Optimization of Removal Rates with Guaranteed Dispersion Stability in Copper CMP Slurry

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Copper metallization has been used in high-speed logic ULSI devices instead of the conventional aluminum alloy metallization. One of the key issues in copper CMP is the development of slurries that can provide high removal rates. In this study, the effects of slurry chemicals and pH for slurry dispersion stability on Cu CMP process characteristics have been performed. The experiments of copper slurries containing each different alumina and colloidal silica particles were evaluated for their selectivity of copper to TaN and SiO_2 films. Furthermore, the stability of copper slurries and pH are important parameters in many industries due to problems that can arise as a result of particle settling. So, it was also observed about several variables with various pH.

Keywords : Chemical mechanical polishing, Copper, Slurry, Dispersion stability, Removal rate

1. INTRODUCTION

The chemical mechanical polishing (CMP) process is now widely used to provide global planarity of layers, reducing the defect density with the advent of multilevel metallization technology during the fabrication of integrated circuits. Recently, copper has emerged as an attractive material because it can be overcome the fundamental limits of aluminum interconnects and can support next generation subquarter-micron integrated circuits with low resistivity and high electromigration resistance[1-3]. But, there remain many uncertainties and problems occurring from a shortage of experince. Presently, in copper CMP process the most issued keys are slurry and pad. In this paper, we focused to understand, develop, characterize and improve the CMP technology using alumina slurry and colloidal silica slurries. Alumina slurries are known as produce higher polish rates compared to silica-bases slurries[4,5]. Then, we reviewed general characteristics of removal result and we observed that removal rate if added in slurry H_2O_2, benzotriazole, tartaric acid case of removal rate; H_2O_2 as an oxidizer, benzotriazole (BTA) as a film forming agent, and tartaric acid as a complexing agent. Also pH has a very strong influence on the removal rate of Cu and TaN. It not only affects the slurry stability but also alters the electrostatic interaction between the abrasive particles and the film being polished[6,7]. Then we invested pH removal rate each pH. In CMP processes, polishing slurries have to be stabilized under extreme environments of pH, ionic strength, pressure and temperature, in the presence of reactive additives. Most of the commonly used stabilization techniques, such as electrostatic stabilization, inorganic or polymeric dispersion may not perform adequately under these severe environments[8]. In this work, it was investigated the effective slurry condition using various slurry chemistries for Cu CMP process.

2. EXPERIMENTAL DETAILS

This experiment was carried out by the G&P technology POLI-500CE chemical mechanical polisher using a Rodel IC-1400 k-groove polyurethane pad. The down force on the wafer is set by air pressure applied uniformly to the wafer carrier via a tube connected to an air supply source. The flow rate of slurries was 100 ml/min and the down pressure of the head was 7 psi. The head and pad speed were 40 rpm. The removal rates were determined by measuring the thickness of samples before and after polishing using the four point probe method. It was observed the variation of $Cu/TaN/SiO_2$ by the concentrations of H_2O_2 as an oxidizer, tartaric acid as a complexing agent and BTA as a film forming agent to find out suitable amounts of each chemical.

Then, the particle size, settling rate and removal rate of Cu/TaN/SiO_2 were examined with alumina slurries to investigate the effect by pH. The pH of the slurry was adjusted by adding the appropriate amounts of NH_4OH to the solution. The slurry chemistries used in these experiments are presented in Table 1. Table 1 shows the corrosion characteristics after adding several 1 wt% complexing agents to 2 wt% H_2O_2. The corrosion rate of the solution with just H_2O_2 2 wt% without any complexing agent was 0.0513 mpy and it increased generally after the addition of complexing agent.

Table 1. The reference recipe of slurry chemichals used in this used in this experiment.

