Treatment of Chemical Mechanical Polishing Wastewater Using Electro-Chemical Processes

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Abstract
Treatment of spent CMP slurry has become increasingly critical to waste management for IC fabs. In this study, we designed and operated a vertical-flow electro-chemical cell to investigate the particle (fume silica) removal efficiency, and to examine the physicochemical properties of the particle suspensions before and after treatment. In particular, the studies were categorized into three distinct phases, namely electro-coagulation, electro-decantation, and chemical coagulation of electrolyzed suspensions. The results showed that all three phases were favorable to enhance particle separation from the dilute suspensions, with different mechanisms that could be induced under appropriate operating conditions. The merits demonstrated by these processes bear important implications to treatment strategies depending on the objective of the waste management. This article described the detail experimental results associated with the different mechanisms occurred in the proposed electro-chemical pretreatment process.

Introduction
Chemical mechanical polishing (CMP) has become an integral process in the manufacturing of multi-level integrated circuit involving both dielectric barrier layer and metal interconnection. Due to the nature of CMP process, however, an enormous quantity of ultra-pure water is required, and consequently a large volume of dilute spent slurry is generated; the latter of which often causes operational problems in wastewater treatment facilities. Presently, majority of the chip-making fabs still relies on the conventional coagulation-flocculation process to treat CMP wastewater. As a result, system operators frequently need to increase the coagulant dosage, or to prolong the settling time in order to achieve the necessary particle removal efficiency. The overall objective of this study, therefore, is to propose an electro-chemical treatment method for CMP wastewater, and to evaluate the solid-liquid separation efficiency under various operating conditions.

In principal, slurry abrasives possess highly negative surface charge and repel adjacent particles when they are immersed in base solutions. Particle dispersed in polarized medium (e.g., water or alcohol) may also result in stable suspense in the solution by carrying surface electrical
charges. The dispersibility of the suspensions can be determined from important physicochemical slurry characteristics such as pH value, conductivity, and zeta potential. For instance, pH value affects the surface charged of the particle; conductivity dictates the extent of metal ions adsorbed on particle surface; and zeta potential is indicative to the surface potential of the particle. In this regard, chemical coagulation generally follows particle destabilization mechanisms of adsorption charged neutralization, electric double-layer compression, or sweep coagulation, all of which involve reduction of electrostatic repulsive force between adjacent particles. Therefore, external driving forces by means of an electric field to induce polarization and to reduce the stabilization of the dispersion particle [1] should theoretically alter the surface properties of the particles, and consequently influence the chemical coagulation conditions. In this work, the feasibility of the electro-chemical coagulation process for treating a well-defined CMP suspension will be evaluated, and its performance will be compared to those without electrolytic pretreatment.

Due to the experience of difficulties to treat CMP waste slurry by chemical coagulation and flucululation method, a number of processes have been proposed in recent years to improve the removal efficiency of the fine particles. Relevant studies on chemical coagulation and electro-coagulation for treating CMP wastewater have been reported in the past few years. Matteson et al. [2] developed a model to simulate the kinetics of electro-coagulation process for ultra-fine particles. Their model was based on the concept that particles are electrophoretically moved toward the proximity of anode, followed by charge neutralization with ions that had been electrolytically generated, leading to particle agglomeration and settling. Belongia et al. [3] investigated the feasibility of applying an electric field to agglomerate charged particles without chemical additives in CMP wastewater. They observed two distinct solid separation phenomena by means of “electro-decantation” and “electro-coagulation”. The occurrence of these phenomena strongly depends on the type of slurry and well as the conductivity of the suspension. In the presence study, both mechanisms will be studied, and their implications to the treatment applications will be discussed in this article.

