Roles of Phosphoric Acid in Slurry for Cu and TaN CMP

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The purpose of this study was to investigate the characteristics of slurry including phosphoric acid for chemical-mechanical planarization of copper and tantalum nitride. In general, the slurry for copper CMP consists of alumina or colloidal silica as an abrasive, organic acid as a complexing agent, an oxidizing agent, a film forming agent, a pH control agent and additives. Hydrogen peroxide (H_2O_2) is the material that is used as an oxidizing agent in copper CMP. But, the hydrogen peroxide needs some stabilizers to prevent decomposition. We evaluated phosphoric acid (H_3PO_4) as a stabilizer of the hydrogen peroxide as well as an accelerator of the tantalum nitride CMP process. We also estimated dispersion stability and zeta potential of the abrasive with the contents of phosphoric acid. An acceleration of the tantalum nitride CMP was verified through the electrochemical test. This approach may be useful for the development of the 2nd step copper CMP slurry and hydrogen peroxide stability.

Keywords : Copper CMP, Tantalum Nitride CMP, Slurry, Hydrogen Peroxide, Phosphoric Acid

1. INTRODUCTION

Copper metallization has been used in high-speed logic ultralarge-scale integrated circuits instead of the aluminum metallization because it has a low electrical resistivity and high electromigration resistance. Also chemical-mechanical planarization (CMP) process for copper dual damascene has been introduced as a new technology in IC manufacturing[1-3].

The first step in copper CMP is to remove the bulk of the copper, typically stopping on the underlying Ta/TaN diffusion barrier. At this point, since tantalum nitride has quite different polishing properties than copper, it is necessary to switch to a different polishing slurry as a 2nd step. The overpolishing time means the amount of time between when the diffusion barrier is first exposed and the last remaining copper. Once the barrier is removed, a third step is used to buff, clean and passivate the wafer. Usually a result of overpolishing, as shown in Fig. 1, 2nd step copper CMP slurry needs TaN to Cu selectivity of >1:1[4].

A copper CMP slurry is typically made of suspended abrasive particles, an oxidizing agent, a film forming agent, a pH controller, plus one or more of a long list of additives including dispersants, chelators, accelerators, colorants and lubricants[5,6]. Hydrogen peroxide is the material that is used as an oxidizing agent. But because of the decomposition, the hydrogen peroxide needs a stabilizer. In the application we setup a good recipe so that slurry has an acceleration of the tantalum nitride CMP and a stability of the hydrogen peroxide.

2. EXPERIMENTAL DETAILS

This experiment was done on G&P Technology POLI-500CE™ chemical mechanical polisher using Rodel IC-1400 k-groove polyurethane pad. The electroplated

