IMPROVED SILICON NITRIDE FILMS AND METHODS

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority benefit under 35 USC § 119(e) of US provisional patent application number 61/324,710, filed April 15, 2010, and US provisional patent application number 61/372,367, filed August 10, 2010, and US provisional patent application number 61/379,081, filed September 1, 2010, and US provisional patent application number 61/417,807, filed November 29, 2010, and US utility patent application number 13/084,305, filed April 11, 2011, each of which is incorporated herein by reference in its entirety and for all purposes.

INTRODUCTION

Field

The present disclosure relates generally to formation of SiN materials on substrates. More particularly, the disclosure relates to formation of SiN films on semiconductor substrates.

Background

Silicon nitride (SiN) thin films have unique physical, chemical and mechanical properties and thus are used in a variety of applications, particularly semiconductor devices, for example in diffusion barriers, gate insulators, sidewall spacers, encapsulation layers, strained films in transistors, and the like. One issue with SiN films is the relatively high temperatures used to form the films, for example, in Front End of Line (FEOL) applications, SiN films are typically deposited by chemical vapor deposition (CVD) in a reactor at greater than 750°C using dichlorosilane and ammonia. However, as SiN films are used in late-stage semiconductor fabrication processes, and as device dimensions continue to shrink, there is an increasing demand for SiN films to be formed at lower temperatures, for example less than 600°C.

Another issue with SiN film depositions is the occurrence and/or buildup of amine salts in the reaction chamber. These salts are formed by reaction of amine reactants and acid by products, for example, hydrogen chloride and amine reactants combining. It would be useful to have methods which reduce the amount of salts formed and thus

improve processing by, for example, reducing downtime needed to clean reactors and improving film quality.

Another issue with SiN films is, in certain instances, unwanted carbon content in the film due to carbon content of reactants used to form the SiN film. One way that such carbon content is removed is by high temperature anneal, for example, greater than 600°C, and thus the aforementioned finer features are jeopardized. Of course there are instances where carbon content is desirable, and it would be helpful if one could more precisely tailor the carbon content of the film.

A useful way to deposit SiN films is atomic layer deposition (ALD) and variants thereof, for example, plasma enhanced ALD (PEALD). Under ALD processes, the reaction chamber is purged after every reactant is introduced for adsorption onto the substrate surface. It would be helpful to have processes where one or more purges were unnecessary and thus, for example, throughput would be increased.

What is need are improved SiN films and methods of making them.

SUMMARY

Described are methods of making SiN materials on substrates, particularly SiN thin films on semiconductor substrates. Improved SiN films made by the methods are also included.

One embodiment is a method of forming a silicon nitride material on a substrate, including: (a) providing the substrate in a reaction chamber; (b) continuously exposing the substrate to a vapor phase flow of a nitrogen-containing reactant wherein the nitrogen-containing reactant is adsorbed onto the surface of the substrate; (c) periodically exposing the substrate to a vapor phase flow of a silicon-containing reactant wherein the silicon-containing reactant is adsorbed onto the surface of the substrate; and (d) periodically igniting a plasma in the reaction chamber when the vapor phase flow of the silicon-containing reactant has ceased. In this embodiment, the plasma is ignited to form a plasma from the nitrogen-containing reactant flowing in the reaction chamber. In one embodiment, a carrier gas is flowed continuously through the reaction chamber, thus the plasma may also contain components of the carrier gas, such as argon or nitrogen ions and/or radicals. Generally, the concentration of the silicon-containing reactant in the reaction chamber is allowed to decrease substantially prior to striking the plasma. The

flow of nitrogen-containing reactant, and carrier gas if present, sweeps the excess silicon-containing reactant (that not adsorbed onto the surface of the substrate) out of the chamber without the need for a vacuum purge step, although, in one embodiment, a purge is performed prior to striking the plasma.

In some embodiments, the SiN film produced has an undesirable carbon content. This in-film carbon may result in electrical leakage and may render the film unusable for some dielectric barrier applications. Methods described herein produce SiN films with less than 2% carbon, in one embodiment less than 1% carbon, in yet another embodiment less than 0.5% carbon. In some embodiments, the reduction in carbon residue is readily observable in FTIR spectra. One embodiment is a method of forming a silicon nitride material on a substrate, including: (a) forming a silicon nitride film on the substrate, said formation including: (i) providing the substrate in a reaction chamber; (ii) exposing the substrate to a silicon-containing reactant in the vapor phase so that the silicon-containing reactant is adsorbed onto the surface of the substrate; (iii) exposing the substrate to an nitrogen-containing reactant in the vapor phase so that the nitrogen-containing reactant is adsorbed onto the surface of the substrate; (iv) igniting a plasma while the nitrogen-containing reactant is present in the vapor phase; and then, (b) exposing the silicon nitride film to a hydrogen containing plasma. The hydrogen plasma reduces carbon content of the film. In one embodiment, the hydrogen plasma is generated using hydrogen (H_2) and a carrier gas such as nitrogen, helium or argon.

In general, any method described herein can include heating the substrate to between about 50°C and about 550°C during formation of the SiN film. Certain methods described herein take advantage of a thermally removable groups, attached either to a silicon-containing reactant or a nitrogen-containing reactant, in order to lower carbon content. One embodiment is a method of forming a silicon nitride material on a substrate, including: (a) providing the substrate in a reaction chamber; (b) providing a carrier gas flow through the reaction chamber; (b) exposing the substrate to a vapor phase flow of a nitrogen-containing reactant wherein the nitrogen-containing reactant is adsorbed onto the surface of the substrate and then purging the reaction chamber; (c) exposing the substrate to a vapor phase flow of a silicon-containing reactant wherein the silicon-containing reactant is adsorbed onto the surface of the substrate; (d) igniting a plasma in the reaction chamber after the vapor phase flow of the silicon-containing reactant has ceased; and (e) heating the substrate to between about 200°C and about 550°C; where at least one of the

nitrogen-containing reactant and the silicon-containing reactant bears one or more of a thermally removable group, wherein said thermally removable group decomposes at between about 200°C and about 550°C.

These and other features and advantages of the present invention will be described in more detail below with reference to the associated drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a temporal progression of exemplary phases in a CFD process.

Figure 2 is an exemplary process flow outlining a CFD process for making a SiN film.

Figure 3 is an exemplary process flow outlining a method of making a SiN film.

Figure 4 is an exemplary process flow outlining a method of making a SiN film.

Figure 5 depicts a CFD processing station.

Figure 6 depicts a schematic view of a multi-station processing tool

DETAILED DESCRIPTION

Overview

The present disclosure relates to formation of SiN films, particularly on semiconductor substrates. Methods described herein include ways of controlling the carbon content in SiN films, particularly forming low-carbon content SiN films, as well as conformal film deposition (CFD) methods of forming SiN films.

Definitions

As used herein, the following definitions shall apply unless otherwise indicated.

A "silicon-containing reactant" is a reagent, single or mixture of reagents, used to make a SiN material, where the reagent contains at least one silicon compound. The silicon compound can be, for example, a silane, a halosilane or an aminosilane. A silane contains hydrogen and/or carbon groups, but does not contain a halogen. Examples of silanes are silane (SiH_4), disilane (Si_2H_6), and organo silanes such as methylsilane, ethylsilane, isopropylsilane, t-butylsilane, dimethylsilane, diethylsilane, di-t-butylsilane, allylsilane, *sec*-butylsilane, thexylsilane, isoamylsilane, t-butyldisilane, di-t-butyldisilane,

and the like. A halosilane contains at least one halogen group and may or may not contain hydrogens and/or carbon groups. Examples of halosilanes are iodosilanes, bromosilanes, chlorosilanes and fluorosilanes. Although halosilanes, particularly fluorosilanes, may form reactive halide species that can etch silicon materials, in certain embodiments described herein, the silicon-containing reactant is not present when a plasma is struck. Specific chlorosilanes are tetrachlorosilane ($SiCl_4$), trichlorosilane ($HSiCl_3$), dichlorosilane (H_2SiCl_2), monochlorosilane ($ClSiH_3$), chloroallylsilane, chloromethylsilane, dichloromethylsilane, chlorodimethylsilane, chloroethylsilane, t-butylchlorosilane, di-t-butylchlorosilane, chloroisopropylsilane, chloro-sec-butylsilane, t-butyldimethylchlorosilane, thexyldimethylchlorosilane, and the like. 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 ($H_3Si(NH_2)_4$, $H_2Si(NH_2)_2$, $HSi(NH_2)_3$ 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, $SiH(CH_3)$-$(N(CH_3)_2)_2$, $SiHCl$-$(N(CH_3)_2)_2$, $(Si(CH_3)_2NH)_3$ and the like.

A "nitrogen-containing reactant" contains at least one nitrogen, for example, ammonia, hydrazine, amines (amines bearing carbon) such as methylamine, dimethylamine, ethylamine, isopropylamine, t-butylamine, di-t-butylamine, cyclopropylamine, sec-butylamine, cyclobutylamine, isoamylamine, 2-methylbutan-2-amine, trimethylamine, diisopropylamine, diethylisopropylamine, di-t-butylhydrazine, as well as aromatic containing amines such as anilines, pyridines, and benzylamines. Amines may be primary, secondary, tertiary or quaternary (for example, tetraalkylammonium compounds). A nitrogen-containing reactant can contain heteroatoms other than nitrogen, for example, hydroxylamine, t-butyloxycarbonyl amine and N-t-butyl hydroxylamine are nitrogen-containing reactants.

