The CS-100 Series High-precision Chemical Solution Monitor in the Semiconductor Cleaning Process

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Abstract

We have developed and commercialized the CS-100 Series Chemical Solution Monitor for Semiconductor Wet Cleaning Process, which features high responsiveness and compact design. This series includes a model that uses developed new design of monochromator to monitor in real time the concentration of each component in SC-1 (ammonia/hydrogen peroxide solution), SC-2 (hydrochloric acid/hydrogen peroxide solution), SPM (sulfuric acid/hydrogen peroxide solution), and BHF (fluorine/ammonium fluoride solution). This series has been upgraded based on technology seeds that we could get over long years. This paper introduces the features of the new monochromator and the performance of the CS-100.
1 Introduction

In recent years, the semiconductor wet cleaning has become more diversified with development of various kinds of new processes and solutions. In addition, many eco-friendly propositions have been made. In the past, chemical solution monitors were required mainly for the circulation type of wet cleaning system. Lately, this requirement has been expanded to single and spray wafer processing cleaners as well as the batch wafer processing. For chemical solution monitors, performance requirements for faster speed, higher accuracy, and improved reliability as well as general requirements for downsizing, energy saving, and safety have become intensified. These requirement changes show that solution concentration monitors have been increasingly used for controlling the concentration rather than monitoring it. The CS-100 series has been developed while incorporating such requirement changes. Fig.1 shows the visual appearance of the CS-100 series.

2 Measuring Principle

The concentration of a solution used for cleaning wafers can be measured relatively easily so far as the solution consists of a single component. A mixed solution of multiple components, such as SC-1, is difficult to be measured by separating the solution into each component because the components interfere with each other. The measuring method used for the CS-100 series is basically analytical absorption spectroscopy. Through multivariate analysis of the absorbance of some wavelengths, the concentrations of individual components in the cleaning solution are derived

3 System Configuration

In the CS-100 series, the basical hardware design is common and the sampling system is modified by adopting the most suitable flow schematic design for the characteristics of the solution to be monitored. For the wetted parts, tetrafluoroethylene perfluoroalkylvinylether copolymer (PFA) or polytetrafluoroethylene (PTFE) is used. For the cells, either quartz or sapphire is used depending upon kinds of the solution.

3.1 Optical System

For the monochromator, the asymmetrical Czerny-Turner type has been adopted. As shown in Fig.2, the optical system of the CS-100 series has been designed so as to provide smaller size, higher speed, and improved reliability. The system uses array sensors while maintaining the grating stationary rather than rotating the grating to allow the incident light at the necessary wavelength to detector one by one. This has enabled faster data acquisition. Smaller size has been achieved by eliminating the grating drive and making the optical path simpler. In order to ensure longer stability, the design of driving the cell has been adopted for switching between the optical path for reference and that for sample. Since this monitor calculates the absorbance (based on light intensity ratio of sample and reference) as input, this design eliminates the adverse influence brought by the long-term change and deterioration of the optical parts by using a single optical path for both reference and sample.
3.2 Sampling System

Fig. 3 shows sampling flow schemes. A cleaning solution often contains hydrogen peroxide and is therefore liable to generate bubbles. If such bubbles enter the sample cell, noise is generated causing abnormal values to be measured. The CS-100 series uses its software to be able to evaluate the obtained optical signals and eliminate any signal that might contain noise resulting from bubbles. It is also important at the hardware level to ensure that no bubble enters the cell. For this purpose, a unit with the bubble separation capability is installed before the sample cell. For highly viscous solutions such as the SPM solution, unlike the SC-1 solution, the piping diameter has been changed and the internal flow has been optimized. For solutions that are liable to generate bubbles like the SC-1 and SC-2, a capillary has been provided at the solution outlet to increase the pressure in the system piping so that the generation of bubbles can be suppressed. The version with an air-cooling unit (CS-100C series) is available to allow for directly sending a high-temperature solution.

![Sampling Flow Schemes (a) and (b)](image)

<table>
<thead>
<tr>
<th>Model</th>
<th>CS-131</th>
<th>CS-152</th>
<th>CS-150</th>
<th>CS-137</th>
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<tbody>
<tr>
<td>Measurement sample</td>
<td>SC-1(NH₃/H₂O₂/H₂O)</td>
<td>SC-2(HCl/H₂O₂/H₂O)</td>
<td>SPM(H₂SO₄/H₂O₂/H₂O)</td>
<td>BHF(NH₄F/HF/H₂O)</td>
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<tr>
<td>Measurement principle</td>
<td>Absorption spectrometry</td>
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<tr>
<td>Concentration computation principle</td>
<td>Temperature-compensated multivariate analysis</td>
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<tr>
<td>Measurement range</td>
<td>NH₃ : 0.00 to 5.00% H₂O₂ : 0.00 to 10.00% H₂O : 85.0 to 100.0%</td>
<td>HCl : 0.00 to 10.00% H₂O₂ : 0.00 to 10.00% H₂O : 80.0 to 100.0%</td>
<td>H₂SO₄ : 50.0 to 90.0% H₂O₂ : 0.00 to 10.00% H₂O : 0.0 to 100.0%</td>
<td>NH₄F : 15.0 to 25.0% HF : 0.00 to 3.00% H₂O : 72.0 to 85.0%</td>
</tr>
<tr>
<td>Reproducibility</td>
<td>NH₃ : ±0.25% H₂O₂ : ±0.3% H₂O : ±1.5%</td>
<td>HCl : ±0.2% H₂O₂ : ±0.2% H₂O : ±1.5%</td>
<td>H₂SO₄ : ±0.5% H₂O₂ : ±0.5% H₂O : ±1.5%</td>
<td>NH₄F : ±0.2% H₂O : ±0.3%</td>
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<tr>
<td>Measurement cycle</td>
<td>Approx. 2 seconds minimum</td>
<td></td>
<td></td>
<td>Approx. 3 seconds minimum</td>
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<tr>
<td>Equipment temperature</td>
<td></td>
<td></td>
<td></td>
<td>20 to 25°C</td>
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<tr>
<td>Power</td>
<td></td>
<td></td>
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<td>24V DC±10%, Approx. 2A</td>
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<table>
<thead>
<tr>
<th>[Difference between CS-100 series and CS-100C series]</th>
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<tr>
<td>Model specification</td>
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<tr>
<td>Chemical conditions</td>
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<tr>
<td>Temperature</td>
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<td>Flow rate</td>
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<tr>
<td>Dimensions</td>
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<td>Mass</td>
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*1: except Model CS-137C, because it is not existing.
3.3 Electrical System

