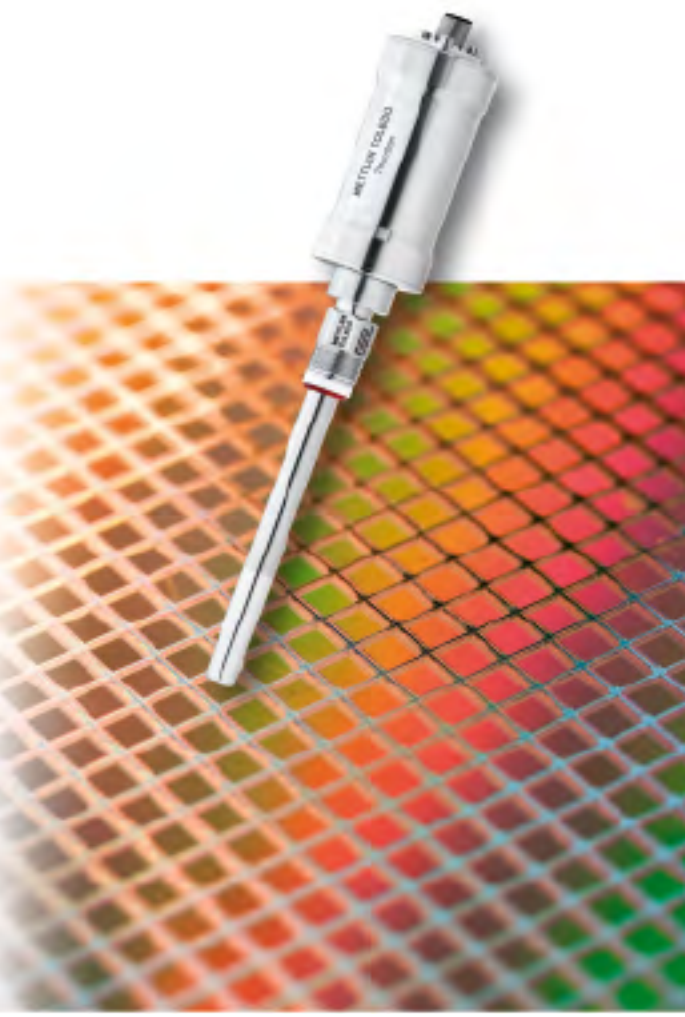
Microelectronics
Perspectives in Pure Water Analytics

10
News

THORNTON
Leading Pure Water Analytics

Optical DO Sensor
for Pure Water Quality Assurance

Eliminating silica oxidation at the surface of a wafer is vitally important in semiconductor manufacturing. An intelligent dissolved oxygen sensor with optical measurement technology provides fast response, high accuracy, and increased stability in demanding low ppb-level ultrapure water applications.



Keeping dissolved oxygen at a minimum

The need for measurement and control of dissolved oxygen at very low concentrations in ultrapure water for certain wafer production processes is widely recognized. In water purification itself, DO can oxidize ion exchange resins in mixed bed polishers, leading to contamination downstream. High DO levels may also support microbiological growth in water systems. DO in rinse water influences the oxidation of the active silicon surface on wafers and can have a direct impact on chip yield.

Ultrapure water monitoring and control therefore requires accurate and reliable DO measurement at very low concentrations. Since ppb-level DO determination can be a significant challenge, such instrumentation must be highly dependable.

Amperometric sensors have been the standard for many years, but now, DO sensors that utilize optical measurement technology are rapidly replacing them due to their accuracy, low drift, and easy maintenance.

Simple servicing

Instead of membrane body, inner body, and electrolyte that have to be replaced on amperometric sensors, the Thornton Pure Water Optical DO sensor has only one consumable component, the OptoCap. It contains a fluorescing, oxygen-sensitive membrane which is the key to the sensor's superb accuracy and speed of response. Replacement of the OptoCap can be done by even un-skilled personnel in only a few minutes. In typical applications, the Opto-

METTLER TOLEDO

Cap needs to be replaced annually, compared with maintenance every three to six months for amperometric sensors.

The long lifetime of the OptoCap, together with its fast and easy replacement, drastically reduces maintenance costs and the risk of handling errors.

Calibration is a quick and straightforward procedure, and in-line calibration within the process is even possible. After calibration, system status information is displayed on the transmitter in real time, increasing the reliability of the measurement point.

Plug and Measure for error-free start up

The Pure Water Optical DO features METTLER TOLEDO's unique Intelligent Sensor Management (ISM®) technology. ISM provides an array of features that simplify sensor operations and improve process reliability. All sensor data, including calibration history, are stored in the sensor itself. After performing maintenance and calibration, installation in the process is simple. Upon connecting the sensor to an ISM M800 transmitter, all relevant data is automatically uploaded to the instrument and an oxygen reading is available immediately – no pre-polarization is required. The Pure Water Optical DO can even be calibrated in advance and stored ready for use, making sensor replacement even quicker and more convenient.

