*Transactions of the Materials Research Society of Japan* 29 [3] 657-660 (2004)

# Annealing Effects on the Mixed Abrasive Slurry in the Oxide Chemical Mechanical Polishing

Y.-J. Seo* and S.-W. Park
Department of Electrical and Electronic Engineering, DAEBUL University, Chonnam-do 526-702, KOREA
Fax: 81-61-469-1260, *e-mail: syj@mail.daebul.ac.kr

In this paper, in order to investigate the effects of agglomeration on the performance of oxide CMP using mixed abrasive slurry (MAS), we have studied an aging effect as a function of different slurry composition. Also, the effects of each slurry composition on the oxide CMP characteristics were investigated to obtain the higher removal rate and lower non-uniformity. We prepared the various kinds of MAS. In order to save the costs of slurry, the original slurry was diluted by de-ionized water (DIW). And then, silica and alumina abrasives before and after annealing were added in the diluted silica slurry in order to promote the mechanical force of diluted slurry. As an experimental result, the CMP characteristics of 1:10 diluted silica slurry containing annealed alumina abrasives were showed higher removal rate and lower non-uniformity. We think that it is due to the increase of mechanical strength of abrasive particles after annealing. Therefore, we can anticipate the saving of CMP run cost for ULSI fabrication industry.

Key words: CMP (chemical mechanical polishing), COO (cost of ownership), MAS (mixed abrasive slurry), alumina abrasive, aging time

## 1. INTRODUCTION

Chemical mechanical polishing (CMP) has been widely used for the planarization of multi-layer structures in semiconductor manufacturing [1]. The results of CMP can be optimized by several process parameters such as equipment and consumables (pad, backing film and slurry). Among the consumables for CMP process, especially, slurry and their chemical compositions play a very important role in the removal rates and within-wafer non-uniformity (WIWNU%) for global planarization ability of CMP process [2, 3]. However, the COO (cost of ownership) is very high, because of high consumable cost. Especially, among the consumables, slurry dominates more than 40 % [4, 5]. Therefore, we focused how to reduce the consumption of raw original slurry and improvement of oxide CMP characteristics using mixed abrasive slurry (MAS) [6].

In this paper, to investigate the effects of agglomeration on the performance of oxide CMP using MAS [7,8], we have studied an aging effect of silica slurry as a function of particle size distribution during one month. We prepared the self-developed mixed abrasive slurry (MAS) [6] by adding of alumina powder before and after annealing in the 1:10 diluted silica slurry and compared the particle size distribution as a function of aging time. Also, we have studied the oxide CMP characteristics in order to evaluate the possibility of MAS for CMP applications. The performances of the mixed abrasive slurries were evaluated based on the removal rate, WIWNU% and surface roughness performed on the polished wafers.

## 2. EXPERIMENTS

Table I. Slurry composition.

| No. | Slurry compositions |
|---|---|
| 1 | Original silica slurry |
| 2 | 1:10 Diluted silica slurry |
| 3 | Adding of non-annealed $Al_2O_3$ 0.5wt% powder at 1:10 diluted silica slurry |
| 4 | Adding of 1500℃ annealed $Al_2O_3$ 0.5wt% powder at 1:10 diluted silica slurry |

In order to save the costs of slurry, the original KOH-based silica slurry was diluted by de-ionized water. And then, silica and alumina abrasives before and after annealing were added in the diluted silica slurry. Also, to study the role of agglomerated aging effects on polishing efficiency, we have prepared four kinds of slurry as shown in table I. Among them, the slurry number 3 and 4 are self-developed mixed abrasive slurry by adding of alumina powder before and after annealing in the 1:10 diluted silica slurry. The contents of alumina abrasive were 0.5 wt% and the annealing temperature was a 1500℃. Particle size analysis of the slurries was conducted by AccuSizer 780 system during one month. Thermal oxide layer of 360 nm was grown during six hour in electric furnace. The CMP polishing of all test wafers were performed with a G&P POLI-380 CMP polisher as shown in figure 1. The polishing pad was a stack-type IC-1300/Suba-IV double pad from Rodel Company. A diamond pad conditioner was utilized to abrade the pad before conducting each polishing test. The parameter ranges of the optimized CMP process is summarized in table II. The SC-1 chemicals, DHF (diluted HF) and ultrasonic were used for the post-CMP cleaning. Nanospec/AFT 2100 system was used to measure the oxide thickness. The surface roughness of the polished wafers was evaluated by atomic force microscopy (AFM) technique.

