Feature Article

Industrial In-line and Multi Component Monitor Using Absorption Spectroscopy and Its Application

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HORIBA's CS-Series chemical concentration monitors that use ultraviolet (UV) and near-infrared (NIR) absorption spectroscopy are widely used in semiconductor wet processes, and make it possible to measure multiple components in line and in real time. The monitor can measure various types of samples, from general ammonia and hydrogen peroxide mixtures in semiconductor cleaning processes to 5-component chemistry including by-products from etching and metal ions in solutions, and things like CMP slurries including solid particles. This paper will introduce specific examples of applications.

Introduction

The HORIBA Group applies various fundamental technologies such as electrochemical, optical, and X-ray technology to provide analysis and measurement solutions. Out of those, an example that makes use of optical technology is the CS-series chemical concentration monitors that use ultraviolet (UV) and near-infrared (NIR) absorption spectroscopy, which have been widely used in semiconductor wet processes for many years and enables to take in-line, real-time measurements. This paper will introduce specific examples of applications.

Measurement principle and structure of CS-Series chemical concentration monitors

Absorption spectroscopy is a technique that is suited to measure chemical concentrations in a non-destructive, non-contact manner in real time. Incident light passes through sample cell and it is absorbed by the sample. The absorbed wavelength and absorption level differ based on the substance and concentration. The light absorbance $A(\lambda)$ at a certain wavelength is expressed in Equation 1.

$$A(\lambda) = \log_{10}[I_0(\lambda)/I(\lambda)] \quad \cdots\cdots \quad (1)$$

$I_0(\lambda)$: Incident light intensity
$I(\lambda)$: Transmitted light intensity
λ: Wavelength

The light absorbance and sample concentration is also expressed as follows, according to the Beer-Lambert law.

$$A(\lambda) = \alpha(\lambda)LC \quad \cdots\cdots \quad (2)$$

$\alpha(\lambda)$: Absorption coefficient
L: Sample cell length
C: Sample concentration

The Beer-Lambert law is the basic principle in the CS Series. The light absorbance is calculated by measuring the light intensity of each wavelength, and the chemical concentration is calculated based on the absorption coefficient and cell length that were set in advance. In actual measurement systems, it is difficult to directly measure the incident light, so we actually measure the reference light intensity I_r instead of the incident light I_0.

With regard to wavelengths for CS-series, the measurements are limited to the UV range and NIR range. The NIR range contains the absorption range for O-H bonding and N-H bonding, etc. The UV range contains the absorption range for H_2O_2 and HNO_3 which are generally used in semiconductor cleaning processes. To make use of these characteristics, the monitor equips a Czerny-Turner spectrometer that can simultaneously conduct spectroscopy and detection in the UV and NIR ranges and use the multi-channel detector to simultaneously measure the amount of light at multiple wavelength points. In this way, we have achieved a fast response with a measurement interval of approximately 0.5 - 3 seconds, even when signal integration and moving average processing are included. There is also no moving part in the spectroscopy area, which means that measurements have good reproducibility. This design is suitable for industrial applications that require high reliability and reproducibility.[1]

In addition, the sample cell is high-purity quartz or

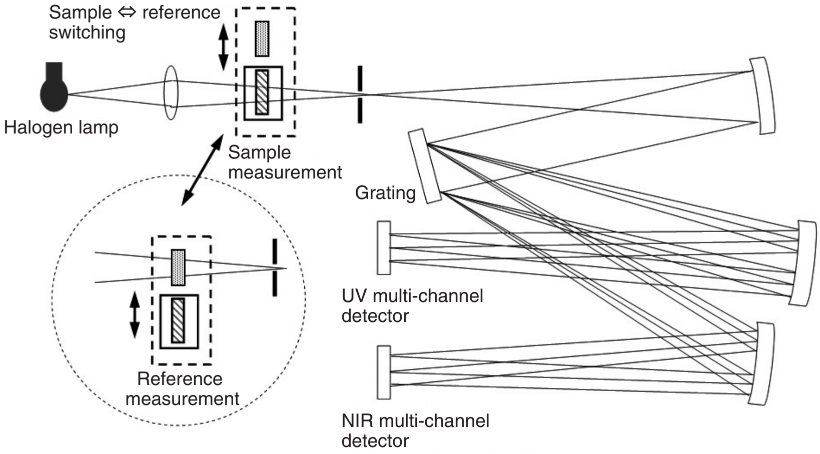

Figure 1 Structure of CS-100 series

high-purity sapphire, and the other wetting materials are PFA (perfluoroalkoxy polymer) and PTFE (polytetrafluoroethylene), that are suitable for use in semiconductor processes that require chemical resistance and high level of cleanliness.

