

Improved Technology for Dissolved Oxygen Measurement

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Abstract

The need for measurement and control of dissolved oxygen at very low concentrations in ultrapure water for some wafer processes has been recognized for many years. Dissolved oxygen instrumentation has been developed that increases the reliability and greatly reduces the maintenance requirements and costs of this specialized measurement. Combining the strengths of traditional diffusion membrane sensors with those of equilibrium-type sensors provides a new capability for successful monitoring. The theory of operation of these types of sensors as well as their benefits and limitations are described. In addition, a multi-parameter instrument concept opens up opportunities for pairing dissolved oxygen with other important measurements such as resistivity or pH. Test results of this measurement system are presented.

Introduction

DO (dissolved oxygen) is undesirable in pure waters for microelectronics manufacturing for several reasons. In the purification itself, there is concern that DO can oxidize ion exchange resins in mixed bed polishers, producing contamination downstream—the justification for an efficient degasifier. There has also been concern that high DO levels support microbiological growth in water systems. In some processes, DO levels influence the oxidation of the active silicon surface during rinse steps and can have a significant impact on chip yields.[1] “This...can affect the quality of thin gate oxide, quality of polysilicon and dielectric thin film, and selective CVD, and atomic layer epitaxy.”[2] Industry guidelines have set DO limits for ultrapure water used for various microelectronics line widths.[3]

DI water monitoring and control for these critical processes requires accurate and reliable DO measurement at low concentrations. Since there is a variety of instrumentation available for this purpose, such equipment must be selected, operated and maintained carefully to obtain optimum results. Presented here is an overview of the technologies available and a new approach to address this need.

Oxygen Solubility

Oxygen has a temperature-dependent solubility in water at atmospheric pressure as shown in Figure 1. If the curve were extrapolated, the solubility at 100°C would be zero as water vapor pressure reaches 100% at boiling, again, at atmospheric pressure. The entire curve would be shifted upwards if the pressure over the water were increased. Working in the opposite direction, deaerators depend on partial vacuum and elevated temperatures to remove dissolved gases.

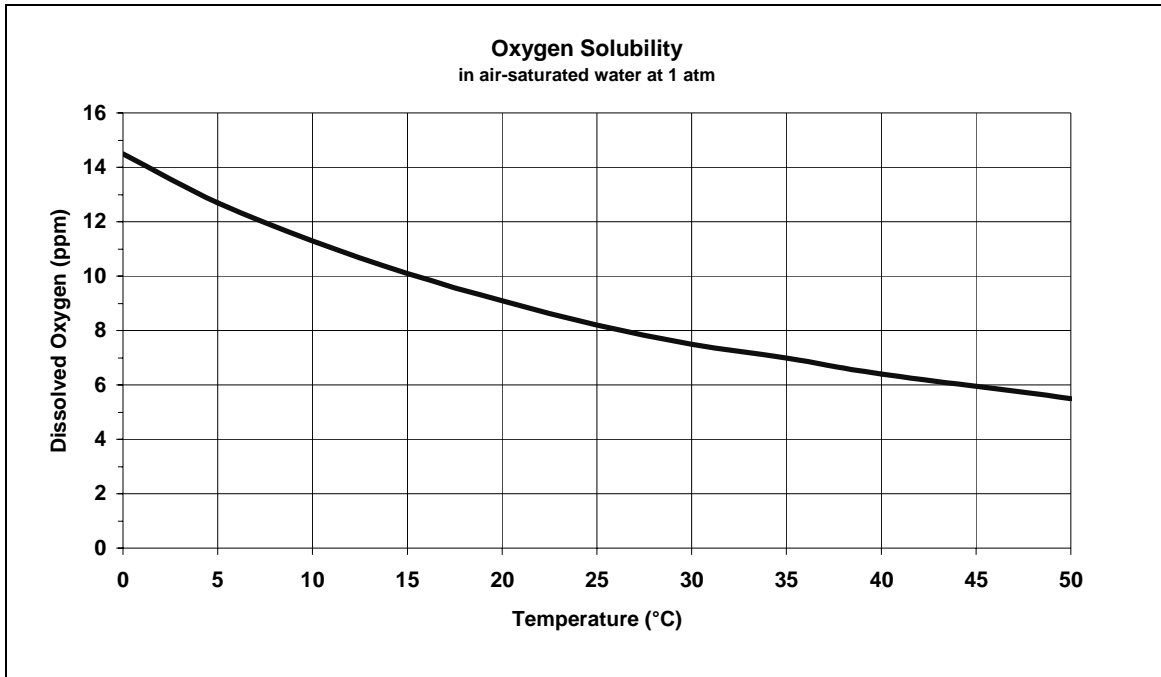


Figure 1 – Solubility of Dissolved Oxygen

Dissolved Oxygen Sensor Operation

DO sensors are electrochemical devices that take advantage of the gas permeability of polymer membranes to separate the heart of the sensor from the sample. This separation provides a controlled environment for the electrodes and electrolyte while allowing oxygen to enter from the sample and react. It keeps the electrochemistry contained and clean. Figure 2 is a simplified illustration of a DO sensor.

