[0133] In various embodiments, a remote plasma may be used. The plasma introduced to the process chamber may be primarily radical based. In some embodiments, the substrate is exposed to N* only radicals or a mixture of N*, and NH* radicals. In some embodiments, the ratio of H* to NH* radicals may be about 0.1:1 to about 0:1.

[0134] Different gas mixtures in the plasma may generate different mixtures of radicals. For example, in some embodiments, plasma generated from a nitrogen-only gas may contain N* radicals, or mostly N* radicals, or only N* radicals. In some embodiments, plasma generated from a nitrogen-containing gas mixture having nitrogen gas, ammonia gas, and/or hydrogen gas may include N* radicals as well as H* radicals and NH* radicals. In some embodiments, an abundance of N* is present in the chamber and the relative concentration of N* is a few order of magnitudes higher than that of NH*.

[0135] In operation 114, the process chamber is optionally purged. Purging may be performed using any one or more of the process gases and conditions described above with respect to operation 106 or operation 110. In one example, nitrogen gas is flowed at a flow rate of about 10000 sccm for about 10 seconds in a chamber having a chamber pressure of about 9.5 Torr.

[0136] In operation 116, it is determined whether the film is deposited to an adequate thickness. If not, operations 104, 108, and 112 may be optionally repeated, or operations 104-114 may be optionally repeated, in cycles.

[0137] Certain disclosed embodiments are capable of depositing silicon nitride films into features whereby growth rate on sidewalls of the feature improves by about 1.7 times or about 2 times or more as compared to performing thermal conversion only (such as only exposing to cycles of silicon-containing precursor and a nitrogen-containing gas without a plasma, and without additionally adding an operation of exposing to a nitrogen-containing plasma after or during the cycles). For example, the growth rate may be about 0.75Å per cycle (where one cycle includes a silicon-containing precursor dose, thermal conversion using ammonia gas, and exposure to RF plasma generated from ammonia and nitrogen gas) as compared to thermal conversion, which may have a growth rate of about 0.44Å per cycle (where one cycle includes a silicon-containing precursor dose and thermal conversion using ammonia gas).

[0138] Additionally, incorporating both thermal conversion and an exposure to nitrogen-containing plasma operation results in increased step coverage, as compared to a plasma-only process (for example, cycles of a silicon-containing precursor dose and exposure to nitrogen-containing plasma without also performing thermal conversion may result in a step coverage of about 75%).

[0139] Provided herein are also methods for depositing and apparatuses having undercoat films on metal-containing chamber components using a halogen-free deposition precursor. Methods

to nitrogen gas. During operation 124, the chamber pressure may be set at a pressure of at least about 0.5 Torr and about 4 Torr to about 8 Torr. Without being bound by a particular theory, it is believed that flow dynamics with pressure affect the effectiveness of certain disclosed embodiments and pressure of at least about 0.5 Torr is used to allow sufficient cleaning of the chamber using certain disclosed embodiments. During operation 124, a substrate is still not present in the process chamber.

[0143] In operation 126, a halogen-free aminosilane precursor is introduced to the process chamber. In operation 126, the process chamber still contains no substrate, or is substrate-free. The aminosilane precursor is introduced to provide a precursor for forming the undercoat film. In some embodiments, the aminosilane precursor is diisopropylaminosilane (DIPAS). Additional examples of precursors are described elsewhere herein in the Precursors section.

[0144] In operation 126 of Figure 1B, the undercoat film may be deposited using atomic layer deposition (ALD). The undercoat may be deposited by plasma-enhanced atomic layer deposition (PEALD). That is, in various embodiments, the reaction between an aminosilane and a nitrogen-containing reactant to form a silicon nitride undercoat is performed using a plasma. 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 the partial layer of film. As another example, a silicon nitride deposition cycle may include the following operations: (i) delivery/adsorption of an aminosilane precursor, (ii) purging of the aminosilane precursor from the chamber, (iii) delivery of plasma species generated from a nitrogen-containing gas, and (iv) purging of the plasma species from the chamber.

[0145] 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-containing 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 an aminosilane precursor may include the aminosilane precursor as well as derivatives of the aminosilane precursor. After a first precursor dose, the chamber is then evacuated to remove most or all of the aminosilane 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

0.1:1 to about 10:1.

[0149] During operation 126, the chamber pressure may be set at a pressure of about 1 Torr to about 25 Torr. Operation 126 may be performed for a duration of about 0.1 second to about 10 seconds.

[0150] Returning to Figure 1B, in operation 128, the chamber is optionally purged. Purging the chamber may involve flowing a purge gas or a sweep gas, which may be a carrier gas used in other operations or may be a different gas. In some embodiments, purging may involve evacuating the chamber. Examples of purge gases include argon (Ar), nitrogen (N_2), hydrogen (H_2), helium (He), oxygen (O_2), krypton (Kr), xenon (Xe), neon (Ne), and combinations thereof. In various embodiments, the purge gas is an inert gas. The purge gas may include one or more gases. In some embodiments, operation 128 may include one or more evacuation subphases for evacuating the process chamber. Alternatively, it will be appreciated that operation 128 may be omitted in some embodiments. In some embodiments, increasing a flow rate of one or more purge gases may decrease the duration of operation 128. For example, a purge gas flow rate may be adjusted according to various reactant thermodynamic characteristics and/or geometric characteristics of the process chamber and/or process chamber plumbing for modifying the duration of operation 128. In one non-limiting example, the duration of a purge phase may be adjusted by modulating purge gas flow rate. This may reduce deposition cycle time, which may improve substrate throughput. After a purge, the aminosilane molecules remain adsorbed onto the substrate surface.