	Chemical		Percentage
Abrasive	Alumina-C	Colloidal silica	5.0 %
Complexing agent	Tartaric acid		1.0 %
Film forming agent	BTA		0.05 %
Oxidizer	H_2O_2		5.0 %
pH control	NH_4OH		0.8 %
Solvent	DI		88.15 %

3. RESULTS AND DISCUSSION

Figure 1 shows the removal rate of Cu, TaN and SiO_2 layer obtained by variation of the concentration of oxidizer in slurries. In case of alumina slurries, Cu removal rate dramatically increased as H_2O_2 concentration increases from 0 wt% and reached about 400 nm/min at 2 wt%. TaN was also increased gradually in proportion to the addition of H_2O_2. It was not generally visible great variation after 2 wt%. In case of colloidal silica slurries, TaN removal rate was decreased with adding of H_2O_2 contrary to alumina slurries. In conclusion, it is assumed that 2 wt% is appropriate H_2O_2 concentration that a high Cu removal rate and good slurry stability are satisfied simultaneously because it causes some problems about slurry dispersion stability when H_2O_2 is added so much.

The removal rate obtained using tartaric acid was also low when it isn't added entirely like case of H_2O_2. As shown in Fig. 2, there was a great difference of Cu/TaN/SiO_2 removal rate using by tartaric acid. The removal rate of Cu and TaN film was just 70 nm/min equally without tartaric acid for alumina abrasive, but it showed the significant increase of removal rate (Cu : TaN = 370 : 200 nm/min) by the addition of only 1 wt% tartaric acid. However, the addition of tartaric acid to alumina slurry causes low pH and the dispersion stability becomes unstable after all. Consequently, it was supposed that the suitable concentration of tartaric acid is about 1 wt%. When tartaric acid is added in colloidal silica, there was not much change of film removal rate by tartaric acid concentration.

Figure 3 shows the removal rate of Cu/TaN/SiO_2 with BTA as a corrosion inhibitor for CMP slurries. Contrary to our expectations, it was presented low change of Cu removal rate with BTA concentration in alumina slurries, as shown in Fig. 3. However, Cu removal rate with colloidal silica was decreased in proportion to BTA concentration. It is considered to be phenomenon by difference of a chemical composition. In short, it is assumed that 0.05 wt% is appropriate BTA concentration as a controller of polishing rate. Because, BTA worsens the slurry stability. Especially, at higher concentrations above 0.05, by reducing the electrostatic repulsion between particles.

Subsequently, it was investigated the slurry characteristics by various pH value. Figure 4 presents the particle size of alumina slurries as a function of pH. In order to achieve an optimal polishing performance with minimal surface deformations, it is necessary to use mono-sized particles for the CMP slurries. In practical applications, however, there may be a few oversize particles in the slurries in the form of larger size particles (hard agglomerates) due to in sufficient filtration, or the agglomerates of the primary slurry particles (soft agglomerates) due to poor stability. The large particles that cause the observed scratches in defective wafers are being formed during the CMP process as the result of agglomeration. Therefore, it is necessary to adjust pH for proper particle size. As shown in Fig. 4, there was a great difference of particle size depending on pH. The particle size was not much change until pH 4.01. But it was increased significantly from 59 to 332 nm as pH increases from 4.01 to 11.78 and it was decreased again after pH 12. In addition, to investigate the appropriate pH, it was considered about settling rate as a function of time with various pH in alumina slurries. As shown in Fig. 5, it was discovered that it has fine settling rate under pH 5 (pH 0.83, 4.01, 4.92) and the settlement occurred after pH 11 (pH 11.78, 13.33, 13.75). At high pH, the settling rate was disappeared after long time. The results of Figs. 4 and 5 suggest that pH 5 is a desirable in chemical system like reference.

With these results, it was examined removal rate of Cu, TaN, and SiO_2 as a function of pH. In case of alumina slurries, the Cu and TaN removal rate was very large at pH 3.65, as shown in Fig. 6. However, the dispersion stability is unstable at low pH (pH 2.7, 3.65) and it was presented stable state at high pH.

