HORIBA Advanced Techno

Beyond Water with You

Development of Monitoring Technique for High Temperature Phosphoric Acid by Spectroscopy

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Introduction

■ Selective removal of silicon nitride in 3D NAND process

Selective removal of silicon nitride (Si_3N_4) in multi-layers of silicon oxide and silicon nitride is a crucial step in the production of 3D-NAND devices[1]. **Phosphoric acid is a typical etchant used for the removal of Si_3N_4** due to its high selectivity of Si_3N_4 to SiO_2[2].
In this process, concentration of H_3PO_4 and the temperature are the key parameters for process control because the etching rate depends on both of them [2].

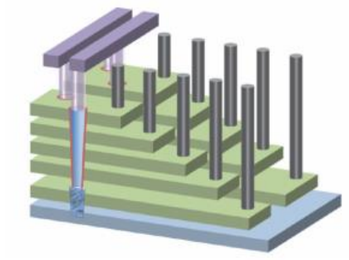


Fig.1 Schematic Diagram of Multi Stuck Layer in 3D-NAND[3]

■ Measurement metrology for hot phosphoric acid

For the measurement of H_3PO_4 concentration, **conductivity measurement and optical measurement** are strong candidate for this purpose[4]. Table1 shows the comparison of advantage and disadvantage for each metrology. Usually, the process temperature is generally over 140 deg.C, making it difficult to measure the concentration with conductivity.

Table.1 Comparison of advantage for metrology of hot phosphoric acid measurement

Metrology	Conductivity	Monochromatic	Spectroscopy
Picture			
High temp. (>100 deg.C)	×	× (PFA cell)	✔
Effect of temp. change	✔	△	✔
Repeatability	✔(<100 deg.C)	△	✔
Cost	✔	✔	△

■ Objective

1. To develop spectroscopy that can directly measure hot phosphoric acid over 140 deg.C
2. To show the results of feasibility study for the performance of newly developing monitor and compared with the performance of conductivity measurement

Materials & Method

■ Materials

- **Sample preparation**

Aqueous solutions of H_3PO_4 were prepared by diluting 85 wt% phosphoric acid solution with deionized water.

H_3PO_4 conc. range : 70 – 85 wt%
Temp. range : 25 – 160 deg.C

- **Experiment system**

Sample temperature was controlled between 25 and 160 deg.C using an oil bath. The image of experiment system is showed in Fig.2.

- **Apertures**

NIR Spectrometer

Type : Not decided (HORIBA)
Principal : Near Infrared Spectroscopy
Wavelength region : 1400 – 1600 nm
Sample temp. : 5 – 180 deg.C (Tentative)
Measurem. Range : 80 – 90 wt% (H3PO4)

Conductivity meter

Type : FES-510-1/4 (HORIBA)
Principal : 4 electrode method
Cell constant : About 1.4/cm
Sample temp. : 5 – 100 deg.C
Measurem. Range : 80 – 90 wt% (H_3PO_4)

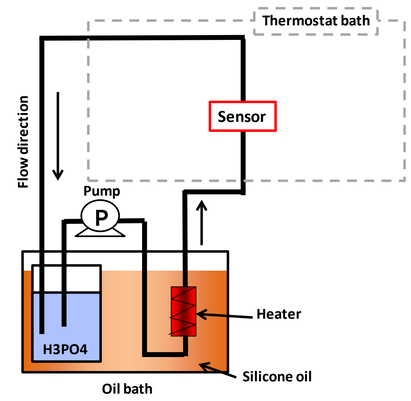


Fig.2 Experiment system

Fig.3 NIR Spectrometer (Prototype)

Fig.4 Conductivity meter FES-510S-1/4S

■ Methods

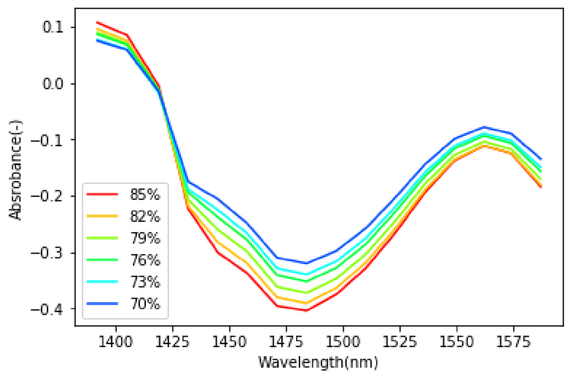
- **Data aquisition**

Investigation of the major performance parameters (ex. linearity between H_3PO_4 concentration & conductivity,absorbance, long term measurement stability etc.) was performed as basic investigations.

Results & Discussion

■ Performance test for H_3PO_4 sample with low temp.

