

Optimum physical–chemical pre-treatment of copper damascene wastewater

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Abstract Chemical and mechanical polishing (CMP) of copper damascene circuits will typically produce copper levels in excess of regulatory limits in wastewater with a unique process chemistry, including high solids. Physical–chemical methods were investigated to determine the optimum treatment depending upon pre-treatment and/or water reuse requirements. Jar test studies revealed that an alum dose of 150–200 mg/L together with anionic polymer aid provided a good removal of turbidity. If the treatment objective is simply solids and copper reduction for discharge to a sewer system, then solids removal can be combined with precipitation of copper hydroxide for relatively inexpensive pre-treatment. The presence of peroxide from the process solution, however, may make it difficult to achieve copper values below 5 mg/L, depending on the associated process conditions. If the objective is to remove solids and recover copper, which may also allow recovery of water for reuse, then solids removal by alum and polymer can be followed by ion exchange by a strong acid cation resin. As with precipitation, however, effective copper removal by ion exchange requires pre-treatment of peroxide by chemical reduction. The exchange of dissolved aluminum also reduces the capacity of the resin for copper.

Keywords Copper; high-solids wastewater; industrial wastewater treatment; physical–chemical treatment; semiconductor wastewater

Introduction

The semiconductor industry is exploring the use of copper damascene technology as a lower resistance interconnect in the manufacturing of circuit devices (Muraka and Hymes, 1995). In the damascene process, grooves and vias are etched into an oxide layer, barrier and adhesion metals are applied, and then copper is used to fill the vias and lines (Carpio *et al.*, 1995). Typically, a seed layer of copper is deposited, followed by electroplating to a thickness of one to two micrometres. The copper overburden is removed by chemical mechanical polishing (CMP) using a mildly abrasive suspension e.g., α -alumina, together with an oxidizing agent (peroxide) and buffers to create a passivation-type slurry chemistry. Copper levels in wastewater discharges from CMP may be more than 50 mg/L, with a total release of tens of kilograms of copper per month depending on water flow rates and the CMP process equipment employed. Wastewater generation in a copper CMP unit is illustrated in Figure 1. It is likely that the copper concentration in CMP discharges will exceed USEPA metal finishing limits which are of an order of 2 mg/L (USEPA, 1983). Pre-treatment, therefore, is necessary and in some instances may prove economical where water and/or metal recovery can be achieved. Various physical–chemical and electrochemical methods have been successfully employed for copper removal from industrial wastewaters that are both thermodynamically and kinetically favorable (Chang, 1996; Kanzelmeyer and Adams, 1996; Suzuki *et al.*, 1995). Treatment of copper CMP wastewater is complicated, however, by high suspended solids in the form of colloidal-sized alumina, and the unique process chemistry. The objective of this study is to evaluate

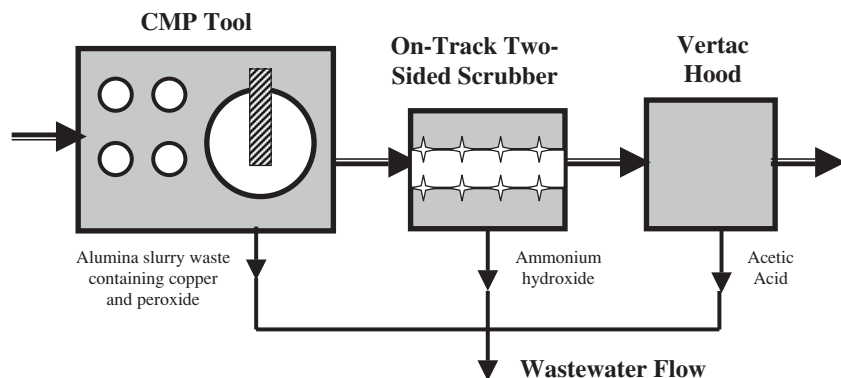


Figure 1 Copper chemical mechanical polishing wastewater generation

physical–chemical methods, singly and/or in sequence, to determine the optimum scheme for the treatment of copper CMP wastewater depending upon pre-treatment and reuse requirements for a given application. Laboratory investigations focus on coagulation, chemical precipitation, and ion exchange utilizing both synthetic and actual wastewater from a pilot copper CMP unit.

