CHARACTERIZATION AND BEHAVIOR OF NANO-SIZED PARICLES IN CHEMICAL, MECHANICAL POLISHING WASTEWATER

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ABSTARCT

Wastewater discharged from semiconductor industry contains high organic and inorganic compounds as well as turbidity. When membrane systems are used for semiconductor wastewater reclamation without pre-treatment, membranes will soon be clogged by the nano-size particles. Wastewater from semiconductor manufacturing is usually separated in three different streams; acid-base, chemical mechanical polishing (CMP) and fluoride-containing wastewater. The coagulation behaviour of aluminium salts and anionic polymer in SiO_2 containing polishing and fluoride-containing wastewater was investigated using dynamic light scattering technique that is applied as an alternative methodology to pre-determine the optimum pH and dosage range. The stability and behavior of SiO_2 nanopartices and the coagulants were studied in terms of zeta potential and z-average hydrodynamic diameter profiles as a function of pH (pH 2 to 12). It was found that the point of zero charge of CMP wastewater that contains SiO_2 is at pH 2.1, while at initial pH of CMP wastewater (pH 9.3) had a negative zeta potential value of -60.5 mV with mean particle size of 150 d.nm. On the other hand, fluoride-containing wastewater showed the initial pH at 6.4 with positive zeta potential of 15 mV and particle size of 1800 d.nm. Results indicated that the combined treatment of both CMP and fluoride-containing wastewater was beneficial as it dramatically increased in the mean particle size to 12 590d.nm. It is proposed that silica in CMP wastewater become adsorbed on the surface of positively charged particles present in fluoride-containing wastewater, and enhances flocculation since repulsive force of both wastewater is decreased. In addition, silica in CMP wastewater may act as nuclei for precipitation with fluoride-containing wastewater as well and facilitate agglomeration. Potential advantages include lower chemical dosage, better control and smaller footprint.

Keywords: Chemical mechanical polishing wastewater (CMP), fluoride-containing wastewater, semiconductor, zeta potential.

INTRODUCTION

Semiconductor is an important electronic product, and it is widely used in electronic control devices, consumer electronic products, communication equipment, computers and medical test equipment [1]. The semiconductor industry has become a representative and major industry. Wastewater from semiconductor manufacturing is usually separated in three different streams; acid-base, chemical mechanical (CMP), and fluoride-containing wastewater [2]. CMP is a highly favoured planarization technology in the manufacturing of multilevel integrated circuits (IC) [3]. Dielectric films such as silica dioxide (SiO_2) are generally planarized using highly alkaline, silica-based slurries, in which silica particles are in nano-sized. However, the rapid development of semiconductor industry also results in some environmental problems including difficulty on its wastewater treatment and high water demand [4, 5].

CMP processes consume as much as 40% of the ultra-pure water used in semiconductor manufacturing and generates 30L-50L of waste slurry per 200 mm wafer at each level of planarization [6-8]. The major contaminants in the CMP wastewater are many nano-sized particles and organic solvents. The wastewater from dielectric planarization is a suspension of silica particles at a concentration of 500 mg/L to 2000 mg/L [9, 10]. Thus, the semiconductor wastewater is distinctly different from most of the industrial wastewaters. Removal of the total solids (TS) and nano-sized particles thus has received the most attention [11].

Many researchers have investigated different methods to treat CMP wastewater. Belongia et. al., [12] used electrochemical method to remove silica and alumina from CMP wastewater. The electro-microfiltration processes can effectively remove SiO_2 from CMP wastewater [13]. The dispersed air flotation has been shown to be effective to remove silica from CMP wastewater [14]. Coagulation and flocculation method is one of the most prevalent procedures for treating CMP wastewater [15]. During treatment processes, CMP wastewater need to recycle large quantities of water, thus over dosing the coagulant to form sufficient hydroxide precipitates to ensure that the particles are effectively separated from the water [16]. This approach is commonly known as sweep flocculation as is especially important when the particle concentration is low and inter-particle collisions are infrequent [17]. This method produces large amount of sludge and increases its treatment cost. Accordingly, the effective removal of particulate and SiO_2 are necessary to fulfil economically the strict requirements of the quantity and quality of recycled water [18].

