

SUBSTRATE PROCESSING METHOD AND SUBSTRATE PROCESSING
APPARATUS

CROSS REFERENCE TO RELATED APPLICATIONS

5 [0001] The present application claims the benefit of
priority based on Japanese Patent Application No. 2018-234733
filed on December 14, 2018. The entire contents of which are
incorporated herein by reference.

10 BACKGROUND OF THE INVENTION

1. Field of the Invention

[0002] The present invention relates to a substrate
processing method and a substrate processing apparatus for
processing substrates. Examples of substrates to be processed
15 include substrates such as semiconductor wafers, substrates
for liquid crystal display devices, substrates for FPDs (flat
panel displays), such as organic EL (electroluminescence)
display devices, etc., substrates for optical disks,
substrates for magnetic disks, substrates for magneto-optical
20 disks, substrates for photomasks, ceramic substrates,
substrates for solar cells, etc.

2. Description of the Related Art

[0003] In a manufacturing process of semiconductor
25 devices, a cleaning step is executed in order to remove various

contaminants attached to a substrate, residue of a processing liquid or a resist, etc., used in a prior step, and various particles, etc. (these may hereinafter be referred to collectively as the "removal object").

5 [0004] In the cleaning step, in general, a cleaning liquid, such as deionized water (DIW), etc., is supplied to the substrate to remove the removal object by physical actions of the cleaning liquid, or a chemical liquid that chemically reacts with the removal object is supplied to the substrate
10 to chemically remove the removal object.

[0005] However, progress is being made in making an uneven pattern formed on a substrate finer and more complex. Therefore, it is becoming difficult to remove a removal object using a cleaning liquid or a chemical liquid while suppressing
15 damage to the uneven pattern.

[0006] Thus, a method has been proposed where a processing liquid, containing a solute and a solvent having volatility, is supplied to an upper surface of a substrate, the processing liquid is solidified or cured to form a processing film, and
20 thereafter, the processing film is dissolved and removed (refer to United States Patent Application Publication No. 2014/041685 and United States Patent Application Publication No. 2015/128994).

[0007] With the method described above, a removal object
25 is pulled away from the substrate when the processing liquid

is solidified or cured to form the processing film. The removal object that has been pulled away is then held inside the processing film.

[0008] Next, a dissolution processing liquid is supplied
5 to the upper surface of the substrate. Since the processing film is thereby dissolved on the substrate and removed, the removal object is removed from the upper surface of the substrate together with dissolved matter of the processing film (refer to United States Patent Application Publication No.
10 2014/041685).

[0009] Alternatively, there is also a case in which a peeling processing liquid is supplied to an upper surface of a substrate. Thereby, the processing film is peeled from the upper surface of the substrate. The dissolution processing
15 liquid is then supplied by which the processing film is dissolved on the substrate (refer to United States Patent Application Publication No. 2015/128994).

SUMMARY OF THE INVENTION

20 [0010] However, with both the method disclosed in United States Patent Application Publication No. 2014/041685 and the method disclosed in United States Patent Application Publication No. 2015/128994, the processing film is dissolved on the substrate. Therefore, the removal object may fall off
25 from the processing film on the substrate and the fallen removal

object may become reattached to the substrate. There is thus a risk that the removal object may not be efficiently removed from the substrate. A method for removing the processing film from the substrate in the state where the removal object is
5 held by the processing film is thus being demanded.

[0011] However, a peeling liquid capable of peeling and removing the processing film from a surface of substrate in a state where the removal object is held by the processing film is comparatively expensive. When the peeling liquid is
10 supplied toward the upper surface of the substrate, the peeling liquid will be consumed in a large amount and cost may thus increase.

[0012] Thus, an object of the present invention is to provide a substrate processing method and a substrate
15 processing apparatus by which a removal object present on a surface of a substrate can be removed efficiently while suppressing cost increase.

[0013] A preferred embodiment of the present invention provides a substrate processing method including a processing
20 liquid supplying step of supplying a processing liquid having a solute and a solvent to a surface of a substrate, a processing film forming step of solidifying or curing the processing liquid supplied to the surface of the substrate to form, on the surface of the substrate, a processing film that holds a
25 removal object present on the surface of the substrate, a

peeling step of supplying a peeling liquid forming liquid to the surface of the substrate to put the peeling liquid forming liquid in contact with the processing film and form a peeling liquid, and peeling the processing film, in the state of holding the removal object, from the surface of the substrate by the peeling liquid, and a removing step of continuing the supply of the peeling liquid forming liquid after the peeling of the processing film to remove the processing film from the surface of the substrate in the state where the removal object is held by the processing film.

[0014] According to the present method, by putting the peeling liquid forming liquid, supplied to the surface of the substrate, and the processing film in contact, the peeling liquid that peels the processing film from the surface of the substrate is formed on the substrate. By the peeling liquid that is formed spontaneously on the substrate, the processing film in the state of holding the removal object is peeled from the surface of the substrate. By then continuing the supply of the peeling liquid forming liquid, the processing film can be removed from the surface of the substrate in the state where the removal object is held by the processing film. That is, the removal object can be removed from the surface of the substrate by just supplying the peeling liquid forming liquid without supplying the peeling liquid toward the surface of the substrate. That is, the removal object can be removed from

the surface of the substrate without consuming the comparatively expensive peeling liquid in a large amount. The removal object present on the surface of the substrate can thus be removed efficiently while suppressing cost increase.

5 [0015] In the preferred embodiment of the present invention, the solute has a peeling liquid forming substance. Also, the processing film forming step includes a step of forming the processing film having the peeling liquid forming substance in a solid state. Also, the peeling step includes
10 a step of dissolving the peeling liquid forming substance that is in the solid state inside the processing film in the peeling liquid forming liquid supplied to the surface of the substrate to form the peeling liquid.

[0016] According to the present method, the peeling liquid
15 is formed by dissolving the peeling liquid forming substance, that is in the solid state inside the processing film, in the peeling liquid forming liquid. The peeling liquid can thus be formed in a vicinity of the processing film by dissolving the peeling liquid forming substance in the peeling liquid
20 forming liquid in the vicinity of the processing film. The peeling liquid, that is comparatively high in concentration of the peeling liquid forming substance before the peeling liquid forming substance eluted into the peeling liquid forming liquid diffuses uniformly throughout the entire peeling liquid
25 forming liquid, can thus be made to act on the processing film.

The processing film can thereby be peeled efficiently and the removal object present on the surface of the substrate can be removed efficiently.

[0017] As with the peeling liquid, the peeling liquid forming substance required for forming the peeling liquid is also comparatively expensive. Also, a time required to supply an amount of the processing liquid required to form the processing film to the substrate is shorter than a time required for peeling and removing the processing film from the substrate. Thus, in the present method, the processing liquid that contains the peeling liquid forming substance is supplied to the substrate for forming the processing film and the peeling liquid forming liquid that does not contain the peeling liquid forming substance is supplied to the substrate for peeling and removing the processing film. A supply time (consumption amount) of the peeling liquid forming substance to the substrate can thus be reduced in comparison to a method where a processing liquid that does not contain the peeling liquid forming substance is supplied to the substrate for forming the processing film and the peeling liquid (the peeling liquid forming liquid with the peeling liquid forming substance dissolved therein) is supplied to the substrate for peeling and removing the processing film. Cost increase can thus be suppressed.

[0018] Consequently, the removal object present on the

surface of the substrate can be removed efficiently while suppressing cost increase.

[0019] In the preferred embodiment of the present invention, the peeling liquid is an alkaline liquid. The alkaline liquid, although capable of peeling the processing film efficiently, is comparatively expensive. Now, with the method where the alkaline liquid is formed by contact of the peeling liquid forming liquid and the processing film, the alkaline liquid can be formed spontaneously on the substrate. The removal object can thus be removed from the surface of the substrate by just supplying the peeling liquid forming liquid without supplying the alkaline liquid toward the surface of the substrate. That is, the removal object can be removed from the surface of the substrate without consuming the comparatively expensive alkaline liquid in a large amount. A consumption amount of the alkaline liquid can thus be reduced and therefore cost increase can be suppressed. The removal object present on the surface of the substrate can thus be removed efficiently while suppressing cost increase.

[0020] In the preferred embodiment of the present invention, the peeling liquid forming liquid is pure water. The processing film can thus be peeled and removed from the surface of the substrate using pure water, which is comparatively inexpensive, as the peeling liquid forming liquid. The removal object present on the surface of the

substrate can thus be removed efficiently while suppressing cost increase.

[0021] In the preferred embodiment of the present invention, the peeling step includes a penetrating hole forming
5 step of supplying the peeling liquid forming liquid to the surface of the substrate to dissolve the processing film partially and form a penetrating hole in the processing film.

[0022] According to the present method, by supplying the peeling liquid forming liquid to the surface of the substrate,
10 the processing film is partially dissolved to form the penetrating hole in the processing film. By the penetrating hole being formed in the processing film, the peeling liquid is enabled to readily reach a vicinity of the surface of the substrate. Therefore, the peeling liquid can be made to act
15 on an interface between the processing film and the substrate to enable the processing film to be peeled efficiently from the surface of the substrate. On the other hand, although the processing film is partially dissolved for forming the penetrating hole, a remaining portion thereof is kept in a solid
20 state, that is, in the state of holding the removal object. Consequently, the processing film can be peeled quickly from the surface of the substrate and the removal object can be removed efficiently together with the processing film from the surface of the substrate.

25 [0023] In the preferred embodiment of the present

invention, the solute has a high solubility substance and a low solubility substance that is lower in solubility in the peeling liquid than the high solubility substance. Also, the processing film forming step includes a step of forming the processing film having the high solubility substance and the low solubility substance in solid states. Also, the penetrating hole forming step includes a step of dissolving the high solubility substance that is in the solid state inside the processing film in the peeling liquid formed on the substrate to form the penetrating hole in the processing film.

[0024] According to the present method, the high solubility substance is higher in solubility in the peeling liquid than the low solubility substance. The penetrating hole can thus be formed reliably in the processing film by the peeling liquid dissolving the high solubility substance that is in the solid state inside the processing film. On the other hand, the low solubility substance inside the processing film is kept in the solid state without being dissolved. Therefore, the peeling liquid can be made to act on an interface between the low solubility substance in the solid state and the substrate while the removal object is held by the low solubility substance in the solid state. Consequently, the processing film can be peeled quickly from the surface of the substrate and the removal object can be removed efficiently together with the processing film from the surface of the substrate.

[0025] In the preferred embodiment of the present invention, a solubility of the low solubility substance in the peeling liquid forming liquid is lower than a solubility of the high solubility substance in the peeling liquid forming liquid. Also, the penetrating hole forming step includes a step of dissolving the high solubility substance, which is in the solid state inside the processing film, in the peeling liquid forming liquid supplied to the surface of the substrate to form the penetrating hole in the processing film.

[0026] According to the present method, the high solubility substance is higher in solubility in the peeling liquid forming liquid than the low solubility substance. The penetrating hole can thus be formed reliably in the processing film by the peeling liquid forming liquid dissolving the high solubility substance that is in the solid state inside the processing film. On the other hand, the low solubility substance in the solid state inside the processing film is kept in the solid state without being dissolved. Therefore, the peeling liquid can be made to act on the interface between the low solubility substance in the solid state and the substrate while the removal object is held by the low solubility substance in the solid state. Consequently, the processing film can be peeled quickly from the surface of the substrate and the removal object can be removed efficiently together with the processing film from the surface of the substrate.

[0027] In the preferred embodiment of the present invention, the solute has a high solubility substance and a low solubility substance that is lower in solubility in the peeling liquid forming liquid than the high solubility substance. Also, the processing film forming step includes a step of forming the processing film having the high solubility substance and the low solubility substance in solid states. Also, the penetrating hole forming step includes a step of dissolving the high solubility substance, which is in the solid state inside the processing film, in the peeling liquid forming liquid supplied to the surface of the substrate to form the penetrating hole in the processing film.

[0028] According to the present method, the high solubility substance is higher in solubility in the peeling liquid forming liquid than the low solubility substance. The penetrating hole can thus be formed reliably in the processing film by the peeling liquid forming liquid dissolving the high solubility substance that is in the solid state inside the processing film. On the other hand, the low solubility substance inside the processing film is kept in the solid state without being dissolved. Therefore, the peeling liquid can be made to act on the interface between the low solubility substance in the solid state and the substrate while the removal object is held by the low solubility substance in the solid state. Consequently, the processing film can be peeled

quickly from the surface of the substrate and the removal object can be removed efficiently together with the processing film from the surface of the substrate.

[0029] A preferred embodiment of the present invention provides a substrate processing method including a processing liquid supplying step of supplying a processing liquid having a solute that contains an alkaline component and a solvent toward a surface of a substrate, a processing film forming step of solidifying or curing the processing liquid supplied to the surface of the substrate to form, on the surface of the substrate, a processing film that contains the alkaline component and holds a removal object present on the surface of the substrate, a peeling step of supplying pure water to the surface of the substrate to put the pure water in contact with the processing film to elute the alkaline component from the processing film into the pure water and form an alkaline aqueous solution, and peeling the processing film, in the state of holding the removal object, from the surface of the substrate by the alkaline aqueous solution, and a removing step of continuing the supply of the pure water, after the peeling of the processing film, to wash away and remove the processing film from the surface of the substrate in the state where the removal object is held by the processing film.

[0030] According to the present method, by putting the pure water, supplied to the surface of the substrate, and the

processing film in contact, the alkaline component is eluted into the pure water from the processing film and the alkaline aqueous solution is formed (prepared) on the substrate. By the alkaline aqueous solution that is formed spontaneously on the substrate, the processing film in the state of holding the removal object is peeled from the surface of the substrate. By then continuing the supply of the pure water, the processing film can be removed from the surface of the substrate in the state where the removal object is held by the processing film. That is, the removal object can be removed from the surface of the substrate by just supplying the pure water without supplying the alkaline aqueous solution toward the surface of the substrate. That is, the removal object can be removed from the surface of the substrate without consuming the comparatively expensive alkaline aqueous solution in a large amount. The removal object present on the surface of the substrate can thus be removed efficiently while suppressing cost increase.

[0031] Another preferred embodiment of the present invention provides a substrate processing apparatus including a processing liquid supplying unit that supplies a processing liquid having a solute and a solvent to a surface of a substrate, a solid forming unit that solidifies or cures the processing liquid, a peeling liquid forming liquid supplying unit that supplies a peeling liquid forming liquid to the surface of the

substrate, and a controller that controls the processing liquid supplying unit, the solid forming unit, and the peeling liquid forming liquid supplying unit.

[0032] The controller is programmed to execute a
5 processing liquid supplying step of supplying the processing liquid from the processing liquid supplying unit to the surface of the substrate, a processing film forming step of making the solid forming unit solidify or cure the processing liquid supplied to the surface of the substrate to form, on the surface
10 of the substrate, a processing film that holds a removal object present on the surface of the substrate, a peeling step of supplying the peeling liquid forming liquid from the peeling liquid forming liquid supplying unit to the surface of the substrate to put the peeling liquid forming liquid in contact
15 with the processing film and form a peeling liquid and peeling the processing film, in the state of holding the removal object, from the surface of the substrate by the peeling liquid, and a removing step of continuing the supply of the peeling liquid forming liquid from the peeling liquid forming liquid supplying
20 unit, after the peeling of the processing film, to remove the processing film from the surface of the substrate in the state where the removal object is held by the processing film.

[0033] According to the present configuration, by putting the peeling liquid forming liquid, supplied to the surface of
25 the substrate, and the processing film in contact, the peeling

liquid that peels the processing film from the surface of the substrate is formed on the substrate. By the peeling liquid that is formed spontaneously on the substrate, the processing film in the state of holding the removal object is peeled from the surface of the substrate. By then continuing the supply of the peeling liquid forming liquid, the processing film can be removed from the surface of the substrate in the state where the removal object is held by the processing film. That is, the removal object can be removed from the surface of the substrate by just supplying the peeling liquid forming liquid without supplying the peeling liquid toward the surface of the substrate. That is, the removal object can be removed from the surface of the substrate without consuming the comparatively expensive peeling liquid in a large amount. The removal object present on the surface of the substrate can thus be removed efficiently while suppressing cost increase.

[0034] In the other preferred embodiment of the present invention, the solute has a peeling liquid forming substance. Also, in the processing film forming step, the processing film having the peeling liquid forming substance in a solid state is formed. Also, in the peeling step, the peeling liquid forming liquid supplied to the surface of the substrate dissolves the peeling liquid forming substance in the solid state inside the processing film to form the peeling liquid.

