Paper

Anode Effects in Electroplated Cu Film

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In order to study anode effects in Cu electroplating, we investigated the characteristics of the Cu films electrodeposited on Cu seed layer and the surface change of anodes, by using Cu (soluble) and Pt (insoluble) anodes. For the case of Cu anode, the brownish passivation layer was formed on the surface of Cu anode, and this was mainly composed of by-products which was formed by reaction of impurities in electrolyte with copper anode. In use of Pt anode, the O_2 bubbles on the anode surface were occurred. The current density in bath for the case of Cu anode was larger than that of Pt anode and increased after 300 s of plating time had elapsed. In formation of the electroplated Cu films, the deposition rate of Cu films electroplated by using Cu anode was larger and the density of film plated by using Cu anode was higher than those by Pt anode.

1. Introduction

Electroplating (EP) is presently the most popular method used for Cu deposition in semiconductor fabrication processes since it is simple, safe and inexpensive. It has low growth temperature, high throughput, and excellent gap-filling capability [1-3]. The copper EP process is that copper metal is deposited on the surface of cathode when a wafer with conducting Cu seed layer (=cathode) and the anode immersed in a solution (electrolyte) are electrically connected to a power supply that supplies current through the surfaces to the solution. The electrolyte for Copper EP deposition is commonly containing H_2SO_4 and $CuSO_4$ with small amounts of Cl^- [4-6].

Generally, we can be faced with a problem of anode passivation during the plating process because of a reaction with impurities contained within the electrolytes [7,8]. This anode passivation can give rise to several problems. Therefore, the anode is one of the important parameters in optimization of Cu electroplating condition.

In the anode type, there are soluble and insoluble anodes. In conventional acid Cu electrolyte, the dissolution of Cu ($Cu \rightarrow Cu^{2+} + 2e^-$) takes place at soluble anode such as Cu, in addition, oxygen (O_2) is evolved at the insoluble anode surface by the degradation of water ($H_2O \rightarrow 1/2\ O_2 + 2e^- + 2H^+$: by

the following process) [9,10].
$$H_2O \rightarrow H^+ + OH^-$$
$$2OH^- \rightarrow 1/2\ O_2 + 2e^- + 2H^+$$
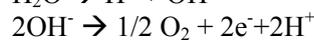
In this study, we investigated the Cu films electrodeposited on Cu seed layer and the passivated film formed on pure Cu anode for comparison with pure Cu (soluble) and pure Pt (insoluble) anodes.

2. Experimental

Potentiostat electrodeposition was conducted using the three-electrode system with a pure Cu (99.99 %) or a pure Pt (99.99 %) plate as a counter electrode (=anode), an Ag/AgCl as a reference electrode and the seed layer as a working electrode (=cathode). The plating was carried out with all the electrodes immersed in the plating cell. The plating voltage was - 0.3 V and - 0.6 V. All Cu films were deposited for 60 min at room temperature.

The substrate was p-type Si(100) with a 20-nm titanium (Ti) thin film as an adhesion/diffusion-barrier layer on the surface. A 20-nm-thick Cu seed layer was deposited onto the substrate by using sputter deposition. The electroplating bath was fixed $CuSO_4 \cdot 5H_2O$ 40 g/L, H_2SO_4 10 g/L, HCl 50 ppm, and three organic additives (Viaform : accelerator 6 mL/L, suppressor 2.5 mL/L, and leveler 2 mL/L).

The film thickness of thin films was measured by using field emission scanning electron microscopy (FE-SEM; HITACHI 4800) in the National Nanofab Center (NNFC), Korea. The chemical states of the films were investigated by using 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). Dual beam charge neutralization was also used to prevent the sample charging due to the ejection of electrons. The binding energies were calibrated to Cu $2p_{3/2}$ at 932.6 eV for the Cu films. For all samples, the surface cleaning was performed with 2 keV Ar^+ ion for 0.2 min. 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.).
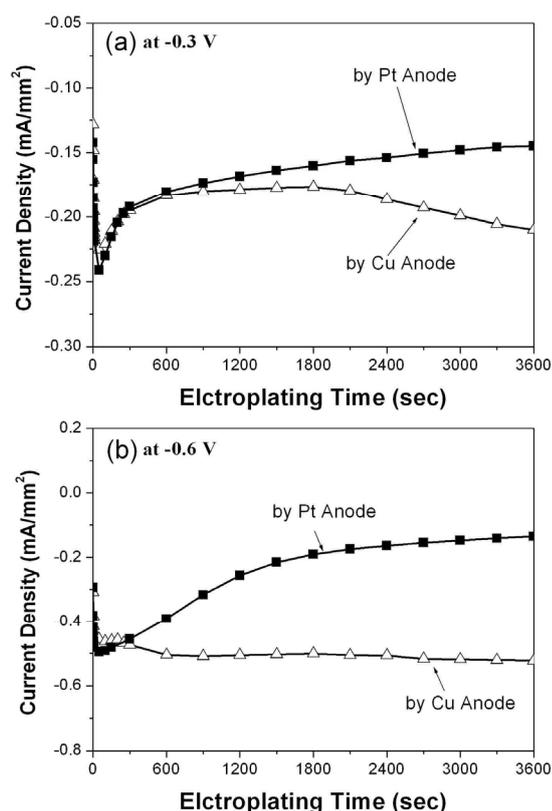

