

# MICROELECTRONICS

## MEMBRANE PROCESSES FOR WATER TREATMENT IN THE SEMICONDUCTOR INDUSTRY

It is the aim of high-purity water production to either fully eliminate organic and inorganic compounds, particles, and microorganisms from the water or to reduce their concentrations to values below the detection limits of the most advanced analysis methods. Currently, this problem is solved by means of a multi-stage process chain, in which membrane technology plays a special role at several points. With the introduction of the 0.25 micron ( $\mu\text{m}$ ) and 0.18  $\mu\text{m}$  wafer technology, the requirements for the high-purity water treatment plants with regard to the specification as well as flexibility, safety, and lead time will be even higher.

Product cycle times in the microelectronics industry are approximately 2 years. This requires an increasing demand on the high-purity water quality. Table A shows how high-purity water specifications have developed over the past decades as the structure of integrated circuits have changed.

Large quantities of high-purity water are required for wafer production; the demand of high-purity water even increases with the wafer size. For instance, the production of a 200-millimeter (mm) wafer with a 16 MB DRAM needs 4 to 5 cubic meters ( $\text{m}^3$ ) of high-purity water. Therefore, state-of-the-art wafer fabs commonly consume 100 to 300  $\text{m}^3$  of high-purity water per hour.

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### Semiconductor High-Purity Water Systems

Figure 1 shows an example of a commonly used high-purity water treatment system in the semiconductor industry for 0.35- $\mu\text{m}$  and 0.25- $\mu\text{m}$  structures, respectively. Membrane processes are highlighted to show their leading role.

The raw water is first fed into the pretreatment system to remove suspended solids and to condition the water for the next step. The components applied in this step may vary dependent on the raw water quality. The goal is to get water to at least drinking water quality.

Then the water is fed to a reverse osmosis (RO) plant. Most of the ionic and organic substances are removed in this step. The pure water flowing off the RO plant (permeate) is collected and ozonated in a tank from where it is pumped through an ultraviolet (UV) system in order to remove the residual total organic carbon (TOC) and to sterilize the water. The UV radiation has the ability to destroy certain bondings in molecules, thus decomposing them. In the vacuum degasifier, dissolved gases, in particular oxygen and carbon dioxide, are removed. A reduction of oxygen down to a level of 10 parts per billion (ppb) and lower is feasible.

A further reduction of the oxygen can be achieved by using a catalytic oxygen removal process. The oxygen can be reduced down to a level of less than 1 ppb.

Residual ionic substances are removed in a mixed-bed ion exchanger (IX). Normally a mixed-bed IX with external regeneration is used to prevent any contamination with regeneration chemicals as well as "dead" zones and to maintain a highly efficient regeneration of the resin. Downstream of such mixed-bed IX systems, the conductivity is approaching the theoretical value of 18.2 megohm-cm or 0.055 microSiemens per centimeter ( $\mu\text{S}/\text{cm}$ ). In addition, most of the organics resulting as a reaction product from the UV oxidation are removed.

In the second RO plant that is equipped with special membranes, TOC and particles are mainly removed. The perme-

ate is then fed into a high-purity water tank that is blanketed with nitrogen to prevent other gases from dissolving in the water.

Downstream of the high-purity water tank, the water enters the polishing loop. A second UV oxidation unit is used that destroys the residual TOC and at the same time sterilizes the water. Then a mixed-bed polisher with special, non-regenerable IX resins is applied to remove the remaining ionic substances.

After passing through an absolute microfilter, the water is fed into an ultrafiltration (UF) system to retain particles.

Downstream of this finishing step, the water passes the quality control. Normally on-line instruments are used to measure and monitor TOC, particles, conductivity, and silica. The water is then supplied to the points of use via a loop system.

It is very important that the water is always circulating in the loop to ensure a flowrate that is sufficient to prevent the accumulation of impurities or bacteria.

### Requirements for a Future Water Plant

As mentioned earlier, the requirements for a future high-purity water plant for the

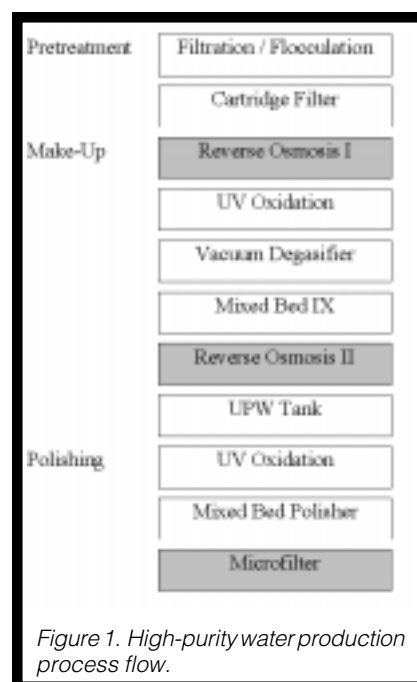


Figure 1. High-purity water production process flow.