[0035] According to the present configuration, the

peeling liquid is formed by dissolving the peeling liquid forming substance, that is in the solid state inside the processing film, in the peeling liquid forming liquid. The peeling liquid can thus be formed in a vicinity of the processing film by dissolving the peeling liquid forming substance in the peeling liquid forming liquid in the vicinity of the processing film. The peeling liquid, that is comparatively high in concentration of the peeling liquid forming substance before the peeling liquid forming substance eluted into the peeling liquid forming liquid diffuses uniformly throughout the entire peeling liquid forming liquid, can thus be made to act on the processing film. The processing film can thereby be peeled efficiently and the removal object present on the surface of the substrate can be removed efficiently.

[0036] As with the peeling liquid, the peeling liquid forming substance required for forming the peeling liquid is also comparatively expensive. Also, a time required to supply an amount of the processing liquid required to form the processing film to the substrate is shorter than a time required for peeling and removing the processing film from the substrate. Thus, in the present configuration, the processing liquid that contains the peeling liquid forming substance is supplied to the substrate for forming the processing film and the peeling liquid forming liquid that does not contain the peeling liquid

forming substance is supplied to the substrate for peeling and removing the processing film. A supply time (consumption amount) of the peeling liquid forming substance can thus be reduced in comparison to an configuration where a processing liquid that does not contain the peeling liquid forming substance is supplied to the substrate for forming the processing film and the peeling liquid (the peeling liquid forming liquid with the peeling liquid forming substance dissolved therein) is supplied to the substrate for peeling and removing the processing film. Cost increase can thus be suppressed.

[0037] Consequently, the removal object present on the surface of the substrate can be removed efficiently while suppressing cost increase.

[0038] In the other preferred embodiment of the present invention, the peeling liquid is an alkaline liquid. The alkaline liquid, although capable of peeling the processing film efficiently, is comparatively expensive. Now, with the configuration where the alkaline liquid is formed by contact of the peeling liquid forming liquid and the processing film, the alkaline liquid can be formed spontaneously on the substrate. The removal object can thus be removed from the surface of the substrate by just supplying the peeling liquid forming liquid without supplying the alkaline liquid toward the surface of the substrate. That is, the removal object can

be removed from the surface of the substrate without consuming the comparatively expensive alkaline liquid in a large amount. A consumption amount of the alkaline liquid can thus be reduced and therefore cost increase can be suppressed. The removal
5 object present on the surface of the substrate can thus be removed efficiently while suppressing cost increase.

[0039] In the other preferred embodiment of the present invention, the peeling liquid forming liquid supplying unit supplies pure water as the peeling liquid forming liquid to
10 the surface of the substrate. The processing film can thus be peeled and removed from the surface of the substrate using pure water, which is comparatively inexpensive, as the peeling liquid forming liquid. The removal object present on the surface of the substrate can thus be removed efficiently while
15 suppressing cost increase.

[0040] In the other preferred embodiment of the present invention, in the peeling step, the peeling liquid forming liquid is supplied to the surface of the substrate to dissolve the processing film partially and form a penetrating hole in
20 the processing film.

[0041] According to the present configuration, by supplying the peeling liquid forming liquid to the surface of the substrate, the processing film is partially dissolved to form the penetrating hole in the processing film. By the
25 penetrating hole being formed in the processing film, the

peeling liquid is enabled to readily reach a vicinity of the surface of the substrate. Therefore, the peeling liquid can be made to act on an interface between the processing film and the substrate to enable the processing film to be peeled
5 efficiently from the surface of the substrate. On the other hand, although the processing film is partially dissolved for forming the penetrating hole, a remaining portion thereof is kept in a solid state, that is, in the state of holding the removal object. Consequently, the processing film can be
10 peeled quickly from the surface of the substrate and the removal object can be removed efficiently together with the processing film from the surface of the substrate.

[0042] In the other preferred embodiment of the present invention, the solute has a high solubility substance and a
15 low solubility substance that is lower in solubility in the peeling liquid than the high solubility substance. Also, in the processing film forming step, the processing film having the high solubility substance and the low solubility substance in solid states is formed. Also, in the peeling step, the
20 peeling liquid formed on the substrate dissolves the high solubility substance, that is in the solid state inside the processing film, to form the penetrating hole in the processing film.

[0043] According to the present configuration, the high
25 solubility substance is higher in solubility in the peeling

liquid than the low solubility substance. The penetrating hole can thus be formed reliably in the processing film by the peeling liquid dissolving the high solubility substance that is in the solid state inside the processing film. On the other
5 hand, the low solubility substance inside the processing film is kept in the solid state without being dissolved. Therefore, the peeling liquid can be made to act on an interface between the low solubility substance in the solid state and the substrate while the removal object is held by the low solubility
10 substance in the solid state. Consequently, the processing film can be peeled quickly from the surface of the substrate and the removal object can be removed efficiently together with the processing film from the surface of the substrate.

[0044] In the other preferred embodiment of the present
15 invention, a solubility of the low solubility substance in the peeling liquid forming liquid is lower than a solubility of the high solubility substance in the peeling liquid forming liquid. Also, in the processing film forming step, the peeling liquid forming liquid, supplied to the surface of the substrate,
20 dissolves the high solubility substance in the solid state inside the processing film to form the penetrating hole in the processing film.

[0045] According to the present configuration, the high solubility substance is higher in solubility in the peeling
25 liquid forming liquid than the low solubility substance. The

penetrating hole can thus be formed reliably in the processing film by the peeling liquid forming liquid dissolving the high solubility substance that is in the solid state inside the processing film. On the other hand, the low solubility substance in the solid state inside the processing film is kept in the solid state without being dissolved. Therefore, the peeling liquid can be made to act on the interface between the low solubility substance in the solid state and the substrate while the removal object is held by the low solubility substance in the solid state. Consequently, the processing film can be peeled quickly from the surface of the substrate and the removal object can be removed efficiently together with the processing film from the surface of the substrate.

[0046] In the other preferred embodiment of the present invention, the solute has a high solubility substance and a low solubility substance that is lower in solubility in the peeling liquid forming liquid than the high solubility substance. Also, in the processing film forming step, the processing film having the high solubility substance and the low solubility substance in solid states is formed. Also, in the peeling step, the peeling liquid forming liquid supplied to the surface of the substrate dissolves the high solubility substance in the solid state inside the processing film to form the penetrating hole in the processing film.

[0047] According to the present configuration, the high

solubility substance is higher in solubility in the peeling liquid forming liquid than the low solubility substance. The penetrating hole can thus be formed reliably in the processing film by the peeling liquid forming liquid dissolving the high solubility substance that is in the solid state inside the processing film. On the other hand, the low solubility substance inside the processing film is kept in the solid state without being dissolved. Therefore, the peeling liquid can be made to act on the interface between the low solubility substance in the solid state and the substrate while the removal object is held by the low solubility substance in the solid state. Consequently, the processing film can be peeled quickly from the surface of the substrate and the removal object can be removed efficiently together with the processing film from the surface of the substrate.

[0048] Another preferred embodiment of the present invention provides a substrate processing apparatus including a processing liquid supplying unit that supplies a processing liquid having a solute that contains an alkaline component and a solvent to a surface of a substrate, a solid forming unit that solidifies or cures the processing liquid, a pure water supplying unit that supplies pure water to the surface of the substrate, and a controller that controls the processing liquid supplying unit, the solid forming unit, and the pure water supplying unit.

[0049] The controller is programmed to execute a processing liquid supplying step of supplying the processing liquid from the processing liquid supplying unit to the surface of the substrate, a processing film forming step of making the solid forming unit solidify or cure the processing liquid supplied to the surface of the substrate to form, on the surface of the substrate, a processing film that contains the alkaline component and holds a removal object present on the surface of the substrate, a peeling step of supplying the pure water from the pure water supplying unit to the surface of the substrate to put the pure water in contact with the processing film to elute the alkaline component from the processing film into the pure water and form an alkaline aqueous solution, and peeling the processing film, in the state of holding the removal object, from the surface of the substrate by the alkaline aqueous solution, and a removing step of continuing the supply of the pure water from the pure water supplying unit, after the peeling of the processing film, to remove the processing film from the surface of the substrate in the state where the removal object is held by the processing film.

[0050] According to the present configuration, by putting the pure water, supplied to the surface of the substrate, and the processing film in contact, the alkaline component is eluted into the pure water from the processing film and the alkaline aqueous solution is formed (prepared) on the substrate.

By the alkaline aqueous solution that is formed spontaneously on the substrate, the processing film in the state of holding the removal object is peeled from the surface of the substrate. By then continuing the supply of the pure water, the processing
5 film can be removed from the surface of the substrate in the state where the removal object is held by the processing film. That is, the removal object can be removed from the surface of the substrate by just supplying the pure water without supplying the alkaline aqueous solution toward the surface of
10 the substrate. That is, the removal object can be removed from the surface of the substrate without consuming the comparatively expensive alkaline aqueous solution in a large amount. The removal object present on the surface of the substrate can thus be removed efficiently while suppressing
15 cost increase.

[0051] The above and other elements, features, steps, characteristics and advantages of the present invention will become more apparent from the following detailed description of the preferred embodiments with reference to the attached
20 drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0052] FIG. 1 is a schematic plan view of a layout of a substrate processing apparatus according to a first preferred
25 embodiment of the present invention.

[0053] FIG. 2 is a schematic partial sectional view of the general configuration of a processing unit included in the substrate processing apparatus.

[0054] FIG. 3 is a block diagram of the electrical configuration of a main portion of the substrate processing apparatus.

[0055] FIG. 4 is a flowchart for describing an example of substrate processing by the substrate processing apparatus.

[0056] FIG. 5A is a schematic view for describing conditions of a processing liquid supplying step (step S5) in the substrate processing.

[0057] FIG. 5B is a schematic view for describing conditions of a film thinning step (step S6) in the substrate processing.

[0058] FIG. 5C is a schematic view for describing conditions of a heating step (step S7) in the substrate processing.

[0059] FIG. 5D is a schematic view for describing conditions of a peeling/removing step (step S8) in the substrate processing.

[0060] FIG. 5E is a schematic view for describing conditions of a second rinsing step (step S9) in the substrate processing.

[0061] FIG. 5F is a schematic view for describing conditions of a second organic solvent supplying step (step

S10) in the substrate processing.

[0062] FIG. 5G is a schematic view for describing conditions of a spin drying step (step S11) in the substrate processing.

5 [0063] FIG. 6A is a schematic sectional view for describing conditions in a vicinity of a surface of a substrate after the heating step (step S7).

[0064] FIG. 6B is a schematic sectional view for describing conditions in the vicinity of the surface of the substrate
10 during execution of the peeling/removing step (step S8).

[0064] FIG. 6C is a schematic sectional view for describing conditions in the vicinity of the surface of the substrate during execution of the peeling/removing step (step S8).

[0065] FIG. 6D is a schematic sectional view for describing
15 conditions in the vicinity of the surface of the substrate during execution of the peeling/removing step (step S8).

[0067] FIG. 7 is a schematic partial sectional view of the general configuration of a processing unit included in a substrate processing apparatus according to a second preferred
20 embodiment.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0068] In the present Specification, unless restrictedly mentioned otherwise, the singular form includes the plural form
25 and "one" and "the" signify "at least one." In the present

Specification, unless mentioned otherwise, an element of a concept is capable of being expressed by a plurality of types and when an amount (for example, mass % or mole %) thereof is indicated, the amount signifies the sum of the plurality of types.

[0069] "And/or" includes all combinations of the elements and also includes use as a singular element.

[0070] In the present Specification, when a numerical range is indicated using "~" or "-", unless restrictedly mentioned otherwise, both endpoints are included and the units are the same. For example, 5 ~ 25 mole % signifies not less than 5 mole % and not more than 25 mole %.

[0071] In the present Specification, expressions of " C_{x-y} ," " $C_x \sim C_y$," and " C_x ," etc., indicate the number of carbons in a molecule or a substituent. For example, C_{1-6} alkyl indicates an alkyl chain (methyl, ethyl, propyl, butyl, pentyl, hexyl, etc.) having not less than one and not more than six carbons.

[0072] In the present Specification, when a polymer has plural types of repeating units, these repeating units are copolymerized. Unless restrictedly mentioned otherwise, the copolymerization may be any one of alternating copolymerization, random copolymerization, block copolymerization, graft copolymerization or a mixture thereof. When a polymer and a resin is expressed by a structural formula, n, m, etc., which are written together in parentheses indicate

the number of repetitions.

[0073] <First Preferred Embodiment>

[0074] FIG. 1 is a schematic plan view of a layout of a
5 substrate processing apparatus 1 according to a first preferred
embodiment of the present invention.

[0075] The substrate processing apparatus 1 is a single
substrate processing type apparatus that processes a substrate
W, such as a silicon wafer, etc., one at a time. In the present
10 preferred embodiment, the substrate W is a disk-shaped
substrate.

[0076] The substrate processing apparatus 1 includes a
plurality of processing units 2 for processing substrates W
with fluids, load ports LP on which are placed carriers C that
15 house a plurality of the substrates W to be processed by the
processing units 2, transfer robots IR and CR that transfer
the substrates W between the load ports LP and the processing
units 2, and a controller 3 that controls the substrate
processing apparatus 1.

20 [0077] The transfer robot IR transfers the substrates W
between the carriers C and the transfer robot CR. The transfer
robot CR transfers the substrates W between the transfer robot
IR and the processing units 2. The plurality of processing
units 2 have, for example, the same configuration. Although
25 the details will be described later, a processing fluid

supplied to the substrate W inside the processing unit 2 includes a chemical liquid, a rinse liquid, a processing liquid, a peeling liquid forming liquid, a heating medium, an inert gas, etc.

5 [0078] Each processing unit 2 includes a chamber 4 and a processing cup 7 disposed inside the chamber 4 and executes processing of the substrate W inside the processing cup 7. An inlet/outlet (not shown) for carrying in the substrates W and carrying out the substrates W by the transfer robot CR is formed
10 at the chamber 4. The chamber 4 is provided with a shutter unit (not shown) for opening/closing the inlet/outlet.

[0079] FIG. 2 is a schematic view for describing an configuration example of the processing unit 2. The processing unit 2 includes a spin chuck 5, a facing member 6,
15 a processing cup 7, a first moving nozzle 8, a second moving nozzle 9, a third moving nozzle 10, a central nozzle 11, and a lower surface nozzle 12.

[0080] The spin chuck 5 rotates the substrate W around a vertical rotational axis A1 (a vertical axis), passing through
20 a central portion of the substrate W, while holding the substrate W horizontally. The spin chuck 5 includes a plurality of chuck pins 20, a spin base 21, a rotating shaft 22 and a spin motor 23.

[0081] The spin base 21 has a disk shape oriented along
25 a horizontal direction. On an upper surface of the spin base

21, a plurality of chuck pins 20 that grip a peripheral edge of the substrate W are disposed at intervals in a circumferential direction of the spin base 21. The spin base 21 and the plurality of chuck pins 20 constitute a substrate holding unit that holds the substrate W horizontally. The substrate holding unit is also referred to as a substrate holder.

[0082] The rotating shaft 22 extends in a vertical direction along the rotational axis A1. An upper end portion of the rotating shaft 22 is coupled to a lower surface center of the spin base 21. The spin motor 23 applies a rotating force to the rotating shaft 22. The spin base 21 is rotated by the rotating shaft 22 being rotated by the spin motor 23. The substrate W is thereby rotated around the rotational axis A1.

The spin motor 23 is an example of a substrate rotating unit that rotates the substrate W around the rotational axis A1.

[0083] The facing member 6 faces the substrate W, held by the spin chuck 5, from above. The facing member 6 is formed to a disk shape having substantially the same diameter as or a diameter equal to or larger than that of the substrate W. The facing member 6 has a facing surface 6a that faces an upper surface (surface on the upper side) of the substrate W. The facing surface 6a is disposed substantially along a horizontal surface higher than the spin chuck 5.

[0084] A hollow shaft 60 is fixed to the facing member 6

at an opposite side to the facing surface 6a. A communicating hole 6b that penetrates up and down through the facing member 6 and is in communication with an internal space 60a of the hollow shaft 60 is formed at a portion of the facing member 5 6 overlapping with the rotational axis A1 in plan view.

[0085] The facing member 6 blocks an atmosphere inside a space between the facing surface 6a and the upper surface of the substrate W from an atmosphere outside the space. The facing member 6 is thus also referred to as a blocking plate.

10 [0086] The processing unit 2 further includes a facing member elevating/lowering unit 61 that drives elevation and lowering of the facing member 6. The facing member elevating/lowering unit 61 is capable of positioning the facing member 6 at any position (height) from a lower position to an 15 upper position. The lower position is a position within a movable range of the facing member 6 at which the facing surface 6a is positioned most proximate to the substrate W. The upper position is a position within the movable range of the facing member 6 at which the facing surface 6a is separated farthest 20 from the substrate W.

[0087] The facing member elevating/lowering unit 61 includes, for example, a ball-screw mechanism (not shown) coupled to a supporting member (not shown) that supports the hollow shaft 60 and an electric motor (not shown) that applies 25 a driving force to the ball-screw mechanism. The facing member

elevating/lowering unit 61 is also referred to as a facing member lifter (blocking plate lifter).

