

Dissolved Oxygen Monitor (HD-960L) for Semiconductor Wet Process Performance of the Dissolved Oxygen Monitor Used in the Semiconductor Wet Process; Low Concentration Monitoring, High Temperature, Small Amount of Sampling Volume, Chemical Resistance

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The HD-960L dissolved oxygen monitor was launched for etching chemicals (HF and TMAH aqueous solutions) in semiconductor wet processes. The polarographic sensor has a guard electrode to improve the response in the low-concentration range. Optimizing the concentration of the electrolyte solution volume and configuring a current-restricting resistor for the guard electrode made it possible to measure high-temperature solutions and extend the life of the electrolyte solution. The evaluation test results showed that the saturated dissolved oxygen signal is not affected even if the chemical concentration changes, that the response to the concentration changing in the low-concentration range was fast enough, and that the signal was linear with respect to the concentration. A magnetic stirrer was installed in the flow chamber, which made it possible to take stable measurements of the dissolved oxygen, even in cases of samples with low flow rates.

Introduction

In semiconductor device manufacturing processes, aqueous solutions of substances such as hydrofluoric acid and TMAH (tetramethyl ammonium hydroxide) are used. The chemicals used in these processes normally contain a few $\mu\text{g/L}$ to a few mg/L of oxygen, and it has been pointed out that this oxygen dissolved in the chemicals affects wafer processing.

The speed of etching using TMAH and the surface uniformity are related to the dissolved oxygen concentration, and it has been found that this can affect finishing, and the dissolved oxygen in the hydrofluoric acid can corrode the copper wires and cause the device characteristics to deteriorate. As such, there is an increased need to monitor the dissolved oxygen in these chemicals.

Cutting off the oxygen in the atmosphere can be achieved by purging the nitrogen, but when the oxygen in the chemicals also needs to be controlled at a low concentration, it needs to be checked using a dissolved oxygen concentration monitor. Here we would like to introduce the performance and structure of our dissolved oxygen monitor (HD-960L) for low concentrations and high temperatures that is specialized for chemicals used in semiconductor device manufacturing processes.

Measurement principle (membrane polarographic method)

This dissolved oxygen monitor uses an electrochemical sensor that operates with the membrane polarographic method, and the sensor is composed of an anode, a cathode, and a guard electrode. The area inside the sensor is filled with electrolyte solution, and the area between the fluid to be measured and the sensor is segregated by a gas-permeable polymeric membrane.

When the oxygen gas has passed through the membrane that separates the aqueous solution to be measured and the electrode, and diffusion allows it to reach the cathode (Au) covered by a thin electrolyte solution coat, the oxygen receives electrons from the cathode, is reduced, and becomes hydroxide ions. With the anode (Ag), part of the anode is oxidized, is ionized, and breaks away from the anode, and at the same time, leaves electrons on the anode. At this time, electrons move from the anode to the cathode, so if measurements are taken with an ammeter, a signal can be obtained that is proportional to the number of the reaction associated with the oxygen gas reduction per unit time. The main components of the electrolyte solution are a KCl aqueous solution with a pH buffer added to decrease the changes in pH that go along with the reaction. To promote the reaction, the cathode electrode is applied about -0.6 V with respect to the anode. The chemical reaction associated with oxygen gas reduc-

tion is shown below.

Cathode: $O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$

Anode: $4Ag + 4KCl + 4OH^- \rightarrow 4AgCl + 4KOH + 4e^-$

The chloride ions are consumed along with the reaction, which leads to the electrolyte solution having a life. At the same time, the silver on the anode gradually oxidized, but the anode has a sufficient amount secured, so this can be ignored compared to the consumption of the electrolyte solution.

If the sample is a solution of hydrofluoric acid or TMAH, etc., the ions can't move through the membrane, so they don't affect the reaction. It is possible to correct the salinity if the chemical concentration is known, but with this device, the output is as dissolved oxygen in pure water.