"Plasma" refers to a plasma ignited in a reaction chamber or remotely and brought into the reaction chamber. Plasmas can include the reactants described herein and may include other agents, for example, a carrier gas, or reactive species such as hydrogen gas. The reactants and other agents may be present in a reaction chamber when a plasma is struck, or a remote plasma may be flowed into a chamber where the reactants are present and/or the reactants and/or carrier gas may be ignited into a plasma remotely and brought

into the reaction chamber. A "plasma" is meant to include any plasma known to be technologically feasible, including inductively-coupled plasmas and microwave surface wave plasmas. One of ordinary skill in the art would appreciate that advancements in technology will occur, and thus as yet developed plasma generating techniques are contemplated to be within the scope of the invention.

"Thermally removable group" refers to a moiety, on either or both of the nitrogen-containing reactant and the silicon-containing reactant, that breaks down into volatile components at between about 200°C and about 550°C. Described herein are non-limiting examples such as secondary and tertiary carbon group, which undergo elimination reactions in this temperature range. One of ordinary skill in the art would recognize that other groups thermally decompose as described by other mechanisms, for example, a t-butyloxycarbonyl (t-BOC or "BOC") group thermally decomposes via both an elimination mechanism where the t-butyl portion of the group forms isobutylene, but also the decomposition forms carbon dioxide. Thus a thermally removable group is not limited to a particular mechanism or combination of mechanisms. As long as the group breaks down under the specified temperature range to produce at least one volatile component, then it qualifies as a thermally decomposable group. For example, under a given set of conditions, t-butylethylamine will undergo thermal decomposition of the t-butyl group to form isobutylene while the ethyl group remains, and thus isobutylene and ethylamine are the products of the thermal decomposition. One of ordinary skill in the art would recognize that the volatility of a component depends, in part, on the reaction conditions under which the component is generated. For example, isobutylene may be volatile and be removed from a reaction chamber under the conditions of heating and low press because it does not react with the adsorbed reactants, while, for example, ammonia, although generally a volatile compound, undergoes reaction with a silicon-containing reactant adsorbed on the surface of a substrate.

Methods

Described herein are methods of making SiN films. In particular embodiments SiN films are made using plasma-activated conformal film deposition (CFD). In some embodiments, SiN films are deposited and treated with a hydrogen plasma to reduce the carbon content of the film. In some embodiments, a silicon-containing reactant and a nitrogen-containing reactant are used to make a SiN film, where one or both of the

reactants includes a thermally removable group. In these embodiments, a hydrogen plasma may not be necessary to remove unwanted carbon from the film, for example when the carbon content is substantially embodied by the thermally removable group or groups' volatile component. When the SiN film is heated, the carbon is driven off via the thermally removable group or groups breaking down into volatile components that are removed in the gas phase. In certain embodiments, although some of the carbon content of the SiN film is removed via exploiting a thermally removable group or groups, there may be some unwanted carbon remaining, and thus a hydrogen plasma treatment may be employed as well. Each of the aforementioned aspects are described in more detail below.

In certain embodiments, CFD is used to deposit the SiN films, although methods described herein are not limited to CFD. Other suitable methods include ALD, PEALD, CVD, PECVD, and plasma enhanced cyclic chemical vapor deposition (PECCVD). Methods for forming films using CFD are described in US Patent application, serial number 13/084,399, filed on the same day as the instant disclosure, and which is incorporated by reference herein for all purposes. For context, a short description of CFD is provided.

Manufacture of semiconductor devices typically involves depositing one or more thin films on a non-planar substrate in an integrated fabrication process. In some aspects of the integrated process it may be useful to deposit conformal thin films. For example, a silicon nitride film may be deposited on top of an elevated gate stack to act as a spacer layer for protecting lightly-doped source and drain regions from subsequent ion implantation processes.

In spacer layer deposition processes, chemical vapor deposition (CVD) processes may be used to form a silicon nitride film on the non-planar substrate, which is then anisotropically etched to form the spacer structure. However, as a distance between gate stacks decreases, mass transport limitations of CVD gas phase reactions may cause "bread-loafing" deposition effects. Such effects typically exhibit thicker deposition at top surfaces of gate stacks and thinner deposition at the bottom corners of gate stacks. Further, because some die may have regions of differing device density, mass transport effects across the wafer surface may result in within-die and within-wafer film thickness variation. These thickness variations may result in over-etching of some regions and under-etching of other regions. This may degrade device performance and/or die yield.

Some approaches to addressing these issues involve atomic layer deposition (ALD). In contrast with a CVD process, where thermally activated gas phase reactions are used to deposit films, ALD processes use surface-mediated deposition reactions to deposit films on a layer-by-layer basis. In one example ALD process, a substrate surface, including a population of surface active sites, is exposed to a gas phase distribution of a first reactant (A). Some molecules of reactant A may form a condensed phase atop the substrate surface, including chemisorbed species and physisorbed molecules of reactant A. The reactor is then evacuated to remove gas phase and physisorbed reactant A so that only chemisorbed species remain. A second film reactant (B) is then introduced to the reactor so that some molecules of reactant B adsorb to the substrate surface. Thermal energy provided to the substrate activates surface reactions between adsorbed molecules of reactants A and B, forming a film layer. Finally, the reactor is evacuated to remove reaction by-products and unreacted reactant B, ending the ALD cycle. Additional ALD cycles may be included to build film thickness. Plasma, or other energetic means, may be used in conjunction with heating, or as alternatives to heating the substrate in order to drive the reaction between reactant A and B.

Depending on the exposure time of the reactant dosing steps and the sticking coefficients of the reactants, each ALD cycle may deposit a film layer of, in one example, between one-half and three angstroms thick. Thus, ALD processes may be time consuming when depositing films more than a few nanometers thick. Further, some reactants may have long exposure times to deposit a conformal film, which may also reduce wafer throughput time.

Conformal films may also be deposited on planar substrates. For example, antireflective layers for lithographic patterning applications may be formed from planar stacks comprising alternating film types. Such antireflective layers may be approximately 100 to 1000 angstroms thick, making ALD processes less attractive than CVD processes. However, such anti-reflective layers may also have a lower tolerance for within-wafer thickness variation than many CVD processes may provide. For example, a 600-angstrom thick antireflective layer may tolerate a thickness range of less than 3 angstroms.

Accordingly, various embodiments described herein include CFD to deposit SiN films. Generally, CFD does not rely on complete purges of one or more reactants prior to reaction to form SiN. For example, there may be one or more reactants present in the vapor phase when a plasma (or other activation energy) is struck. Accordingly, one or

more of the process steps described in the ALD process may be shortened or eliminated in an example CFD process. Further, in some embodiments, plasma activation of deposition reactions may result in lower deposition temperatures than thermally-activated reactions, potentially reducing the thermal budget of an integrated process.

Figure 1, shows a temporal progression of exemplary phases in a CFD process, 100, for various process parameters, for example, inert gas flow, reactant A, reactant B and when a plasma is struck. In FIGURE 1, two deposition cycles 110A and 110B are shown. One of ordinary skill in the art would appreciate that any suitable number of deposition cycles may be included in a CFD process to deposit a desired film thickness. Example CFD process parameters include, but are not limited to, flow rates for inert and reactant species, plasma power and frequency, substrate temperature, and process station pressure.

The concept of a CFD "cycle" is relevant to the discussion of various embodiments herein. Generally a cycle is the minimum set of operations required to perform a surface deposition reaction one time. The result of one cycle is production of at least a partial film layer on a substrate surface. Typically, a CFD cycle will include only those steps necessary to deliver and adsorb each reactant to the substrate surface, and then react those adsorbed reactants to form the partial layer of film. Of course, the cycle may include certain ancillary steps such as sweeping one of the reactants or byproducts and/or treating the partial film as deposited. Generally, a cycle contains only one instance of a unique sequence of operations. As an example, a cycle may include the following operations: (i) delivery/adsorption of reactant A, (ii) delivery/adsorption of reactant B, (iii) sweep B out of the reaction chamber, and (iv) apply plasma to drive a surface reaction of A and B to form the partial film layer on the surface.

Referring to FIGURE 1, an inert gas is flowed during all phases of process 100. At reactant A exposure phase, 120A, reactant A is supplied at a controlled flow rate to a process station to saturate exposed surfaces of a substrate. Reactant A may be any suitable deposition reactant, for example, a nitrogen-containing reactant. In the embodiment shown in FIGURE 1, reactant A flows continuously throughout deposition cycles 110A and 110B. Unlike a typical ALD process, where film precursor (reactant) exposures are separated to prevent gas phase reaction, reactants A and B may be allowed to mingle in the gas phase of some embodiments of a CFD process. Continuously supplying reactant A to the process station may reduce or eliminate a reactant A flow rate

turn-on and stabilization time compared to an ALD process where reactant A is first turned on, then stabilized and exposed to the substrate, then turned off, and finally removed from a reactor. While the embodiment shown in FIGURE 1 depicts reactant A exposure phase 120A as having a constant flow rate, it will be appreciated that any suitable flow of reactant A, including a variable flow, may be employed within the scope of the present disclosure. In some embodiments, reactant A exposure phase 120A may have a duration that exceeds a substrate surface saturation time for reactant A. For example, the embodiment of FIGURE 1 includes a reactant A post-saturation exposure time 130 in reactant A exposure phase 120A. Optionally, reactant A exposure phase 120A may include a controlled flow rate of an inert gas. Example inert gases include, but are not limited to, nitrogen, argon, and helium. The inert gas may be provided to assist with pressure and/or temperature control of the process station, evaporation of a liquid reactant, more rapid delivery of the reactant and/or as a sweep gas for removing process gases from the process station and/or process station plumbing.