The diffusion rate of oxygen through a membrane is proportional to the partial pressure of oxygen in the sample. Of course the membrane material and thickness also affect the diffusion rate, but they are fixed and those properties are accommodated in calibration.

The oxygen which permeates the membrane reacts at the cathode, producing a current in direct proportion to the quantity of oxygen. That current is the measurement signal which matches the oxygen partial pressure and the concentration of DO, at least at constant temperature.

To derive a concentration measurement from partial pressure with varying temperature, the signal must be compensated, based on a relationship similar to Figure 1. That is, the DO concentration in water that a partial pressure represents, depends on temperature. The sensor's temperature signal is used by the instrument microprocessor to temperature compensate the measurement. Further background on the use of these types of DO sensors is described in an ASTM standard test method.[4]

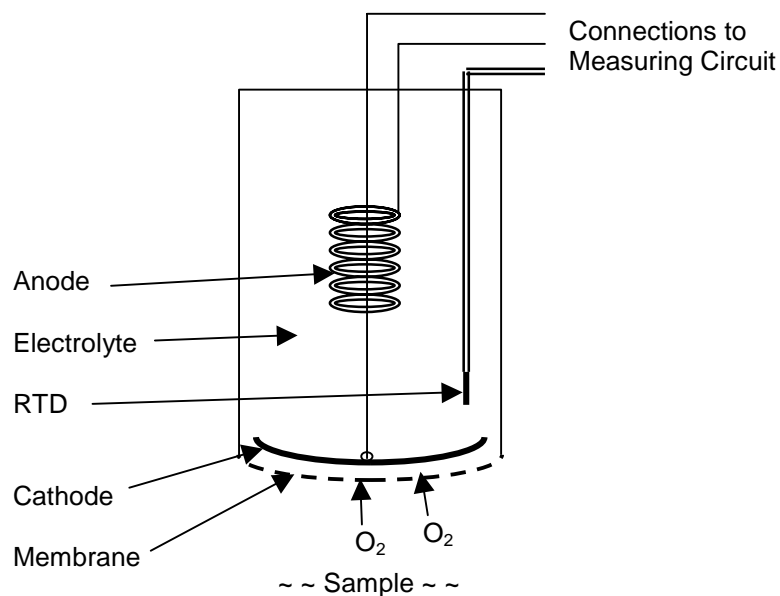


Figure 2 – Dissolved Oxygen Sensor Components

Improved Dissolved Oxygen Sensor Design

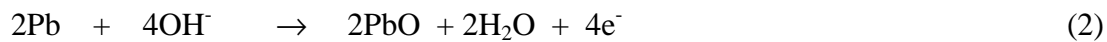
Membrane DO sensors have been around for many decades but the design choices made in electrochemistry, membrane type, mechanics, and electronics can make a substantial difference in maintenance requirements and performance. Described here are these differences for an improved design sensor.

The electrochemical reactions occurring within this probe take place in many stages but the overall result is summarized in equations 1 – 3.

Cathode



Anode



Net



From this it can be seen that there is no consumption of electrolyte. Only the anode is oxidized. However, with suitable electrolyte composition to maintain an active anode surface in spite of its oxidation, a vastly extended operating life can be obtained. With this limitation out of the way, the maintenance interval for this type of sensor is upwards of 3 years.

The choice of electrodes and electrolyte for this sensor provides a self-polarizing voltage that is inherent in the design. This feature allows the sensor to maintain consistent electrochemical characteristics even when disconnected from the instrument, minimizing startup time and upset recovery time if power is lost or if the sensor must be disconnected for any reason.

Additional benefits are provided by a membrane with low permeability yet fast response. By reducing the amount of oxygen permeating the membrane, sensitivity to low flows is greatly reduced. Conventional probe designs allow a larger amount of oxygen to pass through the membrane and more readily deplete the oxygen concentration from the sample layer next to the membrane at low flowrates, resulting in lower than actual readings. The same effect applies to membrane fouling: conventional probes have greater sensitivity to coatings because of their faster consumption of oxygen from the sample and they will produce greater negative errors as a coating builds up.

