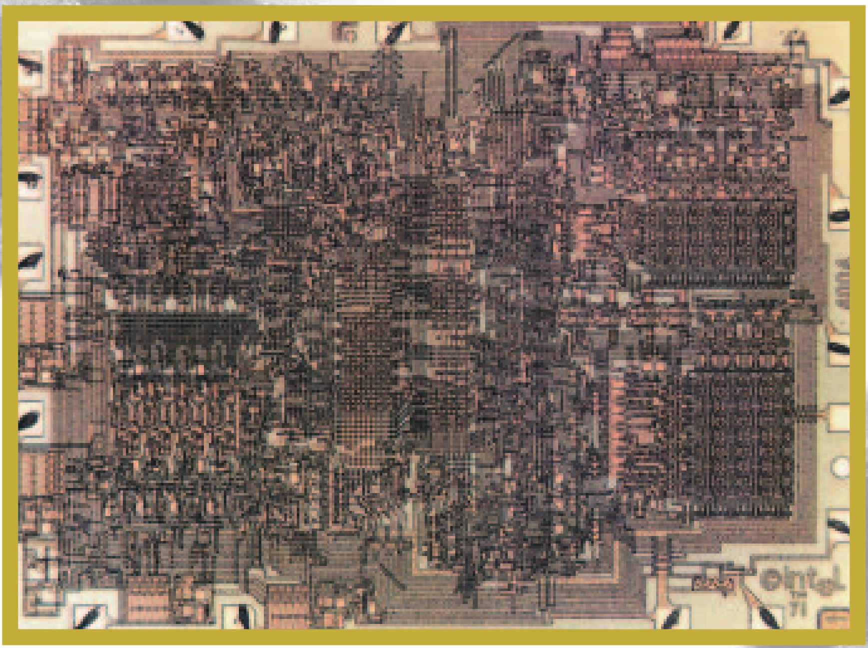
Corrosion Control for Metallized MCMs & Hybrid Circuits

By Don Baudrand, CEF

In this edited version of a presentation given at SUR/FIN® '97—Detroit, corrosion is defined and described for electronic devices. The results of corrosion, including oxidation, loss of contact resistance, current leakage, shorts and diffusion changes in hybrid circuits are discussed. Diffusion of metals resulting in a nickel, copper or silver on the surface, which corrode or change the surface characteristics, as well as the characteristics of the body of the conductor are also discussed. Corrosion minimization and prevention, diffusion barriers and corrosion protection methods are suggested.

Corrosion is defined as the destructive alteration of a metal by reaction with its environment. Corrosion is nature obeying its own rules. Entropy is the measure of the degree of disorder in a system or substance. The second law of thermodynamic teaches us that the entropy is always increasing in our universe. In other words, everything we build tries to fall apart.

Corrosion is the process of changing, usually in an undesirable fashion. We know that corroding of an anode in an electroplating solution is most often desirable, because it supplies metal to the plating solution and is typically less expensive than when metal salts are used to supply metal. It is hard to think of other examples of "good corrosion." Billions of dollars are spent each year replacing corroded things, such as bridges, building components, automobiles, tractors, etc. Many computer failures are the result of corrosion. Failure of control devices can be life threatening, such as aircraft controls, radar or navigation devices. These are just a few examples.



This early Intel microprocessor, commonly called a "chip," is .11 in. by .15 in. in size and has about 4,500 transistors.

Corrosion of electronic components is destructive in many ways. Oxidation of metals is an obvious form of destruction that leads to deterioration of the component, loss of surface conductivity and an increase in contact resistance. Sometimes connections are broken. Soldering, brazing and wire bonding are made difficult or impossible.

Reactions with sulfides in the environment can be equally destructive to electronic components and devices. Although silver sulfide is conductive, it also can interfere with bonding processes. Most sulfides are non-conductors and act similarly to that of metal oxides.

One expert[1] describes failures in dielectric between metal lines caused by accelerated corrosion when voltage gradients are applied this way: "With the presence of moisture and ionic impurities, metal corrosion is also accelerated with voltage gradient. In the absence of a voltage gradient, corrosion was only just apparent after 2000 hr, but corrosion was observed within 50 hr with a 25-volt potential difference between two conductors 0.5 mm apart. The metal corrosion rate was also found to increase linearly with increasing voltage differentials between the metal lines spaced at 0.5 mil in a plastic package in the range of 5-100 volts." The metal conductors used were Al-Cu-Si sputtered on silicon nitride, with one-mil gold wire thermocompressively bonded to the Al-Cu-Si bonding pad. The failure mode was leakage of current between metal conductors. Moisture and electrolytes, such as chlorides, accelerate corrosion and failure.

