Bottom-up Fill of Copper in Deep Sub Micron Holes by Electroless Plating with Addition of Alkane-Thiol as an Inhibitor

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1. Introduction

Copper is used widely for metal interconnection in ULSI. Bottom-up fill of Cu in an electroplating solution has been studied extensively [1]. With shrinkage of interconnections size, it is getting more difficult to use a sputtered Cu seed layer prior to electroplating. Electroless plating on the TaN or WN barrier metals were possible by displacement reaction [2], which suggests electroless plated Cu as a seed layer. The authors found that bottom-up fill was possible for electroless plating with additions of SPS [3,4]. In the present study, we investigate the effect of addition of alkane thiol to control bottom up filling characteristics.

2. Experimentals

The electroless Cu plating bath typically contains $CuSO_4 \cdot 5H_2O$, EDTA, glyoxylic acid, polyethylene glycol, and TMAH as a pH controller. The pH of the plating solution was adjusted to about 12.5, and the bath temperature was 70°C.

We examined the effect of alkane thiol concentration as well as molecular length on the bottom-up filling characteristics of a submicron holes. For this purpose, addition of alkane thiol with alkyl chain number of 3, 11,16 were compared.

Figure 1 shows deposited Cu thickness as a function of alkane thiol with alkyl chain number 3. With the addition of alkane thiol, deposition rate decreased significantly, which suggests that alkane thiol acts as an inhibitor. It is well known that sulfur atoms interact with bare metal surface strongly, and forms self-assembled monolayer after long time immersion. Figure 2 shows time dependence of filling characteristics of submicron hole by electloless plated Cu. The hole was filled from bottom to top.

We investigated the effect of molecular weight by changing alkyl chain number of alkane thiol. In other words, effect of diffusion coefficient of additives were compared. Figure 3 shows cross-sectional micrographs of the hole filled with additives using different number of molecular chains. Bottom-up tendency was enhanced when molecular chain number was increased. The results strongly suggest that suppression of the diffusion flux of inhibitor molecules plays an essential role on bottom-up filing.

3. Conclusions

Bottom-up filling of Cu by electroless plating was observed by addition of alkane thiol. There was a significant change in hole filling characteristics by a change in alkyl chain number, and the bottom-up tendency was enhanced with an increase in the moler weight of inhibitors. These results suggest possibility of controlling bottom-up fill ability of electroless plating solutions by a choice of inhibitor molecules.

References

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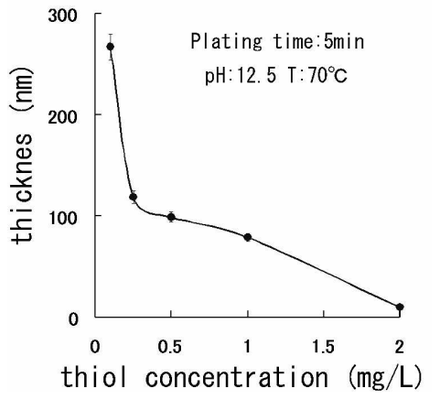

Fig.1 Cu thickness as a function of alkane thiol concentration.

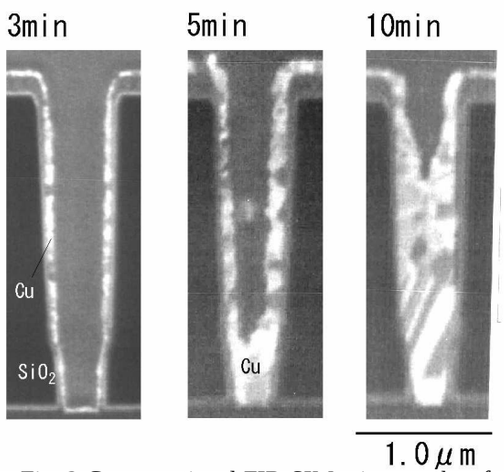

Fig. 2 Cross-sectional FIB-SIM micrographs of electroless Cu deposition profiles for various plating times.

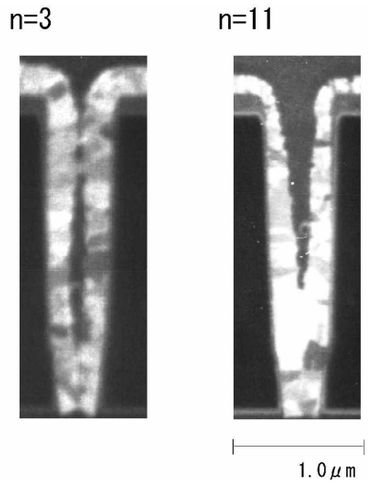

Fig. 3 Diameter dependence of the bottom-up ratio of the electroless plated Cu. Deposition time was 10 min. Moler concentration is 0.94 x 10-6 mol/L.