

METHOD AND APPARATUS FOR REMOVING PARTICLES OR PHOTORESIST ON SUBSTRATES

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention generally relates to a semiconductor wet cleaning field, and more particularly to a method and an apparatus for removing particles or photoresist on semiconductor substrates.

2. The Related Art

[0002] Conventionally, organic photoresist strip processes were developed via using a combination of dry and wet treatments. However, dry treatments based on reactive plasma ashing have been shown to present issues, such as plasma induced damage, resist popping, incomplete resist removal, and byproduct redeposition, consequently, it requires follow up with a wet stripping/cleaning. To avoid plasma issues, wet stripping processes based on organic solvents and aggressive acid chemistries, such as aqueous mixtures of sulfuric acid and hydrogen peroxide (SPM), were developed. Nowadays, SPM is widely used for photoresist stripping and post-resist strip cleaning processes.

[0003] In the past tens of years, SPM wet stripping process is typically carried out in a wet bench tool because of its high throughput, while maintaining a low cost of operation. However, today's SPM bench-only wet process cannot achieve the cleaning performance required for advanced technology nodes due to (1) the particle removal efficiency by wet bench tool has been reduced significantly when the particle sizes are reduced to 45 nm and below; (2) not able to remove photoresists treated by high dose ($>1E17$ ions/cm²) of ion implantation because of limited temperature of SPM bath with normal temperature of 145 °C. Single substrate wet stripping process seems to be an alternative solution for new generation of IC manufacture node which needs to remove particles smaller than 45 nm and clean photoresist treated by high dose of ion implantation due to its higher temperature of SPM (180 °C) . However, single substrate SPM

process requires the SPM mixture to be heated to high temperatures with only a fraction of the hot SPM touching the substrate surface and most of the SPM spinning off from the substrate, which cannot be reused due to loss of chemical energy. This process results in a great consumption of sulfuric acid, what's worse, disposal of waste is expensive and harmful to the environment.

[0004] In order to reduce environmental impact caused by large amount of SPM consumption, utilizing ozone chemistry for photoresist removal to replace SPM wet stripping process has been tried and tested. However, the cleaning efficiency especially for photoresist treated by medium dose ($1\text{E}15\text{ ions/cm}^2$) and high dose ($>1\text{E}17\text{ ions/cm}^2$) of ion implantation was much lower than that of high temperature ($>180^\circ\text{C}$) of single substrate SPM process.

[0005] From a removal efficient and environmental point of view, an integrated cleaning system and process method that combines a traditional bench SPM cleaning module and a single substrate cleaning module into one wet-clean system is disclosed in PCT patent application No. PCT/CN2018/090227, filed on Jun 7, 2018. This system overcomes the challenges of traditional bench-only and single-only wet cleaning systems, using a two-step approach to optimize the advantages of wet bench and single substrate cleaning, achieving a cleaning efficiency that is comparable to the single substrate SPM cleaning while, at the same time, it allows the SPM to be recycled and reused and it greatly reduces the consumption of sulfuric acid. However, SPM temperature in bath is critical for wet stripping process for photoresist treated by high dose of ion implantation. But, a higher temperature can cause rapid decomposition of H_2O_2 or fast depletion of the H_2O_2 , therefore SPM used in this system can only be heated as high as 150°C . It is clear that for the high energy-high dose implanted resist, 150°C SPM cannot remove thick crust formed during ion implantation.

SUMMARY

[0006] The present invention discloses a method and an apparatus to remove fine particles at high efficiency and to remove photoresist and residuals treated by high energy and high dose ion implantation with much lower consumption of SPM chemicals.

[0007] More specifically, the present invention discloses a combination of DIO_3 and SPM substrate photoresist wet stripping method and a substrate photoresist wet stripping apparatus.

[0008] According to one embodiment of the present invention, a method for removing particles or photoresist from substrates comprises the following procedures: processing one or more substrates in a SPM bath and then in a DI water rinsing bath in a bench module, then keeping the one or more substrates being in wet state and transferring the one or more substrates to subsequent one or more single chambers of a single module to perform single substrate DIO_3 cleaning for remaining residues removal and final cleaning.

[0009] According to another embodiment of the present invention, a method for removing particles or photoresist from substrates comprises the following procedures: processing one or more substrates in a DIO_3 bath then in a SPM bath and then in a DI water rinsing bath in a bench module, then keeping the one or more substrates being in wet state and transferring the one or more substrates to subsequent one or more single chambers of a single module to perform single substrate cleaning for remaining residues removal and final cleaning.

[0010] According to another embodiment of the present invention, a method for removing particles or photoresist from substrates comprises the following procedures: processing one or more substrates in a HF bath then in a DIO_3 bath then in a SPM bath and then in a DI water rinsing bath in a bench module, then keeping the one or more substrates being in wet state and transferring the one or more substrates to subsequent one or more single chambers of a single module to perform single substrate cleaning for remaining residues removal and final cleaning.

[0011] According to another embodiment of the present invention, a method for removing particles or photoresist from substrates comprises the following procedures: processing one or more substrates in one or more single chambers of a single module to perform single substrate DIO_3 cleaning, then processing the one or more substrates in a SPM bath and then in a DI water rinsing bath in a bench module, then keeping the one or more substrates being in wet state and transferring the one or more substrates to the one or more single chambers of the single module to perform single substrate cleaning for remaining residues removal and final cleaning.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 illustrates cleaning performance comparison between stand-alone bench SPM cleaning plus stand-alone single cleaning and a Bench-Single integrated cleaning.

[0013] FIG. 2 illustrates a bench DIO_3 -SPM combination process and a subsequent single substrate cleaning process in an integrated sequence according to an exemplary embodiment of the present invention.

[0014] FIG. 3 illustrates another bench DIO_3 -SPM combination process and a subsequent single substrate cleaning process in an integrated sequence according to another exemplary embodiment of the present invention.

[0015] FIG. 4 illustrates a bench SPM-based process and a subsequent single substrate cleaning process including a DIO_3 process in an integrated sequence according to an exemplary embodiment of the present invention.

