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Ultrapure water: systems for microelectronics

Of all the potential sources of contamination in microelectronics manufacturing, water is the most significant – being necessary at different stages of the production process. John Hutcheson of Hutch$_2$O looks at how this potential problem can be avoided.

The burgeoning electronics industry

Electronics are the heartbeat of the products and services of many industries – including aerospace, communications, entertainment, defence, and health – and, as a consequence, the global electronics market is valued at US$1 trillion worldwide.

The electronics market is a stage for intense competition, primarily among US and Asian firms. This in turn spurs rapid product obsolescence and demands high levels of investment in all areas of semiconductor, board, and assembly technologies, and at all stages of research and development (R&D).

Electronic products are steadily becoming smaller, thinner, lighter, faster, and less expensive. Advances now occur so rapidly that, to cite just one example, portable communication products are conceived, designed, and produced in 12 to 15 months, compared to 21 to 27 months a few years ago.

These trends are expected to continue and accelerate, thus challenging the foundation of today's electronics technology. However, rapid change is possible only with an agile, responsive supply and manufacturing infrastructure.

This article will look at only one aspect of this technological arena – **high-purity water systems for the microelectronics industry** – although the same general design principles apply in all areas of this high-tech market.

The manufacture of all electronic products involves the use of high purity water, frequently in large quantities. In the microelectronics industry, manufacturing processes are cumulative, meaning that each process in a facility is affected by the output of the previous processes. When particles and other impurities are present in the chemicals, water and gases used in the process, product yield is reduced.

Of these three potential sources of contamination, water is arguably the most significant one, since water comes into contact with the product many times, and at every stage of the manufacturing process.

The challenge of microelectronics

Microelectronics facilities demand large volumes of water – as much as two thousand gallons per minute – to manufacture a product. And while products increase in complexity and decrease in size, quality requirements for water increase proportionately.

As the industry continues to expand and develop even more advanced technologies, an increasing burden is being placed on the purification technologies used in water generation systems. And the increased demand on limited water resources and local water support infrastructures goes hand in hand with increasingly tougher environmental regulations. As a result, the cost of water usage, treatment and discharge is rising – and will continue to rise.

Some years ago, it was not particularly common for a microelectronics manufacturing facility to reuse water. The perceived wisdom was that the risks involved in reclaiming and recycling water within the facility were greater than the risks involved in processing 'clean' potable water. This meant that very large quantities of relatively high purity water were being sent to waste.

There now appears to be a trend reversing this and modern facilities are now more frequently reclaiming and recycling water, although there will still be some waste streams that must be disposed of.

Carefully planned filtration and purification can optimise the output of each process, resulting in

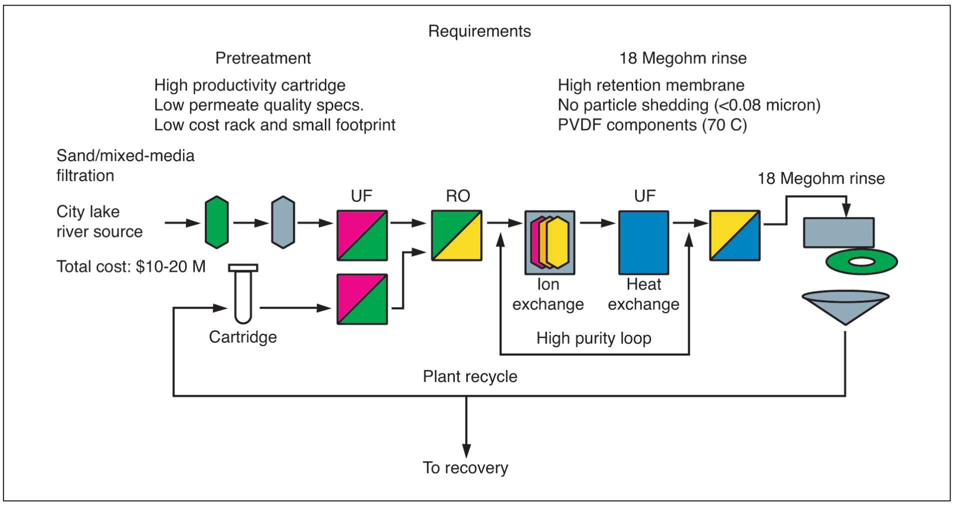


Figure 1: high-purity water production.

