Journal of Hazardous Materials B136 (2006) 183–187

Journal of Hazardous Materials

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Sludge conditioning characteristics of copper chemical mechanical polishing wastewaters treated by electrocoagulation

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Received 7 November 2004; received in revised form 18 February 2005; accepted 15 May 2005

Available online 9 June 2006

Abstract

Treatment of copper chemical mechanical polishing (Cu-CMP) wastewaters by batch electrocoagulation was found effective in simultaneously removing the very fine metal oxide particles, copper ion and organic pollutants in the previous investigations. In the present work, the continuous electrocoagulation tests were performed to explore their treatment efficiencies and to identify the optimum operating conditions. Inherently, this electrocoagulation process, in either batch or continuous operating mode, generates a significant amount of sludge that needs to be properly disposed. In this study, the freeze/thaw conditioning of sludge obtained from this process was investigated in an aim to greatly reducing the sludge volume. Experimental tests were conducted to identify proper freeze/thaw operating conditions. Several fundamental aspects, such as the moisture bonding energy estimated using DSC test data, were examined to elucidate the conditioning results.

Keywords: CMP wastewater; Electrocoagulation; Copper ion; Freeze/thaw conditioning

1. Introduction

In the sub-micron semiconductor interconnects, chemical mechanical polishing (CMP) is fast becoming the established technology for planarization of multi-layer integrated circuit (IC) devices [1,2]. In this process, a large quantity of CMP wastewater is generated. The CMP wastewater is distinctly different from other industrial wastewaters owing to its high solid content and turbidity along with significant amounts of copper ion and organic pollutants. Therefore, total solids (TS) removal has received much attention in the previous investigations [3–10].

Currently, chemical coagulation or membrane separation process has been popular for treating the CMP wastewater in the semiconductor industries. Browne et al. [3] utilized ultrafiltration (UF) for removal of fine oxide particles. Golden et al. [4] had investigated the effectiveness of combined chemical coagulation and microfiltration process in removing the suspended oxide particles. Belongia et al. [5] had also studied the particle removal phenomena of simulated alumina and silica solution by electrodecantation and electrocoagulation. Recognizing the fact that during a CMP operation, the ultrafine oxide particle content of the CMP effluent varies considerably with time. Browne et al. [6] and Corlett [7] employed an online particle monitoring device in separating the cleaner CMP wastewater effluent from the dirtier one so that the former can be recycled without treatment for non-critical applications. The remaining smaller portion of concentrated CMP wastewater effluent needs to be treated by the chemical or physical methods. By combining chemical pretreatment, microfiltration and ion exchange, James et al. [8] were able to remove fine oxide particles and copper ion from the Cu-CMP wastewater. Kruilik et al. [9] found that the treatment process of Golden et al. [4] using proprietary polymer coagulant and microfiltration was also effective in removing copper from the Cu-CMP wastewater. In two recent publications, Lai and Lin [10,11] reported the test results of electrocoagulation for treatment of Cu-CMP wastewater. It

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0304-3894/$ – see front matter © 2006 Published by Elsevier B.V.

doi:10.1016/j.jhazmat.2005.05.042

was found that this method was capable of efficient removal of ultrafine oxide particles, copper ions and CMP wastewater contamination of chemical oxygen demand (COD).

The test results of electrocoagulation reported by Lai and Lin [10,11] were obtained from batch experiments. From the practical viewpoint, continuous tests will be necessary in order to evaluate the true process performances of electrocoagulation under continuous operating conditions and to identify the optimum operating conditions. As noted in the previous studies [10,11], moreover, electrocoagulation or chemical coagulation of the Cu-CMP wastewater generates a significant amount of sludge that needs to be properly disposed. The sludge generated by these processes consists primarily of water, usually in excess of 80%, which complicates the final sludge disposal. Dewatering of sludge is very energy consuming and not easy to do in large-scale industrial applications. Therefore, in order to overcome this problem, the present work was to utilize the freeze/thaw method to reduce the sludge volume that is conducive to the final sludge disposal. The freeze/thaw process had been also found effective in dealing with the sludge dewatering problems in many previous investigations [12,13]. Experiments were conducted to investigate the freeze/thaw dewatering characteristics the CMP sludge obtained by electrocoagulation and to identify the optimum operating conditions.

