

5.0. Wafer cleaning and photoresist stripping

ICs are so sensitive to contaminants that prior to any high temperature or deposition operations the wafers are cleaned. There are also specialized cleans such as post CMP cleans that are required. This chapter focuses on pre thermal and deposition cleaning as well as photoresist stripping, post CMP cleaning will be covered in chapter 11 along with CMP. The objective of any clean is to removed unwanted contaminants without damaging the wafer surface.

5.1. Surface types

The effectiveness of different cleaning methods is heavily dependent on the surface being cleaned and what is being removed from the surface. The wafer fabrication process may be broadly broken up into front end of line (FEOL) and back end of line (BEOL). The FEOL is focused on the fabrication of the different devices that make up the circuit and the BEOL is focused on interconnecting the devices. In FEOL cleaning the surfaces being cleaned are typically silicon (Si) or silicon dioxide (SiO₂). In BEOL cleaning, metal layers are present on the wafers and the allowable cleaning solutions are limited versus FEOL cleaning.

Surfaces may also be characterized as hydrophobic or hydrophilic. SiO₂ surfaces are hydrophilic. Hydrophilic surfaces are easily wet by cleaning solutions and during drying any particles on the surface tend to stay in solution until the solution is removed from the surface. Si surfaces free of oxide are hydrophobic. Hydrophobic surfaces are more difficult to clean, cleaning solutions do not wet as well and during drying the solutions tend to “bead” up on the surface leaving particles on the surface instead of keeping the particles in solution.

The analytical method for describing wetting and determining whether a surface is hydrophobic or hydrophilic is to measure contact angle, see figure 5.1.

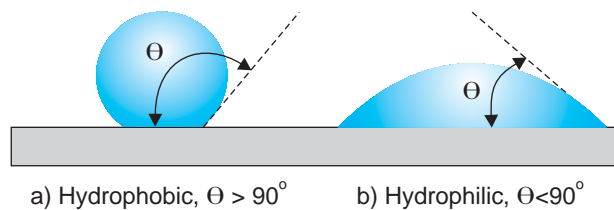


Figure 5.1. Wetting behavior and contact angle.

5.2. Contaminants

The contaminant being removed along with the surface type determines the cleaning solution. The contaminants of concern during IC fabrication can be grouped into five general categories:

- Particles - disturb photoresist patterns and deposited or grown films. Particles may result in shorts or open conductors. As a general rule, particles 1/3 to 1/2 the size of the technology minimum feature size can “kill” an IC.
- Metals - reduced minority carrier lifetimes, increased junction leakage and reduced oxide breakdown voltages. Sources of metals include ion implanters and dry stripping and etching equipment.
- Organics - reduce the breakdown voltage yield of oxides, interfere with contacts and silicide processes, impair adhesion, nucleate defects in thin films and effect oxidation rates. Sources of organics include airborne vapors, incomplete photoresist stripping and outgassing from plastic wafer carriers.
- Native oxide - native oxides are generally of poor quality and can degrade critical gate oxides as well as interfere with contacts, silicide reactions and epitaxial growth. Native oxides form quickly on unprotected silicon surfaces particularly in the presence of moisture.
- Microroughness - reduced surface mobility and low oxide breakdown voltage. Sources include starting material and cleans.

Table 5.1 presents selected cleanliness requirements from the 2004 International Technology Roadmap for Semiconductors [1].

The first two sections of the table cover front and back side particles, the next section covers metals followed by mobile ions. Surface carbon is a measure of organic contaminants and surface oxygen is a measure of native

oxide. For comparison, the areal density of Si atoms on the (100) surface is $6.78 \times 10^{14}/\text{cm}^2$. Finally surface roughness and silicon and oxide loss from cleaning are covered. Surface roughness, and silicon and oxide loss requirements severely limit the aggressiveness of allowable cleans making the contamination goals even harder to meet.

Table 5.1. ITRS surface cleanliness guidelines [1].

Parameter	Linewidth (nm)			
	90	65	45	32
Front surface particles				
Killer defect density (n/cm ²)	0.022	0.023	0.025	0.025
Critical particle diameter (nm)	45	32.5	22.5	16
Critical particle count (n/wafer)	75	80	86	195
Back surface particles				
Lithography and measurement				
Particle diameter (µm)	0.16	0.12	0.10	NA
Particle count (n/wafer)	600	200	200	NA
All other tools				
Particle diameter (µm)	0.2	0.16	0.14	NA
Particle count (n/wafer)	600	200	200	NA
Critical surface metals (10 ¹⁰ atoms/cm ²)				
Gate oxide integrity	0.5	0.5	0.5	0.5
Other surfaces	1	1	1	1
Mobile ions (10 ¹⁰ atoms/cm ²)	1.9	2.2	2.5	2.4
Surface carbon (10 ¹⁰ atoms/cm ²)	1.6	1.2	0.9	0.9
Surface oxygen (10 ¹⁰ atoms/cm ²)	0.1	0.1	0.1	0.1
Surface roughness RMS (nm)	0.4	0.4	0.2	0.2
Silicon loss per cleaning step (nm)	0.1	0.05	0.04	0.04
Oxide loss per cleaning step (nm)	0.1	0.05	0.04	0.04

5.3. Cleaning chemicals

Before discussing the various cleans in use in the industry, it is useful to first present some of the commonly used cleaning chemicals, see table 5.2.

Table 5.2. Properties of cleaning chemicals.

Chemical	Formula	%	Kg/L
Acetic acid	CH ₃ COOH	100	1.05
Ammonium Fluoride	NH ₄ F	40	1.11
Ammonium Hydroxide	NH ₄ OH	30	0.90
Hydrochloric acid	HCL	37	1.19
Hydrofluoric acid	HF	49	1.17
Hydrogen Peroxide	H ₂ O ₂	30	1.10
Isopropyl Alcohol, IPA or 2-Propanol	CH ₃ CHOHCH ₃	100	0.78
Methanol	CH ₃ OH	100	0.79

Table 5.2. Properties of cleaning chemicals.

Chemical	Formula	%	Kg/L
Nitric acid	HNO ₃	70	1.42
Sulfuric acid	H ₂ SO ₄	98	1.84

5.4. The RCA clean

In 1970 the “first systematically developed wafer cleaning process for bare and oxidized Si” was published by Werner Kern of RCA [2],[3]. The clean that Kern disclosed had been in use at RCA since 1965 [3] and went on to become known as the “RCA clean” - the most widely used clean in the industry.

