IN-SITU CONTROL OF FILM PROPERTIES DURING ATOMIC LAYER DEPOSITION

INCORPORATION BY REFERENCE

[0001] A PCT Request Form is filed concurrently with this specification as part of the present application. Each application that the present application claims benefit of or priority to as identified in the concurrently filed PCT Request Form is incorporated by reference herein in their entireties and for all purposes.

BACKGROUND

[0002] Many semiconductor device fabrication processes involve formation of films including silicon-containing films such as silicon nitride and silicon oxide. Some deposition of silicon-containing films involves plasma enhanced chemical vapor deposition (PECVD) and/or atomic layer deposition (ALD) but in some cases it may be difficult to achieve high quality films.

[0003] The background description provided herein is for the purposes of generally presenting the context of the disclosure. Work of the presently named inventors, to the extent it is described in this background section, as well as aspects of the description that may not otherwise qualify as prior art at the time of filing, are neither expressly nor impliedly admitted as prior art against the present disclosure.

SUMMARY

[0004] Provided herein are methods and apparatuses for processing substrates. One aspect involves a method for processing substrates, the method including: providing a semiconductor substrate to a reaction chamber; performing cycles of atomic layer deposition to deposit a film, each cycle including: introducing a first reactant in vapor phase into the reaction chamber to adsorb the first reactant onto a surface of the semiconductor substrate; introducing a dose of a second reactant in vapor phase into the reaction chamber for a dose time; and generating a first plasma in the reaction chamber while the second reactant in vapor phase is in the reaction chamber; and after every n cycles of the atomic layer deposition, exposing the film to a second plasma generated from flowing argon and a second gas, where either (1) the second gas is selected from the group consisting of hydrogen, oxygen, and combinations thereof and a ratio of flow rate of argon to the second gas is between about 50:1 and about 1:1, or (2) the second gas is nitrous oxide and a ratio of flow rate of argon to the second gas is between about 10:1 and about 20:1.

[0005] In some embodiments, the method also includes flowing one or more additional gases during the exposing of the film to the second plasma, the one or more additional gases being any one or more of oxygen, nitrous oxide, and helium.

[0006] Another aspect involves a method for processing substrates, the method including: providing a semiconductor substrate to a reaction chamber; performing cycles of atomic layer

deposition to deposit a film, each cycle including: introducing a first reactant in vapor phase into the reaction chamber to adsorb the first reactant onto a surface of the semiconductor substrate, introducing a dose of a second reactant in vapor phase into the reaction chamber for a dose time, and generating a first plasma in the reaction chamber while the second reactant in vapor phase is in the reaction chamber; and after every n cycles of the atomic layer deposition, exposing the film to a second plasma generated from flowing argon and a second gas having an argon to second gas flow rate ratio of between about 50:1 and about 1:1 to achieve a wet etch rate of less than about 40 Å/min in 100:1 HF.

[0007] In various embodiments, the second gas is one or more of hydrogen and oxygen and combinations thereof. The method may also include flowing a third gas during the exposing of the film to the second plasma, where the third gas is one or more of nitrous oxide, helium, and combinations thereof. In some embodiments, a ratio of flow rate of argon to flow rate of the third gas is between about 10:1 and about 20:1.

[0008] In some embodiments, the second plasma is generated at a power between about 750W and about 1625W per substrate. In some embodiments, the method also includes exposing the deposited film to the second plasma further comprises introducing a mixture of argon and oxygen gas having a flow rate ratio of argon to oxygen gas is about 12:1.

[0009] Another aspect involves a method for processing substrates, the method including: providing a semiconductor substrate to a reaction chamber; performing cycles of atomic layer deposition to deposit a film, each cycle including: introducing a first reactant in vapor phase into the reaction chamber to adsorb the first reactant onto a surface of the semiconductor substrate; introducing a dose of a second reactant in vapor phase into the reaction chamber for a dose time; and generating a first plasma in the reaction chamber while the second reactant in vapor phase is in the reaction chamber; and after every n cycles of the atomic layer deposition, exposing the film to a second plasma generated using a power between about 1000W and about 2000W at a chamber pressure between about 1 Torr and about 10 Torr to reduce stress of the film to less than about -290 MPa to 55 MPa.

[0010] Another aspect involves a method for processing substrates, the method including: providing a semiconductor substrate to a reaction chamber; performing n cycles of atomic layer deposition to deposit a film, each cycle including: introducing a first reactant in vapor phase into the reaction chamber to adsorb the first reactant onto a surface of the semiconductor substrate; introducing a dose of a second reactant in vapor phase into the reaction chamber for a dose time; and generating a first plasma in the reaction chamber while the second reactant in vapor phase is in the reaction chamber; and after every n cycles of the atomic layer deposition, exposing the deposited film to a second plasma using a power between about 3000W and about 6500W at a

chamber pressure between about 1 Torr and about 5 Torr to reduce electrical leakage to less than about 1E-9 A/cm^2 at 2 MV field.

[0011] Another aspect involves a method for processing substrates, the method including: providing a semiconductor substrate to a reaction chamber; performing n cycles of atomic layer deposition to deposit a film, each cycle including: introducing a first reactant in vapor phase into the reaction chamber to adsorb the first reactant onto a surface of the semiconductor substrate; introducing a dose of a second reactant in vapor phase into the reaction chamber for a dose time; and generating a first plasma in the reaction chamber while the second reactant in vapor phase is in the reaction chamber; and after every n cycles of the atomic layer deposition, exposing the deposited film to a second plasma using a power between about 3000W and about 6500W at a chamber pressure between about 1 Torr and about 5 Torr to yield a treated film, where the treated film has a breakdown voltage greater than 10 MW/cm.

[0012] Another aspect involves method for processing substrates, the method including: providing a semiconductor substrate to a reaction chamber; performing n cycles of atomic layer deposition to deposit a silicon-containing film, each cycle including: introducing a first reactant in vapor phase into the reaction chamber to adsorb the first reactant onto a surface of the semiconductor substrate; introducing a dose of a second reactant in vapor phase into the reaction chamber for a dose time; and generating a first plasma in the reaction chamber while the second reactant in vapor phase is in the reaction chamber; after every n cycles of the atomic layer deposition, exposing the deposited silicon-containing film to a second plasma; and introducing fluorine-containing reactive species to form a fluorine-terminated silicon surface.

[0013] Another aspect involves a method for processing substrates, the method including: providing a semiconductor substrate to a reaction chamber; performing n cycles of atomic layer deposition to deposit a film, each cycle including: introducing a first reactant in vapor phase into the reaction chamber under conditions allowing the first reactant to adsorb onto a surface of the semiconductor substrate; introducing a dose of a second reactant in vapor phase into the reaction chamber for a dose time; and generating a plasma in the reaction chamber while the second reactant in vapor phase is in the reaction chamber; and during the nth cycle of atomic layer deposition, introducing the dose of the second reactant for an extended dose time of at least 1.5 times longer than the dose time used for the first through (n-1)th cycles of atomic layer deposition.

[0014] For any of the above aspects, the film deposited may be silicon oxide. In some embodiments, the film deposited is silicon oxynitride. In some embodiments, the film deposited is boron-doped silicon oxide. In some embodiments, the film deposited is doped silicon oxide to form an n-type semiconductor. In some embodiments, the film deposited is doped silicon oxide to form an p-type semiconductor.

[0015] For any of the above aspects, the first reactant may be a silicon-containing precursor.

[0016] For any of the above aspects, the second reactant may include one or more oxygen-containing gases. The oxygen-containing gas may be any of oxygen, nitrous oxide, water, carbon dioxide, and combinations thereof.

[0017] For any of the above aspects, n may be an integer between and including 5 and 10. For any of the above aspects, the second plasma may be generated by igniting an inert gas. For any of the above aspects, the exposing of the film to the second plasma and the performing of the cycles of the atomic layer deposition may be performed in the same chamber. For any of the above aspects, the exposing of the film to the second plasma and the performing of the cycles of the atomic layer deposition may be performed without breaking vacuum. For any of the above aspects, the exposing of the film to the second plasma may include pulsing the second plasma.

[0018] For any of the above aspects, the second plasma may be generated using a plasma density between about 0.4421 W/cm^2 and about 1.7684 W/cm^2.

[0019] Another aspect involves an apparatus for processing substrates, the apparatus including: one or more process chambers, each process chamber including a chuck; one or more gas inlets into the process chambers and associated flow-control hardware; and a controller having at least one processor and a memory, where the at least one processor and the memory are communicatively connected with one another, the at least one processor is at least operatively connected with the flow-control hardware, and the memory stores computer-executable instructions for controlling the at least one processor to at least control the flow-control hardware to: cause introduction of a first reactant in vapor phase to the one or more process chambers from the one or more gas inlets; cause introduction of a second reactant in vapor phase to the one or more chambers from the one or more gas inlets; cause stopping of the introduction of the first reactant; cause stopping of the introduction of the second reactant; and after causing stopping of the introduction of the first reactant and stopping of the introduction of the second reactant, cause generation of a plasma using a combination of an inert gas and an additional gas at a flow rate ratio between the inert gas and the additional gas of between about 50:1 and about 1:1. In some embodiments, where the controller includes instructions to cause introduction of the inert gas and the additional gas after causing stopping of the introduction of the first reactant and stopping of the introduction of the second reactant, without breaking vacuum from causing introduction of the first reactant in vapor phase to the one or more process chambers from the one or more gas inlets and causing introduction of the second reactant in vapor phase to the one or more process chambers from the one or more gas inlets.

[0020] Another aspect involves an apparatus for processing substrates, the apparatus including: one or more process chambers, each process chamber including a chuck; one or more gas inlets

into the process chambers and associated flow-control hardware; and a controller having at least one processor and a memory, where the at least one processor and the memory are communicatively connected with one another, the at least one processor is at least operatively connected with the flow-control hardware, and the memory stores computer-executable instructions for controlling the at least one processor to at least control the flow-control hardware to: cause introduction of a first reactant in vapor phase to the one or more process chambers from the one or more gas inlets; cause introduction of a second reactant in vapor phase to the one or more chambers from the one or more gas inlets; cause stopping of the introduction of the first reactant; cause stopping of the introduction of the second reactant; and after causing stopping of the introduction of the first reactant and stopping of the introduction of the second reactant, cause generation of a plasma using a combination of an inert gas and an additional gas at a flow rate ratio between the inert gas and the additional gas of between about 10:1 and about 20:1. In some embodiments, where the controller includes instructions to cause introduction of the inert gas and the additional gas after causing stopping of the introduction of the first reactant and stopping of the introduction of the second reactant, without breaking vacuum from causing introduction of the first reactant in vapor phase to the one or more process chambers from the one or more gas inlets and causing introduction of the second reactant in vapor phase to the one or more process chambers from the one or more gas inlets.

[0021] For any of the above aspects, the apparatus may include four process chambers and the controller may include instructions for generation of the plasma using a plasma power between about 3000W and about 6500W.

[0022] These and other aspects are described further below with reference to the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] Figures 1 and 2 are process flow diagrams depicting operations for methods performed in accordance with certain disclosed embodiments.

[0024] Figure 3 is a timing sequence diagram showing an example of a method in accordance with certain disclosed embodiments.

[0025] Figure 4 is a schematic diagram of an example process chamber for performing certain disclosed embodiments.

[0026] Figure 5 is a schematic diagram of an example process tool for performing certain disclosed embodiments.

[0027] Figure 6 is a graph showing in-feature wet etch rate at the top, middle, and bottoms of features for various films.

[0028] Figure 7 is a graph showing stress of films deposited using different processes.

[0029] Figure 8 is a graph depicting fluorine concentration of films exposed to varying durations

of plasma as a function of normalized depth.

[0030] Figure 9 is a graph depicting dielectric k-values for a film deposited by plasma-enhanced atomic layer deposition (PEALD) and a film deposited by PEALD with intermittent plasma treatment.

