Polishing characteristics of micron particles aggregated by nanosilica

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Abstract

Colloidal silica slurry has been widely used in mirror finishing of various microelectronic materials, including Si wafer. However, in the last decade, there has been a tendency to replace the polishing slurry with fixed-abrasive pads because of environmental issues related to the use of slurry and poor finishing surface shape accuracy. Unfortunately, the fixed-abrasive pad is still unsatisfactory for both material removal rate and finishing surface quality. Therefore, various silica abrasives added into fixed-silica pads for polishing Si wafer were investigated in this study. Both loose and fixed abrasive polishing experiments were performed. Instead of conventional nanosilica abrasive, the micron spherical particle aggregated by nanosilica (hereafter, aggregate silica) was proposed as an abrasive of fixed-silica pad, and were compared with micron natural crystal silica abrasive and micron spherical fused silica particle. Experimental results demonstrated that the nano-aggregating structure of aggregate silica with a mean diameter of about 5 μ m has approximately 100 times higher specific surface area than the natural and fused silica abrasive, and can easily absorb more [-OH] onto the aggregate silica surface, which is approximately 5 times when each of them is added to the alkaline aqueous solution at pH 12. Thus, a strong chemical removal effect was observed. This condition caused not only higher material removal rate but also better finishing surface roughness, which can be comparable to that of colloidal silica slurry with 10 nm to 20 nm particle size (5 wt%, pH 10.5). The chemical removal effect can also be enhanced by increasing nanopore volume of aggregate silica.

Key words :Fixed-silica pad, Nano-aggregate silica, Micron spherical particle, Chemical removal, Si wafer

1. Introduction

Nanosilica slurry remains widely used to polish various substrate materials in the microelectronic industry. This material is typically utilized to polish Si wafer. Generally, nanosilica slurry is employed with a polishing pad made of viscoelastic material to ensure that the polishing process is less susceptible to vibration interference, thereby making the mirror finishing process easier. However, nanosilica slurry should be replaced by fixed abrasive because of the environmental problems caused by using slurry and the poor precision of post-polish surface shape, among others. A fixed-abrasive pad will not only achieve a final finishing surface without a damaged layer compared with other fixed-abrasive tools (such as grinding wheel), but will also gain higher hardness than the conventional pad. This result is beneficial to improve the oxide dishing in over polishing of CMP and the roll off of the edge in polishing wafer. The motion of fixed-abrasive is also more deterministic than that of loose abrasive during polishing. Thus, prediction of the material removal rate is possible with a fixed-abrasive model. Fixed silica pad typically use an irregularly shaped sub-micron hard silica abrasive. Gagliardi et al. (2002) developed a fixed-abrasive pad with multilayer structure for direct STI CMP. The fixed abrasives was manufactured as rows of micron pyramids or convex cylinders that allowed the polishing chips to drain away smoothly, and avoid clogging the pad surface and shed abrasive to scratch the

polished surface. However, the polishing performance cannot meet the demands for practical use. Y.Kim et al attempted to develop a self-conditioning fixed-abrasive pad by controlling the adhesion between ceria abrasive and matrix material and allowing the fixed-abrasive to come off by itself during polishing. However, both polishing efficiency and surface quality with fixed silica pad remain unsatisfactory compared with those of conventional colloidal silica slurry.

Therefore, a fixed-silica pad was developed in the present study to utilize micron spherical particle aggregated by nanosilica. Experiments were conducted for fixed silica pad with polyurethane matrix material, and the characteristics of mirror finishing was investigated with aggregate and conventional silica. The report is mentioned below.