[0151] The flow rate of the purge gas may about 1000 sccm to about 40000 sccm for a single-wafer chamber. The duration of operation 128 may be about 0.1 seconds to about 10 seconds. The chamber pressure during operation 128 may be about 0.5 Torr to about 25 Torr.

[0152] In operation 130, a nitrogen-containing gas is introduced and a plasma is generated to convert adsorbed aminosilane precursor molecules to silicon nitride. In various embodiments, the nitrogen-containing gas is nitrogen gas. The flow rate of the nitrogen-containing gas may be about 5000 sccm to about 25000 sccm for a single-wafer chamber. The duration of operation 130 may be about 0.1 second to about 30 seconds. The chamber may be set to a pressure of about 1 Torr to about 10 Torr.

[0153] Plasma is used during this operation to generate a plasma or reactive species containing nitrogen. Plasma may be generated using a single frequency or a dual frequency plasma. For a dual frequency plasma, high frequency plasma is generated at a plasma power of about 100W to about 6000W for a single-wafer chamber and low frequency plasma is generated at a plasma power of about 0W to about 2500W for a single-wafer chamber. Inductively coupled plasma, microwave plasma, and capacitively coupled plasmas may be used. Relative to operation 126, the ratio of

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.

[0161] 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.

[0162] In some implementations, ALD methods may include plasma activation. In some implementations, ALD methods may not 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.

[0163] Figure 1C shows a process flow diagram depicting operations that may be performed in accordance with certain disclosed embodiments. It will be understood that the selection of gases in operations 148 and 152 determine the type of material and level of gradation or relative concentrations of oxygen and nitrogen, as well as process conditions used for various operations described herein.

[0164] In operation 142, a substrate is provided to a process chamber. In various embodiments, the process chamber is a single-wafer chamber. In some embodiments, the process chamber is a station within a multi-station chamber. Process conditions described herein are suitable for a single-wafer chamber.

[0165] The process chamber may be set to a chamber pressure about 5 mTorr to about 25 Torr or about 10 Torr to about 25 Torr. Such chamber pressures may be used throughout operations 142-154 as described herein. In some embodiments, chamber pressure may be different during different operations. The chamber pressure may also depend on the chemistries selected for various operations described herein.

[0166] The substrate may be heated to a substrate temperature about 25°C to about 800°C, or

containing plasma, respectively. The plasma may be ignited remotely, such that an oxygen-containing plasma species or nitrogen-containing plasma species is introduced to the process chamber instead of or with an oxygen-containing gas or nitrogen-containing gas. Where operation 148 involves forming silicon oxide, operation 152 may involve nitridation. Where operation 148 involves forming silicon nitride, operation 152 may involve oxidation. In some embodiments, one or more operations of introducing an oxygen-containing gas or nitrogen-containing gas may be used to modulate or control the relative amounts of oxygen and nitrogen in the deposited film.

[0182] The following description is related to embodiments where conversion in operation 148 is used to form an oxide.

[0183] If oxygen-containing gas or oxygen-containing plasma species (generated from an oxygen-containing gas) are introduced in operation 148, one or more of the following process conditions may be used. The oxygen-containing gas may be any suitable oxygen-containing gas, such as but not limited to oxygen (O_2), carbon dioxide, carbon monoxide, hydrogen peroxide, other peroxides, and ozone. The oxygen-containing gas may be mixed with or diluted with one or more inert gases. In some embodiments, the oxygen-containing gas is mixed with or diluted with hydrogen gas. In some embodiments, the oxygen-containing gas is mixed with hydrogen gas and diluted with nitrogen gas. The flow rate of oxygen-containing gas may be about 100 sccm to about 5000 sccm for a single-wafer chamber. The flow rate of hydrogen or inert gas may be about 0 sccm to about 5000 sccm. The flow rate of a dilution gas or nitrogen gas may be about 500 sccm to about 2000 sccm. Operation 148 may be performed for a duration of about 1 second to about 30 seconds, or about 5 seconds to about 15 seconds. After a few cycles of deposition, such as about 25 cycles of deposition, a longer conversion time of about 300 seconds to about 900 seconds, or about 300 seconds, or about 900 seconds may be used. In a mixture of oxygen and hydrogen gas, the ratio of oxygen to hydrogen may be about 1:10 to about 10:1. In some embodiments, hydrogen is not used. In some embodiments, the flow rate of hydrogen gas is 0 sccm.

[0184] In some embodiments, hydrogen is ignited to form a hydrogen plasma. In some embodiments, an oxygen and hydrogen-containing plasma may be used in operation 148. In some embodiments, and in some cycles of deposition, operation 148 may be oxygen-free. In some embodiments and in some cycles of deposition, operation 148 may involve only introducing a hydrogen plasma. In some embodiments, operation 148 uses a hydrogen plasma and is oxygen-free. A hydrogen plasma may be used to reduce the chlorine content or fluorine content in the deposited film.

[0185] Process conditions used in operation 148 may be used to tune film properties, such as change the stress of the deposited film. In some embodiments, this operation may also involve subsequently exposing to a nitrogen plasma. In some embodiments, an inert plasma may be used

above with respect to operation 148.

