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# Completely Planarized W Plugs using MnO<sub>2</sub> CMP

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## Abstract

In tungsten (W) polishing, MnO<sub>2</sub> has been used as an abrasive to form plugs without etching holes in seams during CMP. We found that MnO<sub>2</sub> polishes 1.5 times faster than the standard Al<sub>2</sub>O<sub>3</sub> abrasive, and can be completely removed during the cleaning process.

## Introduction

Chemical Mechanical Polishing (CMP) is used to form tungsten plugs [1, 2]. In CMP, only the tungsten surface is oxidized by the oxidizer in slurry. This oxidized film is removed by an abrasive which is followed by a rapid reformation of oxidized film. Continuous cycles of formation, removal, and reformation of oxidized film continue until the plug is formed [3]. Currently, the standard commercial abrasive used is Al<sub>2</sub>O<sub>3</sub>, and an oxidizer is mixed into the slurry to oxidize the tungsten surface [4]. This added oxidizer may make holes in seams, or abrasive may remain after cleaning because there is no cleaning solution which dissolves the Al<sub>2</sub>O<sub>3</sub>.

We searched for an abrasive which is in itself an oxidizer and readily dissolves in a cleaning solution. We found that MnO<sub>2</sub> satisfies these conditions. Figure 1 is a diagram of the polishing model using the MnO<sub>2</sub>. The MnO<sub>2</sub> polishes the tungsten surface, which was oxidized by the MnO<sub>2</sub> oxidizer. This means that we do not need to add additional liquid oxidizer and can therefore avoid seam etching. The MnO<sub>2</sub> is also readily soluble in an appropriate cleaning liquid, so that no abrasive remains on the surface after cleaning.

## Experiment

First we examined the dependence of the polishing rate on the MnO<sub>2</sub> concentration. Table 1 lists the polishing conditions used for our experiments. We then examined the effects of the MnO<sub>2</sub> abrasive to determine if there were any seam etching effects. We deposited a tungsten layer on our SiO<sub>2</sub> test piece and then used our MnO<sub>2</sub> abrasive for CMP. We then used Scanning Electron Microscopy (SEM) to determine the extent of

plug seam etching. We also examined the process contamination after cleaning by Total X-Ray Fluorescence (TXRF) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

## Results and Discussion

Figure 2 shows the dependence of the polishing rate on the concentration of  $\text{MnO}_2$ . A higher  $\text{MnO}_2$  concentration increases the polishing rate. Polishing slurry with 7 wt% has been used experiments in plug formation. At 7 wt%, the polishing rate is 1.5 times faster than the rate of polishing with the commercially available polishing slurry under the same conditions.

Figure 3 is a photograph of a plug section 1 minute after the tungsten is removed with  $\text{MnO}_2$  (equivalent to 0.15  $\mu\text{m}$ ). The Polishing was completely stopped by the TiN between tungsten and the  $\text{SiO}_2$  and a good plug is formed.

Figure 4 is a photograph of the surface four minutes after the tungsten is removed with both  $\text{MnO}_2$  (equivalent to 0.6  $\mu\text{m}$ ) and a commercially available polishing slurry (equivalent to 0.4  $\mu\text{m}$ ). The figure indicates the degree of seam etching on the plug. The commercially available polishing slurry etches a hole into the seam, whereas  $\text{MnO}_2$  does not make a hole in the seam. The commercially available polishing slurry contains a large quantity of K, so that the  $\text{SiO}_2$  layer becomes the stopper. There is also a possibility that the commercially available polishing slurry will enter the seam and adversely affect the characteristics of the device. However, this cannot occur with  $\text{MnO}_2$ . We polished the TiN film with  $\text{MnO}_2$  and evaluated the contamination on the TiN surface with TXRF. After polishing, we performed two different cleaning steps. First, we scrubbed and dipped in 0.5% HF for 1 minute. Second, we dipped in  $\text{HCl} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$  (1:1:48) for 1 minute and then scrubbed and dipped in 0.5% HF for 1 minute. Table 2 shows a contamination evaluation after TiN is polished with  $\text{MnO}_2$ . The  $\text{HCl} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$  cleaning decreases Mn contamination remarkably. We think this is because  $\text{MnO}_2$  dissolves easily in  $\text{HCl} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$ .

