METHOD FOR FILLING METAL AND SUBSTRATE PROCESSING DEVICE

TECHNICAL FIELD

[0001] The present disclosure relates to a method of embedding a metal and a substrate processing apparatus.

BACKGROUND

[0002] Wiring that constitutes a circuit in a semiconductor device is formed by forming a metal film on a semiconductor wafer (hereinafter referred to as a wafer) provided with recesses using, for example, a chemical vapor deposition (CVD) method or an atomic layer deposition (ALD) method. Meanwhile, as semiconductor devices have become increasingly highly integrated, wiring has become more difficult to form due to reductions in line width and spacing between adjacent wiring lines. Further, since narrower wiring exhibits a higher electrical resistance, the adoption of a metal material having a lower specific resistance has been considered.

[0003] For example, Patent Document 1 discloses a memory array of a semiconductor memory device. The memory cell array is constituted by a stack including a plurality of stacked metal layers serving as control electrodes, intermediate layers, and insulating layers. Patent Document 1 discloses that the metal layers serving as the control electrodes are molybdenum layers having a low electrical resistance.

[Prior Art Document]

[Patent Document]

[0004] Patent Document 1: Japanese Laid-Open Patent Publication No. 2016-201407

SUMMARY

[0005] The present disclosure provides a technique for preventing shape defects in metal

wiring formed in recesses by forming a metal-containing film on a semiconductor wafer, while reducing the resistivity of wiring.

[0006] According to one embodiment of the present disclosure, a method of embedding a metal in a recess formed in a substrate, includes: forming a metal nitride film on the substrate having the recess and embedding a metal nitride in the recess; and subsequently, forming a metal film of a metal contained in the metal nitride on an upper surface of the metal nitride film to cause nitrogen atoms to diffuse from the metal nitride film toward the metal film, and keeping the recess filled with the metal having a reduced nitrogen content.

[0007] According to the present disclosure, it is possible to prevent shape defects in metal wiring formed in recesses by forming a metal-containing film on a semiconductor wafer, and to reduce the specific resistance of wiring.

BRIEF DESCRIPTION OF DRAWINGS

[0008] FIG. 1A is an SEM image illustrating a surface layer of a wafer as a processing target.

FIG. 1B is an SEM image illustrating a surface layer of a wafer on which a metal film has been formed by a method according to a comparative embodiment.

FIG. 2A is a first longitudinal side view of a wafer according to a process of an embodiment.

FIG. 2B is a second longitudinal side view of the wafer according to the process of the embodiment.

FIG. 2C is a third longitudinal side view of the wafer according to the process of the embodiment.

FIG. 2D is a fourth longitudinal side view of the wafer according to the process of the embodiment.

FIG. 2E is a fifth longitudinal side view of the wafer according to the process of the embodiment.

FIG. 2F is a sixth longitudinal side view of the wafer according to the process of the embodiment.

FIG. 3 is a plan view of a substrate processing apparatus according to an embodiment.

FIG. 4 is a longitudinal side view illustrating a processing module of the substrate processing apparatus.

FIG. 5A is a first graph illustrating test results of Experiment 1.

FIG. 5B is a second graph illustrating test results of Experiment 1.

FIG. 5C is a third graph illustrating test results of Experiment 1.

FIG. 5D is a fourth graph illustrating test results of Experiment 1.

FIG. 6 is a sixth graph illustrating test results of Experiment 1.

FIG. 7A is a first SEM image illustrating test results of Experiment 2.

FIG. 7B is a second SEM image illustrating test results of Experiment 2.

FIG. 7C is a third SEM image illustrating test results of Experiment 2.

FIG. 8A is a first SEM image illustrating test results of a reference example.

FIG. 8B is a second SEM image illustrating test results of the reference example.

DETAILED DESCRIPTION

[0009] A method of embedding a metal in a recess of a wafer W as a substrate according to the present disclosure (hereinafter, referred to as a metal embedding method), will be described below. In the following embodiment, descriptions will be given with reference to a processing example in which a wiring metal constituting buried word line structures bWL of a DRAM is formed on the wafer W formed of a silicon (Si) substrate. First, a configuration of the wafer W as a processing target will be described with reference to FIG. 1A. FIG. 1A is an SEM image illustrating a cross-section of a surface layer portion of the wafer W as a processing target.

[0010] Although a detailed shape will be described with reference to FIG. 2A and the like,

the surface layer portion of the wafer W is composed of, for example, a Si layer 10 on a surface of the wafer W and a silicon oxide film (SiO_x film) 10a formed on the Si layer 10. The SiO_x film 10a is formed as an interlayer insulating film. As illustrated in FIG. 2A, which is a schematic cross-sectional view of the surface layer portion, a plurality of convex-concave portions formed by etching are arranged on a surface of the Si layer 10, and surfaces of the convex-concave portions are covered with the SiO_x film 10a. The SiO_x film 10a has a relatively large thickness of, for example, about 60 nm at an upper end portion of a sidewall 14, while the thickness of the other portion is relatively small, for example, about 1 to 3 nm. The surface layer portion of the wafer W composed of the Si layer 10 and the SiO_x film 10a as described above includes recesses 11 and the sidewalls 14 defined on both sides of the recesses 11.

[0011] These recesses 11 are vertically-elongated trenches extending in a direction perpendicular to the paper in the figure and opened toward upper surfaces thereof. As illustrated in FIG. 1A, the plurality of recesses 11 are arranged at intervals of, for example, about 20 to 50 nm. Each of the plurality of recesses 11 forms a relatively deep and narrow groove. Further, each recess has an opening width of about 10 to 20 nm and a depth of about 100 to 250 nm. The width of the recess 11 is smallest at a lower end, gradually increases upward, and is greatest at an opening of the recess. The width of each of the sidewalls 14 on both sides of the recess 11 is greatest at a lower end, gradually decreases upward, and is smallest at a tip end pf each sidewall.

[0012] Each sidewall 14 has a shape that is readily bendable since it has a large dimension from a base end to an upper end thereof and a small width as described above. In the present embodiment, a metal-containing film (metal film) 12 is formed in the recess 11 defined by the sidewalls 14 having such a configuration, thereby forming a wiring metal (metal) 13 having a relatively low specific resistance. An object of this example is to form metal wiring having a specific resistance equal to or higher than that of titanium nitride (TiN), which has been used in the related art, as described in an Example below. From this

viewpoint, molybdenum (Mo) was selected as a wiring material capable of achieving a lower specific resistance than TiN.

[0013] Here, before describing the metal embedding method of the present disclosure, a method according to a comparative embodiment, which is compared with the metal embedding method of the present disclosure, will be described with reference to FIG. 1B. FIG. 1B is an SEM image illustrating a surface layer of the wafer W on which a metal film 12M has been formed by the method according to the comparative embodiment. In addition, the metal film 12M is formed under a condition that a film thickness would be 10 nm when formed on the flat wafer W. Hereinafter, even when a film is formed on the wafer W having the recesses 11, the film may simply be referred to as a film having a film thickness of 10 nm.