[0031] Figure 10 is a graph depicting breakdown voltage of a film deposited by plasma-enhanced atomic layer deposition (PEALD) and a film deposited by PEALD with intermittent plasma treatment.

[0032] Figure 11 is a graph depicting stress and wet etch rate of films treated with pulsed and continuous intermittent plasma treatment.

DETAILED DESCRIPTION

[0033] In the following description, numerous specific details are set forth to provide a thorough understanding of the presented embodiments. The disclosed embodiments may be practiced without some or all of these specific details. In other instances, well-known process operations have not been described in detail to not unnecessarily obscure the disclosed embodiments. While the disclosed embodiments will be described in conjunction with the specific embodiments, it will be understood that it is not intended to limit the disclosed embodiments.

[0034] Semiconductor manufacturing processes often involve fabrication of silicon-containing films, such as silicon oxide, silicon nitride, and silicon carbide. Such films are sometimes deposited onto patterned substrates to form conformal films for various applications, such as barrier layers for contacts. Silicon nitride and silicon carbide layers may be used as encapsulation films, spacers, and barrier films in advanced devices for logic and memory structures, such as FinFETs, MRAM, 3DXPoint, ReRAM, and PCRAM. As devices shrink and technologies become more advanced, higher quality, denser, and more conformal films are desired. Conventional techniques for depositing conformal films involve atomic layer deposition (ALD) but efforts to modify resultant properties of films deposited with this process scheme generally leads to a trade-off with wafer throughput, particularly if qualities such as low wet etch rate or higher breakdown field are desired. Some schemes involve the use of secondary chemistries to affect anisotropic depositions in structures but the process does not regulate or control the resultant contamination in the film.

[0035] Provided herein are methods of performing intermittent plasma treatments during ALD of thin films to control the desired physical properties of resultant films. In various embodiments, the film deposited is silicon oxide. Thin silicon oxide films have a thickness of less than about 3kÅ. The plasma used in such operations can be generated using the same chemistry and process conditions as the plasma used in the activation operation of deposition of silicon oxide by ALD or can involve additional chemistries, frequencies, and/or power levels to achieve desired film

properties, the details of which are provided herein as examples. Physical properties that can be modified using this process can include but are not limited to film wet etch rate, breakdown field, film dielectric, atomic composition, and density. Depending on the chemistries used during the intermittent plasma treatment, improvement to sidewall wet etch rate can also be achieved by more active bombardment of incident ions onto surfaces normal to the wafer plane. Intermittent plasma treatment can also be used to affect film conformality on patterned structures via sputtering action at the top of the structure. For deposition processes involving inhibition operations as part of the ALD cycle or after ALD of thin films, intermittent plasma exposure can help modulate certain film properties to achieve high quality films and reduce contamination build-up.

[0036] Intermittent plasma treatment can occur after any number of ALD cycles. In some example, plasma treatment is performed every *n* cycles, where n is between and including 1 and 200, such as n=5, n=10, n=15, or n=20. Plasma composition, power, and treatment time depends on desired film properties and can be tuned to provide particular physical properties, the optimum critical ranges provided herein.

[0037] As described above, embodiments described herein involve deposition by ALD. ALD is a technique that deposits thin layers of material using sequential self-limiting reactions. Typically, an ALD cycle includes operations to deliver and adsorb at least one reactant to the substrate surface, and then react the adsorbed reactant with one or more reactants to form at least a partial layer of film. As an example, a silicon oxide deposition cycle may include the following operations: (i) delivery/adsorption of a silicon precursor, (ii) purging of the silicon precursor from the chamber, (iii) delivery of an oxygen-containing reactant with an optional plasma, and (iv) purging of the oxygen-containing reactant and/or plasma from the chamber. When a plasma is used during delivery of the second reactant, in some embodiments, this is referred to as plasma-enhanced atomic layer deposition (PEALD). Delivery or adsorption of the silicon precursor may be referred to as a "dose" operation and delivery of the second reactant to react with the adsorbed precursor may be referred to as a "conversion" operation.

[0038] Unlike a chemical vapor deposition (CVD) technique, ALD processes use surface-mediated deposition reactions to deposit films on a layer-by-layer basis. In one example of an ALD process, a substrate surface that includes a population of surface active sites is exposed to a gas phase distribution of a first precursor, such as a silicon precursor, in a dose provided to a chamber housing a substrate. Molecules of this first precursor are adsorbed onto the substrate surface, including chemisorbed species and/or physisorbed molecules of the first precursor. It should be understood that when the compound is adsorbed onto the substrate surface as described herein, the adsorbed layer may include the compound as well as derivatives of the compound. For example, an adsorbed layer of a silicon precursor may include the silicon precursor as well as

derivatives of the silicon precursor. After a first precursor dose, the chamber is then evacuated to remove most or all of first precursor remaining in gas phase so that mostly or only the adsorbed species remain. In some implementations, the chamber may not be fully evacuated. For example, the chamber may be evacuated such that the partial pressure of the first precursor in gas phase is sufficiently low to mitigate a reaction. A second reactant, such as an oxygen-containing reactant, is introduced to the chamber so that some of these molecules react with the first precursor adsorbed on the surface. In some processes, the second precursor reacts immediately with the adsorbed first precursor. In other embodiments, the second reactant reacts only after a source of activation is applied temporally. In some embodiments, a plasma is ignited during the second reactant dose. The chamber may then be evacuated again to remove unbound second reactant molecules. As described above, in some embodiments the chamber may not be completely evacuated. Additional ALD cycles may be used to build film thickness.

[0039] In certain embodiments, an ALD first precursor dose partially saturates the substrate surface. In some embodiments, the dose phase of an ALD cycle concludes before the precursor contacts the substrate to evenly saturate the surface. Typically, the precursor flow is turned off or diverted at this point, and only purge gas flows. By operating in this sub-saturation regime, the ALD process reduces the cycle time and increases throughput. However, because precursor adsorption is not saturation limited, the adsorbed precursor concentration may vary slightly across the substrate surface. Examples of ALD processes operating in the sub-saturation regime are provided in U.S. Patent Application No. 14/061,587 (now U.S. Patent No. 9,355,839), filed October 23, 2013, titled "SUB-SATURATED ATOMIC LAYER DEPOSITION AND CONFORMAL FILM DEPOSITION," which is incorporated herein by reference in its entirety.

[0040] As described, in some implementations, the ALD methods include plasma activation. As described herein, the ALD methods and apparatuses described herein may be conformal film deposition (CFD) methods, which are described generally in U.S. Patent Application No. 13/084,399 (now U.S. Patent No. 8,728,956), filed April 11, 2011, and titled "PLASMA ACTIVATED CONFORMAL FILM DEPOSITION," and in U.S. Patent Application No. 13/084,305, filed April 11, 2011, and titled "SILICON NITRIDE FILMS AND METHODS," which are herein incorporated by reference in their entireties.

[0041] Figure 1 shows a process flow diagram depicting operations that are performed in accordance with certain disclosed embodiments.

[0042] In operation 110, a first ALD cycle is performed. An ALD cycle involves alternating between doses of two or more reactants with a purge step in between to remove excess reactant/by-products. An example is described below with respect to operations 211-214 of Figure 2. In some embodiments, the ALD cycle is a PEALD cycle. In operation 120, a second ALD cycle is

performed. The second ALD cycle may be performed such that the cycle is identical to the first ALD cycle used in operation 110. ALD may be performed using plasma having a plasma power between about 150W and about 6000W. In some embodiments, plasma power in operation 110 is different from plasma power used in operation 140. In some embodiments, plasma power in operation 110 is the same as the plasma power used in operation 140.

[0043] In operation 130, the nth ALD cycle may be performed after potentially numerous intervening cycles. That is, any n cycles, or any two or more ALD cycles may be performed in accordance with disclosed embodiments. In various embodiments, each of 1st, 2nd . . . nth ALD cycles may be distinct from one another. In some embodiments, each of the 1st, 2nd, and nth ALD cycles are identical with identical dose, purge, and conversion chemistries and process conditions. In disclosed embodiments, n may be any integer greater than or equal to 2.

[0044] In operation 140, an intermittent plasma treatment is performed. The intermittent plasma treatment involves exposure to one or more treatment gases provided using particular gas mixture chemistries and process conditions to achieve a particular film property. The one or more treatment gases include argon. The one or more treatment gases can also include one or more of the following gases: hydrogen, oxygen, nitrous oxide, and helium. In one non-limiting example, gases used to generate the plasma for intermittent plasma treatment includes argon and hydrogen. In one non-limiting example, gases used to generate the plasma for intermittent plasma treatment includes argon, hydrogen, and oxygen. In one non-limiting example, gases used to generate the plasma for intermittent plasma treatment includes argon, hydrogen, oxygen, nitrous oxide, and helium. In one non-limiting example, gases used to generate the plasma for intermittent plasma treatment includes argon, oxygen, nitrous oxide, and helium. In one non-limiting example, gases used to generate the plasma for intermittent plasma treatment includes argon, nitrous oxide, and helium.

[0045] In some embodiments, the ratio of flow rate of argon to flow rate of hydrogen is between about 50:1 and about 1:1. In some embodiments, the ratio of flow rate of argon to flow rate of oxygen is between about 50:1 and about 1:1. In some embodiments, the ratio of flow rate of argon to flow rate of nitrous oxide is between about 10:1 and about 20:1. In some embodiments, the ratio of flow rate of argon to flow rate of helium is between about 10:1 and about 20:1.

[0046] In general, the number of ALD cycles performed per intermittent plasma treatment and the conditions used during intermittent plasma treatment affects the film properties in such way that certain properties can be tailored depending on the application of the film being deposited.

[0047] In some embodiments, the intermittent plasma is pulsed. Pulsing of the intermittent plasma may be performed at a particular duty cycle (duration plasma is on during a period). It will be understood that plasma pulsing may involve repetitions of periods, each of which may last a

duration T. The duration T includes the duration for pulse ON time (the duration for which the plasma is in an ON state) and the duration for plasma OFF time (the duration from which the plasma is in an OFF state) during a given period. The pulse frequency will be understood as 1/T. For example, for a plasma pulsing period T = 100 μs, frequency is 1/T = 1/100μs, or 10 kHz. The duty cycle or duty ratio is the fraction or percentage in a period T during which the plasma is in the ON state such that duty cycle or duty ratio is pulse ON time divided by T. For example, for a plasma pulsing period T = 100 μs, if a pulse ON time is 70 μs (such that the duration for which the plasma is in an ON state in a period is 70 μs) and a pulse OFF time is 30 μs (such that the duration for which the plasma is in an OFF state in a period is 30 μs), the duty cycle is 70%.

[0048] In some embodiments, the intermittent plasma is pulsed between an ON state and an OFF state, where the voltage applied during the OFF state is 0W. In various embodiments, for example, a pulsed intermittent plasma is pulsed between an OFF state of 0W and an ON state of 1250W over a particular duration, such as 10 seconds.

[0049] Chamber pressure during operation 140 may be used to modulate stress, form a compressive or tensile film, or reduce contaminates. For example, a lower pressure (such as less than about 6 Torr) can be used to form a compressive film, form a film having reduced wet etch rate, eliminate contaminates, or all of the above. A high pressure (such as greater than about 6 Torr) can be used to form a tensile film, form a film having higher wet etch rate, eliminate contaminates, or all of the above. Operation 140 may be performed at a chamber pressure between about 2 Torr and about 10 Torr.

[0050] Chamber pressure during operation 140 may be different from that of operation 110. For example, chamber pressure during operation 140 may be between about 2 Torr and about 6 Torr while operation 110 may be performed at a chamber pressure between about 0.6 Torr and about 20 Torr. In some embodiments, chamber pressure during operation 140 may be the same as during that of operation

[0051] Example process condition sets for achieving certain properties are provided below.

