In-Process Treatment of Copper-CMP Wastewater Using Electrical Mediation

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The semiconductor industry has made tremendous advances in submicron plating. With copper being the material of choice, large amounts of copper-laden wastewater are being generated. An electrically mediated waste treatment system can be used to electrochemically remove Cu^{+2} from the waste stream, eliminating the problems associated with hazardous waste storage and treatment. This system joins ion-exchange with electrowinning to provide a powerful tool for the removal of cations. After treatment through the cell, ionic contaminants and TDS are reduced to discharge levels and the pH is neutralized. In addition the ion-exchange resin may be generated *in-situ* simply by reversing the polarity.

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Introduction

The semiconductor industry has maintained an average annual growth of 15% over the past 15 years, and has become the largest industry in the world after agriculture.¹ This industry revolves around the ability of semiconductor manufacturers to produce increasingly faster circuits. The speed of the signal through sub-micron integrated circuits is often limited by the interconnect delay associated with conventional scaling. Aluminum was the material of choice for many years due to its relatively low electrical resistance and ease of deposition and etching onto circuits. However, as the interconnections shrink in size, the ability of aluminum to reliably carry a current diminishes. This has led semiconductor manufacturers to investigate other metals for this application. Copper was found to be a good substitute since it has a lower resistivity than aluminum; copper has approximately 40% lower resistivity than aluminum alloys.² This allows copper to carry a greater amount of current in a smaller area, enabling faster, more compact electrical devices.

The performance of an interconnect within a circuit can be further enhanced by multilevel metallization. However, in order to achieve multilevel metallization, the surface of the wafer in which the copper is plated must be planar, varying less than 150 nm across the entire surface. This can be achieved by a process known as chemical mechanical planarization. Chemical mechanical planarization (CMP) is a surface finishing process that is achieved by both chemical and mechanical forces. Conceptually, this process involves mechanically moving a sample across a polishing pad while allowing a constant flow of chemical slurry between the two surfaces. The surface of the sample is effectively planarized and the slurry is present to dissolve any abraded material and prevent the damage incurred by mechanical grinding alone. The chemistry of the slurry is vital, and selected so that the metal dislodged from the surface has high solubility and a high dissolution rate into the slurry. This is often maximized by the addition of oxidizing and complexing agents. CMP can be used for a variety of applications, some of which include optically flat and mirror surfaces, damage-free glass, interlayer dielectrics, and semiconductor surfaces. The use of CMP for interlayer dielectrics and semiconductor surfaces is important, since they are at the heart of the electronics industry.

The composition of copper CMP slurry will vary with manufacturer, however, representative wastewater samples have been analyzed. These findings indicate that CMP wastewater is usually composed of the following components: solids from the abrasive and polishing pad, inorganic material such as complexed copper, copper oxides, copper hydroxides, and iron (Fe^{+2}, Fe^{+3}) , oxidizing agents, acids or bases, corrosion inhibitors, complexing agents and surfactants. The oxidizing agents are added to increase the efficiency of the CMP process by oxidizing the abraded material, in this case copper metal, in order to dissolve the material, eliminating the tendency of undissolved metal to scratch and damage the wafer surface. Any acid or base added is to adjust and control the pH of the mixture. Corrosion inhibitors have an obvious function, and work effectively by forming a surface film in recessed areas to ensure these areas are not further dissolved by the oxidizing conditions of the slurry/wastewater. Complexing agents also aid in dissolution of abraded material; surfactants are added to increase the wetting of the hydrophobic surface of the wafer.

The implementation of copper CMP into industry is rapidly emerging, thus increasing the amount of chemical slurry being consumed and even larger amounts of generated wastewater. The CMP process generates between 30 and 50 liters of waste slurry per 8-inch wafer processed. In addition, the use of slurries is expected to increase by 21% per year up through the year 2010, to an estimated \$1.2 billion dollar industry by the year 2010.³ It is estimated that for each liter of slurry used in the CMP processes, 6-30 gallons of water is expended.³ Large volumes of water are consumed in both the planarization steps as well as the post-CMP clean-up step. The wastewater generated from this process is expected to increase from 328 million gallons in 1997 to an astounding 1.6 billion gallons in 2010.³ This illustrates the need of

treatment technology for the CMP wastewater, which decontaminates the wastewater through removal of dissolved copper.

