Investigation of cleaning solution composed of citric acid and 5-aminotetrazole

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Abstract−In a damascene process for a copper metallization, the planarization method based on a chemical mechanical polishing (CMP) has been used for multilevel metallization. Although a buffing step was adopted in this CMP process, numerous residual abrasives, capable of increasing the resistance of copper lines, still existed after the second CMP step. For this reason, more research has focused on identification of an effective cleaning solution. We investigated a new cleaning solution consisting of citric acid and 5-aminotetrazole (ATRA) as a complexing agent and corrosion inhibitor, respectively. The citric acid was added to achieve a lift-off effect by removing the underlying copper oxide layer, whereas the ATRA was adopted to prevent abrasive re-adsorption by forming a passivation layer on the copper surface. The cleaning solution consisting of 0.006 M citric acid and 0.006 M ATRA displayed a particle density of 0.07 #/μm^2 in an immersion test, and no particles were observed on a 4 cm^2 coupon wafer in a real process test at pH 12.

Key words: Cleaning Solution, Citric Acid, 5-Aminotetrazole, Particle Density, Etch Rate

INTRODUCTION

To solve the problem of resistance-capacity (RC) delay, which is caused by a high-density integration, copper was introduced as an alternative interconnection material due to its low resistivity and high resistance against electromigration compared to aluminum [1,2]. However, reactive ion etching (RIE) process, which had been used in a conventional aluminum interconnection process, could not be adopted for metallization process with the introduction of copper due to its non-volatile byproduct. Therefore, a new patterning method known as the damascene process was introduced. Chemical mechanical polishing (CMP), one of the key technologies of the damascene process, has advanced together with the metallization process since it can be used to solve a topology problem originating from the damascene process. Thus many research groups have been studying the CMP process [3,4].

Generally, the copper CMP process is composed of three steps, including a first copper CMP process for rapid copper removal, a second copper CMP process with low selectivity for wide planarization, and a cleaning step for removing residuals after CMP [5]. In copper CMP, the planarization of a copper wafer is obtained by the chemical and mechanical etching between a wafer carrier, a pad, and the slurry. First, a chemical process forms an activated layer on the copper wafer surface. Second, a mechanical process removes the activated layer by using the friction between the wafer surface, abrasive, and the pad. Third, a chemical reaction occurs again on the surface [6,7]. These three steps are performed simultaneously on the wafer surface. After the CMP process is completed, a buffing step is performed to remove abrasives that could reduce the performance of the device interconnection. Despite the buffing treatment, however, numerous residual abrasives still remain on the wafer, so the cleaning process should be introduced to remove the abrasives.

Although there are some differences among research groups, conventional cleaning solutions are made up of a complexing agent, oxidizer, corrosion inhibitor, surfactant, and pH adjustor. The role of the complexing agent is to remove abrasives by etching underlying copper oxide through soluble complex formation. It has been reported that representative complexing agents are citric acid, tartaric acid, oxalic acid, succinic acid, and glycine. Among them, citric acid, oxalic acid, and succinic acid, all of which have carboxyl groups, are considered as more promising than others since they prevent particle re-adsorption and form a soluble complex with copper oxide. Moreover, they enhance the electrostatic repulsion force between a substrate and particles by increasing the absolute zeta potential of the particles toward the negative direction under the condition at which copper surface has negative charge [8,9].

To protect the copper surface from excessive corrosion, a corrosion inhibitor is added to slurry and cleaning solution. A passivation layer produced by the adsorption of inhibitor onto the Cu surface inhibits corrosion and prevents re-adsorption of the abrasive [10,11]. Benzotriazole (BTA), imidazole, and amino-triazole, all of which contain an azole group, are usually used as corrosion inhibitors. BTA is known as the most effective corrosion inhibitor; however, recent studies have shown that ATRA is more stable than the BTA regarding passivation layer formation [12].

In this research, the optimum composition of citric acid and ATRA that demonstrates similar or more enhanced cleaning properties compared to commercial cleaning solution was determined. The cleaning effects were compared by varying the concentrations of citric acid and ATRA as well as the pH of the solution.