The ability to measure accurately at low sample flowrates is also enhanced by a flow chamber design that directs the sample flow as a jet, directly at the membrane. This assures that the flow against the membrane is turbulent and will not be depleted of oxygen. Operating with sample flowrates down to 50 mL/min, without compromising accuracy, can save a substantial amount of pure water on a continuous basis. For example, a probe requiring a 150 mL/min sample flowrate would consume nearly 53,000 liters (14,000 gallons) of ultrapure water per year more than one that can operate at 50 mL/min.

The membrane material used in this sensor has a faster transport rate for oxygen. Although the *quantity* of oxygen passing through the membrane is less, it actually travels *faster* than through conventional fluoropolymer membranes since fluorine has a particular affinity for oxygen.

When these improvements are all incorporated into a sensor design, the result is a very long-lived assembly where membrane, electrolyte and anode surface require service only if the membrane is damaged. Installations of 3-5 years with no internal service are typical. Only occasional external cleaning is needed when measuring solids-bearing samples. A summary of these improvements is given in Table I.

Table I - Summary of Sensor Improvements

Sensor Characteristic	Conventional	Improved
Flow sensitivity	Minimum flow required	Lower flows tolerated
Membrane fouling	Major interference	Interference reduced
Response time	Slowed by fluoropolymer membrane	Non-fluoropolymer membrane response
Startup time	Extended for polarization equilibration	Shortened by continuous self-polarization
Membrane maintenance	~ 6 months	> 3 years typical
Electrolyte replacement	~ 6 months	> 3 years typical
Anode rejuvenation	~ 6 months	> 3 years typical

Instrumentation

This sensor design was developed by the Danish company OxyGuard International in the early 1990s and was evaluated successfully by the independent Dutch organization, KEMA.[5,6] Its long-term performance at low ppb levels has been proven in numerous European and Asian power plants. A more recent partnership with Thornton / Mettler Toledo provides enhanced analyzer / transmitter capabilities.

This instrumentation complements the sensor design with extremely stable, self-calibrating amplification, accurate temperature compensation, convenient calibration with atmospheric pressure correction, plus digital and dual-analog outputs. Analog output options include bi-linear scaling, to enable high resolution data acquisition in the ppb range yet include on-scale records of ppm range measurements from the same 4-20 mA signal. For example, a normal operating range could be 0-100 ppb with the lower half of the analog output signal (4-12 mA) scaled to that range. The upper half of the signal (12-20 mA) can be scaled for 100 ppb to 10 ppm to allow tracking the progress of startup or any upset as shown in Figure 3. It can also be used to document air calibrations in the same measurement record. An RS232 output is also available that can track the full ranges of measurement with maximum resolution.

The instrumentation can also couple a DO measurement with a second channel of resistivity, pH or ORP in the same instrument. This can be especially convenient when the pair of measurements is needed to assure water purity. Combined measurements are also very helpful in maximizing the number of measurements in a given panel space and in reducing instrumentation costs.

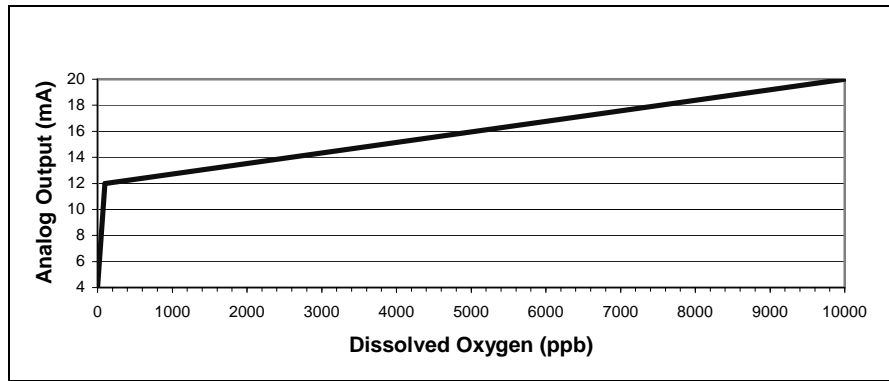


Figure 3 - Bi-Linear Output Scaling

Operating Experience

This DO instrumentation has been thoroughly tested in semiconductor and power plant applications. Examples are illustrated in the following figures. Figure 4 is a plot of operating data comparing the new instrumentation with existing, higher maintenance dissolved oxygen equipment on the same plant sample. This sample is taken following the cation exchanger and deaerator in the water treatment system of a U.S. semiconductor plant. DO is used for continuous monitoring of deaerator operation. The parallel tracking provides confirmation of performance though the operator acknowledged the reference instrument was in need of maintenance and calibration.