**TABLE A**  
**Development of High-Purity Water Specifications**

Structure	1.5 $\mu\text{m}$	0.9 $\mu\text{m}$	0.7 $\mu\text{m}$	0.5 $\mu\text{m}$	0.35 $\mu\text{m}$	0.25 $\mu\text{m}$
DRAM	256 K	1 M	4 M	16 M	64 M	256 M
Resistivity, megohm-cm	17,7	17,8	18,0	18,2	18,2	18,24
TOC, ppb	100	50	10	5	1	0,5
SiO <sub>2</sub> , ppb	10	5	3	1	1	0,2
Ions, ppt	1000	1000	500	50	5	1
Oxygen, ppb		500	100	10	1	1
Particles > 1 $\mu\text{m}$ , 1/L	2.000					
Particles > 0,5 $\mu\text{m}$ , 1/L	10.000	2.500	100			
Particles > 0,2 $\mu\text{m}$ , 1/L		15.000	1.000	100		
Particles > 0,1 $\mu\text{m}$ , 1/L			5.000	500	100	
Particles > 0,05 $\mu\text{m}$ , 1/L				5.000	1.000	200
Particles > 0,03 $\mu\text{m}$ , 1/L						1000

semiconductor industry will further increase. In general, when designing an advanced high-purity water plant, the following principles have to be considered:

**Continuous operation.** Because of the specification requirements, any deviation from a continuous operation in any stage of the high-purity water system should be prevented. Batch processes will cause fluctuations in the water quality. An unstable water flow in a process may lead to a contamination of the water such as the generation of particles.

**Modularity.** A high-purity water system is not allowed to have any shutdown. Therefore, a system with redundancies (i.e., of the so-called N+1 concept) has to be designed. This can easily be achieved by using a modular system. N means the number of aggregates required to achieve 100% capacity. A system of such a modular design offers more flexibility with regard to the capacity as well as to a future extension that may become necessary, because of fluctuations in the production capacity of the fab.

**No bottle necks.** To increase the operation safety bottle necks should be prevented and redundancies should be provided (bottle neck => N=0 ).

**Compact design.** A compact plant design renders savings with regard to the possible building and offers a high flexibility with regard to future extension.

**Lead time.** Due to the price pressure on

the DRAM market, it is very important to minimize the time between making the decision of producing a specific product and starting the production. This of course has an influence on the lead time of all the equipment being used in a fab. To reduce the lead time of a high-purity water plant, both the manufacturing as well as the installation time have to be optimized. A modular and compact design has to be chosen and the modules have to be pre-assembled in the factory. The appropriate conditions, such as the availability of clean rooms, high-purity water and N<sub>2</sub> for equipment flushing have to be provided in the supplier's workshop.

**Future Membrane Processes**

With regard to the above-mentioned requirements new or modified membrane processes will be used in future high-purity water plants

**Ultrafiltration in the pretreatment.** The design of the pretreatment depends on the given raw water quality and has a very important impact on a successful, stable, and safe operation of the processes in the make-up and polishing systems. A pretreatment system that is quite independent from the raw water quality is the UF unit. Table B shows a general comparison between an ultrafiltration and a conventional pre-filter.

Figure 2 shows the operation principles of UF plants. "crossflow" uses a recirculation pump to allow a high flow velocity across the membrane. "Feed and Bleed" means to operate the system with a constant, high concentration. The disadvantages are high energy con-

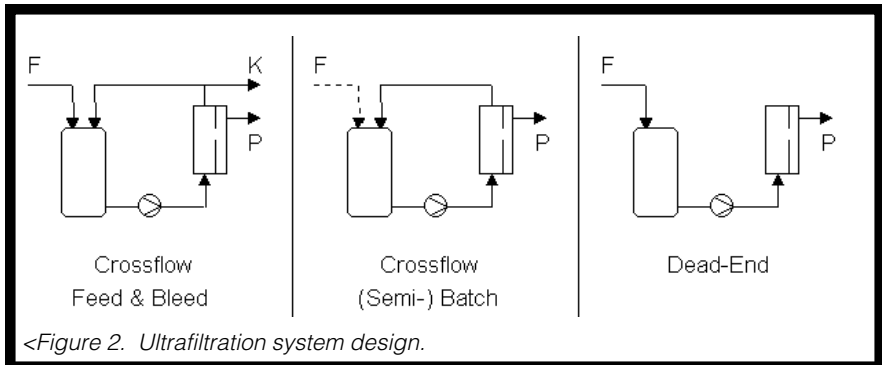
sumption and low membrane flux. "Crossflow - Feed and Bleed" is, therefore, not common to treat large quantities of water. Batch operation starts with a low concentration and ends with a definite end concentration. Batch operation is useful for smaller plants in the field of wastewater treatment.

