Paper

Surface Pretreatments for Remove of Native Cu Oxide Layer

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In order to remove native Cu oxides formed on Cu seed layer, TS-40A and H_2SO_4 solutions were used. After various pretreatments, the changed surface of Cu seed layer was estimated by SEM and XPS. For all pretreatments, the mass of samples was decreased. The mass loss of sample treated in H_2SO_4 solution for 60 s was the largest. After TS-40A pretreatment, native Cu oxide layer is not at all removed although the carbon on Cu seed layer was removed mainly with a few loss of sample mass. By H_2SO_4 treatment after TS-40A pretreatment, most of native Cu oxides on Cu seed layer were removed with a lot of mass loss and the oxides will be eliminated by control of dipping time. Consequently, we found that the pretreatment by H_2SO_4 is suitable to obtain a Cu seed layer removed native oxide for electrodeposition

1. Introduction

The scaling of integrated circuits(ICs) requires the use of alternative metals as the replacement for Al metal line, due to a limit of step coverage by chemical vapor deposition (CVD) process. The use of alternative metal with low resistivity will lead future memory and logic device industry.

Cu has recently been used for memory and logic devices [1-4]. A number of research groups have successfully used it to fill damascene structure by electroplating method [5,6]. The electroplating is presently the most popular method used for Cu deposition in semiconductor fabrication processes because of lower cost, lower growth temperature, higher throughput, and excellent gap-filling capability [7,8]. However, the electroplating technique necessitates a clean Cu seed layer without Cu oxides conducting the currents during plating operation due to the use of highly resistive barrier materials. In general, Cu native oxide formed on a seed layer makes the resistivity higher than itself. Therefore, a native oxide on Cu seed layer has to be removed before using [9]. The pretreatment to obtain the clean Cu seed layer is one of the most important issues in the development of a suitable Cu electroplating method because an oxide film on the surface disturbs the current flow through itself [10,11].

In this study, we investigated the changed surfaces of Cu seed layer by pretreatment of wet chemicals such as H_2SO_4 solution, for removing of native Cu oxide formed on the Cu seed layer. Wet chemical cleaning process is one of the widely used cleaning techniques for obtaining extremely clean surface.

2. Experimental

In order to remove native Cu oxides on Cu seed layer, we carried out the pretreatment methods of 3 types (Table. 1). Cu seed layer (20nm) on Ti diffusion- adhesion barrier film (20nm) / p-type Si (100) was deposited by sputter deposition. This wafer was exposed to air to grow the native oxide of Cu.

Table 1. Pretreatment methods.

Types	Methods
Type 1	No pretreatment (=bare Cu seed)
Type 2	TS-40A
Type 3	TS-40A $\rightarrow H_2SO_4$ (30 s)
Type 4	TS-40A $\rightarrow H_2SO_4$ (60 s)

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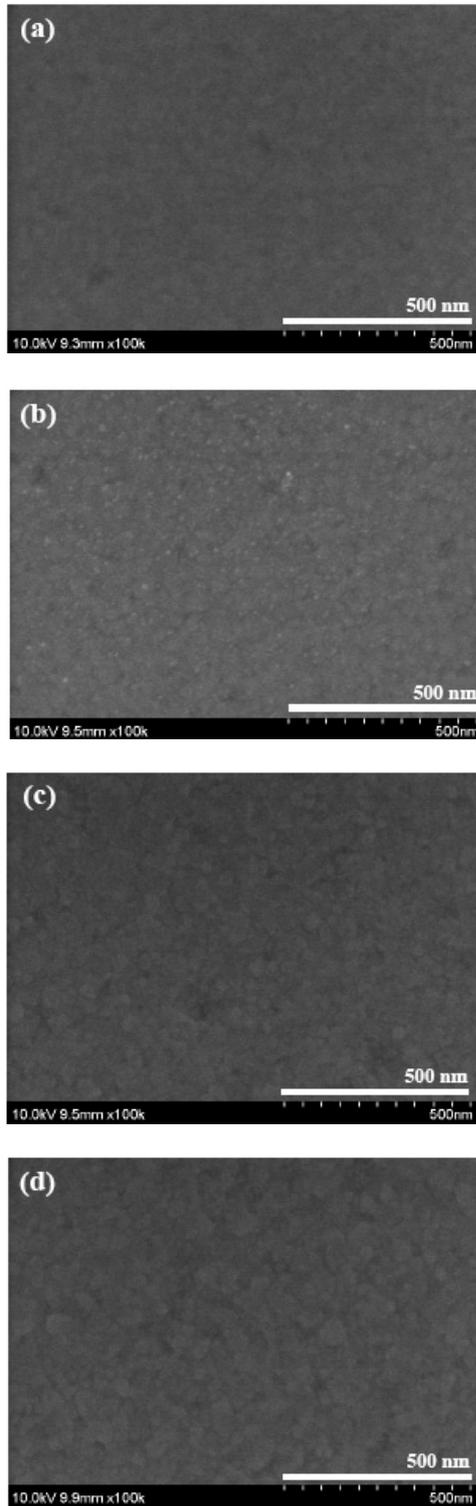
Fig. 1. FE-SEM images of (a) the bare Cu seed layer and the cleaned Cu seed layer by pretreatment of (b) TS-40A, (c) TS-40A+H_2SO_4 for 30 s, and (d) TS-40A+H_2SO_4 for 60 s.

