The effect of surfactants on ceria particle removal in the buff clean process and NPM based cleaning solution for post-CMP cleaning

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Ceria-based slurries were adopted for polishing STI structure because of its high removal rate and high selectivity between Si_3N_4 and Poly-Si. However, Formation of the Ce-O-Si bond between ceria particles and SiO_2 makes nanoceria particles difficult to be removed and this has become one of the difficulties of the current process[1]. In this work, we reported the post CMP cleaning of ceria particles by using HNO_3-H_2O_2-DIW (named NPM)[2] solution with surfactant A and investigate the effect of different surfactants used in the buff cleaning process.

A colloidal ceria slurry of 90 nm was used in this experiment to polish the TEOS wafers with a downforce of 3 Psi for 5 min, following with buff clean with downforce of 1.5 psi for 10s to 60s. After the CMP process was completed, a mixed cleaning solution of NPM ((HNO_3:H_2O_2:DIW = 2:10:88) and different surfactants were used for buff clean process and cleaning process after CMP at RT (25℃) for 1 min with assistance of megasonic (MS: 950kHz, 40W). No brush cleaning was used. Two surfactants, A and B were compared in the experiments. Finally, the samples were rinsed in DIW for 1 min and dried with N_2.

The surface tension of the different surfactant was measured by contact angle analyzer (IL4200, Kruss Gmbh Germany). The zeta potential and average diameter of ceria slurries were measured by Zeta potential and particle size analyzer (Nanobrook 90Plus PALS, Brookhaven). Scanning electron microscope (SEM) was used to analyze the sample surface before and after cleaning at 30kX magnification and finally use Image J software to identify the number of particles and calculate the cleaning efficiency (CE).

Fig. 1 shows the SEM images of the polished samples cleaned with/o 0.2% different surfactants in the NPM solution. All the samples were polished with downforce of 3 psi for 5 min and a buff cleaning of 1.5 psi for 60 s using DIW. Fig.1(a) shows that although buff clean process can remove almost particles, there are still 48 ceria particles left on the polished SiO_2 surface without further cleaning. SEM images show that these particles are majorly embedded in the substrate and are difficult to be removed. The NPM cleaning solution, which has excellent CE for the spin-coating contaminated samples[2] , was used for post-CMP cleaning, yet only a CE of only 54.2% was obtained, as shown in Fig. 1(a). With adding 0.2% surfactant A in the NPM, all the particles were removed; while adding surfactant B resulted in a CE of 87.5% with 6 particles left. The surface tension of different surfactants in water was measured and it was found that the surfactant A has lower surface tension than surfactant B. We have found that the redox reaction between NPM and ceria helps to cut the bonding of ceria with SiO_2. Also even at RT, NPM has certain dissolution ability of ceria particles. The low surface tension of A helps to further lift off the particles, resulting in highest CE.

we also tried to investigate the buff clean process on the particle removal. The sample with buff clean of 10s after CMP with 3 psi was used a reference. As can be seen from Fig.2(a), there are 1192 particles left on the surface for the sample with reduced buff clean time of only 10s. With buff clean time of 30s, there are about 187 particles left (Fig.2(c), indicating the importance of buff clean time. With adding surfactant B in the DIW, there are only 4 particles left (Fig.3(d). We also tried to add other surfactants including surfactant A, which effect was just similar as water buff cleaning (Fig.3(b)). The zeta potential values of ceria and SiO_2 in 0.2% surfactants in DIW were measured and are shown in Fig.3. The pH value of DIW is around 6. Results show that in the DIW, the zeta potential of ceria particles is positive while that of SiO_2 is negative. This is the major reason that large amount of ceria particles are left on the SiO_2. However, with surfactant A, the zeta potentials of both ceria and SiO_2 are slightly negative while those values are positive for the DIW with surfactant B. This result show that the buff cleaning efficiency has strong correlation with the repulsion or attraction of ceria particles and SiO_2 substrate. Further work is undergoing.

In this work, we demonstrate two ways to fully clean the ceria particles after CMP. The NPM solution with surfactant A can remove 90 nm ceria

abrasives for the samples polished with downforce of 3 psi and a buff clean of 60s. Adding surfactant B into the DIW during buff cleaning can also remove most particles without further chemical cleaning.

We believe with certain optimization of our cleaning process, the wafers after CMP can be fully cleaned without need of HF etching and brush cleaning.

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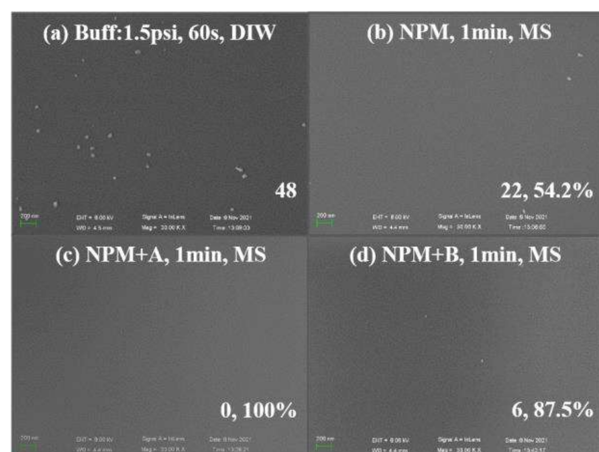

Fig.1 SEM images of megasonic cleaning of polished samples (CMP: 3psi 5min, buff clean: 1.5psi, 60s) with different surfactants added to NPM cleaning solutions.

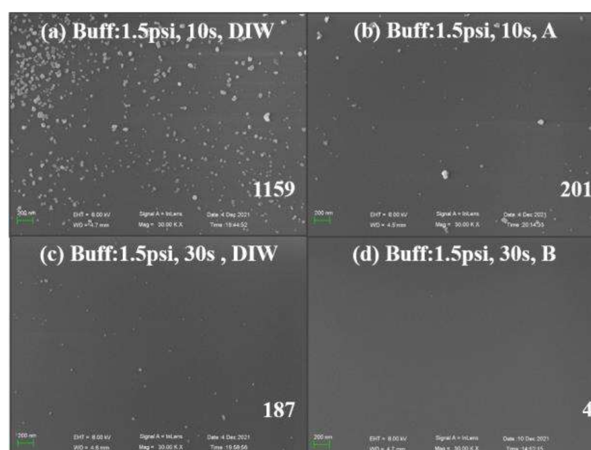

Fig.2 SEM images polished wafers with a downforce of 3 Psi for 5 min after buff clean using DIW with different surfactants.

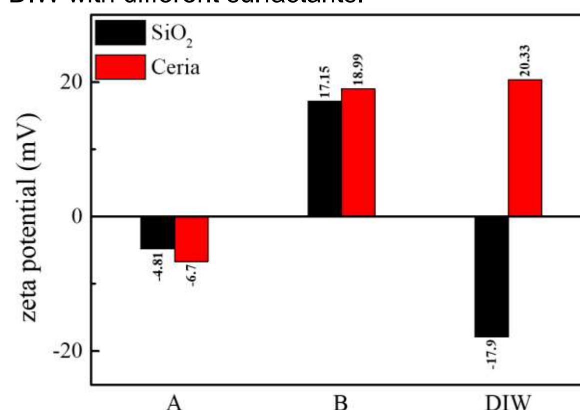

Fig.3 Zeta potential of ceria and SiO_2 in different surfactants.

Preference: ☑ Oral ☐ Poster

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