

Cuprous ion as an Accelerant of Copper Damascene Electrodeposition

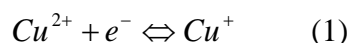
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1. Introduction

The cuprous ion is crucial intermediate and the cuprous ion always produced during the process of the electrodeposition.



It is extremely difficult to detect the cuprous ion and accordingly few works exist which are related to the acceleration effect of cuprous ion.

Rotating ring disk electrode (RRDE) has been used to detect this cuprous ion. The cuprous ion detected at the ring of RRDE is 1000 times larger for the copper dissolution, if it is compared with cuprous ion for the electrodeposition [1]. Hence we formed cuprous ion within the trench of the trench bottom electrodes and experimentally verify the relation between cuprous ion and acceleration.

2. Experimental

Three different widths of trench bottom electrodes are 3, 5, 10 μm . The photo mask pattern consists of lines of 15mm in length and the total area of lines is 0.084cm² for every line widths. Schematic illustration of the trench bottom electrode is illustrated in Fig.1.

Basic bath consists of CuSO₄ · 5H₂SO₄ of 0.6M and H₂SO₄ of 1.85M. The additives are 1ppm of SPS, 400ppm of PEG and 150ppm of HCl. In order to control the cuprous ions, N₂ and O₂ have been purged in the electrodeposition baths. The trench bottom electrode, copper, have been dissolved for 12 seconds at 10mA/cm² in order to form cuprous ion in the trench of the trench bottom electrode.

3. Results

1. With N₂ bubbling, drastic increases in current densities are observed and the current density increased up to -40mA/cm² for 3 μm trench bottom electrode width at -0.05V vs. SCE. Furthermore, the current densities increase with the narrower trench bottom electrode (Fig.2). On the contrary, with O₂ bubbling, the currents show very small value of -1.0mA/cm². The current densities are same with the trench bottom electrode widths of 3, 5, 10 μm (Fig.3). The drastic difference in current densities with the O₂ gas concentration in the electrolyte must be caused by the cuprous ion complex formed in the trench of the trench bottom electrode.

2. By the stirrer rotation of 600rpm, the current densities decrease to few mA/cm² and almost no difference in the current densities for the trench widths of 3, 5, 10 μm . This is because of the free cuprous ion complex flows out of the trenches because of the stirring rate of 600rpm.

3. Basic bath with only Cl⁻, the current shows marked increase and -70mA/cm² for 3 μm at 0.05V vs. SCE. The narrower the trench, the current densities increase. Chloride is an important additive for the acceleration and the acceleration must be related to the free cuprous complex and electron bridge formation of Cl⁻.

SPS alone is not the accelerant. Accelerants are the Cl⁻ and free cuprous ion not absorbing on the electrode.

References

1. J.R.White, J.Electrochem.Soc.17,977(1987)
2. K.Kondo, T.Matsumoto and K.watanabe, J. Electrochem. Soc. 151,C250 (2004).

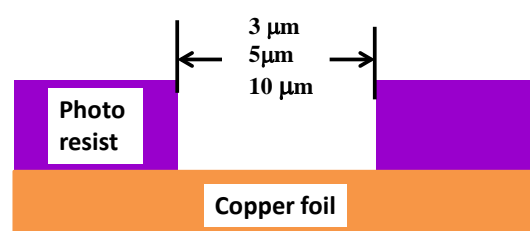


Fig.1 Schematic illustration of trench bottom electrode.

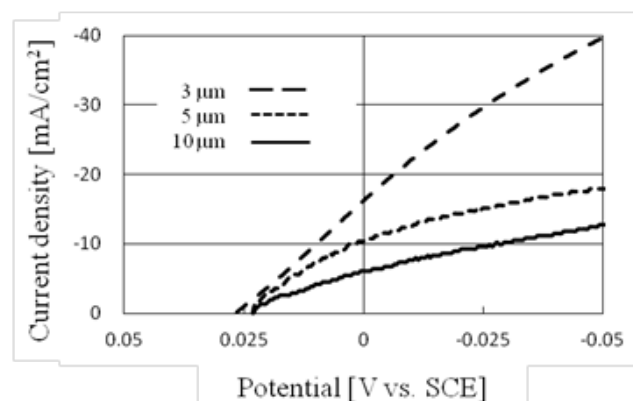


Fig.2 Result of LSV measurements with N₂ bubbling. SPS:1 ppm, Cl:50 ppm, PEG:400 ppm

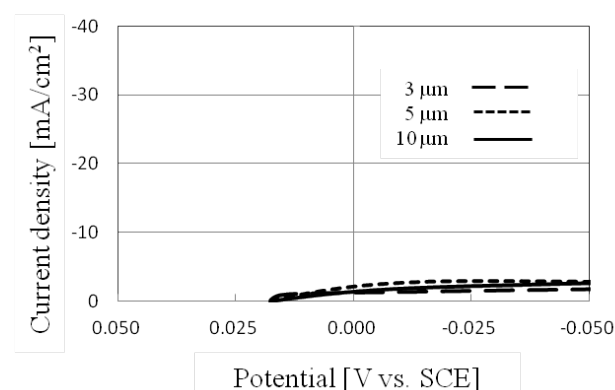


Fig.3 Result of LSV measurements with O₂ bubbling. SPS:1 ppm, Cl:50 ppm, PEG:400 ppm