

Jetalon CS-928

A Compact, Real-time, Point-of-Use Metal Ion Concentration Sensor for Liquids

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Abstract

In this paper, CS-928, a compact, real-time and in-line optical sensor for the detection of metal ions in liquids is presented. Test results show that CS-928 can measure Cu^{2+} for concentrations over the range of 50 ppb to greater than 10 ppm with a less than 10 second response time. Results are presented that show the effectiveness of the sensor for measuring Cu^{2+} concentrations in the presence of typical waste streams constituents found in semiconductor applications.

The results show that the sensor has applications as a process monitor, endpoint detector, breakthrough sensor and environmental compliance sensor for CMP and plating processes and for waste water treatment systems.

The ion selective coating can be engineered to measure nearly any metal ion including Cu, Co, Ni, Pb, Hg, etc.

Figures and analysis:

Figure 1: Sensitivity and accuracy: Cu^{2+} sensor response as a function of Cu^{2+} concentrations in DIW.

Figure 2: Repeatability: Sensor responses are plotted as a function of time for cycling between 5 ppm Cu^{2+} solution and DIW.

Figure 3: pH Response: Sensor responses to 5 ppm Cu^{2+} are plotted for pH values between 3.5 and 10.2

Figure 4: CMP Waste Stream Simulation: Cu sensor responses in the presence of dilute slurry mixture of SS11.

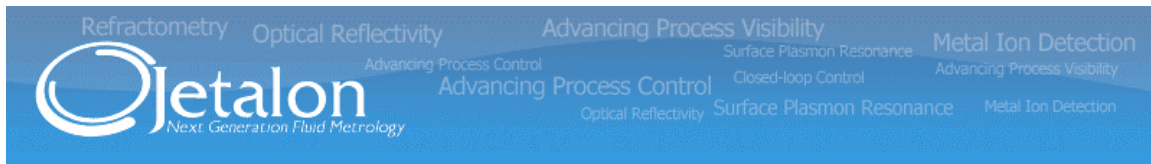


Figure 5: Waste Stream Simulation: Cu sensor responses to Cu^{2+} solution of 50 ppb in DIW (right axis scale) and 10 ppm in DIW(left axis scale).

Introduction

The increased use of metals in semiconductor manufacturing has resulted in a need to monitor and control metal ion concentrations. Specific applications in semiconductor manufacturing include:

- Process monitor for metal ion concentrations in plating liquid chemical deposition operations
- Monitoring metal ion concentrations in waste streams for environmental compliance
- Water quality monitor
- Process end-point detection
- Monitor and control for waste water treatment systems
- Metal ion breakthrough monitor for waste water treatment systems

The metal ion concentration analysis system presented here, CS-928, is designed to meet the requirements of semiconductor manufacturing. These requirements include compact size for in-line and point-of-use applications; process transparency so as not to impact process performance and wafer processing; and real-time response of ≤ 10 seconds per concentration measurement. In addition, sensor systems often require high reliability, accuracy, and precision, and the appropriate dynamic range for specific manufacturing applications.

Results are presented for the measurement of Cu^{2+} concentrations in water and Cu-CMP waste water streams. Sensor resolution and accuracy and data analysis are shown. The effect of typical waste stream constituents, pH and Cu^{2+} concentration changes on sensor performance are presented.

Methods and Apparatus

Cu^{2+} measurements are determined using a compact, optically-based concentration analysis system, Jetalon CS-928. The concentration analysis system consists of an optical-fluidic manifold (OFM), miniaturized optical subsystem, and DSP electronics circuit. The electronics circuit can simultaneously operate up to four sensor heads, has an LCD display that outputs concentration readings and is designed for stand-alone operation. Graphical user interface software (GUI) enables field calibrations, data logging, graphing and analysis, inputs for set points and interface to fab data management systems.

