Quick Dump Rinsing

General Purpose of Quick Dump rinsing

After chemical treatment of semiconductor wafers for cleaning, etching or stripping applications the process media shall be completely removed from the surface in order to stop the chemical reaction and take away chemical residues. When taken out of a chemical bath (or stopping the direct dispense in spray type equipment) typically 50 – 200 ml of medium is carried over with each 25 wafer batch. Chemistry is still covering the wafer surface, in particular within recess structures of the topology (moats, trenches) resulting in continuation of the chemical process outside the bath. This is in particular critical for etch applications, since local over etching might occur which destroys the pattern and therefore causes significant yield loss. Simultaneous the wafer will partly dry off leaving crystallized residues or contaminants which have attached during the transfer of the air liquid interface on the wafer. This typical ionic contamination can interact with the chemical of the subsequent step or create time dependent defect (caused by continuous growth of crystal by taking up airborne moisture. Therefore an immediate replacement of the active chemical is needed, as well as an effective method to remove loosely attached particles. This is achieved by high efficiency rinsing.

The primary objectives of effective rinsing processes after all chemical steps therefore are

1. To quickly and effectively stop the chemical reaction on the surface after the wafers have been removed from the bath. Typically this is achieved by diluting the surface concentration to less than 1 % of the chemistry previously used in the chemical treatment.
2. To fully remove chemical and contaminant residues from the wafer, which are carried over from the chemical bath without ANY impact on the wafer surface. Typically a three orders of magnitude reduction is sufficient not leave residues on the wafer.
3. To take off particulates from the wafer before the next chemical step or drying.

Independent of the type of wet processing equipment like immersion or spray tools this is achieved by rinsing the substrates with Ultra Pure Water (UPW). Basically three types of rinsing are used in Semiconductor manufacturing, depending on the tool type and application:

- Overflow rinsing: immersion of wafers into a rinse bath with continuous introduction of water from the bottom of the tank and overflowing at the top rim.
- Spray rinsing: Dispense of ultra pure water through spray nozzles directly onto the wafer at variable flow, pressure or temperature in a single pass mode (standard process of single wafer equipment)
- Quick dump rinsing: a combination of the above for wet benches consisting of placing the wafer into a overflowing rinse tank, dump the UPW in a very fast manner and refill the tank by spray and /or fill from the bottom.

Overflow rinses are the base method of rinsing providing a continuous exchange of water to take away the media and also allowing methods of agitation like controlled bubbling or megasonics. However fluid dynamic modeling using the double layer approximation, [1,2] reveal that even with high flow rates of > 45 L/min (> 12 GPM) the rinse efficiency (i.e. the change of chemical concentration on the wafer surface by time) is dominated by pure diffusion. Shearing does not happen. As a result overflow rinsing takes a long time (typically 15 – 20 min.) result in huge water consumption and therefore contribute significantly to the Cost of Ownership (CoO) of wet processing tools.

Spray rinses overcome the diffusion limitation by high fluid velocity during dispense and (when the entire batch rotates) centrifugal forces. However coverage on high topology structures is difficult and for some media (f.e. HF based chemistries) spray rinsing results in high particle counts, driven by the preference of particles to attach to hydrophobic (water repellent) solids like Silicon. Megasonics use is limited and significantly less effective than overflow rinsing. Lower water consumption and process times around 10 min result in lower CoO, but in batch systems for the price of reduced performance.

A combination of both techniques has been found to be most effective to utilize the benefits of both techniques. In quick dump rinses short periods of overflow rinsing are enhanced with a fast (< 5 seconds) dump of the water followed by refill with spray and/or bottom fill. While it typically takes to complete tank turnovers (exchange of one entire tank volume) to reduce the concentration of the media on the wafer surface by one order of magnitude, a single quick dump cycle reduces takes off 90 to 95 % of residues, so typically complete rinsing is achieved in three cycles (excepts see below) ending up in process times of 5-7 minutes and half of the water consumption compared to pure overflow rinsing.

Recently some rinses are also used to improve surface conditions of the wafer by adding small amounts of HF (for native oxide removal) or HCl for metal contaminant removal). Although active chemicals are used for these options these are still called rinses since the chemical treatment is typically a single sub-step of the entire recipe and the process is executed in the rinse tank. For details see chapter Functional QDR’s below.

