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Performance of Polishing Slurries containing Silica Particles grown by Sol-Gel Method

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ABSTRACT

Silica slurry used as abrasives in wafer polishing process is made by dispersing silica particles in an alkali solution. Since commercially available colloidal or fumed silica particles need some modifications to be directly used as abrasive slurry due to their small sizes, irregular shapes or broad size distribution, we have prepared silica abrasives by particle growth of fumed silica or colloidal silica as seeds by sol-gel method. Silica slurries prepared by this step-wise growth from commercial seeds were tested using one-armed polisher for the comparison with commercial slurries and showed the performance comparable to commercial slurries. Microstructures of polishing slurries were investigated using transmission electron microscopy and ARES rheometer. From the result, stability of the slurry was found to be more important than the primary particle sizes for the polishing performance.

INTRODUCTION

Semiconductor industry requires silicon wafers with extremely tight specifications with respect to flatness and surface uniformity. Thickness variations in the sub-μm range as well as RMS (root mean square) roughness values in the sub-Å regime are prerequisite to efficient manufacturing of advanced integrated circuits. Wafer polishing process consists of stock removal polishing and final polishing step. Wafer surface is effectively removed in stock removal polishing step and final polishing determines the flatness and surface smoothness of the silicon wafers in the wafer manufacturing process. In the polishing process, silicon wafer is polished by chemical and mechanical action between silica particles in the slurry and silicon wafer surface. Polishing slurry is prepared by dispersing silica particles of nm size in a alkaline solution like ammonium hydroxide solution. Among several additives, surfactants are used for the stabilizing of colloidal slurry since surfactants with amphiphilic radicals provide steric or electrostatic hindrance between particles in the slurry.

Sol-gel method has long been used to prepare silica particles. Stöber *et al*. synthesized monodispersed particles by hydrolysis and condensation of silicon alkoxide using ammonia as catalyst [1]. However, the slurry containing silica particles *per se* prepared by Stöber method has too low solid content to be used as a polishing slurry. Bogush *et al*. used silica particles by Stöber method as seeds to increase the size of particles and developed the relationship between particle size and concentrations of TEOS (tetraethylorthosilicate), ammonia and water [2]. More concentrated particle dispersion with narrow size distribution using Ludox AS-40® (trademark of colloidal silica of Ludox Corp.) as seeds was reported [3]. Commercially available silica particles such as Ludox® or Aerosil® (trademark of fumed silica of Degussa Corp.) have some disadvantages to be directly used for abrasive slurry because of small size of silica particles,

broad size distribution or irregular shapes.

In this study, silica particles were grown by hydrolysis and condensation of TEOS using fumed or colloidal silica as seeds in order to provide proper size of particles for polishing slurry. Then, alcohol-base solvent in the slurry containing grown silica particles is substituted by water solvent through vacuum evaporation. Additives are added to the slurry with water solvent to promote the polishing rate and to enhance the stability of particle dispersion taking advantage of electrostatic hindering action. Polishing test was performed to compare the performance of our slurry with commercially available slurries for stock removal and final polishing. Effects of additives in the slurry and effects of the choice of the seed on the polishing performance are also studied.

EXPERIMENT

Detailed procedures for the growth of silica particles and characteristics of grown silica particles were reported previously [4,5]. The primary particle size and morphology of silica were measured by a transmission electron microscopy (TEM, EM912, Car Zeiss). Microstructure of silica slurry was investigated using rheological measurement by ARES rheometer (Rheometric Scientific).

All the polishing experiments were done using a single platen, single-head chemical mechanical polisher (Model PM5) of Logitech Inc. A wafer is rotated about its center where being pressed down to a rotating pad by a carrier where colloidal silica slurry is injected on the pad. For our experiment, (100)-type, 4-inch wafers, of which one side is lapped, are used. Before polishing silicon wafer is cleaned with SC1 (Standard Cleaning 1, $NH_4OH : H_2O_2 : H_2O$ = 1:1:10) cleaning solution to remove particles on the wafer surface, rinsed with DI water and dried by nitrogen gas following previously published procedure [6].

