TECHNOLOGY

REMOVAL OF NANOPARTICLES FROM SEMICONDUCTOR WATER

A new membrane distillation (MD) technology has the potential to create a total barrier for all particles, regardless of size. This total barrier is an intrinsic character of the technology. Under this approach, particles cannot leave the feed because they cannot overcome the surface tension of the feed surface. Vaporized water escapes the surface tension, passes the membrane, and is then condensed.

Particles will not be pressured through the membrane as in filtration technologies, and no particles are entrained with the vapor as in distillation/evaporation technologies. The membrane permits evaporation and acts at the same time as a perfect demister. Figure 1 illustrates how the technology works.

There are several types of MD. One company[a] has developed a type called "Air Gap Membrane Distillation". While development of this filtration technology can be pictured as an ever tighter mosquito net, the function of MD can be pictured as flypaper. Figure 2 shows how MD relates to other membrane technologies.

Removing Nanoparticles

A major threat to the development of nanoarchitecture in chips is presented by nanoparticles in the clean-room. Both in air and water, there are particles that can be inferred but not correctly measured.

Yield and reliability of all nanodevices are determined by the ability to avoid incorporation of deleterious impurities such as organic contaminants, alkali ions, and metal atoms/ions into the device during fabrication processes. Competitiveness and market share in nanodevices may therefore depend on new cleaning methodology to remove nanoparticles.

The specifications for semiconductor water used in rinsing wafers have for decades been the most stringent in industry. Over time, rinse water production systems have been continuously improved as line width has decreased.

Technologies are being developed in order to remove also these minute particles efficiently and totally. In air purification, a basic method is, for example, to charge all particles and then remove them with charged collectors. In water treatment, nanoparticles that are electrically loaded are quite easily trapped, and removed by electrodialysis (ED), electrodeionization (EDI), or ion-exchange (IX) equipment. However, non-loaded particles are not as easily removed. Typically, materials that are crucial in semiconductor manufacture such as silica, boron, and arsenic are difficult to remove. Other threatening contaminants are small organic particles and acids.

450-mm Technologies

The plan to implement 450-millimeter (mm) wafers and sub-20-nanometer (nm) architecture will require shifts of many paradigms in microelectronics. In any case, the demands on high-purity water will be even more stringent than today. The MD technology[b] can remove even particles that are too small to measure or even detect with present metrology instruments.

