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(54) METHOD OF MANUFACTURING SEMICONDUCTOR DEVICE, SUBSTRATE PROCESSING APPARATUS AND EVAPORATION SYSTEM

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USPC ........... **438/758**; 118/726; 118/724; 55/385.1

(57) **ABSTRACT**

An amount of particles generated when a source material is used is suppressed. A substrate is loaded into a process chamber, and the source material is sequentially flowed into an evaporator, and a mist filter constituted by assembling a plurality of at least two types of plates including holes disposed at different positions to be evaporated and supplied into the process chamber to process the substrate, and then, the substrate is unloaded from the process chamber.

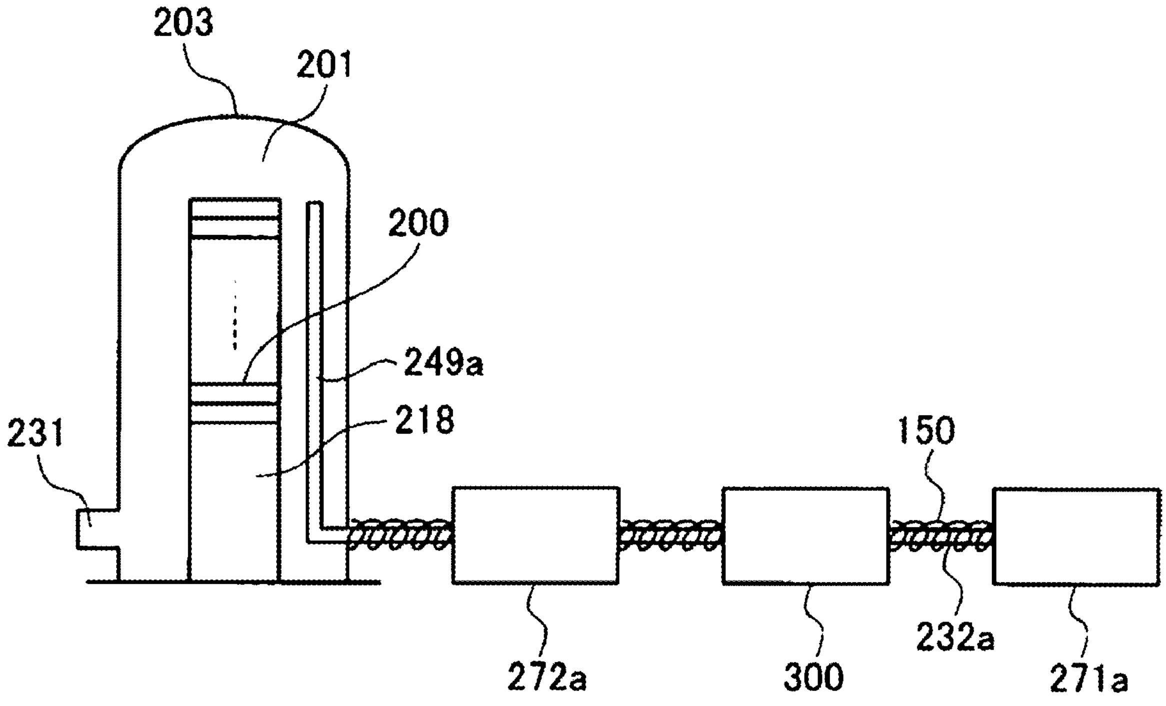
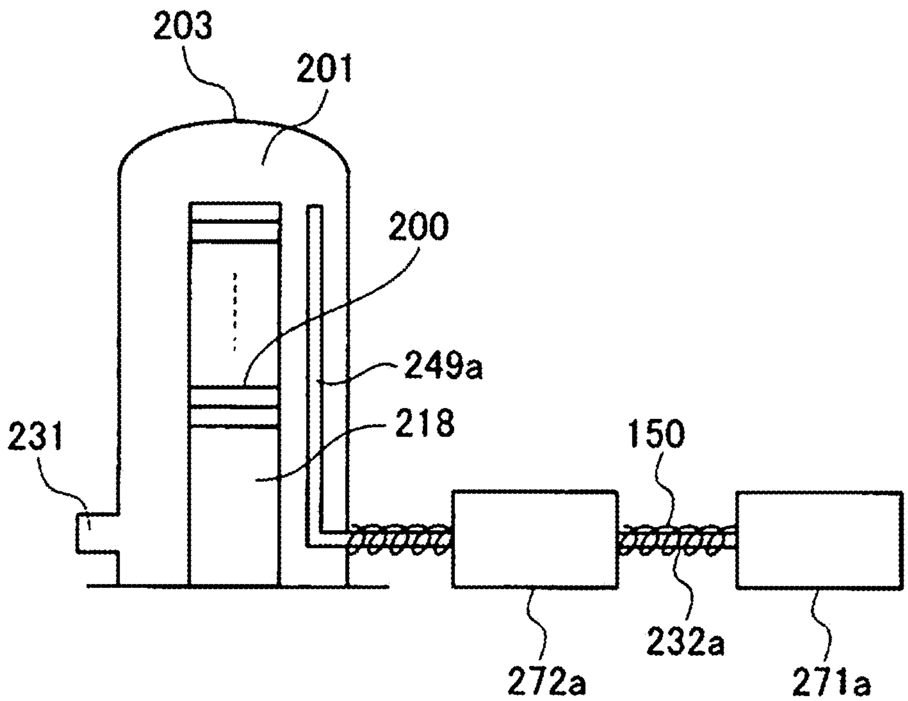


FIG. 1




<PRIOR ART>

FIG. 2

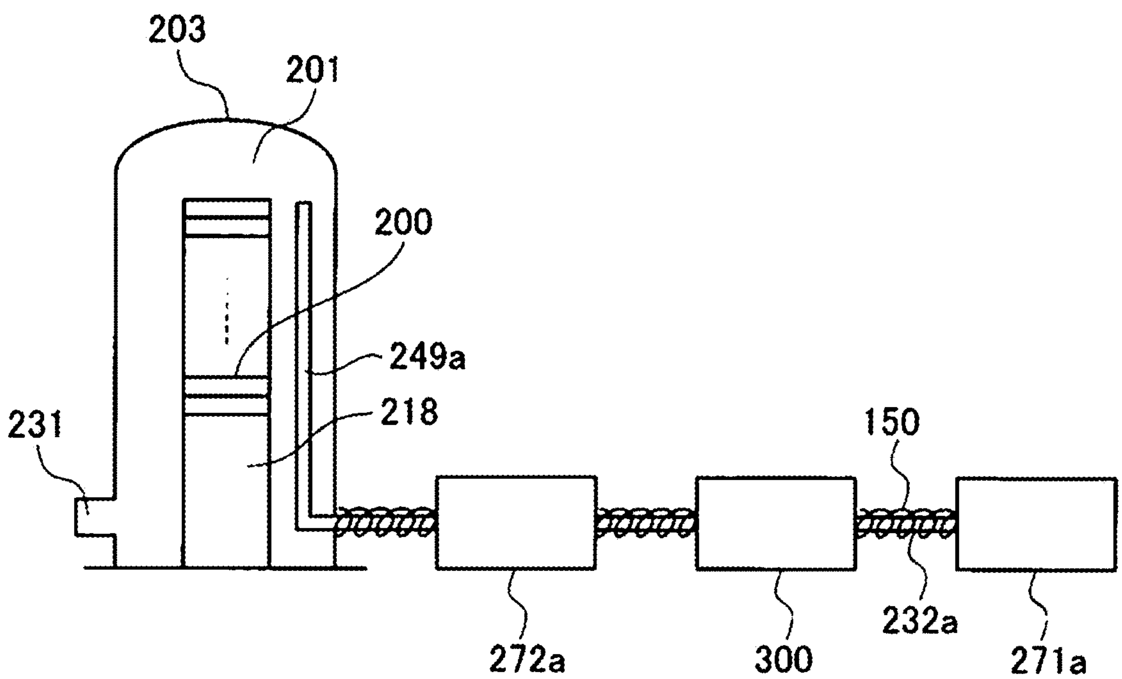


**FIG. 3**

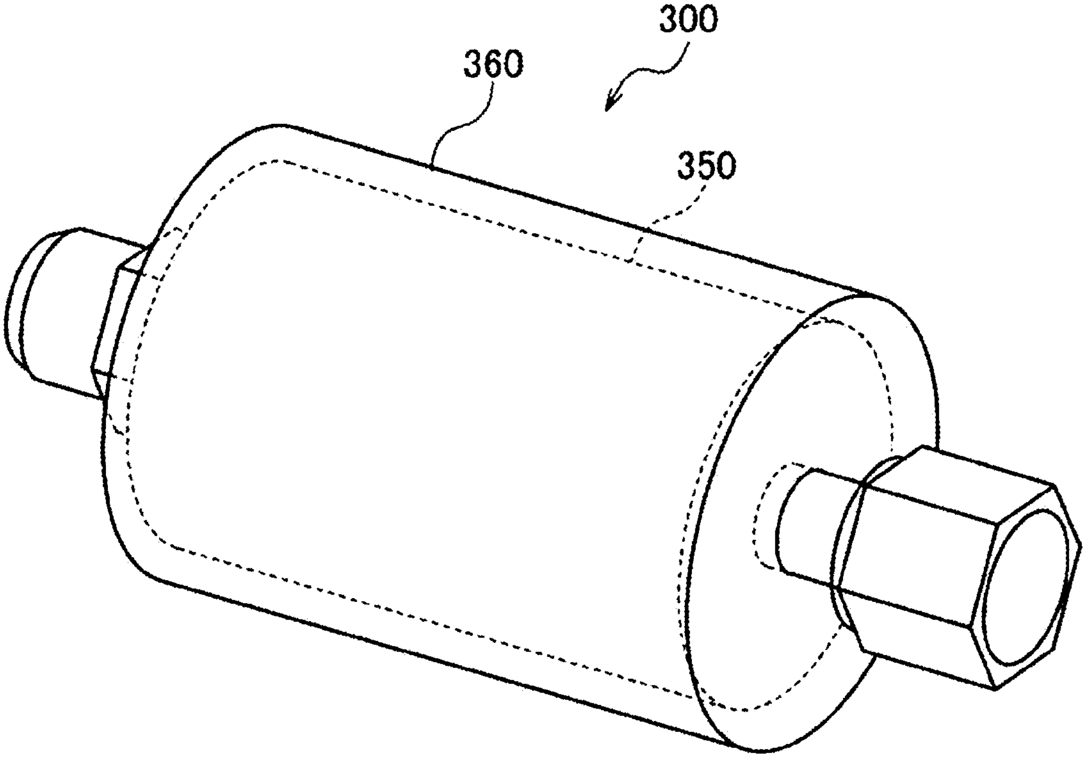


FIG. 4

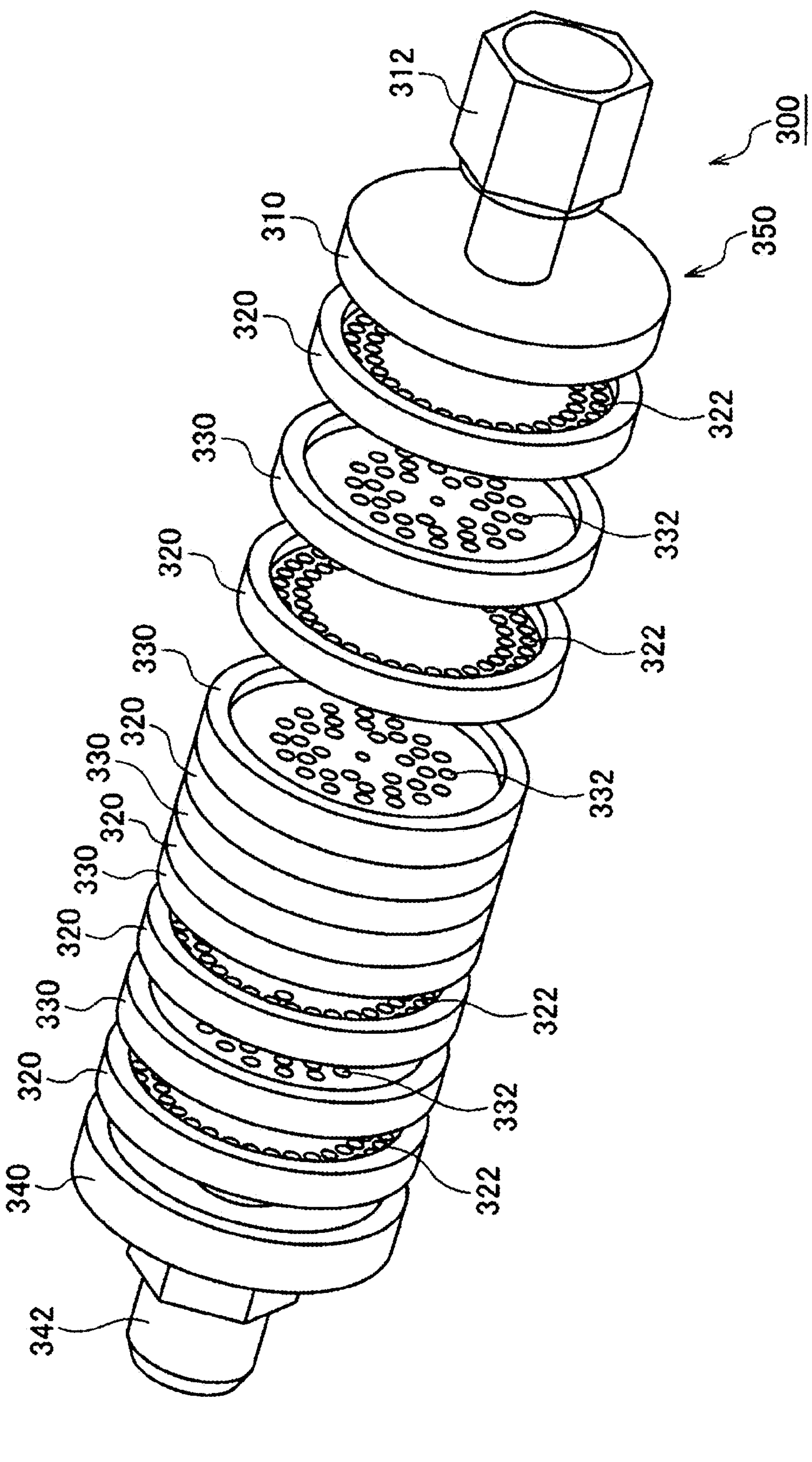

312
300
310
350
320
322
330
332
320
322
330
332
320
330
320
330
320
322
330
332
320
322
340
342

