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(54) SUBSTRATE PROCESSING METHOD AND SUBSTRATE PROCESSING APPARATUS

(75) Inventor: **Hidenori MIYOSHI**, Nirasaki-shi (JP)

(73) Assignee: **TOKYO ELECTRON LIMITED**, Minato-ku (JP)

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(57) **ABSTRACT**

A substrate processing method for removing a copper oxide film on a surface of Cu and a Cu-containing residue adhered to an interlayer insulating film in a Cu wiring structure on a substrate by using an organic acid-containing gas is provided. The substrate processing method includes removing the Cu-containing residue by etching by supplying the substrate with a processing gas containing an organic acid gas, after the temperature of the substrate is set to be maintained at a first temperature; and removing the copper oxide film on the surface of Cu by means of a reduction reaction by supplying the substrate with the processing gas containing the organic acid gas, after the temperature of the substrate is set to be maintained at a second temperature that is higher than the first temperature.

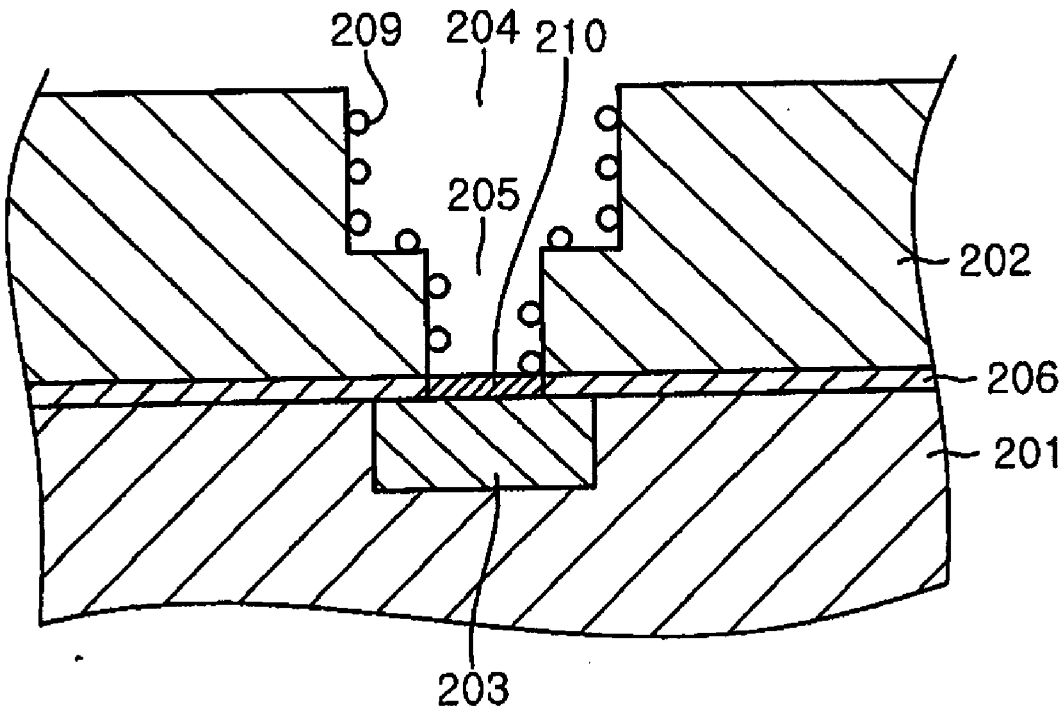


FIG. 1

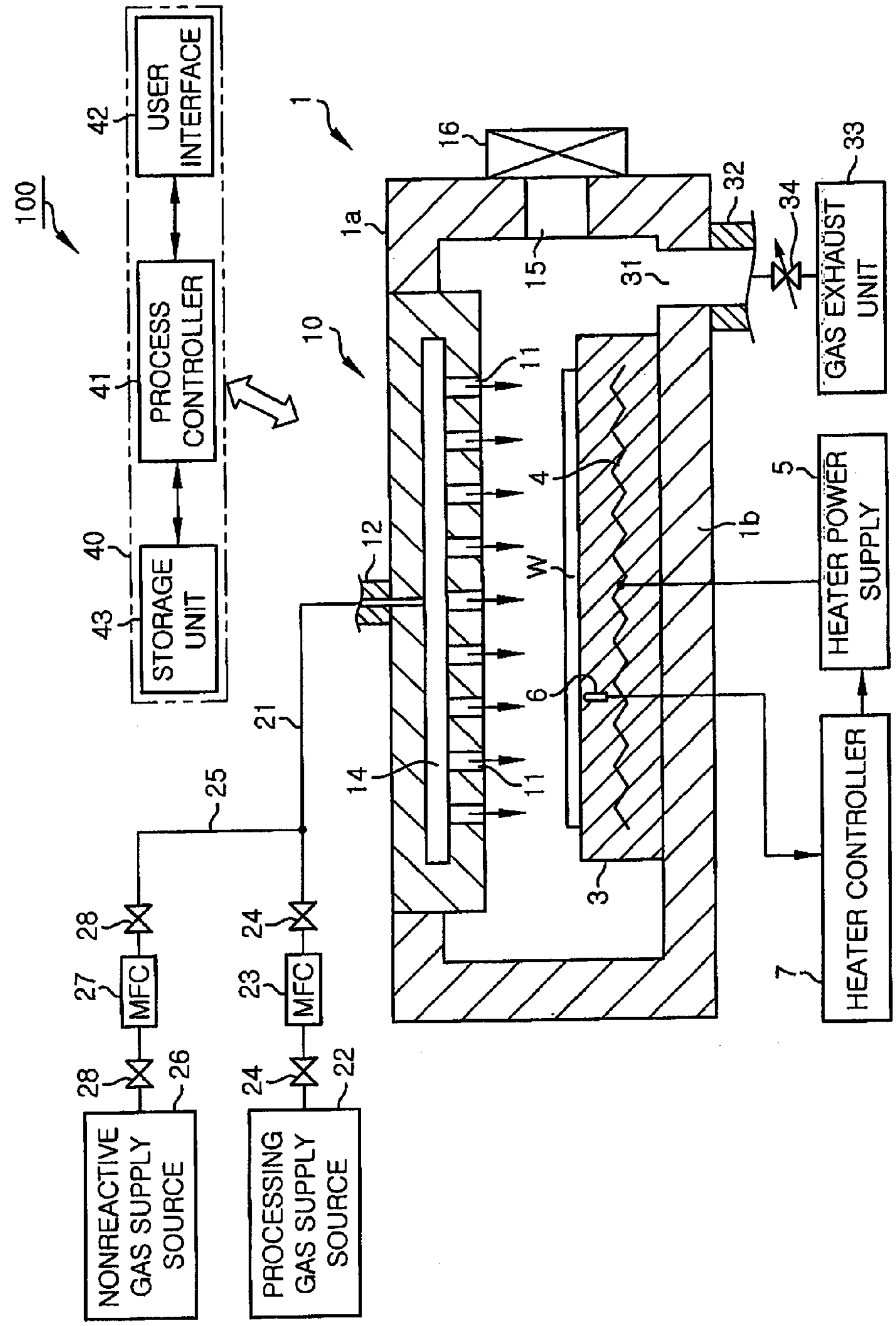

100
STORAGE UNIT
PROCESS CONTROLLER
USER INTERFACE
43
40
41
42
1
10
1a
1b
3
4
5
6
7
W
11
12
14
15
16
21
22
23
24
25
26
27
28
31
32
33
34
MFC
NONREACTIVE GAS SUPPLY SOURCE
PROCESSING GAS SUPPLY SOURCE
HEATER CONTROLLER
HEATER POWER SUPPLY
GAS EXHAUST UNIT

FIG. 2

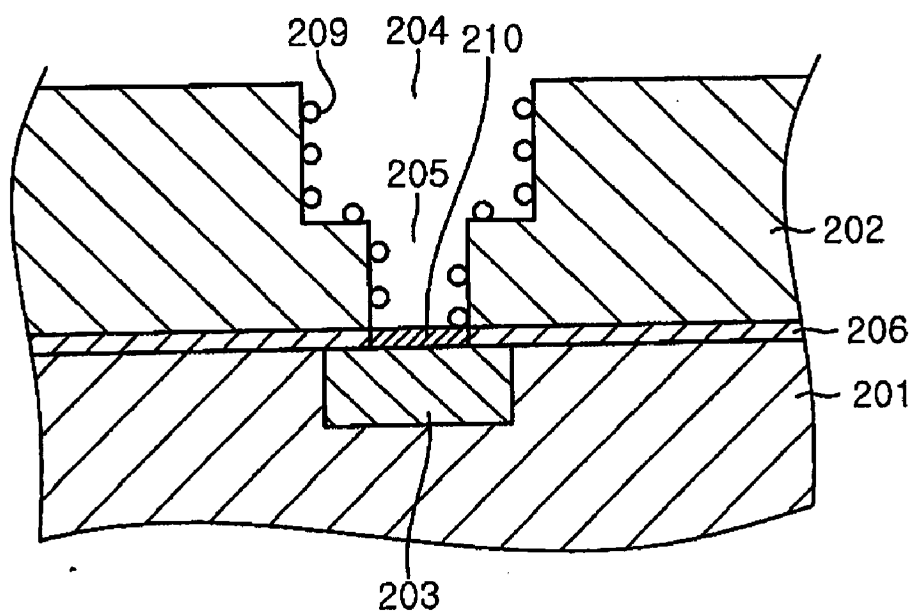


FIG. 3

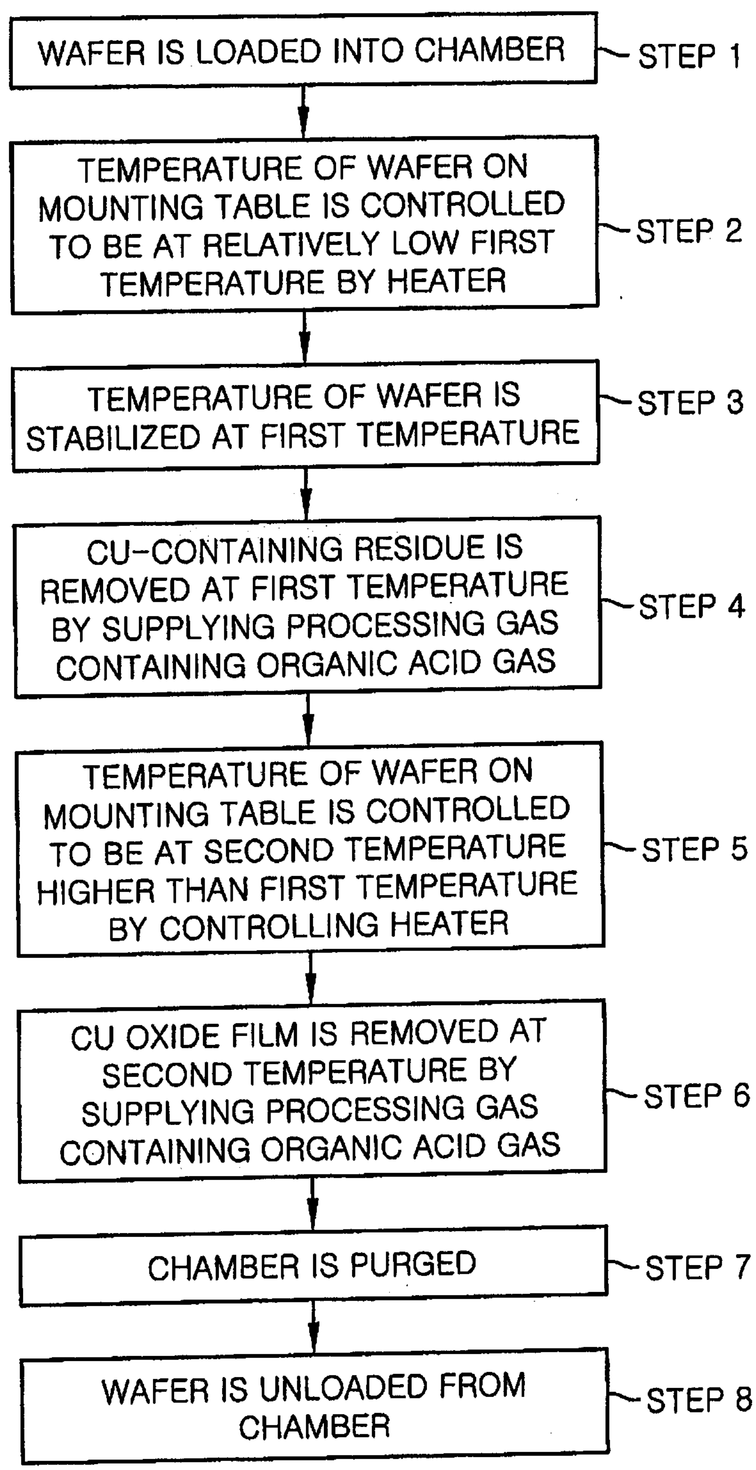

WAFER IS LOADED INTO CHAMBER
STEP 1
TEMPERATURE OF WAFER ON MOUNTING TABLE IS CONTROLLED TO BE AT RELATIVELY LOW FIRST TEMPERATURE BY HEATER
STEP 2
TEMPERATURE OF WAFER IS STABILIZED AT FIRST TEMPERATURE
STEP 3
CU-CONTAINING RESIDUE IS REMOVED AT FIRST TEMPERATURE BY SUPPLYING PROCESSING GAS CONTAINING ORGANIC ACID GAS
STEP 4
TEMPERATURE OF WAFER ON MOUNTING TABLE IS CONTROLLED TO BE AT SECOND TEMPERATURE HIGHER THAN FIRST TEMPERATURE BY CONTROLLING HEATER
STEP 5
CU OXIDE FILM IS REMOVED AT SECOND TEMPERATURE BY SUPPLYING PROCESSING GAS CONTAINING ORGANIC ACID GAS
STEP 6
CHAMBER IS PURGED
STEP 7
WAFER IS UNLOADED FROM CHAMBER
STEP 8