Predictive diagnostics reduce unscheduled downtime

Another useful ISM feature is a set of advanced diagnostics tools. The Dynamic Lifetime Indicator monitors the quality of the OptoCap after each calibration and, together with the current process conditions, calculates and displays on the M800 the remaining lifetime of the OptoCap. Unscheduled downtime due to sudden failure of the sensing element is therefore avoided.

Efficient and reliable

The combination of optical measurement technology, ISM, and METTLER TOLEDO's years of experience in designing sensors for the semiconductor industry means that the Pure Water Optical DO is the most efficient and reliable oxygen sensor on the market.

▶ **www.mt.com/opticalDO**

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Save Time and Cost
Easy to Use Transmitter Configuration Tool

Configuring transmitters can be time-consuming and complex: a task which is particularly frustrating if the same configuration has to be applied to more than one transmitter. A utility for METTLER TOLEDO Thornton transmitters makes the task simple and fast.

Time-saving transmitter software

Transmitter Configuration Tool (TCT) software is included with all METTLER TOLEDO M200, M300, and M800 transmitters. This PC-based program enables users to configure the transmitter and download, upload, save, or print configurations specific to their applications using a USB port on the transmitter connected to a PC or laptop. This unique functionality can save considerable time and effort when setting up multiple transmitters with custom configurations, time after time.

Once a configuration file is created, TCT software permits a user to upload it to all transmitters using any PC or laptop computer, eliminating all configuration at the transmitter and thus greatly reducing setup time. Separate application configurations can be saved and uploaded from a library of previously developed configuration files.

In addition, with the TCT, data can be logged and reviewed at the computer and stored in Excel files for review, troubleshooting or graphing at a later time.

Easy, accurate, and consistent transmitter configuration

Convenience: If a process engineer needs to configure ten transmitters with identical settings, at an average of 10 – 15 minutes each, the potential for error or inconsistency is considerable. However, once a file is created on a PC, TCT software enables the user to upload it accurately to each transmitter, either in a central location before installation, or after mounting on the water system.

Flexibility and consistency: Multiple configurations may be stored for future use. These custom applications can be preconfigured and loaded to transmitters whenever they are needed.

Security: TCT software serves as a security backup to save application-specific configurations in a library folder on a separate computer for future use.

Summary of advantages

- Ensures consistent configuration of several transmitters with the same settings
- Saves time individually configuring multiple transmitters
- Saves time uploading application-specific configurations from the user-developed library
- TCT software is bi-directional – data may be transferred from PC to transmitter and vice-versa
- Transmitter configuration can be completed at a convenient time and location – even remotely or in an office
- Enables real-time data collection
- Data can be logged and reviewed at a computer and stored in Excel™ files for review, troubleshooting or graphing

For further information, contact your local METTLER TOLEDO sales office, or visit:

► **www.mt.com/pro-tct**

Prevention of Ion Exchange Breakthrough
with New Water Monitoring Tool

Methods exist for detecting DI resin exhaustion, but they are inaccurate if feedwater varies in composition. A new tool on the M800 Transmitter monitors the exchange capacity of DI systems and accurately predicts resin exhaustion before breakthrough, regardless of water quality.

The high cost of resin regeneration

During the water purification process, deionization resins eventually reach their exchange capacity, become exhausted, and must be regenerated. The costs of regeneration including acid, caustic, rinse water, and labor are substantial. Anything that can be done to extend run cycles, regenerate more efficiently, or accurately determine the need for resin restoration or replacement can provide significant operating savings. Beyond the cost of regeneration, if the resin is not properly monitored and ionic breakthrough occurs it can cause major upsets downstream that can affect final water quality.

Detecting resin exhaustion

When ion exchange resin capacity is being reached, the resin will begin to leak weakly held ions. This initial leakage needs to be detected immediately, preferably before it even occurs. Conventional monitoring for resin exhaustion uses sodium measurement for cation breakthrough and silica for anion breakthrough. While these are sensitive measurements, they can only detect exhaustion after breakthrough has already happened. The system downstream begins receiving contamination at the same time the measurement detects it. Prediction of exhaustion would enable systems to be taken off-line and regenerated before breakthrough.

Variable feedwater needs to be considered

Predicting resin exhaustion can allow more reliable scheduling of operations; enable longer running; and avoid premature regeneration which would waste time, system capacity, and expensive regeneration chemicals.

Common methods for predicting exhaustion are based on monitoring elapsed time or totalized flow. If the flow rate is nearly constant over the run cycle, then a consistent run time before regeneration should provide an adequate prediction, but only if the water composition is also constant. If the flow rate varies through the run of the exchanger a total flow measurement can accurately account for this, but again, only if the feedwater composition remains unchanged. If the water composition alters, then a total flow value will not be a good predictor of resin exhaustion.

