NEW CERIUM POWDERS

FOR OXIDE FILM PLANARIZATION-CMP

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[Abstract]

ceria(CeO_2) slurry has a strong merit in CMP polishing to give a high removal rate and is more and more used. Polishing efficiency such as removal rate must depend essentially on intrinsic properties of SiO_2 powder .In the present study we investigated the polishing properties and slurry stability of 3 new powders which have been tuned at during synthesis to increase their polishing efficiency .We investigated those properties in the range of pH of 3 to 10 and compared performances to commercial slurries. We could get with the best powder a removal rate 1.5times superior to ceria commercial slurry and 8 times higher than silica commercial slurry. However those 3 powders proved not to have so good sedimentation stability at pH of 7. This should be solved by tuning the formulation by addition of appropriate surfactant.

Key Words: CMP, Ceria slurry, Removal rate, Surface roughness, Zeta potential

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, ceria is still a new comer in CMP polishing and only standard grades of ceria powder have been tested in CMP polishing.

In this study we started from ceria powders designed to increase removal rate and studied their properties of in slurries without addition of surfactant.

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2. Experimental Procedures

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

Tab.1 Measuring equipment

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)

Table 2 shows polishing conditions.

Tab.2 Experimental Conditions

Parameters	Conditions
Work Piece	15mm*15mm Oxide film (P-TEOS)
Apparatus for polishing	LM- 15, (ring type)
Pad	Foamed polyurethane φ340 mm
Slurry	Ceria slurry (P1, P2,P3) Silica slurry commercial Ceria slurry (commercial)
Rotation speed	30 rpm
Pressure during polishing	300 g/cm^2
Slurry feed rate	10 ml/min

We took as a reference a commercial silica slurry (concentration adjusted at 3wt% of silica) and a ceria commercial slurry (concentration adjusted at 3wt% of ceria); both slurries were tested as is (no Ultra Sonic (US) treatment).

High purity ceria powders (provided by Rhodia Electronics & Catalysis) made by 3 different processes (P1, P2 ,P3) were used after being dispersed in pure water and adjusted to appropriate pH by adding HNO_3 and NH_4OH.

Ultra Sonic (US) treatment was carried out for 3 minutes at 38kHz. All experiments were done with slurry containing 3wt% of ceria.

3. Results and discussion

3.1 Effects of pH on agglomeration state of particles

(1) Particle size distribution

Figure 1 shows the average particle size (d 50), we observed that for those 3 products, particle size is quite small at low pH (3) and high pH (10), but quite high at pH 5 or 7.6.

Figure 1:Particle size versus pH

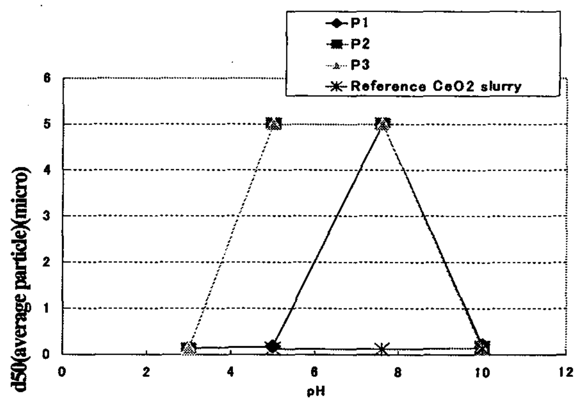
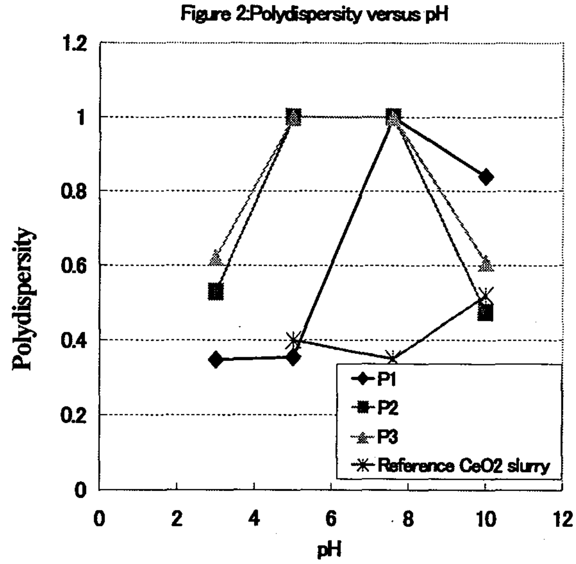


Figure 2 shows the polydispersity of particle in the slurry, those results are in consistant with above average particle size, for low pH (3) and high pH (10), particles are monodispersed, but for intermediate pH (5 and 7.6) dispersion is quite broad, this can be explained by agglomeration.