[0088] The processing cup 7 includes a plurality of guards 71 that receive liquid splashed outside from the substrate W held by the spin chuck 5, a plurality of cups 72 that receive liquid guided downward by the plurality of guards 71, and a circular-cylindrical outer wall member 73 that surrounds the plurality of guards 71 and the plurality of cups 72.

[0089] In the present preferred embodiment, there is shown an example where two guards 71 (a first guard 71A and a second guard 71B) and two cups 72 (a first cup 72A and a second cup 72B) are provided.

[0090] Each of the first cup 72A and the second cup 72B has an annular groove shape that is opened upward.

[0091] The first guard 71A is disposed such as to surround the spin base 21. The second guard 71B is disposed such as to surround the spin base 21 at further outer side in a rotational radius direction of a substrate W than the first guard 71A.

[0092] Each of the first guard 71A and the second guard 71B has a substantially circular cylindrical shape, and an upper end portion of each of the guards (the first guard 71A and the second guard 71B) is inclined inward such as to be directed toward the spin base 21.

[0093] The first cup 72A receives liquid guided downward

by the first guard 71A. The second cup 72B is formed integral to the first guard 71A to receive liquid guided downward by the second guard 71B.

[0094] The processing unit 2 includes a guard
5 elevating/lowering unit 74 that elevates and lowers each of the first guard 71A and the second guard 71B separately. The guard elevating/lowering unit 74 elevates and lowers the first guard 71A between the lower position and the upper position. The guard elevating/lowering unit 74 elevates and lowers the
10 second guard 71B between a lower position and an upper position.

[0095] When the first guard 71A and the second guard 71B are both positioned at the upper position, liquid splashed from the substrate W is received by the first guard 71A. When the first guard 71A is positioned at the lower position and the
15 second guard 71B is positioned at the upper position, liquid splashed from the substrate W is received by the second guard 71B.

[0096] The guard elevating/lowering unit 74 includes, for example, a first ball-screw mechanism (not shown) coupled to
20 the first guard 71A, a first motor (not shown) that applies a driving force to the first ball screw mechanism, a second ball-screw mechanism (not shown) coupled to the second guard 71B, and a second motor (not shown) that applies a driving force to the second ball-screw mechanism. The guard
25 elevating/lowering unit 74 is also referred to as a guard

lifter.

[0097] The first moving nozzle 8 is an example of a chemical liquid supplying unit that supplies (discharges) a chemical liquid toward the upper surface of the substrate W held by the spin chuck 5.

[0098] The first moving nozzle 8 is moved in a horizontal direction and in a vertical direction by a first nozzle moving unit 36. The first moving nozzle 8 is capable of moving between a center position and a home position (retreat position) in the horizontal direction. When positioned at the center position, the first moving nozzle 8 faces a rotation center of the upper surface of the substrate W. The rotation center of the upper surface of the substrate W is a position of intersection of the rotational axis A1 with the upper surface of the substrate W. When positioned at the home position, the first moving nozzle 8 does not face the upper surface of the substrate W and is positioned outside the processing cup 7 in plan view. By moving in the vertical direction, the first moving nozzle 8 can move close to the upper surface of the substrate W and retreat upward from the upper surface of the substrate W.

[0099] The first nozzle moving unit 36 includes, for example, a pivoting shaft (not shown) oriented along the vertical direction, an arm (not shown) that is coupled to the pivoting shaft and extends horizontally, and a pivoting shaft

driving unit (not shown) that elevates, lowers, and pivots the pivoting shaft.

[0100] The pivoting shaft driving unit pivots the pivoting shaft around a vertical pivoting axis, thereby swinging the arm. Further, the pivoting shaft driving unit elevates and lowers the pivoting shaft along the vertical direction, thereby moving the arm up and down. The first moving nozzle 8 is fixed to the arm. The first moving nozzle 8 moves in the horizontal direction and in the vertical direction in accordance with the swinging and elevation/lowering of the arm.

[0101] The first moving nozzle 8 is connected to a chemical liquid piping 40 that guides a chemical liquid. When a chemical liquid valve 50 interposed in the chemical liquid piping 40 is opened, the chemical liquid is discharged continuously downward from the first moving nozzle 8.

[0102] The chemical liquid discharged from the first moving nozzle 8 is, for example, a liquid that contains at least one of sulfuric acid, acetic acid, nitric acid, hydrochloric acid, hydrofluoric acid, ammonia water, hydrogen peroxide water, an organic acid (for example, citric acid, oxalic acid, etc.), an organic alkali (for example, TMAH: tetramethylammonium hydroxide, etc.), a surfactant, and a corrosion inhibitor. As examples of chemical liquids in which the above are mixed, SPM solution (sulfuric acid/hydrogen peroxide mixture), SC1 solution (ammonia-hydrogen peroxide

mixture), etc., can be cited.

[0103] The second moving nozzle 9 is an example of a processing liquid supplying unit that supplies (discharges) a processing liquid toward the upper surface of the substrate W held by the spin chuck 5.

[0104] The second moving nozzle 9 is moved in a horizontal direction and in a vertical direction by a second nozzle moving unit 37. The second moving nozzle 9 is capable of moving between a center position and a home position (retreat position) in the horizontal direction. When positioned at the center position, the second moving nozzle 9 faces the rotation center of the upper surface of the substrate W. When positioned at the home position, the second moving nozzle 9 does not face the upper surface of the substrate W and is positioned outside the processing cup 7 in plan view. By moving in the vertical direction, the second moving nozzle 9 can move close to the upper surface of the substrate W and retreat upward from the upper surface of the substrate W.

[0105] The second nozzle moving unit 37 has the same configuration as the first nozzle moving unit 36. That is, the second nozzle moving unit 37 includes, for example, a pivoting shaft (not shown) oriented along the vertical direction, an arm (not shown) that is coupled to the pivoting shaft and the second moving nozzle 9 and extends horizontally, and a pivoting shaft driving unit (not shown) that elevates,

lowers, and pivots the pivoting shaft.

[0106] The second moving nozzle 9 is connected to a processing liquid piping 41 that guides a processing liquid. When a processing liquid valve 51 interposed in the processing liquid piping 41 is opened, the processing liquid is discharged continuously downward from the second moving nozzle 9.

[0107] The processing liquid discharged from the second moving nozzle 9 contains a solute and a solvent. The processing liquid undergoes solidification or curing by at least a portion of the solvent volatilizing (evaporating). The processing liquid undergoes solidification or curing on the substrate W to form a processing film that holds a removal object, such as particles, etc., present on the substrate W.

[0108] Here, "solidification" refers, for example, to hardening of the solute due to forces acting between molecules or between atoms, etc., in association with the volatilization (evaporation) of the solvent. "Curing" refers, for example, to hardening of the solute due to a chemical change such as polymerization, crosslinking, etc. "Solidification or curing" thus expresses "hardening" of the solute due to any of various causes.

[0109] The third moving nozzle 10 is an example of a peeling liquid forming liquid supplying unit (pure water supplying unit) that supplies (discharges) a peeling liquid forming liquid, such as pure water, etc., toward the upper surface of

the substrate W held by the spin chuck 5.

[0110] The third moving nozzle 10 is moved in a horizontal direction and in a vertical direction by a third nozzle moving unit 38. The third moving nozzle 10 is capable of moving
5 between a center position and a home position (retreat position) in the horizontal direction. When positioned at the center position, the third moving nozzle 10 faces the rotation center of the upper surface of the substrate W. When positioned at the home position, the third moving nozzle 10
10 does not face the upper surface of the substrate W and is positioned outside the processing cup 7 in plan view. By moving in the vertical direction, the third moving nozzle 10 can move close to the upper surface of the substrate W and retreat upward from the upper surface of the substrate W.

15 [0111] The third nozzle moving unit 38 has the same configuration as the first nozzle moving unit 36. That is, the third nozzle moving unit 38 includes, for example, a pivoting shaft (not shown) oriented along the vertical direction, an arm (not shown) that is coupled to the pivoting
20 shaft and the third moving nozzle 10 and extends horizontally, and a pivoting shaft driving unit (not shown) that elevates, lowers, and pivots the pivoting shaft.

[0112] The third moving nozzle 10 is connected to an upper peeling liquid forming liquid piping 42 that guides a peeling
25 liquid forming liquid to the third moving nozzle 10. When an

upper peeling liquid forming liquid valve 52 interposed in the upper peeling liquid forming liquid piping 42 is opened, the peeling liquid forming liquid is discharged continuously downward from a discharge port of the third moving nozzle 10.

5 [0113] The peeling liquid forming liquid is a liquid for forming a peeling liquid to be described below. The peeling liquid forming liquid is, for example, pure water, and DIW (deionized water) is especially preferable. A liquid besides DIW may be used instead as the peeling liquid forming liquid.

10 As a liquid besides DIW that is used as the peeling liquid forming liquid, carbonated water, ammonia water of dilute concentration (for example, approximately 10 ppm ~ 100 ppm), etc., can be cited.

[0114] A low solubility substance, a high solubility

15 substance, and a peeling liquid forming substance are contained in the solute in the processing liquid discharged from the second moving nozzle 9.

[0115] The peeling liquid forming substance is a substance that dissolves in the peeling liquid forming liquid to form

20 a peeling liquid that peels the processing film from a surface of the substrate W. The peeling liquid forming substance is, for example, a salt (alkaline component) that exhibits alkalinity (basicity) upon dissolving in the peeling liquid forming liquid. The peeling liquid forming substance is, for

25 example, a primary amine, a secondary amine, a tertiary amine,

or a quaternary ammonium salt, etc. The peeling liquid is an aqueous solution of a primary amine, a secondary amine, a tertiary amine, or a quaternary ammonium salt, etc., in other words, an alkaline aqueous solution (an alkaline liquid).

5 [0116] Substances mutually differing in solubilities in the peeling liquid forming liquid and the peeling liquid can be used as the low solubility substance and the high solubility substance. Specifically, as the high solubility substance, a substance that is higher in solubility in at least either
10 of the peeling liquid forming liquid and the peeling liquid than the substance used as the low solubility substance can be used.

[0117] As long as it is higher in solubility in one of either of the peeling liquid forming liquid and the peeling
15 liquid than the low solubility substance, the high solubility substance may be as low in solubility in the other of the peeling liquid forming liquid and the peeling liquid as the low solubility substance and may be hardly soluble in the other of the peeling liquid forming liquid and the peeling liquid.
20 Oppositely, even if a high solubility substance is higher in solubility in one of either of the peeling liquid forming liquid and the peeling liquid than the low solubility substance, it cannot be used if it is lower in solubility in the other of the peeling liquid forming liquid and the peeling liquid than
25 the low solubility substance.

[0118] The low solubility substance contained in the processing liquid discharged from the second moving nozzle 9 is, for example, novolac, and the high solubility substance contained in the processing liquid discharged from the second moving nozzle 9 is, for example, 2,2-bis(4-hydroxyphenyl)propane.

[0119] The solvent contained in the processing liquid discharged from the second moving nozzle 9 suffices to be a liquid that dissolves the low solubility substance, the high solubility substance, and the peeling liquid forming substance. The solvent contained in the processing liquid is preferably a liquid having compatibility (is miscible) with the peeling liquid forming liquid. Details of the solvent, the low solubility substance, the high solubility substance, and the peeling liquid forming substance contained in the processing liquid discharged from the second moving nozzle 9 shall be described below together with details of the peeling liquid forming liquid discharged from the third moving nozzle 10.

[0120] The central nozzle 11 is housed in the internal space 60a of the hollow shaft 60 of the facing member 6. A discharge port 11a provided at a tip of the central nozzle 11 faces a central region of the upper surface of the substrate W from above. The central region of the upper surface of the substrate W is a region that includes the rotation center of the substrate W at the upper surface of the substrate W.

[0121] The central nozzle 11 includes a plurality of tubes (a first tube 31, a second tube 32 and a third tube 33) that each discharge a fluid downward and a cylindrical casing 30 that surrounds the plurality of tubes. The plurality of tubes
5 and the casing 30 extend in an up/down direction along the rotational axis A1. The discharge port 11a of the central nozzle 11 also serves as a discharge port of the plurality of tubes.

[0122] The first tube 31 is an example of a rinse liquid
10 supplying unit that supplies a rinse liquid to the upper surface of the substrate W. The second tube 32 is an example of a gas supplying unit that supplies a gas between the upper surface of the substrate W and the facing surface 6a of the facing member 6. The third tube 33 is an example of an organic solvent
15 supplying unit that supplies an organic solvent, such as IPA, etc., to the upper surface of the substrate W.

[0123] The first tube 31 is connected to an upper rinse liquid piping 44 that guides the rinse liquid to the first tube 31. When an upper rinse liquid valve 54 interposed in the upper
20 rinse liquid piping 44 is opened, the rinse liquid is discharged continuously toward the central region of the upper surface of the substrate W from the first tube 31 (central nozzle 11).

[0124] The second tube 32 is connected to a gas piping 45 that guides the gas to the second tube 32. When a gas valve
25 55 interposed in the gas piping 45 is opened, the gas is

discharged continuously downward from the second tube 32 (central nozzle 11).

[0125] The gas discharged from the second tube 32 is an inert gas, for example, nitrogen gas (N_2), etc. The gas
5 discharged from the second tube 32 may be air. The inert gas is not restricted to nitrogen gas and is a gas that is inert with respect to the upper surface of the substrate W and a pattern formed on the upper surface of the substrate W. As examples of the inert gas other than nitrogen gas, noble gases,
10 such as argon, etc., can be cited.

[0126] The third tube 33 is connected to an organic solvent piping 46 that guides the organic solvent to the third tube 33. When an organic solvent valve 56 interposed in the organic solvent piping 46 is opened, the organic solvent is discharged
15 continuously toward the central region of the upper surface of the substrate W from the third tube 33 (central nozzle 11).

[0127] The organic solvent discharged from the third tube 33 is a residue removing liquid for removing residue, that remains on the upper surface of the substrate W after removal
20 of the processing film, by the peeling liquid forming liquid. The organic solvent discharged from the third tube 33 preferably has compatibility with the processing liquid and the rinse liquid.

[0128] As examples of the organic solvent discharged from
25 the third tube 33, a liquid, etc., that contains at least one

of IPA, HFE (hydrofluoroether), methanol, ethanol, acetone, and trans-1,2-dichloroethylene can be cited.

[0129] Also, the organic solvent discharged from the third tube 33 is not required to be constituted of just a single
5 component but may be a liquid that is mixed with other components. The organic solvent discharged from the third tube 33 may, for example, be a liquid mixture of IPA and DIW or may be a liquid mixture of IPA and HFE.

[0130] The lower surface nozzle 12 is inserted into a
10 penetrating hole 21a that is opened at an upper surface central portion of the spin base 21. A discharge port 12a of the lower surface nozzle 12 is exposed from an upper surface of the spin base 21. The discharge port 12a of the lower surface nozzle 12 faces a central region of a lower surface (surface at a lower
15 side) of the substrate W from below. The central region of the lower surface of the substrate W is a region that includes the rotation center of the substrate W at the lower surface of the substrate W.

[0131] One end of a common piping 80 that guides the rinse
20 liquid, the peeling liquid forming liquid and the heating medium in common to the lower surface nozzle 12 is connected to the lower surface nozzle 12. A lower rinse liquid piping 81 that guides the rinse liquid to the common piping 80, a lower peeling liquid forming liquid piping 82 that guides the peeling
25 liquid forming liquid to the common piping 80, and a heating

medium piping 83 that guides the heating medium to the common piping 80 are connected to the other end of the common piping 80.

[0132] When a lower rinse liquid valve 86 interposed in the lower rinse liquid piping 81 is opened, the rinse liquid is discharged continuously toward the central region of the lower surface of the substrate W from the lower surface nozzle 12. When a lower peeling liquid forming liquid valve 87 interposed in the lower peeling liquid forming liquid piping 82 is opened, the peeling liquid forming liquid is discharged continuously toward the central region of the lower surface of the substrate W from the lower surface nozzle 12. When a heating medium valve 88 interposed in the heating medium piping 83 is opened, the heating medium is discharged continuously toward the central region of the lower surface of the substrate W from the lower surface nozzle 12.

[0133] The lower surface nozzle 12 is an example of a lower rinse liquid supplying unit that supplies the rinse liquid to the lower surface of the substrate W. Also, the lower surface nozzle 12 is an example of a lower peeling liquid forming liquid supplying unit that supplies the peeling liquid forming liquid to the lower surface of the substrate W. Also, the lower surface nozzle 12 is an example of a heating medium supplying unit that supplies the heating medium for heating the substrate W to the substrate W. The lower surface nozzle 12 is also a

substrate heating unit that heats the substrate W.

