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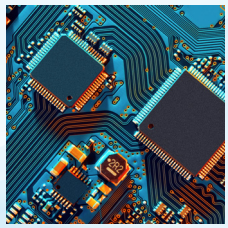
Quantitative Analysis of Common Components in a Chemical Mechanical Polishing (CMP) Slurry Using Raman Spectroscopy



Application Note

Semiconductor
RA91

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Abstract

Chemical Mechanical Polishing (CMP) is a crucial step in semiconductor manufacturing. Quantifying the components of the slurry is crucial to ensuring an effective slurry that will not damage the wafer. Current techniques for quantification, such as Ion Chromatography (IC) and High-Pressure Liquid Chromatography (HPLC) have excellent limits of detection, but they are difficult, costly, and require experienced users. In this application note, Raman spectroscopy is explored as an easier and more flexible technique for quantifying common components in a CMP slurry, such as benzotriazole and glycine, without any sample preparation or costly consumables. Results show that Raman spectroscopy can reach estimated limits of detection and quantification of benzotriazole of less than 0.025% and 0.10% (both in mass percent), respectively, making Raman spectroscopy an ideal alternative to the more costly and time-consuming techniques like IC and HPLC.

Keywords

Semiconductor, CMP Slurry, Raman

Introduction

The Chemical Mechanical Polishing (CMP) process is a critical step in manufacturing semiconductor devices. This process typically involves a slurry as the chemical component and a polyurethane pad as the mechanical component, which are used together to create exceptionally smooth and planar surfaces on the wafer. In this application note, we will focus on the slurry, a mixture of chemicals used to help soften and provide some abrasiveness to the wafer during the polishing process. The common components of a CMP slurry include colloidal particles (usually silica, alumina, or ceria), oxidizers, chelating agents, and corrosion inhibitors. The amounts of these materials and the particle size of the colloidal particles are critical to creating a successful CMP slurry that will be effective, without damaging the wafer. Some of the common chemicals used in a CMP slurry are benzotriazole, colloidal silica, glycine, and water.[1,2,3] This application note will specifically focus on quantifying glycine and benzotriazole, as these are typically measured with chromatographic techniques and may be at a concentration which can be quantified using Raman spectroscopy.

CMP slurry components are typically measured using chromatographic techniques such as Ion Chromatography (IC) or High-Pressure Liquid Chromatography (HPLC). These techniques offer particularly good detection limits and measurement repeatability,z but can require considerable time and effort to create a method, complex and lengthy sample preparation, highly skilled operators, and a significant cost for consumables. Although Raman spectroscopy does not have the same detection limits as chromatographic techniques, it offers a much simpler approach to detecting and quantifying slurry additives, with many benefits over traditional chromatographic techniques. Raman spectroscopy is a quite simple technique allowing for direct measurement of the slurry samples without any sample preparation, no high-cost consumables, and various measurement configurations (directly in the slurry with touch/immersion probes, through bottles/pipes with non-contact probes, in-line, etc.) which make sample measurements fast and easy for anyone. This application note will establish the capability of Raman spectroscopy to detect and quantify some common components found in typical CMP slurry mixtures.

Experimental Methods

Before quantification, measuring each component is required to make sure they are Raman active and can be clearly identified from one another when mixed. For this study, colloidal silica, benzotriazole, and glycine samples were each measured individually and as a mixture, with the MacroRAM and the MarqMetrix® immersion probe. The MacroRAM provides bulk (macroscopic) Raman measurements and does not utilize a microscope, making it simple and easy to use. The MarqMetrix immersion probe is fiber-coupled to the MacroRAM and can be placed directly into the liquid solution for instant Raman measurements. Once it was confirmed that there were Raman peaks to differentiate each component in the mixture, the goal was to move forward with an expanded sample set to quantify the amount of benzotriazole and glycine in different CMP slurry mixtures.