In Type 2 method of Table 1, the chemical pretreatment for elimination of Cu native oxide layer was performed by soaking the wafer in a TS-40A (Metex, MacDermid, Inc.) solution for 60 s (a kind of an alkaline solution to remove organic matters), and then the wafer was dipped in deionized (DI) water for 20 s with stirring. This DI water dipping was carried out three times. Lastly, the rinsed wafer was dried by N_2 gas. In the methods of Type 3 and Type 4, the Cu seed layer exposed in air was soaked in mixture solution (the ratio of 1:20) of H_2SO_4 (95% Sigma Aldrich Co.)and DI water for 30 s and 60 s, respectively, after alkaline cleaning of Type 2. Also, the all wafer were performed DI water rinsing three times for 20 s with stirring and dried in a continuous N_2 stream. The sample size was 2×3 cm^2.

According to various surface treatment methods, the changed surfaces of Cu seed layer were measured by using surface analysis tools such as field emission scanning electron microscopy (FE-SEM; HITACHI 4800) at National Nano Fab Center in Korea and X-ray photoelectron spectroscopy (XPS; PHI VersaProbe XPS Microprobe) at Hanbat National University in Korea. The used X-ray source was the monochromatized Al Kα (1486.6 eV). The binding energies were calibrated to Cu $2p_{3/2}$ at 932.6 eV for the Cu films. All XPS data were obtained without Ar^+ cleaning. The mass density of electroplated Cu film was estimated by measurement of mass difference of sample before and after electroplating by using electronic balance (HR-200, A&D Co. Ltd.).

3. Results and Discussion

Figure 1 shows the surface images for Cu seed layer after various pretreatments. As shown in Fig. 1(a) and 1(b), the surface of sample changed slightly after TS-40A pretreatment. In general, TS-40A as an alkaline soak cleaner is used to remove light rust and other organic coatings. By H_2SO_4 treatments after TS-40A pretreatment [Fig. 1(c) and 1(d)], the surface morphology of samples were so clear and uniform that the grain structure could have been observed.

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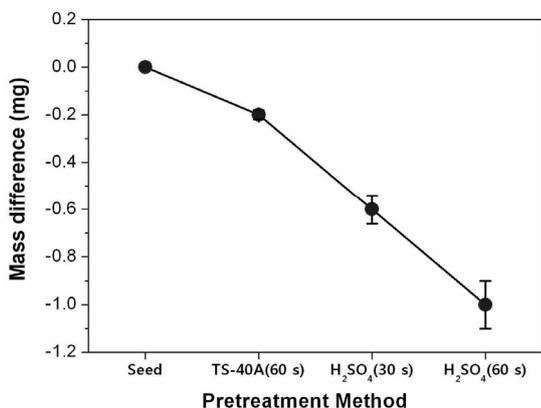
Fig.2. Mass difference of Cu seed layer by various pretreatment methods.