Experimental

Synthetic CMP wastewater was prepared using a 2:1 volume mix of a proprietary α -alumina suspension (6–7% solids) to 30% hydrogen peroxide. To simulate copper contamination, an appropriate volume of copper stock solution was added. The slurry was then diluted up to ten times to simulate the addition of various deionized water sprays and rinses to the wastewater stream from a CMP tool. Selected tests utilized actual wastewater from a CMP unit.

Coagulation and metal precipitation studies

Coagulation and precipitation studies were conducted using conventional jar-test apparatus at room temperature ($\sim 22^{\circ}\text{C}$), with rapid mixing at 100 rpm for 1 minute following coagulant addition, flocculation at 20 rpm for 30 minutes, and quiescent settling for 1 hour. Effectiveness of suspended solids removal was monitored using a turbidimeter. pH adjustment for chemical precipitation was done using NaOH. Copper analysis was done by an inductively coupled plasma spectrometer (ICP) according to EPA Method 6010A (*Test Methods*, 1986).

Ion exchange studies

Ion exchange of copper was investigated in fixed beds using a strong acid cation exchange resin, Dowex HCR-W2 (Dow Chemical Co.). Resin was packed in a 0.75 cm inside diameter stainless steel column supported on glass beads, and wastewater flow delivered at 3.2 mL/min (2 gpm/ft²) using a high pressure solvent delivery pump. Experiments were performed at influent pH values between 2.5 and 7. Both influent and effluent samples were collected at frequent intervals to obtain the relative concentration breakthrough profiles for copper. Copper analysis of samples was by ICP. Copper recovery from resin was determined in selected cases.

Results and discussion

Coagulation and metal precipitation studies

Potentiometric titration of the α -alumina slurry revealed it to have surface charge

characteristics similar to commercial α -alumina suspensions, with a pH_{zpc} of 8.5–9.0 (Hayes *et al.*, 1991). The CMP process slurry contains buffering agents that poise the pH of the wastewater at 3.5–4.0 which is less than the pH of zero point of charge for α -alumina, implying a positive surface charge on suspended particles. Therefore, an anionic polymeric coagulant (POL-E-Z 692, Calgon Corp.) was used in addition to conventional coagulants for suspended solids removal. Considerable agglomeration of solids is observed during the flocculation period in reactors containing polymer.

Alumina particles will settle appreciably without any treatment, but a comparison of treated versus untreated samples for synthetic wastewater (Table 1) illustrates gains in required residence time achieved by coagulation. Results of tests to determine the optimum dosage of coagulant (in this instance, alum) for actual copper CMP wastewater are presented in Figure 2. The most effective removal of turbidity is achieved with an alum dose of 150–200 mg/L alum together with the polymeric aid. Experiments using the polymer alone reduced the turbidity to ~ 120 NTUs at an optimum dosage of 1 mL of 0.5% coagulant emulsion per litre of wastewater. Tests indicated that no Cu(II) is adsorbed by the α -alumina, nor is any appreciable amount removed during the pre-treatment of solids.

If the treatment objective is simply solids and copper reduction for discharge to a sewer, then solids removal can be combined with precipitation of copper hydroxide in sequential mode. However, the presence of peroxide in solution made it difficult to achieve soluble copper values below 5 mg/L. Simultaneous use of coagulants and NaOH achieved better removal of copper (0.5–1 mg/L), as indicated in Figure 3, but final turbidity was higher. The optimum dosage was 1.8 mL/L of 10 N NaOH, yielding a pH of ~ 8.45 . The minimum solubility achieved is still considerably higher and the optimum pH more than one pH unit lower than theoretical solubility calculations for $\text{Cu}(\text{OH})_{2(s)}$ (or $\text{CuO}_{(s)}$), suggesting complexation of Cu(II) with organic materials comprising the proprietary buffer solution.