At Reactant B exposure phase 140A of the embodiment shown in FIGURE 1, reactant B is supplied at a controlled flow rate to the process station to saturate the exposed substrate surface. In this example, reactant B is a silicon-containing reactant. While the embodiment of FIGURE 1 depicts reactant B exposure phase 140A as having a constant flow rate, it will be appreciated that any suitable flow of reactant B, including a variable flow, may be employed within the scope of the present disclosure. Further, it will be appreciated that reactant B exposure phase 140A may have any suitable duration. In some embodiments, reactant B exposure phase 140A may have a duration exceeding a substrate surface saturation time for reactant B. For example, the embodiment shown in FIGURE 1 depicts a reactant B post-saturation exposure time 15 included in reactant B exposure phase 140A.

In some embodiments, surface adsorbed B species may exist as discontinuous islands on the substrate surface, making it difficult to achieve surface saturation of reactant B. Various surface conditions may delay nucleation and saturation of reactant B on the substrate surface. For example, ligands released on adsorption of reactants A and/or B may block some surface active sites, preventing further adsorption of reactant B. Accordingly, in some embodiments, continuous adlayers of reactant B may be provided by modulating a flow of and/or discretely pulsing reactant B into the process station during reactant B exposure phase 140A. This may provide extra time for surface

adsorption and desorption processes while conserving reactant B compared to a constant flow scenario. Additionally, or alternatively, in some embodiments, one or more sweep phases may be included between consecutive exposures of reactant B.

Prior to activation of the plasma, gas phase reactant B may be removed from the process station in sweep phase 160A in some embodiments. Sweeping the process station may avoid gas phase reactions where reactant B is unstable to plasma activation or where unwanted species might be formed. Further, sweeping the process station may remove surface adsorbed ligands that may otherwise remain and contaminate the film. Example sweep gases may include, but are not limited to, argon, helium, and nitrogen. In the embodiment shown in FIGURE 1, sweep gas for sweep phase 160A is supplied by the continuous inert gas stream. In some embodiments, sweep phase 160A may include one or more evacuation subphases for evacuating the process station. Alternatively, it will be appreciated that sweep phase 160A may be omitted in some embodiments.

Sweep phase 160A may have any suitable duration. In some embodiments, increasing a flow rate of a one or more sweep gases may decrease the duration of sweep phase 160A. For example, a sweep 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 sweep phase 160A. In one non-limiting example, the duration of a sweep phase may be optimized by adjustment of the sweep gas flow rate. This may reduce deposition cycle time, which may improve substrate throughput.

At plasma activation phase 180A of the embodiment shown in FIGURE 1, plasma energy is provided to activate surface reactions between surface adsorbed reactants A and B. For example, the plasma may directly or indirectly activate gas phase molecules of reactant A to form reactant A radicals. These radicals may then interact with surface adsorbed reactant B, resulting in film-forming surface reactions. Plasma activation phase 180A concludes deposition cycle 110A, which in the embodiment of FIGURE 1 is followed by deposition cycle 110B, commencing with reactant A exposure phase 120B.

In some embodiments, the plasma ignited in plasma activation phase 180A may be formed directly above the substrate surface. This may provide a greater plasma density and enhance a surface reaction rate between reactants A and B. For example, plasmas for CFD processes may be generated by applying a radio frequency (RF) field to a low-

pressure gas using two capacitively coupled plates. Any suitable gas may be used to form the plasma. In this example, the inert gas such as argon or helium is used along with reactant A, a nitrogen-containing reactant, to form the plasma. Ionization of the gas between the 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. Non-limiting examples of electrodes include process gas distribution showerheads and substrate support pedestals. It will be appreciated that plasmas for CFD processes may be formed by one or more suitable methods other than capacitive coupling of an RF field to a gas.

Plasma activation phase 180A may have any suitable duration. In some embodiments, plasma activation phase 180A may have a duration that exceeds a time for plasma-activated radicals to interact with all exposed substrate surfaces and adsorbates, forming a continuous film atop the substrate surface. For example, the embodiment shown in FIGURE 1 includes a plasma post-saturation exposure time 190 in plasma activation phase 180A.

In some embodiments, extending a plasma exposure time and/or providing a plurality of plasma exposure phases may provide a post-reaction treatment of bulk and/or near-surface portions of the deposited film. In one embodiment, decreasing surface contamination may prepare the surface for adsorption of reactant A. For example, a silicon nitride film formed from reaction of a silicon-containing reactant and a nitrogen-containing reactant may have a surface that may resist adsorption of subsequent reactants. Treating the silicon nitride surface with a plasma may create hydrogen bonds for facilitating subsequent adsorption and reaction events. The SiN films described herein can be exposed to other-than-plasma treatments.

In some embodiments, a treatment other than a plasma treatment is employed to modify the properties the as deposited film. Such treatments include electromagnetic radiation treatments, thermal treatments (e.g., anneals or high temperature pulses), and the like. Any of these treatments may be performed alone or in combination with another treatment, including a plasma treatment. Any such treatment can be employed as a substitute for any of the above-described plasma treatments. In a specific embodiment, the treatment involves exposing the film to ultraviolet radiation. As described below, in a

specific embodiment, the method involves the application of UV-radiation to a film *in situ* (i.e., during formation of the film) or post deposition of the film. Such treatment serves to reduce or eliminate defect structure and provide improved electrical performance.

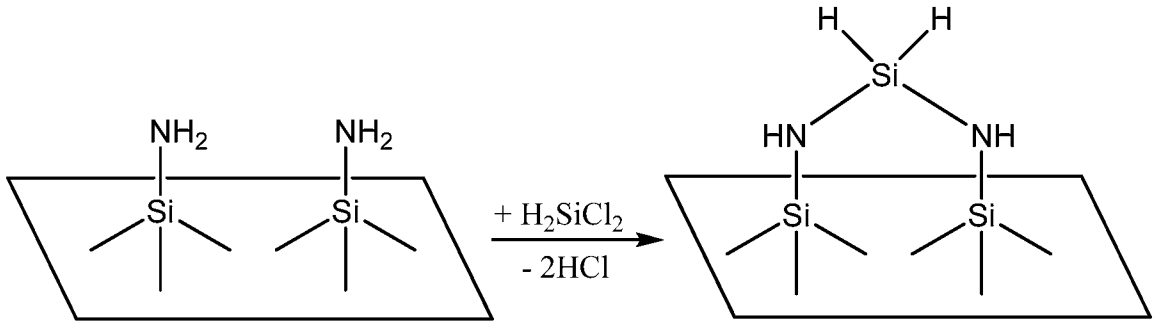
In certain specific embodiments, a UV treatment can be coupled with a plasma treatment. These two operations can be performed concurrently or sequentially. In the sequential option, the UV operation optionally takes place first. In the concurrent option, the two treatments may be provided from separate sources (e.g., an RF power source for the plasma and a lamp for the UV) or from a single source such as a helium plasma that produces UV radiation as a byproduct.

In some embodiments, film properties, such as film stress, dielectric constant, refractive index, etch rate may be adjusted by varying plasma parameters.

While many examples discussed herein include two reactants (A and B), it will be appreciated that any suitable number of reactants may be employed within the scope of the present disclosure. In some embodiments, a single reactant and an inert gas used to supply plasma energy for a surface reaction can be used. Alternatively, some embodiments may use multiple reactants to deposit a film. For example, in some embodiments, a silicon nitride film may be formed by reaction of a silicon-containing reactant and one or more of a nitrogen-containing reactant, or one or more silicon-containing reactants and a single nitrogen-containing reactant, or more than one of both the silicon-containing reactant and the nitrogen-containing reactant.

When multiple reactants are employed and the flow of one of them is continuous, at least two of them will co-exist in the gas phase during a portion of the CFD cycle. Similarly, when no purge step is performed after delivery of the first reactant, two reactants will co-exist in the reaction chamber. Therefore, it may be important to employ reactants that do not appreciably react with one another in the gas phase absent application of activation energy. Typically, the reactants should not react until present on the substrate surface and exposed to plasma or another appropriate non-thermal activation condition. Choosing such reactants involves considerations of at least (1) the thermodynamic favorability (Gibb's free energy <0) of the desired reaction, and (2) the activation energy for the reaction, which should be sufficiently great so that there is negligible reaction at the desired deposition temperature.

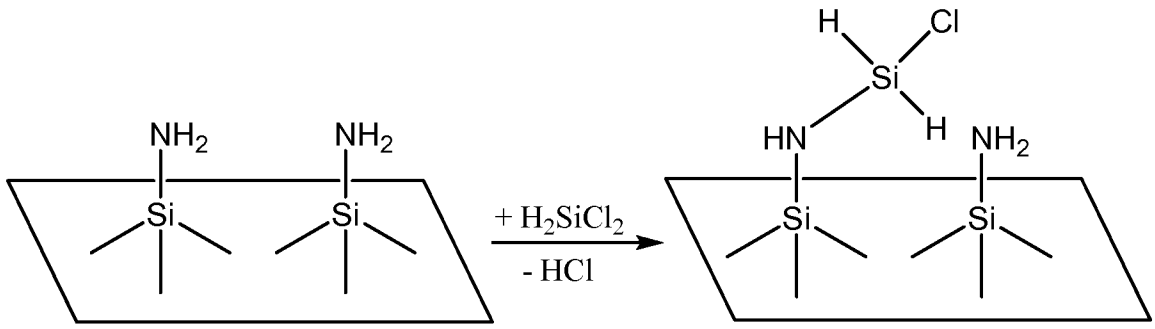
Selection of one or more reactants may be driven by various film and/or hardware considerations. For example, in some embodiments, a silicon nitride film may be formed from reaction of dichlorosilane and a plasma-activated nitrogen-containing reactant, for example ammonia. Chemisorption of dichlorosilane to a silicon surface (indicated by the rectangle in Scheme 1, etc.) may create a silicon-hydrogen terminated surface, liberating hydrogen chloride (HCl). An example of this chemisorption reaction is depicted in Scheme 1.



