Effect of Particle Size of Ceria Coated Silica and Polishing Pressure on Chemical Mechanical Polishing of Oxide Film

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Submicron colloidal silica coated with ceria were prepared by mixing of silica and nano ceria particles and modified by hydrothermal reaction. The polishing efficiency of the ceria coated silica slurry was tested over oxide film on silicon wafer. By changing the polishing pressure in the range of 140~420 g/cm^2 with the ceria coated silica slurries in 100~300 nm, removal rates, WIWNU and friction force were measured. The removal rate was in the order of 200, 100, and 300 nm size silica coated with ceria. It was known that the smaller particle size gives the higher removal rate with higher contact area in Cu slurry. In the case of oxide film, the indentation volume as well as contact area gives effect on the removal rate depending on the size of abrasives. The indentation volume increase with the size of abrasive particles, which results to higher removal rate. The highest removal rate in 200 nm silica core coated with ceria is discussed as proper combination of indentation and contact area effect.

Keywords : CMP, Oxide polishing, Ceria coated silica, Hydrothermal treatment, Friction force

1. INTRODUCTION

It has been required the higher planarity and free of defect of oxide film in CMP(chemical mechanical polishing) process because of ultra-large scale integration circuits with reduction in feature sizes of devices. Recently, many efforts have been made toward decreasing size and preventing keen-edge shape of CMP slurry particles to meet the requirements for the polished wafer. Commercial ceria abrasive prepared by break-down process through milling of the calcined powder which is synthesized from metal salts has inevitably irregular shape and size. The slurry has heterogeneous flow of particles, varied interaction force among abrasive particles, pad and wafer and dissimilar chemical activity. The ceria particle is less stable in solution compared to silica because its Hamaker constant is 28 while the silica is 6. In spite of some defectivity on CMP and low stability, the slurry is applied to ILD(inter layer dielectrics) or STI(shallow trench isolation) process due to high removal rate on oxide film. There have been reports that the ceria prepared from build-up process improved flatness and decreased defect, however, aggregation during manufacturing process may result to unsatisfactory polishing. In contrast, the colloidal silica particles are higher in stability with relatively easier size control, but the removal rate on oxide film is considerably lower than ceria particles.

We have previously reported the possibility of ceria coated silica particle as CMP abrasives, where it showed the considerable removal rate as ceria only abrasives [1,2]. The hydrothermal treatment of ceria coated silica particles improved the removal rate of slurry[3]. There has been doubts whether the nano sized ceria particle can be separated from the surface of silica and afterward aggregated by the pressure that has been applied during the polishing process.

We have prepared mono-dispersed 100, 200, 300 nm size silica coated with ~10 nm size ceria particles by hydrothermal treatment. By changing the polishing pressure in the range of 140~420 g/cm^2 with the ceria coated silica slurries removal rates were measured. The bonding strength between ceria and silica particles will be discussed by comparing the removal rate according to the pressure change for the different size of the ceria coated silica. The CMP slurry composed of ceria coated silica particle shows the merits of silica and ceria, that is the high dispersion and uniformity of silica and the high removal rate of ceria.

2. EXPERMENTAL

2.1 Preparation of nano ceria coated silica particles

Ceria coated silica particles were prepared by the same procedure as previous work[3]. pH condition was chosen to be 6.0, where it is provided the strongest attractive force between ceria and silica. Silica sols (Nissan chemical MP series) with nominal size 100, 200, 300 nm was used as core materials and ~10 nm colloidal ceria (Nyacol co. Ltd) was coated on the surface of silica. The 0.6 wt% ceria slurry was mixed with the 6 wt% silica slurry in 1:1 volume ratio at 25 ℃ for 1hr. pH was adjusted to 6.0 for all reaction conditions at the beginning and monitored during the reaction. The mixture slurry maintained its pH after aging for 3 hr at 96 ℃ and followed by hydrothermal treatment at 150 ℃ for 3 hr. After hydrothermal treatment, ceria adhesion on the surface of silica are expected to get stronger with better dispersion. The slurry was centrifuged at 3200 rpm 3 times to eliminate free ceria particles in the slurry. Finally the concentration of ceria coated silica slurry was adjusted to 1 % for the polishing experiments.

