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Etching and Polishing Behavior of Cu thin film according to the additive chemicals

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The purpose of this study was to characterize the reaction of Cu surface with Cu slurry and CMP performance as a function of additives in CMP slurry. The polish rate of Cu was dependent on the kind of organic acids added in slurry. It was considered that polish rate of Cu was dependent on the concentration of carboxylates and mean particle size. When the etchant and oxidant were added in slurry, the highest removal rate and lower etch rate were measured at neutral pH. The addition of etchant, oxidant and pH adjustor played key roles of CMP ability in slurry. As the pH increased, polish rate of Cu was increased by the enhanced the mechanical effects due to effective dispersion of slurry particles. Alumina abrasives was more desirable for 1st step slurry because of high removal rate of Cu and high selectivity ratio among TaN and Cu.

INTRODUCTION

Copper has been considered as a candidate for the replacement of aluminum in the next generation metal interconnects because of its lower resistivity and higher resistance to electro-migration [1]. Cu CMP process was performed with two step slurries, which were composed of the 1st step slurry for high removal rate of Cu and the 2nd step slurry for adaptable selectivity between Cu and barrier layer in order to reduce the Cu dishing and dielectric erosion [2]. Acidic and neutral alumina slurries are commonly used for 1st step Cu CMP because of its higher Cu removal rate and selectivity to oxide and barrier layer materials [3]. Recently, silica based slurry has been used to Cu CMP during CMP process for the reduction of microscratches and particle contaminations [4]. The 1st step Cu slurry was commonly composed of abrasive particles, etchant, oxidant and corrosion inhibitor. During Cu CMP, Cu surface was planarized by the repetitive process of the oxidation by oxidants and the polish behavior by etchant and abrasive particles [5].

During Cu CMP, there are many issues such as Cu dishing, dielectric erosion, Cu corrosion and post CMP cleaning. These issues are mainly dependent on design of slurry chemistry. The understanding of role of additive chemicals in slurry is very important to Cu CMP mechanism and improve the CMP performance. The effect of additives such as organic acids and H_2O_2 in slurry on Cu CMP performance was not yet reported in detail. The surface reaction of Cu in various slurry chemicals is important in order to understand the of Cu induced oxidation, etching and dishing of Cu. The purpose of this research was to characterize the effects of chemical additives in slurry on Cu polishing and etching rates along with the surface reaction with Cu.

EXPERIMENTAL

γ alumina (99.99%, primary size <50 nm) and fumed silica particles (99.99%, primary size <50 nm) purchased from Degussa were used for the slurry preparation. Three types of organic acids, citric acid ($C_6H_8O_7$), oxalic acid ($C_2H_2O_4$) and succinic acid ($C_4H_6O_4$), with different functional groups, were purchased from Aldrich and added to slurry solutions in this study. Citric acid (pK1 = 5.8, pK2 = 4.3, pK3 = 2.9), a commonly used dispersant for alumina suspensions, was used in the form of naturally occurring tri-carboxylic acid. However, in the neutral pH ranges, the bi-carboxylic group is one of the most dominant species. In order to perform comparisons with citric acid, oxalic (pK1 = 1.2, pK2 = 4.2) and succinic acid (pK1 = 4.2, pK2 = 5.6), bi-carboxylic acids, were chosen for our experiments. H_2O_2 and BTA were used as an oxidant and a corrosion inhibitor of Cu, respectively. Ultrahigh purity DI water (18.2 Mcm, Millipore Milli-Q plus system) was used for the slurry preparation. The Cu films (10000 Å thick) used in this study were deposited on TaN films (~700 Å) by an electroplating system. TaN and TEOS wafers (~12,000 Å thick) were used for the selectivity test. Wafers were cut into 2.0×2.0 cm^2 samples for the polishing test.

Etch and polish rates of Cu were measured by four point probe (Chang Min Tech Co. Ltd, CMT-SR1000N) in various slurries conditions.

For the preparation of slurry, shaking and ultrasonic power were introduced for 60 min and 30 min, respectively. For the polishing experiments, copper CMP slurry was prepared at a constant mixing ratio of abrasives, oxidizer (H_2O_2), corrosion inhibitor (BTA) and organic acids in DI water. All polishing experiments were carried out using a polisher (Logitech, PM5) and Rodels Suba IV pad.

RESULTS AND DISCUSSIONS

Cu CMP slurry is commonly composed of abrasive particles, etchant, oxidant and pH adjustors. The roles of each additives in Cu slurry are very important to understand the polishing behavior of Cu during CMP. In order to understand the role of organic acids in H_2O_2 added slurry, the etch and removal rates of Cu were measured as a function of organic acids concentration at a constant H_2O_2 concentration of 10 vol% at pH 6. Figure 1 shows polish and etch rates of Cu in alumina slurries as a function of the concentration of organic acids. Polish rate of Cu was strongly dependent on the kine of organic acids added in slurry. Polish rates of Cu in slurries with citric and oxalic acids linearly increased to 8000 and 9500 Å/min as their concentrations increased. However, the etch rate of Cu was remained constant at 300~400 Å/min when even 1 wt% organic acids added in slurry.