Materials and Methods

**CMP wastewater preparation**: Silica suspensions were prepared by diluting a commercially available, KOH-based CMP slurry containing 25 % (wt/vol) fume silica. In order to simulate the CMP wastewater from IC manufacturing industries, the original slurry was diluted to 0.05% with DI water, corresponding to a turbidity of approximately 70.7 NTU in our experiment. The physicochemical characteristics such as ultra-fine particle, high pH value, low conductivity and extremely negative surface potential were also similar to the actual CMP wastewater.
Reactor configuration: An 8-L continuous-flow reactor interpolated with five electrodes (20 cm long, 14 cm wide) was designed and fabricated to perform the experiments. The electrodes submerged in the suspensions were arranged equidistant to create vertical flow channels with uniform electric field distribution. The suspension was pumped into the reactor continuously at variable rates to examine the effects of hydraulic retention time. Intensity of electric field up to 10 V/cm was typically applied to the suspension. Both stainless steel and iron plates were used as the electrodes for the purpose of observing the extent of in-situ coagulation with Fe ions released from the electrode.

Jar test experiments: Jar tests (PB-700 Jar tester, Phipps & Bird Inc.) were performed on the synthetic CMP solutions to evaluate the required coagulant dosage and to determine the predominant coagulation mechanisms. The mixing conditions were provided with 1 minute rapid mixing (200 rpm, G = 350 s⁻¹), followed by 20 minutes slow mixing (30 rpm, G = 25 s⁻¹). Polyaluminum chloride (PACl) was used as the chemical coagulant due to its proven effectiveness for a variety of colloidal particles. The stock PACl solution of 1000 mg/L (as Al) was freshly prepared by dissolving the reagent-grade PACl (Showa Chemicals Inc., Japan) in the DI water. All coagulant dosages reported in this paper were in the unit of mg/L as Al.

Experimental strategies: The experiments involved different arrangement of the electrochemical cell in order to demonstrate the performance by three distinctly different processes, namely 1) chemical coagulation of electrolyzed suspension, 2) in situ electro-coagulation with Fe ions, and 3) electro-decantation without chemical interaction. The experimental conditions for these processes and the characteristics of the synthetic CMP wastewater are summarized in Table 1.

Analytical techniques: The particle size distribution was measured by a Dynamic Light Scattering (UPA-150) with an effective range between 0.001 µm and 6 µm. Zeta potential was determined by means of a Zeta Potential Analyzer (Zeta Plus) using Doppler shift analysis with laser light scattering. Turbidity measurement was performed with a Hach ratio/XR turbidity meter. Triplicate samples were typically prepared and analyzed to ensure data precision.

Results and Discussion
Characterization of synthetic CMP wastewater

When the SiO₂ slurry is in aqueous alkaline media, hydrolysis of Si-O-Si bonding is strongly enhanced due to the increasing OH⁻ activity as shown in Eq. 1 and Eq. 2 [4], and therefore the stability of the colloidal system with large repulsive force is highly dependent on the ambient pH.

\[ \text{Si-O-Si} + \text{H}_2\text{O} \rightleftharpoons \text{Si-OH} \]  \hspace{1cm} \text{Eq. 1}
In this study, we observed that when nitric acid was added, the negativity of the surface (zeta) potential gradually decreased, and reversed to positive at pH between 2 and 3. In addition, particle size distribution grew correspondingly, especially under acidic condition. The silica particles submerged in base solutions such as KOH or NH₄OH tend to adsorb OH⁻ on particle surface and form Si-O⁻ on the surface extension. Therefore, increasing the OH⁻ concentration leads to greater degree of negative surface potential. When acid is added, the OH⁻ ions surrounding the abrasives are neutralized with H⁺, forming relatively unstable agglomerates. It was also noted that, when adding nitric acid to reduce the pH, the solution conductivity also increased. This could lead to compression of electric double layer by the bulk of nitric acid [5].