The OFM measures approximately 2"x2"x6" and could hold up to four optical sensor heads. The materials of construction include ultrahigh purity Teflon compatible with all semiconductor liquid chemicals. In all measurements presented here, the OFM had 1/4" Flaretek™ connections and was used in either a recirculation loop or in a flow-through geometry.

In the typical mode of operation, two optical sensor heads are used. The primary sensor used for measuring Cu^{2+} concentration is based on a combination of surface plasmon resonance (SPR) and ion selective chemistry. The active window of the SPR sensor is coated with a Cu^{2+} selective coating and placed in contact with the liquid under analysis. Cu^{2+} from the liquid adsorbs onto the ion selective coating and changes the SPR signal in a known way. The SPR signal increases with increasing Cu^{2+} concentration in the liquid. In this way, the concentration of Cu^{2+} in the liquid is determined.

The second sensor head is Jetalon's CR-288™ liquid chemical concentration sensor, which has been described elsewhere [1]. The CR-288™ is used to measure the background concentration of constituents other than Cu^{2+} . Depending on background to signal ratio, the background signal is subtracted from the Cu^{2+} concentration signal.

Cu^{2+} detection measurements were done using DIW and slurries and are reported as a function of pH and Cu^{2+} concentrations ranging from 50 ppb to 20 ppm. Cu^{2+} concentration were independently determined to ± 0.1 ppm using a Hatch Colorimeter.

Cu^{2+} solution was prepared using CuCl_2 (99.999%).

Data were recorded from two independent sensors in three consecutive runs. After confirming the sensors' baseline readings in DIW, sensors were exposed for 5 minutes to Cu^{2+} solution of a known concentration and sensor response was recorded.

Results and Discussion

Figure 1 shows the sensor response plotted as a function of Cu^{2+} concentrations of 10, 5, 1, 0.5 and 0.1 ppm in DIW. The solid line drawn through the data is a logarithmic trend line. The sensors' characteristic behavior include an initial rapid increase in its response (as a function of Cu^{2+} concentrations from 0-1 ppm), followed by an asymptotic behavior of the sensor response. This behavior suggests that the highest sensor resolution is achieved within the concentration range 0-5 ppm Cu^{2+} . Higher Cu^{2+} concentrations can also be detected but with lower accuracy.

