Feature Article

Conductivity Meter with Carbon Electrodes and Application for Densitometers
Technologies for a Practical Densitometer

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HORIBA developed 2-pole electrical conductivity sensors with chemical-resistant carbon electrodes in 2002. These sensors are installed in semiconductor wet processes and are put into practical use as densitometers. In addition, HORIBA developed a new circuit for 4-pole conductivity measurement, which was an innovation that improved the precision with any 4-pole sensors. Concentration of single-component such as hydrofluoric acid or TMAH are measured based on precise electrical conductivity and temperature measurements. Temperature compensation calculations for the conductivity of the individual component are necessary to convert the conductivity into the concentration. Etching and developing solutions, etc. need to be controlled at a constant level, and the demand for various types of densitometers that use electrical conductivity systems is increasing.

Introduction

Dozens of types of aqueous solutions are used for cleaning and etching in semiconductor wet processes. These are often prepared by diluting stock solutions on site, and densitometers are needed to check the operation of the dilution devices and adjust the concentrations. With electrolytes, there is a correlation between concentration and electrical conductivity, and concentrations can be converted from electrical conductivity. Electrical conductivity measurement systems that can obtain concentration information in real time don't need reagents and can easily be incorporated into in-line processes, so these are essential for measuring single-component concentrations. Metals cannot be used as a material of electrode for semiconductor applications because of problems with chemical resistance. On the other hand, carbon has durability when exposed to normal acids and alkalis such as hydrofluoric acid, and also has the feature of having few surface impurities. This paper will discuss the performance, features, and applications of densitometers with carbon electrodes used as standard equipment in semiconductor processes.

Electrical conductivity of aqueous solutions

Water molecules have one oxygen atom in the center with 2 hydrogen atoms configured at approximately 104-degree angles, and the electric charge is distributed so that the hydrogen atoms have a positive electric charge and the oxygen atom has a negative electric charge. For that reason, water is a dissolving agent that has polarity. When electrolytes dissolve in water, the oxygen in the water molecules orients toward the positive ions, the hydrogen in the water molecules orients around the negative ions, ionizing the ions in the thermal motion. Ion crystals such as sodium chloride (NaCl) that have weak bonding are 100% ionized in dilute solutions, but there are some substances with strong bonding such as silver chloride (AgCl) that only ionize slightly, and mostly don't dissolve in water.[1]

Ions in aqueous solutions receive Coulomb force through electric fields and move, so that movement can be detected using current meter. The electrical conductivity of aqueous solutions depends on the concentration of the ions and the mobility. Electrical conductivity is equivalent to the inverse of the resistance of a sample cut into a 1-m^3 shape, and the unit is expressed as S/m.

Two-pole method, four-pole method, and electromagnetic induction method

Even if constant voltage is applied to a pair of electrodes located in an aqueous solution, the electric field in the aqueous solution is not constant over time, and the current also is not constant. The rate of change in the current also depends on the electrical conductivity. This is because with electrodes and aqueous solutions, the electric charge is carried by the respective electrons and ions, and these can't penetrate each other's territories, so a phenomenon

occurs in which both electric charges approach each other on the junction surface, forming a so-called electrical dielectric layer. The electrical dielectric layer demonstrates the same characteristics as an electric circuit capacitor, and the potential difference concentrates on the junction surface as time passes, so the electric field (potential gradient) in the aqueous solution decreases. When this happens, current doesn't flow, so in the 2-pole method, electrical conductivity is measured using a method in which alternating-current (AC) potential is applied to the electrode and the movement of the ions in the AC electric field is detected as AC current. The impedance of the electrical dielectric layer is expressed as $1/i\omega C$, and the higher the angular frequency ω and the larger the junction capacitance C, the lower the resistance is, and errors can be decreased. These errors become conspicuous in the range with high electrical conductivity.

