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Yi-Koan Hong

Samsung Electronics, South Korea

Ja-Hyung Han

Samsung Electronics, South Korea

Tae-Gon Kim

Hanyang University

Jin-Goo Park

Hanyang University

Ahmed A. Busnaina

Northeastern University

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The Effect of Frictional and Adhesion Forces Attributed to Slurry Particles on the Surface Quality of Polished Copper

Yi-Koan Hong, Ja-Hyung Han,^a Tae-Gon Kim,* Jin-Goo Park,** and Ahmed A. Busnaina^b

Division of Materials and Chemical Engineering, Hanyang University, Ansan 426-791, Korea

The effect of frictional and adhesion forces attributed to slurry particles on the quality of copper surfaces was experimentally investigated during copper chemical mechanical planarization process. The highest frictional force of 9 Kgf and adhesion force of 5.83 nN were observed in a deionized water-based alumina slurry. On the other hand, the smallest frictional force of 4 Kgf and adhesion force of 0.38 nN were measured in an alumina slurry containing citric acid. However, frictional (6 Kgf) and adhesion (1 nN) forces of silica particles in the slurry were not significantly changed regardless of the addition of citric acid. These differences were explained by the strong adsorption of citric ions on alumina but not on silica, which was verified by the charge reversal of alumina in zeta potential measurements. Higher particle adhesion forces resulted in higher friction. A higher magnitude of particle contamination and scratches was observed on polished copper surface in slurry condition with higher adhesion and friction forces.

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Copper has been widely used as an interconnection material in submicrometer multilevel device fabrication because of its many benefits including lower resistivity ($1.7 \mu\Omega \text{ cm}$), superior resistance to electromigration, and the reduction of resistance-capacitance (RC) time delay when compared with aluminum ($2.66 \mu\Omega \text{ cm}$).¹ The formation of the copper interconnection is only possible by a novel damascene chemical mechanical planarization (CMP) process. During copper CMP, wafer surfaces are usually exposed to at least two different slurry solutions. Despite that the CMP process is well recognized as a powerful method for global planarization, several issues remain, such as local erosion, dishing, scratches, and abrasive particle contamination after the CMP process. After polishing, the residue of abrasive particles and scratches that remain on the wafer surfaces become a great challenge.²

Any adhesion forces between two surfaces will induce the increase of contact area and generally contributes to the overall frictional force.³ Adhesion force might act as an additional normal load and increase the frictional force. The frictional force could also increase the contamination on the surface.^{4,5} Past research has focused on the relation between the adhesion force and frictional behavior on microelectromechanical system (MEMS) structures and thin films.⁶⁻⁸ We have studied the effect of the pH on the removal and adhesion of silica particles in slurry solutions.^{9,10} No study has yet reported, however, on the effect of the adhesion force of slurry particles on the frictional behavior and the defects such as scratches and particles in the copper CMP process.

The objective of this research was to see the relationship among friction force, removal rates, adhesion forces, and defects such as scratches and particle contaminations in copper polishing. Because low adhesion forces and the minimal friction between abrasive particles and wafer surfaces are required for reducing particle contamination and scratches on the surfaces, the adhesion forces and frictional curves of silica and alumina particles on copper surfaces were studied in copper CMP slurry solutions. These friction and adhesion forces are a strong function of chemistry in slurry. The effect of additives on these forces was also evaluated. The magnitude of abrasive particle contamination and scratches on the copper surfaces was observed after polishing to relate copper surface quality with the adhesion forces and frictional characteristics.

Experimental

The adhesion forces of particles on copper surfaces was measured using an atomic force microscope (AFM, Park Scientific Instruments CP Research) by directly measuring the force required to remove them from a surface.^{9,10} Both spherical silica (Duke Scientific Co.) and alumina (α phase, Micron Co., Japan) particles with a diameter of $40 \mu\text{m}$ were attached to a Si_3N_4 tipless cantilever as shown in Fig. 1. A spherical particle of silica and alumina was, respectively, attached on a tipless cantilever of spring constant, 1.75 N/m (ULCT-NT, Veeco) by epoxy glue and then dried in air. The adhesion force was measured between the particles and the copper surface in a liquid cell. The normal force was set at 13.2 nN and the area of $45 \times 45 \mu\text{m}$ was scanned at a rate of $0.5 \mu\text{m/s}$.