2. Fixed-nanosilica pad

In order to obtain the same polishing surface with colloidal silica slurry for current precision polishing, nano silica abrasive is used for fixed silica pad first. Thus silica abrasive (Nippon Aerosil Co. Ltd., Japan) with mean diameter of approximately 150nm was added into matrix material of polyurethane (MITSUI Chemicals, Inc., Japan), similar to the material of IC1000 pad. The surface activity of nanosilica is higher than that of micron silica abrasive because of the former's larger specific surface area. Nanosilica abrasive is easily gelled when mixed with the pre-polymer of polyurethane. Thus, silica addition is only allowed to 6 vol%, resulting in poor dispersion (Figure. 1). A 4" Si wafer was polished using a fixed-nanosilica pad with pH 10 alkaline solution prepared by KOH on the high -precision single-sided polishing machine SPL-15 (Okuma Corporation, Japan). Each polishing experiment was conducted at polishing conditions listed in Table 1. For comparison, the conventional polishing of Si wafer was performed using 10-20 nm colloidal silica slurry (5 wt%, pH 10.5) made by Nissan Chemical Industries, Ltd. and IC1000 pad made by Dow Electronic Materials (Newark, DE, USA). The difference in the weight of the wafer before and after polish was used to calculate the material removal rate (R). The pre- and post-polish surface characteristics (R_a roughness) of the wafers were measured using ultra precision surface profiler nanostep2 (Taylor Hobson Ltd., UK). The experimental results showed that the removal rate of nanosilica abrasive fixed in the matrix material of polyurethane significantly decreased compared with the loose abrasive processing of colloidal silica slurry (Fig. 2). This might be attributed to the fixed nanosilica that was easily embedded in the viscoelastic material of the pad during processing. Thus, the polishing pressure on the silica abrasive decreased and became insufficient to remove the material with low addition of abrasive, and so on. The micron particle size of silica abrasive was investigated on the basis of the abovementioned results.

Table 1 Polishing conditions

Workpiece	4" Si wafer
Surface roughness	0.25 μm Ra, 1.8 μm Rz
Polishing pressure	20kPa/50kPa
Rotation speed (Platen, Workpiece)	60 rpm
Polishing time	15 min

Fig. 1 Fixed-silica pad of 150nm silica abrasive

Fig. 2 The comparison of **fixed-silica pad** and conventional loose abrasive polishing

3. Mirror finishing of micron spherical silica

The fixed-abrasive pad with micron abrasive size has long been used in lapping, but not in polishing. Typically, a fixed-ceria pad is usually applied together with ceria slurry for processing glass and crystal. The conventional micron silica abrasive commonly uses hard and brittle natural materials crushed into an irregular shape. Such natural silica

abrasive exhibits a crystal structure with the average particle size of 3.5 μ m (Fujimi Inc., Japan) (Fig. 3a). The average particle diameter (3.2 μ m) spherical fused silica particle (Admatechs Japan Ltd.) was utilized to investigate the relationship between the shape of abrasive and the processing characteristics (Fig. 3b). This silica particle is a typically filler for filling resin. Thus, a uniform fixed silica pad with high addition of abrasive (up to 60 vol%) is easy to manufacture. Both of them have similar specific surface area (Table 2) and smooth surface without any pores (in Fig. 3).

This research start from the loose abrasive processing to investigate processing characteristics of silica abrasive itself, without the effect of matrix material of the pad. Each of the silica slurry was prepared by adding 0.5 wt% each type of silica to D.I. water followed by the addition of KOH powder. The slurry was mixed using a magnetic stirrer for about 15 min till pH 10.5. Comparison experiments of these two types of silica were conducted using the IC1000 pad at 50kPa polishing pressure (Table 1). The results are shown in Fig. 4. Compared with the spherical silica, the irregular silica abrasive exhibits a sharp edge (Fig. 3a). Thus, the removal depth is significant under the same polishing pressure, and a higher material removal rate was obtained but with poor and easy-to-scratch wafer surface (Fig. 3a, upper left). While the fused silica abrasive with spherical shape and smooth surface is not easy to be gripped by a polishing pad, and easily slipped on the wafer during processing. Although the material removal rate R is lower, if R/R_a is obtained to evaluate the characteristics of the material removal, fused silica is better than natural silica (Fig. 4). Nevertheless, both the surface quality and the material removal rate of micron spherical silica were worse than those of nanosilica. In order to retain not only the characteristics of mirror finishing with nanosilica abrasive, but also ensure that fixed nanosilica exposed over the polishing pad to remove material, as well as easy to manufacture fixed-silica pad with high addition of nanosilica. Therefore, following investigation focused on the micron spherical silica particle aggregated by nanosilica.