Experimental conditions for the polishing are listed in table I [7]. In our study polyurethane-based Suba 600 made by Rodel Inc. is used as a pad. Each time after wafer polishing, pad is conditioned to reduce the glazing effect of pad which causes slower slurry delivery to the wafer surface and unstable and lower removal rate. Pad is conditioned by forming microscratches on the pad surface, thereby opens the pores of the pads and helps the flow of the slurry between the wafer surface and the pad [8]. Removal rate is calculated by the following equation,

$$\text{Removal rate}\left[\frac{\mu\text{m}}{\text{min}}\right] = 10000\frac{w_L}{\rho A t_p} \qquad (1)$$

Table I. Experimental condition for polishing

Specification	Stock removal polishing	Final polishing
Wafer carrier type	Flat	Flat
Platen rotation speed	70 RPM	40 RPM
Down load	3.17 psi	1.34 psi
Polishing time	30 min.	30 min.
Polishing pad	SUBA 600	UR 100
Polishing pad temp.	25 ~ 32 °C	25 ~ 32 °C
Pad conditioning	3 min. conditioning time & 10 min. relaxation time	

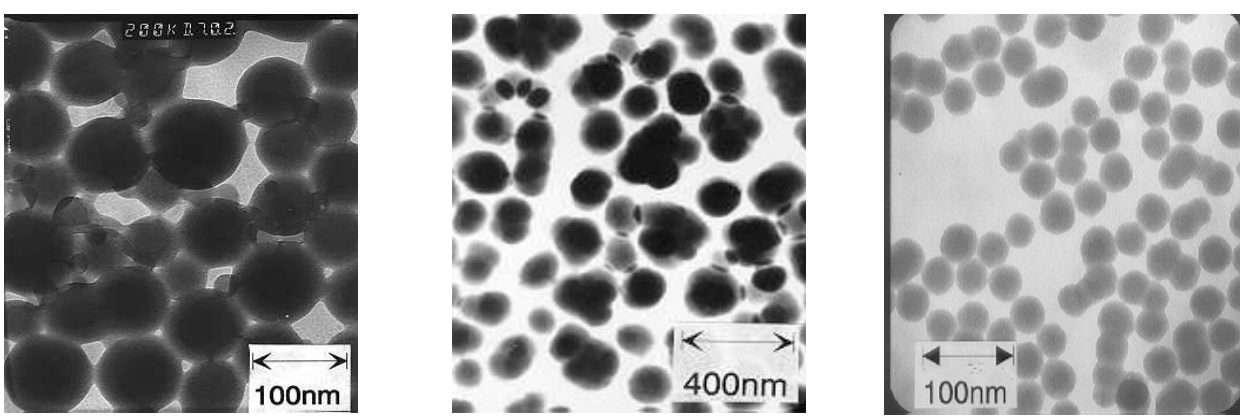
where w_L, ρ, A and t_p are weight loss(g), silicon density(g/cm^3), area of silicon wafer(cm^2) and polishing time(min).

RESULT AND DISCUSSION

Polishing slurry for stock removal usually has average particle size of 50 ~ 150nm and is recycled for over 500 minutes. Its main purpose is to smooth a wafer surface effectively by removing micro peaks on the silicon wafer. In the stock removal process, removal rate is more important than surface roughness, where surface roughness of 20 ~ 40Å is sufficient. Stock removal polishing slurry was prepared by adding polishing accelerator and dispersing agent to the silica slurry with particles grown from fumed or colloidal silica as seeds. Stock removal slurries made in this way were labeled as SRAG and SRLG according to the sort of seeds. SRAG and SRLG are slurries containing silica particles grown from Aerosil OX-50® and Ludox AS-40® as seeds, respectively. The average particle diameter of SRAG was much larger than that of SRLG as shown in Figure 1. Sizes of particles in the commercially available Slurry-N were found to be between those of SRAG and SRLG. Since silica particles are grown in a alcohol base solvent by Stöber method, alcohol in a slurry should be substituted with water for the use in a polishing slurry. Alcohol is evaporated by vacuum evaporation while distilled water is added to the slurry simultaneously. For more hardness of particles, prepared slurry was treated hydrothermally in the autoclave for 90 min at the temperature of 120°C.

Detailed compositions of additives and polishing rates are shown in table II. Removal rates with SRAG and SRLG are comparable to that of commercially available Slurry-N which has a removal rate around 0.35μm/min in our polishing test. Surface roughness of 20 ~ 40Å is sufficient in stock removal step. Surface roughnesses of the wafers polished with SRAG and SRLG are 29.7 Å and 19.1Å, respectively, which are better than the roughness value of 33.9 Å obtained with commercial Slurry-N in our test.

