Description

METHOD FOR CLEANING A SURFACE

[0001] The invention relates to a method for cleaning a surface of a plate-like article.

[0002] Such plate-like articles can be disc-like articles such as semiconductor wafers, or compact discs as well as polygonal articles such as flat panel displays. Such cleaning methods are typically used for removing particles from structured surfaces of semiconductor wafers.

[0003] A so far unsolved dilemma of removing particles from a surface is the following. Particles typically adhere to the surface and can only be removed by mechanical energy. The higher the mechanical energy, which is introduced to the surface the better the removal efficiency. The negative effect is that the higher the mechanical energy, which is used in a particle removing process, the more stress is applied to the surface, which on the other hand shall be unaffected. Therefore it was thought that particle removing efficiency cannot be improved for a given removing technique without accepting more damage to the surface.

[0004] For semiconductor structures damages however are unacceptable. Mechanical agitation for particle removal is therefore the existing problem, which increases when structures become smaller.

[0005] It is thus an object of the invention to provide a cleaning method which is capable of effectively removing particles without significantly damaging the surface of a plate-like article (especially of a structured semiconductor wafer.)

[0006] The invention meets the objects by providing a method for cleaning a surface of a plate-like article comprising the steps of treating the surface with free flow cleaning, wherein liquid is dispensed through a dispense nozzle onto the surface in a continuous liquid flow; treating the surface with spray cleaning, wherein liquid is directed through a spray nozzle towards the surface in form of droplets; wherein the surface is treated with a spray cleaning step before the free flow cleaning step and a spray cleaning step after the free flow cleaning step.

[0007] The droplets of the spray have a mean diameter (D_{30}) of between 0.001

mm and 0.1 mm (1 – 100 µm). The mean diameter (D_{30}) as for this is application is based on the volume distribution and calculated as follows: $D_{30} = (\Sigma D_i^3 N_i / \Sigma N_i)^{(1/3)}$.

[0008] In one embodiment a sequence of a free flow cleaning step followed by a spray cleaning step is carried out at least twice.

[0009] Advantageously the sequence of a free flow cleaning step followed by a spray cleaning step is carried out at least three times.

[0010] In another embodiment at least one of the free flow cleaning steps utilizes an alkaline cleaning liquid and/or spray cleaning step B comprises an oxidizing agent selected from the group of ozone, hydrogen peroxide and a mixture of ozone, and hydrogen peroxide.

[0011] Preferably the cleaning liquid comprises ammonia. Useful cleaning liquids are e.g. aqueous solutions including hydrogen peroxide and ammonia with a water content of 80 to 99.8 wt.%.

[0012] In another embodiment at least one of the spray cleaning steps utilizes a cleaning liquid selected from the group comprising water, organic solvent alkaline composition, and acidic composition.

[0013] When the free low cleaning step and the spray cleaning step timely overlap not more than 5 s this helps to keep the surface wet during cleaning however to limit splashes.

[0014] If the plate-like article is rotated during at least one cleaning step cleaning is performed evenly across the wafer. Alternatively the nozzles (spray nozzle and/or free flow nozzle) may scan across the wafer whilst the plate-like article keeps unmoved.

[0015] Advantageously the spray cleaning step utilizes a spray nozzle selected from the group airless spray nozzle, two phase nozzle with inner mixing or two phase nozzle with outer mixing.

[0016] Preferably the spray cleaning step utilizes a two phase nozzle with outer mixing.

[0017] In one embodiment the spray nozzle's orifice is located at a distance d to the plate-like article's surface of d being in a range of 0.1 cm to 10 cm. preferably 0.3 cm to 5 cm.

[0018] In another embodiment at least two of the spray cleaning steps are run for

a time period for each spray cleaning step of 5 s to 45 s each; preferably 8 s to 30 s.

[0019] In yet another embodiment at least two of the free flow cleaning steps are run for a time period for each free flow cleaning step of each 5 s to 45 s each; preferably 8 s to 30 s.

[0020] Preferably the spray nozzle scans laterally across the plate-like article; e.g. whilst the plate-like article is rotating.