Gas-permeable membranes

We used an FEP (fluorinated ethylene propylene) membrane (thickness of 25 μm) for the gas-permeable membrane. The surface that contacts the electrolyte solution has undergone hydrophilic treatment, and the wetting of the electrolyte solution and the cathode and the electrolyte solution and the membrane has been improved.

Innovations for measuring dissolved oxygen in low concentrations

There are 2 types of oxygen gas that reach the cathode: the oxygen that reached the cathode by passing through the membrane directly above the cathode, and the dissolved oxygen in the electrolyte that reached the cathode by diffusion. The dissolved oxygen in the electrolyte solution finally reaches equilibrium with the dissolved oxygen in the sample fluid, but the volume of the electrolyte solution is larger, so it takes several hours to reach equilibrium. For example, if a sensor has been exposed to air for a long time and sufficient oxygen has dissolved into the electrolyte solution, and this sensor is placed in a zero-oxygen environment, regardless of the fact that there is zero oxygen gas reaching the cathode through the membrane, when the dissolved oxygen in the electrolyte solution reaches the cathode, the signal will not be zero, or it will take a long time until it reaches zero. This phenomenon can be ignored when measuring high concentrations, but becomes conspicuous when measuring the oxygen concentration in a low concentration level of a few $\mu\text{g/L}$.

As such, we provided a ring-shaped guard electrode with the same function as the cathode around the cathode, so that the dissolved oxygen in the electrolyte solution will be reduced by this guard electrode and won't reach the

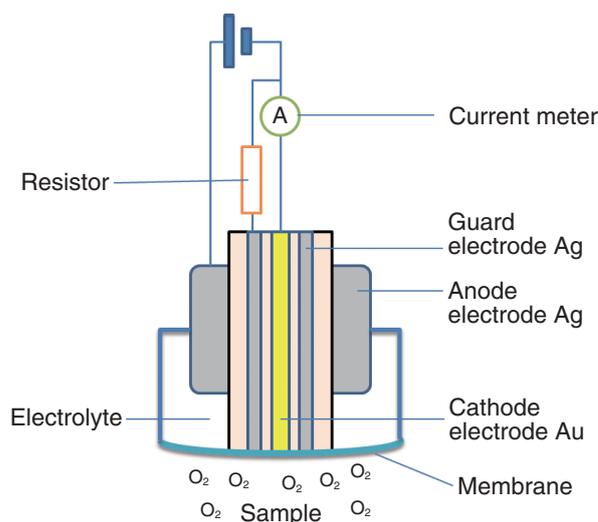


Figure 1 Measurement principle of membrane polarograph method

cathode. This guard electrode blocks oxygen from reaching the cathode by diffusing from the electrolyte solution, which is a problem when taking measurements in low concentrations, and makes it possible to have a high-speed response.

Restricting guard electrode current

The guard electrode is necessary to speed up the response for low concentrations, but is not necessary for high concentrations. However, the guard electrode has approximately 1.4 times the surface area of the cathode, so if the sensor has been exposed to a high concentration of oxygen for a long time, the oxygen will be reduced by the guard electrode, which has the disadvantage of speeding up the degradation of the electrolyte solution. As such, we provided a resistor to restrict current in order to control reduction reactions by the guard electrode in states where the oxygen concentration is high, to prevent the electrolyte solution from degrading. This current-restricting resistor controls unnecessary electrolyte solution consumption by only restricting the guard electrode function when the oxygen concentration is high, while maintaining the true function of the guard electrode when there is low dissolved oxygen. Figure 1 shows the membrane polarographic measurement principle with the guard electrode.

Benefits of the guard electrode

To provide electrons to the oxygen more easily, we decreased the cathode potential and increased the electron density. For that reason, when metal ions reach the cathode, they receive electrons, are reduced, and are deposited on the cathode surface. When this phenomenon occurs, the cathode surface area increases, and the sensitivity changes by that percentage. The guard electrode reduces and traps metal ions in the electrolyte solution, so it has the advantage of stopping metal from being deposited on the cathode.