AFM image of lapped wafer before polishing is shown in Figure 2 (a), of which surface roughness is 1642 Å (scan area: 100μm × 100μm). AFM images of polished wafer using commercial Slurry-N, SRAG and SRLG are shown in Figure 2 (b)-(d), respectively (scan area: 5μm × 5μm). Even though the size difference between SRAG and SRLG is not small, noticeable differences are not seen in removal rate and surface roughness. This can be explained in two



(a) (b) (c)

***Figure 1**. Shape of particles in the slurry; (a) Slurry-N(commercial), (b) SRAG and (c) SRLG.*

Table II. Properties and polishing results of slurries

Additives	SRAG	SRLG
SiO_2(wt%)	11.5wt%, 1000ml	12wt%, 1000ml
Ethanol amine (ml)	35	35
TMAH (ml)	10	15
NH_4OH (ml)	0	10
Glycerol (ml)	5	5
Dilution pH	11.24	11.04
Removal rate (μm/min)	0.3097	0.3305

ways. First, since wafer polishing is carried out via chemical and mechanical actions between silica slurry and wafer surfaces, chemical contributions caused by additives such as polishing accelerator may be more dominant in polishing step than mechanical contribution which depends more on the abrasive particle size. Second explanation with respect to the stability of silica slurry may be more appropriate. That is, in spite of large differences in the primary particle size, silica particles of SRLG might form a flocculated structure and show similar polishing performances in removal rate and surface roughness. In order to clarify this possibility, rhelogical measurement was made using ARES rheometer. As shown in Figure 3, SRAG slurry shows stable Newtonian flow behavior up to 10wt% silica content indicating that SRAG slurry is composed of primary particles rather than flocculated structure. As silica content is increased to 20wt%, weak shear thinning behavior is observed. On the other hand, SRLG slurry (10wt% of silica) shows drastic shear thinning behavior and the slope of shear viscosity versus shear rate in log-log scale is –1 at low shear rate. This is indicative of the existence of yield stress and the formation of flocculated structure. The ready formation of flocculated structure of SRLG can explain the little differences in polishing performance between SRAG and SRLG. This simple comparison shows the importance of the dispersion stability of slurry particles in wafer polishing process.

Compared to stock removal polishing slurry, final polishing slurry has usually smaller

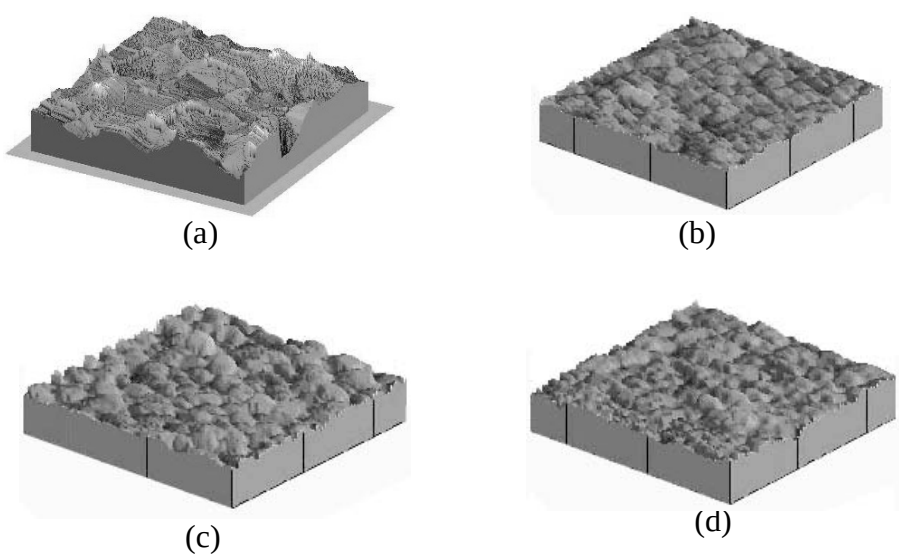


Figure 2. *AFM images of (a) lapped wafer and stock removal polished wafer using (b) Slurry-N, (c) SRAG and (d) SRLG, respectively*.

