

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 a nitrogen-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 reactant reacts immediately with the adsorbed first precursor. 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.

[0028] 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.

[0029] 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.

[0030] Figure 1 provides a process flow diagram depicting example operations of a method performed in accordance with certain disclosed embodiments. In operation 102, a substrate having an exposed silicon oxide surface and exposed silicon surface is provided to a process chamber. The process chamber may be set to a chamber pressure between about 10 mTorr and about 10 Torr, or between about 1 Torr and about 3 Torr. Such chamber pressures may

[0049] 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. Example purge gases include argon, nitrogen, hydrogen, and helium. In various embodiments, the purge gas is an inert gas. The purge gas may include one or more gases. In some embodiments, operation 110 may include one or more evacuation subphases for evacuating the process chamber. Alternatively, it will be appreciated that operation 110 may be omitted in some embodiments. Operation 110 may have any suitable duration, such as between about 0 seconds and about 60 seconds, for example about 0.01 seconds. In some embodiments, increasing a flow rate of one or more purge gases may decrease the duration of operation 110. 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 110. 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 silicon-containing precursor molecules remain adsorbed onto the substrate surface. In some embodiments, the silicon-containing precursor is flowed to a chamber housing the substrate at a flow rate between about 1000 sccm and about 5000 sccm.

[0050] In operation 112, the substrate is exposed to a nitrogen-containing reactant gas without a plasma to selectively form silicon nitride on the unblocked surface, relative to blocked surfaces. In various embodiments, the nitrogen-containing reactant is nitrogen gas. In various embodiments, the nitrogen-containing reactant is a hydrazine. In some embodiments, the nitrogen-containing reactant is ammonia. As shown in Figure 4C, silicon nitride 405 is selectively formed on the unblocked surface (the hydroxyl-terminated silicon oxide surfaces 403) while the blocked silicon surface 412 remains blocked and no silicon nitride is deposited thereon. In Figure 5C, silicon nitride 505 is selectively formed on the unblocked surface (the hydrogen-terminated silicon surface 502) while the blocked silicon oxide surface 513 remains blocked and no silicon nitride is deposited thereon.

[0051] As described above, in some embodiments, the nitrogen-containing reactant gas may be nitrogen, ammonia, a hydrazine, or combinations thereof. Hydrazines used during operation 112 have the structure:

upstream of a showerhead for delivering the blocking reagent into the chamber. In some embodiments, the carrier gas is an inert gas. In some embodiments, the carrier gas and the blocking reagent gas are both delivered to the substrate. During this phase, silicon-containing precursor gas flow is turned off, nitrogen-containing reactant gas flow is turned off, and blocking reagent gas flow is turned on. This phase may correspond to operation 106 of Figure 1.

[0063] Following blocking reagent exposure phase 601A, deposition cycle 610A is performed. Deposition cycle 610A includes silicon-containing precursor exposure phase 657A, purge phase 659A, nitrogen-containing reactant exposure phase 661A, and purge phase 663A. During silicon-containing precursor exposure phase 657A, the carrier gas flow may continue to be on while the silicon-containing precursor gas flow is turned on. Nitrogen-containing reactant gas flow remains off and blocking reagent gas flow is turned off. This may correspond to operation 108 of Figure 1. During purge phase 659A, the carrier gas may continue to flow. In some embodiments the carrier gas may act as a purge gas to help remove excess molecules from the chamber. During this phase, the silicon-containing precursor gas flow is turned off, the nitrogen-containing reactant gas flow is off, and the blocking reagent gas flow is also turned off. This may correspond to operation 110 of Figure 1. During nitrogen-containing reactant exposure phase 661A, a carrier gas may continue to flow. In some embodiments, the carrier gas is used to help deliver a nitrogen-containing reactant gas to the chamber and may be diverted or flowed into the chamber. During this phase, silicon-containing precursor gas flow is turned off and blocking reagent gas flow is turned off while nitrogen-containing reactant gas flow is turned on. This may correspond to operation 112 of Figure 1. During purge phase 663A, the carrier gas flow may continue to be on and the carrier gas may act as a purge gas to remove excess molecules and/or byproducts from the chamber. Silicon-containing precursor gas flow, nitrogen-containing reactant gas flow, and blocking reagent gas flow are turned off. In this example of Figure 6, it is determined that the silicon nitride film deposited is of insufficient thickness and another deposition cycle 610B is performed. Deposition cycle 610B includes silicon-containing precursor exposure phase 657B, purge phase 659B, nitrogen-containing reactant exposure phase 661B, and purge phase 663B. During silicon-containing precursor exposure phase 657B, a carrier gas may be flowed and a silicon-containing precursor gas flow is turned on, while nitrogen-containing reactant gas flow and blocking reagent gas flow are turned off. This may correspond to a

process stations. While the depicted processing chamber 814 includes 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.

[0081] Figure 8 depicts an embodiment of a wafer handling system for transferring wafers within processing chamber 814. In some embodiments, wafer handling system 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 8 also depicts an embodiment of a system controller 850 employed to control process conditions and hardware states of process tool 800. System controller 850 may include one or more memory devices 856, one or more mass storage devices 854, and one or more processors 852. Processor 852 may include a CPU or computer, analog, and/or digital input/output connections, stepper motor controller boards, etc.

[0082] In some embodiments, system controller 850 controls all of the activities of process tool 800. System controller 850 executes system control software 858 stored in mass storage device 854, loaded into memory device 856, and executed on processor 852. Alternatively, the control logic may be hard coded in the controller 850. 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 858 may include instructions for controlling the timing, mixture of gases, gas flow rates, 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 800. System control software 858 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 858 may be coded in any suitable computer readable programming language.

[0083] In some embodiments, system control software 858 may include input/output control (IOC) sequencing instructions for controlling the various parameters described above.

CLAIMS

1. An apparatus for processing semiconductor substrates, the apparatus comprising:
a process chamber comprising a pedestal for holding a substrate;
at least one outlet for coupling to a vacuum; and
a controller for controlling operations in the apparatus including machine-readable instructions for:
causing delivery of a semiconductor substrate to the pedestal of the process chamber,
causing introduction of a blocking reagent to the process chamber,
causing introduction of a silicon-containing precursor to the process chamber and
causing introduction of a nitrogen-containing reactant without igniting a plasma.
2. The apparatus of claim 1, wherein the controller further comprises machine-readable instructions for causing introduction of a fluorine-containing gas and an oxygen-containing gas and generation of a plasma at a plasma power between about 75W and about 200W.
3. The apparatus of claim 1, wherein the controller further comprises machine-readable instructions for causing introduction of hydrogen prior to introduction of the blocking reagent.
4. The apparatus of claim 1, wherein the pedestal is heated to a temperature between about 25°C and about 300°C.
5. The apparatus of claim 2, further comprising a remote plasma generator for generation of the plasma.
6. The apparatus of claim 2, further comprising a plasma generator for generation of the plasma in the process chamber.