Scheme 1

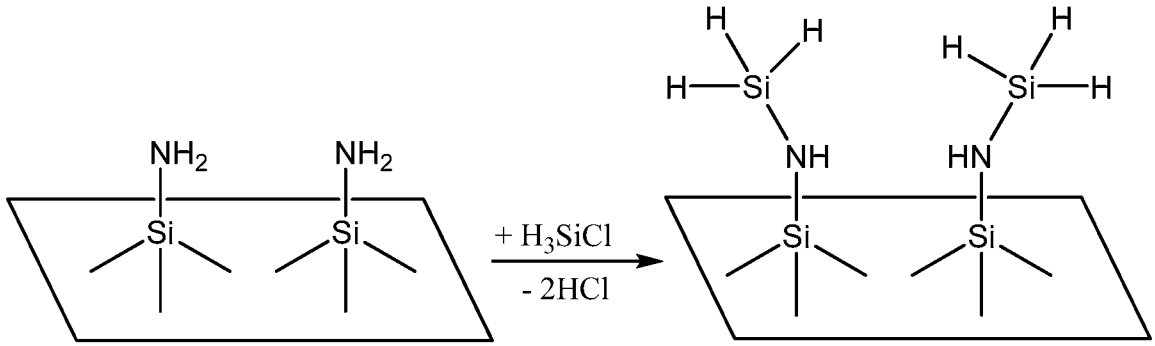
The cyclic intermediate shown in Scheme 1 may then be transformed into a silicon amide terminated surface via reaction with the same or different plasma-activated nitrogen-containing reactant.

However, some molecules of dichlorosilane may chemisorb by alternative mechanisms. For example, surface morphology may hinder the formation of the cyclic intermediate depicted in Scheme 1. An example of another chemisorption mechanism is shown Scheme 2. During subsequent plasma activation of a nitrogen-containing reactant, the remaining chlorine atom of the adsorbed intermediate species shown in Scheme 2 may be liberated and may become activated by the plasma. This may cause etching of the silicon nitride surface, potentially causing the silicon nitride film to become rough or hazy. Further, the residual chlorine atom may readsorb, physically and/or chemically, potentially contaminating the deposited film. This contamination may alter physical and/or electrical properties of the silicon nitride film. Further still, the activated chlorine atom may cause etch damage to portions of the process station hardware, potentially reducing the service life of portions of the process station. Also, excess chloride content of the film may be unwanted.



Scheme 2

Thus, in some embodiments, a monochlorosilane is used rather than a dichlorosilane. This may reduce film contamination, film damage, and/or process station damage. An example of the chemisorption of chlorosilane is shown in Scheme 3. While the example depicted in Scheme 3 uses chlorosilane as the silicon-containing reactant, it will be appreciated that any suitable monosubstituted halosilane may be used. For example there may be applications where a certain carbon content is desirable. In one embodiment, the carbon content of the SiN film is tailored by choice of carbon containing groups, both carbon amount and type, on one or both of the silicon containing reactant and the nitrogen-containing reactant.



Scheme 3

As explained above, the depicted intermediate structures may react with a nitrogen-containing reactant to form a silicon amide terminated surface. For example, ammonia may be activated by a plasma, forming various ammonia radical species. The radical species react with the intermediate, forming the silicon amide terminated surface. Ammonia is a common nitrogen-containing reactant for forming SiN films. Certain embodiments described herein utilize ammonia as a nitrogen-containing reactant.

However, ammonia may physisorb strongly to surfaces of the reactant delivery lines, process station, and exhaust plumbing, which may lead to extended purge and evacuation times. Further, ammonia may have a high reactivity with some gas phase silicon-containing reactants. For example gas-phase mixtures of dichlorosilane (SiH_2Cl_2) and ammonia may create unstable species such as diaminosilane ($SiH_2(NH_2)_2$). Such species may decompose in the gas phase, nucleating small particles. Small particles may also be formed if ammonia reacts with hydrogen chloride, generated during chemisorption of a halosilane, to form ammonium chloride. Such particles may accumulate in the process station where they may contaminate substrate surfaces, potentially leading to integrated device defects, and where they may contaminate process station hardware, potentially leading to tool down time and cleaning. The small particles may also accumulate in exhaust plumbing, may clog pumps and blowers, and may create a need for special environmental exhaust scrubbers and/or cold traps.

Thus, in some embodiments, an amine may be used rather than a nitrogen-containing reactant that does not contain carbon. For example, various radicals formed from plasma activation of alkyl amines, such as t-butyl amine, may be supplied to the process station. Substituted amines, such as t-butyl amine, may have a lower sticking coefficient on process hardware than ammonia, which may result in comparatively lower phyisorbption rates and comparatively lower process purge time.

Further, such alkyl amines form halogenated salts that are more volatile than ammonium salts, for example ammonium chloride. For example, t-butylammonium chloride is substantially more volatile than ammonium chloride and thus less deposits are formed on the interior of the chamber and associated plumbing and deposition hardware. This reduces tool down time, device defect creation, and environmental abatement expense.

In other embodiments, the nitrogen-containing reactant is an amine, having a carbon component and a nitrogen component. In some embodiments, the amine serves as a source of ammonia. That is, for example, t-butylamine is the nitrogen-containing reactant, but after processing, the t-butyl portion of the reactant is volatized and removed from the SiN film, while the amine portion (ammonia) is incorporated into the SiN film. In this way, the nitrogen-containing reactant serves as a delivery vector for ammonia, or an "ammonia equivalent." This avoids having the reaction chamber and associated plumbing and hardware exposed to excess ammonia (although some ammonia is

inevitably lost from the SiN film during decomposition of the t-butyl group and may contact the reactor and other surfaces). Further still, certain amines (nitrogen-containing reactants) may react with silicon-containing reactants to form a new silicon-containing reactant. For example, the reaction of t-butyl amine with dichlorosilane may form BTBAS. Although BTBAS contains silicon, it also contains nitrogen (by convention defined herein, this is a silicon-containing reactant). Because t-butyl amine decomposes at temperatures above 300°C to form isobutylene and ammonia, analogously BTBAS may thermally decompose to form SiN and (2 moles of) isobutylene (BTBAS may also be preformed and used as a silicon-containing reactant with a nitrogen-containing reactant). Thus, certain amines provide alternate routes to form silicon nitride. Described herein are methods of exploiting such alkyl amines.

In some embodiments, where thermal decomposition pathways are exploited, the thermally removable group need not be part of a nitrogen-containing reactant. For example, in certain embodiments the thermally removable group is part of the silicon-containing reactant. In one embodiment the thermally removable group is directly attached to a silicon, nitrogen or oxygen of a silicon-containing reactant. In some embodiments, the reactant, nitrogen or silicon, includes a thermally removable group and at least one group that does not thermally decompose. This may be desirable, for example, when a certain carbon content in the final SiN film is desired, or, for example, when it is desirable to tailor the manner in which the carbon is removed from the SiN film. For example, in one embodiment, among the nitrogen and silicon-containing reactants, there is included both a thermally removable group and a non-thermally removable group, i.e, one that does not thermally decompose under the same conditions. In this way a SiN film is produced where some of the carbon can be removed, if desired, via thermal decomposition and the remainder of the carbon removed, if desirable, via, for example, hydrogen plasma treatment. Thus methods of the invention contemplate carbon removal from a single film in more than one way.

Each of the aforementioned aspects are described in more detail below.

As described above, in one embodiment, CFD is used to make SiN films. One embodiment is a method of forming a silicon nitride material on a substrate, including: (a) providing the substrate in a reaction chamber; (b) continuously exposing the substrate to a vapor phase flow of a nitrogen-containing reactant wherein the nitrogen-containing reactant is adsorbed onto the surface of the substrate; (c) periodically exposing the

substrate to a vapor phase flow of a silicon-containing reactant wherein the silicon-containing reactant is adsorbed onto the surface of the substrate; and (d) periodically igniting a plasma in the reaction chamber when the vapor phase flow of the silicon-containing reactant has ceased. In this embodiment, the plasma is ignited to form a plasma from the nitrogen-containing reactant flowing in the reaction chamber. In one embodiment, a carrier gas is flowed continuously through the reaction chamber, thus the plasma may also contain components of the carrier gas, such as argon or nitrogen ions and/or radicals. Generally, the concentration of the silicon-containing reactant in the reaction chamber is allowed to decrease substantially prior to striking the plasma. The flow of nitrogen-containing reactant, and carrier gas if present, sweeps the excess silicon-containing reactant (that not adsorbed onto the surface of the substrate) out of the chamber without the need for a vacuum purge step, although, in one embodiment, a purge is performed prior to striking the plasma.