Technology History

That rinsewater quality might become a limiting factor in microchip development

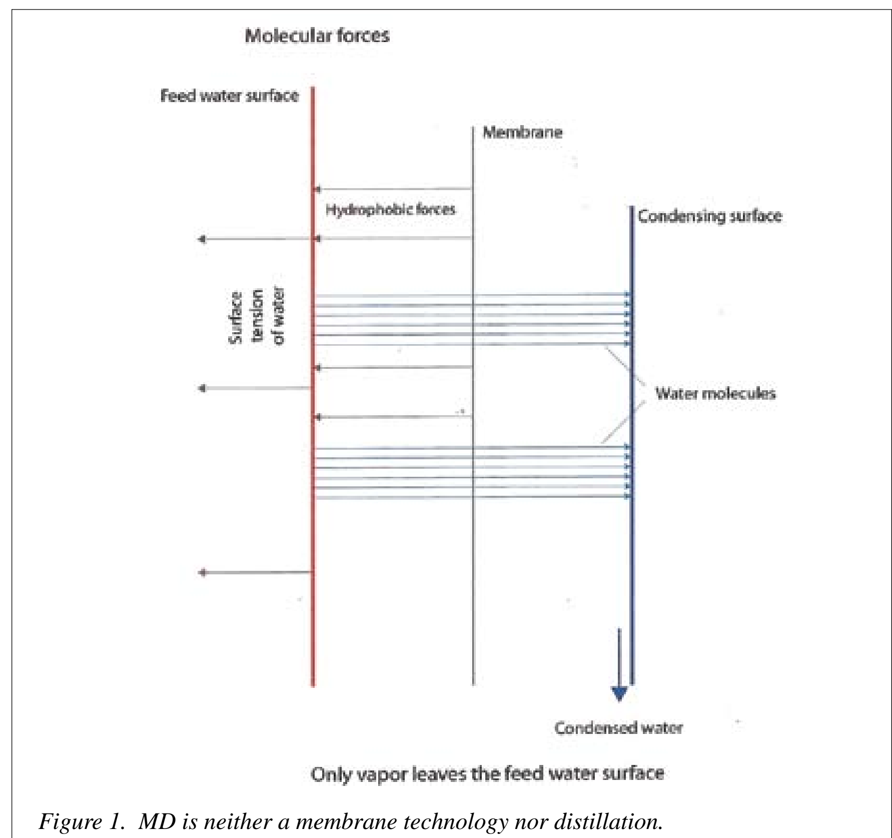

Figure 1. MD is neither a membrane technology nor distillation.

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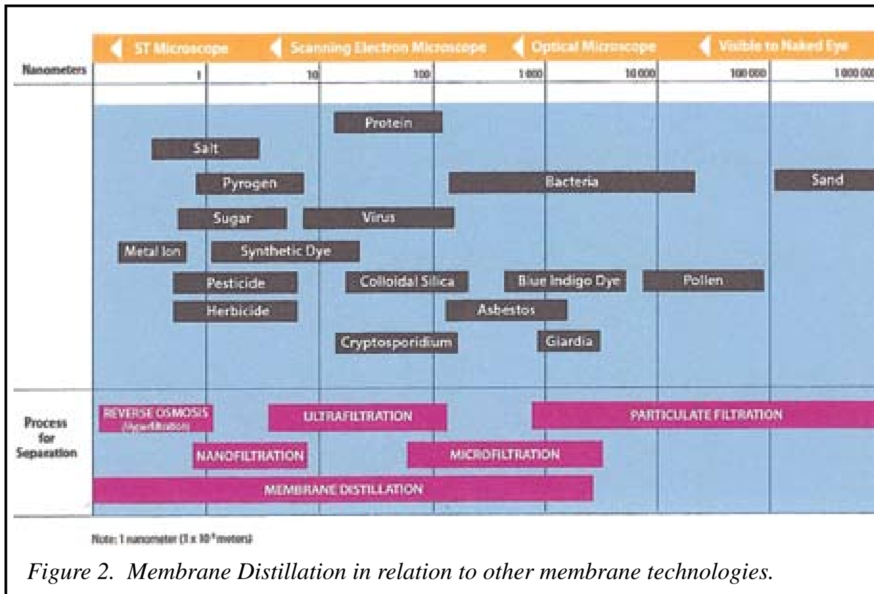

Figure 2. Membrane Distillation in relation to other membrane technologies.

was predicted already in the 1980s. In 1989, a research project was therefore initiated by Scarab Development and ABB Corporate Research to develop MD technology for rinsewater treatment. A new company, Xzero AB, was founded in 1996 to develop the equipment under license from Scarab and a first presentation of the technology was published in *ULTRAPURE WATER* in April 2006 (1). The article was based on a paper given at ULTRAPURE WATER Portland in October 2005.

Since 1996, Xzero has worked on improvements in module efficiency and in manufacturing technology and has tested industrial-scale MD equipment for other applications such as purification of flue gas concentrate, solar desalination, and concentration of reverse osmosis (RO) brine.

As the MD technology works at high concentration factors, it will be well suited to minimize concentrate in reusing spent rinse water. Tests at Sandia National Laboratories (2) that were sponsored by SEMATECH and the U.S. Environmental Protection Agency concluded in 1998 that it was possible to turn spent rinsewater into RO-grade water in one step. Figure 3 shows test equipment used at Sandia National Laboratories.

Killer Particles

To protect yield and reliability from the threat of impurities is as old as the semiconductor industry. In recent years, as devices become more and more compact, the threat has become increasingly ominous. Particles that are large enough to cause damage are called killer particles.

Today, particles that are 20 nm may cause damage. Five years from now, particles as small as 10 nm may cause damage, and soon even 5-nm particles be considered killer particles as semiconductor line widths become narrower. A human hair can have a diameter of more than 100,000 nm. We are referring to particles that are more than 20,000 times smaller than the diameter of human hair. If a human hair were 20 meters in diameter, the killer particle would be 1 millimeter (mm).

