The 6th International Symposium on East Asian Resources Recycling Technology
October 23 - 25, 2001, Gyeongju (慶州), Korea
ISBN: 89-952527-0-7 93530

Recovery of ultrafine particles from Chemical-Mechanical Polishing wastewater discharged by the semiconductor industry

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This study uses traditional alum coagulation and sedimentation process to treat CMP wastewater from cleaning after polishing. The primary goal is to successfully recycle both solid fines and water for semiconductor manufacturing. Results indicated that CMP wastewater may be successfully treated to recover clean water and fine particles by alum coagulation. The optimum operating conditions for coagulation are as following: alum dosage of 10 ppm, pH at 5, rapid mixing speed at 800 rpm, 5 min rapid mixing time, and long slow mixing time. The treated water with low turbidity and an average residual aluminum ion concentration of 0.23 ppm may be considered for reuse. The settled sludge after alum coagulation contains mainly SiO2 particle with a minor content of aluminum (1.7 wt%) may be considered as raw materials for glass and ceramic industry.
Keywords: Chemical mechanical polishing, Alum, Coagulation

Introduction

The Integrated Circuits (IC) industry in the Hsinchu Science Park (Taiwan) in 1999 takes up 55.4% of the total revenue [1], and it is 3.85% of the national production volume in Taiwan[2]. The rapid and complex development of IC requires multi layers of connected metal lines to shorten the delay time, to enhance the working speed of the devices, and to increase the surface usage capacity. Chemo-mechanical Polishing CMP has become an important point of research along with those requirements [3.4]. The parameters which will affect polishing include: rotation speed, the material of the polished device, slurry concentration, slurry viscosity, temperature and pH, etc.. In practice, these parameters are interrelated complicatedly with each other during polishing and the polishing material is crucial towards the successfulness of CMP processing. Among the material, the polishing slurry creates the highest impact. Ultra-pure water is used as a cleaning agent for wafer refinement, which includes masking, film engineering process, photo, etching, polishing and cleaning of other tools in semiconductor processing. This is why tremendous amount of water is necessary for semiconductor manufacturing. Treatment methods for large amounts of processed and non-processed wastewater from semiconductor manufacturing are different. For example, the source of wastewater in CMP processing can be divided into used polishing slurry and wastewater from cleaning after polishing [5,]. The former is mainly used slurry containing particles from the polishing pad, and the latter is the wastewater produced from cleaning the polished wafers (mostly ultra-pure water). Because there is a clear difference in solid concentration between these two wastewaters, wastewater collection will be much more effective if separate ducts are designed in manufacturing plants. This study uses traditional alum coagulation and sedimentation process to treat CMP wastewater from cleaning after polishing. The primary goal is to successfully recycle both solid fines and water for semiconductor manufacturing.

Alum has been proven to be an effective coagulant for the removal of turbidity and color for drinking water treatment [6]. It is thought the alum can coagulate particles in water by means of charge neutralization and enmeshment in aluminum hydroxide precipitate. The exact mechanism depends on the pH, mixing conditions, coagulant dose, type of contaminants and other factors. For low pH conditions, or for high particle concentration of suspensions, charge neutralization is the main destabilization mechanism. Enmeshment is thought to be the important mechanism when pH is high (between 7 and 8), the turbidity is low, and a high dose of alum is used.

Experiment

Materials

The CMP wastewater sample used in this study comes from a semiconductor IC fabrication plant in Hsinchu Science Park. The physical-chemical properties of wastewater sample are shown in Table 1. A SEM image of particles in CMP wastewater sample is shown in Figure 1.
Analytical grade aluminum sulfate, Nitric acid and sodium hydroxide obtained from Kano Chemical Co. were used as received.

Test procedure

500 ml samples of wastewater were used in

coagulation test. Rapid mix was simulated by a high speed stirrer (Eyela model A, Japan). A measure volume of alum solution was injected into the vortex created by the high speed stirrer (90rpm) during rapid mixing. After 5 min rapid mixing the stirrer speed was reduced to 30 rpm for 15 min slow mixing. The sample was taken after 45 min sedimentation and was analyzed for turbidity by a HACH 2100A turbidimeter and expressed in Nephelometric Turbidity Units (NTU).