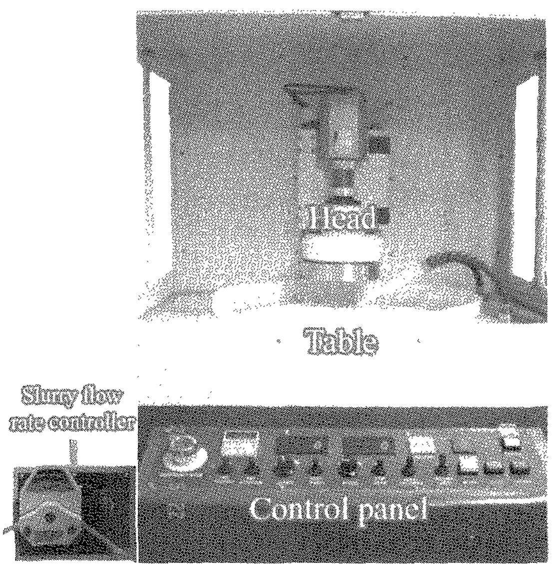


Fig. 1. POLI-380 CMP equipment of G&P Technology Company.

Table II. DOE conditions of CMP equipment.

| | |
|---|---|
| Table speed | 60 [rpm] |
| Head speed | 60 [rpm] |
| Down force | 4.2 [psi] |
| Slurry flow rate | 90 [ml/min] |
| Polishing time | 90 [sec] |

3. RESULTS AND DISCUSSION

Figure 2 shows the particle size distribution of original silica slurry as a function of aging time during one month. As the aging time is elapsed, the small particles of below 1 ㎛ were decreased and large particles were increased. Also, the distribution of larger particles was moved to the right direction due to the agglomeration of slurry particles. The original silica slurry had a mean particle size of 1.32 ㎛. However, after elapsed time of 30$^{th}$ day, the mean particle size was increased to 1.72 ㎛.

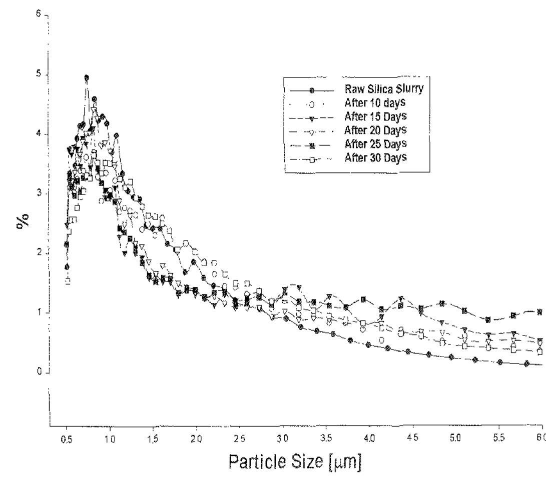


Fig. 2. Particle size analysis of original silica slurry in 30$^{th}$ days.

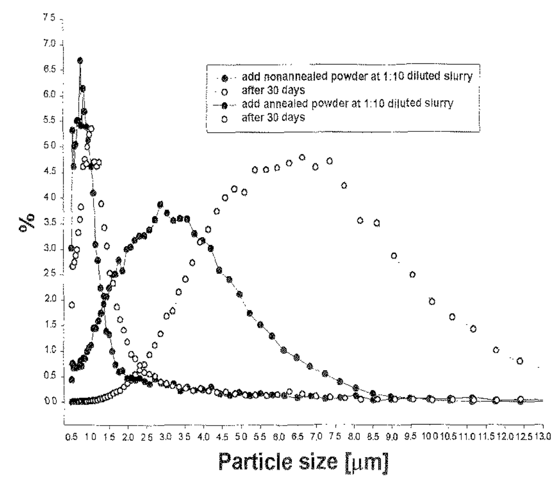


Fig. 3. Particle size analysis of MAS after 30 days.

Figure 3 illustrates the particle size distribution analysis of alumina mixed silica slurry according to the aging time of one month. Slurries containing the non-annealed alumina abrasives, on the other hand, exhibited the particle size distribution with a peak at 3 ㎛-size range. As the aging time is increased, the hump behaviors were moved to right direction. The mean particle size of 3.0 ㎛ at first day was increased to 6.5 ㎛ after one month, which is caused by the agglomeration of slurry particles. However, the slurries containing the 1500℃-annealed alumina abrasive of 0.5 wt% did not reveal the hump-like distribution and peak value was concentrated in the range of below 1 ㎛-size. Also, the size distribution shifts did not occur. This means that the annealed alumina mixed silica slurry did not coagulate. Contrary to the non-annealed slurry, the mean particle size was changed from 1.0 μm to 1.29 μm after one month. Consequently, we can conclude that our self-developed mixed abrasive slurry can prevent the agglomeration effects of inter-particles. By appropriate annealing, the mechanical force of alumina particles was enhanced and its dispersion ability was also dramatically improved.

