the feature **402** may have a high aspect ratio, e.g., an aspect ratio of about 5:1 or more. As used herein, the aspect ratio is the ratio of a depth of the feature to a width of the feature. The feature **402** may be formed by etching the substrate **400** using any suitable etch process. The feature **402** includes a bottom surface **408** and sidewalls **410**.

In some embodiments, and as illustrated by dotted lines in FIGS. **4**A-**4**C, the feature **402** may extend completely through the substrate **400** and an upper surface **426** of a second substrate **428** and may form the bottom surface **408** of the feature **402**. The second substrate **428** may be disposed adjacent to the second surface **406** of the substrate **400**. Further (and also illustrated by dotted lines), a conductive material (e.g., conductive material **420**), for example as part of a device, such as a logic device or the like, or an electrical path to a device requiring electrical connectivity, such as a gate, a contact pad, a conductive line or via, or the like, may be disposed in the upper surface **426** of the second substrate **428** and aligned with the feature **402**.

The method **100** begins at **102** by depositing a layer of material **416** on a substrate **400** by exposing the substrate **400** to a reactive species generated from a remote plasma source and a first precursor, wherein the reactive species reacts with the first precursor (the combination of the reactive species and the first precursor is hereinafter referred to as the reactive precursor **430**), as depicted in FIG. **4**B. In some embodiments, the deposited layer of material **416** may be a suitable semiconductor processing material. In some embodiments, the deposited layer of material **416** may be a dielectric material. In some embodiments, the deposited layer of material **416** may be a metal oxide material such as hafnium oxide, tantalum oxide, manganese oxide, or the like. In some embodiments, the deposited layer of material **416** may be a silicon-containing material, such as silicon carbide (SiC), silicon nitride (SiN), silicon oxide (SiO), silicon oxynitride (SiON), silicon oxycarbide (SiOC) or the like. In some embodiments, the layer of material **416** may be deposited in the process chamber using chemical vapor deposition (CVD), atomic layer deposition, or molecular layer deposition (MLD).

The reactive species is produced by a reactive species precursor introduced into a plasma region of the processing chamber that is separate or removed from the processing region of the chamber in which the substrate resides. The reactive species precursor may include one or more of several precursor materials. For example, the reactive species precursor may be one or more inert gases including argon, helium, nitrogen, etc. Additional gases may alternatively or additionally be used, and may include ammonia (NH_3), hydrogen, or nitrogen and/or hydrogen-containing gases. In some embodiments, the reactive species precursor may exclusively include inert gases.

The separate plasma region may also be referred to as a remote plasma region or remote plasma source and may be within a distinct module separate from the processing chamber, or as a compartment within the processing chamber for example as shown in FIG. **3**. A plasma may be formed within the remote plasma region, generating the reactive species from the reactive species precursor. The generated reactive species is directed into the substrate processing region in a number of ways, including with a pressure differential, generated electric field, or some other known mechanism for directing the flow of ions and/or electrons into the processing region.

Before, after, or concurrently with directing the reactive species into the substrate processing region, a first precursor may be introduced into the substrate processing region. The first precursor is introduced into the processing chamber in a vapor, or substantially vapor, form. In some embodiments, the first precursor is a silicon-containing precursor. In some embodiments, the silicon-containing precursor may be silanes and polysilanes that include or exclusively consist of silicon-silicon and silicon-hydrogen bonds. Exemplary precursors may include at least one silicon-silicon bond, at least two silicon-silicon bonds, at least three silicon-silicon

bonds, etc. For example, the silicon-containing precursor may be selected from any of the polysilane homologues beginning with disilane. The silicon-containing precursor may also be selected from a variety of isomers of the polysilanes. For example, if the silicon-containing precursor has five silicon atoms, the composition could include any of n-pentasilane, isopentasilane, neopentasilane, 2-silyltetrasilane, 2,2-disilyltrisilane, etc. The silicon-containing precursor may include cyclic forms or cyclosilanes, such as cyclohexasilane, for example. The polysilanes may also include any saturated or unsaturated compound such as silenes and silynes. The silicon-containing precursor may also be of a general formula such as SixHy where X may be any number of two or greater up to infinity, and Y may be any number of two or greater up to infinity. For example, such a minimal formula would denote disilyne (Si_2H_2). Y may also be any factor based on X. For example, Y may be 2X, or 2X+N, where n=2, 0, −2, −4, −6, etc., or N may be any number less than or equal to 2. Exemplary silanes can include disilane, tetrasilane, cyclohexasilane, or the like.

