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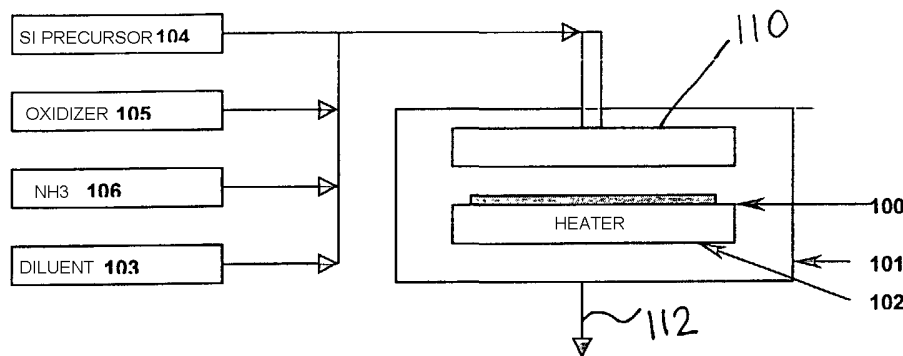
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(54) Title: LOW TEMPERATURE DIELECTRIC DEPOSITION USING AMINOSILANE AND OZONE



(57) Abstract: This invention describes a method of depositing dielectric layers or films with good step coverage and ability to fill high-aspect ratio device structures at low temperature (20 - 400 C) by CVD processes through the use of aminosilane or silicon alkylamide compounds as the silicon precursor with an oxidizer that includes ozone. The present invention further provides a method of depositing silicon oxynitride (SiO_xN_y) films at low temperatures using aminosilane or silicon alkylamide compounds as a silicon precursor, with an oxidizer that includes ozone, and ammonia (NH₃).

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LOW TEMPERATURE DIELECTRIC DEPOSITION USING AMINOSILANE AND OZONE

Cross-Reference To Related Applications

This application is related to, and claims priority to, United States Provisional Patent Application No. 60/396,746, entitled Low Temperature Dielectric Deposition Using Aminosilane and Ozone, filed July 19, 2002, the entire disclosure of which is
5 hereby incorporated by reference.

Field of the Invention

The present invention relates generally to the field of semiconductors. More specifically, the present invention relates to chemical vapor deposition on
10 semiconductor devices and wafers.

BACKGROUND OF THE INVENTION

In the fabrication of semiconductor devices, low pressure thermal chemical vapor deposition (CVD) produces premetal dielectric films with good step coverage
15 characteristics and acceptable gapfill aspect ratio. Some precursors, such as bis(tertiary-butylamino)silane (BTBAS) and Et_2SiH_2 , produce SiO_2 when reacted with O_2 at a temperature of about 400°C by chemical vapor deposition (CVD). Integrated circuits of future generation, however, require lower temperature processes for premetal dielectric (PMD) and spacer applications. One alternative to lowering the process temperature is to
20 use a high-density plasma (HDP) chemical vapor deposition (HDPCVD) process. By this HDPCVD process, phosphorous-doped glass (PSG) or non-doped silicate glass (NSG) are deposited at a temperature range of $300\text{-}550^\circ\text{C}$. However, HDP chemical vapor deposition has drawbacks that limit its usefulness. The HDPCVD process limits gapfill capability to approximately 3:1 aspect ratio, while a higher temperature thermal CVD process achieves a

more desirable gapfill of 6:1 or higher aspect ratios. Thus, the industry is in need of a method of performing chemical vapor deposition on premetal dielectrics at lower temperatures while simultaneously maintaining good step coverage.

5

SUMMARY OF THE INVENTION

The present invention provides a method of depositing SiO₂ and other oxides onto a silicon substrate at a low temperature of about 400°C and below while maintaining good step coverage and gapfill capability.

This method of the present invention can be utilized for both doped and undoped SiO₂ deposition. Typical applications of this process in IC fabrication are, but not limited to, premetal dielectrics (PMD), shallow trench isolation (STI), trench liner, and spacer dielectrics.

The deposition process of the present invention can also be performed with silicon oxynitride using a mixture of O₃ and NH₃ as the reactant gases. Additional aspects of the invention include using substrates other than silicon such as SiC, SOI, flat panels, tungsten or aluminum.

In one aspect of the present invention a method of depositing a dielectric layer on the surface of a substrate in a process chamber is provided, comprising exposing the substrate to reactive gases comprised of an oxidant gas and a silicon precursor and where the oxidant gas includes ozone, and the silicon precursor includes at least one of silicon alkylamide and aminosilane. The method is carried out at a temperature in the range of approximately 20°C to 400°C.

In another aspect of the present invention a method of depositing a silicon oxynitride layer on a substrate in a chamber is provided, comprising exposing the substrate to reactant gases comprised of an oxidant gas, ammonia and a silicon precursor where the oxidant includes ozone and the silicon precursor includes at least one of silicon alkylamide and aminosilane and the method is carried out at a temperature in the range of approximately 20°C to 400°C.

