A NOVEL ELECTROLYTE COMPOSITION FOR COPPER PLATING IN WAFER METALLIZATION

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Copper electroplating from acidified copper sulfate is a classical technology. Critical to its universal appeal has been the ability of the process chemistry to uniformly plate complex parts in multiple bath configurations. This feature is characterized in terms of a high 'throwing power' or a high Wagner number[1]:

$$Wa = \frac{\kappa b}{l i} \quad \text{(defined here for Tafel polarization)}$$

κ is the conductivity; b is the slope of the Tafel polarization curve; *l* is the characteristic length; and i is the current density. To achieve a high Wa number, conventional sulfate based copper plating formulations specify the use of sulfuric acid as a 'supporting electrolyte' with the main purpose of providing high conductivity[2].

Copper metallization of semiconductor interconnects presents a unique application. Here, using a specially designed and *dedicated* tool, a critically uniform copper layer must be electrodeposited onto a resistive seed layer through contacts along the circumference of the wafer. In order to minimize the resistive substrate ('terminal') effect[3], which tends to promote thicker deposit near the contacts, the use of a *low conductivity* electrolyte is particularly beneficial[4]. Since the proton mobility is about 7 times higher than the mobility of copper or sulfate ions, the most effective means of reducing the conductivity is through lowering, or complete elimination, of the acid. Accordingly, the conductivity of a typical copper sulfate plating bath formulated without sulfuric acid drops by about a factor of 10, from about 0.5 S/cm to 0.05 S/cm.

The beneficial effect of lowering the electrolyte conductivity on the copper distribution is demonstrated in computer simulations[5] (Fig. 1) and experimental results (Fig.2). Clearly, the 'no-acid' electrolyte significantly improves the copper thickness uniformity.

Eliminating the acid has a second beneficial effect: its removal shifts the transport number of the copper ion from about zero to 0.5 thus effectively doubling the copper transport rate. Since copper transport within the vias is an important issue (discussed below), this 'chemically induced' transport enhancement supports a higher deposition rate, or (for the same plating rate) permits a lower flow rate.

Additional benefits of the 'no-acid' electrolyte include: (i) the ability to significantly raise the copper concentration without precipitation, (importance of this is discussed below), (ii)'greener', non-toxic and non-corrosive chemistry, (iii) minimize erosion of the seed layer upon prolonged contact with the wafer, and (iv) non-phosphorized anodes may be used, if desired.

A second critical requirement in interconnect metallization is the ability to fill small, micron-scale, features (i.e., cavities) rapidly and reliably. Unlike the current distribution on the macroscopic (wafer) scale which is typically controlled by the electric field (and therefore strongly affected by the conductivity), the current distribution on the micro-scale is dominated by kinetics and mass transport[1]. Since flow is absent within the micron-scale blind vias, the copper is transported there solely by diffusion. Copper ion depletion at the bottom of the vias due to transport limitations will adversely affect the deposit properties. By *raising the copper concentration* in the bath from its typical range of 0.1 – 0.3 M to e.g., over 0.8 M, an enhanced plating rate (by a factor proportional to the concentration increase) can be sustained under the same external flow. Alternatively, since the major function of the electrolyte flow is to minimize copper depletion external to the via, a higher bulk copper concentration enables plating at comparable rates but at lower flow rates, as shown in Table 1.

References:

1. Uziel Landau, The Electrochem. Soc. Proceedings Volume 94-9, 1994.
2. F. A. Loewenheim, "Electroplating", McGraw-Hill, New-York, NY, 1978.
3. O. Lanzi and U. Landau, J. Electrochem. Soc., 137 (4), 1139-113 (1990).
4. U. Landau, Patent Pending
5. "Cell-Design", CAD Software for Electrochemical Cells, L-Chem, Inc., Shaker Heights, OH 44120

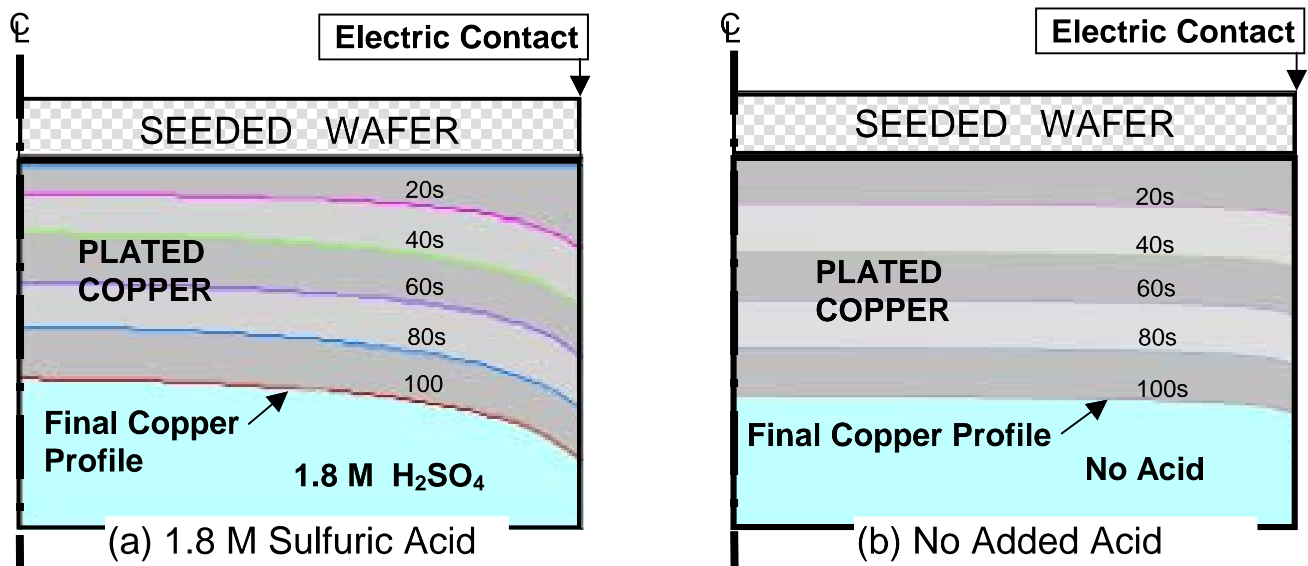

Fig. 1: Computer simulations (CELL-DESIGN©) of copper deposition on a resistive wafer. An axi-symmetric cross section through one half of a 200 mm wafer is shown with center of the wafer on the left and electrical contact (wafer circumference) on the right. The vertical axis is magnified to make the copper profile visible. Copper kinetics (i_0= 1 mA/cm^2, α_C=0.5, α_A=1.5) were assumed. Current density was maintained at ~ 35 mA/cm^2. 5 growth steps, 20 sec. each were simulated. **(a)** electrolyte: 0.24 M $CuSO_4$ + 1.8 M H_2SO_4. Min. copper thickness = 1.08 μ; max. thickness = 1.52 μ **(b)** electrolyte: 0.85 M $CuSO_4$. Min. thickness = 1.28 μ; max. thickness = 1.41 μ. No edge exclusion was assumed.