In today's environment of scarcer water supplies, various raw, recycled, and re-

Ionic load (grains or equivalents) = ∫ Flow × TDS dt

Ionic load (grains or equivalents) – cumulative TDS or ion load
Flow – flow rate entering the DI bed
TDS – total dissolved solids based on conductivity entering the DI bed

Figure 1: Algorithm for DI-Cap tool

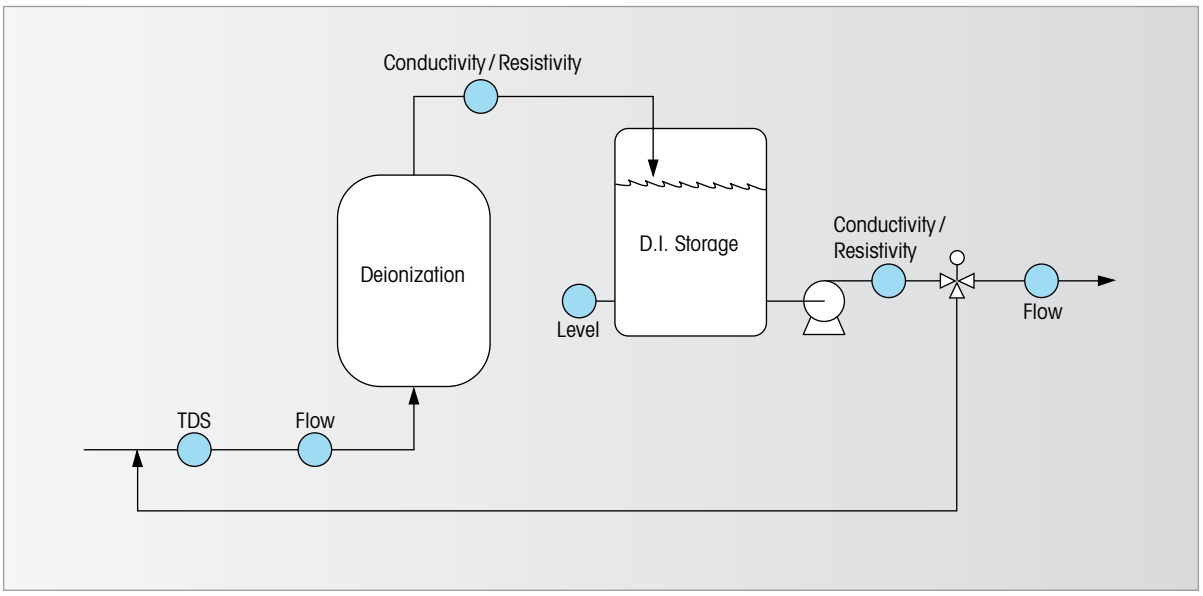


Figure 2: Schematic showing measurements required for the DI-Cap tool for predictive regeneration

claimed water sources can create major variations in feed to the treatment system. As a result, variable composition is commonplace. Therefore, there is a need to account for a varying ionic load due to both flow rate and composition.

More accurate prediction of exhaustion

The capability to predict exhaustion that accounts for variations in both flow rate and composition has been implemented in the METTLER TOLEDO Thornton M800 multi-parameter analyzer / transmitter. The DI-Cap™ tool is a unique deionization capacity monitoring algorithm. Figure 2 illustrates how this method is implemented. First, feedwater conductivity is measured and converted to total dissolved solids (TDS). Flow rate is also measured and multiplied by the TDS value. The product of these is integrated over time to produce a measure of ionic load entering the deionization system as illustrated by the equation (Figure 1). The direct readout allows a choice of units of equivalents, grains, or ppm-gallons.

With this system both variable flow rate and variable water composition are accounted for to accurately monitor ionic loading. Display, output signals, set points, and relays can be assigned to this computed parameter to enable continuous monitoring and control. The total ionic load measurement can be reset manually or automatically by a remote contact closure at the beginning of each run. The METTLER TOLEDO Thornton M800 has additional channels that allow it to measure, alarm, and provide output signals for effluent resistivity as well as other measurements such as dissolved oxygen and TOC.

Assessing resin health

A further benefit from deionization capacity monitoring is for tracking resin bed working capacity over the long term to warn of capacity loss. Lowered working capacity can be due to incomplete regeneration, loss of resin, channeling, or fouling with organics or silica. If a DI bed is run to exhaustion, as detected by effluent conductivity or other means, and the total ionic load for each run cycle is logged, a good historical record of performance can be developed, which is more useful than simply a record of total gallons processed.

With this technique even a gradual deterioration in performance can be identified and corrective action taken before a major loss of efficiency occurs. This represents a substabtial improvement in DI system troubleshooting and maintenance, since the first loss of capacity will be more visible and will allow timely diagnosis of the problem. Issues that continue undetected become harder to pinpoint, and can result in more damage and inefficient operation.