In the 4-pole method, in addition to the electrodes that apply voltage (current electrodes), electrodes that detect the voltage (voltage electrodes) are configured near the current electrodes. By detecting the potential difference induced by the current in the aqueous solution and dividing the current by the potential difference, the 4-pole method can maintain linearity, even in cases with high electrical conductivity where linearity would decrease using the 2-pole method. Figure 1 shows that linear electrical conductivity can be obtained with the method "current signal is divided by the voltage signal" in the 4-pole method.

The 4-pole method has the advantage of not only being able to cancel the effects of the electrical dielectric layer, but also the cable resistance and the resistance of the electrodes themselves. In electromagnetic induction systems that don't use electrodes, there are no problems with the electrical dielectric layer, and these are favorable for measuring high electrical conductivity. They also have the advantage of being able to only use plastic material as wetting material. However, these systems have disadvantages in terms of pursuing precision, such as the linearity of the obtained signals is not guaranteed, temperature changes in the core of the magnetic body that composes the sensor become changes in sensitivity, and it is difficult to measure low electrical conductivity.

Features of sensors that use carbon electrodes

The 2-pole sensors that use carbon electrodes are put into practical use in 2002 and 4-pole sensors are in 2008. The cell constant for the 2-pole sensor is designed larger to avoid disadvantage of dielectric layer. The problem in this case is that these need to be compatible with various pipe diameters in order to be put into practical use as in-line sensors on semiconductor lines. It was necessary to provide sensors that were compatible with sizes from a small diameter of 1/4 inch to a large diameter of 1 inch. To increase the cell constant, it wasn't enough to just make the sensor long and narrow. In the sensor block, we provided a wide main flow path and a narrow flow path that measures electrical conductivity. As a result, a sensor with a cell constant of 4/cm ended up having dimensions of 75 mm. This sensor can obtain linear electrical conductivity up to approximately 8 S/m.

The wetting materials are only PFA (tetrafluoroethylene-perfluoroalkyl vinyl ether copolymer), FFKM (perfluoroelastomer), and carbon, and are mainly used for measuring hydrofluoric acid. We provide a converter for
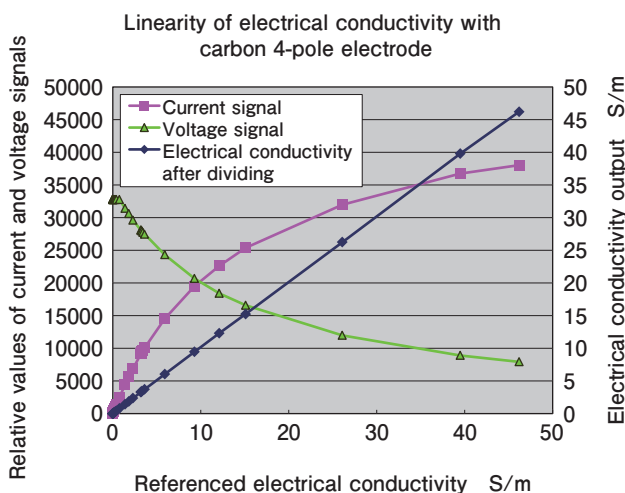

Figure 2   2-electrode carbon sensor

Figure 3   4-electrode carbon sensor

Figure 1   Current, voltage signal and current divided by voltage signal of the 4-electrode carbon sensor

Table 1   Extracted metals from the carbon surface by Hydrogen chloride

Extracted metal	Extracted in Hydrogen chloride solution ppb		
	Blank	One day	Seven days
Fe	110	110	97
Cu	1.9	1.2	1.4
Ni	0.32	0.36	0.36
Cr	0.74	0.76	0.66
Zn	9	11	8.5
Ti	2	2.1	2.2
Al	14	15	16
Ca	33	36	31
Na	250	260	260

this sensor that can obtain hydrofluoric acid concentrations and hydrochloric acid and ammonia concentrations from electrical conductivity.