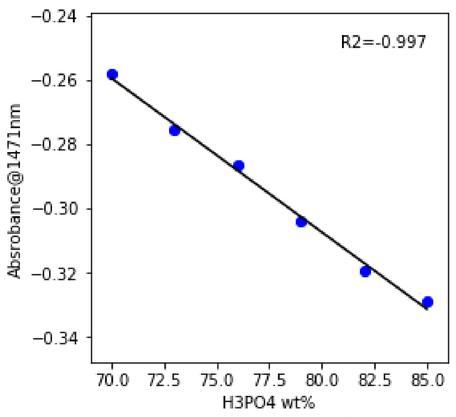
1. Row spectra for H_3PO_4 with NIR spectroscopy



Raw spectra for H_3PO_4 were acquired with developing spectroscopy which can measure the region 1400 – 1600 nm called 1st overtone region of OH stretching vibration. The **peak absorbance around 1480 nm decreased with increasing concentration of H_3PO_4 since this peak derived from OH absorbance for water**.

Fig.5 Raw spectra for H_3PO_4 70 – 85 % aqueous solution sample with RT sample

2. Linearity between single absorbance value and H_3PO_4 conc.



Linearity between the absorbance of 1471 nm and H_3PO_4 concentration was investigated. The result showed **strong correlation between the absorbance and concentration** since the absorbance of OH stretching vibration was changed by increasing H_3PO_4 concentration.

Fig.6 Linearity between the absorbance of 1471 nm and H_3PO_4 concentration.

■ Performance test for H_3PO_4 sample with high temp.

1. Comparison of metrology for H_3PO_4 80wt% sample over 100 deg.C

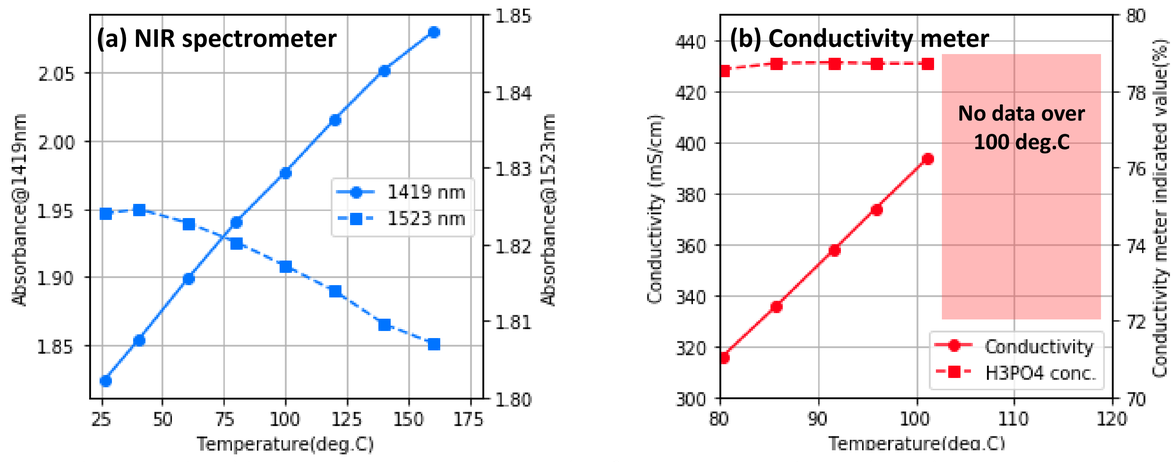
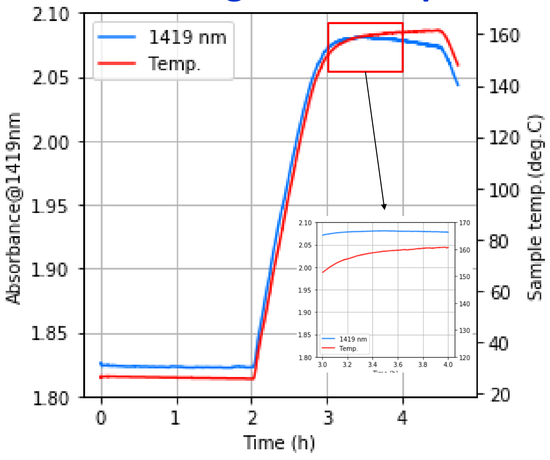


Fig.7 Relationship between measurement value for H_3PO_4 80wt% sample and Temperature (a) NIR Spectroscopy (b) Conductivity meter

2. Monitoring with NIR spectrometer for H_3PO_4 80wt% 25 - 160 deg.C



1. NIR spectra for H_3PO_4 80wt% sample with temperature 25 - 160 deg.C were acquired. Though the absorbance value for 1419 nm and 1523 nm changed with temperature since these wavelengths related to condition of hydrogen bonding, the results showed the potential for measurement of the sample with 160 deg.C or higher. Conductivity meter could measure the sample under 100.degC but couldn't measure it over 100 deg.C since the sample cell deformed.
2. Monitoring data showed the possibility to measure 160.degC sample for long time measurement.

Fig.8 Monitoring data of H_3PO_4 80wt% sample by spectrometer with temperature changing 25 – 160 deg.C

Conclusion

■ This results showed NIR spectroscopy could be applied to measurement of hot H_3PO_4 aqueous solution over 100 deg.C and continuous monitoring for 160 deg.C.

■ Reference

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[4] D. Chin *et al*., *J. Applied Electro. Chem*., **19**, pp.95-99 (1989)