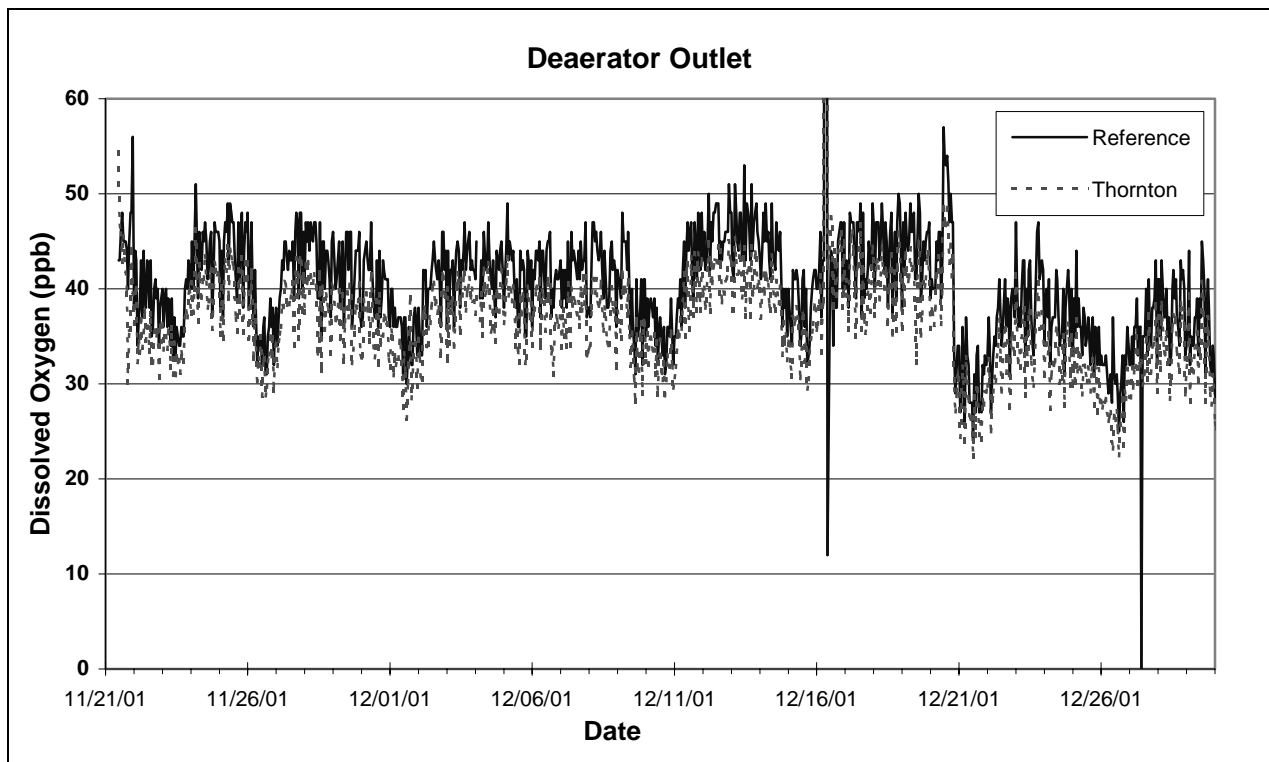


Figure 4 – Evaluation on a Semiconductor Treatment System Deaerator

Figure 5 is a plot of data from a similar comparison test but on a sample in a nuclear power plant. This provides confirmation over a wider operating range, including an incident when the hydrogen treatment was shutdown, allowing the oxygen level to rise. Additional tests have been run in other applications with positive results.