CS-Series chemical concentration monitor line-up

The CS Series is categorized into 2 line-ups: (1) the built-in measurement cell type and (2) the separate measurement cell type.

(1) Built-in measurement cell type

This type includes the CS-100 Series (basic models) and the CS-700 Series (high-end models). The CS-700 Series makes use of the experience HORIBA gained from the CS-100 Series, and has a variety of added improvements in terms of hardware and algorism, etc. The most important point is the optical system, the CS-700 Series equips a detector with a larger number of channels than conventional systems for both UV and NIR, which has resulted in higher wavelength resolution, and improved spectrum separation performance.

(2) Separate measurement cell type (optical fiber type)

In this type, the measurement cell area and main unit area where equips electrical and optical system are separated, and both are connected using optical fibers. CS-100F1 is mainly used to measure corrosive chemicals, high-temperature and large flow rate chemicals. In the CS-600F Series, both the sample light and reference light can be measured by using an air-driven cylinder to move a mirror inside the measurement cell unit. In this way, we were able to significantly reduce the frequency of background corrections, which were necessary on the conventional CS-100F1 Series, from every 6 hours to more than one month.

Preparing the calibration curve

In the CS Series, for specific chemical types and concentration ranges of each component, there are individual conversion coefficients for converting concentrations from light absorbance spectra, and these are called calibration curves. These calibration curves are installed in individual monitors based on the specifications, various adjustments and inspections are conducted for the actual

Table 1 CS series line up (CS-100, CS-700, CS-100F1, CS-600F)

	Build-in measurement cell type		Separate measurement cell type	
	CS-100 Series	CS-700 Series	CS-100F1 Series	CS-600F Series
Appearance				
Note	Basic model	Wider wavelength, higher resolution	Basic model	High stability model
Temperature	20-30°C (Cooler unit can be attached)	20-30°C	20-30°C	20-80°C