Results and Discussion

Effect of alum dose

Considering the relationship between Al3+ solubility and pH, wastewater samples adjusted to pH 5.5 were used in the determination of optimum alum dose. Figure 2 presents the residual turbidity after coagulation at various alum dosages. At an alum dosage range between 6 ppm and 10 ppm, the turbidity may be reduced to under 7.5 NTU. For alum dosages higher than 10 ppp, slight increase in residual turbidity was observer. The optimum alum dose for CMP wastewater sample used in this study was determined to be 10 ppm at pH 5.5.

Effect of pH

The optimum alum dose (10 ppm) obtained on previous tests was applied to determine the optimum pH for the coagulation of the CMP wastewater. Effect of solution pH on the residual turbidity after coagulation was shown in Figure 3. It is evident that the optimum pH range is 4-6. This pH range generally corresponds to the charge neutralization mechanism of alum coagulation. The relatively high particle concentration of this CMP wastewater (184 NTU) probably made charge neutralization as the main destabilization mechanism. Dramatically increase in residual turbidity above pH 6 was observed in Figure 3 due to the formation of negatively charged aluminum species at high pH. The optimum pH for CMP wastewater sample used in this study was determined to be 5.

Effect of mixing conditions

Figure 4 demonstrates the effect of rapid mixing intensity on the coagulation of CMP wastewater. Results indicate that coagulation of CMP wastewater is not very sensitive to rapid mixing intensity. However, an optimum rapid mixing speed of 800 rpm may be observed in Figure 4.

Figure 5 shows the effect of rapid mixing time on the coagulation of CMP wastewater. Results indicate that coagulation of CMP wastewater is not very sensitive to rapid mixing time. However, a too short rapid mixing time (> 5 min) will result in inadequate mixing of alum in water and poor coagulation. A 5 min rapid mixing time is consider to be optimum in Figure 5.

Figure 6 shows the effect of slow mixing time on the coagulation of CMP wastewater. Results indicate that slow mixing did help coagulation of CMP wastewater. Turbidity removal increases with increasing slow mixing time. A long slow mixing time is recommended in the coagulation of CMP wastewater.

Conclusion

CMP wastewater may be successfully treated to recover clean water and fine particles by alum coagulation. The optimum operating conditions for coagulation are : alum dosage of 10 ppm, pH at 5, rapid mixing speed at 800 rpm, 5 min rapid mixing time, and long slow mixing time. The treated water with low turbidity and an average residual aluminum ion concentration of 0.23 ppm may be considered for reuse. The settled sludge after alum coagulation contains mainly SiO2 particle with a minor content of aluminum (1.7 wt%) may be considered as raw materials for glass and ceramic industry.

Reference

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Appendix

Table 1. Characteristics of CMP wastewater used in this study

	CMP wastewater
PH	9.4
Turbidity	184 NTU
Solid Content	0.3%
Zeta Potential	-61.4 mV
Particle Size Range	45-550 nm

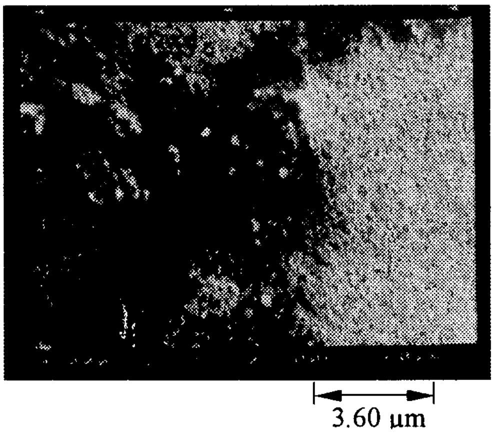

Figure 1. SEM image of particles in CMP wastewater sample.

