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Effect of Organic Additives on Ceria Slurry in Shallow Trench Isolation Chemical Mechanical Planarization

Min Cheol KANG, Jae Jeong KIM* and Doo-Kyung MOON[1]

School of Chemical Engineering, College of Engineering, Seoul National University, San 56-1, Shillim-dong, Kwanak-gu, Seoul 151-742, Korea
[1]*Department of Materials Chemistry and Engineering, Konkuk University, Hwayang-dong, Gwangjin-gu, Seoul 143-701, Korea*

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An increase in the removal selectivity between silicon oxide and silicon nitride was attempted by adding organic additives to a ceria slurry for the application of shallow trench isolation (STI) chemical mechanical planarization (CMP). The protection behavior of poly(acrylic acid) (PAA) and the acceleration behavior of RE-610 in a ceria slurry were studied. PAA served as a protector of the silicon nitride due to the change in zeta potential. RE-610 worked as a hydration accelerator of the silicon oxide. When the two additives were added to the ceria slurry, the removal selectivity increased to 31 : 1. Moreover, PAA improved the stability of the ceria slurry. [DOI: 10.1143/JJAP.44.5949]

KEYWORDS: CMP, ceria, selectivity, zeta potential, hydration

1. Introduction

With the shrinkage of the device design rule, global planarization using chemical mechanical polishing (CMP) becomes one of the most important technologies in ULSI device fabrication.[1)] Local oxidation of silicon (LOCOS) has been extensively used in isolating active areas where transistors are formed. However, the tightened design rule has replaced LOCOS with shallow trench isolation (STI) as an isolation method.[2)] In STI based on CMP, silicon oxide is removed until silicon nitride is exposed. In STI CMP, the use of a slurry with a low removal selectivity, which is the removal ratio of silicon oxide to silicon nitride, results in a nonuniform field oxide thickness depending on pattern density and an overpolishing margin reduction.[3)] Several solutions have been proposed to overcome these problems. One of them is a method in which silicon nitride as a sacrificial layer is deposited on silicon oxide.[4,5)] Another method is the introduction of organic additives, such as anion-type acids, to increase removal selectivity by changing the zeta potential of abrasive particles.[6–8)] Although previous research studies suggested that removal selectivity could be increased by adding organic additives to a slurry, the effect of organic additives in the slurry on STI CMP performance has not been reported yet. In this study, we investigated the effect of organic additives in added to the slurry on the potential change of a wafer and removal selectivity.

2. Experiment

Wafers with a structure of SiO_2 (5500 Å, high-density-plasma chemical vapor deposition)/Si(100) and Si_3N_4 (1450 Å, low-pressure chemical vapor deposition)/Si(100) were used in the study. Lactic acid and poly(acrylic acid) (PAA) were investigated as protectors of silicon nitride. Lactic acid and PAA are widely used as dispersants of silicon nitride particles in the ceramic industry. Therefore, these chemicals were chosen to control the zeta potential of silicon nitride. To maximize the effect of these chemicals on removal selectivity, RE-610, which is a phosphate-ester-based chemical compound used as a wetting agent, was introduced as a hydration accelerator of silicon oxide. The zeta potential of the wafer surface was measured by the electrophoretic light scattering technique with ELS-8000 (Otsuka Electronics). Each wafer was cut into $3 \times 2\,cm^2$ for measuring zeta potential. Prior to measuring zeta potential, a silicon nitride layer was pretreated with 1 : 100 HF aqueous solution for 2 min to remove the native oxide on the wafer surface. The pH of the solution, which was composed of an additive and deionized (DI) water, was controlled from 5 to 9 by adding 0.1 M HNO_3 and 0.1 M KOH.

The mean particle size of ceria abrasive was about 200 nm. The polishing slurries containing 2 wt% ceria were prepared with the additives described earlier. The R&D CMP Machine POLI-380 (G&P Technology) was used to determine polishing rate with a 60 rpm rotating speed. The pressure between the platen and the carrier was maintained at 4 psi, and the flow rate of the slurry was set at 150 mL/min. The ceria slurry was composed of 2 wt% ceria, DI water, and the additives at a fixed concentration of 1 wt%. The removal rates of the wafers were measured at ten points using ellipsometry.