The reactive species and the first precursor may be reacted in the substrate processing region to form a dielectric layer, such as a silicon based dielectric layer, on the substrate. The formed layer of material may be initially flowable when formed or when deposited initially, which may allow the material to flow down into trenches to fill defined patterns on the substrate. The dielectric material may be based on reactions between the first reactive species and the silicon-containing precursor. The reactive species precursor and the first precursor may begin reacting directly upon contacting one another, and accordingly the reactive species precursor and first precursor may be separated until entering the substrate processing region. Such separation may be performed by components such as a dual-channel showerhead as described further below. The showerhead may be configured to maintain separation of the reactive species precursor and first precursor so as to prevent the reactive species precursor and first precursor from contacting one another until they enter or are delivered into the substrate processing region.

Flowability of the dielectric material may be based on a combination of process parameters including the temperature and pressure of the process in relation to the first precursor, plasma power used, and distance between the showerhead or mechanism delivering the reactive species precursor and first precursor and the substrate on which the films are to be formed. During the deposition, the substrate processing region may be relatively, substantially, or completely plasma-free. Although the reactive species may be delivered into the substrate processing region, the plasma used to generate the reactive species may be contained externally to the substrate processing region. The greatest amount of reactions may occur directly under the showerhead, or where the reactive species precursor and first precursor initially interact. The reactive species may have had the least amount of time to recombine, and thus greater reactions between the reactive species precursor and first precursor may occur. These gas phase reactions may be affected further by the material used. Silicon-silicon bonds may be weaker bonds than silicon-hydrogen, silicon-oxygen, and other silicon-based bonds. Accordingly, where these greater reactions occur, or where a higher plasma power is utilized, for the silicon-containing precursors of the present technology, a greater number of bonds may be broken. As a possible result, the dielectric material formed may have reduced or no flowability when deposited on the substrate. During the deposition process, the substrate may be maintained at or below about 500° C., and may be maintained at or below about 400° C., 300° C., 200° C., 100° C., 80° C., 75° C., 50° C., 25° C., 10° C., 0° C., −10° C., −20° C., −30° C., or less, between about 30° C. and −30° C., etc. In some embodiments, the substrate or the substrate support pedestal is controlled from about −150 degrees Celsius to about 500 degrees Celsius. The processing chamber may be maintained at or below about 100 Torr during the processes, and may be maintained at or below about 50 Torr, 25 Torr, 15 Torr, 5 Torr, 1 Torr, 0.1 Torr, etc., or between about 0.1 mTorr and about 10 Torr, or between about 0.05 to about 2 Torr. The temperature and pressure may also be set based at least partially on the vapor pressure of the precursors being used. As one non-limiting example, if tetrasilane is used as the first precursor, and the chamber temperature is about −10° C., the vapor pressure of tetrasilane may be below about 3 Torr. As such, if the chamber pressure is greater than about 3 Torr, then condensation of the tetrasilane may occur. The interaction of the reactive species with the tetrasilane may also impart energy that overcomes the condensation point. The plasma source used may include plasma generated in the chamber, but remote from and fluidly coupled with the substrate processing region, or alternatively generated in a module separate from but fluidly coupled with the processing chamber.

In some embodiments, the layer of material **416** is deposited to a thickness suitable for treatment, as described at **104** below, of all, or substantially all, of the deposited layer of material **416**. For example, in some embodiments, the layer of material **416** is deposited to a thickness of about 5 angstroms to about 25 angstroms per deposition cycle. For example, in some embodiments, a 20 Å thick layer of the material may be deposited during a 1 to 2 second interval, and the treatment of the 20 Å thick layer of the material may be carried out for about 100 milliseconds of the 1 to 2 second interval.

Next, at **104**, all, or substantially all, of the deposited layer of material **416** is treated by exposing the substrate **400** to a plasma **432** generated within the processing chamber from a second plasma source. As used herein treatment of all, or substantially all, of the deposited layer of material **416** refers to treating all, or substantially all of the exposed surface area of the deposited layer of material **416** and all, or substantially all, of the thickness of the deposited layer of material **416**. The energetic ions in the plasma **432** treat the deposited layer of material **416** by breaking or weakening the bonds within the deposited layer of material **416**.