As shown in Fig. 2, the mass of samples after various pretreatments decreased by comparison with bare Cu seed layer. The mass loss after H_2SO_4 treatment was larger than that after TS-40A pretreatment and increased with increasing dipping time. The mass loss by chemical pretreatment means that a part of Cu seed layer is removed. First of all, we estimated the relative atomic concentration of surface of Cu seed layer before and after TS-40A pretreatment [Fig. 3]. After TS-40A pretreatment, carbon content decreased abruptly and then Cu content increased relatively, because oxygen content hardly changed. By this result, the carbon on Cu seed layer was removed mainly by TS-40A pretreatment. Therefore, we think that the decrease of carbon content on Cu seed layer leads to the mass loss of sample in Fig. 2.
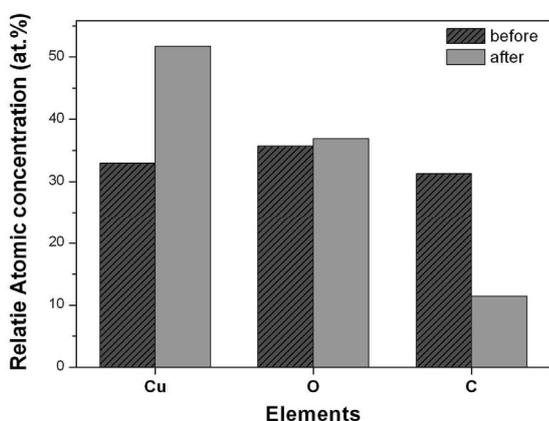
Fig.3. The relative atomic concentration by XPS of Cu seed layer before and after TS-40A pretreatment.

Fig. 4 shows the change of chemical states of Cu (2p) and O (1s) of Cu seed layer before and after TS-40A pretreatment. On the surface of Cu seed layer before pretreatment, Cu oxides and $Cu(OH)_2$ or $CuCO_3$ existed by air contamination. In Cu (2p) spectra, the main peak is corresponding to metallic Cu and/or Cu_2O phase and the broad peak at ~ 935 eV is corresponding to $Cu(OH)_2$ or $CuCO_3$ [12,13]. After TS-40A pretreatment as shown in Fig. 4(a), the broad peak decreased. By this result, we think that the decrease of carbon content in Fig. 3 may be due to the decrease of $CuCO_3$ phase on Cu seed layer. In O (1s) spectra [Fig. 4(b)], Cu_2O peak at ~ 530.3 eV [13] increased slightly. From the results that Cu_2O phase increased slightly and oxygen content hardly changed after TS-40A pretreatment, native Cu oxide layer is not removed by TS-40A.
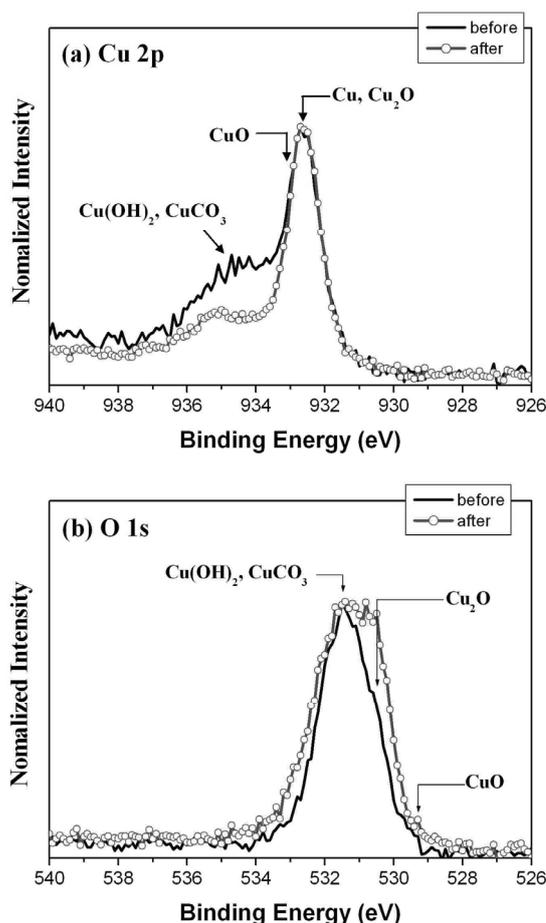
Fig. 4. XPS (a) Cu 2p and (b) O 1s core-level spectra of Cu seed layer before pretreatment and after TS-40A pretreatment.
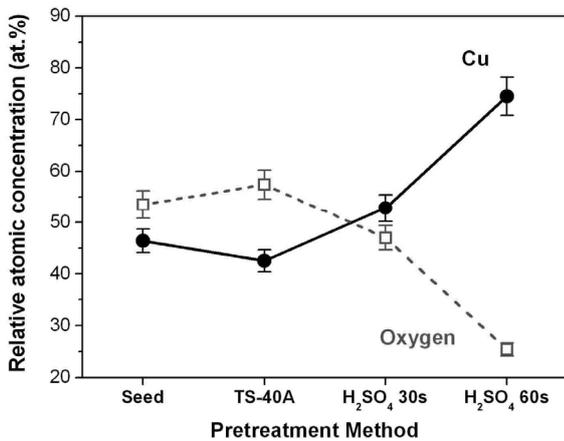
Fig. 5. The relative atomic concentration of remaining Cu and oxygen by XPS on Cu seed layer after various pretreatments.
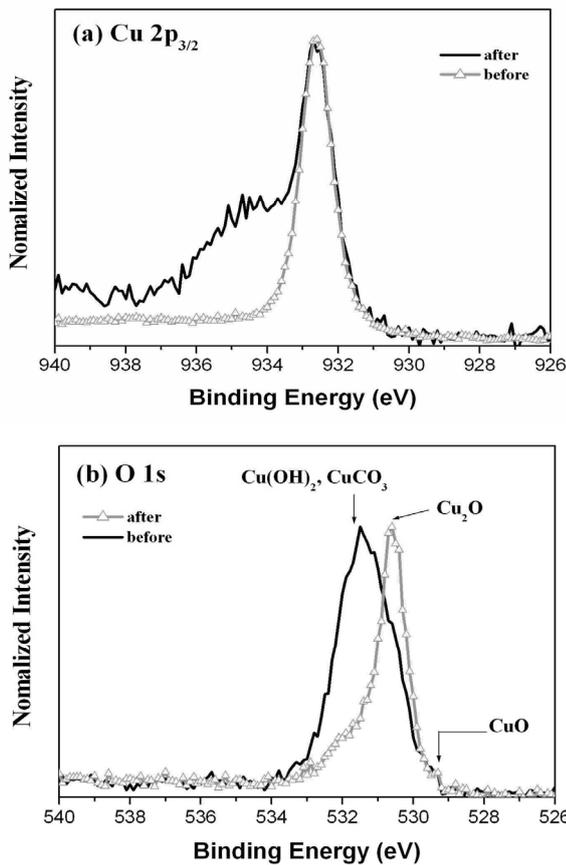
Fig. 6. XPS (a) Cu 2p$_{3/2}$ and (b) O 1s core-level spectra of Cu seed layer before pretreatment and after H$_2$SO$_4$ treatment for 60 s.

