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Interaction Effects of Slurry Chemistry on Chemical Mechanical Planarization of Electroplated Copper

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Abstract

Recent studies have been conducted investigating the effects of slurry chemistry on the copper CMP process. Slurry pH and hydrogen peroxide concentration are two important variables that must be carefully formulated in order to achieve desired removal rates and uniformity. In applications such as through-wafer vertical interconnects, slurry chemistry effects must be thoroughly understood when copper plating thicknesses can measure up to 20 microns thick. The species of copper present on the surface of the wafer can be controlled through formulation of the slurry chemistry resulting in minimizing non-uniformity while aggressively removing copper. Using a design of experiments (DOE) approach, this study was performed investigating the interaction between the two variables during CMP. Using statistical analysis techniques, a better understanding of the interaction behavior between the two variables and the effect on removal rate and uniformity is achieved.

I. INTRODUCTION

Advancements made in integrated circuit (IC) fabrication have allowed new and innovative applications in micro-electronics. One particular area of interest has been in the field of three-dimensional ICs. Building 3-D electronic devices will allow further miniaturization and enhance performance. Through-wafer interconnects (TWIs), combined with damascene architecture are the foundation of electrical connectivity in 3-D microchip structures. In this particular study, the research conducted was part of an effort to support the development of copper (Cu) chemical-mechanical planarization (CMP) methods to be used on TWI applications. Initially, vias are created in silicon wafers with a Bosch etch process[1]. After the vias are formed, a polymer insulation coating, diffusion barrier and Cu seed are deposited on the surface of the wafer lining the wafer surface and via walls. Finally, a thick Cu layer is deposited by an electroplating process filling the vias and depositing a thick layer of copper across the wafer. The thick Cu layer is then removed by CMP leaving only the Cu in the vias intact. The electroplating process results in a non-uniform Cu plating layer 10-20 microns thick. The Cu plating thickness and non-uniformity stretch the capabilities of a conventional CMP process including consumables typically used in Cu CMP. Conventional CMP techniques are designed to planarize and remove metal layers that are typically 1-2 microns[2] thick, however, in TWI applications Cu plating layers are much thicker.

Although the Cu CMP process has been well documented, limited information regarding CMP of TWIs is available. As with any CMP process, slurry chemistry and machine parameters are paramount in obtaining desired removal rates and uniformity. Slurries used in the CMP process provide the chemical and mechanical mechanisms needed for material removal. In Cu CMP, abrasive particles such as alumina or colloidal silica are suspended in the slurry and aid in mechanical removal while slurry pH and hydrogen peroxide (H_2O_2) provide the chemical reactions needed to facilitate the removal of Cu. Although extensive research has been conducted investigating the effects of slurry pH and H_2O_2 during CMP [3-5], limited work has been done exploring the interaction effects between the two variables when dealing with thick Cu layers. The effect of slurry pH and complexing agents such as EDTA, citric acid and glycine on Cu removal rates has been well documented[4]. However, information relating the effect of slurry pH and peroxide concentrations on Cu removal rates is limited to Cu thickness of 1-2 microns.

In Cu CMP applications, H_2O_2 is used as the oxidizing agent and is added to the slurry prior to use. H_2O_2 reacts with the Cu surface and aids in the formation of a thin passivation layer of copper (II) oxide (CuO) or copper (I) oxide (Cu_2O), depending on the H_2O_2 concentration used. The process is repeated until the Cu plating layer has been planarized and removed. Recommended H_2O_2 concentrations vary depending on the slurry manufacturer and can range from 1.5% to 5% by volume.

Slurry pH also plays a significant role in Cu CMP and can be formulated to be either basic or acidic depending on the manufacturer. As mentioned earlier, slurry pH and the concentration levels of H_2O_2 have been found to result in the formation of a hard passivation layer of CuO or Cu_2O on the surface of the Cu[4, 5]. In general, and in accordance with the Cu Pourbaix diagram[6], a number of studies have shown that surface chemistry in the basic region combined with a given peroxide concentration, can lead to the formation of CuO. Conversely, with slurry pH in the acidic region, hydrogen ion concentrations [H^+] are increased resulting in the formation of Cu^{2+} whereas the formation of CuO is not thermodynamically favorable.

For this study, slurry pH levels of 4 and 8 were chosen representing the regions in the Cu Pourbaix diagram where Cu can exist as Cu^{2+} and CuO/Cu_2O, respectively. Surface chemistry of the Cu plating layer can be controlled by slurry pH and H_2O_2 concentration. By generating the ideal Cu species on the surface of the wafer, desired removal rates and uniformity can be achieved. The goal of this study was to use a design of experiments (DOE) approach to systematically investigate and learn the important interactions of pH and peroxide concentrations on the removal rate of Cu and within-wafer-non-uniformity (WIWNU).