In some embodiments, the plasma **432** is formed using a process gas (i.e. treatment gas). In some embodiments, the process gas is introduced directly into the substrate processing region. In some embodiments, the process gas is introduced into the substrate processing region via the remote plasma region. In some embodiments, the process gas is an inert gas such as helium (He), argon (Ar), neon (Ne), krypton (Kr), nitrogen (N_2), ammonia (NH_3), or any combination of these gases. In some embodiments, the process gas may be the same gas as the reactive species precursor gas described above. In some embodiments, the choice of the process gas is dependent on the deposited layer of material **416**. For example, the choice of the process gas can be dependent on providing the deposited layer of material **416** with predetermined film properties. The inventors have observed that different film properties can be achieved by varying the treatment species in the plasma.

During the method **100**, at least one of the remote plasma source or the second plasma source is pulsed to control periods of depositing the layer of material **416** and periods

of treating the layer of material **416**. The inventors have observed that pulsing the remote plasma source helps to control the deposition thickness and to separate deposition and treatment processes. The inventors have observed that pulsing the second plasma source helps to control the treatment time and treatment dose The inventors have observed that pulsing at least one of the remote plasma source or the second plasma source can break the weak bonds of the film and incorporate species into the film (e.g. use nitrogen (N_2) to treat a deposited SiNH film by breaking silicon-hydrogen (Si—H) bonds and incorporate more nitrogen (N) species into the film). The inventors have observed that pulsing at least one of the remote plasma source or the second plasma source improves film properties of the deposited layer of material **416**, such as porosity, film shrinkage, film stress, and wet etch rate ratio (WERR), without additional processing steps such as curing or annealing. For example, the method **100** improves the thermal budget to less than about 450 degrees Celsius, improves the wet etch rate ratio (WERR) to less than about 2, and improves film shrinkage to less than about 10 percent. The pulsing also increases electron density and plasma reactivity, allowing precursor molecules with strong bonds to be cracked. The cracked species can be used to treat the deposited layer of material **416** and improve the film properties listed above. In addition, during the off period of the pulsing, the cracked molecules can recombine to form new larger molecules that can be used during film deposition.

In some embodiments, a suitable plasma power source, operable in a continuous wave (CW) or pulsed mode, is coupled to the remote plasma source. In some embodiments, a suitable plasma power source, operable in a continuous wave (CW) or pulsed mode, is coupled to the second plasma source. In some embodiments, the plasma power source may be an RF power source, a microwave power source, pulsed RF power source or pulsed microwave power source.

In some embodiments, the plasma power source coupled to the remote plasma source may be capable of producing up to 3000 W at a tunable frequency in a range from about 50 KHz to about 13.56 MHz. When in pulse mode, the plasma power source may be pulsed at a pulse frequency of up to about 100 KHz, or in some embodiments, between about 1 Hz to about 100 KHz. The plasma power source may be operated at a duty cycle (e.g., the percentage of on time during the total of on time and off time in a given cycle) of between about 0.1% and about 100%.

In some embodiments, the plasma power source coupled to the second plasma source generally may be capable of producing up to 1500 W at a frequency of approximately 13.56 MHz. When in pulse mode, the plasma power source may be pulsed at a pulse frequency of up to about 100 kHz, or in some embodiments, between about 1 Hz to about 100 KHz. The plasma power source may be operated at a duty cycle (e.g., the percentage of on time during the total of on time and off time in a given cycle) of between about 0.1% and about 100%

In some embodiments, the pulsing of the remote plasma source and/or the second plasma source may be controlled by adjusting the length of time of the treatment of the deposited layer of material **416**. In some embodiments, the pulsing of the remote plasma source and/or the second plasma source may be controlled by adjusting the pulse frequency of the pulsed plasma. In some embodiments, the pulsing of the remote plasma source and/or the second plasma source may be controlled by adjusting the duty cycle of the pulsing of the plasma. In some embodiments, the pulsing of the remote plasma source and/or the second plasma source may be controlled by adjusting the power applied to pulse the remote plasma source and/or the second plasma source. In some embodiments, the pulsing of the remote plasma source and/or the second plasma source may be controlled by adjusting a treatment gas flow.

FIGS. **2**A-**2**I depict a graph in which elapsed time is shown on the horizontal axis and applied power is shown on the vertical axis. FIGS. **2**A-**2**I depict embodiments of the current disclosure in which at least one of the remote plasma source or the second plasma source is pulsed to control periods of depositing the layer of material **416** and periods of treating the layer of material **416**. Line **202** represents the remote plasma source (i.e. the deposition of a layer of material **416** on the substrate **400**) and line **204** represents the second plasma source (i.e. the treatment of the layer of material **416** deposited on the substrate **400**).