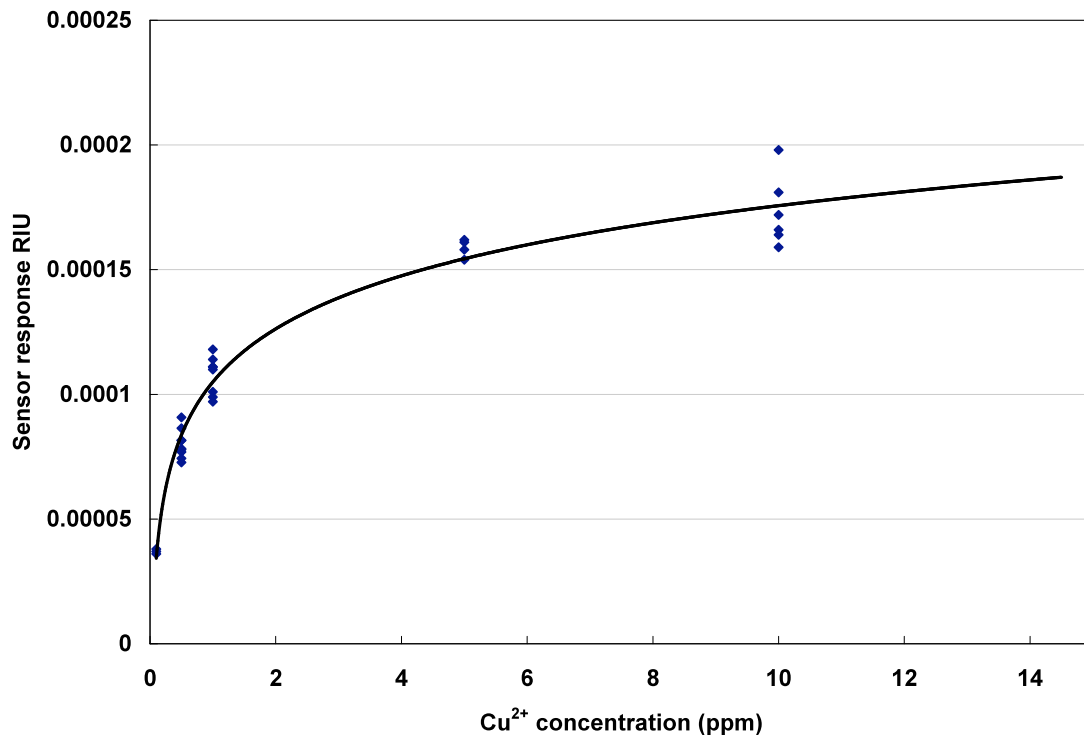


Figure 1. Cu^{2+} sensor response as a function of Cu^{2+} concentrations in DIW.

Figure 2 shows sensor response plotted as a function of time for alternating solutions of 5 ppm Cu^{2+} and DIW (pH = 5.6). These measurements were carried out to determine the sensor surface lifetime; specifically the potential to regenerate the sensor active surface in DIW.

Extended measurements infer that regeneration cycling of this kind could be done for greater than 20 cycles.

Figure 2 shows four consecutive cycles with characteristic sensor behavior. During exposure to the 5 ppm Cu^{2+} solution, the sensor response time is approximately 1 second. Upon subsequent exposure to DIW, the sensor reading is brought back to the baseline level suggesting full sensor regeneration. The same behavior can be observed for solutions at pH values other than DIW (pH=5.6). However the pH of the solution influences Cu^{2+} adsorption/desorption kinetics and as the pH increases, the sensor response time is longer and it takes longer for the sensor to fully regenerate.

The CR-288™ signal is also shown and measures the background refractive index signal for the solutions.

