

PARTICULATE REMOVAL USING A FOAM MEDIUM

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Chemical Process

Semiconductor chips are manufactured in “fabs”, but the conversion of silicon wafers into useful chips is a complex, multi-step, chemical process. In fact, the chips are synthesized like other materials, and, as the feature size becomes smaller and smaller, this similarity increases. Unlike conventional chemical synthesis, where intermediate isolation and purification can improve overall purity and yields, the semiconductor synthesis sequence must approach perfection in order to achieve overall success.

When viewed as a chemical process, semiconductor chip production exhibits some characteristics not often found in conventional chemical manufacturing. These differences include:

- Chemistry is on the wafer surface, not in the bulk medium. The only chemical conversion occurs within the immediate surface layer on the wafer – the bulk fluid phase, filling the tank, is not participating.
- Chemical consumption is low. The number of moles consumed during treatment is small, even though the total moles present in the tank volume may be large.
- Reactants and solvents must be extremely pure. The low molar consumption means low levels of chemical impurities can compete easily, while the cumulative effects of particulate impurities can seriously reduce overall yield.
- The equipment produces significant particulate impurities. The complex chemical storage and delivery systems add to the impurity problem, possibly exceeding that from the chemicals and solvents.

These characteristics suggest a process improvement opportunity.

Why Foam?

Foams are metastable, created by adding mixing energy to a liquid and gas, yielding foam. An example is shaving cream, composed of reduced surface tension water and a low solubility expansion gas, often isobutane. The directions suggest shaking the container, then dispensing, yielding shaving foam. This foam volume is approximately fifteen times larger than the original liquid volume, thereby defining an expansion ratio, $E/R = 15$.

Immediately following production, foam starts to decay, reproducing the expansion gas and the original liquid phase. This process is called draining and the rate of draining is the drain time. In the case of shaving cream, the drain time is long, many hours, but other foams drain quickly – shampoo foam, for instance.^(1, 2)

Characteristics of foam include:

- Energy to create foam can be added to the gas/liquid mixture, and the foam can then be transported to the substrate to be treated – the substrate will not be subjected to the energy input.
- Draining starts immediately, forming a liquid phase equal to the original liquid, defining that substrate treatment will be identical whether delivered as liquid or foam.
- Drainage rate can be controlled.
- Expansion ratio of the foam, generally between 10 and 20, reduces the volume of reactants and solvents by the factor $1.0/(E/R)$. This expansion ratio effect will also reduce the system particulate exposure, as less material will pass through the treatment vessel.
- Foams can be a delivery medium for other ingredients.
- Foams exhibit thixotropic flow properties, flowing best under shear. Shaving cream spreads easily - high shear - but remains stationary when the shear force is removed.
- Foam bubble walls provide surface tension gradients.

Particulates

Megasonic cleaning is an accepted technique for the removal of particulates from semiconductor wafers.⁽³⁾ This process involves subjecting the contents of the liquid bath to a beam of sonic energy of appropriate frequency produced by a transducer assembly attached to the vessel wall.⁽⁴⁾ The higher frequency of megasonic systems produces smaller bubbles/waves and is less damaging to the substrate, while also capable of removing smaller diameter particles.^(3,5) Shwartzman recognized a possible particle size limitation for megasonic cleaning and suggested effective removal down to a size of 0.3 microns.⁽⁴⁾ There have been other suggestions that megasonics cleaning technology would have particle size limitations.^(3,6)

Shortly after Shwartzman's megasonics disclosure, there were two other important cleaning concepts described. The first, Dussault⁽⁷⁾, defined that semiconductor wafers could be effectively cleaned by treating the wafer surface with a thin film of

flowing liquid while at the same time exposing the wafer to ultrasonic energy. During the operation the wafer is slowly rotated, and then finally dried by higher speed rotation. Poor cleaning results are obtained if the initial rotational speed is too fast – an important observation.

