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(71) Applicant: **APPLIED MATERIALS, INC.** [US/US]; 3050 Bowers Avenue, Santa Clara, California 95054 (US).

(72) Inventors: **SINGHA ROY, Susmit**; 426 Escuela Avenue, Apt. 16, Mountain View, California 94040 (US). **CHAN, Kelvin**; 1740 Blakesley Drive, San Ramon, California 94582 (US). **LE, Hien Minh**; 2076 Edgegate Drive, San Jose, California 95122 (US). **KAMATH, Sanjay**; 3440 Brookmill Court, Fremont, California 94536 (US). **MALLICK, Abhijit Basu**; 47863 Masters Court, Fremont, California 94539 (US). **GANDIKOTA, Srinivas**; 2727 Monroe Street, Santa Clara, California 95051 (US). **JANAKIRAMAN, Karthik**; 6181 Countryclub Parkway, San Jose, California 95138 (US).

(74) Agent: **PATTERSON, B. Todd** et al.; Patterson & Sheridan, LLP, 24 Greenway Plaza, Suite 1600, Houston, Texas 77046 (US).

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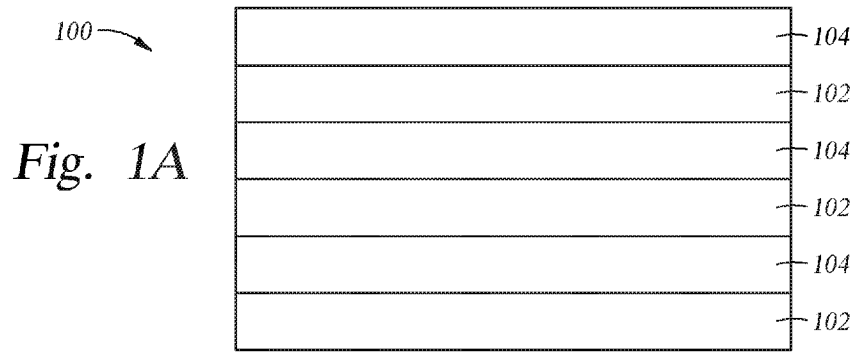

Fig. 1A

(57) Abstract: Implementations described herein generally relate to a method for forming a metal layer and to a method for forming an oxide layer on the metal layer, in one implementation, the metal layer is formed on a seed layer, and the seed layer helps the metal in the metal layer nucleate with small grain size without affecting the conductivity of the metal layer. The metal layer may be formed using plasma enhanced chemical vapor deposition (PECVD) and nitrogen gas may be flowed into the processing chamber along with the precursor gases, in another implementation, a barrier layer is formed on the metal layer in order to prevent the metal layer from being oxidized during subsequent oxide layer deposition process, in another implementation, the metal layer is treated prior to the deposition of the oxide layer in order to prevent the metal layer from being oxidized.

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CVD BASED OXIDE-METAL MULTI STRUCTURE FOR 3D NAND MEMORY DEVICES

BACKGROUND

Field

[0001] Implementations described herein generally relate to a method for forming a metal layer and to a method for forming an oxide layer on the metal layer. Implementations described herein also relate to a method for forming an oxide-metal multilayer structure.

Description of the Related Art

[0002] Designers of computer memory devices are ever in pursuit of smaller geometries with increased capacity at less cost. To this end, components of memory cells are now stacked on top of each other to create three dimensional (3D) cells. One such technology is NAND flash memory, which may be found in memory cards, USB flash drives, solid-state drives and similar products, for data storage and transfer. In NAND flash memory, memory cells made from transistors are connected in series, and can be stacked into vertical layers to create densely packed, high capacity devices. With no moving parts, flash drives use less power and are more durable than ordinary hard drives. Accordingly, there is great interest in increasing the capacity of flash drives, while reducing their size and cost.

[0003] To create 3D structures for memory cells, charge trapping transistors may be stacked into vertical layers. The vertical layers may be alternating oxide and metal layers. However, the metal layer deposited by chemical vapor deposition (CVD) process is known to have large grain size, high surface roughness, and high tensile stress and is prone to oxidation during the subsequent oxide deposition process.

[0004] Therefore, an improved method of forming a metal layer is needed.

SUMMARY

[0005] Implementations described herein generally relate to a method for forming a metal layer and to a method for forming an oxide layer on the metal layer. Implementations described herein also relate to a method for forming an oxide-metal multilayer structure. In one implementation, a method includes placing a substrate into a processing chamber and forming a metal-containing layer on the substrate. The forming a metal-containing layer on the substrate includes increasing a temperature of the substrate to a processing temperature, flowing a metal-containing precursor and nitrogen gas into the processing chamber, wherein a ratio of a flow rate of the metal-containing precursor to a flow rate of the nitrogen gas ranges from 10:1 to 1:3, and forming a plasma inside of the processing chamber by igniting the metal-containing precursor and nitrogen gas with a high frequency radio frequency power and a low frequency radio frequency power.

[0006] In another implementation, a method includes placing a substrate into a processing chamber, forming a metal layer on the substrate, treating a surface of the metal layer with a nitrogen-containing plasma, and forming an oxide layer on the treated surface of the metal layer.

[0007] In another implementation, a method includes placing a substrate into a processing chamber, forming a metal layer on the substrate, and forming an oxide layer on the metal layer. The forming an oxide layer includes flowing an oxygen-free precursor into the processing chamber, wherein the oxygen-free precursor is excited by a plasma to form oxygen-free species, flowing an oxygen-containing gas into the processing chamber, wherein the oxygen-containing gas is excited by the plasma to form oxygen species, and bonding the oxygen-free species to the oxygen species.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] So that the manner in which the above recited features of the present disclosure can be understood in detail, a more particular description

of the disclosure, briefly summarized above, may be had by reference to implementations, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only selected implementations of this disclosure and are therefore not to be considered limiting of its scope, for the disclosure may admit to other equally effective implementations.

[0009] Figures 1A – 1C are schematic cross sectional views of a multilayer structure according to implementations disclosed herein.

[0010] Figures 2A – 2C schematically illustrate formation of a seed layer and a metal layer on the seed layer according to implementations disclosed herein.

[0011] Figure 3 illustrates a process for forming the metal layer according to one implementation disclosed herein.

[0012] Figure 4 illustrates a process for forming the metal layer according to another implementation disclosed herein.

[0013] Figure 5 is a chart illustrates effects of co-flowing nitrogen gas with metal-containing precursor during formation of the metal layer according to implementations disclosed herein.

[0014] Figures 6A – 6C schematically illustrate formation of a barrier layer on a metal layer and an oxide layer on the barrier layer according to implementations disclosed herein.

[0015] Figure 7 illustrates a process for treating a surface of the metal layer according to one implementation disclosed herein.

[0016] Figure 8 illustrates a process for forming an oxide layer according to one implementation disclosed herein.

[0017] Figures 9A – 9E schematically illustrate the formation of the multilayer structure shown in Figure 1A according to implementations disclosed herein.

[0018] To facilitate understanding, identical reference numerals have been used, wherever possible, to designate identical elements that are common to the Figures. Additionally, elements of one implementation may be advantageously adapted for utilization in other implementations described herein.

DETAILED DESCRIPTION

[0019] Implementations described herein generally relate to a method for forming a metal layer and to a method for forming an oxide layer on the metal layer. In one implementation, the metal layer is formed on a seed layer, and the seed layer helps the metal in the metal layer nucleate with small grain size without affecting the conductivity of the metal layer. The metal layer may be formed using plasma enhanced chemical vapor deposition (PECVD) and nitrogen gas may be flowed into the processing chamber along with the precursor gases. In another implementation, a barrier layer is formed on the metal layer in order to prevent the metal layer from being oxidized during subsequent oxide layer deposition process. In another implementation, the metal layer is treated prior to the deposition of the oxide layer in order to prevent the metal layer from being oxidized.