[0191] For plasma conversion, the plasma conditions used for operation 148 varies depending on the chemistries used. In one example, the plasma may be ignited using a plasma power of about 1000W to about 6000W having a 13.6 MHz frequency. In one example, about 4500 sccm of ammonia is introduced for about 15 seconds at a chamber pressure of about 9.5 Torr to convert a silicon-containing precursor to silicon nitride.

[0192] Referring to Figure 1C, in operation 150, the process chamber may again be optionally purged. Purging may be performed using any of the techniques, gases, and process conditions described above with respect to operation 146.

[0193] Operations 144-150 may be optionally repeated in cycles. Operations 144-150 may constitute one ALD cycle. In some embodiments, about 1 to about 1000 or about 1 to about 100 cycles of ALD are performed.

[0194] In operation 152, an in-situ nitridation or oxidation operation is performed to convert the first silicon-containing film into a second silicon-containing film, which may be a converted film by nitriding or oxidizing the film deposited from operations 144 and 148. In one example of in-situ oxidation, a mixture of hydrogen gas, oxygen gas, and inert gas (such as nitrogen gas and/or argon gas) may be used. A higher partial pressure of P_{O_2} and P_{H_2} may cause oxidation to occur faster. In some embodiments, a higher partial pressure of P_{O_2} and P_{H_2} may be caused by lowering inert gas flow and increasing pressure. In a specific, non-limiting example, in an experiment implementing oxidation at a pressure of 22 Torr with hydrogen flow of about 4500 sccm and oxygen flow of about 4500 sccm with inert gas flow of about 4200 sccm, when inert gas flow is increased, oxidation effectiveness decreased. When pressure was decreased, oxidation effectiveness decreased.

[0195] Operation 152 may be performed in-situ. In some embodiments, operation 152 is performed in the same chamber as performing any one or more of operations 144 and 148. The selection of nitridation versus oxidation depends on whether the film already deposited is to be tailored to include more nitrogen atoms or more oxygen atoms. For example, in some embodiments, operations 144 and 148 may be performed to form a silicon nitride layer. To oxidize the silicon nitride to form SiON, in-situ oxidation may be performed. In another example, in some embodiments, operations 144 and 148 may be performed to form a silicon oxide layer. To nitridize the silicon oxide to form SiON, in-situ nitridation may be performed. In some embodiments, after oxidation or nitridation or other cycles of ALD, nitridation and/or oxidation may further be performed to tailor the composition of the deposited film. In some embodiments, operation 152 is performed so as to form a graded layer, with either graded oxygen content, graded nitrogen content, or both. In some embodiments, the graded layer includes graded oxygen content and

graded nitrogen content whereby regions with increased amount of oxygen also have increased amount of nitrogen, or regions with decreased amount of oxygen also have decreased amounts of nitrogen.

[0196] In-situ oxidation may be performed by introducing a oxygen-containing reactant such as a oxygen-containing gas or plasma species. A oxygen-containing plasma species may be generated by igniting a oxygen-containing gas. An example oxygen-containing reactant is oxygen gas. Another example oxygen-containing reactant is carbon dioxide. In some embodiments, any one or more of the chemistries used and/or process conditions used as described above for exposing to a oxygen-containing gas or plasma to form silicon oxide in operation 148 may be performed in operation 152 as an in-situ oxidation operation. For example, in some embodiments, if oxygen-containing gas or oxygen-containing plasma species (generated from an oxygen-containing gas) are introduced in operation 152, one or more of the following process conditions may be used. The oxygen-containing gas may be any suitable oxygen-containing gas, such as but not limited to oxygen (O2), carbon dioxide, carbon monoxide, hydrogen peroxide, other peroxides, and ozone. The oxygen-containing gas may be mixed with or diluted with one or more inert gases. In some embodiments, the oxygen-containing gas is mixed with or diluted with hydrogen gas. In some embodiments, the oxygen-containing gas is mixed with hydrogen gas and diluted with nitrogen gas. The flow rate of oxygen-containing gas may be about 100 sccm to about 5000 sccm for a single-wafer chamber. The flow rate of hydrogen or inert gas may be about 0 sccm to about 5000 sccm. The flow rate of a dilution gas or nitrogen gas may be about 500 sccm to about 2000 sccm. Operation 152 may be performed for a duration of about 1 second to about 900 seconds. In a mixture of oxygen and hydrogen gas, the ratio of oxygen to hydrogen may be about 1:2 to about 1:1.

[0197] In some embodiments, hydrogen is ignited to form a hydrogen plasma. In some embodiments, an oxygen and hydrogen-containing plasma may be used in operation 148. In some embodiments, and in some cycles of deposition, operation 148 may be oxygen-free. In some embodiments and in some cycles of deposition, operation 148 may involve only introducing a hydrogen plasma. In some embodiments, operation 148 uses a hydrogen plasma and is oxygen-free. A hydrogen plasma may be used to reduce the chlorine content or fluorine content in the deposited film.

[0198] Process conditions used in operation 152 may be used to tune film properties, such as change the stress of the deposited film. In some embodiments, this operation may also involve subsequently exposing to a nitrogen plasma. In some embodiments, an inert plasma may be used to anneal the film after conversion to improve film quality.

[0199] The plasma conditions used for operation 152 varies depending on the chemistries used.

six process conditions but it will be understood that fewer or more process conditions may be toggled during each phase in accordance with certain disclosed embodiments and that while specific gases are listed (Ar, N2, and NH3), other suitable gases as described herein may be used.