Another study[2] reported failure of under-hood automotive electronic devices as shorting and blistering

Approximate Resistivity of Various Metals

Metal	Micro-ohm-cm
Pure electrodeposited nickel	8
Nickel phosphorus 7-9% P	40-60
Nickel phosphorus 9.5-10.5% P	90-120
Nickel phosphorus 4-4%	20-35
Nickel Boron 0.5-1% B	6-9
Palladium, electrodeposited	10.5
Palladium, electroless	10.5
Molybdenum	52
Tungsten	55

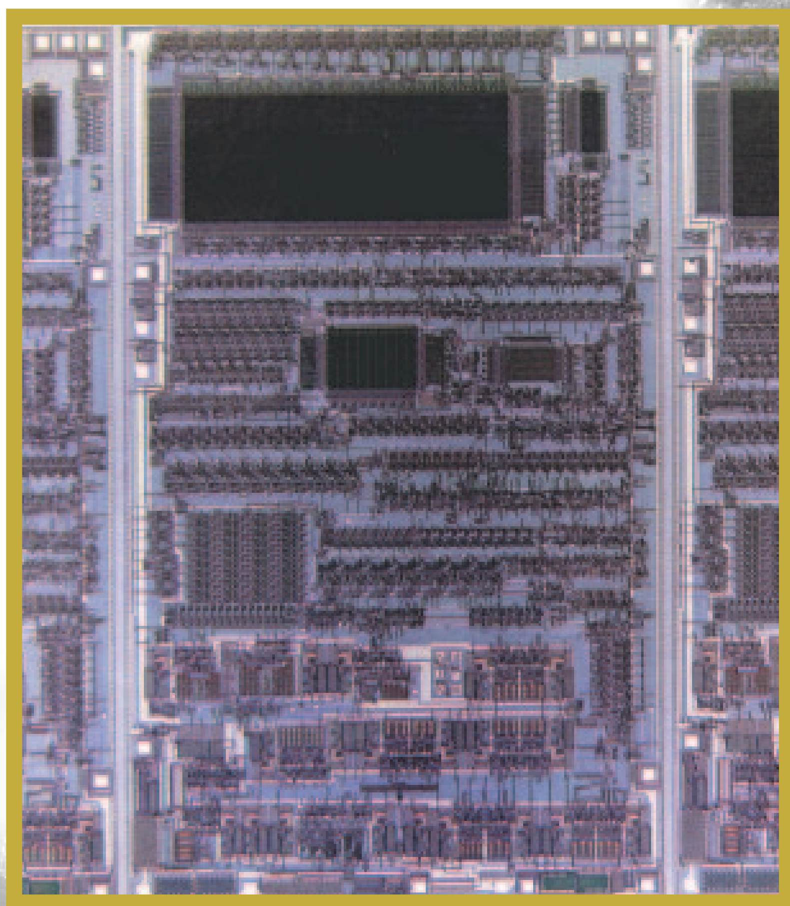
because of "electrolytic migration" using palladium-silver conductors on dielectric materials. Moisture and the presence of electrolytes (any soluble material, which when dissolved increases the conductivity of water) create the conditions for corrosion and electrolytic migration, resulting in current leaks or shorts.

Diffusion of metals can lead to corrosion of electronic devices. For example, when gold is plated over copper, diffusion of gold into copper and copper into gold can, and usually does, take place. If accelerated by heat, when copper reaches the surface of the gold plate, oxidation can easily take place (unless the component is hermetically sealed). Copper oxide, in addition to causing bonding failures and high contact resistance, can cause malfunction of the device. Copper oxide is a semiconductor, meaning it passes current in one direction and not the other. Even though it is somewhat conductive in one direction, the resistance is higher than gold or non-oxidized copper. High-frequency signals traveling through copper oxide can be modified to cause "noise" in the circuit or loss of signal amplitude, or rectification of the signal. Rectification means that half of the signal may be lost entirely.

Another consequence of diffusion is the change in electrical and mechanical properties of the device. Mutually soluble metals include: Silver and gold, copper and silver, copper and gold. Whenever any of these metals are in contact with each other, diffusion will take place, often leading to destructive failure of the electronic device, even when corrosion, *per se*, is not present. It is difficult to prevent oxidation or sulfidation of silver and copper. Corrosion is, therefore, usually associated with the diffusion of these metals. Barrier layers between these metals are one way to minimize or eliminate diffusion. Nickel and electroless nickel deposits are commonly used as diffusion barriers in plated components. The addition of cobalt to nickel plating solutions improves the diffusion barrier.[3] Electroless and electroplated palladium and palladium/nickel alloys are also used for barrier purposes.

