586d An Electrochemical Impedance Spectroscopy Study of Chloride and 3-Mercapto-1-Propanesulfonic Acid Interactions in Acidic Copper Electroplating Bath

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Along with the decrease in the critical dimension of semiconductor chips, there are strong demands for higher electron mobility metal interconnects to permit faster signal transmission and reduce RC delay of the integrated circuit (IC). In addition, the metal deposition process must be able to create void-free deposits in the chip interconnects, which could be as narrow as 90 nm. Replacing the traditional aluminum interconnect with copper could reduce the wiring resistance by as much as 45%. The void-free filling capability of copper electrochemical deposition (ECD) on transistor level interconnects was first demonstrated by IBM in 1990 with damascene patterns[1]. The void-free deposition phenomena is often referred to as superfilling or superconformal deposition and is enabled by several additives at optimal concentration ranges and proper processing conditions. Chloride ions are the most common additive in copper plating chemistries and their adsorption affinity onto copper surfaces has been extensively studied with techniques such as in-situ STM, Auger electro spectroscopy, low-energy electron diffraction (LEED), and Auger depth profiling[2,3]. Ehlers et al.[3] immersed the annealed Cu (100) into a 1 mM HCl solution and observed a chloride surface coverage of 0.5 by LEED pattern. Auger peak height ratios versus emersion potential also showed that the potential dependent chloride adsorption film on copper surface becomes labile at more negative potentials. While chloride presents at high concentration in the electrolyte, CuCl layer starts to form at copper anode surface[2] due to the anodic polarization and it would dissolved in H_2SO_4 bases on a K_{sp} value of 1.02×10^{-6} M. Trace amounts of chloride ions at the parts-per-million level in the electrolyte are able to catalyze the Cu^{2+}/Cu^{+} reaction by changing the reaction mechanism from an outer-sphere reaction (water-water bridge) to an inner-sphere reaction (chloride bridge)[4], and therefore the copper deposition potential becomes depolarized[5]. An adsorbed thin layer of CuCl consequently forms on the cathode surface. 3-mercapto-1-propanesulfonic acid (MPS) and disodium bis(3-sulfopropyl)disulfide (SPS) are well-known as accelerators or brighteners in the electrochemical deposition bath chemistry. Although SPS is the dimer form of MPS, there is no direct experimental evidence for reduction of SPS to MPS[6]. These two brightening agents are unstable at either open circuit potential or in electrolysis condition[7]. The instability of MPS and SPS is caused by the dissolved oxygen in the electrolyte[7,8], Cu^{2+} ions from electrolyte, Cu^{+} ions from metallic copper surface[6], and incorporation of sulfur atom into copper deposition layer at cathode[8]. The complexation reaction between copper ions and accelerating agent is the key step which leads to the brightening of electrodeposited copper. Electrochemical impedance spectroscopy was used to study the role of chloride ions in the presence of MPS. The electrolyte were bubbled with nitrogen prior measurements and blanketed with nitrogen during measurements preventing back diffusion of oxygen. These measurements were conducted at 25 °C in a temperature controlled cell. We observed an increase in double layer capacitance and reduced charge transfer resistance at high to medium impedance scan frequency with the addition of chloride ions; however, the MPS does not show significant effect in this frequency region. The increase of deposition current does not occur until the addition of chloride and it became more significant at potentials more negative than -150 mV. From the ac impedance measurement results in Figure 1, we observe a change in the spectra when chloride present in the solution with MPS at low frequency. There are two frequency regions of interest; 5 to 0.5 Hz and 0.5 to 0.01 Hz corresponding to the sensitivity of chloride ions and MPS, respectively. The chloride ions at the electrode surface help to facilitate bridging these MPS molecules and an increase in deposition current is thereafter observed. Reference

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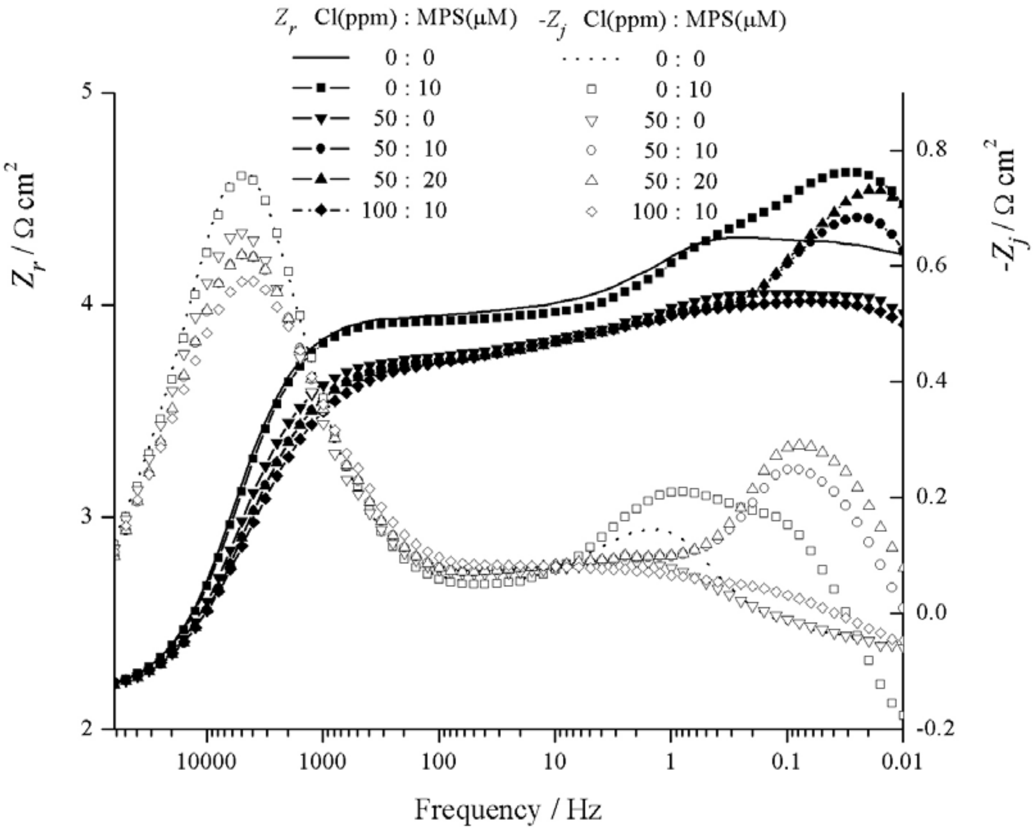

Figure 1. EIS measurements of BE with various concentration levels of chloride and MPS. Rotation speed of RDE is 2000 rpm.