Figure 2:Polydispersity versus pH

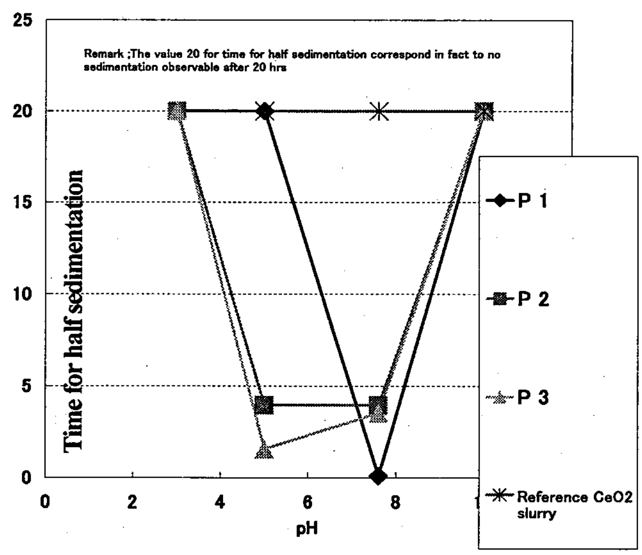


(2) Sedimentation rate of slurries

Figure 3 shows the sedimentation rate of the slurry at the various pH .For all 3 products sedimentation is quite fast at pH 7.6 .On the contrary, for the 2 commercial slurries there is hardly any sedimentation.

Above sedimentation rates can be explained well by particle size as measured in the slurries, formation of big particles at pH of 7.6 leads to quick sedimentation.

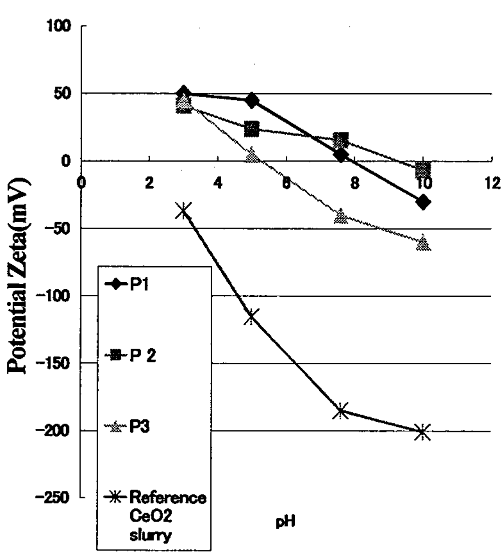
Figure 3:Sedimentation rate



(3) Zeta potential

Figure 4 shows results of zeta potential measurement directly on slurries .It appears that for all 3 slurries made of P products, zeta potential is quite low at pH 7.6, but absolute value is significant at low pH (3) or high pH (10) .On the contrary for commercial slurries absolute value of zeta potential is always high whatever pH is.

Figure 4: Variation of Zeta potential with pH



(4) Interpretation of results

Above results can be interpreted in the following way .It is generally accepted that isoelectric point of ceria is around 7, that is to say at pH 7, the zeta potential is almost zero. Our results have shown that, zeta potential curve for P1, P2, and P3 are different. However in all cases, zeta potential is quite small around pH 7. This zeta potential curves show that around pH 7, zeta potential being quite small, electric repulsion between particles is quite small, that is why there is agglomeration as proved by particle size measurement

Due to this agglomeration, there is formation of big particles, which lead to quick sedimentation.

On the contrary at low pH (3) or high pH (10), zeta potential is high, electric repulsion big, and there is little agglomeration, and sedimentation is quite slow.

For ceria commercial slurry, negative zeta potential, regardless of pH the pH, must be caused by an additive, surfactant, added in the formulation. This gives slurry with no agglomeration nor sedimentation at pH 7.6 and as such sedimentation.

