PulsePlating



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

Nanopulse, Micropulse, Millipulse&Pulse

Note: This column began at the end of 1998. It was not intended to substitute for the collective seminal work "Theory and Practice of Pulse Plating" (available through the AESF Bookstore). Rather, the intention is to explain some aspects and concepts not covered. Authors for column articles are still invited to contribute.

There is so much to say, but so little time and space. The Fifth International Pulse Plating Symposium (held in conjunction with SUR/FIN® 2000 in Chicago) was quite successful. It was well complemented by the general conference concerning electronics, and vice versa. Copper plating presentations abounded. Some data and concepts may have sounded contradictory, but acid copper with pulse plating is a rather complex area.

Three Hundred Pulse Forms The Symposium began with a remark about a Tibetan medical text found recently in Siberia. PBS radio chronicled the finding, which was uncovered in N.E. Russia. Though to be treated with gentle hands, the text cited some 300 different human pulse characters. Could this be compared to the art and science of pulse plating? You be the judge.

Occidentally, taking the pulse indicates frequency of heart contractility, and blood pressure measures heart/artery blood flow resistance. However, there are more indicators. The heartbeat is handled by artery smooth muscle tone, resulting in a

sinusoidal pressure curve. It is characterized by many influences, such as vasodilator/vasoconstrictor release, artery structure, plaque formation, collagen composition, etc. Capillaries are the smallest regions between arteries and veins. There, nutrients are disbursed. Capillary diameter can be less than that of a red blood cell and (resistance) varies under hormone influence. Artery/ precapillary diameter is also modulated by neuronal and endocrinemediated hormones. Control of brain function is by this type, delivering glucose by coordinated vascular engorgement. Blood viscosity and composition are influential. The flow of blood is indeed complex. The timing, force and rate of cardiac output defines the potential for pulsed blood flow.

Similarly, the current delivered in pulse plating could be diagnosed. The resistances come from corroded wires or connections, current weakening due to inductive losses from unbraided wiring, length of the conduit, incompletely clean plating surface, etc. A nearer neutral pH of the electrolyte increases resistivity, and the power supply can have losses for all sorts of reasons.

The complex sensing of the pulse gives rise to a multiplicity of detectable tones. And so it goes with pulse plating. The influences and interferences between theory and practice are not all worked out. Whether there are 300 diagnoses in pulse plating remains to be seen. One of the last incompletely charted areas concerns the interface between surface and solution.

Surface Solution Interface

Water stuck to the surface of metals can be difficult to remove. In order to do so, vacuum and/or evaporation at a temperature of about 400-450 °F is required. This "chemically" bound water just doesn't want to go away. It is significantly present during plating and can even be incorporated in the deposit somewhat. Surface-bound water contributes to a double-layer capacity. The current required to overcome the surface impedance is the desorption energy required prior to plating. I remember from high school chemistry that one can store pressurized hydrogen and oxygen in a single cylinder if "chemically" bound water has been removed.

Water may be harder or easier to remove from the metallic crystal lattice terrace than the steps between terraces. In the case of crystalline nickel, a step at a particular surface orientation gives rise to a well-fitting pocket for water to fit. That site has the ability to spontaneously hydrolyze water to hydrogen, which eventually gases off, and oxygen, which migrates onto the center of the superior terrace and forms oxygen islands. Removing ligands such as this adsorbed water by cathodic currents would require higher-than-normal plating currents; anodic currents more easily affect desorption. Such terrace edges would either constantly hydrolyze water or

terminate edge growth. Sulfate has a similar effect in silver plating, in that it stops the terrace growth.

In fact, plating silver with sulfide may "neutralize" those characteristic sites that would otherwise allow the tarnishing to take place. As plated, the sites are either all occupied by sulfide, which means that the sulfidation process of silver tarnishing cannot begin, or the presence of sulfide prevents the growth of the sulfidesensitive silver surface. There is also a commercial silver tarnish prevention product that allows a chemical to evaporate over silver stored in a confined space. Tarnishing is also removed by galvanic reduction. Immersing a tarnished silver object into hot, dissolved salt and soda in an aluminum vessel will not remove the dark sulfides until contact is made between the silverware and aluminum. There is no loss of silver plate in the process.

Ligand double-layer desorption energy (surface water removal) contributes to the charging time at the beginning of a pulse. Each metal's different crystal surfaces possess relative affinities for organic constituents containing sulfur, nitrogen, oxygen, etc. This is the basis for brightening action and other effects seen by the suppression of terrace and step-edge grain growth.¹⁻⁶ All waterbased electroplating, therefore, is inherently affected by water itself and, in the case of nickel electroplating, affected in several ways.

Surface capacitance and specific electrolyte resistivity can be measured to calculate the current-time it takes for plating to begin. If that currenttime value is not achieved, perhaps due to excessive electrode separation, plating will appear to be more like direct-current plating—if it occurs at all. Brush plating takes advantage of small, inter-electrode dimensions. A special case using charging time with close electrode proximity is pulse micro-machining.

Electrochemical Micro-machining

Applying ultrashort voltage pulses between electrode and work piece in a plating bath allows for both threedimensional (3D) machining with submicron precision, and 2-mil dot plating.⁷ The 3D Micro-machining applies nanosecond voltage pulses at inter-electrode separations on the nanometer-to-micrometer range. The time constant for charging the double layers is the electrolyte resistance times the double-layer capacity. Because electrochemical reaction rates are exponentially dependent on double-layer potential drop, such reactions are strongly confined to these polarized electrode regions.

Machining resolution of one micrometer is possible using 30 nanosecond pulses. This is in accordance with calculations using an electrolyte resistance of ~30 ohm.cm for 0.1 M HClO₄ and double-layer capacity of ~10 microfarads for metal electrodes, where charging of the double layer is achieved at the onemicrometer separation. Machining precision can be significantly enhanced by reducing the pulse duration or the electrolyte concentration, ensuring that a buildup of polarization occurs in such small electrode spacing with a sufficient presence of electrolyte ions. A 0.3-M electrolyte with 100 picosecond (0.0001 millisecond), therefore, that pulses a spatial resolution in the 100-Å range, is theoretically possible.

Copper (2 mil) dots were deposited onto gold film in 0.01 M HClO₄ and 0.1 M CuSO₄ with positive 2 V, 400 nanosecond pulses. The gold surface was kept at the Cu/Cu²⁺ redox equilibrium to prevent large-scale deposition and dissolution of the plating. Forming copper crystallites requires a critical Cu adatom concentration on the gold surface during the pulse. Kinetics of the plating constraints assists in the strongly localized Cu deposition. PASE

References

- 1. Koelzer, S., Pulse Plating Column: "Tackling Current Distribution," *Plat. & Surf. Fin.*, April 1999.
- 2. *ibid.*, Koelzer, S., "Pulsed Electroforming," June 1999.
- 3. *ibid.*, Koelzer, S., "Pulse Electronics," July 1999.
- *ibid.*, Koelzer, S., "State of Electronics Pulse Plating," October 1999.
- 5. *ibid.*, Koelzer, S., "Sample Wave Analysis," December 1999.
- 6. *ibid.*, Koelzer, S., "How I Learned to Love Pulse Plating," July 2000.
- Schuster, R., Kirchner, V., Alongue, P. & Ertl, G., *Science* 289, pp. 98-101, 7 July 2000.





Get QUICK responses on line with AESF's



www.aesf.org/psf-qwiklynx.htm

QwikLynx • QwikLynx • QwikLynx