Electroplated copper wafers (1000 nm , $0.016 \Omega/\square$) and copper disks (99%, diameter 100 mm) were used to measure the adhesion and frictional forces, respectively. Copper wafers were precleaned in diluted HF (DHF, 0.01 vol %) solution for 60 s followed by a rinse with deionized (DI) water for 30 s. The copper slurry was prepared in a solution mixture of 3 wt % citric acid, 10 vol % H_2O_2 , and 0.01 wt % benzotriazole (BTA) by adding 3 wt % fumed silica particles (Degussa, Aerosil, 30 nm) and alumina particles (Degussa, 13 nm). The pH of the copper slurry was adjusted to 6 using NH_4OH . To investigate the adsorption of citrate ions on the surfaces

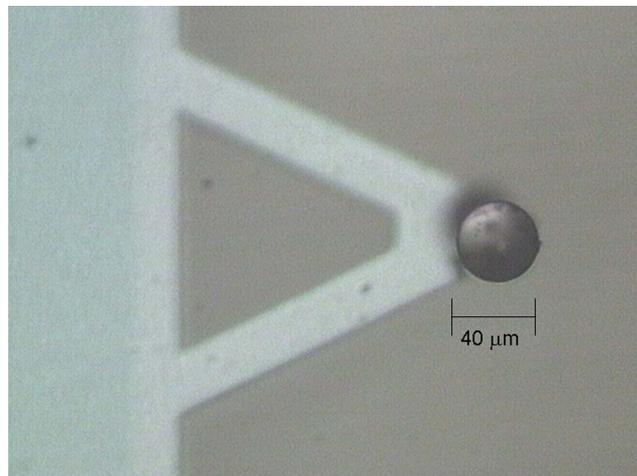


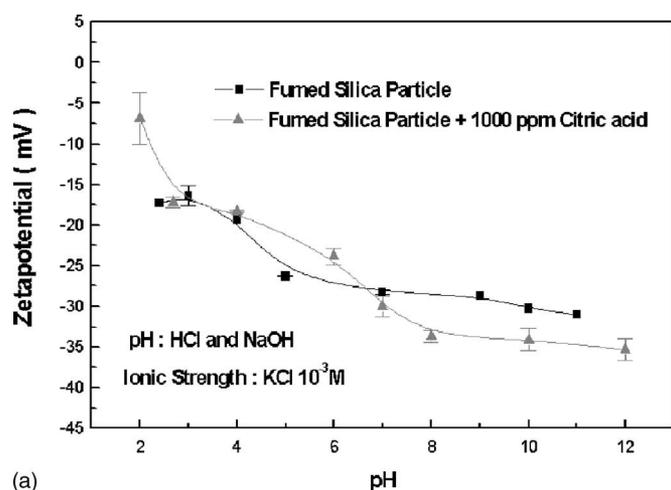
Figure 1. Optical micrograph of a spherical $40 \mu\text{m}$ abrasive particle attached to a tipless cantilever ($\times 200$).

* Electrochemical Society Student Member.

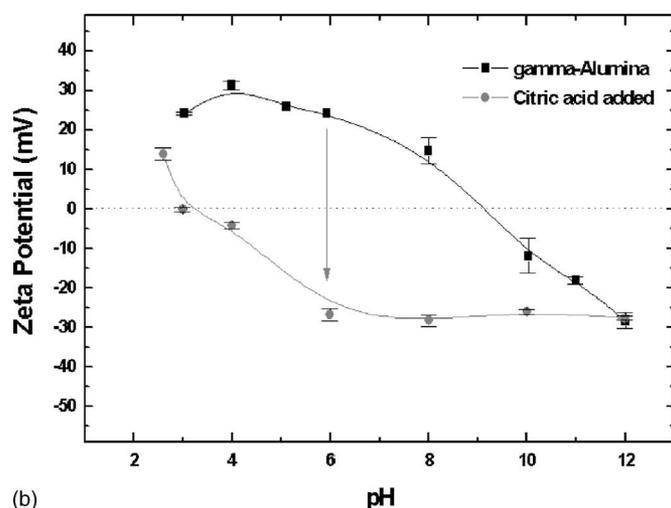
** Electrochemical Society Active Member.

