

WHAT IS CLAIMED IS:

1. A substrate processing method comprising:

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

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

15 a peeling step of supplying a peeling liquid to the front surface of the substrate (W) to peel the processing film (100) from the front surface of the substrate (W) together with the removal object (103), wherein the peeling step includes a penetrating hole forming step of dissolving partially the processing film (100) in the peeling liquid to form a penetrating hole (102) on the processing film (100),

20 the solute of the processing liquid has a first component and a second component which is lower in solubility in the peeling liquid than the first component,

the processing film forming step includes a step of forming the processing film (100) which has a first solid (110) formed by the first component and a second solid (111) formed by the second component, and

25 the penetrating hole forming step includes a step of dissolving the first solid (110) by the peeling liquid to form the penetrating hole (102) on the processing film (100).

2. The substrate processing method according to Claim 1, wherein the peeling step includes a peeling liquid entry step of entering the

peeling liquid between the processing film (100) and the front surface of the substrate (W) via the penetrating hole (102).

3. ~~The substrate processing method according to Claim 1 or Claim~~
 5 ~~2, wherein the solute of the processing liquid has a first component~~
~~and a second component which is lower in solubility in the peeling liquid~~
~~than the first component,~~
~~the processing film forming step includes a step of forming the~~
~~processing film (100) which has a first solid (110) formed by the first~~
 10 ~~component and a second solid (111) formed by the second component, and~~
~~the penetrating hole forming step includes a step of dissolving~~
~~the first solid (110) by the peeling liquid to form the penetrating~~
~~hole (102) on the processing film (100).~~

15 34. The substrate processing method according to ~~Claim 3~~Claim 1 or
2, wherein the contained amount of the second component in the
 processing liquid is larger than the contained amount of the first
 component in the processing liquid.

20 45. The substrate processing method according to ~~Claim 3~~Claim 1 or
2, wherein the contained amount of the second component in the
 processing liquid is smaller than the contained amount of the first
 component in the processing liquid.

25 56. The substrate processing method according to any one of Claim
31 to Claim 45, wherein the solute further includes a third component
 higher in degree of solubility in the peeling liquid than the second
 component and lower in degree of solubility in the peeling liquid than
 the first component, and

the processing film forming step includes a step of forming the processing film (100) which has a third solid (112) formed by the third component at least at a portion adjacent to the front surface of the substrate (W).

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67. The substrate processing method according to any one of Claim 13 to Claim 45, further comprising: a preprocessing liquid supplying step of supplying to the front surface of the substrate (W) a preprocessing liquid which contains a solute having a third component higher in degree of solubility in the peeling liquid than the second component and lower in degree of solubility in the peeling liquid than the first component before supply of the processing liquid to the front surface of the substrate,

wherein the processing film forming step includes a step of forming the processing film (100) which has a third solid (112) formed by the third component at least at a portion adjacent to the front surface of the substrate (W).

78. The substrate processing method according to any one of Claim 31 to Claim 54, further comprising: a preprocessing liquid supplying step of supplying to the front surface of the substrate (W) a preprocessing liquid which contains a solute having a third component higher in degree of solubility in the peeling liquid than the second component and lower in degree of solubility in the peeling liquid than the first component before supply of the processing liquid to the front surface of the substrate (W); and

a preprocessing film forming step of solidifying or curing the preprocessing liquid before supply of the processing liquid to the front surface of the substrate (W) to form a preprocessing film (120) formed

by the third component on the front surface of the substrate (W),
 wherein the peeling step includes a step of supplying the peeling liquid
 to the front surface of the substrate (W) to peel the processing film
 (100) and the preprocessing film (120) from the front surface of the
 5 substrate (W) together with the removal object (103).

89. The substrate processing method according to any one of Claim
~~31~~ to Claim 87, wherein the second component contains at least any one
 of novolac, polyhydroxystyrene, polystyrene, a polyacrylic acid
 10 derivative, a polymaleic acid derivative, polycarbonate, a polyvinyl
 alcohol derivative, a polymethacrylic acid derivative and a copolymer
 of a combination thereof.

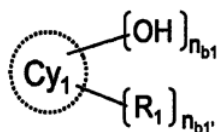
~~910~~. The substrate processing method according to any one of Claim
 15 ~~13~~ to Claim 89, wherein the first component is a crack promoting
 component, and

the crack promoting component contains hydrocarbon, and a
 hydroxy group and/or a carbonyl group.