In some embodiments, as depicted in FIGS. **2**A-**2**C one of the remote plasma source (at line **202**) or the second plasma source (at line **204**) is operated in a continuous wave (CW) mode and the other is pulsed. In some embodiments, as depicted in FIG. **2**A, the remote plasma source (at line **202**) is operated in a continuous wave (CW) mode for a first interval **206** to deposit the layer of material **416** and the second plasma source (at line **204**) is pulsed during the first interval **206** to treat the deposited layer of material **416** while depositing additional layers of material **416**. The first interval **206** is an amount of time suitable for depositing a predetermined amount of the layer of material **416** and treating all, or substantially all, of the layer of material **416**.

In some embodiments, as depicted in FIG. **2**B, the remote plasma source (at line **202**) is operated in a continuous wave (CW) mode for a first interval **206** to deposit the layer of material **416** and turned off for a second interval **208** following the first interval **206**. The second plasma source (at line **204**) is pulsed during the second interval **208** to treat the deposited layer of material **416** while depositing additional layers of material **416**. The first interval **206** is an amount of time suitable for depositing a predetermined amount of the layer of material **416**. The second interval **208** is an amount of time suitable for depositing an additional predetermined amount of the layer of material **416** and treating all, or substantially all, of the layer of material **416**.

In some embodiments, as depicted in FIG. **2**C, the remote plasma source (at line **202**) is pulsed for a first interval **206** to deposit the layer of material **416**. The second plasma source (at line **204**) is operated in a continuous wave (CW) mode during the first interval **206** to continuously treat the deposited layer of material **416**. The first interval **206** is an amount of time suitable for depositing a predetermined amount of the layer of material **416** and treating all, or substantially all, of the layer of material **416**.

In some embodiments, as depicted in FIGS. **2**D-**2**I both of the remote plasma source (at line **202**) and the second plasma source (at line **204**) are pulsed. In some embodiments, as depicted in FIG. **2**D, the remote plasma source (at line **202**) and the second plasma source (at line **204**) are pulsed in phase such that the remote plasma source and the second plasma source are simultaneously on during a first interval **206** and simultaneously off during a second interval **208** to simultaneously deposit and treat the layer of material **416**. The first interval **206** is an amount of time suitable for depositing a predetermined amount of the layer of material **416** and treating all, or substantially all, of the layer of material **416**.

In some embodiments, as depicted in FIG. **2**E, the remote plasma source (at line **202**) and the second plasma source (at line **204**) are pulsed out of phase such that when the remote

plasma source is on the second plasma source is off and when the remote plasma source is off the second plasma source is on. The embodiment depicted in FIG. **2**E allows for deposition of the layer of material **416** and then subsequent treatment of the deposited layer of material **416**, without depositing additional layers of the material **416**

In some embodiments, as depicted in FIG. **2**F, the remote plasma source (at line **202**) and the second plasma source (at line **204**) are pulsed out of phase for a first interval **206** such that when the remote plasma source is on the second plasma source is off and when the remote plasma source is off the second plasma source is on. The embodiment depicted in FIG. **2**F allows for alternating deposition of the layer of material **416** and treatment of the layer of material **416** without depositing additional layers of the material **416**. The remote plasma source (at line **202**) and the second plasma source (at line **204**) are then pulsed in phase for a second interval such that when the remote plasma source is on the second plasma source is on and when the remote plasma source is off the second plasma source is off. The embodiment depicted in FIG. **2**F allows for simultaneously depositing the layer of material **416** and treating the deposited layer of material **416**. The first interval **206** is an amount of time suitable for depositing a predetermined amount of the layer of material **416** and then treating all, or substantially all, of the layer of material **416**. The second interval **208** is an amount of time suitable for depositing a predetermined amount of the layer of material **416** and simultaneously treating all, or substantially all, of the layer of material **416**.

In some embodiments, as depicted in FIG. **2**G, the remote plasma source (at line **202**) and the second plasma source (at line **204**) are pulsed in phase for a for a first interval **206** such that when the remote plasma source is on the second plasma source is on and when the remote plasma source is off the second plasma source is off. The embodiment depicted in FIG. **2**G allows for simultaneously depositing the layer of material **416** and treating the deposited layer of material **416**. The remote plasma source (at line **202**) and the second plasma source (at line **204**) are then pulsed out of phase for a second interval such that when the remote plasma source is on the second plasma source is off and when the remote plasma source is off the second plasma source is on to deposit and treat a layer of the material **416**. The first interval **206** is an amount of time suitable for depositing a predetermined amount of the layer of material **416** and simultaneously treating all, or substantially all, of the layer of material **416**. The second interval **208** is an amount of time suitable for depositing a predetermined amount of the layer of material **416** and then treating all, or substantially all, of the layer of material **416**.