Table 1 Turbidity versus time during quiescent settling

Time (min.)	Untreated (NTU)	Treated (NTU)
0	1050	318
15	123	13.6
30	73.3	8.50
45	51.9	6.16
60	40.2	2.92

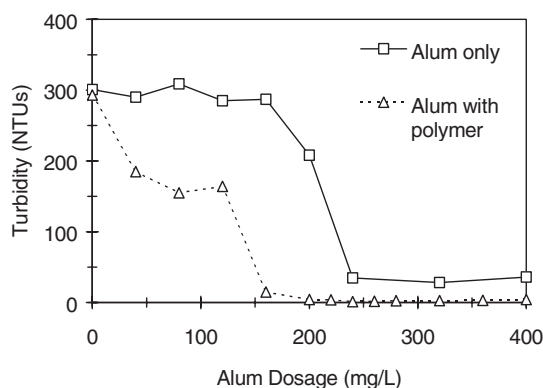


Figure 2 Solids removal from actual copper CMP wastewater using alum coagulation with and without anionic polymer

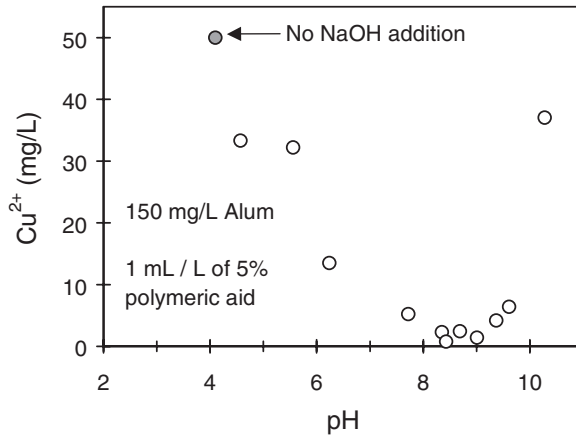


Figure 3 Copper removal from actual copper CMP wastewater using simultaneous alum coagulation with anionic polymer and NaOH

Ion exchange studies

If the objective is to remove solids and recover copper, which may also allow recovery of water for reuse, then solids removal by alum and polymer can be followed by ion exchange. Pilot CMP tool tests generated wastewater containing up to 50 mg/L of soluble Cu(II). Therefore, initial ion exchange treatability studies were run for synthetic copper wastewater at this influent concentration and free of suspended solids. For an influent pH of 4, the pH of actual slurry wastewater, the adsorption capacity (i.e. mg copper adsorbed per g dry resin) for pre-swelled HCR-W2 resin is about 120 mg/g. This is nearly the same capacity as achieved for an influent pH of 2, and 20% higher than that obtained at pH 5.5. Additional, experimental and modeling investigations were conducted to evaluate both the impacts of process variables and strategies for resin regeneration and copper recovery. A dynamic, fixed-bed model for metal adsorption onto porous solids (Smith, 1998) was verified using equilibrium and kinetic parameters derived from experimental data to simulate the relationship between process variables and copper breakthrough as a function of bed volumes treated. The model accounts for dual-resistant mass transfer with negligible axial dispersion. The liquid phase material balance is:

$$\frac{\partial C_{z,t}}{\partial t} = -v_z \frac{\partial C_{z,t}}{\partial z} - \rho \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial Q_{\text{avg},z,t}}{\partial t} \quad (1)$$

where z = axial coordinate (L); C = liquid phase concentration of solute (M/L^3); Q = solid phase loading of solute (M -solute/ M -solid); v_z = interstitial axial velocity (L/t); ρ = density of sorbent (M/L^3); and ε = bed void fraction. The solid phase material balance is:

$$\frac{\partial Q_{r,z,t}}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial Q_{r,z,t}}{\partial r} \right) \quad (2)$$