Corrosion Control In MCMs & Hybrid Circuits

Metallization of circuit elements can take many forms. For example, ceramic multi-chip modules (MCM-C) can use tungsten, molybdenum and molybdenum-manganese alloys (some times called "moly-mag"). These metals or alloys are usually mixed with silicon (glass) and an organic binder, then fired onto the ceramic to form a bonded circuit element. Silver and its alloys, copper and its alloys, and palladium and its alloys are common materials for circuits, resistors, capacitors, etc. All of these metallizing conductors, except tungsten, are subject to corrosion unless they are protected.[4] Even tungsten will dissolve in alkaline anodic conditions. Many oxide films can be used to protect the metal, but corrosion can take place when there is current passing through, or where a corrosion cell is formed. A corrosion cell is a spot where there is a potential (voltage) caused by the presence of an anode and cathode. This condition occurs at dissimilar metals in contact with one another, or where oxides form while passivating one area adjacent to an area not being passivated. Frequently, corrosion cells form



This speech synthesizer chip is about the same size as the Intel chip, but has more than 30,000 transistors. The least bit of corrosion on any microprocessor can cause failure.

because of alloying constituents, pits, nodules or particles included in the plated deposits, and where a non-metal protective layer starts or ends and excludes oxygen from one part of the component—this is known as crevice corrosion.

Sputtered and evaporated metals used for metallizing non-conductive materials have characteristics similar to electrodeposited metals. Diffusion, corrosion, electrochemical cells, impurities, nodules and porosity can increase corrosion rates and cause failures. Electro and electroless plated deposits can also protect these metals and alloys, if properly applied.

Corrosion, metal diffusion and/or surface imperfections can alter the electrical characteristics of an electronic device. This can lead to problems ranging from noisy circuits to failures. When nickel is plated over metallized circuits, semiconductors (via holes), or on surfaces intended for electromagnetic interference (EMI) or radio frequency (RF) shielding, it is important to:

- Plate with sufficient thickness to provide a good diffusion barrier; (150-200 micro inches are usually sufficient for most applications).
- Use clean plating solutions with sufficient filtration to remove all particles from the bath: Use good cleaning and activation pre-plate steps to insure removal of any particles from the basis material and be sure of a clean active surface.
- Monitor all plating solution constituents and operating conditions so as to produce a high-quality deposit.
- EMI shielding of non-conducting packages and enclosures is often accomplished using electroless copper followed by electroless nickel or electroplated nickel to prevent oxidation of the copper. Copper provides efficient shielding. Thickness of copper ranges from 30 to 150 micro-in. (0.75 to 3.74 micrometers). The nickel layer varies from 30 to 100 micro-in. (0.75 to 2.5 micrometers).

These known good practices will minimize or help to eliminate corrosion problems in the majority of electronic devices.

Elevated Temperatures

Why won't these good practices solve all the problems? What about the rest of the devices?

Some devices operate at elevated temperatures. Diffusion rate is increased because of the heat.

Thicker deposits may be required. Pure nickel electroplate may not be good enough. Electroless nickel provides a somewhat better barrier, but at a little higher electrical resistance.

Approximate numbers are given for the resistivity in the accompanying table, because alloys vary and impurities in deposited metals can alter the values. It is interesting to note that nickel is more conductive than 60:40 tin-lead solder. Other solder alloys of tin lead may have different resistivities. Separately, however, tin has about 11 micro-ohm-cm as does lead.

Diffusion of metals, and in some cases non-metals, can lead to changes in resistivity, or accelerated corrosion because of a greater potential between layers or other metals that may be in contact with the temperature-altered materials. Most metals oxidize in the presence of oxygen from the air. But there are other sources of oxygen. Under the influence of an anodic condition, water can liberate oxygen at the anode and hydrogen at the cathode. Water in the form of moisture or vapors can, under these conditions, contribute oxygen. If a steel component is plated and heated, iron can migrate to the surface and oxidize, it can interfere with contacts, soldering, brazing wire bonding and most any type of bonding method. As an underlayer, copper diffuses readily into silver, gold, nickel, etc. Oxidation of copper at the surface interferes with most types of bonding. There is a change in contact resistance, in addition to changes in volume resistance and copper oxide at the surface is a semiconductor, causing noise in high-frequency circuits. Careful selection of diffusion barriers can minimize these problems in palladium, nickel, electroless nickel, nickel-cobalt alloy (up to 40-percent cobalt can be used [4, 5, 6]), sputtered or evaporated chromium and platinum. Most refractory metals serve as diffusion barriers as well, such as tungsten and vanadium. Some rare earth metals are being used via sputtering or chemical vapor deposition methods.

