In-Line Refractive Index In Assay Characterization Of Incoming Fresh And Effluent Spent CMP Slurry

Jason Kiernan, Leticia Vázquez Bengochea, Robert Johnston, Marcus Kavaljer
GLOBALFOUNDRIES Fab 8 facilities, Malta NY 12020, United States of America
University of Arizona, Tucson AZ 85721, United States of America
Yarbrough Solutions Worldwide, Austin TX 78758, United States of America
K-Patents Oy, 01510 Vantaa, Finland

E-mail: marcus.kavaljer@vaisala.com

In-line refractive index (RI) measurements are the technique of choice for qualifying the hydrogen peroxide content in CMP slurries. However, peroxide content is not the only slurry metric of interest. Typically, slurries are delivered from the manufacturer in concentrated form, then diluted with water and peroxide at the fab. Though slurry density is a critical parameter for CMP performance, incoming density can vary from batch to batch. Simply adding specified amounts of peroxide and water will give inconsistent results at the process tool. Provided the blender system can circulate incoming slurry through the refractive index unit, RI can be used to monitor the density of slurry in the blender tank, ensuring that the specified density is maintained regardless of fluctuations in the incoming material. We considered industrially-relevant slurries used for polishing copper, dielectrics, and tungsten, and found a strong correlation between density and refractive index in all three cases. Slurry density was characterized both offline and under high-volume manufacturing process conditions. The offline work showed that RI measurements reported smaller changes in water content as compared to the densitometer in all slurries tested indicating that it could provide a more precise data which would lead to a tighter control of the slurry composition. On the effluent side of the CMP tool, RI measurements were used to determine the ratio of polyurethane pad shavings to silica slurry particles after pad conditioning. Dynamic light scattering measurements were not able to report these values independently.

Keywords: *Monitoring incoming CMP slurries, inline refractive index measurements, CMP slurry density correlation*

1. Introduction

As the semiconductor industry moves toward sub-28nm process nodes, two key trends are combining to dramatically increase the number of CMP steps. First, the slow introduction of extreme ultraviolet lithography is forcing the industry to make increasing use of pitch doubling techniques. For example, self-aligned double-patterning (SADP) creates lines and spaces at half the nominal process pitch, and even more complex quadruple-patterning schemes are being investigated. These processes involve complex CMP steps that have continuously narrower error margins. A second major driver of increased use of CMP is the introduction of FinFET transistor architectures, in which the channel is composed of a series of vertical fins, connected by a metal gate. The gate is perpendicular to the long axis of the fins, and can be deposited by filling an appropriately sized oxide trench. Both the fin structure and the gate may require multiple patterning steps, depending on the specific process flows being used. CMP has been used in the interconnect stack since before the introduction of copper metallization. Still, the number of interconnect CMP steps continues to increase. Not only is the number of metal layers increasing, but the tighter metal pitch needed for connections to highly scaled transistors is driving the adoption of multi-patterning regimes for interconnects as well. As smaller feature sizes reduce the error margin available for CMP, slurries must meet stricter specifications and their components must be monitored tightly at the mixing tank and at the point of use.

2. Consistent results need consistent slurries

Consistent CMP results depend on both “chemical” and “mechanical” components of the slurry. Mechanically, the slurry should have a narrow, uniform particle size distribution and a uniform density of solids in a given volume. Density fluctuations indicate a non-uniform slurry and will change the polishing removal rate. Filters in the blender system can eliminate agglomerations and large particles, but density fluctuations are more insidious. The slurry particles may very well meet the specified size and size distribution requirements, and will pass through the process filters. Typically, slurry is shipped in concentrated form, then diluted with water or hydrogen peroxide at the fab. Inadequate mixing can allow the mixture to separate and stratify, and so the density at the bottom of a slurry tote or drum may be higher. Slurry manufacturers provide recommendations for onsite mixing and storage time, but the incoming material quality at the CMP tool ultimately depends on fab practices. Monitoring the density of slurry as it leaves the blending tank ensures that the correct blend is delivered to process tools. If the fab’s slurry inventory has aged due to over-stocking or a drop in usage, additional mechanical mixing may be needed to homogenize it prior to use. For example, W2000 slurry, commonly used for tungsten CMP, remains stable for 3-4 months. After that, stratification can create a difference in solids concentration from the bottom to the top of the container. Past 5 months, there can even be some loose agglomerate settling in some circumstances. Using stratified material gives a "sawtooth" pattern to mix batch solids and polishing rates (Fig. 1). Settled material tends to have low overall solids and polishing rates with a possible decrease in Loop and POU filter life due to broken up but not fully re-dispersed agglomerated abrasives [1].