Copper Toxicity

Any dissolved copper that gets into groundwater can have adverse environmental effects. Copper is an essential metal in trace amounts for normal physiological processes, in both plants and animals, but in excess copper can be quite toxic. In humans, absorption of copper occurs through the lungs, gastrointestinal tract, and skin.⁴ The degree of copper absorption is heavily reliant upon its oxidation state, Cu⁺² is the most bioavailable form of copper and therefore it is commonly the most toxic. Once absorbed by the body, copper targets the liver, kidneys, spleen, heart, lungs, stomach, intestines, nails and hair.⁴ Symptoms of acute copper toxicity include abdominal pain, diarrhea, vomiting, and tachycardia.⁴ Long-term copper ingestion can result in cirrhosis and other debilitating liver conditions.⁵ Humans also appear to experience detrimental effects in reproduction and development as a result of toxic copper exposure; it has be suggested that the presence of copper in human spermatozoa affects sperm mobility.⁴ Children are especially sensitive to long-term ingestion of high levels of copper, which can result in liver damage and even death.

Other animals are adversely affected by an excess of copper in their diet and in their surrounding environment. To most freshwater and marine invertebrates, copper is highly toxic, although the effect is felt most by freshwater animals. The only metal surpassing copper's toxicity in freshwater fish is mercury.⁷ Copper is highly toxic to freshwater fish, but is selectively toxic to certain species. Copper ions present in the freshwater environment kill fish mainly by asphyxiation; when copper ions come into contact with the fish the copper ions precipitate gill secretions causing death. Copper also causes an osmotic imbalance in the gill filaments that reduces its oxidative activites.⁶ Microorganisms are also adversely affected by toxic levels of copper. It has been suggested that microbial biomass and microbial activities decrease in soil containing relatively high levels of copper.⁷ Any effect felt in the bottom of the food chain will have repercussions in the higher levels, resulting in an overall disturbance in the delicately-balanced ecosystem.

Current technologies to remove copper from the CMP waste stream are either chemical or electrochemical in nature. Generally these technologies are aimed to remove the suspended solids contained in the wastewater matrix, and do little for the removal of the dissolved species contained in the wastewater. Chemical technologies include flocculation, filtration, and gravity settling. Again these technologies are inefficient for treatment of this type of waste as they do not remove dissolved copper species. Elaborate chemical schemes may be devised to chemically treat all chemical components of the CMP wastewater, but these schemes are complex and involve the addition of several chemicals to treat the water. This results in increased capital costs for the consumer as well as an increase in the problems associated with the storage and handling of strong chemical species. CMP wastewater may be treated electrochemically via electrofloccualtion and electrodecantation, but these methods have associated shortcoming as well. Our novel patented electrochemical treatment systems may succeed where others experience shortcomings. Our system uniquely combines the power of off-the-shelf ion-exchange resin with integrated ion-exchange electrodes for the effective removal of soluble species, namely Cu^{+2} , under the influence of an electric field. The nonpareil feature of the system is its ability to be regenerated insitu, allowing for an efficient treatment and regeneration technology that offers both simplicity of operation and worry-free maintenance for the consumer.

