MEMBRANES

HOW TO MEET TODAY'S DISSOLVED OXYGEN SPECIFICATIONS WITH DEGASIFICATION MEMBRANES

Membrane contactors are widely used in the semiconductor industry to control the dissolved gas levels in high-purity water. They have been commercially available for almost 10 years and the technology has rapidly advanced to meet the demanding needs of the semiconductor industry. The industry is in the midst of moving to 300-millimeter (mm) wafer sizes, while at the same time decreasing the line widths of the integrated circuits. This article discusses the changing specifications and offers the reader advice on how to meet the dissolved oxygen specifications using membrane contactors.

The semiconductor industry is now in the middle of two major transitions. The first is a shift from 200- to 300-mm wafer diameters. The driving force behind this shift is a cost-reduction effort. The cost savings will come from higher volumes of chips per unit wafer as well as expected yield improvements. A 300-mm wafer has 2.25 times the surface area of a 200-mm wafer. This means that 2.25 times the number of chips can be produced on a 300-mm line as compared to a 200-mm line. Studies at Taiwan Semiconductor Manufacturing Company (TSMC) have found that when comparing 200- and 300-mm wafers, the numbers of particles per wafer were unrelated to the wafer size. This indicates that the number of defects per wafer caused by particles was the same for 200- and 300-mm wafers. In other words, the particle defect ratio of a 300-mm wafer was actually lower than a 200-mm wafer (1).

The second transition is a move from 0.18-micron (µm) to 0.13-µm geometries. This transition is fueled by the constant technological drive for improved semiconductor performance. This trend is typically referred to as Moore's law. Intel founder Gordon Moore originally observed this trend in 1965. He observed that the number of transistors per square inch doubled in number every year. As the industry developed, this trend has actually slowed down to doubling every 18 months. This trend is expected to continue through the year 2017, at which time the physical processes of today will reach a finite limit (2).

Based on these two transitions, the volume and purity of water used to manufacture these state-of-the-art semiconductors is increasing. Water treatment system designers are both challenged with making a larger system and producing higher quality water.

The shift in chip size has increased the high-purity water demand per wafer. A typical 200-mm line producing 40,000 wafers/month will require approximately 210 cubic meters per hour (m^3/h) (925 gallons per minute [gpm]) of high-purity water. A 300-mm line with the same capacity will require about 300 m^3/h (1,320 gpm) of high-purity water. This flow increase must be taken into account when designing the system and sizing water treatment unit operations.

Table A compares the requirements for water used to manufacture 0.18-µm and 0.13-µm technologies as proposed by the *International Technology Roadmap for Semiconductors* (ITRS) (3). This Roadmap is a worldwide effort organized by International Sematech. The sponsors of the Roadmap include the Semiconductor Industry Association in San Jose, Calif., The European Electronic Component Manufacturers Association, The Japan Electronics & Information Technology Industries Association, The Korean Semiconductor Industry Association, and the Taiwan Semiconductor Industry Association.

As the line width decreases, there are significant changes in the high-purity water specifications. First, critical particle size has been reduced by almost 50%. There is also a 50% reduction in total organic carbon (TOC) and silica levels. The most dramatic change is a decrease in dissolved oxygen. The dissolved oxygen specification is lowered by an order of magnitude from 10 ppb to 1.0 ppb. These specifications push the limit of conventional technologies. In order to meet this specification, new water treatment concepts must be evaluated.

Meeting these new specifications is a challenge. Each component must be removed and controlled using distinctly different technologies. Feedwater quality and water recycling must be carefully evaluated and considered when designing a system that can reliably meet these specifications. The order of magnitude reduction in dissolved oxygen is

TABLE A
Requirements To Produce 0.18-µm and 0.13-µm Technologies

High-Purity Water Requirements	*180 nm*	*130 nm*
Critical particle size (nm)	90	58
TOC (ppb)	2	1
Bacteria cfu/L	<1	<1
Total silica (ppb)	0.1	0.05
Dissolved oxygen (ppb)	10	1
Particles – critical size (/mL)	<0.2	<0.2
Critical cation, anion, metals (ppt, each)	20	< 20

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a difficult requirement to meet without new technologies and strategies. This article focuses on dissolved gas management in a high-purity water system.

Dissolved Gasses

First, it is important to understand how and why gasses dissolve into water.