[0014] The metal film 12M is made of molybdenum (Mo). In the metal embedding method of the comparative embodiment, the metal film 12M is formed on the wafer W having the structure illustrated in FIG. 1A by an ALD method, which provides isotropic film formation, so as to fully fill the entire recess 11. At this time, the metal film 12M formed on each sidewall 14 of the recess 11 increases in thickness along a surface of the sidewall 14. Therefore, the metal films 12M formed on the both surfaces of the sidewalls 14 become closer to each other as the thickness increases.

[0015] Here, it has been confirmed that, when the metal films 12M facing each other in the recess 11 have a thickness of, for example, about 10 nm, and a gap therebetween becomes narrow, the two sidewalls 14 defining the recess 11 bend toward the center of the recess 11 so as to be attracted to each other, thereby reducing the opening width of the recess 11, as illustrated in FIG. 1B. This phenomenon is considered to be caused by van der Waals forces that attract the metal films 12M growing along the respective sidewalls 14 toward each other. On the other hand, when the sidewalls 14 bend toward the center of the recess 11 and the opening width thereof is reduced as described above, the sidewalls 14 of the adjacent recess 11 bend outward, thereby increasing the opening width of the adjacent recess 11. This

phenomenon is also referred to as line bending since it occurs along the extending direction of the trench formed by the recess 11.

[0016] In the example illustrated in FIG. 1B, the recesses 11 having a reduced opening width and the recesses 11 having an increased opening width are substantially alternately arranged. When the metal film 12M is formed in the recess 11 deformed as described above until it fully fills the entire recess 11, a wiring metal having a small wiring width and a wiring metal having a large wiring width are formed in the recesses 11, resulting in shape defects. As described above, according to the metal embedding method of the comparative embodiment in which a metal such as Mo is embedded in the trench formed by the recess 11, it has been found that the specific resistance of the wiring metal may be reduced as compared with TiN, but the wiring metal may exhibit shape defects.

[0017] Hereinafter, a plurality of other comparative embodiments that were investigated will be briefly described. In order to prevent shape defects caused by the metal film 12M in the comparative embodiments, a technique may be employed in which, for example, a metal nitride film having weaker van der Waals forces than a metal film is formed, as in an Example (FIG. 7A) described later. The metal nitride film contains Mo and nitrogen (N) as constituent elements and contains no other elements. Specifically, the metal nitride film is made of molybdenum nitride (Mo_2N).

[0018] The metal nitride film, which has weaker van der Waals forces than a metal film, exerts a small bending force on the opposing sidewalls 14 even when being formed on an inner surface of the recess 11, thereby preventing variations in the width of the wiring metal. However, since the metal nitride film has a higher specific resistance than the metal film, specifically about 100 times that of the metal film, the wiring metal has a high resistance when it has an extremely small width as in the present embodiment.

[0019] Accordingly, in order to eliminate such a high specific resistance state, it was investigated to form the metal nitride film and then perform annealing multiple times to release nitrogen from the metal nitride film. However, as illustrated in a reference example

(FIGS. 8A and 8B) described later, the metal nitride film after the annealing underwent significant shrinkage, resulting in structural collapse. As described above, the problem addressed by the present disclosure could not be solved even when the annealing was performed multiple times on the metal nitride film,.

[0020] Further, as another approach, it was also investigated to form a metal film after forming a metal nitride film. It was considered that, by providing the metal nitride film on the surface of the sidewall 14, which is thin in the width direction and long in the depth direction, the sidewall 14 would be reinforced and thereby become less susceptible to bending. It was further intended that, by forming the metal film on the metal nitride film, the specific resistance of a wiring metal itself would be reduced. However, the opposing metal films in the recess 11 still exhibit relatively strong van der Waals forces, the sidewalls 14 were still bent toward each other as if attracted to each other. As a result, shape defects of a wiring metal composed of the metal nitride film and the metal film could not be prevented.

[0021] As described above, after investigating various comparative embodiments, the present inventors found processing according to the present embodiment, which is capable of reducing both the shape defects of the wiring metal 13 and a reduction in the specific resistance thereof. Hereinafter, a wiring technique according to the present embodiment will be described with reference to FIGS. 2A to 2F. FIGS. 2A to 2F are enlarged cross-sectional views illustrating the recess 11 and the two sidewalls 14 defining the recess 11. As illustrated in FIG. 2D, the metal-containing film 12 formed in the present embodiment includes a lower metal film 12a, a metal nitride film 12b, and an upper metal film 12c. Hereinafter, the lower metal film 12a and the upper metal film 12c may collectively be referred to as the metal films 12a and 12c, and the lower metal film 12a, the metal nitride film 12b, and the upper metal film 12c may simply be referred to as the films 12a, 12b, and 12c, respectively.

[0022] In the processing according to the present embodiment, the lower metal film 12a

(FIG. 2A), the metal nitride film 12b (FIGS. 2B and 2C), and the upper metal film 12c (FIG. 2D) are formed on the wafer W illustrated in FIG. 1A in this order. Thereafter, annealing (FIG. 2E) is performed to form the wiring metal 13 (FIG. 2F).

[0023] Like the metal film 12M of the comparative embodiment, the lower metal film 12a is made of Mo, and contains neither nitrogen (N) nor any other metal as a constituent element. Then, as illustrated in FIG. 2A, the lower metal film 12a is formed on an unprocessed surface of the wafer W, for example, by an ALD method, as in the comparative embodiment. At this time, the lower metal film 12a is formed to have a relatively small film thickness such that bending of the sidewall 14 does not occur, as in the above-described comparative embodiment. Specifically, the film thickness of the lower metal film 12a is preferably about 2 to 3 nm, for example, although it may be as great as about 7.5 nm. The film thickness of the lower metal film 12a at which bending of the sidewalls 14 does not occur may be determined in advance through, for example, a preliminary test.

[0024] As illustrated in FIG. 2A, the lower metal film 12a formed under this film thickness condition is formed at a substantially uniform film thickness on a surface of the SiO_x film 10a, specifically, on the inner surface of the recess 11 and on the surface of the SiO_x film 10a outside the recess 11. Since the lower metal film 12a is thin, van der Waals forces acting between opposing films 12a are small, thereby preventing bending of the sidewall 14. On the other hand, by providing the lower metal film 12a, which has a relatively low specific resistance, so as to be in contact with the SiO_x film 10a constituting a side surface and a bottom surface of the recess 11, a resistance value in an interfacial region between the SiO_x film 10a and the wiring metal 13 (FIG. 2F) may be reduced.

[0025] The lower metal film 12a is formed by alternately supplying a molybdenum-containing gas, which serves as a raw material gas, and a reducing gas to the wafer W, with the supply of a purge gas interposed therebetween, while the wafer W illustrated in FIG. 1A is heated to, for example, 580 degrees C. The molybdenum-containing gas is, for example, a molybdenum dioxide dichloride (MoO_2Cl_2) gas, the reducing gas is, for example, a H_2 gas,

and the purge gas is, for example, an inert gas such as argon (Ar) gas. The molybdenum-containing gas, the reducing gas, and the purge gas do not contain nitrogen as a constituent element.