^a Present address: Samsung Electronics, Korea.

^b Present address: Northeastern University, Boston, Massachusetts 02115.



(a)



(b)

Figure 2. The zeta potentials of (a) silica and (b) alumina particle as a function of pH in the presence and absence of citric acid.

in the solutions, the zeta potentials were measured by electrophoresis method¹¹ using a laser zeta potential analyzer (LEZA600, Otsuka Electronics Co.). For the zeta potential measurements, copper particles (Aldrich, 1 μm) were used instead of copper wafers.

The frictional behavior of alumina and silica abrasive particles was measured using a polisher (Poli-500, G&P Tech, Korea) which could measure the friction force in situ. Normal and lateral force signals were measured during copper polishing by preinstalled two piezoelectric sensors at a rate of 1000 times/s copper disks were used for the polishing experiments. Removal rates were calculated by measuring the weight difference before and after polishing using a microbalance with a sensitivity of 0.01 mg. Head and platen velocity were set at 50 and 83 rpm, respectively. Flow rate of slurry was set at 140 mL/min during copper CMP process. The polishing pressure on wafer was 4.2 psi.

Results and Discussion

To investigate the adsorption of citrate ions onto silica and alumina particles the zeta potential of these particles was measured as a function of pH in the presence and absence of 1000 ppm of citric acid in a 10^{-3} M KCl solution as shown in Fig. 2. Although little change in the zeta potential was observed with silica particles in a citric acid solution, a significant change was observed on alumina particles in the presence of citric acid. The adsorption of negative citrate ions on the positively charged alumina particle surfaces was

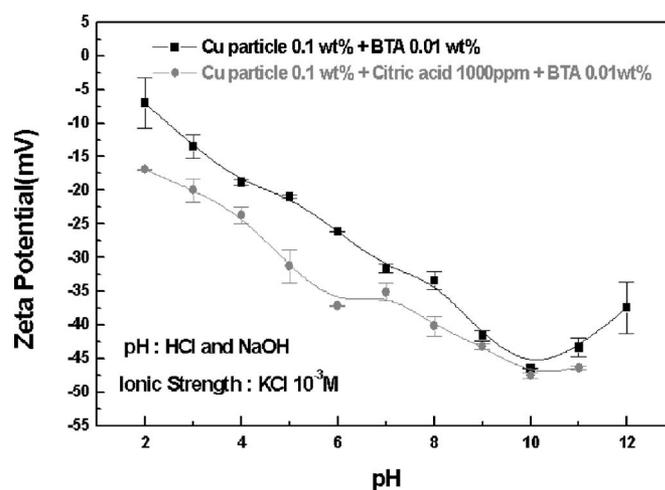


Figure 3. The zeta potential of the copper particles as a function of pH in the presence and absence of citric acid.

studied by observing C = O stretching peaks of the attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra on alumina surface.^{12,13} The adsorption of citrates on alumina caused the reversal of zeta potentials from positive to negative values as shown in Fig. 2a. Little adsorption of citrates on silica was observed by FTIR¹⁰ which led no change in zeta potentials as indicated in Fig. 2b.

Figure 3 shows the zeta potential of the copper particles as a function of pH both with and without the addition of citric acid. BTA was added to prevent copper dissolution at the acidic pH levels. Slightly more negative zeta potentials were measured on the copper surfaces in the presence of citric acid which might indicate the slight adsorption of citrates on copper surfaces.

The adhesion forces of silica and alumina particles in the DI water and slurry solution were measured by AFM as shown in Fig. 4. The smallest adhesion force, 0.38 nN, was observed between the copper surface and alumina particles in a citric acid solution at pH 6. The largest adhesion force of alumina particles, 5.83 nN, was measured in DI water. The largest adhesion force of alumina particle in DI water was attributed to a stronger electrostatic attraction between alumina particle and copper surface in DI water due to their opposite signs of zeta potentials. The smallest adhesion force of alumina particles in the citric acid slurry was attributed to the selective ad-