Table III summarizes the comparison of mean particle size as a function of slurry compositions.

Table III. Comparison of mean particle size as a function of each slurry composition after 30th day.

| Slurry composition | 1st day [μm] | 30th day [μm] |
|---|---|---|
| Original silica slurry (No. 1) | 1.32 | 1.72 |
| Non-annealed alumina mixed slurry (No. 3) | 3.0 | 6.5 |
| Annealed alumina mixed slurry (No. 4) | 1.0 | 1.29 |

Figure 4 shows the removal rates as a function of dilution ratio. As the increase of dilution ratio, the removal rates and non-uniformity were linearly decreased.

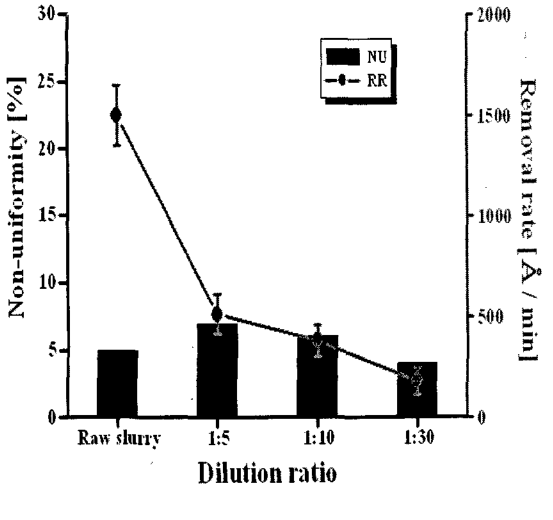


Fig. 4. Removal rates and non-uniformity as a function of dilution ratio.

Figure 5 shows the polishing removal rates and non-uniformity according to the addition amount of silica abrasive in case of 1:10 diluted silica slurry. As the added silica contents were increased, the removal rate and non-uniformity was linearly increased.

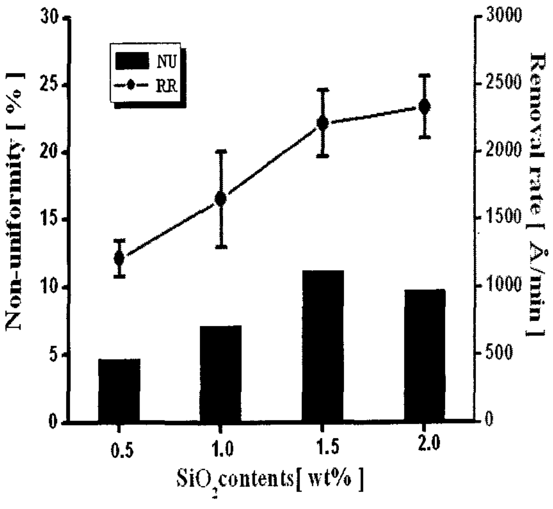


Fig. 5. Removal rates and non-uniformity as a function of $SiO_2$ contents in the 1 : 10 diluted silica slurry.

Figure 6 shows the removal rates and non-uniformity as a function of non-annealed $Al_2O_3$ abrasive contents in the 1:10 diluted silica slurry. The original raw slurry showed a removal rate of 1400 Å /min and within-wafer non-uniformity (WIWNU) of 5 %. The 0.5 wt% of non-annealed alumina mixed slurry had a removal rate of 900 Å/min and WIWNU of 7 %. As the alumina contents are increase, the removal rate was decreased and saturated in 400 Å/min. The maximum in the non-uniformity is observed in the 1.5 wt% of alumina mixed slurry.

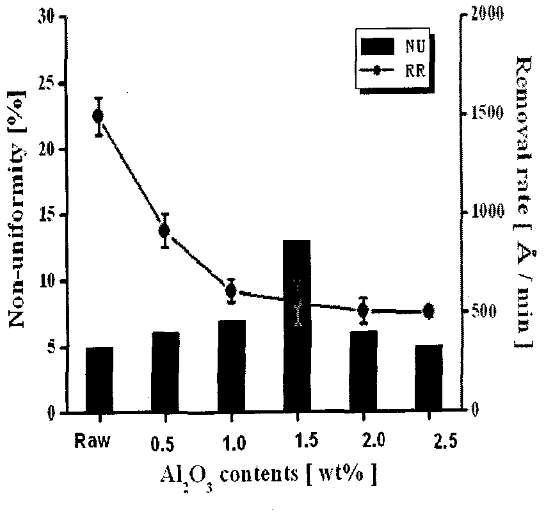


Fig. 6. Removal rate and non-uniformity as a function of $Al_2O_3$ abrasive contents in the 1:10 diluted silica slurry.