[0052] For modulating wet etch rate (as measured by dipping for 60 seconds in 100:1 dilute hydrofluoric acid (HF)), the intermittent plasma treatment can be performed by introducing a mixture of argon and oxygen gas, the argon gas delivered at a flow rate between about 5 slm and about 50 slm, and the oxygen gas delivered at a flow rate between about 500 sccm and about 10000 sccm using an argon to oxygen ratio of between about 50:1 and about 1:10, and between about 50:1 and about 100:1 or about 36:1 and igniting a plasma using a plasma power between about 50W and about 6500W or between about 3000W and about 6500W for a 4-station tool, or about 5000W for a 4-station tool for high frequency plasma. For low frequency plasma, the plasma power for a 4-station tool may be between about 50W and about 4500W, or between about 50W

and about 2000W. In some embodiments, plasma power during operation 110 is less than plasma power during operation 140. The chamber pressure may be set to between about 0.6 Torr and about 20 Torr, or between about 1 Torr to about 5 Torr, and the intermittent plasma treatment can be performed for a duration between about 0.1 seconds and about 30 seconds. The longer the intermittent plasma treatment duration, the lower the wet etch rate. In various embodiments, such intermittent plasma treatment is performed every 15 cycles of ALD, or every less than 15 cycles of ALD. The wet etch rate achieved may be less than about 40Å, or as low as about 30Å/min in 100:1 HF.

[0053] In one non-limiting example of modulating wet etch rate (as measured by dipping for 60 seconds in 100:1 dilute HF), the intermittent plasma treatment can be performed by introducing a mixture of argon, hydrogen, and oxygen gas where the ratio of flow rate of argon to flow rate of hydrogen is between about 50:1 and about 1:1 and the ratio of flow rate of argon to flow rate of oxygen is between about 50:1 and about 1:1.

[0054] In one non-limiting example of modulating wet etch rate (as measured by dipping for 60 seconds in 100:1 dilute HF), the intermittent plasma treatment can be performed by introducing a mixture of argon, oxygen, nitrous oxide, and helium where the ratio of flow rate of argon to oxygen is between about 50:1 and about 1:1, the ratio of flow rate of argon to flow rate of nitrous oxide is between about 10:1 and about 20:1 and the ratio of flow rate of argon to flow rate of helium is between about 10:1 and about 20:1.

[0055] In one non-limiting example of modulating wet etch rate (as measured by dipping for 60 seconds in 100:1 dilute HF), the intermittent plasma treatment can be performed by introducing a mixture of argon, oxygen, and nitrous oxide where the ratio of flow rate of argon to flow rate of oxygen is between about 50:1 and about 1:1, and the ratio of flow rate of argon to flow rate of nitrous oxide is between about 10:1 and about 20:1.

[0056] For modulating film stress, the intermittent plasma treatment can be performed by introducing a mixture of argon and oxygen gas and optionally one or more inert gases such as hydrogen gas or nitrous oxide gas. The mixture of gases delivered does not include ammonia for certain embodiments of modulating film stress. The film stress achieved may be less than about -290MPa, or less than about 55MPa, or between about -290 MPa and about 55 MPa. The argon gas can be delivered at a flow rate between about 5 slm and about 50 slm, and the oxygen gas can be delivered at a flow rate between about 1000 sccm and about 10000 sccm using an argon to oxygen ratio of between about 50:1 and about 1:10, and between about 50:1 and about 100:1 or about 36:1 and igniting a plasma using a plasma power between about 1000W and about 2000W for a 4-station tool, or about 1200W for a 4-station tool. The chamber pressure may be set to about 1 Torr to about 20 Torr, or about 10 Torr, and the intermittent plasma treatment can be performed

for a duration between about 1 second and about 20 seconds, or about 5 seconds to about 10 seconds. In various embodiments, such intermittent plasma treatment is performed every 15 cycles of ALD, or every less than 15 cycles of ALD. The combination of reduced plasma power and chamber pressure helps achieve lower stress films.

[0057] In one non-limiting example of modulating film stress, the intermittent plasma treatment can be performed by introducing a mixture of argon, oxygen, and nitrous oxide where the ratio of flow rate of argon to flow rate of oxygen is between about 50:1 and about 1:1, and the ratio of flow rate of argon to flow rate of nitrous oxide is between about 10:1 and about 20:1.

[0058] For modulating electrical properties of the deposited film, the intermittent plasma treatment can be performed by introducing a mixture of argon, helium, oxygen gas, and one or more of hydrogen gas and nitrous oxide. Electrical properties of a film can be determined by using a mercury probe analytical tool to determine current leakage and breakdown voltage. Certain disclosed embodiments are capable of depositing films having a breakdown voltage of greater than about 10 MW/cm. During intermittent plasma treatment, hydrogen gas can be used to improve particular properties and reduce leakage and increase breakdown voltage in films such as thermal oxide films. The argon gas is delivered at a flow rate between about 5 slm and about 50 slm, and the oxygen gas is delivered at a flow rate between about 500 sccm and about 10000 sccm using an argon to oxygen ratio of between about 50:1 and about 1:10, and between about 50:1 and about 100:1 or about 36:1 and igniting a plasma using a plasma power between about 3000W and about 6500W for a 4-station tool, or about 5000W for a 4-station tool. The chamber pressure may be set to about 1 Torr to about 5 Torr, and the intermittent plasma treatment can be performed for a duration between about 0.1 seconds and about 30 seconds. This particular combination of plasma power and chamber pressure helps achieve reduced leakage and improved breakdown voltage.

[0059] In one non-limiting example of modulating electrical properties of the deposited film, the intermittent plasma treatment can be performed by introducing a mixture of argon, oxygen, and nitrous oxide where the ratio of flow rate of argon to flow rate of oxygen is between about 50:1 and about 1:1, and the ratio of flow rate of argon to flow rate of nitrous oxide is between about 10:1 and about 20:1.

[0060] The longer the intermittent plasma treatment duration, the lower the wet etch rate. In various embodiments, such intermittent plasma treatment is performed every 15 cycles of ALD, or every less than 15 cycles of ALD.

[0061] For modulating film impurities (e.g., impurities of carbon, nitrogen, and/or fluorine atoms), the intermittent plasma treatment can be performed by introducing a mixture of argon, hydrogen, and optionally oxygen gas. Film impurities can be determined by obtaining an IR spectrum of the as-deposited film.

[0062] In one non-limiting example of modulating film impurities, the intermittent plasma treatment can be performed by introducing a mixture of argon, hydrogen, and oxygen gas where the ratio of flow rate of argon to flow rate of hydrogen is between about 50:1 and about 1:1 and the ratio of flow rate of argon to flow rate of oxygen is between about 50:1 and about 1:1.

[0063] In one non-limiting example of modulating film impurities, the intermittent plasma treatment can be performed by introducing a mixture of argon, oxygen, nitrous oxide, and helium where the ratio of flow rate of argon to oxygen is between about 50:1 and about 1:1, the ratio of flow rate of argon to flow rate of nitrous oxide is between about 10:1 and about 20:1 and the ratio of flow rate of argon to flow rate of helium is between about 10:1 and about 20:1.

[0064] For modulating elemental composition of the deposited film, the intermittent plasma treatment can be performed in combination with an inhibition or passivation operation using a fluorine-containing gas. An inhibition or passivation operation can help provide more control over a deposition fill process of ALD. Details of an example process are described below with respect to operation 260 of Figure 2. The intermittent plasma treatment can be performed by introducing a treatment gas mixture.

[0065] The treatment gas mixture may include helium and one or more of argon, oxygen, and hydrogen gas. The flow rate of helium may be between about 1000 sccm and about 10000 sccm, the flow rate of argon may be between about 500 sccm and about 20000 sccm, the flow rate of oxygen may be between about 1000 sccm and about 10000 sccm, and the flow rate of hydrogen may be between about 500 sccm and about 5000 sccm. The treatment gas mixture is introduced and a plasma is ignited using a plasma power between about 1000W and about 1500W for a 4-station tool for a 4-station tool. The chamber pressure may be set to about 5 Torr to about 10 Torr, or about 6 Torr, and the intermittent plasma treatment can be performed for a duration between about 1 second and about 10 seconds.

[0066] The treatment gas mixture may include argon, hydrogen, and oxygen, with gas flow ratios of $Ar:H_2:O_2$ of about 50:1:1 to about 1:1:1, such as about 5:1:1, with no nitrous oxide or helium gas.

[0067] The treatment gas mixture may include argon, nitrous oxide, and helium, with gas flow ratios of $Ar:N_2O:He$ of about 1:1:0.2 to about 0.2:0.5:0.2, such as about 0.2:0.5:0, with no hydrogen or oxygen gas.

[0068] For achieving a void-free fill of material, the intermittent plasma treatment can be performed by introducing a mixture of argon and oxygen gas. The argon gas can be delivered at a flow rate between about 10 slm and about 150 sccm, or about 50 slm, and the oxygen gas can be delivered at a flow rate between about 1 slm to about 10 slm using an argon to oxygen ratio of about 1.5:1 and igniting a plasma using a plasma power between about 1000W and about 2000W

for a 4-station tool, or about 1200W for a 4-station tool. The chamber pressure may be set to about 1 Torr to about 10 Torr, and the intermittent plasma treatment can be performed for a duration between about 1 second and about 20 seconds, or about 5 seconds to about 10 seconds.

[0069] In operation 150, operations 110-140 may be repeated. That is, operation 150 is performed every n cycles of ALD, and the overall n cycles of ALD and intermittent plasma treatment can be repeated. Disclosed embodiments are suitable for depositing any material using ALD, such as oxides, nitrides, and carbides of silicon.

[0070] Further examples of in-situ modulated ALD process cycles are provided herein. Figure 2 shows an example process cycle including an ALD cycle with intermittent plasma treatment and optional inhibition operations which may be used in some embodiments. Figure 3 corresponds to example timing schematic diagram Figure 2 without the optional inhibition operation; the timing schematic in Figure 3 provides the various pulses and flows for the ALD cycles and periodic intermittent plasma treatment repeated once.

[0071] Embodiments herein are described with respect to deposition of silicon oxide but it will be understood that similar processes may be used for depositing other silicon-containing films.

[0072] In operation 211 of Figure 2, a substrate is exposed to a deposition precursor. In various embodiments, the substrate is provided to a chamber prior to exposing to a deposition precursor such that the deposition precursor is introduced to the chamber to expose the substrate to the deposition precursor. In various embodiments, the chamber itself includes a controller, further described below with respect to Figure 4 that includes machine-readable instructions for causing delivery of a deposition precursor to a chamber in which the substrate is housed.

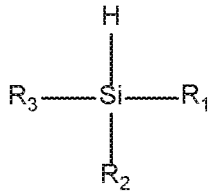
[0073] The substrate may be a semiconductor substrate. The substrate may be a silicon wafer, e.g., a 200-mm wafer, a 300-mm wafer, or a 450-mm wafer, including wafers having one or more layers of material, such as dielectric, conducting, or semi-conducting material deposited thereon. In various embodiments, the substrate is patterned. A patterned substrate may have "features" such as via or contact holes, which may be characterized by one or more of narrow and/or re-entrant openings, constrictions within the feature, and various aspect ratios including high aspect ratios. One or more features may be formed in one or more of the above described layers. One example of a feature is a hole or via in a semiconductor substrate or a layer on the substrate. Another example is a trench in a substrate or layer. In various embodiments, the feature may have an under-layer, such as a barrier layer or adhesion layer. Non-limiting examples of under-layers include dielectric layers and conducting layers, e.g., silicon oxides, silicon nitrides, silicon carbides, metal oxides, metal nitrides, metal carbides, and metal layers.

