

INSTRUMENTS

DEVELOPMENTS TOWARD A NEW TOC MONITORING SYSTEM

The measurement of total organic carbon (TOC) within the semiconductor industry continues to be an area of increasing interest. With ever increasing wafer sizes, the requirements for high-purity water production, specifically TOC measurement, are of constant concern. Therefore, trend monitoring of TOC, even in small single loops, is becoming more important. Although on-line instruments have been available for quite some time, operators are hesitant to switch to continuous on-line monitoring because of high cost of ownership, complicated and expensive maintenance, and rather large investments.

This article highlights the most commonly used measuring techniques for TOC monitoring and introduces ways to reduce maintenance by implementing new, automatic Quality Assurance procedures. Furthermore, implementing automatic instrument verification procedures and integrated sample preparation also enhances reproducibility and reliability of online data. These are both illustrated in this paper, along with examples from various semiconductor applications.

Background

Today the methods of TOC determination are mainly the following: thermal decomposition, NDIR detection, UV-persulfate oxidation, and direct UV oxidation.

All of these methods have their particular advantages and disadvantages,

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according to each system's limitations. For this reason, it is especially important to choose the instrument exactly for its application and environment.

This article will demonstrate the possibilities and limitations of modern TOC instruments by means of concrete examples. We would particularly like to delve into the details of the characteristics of direct UV on-line monitors to show the latest developments (e.g., functional test), which simplify daily routines and ensure safety.

Direct UV Oxidation

During the last two years, a new generation of instruments for TOC analysis has been introduced by a supplier*. The development of these TOC analyzers placed its emphasis on these principles:

- Simplification of the measurement
- Improvement of the instrument's dependability
- Reduction and Ease of maintenance procedures

During the development process of a new monitor generation, new paths were explored to improve the measuring principle for TOC analysis. These paths resulted in a:

- New design of a UV-reactor to improve the performance.
- Reduction of temperature influence

to the measurement.

- Introduction of a Function-Test to optimize the operational reliability.

Increase of the UV-reactor performance. After the first conductivity measurement (COND 1), the sample flows into the UV-reactor and from there to the second conductivity measurement cell (COND 2). The TOC concentration is then calculated from the differences in the two conductivity values; this method being the standard measuring principle. A strong UV radiation is an essential part of the Direct UV method. To increase this UV radiation and the overall performance, this TOC instrument uses a different type of a compact UV reactor. To achieve this target, the developers defined a series of constructive preconditions.

1. The probe should be positioned as close to the UV source as possible.
2. Low dead volume should be attained.
3. Stable thermal conditions should be achieved.
4. Easy maintenance.

Figure 1 illustrates the water flow in a direct stream reactor. The probe that is directly channeled over the UV-lamp surface has a core distance of 8 mm, which causes any loss due to scat-

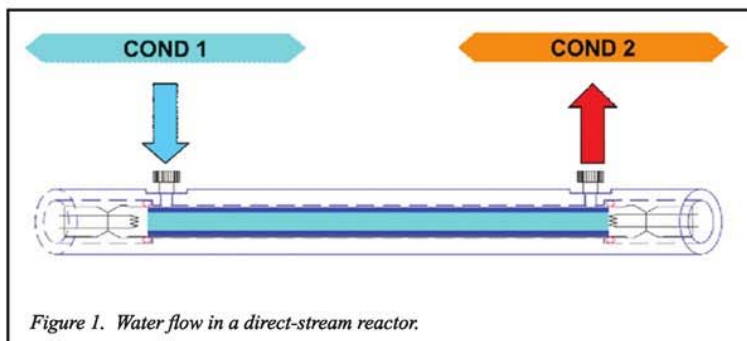


Figure 1. Water flow in a direct-stream reactor.