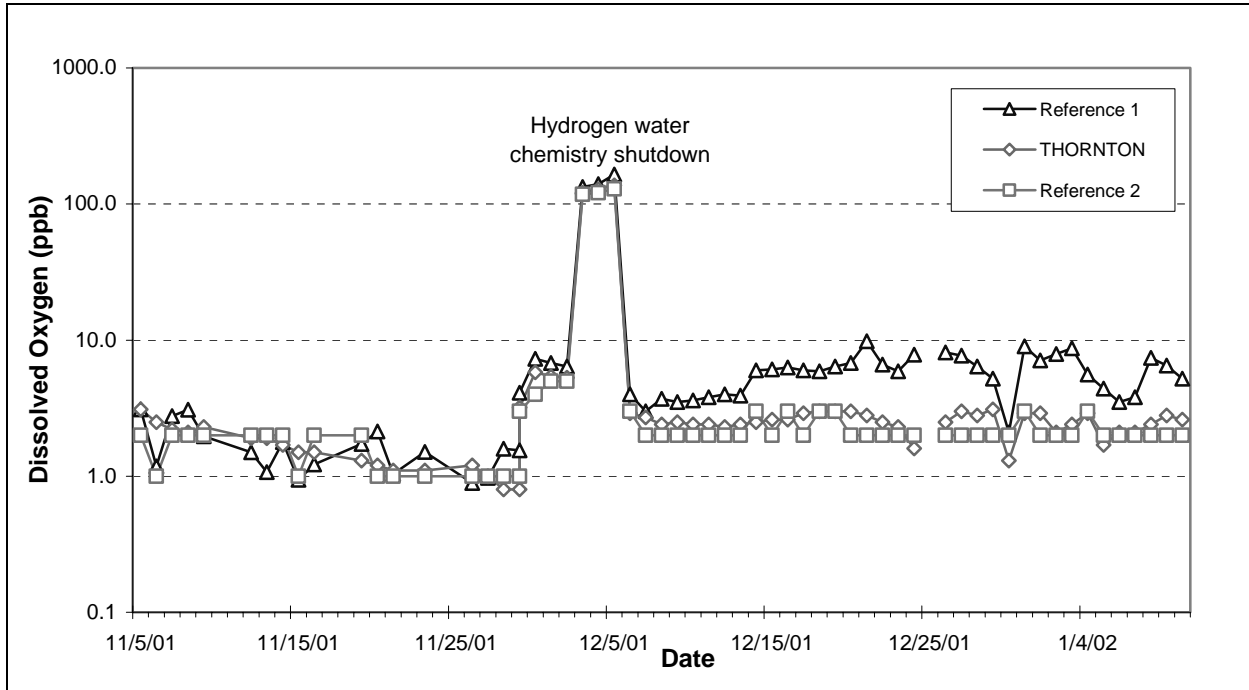


Figure 5 - Evaluation on a Nuclear Power Plant Sample

Interferences

Although improved sensor and instrument design can remove many obstacles from DO measurement, there still remain a number of interferences that must be recognized and properly addressed. Probably the most common problem is air leaks into the sample line. Although the sample is usually under positive pressure, air may still leak through any thin water film at a loose fitting and contaminate a low ppb sample. It always causes a high, flow-sensitive reading. Rotameters, some valves and fittings are particularly prone to air leakage. It is a good practice to install a sample rotameter downstream of a DO sensor for this reason.

A similar problem can occur if using a section of polymer tubing sample line since it is gas permeable. The ubiquitous laboratory vinyl tubing is *not* recommended for DO samples. A recent study has shown that PVDF has a much lower permeability, with Nylon and polypropylene also considerably better than vinyl.[7] Stainless steel or other non-permeable material is preferred but if a flexible connection is needed, the tubing should be of one of the low-permeability materials, have a thick wall and be as short as possible in order to minimize oxygen ingress.

Interference from either leaks or permeation through the sample line can be diagnosed by increasing the sample flowrate. If there is no oxygen intrusion, the reading should remain nearly constant. If the DO reading decreases, a leak or permeation should be suspected since the higher flowrate dilutes the oxygen ingress. If there is an *increase* in the reading, then the original flowrate was too low or the probe requires cleaning. Accumulation of a coating on the membrane surface will cause lower than actual, flow-sensitive readings. Cleaning with a soft cloth and/or dilute hydrochloric acid is needed.

Under some conditions, oxygen-consuming bacteria can grow on DO sensor membranes or inside polymer sample lines. This will affect the readings of any type of sensor by lowering the actual concentration at the surface of the membrane which, in turn, causes low readings. Here also, an increase in flowrate would cause an increase in DO reading. Chemical sterilization with very dilute hydrochloric acid or very dilute hypochlorite bleach can eliminate the bacteria.

Summary

The improvements in dissolved oxygen measurement described here should go a long way to reducing maintenance and operating costs of this type of instrumentation. The accompanying increased reliability of the measurement will enable more confidence among operating personnel in reacting to water treatment system upsets and should improve their responsiveness in correcting them.

Biography

David Gray has a B.S. in Chemical Engineering from Case Western Reserve University and over 30 years experience in the design, application and marketing of process analytical and control instrumentation. He has authored numerous articles and contributed to books on the measurement and control of conductivity/resistivity, pH, ORP, specific ion, and dissolved oxygen in the semiconductor and power industries. He is a senior member of ISA (Instrument Society of America) and a task group chairman on the ASTM (American Society for Testing and Materials) D19 Water Committee.

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