Figure 5 shows the change of relative concentration of Cu and oxygen on Cu seed layer after various pretreatments. After H$_2$SO$_4$ treatments, the oxygen content decreased with increasing dipping time. This result agrees well with the mass difference in Fig. 2. From the decrease of oxygen content and the mass loss of samples after H$_2$SO$_4$ treatment, a lot of Cu oxides on Cu seed layer are removed by H$_2$SO$_4$.

Fig. 6 shows the Cu 2p and O 1s spectra of Cu seed layer before pretreatment and after H$_2$SO$_4$ treatment. After H$_2$SO$_4$ treatment for 60 s, Cu$_2$O phase on Cu seed layer showed as ever and Cu(OH)$_2$ and/or CuCO$_3$ phases vanished almost in Fig. 6. The metallic Cu peak at 932.6 eV just showed in Cu (2p) spectrum after H$_2$SO$_4$ treatment. By the result, most of native Cu oxides formed on Cu seed layer can be removed by control of dipping time in H$_2$SO$_4$ treatment.

4. Conclusion

In order to remove native Cu oxides formed on Cu seed layer, we used TS-40A and H$_2$SO$_4$ solutions. For all pretreatments, the mass of samples was decreased. The mass loss of sample treated in H$_2$SO$_4$ solution for 60 was the largest. By TS-40A pretreatment, native Cu oxide layer is not at all removed although the carbon on Cu seed layer was removed mainly with a few loss of sample mass because of the decrease of CuCO$_3$ phase. By H$_2$SO$_4$ treatment after TS-40A pretreatment, most of Cu oxides on Cu seed layer were removed with a lot of mass loss, in addition, can be eliminated by control of dipping time. Consequently, we found that the pretreatment by H$_2$SO$_4$ is suitable to obtain a Cu seed layer with clean surface for electrodeposition.

5. Acknowledgment

6. References

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