METHOD OF FORMING DIELECTRIC FILMS WITH REDUCED METAL CONTAMINATION

Related Applications

This is a continuation-in-part of U.S. Patent Application Serial No. 08/573,318, filed December 15, 1995.

Brief Summary of the Invention

This invention relates generally to the formation of films on semiconductor and integrated circuit substrates, and more particularly to a method of forming dielectric layers having reduced metal contamination by chemical vapor deposition (CVD).

Background of the Invention

In the manufacture of semiconductors and integrated circuits, various layers of materials are deposited in formation of such devices. Dielectric layers are generally used to electrically isolate conductive layers and enable useful interconnects between such layers.

Dielectric layers are often formed by chemical vapor deposition (CVD). The CVD process deposits a material on a surface by transport and reaction of certain gaseous precursors on the surface. CVD reactors come in many forms. Low pressure CVD systems (LPCVD) and atmospheric pressure CVD systems (APCVD) operate on thermal CVD principles. Plasma may be employed to assist decomposition of chemicals for reaction in plasma enhanced CVD systems (PECVD).

Since CVD deposits the components of the precursor chemicals, it is important for the precursors to be of high purity and substantially free of contaminants because such contaminants may react and become deposited in the resultant film. Contaminants in the film damage the function of the devices on the wafer and reduce the device yields.

Of particular concern are metal contaminants found in oxide layers, which is a problem in the semiconductor industry. CVD systems are comprised of a variety of metal components and the potential source of metal contamination has proven difficult to locate and eliminate. One widely used CVD process employs tetraethylorthosilicate (TEOS) and ozone to react and deposit a silicon oxide film. To generate the ozone

precursor, conventional CVD systems in the semiconductor industry use a plasma discharge cell, through which high purity oxygen and small amounts of nitrogen (typically 1%-5% by weight) are flowed. When power is applied to the discharge cell, the plasma accelerates the reaction with the oxygen and nitrogen to form ozone (O_3), generally in a mixture of up to 5.5 weight % O_3 in oxygen (O_2). The nitrogen acts as a catalyst to the reaction, aiding in the generation of ozone at high concentrations with a concentration stability in the range of approximately +/- 1.4%.

The inventors have discovered, after much study and investigation, that a serious source of metal contamination is derived from nitric acid formed in the ozone system during ozone generation. Moisture is the main contaminant in the system. Nitrogen and moisture in the ozone system generate nitric acid when subjected to oxygen and the plasma discharge. The nitric acid affects the CVD system in a variety of ways. One occurrence is that nitric acid collects in small orifices with low flow rates, such as mass flow controller (MFC) sensor tubes used in the CVD system. This causes clogging of the MFC sensor tubes, and ultimately leads to failure of gas flow control.

Of significant further detriment, the nitric acid has been found to attack the metal conduits and components of the CVD system. In particular, nitric acid attacks surface hydroxide layers of the stainless steel conduits which causes the release of metal contaminants such as volatile chromium oxides into the gas stream. The contaminant is delivered, along with the ozone, to the semiconductor substrate where it deposits as a contaminant in the film.

Thus, it is desirable to provide a method which reduces the generation of such contaminants in the ozone delivered through out the CVD system and results in deposition of films with low metal contamination and desirable film quality.

Objects and Summary of the Invention

It is an object of this invention to provide an improved method for formation of dielectric layers.

More particularly, it is an object of this invention to provide a method for reducing metal contamination in dielectric layers deposited by chemical vapor deposition.

Moreover, it is an object of the present invention to provide a method adapted for minimizing the formation of metal contamination in an ozone gas stream.

A further object of this invention is to provide a method of delivering ozone from an ozonator through a system containing metal conduits wherein the ozone is substantially free of corrosive contaminants.

These and other objects are achieved by the method herein disclosed comprising the steps of delivering gases containing ozone through metal conduits from an ozonator into which oxygen and dilution gases are introduced. The dilution gases do not contain nitrogen, and corrosive vapors which would corrode the conduits are not substantially formed, and the gases provided are substantially free of metal contamination.

An alternative embodiment of the invention provides for a method of depositing oxide layers having reduced metal atom concentration on the surface of a substrate in a chemical vapor deposition (CVD) system. The CVD system includes an ozone system and a CVD reactor Oxygen gas and a dilution gas, excluding nitrogen, are introduced into the ozone system where a gas stream including ozone is produced. The gas stream is delivered through metal conduits to the CVD reactor. The gas stream is substantially free from corrosive elements and as the gas stream flows throughout the system the gas does not substantially react with the metal conduits, thereby generally eliminating metal atom contamination in the gas stream. The gas stream and a reactive gas are separately conveyed through an injector whereby they exit the injector and enter the CVD reactor, wherein said gases interact and deposit a layer of material substantially free of metal contamination on the surface of a wafer positioned proximate to said injector.

Brief Description of the Drawings

Other objects and advantages of the invention become apparent upon reading of the detailed description of the invention provided below and upon reference to the drawings in which:

FIG. 1 is a schematic view, partially in cross-section, of a chemical vapor deposition (CVD) system apparatus which may be employed to practice the method of the invention.

FIG. 2 is a schematic of an ozonator apparatus suitable for delivering a gas stream in accordance with one embodiment of the invention.

FIG. 3 is a table illustrating metal contamination levels achieved according to one embodiment of the method of the invention set forth in Example 1.

FIG. 4 is a table showing resultant metal contamination levels according to an alternative embodiment of the invention set forth in Example 3.

FIGs. 5A and 5B are a photographs made by Scanning Electron Microscope (SEM) of a cross-section of a dielectric layer showing the gap fill and step coverage achieved according to the method of the invention.

FIG. 6 is a graph showing a SIMS plot of Cr content in a film deposited in accordance with the invention.

Detailed Description of the Invention

Turning to the drawings, wherein like components are designated by like reference numerals, FIGs. 1 and 2 are schematical representations of apparatus that can be employed to deliver a gas stream containing low metal contamination according to the method of the present invention. FIG. 1 depicts a chemical vapor deposition (CVD) system 10 which can be used with the inventive method The system 10 generally includes an ozone generator 15 which generates a gas stream containing ozone and other gaseous chemicals. The gas stream is delivered via metal conduits 16 and mass flow controller 17 to a CVD reactor 20. CVD reactor 20 is shown as a conveyorized atmospheric pressure CVD (APCVD) type reactor, which is more fully described in U.S. Patent No. 4,834,020, and which is incorporated by reference herein. It is important to note that although an APCVD reactor is shown, the inventive method may be practiced using other types of CVD reactors such as low pressure CVD (LPCVD) and plasma enhanced CVD (PECVD) reactors. APCVD reactor 20 shown in FIG. 1 typically includes a muffle 31, a plurality of injectors 30 defining multiple stages (for simplicity only one injector 30, and thus one stage is shown) and a conveyor belt 34. Typically the reactor 20 comprises four stages, each of which are substantially identical. Within the muffle 31, a plurality of curtains 32 are placed around both sides of the injector 30 to isolate an area, and therebetween forming a deposition chamber area 33. The curtains 32 include a plurality of inert gas plenums 36 which causes inert gases to flow downwardly and along the belt 34, thereby aiding to isolate the deposition chamber area 33.

