

Inline Real-Time Monitoring of Hydrogen Peroxide Concentration in CMP Slurries Using Ultrasonic Technology for Advanced Process Control

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1. Introduction

Chemical Mechanical Planarization (CMP) is an essential process in semiconductor manufacturing, used to achieve highly planarized wafer surfaces. As semiconductor devices become smaller and more complex, increasingly stringent requirements are placed on process stability, throughput, and manufacturing yield. Accurate control of the chemical and physical properties of CMP slurries is therefore essential for maintaining consistent polishing performance. Hydrogen peroxide (H_2O_2) is commonly used as an oxidizing agent in CMP slurries, and variations in its concentration can significantly influence the polishing process. Changes in slurry composition may also affect physical properties. Monitoring both H_2O_2 concentration and changes in slurry composition can therefore provide important information about slurry condition and contribute to stable and reproducible process operation. H_2O_2 concentration is conventionally determined using offline methods such as titration. Although titration can provide accurate concentration measurements, it requires samples to be taken from the process and analyzed separately. Consequently, changes in slurry conditions are detected only after sampling and analysis have been completed. Furthermore, these measurements provide no continuous information about changes in slurry composition. Laboratory analyses are also generally performed under controlled conditions, while slurry temperature may vary during CMP operation and influence its measured physical properties. Inline measurement offers the possibility of continuously monitoring slurry properties and detecting process changes with minimal delay. However, reliable inline measurement requires the effects of concentration and temperature on the measured parameters to be understood and distinguished from each other. This study investigates the feasibility of using the Rhosonics Chemical Concentration Meter (CCM) for inline monitoring of H_2O_2 concentration and slurry composition under conditions relevant to CMP applications. The study focuses particularly on the influence of temperature and evaluates whether concentration-related changes can be distinguished from temperature-induced variations. The aim is to establish whether a calibrated inline measurement approach can provide reliable, continuous information on slurry conditions, thereby reducing dependence on offline analysis and supporting improved CMP process control and reproducibility.

2. Inline measurement

For continuous monitoring of CMP slurry, the Chemical Concentration Meter (CCM) is installed inline in the slurry circulation system. The instrument monitors the slurry in the mixing tank before distribution to the polishing equipment, allowing changes in composition to be detected before the slurry enters the polishing process. Titration samples were collected and used as reference measurements to validate the H_2O_2 concentrations measured by the CCM. As illustrated in **Figure 1**.

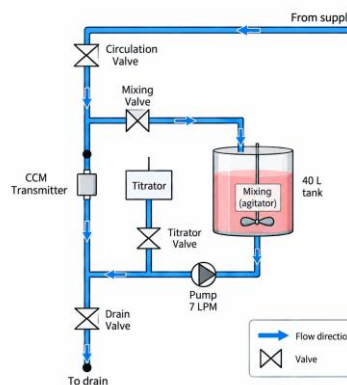


Figure 1. Process diagram

The CCM consists of an inline transmitter and a control unit with a 7-inch touchscreen. Measurement results are displayed on the HMI and can be transmitted to the plant control system through 4–20 mA outputs for integration into the process control strategy. As illustrated in **Figure 2**.

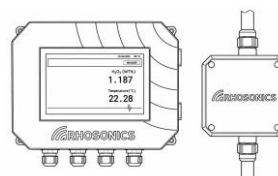


Figure 2. Drawing of the CCM, with the HMI on the left and the transmitter on the right.

The transmitter combines ultrasonic, conductivity, and temperature measurements. The ultrasonic system uses two opposing sensors containing 2 MHz piezoelectric elements. When an ultrasonic pulse reaches the sensor liquid interface, part of the acoustic energy is reflected [1], while the remainder is transmitted into the slurry. For normal incidence, the amplitude reflection coefficient is:

$$R = \left(\frac{Z_2 - Z_1}{Z_1 + Z_2} \right)^2 \quad (1)$$

where (r) is the reflection coefficient and (Z_1) and (Z_2) are the acoustic impedances of the two media. The reflected signal is quantified from the energy of the interface echo, referred to as the Power of the Interface Echo (PIE) [2]. Since the acoustic properties of the sensor material are known, this reflection can be used to determine the acoustic impedance of the slurry. Acoustic impedance is related to density and speed of sound by:

$$Z_l = \rho_l * c_l \quad (2)$$

where (Z) is acoustic impedance, (ρ_l) is density, and (c) is speed of sound. The speed of sound is independently determined from the ultrasonic time of flight between the two opposing sensors [3]. Combining acoustic impedance and speed of sound therefore enables calculation of the slurry density. **Figure 3** shows the schematic representation of the ultrasonic measurement.