For the pretreatment of larger quantities of raw water, dead-end operation is the most economical process. It is a kind of "frontal filtration", well known as conventional filtration. The concentrate outlet during filtration is closed. Frequent backwashing cleans the membrane and drains the concentrate. Dead end UF is the preferred process to treat large quantities of water.

The advantages of UF are the independence from the raw water quality and the steadily good quality of the treated water causing less fouling and resulting in a smaller membrane area required in the RO-I and a higher concentration factor respectively. Figure 3 shows the performance of a UF system in the dead-end operation mode as pretreatment for an RO plant. The raw water source is surface water from a river. The turbidity of the filtrate is constant below 0.05 Nephelometric Turbidity Units (NTU) at a raw water turbidity of between 8 and 80 NTU.

**Reverse osmosis.** The RO system is established in the high-purity water production and offers all the advantages to meet the aforementioned general requirements for future membrane processes in the high-purity water production in the semiconductor industry.

New developments of the membrane



<Figure 2. Ultrafiltration system design.

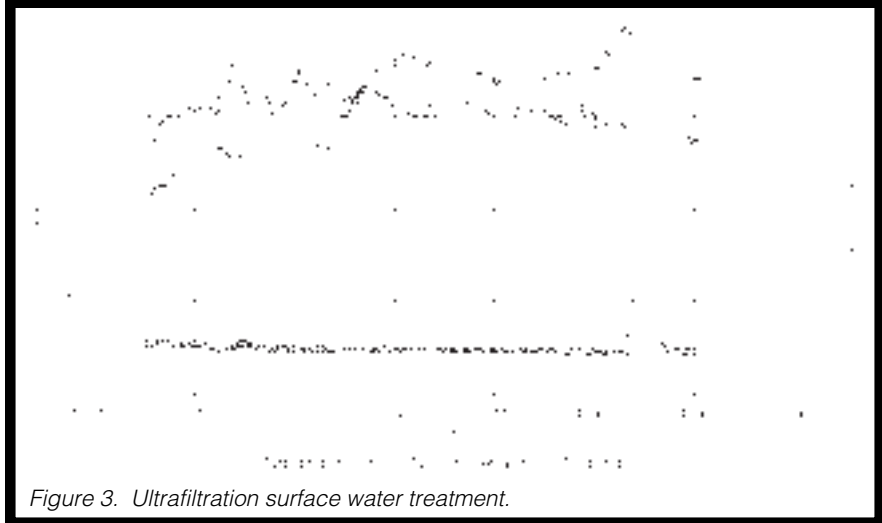


Figure 3. Ultrafiltration surface water treatment.

manufacturers are thin-film composite low-pressure membranes that allow the operation of a RO with a pressure in the range of 8 to 15 bar compared to an operating pressure of up to 40 bar in the past.

To achieve a very high reduction of the ionic load of the water, it may also be worthwhile considering to have two RO-systems connected in series, a so-called double-pass RO. This is also possible with high reject, low pressure membranes. This example shows the salt rejection of a two-pass plant with operation at a higher pH in the first stage.

The thin-film composite membranes can also be operated at a high pH, offering advantages with regard to a better boron rejection.

**Membrane degasification.** In the past, the vacuum degasifier was the only process to achieve low oxygen levels. To reach oxygen levels of less than 1 ppb, the vacuum degasification was designed as a two-stage degasification in combination with a catalytic oxygen removal.

With decreasing oxygen levels downstream of the process, the height of the packing in the vacuum degasifier is increasing. To save energy in some cas-

es, the operational temperature has to be very low (20 to 25 °C), which results in a very low vacuum level requirement. These facts finally lead to an overall height of the vacuum degasifier of about 10 to 13 meters (m), which has an impact on the building design and has to be considered in an early design stage. Because of the highly sophisticated design of the vacuum degasifier, this process is normally designed without redundancy. Together with the fact, that the vacuum degasifier has to be designed for a particular flowrate, this process must be considered as a bottle neck in the process chain.

