Stability of H_2O_2 as an Oxidizer for Cu CMP

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Chemical mechanical polishing is an essential process in the production of copper-based chips. On this work, the stability of hydrogen peroxide (H_2O_2) as an oxidizer of copper CMP slurry has been investigated. H_2O_2 is known as the most common oxidizer in copper CMP slurry. But H_2O_2 is so unstable that its stabilization is needed using as an oxidizer. As adding KOH as a pH buffering agent, stability of H_2O_2 decreased. However, H_2O_2 stability in slurry went up with putting in small amount of BTA as a film forming agent. There was no difference of H_2O_2 stability between pH buffering agents KOH and TMAH at similar pH value. Addition of H_2O_2 in slurry in advance of bead milling led to better stability than adding after bead milling. Adding phosphoric acid resulted in the higher stability. Using alumina C as an abrasive was good at stabilizing for H_2O_2.

Keywords : Copper chemical mechanical polishing (CMP), Oxidizer, Hydrogen peroxide (H_2O_2), Stability

1. INTRODUCTION

Recently, copper CMP has been investigated as a key for interconnect layers to obtain global planarization[1]. Copper has attractive properties as a multi-level interconnection material due to lower resistivity and higher electromigration resistance as compared with alumina and its alloy with copper (0.5 %). Hence, use of copper interconnection leads higher speed by reducing RC delay, enhanced electroromigration lifetime reliability, reduced power consumption, and reduced manufacturing cost for silicon ICs[2,3]. Slurry in CMP process provides both the chemical roll through the solution chemistry and the mechanical roll through the abrasive. Slurry contains various chemicals such as oxidizer, pH buffering agent, complexing agent, abrasive and so on. Among a variety of agents in copper CMP slurry, H_2O_2 has commonly been used as an oxidizer. Stavereva et al.[4] has been reported the effect of slurry using H_2O_2 as an oxidizer. H_2O_2 is powerful yet versatile oxidizer that is both safe and effective. It is miscible with cold water and is soluble in alcohol and ether. H_2O_2 is so unstable that it requires stabilization to use as an oxidizer. Although pure hydrogen peroxide is fairly stable, it decomposes into water and oxygen when heated above about 80 °C; it also decomposes in the presence of numerous catalysts, e.g., most metals, acids, or oxidizable organic material. The chemical composition of copper CMP slurry has an effect on H_2O_2 decomposition. Hence, a variation of H_2O_2 concentration in slurry makes a serious influence on polishing in practical process. Thus durable maintenance of H_2O_2 concentration has to be required. In brief, stabilization of H_2O_2 is a vital process to get better yield in practical CMP process. In this work, the improvement of stability of H_2O_2 as an oxidizer of copper CMP slurry has been investigated through various experiments.

2. EXPERIMENTAL DETAILS

Appropriate H_2O_2 concentration.

To get appropriate H_2O_2 concentration which was applied to stability experiments for copper CMP slurry with alumina abrasive, polishing test of copper CMP was performed. The experiment was done on G&P Technology POLI-500CE™ chemical mechanical polisher. Head speed, table speed and the slurry flow rate were 40 rpm, 7 psi, and 150 ml/min, respectively. Rodel IC-1400 k-groove polyurethane pad, the electroplated copper wafer, and sputtered tantalum nitride wafer with 1,000 nm thickness were used for polishing test. Polishing time was set for 1 min. The reference slurry of polishing test was compounded to alumina C 5 wt% as abrasive, tartaric acid 1.0 wt% as a complexing agent, BTA 0.05 wt% as film forming agent, NH_4OH 0.6 wt% as a pH buffering agent, and DI water 88.35 wt% as solvent. Hydrogen peroxide (H_2O_2, 30 %) was purchased from Aldrich. TitroProcessor measured the concentration of hydrogen peroxide and Turbiscan was used to get dispersion stability.

α-particle alumina as an abrasive.

On experiment of the slurry with α-particle alumina as abrasive, the reference slurry was compounded to α-particle P-4 5.0 wt% as an abrasive, H_2O_2 5.0 wt% as oxidizer, Tartaric acid 2.0 wt% as a complexing agent, and KOH 1.0 wt% as pH buffering agent. After various agents were added and their concentrations were changed in reference slurry, a decrease of H_2O_2 with the lapse of time was measured.