[0219] Example 200 includes two deposition cycles – deposition cycle 220A and deposition cycle 220B. It will be understood that more or less than two deposition cycles may be performed, and that multiple sub-cycles may be performed within one deposition cycle. For example, phases 204A, 206A, 208A, and 210A may constitute a sub-cycle, which may be repeated in multiple cycles within one deposition cycle 220A or 220B. However, repetitions of sub-cycles are not depicted in this particular example in Figure 2.

[0220] Deposition cycle 220A includes silicon-containing precursor exposure phase 204A, purge phase 206A, thermal conversion phase 208A, purge phase 210A, plasma exposure phase 212A, and purge phase 214A. Silicon-containing precursor exposure phase 204A may correspond to operation 104 of Figure 1A. During silicon-containing precursor exposure phase 204A, argon flow is on and constant, and may be used as an inert gas, dilution gas, or carrier gas; silicon-containing precursor flow is on and constant; nitrogen gas flow is on, lower as compared to other phases, and constant; ammonia gas flow is off; plasma is off; and pressure is higher as compared to some other phases. Purge phase 206A may correspond to operation 106 of Figure 1A. In purge phase 206A, argon flow continues to flow as it may be used as a purge gas; silicon-containing precursor flow is turned off; nitrogen gas continues to flow and its flow rate may be slightly increased to a medium flow (as compared to other phases); ammonia gas flow continues to be turned off; plasma continues to be turned off; and pressure may stay constant. Thermal conversion phase 208A may correspond to operation 108 of Figure 1A. In thermal conversion phase 208A, argon flow continues to flow as it may be used as a carrier gas or inert gas or dilution gas; silicon-containing precursor flow remains off; nitrogen gas may continue to flow and may be reduced relative to purge phase 206A; ammonia gas flow may be turned on; plasma remains off; and pressure may remain constant. Purge phase 210A may correspond to operation 110 of Figure 1A. During purge phase 210A, argon flow continues to flow as it may be used as a purge gas; silicon-containing precursor flow remains off; nitrogen gas continues to flow and its flow rate may be slightly increased to a medium flow (as compared to thermal conversion phase 208A); ammonia gas flow is turned off; plasma continues to be turned off; and pressure may stay constant. Plasma exposure phase 212A may correspond to operation 112 of Figure 1A. During plasma exposure phase 212A, argon flow continues to flow as it may be used as a carrier gas or inert gas or dilution gas; silicon-containing precursor flow remains off; nitrogen gas flow may be increased which may be used to facilitate generation of nitrogen-containing plasma such as N* radicals; ammonia gas flow may be turned on but may have a lower flow rate relative to thermal conversion phase 208A;

plasma is turned on; and chamber pressure is lowered relative to other phases. Purge phase 214A may correspond to operation 114 of Figure 1A. During purge phase 214A, argon flow continues to flow as it may be used as a purge gas; silicon-containing precursor flow remains off; nitrogen gas continues to flow and its flow rate may be slightly reduced relative to the plasma exposure phase 212A; ammonia gas flow is turned off; plasma is turned off; and pressure is increased to a pressure that may be the same as during phases other than the plasma exposure phase 212A.

[0221] It may be determined that the film thickness of deposited silicon nitride is insufficiently thick and the cycle may be repeated in accordance with operation 116 of Figure 1A such as shown in the example in deposition cycle 220B of Figure 2, which includes silicon-containing precursor exposure phase 204B, purge phase 206B, thermal conversion phase 208B, purge phase 210B, plasma exposure phase 212B, and purge phase 214B.

[0222] Silicon-containing precursor exposure phase 204B may correspond to a repeated operation 104 of Figure 1A. During silicon-containing precursor exposure phase 204B, argon flow is on and constant, and may be used as an inert gas, dilution gas, or carrier gas; silicon-containing precursor flow is on and constant; nitrogen gas flow is on, lower as compared to other phases, and constant; ammonia gas flow is off; plasma is off; and pressure is higher as compared to some other phases. Purge phase 206B may correspond to a repeated operation 106 of Figure 1A. In purge phase 206B, argon flow continues to flow as it may be used as a purge gas; silicon-containing precursor flow is turned off; nitrogen gas continues to flow and its flow rate may be slightly increased to a medium flow (as compared to other phases); ammonia gas flow continues to be turned off; plasma continues to be turned off; and pressure may stay constant. Thermal conversion phase 208B may correspond to a repeated operation 108 of Figure 1A. In thermal conversion phase 208B, argon flow continues to flow as it may be used as a carrier gas or inert gas or dilution gas; silicon-containing precursor flow remains off; nitrogen gas may continue to flow and may be reduced relative to purge phase 206B; ammonia gas flow may be turned on; plasma remains off; and pressure may remain constant. Purge phase 210B may correspond to a repeated operation 110 of Figure 1A. During purge phase 210B, argon flow continues to flow as it may be used as a purge gas; silicon-containing precursor flow remains off; nitrogen gas continues to flow and its flow rate may be slightly increased to a medium flow (as compared to thermal conversion phase 208B); ammonia gas flow is turned off; plasma continues to be turned off; and pressure may stay constant. Plasma exposure phase 212B may correspond to a repeated operation 112 of Figure 1A. During plasma exposure phase 212B, argon flow continues to flow as it may be used as a carrier gas or inert gas or dilution gas; silicon-containing precursor flow remains off; nitrogen gas flow may be increased which may be used to facilitate generation of nitrogen-containing plasma such as N* radicals; ammonia gas flow may be turned on but may have a lower flow rate relative to thermal

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 303 may be heat traced. In some examples, the mixing vessel 304 may also be heat traced. In one non-limiting example, piping downstream of vaporization point 303 has an increasing temperature profile extending from approximately 40°C to approximately 55°C or from about 60°C to about 65°C at mixing vessel.