Whenever a gas comes into contact with a liquid, it will tend to dissolve into the liquid. The amount of gas that will dissolve into the liquid is proportional to the partial pressure of the gas in contact with the liquid. This relationship is governed by Henry's Law (Equation 1).

$pi = Hxi$ – Henry's Law Eq. 1

Where:
pi = pressure of gas component I
H = Henry's Law coefficient, a function of water temperature
xi= concentration of dissolved solute at equilibrium

The partial pressure of a gas is defined as the product of the molar fraction of the gas in a gas mixture and the total pressure of the gas mixture. This is governed by Dalton's Law (Equation 2).

$$pi=yi*Pt + yj*Pt \qquad \text{Eq. 2}$$

Where:
pi = partial pressure of gas component i
yi = molar component of gas component i
yj = molar component of gas component j
Pt = total pressure of the gas mixture

From these two relationships, we can see that the amount of a specific gas component that will dissolve into a liquid is directly proportional to the total pressure of the gas in contact with the water and the molar fraction of the gas.

As the gases in the atmosphere come in contact with water, the gasses will tend to dissolve into the water. Since the atmosphere is made up 79% nitrogen, 21% oxygen, and trace amounts of carbon dioxide (CO_2) and other gases, water exposed to the atmosphere will also contain these gases. Under one atmosphere of pressure, water at 25 °C typically contains about 8.5 parts per million (ppm) of dissolved oxygen and 14.5 ppm of dissolved nitrogen.

By controlling the gas pressure and concentration in contact with the water, we can control the gas concentrations in the water (4).

Dissolved Gas Removal Techniques

Vacuum tower. A vacuum tower consists of a baffled tower. Water is sprayed into the top of the tower and is broken into thin films as it flows through the tower. This process creates a large contact area between the gas and the water.

Inside the tower a vacuum is drawn. The vacuum essentially lowers the gas pressure in contact with the water, creating a driving force to remove dissolved gasses from water. Hybrid variants of this technology are commercially available that include adding nitrogen to the tower to dilute the concentration of oxygen in the gas phase, and heating the water into the tower to lower the solubility of the gases.

These technologies have successfully been used to lower the dissolved gas level in a high-purity water system. A well-designed tower can produce water that contains less than 5 parts per billion (ppb) of dissolved oxygen. Some may even deliver a less than 2 ppb of dissolved oxygen. The limits of the technology are stretched when trying to routinely deliver less than 1.0 ppb of dissolved oxygen.

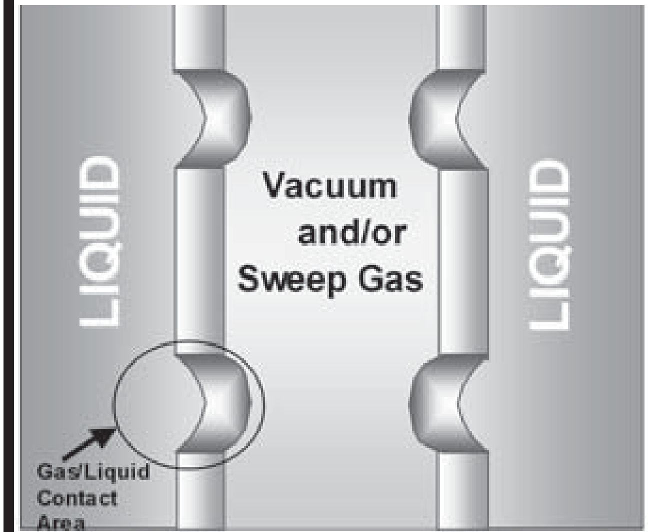

Figure 1. An illustration of pores in a contactor membrane.

Figure 2. A membrane system installed in a semiconductor plant in Singapore.

Membrane contactor. Over the last five years, membrane-based degasification has become increasingly popular. Membrane-based degasification uses a microporous hydrophobic membrane with a pore size on the order of 0.03 µm. Water is passed on one side of the membrane and a gas is passed on the other. Since the membrane is manufactured using a hydrophobic material and the pores are small, water does not easily pass through the pores. Gases, however, freely pass through the pore on a molecular level. By controlling the pressures and concentrations of the gas, precise control of the dissolved gas level can be achieved.

