Effect of Ceria Abrasive Synthesized by Supercritical Hydrothermal Method for Chemical Mechanical Planarization

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Scratches on the wafer surface are one of the significant issues during chemical mechanical planarization process. In order to satisfy wiring width shrinking with time, after polishing process, the presence of small scratches on the wafer is considerable issue. To reduce mechanically induced scratches, small-sized ceria particles are synthesized by a supercritical hydrothermal method. Spherical shaped nano ceria primary abrasive size is about 10 nm and secondary particles are uniformly distributed around 40 nm. The SiO2 wafer removal rate is improved through increasing Ce3+ concentration by metal doping during the synthesis. The detailed principle of the material removal is introduced. The polishing test and its removal rates by the supercritical-hydrothermal-synthesized ceria slurries (SHC) are compared to a commercial ceria slurry. Removal rate of SHC catches up about 85% of the commercial one. The Ce3+ concentration of the slurry samples is compared, and the wafer surfaces are scanned for morphology characteristics. Scratch and roughness results of SHC are significantly improved against the results of commercial ceria slurry.

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With the advancement in technology, electronic devices and their semiconductors are becoming smaller and more compact. According to the roadmap for semiconductors, wiring width of semiconductor has reduced less than 20 nm since 2015.1 Manufacturing processes have to follow up the design rule. Therefore, it is inevitable for integrated nano-scale circuit to require the planarization process.2 Chemical mechanical planarization (CMP) allow the circuit to be compact and well-integrated. The main objective of CMP process is a polished wafer with high quality of the surface finish. The main consumables, which are pad, slurry, and conditioner, determine the results of a surface quality during the CMP process.3 Especially, the slurry that contacts both wafer and pad under the high pressure has potentials that can control various specifications such as scratches or material removal rate (MRR) and so on. Thus, the slurry is an important part for these research fields.

Requirements of satisfactory CMP results include less scratch and roughness. They are significant criteria for designing the next level semiconductor. Scratch and bad wafer roughness can cause functional failure on electronic structure and also affect its yield, reliability etc.4 Commonly, a SiO2 wafer is polished by a silica slurry; however, they are prone to leave scratches which is not suitable for next semiconductor generation that requires even a smaller and compact structure. Those defects are usually brought from mechanical forces by the abrasive. In this study, it is proposed that improvement of chemical force in the slurry makes roughness and scratches decrease during the CMP. Thus, a ceria slurry whose chemical force is considerable than other slurries is investigated as an alternative to existing common slurry.

The ceria slurry cannot be analyzed without the chemical effect. Many studies have attempted to explain the chemical mechanism of oxide layer removal.5 Both silanol groups of the SiO2 wafer and the ceria abrasive take part in the chemical reaction and mechanical tearing.6 Ce3+ and Ce4+ are present in the ceria particle.7 The key element that reacts with the SiO2 surface is Ce3+, which reaches the Si-O structure and weakens a bonding between Si and O.8 Mechanical friction from the polishing pad tears the wafer film off under the soften condition. Ce4+ is formed by an oxygen vacancy in the ceria molecules.7 According to the structural characteristics of ceria particle, some oxygen ions are unoccupied between the molecules. Among them, Ce3+ is formed around the vacancy where the area is reactive with SiO2.9,10 In this study, the concentration of Ce3+ is increased, which influences the wafer MRR. A conventional ceria slurry is prepared by calcination. Its abrasive particles are formed in different sizes and shapes, even sharp fragments. This mechanical component of abrasive is expected that the existing CMP acquire a high removal rate but leave the coarse surface.11 In this research, nano sized and spherical ceria abrasive is synthesized to improve scratches and roughness. The manufacturing of 10 nm sized abrasive is conducted by supercritical hydrothermal synthesis. However, the mechanical impact is also reduced and lower MRR is followed.12 Thus, increasing chemical impact of Ce3+ is studied to improve the issue. Figures of the supercritical-hydrothermal-synthesized ceria slurry (SHC) and a commercial calcined ceria slurry are compared. The MRR of SHC was almost kept up with that of the commercial slurry’s result. Forming Ce3+ on the ceria particle is introduced, and its concentration in the slurry is correlated by UV intensity.