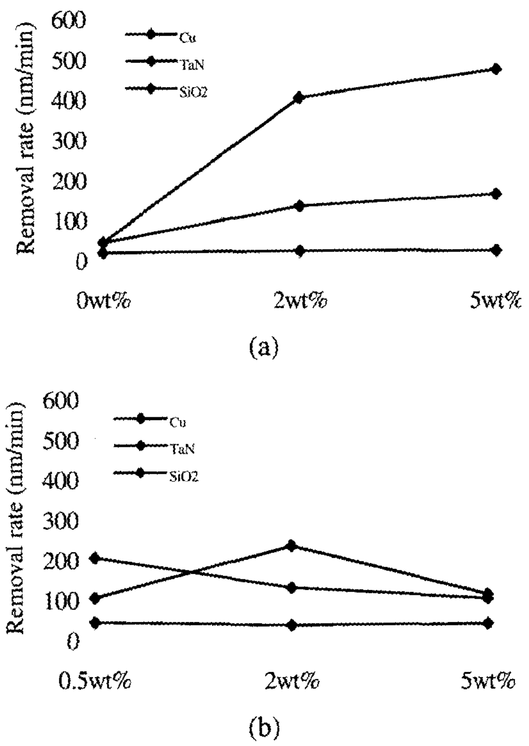


Fig. 1. Removal rate of Cu, TaN, and SiO_2 as a function of H_2O_2 concentration for (a) alumina slurries and (b) colloidal silica slurries.

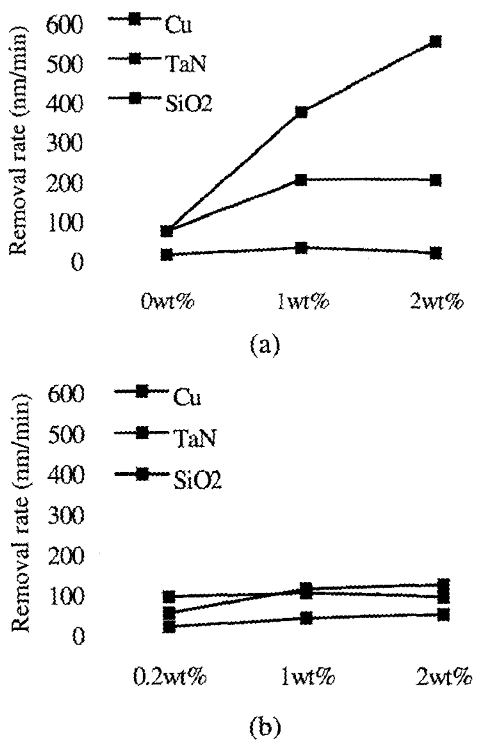


Fig. 2. Removal rate of Cu, TaN, and SiO_2 as a function of tartaric acid concentration for (a) alumina slurries and (b) colloidal silica slurries.

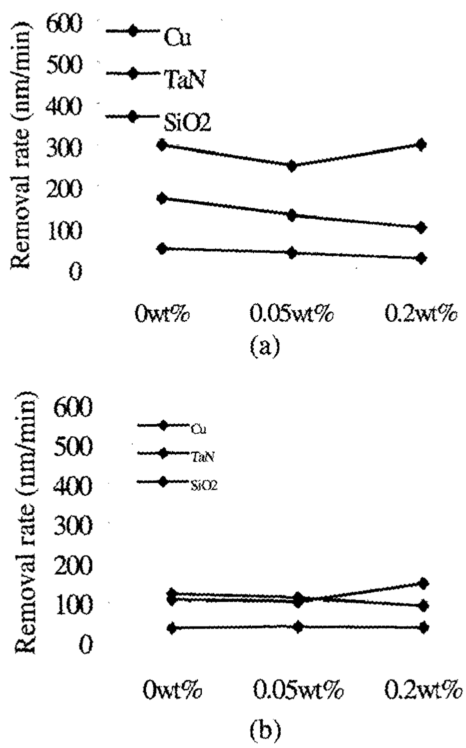


Fig. 3. Removal rate of Cu, TaN, and SiO_2 as a function of BTA concentration for (a) alumina slurries and (b)colloidal silica slurries.