30

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention is further described in the detailed description and with reference to the figures, in which:

FIG. 1 illustrates a CVD apparatus suitable for performing process of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

5 The present invention provides a novel low thermal budget method that deposits dielectric layers or films on semiconductor substrates at temperatures equal to and below approximately 400°C by chemical vapor deposition (CVD). In one embodiment of the present invention, the CVD reaction is summarized by the following equation:



10 where the silicon precursor is $\text{Si}(\text{NR}^1\text{R}^2)_4$ and R^1 or $\text{R}^2 = \text{H}$, $\text{C}_1\text{-C}_6$ alkyl, cyclic alkyls, F substituted alkyls,

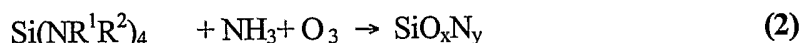
or $\text{Si}(\text{NR}^1\text{R}^2)_{4-x}\text{L}_x$ ($X=1, 2, \text{ or } 3$), where $\text{L} = \text{H}$ or Cl

In equation (1), the Si-N bond in aminosilane and silicon alkylamide
 15 compounds (referred to as silicon precursors) is labile and reacts with an oxidant gas at a lower temperature than will other Si-containing precursors. The preferred silicon precursors from these classes of compounds have smaller R groups, such as methylethylamide. The reaction is carried out in a reactor or chamber in which a substrate is present. In conjunction with the use of ozone as a component of the
 20 oxidant gas, the SiO_2 CVD process temperature can be reduced to below 400°C while maintaining a good step coverage characteristic and gapfill capability of a low pressure thermal CVD process. Ozone gas provides atomic oxygen at lower temperature than can be achieved with other oxidizers such as water or O_2 . Oxidation of the silicon precursor in this reaction gives good results at temperatures
 25 of about 200°C or lower, with a temperature range of 20°C to 300°C being the preferred range. Process gas flow rates are in the range of about 1 sccm to 1000 sccm for the precursor gas flow, preferably in the range of about 10 to 500 sccm. Oxidizer gas flow rates are in the range of about 10 to 2000 sccm, preferably in the range of about 100-2000 sccm.

30 Diluent gas flow may also be used in some cases to improve uniformity but is not required. Inert gases such as nitrogen, helium, neon, argon, xenon and combinations thereof can be used as the diluent gas. Nitrogen and argon are

preferred diluent gases for cost reasons. Diluent gas flow rates are in the range of about 1 sccm to 1000 sccm. In all cases the gas flow rates depend on the size of the chamber and pumping capability, as the pressure must be within the required range, and such variables can be determined by those of ordinary skill in the art with
 5 routine experimentation.

In another aspect of the present invention, the formation of silicon oxynitride is provided. A substrate placed in a chamber is exposed to the following reactants and the CVD reaction is summarized by the following equation:



10 where the silicon precursor is $\text{Si}(\text{NR}^1\text{R}^2)_4$ and R^1 or $\text{R}^2 = \text{H}$, $\text{C}_1\text{-C}_6$ alkyl, cyclic alkyls, F substituted alkyls

or $\text{Si}(\text{NR}^1\text{R}^2)_{4-x}\text{L}_x$ ($X=1, 2, \text{ or } 3$) where $\text{L} = \text{H}$ or Cl

In equation (2), silicon oxynitride (SiO_xN_y) is deposited at a low temperature using a mixture of NH_3 and O_3 gases. In addition to semiconductor applications, SiO_xN_y is an
 15 important material for optical application due to the variable refractive index between 1.45 for SiO_2 and 2.0 for silicon nitride. As in the reaction of equation (1), the Si-N bond in aminosilane or silicon alkylamide compounds is quite labile and reacts with the ozone at a low temperature allowing for a low temperature CVD method that occurs below 400°C . In this aspect of the present invention, the gas flow rate of ammonia
 20 (NH_3) is in the range of about 10 sccm to 2000 sccm, and preferably in the range of about 100 to 2000 sccm. This novel method can be utilized for both doped and undoped SiO_2 formation. Applications of this method in IC fabrication include, but not limited to, premetal dielectrics (PMD), shallow trench isolation (STI), trench liner, and spacer dielectrics.

25 In another aspect of the invention, the pressure is varied to optimize the process for different applications. Referring to equations (1) and (2), the reactions can be performed at atmospheric pressure with good results, or the reactions can be performed at a pressure in the range of about 1 milli Torr up to about 800 Torr. For example, the reaction can be performed at decreased pressure for an increased improvement in step
 30 coverage on non-planar substrates. Alternatively, a higher pressure can be used in PMD applications with less stringent step coverage requirements. Generally, the higher the pressure, the faster the rate of reaction and resulting deposition rate.