Greater efficiency of DI systems

Deionization capacity monitoring with the unique DI-Cap features on the METTLER TOLEDO Thornton M800 provides a significant contribution to the efficient operation and troubleshooting of large DI systems. Whether deionizing raw water, reverse osmosis permeate, or condensate systems can benefit from this water treatment monitoring tool.

Discover more about the M800 at:
► **www.mt.com/M800**

New Trends in Pure Water Analytics
for the Microelectronics Industry

Jim Cannon at METTLER TOLEDO Thornton is an expert in Ultrapure Water for the microelectronics industry. He travels around the globe conducting seminars on advances in UPW monitoring and control as well as the current industry recommendations and regulations. Microelectronics News spoke to him about pure water analytics.

Pure water analytics has been critical in the advancement of microelectronics over the years. Can you explain its importance?

Since the beginning of the semiconductor industry in the 1960's, pure water has been critical to wafer cleaning and production.

Originally, the highest water quality was described by ASTM (American Society for Testing and Materials) as Type 1 water. That evolved into a set of standards dedicated to the semiconductor industry called Type E-1. The term Ultrapure Water, or UPW, became popular in the early 80's and is most often associated with the semiconductor industry. The standards set for Ultrapure Water focused on the electrical conductance for ions, TOC for organic carbon, bacteria, particles and specific ions like silica.

As the size of silicon wafers has increased from 100 mm to 450 mm, the number of chips per wafer has grown exponentially. More significant is the reduction in line-width between circuits on the chips. In 1989, line-widths were in the range of 800 nm. Today that spacing has dropped below 14 nm and will be around 5 nm by 2020. To put this in perspective, a sheet of paper is approximately 100,000 nm thick. Any contaminant, ionic, organic, specific ions or particle that dries on a circuit will create a fault and reduce the yield of the process.

With the circuitry on integrated chips continuing to get smaller and more tightly packed, the need for accurate water analytic measurements will grow to ensure product quality and yield.

What are the critical parameters in the production of UPW?

There are several. The measurement of ionic contaminants is critical and electrolytic conductivity or resistivity is the measurement parameter. The current resistivity standard for UPW is $18.18\,M\Omega \times cm^{-1}$ at 25 °C. The industry has also established standards for TOC which is < 1 ppb, dissolved oxygen is < 10 ppb and the silica standard is < 0.3 ppb. There are numerous other parameters utilized for the preparation of UPW including pH, ORP, ozone, pressure and flow. Conductivity / resistivity, TOC, silica and DO are not only used for production but also for monitoring and control of the distribution of UPW to manufacturing.