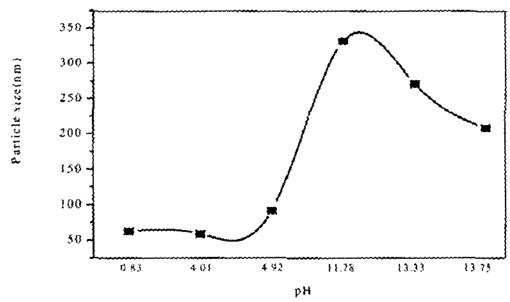


Fig. 4. Particle size with a variation of pH in alumina slurries.

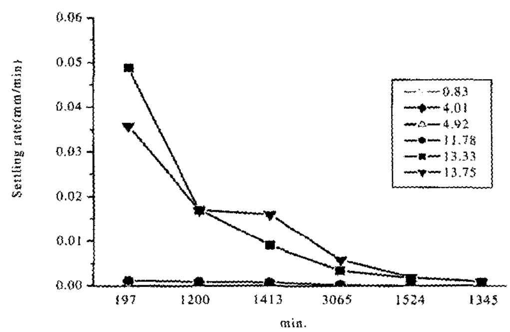
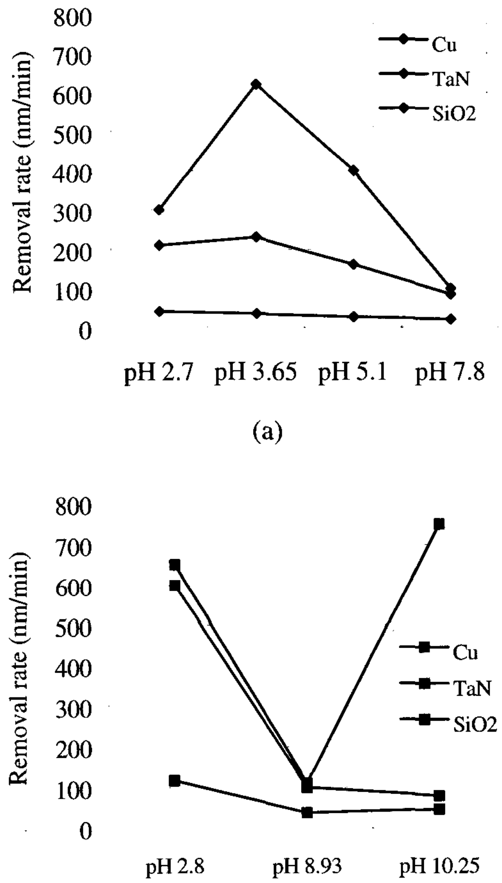


Fig. 5. Settling rate by elapsed time of alumina slurry with various pH.

And moreover, it was considered to be suitable in 2nd stepslurry because the selectivity of TaN over SiO_2 was about 4:1 at alkali (pH 7.8). In case of colloidal silica slurries, the removal rate of Cu/ TaN was great at acid and it was dropped gradually in proportion to pH. But only Cu removal rate increased suddenly at strong alkali. From these results, it is supposed that colloidal silica abrasive can be used both 1st and 2nd step slurry.

4. CONCLUSION



(a)

(b)

Fig. 6. Removal rate of Cu, TaN and SiO_2 with a variation of pH for (a) alumina slurries and (b) colloidal silica slurries.

In this study, it was investigated the best condition of alumina and colloidal slurries which a high film removal rate and good dispersion stability are satisfied simultaneously. As the results of this work, the removal rate of SiO_2 layer has little change by slurry chemicals regardless of slurry abrasive. The removal rate of Cu/TaN was remarkably low without H_2O_2 and tartaric, but it was increased dramatically in proportion to rise in concentration. It was found that the appropriate concentration of H_2O_2 and tartaric acid to be each 2.0 and 1.0 wt%, at which a high removal rate was obtained within the scope which does not cause trouble in dispersion stability. In the case of alumina slurries, it was presented that it has good dispersion stabilization and selectivity between TaN and SiO_2 is about 4 : 1 at high pH. Therefore, it was supposed that it is suitable in 2nd step slurry at alkali. The particle size increases with a variation of pH after pH 5. Besides, it has been observed that the settlement was not occurred under pH 5. In this work, it was obtained that pH is important variable with many influence in Cu CMP slurry.

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