Pulse Plating



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To Fuse or Not Diffuse

Several years of columns touched many facets of pulse plating, even as they were discovered. I find it interesting that types of pulsed plating appear categorizable. For example, plating with very short, high-current bursts on the order of 10 to 100 millionths of a second at 3,000 to 10,000 ASF is a region that can give fine grains with good reflectivity. Another extremity is the combined timing of ultrasonic with cathodic pulsing and reversing at 150,000 Hz to give hard, reflective surfaces. These constitute different categories because the former requires long offtimes so it will not become like direct current (surface adatom diffusion crystallization, as well as replenish ions depleted at surface), while the latter deposits in both forward and reverse currents.

No matter how you look at it, pulse plating is an extension of the mathematics of plating. In the past several months, we looked at the influences of diffusion and calculating on- and off-times, duty cycle, average pulse current density, etc. Another important area is calculating diffusion layer thickness. It is important, because it can define whether conformal plating or roughening occurs. The diffusion layer thickness basically depends on the length of time of the pulse. Its value is used in other calculations, as we shall see in future columns.

Limiting Current Density

The (Nernst) diffusion layer thickness in DC plating is usually around 10-300 micron (0.4-11.8 mil). It is a vertical dimension from the surface and has a nebulous value, owing to the many variables that influence its apparent functional height. Such variables include temperature, surface rugosity, type and degree of agitation, including non-laminar regions of leading and leaving edges, etc. They affect the rate at which the plating ions are replenished at the existent potential *and* concentration gradients. Increasing the potential past its limit electro-reduces water, which makes hydrogen. Before this happens, there will probably be burning—uncontrolled plating in higher current density areas.

So, the DC limiting current density (j_{gg}) in amps per cm² equals the diffusion coefficient of the depositing ion (D, cm²/sec) x its concentration in solution (c, or C₀) in moles per cm² x the ionic charge of the depositing metal (z or n) x the Faraday constant (F, 96500 Coulombs per equivalent), all divided by the diffusion layer thickness (delta, δ , in cm),

$$j_{gg} = DC_0 z F/\delta$$

The mole (or mol) is the molecular weight (MW) expressed in grams $[gm/L \div MW]$. By the way, the average pulse plating current density ought to be less than half of the DC limiting current density in order to avoid burning and powder formation. In this calculation, δ should be made equivalent under similar DC and pulse hydrodynamic conditions. Nonetheless, some powder makers size their product in this manner.

Pulse Diffusion Layer Thickness, δ_p

A real diffusion layer is influenced somewhat by convection (temperature- or gravity-driven) conditions. The much larger hydrodynamic layer's mechanical movement of solution approaching the surface has stopped as a result of frictional forces. However, the Nernst diffusion layer is stagnant and not influenced by convection, wherein types of plating ions diffuse at their characteristically constant rate. Electrochemical calculations utilize the Nernst diffusion layer.

When the δ_p is about the same size or less than the average surface roughness profile (RMS), pulse plating will conform to a macroprofile and uniform (tertiary) current distribution with surface replication. Again, the solution flow (parallel leading and leaving edges, etc.) becomes important for local dimensions of δ_p , but this will be addressed in a later column evaluating peak pulse current density to convert a DC microprofile into a macroprofile.

When the δ_p is larger than surface RMS, pulse plating increases surface roughness (microprofile) as diffusion of metallic ions to nearest surface projections increases their growth. This concept has been used to some advantage to enhance smoothness,¹ and a similar concept to fill submicron trenches and vias.² Limited diffusion of inhibitors of grain growth (brighteners, etc.) therefore become functionally consumed at the uppermost surfaces (peaks) before being able to reach valleys (trenches).

The pulse diffusion layer³ is calculated as the square root of: $4/\pi x$ the plating ion diffusion coefficient x on-time x 1 minus % duty, and is best set up on a spreadsheet as:

$$\begin{split} \delta_{\mathrm{p}} &= [1.27323954DT_{\mathrm{on}}(1\text{-}[T_{\mathrm{on}}(T_{\mathrm{on}}+T_{\mathrm{off}})])]^{0.5} \end{split}$$

Obviously, the main determinants are the on- and off-times, because

0.010 0.010 0.500 0.000189 1.8881 0.0743 As copper su 0.010 0.100 0.091 0.000255 2.5460 0.1002 increased for

ionic diffusion coefficients are all within an order of magnitude. The pulse diffusion layer increases with increasing on-time and decreases with decreasing off-time (increased duty cycle).

For the spreadsheet calculations of δ_n above, the value of D is:

D=0.0000056 cm²/sec

Synopsis

When current is enabled, surface capacitive resistance must be overcome in a time- and current densitydependent manner before plating gets up to speed. The first part of plating reduces depositable metal ions nearest the surface. If plating current is stopped early, a resultant macroprofile will not depend on diffusion, so long as off-time allows solution equilibration prior to the next pulse. The diffusion layer dimension operates on diffusion rate, which is a time function. Longer off-times allow crystallization growth of existing nuclei, but also decrease duty, increasing diffusion layer thicknesses. However, extending pulse on-time has a more pronounced effect on diffusion layer thickness increase. Higher current densities nucleate more so for a higher grain density, to a point.

When the average pulse current density approaches half of the direct current limiting current density under equivalent conditions, dendritic burning occurs. At this point, plating is limited by bulk solution ionic strength. This situation is one of slight diminishing returns because electrolimiting pulse current density would increase 65 percent—not 70 percent—due to a concomitant kinematic viscosity increase. As sulfuric acid increases from 6 to 10 percent, its kinematic viscosity would reduce the pulse limiting current density 2 percent, in spite of a 65-percent increase in conductivity. *PassF*

References

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- 3. J. Cl. Puippe & F. Leaman, eds., *Theory and Practice of Pulse Plating*, AESF, Orlando, FL, 1986, p. 63.
- 4. S. Koelzer, *Proc., AESF SURFIN*[®], Session T—Pulse Plating, 779 (1998).