Banks described a deposit cleaning technique, primarily for boilers and heat exchangers, in which the chemical cleaning solution was agitated by allowing a dissolved gas to “boil” as the pressure was reduced, followed by re-pressurization, and the cycle repeating.⁽⁸⁾ The final cleaning was achieved by dissolution of the deposit material in the liquid phase, but the pressure variations caused agitation, helping to loosen the deposits. This technique is different than that offered by Crowe⁽⁹⁾, for instance, where foam is prepared externally and then passed through the device to be cleaned.

Particulates & Liquid Interface

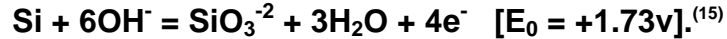
Leenaars⁽¹⁰⁾ apparently recognized the link between megasonics and the Dussault technique. He observed, later confirmed by others:^(3,11)

In the known method [megasonics], the force by which the particles are removed from the surface of the substrate depends upon the cross-section of the particle to be removed and hence is proportional to the square of its radius. The force by which the particle adheres to the substrate, on the contrary, is directly proportional to the radius of the particle.

The experimental work⁽¹⁰⁾ developed the concept that “...the removing force which can be exerted by an “interface of a liquid” on a particle is a force which is caused by the surface tension of the interface and ...is directly proportional to the radius of the particle.” Leenaars specifically identifies the term “interface of a liquid”: (a) the surface of a liquid; (b) the phase boundary between a liquid and a gas; and, (c) the phase boundary between two liquids.

When this information was coupled to the wafer/interface contact rate concept, identified by Dussault⁽⁷⁾, the result was the commonly accepted idea that wafers exiting solution tanks will be more particle free if the rate of exit is relatively slow, preferably at a speed lower than 10 centimeters/second.⁽¹⁰⁾ The first application of this particle removal concept was wafer drying, particularly emphasizing watermarks.

Watermarks are special particulates, which occur during the drying process on clean silicon wafer surfaces.^(12,13) These watermarks are the result of hydrolysis of the very pure water, producing small amounts of hydroxide ion, which, in the presence of oxygen, allow the silicon substrate to oxidize, creating an oxide deposit upon final drying:



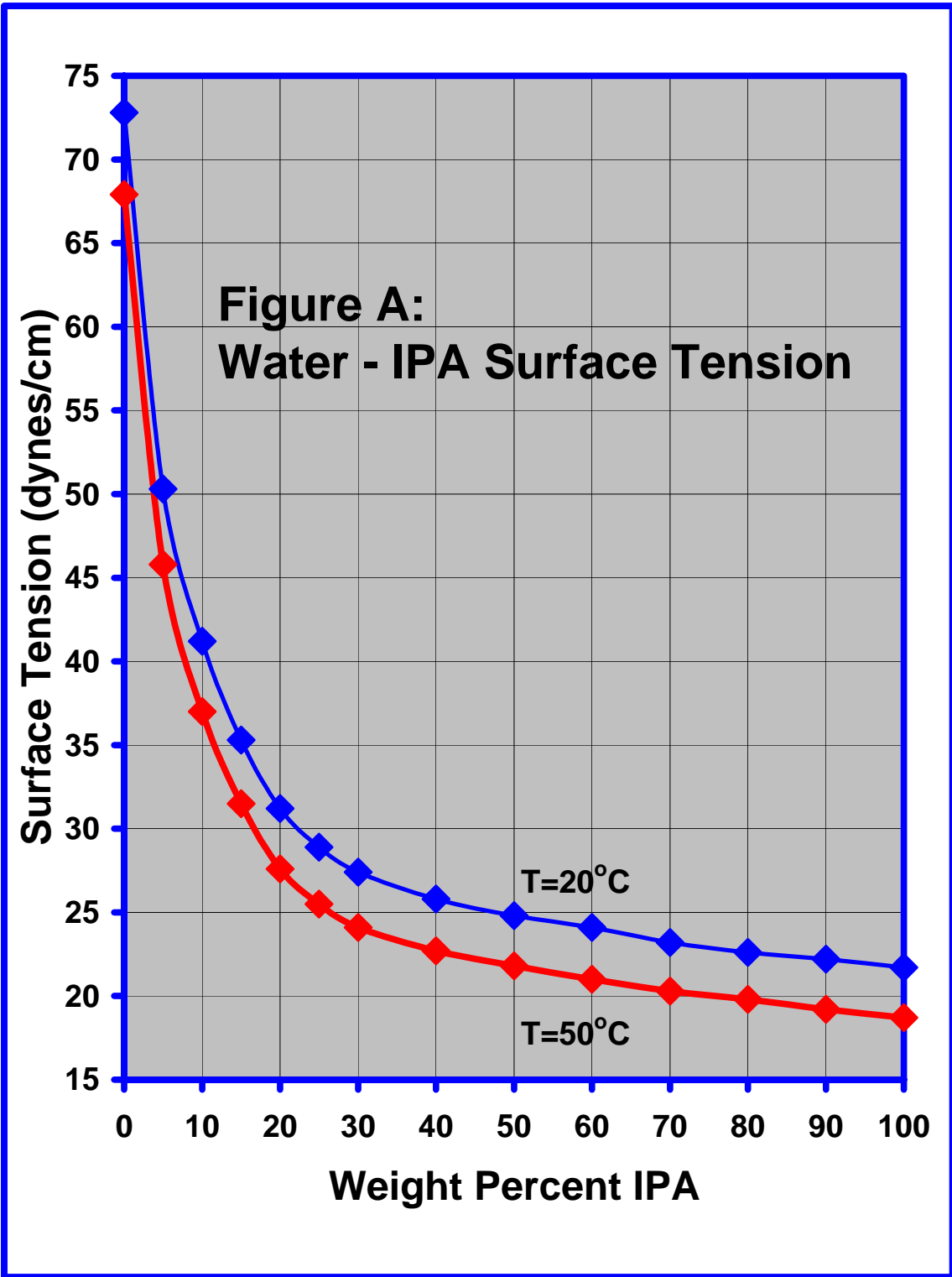
This conclusion is supported by: (a) watermarks are eliminated if the clean wafer has the surface water displaced with a hydrophobic liquid prior to final drying⁽¹³⁾; and, (b) the oxidation may be prevented by eliminating oxygen during the drying process.^(16,17) In addition, the semiconductor industry recognizes the corrosive characteristics of ultrapure water.⁽¹⁸⁻²¹⁾

The generally accepted remedy for watermarks is drying with a water-soluble organic solvent, like isopropyl alcohol, utilizing Marangoni, or surface tension gradient, drying⁽²²⁻²⁶⁾, where, in each case, the surface tension gradient is slowly tracked across the substrate surface being dried. Process equipment using this drying technique include boiling isopropyl alcohol units⁽²⁷⁾, spin rinse units with low levels of isopropyl alcohol⁽²⁸⁾, as well as systems which can reduce the isopropyl alcohol level to zero^(16,17), a concept apparently first suggested by Leenaars.⁽²²⁾ The combination of these results, and the fact that a variety of other organic liquids can be used^(22,25,26), suggests the organic liquid may not be required.⁽²⁹⁾

If these three drying schemes^(16,17,22,23) are compared on the basis of surface tension, which is known to be the important parameter^(24,25), the data definitely define that isopropyl alcohol, or its equivalent, is unnecessary. Figure A displays the surface tension of mixtures of isopropyl alcohol and water, from 100% water to 100% isopropyl alcohol in the temperature range from 20-50°C.⁽³⁰⁾ If the results from the three drying schemes are compared on the surface tension scale, the 100% boiling alcohol system⁽²⁷⁾ corresponds to about 15-20 dynes/cm, while the lower level alcohol system⁽²⁸⁾ corresponds to perhaps 60-65 dynes/cm, although the exact concentration is not specified. These systems are known to produce satisfactory results and they are both used commercially. They are accepted as Marangoni or surface tension gradient wafer dryers.