FIG. 4

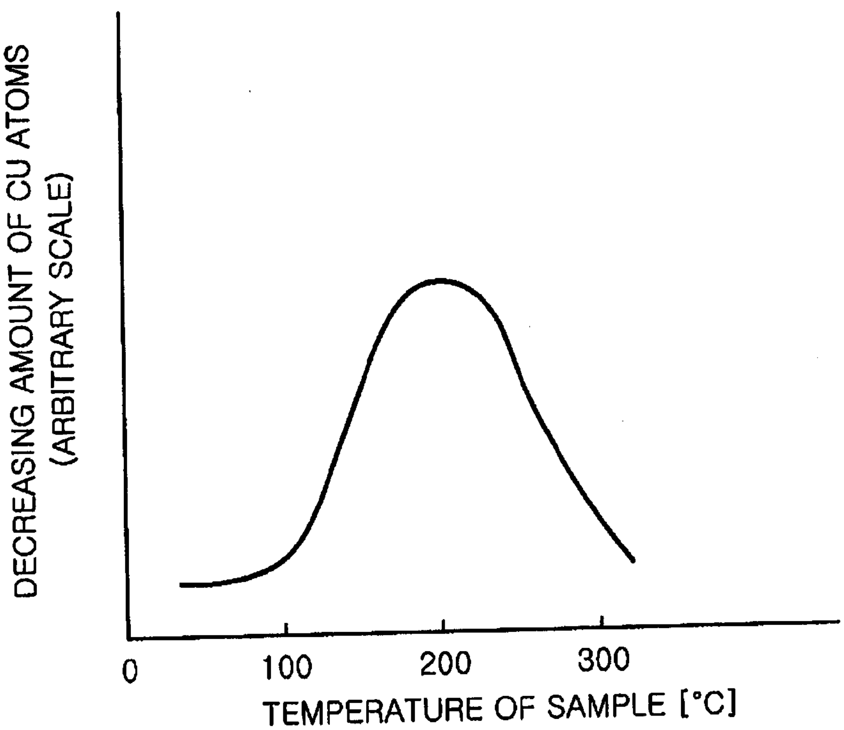

DECREASING AMOUNT OF CU ATOMS
(ARBITRARY SCALE)
0
100
200
300
TEMPERATURE OF SAMPLE [°C]

FIG. 5

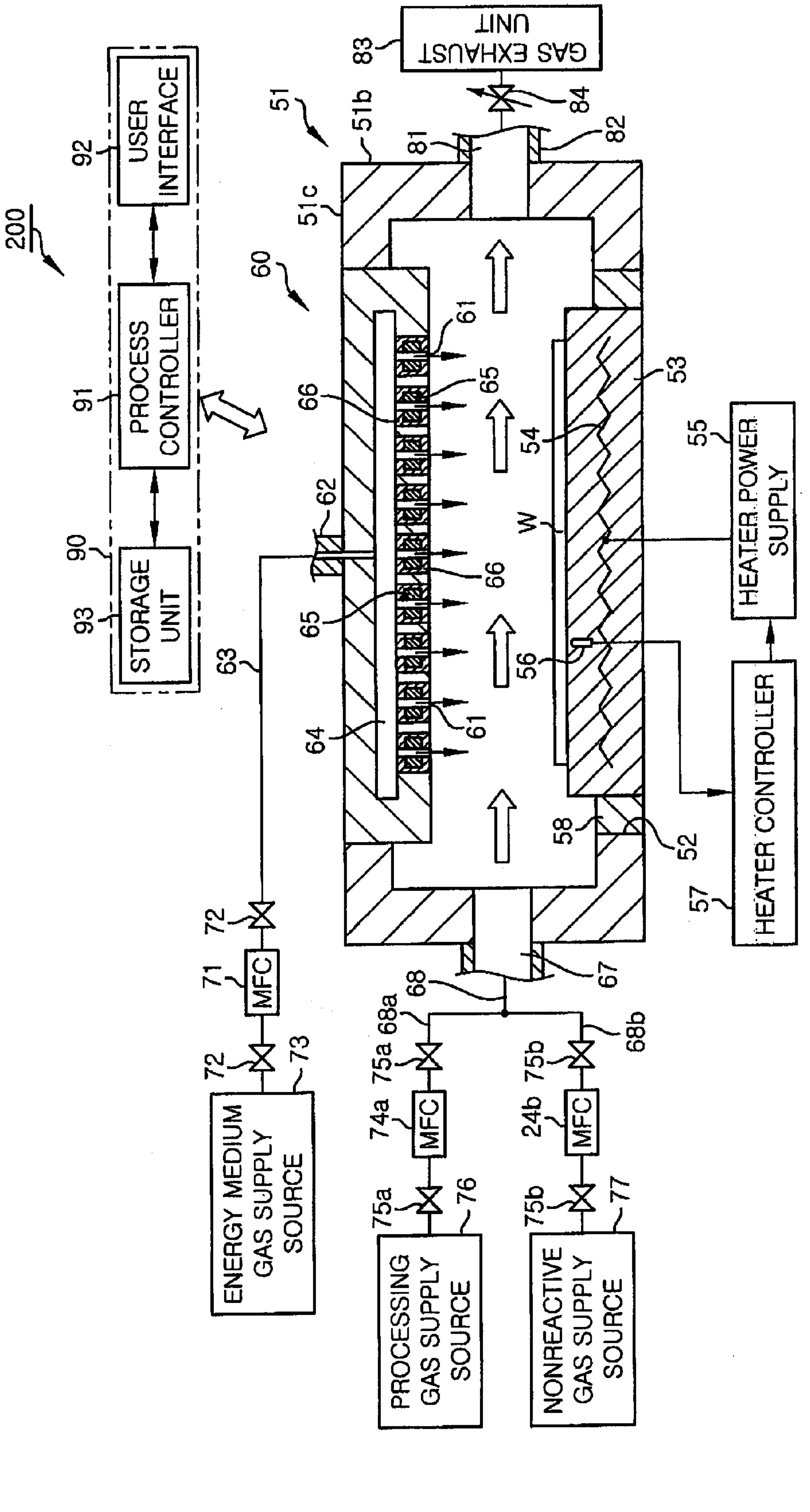

200
90
91
92
93
STORAGE UNIT
PROCESS CONTROLLER
USER INTERFACE
GAS EXHAUST UNIT
ENERGY MEDIUM GAS SUPPLY SOURCE
PROCESSING GAS SUPPLY SOURCE
NONREACTIVE GAS SUPPLY SOURCE
HEATER POWER SUPPLY
HEATER CONTROLLER
MFC
W

FIG. 6

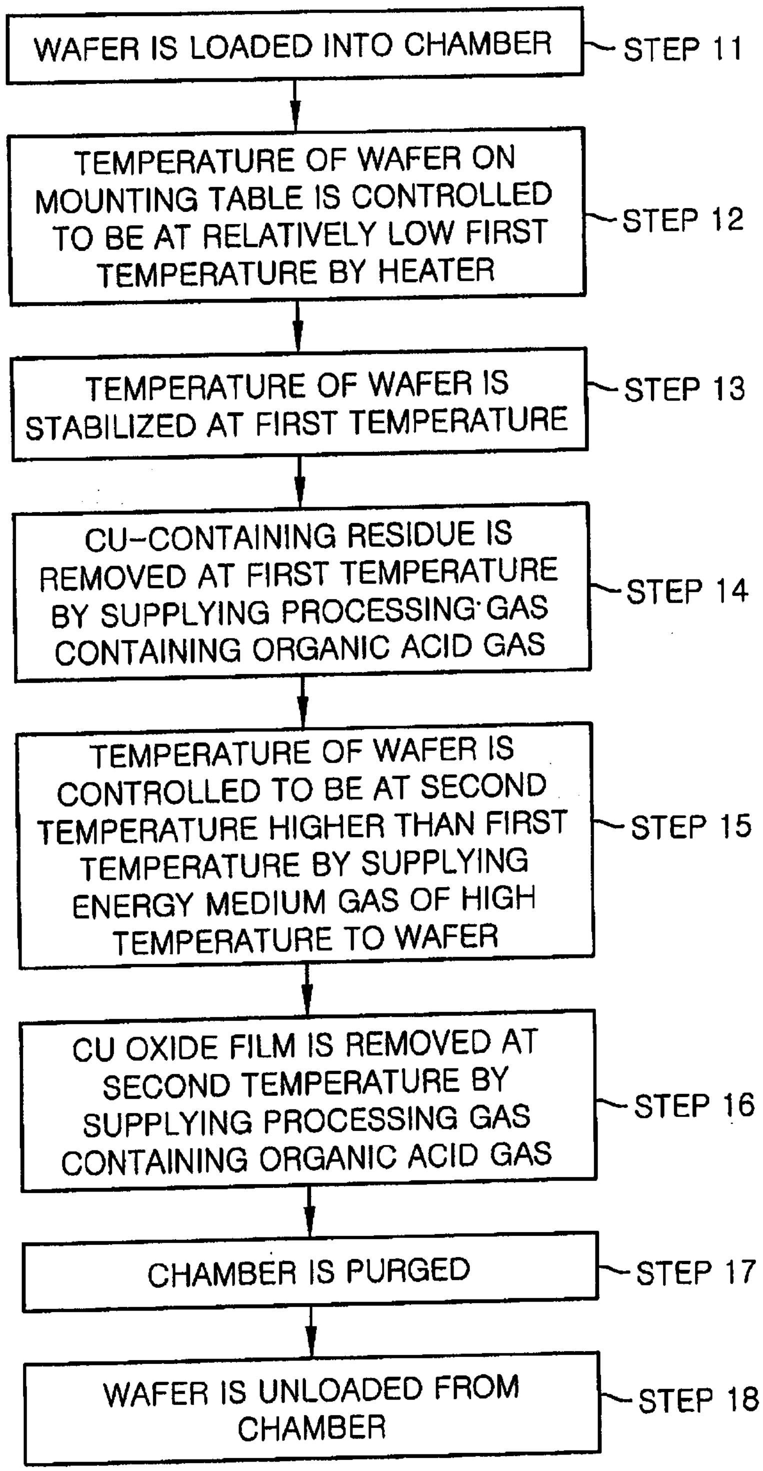

WAFER IS LOADED INTO CHAMBER
STEP 11
TEMPERATURE OF WAFER ON MOUNTING TABLE IS CONTROLLED TO BE AT RELATIVELY LOW FIRST TEMPERATURE BY HEATER
STEP 12
TEMPERATURE OF WAFER IS STABILIZED AT FIRST TEMPERATURE
STEP 13
CU-CONTAINING RESIDUE IS REMOVED AT FIRST TEMPERATURE BY SUPPLYING PROCESSING GAS CONTAINING ORGANIC ACID GAS
STEP 14
TEMPERATURE OF WAFER IS CONTROLLED TO BE AT SECOND TEMPERATURE HIGHER THAN FIRST TEMPERATURE BY SUPPLYING ENERGY MEDIUM GAS OF HIGH TEMPERATURE TO WAFER
STEP 15
CU OXIDE FILM IS REMOVED AT SECOND TEMPERATURE BY SUPPLYING PROCESSING GAS CONTAINING ORGANIC ACID GAS
STEP 16
CHAMBER IS PURGED
STEP 17
WAFER IS UNLOADED FROM CHAMBER
STEP 18