We polished an  $\text{SiO}_2$  film with  $\text{MnO}_2$  and the commercially available slurry to evaluate contamination with ICP-MS. Figure 5 shows a contamination evaluation after the  $\text{SiO}_2$  was polished with  $\text{MnO}_2$  and with commercially available polishing slurry, and then cleaned. The commercially available polishing slurry remains a large quantity of Al ( $1.3 \times 10^{12}$  atoms/ $\text{cm}^2$ ), which is an abrasive element on the  $\text{SiO}_2$  surface. For the  $\text{MnO}_2$  slurry, the remaining quantity of Mn atoms was  $1 \times 10^{10}$  atoms/ $\text{cm}^2$  or less. This indicates that  $\text{MnO}_2$  is considered to have been completely removed from the surface, whereas the abrasive of the commercially available polishing slurry remains in high

concentration. Mn is readily soluble in  $\text{HCl} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$  (1:1:48), whereas there is no appropriate liquid that dissolves  $\text{Al}_2\text{O}_3$ . Even after dipping in  $\text{HCl} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$  (1:1:48) for 1 minute, no holes developed in the plug seam. In the actual cleaning process, both TiN and W are exposed on the surface after cleaning. The etching rate in  $\text{HCl} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$  was 5.4 nm per minute for TiN and 5.1 nm per minute for W. Table 3 compares the  $\text{MnO}_2$  slurry with the commercially available polishing slurry.

### **Other Applications**

$\text{MnO}_2$  slurry can also effectively polish Al and Cu. Currently, the polishing rate for Al and Cu are a few hundred angstroms per minute.  $\text{MnO}_2$  will also be used for Al- and Cu-embedded wiring.

### **Conclusion**

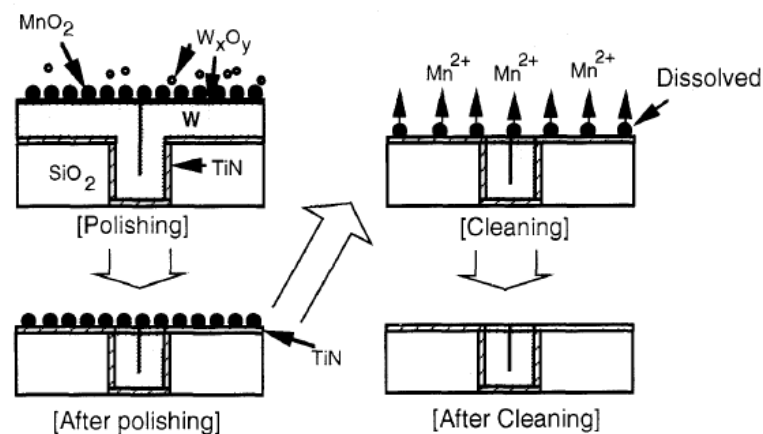
We examined the effects of using  $\text{MnO}_2$  slurry as new abrasive CMP. We compared the  $\text{MnO}_2$  performance and contamination against the standard  $\text{Al}_2\text{O}_3$  slurry. We found that the polishing rate of  $\text{MnO}_2$  is 1.5 times faster than the commercially available polishing slurry. Unlike the standard polishing abrasive, the  $\text{MnO}_2$  slurry does not etch the seam and does not contain metal. After cleaning, the abrasive element of commercially available polishing slurry remains, but the  $\text{MnO}_2$  slurry can effectively be completely removed with a simple cleaning solution.

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### **References**

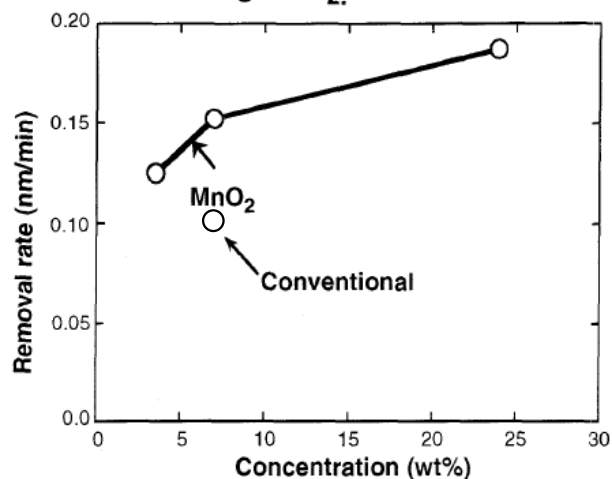
- (1) R. R. Uttecht and R. M. Geffken, proceeding of 18th VMIC, pp. 20 (1991).
- (2) C. Yu, et al., proceedings of 21st VMIC, pp. 144 (1994).
- (3) F. B. Koufman, D. B. Thompson, R. E. Broadie, M. A. Jaso, W. L. Guthrie, D. J. Pearson, and M. B. Small, J. Electrochemical Soc. Vol. 138, 3460 (1991).
- (4) D. L. Hetherington, et al., Surface Technology (Rodel publication), Vol. 2, pp. 2 (1995).