EXPERIMENTAL

An immersion test was performed by using a 1.5 cm×1.5 cm coupon wafer that had the structure of Cu (1,000 nm, PVD)/Ta (25 nm,

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PVD)/TaN (10 nm, PVD)/SiO$_2$ (1,000 nm, thermal oxidation)/Si by varying the cleaning solution composition and cleaning process conditions. The immersion test consisted of a contamination step implemented in the second CMP slurry of LK393C4 (colloidal silica, Dow Chemical Company), a buffing step, a cleaning step, and a rinsing step. The effect of the cleaning solution was investigated by varying pH, citric acid concentration, and ATRA concentration. The performance of the cleaning solution was examined based on etch rate, surface roughness, zeta potential, and particle density. They are measured with a 4-point probe, FE-SEM (field emission scanning electron microscopy, S-4800, Hitachi), AFM (atomic force microscopy, XE-150, Park Systems), and a zeta potential analyzer (ELS - Z2, Otsuka), respectively.

The real process evaluation test consisting of a polishing step using LK393C4, as well as buffing, cleaning, and rinsing step was carried out under the optimized condition obtained in the immersion test. In the polishing step, Cu wafers were polished by using a POLI 400 (G&P Tech., Korea) composed of an 8 in platen and 4 in carrier. The speeds of the platen and carrier were fixed at 94 rpm and 87 rpm, respectively. The applied pressure between the platen and carrier was maintained at 100 g/cm^2 during the polishing time of 10 sec. The buffing, cleaning, and rinsing steps were performed at the wafer speeds of 240, 515, and 238 rpm, respectively, with the Lab. made cleaner. The flow rates of D.I. water and cleaning solution were kept at 150 ml/min. The buffing step and cleaning step were performed for 1 min each, and the rinsing step proceeded for 30 sec. The same analyses as those for the immersion test were also carried out to obtain the results of the real process.

RESULTS AND DISCUSSION

To determine the optimum composition of citric acid-based cleaning solution, etch rate, particle density, and surface characteristics of the copper wafer treated with the citric acid cleaning solution were analyzed at various pHs. Since the cleaning solution showed better performance under basic conditions in a preliminary experiment, the following experiments were carried out on the pH range between 8 and 12. Fig. 1 shows the etch rate of the cleaning solution
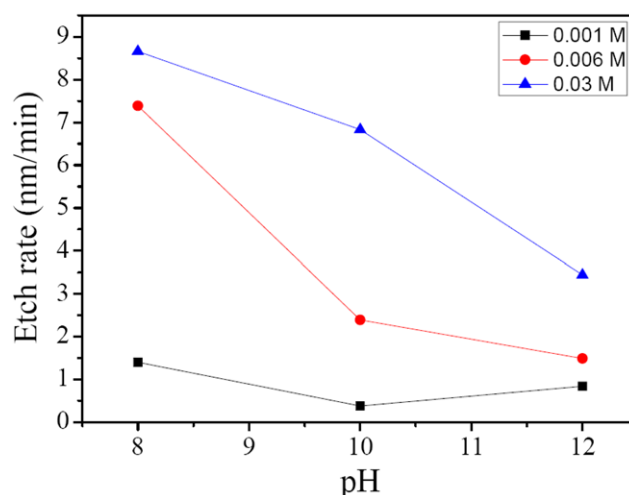