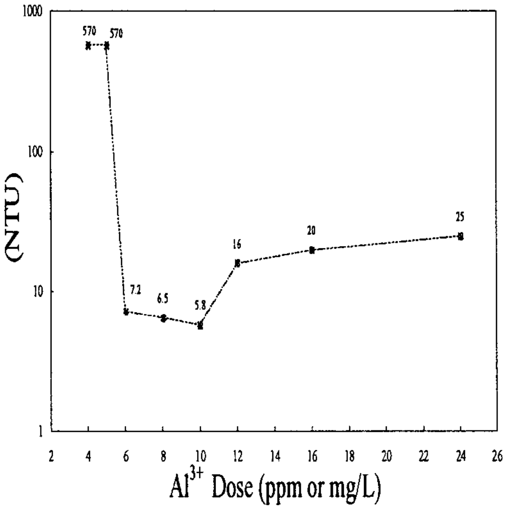

Figure 2. Residual turbidity after coagulation at various alum dosages.

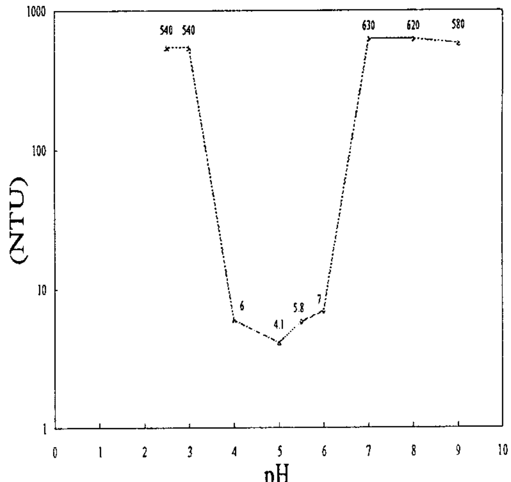

Figure 3.Effect of pH on the residual turbidity after coagulation.

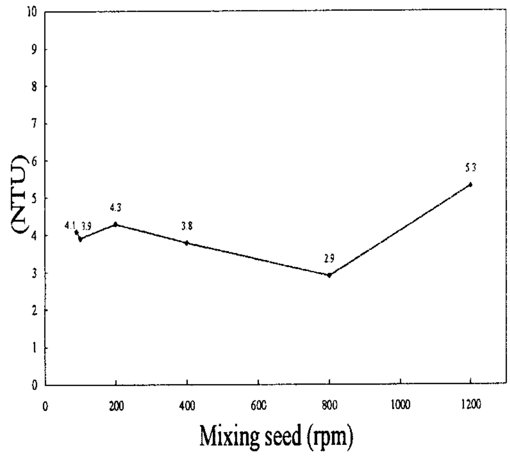

Figure 4 Effect of rapid mixing intensity on the coagulation of CMP wastewater.

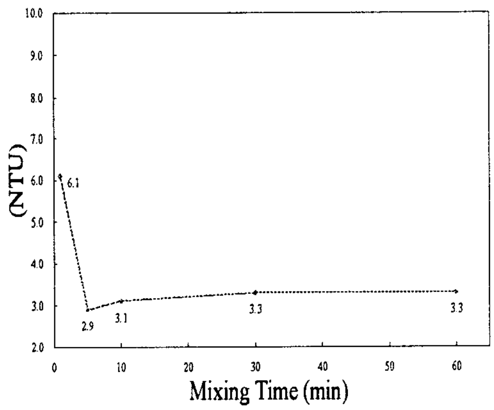

Figure 5 Effect of rapid mixing time on the coagulation of CMP wastewater.

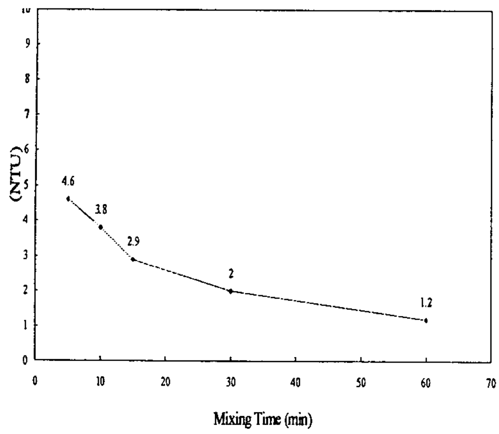

Figure 6 Effect of slow mixing time on the coagulation of CMP wastewater.