

Dielectric Planarization using Mn₂O₃ Slurry

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Dielectric Planarization using Mn_2O_3 Slurry

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Abstract

We have developed an Mn_2O_3 slurry for dielectric planarization for the first time. Our Mn_2O_3 slurry has 4 times the removal rate of conventional slurry. The removal rate for this slurry remains constant for between 1 wt% and 10 wt% solid concentration. Pad-conditioning-free polish was successfully realized. We demonstrated that this slurry is reproducible.

Introduction

Chemical mechanical polishing (CMP) is used for dielectric planarization and colloidal silica slurry is widely used [1]. However, the CMP process has several problems such as low throughput, high cost, difficulties in slurry and pad management, and increasing amounts of used slurry waste [2]. In order to solve these problems, the slurry must offer a high removal rate, a constant removal rate which is less dependent of abrasive concentration, the realization of pad-conditioning-free polish, and slurry reproduction from the used slurry. Previously, we had developed an MnO_2 slurry which offered just a high removal rate and pad-conditioning-free polish [3, 4]. In this study, we have developed an Mn_2O_3 slurry which meets all the aforementioned requirements.

Experiment

Figure 1 shows the Mn_2O_3 slurry formation method. 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 to get Mn_2O_3 . X-ray diffraction analysis identified this sample Mn_2O_3 (Figure 2). Next, we milled this Mn_2O_3 into a powder to get an appropriate size for slurry abrasive.

Figure 3 shows the polishing conditions. The turntable diameter is 12 inches. Rodel IC1000/Suba400 stacked pads were used. The head pressure was 0.21 kg/cm². The wafers used in this study were unpatterned 150 mm diameter silicon wafers with 1.0 um of thermally grown oxide.

We examined the removal rates for Mn_2O_3 , MnO_2 , and conventional colloidal silica slurries. Next, we examined the dependence of the removal rate on concentration.

Next, we examined the removal rate examined the removal rates as a function cumulative polishing cycles without pad conditioning. Finally, we reproduced Mn_2O_3 slurry (figure 4). Our collected waste materials contained the used conventional slurry, pad dregs caused by conditioning, and crushed wafers, in addition to the used Mn_2O_3 and MnO_2 slurries. We put these collected materials in a $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ mixed solution in order to resolve only MnO_2 and Mn_2O_3 to Mn^{2+} , as showing Figure 4. After filtration, we reproduced the Mn_2O_3 slurry as shown in figure 1, and then we examined its removal rate.

Results and Discussion

The removal rate of our newly developed Mn_2O_3 slurry is 4 times higher than that of conventional slurry, and 3 times higher than that of our previous MnO_2 slurry (Figure 5).

Figure 6 shows dependence of the removal rate on the solid concentration. The removal rate for the conventional slurry decreases almost linearly as the concentration is reduced. The removal rate for MnO_2 also drops at below 7 wt% concentration. On the contrary, the removal rate for Mn_2O_3 remains constant from 1 to 10 wt% solid concentration. Thus, Mn_2O_3 slurry gives us a constant removal rate without careful control of the solid concentration, which is very useful especially in recycling the slurry.

Figure 7 shows the removal rate as a function of cumulative polish cycles without conditioning. Although the removal rate for the conventional slurry decreases as the polish cycles increase, Mn_2O_3 slurry maintains a high constant removal rate. Thus, the Mn_2O_3 slurry realizes the conditioning-free polish. Conditioning-free polish helps us to get higher throughput and a longer pad lifetime.

Figures 8 (a) to (c) show the photographs of the used slurry after collection, in $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ solution, and after filtration. The black area is the color of the MnO_2 and Mn_2O_3 in Figure 8 (a). As there are some silica and pad dregs in the used slurry, the solution in Figure 8 (b) is turbid. After filtering off these impurities, we got the transparent solution in Figure 8 (c). As the MnO_2 and Mn_2O_3 readily resolves in a $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ solution, we can easily filter off impurities. Conversely, in the case of conventional silica slurry, silica is stable, so it is extremely difficult to remove impurities from the used slurry. After filtration, we reproduced Mn_2O_3 slurry as shown in Figure 1. We examined the removal rates for unused slurry and reproduced slurry. Conditioning was not performed. The removal rate for the reproduced Mn_2O_3 slurry perfectly corresponds with that for the unused slurry (Figure 9). Slurry reproduction reduces the amount of used slurry waste drastically.

Conclusion

We have developed an Mn_2O_3 slurry for dielectric planarization. Its removal rate is 4 times higher than that of conventional slurry, is constant for a concentration of 1 wt% to 10 wt%, and remains constant without pad conditioning. We successfully reproduce Mn_2O_3 slurry from used Mn_2O_3 slurry containing various impurities.

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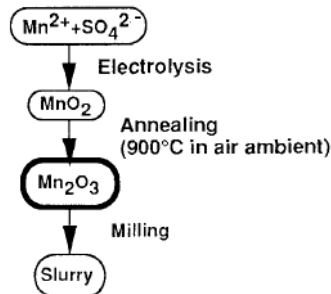


Fig. 1. Mn_2O_3 slurry formation process.

