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The Condition of Optimum Coagulation for Recycling Water from CMP Slurry

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Water usage in the semiconductor industries is dramatically increased by not only using bigger wafer from 8inches to 12 inches but also by adapting new process such as Chemical Mechanical Planarization (CMP) process invented by IBM in late '80. However, The document published by International Semiconductor Association suggests the decreasing ultra pure water (UPW) use from 22 gallon/in^2 in 1997 to 5 gallon/in^2 in 2012. The criteria will possibly used as exporting obstacle in the future. Generally, Solid content of CMP slurry is about 15wt%. The slurry is diluted with UPW before fed to a CMP process. When the slurry is discharged from the process as waste, it contains 0.1～0.6wt% of solid content and 9～10 at pH. The CMP waste slurry is discharged to stream with minimum treatment. In this study, to find optimum condition of coagulation for water recovery from the waste CMP slurry various condition of coagulation were examined. After coagulation for 0.1 wt% solid content of waste CMP slurry, the sludge volume was 10～15% after 30 min of sedimentation time. For the 0.5 wt%, sludge volume was 50～55% after one hour of sedimentation time. For more than 80% of water recycling, the solid content should be in the range of 0.1 to 0.2wt%. Based on the result of the turbidity removal, the Zeta Potential and the analysis of heavy metals, the optimum condition for 0.1 wt% of waste CMP slurry was with 20 mg/L of PACl at 4 to 5 of pH. The result showed that the optimum conditions for the 0.1 wt% waste CMP slurry were 100mg/L of Alum at 4～5 of pH, 100 mg/L of $MgCl_2$ at pH 10 to 11 and 100 mg/L of $Ca(OH)_2$ at pH 9 to 11, respectively.
Keywords: CMP Slurry, Coagulation, Turbidity, UPW

Introduction

Semiconductor industries have been gotten attention from early 1980's in Korea. Mainly, the companies produce the memory chips. Most of people think that the industry is environmentally friendly but it is not true because of using many toxic chemicals and large amount of water. According to use large amount of chemicals and water it produces large amount of wastewater. The wastewater can be divided into three main categories- organic wastewater, acid wastewater and base wastewater- based on the containing chemicals. Especially, the wastewater contains particulate matters caused by the etching processes. In 1996, 138,000 ton of waste was generated and only 25% of the waste was recycled.

The semiconductor industries use very high quality water called ultra pure water (UPW), which should be free from all the contaminants. Production cost of the UPW is as much as ten times higher than drinking water. Therefore, most of the company use about 10 to 15% of total investment to build the UPW process. It can be very critical to reduce the water usage not only save the water but also minimize the wastewater treatment cost. Using less water can give environmentally friendly process as well as reduce the production cost.

The UPW is used most in the process such as wet station and chemical mechanical plnarization (CMP). The CMP process is used to overcome the limit of complexity of wire and multi layer plate. IBM has invented the CMP process in late 1980. Figure 1 showed the schematic diagram of water flow in CMP process. Recently, oxide slurry is mainly used and in the future metal slurry will be adapted. The oxide slurry is base and size of particle is 100 to 200nm. The slurry is diluted with UPW before introduced into process based on the purpose. The produced wastewater contains 0.1 to 0.6wt% of solid in pH 9 to 10. Recently the CMP waste mixed with hydrofluoric acid (HF) wastewater for treatment and then discharged to stream. When the CMP slurry is mixed with HF wastewater possibly reduce the efficiency of wastewater treatment. However, still most of the CMP waste is treated with HF wastewater.

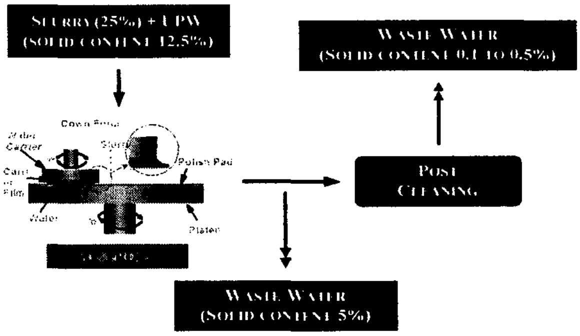

Fig. 1. Schematic diagram of water flow in CMP process

In this study, coagulation was applied to the CMP wastewater to recycle the water instead of discharging the wastewater to stream. The coagulation has some advantages such as easy to operate and relatively low investment and operation cost. The objectives of the study were to find optimum condition of coagulation for water recovery from the CMP slurry and to investigate the characteristics of treated water. To achieve the purpose, different coagulants was tested at different condition such as pH and dosage. Also, experiment was conducted based on the solid content in the CMP slurry to find recyclable water quantity.