Typical amount of fluoride-containing wastewater generated for an 8-in. semiconductor fabrication facilities ranges from 350 to 700 m^3/d with fluoride concentration varying from 50 to 1000 mg/L [19]. According to Lin and Yang [20] indicate that fluoride-containing wastewater contributes 40% of hazardous waste produced from semiconductor manufacturer.

Various methods have been developed to remove fluoride from wastewater. A packed-bed reactor with calcite has been found to remove fluoride effectively from electronic wastewater [20]. Toyoda and Taira [21] modify the conventional chemical precipitation process for treating fluoride-containing wastewater by the addition and regeneration of $Al(OH)_3$ and make process more efficient. Precipitation flotation methods including dispersed air flotation (DiAF) and dissolved air flotation (DAF), are feasible alternative processes for the removal of fluoride from semiconductor wastewater [21]. A fluidized-bed reactor with seeding materials is very effective to convert fluoride to crystalline minerals, such as fluorite (CaF_2) or cryolite ($NaAlF_6$) [20].

Semiconductor manufacturer rarely combined treatment process for CMP wastewater and fluoride-containing wastewater [22]. When these two streams are mixed, then wastewater is expected to be high in turbidity, total solid content, silica and fluoride. There has been no study on the efficiency of combined both wastewater in terms of dynamic light scattering technique to pre-determine the optimum pH and dosage range. Therefore, in this pilot-scale study, the combination of both wastewater; CMP wastewater and fluoride-containing wastewater will be studied by analysing the zeta potential and hydrodynamic diameter of each wastewater in which to determine the optimum pH conditions for both. This research project serves a novel approach that is much faster and accurate in measuring the surface charge and particle size of the SiO_2 nanoparticles within a minute range of 0.2 nm to 6 µm.

METHODOLOGY

The source of water regeneration came from the effluent of the wastewater treatment plant of an industrial park located at Kulim Hi-Tech Park, Kulim, Kedah. Due to high water demand of semiconductor industry was more than 90% of the wastewater of the studied industrial park was from the semiconductor factories. Wastewater samples were collected trimonthly from the effluent location of the wastewater treatment plant. Sodium hydroxide (NaOH and hydrochloric acid (HCL) of 1 M respectively was used to adjust pH from pH 2 to 12.

The functional group and compositions present in the semiconductor wastewater was determined by Fourier Transform Infrared Spectroscopy (FTIR) method using Perkin-Elmer System 2000 FTIR spectrometer. Meanwhile, the value of zeta potential was measured by Laser Doppler electro-phoresis light scattering method from Malvern Zetasizer Nano ZS. The semiconductor wastewater collected was undergo full details of characterization of SiO_2 nanoparticles, in terms of pH study which investigating the development of zeta potential and particles size, simultaneously.

RESULTS AND DISCUSSION

Semiconductor Wastewater Characteristics

The concept of surface potential (i.e., zeta potential) appears to be a valuable practical parameter for coagulation and the resultant separation from the wastewater, providing a direct indicator of the semiconductor wastewater stability. Fig. 1 and 2 shows the zeta potential of the CMP wastewater and the corresponding particle size as a function of the CMP wastewater pH. The solution pH was adjusted and maintained by the addition of the required amount of NaOH or HCL.

The pH of semiconductor wastewater was at pH 9.37 ± 0.2 with zeta potential value was - 60.2 mV. As can be seen from Fig. 1 and 2, an increase in pH resulted in a greater degree of negative zeta potential and a decrease in the corresponding particle size. From the graph, by increasing the pH of the CMP wastewater from 2 to 12, the zeta potential varied from - 4.8 to - 65.2 mV and the mean particle size decreased from 200 to 105 d.nm. This may be due to the pH increase in CMP wastewater tended to adsorb more OH^- ions on the particle surface and created Si-O^- on the surface, thus causing greater negative zeta potential [23].