To deposit a layer of material on the surface of a semiconductor device, a substrate 35 is placed on the conveyor belt 34 and is delivered into the muffle 31 and through the deposition chamber area 33. In the deposition chamber area 33, gaseous chemicals are conveyed by the injector 30 to the area proximate the surface of the

substrate 35, wherein the gaseous chemicals react and deposit a layer of material on the surface of the substrate 35.

The gaseous chemicals are delivered to the reactor 20 via gas delivery system 39, wherein said gaseous chemicals are individually conveyed to the injector 30 through gas delivery lines 16, 26 and 27. In an exemplary embodiment, the gases conveyed though gas delivery lines 16, 26 and 27 are: ozone/oxygen mixture, TEOS, and a nitrogen/ oxygen mixture (separator N_2), respectively. In this embodiment, the TEOS and ozone gases react to form a layer of silicon dioxide (SiO_2) on the surface of the substrate 35. As the gases react in the deposition chamber area 33, byproducts and unreacted chemicals are generally removed through exhaust lines 37 as shown by the general direction of the arrows.

In order to deposit layers of a desired composition and purity on the surface of the substrate 35, it is important to minimize the contaminants in the CVD system, and particularly the contaminants present in the gas streams delivered to the substrate. The present invention promotes the deposition of such desired films by the method of delivering an ozone gas stream substantially free of metal contamination. Referring to FIG. 2, the method is described in detail with reference to the ozone system depicted therein. As referred to above, after much investigation and analysis, the inventor discovered that a significant source of metal contamination in the deposited film is due to corrosive contaminant vapors present in the ozone gas stream produced by the ozone generator. These corrosive contaminant vapors attack metal conduits in the system causing the release of metal atoms, most notably Cr atoms. The Cr atoms pass through the system along with the ozone gas stream, and are delivered into the CVD system whereby the Cr ends up as a metal contaminant in the deposited film.

To reduce such metal contamination, the inventive method employs particular dilution gases in the ozone generator to generate the ozone gas stream. A conventional plate discharge ozonator 40 is shown in FIG. 2. The ozonator 40 is generally comprised of two discharge plates, 41 and 42, spaced apart and opposed by way of a discharge area 47. Discharge plates 41 and 42 are coated with a dielectric material 43. High voltage 48 is applied to one plate 41, while the other plate 42 is grounded. A heat exchanger 49 is placed in contact with the discharge plates 41 and 42 to remove heat generated during the process. To create ozone, oxygen and a dilution gas are introduced via gas lines 12 and 14, respectively, and then gases mix and are conveyed to the ozone generator via gas line 18 and are passed between the plates 41 and 42. In

prior art systems, high purity oxygen, and relatively small amounts of nitrogen (typically 1% to 5% by weight) used as a dilution gas, are introduced into the ozonator 40. Power is applied through voltage source 48 to the ozonator which excites a plasma in the gases. The plasma accelerates a reaction whereby oxygen (O_2) forms ozone (O_3). Nitrogen acts as a catalyst to the reaction, aiding in the generation of ozone at high concentrations. Typically, the ozone gas stream produced is a mixture of up to 5.5 weight % O_3 in O_2. The ozone gas stream comprises ozone, oxygen and the dilution gas, and said gas stream exits the ozonator through gas line 16.

In contrast, the method of the present invention provides for the use of different dilution gases to produce an ozone gas stream which is characterized in that the ozone gas stream is substantially free of corrosive contaminant vapors that attack metal; while maintaining acceptable ozone concentration and stability. Referring again to FIG. 2, the present invention provides for the use of helium, argon or carbon dioxide as the dilution gas which is introduced through gas line 14. Oxygen is introduced through gas line 12. The gases are mixed and introduced into ozonator 40 via line 18. Power is applied to discharge plate 41 which creates a plasma discharge within discharge area 47. The plasma in association with the dilution gas aids the reaction of the oxygen into ozone. The ozone gas stream exits the ozonator 40 through gas line 46, and generally comprises a mixture in the range of substantially 2 to 5.5 wt % O_3 in O_2. Referring now to FIG. 1, the ozone gas stream is conveyed throughout the gas delivery system 39, where said gas stream passes through metal conduits 16 to the mass flow controller 17, and then through more metal conduits 16 into the injector 30, where the ozone gas stream exits the injector 30 into the deposition chamber area 33 proximate the surface of the substrate 35. The ozone gas stream interacts with reactive gases also exiting the injector 30 and forms a layer of material on the surface of the substrate 35. Of particular advantage, throughout the entire gas delivery system 39, the ozone gas stream does not substantially react with the metal conduits and components, thereby enabling the delivery of an ozone gas stream substantially free of metal contamination. Moreover, the ozone gas stream is substantially free of nitrates which are found to clog MFC sensor tubes and ultimately lead to failure of the MFC in prior art systems. The ozone gas stream will contain a metal atom contamination level of equal to or less 0.07 ng metal atoms per gas-liter, and preferably less than or equal to 0.02 ng metal atoms per gas-liter after the ozone gas stream has traveled the delivery system and at the point where the gas stream exits the injector 30. Such a low metal atom contamination level

in the ozone gas stream results in a film deposited on the surface of the substrate 35 in the deposition chamber area 33, such film having desirable metal contamination concentration at equal to or less than $1x10^{15}$ metal atoms/cm^3, which is below the level where device damage will occur.

Although the foregoing description is described with reference to an ozone generator of the plate discharge type, it will be understood by those of ordinary skill in the art that the inventive method may be practiced with other types of ozone generators. Moreover, the method of the present invention may be employed using any one of the recited dilution gases, i.e. Ar , He or CO_2, with various types of ozone generators. In the preferred embodiment, described in detail below, CO_2 is employed as the dilution gas with an ASTeX type ozonator known in the art. The ASTeX ozonator is of the all-metal, sealed-cell plasma discharge type with water cooling

Several experiments were conducted which present different embodiments of the invention. In the following three examples, three different ozonators were operated and produced gas streams according to the method of the present invention with apparatus as shown generally in FIG. 2. The method was first tested using an oil cooled discharge ozone generator, known in the art, as the generator depicted at element 40 in FIG. 2. The second experiment utilized a water cooled 4-module ozone generator known in the art. The third experiment employed an ASTeX ozone generator. Dilution chemistries were separately tested with each ozone generator and metal atom contamination levels were analyzed. The experiments consistently demonstrate the reduction of metal atom contamination in the ozone gas stream to a desired level. The experiments are described in detail below.

Example 1

In this example, an oil-cooled discharge ozone generator was used. Two separate tests were conducted, each test using a different gas (Ar and He) as the dilution gas. Typical test process conditions are set forth in Table 1.