Experimental

The ceria abrasive whose primary particle size is about 10 nm is prepared by supercritical hydrothermal synthesis. In this process, it is necessary to maintain the water pressure above 221 bar and temperature at 374°C. A precursor, aqueous cerium nitride, is dissolved in deionized (DI) water and it decomposes as follows.13

\[
\text{Ce(NO}_3\text{)}_3 + \text{H}_2\text{O} \rightarrow \text{Ce(OH)}_3 + \text{HNO}_3
\]

This solution is mixed with the water that is in supercritical condition. The synthesis is performed in a mixer-T as shown in Fig. 1. The hydroxide solution is dehydrated in supercritical condition. The solution is rapidly formed as an oxide which is the ceria nanoparticle.

\[
\text{Ce(OH)}_3 \rightarrow \text{CeO}_2 + \text{H}_2\text{O}
\]

Additionally, as indicated in Fig. 2, a reactant (metal ion) is added at the mixing point to increase the oxygen vacancy as well as concentration of Ce3+. This formation mechanism is discussed on the later...
section. The particles are allowed to pass through the cooling jacket and filtered to remove the unnecessary residual before the output. In order to control the concentration of Ce\(^{3+}\) on ceria particle surface, concentration of metal reactant is varied from 0 to 4 wt%. SHC 0–4 (lower to higher concentration of reactant added) and the calcined commercial ceria slurry (KCS-1200MS, KCTech) which particle size is distributed around 150 nm are prepared to compare a polishing experiment.

The ceria particles are observed through a transmission electron microscope (TEM; JEM-3010, JEOL). The secondary particle size distribution is analyzed by a scanning mobility particle sizer (SMPS; NANO-5416, GRIMM Aerosol Technik). The polishing experiment is performed by a tablet tribometer (CP-4, Bruker). The polishing time is 120 s under 3 psi fixed head pressure and the 40 × 40 mm thermal oxide wafer coupon is polished with the polyurethane pad (IC1000, Dow Chemical). Ceria abrasive in all the slurry samples is diluted to 10 wt% with deionized water and the slurry is spread by the flow rate of 85ml/min. After planarization, MRR is measured by a reflectometer (ST5000-DLX, K-Mac). 15 different locations on the center of thermal oxide wafer that are divided by 2 mm from each other points are measured. Surface scratch and roughness are investigated through the tapping mode of an atomic force microscope (AFM; Innova, Bruker). Correlating the MRR with the concentration of Ce\(^{3+}\), a radiation intensity is measured by an ultraviolet visible spectrophotometer (UV-Vis; UV-3600, Shimadzu).

**Results and Discussion**

The ceria particles were observed to investigate their shape and size. Their TEM images are shown in Fig. 3. Due to the rapid reaction by supercritical hydrothermal synthesis, 10 nm sized particles were possible to be synthesized. Analyzing through the SMPS (Fig. 4) and
Figure 4. Particle Size distribution of SHC slurries and commercial ceria slurry (3 times repeatability).

TEM results, the primary particle size is 10 nm and secondary particle size is agglomerated as 41 nm. Comparing SHC 0 and other SHC slurries, adding metal ion during the synthesis hardly effects on particle configurations such as size or distribution but the surface chemical formation. The SHC abrasives are uniform and spherical which illustrates a positive result on the wafer morphology. On the other hand, the calcined commercial ceria slurry particles are irregular and sharp. Due to a milling process in the synthesis of abrasives, their particle sizes vary from 50 to 200 nm or even larger. These factors reach the insufficient result after CMP process.

After the evaluation of the SHC particles’ figurations, the CMP experiment was performed with SHC 0–4 slurries. The results were compared to the polishing result of the commercial ceria slurry. The measured data is shown in Fig. 5. For the SHC slurry without any...
The highest MRR was found to be 4344 Å/min, which was obtained for SHC 3. The MRR of SHC slurries increased in proportion to the reactant concentration, but there seems to be a critical point around SHC 3. This indicates that a certain concentration of the reactant in the synthesis improves adhesion between the ceria particles and the SiO₂ wafer. Planarization result of SHC was almost reached to the result of commercial ceria slurry by 85%. It is possible that smaller particle slurry can reach comparable rank with larger particle slurry by chemical modification.

Surface chemistry has a significant impact in this field. Thus, ultra-violet (UV) absorption spectroscopy was carried out for SHC slurries. The absorbance peaks were measured to correlate with CMP results. The absorbance peak of Ce³⁺ is located at around 295 nm. As seen from Fig. 6, SHC 3 has the highest Ce³⁺ absorbance (it also achieved the maximum MRR). The lowest peak was found for SHC 0, which was synthesized without a reactant. It can be concluded that MRR are possibly correlated to the concentration of Ce³⁺. All the ceria absorbance results correspond to each MRR.

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improve the CMP process for the SiO₂ wafer, ceria abrasive nanoparticles were synthesized by these methods. Uniform and spherical abrasive particles were observed. The polishing tests were performed with the SHC slurries and the results were compared to those of the commercial ceria slurry. A CMP experiment gave an account to determine the improvement of the MRR outcome. The MRR of SHC was caught up to 85% by the MRR of the commercial ceria slurry. The UV absorbance for each SHC sample agreed well with the MRR results. After the planarization experiments, the SiO₂ wafer surfaces were scanned by AFM. Their roughness and scratches were considerably improved than those of the commercial ceria slurry.

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