[0074] In some embodiments, the feature may have an aspect ratio of at least about 1:1, at least about 2:1, at least about 4:1, at least about 6:1, at least about 10:1, or higher. The feature may also

have a dimension near the opening, e.g., an opening diameter or line width of between about 10 nm to 10 μm, for example between about 25 nm and about 1 μm. Disclosed methods may be performed on substrates with features having an opening less than about 250 nm. A via, trench or other recessed feature may be referred to as an unfilled feature or a feature. According to various embodiments, the feature profile may narrow gradually and/or include an overhang at the feature opening. A re-entrant profile is one that narrows from the bottom, closed end, or interior of the feature to the feature opening. A re-entrant profile may be generated by asymmetric etching kinetics during patterning and/or the overhang due to non-conformal film step coverage in the previous film deposition, such as deposition of a diffusion barrier. In various examples, the feature may have a width smaller in the opening at the top of the feature than the width of the bottom of the feature.

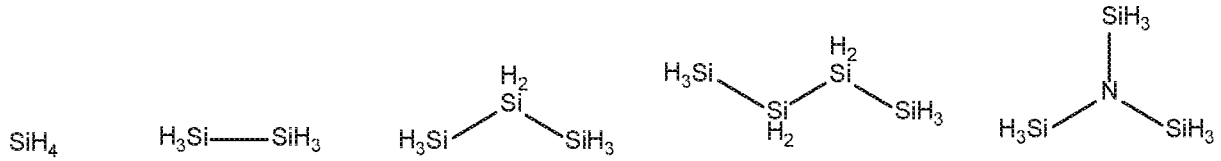
[0075] During operation 211, the substrate is exposed to the deposition precursor. In various embodiments, the substrate is exposed for a duration sufficient to adsorb the deposition precursor onto the surface of the substrate. In some embodiments, the substrate may be exposed to a precursor for a duration sufficient to saturate less than 100% of the substrate surface. Example durations depend on wafer chemistry, type of precursor, precursor flow rate, patterns on the wafer, and other factors. Duration may be selected depending on the desired properties of the material. In some embodiments, the substrate may be exposed during operation 211 for a duration less than about 5 seconds, or between about 0.05 second and about 3 seconds. For deposition of oxides, the dose time may be between about 0.05 seconds and about 0.5 seconds. The deposition precursor is selected depending on the type of material to be deposited. For example, to deposit a silicon nitride or a silicon oxide film, a silicon-containing precursor may be used during operation 211.

[0076] During operation 211, the one or more process gases may be introduced. In some embodiments, the deposition precursor is a silicon-containing precursor, such as silane. A silicon-containing precursor used in certain methods described herein may have the structure:



where R1, R2, and R3 may be the same or different substituents, and may include silanes, amines, halides, hydrogen, or organic groups, such as alkylamines, alkoxy, alkyl, alkenyl, alkynyl, and aromatic groups.

[0077] Example silicon-containing precursors include polysilanes (H3Si-(SiH2)n-SiH3), where $n > 1$, such as silane, disilane, trisilane, tetrasilane; and trisilylamine :



silane disilane trisilane tetrasilane trisilylamine

[0078] In some embodiments, the silicon-containing precursor is an alkoxysilane. Alkoxysilanes that may be used include, but are not limited to, the following:

[0079] H_x-Si-$(OR)_y$ where x = 1-3, x+y = 4 and R is a substituted or unsubstituted alkyl group; and

[0080] $H_x(RO)_y$-Si-Si-$(OR)_yH_x$ where x = 1-2, x+y = 3 and R is a substituted or unsubstituted alkyl group.

[0081] Examples of silicon-containing precursors include: methylsilane; trimethylsilane (3MS); ethylsilane; butasilanes; pentasilanes; octasilanes; heptasilane; hexasilane; cyclobutasilane; cycloheptasilane; cyclohexasilane; cyclooctasilane; cyclopentasilane; 1,4-dioxa-2,3,5,6-tetrasilacyclohexane; diethoxymethylsilane (DEMS); diethoxysilane (DES); dimethoxymethylsilane; dimethoxysilane (DMOS); methyl-diethoxysilane (MDES); methyl-dimethoxysilane (MDMS); octamethoxydodecasiloxane (OMODDS); tert-butoxydisilane; tetramethylcyclotetrasiloxane (TMCTS); tetraoxymethylcyclotetrasiloxane (TOMCTS); triethoxysilane (TES); triethoxysiloxane (TRIES); and trimethoxysilane (TMS or TriMOS).

[0082] In some embodiments, the silicon-containing precursor may be an aminosilane, with hydrogen atoms, such as bisdiethylaminosilane, diisopropylaminosilane, tert-butylamino silane (BTBAS), or tris(dimethylamino)silane. Aminosilane precursors include, but are not limited to, the following: H_x-Si-$(NR)_y$ where x = 0-3, x + y = 4 and R is an organic or hydride group. In some embodiments, the silicon-containing precursor is a tetrakisaminosilane, such as tetrakis(dimethylamino)silane (4DMAS).

[0083] In some embodiments, a halogen-containing silane may be used such that the silane includes at least one hydrogen atom. Such a silane may have a chemical formula of SiX_aH_y where $y \geq 1$. For example, dichlorosilane (H_2SiCl_2) may be used in some embodiments.

[0084] In addition to a silicon-containing precursor, one or more other gases, including inert gases such as argon, nitrogen, helium, hydrogen, or combinations thereof, may also be flowed. In various embodiments, argon gas may be introduced using a flow rate between about 1 slm and about 20 slm. In some embodiments, nitrogen gas is introduced using a flow rate between about 0 slm and about 30 slm (with the understanding that 0 slm refers to no nitrogen gas being flowed). In some embodiments, hydrogen gas is introduced using a flow rate between about 0 slm and about 5 slm (with the understanding that 0 slm refers to no hydrogen gas being flowed). During operation

211, the chamber pressure may be between about 0.6 Torr and about 10 Torr and a pedestal holding the substrate being processed may be set to a temperature between about 150°C and about 650°C, or between about 150°C and about 550°C, or between about 200°C and about 650°C, or between about 550°C and about 650°C.

[0085] In operation 212, the chamber housing the substrate is optionally purged to remove excess precursor molecules in gas phase that did not adsorb onto the surface of the substrate. Purging may involve a purge or sweep gas, which may be a carrier gas used in other operations or a different gas. In some embodiments, the purge gas may be nitrogen, argon or other inert gas, oxygen, nitrous oxide, a combination of inert gases, or combinations thereof. In some embodiments, the argon gas is introduced using a flow rate between about 1 slm and about 20 slm, and nitrogen gas may be flowed using a flow rate between about 0 slm and about 30 slm, hydrogen gas may be flowed using a flow rate between about 0 slm and about 5 slm, and in some embodiments, some oxygen may also be flowed using a flow rate between 0.5 slm and about 5 slm. In some embodiments, nitrous oxide may also be flowed using a flow rate between about 0 slm and about 5 slm.

[0086] In some embodiments, the purge gas is the same chemistry as the carrier gas used during precursor doses. In some embodiments, the purge gas is the same gas flowed during a plasma operation as further described below. In some embodiments, the purge gas is flowed from the same gas source from where carrier gas is flowed. In some embodiments, purging may involve evacuating the station. In some embodiments, a purge may include one or more evacuation purges for evacuating the process station. In some embodiments, the purge may be performed for any suitable duration, such as between about 0 seconds and about 60 seconds, or between about 0 seconds and about 0.8 seconds. In some embodiments, increasing a flow rate of a one or more sweep gases may decrease the duration of the purge. For example, a purge gas flow rate may be adjusted according to various reactant thermodynamic characteristics and/or geometric characteristics of the process station and/or process station plumbing for modifying the duration of operation 212. In one non-limiting example, the duration of a sweep phase may be adjusted by modulating sweep gas flow rate. This may reduce deposition cycle time, which may improve substrate throughput. After a purge, some precursor molecules may remain adsorbed onto the substrate surface.

[0087] The chamber pressure during operation 212 may be between about 0.6 Torr and about 10 Torr, and in some embodiments may be the same as during operation 211. The temperature of the pedestal may be set to a temperature between about 50°C and about 650°C, or between about 50°C and about 550°C, between about 150°C and about 650°C, or between about 150°C and about 550°C, or between about 200°C and about 650°C, or between about 550°C and about 650°C. In

some embodiments, the temperature is the same as during operation 211.

[0088] In operation 213, the substrate is exposed to a second reactant plasma, which may be generated by introducing a second reactant and igniting a plasma. In various embodiments, the second reactant is an oxygen-containing reactant. The oxygen-containing reactant may be oxygen, nitrous oxide, water, carbon dioxide, or combinations thereof. The substrate may be exposed to a second reactant capable of reacting with the precursor to form a material on the surface of the substrate while a plasma is ignited to catalyze the reaction. The second reactant may be selected depending on the type of film to be deposited. For a silicon oxide film, the substrate may be exposed to an oxygen-containing reactant or an oxidant while a plasma is ignited in operation 213 to deposit a silicon oxide film. In various embodiments, the second reactant is oxygen gas. In some embodiments, the second reactant includes two or more gases, such as a mixture of oxygen and nitrous oxide gas.

[0089] In some embodiments, the argon gas is introduced using a flow rate between about 1 slm and about 20 slm, and nitrogen gas may be flowed using a flow rate between about 0 slm and about 30 slm, hydrogen gas may be flowed using a flow rate between about 0 slm and about 5 slm, and in some embodiments, some oxygen may also be flowed using a flow rate between 0.5 slm and about 5 slm. In some embodiments, nitrous oxide may also be flowed using a flow rate between about 0 slm and about 5 slm.

[0090] Plasma energy may be provided to activate the second reactant into ions and radicals and other activated species, which react with the adsorbed layer of the deposition precursor. In various embodiments, the plasma is an in-situ plasma, such that the plasma is formed directly above the substrate surface in the chamber. The in-situ plasma may be ignited at a power per substrate area between about 0.2122 W/cm^2 and about 2.122 W/cm^2, or between about 0.4421 W/cm^2 and about 1.7684 W/cm^2. For example, the power for a single wafer may range from about 150W to about 6000W, or from about 500W to about 6000W, or from about 600W to about 6000W, or from about 800 W to about 4000W, or from about 310W to about 1250W. The power for four 300mm wafers may range from about 150W to about 6000W, or from about 1250W to about 5000W. Ranges described herein are inclusive of their end points.

[0091] Plasmas for ALD processes may be generated by applying a radio frequency (RF) field to a gas using two capacitively coupled plates. Ionization of the gas between plates by the RF field ignites the plasma, creating free electrons in the plasma discharge region. These electrons are accelerated by the RF field and may collide with gas phase reactant molecules. Collision of these electrons with reactant molecules may form radical species that participate in the deposition process. It will be appreciated that the RF field may be coupled via any suitable electrodes. In various embodiments, a high frequency plasma is used having a frequency of at least about

13.56 MHz, or at least about 27 MHz, or at least about 40 MHz, or at least about 60 MHz. In some embodiments, a microwave-based plasma may be used. Non-limiting examples of electrodes include process gas distribution showerheads and substrate support pedestals. It will be appreciated that plasmas for ALD processes may be formed by one or more suitable methods other than capacitive coupling of an RF field to a gas. In some embodiments, the plasma is a remote plasma, such that a second reactant is ignited in a remote plasma generator upstream of the chamber, then delivered to the chamber where the substrate is housed.

[0092] The chamber pressure during operation 213 may be between about 0.6 Torr and about 10 Torr, and in some embodiments may be the same as during operation 211 and 212. The temperature of the pedestal may be set to a temperature between about 50°C and about 650°C, between about 150°C and about 650°C, or between about 150°C and about 550°C, or between about 200°C and about 650°C, or between about 550°C and about 650°C. In some embodiments, the temperature is the same as during operation 211 and 212.

[0093] In operation 214, the chamber is again optionally purged. The purge conditions in some embodiments may be the same as the purge conditions in operation 212. In some embodiments, purge conditions may be varied. For purposes of this example, the purge conditions may be the same as those in operation 212.