Treatment of Wastewater

Our patented technology has proven to be an effective means for the treatment and recycling of copper rinse water from industrial plating lines. The inventiveness of this design lies in several fundamental It can simultaneously remove features. anionic and cationic contaminants, resulting in decreased metal concentration. TDS and a neutralized pH. The treatment of rinse water from a copper plating line is illustrated in Figure 1. First, the rinse water contaminated with $CuSO_4$ is pumped to the anode compartment, and an electric field is applied. Under the influence of the electric field, Cu²⁺ ions transmigrate through the cation selective membrane to the integrated ion exchange cathode, which contains standard, off-the-shelf cation exchange resin mixed with graphite. The Cu^{2+} ions are removed from the wastewater through 1) a



Figure 1: In-process recycling system for copper rinse water, an example of prior work.

cation exchange reaction and 2) an electrodeposition reaction. Simultaneously, SO_4^{2-} ions migrate toward the integrated ion exchange anode, and are removed through the anion exchange reaction. At the cathode, H⁺ is generated from the cation exchange reaction; this combines with the OH⁻ generated at the cathode via water electrolysis to form water, shown by the following reactions:

$$2R - SO_{3}^{-}H^{+} + Cu^{+2} \rightarrow (R - SO_{3}^{-})_{2}Cu + 2H^{+}$$

$$2H_{2}O + 2e^{-} \rightarrow H_{2}(g) + 2OH^{-}$$

$$2H^{+} + 2OH^{-} \rightarrow 2H_{2}O$$
(1)

Similarly, the OH⁻ generated via the anion exchange reaction combines with H⁺ generated via oxygen evolution occurring at the anode to form water, shown in the following reactions.

$$2R - OH + SO_{4}^{2-} \rightarrow R_{2} - SO_{4}^{2-} + 2OH^{-}$$

$$H_{2}O \rightarrow 2H^{+} + \frac{1}{2}O_{2}(g) + 2e^{-}$$

$$2OH^{-} + 2H^{+} \rightarrow 2H_{2}O$$
(2)

The small volume of gases produced as a consequence of water electrolysis may be burped with a special valve to ensure there is no pressure build up. After treatment, the rinse water is free of Cu^{2+} and SO_4^{2-} ions, and the pH is neutralized, enabling the water to be recycled to rinse operation. A typical treatment in the electrochemical cell results in a reduction in copper concentration from 24 to 0.1 ppm. Once the ion-exchange resin ceases to remove Cu^{2+} and SO_4^{2-} , the cell can be electrochemically regenerated, restoring it

to its initial state. The result of cell regeneration is a small volume of highly concentrated copper sulfate, which then can be used as a starter plating solution.

The treatment step requires an electric field to enhance the removal of ionic contaminants; this can be facilitated through the application of constant direct current (DC) or Faradiac processes.

Cell Regeneration

The ingenuity of this design resides in the ability of the system to be regenerated in-situ without the need of strong chemical species. Figure 2 shows a schematic of the regeneration process. Typically, ion-exchange resin must be regenerated through treatment with a strong chemical species. This process involves slowly flowing a strong acid through cation-exchange resin followed by several slow rinses with water, all steps requiring a relatively long period of time. The use of chemical species and time requirement translate into higher capital costs. Another disadvantage of chemical regeneration is the large required footprint.



Figure 2: Regeneration Process.

Our system does not require the addition of chemicals, but instead utilizes the applied electric field for the regeneration of ion-exchange resin. This is achieved simply by reversing the polarity of the applied electric field. Upon reversing the polarity of the electric field, the electrode previously functioning as the cathode now becomes the anode. At this terminal, water is electrolyzed, producing oxygen gas and H^+ ions. These H^+ ions are preferentially absorbed by the cation-exchange resin, which consequently liberates copper ions back into solution and fully regenerates the cation-exchange resin. These reactions are shown in Equation 3:

$$H_{2}O \rightarrow 2H^{+} + \frac{1}{2}O_{2} + 2e^{-}$$

$$(R - SO_{3}^{-})_{2}Cu^{+2} + 2H^{+} \rightarrow 2R - SO_{3}^{-}H^{+} + Cu^{+2}$$
(3)

Similarly, the electrode functioning as the anode in the treatment step becomes the cathode when the electric field polarity is reversed. Water electrolysis at this terminal yields hydrogen gas and OH⁻. The anion-exchange resin will absorb the OH⁻ generated, releasing the anions absorbed onto the anion-exchange resin and fully regenerating the anion-exchange resin, as illustrated by Equation 4.

$$2H_2O + 2e^- \rightarrow H_2 + OH^-$$

$$R_2 - SO_4^{2-} + 2OH^- \rightarrow 2R - OH + SO_4^{2-}$$
(4)

The result of this process is a small volume of concentrated solution, which can be disposed of properly of or depending upon the application, recycled back to CMP operation.