Fourier transform infrared (FTIR) spectroscopy was used to monitor the additive adsorption.

3. Results and Discussion

Figure 1 shows the changes in zeta potential of the wafer surface with or without additives. The isoelectric point (IEP), the pH at which the zeta potential is zero, of the silicon nitride wafer was 5.2; that of silicon oxide did not exist within the pH measurement range of 5 to 9, which was consistent with the values reported the previously.[9,10)] Without any organic additives, the zeta potentials of both wafer surfaces exhibited decreasing tendencies with increasing pH, and the silicon nitride surface had a higher decreasing rate. When 1 wt% PAA was added, the zeta potential of the silicon nitride varied in the range of −55.8 to −91.1 mV, the absolute values of which were higher than those of silicon oxide because of an increase in the negative charge of the carboxylate ion group on the silicon nitride surface. However, lactic acid, which has no excessive carboxylate ion groups like PAA, showed a negligible change in the zeta potential of silicon nitride.

To investigate the adsorption of the additives on the substrates contributing to the change in the zeta potential, FTIR analysis was performed, as shown in Fig. 2. The transmittance spectra of additives were obtained using KBr

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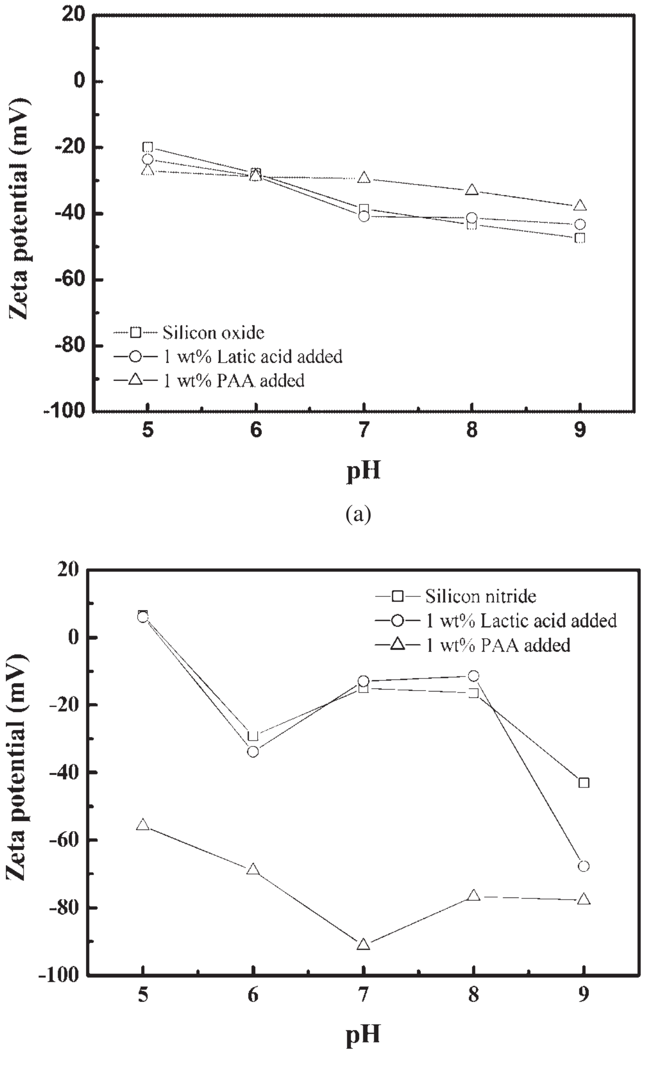
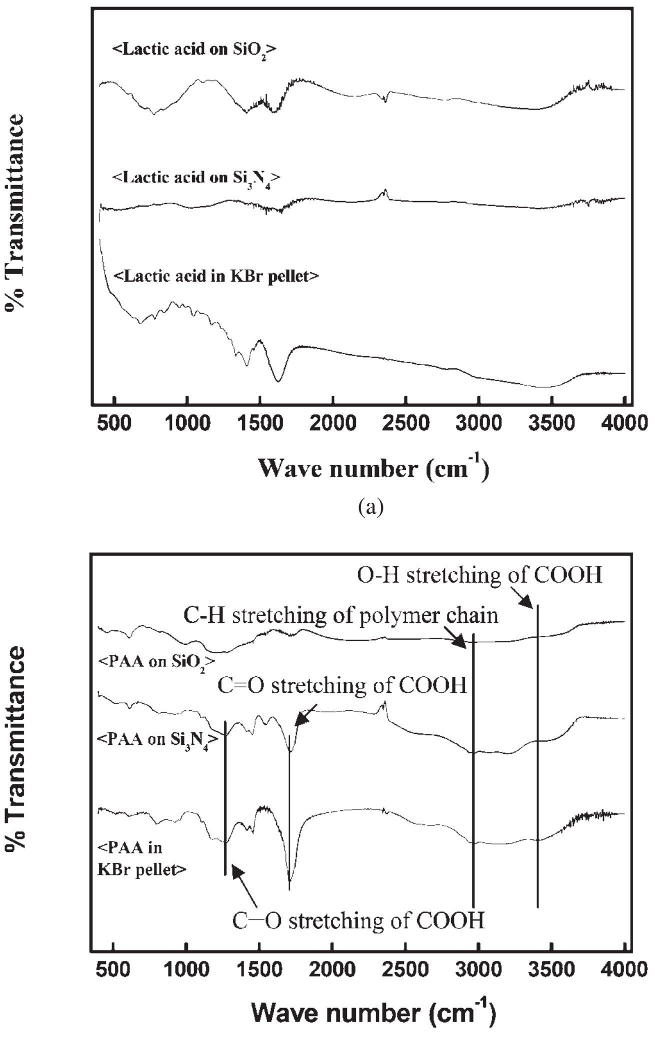
*E-mail address: jjkimm@snu.ac.kr