II. Materials and Experimental Methods

The slurry used throughout the experiment was Cabot 5001. The slurry contains alumina based abrasives and is batch processed to a pH of ~8. The slurry is formulated to remove Cu at a rate of up to 1.0 micron per minute under typical machine conditions. Each slurry batch was prepared prior to each experiment with nitric acid added to obtain the desired pH level. To eliminate problems with slurry deterioration between repeated conditions, a new batch of slurry was mixed prior to each run.

The type of pad used was a Cabot EPAD-A100 CMP polishing pad. Prior to beginning the experiment, the pad was conditioned, *ex-situ*, using a Morgan Advanced Ceramics Diamonex^{TM} pad conditioner. In addition, single conditioning routines were performed between each run to ensure pad consistency during the experiment.

The experiments were performed on a Strasbaugh 6DS-SP Planarizer using a standard wafer carrier. Machine parameters such as down force, table speed and spindle speed were held constant throughout the experiment to ensure data collection consistency. Listed in Table 1 are the machine parameters used during the experiment.

To investigate the effects of slurry pH and H_2O_2 on the CMP process, a design of experiment (DOE) approach was used. By using a DOE approach, a systematic method to perform experiments investigating slurry pH and H_2O_2 interactions could be performed. Any significant effects or interactions dominant during the CMP process could be properly identified. The DOE structure used was a 2^2 full factorial experiment with three replicates for a total of 12 runs. Table 2 contains the factors and respective levels used in the DOE.

Cu removal rates and the change in WIWNU were chosen as the response variables. After the factors and response variables were determined, the data was entered into the DOE software JMP[7], which generated the experimental matrix and run order.

Table 1. Machine parameter settings used throughout the experiment

Machine Parameters	
Down Force(psi)	4
Table Speed(rpm)	60
Spindle Speed(rpm)	60
Slurry Flow Rate(ml/min)	200
Time(sec)	60

Table 2. Factors and levels used in factorial experiment

FACTOR	LEVEL Low	High
Slurry pH	4.0	8.0
% H_2O_2	1.5	3.5

As-received slurry pH and H_2O_2 concentrations amounts were used based on supplier specifications. Each experimental condition was run three times in random order in an attempt to normally distribute any unknown sources of error about zero. Cu removal rates were determined from the change in Cu thickness after each run as measured by an Automatic Four Point Probe (AFPP). To calculate the change in WIWNU, the sample standard deviation from each measurement set was divided by the sample mean and used as the percentage of non-uniformity across the wafer.

The experiments were performed with four-inch diameter wafers electro-plated with approximately 0.5 microns to 2 microns of Cu. Incoming plating thickness and uniformity varied across all wafers used in the experiment and may have contributed to variation experienced in repeated runs.

III. Results

After completing the experiment, the data was entered into the DOE software and analyzed. Table 3 contains the average results of both removal rate and WIWNU. Using analysis of variance (ANOVA), both factors and levels were analyzed to determine if any single variable or combination had any statistical significance on removal rate and WIWNU.

A. Removal Rate

Slurry pH and the interaction between pH and H_2O_2 concentration were the main contributors to removal rate based on p-values of 0.0021 and 0.0207, respectively. With a p-value of 0.588, the concentration of H_2O_2 alone, did not indicate any significance to the model and was rejected as having any significance.

Table 3. Average results of removal rate and WIWNU. Negative WIWNU results indicate an increase in non-uniformity.

Factors and Levels	Average Removal Rate (Ang/min)	Average WIWNU (%)
pH – High %H_2O_2 – High	243	4
pH – High %H_2O_2 – Low	1743	-32
pH – Low %H_2O_2 – High	2908	-38
pH – Low %H_2O_2 – Low	1953	-12

The model adequacy was checked by reviewing the adjusted-R^2 value of 0.69 which did prove to be adequate, although higher values are desired to account for variability in the model.

Interaction between slurry pH and H_2O_2, were shown to have a significant impact on Cu removal as seen in Figure 1. Slurry pH had the greatest impact on removal rate when combined with a high level of H_2O_2 concentration. Conversely, at low concentration levels of H_2O_2, changes in slurry pH did not have a significant impact on removal rate. The decrease in the removal rate at high pH and high concentrations of H_2O_2 may be explained in terms of the formation of CuO, which impedes the removal of Cu. In contrast, the increase in removal rate at low pH and high levels of H_2O_2 concentration may be explained by the formation of Cu^{2+} ion which is easier to remove during CMP. Insignificant differences with low levels of H_2O_2 concentration at both pH levels may also be explained by the formation of Cu_2O at high pH which is preferred for CMP compared to the CuO. This line of argument is supported by the report of Wei et al.[5] who observed and measured the formation of Cu_2O with the addition of 0.06%H_2O_2 and the formation of CuO with the addition of 2.5% H_2O_2 at a slurry pH of 8.

