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(71) Applicant: LAM RESEARCH CORPORATION

[US/US]; 4650 Cushing Parkway, Fremont, California 94538 (US).

(72) Inventors: SIRARD, Stephen M.; 4650 Cushing Parkway,

Fremont, California 94538 (US). LIMARY, Ratchana;

4650 Cushing Parkway, Fremont, California 94538 (US).

PAN, Yang; 4650 Cushing Parkway, Fremont, California 94538 (US). HYMES, Diane; 4650 Cushing Parkway, Fremont, California 94538 (US).

(74) Agent: BERGIN, Denise S. et al.; WEAVER AUSTIN

VILLENEUVE & SAMPSON LLP, P.O. Box 70250, Oakland, California 94612-0250 (US).

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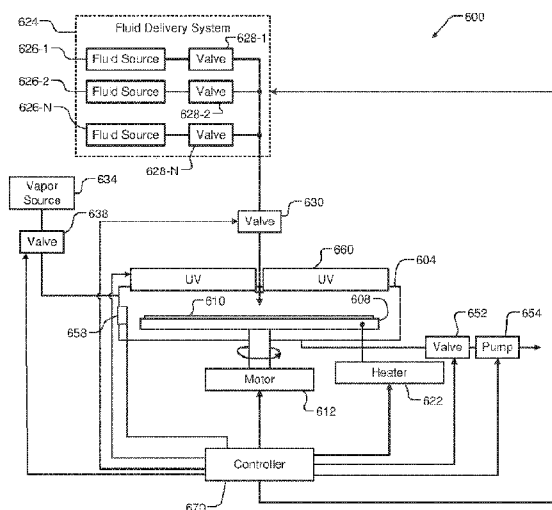


FIG. 6

(57) **Abstract:** A method for protecting a surface of a substrate during processing includes a) providing a solution forming a co-polymer having a ceiling temperature; b) dispensing the solution onto a surface of the substrate to form a sacrificial protective layer, wherein the co-polymer is kinetically trapped to allow storage at a temperature above the ceiling temperature; c) exposing the substrate to ambient conditions for a predetermined period; and d) de-polymerizing the sacrificial protective layer by using stimuli selected from a group consisting of ultraviolet (UV) light and heat.



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SACRIFICIAL PROTECTION LAYER FOR ENVIRONMENTALLY SENSITIVE SURFACES OF SUBSTRATES

INCORPORATION BY REFERENCE

- 5 [0001] A PCT Request Form is filed concurrently with this specification as part of the present application. Each application that the present application claims benefit of or priority to as identified in the concurrently filed PCT Request Form is incorporated by reference herein in its entirety and for all purposes.

FIELD

- 10 [0002] The present disclosure relates to substrate processing, and more particularly to systems and methods for adding and removing sacrificial protective layers to environmentally sensitive surfaces of substrates.

BACKGROUND

- 15 [0003] The background description provided here is for the purpose of generally presenting the context of the disclosure. Work of the presently named inventors, to the extent it is described in this background section, as well as aspects of the description that may not otherwise qualify as prior art at the time of filing, are neither expressly nor impliedly admitted as prior art against the present disclosure.

- 20 [0004] Semiconductor processing systems may be used to perform treatments on substrates such as semiconductor wafers. During processing, the substrates are transported to and from different substrate processing tools for different treatments. During transfer and/or storage, surfaces of the substrates may be exposed to contaminants, ambient air, light, moisture, etc. Exposure during transfer and/or storage may cause defects, material modifications, and/or otherwise adversely impact a downstream process.

- 25 SUMMARY

- [0005] A method for protecting a surface of a substrate during processing includes a) providing a solution forming a co-polymer having a ceiling temperature; b) dispensing the solution onto a surface of the substrate to form a sacrificial protective layer, wherein the co-polymer is kinetically trapped to allow storage at a temperature above the ceiling
30 temperature; c) exposing the substrate to ambient conditions for a predetermined period; and d) de-polymerizing the sacrificial protective layer by using stimuli selected from a group consisting of ultraviolet (UV) light and heat.

[0006] In other features, the co-polymer comprises a poly(aldehyde) co-polymer. The ceiling temperature is lower than room temperature. The method includes dispensing a casting solvent on the substrate prior to dispensing the solution on the substrate.

The method includes adding a thermal catalyst to the solution prior to dispensing the solution. The thermal catalyst is selected from a group consisting of a thermal acid generator and a thermal base generator.

[0007] In other features, the method includes adding a photocatalyst to the solution prior to dispensing the solution. The photocatalyst is selected from a group consisting of a photo acid generator and a photo base generator. The method includes adding a dye to the photocatalyst.

[0008] In other features, d) includes d1) dispensing a thermal catalyst onto the sacrificial protective layer; and d2) heating the substrate to a temperature that is greater than a catalyzed co-polymer degradation temperature and less than an un-catalyzed co-polymer temperature.

[0009] In other features, the method includes repeating d1) and d2) one or more times until the sacrificial protective layer is removed.

[0010] In other features, the method includes d3) heating the substrate to a temperature that is greater than the un-catalyzed co-polymer temperature to remove remaining portions of the sacrificial protective layer.

[0011] In other features, the thermal catalyst is selected from a group consisting of a thermal acid generator and a thermal base generator.

[0012] In other features, prior to b), performing a first treatment process on the substrate in a first substrate processing tool; performing a) and b) in the first substrate processing tool; performing d) in a second substrate processing tool; and performing a second treatment process on the substrate in the second substrate processing tool.

[0013] In other features, the first treatment process is selected from a group consisting of deposition, etching, stripping, cleaning, chemical mechanical planarization (CMP), patterning, or modification of electrical properties of the substrate. The second treatment process is selected from a group consisting of deposition, etching, stripping, cleaning, chemical mechanical planarization (CMP), patterning, or modification of electrical properties of the substrate.

[0014] A method for protecting a surface of a substrate during processing includes a) providing a solution forming a co-polymer having a ceiling temperature; b) dispensing the solution onto a surface of the substrate to form a sacrificial protective layer, wherein the

co-polymer is kinetically trapped to allow storage at a temperature above the ceiling temperature; c) exposing the substrate to ambient conditions for a predetermined period; and d) de-polymerizing the sacrificial protective layer by exposing the substrate to an acidic vapor.

5 **[0015]** In other features, the ceiling temperature is lower than room temperature. The method includes dispensing a casting solvent on the substrate prior to dispensing the solution on the substrate. In other features, the method includes, prior to b), performing a first treatment process on the substrate in a first substrate processing tool; performing a) and b) in the first substrate processing tool; performing d) in a second substrate processing
10 tool; and performing a second treatment process on the substrate in the second substrate processing tool.

[0016] In other features, the first treatment process is selected from a group consisting of deposition, etching, stripping, cleaning, chemical mechanical planarization (CMP), patterning, or modification of electrical properties of the substrate. The second treatment
15 process is selected from a group consisting of deposition, etching, stripping, cleaning, chemical mechanical planarization (CMP), patterning, or modification of electrical properties of the substrate.

[0017] Further areas of applicability of the present disclosure will become apparent from the detailed description, the claims and the drawings. The detailed description and specific
20 examples are intended for purposes of illustration only and are not intended to limit the scope of the disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] The present disclosure will become more fully understood from the detailed description and the accompanying drawings, wherein:

25 **[0019]** FIG. 1 is a functional block diagram of an example of a substrate processing system including multiple substrate processing tools and a storage buffer according to the present disclosure;

[0020] FIG. 2A is a side cross-sectional view of an example of a substrate according to the present disclosure;

30 **[0021]** FIG. 2B is a side cross-sectional view of an example of a substrate including a sacrificial protective layer according to the present disclosure;

[0022] FIG. 3A is a side cross-sectional view of an example of a substrate including a sacrificial protective layer and a first catalyst layer according to the present disclosure;

[0023] FIG. 3B is a side cross-sectional view of an example of a substrate including the sacrificial protective layer that is partially removed according to the present disclosure;

[0024] FIG. 3C is a side cross-sectional view of an example of a substrate including the sacrificial protective layer and a second catalyst layer according to the present disclosure;

5 [0025] FIG. 3D is a side cross-sectional view of an example of a substrate including the sacrificial protective layer that is further removed according to the present disclosure;

[0026] FIG. 4 is a flowchart of an example of a method for adding and removing a sacrificial protective layer from a substrate according to the present disclosure;

[0027] FIG. 5 is a flowchart of an example of a method for adding and removing a
10 sacrificial protective layer from a substrate in steps to prevent collapse using a catalyst according to the present disclosure;

[0028] FIG. 6 is a functional block diagram of an example of a substrate processing chamber for adding and removing the sacrificial protective layer according to the present disclosure; and

15 [0029] FIG. 7 is a graph illustrating a thermographic analysis of an example of a process window for removing the sacrificial protective layer in steps using a catalyst according to the present disclosure.