By increasing the number of membrane contactors in a system the surface area of the system can be increased. By using this concept, the dissolved oxygen level in the water can

TABLE B
Summary of Results from the Use of a Membrane Contactor System

Parameter	*Time*	
Particle contributions	Time to add < 10 particles/ mL (h):	4.5
(particles $\geq$ 0.10 µm)	Time to add < 1 particle /mL (h):	32
TOC	Time to reach 2 ppb added (h):	9.2
	Time to reach background (h):	70

be lowered to far below 1.0 ppb. The achieved level of dissolved oxygen is limited by the purity of the nitrogen gas used.

By using a membrane to bring the gas phase and liquid phase in contact with each other, a very high contact area per unit volume can be achieved. In fact, this technology has an order of magnitude contact area per unit volume as compared to a vacuum tower.

An illustration of a single hollow fiber is shown in Figure 1. In this figure, water flows on the outside of the hollow fiber and gas flows through the inside. The membrane acts as a support that allows that gas and liquid phases to come in direct contact with each other at the pore. Water will not easily pass through the membrane because it is hydrophobic and has small pores. The water pressure would need to exceed 500 pounds per square inch gauge (psig) in order for the water to physically flow through the pore. These properties allow the gas and liquid to come into direct contact with each other at the pore.

System Design Challenges

In order to meet the low dissolved oxygen requirements, new strategies and system designs are currently being employed to make this possible. The first hurdle is designing a system that can deliver less than 1.0 ppb; the second is keeping the dissolved gas level less than 1.0 ppb.

Membrane contactors have been commercially available for almost 10 years and they are a viable technology that can be used to meet the 1.0 ppb of dissolved oxygen requirement. However, the overall water treatment system design must be properly laid out to keep it there.

Source of oxygen contamination. Here is a summary of ways oxygen may enter a treatment system.

1. Air leaks into the high-purity water system. Since a high-purity water system is essentially surrounded by gas that contains oxygen, any small leak will allow oxygen to re-dissolve back into the water. It is not uncommon to see 2 to 3 ppb of dissolved oxygen in a makeup system and 5 to 10 pbb of dissolved oxygen being delivered to the fab. Oxygen can enter the system through pump seals, oxygen permeable polymers, and essentially any fitting or connection that may have a small leak.

2. During routine operations in the fab, when tools are brought on and off line. When a line is broken and exposed to the atmosphere, air will enter the system and potentially dissolve back into the water.

3. When the final polisher is replaced, air trapped inside the vessel will dissolve back into the high-purity water when the tank is brought back on line.

In a system that is designed to deliver less than 1.0 ppb of dissolved oxygen, these issues need to be carefully considered. In order to keep the dissolved oxygen low, it is recommended that dissolved gases be removed in both the makeup and polishing system. By continuously removing dissolved gases from water, the designer can be certain that the dissolved oxygen level remains low.

The relatively large size, uncleanliness, and possible source of vibrations make vacuum tower technology unsuitable for the final polishing system. Vacuum tower technology can only be used in the makeup system. This limitation makes it difficult to reliably deliver 1.0 ppb dissolved oxygen to the fab.

Membrane Contactor System Design

A photo of a membrane system installed in a semiconductor plant in Singapore is shown in Figure 2. The system was built by Vivendi Water systems. A typical piping schematic of a membrane system is shown in Figure 3.

Equipment selection. The major components of a membrane-based system include the membranes, a nitrogen source, and a vacuum pump.

One supplier[a] has developed a sizing program that can be used to determine the overall performance of a system. The program also calculates the required vacuum capacity and nitrogen consumption of the system. This program can be used to size and select vacuum pumps for the membrane system.

A water-sealed vacuum pump is recommended for drawing a vacuum on the membrane system. The system designer has the option of selecting stainless steel or cast iron pumps. Cast iron can be considered, because in a membrane-based system, the vacuum and gasses are separated from the high-purity water by a membrane. In the event of a loss in vacuum, the seal water will not contaminate the high-purity water because the membrane acts as a barrier.

Gas piping is typically fabricated with stainless steel components. Other materials can be used but care should be taken in their selection due to possible oxygen permeation. All connections in the gas line should be welded or flanged. The gas line is under a vacuum and any leak in this portion of the system will prevent the system from delivering low levels of dissolved oxygen. All valves and instruments in the gas line should also be rated for vacuum service.

The vacuum line can be fabricated of stainless steel, carbon steel, or polyvinyl chloride (PVC). Connections in this line are not as critical and threaded connections can be used. A vacuum relief valve is recommended in order to prevent cavitation of the vacuum pump.