[0021] The lateral movement parameters as speed, width and the derivation of speed over width may be controlled, so that the nozzle scans across the plate-like article so that each point of the plate-like article's surface is treated for the same period of time.

[0022] Advantageously the plate-like article rotates during spray cleaning and the spray nozzle moves radially across the surface from the rotational center to the plate-like article's edge.

[0023] Further details of the invented method become apparent when reading the description of a preferred embodiment.

[0024] A structured 300 mm semiconductor wafer is placed onto a spin chuck of a spin processor. Alternatively, before the cleaning process a layer on the wafer can be etched or stripped (e.g. with a mixture of concentrated sulfuric acid and hydrogen peroxide)

[0025] 1st step (pre-rinsing step R): rinsing liquid (de-ionized water) at a flow rat of 5 l/min is supplied onto the center of the wafer while it is spun at a spin speed of 300 rpm.

[0026] 2nd step (free flow step A): a diluted SC1 (0.7 vol.-% 32% hydrogen peroxide; 28.4 vol.-% 35% ammoniac water; 70.9 vol.-% water) is dispensed at 40°C at a flow rate of 10 l/min onto the wafer while it is spun at a spin speed of 600 rpm.

[0027] 3rd step (spray step B): a DI-water spray with nitrogen as the carrier gas (continuous phase (cp) = nitrogen ; disperse phase (dp) = DI-water) is sprayed onto the wafer at 25°C at a spin speed of 1000 rpm. Nitrogen flow rate 90 sl/min (sl = standard liter 1013 hPa, 25°C); DI-water flow rate 70 ml/min. During spraying the spray nozzle slowly scans across the wafer from the center to the edge at a speed of 10mm/s (0.01 m/s).

[0028] 4th step (final rinsing step R): rinsing liquid (de-ionized water) at a flow rate of 5 l/min is supplied onto the center of the wafer while it is spun at a spin speed of 300 rpm.

[0029] 5th step (drying step D): rinsing liquid (de-ionized water) is removed with nitrogen-gas with 2 vol.-% 2-propanol while water is supplied onto the wafer so that a liquid-gas boundary layer is scanned from the center to edge so that the wafer remains perfectly dry after liquid removing.

[0030] This process can be summarized as the sequence of the process steps in this order R-A-B-R-D (prior art), wherein the step A takes 60 s and step B takes 45 s.

[0031] According to the current invention (example 1) the 2nd and 3rd process steps are repeated once leading to the order R-A-B-A-B-R-D, wherein each step A takes 30 s and step B takes 22.5 s.

[0032] Surprisingly the particle removing efficiency could be significantly increased (by more than 20%) without changing the process parameters of each step and without increasing the overall process time.

[0033] Each process step may overlap with the previous step, which helps to keep the surface wet during cleaning until it is finally dried. Such overlapping may be in a range of 0.5 s to 5 s.

[0034] Alternatively (example 2) the 2nd and 3rd process steps are repeated twice leading to the order R-A-B-A-B-A-B-R-D, wherein each step A takes 20 s and step B takes 15 s. Again the overall process time has not increased. This process order leads to a further increase of particle removing efficiency, although not in this significance.

[0035] Table 1 shows the two examples of the invented method (1 and 2) as well as the one comparative example (0 = prior art)

Table 1

Example	first fluid (A) (continuous liquid flow A)	second fluid (B) (spray step B) continuous phase (cp) disperse phase (dp))	sequence
0 (prior art)	SC1 – 60 s	cp: nitrogen; dp: DI-water – 45 s	R-A-B-R-D

1	SC1 – 30 s	cp: nitrogen; dp: DI-water – 22.5 s	R-A-B-A-B-R-D
2	SC1 – 20 s	cp: nitrogen; dp: DI-water – 15 s	R-A-B-A-B-A-B-R-D

[0036] Table 2 shows the cleaning efficiency of the two examples of the invented method (1 and 2) as well as of the cited comparative example.