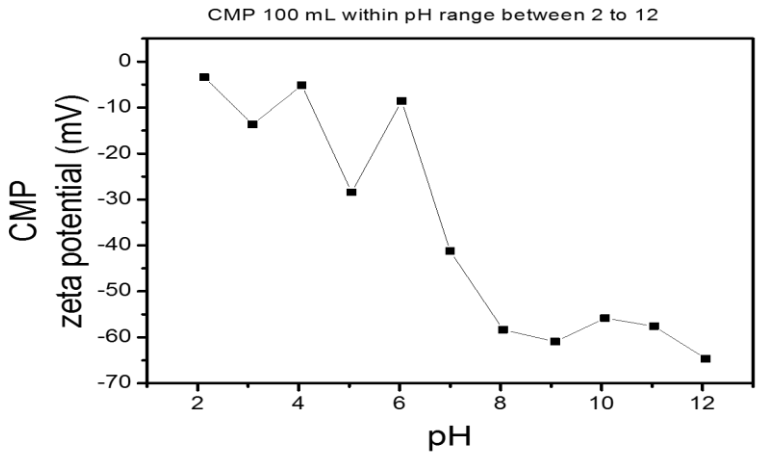

Figure 1. Zeta potential of CMP varies with pH

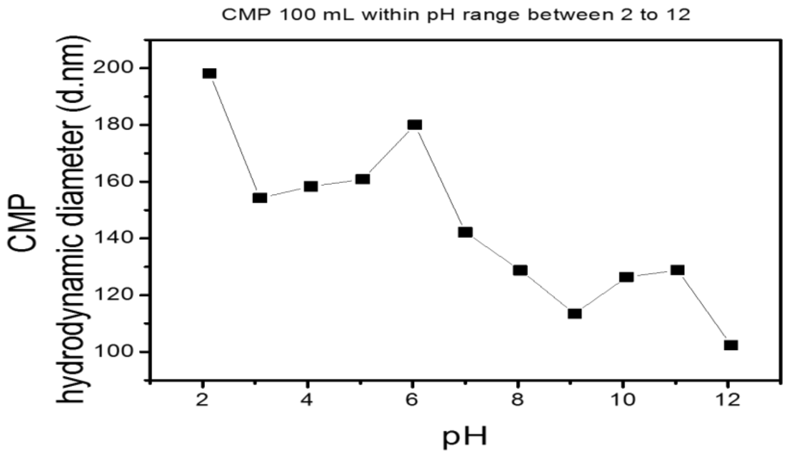

Figure 2. Hydrodynamic diameter of CMP varies with pH

According to the equations for SiO_2 dissolution [Eqs (1) and (4)], the dissolution of SiO_2 raises with pH increasing [24].

$$SiO_{2(s)} + 2H_2O = Si(OH)_{4\,(aq)} \qquad pK = 2.7 \qquad (1)$$

$$Si(OH)_{4\,(aq)} = Si(OH)_3O^-_{\,(aq)} + H^+ \qquad pK_{a1} = 9.9 \qquad (2)$$

$$Si(OH)_3O^- = Si(OH)_2O_2^{2-} + H^+ \qquad pK_{a2} = 11.8 \qquad (3)$$

$$Si(OH)_2O_2^{2-} = Si(OH)O_3^{3-} + H^+ \qquad pK_{a3} = 12 \qquad (4)$$

In other words, electrostatic repulsion between the particles of the electric double layers with greater negative potential drives suspended particles apart, achieving particle stability and reducing a smaller particle size. Therefore, a relatively smaller mean particle size associated with CMP wastewater could be attributed to its relatively large negative zeta potential [23].

The CMP wastewater mainly contains suspended, nano-sized solids originated from slurry abrasive particles of SiO_2, Al_2O_3 or CeO_2, depending on the nature of the CMP applications [17]. Based on the FT IR obtained (Fig. 3) proved that the present of silica group (Si-H group) in the CMP wastewater from 2085 to 2115 cm^{-1}. While the hydroxyl group was also found in the wastewater at 3333 cm^{-1}.