Particles of this size cannot be detected by state-of-the-art instruments.

In a November 2009 *ULTRAPURE WATER* article, Grant and Beuscher (3) introduced their technical paper with the following statement: "The critical features size of state-of-the-art semiconductor devices is on the order of 50 nm and expected to decrease to approximately 20 nm by 2015. Particles on the order of one-half the feature size in the high-purity water used during device manufacturing can reduce device manufacturing yield and finished device reliability. Microfilters and ultrafilters (UF) with particle removal ratings below 50 nm are often used to control particle concentrations in the process water used in device manufacturing. However, the ability of the filters to remove particles is typically measured using optical particle counters with a minimum detection limit of 50 nm or larger."

While *in-situ* filters today generally can test down to 50-nm, dynamic light scattering lab methods may confirm retention down to 5 nm; and 10-nm filtration has been demonstrated. What might be the most important criteria is the residue after the rinsewater has evaporated (water marks). However, measuring on the surface presents obvious problems because any arrangement for measuring may in itself distort the values obtained.

In any case the number of 50-nm particles will definitely have to be reduced and it is hoped that quality of high-purity water will be far below present best detection limits of 0.5 to 15 parts per trillion (ppt) for various metal ions. The problems caused by particles can become acute and increase exponentially since the number of particles in semiconductor water increases with smaller particle sizes.

Membrane Distillation Technology

As noted earlier, membrane distillation is a new chemical unit operation. It is especially appropriate for making high-purity water because unlike traditional distillation technologies, there is no entrainment, and unlike filter technologies, the removal efficiency does not depend on the pore size of the membrane— all particles are contained by the surface tension of the water.

MD equipment has been tested for other applications such as purification of flue gas concentrate at a biopower plant in Sweden, desalination at a solar power plant in Spain, and concentration of brine at an RO desalination plant in Saudi Arabia (4).

Initial testing of lab equipment has verified in practice that the technology is able to remove all non-volatile contaminants absolutely, and all volatiles to a very high degree. The next step is to design and build commercial equipment that can live up to the full potential of the technology.

Organics that are non-volatile at the actual operational temperature do not pass the membrane. Organics that are volatile will go through the membrane, and the ones that recondense must be removed by a degasser. Degassing can be

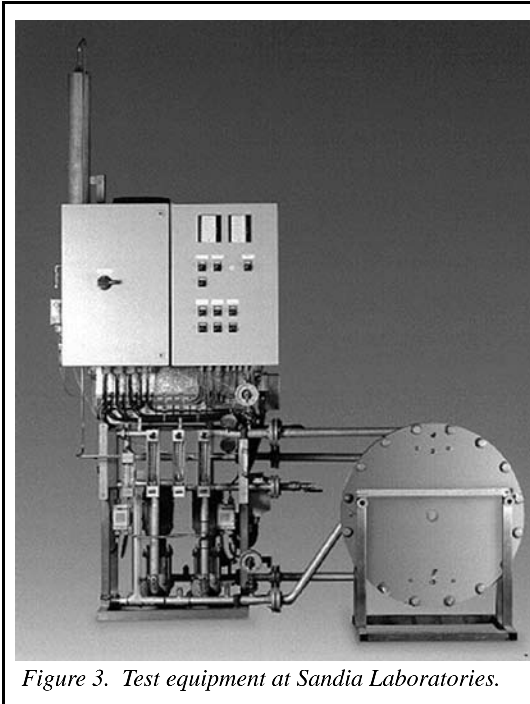

Figure 3. Test equipment at Sandia Laboratories.

Figure 4. Test unit for removal of trace pharmaceuticals in Stockholm.

accomplished by heating; preferentially before the MD, or between the MDs if a redundancy module is added.

Ions or particles will not pass the membranes. They cannot leave the surface of the feedwater because they are restrained by the surface tension of the water. Therefore there is no need from a purification aspect to include ED, EDI, IX, RO, or UF, and the like to the system. Pretreatment is needed to protect the equipment from scaling and fouling, and to prevent surfactants from entering the system. The latter would disrupt the surface tension of the water.