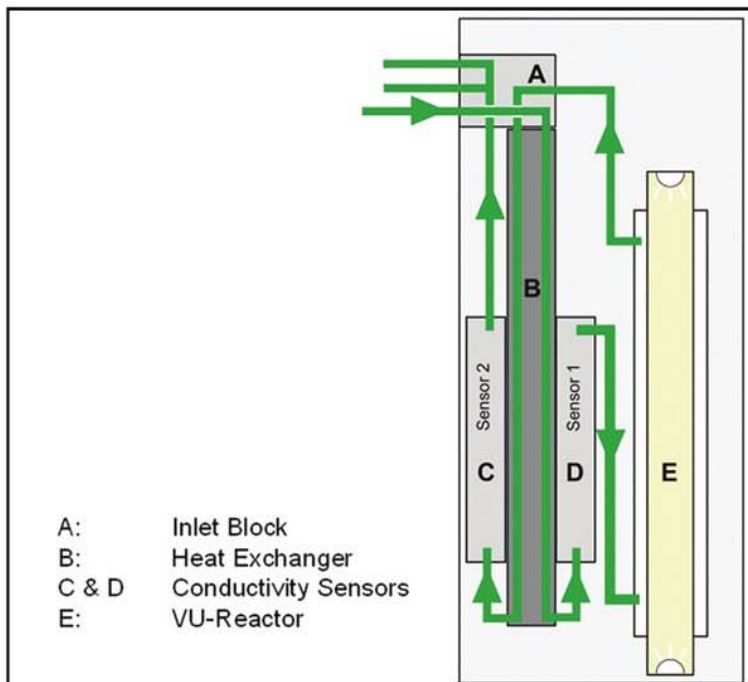


Figure 2. Heat exchanger in instrument to minimize the influence of water temperature on instrument readings.

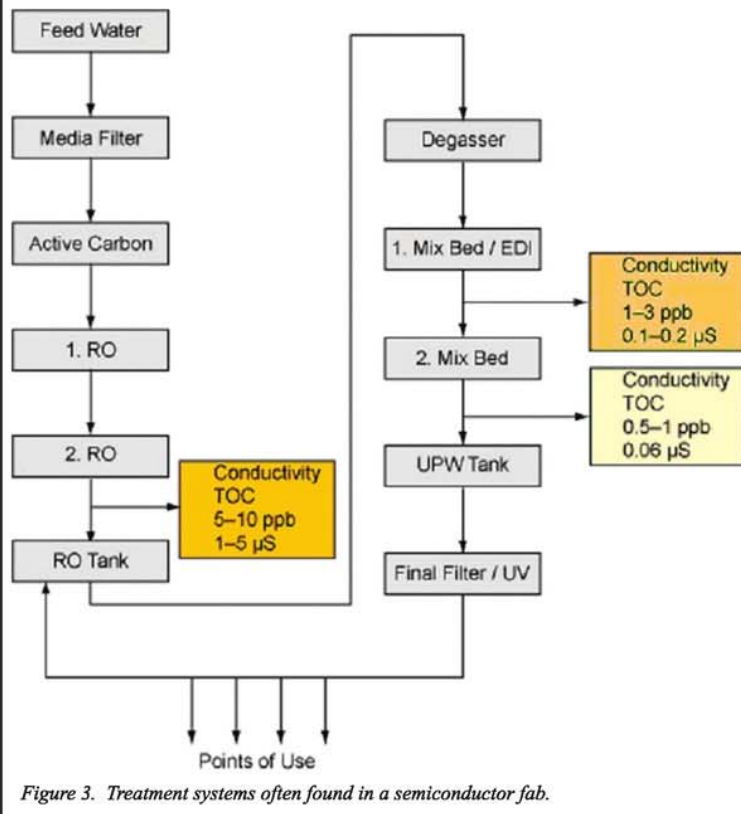


Figure 3. Treatment systems often found in a semiconductor fab.

tering to be eliminated. The emitted UV radiation can then be used for the complete degradation. The dimensions are extremely compact and when compared to other instruments, a much higher irradiance (around 25%), can be achieved. The water layer is about 0.5 millimeter (mm). Due to the compact construction, the resulting dead volume is lower than 3 milliliters (mL). The UV-lamp and the reactor are a fully, preassembled unit which allows for easy replacement. The instrument has "direct stream" construction that allows for constant cooling of the UV-reactor and elimination of overheating effects. This design also enables the achievement of stable thermal conditions.