This document focuses on quick dump rinsing (QDR) for wet bench applications in particular, however since QDR combines spray and overflow rinsing most relevant information for these rinses can be derived as well.

Quick dump process step and parameters

The basic idea of the quick dump is to overcome the (fluid-dynamically inactive) diffusion layer at the wafer surface which is not exchanged during overflow rinsing (thus acts a diffusion barrier for the chemicals to dissolve in the rinse water) by high vertical flow velocities of 50 mm / sec. With such high flows the static layers is reduced to a few microns and at the same time introduce shear forces that physically remove the chemical residues from the surface. In order to prevent the wafer to dry off partially often a top spray is applied during draining. After complete emptying the process tank it is re-filled at highest possible flow (to reduce process time) and allow megasonics agitation before the next is initiated.

A typical process flow for quick dump rinsing etch consists of the following steps.

Fast transfer of wafers into the filled rinse tank running at high flow rates (> 30 L /min, hot or cold) Step 1

10 - 30 sec hot or cold overflow rinse (> 30 L/ min) megasonics optional Step 2

Quick dump of tank content within 2- 5 sec with top spray (optional) Step 3

Re-fill of tank (hot or cold) by bottom fill and top spray at max. flow. Megasonics agitation optional. Step 4

Hot or cold overflow rinse at reduced flow (5 -10 L/min) for 60-90 sec, megasonics optional Step 5

Repeat steps 2 -5 two or three times with extended (2-5) min final overflow step -12 (16)

The table below provides an overview of typical parameters for each of the steps in a three cycle quick dump process as shown above. These might vary by customer and application, but serve well for setting up a general base process.

Rinse step	Description	Mode	Flow	Time	Temperature	Megasonics
1	Transfer	OFL	>30 L /min	Until wafers are fully immersed	Application dependent	No
2	Initial rinse	OFL	>30 L/min	30 -60 sec	Application dependent	Yes
3 / 6 / 9	Fast tank drain	Dump / Spray	15 L/ min (Spray)	5 sec (or tank is completely empty)	Ambient (hot only during first cycle in SPM or H_3PO_4)	no
4 / 7 / 10	Tank refill	OFL / Spray	>30 L/min (bottom fill); 15 L/min (spray)	45 sec (or until is completely refilled)	Ambient (hot only during first cycle in SPM or H_3PO_4)	yes
5 / 8	Low Overflow	OFL	5-10 L /min	30 – 60 sec	Ambient (hot only during first cycle in SPM or H_3PO_4)	yes
11	Final overflow	OFL	5-10 L/min	120 – 300 sec	Ambient	yes

The parameters of a quick dump process can be optimized by considering various effects:

- A fourth cycle does not provide general benefits, however might be necessary for removal of chemical residues after H_3PO_4 and SPM chemistries.
- Since the quick dump rinse is mostly followed by a low temperature chemical step, final rinse or dry process the final step should end at ambient temperature.
- Since during overflow rinsing the efficiency is driven by diffusion only the water consumption during steps 5, 8 and 11 is reduced to minimize water consumption.
- The flow of the spray is primarily determined by the spray profile of the nozzles. It is mandatory that the entire wafer is covered by the spray. This is in particular critical for the front and back wafer.
- Megasonics can typically used whenever the wafer is fully immersed, thus only during dump and re-fill megasonics shall be switched off.
- During initial transfer the tank should operate at maximum overflow rates to take off particulates that by adhere to the surface during passing the air liquid interface when leaving the chemical bath.
- Depending on the previous and following chemical step the rinse can be done with hot (> 70 deg C) or cold (ambient) water. Hot water rinsing reduces temperature stress after high temperature processes like nitride etching and SPM treatment and typically are more effective to remove chemical residues since mostly solubility increases with temperature. However they might have negative impact on the wafer surface. Two prominent effects are often observed:

    - forming an unwanted chemical oxide on the surface
    - enhanced etching of Si by the UPW water

  Therefore (and because of operational costs for heating) the use of hot quick dump rinse step should be minimized to the specific applications need (see below).

