Introduction

Cleaning processes in sub-10 nm node have an increase challenge due to smaller geometry, increased number of wetter materials, and increased functionality/selectivity demands where some components have to be removed at a fast rate with a minimum etch rate for other components. As a result, most modern formulations include at least 6 subcomponents with a special emphasize on corrosion inhibitors and promoters. As an example, fluoride is a potent etching agent for W, Al and SiO₂ while BTA and similar compounds are effective corrosion inhibitors for Cu.

Measuring Inhibitors by UV-VIS spectroscopy

Cu inhibitors are commonly used to passivate previously plated Cu layers. Organic groups in inhibitor compounds usually have good UV-VIS signals. Such inhibitors can be measured by UV-VIS spectroscopy. In case multiple inhibitors are used, spectral features can overlap, multivariate analysis (MVA) is needed. The inhibitor concentration is expressed as:

$$c_{Inhibitor} = c_{\lambda_1} \times A_{\lambda_1} + \cdots c_{\lambda_i} \times A_{\lambda_i} + \cdots c_{\lambda_n} \times A_{\lambda_n}$$  (1)

where $c_{\lambda_i}$ is the coefficient at wavelength $\lambda_i$ and $A_{\lambda_i}$ is the absorbance at wavelength $\lambda_i$. The coefficient set is predetermined by a large amount of calibration data and multivariate analysis.

Measuring Fluoride by ISE

Low concentration of Fluoride is measured by Fluoride Ion Selective Electrode (FISE) method. Under ideal conditions, the potential ($E$) of a FISE is given by the well-known Nernst equation:

$$E = E_0 - \frac{2.303 \cdot RT}{nF} \log [F^-]$$  (2)

Measuring contaminant Ti in TiN removal

Titanium is a contaminant from the TiN removal. Monitoring of Ti level is needed for the process control. Figure below shows an excellent correlation of spectroscopic signal to the Ti concentration at ppm level.

Conclusion

With the combination of various metrology techniques (spectroscopy, ISE, HPLC, etc.), multiple components in the cleaning solutions, including contaminant can be measured with fast, accurate, and repeatable results.

References:
Eugene Shalyt, Guang Liang, Jingjing Wang, Michael Pavlov, Vladimir Dozortsev, Chuannan Bai and Peter Bratin ECS Trans. 2013 volume 58, issue 6, 159-167