Removing Particles With A Foam Medium, Paul A. Kittle, PH.D.

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Removing Particles With A Foam Medium

To achieve acceptable yields, synthesis sequences must approach perfection.

The conversion of silicon wafers into useful chips is a complex, multi-step, chemical process. Unlike conventional chemical synthesis, in which intermediate isolation and purification can improve overall purity and yields, as the feature size of chips diminish, semiconductor synthesis sequences must approach perfection in order to achieve acceptable yields.

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

- Chemistry is on the wafer surface, not in the bulk medium. 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.

- The equipment produces significant particulate impurities.

Why foam? Foams are metastable, created by adding mixing energy to a liquid and gas, yielding foam, such as shaving cream. The foam volume is approximately 15 times larger than the original liquid volume, or has an expansion ratio of E/ R= 15. Immediately following production, foam starts to decay, reverting to the expansion gas and the original liquid state. This is called *draining* and the rate of draining is the *drain time.* Advantages of foam include:

- Energy to create foam can be added to the gas/ liquid mixture and then transported to the substrate so that the substrate will not be subjected to the energy input.

- Draining starts immediately, forming the original liquid phase. The substrate is treated with the same composition whether delivered via foam or condensed phase liquid.

- Drainage rate can be controlled.

- E/ R of the foam is generally between 10 and 20, reducing the volume of reactants and solvents by a factor of 1.0/(E/ R). This E/ R 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.

- Foam bubble walls provide surface tension gradients.

Megasonic cleaning is an accepted technique for the removal of particulates from wafers. 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. The higher frequency of mega-sonic systems produces smaller bubbles/ waves and is less damaging to the substrate, while also capable of removing smaller diameter particles. Shwartzman recognized a possible particle size limitation for megasonic cleaning and suggested effective removal down to a size of 0.3 microns. [1]

Shortly after Shwartzman's megasonic disclosure, there were two other important cleaning concepts

described. The first, Dussault [2] , 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. The second was Banks [3] , who 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.

Leenaars [4] apparently recognized the link between megasonics and the Dussault technique. He stated that in the megasonics method, 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.

Experimental work has shown that the removing force, which can be exerted by an "interface of a liquid" on a particle, is a force 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" as the surface of a liquid, the phase boundary between a liquid and a gas, and the phase boundary between two liquids.

Figure A: Water - IPA Surface Tension

Figure B: Surface Tension of Water
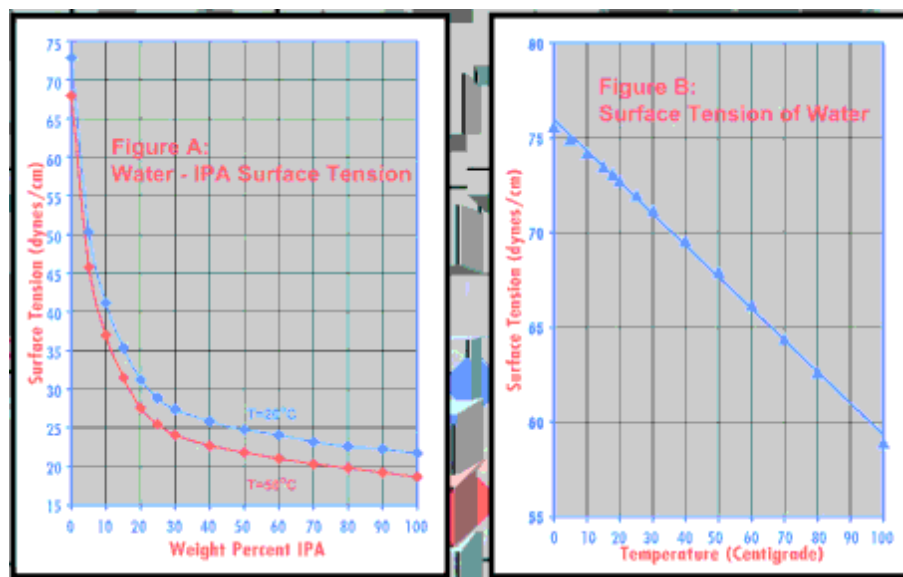
When this information was coupled to the wafer/ interface contact rate concept, identified by Dussault [2] , the result was the commonly accepted idea that wafers exiting solution tanks will be more particle free if the rate of exit is relatively slow, preferably at a speed lower than 10 cm/ sec. [4] The first application of this particle removal concept was wafer drying, particularly emphasizing watermarks, which occur during the drying process on clean silicon wafer surfaces. 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:

$$H_2 O = H+ + OH-[K = 10^{-14}] \quad Si + 6OH- = SiO_{3-2} + 3H_2 O + 4e-[E_0 = +1.73 \text{ v}]$$
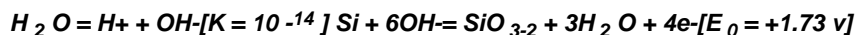
This conclusion is supported by the fact that watermarks are eliminated if the clean wafer has the surface water displaced with a hydrophobic liquid prior to final drying and that the oxidation may be prevented by eliminating oxygen during the drying process. In addition, the semiconductor industry recognizes the corrosive characteristics of ultrapure water.

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

If these three drying schemes are compared on the basis of surface tension, which is known to be the important parameter, 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. 5 If the results from the three drying schemes are compared on the surface tension scale, the 100% boiling alcohol system corresponds to about 15-20 dynes/ cm, while the lower level alcohol system 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 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. The surface tension of water at 70° C is approximately 64 dynes/ cm, a value similar to the lower level alcohol system.

The concept of interface particle removal as outlined by Leenaars [4] , 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 indeed satisfies the original concept in that the surface tension gradient is generated with warmer water 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.

Leenaars and Marra found that "no drying could be induced with pure room temperature N_2 gas or with, for example, alkane vapors." This observation reinforced the soluble organic liquid concept and eliminated the effect of nitrogen from the "no alcohol" system, leaving only the 70° C temperature as the factor responsible the surface tension gradient.

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 is that 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. In the "no alcohol" system, this process liability would not occur as the surface tension gradient is generated thermally. 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 confirmed commercially through a variety of devices and applications. A significant feature of this surface tension gradient concept has, however, 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 and experimentally confirmed in the original work. [4]

Leenaars outlines three preferred embodiments of the method:

- The "interface of a liquid" is moved over the surface of the substrate, by immersing the substrate into the liquid -- an advancing liquid;

- The "interface of a liquid" is moved over the surface of the substrate, by withdrawing the substrate from the liquid -- a retracting liquid; and,

- 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 provides two advantages. Since the liquid is both advancing and retracting, the particle removal efficiency is independent of the wetting characteristics of the particle and the substrate. Also, the efficiency of the sys-tem can be easily increased by moving several gas bubbles at

a time over the surface of the substrate. [4]

Example 6 of the patent [4] 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/sec. 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 -- is equivalent to one of Leenaars' definitions (the "interface of a liquid" is its phase boundary with a gas bubble.) [4]

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.

The Banks cleaning technique [3] 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 [6] -- 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.

Ogaya [7] and Liu [8] 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 pres-sure in a cleaning fluid containing a soluble expansion gas. The pressure is quickly reduced to ambient pressure causing vigorous effervescence, resulting in cleaning.

Storing energy in a compressed system, external to the cleaning vessel, followed by energy discharge in the vessel in order to clean the substrate, is a positive feature. The negative feature is 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.

Conclusions Leenaars [4] 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 [3] has shown that decompression of a solution containing a soluble gas will transfer energy to the surroundings as the effervescing bubbles collapse. Beery [9] 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 pro-vide these results because foam is an agglomeration of gas bubbles separated from each other by thin liquid films, and because foam can be produced by simple mixing of non-soluble expansion gases, such as air, or by decompression of solutions containing soluble expansion gases.

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