2. Experimental

The CMP wastewater was obtained from a large semiconductor manufacturer in northern Taiwan. The detail composition of CMP slurries is a closely guarded secret among the various suppliers. In addition, different types of CMP slurries are generally used in the semiconductor manufacturing process. Hence, the exact contents of the CMP wastewater were very difficult to ascertain. The water quality of the CMP wastewater was therefore quantified in terms of COD, turbidity (in terms of NTU), pH and conductivity. These water quality parameters were measured by the standard methods [14] before and after electrocoagulation. A Malvern zeta potential analyzer (Model Zetasizer 3000HS, Malvern Instrument, Ltd., Worcester, UK) was used to determine the size distribution of the ultrafine oxide particles of the CMP wastewater during the electrocoagulation process. An atomic absorption spectrophotometer (Model 932, GBC Scientific Equipment, Ltd., Vic., Australia) was used to measure the copper concentration. A differential scanning calorimetry (DSC) (Model DSC-7, Perkin-Elmer Instruments, Inc., CT, USA) was employed for measuring the enthalpy change during sludge freezing. A freezer (Model RI-102, Firstek Scientific, Inc., Taipei, Taiwan) was used for freezing the sludge samples.

The electrocoagulation experimental apparatus is shown in Fig. 1. The electrolytic cell was a 1-L Pyrex glass reactor, which was equipped with temperature control. Cast aluminum (Al) and iron (Fe) plates (20 cm $L \times 3$ cm W) were

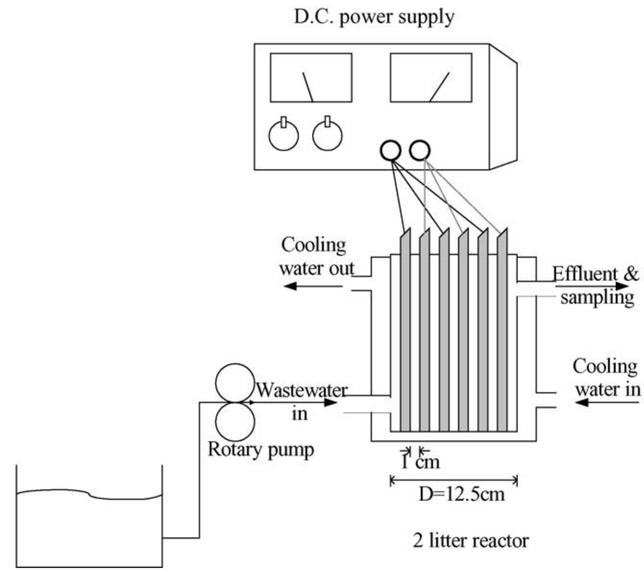

Fig. 1. Schematic diagram of electrocoagulation apparatus used for the treatment of copper chemical mechanical polishing wastewaters.

used as the anode/cathode pair and the electrodes were situated approximately 1 cm apart. Three pairs of electrodes were adopted in the experimental tests, as shown in Fig. 1. The electrode pairs were dipped in the CMP wastewater to a depth of 12 cm, yielding an effective electrode surface area of 72 cm^2. The direct current (DC) power supply was controlled by a voltmeter and was maintained constant at 30 V for most test runs unless noted. A magnetic stirrer was employed in the reactor to maintain well mixing of the CMP wastewater during electrocoagulation process.

During each test run, 1 L of CMP wastewater was placed in the reactor. A steady temperature of 293 K was maintained for all test runs and a constant DC power supply of 30 V was also adopted, as noted earlier. After a test run was completed, wastewater sludge was allowed to settle for at least 3 h. For the freeze/thaw test, 100 mL of the settled sludge was put a plastic bottle. The sludge bottle was then placed in the freezer whose temperature was set at 255 K for all test runs. After 24 h, the frozen sludge bottle was taken out and was allowed to thaw under room temperature conditions for 12 h. Finally, the volumes of surpernatant and settled sludges were then recorded. For sake of accuracy of the test results, two to three sludge bottles were usually tested simultaneously and the average of the observed data was also accepted.

3. Results and discussion

The voltage would be of practical importance and it strongly affected the performances of electrocoagulation. Fig. 2(a and b) illustrate the effect of an applied potential on the copper species removal and final turbidity of wastewater, respectively. It is observed that copper removal increases and but the turbidity of wastewater decreases with time. When a