In some embodiments, as depicted in FIG. **2**H, the remote plasma source (at line **202**) is pulsed on for a first interval **206** and pulsed off for a second interval **208**. The second plasma source (at line **204**) is pulsed on and off multiple times during the first interval **206** and is off during the second interval **208**. The embodiment depicted in FIG. **2**H allows for depositing the layer of material **416** while treating the deposited layer of material **416** for portions of the first interval **206**. The first interval **206** is an amount of time suitable for depositing a predetermined amount of the layer of material **416** and treating all, or substantially all, of the layer of material **416**. The second interval **208** is an amount of time suitable for allowing reactive species in the processing chamber to dissipate.

In some embodiments, as depicted in FIG. **2**I, the remote plasma source (at line **202**) is pulsed on for a first interval **206** and pulsed off for a second interval **208** and the second plasma source (at line **204**) is pulsed on a predetermined time **210** after the first interval **206** and during the second interval **208**. The embodiment depicted in FIG. **2**I allows for depositing the layer of material **416** and then allowing the reactive precursor **430** to dissipate prior to treating the deposited layer of material **416**. The first interval **206** is an amount of time suitable for depositing a predetermined amount of the layer of material **416**. The predetermined time **210** after the first interval **206** is an amount of time suitable for allowing the reactive precursor **430** to dissipate.

In some embodiments, **102**-**104** are each repeated until a predetermined thickness of the layer of material **416** is deposited and treated on the substrate **400**. Following deposition and treatment of a predetermined thickness of the layer of material **416**, the method **100** generally ends. In some embodiments, the method **100** is repeated to fill the feature **402** with the layer of material **416**. In some embodiments, a fill material **424**, for example a conductive material, may be deposited within the feature **402**, for example via a chemical vapor deposition. The feature **402** may be filled above the level of the upper surface of the substrate **400** and the deposited layer of material **416** and the fill material **424** may remain on the upper surface of the substrate **400**. Accordingly, techniques, such as wet clean in an acidic solution, chemical or electrochemical mechanical polishing, or the like may be used to remove excess deposited material from the upper surface, such that the feature **402** is filled up to about an equivalent level with the upper surface of the substrate, as depicted in FIG. **4**C.

Deposition chambers that may implement embodiments of the present disclosure may include high-density plasma chemical vapor deposition (HDP-CVD) chambers, plasma enhanced chemical vapor deposition (PECVD) chambers, sub-atmospheric chemical vapor deposition (SACVD) chambers, and thermal chemical vapor deposition chambers, among other types of chambers. Specific examples of CVD systems that may implement embodiments of the disclosure include the CENTURA ULTIMA® HDP-CVD chambers/systems, and PRODUCER® PECVD chambers/systems, available from Applied Materials, Inc. of Santa Clara, Calif.

FIG. **3** is a schematic cross sectional view of an example of a process chamber **301** suitable for performing a method of depositing a material on a substrate in accordance with some embodiments of the present disclosure.

A remote plasma system (RPS) **310** may process a gas which then travels through a gas inlet assembly **311**. Two distinct gas supply channels may be present within the gas inlet assembly **311**. A first channel **312** may carry a gas that passes through the remote plasma system (RPS) **310**, while a second channel **313** may bypass the remote plasma system (RPS) **310**. The first channel **312** and the second channel **313** may be used for a reactive species precursor or a treatment gas in disclosed embodiments. The lid (or conductive top portion) **321** and a perforated partition, such as showerhead **353**, are shown with an insulating ring **324** disposed between, which may allow an AC potential to be applied to the lid **321** relative to showerhead **353**. The reactive species precursor may travel through first channel **312** into chamber plasma region **320** and may be excited by a plasma in chamber plasma region **320** alone or in combination with remote plasma system (RPS) **310**. The combination of chamber plasma region **320** and/or remote plasma system (RPS) **310** may be referred to as a remote plasma system herein. The perforated partition or showerhead **353** may separate chamber plasma region **320** from a substrate processing region **370** beneath showerhead **353**. Showerhead **353** may allow a plasma present in chamber plasma region

320 to avoid directly exciting gases in substrate processing region **370**, while still allowing excited species to travel from chamber plasma region **320** into substrate processing region **370**.

