Electrochemical and Solid-State Letters, **12** (9) H340-H343 (2009)
1099-0062/2009/12(9)/H340/4/$25.00 © The Electrochemical Society

In Situ Formation of Ag Capping Layer for Preventing Oxidation in Copper Chemical Mechanical Polishing

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An Ag capping layer as a metal barrier was proposed to hinder the oxide formation of Cu, which is exposed after chemical mechanical polishing (CMP). To simplify the process step, the in situ formation of the Ag barrier during the Cu CMP process was investigated using a displacement reaction at either the second step of Cu CMP or the buffing step. The Ag capping layer effectively disturbed the contact between oxygen and Cu, which led to preventing Cu oxidation. Moreover, through the capping formation at the buffing step, the depth of dishing was diminished to about 20 nm regardless of the linewidth.
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Manuscript submitted April 10, 2009; revised manuscript received May 13, 2009. Published July 1, 2009.

The introduction of the damascene process based on chemical mechanical polishing (CMP) enables the multilayer metallization. Copper (Cu) has replaced tungsten (W) and aluminum (Al) as an interconnection material due to its comparatively low electrical resistance and good resistance to electromigration.[1-3] In the damascene process, the Cu interconnection is formed by CMP, which is used to remove excessively electroplated Cu during electroplating. The top surface of the Cu is exposed to the atmosphere during the CMP. This exposed Cu layer is easily oxidized. It continues to oxidize because Cu cannot form a passivated layer like other materials such as W and Al. Because the Cu oxide has a higher resistivity than pure Cu, the overall resistivity of interconnection increased. Therefore, to achieve a reliable Cu interconnection in the damascene process, it is important to prevent Cu oxidation.

Presently, a Si_3N_4 film is deposited as a barrier layer. Various methods to prevent Cu oxidation have been attempted, including ion implantation[4,5] and silicide formation,[6] where the top surface of Cu reacted with boron ions or SiH_4. Recently, some research has been exploring the selective deposition of CoWP or CoWB, which acts as barrier layer, onto the exposed Cu surface through electroless plating.[7,8] All these methods are effective in preventing Cu oxidation; however, the aforementioned methods must be conducted after the CMP. Also, Cu oxidation could be prevented effectively through the codeposition of magnesium (Mg, several atom percent) into Cu. Although the resistance of Cu decreased when applying the annealing process to diffuse Mg to the Cu surface to form Mg oxide as a passivation layer on Cu, the resistance increased as Mg concentrations increased.[9,10]

Kim et al. showed that an Ag film formed on a Cu surface after Cu electroplating is effective in preventing Cu oxidation.[11] Moreover, the resistance might not increase even though the Ag layer is formed onto the Cu surface because the resistivity of Ag is lower than that of Cu. In this study, a method of forming an Ag capping layer during the CMP process was investigated without the additional process.

Experimental

The structure of the wafer used in this study was Cu [9000 Å, physical vapor deposition (PVD)]/Ta (500 Å, PVD)/TaN (300 Å, PVD)/SiO_2 (10,000 Å, thermal oxidation)/Si. Cu CMP consists of three steps; at the first step of CMP, overdeposited Cu was removed using alumina-based slurry. The slurry for the first step CMP consisted of 2 wt % H_2O_2, 0.02 M citric acid, and 0.01 M 5-aminotetrazole (ATRA),[12] which were used as an oxidizing agent, a complexing agent, and a corrosion inhibitor, respectively. At the second step of CMP, residual Cu and the barrier layer were removed using a colloidal silica-based slurry with an abrasive size of 50 nm. The slurry for the second step CMP consisted of 1 wt % H_2O_2, 0.02 M glycine as a complexing agent, and 0.01 M ATRA. At the third step, the buffing step removed residual slurry on the polished wafer using deionized water preferentially before a postcleaning process to prevent brush contamination. The formation of the Ag capping layer on the Cu surface was attempted; either the slurry in the second step of CMP or the solution in the buffing step contained 0.01 M Ag ions. The Cu wafer was polished using the R&D CMP machine POLI-500 (G&P Technology, Korea). This polisher is composed of a 20 in. platen and a 4 in. carrier with the listed polishing and buffing conditions (Table I). The oxidation process was carried out in an atmospheric condition in a horizontal quartz tube furnace by feeding compressed air continuously after filtration of oil impurity and moisture. The pressure inside the tube was kept at 1 atm by controlling the flow rate of air and the pumping valve.