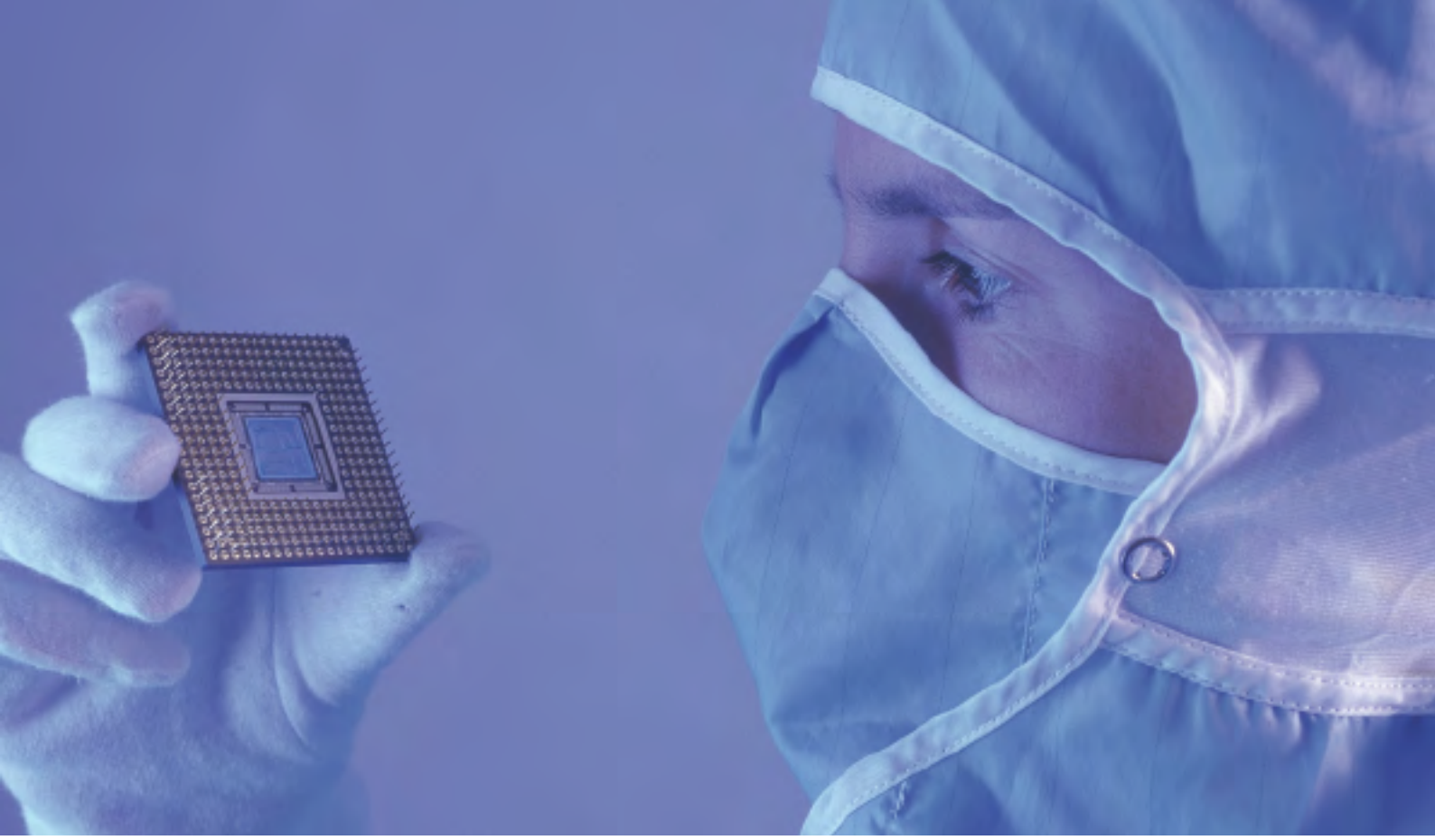
Silica monitoring plays a dual role in semiconductor production. If the silica ion dries on a circuit it will create a fault on the chip, so measurement is critical. Also, silica is a key indicator of the performance of the UPW production system and is used to monitor breakthrough and the requirement for maintenance.

In addition to the production and control of UPW, the mentioned parameters are also utilized in several other critical manufacturing processes within the semi fab. Pure water analytics is required for the control of functional waters (ozonated water, ion water, hydrogentated water), wafer etching, wafer cleaning, wafer stripping, ion implantation, cleaning for metal removal and RCA cleaning (SC-1 and SC-2).

Are there any specific industry trends related to pure water analytics?

As wafer size continues to increase and line-width decreases, higher measurement accuracy with real-time sensor diagnostics for critical parameters has become a growing trend in the industry, so our Intelligent Sensor Management technology with its diagnostic tools, really fits the bill here.

In regards to conductivity / resistivity, the introduction of digital sensors with improved accuracy, stability and expanded measurement range, like the METTLER TOLEDO UniCond® sensors, are meeting



requirements. For dissolved oxygen, optical technology has brought to the industry improved analytics and much lower sensor maintenance. The measurement of TOC has always been critical in UPW, but being able to measure organics in real time with on-line sensors, versus batch process has provided the industry with the rapid response it requires.

These analytical parameters are also utilized in the control and measurement of recycle, reuse and reclaim systems in the semi fab. The increasing costs for water and the cost to produce Ultrapure Water are driving the industry towards recycle / reuse / reclaim. While reuse and reclaim have been fairly common practice, the industry trend is to recycle UPW after use in the process. The UPW waste stream contains a variety of contaminants and to treat this stream to the levels utilized in production requires advanced analytics. These UPW recycle systems need constant monitoring of conductivity / resistivity, TOC, ORP, DO, pH and other physical parameters to control the process to the stringent requirements.

What challenges does pure water analytics face in the semiconductor industry?

People want better smart phones, faster tablets, increased memory laptops and advanced flat screens. To accomplish this, the semiconductor industry will depend on pure water analytics to help increase the processing power of integrated circuits with smaller line-widths and larger wafers. And the drive to recycle / reuse / reclaim more and more of the water used until the semiconductor fabs are entirely water self-sufficient can only be accomplished with pure water analytics. The semiconductor industry requires an advanced water management plan to achieve these goals and that demands real-time sample data, real-time measurements and very accurate analysis.

The challenge for METTLER TOLEDO is to ensure that we're always ahead of the curve in relation to the needs of the semi industry. With our advanced sensors and ISM technology, I'm confident we'll continue to do just that.

For further information, or if you have any questions, please contact Jim Cannon: jim.cannon@mt.com

Measurement of Conductivity and pH
in Semiconductor Hydrofluoric Acid Processes

The extremely corrosive and toxic nature of hydrofluoric acid (HF) makes it difficult to handle and requires special measuring equipment. METTLER TOLEDO Thornton sensors are perfectly suited for these applications.