[0030] In the drawings, reference numbers may be reused to identify similar and/or identical elements.

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DETAILED DESCRIPTION

[0031] Substrate surfaces may be exposed to ambient conditions during semiconductor fabrication. Many of the substrate surfaces are sensitive to modification due to ambient or environmental exposure. The surface changes that occur can adversely impact a subsequent process and/or degrade device performance. This exposure phenomena may
25 be referred to herein as queue time effects.

[0032] In order to manage queue time effects, integrated substrate processing tools have been developed to allow processing to take place in a highly controlled environment with little or no exposure to ambient conditions. This approach usually requires substantial design changes to the substrate processing tools. In addition, there are substantial logistical
30 problems when the integrated substrate processing tool is taken offline for repair.

[0033] Another solution for mitigating queue time effects is to control the environment during transfer. For example, front opening unified pods (FOUPS) may be modified to provide a controlled atmosphere during transfers of the substrates between the substrate processing tools. For example, the FOUP may provide a molecular nitrogen atmosphere.

However, there are still risks associated with outgassing, leaks, and/or wafer transport that may contaminate the surfaces of the substrates.

[0034] Polymers have been used as barriers in several industries including food packaging and pharmaceuticals. The polymer film is applied and then later removed. The polymer film can be used to protect the surfaces of the substrates from environmental threats. At some point, however, the polymer film needs to be removed. Common removal processes include both dry plasma and/or wet clean processes. However, the removal processes tend to be aggressive and usually modify the surfaces of the substrates.

[0035] Polymers that are stable at room temperature (e.g. 20 - 25°C) have been used in sacrificial polymer applications. For example, poly(carbonates) can be used. However, there are some disadvantages with using these types of polymers. During the removal process, relatively high temperatures are needed (i.e. 160°C to 300°C) to assist in chemical bond-breaking because the polymers are stable at room temperature. The removal process is slow because each chemical unit needs to be activated.

[0036] In addition, these types of polymers include inadvertent, non-carbonate bonds (e.g. ether linkages) which, when decomposed, create non-volatile residues. Thus, these polymers have limited usefulness in applications where monolayer impurities cannot be tolerated. Pure poly(carbonates) are not currently available.

[0037] Systems and methods according to the present disclosure apply a sacrificial protection layer on a substrate including a low ceiling temperature (T_c) co-polymer. T_c is the equilibrium temperature between the co-polymer and its monomers. As used herein, the term low T_c refers T_c values below room temperature. In other words, the co-polymers are thermodynamically unstable at room temperature. Instead, the low T_c co-polymer is kinetically trapped to allow prolonged storage at room temperature. In some examples, the stable storage period is on the order of months or years. Low T_c co-polymers will rapidly de-polymerize to its monomer constituents if an end-group or main chain bond is broken. Thus, the co-polymer de-polymerizes in response to stimuli such as ultraviolet (UV) light, heat, or an acidic/basic catalyst.

[0038] The sacrificial protection layer provides protection for the exposed surfaces of the substrates during integrated circuit (IC) fabrication and/or after processing. For example, the sacrificial protection layer protects sensitive thin film for extended periods when the substrate is exposed to ambient conditions by acting as a diffusion barrier to ambient contaminants and by blocking reactive surface sites.

[0039] The sacrificial protection layer is removed at relatively low temperature without requiring the use of plasma or wet processing (which cause surface modification). The heat, UV light, and/or acidic/basic catalysts trigger spontaneous de-polymerization and vaporization of the sacrificial protection layer. This type of removal process minimizes the impact on the sensitive surfaces of the substrate. Examples of substrate surfaces that can be sensitive to environmental queue time effects include silicon, silicon germanium, and germanium structures such as fins and nanowires, tungsten contacts, and/or other structures and materials.

[0040] As described above, the low T_c co-polymers are thermodynamically unstable at room temperature. Below T_c , the material is a co-polymer. Above T_c , the material includes two or more volatile monomers. Low T_c co-polymers can be kinetically trapped at temperatures well above T_c with excellent shelf-life. Stability is achieved by kinetically inhibiting the mechanism of de-polymerization.

[0041] In some examples, the low T_c co-polymers include poly(aldehydes). For example, poly(phthalaldehyde) (PPHA) ($T_c = -40^\circ\text{C}$) is stable at room temperature for 2.5 years. Additional examples of low T_c co-polymers are described in U.S. Patent Application Publication Serial No. 2018/0155483, which was published on June 7, 2018 and which is hereby incorporated herein by reference in its entirety.

[0042] Systems and methods described herein apply a sacrificial protective layer including the low T_c co-polymer onto environmentally sensitive surfaces of substrates such as semiconductor wafers. The sacrificial protective layer provides a barrier against atmospheric contaminants such as oxygen and water. In another example, the sacrificial protective layer provides a barrier against halogens such as fluorine which can outgas from FOUP carriers. As a result, the surfaces of the substrates have extended queue time stability by slowing the permeation (sorption and diffusion) of undesired contaminants to the surface. Furthermore, the sacrificial protective layer can block reactive sites on the surface.

[0043] The low- T_c co-polymers described herein can be readily removed at moderate temperatures ($< 150^\circ\text{C}$) by exposure to heat, UV light, acidic/basic catalysts, and/or acidic vapors. In some examples, the catalyst includes a photocatalyst or a thermal catalyst. In some examples, the photocatalyst includes a photo acid generator (PAG) or a photo base generator. In some examples, the thermal catalyst includes thermal acid generator (TAG) or a thermal base generator. Some of the co-polymers described herein are sensitive to acids or bases. Release of acids or bases cause de-polymerization into volatile monomers.

The catalysts cause the sacrificial protective layer to de-polymerize into volatile monomers in response to UV light and/or heat. In some examples, the solution forming the co-polymer is mixed with the photocatalysts or thermal catalysts when they are cast. In some examples, a dye may be added to the solution before casting to control photon penetration depth and hence degradation depth when the PAG catalyst is used.

[0044] In other examples, the TAG or PAG catalyst is added as an additional layer above an un-catalyzed co-polymer layer prior to the removal of the sacrificial co-polymer layer. When the TAG catalyst is used, the un-catalyzed co-polymer has a higher degradation temperature than the catalyzed co-polymer. Therefore, partial degradation can be performed to prevent collapse of HAR structures. The temperature of the substrate is increased above the degradation temperature of the catalyzed co-polymer but below the degradation temperature of the un-catalyzed co-polymer.

[0045] As will be described further below, the volume of the catalyst that is applied may be used to control the vertical thickness of the un-catalyzed co-polymer that is removed in a step. In some examples, when applying the TAG or PAG catalyst to remove the uncatalyzed copolymer in successive steps, the degraded monomer is removed faster than the diffusion/reaction of the catalyst.

[0046] Low T_c co-polymers have several advantages when used for the sacrificial protection layer. The low T_c co-polymers such as poly(aldehydes) are simple to synthesize and only poly(aldehydes) are formed with no unwanted side products. Therefore, residue-free vaporization of the low T_c co-polymer can be achieved.

[0047] Since poly(aldehydes) are depolymerized at temperatures well above T_c , only one (or few) chemical bonds need to be broken to overcome the kinetic stabilization and initiate full, rapid de-polymerization. Since all of the bonds are the same (no inadvertent impurities), little or no residue remains after removal. The sacrificial protection layers eliminate the need for the integrated substrate processing tool platforms or the specialized FOUP environments.

[0048] In some examples, the sacrificial protective layer is applied in a substrate processing tool after processing and prior to exposure to ambient conditions during transfer or storage. In some examples, the substrates may be exposed to ambient conditions during transfer to and/or storage in a storage buffer or other location. In other examples, the substrates may be exposed to ambient conditions during transfer from one substrate processing chamber or tool to another substrate processing chamber or tool.

[0049] After storage and/or transfer and prior to additional substrate processing, the sacrificial protective layer is removed. In some examples, removal of the sacrificial protective layer is performed in a substrate processing tool and then other processes are performed on the substrate in the same substrate processing tool without exposure to ambient conditions. In some examples, a single substrate has the sacrificial protection layer applied and removed a plurality of times during substrate processing.