[0016] FIG. 5 illustrates another bench SPM-based process and a subsequent single substrate cleaning process including a DIO_3 process in an integrated sequence according to another exemplary embodiment of the present invention.

[0017] FIG. 6 illustrates a single substrate DIO_3 -based cleaning process, a bench SPM-based process and a subsequent single substrate cleaning process in an integrated sequence according to an exemplary embodiment of the present invention.

[0018] FIG. 7 illustrates another single substrate DIO_3 -based cleaning process, a bench SPM-based process and a subsequent single substrate cleaning process in an integrated sequence according to another exemplary embodiment of the present invention.

[0019] FIG. 8 illustrates a top view of an apparatus for removing particles or photoresist on substrates according to an exemplary embodiment of the present invention.

[0020] FIG. 9 illustrates a perspective view of a bench module of the apparatus shown in FIG. 8.

[0021] FIG. 10 illustrates a top view of an apparatus for removing particles or photoresist on substrates according to another exemplary embodiment of the present invention.

[0022] FIG. 11 illustrates a perspective view of a bench module of the apparatus shown in FIG. 10.

[0023] FIG. 12A illustrates a perspective view of a DIO_3 bath according to an exemplary embodiment of the present invention.

[0024] FIG. 12B illustrates a perspective view of the DIO_3 bath of which shutter is open.

[0025] FIG. 12C illustrates a cross-sectional view of the DIO_3 bath shown in FIG. 12B.

DETAILED DESCRIPTION OF EMBODIMENTS

[0026] During the SPM cleaning process, the challenges experienced are that viscous SPM is hard to rinse off and hygroscopic sulfur (S) residues adhere to the substrate surface and absorb moisture, which causes particulate defects are hard to remove after drying. Therefore, after the bench SPM processing, the substrate has to be transferred into a single process chamber with a wet status, which prevents the substrate surface from drying out to form watermark defects or to absorb ionic and particulate pollutants from the external environment.

[0027] As shown in FIG. 1, a comparison test was designed to clarify cleaning performance between stand-alone bench SPM cleaning plus stand-alone single cleaning process and a Bench-Single integrated cleaning process.

[0028] **Test 1: stand-alone bench SPM cleaning plus stand-alone single cleaning**

[0029] a) Sequence 1: bench process: SPM +QDR (quick dump rinse) + Dry;

[0030] More specifically, the bench process is performed in a bench tool. The bench process comprises the steps: processing at least one wafer with SPM, rinsing the wafer by a way of QDR, and at last drying the wafer.

[0031] b) Sequence 2: the wafer stays in a FOUP for 3 hours; and

[0032] c) Sequence 3: single process: $\text{SC1}+\text{N}_2$ Spray $\text{SC1}+\text{N}_2$ Dry.

[0033] More specifically, the single process is performed in a single wafer cleaning tool. The single process comprises the steps: processing the wafer with SC1 , processing the wafer with SC1 which is atomized to generate fine droplets and accelerated by pressurized nitrogen gas

through a gas-liquid atomizing spray nozzle (N_2 Spray SC1), rinsing the wafer with DIW, and at last drying the wafer with N_2 .

[0034] Test 2: Bench-Single integrated cleaning

[0035] Bench process of Bench-Single integrated cleaning: SPM + QDR, and

[0036] Single process of Bench-Single integrated cleaning: SC1+ N_2 Spray SC1+ N_2 Dry.

[0037] More specifically, the bench process and the single process are performed in a Bench-Single integrated cleaning tool. The Bench-Single integrated cleaning process comprises the steps: processing at least one wafer with SPM and then rinsing the wafer by a way of QDR in a bench module of the Bench-Single integrated tool, then transferring the wafer to a single module of the Bench-Single integrated tool to perform the single process which further comprises processing the wafer with SC1, processing the wafer with SC1 which is atomized to generate fine droplets and accelerated by pressurized nitrogen gas through a gas-liquid atomizing spray nozzle (N_2 Spray SC1), rinsing the wafer with DIW, and at least drying the wafer with N_2 .

[0038] Test 1 shows 40nm particle add amount after the wafers have been run through the stand-alone bench SPM cleaning is 297~331. The wafers are then stored in the FOUP for 3 hours before being processed in the stand-alone single wafer cleaning tool, and 40nm particle add amount shown in test 1 is decreased to 117~130. Also as shown in FIG. 1, the test 2 of Bench-Single integrated cleaning shows 40nm particle add amount is decreased to -1~ -9. FIG. 1 shows that the cleaning effect of the Bench-Single integrated cleaning is significantly better than the stand-alone bench SPM cleaning plus the stand-alone single cleaning. The key conclusion for getting better defect removal performance is to keep the wafer surface in a wet state between the post bench SPM cleaning process and the pre single wafer cleaning process. Because the defects are very difficult to remove even by a single wafer cleaning process after the wafer has been dried.

[0039] During the SPM cleaning process, it is very critical to control and keep a certain thickness of liquid film on the wafer surface between the post bench SPM cleaning process and the pre single wafer cleaning process, which can prevent the wafer surface from drying out to form watermark defects or to absorb ionic and particulate pollutants from the external environment. However, it should be noted that in actual application, even with a Bench-Single

integrated cleaning system, a perfect wafer wetting status is hard to achieve, so that a DIO_3 and SPM combination cleaning process is disclosed in the present invention to eliminate the impacts during the wafer being transferred from the bench module to the single module. Furthermore, the residua of sulfur by products and particles attached on the wafer surface after the SPM process is harder to remove by SC1 only process.

[0040] In order to clarify a DIO_3 enhanced SPM cleaning performance, tests are carried out in a Bench-Single integrated cleaning tool with 12 inch bare silicon wafer, and particle amounts are measured on a KLA-Tencor Surfscan SP5 with 19nm metrology recipe. As shown in Table 1, the test conditions are below:

[0041] **Test 1:** Bench process in the Bench-Single integrated cleaning tool: SPM + Hot QDR, *plus* Single process in the Bench-Single integrated cleaning tool: SC1+N₂ Spray SC1+N₂ Dry.