FIG. 7

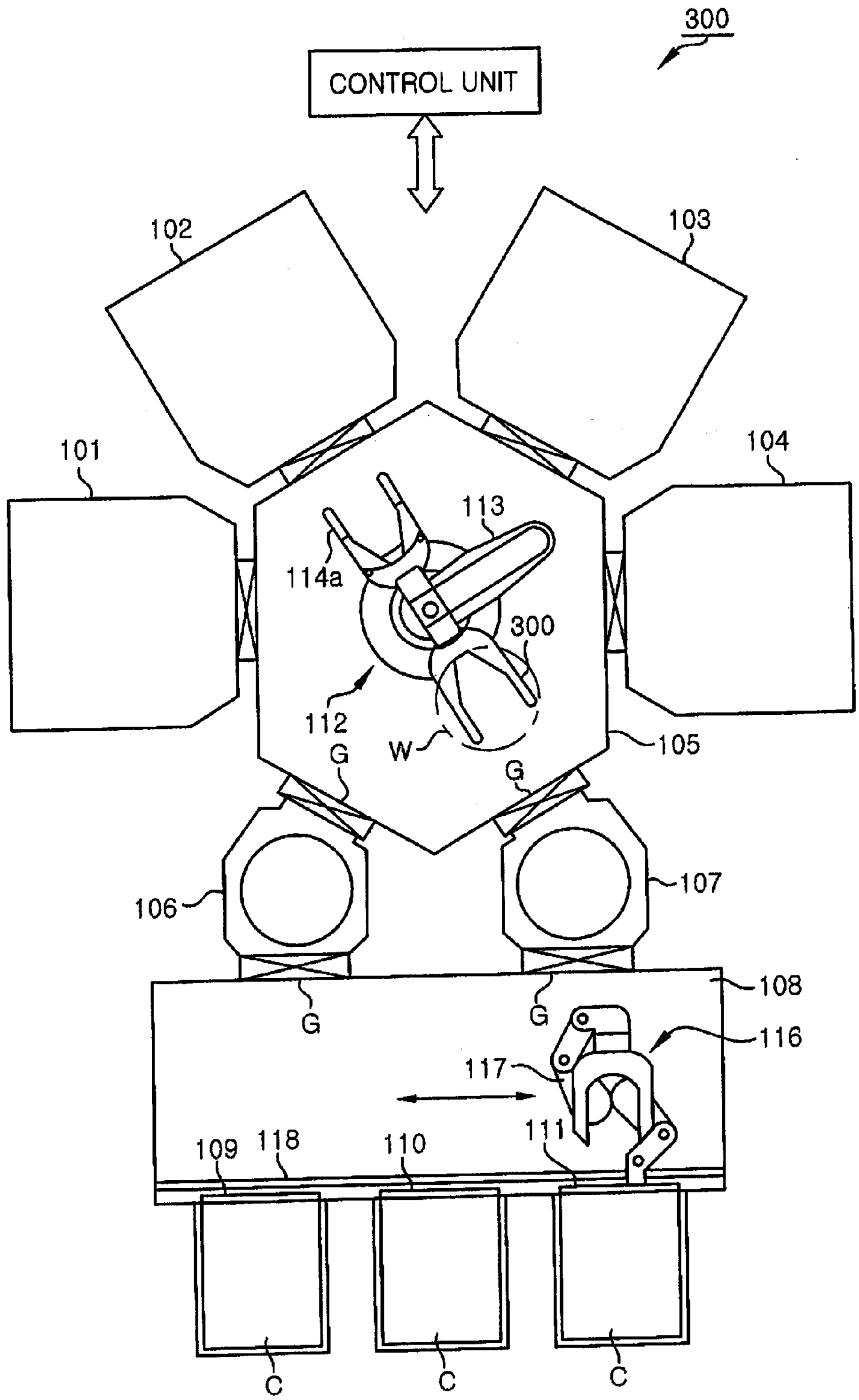

300
CONTROL UNIT
102
103
101
104
113
114a
300
112
W
105
G
G
106
107
108
G
G
116
117
109
118
110
111
C
C
C

FIG. 8

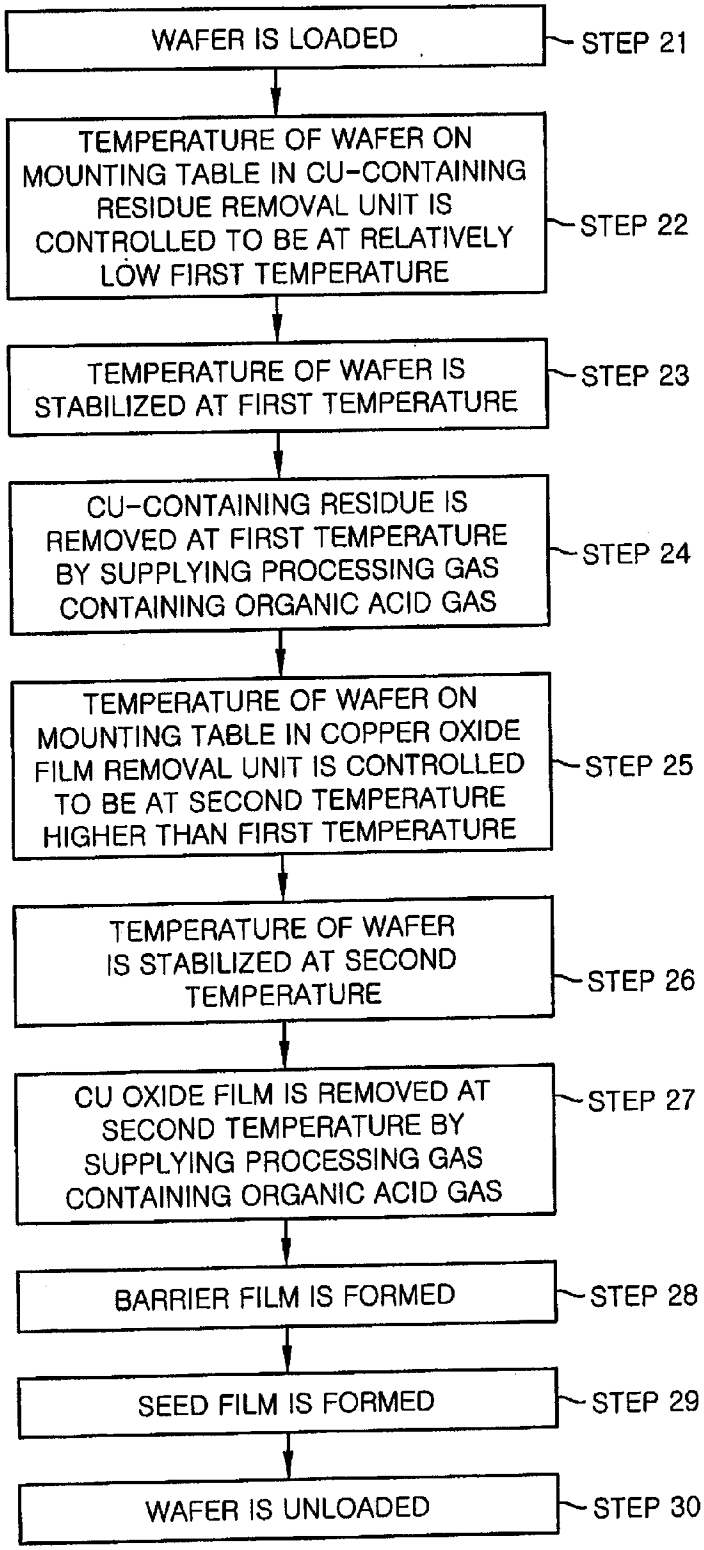

WAFER IS LOADED
STEP 21
TEMPERATURE OF WAFER ON MOUNTING TABLE IN CU-CONTAINING RESIDUE REMOVAL UNIT IS CONTROLLED TO BE AT RELATIVELY LOW FIRST TEMPERATURE
STEP 22
TEMPERATURE OF WAFER IS STABILIZED AT FIRST TEMPERATURE
STEP 23
CU-CONTAINING RESIDUE IS REMOVED AT FIRST TEMPERATURE BY SUPPLYING PROCESSING GAS CONTAINING ORGANIC ACID GAS
STEP 24
TEMPERATURE OF WAFER ON MOUNTING TABLE IN COPPER OXIDE FILM REMOVAL UNIT IS CONTROLLED TO BE AT SECOND TEMPERATURE HIGHER THAN FIRST TEMPERATURE
STEP 25
TEMPERATURE OF WAFER IS STABILIZED AT SECOND TEMPERATURE
STEP 26
CU OXIDE FILM IS REMOVED AT SECOND TEMPERATURE BY SUPPLYING PROCESSING GAS CONTAINING ORGANIC ACID GAS
STEP 27
BARRIER FILM IS FORMED
STEP 28
SEED FILM IS FORMED
STEP 29
WAFER IS UNLOADED
STEP 30

FIG. 9

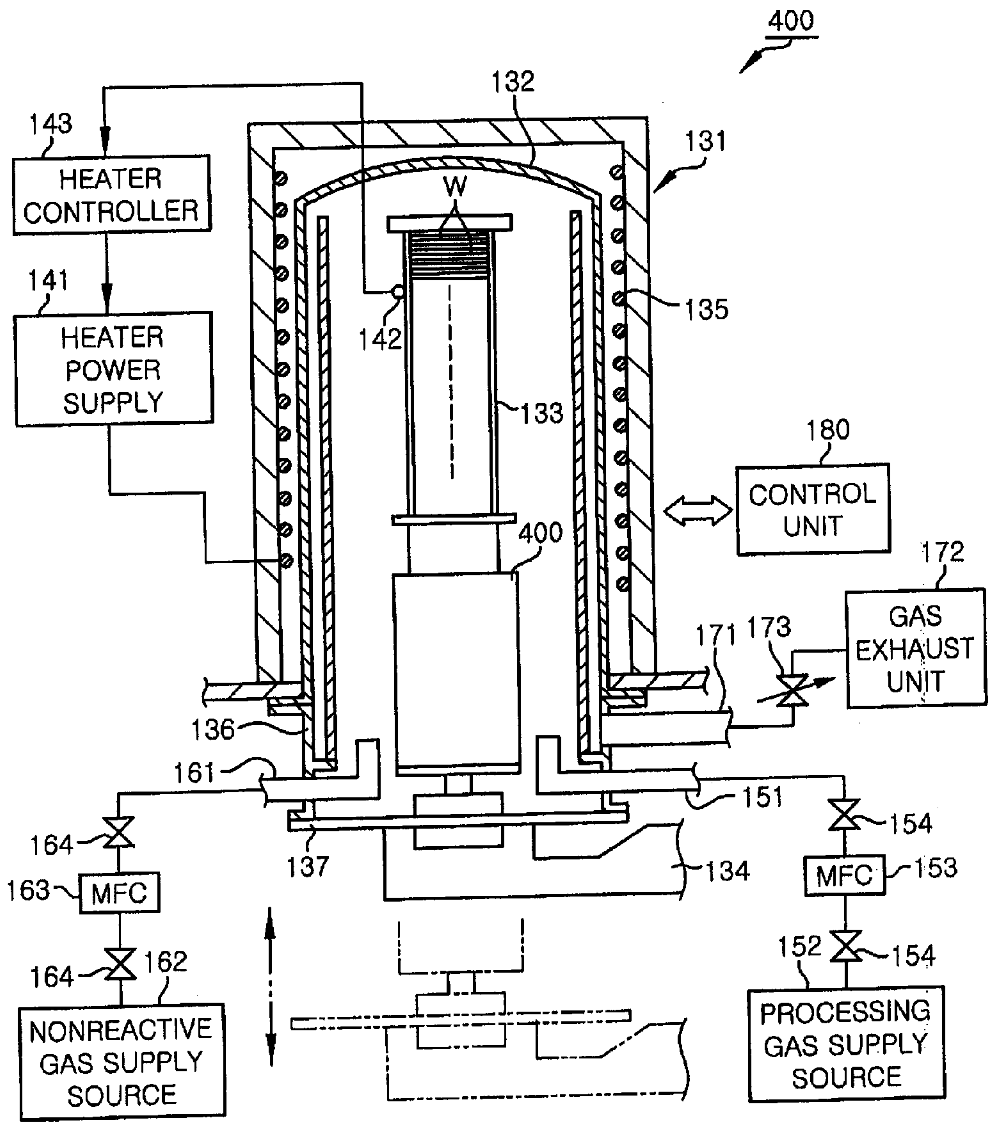
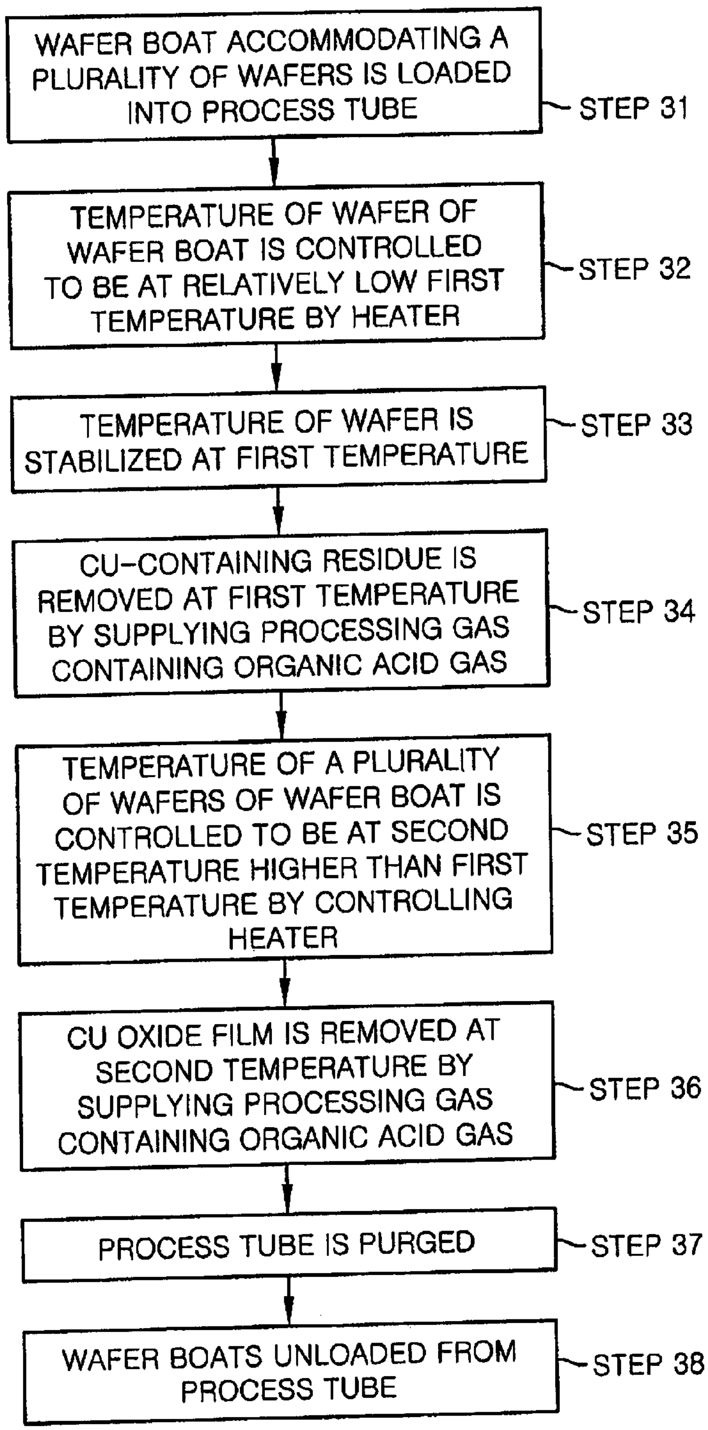