Overall Water Treatment System Design

A membrane-based system offers the designer many options. The contactors are very clean so they can be installed almost anywhere in the system. Membranes manufactured by the supplier[b] have been tested by an independent lab to determine the cleanliness of the devices. A summary of the results is listed in Table B. It is important to note that the contactor typically treats water at a flowrate of 35 to 45 m^3/h (154 to 198 gpm). These tests were done at a 1.14 m^3/h (5 gpm) because of the flow limitations found in extractable test facilities. In practice, actual rinse-up times are much faster.

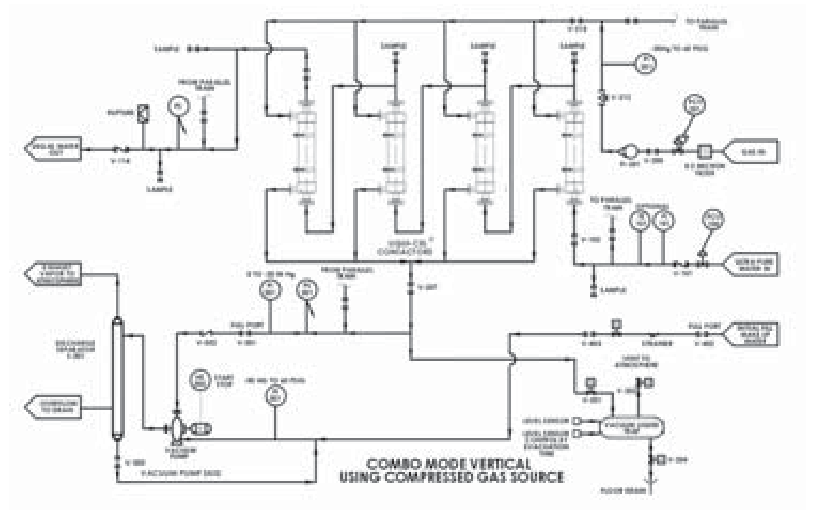

Figure 3. A typical piping schematic of a membrane system.

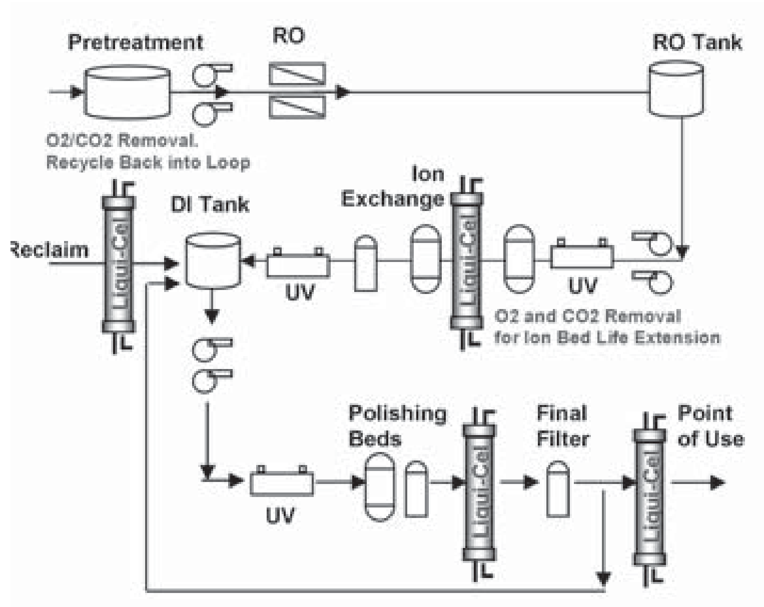

Figure 4. A basic layout for a typical high-purity water system.

Make-up system. The basic layout for a typical high-purity water system is given in Figure 4. In this system, there is a makeup system and a polishing loop. The make-up system typically consists of a pretreatment system, reverse osmosis (RO) membrane system, degasification system (contactors), and an ion-exchange (IX) system. Ultraviolet (UV) light systems are also used for biological control and TOC destruction.

The make-up system feeds a storage tank. The storage tank is blanketed with nitrogen in order to keep atmospheric gasses, such as oxygen, from dissolving back into the water.

Polishing system. The polishing system is typically made up of IX, degasification, and UV lights for TOC destruction and final filtration. The polishing system typically recirculates about 20% of the water used.