The 4-pole carbon sensor has leeway to measure up to 200 S/m with linearity. We provide a densitometer for this sensor that works for up to 50% hydrofluoric acid, 10% hydrochloric acid, and 10% TMAH (tetramethylammonium hydroxide). The nature of the carbon electrodes is somewhere between that of graphite and glassy carbon, and airtight, but machinable. The carbon electrodes have high corrosion resistance and can withstand acids such as hydrofluoric acid, hydrochloric acid, dilute sulfuric acid, dilute nitric acid, and phosphoric acid, as well as most alkalis. Furthermore, carbon has good thermal conductivity, and has the value that it can be used as a sheath for temperature elements.

With regard to the impurities that can become problems in semiconductor processes, if the surface of the carbon electrodes are cleaned with acid and the surface impurities are removed, it is possible to create a state in which there is almost no elution of impurities. Table 1 shows the concentration measurement results from the Kinki Analysis Center. The sample fluid is based in hydrochloric acid, and the table shows the number of days the carbon electrodes were soaked and the concentration of the extracted components in ppb.

Four-pole electrical conductivity measurement circuit

In the 4-pole method, the current flowing to a pair of current electrodes is divided by the potential difference detected by a pair of voltage electrodes. In conventional systems, an operational amplifier changed the applied voltage of the current electrode so that a constant potential difference is generated in the voltage electrode (that is, so that a constant current flows) and a circuit was used that used the maximum amplitude of that applied voltage as electrical conductivity. In this type of circuit, the applied voltage to cause a constant current to flow differed based on factor such as sensor shape and electrode contact area, so it was necessary to design an optimal circuit for every sensor. Furthermore, these systems also had a problem where there was a danger of not noticing even if operation failed due to things like the amplitude of the applied voltage being thrown off, and a problem where the following of the operational amplifier was delayed when the frequency was increased. For this reason, we developed a new 4-pole electrical conductivity measurement circuit that can be used as common equipment for any type of sensor. That circuit uses a method where triangular wave applied voltage is applied to the current electrodes, and before the triangular wave peak, the current and voltage are detected, and a signal that has been converted to DC is divided by a computer. Using this method, constant voltage is applied, so it is possible to increase the frequency without circuit operation failure. When the electrical conductivity increases, the current finally stops changing because the electrical dielectric layer is
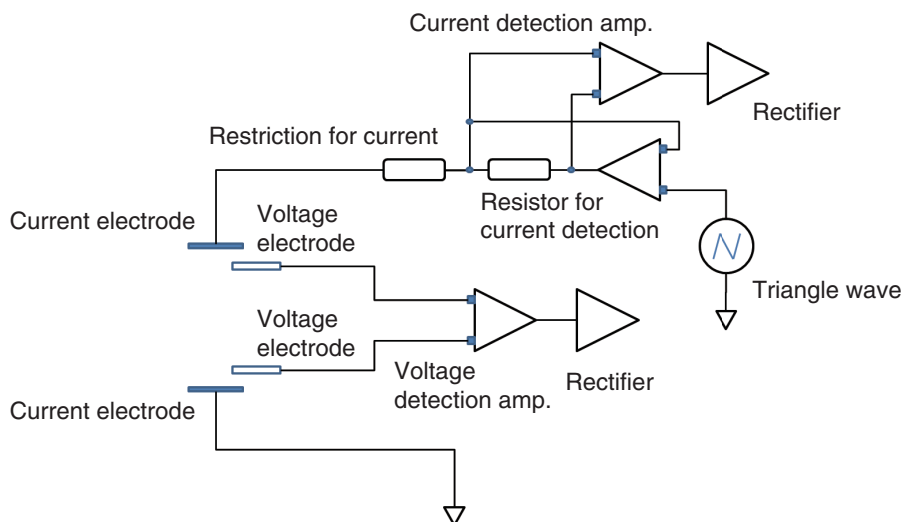