The morphology of the not coated particles were characterized by transmitted electron microscopy (JEM-200EX, JEOL). The particle size distribution was measured by dynamic electrophoretic light scattering method using particle size analyzer (ELS-9000, Photal). The crystalline structure was checked by X-ray diffraction (MXP, MAC Science Co. Ltd) at 2 theta of 20~80 degree. The specific surface area was characterized by nitrogen adsorption (BET, Tristar 3000, Micromeritrics). The zeta potential of silica, ceria and ceria coated silica slurries were measured with pH variation to determine iso-electric point.

2.2 Polishing experiment

Polishing experiments were carried out with oxide film on 4-inch silicon wafers by POLI-500R (G&P technology, Korea) polisher using IC-1400 k-groove pads. To understand the effect of polishing pressure and abrasive size on the removal rate, 4 factors were chosen in 3 levels by response surface methodology. The polishing experiments were performed by changing polishing abrasive size (nominal size of 100, 200, 300 nm), polishing pressure(140, 280, 420 g/cm^2), slurry flow rate(100, 150, 200 ml/min), and table speed(50, 100, 150 rpm). The removal rates for wafers were determined from the differences of the film thicknesses measured by Ellisometer (Rudolph, AutoELⅢ).

At every slurry exchange, there were pre-conditioning of groove pad and polishing of dummy wafer for 1 min, respectively, before polishing tests. The friction force on the wafer during polishing tests was measured for 1 min by piezoelectric force sensor (Kistler).