[0227] 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 303. In one scenario, a liquid injector may be mounted directly to mixing vessel. In another scenario, a liquid injector may be mounted directly to showerhead 306.

[0228] In some embodiments, a liquid flow controller (LFC) upstream of vaporization point 303 may be provided for controlling a mass flow of liquid for vaporization and delivery to ALD process station 300. 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.

[0229] Showerhead 306 distributes process gases toward substrate 312. In the embodiment shown in Figure 3, the substrate 312 is located beneath showerhead 306 and is shown resting on a pedestal 308. Showerhead 306 may have any suitable shape, and may have any suitable number and arrangement of ports for distributing process gases to substrate 312.

[0230] In some embodiments, pedestal 308 may be raised or lowered to expose substrate 312 to a volume between the substrate 312 and the showerhead 306. It will be appreciated that, in some embodiments, pedestal height may be adjusted programmatically by a suitable computer controller 350.

[0231] In another scenario, adjusting a height of pedestal 308 may allow a plasma density to be varied during plasma activation in the process in embodiments where a plasma is ignited. At the conclusion of the process phase, pedestal 308 may be lowered during another substrate transfer phase to allow removal of substrate 312 from pedestal 308.

[0232] In some embodiments, pedestal 308 may be temperature controlled via heater 310. In some embodiments, the pedestal 308 may be heated to a temperature of about 25°C to about 800°C, or about 200°C to about 700°C, during deposition of silicon nitride films as described in disclosed embodiments. In some embodiments, the pedestal is set at a temperature of about 45°C to about 800°C, or about 500°C to about 700°C. In some embodiments, the same pedestal 308 is used for multiple operations in accordance with certain disclosed embodiments.

[0233] Further, in some embodiments, pressure control for ALD process station 300 may be provided by butterfly valve 318. As shown in the embodiment of Figure 3, butterfly valve 318 throttles a vacuum provided by a downstream vacuum pump (not shown). However, in some embodiments, pressure control of ALD process station 300 may also be adjusted by varying a flow rate of one or more gases introduced to the ALD process station 300.

[0234] In some embodiments, a position of showerhead 306 may be adjusted relative to pedestal 308 to vary a volume between the substrate 312 and the showerhead 306. Further, it will be appreciated that a vertical position of pedestal 308 and/or showerhead 306 may be varied by any suitable mechanism within the scope of the present disclosure. In some embodiments, pedestal 308 may include a rotational axis for rotating an orientation of substrate 312. 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 350.

[0235] In some embodiments where plasma may be used as discussed above, showerhead 306 and pedestal 308 electrically communicate with a radio frequency (RF) power supply 314 and matching network 316 for powering a plasma. For example, plasma may be used for igniting a nitrogen-containing plasma in hybrid ALD. 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. For example, RF power supply 314 and matching network 316 may be operated at any suitable power to form a plasma having a desired composition of radical species. Examples of suitable powers are about 150W to about 10000W or about 500 W to about 6000 W for a single-station chamber. For a 3-station chamber, the plasma power may include three generators each powered up to about 10000W, for a total of about 30000W.

[0236] In some embodiments, the substrate may be exposed to nitrogen-containing gas while igniting a plasma during a plasma exposure phase. The plasma may be generated remotely (such

426 through the first wafer transfer module, or VTM, and into the processing chamber 414. In order to achieve this substrate movement, the first robot arm unit 426 uses end effectors on each of its arms.

[0246] Figure 4 also depicts an embodiment of a system controller 450 employed to control process conditions and hardware states of process tool 400. System controller 450 may include one or more memory devices 456, one or more mass storage devices 454, and one or more processors 452. Processor 452 may include a CPU or computer 458, analog and/or digital input/output connections, stepper motor controller boards, etc. In some embodiments, system controller 450 includes machine-readable instructions for performing operations such as those described above with respect to Figure 4 and below with respect to Figure 5.

[0247] As described above, one or more process stations may be included in a multi-station processing tool. Figure 5 depicts an example processing apparatus according to disclosed embodiments. Tool 500 includes a first processing chamber 502 and a second processing chamber 504. The first processing chamber 502 includes a plurality of processing stations, four stations 580A–D, that each may process a wafer. The first processing chamber 502 is configured to perform plasma treatment operations on the wafers. The second processing chamber 504 is configured to perform deposition on the wafer and may be considered a deposition chamber. The second processing chamber 504 also includes a plurality of processing stations, four stations 582A–D, that each may process a wafer and may be controlled by a module 590. The first and second processing chambers 502 and 504 may be considered multi-station processing chambers.

[0248] Tool 500 also includes a wafer transfer unit configured to transport one or more wafers within the tool 500. Additional features of tool 500 will be discussed in greater detail below, and various features are discussed here with respect to some of the described techniques. In the depicted illustration, the wafer transfer unit includes a first robotic arm unit 508 in a first wafer transfer module 510 and a second robotic arm unit 512 in a second wafer transfer module 514 that may be considered an equipment front end module (EFEM) configured to received containers for wafers, such as a front opening unified module (FOUP) 516. The first robotic arm unit 508 is configured to transport a wafer between the first processing chamber 502 and the second processing chamber 504, and between the first processing chamber 502 and the second robotic arm unit 512. The second robotic arm unit 512 is configured to transport the wafer between a FOUP and the first robotic arm unit 508. After a wafer has been treated in the first processing chamber 502, the wafer transfer unit is able to transfer the wafer from the first processing chamber 502, to the second processing chamber 504 where one or more layers of encapsulation material may be deposited on one or more wafers.

