CMP 슬러리의 제조 – 콜로이드 화학과 재료의 관점

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Preparations of CMP slurry – Colloid chemistry and material aspects

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Introducton

As the design rule of semiconductor device decreases, chemical mechanical polishing (CMP) step have been highlighted in the point of multi-layer interconnections, such as planarization and damascene. Particularly, CMP slurries, which were used in shallow trench isolation (STI) CMP technologies, are strongly required high uniformity and selectivity as well as low scratch characteristics because of suitable process margin [1,2]. Generally, as STI structures are composed of various pattern densities and feature size and adopt silicon nitride layer as a stopping layer, conventional silica-based slurries are not adequate for STI CMP below 0.14μm design rules. Particularly, as design rules shrink further, high uniformities are required in not only STI CMP not also ILD process [3,4]. Therefore, CMP slurries, which have both higher chemical reactivity and more uniformed polished profiles than those of commercial silica slurries, are strongly recommended. In this presentation, we are to report silica-based slurry, which showed highly uniformed polished layer. Moreover, ceria slurry additives were developed, which accomplish low defect as well as high nitride selectivity during CMP process.

Experiment

In polishing experiments, PETEOS blanket wafer(6000Å or 16000 Å) and Si_3N_4 blanket wafer(1500Å) were used and Strasbaugh 6EC was used to polish those wafers. Silica and ceria abrasives were supplied by Cheil Industry and Hitachi Chem., respectively. And functional additives of each slurry prepared as given in Table 1 and 2, and they were mixed with them just before polishing. Polishing was carried with the following condition; down force/ back pressure/ platen rpm/ head rpm = 3.5psi/1.5psi/103/97. After polishing test, polished wafer was cleaned with DNS brush-type cleaner and remained thickness was measured OPTI-PROBE. In case of defects and μ-scratch counts, polished wafer was decorated with 1% HF etching for 100sec.

Results and Discussions

(1) Uniformity Improved Silica-based Slurry

Uniformity improved noble silica slurry was designed to be used in STI CMP process by controlling primary particle size of abrasives and using cationic additives as a dispersing agent. As shown in Fig. 1, polished profiles of blanket PETEOS wafer are highly dependent on the primary particle size of silica abrasives. Therefore, adopting of silica slurry with very small primary particle size could give improved uniformity. However, as primary particle size of abrasives is decreased, PETEOS removal rates were also reduced about 600Å/min as given in Fig.2.

In order to compensate for reduced removal rate, amine additive (TMAH, tetramethylammonium hydroxide) was added during dispersion process. As shown in Fig. 3, by adopting TMAH, material removal rates were nearly recovered and uniformities were not changed. Moreover, additional advantages were observed such as defect reduction and improved nitride selectivity as shown in Fig. 4 and Table 1.

Table 1. Si_3N_4 removal rate and Si_3N_4 selectivity according to additives (each additive concentration is 0.1wt% of abrasives).

Additives	Si_3N_4 selectivity
No additives	4.0
Ethanolamine	4.2
Dimethanolamine	4.1
Trimethanolamine	4.6
Ethylenediamine	4.8
TMAH	6.1
CPC (CetylPyridiniumChloride)	5.9
CTAB (CetylTrimethylAmmoniumBromide)	6.6

Table 1. Additive compositions of ceria slurry

	Additive Compositions
1	Poly(acrylic acid), M.W.=3,000 $[-CH_2CH(COOR)-]_n$
2	Poly(acrylic acid-co-maleic acid), M.W.=3,000 $[-CH_2CH(COOH)-]_x[-CH(COOH)CH(COOH-)_y$
3	Poly(methyl vinyl ether-alt-maleic acid), M.W.=3,000 $[-CH_2CH(OCH_3)CH(COOH)CH(COOH)-]_n$
4	Poly(acrylic acid), M.W.=2,000 (100%)
5	Mixture of poly(acrylic acid), M.W.=2,000 and M.W.=450,000 (weight ration=8:2)
6	Mixture of poly(acrylic acid-co-maleic acid), M.W.=2,000 and poly(acrylic acid), M.W.=450,000 (weight ration=8:2)