FIG. 5

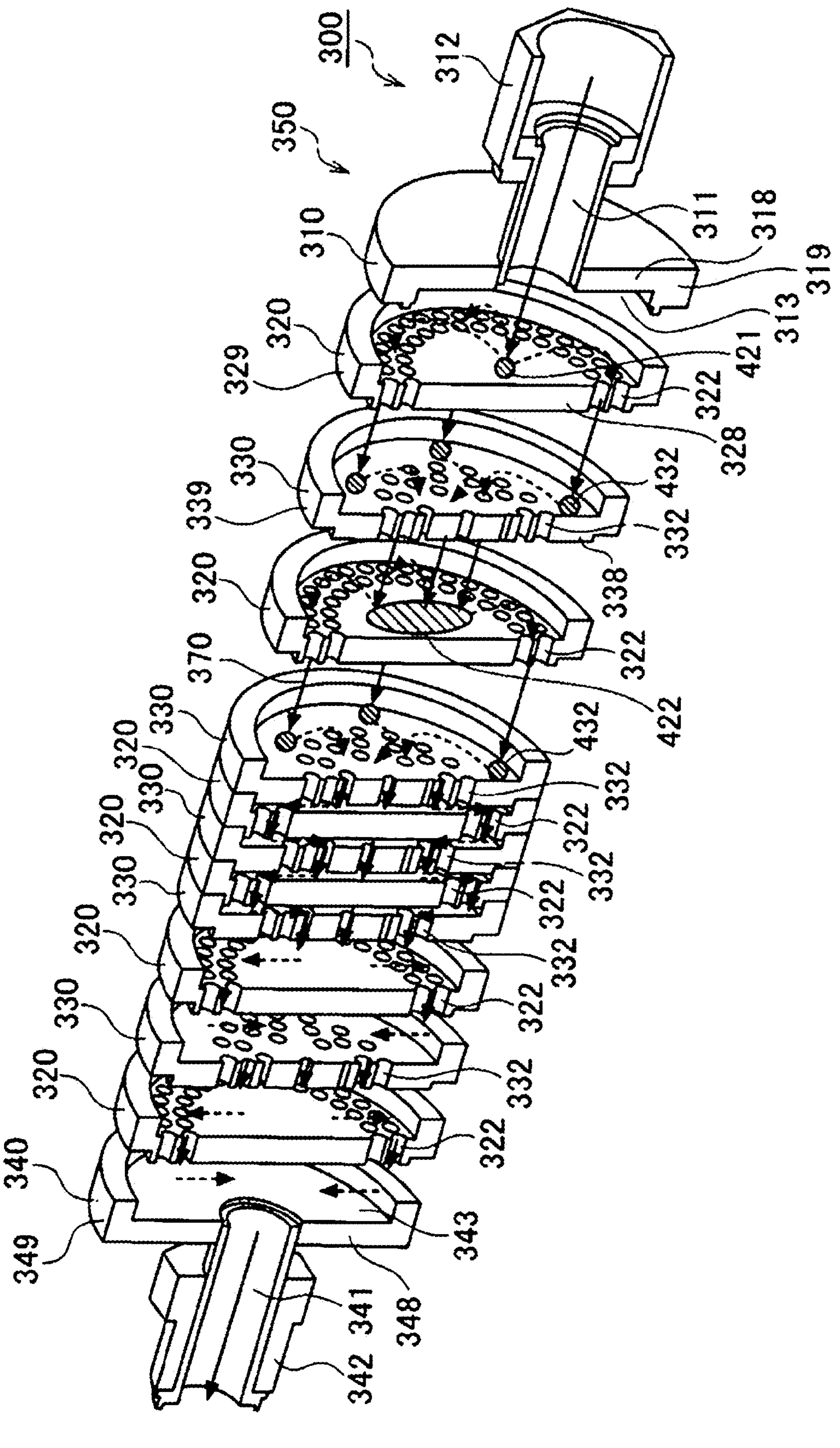
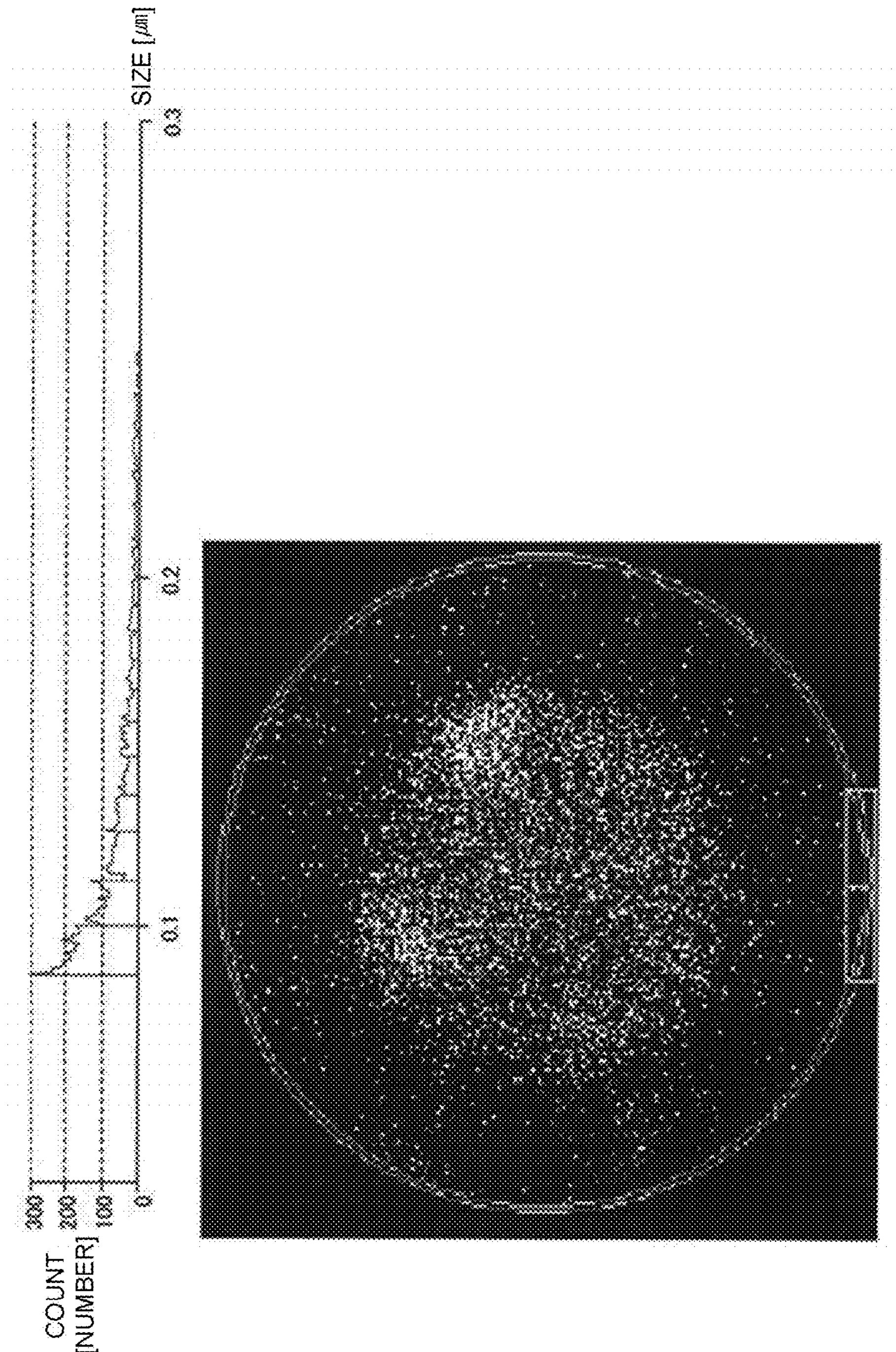

300
312
350
311
318
310
319
313
320
421
329
322
328
330
432
339
332
338
422
370
342
341
348
349
340
343

**FIG. 6**




**<PRIOR ART>**

FIG. 7

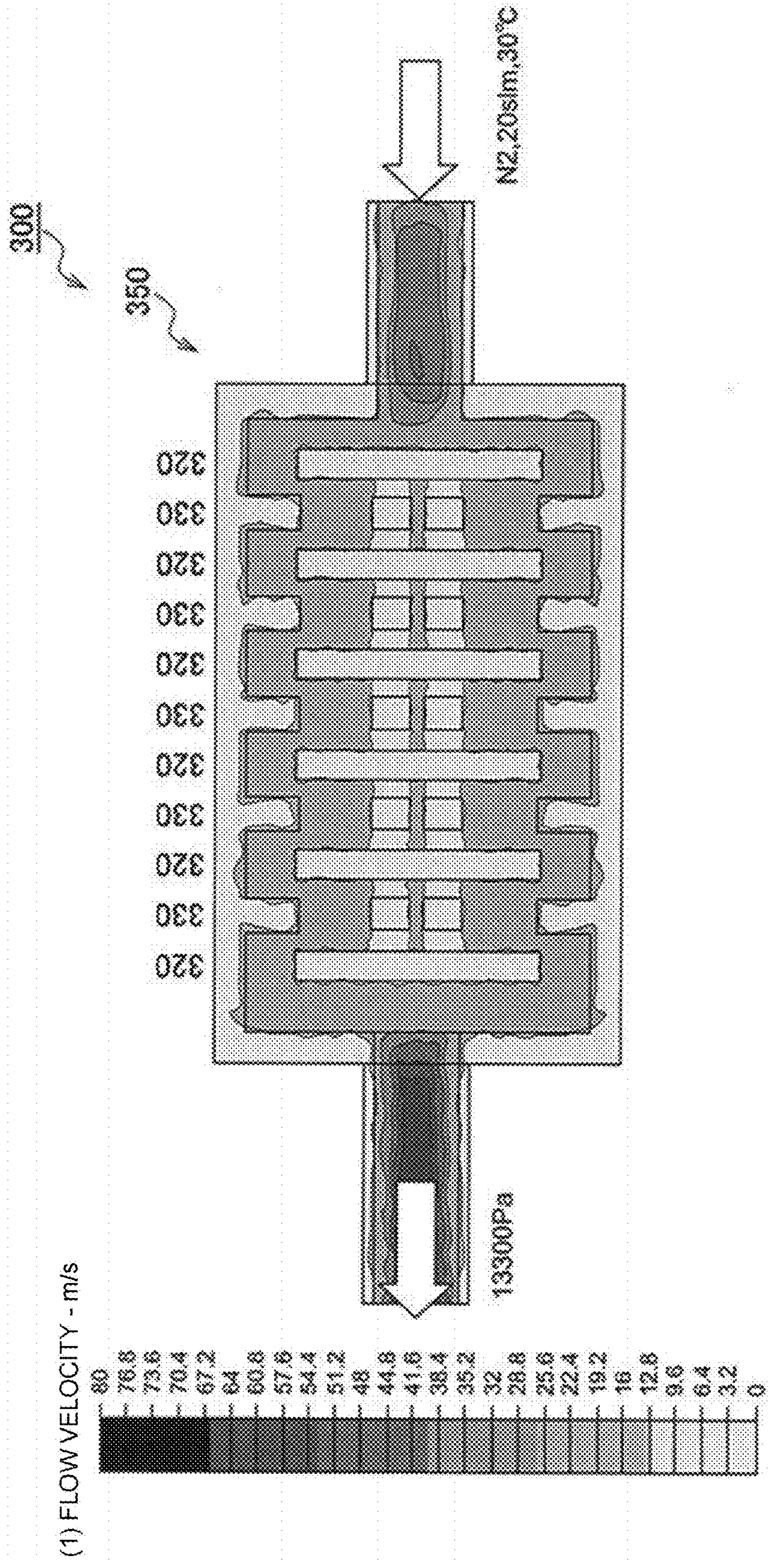

N2,20slm,30°C
300
350
320
330
320
330
320
330
320
330
320
330
320
13300Pa
(1) FLOW VELOCITY - m/s
80
76.8
73.6
70.4
67.2
64
60.8
57.6
54.4
51.2
48
44.8
41.6
38.4
35.2
32
28.8
25.6
22.4
19.2
16
12.8
9.6
6.4
3.2
0

FIG. 8

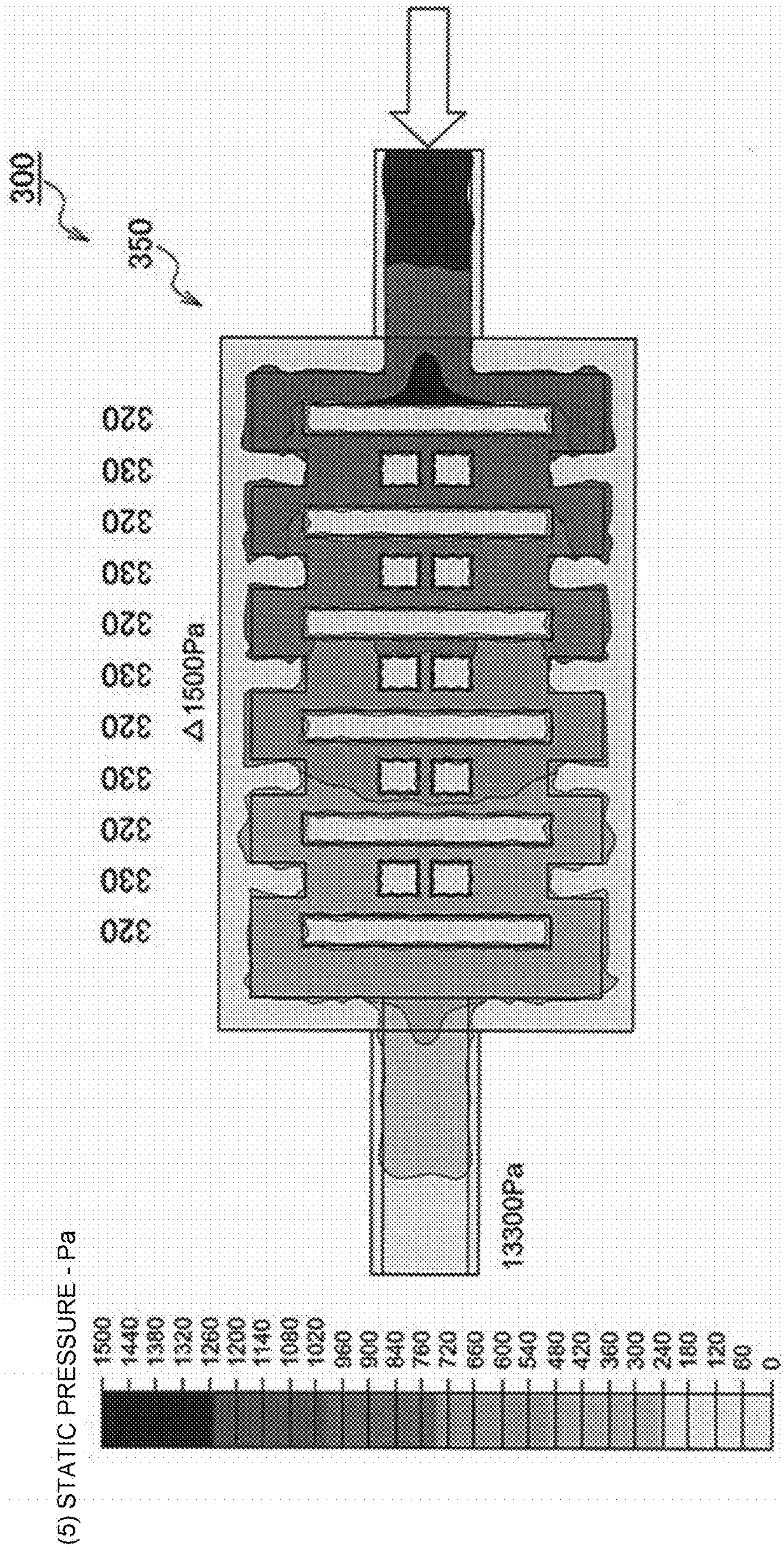

300
350
320
330
320
330
320
330
320
330
320
330
320
Δ1500Pa
13300Pa
(5) STATIC PRESSURE - Pa
1500
1440
1380
1320
1260
1200
1140
1080
1020
960
900
840
780
720
660
600
540
480
420
360
300
240
180
120
60
0