Figure 7 shows the removal rates and non-uniformity as a function of annealed $Al_2O_3$ abrasive contents in the 1:10 diluted silica slurry. The mixed abrasive slurry with non-annealed raw alumina powder showed a removal rate of 900 ~ 1000 Å/min and WIWNU of 7 ~ 9 %. However, the 0.5 wt% of 1500℃-annealed alumina mixed slurry had a removal rate of 1350 Å/min and WIWNU of below 4 %. As the annealing temperature is increases, the removal rate was increased and WIWNU (%) was slightly decreased. As shown in Figure 7, excellent CMP characteristics were seen at high temperature annealed $Al_2O_3$ abrasives. That is, we can anticipate the saving of high cost slurry using mixed abrasive slurry. Finally, the WIWNU (%) and surface roughness were summarized in table IV.

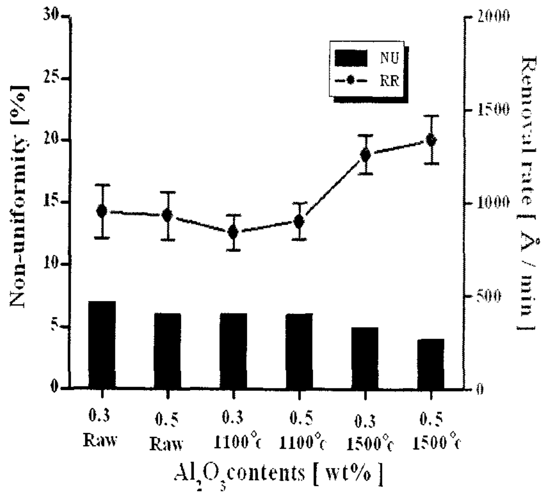


Fig. 7. Removal rate and non-uniformity as a function of annealed $Al_2O_3$ abrasive contents in the 1:10 diluted slurry.

Table IV. Summarized CMP characteristics of MAS.

| | Removal rate [Å/min] | WIWNU [%] | RMS |
|---|---|---|---|
| Original slurry | 1400 | 5 | 2.8 |
| Non-annealed $Al_2O_3$ | 900 | 7 | 9.6 |
| 1100℃ -annealed $Al_2O_3$ | 1000 | 6 | 7.5 |
| 1500℃ -annealed $Al_2O_3$ | 1350 | 4 | 9.1 |

4. CONCLUSION

In summary, to investigate the effects of agglomeration on the performance of oxide CMP using MAS, we have studied an aging effect of silica slurry as a function of particle size distribution and aging time during one month. The mechanical force of alumina particles was enhanced and its dispersion ability was also dramatically improved by appropriate annealing. These observations indicate that to design optimally performing CMP slurries inter-particles and pad-particle-surface interaction forces must be taken into account. In addition, it became clear that not only small particles but also the agglomeration of annealed alumina mixed silica slurry must be avoided in the polishing slurries to ensure acceptable surface quality and comparable to the commercial slurry.

As the dilution ratio is increases, the polishing removal rate was decreased. However, as the addition amount of slurry abrasives is increases, the removal rate was again recovered. Annealed abrasive were showed high removal rate and low non-uniformity. Above result is very useful promise for the saving of high cost slurry as well as the replacement of Cu-CMP slurry.

ACKNOWLEDGEMENT

This work was supported by Korea Research Foundation Grant (KRF-2002-041-D00235).

REFERENCES

[1] W. J. Patrick, et al, *J. of Electrochemical Soc.*, **138**, 555 (1991).

[2] J. M. Steiferwald, S. P. Murarka, and R. J. Getmann,"Chemical Mechanical planarization of Microelectronic Materials", Chapter. 3, John wiley & Sons, Inc., (1997).

[3] S. Y. Kim, S. Y. Jeong, and Y. J. Seo, *J. of Material Sci.; Materials in Electronics*, **13**(50) 299 (2002).

[4] K. J. Lee, W. S. Lee, C. J. Park, S. Y. Kim, J. S. Park, and Y. J. Seo, *CMP-MIC-2003*, 403 (2003).

[5] J. Luo and D. Dorfeld, *Proceeding of VMIC*, 281 (2001).

[6] A. Jindal, S. Hegde, and S. V. Babu, *Electrochemical and Solid-Stated Letters*, **5**(7) G48 (2002).

[7] T. Hara, T. Tomisawa, T. Kurosu, and T. Doy, *J. Electrochemical Soc.*, **146**(6) 2333 (1999).

[8] T. Hara, T. Kurosu, and T. Doy, *Electrochemical and Solid-State Letters*, **4**(12) G109 (2001).

(Received October 10, 2003; Accepted March 20, 2004)