Showerhead **353** may be positioned between chamber plasma region **320** and substrate processing region **370** and allow a first reactive species or excited derivatives of precursors or other gases created within the chamber plasma region **320** to pass through a plurality of through-holes **356** that traverse the thickness of the plate or plates included in the showerhead. The showerhead **353** may also have one or more hollow volumes **351** that can be filled with a precursor in the form of a vapor or gas, such as a first precursor, and pass through small holes **355** into substrate processing region **370**, but not directly into chamber plasma region **320**. Showerhead **353** may be thicker than the length of the smallest diameter **350** of the through-holes **356** in disclosed embodiments. In order to maintain a significant concentration of excited species penetrating from chamber plasma region **320** to substrate processing region **370**, the length **326** of the smallest diameter **350** of the through-holes may be restricted by forming larger diameter portions of through-holes **356** part way through the showerhead **353**. The length of the smallest diameter **350** of the through-holes **356** may be the same order of magnitude as the smallest diameter of the through-holes **356** or less in disclosed embodiments.

In the embodiment shown, showerhead **353** may also distribute, via through-holes **356**, process gases which contain a plasma vapor/gas such as argon, for example. Additionally, the showerhead **353** may distribute, via smaller holes **355**, a precursor that is maintained separately from the chamber plasma region **320**. The process gas or gases and the precursor may be maintained fluidly separate via the showerhead **353** until the precursors separately enter the substrate processing region **370**. The precursors may contact one another once they enter the processing region and react to form a flowable dielectric material on a substrate **380**.

In embodiments, the number of through-holes **356** may be between about 60 and about 2000. Through-holes **356** may have a variety of shapes but may be made round. The smallest diameter **350** of through-holes **356** may be between about 0.5 mm and about 20 mm or between about 1 mm and about 6 mm in disclosed embodiments. There is also latitude in choosing the cross-sectional shape of through-holes, which may be made conical, cylindrical or a combination of the two shapes. The number of small holes **355** used to introduce a gas into substrate processing region **370** may be between about 100 and about 5000 or between about 500 and about 2000 in different embodiments. The diameter of the small holes **355** may be between about 0.1 mm and about 2 mm.

An exemplary film may be created on a substrate supported by a pedestal, such as pedestal **375** having a substrate **380** disposed on the pedestal **375**, within substrate processing region **370** when a reactive species arriving through through-holes **356** in showerhead **353** combine with, for example, a silicon-containing precursor arriving through the small holes **355** originating from hollow volumes **351**. Though substrate processing region **370** may be equipped to support a plasma for other processes such as curing, no plasma may be present during the growth or deposition of the exemplary films.

A plasma may be ignited either in chamber plasma region **320** above showerhead **353** or substrate processing region **370** below showerhead **353**. Alternatively, no plasma may be formed in any portion of the chamber, and may be only formed in remote plasma system (RPS) **310**. A plasma may be present in chamber plasma region **320** to produce radical reactive species, such as from an inflow of one or more of argon, helium, hydrogen, or ammonia. An AC voltage typically in the radio frequency (RF) range is applied between the conductive top portion, such as lid **321**, of the processing chamber and showerhead **353** to ignite a plasma in chamber plasma region **320** during deposition. An RF power supply generates a high RF frequency of 13.56 MHz but may also generate other frequencies alone or in combination with the 13.56 MHz frequency. The plasma in chamber plasma region **320** may be pulsed as described above. For example, in some embodiments, a power source operable in a continuous wave (CW) mode or pulsed mode, such as a microwave power source, a RF power source, or a DC power source is coupled to the remote plasma system (RPS) **310**.

The top plasma may be left at low or no power when the bottom plasma in the substrate processing region **370** may be turned on during the formation of the dielectric layer. A plasma in substrate processing region **370** may be ignited by applying an AC voltage between showerhead **353** and the pedestal **375** or bottom of the chamber. The plasma in substrate processing region **370** may be pulsed as described above. For example, in some embodiments, a power source operable in a continuous wave (CW) mode or pulsed mode, such as a microwave power source, a RF power source, or a DC power source is coupled to the pedestal **375**.