Table 2 Comparison of different types of SiO₂ abrasive

silica		Pore volume (cm ³ /g)	Specific surface area (m ² /g)	Elastic coefficient (N/ μ m)
Fused silica		0	1.38	
Natural silica		0	1.39	88
Aggregate silica	A	0.1	115	52
	B	0.3	145	17
	C	0.8	200	1.24

Fig. 4 Comparison of the mirror finishing of natural silica and fused silica (loose abrasive)

a. Nature silica

b. Fused silica

c. Aggregate silica C

Fig. 3 Comparison of the SEM photos of different types of silica

4. Characteristics of polishing with aggregate silica

4.1 Chemical removal of aggregate silica

This study investigated silica with average particle size of approximately 5 μ m, which was aggregated by 10 nm to 20 nm primary particles (JGC C & C, Japan). SEM photographs in Fig. 3c show that the nanoscale uneven surface of

the aggregate silica particle is noticeable compared with the smooth surface of the conventional natural silica. These two types of silica abrasives are prepared into a concentration of 5 wt% slurries, which are near the neutral and alkaline slurry with D.I.water and KOH respectively. Their loose abrasive processing experiments were performed at conditions described in Table 1 (polishing pressure: 50 kPa). The result is shown in Fig. 5. The material removal rate of the aggregate silica C slurry with pH 6.2 prepared by D.I. water is only about one-fourth that of the natural silica slurry with pH 7. This is due to the natural silica abrasive with the sharp edge come from its irregular shape; furthermore, elastic coefficient is approximately 70 times that of the aggregate silica C (Table 2). Therefore, the mechanical removal effect is strong. However, when the pH value of slurries gradually increased to the alkaline range of approximately 10.2, the removal rate of the aggregate silica C slurry increased to approximately 84%, which is more than that of the natural silica. Moreover, the motor current consumed to drive the work table of polisher significantly decreased (Fig. 6). This result shows that aggregate silica abrasive in an alkaline environment demonstrates chemical removal action. The processed surface roughness is also approximately 0.8 nmRa, which is significantly better than that of conventional natural silica abrasive and fused silica particle, close to the conventional colloidal silica slurry (0.75 nmRa). By contrast, the conventional natural silica mainly based on mechanical rather than chemical removal. A comparative analysis of physical chemical properties on the surface of two types of silica particle was conducted to further understand the cause of chemical removal of nano-aggregate silica particle. Natural silica abrasive has a smooth surface and is pore-free, whereas aggregate silica has not only nano-sub-particles (Fig. 3) but also nanosized ultrafine pores on the micron particle surface (Table 2). This condition leads to a decrease in elastic coefficient of silica, thereby reducing mechanical removal. Nano pores may generated a high specific surface area and the capillary phenomenon, it can produce physical adsorption on the silica surface. Therefore, the amount of $[-OH]$ adsorbed on the aggregate silica particle surface was compared with that of conventional natural silica abrasive and fused silica. Each type of silica powder was added to the aqueous alkaline solution of pH 12 to prepare slurry with 1 wt% concentration, and the pH value of each slurry was measured in terms of the time variation until the saturated condition was achieved. The results of Fig. 7 show the pH values of both natural and fused silica slurries are more stable, whereas those of aggregate silica C significantly decrease. And the amount of $[-OH]$ on the silica surface was calculated based

Fig. 5 The removal rate of Aggregate silica and natural silica slurry changes with pH

