Electroless Plating Processes

Developing Technologies for Electroless Nickel, Palladium and Gold

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Abstract

Many types of electroless nickel, electroless palladium and gold, are in use today. These deposits and tirtiary alloys of these processes will find greater use in the future as technology advances, demanding different surface characteristics, and different metallurgical properties. A basic understanding of the types of processes and some applications may give rise to new uses for these and other electroless processes. Formulas for electroless nickel solutions, electroless gold and palladium may lead to better understanding and encourage use of some of them, or better still modifications of the formulas included in this paper. In general, proprietary formulas that have been based on solid research and development will be better than the ones included here from published literature.

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Introduction

Electroless plating has become somewhat commonplace in the world of certain types of electronic devices such as hybrid circuits, multi-chip modules, capacitor, resisters, and on the chips (semiconductors) for selective metallization for conductors, via hole filling and solder bumps used to mount chips, pins and connect circuits. Electroless nickel has wide acceptance for hardware applications. Electroless plating of palladium, and gold are used more every day for special applications.

Electroless nickel

Electroless nickel has many forms. Examples are: Nickel phosphorus having differing phosphorus (P) content. The physical, electrical and surface characteristics are different for each level of phosphorus. (see appendix for formulations) For example, high phosphorus deposits provide better corrosion resistance in acid environments, while low phosphorus deposits are better in alkaline environments.

Heat treating can increase hardness in the range of 300 to 400 degrees C. different amounts of Phosphorus in the deposits will heat treat to different final hardness, and maximum hardness is obtained as different temperatures. In addition, the reaction to heat treat conditions differ widely. It is well known that heating nickel phosphorus deposits to temperatures of 300 degrees C to 400 degrees C cause the formation of nickel phosphide which hardens the deposit the degree of hardening depends on the amount of P and the heat treat temperature and time. For example, low P deposits (3 to 4%) heat treat to a harder value and at a lower temperature than high P (10.5-12%) deposits.

Nickel phosphorus plating solutions can also host alloying metals which further change the deposit characteristics. Sometimes as little as 1/2 ppm can cause a profound change. Alloys containing more than nickel and phosphorus are sometimes called poly alloys.

Electroless nickel with particulate materials can provide many different and useful applications. Hard materials, lubricating and phosphorescent materials, materials can be co-deposited.

Nickel (B) boron deposits have different characteristics from those of nickel P deposits. Similarly, nickel boron deposit characteristics change with boron content. Low B deposits are best suited for most applications. A nickel boron deposit containing 0.25% B has a melting point of 1455 degrees C. Nickel P with 11 wt.% P melts at 880 degrees C. (a eutectic alloy)

Numerous papers have been published and presented at conferences dealing with the virtues of electroless nickel for many engineering and hardware applications. Hardness, wear resistance and corrosion protection are characteristics which make electroless popular. The ability to plate uniform thickness over all surfaces enhance these characteristics. One place where advanced applications are found is in the electronics industry. Electronic microcircuits and packaging requires a suitable barrier layer which can sustain a long period of service. Nickel has the slowest dissolution rate in solder and the slowest intermetallic compound formation rate compared with gold, silver, copper palladium or cobalt. Electroless nickel serves both functions well.

Heat Excursions

Let us examine what happens to electroless nickel phosphorus when it is heated under certain conditions. “Nickel P starts to oxidize about 400 degrees C and above 800 degrees D, decomposition of phosphorus and evaporation of phosphorus from the coating occurs. Above 600 degrees C migration of phosphorus to the surface and formation of phosphorus oxide has been observed.. A kinetic study at 800 to 1000 Degrees C showed that a Ni-P deposit oxidized about 100 times faster than pure nickel. The addition of even a small amount of boron to the deposit decreased the amount of oxidation. Phosphorus in the Ni-P coating is the cause of the poor oxidation resistance of the alloy and the much purer Ni-B coatings may be expected to have a much improved resistance to oxidation."

Heating nickel-P deposits in air or in moist hydrogen results in removal of phosphorus from the surface of the deposit making it much more solderable, brazable and wire bondable. It is interesting that moist hydrogen atmosphere is reducing for nickel but oxidizing for phosphorus.