Results and Discussion

A displacement reaction occurred spontaneously because the reduction potential of Ag [0.799 V vs normal hydrogen electrode (NHE)] is higher by 0.460 V compared to Cu (0.339 V vs NHE) (Eq. 1). The displacement reaction results in the formation of an Ag film on the Cu surface

$$Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag \qquad [1]$$

Cu CMP was conducted with two consecutive polishing steps, where bulk Cu at the first step or residual Cu, the barrier layer, and the dielectric layer were removed sequentially, and at the buffing step residual slurry was removed on the polished wafer. In this study, to minimize loss of the Ag capping layer, the displacement reaction was applied to the second step of CMP or to the buffing step.

The color of the Cu surface changed from coppery to silvery using the Ag-ion-based slurry, indicating the selective formation of an Ag-like layer on the Cu surface (Fig. 1a). X-ray diffraction (XRD) and Auger electron spectroscopy (AES) depth profile analyses were performed to examine a polished Cu surface. As shown in Fig. 1b, the Ag peak, which was attributed to the (111) texture, was observed on the surface polished by the Ag-ion-based slurry. An analysis of the AES depth profile confirmed that the Ag layer, derived from the displacement reaction, was formed restrictively on the Cu surface (Fig. 1c). The sheet resistances of Cu with the Ag

Table I. The conditions of CMP at each CMP step and buffing step.

Conditions	First step of CMP	Second step of CMP	Buffing step
Applied pressure (psi)	2.5	1.5	1.5
Platen speed (rpm)	80	93	60
Head speed (rpm)	75	87	60
Slurry flow rate (mL/min)		150	

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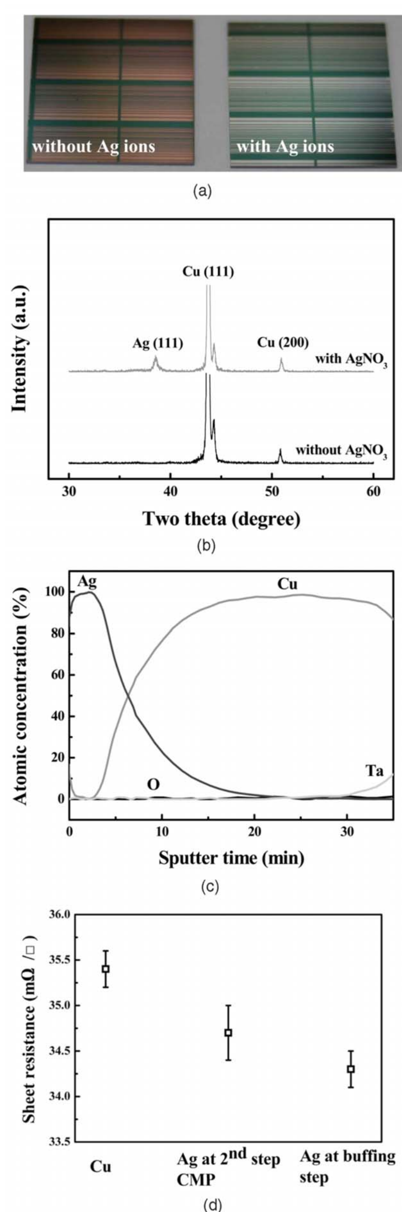

Figure 1. (Color online) Characteristics of polished wafer after second step of CMP using slurry with and without $AgNO_3$; (a) photo images, (b) XRD spectra, (c) AES depth profile, and (d) sheet resistance.

capping layer, which is formed at the second step of CMP or the buffing step, were reduced by 2 and 3%, respectively. The thickness of Ag on Cu could not be measured through field-emission-scanning electron microscopy (FESEM) because the boundary between Ag and Cu was not clear. According to a previous study, the thickness of Ag was around 40 nm when electroplated Cu was dipped into the Ag-based solution.