Fig. 6 Comparison of motor currents during polishing by aggregate silica C slurry

Fig. 7 Changes of pH of silica slurries and amount of $[-OH]$ added onto silicas

Fig. 8 The changes of material removal

on the change in pH value. Natural silica abrasive and fused silica were compared, and the aggregate structure with ultrafine pore showed a specific surface area of more than 100 times. Thus, the amount of $[-OH]$ adsorbed on silica is five times or more. Forming weakly adhered $Si(OH)_4$ was easy, and it was subsequently removed by the abrasive action of the silica particles. Thus, the solid-liquid phase chemical removal was obvious.

4.2 Aggregate structure of silica and polishing characteristics

The aggregate structure of silica can be controlled by prepared method and preparation conditions. The aggregating density of nanosilica was investigated in this study to evaluate the characteristics of aggregate structure of silica. This density is inversely proportional to ultra-fine pore volume, ultra-fine pore size, and particle size of sub-particle, among others. The three types of silica particles, namely, A, B, and C, with high to low aggregating density, were investigated in this study. The pore volume have been sequentially changed from low to high, as listed in Table 2 of silica properties. Three basic aggregate silica were prepared into the slurry with 5 wt% and pH 10.2. The polishing experiments were also performed using IC1000 polishing pad based on the polishing conditions (polishing pressure: 50 kPa) listed in Table 1. The experimental results are shown in Fig. 8. With the increase of the pore volume of silica, the material removal rate gradually increased in the experiment within the range. Among them, the removal rate for the smallest pore volume of silica A decreased with time compared with the stable removal rate of silica B and C. Meanwhile, the output motor current driving worktable was also at a low level (Fig. 9). This result implies that the nano uneven surface of aggregate silica tends to be smooth with decrease of pore volume. Thus, frictional resistance is insufficient to remove material, and silica abrasives just slip over the wafer; while the concentration of slurry decreases to 1 wt% and at the same polishing conditions, the removal rate becomes stable, and the motor current returns to normal level (Fig. 9). This result is similar to that of spherical fused silica described in Chapter 3. Both of them are unsuitable for loose abrasive at normal pressure.

The polishing characteristics of aggregate silica particles in D.I.water and alkaline aqueous environment are investigated to understand the relationship of the aggregating density of silica and material removal of Si wafer. The experimental results (Fig. 10) show that the removal rate of aggregate silica in D.I.water environment decreased with pore volume of silica, which is caused by the elastic coefficient of silica that was inversely proportional to the pore volume (Table 2); however, as the pore volume of silica increased, the part of the removal rate from the alkaline environment of pH 10.2 increased. This result is caused by the fact that increasing the pore volume of aggregate silica also increased the specific surface area of silica (Table 2). Thus, the amount of $[-OH]$ adsorbed on the silica surface increased, thereby enhancing the chemical removal effect. The increase of the pore volume also means the "chip pockets" of nano-sub-particles increased. These "chip pockets" are good for the material removal of aggregate silica.

Additionally, the used aggregate silica particles C with high material removal rate were observed by SEM. The oversize silica is easy to flatten during polishing. The silica particle in 1wt% slurry shows a higher polishing pressure than the silica particles with concentration of 5 wt% slurry and is observed to be easily shaped into an oval (Fig. 11). The result also implies that sub-nanosilica abrasive may directly remove the material. Based on the results, controlling the pore volume or aggregate structure of silica can not only change uneven surface of the silica particle, thereby affecting its frictional behavior during

Fig. 9 Changing of motor current

Fig. 10 Polishing characteristics of silica with different aggregating structure (loose abrasive)

polishing, but also change its surface property of physical chemistry, for example, adsorption of $[-OH]$, which improves the chemical removal effect and material removal rate of silica abrasive, possibly changing the material removal behavior and abrasive size during polishing.

