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Chemical evidences for the optimal coagulant dosage and pH adjustment of silica removal from chemical mechanical polishing (CMP) wastewater

Wen-Hui Kuan [a], Ching-Yao Hu [b,*]

[a] Department of Safety Health and Environmental Engineering, Ming-chi University of Technology, 84, Gunjuan Road, Taishan, Taipei Hsien 24301, Taiwan, ROC
[b] School of Public Health, Taipei Medical University, 250 Wu-Xin Street, Taipei, Taiwan, ROC

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ABSTRACT

The coagulation behavior of aluminum salts in $SiO_{2(s)}$-containing chemical mechanical polishing (CMP) wastewater was investigated using jar tests and with reference to the coordination chemistry of Al(III) and Si(IV). The results of the jar tests show that the alum dosage did not influence the removal of silica when more than a particular amount of coagulant was added. However, the removal efficiency of the CMP wastewater depended more strongly on pH than on coagulant dosage. Insight into these results was given by the surface complexation model/surface precipitation model (SCM/SPM) and electrophoresis measurements. Simulation results thus obtained demonstrate that the Al(III) released from the coagulant underwent a two-stage reaction in a narrow range of 1.5 pH under under-saturated solution conditions with respect to the Al-hydroxide solid phase. At low pH (3.5–4.3), the Al(III) prevents the natural dissolution of $SiO_{2(s)}$ particles by forming bi-nuclear surface complexes which energetically disfavor the simultaneous removal of two metal centers. In the pH range 4.3–5, the surface precipitation reaction dominated, and both Al(III) and Si(IV) formed a new oxide film in the original surface, protecting against dissolution of $SiO_{2(s)}$ by OH^-.

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1. Introduction

Chemical mechanical polishing (CMP) is a highly favored planarization technology in the manufacturing of multilevel integrated circuits (IC). Both dielectric and metal films on IC are planarized using this method, but with different slurries. Dielectric films such as SiO_2 are generally planarized using highly alkaline, silica-based slurries, in which silica particles are submicron in size and so may be regarded as being in colloidal regime.

Available information demonstrates that CMP process consumes as much as 40% of the ultra-pure water used in semiconductor manufacturing and generates 30–50 L of waste slurry per 200 mm wafer at each level of planarization [1–5]. The major contaminants in the CMP wastewater are many nano-sized particles. The wastewater from dielectric planarization is a suspension of silica particles at a concentration of 500–2000 mg/L [1,6]. To satisfy the requirement of the recycling of 80% of water for an IC factory, and to comply with the environmental regulations of Taiwan, ROC, CMP wastewater must be properly treated to separate solids from the liquid dispersions.

Coagulation/flocculation is one of the most prevalent procedures for treating CMP wastewater in an IC foundry [7]. Because of the need to recycle large quantities of water, operators of wastewater treatment plant usually add over-dosing coagulant to form sufficient hydroxide precipitates to ensure that the particles are effectively separated from the water [4,8]. This approach is commonly known as "sweep flocculation" and is especially important when the particle concentration is low and interparticle collisions are infrequent [9]. This approach produces large amounts of sludge and increases its treatment cost. Membrane separation is another procedure for treating CMP wastewater. However, a number of investigations have demonstrated that a pre-coagulation/flocculation process before membrane separation must be performed because the high concentration of Si in raw CMP wastewater causes membrane fouling and substantially shortens the lifetime of the membrane [8,10]. Moreover, since silica is highly soluble ($\log K_{sp} = -2.74$, [11]) the CMP wastewater also contained considerable dissolved Si, which may re-precipitate and cause membrane fouling in a reverse osmotic (RO) process during the regeneration of ultra-pure water from the wastewater. Accordingly, the effective removal of particulate and dissolved Si is necessary to fulfill economically the strict requirements of the quantity and quality of recycled water.

The interaction between silica substrate and Al(III) in solution has for decades preoccupied researchers not only in natural and

* Corresponding author. Tel.: +886 2 27361661x6514; fax: +886 2 27384831.
E-mail addresses: whkuan@mail.mcut.edu.tw (W.-H. Kuan), cyhu@tmu.edu.tw (C.-Y. Hu).

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basic science (geochemistry, colloids, and other fields) but also in applied science and technology (as in the fields of zeolites, catalysts, material science, environmental science and others), but several questions remain unanswered [12–17]. Stumm [18] identified the general trend that (anionic) ligand adsorption increases the dissolution rate of oxides or silicates while cation adsorption reduces them. More precisely, alkaline ions increase the rate of silica dissolution, whereas multivalent ions, such as Zn^{2+}, Cu^{2+}, Al^{3+}, and Fe^{3+}, inhibit dissolution [19,20]. However, Bouallou et al. [21] concluded that no straightforward answer exists to the general question of whether Al enhances or reduces the dissolution of pure amorphous silica; each case should be considered on its own merits. Duan and Gregory [9] noted that dissolved silicic acid can promote or prevent the process in which aggregates of primary aluminum crystallites are formed by the hydrolysis of Al(III) salts, depending on the solution pH and the concentration of silicic acid. Besides the uncertainty in the effects of Al(III) on the dissolution of silica, the sorption type of Al(III) on the silica surface, which is the first stage of the interactions between Al(III) and silica surface, also plays a significant role in the overall interaction processes. Lartiges et al. [22] adopted NMR to investigate the flocculation of colloidal silica with hydrolyzed aluminum and determined that the formation of four coordinated aluminum retained at the silica surface as negatively charged aluminosilicate sites. These sites are potential anchors for aluminum polycations; therefore, the aggregation of silica particles proceeds via either charge neutralization or bridging. Stumm [18] stated that bi-nuclear surface complexes formed from multivalent cations are efficient inhibitors of oxide dissolution, because they form bi- or multi-nuclear inner-sphere surface complexes that can bridge two or more metal centers in the surface lattice. Houston et al. [17] proposed the formation of bidentate tetrahedral Al at the silanol surface during the sorption of Al(III) on the silica surface. However, bi-nuclear complexes and bidentate complexes differ substantially in their coordination chemistry [23].