Materials and Methods

Four different coagulants-Polyaluminum Chloride(PACl), Aluminum Sulfate, Calcium Hydroxide and Magnesium Chloride- were used in this study. The properties of the coagulants are listed in the Table 1. The coagulants are prepared at 1% every week to prevent aging problems. HCl and NaOH were used as pH controller at concentration of 0.1 to 0.5N.

Table 1. Properties of PACl, Alum, $Ca(OH)_2$ and $MgCl_2$

Coagulant	Properties	
PACl $[Al_2(OH)_nCl_{6-n}]_m$	Specific gravity (20/4℃) Viscosity (20℃) PH Al_2O_3	1.19 이상 3~6 cps ± 3.5~5 10.~11.0 %
Alum $Al_2(SO_4)_3 \cdot 13{\sim}14\ H_2O$	Molecular weight Assay	586 56~59 % $Al2(SO_4)_2$
Calcium Hydroxide $Ca(OH)_2$	Molecular weight Assay	74.09 93.0%
Magnesium chloride $MgCl_2 \cdot 6H_2O$	Molecular weight Assay	203.30 97% $MgCl_2$

The waste CMP slurry is obtained from a company in Korea. The CMP slurry is fumed silica type named SS-25. The properties of the waste CMP are listed in the Table 2. Also, concentration of heavy metal in the 0.1 and 0.5wt% waste CMP slurry is shown in Figure 1 and 2.

Table 2. Characteristics of waste CMP slurry

Item	Waste CMP slurry	
Solid content (wt%)	0.1	0.5
Turbidity (NTU)	100	380
Alkalinity CaCO3 mg/L	33.3	126.7
pH	9.5~9.7	9.9~10.1
Size distribution (nm)	163.7	171
Zeta potential (mV)	-42.1	-43.1

The coagulation experiments were conducted using Jar-tester. The reactor volume was 2L. Dimension of impeller was 7x2cm.

The coagulation experiments were divided into three main steps. The first step was rapid mixing which was conducted at 130rpm for 2minute. The second step was slow mixing or flocculation that was conducted at 5 to 30 rpm for various times. The last step was sedimentation. Generally, the rapid mixing time does not effect very much to the over all process so the time was fixed at 2minute. However, the slow mixing speed can be variable for the process. The effect of speed was evaluated. Also, the sedimentation time was evaluated to find the best time.

The turbidity was measured by turbidimeter (Model 2100A) manufactured by HACH. Zeta-potential was measured by using Zeta Sizer (Model Malvern DTS 2000) manufactured by Malvern Instruments. The heavy metals were measured using ICP manufactured by Plasma Lab.

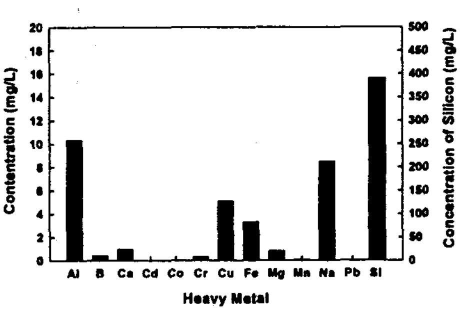

Fig. 1. The concentrate of heavy metals in the 0.1wt% CMP slurry

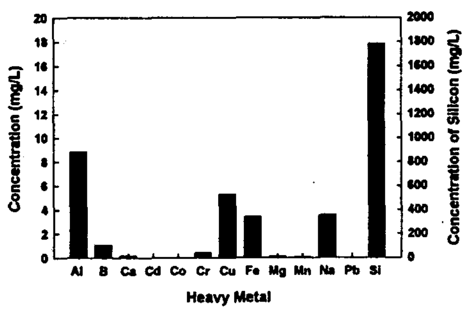

Fig. 2. The concentrate of heavy metals in the 0.5wt% CMP slurry

Results and Discussion

The effect of flocculation speed and sedimentation time

Main parameters affected on the performance of coagulation are pH and coagulant dose. However, the flocculation speed and sedimentation time are also very important because size and density of floc can be varied by flocculation speed and sedimentation time.

From Figure 3 to 6 showed the effect of flocculation speed and sedimentation time for PACl, Alum, $Ca(OH)_2$ and $MgCl_2$. Figure 3 showed the results for PACl. When 50mg/L of PACl was added the final turbidity with 5rpm of flocculation speed for 5minutes of sedimentation time was 2.5NTU. At the same condition, it showed 2NTU after 20minutes. However, when the flocculation speed was 10 to 30rpm the final turbidity was 0.5NTU after 20minutes. When 100mg/L of PACl was added the final turbidity with 5 rpm of flocculation speed after 20minutes was 0.2NTU.