In a typical high-purity water system, the dissolved gas removal system is typically installed in both the makeup and the polishing system. Bulk oxygen removal is typically performed in the make-up system upstream of the primary polisher. This is done for several reasons.

1. The flowrate in the makeup system is 20% lower than the flow in the final polishing system. This means that 20% less membrane area can be used if the membranes are installed in the makeup system.

2. In order to reach low levels of dissolved oxygen, the contactors are typically operated in series. Each membrane in series will contribute to the pressure losses in the system. By removing the bulk of the oxygen in the makeup system, pressure losses in the final polish loop can be minimized and the need for repressurization is eliminated. Typically, the dissolved oxygen content of the water is lowered to 10 to 20 ppb in the make-up system.

3. The membranes should be installed upstream of the primary IX system in an effort to remove any dissolved carbon dioxide that may be present in the water. Carbon dioxide can be present because of the destruction of organics or the by-product of pH adjustment upstream of the RO. Removal of the carbon dioxide will lower the load on the IX resin and can double the life of the resin.

In the final polishing loop, we recommend placing the membrane contactors between the ion exchange and the final polisher. If the organic level is very low, the energy generated by the UV light will be absorbed by the water and hydrogen peroxide may be formed. The amount of hydrogen peroxide generated will depend on the dosage of the UV light and the amount of organics in the water. Hydrogen peroxide may tend to oxidize downstream equipment if not controlled. If the hydrogen peroxide is formed, it may react with downstream equipment and form dissolved oxygen downstream of the membrane contactor that could bring the dissolved oxygen level in the water out of specification.

System Advantages

In addition to the membrane's ability to deliver less than 1.0 ppb of dissolved oxygen, it offers the system designer several key useful improvements over the conventional high-purity water design.

Redundancy. In a system designed with a vacuum tower, redundancy is not practical. A membrane-based system is generally designed in two stages. The first stage is in the makeup system and the second stage is in the polishing system. Each system can be equipped with two vacuum pumps. One is on standby to be used during routine maintenance and one is for use in case of failure of the primary pump.

A membrane-based system typically contains multiple membrane contactors arranged in a series and parallel configuration. Often the system is designed with a plus one-train concept. In this design, an extra train of contactors is arranged in the system so in the event that one train needs to be shut down for servicing, the dissolved oxygen specification can be met. A redundant degas system is not practical in a system that uses a vacuum tower.

System stability. Membrane-based systems operate over a wide range of flowrates. This offers the designer the ability to design the system such that it can operate over a wide range of flows. In the event that the water flowrate fluctuates, the system will not be compromised. The system will actually remove more dissolved oxygen at a lower flowrate.

Since a membrane-based system contains degasification in the polishing loop, the system may be started up much faster. In a system that that does not have degasification in the final polishing system, the water may need to be purged or the system may take a long time to reach the low levels of dissolved oxygen specified by the plant.

System versatility. A membrane system is essentially a modular system. A system that is designed to treat 300 m^3/h in the first phases can easily be expanded to treat 400 or 500 m^3/h in the second phase.

Conclusions

Meeting the water specifications used to manufacture today's state-of-the-art semiconductor device is a challenging task. The specification for dissolved oxygen has been lowered to 1.0 ppb as the line width shifted to 0.13-µm manufacturing.

The unique properties of membrane contactors allow them to be installed in almost any location in the high-purity water system. This allows them to be installed in the final polishing loop of a high-purity water system. Installing a degasification device in this location is essential to properly designing a system that can deliver 1.0 ppb of dissolved oxygen to the fab.

In addition to the membrane contactor's ability to reach less than 1.0 ppb, they also offer the system designer improvements to the conventional high-purity water system design. These improvements include redundancy, system stability, and versatility.■

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Endnote

[a] Membrana Charlotte of Charlotte, N.C., has developed GASCAD™, a sizing program that can help determine the overall performance of a system.
[a] Membrana Charlotte of Charlotte, N.C., is the supplier.

Author Fred Wiesler is a key account manager, Asia, with Membrana Charlotte, which was formerly Celgard Inc. He has more than 15 years of membrane-based experience. His past experience includes sales and servicing of disposable filtration elements, ultrafiltration membranes and systems, and membrane contactors and systems. Mr. Wiesler holds a B.S. in mechanical engineering from the State University of New York at Stony Brook, N.Y.

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