Polish rate of Cu was dependent on the types of organic acids as etchant added in slurry. Effects of other additives on Cu polishing were investigated as shown in Figure 3. Figure 2 shows the polish and etch rates of Cu in alumina slurries with different chemical composition and pH. When citric acid as the etchant and H_2O_2 as oxidant exist in slurry independently, polish and etch rates were almost nil due to the insufficient chemical reaction. The addition of NH_4OH to citric acid slurry did not change them either. Cu removal and etch rates did not increase without the presence of both oxidant and etchant in the slurry.

Polish and etch rates of Cu drastically increased to 2000 Å/min and 1500 Å/min from almost nil, respectively, as the H_2O_2 and citric acid added in slurry at the same time. In this slurry composition, the chemical reaction between Cu surface and slurry was more dominant than the mechanical reaction. Cu CMP performance could be enhanced by the competitive action between chemical and mechanical reaction. The addition of NH_4OH to citric acid-H_2O_2 based slurry enhanced the formation of Cu complexes and further increased the removal rate.

The decrease of etch rate with the addition of NH_4OH might be due to the rapid decomposition of H_2O_2 and the decrease of redox potential in citric acid slurry. The etch rate in slurry solution is very important because it determines the degree of Cu dishing and corrosion during CMP. When the etchant and oxidant were added in slurry, the highest removal rate and lower etch rate were measured at neutral pH.

In order to evaluate the chemical reaction of slurry with Cu, the static etch rate and chemical polish rate were measured as a function of pH. Figure 3 shows the polish and etch rate of Cu with and without the alumina particles as a function of slurry pH. The static etch and chemical polish rates in the mixture of citric acid and H_2O_2 drastically decreased as the pHs of slurries increased. The increase of pH value causes the reduction of Cu etch rate due to decrease of redox potential and the rapid decomposition of H_2O_2. It indicates that pH is one of factors determining the etch rate. As previously mentioned, however, the polish rate of Cu with citric acid based alumina slurry increased to 8000 Å/min as the pH of slurry increased. It should be mentioned that the high static etch rate does not indicate the high polish rate.

The polishing was performed in slurry without the alumina particles. The chemical polish rate was larger than the polish rate in slurry with alumina particles at pH 2. Alumina particles were agglomerated easily at pH 2 because IEP value of alumina particles was 2 in the presence of citric acids. It was considered that the heavy agglomeration of slurry particles disrupted the abrasion reaction of Cu. As the pH of slurry increased, polish rate was increased by the enhanced mechanical effects due to effective dispersion of slurry particles in the abrasive contained slurry. The decrease of polishing rate in chemical polishing without particles at higher pH values the reduction of chemical etch rate of citric acid. It should be mentioned that the chemical polishing rate followed the same tendency as the etch rate of Cu as shown in Figure 3.

Figure 4 shows the polish rate of Cu with citric and oxalic acids added slurries as a function of BTA concentration. As the BTA concentration increased to 0.05 wt%, the polish rate decreased to 7000 Å/min and 4000 Å/min in oxalic and citric acid based slurries, respectively.

Table 1. Polish rate and selectivity among Cu, TaN and TEOS with various slurries

	3wt% Al2O3 at pH 6	3wt% SiO2 at pH 6	9wt% SiO2 at pH 6
Cu RR	8022Å	3600Å	5200Å
TaN RR	211Å	277Å	510Å
TEOS RR	80Å	300Å	700Å
Selectivity Cu:TaN	40 : 1	13 : 1	10 : 1
Selectivity Cu:TEOS	100 : 1	12 : 1	7.5 : 1

Alumina and silica abrasive particles were commonly used for the formulation of Cu CMP slurry. Figure 5 shows the polish rate of Cu in citric and oxalic acid based slurries as a function of abrasive types. The high polish rate of Cu was shown with slurry formulated with alumina when compared with silica abrasives. Also, higher polishing selectivity ratio among Cu, TaN and TEOS was measured with alumina abrasive as shown in Table 1. The removal rates of TaN and TEOS were increased as the solid content of silica abrasive increased. It was interesting to note that the polish rate of Cu was decreased as the concentration of silica was increased from 3 wt% to 9 wt%. Because the high removal rate of Cu and high selectivity ratio to TaN and TEOS are required in the 1st step polishing of Cu, alumina abrasives are more desirable than silica particles in the 1st step slurry.