where r = radial distance in the particle from its center (L) and D_s = intraparticle diffusion coefficient (L^2/t), which for this case is considered to be surface diffusion. The initial and boundary conditions include an expression equating the flux from the bulk phase to the liquid-particle boundary layer (i.e., film diffusion) to the intraparticle flux (Smith, 1991):

$$k_f (C_{z,t} - C_{s,z,t}) = \rho D_s \frac{\partial Q_{r,z,t}}{\partial r} \quad (3)$$

where k_f = the film diffusion coefficient (L/t); and C_s is the liquid phase concentration of solute at the particle surface, versus bulk phase (M/L^3). The Freundlich isotherm equation was used to describe equilibrium at the particle surface. Model constants for Cu(II) adsorption on HCR-W2 resin were evaluated from batch isotherm data and are given in Eq. (4) for C_e in mg/L and Q_e in mg/g.

$$Q_e = K_F C_e^n = 54.7 C_e^{0.20} \quad (4)$$

Using these parameters, breakthrough data from a short laboratory column (4-cm length) was used to calibrate the dynamic model and evaluate the mass transfer coefficients; namely, $k_f = 4.8 \times 10^{-3}$ cm/s and $D_s = 1.5 \times 10^{-8}$ cm²/s. Using both equilibrium and rate constants, good prediction of breakthrough data from a deeper bed experiment (8-cm length) demonstrated the ability of the model to serve as a scale-up tool for design of an exchanger column. Figure 4 depicts the effect of empty bed contact time (EBCT) on copper breakthrough in laboratory-scale columns. The results suggest that, for the given loading rate, an EBCT of at least 1 minute is needed to obtain acceptably low copper effluent levels for water reuse.

Figure 5 illustrates the effects of pre-treatment on copper recovery for actual CMP wastewater with a Cu(II) concentration of ~50 mg/L. While copper removal by ion

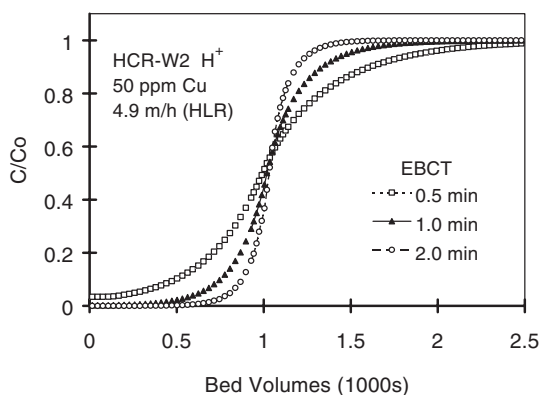


Figure 4 Model simulations of Cu(II) breakthrough versus EBCT at pH 4

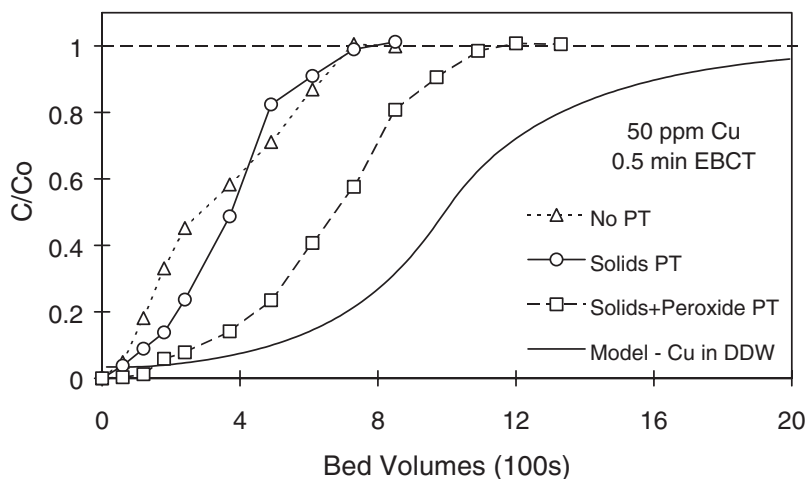


Figure 5 Effect of pretreatment (PT) on Cu(II) removal by ion exchange in fixed bed