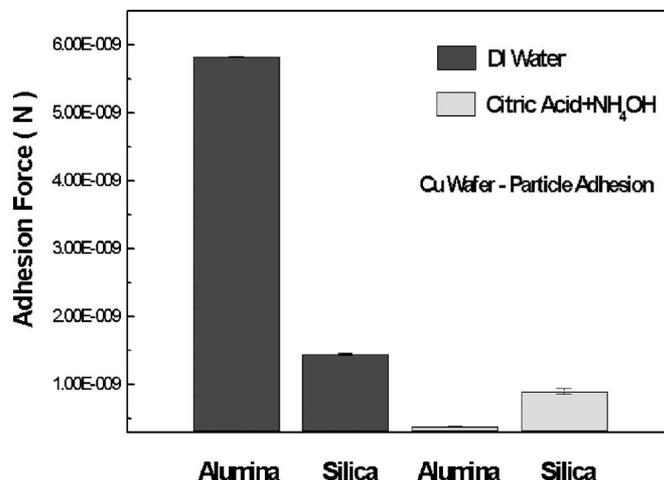


Figure 4. The adhesion forces of the particles on copper in DI water and citric acid solutions.

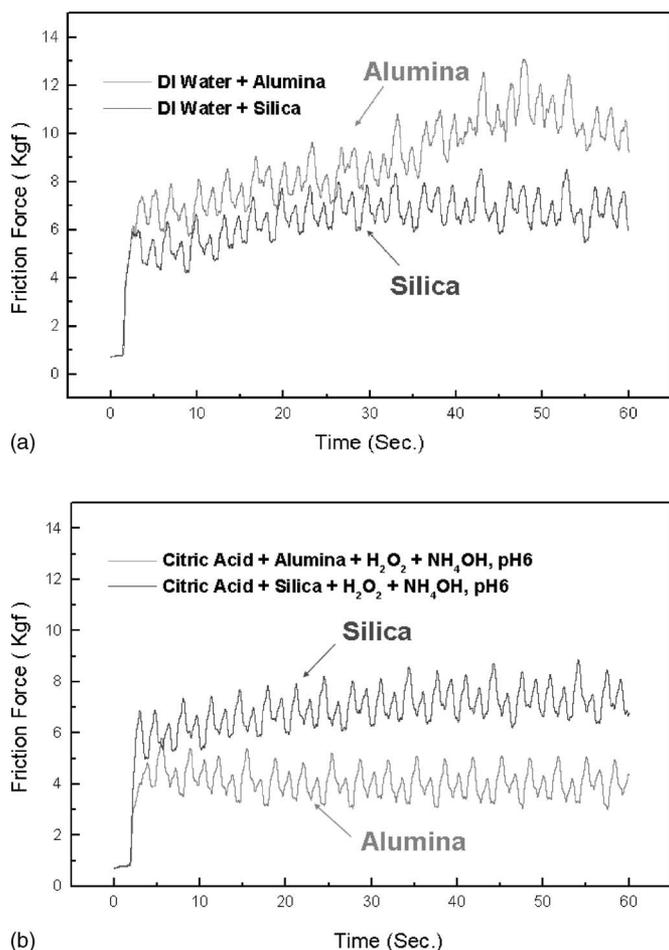


Figure 5. The friction curves of abrasive particles in (a) DI water- and (b) a citric acid-based solution during copper polishing.

sorption of citrate on the alumina surface. However, the presence or absence of citric acid did not change the adhesion forces of the silica particles. This indicates that the adsorption of citrate reduces the adhesion forces of the alumina particles significantly. These results clearly show that the amount of adsorbed chemicals on the particle surfaces can affect the magnitude of the adhesion forces of the particles on wafer surfaces, which indicates that the choice of chemical additives directly influences the adhesion force between slurry particle and substrate.

The frictional characteristics of abrasive alumina and silica particles were experimentally investigated during the copper CMP process as shown in Fig. 5. The frictional curves between the abrasive particles and the copper surfaces were measured using alumina and silica slurries both with and without citric acid. The alumina slurry was very sensitive to the chemistry of slurry. The highest frictional force of 9 Kgf was observed in a DI water-based alumina slurry. However, the lowest frictional force of 4 Kgf was measured when citric acid was added in alumina slurry. The frictional forces of the silica particles (6 Kgf) in the slurry were not significantly changed during CMP process regardless of the presence or absence of citric acid as observed in adhesion force measurements. The greater adhesion forces of particles on surface, the higher friction forces on copper. Yoon et al.¹⁴ already reported that higher adhesion force between two surfaces caused higher friction force on them.