[0050] Referring now to FIG. 1, a substrate processing system 100 includes one or more substrate processing tools 102 (substrate processing tools 102-1 and 102-2 are shown for illustration purposes) and substrate buffer 130 or other substrate storage. Each of the substrate processing tools 102-1 and 102-2 includes a plurality of processing chambers 104-1, 104-2, ... and 104-M (collectively processing chambers 104) (where M is an integer greater than one). For example only, each of the processing chambers 104 may be configured to perform a substrate treatment. In some examples, the substrates may be loaded into one of the processing chambers 104, processed, and then moved to one or more other ones of the processing chambers 104 and/or removed from the substrate processing tool 100 (e.g., if all perform the same treatment).

[0051] Substrates to be processed are loaded into the substrate processing tools 102-1 and 102-2 via ports of a loading station of an atmosphere-to-vacuum (ATV) transfer module 108. In some examples, the ATV transfer module 108 includes an equipment front end module (EFEM). The substrates are then transferred into one or more of the processing chambers 104. For example, a transfer robot 112 is arranged to transfer substrates from loading stations 116 to load locks 120. A vacuum transfer robot 124 of a vacuum transfer module 128 is arranged to transfer substrates from the load locks 120 to the various processing chambers 104.

[0052] After processing in one or more of the substrate processing tools 102-1 and 102-2, the substrates may be transported outside of a vacuum environment. For example, the substrates may be moved to a location for storage (such as the substrate buffer 130). In other examples, the substrates may be moved directly from the substrate processing tool to another substrate processing tool for further processing or from the storage buffer 130 to another substrate processing tool for further processing.

[0053] As was previously described above, exposure of the substrate to ambient conditions may cause defects or otherwise adversely impact downstream processing. Systems and methods according to the present disclosure are used to add the sacrificial protective layer to the substrate prior to exposure to ambient conditions. In some

examples, the sacrificial protective layer is applied in the substrate processing tool prior to transferring the substrate to the substrate buffer for storage or to another substrate processing tool. In other examples, the sacrificial protective layer is applied in another processing chamber (not associated with the substrate processing tool).

5 **[0054]** Prior to performing another treatment on the substrate, the sacrificial protective layer is removed. For example, the substrate may be transferred to the substrate processing tool 102-2 after a period of storage in the storage buffer 130 or after processing in the substrate processing tool 102-1. The sacrificial protective layer may be removed by one of the processing chambers in the substrate processing tool 102-2 or another processing
10 chamber (not associated with the substrate processing tool 102-2).

[0055] In some examples, the sacrificial protective layer is applied by a processing chamber in the same substrate processing tool (that performed substrate treatment) prior to exposure to ambient conditions. Since the substrate processing tool operates at vacuum, exposure of the substrate to ambient conditions is prevented.

15 **[0056]** In some examples, the sacrificial layer is deposited after a wet clean process. In this case, oxides and residues may be removed by the wet clean process and the sacrificial layer is deposited in sequence prior to drying the wafer. In some examples, this process is not done under vacuum and is done without any exposure of the dry pristine surface to the ambient.

20 **[0057]** In other examples, the substrate is transported from the substrate processing tool to another processing chamber located outside of the substrate processing tool that adds the sacrificial protective layer. Using this approach limits or reduces the period of exposure of the substrate to ambient conditions. Exposure is limited to a brief period of transport from the substrate processing tool to the processing chamber where the sacrificial
25 protective layer is applied. Storage of the substrate may be performed for longer periods without additional exposure to ambient conditions.

[0058] Subsequently, the sacrificial protective layer may be removed prior to further processing. In some examples, the sacrificial protective layer is removed in another substrate processing tool under vacuum conditions prior to substrate treatment in
30 processing chambers of the same substrate processing tool. In other examples, the substrate is transported to a processing chamber that removes the sacrificial protective layer and then to the substrate processing tool for further processing. This approach also limits exposure to ambient conditions between the processing chamber and the substrate processing tool or other environment.

[0059] Referring now to FIGs. 2A and 2B, a sacrificial protective layer can be added to a substrate to prevent or reduce the effect of exposure of the substrate to ambient conditions. In FIG. 2A, a substrate 200 is shown. The substrate includes a layer 204 arranged on one or more underlying layers 212. In some examples, the layer 204 includes features such as pillars 216 and trenches 220. In other examples, the layer 204 can be planar and/or can have other types of features. As can be appreciated, a single material or two or more different types of materials or films may be exposed. In FIG. 2B, a sacrificial protective layer 224 is deposited on the substrate 200 and covers the layer 204.

[0060] After the sacrificial protective layer 224 is added, the substrate 200 can be transported and/or stored in ambient conditions for extended periods with a significant reduction in or elimination of contamination. The sacrificial protective layer 224 is removed by applying heat, UV light, exposing the substrate to acidic vapor and/or using a catalyst, as will be described further below.

[0061] Referring now to FIGs. 3A and 3D, the sacrificial protective layer can be removed in one step as shown in FIGs. 2A and 2B or removed in steps to prevent collapse of features. In FIG. 3A, a substrate 300 is shown to include a layer 304 arranged on one or more underlying layers 312. In some examples, the layer 304 includes high aspect ratio (HAR) features such as pillars 316 and trenches 320.

[0062] A sacrificial protective layer 324 (similar to FIG. 2B) is deposited on the substrate 300 and covers the layer 304. After the sacrificial protective layer 324 is added, the substrate 300 can be transported and/or stored in ambient conditions for extended periods with a significant reduction in or elimination of contamination.

[0063] When it is time to remove the sacrificial protective layer 324, a catalyst layer 310 is cast, sprayed, applied or deposited onto the sacrificial protective layer 324. The volume of catalyst solution that is used is determined by how much of the sacrificial protective layer 324 is to be removed. After depositing the catalyst layer 310, the substrate 300 is exposed to heat or UV light to activate the catalyst layer 310. The catalyst layer 310 locally lowers a temperature that is needed to remove a portion 340 of the sacrificial protective layer 324. The portion 340 of the sacrificial protective layer 224 is removed as shown in FIG. 3B.

[0064] The process of incrementally removing the sacrificial protective layer 324 may include additional cycles of depositing the catalyst layer and/or may be done with a single catalyst layer by controlling the top down diffusion of catalyst and removing other portions of the sacrificial protective layer 324. In FIG. 3C, a catalyst layer 344 is cast, sprayed,

applied or deposited. In FIG. 3D, heat or UV light is applied and another portion 350 of the sacrificial protective layer 324 is removed. The process continues until all of the sacrificial protective layer 324 is removed. As can be appreciated, the process for incrementally removing the sacrificial protective layer in a controlled manner reduces or prevents damage (such as collapse) to the features that otherwise may occur with a single step removal process. Collapse may occur as the triggered degradation causes the sacrificial protective layer to temporarily transition to a liquid-like material that collapses HAR structures due to capillary force prior to evaporation of the monomers.

5 [0065] Referring now to FIG. 4, a method 400 for adding and removing the sacrificial protective layer from the substrate is shown. At 422, a process is performed on the substrate 200. In some examples, the process includes deposition, etching, stripping, cleaning, chemical mechanical planarization (CMP), patterning, modification of electrical properties (e.g. doping and optionally annealing or exposure to ultraviolet (UV) light to alter the dielectric constant) or another process. At 424, the substrate is cleaned by performing a post processing rinse with a post rinse solution. In some examples, dilute hydrofluoric (HF) acid or another solution is used to remove native oxide.

10 [0066] At 426, the post rinse solution is optionally displaced by a casting solvent. At 428, a solution that will form the sacrificial protective layer is cast, sprayed, applied or deposited on the substrate. In some examples, the solution includes the TAG catalyst. In some examples, the solution includes the PAG catalyst and/or the dye. At 430, the substrate is optionally rotated or spun to dry the substrate. At 434, the substrate is transported and/or stored in an ambient environment.

15 [0067] At 436, the method determines whether the sacrificial protective layer needs to be removed (e.g. when the substrate is ready for additional processing). If 436 is true, the substrate is transported to a processing chamber or substrate processing tool at 438. At 440, the sacrificial protective layer is removed.