Application specific quick dump rinses

Requirements for rinsing vary slightly for the precedent chemical step. While above described base process is applicable for all processes, QDR’s may be optimized for typical wet chemical applications in semiconductor manufacturing as follows:

- SC1: Typical diluted ammonia peroxide mixtures can be rinsed of quite easily. Two quick dump cycles are sufficient in particular if followed by another chemical step or final rinse. All steps shall be done at ambient temperature. Megasonic agitation greatly improves particle performance.
- SC2: similar to SC1 SC2 rinsing can be done with two cycles only to reduce water consumption. Advanced cleaning technology has shown that the SC2 can be fully replaced by adding HCl into the rinse post SC1, shortening the tool configuration and process cycle time. Details are given in the chapter functional rinses.
- HF based chemistries (dHF, BOE, BHF): Rinsing post HF chemistries is typically done by overflow only. Quick dump rinses result in high particle addition, due to partial drying of hydrophobic surfaces and strong adhesion of particles during the dump and re-fill steps when a spray is used. If required quick dump rinsing maybe done, but the spray should be switched off during all steps.
- SPM: Residues of the sulfuric acid will adhere to the wafer surface as sulfates that will crystallize over time by picking up airborne water. Although a wafer might be found clean directly after drying, sulfate particles can be found after waiting time. Therefore the chemical residues require special attention during rinsing. Proven optimizations are using hot (>70°C water for the first or maybe second quick dump cycle to improve sulfate solubility in the rinse medium and adding a fourth quick dump cycle. Megasonic agitation has been reported to be beneficial to the process, but is not commonly used in the industry.
- H_3PO_4: Nitride etching is performed typically at temperatures of 160 °C. Thus transferring the hot wafer from chemical treatment directly into ambient wafer causes significant stress and may cause wafer breakage. Hot water in the first two cycles reduces the temperature shock and similar to post SPM rinsing increases the solubility of nitride residues in water. Hot quick dumps rinses have become standard for nitride etching applications. Since nitride residues stick to the wafer strongly, a fourth quick dump cycle or an extended final overflow step (up to 20 min.) is often used to achieve acceptable particle results. Megasonic agitation is strongly recommended, and replaces the extended overflow rinsing step, thus reducing process cycle time and water consumption significantly. For some application Megasonic rinsing even has been found mandatory [3]
- Solvents or semi-aqueous chemistry: While the basic quick dump rinse is fully applicable for semi-aqueous chemistries it is not commonly used in the industry. Non water soluble solvents are typically rinsed with IPA to dissolve the solvent and then in a cold overflow rinse to replace the IPA in a second step. QDR’s have not been found useful for these applications.

Functional rinses

Recent developments in wet chemical processing for semiconductors focus on enhancing the functionality of rinse processes by adding traces of chemicals for surface conditioning and better removal of surface metals. In particular four types of functional rinses, which are performed in QDR sequences shall be mentioned here:

1. HCl rinse: With investigation of diluted chemistries in particular for cleaning it has been found that adding HCl into the rinse enhanced metal performance of both RCA and HF-based cleans up to the point of full replacement of the traditional SC2 step. When HCl is added to the water the water is acidified and the zeta potential of most elements towards Si or SiO_2 becomes positive, causing repulsive forces between metal dissolved in the liquid and the wafer surface [4]. Already small dilutions of HCl are sufficient to remove typical surface metals effectively.