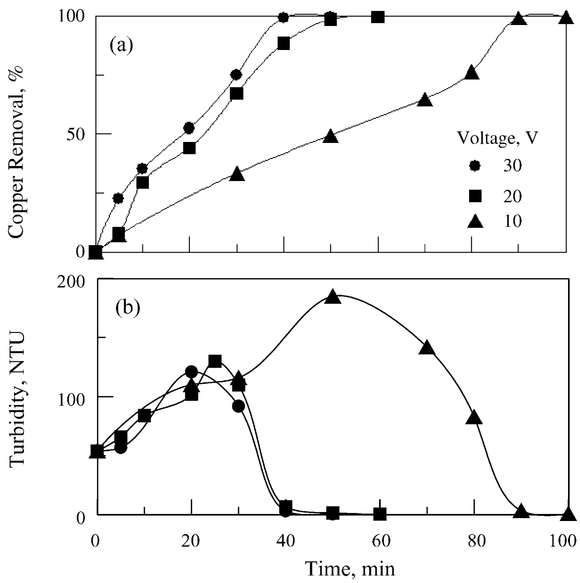

Fig. 2. Effect of applied potential on the removal of copper ions and final turbidity (NTU) of wastewaters with Al/Fe electrode pair at initial conditions of 180 NTU turbidity, copper concentration of 83 mg/L and COD value of 277 mg/L for the treatment of Cu-CMP wastewaters: (a) removal efficiency of copper ions and (b) turbidity of CMP wastewaters.

30 V potential was applied, the time for achieving over 99% copper ions removal was 12 min and the time was 20 min at 20 V. Fig. 2(b) shows that NTU value of final wastewater were 1.1 and 2.1 for 30 and 10 V power supplies, respectively.

In all electrocoagulation test runs, 30 min were found sufficient for floc settling. The amount of sludge collected hence was an important factor in assessing the electrocoagulation performances. Fig. 3(a and b) show the sludge volume and the average sludge particle size, respectively, for various electrode pairs. The corresponding quantities after freeze/thaw conditioning are also shown here. It is apparent that the Fe–Fe electrode pair generated only 83 mL of sludge from the 1 L of original CMP wastewater while the three other electrode pairs yielded a sludge volume ranging from 160 to 215 mL. After freeze/thaw conditioning, the sludge volume was greatly reduced to between 10 and 15 mL. Fig. 3(b) indicates that the Al–Fe pair yielded the smallest average particle size, followed by the Fe–Fe, Al–Fe and Al–Al pairs. After freeze/thaw treatment, there showed a significant increase in the average particle size. These two figures clearly show that freeze/thaw conditioning considerably facilitates the sludge disposal of the electrocoagulation process.

Moisture content of the sludge from after complete settling all exceeded 99%, as demonstrated in Fig. 4(a). After freeze/thaw conditioning, the moisture content was reduced to the ranges of 72 and 82%. Such a sludge moisture content in general was better than that achieved using a mechanical dewatering device. Therefore, comparing Figs. 3(a) and 4(b), considering all aspects of performance, the Al/Fe electrode pair is deemed to be a best choice out of the five electrode combinations tested in the present electrocoagulation. This

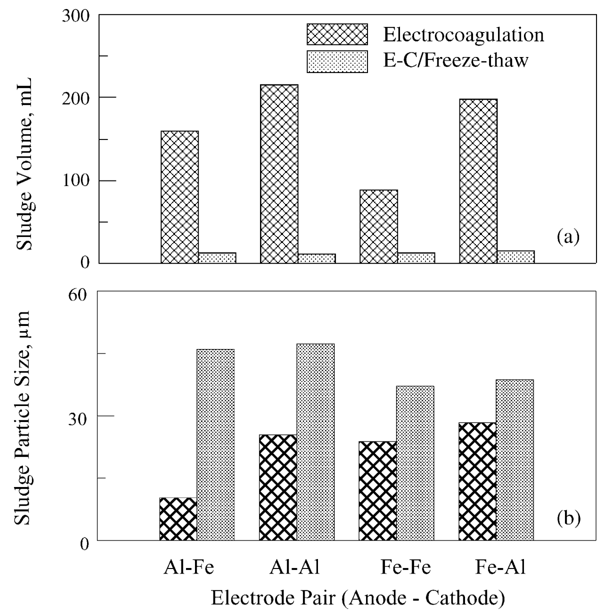

Fig. 3. Effect of before and after freeze–thaw conditioning on (a) sludge volume, (b) average particle size and (c) turbidity for different electrode pairs for the treatment of Cu-CMP wastewaters with initial COD 290 mg/L, turbidity 180 NTU, copper 79 mg/L and 30 min electrocoagulation followed by 30 min sedimentation.

electrode pair offers low final turbidity of wastewater and reasonably low sludge production. Moreover, after freeze/thaw conditions, meltwater has low turbidity and large particle size which was easy for filtration.

