

セリアスラリーによる酸化膜の平坦化 CMP に関する基礎的検討

BASIC STUDY OF OXIDE FILM PLANARIZATION-CMP WITH CERIA SLURRY

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[Abstract]

Ceria(CeO₂) slurry has a strong merit in CMP polishing to give a high removal rate. However, it has an unfavorable reputation of problems linked to its quick sedimentation, agglomeration of particles, purity, difficult cleaning, and high cost. In the present study, focusing on the particular issue of the slurry dispersibility, we examined the effect of ultra-sonic (US) treatment of slurry on its stability and its CMP polishing characteristics in order to make ceria slurry stably applicable to the planarization CMP. As a result, the US treatment has proved remarkably effective in the elimination of agglomerates, improvement of slurry stability, increase of removal rate and better roughness, offering a breakthrough for the realization of high performance ceria slurry for CMP planarization. Comparing to silica slurry, we thus obtained ceria slurry that produces same polished roughness but six times higher removal rate when polished at the pressure of 500g/cm².

Key Words: CMP, Ceria slurry, Ultra sonic treatment, Removal rate, Surface roughness, Zeta potential, Stability, Concentration

1. Introduction

For the polishing of next generation LSI devices, CMP is under rapid expansion. In the CMP process, slurry is critical to the realization of high quality device wafers. Ceria is known to have a high polishing efficiency for oxide film and is actually being used in glass polishing. However, besides impurity problem, such ceria slurry contains a high proportion of large particles compared with silica slurry,

which induces quick sedimentation detrimental to use in CMP. This is the reason why ceria developed for glass polishing cannot be used as-is for CMP. Tailoring of ceria slurry to CMP requirements is necessary.

Aiming to introduce planarization CMP into oxide film polishing, we investigated the effect of surfactant-free slurry using high purity ceria slurry. In the experiment, slurry was US-treated hoping to improve its dispersibility.

2. Experimental Procedures

The measuring instruments employed in the experiment are indicated in Table 1.

Table 2 shows polishing conditions.

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Tab.1 Measuring instruments

Items to be measured	Measuring instrument
Particle size	LB500 (HORIBA).
Zeta potential	ESA9800 (Matec Applied Sciences)
SiO ₂ film thickness	FTP 500 (SENTECH)
Roughness of SiO ₂ film	Interferometer (WYKO.)
Film profile	AFM NPX100(SEIKO Instruments)

Tab.2 Experimental Conditions

Parameters	Conditions
Work Piece	15mm×15mm Oxide film (P-TEOS)
Apparatus for polishing	LM- 15, (ring type)
Pad	Foamed polyurethane (φ 340 mm)
Slurry	Ceria slurry (A-1, A-2) Silica slurry (Cabot SS25)
Rotation speed	30 rpm
Pressure during polishing	56g/cm ² ~500g/cm ²
Slurry feed rate	10 ml/min

3. Results and discussion

3.1 Effects of dispersion by US treatment

(1) Particle size distribution

We took as a reference a commercial silica slurry (containing 3wt% of silica); this slurry was tested as is (no US treatment)

High purity ceria powders (provided by Rhodia Electronics & Catalysis) of two different particle sizes (A1, A2) were used after being dispersed in pure water and adjusted to pH 7.6 by adding HNO₃ and NH₄OH. US treatment was carried out for 3 minutes at 38kHz. Particle size measured before and after the US treatment is shown in Figure 1. As a standard condition the slurry contained 3wt% of ceria.

As for slurry A-1, medium particle size dropped from 3.69 microns to 0.135 microns. As for slurry A-2, medium particle size dropped from 1.136 microns to 0.106 microns. This shows that US is very effective to desagglomerate those powders.

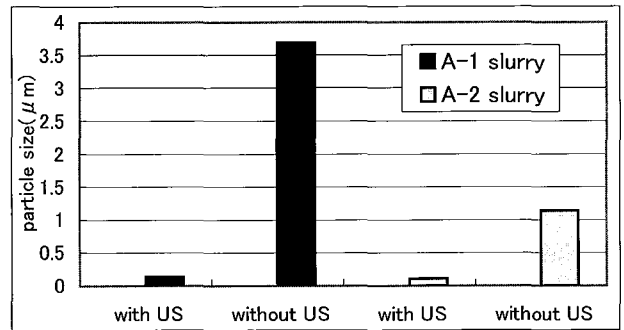
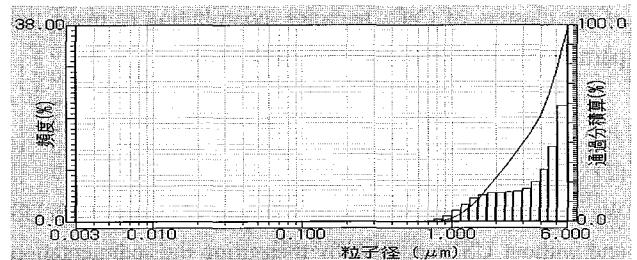
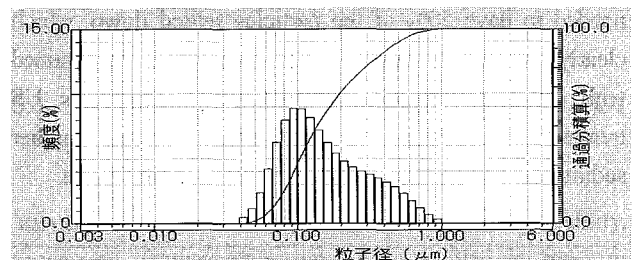