(a)

(b)

Fig. 1. Change in zeta potential with pH with or without additives: (a) silicon oxide and (b) silicon nitride.



(a)

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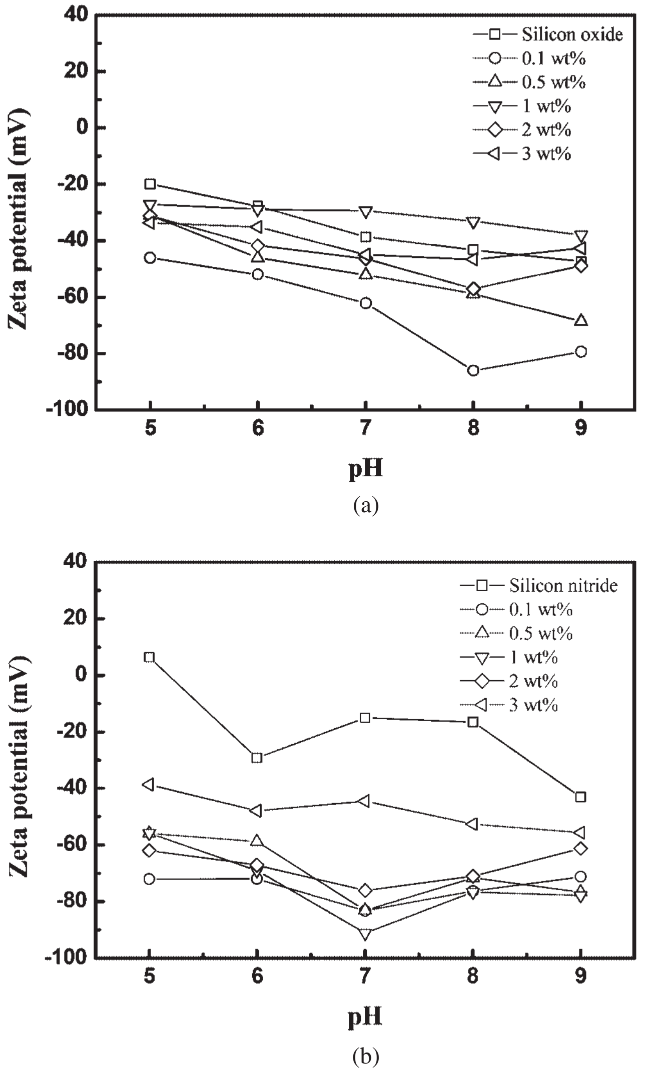
Fig. 2. FTIR spectra of pure additive powders (transmittance) and additives attached to substrates (reflectance) with (a) lactic acid and (b) PAA.