The “no alcohol” system^(16,17) is also used commercially and known to produce satisfactory drying results. The operating directions define that in order to achieve proper drying, without alcohol, but using warm nitrogen gas only, the minimum operating gas temperature is 70°C. Figure B displays the surface tension of water as a function of temperature, which is approximately linear, from 72 dynes/cm at 0°C to 58 dynes/cm at 100°C.⁽³¹⁾ The surface tension of water at 70°C is approximately 64 dynes/cm, a value similar to the lower level alcohol system.⁽²⁸⁾

The concept of “interface particle removal” as outlined by Leenaars⁽¹⁰⁾, specified a surface tension gradient, which has almost always been generated by adding a variety of soluble organic liquids – often defined as polar organic liquids, noting that non-polar organic liquids are not normally water soluble - to the general drying system. This technique has become standardized using isopropyl alcohol at continuously decreasing concentrations. The “no alcohol” system^(16,17) indeed



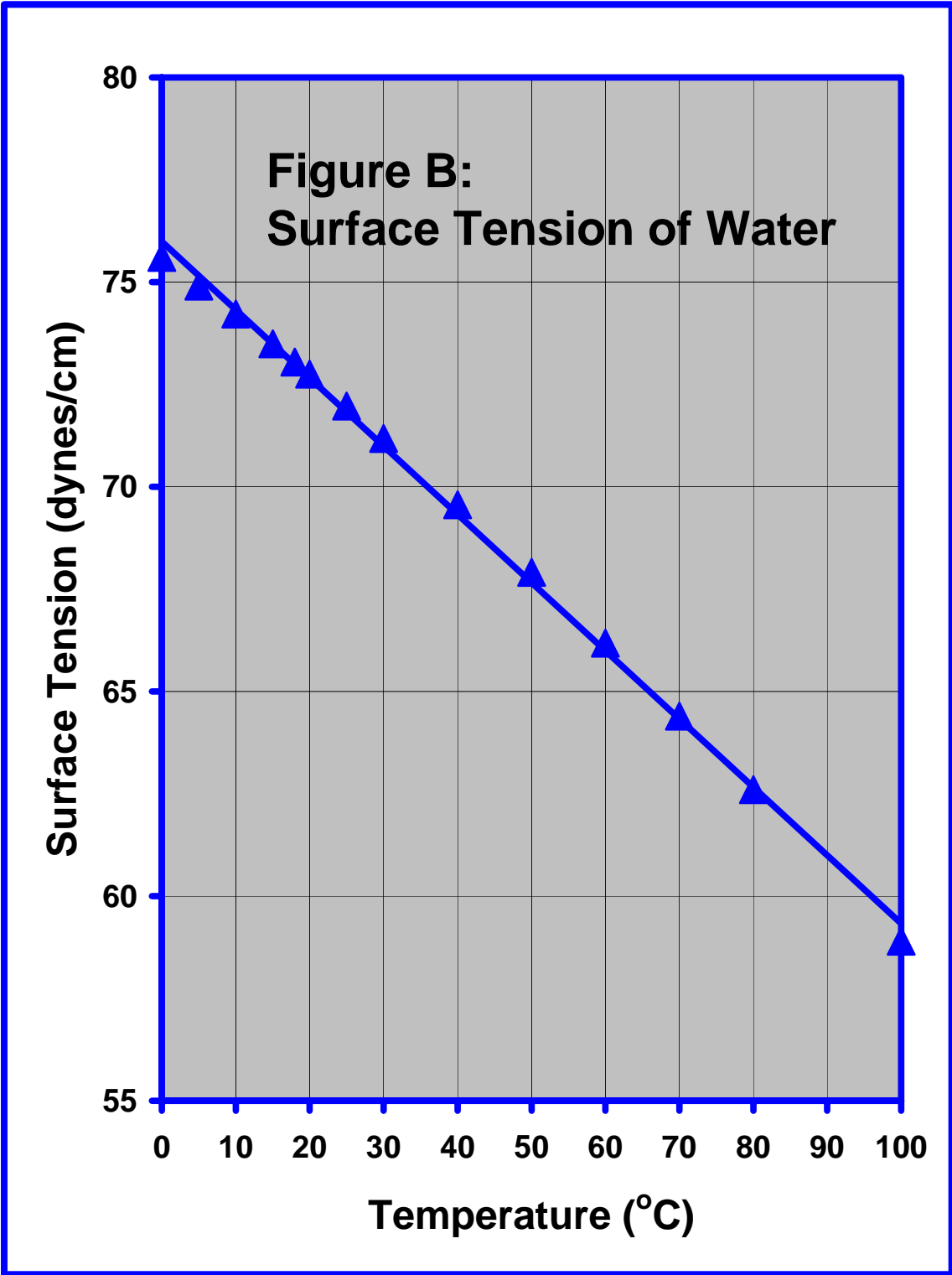
satisfies the original concept in that the surface tension gradient is generated with warmer water⁽²²⁾ providing a lower surface tension medium, identical to the organic liquid systems. No experimental work has demonstrated a requirement for the polar organic liquid; only a requirement for a surface tension gradient, while the “no alcohol” system confirms the same final result can be achieved when the polar organic liquid is omitted.^(16,17,22)