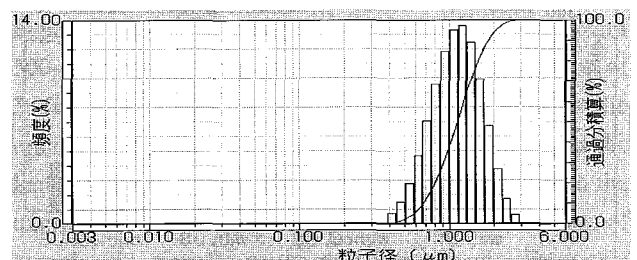
Fig.1 Influence of US on particle size



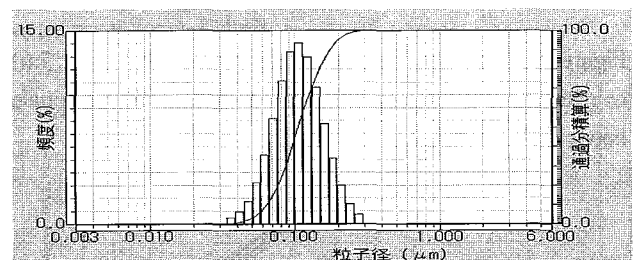
(a) A-1 slurry particle size "without US"



(b) A-1 slurry particle size "with US"



(c) A-2 slurry particle size "without US"



(d) A-2 slurry particle size "with US"

Fig.2 Influence of US on Particle size

Figure.2 shows the particle size distributions of A-1 and A-2 before and after US treatment. With regard to A-1 slurry, the particle size before US treatment was not uniform due to the presence of agglomerates, which later has become uniform with US treatment as agglomerates disappeared. For A-2, the particle size was quite uniform even before US treatment, and has become even smaller after US treatment. Possible reason for achieving stable particle size distribution by US treatment is the generation of physical force through cavitation phenomenon. Big impact between particles produced during such cavitation would lead to a dispersion of the clusters of CeO₂ particles, contributing to make the particle size distribution sharp and uniform.

(2) Stability

We investigated the stability of A-1 and A-2 slurries with US and without US treatment, by measuring the sedimentation rate in test tube (20ml solution). Figure 3 shows the time needed to have 50% of the particles settled down, which clearly indicates that much better stability can be obtained with US treatment than without US treatment as US treatment induces a slower sedimentation. A-1 has a higher sedimentation rate than A-2 due to smaller particle size.

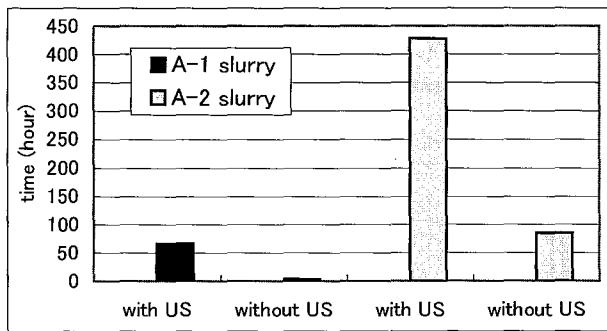


Fig.3 Time for 50% sedimentation

Figure 4 shows the zeta potentials measured (at pH 7.6) over the time treated by US, exhibiting different potentials between A-1 and A-2.

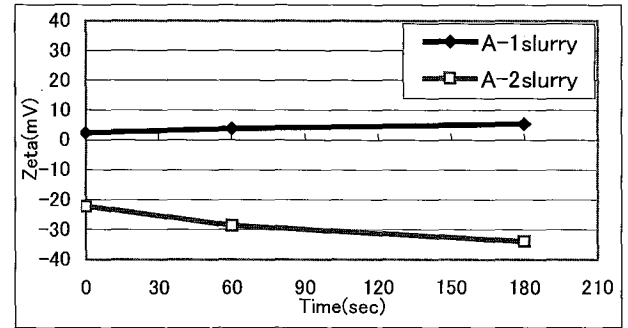


Fig.4 Influence of US treatment time on zeta potential

The bigger the zeta potential is, the less agglomeration of slurry will occur. Therefore, since the potential of A-1 slurry is smaller, A-1 slurry is more apt to become agglomerated. It is also observed that in both cases the potentials turned larger with the time of US treatment.