pellets and the reflection spectra of the additives, which interacted with the wafer, were obtained during immersion in 1 wt % additives for 5 min. The characteristic peaks of the hydroxyl group (3170 cm^{-1}) and carboxyl group (1707 cm^{-1}) could be observed in the lactic acid and PAA transmittance spectra. After the adsorption of lactic acid on the silicon nitride substrate, all characteristic peaks disappeared in the reflection spectra. This indicates that lactic acid was not attached to the silicon nitride substrate. However, in the case of PAA, the peaks of the hydroxyl group and carboxyl group were clearly detected in the reflection spectra, revealing that PAA is strongly absorbed on the silicon nitride surface compared to lactic acid.

The dependency of zeta potential on the concentration of PAA is shown in Fig. 3. In the case of silicon nitride, due to the adsorbed PAA, zeta potential decreased as PAA concentration increased. The decreases in the zeta potentials of silicon oxide and silicon nitride was found to be maximum at approximately 0.1 and 1 wt %, respectively, which was caused by the compression of unabsorbed PAA and the electric double layer that resulted in an increased ion osmotic pressure.[11,12)]

Figure 4 exhibits the effect of pH on the ceria slurry with or without the additives. Without the additives, the zeta potential of the ceria slurry changed from positive to negative with the increase in slurry pH due to the increase in the concentration of the hydroxyl group, and the IEP was measured to be pH 5.6. Meanwhile, when the additives were added, the IEP of the ceria slurry did not exist within the measurement range. The absolute values of the zeta potential of the slurry with the additives were higher compared to those of the slurry without additives. The addition of 1 wt % PAA resulted in the highest negative zeta potential of -52.4 mV at pH 7 and a 60 mV difference between silicon nitride and silicon oxide.

The magnitude of the zeta potential difference contributes the electrostatic force between the substrates and the ceria particle, resulting in an extensive adsorption of the ceria particles on the substrate (Fig. 5). The electrostatic repulsion force arose from increase in the absolute value of the zeta potential of both the substrates and particles, which had the same signs. When 1 wt % PAA was added the ceria slurry, the zeta potentials of the silicon nitride and ceria particles were -91.1 and -52.4 mV, respectively, which were the



(a)

(b)

Fig. 3. Change in zeta potential with pH at various concentrations of PAA: (a) silicon oxide and (b) silicon nitride.