In this study, the passivation and etching behaviors of Cu were evaluated in various slurry composition and related to Cu CMP performance. The effects of parameters such as etchant, abrasive particles and pH on CMP were evaluated. Organic acids as etchant and H_2O_2 as oxidant were very important additives to determine the polish rate and etch rate of Cu. The polish rate of Cu was dependent on the types of organic acids added in slurry. It was considered that polish rate of Cu was dependent on the concentration of carboxylates and mean particle size. High polish rate of Cu was observed in citric and oxalic acids based alumina slurries. When the etchant and oxidant were added in slurry, the highest removal rate and lower etch rate were measured at neutral pH. As the pH increased, polish rate of Cu was increased by the enhanced the mechanical effects due to effective dispersion of slurry particles. Alumina abrasives was more desirable for the 1st step slurry because of high removal rate of Cu and high selectivity ratio to TaN and Cu.

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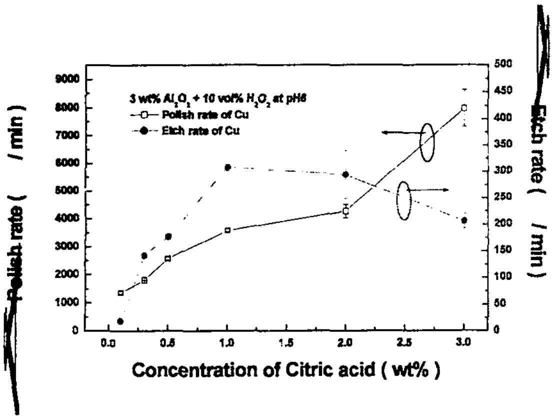

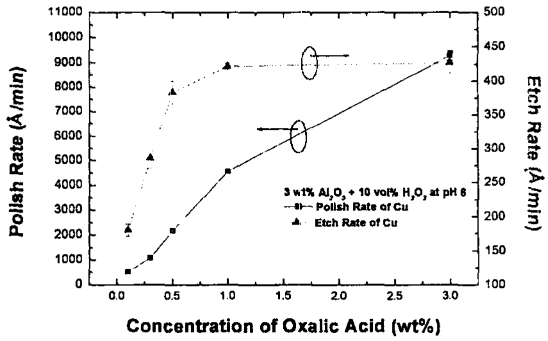

(a) (b)

Figure 1. Polish and etch rates of Cu in alumina slurry with (a) citric, (b) oxalic as a function of their concentration at pH 6

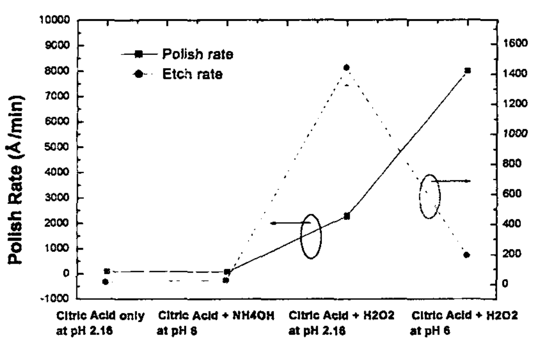

Figure 2. Polish and etch rates of Cu in various compositions of alumina based slurries at different pHs

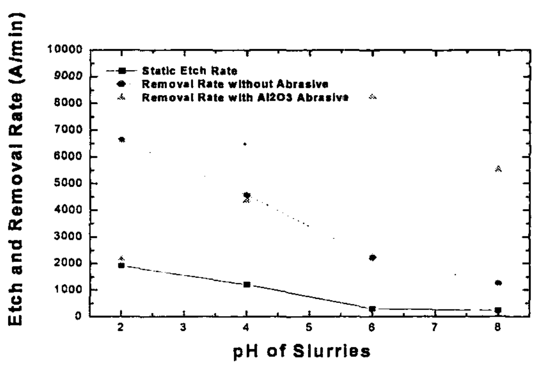

Figure 3. Polish and etch rates of Cu in various slurries with and without abrasive particle

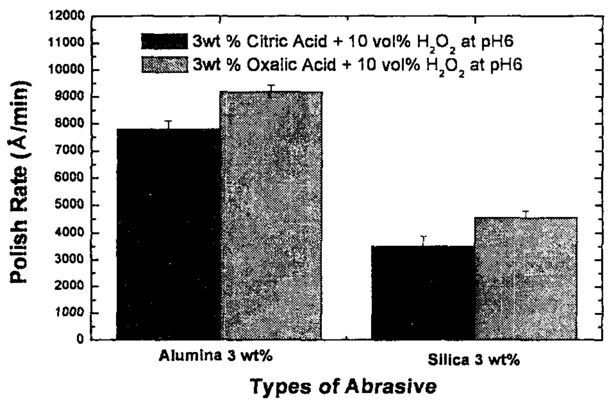

Figure 4. Polish rate of Cu with citric and oxalic acids added slurries as a function of BTA concentration at pH 6