To render surfactants harmless, ozone or ultraviolet (UV) pretreatment can be used. For other purposes, conventional pretreatment will be sufficient. To scour the system, acids can be used. Since the membranes are of polytetrafluoroethylene (PTFE) (also referred to as Teflon®), they can resist strong acids. This also means that acids can be concentrated to high concentrations.

Industrial Development

Recent test of removal efficiency. The MD technology has developed to the point where it is possible to supply industrially made demonstration equipment. Presently, a semi-commercial demo is being run in Stockholm in cooperation with the Royal Institute of Technology (KTH), and the Swedish Environmental Research Institute (IVL-SERI) in order to evaluate separation efficiencies for pharmaceutical residues. This data is shown in Table A. Figure 4 shows a test unit used for removing trace pharmaceuticals in Stockholm.

Total removal of nanoparticles. The next step will be to study the removal of nanoparticles. The purpose of the demonstration will be to show that spent rinsewater can be treated to highest high-purity water standard, including the complete removal of nanoparticles (i.e., higher quality than what is possible today).

Zero liquid discharge (ZLD). With the MD technology, all wastewater can used to make high-purity water. The retentate can be concentrated to a high degree. Supplemented with crystallization, it will enable zero liquid discharge. This will also enable recovery of valuable substances from the wastewater.

The energy-water nexus. MD uses a large amount of heat energy. This must be low temperature (< 100°C) heat. Studies at the Royal Institute of Technology based on information obtained from Intel show that a semiconductor plant may produce enough surplus heat to power an MD-system. For plants with less available heat energy surplus, the process must be integrated in the overall energy system of the plant. Thus far, tests have normally been carried out with a heat input of 70°C. Higher temperatures give higher throughput, but lower temperatures are also feasible. Present tests are conducted at 50°C.

MD actually uses very little energy, but it must be used in symbiosis with a heat flow. Otherwise, a complicated energy recovery system must be added. Typical values (in kilowatt hours [kWh] are as follows:

- Electricity for pumps: 0.5 to 0.9 kWh
- Hot water in: 630 to 645 kWh
- Warm water out: 620 to 630 kWh
- Heat energy used in the process (losses): 6 to 14 kWh

Point-of-use rinsing. One of the ambitions of the MD technology developers is to develop point of use (POU) rinsing that can recover the spent rinsewater. Figure 5 illustrates what a schematic might look like for a single wafer hot water rinse for recovery of spent rinse water.

Challenges

Even though the process itself on a theoretical level can guarantee water without non-volatile impurities of any size, there are several practical systems aspects that

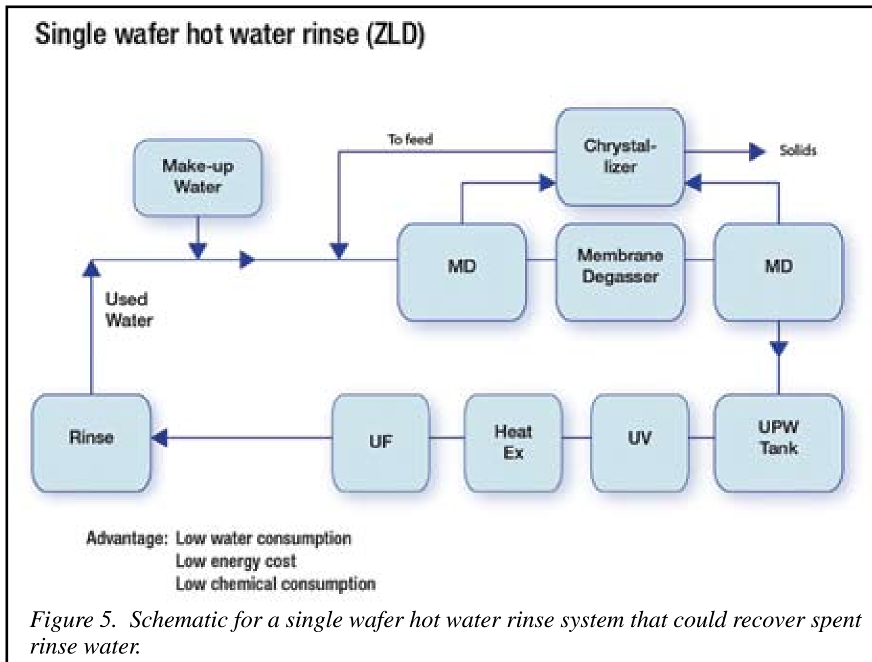

Figure 5. Schematic for a single wafer hot water rinse system that could recover spent rinse water.