[0094] In operation 215, operations 211-214 are optionally repeated for n cycles, where n is an integer equal to or greater than 1, such as between 1 and 200 cycles. The number of cycles may depend on the desired thickness of the film being deposited. Operations 211-214 may constitute one ALD cycle.

[0095] In operation 240, the substrate is exposed to an intermittent plasma treatment. The intermittent plasma treatment may be performed using process conditions and chemistries described above with respect to operation 140 of Figure 1. In some embodiments. In various embodiments, the intermittent plasma treatment is performed every 5 to every 10 cycles of ALD, depending on the particular application. For example, in some embodiments, film stress, fluorine content, and breakdown voltage can be modulated by performing the intermittent plasma treatment every 10 ALD cycles. In some embodiments, wet etch rate can be improved by performing the intermittent plasma treatment every 5 ALD cycles.

[0096] The process conditions of the intermittent plasma treatment, including duration of treatment, frequency of treatment per number of ALD cycles, and gas flow rates used during treatment, can be modulated to achieve desired results, including reduced stress, reduced wet etch rate, reduced fluorine content, reduced dielectric k-value, and improved breakdown voltage tolerance. The wet etch rate achieved may be less than about 40Å, or as low as about 30Å/min in 100:1 HF.

[0097] In some embodiments, the argon gas is introduced using a flow rate between about 1 slm and about 20 slm, and nitrogen gas may be flowed using a flow rate between about 0 slm and about 30 slm, hydrogen gas may be flowed using a flow rate between about 0 slm and about 5 slm, and in some embodiments, some oxygen may also be flowed using a flow rate between 0.5 slm and about 5 slm. In some embodiments, nitrous oxide may also be flowed using a flow rate between about 0 slm and about 5 slm.

[0098] The chamber pressure during operation 240 may be between about 0.6 Torr and about 10 Torr, and in some embodiments may be the same as during operations 211-214. In some embodiments, the chamber pressure during operation 240 is between about 2 Torr and about 10 Torr or between about 2 Torr and about 6 Torr. The temperature of the pedestal may be set to a temperature between about 50°C and about 650°C, between about 150°C and about 650°C, or between about 150°C and about 550°C, or between about 200°C and about 650°C, or between about 550°C and about 650°C. In some embodiments, the temperature is the same as during operations 211-214.

[0099] The duration of operation 240 may be between about 0.02 seconds and about 120 seconds.

[0100] In some embodiments, intermittent plasma treatment can be used to improve deposition in small features by using inhibition in combination with ALD and intermittent plasma treatment. In such embodiments, in operation 260, the substrate is optionally exposed to a fluorine-containing plasma species to inhibit deposition. An example process scheme may be as follows for filling features on a substrate: ALD is performed by exposing the substrate to alternating pulses of a silicon-containing precursor and an oxygen-containing reactant to deposit silicon oxide that partially fills the features, followed by intermittent plasma treatment on the deposited ALD-deposited film, followed by inhibition on surfaces at or near openings of features by exposing the substrate to a dose of fluorine ions and radicals generated from fluorine plasma to form a fluorine-terminated silicon surface that prevents deposition in subsequent ALD cycles, followed by repeating of the above process scheme in cycles (multiple ALD cycles, followed by intermittent plasma treatment, followed by inhibition) to deposit silicon oxide into features.

[0101] As shown in Figure 2, operations 211-240 may be optionally repeated, and operations 211-260 (which may include multiple cycles of operations 211-214) may be repeated in multiple cycles.

[0102] Intermittent plasma treatment in embodiments involving inhibition may be used to control the extent of inhibition from the exposure to fluorine-containing ions and radicals; that is, intermittent plasma treatment can balance the inhibition to allow more active sites and provide an

additional knob to fine-tune the deposition process, particularly in embodiments where inhibition may slow down the deposition too much but may still be used to ensure a bottom-up fill of features.

[0103] Figure 3 is an example timing schematic diagram showing a process having a deposition scheme involving inhibition for a feature fill application. Process 300 shows one complete cycle including multiple deposition cycles in the deposition phase 310, followed by periodic intermittent plasma treatment phase 340, and optional inhibition phase 360. The lines indicate when the flow and/or plasma, as appropriate, are turned on and off. While certain process conditions are depicted in Figure 3, it will be understood that other process parameters may also be modulated depending on the particular application of the film being deposited. It will also be understood that while the example in Figure 3 involves an inhibition phase 360, such phase may not be present in certain embodiments. While process 300 in Figure 3 includes only one cycle, it will be understood that the shown cycle may be repeated in multiple cycles to deposit a film.

[0104] Deposition phase 310 of Figure 3 may correspond to any one of operations 110, 120, or 130 of Figure 1, or may correspond to performing operations 211-214 in Figure 2. During deposition phase 310, an inert gas may be flowed and alternating pulses of a silicon precursor and oxygen-containing reactant are performed while plasma is generated during the oxygen-containing reactant pulse. During this operation, the inhibition gas flow is turned off. While many pulses are shown for the deposition phase, it will be understood that the number of pulses may vary depending on the film to be deposited.

[0105] In periodic intermittent plasma treatment phase 340, the inert gas may continue to flow, while the silicon precursor gas flow and oxygen-containing gas flows are turned off. Plasma is turned on and is ignited continuously in the presence of the inert gas to treat the deposited film and the inhibition gas flow remains off.

[0106] In optional inhibition phase 360, the inert gas may, in some embodiments, be turned off (although it will be understood that in some cases, the inert gas flow may remain on). Silicon precursor flow and oxygen-containing gas flow remains off, and plasma is turned off. Here, the inhibition gas flow is then turned on.

[0107] Although not depicted, the cycle shown in process 300 may be repeated for multiple cycles as desired.

[0108] While silicon oxide is described, it will be understood that disclosed embodiments may be equally applicable to forming doped silicon oxides, n-type semiconductors, p-type semiconductors, silicon oxynitride, boron-doped silicon oxide, and other materials.

[0109] In this application, the terms "semiconductor wafer," "wafer," "substrate," "wafer substrate," and "partially fabricated integrated circuit" are used interchangeably. One of ordinary skill in the art would understand that the term "partially fabricated integrated circuit" can refer to

a silicon wafer during any of many stages of integrated circuit fabrication thereon. A wafer or substrate used in the semiconductor device industry typically has a diameter of 200 mm, or 300 mm, or 450 mm. Unless otherwise stated, the processing details recited herein (e.g., flow rates, power levels, etc.) are relevant for processing 300 mm diameter substrates, or for treating chambers that are configured to process 300 mm diameter substrates, and can be scaled as appropriate for substrates or chambers of other sizes.

APPARATUS

[0110] Figure 4 depicts a schematic illustration of an embodiment of an atomic layer deposition (ALD) process station 400 having a process chamber body 402. The ALD process station 400 may be suitable for processing substrates in a low-pressure environment in some embodiments. In some embodiments, one or more hardware parameter values of ALD process station 400, including those discussed in detail below may be adjusted programmatically by one or more computer controllers 450. In various embodiments, intermittent plasma treatments are performed in situ after deposition of a film in the ALD process station as described herein. Variation of the parameter values may be made in a determined manner or based on real-time feedback. Additional examples and further embodiments are described below.

[0111] ALD process station 400 fluidly communicates with reactant delivery system 401a for delivering process gases to a distribution showerhead 406. Reactant delivery system 401a includes a mixing vessel 404 for blending and/or conditioning process gases for delivery to showerhead 406. For example, the reactant delivery system 401a may include mass flow controllers and liquid flow controllers as described below. One or more mixing vessel inlet valves 420 may control introduction of process gases to mixing vessel 404. In various embodiments, delivery of one or more process gases to the showerhead 406 or to the process chamber 402 may be varied across cycles. For example, the duration of dosing one or more process gases may be varied. In disclosed embodiments, a controller 450 may control the delivery of one or more process gases by controlling one or more inlet valves 420.

[0112] As an example, the embodiment of Figure 4 includes a vaporization point 403 for vaporizing liquid reactant to be supplied to the mixing vessel 404. In some embodiments, vaporization point 403 may be a heated vaporizer. The saturated reactant vapor produced from such vaporizers may condense in downstream delivery piping. Exposure of incompatible gases to the condensed reactant may create small particles. These small particles may clog piping, impede valve operation, contaminate substrates, etc. Some approaches to addressing these issues involve purging and/or evacuating the delivery piping to remove residual reactant. However, purging the delivery piping may increase process station cycle time, degrading process station throughput. Thus, in some embodiments, delivery piping downstream of vaporization point 403 may be heat

traced. In some examples, mixing vessel 404 may also be heat traced. In one non-limiting example, piping downstream of vaporization point 403 has an increasing temperature profile extending from approximately 30°C to approximately 150°C at mixing vessel 404.

[0113] In some embodiments, liquid precursor or liquid reactant may be vaporized at a liquid injector. For example, a liquid injector may inject pulses of a liquid reactant into a carrier gas stream upstream of the mixing vessel. In one embodiment, a liquid injector may vaporize the reactant by flashing the liquid from a higher pressure to a lower pressure. In another example, a liquid injector may atomize the liquid into dispersed microdroplets that are subsequently vaporized in a heated delivery pipe. Smaller droplets may vaporize faster than larger droplets, reducing a delay between liquid injection and complete vaporization. Faster vaporization may reduce a length of piping downstream from vaporization point 403. In one scenario, a liquid injector may be mounted directly to mixing vessel 404. In another scenario, a liquid injector may be mounted directly to showerhead 406.

[0114] In some embodiments, a liquid flow controller (LFC) upstream of vaporization point 403 may be provided for controlling a mass flow of liquid for vaporization and delivery to process station 400. For example, the LFC may include a thermal mass flow meter (MFM) located downstream of the LFC. A plunger valve of the LFC may then be adjusted responsive to feedback control signals provided by a proportional-integral-derivative (PID) controller in electrical communication with the MFM. However, it may take one second or more to stabilize liquid flow using feedback control. This may extend a time for dosing a liquid reactant. Thus, in some embodiments, the LFC may be dynamically switched between a feedback control mode and a direct control mode. In some embodiments, this may be performed by disabling a sense tube of the LFC and the PID controller.

[0115] In some embodiments, a flow-over-vapor process may be used. A discussion of such processes are described in U.S. Patent Application Publication No. 2019/0024233, filed on September 20, 2018, and titled "DYNAMIC PRECURSOR DOSING FOR ATOMIC LAYER DEPOSITION." In some embodiments of flow-over-vapor processes, the timing of the valve operations may be set using line charge time, adsorption time, or some other time. Moreover, the frame of reference for the operation of the valves may be the start of a dose step, the stop of a dose step, any other event during a dose step, and/or any event during an ALD cycle.

[0116] In some implementations, , an amount of precursor may be sent through the gas line that may be more than necessary for a desired adsorption amount. This additional precursor may also be sent such that it arrives before the beginning of the dose step, after the dose step, and/or after the desired adsorption/saturation has been achieved. In some such implementations, some precursor may be dumped to the foreline before and/or after the dose step. In some such

implementations, duration of time for which the ampoule valve may be open, the timing of when the ampoule valve may open and/or close, the duration of time for which the chamber valve may be open, and/or the timing of when the chamber valve may be open may vary. However, to reduce waste, the excess precursor may be limited to about 20% or less (or about 10% or less) of the amount required for adsorption/saturation.

[0117] Furthermore, in some implementations, each event (e.g., the opening of the ampoule valve, the closing of the chamber valve) may not occur precisely at an intended time point.

[0118] Moreover, the timing of the valves may not be exactly equal to the line charge time and/or adsorption time. There may also be a timing delay to account for delays of the system, such as the time it takes a valve to open or close. In some embodiments, an ALD valve may be used which may have a timing delay of 25 milliseconds. There may also be a margin of error within the implementations herein which may also be 25 milliseconds.