Figure 2 depicts an exemplary process flow, 200, outlining aspects of the method. A substrate is provided to the chamber, see 205. A flow of nitrogen-containing reactant is established and continued throughout 200, see 210. The substrate is periodically exposed to a silicon-containing reactant, see 215. Also, periodically, a plasma is struck, but only when the silicon-containing reactant flow has ceased. In one embodiment, the silicon-containing reactant not adsorbed to the surface of the substrate is swept out of the chamber by the flow of the inert gas and/or nitrogen-containing reactant. In another embodiment, a purge may be used. After the plasma treatment, the method is complete. The steps may be repeated a number of times to build up a layer of desired thickness.

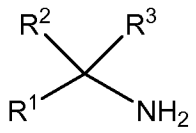
In one embodiment, using any of the methods described herein, the semiconductor wafer is heated to between about 50°C and about 550°C. In one embodiment, the wafer is heated throughout the deposition, in other embodiments the wafer is heated periodically during the deposition or after the deposition steps as an anneal. Heating may also be used in conjunction with thermally removable groups as described in more detail below.

The method is particularly useful for forming SiN films on semiconductor wafers. In one embodiment, steps (b) through (d) are repeated to form a conformal layer on the semiconductor wafer between about 1 nm and about 100 nm thick. In another embodiment, between about 5 nm and about 50 nm thick. In another embodiment, between about 5 nm and about 30 nm thick.

For the methods described herein, generally any silicon-containing reactant is suitable. The SiN material of the films produced may or may not contain carbon. The carbon in the SiN film may come from the silicon-containing reactant or the nitrogen-containing reactant. In one embodiment, the silicon-containing reactant is selected from the group consisting of a silane, a halosilane and an aminosilane, and mixtures thereof. In one embodiment, the silicon-containing reactant is a halosilane, an aminosilane or a mixture thereof. In one embodiment, the silicon-containing reactant is a halosilane. In one embodiment, the halosilane is a chlorosilane. In one embodiment, the halosilane is a mono- or dihalosilane, for example a monochlorosilane or a dichlorosilane. In a particular embodiment, the halosilane is a monochlorosilane. In one embodiment, the monochlorosilane is chlorosilane.

In certain embodiments, a silicon-containing reactant is paired with a particular nitrogen-containing reactant. For example, a monochlorosilane is paired with an alkyl amine, for example t-butyl amine, to make SiN films using the methods described herein. In one embodiment, dichlorosilane is used with t-butylamine to make SiN using a method described herein.

For methods described herein, the nitrogen-containing reactant can be any suitable nitrogen-containing reactant. In one embodiment, the nitrogen-containing reactant is selected from the group consisting of ammonia, a hydrazine, an amine and mixtures thereof. In one embodiment, the nitrogen-containing reactant includes a C_{1-10} alkyl amine or a mixture of C_{1-10} alkyl amines. In one embodiment, the C_{1-10} alkyl amine is a primary alkyl amine or a secondary alkyl amine. In one embodiment, the C_{1-10} alkyl amine is a primary alkyl amine. In one embodiment, the C_{1-10} alkyl amine is according to formula I:



I

wherein each of R^1, R^2 and R^3 is, independent of the others, H or C_{1-3} alkyl; or two of R^1, R^2 and R^3, together with the carbon atom to which they are attached form form a C_{3-7} cycloalkyl and the other of R^1, R^2 and R^3 is H or C_{1-3} alkyl. In one embodiment, the C_{1-10} alkyl amine has a secondary or tertiary carbon attached directly to the nitrogen. In one embodiment, the C_{1-10} alkyl amine is selected from the group consisting of

isopropylamine, cyclopropylamine, sec-butylamine, tert-butyl amine, cyclobutylamine, isoamylamine, 2-methylbutan-2-amine and thexylamine (2,3-dimethylbutan-2-amine). In one embodiment, in the C_{1-10} alkyl amine of Formula I, each of R^1, R^2 and R^3 is C_{1-3} alkyl. In one embodiment, the C_{1-10} alkyl amine is tert-butyl amine. TBA is particularly useful for the reasons described.

In some embodiments, the SiN film produced has an undesirable carbon content. This in-film carbon may result in electrical leakage and may render the film unusable for some dielectric barrier applications. Carbon content can vary, but in some embodiments approximately 10% carbon (by weight) can be considered too high. Methods described herein address unwanted carbon in SiN films. Methods described herein produce SiN films with less than 2% carbon, in one embodiment less than 1% carbon, in yet another embodiment less than 0.5% carbon. In some embodiments, the reduction in carbon residue is readily observable in FTIR spectra, although other analytical methods are known to one of ordinary skill in the art that can measure carbon content in these ranges. One embodiment is a method of forming a silicon nitride material on a substrate, including: (a) forming a silicon nitride film on the substrate, said formation including: (i) providing the substrate in a reaction chamber; (ii) exposing the substrate to a silicon-containing reactant in the vapor phase so that the silicon-containing reactant is adsorbed onto the surface of the substrate; (iii) exposing the substrate to an nitrogen-containing reactant in the vapor phase so that the nitrogen-containing reactant is adsorbed onto the surface of the substrate; (iv) igniting a plasma while the nitrogen-containing reactant is present in the vapor phase; and then, (b) exposing the silicon nitride film to a hydrogen containing plasma to remove at least some carbon content of the silicon nitride film.

Figure 3 depicts an exemplary process flow, 300, outlining aspects of the method. A substrate is provided to the chamber, see 305. The substrate is exposed to a silicon-containing reactant, see 310. The substrate is exposed to a nitrogen-containing reactant, see 315. A plasma is struck while the nitrogen-containing reactant is present in the vapor phase, see 320, thus forming a SiN material is formed on the substrate. In one embodiment, the silicon-containing reactant not adsorbed to the surface of the substrate is swept out of the chamber by the flow of the inert gas and/or nitrogen-containing reactant prior to striking the plasma. In another embodiment, a purge may be used to remove vapor phase silicon-containing reactant. One or more iterations of 310-320 can be performed to build up a SiN layer. After the SiN film is produced to a desired thickness,

the film is exposed to a hydrogen plasma, see 325. After treatment with hydrogen plasma to remove the desired amount of carbon, the method is done. In one embodiment, the hydrogen plasma is generated using hydrogen (H_2) and a carrier gas such as nitrogen, helium or argon. Other hydrogen containing gases, or active hydrogen atoms produced by a remote plasma source, may be used to treat the deposited film. Further, in some embodiments, the carbon content of the film may be tuned to any suitable concentration by varying one or more of the number of treatment pulses and their duration, the intensity of the treatment plasma, the substrate temperature, and the treatment gas composition.

As described in relation to previous methods, in one embodiment, the substrate is a semiconductor wafer. In one embodiment, (ii) is performed prior to (iii). In another embodiment, (iii) is performed prior to (ii). In certain embodiments, (a) is repeated two or more times prior to (b). That is, the hydrogen plasma treatment removes carbon from the SiN film. It is not always necessary to perform the hydrogen plasma treatment after each reaction to form SiN, rather, a number of layers of the SiN (with carbon) may be deposited before requiring a hydrogen plasma treatment. That is, the hydrogen plasma is effective at removing the carbon after two or more layers are deposited. In one embodiment, (a) and (b) are repeated to form a conformal layer on the semiconductor wafer between about 1 nm and about 100 nm thick, in another embodiment, between about 5 nm and about 50 nm thick, in another embodiment, between about 5 nm and about 30 nm thick.

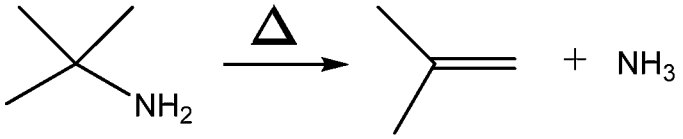
Methods described above employ hydrogen plasma to reduce carbon content in a SiN film. Other methods described herein take advantage of a thermal decomposable groups, attached either to a silicon-containing reactant or a nitrogen-containing reactant, in order to lower carbon content. One embodiment is a method of forming a silicon nitride material on a substrate, including: (a) providing the substrate in a reaction chamber; (b) providing a carrier gas flow through the reaction chamber; (c) exposing the substrate to a vapor phase flow of a nitrogen-containing reactant wherein the nitrogen-containing reactant is adsorbed onto the surface of the substrate and then purging the reaction chamber; (d) exposing the substrate to a vapor phase flow of a silicon-containing reactant wherein the silicon-containing reactant is adsorbed onto the surface of the substrate; (e) igniting a plasma in the reaction chamber after the vapor phase flow of the silicon-containing reactant has ceased; and (f) heating the substrate to between about 200°C and about 550°C; where at least one of the nitrogen-containing reactant and the

silicon-containing reactant bears one or more of a thermally removable group, wherein said thermally removable group decomposes at between about 200°C and about 550°C.

Figure 4 depicts an exemplary process flow, 400, outlining aspects of the method. A substrate is provided to the chamber, see 405. A carrier flow is established, see 410. The substrate is exposed to a nitrogen-containing reactant, see 415. The substrate is exposed to a silicon-containing reactant, see 420. A plasma is ignited after the flow of the silicon-containing reactant is ceased, see 425. This reaction forms SiN. One or more iterations of 410-425 are performed to build a layer of desired thickness. In this method, 415 and 420 are not necessarily done in the order presented. The nitrogen-containing reactant flow may or may not be continuous. The substrate may be heated during formation of the SiN layer, within, or below, the temperature range necessary to decompose the thermally removable groups, but at least at some point after the SiN film is formed, the substrate is heated to between about 200°C and about 550°C in order to break down the thermally removable groups, see 430. After the substrate is heated sufficient time to remove the desired amount of carbon, the process flow ends.