Figure 4   Electric circuit for 4-electrode conductivity measurement
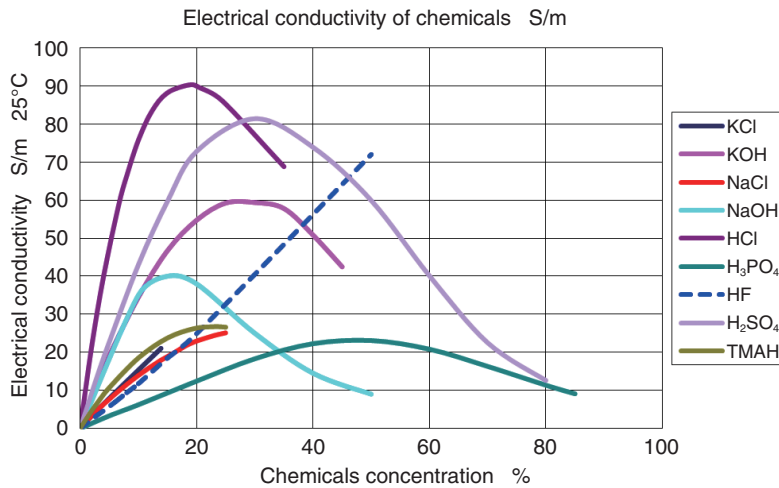
Electrical conductivity of chemicals   S/m

Figure 5   Conductivity characteristics of concerned chemical solution (S/m) (Measured by HORIBA Advanced Techno)

saturated. However, the potential difference decreases because the resistance of the solution decreases, so in terms of the division results, a signal can be obtained that is linear with the electrical conductivity. The objective of applying the triangular wave is to maintain the electric field in the solution. Figure 4 shows the basic circuit 4-pole electrical conductivity measurement.

Electrical conductivity of various chemicals

Figure 5 shows the relationship between various chemical concentrations and electrical conductivity (25°C). The electrical conductivity of hydrofluoric acid is distinctive, and has the characteristic that in low concentrations, the electrical conductivity is low, but in high concentrations of up to 50%, it increases monotonically. Substances such as hydrochloric acid, sulfuric acid, phosphoric acid, and sodium hydroxide have electrical conductivity peaks, and the electrical conductivity decreases as the water content decreases. Substances such as sodium chloride dissolve but reach a saturation point, and do not have such peaks.

Application to industrial processes

In processes where aqueous solutions are mixed, typical chemicals that strongly require concentration control are TMAH (tetramethylammonium hydroxide) and HF acid (hydrofluoric acid). TMAH is an organic alkaline chemical that is used in cleaning and etching silicon oxide film, and photoresist development. A concentration resolution precision to 3 digits after the decimal point is required in order to control the concentration at 2.38%. Hydrofluoric acid is used in etching silicon oxide film, and is mixed in concentrations of 500 ppm to 5,000 ppm. It's not a problem in measuring new chemical concentrations, but measurements of chemicals used in processes may be affected by by-products. An example of this would be the highly conductive silicon hexafluoride, which is generated when

silicon oxide film is etched using hydrofluoric acid.

Compared to other measurement methods (density, sound speed, index of refraction, titration, pH, light absorption, etc.), methods that convert concentrations from electrical conductivity have the advantage of reproducibility and high resolution. However, electrical conductivity won't necessarily increase monotonically as the concentration increases, so the measurable range is limited. Furthermore, the electrical conductivity changes depending on the fluid temperature, and to find the concentration, it is necessary to do temperature compensation for the electrical conductivity at 25°C. In general, temperature compensation is accomplished using a temperature coefficient of 2%/°C, but each chemical has unique temperature characteristics, so we find the electrical conductivity at 25°C using individual temperature compensation functions. Temperature compensation functions can't compensate appropriately using linear equations, there are some cases that require polynomial equations, and there are some cases where they change based on the concentration, so we use special algorithms for temperature compensation. For example, Figure 6 shows the electrical conduc-
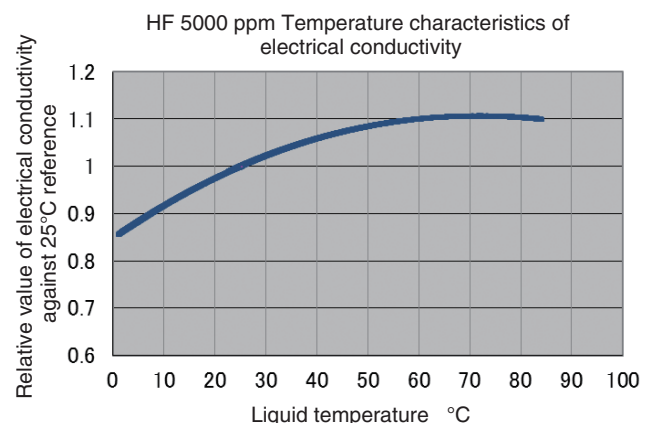

