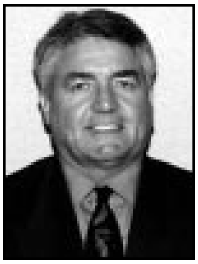

Pulse Plating

Steve Koelzer
Technic, Inc.
709 W. Remington Drive
Sunnyvale, CA 94087
E-mail: smbk@slip.net

Read Between the Pulses

This month, let's talk about what happens to surface-solution equilibrium when current is applied, withdrawn and reversed. If one puts work in a plating solution, there is the possibility of Galvanic deposition while the current is off. This is only possible when the electroactive ions in solution are of a higher reduction potential, as seen on the "galvanic replacement series." This chart is generally true. The exceptions include slight modifications by the supporting electrolyte, in particular, pH, halides, amines and a few others. This is not germane to this month's discussion, but if it were, we would want to explore live pulsing entry (without reversing currents), intermediate oxide layers contributing to non-adhesion, the degree of complete surface replacement and so forth.

As in last month's column, the surface of a metal consists of a sea or cloud of electrons. When in solution without current, wetting needs to occur either by a non-neutral pH or surfactants. An uncleaned surface does not wet in water and a cleaned surface repels water when withdrawn from rinsewater. The reason is that the electron cloud constituting the metallic surface, even without current applied, is repelling molecules of net negative charge or dipole moment. Most plating is done in water that has a negative dipole moment. However, metals always have oxide on their surface unless certain conditions are met.

By applying current in a plating solution, the only guarantee to remove surface oxide depends on the metal's reduction potential (how refractory the metal is) and how much current is applied. For example, copper and nickel are not refractory. Uranium, bismuth, tungsten, tantalum, hafnium, antimony, tin, niobium, zirconium, germanium, titanium, silicon, aluminum, magnesium and beryllium are. That means that when an anodic charge is applied (the "reverse" in pulse reverse plating), oxide will grow and you "anodize" the surface of such "valve" metals.

When current is applied to the work before the plating can occur, due to too low a current density or insufficient potential (EMF, Electromotive Force), underpotential deposition occurs. Here, the laying down of adatoms fills the entire surface of each plane (or terrace) of the lattice before becoming adatoms that adopt the crystal lattice conformation (plate on). Only then will the next layer begin to adsorb. Underpotential deposition IS slow and replicates the structure exactly. When sufficient current is applied to reach plating conditions, overpotential deposition occurs. This is electroplating.

When current exceeds conditions for plating, hydrogen is generated by water electrolysis. This hydrogen overpotential is exactly what is avoided by current withdrawal after a period at current densities that would otherwise "burn" the parts. The degree of current that can be applied for any particular amount of time is limited only by the concentration of electroactive ions in solution. Obviously, very dilute solutions will withstand huge current densities only for infinitesimal pulses, owing to extremely small current-limited diffusion barrier distances.

So, when the current pulse begins, the surface is set to underpotential mode at one-third the speed of light (or so). Then, as platable ions are withdrawn from solution electroreductively, the ionic migration from solution perpendicular to the work surface toward the anode "short circuits" to plate onto apical protuberances until using up diffusible ions by hydrolysis, which is proportional to the current density applied or to the concentration of ions formally in solution. At this point the current has hopefully been withdrawn or switched to reverse. If reversed current is too large, the refractory effect can occur by reverse analogy.

A dissolution rate under reverse conditions is limited by the amount of available water, *i.e.,* how dilute the plating solution is. At first, there would be plenty of water as plating has just depleted platable ions. While electrodissolution occurs, the limit to metal removal would be contingent on available water. When "depleted," an "overpotential" occurs and, again, electrolysis produces oxygen instead of hydrogen in this reverse mode. If refractory or valve metals are present, anodization occurs. If non-refractory, the metal ablates its surface into particles which need to dissolve as they migrate from the surface. The size of the particles depends on the grain sizing and current density applied. Again, the reverse current conditions should be limited to the point at which conditions affecting the surface are desired.

When a pulse of forward current is withdrawn, some residual surface potential exists. It is assumed to be identical to the capacitive current consumed during the initiation of that pulse and plates during its relaxation in a surface conformal manner because there is microscopic reversibility occurring in the solution at the surface interface (solution ion mixing). Such plating conformity also occurs, owing to a lack of driven overpotential as though underpotential conditions existed. Were one to go immediately from forward to reverse, the rate of change in potential would dictate the conditions of surface

Continued on page 63