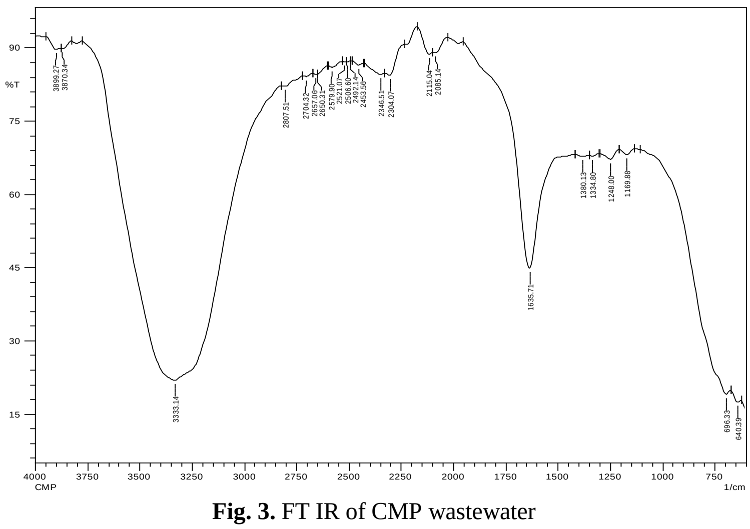

Fig. 3. FT IR of CMP wastewater

Fig 3 and 4 shows the zeta potential and mean particle size with varies of pH of fluoride-containing wastewater. At initial pH of fluoride-containing wastewater of 6.37±0.2 with positive zeta potential of 15 mV shows mean particle size of 1800 d.nm. and achieved its charge neutralisation at pH 11.8 with particle size of 2100 d.nm. From the graph plotted illustrated that increased in pH value resulted in decreased of zeta potential with bigger corresponding particle size. For example, by increasing the pH from pH 4 to 9, the zeta potential varied from 5 to 25 mV and the mean particle size increased from 1500 to 8900 d.nm. This may happen due to the tendency of fluoride particles which is in positively charged to adsorb the OH^- ions on the particle size resulted in reducing zeta potential [21]. Consequently, the electrostatic repulsion between the particles tends to move the particles closer, resulted in particles agglomeration [20]. In addition, from Fig. 6, fluoride-containing wastewater shows the present of functional group containing mainly hydroxyl group (OH^-) at 3328.3 cm^{-1} and also N-H group (1636.7 cm^{-1}).