Figure 6 shows the removal rate of copper in different slurry solutions. Regardless of particle types, removal rates lower than 100 nm/min were observed in DI water-based slurries. These low copper removal rates are attributed to the purely mechanical action

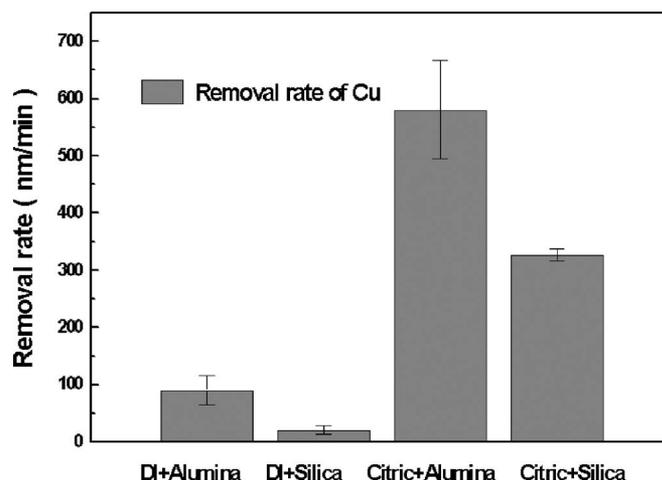


Figure 6. The removal rate of copper in various slurry solutions.

of the abrasive particles although higher friction and adhesion forces were measured in both DI based alumina and silica slurries. Unlike oxide CMP, the oxidation of metal surface is necessary for higher removal rate in metal CMP.¹⁵ Only mechanical action will not provide the removal rate of copper above 100 nm/min. Without chemical reactions (in DI water-based slurries) the friction and adhesion force are well correlated to the magnitude of removal rates. A four times higher removal rate was measured in alumina-based DI water slurry than in silica due to higher adhesion and friction forces of alumina. Note that alumina particle showed four times higher adhesion forces than silica particle on copper in DI water-based slurry.

As explained above, the drastic decrease of adhesion force was measured especially in citric acid added alumina slurry. A slight decrease of adhesion force was measured on silica particles. Higher adhesion and friction forces were measured in silica slurry with citric acid than in alumina due to the adsorption of citric ions on alumina. However, the highest copper removal rate, 600 nm/min, was observed in alumina slurry containing citric acid, H₂O₂, and NH₄OH. This suggested that a high copper removal rate polishing requires not only the mechanical reaction but also the chemical reaction. Abrasives and chemicals in the slurry solutions continuously accelerate oxidation, etching, and abrasion of copper surface by chemical and mechanical effects. However, DI based slurry has only mechanical action on copper. Although the lowest friction force was observed in the alumina-based slurry with the addition of citric acid, the highest removal rate of copper was observed in the slurry due to the chemical reaction with copper surface. The smallest adhesion force also measured in the alumina-based slurry with the addition of citric acid due to the repulsive zeta potentials between alumina and copper surfaces. The material removal process in polishing is commonly described by Preston's equation as shown in Eq. 1¹⁶

$$\text{Material removal rate, } RR = k \cdot P \cdot V \quad [1]$$

where k is Preston constant, P polishing pressure and V platen velocity.

Preston constant, k , is used to account for other factors such as relative hardness of the abrasive and substrate and the density of the abrasive particles. Generally, hardness of the alumina particle (9, Mohs' hardness) is larger than that of silica (6 ~ 7, Mohs' hardness) which leads to higher k value. This may be the reason for higher removal rates in alumina slurry than in silica with citric acid even though the friction and adhesion forces of silica were higher than those of alumina.