3. Measuring slurry density

Many applications measure density with an oscillating U-tube. The volume of the tube is known, and the oscillation frequency varies with mass in a predictable manner. While this method is simple and accurate, systems currently on the market use tubes that allow wetting of metal parts by the fluid being monitored. Abrasive CMP slurries can potentially corrode the tube, contaminating the slurry with metallic impurities. While oscillating U-tubes can provide offline measurements their use for inline monitoring is problematic.

In situ refractive index measurements have become the industry standard for fast, accurate, inline slurry monitoring. In leading fabs, the incoming raw slurry must meet not only chemical composition and particle size specifications, but also an expected refractive index specification. Previous work has shown that refractive index is an accurate tool for monitoring slurry composition [2] and H_2O_2 concentration [3] This paper applies the same technique to density measurements.

In a reflective RI measurement, light from a single wavelength source reflects off the interface between the liquid being measured and an optical window. A CCD camera detector identifies the border between light activated and non-activated pixels on the detector at total reflection. This so-called “critical angle” measurement is independent of light intensity. The critical angle in turn yields the index of refraction of the fluid.

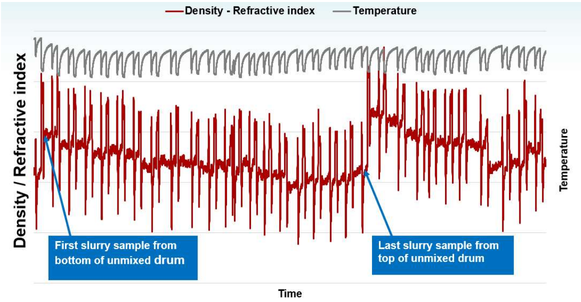

Figure 1. Sawtooth slurry density and polishing rate behavior with stratified slurry.

Because light does not need to pass through the fluid, this method can be used with opaque fluids and is not affected by bubbles and other flow irregularities. Overlapping RI values are rare, even for very similar mixtures, and its monitoring is continuous, collecting data whenever the light source is on. As such, it provides a more accurate picture of variations in slurry composition than any discrete sampling method can.

For this study, we characterized industrially-relevant CMP slurries via inline RI and offline densitometry measurements. All three slurries use colloidal silica abrasives and are optimized for copper, interlayer dielectric, and tungsten CMP (see Table 1). Both density and RI of fresh slurry varied linearly with the addition of ultra pure water to the slurry mix with or without H_2O_2 per the slurry manufacturers´ recommendations. Moreover, the two measurements were highly correlated, with R^2 values exceeding 0.95 (Fig. 2). The smallest detected change (i.e. the smallest quantity of ultra pure water leading to a measurable change) of refractometry was slightly better, depending on the initial slurry composition.

Sample	Volume Initial Solution (mL)	Added UPW (mL)	% Added UPW (v:v)
1	1200	0	**0.00**
2	1200	24	**1.96**
3	1200	48	**3.85**
4	1200	78	**5.66**
5	1200	96	**7.41**
6	1200	120	**9.09**

Table 1. Slurry solids and dilution ratios to the recommended target mix.

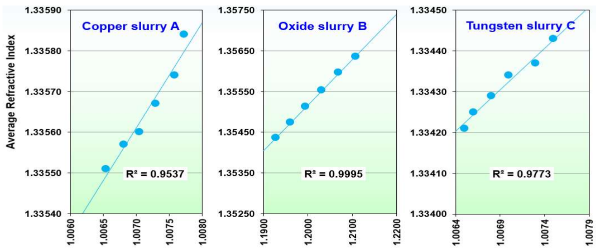

Figure 2. Correlating RI to density g/cm^3 in offline conditions.