[0119] In some embodiments, a dynamic feedback loop may be created in order to deliver exactly the same number of moles of precursor per cycle desired for each cycle, which may be below, equal to, or greater than the adsorption amount. The amount of precursor delivered in a flow-over-vapor system, such as described herein, may depend on several factors including ampoule temperature, headspace pressure, and push gas flow. If one or more of these parameters deviates from the intended set points over the course of the deposition period (for example, due to precursor level changing in the ampoule), the amount of delivered precursor per ampoule valve open time will deviate accordingly. A feedback loop may be created by, among other things, sensor data (e.g. measurements) from, for instance, ampoule thermocouples, pressure gauges, and MFC's, and a controller. In one example, a pressure gauge (e.g., a manometer) is located at the entrance to the process chamber (e.g., by one of the inlet valves 420). The arrival of precursor at the process chamber may be signaled by a pressure variation detected by the pressure gauge. By dynamically controlling the ampoule open/close timing based on such feedback loop, precursor delivery can be made more robust and repeatable cycle-to-cycle. The feedback loop, measurements, and/or adjustments may be made during a dose/deposition step, between steps in a cycle, between cycles, and/or between processes.

[0120] Showerhead 406 distributes process gases toward substrate 412. In the embodiment shown in Figure 4, the substrate 412 is located beneath showerhead 406 and is shown resting on a pedestal 408. Showerhead 406 may have any suitable shape, and may have any suitable number and arrangement of ports for distributing process gases to substrate 412.

[0121] In some embodiments, a microvolume 407 is located beneath showerhead 406. Practicing disclosed embodiments in a microvolume rather than in the entire volume of a process station may reduce reactant exposure and purge times, may reduce times for altering process

conditions (e.g., pressure, temperature, etc.), and may limit an exposure of process station robotics to process gases, etc. Example microvolume sizes include, but are not limited to, volumes between 0.1 liter and 2 liters. This also impacts productivity throughput. In some embodiments, the disclosed embodiments are not performed in a microvolume.

[0122] In some embodiments, pedestal 408 may be raised or lowered to expose substrate 412 to microvolume 407 and/or to vary a volume of microvolume 407. For example, in a substrate transfer phase, pedestal 408 may be raised to position substrate 412 within microvolume 407. In some embodiments, microvolume 407 may completely enclose substrate 412 as well as a portion of pedestal 408 to create a region of high flow impedance.

[0123] Optionally, pedestal 408 may be lowered and/or raised during portions the process to modulate process pressure, reactant concentration, etc., within microvolume 407. In one scenario where process chamber body 402 remains at a base pressure during the process, lowering pedestal 408 may allow microvolume 407 to be evacuated. Example ratios of microvolume to process chamber volume include, but are not limited to, volume ratios between 1:500 and 1:10. It will be appreciated that, in some embodiments, pedestal height may be adjusted programmatically by a suitable computer controller 450. In some embodiments, location of the pedestal 408 may be varied across cycles. For example, in some ALD cycles, the pedestal 408 may be raised, and in some ALD cycles, the pedestal 408 may be lowered. Variations as described herein may be dependent on real-time feedback or a determined recipe.

[0124] In another scenario, adjusting a height of pedestal 408 may allow a plasma density to be varied during plasma activation and/or deposition cycles included in disclosed multi-cyclic ALD processes. At the conclusion of the process phase, pedestal 408 may be lowered during another substrate transfer phase to allow removal of substrate 412 from pedestal 408.

[0125] While the example microvolume variations described herein refer to a height-adjustable pedestal, it will be appreciated that, in some embodiments, a position of showerhead 406 may be adjusted relative to pedestal 408 to vary a volume of microvolume 407. Further, it will be appreciated that a vertical position of pedestal 408 and/or showerhead 406 may be varied by any suitable mechanism within the scope of the present disclosure. In some embodiments, pedestal 408 may include a rotational axis for rotating an orientation of substrate 412. It will be appreciated that, in some embodiments, one or more of these example adjustments may be performed programmatically by one or more suitable computer controllers 450.

[0126] In some embodiments where plasma may be used as discussed above, showerhead 406 and pedestal 408 electrically communicate with a radio frequency (RF) power supply 414 and matching network 416 for powering a plasma. In some embodiments, the plasma energy may be controlled by controlling one or more of a process station pressure, a gas concentration, an RF

source power, an RF source frequency, and a plasma power pulse timing. Such parameter values may be varied from ALD cycle to ALD cycle in a multi-cyclic ALD process as described herein. For example, RF power supply 414 and matching network 416 may be operated at any suitable power to form a plasma having a desired composition of radical species during one or more ALD cycles. Examples of suitable powers are included above. Likewise, RF power supply 414 may provide RF power of any suitable frequency. In some embodiments, RF power supply 414 may be configured to control high- and low-frequency RF power sources independently of one another. Example low-frequency RF frequencies may include, but are not limited to, frequencies between 50 kHz and 500 kHz. Example high-frequency RF frequencies may include, but are not limited to, frequencies between 1.8 MHz and 2.45 GHz. It will be appreciated that any suitable parameter values may be modulated discretely or continuously to provide plasma energy for the surface reactions. In one non-limiting example, the plasma power may be intermittently pulsed to reduce ion bombardment with the substrate surface relative to continuously powered plasmas. In some embodiments, the plasma power can be between about 50W and about 6000W. In various embodiments, the RF power or RF frequency or both may be used for both deposition and intermittent plasma treatment. The RF power and/or frequency may be modulated to change the properties of the deposited film, such as wet etch rate, stress, fluorine concentration, dielectric k-value, and breakdown voltage tolerance.

[0127] In some embodiments, the plasma may be monitored in-situ by one or more plasma monitors. In one scenario, plasma power may be monitored by one or more voltage, current sensors (e.g., VI probes). In another scenario, plasma density and/or process gas concentration may be measured by one or more optical emission spectroscopy sensors (OES). In some embodiments, one or more plasma parameter values may be programmatically adjusted based on measurements from such in-situ plasma monitors. For example, an OES sensor may be used in a feedback loop for providing programmatic control of plasma power. It will be appreciated that, in some embodiments, other monitors may be used to monitor the plasma and other process characteristics. Such monitors may include, but are not limited to, infrared (IR) monitors, acoustic monitors, and pressure transducers.

[0128] In some embodiments, instructions for a controller 450 may be provided via input/output control (IOC) sequencing instructions. In one example, the instructions for setting conditions for a process phase may be included in a corresponding recipe phase of a process recipe. In some cases, process recipe phases may be sequentially arranged, so that all instructions for a process phase are executed concurrently with that process phase. In some embodiments, instructions for setting one or more reactor parameter values may be included in a recipe phase. For example, a first recipe phase may include instructions for setting a flow rate of an inert and/or a reactant gas

(e.g., the first precursor such as silane), instructions for setting a flow rate of a carrier gas (such as nitrogen or argon), and time delay instructions for the first recipe phase. A second, subsequent recipe phase may include instructions for modulating or stopping a flow rate of an inert and/or a reactant gas, and instructions for modulating a flow rate of a carrier or purge gas and time delay instructions for the second recipe phase. A third recipe phase may include instructions for setting a flow rate of an inert and/or reactant gas which may be the same as or different from the gas used in the first recipe phase (e.g., the second precursor such as oxygen), instructions for setting a plasma RF power, instructions for modulating a flow rate of a carrier gas which may be the same as or different from the flow rate in the first recipe phase, plasma conditions, and time delay instructions for the third recipe phase. A fourth recipe phase may include instructions for modulating or stopping a flow rate of an inert and/or a reactant gas, instructions for modulating the flow rate of a carrier or purge gas, and time delay instructions for the fourth recipe phase. A fifth recipe phase may include instructions for setting a flow rate of an inert and/or reactant gas (e.g., the oxygen and/or argon), instructions for setting a different or same plasma RF power, instructions for modulating a flow rate of a carrier gas, plasma conditions, and time delay instructions for the fifth recipe phase for performing an intermittent plasma treatment. In some cases, the recipe phase may also include instructions for pulsing the plasma between ON and OFF states. More recipe phases may also be used. It will be appreciated that these recipe phases may be further subdivided and/or iterated in any suitable way within the scope of the present disclosure.

[0129] In some embodiments, pedestal 408 may be temperature controlled via heater 410. Further, in some embodiments, pressure control for process station 400 may be provided by butterfly valve 418. As shown in the embodiment of Figure 4, butterfly valve 418 throttles a vacuum provided by a downstream vacuum pump (not shown). However, in some embodiments, pressure control of process station 400 may also be adjusted by varying a flow rate of one or more gases introduced to the process station 400. The process station 400 may include a control 450 for controlling example recipes as described above.

[0130] In some implementations, a controller 450 is part of a system, which may be part of the above-described examples. Such systems can comprise semiconductor processing equipment, including a processing tool or tools, chamber or chambers, a platform or platforms for processing, and/or specific processing components (a wafer pedestal, a gas flow system, etc.). These systems may be integrated with electronics for controlling their operation before, during, and after processing of a semiconductor wafer or substrate. The electronics may be referred to as the "controller," which may control various components or subparts of the system or systems. The controller 450, depending on the processing requirements and/or the type of system, may be programmed to control any of the processes disclosed herein, including the delivery of processing

gases and/or variation of different dose times for delivery of process gases including diversion of one or more gases, temperature settings (e.g., heating and/or cooling), pressure settings, vacuum settings, power settings, radio frequency (RF) generator settings and/or variation of RF power settings, RF matching circuit settings, frequency settings, flow rate settings, fluid delivery settings, positional and operation settings, wafer transfers into and out of a tool and other transfer tools and/or load locks connected to or interfaced with a specific system.

[0131] Broadly speaking, the controller 450 may be defined as electronics having various integrated circuits, logic, memory, and/or software that receive instructions, issue instructions, control operation, enable cleaning operations, enable endpoint measurements, and the like. The integrated circuits may include chips in the form of firmware that store program instructions, digital signal processors (DSPs), chips defined as application specific integrated circuits (ASICs), and/or one or more microprocessors, or microcontrollers that execute program instructions (e.g., software). Program instructions may be instructions communicated to the controller 450 in the form of various individual settings (or program files), defining operational parameters for carrying out a particular process on or for a semiconductor wafer or to a system. The operational parameters may, in some embodiments, be part of a recipe defined by process engineers to accomplish one or more processing steps during the fabrication of one or more layers, materials, metals, oxides, silicon, silicon dioxide, surfaces, circuits, and/or dies of a wafer.

[0132] The controller 450, in some implementations, may be a part of or coupled to a computer that is integrated with, coupled to the system, otherwise networked to the system, or a combination thereof. For example, the controller 450 may be in the "cloud" or all or a part of a fab host computer system, which can allow for remote access of the wafer processing. The computer may enable remote access to the system to monitor current progress of fabrication operations, examine a history of past fabrication operations, examine trends or performance metrics from a plurality of fabrication operations, to change parameters of current processing, to set processing steps to follow a current processing, or to start a new process. In some examples, a remote computer (e.g. a server) can provide process recipes to a system over a network, which may include a local network or the Internet. The remote computer may include a user interface that enables entry or programming of parameters and/or settings, which are then communicated to the system from the remote computer. In some examples, the controller 450 receives instructions in the form of data, which specify parameters for each of the processing steps to be performed during one or more operations. It should be understood that the parameters may be specific to the type of process to be performed and the type of tool that the controller 450 is configured to interface with or control. Thus as described above, the controller 450 may be distributed, such as by including one or more discrete controllers that are networked together and working towards a common purpose, such as the

processes and controls described herein. An example of a distributed controller for such purposes would be one or more integrated circuits on a chamber in communication with one or more integrated circuits located remotely (such as at the platform level or as part of a remote computer) that combine to control a process on the chamber.