**Fig.1. Process model using MnO<sub>2</sub>.**

**Table1. Polishing Condition.**

Pressure	378 g/cm <sup>2</sup>
Polishing pad	SUBA 400
Haed/Platten speed	40/40 rpm
Slurry flow rate	100 cc/min
Platten diameter	12 inch
Wafer diameter	6 inch



**Fig. 2 Dependence of polishing rate on MnO<sub>2</sub> concentration.**

**Table 2. Contamination evaluation.**

	Mn	Fe	Ni	Cu
scrubber ➔ 0.5%HF	140000	<0.8	<1	<1
HCl + H <sub>2</sub> O <sub>2</sub> + H <sub>2</sub> O ➔ scrubber ➔ 0.5%HF	<1	<0.8	<1	<1
As recieved	<1	<0.8	<1	<1

$\times 10^{10}$  atoms/cm<sup>2</sup>

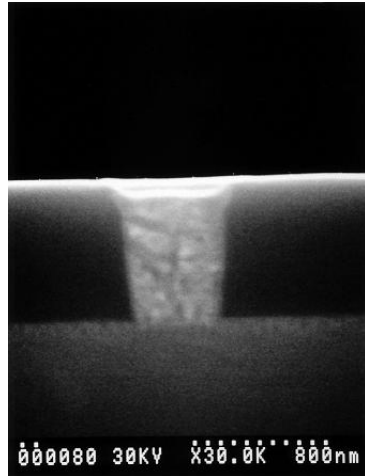


Fig. 3 Plug formed by polishing with  $\text{MnO}_2$ .

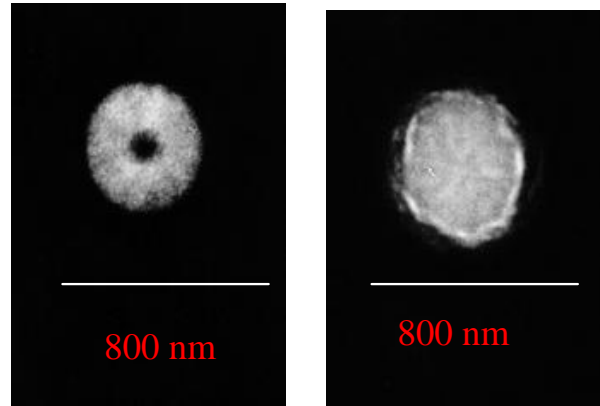


Fig. 4 Comparison of seam etching for (a)  $\text{Al}_2\text{O}_3$  and (b)  $\text{MnO}_2$ .

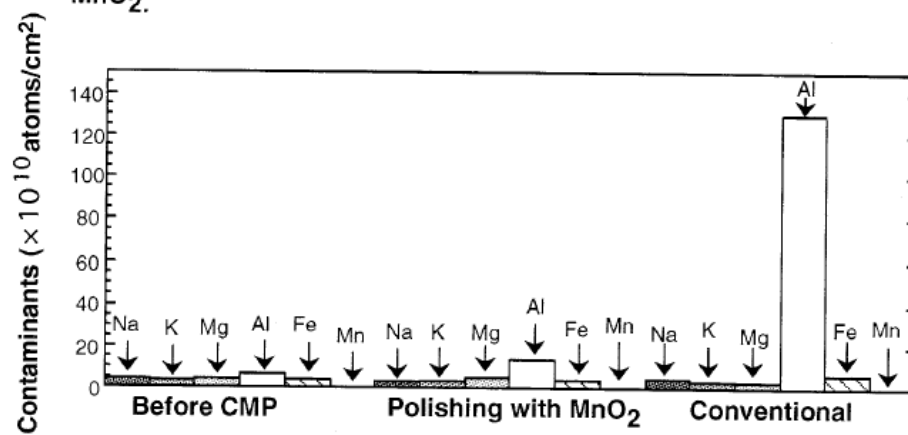


Fig. 5 Comparison contamination between surface after polishing and cleaning.

Table 3. Comparison of  $\text{MnO}_2$  to commercially available polishing slurry.

	Seam etching	Alkaline Metal	Remaining Abrasive
$\text{MnO}_2$	None	not added	N.D.
Commercially available polishing abrasive	Some	added	$>10^{12}$ atoms/cm <sup>2</sup>