20 [0068] In some examples, the sacrificial protective layer is removed using heat at a temperature in a predetermined temperature range from 50° C to 300° C. In some examples, the sacrificial protective layer is removed using heat at a temperature in a predetermined temperature range from 50° C to 150° C. In some examples, the sacrificial protective layer is removed using exposure to ultraviolet (UV) light. In some examples, the catalyst is added to the solution forming the co-polymer. In some examples, the dye is also added to the solution when the photocatalyst is added to control degradation of the co-polymer. In other examples, an un-catalyzed co-polymer is deposited and the catalyst

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is dispensed onto the substrate during removal of the sacrificial protection layer (see FIG. 5).

[0069] In some examples, the sacrificial protective layer is removed by exposure to an acidic vapor species. In some examples, the acidic vapor includes hydrogen bromide (HBr) or other acidic vapor. In some examples, when HBr vapor is used, the temperature of the substrate is maintained at a pressure in a range from 5mT to 5000mT) and a temperature in a range from 0°C to 100°C. In some examples, the temperature of the substrate is maintained at a pressure in a range from 750mT to 1500mT) and a temperature in a range from 35°C to 70°C. In some examples, the temperature of the substrate is maintained at a pressure of 1000mT and a temperature of 60°C. At 442, further processing of the substrate may be performed in a substrate processing tool, processing chamber or other location.

[0070] Referring now to FIG. 5, a method 500 for adding the sacrificial protective layer to the substrate and sequentially removing the sacrificial protective layer in steps is shown. At 422, a process is performed on the substrate. In some examples, the process includes deposition, etching, stripping, cleaning, chemical mechanical planarization (CMP), patterning, modification of electrical properties (e.g. doping and optionally annealing or exposure to ultraviolet (UV) light to alter the dielectric constant) or another substrate treatment process. At 424, the substrate is cleaned by performing a post processing rinse.

[0071] At 426, the post rinse solution is optionally displaced with a casting solvent. At 428, a solution that will form the sacrificial protective layer is cast, sprayed, applied or deposited on the substrate. At 430, the substrate is optionally rotated or spun to dry the substrate. At 434, the substrate is ready to be transported and/or stored in an ambient environment.

[0072] At 436, the method determines whether the substrate is ready for the sacrificial protective layer to be removed (for example prior to further processing). If 436 is true, the substrate is transported to a processing chamber or substrate processing tool at 438 where the sacrificial protective layer is removed. At 510, a solution that will form a catalyst layer is cast, sprayed, applied or deposited to the sacrificial protective layer. At 514, the sacrificial protective layer is partially removed by exposing the substrate to heat or UV light. At 518, the method determines whether the sacrificial protective layer has been fully removed. If not, the method continues at 520 and removes the remaining portion of the sacrificial protective layer using stimuli such as light or heat. In some examples, the heat or light is sufficient to remove the remaining portion of the sacrificial protecting layer in

the absence of the catalyst. In other examples, the method returns to step 510 one or more times until the protective layer is gone.

5 [0073] When the thermal catalyst is used, the un-catalyzed co-polymer has a higher degradation temperature than the catalyzed co-polymer. Therefore, partial degradation can be performed to prevent collapse of HAR structures. The temperature of the substrate is increased above the degradation temperature of the catalyzed co-polymer but below the degradation temperature of the un-catalyzed co-polymer. When the PAG catalyst is used, the dye can be used to limit degradation.

10 [0074] Referring now to FIG. 6, a substrate processing chamber 600 for adding and removing the sacrificial protective layer is shown. A substrate processing chamber 604 includes a substrate support 608 that supports a substrate 610. A heater 622 may be used to heat the substrate support 608. In some examples, the heater 622 includes one or more resistive heaters. In other examples, coolant may be used alone or in combination with the heater 622 to heat and/or cool the substrate support 608. A motor 612 may be used to rotate
15 the substrate support 608.

[0075] A fluid delivery system 624 includes one or more fluid sources 626-1, 626-2, ..., and 626-N (collectively fluid sources 626). The fluid sources 626 may supply liquid such as a solution that will form the sacrificial protective layer, a solution that will form the catalyst and/or other solutions. In some examples, a vapor source 634 including an
20 ampoule or bubbler (not shown) can be used to supply a vapor such as HBr vapor via a valve 638. Outputs of the fluid sources 626 are delivered by valves 628-1, 628-2, ..., and 628-N (collectively valves 628) and a valve 630 to the processing chamber 604.

[0076] A valve 652 and a pump 654 may be used to control pressure in the processing chamber 604 and/or to evacuate reactants from the processing chamber 604 as needed. A
25 pressure sensor 658 may be used to sense pressure within the processing chamber 604. One or more light sources such as ultraviolet (UV) light sources 660 may be used to expose the substrate during processing. A controller 670 may be used to control the valve 652 and the pump 654, the valve 630, the valve 638, the fluid delivery system 624, the motor 612, and/or other components of the processing chamber 600. In some examples, the
30 controller 670 controls pressure within the processing chamber based on feedback from sensors such as pressure sensors, temperature sensors and the like.

[0077] Referring now to FIG. 7, a graph illustrates an example of a process window for removing a portion of the sacrificial protective layer using a catalyst. Portions of the sacrificial protective layer that are not catalyzed require a higher degradation temperature

as compared to catalyzed portions of the sacrificial protective layer. Therefore, the catalyst layer can be used to incrementally remove portions of the sacrificial protective layer by controlling the temperature in a temperature window below the upper degradation temperature that will de-polymerize the sacrificial protective layer and above a lower degradation temperature that will de-polymerize the catalyzed sacrificial protective layer. In other words, when the thermal catalyst is used, the un-catalyzed co-polymer has a higher degradation temperature than the catalyzed co-polymer. Therefore, partial degradation can be performed to prevent collapse of HAR structures. The temperature of the substrate is increased above the degradation temperature of the catalyzed co-polymer but below the degradation temperature of the un-catalyzed co-polymer. When the PAG catalyst is used with dye, the degradation using UV light is also limited by the dye.

[0078] In some examples, the catalyst is applied a limited number of times (e.g. once or a predetermined number of times) and the substrate is heated to the degradation temperature of the catalyzed co-polymer (once or a predetermined number of times), respectively. If the protective layer remains after a last one of the predetermined number of catalyst applications, the temperature of the substrate can be raised to the degradation temperature of the un-catalyzed co-polymer if needed to remove the remaining portion of the protective layer.

[0079] The foregoing description is merely illustrative in nature and is in no way intended to limit the disclosure, its application, or uses. The broad teachings of the disclosure can be implemented in a variety of forms. Therefore, while this disclosure includes particular examples, the true scope of the disclosure should not be so limited since other modifications will become apparent upon a study of the drawings, the specification, and the following claims. It should be understood that one or more steps within a method may be executed in different order (or concurrently) without altering the principles of the present disclosure. Further, although each of the embodiments is described above as having certain features, any one or more of those features described with respect to any embodiment of the disclosure can be implemented in and/or combined with features of any of the other embodiments, even if that combination is not explicitly described. In other words, the described embodiments are not mutually exclusive, and permutations of one or more embodiments with one another remain within the scope of this disclosure.

[0080] Spatial and functional relationships between elements (for example, between modules, circuit elements, semiconductor layers, etc.) are described using various terms, including “connected,” “engaged,” “coupled,” “adjacent,” “next to,” “on top of,” “above,”

“below,” and “disposed.” Unless explicitly described as being “direct,” when a relationship between first and second elements is described in the above disclosure, that relationship can be a direct relationship where no other intervening elements are present between the first and second elements, but can also be an indirect relationship where one or more intervening elements are present (either spatially or functionally) between the first and second elements. As used herein, the phrase at least one of A, B, and C should be construed to mean a logical (A OR B OR C), using a non-exclusive logical OR, and should not be construed to mean “at least one of A, at least one of B, and at least one of C.”

5 [0081] In some implementations, a controller is part of a system, which may be part of the above-described examples. Such systems can comprise semiconductor processing equipment, including a processing tool or tools, chamber or chambers, a platform or platforms for processing, and/or specific processing components (a wafer pedestal, a gas flow system, etc.). These systems may be integrated with electronics for controlling their operation before, during, and after processing of a semiconductor wafer or substrate. The electronics may be referred to as the “controller,” which may control various components or subparts of the system or systems. The controller, depending on the processing requirements and/or the type of system, may be programmed to control any of the processes disclosed herein, including the delivery of processing gases, temperature settings (e.g., heating and/or cooling), pressure settings, vacuum settings, power settings, radio frequency (RF) generator settings, RF matching circuit settings, frequency settings, flow rate settings, fluid delivery settings, positional and operation settings, wafer transfers into and out of a tool and other transfer tools and/or load locks connected to or interfaced with a specific system.