γ-particle alumina as an abrasive.

An experiment on H_2O_2 stability with γ-particle alumina as an abrasive was made. Reference slurry was compounded to γ-particle alumina C 5.0 wt% as an abrasive, H_2O_2 5.0 wt% as an oxidizer, Tartaric acid 2.0 wt% as complexing agent, BTA 0.05 wt% as a film forming agent, and KOH 1 wt% as pH a buffering agent.

3. RESULTS AND DISCUSSION

Figure 1 shows that the removal rate was lower comparing with others when reference slurry did not contain H_2O_2. In slurry with H_2O_2 2.0 wt% or more, removal rates of copper and TaN were higher. Moreover, the highest removal rate of copper was shown in slurry with H_2O_2 5.0 wt%. The removal rate in H_2O_2 10 wt% was drop. This reduction in the chemical reactivity at higher H_2O_2 concentration is possibly due to the formation of a copper oxide film on the copper surface, proving some protection to the copper surface from chemical attack[5].

To get H_2O_2 stability as a function of concentration of KOH as a pH buffering agent, KOH 0.5 wt%, KOH 1.0 wt%, and KOH 1.0 wt% with BTA 0.05 wt% were added in reference slurry, respectively. As shown in Fig. 2, a decrease of H_2O_2 in slurry with KOH 0.5 wt% was smaller than that of with KOH 1.0 wt%. It is assumed to be multiple effects by decreasing metal component K and lower pH value. Stability of slurry is very sensitive to the solution pH[6]. As adding BTA 0.05 % as film forming agent in slurry with KOH 1 wt%, H_2O_2 stability was increased. To get H_2O_2 stability at the same pH condition adding different pH buffering agents, fixing amounts of KOH and TMAH were added in reference slurry respectively. First sample was set to pH 4.57 with adding KOH 1.0 wt% and second sample was set to pH

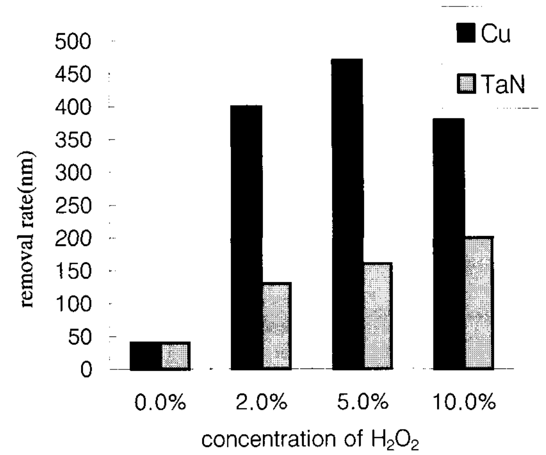

Fig. 1. Removal rate of Cu and TaN as a function of H_2O_2 concentration.

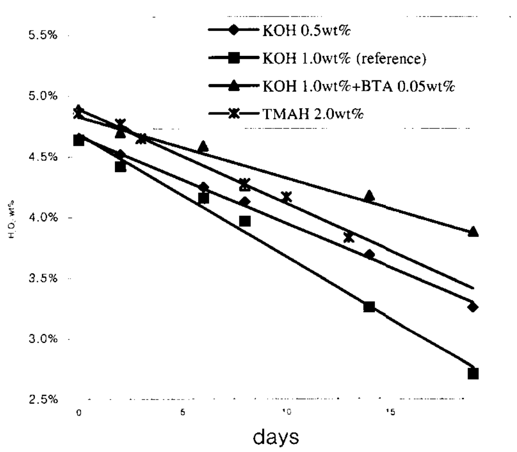

Fig. 2. Stability of H_2O_2 in slurry with KOH and TMAH as a pH buffering agent, and BTA as a film forming agent.

4.65 with TMAH 2.0 wt%. As shown in Fig. 2, there is no difference between H_2O_2 stabilities on same pH condition adding KOH and TMAH. It is estimated that ammonium ions of TMAH facilitate decomposition of H_2O_2. Dispersion stability of TMAH was lower than that of KOH.