Figure 4 showed the results for Alum. When 50mg/L of Alum was added the final turbidity with 5rpm of flocculation speed for 30minutes of sedimentation time was 20NTU. However, when the flocculation speed was 10 to 30rpm the final turbidity was 2NTU after 30minutes. When 100mg/L of Alum was added the final turbidity was 1NTU after 20minutes sedimentation time with all the flocculation speed. Other two coagulants-$MgCl_2$ and $Ca(OH)_2$ showed similar to the results of Alum. Therefore, the coagulation experiments were conducted at 20rpm of flocculation speed for 20minutes and 30minutes of sedimentation time.

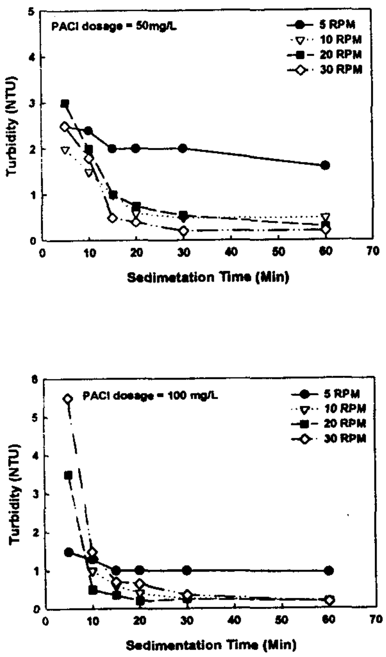

Fig. 3. The effect of flocculation speed and sedimentation time on the removal of turbidity with 0.1wt% solid content waste CMP slurry and dosage of PACl 50, 100 mg/L

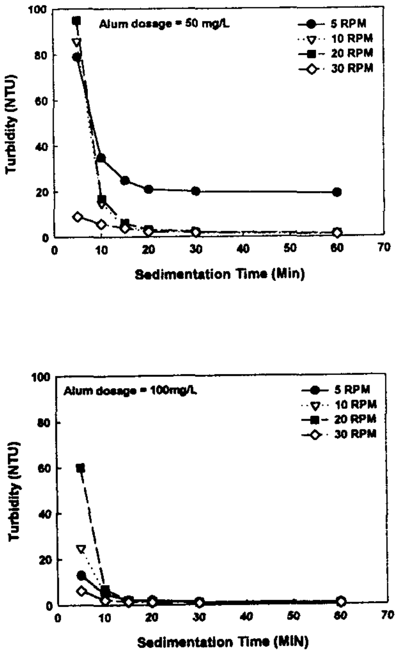

Fig. 4. The effect of flocculation speed and sedimentation time on the removal of turbidity with 0.1wt% solid content waste CMP slurry and dosage of Alum 50, 100 mg/L

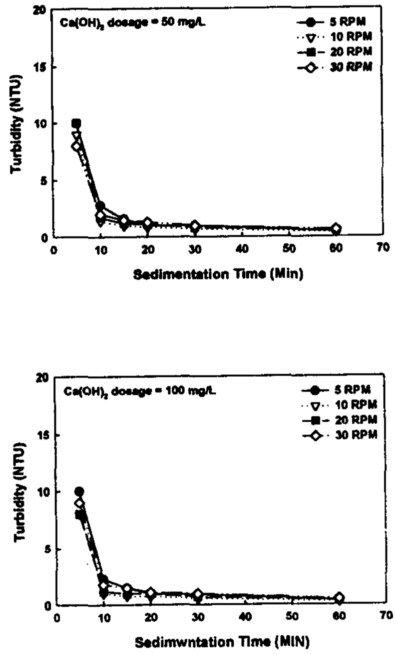

Fig. 5. The effect of flocculation speed and sedimentation time on the removal of turbidity with 0.1wt% solid content waste CMP slurry and dosage of $Ca(OH)_2$ 50, 100 mg/L