The RCA clean is a FEOL clean. The original RCA clean sequence is: [3]

- Standard Clean 1 (SC1) - 5 volumes of H₂O, 1 volume hydrogen peroxide (H₂O₂) 30%, 1 volume ammonium hydroxide (NH₄OH) 29% at 70 - 80°C.
- Ultrapure water rinse.
- Standard Clean 2 (SC2) - 6 volumes H₂O, 1 volume H₂O₂ 30%, 1 volume hydrochloric acid (HCl) 37% at 70°C.
- Ultrapure water rinse and dry.

The SC1 clean removes organic residues and particles. The SC1 clean works by forming and dissolving hydrous oxide films. The SC2 clean removes alkali metal and hydroxides - Li, Al, Ti, Zn, Cr, Fe, Ag, Pd, Au, S, Cu, Ni, Co, Pd, Mg, Nb, Te, W, Na, Fe (leaves Cl residues).

The implementation of the RCA clean is very critical. H₂O₂ is commonly provided with stabilizers such as sodium phosphate, sodium stannate and may contain high levels of aluminum. In order to prevent recontamination of wafers high purity semiconductor grade chemicals with un-stabilized H₂O₂ must be used. H₂O₂ also has a limited bath life and breaks down over time. Solution change-outs must be designed to insure proper cleaning activity. Insufficient H₂O₂ levels in SC1 baths can lead to surface pitting and insufficient H₂O₂ levels in SPM baths lead to carbon build-up in the bath and poor stripping of organics.

Several variants of the RCA clean have been used in the industry. Prior to 1997 a “typical” implementation would be:

- Sulfuric Peroxide (SPM) - 4 volumes of sulfuric acid (H₂SO₄) 98%, 1 volume H₂O₂ 30% at 130°C for 10 to 15 minutes.
- Ultrapure water rinse.
- Dilute hydrofluoric acid (DHF) 50 volumes H₂O, 1 volume hydrofluoric acid (HF) 49% at room temperature for 10 seconds.
- Ultrapure water rinse.
- SC1 for 20 minutes.
- Ultrapure water rinse.
- SC2 for 15 minutes.
- Ultrapure water rinse and dry.

In the preceding sequence the SPM performs bulk organic removal and chemically oxidizes the wafer surface, the DHF removes the chemical oxide, SC1 removes particles and SC2 removes metals.

If the RCA clean is performed prior to metallization, epitaxial growth or thin gate-oxidation, the thin chemical oxide left on the wafer surface by the RCA clean cannot be tolerated and the sequence is modified to the so called HF last process where DHF is the last chemical step prior to rinse and dry. When the HF last process is used a hydrophobic surface results and special care must be taken in rinsing and drying.

5.5. IMEC clean

IMEC (Interuniversity Microelectronics Center) has done a great deal of research into cleaning technologies. One of the major findings of the IMEC work is that dilute versions of SC1 and SC2 are still effective cleans [4]. Dilute chemistries can result in significant reductions in chemical consumption and thus lower costs and environmental impact. IMEC has developed a roadmap of cleaning technology, see figure 5.2.

The IMEC roadmap is [5]:

- RCA Clean - The IMEC wafer cleaning roadmap begins with the standard RCA clean discussed in section 5.4.
- Dilute Clean - The dilute clean replaces hydrogen peroxide with ozone in the sulfuric acid bath. Sulfuric acid breaks down organic layers effectively but over time carbon from organic layers builds up in the sulfuric acid bath. Hydrogen peroxide is added to sulfuric acid to oxidize the carbon into carbon dioxide or carbon monoxide gases which volatilize the carbon out of the bath. The dilute clean replaces hydrogen peroxide with ozone gas as the oxidizer in sulfuric acid baths, the use of ozone extends the bath life by 3X over hydrogen peroxide. The dilute cleans also replace the SC1 - ammonium hydroxide-hydrogen peroxide - water (1:1:5) and the SC2 hydrochloric acid - hydrogen peroxide - water (1:1:6) baths with more dilute versions of the same chemistries (1:1:50 for SC1 and 1:1:60 to 1:1:100 for SC2). The final dry after the dilute clean uses a Marangoni technique that will be discussed in section 5.7.
- Reduced Clean (IMEC) - The reduced clean combines the HF oxide removal step with the HCl metal removals into a single step. An optional rinse in ultrapure water with added ozone can be used to grow a thin protective chemical oxide on the clean surface.
- Reduce Clean (IMEC Ozone) - The reduced clean IMEC Ozone replaces the sulfuric acid bath with an ozone-ultrapure water bath for organic removal. Utilizing ozone-ultrapure water allows the wafers to proceed directly from organic removal to the HF-HCL bath.
- Next Generation Cleans - next generation cleans are projected to evolve to single tank and then single wafer cleaning and finally to dry/wet hybrid cleans.

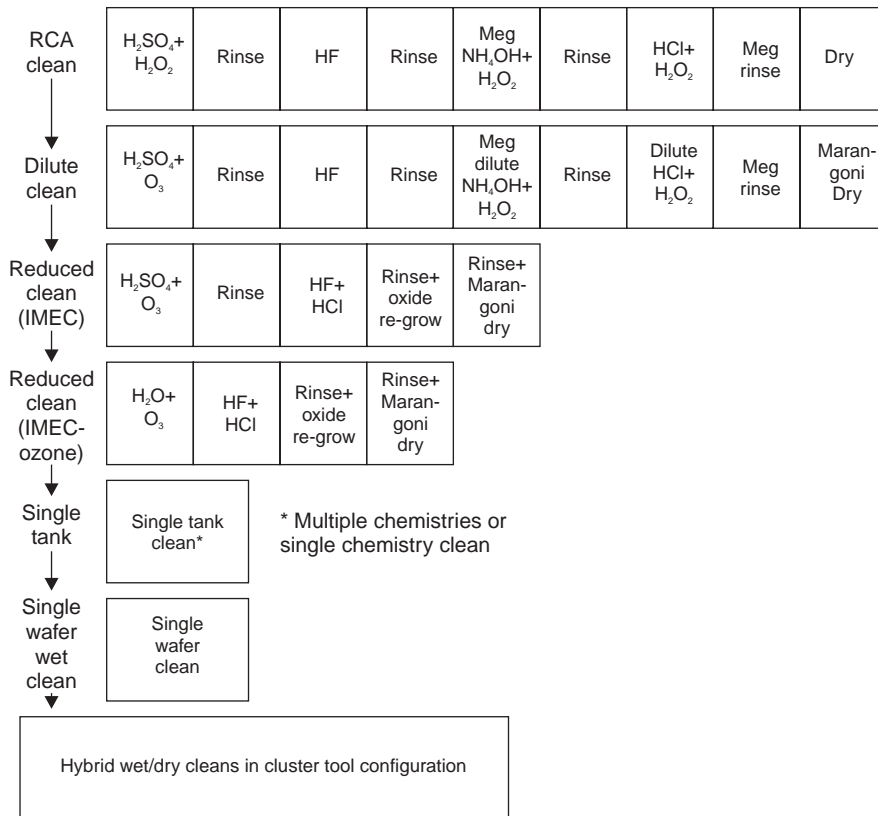


Figure 5.2. IMEC cleaning roadmap [5].

