Analysis of Additive Role for Copper Electroplating using Microfluidic Channel

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Copper electroplating is used in various electronics production. Especially, copper superfilling for on-chip interconnection revealed that electroplating has unique advantages by using some additives in the plating bath. Therefore, understanding of additive roles is very important, and it was found that accelerating additive, such as SPS (bis (3-sulfopropyl) disulfide), remains on the plating surface and concentrates on concave, and this feature leads into the bottom-up superfilling.

On the other hand, additives to suppress electrodeposition are also essential for industrial electroplating. Usually two suppressing addtives, called as suppressor and leveler, are used in the plating bath. It is assumed that suppressor is needed to obtain bright film surface with the accelerator and is used in almost all cases, while leveler has important role for obtaining smooth surface on rough substrates. Both additives are assumed to cover the plating surface and block the electrodeposition. However, the difference in roles between suppressor and leveler is not well known. Recently, leveler is widely used for filling copper into various scale of trench and hole. In these process, it is empirically known that leveler is sensitive to bath agitation. Generally, flow of electrolyte solution in the plating bath is turbulent, and mass transport is complicated. Then, rotating disk electrode is often employed for basical study to obtain steady fluidic flow. To obtain steady flow, microfluidic channel is also an attractive device. In the microfluidic channel, usually flow is laminar, and material balance can be estimated relatively easily. Besides, real time observation by optical microscope of plating surface may be available using the microfluic channel. In this study, in order to understand the role of additives in the plating bath, a simple microfluidic channel was introduced, and impact of additives on polarization behavior was investigated with various electrolyte flow velocity.

Experimental

Figure 1 shows the schematic view of the microfluidic channel. Pt wire of 100μm in diameter, which works as a working electrode, was embedded in an epoxy resin, and the top surface was polished. Microfluidic channel was formed by 45μm thick film resist, and the dimension of cross-section was 45μm$\times$4mm. Glass cover was clamped together with the epoxy resin by a metal frame, and elasticity of the film resist showed good sealing. A copper wire in the outlet hole was worked as a counter electrode. As the counter copper electrode surface was quite large compared to the working electrode, we also use the copper electrode as a reference electrode, and overpotential was estimated with the copper electrode.

Acid copper sulfate solution with commercial plating additives, which consist of chloride ion, accelerator, suppressor and leveler, was prepared. Cyclic voltammetry was performed in several conditions varying additive concentration and electrolyte flow rate. Figure 2 shows example microscopic view of the working electrode. Electrolyte flowed from bottom of the picture. It was found that scar on the working electrode disappeared by the plating, and deposited copper dissolved from the upper stream of the flow.

Figure 3 shows the current densities versus electrolyte flow velocity at overpotential of 200 mV at first forward scan on cyclic voltammetry. Leveler concentration was varied from 0 to twice of recommended concentration. It was found that suppression was weakened at high velocity when no leveler was added, while suppression was strengthened with leveler.

Conclusion

In order to evaluate the impact of bath agitation on copper electroplating, a simple microfluidic device was proposed and some results were demonstrated.

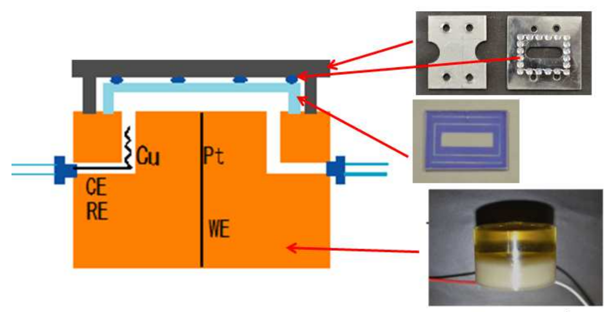
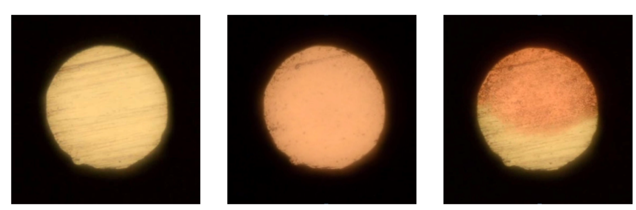


Figure 1 Schematic view of the microfluidic device for the electroplate analysis.



(a) before plating (b) at plating (c) at dissolution

Figure 2 Microscopic observation of working electrode.

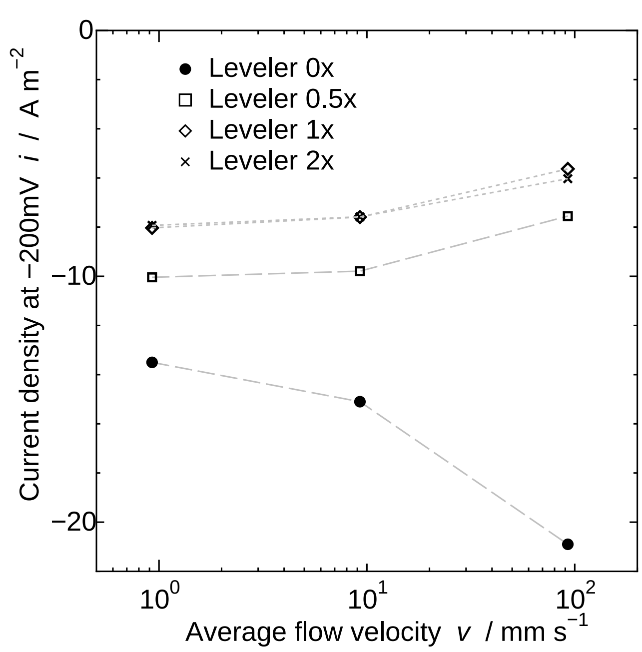


Figure 3 Impact of flow velocity and leveler concentration on suppression.