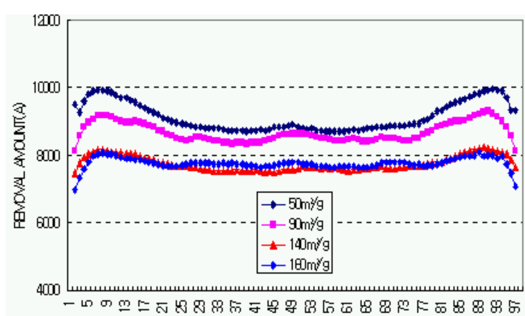

Fig. 1 Polished profile according to the primary particle size of silica abrasives

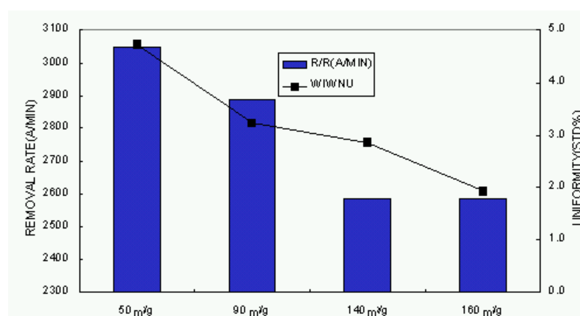

Fig. 2 PETEOS R/R and uniformity according to the primary particle size of silica abrasives

Generally, as primary particle size decreases, dispersion process is very hard to be accomplished and requires much higher dispersion energy. Therefore, usual dispersion systems could not be used to slurry production systems and incompletely dispersed slurry might cause defects on the polished wafer surfaces, such as micro-scratch. By using TMAH additives during normal dispersion process (such as high shear mixer or homogenizer), this dispersion problem could be resolved and defect reduction was clearly indicated in Fig. 4. This defect reduction can be explained by adsorption

behavior of additives onto the abrasive surface. When additives are brought into dispersion step, they adsorb onto negatively charged abrasive surfaces and their adsorption layer acts as a steric barrier of aggregation of abrasive particles. However, main reasons of selectivity increase are not yet clearly understood.

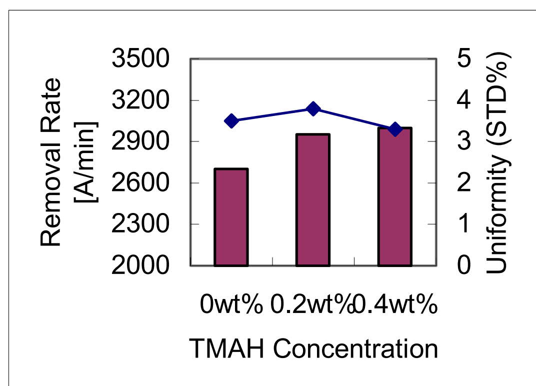

Fig. 3 PETEOS R/R and uniformity as a function of TMAH concentration (abrasive surface area=120m^2/g)

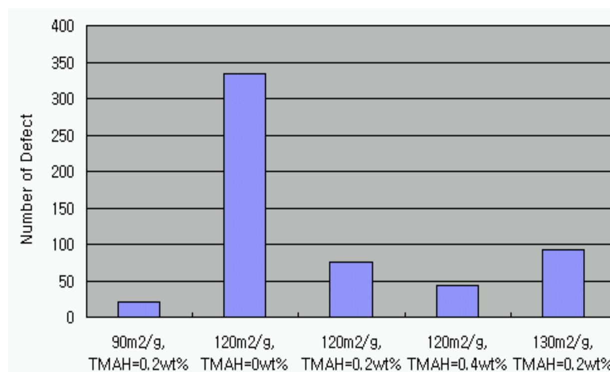

Fig. 4 Defect level comparisons of blanket PETEOS wafer after polishing.

(2) High Selectivity Additives in Ceria Slurry

First, three types of low molecular weight polyelectrolytes were used as shown in Table 2. #1~3 and their blanket polishing performances (SiO_2 and Si_3N_4 removal rate, selectivity) were shown in Fig. 5. Each polyelectrolyte was used as an ammonium salt (with almost neutral pH) before polishing and showed high selectivity above 50. These high selectivity characteristics might be originated from carboxyl groups ($-COO^-$), which have negative charge.