Table 1 - Oil Cooled Discharge Ozone Generator Operating Parameters

Dilution Gas	
Ar	He
Dilution Gas Flow Rate	
210 sccm	528 sccm

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Concentration of Dilution Gas		
3.5 volume % 8.8 volume %		
O2 Gas Flow Rate		
6 slm 6 slm		
Ozone Concentration		
actual	124 g/m^3 (4.74 wt% O_3 in O_2)	128 g/m^3 (4.89 wt% O_3 in O_2)
Ozone Generator Power (% of full power)	52%	52%

Referring generally to FIG.2, for each experiment, oxygen was introduced through gas line 44 at the flow rate depicted in Table 1. Ar and He were separately introduced via gas line 45 according to the flow rates and concentrations depicted in Table 1. As shown in Table 1, the concentration and flow rate of the dilution gas depends on the gas being used, and as will be apparent in the examples below also varies depending on the type of ozone generator used. Accordingly, it should be apparent to one of ordinary skill in the art, that the method of the present invention may be practiced with a variety of ozone generators and associated process conditions in addition to the three types presented herein.

To produce ozone, power is applied to plate 41 via power source 48, thereby creating a plasma discharge in discharge area 47. In the discharge area 47, oxygen reacts to form ozone, and a gas stream of approximately 2 to 5.5 O_3 wt % in O_2 is produced and delivered through gas outlet line 46. The concentration of ozone in the gas stream is shown in Table 1 for each test, and is within desired specifications.

The ratio of dilution gas to oxygen introduced in the ozone generator was found to affect the concentration and stability of the ozone produced in the ozone gas stream. Experiments were conducted to determine the most desirable ratio, and preferably the volume % ratio of Ar ranges substantially from 3.5% to 9.4%, when Ar is used as the dilution gas; and the preferred volume % ratio of He is substantially from 8.8% to 18% when He is used as the dilution gas.

Metal contamination in the ozone gas stream was tested using a bench test whereby measurements were made using the following procedure: the ozone generator 40 and CVD system 20 were employed as generally shown in Fig. 1. A single wafer

sampling device 38 was installed in the ozone gas line 16 between the MFC 21 and the injector 30 as shown in FIG. 1. The device 38 serves to test contaminant levels in the ozone gas stream by exposing a wafer to the ozone gas stream for a specified amount of time, at a particular flow rate and ozone concentration. Typical test conditions are an ozone gas stream flow rate of 6 slm for 15 minutes at 4.0 - 4.5 wt% O_3 in O_2. To perform the test a wafer is placed in the device 38, and the ozone gas stream is generated in ozonator 40 and is conveyed through lines 16 and then sprayed into the top of the device 38 and onto the topside of the wafer surface. The effluent is directed out of the bottom of the device 38 and into the injector 30, where the gases were exhausted. After the specified time, the wafer was removed from the device. The wafer surface contains the ozone stream contaminants which can now be measured. The contaminants are removed by a Hydro-fluoric Vapor Phase Decomposition process known in the art. The resulting chemical was them analyzed using a known Graphite Furnace Atomic Absorption Spectroscopy or Inductively Coupled Plasma Mass Spectrometry technique to quantify metal contaminants found on the surface of the wafer after exposure to the ozone gas stream. For comparison a wafer was tested using an ozone gas stream produced by using nitrogen as the dilution gas as employed in the prior art methods. The results of the foregoing bench tests are depicted in FIG. 3. As shown the level of Cr contamination is dramatically reduced by use of Ar or He as the dilution gas in accordance with the invention.

Example 2

In another experiment, a conventional water cooled 4-stack discharge ozone generator was used to generate a ozone gas stream in accordance with a second embodiment of the invention. Two dilution gases, Ar and He, were tested in two separate experiments pursuant to the process conditions set forth in Table 2A.

Table 2A - Water Cooled 4-Stack Ozone Generator

Dilution Gas	Ar	He
Dilution Gas Flow Rate	1.26 slm	1.32 slm
Concentration of Dilution Gas	5.25 volume %	5.5 volume%
O2 Gas Flow Rate	24 slm	24 slm

Ozone Concentration actual	107 g/m3	107 g/m3
Ozone Generator Power (% of full power)	62%	62%

An ozone gas stream was produced as generally described in Example 1. To measure contaminant levels in the ozone gas stream, dielectric layers were deposited on substrates using the ozone gas stream as a precursor. The substrates were placed in the deposition chamber area 33, under the injector 30 in the CVD reactor 20 as shown in FIG. 1. Specifically, the dielectric layers were deposited utilizing the ozone gas stream generated with Ar as the dilution gas pursuant to the operating conditions associated with the Ar test in Table 2A. CVD deposition was achieved according to the parameters set forth below in Table 2B.

Table 2B - CVD Process Conditions

	Injector 1 flow (slm)	Injector 2 flow (slm)	Injector 2/3 flow (slm)	Injector 3 flow (slm)	Injector 4 flow (slm)
O2/O3	4.87	4.85	--	4.83	4.86
Dilution N2	2.09	2.07	--	2.07	2.03
Separator N2	9.98	9.97	--	9.95	9.89
Liquid Source - Dopants Dilution N2	3.39	--	6.79	--	3.89
Si Source N2	1.898	--	3.781	--	1.895
Deposition Temperature	550 degrees C				
Belt Speed	3"/min.				
Chamber Pressure	1.18"H2O				

As shown in Table 2B, dielectric layers were deposited by passing a substrate 35 through four separate injector and associated deposition chamber area 33 stages with the CVD reactor 20. In this exemplary embodiment, the ozone gas stream is conveyed through each of the four injectors at the gas flow rates depicted in Table 2. Dilution N_2 is provided to each injector, and is tied into the ozone gas stream line generally at point A on FIG. 1. Since nitrogen is introduced down stream from the

plasma discharge ozonator, none of the aforementioned prior art problems of formation of nitric acid and associated metal contamination occur. The Separator N_2 is conveyed into one port of each of the four injector stages as shown by reference 27 in FIG. 1. The Liquid Source Dilution N_2 flow rate represents the introduction of dopants to the chamber, such as boron or phosphorous, using nitrogen as the carrier gas. Such dopants may be used to deposit a boro-phospho-silicate glass (BPSG) oxide film. TEOS is introduced via delivery line 24 with nitrogen as the carrier gas, as shown in Table 2B as the row Si Source N_2. The liquid source dilution nitrogen and Si source nitrogen flow rates are represented on Table 2B as "Injector 2/3 flow" since each gas shares a common delivery line for the two injectors.

Example 3

In a third set of experiments, an ASTeX ozone generator known in the art was used to generate the ozone gas stream in accordance with a third embodiment of the present invention. Three dilution gases, Ar, He and CO_2 were tested independently in three experiments pursuant to the exemplary ozone generating process conditions set forth in Table 3A. Again, an ozone gas stream is produced as described above. From the experiments conducted the preferred method of practicing the invention utilizes the ASTeX generation with CO_2 as the dilution gas and preferably the weight % ratio of CO_2 ranges substantially from 2% to 3.6%. The concentration level of contaminants present in the various ozone gas streams was tested by a number of means. First, a bench test was conducted on the ozone gas stream produced using CO2 as the dilution gas. The bench test was similar to that performed in Example 1 above, whereby the single wafer sampling device 38 was installed in the ozone gas line 16 between the MFC 21 and the injector 30 as shown in FIG. 1. Generally, wafers placed in device 38 were sprayed with the ozone gas stream at a flow rate of 6 slm and a concentration of 4.0 - 4.5 wt% O_3 in O_2 for 15 minutes. The results of the bench test are shown in FIG. 4, and show that the level of Cr contamination is dramatically reduced by use of CO_2 as the dilution gas accordance with the present invention, and in contrast to the wafer tested using N_2 as the dilution gas in FIG. 4.