When reducing an ionized metal with a higher reduction potential, the substrate generally dissolves to provide an electron during the displacement reaction. Table II shows the values of root-mean-square (rms) roughness for a Cu surface immersed in an Ag-ion-based slurry and for a polished surface following the second step of CMP or the buffing step with and without Ag ions. The rms roughness of the Cu wafer just immersed into a slurry containing 0.01 M Ag ions for 30 s increased from about 7 to about 13 nm, resulting from the dissolution of the Cu surface. However, there was no significant difference in the rms roughness of the Cu wafers when they

Table II. The rms roughness of Cu in various solutions.

Conditions	RMS roughness (nm)
As-prepared Cu	7.2
Immersed surface in slurry containing 0.01 M Ag ions for 30 s	13.6
Polished surface after second step CMP without 0.01 M Ag ions	0.9
Polished surface after second step CMP with 0.01 M Ag ions	1.1
Surface after buffing step with 0.01 M Ag ions	1.7

were polished using the slurry with and without Ag ions because the mechanical abrasion during the polishing outweighed that of Cu dissolution. When the Ag-ion-based solution was used at the buffing step, the rms roughness was about 1.7 nm. Regarding surface roughness, the Ag capping layers, which were formed at the second step of CMP or at the buffing step, were more favorably compared with a Cu wafer dipped into an Ag-based solution. The larger roughness of the Ag film just after dipping into the slurry with Ag ions may originate from the complex chemical reactions, including the oxidation of the Cu surface, the continuous corrosion of copper during the Ag displacement reaction, etc. The slurry contains a strong oxidizing agent such as hydrogen peroxide, which can cause the oxidation of the Cu surface. The oxidized surface may block the replacement reaction that induced nonuniform Ag deposition, and the oxidized surface could generate some defects on the surface. All these effects would be the reason for the rough surface after the dipping in the slurry. Compared to that, the buffing step includes the application of mechanical forces to the wafer by contact with a polishing pad, and the addition of Ag ion during the buffing step has a simple chemical reaction pathway (just displacement between Ag and Cu). Furthermore, the strong stream of solution during the buffing step with applied pressure by a polishing pad may lead to an excellent redistribution of Ag or Cu ions (generated during the dissolution of Cu), which ensures a good uniformity and low surface defect generation.

To investigate the oxidation resistance of the Cu wafer with the Ag capping layer, an oxidation experiment was performed at 300°C for various oxidation times. The resulting changes in sheet resistance are presented in Fig. 2. In a pure-Cu wafer, the sheet resistance of Cu dramatically increased after oxidation. For example, the sheet resistance of the Cu wafer without an Ag capping layer, which was oxidized for 30 min, increased by 5000 times. In the AES depth profile after oxidation (Fig. 3a), oxygen can be distinctly observed throughout the Cu layer. This means that a complete Cu oxidation caused an increase in sheet resistance. However, for the Ag capping layer onto the Cu wafer, there was no significant difference in the

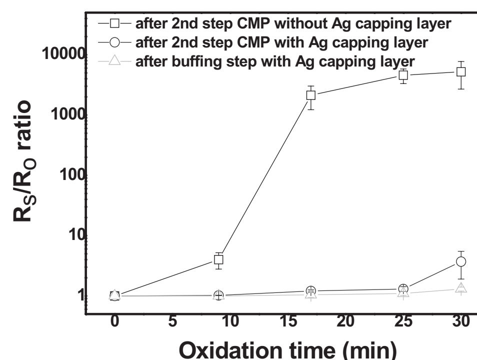

Figure 2. Change in sheet resistance of polished wafer using slurry with and without 0.01 M Ag ions before (R_O) and after (R_S) various oxidation times at 300°C atmospheric conditions.