[0249] Similar to above, the first wafer transfer module 510 may a vacuum transfer module

substrate to one or more deposition cycles, each deposition cycle including: a silicon-containing precursor dose, purge, ammonia thermal conversion, purge, ammonia and nitrogen plasma exposure, and purge.

[0290] The results are in Table 2 below. These show that stress can be tuned by changing plasma time and that tensile to compressive films may be achieved by modulating process conditions, and that the density increased and wet etch rate decreased when hybrid ALD was used, suggesting improvement in film quality.

Table 2. Density, Wet Etch Rate, and Stress of Hybrid ALD Silicon Nitride and Thermal-only ALD Silicon Nitride

		Thermal ALD	**Hybrid ALD**
Density (g/cc)	XRR	2.843	2.909
WER (A/min)- 100:1 DHF	Ellipsometry	2.02	1.26
Stress	Ellipsometry	615 Mpa	-406 Mpa

EXPERIMENT 8

[0291] Growth of an undercoat film deposited as a blanket film was evaluated. A film was deposited at 650°C using 100 atomic layer deposition cycles, where each cycle involved flowing 100 sccm diisopropylaminosilane for 1 second at 3 Torr, followed by purging for 3 seconds, followed by flowing 20 slm of nitrogen gas at 3 Torr and igniting a plasma at 6000W for 5 seconds (then 10 seconds, then 15 seconds, then 20 seconds, to evaluate variable time), followed by purging for 3 seconds. Figure 11A shows a trend for the growth per cycle versus plasma on time. Figure 11B shows a trend for refractive index versus plasma on time. Refractive index saturation was observed at about 20 seconds.

EXPERIMENT 9

[0292] Growth of an undercoat film deposited as a blanket film was evaluated. A film was deposited at 650°C using 100 atomic layer deposition cycles, where each cycle involved flowing 100 sccm diisopropylaminosilane for variable time in seconds at 3 Torr, followed by purging for 3 seconds, followed by flowing 20 slm of nitrogen gas at 3 Torr and igniting a plasma at 6000W for 5 seconds, followed by purging for 3 seconds. Figure 12A shows a trend for the growth per cycle versus dose time. Figure 12B shows a trend for refractive index versus dose time. Sub-saturation of dose time occurred within about 1.5 seconds.

EXPERIMENT 10

[0293] Growth of an undercoat film deposited as a blanket film was evaluated. A film was deposited at 650°C using 100 atomic layer deposition cycles, where each cycle involved flowing

100 sccm diisopropylaminosilane for 1 second at variable pressure, followed by purging for 3 seconds,

followed by flowing 20 slm of nitrogen gas at variable pressure and igniting a plasma at 6000W for 5 seconds, followed by purging for 3 seconds. Figure 13A shows a trend for the growth per cycle versus pressure. Figure 13B shows a trend for refractive index versus pressure. As pressure increased, growth and refractive index also increased. Overall, growth per cycle of about 0.45 Å/cycle with a refractive index of about 2.05 was achieved with less than about 10 seconds cycle time.

EXPERIMENT 11

[0294] A Fourier-transform infrared spectroscopy (FTIR) spectrum for a non-graded SiON film and an FTIR spectrum for a silicon oxide film were obtained. The refractive index of the silicon oxide film was 1.46. The refractive index of the SiON film was 1.63. The FTIR peak shift to lower wavenumber indicates an increased amount of nitrogen in the film.

[0295] An FTIR spectrum for a non-graded silicon nitride film, a graded silicon nitride film with in-situ oxidation for 10 minutes, and a graded silicon nitride film with in-situ oxidation for 15 minutes were obtained. The results are in Figure 14; the bottom graph shows the non-graded silicon nitride film, the center graph shows the graded silicon nitride film with in-situ oxidation for 10 minutes, and the top graph shows the graded silicon nitride film with in-situ oxidation for 15 minutes. The peaks show the bending mode of Si-O bonds. For graded SiON films, both the SiN and SiO peaks are visible. Longer in-situ oxidation increased the Si-O peak, suggesting that more oxygen was incorporated and more Si-O-Si bonds were formed, which means there is deeper oxidation of the SiN film. These results suggest that the amount of oxidation and the depth of oxidation can be controlled using certain disclosed embodiments.

EXPERIMENT 12

[0296] An experiment was conducted that measured the sidewall thickness as compared to in-feature depth of silicon oxynitride deposited using certain disclosed embodiments. The step coverage achieved was about 90% to about 102% as shown in Figure 15.