Table 2 Cu(II) removal by Dowex HCR-W2 resin

Case	mg/g	meq/g
1: Cu in DI water	120	3.77
2: Cu-CMP (untreated)	36.4	1.15
3: Cu-CMP (pretreatment: solids only)	36.4	1.15
4: Cu-CMP (pretreatment: solids and H ₂ O ₂)	61.1	1.92
5: Cu-CMP (aluminium removal)	–	1.24

exchange is relatively unaffected by pre-treatment for solids removal, the solid phase loading capacity is improved by ~70% from 1.15 meq/g to 1.95 meq/g when peroxide is first removed by chemical reduction (e.g., using sodium metabisulfite). While the 1.95 meq/g is still short of the exchange capacity of a 50 mg/L solution of Cu(II) in a deionized water background, further analysis revealed that a portion of the aluminium in solution (deriving from dissolution from α -alumina based on analysis of raw CMP wastewater samples) was adsorbed onto the resin at a loading of 1.25 meq/g. The combined loading of Cu and Al is ~85% of the exchange capacity in deionized water. These results are summarized in Table 2.

Figure 5 also indicates the overprediction of copper removal in the fixed bed by the model. This is expected given the reduced ion exchange capacity in the case of the actual CMP wastewater. The shape of the experimental and model breakthrough curves is very similar, however, indicating that rate constants evaluated for the case of distilled-deionized water background essentially hold for the actual pre-treated wastewater. In fact, a subsequent model run reducing only the Freundlich coefficient, K_F , (keeping $n = 0.20$ as before) produced a very good fit of the breakthrough data in Figure 5. This suggests that copper removal from CMP wastewater is likely inhibited by a combination of surface site competition with aluminium and a reduction of affinity for exchange sites due to complexation with organic agents in the buffering solution. With an adjusted Freundlich capacity coefficient, K_F , model runs resulted in the same conclusion derived from Figure 4, namely that an EBCT of 1–2 minutes is required for copper levels to allow for water reuse.

Five bed volumes of 5% HCL was sufficient for regeneration of the spent resin for subsequent use. After five adsorption–regeneration cycles, Cu loading was still greater than 1.85 meq/g, or ~95% of the initial capacity. One of the potential disadvantages of this option is that the presence of aluminium in the eluent inhibits Cu recovery. It may be possible to separate the metals electrolytically, but the effectiveness and cost of the separation has not yet been evaluated. An advantage of this scheme, however, is that chemical sludge from the solids removal step contains virtually no Cu in contrast to the case of simultaneous coagulation and hydroxide precipitation. In both of these cases, dry sludge generation for respective optimum conditions ranged from 225–250 kg per 1,000 m³ of wastewater treated owing to the high solids concentration contributed by the α -alumina.

Conclusions

1. Copper damascene wastewater has a unique process chemistry, necessitating optimization of existing physical–chemical treatment methods to design a suitable treatment strategy that responds to pre-treatment and/or reuse requirements.
2. If the goal is simply solid and copper reduction for permitted discharge to a sewer system, simultaneous coagulation by alum with an anionic polymer and NaOH, followed by flocculation and settling, should produce a satisfactory result.
3. If water reuse and/or copper recovery is required, then solid removal can be achieved by the above processes using only alum and polymer. Copper can then be removed by ion

exchange. However, for efficient use of the ion exchange resin, chemical reduction of the peroxide in solution must first be achieved.

4. The dynamics of ion exchange removal of copper can be described and predicted by a dual-rate mass transfer sorption model. Model predictions indicate that an EBCT of at least 1 minute is required to obtain copper levels that permit water reuse.

An important difference between the two treatment strategies (numbers 2 and 3 above) is that in the former, the chemical sludge produced contains copper, while in the second scheme it does not. This may have a significant impact on the relative costs of the strategies depending on local hazardous waste handling and disposal regulations.

Acknowledgement

This work was sponsored by a grant to Edward Smith at the Southern Methodist University by Texas Instruments, Inc.

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