Faradaic Processes

It is possible to enhance the performance of the proposed technology compared to DC processes, by use of a Faradaic process (Figure 3). The Faradaic electric field consists of an anodic voltage, applied for time $t_{a,on}$, followed by zero voltage for a period of time t_{bff} . The sum of the on-time and off-time is the period and the inverse of the period is the frequency. The percent anodic on-time is defined as the anodic duty-cycle. The voltage during the on-time is known as the peak voltage and the average voltage is defined as the time-average of the instantaneous voltage over a period. It should be noted that in Faradaic electrolysis, the peak voltage, duty cycle, and frequency are additional parameters available to control the mass transfer process and current distribution, as compared to DC electrochemical processes.



Unlike DC electrolysis, the mass transfer characteristics of charge modulated electric field electrolysis are a time dependent process. Faradaic electrolysis causes concentration fluctuations near the electrode surface and reduces the effective Nernst diffusion layer thickness. Consequently, very high instantaneous limiting current densities can be obtained with Faradaic electrolysis as compared to DC electrolysis.

To qualitatively illustrate how Faradaic electrolysis enhances the instantaneous mass transfer rate, consider the case of a single rectangular cathodic current modulation. Before the current is turned on, the concentration of the diffusing ion is equal to the bulk concentration, C_b . After the current is turned on, the concentration near the cathode drops and a diffusion layer builds up. Using the non-steadystate Fick's law of diffusion, this concentration profile as a function of the distance from the electrode surface, X, is depicted in Figure 5. The corresponding thickness of the Nernst diffusion layer, δ , is also shown in Figure 5 for



Figure 4: Mass transfer in Faradaic electrolysis by diffusion.

various time periods. The mass transfer limited current density is related to the concentration gradient at the electrode surface and to the thickness of the Nernst diffusion layer by:

$$i = nFD[dC/dx]_{x=0} = -nFD[(C_b - C_s)/\delta]$$
(5)

In steady state DC electrolysis, δ is a time-invariant quantity for given electrode geometry and hydrodynamics; this quantity is represented by δ_{∞} . In Faradaic electrolysis, however, δ varies from 0 at the beginning of the process to a value of δ_{∞} when the steady state Nernst diffusion layer is fully established. The corresponding diffusion current density would then be equal to an infinite value at t = 0 and decrease to a steady state value of the DC limiting current density at t = t_{\omega}. The advantage of Faradaic electrolysis is that

the current can be interrupted (*e.g.*, at $t = t_a$) before δ has a chance to reach the steady-state value. This allows the reacting ions to diffuse back to the electrode surface or membrane surface and replenish the surface concentration to its original value before the next current modulation. In this way, one obtains a diffusion controlled modulated current density greater than the steady state limiting current density. This diffusion controlled modulated current density can be made very large if one employs a current modulation of very short duration followed by very long relaxation time to permit the surface concentration to recover to the bulk value. Modeling work by Chin has indicated that limiting current densities obtained under pulse reverse current (PRC) conditions of low duty cycle and high frequency, can be two to three orders of magnitude greater than the DC limiting current density. Vilambi and Chin confirmed the earlier modeling work with experimental studies for a copper sulfate bath for selected pulse periods and duty cycles in PRC electrolysis. They reported peak current densities as high as several hundred A/cm² for PRC electrolysis, while the corresponding values for DC electrolysis were less than 1 A/cm².