[0042] **Test 2:** Bench process in the Bench-Single integrated cleaning tool: SPM + Hot QDR, *plus* Single process in the Bench-Single integrated cleaning tool: O₃+SC1+N₂ Spray SC1+N₂ Dry.

[0043] **Test 3:** Bench process in the Bench-Single integrated cleaning tool: SPM + Hot QDR, *plus* Single process in the Bench-Single integrated cleaning tool: DHF+O₃+SC1+N₂ Spray SC1+N₂ Dry.

[0044] Table 1: DIO_3 enhanced SPM cleaning tests in a Bench-Single integrated cleaning tool

Item	Bench process	Single process	PRE Count		POST Count		Delta (Post-Prec)				Total	Total
			19nm	1um	19nm	1um	19-30nm	30-10nm	40-60nm	>60nm		
Bench-Single integrated cleaning process	SPM+Hot QDR	Test 1: SC1-N ₂ Spray	521	0	528	0	-11	7	3	-2	-5	1%
		SC1-DWF+N ₂ Dry	301	0	308	0	-8	11	9	-7	5	-2%
		Test 2: O ₃ -SC1-N ₂ Spray	381	0	392	0	-62	-3	-7	-2	-79	28%
		SC1-DWF+N ₂ Dry	272	0	292	0	-55	-5	1	-15	-74	27%
		Test 3: DHF-O ₃ -SC1-N ₂ Spray	251	0	291	0	-56	-3	-2	-3	-70	37%
		SC1-DWF+N ₂ Dry	283	0	298	0	-64	-3	-3	-2	-97	34%

[0045]

[0046] Test shows combine bench SPM- hot QDR cleaning and the single cleaning in one sequence, after the single cleaning process with SC1-N₂ Spray SC1, particle has a little added. The single cleaning process with O₃-SC1-N₂ Spray SC1 can enhance particle remove. The single cleaning process with DHF-O₃-SC1-N₂ Spray SC1 has the best particle remove efficiency. The DIO_3 and SPM combination cleaning process shows a positive cleaning effect. Here, HF

will undercut particles attached on the wafer surface, and DIO_3 will further remove sulfur by products and conditioning the wafer surface after the HF process.

[0047] For photoresist irradiated or treated by high dose ($>1\text{E}17$ ion/ cm^2) and high energy (>10 KeV) ion implantation, the C-H inside photoresist are disordered, cross-linked and formed double bonds $\text{C}=\text{C}$ or graphite structure. Those graphite structure materials form hard crust on the surface of photoresist, and are hard to remove unless using very high temperature ($>180^\circ\text{C}$) SPM with single wafer cleaning tool. However, with wet bench process, the temperature of SPM in a bath can only be heated to 150°C or less due to quick decomposition of H_2O_2 . Therefore it is critical to remove the crust which is being hardened in the ion implantation.

[0048] O_3 is a very strong oxidant. The DIO_3 process directly oxidizes $\text{C}=\text{C}$ double bonds, and the resist becomes thinner during this reaction. Taking the ozonolysis of alkenes mechanism for example, it involves the attack of ozone on the $\text{C}=\text{C}$ double bonds and forms the molozonide intermediate which is quite unstable. Due to this unstable nature, the molozonide continues reacting - breaking apart to form a carbonyl molecule and a carbonyl oxide molecule. The carbonyl molecule and the carbonyl oxide molecule formed in the first step rearrange themselves, reforming to create a more stable ozonide intermediate. This ozonide intermediate can be subjected to either an oxidative workup or a reductive workup. The oxidative workup will give carboxylic acid as the product whereas the reductive workup will yield aldehydes or ketones.

[0049] After the crust being treated by DIO_3 , and the remaining by products will be removed by SPM with temperature less than 150°C .

[0050] Therefore, for removing particles or photoresist, especially for removing photoresist treated by medium dose or high dose of ion implantation, the present invention discloses a plurality of methods which combine DIO_3 and SPM in one cleaning sequence.

[0051] According to one embodiment of the present invention, a method for removing particles or photoresist on substrates comprises a bench DIO_3 -SPM combination process and a subsequent single cleaning process in an integrated sequence, the method comprising:

[0052] transferring one or more substrates into a DIO_3 solution accommodated in a DIO_3 bath;

[0053] after the one or more substrates are processed in the DIO_3 bath, taking the one or more substrates out from the DIO_3 bath and transferring the one or more substrates into a SPM solution accommodated in a SPM bath;

[0054] after the one or more substrates are processed in the SPM bath, taking the one or more substrates out from the SPM bath and rinsing the one or more substrates; and

[0055] transferring the one or more substrates to one or more single chambers to perform single substrate cleaning and drying process.

[0056] More specifically, referring to FIG. 2, the bench DIO_3 -SPM combination process is performed in a bench module of a Bench-Single integrated cleaning apparatus. The bench DIO_3 -SPM combination process comprises:

[0057] transferring one or more substrates into a DIO_3 solution accommodated in a DIO_3 bath to perform a DIO_3 oxidizing process, wherein the DIO_3 is used here for photoresist pre-treatment, including oxidizing $\text{C}=\text{C}$ double bonds and softening the photoresist crust, which would facilitate the subsequent photoresist stripping process;

[0058] after the one or more substrates are processed in the DIO_3 bath, taking the one or more substrates out from the DIO_3 bath and transferring the one or more substrates into a SPM solution accommodated in a SPM bath to perform a SPM stripping process, wherein the SPM is used here for removing the softened photoresist crust and the bulk resist by the intense chemical reaction; and

[0059] after the one or more substrates are processed in the SPM bath, taking the one or more substrates out from the SPM bath and transferring the one or more substrates to a DIW bath to perform a rinsing process.

[0060] The sulfuric mixtures act as aggressive strippers during SPM cleaning process. Two types of stripping mechanisms are widely accepted. The first is dehydration mechanism: the first action is that sulfuric acid can cause organic carbonization and dehydration, by which the resist is firstly undercut and then floats away of the substrate. The second is oxidation mechanism: the mixing of sulfuric acid and hydrogen peroxide forms Caro's acid (H_2SO_5), which oxidizes the carbonized resist product into CO and CO_2 as an extremely strong oxidant.