The model system is still highly complicated and fingerprint experiments must be performed to elucidate various conditions. Any link between the treatment of real silica-containing CMP wastewater with the model system of silica substrate is currently lacking and the optimal operating conditions must be determined theoretically and systematically to help the operators of wastewater treatment plants. Accordingly, the objectives of this study are (1) to determine the optimal coagulant dosage and pH for treating CMP wastewater; (2) to model and predict the optimal operating conditions; (3) to interpret chemically and give direct evidences of the optimal operating conditions.

2. Materials and methods

2.1. Characteristics of wastewater

Raw wastewater was sampled from the effluent of oxide layer CMP in an IC manufacturing factory in the south of Taiwan. The main products of this factory are 12 in. wafers, with a designated output of 20,000 wafers/month. Table 1 presents the characteristics of the wastewater. Fig. 1 shows the number in class and accumulative number distribution of particle sizes (Malvern, Zetasizer 3000HSA) in raw wastewater. The particles of the CMP wastewater were substantially composed of the nano-sized $SiO_{2(s)}$ existing in the original CMP agents and the $SiO_{2(s)}$ detritus arising from the planarization process on the dielectrical SiO_2 layers of integrated circuits. Therefore, the particles size shows a bimodal distribution of number attributed respectively to nano-sized $SiO_{2(s)}$ of CMP agents and micro-sized detritus of SiO_2 layers. Although the particles larger than around 10,000 nm represent overwhelming proportion on a mass basis, the abundant numbers (70% of total particles) of the smaller particles prohibit the effective treatment of CMP wastewater.

Table 1
Characteristics of oxide layer wastewater of CMP.

pH	8.54
Turbidity (NTU)	315.5
Conductivity (μs/cm)	247
Total solid (g/L)	3.836
Total Si (mg/L)	1580
Dissolved Si (mg/L)	398
Zeta potential (mv)	−41.6
Specific surface area of solid (m^2/g)	63
Minimum particle size (nm)	42[a]

[a] The minimum particle size was extracted from the measurement of particle size distribution shown in Fig. 1.

2.2. Batch experiments

Batch experiments were conducted in 1 L beakers that were filled with 500 mL wastewater, and placed on a multiple stirring apparatus with a stirrer with an adjustable speed. The desired quantity of coagulant was added and/or the desired pH value was obtained by adding NaOH and H_2SO_4 solution to each sample. The contents of the beakers were mixed at a high speed of 800 rpm for 5 min and then at a low speed of 30 rpm for 15 min. Agitation was then stopped and flocs were allowed to settle for 30 min. After the reaction, a subsample of the suspension was taken to measure total Si content (by digestion using the standard method 3030F and analyzed using standard method 3120B [24]), turbidity (WTW, Turb 350IR) and electrophoresis (Malvern, Zetasizer 3000HSA); some of the suspension was centrifuged (Kubota 6800) at 20,000 rpm for 15 min and the supernatant was passed through a 0.2 μm membrane filter to measure the amount of soluble Al and soluble Si using an ICP-AES (PerkinElmer, Optima 2000DV). A jar test was designed and conducted in the laboratory to determine the optimal coagulant dosage and operating pH during coagulation in the wastewater plant. The following three procedures were implemented; (1) determining the rough coagulant dosage without adjusting pH, (2) determining the optimal pH at fixed coagulant dosage, and (3) ascertaining the coagulant dosage with fixed pH.

The prevalent coagulant alum ($Al_2(SO_4)_3 \cdot 18H_2O$) was employed herein. Since only the Al content in alum influences the coagulation process, the alum dose is expressed as an Al dose and the conversion ratio is 0.081 mg Al/g alum.

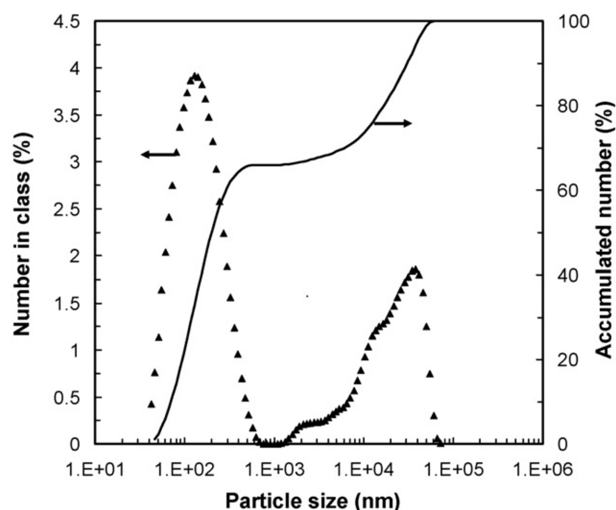

Fig. 1. The distribution of particle size in raw wastewater.

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