The adhesion force is directly related to the friction force during polishing. Whatever the removal rates are, the higher the friction force, the higher level of scratches on polished surfaces. The low copper removal rates observed at high frictional forces may result in

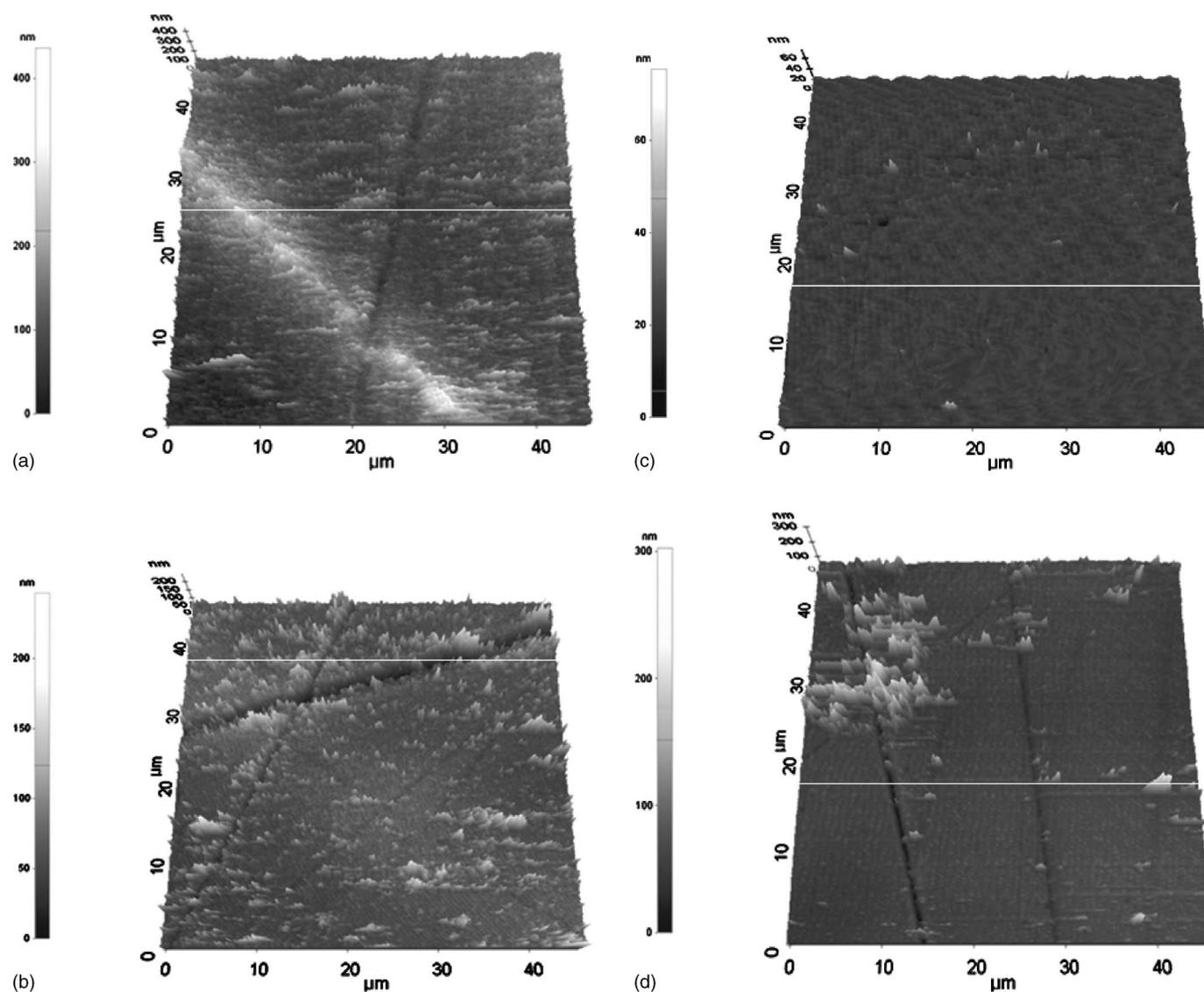


Figure 7. AFM images of the copper surface after polishing in (a) a DI water-based alumina slurry, (b) a DI water-based silica slurry, (c) a citric acid-based alumina slurry, and (d) a citric acid-based silica slurry at pH 6.

severe scratches on the copper surface. To investigate the relationships among the magnitudes of particle adhesion, frictional forces and scratching during the CMP process, AFM was used to observe the copper surfaces after the copper CMP process. Figure 7 shows the magnitude of particle contamination and scratches on the copper surfaces. The scan area of copper surface was $45 \times 45 \mu\text{m}$, and each R_{p-v} value of copper surface was obtained through the analysis of the cross-sectional height of polished surfaces. The depth of the scratches and magnitude of particle contamination on the copper surface are shown in Fig. 7 and summarized in Table I. Large numbers of residual particles and scratches are observed on the polished copper surfaces in DI water with alumina particles. Silica particles also generated particle contamination and scratches on the copper surface when in either a DI water- or a citric acid-based slurry. The depth of the scratches on the copper surface was dependent on the magnitude of the friction force. Higher frictional forces correlated to the observation of deeper scratches on the copper surfaces.