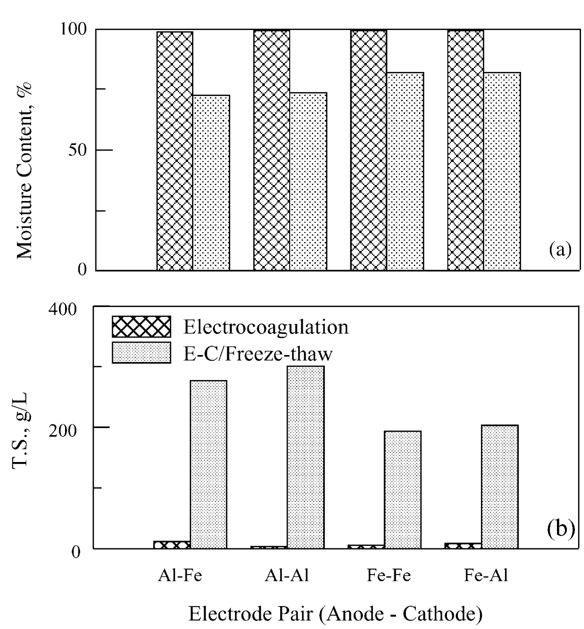

Fig. 4. Effect of before and after freeze–thaw conditioning on (a) sludge moisture content and (b) sludge total solids for different electrode pairs for the treatment of Cu-CMP wastewaters with initial COD of 290 mg/L, turbidity 180 NTU, copper of 79 mg/L and 30 min electrocoagulation followed by 30 min sedimentation.

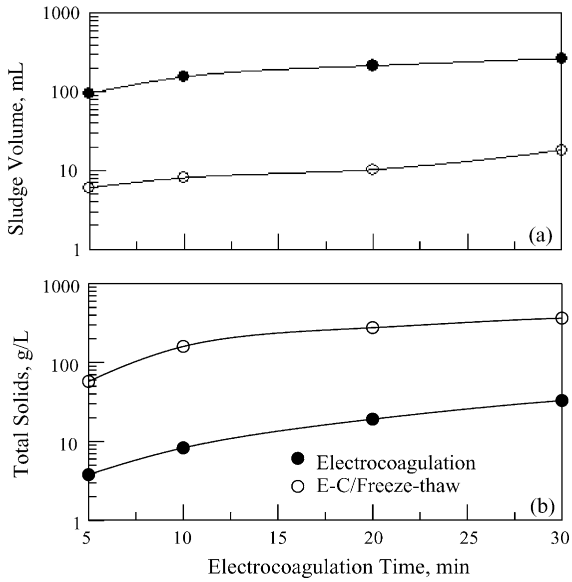

Fig. 5. Effect of before and after freeze–thaw conditioning of (a) sludge volumes and (b) sludge total solids for electrocoagulation time with Al/Fe electrode pair for the treatment of Cu-CMP wastewaters with initial COD of 290 mg/L, turbidity 180 NTU, copper of 79 mg/L and 30 min electrocoagulation followed by 30 min sedimentation.

Addition of electrocoagulation (EC) time to the CMP wastewater however was accompanied by a steady increase in sludge volume as shown in Fig. 5(a). Although rising electrocoagulation time can improve the effect on decontaminating dissolved solids and turbidity of the CMP wastewater, the drawback of sludge volumes after treatment may increase. The problem can be improved dramatically by freeze/thaw condition, which decrease sludge volume 94.3% in average. In this situation, total solids of sludge augmented 15 times in average shown in Fig. 5(b).

The Cu species in wastewater adsorbed in sludge which component by dissolved solids and Al ions, may be released from electrode. Therefore, the concentration of Cu ions in sludge increases with electrocoagulating time. The sludge particle size decreased as dissolved solids content. Because the some particle size can only carry few boundary water, therefore moisture content in electrocoagulated sludge before and after freeze–thaw conditioning decrease with electrocoagulation time, as demonstrated in Fig. 6.

Freeze–thaw conditioning commonly application in the freezing time and the energy required. Longer freezing time may cause an over accumulation of waste in continuously operating factory. Considering the evaluation of operational cost, differential scanning calorimetry was measured and calculated. By using Al–Al and Al–Fe electrodes, electrocoagulated sludges were frozen completely between 267.9 and 269.9 K shown in Fig. 7, it is not far from pure water freezing point. Heat of condensation analysis by field-emission scanning electron microscopy/energy dispersive spectroscopy (FE-SEM/EDS) was shown in Table 1. The

