Cu CMP중 BTA에 의한 Particle의 흡착에 관한 연구

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Effect of Corrosion inhibitor, Benzotriazole (BTA), on Particle Adhesion in Cu CMP

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Abstract : The effect of benzotriazole (BTA) on the adhesion force of silica and pad particle on Cu/TEOS wafer surfaces was investigated with and without the addition of BTA. Cu-BTA had the isoelectric point (IEP) at around pH 4~8. Pad particles were more positive zeta potentials than silica. The adhesion force initially decreased of silica and pad particle on Cu surfaces when BTA was added. However, the more BTA was added, the more adhesion force gradually increased with the increase of BTA concentrations. Then the adhesion force of pad particle was higher than silica. And TEOS didn't resulted increasing adhesion force like Cu when BTA was added in DI water.

Key Words : BTA, Pad Particle, Zeta Potential, Adhesion Force

1. Introduction

The corrosion of rate of Cu decreases with increase BTA concentration[1]. So, an amount of BTA concentration is important factor in the slurry so that Cu had not been etching during polishing. However, If the BTA was lots of added to inhibit the corrosion of Cu, organic residues will be appeared on Cu surfaces since BTA was a source of organic residues. And another source of organic residues included the polishing pad. Pad conditioning was a necessary process during CMP. However, the pad particles were generated during pad conditioning. The focus of this study was to investigate the effect of BTA on the adhesion of silica and pad particles on Cu/TEOS wafer surfaces. This work, which measurement of zeta potentials of particles and wafer surfaces, was expected to predict the adhesion force between them. It also included an experimental investigation of the real adhesion force to remove silica and pad particles to Cu/TEOS in a variety of environments using an atomic force microscope (AFM).

2. Experimental Procedure

The adhesion force of particles on surface was measured using an atomic force microscope (AFM, XE-100, PSIA Co., Korea) by directly measuring the force required to remove them from surfaces [2]. The 40 m spherical silica and dry ground irregular pad (IC 1000, Rohm and Haas Co.) particles were attached on tipless cantilevers. The adhesion force was measured between particles and Cu/TEOS surfaces in a liquid cell as a function of BTA concentration. Cu and TEOS wafer surfaces were pre-cleaned in dilute HF (DHF, 0.01 vol %) solution for 30sec and the SPM (Sulfuric-peroxide mixture) solution for 10min, respectively, before the experiments. In order to investigate the electro-kinetic behavior of surfaces, the zeta potentials were measured using a laser electrophoresis zeta potential analyzer (LEZA 600, Otsuka Electronics, Co.) as a function of pH. To measure the zeta potentials of particles and wafer surfaces, two types of electrokinetic methods, such as an electrophoresis and electroosmosis methods. The ionic strength of solution was set to 10^{-3} M KCl for particles and 10^{-3} M NaCl for wafer surfaces. Then pad particles were prepared by grinding of the pad. Zeta potentials of Cu-BTA/TEOS surfaces were measured of electroosmosis. pH of solutionswas adjusted with HCl and NaOH to measure the zeta potentials.

3. Results and Discussion

In order to investigate the surface charge silica and pad particles, the zeta potentials were measured as a function of pH of solutions as shown in Fig. 1.

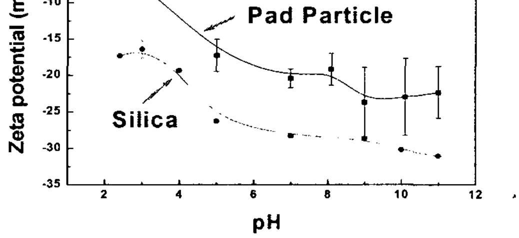

Fig. 1. The zeta potentials of silica and pad particle as a function of pH

Both of Silica and pad particles decreased with the increase of pH and negative zeta potentials were measured at all pH ranges. It should indicate that pad particles were more positive zeta potentials than silica. Fig. 2 illustrates the zeta potentials of Cu-BTA/TEOS wafer surfaces. It was measured using a way of electro-osmosis. Zeta potentials of Cu-BTA had an isoelectric point (IEP) at around 4~8. Zeta potentials of TEOS was decreasing steadily with the increase of pH. And Zeta potentials of Cu-BTA were more positive than TEOS