Table 2

Example	repeating A-B	total cleaning time	particle removing efficiency
0 (prior art)	1x (not repeated)	105 s	64.2
1	2x	105 s	77.7
2	3x	105 s	78

[0037] Further embodiments of the invention are summarized below. Herein the abbreviations are used as follows:

[0038] A: free flow cleaning step wherein the liquid is poured onto the surface in a continuous free flow

[0039] B: spray cleaning step, wherein liquid is dispensed onto the surface with a spray nozzle

[0040] R: a rinsing step, wherein DI (de-ionized water) is supplied in a free flow. (in the DI-water gases such as CO_2 may be dissolved)

[0041] D: a drying step, which removes liquid from the surface.

[0042] R-B-A-B-R-D: This is a basic process according to the current invention wherein the core sequence B-A-B is preceded with a pre-rinse and succeeded by a rinse and dry sequence.

[0043] R-B-A1-A2-B-R-D: This example shall indicate that between the at least two spray cleaning steps two or more free flow cleaning steps may be conducted; e.g. with two different cleaning liquids.

[0044] R-B-A-B-A-R-D: The sequences may start with a spray cleaning step after the pre-rinse step.

[0045] B-A-B-A-R-D: The sequences may start with a spray cleaning step without a pre-rinse.

[0046] B-A-B-R-D: The sequences may start with a spray cleaning step without a pre-rinse and no final free flow cleaning step.

[0047] B-A-B-D: With this cleaning sequence the last (second) spray step B (between A and D) serves simultaneously as rinsing step. Thus it is preferred that a liquid is used, which evaporates without leaving any residues.

[0048] A-B-A-B-A-R-D

[0049] For step A SC1 (an aqueous solution of hydrogen peroxide and ammonia) is used. Alternatively an aqueous solution of choline (or other quaternary amines) may be used.

Claims

1. Method for cleaning a surface of a plate-like article comprising the steps
   - treating the surface with free flow cleaning, wherein liquid is dispensed through a dispense nozzle onto the surface in a continuous liquid flow,
   - treating the surface with spray cleaning, wherein liquid is directed through a spray nozzle towards the surface in form of droplets,
   wherein the surface is treated with a spray cleaning step before the free flow cleaning step and a spray cleaning step after the free flow cleaning step.
2. Method according to claim 1 wherein the sequence of a free flow cleaning step followed by a spray cleaning step is carried out at least twice.
3. Method according to claim 1 wherein at least one of the free flow cleaning steps and/or the spray cleaning steps utilizes an alkaline cleaning liquid.
4. Method according to claim 3 wherein alkaline cleaning liquid comprises an oxidizing agent selected from the group of ozone, hydrogen peroxide, and a mixture of ozone and hydrogen peroxide.
5. Method according to claim 4 wherein the cleaning liquid comprises ammoniac.
6. Method according to claim 1 wherein at least one of the spray cleaning steps utilizes a cleaning liquid selected from the group comprising water, organic solvent alkaline composition, and acidic composition.
7. Method according to claim 1 wherein the free low cleaning step and the spray cleaning step timely overlap not more than 5 s.
8. Method according to claim 1 wherein the plate-like article is rotated during at least one cleaning step.
9. Method according to claim 1 wherein the spray cleaning step utilizes a spray nozzle selected from the group airless spray nozzle, two phase nozzle with inner mixing or two phase nozzle with outer mixing.
10. Method according to claim 9 wherein the spray cleaning step utilizes a two phase nozzle with outer mixing.
11. Method according to claim 9 wherein the spray nozzle's orifice is located at a distance d to the plate-like article's surface of d being in a range of 0.1 cm to 10 cm preferably 0.3 cm to 5 cm.
12. Method according to claim 1 wherein at least two of the spray cleaning steps are run for 5 s to 45 s each; preferably 8 s to 30 s.

13. Method according to claim 2 wherein at least two of the free flow cleaning steps are run for 5 s to 45 s each; preferably 8 s to 30 s.
14. Method according to claim 9 wherein the spray nozzle scans laterally across the plate-like article.