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Mn_2O_3 Slurry Reuse for SiO_2 Film CMP

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1. Introduction

Nowadays, reducing the amount of the used slurry waste is extremely important from an ecological point of view. Chemical mechanical polishing (CMP) slurry reuse enables us to drastically reduce the cost and waste of slurry. Many researches have studied on the reuse of conventional slurry [1, 2, 3, 4]. As the removal rate of the conventional slurry strongly depends on the solid concentration and the pH, the conventional slurry must be severely controlled during the reuse of slurry [1, 4, 5]. This makes it difficult to reuse the conventional slurry in manufacturing.

In our prior work, we reported that Mn_2O_3 slurry can polish SiO_2 film, while offering a high removal rate and the realization of pad-conditioning-free polish [6]. In this paper, we have studied on the reuse of Mn_2O_3 slurry by circulating slurry.

2. Experimental

Figure 1 shows the Mn_2O_3 slurry formation. We dissolved the manganese sulfate in a sulfuric acid solution and performed electrolysis to get MnO_2. We then annealed this MnO_2 at 900 °C in air ambient for about 5min to get Mn_2O_3 [6]. Figure 2 shows the polishing conditions with the reuse of slurries by circulation. We reused the conventional slurry (silica based) and our Mn_2O_3 slurry many times. In both cases, the total slurry is 2 litters, and the flow rate of slurry is 80 cc/min. Rodel IC1000 (lattice grooved)/Suba400 stacked pads were used. The wafers used in this study were unpatterned 150 mm diameter silicon wafers with 1.0 µm of thermally grown oxide. In the case of the conventional slurry, ex-situ pad conditioning was performed to get a constant removal rate [7]. To keep the slurry solid concentration constant, we supplied the conventional slurry in stead of water during pad conditioning. We removed the pad dregs caused by conditioning by filtering. As Mn_2O_3 slurry maintains a constant removal rate without pad conditioning, pad conditioning was not performed [6]. Thus we did not use the filter in the case of Mn_2O_3 slurry. We measured the removal rate, the pH, the specific gravity (solid concentration), and secondary abrasive particle distributions of both slurries.

3. Results and Discussion

Figure 3 shows the pad dregs size distribution caused by conditioning. We removed the pad dregs by filtering. Mn_2O_3 slurry maintains about 4 times higher removal rate even without pad conditioning. On the contrary, the removal rate of the conventional slurry reduces from 0.077 µm/min to 0.049 µm/min as the reuse of polishing time increases (Fig. 4). This means the initial removal rate of the conventional slurry reduced to 64 % of the initial removal rate after the reuse of slurry. In both cases, no scratches were found on the polished surfaces.

Figure 5 shows the difference between the removal rate of reused conventional slurry and that of only fresh conventional slurry. The removal rate of the reused slurry clearly decreases as the cumulated polishing time increases. On the contrary, the removal rate of the fresh slurry maintains a constant removal rate. The pH of the conventional slurry slightly reduced as the polishing time increased while that of the Mn_2O_3 slurry maintained a constant value (Fig. 6). We think the pH of the conventional slurry reduces because OH^- is consumed during polishing [5]. Thus the pH control of Mn_2O_3 is much easier than that of the conventional slurry. The specific gravity of both slurries decreases as the polishing time increases (Fig. 7). Figure 8 shows the dependence on the solid concentration. Undiluted solid concentration of conventional slurry is 12 wt%, and that of Mn_2O_3 slurry is 10 wt%. Undiluted slurries are diluted by DI water to reduce the solid concentration. The removal rate of the conventional slurry drops almost linearly as the solid concentration reduces. Since the removal rate of Mn_2O_3 slurry is almost constant between 1.0 wt% and 10 wt%, Mn_2O_3 slurry can maintain a constant removal rate even the specific gravity reduces during the reuse of slurry.

The secondary conventional abrasive distribution does not change during reuse of slurry (Fig.

9). Although, the size of the secondary Mn_2O_3 abrasive decreases during reuse (Fig. 10). Even though the secondary abrasive size becomes smaller, the removal rate remains constant and high. Figure 11 shows TEM image of primary Mn_2O_3 abrasive. This indicates that the primary abrasive particle is almost or less than 0.2 μm. Since Mn_2O_3 abrasive is easily aggregated like CeO_2 abrasive, the secondary abrasive size of Mn_2O_3 is larger than that of the conventional slurry (silica abrasive).

4. Conclusion

We reused Mn_2O_3 slurry many times by circulating slurry without pad conditioning. We obtained approximately 4 times higher removal rate than conventional slurry. We also obtained a constant removal rate during the reuse of Mn_2O_3 slurry. On the contrary, the initial removal rate of the conventional slurry reduces to 64% of the initial removal rate during the reuse of slurry. We clarified that since the removal rate of Mn_2O_3 slurry is almost constant between 1.0 wt% and 10 wt%, Mn_2O_3 slurry can maintain a constant removal rate even the specific gravity reduces during the reuse of slurry. Thus, Mn_2O_3 slurry has excellent characteristics for slurry reuse.

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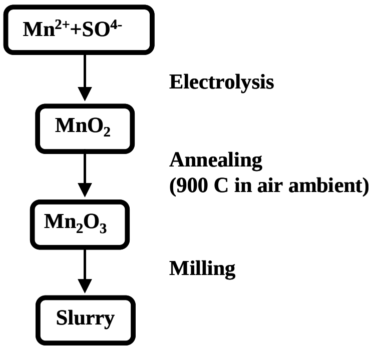

Fig. 1. Mn_2O_3 slurry formation process.