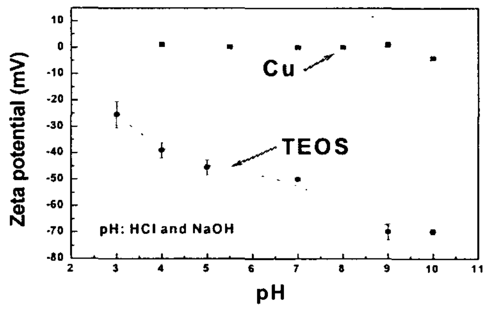

Fig. 2. The zeta potentials of Cu and TEOS wafer surfaces as a function of pH

The adhesion force between particles and wafer surfaces was experimentally measured using an AFM. Fig. 3 shows the adhesion forces between silica, pad particles and Cu surfaces as a function of BTA concentrations in DI water. The adhesion forces initially decreased of both silica and pad particle on Cu surfaces when BTA wad added 0.01 wt %. However, the more BTA was added to 0.05 wt % in DI water, the more adhesion force then gradually increased with the increase of BTA concentrations. In DI water, the adhesion force of silica on Cu was higher than that of pad particle. However, the addition of BTA in DI water resulted in a higher adhesion forces on pad particles. If there were silica and pad particles in slurry with BTA as contaminant sources, more pad particles will be appeared on Cu surfaces.

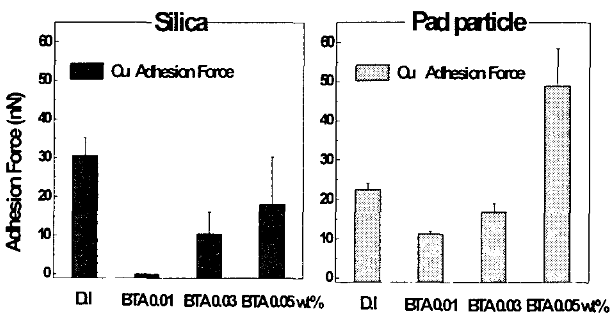

Fig. 3. The adhesion forces of silica and pad particles on Cu as a function of BTAconcentration in DI water.

Fig. 4 shows the adhesion forces between silica, pad particles and TEOS surfaces as a function of BTA concentrations in DI water. The addition of BTA in DI water resulted not increasing adhesion force like Cu as shown in Fig. 5. Overall, Silica was higher adhesion force than pad particle. And adhesion force of TEOS surface was smaller than Cu. It indicates that more organic residues will be appeared on Cu than TEOS

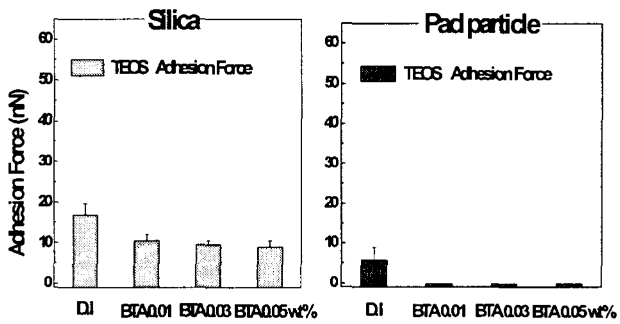

Fig. 4. The adhesion forces of silica and pad particles on TEOS as a function of BTA concentration in DI water.

4. Conclusion

Zeta potentials of Cu-BTA was more positive than TEOS. Cu-BTA had the isoelectric point (IEP) at around pH 4~8. And zeta potentials of silica and pad particle showed negative charges at all pH ranges. Then pad particle was more positive zeta potentials than silica.

In DI water, the adhesion forces initially decreased of both silica and pad particle on Cu surfaces when BTA wad added 0.01 wt %. However, the more BTA was added to 0.05 wt % in DI water, the adhesion force then gradually increased with the increase of BTA concentrations. It was contributed Cu had different Cu-BTA films with the addition of BTA. And the adhesion force of pad particle was higher than silica. So, pad particles had more potentials of adhering on Cu surfaces than silica. TEOS didn't resulted increasing adhesion force like Cu when BTA was added in DI water. And adhesion force of TEOS was much smaller than Cu. It indicates that more organic residues will be appeared on Cu than TEOS

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