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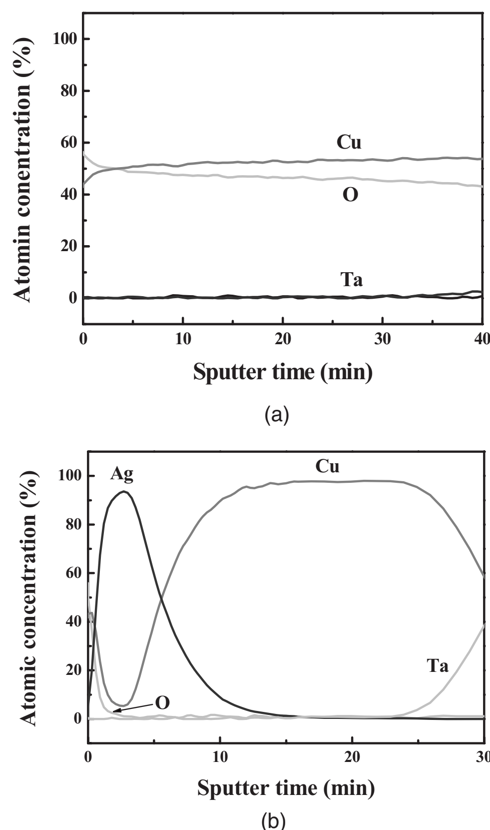

Figure 3. AES depth profiles of polished wafer after 25 min oxidation at 300°C atmospheric condition; (a) without and (b) with Ag capping layer.

change in the sheet resistance before and after oxidation, which indicated that the Ag capping layer effectively hindered the contact between oxygen and Cu (Fig. 3b). The increase in the sheet resistance of the Ag capping layer might be from the oxidation of Cu: Ag capping decelerates the diffusion of Cu onto the surface; it does not block the diffusion completely above 300°C. It consumes the copper under the capping layer and also induces the increase in sheet resistance. The formation of a thin oxide layer at the surface after 30 min of oxidation at 300°C is observed at the surface of the Ag capping layer in Fig. 3b.

The previous oxidation test showed that the Cu wafer with the Ag capping layer tolerated the oxidation thermal budget of 30 min at 350°C. Figure 4 shows the oxidation resistance of the Ag capping layer after exposure to various oxidation temperatures for 30 min.

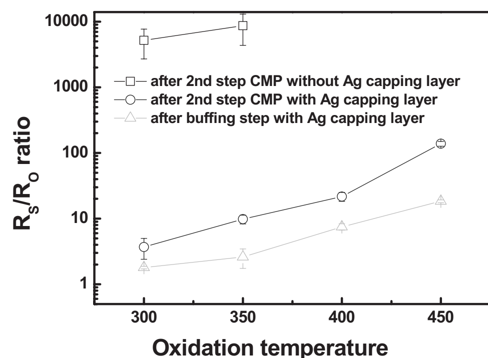

Figure 4. Change in sheet resistance of polished wafer using slurry with and without 0.01 M Ag ions before (R_O) and after (R_S) various oxidation temperatures for 30 min.

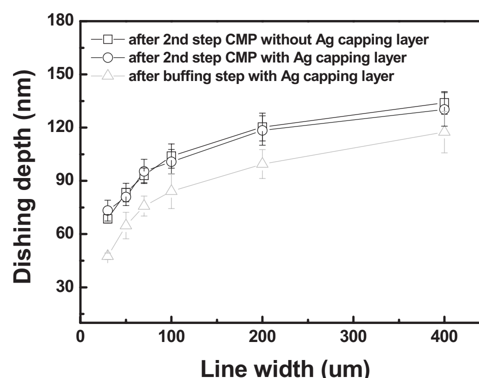

Figure 5. Dishing results measured by alpha step at wide metal line of various widths.