[0020] Figures 1A – 1C are schematic cross sectional views of a multilayer structure 100 according to implementations disclosed herein. As shown in Figure 1A, the multilayer structure 100 includes alternating metal and oxide layers 102, 104. The oxide layer 104 may be silicon oxide or any other suitable oxide layer. The metal layer 102 may be tungsten or any other suitable metal layer. The metal layer 102 may include one or more of the following elements: cobalt, molybdenum, tungsten, tantalum, titanium, ruthenium, rhodium, copper, iron, manganese, vanadium, niobium, hafnium, zirconium, yttrium, aluminum, tin, chromium, or lanthanum. In this illustrative

example, a first or bottom metal layer 102 is deposited, followed by an oxide layer 104, then another metal layer 102, followed by another oxide layer 104, followed by another metal layer 102, and then another oxide layer 104. It should be understood that additional layers will also be provided in practice. In one implementation, the multilayer structure 100 includes 100 layers of alternating metal and oxide layers 102, 104. Further, the bottom layer may be an oxide layer 104 (not shown). Alternatively, the bottom layer may be a metal layer 102, as shown in Figure 1A.

[0021] Next, a plurality of channels 106 (two are shown) are formed in the multilayer structure 100, as shown in Figure 1B. The plurality of channels 106 may be formed by any suitable method, such as dry etching. Next, a material 108 is deposited in each of the plurality of channels 106, as shown in Figure 1C. The material 108 may be any suitable material, such as polysilicon.

[0022] Conventionally, the metal layer is deposited on the oxide layer using CVD, and the CVD based metal layer is known to have large grain size, high surface roughness, high tensile stress and is prone to oxidation during the subsequent oxide deposition process. One method of reducing grain size in the metal layer is to deposit the metal layer on a seed layer.

[0023] Figures 2A – 2C schematically illustrate formation of a seed layer 202 and a metal layer 204 on the seed layer 202 according to implementations disclosed herein. Figure 2A is a schematic cross sectional view of a substrate 200. The substrate 200 may be any suitable substrate and may include one or more layers already formed thereon. Next, as shown in Figure 2B, a seed layer 202 is formed on the substrate 200. The seed layer 202 may be titanium nitride, molybdenum nitride, tungsten nitride, amorphous boron, or amorphous silicon. In one implementation, the seed layer 202 is an amorphous boron layer. The seed layer 202 may be deposited by any suitable method, such as CVD or PECVD.

[0024] Next, as shown in Figure 2C, a metal layer 204 is deposited on the seed layer 202. The metal layer 204 may be the metal layer 102 shown in Figure 1A. The metal layer 204 may be a metal layer in a suitable electronic device. In one implementation, the metal layer 204 is tungsten. The seed layer 202 nucleates the metal layer 204 with the smallest grain size without affecting the conductivity of the metal layer 204. The seed layer 202 also serves as an adhesion layer for the adhesion of the metal layer 204 to the substrate 200 or to an oxide layer, such as the oxide layer 104 shown in Figure 1A. In one implementation, the metal layer 204 has a thickness of about 200 Angstroms and has an electrical resistivity of less than about 30 μohm*cm. Each metal layer 102 shown in Figure 1A may be deposited on a seed layer, such as the seed layer 202. In order to further reduce the grain size of the metal layer 204, the metal layer 204 is deposited using methods shown in Figures 3 and 4. In some implementations, the metal layer 102 or the metal layer 204 is a metal-containing layer, which may be metal nitrides, metal silicides, or metal silicon nitrides. In one implementation, the metal layer 102 or the metal layer 204 is titanium nitride or tungsten nitride.

[0025] Figure 3 illustrate a process 300 for forming the metal layer according to implementations disclosed herein. The process 300 starts at block 302, which is placing a substrate into a processing chamber. The substrate may be the substrate 200 shown in Figure 2A. The processing chamber may be any suitable processing chamber, such as a PECVD processing chamber. The substrate is heated to a processing temperature of about 350 degrees Celsius to about 450 degrees Celsius, such as about 400 degrees Celsius, as shown at block 304. The substrate may be heated by any suitable heating method, such as by heating elements embedded in a substrate support that is used to support the substrate inside the processing chamber. Next, at block 306, a metal-containing precursor and nitrogen gas (N_2) are introduced into the processing chamber. Additional gases such as hydrogen and/or argon gases may be flowed into the processing chamber along with the metal precursor and the nitrogen gas. The metal-containing

precursor may be any suitable metal-containing precursor, such as tungsten hexafluoride. The flow rate of the nitrogen gas is controlled so the metal layer formed on the substrate is pure metal (99.9%) and is not a metal nitride. The ratio of the flow rate of the metal-containing precursor to the flow rate of the nitrogen gas ranges from about 10:1 to about 1:2. In one implementation, the ratio of the flow rate of the metal-containing precursor to the flow rate of the nitrogen gas is about 3:1.

[0026] Next, at block 308, a plasma is formed inside of the processing chamber by igniting the metal-containing precursor and the nitrogen gas with a high frequency radio frequency (HFRF) power and a low frequency radio frequency (LFRF) power. The HFRF power may have a frequency of about 13.56 MHz and a power density of about 0.707W/cm^2. The LFRF power may have a frequency ranging from about 200 kHz to about 500 kHz, such as about 350 kHz and a power density ranging from about 0.071W/cm^2 to about 0.283W/cm^2. Next, at block 310, a metal layer is formed on the substrate. The metal layer may be the metal layer 102 shown in Figure 1A or the metal layer 204 shown in Figure 2C. The metal layer may be any suitable metal, such as tungsten. The combination of having a seed layer, such as the seed layer 202 shown in Figure 2C, forming the metal layer using PECVD, co-flowing nitrogen gas along with the metal-containing precursor at a specific ratio range, and using both HFRF power and LFRF power to form the plasma lead to the metal layer having a smooth surface, the smallest grain size and lowest electrical resistivity. The metal layer has an electrical resistivity that is less than about 30 μohm*cm, and the surface roughness of the metal layer is less than about 1 nm. The addition of nitrogen gas in the process of forming the metal layer does not lead to a metal nitride layer. The nitrogen radicals and/or ions in the metal layer are not chemically bonded to the metal, and the nitrogen radicals and/or ions are acting more like a dopant in the metal layer, which helps reducing the grain size of the metal layer. In addition, the nitrogen flow rate may be adjusted to control the stress of the metal layer.

[0027] Figure 4 illustrate a process 400 for forming the metal layer according to implementations disclosed herein. The process 400 starts at block 402, which is placing a substrate into a processing chamber. The substrate may be the substrate 200 shown in Figure 2A. The processing chamber may be any suitable processing chamber, such as a PECVD processing chamber. The substrate is heated to a processing temperature of about 500 degrees Celsius to about 600 degrees Celsius, such as about 550 degrees Celsius, as shown at block 404. The substrate may be heated by any suitable heating method, such as by heating elements embedded in a substrate support that is used to support the substrate inside the processing chamber. The benefit of heating the substrate to about 550 degrees Celsius is that the subsequent layer, such as an oxide layer, formed on the metal layer may be deposited at about 550 degrees Celsius. Thus, the time used for heating of the substrate from about 400 degrees Celsius to about 550 degrees Celsius between depositing the metal layer and depositing the oxide layer can be omitted.

[0028] Next, at block 406, a metal-containing precursor and nitrogen gas (N_2) are introduced into the processing chamber. Additional gases such as hydrogen and/or argon gases may be flowed into the processing chamber along with the metal precursor and the nitrogen gas. The metal-containing precursor may be any suitable metal-containing precursor, such as tungsten hexafluoride. The flow rate of the nitrogen gas is controlled so the metal layer formed on the substrate is pure metal (99.9%) and is not a metal nitride. At a higher temperature, such as about 550 degrees Celsius, a higher flow rate of the nitrogen gas is utilized compared to depositing the metal layer at a lower temperature, such as about 400 degrees Celsius. The ratio of the flow rate of the metal-containing precursor to the flow rate of the nitrogen gas ranges from about 5:1 to about 1:3. In one implementation, the ratio of the flow rate of the metal-containing precursor to the flow rate of the nitrogen gas is about 2:1.