(a) Slurry: 5 wt%

(b) Slurry: 1 wt%

Fig. 11 SEM photos of aggregate silica C after polishing

5. Characteristics of polishing by fixed-abrasive pad with aggregate silica

The fixed-silica pads that utilized the abovementioned three types of silica abrasive were manufactured. A total of 26 vol% of silica and 25 vol% porosity were added to each pad, and the surface of the fixed-silica pad was faced by a diamond blade (ASAHI Diamond Co. Ltd. Japan, 90°, the tip radius 0.5mm). Compared with natural and fused silica, the surface of aggregate silica particle can easily absorb moisture because of its high specific surface area. Thus, vacuum relief for more than 1 hour is required for the process (pressure of approximately -95 kPa gauge) before the aggregate silica was added into the pre-polymer of polyurethane of the pad. And the surface of the fixed-aggregate silica pad is also rougher than those of other two types of pads at the same facing conditions (Fig. 13). Comparative experiments of the three types of fixed silica pads with pH 10 alkaline aqueous solution of KOH were conducted at polishing conditions listed in Table 1 (polishing pressure 20kPa).

Fig. 13 shows that the hardness of these fixed-silica pads is almost the same. The surface roughness of Si wafer decreased after silica fixed from loose abrasive, but except aggregate silica. It may imply weak associations with the polished surface roughness and the micron particle size of aggregate silica. For the fixed-silica pad, the conventional natural silica abrasive was utilized. Given its mechanical and geometrical properties described in Chapter 3, it is easy to scratch the processed Si wafer surface (Fig. 12). The fused silica is fixed on a polishing pad, and then it easily removes material. Processing can even be performed at the pressure of 20 kPa. Similar to the fused silica, nano aggregate silica A that was fixed on the pad did not slipping during polishing. The material removal rate of fixed-aggregate silica pad gradually improved by increasing the pore volume of aggregate silica. The fixed-silica pad that used particle C was significantly higher than that of the conventional natural and fused silica. Its polished surface roughness is also lower than those of two types of fixed-silica pad. However, the preparation of fixed-silica pad with high added rate of aggregate silica is not as easy as that of fused silica. Thus, further improvement on the preparation process is necessary in the future.

Fig. 12 Comparison of fixed silica pad of aggregate silica and natural silica

Fig. 13 Comparison of fixed silica pad utilized different types of silica

6. Conclusion

The use of micron spherical particle aggregated by nanosilica as an abrasive of fixed-silica pad was proposed in this study. The processing experiments of both loose and fixed abrasive on aggregate silica were compared with the conventional irregular natural and spherical fused silica. The following conclusions were given:

1. Compared with the conventional irregular natural silica with an average particle size of 3.5 μm , the spherical fused silica particle with an average particle size of 3.2 μm did not easily scratch Si wafer surface. The processed surface roughness was better because of the small cutting depth of the spherical edge under the processing pressure. However, it easily slipped during processing. The material removal rate was low, but the material removal rate per surface roughness R/R_a was high.

2. Compared with the abovementioned natural and fused silica, 5 μm average particle size of spherical particle aggregated by 10 nm to 20 nm silica, with specific surface area of more than 100 times because of its aggregating structure, allowing [-OH] adsorbed on the silica surface to approximately five times more in an aqueous alkaline solution of pH12. With the increase of pH in the polishing solution, removal rate was substantially enhanced, and the driving motor current decreased. Thus, the chemical removal effect significantly increased.

3. When the ultrafine nanopore volume of the aggregating structure increased, the mechanical removal of spherical silica abrasive decreased. However, the chemical removal, as well as the material removal rate, substantially increased. The microscopic unevenness of the silica surface also increased, which eliminate slipping and improve the friction behavior of silica during the polishing process.

4. Compared with fixed abrasive pad used the conventional natural silica (silica addition rate 26 vol%, porosity 25 vol%), not only the material removal rate is high, but also surface roughness is good and close to conventional colloidal silica slurry by fixed abrasive pad used aggregate silica C.

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