Table 3A-ASTeX Ozone Generator

Dilution Gas	Ar	He	CO_2
Dilution Gas Flow Rate	4.62 slm	9.30 slm	900 sccm
Concentration of Dilution Gas	18.9 volume %	38 volume %	3.6 volume%

O2 Gas Flow Rate	24 slm	24 slm	24 slm
Ozone Concentration (actual)	48.6 g/m^3	46.4 g/m^3	107 g/m^3
Ozone Generator Power (% of full power)	100%	100%	52%

In addition to the bench test described above, dielectric layers were deposited on substrates according to the method of the present invention. Such layers were formed with the desirable result of low metal contamination in the film. In particular, dielectric layers were deposited using an APCVD reactor generally as depicted in FIG. 1, and pursuant to the process conditions set forth in Table 3B below:

Table 3B - CVD Process Conditions

	Injector 1 flow (slm)	Injector 2 flow (slm)	Injector 2/3 flow (slm)	Injector 3 flow (slm)	Injector 4 flow (slm)
O2/O3	5.96	5.99	--	5.97	5.97
Dilution N2	0.98	0.98	--	0.98	1.00
Separator N2	9.96	9.92	--	9.95	9.96
Liquid Source Dilution N2	3.88	--	3.96	--	3.88
Si Source N2	0.867	--	1.728	--	0.868
Deposition Temperature	500 degrees C				
Belt Speed	3.75"/min				
Chamber Pressure	1.11"H2O				

Dielectric films of 4800 angstroms to 7000 angstroms thickness were deposited on 6" silicon substrates by placing the silicon substrates 35 on the conveyor belt 34 and passing the substrate through each of four stages. Within each stage, the substrate 35 passes under the injector 30 in deposition area 33. Reactive gases O_3 and TEOS, among other gases, exit injector 30 and interact proximate the surface of the substrate 35 whereby the gases form a layer of material on said surface.

Each film was tested for metal contamination level, and the quality of the film was evaluated. In particular, substrates were tested for metal contamination levels using known analysis techniques, and in particular the Secondary Ion Mass Spectrometry (SIMS) technique was used as shown in FIG. 6. The standard SIMS analysis shows a Cr content of less than $1x10^{14}$ metal atoms/cm^3 deposited in a dielectric film atop the

substrate placed under the injector 30 in deposition chamber area 33. Referring to FIG. 6, depicted is the Cr content in a film deposited by conveying a wafer 35 through the CVD apparatus 20 shown in FIG. 1. In this instance the apparatus 20 contains containing four deposition chamber area 33 stages, each chamber area 33 containing an injector 30, and the film was deposited by conveying the wafer through the apparatus 20 in two passes. The dielectric film is deposited on the wafer as it travels through the muffle 31 and passes under four separate injectors 30 which deliver reactive chemical precursors in each of the four deposition chamber area 33 stages. The wafer also passes through an entry nitrogen curtain (not shown), inter-injector nitrogen curtains 32, and an exit nitrogen curtain (not shown) as it is carried on the conveyor belt 34 through the muffle 31. Referring again to FIG. 6, each deposition chamber area 33 stage is represented by a letter A through H. Letters A-D represent the first pass with four deposition chamber area 33 stages, and Letters E-H represent the second pass with four deposition chamber area 33 stages. The film was deposited using He as the dilution gas to generate the ozone gas stream 16 from the ozone generator 15, and the CVD apparatus 20 was operated generally according to the process conditions set forth in Table 3B.

Referring again to FIG. 6, the graph shows the Cr abundance (Cr atoms/cm^3) as a function of the film thickness (microns) deposited on the silicon wafer. Chromium is deposited onto the wafer in varying amounts depending on the location of the wafer as it travels through the apparatus 20. As shown at points A-H, the dielectric film exhibits a Cr content of less than $1x10^{14}$ metal atoms/cm^3 deposited in the film placed under each of the injectors 30 in each deposition chamber area 33. The chromium values greater than 10^{14} are in the areas outside of the deposition chamber areas 33, in the so called inter-injector zones, where vapor phase Cr accumulation occurs. The Cr content in this area is within a standard deviation value of 10^{15} which meets desired target content levels sought by the semiconductor industry.

Of particular advantage is the excellent step coverage and gap fill achieved by the method of this invention. Such film qualities are appreciated with reference to FIGs. 5a and 5b, which show SEM photographs of a portion of the cross-section of wafers with a dielectric layer formed according to two embodiments of the present invention. In FIG. 5a the wafer contains aluminum lines 51 and 52 formed on the surface of substrate 35. The lines 51 and 52 were spaced apart at one micron. The aspect ratio of the gap between lines 51 and 52 was 0.4 microns high to 1.0 microns wide. A

silicon oxide dielectric layer 53 was deposited atop the lines 51 and 52 and the substrate 35 using ozone and TEOS as precursor gases. The ozone gas stream was produced by the water cooled 4-stack ozone generator using Ar as the dilution gas pursuant to the operating conditions shown in Table 2A. CVD deposition was performed pursuant to the operating parameters in Table 2B. As shown in FIG. 5a, the dielectric layer has uniformly filled the one micron gap without any voids, hillocks or other defects.

FIG. 5b is a SEM photograph of a cross-section portion of a wafer and a dielectric layer deposited according to the preferred embodiment of the invention. The wafer contains aluminum lines 55 and 56 formed on the surface of substrate 35 and spaced apart at 1.5 microns. The aspect ratio of the gap between lines 55 and 56 was 0.4 micron high to 1.0 microns wide. Silicon oxide dielectric layer 57 was deposited using ozone and TEOS as precursor gases. In this preferred embodiment, the ozone gas stream was produced by using CO_2 as the dilution gas pursuant to the operating conditions shown in Table 3A. CVD deposition was performed pursuant to the operating parameters in Table 3B. Again referring to FIG. 5b, the dielectric layer has uniformly filled the one micron gap without voids, hillocks and other defects.

The foregoing description of specific embodiments of the invention have been presented for the purpose of illustration and description. They are not intended to be exhaustive or to limit the invention to the precise forms disclosed, and obviously many modifications, embodiments, and variations are possible in light of the above teaching. It is intended that the scope of the invention be defined by the claims appended hereto and their equivalents.

WHAT IS CLAIMED:

1. A method of depositing oxide layers having low metal atom concentration on the surface of a substrate in a chemical vapor deposition (CVD) system, said CVD system including an ozone generating system and including metal conduits and a CVD reactor, comprising the steps of:

introducing an oxygen gas stream into said ozone generating system;

introducing a nitrogen free dilution gas into said ozone system, to produce thereby a gas stream including ozone which does not substantially react with the metal conduits;

delivering said gas stream through the metal conduits to said CVD reactor, whereby to deliver a gas stream substantially free of metal atom contamination; and

reacting said gas stream with a reactive gas in said CVD reactor to deposit a layer substantially free of metal atoms on the surface of said substrate.