5.6. Ohmi Cleans

The Ohmi clean is another simplified cleaning methodology incorporating ozone and adding hydrogen peroxide to hydrofluoric acid to improve metallic removal.

The basic steps to the Ohmi clean are [6]:

- Water and ozone mixture is used for organic removal (2ppm ozone).
- Hydrofluoric acid and water (1:100) is used to remove the thin oxide grown in step 1 and to remove metals.
- A dilute ammonium hydroxide - hydrogen peroxide - water (0.05:1:5) mixture is used for organic, particles and metals removal.
- A hydrofluoric acid - hydrogen peroxide - water (1:35:65) mixture is used to remove the oxide grown in the previous step and to remove metals. The use of hydrofluoric acid as the last step - the so called HF last method requires very careful rinsing to minimize particles.

Ohmi has also observed that while ammonium hydroxide - hydrogen peroxide solutions are effective at removing particles from silicon and silicon dioxide surfaces, ammonium hydroxide-hydrogen peroxide tends to deposit particles onto silicon nitride surfaces. Ohmi has proposed the addition of anionic surfactants to ammonium hydroxide-hydrogen peroxide mixtures to prevent particle deposition on silicon nitride surfaces [7].

5.7. Evolution of cleaning

The requirements outlined in table 5.1 are driving continual improvements in cleaning chemistries. The need to reach ever higher levels of cleanliness without surface damage are difficult to achieve. Standard SC1 chemistries remove particles well but also remove silicon and can roughen the surface, dilute chemistries, new chemistries, highly optimized meagsonics and drying techniques (see sections 5.8 and 5.9) are also required. There is also a continuing push to move to dry cleaning techniques for easier process integration and waste reduction (see section 5.12).

5.8. Rinsing and drying

The quality of a cleaning sequence is highly dependent on rinsing and drying. Rinsing removes chemicals between each cleaning step to prevent cross contamination and at the end of the cleaning sequence to prevent chemical residues from being left on the wafer. Drying must be performed correctly to prevent particles and water spots from being left behind on the wafer surface.

Rinsing between cleaning steps is accomplished with either a dump rinser or a cascade overflow rinser.

5.8.1. Dump rinse

A dump rinser is a tank with spray bars at the top and a large “dump” valve at the bottom, see figure 5.3. When a cassette of wafers is inserted into a dump rinser, the tank is typically full. Once the start button is pressed the spray bars turn on and the dump valve opens in the bottom of the tank rapidly emptying out the dump rinser. The ultra-pure water spraying out of the spray bars provides mechanical agitation rapidly removing any chemicals from the wafer surface. Once the tank has emptied, the dump valve closes and the tank refills from the spray. A typical rinsing sequence would included 3 or more dump and fill cycles before the spray shuts off and the wafers are removed from the rinser. The strength of dump rinsers is that the mechanical action of the sprays rapidly removes chemicals, the weakness is that the sprays may increase particle deposition on the wafer surfaces.

5.8.2. Overflow rinser

An overflow rinser is a tank with a bottom fill inlet, a dump valve similar to a dump rinser and a tank within a tank design to allow the rinser to overflow, see figure 5.4. Similar to a dump rinser the tank would typically be full when the wafers are first put into the rinser. The bottom dump valve opens emptying the tank, once the tank is empty the bottom fill valve opens and the tank is refilled until it overflows. The action of an overflow rinser is gentler than a dump rinser providing a less aggressive chemical removal process and also a lower tendency to deposit particles. Overflow rinsers are preferred over dump rinser when rinsing hydrophobic surfaces.

5.8.3. Spin rinse dryer

Following the completion of the cleaning sequence and the final rinse step, the wafers need to be dried. For many year the standard method of drying wafers was the spin rinse dryer. In a spin rinse dryer, a cassette of wafer is inserted into a rotor that holds the cassette in place and the rinse dryer chamber is closed. Water sprayers come

on and the rotor begins to spin at a relatively low speed while the wafers are rinsed. The drain of the rinse dryer typically has a probe that measures the resistivity of the water and the wafers are rinsed until some specified resistivity is reached. Tap water has a resistivity of approximately 50 thousand ohms, high quality water used in IC processing has a resistivity of greater than 18 megaohms. Acids and other cleaning solutions lower the water resistivity and wafers following cleaning may initially have a resistivity of 1 to 2 megaohms when a rinse dryer starts. Once the drain water reaches a specified resistivity the water spray shuts off, the wafers are spun at high speed and heated nitrogen spray comes on to dry the wafers. Following drying the wafers are removed from the rinse dryer. See figure 5.5 for an illustration of a spin rinse dryer.

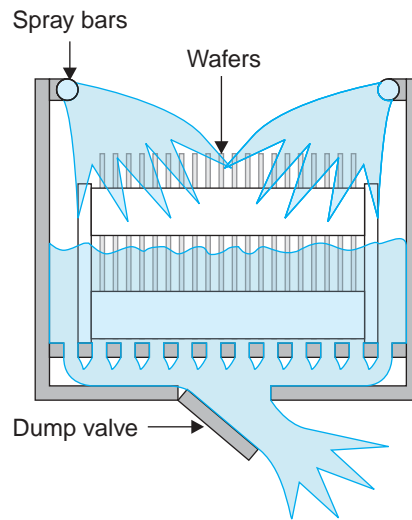


Figure 5.3. Dump rinser.

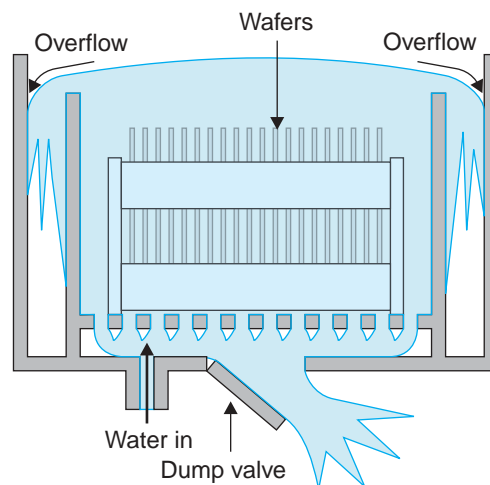


Figure 5.4. Overflow rinser.