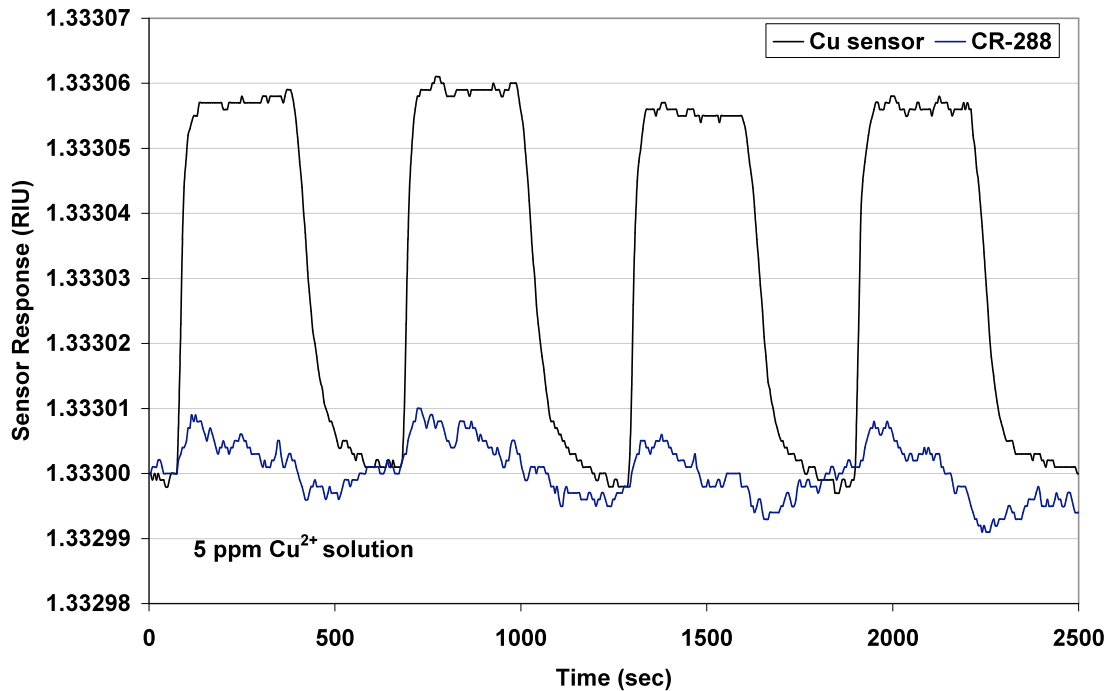


Figure 2. Sensor responses are plotted as a function of time for cycling between 5 ppm Cu^{2+} solution and DIW.

Figure 3 shows the sensor's response to 5ppm Cu^{2+} for pH values between 3.5 and 10.2. The data shows that the sensor response is pH dependent. DIW was adjusted with either concentrated H_2SO_4 or NaOH to obtain the desired pH value. The sensor response (absolute change in RI) was recorded after 5 minutes of sensor exposure to Cu^{2+} solution. As apparent from the graph, sensor response is the highest within pH range 7-8 reaching a value of about $9\text{e-}4$ RIU. Below and beyond this pH range, sensor response sharply decreases in a Lorentzian-like fashion. Below pH 3.5 and above 10.5, Cu^{2+} adsorption was no longer detected by the sensor.

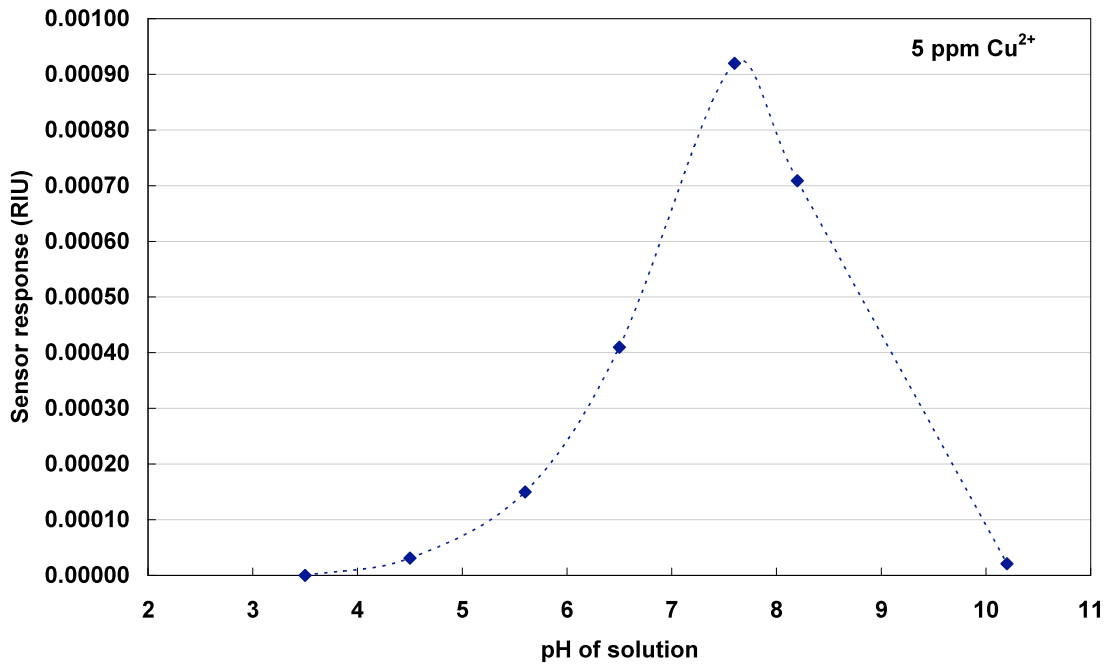


Figure 3 Sensor responses to 5 ppm Cu²⁺ are plotted for pH values between 3.5 and 10.2

Figure 4 shows Cu sensor and CR-288™ responses plotted as a function of time for 5 ppm Cu²⁺ in the presence of diluted SS11 slurry. These measurements were done to simulate CMP waste stream conditions.