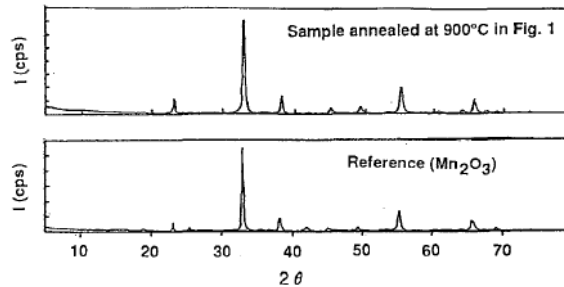


Fig. 2. XRD analysis of the sample annealed at 900 °C in Fig. 1. This identifies the sample Mn_2O_3 .

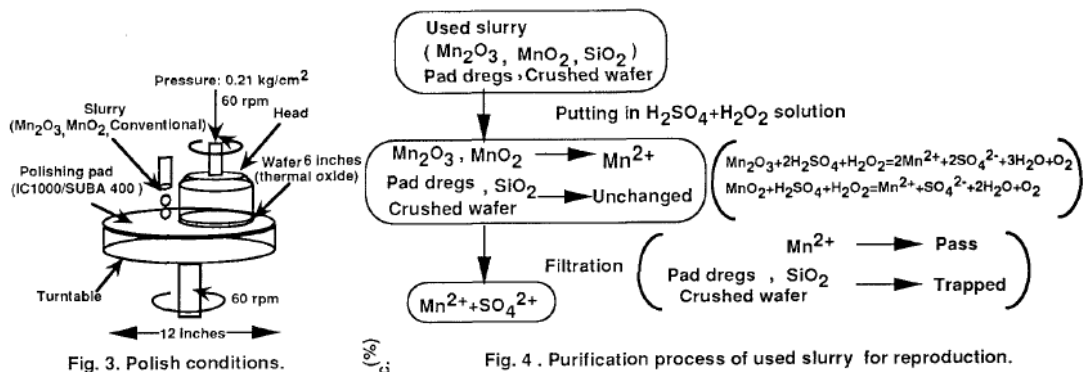


Fig. 4. Purification process of used slurry for reproduction.

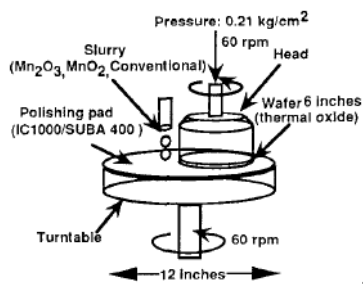


Fig. 3. Polish conditions.

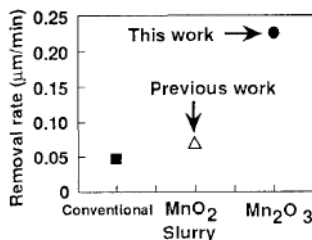


Fig. 5. Removal rate comparison. Polish time is 5 minutes for each case.

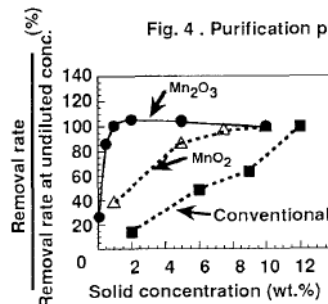


Fig. 6. Solid concentration dependence on removal rate. Slurries were diluted with water to reduce the concentration. Undiluted slurry of conventional, MnO_2 , and Mn_2O_3 are 12 wt%, 10 wt%, and 10 wt%, respectively.

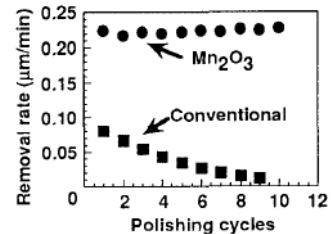


Fig. 7. Removal rates for Mn_2O_3 and the conventional slurries as a function of cumulated polish cycles. Each polish cycle is 100 sec. Pads were not conditioned.

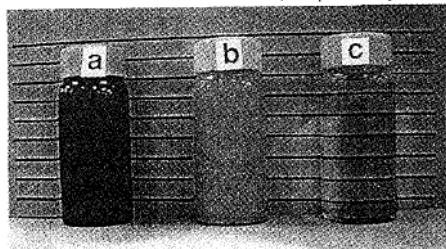


Fig. 8. Photograph of the used slurry in purification process a) after collection, b) in $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ solution, and c) after filtration. After filtration, contaminants were removed. This solution can be given electrolysis to reproduce slurry.

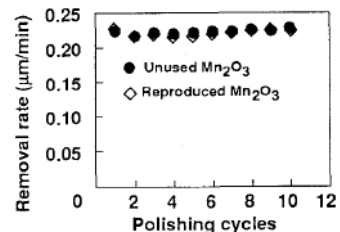


Fig. 9. Removal rates for unused and reproduced Mn_2O_3 slurries as a function of cumulated polish cycles. Pads were not conditioned.