Conductivity measurement for etching solution control

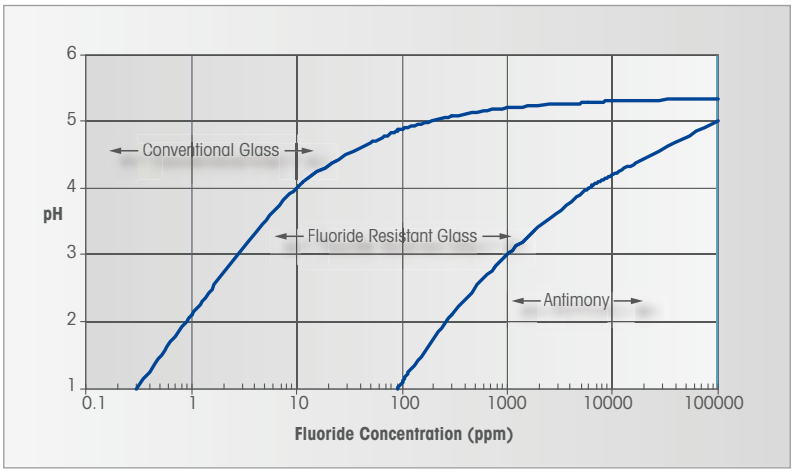
Hydrofluoric acid is commercially available at concentrations near 50 %. In etching solutions this concentration must be diluted and maintained within close tolerances to achieve controlled etching rates and high yields.

This concentration can be monitored using inductive conductivity instrumentation, which allows measurement without any metal being in contact with the fluid. The sensor consists of two adjacent coils encapsulated in a single polymer body. The first coil is energized with AC current. The fluid surrounding the doughnut shaped sensor induces a signal into the second coil in proportion to the conductivity of the fluid. This signal is then measured, temperature compensated and provided for display and control. Inductive conductivity sensors that use PFA (perfluoroalkoxy), such as the InPro 7250, and PTFE (polytetrafluoroethylene) wetted materials withstand the severe conditions of HF-containing baths.

Rinsing assurance is vital

Wafers and other products etched in hydrofluoric acid baths must be rinsed extensively before further processing. Usually this is done with ultrapure water. The initial rinse water will contain enough HF to be highly corrosive while the final rinse must reach ultrapure water levels of purity. To assure thorough rinsing, an ultrapure level contact conductivity / resistivity sensor must monitor the used water quality. At the same time, this sensor must withstand the initial acid conditions.

Resistivity sensors for monitoring etching rinse water are available with Monel electrodes which have excellent resistance to HF, whereas standard stainless steel or titanium sensors are rapidly attacked. Monel sensors are calibrated and measure with the same high accuracy available with other Thornton ultrapure resistivity sensors and will tolerate occasional dumps of hydrofluoric acid etchant as well as the dilute rinse water.



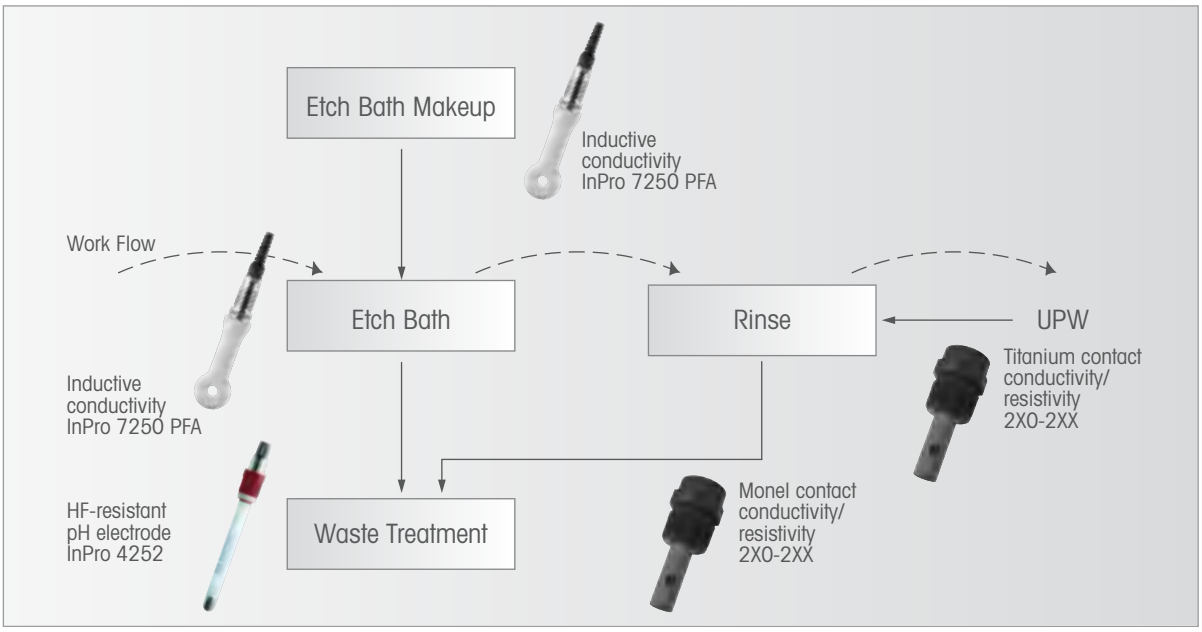
Selection of pH electrode type for fluoride-containing processes at 20 °C (68 °F)