Experimental

Prior work accomplished for the recycling of copper from copper-plating operations laid the groundwork for treatment of copper from CMP wastewater. This work was sought after, and funded by a commercial client specializing in waste treatment for the semiconductor industry. This study explores treatment and regeneration utilizing both direct current (DC) and the Faradaic process with variations in waveform parameters. A couple baseline type tests were run in the absence of current to give a direct comparison of the treatment or regeneration efficiency with applied current. The matrix used for treatment and regeneration is given in Table 1. Table 1 lists a total of 14 tests; a treatment test and a regeneration test were run for each set of DC and Faradaic parameters. Other tests were run outside of these parameters for comparison purposes, for example a couple tests were run at 75% duty cycle to compare effects of treatment run with 25% and 50% duty cycles.

Treatment / Regeneration Tests					
Test No.	Test Type	Flow Rate (L min ⁻¹)	Current (Amps)	Frequency (Hz)	Duty Cycle (% On-Time)
1	No Current	0.2	-	-	-
2	No Current	0.4	-	-	-
3	DC	0.2	3	-	-
4	DC	0.2	5	-	-
5	DC	0.2	10	-	-
6	DC	0.4	5	-	-
7	Faradaic	0.2	3	10	25
8	Faradaic	0.2	3	50	50
9	Faradaic	0.2	5	10	25
10	Faradaic	0.2	5	50	50
11	Faradaic	0.2	5	50	25
12	Faradaic	0.2	5	10	50
13	Faradaic	0.2	3	50	25
14	Faradaic	0.2	3	10	50

 Table 1: Test Matrix for Treatment of Cu-CMP Wastewater and Cell Regeneration

All tests were run with industrially generated CMP waste, supplied by the commercial client. This slurry contained the following materials as specified by the supplier: water, sulfuric acid (H₂SO₄), aluminum oxide (A $_{\rm b}O_3$), copper (II) sulfate (CuSO₄), along with some proprietary additives. Since copper is not only removed via ion-exchange reactions, but also through deposition, two 1.5-hour treatment tests were run before the cell was regenerated. Prior work demonstrated that regeneration of the cell occurs on a shorter time scale than adequate treatment. Therefore, all regeneration tests were run for 40 minutes, although maximum copper concentration was achieved much earlier than 40 minutes. This means that the cell may be regenerated for further treatment after only 5-15 minutes.

The unit cell (Figure 5) used to conduct these treatment and regeneration tests consisted of two one-inch anode frames, sandwiching a half-inch cathode frame. The cathode frame contained the ion-exchange resin/graphite and was separated from anode frames by Nafion membranes. The ion-exchange resin used in the cell was a strong-acid type resin, hydrogen form, (CG8-H from ResinTech) with a capacity of 1.85 meq mL⁻¹. The cathode compartment of the cell contained 210 g of graphite chips and 70 g of the cation-exchange resin. The membranes are present to permit the passage of current and cations, while inhibiting the passage of anions. Solution to be treated was pumped through the



Figure 5: Photograph of cell used for treatment and regeneration tests.

cathode frame. A dilute solution of H_2SO_4 (0.1 M) was pumped through the anode frames to maintain conductivity, and therefore carry current.

Figure 6 shows the entire set-up for treatment and regeneration tests. The set-up consists of a rectifier power supply (Kraft Dynatronix Model DPR20-100-400), a Hall-effect cell (assembled by Mr. R. Renz of Faraday Technology, Inc.), an oscilloscope (Tektronix TDS 210), a control panel to control flow rate as well as pump functions, an exchange cell and four tanks fitted with pumps. The four tanks contained the following: Tank 1 is a treatment tank filled with Cu-CMP slurry, Tank 2 is a regeneration tank filled with 0.1 M H₂SO₄ (made with DI H₂O), Tank 3 is an anolyte tank filled with 0.1 M H₂SO₄ (made with DI H₂O) which is cycled through cell to maintain conductivity, and Tank 4 is the effluent tank for the treated Cu-CMP slurry.