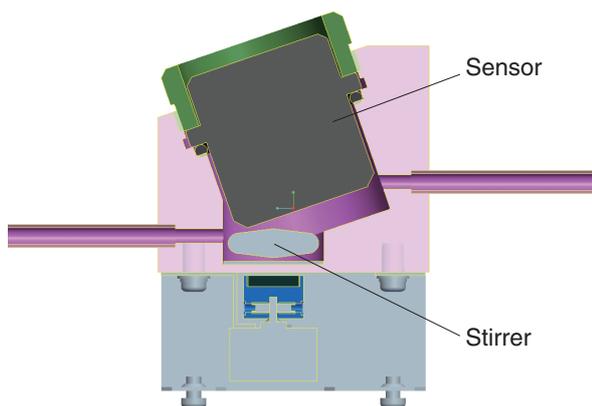


Figure 2 Cross section of the flow chamber with a sensor attached

Measuring high-temperature samples

The sensor can measure high-temperature samples up to 60°C. When the temperature of the fluid supplied to the sensor increases, the volume of the electrolyte solution increases and the internal pressure increases, which causes force to push the membrane from the inner side. When this happens, the gap between the membrane and the cathode spreads, and the diffusion distance becomes longer, so the response deteriorates. As a countermeasure, we increased the diameter of the membrane and used a method in which we decreased the amount of electrolyte solution. Using this method, the gap between the membrane and cathode doesn't increase, even when the volume of the internal electrolyte solution expands. From the perspective of electrolyte solution life, a larger amount of fluid is desirable, but we optimized the concentration and fluid amount to increase the measurement temperature.

Flow chamber structure

The measured sample fluid cannot be returned to the process, so there is a need to minimize the chemical sampling amount. It is desirable to be low sampling flow rate, but the dissolved oxygen is consumed by this sensor which is not the potential sensor that does not consume oxygen, so errors increase when measurements are taken in still samples. To get accurate measurements, a fresh sample always needs to be supplied to the surface of the sensor membrane. Even when supplying sample fluid for low flow rates, agitating the sample fluid is effective in order to maintain the surface concentration as a fresh concentration. On the bottom of the flow chamber, there is a magnetic stirrer that agitates the sample fluid, which makes it possible to measure the dissolved oxygen, even in sample fluid that isn't flowing.

We made the main unit out of PFA (tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer) so that PFA pipes

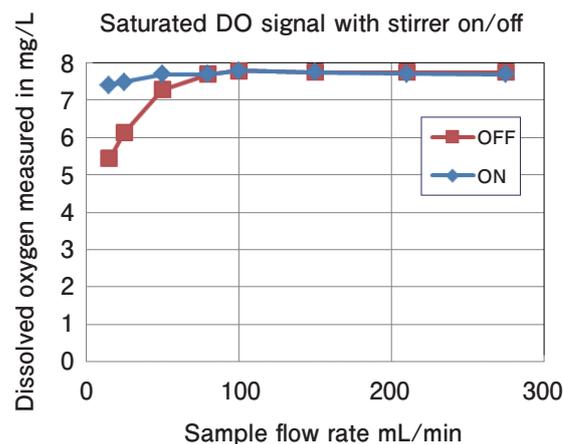


Figure 3 Efficacy of the imbedded stirrer resulted from evaluation test (Possible to measure in low flow rate)

can be directly welded for semiconductor processes. We installed the temperature sensor in the flow chamber so that fluid temperatures can be measured at higher speeds. Figure 2 shows a cross-section of the flow chamber with the sensor installed.

In Figure 3, we compared the measurement values with respect to the flow rates when the magnetic stirrer was operated and when it was stopped. We found that when the stirrer is stopped, when the flow rate is low, the indications decrease drastically.

