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The influence of abrasive particle size in copper chemical mechanical planarization

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ABSTRACT

There are many kinds of commercial slurries used in Cu CMP. Major components include an oxidizing agent, complexing agents, inhibitors, and abrasives. We analyze the abrasive particle size by TEM and light scattering. Cu CMP polishing mechanism is also discussed under different particle size distribution. The complexing agent transportation will be the rate determining step when a small abrasive is insufficient, but the copper hydroxide removal rate will determine the overall polishing rate when the amount of smaller particles is enough.

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1. Introduction

The chemical mechanical planarization (CMP) process is widely accepted in the semiconductor industry for oxide dielectric and metal layer planarization [1]. Especially in the field of copper (Cu) CMP, the slurry components and reaction mechanism are widely discussed. The major components consist of an oxidizing agent, complexing agents, inhibitors, and abrasives [2]. The most frequently used oxidizing agent is hydrogen peroxide, which accelerates copper removal during polishing. Glycine is also a well-known complexing agent, which forms a complex with the copper ions generated during polishing. Benzotriazole (BTA) and its derivatives are usually used as the corrosion inhibitor in commercial slurries. Among these, the abrasives play the role of removing the reaction product in copper oxidation.

In studies of abrasive particles, the solid–solid contact mode of CMP polishing is developed as a function of the abrasive weight concentration [3,4]. In Zhang's study [5], the material removal rate (MRR) increases in the particle range from 40 to 60 nm, but decreases as the particle size increases to 120 nm. In Zhou's literature [6], the polishing rate decreases with a decrease in particle size because the contact area decreases. But in these studies, the particle size distribution (PSD) of slurry abrasive is always similar to normal distribution, showing a single peak in the PSD plot. In some commercial slurries, their abrasive distributions are sometimes shown as bimodal or trimodal peaks in the PSD plot. In order to identify the function of bimodal particle size distribution, two colloidal silica particles with different sizes were prepared for the experiment.

2. Experimental

In the preparation of slurry solutions, two colloidal silica-based abrasive particles are provided by Wah Lee Industrial Corp. The concentration of glycine and hydrogen peroxide are 1 wt.% in all solution samples. For the experiment of abrasive-B only, the solid content is also 1 wt.%. For the solution of two abrasive mixtures, the individual concentrations of each abrasive are 0.5 wt.%. In the experiment of adding extra abrasive-A, the dosing amount is 0.25 wt.%.

A particle sizing system (PSS Nicomp 380, USA) dynamic light scattering particle size analyzer is used to measure the particle size distribution. The MRR is measured by RS-100, and the defect inspection is scanned by SP2. Both these tools are manufactured by KLA-Tencor. And Cu removal experiments are all performed with an Ebara F-REX300S2 tool with D100 grooved pads (Cabot Microelectronics). The rotation speeds of polishing head and platen are 87 and 93 rpm, individually. Down force of polishing head is around 150 hPa. In all experiments, the slurry flow rate is kept constant at 250 cm^3/min.

3. Results and discussion

3.1. Results

The silica particles used in these experiments are colloidal silica and possess a spherical morphology with different sizes, shown in Fig. 1. In order to describe the property of particle size, particle size distribution (PSD) is one of the common methods to show the ratio

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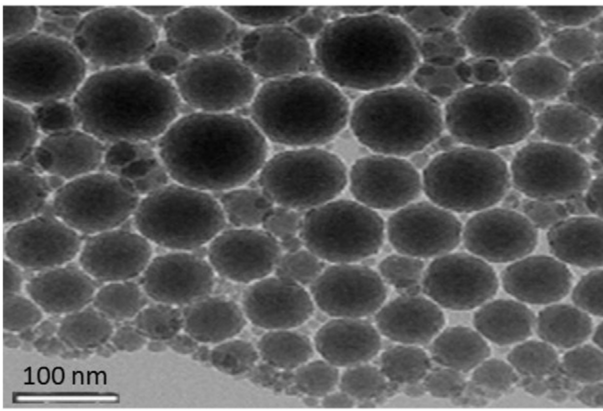


Fig. 1. TEM image of colloidal silica particles.