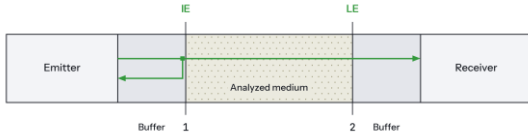


Figure 3. Schematic representation of the ultrasonic measurement

The CCM additionally measures electrical conductivity using an inductive conductivity principle. An alternating current applied to a drive coil generates a magnetic field, which induces an electrical current in the conductive slurry. This current produces a secondary magnetic field detected by a sense coil. The magnitude of the detected signal is related to the electrical conductivity of the slurry. As illustrated in **Figure 4**.

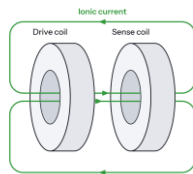


Figure 4. Drive and sense coil conductivity

Together, speed of sound, acoustic impedance, conductivity, density, and temperature provide complementary parameters that respond to changes in slurry composition. After calibration, these measurements can be used to continuously determine and monitor the H_2O_2 concentration and density of CMP slurry.

3. Calibration model

Previous studies have shown that the speed of sound in CMP slurry changes with H_2O_2 concentration, while conductivity can be used as an

indicator of slurry concentration and density [4]. Based on these relationships, a multivariable polynomial calibration model was developed to determine H_2O_2 concentration and slurry density from the CCM measurements. The addition of H_2O_2 produces a measurable change in speed of sound. However, speed of sound is also strongly temperature dependent. The measured speed of sound and temperature are therefore correlated with the known H_2O_2 concentrations to establish the calibration model. A similar procedure is applied to measure the change in the slurry composition. The original CMP slurry is diluted to obtain samples with different slurry concentrations and corresponding densities. Conductivity and density are measured for each sample over a range of temperatures. These data are used to establish the relationship between conductivity, temperature, and slurry density. An important consideration is that the temperature dependence of speed of sound is not identical at all H_2O_2 concentrations. Therefore, applying a single temperature compensation factor over the complete concentration range would introduce measurement errors. **Figure 5** illustrates the different slopes for the temperature compensation.

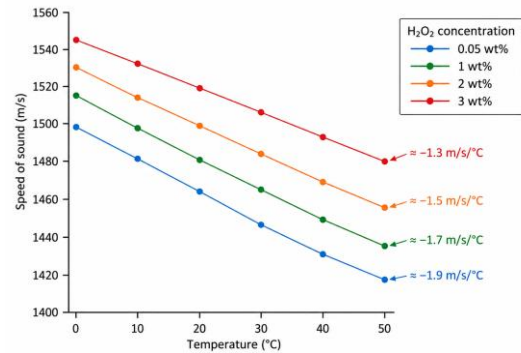


Figure 5. Different slopes for the temperature compensation

Instead, the interaction between speed of sound, H_2O_2 concentration, and temperature is incorporated directly into the multivariable polynomial model. This allows the temperature compensation to vary with H_2O_2 concentration. By combining the relationships between speed of sound, conductivity, temperature, H_2O_2 concentration, and density, the calibration model converts the continuously measured CCM parameters into H_2O_2 concentration.

4. Measurements

Copper CMP slurry samples with different H_2O_2 concentrations were measured between 20 and 28 °C to obtain data for development and evaluation of the calibration model. In addition, the influence of changes in the base slurry composition was investigated. A copper CMP slurry containing approximately 1 wt% H_2O_2 was continuously circulated for more than two months to induce and observe gradual changes in slurry properties. This

extended circulation does not represent normal CMP operating conditions but was used as an accelerated test. During circulation, gradual changes in conductivity and speed of sound were observed. Possible causes include water loss through evaporation, H_2O_2 decomposition, and changes in slurry stability. Since speed of sound is used to determine H_2O_2 concentration, changes in the base slurry can introduce deviations in the calculated concentration. Without compensation for changes in slurry composition, the H_2O_2 concentration calculated by the CCM deviated from the reference titration values. After incorporating conductivity-based slurry compensation into the calibration model, improved agreement with titration was observed. As illustrated in **figure 6**.