Water purification technologies

Reclamation:

- CMP effluents;
- Low TDS/TOC rinses;
- Backside grind/effluent;
- HF rinses;
- Copper plating rinses;
- Ultrapure water system effluents;

Wastewater treatment:

- pH neutralisation;
- Fluoride removal;
- Ammonia reduction;
- TOC/BOD/LOD reduction;
- Arsenic removal;
- CMP effluent treatment (with or without copper);
- Phosphate reduction;
- Suspended solids removal;

Ultrapure water:

- Reverse Osmosis (RO);
- Continuous electrodeionisation;
- Degasification;
- Deionisation;
- Advanced oxidation;
- Ultrafiltration (UF);
- Microfiltration (MF).

improved yields and manufacturing cost reductions. Thus, by effectively filtering contaminants out of the effluent, waste disposal costs can be significantly reduced, and clean permeate can be reused, resulting in additional savings.

To efficiently control the full cycle of water within a facility, and thereby control costs and increase yield, knowledgeable filtration and water experts should manage all the fluids in a manufacturing process.

A variety of different technologies are used in the water purification system and the reclaim/wastewater treatment plant – many of which are membrane-based technologies (*see box, 'water purification technologies'*).

A need for high purity water

Semiconductor companies have expanded globally over the past few years. According to Thomas Flude in *Ultrapure Water*, November 2004, semiconductor device fabricators have benefitted from many significant technology advances developed over the last decade. For example, the production of 200-mm wafers is becoming more common for all new fab investments.

Achieving a line-width geometry of less than 0.13 µm is a normal development today, and many major companies have successfully ventured into the 0.09 µm line-width technology. Just a few years ago, a definition of 'high-purity' water referred to impurities in the parts per billion (ppb) range – while now it is common to set limits in the parts per trillion (ppt) range.

However, it is difficult to grasp what these very low limits actually mean. It used to be said (rather glibly) that if it was possible to measure any impurity, then there was too much of it there. In other words, it is developments in chemical analysis that drive the move towards the lower and lower limits of impurities. It is certainly true that there is no such thing as 'zero', only 'too low to measure'.

To give some idea of what we mean, here is a comparison. The chances of winning the jackpot in the UK National Lottery are one in 13,983,816, i.e. 71.5 in a billion or 71,511 in a trillion. The level of impurities that we are seeking to achieve is less than one in a billion for all the important elements.

Put another way, 1 ppb is equivalent to an accuracy of 1 mm in 1,000 km or 1 second in 11,574 days (over 31 years). A human hair is around 60 – 100 µm; bacteria used to test sterilising grade filters are around 0.2 – 0.3 µm; the largest viruses are just under 0.1 µm, and chips are being manufactured with a line width of 0.09 µm or less.

High-purity water is a very aggressive solvent, and it has an excellent ability to dissolve the impurities out of every material it comes into contact with. It is therefore not only very difficult to achieve the required water quality standards but to maintain them; all the while, transporting the high-purity water from the location where it is purified to the location where it is used.

It is clear that great care must be taken with any chemical used in the generation system or regeneration steps, as well as the materials used to build the purification system and the storage and distribution system. It is also important to ensure accuracy while using the analysers that measure down to these very low ppt levels, and have to cope with the high-purity water environment.

While most 'impurities' are relatively simple to remove and do not pose much of a challenge, others are much tougher and are typically the focus of every system. These include total organic carbon (TOC), boron, silica, metals, oxygen and particles (including bacteria).

So what limits are set for these impurities? Flude, quoted above, included a table in his article, part of which is reproduced below. At this level of purity, conductivity becomes a rather meaningless measurement and the resistivity will always be expected to be 18.2 MegOhm at 25°C.

System design and technologies used

Interestingly, there are no revolutionary new technologies used in achieving these exceptionally high levels of purity. The systems use combinations of technologies that have been available for some years, but the performance of these technologies has been refined consistently over the years. (*Figure 1* on page 22 illustrates one possible example of a microelectronics water system).