Fig. 1. Etch rates of copper coupon wafer cleaned with 0.001 M, 0.006 M, and 0.03 M citric acid at various pH levels.
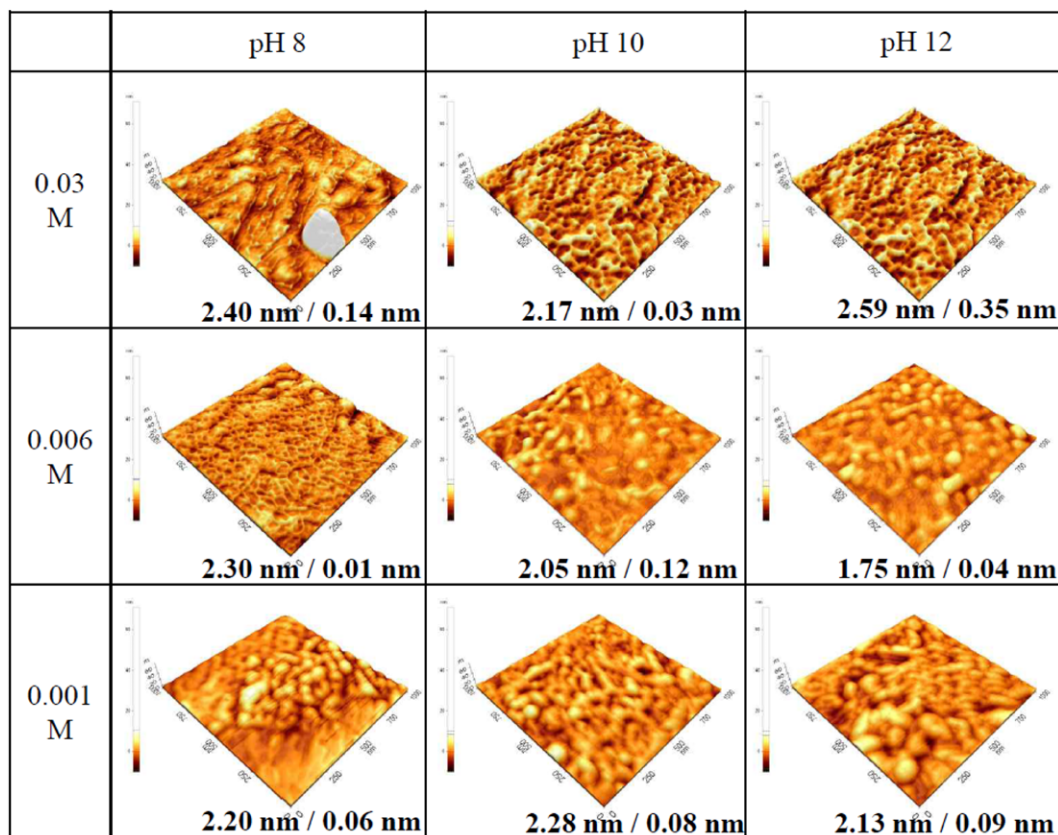

Fig. 2. AFM images of copper coupon wafers obtained varying citric acid concentration and pH.

under various citric acid concentrations and pHs. As expected, etch rates were proportional to the citric acid concentration and inversely proportional to pH. Dissolution of copper oxide decreased at high pH and low citric acid concentration. However, the surface roughness of the copper was not seriously affected by the etch rate of the cleaning solution, as shown in Fig. 2. The difference between the highest and lowest values was 0.84 nm, and there was any relation between surface roughness and etch rate.

The lowest particle density of 0.05 #/μm^2 (particle removal efficiency=98.6% based on Fig. 3(a)) was observed at a citric acid concentration of 0.006 M and a pH of 12. The particle density declined according to the pH of the solution, as shown Fig. 3. It is thought that this phenomenon was due to a difference in zeta potential between the silica particle and copper surface. The copper surface might have a negative zeta potential in the pH range we investigated, as shown in Fig. 4(a). Furthermore, the zeta potential of the particles in the solution was also negative and decreased as pH increased (Fig. 4(b)). These data suggest that the particle density was inversely proportional to the pH. The difference of zeta potential between the abrasive and the copper surface was bigger at higher pH. Considering the results of etch rate, surface roughness and particle density, it can be concluded that a cleaning solution composed of 0.006 M citric acid at the pH 12 is most appropriate for the citric acid-based cleaning solution. 0.05 #/μm^2 of particle density obtained with 0.006 M citric acid at pH 12 was even superior to the results of two commercial solutions as shown in Fig. 3. The results with the commercial solutions were obtained under the conditions recommended by the providers.

After optimizing the citric acid concentration and pH, we introduced ATRA to examine its effect on etch rate and particle density. Etch rates, investigated using 4-point probe and FE-SEM, are shown in Fig. 5. The etch rate steadily decreased from 0.29 nm/min to 0.129 nm/min as the concentration of ATRA increased. Fig. 5 also shows the particle density on the Cu wafer that was cleaned by using a cleaning solution containing ATRA. The lowest particle density, which was comparable to the data obtained using citric acid only (0.006 M), was achieved at an ATRA concentration of 0.006 M. This means that the addition of ATRA not only reduced the etch rate (1/10 of citric acid only), thus improving surface roughness, but also maintained the ability to remove residual particles.