The pedestal **375** may be moveable, and may be configured to be raised or lowered in disclosed embodiments, and may similarly be configured to rotate. The pedestal **375** may have a heat exchange channel through which a heat exchange fluid flows to control the temperature of the substrate. The heat exchange channel allows the substrate temperature to be cooled or heated to maintain relatively low temperatures, such as from about 0° C. or lower up to about 200° C. or higher. The heat exchange fluid may comprise ethylene glycol, water, or some other fluid capable of introducing or removing heat from the system. The wafer support platter of the pedestal may also be resistively heated in order to achieve relatively high temperatures from about 200° C. or lower up to about 1100° C. or higher using an embedded resistive heating element. An outer portion of the heater element may run adjacent to a perimeter of the support platter, while an inner portion runs on the path of a concentric circle having a smaller radius. The resistive heating element may additionally be coiled through the platter to provide more uniform temperatures. The wiring to the heater element may pass through the stem of the pedestal.

The chamber plasma region or a region in an remote plasma system (RPS) may be referred to as a remote plasma region. In embodiments, the radical precursor, e.g. an argon precursor, may be created in the remote plasma region and travel into the substrate processing region to combine with the silicon-containing precursor. In embodiments, the silicon-containing precursor is excited only by the radical-argon precursor. Plasma power may essentially be applied only to the remote plasma region, in embodiments, to ensure that the radical-argon precursor provides the dominant excitation to the silicon-containing precursor.

In embodiments employing a chamber plasma region, the excited reactive species may be generated in a section of the substrate processing region partitioned from a deposition region. The deposition region, also known herein as the substrate processing region, may be where the reactive species mix and react with the first precursor to deposit dielectric material on the substrate, e.g., a semiconductor

wafer. The excited reactive species may also be accompanied by additional gases including other inert gases or ammonia, for example. The first precursor may not pass through a plasma before entering the substrate plasma region, in embodiments. The substrate processing region may be described herein as "plasma-free" during the deposition of the dielectric material. "Plasma-free" does not necessarily mean the region is devoid of plasma. Ionized species and free electrons created within the plasma region may travel through pores or apertures in the partition or showerhead, but the first precursor may not be substantially excited by the plasma power applied to the plasma region. The borders of the plasma in the chamber plasma region are hard to define and may encroach upon the substrate processing region through the apertures in the showerhead. In the case of an inductively-coupled plasma, a small amount of ionization may be effected within the substrate processing region directly. Furthermore, a low intensity plasma may be created in the substrate processing region without eliminating specific features of the forming film. All causes for a plasma having much lower intensity ion density than the chamber plasma region, or a remote plasma region, during the creation of the excited first reactive species do not deviate from the scope of "plasma-free" as used herein.

Plasma power can be a variety of frequencies or a combination of multiple frequencies. In the exemplary processing system, the plasma may be provided by RF power delivered to lid **321** relative to showerhead **353**. The plasma power may be capacitively-coupled (CCP) or inductively-coupled (ICP) into the remote plasma region.

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.

The invention claimed is:

1. A method of processing a substrate disposed in a processing chamber, comprising:

(a) depositing a layer of dielectric material on a substrate by exposing the substrate to a first reactive species generated from a remote plasma source and to a first precursor, wherein the first reactive species reacts with the first precursor; and

(b) treating all, or substantially all, of the deposited layer of dielectric material by breaking at least one chemical bond within the deposited layer of dielectric material by exposing the substrate to a plasma generated within the processing chamber from a second plasma source, wherein at least the remote plasma source is pulsed at least once to control periods of depositing.

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

(c) repeating (a) and (b) until a predetermined thickness of the layer of material is deposited and treated on the substrate.

3. The method of claim **1**, wherein the second plasma source is coupled to a substrate support pedestal within the processing chamber.

4. The method of claim **1**, wherein the remote plasma source is operated in a continuous wave (CW) mode for a first interval to deposit the layer of material and wherein the second plasma source is pulsed during the first interval to treat the deposited layer of dielectric material while depositing an additional layer of dielectric material.

5. The method of claim **1**, wherein the remote plasma source is operated in a continuous wave (CW) mode for a first interval to deposit the layer of dielectric material and turned off for a second interval following the first interval, wherein the second plasma source is off for a first interval and pulsed during the second interval to treat the deposited layer of dielectric material.

6. The method of claim **1**, wherein the remote plasma source is pulsed for a first interval to deposit the layer of dielectric material and the second plasma source is operated in a continuous wave (CW) mode during the first interval to continuously treat the deposited layer of dielectric material.

7. The method of claim **1**, wherein the remote plasma source and the second plasma source are both pulsed.

8. The method of claim **7**, wherein the remote plasma source and the second plasma source are pulsed in phase such that the remote plasma source and the second plasma source are simultaneously on during a first interval and simultaneously off during a second interval to simultaneously deposit the layer of dielectric material and treat the deposited layer of dielectric material.

