Effect of Differential Additive Concentrations in Damascene Copper Electroplating

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Since the development of copper damascene plating [1] and the subsequent implementation of copper interconnects in microelectronics, a renewed interest in the role of the organic additives in copper electroplating has emerged. Typical copper sulfate based electroplating chemistries consist of an organic polymer (e.g., polyethylene glycol (PEG)) as a suppressor additive, bis(sodiumsulfopropyl) disulfide (SPS) or similar molecule as an accelerator or brightening agent, and possibly an additional organic molecule that acts as a leveling agent to produce mirror-like plated surfaces. In combination, these additives can also achieve accelerated, bottom-up electrodeposition of copper into submicron inlaid features which permits void-free interconnect wiring in damascene structures.

In recent years several models have been proposed in an attempt to describe the roles of these additives in the so-called superconformal or superfilling mechanism [1-3]. In general, two distinct models can be found, a leveler dominated system and a suppressor-accelerator dominated system. Which mechanism prevails depends on solution composition. The copper plating chemistries used to fill early generation damascene structures were characterized by relatively high leveler content. In this case the superfilling mechanism was found to be dominated by diffusion and adsorption of the leveler [1]. In the case of the more recently developed two component (suppressor and accelerator) or three component (with low leveler concentration) copper plating chemistries, it has been found that competition between the accelerator and suppressor for adsorption sites can describe the superfilling of sub-micron features [2]. The accumulation of the catalyst due to a rapid change in surface to volume ratio inside a trench or via is believed to be responsible for the observed bottom-up filling [2,3]. However, the exact nature of the acceleration or the formation of the catalyst species is not well understood.

In this paper we describe how a concentration difference of inorganic and organic additives in features and in the field may explain the differential copper deposition kinetics observed during superfilling of features in damascene copper electroplating. The "differential effective additive concentration" is the result of chemical and electrochemical interactions at the copper surface that cause depletion of certain additives and accumulation of in-situ generated species. The resulting differential depletion and accumulation of species is responsible for the observed superfilling of sub-micron features.

The electrochemical behavior of the accelerator additive was examined with cyclic voltammetry. The equilibrium potential for SPS reduction was extracted from the data.

The formation of soluble and insoluble cuprous 1-propane sulfonic-3-thiolate complexes ($Cu(I)(S-C_3H_6-SO_3H)_n^{1-n}$, or cuprous thiolate for short) was demonstrated using a rotating ring-disk technique. Figure 1 shows the disk and ring current densities versus disk potential for a GC-Pt rotating ring-disk electrode. The ring current density, i_{RING} (the measured ring current divided by the collection efficiency and the disk area) corresponds to the actual partial currents at the disk. Ring currents are shown for rotating ring-disk voltammograms measured with the GC ring polarized at 0.5V (curve A) and 0.9V (curve B). At 0.5V any free or complexed Cu^+ ions formed at the disk are oxidized at the ring (collection mode). The charge under the current peak at -0.5V (curve A) is 0.24 mC cm^{-2}, equivalent to about one monolayer of copper (n=1). At 0.9V also SPS and its monomer MPS (3-mercapto-1-propane sulfonic acid) are oxidized at the ring. Since SPS is present at all times a constant ring current is measured with the disk at open-circuit. Any consumption of SPS at the disk will be detected as a decrease in the ring current (shielding mode), whereas any additional formed MPS or its thiolate anion is detected as a ring current increase (collection). Curve C is the difference between curves B and A. The residual peak between -0.3V and -0.6V is due to the oxidation of thiolate ions from the soluble cuprous thiolate complex. The charge under the peak in curve C is 0.47 mC cm^{-2}, twice the amount for Cu^+ (n=2). Note that the dissolved cuprous thiolate complex is detected in a potential range were typical copper plating currents are obtained
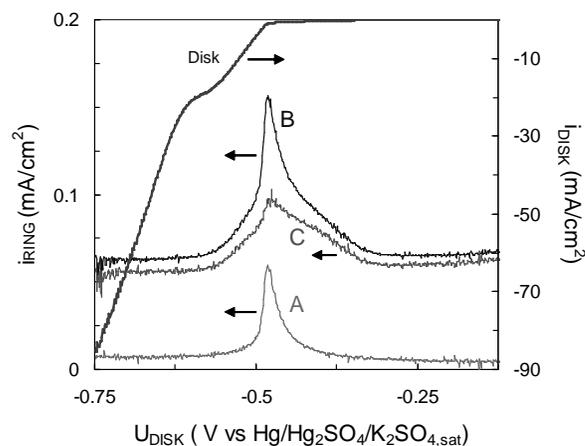

Figure 1: Rotating ring-disk voltammogram (10 mV/s; 1000 rpm) in 0.28M $CuSO_4$ + 40 μM SPS in 10 vol.% H_2SO_4 for GC ring – Pt disk electrode. A) U_{RING} = + 0.5V; B) U_{RING} = + 0.9V; C) current difference between B and A.

Electrochemical impedance spectroscopy was used to measured the adsorption and desorption of suppressor and cuprous thiolate on the copper surface. The influence of different additive concentrations was investigated. The Nyquist frequency plot could typically be described with an equivalent diagram comprising one or two constant phase elements for the capacitance of the electrode interface, one or two charge transfer resistances and an inductance for the adsorpted species, when necessary.

References:
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