The SS11 slurry was diluted 1:100 with DIW. The pH of the resulting mixture was 10.1. For comparison, CR-288™ response is included on the graph showing the bulk RI of the solutions.

Initial response of both sensors to the slurry mixture is similar. When Cu^{2+} ions are introduced, CR-288™ shows no change in response (RI of the mixture does not change). The Cu sensor shows considerable increase in response upon the addition of Cu^{2+} .

Due to the pH value of 10.1 of the mixture, the Cu^{2+} adsorption kinetics are slower than in DIW resulting in a longer, continuous uptake at the sensor active surface and therefore in the Cu sensor reading.

Exposing the sensor to the Cu^{2+} free slurry mixture the uptake ceases and the Cu sensor reading is constant. Cu sensor regeneration is quite slow in the presence of the slurry mixture, again due to $\text{pH} = 10.1$. Upon the reintroduction of Cu^{2+} , the active sensor surface uptake continues and the continuous increase in Cu sensor reading also continues. Upon subsequent exposure to DIW ($\text{pH}=5.6$) the Cu sensor active surface quickly regenerates.

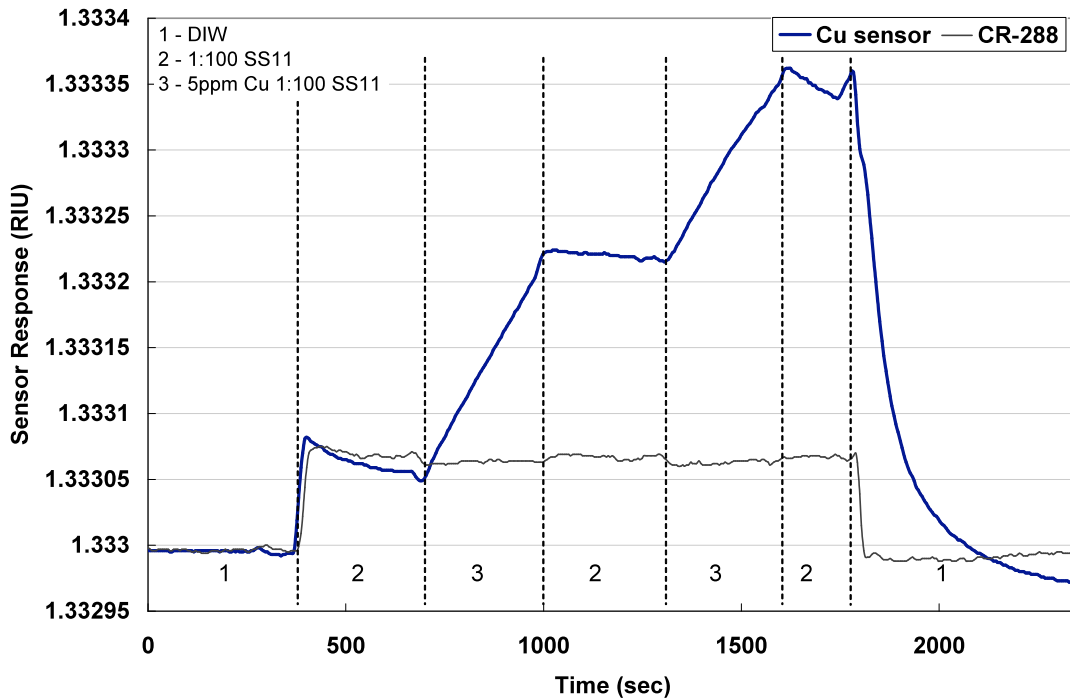


Figure 4 Cu sensor responses in the presence of dilute slurry mixture of SS11.