The favorable characteristics of the cleaning solution with ATRA were not due to improvement in zeta potential but due to the preven-
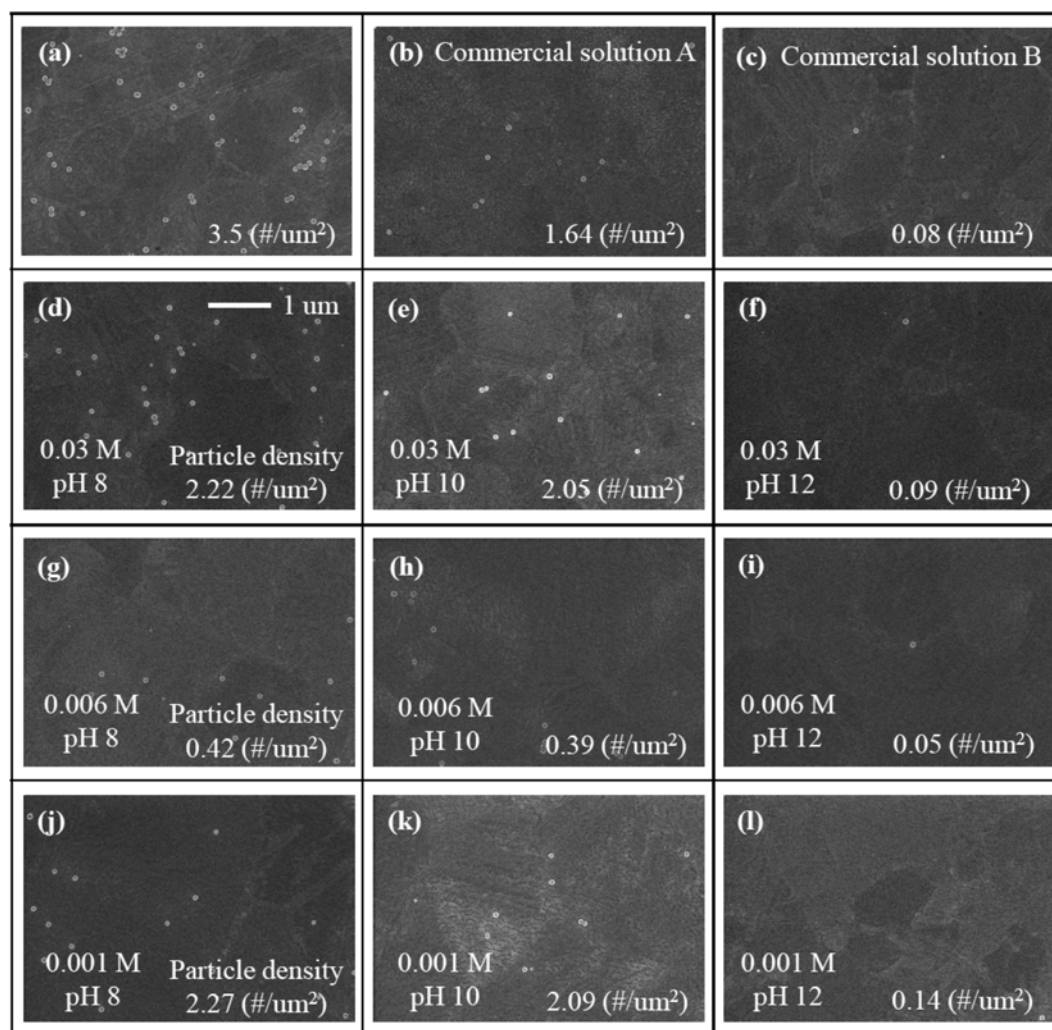