Ohmic contacts are made to thick film deposits on ceramic semiconductors by the use of electroless nickel and heat treat processes. Thick film conductors of gold, silver platinum etc. have DC resistivity which is several orders of magnitude higher than calculated values. Stable low resistance ohmic contacts having ease of solderability and reliable lead attachments using heat treated nickel-P alloys. This technique can be used to make ohmic contacts to intermetallic compounds such as gallium arsenide, thermoelectric semiconductors, bismuth-telluride, silicon and ceramic materials. Heat treating to 350 400 degrees C for 10-15 minutes provides the improved contact. If air oxidation increased the resistance, re-heating will restore the good ohmic contact characteristics. (2)

Electroless nickel Phosphorus for die bonding requires a heat excursion above 700 degrees C, usually about 800 degrees C in Nitrogen/hydrogen for atmosphere for 8-10 minutes, leaves a nearly pure nickel surface that when gold plated will alloy for the formation of a nickel suicide thereby giving rise to an excellent die bond.(3) Nickel boron can be die bonded without this thermal excursion.

Electroless Palladium

Palladium and palladium alloys have been developed as an economic alternative to gold plating. Palladium has some characteristics different from gold such a harder and deposit thermal stability. Electroless palladium is desirable because it can plate uniform thickness, electrically isolated areas and the number of parts in a given size tank can be greater than for electrodeposited palladium, and small complex configurations can be plated easily. Multi-chip modules (MCM'S), Dual-in Line packages (DIP's) and other multi layer hybrid circuits are examples. Soldering and wire bonding to palladium and electroless palladium deposits is made easier by the use of a thin gold over- plate of 1-2 millionths of an inch (0.025 -0.05 micrometers). Thin layers of palladium are as effective as thicker deposits so that 12-30 micro inches (0.3-0.75 micrometers) result in an economical process.(4) Electroless, or immersion gold completes the system for complex devices. Solderability to electroless palladium has been reported as good without a gold strike over the palladium deposit. Palladium is less soluble in solder than gold, thus soldering directly to electroless palladium eliminates the gold migration into the solder. Gold contaminated solder form a weak dull solder joint. Palladium can be plated over copper since the diffusion rate is slow, wire bonding to palladium is possible without copper migration. ft is suggested that electroless palladium deposits onto ceramic sponge or other support materials could be used effectively as reaction catalysts, including automotive emission catalysts. Most palladium is plated over a nickel deposit which enhances the protection and barrier functions.

<u>Deposit properties of palladium</u>

Density	11.5-12.0
Melting point	1552 C
Resistivity	6x of silver, 10.55 (Micro-ohm-cm)
Hardness	100-200 Hv
Appearance	matte white, will not tarnish
Magnetic properties	Non magnetic (unless alloyed)

Nickel an cobalt alloys are strongly magnetic

The future is good for electroless palladium. The first generation has been plagued by bath instability. As the chemistry becomes more friendly, applications will be evident. This will follow a similar development like electroless nickel, but operating problems must be corrected.

Electroless Gold

The advantages of depositing gold by electroless means are will known. Intricate designs and miniaturization necessary in today's' devices and even more intricate designs predicted for the future make electroless deposition mandatory to fabricate many of these devices. There is need for faster and less expensive methods for depositing the minimum required thickness of gold with characteristics necessary to be useful. Bonding characteristics are of paramount importance. Bonding includes soldering, brazing, wire bonding and die bonding. Much research has been done over the last 20 or more years to achieve these objectives. However, much additional research is still needed before a completely reliable electroless gold bath that is suitable for broad application becomes available.

There are a number of formulation types available which with careful attention to monitoring and control produce satisfactory deposits for specific applications. (see appendix) A variety of gold sources have been tried, including (potassium gold cyanide, the gold source for most), Gold chloride, various organic and inorganic gold compounds. Reducing agents include sodium hypophosphite, dimethylamineborane, sodium borohydride, hydrazine, and benzyl alcohol. Z. Mathe lists a larger number of gold sources and reducing agents.(5)

An example of an electroless gold plating solution is one developed by G. Ganu:

TABLE 1

KAu(CN)2	12-16 g/L
Diammonium citrate	15-20 g/L
Citric acid	1-2g/L
Benzyl alcohol	2-4% v/v
Temperature	50-70 Degrees C
pH	4-9

plating rate is from 12-17 micro-inches per hour, dependant on the concentration of benzyl alcohol and temperature (70 C). About 35 micro-inches (0.87 micrometers) deposits in two hours .Gold is first deposited by chemical replacement (also called immersion plate or galvanic displacement) then proceeds by reduction of gold at the surface and oxidation of benzyl alcohol to benzoic acid. Most electroless gold deposits are sensitive to nickel contamination, therefore require an immersion gold strike prior to the electroless plating solution. The benzyl alcohol system appears to be successful without a gold strike. (6)

Others report a plating rate of 1.5 micrometers per hour (60 micro inches) plating rate (GEC Research Laboratories).(7)

Summary

Electroless nickel, of many types, electroless gold, electroless palladium and their alloys will find greater use in the future as technology advances, demanding different surface properties and a wider variety of deposit characteristics.