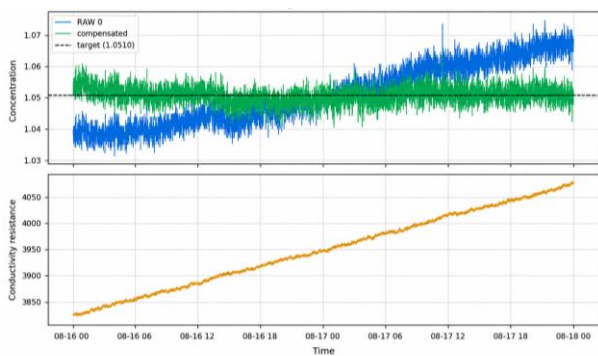


Figure 6. Influence of long-term slurry circulation on conductivity, speed of sound, and calculated H_2O_2 concentration. Target is the titration value

Following implementation of the slurry compensation, measurements were performed at both low and high H_2O_2 concentrations. At low concentrations, samples containing 0.040 and 0.070 wt% H_2O_2 showed distinguishable differences in speed of sound. Using speed of sound together with the compensation parameters, the calibration model inside the CCM calculated the corresponding H_2O_2 concentrations (**Figures: 7 & 8**). The values are compared with the target concentration measured by titration.

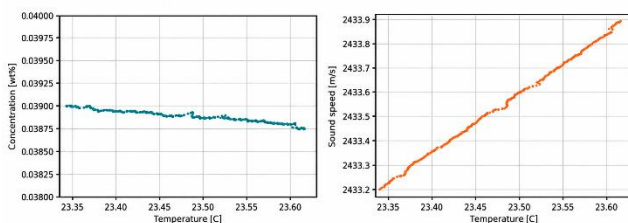


Figure 7. The target concentration determined by titration was 0.03895 wt% H_2O_2 . The left plot shows the concentration calculated by the CCM, while the right plot shows the measured sound speed as a function of temperature

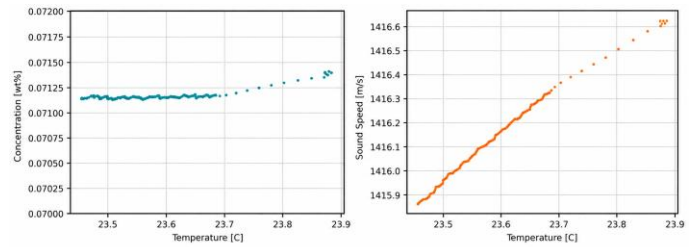


Figure 8. The target concentration determined by titration was 0.07112 wt% H_2O_2 . The left plot shows the concentration calculated by the CCM, while the right plot shows the measured sound speed as a function of temperature

At higher concentrations, measurements were performed between 1 and 3 wt% H_2O_2 . Different speed-of-sound levels were observed for the investigated concentrations and were converted by the calibration model into calculated H_2O_2 concentrations (**Figures: 9,10,11 & 12**).

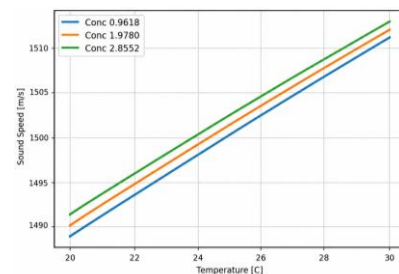


Figure 9. Sound speed of the measured concentration at different temperatures

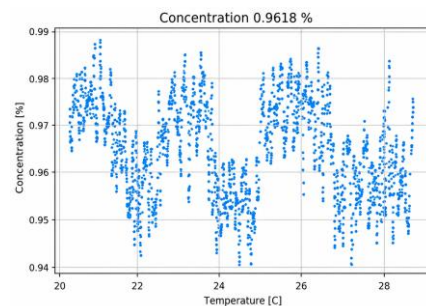


Figure 10. Measured concentration as a function of temperature. Titration value 0.9618 wt% H_2O_2

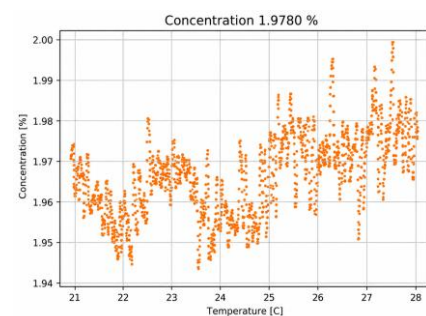


Figure 11. Measured concentration as a function of temperature. Titration value 1.9780 wt% H_2O_2