Fig. 3. FESEM images of copper coupon wafer cleaned by (a) D.I. water, (b) commercial solution A, and (c) commercial solution B, and (d)-(*l*) the images obtained varying citric acid concentration and pH.
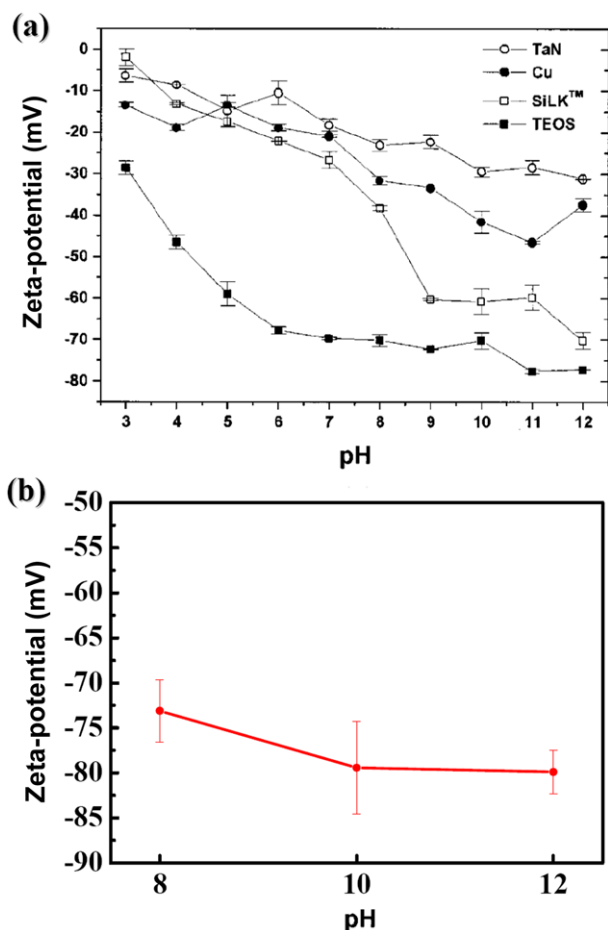
(a)

(b)

Fig. 4. (a) Zeta potential of copper wafer as a function of solution pH, and (b) zeta potential of abrasive ((a) was reproduced upon obtaining permission of ECS - The Electrochemical Society (Ref. 9)).
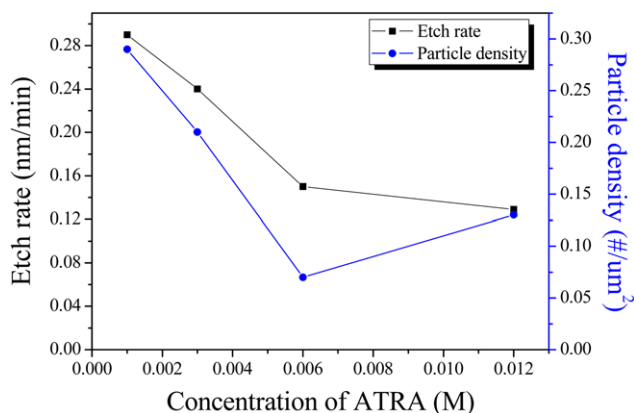

Fig. 5. Etch rate and particle density of Cu coupon wafer cleaned by 0.006 M citric acid with various concentrations of ATRA.

Fig. 6. Zeta potential of silica particle in the cleaning solution composed of 0.006 M citric acid and various concentrations of ATRA at pH 12.

(a)

(b)

Fig. 7. (a) Zeta potential and (b) particle density of the cleaning solution according to storage time.