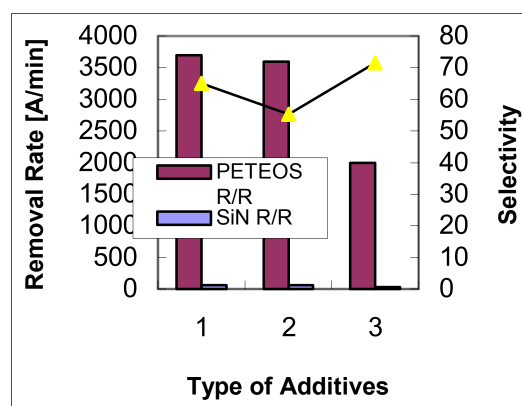

Fig. 5 Material removal rates of SiO2 & SiN wafer & selectivity according to additive compositions.

As mentioned above, high selectivity mechanism in ceria slurry is believed to arise in surface charge differences between SiO_2 and Si_3N_4 substrate. In order to confirm this, surface charge of each blanket wafer was measured with plate-type cell with commercialized electrophoretic apparatus (ELS-8000, Ostuka Electronics, Japan) with a He-Ne laser. Considering data reported by other [6], somewhat different behavior was observed. These deviations might be explained by the materials difference in measurement. In this work, each zeta-potential was measured using blanket wafer, and, wafer surface charge might be changed according to surface moieties determined by deposition condition. Anyway, whole trend of surface charge according to pH changes was well coincided. Those surface charge differences in each substrate could be one of high selectivity mechanisms. Moreover, polyacrylic acid, which has functional such as carboxyl groups ($-COO^-$), is most common dispersant or flocculent in silicon nitride particles because of its high adsorption characteristics [7]. Therefore, high selective SiO_2 over Si_3N_4 polishing

characteristics are originated surface charge differences in substrate surface and highly adsorbing characteristics of additives on Si_3N_4 wafer surface.

To confirm the surface charge effect on high selectivity mechanism, polyacrylic acid ammonium salt additives was used and monitored material removal rates and selectivities with the variation of pH using the composition of #6. PETEOS and Si_3N_4 removal rates and selectivity changes according to pH were given in Fig. 6. As shown in Fig. 6, PETEOS removal rates and silicon nitride selectivity were drastically changed with pH, which clearly indicates that high selectivity mechanism is highly dependent on the surface charge differences between oxide and nitride substrates. Particularly, according to zeta-potential measurements, pH difference was maximized and PETEOS removal rate was highly dependent on pH difference.

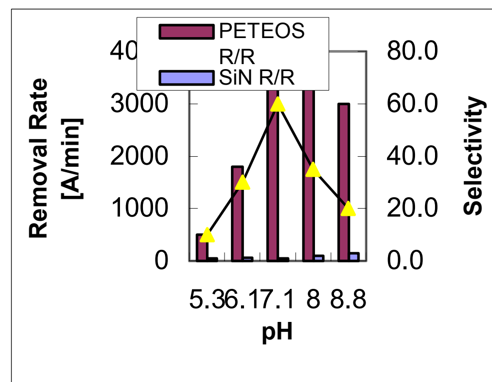

Fig. 6 Material removal rates of SiO_2 & Si_3N_4 wafer & selectivity according to additive pH.

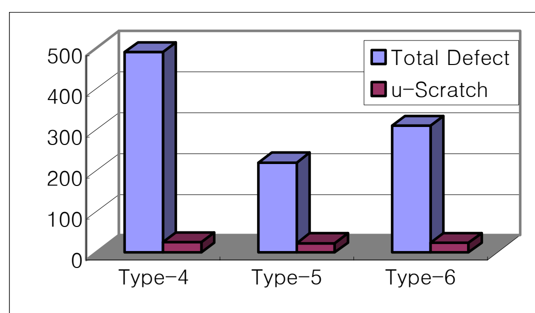

Fig 7. Numbers of total defect & m-scratch per wafer according to the type of additives.

Finally, total defects and μ-scratch counts were measured by KLA (after 1% HF etching for 100sec) using additives given in Table 2. as #4~6. All additives were used as an amine-salt type. In case of additives composed with only low molecular weight, total defect count showed higher value than those of other mixtures of low and high molecular weight. Moreover, additive made as mixture of poly(acrylic acid), M.W.=2,000 and M.W.=450,000 (weight ration=8:2) showed lowest defect level and μ-scratch as shown in Fig. 7.

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