Inline Refractive Index Replaces Auto-titration in Qualifying H_2O_2 Concentration in CMP of Tungsten

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Refractive index measurements have established themselves as the technique of choice for qualifying peroxide content in slurries for CMP of tungsten. Many emerging process flows use CMP as a critical tool for building circuit structures, dramatically increasing the number of CMP steps — and thus the number of opportunities for yield loss if slurry composition deviates from the specification. While auto-titration measurements can give extremely accurate results, they impose large capital equipment and ongoing maintenance costs and offer only discrete sampling at specified intervals. Refractive index, a continuous, non-slurry-consuming measurement, helps fabs identify slurry composition faults quickly, reducing the number of wafers at risk. Once calibrated to a specific slurry's temperature/refractive index characteristics, refractive index measurements can determine the concentration of hydrogen peroxide in tungsten slurry to within ±0.03% by weight. Moreover, unlike conductivity probe tests, refractive index measurements can monitor slurry density, an indicator of settling and degradation of the slurry over time. Therefore, refractive index is used to qualify not only the final product for supply, but also to monitor batch to batch variation of incoming raw slurry and validate the blend addition steps.

In long-term studies at a leading-edge analog device fab, refractive index measurements have replaced auto-titration in qualifying H_2O_2 concentration in slurry delivery systems. The measurements have remained stable for four years with no instrument maintenance beyond routine flushing of the slurry blender. An attractive feature in some slurry delivery systems has been the ability to use an automated chemical spiking function in the day tank.

Keywords: *Slurry delivery system with H2O2 spike function in day tank, inline refractive index concentration measurements, monitoring of incoming raw material*

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 lack of an alternative to 193-nm optical 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. The fab first creates an array of lines and spaces in a sacrificial layer (material A), then deposits a second layer of a spacer, material B. Etching removes material B from the horizontal surfaces, exposing material A and leaving material B on the trench sidewalls. Material B is then used as a hard mask for both removal of material A and pattern transfer to the underlying layer. Finally, the resulting trenches — spaced at half the nominal pitch — are filled with the desired material C, and excess is removed by CMP. Even more complex quadruple-patterning schemes use an additional pitch-doubling step to create lines and spaces at one-quarter the nominal pitch.

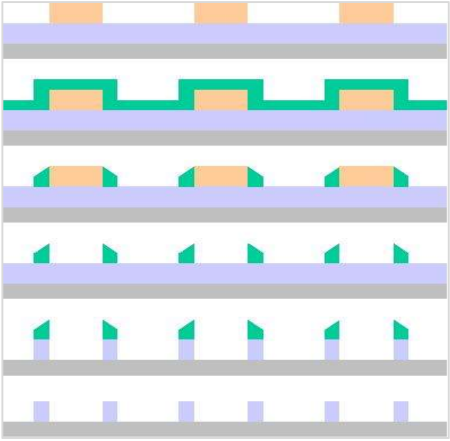

Fig. 1 SADP process flow

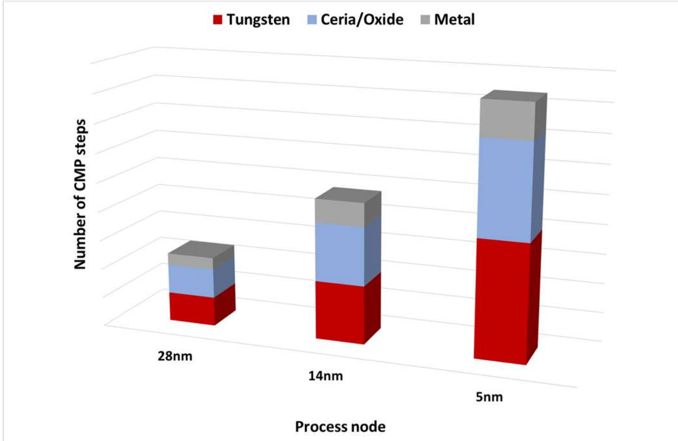

Fig. 2 Number of CMP steps increasing with shrinking process technology nodes

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 use of multi-patterning in more of those layers.

2. Consistent results need consistent slurries

To achieve consistent CMP results, manufacturers must carefully monitor both “chemical” and “mechanical” components of the slurry. Mechanically, the slurry should have a narrow, uniform distribution of particle sizes. Both agglomeration and settling can degrade the quality of slurry delivered to the wafer.

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. Settled material tends to have low overall solids and polishing rates with (perhaps) a decrease in Loop and POU filter life due to broken up but not fully re-dispersed agglomerated abrasive [1]. Where a fab has an aged slurry inventory due to over-stocking or a reduction in usage, mechanical mixing may be needed to make sure that the slurry is homogenized prior to use.