FIG. 9

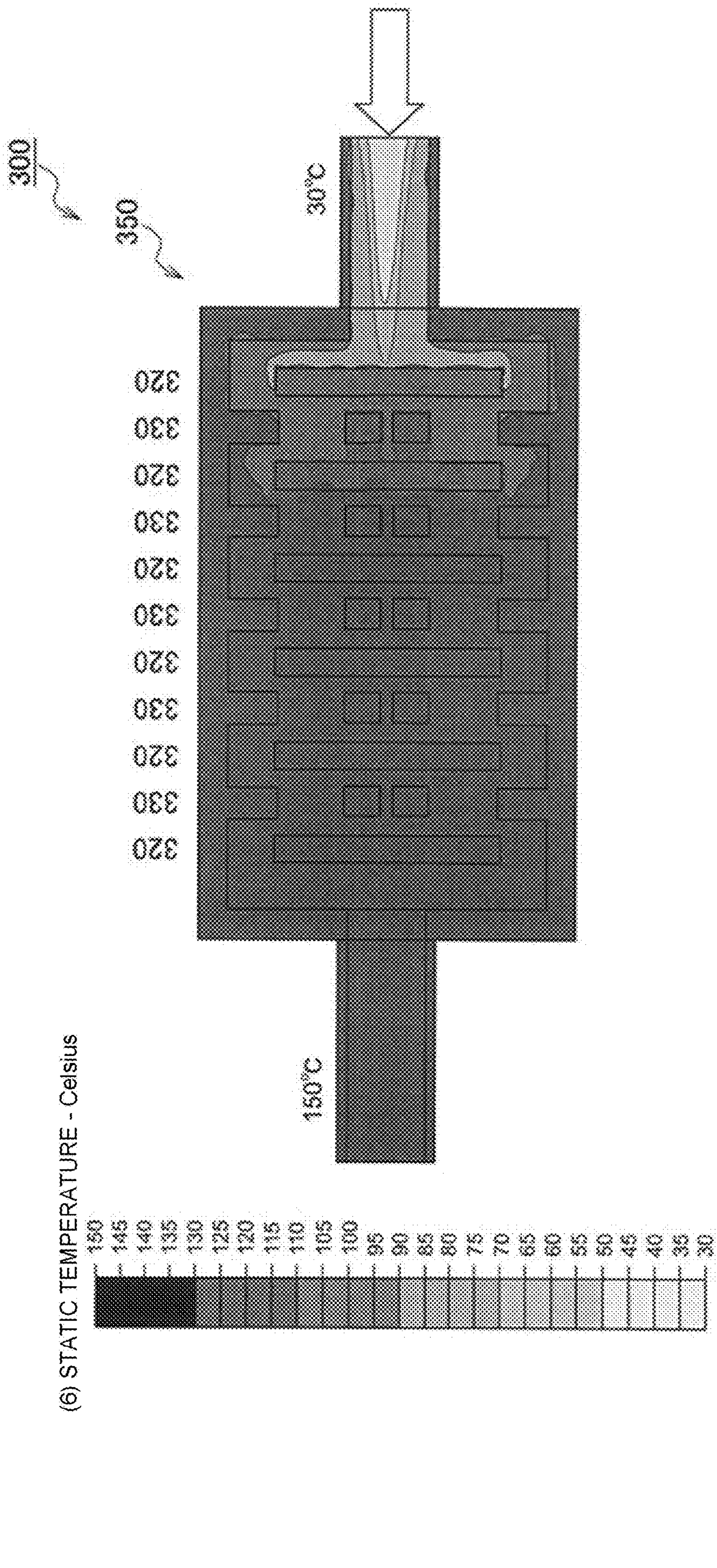

300
350
30°C
320
330
320
330
320
330
320
330
320
330
320
150°C
(6) STATIC TEMPERATURE - Celsius
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30