Figure 6: Photograph of Set-Up Used for Treatment and Regeneration Tests

Results and Discussion

Direct Current Treatment Tests

The starting point, in terms of current, was selected from previous work done to remove copper from copper plating rinse waters. Upon baseline testing, more appropriate current magnitudes became apparent. The first test was run at 5 Amps DC with a flow rate of 0.2 L min^{-1} , and the second test was run at 5 Amps DC with a flow rate of 0.2 L min^{-1} reduced Cu^{2+} concentration from 25 ppm to 3.2 ppm after treatment for 90 minutes. Similarly, the test run at 0.4 L min⁻¹ reduced Cu^{2+} concentration from 28 ppm to 4.5 ppm after 90 minutes of treatment. These results would suggest that there was little difference between the two flow rates, however at the higher flow, more solution will be passing through the cell and therefore a higher volume of solution will be treated. The results of these tests, in terms of concentration, are given in Table 2. The results were then plotted in terms of mass removed during treatment, as shown in Figure 7.

DC Treatment Tests					
	5 Amps	5 Amps	3 Amps	10 Amps	
	0.2 L min-1 Flow	0.4 L min-1 Flow	0.2 L min-1 Flow	0.2 L min-1 Flow	
Initial [Cu ²⁺] (ppm)	25	28	25	30	
Final [Cu ²⁺] (ppm)	3.2	4.5	2.8	7.1	

Table 2: Numerical Results of Concentrations Before and After DC Tests Run with 3,5, and 10 Amps Average Current



Figure 7: Mass of Cu²⁺ Removed as a Function of Treatment Time

As expected, the treatment test run at a flow of 0.4 L min⁻¹, removed approximately double the mass of copper ion over the same treatment time interval. However, further testing was limited by the amount of slurry available, so testing was only run at one flow rate, 0.2 L min⁻¹. Each DC test was conducted for 1.5 hours at current magnitudes of 3 Amps, 5 Amps and 10 Amps. The results are shown in Figure 8. Figure 8 gives the results in terms of percent Cu²⁺ concentration remaining after each time interval. DC treatment at 3 Amps current reduced Cu²⁺ concentration from 25 to 2.8 ppm after 90 minutes, and at 5 Amps current Cu²⁺ was reduced from 25 ppm to 3.2 ppm. Additionally, DC treatment at 10 Amps reduced Cu²⁺ concentration from 30 ppm to 7.1 ppm after 90 minutes.



Figure 8: DC Treatment Current Comparisons, Mass of Cu²⁺ Removed vs. Treatment Time

Faradaic Treatment Tests

The first set of electrically mediated current tests was run with previously optimized electric field parameters determined from treatment tests on copper rinse water. The parameters for the first test are as follows: 5 Amps average current (10 peak Amps), 50% duty cycle, and frequency of 100 Hz. The second test was run with similar parameters with a variation in duty cycle, 75% duty cycle. The test run with a 50% duty cycle gave marginally better results. Therefore, another test with a duty cycle of 25% was conducted for comparison. The results are shown in Figure 9. After treatment for 90 minutes, the

electrically mediated current tests shown in Figure 9 gave the following reductions in Cu^{2+} concentration: at 25% duty cycle Cu^{2+} reduced from 26 ppm to 1.3 ppm, at 50% duty cycle Cu^{2+} reduced from 24 ppm to 3.3 ppm, and at 75% duty cycle Cu^{2+} reduced from 22 to 3.0 ppm.



Figure 9: Comparison of Duty Cycle for Electrically Mediated Current Treatment Tests

Since the 25% duty cycle was shown to have advantage over the 75% duty cycle, the treatment/regeneration tests for this study were run at 25% and 50% duty cycles.

Electrically mediated treatment tests utilizing 3 Amps of current were run according to the test matrix given in Table 1. Table 3 summarizes the results obtained for these treatment tests. The results are plotted in Figure 10 in terms of the mass of copper removed from the CMP waste stream as a function of time. Figure 10 also includes the results of the DC treatment test run at 3 Amps.