For quantification, a series of 28 CMP slurry mixtures were created with varying amounts of colloidal silica (0, 1%, 2%), benzotriazole (0, 0.2%, 0.6%), glycine (0.5%, 1.0%, 1.5%), and water (96-100%), as shown below in Table 1. The goal of this study was to use Raman spectroscopy to quantify benzotriazole and glycine concentrations. Colloidal silica is not a strong Raman scatterer, but it does provide some opaqueness to the sample, which can affect the overall Raman signal, especially when trying to quantify concentrations. For that reason, colloidal silica was added to some of the samples, and concentrations were varied to determine if there were any effects on the overall quantification of the two main components, benzotriazole and glycine.

run	silica	benzotriazole	glycine	water
1	0.00%	0.00%	0.00%	100.00%
2	1.01%	0.00%	0.57%	98.42%
3	1.01%	0.00%	1.22%	97.77%
4	1.00%	0.00%	1.74%	97.26%
5	1.00%	0.20%	0.52%	98.28%
6	0.91%	0.18%	1.11%	97.80%
7	1.01%	0.20%	1.71%	97.08%
8	0.99%	0.60%	0.51%	97.90%
9	1.00%	0.60%	1.02%	97.38%
10	1.01%	0.60%	1.52%	96.87%
11	2.00%	0.00%	0.52%	97.48%
12	1.99%	0.00%	1.02%	96.99%
13	1.99%	0.00%	1.49%	96.52%
14	2.00%	0.20%	0.51%	97.28%
15	2.00%	0.20%	1.01%	96.80%
16	2.00%	0.20%	1.53%	96.28%
17	2.11%	0.60%	0.52%	96.77%
18	2.01%	0.60%	1.02%	96.37%
19	1.99%	0.60%	1.49%	95.92%
20	0.00%	0.00%	0.52%	99.48%
21	0.00%	0.00%	1.03%	98.97%
22	0.00%	0.00%	1.51%	98.49%
23	0.00%	0.20%	0.52%	99.28%
24	0.00%	0.20%	1.00%	98.80%
25	0.00%	0.20%	1.50%	98.30%
26	0.00%	0.60%	0.50%	98.90%
27	0.00%	0.60%	1.00%	98.40%
28	0.00%	0.60%	1.48%	97.92%

Table 1: Known concentrations for 28 CMP slurry mixtures created with varying amounts of colloidal silica, benzotriazole, glycine, and water.

All samples were measured directly in the liquid using the MacroRAM with 785 nm excitation and a ½" MarqMetrix® immersion ballprobe. For each sample, the acquisition time was 20 seconds, and ten spectra were averaged to give the final spectrum (200 seconds total integration time). The setup is shown below in Figure 1. All data were acquired, processed, and analyzed using the HORIBA LabSpec 6 software suite.

The data were then processed using both a single peak calibration and a multivariate partial least squares (PLS) model calibration for comparison. The single peak calibration was done directly through LabSpec 6 and Excel®, and the multivariate model was created using the MVA (MultiVariate Analysis) EVRI application within LabSpec 6.

In addition to measuring these samples directly in the liquid, there are other measurement configurations available including non-contact probes, flow cells, or standard cuvette-based measurements inside the MacroRAM.

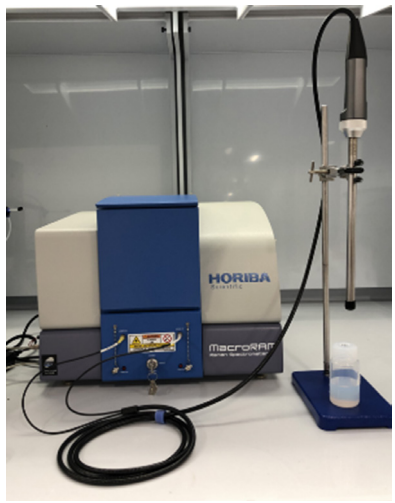

Figure 1: MacroRAM and MarqMetrix immersion probe setup used to measure the CMP slurry samples.

Results and Discussion

Shown in Figure 2 are the Raman spectra of colloidal silica plus benzotriazole, colloidal silica plus glycine, and colloidal silica in water. The spectrum of colloidal silica in water is quite flat and featureless, except for the water peak around 1620 cm^{-1}. Colloidal silica is important, because it causes the slurry to become opaque and scatter light, which could lead to incorrect quantification of the slurry components. For this reason, of the 28 sample mixtures used for the overall experiment, varying amounts of colloidal silica were used to see any matrix effects, with the main interest in quantifying benzotriazole and glycine. As shown in Figure 2, benzotriazole and glycine have distinct Raman peaks that will change in intensity as a function of concentration.