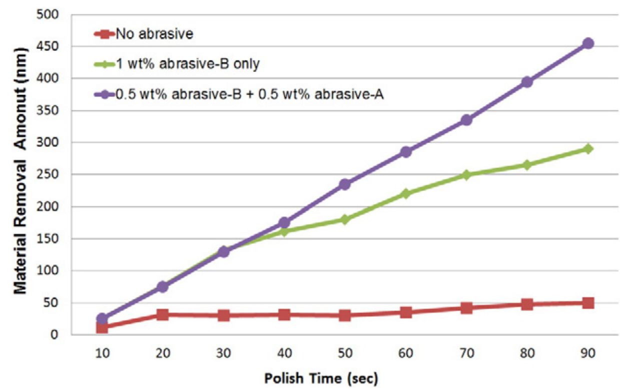
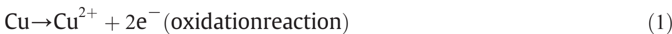


Fig. 3. Cu MRA of three slurry solutions with different abrasive particle types.

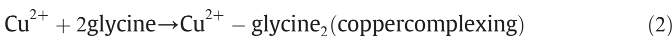
of each size. In Fig. 2, the PSD plot of 3 different types of particles is shown. Both abrasive-A and abrasive-B are close to normal distribution, whose major particle sizes are 60 and 75 nm individually. But the commercial abrasive has dual distribution peaks. It seems the commercial abrasive particle is one mixture of abrasive-A and -B with one specific ratio.

Fig. 3 shows the experiment results of Cu material removal amount (MRA) in 3 different slurry solutions. For the slurry solution without abrasive particles, the Cu MRA is lower and limited in the 90 s polishing. As long as the abrasive particles are added into the solution, the MRA is increased obviously. In the solution with abrasive-B only, the MRA is kept linearly increased in the first 40 s. But after that, the polishing rate is slowed down and MRA is increased by another lower slope. In the solution with both abrasive-A and abrasive-B, the MRA is stably increased with a high slope. Its polishing rate doesn't go down in the whole polishing experiment.

The reaction mechanism of copper polishing in glycine and hydrogen peroxide solution is discussed in Xu's study [7],



$$Cu \rightarrow Cu^{2+} + 2e^{-} (\text{oxidation reaction}) \quad (1)$$



$$Cu^{2+} + 2\text{glycine} \rightarrow Cu^{2+} - \text{glycine}_2 (\text{copper complexing}) \quad (2)$$

$$H_2O_2 + 2e^{-} \rightarrow 2OH^{-} (\text{reduction reaction}) \quad (3)$$

$$Cu^{2+} + 2OH^{-} \leftrightarrow Cu(OH)_2 (\text{precipitation formation}) \quad (4)$$

$$Cu(OH)_{2(s)} \rightarrow Cu(OH)_{2(aq)} (\text{precipitation removal}) \quad (5)$$

And, the abrasive particles play the role of removing $Cu(OH)_2$ in the tribological mechanism. In Li's study [8], slurries containing a larger abrasive increase the removal rate. It's easy to understand why the removal rate is lower in the slurry solution without abrasive particles. In Zhang's research [5], for low solid loading (less than 2 wt.%), the increase in particle size leads to an increase in the material removal rate.

In our experiment results, the mean particle size of abrasive-B is larger than that of abrasive-A and the mixture of the 2 abrasives. But the material removal rate of abrasive-B is lower than the MRR of the 2 abrasive mixtures. It means the small particles perform other roles in chemical reaction rather than mechanical removal.

Fig. 4 shows another experiment result after adding 0.25% abrasive-A into the original 3 slurry solutions. The MRA with no abrasive solution is increased obviously. Material removal rate (MRR) jumped around six-fold from 33 to 197 nm/min. The MRR of the solution with abrasive-B only also showed a 35% increase from 193 to 263 nm/min. But the MRR of the 2 abrasive mixtures doesn't show any obvious change after dosing more abrasive-A.

About the wafer finishing quality, very few scratches are found when using spherical colloidal silica particles as slurry abrasive. Fig. 5 shows the defect inspection result in the experiment with both abrasive-A and abrasive-B. The only defect scanned by the SP2 tool is wafer roughness. No any ";scratch defect is found.

3.2. Discussion

Copper CMP is a successive chemical reaction and mechanical removal. In the slurry solution, the abrasive particles take the role of removing the product, $Cu(OH)_2$, from the Cu surface into the solution and transporting the glycine molecule onto the Cu surface, shown in Fig. 6. The larger abrasive particle, abrasive-B, makes contact easier between polishing pad and wafer. The precipitated by-product can be

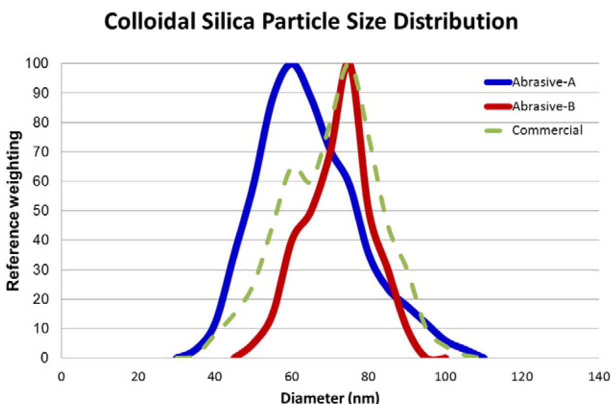


Fig. 2. Particle size distribution for different types of silica particles.