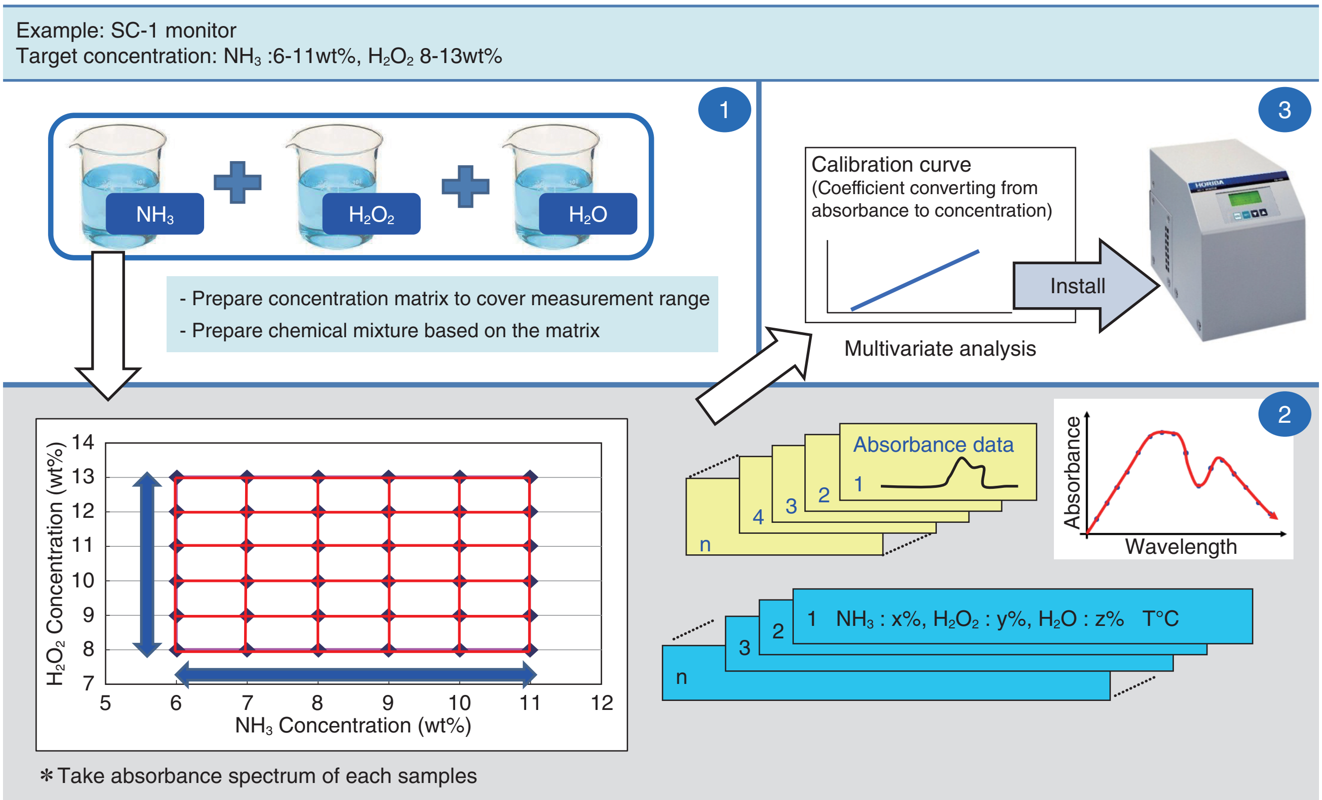

Figure 2 Schematic flow of making calibration curve

chemical, and then the monitors are shipped.

To make a calibration curve, samples with known concentration are adjusted in matrix form within the concentration range for the applicable chemical, and these spectrums are obtained. Multivariate analysis is used to make the calibration curve based on this concentration information and the light absorbance spectrum.

Measurement examples

As a typical example of measurements with the CS-100 Series, we will give an example of measuring a chemical used in semiconductor cleaning processes that is mainly made from 2-3 components, such as $NH_3/H_2O_2/H_2O$ or $HCl/H_2O_2/H_2O$. In recent years substances are not limited to this number of components, and chemicals are measured that are used in manufacturing processes in various fields, such as cases when by-products are generated, cases when organic substances are included, cases when metal ions are also present, and fields outside semiconductor, such as plating and lithium-ion batteries. Some of these are introduced below.

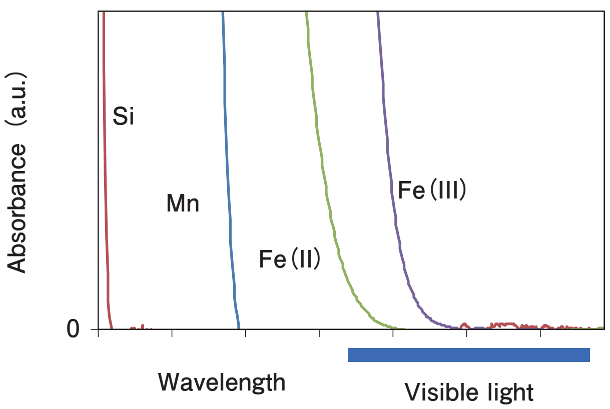

Figure 3 Absorbance spectra of metal ions

Measuring metal ion concentrations in chemicals

Here is an example of measuring the iron ion concentration. When iron dissolves into hydrochloric acid, the majority of it is bivalent, but some is trivalent, because it is oxidized in air.[2] We tried to measure the separation of Fe^{2+} and Fe^{3+} in hydrochloric acid. We set up the following as the measurement concentration range.

HCl: 5-10 mass %
Fe^{2+}: 5-10 mass %
Fe^{3+}: 0.05-0.2 mass %

To measure these components, when we made the calibration curve, we incorporated the iron chloride ions as one component in advance. That is, for Fe^{2+}, we used $FeCl_2$ and $4H_2O$ powder, and for Fe^{3+}, we used an $FeCl_3$ aqueous solution, and mixed these with HCl and water, and made adjustments until the ion concentration became the prescribed concentration.

When the iron ions dissolved, we saw that with Fe^{2+}, the solution turned a yellowish green color, and with Fe^{3+} it