FIG. 10A

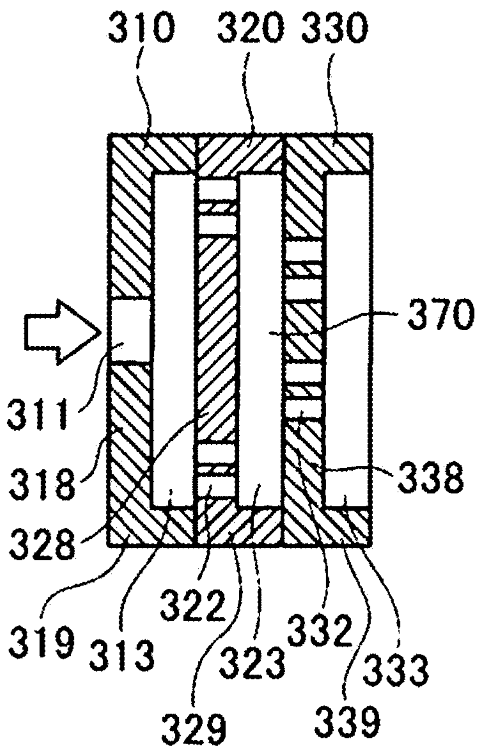


FIG. 10B

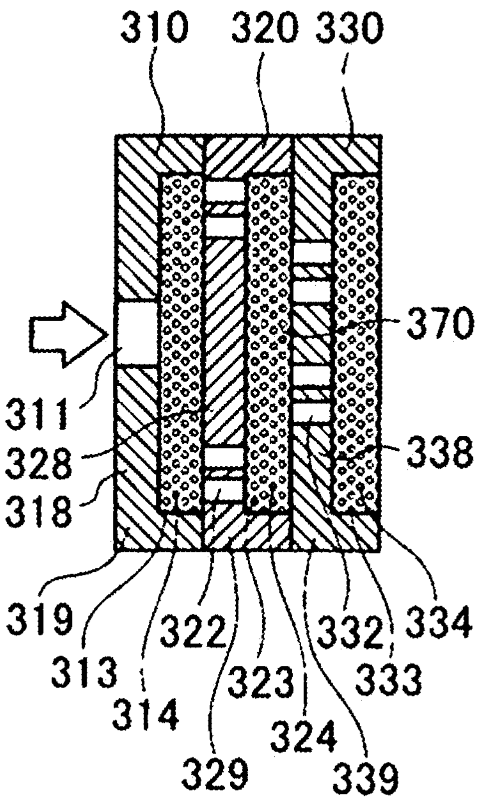

310
320
330
370
311
328
338
318
319
313
314
322
329
323
324
332
333
339
334

FIG. 10C

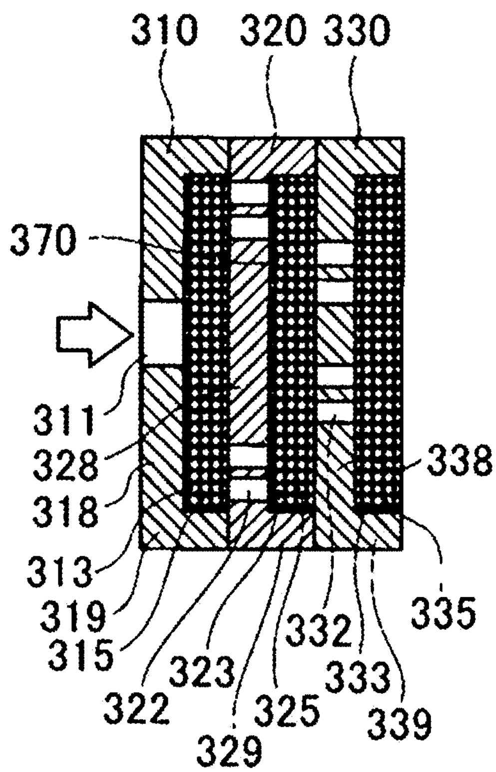

310
320
330
370
311
328
318
313
319
315
322
323
329
325
332
333
339
335
338

FIG. 11A

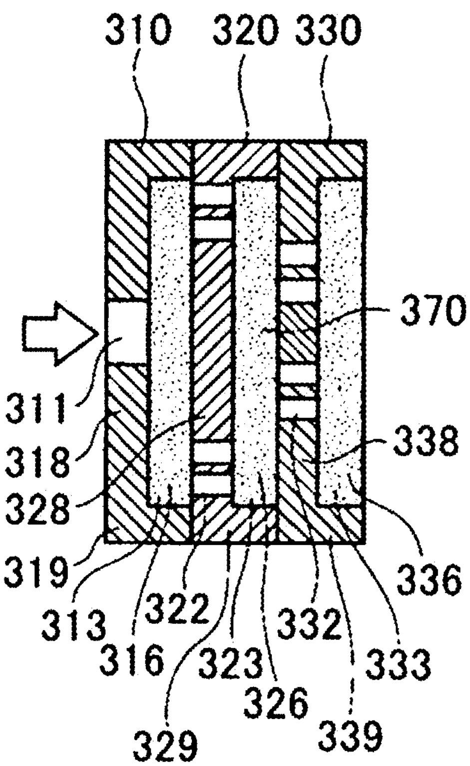

310
320
330
370
311
318
328
338
319
313
316
322
323
329
326
332
333
339
336

FIG. 11B

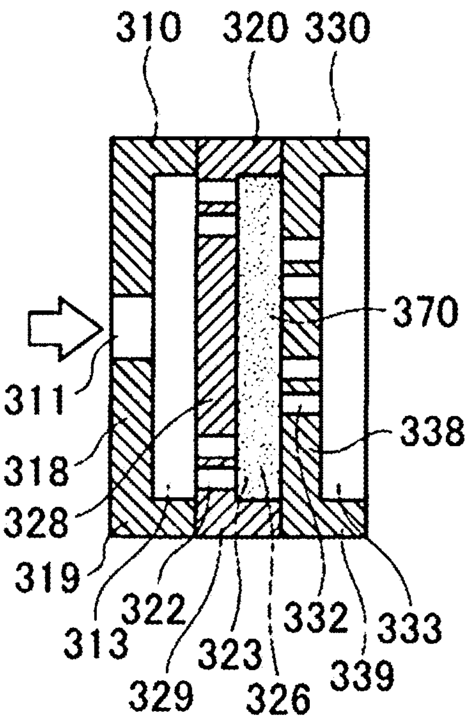

310
320
330
370
311
338
318
328
319
322
313
332
333
323
329
326
339

FIG. 11C

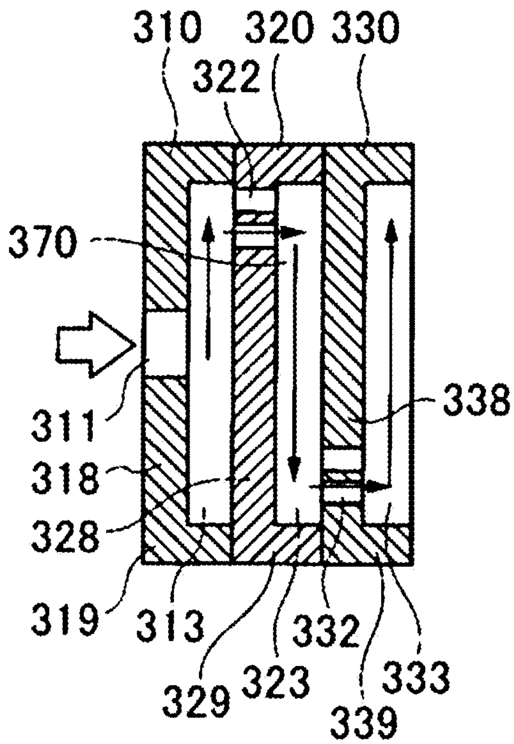


FIG. 12A

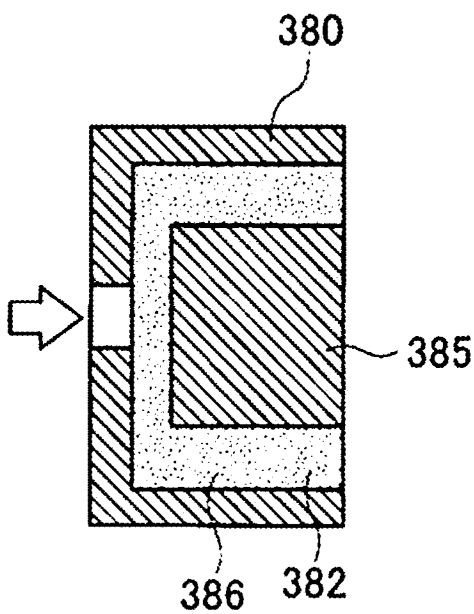


FIG. 12B

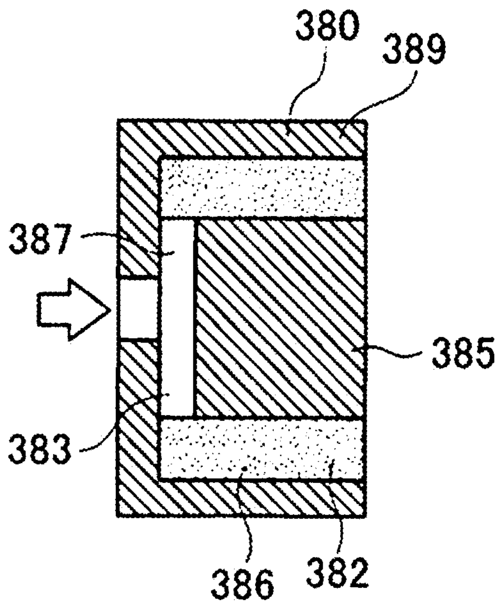


FIG. 13

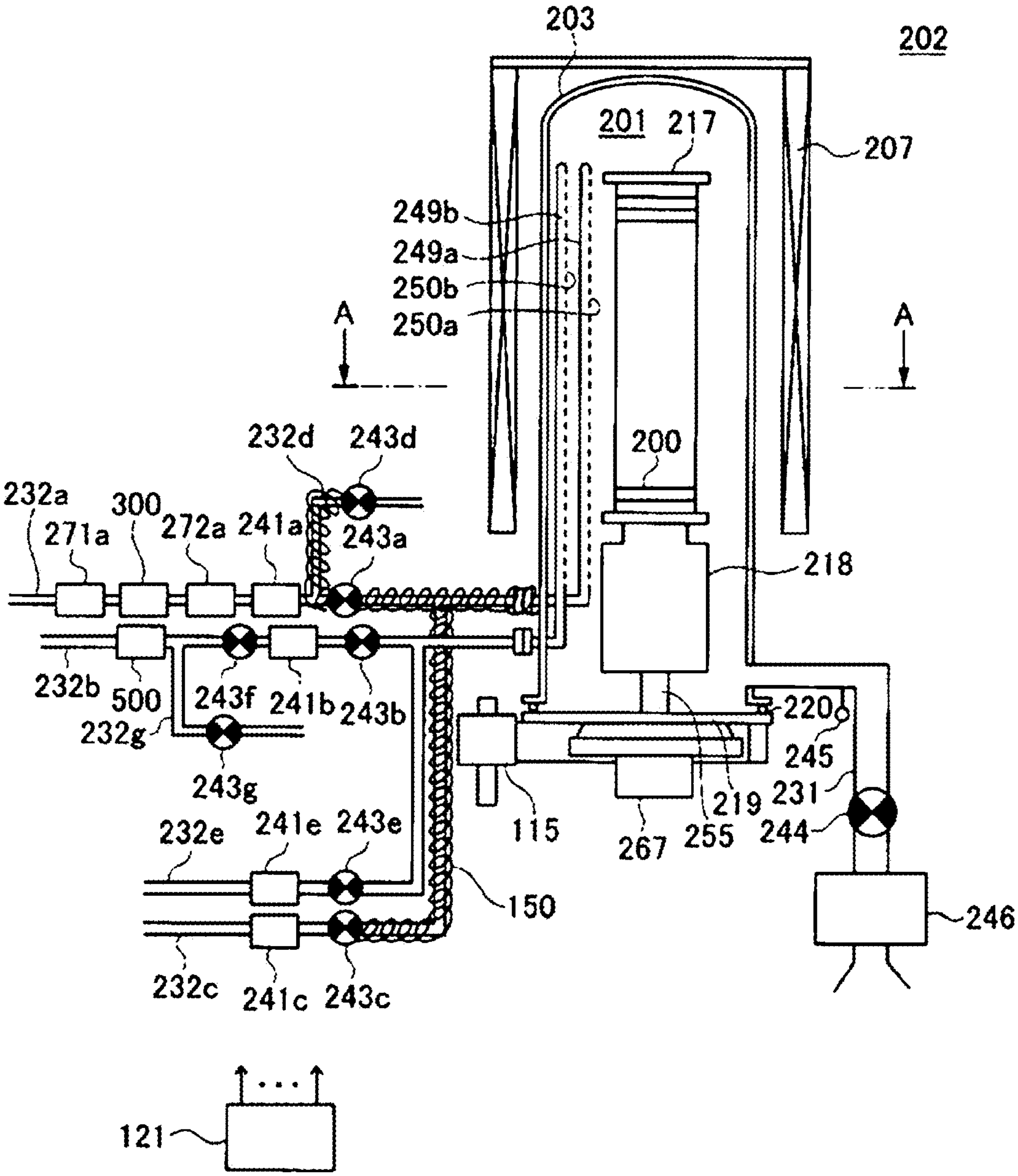
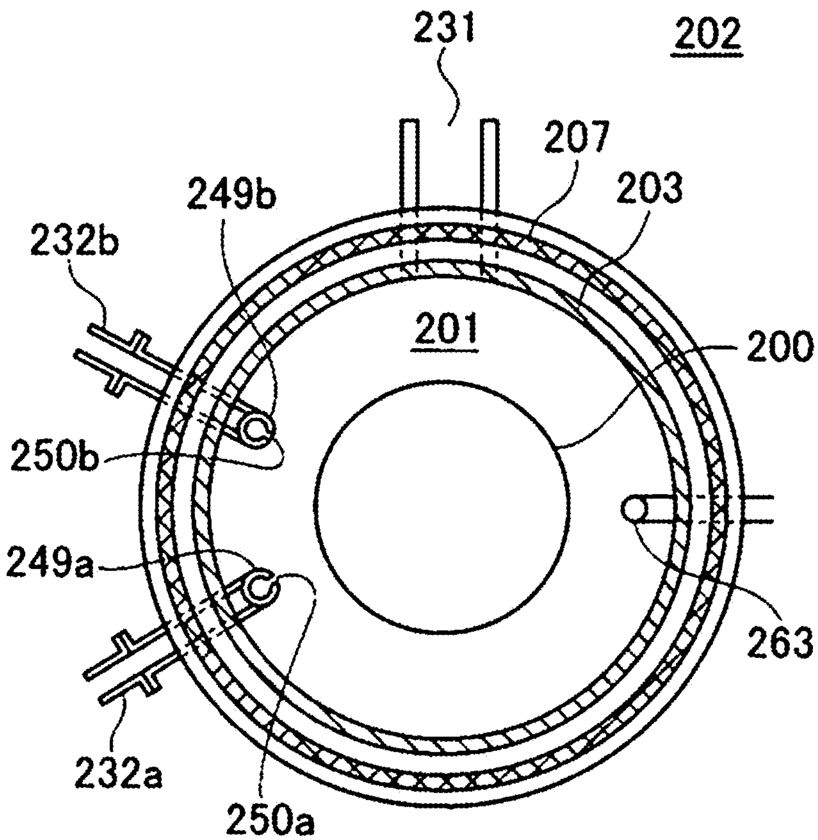
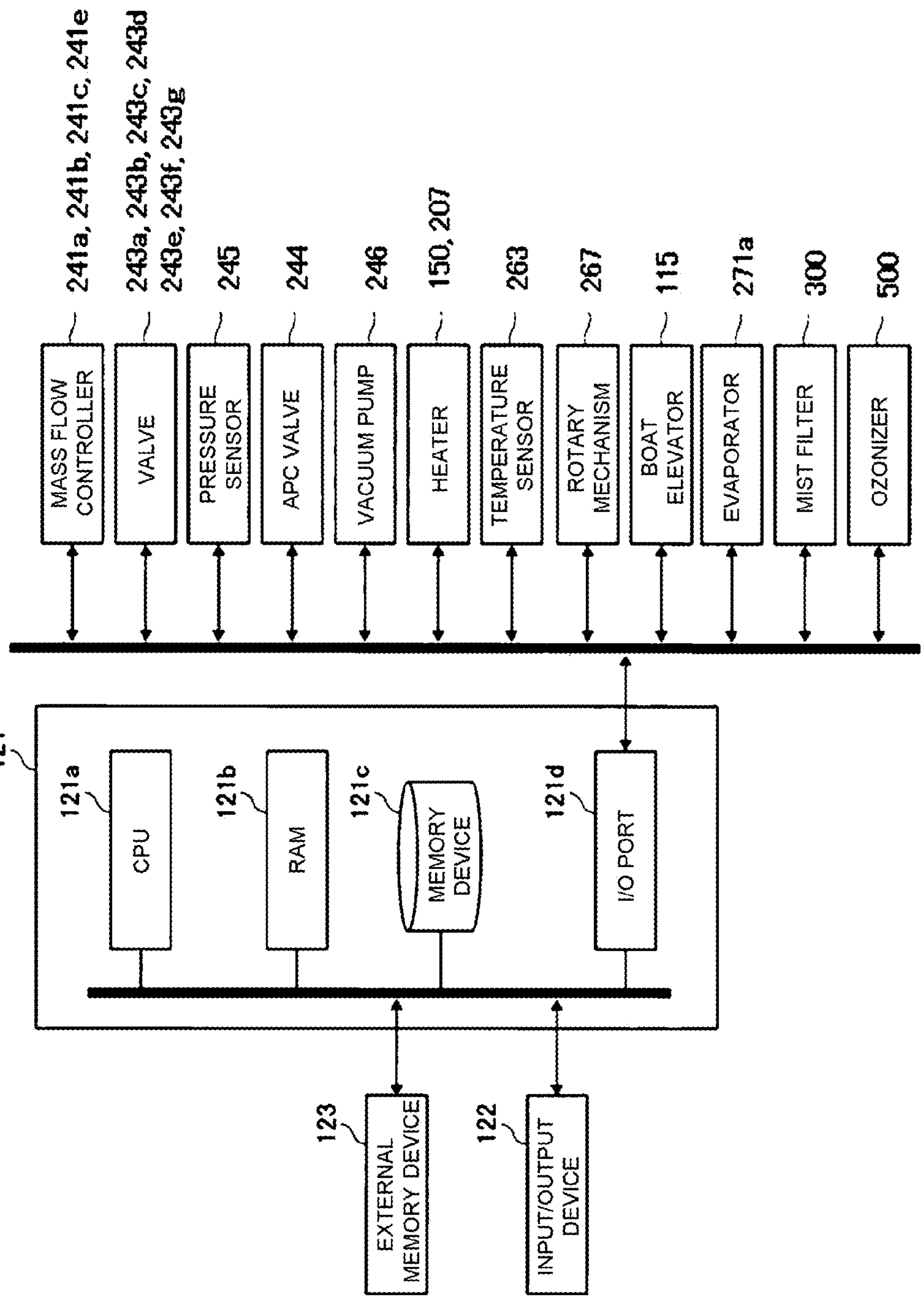

203
202
201
217
207
249b
249a
250b
250a
A
A
232d
243d
200
232a
300
271a
272a
241a
243a
218
232b
500
243f
241b
243b
232g
243g
220
245
231
244
219
255
115
267
232e
241e
243e
150
246
232c
241c
243c
121

FIG. 14





241a, 241b, 241c, 241e
MASS FLOW CONTROLLER
243a, 243b, 243c, 243d
243e, 243f, 243g
VALVE
245
PRESSURE SENSOR
244
APC VALVE
246
VACUUM PUMP
150, 207
HEATER
263
TEMPERATURE SENSOR
267
ROTARY MECHANISM
115
BOAT ELEVATOR
271a
EVAPORATOR
300
MIST FILTER
500
OZONIZER
121
121a
CPU
121b
RAM
121c
MEMORY DEVICE
121d
I/O PORT
123
EXTERNAL MEMORY DEVICE
122
INPUT/OUTPUT DEVICE


FIG. 15

FIG. 16

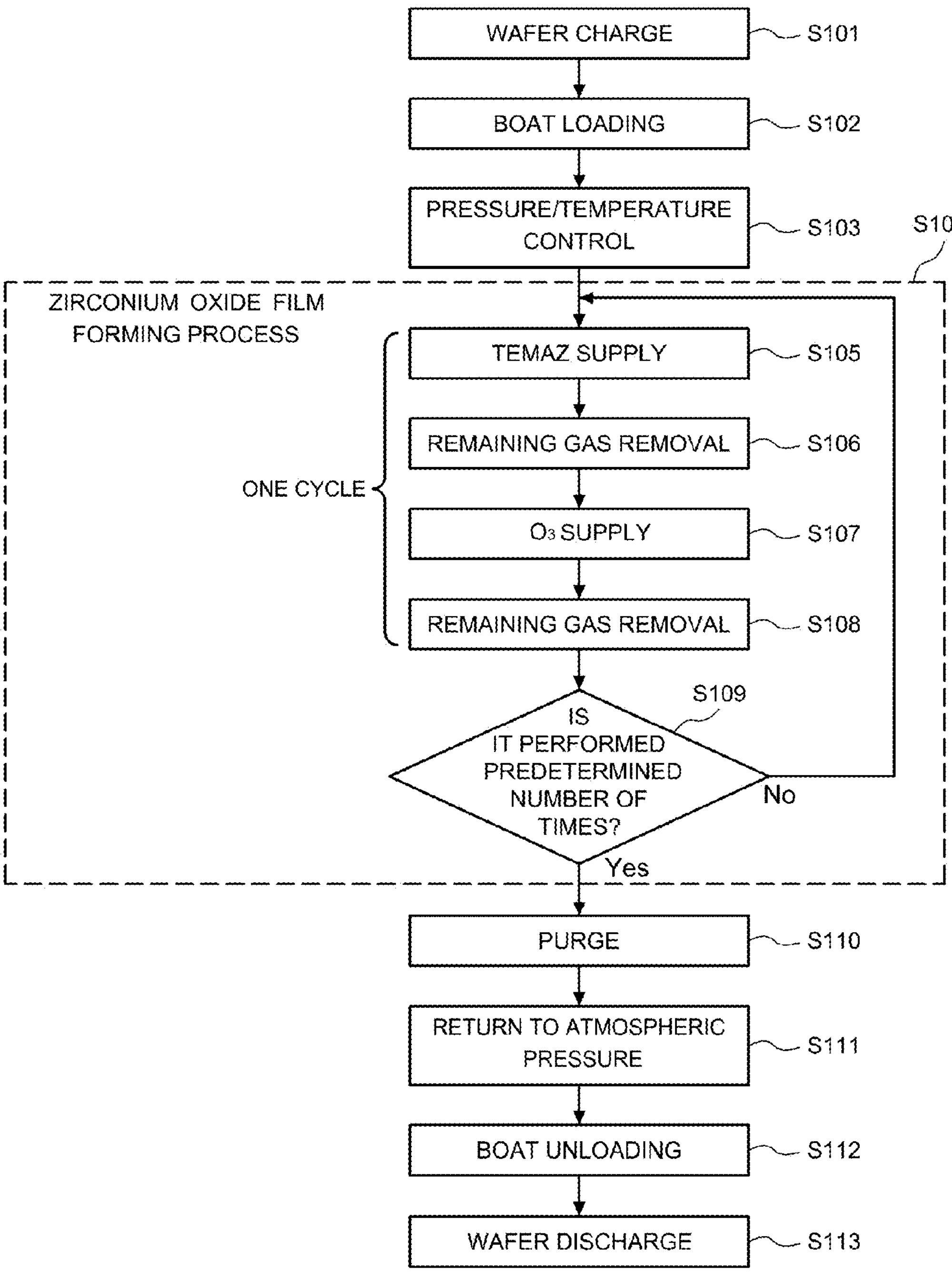
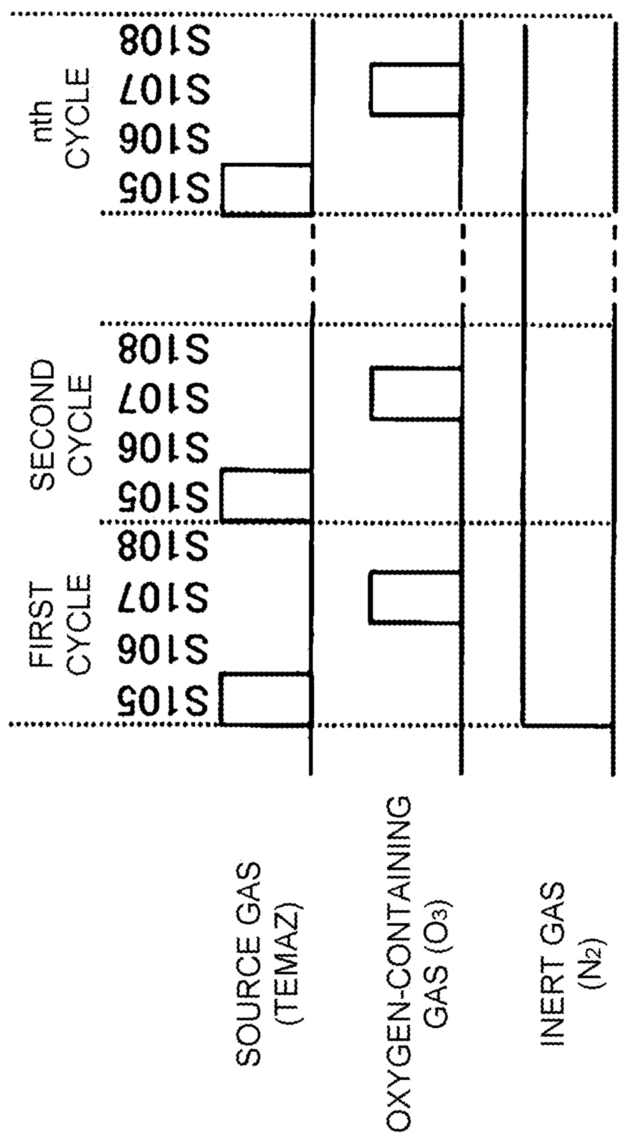

WAFER CHARGE
S101
BOAT LOADING
S102
PRESSURE/TEMPERATURE CONTROL
S103
S104
ZIRCONIUM OXIDE FILM FORMING PROCESS
ONE CYCLE
TEMAZ SUPPLY
S105
REMAINING GAS REMOVAL
S106
O3 SUPPLY
S107
REMAINING GAS REMOVAL
S108
S109
IS IT PERFORMED PREDETERMINED NUMBER OF TIMES?
No
Yes
PURGE
S110
RETURN TO ATMOSPHERIC PRESSURE
S111
BOAT UNLOADING
S112
WAFER DISCHARGE
S113

FIG. 17


FIRST CYCLE
SECOND CYCLE
nth CYCLE
S105
S106
S107
S108
SOURCE GAS (TEMAZ)
OXYGEN-CONTAINING GAS ($O_3$)
INERT GAS ($N_2$)

# METHOD OF MANUFACTURING SEMICONDUCTOR DEVICE, SUBSTRATE PROCESSING APPARATUS AND EVAPORATION SYSTEM

## CROSS-REFERENCE TO RELATED PATENT APPLICATION

**[0001]** This U.S. non-provisional patent application claims priority under 35 U.S.C. §119 of Japanese Patent Application Nos. 2012-087838 and 2013-025544 filed on Apr. 6, 2012 and Feb. 13, 2013 respectively, in the Japanese Patent Office, the entire contents of which are hereby incorporated by reference.

## BACKGROUND OF THE INVENTION

**[0002]** 1. Field of the Invention

**[0003]** The present invention relates to a method of manufacturing a semiconductor device, a substrate processing apparatus and an evaporation system, and more particularly, to a method of manufacturing a semiconductor device including a process of processing a semiconductor wafer using liquid source and a substrate processing apparatus and an evaporation system which are exemplarily used therein.

**[0004]** 2. Description of the Related Art

**[0005]** A technique of forming a film on a substrate using liquid source is disclosed in Patent Document 1 as one process of processes of manufacturing a semiconductor device.

## RELATED ART DOCUMENT

### Patent Document

**[0006]** Japanese Patent Application Laid-Open No. 2010-28094

## SUMMARY OF THE INVENTION

**[0007]** When substrate processing such as film-forming is performed using liquid source, a source gas, which is gasified by evaporating the liquid source, is used. However, when a film is formed on a semiconductor wafer using such a source material, particles may be generated on the wafer due to bad evaporation. In addition, the evaporated source gas may be reliquefied such that the liquid source cannot be efficiently supplied into a process chamber.

**[0008]** It is an aspect of the present invention to provide a method of manufacturing a semiconductor device, a substrate processing apparatus, and an evaporation system that are capable of suppressing an amount of particles generated when liquid source is used and efficiently evaporating liquid source to supply the evaporated fuel into a process chamber.

**[0009]** According to an aspect of the present invention, there is provided a method of manufacturing a semiconductor device, including: (a) loading a substrate into a process chamber; (b) evaporating a source material by sequentially flowing the source material to an evaporator and a mist filter including one or more first plates and one or more second plates; (c) supplying the source material evaporated in the step (b) into the process chamber to process the substrate; and (d) unloading the substrate from the process chamber, wherein each of the one or more first plates includes one or more first holes, and each of the one or more second plates includes one or more second holes disposed at different positions from those of the one or more first holes.

**[0010]** According to another aspect of the present invention, there is provided a substrate processing apparatus including: a process chamber configured to accommodate a substrate; a process gas supply system configured to supply a process gas into the process chamber; and an exhaust system configured to exhaust the process chamber, wherein the process gas supply system includes: an evaporator configured to receive a source material; and a mist filter disposed at a downstream side of the evaporator, and including one or more first plates and one or more second plates, wherein each of the one or more first plates includes one or more first holes, and each of the one or more second plates includes one or more second holes disposed at different positions from those of the one or more first holes.