Fig. 1. Current density as a function of plating time by Pt and Cu anodes at supply voltage (a) -0.3 V and (b) -0.6 V.

3. Results and Discussion

Figure 1 shows the variation of current density (J) by Cu and Pt anodes as a function of electroplating time and supply voltage (potentiostat method). In variation of supply voltages, the current density J at -0.6 V [Fig. 1(b)] was larger than that at -0.3 V[Fig. 1(a)] for all anodes. In case of Cu anode, the current density increased largely according to increase of supply voltage; from $J_{(-0.3 V)} = \sim 0.20$ to $J_{(-0.6 V)} = \sim 0.50$ mA/mm^2. However, the current density by Pt anode increased slightly with increasing supply voltage; from $J_{(-0.3 V)} = \sim 0.15$ to $J_{(-0.6 V)} = \sim 0.20$ mA/mm^2.

As shown in Fig.1, the current density J changed according to increase of electroplating time. On the whole, the current density by Pt decreased and by Cu anode increased with increasing plating time for all supplied voltages (-0.3 V and -0.6 V). At below electroplating time 300 s, the current density by Pt anode was slightly larger than that by Cu anode for all supply voltages although the value was very similar. However, above electroplating time 300 s, the current density by Cu anode was larger than that by Pt anode. The increase of J in use of Cu anode according to increase of plating time may be due to the supplement of the Cu ion in electrolyte. Cu as a soluble anode should be dissolved in electrolyte. From this result, we found that the reaction time for dissolution of Cu anode is needed.

During the electroplating Cu deposition by Pt anode, the bubbles have arisen on the surface of Pt anode and then have risen to the solution surface. In addition, the amount of bubble that occurs on the surface of Pt anode increased with increasing supply voltage. We guess that the bubble is oxygen gas (O_2) by a decomposition of water in solution. On the other hand, the brownish film on Cu anode during the Cu electrodeposition at all supplying voltages, was formed although any bubble didn't occur in bath. We think that the brownish film is passivated film formed by reaction with impurities in solution.

In order to understand the reactants of surface of passivated Cu anode, we measured XPS. The only peaks of copper (Cu), sulfur (S), chlorine (Cl) included oxygen (O) and carbon (C) are visible in the wide scan spectrum of Fig. 2. Fig. 3(a) and 3(b) show the XPS Cu 2p and O 1s core level spectra for brownish film formed on surface of Cu anode. In Cu 2p spectra [Fig. 3(a)], the main peak at 932.6 eV is corresponded to metallic Cu, Cu_2O, Cu_2S, and CuCl [11,12]. After Ar^+ cleaning for 2 min, the peaks of $Cu(OH)_2$ at 934.4 eV, $CuSO_4$ at 935.4 eV, and CuS at 932.2 eV in the Cu 2p spectra decreased,

and consequently the width of the Cu 2p peak narrowed. However, the width of O 1s peak [Fig. 3(b)] expanded after cleaning by the relative increase of Cu_2O peak at 530.3 eV increased in comparison with $Cu(OH)_2$ or sulfates peak at ~531.5 eV.
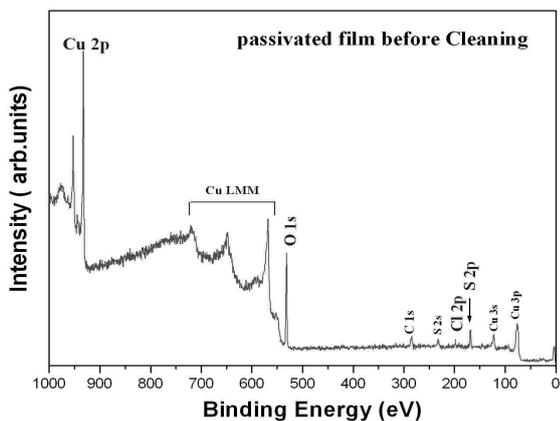

Fig. 2. XPS wide scan spectrum for surface of passivated Cu anode before cleaning.