The membrane degasification meets all the above-mentioned requirements for future high-purity water plants and can be designed to achieve the lowest possible oxygen levels.

For the membrane degasification process, modules with capillary membranes are used. The water flows through the capillaries. At the outside of the capillaries, nitrogen as a sweep gas flows in the opposite direction to the water flow through the modules. Following the physical laws, the oxygen that is dissolved in the water passes the membrane into the sweep gas, the water is

retained by the membrane. The result can be improved by using a combination of nitrogen as sweep gas under vacuum. Figure 4 shows a basic sketch of a three-stage membrane degasification, the respective results are shown in Figure 5.

**Electrodeionization (EDI).** Similarly to the vacuum degasifier, the mixed bed has to be designed on basis of a certain flowrate. Therefore, it is quite inflexible with regard to changes in the flow and has, therefore, to be considered as a bottle neck. Since the mixed-bed exchangers have to be regenerated from time to time, the design according to the N+1 philosophy leads to a 100% redundancy. To achieve a resistivity downstream of the mixed bed of greater than 18 megohm-cm and to prevent any contamination of the high-purity water with chemicals, the actual installed systems are designed as externally regenerated systems. Rather than a highly sophisticated process being developed, a contamination with particles and TOC during the regeneration process cannot be prevented and requires further consideration in the process chain.

The EDI system is gaining more and more in importance as an alternative to the mixed-bed IX. The modular and compact design makes this system highly flexible. The system is continuously in operation and does not require any chemicals for regeneration. A contamination of the water is out of question. However the quality in the outlet of the EDI will not presently achieve greater than 18 megohm-cm. Therefore, a mixed bed polisher has to be considered downstream of the EDI to reduce the ionic load on the polishing loop. Table C compares between mixed-bed IX and EDI plus a mixed-bed IX.

**Reverse osmosis II.** The RO-II is mainly used to reduce TOC and particles downstream of a mixed-bed exchanger and upstream of the polishing system. As mentioned earlier, TOC and particles are produced during the regeneration process of the mixed bed. If the primary mixed bed is replaced by an EDI system, the RO-II will no longer be required (Figure 6).

**Polishing ultrafiltration.** For years, the polishing UF system has been used in high-purity water production for achieving the required particle specification. All the initial requirements for future

membrane processes are already fulfilled.

However, there are some improvements or new developments with regard to this process. In many cases, an absolute filter is installed upstream of the UF system, to maintain the UF feed-water quality. A 3-year experience shows that the absolute filter has no impact on the water quality downstream of the UF. A further development is the use of a concentrate UF to optimize the reject flow of the UF system.

**Summary**

Future requirements on high-purity water plants will lead to a compact and modular design of the individual processes and continuous operation.

The presented membrane processes of UF in the pretreatment, reverse osmosis, membrane degasification, and EDI in the make-up as well as UF in the polishing system will meet these requirements.

An optimization of the currently used membrane systems with regard to the number of membrane steps in a process chain, the way of operation of these processes, the required specification and the overall costs can be done based on the experience gained. ■

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**Key words:** EDI, ION EXCHANGE, REVERSE OSMOSIS, SEMICONDUCTORS, ULTRAFILTRATION, ULTRAVIOLET