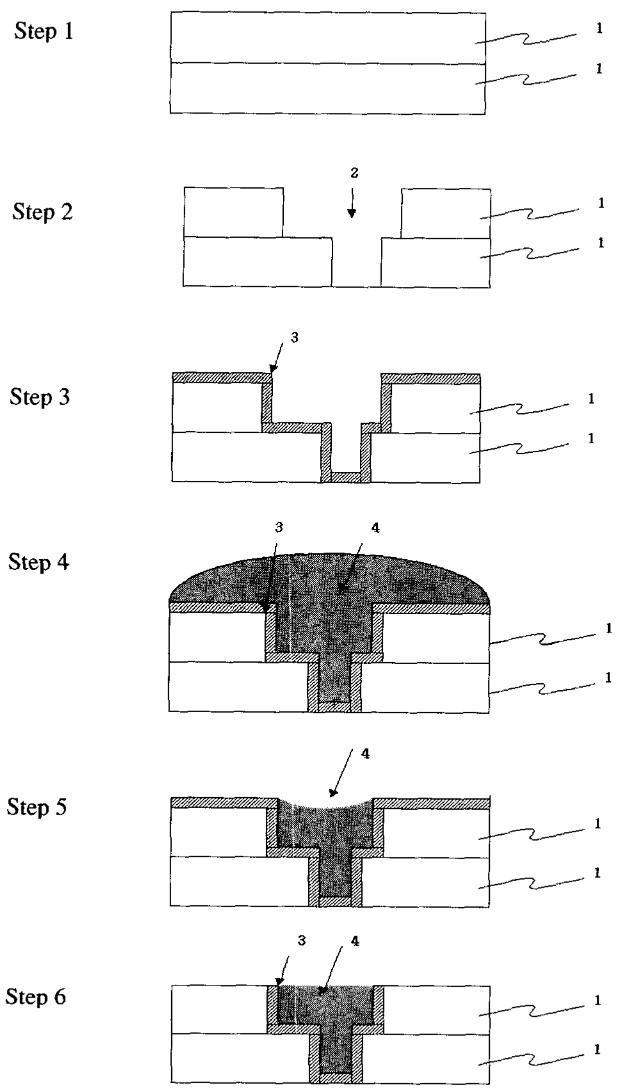


Fig. 1. Cu Damascene and CMP Process (1: Silicon oxide, 2: Trench, 3: Tantalum nitride, 4: Copper, 5: Overpolishing).

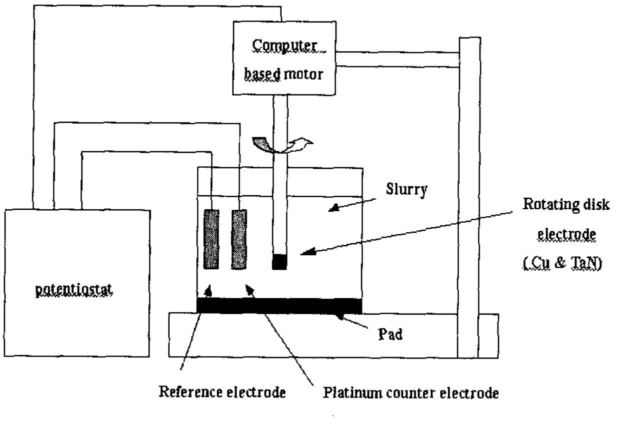


Fig. 2. Diagram of potentiostat equipment.

copper, sputtered tantalum nitride, and PETEOS wafer with 10,000 Å thickness were prepared for polishing. For the polishing, the head speed was set at 40 rpm and the table speed was 40 rpm. The down pressure of the head was 7 psi and the slurry flow rate was 150 ml/min. Polishing time was set for 1 min.

Zeta potential and particle size measurement of the slurries were carried out using a Brookhaven ZetaPlus instrument. This technique allowed the simultaneous determination of both the mobility and the zeta potential of suspended slurry particles. About particle size, this instrument works on the principle of dynamic light scattering (DLS) to determine mean aggregate particle size and size distribution of the particle dispersed.

The electrochemical curves were recorded with an EG&G 273A Potentiostat. Electrochemical data are obtained with an electrode rotation of 100 rpm with the rotator and the electrode in contact with an abrasive pad as shown in Figure 2. Thus metal dissolution could be evaluated as its surface was abraded as well as after abrasion. In a typical test, the electrochemical data were recorded as Tafel plot. Polarization is begun at approximately –250 mV from open circuit potential (OCP) and increased until the potential is +250 mV from OCP. Phosphoric acid (H_3PO_4,85%) and Hydrogen peroxide (H_2O_2,30%) were purchased from Aldrich. TitroProcessor measured the content of hydrogen peroxid

3. RESULTS AND DISCUSSION

The typical chemistry used to polish copper is significantly more complex than the chemistry applied in tungsten or ILD polishing. Copper CMP slurries require many chemicals. As is typical for copper slurries, the oxidizing agent is present to oxidize the surface to the copper ions such as Cu_2O, CuO, and $Cu(OH)_2$. A common oxidizing agent is hydrogen peroxide which is unstable. We evaluated phosphoric acid (in Figure 3) as a stabilizer of the hydrogen peroxide. As shown in Figure 4, the stability of the hydrogen peroxide in slurry including the phosphoric acid was increased, indicating that the decomposition rate of the active peroxide including 0.5wt% H_3PO_4 is much slower than that of other stabilizers. The decomposition rate of hydrogen peroxide was –0.002wt%/day.