From the above results, US treatment has proved highly effective to improve stability of slurries.

3.2 Results of CMP polishing with P-TEOS

We conducted an experiment with P-TEOS with the polishing conditions shown in Table 2.

(1) CMP characteristics with A-1 slurry

Figure 5 shows the relationship between removal rates and polishing pressures with US and without US treatment. The US treated slurry gave a removal rate more than two times higher.

We can interpret it as follows;

- for the slurry treated with US, particles are uniformly dispersed, allowing slurries to be supplied efficiently and uniformly onto the work pieces.
- on the other hand, non-treated slurry was observed to have sedimentation phenomenon even during the polishing, which caused poor removal rate.

For Ceria slurry with US, removal rate is about 6 times higher than for silica slurry. This is due to intrinsic properties of Ceria compared to silica.

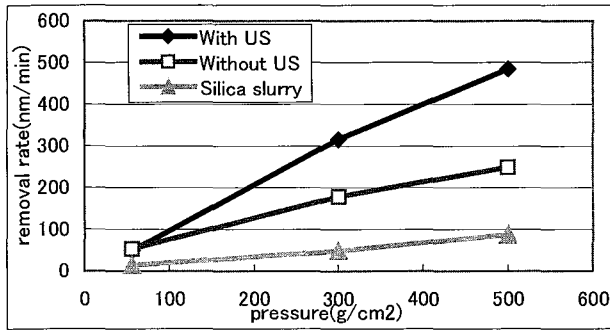


Fig.5 Influence of US on removal rate for A-1 slurry

Figure 6 shows the surface roughness obtained with A1 slurry. US treated slurry gave better results, which can be explained by the presence of less agglomerate after US treatment, leading to the generation of less defects.

Moreover, we have observed that roughness of a work piece with US turned similar to the one with Silica slurry.

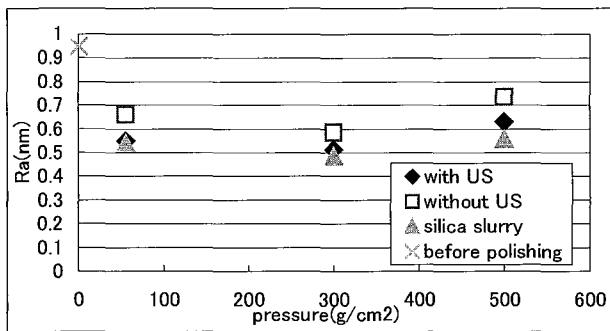


Fig. 6 Influence of US on Ra for A-1 slurry

(2) CMP characteristics with A-2 slurry

Figure 7 shows relationship between removal rates and polishing pressures using A-2 slurry. No significant effect of US treatment on the removal rates was observed. This can be correlated with the smaller effect of US treatment on particle size and stability of slurry observed previously.

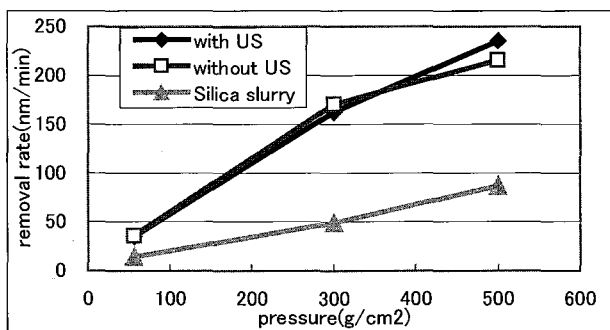


Fig.7 Influence of US on removal rate for A-2 slurry

Roughness of processed surfaces with A-2 slurry is shown in Figure 8. US treatment gives a slightly better surface roughness.

The comparison conducted between A-1 and A-2 slurries shows that A-1 slurry produces better processing characteristics than the other.

As a consequence, we decided to focus on US-treated A1 slurry in our next investigations.