Leenaars⁽²²⁾ and Marra⁽²³⁾ found that “[n]o drying could be induced with pure room temperature N₂ gas or with, for example, alkane vapors.” This observation: (a) reinforced the soluble organic liquid concept; and, (b) eliminated the effect of nitrogen from the “no alcohol” system^(16,17), leaving only the 70°C temperature as the factor responsible for the surface tension gradient.⁽²²⁾

They also identified another important feature. Depending upon the physical properties of the organic compound being used, they found that the liquid bath had to be operated at an overflow condition. The reason for this, as they noted, was in certain instances the organic compound concentration in the bulk fluid increased, independently, via surface transport, while the surface tension gradient was also operating, drying the substrate. This resulted in the surface tension gradient vanishing because the concentration of the organic compound in the bulk fluid was approaching the concentration in the drying fluid film – no gradient. In the “no alcohol” system^(16,17) this process liability would not occur as the surface tension gradient is generated thermally.⁽²²⁾ In this case the drying fluid film temperature would equilibrate to the bulk fluid temperature, thereby maintaining the thermal gradient as well as the surface tension gradient.

The developments from Leenaars and his coworkers have produced a comprehensive and uniform concept for cleaning and drying semiconductor wafers and this concept has been commercially confirmed through a variety of devices and applications. However, a significant feature of this surface tension gradient concept has been overlooked, or, at least, not developed. Although all the current commercial applications involve the liquid surface as the “interface of a liquid” the phase boundary between a liquid and a gas was also identified in the original work.⁽¹⁰⁾ Not only was this interface identified, it was experimentally confirmed.

Leenaars outlines three preferred embodiments of the method: (a) the “interface of a liquid” is moved over the surface of the substrate, by immersing the substrate into the liquid – an advancing liquid; (b) the “interface of a liquid” is moved over the surface of the substrate, by withdrawing the substrate from the liquid – a retracting liquid; and, (c) the “interface of a liquid” is its phase boundary with a gas bubble which is moved over the surface of the substrate, the substrate being immersed in the liquid – both an advancing and a retracting liquid.



The gas bubble embodiment, (c), provides two advantages: (a) since the liquid is both advancing and retracting, the particle removal efficiency is independent of the wetting characteristics of the particle and the substrate; and, (b) the efficiency of the system can be simply increased by moving several gas bubbles at a time over the surface of the substrate.⁽¹⁰⁾

Example 6 of the patent⁽¹⁰⁾ describes this bubble cleaning:

The whole wafer was immersed into a water containing beaker, after which a beam of monochromatic laser radiation having a wavelength of 514 nm and a cross section of about 20 microns was directed by means of an argon laser onto the surface of the substrate, as a result of which vapor bubbles were formed in the proximity of the beam on the surface of the substrate. The beam was moved in a lateral direction over the substrate at a speed of 16 microns/second. This resulted in the removal of about 95% of the particles.

The conversion of this laser generated bubble technique into a commercial system requires development of a medium with a very large number of phase boundaries between a liquid and a gas, so the multiple bubble efficiency can be utilized. Fortunately, the required system already exists – it is aqueous foam. The technical definition of foam - agglomerations of gas bubbles separated from each other by thin liquid films⁽¹⁾ - is equivalent to one of Leenaars' definitions – the “interface of a liquid” is its phase boundary with a gas bubble.⁽¹⁰⁾

This technology is complete and clearly presents a uniform and consistent understanding of particle removal as well as wafer drying, starting with surface tension gradients, simple liquid/gas interfaces, graduating to interfaces at bubble walls, multiple bubble wall interfaces, and then, by extrapolation, extending to aqueous foam, a medium containing millions of bubble wall interfaces.