**[0011]** According to another aspect of the present invention, there is provided an evaporation system including: an evaporator configured to receive a source material; and a mist filter disposed at a downstream side of the evaporator and including one or more first plates and one or more second plates, wherein each of the one or more first plates includes one or more first holes, and each of the one or more second plates includes one or more second holes disposed at different positions from those of the one or more first holes.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0012]** FIG. **1** is a schematic view for describing a conventional source material supply system for the purpose of comparison;

**[0013]** FIG. **2** is a schematic view for describing a source material supply system of an exemplary embodiment of the present invention;

**[0014]** FIG. **3** is a schematic perspective view for describing a mist filter exemplarily used in the exemplary embodiment of the present invention;

**[0015]** FIG. **4** is a schematic exploded perspective view for describing the mist filter exemplarily used in the exemplary embodiment of the present invention;

**[0016]** FIG. **5** is a schematic exploded perspective view for describing the mist filter exemplarily used in the exemplary embodiment of the present invention;

**[0017]** FIG. **6** is a view for describing a status of particles when the conventional source material supply system is used;

**[0018]** FIG. **7** is a schematic cross-sectional view for describing a flow velocity distribution in the mist filter exemplarily used in the exemplary embodiment of the present invention;

**[0019]** FIG. **8** is a schematic cross-sectional view for describing a pressure distribution in the mist filter exemplarily used in the exemplary embodiment of the present invention;

**[0020]** FIG. **9** is a schematic cross-sectional view for describing a temperature distribution in the mist filter exemplarily used in the exemplary embodiment of the present invention;

**[0021]** FIGS. **10**A, **10**B and **10**C are schematic cross-sectional views for describing a variant of the mist filter exemplarily used in the exemplary embodiment of the present invention;

**[0022]** FIGS. **11**A, **11**B and **11**C are schematic cross-sectional views for describing a variant of the mist filter exemplarily used in the exemplary embodiment of the present invention;

**[0023]** FIGS. **12**A and **12**B are schematic cross-sectional views for describing a variant of the mist filter exemplarily used in the exemplary embodiment of the present invention;

**[0024]** FIG. **13** is a schematic longitudinal cross-sectional view for describing a substrate processing apparatus of an exemplary embodiment of the present invention;

**[0025]** FIG. **14** is a schematic horizontal cross-sectional view taken along line A-A of FIG. **13**;

**[0026]** FIG. **15** is a block diagram showing a configuration of a controller included in the substrate processing apparatus shown in FIG. **13**;

**[0027]** FIG. **16** is a flowchart for describing a process of manufacturing a zirconium oxide film using the substrate processing apparatus of the exemplary embodiment of the present invention; and

**[0028]** FIG. **17** is a timing chart for describing a process of manufacturing a zirconium oxide film using the substrate processing apparatus of the exemplary embodiment of the present invention.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0029]** Next, an exemplary embodiment of the present invention will be described.

**[0030]** First, a source material supply system exemplarily used in a substrate processing apparatus of an exemplary embodiment of the present invention will be described.

**[0031]** When the substrate processing such as film-forming or the like is performed using the liquid source as described above, a source gas, which is gasified by evaporating the liquid source, is used. In order to evaporate the liquid source, (1) raising a temperature, and (2) lowering a pressure are very important. However, in a process of manufacturing a semiconductor device, since various restrictions due to apparatus configurations or process conditions are provided, for example, when the temperature cannot be excessively increased or the pressure cannot be sufficiently lowered, it is difficult to form an appropriate evaporation line.

**[0032]** When the processing such as the film-forming is performed on the semiconductor wafer using the source gas, which is gasified by evaporating the liquid source as described above, particles may be generated on the wafer or the evaporated gas may be reliquefied. The inventors have keenly researched these problems and obtained the following knowledge.

**[0033]** As shown in FIG. **1**, in the substrate processing apparatus in which a gas filter **272***a* is installed in a gas supply pipe **232***a* from an evaporator **271***a* configured to evaporate the liquid source to a process chamber **201**, the gas filter **272***a* can collect droplets or particles which are caused to be badly evaporated from the evaporator **271***a* or particles from the gas supply pipe **232***a*. In addition, a heater **150** may be installed at the gas supply pipe **232***a* from the evaporator **271***a* to the process chamber **201** to heat the source gas passing through the gas supply pipe **232***a*.

**[0034]** However, when the liquid source that cannot be easily evaporated by the evaporator **271***a* (a vapor pressure is low) is used or a required evaporation flow rate is high, the particles or the droplets due to bad evaporation cannot be completely collected by the gas filter **272***a*. When the film-forming is performed in this state, as shown in FIG. **6**, particles are increased on a wafer **200**. In addition, the gas filter **272***a* may be clogged and become a particle source. Further, when the clogging occurs, the filter of the gas filter **272***a* should be replaced with a new one.

**[0035]** For this reason, as shown in FIG. **2**, the inventors proposed installing a mist filter (mist killer) **300** at the gas supply pipe **232***a* between the evaporator **271***a* and the gas filter **272***a*. In addition, the heater **150** is installed at the gas supply pipe **232***a* from the evaporator **271***a* to the process chamber **201** to heat the source gas passing through the gas supply pipe **232***a*.

**[0036]** Referring to FIG. **3**, the mist filter **300** includes a mist filter main body **350**, and a heater **360** installed outside the mist filter main body **350** and configured to cover the mist filter main body **350**.

**[0037]** Referring to FIGS. **4** and **5**, the mist filter main body **350** of the mist filter **300** includes end plates **310** and **340** of both ends, and two types of plates **320** and **330** disposed between the end plates **310** and **340**. The two types of plates **320** and **330** include a first plate **320** and a second plate **330**. A joint **312** is installed at the end plate **310** of an upstream side. A joint **342** is installed at the end plate **340** of a downstream side. A gas path **311** is disposed in the end plate **310** and the joint **312**. A gas path **341** is disposed in the end plate **340** and the joint **342**. The joint **312** and the joint **342** (the gas path **311** and the gas path **341**) are connected to the gas supply pipe **232***a*.

**[0038]** Each of the two types of plates **320** and **330** is installed in plural and alternately disposed between the end plates **310** and **340**. The plate **320** includes a flat plate section **328**, and an outer circumferential section **329** disposed at an outer circumference of the plate section **328**. A plurality of holes **322** are disposed in the plate section **328** only near the outer circumference thereof. The plate **330** includes a flat plate section **338**, and an outer circumferential section **339** disposed at an outer circumference of the plate section **338**. A plurality of holes **332** are disposed in the plate section **338** only near a center thereof (i.e., at different positions from the positions at which the holes **322** are disposed in the plate section **328**). The mist filter **300** is constituted by assembling the plates **320** and the plates **330**.

**[0039]** The plates **320** and the plates **330** have the same or substantially the same shape except for formation positions of the holes **322** and **332**. The flat plate section **328** and the plate section **338** have circular shapes when seen in a plan view, and have the same or substantially the same shape except for formation positions of the holes **322** and **332**. The holes **322** are disposed on concentric circles around the outer circumference of the plate section **328**. The holes **332** are disposed in concentric circles around a center of the plate section **338**. Here, the circles in which the holes **322** are disposed and the circles in which the holes **332** are disposed have different radii. Specifically, the radii of the circles in which the holes **322** are disposed are larger than those of the circles in which the holes **332** are disposed. On other words, a region of the plate section **328** in which the holes **322** are disposed is different from a region of the plate section **338** in which the holes **332** are formed. The regions are disposed not to overlap each other in a stacking direction when the plates **320** and the plates **330** are alternately disposed (stacked or assembled). As the plates **320** and **330** are alternately disposed as described above, the holes **322** and the holes **332** are disposed to be deviated from an upstream side toward a downstream side of the mist filter **300**. That is, the holes **322** and the holes **332** are disposed not to overlap each other from the upstream side to the downstream side of the mist filter **300**.

**[0040]** The outer circumferential sections **329** and **339** of the plates **320** and **330** are thicker than the plate sections **328** and **338**. As the outer circumferential sections **329** and **339** come in contact with the outer circumferential sections **329** and **339** of the adjacent plates, a space (to be described below) is disposed between the plate sections **328** and **338**. In addition, the outer circumferential sections **329** and **339** are disposed at positions offset with respect to the plate sections **328** and **338**. That is, a stepped portion is disposed between side surfaces of the outer circumferential sections **329** and **339** and side surfaces of the plate sections **328** and **338**. More specifically, one surface of the outer circumferential sections **329** and **339** (one surface in the stacking direction of the plate **320** and the plate **330**) protrudes from planes of the plate sections **328** and **338**, and the other surface of the outer circumferential sections **329** and **339** is disposed on edge sections of the plate sections **328** and **338**. Accordingly, when the plates **320** and the plates **330** are stacked, the outer circumferential section **329** of the plate **320** is inserted into the edge section of the plate section **338** of the plate **330**, the outer circumferential section **339** of the plate **330** is inserted into the edge section of the plate section **328** of the plate **320**, and thus the plates **320** and **330** are correspondingly coupled to each other.

**[0041]** As the plates **320** and **330** are alternately disposed as described above, a gas path **370** may become complicated, and probability of colliding droplets generated due to bad evaporation or reliquefaction with heated wall surfaces (the plate sections **328** and **338**) may be increased. In addition, the size of the holes **322** and **332** is set depending on a pressure in the mist filter main body **350**, which is preferably a diameter of 1 to 3 mm. A basis of the lower limit value is that the holes are clogged when the size of the holes is too small. In addition, in the holes **332** disposed in the plate **330**, the size of the holes disposed at the center may be smaller than that of the holes disposed around the center.

**[0042]** The source gas gasified by evaporating the liquid source using the evaporator **271***a* (see FIG. **2**) and the droplets generated due to bad evaporation or reliquefaction are introduced into the mist filter main body **350** through the gas path **311** in the end plate **310** and the joint **312**, and collide with a center portion **421** (a portion in which the holes **322** are not formed) of the plate section **328** of the one first plate **320**. Then, they pass through the holes **322** disposed near the outer circumference of the plate section **328** and collide with an outer circumferential section **432** (a portion in which the holes **332** are not formed) of the flat plate section **338** of the second plate **330**. Then, they pass through the holes **332** disposed near the center of the plate section **338** and collide with a center portion **422** (a portion in which the holes **322** are not formed) of the plate section **328** of the other first plate **320**. Then, in the same method as described above, they sequentially pass the plates **330** and **320** to be ejected from the mist filter main body **350** through the gas path **341** in the end plate **340** and the joint **342**, and are delivered to the gas filter **272***a* (see FIG. **2**) of the downstream side.

**[0043]** The mist filter main body **350** is heated by the heater **360** (see FIG. **3**) from the outside. The mist filter main body **350** includes the first plates **320** and the second plates **330**, the first plate **320** includes the flat plate section **328** and the outer circumferential section **329** disposed at the outer circumference of the plate section **328**, and the second plate **330** includes the flat plate section **338** and the outer circumferential section **339** disposed at the outer circumference of the plate section **338**. Since the plate section **328** and the outer circumferential section **329** are integrally formed and the plate section **338** and the outer circumferential section **339** are integrally formed, when the mist filter main body is heated by the heater **360** from the outside, the heat is efficiently transferred to the flat plate sections **328** and **338**. In addition, even if the plate section **328** and the outer circumferential section **329** are not integrally formed but are in full contact with each other, or if the plate section **338** and the outer circumferential section **339** are not integrally formed but are in full contact with each other, the heat from the heater **360** is also sufficiently transferred to the plate sections **328** and **338** efficiently.

**[0044]** In the mist filter main body **350**, since the gas path **370** is configured to be complicated by the first plates **320** and the second plates **330** as described above, probability of the evaporated source gas and the droplets generated due to bad evaporation or reliquefaction colliding with the heated plate sections **328** and **338** can be increased without excessively increasing pressure loss in the mist filter main body **350**. In addition, the droplets generated due to bad evaporation or reliquefaction collide with the heated plate sections **328** and **338** in the mist filter main body **350** having a sufficient calorie and is reheated and evaporated.

**[0045]** A material of the mist filter main body **350** may have heat conductivity equal to or higher than that of the material used in the evaporator **271***a* or a pipe **232***a*. In addition, the material may have corrosion resistance. Stainless use steel (SUS) may be used as a general material.

**[0046]** While the above description has been given as to a case where each of the plates **320** and the plates **330** are provided in plural numbers, it is also possible that the mist filter main body **350** includes at least one plate **320** and at least one plate **330**. Similarly, although the above description has been given as to a case where each of the holes **322** and the holes **332** are provided in plural numbers, there may exist at least one hole **322** and at least one hole **332**.

**[0047]** Next, a result of performing analysis of the mist filter main body **350** using numerical fluid mechanics analysis software (CFdesign) will be described. Dimensions of the mist filter main body **350**, which is an analysis target, are set such that an outer diameter is 40 mm and an overall length is 127 mm.

**[0048]** Referring to FIG. **7**, the analysis was performed under the condition in which nitrogen ($N_2$) gas of 30° C. was supplied into the mist filter main body **350** at 20 slm and a pressure of an outlet side of the mist filter main body **350** was set as 13300 Pa. The pressure loss was 1500 Pa (see FIG. **8**), and a $N_2$ gas of 30° C. arrived at 150° C. at a fourth plate among a first plate of the first plates **320**, a first plate of the second plates **330**, a second plate of the first plates **320**, and a second plate of the second plates **330** (i.e., the second plate of the second plates **330**) (see FIG. **9**). The analysis was performed to satisfy the condition that, while different from an actual condition, was more unfavorable than the actual condition.

**[0049]** When the mist filter **300** is installed at the gas supply pipe **232***a* between the evaporator **271***a* and the gas filter **272***a* (see FIG. **2**), the liquid source that cannot be easily evaporated or the droplets generated due to bad evaporation when the evaporation flow rate is large collide with the wall surface (the plate section **328**) of the first plate **320** and the wall surface (the plate section **338**) of the second plate **330** in the mist filter **300** having a sufficient calorie and are reheated and evaporated. Then, the droplets due to bad evaporation or the particles generated in the evaporator **271***a* and the mist filter **300**, which minutely remain, are collected by the gas filter **272***a* just before the process chamber **201**. The mist filter **300** functions to assist the evaporation, and supply a reaction gas with no droplets or particles generated due to bad evaporation into the process chamber **201** to perform the processing such as good film-forming or the like. In addition, the mist filter **300** can function to assist the gas filter **272***a* and suppress the clogging of the gas filter **272***a* to reduce maintenance of the gas filter **272***a* or lengthen a filter exchange period of the gas filter **272***a*.

**[0050]** As described above, the first plate **320** includes the flat plate section **328** and the outer circumferential section **329** disposed at the outer circumference of the plate section **328**, and the second plate **330** includes the flat plate section **338** and the outer circumferential section **339** disposed at the outer circumference of the plate section **338** (see FIGS. **4** and **5**).

**[0051]** In addition, the end plate **310** also includes a flat plate **318** and an outer circumferential section **319** disposed at an outer circumference of the plate **318**, and the end plate **340** also includes a flat plate **348** and an outer circumferential section **349** disposed at an outer circumference of the plate **348** (see FIGS. **4** and **5**). Further, spaces **323**, **333**, **313** and **343** are disposed inside the outer circumferential sections **329**, **339**, **319** and **349**, respectively (see FIGS. **4**, **5**, and **10**A). In addition, the end plate **310**, the end plate **340**, the first plate **320** and the second plate **330** are adhered to each other, for example, by welding at the outer circumferential sections **319**, **349**, **329** and **339** thereof to be hermetically connected to each other. Further, while the above-mentioned mist filter **300** is configured to include the first plate **320** and the second plate **330**, the mist filter may include three or more plates having different formation positions of holes.

**[0052]** In the above-mentioned embodiment, no member is installed in the spaces **313**, **323**, **333** and **343** (see FIG. **10**A). However, when the pressure loss of the entire mist filter main body **350** is within an allowable range, a sinter metal or the like may be filled in the spaces **313**, **323**, **333** and **343**. The filled sintered metal is a material that can efficiently transfer the heat heated from the outside of the mist filter main body **350**, and may have any shape such as a spherical shape, a granular shape, a non-linear shape, or the like, as long as the material can be filled into the spaces **313**, **323**, **333** and **343**. Hereinafter, a variant of the above-mentioned embodiment will be described.

**[0053]** For example, as shown in FIG. **10**B, sintered metals **314**, **324** and **334** having a spherical shape such as a metal bowl, or the like, may be filled in the spaces **313**, **323**, and **333** (**343**). Since the size of the sphere and the pressure loss have a correlation, the size of the sphere is selected according to its purpose.