[0133] Without limitation, example systems may include a plasma etch chamber or module, a deposition chamber or module, a spin-rinse chamber or module, a metal plating chamber or module, a clean chamber or module, a bevel edge etch chamber or module, a physical vapor deposition (PVD) chamber or module, a chemical vapor deposition (CVD) chamber or module, an atomic layer deposition (ALD) chamber or module, an atomic layer etch (ALE) chamber or module, an ion implantation chamber or module, a track chamber or module, and any other semiconductor processing systems that may be associated or used in the fabrication and/or manufacturing of semiconductor wafers.

[0134] As noted above, depending on the process step or steps to be performed by the tool, the controller 450 might communicate with one or more of other tool circuits or modules, other tool components, cluster tools, other tool interfaces, adjacent tools, neighboring tools, tools located throughout a factory, a main computer, another controller, or tools used in material transport that bring containers of wafers to and from tool locations and/or load ports in a semiconductor manufacturing factory.

[0135] As described above, one or more process stations may be included in a multi-station processing tool. Figure 5 shows a schematic view of an embodiment of a multi-station processing tool 500 with an inbound load lock 502 and an outbound load lock 504, either or both of which may comprise a remote plasma source. A robot 506, at atmospheric pressure, is configured to move wafers from a cassette loaded through a pod 508 into inbound load lock 502 via an atmospheric port 510. A wafer is placed by the robot 506 on a pedestal 512 in the inbound load lock 502, the atmospheric port 510 is closed, and the load lock is pumped down. Where the inbound load lock 502 comprises a remote plasma source, the wafer may be exposed to a remote plasma treatment in the load lock prior to being introduced into a processing chamber 514. Further, the wafer also may be heated in the inbound load lock 502 as well, for example, to remove moisture and adsorbed gases. Next, a chamber transport port 516 to processing chamber 514 is opened, and another robot (not shown) places the wafer into the reactor on a pedestal of a first station shown in the reactor for processing. While the embodiment depicted in Figure 5 includes load locks, it will be appreciated that, in some embodiments, direct entry of a wafer into a process station may be provided.

[0136] The depicted processing chamber 514 comprises four process stations, numbered from 1 to 4 in the embodiment shown in Figure 5. Each station has a heated pedestal (shown at 518 for

station 1), and gas line inlets. It will be appreciated that in some embodiments, each process station may have different or multiple purposes. For example, in some embodiments, a process station may be switchable between an ALD and plasma-enhanced ALD process mode. Additionally or alternatively, in some embodiments, processing chamber 514 may include one or more matched pairs of ALD and plasma-enhanced ALD process stations. While the depicted processing chamber 514 comprises four stations, it will be understood that a processing chamber according to the present disclosure may have any suitable number of stations. For example, in some embodiments, a processing chamber may have five or more stations, while in other embodiments a processing chamber may have three or fewer stations.

[0137] Figure 5 depicts an embodiment of a wafer handling system 590 for transferring wafers within processing chamber 514. In some embodiments, wafer handling system 590 may transfer wafers between various process stations and/or between a process station and a load lock. It will be appreciated that any suitable wafer handling system may be employed. Non-limiting examples include wafer carousels and wafer handling robots. Figure 5 also depicts an embodiment of a system controller 550 employed to control process conditions and hardware states of process tool 500. System controller 550 may include one or more memory devices 556, one or more mass storage devices 554, and one or more processors 552. Processor 552 may include a CPU or computer, analog and/or digital input/output connections, stepper motor controller boards, etc.

[0138] In some embodiments, system controller 550 controls all of the activities of process tool 500. System controller 550 executes system control software 558 stored in mass storage device 554, loaded into memory device 556, and executed on processor 552. Alternatively, the control logic may be hard coded in the controller 550. Applications Specific Integrated Circuits, Programmable Logic Devices (e.g., field-programmable gate arrays, or FPGAs) and the like may be used for these purposes. In the following discussion, wherever "software" or "code" is used, functionally comparable hard coded logic may be used in its place. System control software 558 may include instructions for controlling the timing, mixture of gases, amount of sub-saturated gas flow, chamber and/or station pressure, chamber and/or station temperature, wafer temperature, target power levels, RF power levels, substrate pedestal, chuck and/or susceptor position, and other parameters of a particular process performed by process tool 500. System control software 558 may be configured in any suitable way. For example, various process tool component subroutines or control objects may be written to control operation of the process tool components used to carry out various process tool processes. System control software 558 may be coded in any suitable computer readable programming language.

[0139] In some embodiments, system control software 558 may include input/output control (IOC) sequencing instructions for controlling the various parameters described above. Other

computer software and/or programs stored on mass storage device 554 and/or memory device 556 associated with system controller 550 may be employed in some embodiments. Examples of programs or sections of programs for this purpose include a substrate positioning program, a process gas control program, a pressure control program, a heater control program, and a plasma control program.

[0140] A substrate positioning program may include program code for process tool components that are used to load the substrate onto pedestal 518 and to control the spacing between the substrate and other parts of process tool 500.

[0141] A process gas control program may include code for controlling gas composition (e.g., silane, nitrogen, and purge gases as described herein) and flow rates and optionally for flowing gas into one or more process stations prior to deposition in order to stabilize the pressure in the process station. For example, a process gas control program may include code for changing duration of process gas doses across cycles in a multi-cyclic ALD process. A pressure control program may include code for controlling the pressure in the process station by regulating, for example, a throttle valve in the exhaust system of the process station, a gas flow into the process station, etc.

[0142] A heater control program may include code for controlling the current to a heating unit that is used to heat the substrate. Alternatively, the heater control program may control delivery of a heat transfer gas (such as helium) to the substrate.

[0143] A plasma control program may include code for setting RF power levels applied to the process electrodes in one or more process stations in accordance with the embodiments herein. For example, a plasma control program may include code for varying RF power levels across cycles.

[0144] A pressure control program may include code for maintaining the pressure in the reaction chamber in accordance with the embodiments herein.

[0145] In some embodiments, there may be a user interface associated with system controller 550. The user interface may include a display screen, graphical software displays of the apparatus and/or process conditions, and user input devices such as pointing devices, keyboards, touch screens, microphones, etc.

[0146] In some embodiments, parameter values adjusted by system controller 550 may relate to process conditions. Non-limiting examples include process gas composition and flow rates and dose times, temperature, pressure, plasma conditions (such as RF power levels), and variation of one or more parameter values across ALD cycles, etc. These parameter values may be provided to the user in the form of a recipe, which may be entered utilizing the user interface.

[0147] Signals for monitoring the process may be provided by analog and/or digital input

connections of system controller 550 from various process tool sensors. The signals for controlling the process may be output on the analog and digital output connections of process tool 500. Non-limiting examples of process tool sensors that may be monitored include mass flow controllers, pressure sensors (such as manometers), thermocouples, etc. Appropriately programmed feedback and control algorithms may be used with data from these sensors to maintain process conditions.

[0148] System controller 550 may provide program instructions for implementing the above-described deposition processes. The program instructions may control a variety of process parameters, such as DC power level, RF bias power level, pressure, temperature, etc. The instructions may control the parameter values to operate in-situ deposition of film stacks according to various embodiments described herein.

[0149] The system controller 550 will typically include one or more memory devices and one or more processors configured to execute the instructions so that the apparatus will perform a method in accordance with disclosed embodiments. Machine-readable media containing instructions for controlling process operations in accordance with disclosed embodiments may be coupled to the system controller. The controller 550 may have any of the features described above with respect to Figure 4.

[0150] An appropriate apparatus for performing the methods disclosed herein is further discussed and described in U.S. Patent Application Nos. 13/084,399, filed April 11, 2011, and titled "PLASMA ACTIVATED CONFORMAL FILM DEPOSITION"; and 13/084,305, filed April 11, 2011, and titled "SILICON NITRIDE FILMS AND METHODS," each of which is incorporated herein in its entireties.

[0151] The apparatus/process described herein may be used in conjunction with lithographic patterning tools or processes, for example, for the fabrication or manufacture of semiconductor devices, displays, LEDs, photovoltaic panels and the like. Typically, though not necessarily, such tools/processes will be used or conducted together in a common fabrication facility. Lithographic patterning of a film typically includes some or all of the following operations, each operation enabled with a number of possible tools: (1) application of photoresist on a workpiece, i.e., substrate, using a spin-on or spray-on tool; (2) curing of photoresist using a hot plate or furnace or UV curing tool; (3) exposing the photoresist to visible or UV or x-ray light with a tool such as a wafer stepper; (4) developing the resist so as to selectively remove resist and thereby pattern it using a tool such as a wet bench; (5) transferring the resist pattern into an underlying film or workpiece by using a dry or plasma-assisted etching tool; and (6) removing the resist using a tool such as an RF or microwave plasma resist stripper.

EXPERIMENTAL

EXPERIMENT 1

[0152] An experiment was conducted on two silicon oxide films to determine the wet etch rate of each. Both silicon oxide films were deposited into features having an aspect ratio of 7:1. Both silicon oxide films were deposited by atomic layer deposition using alternating pulses of a silicon precursor and a mixture of oxygen and nitrous oxide which used to generate a plasma using a power of 5000W. Argon and nitrogen gas were also flowed during deposition. The flow rate of oxygen was 5000 sccm, the flow rate of nitrous oxide was 5000 sccm, the flow rate of argon was 5000 sccm, and the flow rate of nitrogen was 25000 sccm. A carrier gas was used having a flow rate of 1500 sccm. The pulses of plasma used during ALD had a duration of 0.3 seconds and the film was deposited into a chamber having a pressure of 6 Torr.

[0153] The first silicon oxide film was deposited without an intermittent plasma treatment and wet etch rate was determined for the top, middle, and bottom of the feature. The measured wet etch rates in 100:1 hydrofluoric acid for 30 seconds are graphed in Figure 6 as the solid bars.

[0154] The second silicon oxide film was deposited with an intermittent plasma treatment by flowing oxygen gas, argon, helium, and hydrogen gas and generating a plasma at a power of 1500W for 10 seconds in a 2 Torr chamber. The flow rate of oxygen gas was 2000 sccm, the flow rate of argon was 3200 sccm, the flow rate of helium was 2000 sccm, and the flow rate of hydrogen was 2000 sccm. The intermittent plasma treatment was performed every 5 cycles of ALD. The measured wet etch rates in 100:1 hydrofluoric acid for 30 seconds for the top, middle, and bottom of the features is graphed in Figure 6 as the diagonally shaded bars.

[0155] As shown in Figure 6, the wet etch rate of the film that was subject to intermittent plasma treatment achieved substantially lower wet etch rate than the film without intermittent plasma treatment.

EXPERIMENT 2

[0156] An experiment was conducted on seven different films. Each film was deposited by atomic layer deposition using cycles of silicon precursor exposure, purge, oxygen and nitrous oxide gas mixture with 1250W plasma, and purge. Argon and nitrogen gas were used as inert carrier gases and were used during the purge. The oxygen gas flow rate was 5000 sccm, the nitrous oxide gas flow rate was 5000 sccm, the argon gas flow rate was 5000 sccm, and the nitrogen gas flow rate was 25000 sccm. The carrier flow rate was 1500 sccm. The plasma used during oxygen and nitrogen gas exposure was turned on for a duration of 0.3 seconds. ALD was performed using a chamber pressure of 6 Torr.

[0157] The first silicon oxide film was deposited by this ALD process with no intermittent plasma treatment and the stress was measured for the film and depicted in Figure 7 as Process 1.

[0158] The second through seventh silicon oxide films were deposited by this ALD process with intermittent plasma treatment every 10 cycles and is depicted in Process 2-7 in Figure 7. The

process conditions for each of these processes are provided in Table 1 below. Pressure during intermittent plasma treatment for all processes was 10 Torr and RF ON time was 10 seconds. For the cyclic processes 4 and 7, the RF was ON for 10 seconds, then off, for 100 cycles of pulsed plasma treatment.