[0134] The heating medium discharged from the lower surface nozzle 12 is, for example, high temperature DIW, the temperature of which is higher than room temperature and lower than a boiling point of the solvent contained in the processing liquid. If the solvent contained in the processing liquid is IPA, for example, DIW of 60°C ~ 80°C is used. The heating medium discharged from the lower surface nozzle 12 is not restricted to the high temperature DIW and may be a high temperature gas, such as a high temperature inert gas or high temperature air, etc., the temperature of which is higher than room temperature and lower than the boiling point of the solvent contained in the processing liquid.

[0135] FIG. 3 is a block diagram of the electrical configuration of a main portion of the substrate processing apparatus 1. The controller 3 includes a microcomputer and controls control objects included in the substrate processing apparatus 1 in accordance with a predetermined control program.

[0136] Specifically, the controller 3 includes a processor (CPU) 3A and a memory 3B that stores control programs. The controller 3 is configured such that various types of control for substrate processing are executed by the processor 3A executing the control programs.

[0137] The controller 3 is programmed to control, in particular, the transfer robots IR and CR, the spin motor 23,

the first nozzle moving unit 36, the second nozzle moving unit 37, the third nozzle moving unit 38, the facing member elevating/lowering unit 61, the guard elevating/lowering unit 74, the chemical liquid valve 50, the processing liquid valve 51, the upper peeling liquid forming liquid valve 52, the upper rinse liquid valve 54, the gas valve 55, the organic solvent valve 56, the lower rinse liquid valve 86, the lower peeling liquid forming liquid valve 87 and the heating medium valve 88.

10 [0138] FIG. 4 is a flowchart for describing an example of substrate processing by the substrate processing apparatus 1. FIG. 4 mainly shows processing realized by execution of a program by the controller 3. FIG. 5A to FIG. 5G are schematic views for describing conditions of respective steps of the substrate processing.

[0139] In the substrate processing by the substrate processing apparatus 1, for example, as shown in FIG. 4, a substrate carry-in step (step S1), a chemical liquid supplying step (step S2), a first rinsing step (step S3), a first organic solvent supplying step (step S4), a processing liquid supplying step (step S5), a film thinning step (step S6), a heating step (step S7), a peeling/removing step (step S8), a second rinsing step (step S9), a second organic solvent supplying step (step S10), a spin drying step (step S11), and a substrate carry-out step (step S12) are executed in that order.

25

[0140] First, an unprocessed substrate W is carried from a carrier C into a processing unit 2 by the transfer robots IR and CR (see FIG. 1) and transferred to the spin chuck 5 (step S1). The substrate W is thereby held horizontally by the spin chuck 5 (substrate holding step). The holding of the substrate W by the spin chuck 5 is continued until the spin drying step (step S11) ends. When the substrate W is carried in, the facing member 6 is retreated at the upper position.

[0141] Next, after the transfer robot CR has retreated outside the processing unit 2, the chemical liquid supplying step (step S2) is started. Specifically, the spin motor 23 rotates the spin base 21. The horizontally held substrate W is thereby rotated (substrate rotating step). The guard elevating/lowering unit 74 then moves the first guard 71A and the second guard 71B to the upper positions.

[0142] The first nozzle moving unit 36 moves the first moving nozzle 8 to a processing position. The processing position of the first moving nozzle 8 is, for example, a central position. The chemical liquid valve 50 is then opened. The chemical liquid is thereby supplied (discharged) from the first moving nozzle 8 toward the central region of the upper surface of the substrate W in the rotating state. The chemical liquid supplied to the upper surface of the substrate W spreads radially by receiving a centrifugal force and spreads across the entire upper surface of the substrate W. The upper surface

of the substrate W is thereby processed by the chemical liquid. The discharge of the chemical liquid from the first moving nozzle 8 is continued for a predetermined time of, for example, 30 seconds. In the chemical liquid supplying step, the substrate W is rotated at a predetermined chemical liquid rotational speed of, for example, 800 rpm.

[0143] Next, the first rinsing step (step S3) is started. In the first rinsing step, the chemical liquid on the substrate W is washed away with the rinse liquid.

10 [0144] Specifically, the chemical liquid valve 50 is closed. The supply of the chemical liquid to the substrate W is thereby stopped. The first nozzle moving unit 36 then moves the first moving nozzle 8 to the home position. The facing member elevating/lowering unit 61 then moves the facing member 6 to a processing position between the upper position and the lower position. When the facing member 6 is positioned at the processing position, a distance between the upper surface of the substrate W and the facing surface 6a is, for example, 30 mm. In the first rinsing step, the positions of 15 the first guard 71A and the second guard 71B are kept at the upper positions.

[0145] The upper rinse liquid valve 54 is then opened. The rinse liquid is thereby supplied (discharged) from the central nozzle 11 toward the central region of the upper surface of the substrate W in the rotating state. The rinse liquid 25

supplied to the upper surface of the substrate W from the central nozzle 11 spreads radially by receiving a centrifugal force and spreads across the entire upper surface of the substrate W. The chemical liquid on the upper surface of the substrate W is thereby washed away outside the substrate W. In the first rinsing step, the substrate W is rotated at a predetermined first rinsing rotational speed of, for example, 800 rpm.

[0146] Also, the lower rinse liquid valve 86 is opened. The rinse liquid is thereby supplied (discharged) from the lower surface nozzle 12 toward the central region of the lower surface of the substrate W in the rotating state. The rinse liquid supplied to the lower surface of the substrate W from the lower surface nozzle 12 spreads radially by receiving a centrifugal force and spreads across the entire lower surface of the substrate W. Even when the chemical liquid splashed from the substrate W by the chemical liquid supplying step is attached to the lower surface, the chemical liquid attached to the lower surface is washed away by the rinse liquid supplied from the lower surface nozzle 12. The discharges of the rinse liquid from the central nozzle 11 and the lower surface nozzle 12 are continued for a predetermined time of, for example, 30 seconds.

[0147] Next, the first organic solvent supplying step (step S4) is started. In the first organic solvent supplying

step, the rinse liquid on the substrate W is replaced with the organic solvent.

[0148] Specifically, the upper rinse liquid valve 54 and the lower rinse liquid valve 86 are closed. The supplies of the rinse liquid to the upper surface and the lower surface of the substrate W are thereby stopped. The guard elevating/lowering unit 74 then moves the first guard 71A to the lower position in a state of keeping the second guard 71B at the upper position. The facing member 6 is kept at the processing position.

[0149] The organic solvent valve 56 is then opened. The organic solvent is thereby supplied (discharged) from the central nozzle 11 toward the central region of the upper surface of the substrate W in the rotating state.

[0150] The organic solvent supplied from the central nozzle 11 to the upper surface of the substrate W spreads radially by receiving a centrifugal force and spreads across the entire upper surface of the substrate W. The rinse liquid on the substrate W is thereby replaced with the organic solvent. The discharge of the organic solvent from the central nozzle 11 is continued for a predetermined time of, for example, 10 seconds.

[0151] In the first organic solvent supplying step, the substrate W is rotated at a predetermined first organic solvent rotational speed of, for example, 300 rpm ~ 1500 rpm. It is

not necessary to rotate the substrate W at a fixed rotational speed in the first organic solvent supplying step. For example, the spin motor 23 may rotate the substrate W at 300 rpm at the start of supplying the organic solvent and may accelerate the rotation of the substrate W until the rotational speed of the substrate W reaches 1500 rpm while the organic solvent is being supplied to the substrate W.

[0152] Next, the processing liquid supplying step (step S5) is started. Specifically, the organic solvent valve 56 is closed. The supply of the organic solvent to the substrate W is thereby stopped. The facing member elevating/lowering unit 61 then moves the facing member 6 to the upper position. The guard elevating/lowering unit 74 moves the first guard 71A to the upper position. In the processing liquid supplying step, the substrate W is rotated at a predetermined processing liquid rotational speed of, for example, 10 rpm ~ 1500 rpm.

[0153] Then, as shown in FIG. 5A, the second nozzle moving unit 37 moves the second moving nozzle 9 to a processing position. The processing position of the second moving nozzle 9 is, for example, the central position. The processing liquid valve 51 is then opened. The processing liquid is thereby supplied (discharged) from the second moving nozzle 9 toward the central region of the upper surface of the substrate W in the rotating state (processing liquid supplying step, processing liquid discharging step). The organic solvent on

the substrate W is thereby replaced with the processing liquid, and a liquid film 101 of the processing liquid (processing liquid film) is formed on the substrate W (processing liquid film forming step). The supply of the processing liquid from the second moving nozzle 9 is continued for a predetermined time of, for example, 2 seconds ~ 4 seconds.

[0154] Next, the processing film forming step (step S6 and step S7) is executed. In the processing film forming step, the processing liquid on the substrate W is solidified or cured to form, on the upper surface of the substrate W, a processing film 100 that holds a removal object present on the substrate W (see FIG. 5C).

[0155] In the processing film forming step, the film thinning step (spin off step) (step S6) is executed. In the film thinning step, first, the processing liquid valve 51 is closed. The supply of the processing liquid to the substrate W is thereby stopped. The second moving nozzle 9 is then moved to the home position by the second nozzle moving unit 37.

[0156] As shown in FIG. 5B, in the film thinning step, a portion of the processing liquid is eliminated from the upper surface of the substrate W by the centrifugal force in a state where the supply of the processing liquid to the upper surface of the substrate W is stopped such that a thickness of the liquid film 101 on the substrate W becomes an appropriate thickness. In the film thinning step, the facing member 6, the first guard

71A, and the second guard 71B are kept at the upper positions.

[0157] In the film thinning step, the spin motor 23 changes the rotational speed of the substrate W to a predetermined film thinning speed. The film thinning speed is, for example, 300 rpm ~ 1500 rpm. The rotational speed of the substrate W may be kept fixed within a range of 300 rpm ~ 1500 rpm or may be changed whenever necessary within the range of 300 rpm ~ 1500 rpm in the middle of the film thinning step. The film thinning step is executed for a predetermined time of, for example, 30 seconds.

[0158] In the processing film forming step, the heating step (step S7) of heating the substrate W is executed after the film thinning step. In the heating step, the liquid film 101 (see FIG. 5B) on the substrate W is heated to volatilize (evaporate) a portion of the solvent of the processing liquid on the substrate W.

[0159] Specifically, as shown in FIG. 5C, the facing member elevating/lowering unit 61 moves the facing member 6 to a proximity position between the upper position and the lower position. The proximity position may be the lower position. The proximity position is a position where a distance from the upper surface of the substrate W to the facing surface 6a is, for example, 1 mm. In the heating step, the first guard 71A and the second guard 71B are kept at the upper positions.

[0160] The gas valve 55 is then opened. The gas is thereby

supplied to the space between the upper surface of the substrate W (an upper surface of the liquid film 101) and the facing surface 6a of the facing member 6 (gas supplying step).

[0161] The evaporation (volatilization) of the solvent in the liquid film 101 is promoted by the gas being blown onto the liquid film 101 on the substrate W (solvent evaporating step, solvent evaporation promoting step). A time required to form the processing film 100 can thus be reduced. The central nozzle 11 functions as an evaporating unit (evaporation promoting unit) for evaporating the solvent in the processing liquid.

[0162] Also, the heating medium valve 88 is opened. The heating medium is thereby supplied (discharged) from the lower surface nozzle 12 toward the central region of the lower surface of the substrate W in the rotating state (heating medium supplying step, heating medium discharging step). The heating medium supplied from the lower surface nozzle 12 to the lower surface of the substrate W spreads radially by receiving a centrifugal force and spreads across the entire lower surface of the substrate W. The supply of the heating medium to the substrate W is continued for a predetermined time of, for example, 60 seconds. In the heating step, the substrate W is rotated at a predetermined heating rotational speed of, for example, 1000 rpm.

[0163] By the heating medium being supplied to the lower

surface of the substrate W, the liquid film 101 on the substrate W is heated via the substrate W. The evaporation (volatilization) of the solvent in the liquid film 101 is thereby promoted (solvent evaporating step, solvent evaporation promoting step). A time required to form the processing film 100 can thus be reduced. The lower surface nozzle 12 functions as an evaporating unit (evaporation promoting unit) for evaporating the solvent in the processing liquid.

10 [0164] By the film thinning step and the heating step being executed, the processing liquid is solidified or cured to form the processing film 100 on the substrate W. The substrate rotating unit (the spin motor 23), the central nozzle 11, and the lower surface nozzle 12 thus constitute a solid forming unit that solidifies or cures the processing liquid to form
15 a solid (the processing film 100).

[0165] In the heating step, it is preferable for the substrate W to be heated such that a temperature of the processing liquid on the substrate W is lower than the boiling
20 point of the solvent. By the processing liquid being heated to the temperature lower than the boiling point of the solvent, the solvent can be made to remain appropriately in the processing film 100. The peeling liquid forming liquid is thereby readily compatibilized with the processing film 100
25 in the subsequent peeling/removing step by interaction of the

solvent remaining inside the processing film 100 and the peeling liquid forming liquid in comparison to a case where the solvent does not remain within the processing film 100. The peeling liquid can thus be formed readily.

5 [0166] The heating medium that splashed outside the substrate W due to the centrifugal force is received by the first guard 71A. The heating medium received by the first guard 71A may splash back from the first guard 71A. However, since the facing member 6 is kept close to the upper surface
10 of the substrate W, the upper surface of the substrate W can be protected from the heating medium that splashed back from the first guard 71A. Therefore, attachment of the heating medium to an upper surface of the processing film 100 can be suppressed, and forming of particles due to the splashing back
15 of the heating medium from the first guard 71A can thus be suppressed.

[0167] Further, by the supply of the gas from the central nozzle 11, a gas stream F that moves from the central region of the upper surface of the substrate W toward a peripheral
20 edge of the upper surface of the substrate W is formed in the space between the facing surface 6a of the facing member 6 and the upper surface of the substrate W. By forming the gas stream F that moves from the central region of the upper surface of the substrate W toward the peripheral edge of the upper surface
25 of the substrate W, the heating medium splashed back from the

first guard 71A can be pushed back toward the first guard 71A. The attachment of the heating medium to the upper surface of the processing film 100 can thus be suppressed further.

[0168] Next, the peeling/removing step (step S8) of
5 peeling and removing the processing film 100 from the upper surface of the substrate W is executed. Specifically, the heating medium valve 88 is closed. The supply of the heating medium to the lower surface of the substrate W is thereby stopped. Also, the gas valve 55 is closed. The supply of the
10 gas to the space between the facing surface 6a of the facing member 6 and the upper surface of the substrate W is thereby stopped.

[0169] The facing member elevating/lowering unit 61 then moves the facing member 6 to the upper position. Then, as shown
15 in FIG. 5D, the third nozzle moving unit 38 moves the third moving nozzle 10 to a processing position. The processing position of the third moving nozzle 10 is, for example, the central position.

[0170] The upper peeling liquid forming liquid valve 52
20 is then opened. The peeling liquid forming liquid is thereby supplied (discharged) from the third moving nozzle 10 toward the central region of the upper surface of the substrate W in the rotating state (upper peeling liquid forming liquid supplying step, upper peeling liquid forming liquid
25 discharging step). The peeling liquid forming liquid supplied

to the upper surface of the substrate W spreads across the entire upper surface of the substrate W due to a centrifugal force.

[0171] The supply of the peeling liquid forming liquid to the upper surface of the substrate W is continued for a predetermined time of, for example, 60 seconds. As mentioned above, the supply time of the processing liquid to the upper surface of the substrate W in the processing liquid supplying step is, for example, 2 ~ 4 seconds. The supply time of the peeling liquid forming liquid to the upper surface of the substrate W in the peeling/removing step is thus longer than the supply time of the processing liquid to the upper surface of the substrate W in the processing liquid supplying step.

[0172] In the peeling/removing step, the substrate W is rotated at a predetermined peeling rotational speed of, for example, 800 rpm.

[0173] Also, the lower peeling liquid forming liquid valve 87 is opened. The peeling liquid forming liquid is thereby supplied (discharged) from the lower surface nozzle 12 toward the central region of the lower surface of the substrate W in the rotating state (lower peeling liquid forming liquid supplying step, lower peeling liquid forming liquid discharging step). The peeling liquid forming liquid supplied to the lower surface of the substrate W spreads across the entire lower surface of the substrate W due to a centrifugal

force.

[0174] By the peeling liquid forming liquid being supplied to the upper surface of the substrate W, the peeling liquid forming liquid and the processing film 100 are put in contact and the peeling liquid is formed. The processing film 100 is then peeled together with the removal object from the upper surface of the substrate W by a peeling action of the peeling liquid (peeling step). In being peeled from the upper surface of the substrate W, the processing film 100 splits into film fragments. Then, after the peeling of the processing film 100, the film fragments of the split processing film 100 are eliminated outside the substrate W together with the peeling liquid forming liquid by the supply of the peeling liquid forming liquid to the upper surface of the substrate W being continued. The film fragments of the processing film 100 in the state of holding the removal object are thereby removed from the upper surface of the substrate W (removing step).