**[0054]** In addition, as shown in FIG. **10**C, sintered metals **315**, **325** and **335** having a granular shape may be filled in the spaces **313**, **323**, and **333** (**343**). The sintered metal having the granular shape has a size smaller than that of the sintered metal having the spherical shape.

**[0055]** Further, as shown in FIG. **11**A, sintered metals **316**, **326** and **336** used in the gas filter or the like may be filled in the spaces **313**, **323**, and **333** (**343**).

**[0056]** In addition, as shown in FIG. **11**B, the sintered metal **326** used in the gas filter may be filled in the space **323** only, and no metal may be filled in the spaces **313**, **333** and **343**. A metal particle size and a fiber form before sintering of the sintered metal used in the gas filter are determined by the size of the collected particles. Since a shape that can collect more fine particles is densified, the pressure loss is also increased. Accordingly, it may be more effective and preferable for the sintered metal to be selectively filled into some of the spaces **313**, **323**, **333** and **343**, rather than all of the spaces **313**, **323**, **333** and **343**.

**[0057]** Further, as shown in FIG. **11**C, as the plate section **328** of the first plate **320** has the holes **322** disposed at only one side of the outer circumference (a portion near the outer circumference) of the plate section **328** and the plate section **338** of the second plate **330** has the holes **332** disposed at only the other side of the outer circumference (a portion near the outer circumference and a position not overlapping the holes **322**) of the plate section **338**, the gas path **370** may be longer in comparison with the above-mentioned embodiment in which the holes **322** are disposed near the outer circumference of the plate section **328** and the holes **332** are disposed near the center of the plate section **338**. In addition, in the embodiment, the same plates are used as the first plate **320** and the second plate **330** but may be stacked not to overlap the holes.

**[0058]** In addition, as shown in FIG. **12**A, the mist filter main body **350** includes an outer vessel **380** having a cylindrical shape, an inner member **385**, and a filling member **386** such as a sintered metal or the like filled in a gas path **382** disposed between the outer vessel **380** and the inner member **385**. As the gas path **382** disposed between the outer vessel **380** and the inner member **385** is filled with the filling member **386** such as the sintered metal or the like, the entire mist filter main body **350** may be integrated such that the heat can be effectively transferred to the inner member **385**. The outer vessel **380** and the inner member **385** may be made of, preferably, a metal member, and more preferably, stainless used steel (SUS).

**[0059]** In addition, as shown in FIG. **12**B, the mist filter main body **350** includes the outer vessel **380** having a cylindrical shape, the inner member **385**, and the filling member **386** such as the sintered metal or the like filled in the gas path **382** disposed between the outer vessel **380** and the inner member **385**. In a structure shown in FIG. **12**A, while the entire gas path **382** disposed between the outer vessel **380** and the inner member **385** is filled with the filling member **386** such as the sintered metal or the like, in a structure shown in FIG. **12**B, a space between a side surface **389** of the cylindrical outer vessel **380** and the inner member **385** in the gas path **382** disposed between the outer vessel **380** and the inner member **385** is filled with the filling member **386**, and a space between an upper surface and a lower surface of the cylindrical outer vessel **380** and the inner member **385** is not filled with the filling member **386**. Even in this case, the entire mist filter main body **350** may be integrated such that the heat can be effectively transferred to the inner member **385**. The outer vessel **380** and the inner member **385** may be made of, preferably, a metal member, and more preferably, stainless used steel (SUS).

**[0060]** In a variant of the above-mentioned embodiment, stainless used steel (SUS) may be used as the sintered metal filled in the spaces **313**, **323**, **333** and **343** or the gas path **382**. Otherwise, nickel (Ni) may be used. In addition, a Teflon (a registered trademark)-based material or ceramics may be used instead of the sintered metal.

**[0061]** In addition, as shown in FIG. **2**, the pipe **232***a* is installed between the evaporator **271***a* and the mist filter **300**, and the evaporator **271***a* and the mist filter **300** are separately installed. Since the process chamber **201** is reduced in pressure and the mist filter **300** is installed closer to the process chamber **201** than the evaporator **271***a*, the mist filter **300** is installed at a lower pressure side than the evaporator **271***a*. Since the gas flows toward the low pressure side, separation of the evaporator **271***a* and the mist filter **300** may provide a fore flow period of the gas from the evaporator **271***a* toward the mist filter **300**. As a result, the gas can collide with the plate **320** and the plate **330** in the mist filter **300** at a higher flow velocity.

**[0062]** Further, as shown in FIG. **2**, the mist filter **300** is installed at a downstream side of the evaporator **271***a*, the gas filter **272***a* is installed at a downstream side thereof, and the gas filter **272***a* is connected to the process chamber **201** via the pipe **232***a*. The mist filter **300** and the gas filter **272***a* may be installed as close to the process chamber **201** as possible. This is because the pressure in the mist filter **300** can be further reduced due to the pressure loss of the pipe **232***a* from the evaporator **271***a* to the process chamber **201** as they are installed near the process chamber **201**. As the pressure in the mist filter **300** is further reduced, the evaporation can be easily performed and the bad evaporation can be suppressed.

**[0063]** The substrate processing apparatus of the exemplary embodiment of the present invention will be described with reference to the accompanying drawings. The substrate processing apparatus is exemplarily configured as a semiconductor manufacturing apparatus configured to perform a film-forming process, which is a substrate processing process of a method of manufacturing an integrated circuit (IC) serving as a semiconductor device. In addition, hereinafter, the case in which a batch type vertical apparatus (which may hereinafter be simply referred to as a processing apparatus) configured to perform oxidation, nitridation, diffusion processing or CVD processing on a substrate is used as the substrate processing apparatus will be described.

**[0064]** FIG. **13** is a schematic configuration view of a vertical processing furnace of the substrate processing apparatus of the embodiment, showing a processing furnace **202** in a longitudinal cross-sectional view, and FIG. **14** is a schematic configuration view of the vertical processing furnace of the substrate processing apparatus of the embodiment, showing the processing furnace **202** in a horizontal cross-sectional view. FIG. **15** shows a configuration of a controller included in the substrate processing apparatus shown in FIG. **13**.

**[0065]** As shown in FIG. **13**, the processing furnace **202** includes a heater **207** serving as a heating unit (a heating mechanism). The heater **207** has a cylindrical shape, and is supported by a heater base (not shown) serving as a holding plate to be vertically installed. A reaction tube **203** constituting a reaction vessel (a processing vessel) is installed concentrically with the heater **207** inside the heater **207**.

**[0066]** A seal cap **219** serving as a furnace port cover configured to hermetically seal the lower end opening of the reaction tube **203** is installed under the reaction tube **203**. The seal cap **219** abuts a lower end of the reaction tube **203** from a lower side in a vertical direction. The seal cap **219** is made of a metal such as stainless steel or the like, and has a disc shape. An O-ring **220** serving as a seal member configured to abut the lower end of the reaction tube **203** is installed at the upper surface of the seal cap **219**. A rotary mechanism **267** configured to rotate the boat is installed at the seal cap **219** opposite to the process chamber **201**. A rotary shaft **255** of the rotary mechanism **267** passes through the seal cap **219** to be connected to a boat **217** (to be described below), and is configured to rotate the boat **217** to rotate the wafer **200**. The seal cap **219** is configured to be raised and lowered in the vertical direction by a boat elevator **115** serving as an elevation mechanism vertically installed at the outside of the reaction tube **203**, and thus the boat **217** can be loaded and unloaded into/from the inside of the process chamber **201**.

**[0067]** The boat **217** serving as a substrate holding unit (a holder) is vertically installed at the seal cap **219** via a quartz cap **218** serving as an insulating member. The quartz cap **218** is a holding body made of a heat resistance material such as quartz, silicon carbide, or the like, serving as an insulating section, and configured to hold the boat. The boat **217** is made of a heat resistance material such as quartz, silicon carbide, or the like, and configured to concentrically support the wafers **200** in a horizontal posture and in a tube axis direction in a multi-stage.

**[0068]** A nozzle **249***a* and a nozzle **249***b* are installed in the process chamber **201** and under the reaction tube **203** to pass through the reaction tube **203**. The gas supply pipe **232***a* and a gas supply pipe **232***b* are connected to the nozzle **249***a* and the nozzle **249***b*, respectively. As described above, the two nozzles **249***a* and **249***b* and the two gas supply pipes **232***a* and **232***b* are installed at the reaction tube **203** so that multiple types of gases can be supplied into the process chamber **201**. In addition, as will be described below, inert gas supply pipes **232***c* and **232***e* or the like are connected to the gas supply pipe **232***a* and the gas supply pipe **232***b*, respectively.

**[0069]** The evaporator **271***a* serving as an evaporating apparatus (an evaporating unit) and configured to evaporate the liquid source to generate an evaporated gas serving as a source gas, the mist filter **300**, the gas filter **272***a*, a mass flow controller (MFC) **241***a* serving as a flow rate controller (a flow rate control unit), and a valve **243***a* serving as an opening/closing valve are installed at the gas supply pipe **232***a* in sequence from the upstream direction. As the valve **243***a* is opened, the evaporated gas generated in the evaporator **271***a* is supplied into the process chamber **201** via the nozzle **249***a*. A vent line **232***d* connected to an exhaust pipe **231** (to be described below) is connected to the gas supply pipe **232***a* between the mass flow controller **241***a* and the valve **243***a*.

**[0070]** A valve **243***d* serving as an opening/closing valve is installed at the vent line **232***d* to supply the source gas to the vent line **232***d* via the valve **243***d* when the source gas (to be described below) is not supplied into the process chamber **201**. As the valve **243***a* is closed and the valve **243***d* is opened, the supply of the evaporated gas into the process chamber **201** can be stopped while maintaining generation of the evaporated gas in the evaporator **271***a*. While a predetermined time is needed to stably generate the evaporated gas, supply/stoppage of the evaporated gas into the process chamber **201** can be switched for an extremely short time by a switching operation of the valve **243***a* and the valve **243***d*. In addition, an inert gas supply pipe **232***c* is connected to the gas supply pipe **232***a* at a downstream side of the valve **243***a*. A mass flow controller **241***c* serving as a flow rate controller (a flow rate control unit) and a valve **243***c* serving as an opening/closing valve are installed at the inert gas supply pipe **232***c* in sequence from the upstream direction. The heater **150** is installed at the gas supply pipe **232***a*, the inert gas supply pipe **232***c*, and the vent line **232***d* to prevent reliquefaction.

**[0071]** The above-mentioned nozzle **249***a* is connected to the tip section of the gas supply pipe **232***a*. The nozzle **249***a* is installed to be raised in an arc-shaped space between the inner wall of the reaction tube **203** and the wafer **200** from a lower portion to an upper portion of the inner wall of the reaction tube **203** upward in the stacking direction of the wafers **200**. The nozzle **249***a* is constituted as an L-shaped long nozzle. A gas supply hole **250***a* configured to supply a gas is installed at a side surface of the nozzle **249***a*. The gas supply hole **250***a* is opened toward a center of the reaction tube **203**. The gas supply holes **250***a* are installed from the lower portion to the upper portion of the reaction tube **203**, have the same opening area, and are disposed at the same opening pitch.

**[0072]** A first gas supply system is mainly constituted by the gas supply pipe **232***a*, the vent line **232***d*, the valves **243***a* and **243***d*, the mass flow controller **241***a*, the evaporator **271***a*, the mist filter **300**, the gas filter **272***a*, and the nozzle **249***a*. In addition, a first inert gas supply system is mainly constituted by the inert gas supply pipe **232***c*, the mass flow controller **241***c*, and the valve **243***c*.

**[0073]** An ozonizer **500** serving as an apparatus for generating ozone ($O_3$) gas, a valve **243***f*, a mass flow controller (MFC) **241***b* serving as a flow rate controller (a flow rate control unit), and a valve **243***b* serving as an opening/closing valve are installed at the gas supply pipe **232***b* in sequence from the upstream direction. An upstream side of the gas supply pipe **232***b* is connected to an oxygen gas supply source (not shown) configured to supply oxygen ($O_2$) gas. The $O_2$ gas supplied into the ozonizer **500** becomes the $O_3$ gas in the ozonizer **500** to be supplied into the process chamber **201**. A vent line **232***g* connected to the exhaust pipe **231** (to be described below) is connected to the gas supply pipe **232***b* between the ozonizer **500** and the valve **243***f*. A valve **243***g* serving as an opening/closing valve is installed at the vent line **232***g* to supply the source gas to the vent line **232***g* via the valve **243***g* when the $O_3$ gas is not supplied into the process chamber **201** (to be described later). As the valve **243***f* is closed and the valve **243***g* is opened, the supply of the $O_3$ gas into the process chamber **201** can be stopped while maintaining generation of the $O_3$ gas by the ozonizer **500**. While a predetermined time is needed to stably refine the $O_3$ gas, the supply/stoppage of the $O_3$ gas into the process chamber **201** can be switched for an extremely short time by the switching operation of the valve **243***f* and the valve **243***g*. In addition, an inert gas supply pipe **232***e* is connected to the gas supply pipe **232***b* at the downstream side of the valve **243***b*. A mass flow controller **241***e* serving as a flow rate controller (a flow rate control unit) and a valve **243***e* serving as an opening/closing valve are installed at the inert gas supply pipe **232***e* in sequence from the upstream direction.

**[0074]** The above-mentioned nozzle **249***b* is connected to the tip section of the gas supply pipe **232***b*. The nozzle **249***b* is installed to be raised and lowered in an arc-shaped space between the inner wall of the reaction tube **203** and the wafer **200** from the lower portion to the upper portion of the inner wall of the reaction tube **203** upward in the stacking direction of the wafers **200**. The nozzle **249***b* is constituted as an L-shaped long nozzle. A gas supply hole **250***b* configured to supply a gas is installed at a side surface of the nozzle **249***b*. The gas supply hole **250***b* is opened toward the center of the reaction tube **203**. The gas supply holes **250***b* are installed from the lower portion to the upper portion of the reaction tube **203**, have the same opening area, and are disposed at the same opening pitch.

**[0075]** A second gas supply system is mainly constituted by the gas supply pipe **232***b*, the vent line **232***g*, the ozonizer **500**, the valves **243***f*, **243***g* and **243***b*, the mass flow controller **241***b*, and the nozzle **249***b*. In addition, a second inert gas supply system is mainly constituted by the inert gas supply pipe **232***e*, the mass flow controller **241***e*, and the valve **243***e*.

**[0076]** For example, a zirconium source gas, i.e., a gas containing zirconium (Zr) (a zirconium-containing gas), which is a first source gas, is supplied from the gas supply pipe **232***a* into the process chamber **201** via the evaporator **271***a*, the mist filter **300**, the gas filter **272***a*, the mass flow controller **241***a*, the valve **243***a*, and the nozzle **249***a*. For example, tetrakis(ethylmethylamino)zirconium (TEMAZ) may be used as the zirconium-containing gas. Tetrakis(ethylmethylamino)zirconium (TEMAZ) is a liquid at a normal temperature and a normal pressure.

**[0077]** A gas containing oxygen (O) (an oxygen-containing gas), for example, $O_2$ gas, is supplied into the gas supply pipe **232***b*, becomes $O_3$ gas in the ozonizer **500**, and is supplied into the process chamber **201** via the valve **243***f*, the mass flow controller **241***b*, and the valve **243***b* as an oxidizing gas (oxidant). The $O_2$ gas serving as the oxidizing gas may be supplied into the process chamber **201** without generating the $O_3$ gas in the ozonizer **500**.

**[0078]** For example, nitrogen ($N_2$) gas is supplied from the inert gas supply pipes **232***c* and **232***e* into the process chamber **201** via the mass flow controllers **241***c* and **241***e*, the valves **243***c* and **243***e*, the gas supply pipes **232***a* and **232***b*, the nozzles **249***a* and **249***b*.

**[0079]** The exhaust pipe **231** configured to exhaust an atmosphere in the process chamber **201** is installed in the reaction tube **203**. A vacuum pump **246** serving as a vacuum exhaust apparatus is connected to the exhaust pipe **231** via a pressure sensor **245** serving as a pressure detector (a pressure detection unit) configured to detect the pressure in the process chamber **201** and an auto pressure controller (APC) valve **244** serving as a pressure regulator (a pressure regulation unit) to perform vacuum exhaust so that the pressure in the process chamber **201** arrives at a predetermined pressure (a vacuum level). In addition, the APC valve **244** is an opening/closing valve configured to open and close the valve to perform the vacuum exhaust and stop the vacuum exhaust of the inside of the process chamber **201** and adjust the valve opening angle to regulate the pressure. An exhaust system is mainly constituted by the exhaust pipe **231**, the APC valve **244**, the vacuum pump **246**, and the pressure sensor **245**.