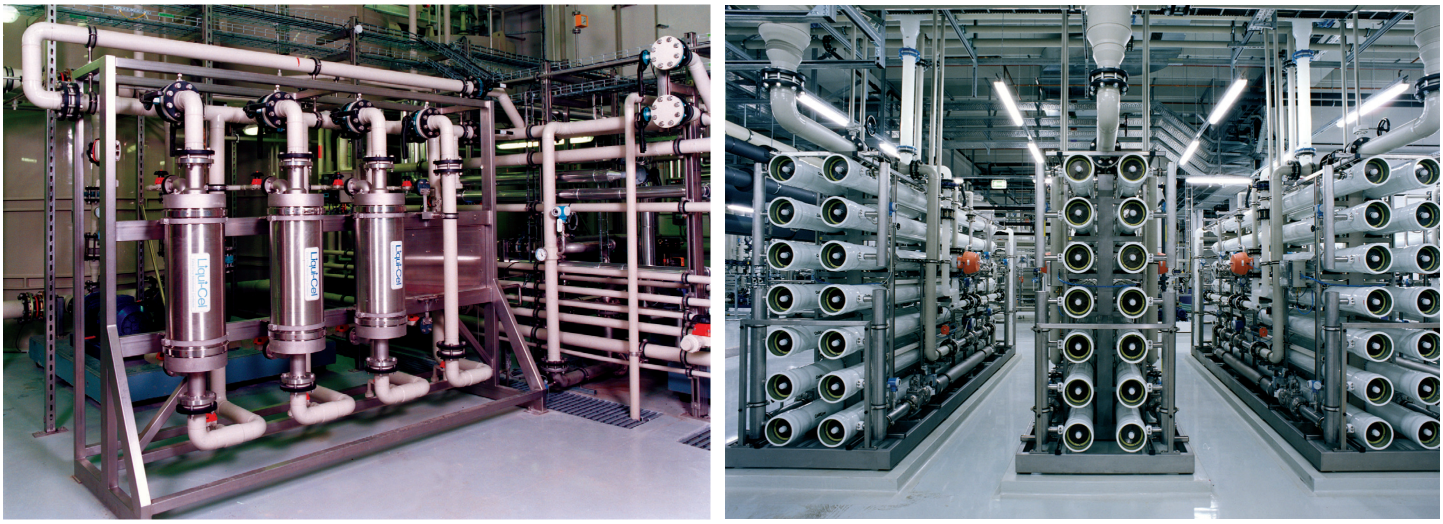
This diagram is from the website of Koch Membrane Systems (*www.kochmembrane.com*) and is generally similar to the system illustrated in the Fulde article.

Membrane technologies

The key membrane separation technologies used are RO, UF and microporous membrane filtration. Degassing membranes and ion-

Memory Size	**256M**	**1G**	**1G**	**4G**	**16G**	**64G**
Geometry rules (µm)	0.25	0.18	0.15	0.13	0.10	0.07
Manufacturing date	1997	1999	2001	2003	2006?	2009?
TOC (ppb)	< 1	< 1 - < < 0.5	1 - < 0.5	< 1 - < 0.5	< 1 - < 0.5	< 0.5 ?
Particle counts / L <= 0.03 µm	-	< 500 ?	< 300 >			
Particle counts / L <= 0.05 µm	< 500	< 300	< 300	< 300	< 100	< 100 ?
Boron (ppt)	< 100	< 50	< 50	< 50	10 - 50	10 - 50 ?
Na^+ (ppt)	< 7	< 5	< 5	< 2	< 2	< 1 ?
K^+ (ppt)	10	< 5	< 5	< 2	< 2	< 1 ?
F^- (ppt)	30	30	30	< 10	< 10 ?	< 5 ?
Cl^- (ppt)	< 20	< 20	< 20	< 10	< 5 ?	< 5 ?
Chromium (Cr) (ppt)	4	2	2	2	2	< 1 ?

Table 1: Impurity removal.



Techniques and equipment used in the production of ultrapure water (*courtesy of Christ Water Technologies*).

selective membranes in CEDI systems also play an increasingly key role in these types of systems.

While it is beyond the scope of this article to discuss the system designs in detail, the remainder of this article will consider the use of each membrane technology in the system and how it contributes to the final water quality.

The overall design of microelectronics water systems is similar to that of all other systems:

- **Pretreatment** – designed for the local incoming water supply. Its purpose is to minimise the fouling or damage of membranes and ion exchange resins in the purification stage;
- **Purification** – designed to remove the contaminants present in the water to achieve the required final level of purity;
- **Storage and distribution** – designed to transport the water to the points of use at the required flow and pressure with minimal degradation of the quality. However, in microelectronics water systems, further purification steps are included in the distribution system and at point of use because of the difficulties in obtaining, then maintaining, the very high purity levels required.

Membrane-based technologies are used in all three sections of a microelectronics water system.

Ultrafiltration (UF)

UF membranes are typically considered to have an effective molecular weight filtration range of 10,000 – over 100,000 Daltons, which equates to a size of around 0.005 – over 0.1 µm.