Sensor selection is critical in wastewater treatment

The rinse waters and the etch baths themselves, when they are spent, must be treated before discharge or reclaim. This treatment typically consists of neutralization, coagulation and settling of the fluoride by adding calcium chloride, lime and / or limestone to produce insoluble calcium fluoride. The measurement of pH to control the neutralization is complicated by the corrosive nature of acidic fluoride solutions. HF attacks the glass membrane of most pH sensors as readily as it etches silicon wafers.

The rate of attack is dependent on fluoride concentration, pH and temperature as well as the glass composition. If the fluorides are consistently neutralized upstream of the pH sensor, then there is less opportunity for attack.

The exposure to acidic conditions may depend on the treatment strategy. If treatment is done in batches with filling, neutralizing and pumping out, then the pH sensor could be exposed to hydroflu-



Suitable sensors for hydrofluoric acid measurement in wafer production

oric acid all through the long filling cycle. In those situations a special HF-resistant glass or even an antimony pH sensor may be needed since they have greater resistance to hydrofluoric acid. On the other hand, if treatment is continuous with gravity overflow then control could maintain the pH near neutral most of the time and the pH sensor would not be subjected to hydrofluoric acid. A conventional glass electrode should be satisfactory in this case unless there is poor mixing or frequent control upsets occur.

Specialized electrodes for high measurement performance

Fluoride treatment typically involves precipitation of calcium fluoride which can rapidly coat any kind of pH sensor as well as the process equipment itself. The pH sensor installation should be designed to enable easy access to the electrode for maintenance which usually includes cleaning with dilute hydrochloric acid (HCl) to dissolve the calcium scaling.

The pH vs. Fluoride figure on page 8 shows the initial recommendation for sensor type for various operating conditions at 20 °C (68 °F). It is always desirable to use a conventional glass pH sensor which provides accurate measurement at moderate cost. The next alternative is the HF-resistant glass sensor, such as the InPro 4252.

The most severe conditions require an antimony electrode. This graph shown is only a guide and cannot account for variations in temperature, additional materials present or other conditions which may affect the rate of attack of a glass sensor. Other factors may also be important in selecting the best sensor for a particular application but this provides a starting point.

An antimony electrode is the choice only after other sensors show too short a life. Antimony has lower accuracy and requires more frequent cleaning compared with glass electrodes.

Titanium conductivity/ resistivity sensor | pH electrode InPro 4252 | Inductive conductivity sensor InPro 7250 PFA

Conclusion

HF is an extremely useful acid in wafer production, but in out-of-spec concentrations can be highly damaging in etch baths, rinse water and wastewater treatment. Choosing the correct sensor can help ensure such out-of-spec situations do not occur.

To find the right sensor for your application, visit:

- ► **www.mt.com/conductivity**
- ► **www.mt.com/PRO-pH**

Predictive Maintenance
from Intelligent Sensor Diagnostics

The multi-parameter, multi-channel M800 transmitter platform covers all major parameters in one instrument. Intelligent Sensor Management (ISM®) technology offers predictive diagnostics, allowing you to fix a sensor issue before measurements are affected.

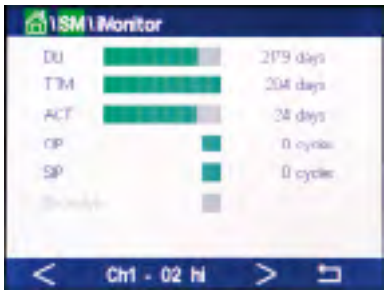
The M800 transmitter for ISM digital sensors incorporates a highly intuitive user interface, expanded measurement parameters and, most significantly, diagnostic maintenance capabilities.

iMonitor is an advanced sensor diagnostics utility. It anticipates maintenance intervals based on real-time sensor performance information rather than sensor failure alarms or imprecise estimates.

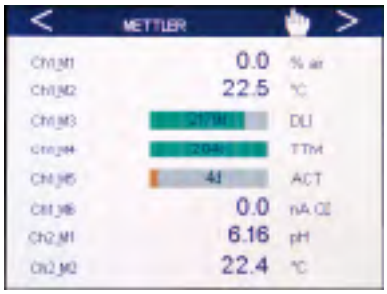
iMonitor evaluates each sensor's condition and calculates remaining sensor (or integrated consumable) lifetime to predict when service or replacement will be necessary. The number of days until maintenance should be performed is displayed on the M800 with a red, yellow or green indicator bar, providing at-a-glance information based on traffic light color coding.