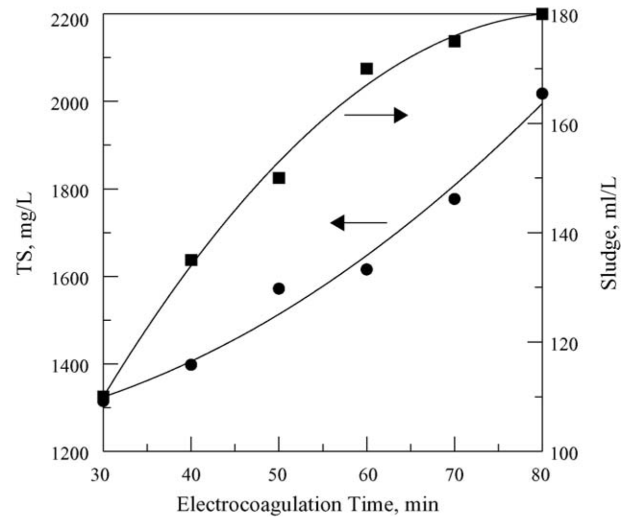

Fig. 6. Effect of electrocoagulation time on the total solids and sludge volumes per liter wastewater of electrocoagulation with Al/Fe electrode pair at 293 K for the treatment of Cu-CMP wastewaters with initial turbidity 180 NTU, and operating 30 V voltage.

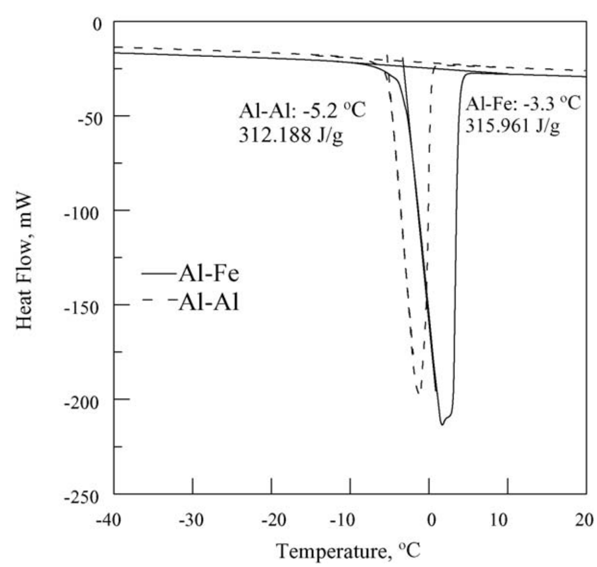

Fig. 7. The DSC curves of the electrocoagulated sludges with Al–Fe and Al–Al electrode pairs for the treatment of Cu-CMP wastewaters in a heating rate of 5 K/min.

measured enthalpy changes of Al–Fe and Al–Al electrode pairs are 288.99 and 285.54 J/g, respectively. Deliberation energy for freezing sludges was produced from every litter of CMP wastewater. Owing to the density of Al–Fe sludges

Table 1
DSC analysis of electrocoagulated sludges produced from Cu-CMP wastewater with a heating rate of 5 K/min.

Electrode pair	Enthalpy (J/g)	Density (g/mL)	Sludge volume (mL/L)	Freeze/thaw energy (J/L)
Al–Fe	288.99	1.39	160	64534
Al–Al	285.54	1.01	215	62005

was higher than the one of Al–Al electrode pairs' sludges, the sludges produced from Al–Fe electrode pairs need more heat energies for freezing. Therefore, even the volumes of Al–Fe sludges less than the ones of Al–Al electrocoagulated products, every litter CMP wastewater still needed more heat energies to be frozen.

4. Conclusions

Electrocoagulation treatment of Cu-CMP wastewater from a semiconductor manufacture was investigated. This method was employed for removal of ultrafine oxide particles, CMP wastewater contamination of COD and copper ions, accessorily freeze–thaw condition for minimizing sludge volumes. Based on the results of experimental tests, the conclusions can be described as following:

(1) Electrocoagulation of the CMP wastewater was able to realize a 96% reduction efficiency of turbidity (NTU) and over 96–99% copper ions removal efficiency with an applied potential of 30 V in 30 min. The COD removal efficiency was achieved acceptably of 88.7%, which was much higher than the one of wastewater effluent standard of 100 mg/L for Taiwan's legislation. The effluent wastewater was clear and can be considered for recycling in the Cu-CMP processes.
(2) Freeze–thaw condition decreases the sludge volumes, increase the particle size and total solids from electrocoagulation process effectively. The decreasing sludge volumes were over 94% in average, independently what kind of electrode pairs were used.
(3) Due to the reducing turbidity, using alumina anode was better than iron ones. $Fe(OH)_2$ was formed during the electrocoagulation process and the particles much more difficult to settle than those formed in the other cases.
(4) By the DSC analysis, iron cathode was needed more heat of condensation than alumina cathode.

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