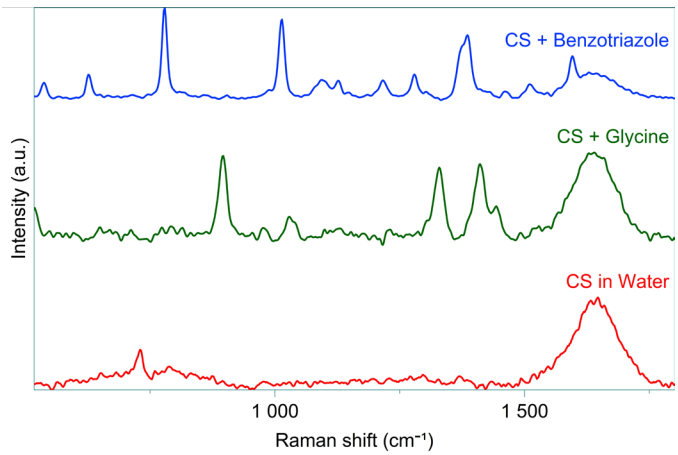

Figure 2: Raman spectra of colloidal silica plus benzotriazole, colloidal silica plus glycine, and colloidal silica in water. Colloidal silica is mostly featureless, but benzotriazole and glycine (the chemicals of interest) show distinct peaks to distinguish one from the other (e.g. ~780 cm^{-1} for benzotriazole and ~900 cm^{-1} for glycine); these peaks can be used for quantification of each material in the CMP slurry mixture.

The first method applied for quantification was a single peak calibration, where the peak intensities of the 780 cm^{-1} peak in benzotriazole and the 900 cm^{-1} peak in glycine were plotted as a function of known concentration. The corresponding calibration curves resulting from a single peak calibration are shown below in Figure 3(a) for benzotriazole and Figure 3(b) for glycine.

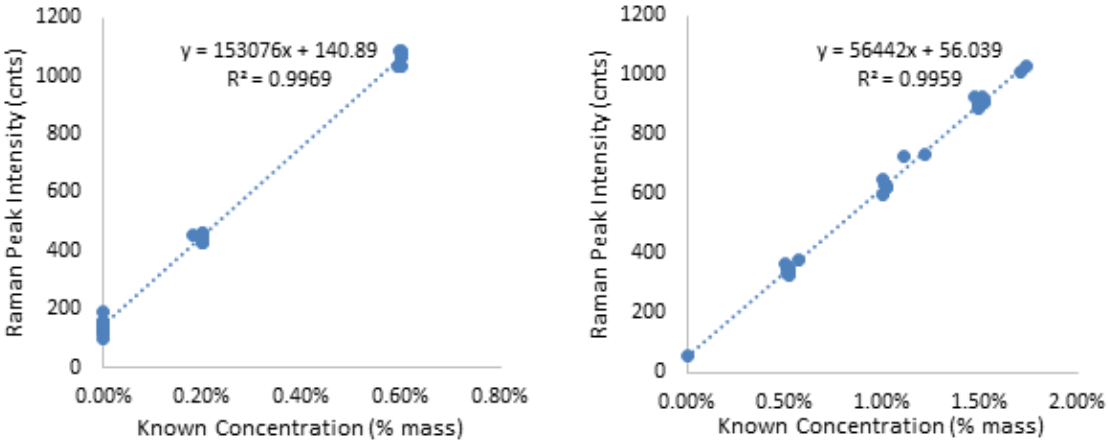

Figure 3: Single peak calibration curve for (a) benzotriazole and (b) glycine, resulting from determining the peak intensity of the Raman bands around 780 cm^{-1} and 900 cm^{-1}, respectively.

To assess the quality of this calibration model, one sample of known concentration was measured 30 times and the resulting concentration obtained from the calibration model for each run was plotted on the same graph as the known concentration for both benzotriazole and glycine, as shown in Figures 4(a) and 4(b) respectively. The single peak calibration model works well for glycine but gives less accurate results for benzotriazole.