In recent years, the life cycle of semiconductor devices has become very short. When a commercially available CPU is installed, the production of related parts is discontinued later and this requires changing the design in not a few cases. For this reason, we have designed our original high-integrated module called the HSBUS system, which allows us to easily comply with improved reliability, higher integration of circuits, and upgrading of the CPU and to achieve easy maintenance. For the readout part, an LCD with LEDs as the backlight has been used because mercury contained in the cold cathode fluorescent backlight can cause pollution. The measuring section in which a solution flows has been separated from the control section where electronic parts are located. In addition, a power source of 24 VDC has been used instead of commercial power. These two features have greatly improved the safety.

4 Basic Performance

The CS-100 has been designed to allow for using a maximum of 4 different solutions and setting their concentration ranges. Individual models will be commercialized by taking account of the future market needs. Table 1 shows main specifications.

4.1 Traceability

The CS-100 series secures traceability based the titrimetric analysis method. Fig.4(a) and (b) show comparison between the measurement results by the SC-1 Monitor and those by the titrimetric analysis method. The measured samples are not single-component solutions, but mixture solutions (the SC-1 in this case) in which the mixing ratios are changed. Therefore, the given correlation data includes the effects of separation and interference.

4.2 Stability

Fig.5 shows data obtained by monitoring for 60 hours the SC-2 solution consisting of hydrochloric acid at concentration of about 0.8% and hydrogen peroxide at concentration of about 0.5%. The maximum deviation from the mean value is 0.034% in the concentration of hydrochloric acid and 0.025% in the concentration of hydrogen peroxide, which show high stability.

4.3 Response

The CS-100 series has achieved high-speed response at a short measurement cycle of about 2 or 3 seconds, thereby allowing for practically obtaining moving averages. Fig.6 shows the response characteristics with hydrogen peroxide through 16 moving averages by the SC-2 Monitor. The number of moving averages is initially set for each solution. Of course, if this number is decreased, the response as shown in Fig.6 will become faster. In practice, the response characteristics vary depending on the piping up to the CS-100, the pressure, and the installation height from the ground.

Fig.4 Correlation between Actually Measured Concentrations and Titrimetric Concentrations
(a) NH₃, (b) H₂O₂

Fig.5 Stability of Measured Values (CS-152)

Fig.6 Response Characteristics
(CS-152, Inlet pressure: 0.20MPa, 16 moving average)
Typical Installation

5.1 Concentration Control

Lately, there have been increasing needs for maintaining the concentration at a certain level, as well as detecting any abnormality of the solution and the time of changing the solution. To provide the optimal control by automatically adding the solution based on the measurement results, the CS-100 itself must respond accurately at high speed. In addition, it is also necessary to grasp the evaporation of the solution and the solution taken by wafers. Fig. 7 shows the results obtained by experimentally measuring concentration changes when our control to maintain the concentration at a certain level was discontinued. During the control, the concentration remained stable within a range of 5.28±0.08%, but the concentration suddenly changed after the control was discontinued.

![Fig.7 Example of Concentration Control](CS-152, sample : 80°C/SC-2)

5.2 Example of Casing

Fig. 8 shows an example of casing with the CS-100 installed inside, which has been increasingly required in these days. The air taken from the front is sent to the CS-100 and then exhausted through the duct located at the rear. This ensures that the internal optical parts are not corroded with a trace of corrosive gas in the atmosphere and that the heat from the light source is also discharged from the case. Of course, the bottom of the case is provided with a liquid leakage tray and a drain line that allows for complying with a leak accident.

![Fig.8 Example of Casing](CS-152, sample : 80°C/SC-2)

Conclusion

The semiconductor wafer cleaning process has been considered from various angles to decrease the environmental load. At the same time, it has become necessary to control the concentration of the solution in response to the needs for high-accurate wet etching. Thus, the situation and applications using solution monitors have become more diverse in a broader range. To meet such different needs with standard solution monitors, harmonization between needs and seeds will become a critical issue. We have made efforts for developing high-performance products as well as the CS-100 series. For the future, our efforts will be required for proposing the most suitable uses of those products as a manufacturer.

Reference


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