15 [0082] Broadly speaking, the controller may be defined as electronics having various integrated circuits, logic, memory, and/or software that receive instructions, issue instructions, control operation, enable cleaning operations, enable endpoint measurements, and the like. The integrated circuits may include chips in the form of firmware that store program instructions, digital signal processors (DSPs), chips defined as application specific integrated circuits (ASICs), and/or one or more microprocessors, or microcontrollers that execute program instructions (e.g., software). Program instructions may be instructions communicated to the controller in the form of various individual settings (or program files), defining operational parameters for carrying out a particular process on or for a semiconductor wafer or to a system. The operational parameters may, in some embodiments, be part of a recipe defined by process engineers to accomplish one

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or more processing steps during the fabrication of one or more layers, materials, metals, oxides, silicon, silicon dioxide, surfaces, circuits, and/or dies of a wafer.

[0083] The controller, in some implementations, may be a part of or coupled to a computer that is integrated with the system, coupled to the system, otherwise networked to the system, or a combination thereof. For example, the controller may be in the “cloud” or all or a part of a fab host computer system, which can allow for remote access of the wafer processing. The computer may enable remote access to the system to monitor current progress of fabrication operations, examine a history of past fabrication operations, examine trends or performance metrics from a plurality of fabrication operations, to change parameters of current processing, to set processing steps to follow a current processing, or to start a new process. In some examples, a remote computer (e.g. a server) can provide process recipes to a system over a network, which may include a local network or the Internet. The remote computer may include a user interface that enables entry or programming of parameters and/or settings, which are then communicated to the system from the remote computer. In some examples, the controller receives instructions in the form of data, which specify parameters for each of the processing steps to be performed during one or more operations. It should be understood that the parameters may be specific to the type of process to be performed and the type of tool that the controller is configured to interface with or control. Thus as described above, the controller may be distributed, such as by comprising one or more discrete controllers that are networked together and working towards a common purpose, such as the processes and controls described herein. An example of a distributed controller for such purposes would be one or more integrated circuits on a chamber in communication with one or more integrated circuits located remotely (such as at the platform level or as part of a remote computer) that combine to control a process on the chamber.

[0084] Without limitation, example systems may include a plasma etch chamber or module, a deposition chamber or module, a spin-rinse chamber or module, a metal plating chamber or module, a clean chamber or module, a bevel edge etch chamber or module, a physical vapor deposition (PVD) chamber or module, a chemical vapor deposition (CVD) chamber or module, an atomic layer deposition (ALD) chamber or module, an atomic layer etch (ALE) chamber or module, an ion implantation chamber or module, a track chamber or module, and any other semiconductor processing systems that may be associated or used in the fabrication and/or manufacturing of semiconductor wafers.

[0085] As noted above, depending on the process step or steps to be performed by the tool, the controller might communicate with one or more of other tool circuits or modules, other tool components, cluster tools, other tool interfaces, adjacent tools, neighboring tools, tools located throughout a factory, a main computer, another controller, or tools used
5 in material transport that bring containers of wafers to and from tool locations and/or load ports in a semiconductor manufacturing factory.

CLAIMS

What is claimed is:

1. A method for protecting a surface of a substrate during processing, comprising:
 - a) providing a solution forming a co-polymer having a ceiling temperature;
 - 5 b) dispensing the solution onto a surface of the substrate to form a sacrificial protective layer,
wherein the co-polymer is kinetically trapped to allow storage at a temperature above the ceiling temperature;
 - c) exposing the substrate to ambient conditions for a predetermined period;
 - 10 and
 - d) de-polymerizing the sacrificial protective layer by using stimuli selected from a group consisting of ultraviolet (UV) light and heat.
2. The method of claim 1, wherein the co-polymer comprises a poly(aldehyde) co-polymer.
- 15 3. The method of claim 1, wherein the ceiling temperature is lower than room temperature.
4. The method of claim 1, further comprising dispensing a casting solvent on the substrate prior to dispensing the solution on the substrate.
5. The method of claim 1, further comprising adding a thermal catalyst to the solution
20 prior to dispensing the solution.
6. The method of claim 5, wherein the thermal catalyst is selected from a group consisting of a thermal acid generator and a thermal base generator.
7. The method of claim 1, further comprising adding a photocatalyst to the solution prior to dispensing the solution.
- 25 8. The method of claim 7, wherein the photocatalyst is selected from a group consisting of a photo acid generator and a photo base generator.
9. The method of claim 7, further comprising adding a dye to the photocatalyst.
10. The method of claim 1, wherein d) includes:
 - d1) dispensing a thermal catalyst onto the sacrificial protective layer; and
 - 30 d2) heating the substrate to a temperature that is greater than a catalyzed co-polymer degradation temperature and less than an un-catalyzed co-polymer temperature.
11. The method of claim 10, further comprising repeating d1) and d2) one or more times until the sacrificial protective layer is removed.

12. The method of claim 10, further comprising d3) heating the substrate to a temperature that is greater than the un-catalyzed co-polymer temperature to remove remaining portions of the sacrificial protective layer.
13. The method of claim 10, wherein the thermal catalyst is selected from a group consisting of a thermal acid generator and a thermal base generator.
14. The method of claim 1, further comprising:
prior to b), performing a first treatment process on the substrate in a first substrate processing tool;
performing a) and b) in the first substrate processing tool;
performing d) in a second substrate processing tool; and
performing a second treatment process on the substrate in the second substrate processing tool.
15. The method of claim 14, wherein:
the first treatment process is selected from a group consisting of deposition, etching, stripping, cleaning, chemical mechanical planarization (CMP), patterning, or modification of electrical properties of the substrate; and
the second treatment process is selected from a group consisting of deposition, etching, stripping, cleaning, chemical mechanical planarization (CMP), patterning, or modification of electrical properties of the substrate.
16. A method for protecting a surface of a substrate during processing, comprising:
a) providing a solution forming a co-polymer having a ceiling temperature;
b) dispensing the solution onto a surface of the substrate to form a sacrificial protective layer,
wherein the co-polymer is kinetically trapped to allow storage at a temperature above the ceiling temperature;
c) exposing the substrate to ambient conditions for a predetermined period;
and
d) de-polymerizing the sacrificial protective layer by exposing the substrate to an acidic vapor.
17. The method of claim 16, wherein the ceiling temperature is lower than room temperature.
18. The method of claim 16, further comprising dispensing a casting solvent on the substrate prior to dispensing the solution on the substrate.

19. The method of claim 16, further comprising:
prior to b), performing a first treatment process on the substrate in a first substrate processing tool;
performing a) and b) in the first substrate processing tool;
5 performing d) in a second substrate processing tool; and
performing a second treatment process on the substrate in the second substrate processing tool.
20. The method of claim 19, wherein:
10 the first treatment process is selected from a group consisting of deposition, etching, stripping, cleaning, chemical mechanical planarization (CMP), patterning, or modification of electrical properties of the substrate; and
the second treatment process is selected from a group consisting of deposition, etching, stripping, cleaning, chemical mechanical planarization (CMP), patterning, or
15 modification of electrical properties of the substrate.