Spin rinse dryers provide effective rinsing but are prone to particles and water spots left on the wafer and can induce too much stress on larger wafers with high spin speeds. Critical drying applications have switched over to the alternate drying technologies covered in the next two sections.

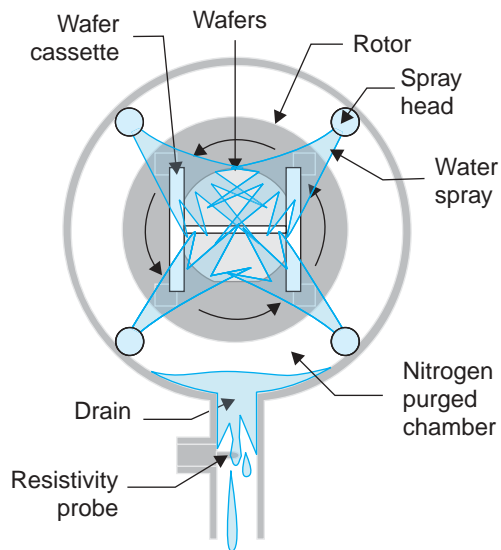


Figure 5.5. Spin rinse dryer.

5.8.4. IPA vapor dryer

In an IPA vapor dryer, a cassette of wafers is placed in a stainless steel chamber with a heated reservoir of isopropyl alcohol in the bottom of the chamber. The isopropyl alcohol (IPA) vapor rises up from the heated bath and displaces the water from the surface of the wafer drying them. The IPA vapors are then condensed at the top of the chamber by a set of cooling coils and returned to the bottom of the chamber. A small catch basin directly under the cassette of wafers catches most of the water and water contaminated IPA that can then be sent to the waste drain, see figure 5.6.

Isopropyl alcohol dryers do a good job of producing dry - clean wafers, but consume a great deal of alcohol doing so, present a fire risk that must be controlled and add organic contaminants to rinse water.

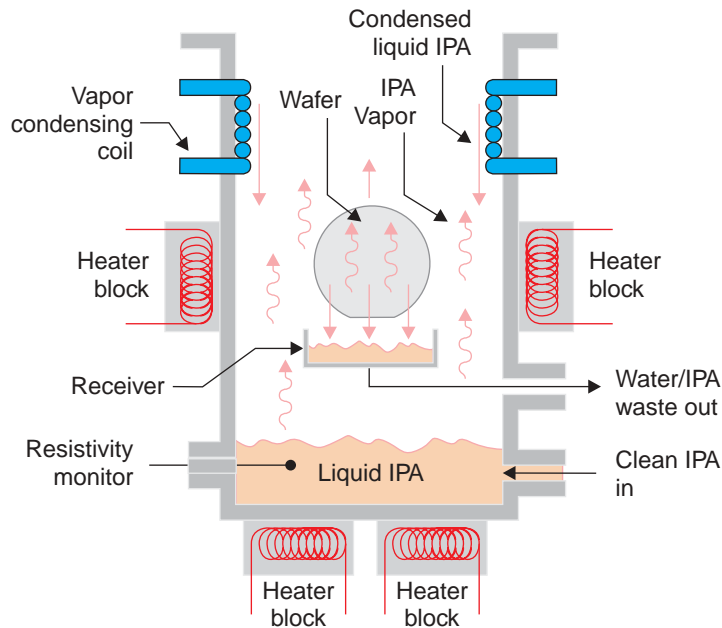


Figure 5.6. Isopropyl alcohol wafer dryer.

5.8.5. Marangoni dryers

A moving zone marangoni dryer uses surface tension gradients in a thin aqueous film to induce a film of water to flow off of the wafer surface [8]. The advantage of Marangoni dryers is that they use very small quantities of IPA to produce a clean and dry wafer surface, see figure 5.7. One potential limit to marangoni drying is the drain speed (the rate that the boundary layer moves across the wafer). Typical drain speeds today are $\sim 1 - 1.5\text{mm/sec}$ [28]. A proposed solution to this limit is the addition of ultrasonic nozzles with drain speeds of $0.3 - 2.5\text{mm/sec}$ and the potential to reach 3.5mm/sec [28].

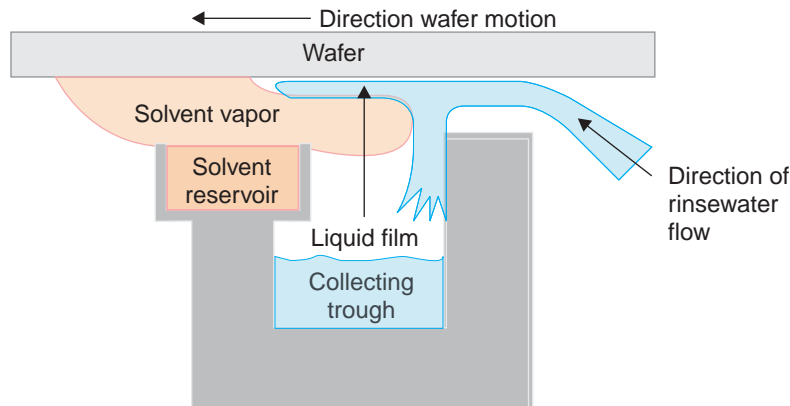


Figure 5.7. Marangoni dryer.

5.9. Sonic cleaning

Small particles are very difficult to remove from the surface of a wafer. One technique used to increase the efficiency of particle removal during wet cleans is to introduce sound waves into the cleaning solution.

Sonic cleaning is characterized by frequencies with 50kHz to 150kHz referred to as ultrasonic, 150kHz to 800kHz as high ultrasonic and greater than 800kHz as megasonic. In the ultrasonic cleaning region the sound waves create cavities in the cleaning solution and then collapse the cavities as the sound wave goes through the positive and negative phase of the wave in a process known as cavitation, see figure 5.8 [9]. The rapid collapse of the cavities created during cavitation mechanically dislodges particles from the surface of the wafer.

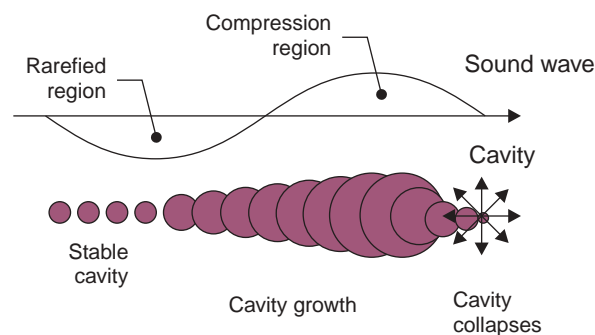


Figure 5.8. Cavitation. Adapted from [9].