[0029] Next, at block 408, a plasma is formed inside of the processing chamber by igniting the metal-containing precursor and the nitrogen gas with a high frequency radio frequency (HFRF) power and a low frequency radio frequency (LFRF) power. The HFRF power may have a frequency of about 13.56 MHz and a power density of about 0.707W/cm^2. The LFRF power may have a frequency ranging from about 200 kHz to about 500 kHz, such as about 350 kHz and a power density ranging from about 0.071W/cm^2 to about 0.566W/cm^2. Next, at block 410, a metal layer is formed on the substrate. The metal layer may be the metal layer 102 shown in Figure 1A or the metal layer 204 shown in Figure 2C. The metal layer may be any suitable metal, such as tungsten. The combination of having a seed layer, such as the seed layer 202 shown in Figure 2C, forming the metal layer using PECVD, co-flowing nitrogen gas along with the metal-containing precursor at a specific ratio range, and using both HFRF power and LFRF power to form the plasma lead to the metal layer having a smooth surface, the smallest grain size and lowest electrical resistivity. The metal layer has an electrical resistivity that is less than about 30 μohm*cm, and the surface roughness of the metal layer is less than about 1 nm. The addition of nitrogen gas in the process of forming the metal layer does not lead to a metal nitride layer. The nitrogen radicals and/or ions in the metal layer are not chemically bonded to the metal, and the nitrogen radicals and/or ions are acting more like a dopant in the metal layer, which helps reducing the grain size of the metal layer. In addition, the nitrogen flow rate may be adjusted to control the stress of the metal layer. The effects of co-flowing the nitrogen gas with metal-containing precursor during formation of the metal layer on the stress and electrical resistivity of the metal layer are shown in Figure 5.

[0030] Figure 5 is a chart 500 illustrates effects of co-flowing nitrogen gas with metal-containing precursor during formation of the metal layer according to implementations disclosed herein. As shown in Figure 5, the nitrogen flow rate ranges from 100 standard cubic centimeters per minute (sccm) to 500 sccm, the stress of the metal layer ranges from compressive (negative values)

to tensile (positive values), and the electrical resistivity of the metal layer ranges from about 14 μohm*cm to about 39 μohm*cm. When the nitrogen flow rate is between 100 sccm and 300 sccm, the electrical resistivity of the metal layer is less than 20 μohm*cm, and the stress of the metal layer can be tuned between about -400 MPa and about 200 MPa.

[0031] Figures 6A – 6C schematically illustrate formation of a barrier layer 602 on a metal layer 600 and an oxide layer 604 on the barrier layer 602 according to implementations disclosed herein. As shown in Figure 6A, the metal layer 600 may be the metal layer 102 shown in Figure 1A or the metal layer 204 shown in Figure 2C. The metal layer 600 may be a metal layer in any suitable electronic device. In one implementation, the metal layer 600 is tungsten and has a thickness ranging from about 100 Angstroms to about 300 Angstroms.

[0032] Next, as shown in Figure 6B, the barrier layer 602 is deposited on the metal layer 600. The barrier layer 602 may be an oxide, such as a metal oxide, or a high k oxide. The barrier layer 602 may be a nitride, such as a metal nitride or any transition metal nitride. In one implementation, the barrier layer 602 is titanium nitride. In another implementation, the barrier layer 602 is silicon nitride. The barrier layer 602 may be deposited by any suitable method, such as atomic layer deposition (ALD), CVD, or PECVD. The barrier layer 602 may have a thickness ranging from about 5 Angstroms to about 100 Angstroms, such as from about 20 Angstroms to about 70 Angstroms, for example about 50 Angstroms.

[0033] Next, as shown in Figure 6C, the oxide layer 604 is deposited on the barrier layer 602. The oxide layer 604 may be the oxide layer 104 shown in Figure 1C. Due to the barrier layer 602 formed between the metal layer 600 and the oxide layer 604, the metal layer 600 is not oxidized by the oxide layer 604 formed on the barrier layer 602.

[0034] In another implementation, oxidization of the metal layer is avoided without forming a barrier layer between the metal layer and the oxide layer. Figure 7 illustrates a process 700 for treating a surface of the metal layer according to one implementation disclosed herein. The process 700 starts at block 702, which is placing a substrate into a processing chamber. The substrate may be the substrate 200 shown in Figure 2A. A metal layer, such as the metal layer 102 shown in Figure 1C or the metal layer 204 shown in Figure 2C, may be deposited on the substrate in the processing chamber or in a different chamber. The processing chamber may be any suitable processing chamber, such as a PECVD processing chamber. Next, at block 704, a nitrogen-containing gas is flowed into the processing chamber, and the nitrogen-containing gas is ignited to form a nitrogen-containing plasma. The nitrogen-containing gas may be any suitable nitrogen-containing gas, such as nitrogen gas or ammonia.

[0035] The surface of the metal layer is treated by the nitrogen-containing plasma, as shown at block 706. The nitrogen-containing plasma includes nitrogen species, such as nitrogen radicals or ions, and the nitrogen species may be bonded to the metal on the surface of the metal layer, converting the surface of the metal layer to metal nitride. The power used to ignite the nitrogen-containing gas and the time the surface is treated by the nitrogen-containing plasma are controlled so the surface of the metal layer is converted from metal to metal nitride, while no nitride layer is formed on the metal layer. In one implementation, the metal layer is tungsten, and the surface of the metal layer is tungsten nitride.

[0036] Next, at block 708, an oxide layer is formed on the treated surface of the metal layer. A purge process may be performed between the treating the surface of the metal layer and the forming the oxide layer on the treated surface of the metal layer. The oxide layer may be formed on the treated surface of the metal layer in the processing chamber or in a different chamber. The oxide layer may be the oxide layer 104 shown in Figure 1C.

Due to the treated surface of the metal layer, the metal layer is not oxidized by the oxide layer formed thereon.

[0037] In another implementation, the method for forming the oxide layer is modified in order to form the oxide layer on the metal layer without oxidizing the metal layer. In such implementation, oxidation of the metal layer is avoided without forming a barrier layer between the metal layer and the oxide layer or without treating the surface of the metal layer.

[0038] Figure 8 illustrates a process 800 for forming an oxide layer according to one implementation disclosed herein. The process 800 starts at block 802, which is placing a substrate into a processing chamber. The substrate may be the substrate 200 shown in Figure 2A. A metal layer, such as the metal layer 102 shown in Figure 1C or the metal layer 204 shown in Figure 2C, may be deposited on the substrate in the processing chamber or in a different chamber. The processing chamber may be any suitable processing chamber, such as a PECVD processing chamber. Next, at block 804, one or more non-reactive gases are flowed into the processing chamber. The one or more non-reactive gases may be any suitable gases, such as argon gas. Hydrogen gas may be also considered non-reactive. In one implementation, hydrogen gas and argon gas are flowed into the processing chamber. Next, at block 806, the one or more non-reactive gases are ignited to form a plasma. The plasma may be utilized to remove any native oxide formed on the metal layer. Next, at block 808, an oxygen-free precursor is flowed into the processing chamber, and the oxygen-free precursor is excited by the plasma formed in the processing chamber. The oxygen-free precursor may be any suitable oxygen-free precursor, such as a silicon-containing precursor, for example silane. The excitation of the oxygen-free precursor forms oxygen-free species, such as radicals or ions, and the oxygen-free species may be floating in the processing chamber between a showerhead and the surface of the metal layer. Some oxygen-free species may fall on the

surface of the metal layer. In one implementation, a monolayer of amorphous silicon may be formed on the surface of the metal layer.

[0039] Next, at block 810, an oxygen-containing gas is flowed into the processing chamber, and the oxygen-containing gas is excited by the plasma formed inside the processing chamber. In one implementation, no purge process is performed between flowing the oxygen-free precursor into the processing chamber and flowing the oxygen-containing gas into the processing chamber. The oxygen-containing gas may be any suitable oxygen-containing gas, such as oxygen gas. The excitation of the oxygen-containing gas forms oxygen species, such as radicals or ions, and the oxygen species bond with oxygen-free species floating in the processing chamber and/or on the surface of the metal layer, as shown at block 812. Bonding of the oxygen species to the oxygen-free species forms an oxide layer on the surface of the metal layer on the substrate, as shown at block 814. The oxide layer may be any suitable oxide layer, such as silicon oxide layer. Because the oxygen-free precursor is flowed into the processing chamber prior to flowing the oxygen-containing gas into the processing chamber, the oxygen-containing gas or species are bonded to the oxygen-free precursor or species. Thus, the metal layer is not oxidized. The modified method for forming the oxide layer may be performed by PECVD, CVD, ALD, or physical vapor deposition (PVD). The plasma (oxygen-free precursor and/or oxygen-containing gas) may be formed in-situ or formed at a remote location, such as in a remote plasma source.