On the chemical side, the concentrations of water and solvents such as hydrogen peroxide must be maintained at a consistent value, even as larger and larger quantities of slurry are prepared and used. CMP slurries are typically delivered to the fab in concentrated form and diluted to the desired concentration with hydrogen peroxide and water immediately before use.

Since hydrogen peroxide typically degrades over time in tungsten slurries, this approach ensures that a “fresh” slurry at the desired concentration is always available for the process tool.

CMP was used for only a limited number of process steps, it was mixed in small batches near the point of use. Initial composition was monitored, but the batch was generally consumed before any significant degradation could occur. As the number of CMP steps increases, though, slurry distribution in the fab is beginning to resemble the distribution architecture used for other bulk chemistries, with a continuous flow from a central tank to multiple tools. It’s no longer enough to check the slurry composition once a day, once every few hours, or whenever a new batch is prepared. The fab needs to be able to detect and respond to deviations from the optimal composition as they occur.

For example, a fab’s slurry delivery system (SDS) might “spike” the day tank with hydrogen peroxide to maintain the desired concentration. In its simplest form, this approach uses a concentration set-point with monitoring of high and low values for a single chemical component within a slurry, creating a trigger on / off point. The chemical dispense valve opens and closes when below or above the established low point. This creates a pulsing injection cycle of H_2O_2 flow that decreases as the sensor sees the increase in H_2O_2 concentration over time, until the monitored value is above the low point. The concept is simple, but monitoring the chemical composition and particle distribution of a CMP slurry, in real time, is not a trivial task.

3. Monitoring balances cost, speed, accuracy

The ideal monitoring method would provide fast, accurate measurements, obtained without immersing probes into the chemical, made instantly available through the fab’s information network. Keeping the cost per measurement down — by minimizing consumables, chemical waste, and equipment costs — allows fabs to limit process risk by sampling frequently.

Since few technologies can meet all of these requirements, fabs must constantly balance cost, accuracy, and other factors. For example, titration — the gold standard for measurement accuracy — is slow and expensive. It requires consumable reagents, creates a new waste stream of sampled chemicals and their reaction products, and introduces possible contamination through the probe used to collect samples.

While auto-titration is used in some composition-monitoring applications, the three or four hours needed to process each sample is simply not fast enough to provide the real-time feedback required for peroxide spiking.

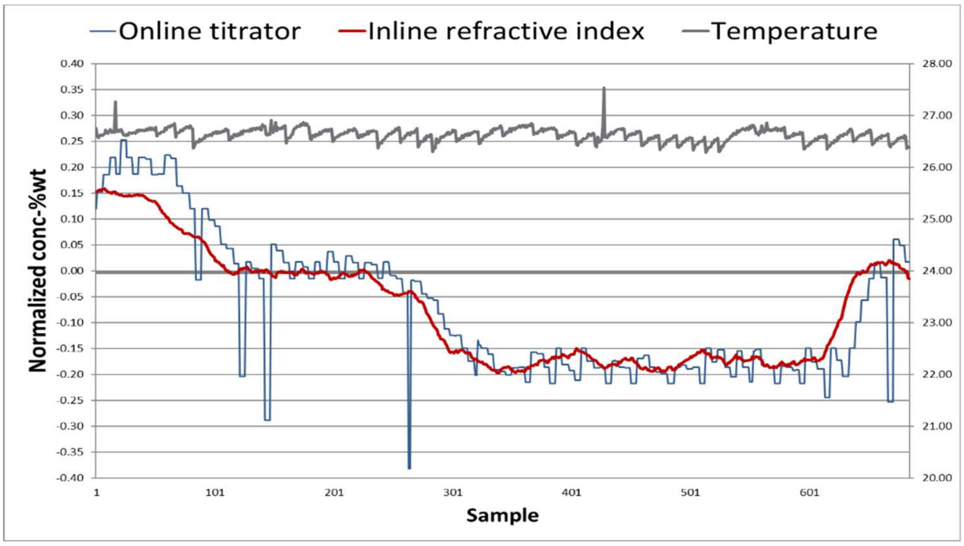

Fig. 3 Inline refractive index vs. online titration of H_2O_2 in slurry conc%

Conductivity, pH, and IR spectroscopy methods can be useful in some situations, but are not universally applicable across the many compositions encountered in a semiconductor fab. Conductivity measurements require ionic solutions. Neither conductivity nor pH is precise enough, as several different compositions might produce the same measured value. IR spectroscopy is an optical, non-contaminating method, and can identify individual components in a solution. It cannot easily determine their relative concentrations, though, and is difficult to calibrate.

