PulsePlating



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Back to Basics: The Diffusion Zone

Last month we looked at a practical way to assess throwing power and covering power. Now we will look at the diffusion zone in direct current and pulse plating.

DiffusionLayer

At the solid-solution interface, there is no solution movement—just a fluid film. Gradually, next to this film, solution convection can be effective, coming from a heat source, mechanical stirring, or flowing electrolyte. The tenacious surface fluid film is impervious to any influence by solution convection. Only diffusionmigration operates in this electrochemical gradient zone.

Ions always move about in solution, even in the stagnant fluid film adjacent to the surface. Ions move for the same reason water molecules do: they tend to maintain an even distribution. When ion concentrations diminish, as in plating, they will diffuse to replenish those that are lost. Diffusion occurs per Fick's first law, which is the ionic species' temperature-dependent constant times (x) a changing ratio of its concentrationper-distance. This diffusion occurs when plating current stops.

When a potential (voltage) is applied to a cathode, ionic migration occurs, but not immediately. The first step in potential is used to charge the electrode (capacitative layer charging current). Negative potential induces surface ions to plate, reducing their concentration and stimulating diffusion. The current density is proportional to the reduction rate of the ions at that potential. At a certain negative potential, the reduction rate will match the rate of diffusing ions. Beyond this potential, the current density and plating rate are under diffusion control. When a pulse consumes all of the platable ions from the diffusion zone, the transition time is reached wherein the potential would then hydrolyze water, making hydrogen. Pulse plating allows current densities up to 10,000 times that of normal direct current values, by virtue of very short pulse times not exceeding the transition time.

The migration of ions such as nickel, copper, etc., are very similar under like conditions. At the beginning of plating under a potential gradient (electric field) and with uniform ionic concentration (zero concentration gradient), the ionic migration flux is proportional to the concentration of ions times (x) the voltage at that distance from the surface. Nickel, copper, etc., are divalent cations having slightly different coulombic charges. Monovalent and polyvalent ions are less and more accelerated, respectively, as the coulombic charge of the ionic species is also factored with the concentration times (x) the voltage gradient. As ions are depleted and diffusion occurs, ionic migration is enhanced as well, by the strength of the potential applied at the distance from the surface in an ion-concentration-dependent manner.

Increased ion concentrations allow higher limits of current density. The diffusion layer inversely limits such current density. The diffusion layer effect may be minimized by enhanced convection, to extremes.

Water Layer

As ions plate out, complexed water gets released from hydrated ions. It has nowhere to go except to diffuse

with incoming ions, increasingly diluting the incoming migration. While this is happening, during electroreduction of platable ions, water concentrates at and near the metal surface. It is possible that the leftover water then channels through magnetic flux lines. The more that water concentrates during plating, the more resistance to current flow it has. It is a good thing we have acidic and alkaline pHs to use along with conducting salts. In acidic electrolytes, conductivity excels, yet the presence of hydrogen ions affords a readily reducible substrate once platable ions deplete. Positively charged hydrogen ions migrate to the negatively charged cathode very effectively. Pure water is an insulator at neutral pH.

If the potential or current is not reduced to compensate the increased resistance at the surface, hydrolysis of water may begin. Catalytic surfaces, such as nickel, palladium, and platinum, lower the energy required to hydrolyze water. As hydrogen is made, hydroxide is also locally produced with perhaps other reduction reaction products. These local ions could increase conductivity as they migrate to bulk, except if they were rapidly generated they would tend to precipitate nickel, for example. Nascent hydrogen (H°) can form an essentially covalent bond with the metal, whereas O and OH form largely ionic bonds.1

Escaping hydrogen can help mixing. It can also cause pitting. P&SF

References

1. M.T.M. Kopera & R.A. van Santen, Journal of Electroanalytical Chemistry, 472:2:126-136 (1999).