Reduction of temperature influence to the measurement. A by-product of direct UV-oxidation is the temperature increase between the first and the second conductivity sensor. Depending on the instrument design, it could be higher than 12°C. This difference has to be compensated for using a calculated algorithm. It is important to state that this compensation is only an approximation.

To reduce this effect, the reactor is fitted upstream with a heat exchanger. This is illustrated in Figure 2. Here, the outgoing water warms the counter current incoming water.

A first step is to minimize this temperature difference between COND 1 and COND 2 to a value under 0.2°C. During the development process, we determined that a heating cartridge will stabilize the system even further. In numerous applications, the water temperature is lower than 20°C. To avoid a radiant flux decrease, the working temperature of the UV-lamp must be held in the optimal range between 40 to 50°C. Stable temperature conditions are the basic principles of accurate and reliable test results. However, the compensation method is equally important, as this is how the measured conductivity is converted to a comparative temperature.

Checking a System

Calibration or system tests at low levels are always challenging. Normal available standard solutions are far too high (500 to 1,000 parts per billion [ppb]), and less concentrated or pre-diluted solutions

are unstable and have a reduced shelf life, making them difficult to produce.

So what can be done? Such instances require an on-line, automatic dilution mechanism. This process creates new possibilities for semiconductor applications. With the implementation of a built-in peristaltic pump, a standard solution may be produced of 500 or even 1,000 ppb. The average dilution factor, which depends on the instrument operation time, is approximately 30. Here is a calculation example for the dilution factor.

Calculation example:
1,000 ppb by 30 \approx 35 ppb
500ppb by 30 \approx 18 ppb
Blank \approx 3 ppb

This approach allows for plant operators to produce test solutions without compromising the instrument performance.

Compensations

Often, a carbon dioxide (CO₂) matrix is used; however, a linear compensation is also a suitable choice. Both models have their own features and areas of application.

The CO₂ model. High-purity water does not contain salt. It can only contain traces of organic carbon compounds (TOC) and dissolved CO₂ (total inorganic carbon [TIC]) from the atmosphere. TIC and TOC can be calculated from conductivity of the sample because of the definite correlation between conductivity and carbon dioxide concentration. The corresponding values for the various temperatures are tabulated and stored in the instrument. Table A offers an actual example with rounded figures.

The organic proportion in our example is converted to CO₂ by the UV lamp. Consequently, the value at Sensor 2 is higher than Sensor 1. This determination of TIC and TOC is under the above-mentioned conditions, an absolute method.

Linear compensation. In linear compensation, uniform temperature dependence is adopted over the total measurement range. With a default setting of 2% per degree, the approximation is widely recognized and accepted. This

classical method can be calibrated with external standards, and, as opposed to the CO₂ model, it can also be adjusted. In doing so, the slope is corrected so that the values shown correspond to the applied standards. These calculations are applied when the stipulations for the CO₂ model are not satisfied, or when a calibration with a subsequent adjustment

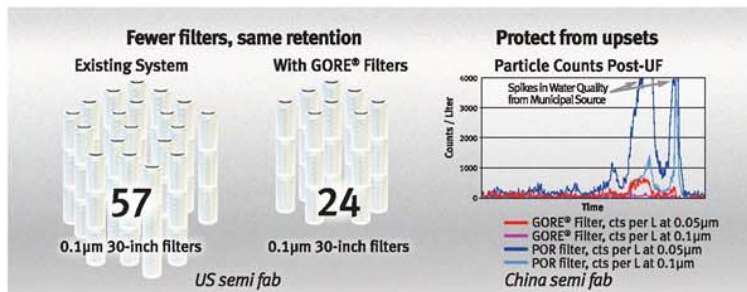
on site is necessary.