[0026] Next, as illustrated in FIG. 2B, the metal nitride film 12b is formed on a surface of the lower metal film 12a by, for example, an ALD method. The metal nitride film 12b contains Mo and N as constituent elements and contains no other elements. Specifically, the metal nitride film 12b is made of molybdenum nitride (Mo_2N). The Mo_2N constituting the metal nitride film 12b has a higher specific resistance and weaker van der Waals forces than Mo. Accordingly, even when the metal nitride film 12b is formed on the inner surface of the recess 11, bending of the opposing sidewalls 14 as if attracted to each other with the recess 11 interposed therebetween may be prevented.

[0027] As the thickness of the metal nitride film 12b on the lower metal film 12a increases, the recess 11 is gradually filled with the metal nitride, and eventually the entire recess 11 is fully filled (FIG. 2C). The metal nitride film 12b fully filling the entire recess 11 has a longitudinal cross-sectional shape that is wedge-shaped, with the width decreasing toward the bottom.

[0028] The expression "fully filling the entire recess 11 with the metal nitride film 12b" means that an internal space of the recess 11 is substantially filled with the metal nitride film 12b, but the upper side of the internal space of the recess 11 may remain slightly unfilled after the formation of the metal nitride film 12b. Once the entire recess 11 has been fully filled with the metal nitride film 12b, the formation of the metal nitride film 12b is terminated.

[0029] The metal nitride film 12b is formed, for example, using an ALD method by alternately supplying a molybdenum-containing gas and a nitrogen-containing gas, which are raw material gases, to the wafer W, with the supply of a purge gas interposed therebetween, while the wafer W illustrated in FIG. 1A is heated to, for example, 400 degrees C. The molybdenum-containing gas is, for example, a MoO_2Cl_2 gas, and the nitrogen-containing gas

is, for example, an ammonia (NH_3) gas. Alternatively, the nitrogen-containing gas may be a nitrogen (N_2) gas. The purge gas is, for example, an inert gas such as argon (Ar) gas. The molybdenum-containing gas and the purge gas may contain nitrogen as a constituent element. When a purge gas containing nitrogen is supplied, the supply of the nitrogen-containing gas described above may be omitted.

[0030] Next, as illustrated in FIG. 2D, the upper metal film 12c is formed on a surface of the metal nitride film 12b using an ALD method, so as to have an approximately uniform thickness. At this time, the upper metal film 12c may alternatively be formed by another anisotropic film forming method. Like the lower metal film 12a, the upper metal film 12c contains Mo as a constituent element, and contains neither nitrogen nor any other metal. Since the upper metal film 12c is provided on the surface of the metal nitride film 12b, the thickness thereof does not need to be limited as in the case of the lower metal film 12a. The lower metal film 12a is preferably formed to have a thickness sufficient for carrying out a process described later for releasing nitrogen atoms from the metal nitride film 12b. Specifically, the thickness of the upper metal film 12c is preferably, for example, about 10 to 30 nm. However, the thickness of the upper metal film 12c may be approximately the same as that of the lower metal film 12a as long as the release of the nitrogen atoms from the metal nitride film 12b is possible.

[0031] The metal nitride film 12b provided between the lower and upper metal films 12a and 12c has a lower surface and an upper surface in contact with the lower and upper metal films 12a and 12b, respectively, each of which has a lower nitrogen concentration than the metal nitride film 12b. Therefore, nitrogen in the metal nitride film 12b is diffused into the metal films 12a and 12c via respective interfacial regions between the metal films 12a and 12c and the metal nitride film 12b (as indicated by solid arrows in FIG. 2E). Then, in the case of the upper metal film 12c, which is exposed to, for example, a clean depressurized atmosphere or an atmospheric atmosphere, for example, nitrogen is released from a surface of the upper metal film 12c when the concentration of the diffused nitrogen increases to a

certain level. In order to allow this phenomenon to proceed sufficiently throughout the metal-containing film 12, annealing is performed on the wafer W on which the upper metal film 12c has been formed.

[0032] In the annealing, the wafer W placed, for example, in a depressurized atmosphere is heated to, for example, 580 degrees C while the reducing gas is supplied. The reducing gas is, for example, a hydrogen (H_2) gas, which may prevent oxidation of the metal-containing film 12. Such annealing allows nitrogen to be diffused from the entire metal nitride film 12b, including a deep region provided inside the recess 11 having a relatively high aspect ratio, thereby equalizing the nitrogen concentration throughout the metal-containing film 12 including a deep region. Further, the annealing promotes the release of nitrogen from the surface of the upper metal film 12c. During the release of nitrogen, nitrogen atoms may be directly released from the surface of the upper metal film 12c, and reaction products (nitrogen compounds) of nitrogen with, for example, oxygen contained in the film and derived from the reducing gas or the molybdenum-containing gas as a raw material gas may also be released.

[0033] In the upper metal film 12c having a relatively low nitrogen concentration due to such release, nitrogen continues to be diffused from the metal nitride film 12b having a relatively high nitrogen concentration. As a result, the nitrogen concentration in the metal nitride film 12b gradually decreases. It is also considered that, in the lower metal film 12a which is in contact with the metal nitride film 12b, the nitrogen concentration temporarily increases due to the diffusion of nitrogen from the metal nitride film 12b, but thereafter, the direction of nitrogen diffusion changes toward the metal nitride film 12b in which the nitrogen concentration has decreased, and the nitrogen concentration in the lower metal film 12a decreases again.

[0034] By performing the annealing on the wafer W on which the upper metal film 12c has been formed as described above, the wiring metal 13 having a low specific resistance may be formed with a reduced nitrogen content. In this example, the wiring metal 13 is composed of the lower metal film 12a and the metal nitride film 12b, but, for example, the upper central

side of the wiring metal 13 may be constituted by the upper metal film 12c by embedding the upper metal film 12c in an upper region of the recess 11. Further, any unnecessary portion of the upper metal film 12c may be removed by, for example, etching. According to the method of the present embodiment as described above, after the recess 11 is filled with the metal nitride film 12b having relatively weak van der Waals forces, the upper metal film 12c is formed on the metal nitride film 12b and is then removed by the diffusion of nitrogen. This may reduce the specific resistance of the wiring metal 13 and enable the formation of the wiring metal 13 having a favorable shape and a uniform width.

[0035] A substrate processing apparatus 1 capable of performing the above-described series of processes will now be described with reference to the plan view of FIG. 3. The substrate processing apparatus 1 is configured, for example, as a vacuum processing apparatus of a multi-chamber system. Then, the substrate processing apparatus 1 includes, for example, an atmospheric-pressure transfer chamber 22 maintained in an atmospheric-pressure atmosphere. A load port 21 is provided at the front of the atmospheric-pressure transfer chamber 22 for performing delivery of the wafer W to and from, for example, a transfer container C accommodating the wafer W therein. An opening/closing door 27 is provided in a front wall of the atmospheric-pressure transfer chamber 22 and is opened when performing loading and unloading of the wafer W into and from the transfer container C. Further, a transfer arm 25 for transferring the wafer W is provided inside the atmospheric-pressure transfer chamber 22. Further, when the atmospheric-pressure transfer chamber 22 is viewed from the load port 22 side, an alignment chamber 26 for adjusting the orientation and eccentricity of the wafer W is provided on a left sidewall of the atmospheric-pressure transfer chamber 22.