tion of particle re-adsorption. As shown in Fig. 6, even though there was not a significant change in zeta potential, the overall potential shifted toward positive direction compared to that of solution without ATRA. This indicated a decrease in the electrostatic repulsion force. Therefore, increased abrasive removal upon the addition of
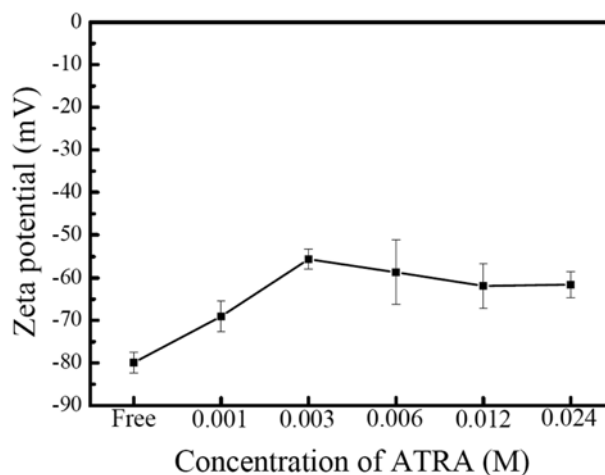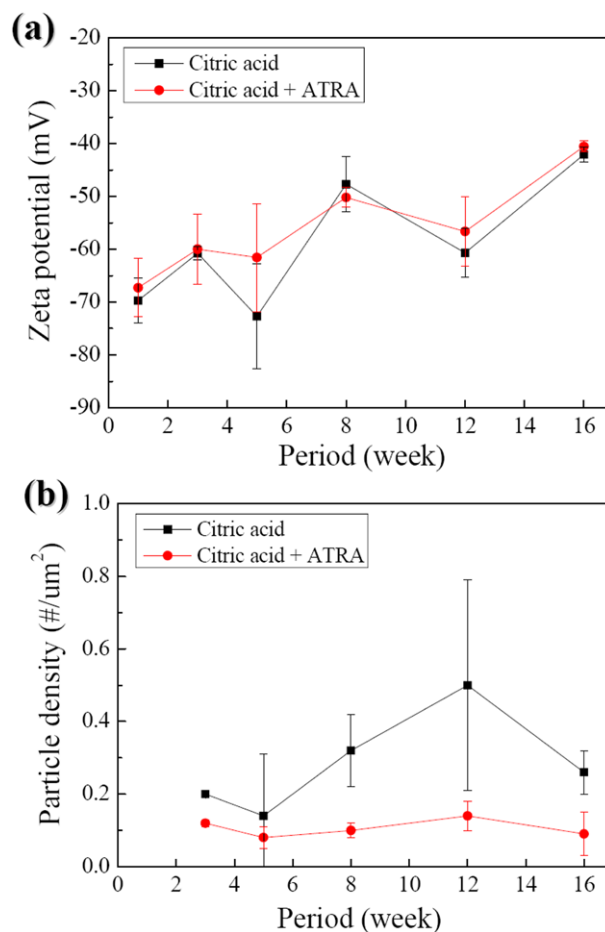
ATRA was possibly due to the inhibition of re-adsorption of abrasives and not due to the zeta potential.

Cleaning solution composed of 0.006 M citric acid and 0.006 ATRA had a shelf life time of over 16 weeks as shown in Fig. 7.