[0040] Figures 9A – 9E schematically illustrate the formation of the multilayer structure 100 shown in Figure 1A according to implementations disclosed herein. Figure 9A is a schematic cross sectional view of a substrate 900. The substrate 900 may be any suitable substrate and may include one or more layers already formed thereon. Next, as shown in Figure 9B, a seed layer 902 is formed on the substrate 200. The seed layer 902 may be titanium nitride, molybdenum nitride, tungsten nitride, amorphous boron, or

amorphous silicon. In one implementation, the seed layer 902 is an amorphous boron layer. The seed layer 902 may be deposited by any suitable method, such as CVD or PECVD.

[0041] Next, as shown in Figure 9C, a metal layer 904 is deposited on the seed layer 902. The metal layer 904 may be the metal layer 102 shown in Figure 1A. In one implementation, the metal layer 904 is tungsten. The seed layer 902 nucleates the metal layer 904 with the smallest grain size without affecting the conductivity of the metal layer 904. The seed layer 902 also serves as an adhesion layer for the adhesion of the metal layer 904 to the substrate 900 or to an oxide layer, such as the oxide layer 104 shown in Figure 1A. In one implementation, the metal layer 904 has a thickness of about 200 Angstroms and has an electrical resistivity of less than about 30 μohm*cm. In order to further reduce the grain size of the metal layer 904, the metal layer 904 is deposited using methods shown in Figures 3 and 4. The combination of having a seed layer, such as the seed layer 902, forming the metal layer 904 using PECVD, co-flowing nitrogen gas along with the metal-containing precursor at a specific ratio range, and using both HFRF power and LFRF power to form the plasma lead to the metal layer 904 having a smooth surface, the smallest grain size and lowest electrical resistivity.

[0042] Next, an oxide layer 906 is deposited on the metal layer 904, as shown in Figure 9D. Prior to the deposition of the oxide layer 906 on the metal layer 904, the surface of the metal layer 904 may be treated in order to prevent the oxidation of the metal layer 904 by the oxide layer 906. The treating of the surface of the metal layer 904 may include flowing a nitrogen-containing gas into the processing chamber, and igniting the nitrogen-containing gas to form a nitrogen-containing plasma. The nitrogen-containing gas may be any suitable nitrogen-containing gas, such as nitrogen gas or ammonia. The surface of the metal layer 904 is treated by the nitrogen-containing plasma. The nitrogen-containing plasma includes nitrogen species, such as nitrogen radicals or ions, and the nitrogen species may be

bonded to the metal on the surface of the metal layer 904, converting the surface of the metal layer 904 to metal nitride. The power used to ignite the nitrogen-containing gas and the time the surface is treated by the nitrogen-containing plasma are controlled so the surface of the metal layer 904 is converted from metal to metal nitride, while no nitride layer is formed on the metal layer 904. In one implementation, the metal layer 904 is tungsten, and the surface of the metal layer is tungsten nitride.

[0043] Alternatively, a barrier layer (not shown) may be formed on the metal layer 904 prior to the deposition of the oxide layer 906 in order to prevent the oxidation of the metal layer 904 by the oxide layer 906. The barrier layer may be an oxide, such as a metal oxide, or a high k oxide. The barrier layer may be a nitride, such as a metal nitride or any transition metal nitride. In one implementation, the barrier layer is titanium nitride. In another implementation, the barrier layer is silicon nitride. The barrier layer may be deposited by any suitable method, such as atomic layer deposition (ALD), CVD, or PECVD. The barrier layer may have a thickness ranging from about 5 Angstroms to about 100 Angstroms, such as from about 20 Angstroms to about 70 Angstroms, for example about 50 Angstroms.

[0044] In another implementation, the oxide layer 906 is deposited on an untreated surface of the metal layer 904 without a barrier layer formed between the metal layer 904 and the oxide layer 906, and the metal layer 904 is not oxidized by the oxide layer 906. The oxide layer 906 may be formed by first flowing one or more non-reactive gases into the processing chamber. The one or more non-reactive gases may be any suitable gases, such as argon gas. Hydrogen gas may be also considered non-reactive. In one implementation, hydrogen gas and argon gas are flowed into the processing chamber. Next, the one or more non-reactive gases are ignited to form a plasma. The plasma may be utilized to remove any native oxide formed on the metal layer. Next, an oxygen-free precursor is flowed into the processing chamber, and the oxygen-free precursor is excited by the plasma formed in

the processing chamber. The oxygen-free precursor may be any suitable oxygen-free precursor, such as a silicon-containing precursor, for example silane. The excitation of the oxygen-free precursor forms oxygen-free species, such as radicals or ions, and the oxygen-free species may be floating in the processing chamber between a showerhead and the surface of the metal layer. Some oxygen-free species may fall on the surface of the metal layer 904. In one implementation, a monolayer of amorphous silicon may be formed on the surface of the metal layer 904.

[0045] Next, an oxygen-containing gas is flowed into the processing chamber, and the oxygen-containing gas is excited by the plasma formed inside the processing chamber. In one implementation, no purge process is performed between flowing the oxygen-free precursor into the processing chamber and flowing the oxygen-containing gas into the processing chamber. The oxygen-containing gas may be any suitable oxygen-containing gas, such as oxygen gas. The excitation of the oxygen-containing gas forms oxygen species, such as radicals or ions, and the oxygen species bond with oxygen-free species floating in the processing chamber and/or on the surface of the metal layer 904. Bonding of the oxygen species to the oxygen-free species forms the oxide layer 906 on the surface of the metal layer on the substrate. Because the oxygen-free precursor is flowed into the processing chamber prior to flowing the oxygen-containing gas into the processing chamber, the oxygen-containing gas or species are bonded to the oxygen-free precursor or species. Thus, the metal layer 904 is not oxidized. The modified method for forming the oxide layer 906 without oxidizing the metal layer 904 may be performed by PECVD, CVD, ALD, or physical vapor deposition (PVD). The plasma (oxygen-free precursor and/or oxygen-containing gas) may be formed in-situ or formed at a remote location, such as in a remote plasma source.

[0046] Next, as shown in Figure 9E, another seed layer 908 is formed on the oxide layer 906, and the seed layer 908 may be the same as the seed layer 902. Another metal layer 910 is formed on the seed layer 908, and the

metal layer 910 may be the same as the metal layer 904. The metal layer 910 may be formed by the same method for forming the metal layer 904. Another oxide layer 912 is formed on the metal layer 910, and the oxide layer 912 may be the same as the oxide layer 906. The oxide layer 912 may be formed by the same method for forming the oxide layer 906. By repeating the processes shown in Figures 9A – 9E, the multilayered structure including multiple pairs of alternating oxide layers and metal layers can be formed.

[0047] While the foregoing is directed to implementations of the present disclosure, other and further implementations of the disclosure may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

Claims:

1. A method, comprising:

placing a substrate into a processing chamber; and

forming a metal-containing layer on the substrate, wherein the forming a metal-containing layer on the substrate comprises:

increasing a temperature of the substrate to a processing temperature;

flowing a metal-containing precursor and nitrogen gas into the processing chamber, wherein a ratio of a flow rate of the metal-containing precursor to a flow rate of the nitrogen gas ranges from 10:1 to 1:3; and

forming a plasma inside of the processing chamber by igniting the metal-containing precursor and nitrogen gas with a high frequency radio frequency power and a low frequency radio frequency power.

2. The method of claim 1, further comprising forming a seed layer on the substrate, wherein the metal-containing layer is formed on the seed layer.

3. The method of claim 2, wherein the seed layer comprises titanium nitride, molybdenum nitride, tungsten nitride, amorphous boron, or amorphous silicon.

4. The method of claim 1, wherein the metal-containing layer comprises cobalt, molybdenum, tungsten, tantalum, titanium, ruthenium, rhodium, copper, iron, manganese, vanadium, niobium, hafnium, zirconium, yttrium, aluminum, tin, chromium, or lanthanum.

5. The method of claim 1, wherein the metal-containing layer comprises metal nitrides, metal silicides, or metal silicon nitrides.

6. The method of claim 1, wherein the processing temperature ranges from about 350 degrees Celsius to about 450 degrees Celsius.

7. The method of claim 6, wherein the ratio of a flow rate of the metal-containing precursor to a flow rate of the nitrogen gas ranges from 10:1 to 1:2.

8. The method of claim 6, wherein the low frequency radio frequency power ranges from about 0.071W/cm^2 to about 0.283W/cm^2.