As critical particle sizes shrink into the submicron range ultrasonic cleaning loses its cleaning efficiency. When fluids are flowing in contact with a static surface, a stagnant boundary layer forms at the surface of the wafer shielding the particles from the effect of cavitation. When cleaning frequencies are increased into the megasonic frequencies, two changes take place in the action of the sonic energy, first cavitation strength decreases and is replaced by acoustic streaming - high velocity pressure waves in the cleaning fluid, secondly, the width of the

boundary layers shrinks. The net effect is that for each frequency of sonic energy, there is a peak in particle removal size and for deep sub-micron particles megasonic frequencies are required, see figure 5.9

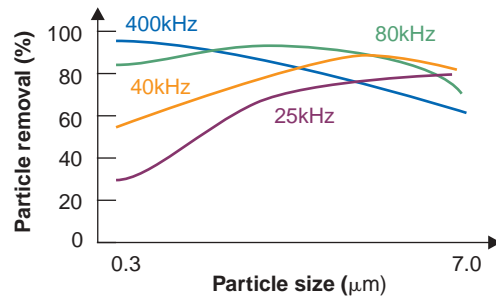


Figure 5.9. Particle removal efficiency versus frequency [9].

Megasonic cleaning tanks must be carefully designed to achieve good cleaning uniformity. Acoustic streaming is a line of sight phenomenon and so the path from the transducer introducing the energy into the tank and the wafers being cleaned must be unobstructed. Figure 5.10 illustrates a megasonic cleaning tank. Megasonic cleaning is frequently used in SC1 tanks to increase cleaning efficiency and may also be used in rinsers.

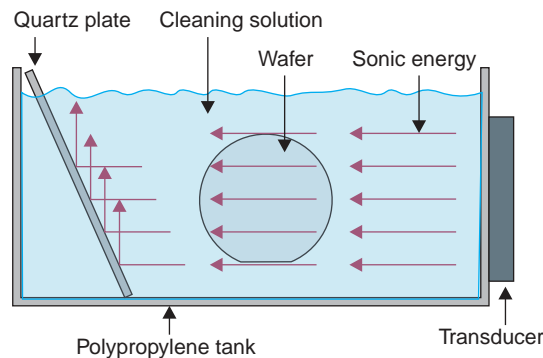


Figure 5.10. Megasonic cleaning tank [10].

As linewidths have continued to shrink to 90nm and smaller, a new problem with Megasonic cleaners have emerged. The energy required to remove a particles is now in the same realm as the energy required to damage the pattern being formed requiring careful optimization of megasonic cleans and pushing some vendors to single wafer cleaners in place of the traditional batch cleaner [29],[30].

Recently Applied Materials announced the development of a unique triple transducer megasonic cleaning system optimized for single wafer cleaning, see figure 5.11.

The system illustrated in figure 5.11 utilizes three megasonic transducers with the top two transducers focused at the liquid-air-wafer interface triple boundary point. The system scans the triple boundary point across the face of the wafer and is reported to achieve damage free cleaning [33].

5.10. Ozone

Hydrogen peroxide is used in cleaning baths as an oxidant, for example, in a sulfuric acid - hydrogen peroxide bath, sulfuric acid will break down photoresist but quickly becomes saturated with carbon. The addition of hydrogen peroxide oxidizes the carbon from the bath in the form of carbon dioxide and carbon monoxide. The drawbacks of hydrogen peroxide are several, hydrogen peroxide decomposes in the bath leaving behind water and diluting the bath, hydrogen peroxide reacts with water in the baths resulting in an exothermic reaction and high

temperatures, and hydrogen peroxide processes result in large amounts of chemical waste. Ozone (O_3) is a replacement for hydrogen peroxide that allows lower temperature processing and the potential for longer baths life with lower waste generation. Several studies of dilute ozone cleaning systems have found ozone and ultrapure water as effective at stripping photoresist, as a sulfuric acid - hydrogen peroxide bath, and ozone - hydrofluoric acid or ozone - hydrofluoric acid cleans with the addition of hydrochloric acid as a replacement for the entire RCA clean sequence. These systems reduce a four step clean to two or three steps [11],[12],[13].

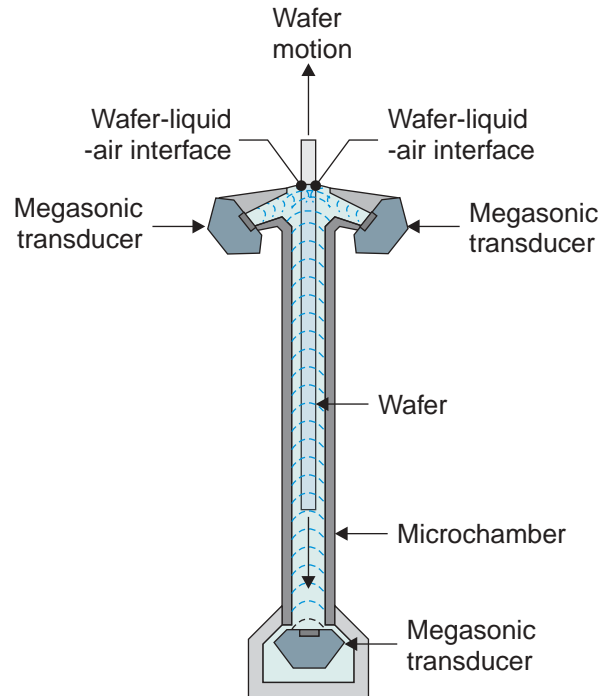


Figure 5.11. Triple transducer megasonic cleaning system. Adapted from [33].

Ozone cleaning does require careful optimization of conditions. The solubility of ozone is highly dependent of temperature and pH, see figure 5.12. In figure 5.12, the pH has been adjusted down with nitric acid and up with sodium hydroxide, note the reduced solubility with increasing pH or temperature.

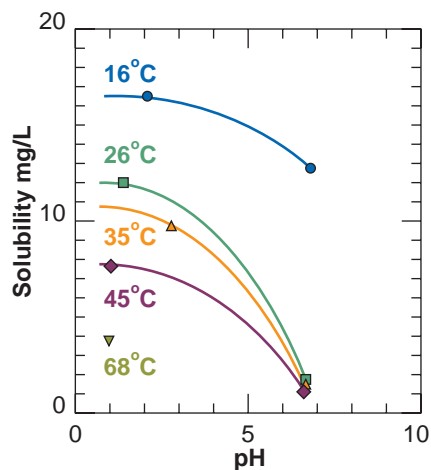


Figure 5.12. Ozone solubility versus temperature and pH [14].