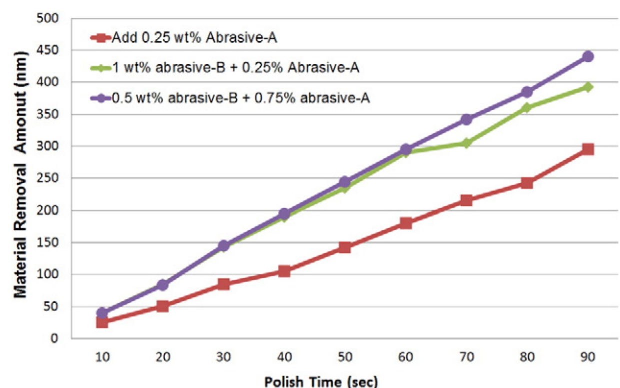


Fig. 4. Cu MRA changes after adding 0.25% abrasive-A into 3 slurry solutions.

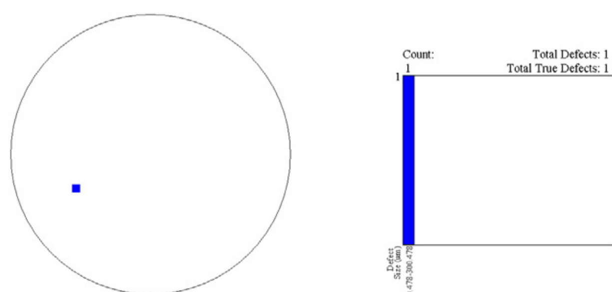


Fig. 5. Defect inspection result of the polishing experiment with both abrasive-A and abrasive-B.

removed by applying down force from polishing wafer. But the smaller abrasive particle, marked “A” in Fig. 6, would not receive the applied force due to the particle size. It's not big enough to make a full contact between pad and wafer. Abrasive-A plays the role of transporting glycine from solution to wafer surface.

In the experimental slurry solution with abrasive-B only, there are plenty of larger particles, but the amount of smaller particles is not enough. In other words, reaction-2 became the rate determining step in the whole Cu CMP polishing mechanism. After adding 0.25% abrasive-A particles, more and more glycine molecules are brought to the Cu surface. Therefore, the overall material removal rate is increased around 35%.

In the experimental slurry solution with both abrasive-A and -B, even the amount of larger particle is only 50% of the above solution, the large abrasive particles are still enough to remove all precipitated $Cu(OH)_2$. After adding extra 0.25% abrasive-A, there is no obvious change in overall material removal rate. It means the rate determining step is reaction-5.

4. Conclusions

This study discusses the effect of different abrasive particle sizes in copper chemical mechanical planarization. The particle size of colloidal abrasive is usually presented by particle size distribution. Based on the TEM result, the abrasive particles have a wide distribution.

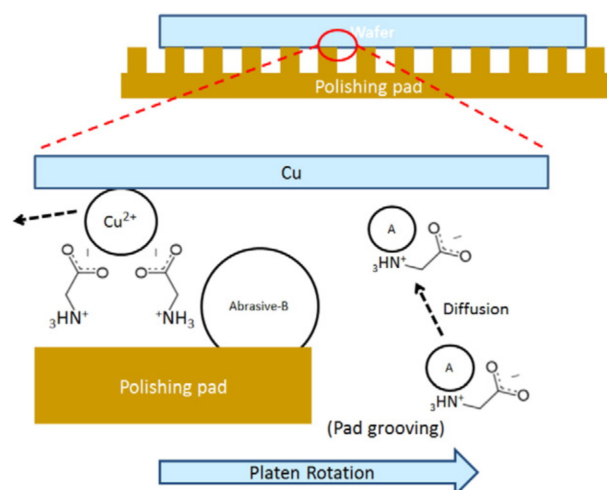


Fig. 6. Working mechanism of larger abrasive particle (abrasive-B) and smaller abrasive particle (abrasive-A).

Nevertheless, the transportation of the complexing agent will be the rate determining step when smaller abrasive particles are insufficient in the slurry solution. On the other hand, the removal rate of copper oxide or its derivate will determine the overall polishing rate when the smaller abrasive particles are enough. That is also why the PSD of commercial Cu CMP slurries sometimes show two or more peaks.

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