Even more interesting, this general interface technology, especially related to foam, is not unique to semiconductor wafer cleaning, but has been studied, developed, and exploited extensively in other commercial applications. Foam use in the petroleum industry - specifically oil recovery - is particularly important. The mass of information is too extensive for review here, but many good references are available.^(11,32-36)

Particulates & Gas Agitation

The Banks cleaning technique⁽⁸⁾ was followed by a similar gas agitation cleaning of magnetic separators involving the addition of the compressed gas from an external source while the unit was submerged in the cleaning fluid⁽³⁷⁾ – same result, different procedure. These cleaning techniques would not be directly applicable to wafer cleaning, but the concept does have merit, especially in the case of wafers with complex surface patterns. This “gas agitation cleaning” is accomplished

because of the bubble collapse.⁽²⁾ The energy balance sequence is: (a) adding energy from the compressed gas in order to produce the foam (bubbles); (b) energy release upon the collapse of the foam (bubbles); and (c) the released energy is transferred to the deposit to be removed and the surroundings.

Ogaya⁽³⁸⁾ and Liu⁽³⁹⁾ advanced the concept of wafer cleaning by internal gas generation. Ogaya used carbonated water under pressure, which was slowly discharged into a vessel containing submerged wafers. The cleaning mechanism suggested involves the particulates acting as a nuclei for the bubble formation caused by depressurization. The approach used by Liu is similar to the Banks technique. The wafers are submerged under pressure in a cleaning fluid containing a soluble expansion gas. The pressure is quickly reduced to ambient pressure causing vigorous effervescence, resulting in cleaning.

These techniques^(8,37-39) exhibit one positive feature – storing energy in a compressed system, external to the cleaning vessel, followed by energy discharge in the vessel in order to clean the substrate – and one negative feature – not accommodating the problem of particle redeposition – as the substrate is not progressively removed from the cleaning medium containing the particulates as the cleaning process proceeds.

Patterns, Sonics, and Foam

The current semiconductor cleaning challenge involves patterned wafers, ever smaller feature sizes, and ever smaller particles. Post etch residue removal involves metal organic ash compositions entangled in the wafer surface structure, in some respects, almost “inside” the wafer as opposed to on the surface. Since the surface features are less than 0.2 microns with an unfavorable aspect ratio, the cleaning must be accomplished from the inside, pushing away from the surface, as opposed to applying cleaning energy parallel to the surface from the outside.

Beery⁽⁴⁰⁾ defines that current small structure can be successfully penetrated with low viscosity and low surface tension fluids, like anhydrous ammonia – surface tension about 20 dynes/cm and viscosity about 0.25 centipoise.⁽⁴¹⁾ This small structure can also be penetrated by aqueous compositions, as these physical properties are similar to aqueous compositions, which can be foamed.⁽¹⁾

Conclusions

Leenaars has shown that a surface tension gradient can produce positive drying results, and, in the form of an “interface of a liquid,” can remove particles on wafer surfaces. Particle removal is improved if the “interface of a liquid” is produced by the phase boundary with a gas bubble, producing both an advancing and retracting interface. Multiple bubbles provide more efficient performance.

Banks has shown that decompression of a solution containing a soluble gas will transfer energy to the surroundings as the effervescing bubbles collapse.

Beery has shown that fluids with low surface tension and low viscosity can penetrate vias and trenches producing positive cleaning results when the proper chemistry is chosen.

Aqueous foam compositions can provide these results because:

- **Foam** is an agglomeration of gas bubbles separated from each other by thin liquid films.
- **Foam** can be produced by simple mixing of non-soluble expansion gases, like air, or by decompression of solutions containing soluble expansion gases.
- **Foam** is normally produced from liquid composition with low viscosity and low surface tension.

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