[0175] Here, the processing liquid supplied to the upper surface of the substrate W in the processing liquid supplying step (step S5) shown in FIG. 5A may flow along the peripheral edge of the substrate W and flow around to the lower surface of the substrate W. Also, the processing liquid that splashed from the substrate W may splash back from the first guard 71A and become attached to the lower surface of the substrate W. Even in these cases, the heating medium is supplied to the lower

surface of the substrate W in the heating step (step S7) as shown in FIG. 5C, and the processing liquid can thus be eliminated from the lower surface of the substrate W by a flow of the heating medium.

5 [0176] Further, the processing liquid that became attached to the lower surface of the substrate W due to the processing liquid supplying step (step S5) may become solidified or cured and form a solid. Even in such a case, the solid can be peeled and removed from the lower surface of
10 the substrate W by the peeling liquid forming liquid being supplied (discharged) from the lower surface nozzle 12 to the lower surface of the substrate W while the peeling liquid forming liquid is supplied to the upper surface of the substrate W in the peeling/removing step (step S8) as shown in FIG. 5D.
15 In detail, the peeling liquid is formed by the contact of the peeling liquid forming liquid and the solid, and the solid is peeled from the lower surface of the substrate W by the peeling action of the peeling liquid.

[0177] After the peeling/removing step (step S8), the
20 second rinsing step (step S9) is executed. Specifically, the upper peeling liquid forming liquid valve 52 and the lower peeling liquid forming liquid valve 87 are closed. The supplies of the peeling liquid forming liquid to the upper surface and the lower surface of the substrate W are thereby
25 stopped. The third nozzle moving unit 38 then moves the third

moving nozzle 10 to the home position. Then, as shown in FIG. 5E, the facing member elevating/lowering unit 61 moves the facing member 6 to the processing position. In the second rinsing step, the substrate W is rotated at a predetermined
5 second rinsing rotational speed of, for example, 800 rpm. The first guard 71A and the second guard 71B are kept at the upper positions.

[0178] The upper rinse liquid valve 54 is then opened. The rinse liquid is thereby supplied (discharged) from the central
10 nozzle 11 toward the central region of the upper surface of the substrate W in the rotating state (second upper rinse liquid supplying step, second upper rinse liquid discharging step). The rinse liquid supplied to the upper surface of the substrate W spreads across the entire upper surface of the substrate W
15 due to a centrifugal force. The peeling liquid forming liquid attached to the upper surface of the substrate W is thereby washed away with the rinse liquid.

[0179] Also, the lower rinse liquid valve 86 is opened. The rinse liquid is thereby supplied (discharged) from the
20 lower surface nozzle 12 toward the central region of the lower surface of the substrate W in the rotating state (second lower rinse liquid supplying step, second lower rinse liquid discharging step). The peeling liquid forming liquid attached to the lower surface of the substrate W is thereby washed away
25 with the rinse liquid. The supplies of the rinse liquid to

the upper surface and the lower surface of the substrate W are continued for a predetermined time of, for example, 35 seconds.

[0180] Next, the second organic solvent supplying step (step S10) is executed. Specifically, the upper rinse liquid valve 54 and the lower rinse liquid valve 86 are closed. The supplies of the rinse liquid to the upper surface and the lower surface of the substrate W are thereby stopped. Then, as shown in FIG. 5F, the guard elevating/lowering unit 74 moves the first guard 71A to the lower position. The facing member 6 is then kept at the processing position. In the second organic solvent supplying step, the substrate W is rotated at a predetermined second organic solvent rotational speed of, for example, 300 rpm.

[0181] The organic solvent valve 56 is then opened. The organic solvent is thereby supplied (discharged) from the central nozzle 11 toward the central region of the upper surface of the substrate W in the rotating state (second organic solvent supplying step, second organic solvent discharging step, residue removing liquid supplying step). The supply of the organic solvent to the upper surface of the substrate W is continued for a predetermined time of, for example, 30 seconds.

[0182] The organic solvent supplied to the upper surface of the substrate W spreads radially by receiving a centrifugal force and spreads across the entire upper surface of the substrate W. The rinse liquid on the upper surface of the

substrate W is thereby replaced with the organic solvent. The organic solvent supplied to the upper surface of the substrate W dissolves residue of the processing film 100 remaining on the upper surface of the substrate W and is thereafter expelled from the peripheral edge of the upper surface of the substrate W (residue removing step).

[0183] Next, the spin drying step (step S11) is executed. Specifically, the organic solvent valve 56 is closed. The supply of the organic solvent to the upper surface of the substrate W is thereby stopped. Then, as shown in FIG. 5G, the facing member elevating/lowering unit 61 moves the facing member 6 to a drying position lower than the processing position. When the facing member 6 is positioned at the drying position, the distance between the facing surface 6a of the facing member 6 and the upper surface of the substrate W is, for example, 1.5 mm. The gas valve 55 is then opened. The gas is thereby supplied to the space between the upper surface of the substrate W and the facing surface 6a of the facing member 6.

[0184] The spin motor 23 then accelerates the rotation of the substrate W to rotate the substrate W at a high speed. The substrate W is rotated at a drying speed of, for example, 1500 rpm in the spin drying step. The spin drying step is executed for a predetermined time of, for example, 30 seconds. Thereby, a large centrifugal force acts on the organic solvent on the substrate W and the organic solvent on the substrate W is spun

off to a periphery of the substrate W. In the spin drying step, the evaporation of the organic solvent is promoted by the supply of the gas to the space between the upper surface of the substrate W and the facing surface 6a of the facing member 6.

5 [0185] The spin motor 23 then stops the rotation of the substrate W. The guard elevating/lowering unit 74 moves the first guard 71A and the second guard 71B to the lower positions. The gas valve 55 is closed. The facing member elevating/lowering unit 61 then moves the facing member 6 to
10 the upper position.

[0186] The transfer robot CR enters into the processing unit 2, lifts up the processed substrate W from the chuck pin 20 of the spin chuck 5 and carries it outside the processing unit 2 (step S12). The substrate W is transferred from the
15 transfer robot CR to the transfer robot IR and housed in a carrier C by the transfer robot IR.

[0187] Next, conditions in which the processing film 100 is peeled from the substrate W shall be described with reference to FIG. 6A to FIG. 6D. FIG. 6A shows conditions in a vicinity
20 of the upper surface of the substrate W after the heating step (step S7). FIG. 6B to FIG. 6D show conditions in the vicinity of the upper surface of the substrate W during execution of the peeling/removing step (step S8).

[0188] As described above, in the heating step executed
25 in the processing film forming step, the liquid film 101 on

a substrate W is heated by the heating medium via the substrate W. The processing film 100 that holds removal objects 103, such as particles, etc., is thereby formed as shown in FIG. 6A. In detail, by at least a portion of the solvent evaporating, the high solubility substance contained in the solute of the processing liquid forms high solubility solids 110 (the high solubility substance in a solid state). Also, by at least a portion of the solvent evaporating, the low solubility substance contained in the solute of the processing liquid forms a low solubility solid 111 (the low solubility substance in a solid state), and the peeling liquid forming substance contained in the solute of the processing liquid forms a peeling liquid forming solids 112 (the peeling liquid forming substance in a solid state).

[0189] The processing film 100 is divided into portions in which the high solubility solids 110 are biasedly present and portions in which the low solubility solid 111 is biasedly present. The peeling liquid forming solids 112 are formed uniformly across the entire processing film 100.

[0190] Referring to FIG. 6B, when, the peeling liquid forming liquid is supplied to the upper surface of the substrate W in the peeling/removing step, the peeling liquid forming solids 112 become eluted into the peeling liquid forming liquid. By the peeling liquid forming solids 112 dissolving in the peeling liquid forming liquid, the peeling liquid (the alkaline

liquid) is formed.

[0191] Referring to FIG. 6C, due to the supply of the peeling liquid forming liquid, the high solubility solids 110 become dissolved. That is, the processing film 100 becomes
5 partially dissolved. By the dissolution of the high solubility solids 110, penetrating holes 102 are formed in the portions of the processing film 100 at which the high solubility solids 110 are biasedly present (penetrating hole forming step). The penetrating holes 102 are likely to be formed in particular
10 in portions in which the high solubility solids 110 extend in a thickness direction T of the substrate W (that is also a thickness direction of the processing film 100). Each penetrating hole 102 has a size of, for example, several nm in diameter in plan view.

15 [0192] If the high solubility solids 110 have a property of dissolving in both the peeling liquid forming liquid and the peeling liquid, the penetrating holes 102 begin to be formed at the instant the peeling liquid forming liquid lands on the processing film 100, even if the peeling liquid forming
20 substance is not sufficiently eluted into the peeling liquid forming liquid. When the peeling liquid is then formed, the forming of the penetrating holes 102 is promoted. That is, the penetrating holes 102 are formed by both the peeling liquid and the peeling liquid forming liquid.

25 [0193] If the high solubility solids 110 have a property

of hardly dissolving in the peeling liquid forming liquid but dissolves in the peeling liquid, the penetrating holes 102 begin to be formed after the peeling liquid forming substance becomes sufficiently eluted into the peeling liquid forming liquid. That is, the penetrating holes 102 are formed by the peeling liquid.

[0194] If the high solubility solids 110 have a property of hardly dissolving in the peeling liquid but dissolves in the peeling liquid forming liquid, the penetrating holes 102 are formed before the peeling liquid forming substance becomes eluted into the peeling liquid forming liquid. That is, the penetrating holes 102 are formed by the peeling liquid forming liquid.

[0195] By the time the penetrating holes 102 are formed, the peeling liquid forming substance will have become eluted from the processing film 100 into the peeling liquid forming liquid and the peeling liquid will have been formed. The solubility of the low solubility substance in the peeling liquid is low and the low solubility substance is hardly dissolved in the peeling liquid. The low solubility solid 111 is thus dissolved only slightly at a vicinity of a surface thereof by the peeling liquid. The peeling liquid reaching to the vicinity of the upper surface of the substrate W via the penetrating hole 102 thus slightly dissolves a portion of the low solubility solid 111 in the vicinity of the upper

surface of the substrate W. Thereby, as shown in an enlarged view in FIG. 6C, the peeling liquid, while gradually dissolving the low solubility solid 111 in the vicinity of the upper surface of the substrate W, enters gaps G between the processing film 100 and the upper surface of the substrate W (peeling liquid entry step).

[0196] When locations of the processing film 100 at which the high solubility solids 110 are biasedly present are being dissolved, the peeling liquid forming solids 112 present at those locations and the peeling liquid forming solids 112 present at portions of the processing film 100 surrounding the penetrating holes 102 become dissolved by the peeling liquid (peeling liquid forming liquid). Similarly, by the peeling liquid entering the gaps G, the peeling liquid forming solids 112 present at the portions of the processing film 100 in the vicinity of the upper surface of the substrate W become dissolved by the peeling liquid. A concentration of the alkaline component in the peeling liquid is thereby increased further (see the enlarged view in FIG. 6C). Peeling of the low solubility solid 111 of the processing film 100 is thus promoted further.

[0197] Then, for example, with peripheral edges of the penetrating holes 102 as starting points, the processing film 100 becomes split into film fragments, and as shown in FIG. 6D, the film fragments of the processing film 100 become peeled

from the substrate W in a state of holding the removal objects 103 (processing film splitting step, peeling step). By then continuing the supply of the peeling liquid forming liquid, the processing film 100 that has become film fragments is washed
5 away (pushed outside the substrate W) and removed, in the state of holding the removal objects 103, from the upper surface of the substrate W (removing step).

[0198] There may be a case where the peeling liquid hardly dissolves the low solubility solid 111. Even in this case,
10 by entry into the slight gaps G between the processing film 100 and the upper surface of the substrate W, the processing film 100 is peeled from the substrate W.

[0199] According to the first preferred embodiment, by putting the peeling liquid forming liquid (pure water),
15 supplied to the upper surface of the substrate W, and the processing film 100 in contact, the peeling liquid (the alkaline liquid) that peels the processing film 100 from the upper surface of the substrate W is formed. Specifically, the alkaline component inside the processing film 100 becomes
20 eluted into the pure water and the alkaline liquid (the alkaline aqueous solution) is formed. The peeling liquid forming liquid is comparatively inexpensive, and among liquids used as the peeling liquid forming liquid, pure water is especially inexpensive. The alkaline liquid used as the peeling liquid
25 is comparatively expensive.

[0200] By the peeling liquid that is formed spontaneously on the substrate W, the processing film 100 in the state of holding the removal objects 103 is peeled from the upper surface of the substrate W. By then continuing the supply of the peeling liquid forming liquid, the processing film 100 can be washed away and removed from the upper surface of the substrate W in the state where the removal objects 103 are held by the processing film 100. That is, the removal objects 103 can be removed from the upper surface of the substrate W by just supplying the peeling liquid forming liquid without supplying the peeling liquid toward the upper surface of the substrate W. That is, the removal objects 103 can be removed from the upper surface of the substrate W without consuming the comparatively expensive peeling liquid in a large amount. The removal objects 103 present on the upper surface of the substrate W can thus be removed efficiently while suppressing cost increase.

[0201] Also, according to the present preferred embodiment, the peeling liquid is formed by dissolving the peeling liquid forming solids 112 inside the processing film 100 in the peeling liquid forming liquid. The peeling liquid can thus be formed in a vicinity of the processing film 100 by dissolving the peeling liquid forming substance in the peeling liquid forming liquid in the vicinity of the processing film 100. The peeling liquid that is high in concentration

of the peeling liquid forming substance before the peeling liquid forming substance diffuses uniformly throughout the entire peeling liquid forming liquid can thus be made to act on the processing film 100. The processing film 100 can
5 thereby be peeled efficiently. The removal objects 103 are thus removed efficiently together with the processing film 100 from the upper surface of the substrate W.

[0202] As with the peeling liquid, the peeling liquid forming substance required for forming the peeling liquid is
10 also comparatively expensive. Also, a time required to supply an amount of the processing liquid required to form the processing film 100 to the substrate W (for example, 2 seconds ~ 4 seconds) is shorter than a time required for peeling and removing the processing film 100 from the substrate (for
15 example, 60 seconds). Thus, in the present preferred embodiment, the processing liquid that contains the peeling liquid forming substance is supplied to the substrate W for forming the processing film 100 and the peeling liquid forming liquid that does not contain the peeling liquid forming
20 substance is supplied to the substrate W for peeling and removing the processing film 100. The supply time (consumption amount) of the peeling liquid forming substance to the substrate W can thus be reduced in comparison to a method where a processing liquid that does not contain the peeling
25 liquid forming substance is supplied to the substrate W for

forming the processing film 100 and the peeling liquid (the peeling liquid forming liquid with the peeling liquid forming substance dissolved therein) is supplied to the substrate for peeling and removing the processing film 100. Cost increase
5 can thus be suppressed.

[0203] When the peeling liquid, such as the alkaline liquid, etc., is supplied in a large amount toward the upper surface of the substrate W, it may damage the substrate W and respective components of the substrate processing apparatus 1. The
10 substrate W and components having peeling liquid resistance performance (alkaline resistance performance) must thus be used and cost may thus increase.

[0204] In the present preferred embodiment, the peeling liquid can be formed spontaneously by the contact of the pure
15 water or other peeling liquid forming liquid that hardly damages the upper surface of the substrate W and the processing film 100. The removal objects 103 can thus be removed from the upper surface of the substrate W by just supplying the peeling liquid forming liquid without supplying the peeling
20 liquid toward the upper surface of the substrate W. That is, the removal objects 103 can be removed from the upper surface of the substrate W without supplying a large amount of a peeling liquid that readily damages the substrate W and the respective components of the substrate processing apparatus 1 to the
25 substrate W. Damage to the substrate W and the respective

components of the substrate processing apparatus 1 can thus be suppressed. Further, there is also no need to improve the peeling liquid resistance performances of the substrate W and the respective components of the substrate processing apparatus 1 and cost increase can thus be suppressed.

[0205] Also, in the present preferred embodiment, by supplying the peeling liquid forming liquid to the upper surface of the substrate W, the processing film 100 is partially dissolved to form the penetrating holes 102 in the processing film 100. By the penetrating holes 102 being formed in the processing film 100, the peeling liquid is enabled to readily reach the vicinity of the upper surface of the substrate W. Therefore, the peeling liquid can be made to act on an interface between the processing film 100 and the substrate W to enable the processing film 100 to be peeled efficiently from the upper surface of the substrate W. On the other hand, although the processing film 100 is partially dissolved for forming the penetrating holes 102, a remaining portion thereof is kept in a solid state, that is, in the state of holding the removal objects 103. Consequently, the removal objects 103 can be removed efficiently together with the processing film 100 from the upper surface of the substrate W.