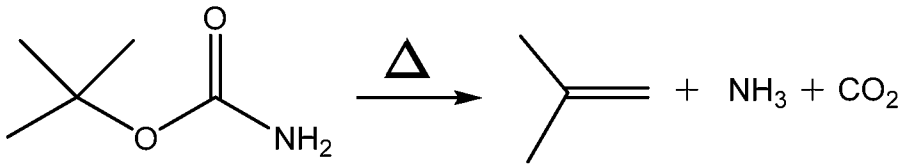
In one embodiment, the substrate is a semiconductor wafer. In one embodiment, the method further includes repeating (b) through (e) to form a conformal layer on the semiconductor wafer between about 1 nm and about 100 nm thick. In one embodiment, (f) is performed throughout (b) through (e). The silicon and nitrogen-containing reactants are as described herein, provided at least one of the silicon and the nitrogen-containing reactant includes at least one thermally removable group.

A thermally removable group is a group that breaks down into volatile components at between about 200°C and about 550°C. For example, secondary and particularly tertiary carbon groups can undergo elimination reactions in this temperature range. In a particular example, t-butyl groups break down to form isobutylene in this temperature range. For example, t-butylamine, when heated, undergoes an elimination reaction to form isobutylene and ammonia as depicted in Scheme 4. As another example, t-butoxycarbonyl groups (t-BOC) groups also thermally decompose, for example at about 150°C, to form isobutylene, carbon dioxide and the



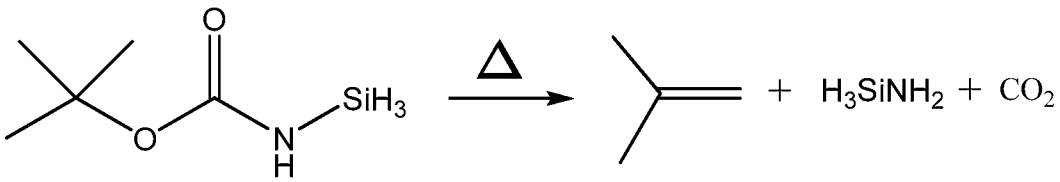
Scheme 4

radical to which the t-BOC group was attached. For example, as depicted in Scheme 5, t-butylcarbamate thermally decomposes to give isobutylene ammonia and carbon dioxide. The thermally removable group need not be on the nitrogen-containing reactant. For example, t-butylsilane,



Scheme 5

when heated, also undergoes an elimination reaction to form isobutylene and a silane. In another example, tert-butyl silylcarbamate thermally decomposes to form isobutylene, silanamine and carbon dioxide, as depicted in Scheme 6.

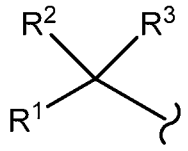


Scheme 6

Thus one or more thermally removable groups can be used on the silicon-containing reactant, the nitrogen-containing reactant, or both. Thus the semiconductor wafer is heated to between about 200°C and about 550°C so that such groups decompose and release their carbon content and thus reduce the carbon content of the SiN film. The reactants are adsorbed onto the substrate, a plasma is used to convert the reactants to a SiN material. Remaining carbon groups are removed by heating the substrate. The heating can be performed during the entire deposition or periodically to decompose the thermally removable groups. In one embodiment, the substrate is heated to between about 200°C and about 550°C, in another embodiment between about 350°C and about 550°C, in another embodiment between about 450°C and about 550°C, and in another embodiment, between about 450°C and about 500°C. In one embodiment, for example

where TBA is used, the SiN film is heated to between about 450°C and about 500°C, for between about 1 second and about 30 seconds, or between about 1 second and about 20 seconds, or between about 1 second and about 10 seconds. Although any particular thermally removable group will breakdown at a certain temperature threshold, a higher temperature may be used to increase the rate of decomposition and/or as an anneal to improve the properties of the SiN film.

As described above, the thermally removable group may include a secondary or tertiary carbon functionality, and either or both of the silicon-containing reactant and the nitrogen-containing reactant can include one or more of the same or different thermally removable groups. In one embodiment, the thermally removable group is according to Formula II:



II

wherein each of R^1, R^2 and R^3 is, independent of the others, H or C_{1-3} alkyl; or two of R^1, R^2 and R^3, together with the carbon atom to which they are attached form form a C_{3-7} cycloalkyl and the other of R^1, R^2 and R^3 is H or C_{1-3} alkyl; and where each of said thermally removable group, when part of the nitrogen-containing reactant, is attached to a nitrogen or an oxygen of the nitrogen-containing reactant, and, when part of the silicon-containing reactant, is attached to a silicon or a nitrogen or an oxygen of the silicon-containing reactant. In one embodiment, each of R^1, R^2 and R^3 is, independent of the others, C_{1-3} alkyl. In one embodiment, the thermally removable group is a t-butyl group.

One embodiment is a SiN film produced by a method described herein.

Apparatus

Another aspect of the invention is an apparatus configured to accomplish the methods described herein. A suitable apparatus includes hardware for accomplishing the process operations and a system controller having instructions for controlling process operations in accordance with the present invention.

It will be appreciated that any suitable process station may be employed with one or more of the embodiments described above. For example, FIG. 5 schematically shows

a CFD process station 1300. For simplicity, CFD process station 1300 is depicted as a standalone process station having a process chamber body 1302 for maintaining a low-pressure environment. However, it will be appreciated that a plurality of CFD process stations 1300 may be included in a common low-pressure process tool environment. While the embodiment depicted in FIG. 5 shows one process station, it will be appreciated that, in some embodiments, a plurality of process stations may be included in a processing tool. For example, FIG. 6 depicts an embodiment of a multi-station processing tool 2400. Further, it will be appreciated that, in some embodiments, one or more hardware parameters of CFD process station 1300, including those discussed in detail below, may be adjusted programmatically by one or more computer controllers.

A CFD process station 1300 fluidly communicates with reactant delivery system 1301 for delivering process gases to a distribution showerhead 1306. Reactant delivery system 1301 includes a mixing vessel 1304 for blending and/or conditioning process gases for delivery to showerhead 1306. One or more mixing vessel inlet valves 1320 may control introduction of process gases to mixing vessel 1304.

Some reactants, like BTBAS, may be stored in liquid form prior to vaporization at and subsequent delivery to the process station. For example, the apparatus of FIG. 5 includes a vaporization point 1303 for vaporizing liquid reactant to be supplied to mixing vessel 1304. In some embodiments, vaporization point 1303 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 sweeping and/or evacuating the delivery piping to remove residual reactant. However, sweeping the delivery piping may increase process station cycle time, degrading process station throughput. Thus, in some embodiments, delivery piping downstream of vaporization point 1303 is heat traced. In some examples, mixing vessel 1304 is also heat traced. In one non-limiting example, piping downstream of vaporization point 1303 has an increasing temperature profile extending from approximately 100°C to approximately 150°C at mixing vessel 1304.

In some embodiments, reactant liquid is 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 vaporizes reactant by

flashing the liquid from a higher pressure to a lower pressure. In another embodiment, a liquid injector atomizes the liquid into dispersed microdroplets that are subsequently vaporized in a heated delivery pipe. It will be appreciated that 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 1303. In one embodiment, a liquid injector is mounted directly to mixing vessel 1304. In another embodiment, a liquid injector is mounted directly to showerhead 1306.

In some embodiments, a liquid flow controller upstream of vaporization point 1303 is provided for controlling a mass flow of liquid for vaporization and delivery to process station 1300. In one example, the liquid flow controller (LFC) includes a thermal mass flow meter (MFM) located downstream of the LFC. A plunger valve of the LFC is 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 is dynamically switched between a feedback control mode and a direct control mode. In some embodiments, the LFC is dynamically switched from a feedback control mode to a direct control mode by disabling a sense tube of the LFC and the PID controller.

Showerhead 1306 distributes process gases toward substrate 1312. In the embodiment shown in FIG. 13, substrate 1312 is located beneath showerhead 1306, and is shown resting on a pedestal 1308. It will be appreciated that showerhead 1306 may have any suitable shape, and may have any suitable number and arrangement of ports for distributing processes gases to substrate 1312.

In some embodiments, a microvolume 1307 is located beneath showerhead 1306. Performing a CFD process in a microvolume rather than in the entire volume of a process station may reduce reactant exposure and sweep times, may reduce times for altering CFD process conditions (e.g., pressure, temperature, etc.), 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.

In some embodiments, pedestal 1308 may be raised or lowered to expose substrate 1312 to microvolume 1307 and/or to vary a volume of microvolume 1307. For example,

in a substrate transfer phase, pedestal 1308 is lowered to allow substrate 1312 to be loaded onto pedestal 1308. During a CFD process phase, pedestal 1308 is raised to position substrate 1312 within microvolume 1307. In some embodiments, microvolume 1307 completely encloses substrate 1312 as well as a portion of pedestal 1308 to create a region of high flow impedance during a CFD process.

Optionally, pedestal 1308 may be lowered and/or raised during portions the CFD process to modulate process pressure, reactant concentration, etc., within microvolume 1307. In one embodiment where process chamber body 1302 remains at a base pressure during the CFD process, lowering pedestal 1308 allows microvolume 1307 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.