9. The method of claim 1, wherein the processing temperature ranges from about 500 degrees Celsius to about 600 degrees Celsius.

10. The method of claim 9, wherein the ratio of a flow rate of the metal-containing precursor to a flow rate of the nitrogen gas ranges from 5:1 to 1:3.

11. The method of claim 9, wherein the low frequency radio frequency power ranges from about 0.071W/cm^2 to about 0.566W/cm^2.

12. A method, comprising:

placing a substrate into a processing chamber;

forming a metal layer on the substrate;

treating a surface of the metal layer with a nitrogen-containing plasma; and

forming an oxide layer on the treated surface of the metal layer.

13. The method of claim 12, wherein the nitrogen-containing plasma is formed by flowing a nitrogen-containing gas into the processing chamber and igniting the nitrogen-containing gas.

14. A method, comprising:

placing a substrate into a processing chamber;

forming a metal layer on the substrate; and

forming an oxide layer on the metal layer, wherein the forming an oxide layer comprises:

flowing an oxygen-free precursor into the processing chamber, wherein the oxygen-free precursor is excited by a plasma to form oxygen-free species;

flowing an oxygen-containing gas into the processing chamber, wherein the oxygen-containing gas is excited by the plasma to form oxygen species; and

bonding the oxygen-free species to the oxygen species.

15. The method of claim 14, further comprising flowing one or more non-reactive gases into the processing chamber prior to flowing an oxygen-free precursor into the processing chamber.