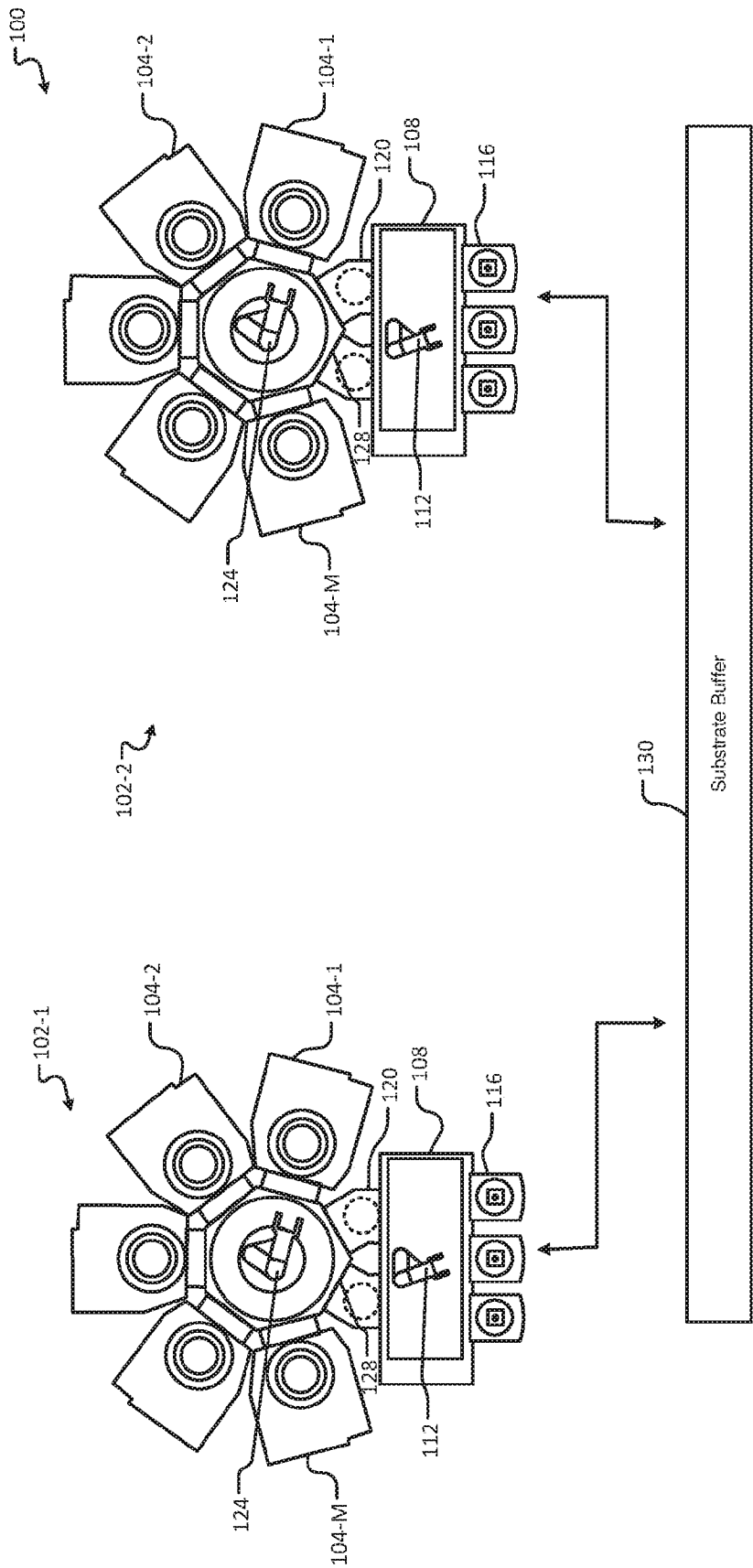


FIG.1

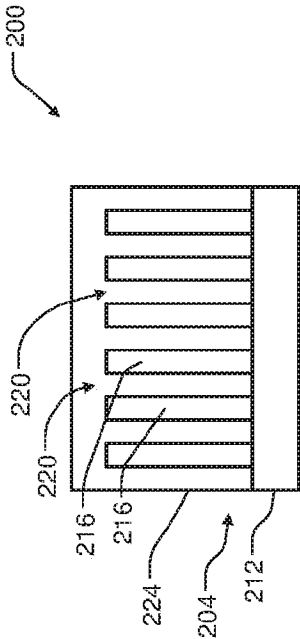


FIG. 2A

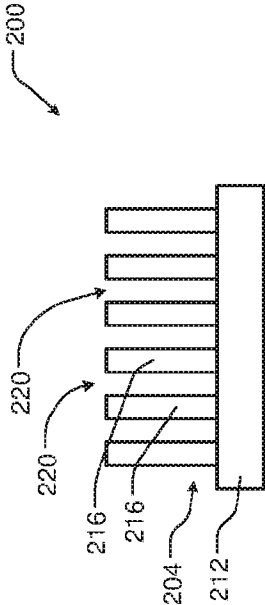


FIG. 2B

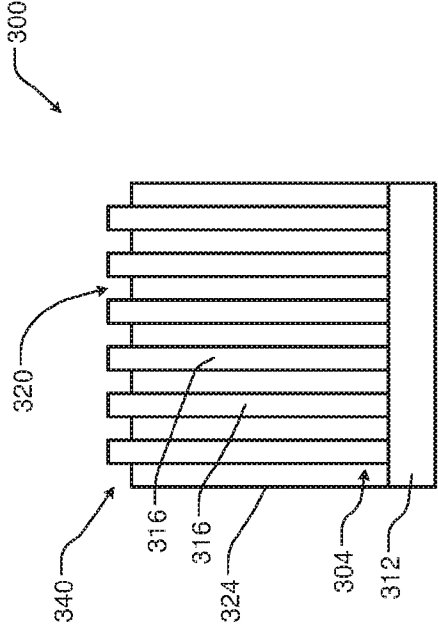


FIG. 3A

