Synergistic and Transient Effects of Plating Additives in Copper Metallization of Semiconductor Interconnects

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Copper electroplating of interconnects on semiconductor wafers has recently become the mainstay for metallizing high-end microprocessors. The metallization process hinges on the ability to produce by plating defect-free fill of many millions of sub-micron vias and trenches distributed across 200 and 300 mm wafers. The key to this breakthrough technology has been a special mixture of plating additives that controls the plating process and shifts its normal tendency to preferentially metallize the more accessible wafer surface towards generating instead a bottom-up fill of the cavities[1]. A number of experimental and modeling studies have addressed this special electrodeposition process and the additives role in particular[2-6].

The technology remains, however, empirical, and the critical role that the additives play in the deposition process is only partially understood. This presentation primarily addresses two heretofore unanswered issues: (i) the characteristics and the significance of the interactions between the additive compounds which play a key role in providing their special function, and (ii) the nature of the transient processes that are critical to the 'bottom-up' fill process.

Steady-state polarization data for different additive combinations characterizes their inhibition or acceleration of the copper deposition process. Observed shifts in the equilibrium potentials and variations between the upward and downward potential scans indicate irreversible, or slow, additives adsorption/desorption effects. Voltage response to current step experiments indicates transient inhibition or acceleration effects. Fig. 1 shows a typical voltage response to a current step from 10 mA/cm^2 to 40 mA/cm^2 in a copper electrolyte with a common additive combination consisting of a chloride ion (Cl^-), polyalkylene glycol (PAG), an organic di-sulfide ($C_6H_{12}Na_2O_6S_4$, SPS) and a quaternary nitrogen compound. It is observed that while the response of most additive combinations is fast, the specific system containing Cl^- + PAG + SPS exhibits a slow response which is indicative of interactions.

The interactions between the various additives, including competitive adsorption, and their effects on the copper deposition are analyzed, providing some rationalization for the selection of the additives combination and guidelines for optimizing the process conditions.

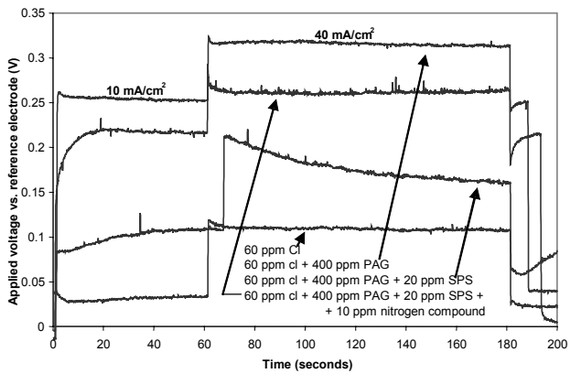

Fig. 1. Voltage response to a current step from 10 mA/cm^2 to 40 mA/cm^2 for a copper electrolyte to which chloride, SPS, PAG and a nitrogen compound have been added. The long transient for the SPS/ PAG/Cl^- combination are noted.

References:

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