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Appendix

Typical Solution Compositions

Electroless Nickel Phosphorus

	I	**II**
Nickel sulfate $6H_20$	21	25
Acetic acid	---	10 ml/L
Lactic acid	30	---
Molybdic acid (85%)	---	0.009 g/L
Propionic acid	2 ml/L	---
Lead acetate	0.001 g/L	0.002 g/L
1 ,3-diisopropylthiourea	---	0.004 g/L
Sodium glycolate	---	30 G/L
Sodium hypophosphite H_20	24 g/L	30 g/L
PH	4.6	5.0
Temperature, ^{0}C	95	85

Formula I will produce a medium phosphorus deposit (5-8% P)
Formula II will produce a lower phosphorus deposit (3-5%)
Tom lower the phosphorus content in general, raise the pH, raise the temperature, use active buffers such as proprionic acid and increase the sulfur containing stabilizer content, These changes increase the deposit rate. Some proprietary formulas contain several different stabilizers.
To make a high phosphorus containing deposit, lower the pH 4.0 to 4.6, lower the temperature and use strong complexing agents such as sodium citrate, or glycine. This slows the deposit rate.

Appendix

Au(lll) Sulfite Solution Comparisons

	Reducing Agent Hypophosphit	Borohyd ride	Formaldehyde
$Na_3Au(S0_3)_2$, g/L	3	1.5	0.6
Na $_2S0_3$,g/L	15	15	15
1 2-diaminoethane,g/L	1	1	---
KBr, g/L	1	1	---
Na_4EDTA, g/L	1	1	---
Na-citrate, g/L	---	---	5
NH_4CI, g/L	---	---	7
Na-hypophosphite, *g*/L	4	---	---
$NaBH_4$, g/L	---		
Formaldehyde (37% solution), g/L	---	---	1
PH	9	10	(not given)
Temperature, degrees C	96-98	96-98	96-98
Rate mg/cm^2/hr	0.95 (0-.5 um/hr)	5.2 (2.7 um/hr.)	19 (10 um/hr.)

Three Au(IIl) sulfite solution formulations are given in the slide as examples.

Both hypophosphite and formaldehyde provide autocatalytic systems with Au(I) sulfite complex, but not with the conventional cyanide complex. On the other hand, it has been shown that gold metal is an excellent catalyst for the anodic oxidation of these reducing agents in solutions containing no cyanide species. Evidently, the catalytic activity of gold is poisoned by $Au(CN)_2$ and/or CN ions.

Appendix

Platinum Group Electroless Solutions

Table 1
Palladium, Palladium-Phosphorus, and Palladium-Boron Hydrazine Solution

	Bath A*	**Bath B**
Pd(NH$_3$)$_4$01$_2$, gIL as Pd	5.4	7.5
Na$_2$EDTA, g/L	33.6	8.0
NH$_4$OH, g/L	350	280
Hydrazine, g/L	0.3	
Hydrazine (1M), mLlhr		8
Temperature, ^{0}C	80	35±5
Plating rate, pm/hr	25.4	0.89
Plating area, cm^{2}IL	100	1000

*Bath A for rack plating, Bath B for barrel plating

Table 2
Palladium, Palladium-Phosphorus, and Palladium-Boron Hypophosphite Solution

PdCI$_2$, gIL	10.0
Na$_2$EDTA, g/L	19.0
Ethylenediamine, g/L	25.6
NaH$_2$PO$_2$, gIL	4.1
pH at 20^{0}C with HCI	8.5
Temperature, ^{0}C	71

Appendix

Table 3
Palladium, Palladium-Phosphorus, and Palladium-Boron Amine Borane Solutions

	A	**B**	**C**
$Pd(NH_3)_4C1_2.H_20$, g/L	3.75		
$PdCI_2$, g/L		4.0	4.0
NH_4OH, M	0.3	4.0	4.0
Trimethylamine borane, g*I*L	3.0		2.5
N-Methylmorpholine borane, g/L		1.0	
Mercaptobenzothiazole mg/L	---	30	3.5
pH	11.4	11.0	
Temperature, ^{0}C	50	45	45
Plating rate, pm/hr	3.2-3.4	0.88	1.6-1.8

Table 4
Palladium, Palladium-Phosphorus, and Palladium-Boron Formaldehyde Solution

$PdCI_2$	0.1M *(1.78* g*I*L*)*
Formic acid*	0.4M
HNO_3**	1.OM
Formaldehyde	2.OM
Saccharin	0.002M
pH	1.0-1.5
Temperature	50^{0}C
Plating rate	0.15 pm/mm

* Oxalic, tartaric, or citric acid may be substituted
**Hydrochloric or sulfuric acid may be substituted