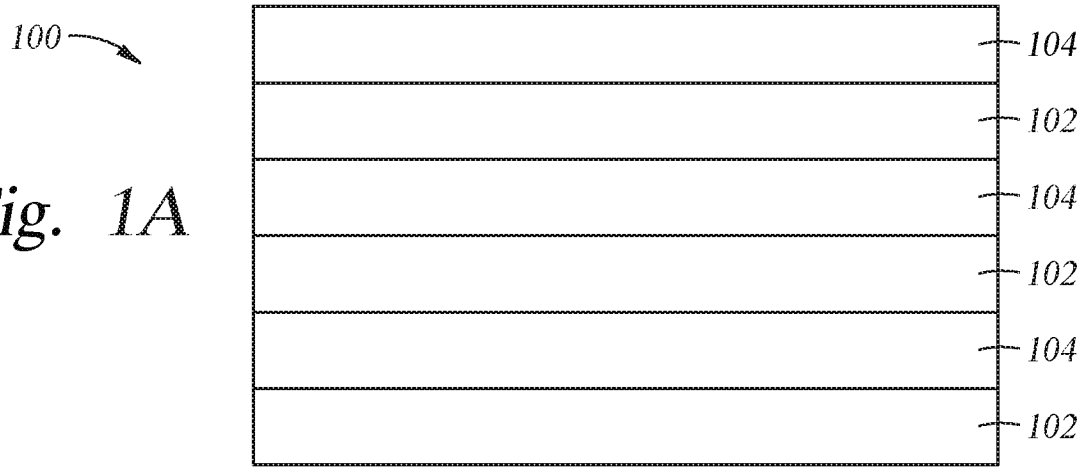

Fig. 1A

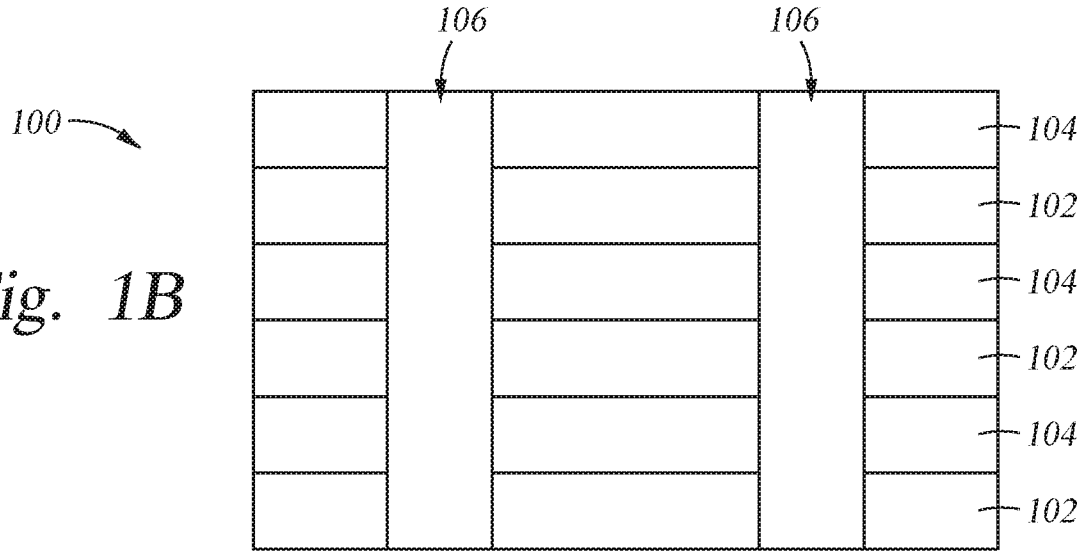

Fig. 1B

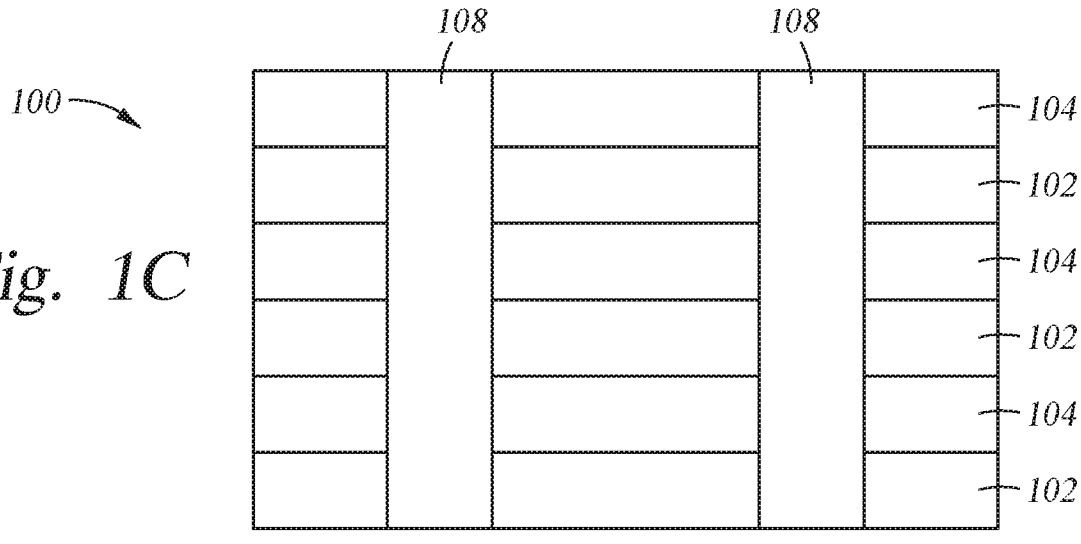

Fig. 1C

Fig. 2A

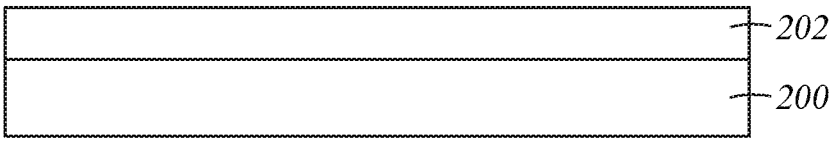

Fig. 2B

Fig. 2C

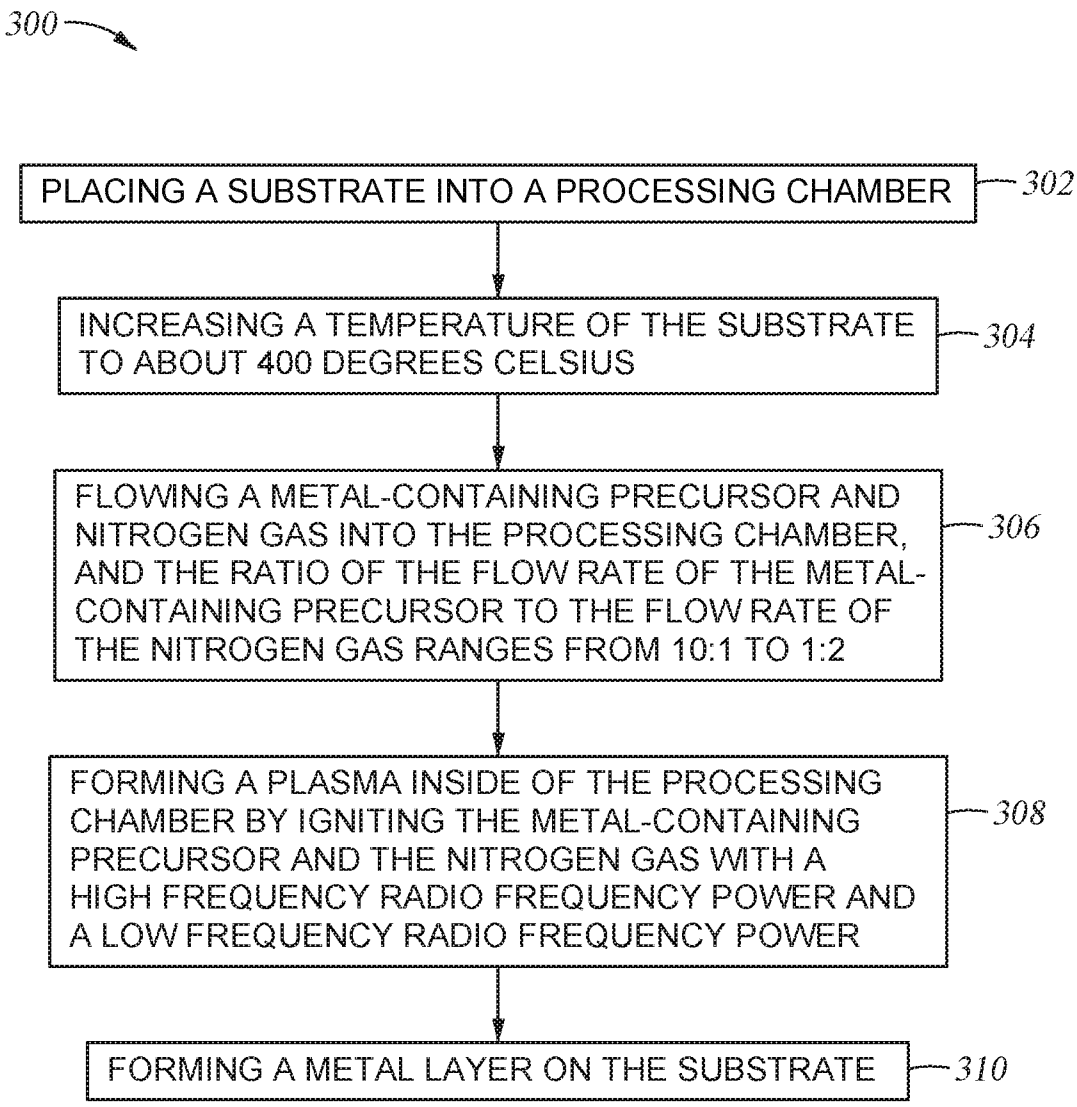
300
PLACING A SUBSTRATE INTO A PROCESSING CHAMBER
302
INCREASING A TEMPERATURE OF THE SUBSTRATE TO ABOUT 400 DEGREES CELSIUS
304
FLOWING A METAL-CONTAINING PRECURSOR AND NITROGEN GAS INTO THE PROCESSING CHAMBER, AND THE RATIO OF THE FLOW RATE OF THE METAL-CONTAINING PRECURSOR TO THE FLOW RATE OF THE NITROGEN GAS RANGES FROM 10:1 TO 1:2
306
FORMING A PLASMA INSIDE OF THE PROCESSING CHAMBER BY IGNITING THE METAL-CONTAINING PRECURSOR AND THE NITROGEN GAS WITH A HIGH FREQUENCY RADIO FREQUENCY POWER AND A LOW FREQUENCY RADIO FREQUENCY POWER
308
FORMING A METAL LAYER ON THE SUBSTRATE
310

Fig. 3

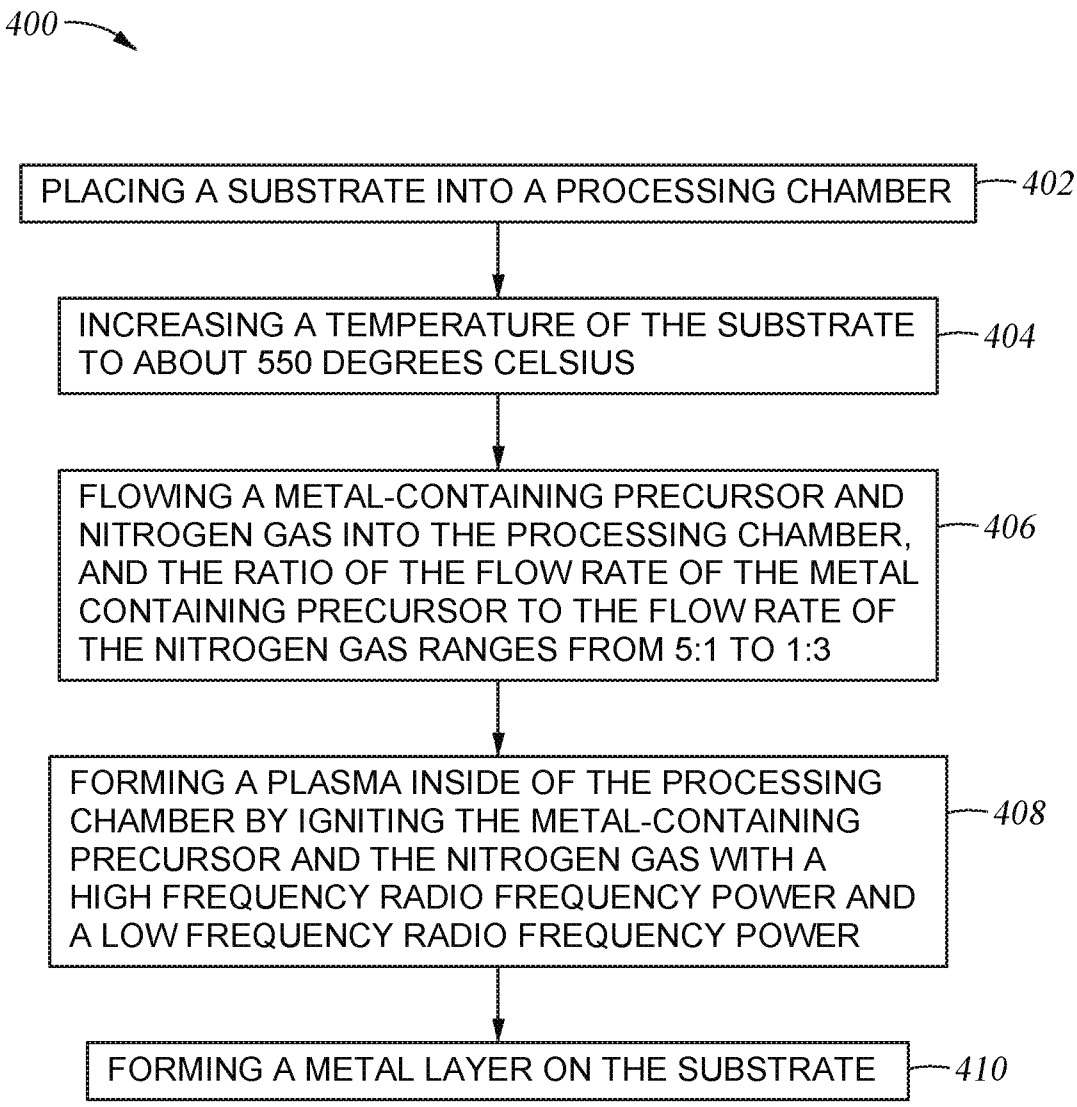
400
PLACING A SUBSTRATE INTO A PROCESSING CHAMBER
402
INCREASING A TEMPERATURE OF THE SUBSTRATE TO ABOUT 550 DEGREES CELSIUS
404
FLOWING A METAL-CONTAINING PRECURSOR AND NITROGEN GAS INTO THE PROCESSING CHAMBER, AND THE RATIO OF THE FLOW RATE OF THE METAL CONTAINING PRECURSOR TO THE FLOW RATE OF THE NITROGEN GAS RANGES FROM 5:1 TO 1:3
406
FORMING A PLASMA INSIDE OF THE PROCESSING CHAMBER BY IGNITING THE METAL-CONTAINING PRECURSOR AND THE NITROGEN GAS WITH A HIGH FREQUENCY RADIO FREQUENCY POWER AND A LOW FREQUENCY RADIO FREQUENCY POWER
408
FORMING A METAL LAYER ON THE SUBSTRATE
410