**[0080]** A temperature sensor **263** serving as a temperature detector is installed in the reaction tube **203**, and an electrical connection state to the heater **207** is controlled based on temperature information detected by the temperature sensor **263** so that the temperature in the process chamber **201** arrives at a desired temperature distribution. The temperature sensor **263** has an L shape similar to the nozzles **249***a* and **249***b*, and is installed along the inner wall of the reaction tube **203**.

**[0081]** As shown in FIG. **15**, a controller **121** serving as a control unit (a control means) is constituted as a computer including a central processing unit (CPU) **121***a*, a random access memory (RAM) **121***b*, a memory device **121***c*, and an I/O port **121***d*. The RAM **121***b*, the memory device **121***c* and the I/O port **121***d* are configured to exchange data with the CPU **121***a* via an internal bus. An input/output device **122** constituted as, for example, a touch panel or the like is connected to the controller **121**. In addition, an external memory device (a recording medium) **123** on which a program (to be described later) is stored is connectable to the controller **121**.

**[0082]** The memory device **121***c* is constituted by, for example, a flash memory, a hard disk drive (HDD), or the like. A control program configured to control an operation of the substrate processing apparatus or a process recipe on which a sequence or condition of substrate processing (to be described later) is disclosed is readably stored in the memory device **121***c*. In addition, the control program or the process recipe can be stored in the memory device **121***c* by storing the control program or the process recipe in an external memory device **123** and connecting the external memory device **123** to the controller **121**. Further, the process recipe is assembled to obtain a predetermined result by causing the controller **121** to perform the sequences of the following substrate processing process, and functions as a program. Hereinafter, the process recipe or the control program is also generally and simply referred to as a program. In addition, the case in which the terms of the program are recited in the description may include the case in which only the process recipe is included, the case in which only the control program is included, and the case in which both are included. Further, the RAM **121***b* is constituted as a memory region (a work area) in which a program or data read by the CPU **121***a* is temporarily held.

**[0083]** The I/O port **121***d* is connected to the mass flow controllers **241***a*, **241***b*, **241***c* and **241***e*, the valves **243***a*, **243***b*, **243***c*, **243***d*, **243***e*, **243***f* and **243***g*, the evaporator **271***a*, the mist filter **300**, the ozonizer **500**, the pressure sensor **245**, the APC valve **244**, the vacuum pump **246**, the heaters **150** and **207**, the temperature sensor **263**, the boat rotary mechanism **267**, the boat elevator **115**, and so on.

**[0084]** The CPU **121***a* is configured to read and perform the control program from the memory device **121***c* and read the process recipe from the memory device **121***c* according to an input of an operation command from the input/output device **122**. Then, the CPU **121***a* performs a flow rate control operation on various gases by the mass flow controllers **241***a*, **241***b*, **241***c* and **241***e*, an opening/closing operation on the valves **243***a*, **243***b*, **243***c*, **243***d*, **243***e*, **243***f* and **243***g*, a pressure regulation operation based on opening/closing of the APC valve **244** and the pressure sensor **245**, a temperature control operation on the heater **150**, a temperature control operation on the heater **207** based on the temperature sensor **263**, control on the evaporator **271***a*, the mist filter **300** (the heater **360**) and the ozonizer **500**, start/stoppage on the vacuum pump **246**, a rotational speed adjustment operation on the boat rotary mechanism **267**, an elevation operation on the boat elevator **115**, or the like, according to the read process recipe.

**[0085]** Next, a sequence example of forming an insulating film on a substrate, which is one process of processes of manufacturing a semiconductor device using a processing furnace of the above-mentioned substrate processing apparatus will be described with reference to FIGS. **16** and **17**. In addition, in the following description, operations of the respective parts constituting the substrate processing apparatus are controlled by the controller **121**.

**[0086]** In a chemical vapor deposition (CVD) method, for example, multiple types of gases including a plurality of elements constituting a film are simultaneously supplied. In addition, a film-forming method of alternately supplying multiple types of gases including a plurality of elements constituting a film is also provided.

**[0087]** First, when the wafers **200** are charged into the boat **217** (wafer charging) (see step S**101** in FIG. **16**), as shown in FIG. **13**, the boat **217** supporting the wafers **200** is raised by the boat elevator **115** to be loaded into the process chamber **201** (boat loading) (see step S**102** in FIG. **16**). In this state, the seal cap **219** hermetically seals the lower end of the reaction tube **203** via the O-ring **220**.

**[0088]** The inside of the process chamber **201** is vacuum-exhausted by the vacuum pump **246** to a desired pressure (a vacuum level). Here, the pressure in the process chamber **201** is measured by the pressure sensor **245**, and the APC valve **244** is feedback-controlled based on the measured pressure (pressure regulation) (see step S**103** in FIG. **16**). In addition, the inside of the process chamber **201** is heated by the heater **207** to a desired temperature. Here, an electrical conduction state to the heater **207** is feedback-controlled based on temperature information detected by the temperature sensor **263** such that the inside of the process chamber **201** arrives at a desired temperature distribution (temperature control) (see step S **103** in FIG. **16**). Next, the boat **217** is rotated by the rotary mechanism **267** to rotate the wafer **200**.

**[0089]** Next, as the TEMAZ gas and $O_3$ gas are supplied into the process chamber **201**, an insulating film forming process of forming a ZrO film serving as an insulating film is performed (see step S**104** in FIG. **16**). The following four steps are sequentially performed in the insulating film forming process.

**[0090]** (Insulating Film Forming Process)<Step S**105**>

**[0091]** In step S**105** (see FIGS. **16** and **17**, a first process), first, the TEMAZ gas flows. As the valve **243***a* of the gas supply pipe **232***a* is opened and the valve **243***d* of the vent line **232***d* is closed, the TEMAZ gas flows into the gas supply pipe **232***a* via the evaporator **271***a*, the mist filter **300** and the gas filter **272***a*. The TEMAZ gas flowing through the gas supply pipe **232***a* is flow-rate-controlled by the mass flow controller **241***a*. The flow-rate-controlled TEMAZ gas is supplied into the process chamber **201** from the gas supply hole **250***a* of the nozzle **249***a* and exhausted from the gas exhaust pipe **231**. Here, simultaneously, the valve **243***c* is opened and an inert gas such as $N_2$ gas or the like flows into the inert gas supply pipe **232***c*. The $N_2$ gas flowing through the inert gas supply pipe **232***c* is flow-rate-controlled by the mass flow controller **241***c*. The flow-rate-controlled $N_2$ gas is supplied into the process chamber **201** and exhausted from the gas exhaust pipe **231** with the TEMAZ gas. The TEMAZ gas is supplied into the process chamber **201** to be reacted with the wafer **200** to form a zirconium-containing layer on the wafer **200**. In addition, before performing step S**105**, the operation of the heater **360** of the mist filter **300** is controlled to maintain the temperature of the mist filter main body **350** at a desired temperature.

**[0092]** Here, the APC valve **244** is appropriately adjusted to regulate the pressure in the process chamber **201** to a pressure within a range of, for example, 50 to 400 Pa. A supply flow rate of the TEMAZ gas controlled by the mass flow controller **241***a* is set to a flow rate within a range of, for example, 0.1 to 0.5 g/min. A time in which the wafer **200** is exposed to the TEMAZ gas, i.e., a gas supply time (an irradiation time) is set to a time within a range of, for example, 30 to 240 seconds. Here, the temperature of the heater **207** is set such that the temperature of the wafer **200** is a temperature within a range of, for example, 150 to 250° C.

**[0093]** <Step S**106**>

**[0094]** In step S**106** (FIGS. **16** and **17**, a second process), after the zirconium-containing layer is formed, the valve **243***a* is closed and the valve **243***d* is opened to stop the supply of the TEMAZ gas into the process chamber **201**, and the TEMAZ gas flows through the vent line **232***d*. Here, the inside of the process chamber **201** is vacuum-exhausted by the vacuum pump **246** in a state in which the APC valve **244** of the gas exhaust pipe **231** is open, and the TEMAZ gas that is not reacted or has contributed to formation of the zirconium-containing layer and remains in the process chamber **201** is removed from the process chamber **201**. In addition, here, supply of the $N_2$ gas into the process chamber **201** is maintained in a state in which the valve **243***c* is open. Accordingly, an effect of removing the TEMAZ gas that is not reacted or has contributed to formation of the zirconium-containing layer and remains in the process chamber **201** from the inside of the process chamber **201** is improved. A rare gas such as Ar gas, He gas, Ne gas, Xe gas, or the like, in addition to the $N_2$ gas may be used as the inert gas.

**[0095]** <Step S**107**)>

**[0096]** In step S107 (FIGS. **16** and **17**, a third process), after removing the remaining gas in the process chamber **201**, the $O_2$ gas flows into the gas supply pipe **232***b*. The $O_2$ gas flowing through the gas supply pipe **232***b* becomes $O_3$ gas in the ozonizer **500**. As the valve **243***f* and the valve **243***b* of the gas supply pipe **232***b* are opened and the valve **243***g* of the vent line **232***g* is closed, the $O_3$ gas flowing through the gas supply pipe **232***b* is flow-rate-controlled by the mass flow controller **241***b*, supplied into the process chamber **201** from the gas supply hole **250***b* of the nozzle **249***b*, and exhausted from the gas exhaust pipe **231**. Here, simultaneously, the valve **243***e* is opened, and the $N_2$ gas flows into the inert gas supply pipe **232***e*. The $N_2$ gas is supplied into the process chamber **201** and exhausted from the gas exhaust pipe **231** with the $O_3$ gas. As the $O_3$ gas is supplied into the process chamber **201**, the zirconium-containing layer formed on the wafer **200** is reacted with the $O_3$ gas to form a ZrO layer.

**[0097]** When the $O_3$ gas flows, the APC valve **244** is appropriately adjusted such that the pressure in the process chamber **201** arrives at a pressure within a range of, for example, 50 to 400 Pa. A supply flow rate of the $O_3$ gas controlled by the mass flow controller **241***b* is set to a flow rate within a range of, for example, 10 to 20 slm. A time in which the wafer **200** is exposed to the $O_3$ gas, i.e., a gas supply time (an irradiation time) is set to a time within a range of, for example, 60 to 300 seconds. Here, the temperature of the heater **207** is set such that the temperature of the wafer **200** is set to a temperature within a range of 150 to 250° C. similar to step **105**.

**[0098]** <Step S**108**)>

**[0099]** In step S**108** (FIGS. **16** and **17**, a fourth process), the valve **243***b* of the gas supply pipe **232***b* is closed and the valve **243***g* is opened to stop the supply of the $O_3$ gas into the process chamber **201**, and the $O_3$ gas flows through the vent line **232***g*. Here, the inside of the process chamber **201** is vacuum-exhausted by the vacuum pump **246** in a state in which the APC valve **244** of the gas exhaust pipe **231** is open, the $O_3$ gas that is not reacted or has contributed to oxidation and remains in the process chamber **201** is removed from the process chamber **201**. In addition, here, supply of the $N_2$ gas into the process chamber **201** is maintained in a state in which the valve **243***e* is open. Accordingly, an effect of removing the $O_3$ gas that is not reacted or has contributed to oxidation and remains in the process chamber **201** from the inside of the process chamber **201** is increased. In addition to the $O_3$ gas, the $O_2$ gas or the like may be used as the oxygen-containing gas.

**[0100]** As the above-mentioned steps S**105** to S**108** are set as one cycle and the cycle is performed at least one time (step S**109**), an insulating film containing zirconium and oxygen and having a predetermined film thickness, i.e., a ZrO film, can be formed on the wafer **200**. In addition, the above-mentioned cycle may be repeated a plurality of times. Accordingly, a deposition film of the ZrO film is formed on the wafer **200**.

**[0101]** After forming the ZrO film, the valve **243***a* of the gas supply pipe **232***a* is closed, the valve **243***b* of the gas supply pipe **232***b* is closed, the valve **243***c* of the inert gas supply pipe **232***c* is opened, the valve **243***e* of the inert gas supply pipe **232***e* is opened, and the $N_2$ gas flows into the process chamber **201**. The $N_2$ gas serves as a purge gas, and thus the inside of the process chamber **201** is purged with an inert gas to remove the gas remaining in the process chamber **201** from the process chamber **201** (purge, step S**110**). After that, the atmosphere in the process chamber **201** is replaced with the inert gas, and the pressure in the process chamber **201** returns to a normal pressure (return to an atmospheric pressure, step S**111**).

**[0102]** After that, the seal cap **219** is lowered by the boat elevator **115** and a lower end of a manifold **209** is opened, and simultaneously, the processed wafer **200**, which is held by the boat **217**, is unloaded from the lower end of the manifold **209** to the outside of the reaction tube **203** (boat unloading, step S**112**). Next, the processed wafer **200** is discharged from the boat **217** (wafer discharge, step S**112**).

## Example 1

**[0103]** The film-forming of the ZrO film was performed using the substrate processing furnace of the above-mentioned embodiment. In addition, for the purpose of comparison, the film-forming of the ZrO film was performed without installing the mist filter **300**. In the configuration in which the mist filter **300** was not installed, the film-forming was performed under conditions in which an evaporation source material TEMAZ was 0.45 g, a supply time was 300 sec, and a cycle number was 75 cycles. Step coverage in the film-forming was 81%. On the other hand, in the configuration in which the mist filter **300** was installed, since an evaporation flow rate could be increased, when the film-forming was performed under conditions in which the evaporation source material TEMAZ was 3 g, the supply time was 60 sec, and the cycle number was 75 cycles, the step coverage was 91%, which led to improvement of the step coverage. In addition, generation of the particles could be suppressed.

**[0104]** As described above specifically, when the liquid source that cannot be easily evaporated is used or a large evaporation flow rate is needed in the exemplary embodiment of the present invention, the bad evaporation can be suppressed. As a result, the following effects can be obtained.

**[0105]** (1) The gas filter clogging can be suppressed, and the maintenance can be reduced or the filter exchange period can be increased.

**[0106]** (2) The film-forming in which the particles are removed or suppressed can be performed.

**[0107]** (3) Step coverage of the pattern wafer is improved.

**[0108]** While the film-forming of the ZrO film has been performed in the above-mentioned embodiment, the technique using the mist filter **300** may be applied to other types of films, for example, a high permittivity (high-k) film such as ZrO, HfO, or the like, or a kind of film using an evaporator (in particular, a kind of film using a gas that can easily cause bad evaporation or requiring a large flow rate). In particular, the technique using the mist filter **300** may be applied to a kind of film using liquid source having a vapor pressure.

**[0109]** The technique using the mist filter **300** may be applied to the case of forming a metal carbide film of a metal nitride film including at least one metal element such as titanium (Ti), tantalum (Ta), cobalt (Co), tungsten (W), molybdenum (Mo), ruthenium (Ru), yttrium (Y), lanthanum (La), zirconium (Zr), hafnium (Hf), nickel (Ni), or the like, or a silicide film in which silicon (Si) is added to the above-mentioned film. Here, titanium chloride ($TiCl_4$), tetrakis (dimethylamino)titanium (TDMAT, $Ti[N(CH_3)_2]_4$), tetrakis (diethylamino)titanium (TDEAT, $Ti[N(CH_2CH_3)_2]_4$), or the like, may be used as a Ti-containing source material, tantalum chloride ($TaCl_4$) or the like may be used as a Ta-containing source material, $Co(AMD)[(tBu)NC(CH_3)N(tBu)_2Co]$ or the like may be used as a Co-containing source material, tungsten fluoride ($WF_6$) or the like may be used as a W-containing source material, molybdenum chloride ($MoCl_3$ or $MoCl_5$) or the like may be used as a Mo-containing source material, 2,4-dimethlypentadienyl(ethylcyclopentadienyl)ruthenium [$Ru(EtCp)(C_7H_{11})$] or the like may be used as a Ru-containing source material, trisethylcyclopentadienylyttrium [$Y(C_2H_5C_5H_4)_3$] or the like may be used as an Y-containing source material, trisisopropylcyclopentadienyllanthanum[$La(i\text{-}C_3H_7C_5H_4)_3$] or the like may be used as a La-containing source material, tetrakis(ethylmethylamino)zirconium[$Zr(N[CH_3(C_2H_5)]_4)$] or the like may be used as a Zr-containing source material, tetrakis(ethylmethylamino)hafnium [$Hf(N[CH_3(C_2H_5)]_4)$] or the like may be used as a Hf-containing source material, nickelamidinate (NiAMD), cyclopentadienylallylnickel ($C_5H_5NiC_3H_5$), methylcyclopentadienylallylnickel[$(CH_3)C_5H_4NiC_3H_5$], ethylcyclopentadienylallylnickel [$(C_2H_5)C_5H_4NiC_3H_5$], $Ni(PF_3)_4$ or the like may be used as a Ni-containing source material, and tetrachlorosilane ($SiCl_4$), hexachlorodisilane ($Si_2Cl_6$), dichlorosilane ($SiH_2Cl_2$), trisdimethyl aminosilane ($SiH[N(CH_3)_2]_3$), bis-tertiary-butyl-amino-silane ($H_2Si[HNC(CH_3]_2$) or the like may be used as a Si-containing source material.

