Final polishing processes are important to produce a clean surface in Si semiconductor wafers. Final polishing is carried out using a slurry that typically comprises colloidal silica, alkaline and a water-soluble polymer. Hydroxyethyl cellulose (HEC) has been widely used as a water-soluble polymer to impart hydrophilic properties to the polished wafer surface in order to reduce defects. In this study, we examined the effects of HEC concentration on the hydrophilicity of the polished wafer surface. We show correlations between the free HEC concentration in slurry liquid phase, friction during polishing, and hydrophilicity of the polished wafer surface. Furthermore, we show that the residual silica abrasive on the wafer enhances its hydrophilicity. These results show that HEC in the slurry not only acts as a hydrophilizing agent but also as an adsorptive medium between the wafer and silica. Silica has a highly hydrophilic surface owing to the presence of Si–O– groups on its surface. Therefore, a highly hydrophilic surface of polished wafer is achieved by adsorptive HEC as well as silica adsorbed on the wafer, bound by HEC. This mechanism is useful to develop new final polishing slurries to produce ultra-clean Si wafers.

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We evaluated the hydrophilicity of polished wafers by measuring the contact angle of a sessile drop using a contact angle meter (KY-OWA CAX-200). The evaluated contact angles were obtained from the average of five measurements per polished wafer surface. The contact angle measurements had variation of 5%.

We also observed the polished wafer surface in detail using a scanning electron microscope (SEM) (HITACH FE-SEM SU-8000) and the surface coverage ratio of the silica abrasive on the wafer was calculated by dividing the adsorbed silica area by the total surface area of the silicon wafer determined from the SEM images. The variation of the surface coverage was 11%.

Finally, we evaluated the wafer surface coverage ratio and the contact angles after the polished wafers were dipped into HF, in order to understand the effect of the silica abrasive on the hydrophilicity. Sample preparation procedures did not change from those mentioned above, except that the wafers were dipped into 5% HF bath for 10–60 s after polishing to dissolve the silica on the wafer surface. These wafers were again rinsed with flowing DIW for 3 s and were stood in an upright position to dry.

Results and Discussion

The adsorptivity of HEC onto the abrasive surface of silica in the SiO$_2$/HEC slurry is shown in Figure 1, with the amount of adsorbed HEC per gram of silica surface shown as a function of the concentration of free HEC, which did not adsorb onto silica but remained in the liquid phase of the slurry. From these results, we confirm that HEC may exist both on the silica surface and in the liquid phase of the slurry as free HEC. The amount of HEC adsorbed onto the silica surface increased with the increase of free HEC concentration in the slurry, until the adsorbed amount became saturated at around 0.024 g/1 g SiO$_2$ with the free HEC concentration at over 0.2 g/L. These results suggest that at low HEC concentrations, the HEC is selectively adsorbed onto the silica surface rather than remaining in the liquid phase, as evidenced by the steep increase in adsorbed HEC with the increase of free HEC concentration. With a further increase in the HEC concentration of the slurry, the rate of increase in the amount of adsorbed HEC diminished. This behavior arises due to the adsorbed HEC preventing further adsorption owing to steric repulsion forces. At higher HEC concentrations, the amount of HEC adsorbed onto the silica surface reached a maximum, and this saturation concentration significantly increased the free HEC concentration in the liquid phase of slurry.

We next investigated the effect of free HEC in the liquid phase on the polishing friction in order to understand how HEC influences the wafer surface during polishing. Figure 2 shows the platen motor current (i.e., polishing friction) as a function of free HEC concentration. The platen motor current decreased with increasing free HEC concentration in the HEC-aq and became saturated at around 0.029 g/L, as indicated by the arrow in Figure 2. After this saturation point, the polishing friction remained stable. The polishing friction arises between the wafer surface and the polishing pad during polishing. If the wafer surface is hydrophobic, it is difficult for the hydrophilic slurry to flow between the wafer and the pad, resulting in a high polishing friction. On the other hand, if the free HEC adsorbs onto the wafer surface and increases the hydrophilicity of the wafer surface, the slurry may flow between the wafer and the pad more easily. In this investigation, the polishing friction decreased and became stable with the increase in the free HEC concentration. This could indicate that the free HEC adsorbed onto the wafer surface and increased its hydrophilicity. Furthermore, the platen motor current of SiO$_2$/HEC slurry shown in Figure 2 also decreased with the increase in free HEC concentration, saturating at over 0.029 g/L. According to these results, the effect of free HEC on the polishing friction did not change either with or without silica, but the platen motor current of SiO$_2$/HEC slurry was higher than that of the HEC-aq once both motor currents were stable. This suggests that the free HEC could be more effective in bringing the silica on the wafer surface, but the silica increases the mechanical energy during polishing.[10,11]

To explore the effect of free HEC on the hydrophilicity of polished wafer surface, we measured the sessile drop contact angle on a wafer...
surface after polishing, shown in Figure 3. It shows that the contact angle decreased with the increase of free HEC in the HEC-aq. Hence, we can confirm that an increase in free HEC increases the hydrophilicity of the wafer surface, as suggested above. On a closer analysis of Figure 3, it is clear that the contact angle shows a significant decrease until a concentration of 0.029 g/L, which is shown by the arrow, and reaches a plateau. This behavior is also shown in Figure 2. These two facts are in good agreement to support the above mentioned model of the free HEC behavior. The SiO2/HEC slurry in Figure 3 also shows a significant decrease and a gradual change of contact angle as the free HEC increases, but the concentration also reached a plateau at 0.029 g/L, as in Figure 2. H. S. Hwang et. al also reported that increase of total HEC concentration in the slurry enhanced the hydrophilicity on the wafer surface. In addition, free HEC acts not only as a hydrophilizing agent, but also as a polishing friction stabilizer by improving the slurry flow between the wafer and the pad. Furthermore, we show the possibility of the silica effect on increasing the hydrophilicity of the polished wafer surface, since the contact angle of SiO2/HEC was lower than that of the HEC-aq. This fact could lead to modification of the previously proposed model that only HEC increases the hydrophilicity of the polished wafer surface.