[0036] Two load lock chambers 23 arranged side by side are connected to a wall surface of the atmospheric-pressure transfer chamber 22 opposite the load port 21. Each load lock chamber 23 has a function of switching the internal atmosphere thereof, with the wafer W accommodated therein, between an atmospheric-pressure atmosphere and a vacuum

atmosphere. A vacuum transfer chamber 24 is disposed behind the load lock chambers 23 as viewed from the atmospheric-pressure transfer chamber 22. The atmospheric-pressure transfer chamber 22 and the vacuum transfer chamber 24 are connected to the respective load lock chambers 23 via gate valves 29.

[0037] An exhaust mechanism (not illustrated) is connected to the vacuum transfer chamber 24, so that an internal space of the vacuum transfer chamber is maintained in a vacuum atmosphere, and a transfer arm 28 is provided in the internal space. Processing modules 101 to 104 are connected to sidewalls of the vacuum transfer chamber 24 in this order in the clockwise direction. The processing module 101 is configured to form the lower metal film 12a, the processing module 102 is configured to form the metal nitride film 12b, and the processing module 103 is configured to form the upper metal film 12c. The processing module 102 corresponds to a metal nitride film forming module, and the processing module 103 corresponds to a metal film forming module. The delivery of the wafer W to and from the processing modules 101 to 104 and the respective load lock chambers 23 is performed by the transfer arm 28.

[0038] Each of the processing modules 101 to 104 includes a processing container 51 configured to be evacuated such that the interior thereof is maintained in a vacuum atmosphere, and a substrate stage 55 (FIG. 4) provided inside the processing container 51 and configured to place the wafer W thereon. Each process is performed inside the processing container 51.

[0039] The substrate processing apparatus 1 includes a controller 20, which is a computer. The controller 20 has a program. The program incorporates instructions (steps) for performing the above-described processing and transfer operation for the wafer W. The program is stored in a storage medium such as a compact disk, a hard disk, a DVD, or non-volatile memory, and is read from the storage medium and installed in the controller 20.

[0040] The controller 20 outputs control signals to the respective parts of the substrate processing apparatus 1 in accordance with the program, thereby controlling operations of the

respective parts. Specifically, the controller 20 controls operations such as the operations of the processing modules 101 to 104, the opening and closing of the respective gate valves 29, the operation of the transfer arm 25, the operation of the transfer arm 28, the operation of the exhaust mechanism, the switching of internal pressures of the load lock chambers 23.

[0041] Regarding a transfer path of the wafer W in the substrate processing apparatus 1, the wafer W is first transferred in the order of the transfer container C→ the load port 21→ the atmospheric-pressure transfer chamber 22→ the load lock chamber 23→ the vacuum transfer chamber 24→ the processing module 101. The wafer W on which the lower metal film 12a has been formed in the processing module 101 is then transferred in the order of the processing module 101→ the vacuum transfer chamber 24→ the processing module 102. The wafer W on which the metal nitride film 12b has been formed in the processing module 102 is then transferred in the order of the processing module 102→ the vacuum transfer chamber 24→ the processing module 103.

[0042] Then, the wafer W on the upper metal film 12c has been formed in the processing module 103 is then transferred in the order of the processing module 103→ the vacuum transfer chamber 24→ the processing module 104. The wafer W that has undergone the annealing in the processing module 104 is transferred in the order of the processing module 104→ the vacuum transfer chamber 24→ the load lock chamber 23→ the atmospheric-pressure transfer chamber 22, and is returned to the transfer container C.

[0043] Next, a configuration example of the processing module 101 will be described as a representative of the processing modules 101 to 104 with reference to the longitudinal side view of FIG. 4. The processing container 51 of the processing module 101 is formed of, for example, aluminum. A transfer port for the wafer W is formed in a sidewall of the processing container 51, and a gate valve G1 for opening and closing the transfer port is provided. An annular exhaust duct 52 having, for example, a rectangular cross-sectional shape is disposed above the sidewall of the processing container 51. A slit 52a is provided along an inner peripheral surface of the exhaust duct 52, and an exhaust port 52b is formed in

an outer wall of the exhaust duct 52. A ceiling wall 54 is provided on an upper surface of the exhaust duct 52 via an insulating member 53 so as to close an upper opening of the processing container 51, and a space between the exhaust duct 52 and the insulating member 53 is hermetically sealed by a seal ring.

[0044] The substrate stage 55 is provided in the interior of the processing container 51 to horizontally support the wafer W. The substrate stage 55 is formed in a disk shape using a ceramic material such as aluminum nitride (AlN) or a metallic material such as aluminum or a nickel alloy. In this example, a heater 56A for heating the wafer W is embedded in the substrate stage 55. The heater 56A heats the wafer W to, for example, the above-described film formation temperature. An outer peripheral region of an upper surface and a side surface of the substrate stage 55 are covered with a cover member formed of a ceramic material such as alumina.

[0045] The substrate stage 55 is connected to a lifting mechanism 57 provided below the processing container 51 via a support member, and is configured to be vertically movable between a processing position indicated by the solid line in FIG. 4 and a delivery position of the wafer W indicated by the one-dot dashed line below the processing position. In FIG. 4, reference numeral 52c denotes a partition member for vertically partitioning the interior of the processing container 51 together with the substrate stage 55 that has been moved up to the processing position. Three support pins 58 (only two of which are illustrated) are provided below the substrate stage 55 inside the processing container 51 so as to be vertically movable by a lifting mechanism provided below the processing container 51. The support pins 58 are configured to be inserted into respective through-holes of the substrate stage 55 located at the delivery position, so as to be able to move upward and downward with respect to an upper surface of the substrate stage 55, and are used to deliver the wafer W between the transfer arm 28 in the vacuum transfer chamber 24 illustrated in FIG. 3 and the substrate stage 55. In the drawings, reference numeral 59 denotes a bellows that isolates the internal atmosphere of the processing container 51 from the outside air and expands and contracts in accordance

with the vertical movement of the substrate stage 55 and the support pins 58.

[0046] The processing container 51 is provided with a shower head 61 facing the substrate stage 55 to supply various gases into the processing container 51 in the form of a shower. The shower head 61 includes a main body fixed to the ceiling wall 54 of the processing container 51, and a shower plate 62 connected below the main body. The interior of the shower head 61 forms a gas diffusion space 63. A downwardly protruding annular protrusion is formed on a peripheral edge of the shower plate 62, and a gas discharge hole 64 is formed in an inner flat surface of the annular protrusion. A gas supply mechanism 6A is connected to the ceiling wall 54 and the main body of the shower head 61.

[0047] The gas supply mechanism 6A includes a raw material gas supply 71A configured to supply a raw material gas to the processing container 51, and a reducing gas supply 72A configured to supply a reducing gas. Further, the gas supply mechanism 6A includes two purge gas supplies 73A configured to supply a purge gas. The raw material gas supply 71A includes a source 74A of the raw material gas and a supply path 75A for the raw material gas. The supply path 75A is provided with a flow rate adjuster M1A, a storage tank T1A, and a valve V1A in this order from the upstream side.