Despite this very 'tight' filtration capability, UF membrane systems are now typically used in both the pre-treatment stage of systems as well as in the high purity stage.

UF membranes are an attractive alternative to conventional chemical and mechanical filtration, because they can provide a more effective and reliable pretreatment process for RO and ion exchange.

UF membranes are available as spiral wound modules or as hollow fibre modules. Theses hollow fibre membranes are typically 'double skinned' i.e. they have a UF membrane on the inside of the hollow fibre, as well as the outside.

The design of the UF system will typically use a cross flow configuration where the feedwater is recirculated around an internal recirculation loop with permeate being taken off through the membranes, and a portion of concentrate being bled off to drain with the concentrated impurities.

The use of UF units in pre-treatment systems is increasing, particularly in locations where the feed water is variable in quality and can have high organic levels. UF membranes give a good balance of physical strength, resistance to fouling and 'cleanability' with economically viable flux rates (flux is a measure of flow per unit area of membrane).

There are various methods of operating such systems, from a high cross flow and lower percentage conversions, through to minimal or no cross flow with periodic backpulsing/backflushing and cleaning cycles.

Some systems – from the likes of **Christ Waterman** for example – are designed to operate with a cross flow, but include the capability of backwashing the UF modules with permeate periodically, as well as carrying out chemical cleaning cycles.

In this type of pretreatment application, the UF membranes are being used to remove contaminants across a wide range of particle sizes – and certainly much larger than 0.1 µm. They are a particularly effective method of reducing the organic contaminant problem, which can cause considerable fouling to first-stage RO membranes and ion exchange units, and which traditional technologies (such as organic scavengers, coagulation/flocculation and filtration) sometimes have difficulty in removing consistently.

The UF membranes used for such applications will typically have a molecular weight cut-off rating of 30,000 – 100,000 Daltons.

As an alternative to UF, continuous membrane filtration (CMF) can be used in this pre-treatment application. One example is the **Memcor** 0.2 µm membrane system, which is periodically backflushed with a compressed gas purge.

UF membranes can also be used very effectively when installed in the distribution pipework system in the high-purity section. The double-skinned design can minimise particle shedding with the permeate exiting the membrane through a UF membrane rather than through a supporting matrix, as is the case with conventional spiral wound modules.

The UF membranes used in this critical application will typically have a molecular weight cut-off rating of 6,000 – 10,000 Daltons (< 0.01 µm). At this level of filtration, the membranes remove not only particles but bacteria, breakdown products from bacterial cells and polymeric organic molecules. By operating UF units with a small reject flow, the rejected contaminants are removed from the system, not retained within the filter where they can build up and cause an increasing challenge.

Finally, smaller UF membranes may be used as point-of-use filters, when the user-take-off points remove any particles that might have been generated within the distribution piping system.

Reverse osmosis (RO)

RO has been the 'work horse' of high purity water systems for many years now. Although even the most modern RO membranes only achieve a percentage removal of contaminants, this percentage removal is both very high and comprehensive across the full range of contaminants present. RO is therefore an excellent first step in removing contaminants in the feed water. Remaining contaminants can be removed with other technologies such as UF, CEDI and Ozone.

In today's systems it is now standard for double-pass RO to be used. In this technology, the permeate from the first bank of RO membranes becomes the feed to the second bank, so that the product water passes through two sets of RO membranes.

RO membrane manufacturers, such as **Filmtec**, have developed new membranes that have a higher overall rejection, and specifically a higher rejection of lower molecular weight organic compounds, silica and boron. They also have an accelerated TOC rinse down profile. The products also have higher surface areas, which allow fewer elements to be used along with lower operating pressure. Developments to the endcaps and interconnectors have also reduced the risk of leakage.

In order to improve RO performance, further pH adjustment using caustic soda injection is sometimes carried out, either prior to the first pass or between the two RO passes (interstage).

Continuous electrodeionisation (CEDI)

Arguably one of the most significant changes in technology usage in microelectronics water systems, is the growth in use of CEDI systems. CEDI technology is now commonly used as a post-RO makeup demineralisation process in a variety of applications, including microelectronics.

Some efforts have been made in the past to develop CEDI technology as a final polishing step, and as a replacement for mixed beds for microelectronics applications. Although these efforts have met with limited success, and have not been cost effective, the latest innovations in the CEDI process, combined with low-cost CEDI modules and system designs – such as the **Ionpure** *VNX* – have resulted in a cost effective alternative to mixed bed DI.