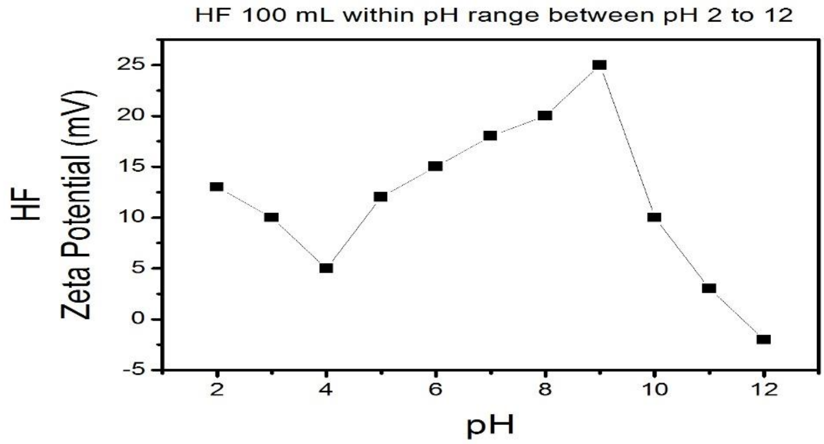

Figure 4. Zeta potential of fluoride-containing wastewater varies with pH

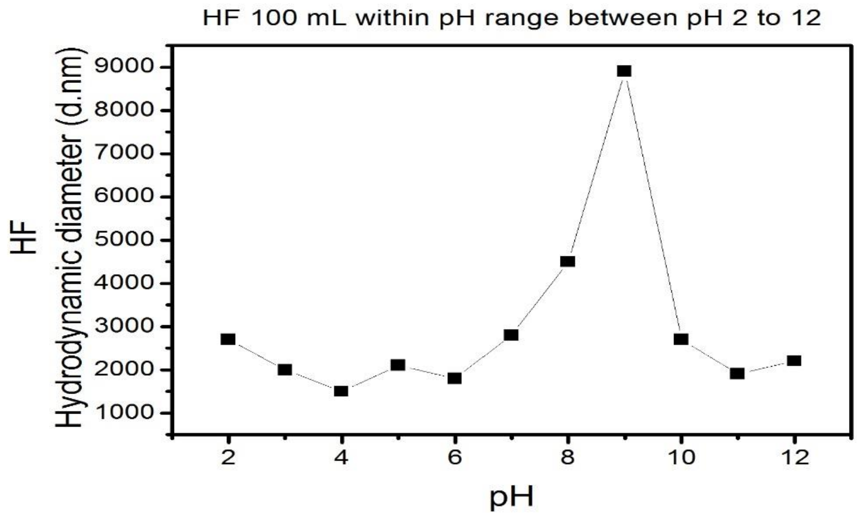

Figure 5. Hydrodynamic diameter of fluoride-containing wastewater varies with pH

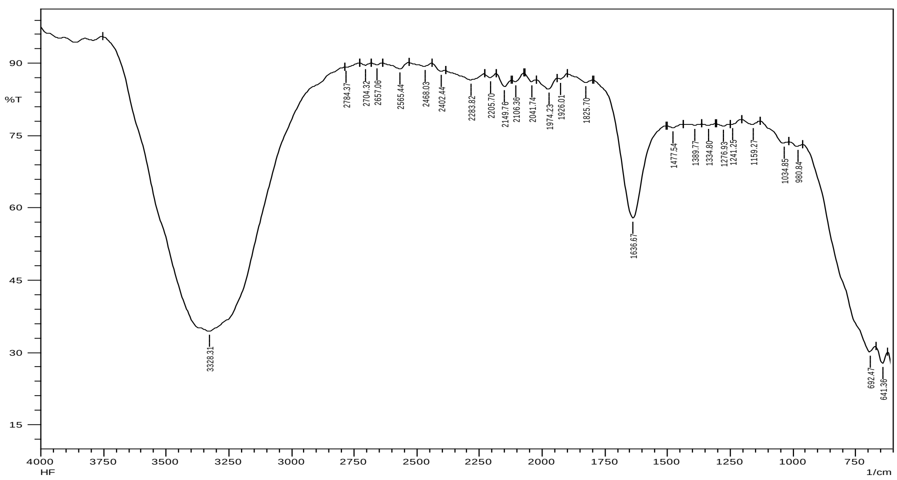

Figure 6. FT IR of fluoride-containing wastewater

Interaction between CMP Wastewater and Fluoride-containing Wastewater

The interaction between CMP wastewater with fluoride-containing wastewater has not being studied in details in terms of zeta potential and hydrodynamic diameter. Very little is known about the advantages and disadvantages of combined treatment. The optimum pH of CMP wastewater is selected to be at pH 6 with negative zeta potential of -10 mV and mean particle of 180 d.nm. Meanwhile, the optimum pH of fluoride-containing wastewater is at pH 9 with positive zeta potential and mean particle size of 25 mV and 8900 d.nm., respectively. Combining both wastewater at each optimum pH has resulted in changes of pH to pH 8.6 ± 0.2 with negative zeta potential of -17.4 mV and corresponding particle size of 3914 d.nm.

From Fig. 7 illustrated that increased in pH from its initial pH value to alkaline also increased the zeta potential from -22.4 to 0.55 mV and achieved its charge of neutralisation at pH 11.8. It is proposed that fine silica particles in CMP wastewater that have negative charge become adsorbed on the surface of positively charged fluoride particles in fluoride-containing wastewater. It is found that at optimum pH 9, the mean particle size has increased dramatically to 12590 d.nm with zeta potential of -16.5 mV (Fig. 8). This may due to the decreased electrostatic repulsion among silica and fluoride particles then results in larger flocs. It is also probable that fine silica particles in CMP wastewater can act as nuclei for precipitation of fluoride particles and facilitates the floc growth.

According to reaction (5) and (6), the reaction of silica and fluoride formed precipitate known as fluorosilicate (SiF_6^{2-}) [20]. The formation of SiF_6^{2-} did not delay the precipitation reaction due to different characteristics of wastewater, since relatively low initial volume was utilized in the experiment [20].

$$SiO_2 + 2HF_2 + 2H^+ \leftrightarrow SiF_4 + 2\,H_2O \qquad (5)$$
$$SiF_4 + 2HF \leftrightarrow H_2SiF_6 \qquad (6)$$

From thermodynamic modelling, it is predicted that most of dissolved silica exits as H_4SiO_4 when pH <9.5 and $H_3SiF_4^-$ when pH > 9.5. Yang *et. al.*, [20] stated that SiF_6^{2-} was unfavourable to form at pH < 9 and recommend keeping the pH at 8 to 9 for precipitation of SiF_6^{2-} in the presence of SiO_2. This supports with the aforementioned for the selected optimum pH to be at pH 9.