400
132
131
143
HEATER CONTROLLER
W
141
HEATER POWER SUPPLY
142
135
133
180
CONTROL UNIT
400
172
GAS EXHAUST UNIT
171
173
136
161
151
154
164
137
134
163
MFC
MFC
153
164
162
152
154
NONREACTIVE GAS SUPPLY SOURCE
PROCESSING GAS SUPPLY SOURCE

FIG. 10


WAFER BOAT ACCOMMODATING A PLURALITY OF WAFERS IS LOADED INTO PROCESS TUBE
STEP 31
TEMPERATURE OF WAFER OF WAFER BOAT IS CONTROLLED TO BE AT RELATIVELY LOW FIRST TEMPERATURE BY HEATER
STEP 32
TEMPERATURE OF WAFER IS STABILIZED AT FIRST TEMPERATURE
STEP 33
CU-CONTAINING RESIDUE IS REMOVED AT FIRST TEMPERATURE BY SUPPLYING PROCESSING GAS CONTAINING ORGANIC ACID GAS
STEP 34
TEMPERATURE OF A PLURALITY OF WAFERS OF WAFER BOAT IS CONTROLLED TO BE AT SECOND TEMPERATURE HIGHER THAN FIRST TEMPERATURE BY CONTROLLING HEATER
STEP 35
CU OXIDE FILM IS REMOVED AT SECOND TEMPERATURE BY SUPPLYING PROCESSING GAS CONTAINING ORGANIC ACID GAS
STEP 36
PROCESS TUBE IS PURGED
STEP 37
WAFER BOATS UNLOADED FROM PROCESS TUBE
STEP 38

SUBSTRATE PROCESSING METHOD AND SUBSTRATE PROCESSING APPARATUS

[0001] This application is a Continuation Application of PCT International Application No. PCT/JP2010/051597 filed on Feb. 4, 2010, which designated the United States.

FIELD OF THE INVENTION

[0002] The present invention relates to a substrate processing method and a substrate processing apparatus for removing an oxide on a surface of a Cu film and a Cu-containing residue adhered to an interlayer insulating film during formation of Cu wiring.

BACKGROUND OF THE INVENTION

[0003] Recently, along with demands for high speed and high integration of semiconductor devices and miniaturization of wiring patterns, it is required to reduce an inter-wiring capacitance and improve conductivity and electromigration resistance of wiring. As a technique therefor, a Cu multilayer interconnection technique attracts attention. In this technique, Cu having a higher conductivity and better electromigration resistance than those of Al or W is used as a wiring material, and an insulating film (low-k film) having a lower dielectric constant than that of SiO_2 is used as an interlayer insulating film.

[0004] Cu is easily oxidized, and copper oxide film having high resistance is easily formed on a surface of Cu, which makes it difficult to become a contact. Therefore, an oxide film formed on the surface of Cu has to be removed.

[0005] In case of forming a Cu wiring structure by using a damascene method, when an interlayer insulating film is etched, a part of Cu wiring as an underlayer which is exposed through a hole or a via for the wiring is etched, and thus a Cu-containing material is adhered as a residue on the sidewall of the via or the wiring groove. If a next process is performed in a state where the residue is adhered, Cu is diffused into the interlayer insulating film, and this leads to a decrease in a production yield of semiconductor devices. For that reason, the Cu-containing residue needs to be removed.

[0006] As for a method for removing an oxide film on a surface of Cu, dry cleaning using a plasma has been used. However, when a plasma is used, Cu as an underlayer may be damaged. Hence, as for a method for dry-cleaning a surface of a substrate without using a plasma, organic acid dry cleaning has been studied (see, e.g., Japanese Patent Application Publication No. 2003-218198).

[0007] Moreover, as for a method for removing a Cu-containing residue adhered to an interlayer insulating film, wet cleaning has been used. However, when a low-k film is used as an interlayer insulating film, moisture is absorbed into the low-k film by wet cleaning, which increases a dielectric constant. Accordingly, a method for removing a Cu-containing residue by organic acid dry cleaning has been studied (see, e.g., Enhancing Yield and Reliability by Applying Dry Organic Acid Vapor Cleaning to Copper Contact Via-Bottom for 32-nm Nodes and Beyond (International Interconnect Technology Conference, 2008. p93-p95)).

[0008] However, a technique for simultaneously and effectively etching a copper oxide film on a surface of Cu and a Cu-containing residue has not yet been developed.

SUMMARY OF THE INVENTION

[0009] In view of the above, the present invention provides a substrate processing method and a substrate processing apparatus capable of effectively removing a copper oxide film on a surface of Cu and a Cu-containing residue adhered to an interlayer insulating film.

[0010] The present invention also provides a storage medium storing a program for performing the substrate processing method.

[0011] The present inventors have repeated examinations in order to achieve the above goals. As a result, the present inventors have found that when copper oxide is subjected to dry cleaning using an organic acid-containing gas, etching easily occurs at a low temperature and reduction easily occurs at a high temperature. As a result of further examination based on the above information, the present inventors have reached to the following conclusion. That is, a Cu-containing residue adhered to an interlayer insulating film in a Cu wiring structure includes mainly copper oxide and needs to be removed by etching, so that dry cleaning using an organic acid-containing gas is performed at a low temperature at which etching easily occurs. Meanwhile, when a copper oxide film on a surface of Cu is removed by dry cleaning using an organic acid-containing gas, it can be removed by etching or reduction. The reaction conducted at a low temperature has a low reaction speed and requires a longer period of time, whereas the reaction conducted at a high temperature has a high reaction speed. Thus, the copper oxide film on the surface of Cu can be reliably removed within a short period of time by performing reaction that is mainly a reduction process at a high temperature at which a high reaction speed is achieved.

[0012] The present invention has been conceived from the above conclusion.

[0013] In accordance with first aspect of the present invention, there is provided a substrate processing method for removing a copper oxide film on a surface of Cu and a Cu-containing residue adhered to an interlayer insulating film in a Cu wiring structure on a substrate by using an organic acid-containing gas, the substrate processing method including: removing the Cu-containing residue by etching by supplying the substrate with a processing gas containing an organic acid gas, after the temperature of the substrate is set to be maintained at a first temperature; and removing the copper oxide film on the surface of Cu by means of a reduction reaction by supplying the substrate with the processing gas containing the organic acid gas, after the temperature of the substrate is set to be maintained at a second temperature that is higher than the first temperature.

[0014] The interlayer insulating film may be a low-k film. The organic acid may be a carboxylic acid. Preferably, the carboxylic acid may be a formic acid. Further, the first temperature may be within a range from about 100° C. to about 200° C., and the second temperature may be within a range from about 200° C. to about 300° C.

[0015] In accordance with second aspect of the present invention, there is provided a substrate processing apparatus for removing a copper oxide film on a surface of Cu and a Cu-containing residue adhered to an interlayer insulating film in a Cu wiring structure on a substrate by using an organic acid-containing gas, the substrate processing apparatus including: a chamber for accommodating a substrate; a mounting table for mounting thereon the substrate in the chamber; a heating mechanism for heating the substrate on the mounting table; a processing gas supply mechanism for supplying a processing gas containing an organic acid gas into the chamber; a gas exhaust mechanism for exhausting an interior of the chamber; and a control mechanism for removing a Cu-containing residue by etching by supplying the substrate with the processing gas containing an organic acid gas after the temperature of the substrate mounted on the mounting table is set to be maintained at a first temperature by the heating mechanism, and then removing a copper oxide film on a surface of Cu by means of a reduction reaction by supplying the substrate with the processing gas containing an organic acid gas after the temperature of the substrate is set to be maintained at a second temperature higher than the first temperature by the heating mechanism.

[0016] In accordance with third aspect of the present invention, there is provided a substrate processing apparatus for removing a copper oxide film on a surface of

[0017] Cu and a Cu-containing residue adhered to an interlayer insulating film in a Cu wiring structure on a substrate by using an organic acid-containing gas, the substrate processing apparatus including: a chamber for accommodating a substrate; a mounting table for mounting thereon the substrate in the chamber; a heating mechanism for heating the substrate on the mounting table; an energy medium gas supply mechanism for supplying a heated energy medium gas to the substrate on the mounting table; a processing gas supply mechanism for supplying a processing gas containing an organic acid gas into the chamber; a gas exhaust mechanism for exhausting an interior of the chamber; a control mechanism for removing a Cu-containing residue by etching by supplying the substrate with the processing gas containing an organic acid gas after the temperature of the substrate mounted on the mounting table is set to be maintained at a first temperature by the heating mechanism, and then removing a copper oxide film on a surface of Cu by means of a reduction reaction by supplying the substrate with the processing gas containing an organic acid gas after the temperature of the substrate is set to be maintained at a second temperature higher than the first temperature by supplying the heated energy medium gas to the substrate on the mounting table.

[0018] In accordance with fourth aspect of the present invention, there is provided a substrate processing apparatus for removing a copper oxide film on a surface of Cu and a Cu-containing residue adhered to an interlayer insulating film in a Cu wiring structure on a substrate by using a processing gas containing an organic acid, the substrate processing apparatus including: a first processing unit, having a mounting table maintained at a temperature for heating the substrate mounted thereon to be maintained at a first temperature, for supplying the processing gas onto the substrate on the mounting table; a second processing unit, having a mounting table maintained at a temperature for heating the substrate mounted thereon to be maintained at a second temperature, for supplying the processing gas onto the substrate on the mounting table; a transfer mechanism for transferring the substrate between the first processing unit and the second processing unit; and a control mechanism for removing a Cu-containing residue by etching by supplying the substrate with the processing gas containing an organic acid gas after the temperature of the substrate mounted on the mounting table of the first processing unit is set to be maintained at the first temperature, and then removing a copper oxide film on a surface of Cu by means of a reduction reaction by supplying a processing gas containing an organic acid gas to the substrate by supplying the substrate with a processing gas containing an organic acid gas after the temperature of the substrate transferred on the mounting table of the second processing unit by the transfer mechanism is set to be maintained at the second temperature.

[0019] In accordance with fifth aspect of the present invention, there is provided a A substrate processing apparatus for removing a copper oxide film on a surface of Cu and a Cu-containing residue adhered to an interlayer insulating film in a Cu wiring structure on a substrate by using an organic acid-containing gas, the substrate processing apparatus including: a processing chamber for processing a substrate; a substrate supporting unit for supporting a plurality of substrates in the processing chamber; a heating mechanism for heating the substrates in the processing chamber; a processing gas supply mechanism for supplying a processing gas containing an organic acid gas into the processing chamber; a control mechanism for removing a Cu-containing residue by etching by supplying the substrates with the processing gas containing an organic acid gas after the temperature of the substrates held by the substrate supporting unit in the processing chamber is set to be maintained at a first temperature by the heating mechanism, and then removing a copper oxide film on a surface of Cu by means of a reduction reaction by supplying the substrates with the processing gas containing an organic acid gas after the temperature of the substrates is set to be maintained at a second temperature higher than the first temperature by the heating mechanism.

[0020] In accordance with sixth aspect of the present invention, there is provided a non-transitory computer-readable storage medium storing a program for controlling a substrate processing apparatus, wherein the program, when executed by a computer, controls the substrate processing apparatus to perform the substrate processing method described in the first aspect of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] FIG. **1** is a cross sectional view schematically showing an example of a configuration of a substrate processing apparatus for performing a substrate processing method in accordance with a first embodiment of the present invention.