5.11. Backend of line cleaning

Once a metal layer has been deposited onto a wafer, wafer cleaning takes on a new set of problems. The chemistries described so far are nearly universally destructive to metal layers. Following plasma metal etch, via etch and plasma photoresist strip, residues can be left behind. For example, following plasma aluminum etching, plasma stripping of photoresist may leave behind residues containing; aluminum oxide, silicon oxide, titanium oxide and aluminum fluoride among other compounds [15].

Organic formulations originally designed for photoresist stripping have now been applied to residue removal, with fully aqueous formulations becoming available more recently. Specifically formulated removers are now available targeted at residue removal. Removers contain an active species, a chelating agent that convert residue to organometallic materials that will dissolve in the remover solvent, and the remover solvent.

In the 1970s the first generation solvent based photoresist stripping formulations were phenol based. Phenol based strippers were typically used above their boiling points raising safety concerns [16]. Phenol based strippers are also very hard to dispose of. Sulfonic acid based formulation provided some improvement but were still difficult to dispose of. In the early 1980s, amine based strippers were introduced [16] with improved safety and easier disposal. Amine based strippers are strictly for positive photoresist and are not effective on negative photoresist. Amine based strippers continued to be the stripper of choice into the 1990s. Around the mid nineties strippers began to transition from photoresist strippers to residue removal. Photoresist stripping was largely off-loaded to dry strippers and “stripper” solutions transitioned to post-strip clean to remove etch and strip residues. Fluorine was added to the formulations providing some etching of silicon dioxide surface drastically reducing metal residue levels. These solutions were very sensitive to water contamination with silicon dioxides etch rates heavily dependent on the amount of water in the solution. By the late 1990s buffering provided consistent silicon dioxide etch rates and in the early 2000s the latest generation of products with corrosion inhibitors and low silicon dioxide etch rates were introduced [16]. Stripper formulations have generally gone through a new transition every four years [16].

Hydroxylamine strippers are widely used on aluminum with newer removers based on solvents that form complexes with the metal residue and solubilize the residue. Water also plays an active role in removers hydrating the aluminum oxide portion of the residue increasing solubility. Amine based removers must be carefully rinsed to prevent corrosion.

Copper layers add additional cleaning issues. Copper corrodes much more easily than aluminum and requires additional corrosion prevention and remover formulation consideration. Newer semi-aqueous or aqueous chemistries are typically based on fluorine and may include hydrofluoric acid, hydrochloric acid and hydrogen peroxide in very dilute concentrations. Mattson Technology has developed a two step clean with $H_2O - H_2O_2$ solution at 36:1 with surfactant and megasonic agitation followed by a $H_2O - HF/HCl$ with HF at 600:1 and HCL at 240:1 [17].

Low-k films also present a new challenge. Ashing can deplete the surface of organic films of carbon changing the surface properties [18]. Pores can also trap chemicals.

5.12. Dry cleans

While wet cleaning is still far and away the most common cleaning technique, there is a great deal of interest in developing more environmentally friendly dry-cleans. Wet cleans generate tremendous amounts of chemical waste in the semiconductor industry each year that must be disposed of. Wet cleans are also difficult to integrate into cluster tools where multiple processes are performed on one tool, dry cleans allow easier integration. Table 5.3 lists some dry cleans currently under investigation or in-use in the semiconductor industry.

5.12.1. Supercritical carbon dioxide

All substances have a liquid, a gas and a solid phase depending on temperature and pressure. Above a critical pressure and temperature a supercritical fluid phase exists, see figure 5.13. For carbon dioxide the critical pressure is approximately 1,070 PSI and the critical temperature is approximately 31°C. Supercritical carbon dioxide has excellent solvent properties and may be used to remove contaminants through it's solvent action. Supercritical carbon dioxide is a particularly desirable solvent because it turns back into carbon dioxide gas that may be vented to the atmosphere producing no direct waste

Table 5.3. Dry cleans

Clean	Description	Contaminants removed	Reference
O ₂ plasma	Downstream oxygen plasma.	Organics	[19]
SCCO ₂	Carbon dioxide at high pressure and slightly elevated temperatures forms a super critical fluid.	Organics	[20]
UV Ozone or UV O ₂	Ultraviolet light is used to create ozone from O ₂ gas.	Organics	[21],[19]
Ar sputter	Argon sputtering.	Oxide	[19]
UV F ₂ /H ₂	Ultraviolet light used to disassociate and activate fluorine and hydrogen.	Oxide	[19]
NF ₃ /H ₂ plasma	Downstream nitrogen trifluoride and hydrogen plasma.	Oxide	[19]
anhydrous HF and H ₂ O or alcohol	Hydrogen fluoride gas and water or alcohol vapor.	Oxide	[22],[19]
H ₂ plasma	Downstream hydrogen plasma.	Metals and oxide	[19]
UVCl ₂ or UVHCl	Ultraviolet light used to disassociate and activate chlorine or hydrogen chloride gas.	Metals	[23],[24]
Cryogenic aerosol Ar/N ₂	Very low temperature aerosol of argon or nitrogen.	Particles	[19]
CO ₂ snow	Low temperature high velocity carbon dioxide.	Particles	[19]

5.12.2. Carbon dioxide snow

Carbon dioxide liquid put through a nozzle under pressure forms carbon dioxide snow. Carbon dioxide snow may be used to remove submicron particles by momentum transfer and the carbon dioxide snow solvent properties can also remove organic films.

5.12.3. Ultraviolet light activated

Ultraviolet light activated cleaning uses ultraviolet radiation to induce chemical reactions, for example converting oxygen to ozone that reacts with organics. An ultraviolet light activated cleaning system is illustrated in figure 5.14).

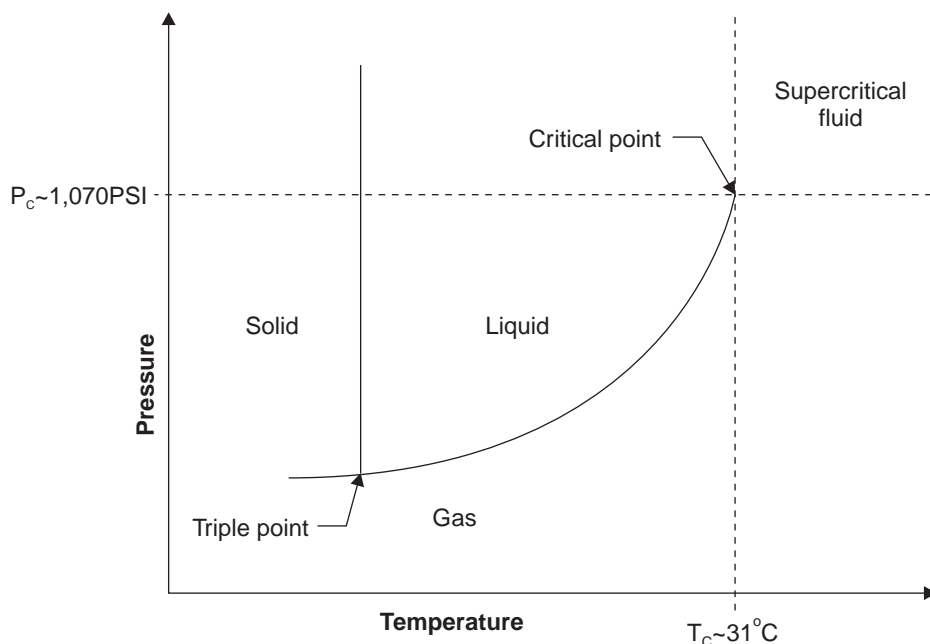


Figure 5.13. Carbon dioxide pressure-temperature diagram.