4. Refractive index gives accurate, non-intrusive measurements

Instead, in situ refractive index measurements have become the industry standard for fast, accurate, inline slurry monitoring. At leading fabs, the incoming raw slurry must meet not only chemical composition and particle size specifications, but also an expected refractive index specification.

In a reflective index of refraction 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 borderline position at total reflection, which is the transition between light activated and non-activated pixels on the detector. This so-called "critical angle" measurement is independent of light intensity. The critical angle in turn yields the refractive index of the fluid [2]. Because the 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 refractive index values are rare: even very similar mixtures generally have unique indices.

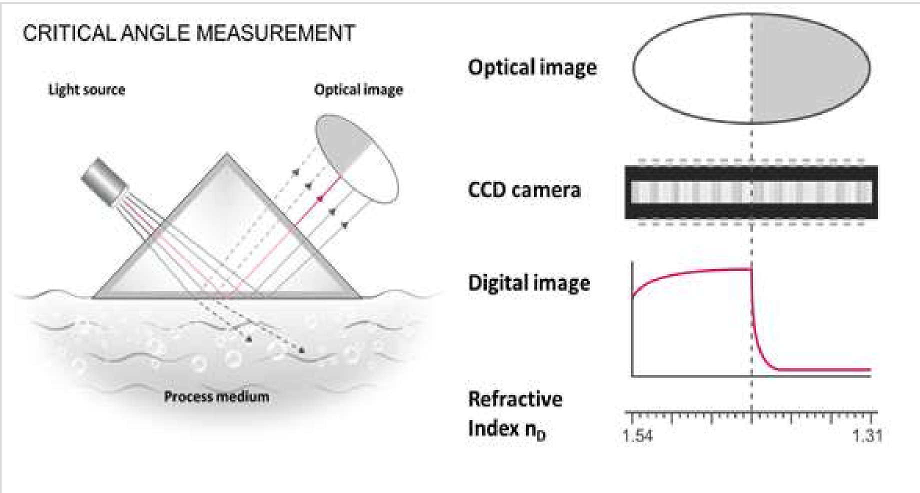

Fig. 4 The optical critical angle of total reflection yield refractive index

Refractive index 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. As Figure 5 shows, refractive index measurements can easily track the introduction and dispersion of a hydrogen peroxide spike. The SDS can determine whether the spike has had the desired effect in real time, avoiding both overshoot and undershoot and ensuring that the desired composition is delivered to the wafer.

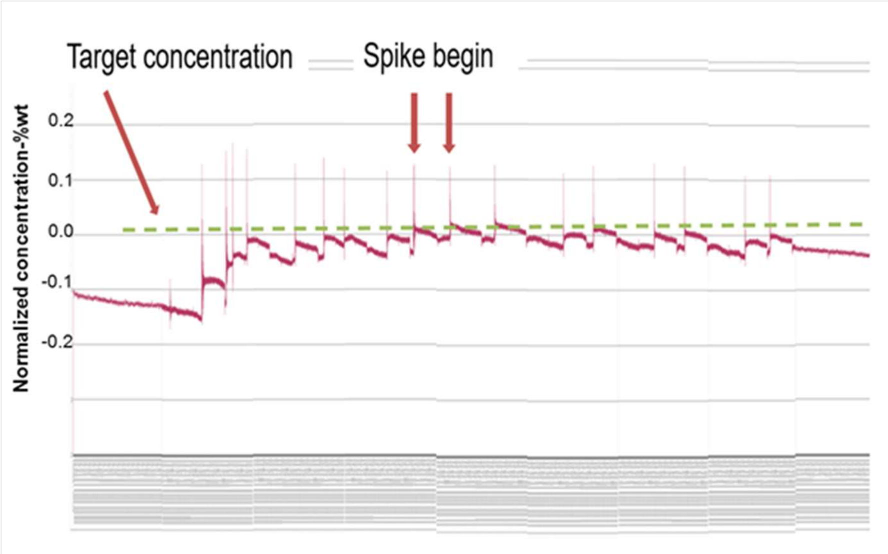

Fig. 5 Spike function designed in the slurry delivery system to maintain nominal H_2O_2 concentration in slurry

Refractive index monitors can be placed at multiple locations along the distribution chain, helping to find the point at which any failure occurred. They are typically installed on the incoming hydrogen peroxide and raw slurry supplies, at the blending tank, and on the process feed. Monitoring of the blending tank in particular can identify settling and stratification of the slurry particles as well as changes in chemical composition, Figure 6.