20 ~~1011~~. The substrate processing method according to any one of Claim
~~31~~ to Claim ~~109~~, wherein the first component is expressed by at least
 any one of (B-1), (B-2) and (B-3) given below;

(B-1) is a compound which contains 1 to 6 of constituent units
 expressed by Chemical Formula 1 and in which each of the constituent
 25 units is bonded by a linking group L₁,

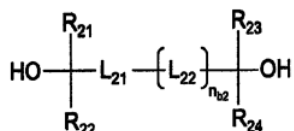
[Chemical Formula 1]



here, L_1 is selected at least from a single bond and any one of C_{1-6} alkylene, Cy_1 is a hydrocarbon ring of C_{5-30} , R_1 is each independently C_{1-5} alkyl, n_{b1} is 1, 2 or 3, and $n_{b1'}$ is 0, 1, 2, 3 or 4;

(B-2) is a compound expressed by Chemical Formula 2,

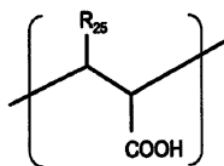
5 [Chemical Formula 2]



here, R_{21} , R_{22} , R_{23} and R_{24} are each independently hydrogen or C_{1-5} alkyl, L_{21} and L_{22} are each independently C_{1-20} alkylene, C_{1-20} cycloalkylene, C_{2-4} alkenylene, C_{2-4} alkynylene or C_{6-20} arylene, these
10 groups may be substituted by C_{1-5} alkyl or hydroxyl, and n_{b2} is 0, 1 or 2; and

(B-3) is a polymer which contains a constituent unit expressed by Chemical Formula 3 and has the weight average molecular weight (M_w) of 500 to 10,000,

15 [Chemical Formula 3]



R_{25} is -H -CH₃ or -COOH.

20 ~~1112~~. The substrate processing method according to any one of Claim ~~31~~ to Claim ~~1110~~, wherein the solubility of the second component in 5.0 mass % ammonia water is less than 100 ppm and the solubility of the first component in 5.0 mass % ammonia water is 100 ppm or more.

~~1213~~. The substrate processing method according to any one of Claim

31 to Claim ~~12~~11, wherein the mass of the second component is 0.1 to 50 mass %, as compared with an entire mass of the processing liquid.

13~~14~~. The substrate processing method according to any one of Claim 31 to Claim ~~13~~12, wherein the weight average molecular weight (Mw) of the second component is 150 to 500,000.

14~~15~~. The substrate processing method according to any one of Claim 13 to Claim ~~8~~7, wherein the first component and the second component are a synthetic resin.

15~~16~~. The substrate processing method according to any one of Claim 1 to Claim ~~15~~14, wherein the processing liquid supplying step includes a liquid film forming step of forming a liquid film (101) of the processing liquid on the front surface of the substrate (W) held horizontally, and

the method further comprises a film thinning step of rotating the substrate (W) around a vertical axis (A1) passing through a central portion of the substrate (W) to eliminate the processing liquid from the front surface of the substrate (W) and to thin the liquid film (101).

16~~17~~. The substrate processing method according to any one of Claim 1 to Claim ~~16~~15, wherein the processing film forming step includes a step of forming the processing film (100) in which the solvent remains in the interior of the processing film (100).

17~~18~~. The substrate processing method according to any one of Claim 1 to Claim 16~~17~~, wherein the processing film forming step includes a solvent evaporating step of evaporating the solvent from the processing

liquid supplied to the front surface of the substrate (W).

1819. A substrate processing apparatus (1, 1P or 1Q) comprising:

5 a processing liquid supplying unit (9) which supplies a processing liquid which has a solute and a solvent to a front surface of a substrate (W);

a solid forming unit (11, 12 or 23) which solidifies or cures the processing liquid;

10 a peeling liquid supplying unit (10) which supplies a peeling liquid to the front surface of the substrate; and

a controller (3) which controls the processing liquid supplying unit (9), the solid forming unit (11, 12 or 23) and the peeling liquid supplying unit (10);

15 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 front surface of the substrate (W), a processing film forming step of solidifying or curing the processing liquid supplied to the front surface of the substrate (W) by using the solid forming unit (11, 12 or 23), thereby forming on the front surface
20 of the substrate (W) a processing film (100) which holds a removal object (103) present on the front surface of the substrate (W), and a peeling step of supplying the peeling liquid from the peeling liquid supplying unit (10) to the front surface of the substrate (W) to peel the processing film (100) and also programmed to execute, in the peeling step, a
25 penetrating hole forming step of partially dissolving the processing film (100) in the peeling liquid to form a penetrating hole (102) on the processing film (100),

wherein the solute of the processing liquid has a first component and a second component which is lower in solubility in the peeling liquid

than the first component, and

the controller (3) is programmed to form the processing film which contains a first solid (110) formed by the first component and a second solid (111) formed by the second component in the processing film forming step and also to form the penetrating hole (102) on the processing film (100) by dissolving the first solid (110) by the peeling liquid in the penetrating hole forming step.

