Cl$^-$ Consumption in Copper Electrodeposition

Masanori HAYASE
Tokyo Institute of Technology
Nagatsuta, Midori-ku, Yokohama 226-8503, JAPAN

Munemasa TAKETANI
Tokyo Institute of Technology
Nagatsuta, Midori-ku, Yokohama 226-8503, JAPAN

Koji AIZAWA
Tokyo Institute of Technology
Nagatsuta, Midori-ku, Yokohama 226-8503, JAPAN

Takeshi HATSUZAWA
Tokyo Institute of Technology
Nagatsuta, Midori-ku, Yokohama 226-8503, JAPAN

Keisuke HAYABUSA
Ebara Research Co., LTD
Honfujisawa, Fujisawa, Kanagawa, 251-8502, JAPAN

The copper superfilling is achieved by the presence of additives (generally PEG, Cl$^-$ and SPS)in the acid copper sulfate electroplating bath. Recently, as one of the superfilling mechanism, we proposed the halide ion consumption model$^{1-2)}$, in which the reduction of halide ion concentration causes the rapid electrodeposition on trench bottoms. The copper bottom-up deposition was also realized by the addition of only PEG and halide ion in acid copper sulfate plating bath. However, the addition of Cl$^-$ was about 10 ppm and it is diluter than the industrial standard of 50 ppm. Therefore, it is unclear whether the Cl$^-$ consumption has impact on the superfilling or not.

In this study, in order to know the extent of Cl$^-$ consumption, SIMS measurements were carried out and the efficiency of electrodeposition was investigated.

SIMS MEASUREMENT

Copper is electroplated for 30s applying 200A/m^2 in a stagnant Cl$^-$ containing acid copper sulfate bath($CuSO_4$ 225g/dm^3, H_2SO_4 55g/dm^3). The specimen was a chip of copper sputter deposited Si wafer. Cl$^-$ is supplied by the addition of HCl and various Cl$^-$ concentrations were examined. Fig.1 shows the depth profile of Cl in deposited copper measured by SIMS(Cameca ims4f). In all cases, Cl counts are high around the starting point of electrodeposition and are reduced toward the specimen surface. Interestingly, the Cl counts at 0.2 mmol/dm^3 are higher than that at 0.5 mmol/dm^3 and 1 mmol/dm^3. It is also found that the Cl peak appears earlier at 10 mmol/dm^3 of Cl$^-$ and less thickness of deposited copper is suggested.

DEPOSITION LOSS

As a cause of Cl$^-$ consumption, Cl incorporation into deposited copper and formation of soluble compounds such as $CuCl_2^-$ can be considered. SIMS measurements suggests that the formation of soluble compunds might be dominant for the Cl$^-$ consumption. In order to grasp the Cl$^-$ consumption by the formation of soluble compounds, loss of electrodeposition was investigated. The electrodeposition was carried out potentiostatically for 30 s using a RDE, then the deposited copper was dissolved anodically. The loss of deposition was calculated by the integration of the current. Fig.2 shows the relation between the deposition loss and Cl$^-$ concentration. The larger loss can be seen at larger concentration of Cl$^-$ and at larger rotational speed.

DISCUSSION

Fig.3 shows the Cl depth profile when PEG of 300ppm was added. The specimen was Pt sputter deposited Si wafer. Though the Cu counts is not constant, it is found that the Cl counts with the addition of PEG and Cl$^-$ are higher than that with addition of only Cl$^-$. This result suggests that PEG blocks the formation of soluble Cl compounds. The deposition loss seems to be limited by Cl$^-$ diffusion in Fig.2. It is supposed that once the inhibition by PEG-Cl breaks, subseaquent quite rapid consumption of Cl$^-$ by formation of soluble compounds might occur. Therefore, large reduction of Cl$^-$ concentration around the trench bottom can be expected even in the higher bulk concentration of Cl$^-$, 50ppm.

REFERENCE

[1] M.Hayase, et al., Electrochem. and Solid State Lett.,**5**, C98(2002)

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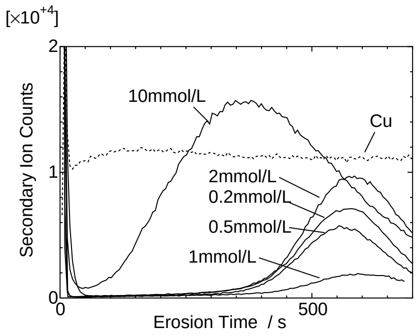

Fig.1 Cl depth profile by SIMS. Copper is electroplated by applying 20mA/cm^2 for 30s in Cl$^-$ containing acid copper sulfate bath.

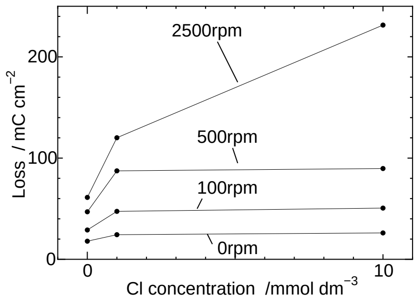

Fig.2 Deposition loss calculated by integration of current density. Copper is electroplated at -100mV vs Ag/AgCl for 30 s and is electrolyzed anodically.

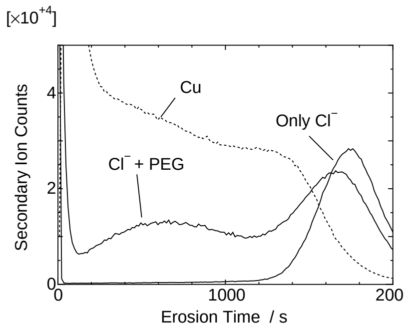

Fig.3 Cl depth profile by SIMS. Copper is electroplated by applying 20mA/cm^2 for 30s with Cl$^-$ 0.2mmol/dm$^-$3 and PEG 300ppm.