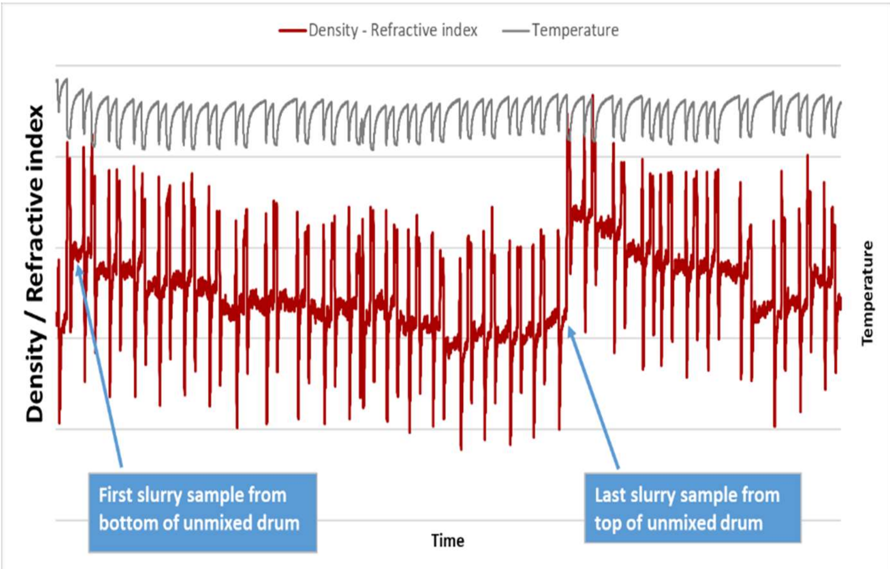

Fig.6 Refractive index of raw incoming slurry indicates density changes over time and sample

Two locations have had these instruments installed for almost four years, replacing the auto-titrator for qualification of the H_2O_2 in slurry concentration. One location learned that the instrument also reveals general process blender dynamics: The system is flushed with DIW after each batch. The instrument also goes through a quarterly mechanical prism clean.

When the instrument was isolated from the process for the mechanical clean, the next batch came in with a high concentration reading. The fab discovered that was the isolation valves had been left closed, so the next tank loading caused the pressure to increase in the tank. The increase in pressure caused the sensor to read high. On the other hand, during a lull in CMP production the slurry system was left idle. That change in flow caused the reading to drop by a statistically significant amount, even though not beyond the alarm limits.

5. Handling different slurry types and process conditions

Successfully implementing refractive index measurements in a fab setting requires attention to a number of subtle details. Among other requirements, the optical window must be able to tolerate the temperatures and chemical compositions of interest, and must itself have a compatible refractive index. For example, a sapphire prism allows measurements over a refractive index (n_D) range from 1.32 to 1.53, covering all concentrations of fab chemicals. While the sensor itself is not in contact with the fluid, only the sapphire prism, and can be isolated from pressure and temperature variations, temperature variations do affect the properties of the fluid being measured. Refractive index varies non-linearly with concentration and temperature. Published refractive index values are usually measured at 20°C [3], while actual in-fab chemical supply temperatures tend to vary seasonally. The sensor must measure and compensate for these temperature variations in order to accurately determine composition of a chemical.

Each slurry's refractive index will have a unique temperature dependence. Each blender tank will have unique hydraulic characteristics. While rough calibration data files are available for commonly used slurries, exact calibration is done in situ at the fab. A slurry of known composition is ramped through a variety of temperature changes and the refractive index measured. This data is then used to calibrate the refractive index for that slurry. Once the dependence of the slurry's refractive index on temperature is known, the instrument can correct for thermal fluctuations. In the event that a sensor needs to be replaced, calibration files from the existing sensor can be used to initialize the replacement.

Slurries for tungsten and copper removal will have different absolute refractive index values, but generally see similar trends as the water and peroxide concentrations change. Similarly, the density of raw slurry will affect its refractive index, but adding water and peroxide will change the value in the same way. In one example, Drum 1 of a slurry had a refractive index of 1.3350, while the refractive index of Drum 2 was 1.3352. In both cases, the target concentration of hydrogen peroxide in deionized water and slurry was 2.00%. And in both cases, the same change in refractive index was measured, even though the absolute refractive index values differed.

6. Conclusion

As advanced process nodes bring increasing numbers of CMP steps, fabs must ensure that the slurries delivered to their polishing tools maintain consistent chemical and mechanical characteristics. Inline refractive index monitoring can evaluate chemical composition of incoming material, qualify blend addition steps, and validate a uniform CMP slurry blend in a single real-time, non-slurry-consuming measurement.

7. References

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