Avoid unnecessary high-heat excursions where possible.[7] Heat-treating electroless nickel deposits results in changes in composition and characteristics of the deposit. For example, heating electroless nickel phosphorus deposits to 350–400 °C for one-half hr will cause the formation of nickel phosphorus intermetallic compound, resulting in hardening of the deposit, changing its structure from amorphous to somewhat crystalline. The deposit becomes magnetic and the specific resistance changes. Heating electroless nickel deposits to higher temperatures results in further changes. Above 600 °C, migration of phosphorus to the surface and formation of phosphorus oxide takes place. At 800–1000 °C, nickel phosphorus oxidizes about 100 times faster than pure nickel. Heating nickel phosphorus in moist hydrogen results in removal of phosphorus from the surface, making it more easily solderable and bondable. Electroless nickel-boron deposits act differently. Even a small amount of boron in the deposit will inhibit (but not prevent) oxidation.[8]

Protecting Completed Devices

Encapsulation, hermetic sealing and coating with potting compounds are some of the methods used to protect electronic devices.

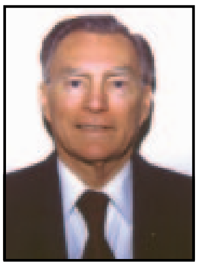
Silicone gels, epoxy coating and potting materials are widely used to protect components from moisture and corrosive materials. New materials appear more frequently than every few years. Keeping abreast of new developments in circuit protection is time well spent.

Electro and electroless plating of alloys can improve performance if the right coatings are selected for the application. Extreme care must be exercised in minimizing the exposure of the completed device to moisture by using the right plating selection and the best sealing materials of process for the application. P&SF

References:

1. Chang, Li-Hsing, "Metal Failure Mechanisms for a High Voltage Integrated Circuit in a Plastic Package," *ISHM 95 Proceedings*, International Symposium on Microelectronics Los Angeles, CA, Oct. 24-26, 1995.
2. Sarma, D.H.R., Richter, F.E., and McDermott, M.G.. ISHM 95, "Multilayer Materials System for Automotive Applications," *Proceedings Symposium on Microelectronics*, Los Angeles, CA., Oct. 24-26, 1995.
3. U.S. Patent Reissue No. 34,48 4. Nagashima, *et al*.
4. E. Winters, W. Baxter and A. Choudhury, "A Comparison of Electrolytic and Electroless Ni/Au Finishing Processes for Multilayer Ceramic IC Packages," *Plating and Surface Finishing*, April, 1994
5. J. Russo, "Nickel-Cobalt Diffusion Barrier Coating," *Plating and Surface Finishing*, July, 1994.
6. S. Wakabayashi, N. Sakabuchi, N. Kaneko, and H. Nezu, "Effects of Underlayer Metals on Die Bond Reliability of Gold-plated Ceramic Packages," *Plating and Surface Finishing*, November 1994.
7. Baudrand, D. "Ceramic Hybrid Circuits," *Plating & Surface Finishing*, Vol. **85**, No. 6, June 1987.
8. Baudrand, D. & Bengston, J., "Electroless Plating Processes, Developing Technologies for Electroless Nickel, Palladium and Gold," *Metal Finishing*, Vol. **93**, No. 9; September 1995.
9. Tomlinson, W. and Wilson, G., "Oxidation of Electroless Ni-B and Ni-P Coatings in Air at 800-1000 °C," *Journal of Materials Science*, 21:97, 1986.

About the Author



Don Baudrand, CEF was founder and president of Electrochemical Laboratories, Los Angeles, CA; vice president of Research and Development for Allied Kelite, Division, Witco Corp.; and vice president and business manager for Allied Kelite. Retired since 1994, he is currently a consultant in electro and electroless plating processes. He has numerous patents in electroless plating and microelectronics, and has written more than 70 papers. He is a contributing author for the ASM Metals Handbook, *the* McGraw-Hill Electronic Materials and Processes Handbook *(chapter 9), and* Electroless Plating Fundamentals & Applications *(chapter 9). He is also the co-author of* Plating of ABS Plastics, the 1960 AES Plating Handbook, *and others.*