[0061] The reactions in the SPM cleaning process are:

[0062] $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2 \rightarrow \text{HO}-(\text{SO}_2)-\text{O}-\text{OH} + \text{H}_2\text{O}$

[0063] $\text{HO}-(\text{SO}_2)-\text{O}-\text{OH} + -(\text{CH}_2)_n \rightarrow \text{CO}_2 + \text{H}_2\text{O}$

[0064] The SPM temperature in the SPM bath is critical for removing photoresist treated by high dose of ion implantation. However, a higher temperature can cause rapid decomposition of H_2O_2 or fast depletion of the H_2O_2 . Therefore, the SPM used in the bench module can only be heated as high as 150°C . It is clear that for the high energy-high dose implanted resist, 150°C SPM cannot remove the thick photoresist crust formed during ion implantation.

[0065] Therefore, the present invention discloses a method by adding DIO_3 (ozonized DIW) process prior to the SPM ($<150^\circ\text{C}$) process. O_3 is a very strong oxidant and can directly oxidize $\text{C}=\text{C}$ double bonds, so that the thick crust of resist formed during high energy and high dose ion implantation can be softened during this reaction. After the crust of resist being softened, the underneath resist can be removed by SPM with temperature less than 150°C .

[0066] In an embodiment, the SPM solution is a mixture of H_2SO_4 and H_2O_2 , and H_2SO_4 and H_2O_2 mix ratio is 3:1 to 50:1, the temperature of the mixture is 80°C to 150°C .

[0067] In an embodiment, the rinsing process in the DIW bath comprises QDR (Quick dump drain) and overflow rinse.

[0068] In an embodiment, the ozone concentration of DIO_3 solution in the DIO_3 bath is 30 ppm to 120 ppm.

[0069] In an embodiment, the flow rate of DIO_3 solution supplied to the DIO_3 bath is 10LPM to 30LPM.

[0070] In an embodiment, before the one or more substrates are transferred to the DIO_3 bath, the liquid in the DIO_3 bath is DIW. A procedure of the DIO_3 oxidizing process further comprises:

[0071] step 1: opening a shutter of the DIO_3 bath, transferring the one or more substrates into the DIW in the DIO_3 bath, closing the shutter of the DIO_3 bath, in order to prevent ozone gas leakage, before the one or more substrates are transferred to the DIO_3 bath, the liquid in the DIO_3 bath is DIW;

[0072] step 2: overflowing an ozonized DIW from the DIO_3 bath bottom to replace the DIW in the DIO_3 bath;

[0073] step 3: after the DIO_3 bath is full of the ozonized DIW, keeping the ozonized DIW overflowing for a calculated time, in an embodiment, the time is 5 to 15 min, better 10 min;

[0074] step 4: quick dump drain the ozonized DIW;

[0075] step 5: filling the DIO_3 bath with pure DIW;

[0076] step 6: opening the shutter of the DIO_3 bath, taking the one or more semiconductor substrates out from the DIO_3 bath.

[0077] In the step 3, in consideration of compensating for half-life of ozone destruction and maintaining a constant ozone concentration, the DIO_3 supply flow rate must be high enough to refill the DIO_3 bath, and make sure the ozone concentration would not drop too much during process. As well known, the ozonized DIW decays rapidly and the half-life of ozonized DIW at 25 °C and pH 7.0 is typically about 15 minutes. How to compensate for half-life of ozone destruction and maintain a constant ozone concentration is important. In order to assure its strong oxidizing property, the decreasing of DIO_3 concentration during process should be controlled less than $D=10$ ppm, and the process should have a full consideration of ozone decomposition rate, fresh ozonized DIW replenishing flow rate, and an optimal DIO_3 process time.

[0078] Assume t is the half-life of DIO_3 , C is the target concentration of DIO_3 , V is the volume of the DIO_3 bath, the average ozone decomposition rate can be estimated as $d = \frac{1}{2} * \frac{C}{t}$

(instant ozone decomposition rate will vary and be bigger at higher concentration and smaller at lower concentration), the fresh ozonized DIW replenishing flow rate is $r=V/(D/d)$. The DIO_3 process time is in the range of 5 min to 15 min, better to be 10 min.

[0079] In an embodiment, the ozone concentration of DIO_3 solution in the DIO_3 bath is 90 ppm, the half-life of DIO_3 is 15min, the volume of the DIO_3 bath is 50 L, the average ozone decomposition rate is $d=0.5*90/15=3\text{ppm/min}$, the fresh ozonized DIW replenishing flow rate is $r=50/(10/3)=15$ LPM. In consideration of using average ozone decomposition rate in the calculation, it is better to use $2r = 30$ LPM in practical application.

[0080] In the present invention, the DIO_3 bath combines both ozonized DIW and pure DIW in one bath, and the DIO_3 process and DIW rinsing process can be performed in one bath,

solving the environment problem caused by ozone gas escaped from DIO_3 liquid which smells pungent and is a toxic gas which may cause harmful effects on the health.

[0081] After the one or more substrates are performed the rinsing process in the DIW bath and before the one or more substrates are transferred to the one or more single chambers of a single module of the Bench-Single integrated cleaning apparatus, keep the one or more substrates being in wet state. More specifically, transferring the one or more substrates to a wetting buffer area to keep the substrates being in wet status.

[0082] Please continue to refer to FIG. 2. In one embodiment of the present invention, the single substrate cleaning and drying process is performed in one single chamber of a single module of the Bench-Single integrated cleaning apparatus. The single substrate cleaning and drying process in one single chamber comprises:

[0083] spraying HF formulation solution on the substrate surface to perform a surface etching process;

[0084] spraying DIO_3 on the substrate surface to perform a DIO_3 oxidizing process;

[0085] spraying SC1 on the substrate surface to perform a particle removal process;

[0086] spraying DIW on the substrate surface to perform a DIW rinsing process; and

[0087] drying the substrate.

[0088] Optionally, after the particle removal process by using the SC1, the single substrate cleaning and drying process can further comprise spraying SC2 on the substrate surface to perform metal removal process.