Table I shows R_a (average roughness), R_{p-v} and depth of scratches on the copper surface after polishing. The largest values of R_a and R_{p-v} were observed on the polished copper surfaces in a DI water-based alumina slurry. On the other hand, the polished copper surface in the citric acid solution and H_2O_2 with alumina particle

had the smallest R_a and R_{p-v} . Adhesion force is known to influence not only the magnitude of the friction force but also the level of particle contamination on substrates which directly relate to the surface roughness and number of scratches after CMP. Even though similar friction forces were measured in both silica slurries with and without citric acid, lower adhesion force was observed in citric-based silica slurry. Lower adhesion force indicates lower friction

Table I. The roughness and depth of scratches of the copper surface after polishing with alumina based and silica based slurry solutions.

(nm)	DI water-based alumina slurry	DI water-based silica slurry	Citric acid-based alumina slurry with H_2O_2	Citric acid-based silica slurry with H_2O_2
R_a	33.8	12.0	0.8	3.9
R_{p-v}	271.1	106.7	6.8	74.0
Depth of scratches	113.2	72.4	3.4	54.5

during polishing which actually resulted in smoother surfaces in citric based silica slurry as shown in Table I. It might suggest that the friction measurement was not as sensitive as AFM measurements. These roughness results clearly show that the amount of citrate ions adsorb on the particle surfaces significantly affected the frictional behavior and the adhesion forces of the particles as well as surface quality during copper polishing.

Conclusions

The frictional and adhesion forces between the abrasive particles and wafer surfaces were experimentally measured using alumina and silica slurries with and without citric acid. Although citric acid did not affect the zeta potential of the silica particles, it resulted in a more negative zeta potential of the alumina particles due to the adsorption of the negatively charged citrate ions on the alumina surfaces. The highest particle adhesion force was measured in an alumina slurry without the addition of citric acid. However, the alumina slurry with the addition of citric acid had the lowest particle adhesion force due to the adsorption of citrate ions on the alumina surfaces. While citrate ions could easily adsorb on alumina particles, the silica particles did not appear to benefit in terms of reduced frictional force when in citric acid solutions.

The frictional curves between the abrasive particles and the copper surfaces were measured using alumina and silica slurries with and without citric acid. The highest frictional force was observed in a DI water-based alumina slurry. On the other hand, the smallest friction force was measured in an alumina slurry containing citric acid. Regardless of the presence or absence of citric acid in the slurry, the frictional curves of the silica particles were not significantly changed during the CMP process. These results clearly show that the magnitude of citrate ions adsorbing on the particle surfaces affects the frictional behavior as well as the adhesion force during the CMP process.

The low copper removal rate was observed in the DI water-based slurry due to the purely mechanical action of the abrasive particles. However, the highest copper removal rate was observed in alumina slurry containing citric acid, H_2O_2 and NH_4OH . This suggests that a high copper removal rate requires not only the mechanical reaction but also the chemical reaction. Abrasives and chemicals in the slurry solutions continuously accelerate oxidation, etching, and abrasion of copper surface by chemical and mechanical effects. Although the lowest friction force was observed in the alumina-based slurry with the addition of citric acid, the highest removal rate of copper was

observed in this slurry due to the chemical reaction with copper surface. The smallest adhesion force resulted in the lowest friction force in the alumina-based slurry with the addition of citric acid.

Large numbers of residual abrasive particles and scratches were observed on the polished copper surfaces in a DI water-based alumina slurry. The depth of the scratches on the copper surface was dependent on the frictional force. Higher frictional forces resulted in deeper scratches on the copper surfaces. Higher particle adhesion forces generated higher frictional forces, abrasive particle contamination and scratches on the copper surfaces during the CMP process. This indicates that the magnitude of particle adhesion on the wafer surfaces in slurries can be directly related to the frictional behavior and surface quality during the CMP process.

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