Separation of solid from the bulk liquid by adjusting pH by itself to reduce particle stability was not effective. Mixing with chemical coagulants or salts for abrasive aggregation is thereby needed to disrupt the dispersion stability. Fig. 1 shows the change of mean particle size distribution and zeta potential with reference to the solution pH when 2 mg/L of PACl was mixed (rapid mix for 30 sec) in the synthetic solution. The results indicated that the pH must be maintained in the range between 4 and 6 to have significant growth in the particle size. Although the zeta potential measurement at pH beyond this range (3<pH<8) also shown particle instability, it is believed that the primary hydrolysis products such as Al(OH)²⁺, Al(OH)₃⁺ and Al(OH)₃ were formed from PACl and interacted with the particles at suitable pH of 5~6 [6]. In addition to zeta potential and particle size measurements, the “sludge volume index” (SVI), defined as the solid settling volume in relation to the liquid volume, can also reflects the coagulation mechanism. During this experiment, the SVI of the settling floc remained within 5~6% with increases in the PACl dosage. The slight variation in SVI and conductivity – the former of which would otherwise have increased significantly had “sweep flocculation” occurred, and the latter of which would have varied substantially had double layer compression occurred – strongly suggested that adsorption charge neutralization was the predominant mechanism controlling the particle coagulation with PACl.

Performance of Chemical Coagulation of Electrolytically Treated Wastewater

Fig. 2 shows the residual turbidity in relation to coagulant (PACl) dosage at various overflow rates of bulk liquid (i.e., synthetic CMP wastewater). It can be seen that, at lower overflow rates (<0.6 m/hr), approximately 3 mg/L of PACl was required to reduce the residual turbidity under 5 NTU; higher overflow rates (less reaction time) required even larger quantity of dosage to achieve similar turbidity reduction. These results serve important implication to fabs’
treatment facility because either large reactor or large sludge volume must be dealt with.

In an effort to reduce the chemical dosage or the settling volume for chemical coagulation, we postulated that by applying an electric field would induce polarization and reduce the dispersion stabilization. Therefore, the solid removal efficiency by electro-chemical coagulation process was evaluated in comparison with that by chemical coagulation without electrolytic pretreatment. Fig. 3 shows a set of the comparative profiles for chemically treated CMP wastewater with and without electrolytic pretreatment. Both experiments involved the use of 3 mg/L of PACl with solution pH maintaining at 6.8. We observed that the residual turbidity of electrolytically treated wastewater was much stable than that without electrolytic pretreatment under similar surface loading and chemical dosage. The residual turbidity of the electrolyzed solution decreased to approximately 5 NTU after 5 min of settling time. Extending settling time to 20 min led to supernatant that was clearer than potable water. These results suggest that the electro-chemical treatment offers the potential advantage of reducing both reactor volume and sludge volume by more efficient settling and less chemical dosage. It is interesting to note, however, that these results were achieved even though the surface potential, particle size, conductivity, and pH did not change significantly after electrolyzing. Therefore, the chemical and structure characteristics of the particles after electrolytic treatment were currently under investigation to rationalize the results.

The Effects of Electro-Coagulation for Solid Removal

Electro-coagulation induced by ferrous ions was conducted as the second phase of the experiments using iron anodic electrodes. The experimental variables include the field intensity (in applied current), the hydraulic retention time, and the settling time. A settling time of 80 min was found to be sufficient for all residual turbidity to reach a steady-state condition. Fig. 4 shows the extent of turbidity reduction in relation to the various retention time and applied current at pH 9.7 and low conductivity range (53~56 μs/cm). It can be seen that the turbidity reduction was strongly dependent on both electric field intensity and retention time. The patterns of the profiles also suggest that there exists a kinetic relationship between these two variables that lead to an extent of solid removal. Therefore we inferred that the electric field strength represented by the applied current dictates the quantity of ferrous ions available for coagulation with the particles. The hydraulic retention time, by contrast, determines the transport of metal ions and particles that strongly influences the re-deposition of coagulated species on the anodic electrodes in the electrochemical cell. Therefore, shorter retention times (or faster flowrates) render the process kinetically unfavorable, and leads to lesser extent of turbidity reduction.
During the experiments, we also observed that excessive quantity of ferrous ions was detrimental to the process performance. This observation implies that an appropriate range of operating field strength and conductivity exist in order to achieve optimum results. The fact that the effluent water exhibited severe yellowish color as the aqueous conductivity was increased from ~53 to ~150 µs/cm confirmed this situation. These results bear significant engineering implication because a relative narrow operating range must be maintained for desirable outcome.