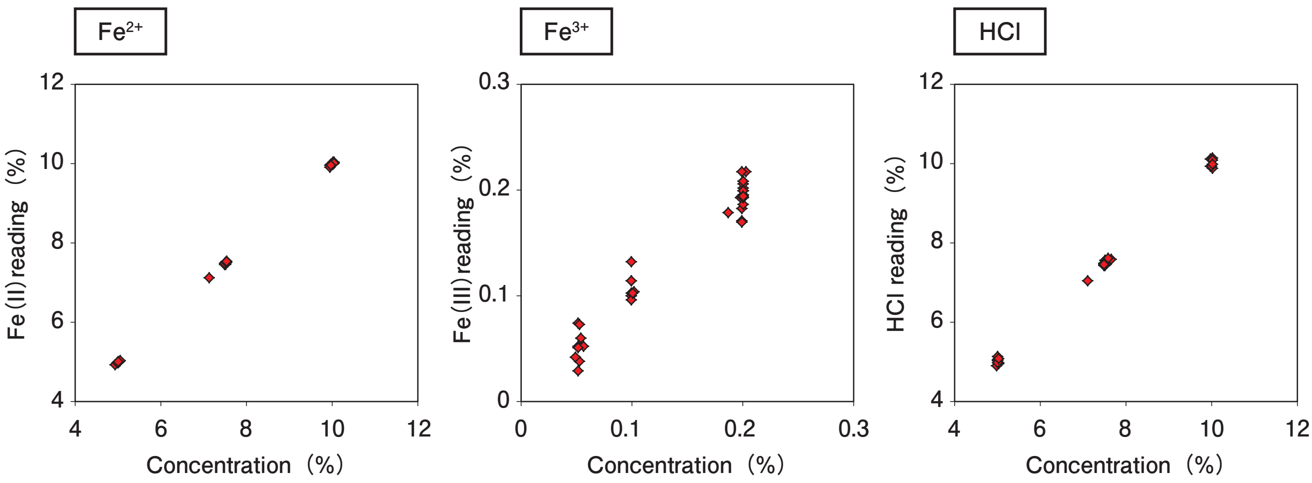

Figure 4 Measurement results of HCl, Fe^{2+} and Fe^{3+}, using monitor which equips spectrometer for VIS region

became a yellowish brown, and based on this we found that there was absorption in the visible range near blue, which is in a complementary color relationship. Figure 3 shows the Fe^{2+} and Fe^{3+} absorption spectrum with air as a reference.

To measure the Fe^{2+} and Fe^{3+} absorption range at the same time, we adjusted the optical system so that we could measure the visible range, measured the above sample, and made a calibration curve. Figure 4 shows that calibration data. In this sample, all the components (HCl, Fe^{2+}, and Fe^{3+}) were adjusted so that they have variation, but the respective components separated and we were able to measure them.

