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Comparison of near-infrared and Raman spectroscopy for on-line monitoring of etchant solutions directly through a Teflon tube

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ABSTRACT

Both near-infrared (NIR) and Raman spectroscopy have been studied for the quantitative measurement of components (H_3PO_4, HNO_3, and CH_3COOH) in an etchant solution and the corresponding prediction robustness has been evaluated. Both measurements were accomplished by illuminating radiation directly through a Teflon tube. Raman spectral features of each component were much clearer and more selective than those observed in the NIR spectrum. Especially, NIR spectral variation pertinent to H_3PO_4 and HNO_3 were mostly based on the displacement and perturbation of water bands rather than due solely to NIR absorption. Therefore, the resulting spectral variations were not highly specific. When the validation set contained minor spectral variations resulting from a slight instrumental change, NIR prediction performance for all three components degraded substantially by showing obvious prediction bias. However, the accuracies of Raman predictions were maintained. Since partial least squares (PLS) models for each component were built using NIR spectra of poor specificity with broadly overlapping features, even minor spectral differences introduced by instrumental variations sensitively influenced the prediction performance of the NIR models. Overall, the selectivity (specificity) of a targeting spectroscopic method should be considered critically to secure prediction robustness for monitoring components in an etchant solution.

1. Introduction

Near-infrared (NIR) spectroscopy has recently been studied for on-line monitoring of components in etchant solutions; these solutions are used extensively in semi-conductor industries to remove impurities in silicon wafers. These etchants are mostly oxidants and diverse acids in an aqueous medium. By providing direct NIR radiation through an existing Teflon line, measurements can be taken without any process modifications, as shown in previous studies [1,2]. In general, the NIR spectral features of the components in etchant solutions broadly overlapped with one other and the water spectral feature. Sometimes the perturbation and/or displacement of the water band was the only information available to build a model for some components, such as H_3PO_4 and HNO_3, which had no separate NIR absorption. Under this circumstance, the selectivity of a multivariate calibration model should be careful considered. Based on a previous study, the spectral range should be carefully determined to achieve an acceptable selectivity [3,4]. When a calibration model is built using spectra of

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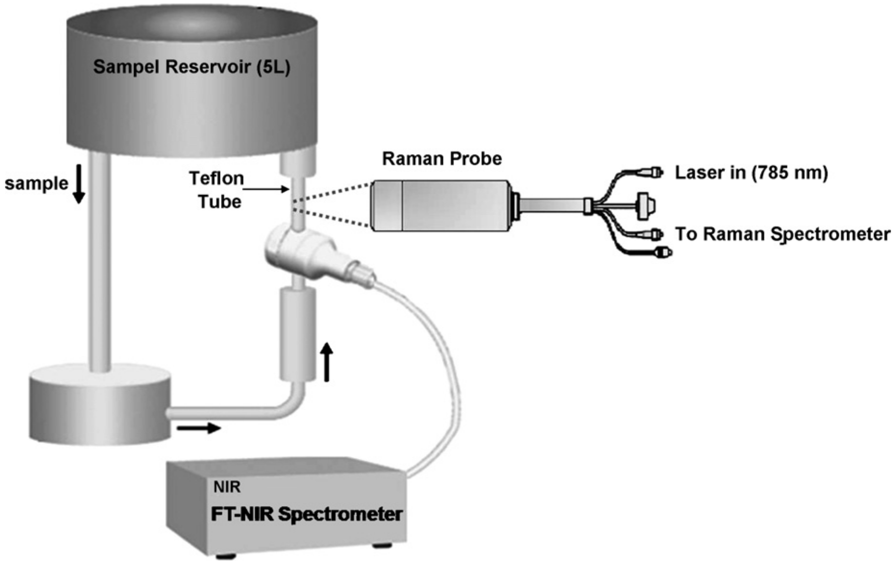

Fig. 1 – The graphical description of a chemical wet bench for circulating samples and the spectral collection scheme for acquiring NIR and Raman spectra directly from a Teflon tube.

low selectivity and sensitivity, such as NIR spectra of etchant solutions, it is highly likely that prediction performance would be affected by minor spectral variations other than the compositional change in the components. Therefore, the long-term robustness of NIR measurements for monitoring etchant solutions is another important issue to consider.

Alternatively, Raman spectroscopy can provide more distinct spectral features (better selectivity) than NIR spectroscopy, especially for inorganic acids, as shown previously [5]. To exploit the superior selectivity of Raman spectroscopy, a Raman collection scheme capable of providing reproducible Raman spectra should be developed. Direct Raman spectral collection through a Teflon tube is advantageous because a non-overlapping Teflon band could be used as a standard to correct Raman intensity variation which is essential for reliable quantitative analysis [6].

In this publication, the analytical performance of NIR and Raman spectroscopy for determining the compositional analysis of a metal aluminum etchant (MAE, a mixture of H_3PO_4, HNO_3, and CH_3COOH) solution, one of the most frequently used etchant solutions, was compared. NIR and Raman spectra of MAE solutions were collected synchronously in an on-line manner by circulating samples using a pilot scale chemical wet bench, as shown in Fig. 1. For NIR measurements, NIR radiation from an optical fiber was illuminated in the center of the Teflon tube. The transmitted radiation was also collected with the use of an optical fiber. The sample holder was designed to hold the Teflon tube firmly. To maintain reproducibility of the Raman measurement, the wide area illumination (WAI) Raman scheme that applied a laser in a circular fashion with a 6-mm diameter (area: 28.7 mm^2) with a focal length of 250 mm, was employed. Previous studies have shown that the use of the WAI scheme helps to improve the reproducibility and accuracy of the Raman measurement [6–9]. As shown in Fig. 1, NIR and Raman spectra were collected simultaneously through the same Teflon tube to ensure fair comparison of the two methods for quantitative analysis of the components in the MAE solution. Using both NIR and Raman spectra, partial least squares (PLS) models [10,11] were built and the corresponding models were validated by predicting the spectra collected after 2 months of initial spectral collection, where some minor spectral variations were observed.

2. Experimental

2.1. NIR and Raman spectral collection

Fig. 1 shows the schematic diagram of the pilot chemical bench used for this study. This chemical bench was designed to control the temperature and flow rate while continuously circulating an etchant sample through a 0.75-in. Teflon tube. The volume of the reservoir (also made of Teflon) was 5 L. Both NIR and Raman spectral collections were performed in the same Teflon tube with continuous flow (flow rate: 4 L min^{-1}) of the sample.

For the NIR measurements, a fiber optic probe designed to transmit NIR radiation through the Teflon tube was used. The tube was held firmly in place by the probe. A detailed description of the fiber optic configuration can be found in a previous publication [1]. An ABB Bomem fiber optic-based FT-NIR spectrometer equipped with a tungsten–halogen source and a Germanium detector was used. All NIR spectra corresponded to an accumulation of 128 scans with a resolution of 32 cm^{-1} (collection time: 60 s). Five spectra were collected per sample.

For Raman spectral collection, the WAI scheme (Kaiser Optical, Inc., Ann Arbor, MI) was used in which a laser beam is used to illuminate a sample in a circular fashion, with a 6-mm diameter (area: 28.3 mm^2) and a focal length of 250 mm. A Teflon tube containing the circulating sample was located in