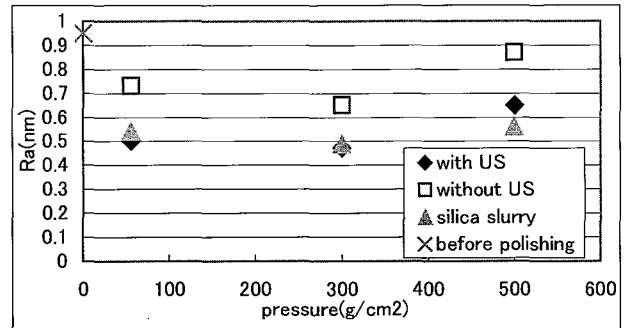


Fig. 8 Influence of US on Ra for A-2 slurry

3.3 Processing characteristics with US-treated A-1 slurry

Varying the ratio of ceria concentration in A-1 slurry, processing characteristics have been studied in order to obtain optimized conditions for oxide films (P-TEOS). Figure 9 shows the results: at the processing pressure of 500g/cm², the removal rates with the ceria concentration of 3~5wt% became about 5 times that of 1wt% while the removal rate of 10wt% slurry began growing slowly in the higher-pressure region. This is believed to be linked to the interference of CeO₂ particles, reducing the number of contributing particles to the polishing process. From this study, it is anticipated that 3wt% ceria concentration is most appropriate for A-1 slurry.

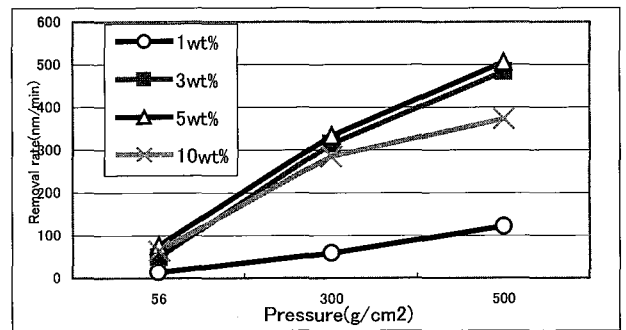
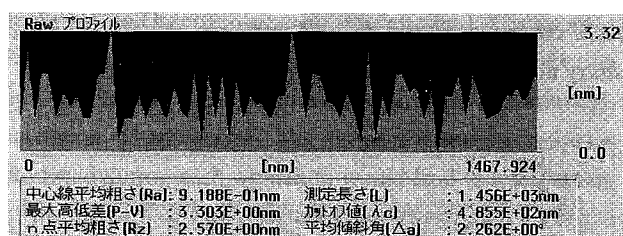
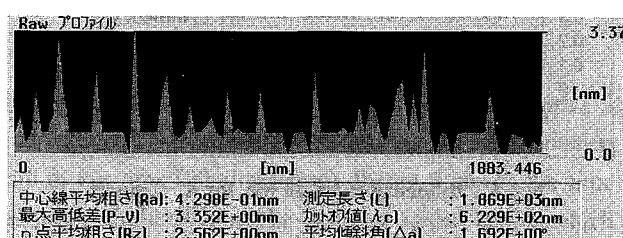


Fig.9 Influence of concentration on removal rate

Figure 10 shows AFM observation of wafers before and after polishing. We observe that average roughness drops from 0.919 nm before polishing to 0.429 nm after polishing. This is in agreement with the results observed on Figure 6 by interferometer (drop from 0.95 nm to 0.5 nm).



(a) Surface state before CMP



(b) Surface state after CMP

Fig. 10 AFM observation of wafers before and after CMP

4. Conclusions

We investigated the effect of US treatment on stability and polishing efficiency of 2 slurries; A-1 and A-2.

It appears that for slurry A-1, US treatment was particularly effective in improving stability (slower sedimentation). This can be explained by the cavitations effect produced by US treatment, which permits to desagglomerate particles as shown by particle size measurement. After US treatment A-2 slurry was found to have a better dispersibility (slower sedimentation) than A-1 by a combination of 2 factors; smaller particles obtained with slurry A-2 and higher zeta potential.

For CMP polishing with slurry A-1, it proved that strong desagglomeration generated by US treatment brings a large improvement in polishing efficiency and quality that can be explained by less sedimentation on pad during polishing.

On the contrary, for slurry A-2 where sedimentation is slow, US pretreatment has no effect on polishing results. This shows that good dispersibility is a necessary condition for the satisfactory polishing, which can be obtained without addition of surfactant (only US is enough).

Comparing slurry A-1 and A-2 with US pretreatment, it proved that despite mean particle size was similar, polishing efficiency was much superior with slurry A-1. This could be due to surface state of ceria (we indeed observed that zeta potential is quite different), to the presence of bigger particles in A-1, or to other factors such as particle shape, agglomerate structure, or crystallite size. Further characterizations to determine the main factor should continue.

Optimum concentration of ceria was found between 1 and 3 %. For a concentration higher than 3%, there is a saturation effect (no increase of removal rate) that remains to be explained. It looks like as if all active sites for polishing get saturated for a concentration in ceria higher than 3 %.

Comparing with silica commercial slurry, we showed that with A-1 slurry with US treatment we could reach same roughness of polished surface and a removal rate six times higher (for the same % of matter). This means that ceria slurry made from well tailored ceria oxide powders is very promising material for CMP.

《References》

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