[0022] FIG. **2** is a cross sectional view showing an example of a Cu wiring structure to which the present invention is applied.

[0023] FIG. **3** is a flowchart showing the method in accordance with the first embodiment of the present invention.

[0024] FIG. **4** shows relationship between processing temperature and a decreasing amount of Cu atoms in case of processing Cu_2O by a formic acid.

[0025] FIG. **5** is a cross sectional view schematically showing an example of a configuration of a substrate processing apparatus for performing a substrate processing method in accordance with a second embodiment of the present invention.

[0026] FIG. **6** is a flowchart showing the film forming method in accordance with the second embodiment of the present invention.

[0027] FIG. **7** is a cross sectional view schematically showing an example of a configuration of a substrate processing apparatus for performing a substrate processing method in accordance with a third embodiment of the present invention.

[0028] FIG. 8 is a flowchart showing the film forming method in accordance with the third embodiment of the present invention.

[0029] FIG. 9 is a cross sectional view schematically showing an example of a configuration of a substrate processing apparatus for performing a substrate processing method in accordance with a fourth embodiment of the present invention.

[0030] FIG. 10 is a flowchart showing the film forming method in accordance with the fourth embodiment of the present invention.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0031] Hereinafter, the embodiments of the present invention will be described with reference to the accompanying drawings which form a part hereof.

First Embodiment

[0032] (Configuration of a Substrate Processing Apparatus for Performing a Substrate Processing Method in Accordance with the First Embodiment of the Present Invention)

[0033] FIG. 1 is a cross sectional view schematically showing an example of a configuration of a substrate processing apparatus for performing a substrate processing method in accordance with the first embodiment of the present invention. Here, the case in which a semiconductor wafer (hereinafter, simply referred to as a “wafer”) is used as a substrate will be described (This is the same in the following embodiments).

[0034] This processing apparatus **100** includes a substantially cylindrical airtight chamber **1**. Provided on a bottom wall of the chamber **1** is a mounting table **3** for horizontally supporting a wafer W as a semiconductor substrate in the chamber **1**.

[0035] A heater **4** is buried in the mounting table **3**, and a heater power supply **5** is connected to the heater **4**. Meanwhile, a thermocouple **6** is provided near the top surface of the mounting table **3**, and a signal of the thermocouple **6** is outputted to a heater controller **7**. The heater controller **7** is configured to transmit an instruction to the heater power supply **6** in accordance with the signal of the thermocouple **6** and control a wafer W to be maintained at a predetermined temperature by controlling heating of the heater **4**. Further, the mounting table **3** is provided with, e.g., three wafer support pins (not shown) for supporting and vertically moving the wafer W. The three wafer support pins can protrude and retract with respect to the surface of the mounting table **3**.

[0036] A shower head **10** is provided at a ceiling wall la of the chamber **1**. A gas inlet port **12** for introducing a gas into the shower head **10** is provided on a top surface of the shower head **10**, and a line **21** for supplying a cleaning gas and a purge gas is connected to the gas inlet port **12**.

[0037] A diffusion space **14** is formed in the shower head **10**, and a plurality of injection openings **11** for injecting a processing gas or a purge gas toward the mounting table **3** is formed on a bottom side of the shower head **10**. The gas introduced into the shower head **10** through the gas inlet port **12** is diffused in the diffusion space **14**, and then is injected through the injection openings **11** in a direction perpendicular to the wafer W mounted on the mounting table **3** in the chamber **1**.

[0038] A processing gas supply source **22** for supplying a processing gas is connected to the other end of the line **21** connected to the gas inlet port **12**. A mass flow controller and valves **24** disposed on both sides thereof are installed in the line **21**. A nonreactive gas line **25** is connected to the line **21**, and a nonreactive gas supply source **26** is connected to the other end of the nonreactive gas line **25**. A mass flow controller **27** and valves **28** disposed on both sides thereof are installed in the nonreactive gas line **25**.

[0039] As for a processing gas supplied from the processing gas supply source **22**, one containing an organic acid gas is used. As for an organic acid forming the processing gas, it is preferable to use a carboxylic acid. The carboxylic acid may be a formic acid (HCOOH), an acetic acid (CH_3COOH), a propionic acid (CH_3CH_2COOH), a butyric acid ($CH_3(CH_2)_2COOH$), a valeric acid ($CH_3(CH_2)_3COOH$) or the like. Among them, it is preferable to use a formic acid (HCOOH). In addition, a nonreactive gas supplied from the nonreactive gas supply source **26** is used as a purge gas, a dilution gas, a carrier gas or the like. For example, Ar gas, He gas, N_2 gas or the like can be used therefor.

[0040] A gas exhaust port **31** is formed on a bottom wall **1***b* of the chamber **1**, and a gas exhaust line **32** is connected to the gas exhaust port **31**. Further, a gas exhaust unit **33** including a high-speed vacuum pump is provided in the gas exhaust line **32**. A conductance variable valve **34** is provided in the gas exhaust line **32** to control a gas exhaust amount from the chamber **1**. The gas in the chamber **1** is exhausted by driving the gas exhaust unit **33**, and the chamber **1** can be depressurized to a predetermined vacuum level via the gas exhaust line **32**.

[0041] Installed on a sidewall of the chamber **1** are a loading/unloading port **15** for loading and unloading a wafer

[0042] W with respect to a transfer chamber (not shown) close to the substrate processing apparatus **100** and a gate valve **16** for opening and closing the loading/unloading port **15**.

[0043] The substrate processing apparatus **100** includes a control unit **40**, and the control unit **40** has a process controller **41**, a user interface **42**, and a storage unit **43**. The process controller **41** is connected to components of the substrate processing apparatus **100**, e.g., the valve, the mass flow controller, the heater controller **7**, the gas exhaust unit **33** and the like. These components are controlled by the process controller **41**

[0044] The user interface **42** is connected to the process controller **41**, and includes a keyboard through which an operator inputs a command to manage the processing apparatus, a display for visually displaying the operational states of the plasma processing apparatus, and the like.

[0045] The storage unit **43** is connected to the process controller **41**, and stores therein control programs to be used in realizing various processes performed by the substrate processing apparatus **100** under the control of the process controller **41**, or programs, i.e., recipes, to be used in operating the respective components of the substrate processing apparatus **100** to carry out processes under processing conditions. The processing recipes are stored in a storage medium provided inside the storage unit **43**. The storage medium may be a fixed medium such as a hard disk or the like, or a portable device such as a CD-ROM, a DVD, a flash memory or the like. Alternatively, the recipes may be suitably transmitted from other devices via, e.g., a dedicated transmission line.

[0046] If necessary, a predetermined processing recipe is read out from the storage unit **43** under the instruction from the user interface **42** and is executed by the process controller **41**. Accordingly, a cleaning process is performed in the substrate processing apparatus **100** under the control of the process controller **41**.

(Substrate Processing Method of the First Embodiment)

[0047] The following is description of the substrate processing method of the present invention which removes a copper oxide film on a surface of Cu and a Cu-containing residue in a Cu wiring structure on a wafer W by using the substrate processing apparatus **100**.

[0048] Here, as shown in FIG. **2**, for example, a wafer W has a structure in which a low-k film **202** as an upper interlayer insulating film is formed on a low-k film **201** as a lower interlayer insulating film via a cap film **206** and a Cu wiring layer **203** is formed on the low-k film **201**. A trench **204** and a hole **205** are formed by plasma-etching a portion of the low-k film **202** which corresponds to the Cu wiring layer **203**. After ashing of a resist, a Cu-containing residue **209** adhered to the sidewalls of the trench **204** and the hole **205** and a copper oxide film **210** formed on the surface of the Cu wiring layer **203** are removed by dry cleaning using a processing gas containing an organic acid gas.

[0049] As can be seen from the flowchart of FIG. **3**, first of all, the gate valve **16** is opened, and the wafer W having the Cu wiring structure is loaded into the chamber **1** through the loading/unloading port **15** and then is mounted on the mounting table **3** (step **1**). Next, the gate valve **16** is closed, and the temperature of the wafer W is controlled to be maintained at a relatively low first temperature at which etching of copper oxide as a main component of the Cu-containing residue **209** mainly occurs by controlling the heater **4** by the heater controller **7** based on the temperature detection signal outputted by the thermocouple **6** (step **2**).

[0050] Then, the chamber **1** is exhausted by the vacuum pump of the gas exhaust unit **33**. At the same time, the valves **28** are opened to introduce, e.g., Ar gas, from the nonreactive gas supply source **26** into the chamber **1**, and the temperature of the wafer W is stabilized to be maintained at the first temperature (step **3**).

[0051] Next, the valves **24** are opened, and a processing gas containing an organic acid gas is supplied from the processing gas supply source **22** into the chamber **1** via the shower head **10** at a flow rate controlled by the mass flow controller **23**, thereby removing mainly the Cu-containing residue **209** by etching (step **4**). This step is performed until the Cu-containing residue **209** is almost completely removed by etching. At this time, however, a part of a copper oxide film **210** is also removed by etching.

[0052] As described above, as for the organic acid forming the processing gas, it is preferable to use a carboxylic acid such as a formic acid (HCOOH), an acetic acid (CH_3COOH), a propionic acid (CH_3CH_2COOH), a butyric acid ($CH_3(CH_2)_2COOH$), a valeric acid ($CH_3(CH_2)_3COOH$) or the like. Among them, it is preferable to use a formic acid (HCOOH). If an organic acid is a carboxylic acid, e.g., a formic acid (HCOOH), the first temperature is preferably set to be within a range from about 100° C. to about 200° C. The etching reaction that occurs when the formic acid is used as an organic acid can be expressed as in the following Eq. (1).

$$Cu_2O+2HCOOH \rightarrow 2Cu(HCOO)+H_2O \quad \text{Eq. (1)}$$

[0053] Here, Cu(HCOO) is volatile, so that the Cu-containing residue **209** is removed by etching.

[0054] The processing gas may be supplied immediately after the wafer W is mounted on the mounting table **3** without performing the stabilization process of step **3**. In step **4**, the flowing nonreactive gas may be stopped to flow.

[0055] After the Cu-containing residue **209** is almost completely removed by the process of step **4**, the supply of the processing gas is stopped and the nonreactive gas is supplied. At the same time, the heater **4** is controlled by the heater controller **7** based on the temperature detection signal obtained by the thermocouple **6**, and the temperature of the wafer W is controlled to be raised to a second temperature higher than the first temperature at which reduction of copper oxide occurs mainly (step **5**).

[0056] After the temperature becomes stable, the processing gas containing an organic acid gas is supplied again from the processing gas supply source **22** into the chamber **1** via the shower head **10** at a flow rate controlled by the mass flow controller **23**, and the copper oxide film **210** on the surface of the Cu wiring layer **203** is removed by reaction which is mainly a reduction process (step **6**). If an organic acid is a carboxylic acid, e.g., a formic acid (HCOOH), the second temperature is preferably in a range from about 200° C. to about 300° C. The reduction reaction that occurs when a formic acid is used as an organic acid can be expressed as in the following Eq. (2).

$$Cu_2O+HCOOH \rightarrow 2Cu+H_2O+CO_2 \quad \text{Eq. (2)}$$

[0057] The processing gas may be supplied before the temperature becomes stable, or may be supplied when the temperature is changed after the completion of step **4**. By supplying the processing gas at a temperature lower than the second temperature, the ratio of removing the copper oxide film by etching is increased.

[0058] The process of removing the copper oxide film **210** by reaction which is mainly a reduction process is continued until the copper oxide film **210** is completely removed. After the copper oxide film **210** is removed, the supply of the processing gas is stopped, and the nonreactive gas is supplied as a purge gas from the nonreactive gas supply source **26** into the chamber **1** via the shower head **10** at a flow rate controlled by the mass flow controller **27**, thereby purging the chamber **1** (step **7**). Next, the gate valve **16** is opened, and the wafer W is unloaded from the loading/unloading port **15** (step **8**).

[0059] In the above-described steps, the Cu-containing residue **209** and the copper oxide film **210** are removed at different temperatures for the following reasons.

[0060] FIG. **4** shows a relationship between a temperature of a sample prepared by forming a Cu_2O film having a thickness of about 300 nm on a Si substrate and a decreasing amount of Cu atoms, which is obtained by measuring an intensity of a Cu—Ka radiation by using fluorescent X-ray, wherein the measurement was performed in the case of increasing the temperature of the sample while supplying a formic acid (HCOOH) gas to the sample. As can be seen from FIG. **4**, the decreasing amount of Cu atoms increases at a low temperature and becomes maximum at about 200° C. However, the decreasing amount of Cu atoms decreases when the temperature becomes higher than about 200° C. As illustrated in FIG. **4**, the etching of Cu_2O mainly occurs at a temperature lower than about 200° C., and the reduction of Cu_2O mainly occurs at a temperature higher than about 200° C.