[0089] In another embodiment of the present invention, the single substrate cleaning and drying process in one single chamber comprises:

[0090] spraying DIO_3 on the substrate surface to perform a DIO_3 oxidizing process;

[0091] spraying SC1 on the substrate surface to perform a particle removal process;

[0092] spraying DIW on the substrate surface to perform a DIW rinsing process; and

[0093] drying the substrate.

[0094] Optionally, after the particle removal process by using the SC1, the single substrate cleaning and drying process can further comprise spraying SC2 on the substrate surface to perform metal removal process.

[0095] In yet another embodiment of the present invention, the single substrate cleaning and drying process in one single chamber comprises:

[0096] spraying HF formulation solution on the substrate surface to perform a surface etching process;

[0097] spraying DIO_3 on the substrate surface to perform a DIO_3 oxidizing process;

[0098] spraying DIW on the substrate surface to perform a DIW rinsing process; and

[0099] drying the substrate.

[0100] Optionally, after the DIO_3 oxidizing process, the single substrate cleaning and drying process can further comprise spraying SC2 on the substrate surface to perform metal removal process.

[0101] In yet another embodiment of the present invention, the single substrate cleaning and drying process in one single chamber comprises:

[0102] spraying SC1 on the substrate surface to perform a particle removal process;

[0103] spraying DIW on the substrate surface to perform a DIW rinsing process; and

[0104] drying the substrate.

[0105] Optionally, after the particle removal process by using the SC1, the single substrate cleaning and drying process can further comprise spraying SC2 on the substrate surface to perform metal removal process.

[0106] Referring to FIG. 3, according to another embodiment of the present invention, a method for removing particles or photoresist on substrates comprises a bench DIO_3 -SPM combination process and a subsequent single cleaning process in an integrated sequence. Comparing with the method disclosed in FIG. 2, the difference is that the method disclosed in FIG. 3 further comprises: transferring one or more substrates into a HF formulation solution accommodated in a HF formulation bath to perform a HF formulation dipping process before the one or more substrates are transferred to the DIO_3 bath.

[00107] In an embodiment, the HF formulation solution is a mixture of HF and DIW, and HF and DIW mix ratio is 100:1 to 1000:1.

[00108] In another embodiment, the HF formulation solution is a BOE mixture. HF weight percentage of the BOE mixture is 0.05% to 10%, and NH_4F weight percentage of the BOE mixture is 10% to 40%.

[00109] According to one embodiment of the present invention, a method for removing particles or photoresist on substrates comprises a bench SPM-based process and a subsequent DIO_3 -based single cleaning process in an integrated sequence, the method comprising:

[00110] transferring one or more substrates into a SPM solution accommodated in a SPM bath;

[00111] after the one or more substrates are processed in the SPM bath, taking the one or more substrates out from the SPM bath and rinsing the one or more substrates; and

[00112] transferring the one or more substrates to one or more single chambers to perform single substrate cleaning and drying process, wherein the single substrate cleaning and drying process comprises at least one DIO_3 oxidizing process.

[00113] The purpose of using DIO_3 is to remove residual of Sulfur by products after SPM process and residuals of photoresist which have not been removed by SPM process in the previous bench module. The ozone concentration of DIO_3 is 30ppm to 120ppm, and 80 ppm is preferred.

[00114] More specifically, referring to FIG. 4, the bench SPM-based process is performed in a bench module of a Bench-Single integrated cleaning apparatus. The bench SPM-based process comprises:

[00115] transferring one or more substrates into a SPM solution accommodated in a SPM bath to perform a SPM stripping process, wherein the SPM is used here for removing photoresist crust and the bulk resist by the intense chemical reaction with concentrated sulfuric acid in the bench module; and

[00116] after the one or more substrates are processed in the SPM bath, taking the one or more substrates out from the SPM bath and transferring the one or more substrates to a DIW bath to perform a rinsing process.

[00117] In an embodiment, the SPM solution is a mixture of H_2SO_4 and H_2O_2 , and H_2SO_4 and H_2O_2 mix ratio is 3:1 to 50:1, the temperature of the mixture is 80 °C to 150 °C.

[00118] In an embodiment, the rinsing process in the DIW bath comprises QDR (Quick dump drain) and overflow rinse.

[00119] After the one or more substrates are performed the rinsing process in the DIW bath and before the one or more substrates are transferred to the one or more single chambers of a single module of the Bench-Single integrated cleaning apparatus, keep the one or more substrates being in wet state. More specifically, transferring the one or more substrates to a wetting buffer area to keep the substrates being in wet status.

[00120] Please continue to refer to FIG. 4. In one embodiment of the present invention, the DIO_3 -based single substrate cleaning and drying process is performed in one single chamber of a single module of the Bench-Single integrated cleaning apparatus. The DIO_3 -based single substrate cleaning and drying process in one single chamber comprises:

[00121] spraying HF formulation solution on the substrate surface to perform a surface etching process;

[00122] spraying DIO_3 on the substrate surface to perform a DIO_3 oxidizing process;

[00123] spraying SC1 on the substrate surface to perform a particle removal process;

[00124] spraying DIW on the substrate surface to perform a DIW rinsing process; and

[00125] drying the substrate.

[00126] Optionally, after the particle removal process by using the SC1, the single substrate cleaning and drying process can further comprise spraying SC2 on the substrate surface to perform metal removal process.

[00127] In another embodiment of the present invention, the DIO_3 -based single substrate cleaning and drying process is performed in one single chamber of a single module of the Bench-Single integrated cleaning apparatus. The DIO_3 -based single substrate cleaning and drying process in one single chamber comprises:

[00128] spraying DIO_3 on the substrate surface to perform a DIO_3 oxidizing process;

[00129] spraying SC1 on the substrate surface to perform a particle removal process;

[00130] spraying DIW on the substrate surface to perform a DIW rinsing process; and

[00131] drying the substrate.

[00132] Optionally, after the particle removal process by using the SC1, the single substrate cleaning and drying process can further comprise spraying SC2 on the substrate surface to perform metal removal process.