For the Cu wafer without the Ag capping layer, the sheet resistance could not be measured due to complete oxidation of the Cu wafer above 400°C, whereas with the Ag capping layer, an increase in the sheet resistance was observed as the oxidation temperature increased. At the maximum oxidation temperature (450°C) used in this study, the sheet resistance of the Cu wafer with the Ag capping layers formed at the second step of CMP and at the buffing step increased about 140 and 20 times, respectively. The Cu wafer showed a better resistance against oxidation when the Ag capping layer was formed at the buffing step, which seemed to be contributed by the thicker Ag formation due to the CMP process mechanism.

The in situ formation of the Ag capping layer also plays an important role in decreasing the dishing during the CMP process. Cu dishing refers to the loss of Cu during the CMP process, often caused by the deformation of the pad and additives in the slurry. Several solutions have been proposed to overcome this problem, such as the insertion of a dummy pattern on the wafer or the addition of a passivation agent into the slurry.[13,14] Although these methods can reduce the amount of Cu dishing when applying the aforementioned methods, the Cu dishing inevitably occurs in the overpolishing step, where residual copper and the barrier layer on the dielectric layer are to be removed completely.

The variation in the Cu dishing according to pattern width after CMP is shown in Fig. 5. Using the Ag-ion-based solution in the buffing step, the depth of Cu dishing was reduced by 20–30 nm regardless of the linewidth. When Cu was consumed to generate electrons to Ag ions, the amount of the formed Ag layer was about 2.26 times larger than that of the consumed Cu layer. Based on the reaction stoichiometry and lattice parameters (Cu and Ag were 361.69 and 408.53 pm, respectively), the calculated thickness of the formed Ag layer and the consumed Cu layer was 34 and 15 nm, respectively. Therefore, the final thickness of the Cu line increased by about 20 nm. There was no difference in the depth of dishing whether an Ag-ion-based slurry was used or not at the second step of CMP. This implies that the relatively thin Ag layer was formed because the majority of the formed Ag layer was polished away by mechanical abrasion. Therefore, the decrease in the formation thickness of the Ag layer at the second step of CMP results in diminishing oxidation resistance (Fig. 4).

Ag capping is expected to have better chemical resistance during the cleaning or etching process due to its noble character compared to copper. The chemical resistance of the Ag film against SC-1 cleaning ($NH_4OH–H_2O_2–H_2O$ mixture) and a dry etching condition of tetraethoxysilane oxide were tested, and there was no obvious damage on the Ag surface morphology by FESEM. The results strongly suggest that the Ag capped Cu film has better process windows in many postcleaning or patterning processes.

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Conclusions

In this work, methods for the prevention of Cu oxidation and restoration of Cu dishing were developed. These methods are suitable to the damascene process, and they require no additional process step. The in situ formation of an Ag layer was attempted through the displacement reaction between the Cu surface and the Ag ions at the second step of CMP or at the buffing step during the CMP. The Cu wafer with the Ag capping layer showed superior oxidation resistance when compared to pure-Cu wafer because the Ag layer effectively hindered the contact between oxygen and Cu. Moreover, because the amount of the formed Ag film due to the displacement reaction is about 2.26 times larger than that of the consumed Cu, the depth of Cu dishing in this experiment was reduced to about 20 nm regardless of the linewidth.

Acknowledgments

This research was supported by the Nano R&D program through the Korea Science and Engineering Foundation (KOSEF) funded by the Ministry of Education, Science and Technology (2008-02857) and by the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Commerce, Industry and Energy, Republic of Korea.

Seoul National University assisted in meeting the publication costs of this article.

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