► **www.mt.com/M800**

Your benefits

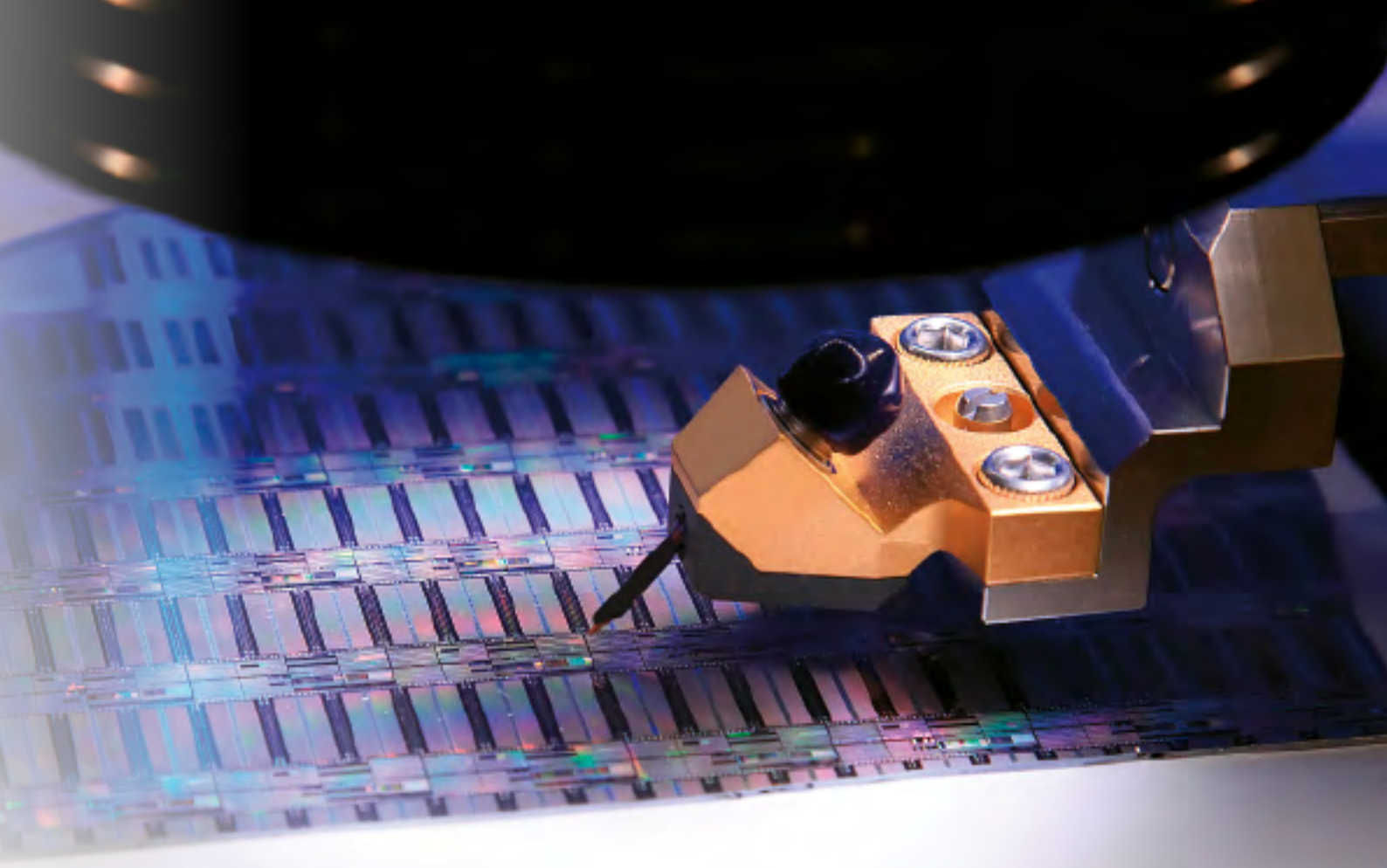


Intelligent diagnostics
With its unique iMonitor predictive diagnostics functionality based on METTLER TOLEDO's ISM technology, the M800 tells you not only what is wrong with a sensor but how to fix it – before an issue arises.



Multi-parameter and multi-channel
The M800's multi-parameter abilities gives you greater flexibility, less complexity, and less training and inventory. Two- and four-channel models provide multiple measurements from a single unit.

Color touchscreen
The color touchscreen provides simple, convenient operation. Just touch and follow the intuitive user interface.



M800 multi-parameter,
multi-channel transmitter

ISM®

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