[0048] The reducing gas supply 72A includes a source 76A of the reducing gas and a supply path 77A for the reducing gas. The supply path 77A is provided with a flow rate adjuster M2A, a storage tank T2A, and a valve V2A in this order from the upstream side. Each purge gas supply 73A includes a source 78A of the purge gas and a supply path 79A for the purge gas. The supply path 79A is provided with a flow rate adjuster M3A and a valve V3A. The supply path 79A for one purge gas supply 73A is connected to the purge gas supply path 75A for purging the raw material gas, and the supply path 79A for the other purge gas supply 73A is connected to the reducing gas supply path 77A for purging the reducing gas. As described above, the raw material gas supply 71A, the reducing gas supply 72A, and the purge gas supplies 73A are configured to independently supply the raw material gas, the reducing gas, and the purge gas to the processing container 51, respectively.

[0049] The processing container 51 is connected to a vacuum exhaust path 66 via the exhaust port 52b. A vacuum exhauster 67, which is configured to execute the evacuation of gas from the processing container 51 and includes, for example, a vacuum pump, is provided on the downstream side of the vacuum exhaust path 66. For example, an APC valve (not illustrated) serving as a pressure regulating valve is provided in the vacuum exhaust path 66 between the processing container 51 and the vacuum exhauster 67.

[0050] The other processing modules 102 to 104 have substantially the same configuration as the above-described processing module 101, and differences from the processing module 101 will be briefly described. The processing module 102 for forming the metal nitride film 12b includes a nitrogen-containing gas supply instead of the reducing gas supply 72A illustrated in FIG. 4, and a nitrogen-containing gas source instead of the source 76A. The processing module 104 for performing the annealing may be configured without the raw material gas supply 71A.

[0051] Using the substrate processing apparatus 1 having the configuration described above, an operation of executing a series of processes on the wafer W will be described with reference to FIGS. 3 to 4 illustrating the substrate processing apparatus 1 and FIGS. 2A to 2E illustrating film changes. First, when the transfer arm 28 receives the wafer W as a processing target from the load lock chamber 23 illustrated in FIG. 3, the transfer arm 28 transfers the wafer W to the processing module 101 located at the front left side. Thereafter, the gate valve G1 of the processing module 101 illustrated in FIG. 4 is opened, and the transfer arm 28 introduces the wafer W into the processing container 51 via the loading port. Then, the wafer W is delivered from the transfer arm 28 to the substrate stage 55 using the support pins 58, the transfer arm 28 is retracted from the processing container 51, and the gate valve G1 is closed.

[0052] As described above, the lower metal film 12a is formed in the processing module 101. Based on a recipe for forming the lower metal film 12a at a predetermined film thickness, the internal pressure of the processing container 51 and the temperature of the

wafer W are adjusted, and the raw material gas, the reducing gas, and the purge gas are repeatedly supplied to the processing container 51 in a predetermined order. Thus, the lower metal film 12a is formed at the predetermined film thickness while preventing the bending of the sidewall 14 (FIG. 2A) (an operation of forming an underlayer film).

[0053] Then, the wafer W on which the lower metal film 12a has been formed is unloaded from the processing module 101 in a reverse order of the loading operation, and is transferred to the processing module 102. The wafer W is then loaded into the processing module 102 in the same order as the loading of the wafer W into the processing module 101 where the metal nitride film 12b is formed. Based on a recipe for forming the film so as to fully fill the recess 11, the internal pressure of the processing container 51 and the temperature of the wafer W are adjusted, and the raw material gas, the nitrogen-containing gas, and the purge gas are repeatedly supplied to the processing container 51 in a predetermined order. Thus, the metal nitride film 12b is formed to an extent sufficient to substantially fill the entire recess 11 while preventing the bending of the sidewall 14 (FIGS. 2B and 2C) (an operation of embedding a metal nitride in the recess 11).

[0054] Next, the wafer W on which the metal nitride film 12b has been formed is unloaded from the processing module 102 in the same order as the unloading of the wafer W from the processing module 101, and is loaded into the processing module 103 where the upper metal film 12c is formed. Based on a recipe for forming the upper metal film 12a at a predetermined film thickness, the internal pressure of the processing container 51 and the temperature of the wafer W are adjusted, and the raw material gas, the reducing gas, and the purge gas are repeatedly supplied to the processing container 51 in a predetermined order. Thus, the upper metal film 12c having the predetermined film thickness is formed.

[0055] Thereafter, the wafer W on which the upper metal film 12c has been formed is unloaded from the processing module 103 and is loaded into the processing module 104 where annealing is performed. Based on a recipe for forming the wiring metal 13 from which nitrogen has been sufficiently removed, the internal pressure of the processing

container 51 and the temperature of the wafer W are adjusted, and the reducing gas and the purge gas are simultaneously supplied for a preset period of time, for example, 3 to 8 hours (an operation of supplying a hydrogen gas). Thus, the diffusion and release of nitrogen may be sufficiently performed throughout the metal-containing film 12, which makes it possible to more reliably remove the nitrogen from the entire metal-containing film 12 (FIG. 2E). Then, after the wiring metal 13 having a reduced specific resistance is formed (FIG. 2F), the annealing is terminated (an operation of diffusing nitrogen atoms and keeping the recess 11 filled with a metal having a reduced nitrogen content).

[0056] The wafer W on which the wiring metal 13 has been formed by the annealing is loaded into the load lock chamber 23, and thereafter, is returned to the transfer container C via the load port 21. As described above, according to the substrate processing apparatus 1 and the metal embedding method of the present disclosure, the wiring metal 13 having a reduced specific resistance and a favorable shape may be formed.

[0057] In addition, the annealing, which requires a processing time of several hours, is not limited to being performed in the single-wafer-type processing module 104. For example, after the upper metal film 12c is formed in the processing module (metal film forming module) 103, the wafer W may be returned to the transfer container C, thereby completing the process in the substrate processing apparatus 1. Thereafter, the annealing may be collectively performed on a plurality of wafers U using, for example, a batch-type annealing apparatus.

[0058] Further, the substrate processing apparatus 1 is not limited to including the single-wafer-type processing modules 101 to 103. For example, the substrate processing apparatus 1 may be configured with a batch-type thermal processing module configured to continuously perform the film formation and the annealing. In this case, after a plurality of wafers W before film formation are loaded into the batch-type thermal processing module, gases supplied to the thermal processing module are sequentially switched so that formation of the lower metal film 12a→ formation of the metal nitride film 12b→ formation of the upper

metal film 12c are performed in this order. Thereafter, the gas to be supplied to the thermal processing module is switched to a reducing gas (H_2 gas), and the annealing is performed.

(Modification)

[0059] As described in the above embodiments, it is preferable to form the lower metal film 12a and the metal nitride film 12b in different processing modules 101 and 102 since the film formation may be made more efficient without requiring the pressure and the temperature to be adjusted for each film formation based on the corresponding recipe. However, the present disclosure is not limited thereto. The lower metal film 12a and the metal nitride film 12b may be formed in either one of the processing module 101 or the processing module 102. In this case, the footprint of the substrate processing apparatus 1 may be reduced. Then, for example, when the films 12a and 12b are formed in the common processing module 101, the gas supply mechanism 6A may be provided with the above-described nitrogen-containing gas supply. Further, by forming the metal film 12c in the processing module 101, all of the films 12a to 12c may be formed in the processing module 101 alone, and the annealing may further be performed therein.