Dissolved oxygen signal in chemicals

When measuring dissolved oxygen in chemicals, ions can't pass through the membrane, so ion components basically don't affect the measurements. Gas components such as chlorine gas and ozone gas can pass through the membrane and do affect measurements. Hydrofluoric acid is not ionized 100%, and mostly exists in a molecular state, but in low concentrations, the vapor pressure of hydrogen fluoride (HF) is low, so it did not affect the test. TMAH is mostly ionized, as it can't pass through the membrane so it doesn't affect the measurements. We bubbled pure water in air and checked the saturated dissolved oxygen signal while adding hydrofluoric acid and TMAH, but this did not have an effect even if the chemical concentration changed. Figure 4 and Figure 5 show the measurement values in an air-saturated state when the concentrations of HF and TMAH were changed.

Signal response

We found that the guard electrode makes it possible to have high-speed response even in the low dissolved oxygen concentration range. We switched the valve before the flow chamber for degassed water and fluid that was prepared by electrolyzing degassed water to generate

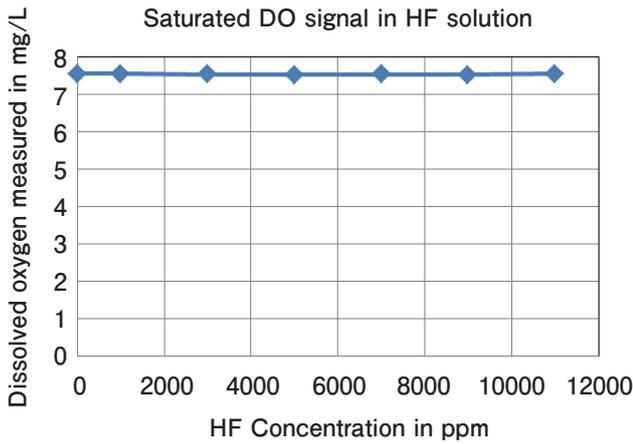


Figure 4 Air saturated DO signal in HF solution

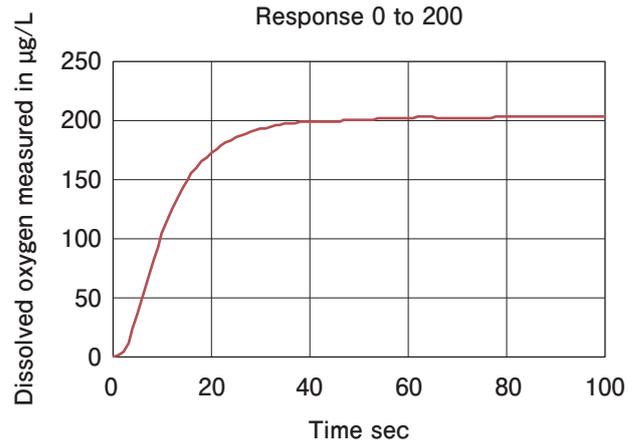


Figure 6 Rising response of DO

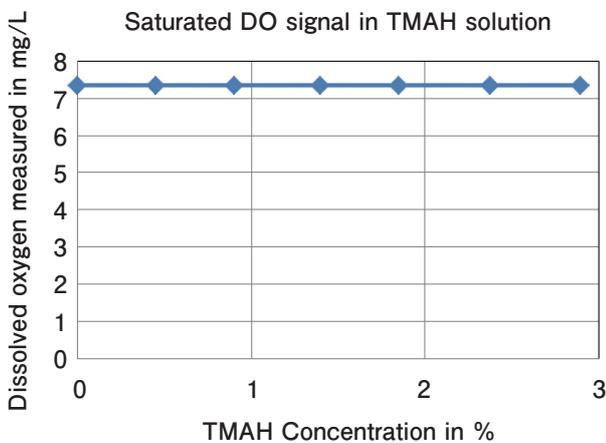


Figure 5 Air saturated DO signal in TMAH solution

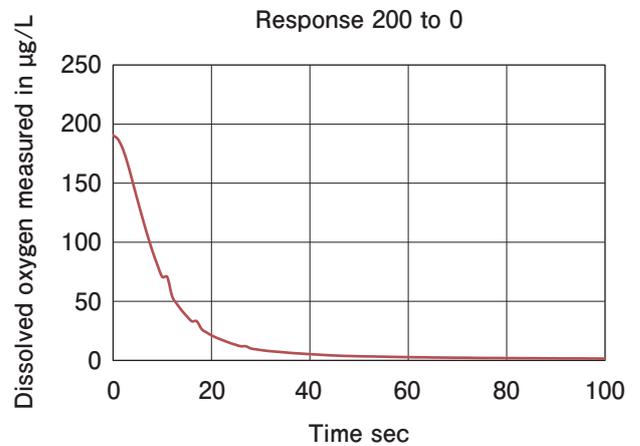


Figure 7 Falling signal of DO

about 200 µg/L of dissolved oxygen, and checked the rising and falling response performance. Figure 6 and Figure 7 show the response in the low-concentration range.

Signal linearity

We adjusted the electrolytic current to change the dissolved oxygen concentration using a method of passing the fluid through an oxygen generator via electrolysis while making degassed water flow through at a constant flow rate. We found that the detected current changes in a manner that is linear with the dissolved oxygen concentration obtained in the calculations. The residual current is low when there is zero oxygen, and the zero point is extremely stable. Figure 8 shows the results of checking linearity by using electrolytic current to adjust the dissolved oxygen concentration.