2. The method of Claim 1 wherein said dilution gas is argon.

3. The method of claim 1 wherein said dilution gas is helium.

4. The method of Claim 1 wherein said dilution gas is carbon dioxide.

5. The method of Claim 1 wherein said gas stream has a metal atom concentration of substantially equal to or less than 0.05 ng metal atoms per gas-liter.

6. The method of Claim 1 wherein the layer has a metal atom concentration of substantially equal to or less than $1x10^{15}$ metal atoms/cm^3.

7. The method of Claim 1 wherein said CVD reactor is an atmospheric pressure CVD reactor having a muffle, at least one CVD chamber area within said muffle, at least one injector for conveying gases into said at least one CVD chamber area, and a conveyorized belt for moving wafers through said chamber area and said muffle.

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8. The method of Claim 1 wherein said CVD reactor includes an injector for conveying said reactive gas stream and said gas stream to deposit said layer having a metal atom concentration of substantially less than or equal to $1x10^{14}$ metal atoms/cm^3.

9. The method of Claim 1 wherein said CVD reactor is a low pressure CVD reactor.

10. The method of Claim 1 wherein said CVD reactor is a plasma enhanced CVD reactor.

11. A method of delivering reactive gases containing low metal atom contamination through an ozone system containing metal conduits, comprising the steps of:

introducing an oxygen gas stream into said ozone system;

introducing a nitrogen free inert gas into said ozone system;

ozonating said oxygen gas and said inert gas thereby producing a reactive gas stream including ozone and being substantially free of acids that attack metal; and

delivering said reactive gas stream through the metal conduits contained in said ozone system, wherein said reactive gas stream does not substantially react with the metal conduit, thereby minimizing the formation of metal atom contamination in said reactive gas stream.

12. The method of claim 11 wherein said reactive gas stream has a metal atom concentration equal to or less than 0.05 ng metal atoms per gas-liter.

13. The method of claim 11 wherein said reactive gas is argon.

14. The method of claim 11 wherein said reactive gas is helium.

15. The method of claim 11 wherein said reactive gas is carbon dioxide.

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16. A method of delivering gases containing ozone through metal conduits from an ozonator into which oxygen and dilution gases are introduced characterized in that the dilution gases do not contain nitrogen, whereby corrosive vapors which would corrode the conduits are not substantially formed, thereby providing gases which are substantially free of metal contamination.

17. The method of Claim 16 wherein said dilution gas is argon.

18. The method of claim 16 wherein said dilution gas is helium.

19. The method of Claim 16 wherein said dilution gas is carbon dioxide.

20. The method of Claim 16 wherein said gases are further characterized in that the metal contamination is said gases is substantially equal to or less than 0.05 ng metal atoms per gas-liter.

21. A method of depositing oxide layers having low metal atom concentration on the surface of a substrate in a chemical vapor deposition (CVD) system, said CVD system including an ozone system and a CVD reactor, comprising the steps of:

introducing an oxygen gas stream into said ozone system;

introducing a dilution gas into said ozone system, the dilution gas excluding nitrogen, to produce thereby a gas stream including ozone which does not substantially react with the metal conduits, thereby substantially eliminating metal atom contamination of said gas stream;

delivering said gas stream through the metal conduits contained in said ozone system to said CVD reactor; and

reacting said gas stream with a reactive gas in said CVD reactor to deposit a layer on the surface of said substrate, said layer having a metal atom concentration equal to or less than $1x10^{14}$ metal atoms/cm3.

22. The method of Claim 21 wherein the flow rate of said gas stream delivered to said CVD reactor is approximately in the range of 4.0 to 10.0 slm.

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23. The method of Claim 21 wherein said reactive gas is delivered to said CVD reactor at a flow rate approximately in the range of 1 0 to 5.0 slm.

24. The method of Claim 21 wherein said reactive gas stream comprises a silicon containing gas and a dopant containing gas, each gas being separately conveyed to said CVD reactor, said silicon containing gas having a flow rate approximately in the range of 1.0 to 5.0 slm, and said dopant containing gas having a flow rate approximately in the range of 3.0 to 8.0 slm.

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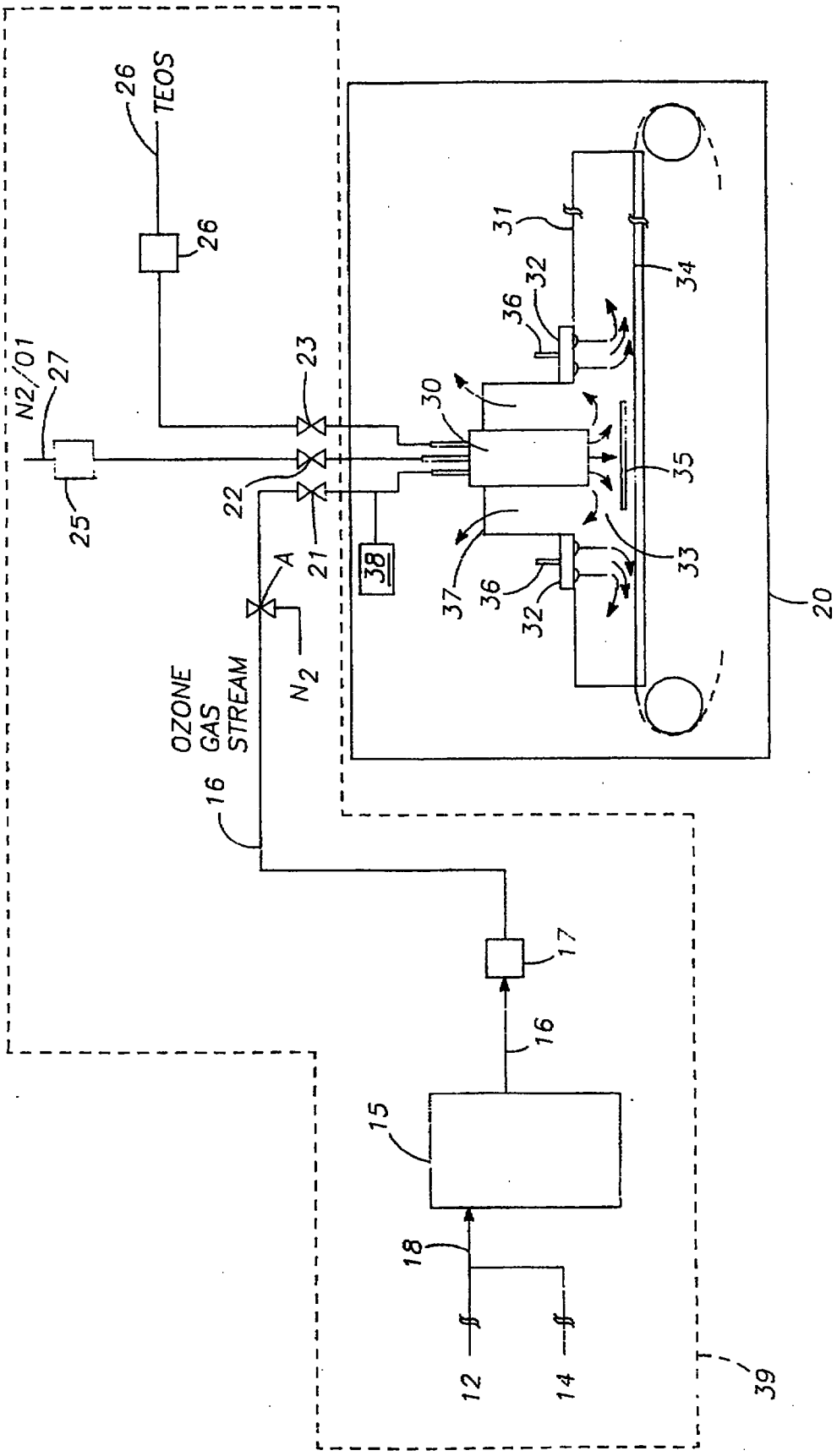

