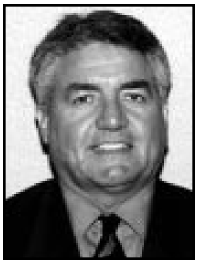

Pulse Plating

Steve Koelzer
Vice President, Research & Development
K & K Consulting
709 W. Remington Drive
Sunnyvale, CA 94087
E-mail: smbk@slip.net

How & When Pulse Plating Works

The fundamental barrier encountered in all of plating is the one that causes burning, hydrogen bubbles, edge buildup and just plain old bad plating. That barrier is involved with the depletion of platable ions adjacent to the work surface. Metal ions from the bulk solution must replace those being consumed by plating and do so by convection, migration and diffusion to transfer their mass to the surface to plate. In electroplating, the rate of deposition is proportional to the current density applied. Steady-state plating conditions allow only so much current to be used, the limiting current density (LCD). Above, one encounters hydrogen formation, burning, etc. You simply run out of gas, a real mass transfer deficiency.

Convection to the cathode surface happens by solution movement—stirring, heating, sparging, cathode rocking and such. It is a thermo-mechanical or hydrodynamic process. Intense, turbulent solution movement raises the LCD. For example, LCDs of 2,800 ASF or more can be achieved by flowing the solution 3.3 to 8 feet per second.[1] Considering metal-to-solution heat transfer, there is a thin film of fluid adjacent to the wall that offers considerable resistance to molecular movement and so reduces heat transfer. Surfactant-like molecules are used in modern coolant systems to increase metal to solution heat transfer. Similar work also has been done with pulse plating to increase leveling power.[2-4] The (micro)rough surface of the wall causes frictional forces at the solid-solution interface and establishes a hydrodynamic boundary. In lubrication systems, additives that act like metal-lipid surfactants facilitate the formation of a film (barrier) to reduce friction. The aforementioned solution modifications affect convection to increase mass transfer of metal ions from solution, but there is still a barrier that is not penetrated by convection.

Diffusion of ions occurs through a layer immediately adjacent to the plating surface. Here no convection occurs. Diffusion comes about from surface metal ion depletion to generate the concentration-dependent diffusion force trying to equalize toward bulk concentration. The rate of diffusion also depends on the metallic ion's "diffusibility," a characteristic of the elemental or complex ion considered in the plating system. The derivation of the ionic mobility for consideration at the plating surface is beyond the scope of most concerned; for all intents and purposes it is represented as a temperature dependent ionic diffusion coefficient. Values of diffusion coefficients are expressed in units of square centimeters per second and typically have values of 0.5 (10^{-7}) $cm^2\ sec^{-1}$. The values of copper in M H_2SO_4 are 0.61 (10^{-7}) and 0.53 (10^{-7}) $cm^2\ sec^{-1}$ at the respective concentrations of 0.05 and 0.1 M.[5]

One perspective on the diffusion process might be the way increased water works, resulting from removal of dissolved metal ions as they plate.[6] Typical metallic ions, like copper, have strongly coordination bound water (Cu has $6H_2O$). These aquated ions also have a primary hydration shell which attempts to neutralize the atomic charge (+2 for Cu). There are more hydration or counter-hydration shells to further neutralize or offset overly neutralized former shells (water is dipolar having more partial negative than positive charge). Finally, there are networks of hydrogen bonding water loosely tying all the ingredients together ("the solution"). Electrochemical reduction of metallic ions requires that all water be removed before deposition. The resultant "free" waters bond to each other, the surface and additives, as well as other ions in solution. Surface-generated water dissolves the gradient solute trying to equilibrate to the bulk concentration and forms a concentration gradient, which constitutes the diffusion barrier.

Proton or hydroxyl transfer occurs by making one hydrogen bind to water whilst breaking another. These are the fastest known of chemical reactions. Because dipolar water will hydrogen-bond to anything possessing a charge, it will tend to "encapsulate" ions by certain number. Thus it would appear that more dilute solutions would have less diffusion. The reason copper is slower diffusing when twice as concentrated[5] is a result of the relative lack of water for the high sulfuric acid strength used[6] with competition by 40 and 20 times as many hydrogen ions as copper. Hydronium ion (H_3O^+) has an higher affinity for (proton) charge neutralization by water and thus 'drags' more waters of hydration. A minor influence on mass transfer is brought about by opposites attracting and like charges repelling.

Continued on p. 94