Semiconductor Applications

Figure 1 shows a possible construction of a high-purity water plant. The following three measuring points for semiconductor production in high-purity water plants are standard:



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TABLE A
Example of Correlation between CO₂ and Conductivity

| | |
|--|-------------------|
| Conductivity value at the first sensor (COND 1) | 0.6 μS/cm at 42°C |
| Conductivity value at the second sensor (COND 2) | 0.8 μS/cm at 42°C |
| The absolute conductance of water at this temperature is about: | 0.12 μS/cm |
| The difference of COND 1 and COND 2 must therefore come from CO ₂ . | 0.48 μS/cm |

1. After the complete desalination (RO).
2. Before and after the mixed-bed ion exchange.
3. Recycling water from the production (not shown in Figure 3).

Depending on the user, extra TOC measurements are found in the branch lines and at the points of use.

The instrument supplier conducted a study of the above-mentioned points with a German semiconductor manufacturer.

The study lasted several weeks. For all of the points, it was possible to compare the results with the manufacturer's existing instruments. Detailed results are not available due to confidential agreements with all customers. The measurement points are detailed below:

Complete desalination. This measurement tests the desalination in the first stages of the high-purity water production. Normally, the values are between 5 and 50 ppb TOC at a conductance of 1 to 2 (maximum 5 μS/cm). The values

were congruent with those of the reference instrument.

Before and after the mixed bed. This measurement is particularly important because the TOC load must not exceed the limit of the inlet to avoid a premature depletion of the mixed bed. The water is tested at the outlet before entering the actual production plant. At the same time, the effectiveness of the last stage is tested. Great importance is placed on a fast response in order to ensure the facility that the measured value is highly accurate.

Here are the representative values:

Inlet: 1 to 3 ppb TOC at 0.1 μS/cm
 Outlet: 0.5 to 1 ppb TOC at 0.06 μS/cm

The values were stable and corresponded to the comparative instrument. In semiconductor fabs, the design of most of the desalination steps within the mixed-bed units is redundant, so one system can run a recycling procedure without any effect on the water production. At the end of this recycling process, the operator is obligated to rinse the system. Often, a TOC instrument is not installed on each ion exchanger or mixed-bed step.

To know the endpoint of a recycling process, and to prove the expected function, a TOC sample is mandatory. At this stage, a sample has to be brought to the lab for a release test. This is not very efficient and can be time intensive. If your TOC system provides you with a sample function, the need for this step is no longer experienced. The sample size of 250 mL is easy to handle and could be filled at a normal sample point. This bottle can be hooked up to the AMI Line TOC in a matter of seconds. The result is displayed within 2 minutes on the transmitter. After the measuring cycle (rinse - measuring grab sample - rinse) the monitor goes back to the default program full automatically.

Recycling water from the production plant. The water from the production process shows strong fluctuations in TOC and conductivity. If wafers are washed, the value of TOC increases rapidly. Therefore, operators are faced

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with a wide fluctuation range between 0 and 500 ppb. After the washing process, the TOC value will fall back to a low, basic level. A fast response is especially important here, as the measurement values are applied in order to remove the highly polluted water out of the cycle and to send it directly into the wastewater plant.

Conclusions

With the measurement of TOC becoming more stringent, the technology used to measure this parameter must be precise, as well as simple to use. The chosen technology must have the ability to provide the facility with the most accurate and most reliable readings. Such technology should incorporate an easy to use, highly precise calibration procedure, as well as functional tests. Of the given methods to measure TOC, the direct UV-oxidation method has been proven to be simple, fast, and reliable.

This method compensates for impor-

tant factors that affect a TOC measurement, such as temperature, for example. New developments including the "direct stream" UV-reactor and the function test with on-line dilution, provide the instrument owner with new possibilities for a smart TOC measurement. The sample function can be used for cross checking or backup measurements. □

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Endnote

*SWAN Analytical Instruments is the supplier of the TOC analyzers mentioned in the text.

Author Roger Schmid joined SWAN Analytical Instruments in 2009, and currently is an industry application manager. He previously worked for Mettler-Toledo in the pharmaceutical and biotech industries. Before that, he was employed by several pharmaceutical companies in Switzerland for 8 years.

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