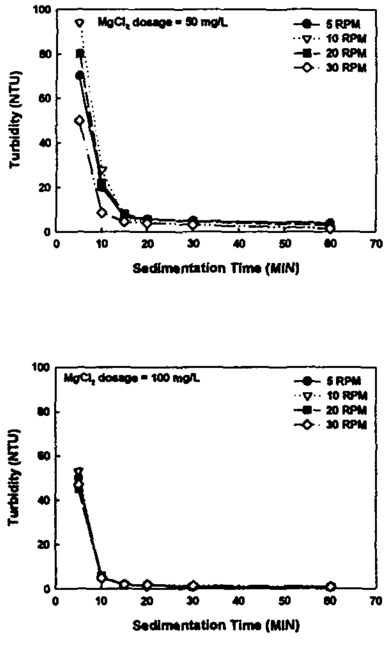

Fig. 6. The effect of flocculation speed and sedimentation time on the removal of turbidity with 0.1wt% solid content waste CMP slurry and dosage of $MgCl_2$ 50, 100 mg/L

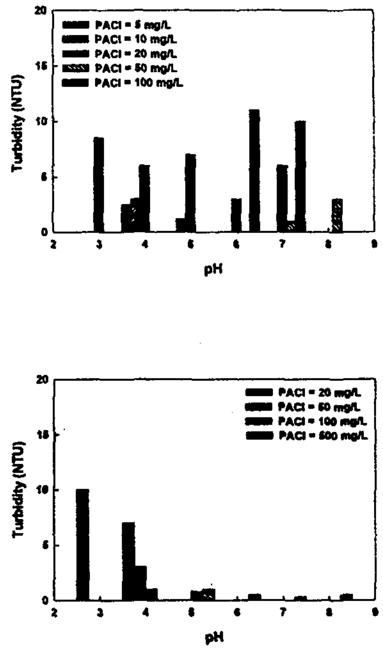

Fig. 7. The effect of pH and PACl dosage on the removal of turbidity over 90% for 0.1wt% and 0.5wt% solid content waste CMP slurry

The effect of coagulants

To find the best coagulant and the optimum condition of coagulation turbidity and Zeta potential were measured in the supernatant. The reason to measure the turbidity is that the waste CMP slurry mainly contains SiO_2 particles and some of organics. Therefore, if particulates were removed effectively from the waste slurry the water could be recycled with minimal treatment either as UPW or conventional use.

When the solid weight percent is 0.1wt% in the waste slurry it showed higher than 90% turbidity removal with 10mg/L of PACl at pH of 4 to 5 and with more than 50mg/L of PACl at pH of 3 to 6. However, when the solid weight percent is 0.5wt% in the slurry it showed higher than 90% turbidity removal at pH of 3 to 5 with less than 100mg/L of PACl and at pH 5 to 8 with more than 100mg/L of PACl. The other condition for the PACl showed less than 1% of turbidity removal. The phenomena can be explained by that the floc was not big enough to be settled within given time period. The minimum coagulant dosage to achieve more than 90% turbidity removal could be obtained at pH 4 with 5mg/L and at pH 3 to 4 with 20mg/L of PACl. The best removal can be obtained at pH 7 with 50mg/L of PACl for 0.1wt% of waste CMP slurry. At the condition the turbidity was 1NTU. The best removal can be obtained at pH 5 with 100mg/L of PACl for 0.5wt% of waste CMP slurry. At the condition the turbidity was 0.8NTU. Generally, the

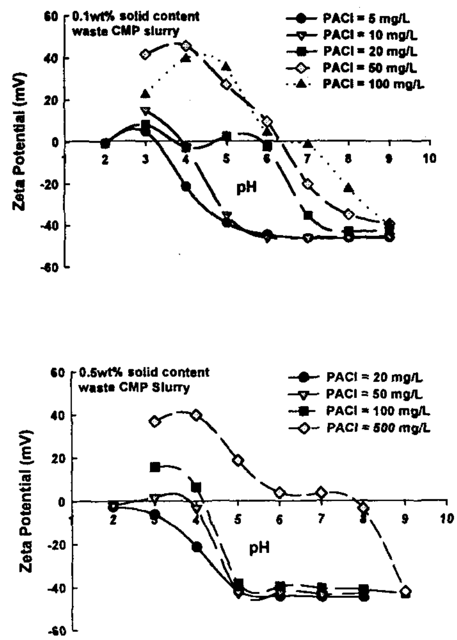

Fig. 8. The variation of zeta potential by pH and dosage of PACl with 0.1wt% and 0.5wt% solid content waste CMP slurry

turbidity of sources water for drinking water is higher than

3NTU. Usually, when the zeta potential is closed to the zero it showed good coagulation. Therefore, the relationship between the coagulation and zeta potential was evaluated. As shown in the Figure 7 and 8, when it shows the higher than 90% of turbidity removal the zeta potential is closed zero except few data point.
When the alum was used as coagulant the following results were obtained. When the solid weight percent is 0.1wt% in the waste slurry it showed higher than 90% turbidity removal with 50mg/L at pH of 4 and with 100mg/L at pH 4 to 6. However, when the solid weight percent is 0.5wt% in the slurry it showed higher than 90% turbidity removal at pH of 3 to 5 with more than 500mg/L of alum. The other condition for the alum showed less than 1% of turbidity removal.