B. Within-wafer-non-uniformity

In analyzing the WIWNU data, the normal probability plot revealed problems with constant variance. Based on the lack of constant variance, a transformation of the data was needed to stabilize the variance distribution and obtain a suitable model. The adjusted-R^2 value also contained issues with model adequacy as did the residual versus predicted plot. Using the Box-Cox method to obtain an appropriate model, a log transformation was chosen to eliminate problems with variation and develop a suitable model to interpret the data. After transformation, the WIWNU data was re-analyzed and did provide information regarding significant factor contributions. Slurry pH, H_2O_2 concentration and the interaction between the two variables did have an impact on WIWNU.

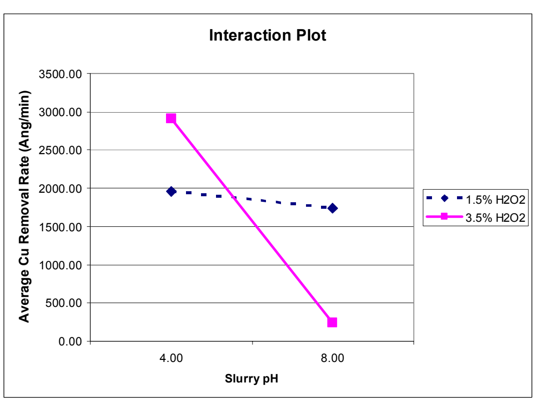

Figure 1. Interaction plot of Cu removal rate between slurry pH and H_2O_2 concentration.

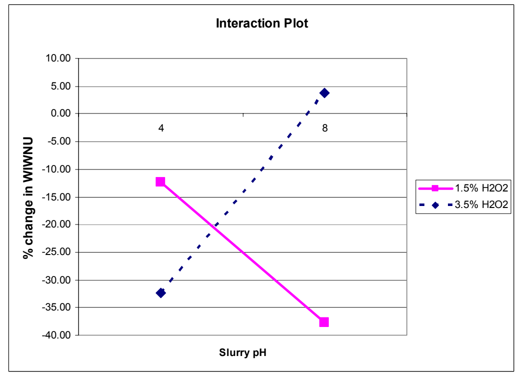

Figure 2. Interaction plot of average percent change in WIWNU between slurry pH and H_2O_2 concentration.

However, with a p-value of 0.93, slurry pH did not have a significant effect as compared to H_2O_2 concentration and the interaction between slurry pH and H_2O_2 concentration. Although the results obtained do require extra caution in interpretation due to the transformation performed of the data, the ANOVA did reinforce the significance of the two factors. In reviewing the interaction plots, both high and low levels of H_2O_2 concentration did result in a significant change in WIWNU based on slurry pH levels.

IV. Conclusions

In conclusion, the analysis did reveal insight into the interaction effects occurring during Cu CMP between two very common slurry chemistry variables. Changes in slurry pH had the greatest impact on the process when H_2O_2 content was at the high level of 3.5%. At 3.5% H_2O_2 and a slurry pH of 4, high Cu removal rates were achieved. In contrast, the lowest changes in WIWNU occurred at low concentrations of H_2O_2 and a pH of 8. This combination also accounted for smaller levels in Cu removal.

Based on Cu Pourbaix diagrams, the type of species generated on the surface of the Cu is important in achieving desired removal rates and WIWNU. In the basic region, the Cu species formed will impede the oxidation process due to formation of the CuO layer. In the acidic region, Cu^{2+} ion is formed which is easily removed during the CMP process creating an aggressive condition to increase removal rate and WIWNU.

With the goal of Cu CMP to be high removal rates while maintaining uniformity, a compromise between both response variables will need to be addressed in order to achieve an optimum process condition. The experiments performed in this study show the impact of surface chemistry in trying to achieve desired removal rates and WIWNU when dealing with thick Cu plating, however, further studies would be required to investigate noise effects contributed by wafer-to-wafer plating variation.

Based on the data collected by this experiment, future efforts will be focused on the development of optimized process conditions for thick Cu removal of TWIs. Research in the area of Cu removal as related to dishing and erosion of TWIs will also be investigated.

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