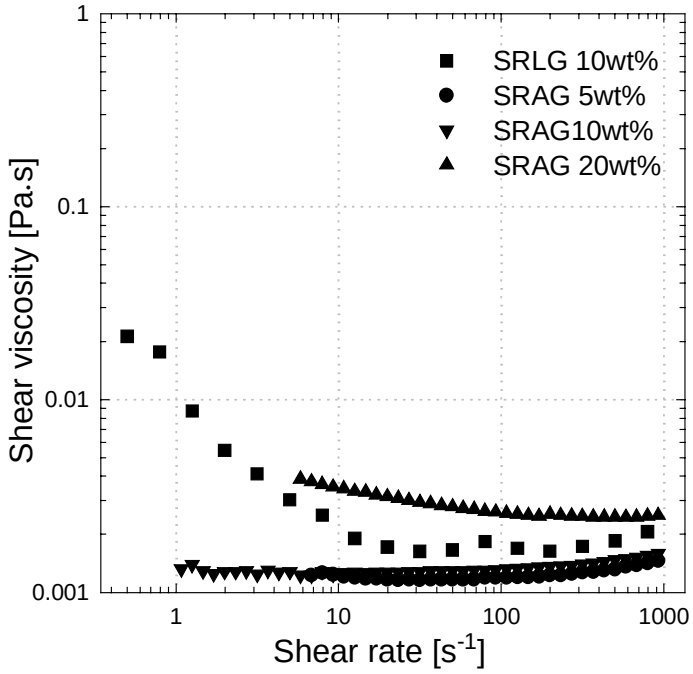


Figure 3. *Shear viscosity as a function of shear rate for various slurries.*

particle size and lower mass concentration for the sake of surface smoothness by sacrificing the high removal rate. Aerosil OX-50® can be used for final polishing slurry due to its high dispersion stability. However, since it has broad size distribution, particles of proper size should be separated to be used for final polishing slurry. Separated particles from Aerosil OX-50® by sedimentation are dispersed in D.I. water and stabilizer and accelerator such as cellulose, TMAH and ethanol amine are added. Cellulose makes a slurry flow to be laminar and TMAH and ethanol amine are used as pH controller, polishing accelerator and bactericide.

Effect of ethanol amine on the surface roughness of polished wafer was investigated by varying its weight fraction at 0, 0.011 and 0.033 wt % and the resulting RMS roughness were found to be 50.2, 7.67 and 33.8, respectively, in accordance with its concentration. Table III shows that roughness is getting better with small addition of ethanol amine but becomes worse with excess amount. It is because small amount of ethanol amine accelerates polishing but excess ethanol amine inhibits chemical reaction between slurry and wafer.

Effect of xanthan and cellulose shows similar tendency to that of ethanol amine. Table III shows that roughness becomes better with small addition of xanthan and cellulose but worse with more addition. Added amounts of xanthan and cellulose are same at 0, 0.005 and 0.01 wt %. From our results, minimum roughness can be expected with the concentration of additives at the vicinity of 0.01 wt % of ethanol amine or 0.005/0.005 wt % of xanthan/cellulose.

Table III. Effects of wt. % of ethanol amine, xanthan and cellulose on RMS roughness

Ethanol Amine (wt %)	Removal rate (Å)	Xanthan / Cellulose (wt %)	Removal rate (Å)
0.0	50.2	0.0/0.0	49.1
0.011	7.67	0.005/0.005	15.3
0.033	33.8	0.01/0.01	37.1

CONCLUSIONS

Performance of wafer polishing silica slurries and effects of additives on the performance were examined in this study. Silica particles for the stock removal polishing slurry was grown to proper size by sol-gel method using commercial fumed silica or colloidal silica as seeds and the resulting slurry was stabilized using electrostatic hindrance effect of surfactants. Colloidal silica (Ludox AS-40®) as seeds were grown to be 60 ~ 70nm in final size and particles showed more regular and mono-dispersed spherical shape than particles grown from fumed silica (Aerosil OX-50®). But, particles grown from fumed silica showed better stability after growth. This was confirmed by rheological measurement and gives the explanation of little difference in performance between the slurries containing large and small primary particles. Final polishing slurry was prepared by dispersing fumed silica in an alkaline solution and stabilized using surfactants' electrostatic and steric hindrance effect. Fabricated stock removal and final polishing slurries showed performance comparable to commercial ones. Study of the effects of additives showed the existence of optimal addition of additives for the best performance of the polishing slurry.

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