26
TEOS
26
N2/O1
27
25
23
22
21
A
N2
38
OZONE
GAS
STREAM
16
17
16
15
18
12
14
39
20
30
31
32
34
36
35
33
37
36
32

FIG. – 1

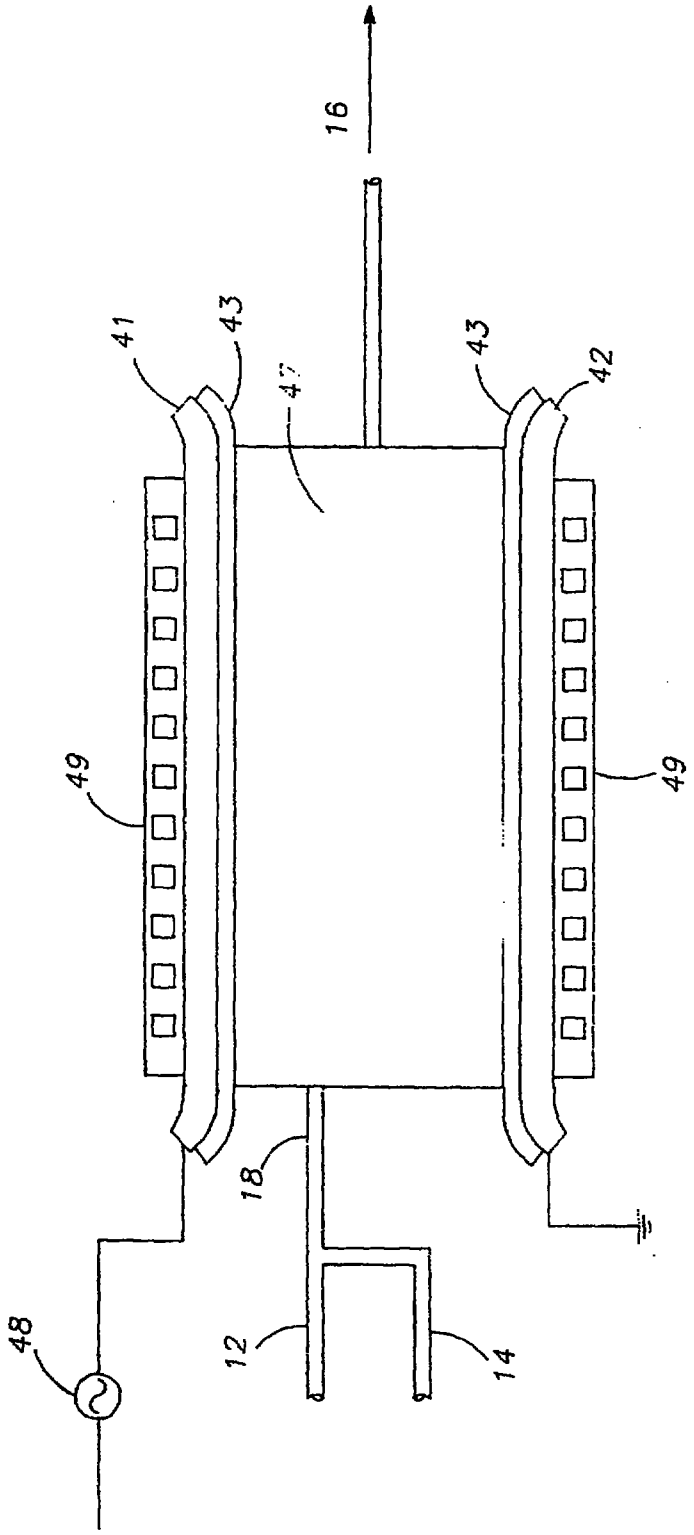


FIG. -2

METAL CONTAMINANT	O3 + Ar	O3 + He	O3 + N2
Cr	4.0	*	1500

All values times: 1x1014 atoms/cm^2

* Indicates measurement was below the detection limit.

FIG.—3

METAL CONTAMINANT	O3 + CO2 – OZONE GAS STREAM
Cr	*

All values times: 1x1014 atoms/cm^2

* Indicates measurement was below the detection limit.