In S (2p) of Fig. 4(a), typical copper sulfate ($CuSO_4$) peak showed on passivated anode surface without any peak, but after Ar+ cleaning, the shoulder peak at ~167 eV and the broad peak at ~162 eV appeared. The broad peak position is corresponding to copper sulfides (CuS and Cu_2S) and the shoulder peak which shifted to lower binding energy in comparison with sulfate peak, may indicate the presence of sulfinate or sulfonate. In Cl (2p) spectra [Fig. 4(b)], the peak at 198.2 eV is corresponded to the CuCl. The CuCl phase may be formed by adsorbed Cl^- ion on surface of Cu anode because the interaction of Cu and Cl is very strong. After cleaning, the peak broadened and the position of main peak shifted to higher binding energy. We guess that the broad peak is due to the coexistence of CuCl and $CuCl_2$ (199.2 eV) [12,13]. As a result, we found that the brownish passivation film was mainly composed of CuO_2, CuCl or $CuCl_2$, $CuSO_4$, Cu-sulfides, and Cu-sulfinate or sulfonate. These by-products would be formed by reaction of impurities in electrolyte.
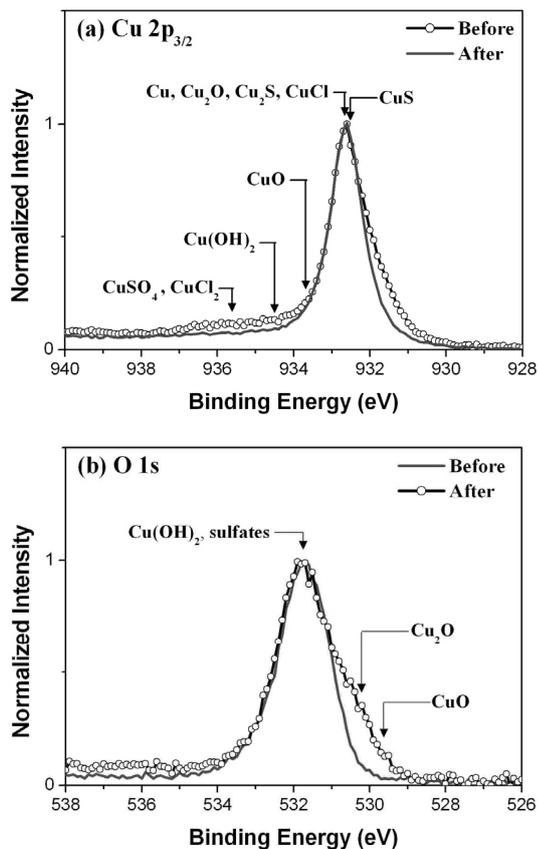

Fig. 3. XPS (a) Cu $2p_{3/2}$ and (b) O 1s core level spectra for surface of passivated Cu anode before and after Ar^+ cleaning.
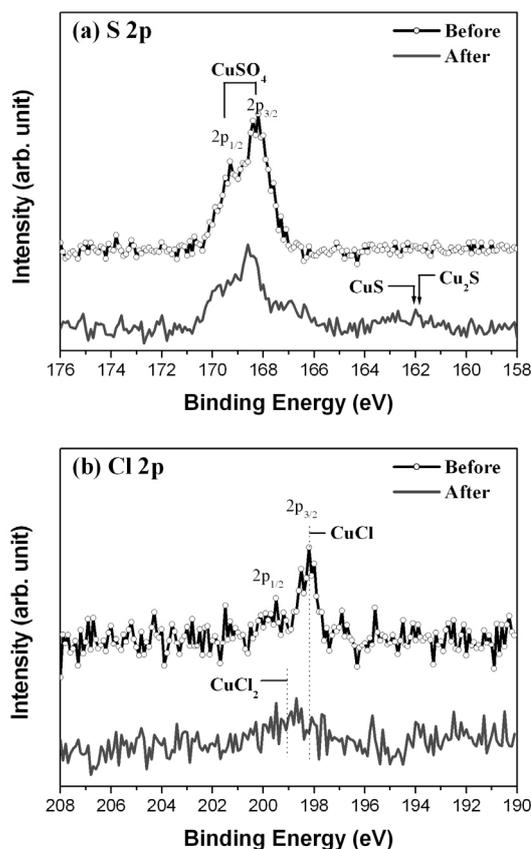

Fig. 4. XPS (a) S 2p and (b) Cl 2p core level spectra for surface of passivated Cu anode before and after Ar^+ cleaning.