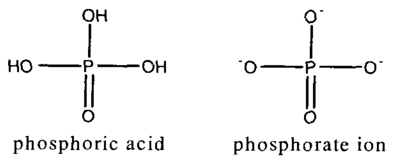


Fig. 3. The structure of phosphoric acid.

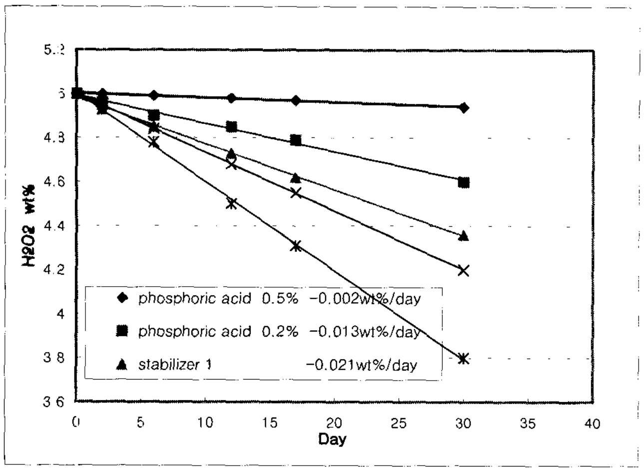


Fig. 4. Stability evaluation of H_2O_2 in slurry.

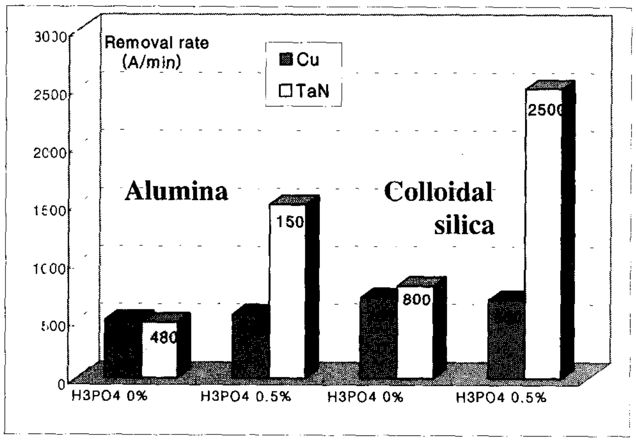
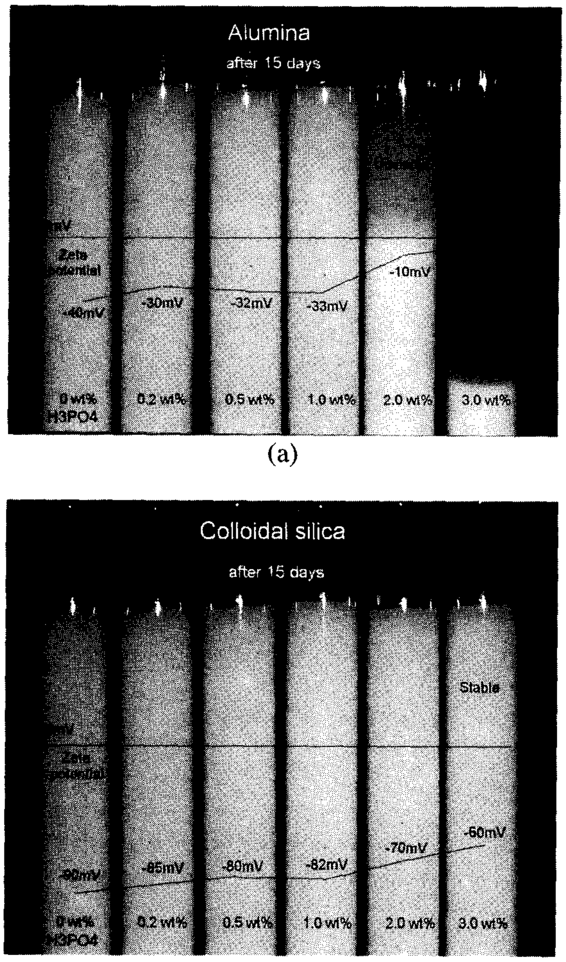


Fig. 5. Cu and TaN polishing results (Head 40rpm, Table 40rpm, Pressure 7psi).