To get an effect of bead milling on H_2O_2 stability, first sample was added H_2O_2 after bead milling and another sample was added H_2O_2 before bead milling in reference slurry. As shown in Fig. 3, the sample which H_2O_2 was added before bead milling has a lower decomposition rate compared with after beading milling. Even though a supplement experiment was needed, it is assumed that H_2O_2 was mixed sufficiently with other components through a bead milling. In the matter of dispersion stability, a sample adding H_2O_2 after milling was shown higher dispersion stability.

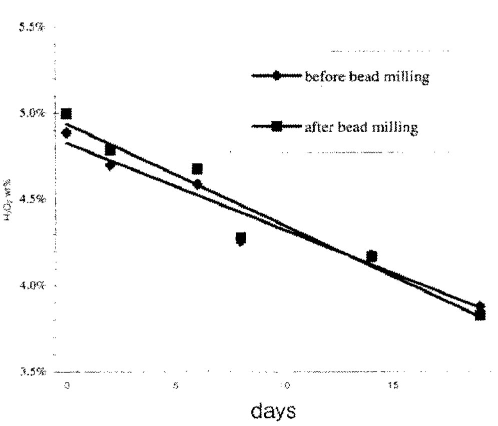

Fig. 3. Stability of H_2O_2 in slurry with addition of H_2O_2 before and after bead milling.

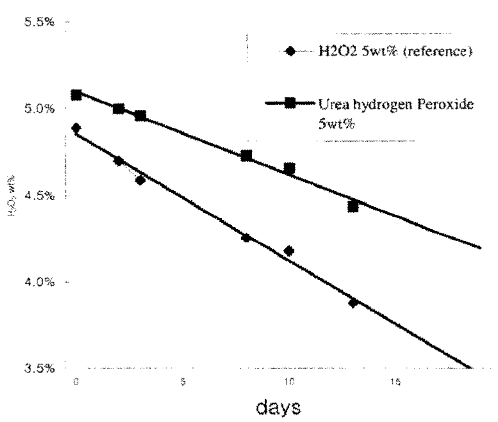

Fig. 4. Stability of H_2O_2 in slurry with urea hydrogen peroxide as an oxidizer.

Figure 4 shows the result when urea hydrogen peroxide 5 wt% was added in slurry to get its actual performance. Using urea hydrogen peroxide as oxidizer led better stability compared with using H_2O_2. Urea hydrogen peroxide is known as an enhanced oxidizer because it inhibits a decomposition of H_2O_2; moreover, it has similar oxidative as H_2O_2. Hence, urea hydrogen peroxide is the solution which is able to be used with H_2O_2.

In addition, the experiment of agents which commonly use as a H_2O_2 stabilizer of STI slurry was performed. Figure 5 shows the result of addition of potassium stannate 0.2 wt%, potassium diphosphate 0.2 wt%, and phosphoric acid 0.2 wt% in reference slurry, respectively. When phosphoric acid was added in slurry, decrease of H_2O_2 was 0.035 %/day which is 60 % rise compared with a reference. On the other hand, adding Potassium stannate and potassium diphophate seldom help to H_2O_2

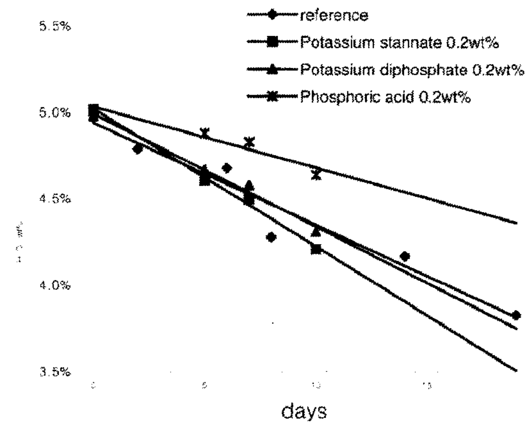

Fig. 5. Stability of H_2O_2 in slurry with H_2O_2 stabilizers of STI slurry.

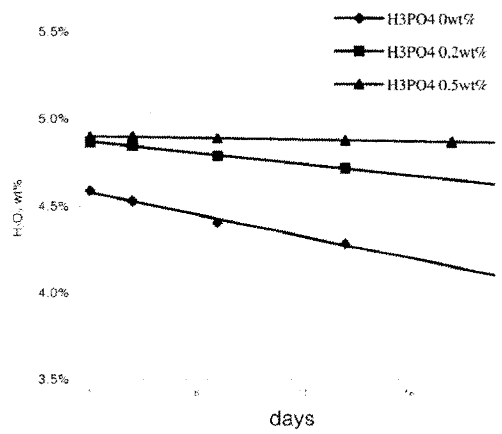

Fig. 6. Stability of H_2O_2 in slurry as a function of concentration of H_3PO_4 as H_2O_2 stabilizer.