will have to be solved.

Pretreatment. Depending on what is used in the manufacture of the integrated circuits, the rinsewater may contain contaminants that may harm the function of the process. Particular danger is posed by surfactants that may disturb the surface tension of the feed. Surfactants are generally macro molecules, and these have to be broken up in order to not reduce the surface tension.

Membrane and backing has to be chosen not only from the point of water purity and yield, but must also be guaranteed not to contaminate the vapor passing through the membrane, or the purified water that is condensed on the other side, and may come in contact with the membrane/backing.

Air-gap. The air gap on the other side of the membrane must be kept entirely clean. Either the air must be continuously cleaned, or nitrogen blanketing used or the air gap could be filled with the purified water. The latter method would solve the air-gap purity issue but reduce the energy efficiency of the process.

Condensing surface. There has to be barrier between the pure water and the coolant, a condensing surface. This surface must be at least as inert as the membrane and the backing. Also here, because of purity issues, a material may have to be used which may cause a lower energy transport efficiency and thus reduced cooling efficiency.

Transport to use. Even for a POU application, the purified water has to be relayed from the equipment to where it is used. This transport must be entirely free from contamination.

Heating. The high-purity water from a membrane distillation unit will normally be around 40 to 50°C. If hotter water is desired, it is possible to achieve that by increasing the temperature of the feed and decreasing the flow of coolant. This may increase energy costs and must be compared to the addition of a heater that may contaminate the pure water.❑

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Endnotes

[a]Scarab Development AB has developed a type called Air Gap Membrane Distillation. Xzero has a license from Scarab to develop the technology for the manufacture of high-purity water for the semiconductor industry. This variation is distinguished as XZERO-MD.
[b]XZERO-MD is the name of the membrane distillation technology referred to in the text.

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Key words: DISTILLATION, MEMBRANES, NANOTECHNOLOGY, PARTICLES, SEMICONDUCTORS, ZERO DISCHARGE

TABLE A
Test Unit for Removal of Trace Pharmaceuticals in Stockholm

Treatment plant: Sjöstadsverket

Date: 2012-11-08

Effluent from: (as ng/L)

Substances:	*Mode of Action:*	*Municipal Wastewater Plant*	*Module 1a 52C*	*Module 1b 54C*
Diclofenac	anti-inflammatory	336	<3	<3
Furosemide	diuretics	592	<5	<5
Sulfamethoxazole	antibiotic	95	<5	<5
Hydrochlorothiazide	antihypertensive	860	<7	<7
Ibuprofen	anti-inflammatory	63	<3	<3
Naproxen	anti-inflammatory	42	<5	<5
Warfarin	blood thinning	12,8	<2	<2
Atenolol	antihypertensive	136	<1	<1
Ciprofloxacin	antibiotic	16	<10	<10
Paracetamol	anti-inflammatory	20	<8	<8
Trimetoprim	antibiotic	15	<3	<3
Ranitidine	anti-acid	46	<5	<5
Metoprolol	antihypertensive	761	<1	<1
Oxazepam	sedatives	187	<2	<2
Carbamazepine	sedatives	190	<1	<1
Ketoprofen	anti-inflammatory	53	<4	<4
Amlodipine	antihypertensive	38	<8	<8
Propranolol	antihypertensive	50	<2	<2
Citalopram	antidepressant	115	<2	<2
Bisoprolol	antihypertensive	25	<3	<3
Sertralin	antidepressant	3,7	<0.8	<0.8

"<" means below the indicated detection limit.
Result for 2012-11-08