Figure 5 shows the Cu sensor signal plotted as a function of time for Cu^{2+} concentrations of 50 ppb and 10 ppm.

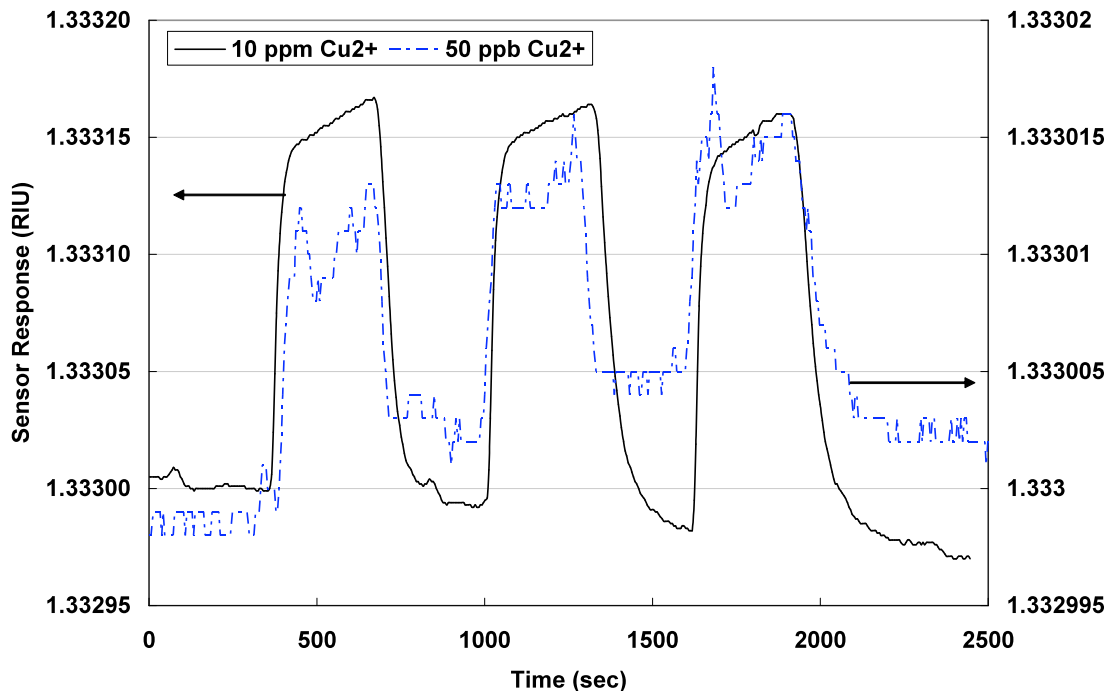


Figure 5. Cu sensor responses to Cu^{2+} solution of 50 ppb in DIW (right axis scale) and 10 ppm in DIW(left axis scale).

Conclusion

In conclusion, results for the Jetalon CS-928, a compact (2"x2"x3"), real-time (< 10 second response time) point-of-use metal ion concentration analysis system for liquids were presented. The CS-928 system combines surface plasmon resonance with ion selective surface chemistry for high sensitivity and selectivity. The ion selective coating can be engineered to measure nearly any metal ion including Cu, Co, Ni, Pb, Hg, etc. As currently configured, the sensor has a measurement range of 50 ppb to greater than 10 ppm for Cu^{2+} . The results presented here show that the sensor has applications as a process monitor, endpoint detector, breakthrough sensor and environmental compliance sensor for CMP and plating processes and for waste water treatment systems.

References

1. Ron Chiarello, C. Eric Boyd, C. Wacinski, Tom Kiez, J. Elkind, B. Presley, R. McDermott, and G. Harakas, "Using a real time point of use sensor to control liquid chemical concentration." Micro Magazine, May, 2005.