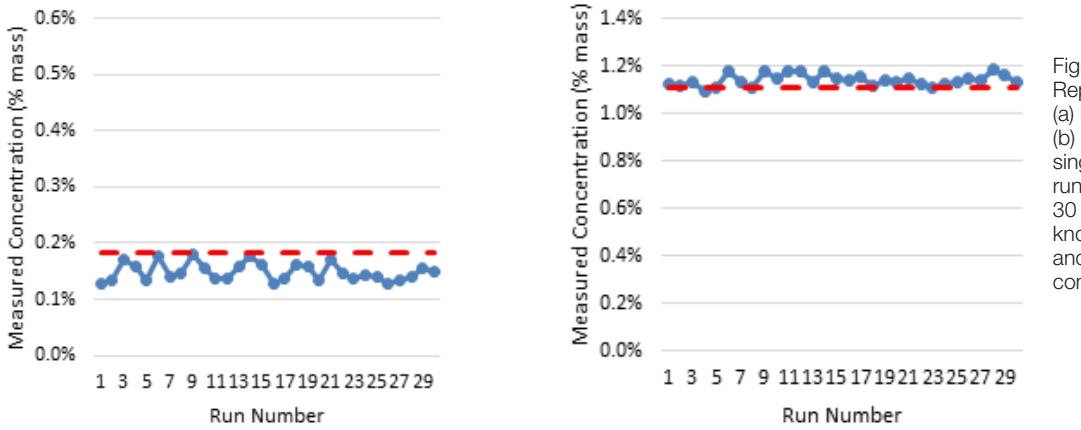

Figure 4: Repeatability results for (a) benzotriazole and (b) glycine obtained from a single peak calibration by running a known sample 30 times (red is the known concentration and blue is the measured concentration).

A more accurate method for quantification, partial least squares (PLS) analysis, was then implemented and evaluated. PLS analysis is a multivariate approach that uses the entire spectral range (instead of a single peak) to create calibration curves for each component in the slurry mixture. PLS analysis is integrated into the LabSpec 6 software, and the calibration curves are obtained by simply loading the Raman data for all samples, loading the known concentrations for all samples, creating a model, and validating the model. Once the model is created, it can be applied to determine the concentration of any component of any sample with the same matrix and concentration range as the original 28 samples measured. Shown below in Figures 5(a) and 5(b) are the resulting PLS calibration curves for both glycine and benzotriazole, respectively, using a 4-factor model and spectral range from 350-3500 cm^{-1}.

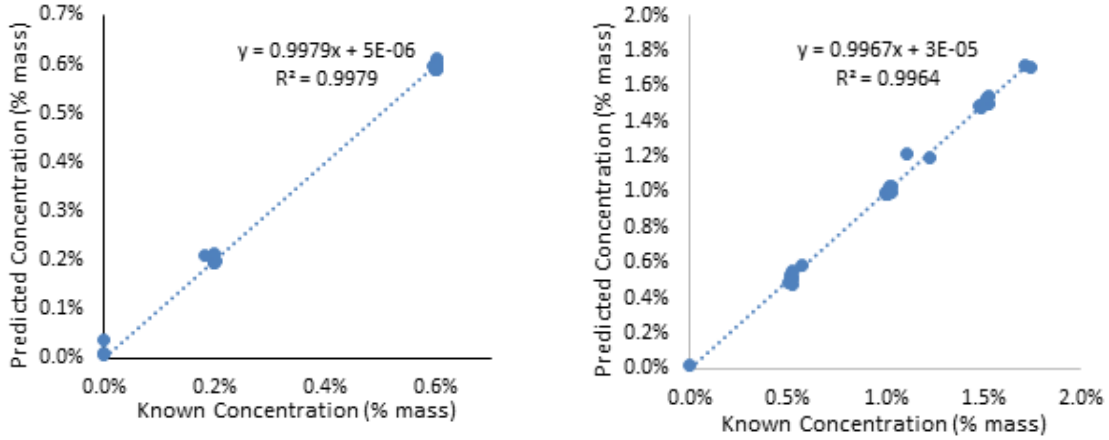

Figure 5: Calibration curves obtained from PLS for (a) benzotriazole and b) glycine, using a 4-factor model and the spectral range from 350-3500 cm^{-1}.

Once again, to check the quality of the model, one sample of known concentration was measured 30 times, and the resulting concentration given by the model was plotted on the same graph as the known concentration, as shown in Figures 6(a) and 6(b), respectively. The concentration values given by the PLS model agree well with the known concentration values for both glycine and benzotriazole.

Statistics for comparing the single peak calibration to the PLS calibration are shown below in Table 2.