CEDI devices are comprised of cation- and anion-permeable membranes alternating in a module with spaces in between, and configured to create liquid flow compartments with inlets and outlets. The diluting compartments are bound by an anion exchange membrane (AEM) facing the positively charged anode, and a cation exchange membrane (CEM) facing the negatively charged cathode. The concentrating compartments are bound by an AEM facing the cathode and a CEM facing the anode. Most CEDI systems use a 'plate and frame' type configuration to build up a complete module, although a spiral configuration is also available, an example being the *Septron* system manufactured by **Christ Water Technology**.

To facilitate ion transfer in low ionic strength solutions, the dilute compartments are filled with ion exchange resins, and in some systems the concentrate compartments are also filled with ion exchange resin.

A transverse DC electrical field is applied by an external power source using electrodes at the bounds of the membranes and compartments. When the electric field is applied, ions in the liquid are attracted to their respective counter-electrodes. The result is that the diluting compartments are depleted of ions and the concentrating compartments are concentrated with ions.

Although mixed bed polishing systems have continued to be used there has been an increasing use of CEDI systems as a polishing technique – for quality and economic reasons. Ongoing developments in CEDI technology continue; for example, Ionpure UP technology has been developed to remove weakly-ionised species such as boron and silica from the feed water, which is typically RO permeate, and attain very high purity (18 M.-cm) in the product water.

Development of layered bed CEDI devices have the advantage of being able to configure the ion exchange layers within the device to optimise the removal of specific contaminants. Over the last few years there has been a shift towards thicker diluting cells and modular system approaches, both of which have lowered costs.

Degassing membranes

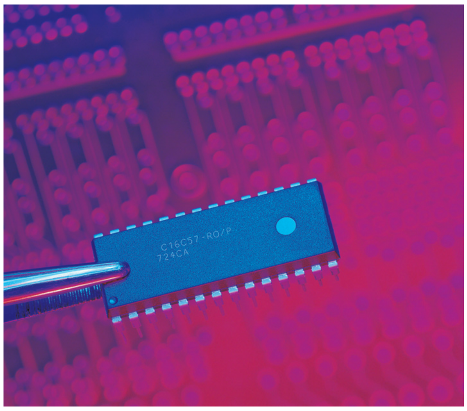
The removal of oxygen has become a very important item with typical levels now being specified at <1 ppb. Vacuum towers were previously the standard but now, in almost all new plants, membrane degasification technology is used.

Typically two-membrane degasification systems are used, the primary one removing oxygen to less than 100 ppb and the polishing system then reducing oxygen to less than 1 ppb. By using two systems, removal of oxygen and THM can be greatly improved and it also allows ozonation of the polishing system without oxygen excursions occurring.

As with CEDI technology, where contaminant ions pass through the membrane material and water does not, in degassing membrane systems the gas being removed passes through the membrane while water is retained.

An example of a degassing membrane system is the *Liqui-Cel* product supplied by **Membrana**. This is a hollow fibre, microporous, naturally hydrophobic, polypropylene filter which has good gas transfer capabilities. The membrane also has relatively high burst and tensile strengths.

For ease in device manufacturing, the hollow fibre is knitted into a fabric array so that the fibres are evenly spaced. Unlike a filter, which membrane contactors are not, the liquid flows over the outside of the hollow fibres while the gas/vacuum phase is on the inside of the hollow fibres. There is much more surface area for gas transfer to occur when the liquid flows shell side or on the outside of the hollow fibres. The oxygen is drawn through the membrane and removed from the system. (Degassing membranes are also increasingly being used to remove carbon dioxide from RO permeate to reduce the challenge onto CEDI modules).



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Benefits of reclaim/recycle

Space does not permit any in-depth review of this area, however, one example given on the Koch website is of a microchip manufacturer whose custom water treatment chemistry enabled reclaimed wastewater to replace municipal water as make-up for cooling towers. The company saved a total of US$300,000 per annum in city water expenses and reduced chemical usage from increased cycles of concentration and lower blowdown volume.

The use of recycling systems today is not only a standard but a must-have in a system. The recycling rate typically lies between 60-80%, and depends on the location (country and end user) where the system is installed. The recycled water is usually used again in the UPW treatment plant so recycled water is returned from the recycling plant to the raw water or the filtered water tank.

A typical recycling system consists of the following equipment:

- Collecting tanks;
- Circulating pumps;
- Booster pumps;
- Activated carbon filters;
- RO units.

The use of membrane systems in the reclaim/recycle/reuse of previously discharged waste streams will increase as water resources become scarcer and more expensive. ●

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