[0206] According to the present preferred embodiment, the high solubility substance is higher in solubility in at least either of the peeling liquid forming liquid and the peeling

liquid than the low solubility substance. The penetrating holes 102 can thus be formed reliably in the processing film 100 by the peeling liquid forming liquid or the peeling liquid dissolving the high solubility solids 110 inside the processing film 100. On the other hand, the low solubility solid 111 inside the processing film 100 is kept in the solid state without being dissolved. Therefore, the peeling liquid can be made to act on an interface between the low solubility solid 111 in the solid state and the substrate W while the removal objects 103 are held by the low solubility solid 111. Consequently, the processing film 100 can be peeled quickly from the upper surface of the substrate W and meanwhile the removal objects 103 can be removed efficiently together with the processing film 100 from the upper surface of the substrate W.

[0207] <Second Preferred Embodiment>

[0208] FIG. 7 is a schematic partial sectional view of the general configuration of a processing unit 2P included in a substrate processing apparatus 1P according to a second preferred embodiment. Referring to FIG. 7, a main point of difference of the processing unit 2P according to the second preferred embodiment with respect to the processing unit 2 according to the first preferred embodiment (see FIG. 2) is that the processing unit 2P according to the second preferred

embodiment includes a fourth moving nozzle 14 in place of the facing member 6 and the central nozzle 11.

[0209] The fourth moving nozzle 14 is an example of the organic solvent supplying unit that supplies an organic solvent to the upper surface of the substrate W. The fourth moving nozzle 14 is also an example of the gas supplying unit that supplies a gas, such as nitrogen gas, etc., to the upper surface of the substrate W.

[0210] The fourth moving nozzle 14 is moved in a horizontal direction and in a vertical direction by a fourth nozzle moving unit 35. The fourth moving nozzle 14 is capable of moving between a center position and a home position (retreat position) in the horizontal direction.

[0211] When positioned at the center position, the fourth moving nozzle 14 faces the rotation center of the upper surface of the substrate W. When positioned at the home position, the fourth moving nozzle 14 does not face the upper surface of the substrate W and is positioned outside the processing cup 7 in plan view. By moving in the vertical direction, the fourth moving nozzle 14 can move close to the upper surface of the substrate W and retreat upward from the upper surface of the substrate W.

[0212] The fourth nozzle moving unit 35 has the same configuration as the first nozzle moving unit 36. That is, the fourth nozzle moving unit 35 includes, for example, a

pivoting shaft (not shown) oriented along the vertical direction, an arm (not shown) that is coupled to the pivoting shaft and the fourth moving nozzle 14 and extends horizontally, and a pivoting shaft driving unit (not shown) that elevates, lowers, and pivots the pivoting shaft.

[0213] An organic solvent piping 90 that guides the organic solvent to the fourth moving nozzle 14 is connected to the fourth moving nozzle 14. When an organic solvent valve 95 interposed in the organic solvent piping 90 is opened, the organic solvent is discharged continuously from the fourth moving nozzle 14 toward the central region of the upper surface of the substrate W.

[0214] A plurality of gas pipings (a first gas piping 91, a second gas piping 92, and a third gas piping 93) each of which guide a gas to the fourth moving nozzle 14 are connected to the fourth moving nozzle 14. In the plurality of gas pipings (the first gas piping 91, the second gas piping 92 and the third gas piping 93) are respectively interposed gas valves (a first gas valve 96A, a second gas valve 97A, and a third gas valve 98A) for opening and closing the corresponding flow passages.

[0215] The fourth moving nozzle 14 has a central discharge port 14a that discharges the organic solvent, that is guided from the organic solvent piping 90, along the vertical direction. The fourth moving nozzle 14 has a linear flow discharge port 14b that discharges the gas, which is supplied

from the first gas piping 91, rectilinearly along the vertical direction. Further, the fourth moving nozzle 14 has a horizontal flow discharge port 14c that discharges the gas, which is supplied from the second gas piping 92, radially along the horizontal direction to a periphery of the fourth moving nozzle 14. Also, the fourth moving nozzle 14 has an inclined flow discharge port 14d that discharges the gas, which is supplied from the third gas piping 93, radially along an obliquely downward direction to the periphery of the fourth moving nozzle 14.

[0216] A mass flow controller 96B configured to accurately adjust a flow rate of the gas flowing inside the first gas piping 91 is interposed in the first gas piping 91. The mass flow controller 96B has a flow control valve. Also, a variable flow valve 97B configured to adjust a flow rate of the gas flowing inside the second gas piping 92 is interposed in the second gas piping 92. Also, a variable flow valve 98B configured to adjust a flow rate of the gas flowing inside the third gas piping 93 is interposed in the third gas piping 93. Further, filters 96C, 97C, 98C configured to remove foreign objects are interposed in the first gas piping 91, the second gas piping 92, and the third gas piping 93, respectively.

[0217] As the organic solvent discharged from the fourth moving nozzle 14, the same organic solvent as the organic solvent discharged from the third tube 33 according to the first

preferred embodiment (see FIG. 2) can be cited. As the gas discharged from the fourth moving nozzle 14, the same gas as the gas discharged from the second tube 32 according to the first preferred embodiment (see FIG. 2) can be cited.

5 [0218] Also, with the processing unit 2P according to the second preferred embodiment, an upper rinse liquid piping 43 that guides a rinse liquid is connected to the third moving nozzle 10. When an upper rinse liquid valve 53 interposed in the upper rinse liquid piping 43 is opened, the rinse liquid
10 is discharged continuously downward from the discharge port of the third moving nozzle 10.

[0219] The upper rinse liquid valve 53, the first gas valve 96A, the second gas valve 97A, the third gas valve 98A, the mass flow controller 96B, the variable flow valve 97B, the
15 variable flow valve 98B, and the fourth nozzle moving unit 35 are controlled by the controller 3 (see FIG. 3).

[0220] The same substrate processing as that by the substrate processing apparatus 1 according to the first preferred embodiment is enabled by using the substrate
20 processing apparatus 1P according to the second preferred embodiment. However, in the first rinsing step (step S3) and the second rinsing step (step S9), the rinse liquid is supplied from the third moving nozzle 10 to the upper surface of the substrate W.

25 [0221] Details of the (A) low solubility substance, the

(B) peeling liquid forming substance, the (C) solvent, and the (D) high solubility substance inside the processing liquid and details of the (F) peeling liquid forming liquid shall now be described.

5 [0222] <Processing Liquid>

[0223] As described above, by the processing liquid being dried on the substrate W and the (C) solvent being removed, the (A) low solubility substance is formed into a film. That is, the processing film 100 is formed. The (B) peeling liquid
10 forming substance and/or the (D) high solubility substance is or are not removed together with the (C) solvent and is or are left in the processing film 100. "Solidification" and "curing" are both a mode of "film formation." Also, the processing film 100 obtained from the processing liquid suffices to have a
15 hardness of a degree enabling holding of the particles (the removal objects 103) and the (C) solvent is not required to be removed completely (for example, by vaporization). The processing liquid becomes the processing film while contracting gradually in accompaniment with volatilization of
20 the (C) solvent. By "not removed together with the (C) solvent," it is meant that removal (e.g. evaporation or volatilization) of a very small amount with respect to the entirety is permissible. For example, removal of 0 ~ 10 mass % with respect to an original amount is permissible.

25 [0224] As described above, the processing film 100 holds

the particles 103 on the substrate W and is removed by being peeled by the (F) peeling liquid forming liquid. If the (B) peeling liquid forming substance remains in the processing film 100, the (B) peeling liquid forming substance is eluted into the (F) peeling liquid forming liquid by the (F) peeling liquid forming liquid being supplied to the substrate W. It is considered that thereby, the pH of the (F) peeling liquid forming liquid increases and the peeling liquid is formed (prepared). The (F) peeling liquid forming liquid is thus not required to be an alkaline solution, such as ammonia water, and it is also considered that when the (B) peeling liquid forming substance and/or the (D) high solubility substance remain or remains in the film, portions that set off the peeling of the processing film 100 are formed.

[0225] <Low Solubility Substance>

[0226] The (A) low solubility substance contains at least one of novolac, polyhydroxystyrene, polystyrene, a polyacrylic acid derivative, a polymaleic acid derivative, polycarbonate, a polyvinyl alcohol derivative, a polymethacrylic acid derivative, and a copolymer of a combination of the above. Preferably, the (A) low solubility substance contains at least one of novolac, polyhydroxystyrene, a polyacrylic acid derivative, polycarbonate, a polymethacrylic acid derivative, and a copolymer of a combination of the above. More preferably, the (A) low

solubility substance contains at least one of novolac, polyhydroxystyrene, polycarbonate and a copolymer of a combination of the above. Novolac may be phenol novolac.

[0227] Obviously, the processing liquid according to the present invention may contain one or a combination of two or more of the above-described preferable examples as the (A) low solubility substance. For example, the (A) low solubility substance may contain both novolac and polyhydroxystyrene.

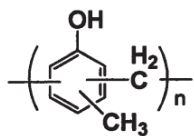
[0228] In a preferred mode, the (A) low solubility substance is formed into a film by being dried, and the film is peeled while still holding the particles and without being largely dissolved in the (F) peeling liquid forming liquid (which may contain the dissolved (B) peeling liquid forming substance) to be described below. A mode where a very small portion of the (A) low solubility substance is dissolved by the (F) peeling liquid forming liquid is permissible.

[0229] Preferably, the (A) low solubility substance does not contain fluorine and/or silicon and more preferably it contains neither element.

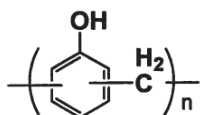
[0230] Preferably, the copolymerization is random copolymerization or block copolymerization.

[0231] Although not intended to restrict the present invention, the compounds expressed by the following Chemical Formulae 1 to 7 can be cited as specific examples of the (A) low solubility substance.

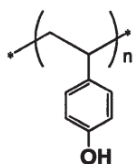
[0232] [Chemical Formula 1]



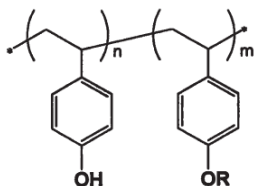
[0233] [Chemical Formula 2]



5 [0234] [Chemical Formula 3]

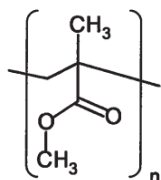


[0235] [Chemical Formula 4]

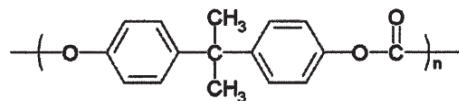


(Here, R signifies a substituent, such as a C₁₋₄ alkyl, etc.)

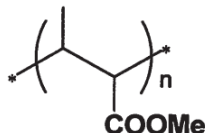
10 [0236] [Chemical Formula 5]



[0237] [Chemical Formula 6]



[0238] [Chemical Formula 7]



[0239] A weight average molecular weight (Mw) of the (A)
 5 low solubility substance is preferably 150 ~ 500,000.

[0240] The (A) low solubility substance can be obtained
 by synthesis. It can also be purchased. In the case of
 purchase, the following can be cited as examples of suppliers.
 The (A) low solubility substance can also be synthesized by
 10 a supplier such as to exhibit the effects of the present
 invention.

Novolac: Showa Kasei Kogyo Co., Ltd., Asahi Yukizai Corp.,
 Gunee Chemical Industry Co., Ltd., Sumitomo Bakelite Co., Ltd.
 Polyhydroxystyrene: Nippon Soda Co., Ltd., Maruzen
 15 Petrochemical Co., Ltd., Toho Chemical Industry Co., Ltd.
 Polyacrylic acid derivative: Nippon Shokubai Co., Ltd.
 Polycarbonate: Sigma-Aldrich

Polymethacrylic acid derivative: Sigma-Aldrich
 [0241] As a mode of the present invention, the amount of
 20 the (A) low solubility substance is 0.1 ~ 50 mass % in comparison
 to a total mass of the processing liquid. In other words, on

basis of the total mass of the processing liquid as 100 mass %, the amount of the (A) low solubility substance is 0.1 ~ 50 mass %. That is, "in comparison to" can be reworded as "on basis of." The same applies in the present Specification, unless mentioned
 5 otherwise.

[0242] <Peeling Liquid Forming Substance>

[0243] The (B) peeling liquid forming substance contains at least one of a primary amine, a secondary amine, a tertiary amine, and a quaternary ammonium salt (preferably at least one
 10 of a primary amine, a secondary amine, and a tertiary amine), and the (B) peeling liquid forming substance contains a hydrocarbon. As a preferred mode, the (B) peeling liquid forming substance remains in the processing film 100 formed from the processing liquid, and the (B) peeling liquid forming
 15 substance is eluted into the (F) peeling liquid forming liquid when the peeling liquid peels the processing film 100. For this to take place, a boiling point at one atmospheric pressure of the alkaline component in the (B) is preferably 20 ~ 400°C.

[0244] Although not intended to restrict the type of the
 20 peeling liquid forming substance, N-benzylethanolamine, diethanolamine, monoethanolamine, 2-(2-aminoethylamino)ethanol, 4,4'-diaminodiphenylmethane, 2-(butylamino)ethanol, 2-anilinoethanol, triethanolamine, ethylenediamine, diethylenetriamine,
 25 tris(2-aminoethyl)amine, and

tris[2-(dimethylamino)ethyl]amine can be cited as preferable examples of (B).

[0245] Although not intended to restrict the type of the peeling liquid forming substance,
5 N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine and N,N,N',N'-tetraethylethylenediamine can be cited as preferable examples of (B).

[0246] Although not intended to restrict the type of the peeling liquid forming substance,
10 1,4-diazabicyclo[2.2.2]octane and hexamethylenetetramine can be cited as specific examples of (B) having a cage type three-dimensional structure. Although not intended to restrict the present invention,
1,4,7,10-tetraazacyclododecane and
15 1,4,7,10,13,16-hexaazacyclooctadecane can be cited as specific examples of (B) having a planar cyclic structure.

[0247] Obviously, the processing liquid according to the present invention may contain one or a combination of two or more of the above-described preferable examples as the (B)
20 peeling liquid forming substance. For example, the (B) peeling liquid forming substance may contain both N-benzylethanolamine and diethanolamine. Also, the (B) peeling liquid forming substance may contain both N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine and
25 1,4-diazabicyclo[2.2.2]octane.

[0248] A molecular weight of the (B) peeling liquid forming substance is preferably 50 ~ 500.

[0249] The (B) peeling liquid forming substance can be obtained by synthesis or by purchase. In the case of purchase,
5 the Sigma-Aldrich and Tokyo Chemical Industry Co., Ltd. can be cited as examples of suppliers.

[0250] As a mode of the present invention, the amount of the (B) peeling liquid forming substance is preferably 1 ~ 100 mass % in comparison to the mass of the (A) low solubility
10 substance inside the processing liquid.

[0251] <Solvent>

[0252] The (C) solvent preferably contains an organic solvent. The (C) solvent has volatility. Having volatility means that the solvent is higher in volatility than water. A
15 boiling point at one atmospheric pressure of the (C) solvent is preferably 50 ~ 200°C. It is permissible for the (C) solvent to contain a small amount of pure water. The amount of pure water contained in the (C) solvent is preferably not more than 30 mass % in comparison to the entire (C) solvent. Not
20 containing pure water (0 mass %) is also a preferred mode. The pure water is preferably DIW.

[0253] As a preferred mode of the present invention, components (including an additive) contained in the processing liquid dissolve in the (C) solvent. The processing liquid that
25 assumes this mode is considered to be satisfactory in embedding

performance or film uniformity.

[0254] As the organic solvent contained in the (C), an alcohol, such as isopropanol (IPA) , etc.; an ethylene glycol monoalkyl ether, such as ethylene glycol monomethyl ether, 5 ethylene glycol monoethyl ether, etc.; an ethylene glycol monoalkyl ether acetate, such as ethylene glycol monomethyl ether acetate, ethylene glycol monoethyl ether acetate, etc.; a propylene glycol monoalkyl ether, such as propylene glycol monomethyl ether (PGME), propylene glycol monoethyl ether 10 (PGEE), etc.; a propylene glycol monoalkyl ether acetate, such as propylene glycol monomethyl ether acetate (PGMEA), propylene glycol monoethyl ether acetate, etc.; a lactic acid ester, such as methyl lactate, ethyl lactate (EL), etc.; an aromatic hydrocarbon, such as toluene, xylene, etc.; a ketone, 15 such as methyl ethyl ketone, 2-heptanone, cyclohexanone, etc.; an amide, such as N,N-dimethylacetamide, N-methylpyrrolidone, etc.; or a lactone, such as γ -butyrolactone, etc., can be cited. These organic solvents can be used alone or two or more types can be mixed and used.

20 [0255] As a preferred mode, the organic solvent contained in the (C) solvent is selected from IPA, PGME, PGEE, EL, PGMEA, and any combination thereof. If the organic solvent is a combination of two types, a volume ratio thereof is preferably 20:80 ~ 80:20.