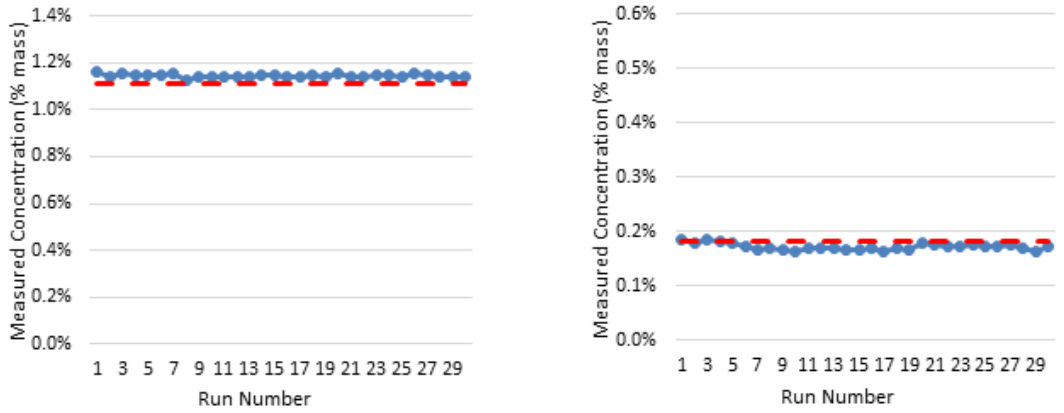

Figure 6: Repeatability results for both (a) benzotriazole and (b) glycine obtained from PLS by running a known sample 30 times (red is the known concentration and blue is the predicted concentration).

Finally, the limits of detection (LOD) and quantification (LOQ) for benzotriazole were estimated using the resulting concentrations from the single peak and PLS calibration curves for all samples which contained 0% benzotriazole. Shown below in Table 3 are the corresponding average concentration and standard deviation values obtained from the single peak and PLS calibration curves, and the estimated limits of detection and quantification obtained from each calibration method. For reference, the limit of detection is calculated as the mean value (of all 0% benzotriazole samples; "blank") obtained by the model plus three standard deviations, and the limit of quantification is calculated as the mean value (of all 0% benzotriazole samples; "blank") obtained by the model plus ten standard deviations. The use of the PLS model allows for a lower limit of detection and quantification, as highlighted in Table 3.

	MultiVariate Analysis		Single Peak	
	Benzotriazole	Glycine	Benzotriazole	Glycine
Target	0.18%	1.11%	0.18%	1.11%
Average	0.17%	1.14%	0.15%	1.14%
St. Dev.	0.006%	0.007%	0.016%	0.024%
6 * St. Dev.	0.036%	0.043%	0.096%	0.147%

Table 2: Statistics for benzotriazole and glycine comparing the MVA results (PLS) to the single peak calibration results for thirty repeat measurements of a known sample.

"Blank" = 0% Benzotriazole	MultiVariate Analysis	Single Peak
"Blank" Average	-0.005%	-0.005%
"Blank" St. Dev.	0.009%	0.013%
LOD ("Blank" mean + 3 St. Dev.)	0.022%	0.034%
LOQ ("Blank" mean + 10 St. Dev.)	0.087%	0.125%

Table 3: Estimated limits of detection (LOD) and quantification (LOQ) for benzotriazole from both MVA (PLS) and single peak calibrations.

Conclusion

Quantifying components in a CMP slurry is important to ensure the slurry will effectively polish the specific device layer without damaging the wafer. Current techniques used for analyzing CMP slurry mixtures, such as Ion Chromatography (IC) and High-Pressure Liquid Chromatography (HPLC) are sensitive to small concentrations but can be costly and require experienced users. Raman spectroscopy was explored as a fast, easy, and inexpensive alternative to these techniques to quantify components in a CMP slurry. Benzotriazole and glycine were successfully quantified with Raman spectroscopy using both a single peak calibration and a PLS calibration, and estimated limits of detection and quantification of benzotriazole were calculated. The estimated limit of detection of benzotriazole with the PLS calibration model was less than 0.025% (mass percent) and the estimated limit of quantification of benzotriazole was less than 0.10% (mass percent), showing that Raman spectroscopy can be an ideal alternative to the more costly and time-consuming methods described here.

References

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