DEFINITIONS AND PRECURSORS

DEFINITIONS

[0297] The term “acyl,” or “alkanoyl,” as used interchangeably herein, represents groups of 1, 2, 3, 4, 5, 6, 7, 8 or more carbon atoms of a straight, branched, cyclic configuration, saturated, unsaturated and aromatic, and combinations thereof, or hydrogen, attached to the parent molecular group through a carbonyl group, as defined herein. This group is exemplified by formyl (-C(O)H), acetyl (Ac or -C(O)Me), propionyl, isobutyryl, butanoyl, and the like. In some embodiments, the

(22) -CO_2R^1, where R^1 is selected from the group consisting of (a) hydrogen, (b) C_{1-6} alkyl, (c) C_{4-18} aryl, and (d) C_{4-18} aryl-C_{1-6} alkyl (e.g., -L-R, in which L is C_{1-6} alkyl and R is C_{4-18} aryl); (23) -$C(O)NR^1R^2$, where each of R^1 and R^2 is, independently, selected from the group consisting of (a) hydrogen, (b) C_{1-6} alkyl, (c) C_{4-18} aryl, and (d) C_{4-18} aryl-C_{1-6} alkyl (e.g., -L-R, in which L is C_{1-6} alkyl and R is C_{4-18} aryl); (24) -SO_2R^1, where R^1 is selected from the group consisting of (a) C_{1-6} alkyl, (b) C_{4-18} aryl, and (c) C_{4-18} aryl-C_{1-6} alkyl (e.g., -L-R, in which L is C_{1-6} alkyl and R is C_{4-18} aryl); (25) -$SO_2NR^1R^2$, where each of R^1 and R^2 is, independently, selected from the group consisting of (a) hydrogen, (b) C_{1-6} alkyl, (c) C_{4-18} aryl, and (d) C_{4-18} aryl-C_{1-6} alkyl (e.g., -L-R, in which L is C_{1-6} alkyl and R is C_{4-18} aryl); and (26) -NR^1R^2, where each of R^1 and R^2 is, independently, selected from the group consisting of (a) hydrogen, (b) an *N*-protecting group, (c) C_{1-6} alkyl, (d) C_{2-6} alkenyl, (e) C_{2-6} alkynyl, (f) C_{4-18} aryl, (g) C_{4-18} aryl-C_{1-6} alkyl (e.g., -L-R, in which L is C_{1-6} alkyl and R is C_{4-18} aryl), (h) C_{3-8} cycloalkyl, and (i) C_{3-8} cycloalkyl-C_{1-6} alkyl (e.g., -L-R, in which L is C_{1-6} alkyl and R is C_{3-8} cycloalkyl), wherein in one embodiment no two groups are bound to the nitrogen atom through a carbonyl group or a sulfonyl group. The alkyl group can be a primary, secondary, or tertiary alkyl group substituted with one or more substituents (e.g., one or more halo or alkoxy). In some embodiments, the unsubstituted alkyl group is a C_{1-3}, C_{1-6}, C_{1-12}, C_{1-16}, C_{1-18}, C_{1-20}, or C_{1-24} alkyl group.

[0310] By "alkylene," "alkenylene," or "alkynylene" is meant a multivalent (e.g., bivalent) form of an alkyl, alkenyl, or alkynyl group, respectively, as described herein. Exemplary alkylene groups include methylene, ethylene, propylene, butylene, etc. In some embodiments, the alkylene group is a C_{1-3}, C_{1-6}, C_{1-12}, C_{1-16}, C_{1-18}, C_{1-20}, C_{1-24}, C_{2-3}, C_{2-6}, C_{2-12}, C_{2-16}, C_{2-18}, C_{2-20}, or C_{2-24} alkylene group. In other embodiments, the alkenylene or alkynylene group is a C_{2-3}, C_{2-6}, C_{2-12}, C_{2-16}, C_{2-18}, C_{2-20}, or C_{2-24} alkenylene or alkynylene group. The alkylene, alkenylene, or alkynylene group can be branched or unbranched. The alkylene, alkenylene, or alkynylene group can also be substituted or unsubstituted. For example, the alkylene, alkenylene, or alkynylene group can be substituted with one or more substitution groups, as described herein for alkyl.

[0311] By "alkylsulfinyl" is meant an alkyl group, as defined herein, attached to the parent molecular group through an -S(O)- group. In some embodiments, the unsubstituted alkylsulfinyl group is a C_{1-6} or C_{1-12} alkylsulfinyl group. In other embodiments, the alkylsulfinyl group is -S(O)-R, in which R is an alkyl group, as defined herein.

[0312] By "alkylsulfinylalkyl" is meant an alkyl group, as defined herein, substituted by an alkylsulfinyl group. In some embodiments, the unsubstituted alkylsulfinylalkyl group is a C_{2-12} or C_{2-24} alkylsulfinylalkyl group (e.g., C_{1-6} alkylsulfinyl-C_{1-6} alkyl or C_{1-12} alkylsulfinyl-C_{1-12} alkyl). In other embodiments, the alkylsulfinylalkyl group is -L-S(O)-R, in which each of L and R is, independently, an alkyl group, as defined herein.

SILICON-CONTAINING PRECURSORS

[0402] In various embodiments, the silicon-containing precursor is a silane. Silanes include but are not limited to substituted and unsubstituted silanes, halosilanes, aminosilanes, organosilanes, alkylsilanes, alkylaminosilanes, and alkylhalosilanes. In particular embodiments, the silicon-containing precursor includes a halosilane precursor. In particular embodiments, the silicon-containing precursor includes an aminosilane precursor.