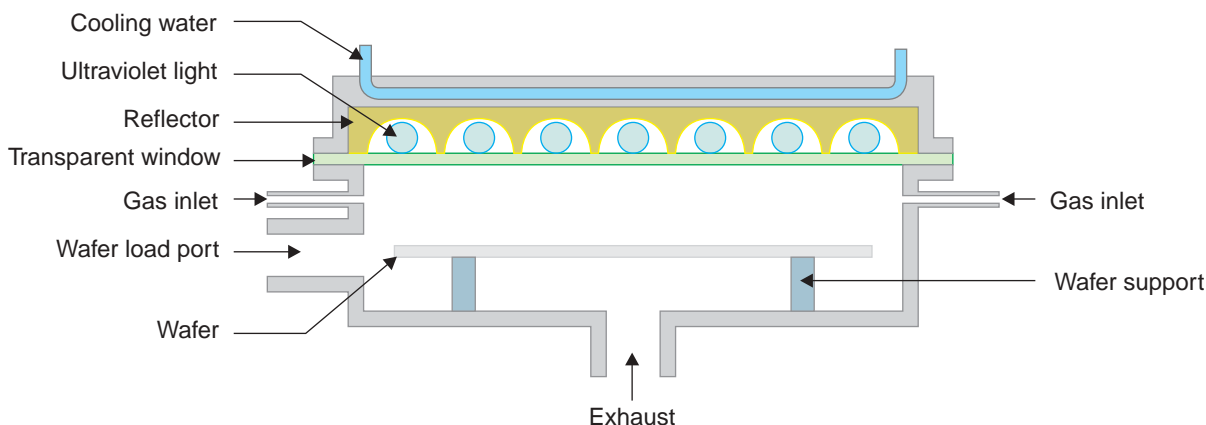


Figure 5.14. Ultraviolet light activated cleaning system

5.12.4. Cryogenic aerosol

Cryogenic aerosol are formed by super cooling gases to less than -150°C freezing the gas into solid aerosol clusters. The aerosol clusters remove contaminants by momentum transfer. Figure 5.15 illustrates schematic of a cryogenic aerosol system.

In figure 5.15 an inert gas such as nitrogen or argon enters the system through a liquid nitrogen jacket that pre-cools the gas. The cold gas enter a movable nozzle through a flexible connection. The gas exits the movable nozzle at an angle to wafer surface and as the gas expands leaving the nozzle the gas further cools forming solid clusters that impact the wafer surface dislodging contaminants such as the particle illustrated in the figure. The chamber is vacuum pumped and a laminar flow of nitrogen flows across the wafer surface sweeping particle out of the chamber once they are dislodged. The process may be tuned by adjusting the inlet gas with argon creating larger higher-momentum clusters than nitrogen, adjusting nozzle angle or system pressure. The larger clusters of argon have better removal but are also more likely to damage the surface of the wafer [32].

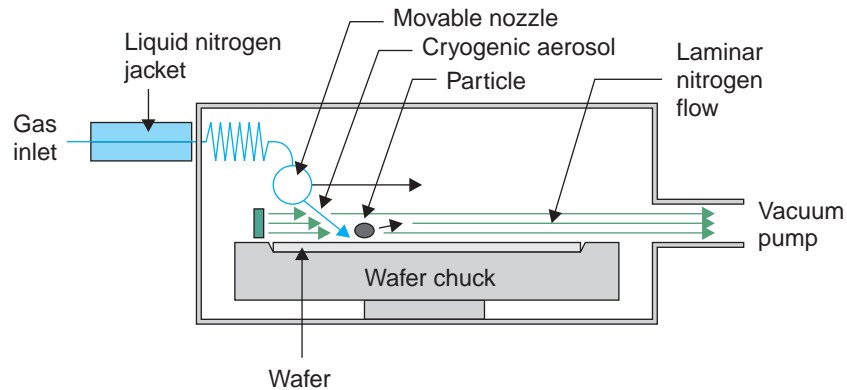


Figure 5.15. Cryogenic aerosol system.

5.13. Automation and single wafer cleaning

All of the cleans presented in this chapter are implemented as fully automated systems in state-of-the-art fabs. Initially, automated systems were huge wet benches with robotic arms moving cassettes of wafers from clean tank to rinse tank and on to the next clean tank, and finally into dryers at the end of the process. More recently cleans are being performed in single wafer at a time cleaning systems utilizing spin processing [25], see figure 5.16. With the advent of copper metallization and very shallow depth of focus lithography it is even becoming necessary to insure the backside of the wafer is free of metals and particles and spin processing techniques are also being applied to this issue as well [26].

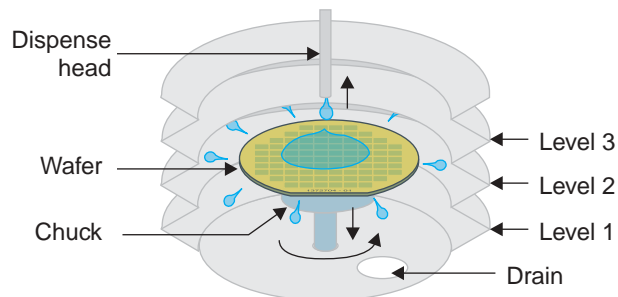


Figure 5.16. Spin etch system.

Advantages of single wafer cleans include [25]:

- Shorter cleaning times (2 to 3 minutes) to meet critical time constraints.
- Megasonic agitation to improve uniformity. Megasonic agitation is also used in batch cleaning but with a single wafer the distribution and cleaning efficiency can be more highly optimized.
- Shorter wafer travel distance and the option of single sided cleaning.
- Reduced scrap.