The Effects of Electro-Decantation for Solid Separation

When stainless steel electrodes replaced iron electrodes at the anode, the phenomenon known as “electro-decantation” was induced. Shortly after applied electrical field, layers of condensed slurry could be clear observed at the bottom of the channels. Electro-decantation was thought to be a result of the charged particles migrating electrophoretically toward the opposite-charge electrode, thereby increasing the localized solid density that leads to solid sinking [3]. Fig. 5 showed the quality of the electro-decanted particles formed under a fixed electrical field with various hydraulic retention times. Samples were extracted from the exact same spot at the bottom of the cell. It can be observed that the decanted particles became increasingly condensed (as in turbidity) with the settling time before reaching a plateau at some point. Furthermore, the hydraulic retention time obviously had substantial impact on both the extent of solid condensation and the duration to reach a steady-state plateau. In this study, the condensed solids at retention time of 100 min showed a turbidity of ~400 NTU, which was roughly two-folds over that at retention time of 30 min, and nearly 6-folds more concentrated than the original slurry.

The formation of condensed slurry at the bottom of the cell causes operational problems because the hydraulic force continuously disturbed the top of the condensed layer, and consequently carried the particles out of the system. As shown in Fig. 6 (solid line), this problem led to ineffective removal with respect to residual turbidity of the effluent water. In order to deal with this problem, we had to regularly extract the condensed solids from the cell. This effort apparently cleared the obstacle, as the residual turbidity gradually reduced below 10 NTU (dotted line). In addition, analysis of the condensed solids showed a similar particle size distribution and purity to the original slurry. These results imply that, if the decanted particles can be effective separated from the bottom of the vessel, the possibility of recycle and reuse of these slurries can be greatly enhanced.

Conclusion

This study investigated the application of a continuous-flow, vertically channeled electrochemical process to induce solid separation from the CMP wastewater. Three distinct processes,
namely chemical coagulation of electrolyzed suspension, electro-coagulation with anodic iron electrode, and electro-decantation with stainless steel electrodes, were demonstrated for their effects on particle removal. The former two methods were capable of reducing effluent turbidity under 1 NTU, but their optimum operating ranges were rather narrow. The electro-decantation did not achieve the same level of residual turbidity, yet the easy of operation and the potential for slurry reuse makes it a viable treatment method.

References


Table 1. The experimental conditions and the characteristics of the synthetic CMP wastewater

<table>
<thead>
<tr>
<th>Item</th>
<th>Chemical coagulation of electrolyzed suspension</th>
<th>Electro-coagulation</th>
<th>Electro-decantation</th>
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<tr>
<td>pH</td>
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<td>zeta potential (mV)</td>
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<td>mean particles size (nm)</td>
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<td>turbidity (NTU)</td>
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<tr>
<td>conductivity, µS/cm</td>
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<td>50, 100, 150</td>
<td>50, 100, 150</td>
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<td>retention time (min)</td>
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<td>20, 30, 60</td>
<td>20, 30, 60</td>
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<td>applied current (A)</td>
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<td>0.5~2 @ 0.5 interval</td>
<td>0.5~2 @ 0.5 interval</td>
</tr>
<tr>
<td>Electrode type</td>
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<td>Iron anodic</td>
<td>S.S. anodic</td>
</tr>
<tr>
<td>PACl dosage (mg/l)</td>
<td>0~3 @ 0.5 interval</td>
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<tr>
<td>overflow rate (m/hr)</td>
<td>0.15~1.2</td>
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Figure 1. Variation of particle size and zeta potential with pH in the presence of 2 mg/L PACl as coagulant.

Figure 2. Residual turbidity profiles vs. PACl dosage for chemical coagulation of synthetic CMP wastewater at various overflow rates.

Figure 3. Residual turbidity with respect to settling time for chemically treated wastewater with and without electrolytic pretreatment.

Figure 4. Effects of applied current to the turbidity reduction during electro-coagulation with various retention times.

Figure 5. The turbidity of concentrates extracted from the electrochemical cell during electro-decantation.

Figure 6. Turbidity reduction by electro-decantation with and without extraction of concentrates.