In another embodiment, adjusting a height of pedestal 1308 allows a plasma density to be varied during plasma activation and/or treatment cycles included in the CFD process. At the conclusion of the CFD process phase, pedestal 1308 is lowered during another substrate transfer phase to allow removal of substrate 1312 from pedestal 1308.

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 1306 may be adjusted relative to pedestal 1308 to vary a volume of microvolume 1307. Further, it will be appreciated that a vertical position of pedestal 1308 and/or showerhead 1306 may be varied by any suitable mechanism. One of ordinary skill in the art would appreciate that such mechanism would include, for example, hydraulics, pneumatics, spring mechanisms, solenoids and the like. In some embodiments, pedestal 1308 may include a rotational mechanis, for example along an axis perpendicular to the surface of the substrate, for rotating an orientation of substrate 1312. 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.

Returning to the embodiment shown in FIG. 5, showerhead 1306 and pedestal 1308 electrically communicate with RF power supply 1314 and matching network 1316 for powering a plasma. In some embodiments, the plasma energy is 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 1314 and matching network 1316 may be operated at any suitable power to form a plasma having a desired composition of radical species. Examples of suitable powers include, but are not limited to, powers between 100W and 5000 W. Likewise, RF power supply 1314 may provide RF power of any suitable frequency. In some embodiments, RF power supply 1314 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 parameters 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 is monitored in-situ by one or more plasma monitors. In one embodiment, plasma power is monitored by one or more voltage, current sensors (e.g., VI probes). In another embodiment, plasma density and/or process gas concentration is measured by one or more optical emission spectroscopy sensors (OES). In some embodiments, one or more plasma parameters are 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 include, but are not limited to, infrared (IR) monitors, acoustic monitors, and pressure transducers.

In some embodiments, the plasma is controlled via input/output control (IOC) sequencing instructions. For example, the instructions for setting plasma conditions for a plasma process phase may be included in a corresponding plasma activation recipe phase of a CFD process recipe. In some embodiments, process recipe phases may be sequentially arranged, so that all instructions for a CFD process phase are executed concurrently with that process phase. It will be appreciated that some aspects of plasma generation may have well-characterized transient and/or stabilization times that may prolong a plasma process phase. Put another way, such time delays may be predictable.

Such time delays may include a time to strike the plasma and a time to stabilize the plasma at the indicted power setting.

In some embodiments, pedestal 1308 may be temperature controlled via heater 1310. Further, in some embodiments, pressure control for CFD process station 1300 may be provided by butterfly valve 1318. As shown in FIG. 5, butterfly valve 1318 throttles a vacuum provided by a downstream vacuum pump (not shown). However, in some embodiments, pressure control of process station 1300 may also be adjusted by varying a flow rate of one or more gases introduced to CFD process station 1300.

As described above, one or more process stations may be included in a multi-station processing tool. Figure 6 shows a schematic view of a multi-station processing tool, 2400, with an inbound load lock 2402 and an outbound load lock 2404, either or both of which may comprise a remote plasma source. A robot 2406, at atmospheric pressure, is configured to move wafers from a cassette loaded through a pod 2408 into inbound load lock 2402 via an atmospheric port 2410. A wafer is placed by the robot 2406 on a pedestal 2412 in the inbound load lock 2402, the atmospheric port 2410 is closed, and the load lock is pumped down. Where the inbound load lock 2402 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 2414. Further, the wafer also may be heated in the inbound load lock 2402 as well, for example, to remove moisture and adsorbed gases. Next, a chamber transport port 2416 to processing chamber 2414 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 FIG. 6 includes load locks, it will be appreciated that, in some embodiments, direct entry of a wafer into a process station may be provided.

The depicted processing chamber 2414 comprises four process stations, numbered from 1 to 4 in the embodiment shown in FIG. 6. Each station has a heated pedestal (shown at 2418 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 a CFD and PECVD process mode. Additionally or alternatively, in some embodiments, processing chamber 2414 may include one or more matched pairs of CFD and PECVD process stations. While the depicted processing chamber 2414 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.

Figure 6 also depicts a wafer handling system 2490 for transferring wafers within processing chamber 2414. In some embodiments, wafer handling system 2490 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 6 also depicts a system controller 2450 employed to control process conditions and hardware states of process tool 2400. System controller 2450 may include one or more memory devices 2456, one or more mass storage devices 2454, and one or more processors 2452. Processor 2452 may include a CPU or computer, analog and/or digital input/output connections, stepper motor controller boards, etc.

In some embodiments, system controller 2450 controls all of the activities of process tool 2400. System controller 2450 executes system control software 2458 stored in mass storage device 2454, loaded into memory device 2456, and executed on processor 2452. System control software 2458 may include instructions for controlling the timing, mixture of gases, 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 2400. System control software 2458 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 necessary to carry out various process tool processes. System control software 2458 may be coded in any suitable computer readable programming language.

In some embodiments, system control software 2458 may include input/output control (IOC) sequencing instructions for controlling the various parameters described above. For example, each phase of a CFD process may include one or more instructions for execution by system controller 2450. The instructions for setting process conditions for a CFD process phase may be included in a corresponding CFD recipe phase. In some embodiments, the CFD recipe phases may be sequentially arranged, so that all instructions for a CFD process phase are executed concurrently with that process phase.

Other computer software and/or programs stored on mass storage device 2454 and/or memory device 2456 associated with system controller 2450 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.

A substrate positioning program may include program code for process tool components that are used to load the substrate onto pedestal 2418 and to control the spacing between the substrate and other parts of process tool 2400.

A process gas control program may include code for controlling gas composition 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. 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.

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.

A plasma control program may include code for setting RF power levels applied to the process electrodes in one or more process stations.

In some embodiments, there may be a user interface associated with system controller 2450. 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.

In some embodiments, parameters adjusted by system controller 2450 may relate to process conditions. Non-limiting examples include process gas composition and flow rates, temperature, pressure, plasma conditions (such as RF bias power levels), pressure, temperature, etc. These parameters may be provided to the user in the form of a recipe, which may be entered utilizing the user interface.

Signals for monitoring the process may be provided by analog and/or digital input connections of system controller 2450 from various process tool sensors. The signals for controlling the process may be output on the analog and digital output connections of process tool 2400. 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.

System controller 2450 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 parameters to operate in-situ deposition of film stacks according to various embodiments described herein.

The system controller 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 the present invention. Machine-readable media containing instructions for controlling process operations in accordance with the present invention may be coupled to the system controller.

Patterning Method/Apparatus:

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 comprises some or all of the following steps, each step 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. In one embodiment, a SiN film is formed using a method as described herein. The SiN film is used, for example, for one of the purposes described herein. Further, the method includes one or more steps (1)-(6) described above.

Examples

The invention is further understood by reference to the following examples, which are intended to be purely exemplary. The present invention is not limited in scope by the exemplified embodiments, which are intended as illustrations of single aspects of the invention only. Any methods that are functionally equivalent are within the scope of the invention. Various modifications of the invention in addition to those described herein will become apparent to those skilled in the art from the foregoing description and accompanying figures. Moreover, such modifications fall within the scope of the appended claims.

Example 1

Table 1 includes a number of reaction partners, and temperature and pressure parameters that may be used to make SiN films in accordance with the embodiments described herein.

Table 1

Reactant A	Reactant B	Reactant C	Temp(°C)	Press. (torr)	Ref. index
BTBAS	NH_3	-	50-550	1-4	1.80-2.05
BTBAS	-	N_2/H_2	50-550	1-4	1.80-2.05
BTBAS	NH_3	N_2/H_2	50-550	1-4	1.80-2.05
SiH_3Cl	NH_3	Optionally N_2/H_2	50-550	1-4	
SiH_3Cl	TBA	Optionally N_2/H_2			
SiH_2Cl_2	NH_3	Optionally N_2/H_2	50-550	1-4	1.80-2.05
SiH_2Cl_2	TBA	Optionally N_2/H_2			
$SiH(CH_3)$-$(N(CH_3)_2)_2$	NH_3	Optionally N_2/H_2	50-550	1-4	1.80-2.05
$SiH(CH_3)(Cl_2)$	NH_3	Optionally N_2/H_2	50-550	1-4	1.80-2.05
$SiHCl$-$(N(CH_3)_2)_2$	NH_3	Optionally N_2/H_2	50-550	1-4	1.80-2.05
$(Si(CH_3)_2NH)_3$	NH_3	Optionally N_2/H_2	50-550	1-4	1.80-2.05

Example 2

A 300 mm wafer is placed into vacuum chamber and the chamber evacuated to 0.5 torr. The wafer is supported within the chamber on an aluminum pedestal which is heated throughout the procedure. For example, the pedestal is heated at a constant temperature that is between about 50°C and about 550°C. The pressure in the chamber is increased to 2 torr using an inert gas such as argon or nitrogen. Dichlorosilane (DCS) is introduced into the reactor as a vapor phase flow at between about 1 slm and about 5 slm (standard liters per minute) for between about 1 second and about 30 seconds in order to adsorb DCS onto the surface of the wafer. After the DCS flow is ceased, the inert gas flow in the reactor purges the remaining vapor phase DCS and any byproducts. Then, a t-butylamine (TBA) vapor phase flow is established in the reactor at between about 1 slm and about 5 slm for between about 1 second and about 30 seconds. A plasma, for example 13.56 MHz at 2.5kW power, is ignited above the wafer for between about 1 second and about 15 seconds. The inert gas flow in the reactor purges the remaining vapor phase TBA and any byproducts. The DCS flow, inert gas purge, TBA flow, plasma and inert gas purge are repeated to deposit a SiN film of desired thickness. Each cycle as described deposits between about 0.5 Å and about 1.5 Å of a SiN film.

