## Novel Alkaline Copper and Copper-alloy Electroplating Processes Offering Extended Capabilities in Semiconductor Interconnect Metallization

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Interconnect metallization in semiconductor applications is currently being carried out by copper electroplating from acidified (pH=0-2) copper sulfate solutions in the presence of special additives that provide bottom-up fill of the plated features<sup>1</sup>. TaN or TiN diffusion barrier and a Cu seed serve as underlayers. However, as the copper interconnects become smaller in advanced devices, the copper plating process from the 'classical' acidified solution can no longer meet future technology requirements: (i) the non-uniform Cu seed layer deposited by PVD occupies too large a fraction of the feature cavity leading to premature closure at the rim. (ii) The need arises for a broader range of plated alloys, which the acidified copper solution cannot accommodate. To overcome the first issue of Cu seed non-uniformity, industry is seeking to replace the Cu sublayer with Ru. However, the acidic copper plating process does not provide sufficient nucleation density and adhesion to Ru. A number of processes had been suggested to provide enhanced Cu nucleation on Ru<sup>2,3</sup>, however, none has been demonstrated to also provide bottom-up fill, or enable alloy co-deposition from the same chemistry.

We present here an alkaline plating electrolyte that addresses all the above stated technology demands by providing (*i*) high nucleation density on Ru, (*ii*) bottomup fill, and (*iii*) copper alloys electrodeposition- all from the same chemical bath. The new electrolyte is complexed copper sulfate at pH > 13. Nucleation density >  $10^{11}$ /cm<sup>2</sup> can be achieved from this electrolyte using high current density pulses (2.5 A/cm<sup>2</sup> amplitude and 200 µs duration)<sup>4</sup>. Furthermore, application of special additives has been shown to provide bottom-up fill from the same alkaline medium (Fig. 1)<sup>5</sup>.

Another roadblock to interconnect scaling is that pure Cu exhibits diminished material properties in extremely small features, e.g., as dimensions approach the electron mean free path in Cu (~39 nm), the rise in Cu resistivity introduces a time delay that deteriorates device performance. Furthermore, the reduced electromigration (EM) lifetime of Cu in smaller geometries, due to increased grain boundary density and stress-induced voiding, contributes to poor reliability. A possible means to circumvent these adverse effects is to utilize Cu-alloys with improved material properties. Cu<sub>3</sub>Ge had recently been suggested for damascene integration due to its low room temperature resistivity and high oxidation resistance. EM reliability of Cu can be significantly improved by 'doping' it with impurities such as Mn. Traditionally, these Cu-alloys are fabricated using PVD or CVD techniques which are not scalable. Hence, electrochemical route for depositing these alloys is highly desirable.

We report here the electrodeposition of the aforementioned Cu alloys from the alkaline complexed solutions. Cu<sub>3</sub>Ge thin films were electrodeposited from a tartrate-complexed electrolyte using a pulse current waveform<sup>6</sup>. Compact and adherent Cu-Mn (2 at. % Mn) films were also electrodeposited from an EDTA-complexed electrolyte using a similar pulse current waveform (Figure 2). Diffusivity of the manganese atoms

in the electroplated Cu-Mn film and its segregation at the interface, which is essential for improving the EM reliability, was verified by X-ray photoelectron spectroscopy (XPS). In addition to offering lower seed layer susceptibility than its acidic counterpart, these high pH, complexed electrolytes offer high versatility that can provide numerous advantages in metallization of future generation interconnects.

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**Figure 1:** Partial-fill profiles for Cu electrodeposition from the alkaline, Cu-tartrate electrolyte containing 15 ppm SPS and 40 ppm PEI. The plating current density (on the flat region of the wafer segment) was 25 mA/cm<sup>2</sup> and the plating time was 45 s. Trench widths are approximately 500 nm.



**Figure 2:** (a) Cross-section of the Cu-Mn film electrodeposited on a Cu seeded wafer using the pulse waveform. (b) Surface morphology of the plated Cu-Mn film (c) EDS spectra of the Cu-Mn film indicating codeposition of Cu and Mn in a 49:1 ratio.