Measuring multiple components using the CS-700 Series

Here we will discuss a case of a mixed acid with 3 or

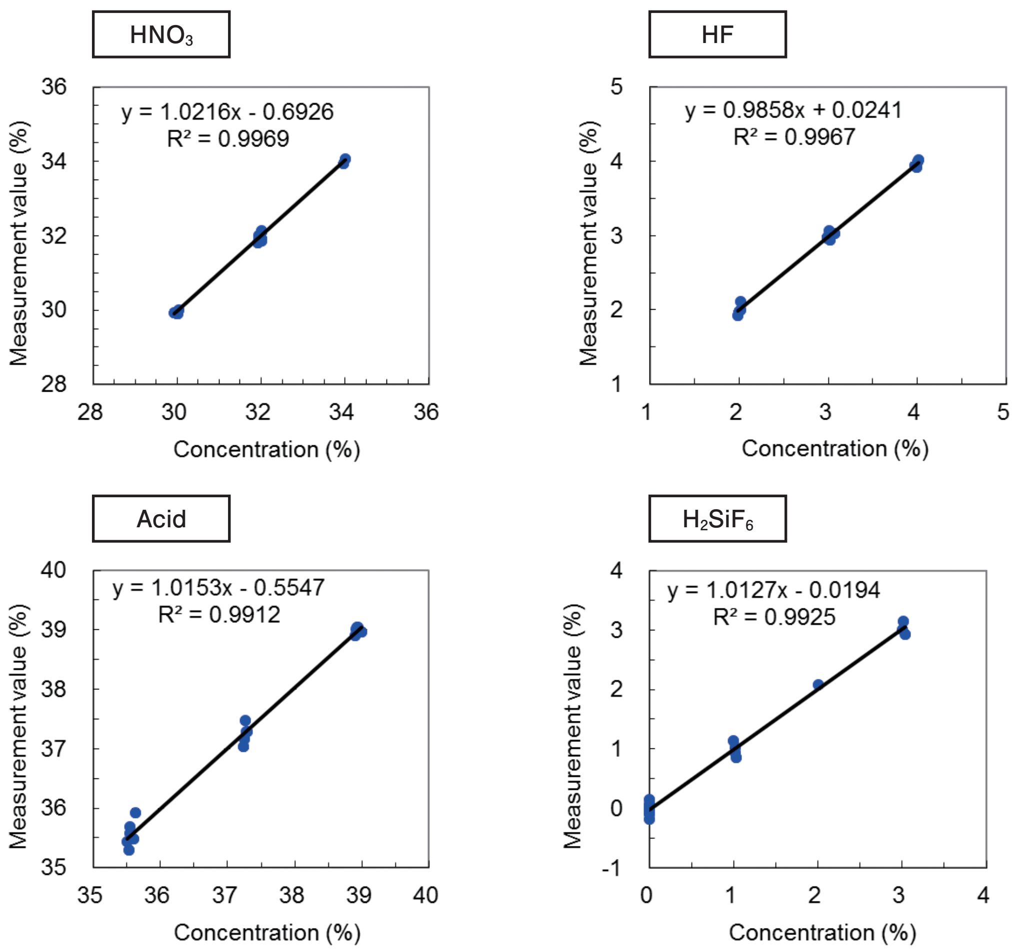

Figure 5 CS-700 measurement results of 5 components acid

more components, where by-products were also generated. In this example, we monitored a case where silicon dissolved during etching into chemical mixture composed of 3 types of acid (HF, HNO_3, and acid), which is generally used in etching silicon wafers. Generally, the acid concentration decreases as etching progresses, and by-products are generated from reactions with silicon. If the by-product concentration is high, it affects the absorption spectrum, and can cause errors in the concentration measurement results of each acid. As such, when we made the calibration curve, in addition to the water and 3 types of acid, we added the etching by-product H_2SiF_6 as one component, prepared the sample as having 5 components, and made the curve based on this information. Figure 5 shows the measurement results using the multi-wavelength, high-resolution CS-700. None of the components were affected by the H_2SiF_6, and the measurement results were good, and we were also able to measure the concentration of H_2SiF_6.

Example of measuring semiconductor CMP slurry

In semiconductor manufacturing, a process called CMP (chemical mechanical polishing) is used, in which wafer surfaces are polished using chemical and mechanical reaction. In processes where metal layers such as copper are polished, hydrogen peroxide is added to the slurry, which increases the polishing efficiency due to the oxidation of the metal. At this time, controlling the concentration of hydrogen peroxide is an important point. In general CMP slurries, the particle diameter of the abrasive is often at the hundred or several-hundred nm level, but in the UV range, where the wavelength is short, the light is scattered by the particles, and this is not suitable for measurement when absorption spectroscopy is used. On the other hand, in the NIR range, the wavelength is long compared to the particle size, and light passes through without being scattered, so this is relatively suitable for measurement. We made use of the characteristic that H_2O_2 also has absorption in the NIR range, although not as much as in the UV range, and tried to measure the H_2O_2 concentration in the CMP slurry using only the NIR range. In addition to abrasive particles and water as a solvent, CMP slurries include various components such as pH regulators and inhibitors. We made a calibration curve to measure the H_2O_2 concentration and set it up for 3 components, considering the overall slurry as one component, along with the H_2O_2 and water[3]. As shown in Figure 6, there is good linearity, and we found that even in chemical mixture that include particles, if things like the particle sizes and concentrations are suitable, it is possible to take measurements.

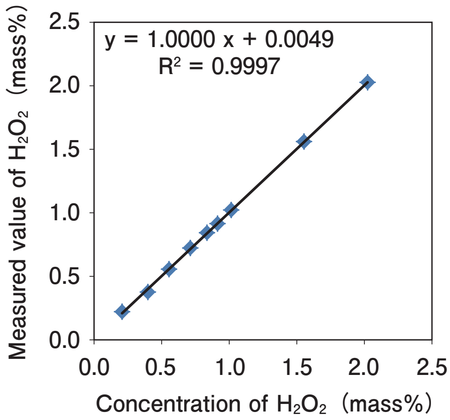

Figure 6 Measurement result of H_2O_2 in CMP slurry

Summary

This paper introduced concentration monitors that apply absorption spectroscopy that is used to measure cleaning chemical and etching chemical that are mainly used in semiconductor manufacturing processes. A wide variety of things can be measured, such as acid and metal ion concentrations dissolved in acid, concentrations of mixed acids that include by-products, hydrogen peroxide concentrations in CMP slurry that include particles, and also other substances that have not been listed here. In addition, there are many variations in the line-up for things like wavelength range and sampling system types, along with sample conditions and integration with customers' manufacturing equipment. We would like to use our technology, starting with absorption analysis in various industrial fields, not just semiconductors, to contribute to solving problems in manufacturing processes and improving quality and production efficiency through in-line monitoring.

References

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