Figure 5 shows actual copper and tantalum nitride polishing results using slurry including phosphoric acid. The removal rate of tantalum nitride with 0.5wt% phosphoric acid was approximately 1500 Å/min using a 5wt% alumina abrasive and 40 rpm, 7 psi polishing conditions. This removal rate was 3.1 times faster than that of the slurry without phosphoric acid. In the case of copper, removal rate did not increase according to the phosphoric acid's addition. Colloidal silica showed the same results (TaN removal rate 800→ 2500Å/min). According to the experimental data, H_3PO_4 enhanced the tantalum nitride removal rate. Therefore, this slurry has an advantage in the 2nd step CMP of copper and tantalum nitride.

The pictures in Fig. 6 show the dispersion stability of slurry after 15days and the plots in the Figure indicate the zeta potential of the abrasive with the contents of phosphoric acid. A high zeta potential, either positive or negative, signifies an unstable dispersion. In the case of alumina abrasive, the dispersion was unstable and zeta potential approached 0 mV above 2wt% of phosphoric acid. But, colloidal silica was stable up to 3wt%. Both alumina and colloidal silica based slurry had no particular problem to 1wt% that was actual addition condition. Therefore, phosphoric acid has applicable ability of copper CMP slurry.



(a)

(b)

Fig. 6. Dispersion stability and Zeta potential test with the contents of phosphoric acid (slurry pH 8).

We recognized an acceleration of the tantalum nitride CMP through electrochemical test. Potentiostat is the equipment used to measure electrochemical and potentiodynamic conduct of copper and tantalum nitride. Using the potentiostat and rotating disk system, a test was done by similar polishing situation (100 rpm). The rotating disk electrode was used to investigate the tantalum nitride and copper dissolution behavior under hydrodynamic conditions. The Tafel curves of Cu and TaN are shown in Fig. 7. In the case of tantalum nitride and slurry including phosphoric acid, there is a increase in the open circuit potential (OCP) and enhancement in the corrosion current density and corrosion rate. These results show indirectly that phosphoric acid influences tantalum nitride.

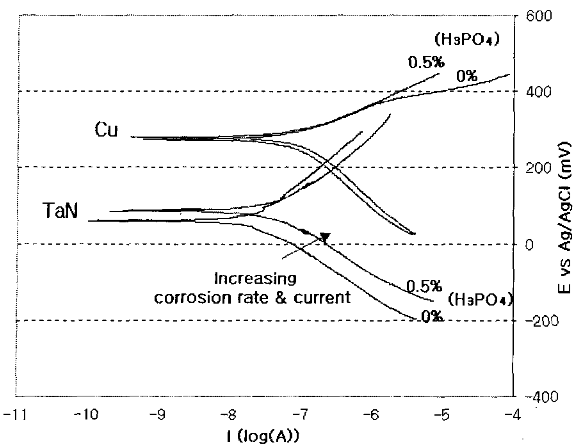


Fig. 7. Tafel curve of Cu & TaN in slurry including (0%, 0.5%) phosphoric acid.

4. CONCLUSION

A slurry including phosphoric acid was proposed. The slurry consists of 5.0wt% abrasive, 5.0wt% hydrogen peroxide, 0.5wt% phosphoric acid and etc. This slurry has good H_2O_2 stability, TaN CMP acceleration and dispersion ability. We present a special chemistry and electrochemical conduct of real polishing. This approach may be useful for the development of the 2nd copper CMP slurry and hydrogen peroxide stability.

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