[0061] From the above, it is clear that the Cu-containing residue **209** which needs to be removed by etching can be removed within a relatively short period of time by performing dry etching using an organic acid-containing gas at a relatively low first temperature within a range, e.g., from about 100° C. to about 200° C., at which the etching mainly occurs. Meanwhile, when the copper oxide film **210** is removed by dry cleaning using an organic acid-containing gas, it can be removed by etching or reduction. Generally, the reaction speed decreases at a low temperature and increases at a high temperature. Therefore, it is possible to reliably remove the copper oxide film **210** within a short period of time by performing the reaction which is mainly a reduction process at a second temperature within a range, e.g., from about 200° C. to about 300° C., at which a high reaction speed is obtained. Hence, in the present embodiment, when the Cu-containing residue **209** and the copper oxide film **210** are removed by dry cleaning using an organic acid-containing gas, the Cu-containing residue is removed at the relatively low first temperature by etching, and the copper oxide film on the surface of Cu is removed by reaction which is mainly a reduction process at the second temperature higher than the first temperature. Accordingly, they can be reliably removed within a short period of time.

[0062] Further, the substrate processing apparatus **100** of the present embodiment is assembled to a cluster tool-type multi-chamber system having a unit for forming a barrier film such as a Ru film, a Ti film or a Ta film to form Cu wiring at the trench **204** and the via **205** and a unit for forming a Cu seed film. Thus, the removal of the Cu-containing residue **209** and the copper oxide film **210**, the formation of the barrier film, and the formation of the Cu seed film can be performed in-situ. Besides, a series of processes from the etching of the low-k film to the formation of the Cu seed film can be performed in-situ by installing in this system a unit for etching the low-k film or ashing a resist.

Second Embodiment

[0063] (Configuration of a Film Forming Apparatus for Performing a Film Forming Method in Accordance with a Second Embodiment of the Present Invention)

[0064] FIG. **5** is a cross sectional view schematically showing an example of a substrate processing apparatus for performing a substrate processing method in accordance with the second embodiment of the present invention.

[0065] This processing apparatus **200** includes a substantially cylindrical airtight chamber **51**. A circular opening **52** is formed at a central portion of a bottom wall **51***a* of the chamber **51**, and a mounting table **53** for horizontally supporting a wafer W in the chamber **51** is provided at the opening **52**. An insulating unit **58** is provided between the mounting table **53** and the bottom wall **51***a,* and is airtightly coupled to the bottom wall **51***a* of the chamber **1**.

[0066] A heater **54** is buried in the mounting table **53**, and a heater power supply **55** is connected to the heater **54**. Meanwhile, a thermocouple **56** is provided near a top surface of the mounting table **53**, and a signal of the thermocouple **56** is transmitted to the heater controller **57**. Further, the heater controller **57** is configured to transmit an instruction to the heater power supply **55** in accordance with the signal of the thermocouple **56**, and control the wafer W to be maintained at a predetermined temperature by controlling the heating of the heater **54**. Moreover, the mounting table **53** is provided with, e.g., three wafer support pins (not shown) for supporting and vertically moving the wafer W. The three wafer support pins can protrude and retract with respect to the surface of the mounting table **53**.

[0067] A shower head **60** is provided at a ceiling wall **51***c* of the chamber **51**. A gas inlet port **62** for introducing a gas into the shower head **10** is provided on a top surface of the shower head **60**, and a line **63** for supplying an energy medium gas is connected to the gas inlet port **62**.

[0068] A diffusion space **64** is formed in the shower head **60**, and a plurality of injection openings **61** for injecting an energy medium gas toward the mounting table **53** is formed on a bottom side of the shower head **60**. Further, the gas introduced into the shower head **60** through the gas inlet port **62** is diffused in the diffusion space **64**, and then is injected through the injection openings **61** in a direction perpendicular to the wafer W mounted on the mounting table **53** in the chamber **51**.

[0069] Heaters **65** as heating units for heating the energy medium gas in the shower head **60** are provided around the injection openings **61** of the shower head **60**. Insulating units **66** made of a material having a low thermal conductivity, e.g., heat-resistance synthetic resin, quartz, ceramic or the like, are provided around the heaters **65** to insulate the heaters **65**. Further, an energy medium gas which passes through the heaters **65** is instantly and effectively heated.

[0070] An energy medium gas supply source **73** for supplying an energy medium gas is connected to the other end of the line connected to the gas inlet port **62**. A mass flow controller **71** and valves **72** disposed on both sides thereof are installed in the line **63**. As for the energy medium gas, it is preferable to use a nonreactive gas such as He, Ar, Kr, Xe, N_2 or the like. In addition, an organic acid gas may be used.

[0071] A gas inlet port **67** is formed on a sidewall **51***b* of the chamber **51**, and a line **68** is connected to the gas inlet port **67**. The line **68** is branched into a line **68***a* and a line **68***b,* and a processing gas supply source **76** for performing a cleaning process is connected to one end of the line **68***a*. A mass flow controller **74***a* and valves **75***a* disposed on both sides thereof are installed in the line **68***a*. A nonreactive gas supply source **77** for supplying a nonreactive gas is connected to the other end of the line **68***b*. A mass flow controller **74***b* and valves **75***b* disposed on both sides thereof are installed in the line **68***b*.

[0072] As for a processing gas supplied from the processing gas supply source **76**, it is preferable to use one containing an organic acid gas, as in the first embodiment. As for an organic acid gas, it is preferable to use a carboxylic acid. The carboxylic acid may be a formic acid (HCOOH), an acetic acid (CH_3COOH), a propionic acid (CH_3CH_2COOH), a butyric acid ($CH_3(CH_2)_2COOH$), a valeric acid ($CH_3(CH_2)_3COOH$) or the like. Among them, it is preferable to use a formic acid (HCOOH).

[0073] Meanwhile, a nonreactive gas supplied from the nonreactive gas supply source **77** is used as a carrier gas, a dilution gas and a purge gas for purging a processing gas remaining in a gas phase, a by-product generated in a gas phase by reaction, and an energy medium gas containing a large amount of thermal energy. For example, Ar gas, He gas, N_2 gas or the like can be used.

[0074] A gas exhaust port **81** is provided at an opposite side of the gas inlet port **67** provided at the sidewall **51***b* of the chamber **51**, and a gas exhaust line **82** is connected to the gas exhaust port **81**. A gas exhaust unit **83** including a high-speed vacuum pump is provided in the gas exhaust line **82**. A conductance variable valve **84** is provided in the gas exhaust line

82, so that a gas exhaust amount from the chamber 51 can be controlled. By driving the gas exhaust unit 83, the gas in the chamber 51 is exhausted, and the chamber 51 can be depressurized via the line 82 to a predetermined vacuum level at a high speed.

[0075] A loading/unloading port for loading and unloading a wafer W with respect to a transfer chamber (not shown) close to the processing apparatus 200 and a gate valve for opening and closing the loading/unloading port are installed on the sidewall of the chamber 51 where the gas inlet port 67 and the gas exhaust port 81 are not formed (all not shown).

[0076] The processing apparatus 200 includes a control unit 90, and the control unit 90 has a process controller 91, a user interface 92, and a storage unit 93. The process controller 91, the user interface 92, and the storage unit have the same configurations as those of the process controller 41, the user interface 42 and the storage unit 43 of the first embodiment.

(Substrate Processing Method of the Second Embodiment)

[0077] The following is description of a substrate processing method of the present embodiment which performs cleaning by removing a copper oxide film on a surface of Cu and a Cu-containing residue adhered to an interlayer insulating film in a Cu wiring structure on a wafer by using the processing apparatus 200.

[0078] Here, as in the first embodiment, the Cu-containing residue 209 and the copper oxide film 210 in the structure of FIG. 2 are removed by dry cleaning using an organic acid.

[0079] FIG. 6 is a flowchart showing the substrate processing method of the second embodiment. First of all, a gate valve (not shown) is opened, and the wafer W having the Cu wiring structure of FIG. 2 is loaded into the chamber 51 via a loading/unloading port (not shown) and then is mounted on the mounting table 53 (step 11). Next, the gate valve is closed, and the temperature of the wafer W is controlled to be maintained at a relatively low first temperature at which etching of copper oxide as a main component of the Cu-containing residue 209 mainly occurs by controlling the heater 54 by the heater controller 57 based on the temperature detection signal obtained by the thermocouple 56 (step 12).

[0080] Then, the chamber 51 is exhausted by the vacuum pump of the gas exhaust unit 83, and the valve 75*b* is opened to introduce thereinto, e.g., Ar gas, from the nonreactive gas supply source 77, then the temperature of the wafer W is stabilized to be maintained at the first temperature (step 13).

[0081] Thereafter, the valve 75*a* is opened to supply a processing gas containing an organic acid gas from the processing gas supply source 76 into the chamber 51 via the gas inlet port 67 at a flow rate controlled by the mass flow controller 74*a*, thereby removing mainly the Cu-containing residue 209 by etching (step 14). At this time, the processing gas flows in a horizontal direction indicated by white arrows in FIG. 5. This step is performed until the Cu-containing residue 209 is almost completely removed by etching. At this time, however, a part of the copper oxide film 210 is also removed by etching. As described above, as for the organic acid forming the processing gas, it is preferable to use a carboxylic acid. Especially, it is preferable to use a formic acid (HCOOH). If the organic acid is a carboxylic acid, e.g., a formic acid (HCOOH), the first temperature is preferably within a range from about 100° C. to about 200° C. as in step 4 of the first embodiment, and the reduction reaction occurs as expressed in the Eq. (1).

[0082] The processing gas may be supplied immediately after the wafer W is mounted on the mounting table 3 without performing the stabilization process of step 13. In step 14, the flowing nonreactive gas may be stopped to flow.

[0083] Next, the supply of the processing gas is stopped by closing the valve 75*a*. Then, the valves 72 are opened to introduce an energy medium gas from the energy medium gas supply source 73 into the diffusion space 64 of the shower head 60 via the line 63 and the gas inlet port 62 at a flow rate controlled by the mass flow controller 71. Further, the high-temperature energy medium gas heated by the heaters 65 is injected into the chamber 51 and supplied to the wafer W. The temperature of the wafer W is raised by the thermal energy, and controlled to be maintained at a second temperature higher than the first temperature at which the reduction of copper oxide occurs mainly (step 15). In this case, the energy medium gas is injected in a direction perpendicular to the wafer W as indicated by a black arrow in FIG. 5, so that the temperature of the wafer W can be rapidly raised by the energy medium gas. Accordingly, the temperature of the wafer W can be raised from the first temperature to the second temperature within an extremely shorter period of time compared to that in the first embodiment.

[0084] In the case of using a gas other than an organic acid gas, e.g., a nonreactive gas, as an energy medium gas, the supply of the energy medium gas is stopped by closing the valves 72 when the temperature of the wafer W becomes stable at the second temperature. Then, the valves 75*a* are opened to supply the processing gas containing an organic acid gas from the processing gas supply source 76 into the chamber 51 via the gas inlet port 67 at a flow rate controlled by the mass flow controller 74*a*, thereby removing mainly the copper oxide film 210 on the surface of the Cu wiring layer 203 by the reaction which is mainly a reduction process (step 16). At this time, when the organic acid is a carboxylic acid, e.g., a formic acid (HCOOH), the second temperature falls within a range preferably from about 200° C. to about 300° C., as in step 6 of the first embodiment, and the reduction reaction occurs as described in the Eq. (2).

[0085] When the organic acid gas is supplied as an energy medium gas, the copper oxide film 210 is removed by supplying the organic acid gas to the wafer W maintained at the second temperature in step 15.

[0086] The process of removing the copper oxide film 210 by reaction which is mainly a reduction process is continued until the copper oxide film 210 is completely removed. After the copper oxide film 210 is removed, the supply of the processing gas is stopped by closing the valves 75*a*, and the valves 75*b* are opened to supply a nonreactive gas as a purge gas from the nonreactive gas supply source 77 into the chamber 51 via the gas inlet port 67 at a flow rate controlled by the mass flow controller 74*b* (step 17). Thereafter, the wafer W is unloaded from the loading/unloading port by opening a gate valve (not shown) (step 18).

[0087] In the present embodiment as well as in the first embodiment, when the Cu-containing residue 209 and the copper oxide film 210 are removed by dry cleaning using an organic-containing gas, they can be reliably removed within a short period of time by removing the Cu-containing residue by etching at the relatively low first temperature and removing the copper oxide film on the surface of Cu by reaction which is mainly a reduction process at the second temperature higher than the first temperature.

[0088] In the first embodiment, the time for raising the temperature of the wafer from the first temperature to the second temperature is required. Further, when a plurality of wafers is consecutively processed, the time for lowering the temperature of the mounting table from the second temperature to the first temperature is required. On the other hand, in the present embodiment, the high-temperature energy medium gas is injected to the wafer W, so that the temperature of the wafer W can be raised from the first temperature to the second temperature within an extremely short period of time. Hence, the throughput of processing is increased.

[0089] As in the case of the substrate processing apparatus **100** of the first embodiment, the substrate processing apparatus **200** of the present embodiment is assembled to a cluster tool-type multi-chamber system including a unit for forming a barrier film such as a Ru film, a Ti film or a Ti film to form Cu wiring at the trench **204** and the via **205** and a unit for forming a Cu seed film. Therefore, the removal of the Cu-containing residue **209** and the copper oxide film **210**, the formation of the barrier film, and the formation of the Cu seed film can be performed in-situ. Further, a series of processes from the etching of the low-k film to the formation of the Cu seed film can be performed in-situ by installing at this system a unit for etching the low-k film or ashing a resist.

