Application Note 6.02

Dissolved oxygen measurement in ultrapure water for semiconductor manufacturing

- Measures in the sub-10 ppb range for today's demanding analysis requirements, for trace level accuracy
- Enables elimination of film buildup during manufacturing
- Compatible with all common deaeration methods described below.

Application Description

Semiconductor manufacturing is commonly thought to comprise two basic components, the "wet process" and "packing process." Since the inception of large-scale integration techniques, the presence of dissolved oxygen in ultrapure water during the wet process has been a growing concern.

Prior to the 1990s, dissolved oxygen (DO_2) levels as high as 100 parts per billion were commonly accepted. This was considered adequate to suppress microorganism growth. More recently, a sub-1 0 ppb DO_2 level has been sought to prevent the formation of oxide film that would otherwise appear on the surface of silicon wafers.

This oxide film is detrimental to submicron or deep submicron circuitry for several reasons, including epitaxial growth on high quality silicon film at lower temperatures or in the quality of thin gate oxide film. In addition, the film increases contact resistance between silicon and metal leads. Unfortunately, the oxide film can be formed in air, in ultrapure water, and in chemicals. In the case of ultrapure water, the lower the DO_2 level, the slower the formation of film oxide. This can be explained by the reaction of H-radicals on the interfacial molecular structure of silicon wafers, which is oxidized by DO_2 and water.

Of the three current methods of deaeration, using a *hollow fiber membrane* under negative pressure is perhaps most widely used, where oxygen is extracted from water through a membrane. While this is costeffective and compact, it is not generally capable of achieving satisfactorily low DO_2 levels. It is generally used as a primary method and combined with one of the two described forthwith.

The *reduction method* recombines DO_2 with hydrogen introduced to the line under the presence of a palladium catalyst or ultraviolet light. This can produce very low DO_2 levels, but it becomes necessary to monitor H2 levels to keep stoichiometrical volume for O_2.

Nitrogen gas bubbling (sparging) usually connects three or four columns in series where N_2 is introduced at the bottom and water flows to the top. Very high levels of very pure N_2 are required, but theoretically, DO_2 levels of less than 0.1 ppb are possible.

In normal manufacturing, levels of 3–6 ppb are sought, although it is reported that a miniature plant in Dr. Ohomi's laboratory at Tohoku University managed a 0.4 ppb level. Orbisphere's electrochemical sensors, as used with the current 3660 series analyzers, were used to measure at both the inlet and outlet ports for the N_2 sparging method described above, with the more useful information derived at the latter end.

Typical Installation

It is recommended that the DO_2 sensor be installed in a flow chamber on a side stream. Ultrapure water is run past the sensor and routed to waste. This method is preferred to placing the sensor directly in-line, to assure that no chemical impurities will be introduced into the sample by the sensor itself. The flow requirement is only 100 ml/minute. Depending upon the method of deoxygenation, users should be wary of high levels of dissolved gases that have the potential to require higher levels of maintenance. For example, N_2 sparging could cause high levels of nitrogen in the wash water, which could degas in the side stream sample line. To guard against this, a flow control valve on the outlet of the flow chamber is recommended, and a membrane protection grill would be advised.

Analog 0/4-20 mA current output of O_2 concentration is available. Often an application requires the instrument's output to match a specific measurement range. This output level can be adjusted with the supplied Windows® software.

Recommended System Components

Model	Description
3660EX/ 106.B	Orbisphere 3660EX ATEX Controller for Oxygen (O_2) measurement, wall mount, 230 V AC, units : %/ppm
GA2400-S0S	Orbisphere GA2400 Stainless Steel Oxygen Sensor (EC), 100 bar, EPDM O-rings
32502.03	Sensor cable, standard length 3 meters (longer cables can be specified)
32001.011	Flow chamber, stainless steel construction with Swagelok inlet/outlet tube fittings (6-mm or 1/4" available)
32541.03	RS-232 communication cable, standard length 3 meters (longer cables can be specified); for applications over 20 meters, an optional RS-422 output is available
32685	Windows® software

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