Both cleaning solutions consisting of citric acid only or citric acid with ATRA showed a shift in zeta potential toward the positive direction with increased storage time. However, there were obvious differences in particle density as shown in Fig. 7(b). In the case of citric acid only, particle density was affected by the zeta potential of silica particle. Particle density increased, and the deviation became larger as the zeta potential of the silica particles became more positive. On the other hand, the particle density of citric acid with ATRA was maintained at its initial value independent of storage time, even if the zeta potential shifted to a positive value. From the result, it can be assumed that ATRA extends the lifetime of the cleaning solution by maintaining its ability which prevents the re-adsorption of particles.
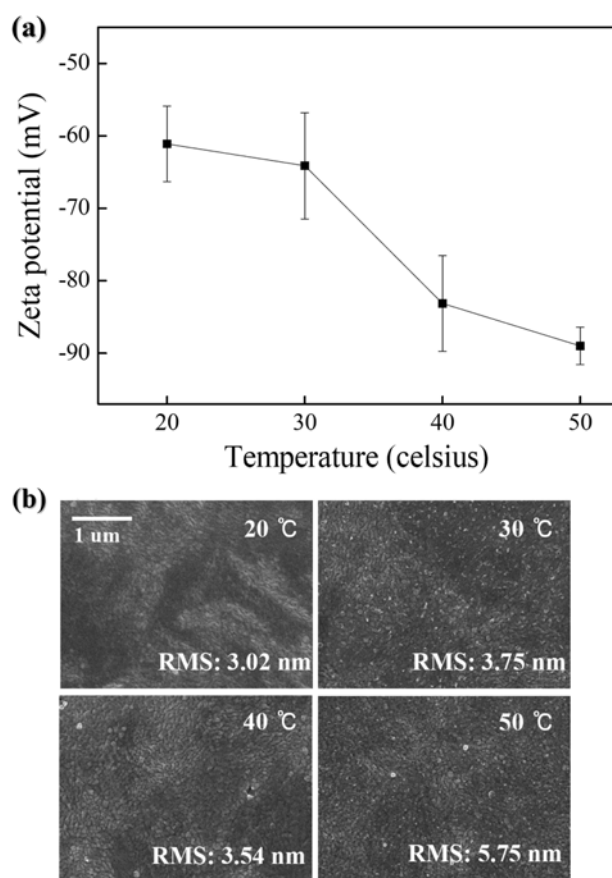
One factor that is often overlooked but should be considered during the cleaning step is the temperature of the cleaning solution. Thus, the effect of temperature on particle density and surface morphology was investigated by using cleaning solution composed of 0.006 M citric and 0.006 M ATRA. Fig. 8(a) shows the zeta potential of silica particles according to the temperature of the solution. From the results, it could be expected that the cleanability might be improved with the elevation of solution temperature. However, the surface of the Cu wafer was severely damaged as the temperature of the cleaning solution increased as well as the particle density was higher than that at room temperature. Specifically, the occurrence of voids increased and the surface became rougher at higher temperature. Thus, the temperature should be kept at room temperature in order to maintain the characteristics of the cleaning solution during a cleaning step.

The performance of the cleaning solution composed of 0.006 M citric acid and 0.006 M ATRA was tested using LK393C4 (colloidal silica, Wako Co.) slurry following real process steps. Experimental conditions are described in detail in the experimental section. POLI 400 (G & P tech, Korea) polishing machine and a 2×2 cm^2 Cu coupon wafer were used to investigate particle density. The cleaning solution composed of 0.006 M citric acid and 0.006 M ATRA showed outstanding results, as shown in Fig. 9(a), (b), and (c). It was difficult to find any particle on the 2×2 cm^2 wafer surface. This result was superior to the results obtained in D.I. water or citric acid only.

CONCLUSION

A cleaning solution composed of citric acid and ATRA was investigated in this study. The effects of composition, pH, and process temperature were examined through immersion test and real process test. From the results, it was found that a cleaning solution consisting of 0.006 M citric acid and 0.006 M ATRA was superior to other combinations. Furthermore, pH 12 and room temperature were revealed to be the optimum conditions for the cleaning solution. No particle was found on the 2×2 cm^2 wafer surface in the real process test. Lastly, a shelf life of over 16 weeks was one more advantage offered by the cleaning solution.

Fig. 8. (a) Zeta potential of silica particles and (b) FESEM images of the Cu surface cleaned at solution temperatures of 20, 30, 40, and 50 ºC.
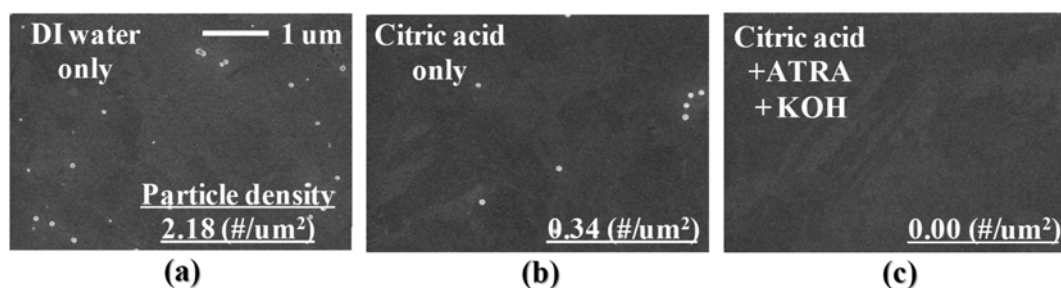

Fig. 9. FESEM images of the Cu coupon wafer cleaned with (a) D.I. water only, (b) citric acid, and (c) citric acid and ATRA.

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