Third Embodiment

[0090] (Configuration of a Film Forming Apparatus for Performing a Film Forming Method in Accordance with a Third Embodiment of the Present Invention)

[0091] FIG. **7** is a cross sectional view schematically showing an example of a substrate processing apparatus for performing a substrate processing method in accordance with the third embodiment of the present invention.

[0092] This substrate processing apparatus **300** is configured as a cluster tool-type multi-chamber system including a unit for removing a Cu-containing residue, a unit for removing a copper oxide film, a unit for forming a barrier film, and a unit for forming a Cu seed film.

[0093] In other words, the substrate processing apparatus **300** includes a Cu-containing residue removal unit **101** for mainly removing a Cu-containing residue, a copper oxide film removal unit **102** for removing a copper oxide film, a barrier film formation unit **103** for forming a barrier film on a sidewall of a via and/or a trench, and a Cu seed film formation unit **104** for forming a Cu seed film on the barrier film. These units **101** to **104** are maintained in a vacuum state and connected to a transfer chamber **105** maintained in a vacuum state via gate valves G. Moreover, load-lock chambers **106** and **107** are connected to the transfer chamber **105** via gate valves G. A loading/unloading chamber **108** in an atmospheric atmosphere is provided at the side of the load-lock chambers **106** and **107** which is opposite to the side where the transfer chamber **105** is provided, and three carrier attachment ports **109**, **110** and **111** to which the carriers C capable of accommodating wafers W are attached are provided at the side of the loading/unloading chamber **108** which is opposite to the side where the load-lock chambers **106** and **107** are connected.

[0094] Provided in the transfer chamber **105** is a transfer device **112** for loading and unloading a wafer W with respect to the Cu-containing residue removal unit **101**, the copper oxide film removal unit **102**, the barrier film formation unit **103**, the Cu seed film formation unit **104**, and the load-lock chambers **106** and **107**. The transfer device **112** is disposed at a substantially central portion of the transfer chamber **105**, and has at a leading end of a rotatable and extensible/contractible portion **113** two support arms **114*a*** and **114*b*** for supporting wafers W. The two support arms **114*a*** and **114*b*** are attached to the rotatable and extensible/contractible portion **113** to face the opposite directions.

[0095] Installed in the loading/unloading chamber **108** is a transfer device **116** for loading/unloading wafers W with respect to the carriers C and the load-lock chambers **106** and **107**. The transfer device **116** has a multi-joint arm structure and can move on a rail **118** in a direction in which the carriers C are arranged, to transfer a wafer W mounted on the support arms **117** provided at the leading end thereof.

[0096] This film forming apparatus **300** includes a control unit **120** for controlling each component thereof. The control unit **120** controls each component of the units **101** to **104**, the transfer devices **112** and **116**, a gas exhaust system (not shown) of the transfer chamber **105**, opening and closing of the gate valves G and the like. The control unit **120** has the same configuration as that of the control unit **40** shown in FIG. **1**.

[0097] The Cu-containing residue removal unit **101** and the copper oxide film removal unit **102** have the same configurations as that of the film forming apparatus of the first embodiment. In the Cu-containing residue removal unit **101**, the temperature of the mounting table is set such that the wafer is heated to be maintained at the first temperature within a range, e.g., from about 100° C. to about 200° C. In the copper oxide film removal unit **102**, the temperature of the mounting table is set such that the wafer is heated to the second temperature that falls within a range, e.g., from about 200° C. to about 300° C.

(Substrate Processing Method of the Third Embodiment)

[0098] The following is description of the substrate processing method of the present embodiment which performs cleaning by removing a copper oxide film on a surface of Cu and a Cu-containing residue in a Cu wiring structure on a wafer W by using the substrate processing apparatus **300** configured as described above.

[0099] Here, as in the first embodiment, the Cu-containing residue **209** and the copper oxide film **210** in the structure of FIG. **2** are removed by dry cleaning using an organic acid.

[0100] FIG. **8** is a flowchart showing the substrate processing method of the third embodiment. First of all, a wafer W is loaded from a carrier C into one of the load-lock chambers **106** and **107** by a transfer device **116** of the loading/unloading chamber **108** (step **21**). Next, the load-lock chamber is exhausted to a vacuum state, and the wafer W is unloaded by the transfer device **112** of the transfer chamber **105**. Then, the wafer W is loaded into the Cu-containing residue removal unit **101** and then is mounted on the mounting table (step **22**). The temperature of the mounting table is controlled such that the wafer W mounted on the mounting table is set to be maintained at the relatively low first temperature.

[0101] In the Cu-containing residue removal unit **101**, the temperature of the wafer W is stabilized to be maintained at the first temperature by introducing a nonreactive gas into the chamber (step **23**). Then, the processing gas containing an organic acid gas is supplied into the chamber, and the Cu-containing residue **209** is mainly removed at the first temperature by etching (step **24**). As described above, as for an organic acid forming the processing gas, it is preferable to use a carboxylic acid. Especially, a formic acid (HCOOH) is preferably used. If an organic acid is a carboxylic acid, e.g., a formic acid (HCCOH), the first temperature falls preferably within a range from about 100° C. to about 200° C. as in step **4** of the first embodiment, and the reduction reaction occurs as expressed in the Eq. (1). This step is executed until the Cu-containing residue **209** is almost completely removed. At this time, a part of the copper oxide film **210** is also removed by etching.

[0102] Moreover, the processing gas may be supplied immediately after the wafer W is mounted on the wafer W without performing the stabilization process of step **23**. In step **24**, the flowing nonreactive gas may be stopped to flow.

[0103] After the Cu-containing residue is removed by etching in step **24**, the wafer W is unloaded from the Cu-containing residue removal unit **101** by the transfer device **112**. Then, the wafer W is loaded into the copper oxide film removal unit **102** and then is mounted on the mounting table (step **25**).

[0104] The temperature of the mounting table is controlled such that the wafer W mounted thereon is set to be maintained at the second temperature higher than the first temperature.

[0105] In the copper oxide film removal unit **102**, the temperature of the wafer W is stabilized at the second temperature by introducing the nonreactive gas into the chamber (step **26**). Thereafter, the processing gas containing an organic acid gas is supplied into the chamber, and the copper oxide film **210** is removed at the second temperature mainly by reduction (step **27**). If the organic acid is a carboxylic acid, e.g., a formic acid (HCOOH), the second temperature is preferably set to be within a range from about 200° C. to about 300° C. as in step **6** of the first embodiment, and the reduction reaction occurs as expressed in the Eq. (2).

[0106] The processing gas may be supplied immediately after the wafer W is mounted on the wafer W without performing the stabilization process of step **26**. In step **27**, the flowing nonreactive gas may be stopped to flow.

[0107] The process of removing the copper oxide film **210** by reaction which is mainly a reduction process is continued until the copper oxide film **210** is completely removed. The cleaning process of the present embodiment is completed when the removal process of the copper oxide film **210** is completed. However, in the substrate processing apparatus **300**, the wafer W is unloaded via one of the load-lock chambers **106** and **107** after the barrier film formation in the barrier film formation unit **103** and the Cu seed film formation in the Cu seed film formation unit **104** (step **29**) are carried out (step **30**).

[0108] In the present embodiment as well as in the first embodiment, when the Cu-containing residue **209** and the copper oxide film **210** are removed by dry cleaning using an organic-acid gas, the Cu-containing residue is removed at the relatively low first temperature by etching, and copper oxide film is removed at the second temperature higher than the first temperature by reaction which is mainly a reduction process. As a consequence, they can be reliably removed within a short period of time.

[0109] As described above, in the first embodiment, the time for raising the temperature of the wafer from the first temperature to the second temperature is required. Further, when a plurality of wafers is consecutively processed, the time for lowering the temperature of the mounting table from the second temperature to the first temperature is required. On the other hand, in the present embodiment, the Cu-containing residue **209** and the copper oxide film **210** are removed by using two units having mounting tables respectively preset to be maintained at the first and the second temperature. Hence, the temperature changing time is not required, and the throughput can be increased by the corresponding amount.

[0110] In the cluster tool-type substrate processing apparatus **300** of the present embodiment, a series of processes from the etching of the low-k film to the formation of the Cu seed film can be performed in-situ by providing a unit for etching the Low-k film and ashing a resist.

Fourth Embodiment

[0111] (Configuration of a Film Forming Apparatus for Performing a Film Forming Method in Accordance with a Fourth Embodiment of the Present Invention)

[0112] FIG. **9** is a cross sectional view schematically showing an example of a substrate processing apparatus for performing a substrate processing method in accordance with the fourth embodiment of the present invention.

[0113] This substrate processing apparatus **400** is a batch-type apparatus for heating a plurality of wafers W simultaneously, and includes a substantially cylindrical processing chamber **131** for accommodating and processing a wafer W. A process tube **132** made of quartz and having a double pipe structure is provided in the processing chamber **131**, and a cylindrical manifold **136** made of metal is connected to the lower end of the process tube **132**. Various lines are connected to the manifold **136**.

[0114] A wafer boat **133** for holding a plurality of wafers W in the processing chamber **131** is loaded into the process tube **132**. The wafer boat **133** is supported by a boat elevator **134** via a thermal insulation container **138**, and is loaded and unloaded by vertical movement. A cover **137** is adhered to the boat elevator **134**. When the wafer boat **133** is loaded into the process tube **132** by raising the boat elevator **134**, the cover **137** covers the lower opening of the manifold **136** in a sealed state. Accordingly, the interior of the process tube **132** becomes a sealed space.

[0115] A heater **135** for heating a wafer W is provided in the processing chamber **131** so as to surround the process tube **132**. A heater power supply **141** is connected to the heater **135**. Meanwhile, a thermocouple **142** is provided near the wafer W mounted on the wafer boat **133**, and a signal of the thermocouple **142** is transmitted to the heater controller **143**. The heater controller **143** transmits an instruction to the heater power supply **141** in accordance with the signal of the thermocouple **142** and controls the wafer W to be maintained at a predetermined temperature by controlling the heating of the heater **135**.

[0116] A processing gas line **151** for supplying a processing gas containing an organic acid gas into the process tube **132** is connected to the manifold **136**. The processing gas line **151** extends in a horizontal direction toward the inside of the manifold **136**, and extends upward such that the processing gas can be supplied toward the upper portion of the process tube **132**. A processing gas supply source **152** for supplying a processing gas is connected to the other end of the processing gas line **151**. A mass flow controller **153** and valves **154** disposed on both sides thereof are installed in the processing gas line **151**. As for an organic acid forming the processing gas, it is preferable to use a carboxylic acid. As for a carboxylic acid, it is preferable to use a formic acid (HCOOH), an acetic acid (CH_3COOH), a propionic acid (CH_3CH_2COOH), a butyric acid ($CH_3(CH_2)_2COOH$), a valeric acid ($CH_3(CH_2)_3COOH$) or the like. Among them, it is preferable to use a formic acid (HCOOH).

[0117] A nonreactive gas line **161** for supplying a nonreactive gas into the process tube **132** is connected to the manifold **136**. The nonreactive gas line **161** extends in a horizontal direction toward the inside of the manifold **136**, and extends upward such that the nonreactive gas can be supplied toward the upper portion of the process tube **132**. A nonreactive gas supply source **162** for supplying a nonreactive gas is connected to the other end of the nonreactive gas line **161**. A mass flow controller **163** and valves **164** disposed on both sides thereof are installed in the processing gas line **161**. The nonreactive gas may be used as a purge gas, a dilution gas, a carrier gas or the like. For example, Ar gas, He gas, N_2 gas or the like can be used therefor.

[0118] A line **171** is connected to the manifold **136**, and a gas is exhausted between an inner line and an outer line of the process tube **132**. A gas exhaust unit **172** including a high-speed vacuum pump is provided in the gas exhaust line **171**. A conductance variable valve **173** is provided in the gas exhaust line **171**, so that a gas exhaust amount from the process tube **132** can be controlled. By driving the gas exhaust unit **172**, the gas in the process tube **132** is exhausted, and the process tube **132** can be depressurized via the line **171** to a predetermined vacuum level at a high speed.

[0119] The substrate processing apparatus **400** includes a control unit **180** for controlling each component thereof. The control unit **180** has the same configuration as that of the control unit **40** of FIG. **1**.

(Substrate Processing Method of the Fourth Embodiment)

[0120] The following is description of the substrate processing method of the present embodiment which performs cleaning by removing a copper oxide film on a surface of Cu and a Cu-containing residue adhered to an interlayer insulating film in a Cu wiring structure on the wafer W by using the processing apparatus **400**.

[0121] Here, as in the first embodiment, the Cu-containing residue **209** and the copper oxide film **210** in the structure of FIG. **2** are removed by dry cleaning using a processing gas containing an organic acid.