[00133] In yet another embodiment of the present invention, the DIO₃-based single substrate cleaning and drying process is performed in one single chamber of a single module of the Bench-Single integrated cleaning apparatus. The DIO₃-based single substrate cleaning and drying process in one single chamber comprises:

[00134] spraying HF formulation solution on the substrate surface to perform a surface etching process;

[00135] spraying DIO₃ on the substrate surface to perform a DIO₃ oxidizing process;

[00136] spraying DIW on the substrate surface to perform a DIW rinsing process; and

[00137] drying the substrate.

[00138] Optionally, after the DIO₃ oxidizing process, the single substrate cleaning and drying process can further comprise spraying SC2 on the substrate surface to perform metal removal process.

[00139] Referring to FIG. 5, according to another embodiment of the present invention, a method for removing particles or photoresist on substrates comprises a bench SPM-based process and a subsequent DIO₃-based single cleaning process in an integrated sequence. Comparing with the method disclosed in FIG. 4, the difference is that the method disclosed in FIG. 5 further comprises: transferring one or more substrates into a HF formulation solution accommodated in a HF formulation bath to perform a HF formulation dipping process before the one or more substrates are transferred to the SPM bath. Specifically, transferring the one or more substrates into a HF formulation solution accommodated in a HF formulation bath, after the one or more substrates are processed in the HF formulation bath, taking the one or more substrates out from the HF formulation bath and rinsing the one or more substrates, and then transferring the one or more substrates to the SPM bath. The HF formulation solution can attack photoresist,

and remove Si-containing polymers and fluorocarbon polymers from the substrate sidewall, and would be benefit for subsequent SPM photoresist removal.

[00140] In an embodiment, the HF formulation solution is a mixture of HF and DIW, and HF and DIW mix ratio is 100:1 to 1000:1.

[00141] In another embodiment, the HF formulation solution is a BOE mixture. HF weight percentage of the BOE mixture is 0.05% to 10%, and NH₄F weight percentage of the BOE mixture is 10% to 40%.

[00142] According to one embodiment of the present invention, a method for removing particles or photoresist on substrates comprises a DIO₃-based single substrate cleaning and drying process for photoresist attacking and thinning, a subsequent bench SPM-based process, and a final single substrate cleaning and drying process in an integrated sequence, the method comprising:

[00143] transferring one or more substrates to one or more single chambers to perform single substrate cleaning and drying process, wherein the single substrate cleaning and drying process comprises at least one DIO₃ oxidizing process;

[00144] after the one or more substrates are processed in the one or more single chambers, transferring the one or more substrates into a SPM solution accommodated in a SPM bath;

[00145] after the one or more substrates are processed in the SPM bath, taking the one or more substrates out from the SPM bath and rinsing the one or more substrates; and

[00146] transferring the one or more substrates to the one or more single chambers to perform single substrate cleaning and drying process.

[00147] More specifically, referring to FIG. 6, in an embodiment, the DIO₃-based single substrate cleaning and drying process prior to the bench SPM-based process is performed in one single chamber of a single module of a Bench-Single integrated cleaning apparatus. The DIO₃-based single substrate cleaning and drying process comprises: a HF formulation surface etching process, a DIO₃ oxidizing process, a DIW rinsing process and a drying process.

[00148] In another embodiment, the DIO₃-based single substrate cleaning and drying process prior to the bench SPM-based process is performed in one single chamber of a single module of

a Bench-Single integrated cleaning apparatus. The DIO₃-based single substrate cleaning and drying process comprises: a DIO₃ oxidizing process, a DIW rinsing process and a drying process.

[00149] In an embodiment, the bench SPM-based process is performed in a bench module of the Bench-Single integrated cleaning apparatus. The bench SPM-based process comprises: a SPM stripping process and a DIW rinsing process.

[00150] After the one or more substrates are performed the DIW rinsing process in the bench module and before the one or more substrates are transferred to the one or more single chambers, keep the one or more substrates being in wet state. More specifically, transferring the one or more substrates to a wetting buffer area to keep the substrates being in wet status.

[00151] Similar to the method disclosed in FIG. 2, in one embodiment, the single substrate cleaning and drying process after the bench SPM-based process is performed in one single chamber of the single module of the Bench-Single integrated cleaning apparatus. The single substrate cleaning and drying process comprises: a HF formulation surface etching process, a DIO₃ oxidizing process, a SC1 particle removal process, a DIW rinsing process and a drying process. Optionally, after the SC1 particle removal process, the single substrate cleaning and drying process can further comprise a SC2 metal removal process.

[00152] In another embodiment, the single substrate cleaning and drying process after the bench SPM-based process is performed in one single chamber of the single module of the Bench-Single integrated cleaning apparatus. The single substrate cleaning and drying process comprises: a DIO₃ oxidizing process, a SC1 particle removal process, a DIW rinsing process and a drying process. Optionally, after the SC1 particle removal process, the single substrate cleaning and drying process can further comprise a SC2 metal removal process.

[00153] In yet another embodiment, the single substrate cleaning and drying process after the bench SPM-based process is performed in one single chamber of the single module of the Bench-Single integrated cleaning apparatus. The single substrate cleaning and drying process comprises: a HF formulation surface etching process, a DIO₃ oxidizing process, a DIW rinsing process and a drying process. Optionally, after the DIO₃ oxidizing process, the single substrate cleaning and drying process can further comprise a SC2 metal removal process.

[00154] In yet another embodiment, the single substrate cleaning and drying process after the bench SPM-based process is performed in one single chamber of the single module of the Bench-Single integrated cleaning apparatus. The single substrate cleaning and drying process comprises: a SC1 particle removal process, a DIW rinsing process and a drying process. Optionally, after the SC1 particle removal process, the single substrate cleaning and drying process can further comprise a SC2 metal removal process.

[00155] Referring to FIG. 7, according to another embodiment of the present invention, a method for removing particles or photoresist on substrates comprises a DIO_3 -based single substrate cleaning and drying process for photoresist attacking and thinning, a subsequent bench SPM-based process, and a final single substrate cleaning and drying process in an integrated sequence. Comparing with the method disclosed in FIG. 6, the difference is that the method disclosed in FIG. 7 further comprises: a HF formulation dipping process prior to the SPM stripping process.