IMEC has developed a clean based on ammonium hydroxide - hydrogen peroxide (APM) solution with an added complexing agent for metals removal. The APM solution is implemented in a spin cleaner with megasonic agitation and marangoni drying.

Hattori [27] has reported a spin cleaning method utilizing alternating deionized water - ozone and dilute hydrofluoric acid applications. Hattori's clean reportedly reduces chemical and water usage compared to batch cleans, see table 5.4.

Table 5.4. Chemical consumption for batch versus spin cleaning [27].

Clean	Chemical usage (liters)	Water usage (liters)
Standard RCA clean	19	1.1
Dilute RCA	2	1.1
Spin rinse (6 cycles)	<1	<0.1

5.14. Photoresist stripping

Section 5.11 includes a brief description of the evolution of solvent based photoresist strippers. In the early days of the IC industry stripping choices were acid or solvent based strippers. Acid based strippers were typically sulfuric acid with hydrogen peroxide added. The sulfuric acid breaks down the photoresist but quickly becomes contaminated with carbon from the photoresist. The addition of hydrogen peroxide oxidizes the carbon into carbon dioxide gas that then evaporates from the bath. This sulfuric acid - hydrogen peroxide mixture (SPM) is an excellent photoresist stripper and so popular that sulfuric acid waste is the single largest hazardous waste stream produced by the IC industry. There are a couple of problems with this method of photoresist stripping - SPM can leave sulfur residues on the wafer surface, the solution is unstable requiring frequent replenishments of the hydrogen peroxide and generating a lot of waste and SPM attacks most metals so it cannot be used after the first layer of interconnect is deposited.

Solvent strippers present disposal problems although newer strippers are much more environmentally friendly. For most applications today strippers have become cleaners as noted in section 5.11 and photoresist removal is mainly handled by dry strip techniques.

5.14.1. Basic theory

Photoresist is made up of organic solvents, polymers and photoactive compounds. The vast majority of the elemental constituents are carbon (C), oxygen (O) and nitrogen (N). The main issue in photoresist stripping is volatilizing the carbon. Dry strippers either break down oxygen molecules (O_2) into reactive atomic oxygen or form ozone (O_3) that then reacts with the carbon in photoresist to form carbon dioxide (CO_2) or carbon monoxide (CO). The activation for the oxygen reaction may come from an RF plasma or from ultraviolet light (see section 5.12.3 for UV activated process equipment).

5.14.2. Downstream strippers

Early dry strip systems were barrel systems with the wafers sitting in the middle of the plasma (see chapter 7 for a discussion of plasmas). The need to minimize ion bombardment and damage while maximizing throughput led to the development of downstream systems. Downstream systems generate the plasma using microwaves in a remote chamber and then strip the photoresist with the resulting oxygen products in a second chamber. Downstream systems virtually eliminate ion bombardment of the wafer and can generate high plasma densities. Figure 5.17 illustrates a downstream, plasma stripper.

5.14.3. Dry strip issues

Photoresist that has not been exposed to high energy processes such as ion implantation is relatively easy to strip with weak chemical bonds of approximately 0.15-0.18 eV [30], however, following ion implantation photoresist has a crust layer that behaves more like diamond and has bond strengths of 2.5-3.0 eV [30]. The activity of the dry stripper can be increased by raising the temperature but this can lead to the photoresist popping - putting unacceptable stresses on the wafer. Alternately ions can be used to bombard the photoresist or fluorine can be added to the dry stripper chemistry (oxygen based). Ions and fluorine have been effective solutions in the past but as device linewidths shrink, substrate damage from ions and oxide etching from the fluorine are reaching unacceptable levels requiring new solutions.

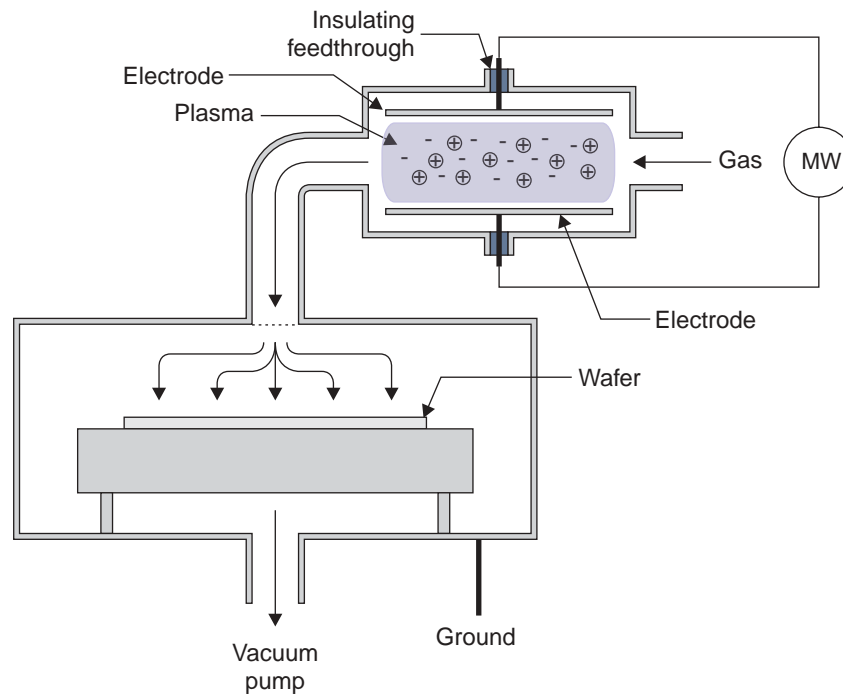


Figure 5.17. Downstream plasma stripper.

The other big issue in photoresist stripping is stripping photoresist off of the new low-k materials (see chapter 20). The bonds that make low-k materials - low-k are easily broken and the photoresist stripping process can raise the k of the films. Possible solutions being worked on are [30]:

- Oxygen at low temperatures with directional ion bombardment so the low-k films see very little ion bombardment. This results in about 10nm of damage.
- Strip with atomic hydrogen or protons although this technique is slower.
- Heat the photoresist until it starts to decompose and then use hydrogen to strip the resist (technique used by Axcellis).

Another approach that can be used albeit at the cost of increased complexity is a hard mask between the photoresist and the low-k film that is patterned by the photoresist and then blocks the stripper ions from bombarding the low-k film. After photoresist stripping the hard mask must then be removed.

5.15. Conclusion

Reduction in chemical and water consumption, better integration with single wafer tools, the need to minimize damage and new material requirements are the main drivers for changes in cleaning and stripping methods. Critical wafer cleaning is evolving to simpler cleaning sequences with dilute chemistries and single wafer processing. As cleans continue to evolve, wet - dry clean approaches and one day completely dry cleaning sequences will be implemented.

5.16. References

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