25 [0256] In comparison to the entire mass of the processing

liquid, the amount of the (C) solvent is 0.1 ~ 99.9 mass %.

[0257] <High Solubility Substance>

[0258] The (D) high solubility substance contains a hydrocarbon and further contains a hydroxy group (-OH) and/or
5 a carbonyl group (-C(=O)-). If the (D) high solubility substance is a polymer, one type of constituent unit contains a hydrocarbon in each unit and further contains a hydroxy group and/or a carbonyl group. As the carbonyl group, carboxylic acid (-COOH), aldehyde, ketone, ester, amide, and enone can
10 be cited, and carboxylic acid is preferable.

[0259] As described above, the (D) high solubility substance remains in the processing film formed on the substrate when the processing liquid is dried. In the peeling of the processing film by the (F) peeling liquid forming liquid,
15 the (D) high solubility substance gives rise to the portions that induce the peeling of the processing film. For this to take place, it is preferable for the (D) high solubility substance to be that which is higher in solubility in the (F) peeling liquid forming liquid than the (A) low solubility
20 substance is used.

[0260] As a mode of the (D) high solubility substance that contains ketone as the carbonyl group, a cyclic hydrocarbon can be cited. As specific examples, 1,2-cyclohexanedione and 1, 3-cyclohexanedione can be cited.

25 [0261] Although not intended to restrict the scope of the

claims, 2,2-bis(4-hydroxyphenyl)propane,
 2,2'-methylenebis(4-methylphenol),
 2,6-bis[(2-hydroxy-5-methylphenyl)methyl]-4-methylphenol,
 1,3-cyclohexanediol, 4,4'-dihydroxybiphenyl,
 5 2,6-naphthalenediol, 2,5-di-tert-butylhydroquinone, and
 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane can be cited as
 preferable examples of (D). These may be obtained by
 polymerization or condensation.

[0262] Although not intended to restrict the scope of the
 10 claims, 3,6-dimethyl-4-octyne-3,6-diol and
 2,5-dimethyl-3-hexyne-2,5-diol can be cited as preferable
 examples of (D). As other modes, 3-hexyne-2,5-diol,
 1,4-butyne-1,3-diol, 2,4-hexadiyne-1,6-diol, 1,4-butanediol,
 cis-1,4-dihydroxy-2-butene, and 1,4-benzenedimethanol can
 15 also be cited as preferable examples of (D).

[0263] Although not intended to restrict the scope of the
 claims, polymers of acrylic acid, maleic acid, or combinations
 thereof can be cited as preferable examples of the (D) polymer.
 Polyacrylic acids and maleic acid/acrylic acid copolymers are
 20 more preferable examples.

[0264] In the case of copolymerization, random
 copolymerization or block copolymerization is preferable, and
 random copolymerization is more preferable.

[0265] Obviously, the processing liquid may contain one
 25 or a combination of two or more of the above-described

preferable examples as the (D) high solubility substance. For example, the (D) high solubility substance may contain both 2,2-bis(4-hydroxyphenyl)propane and 3,6-dimethyl-4-octyne-3,6-diol.

5 [0266] A molecular weight of the (D) high solubility substance may be 80 ~ 10,000. If the (D) high solubility substance is a resin, a polymeride, or a polymer, the molecular weight is expressed by the weight average molecular weight (Mw) .

10 [0267] The (D) high solubility substance can be obtained by synthesis or purchase. As suppliers, Sigma-Aldrich, Tokyo Chemical Industry Co., Ltd., and Nippon Shokubai Co., Ltd. can be cited.

[0268] As a mode of the present invention, the amount of 15 the (D) high solubility substance is preferably 1 ~ 100 mass % in comparison to the mass of the (A) low solubility substance inside the processing liquid.

[0269] <Other Additive>

[0270] The processing liquid of the present invention may 20 further contain (E) another additive. The (E) other additive may include a surfactant, an antibacterial agent, a bactericide, an antiseptic, an antifungal agent, or a base (a surfactant is preferable) or may include a combination of any of the above.

[0271] The amount of the (E) other additive (the sum amount 25 in the case of a plurality of additives) is preferably 0 ~ 10

mass % in comparison to the mass of the (A) low solubility substance inside the processing liquid. The processing liquid does not have to contain (E) another additive (0 mass %).

[0272] <Peeling Liquid Forming Liquid>

5 [0273] As described above, the processing liquid supplied to the substrate W is dried and by the (C) solvent thereby being removed, the (A) low solubility substance is formed into a film. That is, the processing film is formed. The (B) peeling liquid forming substance and/or the (D) high solubility substance
10 remain or remains in the processing film without being removed together with the (C) solvent. The processing film is capable of holding the particles present on the substrate and is removed by the (F) peeling liquid forming liquid while still holding the particles.

15 [0274] Here, the (F) peeling liquid forming liquid is preferably neutral or weakly acidic. The (F) peeling liquid forming liquid is preferably 4 ~ 7 in pH, more preferably 5 ~ 7 in pH, and even more preferably 6 ~ 7 in pH. For measurement of the pH, performing measurement upon degassing is preferable
20 to avoid influences due to dissolution of carbon dioxide in air.

[0275] Preferably, the (F) peeling liquid forming liquid contains pure water. As described above, the processing liquid of the present invention contains the (B) peeling liquid
25 forming substance by which the peeling liquid is formed

(prepared) through elution into the (F) peeling liquid forming liquid and increasing the pH of the (F) peeling liquid forming liquid. A large portion of the (F) peeling liquid forming liquid may thus be pure water. In comparison to a total mass
5 of the (F) peeling liquid forming liquid, the amount of pure water contained in the (F) is preferably 80 ~ 100 mass %, more preferably 90 ~ 100 mass %, even more preferably 95 ~ 100 mass %, and yet even more preferably 99 ~ 100 mass %. A mode where the (F) peeling liquid forming liquid is constituted of just
10 pure water (100 mass %) is also preferable.

[0276] When the processing liquid is constituted of the (A) low solubility substance, the (B) peeling liquid forming substance, and the (C) solvent, conditions of forming of the processing film and conditions of peeling of the processing
15 film from a substrate can also be described as follows.

[0277] By the processing liquid being dropped and dried on the substrate W to which the particles are attached, the low solubility substance (polymer) is formed into the film. By the low solubility substance being formed into the film,
20 the processing film is formed. The peeling liquid forming substance (alkaline component) remains in the processing film. Thereafter, the peeling liquid forming liquid is supplied to the processing film and the alkaline component becomes eluted into the peeling liquid forming liquid. It is considered that
25 by the elution of the alkaline component, the pH of the peeling

liquid forming liquid in the vicinity of the processing film increases and the peeling liquid that peels the processing film from the substrate W is formed (prepared). By the alkaline component being eluted, marks (void holes) resulting from the elution of the alkaline component are formed in the processing film. It is considered that by the elution of the alkaline component, a pH of the peeling liquid in the vicinity of the processing film is increased and an effect of peeling the processing film is improved. Further, the marks formed by the elution of the alkaline component induce the peeling of the processing film and cracks spread with these as the starting points. The processing film that is split by the spreading of the cracks is removed from the substrate while still holding the particles.

[0278] When the processing liquid is constituted of the (A) low solubility substance, the (B) peeling liquid forming substance, the (C) solvent, and the (D) high solubility substance, conditions of forming of the processing film and conditions of peeling of the processing film from a substrate can also be described as follows.

[0279] By the processing liquid being dropped and dried on the substrate W to which the particles are attached, the low solubility substance (polymer) is formed into the film. By the low solubility substance being formed into the film, the processing film is formed. The peeling liquid forming

substance (alkaline component) remains in the processing film. Thereafter, the peeling liquid forming liquid is supplied to the processing film and the alkaline component becomes eluted into the peeling liquid forming liquid. It is considered that
5 by the elution of the alkaline component, the pH of the peeling liquid forming liquid in the vicinity of the processing film increases and the peeling liquid that peels the processing film from the substrate W is formed (prepared). Also, the high solubility substance (crack promoting component) remains in
10 the processing film. The crack promoting component becomes eluted into the peeling liquid forming liquid/peeling liquid and marks (void holes) resulting from the elution of the crack promoting component are formed in the processing film. The marks formed by the elution of the crack promoting component
15 induce the peeling of the processing film and cracks spread with these as the starting points. The processing film that is split by the spreading of the cracks is removed from the substrate W while still holding the particles.

[0280] It is considered that, in the removal (peeling) of
20 the processing film (particle holding layer) by the (F) peeling liquid forming liquid, the (B) peeling liquid forming substance and/or the (D) high solubility substance that remain or remains in the processing film give or gives rise to the portions that induce the peeling of the film. It is thus preferable for the
25 (B) peeling liquid forming substance and the (D) high

solubility substance to be those that are higher in solubility in the (F) peeling liquid forming liquid than the (A) low solubility substance. The solubility can be evaluated by a known method. For example, the solubility can be determined
5 by checking that the (A) or (B) described above is dissolved by adding the (A) or (B) at 100 ppm to pure water in a flask and then capping and shaking the flask for 3 hours by a shaker under conditions of 20 ~ 35°C (more preferably 25±2°C). For the evaluation of solubility, the pure water may be changed
10 to an alkaline liquid (for example, ammonia water of 5.0 mass %).

[0281] A preferred mode of the present invention is that the processing film is removed from the substrate while still holding the particles and without being completely dissolved
15 by the (F) peeling liquid forming liquid. It is considered that the processing film is removed, for example, upon being put in a state of being cut finely by the "portions that induce the peeling."

[0282] The present invention shall now be described by way
20 of various examples. The processing liquid and the peeling liquid forming liquid are not restricted to just these examples.

[0283] Preparation of Patterned Substrate

[0284] A KrF resist composition (AZ DX-6270P, Merck
25 Performance Materials Ltd., hereinafter referred to as "MPM

Ltd.") is dropped onto an 8-inch Si substrate and spin-coated on the substrate at 1500 rpm. The substrate is soft-baked at 120°C for 90 seconds. The substrate is then exposed at 20 mJ/cm² using a KrF stepper (FPA-3000 EX5, Canon) and subject
5 to PEB (post exposure baking) at 130°C for 90 seconds and developed with a developing fluid (AZ MIF-300, MPM Ltd.). A line/space resist pattern having a pitch of 360 nm and a duty ratio of 1:1 is thereby obtained. The resist pattern is used as an etching mask to etch the substrate with a dry etching
10 apparatus (NE-5000N, ULVAC). Thereafter, the substrate is cleaned with a stripper (AZ 400T, MPM Ltd.) to peel the resist pattern and a resist residue. A patterned substrate having a pattern with a pitch of 360 nm, a duty ratio of 1:1, and a line height of 150 nm is thereby prepared.

15 [0285] Preparation of Bare Substrate

[0286] An 8-inch Si substrate is used.

[0287] Preparation of Evaluation Substrate

[0288] Particles are attached to the patterned substrate and the bare substrate described above. As experimental
20 particles, ultra-high purity colloidal silica (PL-10H, Fuso Chemical Co., Ltd., average primary particle diameter: 90 nm) is used. 50 mL of a silica microparticle composition is dropped and rotation at 500 rpm is performed for 5 seconds to perform coating. Thereafter, rotation at 1000 rpm is
25 performed for 30 seconds to spin-dry a solvent of the silica

microparticle composition. An evaluation substrate is thereby obtained.

[0289] Comparison Test of Presence/Non-Presence of Respective Components in Processing Liquid

5 [0290] 5 g of novolac (Mw: approximately 5,000; the (A) low solubility substance) is added to 95 g of isopropanol (the (C) solvent). The mixture is stirred with a stirrer for 1 hour and a liquid with which the concentration of the (A) low solubility substance is 5 mass % is obtained. 2.5 g each of
10 diethanolamine (the (B) peeling liquid forming substance) and 3,6-dimethyl-4-octyne-3,6-diol (Tokyo Chemical Industry Co., Ltd., hereinafter referred to as "TCI Co., Ltd."; the (D) high solubility substance) are added to the liquid. The mixture is stirred with a stirrer for 1 hour. The liquid is then
15 filtered with Optimizer UPE (Nihon Entegris G.K.). A processing liquid containing the (A), the (B), and the (D) is thereby obtained.

A processing liquid containing the (A) and the (B) is obtained by performing the same with the exception of not adding
20 the (D) component.

A processing liquid containing the (A) and the (D) is obtained by performing the same with the exception of not adding the (B) component.

A processing liquid containing the (B) and the (D) is
25 obtained by performing the same with the exception of not adding

the (A) component.

[0291] Using Coater-Developer RF3 (Sokudo Co., Ltd.), 10 cc of the respective processing liquids are dropped onto the respective evaluation substrates and rotation at 1,500 rpm is performed for 60 seconds to perform coating and drying. While rotating each substrate at 100 rpm, DIW is dropped for 10 seconds to cover the entire substrate with DIW and this state is kept for 20 seconds. The substrate is dried by rotating the substrate at 1,500 rpm. If a film is present, the film is peeled and removed by the rotation.

[0292] Residual particle amounts of the substrates are compared. A bright field defect inspection apparatus (UVision 4, AMAT Ltd.) is used to evaluate the patterned substrates and a dark field defect inspection apparatus (LS-9110, Hitachi High-Technologies Corporation) is used to evaluate the bare substrates.

[0293] Preparation Example 1 of Cleaning Liquid 1

[0294] 5 g of novolac (Mw: approximately 5,000; the (A) low solubility substance) are added to 95 g of isopropanol (the (C) solvent). The mixture is stirred with a stirrer for 1 hour and a liquid with which the concentration of the (A) low solubility substance is 5 mass % is obtained. 2.5 g each of N-benzylethanolamine (TCI Co., Ltd.; the (B) peeling liquid forming substance) and 2,2-bis(4-hydroxyphenyl)propane (TCI Co., Ltd.; the (D) high solubility substance) are added to the

liquid. The mixture is stirred with a stirrer for 1 hour. The liquid is then filtered with Optimizer UPE (Nihon Entegris G.K.). A cleaning liquid 1 is thereby obtained. Results thereof are indicated in Table 1.

5 [0295] In Tables 1 to 3 below, the novolac is abbreviated as A1, N-benzylethanolamine is abbreviated as B1, isopropanol is abbreviated as IPA, and 2,2-bis(4-hydroxyphenyl)propane is abbreviated as D1. Also, the numerals in parentheses in the (A) column each signify the concentration (mass %) when the (A) low solubility substance is added to the (C) solvent. The
10 numerals in parentheses in the (B) column each signify the concentration (mass %) in comparison to the (A) low solubility substance when the (B) peeling liquid forming substance is added to the corresponding liquid. The numerals in
15 parentheses in the (D) column each signify the concentration (mass %) in comparison to the (A) low solubility substance when the (D) high solubility substance is added to the corresponding liquid.

[0296] [Table 1]

Table 1

	(A)	(B)	(D)	(C) Solvent	Removal evaluation Patterned substrate	Removal evaluation Bare substrate
Cleaning liquid 1	A1 (5%)	B1 (1%)	D1 (1%)	IPA	A	A
Cleaning liquid 2	A1 (5%)	B1 (10%)	D1 (1%)	IPA	AA	AA
Cleaning liquid 3	A1 (5%)	B1 (50%)	D1 (1%)	IPA	AA	AA

Cleaning liquid 4	A1 (5%)	B1 (100%)	D1 (1%)	IPA	A	AA
Cleaning liquid 5	A1 (5%)	B1 (1%)	D1 (10%)	IPA	AA	A
Cleaning liquid 6	A1 (5%)	B1 (10%)	D1 (10%)	IPA	AA	AA
Cleaning liquid 7	A1 (5%)	B1 (50%)	D1 (10%)	IPA	AA	AA
Cleaning liquid 8	A1 (5%)	B1 (100%)	D1 (10%)	IPA	A	A
Cleaning liquid 9	A1 (5%)	B1 (1%)	D1 (50%)	IPA	A	AA
Cleaning liquid 10	A1 (5%)	B1 (10%)	D1 (50%)	IPA	A	AA

[0297] [Table 2]

Table 2

	(A)	(B)	(D)	(C) Solvent	Removal evaluation Patterned substrate	Removal evaluation Bare substrate
Cleaning liquid 11	A2 (5%)	B2 (50%)	D2 (50%)	PGEE	AA	AA
Cleaning liquid 12	A3 (5%)	B2 (50%)	D2 (50%)	PGEE	AA	AA
Cleaning liquid 13	A4 (5%)	B2 (50%)	D2 (50%)	PGEE	AA	AA
Cleaning liquid 14	A5 (5%)	B2 (50%)	D2 (50%)	PGEE	AA	AA
Cleaning liquid 15	A6 (5%)	B2 (50%)	D2 (50%)	PGEE	A	AA
Cleaning liquid 16	A7 (5%)	B2 (50%)	D2 (50%)	PGEE	AA	AA
Cleaning liquid 17	A8 (5%)	B2 (50%)	D2 (50%)	PGEE	AA	AA
Cleaning liquid 18	A9 (5%)	B2 (50%)	D2 (50%)	PGEE	A	AA

[0298] [Table 3]

Table 3

	(A)	(B)	(D)	(C) Solvent	Removal evaluation Patterned substrate	Removal evaluation Bare substrate
Cleaning liquid 19	A10 (5%)	B2 (50%)	D3 (50%)	EL	AA	AA
Cleaning liquid 20	A10 (5%)	B2 (50%)	D4 (50%)	EL	AA	AA
Cleaning liquid 21	A10 (5%)	B2 (50%)	D5 (50%)	EL	AA	AA

Cleaning liquid 22	A10 (5%)	B3 (50%)	D2 (50%)	EL	AA	AA
Cleaning liquid 23	A10 (5%)	B4 (50%)	D2 (50%)	EL	AA	AA
Cleaning liquid 24	A10 (5%)	B5 (50%)	D2 (50%)	EL	AA	AA
Cleaning liquid 25	A10 (5%)	B6 (50%)	D2 (50%)	EL	AA	AA
Cleaning liquid 26	A10 (5%)	B7 (50%)	D2 (50%)	EL	AA	AA
Cleaning liquid 27	A10 (5%)	B8 (50%)	D2 (50%)	EL	AA	AA

[0299] The following abbreviations are used in Table 1 to Table 3 above.