[00156] In all embodiments described above in the present invention, the DIO_3 is solution dissolved ozone in DIW. The SC1 is a mixture of ammonium hydroxide and hydrogen peroxide in deionized water, sometime called “standard clean-1”. The SC2 is a mixture of hydrochloric acid and hydrogen peroxide in deionized water, sometime called “standard clean-2”.

[00157] It should be recognized that in the single chamber, one DIW rinsing process can be inserted between any two chemical processes. For example, between the DIO_3 oxidizing process and the SC1 particle removal process, one DIW rinsing process can be inserted there between.

[00158] The present invention discloses an apparatus for removing particles or photoresist on substrates. The apparatus includes a bench module configured to implement one or more substrates bench cleaning process, a single module having multiple single chambers configured to implement single substrate cleaning and drying process and a process robot configured to transfer the one or more substrates between the bench module and the single module, wherein the bench module has at least one DIO_3 bath configured to accommodate DIO_3 solution for processing the one or more substrates, at least one SPM bath configured to accommodate SPM solution for processing the one or more substrates, at least one DIW bath configured to accommodate DIW for rinsing the one or more substrates, and at least one second substrate

transfer robot configured to transfer the one or more substrates among the DIO₃ bath, the SPM bath and the DIW bath.

[00159] More specifically, referring to FIG. 8 and FIG. 9, an apparatus for removing particles or photoresist on substrates according to one exemplary embodiment of the present invention is illustrated. The apparatus includes a plurality of, e.g. four load ports 81 each of which receives a FOUP, an index robot 82, a buffer 88, a bench module 83, a process robot 84 and a single module 85 having multiple single chambers 851.

[00160] The bench module 83 includes a substrate loader 8301, a cleaning bath 8302, a first HF formulation bath 8303, a second HF formulation bath 8304, a first DIO₃ bath 8305, a second DIO₃ bath 8306, a SPM bath 8307, a first DIW bath 8308, a second DIW bath 8309, a wetting buffer area 8310, a first substrate transfer robot 8313, a second substrate transfer robot 8314, a third substrate transfer robot 8315, a first lifter 8311, a second lifter 8312, a third lifter 8316, a fourth lifter 8317 and a fifth lifter 8318.

[00161] When the apparatus is used for removing particles or photoresist on substrates, the process sequence is as follow.

[00162] The index robot 82 gets one or more substrates from one FOUP and transfers the one or more substrates to the substrate loader 8301 by one time or several times. The substrate loader 8301 holds the one or more substrates and then makes the one or more substrates rotate 90 degrees along the horizontal axis and rotate another 90 degrees along the vertical axis so that the one or more substrates are vertically held by the substrate loader 8301.

[00163] The first substrate transfer robot 8313 gets the one or more substrates, e.g. 13 pieces of substrates or 12 pieces of substrates from the substrate loader 8301 and transfers the one or more substrates to the first lifter 8311. The first lifter 8311 holds the one or more substrates and brings the one or more substrates to immerse into HF formulation solution accommodated in the first HF formulation bath 8303. The first substrate transfer robot 8313 gets another one or more substrates from the substrate loader 8301 and transfers the one or more substrates to the second lifter 8312. The second lifter 8312 holds the one or more substrates and brings the one or more substrates to immerse into HF formulation solution accommodated in the second HF formulation bath 8304.

[00164] After the process in the first HF formulation bath 8303 or the process in the second HF formulation bath 8304 completes, the second substrate transfer robot 8314 gets the one or more substrates from the first HF formulation bath 8303 and transfers the one or more substrates to the first DIO₃ bath 8305, or the second substrate transfer robot 8314 gets the one or more substrates from the second HF formulation bath 8304 and transfers the one or more substrates to the second DIO₃ bath 8306. In order to reduce the risk of water mark formed on the substrate surface, it is better to control the transfer time to be less than 20 seconds, and better to be less than 10 seconds. The first lifter 8311 and the second lifter 8312 respectively rise to be above the first HF formulation bath 8303 and the second HF formulation bath 8304. In this embodiment, the first HF formulation bath 8303, the second HF formulation bath 8304, the first DIO₃ bath 8305, and the second DIO₃ bath 8306 are arranged in two rows, and each row has one HF formulation bath and one adjacent DIO₃ bath.

[00165] After the process in the first DIO₃ bath 8305 or the process in the second DIO₃ bath 8306 completes, the second substrate transfer robot 8314 gets the one or more substrates from the first DIO₃ bath 8305 or the second DIO₃ bath 8306 and transfers the one or more substrates to the third lifter 8316. The third lifter 8316 brings the one or more substrates to immerse into SPM solution accommodated in the SPM bath 8307.

[00166] After the process in the SPM bath 8307 completes, the third lifter 8316 rises to be above the SPM bath 8307 and the second substrate transfer robot 8314 gets the one or more substrates from the third lifter 8316 and transfers the one or more substrates to the fourth lifter 8317 or the fifth lifter 8318. The fourth lifter 8317 or the fifth lifter 8318 brings the one or more substrates to the first DIW bath 8308 or the second DIW bath 8309 to implement QDR (Quick dump drain) or overflow rinsing process.

[00167] After the one or more substrates are processed in the first DIW bath 8308 or the second DIW bath 8309, the fourth lifter 8317 or the fifth lifter 8318 rises to be above the first DIW bath 8308 or the second DIW bath 8309, and the third substrate transfer robot 8315 gets the one or more substrates from the fourth lifter 8317 or the fifth lifter 8318 and transfers the one or more substrates to the wetting buffer area 8310 by one time or several times. In the wetting buffer area 8310, the one or more substrates can be rotated from vertical to horizontal and kept in wet status before the one or more substrates are transferred to the one or more single chambers

851 of the single module 85. During this waiting period, the substrates in the wetting buffer area 8310 can be sprayed by DI water to keep the substrate surface wet.