Fig. 4

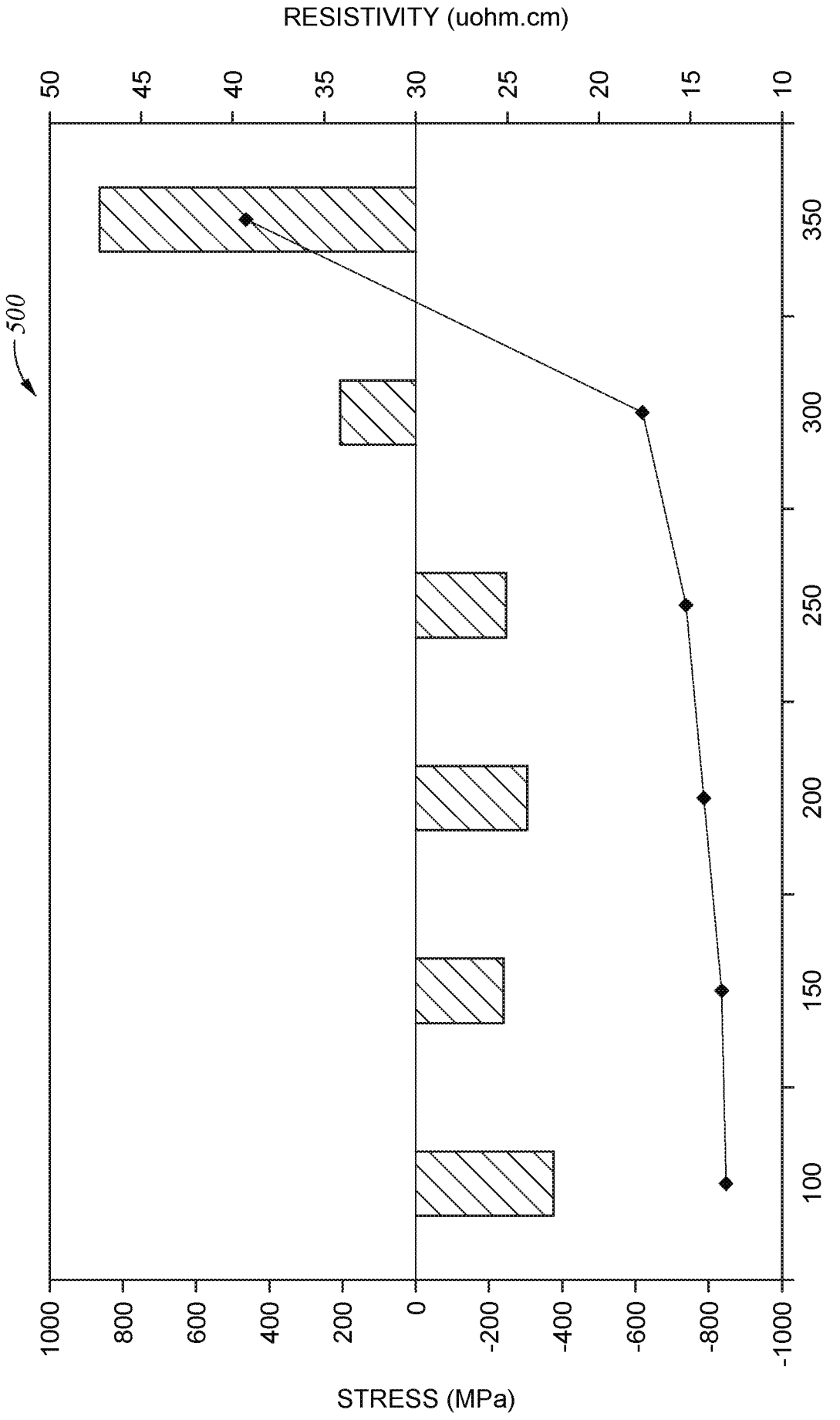
RESISTIVITY (uohm.cm)
50
45
40
35
30
25
20
15
10
500
350
300
250
200
150
100
N2 FLOW (sccm)
1000
800
600
400
200
0
-200
-400
-600
-800
-1000
STRESS (MPa)

Fig. 5

Fig. 6A

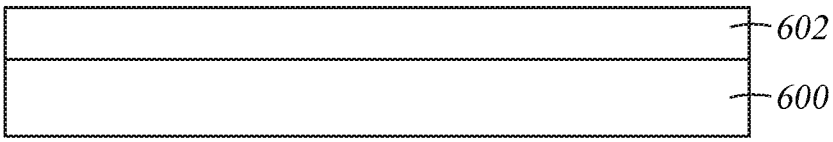

Fig. 6B

Fig. 6C

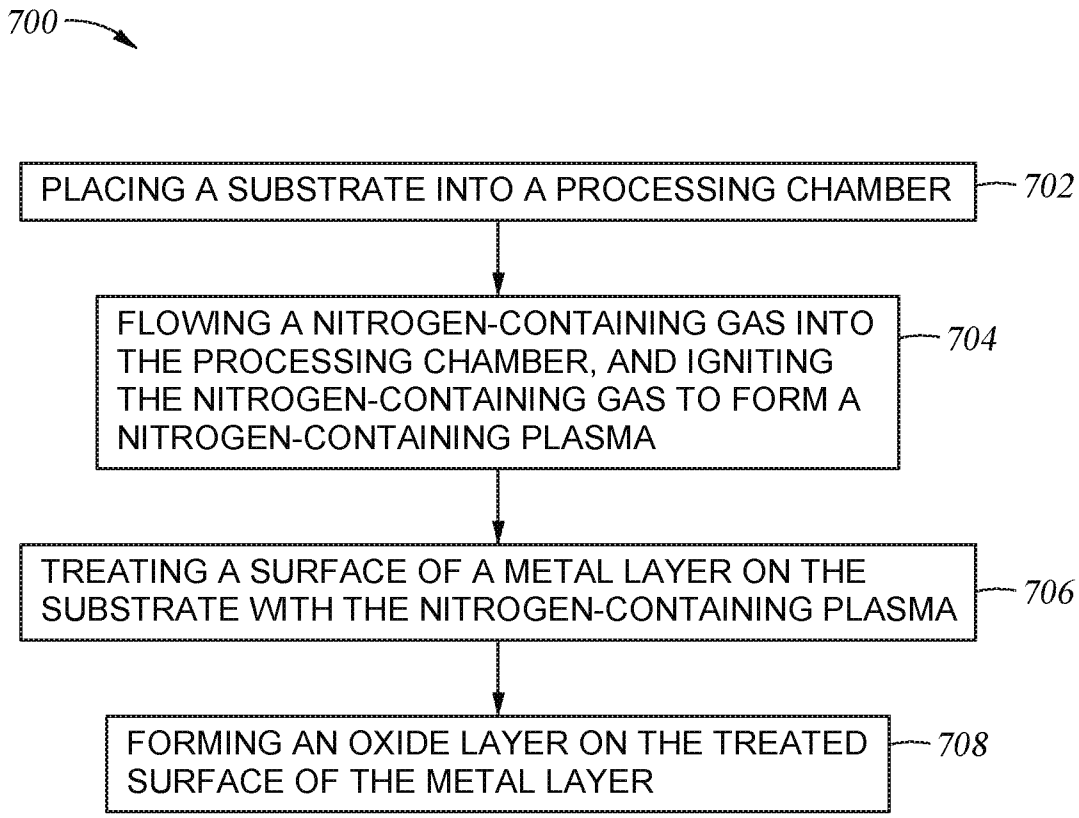
700
PLACING A SUBSTRATE INTO A PROCESSING CHAMBER
702
FLOWING A NITROGEN-CONTAINING GAS INTO THE PROCESSING CHAMBER, AND IGNITING THE NITROGEN-CONTAINING GAS TO FORM A NITROGEN-CONTAINING PLASMA
704
TREATING A SURFACE OF A METAL LAYER ON THE SUBSTRATE WITH THE NITROGEN-CONTAINING PLASMA
706
FORMING AN OXIDE LAYER ON THE TREATED SURFACE OF THE METAL LAYER
708