3. RESULTS AND DISCUSSION

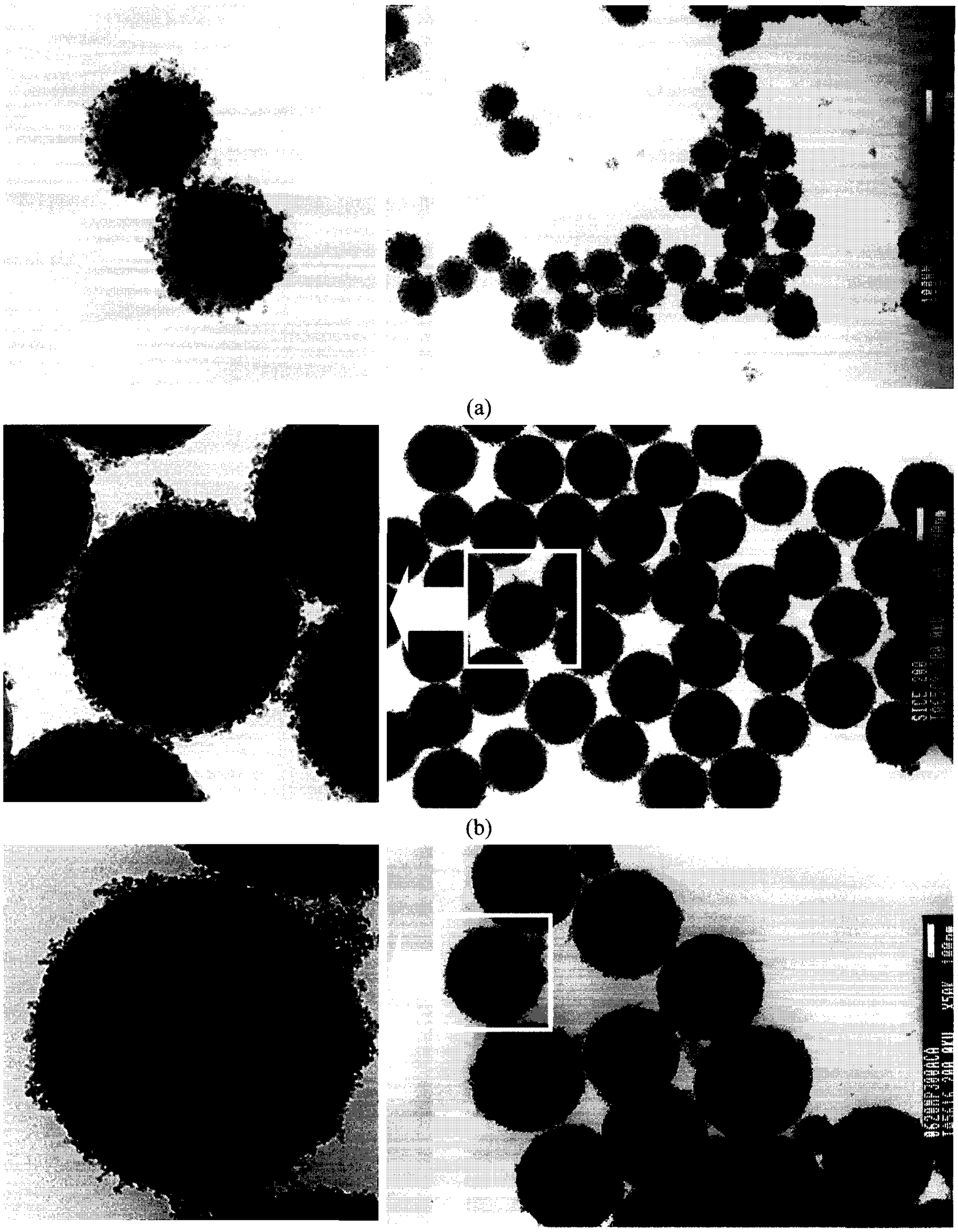
3.1 Properties of particles

The particle size analysis and specific surface area are summarized for colloidal silicas in 100, 200, 300 nm nominal size (Si-100, Si-200, Si-300) and ceria coated on the surface of silica particles in 100, 200, 300 nm (SiCe-100, SiCe-200, SiCe-300). The average particle size of silica core by dynamic light scattering are pretty well consistent with the nominal size of the commercial colloidal silica. After coating process, the particle size increased by 52, 23, and 7 % compared to silica cores Si-100, Si-200, Si-300, respectively. The smaller the size of particle, there is higher increase in size after coating process and smaller increase in BET surface area relative to the cores. The BET surface increased after ceria coating since it has higher surface area than the core. According to the BET surface area of core silica, Si-100 has ~twice and ~four times larger surface area than Si-200 and Si-300. Thereby larger amount of deposition of ceria was expected, but the increased value of BET surface area after ceria coating remained the same and the increased BET surface area fraction relative to the core was the smallest for SiCe-100. We assume that there would be higher adsorption capacity for smaller size of SiO_2 particles, at the same time. Ceria coating seems in Si-100 to be less dense due to curvature of convex surface.

The morphology of ceria coated silica are observed by TEM in Fig. 1. The nano size ceria particles are coated in a single or double layers on the surface of core silica particles, which was checked also by BET surface area increase. The change in the crystalline structure of ceria particles before and after hydrothermal treatment were checked by comparing peak intensity and full width at half maximum, and there was no noticeable change in the ceria crystalline structure.

Table 1. Properties of colloidal silica and ceria coated silica particles.

Property Sample name	Particle size analysis (nm)	Specific surface area (m^2/g)	Particle size Increase rate (%)	Surface area Increase amount (%)
Si-100	90	58	52	28
SiCe-100	140	74		
Si-200	185	23	23	65
SiCe-200	230	48		
Si-300	300	13	7	115
SiCe-300	320	28		



(a)

(b)

(c)

Fig. 1. TEM image of the coated particle (a) SiCe-100, (b) SiCe-200, (c) SiCe-300.