[0122] FIG. **10** is a flowchart showing the substrate processing method of the fourth embodiment. First of all, the wafer boat **133** accommodating a plurality of, e.g., 100 wafers W, is loaded into the process tube **132** by the boat elevator **134** (step **31**). Next, the temperature of the wafer W is controlled to be maintained at a relatively low first temperature at which etching of copper oxide as a main component of the Cu-containing residue **209** mainly occurs by controlling the heater **135** by the heater controller **143** based on the temperature detection signal obtained by the thermocouple **142** (step **32**).

[0123] Next, the process tube **132** is exhausted by the vacuum pump of the gas exhaust unit **172**. Further, the valves **164** are opened to introduce, e.g., Ar gas, from the nonreactive gas supply source **162** into the process tube **132** via the nonreactive gas line **161**, thereby stabilizing the temperature of the wafer W at the first temperature (step **33**).

[0124] Next, the valves **154** are opened to supply a processing gas containing an organic acid from the processing gas supply source **152** into the process tube **132** via the processing gas line **151** at a flow rate controlled by the mass flow controller **153**, thereby mainly etching the Cu-containing residue **209** (step **34**). This step is executed until the Cu-containing residue **209** is almost completely removed by etching. At this time, however, a part of the copper oxide film **210** is also removed by etching. As described above, as for the organic acid forming the processing gas, it is preferable to use a carboxylic acid. Especially, a formic acid (HCOOH) is preferably used. If an organic acid is a carboxylic acid, e.g., a formic acid (HCOOH), the first temperature is preferably set to be within a range from about 100° C. to about 200° C. as in step **4** of the first embodiment, and the reduction reaction occurs as described in the Eq. (1).

[0125] In addition, the processing gas may be supplied immediately after the wafer W is loaded into the process tube **132** without performing the stabilization process of step **33**. In step **34**, the flowing nonreactive gas may be stopped to flow.

[0126] After the Cu-containing residue **209** is almost completely removed by the process of step **34**, the supply of the processing gas is stopped, and the nonreactive gas is supplied. The heater **135** is controlled by the heater controller **143** based on the temperature detection signal outputted by the thermocouple **142**, and the temperature of the wafer W is controlled to be maintained at the second temperature higher than the first temperature at which etching of copper oxide mainly occurs (step **35**).

[0127] After the temperature becomes stable, the processing gas containing an organic acid gas is supplied from the processing gas supply source **152** into the process tube **132** via the processing gas line **151** at a flow rate controlled by the mass flow controller **153**, and the copper oxide film **210** on the surface of the Cu wiring layer **203** is removed by reaction which is mainly a reduction process (step **36**). If an organic acid is a carboxylic acid, e.g., a formic acid (HCOOH), the second temperature is preferably set to be within a range from about 200° C. to about 300° C., and the reduction reaction occurs as described in the Eq. (2).

[0128] The process of removing the copper oxide film **210** by reaction which is mainly a reduction process is continued until the copper oxide film **210** is completely removed. After the copper oxide film **210** is removed, the supply of the processing gas is stopped by closing the valves **154**, and the valves **164** are opened to supply a nonreactive gas as a purge gas from the nonreactive gas supply source **162** into the process tube **132** via the nonreactive gas line **161** at a flow rate controlled by the mass flow controller **163**, thereby purging the process tube **132** (step **37**). Thereafter, the pressure in the process tube **132** is returned to an atmospheric pressure, and the wafer boat **133** is unloaded by lowering the boat elevator **134** (step **38**).

[0129] In the present embodiment as well as in the first embodiment, when the Cu-containing residue **209** and the copper oxide film **210** are removed by dry cleaning using an organic acid-containing gas, the Cu-containing residue is removed at the relatively low first temperature by etching and the copper oxide film on the surface of Cu is removed at the second temperature higher than the first temperature by reaction which is mainly a reduction process. Accordingly, they can be reliably removed within a short period of time.

[0130] As described above, in the first embodiment, the time for raising the temperature of the wafer from the first temperature to the second temperature is required. Moreover, when a plurality of wafers is consecutively processed, the time for lowering the temperature of the mounting table from the second temperature to the first temperature is required. In a single-wafer processing environment of the first embodiment, the throughput of processing is decreased by the effect the temperature changing time. However, the present embodiment employs a batch type in which a plurality of, e.g., 100 wafers, is processed simultaneously. Therefore, even though the time for changing the temperature from the first temperature to the second temperature is required, the temperature changing time corresponding to each wafer is not long. Hence, the throughput of processing is hardly decreased.

Another Application of the Present Invention

[0131] The present invention can be variously modified without being limited to the above embodiments. For example, the above embodiments have described a case in which only a carboxylic acid represented by a formic acid (HCOOH) is used as an organic acid forming the processing gas. However, it is not limited to the case of supplying only an organic acid gas, and an organic acid gas mixed with another gas such as H_2 or the like may be supplied. Further, an apparatus for performing the substrate processing method of the present invention is not limited to those described in the above embodiments, and various apparatuses can be employed. In addition, the structure of the substrate to be processed is not limited to that shown in FIG. **2**, and the substrate to be processed is not limited to a semiconductor wafer.

What is claimed is:

1. A substrate processing method for removing a copper oxide film on a surface of Cu and a Cu-containing residue adhered to an interlayer insulating film in a Cu wiring structure on a substrate by using an organic acid-containing gas, the substrate processing method comprising:

removing the Cu-containing residue by etching by supplying the substrate with a processing gas containing an organic acid gas, after the temperature of the substrate is set to be maintained at a first temperature; and

removing the copper oxide film on the surface of Cu by means of a reduction reaction by supplying the substrate with the processing gas containing the organic acid gas, after the temperature of the substrate is set to be maintained at a second temperature that is higher than the first temperature.

2. The substrate processing method of claim **1**, wherein the interlayer insulating film is a low-k film.

3. The substrate processing method of claim **1**, wherein the organic acid is a carboxylic acid.

4. The substrate processing method of claim **1**, wherein the carboxylic acid is a formic acid.

5. The substrate processing method of claim **3**, wherein the first temperature is within a range from about 100° C. to about 200° C., and the second temperature is within a range from about 200° C. to about 300° C.

6. The substrate processing method of claim **1**, wherein there is used a substrate processing apparatus including a chamber for accommodating a substrate, a mounting table for mounting thereon the substrate in the chamber, a heating mechanism for heating the substrate on the mounting table, a processing gas supply mechanism for supplying the processing gas containing an organic acid gas into the chamber, and a gas exhaust mechanism for exhausting the chamber,

wherein the Cu-containing residue is removed by etching after the temperature of the substrate is set to be maintained at the first temperature by the heating mechanism and, then, the copper oxide film on the surface of Cu is removed after the temperature of the substrate is set to be maintained at the second temperature by the heating mechanism.

7. The substrate processing method of claim **1**, wherein there is used a substrate processing apparatus including a chamber for accommodating therein a substrate, a mounting table for mounting thereon the substrate in the chamber, a heating mechanism for heating the substrate on the mounting table, an energy medium gas supply mechanism for supplying a heated energy medium gas to the substrate on the mounting table, a processing gas supply mechanism for supplying the processing gas containing an organic acid gas into the chamber, and a gas exhaust mechanism for exhausting the chamber,

wherein the Cu-containing residue is removed by etching after the temperature of the substrate is set to be maintained at the first temperature by the heating mechanism and, then, the copper oxide film on the surface of Cu is removed after the temperature of the substrate is set to be maintained at the second temperature by supplying the heated energy medium gas to the substrate on the mounting table from the energy medium gas supply mechanism.

8. The substrate processing method of claim **1**, wherein there is used a substrate processing apparatus including: a first processing unit, having a mounting table for mounting thereon a substrate and maintained at a temperature for heating the substrate mounted thereon to be maintained at the first temperature, for supplying the processing gas to the substrate on the mounting table; and a second processing unit, having a mounting table for mounting thereon the substrate and maintained at a temperature for heating the substrate mounted thereon to be maintained at the second temperature, for supplying the processing gas to the substrate on the mounting table,

wherein the Cu-containing residue is removed by etching after the temperature of the substrate mounted on the mounting table of the first processing unit is set to be maintained at the first temperature and then, the copper oxide film on the surface of Cu is removed after the temperature of the substrate mounted on the mounting table of the second processing unit is set to be maintained at the second temperature.

9. The substrate processing method of claim **1**, wherein there is used a substrate processing apparatus including a processing chamber for processing therein a substrate, a substrate holding unit for holding a plurality of substrates in the processing chamber, a heating mechanism for heating the substrates in the processing chamber, a processing gas supply mechanism for supplying the processing gas containing an organic acid gas into the processing chamber, and a gas exhaust mechanism for exhausting the processing chamber,

wherein the Cu-containing residue is removed by etching after the temperature of the substrate supported by the supporting unit in the processing chamber is set to be maintained at the first temperature by the heating mechanism and, then, the copper oxide film on the surface of Cu is removed after the temperature of the substrates is set to be maintained at the second temperature by the heating mechanism.

10. A substrate processing apparatus for removing a copper oxide film on a surface of Cu and a Cu-containing residue adhered to an interlayer insulating film in a Cu wiring structure on a substrate by using an organic acid-containing gas, the substrate processing apparatus comprising:

a chamber for accommodating a substrate;
a mounting table for mounting thereon the substrate in the chamber;
a heating mechanism for heating the substrate on the mounting table;
a processing gas supply mechanism for supplying a processing gas containing an organic acid gas into the chamber;
a gas exhaust mechanism for exhausting an interior of the chamber; and
a control mechanism for removing a Cu-containing residue by etching by supplying the substrate with the processing gas containing an organic acid gas after the temperature of the substrate mounted on the mounting table is set to be maintained at a first temperature by the heating mechanism, and then removing a copper oxide film on a surface of Cu by means of a reduction reaction by supplying the substrate with the processing gas containing an organic acid gas after the temperature of the substrate is set to be maintained at a second temperature higher than the first temperature by the heating mechanism.

11. A substrate processing apparatus for removing a copper oxide film on a surface of Cu and a Cu-containing residue adhered to an interlayer insulating film in a Cu wiring structure on a substrate by using an organic acid-containing gas, the substrate processing apparatus comprising:
a chamber for accommodating a substrate;
a mounting table for mounting thereon the substrate in the chamber;
a heating mechanism for heating the substrate on the mounting table;
an energy medium gas supply mechanism for supplying a heated energy medium gas to the substrate on the mounting table;
a processing gas supply mechanism for supplying a processing gas containing an organic acid gas into the chamber;
a gas exhaust mechanism for exhausting an interior of the chamber;
a control mechanism for removing a Cu-containing residue by etching by supplying the substrate with the processing gas containing an organic acid gas after the temperature of the substrate mounted on the mounting table is set to be maintained at a first temperature by the heating mechanism, and then removing a copper oxide film on a surface of Cu by means of a reduction reaction by supplying the substrate with the processing gas containing an organic acid gas after the temperature of the substrate is set to be maintained at a second temperature higher than the first temperature by supplying the heated energy medium gas to the substrate on the mounting table.

12. A substrate processing apparatus for removing a copper oxide film on a surface of Cu and a Cu-containing residue adhered to an interlayer insulating film in a Cu wiring structure on a substrate by using a processing gas containing an organic acid, the substrate processing apparatus comprising:
a first processing unit, having a mounting table maintained at a temperature for heating the substrate mounted thereon to be maintained at a first temperature, for supplying the processing gas onto the substrate on the mounting table;
a second processing unit, having a mounting table maintained at a temperature for heating the substrate mounted thereon to be maintained at a second temperature, for supplying the processing gas onto the substrate on the mounting table;
a transfer mechanism for transferring the substrate between the first processing unit and the second processing unit; and
a control mechanism for removing a Cu-containing residue by etching by supplying the substrate with the processing gas containing an organic acid gas after the temperature of the substrate mounted on the mounting table of the first processing unit is set to be maintained at the first temperature, and then removing a copper oxide film on a surface of Cu by means of a reduction reaction by supplying a processing gas containing an organic acid gas to the substrate by supplying the substrate with a processing gas containing an organic acid gas after the temperature of the substrate transferred on the mounting table of the second processing unit by the transfer mechanism is set to be maintained at the second temperature.

13. A substrate processing apparatus for removing a copper oxide film on a surface of Cu and a Cu-containing residue adhered to an interlayer insulating film in a Cu wiring structure on a substrate by using an organic acid-containing gas, the substrate processing apparatus comprising:
a processing chamber for processing a substrate;
a substrate supporting unit for supporting a plurality of substrates in the processing chamber;
a heating mechanism for heating the substrates in the processing chamber;
a processing gas supply mechanism for supplying a processing gas containing an organic acid gas into the processing chamber;
a control mechanism for removing a Cu-containing residue by etching by supplying the substrates with the processing gas containing an organic acid gas after the temperature of the substrates held by the substrate supporting unit in the processing chamber is set to be maintained at a first temperature by the heating mechanism, and then removing a copper oxide film on a surface of Cu by means of a reduction reaction by supplying the substrates with the processing gas containing an organic acid gas after the temperature of the substrates is set to be maintained at a second temperature higher than the first temperature by the heating mechanism.

14. A non-transitory computer-readable storage medium storing a program for controlling a substrate processing apparatus, wherein the program, when executed by a computer, controls the substrate processing apparatus to perform the substrate processing method described in claim **1**.

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