~~1920.~~ The substrate processing apparatus (1, 1P or 1Q) according to Claim ~~18~~¹⁹, wherein the controller (3) is programmed to enter the peeling liquid between the processing film (100) and the front surface of the substrate (W) via the penetrating hole (102) in the peeling step.

~~21. The substrate processing apparatus (1, 1P or 1Q) according to Claim 19 or Claim 20, wherein the solute of the processing liquid has a first component and a second component which is lower in solubility in the peeling liquid than the first component, and~~

~~the controller (3) is programmed to form the processing film (100) which contains a first solid (110) formed by the first component and a second solid (111) formed by the second component in the processing film forming step and also to form the penetrating hole (102) on the processing film (100) by dissolving the first solid (110) by the peeling liquid in the penetrating hole forming step.~~

~~2022.~~ The substrate processing apparatus (1, 1P or 1Q) according to Claim ~~21~~^{18 or 19}, wherein the contained amount of the second component in the processing liquid is larger than the contained amount of the first component in the processing liquid.

2123. The substrate processing apparatus (1,1P or 1Q) according to ~~Claim 21~~ Claim 18 or 19, wherein the contained amount of the second component in the processing liquid is smaller than the contained amount of the first component in the processing liquid.

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2224. The substrate processing apparatus (1, 1P or 1Q) according to any one of Claim ~~1821~~ to Claim 2123, wherein the solute further contains a third component which is higher in degree of solubility in the peeling liquid than the second component and lower in degree of solubility in the peeling liquid than the first component, and

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the controller (3) is programmed to solidify or cure the processing liquid supplied to the front surface of the substrate (W) by the solid forming unit (11, 12 or 23), thereby forming the processing film (100) which has a third solid (112) formed by the third component at least at a portion adjacent to the front surface of the substrate (W).

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2325. The substrate processing apparatus (1, 1P or 1Q) according to any one of Claim ~~1821~~ to Claim 2123, further comprising a preprocessing liquid supplying unit (13) which supplies to the front surface of the substrate (W) a preprocessing liquid which contains a solute having a third component higher in degree of solubility in the peeling liquid than the second component and lower in degree of solubility in the peeling liquid than the first component,

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wherein the controller (3) is programmed to execute a preprocessing liquid supplying step of supplying a preprocessing liquid to the front surface of the substrate (W) from the preprocessing liquid supplying unit (13) before supply of the processing liquid to the front surface of the substrate (W), and to form, in the processing film forming

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step, the processing film (100) which has a third solid (112) formed by the third component at least at a portion adjacent to the front surface of the substrate (W).

5 ~~2426~~. The substrate processing apparatus (1, 1P or 1Q) according to any one of Claim ~~1821~~ to Claim ~~2123~~, further comprising: a preprocessing liquid supplying unit (13) of supplying to the front surface of the substrate (W) a preprocessing liquid which contains a solute having a third component higher in degree of solubility in the peeling liquid
10 than the second component and lower in degree of solubility in the peeling liquid than the first component,
wherein the controller (3) is programmed to further execute a preprocessing liquid supplying step of supplying the preprocessing liquid to the front surface of the substrate (W) from the preprocessing
15 liquid supplying unit (13) before supply of the processing liquid to the front surface of the substrate (W), and a preprocessing film forming step of solidifying or curing the preprocessing liquid by the solid forming unit (11, 12 or 23) before supply of the processing liquid to the front surface of the substrate (W), thereby forming a preprocessing
20 film (120) formed by the third component on the front surface of the substrate (W), and programmed to supply a peeling liquid to the front surface of the substrate (W) from the peeling liquid supplying unit (10) in the peeling step to peel the processing film (100) and the preprocessing film (120) from the front surface of the substrate (W)
25 together with the removal object (103).

~~2527~~. The substrate processing apparatus (1, 1P or 1Q) according to any one of Claim ~~1821~~ to Claim ~~2426~~, wherein the second component contains at least any 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 thereof.

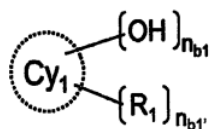
5 ~~2628~~. The substrate processing apparatus (1, 1P or 1Q) according to any one of Claim ~~1821~~ to Claim ~~2527~~, wherein the first component is a crack promoting component, and

the crack promoting component contains hydrocarbon, and a hydroxy group and/or a carbonyl group.