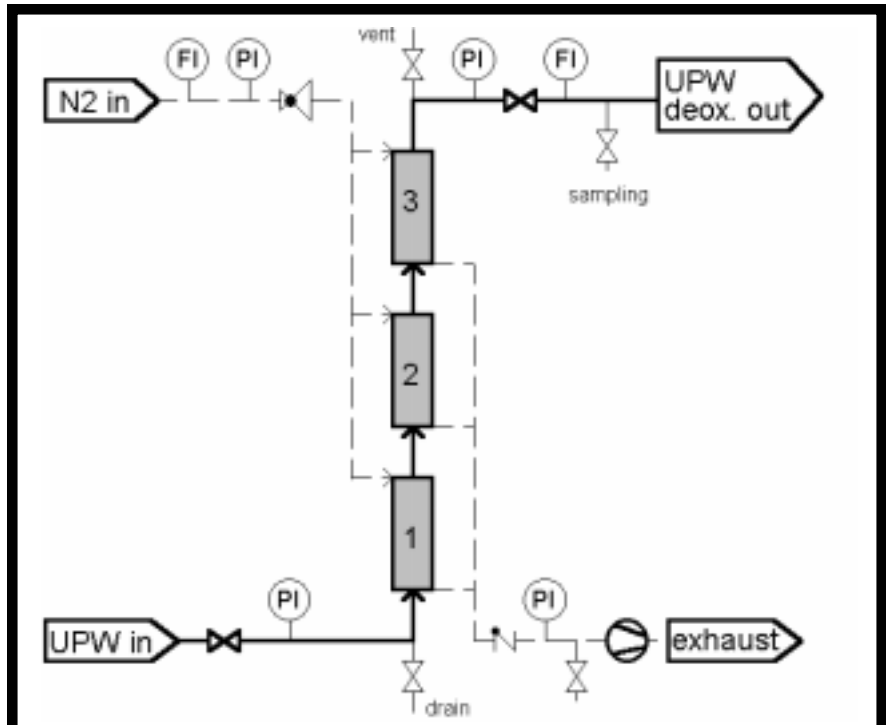


Figure 4. Multi-stage membrane degasifier.

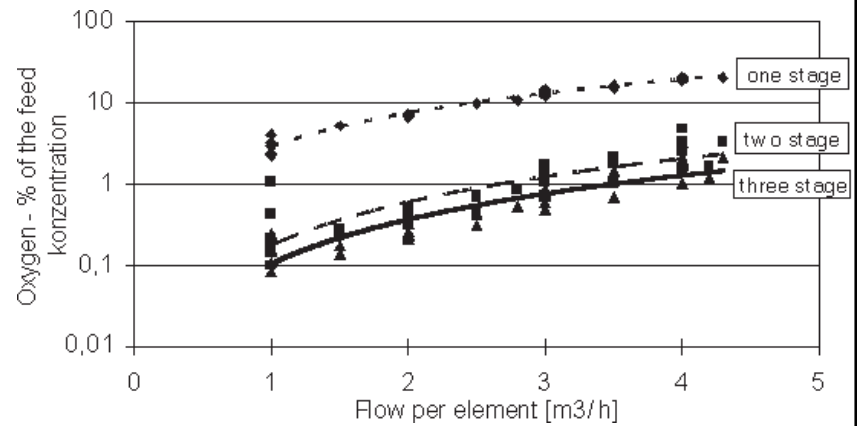


Figure 5. Oxygen reduction with membrane degasifier.

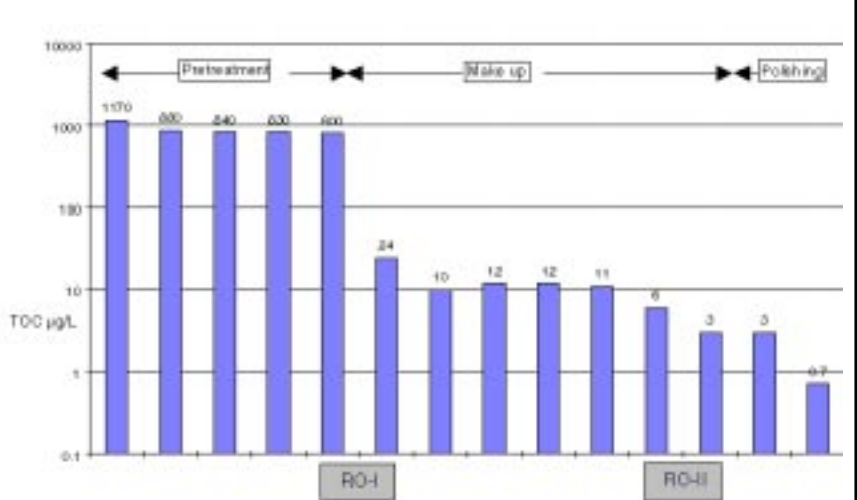


Figure 6. Reverse osmosis TOC reduction.

**TABLE B**  
**Ultrafiltration versus Conventional Filters**

	<i>Multimedia Filter</i>	<i>Ultrafiltration</i>
Continuous	-	++
Modular design ( N+1 )	+	++
No bottle necks	+	++
Compact	-	++
Water quality	+	++
Constant quality	-	+
- = poor		
+ = good		
++ = excellent		

**TABLE C**  
**A Comparison of Mixed-Bed IX versus EDI plus Mixed-Bed IX Polisher**

<i>Feature</i>	<i>Mixed-bed IX Externally Regenerated</i>	<i>EDI + Mixed-bed IX Polisher</i>
Continuous	-	+
Modular design ( N+1 )	-	+
No bottle necks	-	+
Compact	-	+
Water quality	++	++
Constant quality	+	+
- = poor		
+ = good		
++ = excellent		