To investigate the effect of silica abrasive on the hydrophilicity, we imaged the polished wafer surface. Figure 4 shows SEM images of the wafer surface polished with SiO2/HEC slurry without any HEC (Figure 4a) and the SiO2/HEC slurry with various free HEC concentrations between 0.002 and 0.4 g/L (Figures 4b to 4f). As seen in the images, the silica (white dots in the pictures) remains on the polished wafer surface and the number of remaining silica particles increased with the increase of free HEC concentration. This result is difference from the previous report that HEC prevented the adsorption of silica and reduced the residual particles on the wafer. In order to express the silica effect clearly, the surface coverage ratio by the silica on the polished wafer was calculated from the SEM images. A steep increase in the coverage of residual silica abrasives from 0.06% to 0.31% was observed with an increase of free HEC concentration from 0.002 and 0.009 g/L. Further increases in free HEC concentration resulted in only slight increases to the residual silica ratio. These observations may be explained by the increased hydrophilicity of the wafer surface due to the free HEC, which allows for a smooth slurry flow over the wafer surface. Furthermore, HEC can adsorb onto the silica surface, as shown in Figure 1, such that adsorbed HEC on the wafer surface may increase the adhesion of the silica. Thus, HEC may act as an adsorption medium between the wafer and silica.

Furthermore, we show the correlation between the hydrophilicity of the polished wafer and the surface coverage of silica abrasive on the polished wafer. Figure 5 shows the sessile drop contact angle dependence on the surface coverage of silica. The contact angle decreases with increasing of SiO2 surface coverage. These results show that the hydrophilicity increase of the polished wafer surface was affected by the residual silica adsorbed on the surface.

On the basis these findings, we next conducted an examination of the HF treatment used for the dissolution of the silica abrasive, in order to understand the effect of silica on the hydrophilicity of polished wafer surface. Figure 6 shows the silica surface coverage ratio, on the wafers polished with the SiO2-aq and SiO2/HEC slurries, as a function of HF treatment time. The surface coverage ratio decreased with HF treatment time, and it was clear that the silica was almost completely dissolved (from a visual analysis) after 30 s in both SiO2-aq and SiO2/HEC slurries.

In order to further investigate this behavior, Figure 7 shows the sessile drop contact angle, as a function of HF treatment time, on the wafer surface polished with the HEC-aq, SiO2-aq and SiO2/HEC slurry. The contact angle of the HEC-aq treated sample was stable regardless the HF treatment time, suggesting that the adsorbed HEC on the polished wafer surface was not removed by the HF treatment. On the other hand, from Figure 7, the contact angle of the SiO2-aq treated sample reached almost the same base-line value of the water.
in 10 s. In addition, SiO$_2$/HEC treated sample also increased at 10 s and then finally reached the same value of HEC-aq treated sample. From the data in Figures 6 and 7, we confirm the relationship between the decrease of surface coverage ratio by silica and the deterioration of hydrophilicity. Since the silica can introduce hydrophilicity to the wafer surface, it is possible to say that adsorption of both HEC and silica onto the wafer surface during polishing is necessary to generate high hydrophilicity.

Based on these results, we interpret that the hydrophilicity expression mechanism on wafer surfaces polished with the final polishing slurry, typically comprising HEC, colloidal silica abrasive and NH$_4$OH, as follows. HEC can remain in the slurry in two different locations: one is adsorbed onto the silica surface and the other is in the free liquid phase. Under these conditions, the free HEC could adsorb onto the wafer surface and introduce hydrophilicity to the wafer during polishing. This hydrophilicity was effective in allowing a smooth slurry flow between the wafer and the pad; hence, the polishing friction became stable. Furthermore, silica remained adsorbed on the wafer surface through the adsorptive properties of HEC. As silica has a highly hydrophilic surface, derived from the Si-O$^-$ polar group, the remaining silica on the wafer surface produced a high hydrophilicity along with the HEC. In this study, we found that HEC had three different roles in producing a hydrophilic wafer surface, acting as 1) a hydrophilizing agent, 2) a polishing friction stabilizer, and 3) an adsorption medium between the wafer and silica. Moreover, the silica also acts as the hydrophilizing agent and this effect may enhance the hydrophilicity conferred by HEC. We considered that high hydrophilicity on the polished wafer surface by the adsorption of silica and HEC is significantly effective to avoid the adsorption of dried particles, therefore we can expect to achieve a high quality wafer surface after final cleaning.

**Conclusions**

We investigated the polishing friction and hydrophilicity as a function of free HEC concentration. The contact angle measurements show that the hydrophilicity of polished wafer surface improves with increasing free HEC concentration, which did not adsorb onto silica but existed in the liquid phase. This hydrophilicity improvement may be linked to the stabilization of polishing friction. From this, we determined that the free HEC acts not only as a well-known hydrophilizing agent, but also acts to stabilize the polishing friction. Besides this, the free HEC concentration was correlated with the residual silica abrasive adsorbed on the polished wafer surface. This indicated a new role for the free HEC as an adsorption medium between the wafer and silica. We also observed that the residual silica increased the hydrophilicity of the polished wafer more effectively. Hence, it can be concluded that silica acts as a hydrophilizing agent together with HEC, and is effective in improving the hydrophilicity of Si wafer surfaces in the final polishing processes.

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