   A common process solution is adding a diluted HCl cycle into the quick dump process after the first dump. The tank is re-filled with a 1:200 to 1:500 mixture of HCl and water and the concentration is maintained during the subsequent steps up to the final rinse where UPW is used to dilute the HCl mixture and take of easily soluble Cl ions from the solution.
2. H_2-rinse: Adding Hydrogen Ions have a similar effect on the acidity of water for metal removal; additionally the Hydrogen is highly reactive and helps in removing particulates from the surface. In particular in Japan and Korea H_2 functional water is often used to enhance cleaning. The practical application in Quick dump rinsing is to add a second UPW supply line using externally hydrogenated water UPW-H_2-generators are commercially available f. e. by Puretron Inc.) and use this supply in the overflow steps of each quick dump cycle. In order to allow sufficient interaction of the Hydrogen with the surface the overflow steps are extended to 1 – 2 min.
3. O_3-rinse: For some cleaning applications (in particular after HF based cleans like the IMEC or Ohmi clean) a hydrophobic is not desirable. Adding ozone to the rinse water forms a defined chemical oxide of up to 1 nm on the Si surface, thus making it hydrophilic. The growth of chemical oxides is depending on the ozone concentration, but typically only takes minutes; therefore the use of ozonated UPW is applicable for quick dump rinses during an extended final overflow step. Similar to hydrogenated water O_3 water can be formed with external liquid ozone generators (f. e. the Liquozon from AsteX) and introduced at typically overflow rates into the tank after the last quick dump. Since the ozone evaporated from the liquid it is recommended to add a lid to the rinse tank (typically not need for standard rinses) and to adjust exhaust volume to ensure that no ozone gas will diffuse into the operator and service area.
4. HF-Rinse: Other applications require a surface conditioning opposite to the ozone rinse described above: The wafer surface shall be fully hydrophobic. This is typically achieved by an HF last step (i.e. the last chemical step is HF based chemistry). However the transfer through air while the wafers are introduced into the rinse tank and always existing (though fairly low) dissolved oxygen concentration in the water may partially reverse the hydrogen terminated surface achieved n HF etching. This effect can be significantly reduced by adding extremely small concentrations of HF into the rinse water. Dilutions of 1:2000 to 1:5000 in the final overflow step only have been found to be effective to ensure a fully H_2 terminated surface on Si and at the same time sustain a perfect Si-OH termina-

tion on oxides and nitrides. The HF is introduced directly into the UPW stream through metering pumps (allowing to control the concentration precisely for a given UPW flow).

Hardware considerations

Process tank

For efficient rinsing at lowest cost the process tank shall be designed with minimal volume in order to achieve shortest times for the dump and re-fill steps. In particular since the wafers in the bath represent a significant resistance the rinse water tends to flow around the wafers and thus reduces the already low flow velocity during overflow steps. In order to make maximal use of the water at the wafer surface, space around the wafers (distance to front, back and side wall) shall minimal.

The upper rim of the tank shall allow an uniform at least two sided overflow even at flow rates of 10 L/min. Particulates accumulate in areas of no or less surface flow and may re-adhere to the wafers during wafer transfer to the subsequent process. Flow simulations for a given design often reveal weak areas and define potential improvement.

Spray nozzles

In case the QDR tank is equipped with spray nozzles to ensure continuous wetting of the wafers even during the dump and re-fill steps it shall be designed to full cover all wafers in a uniform flow. High pressure at the nozzle outlets is beneficial since it results in smaller droplets and higher spray beam velocity, which favorise media exchange by mechanical energy.

Tank refill manifold

After dumping the tank volume the tank is re-filled through a bottom supply manifold and (if installed) additional spray nozzles from the top. Highest concentration of residual media after the dump will be at the bottom of the wafer. Since the wafers represent a flow resistance fresh UPW tends to flow around the wafers and in worst case media residues near the wafer surface. Therefore using a manifold with multiple outlets positioned in the spacing between and directed to the center of the wafer provides best efficiency results. The manifold shall be capable to provide the required UPW flow uniformly across the batch. A labyrinth at the manifold inlet (connection to supply tubing) preventing a direct path from the incoming tubing to the outlets on the opposite site provides best results.

Quickdump valve

Although not critical for process performance unless the drain velocity is not sufficient, functional problems like wafer lifting and cross slotting or even wafer breakage is often caused during opening of the quick dump valve. Lateral forces due to uneven (i. e not perfectly vertical) opening of the valve result in water flowing sie ways and hit the wafers. In particular thin wafers can break or are being lifted from their support or cassette. It is recommended to use a single valve with large opening area which is controlled by single pneumatic.

Environmental protection

Typically rinse tanks are not equipped with lids in order to save equipment cost. However fo functional rinse with chemicals, in particular ozone rinses a lid is required to protect the environment. For safety reasons also an environmental ozone detect unit is recommended, which switches off the supply of ozone whenever critical concentration of ozone gas in the operator and service area are detected..

References

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