Figure 6   Example of the temperature characteristic of the conductivity of Hydrogen Fluoride solution

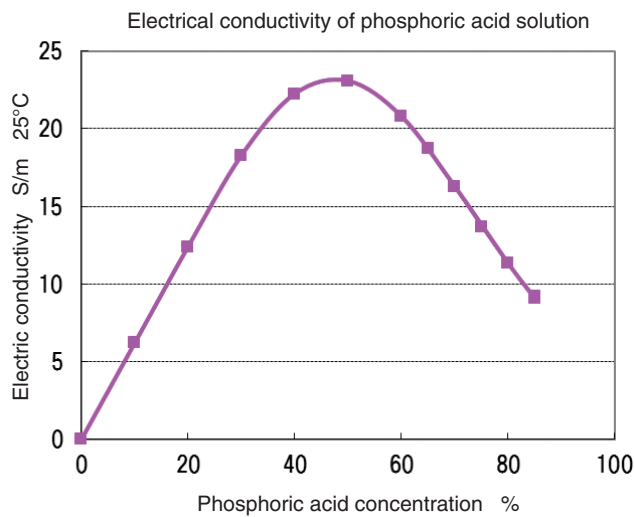Electrical conductivity of phosphoric acid solution

Figure 7   Conductivity of the phosphoric acid at 25°C

tivity temperature changes for a 5,000 ppm concentration of hydrofluoric acid, where the value at 25°C is set as 1. The temperature compensation for 25°C can be found by dividing by the values in this graph.

Even in ranges where electrical conductivity decreases due to the concentration increasing, this can be applied as a densitometer. For example, an algorithm has been developed to find the concentration with 85% phosphoric acid around 160°C. **Figure 7** shows the electrical conductivity at 25°C up to 85% phosphoric acid. Based on a database for various temperatures, we found the concentration of phosphoric acid from the electrical conductivity and temperature.

Chemical densitometer

Table 2 shows the scope of our experience for converting concentrations from electrical conductivity for single-component chemicals. We have actually finished designing conversion software including temperature compensation for use as a densitometer. This has been put into practical use as a densitometer in semiconductor, liquid crystal, and solar panel manufacturing processes for things such as etching and cleaning of silicon oxide

using inorganic alkalis and oxalic-acid-based etching of ITO (indium tin oxide) transparent electrodes.

Conclusion

Carbon has higher chemical resistance performance than metal, it is possible to increase the contact area during etching processing, and the catalytic effect of hydrogen peroxide breaking down is low, which makes it an optimal material for electrically conductive electrodes. However, the difficult point is that there is little freedom in things such as size and shape. There is a need to design a sensor for diverse requirements that has commonized electrode shapes. Furthermore, in the future, we intend to develop an electrically conductive sensor that makes use of the characteristics of carbon for general industrial use beyond semiconductor processes.

Table 2   Practical concentration range converted from the conductivity for each chemical solutions

Component	Concentration range %	Component	Concentration range %
HCl	0-15	NaOH	0-12
H_2SO_4	0-20	TMAH	0-15
HF	0-50	NH_3	0-2
HNO_3	0-15	NaCl	0-23
$(COOH)_2$	0-7	KCl	0-20
H_3PO_4	0-30	K_2CO_3	0-10
KOH	0-20	Na_2CO_3	0-12

References

[1]   Solubility AgCl 1.93 mg/L NaCl 26.43% 25°C (Handbook of Chemistry 3rd Edition)

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