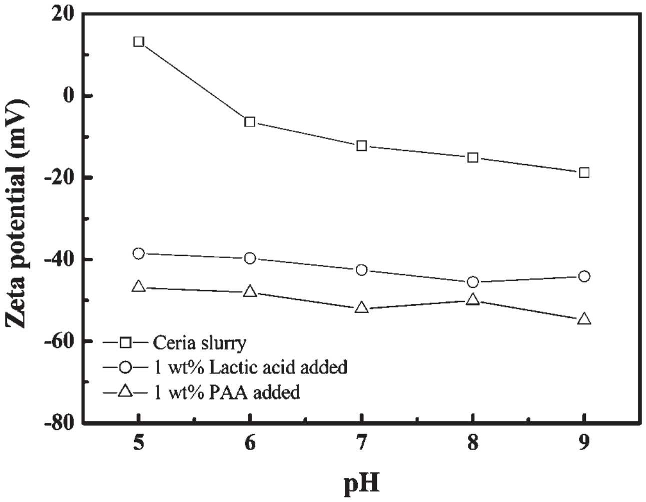
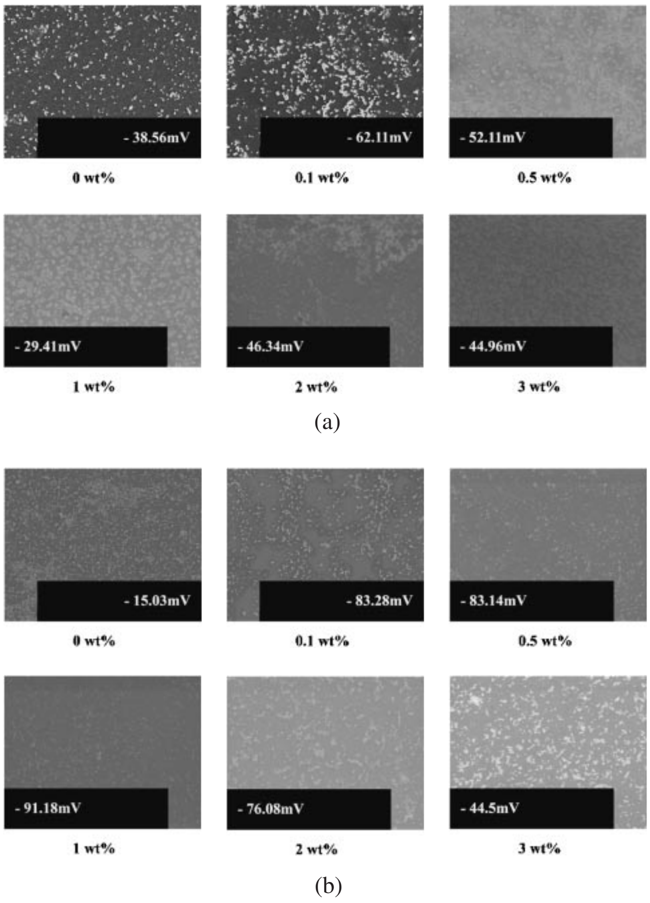


Fig. 4. Change in zeta potential of ceria slurry with pH with or without additives.

highest value, and the density of the adsorbed ceria particles was the lowest.



(a)

(b)

Fig. 5. SEM images of ceria particles adsorbed on (a) silicon oxide and (b) silicon nitride with various concentrations of PAA at pH 7 (numbers in the figure indicate the zeta potentials and numbers below the figure indicate the concentrations of PAA).

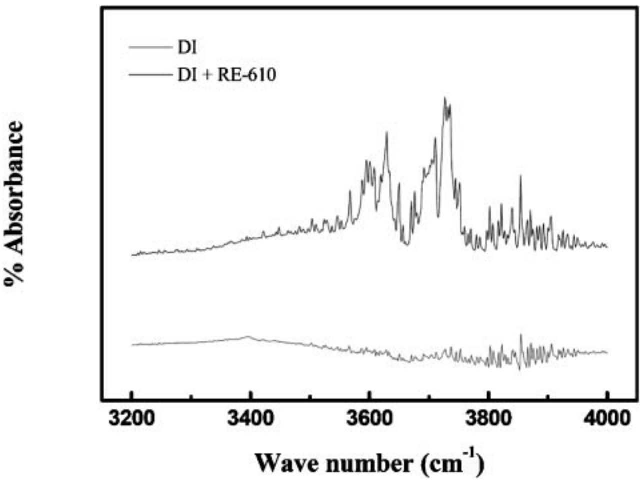


Fig. 6. FTIR measurement of treated silicon oxide surface with or without RE-610.