RI monitors can be placed at multiple locations along the distribution chain. They are typically installed on the incoming hydrogen peroxide and raw slurry supply lines as well at the blend phase and on the process feed lines. The blend phase and process feed locations are especially relevant for monitoring not only H_2O_2 concentration, but also uniformity and density of the slurry. Variations in these parameters can serve as fault detectors for settling and stratification of the slurry particles. We compared results from in-line density monitors and inline refractive index measurements for 23 consecutive blender batches of copper slurry for a high volume process. Fig. 3 shows that the two measurements followed identical trends. Similar results were obtained when comparing density and refractive index measurements for tungsten slurry within the batch, also under high volume manufacturing conditions (Fig. 4).

4. Density monitoring in slurry reclamation

Density measurements are also useful at the effluent side of the CMP tool in slurry reclamation. Slurry is the main contributor to CMP COO, and spent slurry is a major component of the fab waste stream which is associated with substantial disposal costs and a significant environmental impact. As such, one would like to recover and reuse as much of this material as possible. This requires accurate characterization of the spent slurry composition. In addition to slurry particles of unknown size and distribution, reclaimed slurry can include residues of the material being polished as well as shavings from the polyurethane polishing pad or by-products. Offline, nonfactory related tests of spent copper slurry showed that both density, as measured by the densitometer Densito P30X, and K-Patents refractive index were lower than for fresh slurry. The specific gravity SG of polyurethane is approximately 0.805, while it is 1.00 and 1.08 for the fresh slurry. From density measurements, we estimated the amount of pad debris in spent slurry at 0.148 wt. per cent. RI measurements found a distinct difference between fresh and spent slurry. Thus, the density to RI correlation curves were different for the two materials (Fig. 5). The dynamic light scattering particle analyzer Zetasizer Nano ZS was not able to independently measure silica and PU particle sizes in the spent slurry because the RI values for PU and silica were very close to one another (i.e. 1.550 vs. 1.475). As a result, the measured particle size of spent slurry (99.6 nm) was between those of both silica and the pad shavings when they are measured separately.

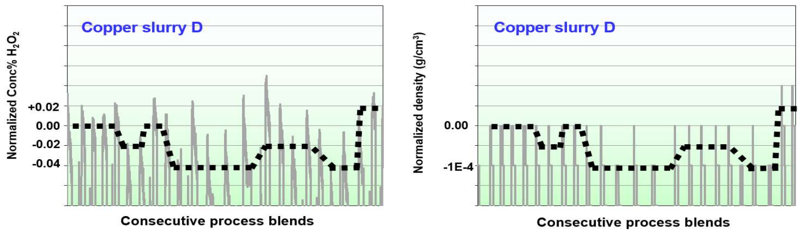

Figure 3. RI (left) and density (right) correlation in consecutive slurry blender batches for CMP tool delivery in high volume manufacturing process.

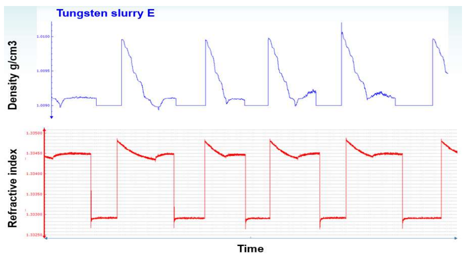

Figure 4. Inline density and inline RI in slurry within the high volume blender batch.

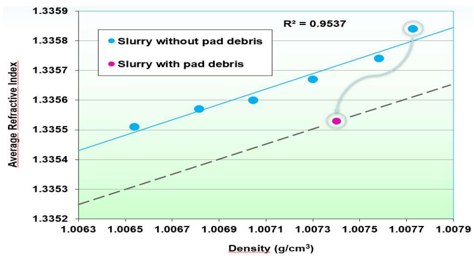

Figure 5. RI and density of spent copper slurry with pad debris.

5. Conclusions

Density is important throughout the slurry's lifecycle, from arrival at the fab in concentrated form through dilution with water or peroxide, and from delivery to the process tool to recovery from treated effluent. At the beginning of the process, accurate density control is necessary to maintain the specified polishing rate and uniformity. At the end, density measurements help the fab understand exactly what is in the material they seek to reclaim. Refractive index RI measurements can monitor slurry characteristics at every point on this journey, without the risk of contamination that conventional densitometers may bring.

6. References

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