9. The method of claim **7**, wherein the remote plasma source and the second plasma source are pulsed out of phase such that when the remote plasma source is on the second plasma source is off and when the remote plasma source is off the second plasma source is on to deposit the layer of dielectric material and then subsequently treat the deposited layer of dielectric material without depositing additional layers of the dielectric material.

10. The method of claim **7**, wherein the remote plasma source and the second plasma source are pulsed out of phase for a first interval such that when the remote plasma source is on the second plasma source is off and when the remote plasma source is off the second plasma source is on and are pulsed in phase for a second interval such that when the remote plasma source is on the second plasma source is on and when the remote plasma source is off the second plasma source is off.

11. The method of claim **7**, wherein the remote plasma source and the second plasma source are pulsed in phase for a first interval such that when the remote plasma source is on the second plasma source is on and when the remote plasma source is off the second plasma source is off and are pulsed out of phase for a second interval such that when the remote plasma source is on the second plasma source is off and when the remote plasma source is off the second plasma source is on to deposit and treat a layer of the dielectric material.

12. The method of claim **7**, wherein the remote plasma source is pulsed on for a first interval and pulsed off for a second interval and the second plasma source is pulsed on and off multiple times during the first interval and is off during the second interval.

13. The method of claim **7**, wherein the remote plasma source is pulsed on for a first interval and pulsed off for a second interval and wherein the second plasma source is pulsed on a predetermined time after the first interval and during the second interval.

14. The method of claim **1**, wherein the remote plasma source and the second plasma source are coupled to a RF power source, DC power source, or a microwave power source.

15. The method of claim **1**, wherein the deposited layer of dielectric material is one of silicon carbide (SiC), silicon nitride (SiN), silicon oxide (SiO), silicon oxynitride (SiON), silicon oxycarbide (SiOC), or metal oxide.

16. The method of claim **1**, wherein the plasma generated within the processing chamber is formed from a second process gas comprising helium (He), argon (Ar), neon (Ne), krypton (Kr), nitrogen (N_2), ammonia (NH_3), or any combination thereof.

17. The method of claim **1**, wherein pulsing the remote plasma source and the second plasma source is controlled by adjusting a pulse frequency, or a duty cycle, or a power applied to the remote plasma source or the second plasma source.

18. The method of claim **1**, wherein a temperature of a substrate support pedestal within the processing chamber is controlled from about −150 degrees Celsius to about 500 degrees Celsius.

19. A method of depositing a material on a substrate disposed atop a substrate support pedestal in a process chamber, comprising:

(a) depositing a layer of dielectric material on a substrate by exposing the substrate to a first reactive species generated from a remote plasma source and to a first precursor, wherein the first reactive species reacts with the first precursor;

(b) treating all, or substantially all, of the deposited layer of dielectric material by breaking at least one chemical bond within the deposited layer of dielectric material by exposing the substrate to a plasma generated within the processing chamber from a second plasma source; wherein the remote plasma source is pulsed for a first interval and the second plasma source is pulsed for a second interval concurrent with the first interval; and

(c) repeating (a) and (b) until a predetermined thickness of the dielectric material is deposited and treated on the substrate, wherein a temperature of the substrate support pedestal during (a)-(c) is controlled from about −150 degrees Celsius to about 500 degrees Celsius.

20. A non-transitory computer readable medium having instructions stored thereon that, when executed, cause a method for processing a substrate disposed atop a substrate support pedestal in a processing chamber to be performed, the method comprising:

(a) depositing a layer of dielectric material on a substrate by exposing the substrate to a first reactive species generated from a remote plasma source and to a first precursor, wherein the first reactive species reacts with the first precursor;

(b) treating all, or substantially all, of the deposited layer of dielectric material by breaking at least one chemical bond within the deposited layer of dielectric material by exposing the substrate to a plasma generated within the processing chamber from a second plasma source; wherein at least the remote plasma source is pulsed at least once to control periods of depositing; and

(c) repeating (a) and (b) until a predetermined thickness of the dielectric material is deposited and treated on the substrate, wherein a temperature of the substrate support pedestal during (a)-(c) is controlled from about −150 degrees Celsius to about 500 degrees Celsius.

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

processing the substrate within a thermal budget of less than about 450 degrees Celsius.

22. The method of claim **1**, wherein the layer of material remains at least partially flowable after deposition or during treatment.

23. The method of claim **19**, further comprising:

processing the substrate within a wet etch rate ratio of less than about 2.

24. The method of claim **19**, further comprising:

processing the substrate with a film shrinkage of less than about 10%.

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