FIG.—4

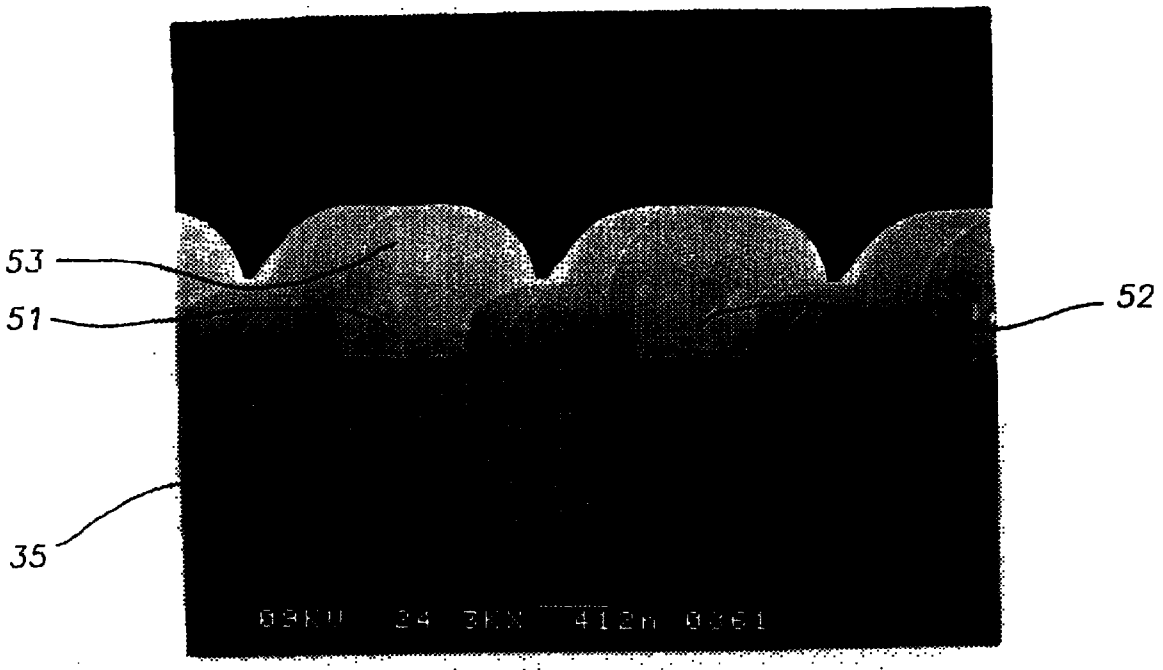


FIG.—5A

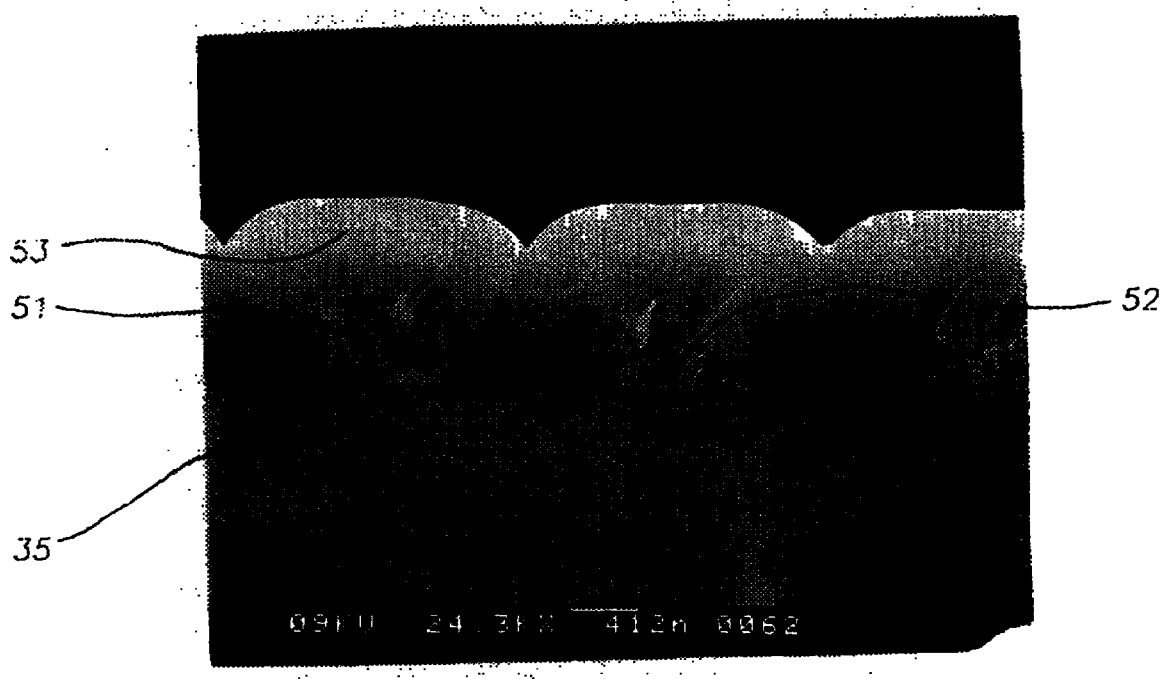


FIG.—5B

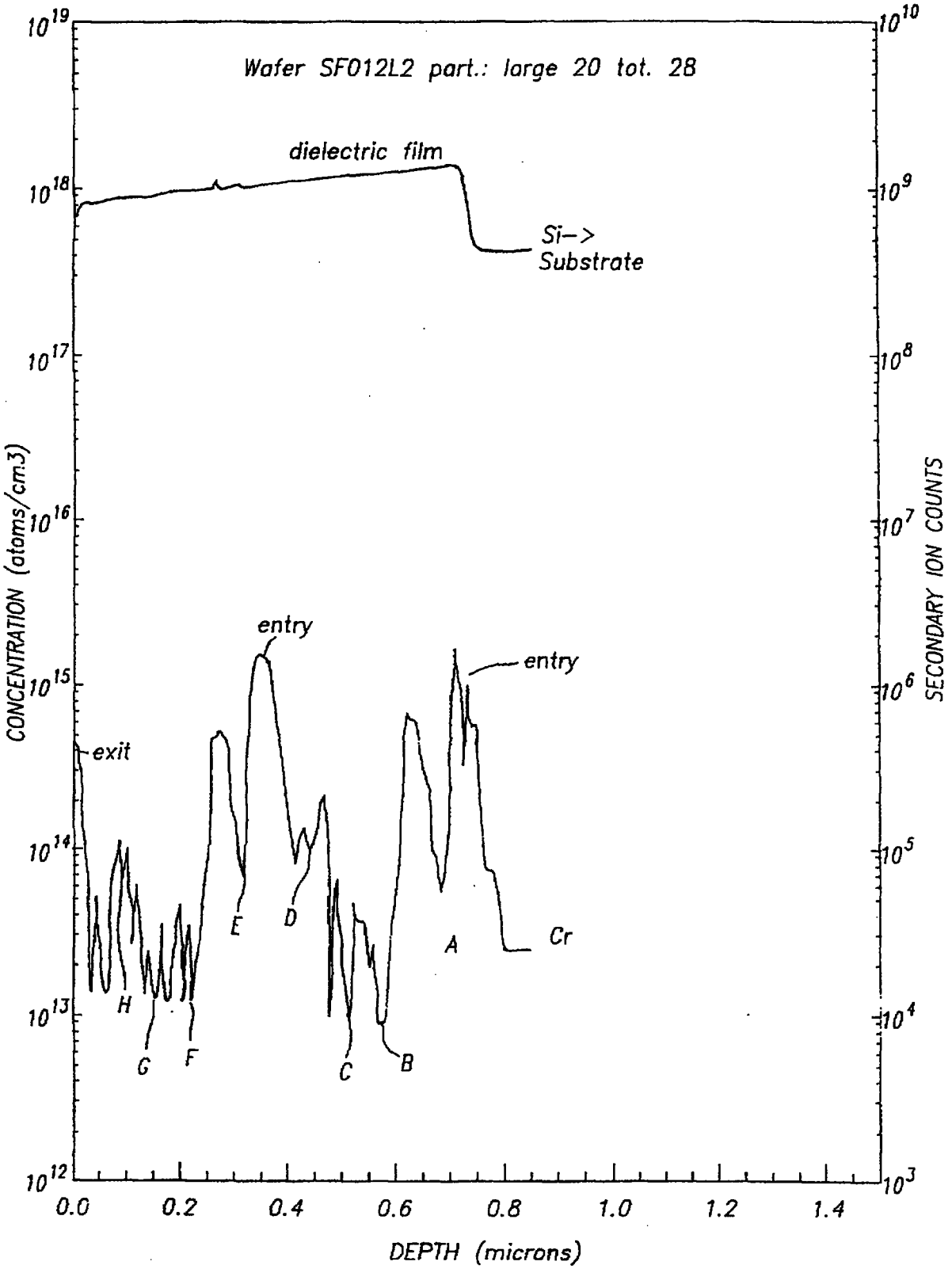

Wafer SF012L2 part.: large 20 tot. 28
dielectric film
Si–>
Substrate
entry
entry
exit
Cr
A
B
C
D
E
F
G
H
CONCENTRATION (atoms/cm3)
SECONDARY ION COUNTS
DEPTH (microns)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4

FIG.—6

in the ozone gas stream results in a film deposited on the surface of the substrate 35 in the deposition chamber area 33, such film having desirable metal contamination concentration at equal to or less than $1x10^{15}$ metal atoms/cm^3 and preferrably equal to or less than $1x10^{14}$ metal atoms/cm^3, which is below the level where device damage will occur.