The substrate used in the present invention is typically silicon. However, alternate substrates such as SiC, SOI, flat panels, tungsten or aluminum may be used instead of silicon and are within the scope and spirit of the invention. The choice of substrate is dependent on the specific application.

5 The present invention may be carried out in known deposition systems such as commonly used CVD, PECVD, spray pyrolysis, arc jet deposition, or ALD systems. Referring to **FIG. 1**, a simplified cross sectional view of a CVD system **10** suitable for carrying out the method of the present invention is shown. A silicon wafer **100** is loaded into the deposition chamber **101** and supported by a wafer support or chuck **102**.
10 The process may be conducted at low or near atmospheric pressure. In the process chamber **101** the wafer **100** is heated to deposition temperature by a heater preferably located within the support **102**. For a CVD process, the process pressure is established by introducing a diluent gas **103** into the chamber **101** via an injector **110**. Then, the silicon precursor **104** and the oxidizer **105** (and also NH_3 **106** if SiO_xN_y is to be
15 deposited) gases are introduced into the chamber using conventional gas delivery methods used in the semiconductor and thin films industries. The reactant gases are conveyed proximate the wafer. The reactant gases mix and react to form a desired layer of material on the surface of the wafer. After an appropriate time required to achieve the target film thickness, the silicon precursor and oxidizer/ NH_3 gas flows are
20 turned off, and preferably diluent inert gas flow is conveyed to the chamber to purge the chamber of remaining reactants through exhaust **112**. After an appropriate purge time, the process is complete and the wafer is removed from of the process chamber.

Although the illustrative embodiment of the present invention is CVD deposition, the reactions and methods described herein are also beneficial for
25 depositing dielectric films by other deposition techniques, including Plasma Enhanced CVD (PECVD), spray pyrolysis, arc jet or cathodic arc spray deposition, and spin-on glass (wet chemical) deposition. This invention can also be applied to atomic layer deposition (ALD), where the reactants may be conveyed independently.

Having thus described the invention with the details and particularity required
30 by the patent laws, what is claimed and desired protected by Letters Patent is set forth in the appended claims.

What is claimed is:

1. A method of depositing a dielectric layer on a substrate in a chamber comprising:
 exposing the substrate to the reactant gases comprised of an oxidant gas and a silicon precursor,
 wherein the oxidant gas includes ozone and the silicon precursor includes at least one of silicon alkylamide and aminosilane, and wherein the chamber is at a temperature in the range of approximately 20°C to 400°C when the set of reactant gases are present in the chamber.
2. The method of claim 1 where the pressure in the chamber is in the range from 1 milliTorr to 760 Torr when the set of reactant gasses are present in the chamber.
3. The method on claim 1 where the substrate is exposed to the set of reactant gasses by flowing the reactant gas over the substrate in the chamber.
4. The method of claim 3 where the flow for the silicon precursor gas is from 1 sccm to 1000 sccm and the flow for the ozone gas flows from 10 to 2000 sccm.
5. The method of claim 4 further comprising flowing a diluent gas in conjunction with the reactant gas.
6. The method of claim 1 wherein said reactant gases further includes ammonia.
7. A method of depositing silicon oxynitride on a substrate in a chamber comprising:
 exposing the substrate to the reactant gases comprised of an oxidant gas, ammonia, and a silicon precursor,
 wherein the oxidant gas includes ozone and the silicon precursor includes at least one of silicon alkylamide and aminosilane, and wherein the chamber is at a temperature in the range of approximately 20°C to 400°C when the set of reactant gases are present in the chamber.
8. The method of claim 7 where the pressure in the chamber is in the range from 1 milliTorr to 760 Torr when the set of reactant gasses are present in the chamber.

9. The method of claim 8 where the substrate is exposed to the set of reactant gasses by flowing the reactant gas over the substrate in the chamber.
10. The method of claim 9 where the flow for the silicon precursor gas is from 1 sccm to 1000 sccm and the flow for the ozone gas flows from 10 to 2000 sccm.
11. The method of claim 10 further comprising flowing a diluent gas in conjunction with the reactant gas.
12. The method of claim 11 wherein the diluent gas is an inert gas.
13. The method of claim 12 wherein the inert gas is argon or nitrogen.
14. A method of depositing silicon oxides on a substrate in a chamber comprising:
reacting ozone and a silicon precursor in the presence of the substrate in the chamber, wherein the chamber is at a temperature under 400°C and the silicon precursor comprises at least one of silicon alkylamide and aminosilane, and the oxidant gas comprises ozone.
15. The method of claim 14 further comprises reacting ammonia with the oxidant gas and silicon precursor.
16. The method of claim 14 further comprising flowing a diluent gas through the chamber during the step of reacting an oxidant gas and a silicon precursor in the presence of the substrate in the chamber.
17. The method of claim 14 wherein the temperature is in the range of 20 to 400°C.

FIG. 1.