Figure 6 shows an influence of H_3PO_4 concentration on H_2O_2 stability. On the whole, an addition of small amount of H_3PO_4 led far better stabilization. Decrease of H_2O_2 was the lowest (0.002 %/day) when a concentration of H_3PO_4 in slurry increased to 0.5 wt%. Although stability was increased significantly with addition of H_3PO_4, the problem was lower dispersion stability[7]. While H_3PO_4 concentration was fixed to 0.2 wt% for meeting the upper result, concentration of KOH as pH buffering agent was changed to KOH 0 wt%, KOH ' wt%, and KOH 1 wt% with potassium diphosphate 0. wt%, respectively.

Figure 7 shows H_2O_2 stability in slurry with them. the concentration of KOH became lower, the stab' was increased. The slurry in absence of KOH had so pH value (1.86) that it met a dispersion prol Addition of potassium diphosphate did not stability and it caused lower dispersion stability in As shown Fig. 8, using urea hydrogen peroxide 5 an oxidizer didn't have a better effect on the decre

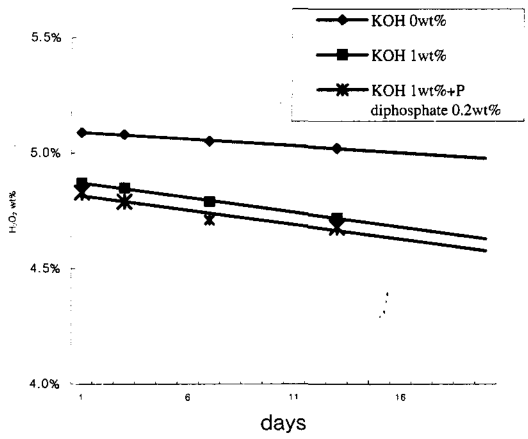

Fig. 7. Stability of H_2O_2 in slurry as a function of concentration of KOH, and addition of potassium diphosphate 0.2 wt%.

of H_2O_2 as compared with using H_2O_2 5 wt%. Otherwise, it improved the stability remarkably as same as the result of α-particle alumina. In addition, H_3PO_4 0.2 wt% was added while urea hydrogen peroxide was used as an oxidizer. Even though addition of H_3PO_4 0.2 wt% improved H_2O_2 stability in slurry with urea hydrogen peroxide, it led worse dispersion stability like other results.

4. CONCLUSION

When H_2O_2 is used as an oxidizer in copper CMP slurry, addition of stabilizer is required. As compared between two kinds of alumina particles, H_2O_2 becomes more stable as using γ-particle alumina C as an abrasive. When KOH is added as a pH buffering agent, the H_2O_2 stability is worse. On the other hand, it prevents dispersion stability from lowering due to the rise of pH value. In the same pH value, the difference of H_2O_2 stability between addition of KOH and TMAH is significantly small. On the same condition, H_2O_2 addition before bead milling in the slurry is better than H_2O_2 addition after bead milling for the stability. H_3PO_4 leads better stability remarkably; nevertheless, addition of small amount of H_3PO_4 is required because of dispersion stability. Urea hydrogen peroxide is an excellent oxidizer in the matter of H_2O_2 stability. Considering just stability of H_2O_2, the uppermost compound of CMP slurry is as follows; alumina C as an abrasive, urea hydrogen peroxide as an oxidizer, H_3PO_4 as a H_2O_2 stabilizer, and NH_4OH as a pH buffering agent.

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Instructions for the Preparation of Article for Transactions on Electrical and Electronic Materials (bold, 15 points)

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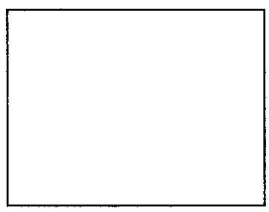

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This work was supported by the Ministry of Science and Technology though the Nano-Structure Technology Project.

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