3 Amps Average Current						
	25% Duty Cycle, 10 Hz	25% Duty Cycle, 50 Hz	50% Duty Cycle, 10 Hz	50% Duty Cycle, 50 Hz		
Initial [Cu ²⁺] (ppm)	23	26	27	28		
Final [Cu ²⁺] (ppm)	1.5	2.8	1.7	2.1		

 Table 3: Numerical Results of Concentrations Before

 and After Tests Run with 3 Amps Average Current



Figure 10: Treatment, DC and Electrically Mediated Current, at 3 Amps Average Current

Figure 10 indicates that in this series of tests, Cu^{2+} is most effectively removed with a duty cycle of 50% at a frequency of 50 Hz, with 50% duty cycle and 10 Hz trailing only slightly. However, it is important to note that end concentrations were not always the lowest concentrations achieved during testing. For the treatment test run at 50% duty cycle and 50 Hz, the lowest concentration of Cu^{2+} was achieved after 75 minutes, while it took 90 minutes to achieve lowest Cu^{2+} concentration at 50% duty cycle and 10 Hz. As stated previously, tests in this series utilizing 25% duty cycle required less treatment time to achieve lower Cu^{2+} concentrations. At 10 Hz, it took only 45 minutes to reduce Cu^{2+} concentration from 23 ppm to 0.63 ppm and at 50 Hz took only 15 minutes to reduce Cu^{2+} concentration from 26 ppm to 1.3 ppm. These processes may be more efficient in terms of treatment time requirements, especially when coupled with a longer residence time.

Next, the results of treatment with 5 Amps average current are shown in Figures 12-13, and results are summarized in Table 4. Figure 12 gives results of Faradaic treatment tests run at 5 Amps average current with variations in duty cycle and frequency. Figure 13 shows the results of these tests with analogous DC treatment tests. Again, 50% duty cycle appears to be the most efficient for removal of Cu^{2+} from the Cu-CMP waste stream. However, for this series of tests 10 Hz frequency coupled with 5 Amps average current and 50% duty cycle gives maximum decontamination efficiency; this is compared to 50% duty cycle and 50 Hz frequency seen in 3 Amps average current tests. However, it is important to note that as with 3 Amps average tests, end concentrations were not always the lowest concentrations achieved during testing. At 25% duty cycle and 50 Hz, the concentration of 1.2 ppm was achieved after just 15 minutes of treatment. Concluding that 45 minutes would be the optimum treatment time for the following parameters: 25% duty cycle and 10 Hz, while the optimum treatment time for tests run at 25% duty cycle and 50 Hz appears to be 15 minutes. In addition to these trends, it appears that at 50% duty cycle and 50 Hz, the optimum treatment time is 75 minutes, since tests at both 3 and 5 Amps give lowest concentrations at this time interval (1.8 ppm in both cases)

5 Amps Average Current					
	25% Duty Cycle, 10 Hz	25% Duty Cycle, 50 Hz	50% Duty Cycle, 10 Hz	50% Duty Cycle, 50 Hz	
Initial [Cu ²⁺] (ppm)	23	23	28	28	
Final [Cu ²⁺] (ppm)	1.5	2.3	2.9	2.1	

 Table 4: Numerical Results of Concentrations Before

 and After Tests Run with 5 Amps Average Current



Figure 12: Electrically Mediated Current Treatment Tests Utilizing 5 Amps Average Current



Figure 13: Mass Cu²⁺ Removed vs. Treatment Time for DC and Electrically Mediated Current Treatment Tests Run at 5 Amps Average Current

At 5 Amps average current, 50% duty cycle coupled with 50 Hz was shown to remove less mass of Cu^{2+} (mg) than 25% duty cycle at both frequencies. The lowest concentration of Cu^{2+} in this series of tests was 1.0 ppm; this concentration was achieved after testing for 45 minutes at 25% duty cycle and 10 Hz frequency. Again, 25% duty cycle appears to be advantageous to 50% duty cycle in terms of treatment time requirements.

The previous graphs suggest that electrically mediated current treatment shows an enhancement over DC treatment. The lowest concentration of Cu^{2+} was achieved at 3 Amps average current, 25% duty cycle and 10 Hz frequency; the highest mass removal was achieved at 3 Amps average current, 50% duty cycle and 50 Hz frequency. Concluding that lower current may give better treatment results in terms of electrically mediated current treatment.