Alternatively, in a CFD run, the TBA flow is run continuously. In these runs, the same conditions as described above are used, except the TBA flow is established first and maintained. The DCS flow is introduced into the reactor at the same rate and time as described above, followed by an inert gas purge as described above. The plasma is ignited as described above, followed by an inert gas purge as described above. The DCS flow, inert gas purge, plasma ignition and inert gas purge are repeated to deposit a SiN film of desired thickness. Each cycle as described deposits between about 0.5 Å and about 1.5 Å of a SiN film.

The SiN films produced have the following characteristics:

- Non-Uniformity 3% - 5% (max-min/average)
- Non-uniformity <1% (1s)
- Refractive Index 1.8-1.9
- Film stress: +20MPa to -180 MPa
- Dielectric constant: 5.5-6.5
- Wet etch ratio 0.1-1.0 (to thermal oxide)

Although the foregoing has 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 described. Accordingly, the described embodiments are to be considered as illustrative and not restrictive.

WHAT IS CLAIMED IS:

1. A method of forming a silicon nitride material on a substrate, comprising:

(a) providing the substrate in a reaction chamber;

(b) continuously exposing the substrate to a vapor phase flow of a nitrogen-containing reactant wherein the nitrogen-containing reactant is adsorbed onto the surface of the substrate;

(c) periodically exposing the substrate to a vapor phase flow of a silicon-containing reactant wherein the silicon-containing reactant is adsorbed onto the surface of the substrate; and

(d) periodically igniting a plasma in the reaction chamber when the vapor phase flow of the silicon-containing reactant has ceased.

2. The method of claim 1, further comprising continuously flowing a carrier gas through the reaction chamber.

3. The method of claim 1 or 2, further comprising purging to remove unabsorbed silicon-containing reactant after (c) but before (d).

4. The method of claim 1, wherein the substrate is a semiconductor wafer.

5. The method of claim 4, further comprising repeating (b) through (d) to form a conformal layer on the semiconductor wafer between about 1 nm and about 100 nm thick.

6. The method of claim 1, wherein the silicon-containing reactant is selected from the group consisting of a silane, a halosilane and an aminosilane, and mixtures thereof.

7. The method of claim 1, wherein the nitrogen-containing reactant is selected from the group consisting of ammonia, a hydrazine, an amine and mixtures thereof.

8. The method of claim 7, wherein the nitrogen-containing reactant comprises a C_{1-10} alkyl amine.

9. The method of claim 8, wherein the C_{1-10} alkyl amine is tert-butyl amine.

10. The method of claim 8, wherein the silicon-containing reactant is a monochlorosilane or a dichlorosilane.

11. The method of claim 4, wherein the semi-conductor wafer is heated to between about 50°C and about 550°C.

12. A method of forming a silicon nitride material on a substrate, comprising:

(a) forming a silicon nitride film on the substrate, said formation comprising:

(i) providing the substrate in a reaction chamber;

(ii) exposing the substrate to a silicon-containing reactant in the vapor phase so that the silicon-containing reactant is adsorbed onto the surface of the substrate;

(iii) exposing the substrate to a nitrogen-containing reactant in the vapor phase so that the nitrogen-containing reactant is adsorbed onto the surface of the substrate;

(iv) igniting a plasma while the nitrogen-containing reactant is present in the vapor phase;

and then,

(b) exposing the silicon nitride film to a hydrogen containing plasma to remove at least some carbon content of the silicon nitride film.

13. The method of claim 12, wherein the substrate is a semiconductor wafer.

14. The method of claim 12, wherein (ii) is performed prior to (iii).

15. The method of claim 12, wherein (iii) is performed prior to (ii).

16. The method of claim 13, wherein (a) is repeated two or more times prior to (b).

17. The method of claim 13, further comprising repeating (a) and (b) to form a conformal layer on the semiconductor wafer between about 1 nm and about 100 nm thick.

18. The method of claim 12, wherein the silicon-containing reactant is selected from the group consisting of a silane, a halosilane and an aminosilane, and mixtures thereof.

19. The method of claim 12, wherein the nitrogen-containing reactant comprises a C_{1-10} alkyl amine.

20. The method of claim 18, wherein the silicon-containing reactant is a chlorosilane.

21. The method of claim 12, further comprising continuously flowing a carrier gas through the reaction chamber after (i).

22. The method of claim 13, wherein the semi-conductor wafer is heated to between about 50°C and about 550°C.

23. A method of forming a silicon nitride material on a substrate, comprising:

(a) providing the substrate in a reaction chamber;

(b) providing a carrier gas flow through the reaction chamber;

(c) exposing the substrate to a vapor phase flow of a nitrogen-containing reactant wherein the nitrogen-containing reactant is adsorbed onto the surface of the substrate and then purging the reaction chamber;

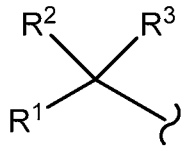
(d) exposing the substrate to a vapor phase flow of a silicon-containing reactant wherein the silicon-containing reactant is adsorbed onto the surface of the substrate;

(e) igniting a plasma in the reaction chamber after the vapor phase flow of the silicon-containing reactant has ceased; and

(f) heating the substrate to between about 200°C and about 550°C;

wherein at least one of the nitrogen-containing reactant and the silicon-containing reactant bears one or more of a thermally removable group, wherein said thermally removable group decomposes at between about 200°C and about 550°C.

24. The method of claim 23, wherein the thermally removable group is according to Formula II:



II

wherein each of R^1, R^2 and R^3 is, independent of the others, H or C_{1-3} alkyl; or two of R^1, R^2 and R^3, together with the carbon atom to which they are attached form form a C_{3-7} cycloalkyl and the other of R^1, R^2 and R^3 is H or C_{1-3} alkyl; and wherein each of said thermally removable group, when part of the nitrogen-containing reactant, is attached to a nitrogen or an oxygen of the nitrogen-containing reactant, and, when part of the silicon-containing reactant, is attached to a silicon or a nitrogen or an oxygen of the silicon-containing reactant.

25. The method of claim 23, wherein the substrate is a semiconductor wafer.

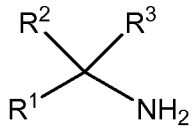
26. The method of claim 25, further comprising repeating (b) through (e) to form a conformal layer on the semiconductor wafer between about 1 nm and about 100 nm thick.

27. The method of claim 23, wherein (f) is performed throughout (b) through (e).

28. The method of claim 23, wherein the silicon-containing reactant is selected from the group consisting of a silane, a halosilane and an aminosilane, and mixtures thereof.

29. The method of claim 23, wherein the nitrogen-containing reactant is selected from the group consisting of ammonia, a hydrazine, an amine and mixtures thereof.

30. The method of claim 29, wherein the nitrogen-containing reactant is a C_{1-10} alkyl amine according to formula I:



I

wherein each of R^1, R^2 and R^3 is, independent of the others, H or C_{1-3} alkyl; or two of R^1, R^2 and R^3, together with the carbon atom to which they are attached form form a C_{3-7} cycloalkyl and the other of R^1, R^2 and R^3 is H or C_{1-3} alkyl.

31. The method of claim 30, wherein the C_{1-10} alkyl amine is selected from the group consisting of isopropylamine, cyclopropylamine, sec-butylamine, tert-butyl amine, cyclobutylamine, isoamylamine, 2-methylbutan-2-amine and thexylamine.

32. The method of claim 31, wherein the C_{1-10} alkyl amine is tert-butyl amine.

33. The method of claim 29, wherein the silicon-containing reactant is a chlorosilane.

34. The method of claim 32, wherein the semi-conductor wafer is heated to between about 450°C and about 500°C.

35. An apparatus for depositing a silicon nitride film on a semiconductor wafer, the apparatus comprising:

(a) a reaction chamber;

(b) a source of activation energy to form the silicon nitride film;

(c) a reactant inlet; and

(d) a controller comprising instructions for:

continuously flowing a nitrogen-containing reactant into the reaction chamber during a deposition cycle;

periodically flowing a silicon-containing reactant into the reaction chamber during the deposition cycle;

periodically igniting a plasma in the reaction chamber when the flow of the silicon-containing reactant has ceased.

36. The apparatus of claim 35, wherein the source of activation energy is a plasma generator.

37. The apparatus of claim 35, further including a vacuum port.

38. The apparatus of claim 36, wherein the plasma generator comprises induction coils and/or a microwave source.

39. An apparatus for depositing a silicon nitride film on a semiconductor wafer, the apparatus comprising:

(a) a reaction chamber;

(b) a source of activation energy to form the silicon nitride film;

(c) a reactant inlet; and

(d) a controller comprising instructions for:

flowing a nitrogen-containing reactant into the reaction chamber during a deposition cycle;

flowing a silicon-containing reactant into the reaction chamber during the deposition cycle;

periodically igniting a plasma in the reaction chamber when the flow of the silicon-containing reactant has ceased and while the nitrogen-containing reactant is present in the vapor phase in the reaction chamber.

40. The apparatus of claim 39, wherein the source of activation energy is a plasma generator.

41. The apparatus of claim 39, further including a vacuum port.

42. The apparatus of claim 40, wherein the plasma generator comprises induction coils and/or a microwave source.