[0060] In the embodiments of the present disclosure, the lower metal films 12a to 12c are preferably formed using an isotropic method. However, when the side surface of the recess 11 is not orthogonal to the surface of the wafer but is inclined such that the width of the recess increases upward as illustrated in the present example, the metal films 12a to 12c may also be formed using an anisotropic method such as a CVD method.

[0061] The annealing performed in the present embodiment is not limited to the above-described processing recipe, and the processing recipe may be appropriately changed according to a composition, shape, and thickness of the metal-containing film 12. Further, the annealing is not necessarily essential to the method of the present disclosure, and other techniques may be employed. For example, the wafer W may be subjected to heat treatment under a depressurized atmosphere without supplying a reducing gas. Alternatively, the

wafer W may be subjected to the heat treatment under an atmospheric atmosphere without supplying the reducing gas. Experiments have confirmed that the heat treatment is effective for diffusing and removing the nitrogen from the metal-containing film 12 as described above, and the temperature of the wafer W may be higher than 580 degrees C and no higher than 850 degrees C. However, the present disclosure is not limited to such a temperature range, but is considered highly likely that the heat treatment may also be implemented at temperatures deviating to some extent from the temperature range, for example, at temperatures of about 550 degrees C to about 900 degrees C.

[0062] In the embodiments of the present disclosure, it is not necessarily essential that the recess 11 is a trench. The metal embedding method of the present disclosure is also useful, for example, when a wiring metal is formed in a via. In particular, when the via is extremely narrow and long and a sidewall defining the via is thin, the method of the present disclosure may form a wiring metal having a reduced specific resistance and a favorable shape.

[0063] In the embodiments of the present disclosure, the metal-containing film 12 has been described as containing Mo as a metal, but the present disclosure not limited thereto. The metal-containing film 12 may be made of another metal having a relatively low specific resistance such as aluminum (Al), copper (Cu), tungsten (W), titanium (Ti), silver (Ag), or an alloy thereof. In this case, the lower metal film 12a and the upper metal film 12c do not contain nitrogen as a constituent element.

[0064] In the embodiments of the present disclosure, the lower metal film 12a is formed to reduce the specific resistance of the wiring metal 13. However, this is not necessarily essential, and the lower metal film 12a may be omitted. Although the metal nitride film 12b is formed so as to fully fill the recess 11, this is also not necessarily essential. The upper metal film 12c may be formed in an upper space of the recess 11 without the metal nitride film 12b fully filling the upper space of the recess 11. In this case, the metal nitride film 12b may need only be formed at a film thickness sufficient to prevent the sidewall 14 from

bending due to van der Waals forces exerted by the upper metal film 12c during film formation.

[0065] Further, the upper metal film 12c is formed so as to cover the entire surface of the metal nitride film 12b in order to efficiently diffuse nitrogen from the metal nitride film 12b. However, this merely means that it is preferable for the upper metal film 12c to cover as much of the surface of the metal nitride film 12b as possible, and does not exclude an embodiment in which the upper metal film 12c covers only a portion of the surface of the metal nitride film 12b. Since the upper metal film 12c serves to diffuse and release nitrogen from the metal nitride film 12b disposed in the recess 11 upward, the upper metal film 12c may, for example, be formed so as to cover only the opening region of the recess 11.

[0066] In addition, the embodiments disclosed herein should be considered to be illustrative and not limitative in all respects. The above embodiments may be omitted, replaced, modified, or combined in various ways without departing from the scope and spirit of the appended claims.

Example

(Experiment 1)

[0067] The present inventors have checked on the action of removing the nitrogen from the metal film in the wafer having the metal film formed on the metal nitride film. Specifically, the present inventors has checked differences in such a nitrogen removal action with respect to metal films having different thicknesses formed on a metal nitride film provided on a surface of a bare wafer.

A. Experimental Conditions

Four unpatterned flat bare wafers were prepared. Each of the wafers was prepared by forming a molybdenum nitride (Mo_2N) film on a surface layer, which is a SiO_2 film, and then forming a molybdenum (Mo) film having a different thickness on the molybdenum film,

as in the embodiment. The thickness of the molybdenum nitride film was 15 nm, while the thickness of the molybdenum film was 0 nm (i.e., no molybdenum film was formed), 5 nm, 10 nm, or 20 nm. The wafers were subjected to the heat treatment under the same condition in the depressurized atmosphere in which the diffusion and removal of nitrogen are sufficient, instead of the annealing. After the heat treatment, the surface region of each wafer was analyzed by X-ray photoelectron spectroscopy (XPS) to determine a composition thereof, and measure a sheet resistance thereof.

B. Experiment Results

(1) Composition Analysis Results

[0068] FIGS. 5A to 5D illustrate composition analysis results for the surface regions of the wafers on which the Mo film was formed. Specifically, the graphs illustrate the atomic percentage (At%) at respective depths from an upper surface of each wafer, where silicon (Si) atoms were excluded from the atomic percentage. FIG. 5A illustrates the composition analysis results for the wafer on which no Mo film was formed. A boundary line is indicated at a position corresponding to an interface between the molybdenum nitride film and the SiO_2 film. A region shallower than the interface corresponds to the molybdenum nitride film, and a region deeper than the interface corresponds to the SiO_2 film.

[0069] In the molybdenum nitride film sufficiently distant from the interface, the proportions of Mo atoms and N atoms were approximately 50% and slightly higher than 40%, respectively, while the proportion of oxygen (O) atoms was approximately 5%. The proportions of these atoms were approximately constant with respect to depth. In addition, it was presumed that O atoms in this region originated from the raw material gas described above.

[0070] A region extending from the interface described above and including both a relatively shallow region and a relatively deep region is an interfacial region between the molybdenum nitride film and the SiO_2 film. In the interface region, the proportions of all

atoms other than O atoms decreased sharply, while the proportion of O atoms increased, toward the SiO_2 film. Then, in the SiO_2 film sufficiently distant from the interface, the proportions of Mo atoms, N atoms, and O atoms converged to 10% or less, approximately 0%, and approximately 65%, respectively.

[0071] FIG. 5B illustrates the composition analysis results for the wafer on which the Mo film having a thickness of 5 nm was formed. As illustrated in FIG. 5B, in the molybdenum nitride film and the Mo film sufficiently distant from the interface with the SiO_2 film, the proportions of Mo atoms, N atoms, and O atoms were substantially constant with respect to depth. From this, it was determined that N atoms had sufficiently diffused throughout the molybdenum nitride film and the Mo film. Then, more specifically, as compared with FIG. 5A, the proportion of O atoms increased slightly by approximately 1% to 2%, the proportion of Mo atoms increased to approximately 65%, and the proportion of N atoms decreased to slightly less than approximately 30%.