Generally, in the removal mechanism of silicon oxide, the hydrated layer on silicon oxide formed through the chemical reaction between water and silicon oxide is dissolved by abrasives and removed from the surface. In this study, to accelerate the hydration of the silicon oxide surface based on the removal mechanism, RE-610 was proposed to be added to 1 wt % PAA ceria slurry. As shown in Fig. 6, the addition of 0.05 wt % RE-610 enabled the peak of hydrated silicon

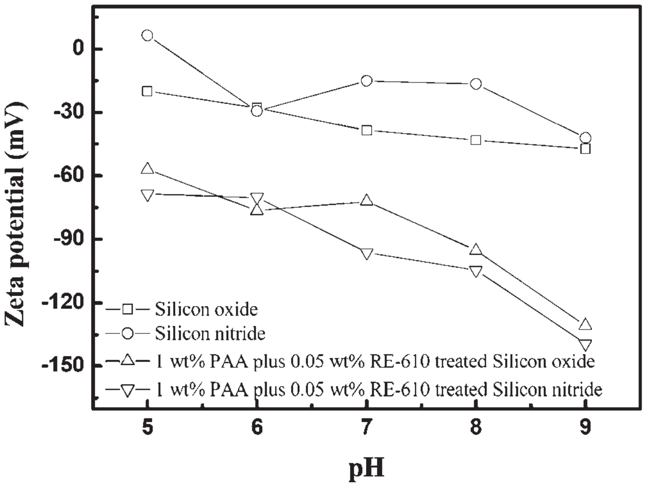


Fig. 7. Change in zeta potential with pH in the presence of PAA and RE-610.

Table I. Removal rates and selectivities of silicon oxide and silicon nitride wafer with or without additives at pH 7.

	Removal rate (nm/min)		Selectivity
	SiO_2	Si_3N_4	
Without additives	320	100	3.2 : 1
1 wt% Lactic acid	248	81	3.1 : 1
1 wt% PAA	230	11 (5.5%)	21 : 1
1 wt% PAA plus 0.05 wt% RE-610	370	12 (6.98%)	31 : 1

(Numbers in brackets indicate uniformity)

oxide ($3500-3700\,cm^{-1}$) in the FTIR analysis to be detected, indicating that the hydration of the silicon oxide wafer was accelerated by RE-610. The increase in the amount of hydrated silicon oxide on silicon oxide contributed to the shift in zeta potential to higher negative values as shown in Fig. 7. It was found that the removal selectivity, the removal rate ratio of silicon oxide to silicon nitride, might be controlled by changing zeta potential with the addition of PAA or RE-610. The removal rates of both substrates and the removal selectivity using ceria slurries containing various additives at pH 7 are listed in Table I. The removal rates of silicon nitride and silicon oxide with no additives were measured to be 100 and 320 nm/min, respectively.

The addition of 1 wt% lactic acid did not make a considerable change in removal rate, whereas the PAA addition resulted in a remarkable increase in removal selectivity from 3.2 : 1 to 21 : 1 due to a reduction in the removal rate of silicon nitride to 11 nm/min, originating from the zeta potential control. As expected from the zeta potential data, the addition inclusion of 0.05 wt% RE-610 increased the removal rate of silicon oxide from 230 to 370 nm/min, while it gave a negligible effect on silicon nitride at pH 7. Therefore, the highest selectivity was obtained to be 31 : 1 with the addition of both 1 wt% PAA and 0.05 wt% RE-610.

4. Conclusions

The effects of organic additives in a ceria slurry on the removal rate between silicon oxide and silicon nitride were investigated. The zeta potential of the silicon nitride wafer was dramatically changed by the selectiveness of the adsorption of PAA and the polishing rate of the silicon nitride wafer decreased from 100 to 11 nm/min through the interaction between the silicon nitride wafer and ceria particles, and removal selectivity increased. The addition of RE-610 to the ceria slurry containing 1 wt% PAA accelerated the hydration of silicon oxide. Therefore, the decrease in the removal rate of silicon oxide caused by adsorbed PAA was restored and removal selectivity was improved.

Acknowledgements

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