Table 1. Process Conditions for Processes 2-7

Process	RF Frequency	RF Power	Flow Rate (sccm)				Pulsed?
			O2	He	H2	Ar	
2	13.56 MHz	1250W	2000	2000	2000	0	No
3	13.56 MHz	1250W	2000	2000	2000	10000	No
4	13.56 MHz	1250W	2000	20000	2000	1200	Yes, 100 cycles of ON/OFF
5	13.56 MHz	1250W	2000	2000	2000	10000	No
6	13.56 MHz	2500W	2000	2000	2000	10000	Yes, 100 cycles of ON/OFF
7	13.56 MHz/ 440 kHz	1250W	2000	2000	2000	10000	No

[0159] The results show that the stress of the film can be modulated by toggling various process conditions of the intermittent plasma treatment alone, including varying the RF frequency, RF power, helium flow rate, argon flow rate, and pulsing scheme.

EXPERIMENT 3

[0160] An experiment was conducted on silicon oxide films deposited by atomic layer deposition involving cycles of silicon precursor dose, purge, oxygen and nitrous gas plasma (with argon and nitrogen gas), and purge. The plasma was generated using 1250W plasma power for 0.3 seconds and carrier gas flow was used at a flow rate of 1500 sccm. The oxygen gas flow rate was 5000 sccm, the nitrous oxide gas flow rate was 5000 sccm, the argon flow rate was 5000 sccm, and the nitrogen gas flow rate was 25000 sccm. The chamber pressure was 6 Torr.

[0161] The films were subject to fluorine-based inhibition by using a dual frequency plasma generated at 750W for the high frequency plasma, 1000W for the low frequency plasma, ignited in an environment having 500 sccm of oxygen gas, 3200 sccm of argon gas, 6000 sccm of helium gas, and 35 sccm of nitrogen trifluoride gas flowed therein for 1 second.

[0162] The films were then subject to intermittent plasma treatments of different durations. The intermittent plasma treatment involved exposing the substrate to 2000 sccm of oxygen, 3200 sccm

of argon, 2000 sccm of helium, and 2000 of hydrogen in a chamber having a pressure of 2 Torr ignited using 1500W of plasma. The three different intermittent plasma treatment durations were 5 seconds, 10 seconds and 20 seconds. The intermittent plasma treatment was performed every 10 cycles of ALD. The fluorine concentration was determined for each of these films as a function of normalized depth of the film which is graphed in Figure 8. Line 801 refers to the 5 second intermittent plasma treatment results, line 802 refers to the 10 second intermittent plasma treatment results, and line 803 refers to the 15 second intermittent plasma treatment results. The results suggest that longer post plasma treatment can be used to reduce fluorine concentration in the silicon oxide film deposited using ALD with inhibition.

EXPERIMENT 4

[0163] An experiment was conducted to measure the k value of silicon oxide films deposited by ALD for a film without and a film with intermittent plasma treatment. The experiment also involved determining the breakdown field for both films.

[0164] These films were deposited using multiple cycles of a silicon precursor exposure, purge, oxygen and nitrous oxide plasma exposure (with argon and nitrogen) and purge. The plasma was generated using a plasma power of 1250W for 0.3 seconds. The flow rate of oxygen gas was 5000 sccm, the flow rate of nitrous oxide gas was 5000 sccm, the flow rate of argon gas was 5000 sccm, the flow rate of nitrogen gas was 25000 sccm, and the carrier flow was 1500 sccm. The chamber pressure was 6 Torr.

[0165] The film deposited using this process without intermittent plasma treatment was evaluated for dielectric k value (Figure 9) and breakdown field (Figure 10).

[0166] The other film was exposed to intermittent plasma treatment after the deposition of the film, whereby the intermittent plasma treatment involved exposure to a 1250W plasma for 10 seconds generated from igniting 2000 sccm of oxygen, 3200 sccm of argon, 2000 sccm of helium, and 2000 sccm of hydrogen for every 10 cycles of ALD. The film deposited using the above process with intermittent plasma treatment was evaluated for dielectric k value (Figure 9) and breakdown field (Figure 10).

[0167] As shown in Figure 9, the dielectric k value for the film exposed to intermittent plasma treatment was substantially lower than that of the film not exposed to intermittent plasma treatment. The breakdown voltage for the film exposed to intermittent plasma treatment was substantially higher than that of the film not exposed to intermittent plasma treatment. These results suggest superior results for a film deposited using the intermittent plasma treatment versus without.

EXPERIMENT 5

[0168] An experiment was conducted comparing stress and wet etch rate of films deposited and

treated using continuous versus pulsed plasma. Figure 11 shows a graph depicting variation in film stress versus wet etch rate by modifying the percent argon flow and type of plasma applied during treatment. Pulsed plasma was performed at a frequency of 10 Hz. The percentage of argon flow is a percentage of the total available argon flow into the chamber.

[0169] Point 1102 represents 80% argon flow with pulsed plasma; point 1104 represents 100% argon flow with pulsed plasma; point 1106 represents 60% argon flow with pulsed plasma; point 1108 presents 40% argon flow with pulsed plasma; point 1110 represents 20% argon flow with pulsed plasma; and line 1101 represents the overall curve and trend of stress with wet etch rate when treated with pulsed plasma.

[0170] In comparison, point 1112 represents 80% argon flow with continuous plasma; point 1114 represents 100% argon flow with continuous plasma; point 1116 represents 60% argon flow with continuous plasma; point 1118 represents 40% argon flow with continuous plasma; point 1120 represents 20% argon flow with continuous plasma; and line 1111 represents the overall curve and trend of stress and wet etch rate of a film treated with continuous plasma.

[0171] As shown, the results are surprising, since the trend for continuous plasma is different from that of pulsed plasma, which appears to have favorable results of both substantially reduced stress and reduced wet etch rate at 40% argon flow and pulsed plasma, whereas the 40% argon flow and continuous plasma achieved the highest wet etch rate compared to all of the other points. The differentiation shown is distinct, and unexpected, given known trends of stress and wet etch rate for various films.

CONCLUSION

[0172] Although the foregoing embodiments have been described in some detail for purposes of clarity of understanding, it will be apparent that certain changes and modifications may be practiced within the scope of the appended claims. It should be noted that there are many alternative ways of implementing the processes, systems, and apparatus of the present embodiments. Accordingly, the present embodiments are to be considered as illustrative and not restrictive, and the embodiments are not to be limited to the details given herein.

CLAIMS

1. An apparatus for processing substrates, the apparatus comprising:

one or more process chambers, each process chamber comprising a chuck;

one or more gas inlets into the process chambers and associated flow-control hardware; and

a controller having at least one processor and a memory,

wherein the at least one processor and the memory are communicatively connected with one another,

the at least one processor is at least operatively connected with the flow-control hardware, and

the memory stores computer-executable instructions for controlling the at least one processor to at least control the flow-control hardware to:

cause introduction of a first reactant in vapor phase to the one or more process chambers from the one or more gas inlets;

cause introduction of a second reactant in vapor phase to the one or more chambers from the one or more gas inlets;

cause stopping of the introduction of the first reactant; cause stopping of the introduction of the second reactant; and

after causing stopping of the introduction of the first reactant and stopping of the introduction of the second reactant, cause generation of a plasma using a combination of an inert gas and an additional gas at a flow rate ratio between the inert gas and the additional gas of between 50:1 and 1:1.

2. The apparatus of claim 1, wherein the controller comprises instructions to cause introduction of the inert gas and the additional gas after causing stopping of the introduction of the first reactant and stopping of the introduction of the second reactant, without breaking vacuum from causing introduction of the first reactant in vapor phase to the one or more process chambers from the one or more gas inlets and causing introduction of the second reactant in vapor phase to the one or more process chambers from the one or more gas inlets.

3. An apparatus for processing substrates, the apparatus comprising:

one or more process chambers, each process chamber comprising a chuck;

one or more gas inlets into the process chambers and associated flow-control hardware; and

a controller having at least one processor and a memory,

wherein the at least one processor and the memory are communicatively connected with one another,

the at least one processor is at least operatively connected with the flow-control hardware, and

the memory stores computer-executable instructions for controlling the at least one processor to at least control the flow-control hardware to:

cause introduction of a first reactant in vapor phase to the one or more process chambers from the one or more gas inlets;

cause introduction of a second reactant in vapor phase to the one or more chambers from the one or more gas inlets;

cause stopping of the introduction of the first reactant; cause stopping of the introduction of the second reactant; and

after causing stopping of the introduction of the first reactant and stopping of the introduction of the second reactant, cause generation of a plasma using a combination of an inert gas and an additional gas at a flow rate ratio between the inert gas and the additional gas of between 10:1 and 20:1.

4. The apparatus of claim 3, wherein the controller comprises instructions to cause introduction of the inert gas and the additional gas after causing stopping of the introduction of the first reactant and stopping of the introduction of the second reactant, without breaking vacuum from causing introduction of the first reactant in vapor phase to the one or more process chambers from the one or more gas inlets and causing introduction of the second reactant in vapor phase to the one or more process chambers from the one or more gas inlets.

5. The apparatus of any of claims 1 and 3, wherein the one or more process chambers comprise four process chambers and wherein the controller comprises instructions for generation of the plasma using a plasma power between 3000W and 6500W.

6. A method for processing substrates, the method comprising:

providing a semiconductor substrate to a reaction chamber;

performing cycles of atomic layer deposition to deposit a film, each cycle comprising:

introducing a first reactant in vapor phase into the reaction chamber to adsorb the first reactant onto a surface of the semiconductor substrate;

introducing a dose of a second reactant in vapor phase into the reaction chamber for a dose time; and

generating a first plasma in the reaction chamber while the second reactant in vapor phase is in the reaction chamber; and

after every n cycles of the atomic layer deposition, exposing the film to a second plasma generated from flowing argon and a second gas,

wherein either

(1) the second gas is selected from the group consisting of hydrogen, oxygen, and combinations thereof and a ratio of flow rate of argon to the second gas is between 50:1 and 1:1, or

(2) the second gas is nitrous oxide and a ratio of flow rate of argon to the second gas is between 10:1 and 20:1.

7. The method of claim 6, further comprising flowing one or more additional gases during the exposing of the film to the second plasma, the one or more additional gases selected from the group consisting of oxygen, nitrous oxide, and helium.

8. A method for processing substrates, the method comprising:

providing a semiconductor substrate to a reaction chamber;

performing cycles of atomic layer deposition to deposit a film, each cycle comprising:

introducing a first reactant in vapor phase into the reaction chamber to adsorb the first reactant onto a surface of the semiconductor substrate;

introducing a dose of a second reactant in vapor phase into the reaction chamber for a dose time; and

generating a first plasma in the reaction chamber while the second reactant in vapor phase is in the reaction chamber; and

after every n cycles of the atomic layer deposition, exposing the film to a second plasma generated from flowing argon and a second gas having an argon to second gas flow rate ratio of between 50:1 and 1:1 to achieve a wet etch rate of less than 40 A/min in 100:1 HF.

9. The method of claim 8, wherein the second gas is selected from the group consisting of hydrogen and oxygen and combinations thereof.

10. The method of claim 8, further comprising flowing a third gas during the exposing of the film to the second plasma, wherein the third gas is selected from the group consisting of nitrous oxide, helium, and combinations thereof.

11. The method of claim 10, wherein ratio of flow rate of argon to flow rate of the third gas is between 10:1 and 20:1.

12. The method of claim 6, wherein the second plasma is generated at a power between 750W and 1625W per substrate.

13. The method of any of claims 6-12, wherein the film comprises silicon oxide.

14. The method of claim 6, wherein exposing the deposited film to the second plasma further comprises introducing a mixture of argon and oxygen gas having a flow rate ratio of argon to oxygen gas is 12:1.

15. The method of any of claims 6-12, wherein the exposing of the film to the second plasma and the performing of the cycles of the atomic layer deposition are performed without breaking vacuum.

16. The method of any of claims 6-12, wherein the exposing of the film to the second plasma comprises pulsing the second plasma.