[00168] The process robot 84 gets the one or more substrates from the wetting buffer area 8310 and transfers the one or more substrates to the one or more single chambers 851 to implement single substrate cleaning and drying process.

[00169] After the single substrate cleaning and drying process complete in one single chamber 851, the process robot 84 gets the substrate from the single chamber 851 and transfers it to the buffer 88, and then the index robot 82 gets the substrate from the buffer 88 and transfers it back to the FOUP.

[00170] In the bench module 83, the cleaning bath 8302 is used for cleaning the second substrate transfer robot 8314 while the second substrate transfer robot 8314 is idle.

[00171] Referring to FIG. 10 and FIG. 11, an apparatus for removing particles or photoresist on substrates according to another exemplary embodiment of the present invention is illustrated. The apparatus includes a plurality of, e.g. four load ports 101 each of which receives a FOUP, an index robot 102, a buffer 108, a bench module 103, a process robot 104 and a single module 105 having multiple single chambers 10501.

[00172] The bench module 103 includes a substrate loader 10301, a cleaning bath 10302, a HF formulation bath 10303, a first DIO₃ bath 10304, a second DIO₃ bath 10305, a SPM bath 10306, a first DIW bath 10307, a second DIW bath 10308, a wetting buffer area 10309, a first substrate transfer robot 10310, a second substrate transfer robot 10311, a third substrate transfer robot 10312, a first lifter 10313, a third lifter 10314, a fourth lifter 10315 and a fifth lifter 10316.

[00173] Comparing with the apparatus shown in FIG. 8 and FIG. 9, the apparatus shown in this embodiment has one HF formulation bath 10303 and the HF formulation bath 10303 is set between the first DIO₃ bath 10304 and the second DIO₃ bath 10305. Comparing with the apparatus shown in FIG. 8 and FIG. 9, since the apparatus shown in this embodiment is lack of a second HF formulation bath, and accordingly, the apparatus shown in this embodiment is lack of a second lifter. The substrate transfer sequence is similar to that of embodiment shown in FIG. 8 and FIG. 9, which will not be repeat described herein.

[00174] Please refer to FIGS. 12A-12C. A DIO₃ bath according to an exemplary embodiment of the present invention is illustrated. The DIO₃ bath has an outer bath 121, an inner bath 122, two overflow grooves 123, a shutter 124 and a driving device 125.

[00175] The bottom of the outer bath 121 sets two exhaust ports 1211. Two exhaust lines 128 are respectively connected to the two exhaust ports 1211 of the outer bath 121. A pressure monitor and a pressure damper 129 are respectively set on the two exhaust lines 128. The material of the outer bath 121 can select PVC.

[00176] The inner bath 122 is set in the outer bath 121 and configured to accommodate DIO₃ solution. The inner bath 122 has a substrate holding pedestal 1221 configured to supporting and holding the one or more substrates. Two liquid inlet pipes 1222 are set in the inner bath 122 and configured to supply liquid to the inner bath 122. A drain port 1223 is set at the bottom of the inner bath 122 and configured to drain the liquid in the inner bath 122 to the outside of the DIO₃ bath. Preferably, the drain port 1223 is a quick drain port. The inner bath 122 is made of high purity quartz materials.

[00177] The two overflow grooves 123 are set at both sides of the inner bath 122. Each overflow groove 123 has two drain holes 1231 configured to drain the liquid in the overflow groove 123 to the outside of the DIO₃ bath.

[00178] The shutter 124 is set on the outer bath 121 to seal the outer bath 121. The shutter 124 has at least one gas intake 1241 set on the top side of the shutter 124 and a plurality of exhaust holes 1242 set on the bottom side of the shutter 124. The driving device 125 is connected to the shutter 124 and configured to open or close the shutter 124.

[00179] For better seal, preferably, a seal ring 126 is set on the top of the outer bath 121. At least one pair of locking devices are set on the outer bath 121 to lock the shutter 124 while the shutter 124 is closed. Each locking device has a lock head 1271 and an actuator 1272 connected to the lock head 1271 and driving the lock head 1271 to rotate and rise and fall. After the shutter 124 is closed, the actuator 1272 drives the lock head 1271 to rotate to be above the shutter 124 and then the actuator 1272 drives the lock head 1271 to fall so that the lock head 1271 locks the shutter 124. When the shutter 124 needs to open, the actuator 1272 drives the lock head 1271 to rise and then the actuator 1272 drives the lock head 1271 to rotate to make the lock head 1271 leave the shutter 124 so that the shutter 124 can be open.

[00180] During process, when the one or more substrates are transferred into the DIO_3 bath and held by the substrate holding pedestal 1221, the shutter 124 is closed to seal the DIO_3 bath to prevent ozone gas from leaking to the peripheral environment. Ozone smells pungent and it is a toxic gas which may cause harmful effects on the health. In that case, for safety protection, how to seal the DIO_3 bath and keep a very low ambient ozone level is challenging and important.

[00181] In this embodiment, the inner bath 122 is used for accommodating DIO_3 . The two overflow grooves 123 are used as a DIO_3 overflow area. The outer bath 121 is used for exhausting gas. There is a gap between the top of the inner bath 122 and the top the outer bath 121, which can ensure enough area for exhausting gas, preventing the ozone gas from leaking from the outer bath 121. Furthermore, the present invention also discloses an ozone gas anti-leakage structure. Specifically, a purge gas, such as N_2 or CDA is supplied to the outer bath 121 through the at least one gas intake 1241 set on the top side of the shutter 124 and a plurality of exhaust holes 1242 set on the bottom side of the shutter 124. Purge gas is provided into the outer bath 121, serving as a gas carrier to prevent the ozone gas from leaking to the peripheral environment. Meanwhile, it's important to control the exhaust pressure in the outer bath 121 to balance the gas intake and output, which can be realized by the pressure monitor and the pressure damper 129.

[00182] The foregoing description of the present invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed, and obviously many modifications and variations are possible in light of the above teaching. Such modifications and variations that may be apparent to those skilled in the art are intended to be included within the scope of this invention as defined by the accompanying claims.