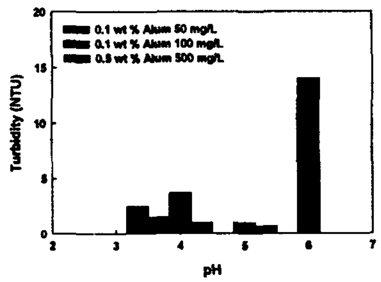

Fig. 9. The effect of pH and Alum dosage on the removal of turbidity over 90% for 0.1wt% and 0.5wt% solid content waste CMP slurry

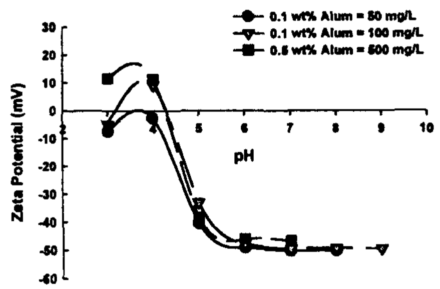

Fig. 10. The variation of zeta potential by pH and dosage of Alum with 0.1wt% and 0.5wt% solid content waste CMP slurry

When the $MgCl_2$ was used as coagulant the following results were obtained. When the solid weight percent is 0.1wt% in the waste slurry it showed higher than 90% turbidity removal with 50mg/L at pH of 12 and with 100mg/L at pH 10 to 12. However, when the solid weight percent is 0.5wt% in the slurry it showed higher than 90% turbidity removal at pH of 9 to 10 with 300mg/L of MgCl2 and at pH of 9 to 11 with 500 mg/L of $MgCl_2$. The other condition for the $MgCl_2$ showed less than 1% of turbidity removal. The best removal can be obtained at pH 9 with 300mg/L of $MgCl_2$ for 0.5wt% of waste CMP slurry. At the condition the turbidity was 0.74NTU. In the case of $MgCl_2$, there was no strong correlation between the reasonable turbidity removal and zeta potential.

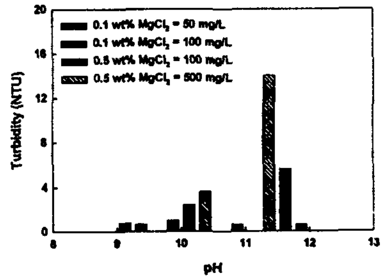

Fig. 11. The effect of pH and $MgCl_2$ dosage on the removal of turbidity over 90% for 0.1wt% and 0.5wt% solid content waste CMP slurry

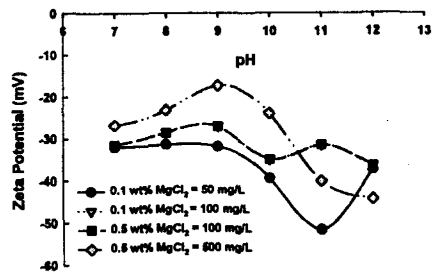

Fig. 12. The variation of zeta potential by pH and dosage of $MgCl_2$ with 0.1wt% and 0.5wt% solid content waste CMP slurry

Conclusion

The objectives of the study were to find optimum condition of coagulation for water recovery from the CMP slurry and to investigate the characteristics of treated water. To achieve the purpose, different coagulants was tested at different condition such as pH and dosage. The following conclusion could be obtained. The optimum flocculation speed was 10 to 30rpm. The required minimum sedimentation time was 30minutes. After coagulation for 0.1 wt% solid content of waste CMP slurry, the sludge volume was 10~15% after 30 min of sedimentation time. For the 0.5 wt%, sludge volume was 50~55% after one hour of sedimentation time. For more than 80% of water recycling, the solid content should be in the range of 0.1 to 0.2wt%. Based on the result of the turbidity removal, the Zeta Potential and the analysis of heavy metals, the optimum condition for 0.1 wt% of waste CMP slurry was with 20 mg/L of PACl at 4 to 5 of pH. The result showed that the optimum conditions for the

0.1 wt% waste CMP slurry were 100mg/L of Alum at 4 ~ 5 of pH, 100 mg/L of $MgCl_2$ at pH 10 to 11 and 100 mg/L of $Ca(OH)_2$ at pH 9 to 11, respectively.

Acknowledgement

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