Direct Current Regeneration Tests

Regeneration tests were run under the same matrix conditions as the treatment tests. However, for regeneration tests, the polarity of the electrodes were switched so that the electrode previously functioning as the cathode became the anode and the electrode previously functioning as the anode became the cathode. Dilute sulfuric acid (0.1 M) was circulated through both anode and cathode frames for regeneration. DC Regeneration tests were performed according to the DC treatment matrix, shown in Table 1. Note, the first regeneration test was run for the same amount of time as the treatment tests (1.5 hrs). Once the results were obtained, it was clear that regeneration at 3, 5, and 10 Amps current. Here, it is observed that regeneration at 5 Amps current is significantly better than regeneration at 3 or 10 Amps current.



Figure 14: Plot of DC Regeneration Tests

Faradaic Regeneration Tests

Electrically mediated current regeneration tests were run according to the electrically mediated current treatment matrix. However, due to time constraints only 6 of the 8 tests listed were conducted. Electrically mediated current regeneration results are shown in Figure 15 and a direct comparison of all regeneration tests in Figure 16. After 5 minutes of regeneration, most tests gave the maximum concentration of Cu^{2+} , indicating relatively short regeneration time requirements. The test utilizing 3 Amps average current, 25% duty cycle and 10 Hz gave the highest concentration of Cu^{2+} observed in the electrically mediated current regeneration portion of this study. However, this result was obtained after regeneration for 10 minutes, which is twice as long as it took for the other tests to reach their maximum concentration. The same duty cycle and frequency at 5 Amps average current gave nearly the same maximum concentration (320 ppm vs. 300 ppm at 5 Amps) in half the amount of time.



Figure 15: Electrically Mediated Current Regeneration Tests



Figure 16: Comparison of All Regeneration Tests

Conclusion

In summary, we demonstrated the technical feasibility of treating copper laden CMP wastewater with our patented system. Over the course of this study we established the following:

- Electrically mediated current enhances the removal efficiency of the system when compared to direct current or no current at all
- Electrically mediated current processes appeared to be further enhanced by the use of low current magnitudes
- Regeneration of the cell appears to be most efficient with direct current
- This system is a cost-effective, environmentally-friendly method to remove copper from the CMP waste stream

More work will be done to explore other waveform parameters that may further enhance this process. Future work will include exploring the effect of smaller current magnitudes, as well as lower duty cycle and varying frequencies. However, this study has effectively demonstrated the feasibility of Cu-CMP waste treatment with our patented waste treatment system.

References

- 1. J.K. Cochran and J.W. Fowler, *Computers in Industry*, **45**, 1 (2001)
- 2. J.M. Steigerwald, S.P. Murarka, R.J. Gutman, and D.J. Duquette, *Materials Chemistry and Physics*, **41**, 217 (1995)
- B.M. Belongia, P.D. Haworth, J.C. Baygents, and S. Raghavan, "Treatment of Alumina and Silica CMP Waste by Electrodecantation and Electrocoagulation" in *Chemical Mechanical Planarization in Integrated Circuit Device Manufacturing*, eds. S. Raghavan, R.L. Opila, L. Zhang, Proceedings Volume 98-7, The Electrochemical Society, Inc, Pennington, N.J., 1998
- 4. http://www.lucidtreatmentsystems.com/arttwo.htm
- 5. http://www.extremehealthusa.com/toxicityheavy.htm
- 6. J. Mueller-Hoecker, U. Meyers, B. Wiebecke et al, Pathol. Red. Pract, 183, 39 (1988)
- 7. D. Brown at http://www.science.mcmaster.ca/Biology/4S03/COPPER.htm
- 8. T. Kunito, K. Saeki, H. Oyaizu, and S. Matsumoto, *Ecotoxicology and Environmental Safety*, Env. Research B, 44, 174 (1999)
- 9. D-T Chin, J. Electrochem. Soc, 130, 1657 (1983)
- 10. N.R.K. Vilambi and D-T Chin, Plating and Surface Finishing, 67 (1988)