[0072] In order to consider the proportion of N atoms in the present test results, a reference value was calculated as an approximate proportion of N atoms when N atoms in the molybdenum nitride film were sufficiently diffused into the Mo film having a film thickness of one-third of the film thickness of the molybdenum nitride film and that the proportion of N atoms in these films became uniform. Specifically, based on FIG. 5A, the reference value was calculated assuming that N atoms, which accounted for, for example, 42% in the molybdenum nitride film having a film thickness corresponding to 1, were diffused and uniformly distributed in the molybdenum nitride film and the Mo film having a total film thickness corresponding to 1+1/3. Assuming that the number of N atoms does not change before and after the diffusion, the following relationship is established: 4/3×(reference value)=1×42. Based on this relationship, the reference value of the uniform N atom proportion was calculated to be 31.5%. In contrast, based on FIG. 5B, the proportion of N atoms was reduced to slightly less than 30% as described above. Therefore, it was presumed in the present test results that N atoms were released from the Mo film and the

number of N atoms was reduced.

[0073] FIG. 5C illustrates the composition analysis results for the wafer on which the Mo film having a thickness of 10 nm, which is twice as thick as the Mo film in FIG. 5B, was formed. As illustrated in FIG. 5C, concentration gradients of respective atoms with respect to depth were observed in the molybdenum nitride film and the Mo film, other than the interfacial region with the SiO_2 film. At a depth corresponding to the Mo film, the proportion of Mo atoms was particularly high in a surface portion, exceeding approximately 95%, and decreased with increasing depth from the surface of the Mo film. The proportion of N atoms was approximately 5% or less in the Mo film, increased with increasing depth from the interfacial region between the Mo film and the molybdenum nitride film, and reached approximately 15% at an intermediate depth of the molybdenum nitride film.

[0074] Similarly to FIG. 5B, the reference value of the uniform N atom proportion was calculated assuming that N atoms in the molybdenum film were sufficiently diffused into the Mo film having a film thickness of two-thirds of the molybdenum nitride film and that the proportion of N atoms became uniform throughout these films. Assuming that N atoms, which accounted for 42% in the molybdenum nitride film having a film thickness corresponding to 1, were diffused and uniformly distributed throughout the molybdenum nitride film and the Mo film having a total film thickness corresponding to 1+2/3, the following relationship is established: 5/3×(reference value)=1×42. Thus, the reference value of the uniform N atom proportion was 25.2%. In contrast, the proportion of N atoms in the composition analysis results was, as described above, significantly lower than the reference value at every depth. Accordingly, it is considered from the composition analysis results that doubling the film thickness of the Mo film increased the amount of N atoms released from the Mo film. In addition, the proportion of O atoms was 0%, particularly in the surface portion of the Mo film, and increased with increasing depth from the surface portion. This is considered to indicate that oxygen was also released along with nitrogen during the release of nitrogen from the Mo film.

[0075] FIG. 5D illustrates the composition analysis results for the wafer on which the Mo film having a thickness of 20 nm, which is four times as thick as the Mo film in FIG. 5B, was formed. As illustrated in FIG. 5D, in a region shallower than the intermediate depth of the molybdenum nitride film, the proportion of Mo atoms was 100%, while the proportion of N atoms and O atoms were 0%. Similarly to the above, assuming that N atoms, which accounted for 42% in the molybdenum nitride film having a film thickness corresponding to 1, were diffused and uniformly distributed throughout the molybdenum nitride film and the Mo film having a total film thickness corresponding to 1+4/3, the following relationship is established: 7/3×(reference value)=1×42. The reference value of the uniform N atom proportion was 18%. However, the proportion of N atoms in the composition analysis results was 0% at every depth. In this way, by increasing the thickness of the Mo film to four times that of the Mo film in FIG. 5B so that it became thicker than the molybdenum nitride film, the amount of N atoms released from the Mo film was further increased. Thus, all N atoms were substantially removed and the molybdenum nitride Mo was substantially converted into a Mo film.

(2) Measurement Results of Sheet Resistance

[0076] FIG. 6 is a graph illustrating sheet resistances of the wafers on which the Mo films having different thicknesses described above were formed respectively. For reference as a comparative example, the graph also illustrates the sheet resistance of bare wafers each having a Mo film or a molybdenum nitride film with a varying film thickness on a SiO_2 film formed on a wafer surface, together with the sheet resistance of a titanium nitride (TiN) film having a specific resistance of, for example, 50 μΩcm and a thickness of 20 nm.

[0077] As illustrated in FIG. 6, the sheet resistance of the wafer including the Mo film having a thickness of 5 nm and the molybdenum nitride film having a thickness of 15 nm was approximately an intermediate value between the sheet resistance of the molybdenum nitride film and the sheet resistance of the Mo film, and the specific resistance of the wafer including

the Mo film and the molybdenum nitride film was also approximately an intermediate value between the specific resistance of the molybdenum nitride film and the specific resistance of the Mo film. It was found that the sheet resistance of the wafer having the Mo film having a thickness of 10 nm and the molybdenum nitride film having a thickness of 15 nm was close to the sheet resistance of the TiN film, and the specific resistance of the wafer having both the Mo film and the molybdenum nitride film is substantially the same as the specific resistance of the TiN film. It was found that the sheet resistance of the wafer including the Mo film having a thickness of 20 nm and the molybdenum nitride film having a thickness of 15 nm was reduced to a level comparable to the sheet resistance of the Mo film, and the specific resistance of the wafer having both the Mo film and the molybdenum nitride film was reduced to a level comparable to the specific resistance of the Mo film. It was confirmed from these sheet resistance measurement results that the Mo film removed nitrogen from the molybdenum nitride film, thereby reducing the specific resistance. Then, it was further confirmed that, by increasing the thickness of the Mo film, nitrogen is removed effectively, thereby achieving the sheet resistance and specific resistance comparable to those of the Mo film.

(Experiment 2)

[0078] The present inventors have checked specific resistance and shape changes with respect to a wafer having no film, a wafer having the Mo film, a wafer having the molybdenum nitride film, a wafer having a mixed film of the Mo film and the molybdenum nitride film, and a wafer having the mixed film after annealing, each wafer having a plurality of recesses formed in s surface of a SiO_2 film.

A. Experimental Conditions

Five wafers each having a plurality of recesses identical to those of the above-described embodiment were prepared. One wafer was not subjected to film formation. The Mo film and the molybdenum nitride film were respectively formed on two wafers

according to a film formation recipe for forming a film having a thickness of 20 nm. Then, a mixed film was formed on the remaining two wafers. The mixed film was formed according to a film formation recipe for sequentially forming the Mo film having a thickness of 7.5 nm, the Mo film having a thickness of 15 nm, and the Mo film having a thickness of 15 nm in this order. One of these two wafers was then subjected to the annealing exemplified in the above-described embodiment (580 degrees C for 3 hours).

Film-formed portions of the wafers were observed using a scanning electron microscope (SEM) to evaluate shape changes, and measure the specific resistance. In addition, the specific resistance was measured using films formed according to the same film formation recipes on flat wafers having no recesses.