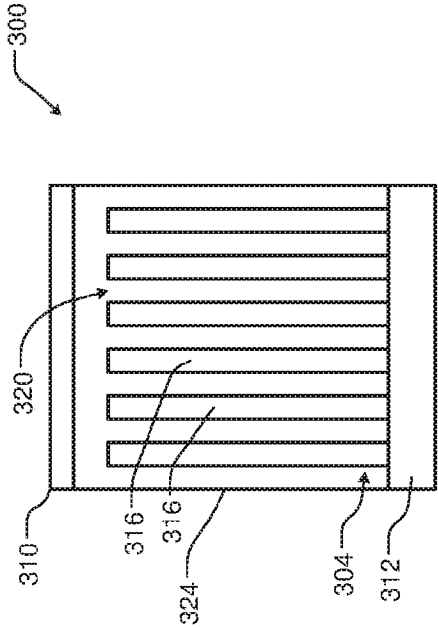


FIG. 3B

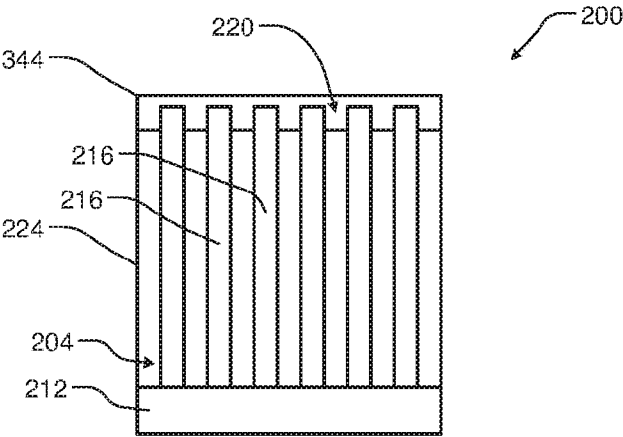


FIG. 3C

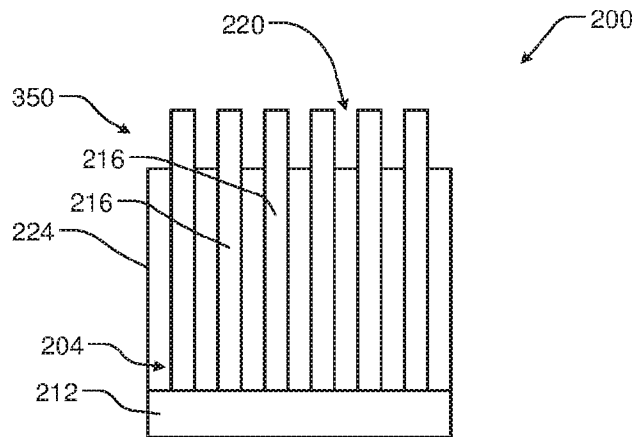
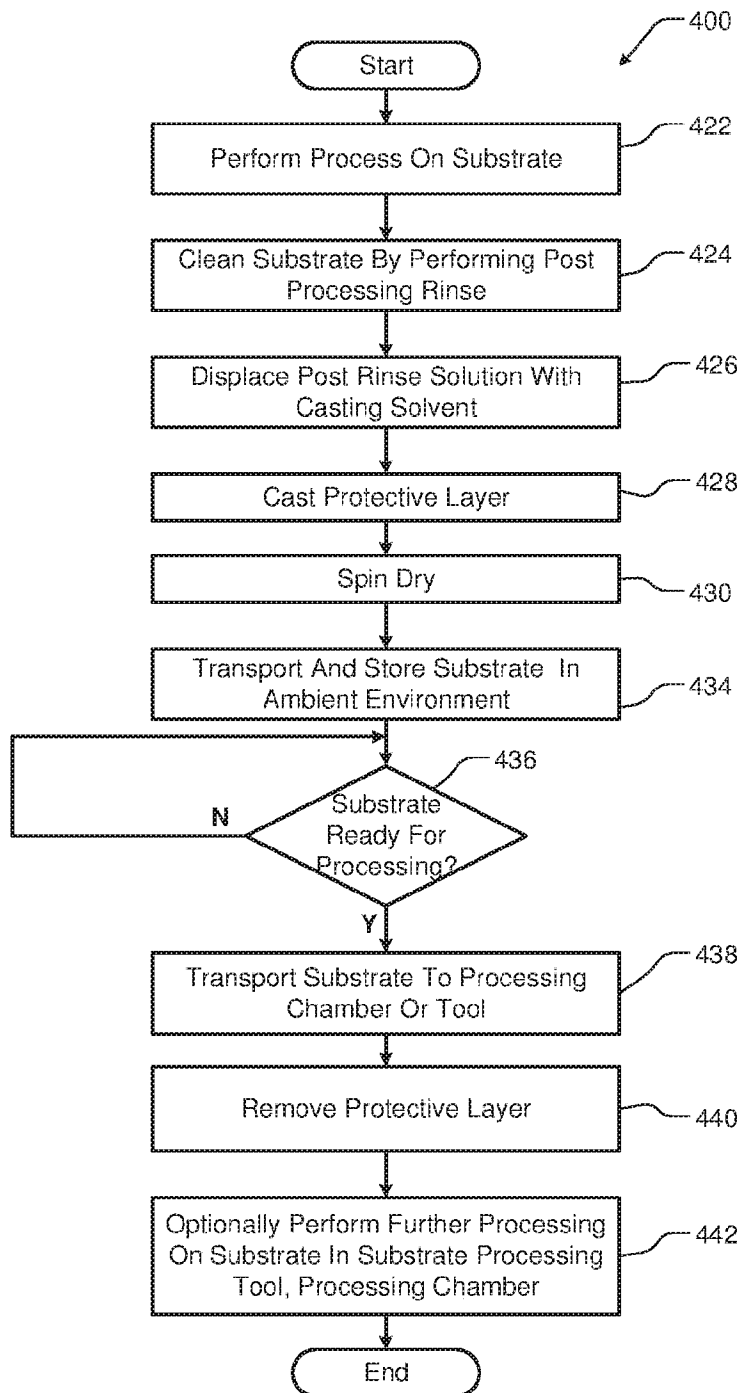
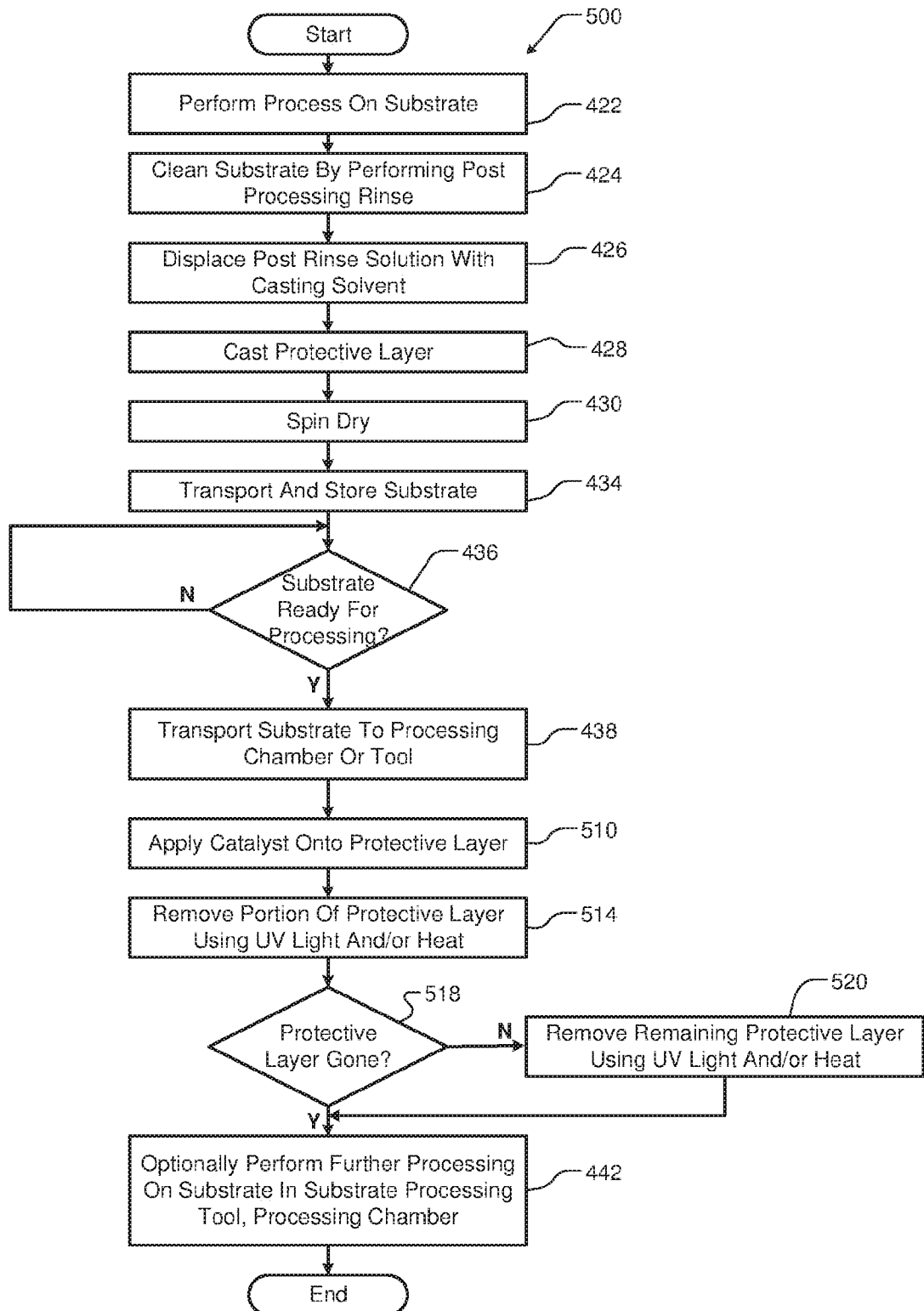