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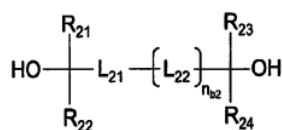
~~2729~~. The substrate processing apparatus (1, 1P or 1Q) according to any one of Claim ~~1821~~ to Claim ~~2628~~, wherein the first component is expressed by at least any one of (B-1), (B-2) and (B-3) given below;

(B-1) is a compound which contains 1 to 6 of constituent units expressed by Chemical ~~Formula 4~~~~Formula 1~~ and in which each of the constituent units is bonded by a linking group L_1 ,
15 [Chemical Formula 4]



here, L_1 is selected at least from a single bond and any one of
20 C_{1-6} alkylene, Cy_1 is a hydrocarbon ring of C_{5-30} , R_1 is each independently C_{1-5} alkyl, n_{b1} is 1, 2 or 3, and $n_{b1'}$ is 0, 1, 2, 3 or 4;

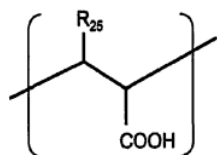
(B-2) is a compound expressed by Chemical Formula 5,
[Chemical Formula 5]



25 here, R_{21} , R_{22} , R_{23} and R_{24} are each independently hydrogen or C_{1-5}

alkyl, L_{21} and L_{22} are each independently C_{1-20} alkylene, C_{1-20} cycloalkylene, C_{2-4} alkenylene, C_{2-4} alkynylene or C_{6-20} arylene, and these groups may be substituted by C_{1-5} alkyl or hydroxyl, and n_{b2} is 0, 1 or 2; and

- 5 (B-3) is a polymer which contains a constituent unit expressed by Chemical Formula 6 and has the weight average molecular weight (M_w) of 500 to 10,000,
[Chemical Formula 6]



- 10 here, R_{25} is -H, -CH₃, or -COOH.

2830. The substrate processing apparatus (1, 1P or 1Q) according to any one of Claim 1821 to Claim 2729, wherein the solubility of the second component in 5.0 mass % ammonia water is less than 100 ppm, and the
15 solubility of the first component in 5.0 mass % ammonia water is 100 ppm or more.

2931. The substrate processing apparatus (1, 1P or 1Q) according to any one of Claim 1821 to Claim 2830, wherein as compared with an entire
20 mass of the processing liquid, the mass of the second component is 0.1 to 50 mass %.

3032. The substrate processing apparatus (1, 1P or 1Q) according to any one of Claim 1821 to Claim 2931, wherein the weight average molecular
25 weight (M_w) of the second component is 150 to 500,000.

3133. The substrate processing apparatus (1, 1P or 1Q) according to any one of Claim 2118 to Claim 2426, wherein the first component and the second component are a synthetic resin.

5 3234. The substrate processing apparatus (1, 1P or 1Q) according to any one of Claim 1819 to Claim 3133, further comprising: a substrate holding unit (20, 21) which holds the substrate (W) horizontally, wherein the solid forming unit (11, 12 or 23) includes a substrate rotating unit (23) which rotates the substrate around a vertical axis
10 (A1) passing through a central portion of the substrate, and
the controller (3) is programmed to execute in the processing liquid supplying step a liquid film forming step of forming a liquid film (101) of the processing liquid on the front surface of the substrate (W) held by the substrate holding unit (20 or 21), and to execute, in
15 the processing film forming step, a film thinning step of rotating the substrate (W) in which the liquid film (101) is formed on the front surface thereof by the substrate rotating unit (23) to eliminate the processing liquid from the front surface of the substrate (W) and to thin the liquid film (101).

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3335. The substrate processing apparatus (1, 1P or 1Q) according to any one of Claim 1819 to Claim 3234, wherein the controller (3) is programmed to allow the solvent to remain in the interior of the processing film (100) when the processing film
25 (100) is formed by the solid forming unit (11, 12 or 23).

3436. The substrate processing apparatus (1, 1P or 1Q) according to any one of Claim 1819 to Claim 3335, wherein the solid forming unit (11, 12 or 23) includes an evaporation promoting unit (11 or 12) which

promotes evaporation of a liquid on the substrate (W), and

the controller (3) is programmed to execute, in the processing
film forming step, a solvent evaporating step of evaporating the solvent
from the processing liquid which is supplied to the front surface of
5 the substrate (W) by the evaporation promoting unit (11 or 12).