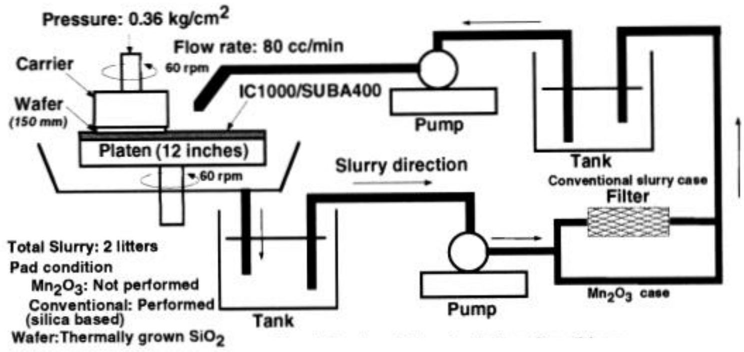

Fig. 2. Polishing conditions with the reuse of slurry by circulation.

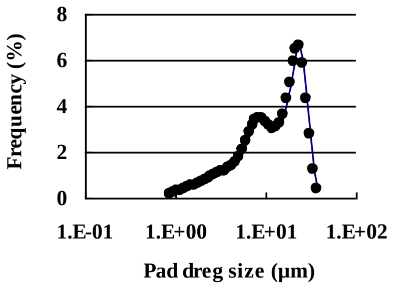

Fig. 3. Pad dreg distribution caused by conditioning. To remove pad dregs, we used filter.

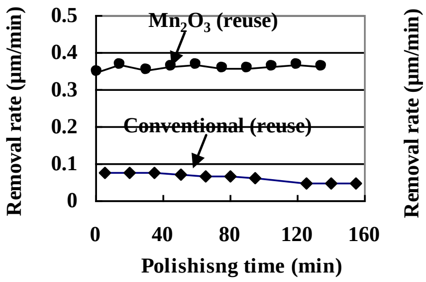

Fig. 4. Relationship between the removal rate and polishing time for Mn_2O_3 slurry and conventional slurry. Both slurries are reused.

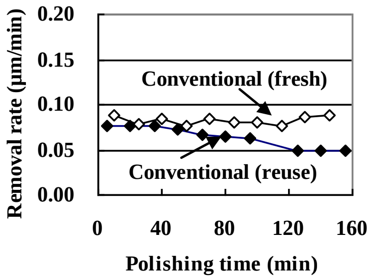

Fig. 5. Relationship between the removal rate and polishing time for reused and fresh conventional slurries.

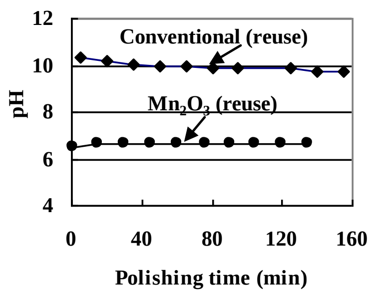

Fig. 6. Relationship between pH and polishing time for Mn_2O_3 slurry and conventional slurry.

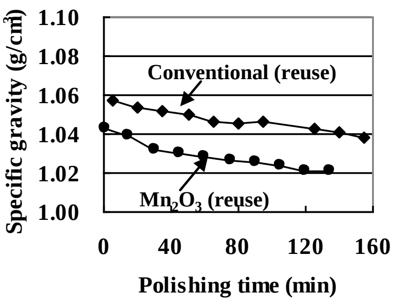

Fig. 7. Relationship between the specific gravity and polishing time for Mn_2O_3 slurry and conventional slurry.

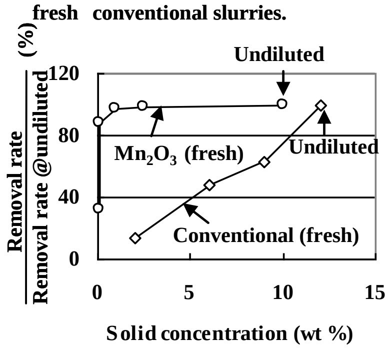

Fig. 8. Relationship between the removal rate and solid concentration of Mn_2O_3 slurry and conventional slurry. Undiluted concentration of conventional is 12 wt%, and that of Mn_2O_3 is 10 wt%.

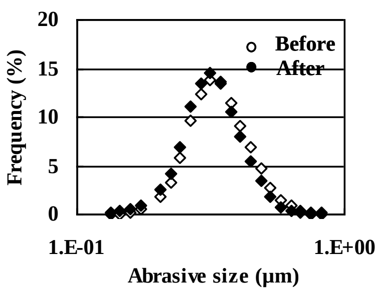

Fig. 9. Secondary abrasive distribution of conventional slurry before and after reuse.

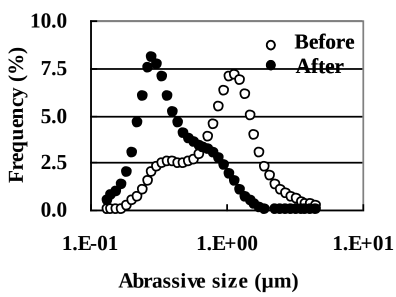

Fig. 10. Secondary abrasive distribution of Mn_2O_3 slurry before and after reuse.

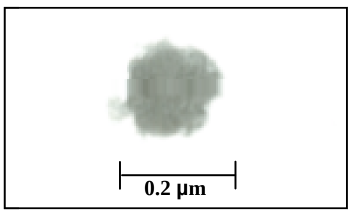

Fig. 11. TEM image of Mn_2O_3 abrasive. Primary abrasive size is almost or less than 0.2 µm.