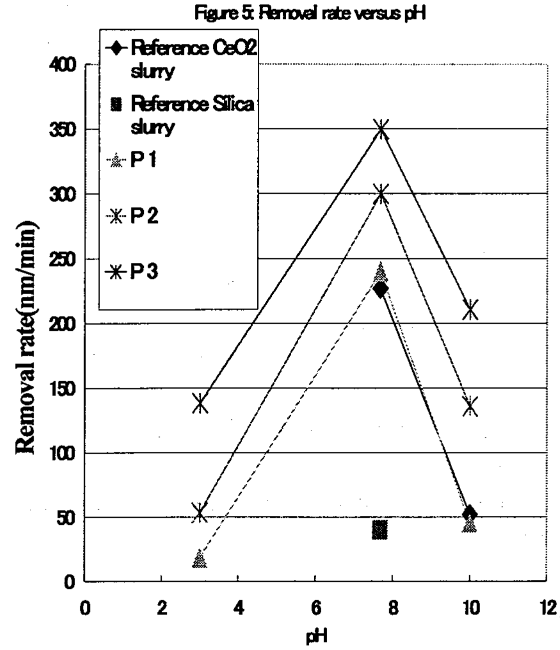
3.2 Results of CMP polishing with P-TEOS

We conducted experiments with P-TEOS with the polishing conditions shown in table 2.

(1) Removal rate

Figure 5 shows the results of removal rate for a pressure of 300 g/cm2 versus pH for various grades.

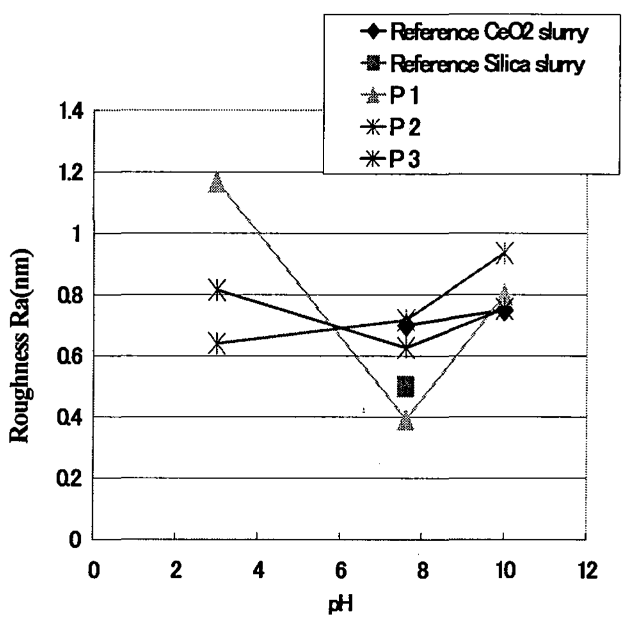
Figure 5: Removal rate versus pH



We can observe following points;
-Whatever the product, the removal rate is highest at pH 7.6 and drops sharply at low pH (3) and at high pH (10).
-P3 is the best product that increases the removal rate 50% superior to reference commercial SiO_2 slurry (350 nm/min compared to 230nm/min)
-P3 has a removal rate more than 8 times higher than silica commercial slurry

(2) Average roughness
Figure 6 shows the average roughness for polishing at various pH.

Figure 6: Roughness versus pH



Results have indicated that;
-A general tendancy that the higher the removal rate, the better the roughness was observed.
-At low pH (3) and high pH (10) obtained roughness is relatively bad
-P3 slurry has an average roughness similar to commercial CeO_2 reference
-Commercial silica seems to give slightly better roughness than other slurries

4. Conclusions

We investigated the effect of pH on physical properties of slurries and polishing properties of slurries made from 3 new powders, and compared to commercial slurries.
It appears these 3 powders, when put in slurry, have rather poor stability around pH 7.This behavior could be explained by zeta potential measurement which showed that, due to surface state of those powders, they have low potential zeta at pH 7 .Due to this low zeta potential, agglomeration occurs at pH 7 and this leads to a quick sedimentation.

However, those powders appeared to have very high intrinsic properties for CMP polishing, and the best one, P3, gave a removal rate 50% higher than commercial ceria slurry, and 8 times superior to commercial silica slurry.
Average roughness after polishing proved to be same level as commercial ceria slurry, but a little inferior to silica slurry.

It is observed that the removal rate is low at low pH and high pH whatever the ceria powder included in the slurry is. This confirms that optimal chemical effect of CMP with ceria is at pH around 7.
In order to develop a superior slurry from powder P3, it is necessary to work on the formulation of slurry, to find the appropriate surfactant that will bring a high zeta potential at pH of 7.

《References》

1) T K Doy : Details of Semiconductor CMP Technology (Kogyo-chosakai publishing Co, 2001) in Japanese
2) T K Doy : Semiconductor planarization CMP technology (Kogyo-chosakai publishing Co, 1999) in Japanese
3) B Pacaud, T K Doy, Y Sasakawa, E Rohart: Basic study of oxide film planarization CMP with ceria slurry, 2002