Although the foregoing description is described with reference to an ozone generator of the plate discharge type, it will be understood by those of ordinary skill in the art that the inventive method may be practiced with other types of ozone generators. Moreover, the method of the present invention may be employed using any one of the recited dilution gases, i.e. Ar , He or CO_2, with various types of ozone generators. In the preferred embodiment, described in detail below, CO_2 is employed as the dilution gas with an ASTeX type ozonator known in the art. The ASTeX ozonator is of the all-metal, sealed-cell plasma discharge type with water cooling

Several experiments were conducted which present different embodiments of the invention. In the following three examples, three different ozonators were operated and produced gas streams according to the method of the present invention with apparatus as shown generally in FIG. 2. The method was first tested using an oil cooled discharge ozone generator, known in the art, as the generator depicted at element 40 in FIG. 2. The second experiment utilized a water cooled 4-module ozone generator known in the art. The third experiment employed an ASTeX ozone generator. Dilution chemistries were separately tested with each ozone generator and metal atom contamination levels were analyzed. The experiments consistently demonstrate the reduction of metal atom contamination in the ozone gas stream to a desired level. The experiments are described in detail below.

Example 1

In this example, an oil-cooled discharge ozone generator was used. Two separate tests were conducted, each test using a different gas (Ar and He) as the dilution gas. Typical test process conditions are set forth in Table 1.

Table 1 - Oil Cooled Discharge Ozone Generator Operating Parameters

Dilution Gas	
Ar	He
Dilution Gas Flow Rate	
210 sccm	528 sccm

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* C L M S *

WHAT IS CLAIMED:

1. A method of depositing oxide layers having low metal atom concentration on a surface of a substrate in a chemical vapor deposition (CVD) system, said CVD system including an ozone generating system and including metal conduits and a CVD reactor, comprising the steps of:

introducing an oxygen gas into said ozone generating system;

introducing a nitrogen free dilution gas into said ozone generating system, and producing a gas stream which includes ozone and which does not substantially react with the metal conduits;

delivering said gas stream through the metal conduits to said CVD reactor, to deliver said gas stream substantially free of metal atom contamination; and

reacting said gas stream with a reactive gas in said CVD reactor to deposit a layer substantially free of metal atoms on the surface of said substrate.

2. The method of Claim 1 wherein said dilution gas is argon.

3. The method of claim 1 wherein said dilution gas is helium.

4. The method of Claim 1 wherein said dilution gas is carbon dioxide.

5. The method of Claim 1 wherein said gas stream has a metal atom concentration of substantially equal to or less than 0.05 ng metal atoms per gas-liter.

6. The method of Claim 1 wherein the layer has a metal atom concentration of substantially equal to or less than $1x10^{15}$ metal atoms/cm^3.

7. The method of Claim 1 wherein said CVD reactor is an atmospheric pressure CVD reactor having a muffle, at least one CVD chamber area within

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said muffle, at least one injector for conveying gases into said at least one CVD chamber area, and a conveyorized belt for moving wafers through said chamber area and said muffle.

8. The method of Claim 1 wherein said CVD reactor includes an injector for conveying said reactive gas stream and said gas stream to deposit said layer having a metal atom concentration of substantially less than or equal to $1x10^{14}$ metal atoms/cm^3.

9. The method of Claim 1 wherein said CVD reactor is a low pressure CVD reactor.

10. The method of Claim 1 wherein said CVD reactor is a plasma enhanced CVD reactor.

11. A method of delivering reactive gases containing low metal atom contamination through an ozone system to a CVD reactor containing metal conduits, comprising the steps of:

introducing an oxygen gas stream into said ozone system;

introducing a nitrogen free dilution gas into said ozone system;

ozonating said oxygen gas and said inert gas thereby producing a reactive gas stream including ozone and being substantially free of acids that attack metal; and

delivering said reactive gas stream through the metal conduits contained in said ozone system and said CVD reactor, wherein said reactive gas stream does not substantially react with the metal conduits, thereby minimizing the formation of metal atom contamination in said reactive gas stream.

12. The method of claim 11 wherein said reactive gas stream has a metal atom concentration equal to or less than 0.05 ng metal atoms per gas-liter.

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13. The method of claim 11 wherein said dilution gas is argon.

14. The method of claim 11 wherein said dilution gas is helium.

15. The method of claim 11 wherein said dilution gas is carbon dioxide.

16. An ozone system for delivering gases containing ozone through metal conduits from an ozonator into which oxygen and dilution gases are introduced characterized in that the dilution gases do not contain nitrogen, and corrosive vapors which would corrode the metal conduits are not substantially formed, thereby providing said gases containing ozone which are substantially free of metal contamination.

17. The ozone system of Claim 16 wherein said dilution gas is argon.

18. The ozone system of claim 16 wherein said dilution gas is helium.

19. The ozone system of Claim 16 wherein said dilution gas is carbon dioxide.

20. The ozone system of Claim 16 wherein said gases are further characterized in that the metal contamination is said gases is substantially equal to or less than 0.05 ng metal atoms per gas-liter.

21. The method of Claim 1 wherein the layer has a metal atom concentration of substantially equal to or less than $1x10^{14}$ metal atoms/cm^3.

22. The method of Claim 1 wherein the flow rate of said gas stream delivered to said CVD reactor is approximately in a range of 4.0 to 10.0 slm.

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* C L M S *

23. The method of Claim 1 wherein said reactive gas is delivered to said CVD reactor at a flow rate approximately in a range of 1.0 to 5.0 slm.

24. The method of Claim 1 wherein said reactive gas comprises a silicon containing gas and a dopant containing gas, each gas being separately conveyed to said CVD reactor, said silicon containing gas having a flow rate approximately in a range of 1.0 to 5.0 slm, and said dopant containing gas having a flow rate approximately in a range of 3.0 to 8.0 slm.

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(54) Title: METHOD OF FORMING DIELECTRIC FILMS WITH REDUCED METAL CONTAMINATION

METAL CONTAMINANT	O3 + Ar	O3 + He	O3 + N2
Cr	4.0	*	1500

All values times: 1x1014 atoms/cm^2

**Indicates measurement was below the detection limit.*

(57) Abstract

A method of forming dielectric layers having reduced metal contamination by Chemical Vapor Deposition (CVD). The CVD system includes an ozone system and a CVD reactor. Oxygen and a nitrogen free dilution gas are introduced into the ozone system where a gas stream including ozone is produced. The gas stream is delivered through metal conduits to the CVD reactor, whereby corrosive vapors which would corrode the conduits are not substantially formed, thereby providing gases which are substantially free of metal contamination which react and deposits layers having reduced metal contamination.