We investigated the characteristics of Cu films electroplated by soluble Cu and insoluble Pt anodes. In the electroplated Cu films, there were no impurities such as Cl and S within the detection level of the XPS (not shown here). Also, Cu-oxides on the electroplated Cu films were almost vanished after surface cleaning. From this result, the impurities in electrolyte don't seem to be having much effect on the electroplated Cu film.
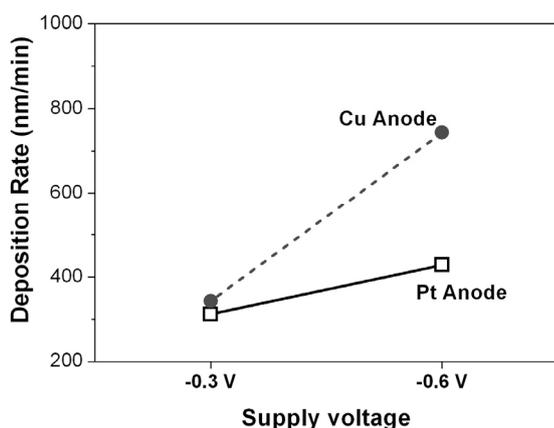

Fig. 5. Deposition Rate of Cu films electroplated by Pt and Cu anodes as a function of supply voltage.

In Fig. 5, at supply voltage -0.3 V, the deposition rate of Cu films was very similar in both of Cu and Pt anodes in spite of increase of current density by Cu anode [Fig. 1(a)]. However, the deposition rate by Cu anode at -0.6 V was remarkably larger than that by Pt anode. This means that Cu anode as soluble anode is inefficient at -0.3 V and proves effective at -0.6 V.
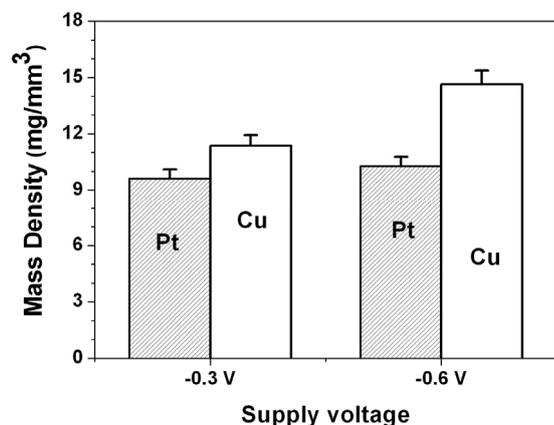

Fig. 6. Mass density of Cu films electroplated by Pt and Cu anodes as a function of supply voltage.

Fig. 6 shows the mass density of electroplated Cu films. On the whole, the mass density of Cu film electrodeposited at -0.6 V was larger than that at -0.3 V, in addition, the electroplated Cu film by using Cu anode was denser than that of Pt anode.

4. Conclusion

We investigated the changes in the anode surface during electroplating and the characteristics of the electroplated Cu films by soluble Cu and insoluble Pt anodes. During electroplating, above plating time 300 s, the current density by Cu anode increased with increasing plating time and was larger than that by Pt anode. In addition, the O_2 bubbles on the surface of Pt anode were occurred during plating and the brownish passivation layer on the surface of Cu anode was formed. From XPS results, the passivation layer formed on Cu anode was mainly composed of CuO_2, $CuCl$ or $CuCl_2$, $CuSO_4$, Cu-sulfides, and Cu-sulfinate or sulfonate. The Cu films electroplated by both Cu and Pt anodes were composed of metallic Cu without impurities such as S and Cl although the reactants formed on surface of anodes were very different. The deposition rate of Cu films electroplated by Cu anode was larger and the film density by Cu anode was higher than those by Pt anode.

5. Acknowledgment

6. References

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