[0403] An aminosilane includes at least one nitrogen atom bonded to a silicon atom, but may also contain hydrogens, oxygens, halogens and carbons. Examples of aminosilanes are mono-, di-, tri- and tetra-aminosilane ($H_3Si(NH_2)$, $H_2Si(NH_2)_2$, $HSi(NH_2)_3$ and $Si(NH_2)_4$, respectively), as well as substituted mono-, di-, tri- and tetra-aminosilanes, for example, t-butylaminosilane, methylaminosilane, tert-butylsilanamine, bis(tertiarybutylamino)silane ($SiH_2(NHC(CH_3)_3)_2$ (BTBAS), tert-butyl silylcarbamate, $SiH(CH_3)$-$(N(CH_3)_2)_2$, $SiHCl$-$(N(CH_3)_2)_2$, $(Si(CH_3)_2NH)_3$, di(sec-butylamino)silane (DSBAS), di(isopropylamino)silane (DIPAS), bis(diethylamino)silane (BDEAS), and the like. A further example of an aminosilane is trisilylamine ($N(SiH_3)_3$). In one example, the silicon-containing precursor is DIPAS. In another example, the silicon-containing precursor is BTBAS.

[0404] A silicon-containing precursor can include one or more optionally substituted amino groups, thereby providing a non-limiting amino silane. In one embodiment, the precursor has a formula of $(R')_{4-x}Si(NR''_2)_x$, wherein:

x is 1, 2, 3, or 4;

each R′ is, independently, H, aliphatic, aliphatic-carbonyl, aliphatic-carbonyloxy, aliphatic-oxy, aliphatic-oxycarbonyl, heteroaliphatic, heteroaliphatic-carbonyl, heteroaliphatic-carbonyloxy, heteroaliphatic-oxy, heteroaliphatic-oxycarbonyl, aromatic, aromatic-carbonyl, aromatic-carbonyloxy, aromatic-oxy, aromatic-oxycarbonyl, heteroaromatic, heteroaromatic-oxy, amino, hydrazino, azido, hydroxyl, silyl, silyloxy, cyanato, isocyanato, cyano, or isocyano, in which any of these may be optionally substituted; and

each R″ is, independently, H, aliphatic, heteroaliphatic, aromatic, heteroaromatic, or amino, in which any of these may be optionally substituted; or optionally in which two R″ can be taken together, with the nitrogen atom to which each is attached, to form an optionally substituted heterocyclyl.

[0405] In another embodiment, the precursor has a formula of $(R''_2N)_x(R')_{3-x}Si{-}L{-}Si(R')_{3-x}(NR''_2)_x$, wherein:

each x is, independently, 0, 1, 2, or 3;

L is a linker, such as a covalent bond, optionally substituted aliphatic, optionally substituted heteroaliphatic, optionally substituted aromatic, optionally substituted heteroaromatic, oxy (-O-),

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;
a plasma generator; 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 silicon-containing precursor to the one or more process chambers for a duration sufficient to adsorb at least some of the silicon-containing precursor to adsorb to a surface of a substrate without igniting a plasma;
cause introduction of a first nitrogen-containing gas without igniting a plasma; and
cause generation of a plasma using a second nitrogen-containing gas to form silicon nitride.

2. The apparatus of claim 1, wherein the plasma generator is a remote plasma generator.

3. The apparatus of claim 1, wherein the chuck is a heated chuck.

4. The apparatus of claim 3, wherein the chuck is heated to a temperature of at least about 650°C.

5. A method for processing substrates, the method comprising:
providing a substrate having a feature thereon;
exposing the substrate to a silicon-containing precursor in vapor phase for a duration sufficient to adsorb at least some of the silicon-containing precursor onto a surface of the substrate to form an adsorbed silicon-containing precursor;
exposing the substrate to a first nitrogen-containing gas in a plasma-free environment; and

exposing the substrate to a plasma generated from igniting a second nitrogen-containing gas to form silicon nitride on the surface of the substrate.

6. The method of claim 5, wherein the plasma comprises radical species selected from the group consisting of nitrogen radicals, hydrogen radicals, and nitrogen hydrogen radicals.

7. The method of claim 5, wherein at least one of exposing the substrate to the first nitrogen-containing gas in the plasma-free environment and exposing the substrate to the plasma generated from igniting the second nitrogen-containing gas further comprises exposing the substrate to hydrogen gas.

8. The method of claim 5, wherein the second nitrogen-containing gas comprises two or more gases.

9. The method of claim 5, wherein the silicon-containing precursor is a halogen-containing precursor.

10. The method of claim 5, wherein the plasma is generated remotely.

11. The method of claim 5, further comprising exposing the formed silicon nitride to an in-situ nitridation or oxidation process to incorporate nitrogen or oxygen to form a second silicon-containing film.

12. The method of claim 5, further comprising prior to providing the substrate having the feature thereon, setting a temperature of one or more chamber components of a process chamber used to house substrates to at least about 650°C; after setting the temperature to at least about 650°C, introducing a halogen-free aminosilane precursor to the process chamber; and introducing a nitrogen-containing reactant and igniting a plasma to form a silicon nitride undercoat on at least one of the one or more chamber components.

13. A method for treating a process chamber having no substrate therein, the method comprising:

setting a temperature of one or more chamber components of the process chamber to at least about 650°C;

after setting the temperature to at least about 650°C, introducing a halogen-free aminosilane precursor to the process chamber; and

introducing a nitrogen-containing reactant and igniting a plasma to form a silicon nitride undercoat on at least one of the one or more chamber components.

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

introducing a substrate having a feature;

exposing the substrate to a silicon-containing precursor for a duration sufficient to adsorb at least some silicon-containing precursor to a surface of the substrate;

exposing the substrate to a reactant species for forming a first silicon-containing film; and

exposing the first silicon-containing film to an in-situ nitridation or oxidation process to incorporate nitrogen or oxygen to form a second silicon-containing film.