**[0110]** TiCN, TiAlC, or the like may be used as a metal carbide film containing Ti. For example, $TiCl_4$, $Hf[C_5H_4(CH_3)]_2(CH_3)_2$ and $NH_3$ may be used as a source material of TiCN. In addition, for example, $TiCl_4$ and trimethylaluminum (TMA, $(CH_3)_3Al$) may be used as a source material of TiAlC. Further, $TiCl_4$, TMA and propylene ($C_3H_6$) may be used as a source material of TiAlC. Furthermore, TiAlN or the like may be used as a metal nitride film containing Ti. For example, $TiCl_4$, TMA and $NH_3$ may be used as a source material of TiAlN.

**[0111]** According to the present invention, an amount of particles generated when liquid source is used can be suppressed, and the liquid source can be efficiently evaporated to be supplied into a process chamber.

**[0112]** (Exemplary Modes of the Invention)

**[0113]** Hereinafter, exemplary modes of the present invention will be supplementarily stated.

**[0114]** (Supplementary Note 1)

**[0115]** A method of manufacturing a semiconductor device, including: (a) loading a substrate into a process chamber; (b) evaporating a source material by sequentially flowing the source material to an evaporator and a mist filter including one or more first plates and one or more second plates; (c) supplying the source material evaporated in the step (b) into the process chamber to process the substrate; and (d) unloading the substrate from the process chamber, wherein each of the one or more first plates includes one or more first holes, and each of the one or more second plates includes one or more second holes disposed at different positions from those of the one or more first holes.

**[0116]** (Supplementary Note 2)

**[0117]** The method of manufacturing the semiconductor device according to Supplementary Note 1, wherein the one or more first holes are disposed near an outer circumference of each of the one or more first plates, the one or more second holes are disposed near a center of each of the one or more second plates, and the one or more first plates and the one or more second plates are alternately disposed, and wherein the step (b) includes evaporating the source material passed through the evaporator by alternately flowing the source material through the one or more first holes and the one or more second holes.

**[0118]** (Supplementary Note 3)

**[0119]** The method of manufacturing the semiconductor device according to Supplementary Note 1 or 2, wherein the step (b) includes evaporating the source material sequentially flown through the evaporator and the mist filter by further flowing the source material through a gas filter.

**[0120]** (Supplementary Note 4)

**[0121]** A method of manufacturing a substrate, including: (a) loading a substrate into a process chamber; (b) evaporating a source material by sequentially flowing the source material to an evaporator and a mist filter including one or more first plates and one or more second plates; (c) supplying the source material evaporated in the step (b) into the process chamber to process the substrate; and (d) unloading the substrate from the process chamber, wherein each of the one or more first plates includes one or more first holes, and each of the one or more second plates includes one or more second holes disposed at different positions from those of the one or more first holes.

**[0122]** (Supplementary Note 5)

**[0123]** The method of manufacturing the substrate according to Supplementary Note 4, wherein the one or more first holes are disposed near an outer circumference of each of the one or more first plates, the one or more second holes are disposed near a center of each of the one or more second plates, and the one or more first plates and the one or more second plates are alternately disposed, and wherein the step (b) includes evaporating the source material passed through the evaporator by alternately flowing the source material through the one or more first holes and the one or more second holes.

**[0124]** (Supplementary Note 6)

**[0125]** The method of manufacturing the semiconductor device according to Supplementary Note 4 or 5, wherein the step (b) includes evaporating the source material sequentially flown through the evaporator and the mist filter by further flowing the source material through a gas filter.

**[0126]** (Supplementary Note 7)

**[0127]** A program performed by a control unit, the program including the sequences of: (a) loading a substrate into a process chamber; (b) evaporating a source material by sequentially flowing the source material to an evaporator and a mist filter including one or more first plates and one or more second plates; (c) supplying the source material evaporated in the step (b) into the process chamber to process the substrate; and (d) unloading the substrate from the process chamber, wherein each of the one or more first plates includes one or more first holes, and each of the one or more second plates includes one or more second holes disposed at different positions from those of the one or more first holes.

[0128] (Supplementary Note 8)

[0129] The program according to Supplementary Note 7, wherein the one or more first holes are disposed near an outer circumference of each of the one or more first plates, the one or more second holes are disposed near a center of each of the one or more second plates, and the one or more first plates and the one or more second plates are alternately disposed, and wherein the step (b) includes evaporating the source material passed through the evaporator by alternately flowing the source material through the one or more first holes and the one or more second holes.

[0130] (Supplementary Note 9)

[0131] The program according to Supplementary Note 7, wherein the sequence (b) includes evaporating the source material sequentially flown through the evaporator and the mist filter by further flowing the source material through a gas filter.

[0132] (Supplementary Note 10)

[0133] A non-transitory computer-readable recording medium on which a program performed by a control unit is recorded, the program including the sequences of: (a) loading a substrate into a process chamber; (b) evaporating a source material by sequentially flowing the source material to an evaporator and a mist filter including one or more first plates and one or more second plates; (c) supplying the source material evaporated in the step (b) into the process chamber to process the substrate; and (d) unloading the substrate from the process chamber, wherein each of the one or more first plates includes one or more first holes, and each of the one or more second plates includes one or more second holes disposed at different positions from those of the one or more first holes.

[0134] (Supplementary Note 11)

[0135] The non-transitory computer-readable recording medium according to Supplementary Note 10, wherein the one or more first holes are disposed near an outer circumference of each of the one or more first plates, the one or more second holes are disposed near a center of each of the one or more second plates, and the one or more first plates and the one or more second plates are alternately disposed, and wherein the step (b) includes evaporating the source material passed through the evaporator by alternately flowing the source material through the one or more first holes and the one or more second holes.

[0136] (Supplementary Note 12)

[0137] The non-transitory computer-readable recording medium according to Supplementary Note 10, wherein the sequence (b) includes evaporating the source material sequentially flown through the evaporator and the mist filter by further flowing the source material through a gas filter.

[0138] (Supplementary Note 13)

[0139] A substrate processing apparatus including: a process chamber configured to accommodate a substrate; a process gas supply system configured to supply a process gas into the process chamber; and an exhaust system configured to exhaust the process chamber, wherein the process gas supply system includes: an evaporator configured to receive a source material; and a mist filter disposed at a downstream side of the evaporator, and including one or more first plates and one or more second plates, wherein each of the one or more first plates includes one or more first holes, and each of the one or more second plates includes one or more second holes disposed at different positions from those of the one or more first holes.

[0140] (Supplementary Note 14)

[0141] The substrate processing apparatus according to Supplementary Note 13, wherein the one or more first holes are disposed near an outer circumference of each of the one or more first plates, the one or more second holes are disposed near a center of each of the one or more second plates, and the one or more first plates and the one or more second plates are alternately disposed.

[0142] (Supplementary Note 15)

[0143] The substrate processing apparatus according to Supplementary Note 13 or 14, wherein the process gas supply system further includes a gas filter disposed at a downstream side of the mist filter.

[0144] (Supplementary Note 16)

[0145] The substrate processing apparatus according to Supplementary Note 15, wherein the evaporator, the mist filter and the gas filter are separate from one another.

[0146] (Supplementary Note 17)

[0147] The substrate processing apparatus according to any one of Supplementary Notes 13 to 16, wherein the mist filter further includes a heater configured to heat the one or more first plates and the one or more second plates.

[0148] (Supplementary Note 18)

[0149] The substrate processing apparatus according to any one of Supplementary Notes 13 to 17, wherein each of the one or more first plates and the one or more second plates includes a metal.

[0150] (Supplementary Note 19)

[0151] The substrate processing apparatus according to any one of Supplementary Notes 13 to 18, wherein a shape of each of the one or more first plates is same as that of each of the one or more second plates except for the one or more first holes and the one or more second holes.

[0152] (Supplementary Note 20)

[0153] The substrate processing apparatus according to any one of Supplementary Notes 13 to 19, wherein each of the one or more first plates and the one or more second plates includes a plate section including one of the one or more first holes and the one or more second holes; and an outer circumferential section disposed at an outer circumference of the plate section, the outer circumferential section being thicker than the plate section, and

[0154] the outer circumferential section of one of the one or more first plates is in contact with the outer circumferential section of one of the one or more second plates adjacent to the outer circumferential section of the one of the one or more first plates in a manner that a space is provided between the plate section of the one of the one or more first plates and the plate section of the one of the one or more second plates.

[0155] (Supplementary Note 21)

[0156] The substrate processing apparatus according to any one of Supplementary Notes 13 to 20, wherein a stepped portion is provided between a side surface of the outer circumferential section and a side surface of the plate section.

[0157] (Supplementary Note 22)

[0158] The substrate processing apparatus according to any one of Supplementary Notes 13 to 21, wherein a sintered metal is filled between the one or more first plates and the one or more second plates.

[0159] (Supplementary Note 23)

[0160] The substrate processing apparatus according to any one of Supplementary Notes 13 to 22, wherein the process gas is a zirconium-containing source material.

[0161] (Supplementary Note 24)

[0162] An evaporation system including: an evaporator configured to receive a source material; and a mist filter disposed at a downstream side of the evaporator and including one or more first plates and one or more second plates, wherein each of the one or more first plates includes one or more first holes, and each of the one or more second plates includes one or more second holes disposed at different positions from those of the one or more first holes.

[0163] (Supplementary Note 25)

[0164] The evaporation system according to Supplementary Note 24, wherein the one or more first holes are disposed near an outer circumference of each of the one or more first plates, the one or more second holes are disposed near a center of each of the one or more second plates, and the one or more first plates and the one or more second plates are alternately disposed.

[0165] (Supplementary Note 26)

[0166] The evaporation system according to Supplementary Note 24 or 25, further including a gas filter disposed at a downstream side of the mist filter.

[0167] (Supplementary Note 27)

[0168] The evaporation system according to Supplementary Note 26, the evaporator, the mist filter and the gas filter are separate from one another.

[0169] (Supplementary Note 28)

[0170] The evaporation system according to any one of Supplementary Notes 24 to 27, wherein the mist filter further includes a heater configured to heat the one or more first plates and the one or more second plates.

[0171] (Supplementary Note 29)

[0172] A mist filter constituted by assembling a plurality of at least two types of plates including holes disposed at different positions.

[0173] (Supplementary Note 30)

[0174] The mist filter according to Supplementary Note 29, wherein the mist filter is constituted by alternately disposing a first plate in which a plurality of holes are disposed near an outer circumference thereof and a second plate in which a plurality of holes are disposed near a center thereof.

[0175] (Supplementary Note 31)

[0176] The mist filter according to Supplementary Notes 29 or 30, including a heater configured to heat the at least two types of plates.

[0177] Hereinabove, while various exemplary embodiments of the present invention have been described, the present invention is not limited thereto. Accordingly, the scope of the present invention is limited by only the scopes of the accompanying claims.

What is claimed is:

**1**. A method of manufacturing a semiconductor device, comprising:

(a) loading a substrate into a process chamber;

(b) evaporating a source material by sequentially flowing the source to an evaporator and a mist filter comprising one or more first plates and one or more second plates;

(c) supplying the source material evaporated in the step (b) into the process chamber to process the substrate; and

(d) unloading the substrate from the process chamber,

wherein each of the one or more first plates comprises one or more first holes, and each of the one or more second plates comprises one or more second holes disposed at different positions from those of the one or more first holes.

**2**. The method of manufacturing the semiconductor device of claim **1**, wherein the one or more first holes are disposed near an outer circumference of each of the one or more first plates, the one or more second holes are disposed near a center of each of the one or more second plates, and the one or more first plates and the one or more second plates are alternately disposed, and

wherein the step (b) comprises evaporating the source material passed through the evaporator by alternately flowing the source material through the one or more first holes and the one or more second holes.

**3**. The method of manufacturing the semiconductor device of claim **1**, wherein the step (b) comprises evaporating the source material sequentially flown through the evaporator and the mist filter by further flowing the source material through a gas filter.

**4**. A substrate processing apparatus comprising:

a process chamber configured to accommodate a substrate;

a process gas supply system configured to supply a process gas into the process chamber; and

an exhaust system configured to exhaust the process chamber,

wherein the process gas supply system comprises:

an evaporator configured to receive a source material; and

a mist filter disposed at a downstream side of the evaporator, and comprising one or more first plates and one or more second plates, wherein each of the one or more first plates comprises one or more first holes, and each of the one or more second plates comprises one or more second holes disposed at different positions from those of the one or more first holes.

**5**. The substrate processing apparatus of claim **4**, wherein the one or more first holes are disposed near an outer circumference of each of the one or more first plates, the one or more second holes are disposed near a center of each of the one or more second plates, and the one or more first plates and the one or more second plates are alternately disposed.

**6**. The substrate processing apparatus of claim **4**, wherein the process gas supply system further comprises a gas filter disposed at a downstream side of the mist filter.

**7**. The substrate processing apparatus of claim **6**, wherein the evaporator, the mist filter and the gas filter are separate from one another.

**8**. The substrate processing apparatus of claim **4**, wherein the mist filter further comprises a heater configured to heat the one or more first plates and the one or more second plates.

**9**. The substrate processing apparatus of claim **4**, wherein each of the one or more first plates and the one or more second plates comprises a metal.

**10**. The substrate processing apparatus of claim **4**, wherein a shape of each of the one or more first plates is same as that of each of the one or more second plates except for the one or more first holes and the one or more second holes.

**11**. The substrate processing apparatus of claim **4**, wherein each of the one or more first plates and the one or more second plates comprises a plate section comprising one of the one or more first holes and the one or more second holes; and an outer circumferential section disposed at an outer circumference of the plate section, the outer circumferential section being thicker than the plate section, and

the outer circumferential section of one of the one or more first plates is in contact with the outer circumferential section of one of the one or more second plates adjacent to the outer circumferential section of the one of the one or more first plates in a manner that a space is provided between the plate section of the one of the one or more first plates and the plate section of the one of the one or more second plates.

**12**. The substrate processing apparatus of claim **11**, wherein a stepped portion is provided between a side surface of the outer circumferential section and a side surface of the plate section.

**13**. The substrate processing apparatus of claim **4**, wherein a sintered metal is filled between the one or more first plates and the one or more second plates.

**14**. An evaporation system comprising:

an evaporator configured to receive a source material; and

a mist filter disposed at a downstream side of the evaporator and comprising one or more first plates and one or more second plates, wherein each of the one or more first plates comprises one or more first holes, and each of the one or more second plates comprises one or more second holes disposed at different positions from those of the one or more first holes.

**15**. The evaporation system of claim **14**, wherein the one or more first holes are disposed near an outer circumference of each of the one or more first plates, the one or more second holes are disposed near a center of each of the one or more second plates, and the one or more first plates and the one or more second plates are alternately disposed.

**16**. The evaporation system of claim **15**, further comprising a gas filter disposed at a downstream side of the mist filter.

**17**. The evaporation system of claim **16**, wherein the evaporator, the mist filter and the gas filter are separate from one another.

**18**. The evaporation system of claim **14**, wherein the mist filter further comprises a heater configured to heat the one or more first plates and the one or more second plates.

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