3.2 Polishing

The removal rate(RR), within wafer non-uniformity (WIWNU), and friction force were measured in the series of conditions designed according to the response surface methodology and listed in Table 2.

The removal rates are plotted in Fig. 2(a), which is varied with polishing pressure and abrasive particle size. The removal rate was proportional to the polishing pressure.

Table 2. Polishing conditions and polishing property of ceria coated silica particles.

Sample	Polishing Pressure (g/cm^2)	Table Speed (rpm)	Slurry flow rate (ml/min)	Removal Rate (nm/min)	WIWNU (%)	Friction force (kgf)
SiCe-100	140	100	150	36	19.2	4.0
	280	50	150	3	53.8	6.7
		100	100	230	11.0	6.1
		100	150	98	8.8	6.1
		100	200	105	27.4	5.8
		150	150	390	13	8.2
	420	100	150	160	17.1	8.2
SiCe-200	140	50	150	90	13.5	7.8
		100	100	240	10.1	7.5
		100	150	170	8.9	7.9
		100	200	160	9.6	7.2
		150	150	220	8.4	7.4
	280	50	100	210	17.5	7.2
		50	200	180	13.3	6.9
		100	150	314	10	5.8
		150	100	447	7.1	4.7
		150	200	380	11.2	4.4
	420	50	150	270	13.1	6.4
		100	100	443	8.4	3.2
		100	150	437	11.2	3.6
		100	200	450	6.5	2.7
		150	150	560	6.5	2.7
SiCe-300	140	100	150	17	23.9	8.7
	280	50	150	4	21.5	8.4
		100	100	47	21.6	7.0
		100	150	35	22.7	7.0
		100	200	23	27.4	7.7
		150	150	90	16.2	6.2
	420	100	150	47	15.0	5.9

which is consistent with Preston equation RR = k×P×V (RR is removal rate, k : Preston constant, P : total pressure, V : relate velocity)[4,5]. The removal rate is known to be higher with smaller abrasive particles in the polishing of copper and tantalum where contact area model is dominant mechanism in the metal polishing. The ceria coated on 200 nm core silica (SiCe-200) exhibit higher removal rate than SiCe-300, however, removal rate of SiCe-100 was lower than that of SiCe-200. The abrasive behaviors are often explained by indentation and surface area model[6,7]. The decrease in removal rate in SiCe-100 might be explained by the structure of porous structure of groove pad. The smaller particle has higher contact area but the SiCe-100 has the smallest indentation volume so that the pressure might not properly transfered to the abrasives on the contact with surface of oxide film. Even with the SiCe-100, it is possible to improve the polishing removal rate by changing the pad structure, which consisted of many cylindrical segments with flat surface as was proved for efficient polishing rate of nano size ceria[2].

Figure 2(b) revealed the correlation between removal rate and table speed depending on abrasive particle size. The removal rate of SiCe-200 and SiCe-300 is proportional to the table speed but the linear regression does not pass the center, so that they follow the Preston equation with some deviation. In the case of SiCe-100 abrasive particles does follow Non-Preston equation.

Wafer in wafer non-uniformity (WIWNU) was obtained from film thickness variation by calculating standard deviation over average of 19 measurements in film thickness. The WIWNU of SiCe-200 was relatively lower than SiCe-100 and SiCe-300. The plot of removal rate vs. friction force is shown in Fig. 3. The removal rate of ceria coated silica decreased with increase of friction force, which is contrary to the previous work by H.S. Lee, et al[8] for the silica abrasives on the chemical mechanical polishing of silicon oxide film. The correlation