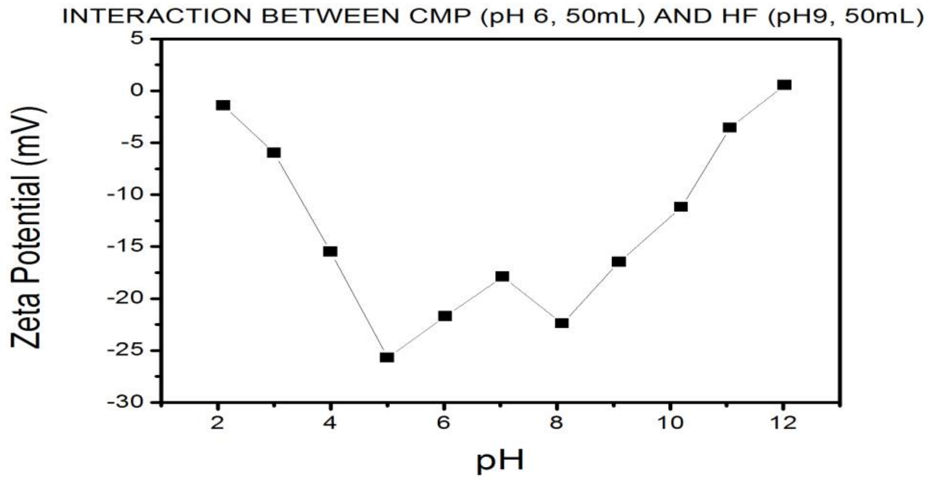

Figure 7. Zeta potential of interaction between CMP wastewater and fluoride-containing wastewater varies with pH

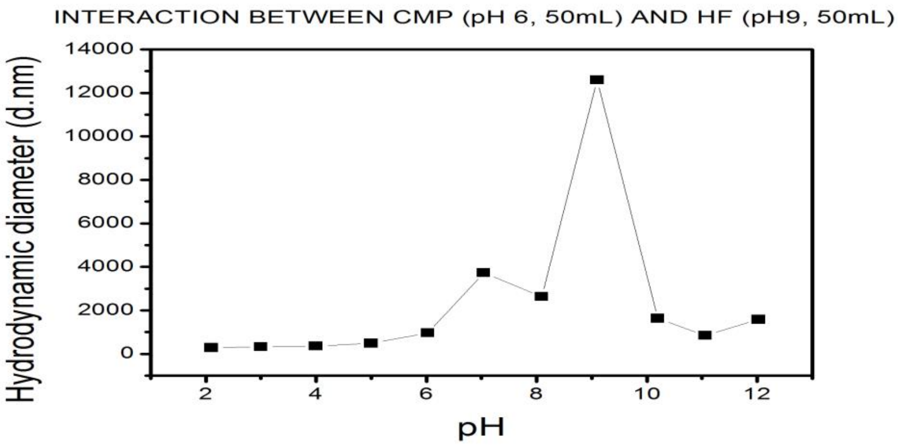

Figure 8. Hydrodynamic diameter of interaction between CMP wastewater and fluoride-containing wastewater varies with pH

CONCLUSION

The current study showed that the combined treatment both polishing and fluoride-containing wastewater is beneficial. At optimum pH of both wastewaters, the size of flocs formed at pH 9 became bigger. It was proposed that two different mechanisms might be included. Firstly, negatively charged silica in CMP wastewater may become adsorbed on the positively charged fluoride particle and enhanced particle agglomeration. Secondly, heterogeneous nucleation might be involved, with nano-sized silica act as nuclei to enhance precipitation of SiF_6^{2-}. Potential advantages for the combined treatment of CMP wastewater with fluoride-containing wastewater include lower chemical dosage, better control of process and smaller footprint.

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