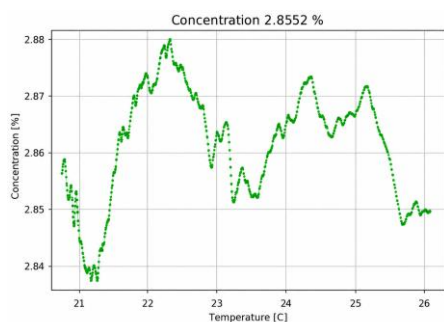


Figure 12. Measured concentration as a function of temperature. Titration value 2.8552 wt% H_2O_2

To evaluate the maximum achievable measurement accuracy under controlled conditions, the slurry temperature was maintained constant within $\pm 0.5^\circ\text{C}$. This minimizes the contribution of temperature variation to the speed-of-sound measurement, allowing the remaining variation in calculated H_2O_2 concentration to be evaluated. The results are presented in **Figure 13**.

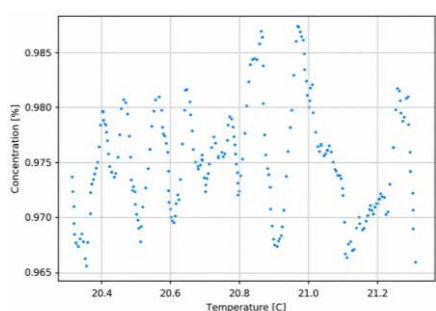


Figure 13. Measured concentration as a function of temperature.

5. Discussion

This study investigated the feasibility of combining ultrasonic and conductivity measurements for inline monitoring of H_2O_2 concentration and slurry properties in CMP processes. The results indicate that changes in H_2O_2 concentration can be detected through changes in acoustic properties, while conductivity provides additional information for compensating for changes in the base slurry composition. CMP slurry formulations differ in additives, abrasive materials, oxidizer concentrations, and physical properties. These differences affect speed of sound, conductivity, density, and their temperature dependencies. Therefore, a single universal calibration is not suitable for all CMP slurries. To address this, a modular calibration model was developed in which the coefficients can be adapted to individual slurry formulations using reference measurements at different concentrations and temperatures. Titration remains important for establishing and validating

the H_2O_2 calibration but provides only a measurement at the sampling moment. In contrast, the CCM continuously measures multiple slurry properties, allowing changes in the base slurry to be identified and compensated for. After slurry-specific calibration, the CCM can perform up to 10 measurements per second, providing substantially higher temporal resolution than periodic sampling.

6. Conclusion

This study demonstrates the feasibility of using combined ultrasonic, conductivity, and temperature measurements for continuous inline determination of H_2O_2 concentration in CMP slurry. The results show that changes in H_2O_2 concentration produce measurable changes in speed of sound and that these changes can be converted into concentration using a slurry-specific multivariable calibration model. Conductivity provides an additional parameter for identifying and compensating for changes in the base slurry composition, which is important for maintaining measurement accuracy over time. Under controlled conditions with a stable slurry temperature, a measurement accuracy of approximately 0.015 wt% H_2O_2 was achieved, demonstrating the high intrinsic measurement resolution of the ultrasonic method. When measurements were evaluated over the complete investigated temperature range, an accuracy of approximately 0.03 wt% H_2O_2 was achieved. The developed calibration approach can be adapted to different CMP slurry formulations by determining slurry-specific calibration coefficients. The CCM provides a practical foundation for real-time monitoring and enhanced process control in CMP applications

7 Literature

- [1] Bamberger J. and Greenwood S. (2004), Measuring fluid and slurry density and solids concentration non-invasively, *Ultrasonics*, Vol. 42, 563-567.
- [2] Higuti, R. T., & Adamowski, J. C. (2002). Ultrasonic densitometer using a multiple reflection technique. *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*, 49(9), 1260–1268.
- [3] Adamowski, Julio & Buiocchi, Flávio & Simon, Claudio & Silva, Emilio & Sigelmann, Rubens. (1995). Ultrasonic measurement of density of liquids. *Acoustical Society of America Journal*. 97. 354-361.
- [4] R. Maas, "Inline Real-Time Process Monitoring of CMP Slurries with Ultrasonic and Conductivity Measurements " in *Proceedings of the ICPT 2024 Conference*, Germany, 2024