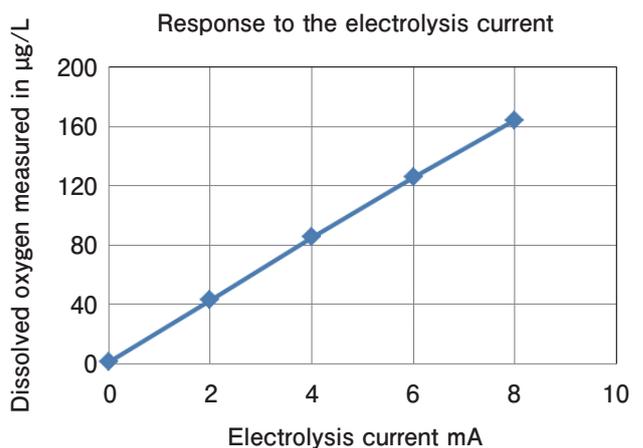


Figure 8 Linearity of DO in low concentration

Product specifications and appearance

Figure 9 shows the product appearance, and Table 1 shows the specifications.



(a) sensor unit: DO-100



(b) Amplifier: HD-960L

Figure 9 Outline view of Dissolved Oxygen monitor

Table 1 Abstract of the specification

Model	Amplifier	HD-960L
	Sensor Unit	DO-100
	Sensor	5600
Measuring principle	Membrane Polarography	
Measuring range	200.0 µg/L 2.000 mg/L 20.00 mg/L	
Measurement cycle	1 sec	
Repeatability	+/- 1%FS	
Linearity	+/- 1%FS	
Response (T90)	30 sec	
Sample condition	Flow rate	15 to 200 mL/min
	Temperature	10 to 45 deg.C
	Pressure	0 to 0.1 MPa
	HF concentration	Less than 5000 ppm
Wetted material	Sensor body	PP
	Membrane	FEP
	Flow chamber	PFA
Facility	Power	DC24 V
	Purge gas	N ₂

than chemical concentrations, such as dissolved oxygen, will become more and more important, in addition to the conventional chemical concentration measurements. We hope that this dissolved oxygen monitor will contribute to improving the quality and yield of semiconductors.

Conclusion

A major feature of this product is that a resistor has been applied to the guard electrode that enables it to control the consumption of electrolyte solution even when exposed to high concentrations of dissolved oxygen, which helps solve the problem of the life of the electrolyte solution being shortened when the electrolyte solution decreases because of high temperatures. In addition, the chemical resistance of the wetting components and the structure of the flow chamber are specialized for semiconductor processes, which means that it can even be used to measure dissolved oxygen in chemicals with the above characteristics.

In semiconductor processes that will become more complex in the future, it is predicted that measurements other



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