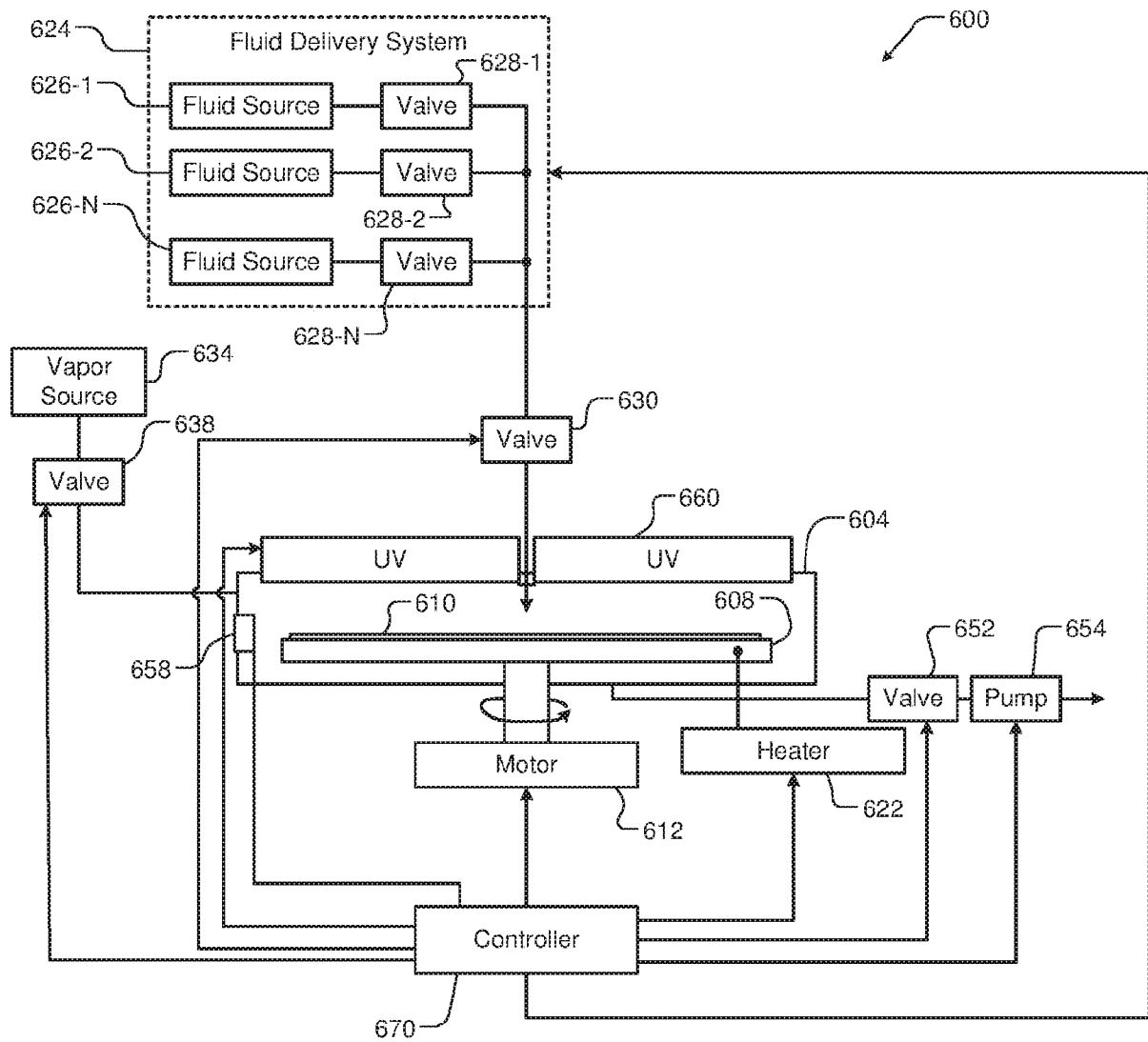
FIG. 3D

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**FIG. 4**

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**FIG. 5**

**FIG. 6**

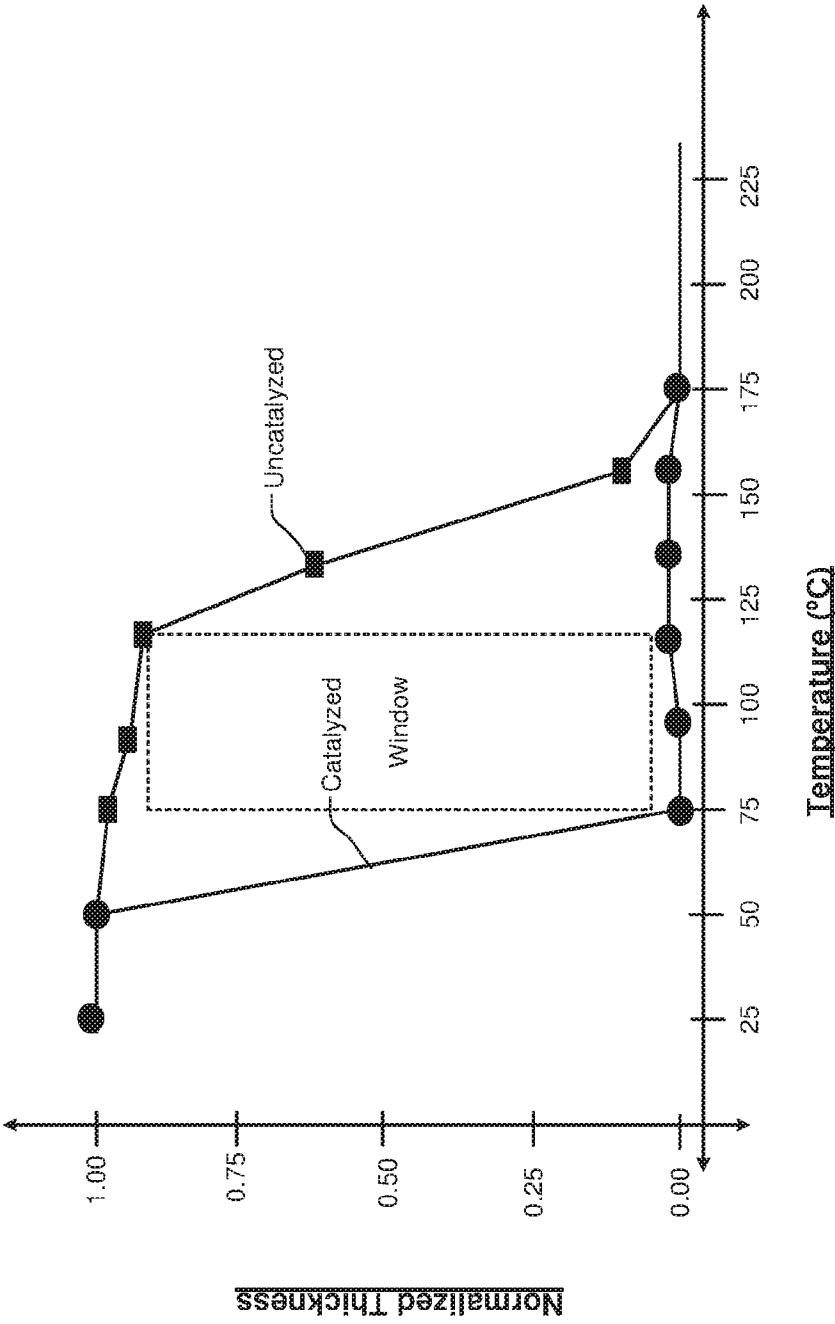


FIG. 7

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2020/015451**A. CLASSIFICATION OF SUBJECT MATTER****H01L 21/56(2006.01)i, C09D 5/16(2006.01)i, H01L 21/02(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01L 21/56; C09D 129/04; C09D 129/12; C09D 5/00; G03F 007/004; H01L 021/31; H01L 21/304; H01L 21/78; C09D 5/16; H01L 21/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: surface-protecting, co-polymer, de-polymerizing, ultraviolet, heating, acidic-vapor

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 10-2009-0006551 A (SILTRON INC.) 15 January 2009 Paragraphs [0005]-[0037]; claim 1; and figure 7.	1-20
Y	JP 1999-021496 A (NIPPON SHOKUBAI CO., LTD.) 26 January 1999 Paragraphs [0021]-[0026]; and claim 1.	1-20
Y	US 2004-0146803 A1 (PAUL A. KOHL et al.) 29 July 2004 Paragraphs [0090]-[0092]; and claim 1.	5-13, 16-20
A	US 2018-0204770 A1 (HONEYWELL INTERNATIONAL INC.) 19 July 2018 Claim 1; and figures 1-5.	1-20
A	US 2004-0087176 A1 (MATTHEW E. COLBURN et al.) 06 May 2004 Paragraphs [0034]-[0035]; and figures 1-5.	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

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Date of mailing of the international search report

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Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea

Facsimile No. +82-42-481-8578

Authorized officer

Kim, Yeonkyung

Telephone No. +82-42-481-3325



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2020/015451

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
KR 10-2009-0006551 A	15/01/2009	KR 10-0931195 B1	10/12/2009
JP 1999-021496A	26/01/1999	None	
US 2004-0146803 A1	29/07/2004	CN 101831163 A CN 101831163 B CN 1717437 A CN 1717437 B EP 1567580 A2 EP 1567580 A4 EP 2228401 A1 JP 2006-504853 A JP 2010-106286 A JP 4608317 B2 KR 10-1032670 B1 KR 10-2005-0071639 A US 2006-0263718 A1 US 2009-0107952 A1 US 2009-0120905 A1 US 7052821 B2 US 7459267 B2 US 7695894 B2 US 7923194 B2 WO 2004-042797 A2 WO 2004-042797 A3	15/09/2010 10/07/2013 04/01/2006 28/03/2012 31/08/2005 30/04/2008 15/09/2010 09/02/2006 13/05/2010 12/01/2011 06/05/2011 07/07/2005 23/11/2006 30/04/2009 14/05/2009 30/05/2006 02/12/2008 13/04/2010 12/04/2011 21/05/2004 07/07/2005
US 2018-0204770 A1	19/07/2018	CN 110168708 A EP 3571712 A1 JP 2020-504454 A KR 10-2019-0100233 A US 0276440 B2 WO 2018-136484 A1	23/08/2019 27/11/2019 06/02/2020 28/08/2019 30/04/2019 26/07/2018
US 2004-0087176 A1	06/05/2004	CN 1305111 C CN 1499290 A KR 10-0561493 B1 KR 10-2004-0040346 A US 2005-0233597 A1 US 2008-0265382 A1 US 2008-0265415 A1 US 6911400 B2 US 7948051 B2 US 8491987 B2	14/03/2007 26/05/2004 20/03/2006 12/05/2004 20/10/2005 30/10/2008 30/10/2008 28/06/2005 24/05/2011 23/07/2013