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Completely Planarized W Plugs using MnO₂ CMP

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Abstract

In tungsten (W) polishing, MnO₂ has been used as an abrasive to form plugs without etching holes in seams during CMP. We found that MnO₂ polishes 1.5 times faster than the standard Al₂O₃ 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 Al₂O₃, 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 Al₂O₃.

We searched for an abrasive which is in itself an oxidizer and readily dissolves in a cleaning solution. We found that MnO₂ satisfies these conditions. Figure 1 is a diagram of the polishing model using the MnO₂. The MnO₂ polishes the tungsten surface, which was oxidized by the MnO₂ oxidizer. This means that we do not need to add additional liquid oxidizer and can therefore avoid seam etching. The MnO₂ 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 MnO₂ concentration. Table 1 lists the polishing conditions used for our experiments. We then examined the effects of the MnO₂ abrasive to determine if there were any seam etching effects. We deposited a tungsten layer on our SiO₂ test piece and then used our MnO₂ 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 MnO_2 . A higher 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 MnO_2 (equivalent to 0.15 μm). The Polishing was completely stopped by the TiN between tungsten and the 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 MnO_2 (equivalent to 0.6 μm) and a commercially available polishing slurry (equivalent to 0.4 μm). The figure indicates the degree of seam etching on the plug. The commercially available polishing slurry etches a hole into the seam, whereas MnO_2 does not make a hole in the seam. The commercially available polishing slurry contains a large quantity of K, so that the 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 MnO_2 . We polished the TiN film with 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 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 MnO_2 dissolves easily in $\text{HCl} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$.

We polished an SiO_2 film with MnO_2 and the commercially available slurry to evaluate contamination with ICP-MS. Figure 5 shows a contamination evaluation after the SiO_2 was polished with MnO_2 and with commercially available polishing slurry, and then cleaned. The commercially available polishing slurry remains a large quantity of Al (1.3×10^{12} atoms/ cm^2), which is an abrasive element on the SiO_2 surface. For the MnO_2 slurry, the remaining quantity of Mn atoms was 1×10^{10} atoms/ cm^2 or less. This indicates that 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 Al_2O_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 MnO_2 slurry with the commercially available polishing slurry.

Other Applications

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. MnO_2 will also be used for Al- and Cu-embedded wiring.

Conclusion

We examined the effects of using MnO_2 slurry as new abrasive CMP. We compared the MnO_2 performance and contamination against the standard Al_2O_3 slurry. We found that the polishing rate of MnO_2 is 1.5 times faster than the commercially available polishing slurry. Unlike the standard polishing abrasive, the 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 MnO_2 slurry can effectively be completely removed with a simple cleaning solution.

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Fig.1. Process model using MnO₂.

Table1. Polishing Condition.

Pressure	378 g/cm ²
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 MnO₂ concentration.

Table 2. Contamination evaluation.

	Mn	Fe	Ni	Cu
scrubber → 0.5%HF	140000	<0.8	<1	<1
HCl + H ₂ O ₂ + H ₂ O → scrubber → 0.5%HF	<1	<0.8	<1	<1
As recieved	<1	<0.8	<1	<1

× 10¹⁰ atoms/cm²

Fig. 3 Plug formed by polishing with MnO_2 .

Fig. 4 Comparison of seam etching for (a) Al_2O_3 and (b) MnO_2 .

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

Table 3. Comparison of MnO_2 to commercially available polishing slurry.

	Seam etching	Alkaline Metal	Remaining Abrasive
MnO_2	None	not added	N.D.
Commercially available polishing abrasive	Some	added	$>10^{12}$ atoms/cm ²