Fig. 7

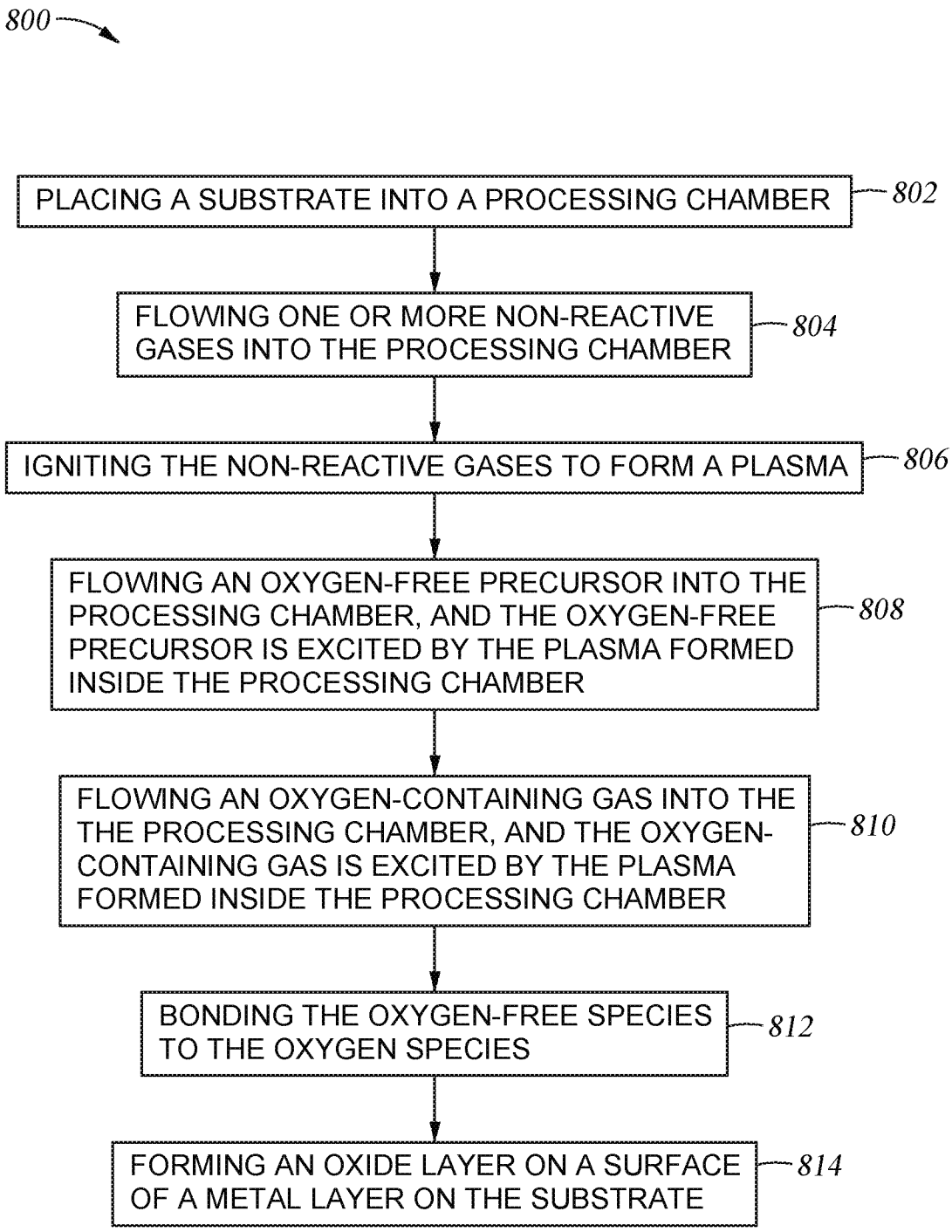
800
PLACING A SUBSTRATE INTO A PROCESSING CHAMBER
802
FLOWING ONE OR MORE NON-REACTIVE GASES INTO THE PROCESSING CHAMBER
804
IGNITING THE NON-REACTIVE GASES TO FORM A PLASMA
806
FLOWING AN OXYGEN-FREE PRECURSOR INTO THE PROCESSING CHAMBER, AND THE OXYGEN-FREE PRECURSOR IS EXCITED BY THE PLASMA FORMED INSIDE THE PROCESSING CHAMBER
808
FLOWING AN OXYGEN-CONTAINING GAS INTO THE THE PROCESSING CHAMBER, AND THE OXYGEN-CONTAINING GAS IS EXCITED BY THE PLASMA FORMED INSIDE THE PROCESSING CHAMBER
810
BONDING THE OXYGEN-FREE SPECIES TO THE OXYGEN SPECIES
812
FORMING AN OXIDE LAYER ON A SURFACE OF A METAL LAYER ON THE SUBSTRATE
814

Fig. 8

Fig. 9A

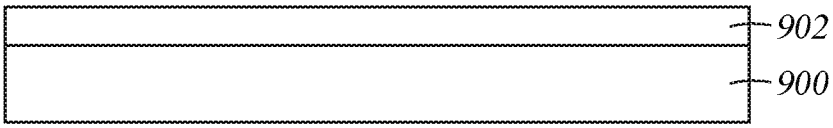

Fig. 9B

Fig. 9C

Fig. 9D

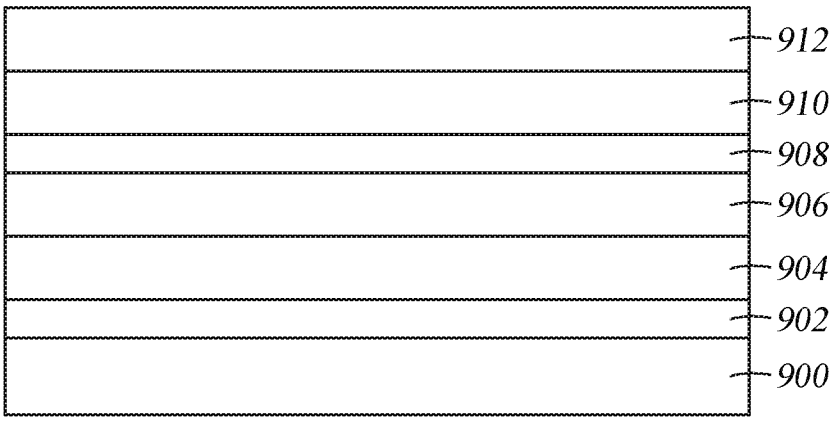

Fig. 9E

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/039317

A. CLASSIFICATION OF SUBJECT MATTER

H01L 21/02(2006.01)i, H01J 37/32(2006.01)i, H01L 21/324(2006.01)i, H01L 27/11551(2017.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L 21/02; H01L 27/115; H01L 21/28; C23C 16/40; H01L 21/316; H01L 21/31; C25D 3/00; C25D 5/10; H01J 37/32; H01L 21/324; H01L 27/11551

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: 3D NAND, metal-oxide stack, nitride, frequency, oxidation

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015-0206757 A1 (APPLIED MATERIALS, INC.) 23 July 2015 See claims 11, 12, 17 and figure 4A.	12,13
A		1-11,14,15
A	US 2010-0173501 A1 (HIRONOBU MIYA et al.) 08 July 2010 See paragraph [0078] and claim 1.	1-15
A	JP 5813303 B2 (HITACHI KOKUSAI ELECTRIC INC.) 17 November 2015 See paragraphs [0064]-[0070].	1-15
A	JP 4595702 B2 (TOKYO ELECTRON LTD.) 08 December 2010 See paragraphs [0031]-[0037] and figure 3.	1-15
A	US 2011-0180413 A1 (JOHN D. WHITAKER et al.) 28 July 2011 See paragraphs [0046]-[0049] and figure 2.	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 September 2017 (14.09.2017)	**15 September 2017 (15.09.2017)**

Name and mailing address of the ISA/KR
International Application Division
Korean Intellectual Property Office
189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea
Facsimile No. +82-42-481-8578

Authorized officer
LEE, Myung Jin
Telephone No. +82-42-481-8474

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2017/039317

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Information on patent family members

International application No.

PCT/US2017/039317

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