Phenol novolac (Mw: approximately 10,000) is abbreviated as A2,

5 phenol novolac (Mw: approximately 100,000) is abbreviated as A3,

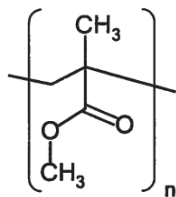
polyhydroxystyrene (Mw: approximately 1,000) is abbreviated as A4,

polyhydroxystyrene (Mw: approximately 10,000) is abbreviated
10 as A5,

polyhydroxystyrene (Mw: approximately 100,000) is abbreviated as A6,

a polyacrylic acid derivative (Mw: approximately 1,000) having the structure shown in Chemical Formula 8 below is abbreviated
15 as A7,

[Chemical Formula 8]



a polyacrylic acid derivative (Mw: approximately 10,000) having the same repeating unit as the above is abbreviated as A8,

5 a polyacrylic acid derivative (Mw: approximately 100,000) having the same repeating unit as the above is abbreviated as A9,

polymethyl methacrylate (Mw: approximately 5,000) is abbreviated as A10,

10 diethanolamine is abbreviated as B2,

monoethanolamine is abbreviated as B3,

2-(2-aminoethylamino)ethanol is abbreviated as B4,

4,4'-diaminophenylmethane is abbreviated as B5,

1,4-diazabicyclo[2.2.2]octane is abbreviated as B6,

15 hexamethylenetetramine is abbreviated as B7,

2-(butylamino)ethanol is abbreviated as B8,

3,6-dimethyl-4-octyne-3,6-diol is abbreviated as D2,

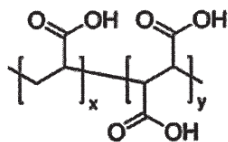
polyacrylic acid (Mw: approximately 1,000) is abbreviated as D3,

20 polyacrylic acid (Mw: approximately 10,000) is abbreviated as D4, and

a maleic acid/acrylic acid copolymer (Mw: approximately 3,000)

having the Chemical Formula 9 below is abbreviated as D5.

[Chemical Formula 9]



[0300] Preparation Examples 1 to 27 of Cleaning Liquids

5 1 to 27

[0301] The cleaning liquids 2 to 27 are prepared in the same manner as the preparation example 1 with the exceptions of using the substances indicated in Table 1 to Table 3 as the (A) low solubility substances, the (B) peeling liquid forming substances, the (C) solvents, and the (D) high solubility substances and preparing the liquids such as to achieve the concentrations indicated in Table 1 to Table 3.

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[0302] Evaluation of Residual Particle Amounts of Cleaning Liquids 1 to 27

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[0303] Evaluation substrates prepared as described in the above description of preparation of evaluation substrates are used.

[0304] Using Coater-Developer RF3 (Sokudo Co., Ltd.), 10 cc of the respective processing liquids are dropped onto the respective evaluation substrates and rotation at 1,500 rpm is performed for 60 seconds to perform coating and drying. While rotating each substrate at 100 rpm, DIW is dropped for 10 seconds to cover the entire substrate with DIW and this state

20

is kept for 20 seconds. The substrate is dried by rotating the substrate at 1,500 rpm. If a film is present, the film is peeled and removed by the rotation.

[0305] The residual particle amounts of the substrates are compared. The bright field defect inspection apparatus (UVision 4, AMAT Ltd.) is used to evaluate the patterned substrates and the dark field defect inspection apparatus (LS-9110, Hitachi High-Technologies Corporation) is used to evaluate the bare substrates.

10 [0306] Coating conditions and film removal conditions are checked and remaining numbers of particles are counted and evaluated according to the following criteria. The evaluation results are indicated in Table 1 to Table 3.

AA: ≤ 10 particles

15 A: > 10 particles and ≤ 100 particles

B: > 100 particles and $\leq 1,000$ particles

C: > 1000 particles

D: The film is not uniformly coated or the film is not removed.

[0307] Other Modifications

20 [0308] The present invention is not restricted to the preferred embodiments described above and can be implemented in yet other modes.

[0309] For example, unlike in the substrate processing in the preferred embodiments described above, the chemical liquid
25 supplying step (step S2), the first rinsing step (step S3),

and the first organic solvent supplying step (step S4) may be omitted.

[0310] Also, in the substrate processing in the preferred embodiments described above, the solvent of the processing liquid evaporates due to heating of the substrate W by the heating medium in the processing film forming step (step S6 and step S7). However, the heating of the substrate W is not restricted to that by the supply of the heating medium and may instead be performed, for example, by a heater, etc. (not shown) incorporated in the spin base 21 or the facing member 6. In this case, the heater functions as the substrate heating unit and the evaporating unit (evaporation promoting unit).

[0311] Also, in the substrate processing in the preferred embodiments described above, the second rinsing step (step S9) is executed after the peeling/removing step (step S8). However, it is also possible to omit the second rinsing step.

[0312] In detail, if pure water is used as the peeling liquid forming liquid in the peeling/removing step and the processing film 100 is expelled outside the substrate W by the pure water as the peeling liquid forming liquid, there is no need to wash away the peeling liquid forming liquid and therefore, the second rinsing step can be omitted. There is also no need to execute the second rinsing step if the peeling liquid forming liquid supplied to the substrate W in the peeling/removing step and the organic solvent (residue removing liquid) supplied to

the substrate W in the second organic solvent supplying step (step S10) executed after the second rinsing step have compatibility.

[0313] Also, the heating of the substrate W does not
5 necessarily have to be performed to form the processing film 100. That is, if the solvent volatilizes sufficiently in the film thinning step (step S6), the subsequent heating step (step S7) does not have to be executed. In particular, if remaining of the solvent in the interior of the processing film 100 is
10 permissible, the solvent can readily be evaporated to a desired degree even if the substrate W is not heated.

[0314] While preferred embodiments of the present invention have been described above, it is to be understood that variations and modifications will be apparent to those
15 skilled in the art without departing from the scope and spirit of the present invention. The scope of the present invention, therefore, is to be determined solely by the following claims.

WHAT IS CLAIMED is:

1. A substrate processing method comprising:

a processing liquid supplying step of supplying a processing liquid having a solute and a solvent to a surface
5 of a substrate (W);

a processing film forming step of solidifying or curing the processing liquid supplied to the surface of the substrate (W) to form, on the surface of the substrate (W), a processing film (100) that holds a removal object (103) present on the
10 surface of the substrate (W);

a peeling step of supplying a peeling liquid forming liquid to the surface of the substrate (W) to put the peeling liquid forming liquid in contact with the processing film (100) and form a peeling liquid and peeling the processing film (100),
15 in the state of holding the removal object (103), from the surface of the substrate (W) by the peeling liquid; and

a removing step of continuing the supply of the peeling liquid forming liquid, after the peeling of the processing film, (100) to wash away and remove the processing film (100) from
20 the surface of the substrate (W) in the state where the removal object (103) is held by the processing film (100).

2. The substrate processing method according to Claim 1, wherein the solute has a peeling liquid forming substance,

25 the processing film forming step includes a step of

forming the processing film (100) having the peeling liquid forming substance (112) in a solid state, and

the peeling step includes a step of dissolving the peeling liquid forming substance (112) that is in the solid state inside the processing film (100) in the peeling liquid forming liquid supplied to the surface of the substrate (W) to form the peeling liquid.

3. The substrate processing method according to Claim 1 or 2, wherein the peeling liquid is an alkaline liquid.

4. The substrate processing method according to any one of Claims 1 to 3, wherein the peeling liquid forming liquid is pure water.

5. The substrate processing method according to any one of Claims 1 to 4, wherein the peeling step includes a penetrating hole forming step of supplying the peeling liquid forming liquid to the surface of the substrate (W) to dissolve the processing film (100) partially and form a penetrating hole (102) in the processing film (100).

6. The substrate processing method according to Claim 5, wherein the solute has a high solubility substance and a low solubility substance that is lower in solubility in the peeling

liquid than the high solubility substance,

the processing film forming step includes a step of forming the processing film (100) having the high solubility substance (110) and the low solubility substance (111) in solid states, and

the penetrating hole forming step includes a step of dissolving the high solubility substance (110) that is in the solid state inside the processing film (100) in the peeling liquid formed on the substrate (W) to form the penetrating hole (102) in the processing film (100).

7. The substrate processing method according to Claim 6, wherein a solubility of the low solubility substance in the peeling liquid forming liquid is lower than a solubility of the high solubility substance in the peeling liquid forming liquid, and

the penetrating hole forming step includes a step of dissolving the high solubility substance (110) that is in the solid state inside the processing film (100) in the peeling liquid forming liquid supplied to the surface of the substrate (W) to form the penetrating hole (102) in the processing film (100).

8. The substrate processing method according to Claim 5, wherein the solute has a high solubility substance and a low

solubility substance that is lower in solubility in the peeling liquid forming liquid than the high solubility substance,

the processing film forming step includes a step of forming the processing film (100) having the high solubility substance (110) and the low solubility substance (111) in solid states, and

the penetrating hole forming step includes a step of dissolving the high solubility substance (110) that is in the solid state inside the processing film (100) in the peeling liquid forming liquid supplied to the surface of the substrate (W) to form the penetrating hole (102) in the processing film (100).

9. A substrate processing method comprising:

a processing liquid supplying step of supplying a processing liquid having a solute that contains an alkaline component and a solvent toward a surface of a substrate (W);

a processing film forming step of solidifying or curing the processing liquid supplied to the surface of the substrate (W) to form, on the surface of the substrate (W), a processing film (100) that contains the alkaline component and holds a removal object (103) present on the surface of the substrate (W);

a peeling step of supplying pure water to the surface of the substrate (W) to put the pure water in contact with the

processing film (100) to elute the alkaline component from the processing film (100) into the pure water and form an alkaline aqueous solution, and peeling the processing film (100), in the state of holding the removal object (103), from the surface of the substrate (W) by the alkaline aqueous solution; and
5 a removing step of continuing the supply of the pure water, after the peeling of the processing film (100), to wash away and remove the processing film (100) from the surface of the substrate (W) in the state where the removal object (103) is
10 held by the processing film (100).

10. A substrate processing apparatus (1, 1P) comprising:
a processing liquid supplying unit (9) that supplies a processing liquid having a solute and a solvent to a surface
15 of a substrate (W);
a solid forming unit (23, 11, 12) that solidifies or cures the processing liquid;
a peeling liquid forming liquid supplying unit (10) that supplies a peeling liquid forming liquid to the surface of the
20 substrate; and
a controller (3) that controls the processing liquid supplying unit (9), the solid forming unit (23, 11, 12), and the peeling liquid forming liquid supplying unit (10),
wherein the controller (3) is programmed to execute a
25 processing liquid supplying step of supplying the processing

liquid from the processing liquid supplying unit (9) to the surface of the substrate (W), a processing film forming step of making the solid forming unit (23, 11, 12) solidify or cure the processing liquid supplied to the surface of the substrate (W) to form, on the surface of the substrate (W), a processing film (100) that holds a removal object (103) present on the surface of the substrate (W), a peeling step of supplying the peeling liquid forming liquid from the peeling liquid forming liquid supplying unit (10) to the surface of the substrate (W) to put the peeling liquid forming liquid in contact with the processing film (100) and form a peeling liquid, and peeling the processing film (100), in the state of holding the removal object (103), from the surface of the substrate (W) by the peeling liquid, and a removing step of continuing the supply of the peeling liquid forming liquid from the peeling liquid forming liquid supplying unit (10), after the peeling of the processing film (100), to remove the processing film (100) from the surface of the substrate (W) in the state where the removal object (103) is held by the processing film (100).

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11. The substrate processing apparatus (1, 1P) according to Claim 10, wherein the solute has a peeling liquid forming substance,

the processing film (100) having the peeling liquid forming substance (112) in a solid state is formed in the

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processing film forming step, and

in the peeling step, the peeling liquid forming liquid
supplied to the surface of the substrate (W) dissolves the
peeling liquid forming substance (112) in the solid state
5 inside the processing film (100) to form the peeling liquid.

12. The substrate processing apparatus (1, 1P) according to
Claim 10 or 11, wherein the peeling liquid is an alkaline
liquid.

10

13. The substrate processing apparatus (1, 1P) according to
any one of Claims 10 to 12, wherein the peeling liquid forming
liquid supplying unit (10) supplies pure water as the peeling
liquid forming liquid to the surface of the substrate (W).

15

14. The substrate processing apparatus (1, 1P) according to
any one of Claims 10 to 13, wherein, in the peeling step, the
peeling liquid forming liquid is supplied to the surface of
the substrate (W) to dissolve the processing film (100)
20 partially and form a penetrating hole (102) in the processing
film (100).

15. The substrate processing apparatus (1, 1P) according to
Claim 14, wherein the solute has a high solubility substance
25 and a low solubility substance that is lower in solubility in

the peeling liquid than the high solubility substance,

the processing film (100) having the high solubility substance (110) and the low solubility substance (111) in solid states is formed in the processing film forming step, and

5 in the peeling step, the peeling liquid formed on the substrate (W) dissolves the high solubility substance (110) in the solid state inside the processing film (100) to form the penetrating hole (102) in the processing film (100).

10 16. The substrate processing apparatus (1, 1P) according to Claim 15, wherein a solubility of the low solubility substance in the peeling liquid forming liquid is lower than a solubility of the high solubility substance in the peeling liquid forming liquid, and,

15 in the processing film forming step, the peeling liquid forming liquid, supplied to the surface of the substrate (W), dissolves the high solubility substance (110) in the solid state inside the processing film (100) to form the penetrating hole (102) in the processing film (100).

20

17. The substrate processing apparatus (1, 1P) according to Claim 14, wherein the solute has a high solubility substance and a low solubility substance that is lower in solubility in the peeling liquid forming liquid than the high solubility
25 substance,

the processing film having the high solubility substance (110) and the low solubility substance (111) in solid states is formed in the processing film forming step, and

5 in the peeling step, the peeling liquid forming liquid supplied to the surface of the substrate (W) dissolves the high solubility substance (110) in the solid state inside the processing film (100) to form the penetrating hole (102) in the processing film (100).

10 18. A substrate processing apparatus (1, 1P) comprising:
a processing liquid supplying unit (9) that supplies a processing liquid having a solute that contains an alkaline component and a solvent to a surface of a substrate (W);
a solid forming unit (23, 11, 12) that solidifies or cures
15 the processing liquid;
a pure water supplying unit (10) that supplies pure water to the surface of the substrate (W); and
a controller (3) that controls the processing liquid supplying unit (9), the solid forming unit (23, 11, 12), and
20 the pure water supplying unit (10),

wherein the controller (3) is programmed to execute a processing liquid supplying step of supplying the processing liquid from the processing liquid supplying unit (9) to the surface of the substrate (W), a processing film forming step
25 of making the solid forming unit (23, 11, 12) solidify or cure

the processing liquid supplied to the surface of the substrate (W) to form, on the surface of the substrate (W), a processing film (100) that contains the alkaline component and holds a removal object (103) present on the surface of the substrate (W), a peeling step of supplying the pure water from the pure water supplying unit (10) to the surface of the substrate (W) to put the pure water in contact with the processing film (100) to elute the alkaline component from the processing film (100) into the pure water and form an alkaline aqueous solution, and peeling the processing film (100), in the state of holding the removal object (103), from the surface of the substrate (W) by the alkaline aqueous solution, and a removing step of continuing the supply of the pure water from the pure water supplying unit (10), after the peeling of the processing film (100), to remove the processing film (100) from the surface of the substrate (W) in the state where the removal object (103) is held by the processing film (100).