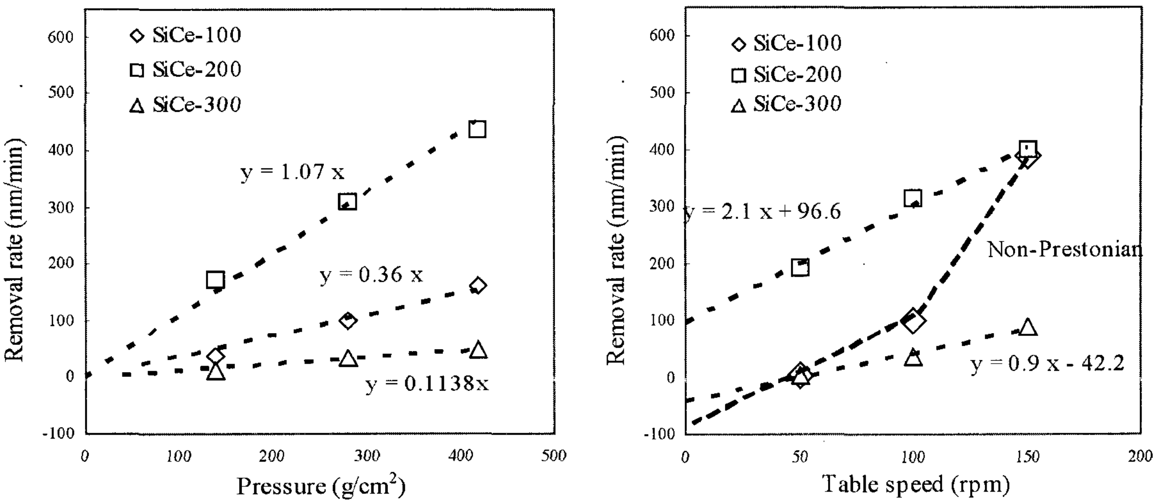


Fig. 2. (a) Removal rates by polishing pressure and at flow rate 100 ml/min, table speed 150 rpm (b) removal rate by table speed and particles size at polishing pressure 280 g/cm^2 and flow rate 150 ml/min.

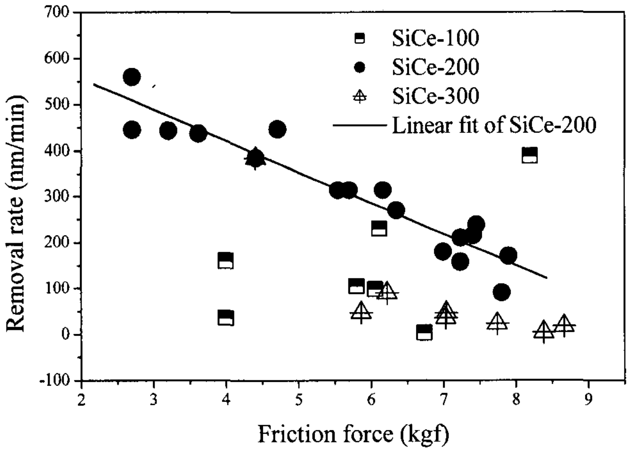


Fig. 3. Relationship between removal rate and friction force from SiCe-200 in table 2.

of removal rate and friction force for SiCe-100 and SiCe-300 was low, but for SiCe-200 the correlation was pretty clear with correlation coefficient $r^2=0.9$. For polishing of oxide film by silica abrasives in high concentration as over 5 wt%, the removal rate is proportional to the friction force since it provides stable slurry fluid layer between wafer and pad even with high polishing pressure. However, for the ceria coated silica slurry in low concentration as 1 wt%, the removal rate decreased by increase of friction force because there is small number of abrasive particles and direct contact of pad to the wafer increased while the contact area of particles to the wafer remained the same in fluid layer between pad and wafer. The other reason of removal rate decrease with friction force is that the exposure of core silica increase because ceria particles may released by increasing shear force during polishing process[9]. The friction force of ceria particles is relatively larger that that of silica. The polishing tests of ceria coated silica with the additional bare silica particles might give further understanding on the correlation of friction force and removal rate in polishing of oxide film by ceria coated silica.

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