B. Experiment Results

(1) Shape Changes

[0079] FIGS. 7A to 7C illustrate SEM images of the molybdenum nitride film, the mixed film without annealing, and the mixed film after annealing, respectively. The SEM images of the wafer having no film and the Mo film are omitted. The widths of the recesses were measured from the acquired SEM images, and the amount of bending displacement, which indicates the degree of bending of the sidewall, was calculated. The bending of the sidewall causes narrow recesses and wide recesses to be arranged alternately. Therefore, the amount of bending displacement was calculated by measuring the width of each recess and determining the difference between the average width of the wide recesses and the average width of the narrow recesses.

[0080] The amount of bending displacement was 7.5 nm for the wafer having no film, 31.1 nm for the Mo film, 4.32 nm for the molybdenum nitride film, 11.2 nm for the mixed film without annealing, and 10.0 nm for the mixed film after annealing. These results demonstrate that the amounts of bending displacement of both the mixed films were significantly reduced as compared with the amount of bending displacement of the Mo film

and approached the amount of bending displacement of the wafer having no film. Then, it was considered that the annealing provides a more favorable film shape since the mixed film after annealing exhibited a slightly smaller amount of bending displacement than the mixed film without annealing.

[0081] As illustrated by the grayscale images in FIGS. 7B and 7C, the respective films in the mixed film without annealing may be distinguished by differences in grayscale intensity. In contrast, the mixed film after annealing exhibits substantially no grayscale contrast and appears as a uniform film. From this, it was confirmed that nitrogen had sufficiently diffused throughout the mixed film by annealing, thereby forming a mixed film having a uniform nitrogen content. On the other hand, as illustrated in FIG. 7B, according to the above-described film formation recipe, a relatively light-gray Mo film was formed as a thin layer covering the sidewall, and a relatively dark-gray molybdenum nitride film was formed so as to cover the Mo film, thereby fully filling the entire recess. Then, the light-gray Mo film uniformly covering the surface of the molybdenum nitride film was formed thicker than the molybdenum nitride film located on the upper end of the sidewall. This is considered to be because nitrogen had diffused during annealing, and the interfacial region of the molybdenum nitride film adjacent to the Mo film was converted into a Mo film.

(2) Specific resistance

[0082] The electrical resistance of each film formed according to the same film formation recipe on a separate wafer having a flat surface was measured, and the specific resistance was calculated based on the measured electrical resistance and the electrical resistance of the wafer before film formation. The Mo film having a film thickness of 20.5 nm exhibited a specific resistance of 14 μΩcm, while the molybdenum nitride film having a film thickness of 14 nm exhibited a specific resistance of 1,294 μΩcm. The mixed film without annealing, having a film thickness of 24.1 nm, exhibited a specific resistance of 15 μΩcm, while the mixed film after annealing, having a film thickness of 28.8 nm, exhibited a specific resistance

of 14 μΩcm. Thus, the mixed films exhibited resistivities comparable to that of the Mo film, regardless of whether annealing was performed. Then, the specific resistance of the mixed film after annealing was lower than that of the mixed film without annealing.

(Reference Example)

[0083] An experiment was conducted to determine whether nitrogen in a molybdenum nitride film could be released and removed by annealing without providing a Mo film. In the experiment, a molybdenum nitride film having a film thickness of 15 nm was formed on a wafer having a plurality of recesses identical to those of the comparative embodiment using a corresponding film formation recipe. Thereafter, the same annealing as that employed in Experiment 2 was performed, and the respective regions were examined by SEM.

[0084] FIG. 8A is an SEM image of a surface of the wafer, and FIG. 8B is an SEM image of a cross section of the wafer. Voids resembling local cracks were observed in several locations on the surface of the annealed molybdenum nitride film. This is considered to be because annealing increased the difference in film density between the molybdenum nitride film and the sidewall, causing the molybdenum nitride film to shrink relative to the sidewall, resulting in delamination and cracking. Further, in the cross-sectional view of the molybdenum nitride film, stress was found to have been generated in the sidewall due to the shrinkage of the molybdenum nitride film, and structural collapse of the sidewall was confirmed.

[0085] The electrical resistance of the annealed molybdenum nitride film was also evaluated. Specifically, the sheet resistance of an annealed molybdenum nitride film formed on a flat wafer using the same film formation recipe and the same annealing was measured. The results showed that the annealed molybdenum nitride film exhibited intermediate sheet resistance and specific resistance values between those of the molybdenum nitride film and the Mo film.

[0086] As described above, even when the molybdenum nitride film not covered with a Mo

film was subjected to annealing, it was not possible to achieve both prevention of shape defects and a reduction in specific resistance. In contrast, it was confirmed that, when a molybdenum nitride film covered with a Mo film was formed as in the present example, both of these objectives could be achieved, and that annealing further enhanced these effects. Further, it is presumed that no structural collapse was observed in the annealed mixed film because Mo atoms in the Mo film, which has a higher film density than the molybdenum nitride film, had diffused into the molybdenum nitride film and inhibited shrinkage thereof. Accordingly, it is considered that, according to the metal embedding method of the present example, a wiring metal capable of preventing shape defects and reducing specific resistance may be formed.

EXPLANATION OF REFERENCE NUMERALS

[0087] W: wafer, 12b: metal nitride film, 12c: upper metal film, 11: recess, 13: wiring metal

WHAT IS CLAIMED IS:

1. A method of embedding a metal in a recess formed in a substrate, the method comprising:

forming a metal nitride film on the substrate having the recess and embedding a metal nitride in the recess; and

subsequently, forming a metal film of a metal contained in the metal nitride on an upper surface of the metal nitride film to cause nitrogen atoms to diffuse from the metal nitride film toward the metal film, and

keeping the recess filled with the metal having a reduced nitrogen content.

2. The method of Claim 1, wherein the keeping the recess filled with the metal having the reduced nitrogen content includes

performing heating at a temperature within a range of 550 to 900 degrees C under a depressurized atmosphere.

3. The method of Claim 2, wherein the performing heating includes supplying a hydrogen gas.

4. The method of Claim 1, further comprising, before the embedding the metal nitride in the recess, forming an underlayer film of the metal in the recess.

5. The method of Claim 1, wherein, in the embedding the metal nitride in the recess, the metal nitride film is formed so that the recess is fully filled with the metal nitride.

6. The method of Claim 1, wherein the metal constituting the metal nitride film and the metal film is molybdenum.

7. The method of Claim 1, wherein the recess includes a plurality of recesses arranged in one direction along a surface of the substrate, and each of the plurality of recesses is formed to extend in a direction intersecting the one direction along the surface of the substrate.

8. The method of Claim 1, wherein the metal having the reduced nitrogen content has a specific resistance within a range of 10 to 50 μΩcm.

9. A substrate processing apparatus for embedding a metal in a recess formed in a substrate, the substrate processing apparatus comprising:

a metal nitride film forming module configured to form a metal nitride film on the substrate having the recess and embed a metal nitride in the recess; and

a metal film forming module configured to form a metal film of a metal contained in the metal nitride on an upper surface of the metal nitride film to cause nitrogen atoms to diffuse from the metal nitride film toward the metal film, and keeping the recess filled with the metal having a reduced nitrogen content.